Società Chimica Italiana

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## Vol III

- Divisione di Elettrochimica
- Divisione di Chimica Fisica
- Divisione di Chimica Teorica e Computazionale
- Divisione di Didattica Chimica

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# SOMMARIO

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- Onofrio Scialdone, Università degli Studi di Palermo
- Alice Soldà, Università degli Studi di Bologna

**Delegato di Divisione**

- Amalia Velardo, Università degli Studi di Salerno

# Programma Scientifico

## Divisione di Elettrochimica

## Lunedì 11 Settembre 2017

| | |
|---|---|
| | ***Hotel Savoy Sala Verdi*** |
| ***Sessione Elettrochimica I*** | |
| ***Chairpersons: Marco Musiani, Amalia Velardo*** | |
| 9:00 - 9:30 | *Saluto Presidente* |
| 9:30 - 9:45 | ELE OR01: Fabio La Mantia, Collins Erinmwingbovo, Dominique Koster, Doriano Brogioli<br>*Dynamic impedance spectroscopy of a Prussian blue derivative thin film* |
| 9:45 - 10:00 | ELE OR02: Sergio Brutti<br>*The mixed olivine $Li(Co_{1/3}Fe_{1/3}Mn_{1/3})PO_4$ material as positive electrode for lithium batteries* |
| 10:00 - 10:15 | ELE OR03: Amedeo Capobianco, Alessandro Landi, Tonino Caruso, Andrea Peluso<br>*Hole site energies and electronic couplings for hole transport in DNA inferred from electrochemistry and quantum chemical predictions* |
| 10:15 - 10:30 | ELE OR04: Giovanni Valenti, Alessandro Boni, Michele Melchionna, Massimo Marcaccio, Stefania Rapino, Marcella Bonchio, Maurizio Prato, Paolo Fornasiero, Francesco Paolucci<br>*Co-axial nanostructures for energy conversion: synergic effects between carbon nanotubes and metal oxide* |
| 10:30 - 11:00 | Coffee Break |
| | ***Hotel Savoy Sala Verdi*** |
| ***Sessione Elettrochimica II*** | |
| ***Chairpersons: Onofrio Scialdone, Gianluca Longoni*** | |
| 11:00 - 11:15 | ELE OR05: Armando Gennaro, Francesca Lorandi, Marco Fantin, Abdirisak A. Isse, Krzysztof Matyjaszewski<br>*The use of rotating disk electrode to measure a complete set of kinetic and thermodynamic ATRP parameters* |
| 11:15 - 11:30 | ELE OR06: Vito Di Noto, Enrico Negro, Keti Vezzù, Angeloclaudio Nale, Yannick Bang, Federico Bertasi, Gioele Pagot, Agnieszka Zlotorowicz, Giuseppe Pace<br>*Graphene-based "core-shell" hierarchical nanostructured low-pt electrocatalysts for proton exchange membrane fuel cells* |
| 11:30 - 11:45 | ELE OR07: Maurizio Passaponti, Luca Rosi, Emanuele Salvietti, Carolina Castello, Andrea Giaccherini, Massimo Innocenti<br>*Microwave assisted pyrolysis of waste tires: evalutation by rotating ring-disk electrode technique of the catalytic efficiency in O.R.R.* |
| 11:45 - 12:00 | ELE OR08: Riccardo Brandiele, Christian Durante, Gian Andrea Rizzi, Armando Gennaro<br>*New evidences of platinum-yttrium alloyed nanoparticles formation on carbon support and catalytic activity for oxygen reduction reaction* |
| 12:00 - 12:15 | ELE OR10: Andrea Zaffora, Francesco Di Franco, Francesco Di Quarto, Ilia Valov, Hiroki Habazaki, Monica Santamaria<br>*Fabrication of Hf-Nb anodic oxides and their use in resistive switching devices* |
| 12:15 - 12:30 | ELE OR11: Eliana Quartarone, Simone Angioni, Luca Millia, Piercarlo Mustarelli, Enrico Doria, Marta Elisabetta Temporiti, Barbara Mannucci, Federica Corana<br>*Photosynthetic microbial fuel cell with polybenzimidazole-type membrane: highly efficient synergy between bacteria and microalgae for simultaneous wastewater removal and biorefinery* |

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| 12:30 - 12:45 | ELE OR12: Carmelo Lo Vecchio, Claudia D'Urso, Antonino Salvatore Aricò, Vincenzo Baglio<br>*Nanoclusters based on CoNC and FeNC for oxygen reduction reaction and their applications in direct methanol fuel cell* |
| 12:45 - 13:00 | ELE OR13: Maria Assunta Navarra, Marco Agostini, Lucia Lombardo, Aleksandar Matic, Stefania Panero<br>*Gel polymer electrolytes for high-loading sulfur composite electrodes in Li-batteries* |
| 13:00 - 14:00 | Intervallo Pranzo |

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| ***Sala Paestum B*** | |
| 14:00 – 15:00 | *Sessione Poster 1 (ELE PO01 – ELE PO24)* |
| ***Hotel Savoy Sala Verdi*** | |
| ***Sessione Elettrochimica III*** | |
| ***Chairperson: Vito Di Noto*** | |
| 15:00 - 15:15 | ELE OR14: Danilo Dini, Matteo Bonomo, Francesco Scorretti, Aldo Di Carlo<br>*Study of the influence of the electrolyte on the photoconversion properties of p-type dye-sensitized solar cells* |
| 15:15 - 15:30 | ELE OR15: Gioele Pagot, Federico Bertasi, Keti Vezzù, Nawn, Sun, Angeloclaudio Nale, Enrico Negro, Vito Di Noto<br>$EMImCl/(TiCl_4)_{1.4}/(\delta\text{-}MgCl_2)_x$ *Ionic Liquid Electrolyte for Mg-ion Batteries* |
| 15:30 - 15:45 | ELE OR16: Giada Tranchida, Hermes Egidio Pituccio, Francesco Di Franco, Francesco Di Quarto, Monica Santamaria<br>*Growth and characterization of atmospheric and anodic oxide films on weathering steels* |
| 15:45 - 16:00 | ELE OR17: Massimiliano Lo Faro, Stefano Trocino, Sabrina C. Zignani, Antonino S. Aricò<br>*Syngas production via co-electrolysis of* $H_2O$ *and* $CO_2$ *fed to a Solid Oxide Cell* |
| 16:00 - 16:15 | ELE OR18: Francesco De Bon, Abdirisak A. Isse, Armando Gennaro<br>*Improvements of electrochemically mediated atom transfer radical polymerization of styrene with ionic liquids* |
| 16:15 - 16:30 | ELE OR19: Francesca Colò, Stèven Renault, Federico Bella, Claudio Gerbaldi, Daniel Brandell<br>*An electrolyte study on* $Na_2BDA$ *anode for Na-based organic batteries* |
| 16:30 - 17:00 | Coffee Break |
| ***Hotel Savoy Sala Verdi*** | |
| ***Sessione Premi*** | |
| ***Chairpersons: Christian Durante, Alice Soldà*** | |
| 17:00 - 17:15 | ELE PZ01: Gianluca Longoni<br>*Investigation of sodium-ion battery materials - Premio di Dottorato "Engitec Technologies"* |
| 17:15 - 17:30 | ELE PZ02: Giorgia Zampardi<br>*In situ analysis of surface and bulk phenomena in lithium-ion batteries by means of scanning electrochemical microscopy - Premio di Dottorato "Fondazione Oronzio e Niccolò De Nora"* |
| 17:30 - 17:45 | ELE PZ03: Marco Fantin, Francesca Lorandi, Francesco De Bon, Xiangchen Pan, Krzysztof Matyjaszewski, Armando Gennaro, Abdirisak A. Isse<br>*Electrochemical methods for atom transfer radical polymerization of aqueous and metal free systems - Premio di Dottorato "Fondazione Oronzio e Niccolò De Nora"* |
| 17:45 - 18:00 | ELE PZ04: Eleonora Pargoletti, Giuseppe Cappelletti, Alberto Vertova, Valentina Pifferi<br>*Bare and titanium-doped manganese dioxide nanoparticles. Their pivotal role in energetic and sensoristic applications - Premio di Laurea "Bio-Logic SAS"* |
| 18:00 - 18:15 | ELE PZ05: Andrea La Monaca, Francesca De Giorgio, Maria Letizia Focarete, Davide Fabiani, Marco Zaccaria, Catia Arbizzani<br>*Electrospun polymer separators based on PVdF-PEO blends for Li-ion batteries - Premio di Laurea "Photo Analytical s.r.l."* |

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| 18:15 - 18:30 | ELE PZ06: Federica Proietto, Alessandro Galia, Onofrio Scialdone<br>*Electrochemical conversion of carbon dioxide to formic acid. Study of the effect of the operating parameters - Premio di Laurea "Ametek Scientific Instruments"* |
| | ***Sala Argiva*** |
| 18:30 - 20:00 | *Assemblea dei Soci della Divisione di Elettrochimica* |

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|---|---|
| | ***Sala Penelope*** |
| ***Sessione Congiunta: Chimica Analitica - Elettrochimica - Gruppo Sensori*** | |
| ***Chairperson: Aldo Roda*** | |
| 11:00 - 11:20 | ANA/ELE/GS KN01: Fabiana Arduini, Stefano Cinti, Giorgio Scordo, Renato Massoud, Danila Moscone, Giuseppe Palleschi<br>*New sustainable and cost-effective paper-based electrochemical (bio)sensors* |
| 11:20 -11:50 | ANA/ELE/GS OR01: Erika Scavetta, Federica Mariani, Isacco Gualandi, Domenica Tonelli, Marta Tessarolo, Beatrice Fraboni<br>*All PEDOT: PSS electrochemical transistors as a platform for sensing* |
| 11:50 - 12:10 | ANA/ELE/GS OR02: Alice Soldà, Marco Giorgio, Pier Giuseppe Pelicci, Nicholas Dale, Francesco Paolucci, Stefania Rapino<br>*Development of enzyme-based microsensors for ex vivo analyses* |
| 12:10 - 12:30 | ANA/ELE/GS OR03: Ornella Abollino, Andrea Ruo Redda, Francesca Durbiano, Eleonora Conca, Mery Malandrino, Agnese Giacomino<br>*Potential and limitations of voltammetric measurements for the characterization of electrode surface* |
| 12:30 - 12:50 | ANA/ELE/GS OR04: Laura Fabiani, Giulia Volpe, Elisabetta Delibato, Eleonora Pucci, Silvia Piermarini, Giuseppe Palleschi<br>*Development of an electrochemical magneto-immunosensor for the detection of Campylobacter: a preliminary study* |

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| 13:00 - 14:00 | Intervallo Pranzo |

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| | ***Sala Paestum A*** |
| ***Sessione Congiunta: Chimica Analitica - Elettrochimica - Gruppo Sensori*** | |
| ***Chairperson: Salvatore Daniele*** | |
| 15:00 - 15:30 | ANA/ELE/GS KN02: Andreas Lesch, Milica Jovic, Victor Costa Bassetto, Hubert H. Girault<br>*Preparing nanoparticles on large electrodes using inkjet printing and flash light irradiation* |
| 15:30 -15:50 | ANA/ELE/GS OR05: Stefania Rapino, Mirella Trinei, Alice Soldà, Marco Giorgio, Luca Bartolini, Matteo Iurlo, Massimo Marcaccio, Francesco Zerbetto, Pier Giuseppe Pelicci, Francesco Paolucci<br>*Rapid, low-cost and portable electrochemical assay for heart injury diagnosis* |
| 15:50 - 16:10 | ANAELE/GS OR06: Maria Rita Tomei, Daniela Neagu, Fabiana Arduini, Danila Moscone<br>*Carbon black modified screen-printed electrodes to detect chlorine dioxide.* |
| 16:10 - 16:30 | ANA/ELE/GS OR07: Vincenzo Mazzaracchio, Daniela Neagu, Alessandro Porchetta, Giuseppe Palleschi, Danila Moscone, Alice Pomponi, Giovanni Faggioni, Florigio Lista, Fabiana Arduini<br>*Bacillus anthracis spore detection by using a label free impedimetric aptasensor* |
| 16:30 - 17:00 | Coffee Break |

# Martedì 12 Settembre 2017

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| ***Hotel Savoy Sala Vivaldi*** | |
| ***Sessione Congiunta: Chimica Fisica - Elettrochimica - Enerchem*** | |
| ***Chairpersons: Moreno Meneghetti, Alessandro Minguzzi*** | |
| 9:00 - 9:30 | ELE KN01: Riccardo Ruffo<br>*Negative electrode materials for sodium ion batteries* |
| 9:30 - 9:45 | FIS OR51: Francesco Lamberti, Lucio Litti, Michele De Bastiani, Roberto Sorrentino, Marina Gandini, Moreno Meneghetti, Annamaria Petrozza<br>*High-quality, ligands-free, mixed-halide perovskite nanocrystals ink for optoelectronic applications* |
| 9:45 - 10:00 | ELE OR20: Marco Musiani, Enrico Verlato, Simona Barison, Stefano Cimino, Luciana Lisi, Gabriella Mancino, Francesco Paolucci<br>*Electrochemical preparation of nanostructured* $CeO_2$*-Pt catalysts on Fe-Cr-Al alloy foams for the low-temperature combustion of methanol* |
| 10:00 - 10:15 | FIS OR52: Simona Binetti, Alessia Le Donne, Maurizio Acciarri, Stefano Marchionna<br>*New earth-abundant thin film solar cells based on* $Cu_2MnSnS_4$ |
| 10:15 - 10:30 | ELE OR21: Christian Durante, Giorgia Daniel, Giorgio Mattiacci, Gian Andrea Rizzi, Armando Gennaro<br>*Platinum free electrocatalyst based on Fe-Nx moieties supported on mesoporous carbon prepared from polysaccharides for oxygen reduction reaction* |
| 10:30 - 11:00 | Coffee Break |
| ***Hotel Savoy Sala Vivaldi*** | |
| ***Sessione Congiunta: Elettrochimica - Chimica Fisica - Enerchem*** | |
| ***Chairpersons: Simona Binetti, Claudio Gerbaldi*** | |
| 11:00 - 11:15 | FIS OR53: Piercarlo Mustarelli, Fabio Invernizzi, Maddalena Patrini, Keti Vezzù, Vito Di Noto<br>*Polyurethane-based Electrostrictive Nanocomposites as High Strain - Low Frequency Mechanical Energy Harvesters* |
| 11:15 - 11:30 | FIS OR54: Gian Luca Chiarello, Massimo Bernareggi, Matteo Pedroni, Mirko Magni, Silvia M. Pietralunga, Espedito Vassallo, Elena Selli<br>*A bilayer* $WO_3$ *n-n heterojunction photoanode prepared by RF diode sputtering for improved photoelectrocatalytic water splitting* |
| 11:30 - 11:45 | ELE OR22: Federico Bella, Francesca Colò, Lorenzo Zolin, Diego Pugliese, Arul M. Stephan, Claudio Gerbaldi<br>*Lignocellulosic materials for electrochemical energy storage and conversion* |
| 11:45 - 12:00 | FIS OR55: Sergio Brutti, Stefania Panero, Annalisa Paolone, Priscilla Reale<br>*Hydrides as high capacity anodes in lithium cells: An Italian "Futuro in Ricerca di Base FIRB-2010" Project* |
| 12:00 - 12:15 | ELE OR23: Gioele Pagot, Federico Bertasi, Vito Di Noto<br>*Secondary magnesium batteries: an overview on ionic liquid -based electrolytes* |
| 12:15 - 12:30 | FIS OR56: Simona La Gatta, Francesco Milano, Roberta Ragni, Angela Agostiano, Gianluca Maria Farinola, Massimo Trotta<br>*Bio-hybrid complexes in artificial photosynthesis* |
| 12:30 - 12:45 | ELE OR24: Alessandro Minguzzi, Martina Fracchia, Alberto Visibile, Alberto Naldoni, Francesco Malara, Cristina Locatelli, Alberto Vertova, Paolo Ghigna, Sandra Rondinini<br>*Operando (photo)electrochemical X-ray absorption spectroscopy for water splitting* |
| 12:45 - 13:00 | FIS OR57: Amerigo Beneduci, Agostina L. Capodilupo, Giuseppina A. Corrente, Eduardo Fabiano, Vito Maltese, Sante Cospito, Giuseppe Ciccarella, Giuseppe Chidichimo, Giuseppe Gigli<br>*Electronic coupling in H-shaped tetra-arylamine mixed-valence compounds* |

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| 13.00 - 14.00 | Intervallo Pranzo |

# Mercoledì 13 Settembre 2017

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| ***Hotel Savoy Sala Verdi*** | |
| ***Sessione Elettrochimica IV*** | |
| ***Chairpersons: Patrizia Romana Mussini, Marco Fantin.*** | |
| 15:00 - 15:15 | ELE OR25: Monica Santamaria, Francesco Di Quarto, Maniscalco, Francesco Di Franco, Fabio La Mantia<br>*Synergistic use of impedance and photoelectrochemical measurements to study the electronic properties of anodic* $TiO_2$ |
| 15:15 - 15:30 | ELE OR26: Alberto Battistel, Danick Reynard, Christopher R. Dennison, Hubert Girault<br>*Recovery of low grade heat by redox flow battery* |
| 15:30 - 15:45 | ELE OR27: Francesca Lorandi, Alessandro Michieletto, Marco Fantin, Pawel Chmielarz, Abdirisak A. Isse, Armando Gennaro, Krzysztof Matyjaszewski<br>*Boosting aqueous atom transfer radical polymerization of hydrophilic and hydrophobic monomers by means of electrochemistry* |
| 15:45 - 16:00 | ELE OR28: Isabella Chiarotto, Marta Feroci, Fabiana Pandolfi<br>*Voltammetric analysis and chemical reactivity of ionic liquids (ILs) used as "green" reaction media and precursors of efficient catalysts* |
| 16:00 - 16:15 | ELE OR29: Onofrio Scialdone, Adriana D'Angelo, Fabrizio Vicari, Alessandro Galia<br>*New processes to produce renewable energy: reverse electrodialysis and thermally regenerative ammonia battery* |
| 16:15 - 16:30 | ELE OR30: Nicola Comisso, Lidia Armelao, Sandro Cattarin, Paolo Guerriero, Luca Mattarozzi, Marco Musiani, Marzio Rancan, Lourdes Vàzquez-Gòmez, Enrico Verlato<br>*Preparation of porous oxide layers by oxygen bubble templated anodic deposition followed by galvanic displacement* |
| 16:30 - 17:00 | Coffee Break |
| ***Hotel Savoy Sala Verdi*** | |
| ***Sessione Elettrochimica V*** | |
| ***Chairpersons: Monica Santamaria, Zampardi*** | |
| 17:00 - 17:15 | ELE OR31: Serena Arnaboldi, Patrizia Romana Mussini, Ivo Franco Buzzi, Rossella Monaco, Francesco Sannicolò, Tiziana Benincori, Giulio Apolloni, Andrea Penoni, Roberto Cirilli<br>*Inherently chiral molecular materials with 2,2'- and 3,3'-bisindole atropoisomeric cores: interactions between equivalent redox sites, configurational stability and enantioselection ability* |
| 17:15 - 17:30 | ELE OR32: Eleonora Macchia, Domenico Alberga, Kyriaki Manoli, Giuseppe F. Mangiatordi, Gerardo Palazzo, Luisa Torsi<br>*Organic bioelectronics probing conformational changes in surface confined proteins* |
| 17:30 - 17:45 | ELE OR33: Francesco Di Franco, Antoine Seyeux, Sandrine Zanna, Vincent Maurice, Philippe Marcus<br>*Physicochemical characterization and corrosion behaviour of surface oxide films on bright annealed ferritic stainless steel* |
| 17:45 - 18:00 | ELE OR34: Sabrina C. Zignani, Rafael M. Reis, Guilherme G.A. Saglietti, Vanessa Oliveira, Stefano Trocino, Susanna Maisano, Edson A. Ticianelli, Aricò, Massimiliano Lo Faro<br>$La_2NiO_4$*@Ni core-shell based catalyst as pre-layer for a commercial Solid Oxide Fuel Cell fed with biofuels* |

# Premi

## Premi di Dottorato

***Premio "Engitec Technologies"***

Gianluca Longoni, Università di Milan-Bicocca,

***Premio "Fondazione Oronzio e Niccolò De Nora"***

Marco Fantin, Università di Padova

Giorgia Zampardi, Ruhr-Universität Bochum

## Premi di Laurea

***Premio "Bio-Logic Sas"***

Eleonora Pargoletti, Università degli Studi di Milano

***Premio "Photo Analytical S.R.L."***

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***Premio "Ametek Scientific Instruments"***

Federica Proietto, Università degli Studi di Palermo

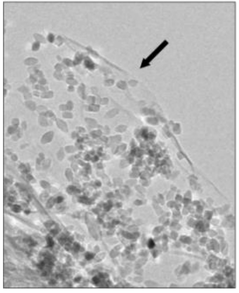
# Premio di Dottorato “Engitec Technologies”: Investigation of Sodium-Ion Battery Materials

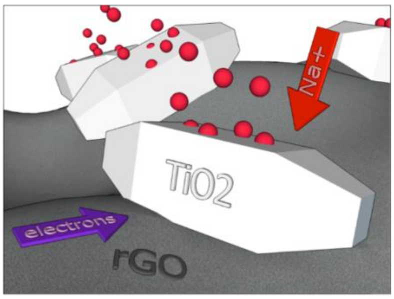
Gianluca Longoni[a,b]

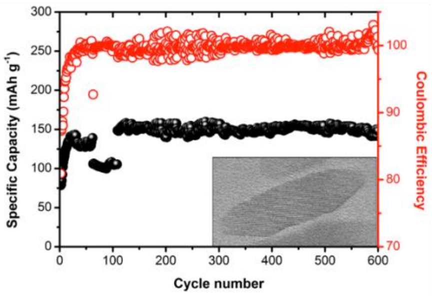
[a]Materials Science Department, University of Milan-Bicocca, via R. Cozzi 55, 20125, Milan, Italy,
[b]Nanochemistry Department, Istituto Italiano di Tecnologia, Via Morego 29, 16163 Genova, Italy

Na-ion battery technology has recently aroused great interest among all the scientific community as a valid and more environmentally friendly alternative to Li-ion batteries. The PhD research activity has been mostly devoted to the investigation of reliable active materials for sodium ion battery technology. All the investigated materials, either anode or cathode, have been investigated trying to highlight the major limits and difficulties connected to sodium intercalation and conversion reactions. Among these, some are: i) assessment of $Na^+$ diffusion in an intercalating host structure, ii)products and reversibility of transition metal oxides conversion reactions, iii) effects of materials crystalline properties on electrochemical performances and iv) features influencing the overall stability of a functional material. In order to keep the broadest view over the problem, it has been chosen to systematically start, for each species electrochemically investigated, from its synthesis and chemical-physical characterization. Rather than a pure electrochemical analysis, a continuous parallelism between morphological features, structural characteristics and performances was encouraged, eventually obtaining a detailed overlook of different classes of active materials for rechargeable (secondary) sodium-ion batteries.

The contribution will mainly focus on the most significant findings related to electrochemical mechanism-crystalline properties correlation of nanostructured anatase-$TiO_2$, investigated as anode material for sodium-ion batteries. A solvothermal surfactants-mediated synthesis was specifically tuned to achieve different crystalline facets expression on nano-sized $TiO_2$ mono crystals. An effective support on reduced graphene oxide sheets was adopted as well, in order to minimize agglomeration and crystal size biasing on sodium diffusion and electron transfer. Electrochemical properties and energy storage mechanism were thus investigated and experimental evidence of the macro-effect of crystalline facets expression on sodium uptake properly addressed. Following an intercalation pseudocapacitance-type of mechanism(1), $TiO_2$ crystals expressing {100} family facets predominance, ensured a relatively high cation exchange rate, accompanied with an outstanding stability over cycling, which eventually resulted in capacities above 150 mAh $g^{-1}$ maintained for over 600 cycles(2). This work is meant to encourage the investigation of crystalline appearance-electrochemical properties correlation of nanostructured materials for energy storage.







References:

1. Augustyn, V.; Come, J.; Lowe, M. a; Kim, J. W.; Taberna, P.-L.; Tolbert, S. H.; Abruña, H. D.; Simon, P.; Dunn, B. High-Rate Electrochemical Energy Storage through Li+ Intercalation Pseudocapacitance. *Nat. Mater.* **2013**, *12* (6), 518–522.
2. Longoni, G.; Pena Cabrera, R. L.; Polizzi, S.; D’Arienzo, M.; Mari, C. M.; Cui, Y.; Ruffo, R. Shape-Controlled $TiO_2$ Nanocrystals for Na-Ion Battery Electrodes: The Role of Different Exposed Crystal Facets on the Electrochemical Properties. *Nano Lett.* **2017**, acs.nanolett.6b04347.

# Premio di Dottorato "Fondazione Oronzio e Niccolò De Nora": In Situ Analysis of Surface and Bulk Phenomena in Lithium-ion Batteries by means of Scanning Electrochemical Microscopy

*Giorgia Zampardi*[a,b]

[a] *Semiconductors and Energy Conversion* - [b] *Analytical Chemistry - Center for Electrochemical Sciences (CES), Ruhr-Universität Bochum, 44780 Bochum, Germany.*

The formation of the solid electrolyte interphase (SEI), which occurs through the irreversible decomposition of the electrolyte components, is of fundamental importance in lithium-ion batteries since it affects the specific irreversible charge loss, the long term stability and the safety of the battery system. Nonetheless, only few *in situ* techniques are available for analysing the SEI in its native environment (1), such as Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy and differential electrochemical mass spectrometry (DEMS), and none of them allows a direct experimental observation of the SEI electronic character.

In this context, scanning electrochemical microscopy (SECM) in its feedback mode of operation has been recently proposed (2) as an *in situ* technique to visualise the conductive or insulating nature of the surface of a Li-ion battery electrode via the recycling of a free-diffusing redox couple present in solution (Fig.1).

After placing a SECM inside a glovebox (traces $H_2O$ and $O_2$ < 2 ppm), the experiments were performed holding at a constant position and at a constant potential a Pt microelectrode in close proximity of a sample surface during its polarisation. Before the SEI formation, the electrode surface is electronically conductive and the current recorded at the micro-electrode in proximity of the sample surface ($I_{Fb}$) is higher than the one recorded in the bulk ($I_{bulk}$), thanks to the redox couple recycle (positive feedback). After the SEI is formed, the sample surface turns to be electronically insulating and the $I_{Fb}$ is lower than the $I_{bulk}$ (negative feedback). In this way, through the observation of the variation of feedback current recorded at the Pt microelectrode, it is possible to monitor the electronic character of the electrode surface under analysis, enabling the *in situ* and *in operando* determination of the SEI.

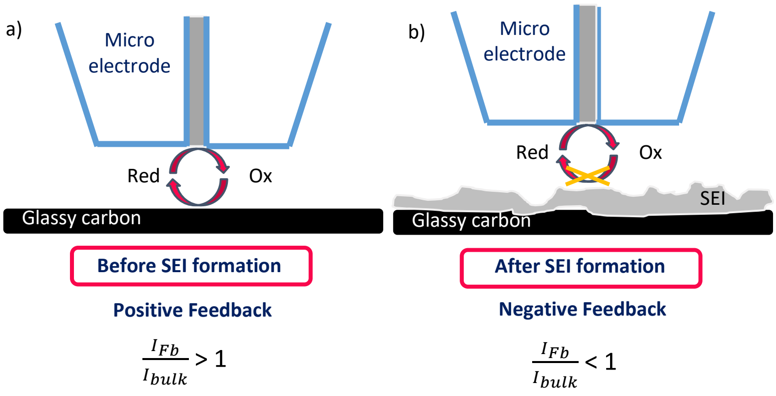


Fig.1 Schematic representation of the working principle of the feedback mode SECM applied to a Li-ion battery electrode. a) Positive feedback: no SEI on the sample surface, b) Negative feedback: SEI formed on the sample surface.

Here, an overview of the method is presented starting from its development up to the most important findings on different lithium-ion battery systems, such as: the formation of a SEI on titanium oxide based electrodes; the influence of the applied potential range on the SEI stability, the role of Li ions on the formation of an insulating layer, and the effect of commonly used additives as vinylene carbonate on the SEI formation on carbonaceous electrodes; and the nature of the surface layer formed on high operating voltage active materials for next generation Li-ion batteries.

References
1. Pallavi V., Pascal M., Novák P., Electrochim. Acta 55 (2010), 633
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# Premio di Dottorato “Fondazione Oronzio e Niccolò De Nora”: Electrochemical Methods for Atom Transfer Radical Polymerization of Aqueous and Metal Free Systems

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In occasion of the 2017 Ph.D. Prize “Fondazione Oronzio e Niccolò De Nora”, I will present some contributions of electrochemistry to the field of atom transfer radical polymerization (ATRP).[1-9] ATRP is a controlled radical polymerization used worldwide to prepare macromolecules with complex but well-defined architectures.

ATRP is generally catalyzed by transition metal catalysts, which can be accurately investigated by electrochemical techniques. Electrochemical methods to understand the mechanism of ATRP will be discussed, together with strategies to reduce the environmental impact of the procedure. An electropolymerization approach will also be introduced.

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# Premio di Laurea "Bio-Logic Sas": Bare and Titanium-doped Manganese Dioxide Nanoparticles. Their Pivotal Role in Energetic and Sensoristic Applications

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The most prominent feature of metal-air batteries is the combination of a metal anode and an air electrode with open structure to draw cathode active materials from air (1). Oxygen reduction is the main cathodic process, but unfortunately it is affected by overpotential loss under operation conditions (1). Thus, an effective catalyst is required. Owing to their structural flexibility and versatility, manganese oxides have been widely applied in several research fields (2,3). Since $MnO_2$ possesses quite a lot polymorphic phases, its controlled synthesis is pivotal. Hence, this Thesis work was focused on *i*) the hydrothermal synthesis of bare and novel Ti-doped $MnO_2$ nanopowders, *ii*) their deep physico-chemical characterization and *iii*) their application as electrocatalysts for the Oxygen Reduction Reaction (ORR). In the synthetic route, the oxidizing agent was varied (*i.e.* $(NH_4)_2S_2O_8$ for samples labelled as MH_N and $KMnO_4$ for MH_K ones) to study the correlation between the physico-chemical properties and the electrochemical performances of the nanopowders. Indeed, it has been possible to observe that both the oxidants cations and Ti-dopant ions play a pivotal role in modifying the nanopowders structural, morphological and surface properties. For the electrochemical tests, Linear Sweep Voltammetries (LSVs) have been carried out in KOH (-1.0 – 0.0 V *vs* SCE). Gas Diffusion Electrodes (GDEs), prepared by adding the synthesized uncalcined $MnO_2$ to the air-cathode slurry, have performed explicitly better than GDEs made of only carbonaceous matrixes, proving synthesized $MnO_2$ to be good electrocatalysts for the ORR (4). Furthermore, GDE(MH_K) seems to have less diffusive limitations probably due to the much higher $O_2$ permeability, which is connected to the greater MH_K pore volume (confirmed by BET analyses). On the kinetic point of view (Tafel elaborations), high values of exchange current densities have been determined for GDEs with Ti-doped nanopowders. In particular, the presence of 5% Ti-doped MH_N has led to an increase of almost six orders of magnitude (4). Parallel to the above investigation, a preliminary forefront study about the use of MH_K sample (chosen for its highest BET surface area) for $CHCl_3$ detection was developed. Thus, Glassy Carbon Electrodes (GCEs) were modified by drop casting of a suspension of the adopted $MnO_2$ in DMF (20 μL, 0.5 g $cm^{-3}$). Contrary to the response obtained with only GCE (no peaks evidence), the presence of $MnO_2$ (at neutral pH) has caused the appearance of two peaks in the Cyclic Voltammetry (CV) anodic scan (ascribable to two characteristic reactions of $MnO_2$) and a further broad peak in the cathodic scan (at -0.5 V *vs* SCE) that can be due to the reduction of $O_2$ (5). The presence of chloroform has led to a linear decreasing of the specific CV peaks currents, because of the adsorption of the pollutant molecules onto the electrode surface (indirect detection method).

In conclusion, the present Thesis work focused on the deep investigation of bare and Ti-doped $MnO_2$ electrocatalytic nanoparticles showing novel and promising results (3,4).

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# Premio di Laurea "Photo Analytical SRL": Electrospun Polymer Separators Based on PVdF-PEO Blends for Li-Ion Batteries

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Li-ion batteries are one of the most mature and most wide spread energy storage systems on the market. Today Li-ion technology is approaching its limits of energy density (200–250 Wh/kg) (1) thanks to new and advanced high-voltage and high-capacity electrode materials. Hence, most electrochemical research seeks to improve cycle life and safety. However, in order to meet the new conditions required by high-voltage electrodes and to enhance the other aforementioned features, the development of so-called inactive materials is mandatory. A key inactive material is the separator. In the last years electrospun polymer separators (EPS) have gained great attention for applications in lithium batteries (2) thanks to their good mechanical properties, high porosity and safety improvements. Polyvinylidenedifluoride (PVdF) and its copolymers are probably the most widely studied (3). PVdF is characterized by excellent electrochemical stability, and its high dielectric constant ($\varepsilon = 8.4$) permits better dissolution of lithium salts and, thus, a larger amount of charge carriers. One PVdF drawback is a high melting point that does not execute the shutdown function (4). We submit a novel strategy to overcome this limitation by blending PVdF with a polymer of lower melting-point such as polyethyleneoxide (PEO), which can also coordinate and transport $Li^+$ through local relaxation and segmental motion of its chains. Two blends with the same composition (PVdF:PEO, 90:10 w/w) were prepared using PEO of different molecular weight (Mv 100,000 and 1,000,000). For the sake of comparison, an EPS of PVdF was also prepared. The PVdF-PEO based separators ensure increased conductivities, greater electrolyte uptake and higher porosities than commercial polyolefines, all factors that improve cell performance (5,6). They are also safer than PVdF separators thanks to lower shutdown temperature, even if their mechanical properties are not yet comparable with those of the latter. The two blends were soaked in 1M $LiPF_6$ – ethylene carbonate:dimethyl carbonate (1:1 w/w) and the electrochemical performance were tested in a Li/EPS/$LiFePO_4$ cell and discussed on the basis of their physical, mechanical, thermal and morphological properties.

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# Premio di Laurea "Ametek Scientific Instruments": Electrochemical Conversion of Carbon Dioxide to Formic Acid. Study of the Effect of the Operating Parameters.

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Electrochemical conversion of $CO_2$ is considered one of the more appealing approaches to introduce renewable energy in the chemical and energy chain and to mitigate the greenhouse gases effect. In this work, the reduction of carbon dioxide was performed in undivided electrochemical cell to produce formic acid, which is one of the highest value-added chemicals and economically feasible for large-scale applications (1). It is well known that the main hurdle of the reduction of $CO_2$ from water solution is the low $CO_2$ solubility in water. In order to overcome this obstacle, a specific investigation on the effect of the $CO_2$ pressure and other operating parameters at tin flat cathodes was carried out. It was shown that an increase of the pressure leads to a drastic enhancement of the formic acid concentration. Indeed, the utilization of moderately high $CO_2$ pressures (15–30 bar) allowed to obtain high concentrations of formic acid (up to 0.46 mol $L^{-1}$) at high current density (up to 90 mA $cm^{-2}$) employing cheap and simple undivided cell (2).

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# Keynote e Conferenze su Invito

- ANA/ELE/GS KN01: Fabiana Arduini, Tor Vergata University, Rome
- ANA/ELE/GS KN02: Andreas Lesch, EPFL Valais Wallis, Laboratory of Physical and Analytical Electrochemistry, Sion
- ELE KN01: Riccardo Ruffo, Università di Milano Bicocca

# New sustainable and cost-effective paper-based electrochemical (bio)sensors

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Electronic equipment generated 9 million tons of waste in 2005 in EU, and it is expected to grow to more than 12 million tons by 2020. To decrease the environmental pollution of electronics, the development of sustainable sensors, including paper-based electrochemical devices, are attracting growing interest thanks to their cost-effectiveness, suitability for in situ analysis, and environmentally friendly.

In this keynote, we reported the recent advancements on paper-based electrochemical (bio)sensors for environmental, biomedical, and agrifood sectors carried out by our group.

We described a novel reagentless paper-based electrochemical phosphate sensor, manufactured with a simple and inexpensive approach. By following three easy steps, consisting of wax patterning, paper chemical modification, and electrode screen-printing, the filter paper provides an effective electroanalytical platform to sense phosphate ions in standard solutions and in real samples (river water). This novel and highly sustainable configuration allows for the determination of phosphate ions with high reproducibility thanks to the use of heptamolybdate as reagent loaded on paper and carbon black as ink nanomodifier, achieving a detection limit of 4 mM. The filter paper has been also combined with the butyrylcholinesterase enzyme (BChE) for the detection of pesticides in rivers and wastewaters. The principle of this approach is based on dual electrochemical measurements, in parallel, of butyrylcholinesterase enzyme activity towards butyrylthiocholine, with and without exposure to contaminated samples. The sensitivity of this device is largely improved using a carbon black/Prussian Blue nanocomposite as a working electrode modifier. A strip of a nitrocellulose membrane, that contains the substrate, is integrated with a paper-based test area that holds a screen-printed electrode and BChE, allowing a reagent-free detection of Paraoxon down to 3 μg/L. Beside the filter paper, the office paper has also been exploited as substrate to print the electrode. An office-paper based sensor has been developed for monitoring Zn(II) in biological fluids. The printed sensor modified with bismuth film has been used to detect it by stripping analysis, with a detection limit of 25 ng/mL and a relative standard deviation of 8%. To highlight the feasibility, reliability, and easiness of the proposed electrochemical sensor, Zn(II) has been detected in serum and sweat at a physiological level (μg/mL). The sensor printed on office paper has been also combined with alcohol oxidase enzyme for the detection of ethanol in beer samples. After optimizing the analytical parameters, such as pH, enzyme, concentration, and working potential, the developed biosensor allowed a facile quantification of ethanol up to 10 mM, with a detection limit equal to 0.52 mM. Recently, we have also combined the sensor fabricated using wax printing and screen-printing technologies with a printed holder made by a 3-D printing technology. This device is able to measure the BChE activity in serum, with a linear range up to 12 UI/mL and a detection limit lower than 1 UI/mL.

# Preparing Nanoparticles on Large Electrodes Using Inkjet Printing and Flash Light Irradiation

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Coating electrodes with catalytically active metal and alloyed metal nanoparticles (NPs) can improve significantly the performance of commercial electrocatalytic and (bio)analytical devices. Nevertheless, the price of many noble and scarce metals requires sustainable strategies to synthesize NPs and to prepare nanoparticle-decorated surfaces. In addition, the cost-effective and high-throughput optimization of the NP properties as a result of the NP size, shape, composition and synergistic effects with support materials is very attractive for academia as well as industry. This is especially true if process conditions are easily tunable, highly reproducible and fully up-scalable.

The fabrication of NP-coated electrode surfaces can be achieved in various ways, usually started with a NP synthesis, with or without support particles and dispersed in solution, before an ink or paste is formulated. Subsequently, this mixture is casted by dropping, dispensing or printing onto the sensing device structure. Afterwards, thermal post-processing results in the removal of solvents and stabilizers achieving electrodes with catalytically active and well-adhered NPs. Alternative strategies apply metal precursors that are electrochemically, (photo)chemically or thermally (thermal decomposition by equilibrium heating in a furnace) converted into the according NPs.

In this contribution, we demonstrate our novel approach where defined thin films of metal precursors, e.g. chloroplatinic acid, are first deposited onto various electrode surfaces by using inkjet printing and then irradiated with a high energy light pulse from a Xenon flash lamp to generate NPs within a fraction of a second (1). Due to the rapid absorption of the flash light by the precursor-coated electrodes temperatures of several hundred degrees Celsius are generated immediately inside the printed films. The result is a rapid thermal decomposition of the precursor into the pure metal or alloyed metal nanoparticles. As for the well-known thermal decomposition processes at equilibrium heating conditions, side products are simply gaseous (e.g. HCl, $Cl_2$ and $H_2O$) leaving pure metal on the electrode surface (2-3).

We use an integrated inkjet printing (with three printheads) and flash light irradiation platform to prepare the NP-decorated electrodes (e.g. Pt deposited on ITO, graphene or carbon nanotubes) of square centimeter size only within few minutes at ambient conditions (4). This allows a rapid optimization and up-scaling of the process outcome. The final electrodes were optically and electrochemically analyzed, the latter in particular with Soft-Probe Scanning ElectroChemical Microscopy (Soft-Probe-SECM) (5).

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# Negative Electrode Materials for Sodium Ion Batteries

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The world annual consumption of energy is in the range of 100 TWh whose largest part of this energy is supplied by fossil fuels or nuclear plants. Both these technologies are nowadays considered as not sustainable, however the global energy demand is still increasing. In this dim picture, renewable energy supplied by sun, wind, earth crust heat, and sea represent a viable and environmental friendly alternative which is leading to the investigation, development, and commercialization of new technology such as solar cells, wind mills, heat pumps, etc. The full exploitation of the energy produced by these primary sources, which are intrinsically intermittent, represents another technological issue which is currently approached by the design of better energy distribution grids and the large use of energy storage devices. Moreover, an important part of the total energy consumption is related to the automotive field, where fossil fuels still play a predominant roles. Just in the last few years the automotive market is showing an exponential growing interest in electrical power units to feed hybrid or full electrical vehicles.

Electrochemical energy storage units are currently used in high or low tech portable devices. The most demanding high tech tools require the use of high energy density system, such as lithium ion batteries. Smart grid developers or automotive engineers are looking with growing interest at the development of better batteries with higher performances, however, the figure of merits depends on the specific applications. Few years ago, due to the large use of lithium, several investigators are questioning about its availability and possible material shortness. There are several answers to this issue: the design of better lithium based systems (lithium air, lithium sulfur), the lithium recycling, actually non convenient, or the development of lithium free battery technology.

Aim of the present contribution will be the description of the current researches performed at the Material Science Department of the University of Milano Bicocca on materials for sodium ion secondary battery, focusing in particular on the negative electrode. Usually, research efforts in this field are directed towards the production of optimized phases by a trial and error procedure focused on the electrochemical performances rather than a full understanding of the mechanism beyond the electrochemical reaction. In our case, however, the scope is to elucidate the structure properties correlations by combining SEM, TEM, XRPD, and Raman measurements with the electrochemical behaviour in half cells vs. metallic sodium. Several phases, representative of different reaction classes have been investigated: conversion oxides ($Co_3O_4$, $Fe_2O_3$), intercalation or pseudo-capacitive oxides ($TiO_2$), and carbons, which show different reaction mechanism depending on their properties. Specific morphologies were designed to optimize the sodium uptake/release from the electrolyte addressing preparation routes towards proper particle size and shape.

# Comunicazioni Orali

# Dynamic impedance spectroscopy of a Prussian blue derivative thin film

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Dynamic multi-frequency analysis (DMFA) has been proposed as a technique to measure non-stationary impedance spectra, in order to extract kinetic parameters of unstable systems under non-stationary conditions. This allows an in-depth understanding of reaction pathways as the evolvement of the kinetic parameters can be monitored. We have demonstrated that the data fitting can be performed with standard equivalent circuits (1). Herein we show the application of DMFA on the measurement of the kinetic parameters for the intercalation reaction of cations in Prussian blue derivatives. The working electrode consists of a 1 mm glassy carbon electrode coated with a layer of electrodeposited Nickel hexacyanoferrate (NiHCF), which is unstable under oxidation. The electrolyte is composed by 0.5 M $A_2SO_4$ [A=Na, K] in water. The DMFA is performed by using multi-sine perturbation, which covers the frequency range from 8 Hz to 100 kHz, and it is added to a quasi-triangular cyclic voltammetry with scan rate equal to 160 mV $s^{-1}$. The impedance of the system is obtained using a modified definition of the dynamic impedance, based on the inverse Fourier transform (iFT):

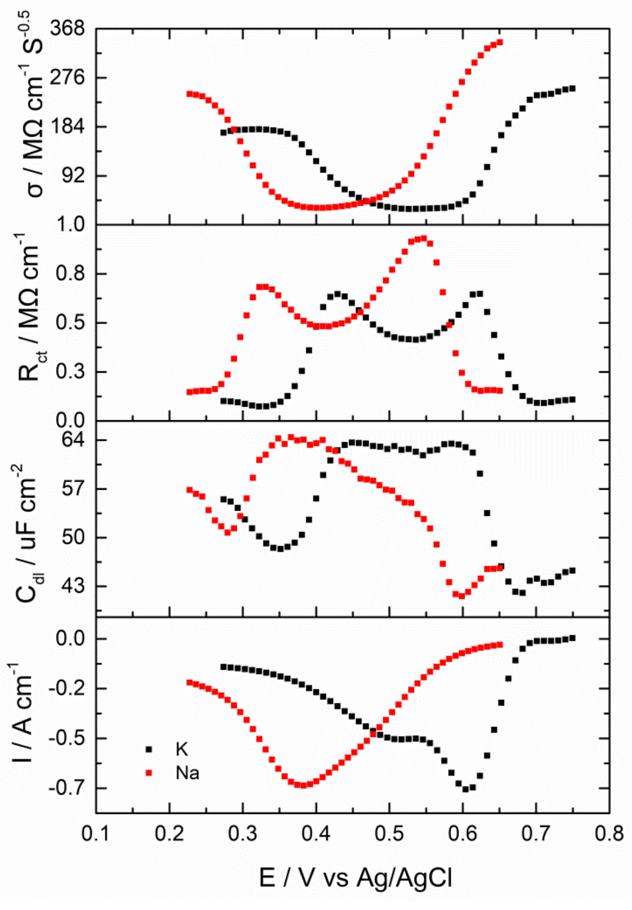

*Figure: Dependence of kinetic parameters on the polarization potential in the cathodic scan.*

$$Z(\omega, t) = \frac{\mathrm{iFT}\left[\Delta U \cdot f(\omega, bw)\right](t)}{\mathrm{iFT}\left[I \cdot f(\omega, bw)\right](t)}$$

where f represents a filter function, ω and bw are the central frequency and the bandwidth of the filter, respectively, and t is time. The obtained impedance spectra were fitted using an algorithm based on the non-linear least squares minimization with an additional constraint on the smoothing of the fitting parameter. The impedance spectra were fitted using a modified porous electrode model, taking into account a single step mechanism for the intercalation of the ion in the host structure. The fitting had a standard deviation $\chi^2$ lower than $9.0 \cdot 10^{-4}$. The dependence of the parameters such as interface capacitance ($C_{dl}$), charge transfer resistance ($R_{ct}$) and Warburg coefficient (σ) on the potential in the cathodic scan is shown in the figure. The evolution of the parameters with the polarization potential will be discussed in the frame of the model for intercalation.

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# The mixed olivine Li($Co_{1/3}Fe_{1/3}Mn_{1/3}$)$PO_4$ material as positive electrode for lithium batteries

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Polyanion-type electrode materials are one of the great success in the field of electrochemistry: within this family, $LiFePO_4$ (LFP) is a now mature material exploited as cathode material in lithium-ion cells. Recently the attention of the scientific community is focusing the advantage of the substitution in the LFP olivine lattice of Fe with Mn, Co or Ni. In fact the $Mn^{3+}/Mn^{2+}$ and $Co^{3+}/Co^{2+}$ couples show increasing redox potentials, thus opening the door to improvements in the energy performances. The mixed $LiCo_{1/3}Fe_{1/3}Mn_{1/3}PO_4$ (LCFMP) stoichiometry is one of the most promising one. Compared to LFP in lithium cells (LIC) the LCFMP cathodes shows a similar practical specific capacity (120 mAhg$^{-1}$) and an higher working potential (4.2 V vs. Li to be compared to 3.5 V vs Li of LFP). In our laboratories developed an original synthetic route by exploiting a solvothermal treatment followed by an high temperature pyrolysis with sucrose. Our characterization suggests that the LCFMP material consisted in an single phase (see figure 1a for the X-ray diffraction pattern, XRD) crystallized in an olivine lattice similar to LFP (space group 62 Pnma with cell parameters a=10.332Å, b=6.014 Å, c=4.720Å) with an homogeneous round-shaped particle morphology of approximately 50-150 nm in diameter (see figure 1b). Moreover the LCFMP material is free from any contamination from pyrophosphates or $Li_3PO_4$ as highlighted by FTIR.

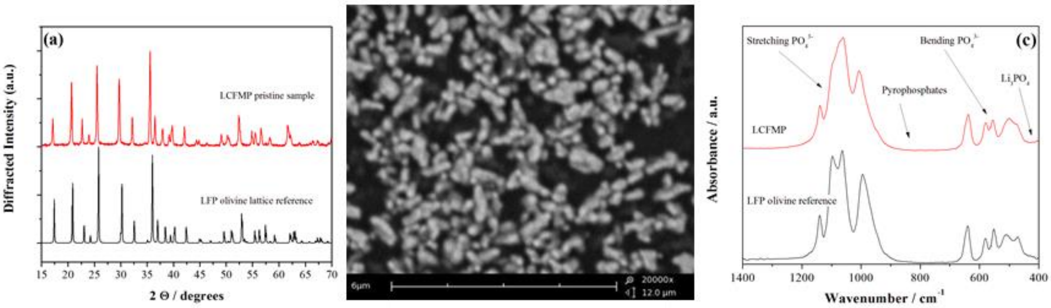

Figure 1. (a) XRD pattern of the LCFMP sample, (b) SEM micrograph and (c) FTIR spectra compared to the reference LFP phase.

The LCFMP electrodes are able to supply a specific capacity in galvanostatic tests on LICs that exceeds 165 mAhg$^{-1}$ in the first charge (corresponding to the full de-lithiation, being the maximum theoretical capacity 167 mAhg$^{-1}$) and 110 mAhg-1 in the first discharge (corresponding to 67% of reversible lithium incorporation). The capacity retention at cycle 20 is approximately >90% in discharge compared to cycle 1.

# Hole site energies and electronic couplings for hole transport in DNA inferred from electrochemistry and quantum chemical predictions

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Singly ionized DNA exhibits long range hole transport (HT) covering distances up to 200 Å (1). Hole transport has great biochemical and technological relevance, as it controls the site distribution of the oxidative damage in DNA and makes DNA a potential conduit for nanoelectronics. Different mechanisms for the hole transport have been invoked so far: ion gated transport, thermal activated hopping, and superexchange among others. Independent of the kinetic mechanism, hole transfer in oxidized DNA is modulated by the complex mosaic of low-lying electronic states, whose accessibility depends on the effective in-situ hole energies of nucleobases and the electronic couplings between interacting nucleobases (2,3).

The hole energies for adenine (A) and guanine sites were quantified by using voltammetry, the influence of hydrogen bonds on the oxidation potential was also determined. Information for cytosine oxidation was inferred by spectroelectrochemistry experiments (4-6).

Herein we have used the above data to obtain a complete set of hole-site energies and electronic couplings covering all nucleobases, including pyrimidines, which are very difficult to oxidize in solution. The above quantities have been estimated by analyzing in terms of the two-state model the oxidation potentials inferred from differential pulse voltammetry and the ionization potentials predicted by quantum chemical computations carried out for oligonucleotides including the sugar-phosphate backbone and solvation

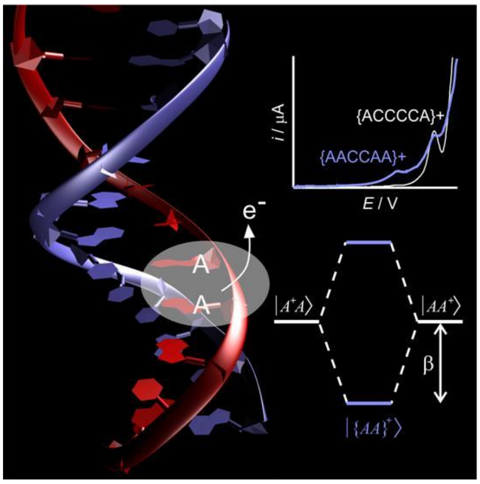

**Figure 1: differential pulse voltammograms of adenine-rich single stranded oligonucleotides rationalized in terms of the two-state model.**

Hole energies and electronic couplings were then used as parameters in a simple tight-binding model Hamiltonian, which allows for the prediction of reliable estimates of the oxidation potential of any DNA sequence. As an example, the lowering of the oxidation potential for single stranded oligonucleotides containing an increasing number of adjacent adenines is predicted to be ca 0.25-0.30 V for the AA step, in good agreement with voltammetric observations (0.27-0.31 eV). That result testifies that adenine tracts give rise to delocalized hole domains (Figure 1), greatly facilitating hole transport in DNA (7). Although stacking interactions are found to be less effective in stabilizing the positive charge on adjacent guanines inside a strand, our model confirms that consecutive guanines constitute a very efficient trap for the hole (8).

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# Co-axial Nanostructures for energy conversion: synergic effects between carbon nanotubes and metal oxide

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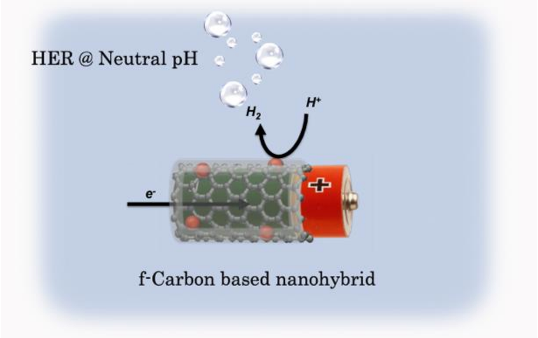
The growing need for energy on global scale and the realization that the so called oil-based economy cannot sustain our world anymore, prompted researchers to find new ways to "power" the planet.(1) In particular a lot of efforts have been done in the field of chemical energy conversion, that remains very challenging because of the requirement for higher efficiencies.(2) The splitting of water to high energy chemical fuels is one of the most attractive and pursued alternatives; among the major issues there is the need to find catalytic systems that are able to boost the overall reaction efficiently and durably.(3)

In this context our group recently focused the attention on the study of catalytic systems for the oxygen reaction (such as oxygen evolution (4) and oxygen reduction (5)). Our last efforts have been done in the development of new C-based nanocomposites that combine the unique properties of multiwall carbon nanotubes (MWCNTs), metal oxides ($TiO_2$ and $CeO_2$) and Pd nanoparticles (Pd NPs).(6) The nanocomposites MWNT@Pd/$TiO_2$ and MWNT@Pd/$CeO_2$ have been designed and evaluated as electrocatalyst for the reaction of hydrogen evolution (HER) and for the $CO_2$ reduction, respectively.

Both systems exhibit very good performances and efficiencies, showing physical and chemical properties that differ to those expected from the simple sum of the individual building blocks. Due to these synergic effects, we shed light on the role of the MWCNTs in terms of their influence on the electronic properties of the two semiconductors (e.g. presence of surface states and different doping levels), resulting in better electrocatalytic activities.



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# The use of rotating disk electrode to measure a complete set of kinetic and thermodynamic ATRP parameters

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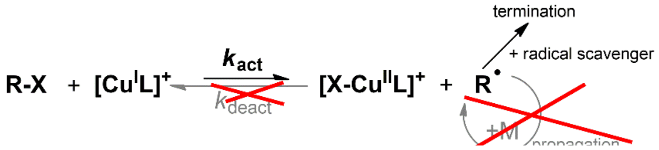
Electrochemical tools are extensively used to study mechanisms and kinetics of various processes. Atom Transfer Radical Polymerization (ATRP) is the foremost technique in the synthesis of macromolecules with predetermined molecular weights (MWs), narrow MW distribution and finely tunable architectures. A thermodynamic and kinetic understanding of this process is required for a wise selection of the proper setup and experimental conditions.

In 2011, we firstly proposed the use of a rotating disk electrode (RDE) to measure the activation rate constant, $k_{act}$, of ATRP, with relative ease and precision compared to traditionally used techniques (UV-Vis, stop-flow) (1,2). The activation reaction is kinetically isolated by adding an excess of a radical scavenger that reacts with generated radicals (**Scheme 1**). $k_{act}$ is measured by monitoring the decrease of limiting current of $[Cu^IL]^+$ oxidation, which is proportional to the amount of catalyst consumed by reaction with the initiator, RX.



**Scheme 1. ATRP mechanism for $k_{act}$ determination.**

Recently, we adapted this approach to measure the equilibrium constant, $K_{ATRP}$. Indeed, by simply omitting addition of the radical scavenger and allowing the system to equilibrate, $K_{ATRP}$ can be determined by using a slightly modified version of an equation proposed by Fischer (3). Under particular conditions, $K_{ATRP}$ can be determined only by using a huge excess of RX, otherwise Cu(I) is consumed by a side reaction known as Cu(I) catalyzed radical termination (CRT) (4). However, once $K_{ATRP}$ is measured, $k_{CRT}$ can be obtained with the same technique if $C_{Cu(I)} = C_{RX}$. Moreover, under the last cited conditions, an excess of radical scavenger can be added after few minutes, allowing the simultaneous determination of $k_{act}$ and $K_{ATRP}$ (**Fig. 1**). $k_{deact}$ is then known as $K_{ATRP}/k_{act}$. Concluding, by means of RDE, the complete set of thermodynamic and kinetic parameters of ATRP can be quickly determined. The reproducibility of the data was also carefully verified.

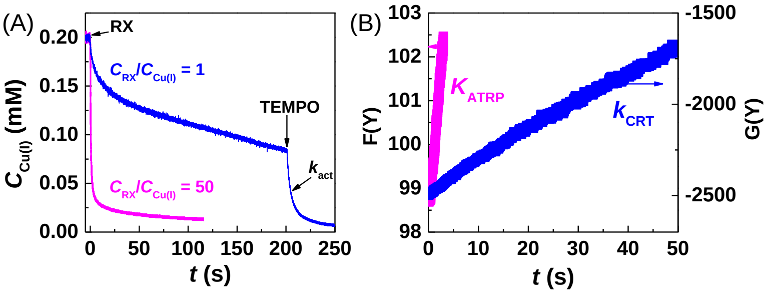


**Figure 1. Disappearance of Cu(I) vs. time (A) and fitting of elaborated data (B) for the reaction of $10^{-3}$ M $[Cu(I)Me_6TREN]^+$ with methyl 2-bromoprorionate in MeCN, T = 40 °C. F(Y) and G(Y) are functions of $C_{Cu(I)}$.**

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# Graphene-Based "Core-Shell" Hierarchical Nanostructured Low-Pt Electrocatalysts for Proton Exchange Membrane Fuel Cells

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The operation of proton exchange fuel cells (PEMFCs) is bottlenecked by the sluggishness of the oxygen reduction reaction (ORR) (1). Accordingly, the development of advanced electrocatalysts (ECs) capable to promote the ORR kinetics is one of the main goals of the research. It is further highlighted that, as of today, the only ORR ECs capable to provide PEMFCs with a performance level compatible with applications require a high loading of strategic elements such as platinum-group metals (PGMs), raising critical issues associated with supply shortages and high costs (1).
This work addresses the above points by the development of innovative ECs characterized by the following features: (i) a low loading of PGMs; (ii) an improved ORR activity in comparison with conventional state-of-the-art ECs (2); (iii) a *"core-shell"* morphology. In the proposed ECs the *"core"* support exhibits a hierarchical structure including the following constituents: (i) graphene flakes, to exploit the benefits associated with the large specific surface area and high electron mobility of graphene (3-6); (ii) carbon black nanoparticles, to further promote the mass and charge transfer processes of the ECs; and (iii) copper nanoparticles, which are introduced as a sacrificial component modulating the EC morphology and the chemical composition of ORR active sites. The hierarchical *"core"* support is covered by a carbon nitride *"shell"*, providing *"coordination nests"* that embed the ORR active sites (7). The latter are based on a very low loading of Pt (*ca.* 3 wt% of the EC) and also include Ni and Cu as *"co-catalysts"*. The proposed L-PGM ECs are obtained customizing the synthetic protocol devised in our research group (7). In this work, the final ECs are obtained after a post-synthesis activation process carried out by electrochemical cycling, that plays a crucial role to modulate the physicochemical properties and the morphology. Preliminary results indicate that the proposed approach is promising, as the proposed L-PGM ECs exhibit an improved specific and mass activity in comparison with the state of the art.
The assay of the metals in the L-PGM ECs is evaluated by inductively-coupled plasma atomic emission spectroscopy (ICP-AES). Vibrational spectroscopies (e.g., confocal micro-Raman) and wide-angle X-ray diffraction (WAXD) are adopted to probe the structure. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM), both conventional and at high resolution, are used to study the morphology. Cyclic voltammetry with the rotating ring-disk electrode method (CV-TF-RRDE) investigates the electrochemical performance and ORR reaction mechanism. Finally, the fuel cell performance in operating conditions is tested on PEMFC prototypes including the proposed L-PGM ECs at the cathode.

Acknowledgements: This work was funded by the Strategic Project of the University of Padova "From Materials for Membrane-Electrode Assemblies to Energy Conversion and Storage Devices – MAESTRA". The research leading to these results has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement n°696656.

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# Microwave Assisted Pyrolysis of Waste Tires: Evaluation by Rotating Ring-Disk Electrode technique of the catalytic efficiency in O.R.R

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In recent years the fossil sources dependence of our society for both fuels and essential raw materials and the global warming have led to an increasing use of renewable sources and waste valorization processes. Nowadays the outstanding increase in the number of vehicles worldwide is among the most environmental problem because of the emission of harmful pollutants and the solid wastes disposal, in particular the removal of the used tires (1). There are several technologies for tires recycling. Thermal treatments may be used such as pyrolysis: a thermal decomposition process performed at higher temperature in an inert atmosphere which allows the transformation of complex substances in simple molecules. Pyrolysis transforms starting materials into three potentially useful classes of products: char, liquid and gas. These products can be easily stored, transported and used as a source of chemicals and energy. Among several heating technologies and apparatus used in pyrolysis process, microwave assisted pyrolysis (MAP) attracted attention, in recent years, due to the considerable advantages of this technology over conventional pyrolysis process (2,3,4). The use of microwaves requires the presence of material: water, carbon, metals or materials able to absorb microwaves and releasing energy. Recently Undri et.al (5) reported the correlation between experimental conditions of pyrolysis (MAP) and some of the characteristics of char. Interesting ICP-MS analysis showed the presence of several metal. It was observed that char obtained from microwave assisted pyrolysis of waste tires showed an interesting electrocatalytic activity in the Oxygen Reduction Reaction (ORR) in alkaline medium. ORR is regarded as one of the most important electrocatalytic reactions in electrochemical energy conversion system such as fuel cells and several industrials process. In order to speed up the ORR kinetics to reach a practically usable level in fuel cell, a cathode ORR catalyst is needed. Platinum-based materials are the most practical catalyst. Nevertheless, owing to the limited reserve in nature of Platinum-group metals, and their high cost, extensive research has focused on developing alternative catalyst. To remove and replace platinum with less expensive materials it was proposed to exploit a synergic mechanism with one metal able to break the O-O bond of molecular oxygen and second metal capable in reducing the adsorbed oxygen so formed. The basic idea of this work comes from the consideration that the presence of specific metals in addition to an appropriate rate together with a high carbon content are mandatory requirements for catalysts for ORR (6).

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# New evidences of platinum-yttrium alloyed nanoparticles formation on carbon support and catalytic activity for oxygen reduction reaction

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Recently, the preparation of Pt bimetallic systems has attracted considerable attention because the amount of Pt could be reduced while the catalytic activity and stability may be maintained or even improved, due to the so called "*geometric effect*" and "*ligand effect*". From theoretical calculations $Pt_3Y$ exhibits the second highest ORR activity ever measured on a polycrystalline electrode, surpassed only by single crystal $Pt_3Ni$ (111) and, above all, it has a catalytic activity greater than pure platinum (1,2).

In this work $Pt_xY$ NPs, where Y atoms are in part alloyed with the Pt, were synthesized via a solid state method involving the chemical reduction of $Pt(acac)_2$ and $Y(NO_3)_3 \cdot 6H_2O$ salt precursors by $H_2/N_2$ flow at high temperature on different carbon supports.(3)

The influence of the $Pt_xY$ formation, NPs shape and dimension, and ORR activity, in terms of mass activity (MA) and specific activity (SA), were investigated with different commercial and homemade carbon support, which possess different surface area, porous distribution, conductivity and surface functional groups. XPS and XRD analysis confirmed the $Pt_xY$ alloy formation. The best syntheses afforded small spherical $Pt_xY$ NPs (2.71 nm) on a commercial Carbon Black ($Pt_xY$@MC7) and on MWCNT ($Pt_xY$@MC5), which showed a higher current densities than the Tanaka catalyst but containing a lower amount of Pt. The mass activity determined at 0.9 V vs RHE were 606 $mA/mg_{Pt}$ and 453 $mA/mg_{Pt}$, respectively. The catalytic activity towards ORR was compared with the commercial Tanaka taken as standard reference (205 $mA/mg_{Pt}$), confirming the increased activity of the $Pt_xY$ alloy.

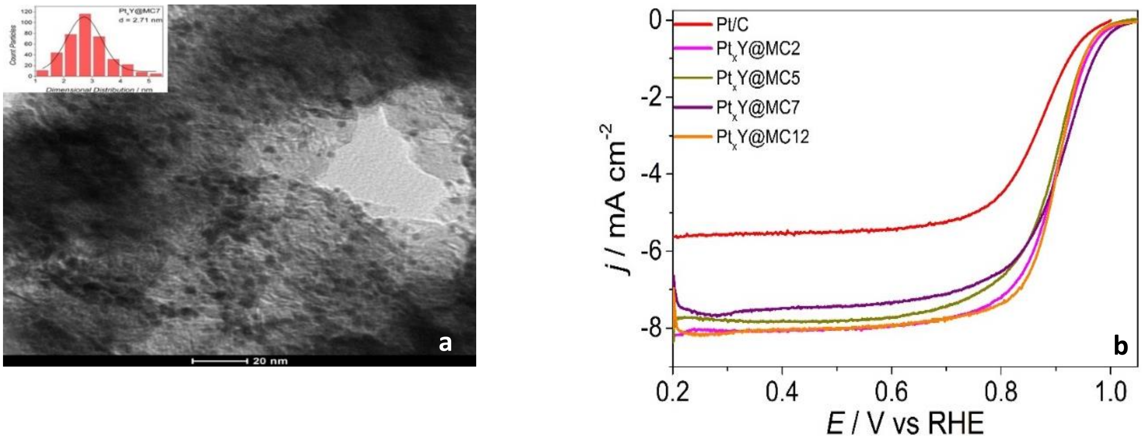

Figure 1 (a) TEM image for the best Pt-Y/C catalysts and particle size distribution; (b) LSV on several prepared catalysts and Tanaka Pt/C 50% in $O_2$ saturated 0.1 M $HClO_4$ recorded at RDE, $v$ = 20 $mVs^{-1}$, rotation rate 1600 rpm.

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# Fabrication of Hf-Nb Anodic Oxides and Their Use in Resistive Switching Devices

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In last decades scientists efforts have been devoted to find new materials to replace $SiO_2$ as dielectric in micro and nanoelectronics devices. Among transitional metal oxides, $HfO_2$ is nowadays one of the most suitable materials due to their peculiar features, such as large band gap (5.1-6.1 eV), high dielectric constant (20-25), low leakage current and thermal stability with Si (1). For electronics applications, such as ReRAMs (Redox-based resistive switching memories), uniform, flaw-free and smooth oxides are necessary, joined with a detailed understanding of chemical and physical properties as a function of the fabrication conditions. Despite the oxide films have macroscopic dielectric (high-*k*) properties, deposited as nanoscale thin films they behave as solid electrolytes (2). Anodizing is a low-cost electrochemical technique which allows to grow barrier-type oxides on valve metals (Hf, Nb, Ta, Ti etc.) surface whose structure, morphology, composition and thickness can be easily tailored by controlling the process parameters. Recently it was also reported that alloying low amounts of Nb to Hf substrate leads to anodic films with higher dielectric constant with respect to that of pure $HfO_2$ (3). In order to properly change anodizing conditions to obtain suitable oxides features, a study about growth kinetics of Hf-Nb mixed anodic films is needed, since amorphous-crystalline transition during the oxide growth was reported in literature for similar anodic films, with consequent detrimental effects on oxides properties (4).

This work is aimed to study the changes of oxides features during anodic films growth of sputtering-deposited Hf-Nb alloys. Mixed oxides were prepared by anodizing alloys with different Nb content (from 4at.% to 76at.% of Nb) in neutral electrolyte with different growth rates and up to different formation voltages. Morphological and structural features were analyzed by *ex-situ* X-Ray Diffraction, Glow Discharge Optical Emission Spectroscopy, Transmission and Scanning Electron Microscopy, X-Ray Photoelectron Spectroscopy. Photoelectrochemical measurements, differential capacitance and impedance measurements were carried out in order to study oxides solid state properties and to estimate their dielectric constant. Finally we fabricated ReRAM-type devices by depositing Pt top electrodes on the anodic films surfaces. Electrical characterization was performed to check, first of all, whether these devices exhibit resistive switching and, in addition, they are suitable for the use in redox-based memories.

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# Photosynthetic microbial fuel cell with polybenzimidazole-type membrane: highly efficient synergy between bacteria and microalgae for simultaneous wastewater removal and biorefinery

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There is growing interest towards simultaneous production of bioenergy and valuable materials by PMFCs. We showed very efficient systems based on polybenzimidazole as separator. Two cells were investigated, Pt-electrocatalysed and Pt-free, operated as microbial carbon capture devices, by using wastewater as anolyte and *Scenedesmus acutus* strain in the catholyte. The Pt-cell generated higher power density over 100 days, resulting in improved wastewater treatment efficiency.

The $CO_2$ fixation of PMFC grown microalgae leaded to high production of valuable compounds. Significant quantity of lutein was obtained, as well as relevant amount of other carotenoids. Lipids were excellently accumulated ($49\%_{dw}$) in the $C_{16-18}$ range, particularly indicated for the biofuel production.

We demonstrate the implemented sustainability of such PMFCs as technology for simultaneous wastewater treatment and biorefinery. The use of PBI is very promising for energy performances and sustainability. It is also autoclavable, so allowing a re-use of the separator with beneficial cost effects.

# Nanoclusters based on CoNC and FeNC for oxygen reduction reactions and their application at the cathode of a direct methanol fuel cell

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Polymer electrolyte fuel cells (PEFCs) are attracting remarkable interest as an alternative power source with low environmental impact. Direct methanol fuel cells (DMFCs) are a subcategory of PEFCs well suited for portable applications. Nowadays, the widespread commercialization of a DMFC is hindered by the cost of the components. This cost is, in part, due to the precious metals, in particular Pt, used as the catalysts of the fuel cell. To solve this problem, the attention of many researchers is focused on the replacement of the expensive Pt catalyst with more abundant non precious metals. Here, in-house CoNC and FeNC have been prepared by, first, chelating the metals with ethylene diamine tetra acetic acid, known as EDTA (nitrogen precursor). UV-Visible (UV-Vis) spectrometry has been used to ensure the chelated metal formation. In the next step, the chelated metals have been deposited on a high surface area oxidized carbon support to increase the electrical conductivity. The latter composite material has been thermally treated at 800°C (CoNC8 and FeNC8) or 1000°C (CoNC10 and FeNC10) in nitrogen atmosphere in order to create the catalytic sites that will be able to perform the oxygen reduction reaction (ORR) in the acid medium. Electrochemical tests have been carried out to investigate the activity of the electro-catalysts for the ORR and the performance and durability in DMFCs. Moreover, some portions of the most performing electro-catalysts have been treated in $HNO_3$ to leach out the unalloyed ions and, then, thermally treated a second time. Informations about the crystalline structure, size and morphologies have been obtained by X-ray diffraction (XRD) and transmission electron microscopy (TEM) techniques, whereas the elementary percentage composition has been studied with CHNS analyser and energy dispersive X-ray spectroscopy. Finally, the nature and the oxidation states of the nanoclusters have been related to the electrochemical results by using X-ray photoelectron spectroscopy (XPS).

# Gel polymer electrolytes for high-loading sulfur composite electrodes in Li-batteries

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Important safety hazards are related to the use of liquid electrolytes in lithium batteries, due to the volatility of organic molecular solvents, the limited temperature range for safe ion conduction and fear of leakage of the solution.

Various attempts have been made to overcome these problems. An approach, which reduces flammability, is the replacement or the hybridization of volatile solvents with ionic liquids (ILs). Moreover, the idea of using IL-Li salt solutions or their mixture with molecular solvents to form gel-type polymer electrolytes (GPE) has been successfully demonstrated, achieving improved safety and stability (1,2,3).

In this work, optimized liquid electrolytes, composed by ether-based solvents with and without an ionic liquid additive, were used to swell selected polymer matrices. The proposed GPEs reveal advanced performance in Li-S batteries, by addressing the issue of sulfide anions dissolution from high-loading sulfur cathodes.

Two different approaches, suited for polymer matrices based on polyethylene oxide (PEO) and polyvinylidene fluoride (PVdF), will be discussed. In both cases, a pristine membrane is first prepared and then activated by the liquid electrolyte, according to a well addressed swelling procedure.

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# Study of the influence of the electrolyte on the photoconversion properties of *p*-type dye-sensitized solar cells

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In the framework of the research on dye-sensitized solar cells of *p*-type (*p*-DSCs) the definition and optimization of the electrolyte have been the most crucial aspects for the reach of the recent records of photo-conversion for this type of photoelectrochemical devices (1-3). At the basis of this progress there was the replacement of the redox shuttle of reference $I_3^-/I^-$ (4) with opportune redox mediators which deliver higher photocurrents and produce larger open circuit photovoltages with respect to $I_3^-/I^-$. In the present study we intend to optimize the chemical composition of the liquid electrolyte for *p*-DSCs employing different couples of redox mediator, various additives for the stabilization of the photocathode surface (made of NiO), and variable concentrations of redox shuttle, supporting electrolyte and surface stabilizers. Beside the general conditioning of the overall performance, the analysis of the influence of *p*-DSC electrolytes has concerned the aspects of the extent of optical self-absorption of the electrolyte, of the chemical aggressiveness of the redox species and of the control of the phenomena of electronic back-donation by the photoreduction product. Non obvious correlations have been found between the four main cell parameters (overall efficiency, short-circuit photocurrent density, open circuit photovoltage, fill factor) and the conductivity of the electrolyte. Another relevant aspect of the investigations here reported has concerned the influence of the electrochemical stability of the electrolyte on the general performance of the *p*-DSC.

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# EMImCl/$(TiCl_4)_{1.4}$/$(\delta\text{-}MgCl_2)_x$ Ionic Liquid Electrolyte for Mg-ion Batteries

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The rapid advance in the fields of portable electronics, load leveling and peak shaving for the power grid and zero-emission automotive applications require the development of new and improved electrical energy storage systems (1). Since the 90's major improvements have been achieved in magnesium battery technology (2-4). In comparison to Li, Mg offers the following advantages: (i) a higher volumetric capacity (3832 vs. 2062 $mAh\cdot cm^{-3}$); (ii) far greater abundance in the Earth's crust, lowering the costs; (iii) a safer operation and a better compatibility with the environment; and (iv) an acceptable standard reduction potential (-2.36 vs. -3.04 V) (5-7). The main roadblock for these devices is the development of an efficient and stable electrolyte that is able to reversibly deposit and strip magnesium. Although Grignard and other organo-magnesium compounds exhibit good electrochemical performances (7), they do not exhibit an optimal stability due to their high vapor pressure and flammability. Ionic liquids dissolving a Mg salt with a high crystalline disorder were proposed as promising alternative electrolytes to organo-Mg systems owing to their good electrochemical performance and lack of flammability and thermal stability issues (8,9).

In the present work a new family of electrolytes is proposed, based on 1-ethyl-3-methylimidazolium chloride (EMImCl), titanium(IV) chloride ($TiCl_4$) and increasing amounts of $\delta$-$MgCl_2$. Specifically, four EMImCl/$(TiCl_4)_{1.4}$/$(\delta\text{-}MgCl_2)_x$ electrolytes, with $0.00 \leq x \leq 0.23$ are prepared and extensively characterized. The chemical composition was determined by Inductively-Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). The thermal stability was gauged using High-Resolution Thermo Gravimetric Analysis (HR-TGA) and the phase transitions are highlighted with Modulated Differential Scanning Calorimetry (MDSC). Chemical interactions were studied through Fourier-Transform spectroscopy in the medium and far infrared (FT-MIR and FT-FIR) regions and confocal micro-Raman spectroscopy. The electrochemical performance was studied with: (i) Cyclic Voltammetry (CV), to probe Mg deposition and stripping; (ii) Linear Sweep Voltammetry (LSV), to evaluate the electrochemical stability window; (iii) Chronopotentiometry (CP) experiments coupled with ICP-AES, to confirm and quantify the Mg deposition; and (iv) Broadband Electrical Spectroscopy (BES), to elucidate the long-range charge migration mechanisms of the electrolytes. High level density functional theory (DFT) based electronic structure calculations were undertaken to elucidate structures and vibrational frequency assignments.

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# Growth and Characterization of Atmospheric and Anodic Oxide Films on Weathering Steels

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Nowadays Weathering Steels are considered a good compromise between Carbon Steel, in terms of their corrosion resistance, and Stainless Steels due to their much lower price (1). They contain less than 3% of elements such as Cr, Ni, Cu and P, providing much higher atmospheric corrosion resistance due to the formation of thick (up to tens μm) passive films. Thanks to their properties COR-TEN (CORrosion resistance and TENsile strength) weathering steels can be widely use in coastal atmospheres for the construction of bridges, transmission tower, buildings, guardrails, lighting poles, ornamental sculptures, facades and roofs, and there has been an increase in the use of this material in recent years as part of the image of contemporary cities (2).

It is known that after a long term exposure in aggressive and corrosive ambient it is formed in WS surface an adherent rust layer with oxides/oxi-hydroxides mainly constituted by magnetite ($Fe_3O_4$), maghemite ($\gamma$-$Fe_2O_3$), lepidocrocite ($\gamma$-FeOOH), akaganeite ($\beta$-FeOOH), goethite ($\alpha$-FeOOH). Several papers tried to highlight the role of alligants in influencing the composition, structure and, consequently, corrosion resistance of passive films on WS (1,3). According to the authors these films show a multilayer structure with an inner compact and adherent layer constituted mainly by Cr, Cu or P enriched $\alpha$-FeOOH, and an outer porous layer working as a barrier toward diffusion of aggressive species toward the metal (1,3,4). Formation of $\alpha$-FeOOH is crucial to provide good corrosion resistance to WS, so it is necessary to understand how corrosion conditions can lead to the formation of a more or less protective compact rust layer.

In this work we studied the corrosion resistance of WS after long term atmospheric corrosion in quasi neutral aqueous solution without and with the addition of chloride ions. For comparison we also prepared anodic films on WS by potentiostatic polarization below and above the transpassive potential. Polarization curves were recorded to estimate the corrosion potential, the corrosion current density, as well as the pitting potential in presence of Cl- ions. Electrochemical impedance spectroscopy (EIS) was employed to estimate the polarization resistance. In order to get information on the electronic properties of the passive films, we also performed a photoelectrochemical investigation to estimate their band gap and conductivity type. We also studied the dependence of the measured capacitance as a function of the potential to highlight the formation of a compact thin barrier layer and a porous thick outer layer. All the experimental findings were finally used to get more insight the passivation mechanism of WS during exposure to atmospheric conditions.

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# Syngas production via co-electrolysis of $H_2O$ and $CO_2$ fed to a Solid Oxide Cell

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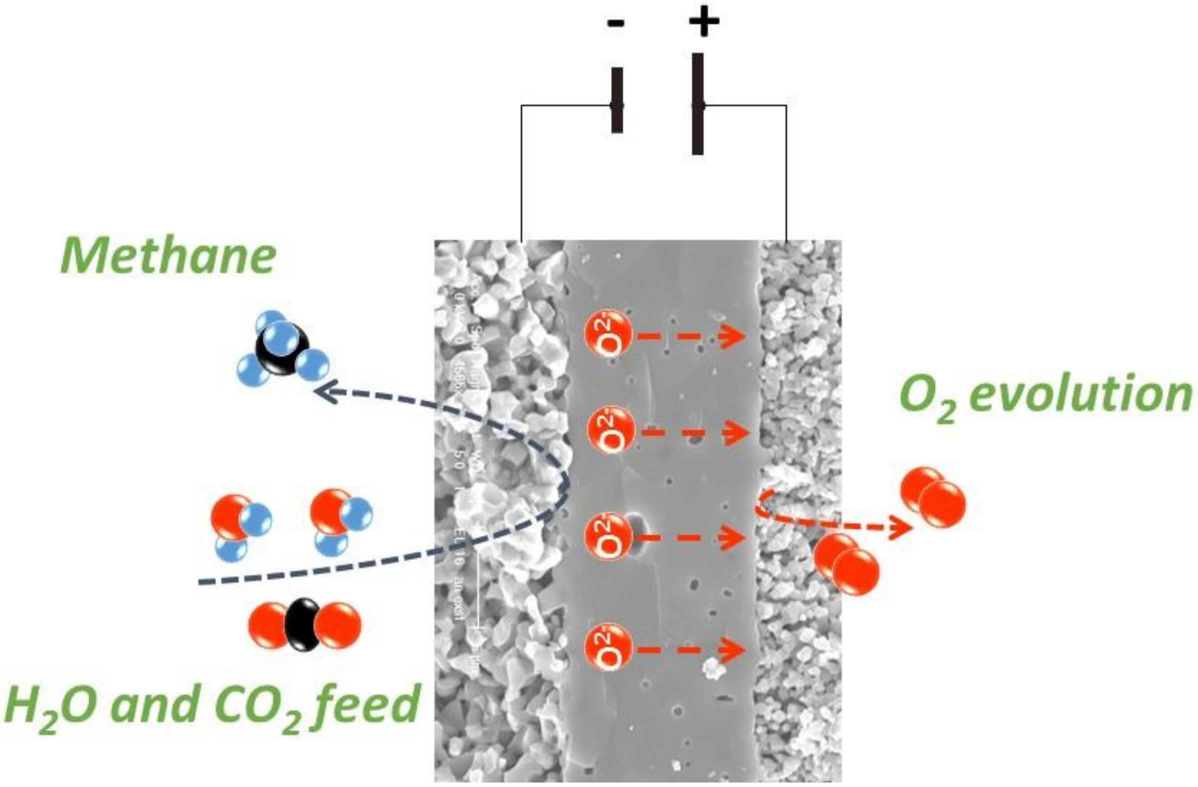
An investigation of syngas production using solid oxide electrolysis was carried out. A conventional solid oxide cell based on Ni supporting cathode, thin yttria-stabilized zirconia electrolyte, yttria-doped ceria interlayer, and strontium-doped lanthanum cobaltite and ferrite-based perovskite anode (Ni-YSZ/YSZ/YDC/LSFC) was used for the reduction of $CO_2$ and water to syngas. This process was assisted by $H_2$ added to the reactant in various amounts to maintain the Ni sites in a metallic state. This is necessary to favour $CO_2$ reaction and to avoid any ohmic constraint that may derive from the occurrence of Ni re-oxidation as consequence of the presence of oxidising species like $CO_2$ and water. The outlet gas was analysed by gas chromatography. The presence of CO and $CH_4$ beside $CO_2$ and $H_2$ was detected in the outlet stream. Analysis of outlet gas composition revealed that CO was produced by both electrochemical and catalytic mechanisms. Suitable conversions were achieved with dry gases.



SEM image of a planar SOEC operating in co-electrolysis mode

# Improvements of electrochemically mediated Atom Transfer Radical Polymerization of Styrene with ionic liquids

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Atom Transfer Radical Polymerization (ATRP) is a powerful and versatile polymerization technique for the synthesis of polymers and copolymers of precise architecture. Polymerization is mainly catalyzed by Cu complexes with amine ligands and a reversible exchange of a halogen atom between a dormant species $P_n$-X and $[Cu^IL]^+$, which produces the propagating radical $P_n^\bullet$ and $[XCu^{II}L]^+$, is at the heart of the process. The equilibrium is strongly shifted toward the dormant state ($K_{ATRP} << 1$), thus the concentration of $P_n^\bullet$ is very low and terminations are negligible (1). Electrochemically mediated ATRP (*e*ATRP) is an advanced ATRP technique allowing fast (re)generation of $Cu^I$ from $Cu^{II}$, easy control of the distribution of Cu(I) and Cu(II) species and the possibility of switching the process from active to dormant state and vice versa (2,3). Room Temperature Ionic liquids (RTILs) are green salts, which are gaining relevance in many applications for their non-volatility, non-flammability and versatility. They solvate a wide range of compounds in a wide range of conditions. In electrochemistry, they act as both solvents and background electrolytes, allowing elimination of additional supporting electrolytes. ATRP of styrene has several drawbacks including long reaction time due to propagation rate, high temperatures (>100 °C), limited conversion and limited solubility of polystyrene in polar solvents. 1-butyl-3-methylimidazolium trifluoromethanesulfonate, [BMIm][OTf] has been used for the first time in *e*ATRP of styrene. The results show that polymerizations performed in this ionic liquid are significantly faster than those in common organic solvents. However, the limited solubility of polystyrene in [BMIm][OTf] caused precipitation and poor control of the reaction. It was found that running the polymerization in ethyl acetate, a green solvent, using the ionic liquid as supporting electrolyte (less than 0.5 M) strongly enhance polymerization rate with narrow dispersity and higher conversion, compared to pure ethyl acetate. The polymerization of styrene was studied also in polar solvents such as dimethylformamide, dimethylsulfoxide and acetonitrile, where longer reaction times, higher dispersity and lower conversions were observed. In conclusion, *e*ATRP of styrene in ethyl acetate using [BMIm][OTf] as supporting electrolyte performs well and provides good results in a system greener than conventional ATRP. Thanks to the use of electricity, no by-products are produced since no chemical reducing agents are involved; moreover, the system requires a low catalyst load that does not contaminate the polymer.

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# An Electrolyte Study on $Na_2BDA$ Anode for Na-Based Organic Batteries

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Energy production and storage plays a key role in the development of portable devices, hybrid and electric vehicles and in the energy storage system for renewable energy, such as wind and solar resources. Lithium ion batteries (LIBs) dominate the global market on these, but the geographically constrained resources and the difficult extraction of metallic lithium lead to prices increment, removing the idea of low-cost technologies.

An alternative on lithium technology is sodium, very abundant, cheap and with suitable electrochemical properties, close to those of lithium. A lot of work on sodium technology has to be done in order to catch up with lithium (1).

Electrode materials research is the first step which must be done for meet the high energy storage demand. At the moment the most common chemistries used in batteries are based on inorganic compounds (e. g. $LiCoO_2$, $LiMn_2O_4$, $Li_4Ti_5O_{12}$, etc…), that are expensive and synthesized from high temperature reactions, and also the end-of-life treatment is difficult and energy greedy. One possible approach as alternative is switching to the organic based materials, in which a lot of synthesis routes can be chosen and a lots of compounds can be synthesized. Furthermore, the possibility to prepare materials from recyclable organic materials (e. g. biomass) is really appealing (2).

However, organic compounds are often associated with drawbacks such as poor conductivity, low energy density and high solubility in liquid electrolytes. Especially for the last point an accurate study on the electrolytes involved in the batteries is mandatory, because is well known how the ion-transport media affect the performances of the batteries system.

In this work we present an overview on our recent results on using disodium benzenediacrylate ($Na_2BDA$) as electrode material for Na-based organic batteries (3,4), in different electrolyte media. In particular, the galvanostatic cycling behaviors in Na|electrolyte|$Na_2BDA$ pouch-cell configuration are shown.

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# Electrochemical preparation of nanostructured $CeO_2$-Pt catalysts on Fe-Cr-Al alloy foams for the low-temperature combustion of methanol

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Methanol is a valuable energy feedstock for the future beyond oil and gas, due to its easy storage as a liquid at room temperature, and an excellent fuel for catalytic combustion, a process that is stable in a wide methanol/air operating range, and produces ultra-low $NO_x$, CO and VOC emissions. Lightweight catalytic burners are often realized using metal foams, due to their outstanding properties in terms of heat and mass transfer coupled with low pressure-drops and thermal resistance. Among the foam materials, Fe-Cr-Al alloy (Fecralloy) have outstanding resistance to high temperatures.

The procedures for depositing firmly anchored, homogeneous catalytic layers onto the foam substrates are often cumbersome and involve many steps. Therefore, there is interest for innovative preparation methods which take advantage of the metallic nature of the foam support, such as electrodeposition and spontaneous deposition through galvanic displacement. Both approaches are capable to form well-dispersed, homogeneously distributed noble metal nano-particles strongly adhering to the substrate (1, 2).

As a part of an ongoing research project, our groups have recently prepared Pt-based structured catalysts for the low-temperature combustion of methanol by electrochemical methods (3). These catalysts consisted of Pt nanoparticles, deposited onto Fecralloy foam supports by pulsed electrodeposition from $H_2PtCl_6$ aqueous solution, and $CeO_2$ thin films electrodeposited from a nitrate baths. Reduction of nitrates induced a local pH increase at the foam/electrolyte interface and caused the precipitation of mixtures of $Ce(OH)_3$ and $CeO_2$, which were converted to $CeO_2$ by heating in air. The Pt loading in the catalysts was measured by ICP-MS, while the noble metal surface area was determined by cyclic voltammetry, through the H desorption charge. Although the presence of a $CeO_2$ film decreased the Pt surface area accessible to electrolyte it enhanced the performance of the catalysts towards methanol combustion, without affecting the activation energy of the process. The enhanced catalytic performance of the $CeO_2$-Pt-Feclalloy catalysts as compared to Pt-Fecralloy was ascribed to the formation of additional active sites along the interface of $CeO_2$-coated Pt nanoparticles.

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# Platinum free Electrocatalyst based on Fe-Nx moieties supported on Mesoporous Carbon prepared from polysaccharides for Oxygen Reduction Reaction

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The physical amount of platinum existing on the Earth is barely enough to cover the world demand in the next forty years for fuel cell vehicles. Furthermore, the high cost and the low durability of platinum-based catalysts are serious obstacles to the large-scale commercialization of PEMFCs. Nitrogen doped mesoporous carbons are emerging as a new class of Pt free materials for ORR (1,2) In particular, it was observed that doped carbons containing small amount of transition metals, such as Fe or Co, can catalyze the $O_2$ reduction to $H_2O$ at overpotentials comparable to that of the most active Pt catalyst (3).
In this paper, nitrogen doped mesoporous carbons containing Fe (Fe@N-MC) were prepared from agarose gel embedding an iron ($FeCl_2$, $FeSO_4$, etc.) and nitrogen (1,10-phenanthroline) precursors. The formation of a hydrogel embedding an iron metalorganic complex, assures an optimal Fe dispersion before pyrolysis. Several types of porogen agents (silica, carbamate, carbonate, etc.) were inserted to induce a hierarchy pore structure in the final pyrolyzed material. After the freeze-drying of the gel, aimed at removing the gelling solvent, the material is subjected to a first thermal treatment at 500 °C, obtaining a crude product, which is further activated at high temperature 900 °C under hydrogen flow. XPS analysis reveals the presence of various forms of iron oxides and a distinct peak due to the Fe−Nx bond at 708.6 eV (Fig. 1a). Beside Fe-Nx not visible from TEM analysis, iron is present as core shell NPs with iron oxide core and carbon shell. The catalytic performances of catalyst ink prepared from Fe@N-MC were investigated by cyclic voltammetry and by rotating ring-disk electrode in 0.1 M $HClO_4$ attesting that $O_2$ is reduced following an almost $4e^-$ pathway at very positive potentials (0.8 V vs RHE) (Fig. 1b).

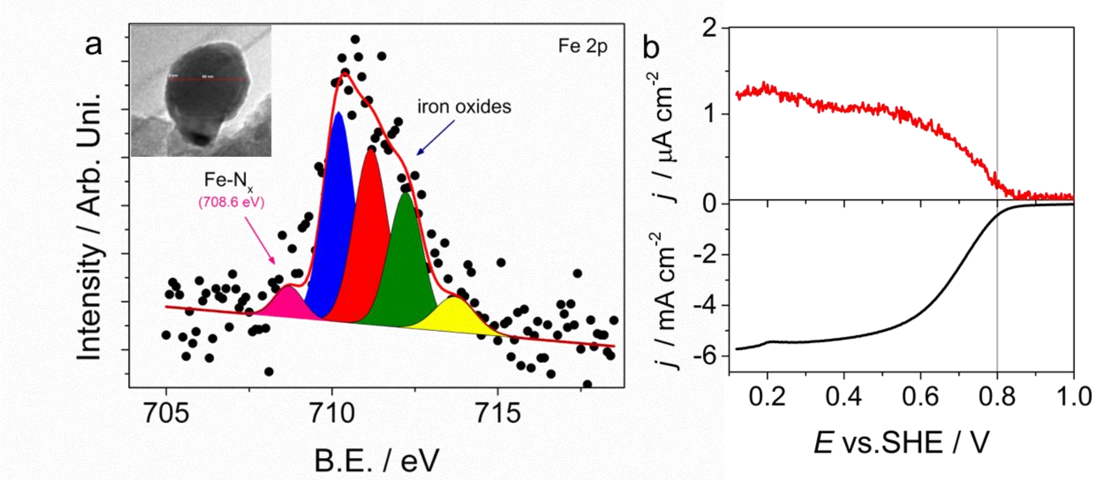

Figure 1. (a) Fe 2p XPS detailed study and deconvolution signals, and Fe NP TEM image. (b) Example of RRDE measurement on Fe@N-MC in 0.1 M $HClO_4$ at 1600 rpm and $\upsilon = 5$ mV/s.

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# Lignocellulosic Materials for Electrochemical Energy Storage and Conversion

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In the last 20 years, the Li-ion battery market has rapidly grown thanks to the extensive diffusion of mobile electronics devices. In order to lower the cost and reduce the environmental impact of batteries, efforts must be devoted to reduce the amount of inactive components in the cell, to substitute synthetic polymer binders/separators and organic solvents with low-cost and biosourced materials and to develop new eco-friendly processes for the manufacture of cell components (both electrodes and electrolyte). Natural nanoscale-microfibrillated cellulose (NMFC) fibers are readily available; they show stiffness, impressive mechanical robustness, low weight and, furthermore, their preparation process is easy and does not involve chemical reactions.
Here we review the use of paper-making technique for manufacturing:

- Bio-inspired all-paper Li-ion polymer cells, constituted by NMFC-binded paper-electrodes, and NMFC reinforced polymer electrolytes (1). The use of NMFC as filler/binder leads to produce high performing, safe and extremely flexible electrolytes for LiBs. No organic solvents or synthetic polymer binders are used during the entire electrode/electrolyte/cell preparation process.
- Cellulosic membranes as separators/electrolytes for post-lithium technologies, such as Na-ion and Li-S (2,3), thus demonstrating the possibility of obtaining “truly green” energy storage devices in the near future.
- Paper-based flexible electrodes and electrolytes for third generation solar cells (4), useful to lower oil-derived components and typical temperatures used to electrodes processing.

This materials platform is promising not only for the sustainable manufacture of energy devices components, but also for their processability at the end of life. For example, the all-paper lithium cell can be easily re-dispersed in water by simple mechanical stirring, as well as common paper handsheets and battery materials can be recovered using well-known water-based recycling process.

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# Secondary Magnesium Batteries: an Overview on Ionic Liquid -based Electrolytes

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A critical roadblock toward the development of post-lithium-ion batteries is the lack of electrolytes that are safe and electrochemically stable whilst demonstrating good compatibility with the electrode materials (1).
It was recently shown that haloaluminate ionic liquids (ILs) can provide a viable alternative to conventional electrolytes due to their low volatility, negligible flammability and good electrochemical performance (2,3,4).
Following this, an overview on recent advancements on electrolytes for secondary Magnesium batteries is presented with particular reference to imidazolium and pyrrolidinium -based ionic liquids. Insights on the interplay between structure and conductivity of $BF_4^-$, $Cl^-/AlCl_3$ and $I^-/AlI_3$ -based systems are given, thus providing an in-depth understanding of the relation between Mg-ion speciation, long-range charge transfer mechanism and electrochemical performance of this very promising class of materials.

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# Operando (photo)electrochemical X-ray absorption spectroscopy for water splitting

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Electrochemical in-situ and operando X-ray absorption spectroscopy (XAS) represents one of the most powerful available tools to study the fine structure and the behavior of electrode materials. This serves to better elucidate important reaction mechanisms and to better define structure/activity relations.

This becomes particularly crucial in electrocatalysis, for studying the oxidation state transitions and during the catalytic cycle, in photoelectrochemistry, for highlighting the local structure and the kinetics of charge recombination/transfer at surface defects and/or to study charge transfer among different layers in composite photoelectrodes.

In our recent work, we developed new methods and techniques to carry out operando XAS on electrodes and photoelectrodes with the aim of highlighting: (i) the kinetics of charge transfer across interfaces (1,2), (ii) the role of the (photo)electrode material during the reaction process (3), (iii) the role of the overlayer in composite photoelectrodes (4).

In particular, we developed FEXRAV (5), that consists in recording the absorption coefficient at a fixed energy while varying at will the electrode potential and allows to quickly map the variation of the oxidation states of the element under consideration in a desired potential window.

More recently, we carried out the first experiment on pump&probe operando XAS on a photoelectrode (6). In addition, we extended the use of energy dispersive XAS to Ir-based electrocatalysts (7) and improved the use of operando XAS for the steady-state study of photoelectrodes by recording parallel dark/light spectra adopting an innovative procedure (4).

This presentation is devoted to review some of our most significant studies, with a particular emphasis on both photoanode, ($\alpha$-$Fe_2O_3$ /$IrO_x$, $\alpha$-$Fe_2O_3$/NiO(OH)) and photocathode ($Cu_xO$) systems.

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# Synergistic use of Impedance and Photoelectrochemical Measurements to study the electronic properties of anodic $TiO_2$

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Anodic titanium oxide has attracted much attention due to its potential widespread applications, including capacitors, photocatalysis and solar energy conversion. For capacitor applications in the microelectronics industry, a dense and flaw-free barrier oxide must be formed as a dielectric layer. In contrast to anodic aluminium oxide ($\varepsilon_{ox} = 10$) and tantalum oxide ($\varepsilon_{ox} = 27$), which are currently used in commercial electrolytic capacitors, anodic oxide films on Ti develop with a high population density of flaws on high purity titanium in aqueous electrolytes. Thus, anodic titanium oxide-based capacitors have not been realized practically despite the large permittivity of the oxide. Effective suppression of crystallisation has been demonstrated by incorporation of silicon species from the metal substrate, i.e., anodizing of a Ti–6at.% Si alloy (1). Another investigated strategy to hinder $TiO_2$ crystallization is to induce incorporation of foreign species from the electrolyte. Their concentration and distribution influence the electronic properties of the anodic oxides and, consequently, the onset of crystallization. In the present work we want to show the effect of anodizing condition on the structure on anodic oxide on Ti.

The anodic films were prepared according to two different procedures: 1) a patented procedure, consisting of a pickling step carried out in a 5% HF/40% $HNO_3$ mixture followed by an anodizing step (potensiostatic polarization at 3.9 V for 30 min) in HCl (18.5%v/v) (Pedeferri's treatment); 2) a pickling step carried out in a 5% HF/40% $HNO_3$ mixture followed by a potenziostatic anodization at 5 V vs. Ag/AgCl for 30 min in 0.1 M sodium biborate aqueous solution (pH = 8.5). Photoelectrochemical measurements were performed in order to estimate band gap, flat band potential and conductivity type of the anodic films as a function of growing conditions, while information of the dielectric constant of the oxides were obtained by impedance measurements. The differential capacitance curves recorded at several frequency of the a.c. signal are interpreted in the frame of amorphous semiconductor Schottky barrier, since the usually employed Mott and Schottky model results to be not suitable to explain the dependence of the measured capacitance as a function of potential. The experimental findings were used to sketch the density of states distribution for amorphous $TiO_2$ as a function of the anodizing conditions.

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# Recovery of Low Grade Heat by Redox Flow Battery

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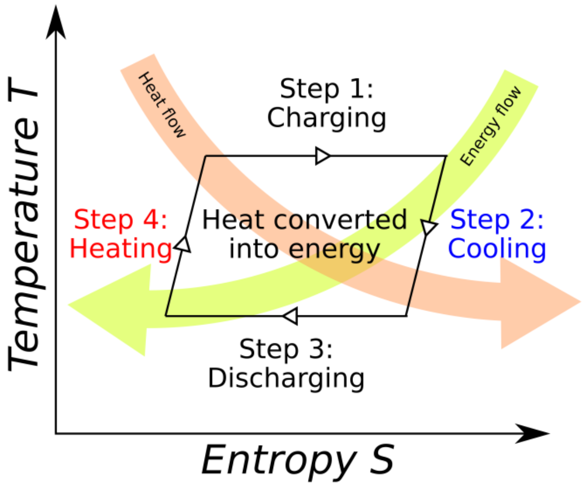
Low grade heat, heat available at temperature lower than 250 °C and even below 100 °C, is everywhere. It is available from solar concentrator and geothermal sources or from domestic and industrial heat waste. It is speculated that only in USA it is possible to recover 8000 TWh of heat per year (1).

However, it is difficult to recover such heat because of the low thermal difference. Recently, an American group introduced the thermal regenerative electrochemical cycle (TREC) as new strategy to recover low temperature heat (2). In the TREC a battery is charged and discharged at two different temperatures as shown in the figure and the variation in cell voltage is used to recover energy. The figure shows the example of a battery charging at higher temperature and discharging at lower temperature. Because of different thermal coefficients in the anodic and cathodic reaction, voltage is larger during discharge than during charge which results in a net conversion of thermal energy into electrical energy.



*Thermodynamic cycle for a TREC with heat and energy flow directions.*

In this work, we demonstrate the use of a redox flow battery to recover low grade heat. All-vanadium redox flow batteries are a promising technology for large scale energy storage. Unlike conventional batteries, the charge is stored in the liquid phase and not in the electrodes. Two acidic electrolytes, one containing $V^{V}/V^{IV}$ redox couple and the other containing $V^{III}/V^{II}$ redox couple, circulate between the tanks reservoirs and the electrode compartment. This kind of battery has the advantage that the reservoirs and the tube connections can be used directly as heat exchangers. In thermal regenerative operations, the battery, as exemplified in figure, absorbs heat during charge storing it as electrical energy in the electrolytes and release it upon discharge rejecting the heat into the environment.

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# Boosting aqueous Atom Transfer Radical Polymerization of hydrophilic and hydrophobic monomers by means of electrochemistry

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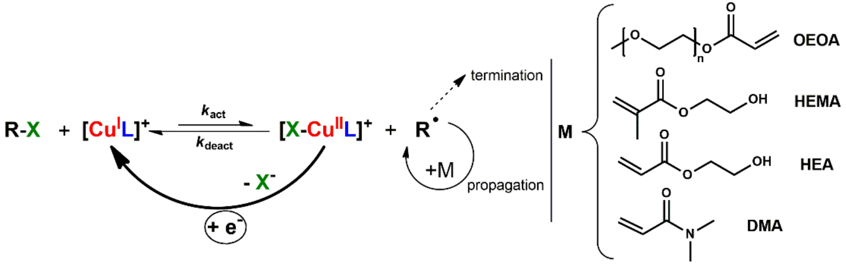
Water is a green, inexpensive, and non-toxic medium, widely used to run controlled radical polymerizations of hydrophilic monomers. Moreover, increasing interest is devoted to the aqueous polymerization of hydrophobic monomers, because water ensures good heat transfer and low viscosity.

Atom Transfer Radical Polymerization (ATRP) is the most used technique to produce polymers with predetermined molecular weights (MWs) and complex architectures. Electrochemistry allows to tune the control over the process, in the so-called Electrochemically mediated ATRP (*e*ATRP). Despite the challenges of aqueous *e*ATRP, oligo (ethylene glycol) methyl ether methacrylate (OEOMA) was successfully polymerized by *e*ATRP, identifying the best conditions over several parameters: monomer loading, pH, nature and amount of halide ions, and applied potential (1,2).

Herein, the *e*ATRP of other hydrophilic monomers is reported (**Scheme 1**). Favorable conditions for OEOMA were adapted to its acrylate equivalent, OEOA, and hydroxyl ethyl (meth)acrylate (HEA and HEMA). Linear kinetics, experimental MWs matching theoretical values and narrow MW distribution confirmed the controlled process. *e*ATRP was successfully applied to another family of hydrophilic monomers, acrylamides, after preliminary electrochemical investigation of the properties of ATRP catalysts in these media.

Moreover, *n*-butyl acrylate which is a hydrophobic monomer, was polymerized in water with good yield and very narrow MW distribution, in a miniemulsion environment (3). To achieve these results a hydrophilic catalyst was combined to an anionic surfactant, forming ion-pairs able to enter the hydrophobic monomer droplets and catalyze the process. This novel catalytic concept was deeply studied by means of Cyclic Voltammetry, determining the amount of complex bound to the surfactant. Overall, *e*ATRP was confirmed as a versatile and robust technique for the aqueous polymerization of both hydrophilic and hydrophobic monomers.



**Scheme 2. Mechanism of eATRP and hydrophilic monomers emploid in the present work.**

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# Voltammetric analysis and chemical reactivity of ionic liquids (ILs) used as "green" reaction media and precursors of efficient catalysts

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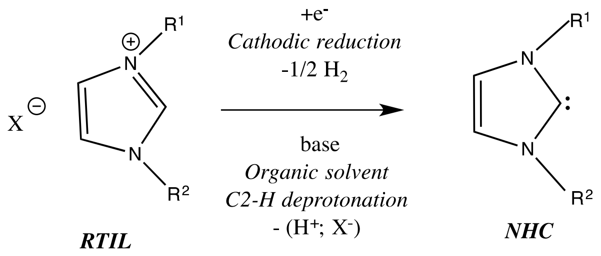
Room temperature ionic liquids (RTILs), owing to their specific properties (chemical and thermal stability, etc.) have been frequently used as "green" reaction media in clean organic syntheses as substitutes for conventional, toxic and volatile organic solvents (VOCs). Considering that an organic synthesis often involves the generation of a significant amount of wastes, the scientific community is strongly interested in alternative methodologies according to the current pressing demand of a sustainable chemistry. Therefore, the discovery of "greener" and efficient catalysts and mild conditions for their generation in the reaction mixture are regarded as significant targets in modern organic synthesis. In the past few decades, N-heterocyclic carbenes (NHCs) have emerged not only as powerful ligands for transition metals (1) but also as organocatalysts (2) for various molecular reactions and as catalysts in metal-free polymer synthesis.(3) Owing to the acidity of the C2-H group of imidazolium salts, NHCs could be prepared by deprotonation of these structures with suitable bases. Also the electrochemical methodology allows obtaining NHCs by cathodic reduction of azolium salts, thus avoiding the utilization of bases.(4) Nevertheless, some NHC-catalysed reactions, or anyhow requiring the presence of NHC, were carried out using imidazolium based acetate or chloride salts in the absence of any base or reducing agent purposely added to the reaction mixture.



Due to its excellent sensitivity, voltammetric measurement can highlight the presence of NHC. The voltammetric analysis will be directed to realize the role of the anion part of the salt as regards the possible presence of free NHC in neat ionic liquids. The electrochemical behaviour of different salts systems will be presented in order to clarify whether the catalytic activity is due to the anion, the NHC or both. Further information can be obtained by evaluating the influence of cation and anion of different salts using them as bases in two classical and important base-catalysed reactions: the Knoevenagel condensation and the transesterification reaction.

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# New processes to produce renewable energy: reverse electrodialysis and thermally regenerative ammonia battery

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In the last years, research activities increasingly focused on renewable energy sources characterized by no emission of environmental unwanted substances, no thermal pollution and without net emission of greenhouse gases. In this frame, various processes were studied in the last years including microbial fuel cells, reverse electrodialysis, microbial reverse electrodialysis and thermally regenerative ammonia battery. Reverse electrodialysis (RED) appears as one of the more promising process for direct electricity production from salinity gradients, based on the use of many pairs of anion and cation exchange membranes situated between two electrodes (1). It is worth mentioning that salinity gradients can be regenerated using waste heat. An alternative approach to convert waste heat to electricity, called a thermally regenerative battery (TRB) based on using ammonia (TRAB), was recently shown (2). TRBs operate using chemical potentials obtained by adding ligands into a metal salt solution. In a TRAB, copper ammine complexes are produced when ammonia is used as the ligand only in the anolyte, necessary to charge the battery. Aside from this difference, anolyte and catholyte contain the same electrolytes: copper nitrate and ammonium nitrate, in the same concentrations. The performances of these processes to generate renewable energy are discussed. In the case of RED, the process is evaluated in both lab and pilot-plant scale for the generation of energy and the treatment of wastewater. For TRAB, the main advantages and disadvantage of the methods will be assessed by a series of experiments performed in lab cells.

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# Preparation of Porous Oxide Layers by Oxygen Bubble Templated Anodic Deposition Followed by Galvanic Displacement

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In recent years, there has been considerable interest in the hydrogen bubble–templated electrodeposition of porous metals (1). In this process, an electrolysis performed at high cathodic current density causes simultaneous metal ion reduction and hydrogen evolution, leading to the formation of highly porous metal films on the cathode, normally consisting of nanocrystals. Our group has recently shown that a symmetric anodic process can be used for producing porous layers of $PbO_2$ which, due to their enhanced surface area, exchange much larger charges than compact layers, when cycled in $H_2SO_4$ solutions (2,3).

The oxygen bubble templated anodic deposition of porous oxides cannot be extended to compounds which electrical resistivity, significantly higher than that of $PbO_2$, prevents the use of large current density. Some of these oxides may be obtained in a two-step process, by combining oxygen bubble templated anodic deposition and galvanic displacement. In the latter, a porous $PbO_2$ layer reacts with a low-valent cation $M^{n+}$ in solution to yield its higher-valence oxide and $Pb^{2+}$, according to:

$$PbO_2 + M^{n+} \rightarrow MO_x + Pb^{2+}$$

We have preliminarily reported on this two-step preparation route for $M^{n+} = Mn^{2+}$ (4), and we have recently extended the process to $M^{n+} = Co^{2+}$.

The main steps of the work were the following.

- Porous $PbO_2$ layers were deposited from either methanesulfonic acid or perchloric acid media. Their porosity was controlled through the deposition current density.
- Galvanic displacement reactions were carried out by immersing porous $PbO_2$ layers in either $Mn^{2+}$ or $Co^{2+}$ solutions at open circuit. Acetate solutions, where $Pb^{2+}$ is soluble, were used, in the temperature range 25-75°C.
- XPS analyses were used to establish that the compounds formed by galvanic displacement were $MnO_2$ and $Co_3O_4$. Due to their amorphous nature, XRD analyses did not provide additional information.
- SEM was used to assess the morphology of Mn-modified and Co-modified $PbO_2$ layers, and showed that porosity was maintained. Inspection of cross-sectional images allowed the determination of the thickness of the $MnO_2$ and $Co_3O_4$ layers as a function of reaction time.
- Recognizing that galvanic displacement is a peculiar corrosion process, methods that are current in corrosion studies were used to determine the deposition rate. Thus, quasi-steady-state curves for $PbO_2$ reduction and $Mn^{2+}$ or $Co^{2+}$ oxidation were compared using Evans' diagrams. Deposition rates were calculated from the current values at which the partial reactions had identical and opposite rates.
- The effects of $Mn^{2+}$ concentration and reaction temperature on the deposition rate were elucidated.

Hence, the proposed method allows the preparation of low conductivity oxides of controlled porosity, not attainable by direct electrodeposition.

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# Inherently chiral molecular materials with 2,2'- and 3,3'-bisindole atropoisomeric cores: interactions between equivalent redox sites, configurational stability and enantioselection ability

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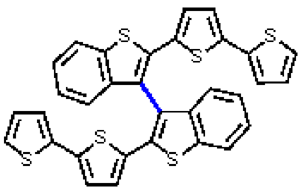
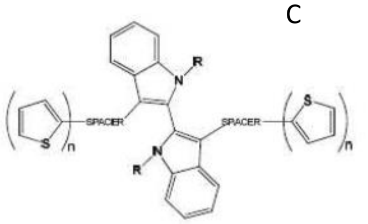
The peculiarity of inherently chiral molecular materials is that the same element endows the molecule with both its key functional property and with chirality, coinciding with the main molecular backbone featuring a tailored torsion; this results in outstanding chirality manifestations. Recently we have presented "inherently chiral" enantiopure electrodes resulting in large potential differences for the enantiomers of chiral probes in voltammetry experiments; they were prepared by electrooligomerization of monomers having atropoisomeric bibenzothiophene (A) or bithiophene cores. (1-5). Concurrently, we have also developed a large family of inherently chiral monomers having 2,2'- or 3,3'-bisindole atropoisomeric cores (B, C).

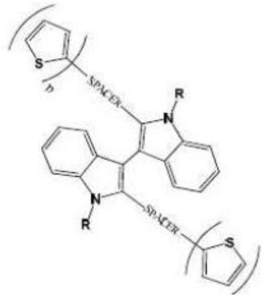
A



B



C



Since indole is electron richer than thiophene, the first two oxidations are shifted at significantly less positive potentials, and localized on the two interacting moieties of the bisindole core rather than on the terminal thiophene wings, and therefore are chemically reversible (oligomerization can be achieved cycling around the third oxidation peak). Moreover, indoles can be N-alkylated, affording modulation of important properties such as solubility and therefore processability.

We will present a detailed electrochemical study on the monomer redox properties and oligomerization ability as a function of the molecular structure in this compound family. A quite original and attractive feature concerns the interaction between the two equivalent redox centers in the biindole cores, (which can be estimated from the potential difference between the corresponding oxidation peaks), since it can be shown to account for the atropoisomeric energy barrier (depending on the 2,2' or 3,3' connectivity and on the N-alkyl substituents), and to be also nicely modulated by temperature and solvent polarity. Thus electrochemistry can provide information on the torsional energy barrier and on the enantiomer stability, confirmed by other approaches.

Finally, enantioselectivity tests on films obtained by electrooligomerization of the more configurationally stable 2,2'-oligomers yield large potential differences for the antipodes of very different chiral probes, also of pharmaceutical interest.

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# Organic bioelectronics probing conformational changes in surface confined proteins

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The study of proteins confined on a surface has attracted a great deal of attention due to its relevance in the development of bio-systems for laboratory and clinical settings. In this respect, organic bio-electronic platforms can be used as tools to achieve a deeper understanding of the processes involving protein interfaces, since the energetic and electrostatic contributions play the main role in shaping the device response.(1, 2) Biotin-binding proteins such as avidin, streptavidin and neutravidin have been integrated in an organic thin-film transistor (TFT) to investigate the changes occurring in the protein-ligand complex morphology and dipole moment.(3) To this end, functional bio-interlayer and the newly introduced pre-formed complex TFTs have been proposed to separately address these two features. This has been achieved by decoupling the output current change upon binding, taken as the transducing signal, into its component figures of merit. In particular, the threshold voltage is related to the protein dipole moment, while the field-effect mobility is associated with conformational changes occurring in the proteins of the layer upon ligand binding, directly impacting on the transport properties of the organic semiconductor. The probing of a protein bio-layer by means of assessed approaches is not capable to provide information on both the electrostatic and the conformational changes. Molecular Dynamics simulations on the whole avidin tetramer in presence and absence of ligands were carried out, to evaluate how the tight interactions with the ligand affect the protein dipole moment and the conformation of the loops surrounding the binding pocket. These simulations allow assembling a rather complete picture of the studied interaction processes and support the interpretation of the experimental results.

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# Physicochemical characterization and corrosion behaviour of surface oxide films on bright annealed ferritic stainless steel

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The corrosion resistance of stainless steels is determined by the thickness, structure, composition and electronic properties of the oxide layers grown on their surface and isolating the metallic substrate from the environment. Surface analytical techniques such as X-Ray Photoelectron Spectroscopy (XPS) and Time-of-Flight Secondary Ion Mass Spectroscopy (ToF-SIMS) have been and still are widely applied to characterize thickness, chemical structure and composition of thin and ultrathin surface oxide films. PhotoCurrent Spectroscopy (PCS) is a technique applied to obtain direct information on the electronic properties of thin photoconducting surface films on metals and alloys. In the present work, XPS and ToF-SIMS have been combined to PCS in order to perform an integrated physico-chemical characterization of surface oxide films grown on bright annealed ferritic stainless steel in different conditions. Ferritic stainless steels are a nickel-free (i.e. cheaper) alternative to austenitic stainless steels. They are process-annealed to high temperature (~ 1000 °C) in order to reduce hardness and achieve the ductility required for mechanical machining. Bright annealing, is performed under inert gas atmosphere (a mixture of hydrogen and nitrogen) in order to minimize the reaction with oxygen and to avoid the growth of oxide scales and preserve a bright appearance. Our results show that on as-received bright annealed samples the surface oxide film is ~ 2.0 nm thick and has a bilayer structure with an inner layer close to pure Cr(III) oxide and an outer layer of mixed Fe(III) and Cr(III) oxide as shown by XPS and ToF-SIMS. By PCS electronic band gaps of the inner and outer layers are measured close to 3.4 eV and 2.8 eV, respectively, and the oxide films behave as an insulator with an inversion potential of ~ - 0.7 V vs. Ag/AgCl at $\lambda = 309$ nm and at pH ~ 9.5. After thermal treatment in air between 350°C and 550 °C, the surface oxide films thickens and the outer layer is enriched in Fe(III) as shown by XPS and ToF-SIMS. PCS confirms iron enrichment of the outer layer with a band gap reduced to 2.0 eV; photocurrent intensity increases according to thickening and iron enrichment. Polarization curves and electrochemical impedance spectra evidence a decrease of the polarization resistance and a cathodic shift of the corrosion potential after thermal treatment. The knowledge of the structure, composition and electronic properties of these surface films will be discussed to rationalise their corrosion behaviour.

# $La_2NiO_4$@Ni core-shell based catalyst as pre-layer for a commercial Solid Oxide Fuel Cell fed with biofuels

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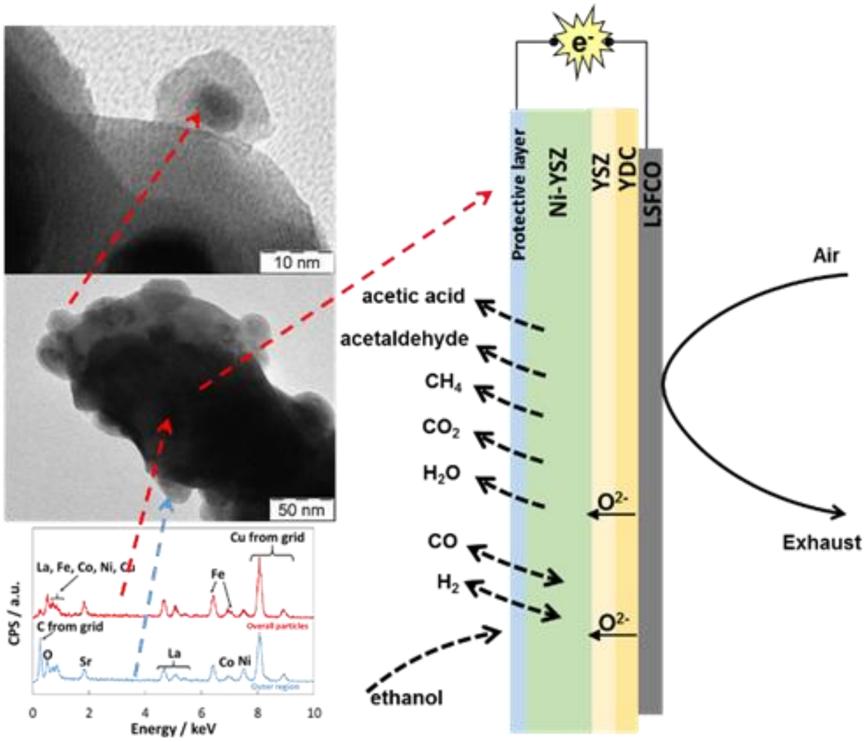
Solid oxide fuel cells (SOFCs) based on conventional nickel-yttria stabilized zirconia (Ni-YSZ) anodes can not be fed directly with organic fuels because of the associated formation of carbon deposits. This work explores a simple approach to solve such relevant limiting factor that affects the utilization of dry biofuels such as ethanol and glycerol directly fed in SOFCs. The approach consists in depositing a composite multifunctional electrocatalyst layer on the SOFC anode to work as an internal integrated fuel processor. A protective layer based on a composite made of Ni-modified perovskite and gadolinia-doped ceria is coated on a conventional SOFC anode based on Ni-YSZ. Beside the oxygen storage properties of ceria, the composite electrocatalyst is characterized by the presence of $La_2NiO_4$@Ni core-shell nanoparticles in the outer layers and surface basicity properties. Efficient dehydrogenation mechanism, carbon deposition-free cracking reactions and internal reforming assisted by a $H_2/H_2O$ "shuttle mechanism" appear as the key steps involved in the direct oxidation of the biofuels at the modified SOFC anode.



Protective layer and scheme of the "shuttle mechanism" suggested in the present paper

# All PEDOT:PSS electrochemical transistors as a platform for sensing

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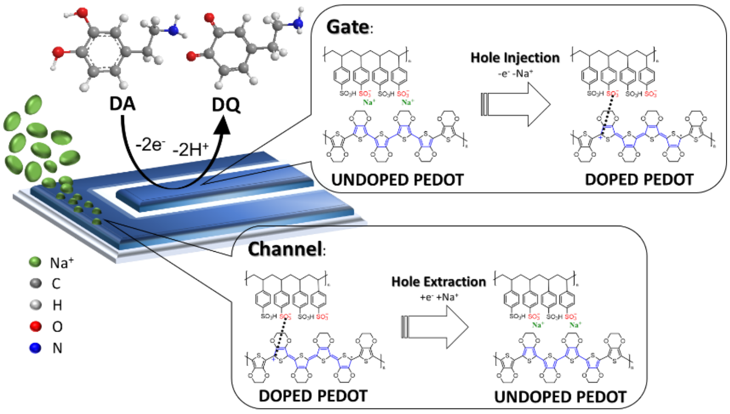
Organic electrochemical transistors (OECTs) are devices which find growing interest in the field of biological and chemical sensing. Although the OECT transduction is based on electrochemical reactions, the transistor architecture offers several advantages respect to amperometric sensors such as signal amplification, the use of an easy and cheap readout electronics, low supply voltage (usually < 1 V), low power operation (< 100 µW), bio-compatibly, and, moreover, they can be easily miniaturized and adapted to non-flat, flexible and even textile devices [1]. This contribution want to report the potentiality of such devices by describing an OECT based only on PEDOT:PSS as conductive material, that can be exploited to obtain low cost sensors [2, 3] with very high performance.

The sensor was optimized by studying the response to different redox compounds of biological interest such as ascorbic acid, dopamine, adrenaline and uric acid. The bio-molecules react with PEDOT:PSS by extracting charge carriers from the transistor channel, and consequently an increase of analyte concentration leads to a decrease of the absolute value of the drain current.



The main drawback of such devices is the lack of selectivity which hinders its wide use in real applications. To address this issue we use a dual approach: on one side we have implemented a potentiodynamic approach that exploits the variation of the operating gate bias voltage in order to obtain a trans-conductance curve wherein the waves due to different redox compounds are separated. On the other side the physical and chemical modification of the PEDOT lactice of the gate electrode offers great opportunities for the implementation of a selective sensor.

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# Development of enzyme-based microsensors for *ex vivo* analyses

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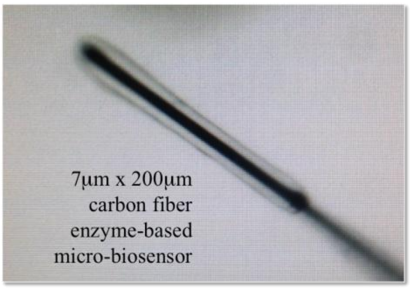
Nowadays real-time quantitative measurements of many proteins, metabolites and cancer biomarkers, are feasible by the use of biosensors for *in vitro* and *in/ex vivo* studies (1). Although, strategies on biosensor design are rapidly increasing, enzymatic biosensors remain a large and important field of study. Enzymes achieve molecular recognition of the substrate based on structural complementarity and exploit an analyte-dependent step to convert an electrochemically inert substrate to an active product, often revealing high selectivity, sensitivity, time scale and information content. Even if, amperometric biosensors have been around since the early 1960s (2-3), it is the production of very tiny micro-electrode biosensors that offers great utility for studying chemical signalling for *in vitro* (at single cell level) and *in/ex vivo* studies. These microelectrode biosensors have the advantage of offering a better spatial and temporal resolution and they are considerably less invasive than other electrode (i.e. microdialysis electrodes) (4). The miniaturization of biosensors is challenging, as they need to be both extremely small and highly sensitive. In fact, smaller is the sensor, smaller is the electrode surface area, and consequently the recorded amperometric signal diminishes (1). The requirement in miniaturizing biosensors is to maintain a signal to noise ratio that enables effective and sensitive detection of the analyte. The tiny sensing surface of the sensor has to be coated with a high density of enzymes in their native active conformation. Furthermore, for *ex vivo* analyses, it is mandatory to control the selectivity of the signal and the mechanical strength of the sensor itself, which has to enter in tissues without damaging.

*In this work, we present the development of small, robust and highly active micro-electrode enzymatic biosensors for detecting metabolites, such as glucose, lactate and ATP from single living cells to tissues analysis.*



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# Potential and limitations of voltammetric measurements for the characterization of electrode surface

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In this work we tested the possibility to use voltammetry for the evaluation of the area of solid electrodes. In the first step of the research study we adopted two voltammetric techniques, well known in the literature: i) cyclic voltammetry (CV) at different scan rates, followed by processing of the peak height with the Randles-Sevcik equation; ii) linear sweep voltammetry (LSV) at different electrode rotation rates, followed by data treatment with Levich equation (1,2).

The ferrocene/ferrocenium redox system was chosen as a probe for its well-known reversible process of diffusion-controlled single electron transfer. Acetonitrile and tetrabutylammonium esafluorophosphate were used as solvent and supporting electrolyte respectively. Initially attention was focused on a solid gold electrode (SGE). The evaluation of its area was made both on the electrode as received, without applying any treatment, and after a drastic surface treatment, to compare the effect of mechanical polishing on the measured area. The results obtained showed that such a treatment gave rise to a significant decrease of the standard deviation of the results and a decrease of the value measured for the area.

Method i) was then applied to a glassy carbon electrode (GCE) in three different conditions: unmodified and modified with an Au-film (AuF-GCE) and with an Au-nanoparticle layer (AuNP-GCE), to investigate the influence of the “roughness” of the electrode surface on the value measured for the area. According to the literature, the above-mentioned electrochemical techniques should respond to the electrode projected areas (2,3): however, we found that the measured areas differ for each modification, suggesting that the morphology of the active surface influences the results of the calculation. Subsequently, method i) was applied to home-made carbon paste electrodes (CPE) of different sizes, to test the relationship between the diameter of the electrode body and the measured area. The calculated areas were compared with those obtained by recording electrode images by scanning electron microscopy (SEM) and processing the data with Wolfram Mathematica software.

In the second step of the study, the actual active surfaces of the SGE and of the two Au-modified GCEs were estimated by CV in $H_2SO_4$, from the areas of the cathodic peak obtained in each voltammogram, through the theoretical charge associated with the reduction of the oxide layer per unit surface area of gold (4).

In conclusion, voltammetry provide information on the area of solid electrodes, but, despite the notoriety of the equations considered in this study, there are some doubts about the kind of “area” actually involved in the measurement process; further studies are required to correctly interpret experimental results.

Finally, the evolution of the SGE surface during an extended period of usage was checked by periodically recording cyclic voltammograms in $H_2SO_4$. Clear differences were observed in the CV curves over time and a relationship between the shapes of the voltammograms and the performance of the electrode was found: therefore CV can be a used to monitor the state of the SGE surface and identify the need for a mechanical polishing or even a substitution of the electrode.

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# Development of an electrochemical magneto-immunosensor for the detection of *Campylobacter*: a preliminary study

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*Campylobacter* is an important pathogen genus that cause acute bacterial diseases in humans worldwide. Most infections (about 90%) are caused by *C. jejuni* species, less frequent are those caused by *C. coli*, while sporadic cases are caused by *C. lari* species and *C. upsaliensis*. Outbreaks of Campylobacteriosis have traditionally been linked to the consumption of food products of animal origin (e.g. meat and eggs) but, more recently, an increasing number of outbreaks have been associated to contaminated fruits and vegetables, especially raw leafy green vegetables (1). Conventional bacterial testing methods rely on specific microbiological media to isolate and enumerate viable bacterial cells in food. These traditional methods are very sensitive and inexpensive, but require several days to generate results because they rely on the ability of microorganisms to multiply to produce visible colonies. Therefore, rapid, sensitive and specific methods to detect pathogens are needed. In this work a sandwich ELIME (Enzyme-Linked Immuno Magnetic Electrochemical) assay to detect *Campylobacter* is reported. The proposed system is similar to that already developed by our research group for *Salmonella enterica* (2,3). Magnetic beads (MBs), coupled to a strip of eight-magnetized screen-printed electrodes, effectively supported a sandwich immunological chain. Enzymatic by-product is quickly measured by differential pulse voltammetry, using a portable instrument. Different antibodies, blocking agents and treatments for bacterial cultures were tested. The final system employs: MBs tosyl-activated blocked with dry milk and coated with a capture polyclonal antibody anti-*Campylobacter*, whole *Campylobacter* cells (inactivated with $NaN_3$) and a detection antibody conjugates with ALP enzyme. For a simple and rapid assay the coating and blocking steps were performed in a preliminary phase, while the two sequential incubations for the immuno-recognition events were merged in a single step of 1 h. The final proposed conditions are those that ensured the best analytical performance for *C. coli*, while, to date, there are still difficulties to detect *C. jejuni*. The future work will focus on improving the response towards *C. jejuni* and the next application of the assay in contaminated matrices, such as irrigation water and vegetables, object of various community alerts in the last few years.

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# Rapid, Low-cost and Portable Electrochemical Assay for Heart Injury Diagnosis

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Early and fast diagnosis and prognosis of heart injury are of paramount importance for a successful treatment of the diseases. Furthermore, heart related pathologies, also caused by anticancer treatment, are determinant in cancer patient survival. Several molecular markers of heart damage are emerging and electrochemically-driven trapping and signal transduction of biomarkers have proven to be effectively employed in the development of sensing devices and assays.

For instance, cytochrome c (cyt c), an inner mitochondrial membrane (IMM) protein, which plays an important role in oxidative phosphorylation, can be detected as heart failure marker. This protein is not detectable in healthy patients' blood but it has been demonstrated that during some diseases, which also involves the cellular apoptosis, cyt c is released [1]. In particular, cyt c is released from cellular membrane as a consequence of the treatment of infarction. [2] A fast monitoring of cyt c concentration can help to control the progression and extension of the heart injury guiding the therapeutic actions.

In this view, there is an urgent need to develop biochips/sensors/devices for the rapid detection of markers, such as cyt c, in very early stages of the diseases to evaluate the real state of the injury and to operate with fast bedside therapies.

Herein, we show some strategies based on optimized chemical affinity for the trapping and the detection of heart injury markers and for signal amplification.

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# Carbon black modified screen-printed electrodes to detect chlorine dioxide

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Chlorine compounds have always been the most used chemical agents for water disinfection. However, alternative disinfectants have been investigated to avoid harmful by-products generated by the reaction between free chlorine and organic substances present in water. Among the different compounds used for the treatment of water, chlorine dioxide can be considered a good alternative to chlorine. Chlorine dioxide is employed in several industrial fields, including food, textile, and paper industries. Furthermore, chlorine dioxide is used to produce disinfected water with satisfactory characteristics in terms of odor and taste. (1,2)

Chlorine dioxide is often used because of its excellent oxidizing and disinfecting properties against bacteria, viruses and algae, combined with the absence of harmful by-products, such as trialomethanes. Moreover, it is active in a wide range of pH, unlike free chlorine. (3)

Actually, the maximum residual disinfectant level using chlorine dioxide in water is 0.8 ppm, accordingly to the United States Environmental Protection Agency (EPA), thus analytical tools are required to control the disinfectant level. (4)

Due to the industrial needs in the control of disinfectant level in different processes, the development of cost-effective and easy to use sensors is highly requested.

The goal of the Tecnosens Spin-off is to fabricate miniaturized and sustainable electrochemical sensors for the monitoring of disinfectant compounds.

Herein, we report a novel and cost-effective probe for the *in-situ* determination of chlorine dioxide in swimming pool water.

This sensor was fabricated using screen-printed electrodes modified with carbon black (CB), a cost effective and raw nanomaterial with excellent electrocatalytic properties as demonstrated by our research group and corroborated by also other groups, like Compton's group. (5,6)

The working electrode was modified by drop casting with 2 µl of a carbon black dispersion (1 mg/ml) prepared in a mixture of N,N-Dimethylformamide/$H_2O$ 1:1 (v/v). Under optimized conditions (potential of + 0.1 V vs Ag/AgCl and Britton-Robinson buffer 0.02 M + KCl 0.02 M, pH =2 as working solution), the sensor showed a linear response up to 10 ppm (R=0.989), sensitivity and LOD equal to 13.4 nA/ppm and 0.03 ppm, respectively.

The interfering species including $NO_3^-$, $SO_4^{2-}$, $CO_3^{2-}$, $HCO_3^-$ and $Cl^-$ were evaluated, demonstrating the selectivity of this device.

The study of matrix effect and the accuracy of the sensor was estimated in swimming pool water, obtaining a satisfactory recovery value (78 ± 8)%.

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# *Bacillus anthracis* spores detection by using a label free impedimetric aptasensor

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Since 1930, biological weapons have been developed and used in different countries; they include microorganisms like virus and bacteria which can be used in terroristic attacks, affecting the human health. For instance, *Salmonella typhimurium* was spread in food samples by a religious sect in the western USA; *Bacillus anthracis* spores were used in 2001 to contaminate letters in the Washington area (1).

For the safety of citizens at worldwide level, there has been a continuous interest in the development of robust and reliable analytical tools for the detection of these agents, to provide an early alarm in case of terroristic attacks. The detection of these agents is usually carried out using laboratory-set techniques like real-time PCR, which are not suitable for in field applications and fast early warning, due to the lack of portability, power requirements, long response time and expensive procedures. In this context, electrochemical biosensors offer advantages in terms of high sensitivity, miniaturization, integration, low cost, and power requirements. For the development of biosensors able to detect these agents, antibodies are mainly used as biocomponents, but their production requires the use of animals; in addition, their stability is often affected by environmental conditions. To overcome these drawbacks, synthetic DNA aptamer sequences were recently employed to develop aptasensors (2).

Herein we describe the development of an impedimetric label free biosensor for the detection of *B. anthracis* spores, using the BAS-6R aptamer as biocomponent. This aptamer sequence has been selected among a library of 92 DNA aptamers by Bruno et al., demonstrating a good selectivity for *Bacillus* spores when tested in fluorescence, using a fluorophore and a quencher as labels (3). We developed a miniaturized label free aptasensor for *B. anthracis* spores using this aptamer as biocomponent and the electrochemical impedance spectroscopy as technique. The aptamer BAS-6R was immobilised on gold screen-printed electrodes by exploiting the affinity between the gold working electrode area and the thiol chain at the 5′ position of BAS-6R, while the spores presence has been detected by evaluating the increase of the charge transfer resistance ($R_{ct}$). To optimise the aptasensor, different working conditions, including the amount of aptamer and blocking agent, the time of aptamer incubation, the type of working buffer have been studied. This aptasensor was then tested against *B. anthracis* spore simulants, namely *Bacillus Cereus 14579*, *Bacillus Subtilis*, *Bacillus Cereus* 11778, observing a significant $R_{ct}$ variation in the presence of *B. Cereus 14579* ($10^5$ CFU/mL), thus demonstrating the binding between the aptamer and this *Bacillus*. This aptasensor has showed the capability to detect *B. anthracis* spores simulant in the range comprised between 0.5 x $10^5$ CFU/mL and 7 x $10^5$ CFU/mL, it has also demonstrated its suitability for a rapid analysis.

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# High-Quality, Ligands-Free, Mixed-Halide Perovskite nanocrystals Ink for Optoelectronic applications

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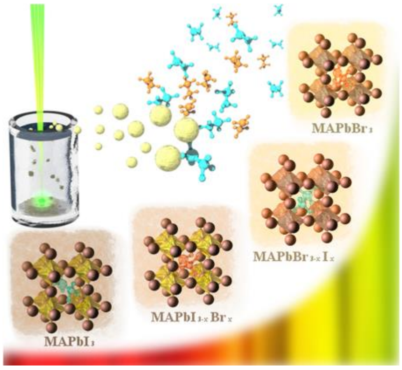
It is now well established that the primary optoelectronic properties of perovskite-halides – such as their tunable direct bandgap, high absorption coefficient, low exciton binding energy, and balanced ambipolar carrier transport – meet many of the requirements for a high-efficiency solar energy conversion technology(1). But in spite of the huge research effort, yet they are far from the market.

Given the simple processability of perovskite-halides, typically from solutions at relatively low temperatures, a non-negligible level of unintentional structural and chemical defects at temperatures relevant for device operation are currently limiting the devices efficiencies and causing instability - i.e. hysteretic behaviours (2) and formation of metastable phases upon photoexcitation which hampers the band-gap tunability (3) - and low reproducibility, especially in view of large area deposition.

In more established semiconductors, such as Si for example, the understanding and control of defects has been a cornerstone of their successful development in devices. Defects thus remain one of the interesting material characteristics in solution processable perovskites that underpin limitations in device operation and influence further progress towards reaching the highest possible power conversion efficiencies. So far, high quality colloidal nanocrystal of perovskites (not necessarily quantum confined) have been demonstrated. However, they all need bulky and insulating organic ligands to remain in suspension, thus hampering the fabrication of conductive thin films.



We demonstrate, for the first time, the synthesis of ligand free metal-halide pervskite nano-crystal inks by Laser Ablation Synthesis in Solution (LASiS).[4] This methodology, simple and easy to use for large scale materials production, allows to produce nano-crystals solutions to print conductive thin films electrically and photo-stable. In fact, we show that such films do not present any hysteretic behavior under polarization, typical in presence of ion migration and permit monotonic tunability of the band gap across the visible spectrum, in absorption and emission, without the formation of sub-band gap emissive phases upon photo-excitation.

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# New Earth-abundant thin film solar cells based on $Cu_2MnSnS_4$

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As it is well known, in the last decade much attention has been focused on $I_2$-II-IV-$VI_4$ thin films as an attractive possibility for the synthesis of In and Ga free chalcogenides which may allow terawatt range photovoltaic (PV) applications. A new alternative to copper zinc tin sulfide/selenide belonging to this class of materials is copper manganese tin sulfide (CMTS), a p-type semiconductor fully based on Earth-abundant and low-cost elements which shows an important advantage with respect to copper zinc tin sulfide/selenide. As a matter of fact, not only the abundance in the Earth's crust of Mn is two order of magnitude higher than that of Zn (1100 ppm vs 79 ppm), but the amount of Zn produced in 2015 was 4'600'000 tons lower than that of Mn (13'400'000 Zn tons vs 18'000'000 Mn tons). Therefore, since Mn is definitely cheaper than Zn, optimized CMTS could potentially provide Wp cost definitely lower than copper zinc tin sulfide/selenide, which is crucial for thin film PV applications. CMTS, which crystallizes into a stannite structure (space group: I-42m), shows high absorption coefficient ($\alpha=10^4$ $cm^{-1}$) and direct band gap suitable for PV applications. So far, CMTS was mainly studied as bulk magnetic semiconductor, while, only in the last two years, the present authors (1) and Chen et al. (2) reported on CMTS thin films for PV applications. The latter reported on CMTS layers prepared by direct liquid coating followed by annealing in nitrogen atmosphere and/or post-sulfurization in sulfur vapors, which provided solar cells with 0.49% maximum efficiency. Our work deals instead with CMTS thin films grown by a two-step vacuum process. The metal precursors deposited on Mo-coated soda lime glass (SLG) by thermal evaporation are annealed in sulfur vapors for 1h at 585°C with an initial 1h step at 115°C to enhance the metal intermixing. Of the many possible stoichiometries, Cu-poor/Mn-rich CMTS films with Mn/Sn ratio around 1 were chosen in order to prevent the development of both highly conductive (e.g. $Cu_{2-x}S$) and insulating (e.g. MnS) secondary phases. Several techniques, including Scanning Electron Microscopy, Energy Dispersive Spectroscopy (EDS) , Raman spectroscopy and Photoluminescence have been used to test the quality of CMTS thin films, while CMTS/CdS/iZnO+AZO solar cells were inspected both by External Quantum Efficiency and current density-voltage (J-V) measurements under 1 sun illumination. The beneficial effects of low temperature post-deposition annealing either in air or inert atmosphere between 200 and 275°C on CMTS solar cells were investigated, both in terms of electrical performance and modification of the material properties. In particular, a 40 min 225°C annealing in air lead to the best overall performance: efficiency 0.83%, open-circuit voltage 354 mV, short-circuit current density 5.8 mA/cm2, fill factor 40%.

The reasons behind these beneficial modifications of the device parameters were investigated by Raman and PL spectroscopies. Results showed that post-deposition thermal treatments in air between 200 and 275°C generally reduce generally reduces the density of the bulk defect, thus reducing recombination losses and increase the of CdS crystalline quality, while red-shifting its absorption edge.

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# Polyurethane-based Electrostrictive Nanocomposites as High Strain - Low Frequency Mechanical Energy Harvesters

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Energy harvesting of wasted energy is increasingly important for powering wearable electronics in Internet-of-Things world [1]. Here, we reported on innovative nanocomposites made of electrostrictive polymer (thermoplastic polyurethane, TPU), and high-k ceramic filler ($CaCu_3Ti_4O_{12}$, CCTO), which offered outstanding results in recovering energy by human gait. The excellent mechanical properties of TPU allowed up to 50 vol% of filler into the composite without loosing film elasticity even for high strains (~30%). CCTO was able to increase of more than one order of magnitude the resistance of the film harvesters with respect to pure TPU, without lowering the dielectric constant and the breakdown voltage. The combined effect of high dielectric strength, high resistance and allowable strain make these composites very promising as energy harvesting actuators.
By means of careful broadband electric spectroscopy coupled with microstructure analysis, we were able to address the mechanisms underlying energy recovery. In particular, long-range charge migration phenomena mainly occurred along conductivity pathways, which are formed at the extended interfaces between the polymer strands and the filler. Our model allowed optimal tailoring of electrostrictive nano-composite actuators.

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# A Bilayer $WO_3$ n-n Heterojunction Photoanode prepared by RF Diode Sputtering for Improved Photoelectrocatalytic Water Splitting

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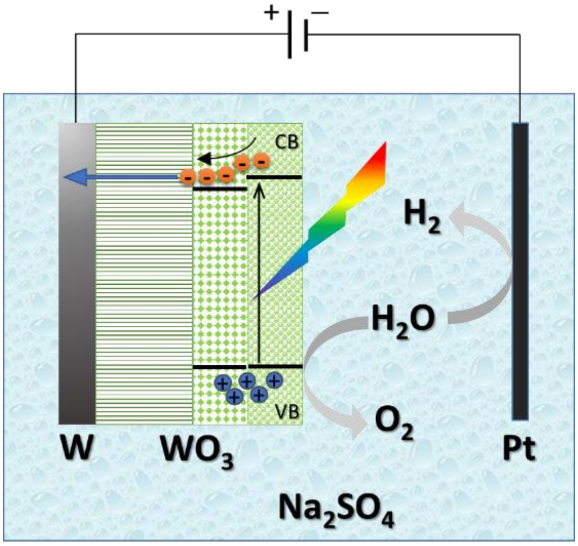
A bilayer $WO_3$ photoelectrode was prepared by radio frequency (RF) plasma sputtering in reactive 40%$O_2$/Ar atmosphere by depositing on a tungsten foil two successive $WO_3$ coatings at two different total gas pressures (3 Pa and 1.7 Pa, respectively), followed by calcination at 600 °C (1). Its photoelectrocatalytic (PEC) activity was evaluated by both Incident Photon-to-Current Efficiency (IPCE) measurements and separate evolution of $H_2$ and $O_2$ by water splitting in a two-compartment PEC cell (2), and compared with those of the corresponding single layer grown at constant pressure (1.7 Pa or 3 Pa). FESEM analysis revealed that the photoanodes have a nanostructured porous double layer surmounting a columnar basement (Staffa-like morphology, after the name of the Scottish island). Tauc plot of the single layer revealed that the sample prepared at lower pressure possesses a 0.1 V wider bandgap (2.94 eV) than that prepared at higher pressure (2.82 eV). Both Mott-Schottky analysis and XPS valence band spectra showed that this difference was essentially due to a shift of the conduction flat band (CB) potential. Thus, this work demonstrates that the total pressure during $WO_3$ deposition by RF diode sputtering affects the position of the CB energy very likely due to the different extent of crystal structure distortion induced by oxygen vacancies (3), in agreement with the crystal field theory (CFT). Lowering the pressure increases the oxygen vacancies, and produces a shift of the CB towards higher energy. The equivalent n-n heterojunction at the interface of the double-layer (see Figure) creates a built-in electric field that facilitates the photopromoted electron transfer toward the lower laying conduction band material, while the columnar innermost layer introduces percolation paths for efficient electron transport toward the conductive tungsten foil. Both phenomena contribute to decrease the interfacial charge transfer resistance ($R_{ct}$) as measured by impedance spectroscopy and lead to a *ca.* 30% increase in the PEC performance compared to the monolayer and to a 93% faradaic efficiency, which is among the highest reported so far for $WO_3$ photoanodes. Upon methanol addition an outstanding 4-fold photocurrent density increase up to 6.3 mA $cm^{-2}$ was attained over the bilayer $WO_3$ photoanode, much larger than the usually observed current doubling effect.



*Acknowledgment*
This work received financial support from the Regione Lombardia and Cariplo Foundation co-funded "SmartMatLab Centre" project (Grant No. 2013-1766)

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# Hydrides as High Capacity Anodes in Lithium Cells: An Italian "Futuro in Ricerca di Base FIRB-2010" Project

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Automotive and stationary energy storage are among the most recently-proposed and still unfulfilled applications for lithium ion devices. Higher energy, power and superior safety standards, well beyond the present state of the art, are actually required to extend the Li-ion battery market to these challenging fields, but such a goal can only be achieved by the development of new materials with improved performances. Focusing on the negative electrode materials, alloying and conversion chemistries have been widely explored in the last decade to circumvent the main weakness of the intercalation processes: the limitation in capacity to one or at most two lithium atoms per host formula unit. Among all of the many proposed conversion chemistries, hydrides have been proposed and investigated since 2008. In lithium cells, these materials undergo a conversion reaction that gives metallic nanoparticles surrounded by an amorphous matrix of LiH. Among all of the reported conversion materials, hydrides have outstanding theoretical properties and have been only marginally explored, thus making this class of materials an interesting playground for both fundamental and applied research. In this communication, we illustrate the most relevant results achieved in the frame of the Italian National Research Project FIRB 2010 Futuro in Ricerca "Hydrides as high capacity anodes in lithium cells" and possible future perspectives of research for this class of materials in electrochemical energy storage devices.

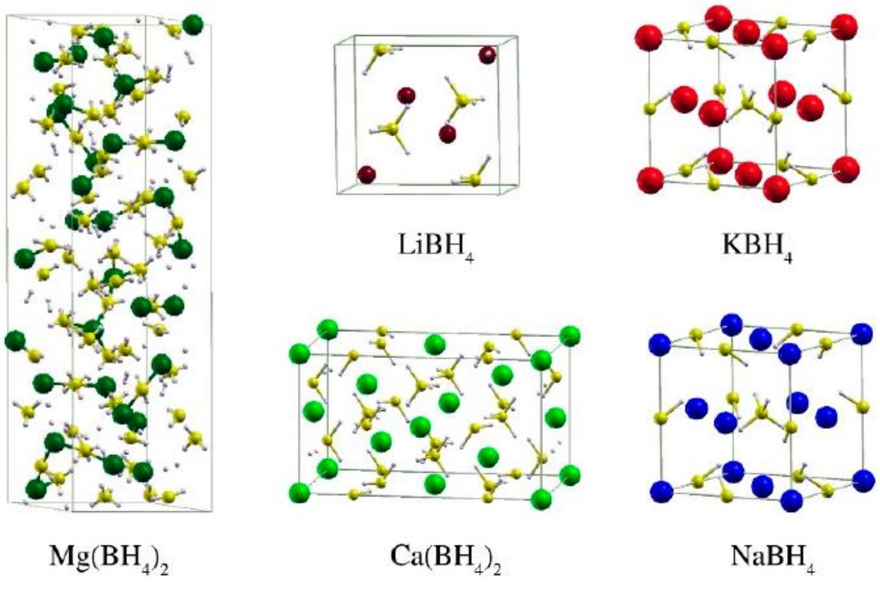

**Figure 1.** Crystal structures of the borohydrides phases.

# Bio-Hybrid Complexes In Artificial Photosynthesis

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The sun was born five billion years ago and it is estimated that it will continue to irradiate the same amount of energy for another five billion years. Sun is a renewable energy source, inexhaustible within the humankind life, and, every year, Earth receives an amount of solar energy ten thousand times greater than that the entire planet population uses (1). The ability to convert solar light into chemical energy is the fundamental feature of photosynthetic systems. Photosynthesis is the most important biological process, supplying Earth's biosphere with oxygen and energy for living organisms' metabolism (2). All life on Earth depends on photosynthesis directly or indirectly, and has been deeply investigated by scientists with the aim of reproducing it in the laboratory, mimicking the Nature, and, consequently, producing green energy efficiently, following the artificial photosynthesis way (3). The complexity of the natural photosynthetic systems is difficult to reproduce *in vitro*; however, it is largely related to their living character and can be reduced in a biomimetic environment. In this regard, ideal biomimetic systems must efficiently harvest the sunlight, with the help of suitable antennas, and convert the energy in a stable charge-separated state with a lifetime long enough to allow ancillary chemistry to take place. In the purple, no sulphur photosynthetic bacterium *Rhodobacter sphaeroides R26*, energy from sunlight is harvested by antennas and transferred to reaction center (RC), a most efficient photoconverting transmembrane protein. During the electron transfer process, the RC, upon photon absorption, promotes one electron sitting on the bacteriochlorophylls dimer (D), the electron donor, in its excited state and then it shuttles to the electron acceptors the ubiquinone-10 Q, generating the charge separated state $D^+Q^-$. In the presence of external electron donors, the oxidized $D^+$ is reduced again and a second photon impinges a second electron so that the quinone Q, now doubly reduced, is doubly protonated and it is released as quinol. Cytochrome $c_2$ is the physiological electron donor to the oxidized dimer. Our idea is to build a supramolecular architecture made up of the photosynthetic bacterial reaction center, an artificial light-harvesting antenna, synthesized *ad hoc*, belonging to the class of heptamethine cyanines, with the task of increasing the RC absorption cross section in the visible range, and an electron donor redox protein, the cytochrome $c_2$. These three components were connected to each other by covalent bonds obtaining a stable bio-hybrid supramolecular complex, easily interfaceable to a semi-conductive surface, with the aim of assembling a sustainable sunlight-to-energy converting device based on proteins.

Insert references in brackets as follows: (1) (1,2,3) and add reference list at the bottom of the abstract using justified Times New Roman 10, with line-spacing 1. As indicated below:

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# Electronic coupling in H-shaped tetra-arylamine mixed-valence compounds

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Organic mixed-valence compounds (MVs) are donor-acceptor compounds that possess an open shell ground state (1). Amongst the MVs particularly interesting are those with arylamines connected through a conjugated bridge. The nature of the bridge as well as that of the substituents on the arylamine moieties, determines the electrooptical properties of such compounds. Specifically, the intervalence charge transfer transition (IVCT) in the near infrared region (NIR), occurring upon photoexcitation of the oxidized monocation species, is heavily affected by the above structural parameters. These compounds can be designed to work as electrochromic materials in smart devices for controlling the solar thermal radiation, as well as for the generation of high charged radical species for high spin magnetic materials (2,3). Here we present organic MVs with an innovative H-shape design, where four redox centres are bridged "vertically" via a dibenzofulvene backbone and "horizontally" via a bis-(dibenzofulvene)-thiophene bridge. They are oxidized to stable high charged radical species, showing IVCT in the NIR, in contrast to the linear systems lacking one dibenzofulvene-bisamine moiety at one end of the thiophene bridge, where band bleaching occurs upon dication formation. Electrochemical, spectroelectrochemical and TD-DFT results, show that the IVCT in high oxidation states of the H-shape MVs is due to the activation of both vertical and horizontal electron transfer pathways (4). The innovative H-shape design may improve the potential electrooptical applications of MVs, highlighting the importance of the coupling between multiple redox centres and paving the way for the development of three-dimensional multicentre mixed valence compounds.

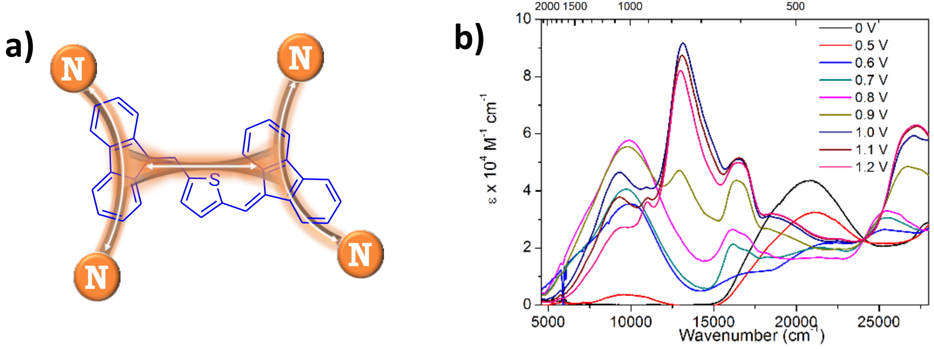

Figure 1. H-shape MVs based on the bis(dibenzofulvene)tiophene bridge a); example of the electrochromic response of an H-shape compound in the Vis-NIR region b).

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# Comunicazioni Poster

# A Solid-Liquid Soggy-Sand Electrolyte for Dye-Sensitized Solar Cells

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The electrolyte is one of the crucial components in dye sensitized solar cells (DSSCs), allowing for fast diffusion of charge carriers between the electrodes and directly affecting photocurrent density ($J_{SC}$), photovoltage ($V_{OC}$), and fill factor (FF). Quasi-solid state DSSC electrolytes typically ensure mechanical properties of a solid and diffusive property of a liquid, circumventing practical problems such as solvent volatility, leakage, photodegradation and corrosion of counter electrode (1). In this study, a polyethylene glycol dimethyl ether (PEGDME, $M_w$ = 150 g mol$^{-1}$) based $I^-/I_3^-$ electrolyte containing mesoporous $SiO_2$ particles (MSU-H, 15 nm pores) is investigated in terms of ionic conduction and DSSC performance. Similarly as in "soggy sand" electrolytes, preferential adsorption of anions is observed by Zeta potential measurements and ionic conductivity of the liquid electrolyte can be enhanced (2). High values of photovoltaic parameters at 1 sun irradiation ($J_{SC}$ = 11.5 mA cm$^{-2}$, $V_{OC}$ = 0.69 V, FF = 0.47, 6.3% efficiency) at 2.8 vol% $SiO_2$ suggests an improved regeneration kinetics of the dye molecules. Transient photocurrent experiments confirmed favorable mass transport. A remarkably high 11.2% efficiency was measured under 0.2 sun irradiation.

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# Metal-Support Interaction in Pt nanoparticle supported on Nitrogen Functionalized Mesoporous Carbon: a combined DFT and Experimental Approach

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Proton exchange membrane fuel cell (PEMFC) wide spreading is still hindered by the bottleneck of the oxygen reduction reaction (ORR). Actually, large amounts of precious Pt metal are required to promote the sluggish kinetics, causing the PEMFCs to be economically uncompetitive with conventional technologies. One way to reduce the metal loading, while increasing the metal nanoparticles (NPs) catalytic activity, is to support them on activated surface able at triggering their activity by increasing the number of active sites or by electronic interaction (1). Pt NPs on nitrogen functionalized mesoporous carbon (NMC) have proved to be interesting materials for ORR (1).

In this paper we employed a new synthetic route for the simultaneous Pt NPs deposition and carbon support doping by using a platinum precursor bearing a nitrogen containing ligand such as 1,10-phenantroline or 2,2'-bipyridine. Metal NPs (average size 3 nm) were successfully synthesized by thermal solid state reduction on a commercial carbon. XPS analysis confirmed that during the treatment the ligand degrades and the nitrogen is embedded in the mesoporous carbon structure obtaining a surface modification of the carbon support, preserving the bulk conductivity and thermal stability (2).

Electrochemical characterization revealed superior mass catalytic activity towards ORR in those catalysts showing higher Pt-N interaction expresses as B.E. shift of nitrogen components (Fig.1a). Pyridinic, pyrrolic and graphitic functional groups were considered in a DFT computational investigation for discriminating the interaction with a single Pt atom and nitrogen defects. DFT analysis confirmed that the interaction between Pt and nitrogen depends on the number and different types of nitrogen functional groups, so that the most stable structure is observed when Pt interacts closely with 4 pyridinic groups (Fig.1b).

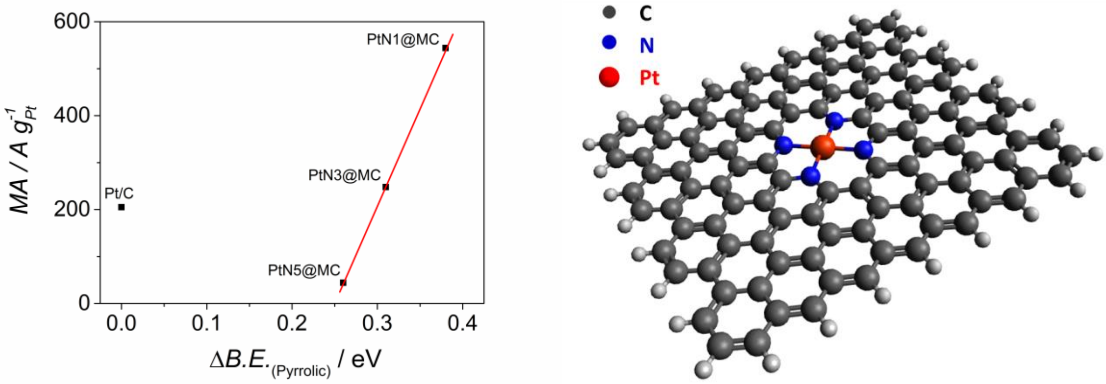

Figure 1. a) correlation between pyrrolic B.E: shift and mass activity towards ORR, b) DFT optimized structure of Pt atom on NMC.

Funding from University of Padova (PRAT CPDA139814/13) is acknowledged.

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# Nitrogen and sulfur doped mesoporous carbon, prepared form templating silica gel, as interesting materials for supercapacitors

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Highly accessible surface area and heteroatom-doping are desired properties for carbon electrode materials to be used in electrochemical supercapacitors (1).

In this paper, nitrogen and sulfur doped carbon materials with wide mesopores (13-14 nm) were synthetized according to a hard template approach by pyrolysis of sucrose, 1,10-phenantholine or dibenzothiophene as carbon, nitrogen- or sulfur-carbon precursors, respectively. The morphology and dimension of mesopores were induced by sacrificial $SiO_2$ nanoparticles (10-20 nm), which after removal by an etching solution reveals a network of hemispherical pores (2,3). The interconnected pore structure was confirmed by scanning electron microscopy and transmission electron microscopy. X-ray photoemission spectroscopy and elemental analysis confirmed the presence of nitrogen and sulfur functional groups. The prepared materials were fully characterized by cyclic voltammetery, chronopotentiometry and electrochemical impedance spectroscopy in 0.5 M $H_2SO_4$. Notwithstanding the small surface (200 $m_2$/g) determined by BET method, the nitrogen doped mesoporous carbon showed high specific gravimetric (~170 F $g^{-1}$) and surface (~835 mF $m^{-2}$) capacitances, comparable with material showing surface area 5 to 10 times higher.

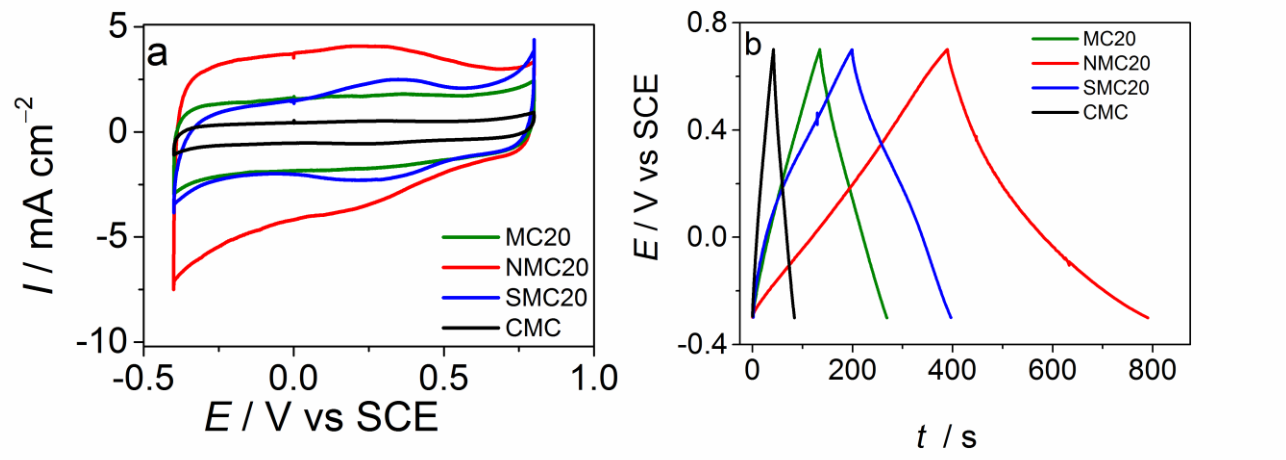

Fig1. Electrochemical data in 0.5 M $H_2SO_4$. (a) CVs of MCs electrodes at 5 mV $s^{-1}$. (b) Galvanostatic charge/discharge curves of MCs at $I$ = 0.26 mA $cm^{-2}$.

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# Electrochemistry of inherently chiral macrocyclic *vs* open-chain oligomers: reciprocal interactions between bibenzothiophene atropoisomeric cores?

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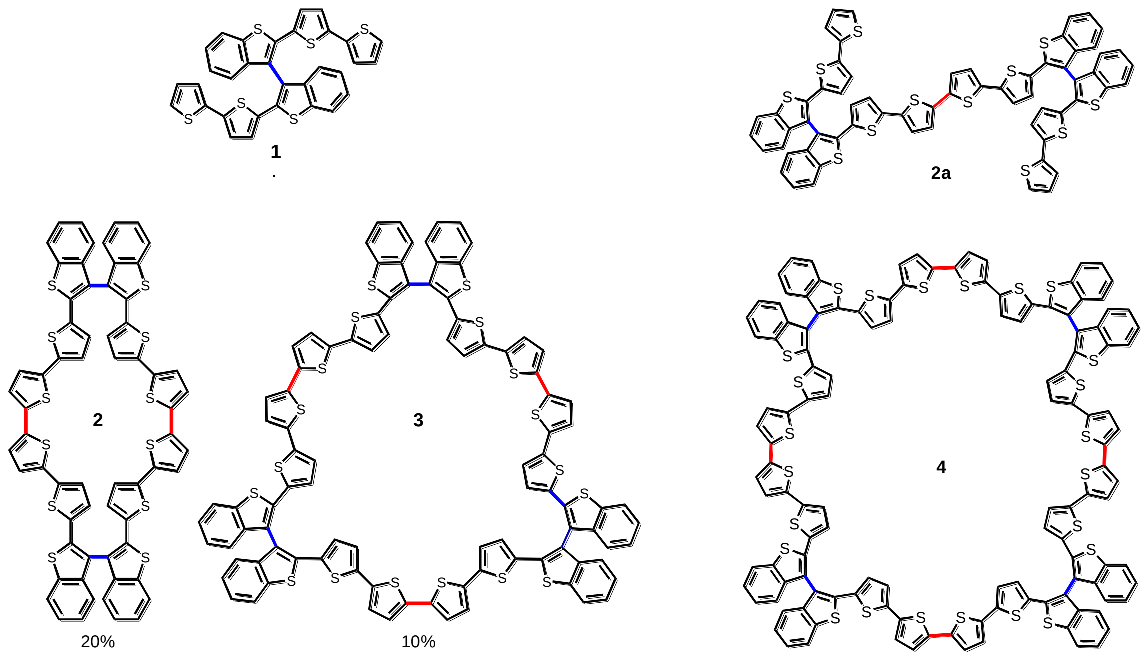
We have recently introduced "inherently chiral" enantiopure electrode surfaces of outstanding chirality manifestations, including large potential differences for the enantiomers of chiral probes in voltammetry experiments. (1-5) They can be prepared by electrooligomerization from monomer 1, having an atropoisomeric dibenzothiophene core, and consist of a mixture of macrocyclic and open-chain oligomers as those represented in the Figure, which we have electrochemically investigated one by one in detail. The results will be presented and discussed. Especially the macrocycles provide a quite attractive casebook of interactions between equivalent redox centers, possibly also requiring to take into account interactions between facing chains, especially in the case of the smaller ringlet.



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# Mitigation of the side reactivity upon cycling of a LTO-LFP Li-ion battery

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Novel and safer Li-ion cells configurations have found commercialization in recent years in substitution to the usual C-NCA standard formulation. In particular the coupling of lithium titanate (LTO) negative electrodes with lithium iron phosphate (LFP) positive electrodes is in theory suitable for a full Li-ion configuration able: (1) to work in a potential range within the thermodynamic stability window of all the typical standard carbonate-based electrolytes; (2) to suffer only a limited performance decrease due to the use of a negative electrode material with a practical specific capacity 50% smaller compared to graphite; and (3) to disclose outstanding improvements in the power performances due to the excellent lithium ion mobility in both the positive and the negative electrode materials obtained by a fine tuning of the morphology, composition and structure.

Here we illustrate our recent studies about the unexpected complex reactivity upon cycling of a LTO-LFP full Li-ion cell. Our aim is to draw a fundamental description of the parasitic side chemistry that takes plane in a LTO-LFP Li-ion cell upon cycling in galvanostatic conditions. In this view coin cells as well as pouch cells have been assembled using commercial materials (Custom cells Gmbh and Solvionic) and electrodes recuperates for post mortem analysis by SEM, FTIR and Raman spectroscopy. Moreover the release of gaseous components upon cycling has been monitored by continuous in operando monitoring of the internal pressure in a LTO-LFP cell assembly and ex situ gas chromatography.

Our results support the occurrence of an unexpected complex parasitic chemistry with remarkable differences in the degradation processes depending on the galvanostatic cycling conditions of the cells.

This detrimental parasitic chemistry has been mitigated by the incorporation of a selective metallic getter able to sequestrate gaseous components released upon cycling. Evidences of the mitigation of the release of gas byproducts due to the side parasitic chemistry are here illustrated.

# Electrochemically mediated Atom Transfer Radical Polymerization in ionic liquid/water mixtures

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Atom transfer radical polymerization (ATRP) is one of the most advanced techniques to produce polymers with precise and complex architectures, predetermined molecular weights, and high chain-end fidelity (1). Usually, ATRP is catalyzed by a copper−amine complex through a reversible equilibrium ($K_{ATRP}$) involving the activator and deactivator complexes, $[Cu^IL]^+$ and $[X\text{-}Cu^{II}L]^+$ (X = Cl, Br), respectively. $K_{ATRP} << 1$ guarantees that the vast majority of the propagating chains is in the dormant state ($P_n$-X), while the concentration of active radicals ($P_n$•) is low to minimize the occurrence of radical termination reactions and promote concurrent growth of all polymer chains (2). In electrochemically mediated ATRP (*e*ATRP), one of the most recent and potent developments of ATRP, $Cu^I$ is (re)generated by reduction of $Cu^{II}$ at the working electrode. This allows to precisely control the $Cu^I/Cu^{II}$ ratio, enhancing the overall polymerization control (3). Room Temperature Ionic liquids are gaining increasing relevance in many applications, especially for their non-volatility, non-flammability and versatility. Water is inexpensive, abundant and non-toxic, but its use in ATRP is limited to few water-soluble monomers. In this study, we explored the possibility of adding water into the polymerization medium to reduce process cost and increase the rate of polymerization ($R_p$) and cleanness of the system. Mixtures of a model ionic liquid, 1-butyl-3-methylimidazolium trifluoromethanesulfonate, [BMIm][OTf], and water have been used for the first time in *e*ATRP of hydrophobic acrylates and methacrylates. In [BMIm][OTf] containing 20 vol% $H_2O$, polymerizations proceeded faster than in the pure ionic liquid and yielded well-defined polymers. The increase of $R_p$ correlates with the amount of $H_2O$ and is consistent with enhanced activation rate of the dormant $P_n$-X. Indeed, the rate of activation of the C-X bond is usually much higher in water than in ionic liquids or organic solvents (4). *e*ATRPs were performed also in aqueous media (60 vol% $H_2O$) using [BMIm][OTf] as co-solvent to help dissolve both monomer and polymer, with excellent results (high conversion and low dispersity) for both hydrophobic and hydrophilic monomers. The prepared polymers were easily isolated by precipitation either with an excess of $H_2O$ or by cooling. The ionic liquid and catalyst were recycled, with high yields, by evaporating water and unreacted monomer from the exhaust mixture. Reactions performed with fresh and recycled ionic liquid provided very similar results. In conclusion, *e*ATRP in [BMIm][OTf]/$H_2O$ truly offers a powerful, fast and clean approach for the synthesis of tailor-made polymers.

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# Electrochemical Conversion of Carbon Dioxide: effect of the cell and of operating parameters on the performances of the process

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Recycling technologies of $CO_2$ allow to introduce renewable energy in the chemical and energy chain, storing a renewable energy in the chemical form. In this context, electrochemical conversion of $CO_2$ is considered one of the more interesting approaches, using excess electric energy from intermittent renewable sources. (1) Furthermore, products can be selectively controlled by changing the operating conditions of electrolysis. In particular, in the last years, an increasing attention has been devoted to the electrochemical conversion of $CO_2$ to formic acid or formate in water. (2,3,4) The main hurdle of the reduction of $CO_2$ from water solution is the low $CO_2$ solubility in water. In this work, a systematic study on the effect of the $CO_2$ pressure and of other operating parameters on the conversion of $CO_2$ at tin flat cathodes to formic acid was performed to overcome this obstacle.

The reduction of $CO_2$ was first studied in a glass undivided cell at atmospheric pressure to evaluate the effect of various operating parameters, including the nature of the anode and of the supporting electrolyte, the mixing rate, the current density and cathode to anode area ratio. Subsequently, in order to improve the performance of the process, a series of electrolysis was performed in a batch stainless steel undivided cell in a wide range of pressure of $CO_2$ and current density. It was shown that an increase of the pressure leads to a drastic enhancement of the final formic acid concentration. Indeed, the utilization of relatively high $CO_2$ pressures (15–30 bar) allowed to achieve high concentrations of formic acid (up to 0.46 mol $L^{-1}$) at high current density (up to 90 mA $cm^{-2}$) and with cheap and simple undivided cell. (5)

Several researchers have discussed the economic feasibility for large-scale design of the $CO_2$ mitigation electrochemistry system, by suggesting that could be operationally profitable. Therefore, in the last stage, the process was performed in a pressurized filter-press cell, suitable for scale-up on applicative scale. The goal of this research is to provide an electrochemical process sustainable at applicative point of view characterized by a high yield and selectivity of the product. Long-term stability has also to be acquired in order to obtain an interesting alternative at commercial level for the conversion of carbon dioxide.

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# Connections at the Interface: Shuttling the Electrochemical Stimulus from Electrode to Monomer Droplets in Dispersed Polymerization

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Electropolymerization under heterogeneous conditions is challenging because in dispersed media electrode and reactants are separated: the electrode is in contact with the continuous aqueous phase, while polymerization reactants (monomer, initiator, and radicals) are dispersed in the organic phase. Therefore, to trigger polymerization the electrochemical stimulus must first reach the aqueous phase (crossing the first electrode | liquid interface) and then shuttle to the dispersed phase (crossing the second liquid | liquid interface). Moreover, controlled radical polymerization (such as atom trasnfer radical polymerization, ATRP) poses an additional challenge in comparison to most organic reactions, because radicals must be continuously activated/deactivated after the electrochemical stimulus has reached the organic phase droplets. We used two strategies to establish efficient electrochemical communication between electrode and droplets in order to obtain ATRP in a miniemulsion. First, we created a dual catalytic system, composed of two distinct copper catalysts (one hydrophilic and one hydrophobic). The two mediators created an unbroken connection from the electrode surface, via the aqueous continuous phase, to the monomer droplets. This enabled controlled polymerization and resulted in the production of well-defined polymeric latexes.(1)

The second—more refined—approach involved the *in situ* generation of hydrophobic ion pairs between anionic surfactants and ATRP cationic complexes. The ion pairs shuttled the active copper catalyst and the electrochemical stimulus to the monomer droplets, enabling controlled polymerization. This catalytic mechanism opens a new avenue for controlled radical polymerization in *ab-initio* emulsion (whereby both small micelles and large monomer droplets are present).(2)

Fast and well controlled polymerization of acrylic and methacrylic monomers in aqueous dispersed media was achieved with as low as 50 ppm of copper. Moreover, catalyst removal (by technique such as electrodeposition) was simple because during purification the hydrophilic cationic copper complexes easily left the hydrophobic polymer particles.

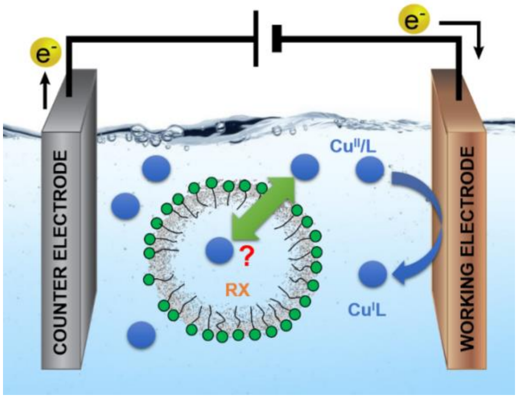

Figure 1. Scheme of electrochemically mediated ATRP in dispersed media (L = amine ligand)

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# Artificial Inherently Chiral Electroactive Membranes

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Low-cost, continuous, high-efficiency resolution technology is clearly needed for commercial-scale preparation of enantiomerically pure substances. Membrane technology, fortunately, fulfils this need very well because of its high efficiency, low energy usage, simplicity, convenience for up- and/or down-scaling, and continuous operability. Membrane-based chiral resolution can be achieved using either enantioselective or non-enantioselective membranes. The enantioselective membranes themselves can carry out chiral separation of enantiomers because they contain chiral recognition sites (1). Considering the outstanding enantioselection ability achieved with our inherently chiral surfaces (2) we have decided to synthesize by electrooligomerization inherently chiral membranes. These membranes were electrodeposited on FTO electrodes from the enanantiopure monomers of our inherently chiral forefather ($BT_2T_4$) dissolved in acetonitrile + tetrabutylammonium hexafluorophosphate 0.1 M as supporting electrolyte. The chiral membrane detachment is then obtained by dipping the FTO in deionized water. Preliminary tests have shown that they are electroactive with a perfectly specular CD spectra. We have also performed experiments by inserting the enantiopure membrane in a support normally used for ISE electrodes.

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# Electrochemical Impedance Spectroscopy Meets Arduino: Can We Make an Open-source Impedance Analyzer?

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Commercial potentiostats which offer modules to perform electrochemical impedance spectroscopy (EIS) have very high specifications like broad frequency range (> 6 orders of magnitude), high accuracy, and low distortions. However, they are much more expensive than standard instruments. Moreover, the instrument is a black box where often the scientist has little or no knowledge of the real operations, such automatic phase corrections or current range selection, or because of software usability some fine features are hidden, like for example the choice of an arbitrary integration time or inspection of harmonic distortions. Although the high quality of the hardware, these limitations hinder more sophisticated or particular applications or simply make troubleshooting more complicated.

On the other hand, the advent of chip, easy-to-program microcontrollers equipped with analog to digital (ADC) and digital to analog converters (DAC) give the possibility to build up a rather inexpensive impedance spectrometer with full control over any feature. Arduino paved the way of an electronic revolution, where almost everybody can be able to interface a computer to an instrument. Some relevant specifications of Arduino and Arduino-compatible microcontrollers are reported in the table.

*Summary table for some microcontrollers.*

| | **Arduino Due (1)** | **Teensy 3.6 (2)** |
|---|---|---|
| **Price** | **~35 €** | **~35 €** |
| **CPU clock frequency** | **84 MHz** | **180-240 MHz** |
| **Memory (flash+SRAM)** | **608 kB** | **1280 kB** |
| **Number of ADC** | **12** | **25** |
| **Number of DAC** | **2** | **2** |
| **ADC resolution** | **12 bits** | **>12 bits** |
| **DAC resolution** | **12 bits** | **12 bits** |

Several open-source projects already showed how to build up and program computer base oscilloscopes (reference (3) for example). Moreover, the high computational power and rather large memory allows to perform fast Fourier transforms on the chip or to buffer the data during streaming to the computer for more involved analysis giving large flexibility in the usage.

In this work we report the results achieved with some Teensy (Arduino-compatible) microcontrollers connected to standard potentiostats in performing EIS. The details of the analog front end, program, and signal processing, following the open-source spirit, are also shown and discussed.

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# Thin films of $MoS_2$ on Ag(111)

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The transition metal dichalcogenides (TMDC) are materials of interest in the fields of the material chemists, physicists and engineers.
TMDC monolayer s are 2-dimensional (2D) material, as graphene, have the general formula $MX_2$, where M is a transition metal (as Ta, Nb, Mo or W) and X is chalcogen (as S, Se or Te) (1). Each layer of $MX_2$ is a trilayer, made up of a sandwich of two chalcogen layers on either side of a transition metal center layer.
The Electrochemical Atomic Layer Deposition (E-ALD) is one of these techniques that allows us to produce thin films of semiconductor. Exploiting Surface Limited Reactions (SLR), it enables the deposition of highly ordered ultra-thin films from diluted aqueous solutions and at room temperature and pressure.
Underpotential deposition (UPD) is a type of electrochemical SLR, where an atomic layer of a first element is deposited on a second, at a potential prior to (under) that needed to deposit the first element on itself, so that the resulting deposit is generally limited to an atomic layer.
It occurs when the depositing element is able to somehow interact with the substrate, so that the deposition of the layer in direct contact with the substrate occurs at a potential preceding bulk deposition, that is, the deposition of the element on itself.
In the study presented here, E-ALD was used to grow molybdenum disulfide $MoS_2$ on crystalline Ag[111] elecrtode. UPD anodic electrodeposition of $Na_2S$ on crystalline Ag[111] electrode are well-known (2). The research move to discover the optimal conditions to deposit Mo on Ag/S from a solution of $MoO_4^{2-}$ in alkaline buffer. This study has been carried by means of voltammetric techniques, and AFM characterizations of the deposit.

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# Influence of Different Porosity Carbon Supports in the RRDE Analysis

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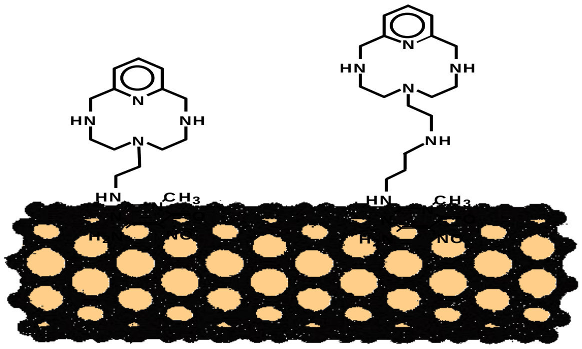
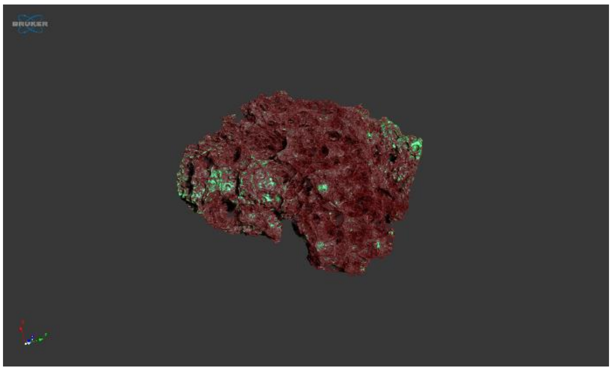
RRDE is an electrochemical technique furnishing information about the mechanism of the Oxygen Reduction Reaction (ORR) and its kinetic parameters (1). One of the most appealing applications of ORR consists in the study of reactions occurring at the cathode in energy converting systems such as fuel cells. In order to speed up the ORR kinetics to reach a practically usable level in fuel cell, a cathode ORR catalyst is needed. Platinum-based materials are the most practical catalysts. Nevertheless, owing to the limited reserve in nature of Platinum-group metals, and to their prohibitive cost, extensive research has focused on developing alternative catalysts. It was observed that the activity of an electrocatalyst increases hand to hand with the reaction surface area. The use of carbon supports is the right compromise to minimize the use of metallic catalysts. The high surface area of carbon supports is due by their high porosity (2). In this work we evaluated, by means of Rotating Ring-Disk Electrode (RRDE), the electrocatalytic properties of different porosity of carbon supports. Measurements were performed by using RRDE from Pine Instruments Co. All cyclic voltammograms (CV) and RRDE were carried out at scan rate of 5 mV/s in the potential range from -1,1 to +0,2 V vs Ag/AgCl/sat. KCl. The number of electrons transferred for $O_2$ molecule for each catalyst were calculate by Koutecky-Levich (K.L.) equation applied to the ORR curves obtained at different rotation rates (rpm) and from RRDE technique. The results were compared with data relating to the Glassy Carbon electrode and Pt-electrode. These results showed a different values on number of electrons between K.L. and RRDE. In fact, a high porosity of carbon supports showed a greater difference between the two techniques of analysis.





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# Electrodeposition of Bismuth Thin Films

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The electrodeposition technique is an interesting approach for the production of materials with application in electronics devices and photovoltaics components, since needs simple conditions and has low costs (1). The EALD (Electrochemical Atomic Layer Deposition) method allows a high control on the deposit by the single-layers surface limited electrodeposition (2). With an automatized system for the repetition of different mono-layers deposition cycles we are able to control the thickness and composition of the entire final material, which is an important requested task in nanoscience.

In this study, we present the electrodeposition of bismuth-based materials, which is a relatively unexplored new field of research that is expected to show many desirable thermoelectric, optoelectronic and electronic properties for technologically innovative devices besides bismuth is a component of nanostructure topological insulators.

Thin films of both bismuth alone and semiconductors compounds have been explored with EALD using a silver (111) mono-crystal as substrate (3). Our goals were to grow a “massive” layer (up to hundreds of nanometers) of crystalline nanostructured bismuth, deposit a multi-layer crystalline structure of bismuth selenide investigating the optimal conditions to obtain these materials in addition to the understanding of the deposition mechanisms.

The synthesized thin films have been characterized electrochemically with cyclic and stripping voltammetry to obtain composition information followed by a morphological and microanalytical SEM-EDX investigation and structural characterization.

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# Effect of Pressure on the Electrochemical Conversion of CO2 to CO

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To minimize the negative effect of carbon dioxide as a greenhouse gas and introduce renewable energy in the chemical and energy chain, an interesting approach is the Carbon Capture and Conversion. In this context, one of more appealing conversion strategies is the electrochemical reduction of $CO_2$, which could combines the utilization of excess electric energy from intermittent renewable sources with $CO_2$. (1) Furthermore, $CO_2$ can be selectively converted into various useful chemicals by changing the operating conditions of electrolysis. In particular, an increasing attention has been devoted to the electrochemical conversion of carbon dioxide to carbon monoxide. (2,3) The main obstacle of that conversion from water solution is the low $CO_2$ solubility in water. In this work, a methodical study on the effect of the $CO_2$ pressure and of other operating parameters on the conversion of $CO_2$ at flat cathodes to carbon monoxide was performed. In detail, the reduction of $CO_2$ was studied in different kind of electrochemical cells to evaluate the effect of various operating parameters, including the nature of the supporting electrolyte and the nature of cathode (Ag and Au), the current density, the pH and the pressure of $CO_2$. It was shown that an increase of the pressure leads to an improvement the stability of the electrode.

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# Operative parameters and bacterial community effect on single chamber membraneless microbial fuel cell

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Municipal, domestic, animal and food processing wastewaters have a theoretical carbon content sufficient to globally sustain the whole water infrastructure. However, it is a common practice to use additional energy to remove it instead of trying to convert it (1). It is possible, indeed, to directly convert this organic content into electricity thanks to microbial fuel cells (MFCs), bio-electrochemical devices in which particular bacterial strains oxidize the organic matter using electrodes as final electron acceptor (2). What has been mainly adopted in this work, is usually reported as Single Chamber Membraneless (SCML) MFC. SCML-MFC were developed without any physical delimitation between the anodic and cathodic environments. With regards to a conventional MFC, SCML have reduced cost, both investment and exercise, avoiding the usage of membranes (3). In some SCML-MFC work, an horizontal cathode is used, lying at the interface between the liquid and the gas phase (4), circumstance that inspired our work (5). Other authors have changed electrode distance in order to asses this parameter influence (6), deducing that a closer distance could increase aeration of the anodic biofilm, lowering the performance. Thus, researchers concern designing SCML-MFC is to limit as much as possible anode oxygenation (8).In the present work, this very same path was followed, exploring the effect of cathode positioning, hydrodynamic regimen and evaluating the possibilities given by the usage of bio-cathodes with both pure *Shewanella putrefaciens* culture and mixed communities.

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# Towards High Energy Density Aging Resistant Li-ion Polymer Batteries

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A wide interest is mounting towards polymer electrolytes, due to their application in energy efficient rechargeable batteries, photo-electrochemical cells, electrochromics, and supercapacitors. Polymer electrolytes exhibit unique advantages such as mechanical integrity, wide variety of fabrication methods in desirable size and shape, possibility to fabricate an intimate electrode/electrolyte interface and adapt to a lightweight, leak-proof construction, and economic packaging structure.

In this communication, we offer a summary of our results regarding the synthesis, physico-chemical and electrochemical characterization of solid polymer electrolytes (SPEs) based on different monomers/oligomers (methacrylic and/or ethylene oxide based) with specific amounts of lithium salt, plasticizers and/or fillers (1,2). Profoundly ion conducting ($\sigma > 10^{-4}$ S cm$^{-1}$ at 20 °C), electrochemically stable (> 5 V vs. Li), self-standing, robust and tack-free SPEs are successfully prepared via a rapid and easily up-scalable process including a light and/or thermally induced polymerization step. The resulting crosslinking allows the incorporation of high amounts of plasticisers (e.g., RTILs) and lithium salt (based on $TFSI^-$ anion), leading to a material with remarkable morphological characteristics in terms of homogeneity and mechanical abusability under highly stressful conditions.

Lab-scale Li-polymer cells assembled show stable charge/discharge characteristics without any capacity fading at C/5 current regime (> 130 mAh g$^{-1}$ in $LiFePO_4$/Li configuration and > 150 mAh g$^{-1}$ in $TiO_2$/Li configuration even @ 20 °C). The overall performance of the SPEs postulates the possibility of effective implementation in the next generation of safe, durable and high energy density secondary all-solid Li-ion polymer batteries working at ambient and/or sub-ambient temperatures.

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# Novel Lithium Battery Single-Ion Block Copolymer Electrolytes based on Poly(Ethylene Oxide) and Methacrylic Sulfonamide

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Polymer electrolytes have been proposed as a replacement for conventional liquid electrolytes in next-generation lithium-based batteries, mainly because of their intrinsic enhanced safety and peculiar chemical structure that can be tailored as desired to display unique properties such as lithium-ion transference number ($t^+$) approaching unity. This new class of materials, namely Single-Ion Conductors, has attracted increasing interest in recent years. Nevertheless, practical application of polymer electrolytes is still limited mainly by low ionic conductivity ($\sigma$), which is far below $10^{-5}$ S $cm^{-1}$ at 25 °C.

Herein, the preparation and characterization of new families of single-ion conducting copolymers based on the specifically designed lithium 1-[3-(methacryloyloxy)propylsulfonyl]-1-(trifluoromethylsulfonyl)imide (LiMTFSI) anionic monomer is described (1,2). RAFT polymerization was employed to prepare well-defined anionic di- and tri-block copolymers comprising poly(LiMTFSI) and poly(ethylene oxide) blocks (1). The effect of the macromolecular architecture and molecular weight on thermal and ionic conduction properties is thoroughly discussed. Block copolymers were semi crystalline, with a single glass transition temperature ($T_g$) due to the miscibility of the amorphous regions of both the blocks. $T_g$, ranging from –55 to 7 ºC, as well as degree of crystallinity ($X_c$, ranging from 51 to 0%) were both composition dependent. Block copolymers showed very high σ as compared to previous examples (up to ≈ $10^{-4}$ S $cm^{-1}$ at 70 ºC) combined with and impressive $t^+ \approx 0.91$, and wide 4.5 V electrochemical stability. In addition to these promising features, solid polymer electrolytes were successfully tested in $LiFePO_4$/Li cell prototypes at different temperatures providing long lifetime up to 300 cycles, and outstanding rate performance up to C/2 (≈100 mAh $g^{-1}$).

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# Solid-state lithium batteries adopting sulfide-based solid electrolytes

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All-solid-state lithium secondary batteries with inorganic solid electrolytes (SEs) attract much attention in terms of safety and reliability. Bulk-type solid-state cells composed of electrode and electrolyte powders have an advantage of achieving large energy density. Key materials to realize bulk-type lithium batteries are SEs with high Liþ ion conductivity and active materials with high capacities which are suitable for all-solid- state lithium batteries. Sulfide based SEs have been studied because of their remarkably high lithium-ion conductivities at room temperature (1).
This work was aimed to select optimized components for a solid-state lithium battery. We studied Li3PS4 (SE1) and LiI-Li3PS4 (SE2) (Samsung R&D Institute Japan) as glass-type electrolytes. Li3PS4 and LiI-Li3PS4 were characterized in terms of transport properties (Impedance spectroscopy) studying the temperature dependence of the ionic conductivity and structure (Raman Spectroscopy and X-ray diffraction). We studied these electrolyte in an all-solid-state-cell in combination with different kind of anodes.

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# Design of bis(fluorosulfonyl)imide-based ionic liquids for lithium ion batteries

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The great demand for batteries with high power and energy densities promotes the need for an advanced lithium-ion battery technology. The electrolyte is a critical component involved in balancing energy and safety specifications. The electrolyte solutions that normally contain organic solvents have been replaced with highly stable ionic liquids (ILs) to combat the flammability. ILs are entirely composed of ions and having negligible vapor pressure. We have been designed novel ILs which are suitable for the battery applications. Heteroatom-modification of simple ILs can cause unexpected change in thermal- and electrochemical-stability. However, we recently revealed that the modification of cation in ILs with an ethoxyethylether chain improves liquid properties of ILs, i.e. suppresses crystallization at sub-zero temperature, without detracting from the stabilities (1). In this case, bis(trifluoromethanesulfonyl)imide ([TFSI]) anion was combined with the designed cation, because TFSI is one of the most common species and suitable to compare fundamental properties in the battery applications. Here we selected bis(fluorosulfonyl)imide ([FSI]) as a counter anion because of its small molecular weight and excellent ion transportation property. Physical and electrochemical properties in terms of density, thermal stability, ionic conductivity, and electrochemical stability will be shown in the presentation. The properties will be compared before and after the addition of lithium salts. The performance of the lithium metal half-cell and the lithium ion full cell will also be evaluated and compared.

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# Electrode Protection by Polymer Deposition in Lithium Batteries

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Recently, a great interest has been focused on electrolytic media with salt concentration higher than 1 molar that is the one commonly used. Electrolytic systems with equimolar ratio between salt and solvent are extremely interesting especially for their thermal and electrochemical stability. In some cases they can be described as solvate ionic liquids (SILs), i.e. salts in which the cation or the anion is strongly coordinated to a third molecule, thus forming a complex ion. The strategy to use SIL for lithium batteries has already been pursued, particularly to ameliorate Li interface stability [1-4].
The ability of SILs in forming good solid electrolyte interphase (SEI) on lithium or on graphite anodes is of utmost importance for the stability of lithium metal and lithium ion batteries. Furthermore, the compatibility with the cathode and with the species that are here produced is mandatory in presence of the high-potential cathodes of lithium-ion batteries, of the cathodes where the reduction of molecular oxygen takes place in lithium/air batteries, or in presence of sulphur-based cathodes and soluble polysulfides in lithium/sulphur batteries [5-8].
In this contribution, we investigate the effect of highly concentrated solutions based on lithium bis (trifluoromethanesulfonyl) imide (LiTFSI), lithium triflate (LiTf) and 1,3-dioxolane (DOL) both on Li and on sulphur-based electrodes. Particularly, DOL polymerization from 5m LiTFSI-DOL and 5m LiTFSI-DOL:dimetoxyethane (1:1) solutions at voltage higher than 4 V [9, 10] is exploited to produce a protective polymer layer in-situ on the sulphur-based cathode, also in presence of a suitable (commercial or electrospun) separator, and the results are reported and discussed.

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# Mixed oxided electrodes containing manganese on pretreated titanium support for environmental applications

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Mixed oxide electrodes have been extensively studied for their electrocatalytic activity. In particular manganese oxide-based (MnOx) films combine low cost with a reduced electrogeneration of chlorinated by-products in the presence of chlorides and low cost.

In previous works (1), we have presented the performance of MnOx films grown on both untreated and microstructured titanium substrates and we have verified that the morphological and electrochemical properties are improved by a surface texturization. The method involves the oxide deposition on substrates modified at a nano-scale with an enhancement of electrocatalytic properties with significant increase in the life time of the electrode.

The present work investigates the electrochemical behavior of new manganese-based electrodes obtained by co-deposition of the manganese oxide in combination with other metals. In particular, different types of anodes have been obtained by co-deposition of Ru (Ruthenium) Mn (Manganese) and Cu (Copper) oxides with different ratio. These thin films have been prepared by thermal decomposition on titanium substrate from alcoholic solutions. The titanium substrates were pretreated by HF etching.

The obtained electrodes have been characterized in terms of chemical and morphological properties by scanning electron microscopy (SEM) and Energy Dispersive X-ray Analysis EDX. Moreover, their electrochemical behaviour was evaluated by potentiodynamic polarization curves and cyclic voltammetry tests. We also tested and compared their oxidizing ability in the degradation of aqueous solutions containing a model compound and small amount of chloride. Galvanostatic experiments were conducted in a membrane-free reactor. The treatment extent was assessed by detection of color and TOC decay. The electrogeneration of active chlorine, chlorate and perchlorate was also monitored. The preliminary results show that ternary oxides coated electrodes exhibit enhanced electrocatalytic activity with negligible formation of undesired chlorinated by-products.

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# Scalable Fabrication of Graphene-based Textile Supercapacitors by Mimicking an Industrial Process

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Graphene-based electronic textiles have drawn significant research interest as the potential components for low-cost multifunctional flexible and wearable electronics for sportswear, military and health care applications (1). One of the key challenges to integrate these electronic devices to textiles is the requirement of being lightweight, flexible, and high performance power supply unit (2). Flexible supercapacitors are promising energy storage device that can meet these requirements while maintaining the same electrochemical properties such as high power density, longer life cycles, and quick charge/discharge (3). Recently, graphene (G) has been focus of much investigation for energy storage applications due to its extremely high specific surface area, excellent mechanical properties, and high thermal and electrical conductivity (4).

However, majority of the textile supercapacitors reported are based on reduced graphene oxide (rGO) and could only be produced at laboratory scale. Here, we report a simple, scalable, and cost-effective padding method for fabricating e-textile electrodes for flexible supercapacitors application. To our best knowledge, we report for the first time the use of electrochemically exfoliated G for textile supercapacitors.

Electrochemically exfoliated Graphene (G) was ultrasonically dispersed in Isopropanol/water 50/50 V.% solution. Then, Polyester-Cotton (PC), Cotton (C), and Nylon (N) fabrics were padded using G dispersion and dried in oven at 150°C for 15 minutes. The quality of both G was assessed by XPS and Raman spectroscopies. As prepared samples were characterized by SEM and Raman to evaluate the dispersion of active materials in the fabric. Fabrics were dip-coated into a gel electrolyte. Three gels were tested: PVA-LiCl, PVA-$H_3PO_4$, and PVA-KOH. Electrochemical characterizations were performed afterwards to evaluate the performance of the coated fabrics.

XPS and Raman confirmed the exfoliation and the quality of the G. SEM images of the padded fabrics (PC, C, and N) show a homogeneous dispersion after the padding procedure. Complete electrochemical characterizations demonstrate significant results for textile supercapacitors applications.

For the first time, a padding procedure mimicking an industrial process allows to obtain textile with suitable power sources for e-textile applications. Moreover, this procedure uses directly G as active material while previous research in this field was focused on rGO.

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# Galvanostatic reduction of cinchona alkaloid-derived ammonium salts: a simple, highly efficient strategy for chiral modification of metal surfaces

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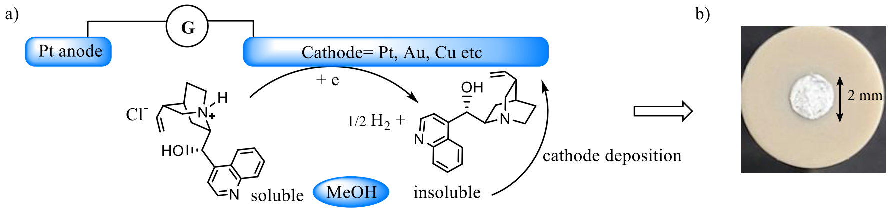
In the field of the asymmetric synthesis, the development of heterogeneous chiral catalysts attracts for a long time intense research efforts. With respect to the homogeneous ones, heterogeneous chiral catalysts offer several advantages for practical applications such as the easy separation from the reaction mixture, high stability and potential reusing for multiple times. In parallel, the flourishing of the "organocatalysis" as a powerful, low-cost and eco-friendly method to induce enantioselective reactions, has led to the development of a related research area which focus on the immobilization of the organocatalysts on different solid supports in order to combine the advantage of this kind of bioinspired chiral inductors with the beneficial to use them in heterogeneous manner. Indeed, several different strategies have been applied to manufacture chirally-modified surfaces, including covalent attachment, "ship-in-a-bottle" entrapment, chemical or electrochemical adsorption (1).

Among the most investigated modified surfaces with adsorbed organic molecules as chirality inductors, metal-cinchona alkaloid systems receive so far widely attention in view of their proven effectiveness, especially in enantioselective hydrogenation processes (2,3).

In this work we demonstrate that an effective deposition of cinchonine (CN) on various different metal surfaces can be easily achieved by cathodic reduction of cinchonine hydrochloride (CN·HCl) methanolic solution (scheme 1). Indeed, as depicted in scheme 1, the electrolysis, under galvanostatic conditions, induces $H_2$ evolution reaction which results in the absorption of insoluble CN at the cathode surface.

**Scheme 1. A)** Schematic depiction of the cell and chemical cathodic process. b) CN-modified Pt-electrode. Deposition time 600 *s*; *j*= 32 mA/cm$^2$



In order to determine coverage and apparent surface area and test the stability of the obtained CN layers, all the chirally modified metal surfaces will be investigated by electrochemical methods (4). In parallel, the catalytic abilities as well as the catalyst leaching of these materials will be tested in the asymmetric addition of aniline to chalcone as model reaction (5).

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# Reliable first principles prediction of oxidation potentials: an important tool to design organic molecules for opto-electronic applications

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Charge separation and charge recombination processes are ubiquitous in modern opto-electronic devices and their kinetics can greatly affect device performances. An effective design of new organic molecules for opto-electronic devices cannot neglect kinetics considerations, which in turns requires highly reliable estimates of the redox potentials of the involved molecular units. Modern computational tools can be of great help in this task. DFT methods offer several advantages for computing oxidation free energy, providing sufficiently reliable results at reasonable computational costs.

Herein we present a benchmark study on the ability of different DFT approaches to predict oxidation potentials for a series of organic molecules, which are commonly used in opto-electronic applications. The comparison between predicted and experimental oxidation potentials, the latter ones obtained by cyclic voltammetry in organic solvents, with suitable supporting electrolytes, shows that standard hybrid functionals are capable of accurate predictions only for molecules with moderate push-pull character, whereas high-exchange meta functionals such as M05-2X and M06-2X provide better results for strong push-pull molecular systems. Noteworthy, by properly choosing the functional, the oxidation potential can be predicted with an accuracy of about 50 mV.

# Elenco degli Autori

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| Fontani Marco | ELE PO12 |
| Fornasiero Paolo | ELE OR04 |
| Fraboni Beatrice | ANA/ELE/GS OR01 |
| Fracchia Martina | ELE OR24 |
| Freschi Stefano | ELE PO13 |
| Galia Alessandro | ELE PO15 |
| | ELE PO07 |
| | ELE PO14 |
| | ELE PZ06 |
| | ELE OR29 |
| Gambinossi Filippo | ELE PO12 |
| Gambuzzi Riccardo | ELE PO20 |
| Gandini Marina | FIS OR51 |

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| Gennaro Armando* | ELE OR05 |
| Gennaro Armando | ELE PO03 |
| | ELE PO06 |
| | ELE PO02 |
| | ELE PO08 |
| | ELE OR08 |
| | ELE OR18 |
| | ELE PZ03 |
| | ELE OR21 |
| | ELE OR27 |
| Gerbaldi Claudio* | ELE PO16 |
| | ELE PO17 |
| Gerbaldi Claudio | ELE PO01 |
| | ELE OR19 |
| | ELE OR22 |
| Ghigna Paolo | ELE OR24 |
| Giaccherini Andrea | ELE PO13 |
| | ELE PO12 |
| | ELE PO11 |
| | ELE OR07 |
| Giacomino Agnese | ANA/ELE/GS OR03 |
| Gigli Giuseppe | FIS OR57 |
| Gigot Arnaud* | ELE PO22 |
| Giorgio Marco | ANA/ELE/GS OR05 |
| | ANA/ELE/GS OR02 |
| Girault Hubert | ELE PO10 |
| | ELE OR26 |
| | ANA/ELE/GS KN02 |
| Giurlani Walter* | ELE PO13 |
| Gualandi Isacco | ANA/ELE/GS OR01 |
| Guerriero Paolo | ELE OR30 |
| Habazaki Hiroki | ELE OR10 |
| Innocenti Massimo | ELE PO13 |
| | ELE PO12 |
| | ELE PO11 |
| | ELE OR07 |
| Innocenti Matteo | ELE PO12 |
| Invernizzi Fabio | FIS OR53 |
| Isse Abdirisak A. | ELE PO06 |
| | ELE OR18 |
| | ELE PO08 |
| | ELE PZ03 |
| | ELE OR05 |
| | ELE OR27 |
| Ito Seitaro | ELE PO18 |
| Iurlo Matteo | ANA/ELE/GS OR05 |
| Jovic Milica | ANA/ELE/GS KN02 |
| Karim Mohammad Nazmul | ELE PO22 |
| Koster Dominique | ELE OR01 |
| la Gatta Simona* | FIS OR56 |
| La Mantia Fabio* | ELE OR01 |

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| La Mantia Fabio | ELE OR25 |
| La Monaca Andrea* | ELE PO20<br>ELE PZ05 |
| Lamberti Francesco* | FIS OR51 |
| Landi Alessandro | ELE OR03 |
| Lavacchi Alessandro | ELE PO13 |
| Le Donne Alessia | FIS OR52 |
| Lesch Andreas* | ANA/ELE/GS KN02 |
| Lin Rongying | ELE PO16 |
| Lisi Luciana | ELE OR20 |
| Lista Florigio | ANA/ELE/GS OR7 |
| Litti Lucio | FIS OR51 |
| Lo Faro Massimiliano * | ELE OR17 |
| Lo Faro Massimiliano | ELE OR34 |
| Lo Vecchio Carmelo* | ELE OR12 |
| Locatelli Cristina | ELE OR24 |
| Lombardo Lucia | ELE OR13 |
| Longoni Gianluca* | ELE PZ01 |
| Lorandi Francesca* | ELE OR27 |
| Lorandi Francesca | ELE PO08<br>ELE OR05<br>ELE PZ03 |
| Macchia Eleonora* | ELE OR32 |
| Magni Mirko | FIS OR54 |
| Maier Joachim | ELE PO01 |
| Maisano Susanna | ELE OR34 |
| Malandrino Mery | ANA/ELE/GS OR03 |
| Malara Francesco | ELE OR24 |
| Maltese Vito | FIS OR57 |
| Mancino Gabriella | ELE OR20 |
| Mangiatordi Giuseppe F. | ELE OR32 |
| Maniscalco Anna | ELE OR25 |
| Mannucci Barbara | ELE OR11 |
| Manoli Kyriaki | ELE OR32 |
| Marcaccio Massimo | ELE OR04<br>ANA/ELE/GS OR05 |
| Marchionna Stefano | FIS OR52 |
| Marcus Philippe | ELE OR33 |
| Maresca Giovanna* | ELE PO18 |
| Maresca Giovanna | ELE PO19 |
| Mariani Federica | ANA/ELE/GS OR01 |
| Martinazzo Rocco | ELE PO04 |
| Massoud Renato | ANA/ELE/GS KN01 |
| Matic Aleksandar | ELE OR13 |
| Mattarozzi Luca | ELE OR30 |
| Mattiacci Giorgio | ELE OR21 |
| Matyjaszewski Krzysztof | ELE PO08<br>ELE OR05<br>ELE PZ03<br>ELE OR27 |
| Maurice Vincent | ELE OR33 |
| Mazzaracchio Vincenzo | ANA/ELE/GS OR7 |
| Mecerreyes David | ELE PO17 |

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| Melchionna Michele | ELE OR04 |
| Meligrana Giuseppina | ELE PO16 |
| Meneghetti Moreno | FIS OR51 |
| Michieletto Alessandro | ELE OR27 |
| Milano Francesco | FIS OR56 |
| Millia Luca | ELE OR11 |
| Minguzzi Alessandro* | ELE OR24 |
| Monaco Rossella | ELE OR31 |
| Montanaro Daniele | ELE PO21 |
| Moreno Margherita | ELE PO16 |
| Moscone Danila | ANA/ELE/GS OR07<br>ANA/ELE/GS KN01<br>ANA/ELE/GS OR06 |
| Musiani Marco* | ELE OR20 |
| Musiani Marco | ELE OR30 |
| Mussini Patrizia Romana* | ELE PO04 |
| Mussini Patrizia Romana | ELE PO09<br>ELE OR31 |
| Mustarelli Piercarlo* | FIS OR53 |
| Mustarelli Piercarlo | ELE OR11 |
| Nair Jijeesh R. | ELE PO16<br>ELE PO17 |
| Naldoni Alberto | ELE OR24 |
| Nale Angeloclaudio | ELE OR06<br>ELE OR15 |
| Navarra Maria Assunta* | ELE OR13 |
| Navarra Maria Assunta | ELE PO18<br>ELE PO19 |
| Nawn Graeme | ELE OR15 |
| Neagu Daniela | ANA/ELE/GS OR06<br>ANA/ELE/GS OR7 |
| Negro Enrico | ELE OR06<br>ELE OR15 |
| Oliveira Vanessa | ELE OR34 |
| Orsini Monica | ELE PO21 |
| Pace Giuseppe | ELE OR06 |
| Pagot Gioele | ELE OR06 |
| Pagot Gioele* | ELE OR15<br>ELE OR23 |
| Palazzo Gerardo | ELE OR32 |
| Palleschi Giuseppe | ANA/ELE/GS OR04<br>ANA/ELE/GS OR7 |
| Palombi Laura | ELE PO23 |
| Pan Xiangchen | ELE PZ03 |
| Pandolfi Fabiana | ELE OR28 |
| Panero Stefania | ELE PO19<br>ELE OR13<br>FIS OR55 |
| Panigati Monica | ELE PO04 |
| Paolone Annalisa | FIS OR55 |
| Paolucci Francesco | ELE OR04<br>ELE OR20 |

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| Valov Ilia | ELE OR10 |
| Vassallo Espedito | FIS OR54 |
| Vàzquez-Gòmez Lourdes | ELE OR30 |
| Velardo Amalia* | ELE PO24 |
| Verlato Enrico | ELE OR30<br>ELE OR20 |
| Vertova Alberto | ELE PZ04<br>ELE OR24 |
| Vezzù Keti | ELE OR06<br>ELE OR15<br>FIS OR53 |
| Vicari Fabrizio | ELE OR29<br>ELE PO15 |
| Visibile Alberto | ELE OR24 |
| Vizza Martina | ELE PO11 |

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| Volpe Giulia | ANA/ELE/GS OR04 |
| Wang Yi | ELE PO08 |
| Yeates Stephen | ELE PO22 |
| Zaccaria Marco | ELE PZ05 |
| Zaffora Andrea* | ELE OR10 |
| Zampardi Giorgia* | ELE PZ02 |
| Zanna Sandrine | ELE OR33 |
| Zerbetto Francesco | ANA/ELE/GS OR05 |
| Zerbetto Mirko | ELE PO02 |
| Zignani Sabrina* | ELE OR34 |
| Zignani Sabrina | ELE OR17 |
| Zilio Stefano | ELE PO05 |
| Zlotorowicz Agnieszka | ELE OR06 |
| Zolin Lorenzo | ELE OR22 |

# DIVISIONE DI CHIMICA FISICA

## Comitato Scientifico

- Elena Selli, Università degli Studi di Milano
- Salvatore Coluccia, Università degli Studi di Torino
- Patrizia Canton, Università Ca' Foscari Venezia
- Gerardino D'Errico, Università degli Studi di Napoli Federico II
- Concetta Giancola, Università degli Studi di Napoli Federico II
- Gianmario Martra, Università degli Studi di Torino
- Moreno Meneghetti, Università degli Studi di Padova
- Ludovico Valli, Università del Salento
- Giovanni Marletta, Università degli Studi di Catania
- Rodorico Giorgi, Università degli Studi di Firenze

**Delegato di Divisione**

- Riccardo Zanasi, Università degli Studi di Salerno

# Programma Scientifico

## Divisione di Chimica Fisica

## Lunedì 11 Settembre 2017

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|---|---|
| | ***Sala Vivaldi - Hotel Savoy*** |
| ***Photoactive Materials*** | |
| *Chairperson: Elena Selli* | |
| 9:00 - 9:15 | FIS OR01: A. Truppi, F. Petronella, T. Placido, C. Giannini, T. Sibillano, A. Agostiano, M. L. Curri, R. Comparelli<br>*$TiO_2$/Au NRs photocatalysts for photodegradation of water pollutants under UV and visible light* |
| 9:15 - 9:30 | FIS OR02: F. Ortica, M. Frigoli, A. Zangarelli, D. Pannacci<br>*Photochromism of N-phenyl-carbazole benzopyrans* |
| 9:30 - 9:45 | FIS OR03: A. Panniello, A. E. Di Mauro, E. Fanizza, M. L. Curri, M. Striccoli, A. Agostiano<br>*Hydrophobic carbon dots with intense phololuminescence towards single white emitting materials* |
| ***New Composite Materials*** | |
| *Chairperson: Moreno Meneghetti* | |
| 9:45 - 10:00 | FIS OR04: F. Cesano, S. Cravanzola, F. Gaziano, D. Scarano<br>*Graphene-like domains on $MoS_2$/$TiO_2$ systems, via acetylene polymerization: in-situ synthesis and characterization* |
| 10:00 - 10:15 | FIS OR05: C. Ingrosso, M. Corricelli, G. V. Bianco, V. Pifferi, P. Guffanti, A. Testolin, F. Bettazzi, F. Petronella, R. Comparelli, A. Agostiano, M. Striccoli, I. Palchetti, L. Falciola, G. Bruno, M. L. Curri<br>*Colloidal Nanocrystal Surface Decorated Graphene based Hybrid Materials for Sensors* |
| 10:15 - 10:30 | FIS OR06: C. Sartorio, V. Campisciano, C. Chiappara, S. Cataldo, M. Gruttadauria, F. Giacalone, B. Pignataro<br>*Enhanced power-conversion efficiency in organic solar cells incorporating polymeric compatibilizers* |
| 10:30 - 11:00 | Coffee Break |
| ***Models & Experiments*** | |
| *Chairperson: Giovanni Marletta* | |
| 11:00 - 11:30 | FIS KN01: P. Ugliengo, A. Rimola, M. Sodupe M. Fabbiani, G. Martra<br>*Amide Bond Formation by Condensation between Unactivated Reagents at Silica Surfaces: Rôle in Prebiotic Chemistry* |
| 11:30 - 11:45 | FIS OR07: A. Painelli, S. Sanyal, F. Terenziani, S. Pati, C. Sissa<br>*Molecular Aggregates: a Fresh Perspective* |
| 11:45 - 12:00 | FIS OR08: F. Sessa, V. Migliorati, A. Serva, P. D'Angelo<br>*On the $Zn^{2+}$ ion speciation in challenging ionic media: a molecular dynamics and X-ray absorption spectroscopy study* |
| ***Materials for Biotechnological Applications 1*** | |
| *Chairperson: Patrizia Canton* | |
| 12:00 - 12:15 | FIS OR09: F. Vischio, N. Depalo, I. Arduino, S. Villa, F. Canepa, E. Fanizza, S. H. Lee, B. C. Lee, R. M. Iacobazzi, V. Laquintana, A. Lapedota, A. Cutrignelli, M. P. Scavo, M. Striccoli, A. Agostiano, M. L. Curri, N. Denora<br>*Magnetic Solid Lipid Nanoparticles for Magnetically Targeted Delivery of Sorafenib for Treatment of Hepatocellular Carcinoma* |
| 12:15 - 12:30 | FIS OR10: A. De Santis, I. R. Krauss, L. Paduano, G. D'Errico<br>*Micro-structural characterization of model membranes containing DHA* |

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| 12:30 - 12:45 | FIS OR11: G. Valente, N. Depalo, E. Fanizza, R. M. Iacobazzi, N. Denora, V. Laquintana, L. Zaccaro, A. Del Gatto, I. De Paola, M. Saviano, P. D. Howes, C. Spicer, M. M. Stevens, M. Striccoli, A. Agostiano, L. M. Curri<br>*Nanoparticles encapsulation in micellar systems for biomedical applications* |
| 12:45 - 13:00 | FIS OR12: R. Gelli, L. Mati, F. Ridi, P. Baglioni<br>*Effect of cellulose ethers on the formation and properties of magnesium phosphate-based cements for biomedical applications* |

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| 13:00 - 14:00 | Intervallo Pranzo – Lunch Break |

| | ***Sala Paestum B*** |
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| 14:00 - 15:00 | *Poster Session 1 (FIS PO01 - FIS PO16)* |
| ***Molecular and Supramolecular Systems*** | |
| *Chairperson: Gerardino D'Errico* | |
| 15:00 - 15:15 | FIS OR13: G. De Filpo, P. Formoso, S. Manfredi, A. I. Mashin, F. P. Nicoletta<br>*Bifunctional polymer-dispersed liquid crystals* |
| 15:15 - 15:30 | FIS OR14: J. Cautela, J. J. Crassous, N. V. Pavel, L. Galantini<br>*Supracolloidal association of microgels and supramolecular tubules of bile salt derivatives* |
| 15:30 - 15:45 | FIS OR15: P. Sassi, B. Gironi, A. Lapini, M. Paolantoni, A. Morresi, P. Foggi<br>*The lipid bilayer of model membranes: news from the inside* |
| ***Physical Studies of Materials and Molecules*** | |
| *Chairperson: Gianmario Martra* | |
| 15:45 - 16:00 | FIS OR16: V. Domenici, A. Resetic, J. Milavec, B. Zupancic, B. Zalar<br>*Physical-chemical study of a new shape-memory material based on liquid crystalline elastomers* |
| 16:00 - 16:15 | FIS OR17: G. Cavallaro, V. Bertolino, G. Lazzara, F. Parisi, S. Milioto, M. Gradzielski<br>*Hybrid nanostructures based on halloysite nanotubes and sustainable polymers* |
| 16:15 - 16:30 | FIS OR18: G. Monaco, F. Aquino, R. Zanasi, W. Herrebout, A. Massa<br>*Absolute Configuration Assignment of two Hybrid Isoindolinone-phthalide Molecules by Vibrational Circular Dichroism* |
| 16:30 - 17:00 | Coffee Break |
| ***Chemistry of Materials and Surfaces*** | |
| *Chairperson: Ludovico Valli* | |
| 17:00 - 17:15 | FIS OR19: E. Groppo, A. Piovano, G. Martino, M. D'Amore, C. Barzan, S. Bordiga<br>*Can we speak of "ancillary ligands" also in heterogeneous catalysis? Selected examples in olefin polymerization catalysts* |
| 17:15 - 17:30 | FIS OR20: E. Fanizza, F. Cascella, A. Panniello, L. Triggiani, N. Depalo, C. Giannini, D. Altamura, A. Agostiano, M. L. Curri, M. Striccoli<br>*Synthesis and post preparative shape control of cesium lead bromide colloidal nanocrystals* |
| 17:30 - 17:45 | FIS OR21: M. L. Saladino, F. Armetta, D. Hreniak, L. Marciniak, W. Stręk, C. Giordano, E. Caponetti<br>*Non conventional based Ce:YAG nanocomposites* |
| ***Materials for Biotechnological Applications 2*** | |
| *Chairperson: Concetta Giancola* | |
| 17:45 - 18:00 | FIS OR22: F. Ridi, R. Gelli, L. Gigli, M. Scudero, M. Bonini, P. Baglioni<br>*Synthesis and characterization of immunologically relevant calcium and magnesium phosphate amorphous nanostructures and strategies for their stabilisation* |
| 18:00 - 18:15 | FIS OR23: E. Gatto, R. Lettieri, A. Colella, F. Leonelli, L. Giansanti, L. Stella, M. Venanzi<br>*Physico-chemical characterization of smart lipid biointerfaces for the detection of a tumor biomarker* |

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| 18:15 - 18:30 | FIS OR24: I. Miletto, L. Invernizzi, C. Gionco, M. C. Paganini, E. Giamello, L. Marchese, E. Gianotti<br>*Luminescent $ZrO_2:Ln^{3+}@SiO_2$ Nanosystems Conjugated with Rose Bengal as Efficient Nanoplatform for Theranostic Applications* |
| 18:30 - 20:00 | Assemblea della divisione di Chimica Fisica<br>***Sala Olimpia – Hotel Ariston*** |

## Martedì 12 Settembre 2017

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| ***Sala Verdi - Hotel Savoy*** | |
| ***Materials*** | |
| *Chairpersons: Debora Berti, Gianmario Martra* | |
| 9:00 - 9:15 | FIS OR25: A. Girlando, N. Castagnetti, M. Masino<br>*Phenomenology of the Neutral-Ionic Valence Instability in Mixed Stack Charge Transfer Crystals* |
| 9:15 - 9:30 | FIS OR26: M. Fabbiani, G. Tabacchi, E. Fois, G. Martra<br>*The effect of temperature in the formic acid - formate system on $TiO_2$ (101) surfaces* |
| 9:30 - 9:45 | FIS OR27: M. Tonelli, R. Moscatelli, M. Sebastiani, F. Martini, L. Calucci, M. Geppi, S. Borsacchi, F. Ridi<br>*Interaction of phosphate-based additives with $MgO/SiO_2$ cements* |
| 9:45 - 10:00 | FIS OR28: L. Triggiani, C. N. Dibenedetto, G. Tartaro, A. Loiudice, T. Sibillano, C. Giannini, G. Bruno, R. Brescia, R. Buonsanti, A. Agostiano, M. Striccoli, E. Fanizza<br>*Composition and architecture engineering of colloidal $TiO_2$ nanocrystals for the enhancement of sunlight conversion ability* |
| 10:00 - 10:15 | FIS OR29: Y. Miele, A. F. Taylor, T. Bánsági Jr, L. Izzo, F. Rossi<br>*Coupling of nonlinear chemical reactions with pH-responsive polymers* |
| 10:15 - 10:30 | FIS OR30: J. Gubitosa, V. Rizzi, P. Fini, A. Petrella, F. Fanelli, A. Agostiano, M. Perrone, I. Arduino, A. Lopedota, P. Cosma<br>*Green synthesis of gold nanoparticles using Punica Granatum Juice for cosmetic applications* |
| 10:30 - 11:00 | Coffee Break |
| ***Materials*** | |
| *Chairpersons: Alberto Girlando, Gerardino D'Errico* | |
| 11:00 - 11:15 | FIS OR31: M. Bonini, A. Gabbani, S. Del Buffa, F. Ridi, P. Baglioni, R. Bordes, K. Holmberg<br>*Adsorption of Amino Acids and Glutamic Acid-Based Surfactants on Imogolite Clays* |
| 11:15 - 11:30 | FIS OR32: M. Corno, I. Miletto, E. Gianotti, M. Cossi, L. Marchese<br>*Organic-inorganic hybrid materials as heterogenous catalysts for pharma industry* |
| 11:30 - 11:45 | FIS OR33: L. Ambrosone, G. Bufalo, F. Cuomo, F. Lopez<br>*Coupling of sieving and thermogravimetric analyzes for studying the activation energy distribution function of complex reactions* |
| 11:45 - 12:00 | FIS OR34: M. Baglioni, C. Montis, F. Brandi, T. Guaragnon, I. Meazzini, P. Baglioni, D. Berti<br>*Dewetting of acrylic polymeric films induced by water/propylene carbonate/surfactant mixtures - Implications for cultural heritage conservation* |
| 12:00 - 12:15 | FIS OR35: V. Rizzi, M. A. Ricci, E. Altamura, P. Fini, S. Sortino, A. Fraix, P. Semeraro, L. De Cola, E. A. Prasetyanto, P. Cosma<br>*Supramolecular Self-Assembly of Chlorophyll A and Mesoporous Silica Nanoparticles in Water Medium* |
| 12:15 - 12:30 | FIS OR36: R. Camerini, D. Chelazzi, R. Giorgi, P. Baglioni<br>*Silica-based composites for the consolidation of earthen materials* |

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| 12:30 - 12:45 | FIS OR37: B. Di Napoli, P. Conflitti, C. Mazzuca, M. Venanzi, M. De Zotti, F. Formaggio, A. Palleschi<br>*Langmuir-Blodgett and MD characterization of peptides at the air/water interface* |
| 12:45 - 13:00 | FIS OR38: L. Litti, A. Ramundo, V. Amendola, M. Meneghetti<br>*Detection and Quantification of Anticancer Drugs with Surface Enhanced Raman Spectroscopy* |

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| 13:00 - 14:00 | Intervallo Pranzo |

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| | ***Sala Paestum B*** |
| 14:00 - 15:00 | *Poster Session 2 (FIS PO17 - FIS PO33)* |

## Mercoledì 13 Settembre 2017

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| | ***Sala Paestum B*** |
| 14:00 - 15:00 | *Poster Session 3 (FIS PO34 - FIS PO51)* |
| | ***Sala Vivaldi - Hotel Savoy*** |
| ***Environmental Physical Chemistry*** | |
| *Chairpersons: Maria Lucia Curri, Riccardo Zanasi* | |
| 15:00 - 15:15 | FIS OR39: A. Tursi, N. De Vietro, A. Beneduci, F. Chidichimo, F. Fracassi, G. Chidichimo<br>*Effective remediation of highly polluted water by petroleum hydrocarbons with functionalized cellulose fiber* |
| 15:15 - 15:30 | FIS OR40: S. Salvestrini<br>*A comparison between the Langmuir rate equation and the pseudo-first and pseudo-second order models for adsorption processes* |
| 15:30 - 15:45 | FIS OR41: F. Venditti, F. Cuomo, L. Ambrosone, A. Ceglie, G. Cinelli, F. Lopez<br>*Microstructured composite for Cr (VI) removal from polluted environment* |
| 15:45 - 16:00 | FIS OR42: F. Lopez, F. Cuomo, F. Venditti, L. Ambrosone, A. Ceglie<br>*Olive mill wastewaters phenol photocatalytic degradation by visible light activated carbon doped titanium* |
| 16:00 - 16:15 | FIS OR43: P. Semeraro, J. A. Gabaldón, P. Fini, J. A. Pellicer, V. Rizzi, A. Longo, E. Núňez, P. Cosma<br>*Removal of an azo textile dye from wastewater using cyclodextrin-epichlorohydrin polymers* |
| 16:15 - 16:30 | FIS OR44: R. Angelico, C. Colombo, G. Palumbo, G. Ventruti<br>*Arsenic Adsorption on Iron Oxides and its Environmental Impact* |
| 16:30 - 17:00 | Coffee Break |
| ***Physical Chemistry of Biological Systems*** | |
| *Chairpersons: Concetta Giancola, Maria Rosaria Tinè* | |
| 17:00 - 17:15 | FIS OR45: F. Tadini-Buoninsegni<br>*Electrophysiological measurements on a solid supported membrane to investigate the transport activity of sarcoplasmic reticulum* $Ca^{2+}$*-ATPase* |
| 17:15 - 17:30 | FIS OR46: F. Sciubba, M. Delfini, M. E. Di Cocco, F. Ferraris<br>*Protein-ligand interaction: a NMR study* |
| 17:30 - 17:45 | FIS OR47: C. Satriano, P. Di Pietro, N. Caporarello, C. D. Anfuso, G. Lupo, A. Magrì, D. La Mendola<br>*Immobilisation of neurotrophin peptides on gold nanoparticles by direct and lipid-mediated interaction: a new multipotential therapeutic nanoplatform for CNS disorders* |

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| 17:45 - 18:00 | FIS OR48: V. De Leo, F. Milano, R. Comparelli, E. De Giglio, A. Trapani, S. Di Gioia, M. Conese, M. Mattioli-Belmonte, A. Agostiano, L. Catucci<br>*Small liposomes for drug delivery* |
| 18:00 - 18:15 | FIS OR49: G. Arrabito, F. Cavaleri, A. Porchetta, F. Ricci, V. Vetri, M. Leone, B. Pignataro<br>*Molecular Confinement in Femtoliter Scale Aqueous Compartments* |
| 18:15 - 18:30 | FIS OR50: S. Rapino, L. Bartolini, C. Albonetti, A. Soldà, G. Valenti, F. Valle, P. G. Pelicci, F. Paolucci, F. Zerbetto<br>*The Influence of Chemical Microenvironment on Living Cell Shape* |

# Joined Sessions

## Lunedì 11 Settembre 2017

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| | ***Sala Afrodite - Hotel Ariston*** |
| ***SessioneABC+ANA+FIS: La trasversalità della chimica per i Beni Culturali*** | |
| *Chairperson: Lucia Toniolo* | |
| 9:00 - 9:25 | ABC/ANA/FIS KN01: Rocco Mazzeo<br>*Macro Mid-Infrared total reflection (MA-FTIR) mapping for the characterization of outdoor bronze surfaces* |
| 9:25 - 9:40 | FIS OR65: C. Berlangieri, E. Carretti, G. Poggi, S. Murgia, M. Monduzzi, L. Dei, P. Baglioni<br>*Formulation and characterization of hydroxypropyl guar based gel-like systems, tailored for the low impact cleaning of works of art surfaces* |
| 9:40 - 9:55 | FIS OR66: P. Ferrari, A. Mirabile, M. Trabace, L. Montalbano, R. Giorgi, P. Baglioni<br>*Chemical poly ethyl methacrylate (PEMA) organogels for the removal of pressure sensitive tapes (PSTs) from paper artworks* |
| 9:55 - 10:10 | FIS OR67: N. Bonelli, R. Mastrangelo, C. Montis, P. Tempesti, P. Baglioni<br>*Surface Cleaning of Artworks: Structure and Dynamics of Nanostructured Fluids Confined in a Polymeric Network* |
| 10:10 - 10:25 | FIS OR68: G. Poggi, R. Giorgi, P. Baglioni<br>*Nanocomposites for the consolidation and deacidification of cellulose-based artifacts* |
| 10:30 - 11:00 | Coffee Break |
| *Chairperson: Elisabetta Zendri* | |
| 11:00 - 11:25 | ABC/ANA/FIS KN02: Erika Ribechini<br>*GC/MS and HPLC/MS characterization of organic residues from ceramic vessels of Basque whalers of the 16th to 17th century* |
| 11:25 - 11:40 | ABC/ANA/FIS OR05: Francesca Di Turo<br>*FIB-FESEM-EDX study of silver Roman coins: characterization of the core microstructure and corrosion products with a multi-analytical approach* |
| 11:40 - 11:55 | ABC/ANA/FIS OR06: Antonella Casoli<br>*I materiali e la tecnica pittorica di Konrad Witz nel suo capolavoro di Ginevra* |
| 11:55 - 12:10 | ABC/ANA/FIS OR07: Elettra Barberis<br>*Towards the Non-invasive Proteomic Analysis of Cultural Heritage and Archaeological Objects* |
| 12:10 - 12:25 | ABC/ANA/FIS OR08: Giuseppe Egidio De Benedetto<br>*Provenance of bitumen from different Apulian Bronze Age settlements through a biomarker based approach* |
| 12:25 - 12:40 | ABC/ANA/FIS OR09: Marzia Fantauzzi |

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| | *From XAES signals to depth-profile reconstruction: the case of copper and copper alloys* |
| 12:40 - 12:55 | ABC/ANA/FIS OR10: Marco Orlandi<br>*Integrated approach for the chemical characterization of archaeological woods* |
| ***Sala Diana - Hotel Ariston*** | |
| ***Sessione: Sistemi Biologici - Fisica*** | |
| *Chairpersons: Carla Isernia, Concetta Giancola* | |
| 11:00 - 11:50 | CSB PL2: Maria Rosaria Tinè<br>*Calorimetry and Thermoanalytical Techniques in the Study of Proteins* |
| 11:50 - 12:05 | FIS OR69: R. Oliva, A. Grimaldi, P. Del Vecchio, V. Cafaro, K. Pane, E. Notomista, L. Petraccone<br>*Biophysical studies of membrane perturbation induced by the antimicrobial peptide GKY20* |
| 12:05 - 12:20 | CSB OR3: Alessandro D'Urso<br>*Exploiting conformation and structural analysis of endogenous miRNAs to refine gene targeting evaluation* |
| 12.20 - 12.35 | FIS OR70: A. Del Giudice, C. Dicko, L. Galantini, N. V. Pavel<br>*The structural response of Human Serum Albumin to oxidation: a biological buffer to local formation of hypochlorite* |
| 12.35 - 12.50 | CSB OR4: Jussara Amato<br>*Identification and characterization of DNA G-quadruplex interacting proteins* |

## Martedì 12 Settembre 2017

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| ***Sala Vivaldi - Hotel Savoy*** | |
| ***Sessione Congiunta: Fisica - Elettrochimica - Enerchem*** | |
| *Chairpersons: Moreno Meneghetti, Alessandro Minguzzi* | |
| 9:00 - 9:30 | ELE KN01: Riccardo Ruffo<br>*Negative Electrode Materials for Sodium Ion Batteries* |
| 9:30 - 9:45 | FIS OR51: F. Lamberti, L. Litti, M. De Bastiani, R. Sorrentino, M. Gandini, M. Meneghetti, A. Petrozza<br>*High-Quality, Ligands-Free, Mixed-Halide Perovskite Nanocrystals Ink for Optoelectronic applications* |
| 9:45 - 10:00 | ELE OR20: M. Musiani, E. Verlato, S. Barison, S. Cimino, L. Lisi, G. Mancino, F. Paolucci<br>*Electrochemical preparation of nanostructured* $CeO_2$*-Pt catalysts on Fe-Cr-Al alloy foams for the low-temperature combustion of methanol* |
| 10:00 - 10:15 | FIS OR52: S. Binetti, A. Le Donne, M. Acciarri, S. Marchionna<br>*New Earth-Abundant Thin Film Solar Cells Based on* $Cu_2MnSnS_4$ |
| 10:15 - 10:30 | ELE OR21: C. Durante, G. Daniel, G. Mattiacci, G. A. Rizzi, A. Gennaro<br>*Platinum free Electrocatalyst based on Fe-Nx moieties supported on Mesoporous Carbon prepared from polysaccharides for Oxygen Reduction Reaction* |
| 10:30 - 11:00 | Coffee Break |
| ***Sessione Congiunta: Elettrochimica - Fisica - Enerchem*** | |
| *Chairpersons: Simona Binetti, Claudio Gerbaldi* | |
| 11:00 - 11:15 | FIS OR53: P. Mustarelli, F. Invernizzi, M. Patrini, K. Vezzù, V. Di Noto<br>*Polyurethane-based Electrostrictive Nanocomposites as High Strain - Low Frequency Mechanical Energy Harvesters* |
| 11:15 - 11:30 | FIS OR54: G. L. Chiarello, M. Bernareggi, M. Pedroni, M. Magni, S. M. Pietralunga, E. Vassallo, E. Selli<br>*A Bilayer* $WO_3$ *n-n Heterojunction Photoanode prepared by RF Diode Sputtering for Improved Photoelectrocatalytic Water Splitting* |

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| 11:30 - 11:45 | ELE OR22: F. Bella, F. Colò, L. Zolin, D. Pugliese, A. M. Stephan, C. Gerbaldi<br>*Lignocellulosic Materials for Electrochemical Energy Storage and Conversion* |
| 11:45 - 12:00 | FIS OR55: S. Brutti, S. Panero, A. Paolone, P. Reale<br>*Hydrides as High Capacity Anodes in Lithium Cells: An Italian "Futuro in Ricerca di Base FIRB-2010" Project* |
| 12:00 - 12:15 | ELE OR23: F. Bertasi, V. Di Noto - *Secondary Magnesium Batteries: an Overview on Ionic Liquid -based Electrolytes* |
| 12:15 - 12:30 | FIS OR56: S. La Gatta, F. Milano, R. Ragni, A. Agostiano, G. M. Farinola, M. Trotta<br>*Bio-hybrid Complexes in Artificial Photosynthesis* |
| 12:30 - 12:45 | ELE OR24: A. Minguzzi, M. Fracchia, A. Visibile, A. Naldoni, F. Malara, C. Locatelli, A. Vertova, P. Ghigna, S. Rondinini<br>*Operando (photo)electrochemical X-ray absorption spectroscopy for water splitting* |
| 12:45 - 13:00 | FIS OR57: A. Beneduci, A. L. Capodilupo, G. A. Corrente, E. Fabiano, V. Maltese, S. Cospito, G. Ciccarella, G. Chidichimo, G. Gigli<br>*Electronic Coupling in H-Shaped Tetra-Arylamine Mixed-Valence Compounds* |
| 13:00 - 14:00 | Intervallo Pranzo |

## Mercoledì 13 Settembre 2017

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| | ***Sala Puccini - Hotel Savoy*** |
| | ***Sessione Congiunta: Fisica - Teorica*** |
| | *Chairperson: Michele Pavone* |
| 15:00 - 15:40 | TEO KN01: C. Cappelli<br>*A Fully Polarizable Embedding Model for Molecular Spectroscopy of Aqueous Solutions* |
| 15:40 - 16:00 | TEO OR01: R. Dovesi, S. Salustro, F. Gentile , Y. Noel<br>*Hydrogen defects in diamond. A quantum mechanical approach* |
| 16:00 - 16:15 | FIS OR58: L. Zamirri, M. Corno, A. Rimola, P. Ugliengo<br>*Forsterite surfaces as models of interstellar core dust grains: computational study of carbon monoxide adsorption* |
| 16:15 - 16:30 | FIS OR59: M. Mattia, D. E. Claudio, D. Luca, P. Cristina, S. Lorenzo<br>*Prebiotic Molecules in Interstellar Space: Aminoacetonitrile and C-Cyanomethanimine* |
| 16:30 - 17:00 | Coffee Break |
| | *Chairperson: Ludovico Valli* |
| 17:00 - 17:15 | FIS OR60: M. V. La Rocca, L. Izzo, S. Losio, M. Mella<br>*Should we introduce pre-equilibria into Markov models for homogeneously catalyzed copolymerization?* |
| 17:15 - 17:30 | FIS OR61: F. Di Maiolo, C. Pieroni, A. Painelli<br>*Intramolecular Energy Transfer in Real Time* |
| 17:30 - 17:45 | TEO OR02: E. Bodo, A. Le Donne<br>*Proton Mobility in Protic Ionic Liquids: New Results from Theoretical Calculations* |
| 17:45 - 18:00 | TEO OR03: N. Tasinato, L. Spada, C. Puzzarini,V. Barone<br>*Computational Tools for the Interpretation of Rotational Spectra within the Virtual Multifrequency Spectrometer* |
| 18:00 - 18:15 | FIS OR62: A. Mariani, R. Caminiti, L. Gontrani<br>*A spotlight on the complex hierarchical structure of some ionic liquid-molecular liquid binary mixtures* |
| 18:15 - 18:30 | FIS OR63: O. Russina, R. Caminiti<br>*Fluorous mesoscopic domains in room temperature ionic liquids* |
| 18:30 - 18:45 | FIS OR64: E. Fois, R. Arletti, L. Gigli, G. Vezzalini, S. Quartieri, G. Tabacchi<br>*Supramolecular Organization of Water–Ethanol Solution in Ferrierite under Pressure* |

# Keynote

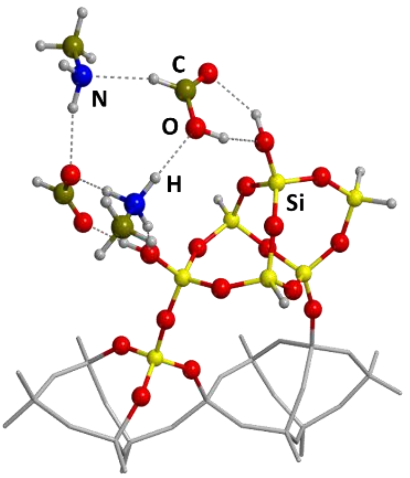
- FIS KN01: Piero Ugliengo, Università degli Studi di Torino
- ELE KN01: Riccardo Ruffo, Università degli Studi di Milano Bicocca
- TEO KN01: Chiara Cappelli, Scuola Normale Superiore, Pisa
- ABC/ANA/FIS-KN01: Rocco Mazzeo, Università di Bologna
- ABC/ANA/FIS-KN02: Erika Ribechini, Università di Pisa

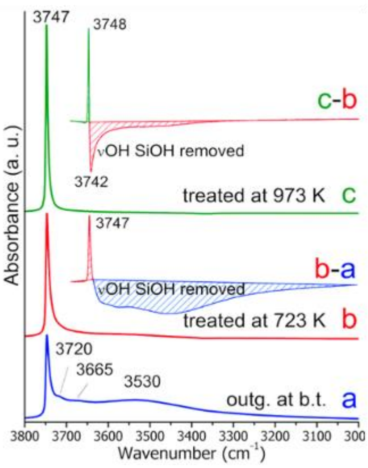
# Amide Bond Formation by Condensation between Unactivated Reagents at Silica Surfaces: Rôle in Prebiotic Chemistry

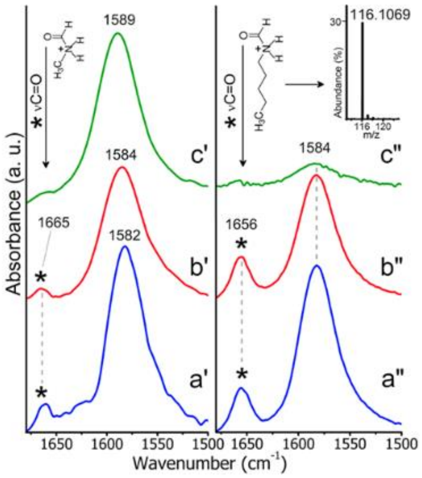
*P. Ugliengo[a], A. Rimola[b], M. Sodupe[b] M. Fabbiani[c], G. Martra[a]*

*[a]Dipartimento di Chimica, Università di Torino, Via P. Giuria 7, 10125 Torino, Italy, piero.ugliengo@unito.it; [b]Departamento de Química, Universitat Autònoma de Barcelona, 08193 Bellaterra, Spain; [c]Dipartimento di Scienza e Alta Tecnologia DiSAT, Università dell'Insubria, via Valleggio 9, 22100 Como, Italy.*

The role of mineral surfaces in promoting the formation of peptides in the prebiotic era by condensation reaction of aminoacids has long been established (1). We contributed to the field through experiment (2) and simulation (3), focusing on common oxides, as potential helpers in the formation of small glycine oligopetides. Here, we propose the mechanism of the amide bond formation between non-activated carboxylic acids and amines (simpler analogous of aminoacids), hosted at the surface of amorphous silica. We elucidate the mechanism by a combined use of molecular simulation through quantum mechanical calculations based on density functional theory (B3LYP-D3/6-311++G(d,p)) and experimental infrared spectroscopic measurements. Experiments based on infrared spectroscopy carried out on carefully thermal treated silica samples, identified very weakly interacting SiOH surface group pairs, as key sites for hosting and activating, ionic and neutral pairs of the reactants, whose simultaneous presence is crucial for the amide bond formation. The atomistic view provided by DFT modelling revealed the catalytic site envisaging pairs of surface silanol (Si-OH) groups ca. 5 Å apart (see figure). The proposed mechanism on dry silica resembles that operative in the ribosome for the peptide bond formation (4), in which the Si-OH groups at silica play the role of water in the biological system.







References: 1. J. D. Bernal, The Physical Basis of Life, Routledge and Kegan Paul, London, 1951. 2. G. Martra, C. Deiana, Y. Sakhno, I. Barberis, M. Fabbiani, M. Pazzi, M. Vincenti, Angew. Chem. Int. Ed. Engl. 2014, 53, 4671-4674. 3. A. Rimola, M. Sodupe, P. Ugliengo, J. Am. Chem. Soc. 2007, 129, 8333-8344. 4. K. Świderek, S. Marti, I. Tuñón, V. Moliner, J. Bertran J. Am. Chem. Soc. 2015, 137, 12024-12034.

# Negative Electrode Materials for Sodium Ion Batteries

*Riccardo Ruffo*

*Università degli Studi di Milano Bicocca, Dipartimento di Scienza dei Materiali; riccardo.ruffo@unimib.it*

The world annual consumption of energy is in the range of 100 TWh whose largest part of this energy is supplied by fossil fuels or nuclear plants. Both these technologies are nowadays considered as not sustainable; however the global energy demand is still increasing. In this dim picture, renewable energy supplied by sun, wind, earth crust heat, and sea represent a viable and environmental friendly alternative which is leading to the investigation, development, and commercialization of new technology such as solar cells, wind mills, heat pumps, etc. The full exploitation of the energy produced by these primary sources, which are intrinsically intermittent, represents another technological issue which is currently approached by the design of better energy distribution grids and the large use of energy storage devices. Moreover, an important part of the total energy consumption is related to the automotive field, where fossil fuels still play a predominant role. Just in the last few years the automotive market is showing an exponential growing interest in electrical power units to feed hybrid or full electrical vehicles.

Electrochemical energy storage units are currently used in high or low tech portable devices. The most demanding high tech tools require the use of high energy density system, such as lithium ion batteries. Smart grid developers or automotive engineers are looking with growing interest at the development of better batteries with higher performances, however, the figure of merits depends on the specific applications. Few years ago, due to the large use of lithium, several investigators are questioning about its availability and possible material shortness. There are several answers to this issue: the design of better lithium based systems (lithium air, lithium sulfur), the lithium recycling, actually non-convenient, or the development of lithium free battery technology.

Aim of the present contribution will be the description of the current researches performed at the Material Science Department of the University of Milano Bicocca on materials for sodium ion secondary battery, focusing in particular on the negative electrode. Usually, research efforts in this field are directed towards the production of optimized phases by a trial and error procedure focused on the electrochemical performances rather than a full understanding of the mechanism beyond the electrochemical reaction. In our case, however, the scope is to elucidate the structure properties correlations by combining SEM, TEM, XRPD, and Raman measurements with the electrochemical behaviour in half cells vs. metallic sodium. Several phases, representative of different reaction classes have been investigated: conversion oxides ($Co_3O_4$, $Fe_2O_3$), intercalation or pseudo-capacitive oxides ($TiO_2$), and carbons, which show different reaction mechanism depending on their properties. Specific morphologies were designed to optimize the sodium uptake/release from the electrolyte addressing preparation routes towards proper particle size and shape.

# A Fully Polarizable Embedding Model for Molecular Spectroscopy of Aqueous Solutions

*Chiara Cappelli*[a]

[a]*Scuola Normale Superiore, Piazza dei Cavalieri 7, I-56126 Pisa (IT)*

The computational modeling of molecular spectra of aqueous solutions is particulary challenging. In fact, it requires at the same time an accurate modeling of the response of the solute to the external radiation field and a reliable account of the effects of the surrounding environment, which can hugely modify the solute's spectral features as a result of specific/directional interactions (1).

A recently developed Quantum-Mechanical (QM)/polarizable molecular mechanics (MM)/polarizable continuum model (PCM) (2) embedding approach has shown extraordinary capabilities, yielding calculated spectra in excellent agreement with experiments.

An overview of the the theoretical fundamentals of this methods, which combines a fluctuating charge (FQ) approach to the MM polarization with the PCM is given, and specific issues related to the calculation of spectral responses (3) are discussed in the context of selected applications (4).

References: 1. F. Egidi, C. Cappelli "Elsevier Reference Module in Chemistry, Molecular Sciences and Chemical Engineering", DOI:10.1016/B978-0-12-409547-2.10881-9 (2015). 2. C. Cappelli, Int, J. Quantum Chem. 116, 1532 (2016). 3. (a) F. Lipparini, C. Cappelli. V. Barone, J. Chem. Theory Comput., 8, 4153 (2012); (b) F. Lipparini, C. Cappelli, N. De Mitri, G. Scalmani, V. Barone, J. Chem. Theory Comput. 8, 4270 (2012); (c) F. Lipparini, C. Cappelli, V. Barone, J. Chem. Phys. 138, 234108 (2013); (d) M. Caricato, F. Lipparini, G. Scalmani, C. Cappelli, V. Barone J. Chem. Theory Comput. 9, 3035 (2013); (e) I. Carnimeo, C. Cappelli, V. Barone, J. Comput. Chem. 36, 2271 (2015). 4. (a) F. Lipparini, F. Egidi, C. Cappelli, V. Barone, J. Chem. Theory Comput. 9, 1880 (2013); (b) F. Egidi, I. Carnimeo, C. Cappelli, Opt. Mater. Express 5, 196 (2015); (c) F. Egidi, R. Russo, I. Carnimeo, A. D'Urso, G. Mancini, C. Cappelli, J. Phys. Chem. A 119, 5396 (2015); (d) T. Giovannini, M. Olszowka, C. Cappelli, J. Chem. Theory Comput. 12, 5483 (2016).

# Macro Mid-Infrared total reflection (MA-FTIR) mapping for the characterization of outdoor bronze surfaces

*Rocco Mazzeo*[a], *Stjin Legrand*[b], *Giorgia Sciutto*[a], *Silvia Prati*[a], *Emilio Catelli*[a], *Paolo Oliveri*[c], *Koen Janssens*[b]

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In the last decades, many research efforts have been devoted to the development of advanced non-invasive approaches for the examination of cultural heritage. However, up to now, too few attentions has been paid on the potentialities of the Macro Mid-Infrared total reflection (MA-FTIR) mapping analysis. Indeed, the infrared reflectance spectroscopy single point investigation has been largely applied in analytical studies of artworks due to its advantage of characterizing both organic and inorganic materials. On the other hand, the possibility to simultaneously obtained information on molecular composition and spatial distribution of constituents is of crucial importance for properly addressing conservation issues.

To this aim, the present research work was focused on the application of an advanced MA-FTIR mapping system for the study of altered bronze surfaces. Moreover, an *ad hoc* multivariate approach has been proposed for the interpretation of data.

A bronze sculpture exposed in the atmosphere deteriorates with time, developing a greenish/blackish layer mainly constituted of corrosion products. The formation of these corrosion products implies complex chemical, electrochemical and physical processes that strongly depend on the constituents of the surrounding environment. In addition, different acrylic resins, synthetic waxes and organic inhibitors may be commonly applied for short-term protection of outdoor bronze sculptures.

To the Authors knowledge for the first time Mid FTIR macro mapping analysis was performed on metal patinas, allowing the location of corrosion products and old coatings, and describing their interactions. The performances of the approach have been initially evaluated on standard bronze samples characterized by the presence of a green basic hydroxysulfate (brochantite) treated with different organic materials. Subsequently, the exceptional case of study of the bronze sculptures of the Neptune Fountain (Bologna, 16th century) has been investigated.

The instrument acquired hyperspectral cubes by scanning the metal surface without any contact, recording sequential total reflection single-point spectra. The big dimension of the data cubes obtained, as well as, the deformation of IR bands induced by specular reflection phenomena, may serious hampering the correct interpretation of the spectral features. Thus, a chemometric method, based on the use of the brushing procedure, was proposed to extract all the useful information embedded in a complex hypercube.

The high specificity of MA-FTIR mapping revealed important outcomes on the state of conservation of the monumental statue. In particular, it was possible to clearly describe well preserved areas in which wax and incralac resulted to be still present, describing their distribution and identifying zones affected by a more aggressive corrosion process.

# GC/MS and HPLC/MS characterization of organic residues from ceramic vessels of Basque whalers of the 16th to 17th century

*Erika Ribechini*[a], *Laura Blanco-Zubiaguirre*[b], *Ilaria Degano*[a], *Jacopo La Nasa*[a], *Javier García-Iñañez*[c], *Maitane Olivares*[b], *Kepa Castro*[b]

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The aim of this work is focused on the identification of the organic residues from ceramic vessels recovered from a deposit in Lekeitio (Basque Country, Northern Spain). These vessels are suspected to have been used by the Basque whalers in the period from 16th to 17th Century to store whale oil. Bearing in mind our aim, different analytical approaches based on chromatography and mass spectrometry (GC/MS and HPLC-ESI-qTOF) were used to study both fresh blubber and whale oil products and the archaeological substances in order to obtain chromatographic profiles and possibly detect highly diagnostic biomarkers. Two hydrolysis approaches were used in order to compare data and obtain as much information as possible; (i) microwave assisted direct hydrolysis of the ceramic samples and (ii) microwave assisted hydrolysis of previously solvent-extracted samples. On the other side, the study of solvent (chloroform:hexane (3:2 v/v)) soluble fraction was carried out by means of HPLC-ESI-qTOF. Preliminary results led to the identification of some interesting organic compounds in the hydrolysable and soluble aliquots from the ceramic vessel such as pristane, phytane, several saturated fatty acids, hydroxyacids and cholesterol along with triacylglycerols in the solvent soluble fraction. On the other hand, the obtained results for the fresh whale oil and blubber suggested a similar lipid profile to the ones obtained for the archaeological samples. The chemical results together with archaeological data seem to indicate the vessels were used to store whale oil.

# Comunicazioni Orali

# TiO2/Au NRs photocatalysts for photodegradation of water pollutants under UV and visible light

*A. Truppi*[a], *F. Petronella*[a], *T. Placido*[a,b], *C. Giannini*[c], *T. Sibillano*[c], *A. Agostiano*[a,b], *M. Lucia Curri*[a], *R. Comparelli*[a]

[a] *CNR-IPCF UOS Bari, c/o Dip. Chimica Via Orabona 4, 70126 Bari, Italy;* [b] *Università degli Studi di Bari, Dip. Chimica, Via Orabona 4, 70126 Bari, Italy;* [c] *CNR-IC-Istituto di Cristallografia, via Amendola 122/O, 70126 Bari,Italy;* a.truppi@ba.ipcf.cnr.it

In the quest to solve environmental remediation and solar energy conversion issues, plasmonic heterostructures composed of noble metals in combination with semiconductors have been attracting tremendous attention (1,2). In particular anisotropic metal nanoparticles are very appealing for photocatalytic applications (1,3). Owing to their tuneable longitudinal plasmon band and their anisotropic shape cylindrical Au nanorods (Au NRs) are among the most studied plasmonic NPs. However, it must be pointed out that the role played by gold nanoparticles in the overall photoactivation mechanism is different according the photoactivation wavelength. Under UV irradiation titania is activated and photo-generated electrons, sink in NPs of noble metal, hindering the recombination of charge carriers ($e^-/h^+$),which results in an increase of the photocatalytic activity. While, under visible light irradiation titania cannot be activated (band-gap: 3–3.2 eV), and thus light must be absorbed by plasmonic NPs. Two possible mechanisms of titania activation by plasmonic NPs under visible light irradiation have been recently proposed, i.e. charge and energy transfer (4).
The present work focuses on the synthesis of $TiO_2$/Au NRs hybrid nanocomposites exploiting pre-synthetized Au NRs as nucleation seeds for the growth of anatase $TiO_2$ nanoparticles according to co-precipitation procedure followed by calcination at different temperatures. The final goal of this work is to obtain a visible light active plasmonic photocatalyst on a gram scale exploiting a user friendly and easy scalable procedure. Photocatalytic experiments were performed under UV irradiation in order to test the degradation of a target compound (methylene blue) in aqueous solution using $TiO_2$ P25 Evonik as a reference material. Moreover, the photocatalytic removal of the antibiotic Nalidixid acid upon visible light irradiation was investigated. $TiO_2$/AuNRs calcined at 450°C presented a photoactivity up to 2.5 times higher than $TiO_2$P25 Evonik under UV light. Interestingly, after 15 min of visible irradiation $TiO_2$/AuNRs 450°C based nanocomposite has achieved a 20% degradation while NA degradation achieved by other $TiO_2$/AuNRs samples, unmodified $TiO_2$ nanoparticles and $TiO_2$ P25 Evonik was negligible. HPLC-MS analyses further confirmed that NA degradation reaction occurred only in presence of $TiO_2$/AuNRs 450°C sample. Furthermore, the photoreduction of $CO_2$ was evaluated for all the samples under study under UV-visible irradiation. In particular, $TiO_2$/Au NRs 450°C catalysed the formation of $CH_3COOH$ in high yield 113 $\mu mol \cdot g^{-1}$ cat. The obtained results point out the promising photoactivity of $TiO_2$/AuNRs samples in the visible range and their potential viability for water remediation and artificial photosynthesis.

References: 1. A. Truppi, et al., “Visible-Light-Active $TiO_2$-Based Hybrid Nanocatalysts for Environmental Applications” *Catalysts* 2017, *7(4)*, 100. 2. F. Petronella, et al., “Nanocomposite materials for photocatalytic degradation of pollutants” *Catalysis Today*, 2017, 281,1, 85-100. 3. F. Petronella, et al., “Multifunctional $TiO_2/Fe_xO_y$/Ag based nanocrystalline heterostructures for photocatalytic degradation of a recalcitrant pollutant” *Catalysis Today*, 2017, 284, 100-106. 4. Bumajdad, A. and M. Madkour, *Understanding the superior photocatalytic activity of noble metals modified titania under UV and visible light irradiation.* Physical Chemistry Chemical Physics, 2014. 16(16): p. 7146-7158.

# Photochromism of N-phenyl-carbazole benzopyrans

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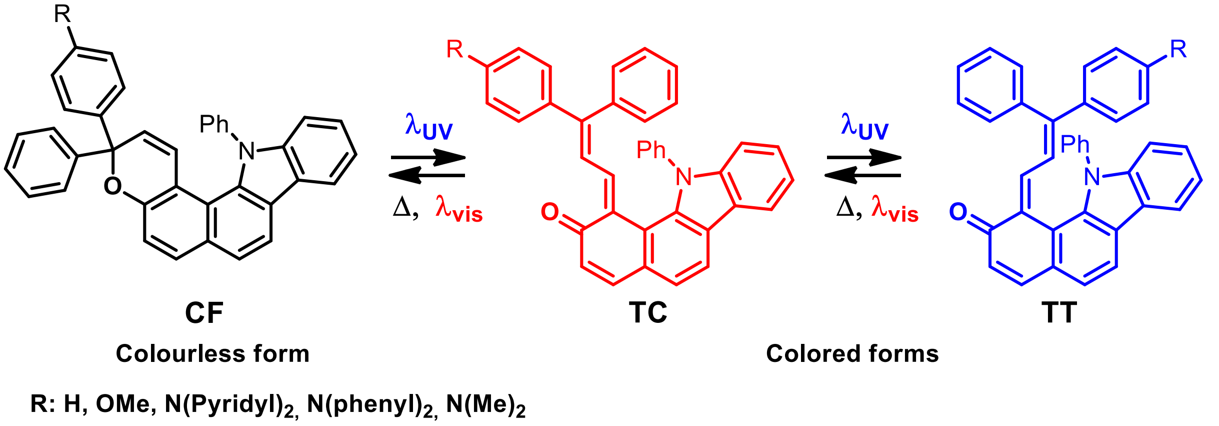
[c] *Institut Lavoisier de Versailles, UMR CNRS 8180, Université de Versailles Saint-Quentin-en-Yvelines, 45 av des Etats-Unis, Versailles Cedex, 78035, France;*
fausto.ortica@unipg.it

In this study, which is part of a wider investigation carried out in our laboratories on photochromic systems belonging to the chromenes class (1,2), we report on the synthesis and the photochromic behaviour of a series of benzopyrans bearing a N-phenyl carbazole moiety (Scheme 1). Unlike most chromenes, these molecules exhibit a significant conversion percentage to the transoid-*trans* coloured isomer (TT), as high as 70% in the case of the unsubstituted compound. This feature, along with the long-lasting thermal stability in the dark of the TT isomer, which can be completely bleached back to the starting material by visible light, suggests the possible use of these compounds as P-type photochromic systems (3) in optical memories and photoswitchable devices.



Scheme 1. Simplified photochromic mechanism of N-phenyl-carbazole benzopyrans.

Various information which shed light on the mechanism of the photochromic reaction have been obtained. The combination of spectral, kinetic and HPLC data allowed the quantitative absorption spectra of the closed colorless form (CF), the transoid-cis (TC) and the transoid-trans (TT) coloured isomers to be measured, along with the quantum yields for the UV photocolouration and visible photobleaching processes. The effect of the substituent located on the phenyl ring linked to the sp3 carbon atom of the pyran ring on the thermal stability of the TT isomer, the spectral features and the kinetic profiles has been investigated.

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# Hydrophobic Carbon Dots with intense phololuminescence towards single white emitting materials

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Carbon dots (C-dots) draw increasing attention as new emitting nanomaterials in different applications, including optoelectronics, bioimaging and biosensing, thanks to their high quantum yield (QY), biocompatibility, low toxicity and cost effective sources (1), compared to inorganic Cd based quantum dots. C-dots are all organic, carbonaceous materials, less than 10 nm in size, with a bright and multi-colored emission that typically depends on the excitation wavelength. Although the origin of C-dot photoluminescence (PL) properties is still a debated topic, two main contributions to their radiative emission, one arising from the intrinsic core, consisting of $sp^2$ carbogenic domains, and the second involving surface states, i.e. emission traps, surface defects, functional groups connected with C-dots surface, were proposed (2). Moreover, when the synthesis of C-dots is performed by means of hydrothermal methods in the presence of amines, high emitting molecular fluorophores can be formed by the condensation reaction and the concomitant loss of water in the synthetic medium between the carboxylic moiety of the carbonaceous precursor and the amine group (3). In this work, the synthesis of oil-soluble C-dots has been investigated (4) by systematically controlling the reaction conditions, in order to assess the role of the preparative conditions on the optical and morphological properties of the nanoparticles. In particular, the carbonization conditions, temperature and time, and surface passivation have been studied. We have demonstrated that, besides the fundamental role of the amine-containing passivating agents in improving the PL emission of C-dots, *via* the formation of molecular fluorophores alongside the carbonization process, also the reaction temperature is decisive in addressing the optical properties of C-dots. Indeed, in specific reaction conditions, additional UV-vis absorption and fluorescence signals appear, whose occurrence has been assigned to further multiple excited states emitting at low energies and/or to the aggregation of intermediate molecular species. Such C-dots, when excited in the blue region, show high intensity white emission, thus resulting potential candidate for the fabrication of all-organic and bio-compatible colloidal white emitting single nano-objects. The white emission appears retained also when the nanoparticles are processed in solid films by incorporation in a PMMA host matrix (QY=23%). In addition, the colour point of the suspension and of the polymeric films still stays in the white colour region of the 1931 CIE diagram after several months, thus proving the colour stability of the nanoparticles.

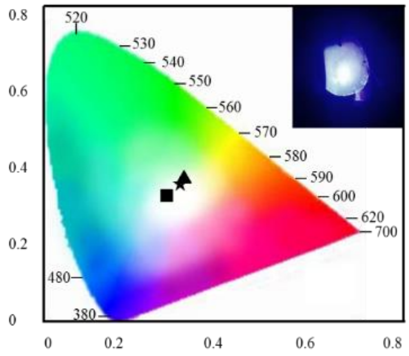

*Fig. 1 1931 CIE diagram of the C-dot /PMMA film showing white emission when excited in the blue region ( 400, ★405 and ■ 410 nm▲). The inset shows the white emission of the C-dot /PMMA film illuminated with a monochromatic radiation of 405 nm.*

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# Graphene-like domains on MoS2/ TiO2 systems, via acetylene polymerization: in-situ synthesis and characterization

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Carbon–based materials with different dimensionality, including graphene, graphene oxide and graphite nanoplatelets have attracted an increasing attention due to their unique electrical conductivity, structural regularity, chemical inertness, biocompatibility, mechanical and thermal stability (1,2). Actually, carbon nanomaterials are ideal templates and supports for the interaction and growth of organic and/or inorganic structures, according to the properties required by the final carbon-based nanocomposite. On the basis of the literature concerning the *in situ* synthesis of carbon nanostructures on the surface of $TiO_2$, via acetylene ($C_2H_2$) polymerization (3) and according to the bottom-up approach, our aim was to obtain graphene-based structures grown at the surface of $MoS_2$ (a layered metal dichalcogenide), via $C_2H_2$ polymerization, to be compared with RGO (reduced graphene oxide)/$MoS_2$ hybrid nanostructures, previously obtained via top down method (exfoliation) (4).

It is relevant to underline that a metal oxide support is crucial for the dilution of dark $MoS_2$ samples. Among the different oxides, $TiO_2$ particles, due to the relatively narrow size distribution and to the good crystallinity, are known to limit the heterogeneity of the supported species. Following this line, the role of $MoS_2$ in $MoS_2/TiO_2$ system in affecting $C_2H_2$ polymerization is highlighted, as compared to pure $TiO_2$. Morphology, structure, optical and vibrational properties of the obtained materials, for each step of the synthesis procedure, have been investigated by means of high-resolution TEM, X-ray diffraction, Raman, UV-vis and FTIR spectroscopies.

HRTEM images provide a simple tool to highlight the effectiveness of the sulfidation process, thus showing 1L, 2L, and few-layer $MoS_2$ nanosheets anchored to the surface of $TiO_2$ nanoparticles. In-situ FTIR spectroscopy investigation gives information on the nature of the polymeric species, showing that the formation of both polyenic and aromatic systems can be taken into account, being their formation plausibly promoted by both Ti and Mo catalytic sites (Fig. 1).

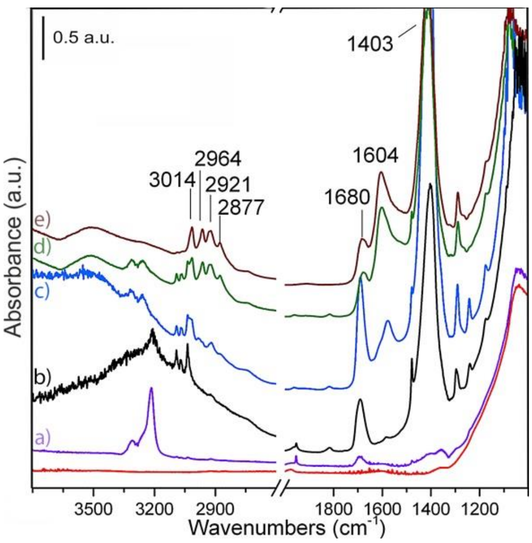

**Fig.1. FTIR spectra of $C_2H_2$ (120 Torr) adsorbed on $MoS_2/TiO_2$ at 298K (0-30' a-c) and at 423K (d,e).**

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# Colloidal Nanocrystal Surface Decorated Graphene based Hybrid Materials for Sensors

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Graphene is an extraordinary structural material for (bio)sensors, solar cells, supercapacitors, batteries and photocatalytic devices, due to its excellent thermal and electrical conductivity, high surface area, mechanical strength and light transparency from visible to infrared (1). The reactivity of graphene as a two-dimensional platform offers the possibility to implement a large variety of strategies of hybridization, including molecular decoration approaches with (bio)molecules or nanostructured compounds, finally resulting in novel functional nanocomposites. Such hybrid materials exhibit novel functionalities and improved pristine properties, further extending the technological applications of graphene. Colloidal nanocrystals (NCs), prepared by means of solution-based colloidal chemistry routes, are particularly suitable for the chemical decoration of graphene. The surface chemistry of these nano-objects can be engineered by playing with the coordinated surfactant molecules that allow their anchoring to graphene. In this way, the original size- and shape-dependent properties of the NCs can be ingeniously combined the unique functionalities of graphene, finally merging in a novel composite material promising for advanced device applications (2). Here, the preparation and characterization of hybrid materials based on graphene and semiconductor NCs (i.e. PbS, $TiO_2$) or Au nanoparticles (NPs) are presented. Nanocomposites based on CVD grown graphene and colloidal NCs were prepared by exposing graphene films to solutions of 1-pyrene butyric acid (PBA) surface coated semiconductor NCs (PbS, $TiO_2$), obtained by a capping exchange procedure onto pre-synthesized NCs (3,4) (see Figure 1 A). As an alternative, composites formed of Reduced Graphene Oxide (RGO), surface modified by a functional pyrene and then decorated by semiconducting NCs or Au NPs grown by using *in-situ* colloidal routes, were prepared. The sensing characteristics of the hybrid nanocomposites have been preliminarily tested and result promising for the materials integration in photodetectors and in electroanalytical sensors for detection of DNA or neurotransmitter molecules (see Figure 1 B).

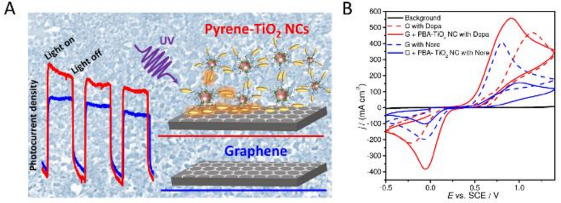

Figure 1. A) (On the left) Sketch of photocurrent density response of graphene decorated with PBA-$TiO_2$ NCs. (On the right) Sketch of the PBA-$TiO_2$ NCs anchored to graphene with scheme of the chemical immobilization by the pyrene linker capping NC surface, B) CVs of 1 mM dopamine (Dopa) and norepinephrine (Nore) registered at 0.1 V $s^{-1}$ in 0.1 M aqueous $NaClO_4$ on ITO electrodes modified with graphene (G) and with PBA-$TiO_2$ NC functionalized G.

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# Enhanced power-conversion efficiency in organic solar cells incorporating polymeric compatibilizers

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Organic Solar Cells (OSCs) have attracted considerable interest because of their flexibility, lightness, and potential for low-cost and simplicity of the manufacturing processes. Devices based on the P3HT:PCBM thin film heterojunctions are among the most studied, providing power conversion efficiency (PCE) of 3-6% and 0.1-3.1% in bulk (BHJ) and planar (PHJ) heterojunctions, respectively (1,2). Although encouraging progress has been made, performances are not yet suitable for large-scale implementation. Many effort has been spent on the development of low band-gap polymers, fullerene derivatives, and additives for obtaining improved performance and controlled morphology of the heterojunctions (3-4). However, the development of most semiconducting polymers or copolymers involves complicated multistep synthetic procedures that affect the yield and the cost of final materials. In the present work, three polymers based on polythiophene and $C_{60}$ units have been designed, easily synthesized, characterized, and employed as compatibilizers in P3HT:PCBM devices.

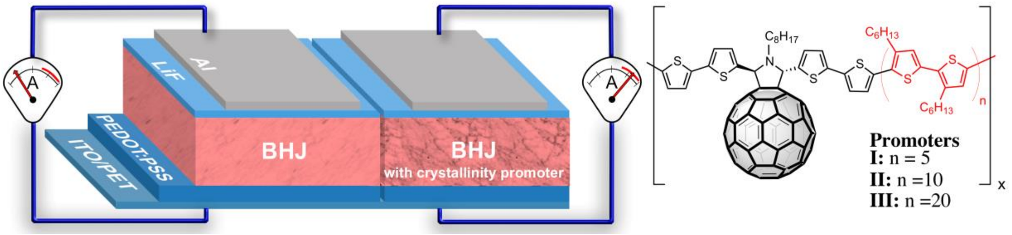

**Figure 2 Schematic representation of devices with and without compatibilizer (left) and its chemical structure (right).**

The effect of the thienyl spacer length between $C_{60}$ monomers on optoelectronic properties, morphology, and structure of heterojunction has been examined using several techniques (NMR, FTIR, XPS, DSC and AFM). We observed that small quantities of these systems can play a critical role in tuning the device morphology by enhancing crystallinity along with charge transport of the thin film heterojunction. In addition, a good matching in the energy levels was observed, so that the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels of these systems form a cascade energy band structure. What above allows for up to a 3-fold enhancement of PCE by adding small amount (about 2%) of compatibilizer. By our approach, we obtained the highest short-circuit current density (~ 16 mA/cm$^2$) and PCE (~ 4.5%) values ever reported for P3HT:PCBM solar cells on plastic/flexible substrates, thus giving new perspectives to applications of flexible photovoltaics.

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# Molecular aggregates: a fresh perspective

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The exciton model for molecular aggregates relies on two major approximations: the neglect of molecular polarizability and the dipolar description of intermolecular interactions. Both approximations are bound to fail in aggregates of organic dyes for NLO applications (1).

Here we discuss aggregates of quadrupolar dyes, a class of conjugated molecules characterized by the presence of electron donor (D) and acceptor (A) groups in structures D-A-D or A-D-A, described by essential state models, and parametrized against TD-DFT calculations on dimeric units. The proposed model predicts sizable excitonic effects in 2-photon absorption spectra and explains the experimental observation of non-fluorescent J-aggregates (2).

We also address linear aggregates of D-A polar dyes (specifically 4-Dimethylamino-4′-nitrostilbene, DANS) molecules aligned into carbon-nanotubes (CNT). In a recent paper (3) the amplified β-response observed for DANS@CNT that was ascribed to ~70 aligned dyes (3). Essential state models, parametrized according to the calculated geometry of DANS dimers in CNT (Fig. 1), demonstrate that the molecular polarizability leads to a superlinear amplification of the response that reduces the required number of aligned dyes to ~10, while quite naturally explaining the large red-shift of the HyperRayleigh scattering signal with respect to the linear absorption peak.

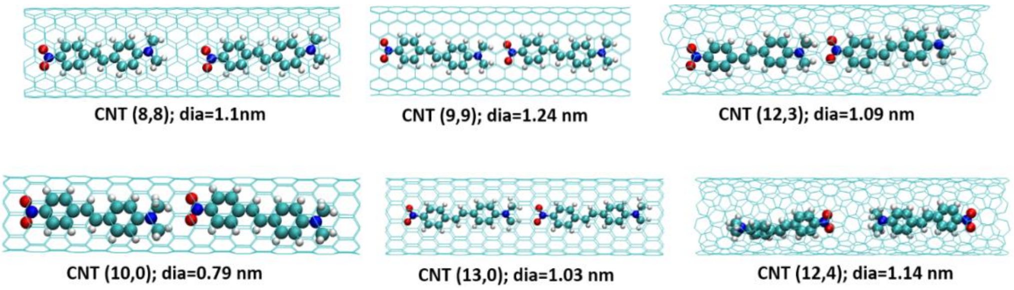

Fig. 1 DANS dimers in CNT (DFT optimized geometry).

Acknowledgements
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# On the Zn2+ ion speciation in challenging ionic media: a molecular dynamics and X-ray absorption spectroscopy study

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Ranging from analytical chemistry to electrochemistry, Ionic Liquids (ILs) are interesting compounds that have seen a wide array of applications, including their use as replacement for organic solvents, lubricants, reaction media and transport media. Due to their low volatility and non-flammability, as well as their high chemical and thermal stability, ILs are safer and more environmental-friendly than the commonly used solvents. Furthermore, the capability to tune their chemico-physical properties with slight changes in the composition makes them appealing from the point of view of efficiency.(1) Among the many applications in which ILs have been employed as solvents, an interesting one is Zn deposition for Zn-air batteries.(2,3) While many studies have been reported on this subject, obtaining reliable structural data and identify species in IL solutions is still a challenging task. Indeed, information on the solvation properties of Zn(II) salts in ILs and on how these properties are influenced by the choice of the IL cation and anion is still lacking.

Here, four solutions of zinc bis(trifluoromethanesulfonyl)imide ($Zn(Tf_2N)_2$) in $Tf_2N$ based ILs were studied by combining molecular dynamics (MD) and X-ray absorption spectroscopy (XAS) in order to shed light on the influence that the IL organic cation has on the structural properties of $Zn-Tf_2N$ solvation complexes. The MD-XAS approach has been already proven a valuable tool for the study of IL solutions: the high selectivity and versatility of the XAS technique allows one to obtain reliable data on liquid samples, while MD simulations provide a dynamic atomistic description of the systems.(4,5) We found the $Zn^{2+}$ ion coordinated in a typical octahedral fashion, with the IL cation having no influence on the short range arrangement of atoms around the metal up to 3.5 Å. Conversely, the choice of the organic cation has a significant impact on the speciation of the metal ion (see Figure 1) and on the dynamic properties of the $Zn-Tf_2N$ solvation complexes.

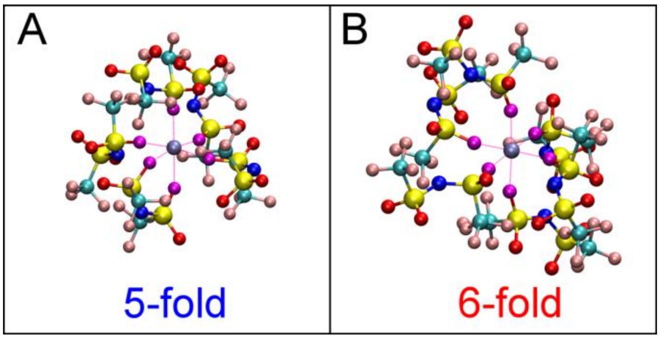

**Figure 1**: Pictorial example of the structural arrangement of $Tf_2N^-$ anions around a $Zn^{2+}$ cation in the 5-fold (A) and 6-fold (B) solvation complexes.

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# Magnetic Solid Lipid Nanoparticles for Magnetically Targeted Delivery of Sorafenib for Treatment of Hepatocellular Carcinoma

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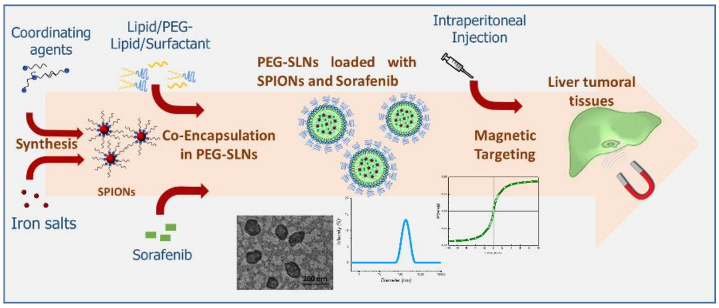
Sorafenib is an orally active multikinase inhibitor and it is only anticancer drug that has proved to significantly prolong the survival time in patients with advanced hepatocellular carcinoma (HCC), when not candidates for potentially curative treatment or transarterial chemoembolization. However, sorafenib is characterized by severe toxic side effects limiting the possible therapeutic response (1,2). Nanoparticle (NP) based approaches offer a valuable alternative for cancer drug delivery, functioning as a carrier for entry through fenestrations in tumor vasculature, thus allowing direct cell access and ensuring the accumulation of high concentrations of drug to the targeted cancer cell, with a concomitant reduced toxicity of normal tissue. In this contest, superparamagnetic iron oxide NPs (SPIONs) are very attractive for delivery of therapeutic agents as they have been reported to enhance the drug delivery to specific locations in the body through the application of an external magnetic field (3,4). Here, solid lipid NPs (SLN) containing sorafenib and SPIONs have been prepared by a hot homogenization technique using cetyl palmitate as lipid matrix and polyethylene glycol modified phospholipids (PEG lipids), in order to achieve a PEG-based anti-fouling coating on SLN surface. These nanoformulations, thoroughly investigated by means of complementary techniques, have finally resulted effective drug delivery magnetic nanovectors with good stability in aqueous medium and high drug encapsulation efficiency (% EE>90%). In addition, the relaxometric characterization has proven that the magnetic SLN loaded with sorafenib are also very efficient contrast agents, with a great potential in magnetic resonance imaging (MRI) technique. The proposed magnetic SLNs loaded with sorafenib represent promising candidates for image guided and magnetic targeting of sorafenib to liver towards an efficacious treatment of HCC.



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# Micro-structural characterization of model membranes containing DHA

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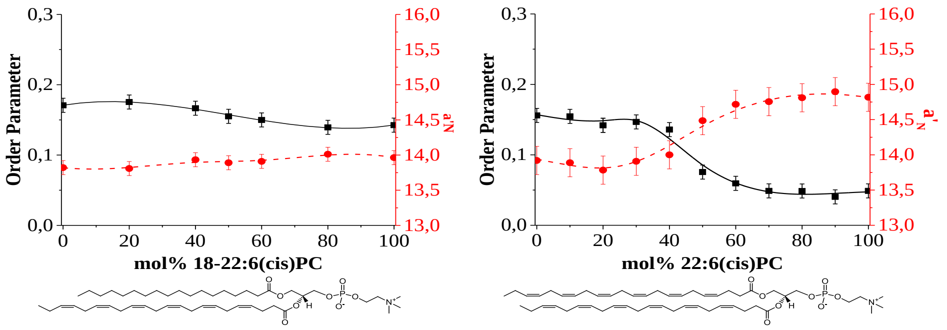
DocosaHexaenoic Acid (DHA) is the longest and most unsaturated fatty acid present in cell membranes, playing a pivotal role in the prevention of cardiovascular diseases and cancer and exerting a strong neuroprotective effect (1). Among other hypotheses, mainly based on their radical-scavenging and anti-inflammatory action (2) it has been proposed that omega-3 fatty acids, to which DHA belongs, once converted to lipids could alter the structure of biological membranes, whose involvement in major biological processes, such as signaling and protein trafficking, is reported. However, how one molecule can be associated to many different beneficial effects is still unclear.

Lipid diversity regulates a wealth of biomembranes processes, because those molecules can tune the physicochemical characteristics of the lipid bilayer, such as elasticity, curvature, surface charge, hydration and the formation of domains by specific interactions involving the chemical structure, conformation and dynamics of the lipid head groups and acyl chains. For instance, it has been shown that certain lipids can promote nonlamellar phase formation, such as inverted hexagonal and cubic phases, as well as favor insertion of proteins into the membrane. These lipids, including sphigolipids and lysolipids, are defined non-bilayer lipids. Moreover, both theoretical and experimental data provide clear indications that, at least transiently, non-lamellar structural intermediates must exist *in vivo (*3).

With the aim to understand the functional role of DHA, we characterized the microstructure of different phospholipid systems containing this fatty acid. A variety of physico-chemical techniques such as Electron Spin Resonance (ESR) spectroscopy with the spin-labelling approach and Neutron Reflectivity (NR) were used to achieve our aims.

ESR results indicates clearly that the di-polyunsaturated phospholipid is able to induce dramatic variation in the fluidity of the bilayer, described by the order parameter, in association with higher hyperfine coupling constant values, index of the polarity experienced by the spin label (Figure 1). These significant changes in the biomembranes micro-structure supports the hypothesis that the phospholipids di-polyunsaturated behaves as a nonbilayer lipid, playing a key role as a morphological element to support the dynamic organization of cellular membrane systems.



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# Nanoparticles encapsulation in micellar systems for biomedical applications

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Increasing interest has been devoted to colloidal inorganic nanoparticles (NPs) in the last decades in order to improve their properties and implement their use in nanomedicine.

As synthesized colloidal inorganic NPs require a proper functionalization in order to be further used in combination with biologically relevant structures for biomedical applications. Among the most common functionalization techniques, the exploitation of the hydrophobic interactions between NPs capping ligands and hydrophobic tails of amphiphilic molecules represents a prompt, versatile and reproducible method. Micelles forming amphiphilic molecules are able to encapsulate NPs in the hydrophobic core preserving their properties, enabling their dispersion in aqueous media and providing, at the same time, suitable functionalities at their surface serving as anchor points for the bioconjugation with peptides, DNA, drugs, proteins *etc*.

Several systems based on micelles forming molecules have been reported able to encapsulate NPs, here the results recently obtained on the phospholipids functionalization of multifunctional anisotropic $Fe_3O_4$-$TiO_2$ heterostructured NPs have demonstrated the success of the technique for achieving peptide bioconjugates, potentially effective for theranostic applications (1).

Another class of materials, namely amphiphilic peptides (APs) have been found able to self-assemble in several supramolecular structures (micelles, fibers, vesicles, *etc.*) and have been used as delivery carriers for drugs, RNA and DNA molecules (2).

Here, APs have been synthesized with hydrophilic backbones and functional groups and hydrophobic acyl chains, as advanced and highly customizable encapsulation agents for emitting NPs (QDs). The comprehensive spectroscopic and morphological investigation of the functionalized QDs has elucidated the role played by the different APs features in the functionalization procedure. Finally, the conjugation of the prepared APs capped QDs with DNA to achieve exceptional probes envisages a great potential for biomolecular detection and imaging applications.

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# Effect of cellulose ethers on the formation and properties of magnesium phosphate-based cements for biomedical applications

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In the field of injectable materials for bone regeneration, magnesium phosphate-based cements (MPCs) represent an underexplored area of research, which is nowadays getting more attention thanks to their attractive features that, in some cases, make it possible to overcome the traditional drawbacks associated to the deeply investigated calcium phosphate cements. MPCs are reported to display an effective combination of mechanical properties, fast setting and resorption rate, while maintaining a good biocompatibility (1). Polymeric additives are commonly employed in calcium phosphate-based cements to improve paste cohesiveness, injectability and rheological properties (2); however, to the best of our knowledge, only few reports investigated the effect of polymers on MPCs. Moreover, little attention is devoted so far to understand why a specific additive works and how the molecular structure and properties of the polymer affect the final properties of the paste.

The present contribution deals with the investigation of the effect of three different biocompatible cellulose ethers (carboxymethyl cellulose, hydroxypropyl cellulose and (hydroxypropyl)methyl cellulose) on the formation and properties of magnesium phosphate-based cements. The pastes were prepared by mixing $Mg_3(PO_4)_2$ with a solution of $(NH_4)_2HPO_4$. First, the powder to liquid ratio and the concentration of the phosphate solution were optimized to obtain a good conversion degree to the final product (struvite, $MgNH_4PO_4 \cdot 6H_2O$), as investigated by X-rays Diffraction experiments. Then, we incorporated into the mixture different percentages of polymeric additives (5% wt and 10% wt) and we investigated their effect on both the formation and final properties of the material. We observed the morphology by means of Scanning Electron Microscopy, while the effect of the celluloses on the crystallinity of the formed mineral phases was explored using X-ray Diffraction. We employed Differential Scanning Calorimetry to investigate the amount of free and confined water in these systems and to get information about the porosity. The microstructure and the porosity were also evaluated by means of nitrogen adsorption measurements. The setting reaction of the pastes at physiological temperature was monitored using calorimetry, while the setting time was determined with the Gillmore needle test. Given the potential of the obtained materials as injectable bone cements, we tested their injectability at different setting times, using a custom-made apparatus. We then investigated the stability in a physiological medium at 37 °C and studied the dissolution behaviour up to 28 days, as well as the modifications in the morphology and in the crystallinity of the cements. We believe that this study represents a step forward in the field of MPCs and in the understanding of the effect that polymeric additives display on this kind of materials.

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# Bifunctional polymer-dispersed liquid crystals

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Reverse mode polymer-dispersed liquid crystals (PDLCs) are transparent films in their OFF state (no applied electric field) and become opaque in their ON state. The addition of a photo-chromic compound allows a colour change of films, when they are UV irradiated. The aim of this work was the preparation and characterisation of bifunctional materials, able to change their transparency by application of an electric field and colour under UV irradiation. In particular, the performance of PDLCs doped with different spiro(indolo)-oxazine molecules was investigated. Both the electro-optical and photo-chromic response of these systems were evaluated and compared (1).

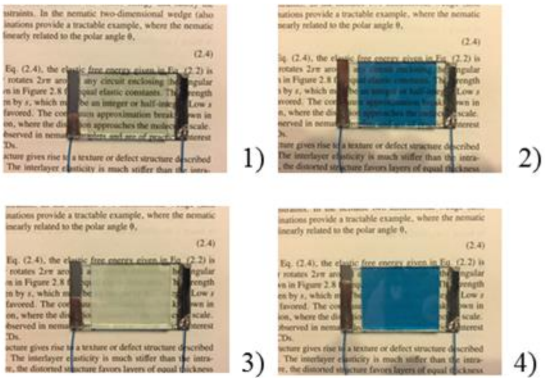

Figure 1. The four independent states of a photo-chromic reverse mode PDLC: 1) Transparent and uncoloured (no electric field and no UV irradiation); 2) Transparent and coloured (no electric field, but in the presence of UV irradiation); 3) Opaque and uncoloured (if the electric field is turned on, but no UV irradiation); 4) Opaque and coloured (if both the electric field and UV irradiation are present).

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# Supracolloidal association of microgels and supramolecular tubules of bile salt derivatives

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The aggregation of colloid-sized particles is a fascinating subject, widely employed in chemistry, physics, and biology. The formation of supracolloidal nanostructures represents nowadays an intriguing approach for building novel artificial nanomaterials and devices (1). However, a fine control over the interactions of colloidal particles is fundamental to approach complex structures. This control is particularly crucial when involving systems of particles of different shapes, where specific interactions can be exploited to provide complex supracolloidal geometries with expanded application potential. With this background, we studied the supracolloidal aggregation of spherical microgels and supramolecular surfactant tubes. The interactions were controlled by changing charge of the particles and parameters like electrolyte concentration and temperature. We used cationic or anionic microgels and catanionic surfactant tubes with tunable charge, formed by mixtures of anionic and cationic derivatives of bile salts (2). The charge of the tubes was tuned by controlling the anionic/cationic derivative molar ratio. A structure of triangular rolled layer were observed for the catanionic mixtures, with the edges of the layer designing spirals along the tubular structure. Tubes with a smooth surface were instead provided by the pure anionic derivative solutions. We demonstrated that specific interactions of the microgels occur with the edges of the layers that form the tubular structures. By properly choosing the tube type and adjusting the interaction conditions, virus like particles, microgel decorated tubules or clusters of tubes interconnected by microgels were formed (Figure 1a, b and c, respectively). Extended forms of these clusters provided the basic framework of low density hybrid gels.

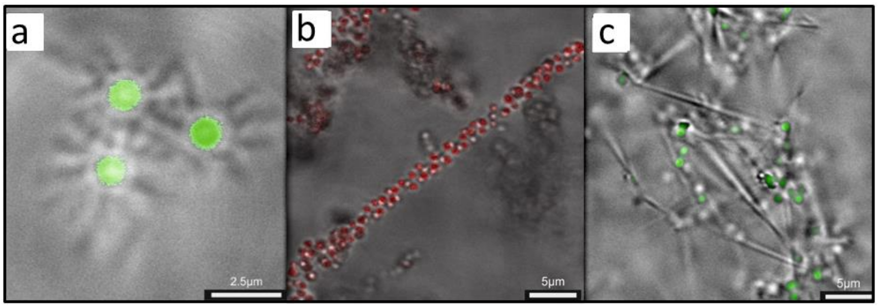

**Figure 2** Virus like particles with a microgel core and a corona of tubes (a), microgel decorated tubes (b), clusters of tubes interconnected by microgels (c).

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# The lipid bilayer of model membranes: news from the inside

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The solubility of small molecules into a lipid bilayer is central to many biological and biotechnological processes. Lieb and Stein (1) proposed that small molecules dissolve and diffuse by "hopping" between empty voids and molecular dynamics studies have shown that the largest voids are located in the center of the membrane (2), that they increase by increasing temperature and unsaturations in the acyl chains (3), decrease by adding cholesterol (4), and that it depends on lipid composition (5). Unfortunately, this description can hardly find an experimental confirmation and the diffusion and permeation routes at the atomic level are still not completely understood.

In the present study we use IR spectroscopy, both stationary and time resolved, to characterize the properties of cholesterol loaded POPC liposomes. To this extent we use a vibrational probe, hexacarbonyl tungsten $W(CO)_6$, to follow the solubility of a small hydrophobic molecule inside the membrane at different temperatures and solvent composition (DMSO/water solutions at different DMSO mole fraction), and to follow the dynamics of fat acid hydrophobic tails in the picosecond time domain.

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# Physical-chemical study of a new shape-memory material based on liquid crystalline elastomers

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In this work, we present a new type of soft-soft composite material based on liquid crystalline elastomers, namely Polymer-Dispersed Liquid Crystal Elastomers (PDLCEs) [1]. PDLCEs are made of isotropic polymer, or elastomer matrix, filled with oriented liquid crystal elastomer (LCE) microparticles as colloidal inclusions. The relative composition of the two soft components as well as the liquid crystalline properties of the LCE microparticles allow for a fine-tuning of the final thermo-actuator properties of the PDLCEs [2]. Respect to previous LCE-based composites, characterized by mono-dimensional and uniaxial actuation [3,4], we are able to obtain different actuation geometries and shapes (*Figure 1*).

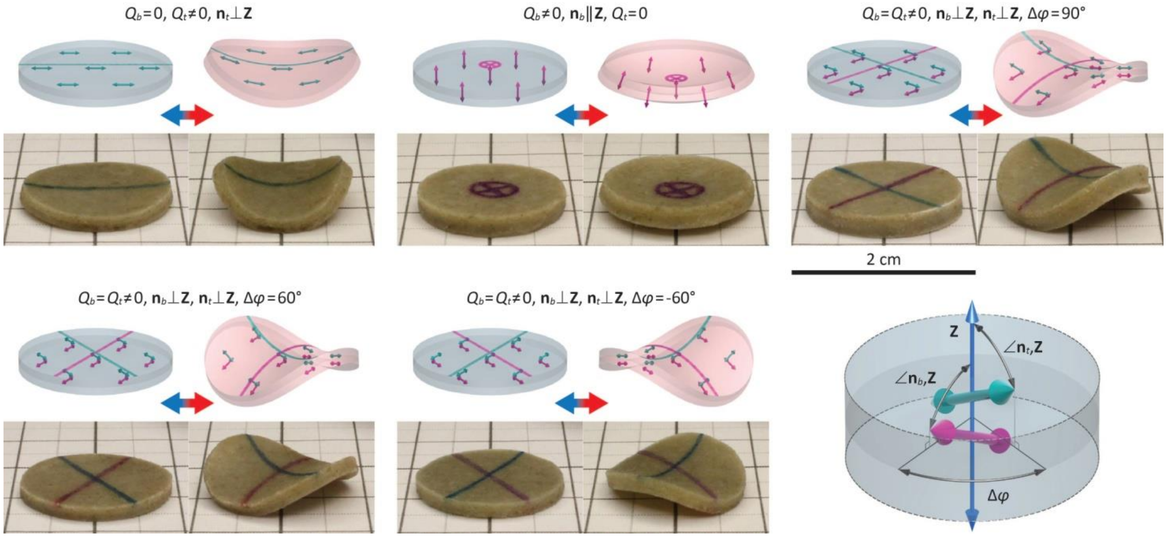

*Figure 1*. Different thermomechanical actuation modes obtained in bilayer PDLCE disks realized by a suitable choice of PDLCE orientational order $Q_b$ and $Q_t$, orientation of $\boldsymbol{n_b}$ and $\boldsymbol{n_t}$ with respect to the surface normal **Z**, and azimuthal angle $\Delta\varphi$ between $\boldsymbol{n_b}$ and $\boldsymbol{n_t}$.(*b*=bottom, cyan; *t*=top, magenta).

The peculiar physical properties of the new PDLCEs is related to their orientational properties, namely the LCE microparticles orientational order (***S***), the overall PDLCE orientational order (***Q***) and the distribution functions of the mesophase director (**n**). $^2$H NMR spectroscopy [5,6] of PDLCEs, prepared under different conditions with $^2$H-selectively labelled LCE microparticles, provided a clear understanding of all these aspects. A magnetic alignment model was proposed and then validated by means of thermo-mechanical, thermo-elastic and $^2$H NMR measurements [1,2].

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# Hybrid nanostructures based on halloysite nanotubes and sustainable polymers

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This work addressed the critical technical challenges in design of functional nanostructures based on halloysite nanotubes (HNTs) and sustainable polymers (both ionic and non-ionic). Chemically, HNTs are composed of gibbsite octahedral sheet (Al−OH) groups on the inner surface and siloxane (Si−O−Si) groups on the external surface. This different chemistry determines a positively charged lumen and a negatively charged shell in the 2−8 pH range. Consequently, the adsorption of ionic biopolymers onto the HNTs surfaces can be controlled by the specific electrostatic interactions as highlighted by the ζ-potential experiments. The thermodynamics of the adsorption process was investigated by isothermal titration calorimetry (ITC), which evidenced that the polymer/HNTs interactions are enthalpy driven (1). The entropic contribution for the polymer adsorption is always negative, demonstrating the loss of configuration freedom for the polymer in the adsorbed state (1). According to the ITC data, non-ionic Hydroxylpropylcellulose is the most efficient polymer in retarding the HNTs sedimentation because of the steric interactions. As a general feature, cationic chitosan is efficient in stabilizing HNT dispersions under acidic pH, whereas anionic pectin is recommended for the same purpose at basic pH values (1). The dynamic behavior of the polymers adsorbed onto the HNTs surfaces was studied by the Fluorescence Correlation Spectroscopy (FCS). To this purpose, the biopolymers were fluorescently labelled with fluorescein derivatives. We observed that the mobility of the polymers is reduced as a consequence of their adsorption onto HNTs surfaces. Structural insights about the polymers adsorbed onto the HNTs surfaces were obtained through Small Angle Neutron Scattering (SANS) and Electric Birefringence (EBR) measurements, which showed that the rotational mobility of the nanotubes decreases in the hybrid systems. The strongest effect was estimated for cationic chitosan that is wrapped onto the HNTs external surface. The studies of the biopolymer/HNTs aqueous dispersions were correlated to the mesoscopic properties of the corresponding bionanocomposite films, which were prepared through the casting method in water. The thermal stabilization of anionic biopolymers can be ascribed to its confinement into the HNTs lumen (2). For both cellulose ethers and chitosan the HNTs addition did not affect the tensile properties, while the presence of HNTs into alginate matrix determined an increase of the elastic modulus. Dynamic mechanical analysis evidenced that the glass transition of the polymers is reduced as consequence of the specific interactions with the HNTs surfaces (2). Mechanical and thermal characteristics of the bionanocomposites were successfully related to their morphology and wettability. In conclusion, this work provides a valuable platform for the development of smart composite nanomaterials with interesting technological properties that can be controlled by the specific biopolymer/HNTs interactions.

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# Absolute Configuration Assignment of two Hybrid Isoindolinone-phthalide Molecules by Vibrational Circular Dichroism

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Vibrational Circular Dichroism (VCD) is more and more used as a sensitive technique to determine the absolute configuration (AC); the many signed signals typical of the mid infra-red region of the spectrum offer a sound basis to discriminate between stereochemical models. Despite the richness of the data, in presence of many low-energy conformers and/or more than one stereocenter, either visual comparison of computed and calculated spectra for all possible diastereomers or use of standard indicators of agreement can be non-straightforward. An ad hoc quantitative indicator of agreement, the similarity index (1), has been advantageously used for that task (2).

We have used VCD spectrsocopy for the AC assignment of the recently synthesized (+)-**1** and (+)-**2**, which are heterocyclic hybrids isoindolinone-phthalide (3), and we have determined their absolute configurations as (*S*,*R*). The study has offered the occasion to compare experimental and computed spectra according to a new similarity index, which can encompass the experience acquired in recent years on the limitations of quantum-chemical calculations (4).

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# Can we speak of "ancillary ligands" also in heterogeneous catalysis? Selected examples in olefin polymerization catalysts

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The role of the ancillary ligands is well known in homogeneous catalysis. Small variations in the composition, geometry and flexibility of the ligands could lead to important changes on the active site functionality, on the catalytic performances and on the selectivity. Paradigmatic examples can be found in the field of olefin polymerization catalysis. For example, homogeneous nickel catalysts can give almost exclusively ethylene oligomers (e.g. Keim's Ni ylides), but also tailored polyolefins (e.g. Brookart's Ni-diimine and Grubbs' Ni-iminophenolate), depending on the type of the ancillary ligand. Similarly, the molecular architecture of single-site metallocene–based catalysts can be tuned to produce selectively isotactic, syndiotactic, hemiisotactic or stereoblock polypropylenes.

Much less explored, if not often neglected, is the role of the ancillary ligands in heterogeneous catalysis. In this contribution, we will show that also for heterogeneous ethylene polymerization catalysts it is possible to speak about "ancillary ligands", and that they take an important part in the definition of the properties of the active sites, in many cases displaying a flexible and dynamic behavior very much similar to that found in homogeneous catalysts. The selected examples will cover the two main categories of industrially employed heterogeneous catalysts for olefin polymerization, i.e. the $MgCl_2/TiCl_4$ Ziegler-Natta catalysts and the Cr-based Phillips catalysts, investigated by means of advanced spectroscopic methods. Depending on the system, the "ancillary ligands" can be added as external components (e.g. the so-called electron donors in Ziegler-Natta catalysis), can be formed "in situ" in the presence of the monomer (e.g. oxygenated by-products during the reduction of the Phillips catalyst), or can be even present as a part of the support (e.g. the siloxane bridges at the surface of the Phillips catalyst). In all the cases, they contribute in creating the three-dimensional (nano-sized) environment around the active sites, acting in a concerted way during the ethylene polymerization.

# Synthesis and post preparative shape control of Cesium Lead Bromide colloidal nanocrystals

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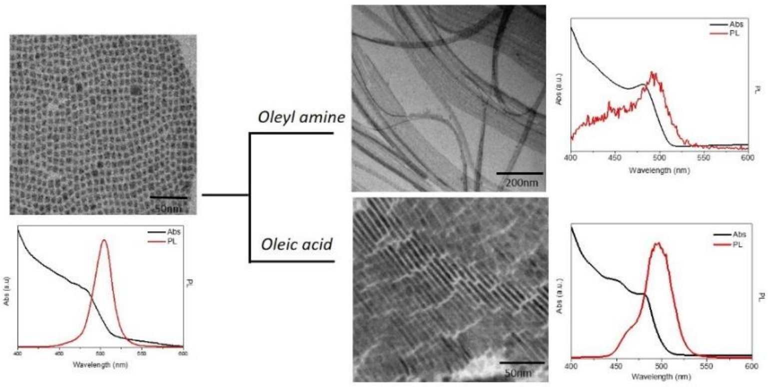
All-inorganic lead halide perovskite materials have attracted significant attention in the context of photovoltaic and other optoelectronic applications, and recently, efforts have been devoted to the fabrication of colloidally stable versions of these materials.(1) Cesium Lead Bromide ($CsPbBr_3$) colloidal nanocrystals (NCs), in particular, exhibits bright, size and shape-tunable photoluminescence in the blue-green region of the visible spectrum, that is usually not easily accessible with conventional quantum dots. While compositional band gap engineering and size tunability of the band-gap energies have been investigated by anion exchange, the role of the ligands in post-synthetic treatments at room temperature is still a critical issue towards the application of this class of material for devices fabrication. It is worth to note that surfactants assist the shape and size regulation during the synthetic step, provide the better stability and help to maintain the optical properties of the final colloidal forms. The ionic nature of the $CsPbBr_3$ NCs and labile interaction of the ligands with the colloidal NC surface suggest a crucial role of surface chemistry on the as prepared NCs. In this regard, this work investigates the shape regulation of the $CsPbBr_3$ NCs played by the ligand composition in a post synthetic treatments based on simply addition of freshly oleylamine and oleic acid to the as prepared NCs. Optical, morphological and structural characterization have been performed in order to depict the ligand role in the colloidal stabilization. This analysis will provide an insight in the surface chemistry and solution processability of this new and widespread investigated class of material, which will be also useful to predict its behavior for future applications in multicomponent complex systems for device fabrication.



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# Non conventional based Ce: YAG nanocomposites

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The interesting technological applications of Yttrium Aluminum Garnet (YAG, Y3Al5O12), whose cubic structure is in the space group Ia-3d, doped with lanthanides ions, in inorganic electroluminescence displays, X-ray scintillators, lasers, and white light LED are nowadays well consolidated. Notwithstanding, the interest of researchers is still growing because the optical properties of nanocrystals are expected to be dependent on the properties of doping agent and on the synthesis route that may influence particle size and its distribution and morphology.

The aim of this work is to prepare Ce:YAG nanoparticles with well-defined morphology, reduced sizes and hindered aggregation, simplifying at the same time the reaction conditions in order to scale up the synthesis. Innovative methodologies of preparation such us Urea glass Route, synthesis in microemulsion and solvothermal method in autoclave have been used.

Some nonconventional nanocomposites have been obtained combining the better nanoparticles with polymetylmetacrylate (PMMA), filter paper, cotton wool and glass wool.

Structure, morphology and optical properties have been thus investigated.

Figure. (From left to right) Nanoparticles dispersed in a solvent, Ce:YAG composites in glass wool, filter paper and cotton wool.

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# Synthesis and characterization of immunologically relevant calcium and magnesium phosphate amorphous nanostructures and strategies for their stabilisation

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Some recent investigations showed that calcium and phosphate ions are secreted from the distal small intestine of humans and other mammals into the lumen, leading to the formation of amorphous magnesium-substituted calcium phosphate nanostructures, which are able to trap macromolecules in the lumen (such as bacterial peptidoglycans) and transport them to immune cells of the intestinal tissue. (1) This sampling process of luminal content is recognized to be a form of local immunosensing and surveillance (2) and it is now confirmed that at least part of this process is mediated by this endogenous amorphous nanomineral. (1) The stability of amorphous magnesium and calcium phosphate (AMCP) towards its crystallization is dramatically affected by the pH and by the composition of the solution in which it forms or it is dispersed in. (3)

In this study, we focused on the preparation and the characterization of AMCP particles, readapting a protocol from the literature. (4) We systematically investigated the parameters affecting AMCP stability against crystallization to brushite. We explored the effect of pH, ionic strength, $Mg^{2+}$ concentration and the presence of small organic molecules commonly found in the gut lumen. The presence of amorphous and/or crystalline phases was assessed by means of infrared spectroscopy and X-ray powder diffraction. The amount of adsorbed organic molecules was evaluated by thermogravimetry, while scanning electron microscopy was used to investigate the morphology of the nanostructures.

We identified a synthetic protocol producing amorphous nanostructures with improved stability against crystallization, *i.e.* stable for several days. We investigated the structural evolution of these particles once freeze-dried and redispersed in buffer solutions, finding that the spontaneous transition of AMCP into brushite (which normally takes place within few minutes) can be slowed down with the addition of organic additives. These protective strategies against crystallization are relevant to tailor a drug or food additive formulation containing AMCP, for the improvement of the immune system functionality. To this aim, the study of the interactions of AMCP with the gut microbiota is currently ongoing.

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# Physico-chemical characterization of smart lipid biointerfaces for the detection of a tumor biomarker

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Supported lipid membranes represent an elegant way to design smart fluid biointerfaces able to mimic the physico-chemical properties of biological membranes. Furthermore, being accessible to a wide variety of surface-specific physico-chemical and analytical techniques, they provide smart biointerfaces to be optimized for specific biotechnological applications (1), such as the design of chemical and biomedical sensors. In this contribution, we describe a new lipid-based sensor for the detection of the thymidine phosphorylase (TP) enzyme, one of the most known biological markers of solid tumors. This enzyme promotes tumor growth and metastasis and is overexpressed in the presence of cancers, so that also its blood levels increase (2). To achieve this goal, a TP target analyte, i.e. the pyrimidine analogue 5-fluorouracil (5-FU) (3) has been properly functionalized with a chain consisting of six (derivative **1**) or seven (derivative **2**) units of glycol, linked to an alkyl moiety of 12 carbon atoms, in order to be inserted into gold supported lipid membranes. The TP affinity towards derivatives (**1**) and (**2**) has been firstly evaluated in solution by fluorescence measurements, then the derivatives have been inserted into a lipid bilayer linked to a gold surface. The supported lipid biointerfaces have been characterized by ellipsometry, AFM and electrochemical techniques (4). The TP interaction with the substrate has been quantitatively evaluated by quartz crystal microbalance, following the oscillation frequency of the QCM crystal, making this system a very promising sensor for the detection of TP concentration in blood.

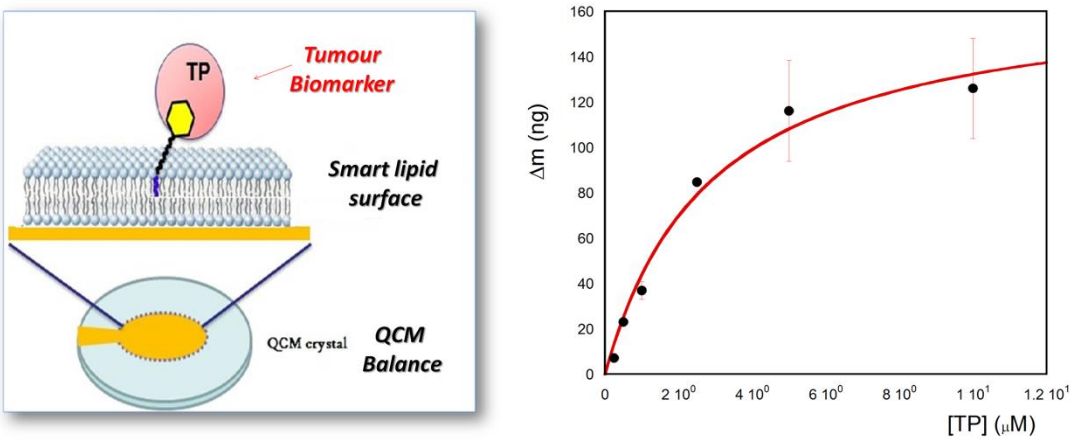

**Figure.** Left: scheme of the gravimetric sensor. Right: gravimetric quantification of the TP in buffer solution with the designed lipid surface.

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# Luminescent $ZrO_2$:$Ln^{3+}$@$SiO_2$ Nanosystems conjugated with Rose Bengal as Efficient Nanoplatform for Theranostic Applications

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Nanocarriers as theranostic agents are of great interest in modern nanomedicine, and several kinds of nanomaterials with interesting chemical and physical properties have been developed and tested, showing encouraging results *in vitro* and *in vivo* (1-3). Zirconium oxide, or zirconia ($ZrO_2$) is a metal oxide which is extensively used, in the bulk form, in many different application fields, such as thermal barrier coatings, dental and bone prostheses, gas sensors, optical devices and catalysts (4,5). Conversely, it is a relatively new material for theranostic applications, with many promising features: it is biocompatible, chemically inert, with good mechanical and thermal properties (4). The doping of $ZrO_2$ matrix with Vis and/or NIR luminescent rare earth ions allow the preparation of intrinsically luminescent nanosystems which can be further functionalized for the introduction of therapeutic and targeting moieties. In this contribution, the preparation and characterization of silica coated $ZrO_2$ nanoparticles doped with Vis and NIR luminescent rare earth ions (hereafter $ZrO_2$:RE, where RE= Er, Pr, Yb) are discussed. $ZrO_2$:RE samples were prepared via a hydrothermal process starting from a 1.0 M aqueous solution containing the stoichiometric ratio of $ZrOCl_2 \cdot 8H_2O$ and the RE precursor ($Er(NO_3)_3 \cdot 5H_2O$; $Pr(NO_3)_3 \cdot 6H_2O$; $Yb(NO_3)_3 \cdot 5H_2O$). For each RE dopant, samples of different concentrations, namely 0.5%, 1% and 5% molar, were prepared. Structural and morphological properties were investigated by X-ray powder diffraction, Dynamic Light Scattering and electron microscopies. Absorption and emission UV-Vis-NIR electronic spectroscopies were used to select the best samples in term of photoluminescence performances. A direct correlation between the dopant concentration, $ZrO_2$ crystalline phase and photoluminescence performances was evidenced, thus allowing the selection of the lowest dopant concentration samples as the best candidates as bioimaging probes. Both non-porous and mesoporous amino-functionalized silica shell was deposed on the selected samples, thus creating anchoring groups for the covalent immobilization of Rose Bengal, a well know photosensitizer for photodynamic therapy. Photodynamic activity was assessed by evaluating $^1O_2$ generation efficiency by a chemical method, evidencing that the photosensitizer maintains its activity upon immobilization on the silica shell. NIR luminescent $ZrO_2$:RE nanosystems are particularly interesting because they can be potentially used in up-conversion modality, with the possibility of using NIR light to trigger, by up-conversion, the photodynamic activity of visible-absorbing photosensitizers.

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# Phenomenology of the Neutral-Ionic Valence Instability in Mixed Stack Charge Transfer Crystals

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Organic charge-transfer (CT) crystals constitute an important class of functional materials, characterized by the directional CT interaction between π-electron Donor (D) and Acceptor (A) molecules, with the formation of one-dimensional ...DADAD… mixed stacks (*ms*). Among the many different and often unique phenomena displayed by this class of crystals, Neutral-Ionic phase transition (NIT) occupies a special place, as it implies a *collective* electron transfer along the stack, involving charge, spin and phonon degree of freedom. NIT can be induced by pressure (1), temperature (2), or even light (3). We present an updated and extensive summary of the phenomenology of the few temperature induced NIT, with emphasis on the spectroscopic signatures of the transition.

NIT are characterized by a valence instability (variation of the degree of CT ρ, with the Neutral-Ionic borderline at ρ ~ 0.5), driven by the 3D Madelung energy, and by a Peierls instability (stack dimerization δ), driven by the 1D electron-lattice phonon interaction. The competition between these two instabilities, respectively first- and second-order, is what makes NIT such a complex and intriguing phenomenon. In the first part of the talk we shall show how properly interpreted single crystals infrared and Raman spectra can provide detailed and reliable information on the evolution of both valence and dimerization instability, inclusive of the detection of the low-frequency soft mode accompanying the Peierls instability (4).

In the second part of the talk we shall present a comprehensive phase space exploration of *ms* CT crystals (Figure 1), showing that the Neutral-Ionic borderline may be crossed at ambient conditions by chemical substitution. This kind of studies have been prompted by the possible exploitation of *ms* CT crystals as ambipolar semicondutors, or as ferroelectrics. We shall also show how a general understanding of the phase diagram can be gained through a modified Hubbard model properly parametrized through simple first principle calculations (5). However, the understanding of the detailed mechanism of NIT and the explanation for the rarity of its occurrence requires consideration of the weak inter-molecular forces determining the packing of the stacks inside the crystals.

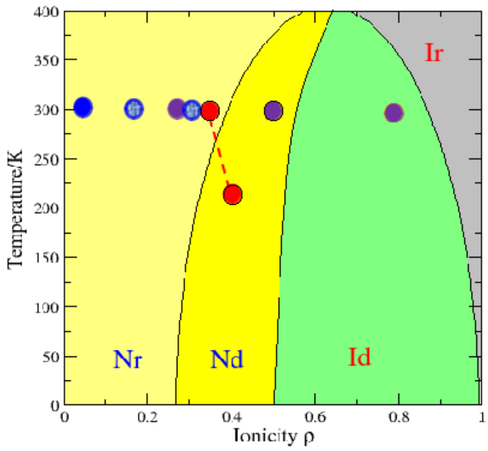

*Figure 1: Empirical ρ vs. T phase diagram of ms CT crystals*

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# The effect of temperature in the formic acid - formate system on $TiO_2$ (101) surfaces

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The interaction between simple organic molecules and $TiO_2$ nanoparticles has received much attention because of its relevance for applications in innovative technologies (1). Among the organic adsorbates, formic acid HCOOH has been the subject of many studies as it represents the smallest organic acid and because of the anchoring capacities of the carboxylic group. Moreover, the interest of HCOOH on top of $TiO_2$ has gathered momentum because of recent reports on solvent-free amide bond formation obtained by dosing gas phase amines on top of {101} anatase surfaces previously treated with HCOOH (2). In spite of its relevance, the actual HCOOH state on {101} anatase facets is yet poorly understood. First-principles modelling investigations on HCOOH@$TiO_2${101} predict, on clean surfaces, a molecularly monodentate adsorption geometry (3). On the other hand, IR studies clearly indicate that HCOOH dissociates on anatase forming a monodentate formiate on not defective {101} facets and a minority of bidendate species associated to defective sites. Moreover, the fate of the proton derived from formic acid deprotonation is unclear as well, indeed after $HCOO^-$ adsorption in IRRAS spectroscopic experiments, no surface OH stretching signal was detected (4). Thus, the picture emerging from modeling seems to be different from that indicated by experiments.

Here we show that the two pictures are only in apparent contradiction and that the keyword capable of settling the question is Temperature. Indeed, the above mentioned modeling studies are mainly energy minimization, resulting in 0 K structures. When considered IR experiments one needs to account for at the least 300 K. In our modeling approach, the HCOOH adsorption problem is considered with both regimes, namely geometry optimizations (0 K) and finite temperature (300 K) molecular dynamics simulations, carried out within the same first-principles theoretical framework focusing on a regular clean and not defective {101} anatase slab model. Four different structures were found carboxyl proton is actually shared between the formate and the surface moieties.

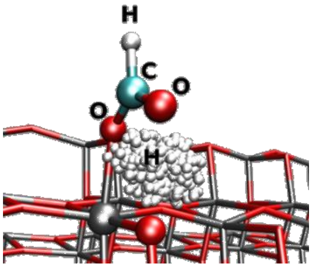

Figure 1. Schematic drawing of the sharing of the carboxyl proton between HCOOH and

For the adsorption of HCOOH on our slab model: two molecularly adsorbed and two dissociated. The two molecularly adsorbed structures, nearly degenerate, were the most stable ones. On the other hand, the finite temperature simulations, performed with either DCOOD or HCOOH, revealed that the acid proton shuttles between a $TiO_2$ surface oxygen and the carboxylic oxygen (Figure 1). The fast interconversion (at the femtosecond-scale) between the dissociated and the non-dissociated formic acid moiety was found to have consequences on the IR signal as well. The fingerprint of the spectroscopic behavior of the system was obtained by linear response approaches using appropriate autocorrelation functions, resulting in the absence of a well-defined and localized signal due to the O-H stretchings involving carboxyl proton shared between the formate and the surface moieties.

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# Interaction of phosphate-based additives with MgO/SiO2 cements

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In the last decade, research efforts on the investigation of MgO/$SiO_2$ cements have significantly grown because they are one of the most promising materials for the encapsulation of radioactive waste (1-4). In the presence of water, MgO/$SiO_2$ mixtures hydrate and form a binder phase, M-S-H (magnesium silicate hydrate), a colloidal gel analogue to calcium silicate hydrate (C-S-H), present in traditional cements. Even if research interest in MgO-based cement is growing, only one additive (sodium hexametaphosphate, HMP) has been used so far with this kind of cement, while in CaO-based cement many additives are commonly used to modulate the performances to specific applications. In fact, it has been recently reported that HMP in MgO-based cements increases the fluidity of the pastes, which is essential for practical applications, but its action mechanism is still unknown (5-7). In this study, we investigated the mechanism of interaction of different phosphate-based salts (i.e. sodium orthophosphate (OP), sodium trimetaphosphate (TMP), and HMP) with MgO-based cements, in order to understand the changes induced by the phosphate presence on the hydration reaction and on the M-S-H structure. The effect of the investigated additives on M-S-H has been studied by comparing data obtained in samples with and without additives with a multi-technique approach. In particular, the kinetics of hydration of the studied pastes was monitored by means of differential scanning calorimetry, while the hydrated phases formed during the reaction were characterized by thermogravimetric analysis, infrared spectroscopy, X-ray diffraction and solid state NMR. The morphology and topography of the pastes were studied by scanning electron microscopy and atomic force microscopy. Moreover, we performed a characterization of the mechanical properties by statistical nanoindentation and Vickers micro-indentation. The results evidenced that phosphate salts influence the hydration reaction, which is more efficient especially in the presence of OP, which enhances M-S-H precipitation even more than the currently used HMP.

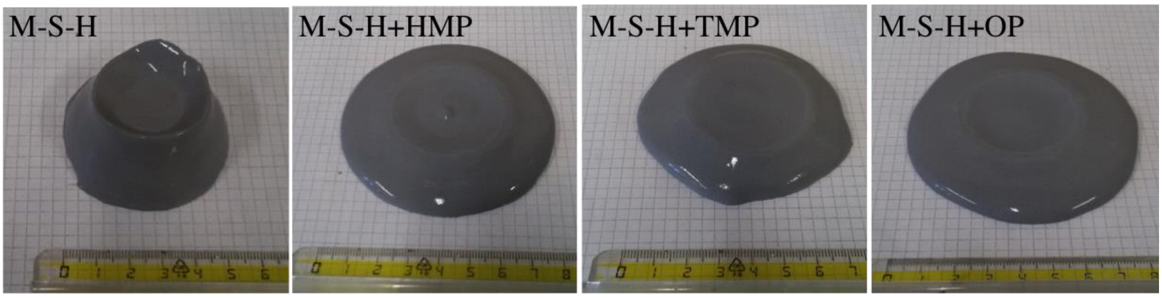

Figure 1. Mini-slump test results.

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# Composition and architecture engineering of colloidal $TiO_2$ nanocrystals for the enhancement of sunlight conversion ability

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Nanometric titanium dioxide ($TiO_2$) has an acknowledged important role as an environmentally friendly and clean photocatalyst, due to its unique properties, such as the strategic position of the band edges on the electrochemical potential scale, energy band structure, high chemical and thermal stability, to name but a few (1).

However, there are still some disadvantages in using $TiO_2$ nanocrystals (NCs) for solar light conversion that limit their practical applications. The most crucial one arises from the intrinsic wide energy gaps of $TiO_2$ phases (3.2 eV for anatase, 3.0 eV for rutile), confining the material photoactivity to the sole ultraviolet region of the solar spectrum (2).

The extension of $TiO_2$ NCs photoactivity in a wider spectral range has been investigated over the last decade in many ways. Among them, colloidal chemistry offers a plethora of tools for engineering the properties and performance of nanomaterials. We explored two strategies for this purpose, taking advantage of the versatility and the potentiality of colloidal methods.

Firstly, we developed a synthetic strategy based on an alcoholytic route (3) to synthesize pure anatase, highly crystalline $TiO_2$ NCs, with average size of 9 nm and narrow size distribution.

In the first approach proposed to enhance the sensitivity towards solar light, we fine-tuned the synthetic protocol to rationally manipulate the NC chemical composition (doping). We achieved the incorporation of iron in place of titanium ions up to 20%, retaining size, shape, and crystalline phase of the pristine NCs, demonstrating that it induces enhanced visible light absorption, but simultaneously also worsens the overall material performances.

In a second approach, we sensitized $TiO_2$ NCs towards visible light by the epitaxial seeded-growth of small lead sulfide nanoparticles (PbS NPs) onto the surface of previously prepared $TiO_2$ NCs. These PbS/$TiO_2$ heterostructures indeed show higher absorption both in the visible and near-infrared ranges, thanks to the peculiar size-dependent optical properties of PbS domains (4).

We present structural, morphologic, and spectroscopic investigations supporting the light-harvesting enhancement, but also evidencing opposite outcomes in the two model systems as for the overall performances in visible light conversion ability.

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# Coupling of nonlinear chemical reactions with pH-responsive polymers

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Chemical reactions with nonlinear kinetics can give rise to a remarkable set of spatiotemporal phenomena like periodic oscillations, traveling waves and stationary patterns. Despite initial skepticism, much progress has been made in the past three decades in characterizing, designing and modeling these phenomena (1). Nowadays, the main goal is to drag nonlinear reactions out of a purely theoretical context and start exploring the potential applications from catalysis to drug delivery systems and others yet to be imagined. One way to achieve this purpose is to develop biocompatible batch oscillators that oscillate for an extended period in a closed system without a continuous flow of fresh reactants. Among all the families of oscillators, the pH-based ones offer the greatest promise for practical applications because of the ubiquity of hydrogen ion in biological and chemical processes (2). In an attempt to design a biocompatible batch pH oscillator, a couple of years ago, our research group recovered the well-known urea-urease reaction (3,4,5). This reaction, that involves the hydrolysis of urea in ammonia and carbon dioxide, occurs in numerous cellular systems and is used, for example, by bacteria H. pylori in order to raise the local pH (6). By taking advantage of the bell-shaped reaction rate as a function of the pH, this reaction can show autocatalysis with a sharp increase in the pH. In order to obtain pH oscillations, the autocatalytic reaction must be properly combined with a negative feedback (e.g. transport of protons) that restores the initial conditions. The strategy we used to achieve this condition was the encapsulation of the enzyme in 1-palmitoyl-2-oleoylphosphatidylcholine (POPC) lipid membranes, where the differential diffusion of the inhibitor (proton or weak acid) and the activator (urea) were ensured by the different permeability of the membrane to the two species (5). Our results showed that the lipid vesicles are permeable to the species involved in the enzymatic reaction: urea, ammonia, and acids; moreover, by varying the initial concentrations we found several experimental conditions yielding the autocatalysis, however oscillations have not been observed yet. The next step in order to develop a pH oscillator is to couple the urea-urease reaction with pH-sensitive polymers that show swelling-deswelling behavior according to the pH of the solution. pH-sensitive polymers can be obtained through the synthesis of A(BC)n block polymers with linear (n=1) and branched (n=2) architectures where A is the hydrophilic block made of monomethoxypoly(ethylene glycol) (mPEG), while BC is a copolymeric random chain formed by the hydrophobic methyl methacrylate (MMA) and the pH sensitive monomer 2-(Dimethylamino)ethyl methacrylate (DMAEMA) (7,8). The polymers will be used in the form of gels or polymersomes.

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# Green synthesis of gold nanoparticles using Punica Granatum Juice for cosmetic applications

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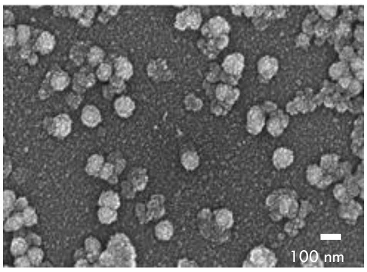

**Figure 1:** SEM image of AuNPs

The green synthesis of gold Nanoparticles (AuNPs) using *Punica Granatum* Juice (PGJ) was the aim of the present work. $HAuCl_4$ and PGJ, without further purification, were used to induce the formation of AuNPs in water medium. (1) Organic solvents or auxiliary capping agents were avoided enabling the environmental friendly synthesis of AuNPs. More specifically, by using appropriate amounts of PGJ and mild conditions of work, interesting results were obtained. Spherical AuNPs with a mean size of 130 ± 20 nm were observed through SEM images (Figure 1) and carefully characterized using several complementary techniques, i.e. UV-Vis spectroscopy, XPS analyses, DLS and Zeta Potential investigations. Changing in pH values, volume of solutions and temperature values were adopted for affecting the formation and the features of AuNPs. Interesting applications could be suggested. A chitosan or like-structures shell around AuNPs, enriched with PGJ active agents, were proposed to modulate their release presenting a novel formulation with antioxidant, skin lightening and anti-aging properties, especially inhibiting UV-induced pigmentation (see Figure 2). Additionally, the obtained AuNPs could be potentially used as agents to enhance the sun protection factor (SPF) of commercial sunscreens formulations as an alternative to traditionally used nanostructured $TiO_2$ and ZnO that suffer from side effects such as irritation, percutaneous absorption, photomutagenicity and immunoreaction.(2,3)

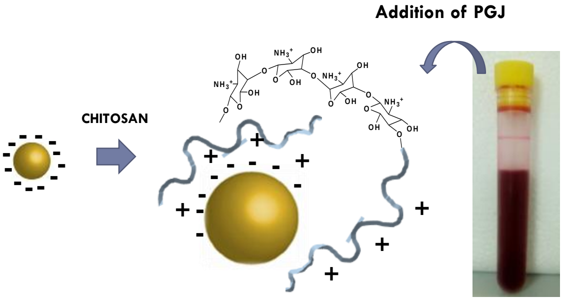

**Figure 2:** Illustration of AuNPs and chitosan enriched with PGJ

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# Adsorption of Amino Acids and Glutamic Acid-Based Surfactants on Imogolite Clays

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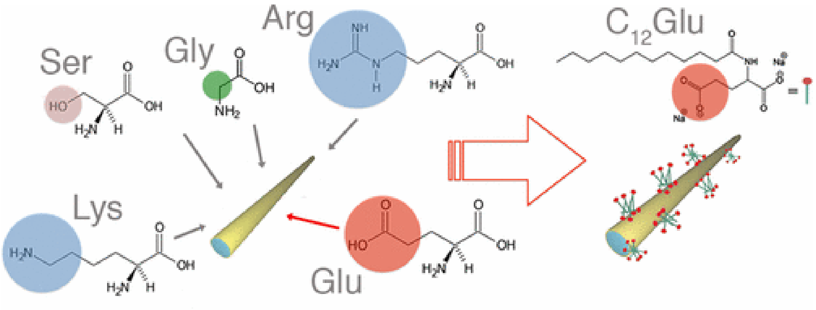
Aluminum oxide surfaces are of utmost interest in different biotech applications, in particular for their use as adjuvants (i.e., booster of the immune response against infectious agents in vaccines production). (1) In this framework, imogolite clays combine the chemical flexibility of an exposed alumina surface with 1D nanostructure. (2) This work reports on the interaction between amino acids and imogolite, using turbidimetry, ζ-potential measurements, and Fourier transform infrared spectroscopy as main characterization tools. (3) Amino acids with different side chain functional groups were investigated, showing that glutamic acid (Glu) has the strongest affinity for the imogolite surface. This was exploited to prepare a composite material made of a synthetic surfactant bearing a Glu polar head and a hydrophobic $C_{12}$ alkyl tail, adsorbed onto the surface of imogolite. The adsorption of a model drug (rhodamine B isothiocyanate) by the hybrid was evaluated both in water and in physiological saline conditions. The findings of this paper suggest that the combination between the glutamate headgroup and imogolite represents a promising platform for the fabrication of hybrid nanostructures with tailored functionalities.



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# Organic-inorganic hybrid materials as heterogenous catalysts for pharma industry

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Developing efficient heterogeneous catalysts for pharmaceutical industrial processes in the C-C coupling reactions is a current major challenge for material scientists, organic chemists, industrial engineers and other researchers. Recently, multifunctional organic-inorganic hybrid materials have become an attractive alternative class of catalysts, for applications in cascade, asymmetric, multi-step reactions. The idea of designing hybrid materials is originated by the observation of the success of nature developing enzymes in living organisms. Indeed, selectivity is a crucial factor for the survival of the species.

Organic-inorganic hybrid materials combine the advantages of inorganic solids (high mechanical, thermal, and structural stability) and organic molecules or macromolecules (flexibility and functionality) and offer a wide class of new heterogeneous catalysis maximizing the chemical efficiency. Beside the different synthetic strategies to produce hybrid catalysts, the covalent interactions among organic and inorganic units to synthesize class II hybrids allow to obtain more robust and stable functional solids. (1) Nevertheless, the family of Class II hybrid materials could suffer of low conversions and low selectivity because of a non-regular distribution of the different active centers.

In this context, also thanks to the recent evolutions in High Performance Computing (HPC) architectures, theoretical methods can be successfully applied to provide structural information and interface properties at an atomistic level to both guide and interpret experimental synthesis and measurements (2,3).

In this contribution, a preliminary study on the role of theoretical approaches to the synthesis and characterization of innovative porous organic-inorganic materials, with several active sites, will be reported. The joint use of experimental and computational techniques will be also highlighted to deeply understand the structure-properties relationship of the hybrid catalysts.

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# Coupling of sieving and thermogravimetric analyzes for studying the activation energy distribution function of complex reactions

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Kinetic parameters of the decomposition of hazardous chemicals can be used for the estimation of the advanced kinetic approach of the thermal behaviour also under adiabatic conditions occurring, e.g. in batch reactors in case of cooling failure. In the present study, a method for analyzing the kinetics of thermal degradation of complex compounds is suggested. Results of thermogravimetric analysis, under nitrogen atmosphere, of ground soft wheat and ground maize have been investigated (1). The thermogravimetric curves reveal two well-distinct jumps of mass loss: volatilization region and decomposition region. We assimilate the global degradation process as a solid state reaction whose kinetics are analyzed separately in each region. By means of a sieving analysis different size fractions of the material are separated and studied (2). A quasi-Newton fitting algorithm is used to obtain the grain size distribution as best fit to experimental data. The individual fractions are thermogravimetrically analyzed for deriving the functional relationship between activation energy of the degradation reactions and the particle size. Such functional relationship turns out to be crucial to evaluate the moments of the activation energy distribution, which is unknown, in terms of the distribution calculated by sieve analysis. From the knowledge of moments the reaction conversion is reconstructed. The comparison with the experimental data reveals that the method reproduces the experimental conversion with an accuracy of 5−10% in the volatilization region and of 3−5% in the decomposition region.

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# Dewetting of acrylic polymeric films induced by water/propylene carbonate/surfactant mixtures - Implications for cultural heritage conservation

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The removal of hydrophobic polymer films from surfaces is one of the top priorities of modern conservation science. Nanostructured fluids containing water, a good solvent for the polymer, either immiscible or partially miscible with water, and surfactants have been used in the last decade to achieve controlled removal.[1–6] The dewetting of the polymer film is often an essential step to achieve efficient removal;[7] however, the role of the surfactant throughout the process is yet to be fully understood. We report on the dewetting of a methacrylate/acrylate copolymer film induced by a ternary mixture of water, propylene carbonate (PC) and $C_{9\text{-}11}E_6$, a nonionic alcohol ethoxylate surfactant. The fluid microstructure was characterized through Small Angle X-Ray Scattering and the interaction between the film and water, water/PC and water/PC/$C_{9\text{-}11}E_6$ was monitored through confocal laser-scanning microscopy (CLSM) and analyzed both from a thermodynamic and a kinetic point of view. The surfactant presence is a prerequisite to induce dewetting of μm-thick films at room temperature, but it is not a thermodynamic driver. The amphiphile lowers the interfacial energy between the phases, favors the loss of adhesion of the polymer on glass, decreasing, in turn, the activation energy barrier, which can be overcome by the thermal fluctuations of polymer film stability, initiating the dewetting process.

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# Supramolecular Self-Assembly of Chlorophyll A and Mesoporous Silica Nanoparticles in Water Medium

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Novel photosensitizing system based on mesoporous silica nanoparticles and Chlorophyll *a* (Chl) as a photoactive agent for possible applications in antimicrobial photodynamic therapy (PDT) is presented in this work. The supramolecular system enhanced the solubility of Chl in water medium maintaining the monomeric form of the pigment, important feature for the photodynamic action of Chl. (1) Indeed, under these conditions, the pigment absorbed the visible light inducing the formation of reactive oxygen species (ROS). Silica nanoparticles with different pore sizes were used. Moreover, the functionalization of nanoparticles with amino groups was obtained. The supramolecular system was characterized by means of spectroscopic, diffraction techniques and microscopic imaging methods including time-resolved absorption spectroscopy. Chl showed a strong affinity toward functionalized nanoparticles with amino groups. Indeed, the ʒ potential value of nanoparticles occurred to decreased after the insertion of Chl, shielding the positive charge of particles. Nanosecond laser flash photolysis technique provides evidence for the population of the excited triplet state of Chl showing the important precursor of ROS. Among them, the photogeneration of singlet oxygen was demonstrated.

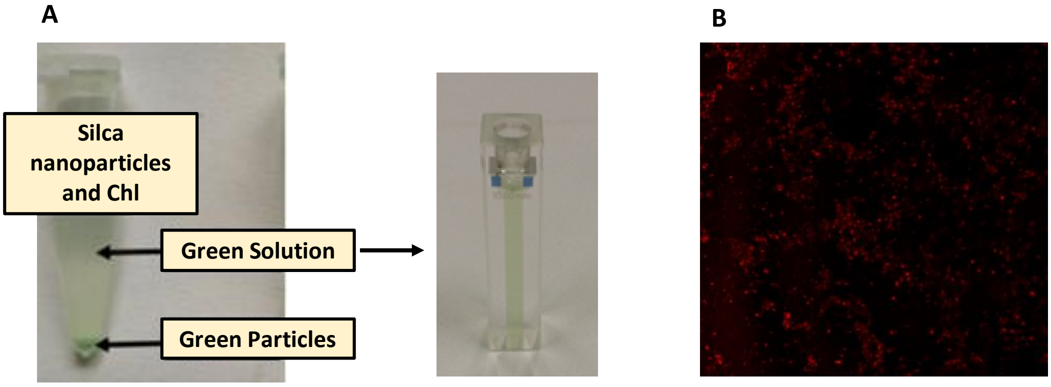

**Figure 1. (A)** Camera Pictures of Silica Nanoparticles in presence of Chl; **(B)** The fluorescence image of the supramolecular assembly: Chl and Nanoparticles

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# Silica-based composites for the consolidation of earthen materials

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Earthen materials are largely used in the architecture of many areas of the world, but the lack of well-established processing techniques and recipes make their conservation challenging. The object of this research is to develop a compatible and long-lasting consolidating treatment for adobe bricks, unbaked mixtures of soil and water, often added with organic matter and/or lime. We are experimenting the formulation and application of a silica-based system, where the combination with a cellulosic derivative and nano-lime aims at obtaining greater effectiveness and compatibility with the substrate.

Mesoporous silica nanoparticles were prepared following a synthesis (1) selected to obtain adequate particle size and porosity (250 nm uniform spheres with 300-600 $m^2/g$ BET surface area were observed with SEM, DLS and porosimetry). Various amounts of *Klucel*®-G (hydroxypropyl cellulose ethanol solution) and *NanorestorePlus*® ($Ca(OH)_2$ nanoparticles ethanol dispersion) were added to the silica aqueous dispersion and kept under stirring to maximize the interaction. Components proportions were chosen according to common restoration applications and in order to minimize the aqueous content. The systems obtained were characterized by DLS, Z Potential, turbidimetry, TGA, FT-IR and SEM-EDS.

Turbidimetric tests confirmed the expected stabilizing effect of hydroxypropyl cellulose on silica, while almost instantaneous flocculation occurs in $Ca(OH)_2$-silica systems, in accordance with surface charge measures. Interestingly, the ternary system maintains a significant stability over several days. FT-IR analyses pointed out an intensification of the stretching band at 965 $cm^{-1}$, characteristic of calcium silicate hydrate (2,3), in all the systems containing silica and $Ca(OH)_2$ nanoparticles. The hypothesis of the formation of a cementing phase is supported by SEM observations of similar structures. Further analyses are underway. Following these first results, one of the ternary formulations was selected for preliminary application tests on adobe samples from Mexico.

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# Langmuir-Blodgett and MD characterization of peptides at the air/water interface

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Molecular monolayers at the air-water interface and on both hard and soft surfaces are deeply studied and well characterized topics. However, a detailed characterization of the behavior of peptides at the air-water interface, in terms of the influence of the peptide concentration on its conformations and on the final film structure is a less examined matter, even if the formation of peptide monolayers is a common established experimental procedure.

In this regard, we studied two different peptides at the air-water interface, namely Trichogin GA IV and Z-(Aib)$_9$-O*t*Bu. The primary structure of Trichogin GA IV is *n*-Oct-Aib-Gly-Leu-Aib-Gly-Gly-Leu-Aib-Gly-Ile-Lol, where Aib is α-aminoisobutyric acid, *n*-Oct is *n*-octanoyl and Lol is leucinol, while, in the homopeptide Z-(Aib)$_9$-O*t*Bu, Z is a benzyloxycarbonyl group, and O*t*Bu is a *tert*-butoxy group. The two peptides differ in hydrophobicity and in the main conformation adopted in solution; Trichogin, indeed, is amphiphilic and can adopt a mixed $3_{10}$/α-helical conformation (1), whilst, the homopeptide Z-(Aib)$_9$-O*t*Bu is hydrophobic and tends to prefer right- or left-helical conformations (2).

To study the molecular arrangement at the interface, in terms of conformation and aggregation propensity, we used both experimental and theoretical approaches. The compression isotherms obtained with the Langmuir-Blodgett technique have been used for obtaining data regarding changes in the aggregated structures as a function of peptide concentration. To reproduce the formation of the monomolecular films of these peptides, we ran several molecular dynamic (MD) simulations, at different peptide concentrations, in order to investigate the influence of the aggregation on the peptide conformational behaviour and film formation.

All these results made us able to characterize the process leading to the formation of the monomolecular films of these peptides and their 3D-structures, also highlighting the conformational changes induced by the increasing concentration and molecular interactions under aggregative conditions.

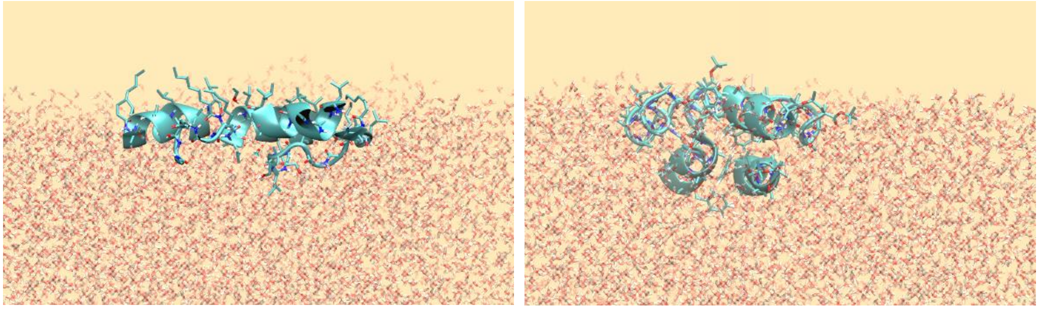

*Figure 1.* Aggregates of six peptides for Trichogin GA IV (*left*) and Z-(Aib)$_9$-OtBu (*right*)

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# Detection and Quantification of Anticancer Drugs with Surface Enhanced Raman Spectroscopy

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Ultrasensitive detection of low-quantity drugs is important for personalized therapeutic approaches in several diseases and, in particular, for cancer treatment. In this field, surface-enhanced Raman scattering (SERS) can be very useful for its ability to precisely identify analytes from their unique vibrational spectra, with very high sensitivity.

Nevertheless, choice of plasmonic substrates for such complex biological samples plays a critical role on the application of this techniques. Zanchi at al. reported a roughened gold surface for the detection of Apomorphine.(1) Calibration curves were also presented for aqueous solutions and the detection was also proved using human blood plasma. Due to the vibrational nature or Raman spectroscopy, signals obtained by complex samples could be usually not trivial to interpret. So, multivariate analysis could often help, as reported by Fornasaro at al. that used Partial Least Square Regression (PLSR) to build calibration curves for Methotrexate in simulated and in real plasma samples. (2)

A further look insight the optical properties of analytes, SERS substrates and the acquisition wavelength could be useful to better understand the relative efficiencies of some setups over others. Our group recently reported a study on five different clinically relevant anticancer drugs over detection and quantification with SERS. (3) The species were Doxorubicin, Paclitaxel, Sunitinib, Irinotecan and it's active metabolite, SN-38. As plasmonic substrate we used Klarite, a commercially available SERS active surface. Our results clearly showed that the quality of the signal arising from these molecules are closely related to their extinction characteristics, taking fixed the substrate and the excitation wavelength. Of course, this also reflect on the quality of calibration curves, that were done for Sunitinib, Irinotecan and SN-38 at detection limits of 20–70 ng, which is below the threshold for applications in cancer therapy. Principal Component Analysis was also used to discriminate between pure spectra of Irinotecan and SN-38 and a mixture of these two, that was not trivial to obtain without multivariate approach due to the similarity of these molecules.

We also present our newest results on a different approach for quantification using SERS. That is using colloidal solution instead of surfaces and, most important, a covalent, specific recognition of the analyte Erlotinib with our functionalized gold nanoparticles. Our method was found able to quantify the drug up to 20 ng/mL into 150 µL of sample. Calibration curves were obtained in hydro-alcoholic solution, using a competition strategy to overcome the low signals of Erlotinib. Firsts results on simulated plasma samples could open interesting perspectives on this method as a point-of-care tool.

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# Effective remediation of highly polluted water by petroleum hydrocarbons with functionalized cellulose fiber

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One of the major environmental problem that needs to be resolved today is the remediation of water bodies such as seabed, lakes and aquifers polluted by hydrophobic organic compounds (HOCs) including BTEX, PCBs, PAHs and some pesticides due to their high toxicity, mutagenicity and carcinogenicity (1). This work gives a first example of remediation, at laboratory level, of water polluted by petroleum hydrocarbons by means of surface functionalized cellulose fiber, extracted from Spanish Broom. In order to transform the hydrophilic character of cellulose surface into the hydrophobic one, therefore to improve its affinity for hydrocarbons, the surface was functionalized with two different methods: in one case, cellulose was allowed to react with 4,4'-methylenebis(phenyl isocyanate) (4,4' MDI) in a home-made reactor. In the other case, the low pressure plasma technique was used to superficially graft with fluorinated groups. The functionalized cellulose was chemically characterized by FT-IR, SEM, XPS and WCA. Batch experiments were performed in order to study the kinetics and thermodynamics of the adsorption process as a function of the initial Total Hydrocarbon concentration and the mass of adsorbent. The kinetics data show that the equilibrium adsorption capacity is reached within an hour, with removal efficiencies as high as 99%. The kinetics of the sorption process can be very well fitted by a pseudo second order model. Moreover, the thermodynamic of adsorption follows a Langmuir isotherm model from which maximum adsorption capacities larger than 200 mg/g can be fitted for the functionalized fiber. Finally, a method for regenerating the cellulose fiber for multiple reuse is discussed.

In conclusion, this work shows a remarkable effectiveness of functionalized cellulose fiber filters for water remediation from petroleum hydrocarbons pollution, since its adsorption capacity is one of the highest ever reported in the literature, showing much higher values than the natural substrates studied so far for such use (2).

Fig.1 **Spanish Broom**

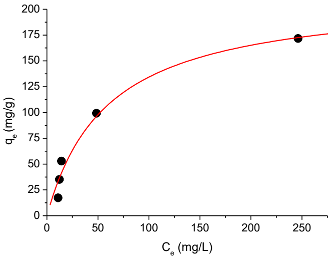

Fig.2 **Hydrocarbons adsorption isotherm at 20 °C for the functionalized fiber and fitting with the Langmuir model**

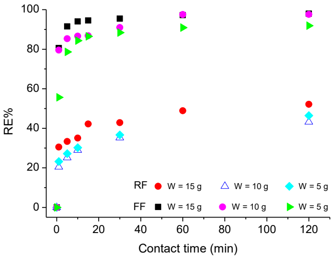

Fig.3 **Removal efficiency of SB Functionalized Fiber (FF) and Raw Fiber (RF) for total hydrocarbons from water**

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# A comparison between the Langmuir rate equation and the pseudo-first and pseudo-second order models for adsorption processes

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The objective of this study is to discuss the applicability of the Langmuir, pseudo-first order (PFO) and pseudo-second order (PSO) models in estimating the kinetic and thermodynamic adsorption parameters. The integrated Langmuir equation depends on five parameters with a direct physical significance, namely the initial solute concentration, the adsorbent dosage, the microscopic adsorption rate constant, the adsorption amount at the equilibrium and the maximum adsorption capacity of the adsorbent. The PFO and PSO models are of common use for describing adsorption kinetics, although both are derived empirically (1,2). An analysis of the factorized form of the differential Langmuir equation shows that the Langmuir kinetics regularly coincides with the PFO model with very low or very high input of solute per mass of adsorbent. By contrast, the PSO model approximates the Langmuir kinetics only when the adsorbent is near saturation and, at the same time, the input of solute per mass of adsorbent is close to the maximum adsorption capacity. The optimal initial solute concentration and adsorbent dosage are determined for approximating the Langmuir kinetics. A graphical method is proposed for assessing the PFO and PSO models as substitutes for the Langmuir equation and estimating the adsorption parameters.

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# Microstructured composite for Cr (VI) removal from polluted environment

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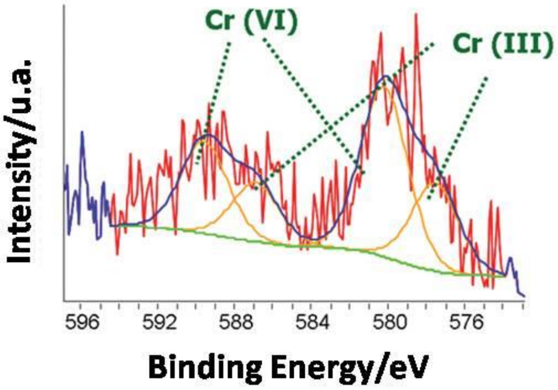
A microstructured composite able to remove hexavalent chromium Cr(VI) from aqueous solutions obtained by adding the silica precursor tetraethoxysilane (TEOS) to the hexadecyltrimethylammonium bromide (CTAB) microemulsion-based gel is here presented (1,2). SEM and NMR analysis showed that this material is made by an interconnected network of gelatin, silicate and surfactant molecules in which water molecules manifest a high mobility. Analyses of the elemental content in the CTAB-silica gelatin composite suggest that the adsorption of chromium takes also places in the internal areas. Remarkably, this composite containing the adsorbed hexavalent chromium left in water for 30 days undergoes a change in colour from yellow to green. This evidence is an indication of the reduction in situ of Cr(VI). X-ray Photoelectron Spectroscopy has been used to characterize the composite materials. Surface analyses performed at different times revealed chromium chemical speciation changes as a function of the pollutant-material interaction time (3). Moreover, the removal of chromate was assessed also through evaluation of the adsorption kinetics of chromate ions on the composite under equilibrium conditions in the presence of sulfate ions and at a slightly acidic pH condition (pH 5.8) (4,5). These findings demonstrated a high specificity of the CTAB–silica gelatin composite for chromium, and highlight the possibility of using this matrix for efficient removal and in situ conversion of chromium from industrial wastewater without the need to eliminate contaminant sulfate ions.



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# Olive mill wastewaters phenol photocatalytic degradation by visible light activated carbon doped titanium

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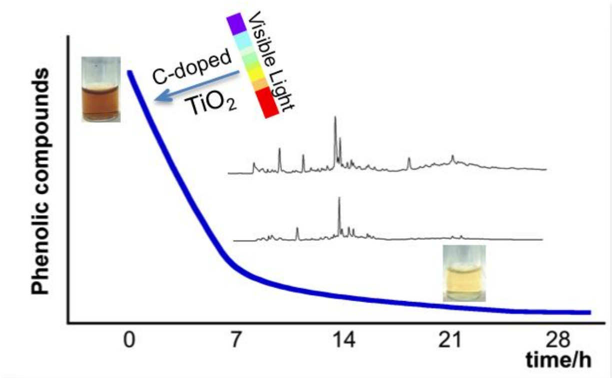
Carbon doped titanium dioxide (CDT) was tested as catalyst for photodegradation of phenolic compounds. Caffeic acid and olive mill wastewater (OMW) phenolic compounds were removed under visible light (1). The cleaning effectiveness of this catalyst towards the polluted wastewater from olive oil industry was demonstrated by means of HPLC and UV-visible spectroscopy combined with phenol compound determination. The photodegradation activity was tested on systems having different initial concentration of phenols and in the presence of different amounts of CDT (2). By introducing a suitable parameter, namely the ratio between the amount of catalyst and the amount of total phenols Ti/TPh, it was demonstrated that the proposed degradation method could be scaled up without losing its effectiveness (3). The OMW decolorization occurring in the presence of CDT particles under visible light radiation is marked enough to be directly appreciated with the naked eye. The decolorization is strongly associated with the removal of phenols. In fact, while bleaching the solutions, CDT successfully removed 70% of the phenols in 24 hours. HPLC analysis demonstrates that CDT was effective in degrading the higher part of the phenols of OMW.

It was found that the whole photodegradation process is governed by a synergic mechanism in which adsorption and photodegradation are involved.



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# Removal of an azo textile dye from wastewater using cyclodextrin-epichlorohydrin polymers

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Textile industries and clothing manufacturing release large amounts of dyes in effluents generating high amount of polluted wastewater (1). Indeed, dyes discharged in water are molecules stable to light irradiation, heat and oxidation agents which influence the photosynthetic activity of aquatic species inhibiting their growth (2). Moreover, azo dyes are toxic, carcinogenic and mutagenic both to some aquatic species and to human beings due to the reduction of the azo groups and the consequential formation of aromatic amines in the wastewater (3). Therefore, the removal of dyes from industrial effluents is a fundamental questions and appropriate treatments of wastewater should be done to decrease the environmental impact. Among all the processes developed for the removal of dyes from industrial effluents, adsorption is one of the most effective and cheap methods which industries employ to reduce hazardous pollutants present in the effluent. In this study, cyclodextrins-epichlorohydrin (CDs/EPI) polymers were used as adsorbent materials to remove a textile dye, Direct Blue 78 (DB78), from aqueous solutions. Since in a recent paper (4), we already demonstrated the ability of some commercial cyclodextrins to encapsulate, in their inner cavity, some azo direct dyes, in this work the adsorption process of DB78 on CDs/EPI polymers was performed and the effect of different variables, such as contact time, adsorbent dosage, initial dye concentration, pH of initial solution and temperature were considered and discussed. The equilibrium isotherms and the adsorption kinetics were analyzed using opportune mathematic models. Results of adsorption showed the good adsorption properties towards azo DB78 of β- and γ-CD EPI polymers. The dye removal efficiency was about 99% with β-CD/EPI polymer and about 98% with γ-CD/EPI polymer. This adsorption method allows indeed to obtain very clean water after 2 hours of treatment with polymers permitting the feasible reuse of water in further industrial processes. Moreover, the chemical-physical characteristics of adsorbent polymers were observed by means of different techniques (FTIR-ATR, DSC, TGA and FESEM). The proposed adsorption mechanism involved several kinds of interactions such as physical adsorption in the polymer network, hydrogen bonding and formation of inclusion complex due to the presence of CD molecules through host–guest interactions.

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# Arsenic Adsorption on Iron Oxides and its Environmental Impact

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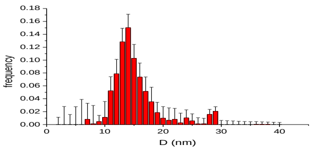
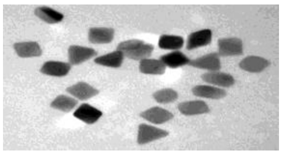
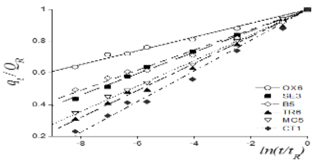
Arsenic occurs naturally in water in many parts of the world. Natural processes, including soil erosion, mineral leaching, and weathering, are responsible for introducing arsenic into surface water. Drinking water is derived from a variety of sources depending on local availability: surface water (rivers, lakes, reservoirs, and ponds), groundwater (aquifers), and rainwater. These sources are very variable in terms of arsenic risk, among which groundwater has high concentration of arsenic (1). Minerals such as iron oxyhydroxide and oxides phases probably play a key and complex role in controlling the mobility and fate of arsenic in groundwater (2). Crystal morphology and surface area often depend on synthesis conditions and several methods are available to enable a range of oxides with specific characteristics to be produced. In this study, laboratory batch experiments were carried out to study the adsorption of arsenic on two of major iron oxide minerals, namely, hematite $\alpha$-$Fe_2O_3$ and magnetite $Fe_3O_4$. To simulate the role played by inorganic and organic ions commonly found in soils in the alteration of crystal morphology of natural hematite, several experimental protocols were applied to synthetize $\alpha$-$Fe_2O_3$ through hydrothermal methods in the presence of Al, Mg, Si and oxalic, citric and tartaric acids. Previous investigations demonstrated that the adsorption efficiency of phosphate anions onto hematite nanocrystals could be affected by different crystal shapes induced in $\alpha$-$Fe_2O_3$ synthetized in the presence of the aforementioned chemical species, without modifying the structure (isomorphous substitution) (3). Therefore, we explored the adsorption properties of hematite prepared in different experimental conditions to verify their capacity in the immobilization of arsenate anion and investigate its environmental impact. A parallel investigation was carried out by using magnetite nanocrystals as adsorbent for arsenate. We proposed a slight modification of its preparative procedure based on the partial oxidation of a Fe(II) salt solution with $KNO_3$ under alkaline conditions at 80°C under inert atmosphere of $N_2$ (4). For both hematite and magnetite adsorbents, kinetic tests were carried out to characterize the mechanism of arsenate adsorption process, by evaluating also the effect of pH. Finally, X-ray diffractograms, FTIR absorption spectra, Atomic Force Microscopy and electron micrographs were included in the present study to link the iron oxide crystal morphology to the arsenate adsorption properties. Overall, these findings improve our knowledge in modeling arsenic adsorption to common soil minerals and provide elucidation of the role played by iron oxides in soil decontamination.







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# Electrophysiological measurements on a solid supported membrane to investigate the transport activity of sarcoplasmic reticulum $Ca^{2+}$-ATPase

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P-type ATPases are a large and varied family of membrane proteins that are involved in many transport processes in virtually all living organisms (1). These membrane proteins couple the energy provided by ATP hydrolysis to the active transport of various ions across biological membranes. Sarcoplasmic reticulum (SR) $Ca^{2+}$-ATPase promotes muscle relaxation by pumping $Ca^{2+}$ ions from the cytoplasm into the SR lumen. The activity of SR $Ca^{2+}$-ATPase is regulated by two small membrane proteins, phospholamban (PLN) and sarcolipin (SLN). PLN is primarily expressed in cardiac muscle, whereas SLN expression predominates in skeletal muscle. The molecular mechanisms of PLN and SLN regulation are not fully understood. Solid supported membranes (SSM) have been employed for the functional characterisation of P-type ATPases (2). The SSM, consisting of a hybrid alkanethiol/phospholipid bilayer supported by a gold electrode, is a convenient model system for a biological membrane. Proteoliposomes or native membranes (vesicles or fragments) incorporating the ATPase are adsorbed on the SSM surface and are subjected to a rapid substrate concentration jump. The substrate concentration jump activates the ATPase and the charge displacement concomitant with the transport activity of the enzyme is recorded as a current transient via capacitive coupling (3). Charge transfer in P-type ATPases was investigated by SSM-based electrophysiological measurements in order to gain insights into the ion transport mechanism. In the case of SR $Ca^{2+}$-ATPase, the SSM technique provided useful information for a detailed characterization of the enzyme's transport cycle, especially as concerns $Ca^{2+}$ binding mechanism, $Ca^{2+}/H^+$ exchange and competitive $Mg^{2+}$ binding (4,5). In a typical SSM experiment, SR vesicles containing the $Ca^{2+}$-ATPase are adsorbed on the SSM and exposed to a concentration jump of a suitable substrate, e.g., ATP. The ATP-induced current transient is related to an electrogenic event corresponding to the translocation and release of bound $Ca^{2+}$ upon phosphorylation by ATP within the first transport cycle (2,4). Recently, SSM-based current measurements were performed to investigate the effects of PLN and SLN on $Ca^{2+}$ translocation by SR $Ca^{2+}$-ATPase. We observed that PLN altered ATP-dependent $Ca^{2+}$ translocation within the first enzyme cycle, while SLN did not. These measurements indicate that PLN can establish an inhibitory interaction with multiple conformational states of the ATPase. The results are discussed in terms of the recently published crystal structures of SR $Ca^{2+}$-ATPase bound to PLN and SLN.

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# Protein-ligand interaction: a NMR study

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Proteins perform numerous tasks within living organisms, some act as structural support for cells and tissues, others are transporters of non-soluble molecules in water and others, such as lysozyme, are involved in defensive mechanisms against bacterial attacks. The growing ease of obtaining proteins in substantial quantities and purity, by means of increasingly sophisticated bio-engineering techniques (1), may lead to their use in pharmaceutical formulations as drug delivery mechanisms or in food as preservatives (2). However, given the chemical nature of these macromolecules, they are vulnerable to oxidative attacks that would lead to their denaturing resulting in loss of activity. Moreover, some of these, such as lysozyme, once denatured, can give rise to aggregation leading to the onset of amyloidogenic diseases such as Alzheimer's disease and transmissible spongiform encephalopathies. The proteins that cause these diseases have no common characteristics in their native state, but once converted into amyloid fibrils they have many analogies (3). The factors that induce the formation of aggregates remain obscure; a hypothesis is the malfunctioning of mechanisms that govern the folding of proteins and the elimination of erroneously folded ones, or even oxidative stress phenomena caused by a malfunction of superoxide dismutase mutation.

Therefore, it is vital to be able to prevent the oxidation of these enzymes in order to maintain their activity unaltered before they can be used on a large scale. The aim of this study is to investigate, through Nuclear Magnetic Resonance, the interaction between a protein with potential industrial applications (lysozyme), with a molecule with known antioxidant potential, the catechin, which has no compatibility issues with the human body being a substance naturally occurring in numerous foods of natural origin. Subsequently, in order to verify the protective effect of catechin on the protein, the effect of an oxidizing system on lysozyme was assessed both in the absence and the presence of catechin. Finally, in order to estimate the magnitude of such protection, a comparison with another known antioxidant system, the ascorbic acid (4), has been carried out.

The study begins with the chemico-physical characterization of the molecules employing advanced spectroscopic techniques such as $^{1}$H-$^{1}$H COSY, TOCSY, NOESY and $^{1}$H-$^{13}$C HSQC and HMBC bidimensional experiments as well DOSY. These experiments aim to evaluate the spatial structure and arrangement of isolated molecules, as well as evaluate their translational mobility. The study proceeds with the evaluation of the interaction based on the variation of the ligand self-diffusion coefficient, is continued by determining the binding constant by acquiring spectra at different concentration ratios and finally identifying the interaction site on the protein.

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# Immobilisation of neurotrophin peptides on gold nanoparticles by direct and lipid-mediated interaction: a new multipotential therapeutic nanoplatform for CNS disorders

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Neurotrophins are essential proteins for the developing and maintenance of neural functions as well as promising drugs in neurodegenerative disorders. Current limits in their effective clinical applications can be overwhelmed by the combined use of peptidomimetic and nanomedicine approaches. Indeed, neurotrophin-mimicking peptides may allow minimising the adverse side effects of the whole protein drug. Moreover, the immobilisation of such peptides on nanomaterials may offer additional advantages, including protection against degradation, enhanced permeability of barrier membranes and intrinsic therapeutic properties of the nanoparticles (e.g., anti-angiogenic and plasmonic features of gold nanoparticles, AuNPs). In the present paper we scrutinize the functionalisation of spherical AuNPs of 12 nm of diameter by peptides owing to the N-terminal domains of nerve growth factor and brain derived neurotrophic factor, NGF1-14 and BDNF1-12, respectively. The hybrid gold-peptide nanobiointerface was investigated, both in the direct physisorption and in the lipid bilayer-mediated adsorption processes, by a multitechnique study that included UV-visible and X-ray photoelectron spectroscopies, dynamic light scattering, zeta potential analyses and atomic force microscopy. Both peptide- and lipid-dependant features were identified, in order to have a modulation in the nanoparticles peptide coverage as well as in the cellular uptake of NGF and BDNF peptides, as investigated by confocal microscopy. The promising potentialities in the capability to cross the blood brain barrier were demonstrated.

# Small liposomes for drug delivery

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Micelle to vesicle transition (MVT) method was applied to the realization of small unilamellar liposomes (<100 nm) useful for different types of applications in the field of drug and bioactive molecule delivery. In particular, mucus-penetrating liposomes for pulmonary delivery of beclomethasone dipropionate (BDP), a known anti-inflammatory drug, were realized. We also decorated vesicles with hydrophilic polymers, capable of giving mucus-penetrating properties to the liposomes. Indeed, some pathologies such as lung diseases result often in the overproduction of mucus that forms a barrier for drugs. The method allows obtaining liposomes always below 100 nm and with good yields of drug encapsulation. Liposomes featured a constant low release of the drug over a period of 48h. In vitro assays showed that liposomes with a hydrophilic cover were well tolerated by pulmonary cells. In vivo experiments on mice also showed a good tolerability of BDP-loaded liposomes. The same strategy was successfully adopted to incorporate natural antioxidants, such as curcumin, aiming to obtain formulations of potential nutraceutical and pharmaceutical interest (1). Finally, the possibility of assembly liposomes on Titanium to develop advanced implant surface was exploited in view of possible strategy to local delivery of bioactive molecules. The opportunity of engineering the surface of implantable materials in order to increase the biocompatibility to host tissues, providing at the same time a surface-mediated drug delivery, is a very attractive solution to limit inflammation and to promote new bone formation in the prosthetic application field (2).

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# Molecular Confinement in Femtoliter scale aqueous Compartments

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Molecular confinement is known to lead to acceleration of molecular dynamics along with surface interaction. Nature employs confinement in molecularly crowded, heterogeneous and, specialized femtoliter (fL) compartments inside living cells for spontaneously achieving higher reaction efficiency and spatial-programming of composite, multi-step biochemical processes (1). We here show the facile production of aqueous fL droplets for studying molecular confinement on a biochip. We prepare fL aqueous droplets in oil drops on solid substrates by a "field-free"- no external electric fields and electrolytes (2) - piezoelectric inkjet printing in which a novel actuating waveform is employed by picoliter sized nozzles (Fig 1.a). The droplets form an almost-regular circular pattern at the border of mineral oil drops (3), (Fig 1.b) and Alexa 647 molecules, at 10-0.01 µM concentrations, form ring patterns at the surfactant/oil interface (Fig.1c) as predicted by numerical adsorption general models (4). At the single droplet level, we show that molecular confinement leads to modify solute-solvent and solvent driven solute-solute interactions. Confinement effects are tested by using Fluorescence lifetime imaging which reveals different characteristic lifetimes of specific molecules in confined volumes with respect to macroscopic solutions. The same method using the signal of a molecular rotor- i.e. 9-(2-Carboxy-2-cyanovinyl)julolidine - did not reveal changes in solution viscosity due to confinement. We exploit the possibility of analyzing molecules "in action" in fL volume solutions to study the behavior of molecular machines in confined environments. At these volume scales, by employing a model DNA beacon machine, we highlight that DNA-machines/ target interaction is favored in confined conditions with respect to microliter/macroscopic volumes.

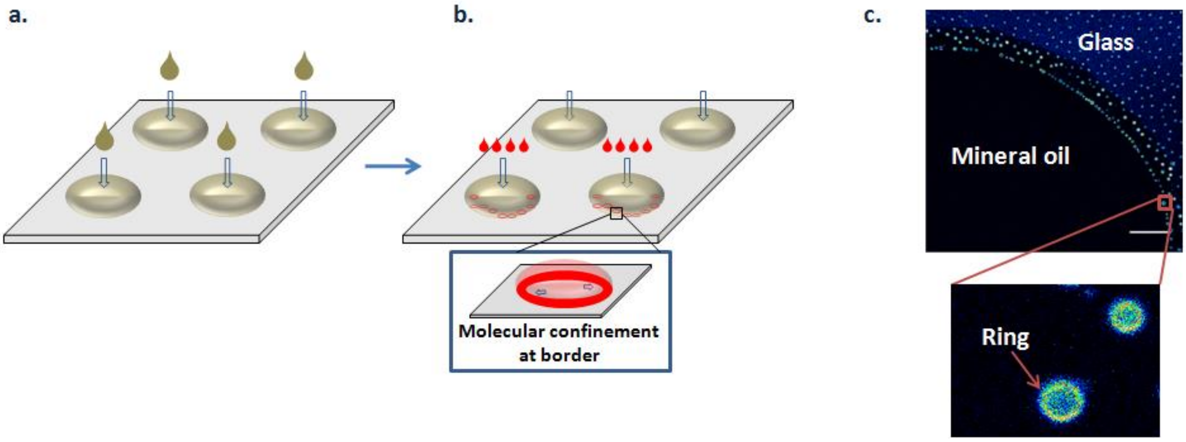

Figure 1. (a-b) Scheme of fL aqueous droplets injection inside mineral oil nanoliter scale droplets. (c) Fluorescence confocal images show the molecular confinement at the border of the droplets (Alexa 647 dye, 10 µM).

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# The Influence of Chemical Microenvironment on Living Cell Shape

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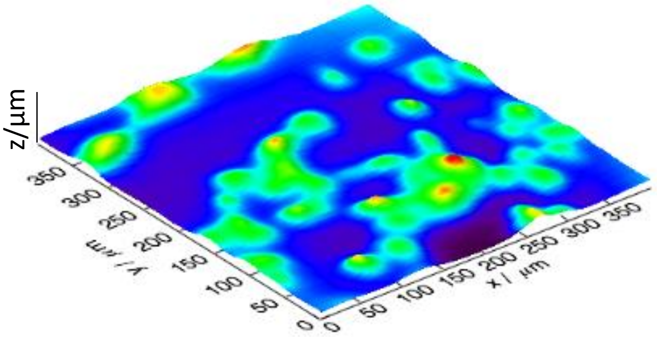
The shape and morphology of cells are related to their health status. Diseases, senescence, and the presence of toxic compounds cause morphological changes. Mechanical forces involved in the interaction with the cell microenvironment influence adhesiveness and morphology. Variations of morphology and motility are present in all cancer cells and are involved in metastasis. Cells adhesion to solid substrates is a multistep and complex process. It involves surface receptors, signaling elements and cytoskeleton. When a cell attaches to a solid substrate, it spreads over the surface. The degree of adhesion can be expressed in terms of shape parameters. Cells sense the physical-chemistry of their microenvironment and modulate their cell shape. We employed 2D nanomaterials, such as organic monolayers with a high surface coverage >95% [1] as culturing surfaces/environment for normal and cancer cells.

We used Scanning Electrochemical Microscopy (SECM) to study the local reactivity [2] and conductivity [3] of the surfaces. Using SECM, fluorescence microscopy and AFM we correlated the local physical chemical characteristics of the environments with the cancer and normal cellular shapes.The investigation of the interactions of living cells with 2D environments can gain fundamental knowledge on the type of environment that retards or accelerates diseases and degeneration and can determine the chemical forces that drive cell recruitment on a bioactive surface. The influence of micro-shaped chemical micro-environments on cell biology was investigated and will be presented as well.



Scanning Electrochemical Image of MCF10A cells growth on a pentacene monolayer

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# High-Quality, Ligands-Free, Mixed-Halide Perovskite nanocrystals Ink for Optoelectronic applications

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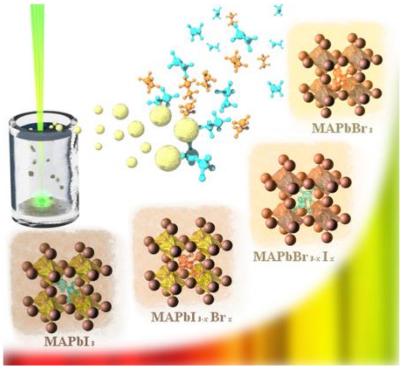
It is now well established that the primary optoelectronic properties of perovskite-halides – such as their tunable direct bandgap, high absorption coefficient, low exciton binding energy, and balanced ambipolar carrier transport – meet many of the requirements for a high-efficiency solar energy conversion technology(1). But in spite of the huge research effort, yet they are far from the market.
Given the simple processability of perovskite-halides, typically from solutions at relatively low temperatures, a non-negligible level of unintentional structural and chemical defects at temperatures relevant for device operation are currently limiting the devices efficiencies and causing instability - i.e. hysteretic behaviours (2) and formation of metastable phases upon photoexcitation which hampers the band-gap tunability (3) - and low reproducibility, especially in view of large area deposition.
In more established semiconductors, such as Si for example, the understanding and control of defects has been a cornerstone of their successful development in devices. Defects thus remain one of the interesting material characteristics in solution processable perovskites that underpin limitations in device operation and influence further progress towards reaching the highest possible power conversion efficiencies. So far, high quality colloidal nanocrystal of perovskites (not necessarily quantum confined) have been demonstrated. However, they all need bulky and insulating organic ligands to remain in suspension, thus hampering the fabrication of conductive thin films.



We demonstrate, for the first time, the synthesis of ligand free metal-halide pervskite nano-crystal inks by Laser Ablation Synthesis in Solution (LASiS).[4] This methodology, simple and easy to use for large scale materials production, allows to produce nano-crystals solutions to print conductive thin films electrically and photo-stable. In fact, we show that such films do not present any hysteretic behavior under polarization, typical in presence of ion migration and permit monotonic tunability of the band gap across the visible spectrum, in absorption and emission, without the formation of sub-band gap emissive phases upon photo-excitation.

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# New Earth-abundant thin film solar cells based on $Cu_2MnSnS_4$

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As it is well known, in the last decade much attention has been focused on $I_2$-II-IV-$VI_4$ thin films as an attractive possibility for the synthesis of In and Ga free chalcogenides which may allow terawatt range photovoltaic (PV) applications. A new alternative to copper zinc tin sulfide/selenide belonging to this class of materials is copper manganese tin sulfide (CMTS), a p-type semiconductor fully based on Earth-abundant and low-cost elements which shows an important advantage with respect to copper zinc tin sulfide/selenide. As a matter of fact, not only the abundance in the Earth's crust of Mn is two order of magnitude higher than that of Zn (1100 ppm vs 79 ppm), but the amount of Zn produced in 2015 was 4'600'000 tons lower than that of Mn (13'400'000 Zn tons vs 18'000'000 Mn tons). Therefore, since Mn is definitely cheaper than Zn, optimized CMTS could potentially provide Wp cost definitely lower than copper zinc tin sulfide/selenide, which is crucial for thin film PV applications. CMTS, which crystallizes into a stannite structure (space group: I-42m), shows high absorption coefficient ($\alpha=10^4$ $cm^{-1}$) and direct band gap suitable for PV applications. So far, CMTS was mainly studied as bulk magnetic semiconductor, while, only in the last two years, the present authors (1) and Chen et al. (2) reported on CMTS thin films for PV applications. The latter reported on CMTS layers prepared by direct liquid coating followed by annealing in nitrogen atmosphere and/or post-sulfurization in sulfur vapors, which provided solar cells with 0.49% maximum efficiency. Our work deals instead with CMTS thin films grown by a two-step vacuum process. The metal precursors deposited on Mo-coated soda lime glass (SLG) by thermal evaporation are annealed in sulfur vapors for 1h at 585°C with an initial 1h step at 115°C to enhance the metal intermixing. Of the many possible stoichiometries, Cu-poor/Mn-rich CMTS films with Mn/Sn ratio around 1 were chosen in order to prevent the development of both highly conductive (e.g. $Cu_{2-x}S$) and insulating (e.g. MnS) secondary phases. Several techniques, including Scanning Electron Microscopy, Energy Dispersive Spectroscopy (EDS) , Raman spectroscopy and Photoluminescence have been used to test the quality of CMTS thin films, while CMTS/CdS/iZnO+AZO solar cells were inspected both by External Quantum Efficiency and current density-voltage (J-V) measurements under 1 sun illumination. The beneficial effects of low temperature post-deposition annealing either in air or inert atmosphere between 200 and 275°C on CMTS solar cells were investigated, both in terms of electrical performance and modification of the material properties. In particular, a 40 min 225°C annealing in air lead to the best overall performance: efficiency 0.83%, open-circuit voltage 354 mV, short-circuit current density 5.8 mA/cm2, fill factor 40%. The reasons behind these beneficial modifications of the device parameters were investigated by Raman and PL spectroscopies. Results showed that post-deposition thermal treatments in air between 200 and 275°C generally reduce generally reduces the density of the bulk defect, thus reducing recombination losses and increase the of CdS crystalline quality, while red-shifting its absorption edge.

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# Polyurethane-based Electrostrictive Nanocomposites as High Strain - Low Frequency Mechanical Energy Harvesters

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Energy harvesting of wasted energy is increasingly important for powering wearable electronics in Internet-of-Things world [1]. Here, we reported on innovative nanocomposites made of electrostrictive polymer (thermoplastic polyurethane, TPU), and high-k ceramic filler ($CaCu_3Ti_4O_{12}$, CCTO), which offered outstanding results in recovering energy by human gait. The excellent mechanical properties of TPU allowed up to 50 vol% of filler into the composite without loosing film elasticity even for high strains (~30%). CCTO was able to increase of more than one order of magnitude the resistance of the film harvesters with respect to pure TPU, without lowering the dielectric constant and the breakdown voltage. The combined effect of high dielectric strength, high resistance and allowable strain make these composites very promising as energy harvesting actuators.

By means of careful broadband electric spectroscopy coupled with microstructure analysis, we were able to address the mechanisms underlying energy recovery. In particular, long-range charge migration phenomena mainly occurred along conductivity pathways, which are formed at the extended interfaces between the polymer strands and the filler. Our model allowed optimal tailoring of electrostrictive nano-composite actuators.

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# A Bilayer $WO_3$ n-n Heterojunction Photoanode prepared by RF Diode Sputtering for Improved Photoelectrocatalytic Water Splitting

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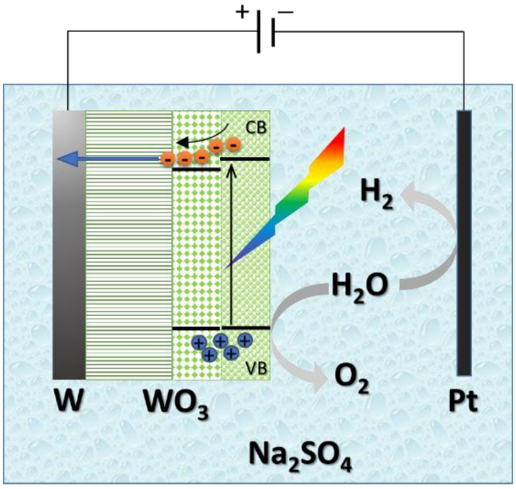
A bilayer $WO_3$ photoelectrode was prepared by radio frequency (RF) plasma sputtering in reactive 40%$O_2$/Ar atmosphere by depositing on a tungsten foil two successive $WO_3$ coatings at two different total gas pressures (3 Pa and 1.7 Pa, respectively), followed by calcination at 600 °C (1). Its photoelectrocatalytic (PEC) activity was evaluated by both Incident Photon-to-Current Efficiency (IPCE) measurements and separate evolution of $H_2$ and $O_2$ by water splitting in a two-compartment PEC cell (2), and compared with those of the corresponding single layer grown at constant pressure (1.7 Pa or 3 Pa). FESEM analysis revealed that the photoanodes have a nanostructured porous double layer surmounting a columnar basement (Staffa-like morphology, after the name of the Scottish island). Tauc plot of the single layer revealed that the sample prepared at lower pressure possesses a 0.1 V wider bandgap (2.94 eV) than that prepared at higher pressure (2.82 eV). Both Mott-Schottky analysis and XPS valence band spectra showed that this difference was essentially due to a shift of the conduction flat band (CB) potential. Thus, this work demonstrates that the total pressure during $WO_3$ deposition by RF diode sputtering affects the position of the CB energy very likely due to the different extent of crystal structure distortion induced by oxygen vacancies (3), in agreement with the crystal field theory (CFT). Lowering the pressure increases the oxygen vacancies, and produces a shift of the CB towards higher energy. The equivalent n-n heterojunction at the interface of the double-layer (see Figure) creates a built-in electric field that facilitates the photopromoted electron transfer toward the lower laying conduction band material, while the columnar innermost layer introduces percolation paths for efficient electron transport toward the conductive tungsten foil. Both phenomena contribute to decrease the interfacial charge transfer resistance ($R_{ct}$) as measured by impedance spectroscopy and lead to a *ca.* 30% increase in the PEC performance compared to the monolayer and to a 93% faradaic efficiency, which is among the highest reported so far for $WO_3$ photoanodes. Upon methanol addition an outstanding 4-fold photocurrent density increase up to 6.3 mA cm$^{-2}$ was attained over the bilayer $WO_3$ photoanode, much larger than the usually observed current doubling effect.



***Acknowledgment.*** This work received financial support from the Regione Lombardia and Cariplo Foundation co-funded "SmartMatLab Centre" project (Grant No. 2013-1766)

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# Hydrides as High Capacity Anodes in Lithium Cells: An Italian "Futuro in Ricerca di Base FIRB-2010" Project

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Automotive and stationary energy storage are among the most recently-proposed and still unfulfilled applications for lithium ion devices. Higher energy, power and superior safety standards, well beyond the present state of the art, are actually required to extend the Li-ion battery market to these challenging fields, but such a goal can only be achieved by the development of new materials with improved performances. Focusing on the negative electrode materials, alloying and conversion chemistries have been widely explored in the last decade to circumvent the main weakness of the intercalation processes: the limitation in capacity to one or at most two lithium atoms per host formula unit. Among all of the many proposed conversion chemistries, hydrides have been proposed and investigated since 2008. In lithium cells, these materials undergo a conversion reaction that gives metallic nanoparticles surrounded by an amorphous matrix of LiH. Among all of the reported conversion materials, hydrides have outstanding theoretical properties and have been only marginally explored, thus making this class of materials an interesting playground for both fundamental and applied research. In this communication, we illustrate the most relevant results achieved in the frame of the Italian National Research Project FIRB 2010 Futuro in Ricerca "Hydrides as high capacity anodes in lithium cells" and possible future perspectives of research for this class of materials in electrochemical energy storage devices.

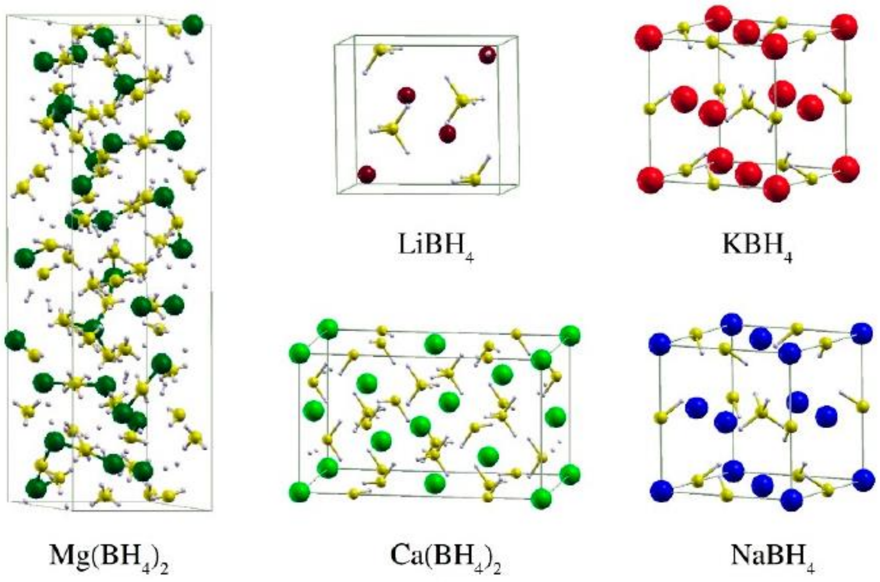

**Figure 1.** Crystal structures of the borohydrides phases.

# Bio-Hybrid Complexes in Artificial Photosynthesis

Simona la Gatta[a], Francesco Milano[b], Roberta Ragni[a], Angela Agostiano[a,b], Gianluca Maria Farinola[a] and Massimo Trotta[b]

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The sun was born five billion years ago and it is estimated that it will continue to irradiate the same amount of energy for another five billion years. Sun is a renewable energy source, inexhaustible within the humankind life, and, every year, Earth receives an amount of solar energy ten thousand times greater than that the entire planet population uses (1). The ability to convert solar light into chemical energy is the fundamental feature of photosynthetic systems. Photosynthesis is the most important biological process, supplying Earth's biosphere with oxygen and energy for living organisms' metabolism (2). All life on Earth depends on photosynthesis directly or indirectly, and has been deeply investigated by scientists with the aim of reproducing it in the laboratory, mimicking the Nature, and, consequently, producing green energy efficiently, following the artificial photosynthesis way (3). The complexity of the natural photosynthetic systems is difficult to reproduce *in vitro*; however, it is largely related to their living character and can be reduced in a biomimetic environment. In this regard, ideal biomimetic systems must efficiently harvest the sunlight, with the help of suitable antennas, and convert the energy in a stable charge-separated state with a lifetime long enough to allow ancillary chemistry to take place. In the purple, no sulphur photosynthetic bacterium *Rhodobacter sphaeroides R26*, energy from sunlight is harvested by antennas and transferred to reaction center (RC), a most efficient photoconverting transmembrane protein. During the electron transfer process, the RC, upon photon absorption, promotes one electron sitting on the bacteriochlorophylls dimer (D), the electron donor, in its excited state and then it shuttles to the electron acceptors the ubiquinone-10 Q, generating the charge separated state $D^{+}Q^{-}$. In the presence of external electron donors, the oxidized $D^{+}$ is reduced again and a second photon impinges a second electron so that the quinone Q, now doubly reduced, is doubly protonated and it is released as quinol. Cytochrome $c_2$ is the physiological electron donor to the oxidized dimer. Our idea is to build a supramolecular architecture made up of the photosynthetic bacterial reaction center, an artificial light-harvesting antenna, synthesized *ad hoc*, belonging to the class of heptamethine cyanines, with the task of increasing the RC absorption cross section in the visible range, and an electron donor redox protein, the cytochrome $c_2$. These three components were connected to each other by covalent bonds obtaining a stable bio-hybrid supramolecular complex, easily interfaceable to a semi-conductive surface, with the aim of assembling a sustainable sunlight-to-energy converting device based on proteins. Insert references in brackets as follows: (1) (1,2,3) and add reference list at the bottom of the abstract using justified Times New Roman 10, with line-spacing 1. As indicated below:

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# Electronic coupling in H-shaped tetra-arylamine mixed-valence compounds

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Organic mixed-valence compounds (MVs) are donor-acceptor compounds that possess an open shell ground state (1). Amongst the MVs particularly interesting are those with arylamines connected through a conjugated bridge. The nature of the bridge as well as that of the substituents on the arylamine moieties, determines the electrooptical properties of such compounds. Specifically, the intervalence charge transfer transition (IVCT) in the near infrared region (NIR), occurring upon photoexcitation of the oxidized monocation species, is heavily affected by the above structural parameters. These compounds can be designed to work as electrochromic materials in smart devices for controlling the solar thermal radiation, as well as for the generation of high charged radical species for high spin magnetic materials (2,3). Here we present organic MVs with an innovative H-shape design, where four redox centres are bridged "vertically" via a dibenzofulvene backbone and "horizontally" via a bis-(dibenzofulvene)-thiophene bridge. They are oxidized to stable high charged radical species, showing IVCT in the NIR, in contrast to the linear systems lacking one dibenzofulvene-bisamine moiety at one end of the thiophene bridge, where band bleaching occurs upon dication formation. Electrochemical, spectroelectrochemical and TD-DFT results, show that the IVCT in high oxidation states of the H-shape MVs is due to the activation of both vertical and horizontal electron transfer pathways (4). The innovative H-shape design may improve the potential electrooptical applications of MVs, highlighting the importance of the coupling between multiple redox centres and paving the way for the development of three-dimensional multicentre mixed valence compounds.

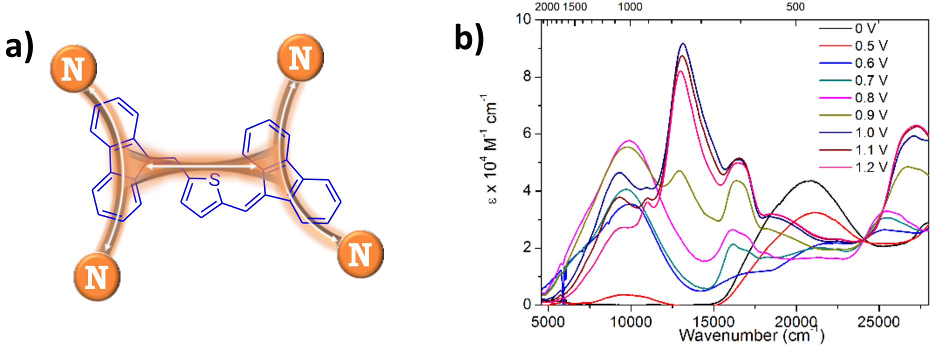

Figure 1. H-shape MVs based on the bis(dibenzofulvene)tiophene bridge a); example of the electrochromic response of an H-shape compound in the Vis-NIR region b).

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# Forsterite surfaces as models of interstellar core dust grains: computational study of carbon monoxide adsorption

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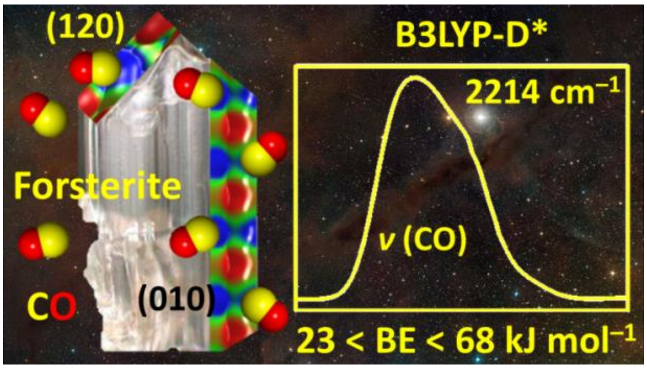
Carbon monoxide (CO) is the second most abundant gas-phase molecule (after hydrogen) of the Interstellar Medium (ISM) (1). In Molecular Clouds (MCs), regions of the ISM where star-forming processes occur, it adsorbs at the surface of grain cores – typically partially crystalline Mg/Fe silicates – or within the icy grain mantle and originate other molecular species through the catalytic power of surface active sites. More than 200 molecular species in the MCs have been observed so far by means of rotational spectroscopic, partly derived from reactions among molecules entrapped at the grains surfaces, while the presence of Mg-silicates has been inferred by IR spectroscopy (1,2,3). Laboratory studies can only partially reproduce the harsh conditions of the ISM (4), thus computational modeling can play a major role in the understanding of the chemical network charactering MCs. In this work, we performed and accurate analysis of the energetic and structural features of CO adsorption on different crystalline forsterite (Fo, $Mg_2SiO_4$) surfaces by means of DFT techniques. Data indicate that CO exclusively physisorbs on Mg exposed cations of Fo surfaces, with binding energies in the 23-68 kJ mol$^{-1}$ range. Not only simple charge-dipole forces are involved, but also quadrupolar and dispersive ones are responsible of the CO adsorption. We also performed a full thermodynamic treatment of the CO adsorption at the very low temperatures and pressures typical of the MCs together with a full spectroscopic characterization of the CO stretching frequency. We proved the CO stretching frequency value to be extremely sensitive to the local nature of the surface active site of adsorption and showed results at variance with what is known about CO adsorbed on flat oxide surfaces due to the complex electrostatic and structural morphologies of the Fo surfaces. The detailed kinetic analysis of CO desorption at different low temperatures suggested that desorption times are higher than the typical evolution times of the ISM, at least until 100 K when they become comparable. Our computed data could be incorporated in the various astrochemical models of interstellar grains developed so far and thus contribute to improve the description of the complex chemical network occurring at their surfaces.



This work is supported by MIUR and SNS Stars in the Caos PRIN2015 cod. 2015F59J3R.

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# Prebiotic Molecules In Interstellar Space: Aminoacetonitrile And C-Cyanomethanimine

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The attempts to detect amino acids in the interstellar medium were so far unsuccessful even for its simplest form, glycine, despite that decades-long efforts have been devoted by many observational studies. From a chemical point of view, it is therefore important to identify the possible precursors of amino acids as well as the astronomical sources where they are abundant. Aminoacetonitrile ($NH_2CH_2CN$) is one of the possible precursors of glycine in the production process known as Strecker reaction, whose synthetic route is shown below:

$$NH_3 + H_2C{=}O \rightarrow HN{=}CH_2 + H_2O$$
$$HN{=}CH_2 + HCN \rightarrow NH_2CH_2CN$$
$$NH_2CH_2CN + H_2O \rightarrow NH_2CH_2CONH_2$$
$$NH_2CH_2CONH_2 + H_2O \rightarrow NH_2CH_2COOH + NH_3$$

Aminoacetonitrile has been already detected toward the giant molecular cloud Sagittarius B2 (1). Its vibrational ground-state rotational spectrum has been characterized in the laboratory up to 1.3 THz (2). Aminoacetonitrile has a few low-lying (below 400 $cm^{-1}$) vibrational excited states (3) and rotational transitions within these states may be observed in hot cores and circumstellar shells. In this study (4), the pure rotational transitions in the 3 lowest vibrational states have been assigned and analyzed in the range 80-450 GHz. It was found very important to include Coriolis coupling between the two lowest vibrational fundamentals, while the other one resulted unperturbed. The spectral data of these vibrational excited states are essential for future observations of the molecule in relatively high kinetic temperature conditions.

Another molecule of astrochemical interest is the dimerization product of hydrogen cyanide, C-Cyanomethanimine (HN=CHCN), that is thought to play an important role as intermediate in the prebiotic formation of purines and proteins. In fact, hydrogen cyanide tends to polymerize, giving biologically important molecules such as adenine (pentamer of HCN) (5). C-Cyanomethanimine exists in two isomeric forms, *Z* and *E*. Although the (*E*)-C-cyanomethanimine is about 210 $cm^{-1}$ less stable than the (*Z*)-C-Cyanomethanimine (6), the former has been detected through radio-astronomical observation (7) in the star-forming region (Sgr)B2(N), while no detection for the latter has been claimed so far. For its astrophysical interest and because its rotational spectrum has been investigated only below 100 GHz, the study of this molecule is being extended to higher frequency (millimeter and sub-millimeter wave regions) in order to facilitate astronomical detection. The sextic centrifugal distortion constants for both isomers of C-Cyanomethanimine were evaluated by means of highly accurate *ab initio* calculations (8). Therefore, the assignment of the rotational spectrum above 200 GHz can rely on accurate predictions.

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# Should we introduce pre-equilibria into Markov models for homogeneously catalyzed copolymerization?

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Polyolefin elastomers based on ethene and propene are important players in the field of synthetic rubbers and the molecular features that control bulk properties are strictly related to the monomer distributions along the chains (1). Usually, the chemical reactivity of a propagating chain is considered to depend only on the identity of monomer units at the growing end. Two reactivity ratios, $r_1$ and $r_2$, were thus defined starting from the kinetic expressions for the uncontrolled radical mechanism in order to describe the radical copolymer micro-structure; mathematical models (e.g. Mayo-Lewis, Fineman-Ross and Kelen-Tudos) derived from such approach have also been exploited to characterize homogeneous catalyzed copolymers despite the latters could present a more complicated mechanism, involving coordination pre-equilibria (2,3).

In this study, we describe a theoretical study of E/P copolymerization by a $C_2$-symmetric metallocene catalyst, *rac*-$Me_2C$-$Ind_2ZrCl_2$ via a synergic DFT/kMC approach offering a robust alternative interpretation of homogeneously catalyzed copolymer process: the mechanism consists of at least two steps, equally important, namely coordination and insertion. If this holds, the application of Markovian models to copolymerization induced by homogeneous catalyst might request extreme care, as they hinge on the mechanism proposed for uncontrolled radical polymerization, which neglects coordination and pre-equilibria.

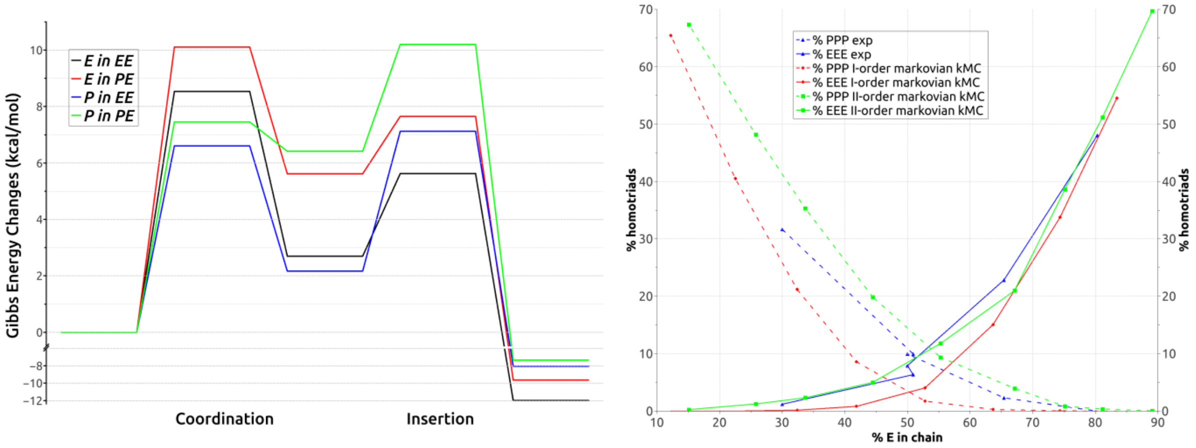

Figure 1. Left, a typical reaction pathway composed of coordination and insertion; right, comparison of experimental and kMC-simulated EEE and PPP triads.

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# Intermolecular Energy Transfer in Real Time

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Essential state models (ESM) have been successfully used to describe low-energy optical properties (1,2,3) of different classes of charge-transfer (CT) chromophores, namely dipolar (D-A, where D=donor and A=acceptor of electrons), quadrupolar (D-A-D or A-D-A) and octupolar (A(-D)3 or D(-A)3) chromophores.

Here we introduce a truly dynamical and non-adiabatic model for resonant energy transfer (RET). More precisely, we consider two different dipolar chromophores, an energy donor ($\mathcal{D}$) and an energy acceptor ($\mathcal{A}$), their main resonating structures being used as electronic basis states and introducing the coupling to one effective molecular vibration per chromophore.

By means of a non-adiabatic dynamical calculation also accounting for energy dissipation, we follow in real time the complete $\mathcal{D}$-to-$\mathcal{A}$ energy transfer process (fig.1, panel a). Coherent oscillations of $\mathcal{D}^*$ as induced by an ultrashort light pulse are washed-out in the few hundred femtoseconds by fast intramolecular energy dissipation, while the $\mathcal{D}^*$-to-$\mathcal{A}$ energy transfer process takes place in the following few picoseconds (fig.1, panel b). The whole process is followed through time-dependent fluorescence spectra (fig.1, panel c).

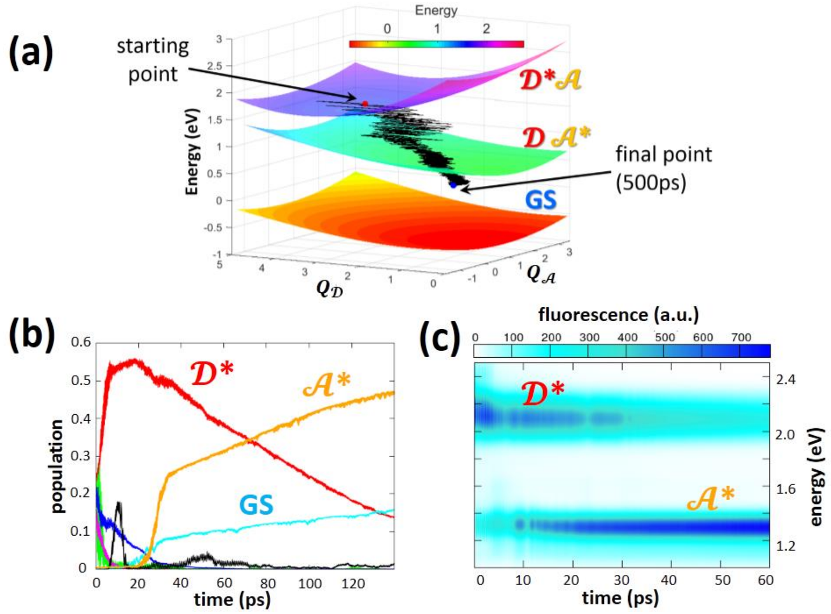

Fig. 1. Energy transfer in real time. Panel a: non-adiabatic $\mathcal{D}\mathcal{A}$ dynamics following impulsive excitation of $\mathcal{D}$; to help the eye, relevant adiabatic energy surfaces are also shown. Panel b: population time-dependence plotted for some relevant $\mathcal{D}\mathcal{A}$ states. Panel c: time-dependent fluorescence spectra for the $\mathcal{D}\mathcal{A}$ system.

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# A spotlight on the complex hierarchical structure of some ionic liquid-molecular liquid binary mixtures

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Ionic Liquids (salts with melting point below 373K) are a class of compounds that are being intensively studied because of their peculiar properties (1). Being neat ions in the liquid phase, they exhibit almost zero vapour pressure, high viscosity, high conductivity, wide electrochemical window and low flammability. While it is possible to find a relatively wide literature for these neat chemicals, works on their mixtures are just about 14% of the total and only ~1% concerning structural properties. These mixtures are innovative materials that are recently reported as even more versatile and cheap than pure ILs. The structure of many neat ILs consists of two segregated micro-domains percolating each other: one is polar and the other is non-polar. This organization, often called "sponge like", is at the basis of the characteristic low-q peak in the SAXS patterns (~2-7 nm$^{-1}$) (2). Adding a second substance into the IL forces some rearrangement in its structure, affecting the domains, for example water enlarges the polar domain, while hexane does so in the apolar. The recent discovery (3) of a more complex structure hierarchy in some ethylammonium nitrate (EAN) + methanol mixtures, opened a new debate on the properties of ILs and the potential applications of such mixtures. A cluster-like organization was suggested then, while almost at the same time Atkin et al. (4) observed the same odd feature in other IL mixtures with longer n-alcohols. They interpreted the "Low q Excess" (LqE) as the fingerprint of self-assembled structures. Recently we have shown that the LqE can be found not only when the co-solvent is amphiphilic (as reported so far), but also when it is highly symmetrical, regardless if the compound is polar or almost apolar. We had the experimental evidence of LqE in EAN+1,4-diaminobutane and EAN+1,2- dimetoxyethane mixtures (5). These molecules cannot self-assembly, thus confuting the hypothesis from Atkin et al.. The results collected using synchrotron radiation together with MD calculations enable us to state that the LqE arise when the mixture is preparing to demix, and is undergoing strong density fluctuations. This appears to be a general behaviour, and not strictly linked to the polar/apolar nature of the co-solvent. Our models are suggesting that some supramolecular structures can be found in the samples showing the LqE. The understanding of the driving force behind this large-scale hierarchical organization could open new landscapes for ionic liquids applications.

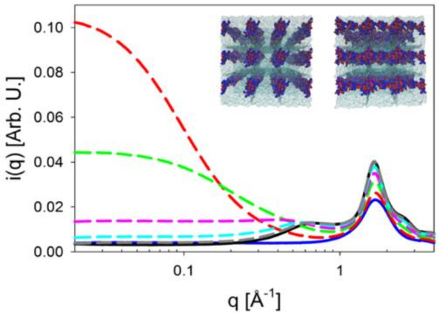

Figure 1: **SAXS patterns for ethylammonium nitrate+acetonitrile mixtures. In the inset two snapshots of the simulation box for the mixture with the highest "Low q Excess".**

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# Fluorous mesoscopic domains in room temperature ionic liquids.

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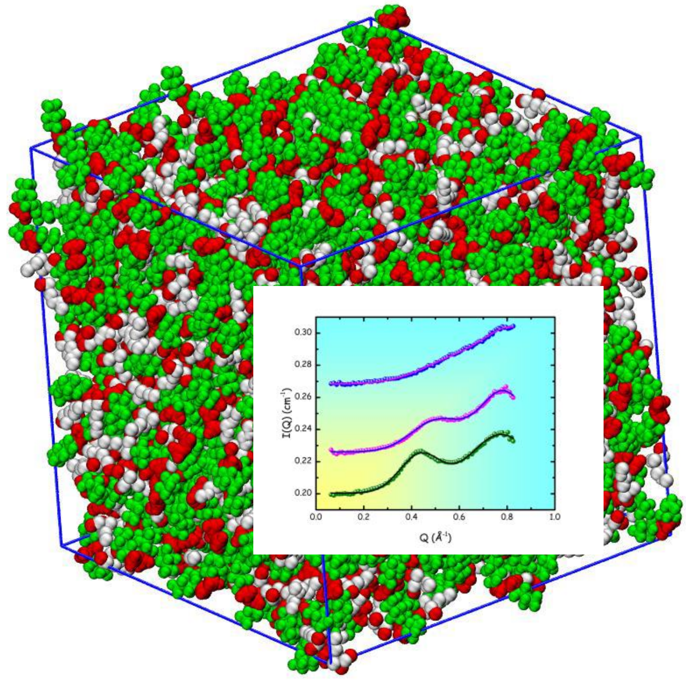
Room temperature ionic liquids (RTILs) are compounds composed solely of ionic species. Recently attention is focusing on the interesting properties of fluorinated RTILs that find application in separation, pharmacology, catalysis etc and show an appealing blending of ionic liquid specific properties and fluorous moieties induced features. Among the relevant properties highlighted in FRTILs, the possibility that fluorous moieties might segregate analogously to their alkyl counterparts in conventional RTILs has been proposed in the past [1–6]. So far however, no direct experimental evidence for such a behavior has been provided.



Simulation box of fluorinated RTILs, highlighting the different alkyl, fluorous and charged moieties. The inset data sets refer to neutron scattering data set collected as a function of the fluorous tail length. [Adapted from Ref. 7 with permission from the PCCP Owner Societies. ]

Here we provide the first direct experimental evidence that RTILs bearing a long enough side fluorous chain are characterized by the occurrence of a well-defined mesoscopic organization, consistent with the segregation of the fluorous tails. [7] By exploiting the synergy between x-ray and neutron scattering coupled with state of the art Molecular Dynamics simulations, we will discuss several consistent examples where such a phenomenology has been observed.

We envisage an important role played by these self-aggregating domains of fluorous moieties in determining specific performances in the fields of separation, catalysis and related fields.

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# Supramolecular Organization of Water–Ethanol Solution in Ferrierite under Pressure

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Turning disorder into organization is a key issue in science. In particular, supramolecular organization induced by external stimuli has opened new paths for the bottom-up fabrication of nanostructures. By using a combined strategy based on the synergy of X-ray powder diffraction experiments and modeling studies (1), we showed that high pressure - in combination with the shape and space constraints of a hydrophobic all-silica zeolite - separate an ethanol–water liquid mixture into ethanol dimer wires and water tetramer squares (Figure 1).

Separation of ethanol from water was accomplished in an all-silica ferrierite (Si-FER), by using as pressure transmitting medium a mixture of (1:3) ethanol and water in the 0.20 to 1.34 GPa pressure range. The system was studied in situ by high-pressure synchrotron X-ray powder diffraction at BM01 beamline at ESRF and refined via first principles modeling.

Upon separation, the confined supramolecular blocks alternate in a binary two-dimensional architecture that remains stable upon complete pressure release. These results support the combined use of high pressures and porous networks as a viable strategy for driving the organization of molecules or nano-objects towards complex, pre-defined patterns relevant for the realization of novel functional nanocomposites and highlight the need of appropriate modeling for an atomistic level understanding of complex phenomena.

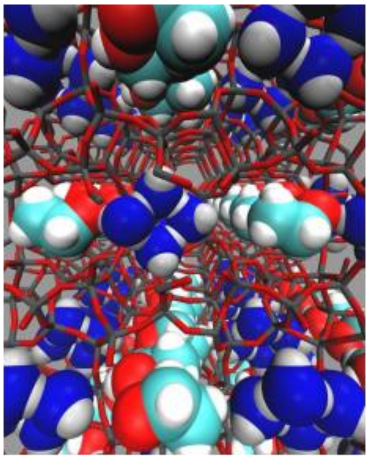

Figure 1.

(1) Arletti, R., Fois, E., Gigli, L., Vezzalini, G., Quartieri, S., Tabacchi, G. (2017) Angew. Chem. Int. Ed. 56, 2105, DOI: 10.1002/anie.201700219

# Formulation and characterization of hydroxypropyl guar based gel-like systems, tailored for the low impact cleaning of works of art surfaces

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The development and characterization of a new family of water based gel-like systems containing hydroxypropyl guar gum (HPG) with borax as crosslinker are presented in this contribution. In the formulation glycerol is introduced as plasticizer, and its role is broadly investigated. The effect of the components on the structure, on the viscoelastic behavior of the system and on the activation energy related to the relaxation process has been investigated by means of rheology, Nuclear Magnetic Resonance (NMR) and Small Angle X-ray Scattering (SAXS) (1,2). Results indicated that the mechanical properties of the systems can be tuned by varying the amount of each component; $^{11}$B-NMR and $^{1}$H-NMR measurements highlighted the role of glycerol in the crosslinking mechanism, with the formation of a glycerol-borate complex. The characterization approach is used to identify the best formulation, in the view of a future application in the field of cultural heritage conservation, in particular for the cleaning of surfaces of historical and artistic interest (3). The main goal is to obtain a system adaptable to the roughness typical of surfaces of many artifacts. The best formulation was used for preliminary cleaning tests on a *stucco* artifact deriving from the decorations of *La Fenice* theatre, in Venice. The tests suggest a promising efficacy in selective cleaning of the surface and make these materials particularly interesting in the field of restoration.

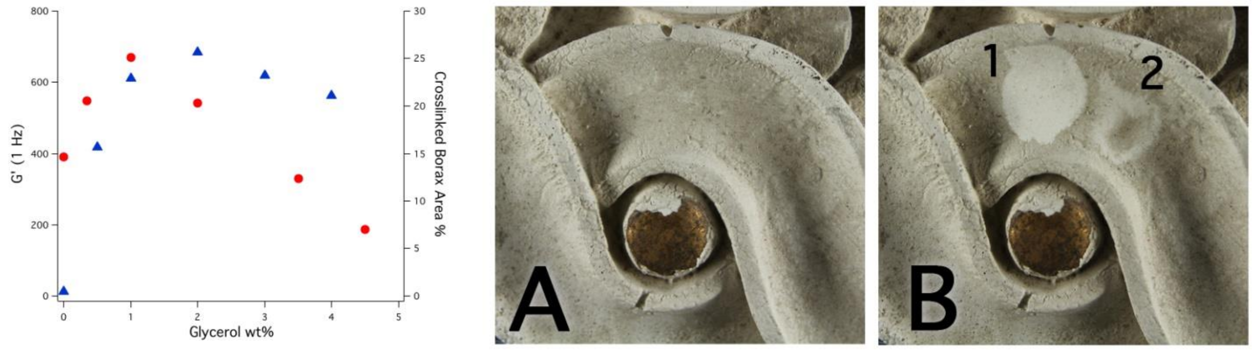

Figure 3: **On the left, Storage modulus values at Frequency=1Hz (■) and Crosslinked Borate Area obtained from NMR measurements (▲) are plotted against glycerol concentration. Pictures on the right show the *stucco* surface before (A) and after (B) the cleaning, with the comparison between the the HPG based system (1) and a wet cotton swab (2).**

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# Chemical poly ethyl methacrylate (PEMA) organogels for the removal of pressure sensitive tapes (PSTs) from paper artworks

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Chemical poly ethyl methacrylate (PEMA) organogels loaded with Diethyl Carbonate (DEC) were synthesized by means of radical polymerization (1, 2). These systems are specifically designed for the removal of degraded Pressure Sensitive Tapes (PSTs) from paper artworks, a very common issue in the field of manuscripts and drawings restoration. DEC, an organic green solvent, shows interesting swelling properties towards PSTs components; besides it is inert to most common inks and dyes, unlike other commonly used cleaning systems such as polar solvents and microemulsions (3).

Several organogels were obtained by changing reaction parameters; on the basis of macroscopic evaluations (e.g. mechanical properties, homogeneity), some systems were chosen for a deep physico-chemical characterization performed by means of different techniques. Thermogravimetry (DTG), Differential Scanning Calorimetry (DSC), and gravimetric analysis were used to assess solvent content and uptake/release behaviour of gels; rheological analysis permitted the evaluation of their viscoelastic properties; Fourier Transform Infrared Spectroscopy (FT-IR) and Attenuated Total Reflection Fourier Transform Infrared Spectroscopy (ATR-FTIR) allowed to investigate the presence of unwanted residues in the exchange solvents and the effectiveness in the removal of PSTs. The penetration of DEC through the backing layer of PSTs and the swelling of the adhesive was investigated by means of Laser Scanning Confocal Microscopy (LSCM).

Cleaning tests on mock-up samples and real artworks were also successfully performed.

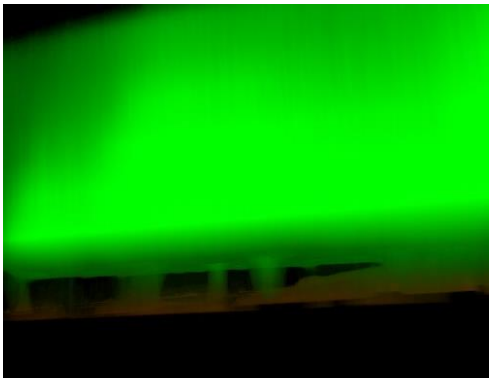

Fig. 1 – Laser Confocal image of a PEMA-DEC gel onto a PST sample: penetration of DEC (in green) through the backing up to the adhesive layer (in red)

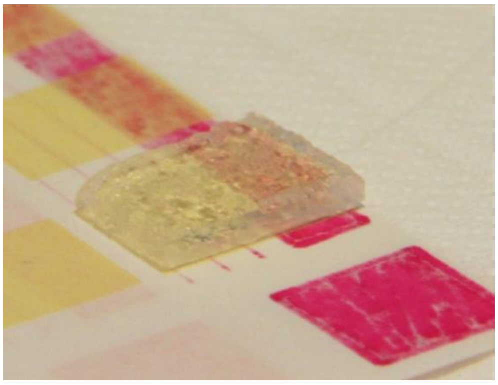

Fig. 2 – Application of a PEMA-DEC organogel for the removal of a Masking Tape from a mock-up sample

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# Surface Cleaning of Artworks: Structure and Dynamics of Nanostructured Fluids Confined in a Polymeric Network

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Nanosystems and confinement tools for the controlled release of a cleaning agent, e.g., hydrogels and microemulsions, have been used for several years for the treatment of delicate surfaces in art restoration interventions. However, notwithstanding the unprecedented achievements from an applicative point of view, a fundamental comprehension of their interaction mechanism is still lacking. In this study PVA hydrogels, obtained via freeze-thaw processes, are prepared as scaffolds for water-based nanostructured fluids for application in the cleaning of artworks: rheological, thermal, microscopic and scattering techniques showed that, depending on the number of freeze-thaw cycles, the hydrogels exhibit different physicochemical and viscoelastic properties, making them suitable for application in a broad range of cleaning issues. The gels have been loaded with an oil-in-water microemulsion and the diffusion of the microemulsion droplets inside the polymeric network has been investigated through Fluorescence Correlation Spectroscopy (FCS), demonstrating that the microemulsion is permanently kept inside the matrix and can freely diffuse in the network. In addition, we show that, when the gel-microemulsion system is put in contact with a layer of hydrophobic grime, a dynamic interaction between the microemulsion droplets and the underlying layer is established, leading to the solubilization of the hydrophobic molecules inside the droplets in the gel matrix. Thus, for the first time, through FCS, insights about the removal mechanism of hydrophobic grime upon interaction with cleaning agent embedded in the polymeric matrix, are obtained. Some examples of significant case studies treated with these innovative materials will be presented.

# Nanocomposites for the consolidation and deacidification of cellulose-based artifacts

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A restoration method designed for the conservation of degraded fibrous-based artifacts should addressed the two main problems concerning these materials. Firstly, a mechanical reinforcement of artifacts is usually needed to ensure that the original material keeps its integrity. Moreover, pH buffering is required to prevent acidic degradation that is inherent to natural materials. (1)
It has been recently shown that these two issues are related. For instance, it takes less than 100 years for acidic compounds to induce a significant loss of mechanical properties in canvases based on natural materials. (2) The same degradation effect of acidic compounds is found in paper-based artworks, drawings and documents. In this regard, several deacidification methods have been proposed and proven efficient in hampering the degradation of cellulose. (3,4,5)

Research efforts have been recently devoted to the development of a nanocomposite material for the consolidation and concomitant pH adjustment of cellulosic works of art and artifacts that is one of the goal within the EU Project NANORESTART.
The use of nanocellulose, in combination with nanoparticles and cellulose derivatives, could ensure the consolidation of fiber-based materials using almost entirely natural materials. The choice of these materials is due to the high compatibility of the proposed treatments with the original fibrous support, which is essential from the conservation point of view.
Considering the high variability of cellulose-based artifacts, several different approaches were followed in order to provide conservators with a wide palette of tools that can be used on different works of art that are in need of both consolidation and deacidification treatments.
Nanocomposite materials were analyzed in order to gain more information about their structure and characteristics. Mechanical tests on not aged and aged reference samples were used to assess the consolidation efficacy of the proposed consolidation treatments before testing on real case studies.

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# Biophysical studies of membrane perturbation induced by the antimicrobial peptide GKY20

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The resistance to conventional antibiotics in pathogen organisms (e.g. bacteria) has become a central problem in the international community. Many efforts have been made on the development of new anti-infective agents and among these the most promising are antimicrobial peptides (AMPs). (1,2) AMPs are small, cationic membrane-active peptides that exhibit broad-spectrum activity against bacteria, fungi and even viruses. Despite of their similar physical properties, AMPs share a limited sequence homology and can assume a wide range of secondary structures (e.g. α-helices and β-sheets) upon interaction with membranes whereas they show essentially a disordered structure in solution (1,3,4).

The mechanism by which AMPs interact with membranes strongly depend on the lipid composition of the membrane and on the molecular properties of the peptide (1). Great efforts have been made to elucidate the mechanism of action of AMPs and different models have been suggested (1). However, a peptide adopting solely one of those mechanisms is not common. Further, the molecular mechanism by which the peptide modify the biophysical properties of the membrane is not fully understood.

In this study, we report the physicochemical characterization of the interaction of the antimicrobial peptide GKY20 with model bio-membranes. The recombinant peptide GKY20, modelled on the $\text{Gly}^{271}$ to $\text{Ile}^{290}$ sequence of the human thrombin, was obtained as described in (5). Liposomes composed by POPC and POPC/POPG lipids were used as model of the eukaryotic plasma membrane and bacterial membrane, respectively. Far-UV circular dichroism (CD) experiments showed that the GKY20 peptide folds from a random-coil structure in solution to a more ordered structure in the presence of lipid bilayers. Steady-state fluorescence measurements revealed that GKY20 binds with higher affinity to the POPC/POPG than POPC liposomes. Further, differential scanning calorimetry (DSC) measurements revealed that GKY20 is able to induce a greater lipid perturbation in the bacterial-mimetic membrane.

The obtained results are consistent with the high antimicrobial activity and low cytotoxicity (6) of GKY20 making this antimicrobial peptide a serious candidate as antibacterial drug for biomedical applications.

*Abbrevations:*
POPC: *1-palmitoyl-2-oleoyl-sn-glycero-3-phosphocholine*
POPG: *1-palmitoyl-2-oleoyl-sn-glycero-3-phospho-1'-rac-glycerol*

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# The structural response of Human Serum Albumin to oxidation: a biological buffer to local formation of hypochlorite

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Human Serum Albumin (HSA), the most abundant protein of body fluids, has a "modular" three-domain structure potentially responding to stress by means of changes of conformation (1). Besides acting as the main carrier protein of the circulation, HSA is also an obvious target of extracellular reactive oxidant species due to its high abundance in plasma. It is for this reason considered the main anti-oxidant defense in blood (2).

This study was aimed at correlating oxidant-induced chemical and structural effects on HSA. The experiments benefited from the use of a multi-technique instrumental platform which combined the simultaneous collection of SAXS, UV-vis absorbance spectra and fluorescence emission on the same sample volume (3).

Despite the chemical modification, the native shape was preserved up to oxidant/HSA molar ratio < 80, above which a structural transition occurred in the critical oxidant/HSA molar ratio range between 80-120. This conformational variation involved the drifting of one of the end-domains from the rest of the protein and corresponded to the loss of one third of the alpha-helix and a net increase of the protein negative charge. The high reproducibility and well-defined nature of this transition suggested that it represents a structural response characteristic of this multi-domain protein that was never observed before (4).

The ability to tolerate high levels of chemical modification in a folded or only partially unfolded state, as well as the stability to aggregation, provides albumin with optimal features as a biological buffer for the local formation of oxidants.

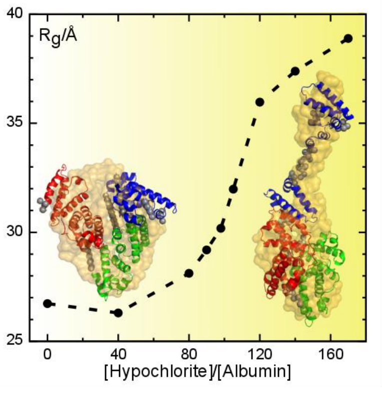

Figure: The variation of the gyration radius of HSA at increasing hypochlorite doses. The low-resolution models obtained by fitting the SAXS experimental profiles of the protein monomer in the native (left) and highly oxidized (right) conditions are also shown.

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# Electrochemical preparation of nanostructured $CeO_2$-Pt catalysts on Fe-Cr-Al alloy foams for the low-temperature combustion of methanol

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Methanol is a valuable energy feedstock for the future beyond oil and gas, due to its easy storage as a liquid at room temperature, and an excellent fuel for catalytic combustion, a process that is stable in a wide methanol/air operating range, and produces ultra-low $NO_x$, CO and VOC emissions. Lightweight catalytic burners are often realized using metal foams, due to their outstanding properties in terms of heat and mass transfer coupled with low pressure-drops and thermal resistance. Among the foam materials, Fe-Cr-Al alloy (Fecralloy) have outstanding resistance to high temperatures.

The procedures for depositing firmly anchored, homogeneous catalytic layers onto the foam substrates are often cumbersome and involve many steps. Therefore, there is interest for innovative preparation methods which take advantage of the metallic nature of the foam support, such as electrodeposition and spontaneous deposition through galvanic displacement. Both approaches are capable to form well-dispersed, homogeneously distributed noble metal nano-particles strongly adhering to the substrate (1, 2).

As a part of an ongoing research project, our groups have recently prepared Pt-based structured catalysts for the low-temperature combustion of methanol by electrochemical methods (3). These catalysts consisted of Pt nanoparticles, deposited onto Fecralloy foam supports by pulsed electrodeposition from $H_2PtCl_6$ aqueous solution, and $CeO_2$ thin films electrodeposited from a nitrate baths. Reduction of nitrates induced a local pH increase at the foam/electrolyte interface and caused the precipitation of mixtures of $Ce(OH)_3$ and $CeO_2$ , which were converted to $CeO_2$ by heating in air. The Pt loading in the catalysts was measured by ICP-MS, while the noble metal surface area was determined by cyclic voltammetry, through the H desorption charge. Although the presence of a $CeO_2$ film decreased the Pt surface area accessible to electrolyte it enhanced the performance of the catalysts towards methanol combustion, without affecting the activation energy of the process. The enhanced catalytic performance of the $CeO_2$-Pt-Feclalloy catalysts as compared to Pt-Fecralloy was ascribed to the formation of additional active sites along the interface of $CeO_2$-coated Pt nanoparticles.

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# Platinum free Electrocatalyst based on Fe-Nx moieties supported on Mesoporous Carbon prepared from polysaccharides for Oxygen Reduction Reaction

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The physical amount of platinum existing on the Earth is barely enough to cover the world demand in the next forty years for fuel cell vehicles. Furthermore, the high cost and the low durability of platinum-based catalysts are serious obstacles to the large-scale commercialization of PEMFCs. Nitrogen doped mesoporous carbons are emerging as a new class of Pt free materials for ORR (1,2) In particular, it was observed that doped carbons containing small amount of transition metals, such as Fe or Co, can catalyze the $O_2$ reduction to $H_2O$ at overpotentials comparable to that of the most active Pt catalyst (3).

In this paper, nitrogen doped mesoporous carbons containing Fe (Fe@N-MC) were prepared from agarose gel embedding an iron ($FeCl_2$, $FeSO_4$, etc.) and nitrogen (1,10-phenanthroline) precursors. The formation of a hydrogel embedding an iron metalorganic complex, assures an optimal Fe dispersion before pyrolysis. Several types of porogen agents (silica, carbamate, carbonate, etc.) were inserted to induce a hierarchy pore structure in the final pyrolyzed material. After the freeze-drying of the gel, aimed at removing the gelling solvent, the material is subjected to a first thermal treatment at 500 °C, obtaining a crude product, which is further activated at high temperature 900 °C under hydrogen flow. XPS analysis reveals the presence of various forms of iron oxides and a distinct peak due to the Fe−Nx bond at 708.6 eV (Fig. 1a). Beside Fe-Nx not visible from TEM analysis, iron is present as core shell NPs with iron oxide core and carbon shell. The catalytic performances of catalyst ink prepared from Fe@N-MC were investigated by cyclic voltammetry and by rotating ring-disk electrode in 0.1 M $HClO_4$ attesting that $O_2$ is reduced following an almost $4e^-$ pathway at very positive potentials (0.8 V vs RHE) (Fig. 1b).

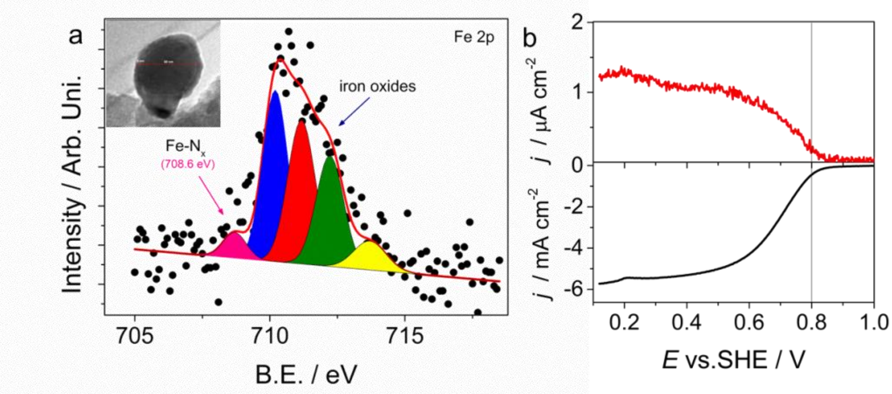

Figure 1. (a) Fe 2p XPS detailed study and deconvolution signals, and Fe NP TEM image. (b) Example of RRDE measurement on Fe@N-MC in 0.1 M $HClO_4$ at 1600 rpm and $\upsilon = 5$ mV/s.

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# Lignocellulosic Materials for Electrochemical Energy Storage and Conversion

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In the last 20 years, the Li-ion battery market has rapidly grown thanks to the extensive diffusion of mobile electronics devices. In order to lower the cost and reduce the environmental impact of batteries, efforts must be devoted to reduce the amount of inactive components in the cell, to substitute synthetic polymer binders/separators and organic solvents with low-cost and biosourced materials and to develop new eco-friendly processes for the manufacture of cell components (both electrodes and electrolyte). Natural nanoscale-microfibrillated cellulose (NMFC) fibers are readily available; they show stiffness, impressive mechanical robustness, low weight and, furthermore, their preparation process is easy and does not involve chemical reactions.

Here we review the use of paper-making technique for manufacturing:

- Bio-inspired all-paper Li-ion polymer cells, constituted by NMFC-binded paper-electrodes, and NMFC reinforced polymer electrolytes (1). The use of NMFC as filler/binder leads to produce high performing, safe and extremely flexible electrolytes for LiBs. No organic solvents or synthetic polymer binders are used during the entire electrode/electrolyte/cell preparation process.
- Cellulosic membranes as separators/electrolytes for post-lithium technologies, such as Na-ion and Li-S (2,3), thus demonstrating the possibility of obtaining “truly green” energy storage devices in the near future.
- Paper-based flexible electrodes and electrolytes for third generation solar cells (4), useful to lower oil-derived components and typical temperatures used to electrodes processing.

This materials platform is promising not only for the sustainable manufacture of energy devices components, but also for their processability at the end of life. For example, the all-paper lithium cell can be easily re-dispersed in water by simple mechanical stirring, as well as common paper handsheets and battery materials can be recovered using well-known water-based recycling process.

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# Secondary Magnesium Batteries: an Overview on Ionic Liquid -based Electrolytes

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A critical roadblock toward the development of post-lithium-ion batteries is the lack of electrolytes that are safe and electrochemically stable whilst demonstrating good compatibility with the electrode materials (1).

It was recently shown that haloaluminate ionic liquids (ILs) can provide a viable alternative to conventional electrolytes due to their low volatility, negligible flammability and good electrochemical performance (2,3,4).

Following this, an overview on recent advancements on electrolytes for secondary Magnesium batteries is presented with particular reference to imidazolium and pyrrolidinium -based ionic liquids. Insights on the interplay between structure and conductivity of $BF_4^-$, $Cl^-/AlCl_3$ and $I^-/AlI_3$ -based systems are given, thus providing an in-depth understanding of the relation between Mg-ion speciation, long-range charge transfer mechanism and electrochemical performance of this very promising class of materials.

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# Operando (photo)electrochemical X-ray absorption spectroscopy for water splitting

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Electrochemical in-situ and operando X-ray absorption spectroscopy (XAS) represents one of the most powerful available tools to study the fine structure and the behavior of electrode materials. This serves to better elucidate important reaction mechanisms and to better define structure/activity relations.

This becomes particularly crucial in electrocatalysis, for studying the oxidation state transitions and during the catalytic cycle, in photoelectrochemistry, for highlighting the local structure and the kinetics of charge recombination/transfer at surface defects and/or to study charge transfer among different layers in composite photoelectrodes.

In our recent work, we developed new methods and techniques to carry out operando XAS on electrodes and photoelectrodes with the aim of highlighting: (i) the kinetics of charge transfer across interfaces (1,2), (ii) the role of the (photo)electrode material during the reaction process (3), (iii) the role of the overlayer in composite photoelectrodes (4).

In particular, we developed FEXRAV (5), that consists in recording the absorption coefficient at a fixed energy while varying at will the electrode potential and allows to quickly map the variation of the oxidation states of the element under consideration in a desired potential window.

More recently, we carried out the first experiment on pump&probe operando XAS on a photoelectrode (6). In addition, we extended the use of energy dispersive XAS to Ir-based electrocatalysts (7) and improved the use of operando XAS for the steady-state study of photoelectrodes by recording parallel dark/light spectra adopting an innovative procedure (4).

This presentation is devoted to review some of our most significant studies, with a particular emphasis on both photoanode, ($\alpha$-$Fe_2O_3$ /$IrO_x$, $\alpha$-$Fe_2O_3$/NiO(OH)) and photocathode ($Cu_xO$) systems.

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# Hydrogen defects in Diamond. A quantum mechanical approach.

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The investigation of native and radiation-induced point-defects in diamond (as well as in other semiconductors) has attracted large theoretical and experimental interest. Diamond is a wide-bandgap material characterized by well-known extreme physical properties (high Young's modulus and thermal conductivity, broad transparency range, high carriers mobility, etc.) with attractive applications in different fields, ranging from microelectromechanical systems to heatsinks, laser windows, particle detectors, etc (1). Hydrogen, with nitrogen, is the most important impurity in diamond. It is included during the growth of natural diamond as well as in chemical vapour deposition (CVD) processes. It is certainly present at the surfaces; a non minor fraction, however, is also thought to be incorporated in the bulk. H atoms are supposed to be involved in several defects combining vacancies and nitrogen aggregates(2). It is identified through its infrared (IR) active modes (stretching and bending), although probably not all hydrogen atoms present in diamond are IR active. The sharp vibrational peaks at 3107 and 1405 $cm^{-1}$ that appear in most natural diamonds (3) have been attributed in the past to various H containing defects. Experimental evidence suggest that H is strongly bonded to a carbon atom, with weak perturbations due to nitrogen atoms (3).

Various H containing defects, in particular VN$_3$H (a vacancy surrounded by three N and one C atom, the latter being saturated with H), have been considered by using a quantum mechanical approach, a local gaussian-type basis set, hybrid functionals, the supercell scheme and the CRYSTAL code (4). The same scheme has recently been used for describing the vacancy (5) and interstitial (6). Various properties (structural, electronic vibrational) have been used for a complete identification of the defect. The Infrared spectra (wavenumbers and intensities, evaluated analytically through the Coupled Perturbed Hartree-Fock method) are generated and compared with experiments.

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# Proton Mobility in Protic Ionic Liquids: New Results from Theoretical Calculations.

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Ionic liquids (ILs) are salts made by bulky, sterically mismatched molecular ions that possess a low melting point because the electrostatic interactions are weakened by charge delocalization and lattice formation frustrated by geometric effects. In contrast to traditional organic solvents, ILs possess negligible flammability and volatility and represent a new class of "green" solvents that are inherently safer than conventional solvents. A Protic Ionic Liquid (PIL) is formed through an acid base reaction. When the difference of pKa between the acid and the conjugate acid of the base is large (>10 pKa units) the ensuing liquid is completely ionized. In this case, the acidic proton is transferred quantitatively from the acid to the base during the synthesis reaction and turns out to be strongly bound to the latter. Subsequent proton transfer is therefore not possible. Conduction in these liquids is therefore due to ion drift (Walden mechanism) and inversely proportional to the liquid viscosity. In order to have a larger conductivity one has to find a way to promote the formation of different charge carriers. One possibility is to have proton transfer from one molecular ion to another. Compounds where amino acids in their deprotonated (anionic) form are combined with inorganic cations such as [Ch][Asp] and [Ch][Cys] might have these features. The former has a weak acid terminal, while the latter has a weak basic proton attached to the sulphur atom. We will show evidences of a non-ordinary behavior of these two materials that have been obtained by carefully validated ab-initio and classical molecular dynamics simulations [1].

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# Computational Tools for the Interpretation of Rotational Spectra within the Virtual Multifrequency Spectrometer

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Spectroscopic techniques provide a wealth of qualitative and quantitative information on the chemical and physical-chemical properties of molecular systems, in a variety of environments. However, the interpretation of experimental data is often a difficult task mainly because the observed spectroscopic properties depend on the subtle interplay of different effects, whose specific impact on the overall behavior is difficult to address. From this point of view, theoretical approaches are invaluable tools for guiding and complementing experiment as well as supporting the interpretation of spectra. For this reason, measurements are increasingly supported by theoretical studies, and computational spectroscopic techniques have become essential tools for understanding spectra in terms of basic physical-chemical process. The widespread use of computational spectroscopy has prompted the development of a virtual multifrequency spectrometer (VMS), which gives access to the latest developments in the field of computational spectroscopy also to non-specialists (1-4). In addition to the computational module (VMS-Comp), which provides the support for a wide range of spectroscopic techniques, it features VMS-Draw. This is a multiplatform graphical user interface (GUI), which offers to the user a powerful integrated environment for processing the outcomes of quantum-chemical calculations and visualizing the relevant information in an intuitive way. In addition, VMS-Draw includes a panel of advanced tools for the comparison of theoretical and experimental spectra, thus assisting their interpretation. In this contribution, we present VMS with particular attention to its newborn rotational spectroscopy module, VMS-Rot. VMS-Rot has been specifically designed for guiding the assignment and interpretation of rotational spectra: from the assignment of the observed transitions to a set of quantum numbers, as well as their fitting with a given model Hamiltonian, to the prediction and simulation of the whole spectrum. Given the general philosophy of VMS and the leading role played by quantum-chemical calculations in modern rotational spectroscopy, unlike other software supporting the analysis of MW spectra, VMS-Rot is intimately related to theoretical calculations, to be used as a starting point for guiding experiments and spectral interpretations. VMS-Rot is composed of four closely related modules, namely (i) the computational engine that allows spectroscopic parameters to be computed from first principles; (ii) the fitting-prediction engine that allows the refinement of the spectroscopic parameters, based on the assigned transitions, and the calculation of the simulated spectrum. (iii) the GUI that allows the comparison between theoretical and experimental spectra, aided by a number of advanced features for spectra manipulation and (iv) the assignment tool that takes care of the assignment of the rotational spectrum recorded experimentally by comparison with the simulated one. An overview of the range of applicability of VMS-Rot is given in order to demonstrate how this module of VMS represents a one-pot solution for the analysis of rotational spectra based on the interpretation of experimental measurements supported by quantum chemical simulations.

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# Calorimetry and Thermoanalytical Techniques in the Study of Proteins

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Thermal analysis and calorimetry, particularly when combined with other analytical and spectroscopic techniques, offer powerful methods for studying biological macromolecules. Here, we present and discuss the application of calorimetry and thermogravimetric analysis to the study of the conformational behavior of proteins in three cases belonging to very different fields, ranging from the use as binders in tempera paintings, to medical or pharmaceutical applications. The first issue concerns with proteinaceous materials used as paint media in order to disperse and apply pigments. Over the centuries, animal glue, egg and milk or casein have been the most common proteinaceous binders used in tempera technique. The characterization of these paints is complex because of the sample size, the high inorganic content, the degradation phenomena undergone with time, and the simultaneous presence of other organic materials. We used a combined approach (Thermogravimetric Analysis, TGA, Differential Scanning Calorimetry, DSC, Fourier Transform Infrared Spectroscopy, FTIR) to investigate the interaction occurring between selected pigments and ovalbumin, casein, and rabbit glue as well as their changes with ageing. This allowed us to characterize the molecular modifications undergone by proteins as an effect of light ageing, and depending on the pigment, in terms of amino acid side chain oxidations, cross linking/aggregation, hydrolysis, and the formation of stable complexes. We highlighted that in most cases the inorganic pigments interact with proteins by decreasing their thermal stability and their intermolecular β-sheet content, and that ageing induces aggregation. The second issue concerns with some biocompatible nanomaterials suitable to be used in biotechnological and medical applications. We focused our attention on alloysite nanotubes (HNTs) which are considered very promising as nanocarriers, because of their low cost, high availability, biocompatibility, atoxicity, anti-inflammatory properties, and capacity to maintain the biological activity of immobilized enzymes. HNTs can be loaded with a wide range of molecules, from antioxidants to antibiotics, anticancer, and anti-inflammatory drugs and can be used for drug delivery, as tablets and capsule fillers. Therefore, to study their interaction with proteins is important because of the general concern regarding the safety of nanoparticles and the modifications that loaded biological material may undergo with alteration of their biological functions. We studied the interaction between HNTs and some proteins (bovine serum albumin, α-lactalbumin and β–lactoglobulin) loaded into HTNs, by using TGA and FTIR. These techniques enable us to assess the protein conformation and thermal stability, respectively, and to estimate the amount of protein loaded into the HNTs.

Finally, as the third issue, we show here some preliminary results on the use of protein-polymer conjugates in order to improve the properties of therapeutic proteins. It is well known that proteins and peptides exhibit great potentialities as therapeutic agents; however, they also show severe drawbacks (low solubility in water, tendency to agglomerate during storage in solution, short shelf-life, rapid kidney clearance, destruction by proteolytic enzymes, propensity to generate neutralizing antibodies). One of the most promising modification for overcoming these drawbacks is the covalent attachment of synthetic polymers (the most common being PEG) to the protein, to form protein-polymer conjugates with the aim of improving both the stability and the pharmacokinetics properties of the drug. In particular, we present some preliminary results obtained by TGA and DSC measurements on Myoglobin-PEG and myoglobin-polyphosphoesters conjugates. In fact, polyphosphoesters (PPEs) are one of the most promising new classes of polymers in biomedicine.

# Exploiting conformation and structural analysis of endogenous miRNAs to refine gene targeting evaluation

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Mature microRNAs (miRNAs) are a class of evolutionally conserved, single-stranded, small (approximately 19−23 nucleotides), endogenously expressed, and non-protein-coding RNAs that act as post-transcriptional regulators of gene expression in a broad range of animals, plants, and viruses.(1,2) The biogenesis of miRNAs is a multiple step process, which complete with the incorporation of the mature miRNA into RNA-induced silencing complex.(3) The RISC complex functions by perfectly or imperfectly matching with its complementary target mRNA, and induces target mRNA degradation or translational inhibition. Thus, alterative expression of miRNAs has been associated with a number of diseases, genetic disorders and tumors progression.(3)

We think that the knowledge of the miRNA structure may give a new insight into miRNA-dependent gene regulation mechanism and be a step forward in the understanding their function and involvement in cancerogenesis. With this aim we characterized the conformation and structures adopted by several endogenous miRNA in physiological conditions. Preliminary data obtained by CD melting experiments, using synthetic miRNA,(4) highlighted the important role played by the structures adopted by miRNA. Indeed the sequences showed a sigmoidal CD melting curves induced a significant inhibition of the luciferase activity for two of the most prominent genes associated to lung cancer, c-MET and Epidermal Growth Factor Receptor (EGFR).

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# Identification and characterization of DNA G-quadruplex interacting proteins

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Guanine-rich DNA sequences can form non-canonical structures known as G-quadruplexes (G4s). These peculiar structural arrangements emerged as biologically significant due to compelling evidence that they participate in several biological processes. Experimental evidences imply that G4 DNA structures are, for example, involved in tumorigenic processes, probably with regulatory functions, and that various proteins are involved in the recognition of these structures and modulate their effect on such processes.

The analysis of the G4–protein interaction network can be considered a crucial point to clarify the elusive biological mechanisms in which such relevant DNA structures could be implicated. Some proteins are able to recognize G4 structures and some are also able to unfold them. The discovery of these proteins raises interesting questions regarding the dynamic nature and function of such structures within the genome, especially at telomere, a region of repetitive G-rich sequences at each end of chromosomes. In this frame, we decided to search for proteins able to recognize G4-forming truncations of human telomeric DNA sequence (1). In particular, we employed a chemoproteomic-driven approach, where the molecule of interest is used as a bait to fish out its interactors from nuclear extracts. In particular, we have used different G4 conformations, namely the parallel and the anti-parallel folds. Very interestingly, novel G4-interacting partners were identified, thus suggesting a possible, and so far unknown, role of these proteins. In this communication, the latest results will be presented, including a preliminary structural study of the interaction between the HMGB1 protein and the parallel telomeric G4 structure.

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# FIB-FESEM-EDX study of silver Roman coins: characterization of the core microstructure and corrosion products with a multi-analytical approach

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Metal artifacts are among the most common materials in the Cultural Heritage field: alloys have been used in several fields of everyday life and their analysis can prove useful information about the technology of the ancient populations. In particular, coins are important for studying provenance, dating, minting and corrosion processes as well as provenance and stratigraphy of the archaeological sites (1,2).

In this work a set of Roman silver coins, dated back to the Antonini's period, has been analyzed using FIB-FESEM-EDX aiming to establish the used technique for the silvering and discriminating different mints. Recently, this approach was used as a complementary technique for the characterization of bronze coins (3) but this is the first application on Roman silver coins. The aim of this work is to investigate the microstructure and the composition of the alloy with a micro-invasive approach. Commonly to investigate the composition of the metal core are used invasive and destructive techniques, therefore the developing of methods with minimal damage on metal is of a great interest.

The study of Antonini's coins is also important as in that historical period Roman Empire underwent to a severe debasement which influenced coinage, so the surface silvering it is still an open question. Diocletian in the 294 A.D. introduced a complex alloy (Cu-Sn-Pb-Ag) with an Ag-rich surface patina of 2 µm. Some coins of the set show a very fine silvered surface with a core composition entirely made of Cu, whereas others have the composition made of Sn-Cu-Pb with a very low concentration of Ag. This technique has been joined with surface analysis (Raman spectroscopy, SEM mapping, voltammetry of microparticles (VMP) and electrochemical impedance spectroscopy (EIS)) for a deeper knowledge of the samples. The results showed the leaching of the Sn and Pb as well as of the Cu that formed several common products on the surface of the coins, *i.e*, $Cu_2O$, CuO, PbO, SnO. The presence of AgCl has been detected in several coins.

In conclusion, FIB-FESEM-EDX analysis provides information about the composition, structure and thickness of the metal patina as well as the composition and microstructure of the metallic core which in turn reflects the technology of minting. As a result, FIB-FESEM-EDX features yield information for the diagnostic, authentication, technologies and historical context in which the coins were fabricated. Such multi-analytical data allow us the possibility of screening the coins minting, obtaining significant differences between those minted in Roma and those minted in the Gallia.

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# I materiali e la tecnica pittorica di Konrad Witz nel suo capolavoro di Ginevra

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Konrad Witz, tedesco di origine, ma attivo soprattutto in Svizzera fra il 1431 e il 1445 circa, è, per dirla con le parole dello storico dell'arte Jonathan Jones, "un gigante della pittura medievale che aspetta solo di essere scoperto". Le opere superstiti di questo artista sono davvero poche; fra queste sicuramente le più importanti sono le due tavole dipinte nel 1444 su entrambi i lati per l'altare maggiore della Cattedrale di Ginevra ed ora conservate nel Musée d'art et d'histoire de Genève (1). Il presente studio illustra i risultati della campagna diagnostica condotta, prima dell'intervento di restauro, sui materiali costitutivi, la tecnica esecutiva e lo stato di conservazione di queste opere. Le indagini scientifiche sono state condotte dapprima mediante tecniche strumentali non invasive, successivamente su microcampioni prelevati in modo mirato dopo l'acquisizione dei dati delle analisi preliminari.

Gli obiettivi delle indagini sono così sintetizzati:

- osservazione in situ della superficie delle opere mediante l'impiego di microscopia a bassi ingrandimenti, in luce visibile e UV, per osservare lo stato di conservazione della pellicola pittorica originale e differenziare le parti originali dalle eventuali ridipinture;
- analisi XRF in più punti delle superfici policrome per avere dati preliminari sulla composizione degli elementi chimici e orientare la scelta dei prelievi di campione;
- esame chimico-stratigrafico di campioni di materiale pittorico per documentare la composizione delle stratificazioni dei materiali costitutivi, dalla preparazione fino alle vernici superficiali, e avere così informazioni circa la tecnica esecutiva;
- identificazione delle cariche minerali negli strati preparatori e dei pigmenti nelle stesure pittoriche;
- riconoscimento, mediante test microchimici ed istochimici, delle classi di appartenenza dei leganti organici nelle varie stratificazioni;
- identificazione dei leganti pittorici mediante gascromatografia abbinata alla spettrometria di massa (GC-MS).

Una prima ricognizione delle superfici pittoriche delle quattro opere è stata effettuata mediante l'impiego di uno stereo-microscopio operativo con sorgenti di luce visibile e UV. Successivamente, sono state analizzate le superfici pittoriche mediante uno spettrofotometro portatile a raggi X (XRF). Sui dipinti sono state, inoltre, eseguite indagini radiografiche e riflettografiche all'IR per studiarne lo stato di conservazione e esaminare i dettagliati disegni preparatori. Una volta acquisite in situ tutte queste informazioni sono stati effettuati sedici microprelievi di materiale pittorico in zone ritenute maggiormente significative in relazione alle domande di conoscenza.

I test microanalitici impiegati sono stati finalizzati alla ricerca di sostanze proteiche, composti saponificabili e polisaccaridi. Le analisi rivolte all'identificazione dei leganti organici sono state condotte mediante microspettroscopia infrarossa a trasformate di Fourier e gascromatografia accoppiata alla spettrometria di massa (GC/MS).

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# Towards the Non-invasive Proteomic Analysis of Cultural Heritage and Archaeological Objects

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During the last years, there has been a growing interest in the identification of proteinaceous material of cultural heritage and archaeological objects. Our group recently developed a new method for the non-invasive analysis of proteins material from precious and ancient artworks. The technique uses a functionalized film that extracts the proteins from the surface of the object. The extracted proteins are then analyzed by LC-MS/MS analysis using shotgun proteomics (1).

In this research, we will present the application of this method to several historical and archaeological samples. Moreover, we will discuss the analytical performances for the identification and quantification of proteins in complex matrixes.

In particular, we will present the developed protocol and the results obtained from the analysis of several artworks: a polychrome wooden altarpiece from the Maestro of Oropa, a polychrome sandstone capital, a rare polychrome alabaster, several wood medieval and renaissance panels (Pietro Gallo from Alba, Defendente Ferrari, Martino Spanzotti, Jean Bapteur, Gerolamo Giovenone) and a detached fresco from Antoine de Lonhy.

Moreover, through the use of this method we were able to identify the animal origin of an old precious manuscript from Domenico della Rovere (XIV century) as well as the binders from a rare sample of painted leather casket from Parisian manufactory (beginning of XIV century).

The analysis of the bottom of several greek vessels (Pyxis, Krater, Kylix cup and Kantharos) revealed the presence of animal origin proteins.

In conclusion, this study will report the first use of this non-invasive method for the characterization of proteins from ancient objects without the need to transport or sampling the artifacts.

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# Comunicazioni Poster

# Single Crystal to Single Crystal Transformations In A Cyclic Hexapeptoid

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Cyclic alpha-peptoids are peptido-mimetic compounds which represent interesting building blocks for the design and synthesis of artificial systems at the frontier between materials science and biology (1). Peptoids differ from peptides in the side chains, which are shifted by one position along the peptide backbone to the nitrogen atom to give N-substituted oligoglycine. The lack of the amide proton prevents the formation of NH•••OC hydrogen bonds and weaker interactions, as CH•••OC hydrogen bonds and CH-pi interactions, play a key role. Inter-annular CH•••OC hydrogen bonds can provide face to face or side by side arrangement of macrocycles mimicking beta-sheet secondary structure in proteins (2). In particular, the side chains have a key role in the solid state assembly of peptoid macrocycles promoting the formation of peptoid nanotubes by acting as pillars, extending vertically with respect to the macrocycle planes (3,4). Moreover conformational flexibility of cyclic peptoids can lead to unexpected solid state dynamic properties (5).

Single crystal X-ray diffraction, hot stage microscopy, DSC and TGA helped in exploring the landscape of crystal forms for a cyclic hexapeptoid decorated with four methoxyethyl and two propargyl side chains (compound **1** in Figure 1). Interestingly single crystal to single crystal transformation were detected and characterized by in situ variable temperature single crystal X-ray diffraction.

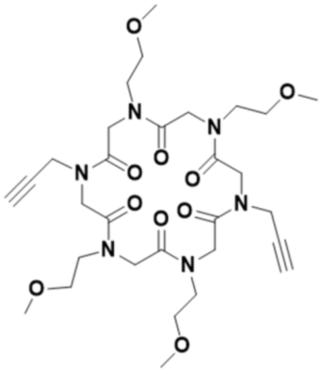

**Figure 1**

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# Hirshfeld Analysis Of The Solid State Assembly Of Cyclic Octapeptoids

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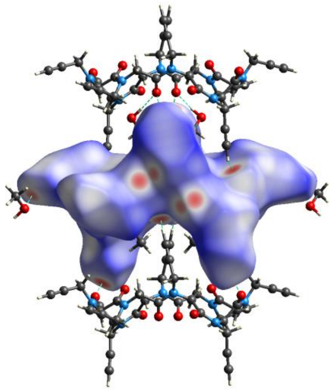
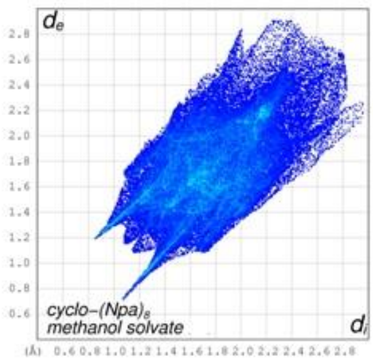
Cyclic peptoids for their biostability and potential diversity seem to be the ideal candidates to evoke biological activities and novel chemical properties (1,2).

Peptoids differ from peptides in the backbone position of the side chains, which are attached to the nitrogen atoms. CH···OC hydrogen bonds play a key role in the solid-state assembly of cyclic α-peptoids: face to face or side by side arrangement of the macrocycles mimick β-sheet secondary structure in proteins (3). In particular side chains may act as pillars, extending vertically with respect to the macrocycle plane, inducing the columnar arrangement of the peptoid macrocycles (3).

The structural diversity of the solid state assembly of cyclic peptoid is accompanied by peculiar host-guest chemistry and sorption properties (4-6). Hirshfeld surface analysis revealed to be extremely useful in fingerprinting the molecular interactions that lead to the solid state molecular assembly with particular reference to the role of the guest molecules (3-5).





In figure as an example it is shown the Hirshfeld surface analysis for the compound cyclo-(Npa)$_8$, *Npa* = *N*-(propargyl)glycine, which crystallizes as methanol solvate. The shortest contacts are depicted as green dotted lines. The Hirshfeld surface mapped with $d_{\mathrm{norm}}$ is shown on the left, as viewed along the *c* axis to allow a better view of the closest contacts leading to the formation of a peptoid nanotube, also the closest contacts with methanol molecules are evidenced. The corresponding fingerprint plot is shown on the right.

We will describe in details the results obtained by applying the Hirshfeld surface analysis to a library of cyclic octapeptoids decorated with propargyl and/or methoxyethyl side chains.

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# Self-assembly of peptide nanostructures driven by graphene oxide nanoplatforms

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Over the last 20 years, self-assembled peptide nanostructures have been investigated as biomaterials due to their impressive potential to be used in different bio-nanotechnological applications such as sensors, drug delivery systems, bioelectronics, tissue reparation, among others (1,2). Through self-assembly, peptides can give rise to a range of well-defined nanostructures such as nanotubes, nanofibers, nanoparticles, nanotapes, gels and nanorods. In the present work, we investigated both experimentally and theoretically the self-assembly process of the hydrophobic phenylalanine (FF) and its analogous tyrosine (YY) dipeptides, in the presence or not of graphene oxide (GO) nanosheets.

The CD, UV-vis and fluorescence spectroscopies revealed that YY is able to form ordered nanostructures similarly to YY, already at short incubation time (< 2 h) and in ultrapure water. In the presence of GO dispersion, the formation of ordered structures was also found, with a conformational stability) higher than the dipeptides alone at longer incubation time (< 72 h). QM calculations well reproduced the experimental findings pointing to the preeminence of intermolecular instead of intramolecular interactions. Atomic force microscopy showed the peptide-specific ‘decoration’ of GO nanosheets, with FF molecules gathering at the GO edges whereas the YY preferentially collect onto the GO basal plans. Moreover, QCM-D analyses, performed to scrutinise the GO-dipeptide interface interactions, highlighted different viscoelastic responses of the GO-YY and GO-FF adlayers, respectively.

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# On the sodium alginate aqueous solutions and nanodispersions flow behavior

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Hydrocolloids are widely used in different industrial fields to perform a number of functions including thickening and gelling of aqueous solutions, stabilizing foams, emulsions dispersions and so on (1).

Sodium alginate, due to its biocompatibility, non toxicity, and biodegradability, is a good candidate for food and biomedical applications (2). An accurate study of the rheological and conductivity behaviors of this polymer could help in the formulation of supramolecular systems that can be used as edible coatings and films to preserve food products (3,4).

In this study, rheological behavior and conductivity of aqueous solutions with different sodium alginate concentrations were evaluated by tuning temperature and polyelectrolyte viscosity. As expected, lower polymer concentrations gave low values of conductivity and viscosity (5).

Two of the polymer aqueous solutions considered were then chosen as continuous phase for the realization of dispersions obtained by adding a surface active agent (Tween 80) and a lipid component, lemongrass essential oil, selected for its antimicrobial activity against pathogenic microorganisms (6).

Viscosity and conductivity were measured on the produced dispersions in order to evaluate how different type energy sources (homogenization and sonication) and the addition of surfactant and lipid phase could affect the dispersion properties. In particular the effect of essential oil amounts on the emulsion properties were evaluated.

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# Food-grade nanocarriers for protection and delivery of bioactive compounds

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The encapsulation of active ingredients into nanoemulsions as carrier systems is a novel approach for drug delivery. Nanoemulsions are considered to be more stable than classical emulsions thanks to the smaller droplet size that minimizes the particle aggregation and gravitation separation. These systems are generally employed for encapsulation of hydrophobic bioactive compounds to improve their solubility, chemical stability and oral bioavailability. One of the most important and extensively researched bioactive molecules is the curcumin. It is considered highly effective against colorectal and pancreatic cancer (1) thanks to its ability to interfere with various biochemical pathways (2). These aspects make curcumin an interesting molecule as a bioactive agent in functional foods, supplements, and pharmaceuticals. Nevertheless, the main challenge that currently limits the incorporation of curcumin into commercial products is its low water-solubility, chemical instability, and poor oral bioavailability (3,4). In this study, an oil-in-water nanoemulsion, stabilized by either surfactant (Tween 20) and/or Sodium Caseinate, was proposed to encapsulate curcumin. The stability of the host emulsion system was studied according to time, temperature and pH changes. The characterization of the proposed system was carried out through dynamic light scattering and rheometry measurements in order to investigate on size, stability and viscosity of the preparation. The loading ability of curcumin, detected through molecular spectroscopy, varied with the emulsifier type and concentration.

The outcomes of this study provide useful information on the relationship between the emulsion composition and the bioavailability of an important molecule, like curcumin and other similar molecules.

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# Encapsulation and release of hydrophilic and lipophilic molecules from layer by-layer assembled capsules

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Polyelectrolyte capsules produced through layer-by-layer (LbL) method have been assembled by alternatively depositing anionic and cationic polymer layers onto liposomes cores (1-3). High and low molecular weight molecules were entrapped into the liposome core before the polyelectrolyte deposition. The release of the loaded molecules from the nanocapsules was demonstrated.

The combination of dynamic light scattering (DLS), ζ-potential, and transmission electron microscopy (TEM) techniques provided detailed information on the stability, dimensions, charge, and wall thickness of these polyelectrolyte globules. TEM microphotographs demonstrate the presence of nanocapsules with an average diameter of below 300 nm and with a polyelectrolyte wall thickness of about 20-25 nm.

Transport behavior through the multishell wall was detected for the diffusion of the entrapped molecules (4,5) Additionally, it was proven that the proposed nanocapsules appear to be appropriate for prolonged molecule compartmentalization and protection, even for molecules having low molecular weight. The influence of pH and wall thickness on the release properties were also considered. As a whole, vesicle templated polyelectrolyte nanocapsules show great potential as novel controllable drug-delivery devices for biomedical and biotechnological applications

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# Supramolecular complexes based on Chlorophyll *a*/Cyclodextrins for Photodynamic Therapy (PDT) applications

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The natural porphyrin Chlorophyll *a* (Chl *a*) has the features of a good photosensitizer for photodynamic therapy (PDT) applications. Indeed, when photoactivated, this molecule is able to induce the production of reactive oxygen species, such as $H_2O_2$, superoxide radical anion ($^{\bullet}O_2^{-}$) and, in particular, $^1O_2$ (1, 2, 3). Since Chl *a* has a lacking solubility in water and high tendency to aggregate, in this study, it was first included into different cyclodextrins (CDs) to form stable water-soluble supramolecular complexes (4), then the PDT performance of Chl *a*/CDs complexes was evaluated. 2-Hydroxypropyl-β-cyclodextrin (2-HP-β-CD), 2-Hydroxypropyl-γ-cyclodextrin (2-HP-γ-CD), Heptakis(2,6-di-*o*-methyl)-β-cyclodextrin (DIMEB) and Heptakis(2,3,6-tri-*o*-methyl)-β-cyclodextrin (TRIMEB) were used to solubilize the Chl *a* into aqueous environments. The chemical physical properties of Chl *a*/cyclodextrins complexes in cellular medium were studied by means of UV–Vis absorption spectroscopy demonstrating the better aptitude of 2-HP-β-CD and 2-HP-γ-CD than the other CDs to solubilize Chl *a* in cell culture medium in monomeric form.

Consequently, Chl *a/*2-HP-β-CD and Chl *a/*2-HP-γ-CD supramolecular complexes were tested *in vitro* on the human colorectal adenocarcinoma HT-29 cell line to evaluate their photodynamic effects. As shown by MTT tests, both supramolecular complexes exhibited no dark toxicity and a high phototoxicity toward HT-29 cells promoting a high percentage of cell death, after illumination, particularly when high concentration of Chl *a* and long incubation time were used. When the higher dose of the photosensitizer was used ($5 \cdot 10^{-5}$ M), the relative survival rate was about 10% after 24 hours of incubation, for both studied systems.

Cellular uptake of porphyrin was determined by means of fluorescence measurements and intracellular localization was evaluated by confocal microscopy proving that Chl *a* was localized primarily in lysosomal organelles of HT-29 cells. Moreover, flow cytometric analysis demonstrated that the cell death occurred by necrotic mechanisms.

Therefore, it is possible to affirm that supramolecular complexes based on cyclodextrins not only are promising formulations for loading natural Chl *a*, but also that Chlorophyll *a*/cyclodextrins complexes have great potentials for therapeutic applications.

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# Cytotoxicity of red-emitting CdSe@ZnS nanocrystals embedded in Liposomes

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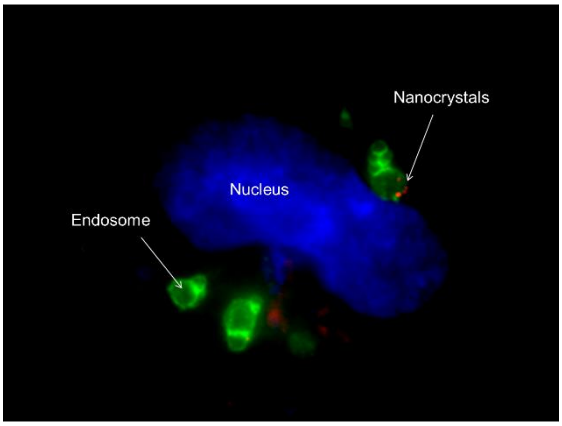

Fluorescent nanocrystals (NCs) are an advantageous alternative to conventional organic fluorescent dyes for bioimaging applications (1) and their toxicological evaluation is currently a primary field of research. In this work, the micelle-to-vesicle transition (MVT) method was applied to the encapsulation of hydrophobic and highly fluorescent CdSe@ZnS NCs into the lipid bilayer of liposomes (2). The obtained aqueous NC−Liposome preserved the spectroscopic characteristics of the pristine NCs. Then, the in vitro toxicological effects on HeLa cells of these red emitting NC-Liposomes were carried out. In addition, we evaluated the effect of the lipid carrier on the cell toxicity by using liposomes of different phospholipid composition. The toxic effects of NCs, evaluated by cells proliferation, cell death study and MTT test on HeLa cells at concentrations up to 20 nM, are negligible compared to those of the lipid carrier, especially when this is constituted by DOTAP, a cationic phospholipid. The obtained data suggest that DOTAP has a dose- and time-dependent toxic effect on HeLa cells, while the addition of PEG to the liposome formulation does not alter significantly the viability of the cells. The ability of NC-Liposomes to penetrate HeLa cells was also assessed by fluorescence and confocal microscopy investigation. Obtained images show that NC-Liposomes are internalized into HeLa cells through the endocytic pathway, enter early endosomes and reach lysosomes in about 1 h. NCs co-localized with endosome vesicles and were positioned at the limiting membrane of these organelles. Experimental results suggest that the system as a whole, hydrophobic NCs and its lipid carrier, should be considered for the development of fully safe biological applications of CdSe@ZnS NCs, providing essential indications to define the optimal conditions to use the proposed system as optical probe for both in vitro and in vivo investigations.

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# A photoelectrochemical transduction system based on solubilized photosynthetic reaction center proteins

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The screen-printing technology in electrochemical applications offers the possibility to produce a large number of electrochemical (bio-)assays at low cost. Intrinsic characteristics and reproducibility of screen-printed electrodes make them extremely versatile in the development of a wide range of electrochemical devices (1). In this work we have characterized a miniaturized photoelectrochemical transduction system represented by a screen-printed electrochemical cell dipped in an aqueous electrolyte, containing photosynthetic reaction center (RC) enzymes, extracted from the phototrophic bacterium *Rhodobacter sphaeroides*, and suitable redox mediators.

*In vivo*, RC enzymes act as photocatalysts promoting the transfer of two electrons from two ferrocytochrome proteins (electron donor) to a ubiquinone molecule (electron acceptor) upon absorption of two photons. Photocurrent generation in RC-based photoelectrochemical cells (PECs) occurs when RC photocycle is sustained by light in the presence of either physiological or synthetic electron donors and acceptors, acting as redox mediators between protein and electrodes (2).

The ability of our device to generate photocurrents under illumination has been assessed and the factors limiting (or enhancing) the photoresponse have been investigated. The efficiency of ferrocenemethanol and decylubiquinone in performing the role of electron donor and acceptor in our PEC has been demonstrated. Moreover, a theoretical model has been proposed, able to describe the chronoamperometry profiles with high accuracy. This model has allowed obtaining, under light and in the dark, the concentration of all involved species as a function of time, both in the bulk and in proximity of working and counter electrodes. The results achieved show that the steady photocurrent is the result of a fine balance between photochemical reaction, reverse chemical reaction and mass transfer processes involving bulk and electrodes/solution interfaces.

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# Functional incorporation of bacterial photosynthetic reaction centers in polydopamine nanospheres

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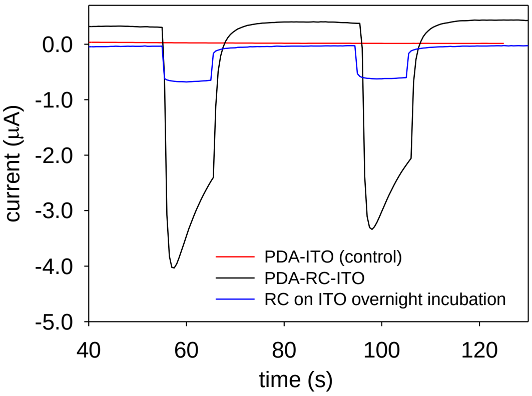
Polydopamine (PDA) nanospheres have recently gained great attention as a new material with the potential to incorporate various molecules meanwhile firmly immobilizing them onto different surfaces (1). The intriguing possibility of incorporating proteins maintaining their biocatalytic activity is currently a “hot” field of investigation with promising perspectives. In this work, we offer a characterization of the behavior of the bacterial photosynthetic reaction center (RC) from *Rhodobacter sphaeroides* incorporated in polydopamine nanospheres either dispersed in solution or immobilized onto ITO-covered glass slides. RC is a membrane-spanning pigment-protein complex that, upon illumination, produces a stable charge-separated state (2). This electron-hole pair can be used, with the help of suitable mediators, to produce photocurrents, making RCs a good model for basic studies of protein activity immobilized in bioactive films (3). Herein, we first report that, upon oxygen-assisted dopamine polymerization in the presence of the protein, RC (a) is incorporated, (b) is capable to generate the charge-separated state, and (c) to produce photocurrents in a properly designed electrochemical setup either when immobilized onto ITO (used as working electrode) and when suspended in solution in the presence of the electron donor ferrocenemethanol (FcnMeOH) and the electron acceptor decylubiquinone (dQ). Upon illumination, RC promotes the reduction of dQ to dQH2 by withdrawing electrons from FcnMeOH. The incorporation of RC into PDA has been carried out either in Tris and in Phosphate buffer at pH 8 at increasing dopamine concentration using an overnight incubation at room temperature. We found that in Tris the complete incorporation of RC occurs at lower dopamine concentration with respect to phosphate. For maximal RC photoactivity when immobilized onto ITO we found that it is important to maximize the RC/PDA ratio, possibly because increasing the PDA matrix decreases the amount of light available for RC excitation and/or the interaction of the mediators with the RC active sites and the electrode surface is unpaired. Moreover, it is possible also to co-incorporate FcnMeOH and dQ in the PDA film, so that the photocurrents can be detected only by using ferrocyanide as electrochemical mediator at the counter electrode.



Photocurrents detected using RC-PDA covered ITO as WE (black trace), bare ITO (red trace) and ITO after overnight incubation with RC (blue trace).

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# Photosynthetic Reaction Centers exposed to ultrasounds: effect on structure and function

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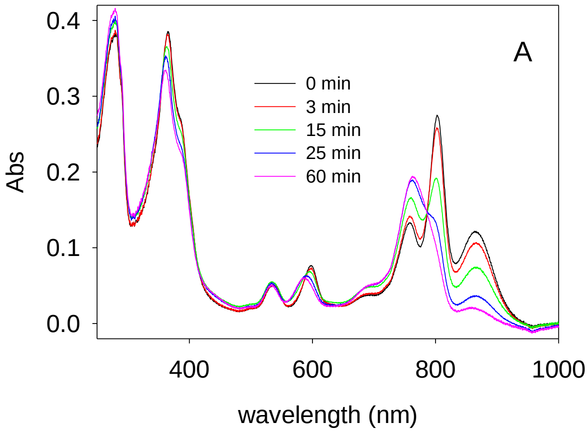

Ultrasounds are used in many industrial, medical and research applications, for example for equipment cleaning, milk homogenization (1), microorganisms and enzymes inactivation (2), liposome preparation, drug delivery (3), liposuction, tumor ablation and kidney stone disruption. Properties and function of proteins are strongly influenced by the interaction with the ultrasonic waves and their bioactivity can be lost because of alteration of protein structure. A systematic study of ultrasounds effect on Integral Membrane Proteins (IMPs), which are responsible for a variety of fundamental biological functions is lacking in literature. We have undertaken this subject using the photosynthetic Reaction Center (RC) of the bacterium *Rhodobacter sphaeroides* as a model for assessing the ultrasound-induced IMP denaturation. Purified RCs were suspended in i) detergent micelles, in ii) detergent-free buffer and iii) reconstituted in liposomes, and then treated with ultrasound at 30 W and 20 kHz at increasing times. The advantage of using RCs is that they have an optical spectrum rich in diagnostic signals that can be used for monitoring the protein integrity. In particular, the bands at 760, 800 and 865 nm are in the ratio 1:2:1 in the native protein, while progressive denaturation results in a decrease of the 865 nm band and increase of the 760 nm one. The optical absorption spectra (shown in the figure for the case of detergent) indicated a progressive and irreversible denaturation in all cases, resulting from the perturbation of the protein scaffold structure, as confirmed by circular dichroism spectra that showed progressive alterations of the RC secondary structure. The functionality of the RC can be assayed with time resolved optical spectroscopy, since after light excitation it forms a charge separated state. The amplitude of the subsequent dark charge recombination signal at 865 nm is diagnostic of protein photoactivity. The lifetime for the loss of RC photoactivity was of 32 min in detergent micelles, ranged from 3.8 to 6.5 min in the different proteoliposomes formulations, and of 5.5 min in detergent-free buffer. Atomic force microscopy revealed the formation of large RC aggregates related to the sonication-induced denaturation, in agreement with the scattering increase observed in solution.

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# Targeting DNA G-quadruplex in KRAS oncogene promoter: computational, calorimetric, and spectroscopic studies

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The discovery of G-quadruplex structures in G-rich DNA sequences has shed light on new functions for DNA in biology. G-quadruplexes (G4) are nucleic acid structures formed in relevant genomic regions, as telomeres and oncogene promoters. Recently, cellular studies proved the *in vivo* existence of G4, confirming their key role in living cells (1). A growing body of evidence supports the idea that G4-DNA formed by promoter sequences is involved in the regulation of gene expression.

KRAS is one of the most frequently mutated oncogenes involved in the pathogenesis of different types of cancers, such as colorectal and pancreatic carcinoma. Its promoter contains a nuclease hypersensitive element (NHE) with repetitive guanine residues able to fold in DNA G4 (2). An effective anticancer therapy may be obtained targeting the G4 formed in this oncogene promoter.

We identified a pool of ligands through receptor-based high-throughput virtual screening (HTVS) starting from the recently determined NMR structure (3). A rapid screening of the affinity of the identified ligands was obtained by circular dichroism melting experiments. After this screening, several derivatives of the best ligand were synthesized to improve the affinity for KRAS G4 and the selectivity against DNA double helix.

The affinity, the binding stoichiometry and all the thermodynamic parameters related to the association processes were obtained by means of Isothermal Titration Calorimetry (ITC), Circular Dichroism (CD) and fluorescence (for the ligands containing chromophoric groups). Differential Scanning Calorimetry (DSC) measurements was also utilized to evaluate the quadruplex stabilization upon ligand binding.

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# Spectroscopic and biochemical characterization of a new bacterial Tyrosinase from *Streptomyces cyaneofuscatus*

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*Streptomycetaceae,* a family of Actinobacteria, are Gram-positive soil bacteria and some members are involved in lignin degradation, melanin formation and in the production of antibiotics and secondary metabolites. Tyrosinases are produced by the genus *Streptomyces* spp. and 40% of them produces melanin-like exopigments on tyrosine containing agar media (1,2). Tyrosinase belongs to the Type 3 copper proteins, where two antiferromagnetically coupled copper ions are present (3); the enzyme catalyzes two different reactions: the ortho-hydroxylation of monophenols (cresolase activity) and the oxidation of o-diphenols to o-quinones (cathecolase activity). As typical substrates of tyrosinases are mono- and diphenols, tyrosinase has biotechnological applications: from wastewater treatment to food and material functionalization (4).
In this study, different Actinomycete strains were isolated from Algerian Saharan soil and the Ms1 strain was selected for its capability to produce melanin in various solid media. Chromosomal DNA was purified and a novel tyrosinase encoding sequence was identified and assigned to *Streptomyces cyaneofuscatus* sp. (99.6%). The tyrosinase was isolated and biochemically characterized to test its stability and activity at different pHs, temperatures, in the presence of inhibitors, reducing agents and metals. The tyrosinase was able to oxidize l-DOPA with an optimum activity at 55°C and pH 7 and also in presence of different concentrations of water-miscible organic solvents. The enzyme activity showed a total inhibition effect with cysteine, sodium metabisulphite, ascorbic acid, whereas a limited inhibition effect was observed with EDTA. Furthermore the X-band EPR spectra were recorded to highlight the "half-met" form after activation of the Type 3 copper center through nitrite and ascorbate addition. The EPR spectra were also recorded in presence of inhibitors like the L-mimosine ligand (5,6). Finally, as the enzyme immobilization increases its stability and allows its reusability (7), the tyrosinase was supported on electrospun Nylon 6 nanofibers and tested; the enzyme immobilization efficiency was also calculated.

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# Transducing light giant lipid vesicles: towards the preparation of autotrophic protocells

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A challenging goal of the synthetic biology is the synthesis of artificial cells from scratch. This research topic sheds insights both on the emergence of life, i.e. the transition between non-living to living matter, and on the preparation of micro-sized confined bio-reactors designed for accomplishing specific tasks, i.e. *bio-robots*.

Lipid vesicles and emulsion droplets have been extensively used as minimal model cells, also called *protocells,* since they have an aqueous core enclosed by a lipid bilayer boundary. Their size can range from few nanometres to tens of micron (*giant vesicles*) and they can encapsulate biomolecules, like proteins, DNA and RNA, in the inner aqueous solution. Some years ago, the water-in-oil (W/O) emulsion transfer method has been presented(0) as a flexible and robust procedure to prepare Giant Unilamellar Vesicles (GUVs). In recent years, we have used this method for the preparation of GUVs encapsulating enzymatic pathways in the internal aqueous core(0), or for the reconstitution of trans-membrane proteins in the GUV lipid bilayer with a defined and uniform orientation(0). Moreover, different theoretical approaches have been also developed in order to describe the time evolution of a population of reactive GUVs taking into account both intrinsic and extrinsic stochastic effects (4, 5).

In this contribution, an example of protocells able to transduce light energy into chemical energy will be presented and discussed(0). In fact, it has been possible to functionalize the lipid membrane of GUVs inserting in the hydrophobic domain an integral membrane protein: the *Photosynthetic Reaction Center* (RC) retaining its physiological orientation (RC@GUV). Under continuous light irradiation, RC@GUVs are able to convert light energy into a trans-membrane pH gradient that can be exploited, in a near future, for sustaining metabolic pathways, like for instance the conversion of ADP in ATP. This represents a genuine first step forward the preparation of semi-synthetic autotrophic protocells.

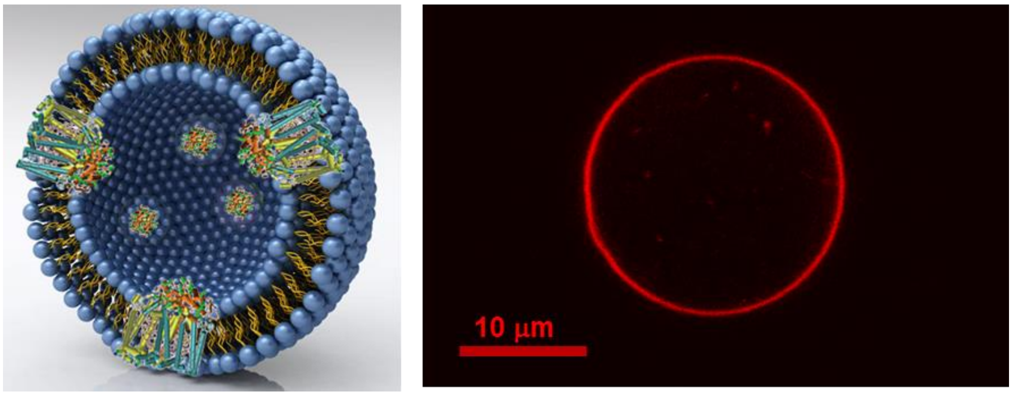

**Figure 1**. Giant Unilamellar Vesicle with RC reconstituted in the lipid membrane: a sketch of the lipid membrane showing the RC physiological orientation on the left, a confocal microscopy image of a RC@GUV whit RCs fluorescently labelled, on the right.

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# Structural and functional characterization of photosynthetic reaction centers in deep eutectic solvents.

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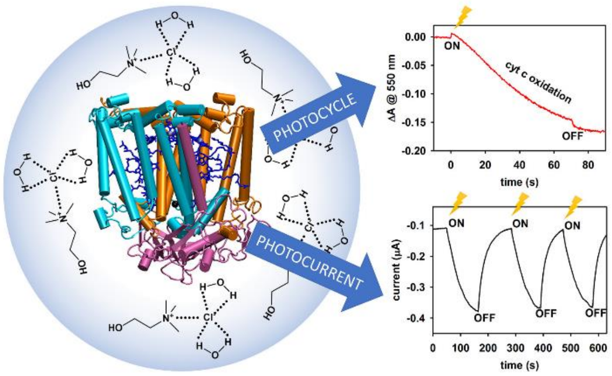

Deep eutectic solvents (DESs) are emerging as a new class of green solvents with the potential to replace organic solvents in many applications both at industrial and academic level (1). In this work, we offer an unprecedented characterization of the behavior of the bacterial photosynthetic reaction center (RC) from *Rhodobacter sphaeroides* in a series of choline-based DESs. RC is a membrane-spanning three-subunit pigment-protein complex that, upon illumination, is capable to produce a stable charge-separated state. Thus, it represents the ideal model for carrying out basic studies of protein-solvent interactions. Herein, we first report that, in many DES mixtures investigated, RC (a) is stable, (b) is capable to generate the charge-separated state, and (c) even to perform its natural photocycle. It proved, indeed, to be effective in reducing quinone molecules to quinol by withdrawing electrons from cytochrome c. As an example of biotechnological application, a photoelectrochemical cell based on DES-dissolved RC has also been designed and successfully employed to generate photocurrents arising from the reduction of the electron-donor ferrocenemethanol.

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# Light Transducing Protocells: reconstituting and characterizing the bc1 complex into the membrane of giant lipid vesicles.

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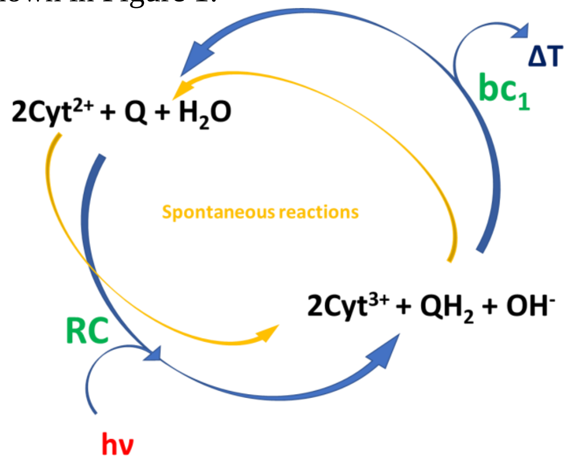
Photosynthesis is responsible for the photochemical conversion of light into the chemical energy that fuels the planet Earth. The photochemical core of this process in all photosynthetic organisms is a transmembrane protein called the reaction center (RC) (1). In purple photosynthetic bacteria a simple version of this photo-enzyme catalyzes the reduction of a quinone molecule, accompanied by the uptake of two protons from the cytoplasm and the oxidation of $cyt^{2+}$ to $cyt^{3+}$ from external medium. In a previous work (2), giant unilamellar vesicles (GUVs) were prepared by the phase transfer method (3) reconstituting in the lipid membrane RCs retaining the physiological orientation at 90%. These synthetic protocells (RC@GUVs) are capable of generating a photo-induced proton gradient 0.061 pH units per min across the membrane under continuous illumination and in presence of an excess of $cyt^{2+}$ and quinone in the external solution. In this contribution, bc1 extracted both from bacteria and mitochondria are reconstituted in giant vesicle membrane (bc1@GUVs) and characterized by studying the enzymatic activity in reducing $cyt^{3+}$ to $cyt^{2+}$ in presence of quinole $QH_2$. This is a forward step towards the coupling of both RC and bc1 in in the synthetic protocells order to implement the complete photo-cycle, as shown in Figure 1:



This pave the way for the construction of more functional protocells for synthetic biology which can be ultimately harnessed to synthesize ATP(4,5).

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# PDMS membranes loaded with $TiO_2$ NPs: antibacterial activity and self-cleaninproperties

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Poly (dimethyl siloxane) "PDMS" is a highly hydrophobic, thermally and mechanically stable polymer whose features are attributable to its Si-O bonds, which have higher bond strengths and larger bond lengths than average C-C bonds. Therefore, PDMS is widely used in different fields, such as sealants, separating membranes and biomedical devices (1). In order to fit the PDMS synthesis to the electrospinning, a sol-gel route was used to synthesize PDMS elastomer. PDMS hydroxyl terminated prepolymers with two different molecular weights and therefore viscosities (20.000 e 50.000 cSt), TEOS (tetraethyl orthosilicate) as multifunctional cross-linking agent, THF as solvent and $HNO_3$ as acid catalyst (2) were used. The sol-gel route is essential for the electrospinning process, which guarantees a fibrous structure with microscale to nanoscale dimensions (figure 1). In order to obtain the crosslinked PDMS membranes coupled with $TiO_2$, a Sn-based catalyst was used (3). $TiO_2$ was synthesized using titanium tetraisopropoxide, 2-propanol and water (1:2:5, V/V) to get an amorphous gel which was then subjected to two different thermal treatments, that are a solid-state and a hydrothermal synthesis, to get crystalline anatase $TiO_2$. This coupled system allows to have membrane sheets loaded with NPs $TiO_2$, combining the high adsorbent capacity and the macroscopic handling of the membrane with the photocatalytic antibacterial and self-cleaning features of $TiO_2$. The photocatalytic activity of this system can be activated by an UV light source, whose photons have an energy at least equal to the $TiO_2$ energy gap (3.2 eV for anatase) and the PDMS membrane showed a high resistance to this type of source. For this work, different synthetic conditions were investigated, varying the PDMS prepolymers ratio, the temperature and the time of the polymer synthesis and the electrospinning conditions (voltage, flow, distance from the electrodes). Two different amounts of titania were loaded (5% and 10% w/w) inside the membranes, by suspending the powders or the sol in a THF solution and then electrospraying together with the PDMS membrane. The samples synthesized were characterized by means of rheological measurements and FE-SEM.

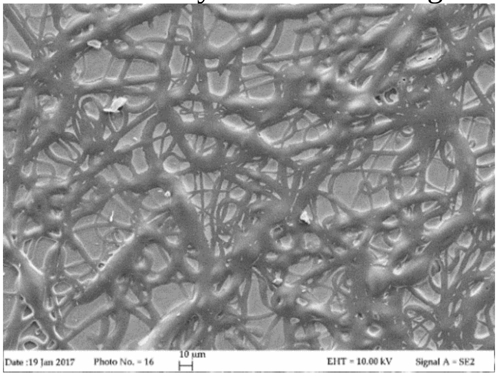

Figure 1. FE-SEM image for a PDMS membrane loaded with 5% w/w $TiO_2$ (solid-state crystallization)

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# Spectroscopic investigations on the effects of hydrophobic silver nanoparticles on peptide conformations

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Protein function is highly dependent on the tridimensional structure of the protein itself; proteins fold into defined structures via a specific pathway to execute their biological function. Since nanomaterials have been widely used in recent years for therapeutical purposes, a deeper knowledge on the effects on protein conformation and folding is fundamental for the development of new therapeutic and diagnostic devices.

Gramicidin A is a linear 15 aminoacid peptide with the ability to adopt single- or double-stranded helical conformations when inserted into phospholipid membranes: the dimerization of two single-stranded helices originates a cation-selective ion channel. Due to its properties, the peptide is an excellent model for membrane proteins and ion channels (1). Silver nanoparticles (AgNPs) are likely among the most used nanomaterials in many consumer applications, mostly because of their well-demonstrated and safe antimicrobial properties (2,3); recent findings on their optical properties (4,5,6) suggest that AgNPs could be a versatile component for therapeutic and diagnostic devices. However limited information are available on the impact of AgNPs on proteins' conformations.

In this work, the effect of silver nanoparticles (AgNPs) on Gramicidin A conformation is presented; in particular, Gramicidin A is inserted into POPC liposomes, to mimic cell membrane. Dodecanethiol-stabilized spherical AgNPs (D-AgNPs) (7) are prepared to have dimensions (5 nm) and an hydrophobic nature compatible with the POPC lipid bilayer.

Tryptophan (Trp) fluorescence, together with Raman signals of Trp residues, were used to probe the position of the peptide inside the bilayer due to their sensitivity to the local environment (8,9). ATR-FTIR spectroscopy was employed to study Gramicidin A conformation: amide I and II vibrational bands are indeed sensitive to secondary structure of peptides and proteins (10). ATR-FTIR spectra revealed the single- and double-stranded conformations of Gramicidin A in the lipid bilayer, and the effects of D-AgNPs addition on peptide conformation.

Our results suggest that D-AgNPs may affect the peptide dimerization and the formation of the ion channel.

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# High-Resolution Molecular Spectroscopy Of Open Shell Molecules: Isotopologues Of The Imidogen ($^{15}$ND) And Amidogen ($^{15}ND_2$) Radicals

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A wide number of studies have been carried out on the imidogen and amidogen radicals, which are thought to be involved in the ion-reaction scheme in which ammonia is produced from $N^+$. The rotational spectrum of the main isotopologue of the imidogen radical NH has been investigated in the THz region (1), as well as in the Far-Infrared-Region (2). In addition, the less common isotopologues ND and $^{15}$NH have been studied by rotational spectroscopy (3,4,5). The interest on this small free radical has increased, since both NH and ND have been detected is several astronomical sources (6,7). However, no data on the rare isotopologue $^{15}$ND were available until now. In this work, $^{15}$ND radical has been produced by electrical DC discharge of $^{15}ND_3$ and Ar as gas buffer and its pure rotational spectrum has been recorded up to 1.2 THz. The fine and hyperfine structure of the $N = 1 \leftarrow 0$ and $N = 2 \leftarrow 1$ transitions has been assigned and all the measured line frequencies have been analyzed, allowing to determine the rotational constant $B$, the centrifugal distortion term $D$ and 9 fine and hyperfine parameters. A global analysis including rotational and vibrational data of all the isotopologues of NH radical is in progress (8). While discharging ammonia, the spectrum of another radical, rapidly identified as $^{15}ND_2$, appeared (Fig. 1). In fact, imidogen and amidogen radicals are usually obtained in the same conditions. Although the amidogen radical has been subjected to numerous studies (9,10,11,12,13), no spectroscopic data on $^{15}ND_2$ are reported. In the second part of our work, the rotational spectrum of the $^{15}ND_2$ radical has been observed in selected frequency region between 264 GHz and 1.2 THz. A total number of 164 transitions have been recorded and assigned, whose analysis allowed us to determine with high accuracy the rotational constants $A$, $B$ and $C$, some centrifugal distortion terms and 21 fine and hyperfine parameters.

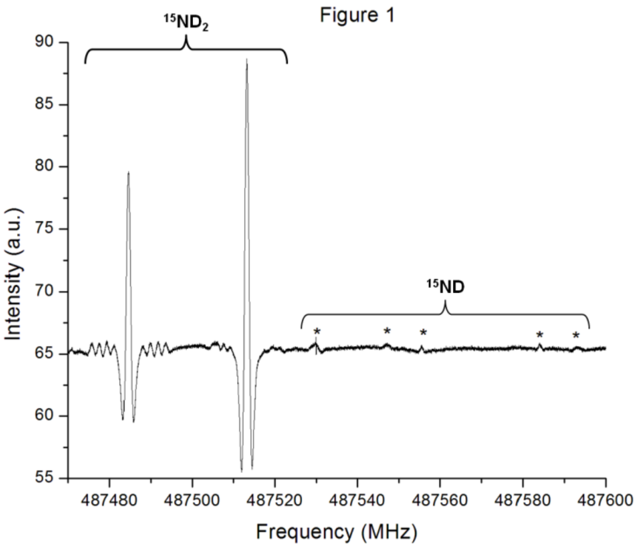
Figure 1

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# New liquid crystalline elastomers investigated by $^2$H NMR and X-ray measurements

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Liquid crystal elastomers (LCEs) are a unique class of soft materials, which combine rubber elasticity with the orientational order typical of liquid crystals. Depending on the chemistry of these materials, LCEs undergo reversible, anisotropic shape change in response to a number of stimuli, such as heat, UV-vis light, type of solvent and electro-magnetic waves. LCEs are indeed very promising materials for nanometer- to centimeter- scale robotic applications. In the recent years, many efforts have been spent in developing new LCE chemistry and processing [1-4], reaching impressing results, such as large and controlled deformations, high motion complexities and multi-step functionality. Most of the investigations are related to LCEs exhibiting a nematic phase, while few studies are known about smectic LCEs. Moreover, the interplay between molecular structure and macroscopic physical properties, such as shape responsiveness, orientational distributions and ordering are poorly understood.

In this work, we report the physical-chemical study of new side-chain liquid crystal elastomers prepared in the form of thin films having uniaxial actuation. A new smectic (semi-flexible) crosslinker (see *Figure 1*) was used to prepare monodomain films [5] showing isotropic-nematic or isotropic-smectic phase transitions, depending on the relative crosslinker/monomers concentration.

Detailed physical-chemical investigations based on $^2$H NMR spectroscopy [6,7] and small angle and wide angle X-ray diffraction measurements, thermo-mechanic and thermo-elastic properties are discussed in view of molecular properties of these new systems and compared with LCEs prepared with conventional flexible crosslinkers [8].

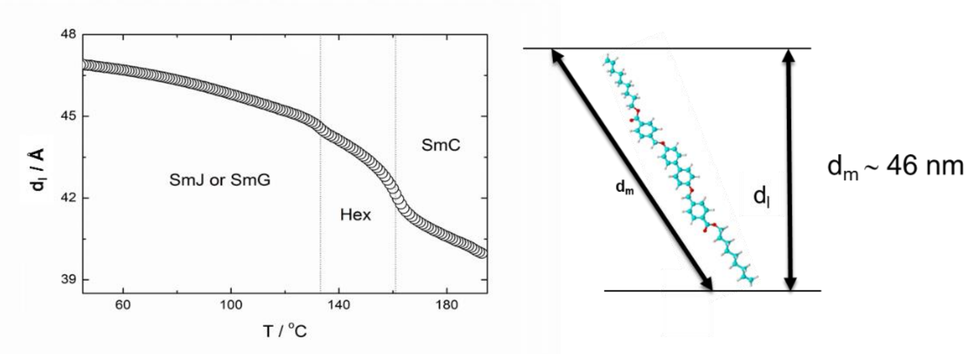

*Figure 1.* Interlayer distance ($d_l$) as a function of temperature (T) in smectic phases formed by the semiflexible crosslinker (on the right) used to prepare new nematic and smectic LCEs [5].

Acknowledgements:
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# Near UV-Visible Absorption Spectroscopy of Extra-Virgin Olive Oils

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Extra-Virgin Olive Oil (EVOO) is an essential food in Mediterranean cuisine, and is nowadays an appreciated and recognized ingredient in many other cultures. Olive oil is produced from the olive fruits of the *Olea europeae L*. trees, and due to the high content of monounsaturated fatty acids and bioactive compounds, olive oil is considered beneficial for human health [1]. Among the quality factors of EVOOs, the colour is very important and several efforts have been devoted to the identification of quantitative parameters related to the colour of olive oils [1,2]. The chemical-physical origin of the colour of EVOOs is related to the presence of pigments, one of the class of minor components present in olive oils. EVOOs contain a relatively rich variety of pigments, divided in carotenoids (i.e., β-carotene, lutein, violaxanthin, neoxanthin, and other xanthophylls) and chlorophyll derivatives (i.e., chlorophylls A and B, pheophytins A and B, and other minor derivatives) [2]. In this work, we present a mathematical approach to analyse the near UV-visible absorption spectrum of edible oils, in particular olive oils [3], able to determine the concentration of four main pigments: β-carotene, lutein, pheophytin A and pheophytin B (*Figure 1*). This approach has been applied to EVOOs produced in several Mediterranean countries from different cultivars [3-6]. A further step in the mathematical devonvolution of near UV-visible absorption spectra of EVOOs in terms of other minor pigments [7,8] is presented and discussed.

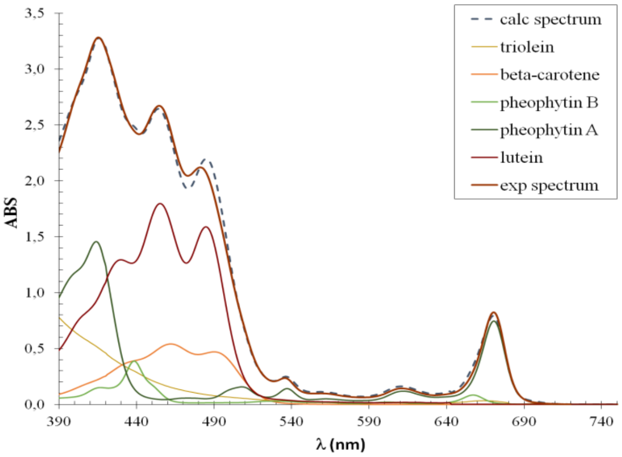

*Figure 1*. Example of spectral deconvolution of the near UV-visible spectrum of an extra-virgin olive oil in terms of main chemical components.

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Authors thank the former students Donatella Ancora, Francesco Buti and Cristina Lazzerini for their contributions. Prof. Maurizio Zandomeneghi and Dr. Andrea Serani are acknowledged for having introduced us to the interesting field of olive oils and for the helpful discussions and suggestions.

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# A method to reduce the OFF-axis haze in polymer-dispersed liquid

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Polymer-dispersed liquid crystals (PDLCs) are composite materials formed by micron-sized droplets of liquid crystals (LCs) dispersed in a polymer matrix, which can be turned from an opaque state to a transparent one by application of a suitable electric field. PDLCs have been proposed in applications related to the control of light transmittance on large surfaces (light shutters, displays, rear mirrors). Despite several advantages, PDLCs' main drawback is haze, i.e. the fast decay of transmission at large viewing angles. In this paper, a method for achieving highly transparent PDLC devices over a wide range of viewing angles is proposed. The method is based on the use of PDLCs with tilted elongated LC droplets and driven by opportune electric fields, which are experimentally calculated and able to ensure an almost constant value for OFF-axis transmittance (1).

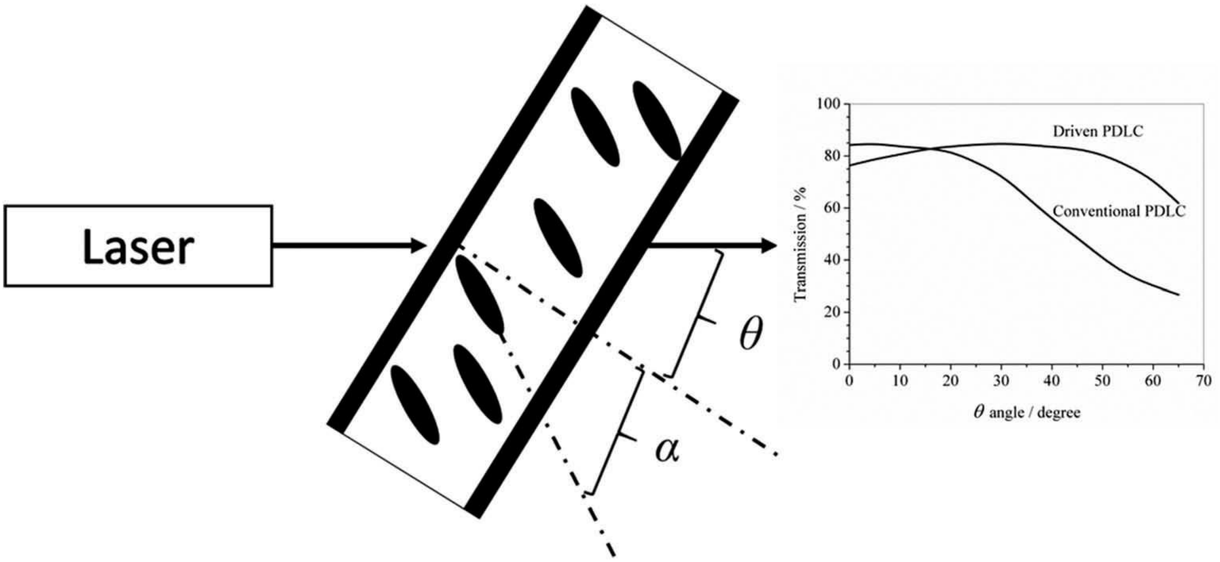

Figure 1. Angular behaviour of the opportunely driven transmittance for a PDLC with 30° tilted directors. The driving field was the sum of 4 V $\mu m^{-1}$ DC bias and a 50 Hz sinusoidal electric field of 24 V $\mu m^{-1}$. The transmittance of similar PDLC with spherical droplets and driven by an electric field of about 20 V $\mu m^{-1}$ at 1 kHz is reported for comparison.

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# Chiral mesoscopic structures obtained by self-assembly of disubstituted steroid-porphyrins

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Aggregation studies carried out on a porphyrin template functionalized with two steroid groups revealed the formation of mesoscopic supramolecular architectures, endowed with peculiar chiral properties.

Aggregation of the steroid-porphyrin building blocks has been induced exploiting hydrophobic effect, by adding increasing volumes of water to micromolar methanol/water solution of the steroid compound investigated. Spectroscopic studies showed that the monomers forming the mesoscopic aggregate attain a J-type conformation, characterized by a slipped-out stacked arrangement of vicinal porphyrin building-blocks. Most interestingly, Circular Dichroism measurements carried out on the mesoscopic aggregates, show a dichroic signal, the shape of which is characteristic of porphyrin units coupled by exciton interaction over long distances.

Atomic Force Microscopy imaging shows that the morphology of the supramolecular architectures strongly depends on the aggregation mechanism, and specifically on the nucleation step seeding aggregation.

The latter is strongly dependent on the concentration of the steroid-porphyrin compound. At low concentration, the hydrophobic effect is predominant, leading to aspecific aggregation and formation of globular species, that, at longer times, self-assemble forming micrometric rod-like structures. At higher concentrations, the globular structures maintain their shape for long times and did not show long-range ordering.

The amphiphilic properties of the steroid-porphyrins allowed for the formation of a porphyrin film by Langmuir-Blodgett deposition. The film, formed at the air-water interface, was transferred on a transparent substrate, allowing optical spectroscopy characterization (UV-Vis absorption, Circular Dichroism, fluorescence). Microscopy techniques with nanometric resolution (AFM, SEM), revealed the formation of micrometric bundles formed by entwined porphyrin nanorods (Figure 1).

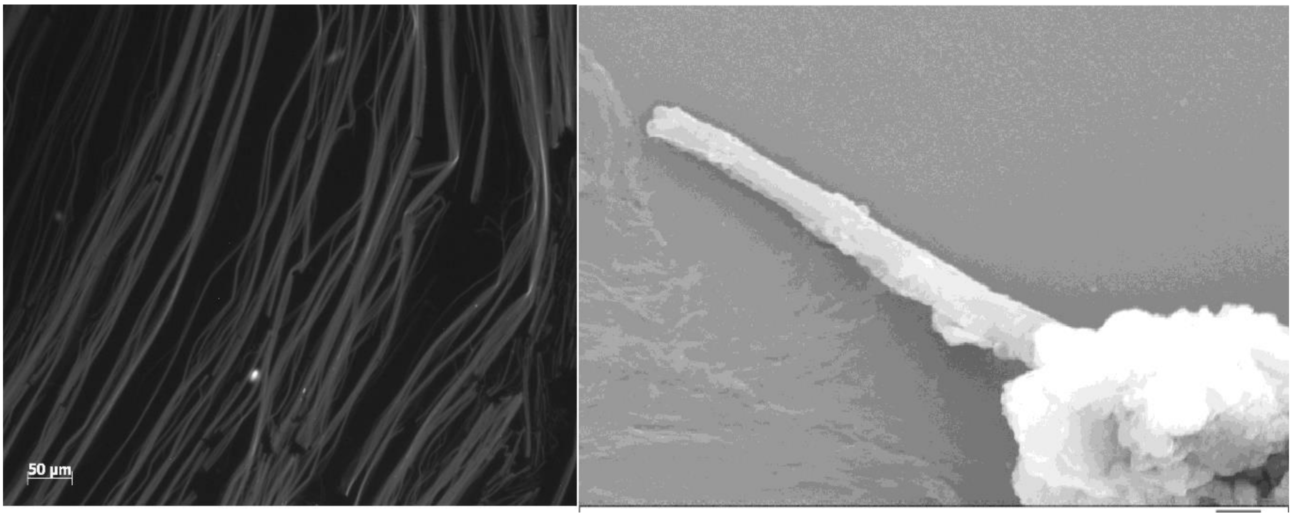

Figure 1. Fluorescence microscopy (left) and Scanning Electronic Microscope image (right) of the micrometric bundles formed by the steroid-porphyrin compound investigated. Note the rod structure originating from a large globular structure in the SEM image reported on the right.

# Excited state interactions of porphyrin units mediated by conformationally constrained oligopeptides: the influence of structure and dynamics

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The excited-state interactions between two tetraphenylporphyrin units separated by conformationally constrained oligopeptides of different length (*n* = 2, 4, 6) (Figure 1) were characterized by time-resolved spectroscopy methods from the micro- to the femtosecond time scale.

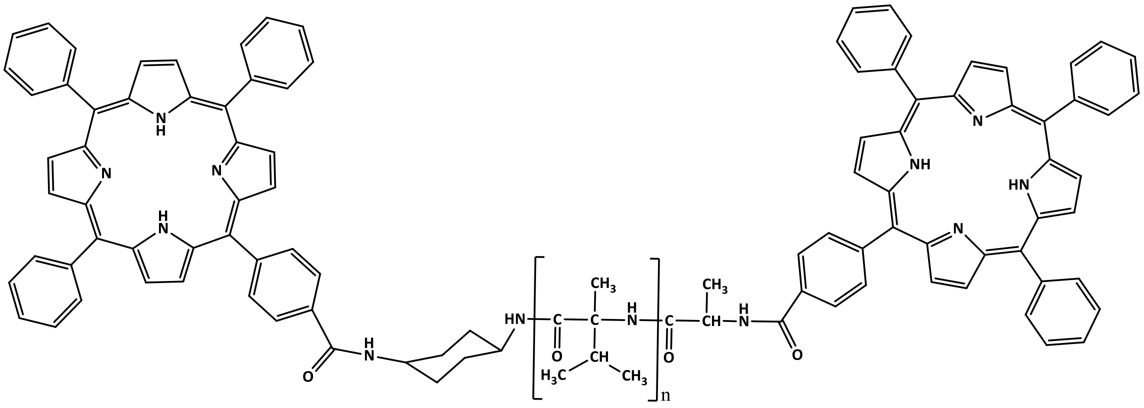

Figure 1. Molecular scheme of the bis-porphyrin-peptide compounds investigated (bPPn, *n*=2,4, 6).

In particular, time-resolved fluorescence and transient absorption techniques were applied to study the electronic coupling between the two porphyrin units mediated by the peptide spacer. The oligopeptides used are predominantly formed by the non-coded, $C^{\alpha}$-tetrasubstituted chiral amino acid $C^{\alpha}$-methylvaline, with the aim at controlling the conformational properties of the compounds investigated, and therefore, the distance and orientation between the two porphyrin moieties.

The application of time-resolved techniques allowed us to distinguish between ground-state and excited-state interactions, and to characterize the dynamical properties of the porphyrin-peptide conjugates. The porphyrin-peptide-porphyrin compounds here investigated have already been shown to be coupled *via* excitonic interaction by circular dichroism measurements (1). Goal of this study is to determine the dependence of the exciton coupling on the time-dependent distance and orientation of the porphyrin moieties, and therefore on 3D-structural properties, *i.e.* on the conformations attained by the peptide main chain, and on dynamic factors, *i.e.* the conversion rate among the populated conformers.

This study is expected to open new perspectives in the design of photosensitizers to be used in photodynamic therapy of tumors.

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# Investigation of gelatin-based composites as scaffolds for bone tissue engineering

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The need of new materials for the treatment of bone defects and diseases has dramatically grown in the last few years, due to the aging of the population and the increase in traumas and tumors (1). Together with the advances in the "traditional" medicine, the developing field of tissue engineering aims at regenerating damaged tissues by combining living cells with highly porous scaffolds, which act as templates for tissue regeneration and guide the growth of new tissue (2). Among the biocompatible and biodegradable materials that can be considered to this purpose, gelatin holds an important role, since it has the same composition of the organic component of the natural extra-cellular matrix. The use of gelatin in this field is nevertheless limited by its fast dissolution rates in physiological conditions, making it necessary to increase the stability of gelatin-based materials by means of chemical crosslinking and/or integration with fillers (3). In our research group, a great interest lies in the preparation and characterization of composite gelatin-based materials: we are mainly focused in the understanding of the interactions between gelatin matrix and inorganic fillers, as well as with others biocompatible polymers, that can lead to the design of a scaffold endowed with the right features to become a potential candidate for bone regeneration. In this contribution, we report on two case studies that address this issue. First, we describe the inclusion of imogolite clays within a macroporous gelatin matrix, whose dissolution at physiological temperature is slowed down using a non-toxic chemical cross-linker, namely glycerol diglycidyl ether (GDE). The effect of imogolite and GDE on the formation of gelatin network was evaluated by means of Differential Scanning Calorimetry (DSC) and Small Angle X-rays Scattering (SAXS), while the morphology of the corresponding xerogels was observed using Scanning Electron Microscopy (SEM). Using a cryo-formation process, we were then able to generate macropores in the hydrogel network, matching the proper dimensions for the permeation of cells. Such hybrid material was used as a scaffold for the formation of hydroxyapatite. By means of X-ray Diffraction (XRD) and Thermogravimetric Analysis (TGA) we demonstrated that imogolite acts as nucleation site for the formation of the mineral phase and promotes the formation of hydroxyapatite enriched in carbonate ions, mimicking the composition of bone mineral phase. The second case study deals with the characterization of gelatin and poly(vinyl alcohol) (PVA) hydrogels, especially in terms of the self-assembly and interaction with water, and with the evaluation of their use as scaffolds for bone mineralization. We constructed a ternary phase diagram at varying concentration and gelatin/PVA ratio and we evaluated the stability at 37 °C. A point of the phase diagram was then selected and characterized at multi-scale levels by means of SEM, DSC, SAXS and rheology. The selected specimen was cross-linked with GDE and BDGE (1,4-butanediol diglycidyl ether). The freeze-dried cross-linked hydrogels were soaked in a simulated body fluid (SBF) at 37 °C and the mineral phase formed was characterized through TGA, SEM and XRD. The results demonstrate that hydrogels cross-linked with BDGE show in SBF very promising stability and mineralization properties.

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# [10]Cyclophenacene: one more case of NICS failure

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Nucleus independent chemical shift (NICS) (1) is considered to be a useful measure of the magnetic shielding effect caused by the aromatic ring current. Owing to the easiness of the calculation and the presumed accuracy, NICS has become very popular especially among organic chemists. However, several criticisms have been raised so far concerning its validity (2). Here, we show a very clear example of a wrong application of the NICS, leading to the conclusion that [10]cyclophenacene is an aromatic molecule (3). Actually, the NICS value calculated in the center of gravity at B3LYP/6-31G(d) is -5.3, which indicates a substantial aromatic character; but, quite remarkably, this is the negative of the isotropic component of the shielding tensor formed by three large and opposing diagonal components, whose values are: xx=16.14, yy=16.08, zz=-16.34. The zz component is the result of a large paratropic, i.e., antiaromatic, global ring current induced by a magnetic field parallel to the main symmetry axis of the molecule.

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# A new 3D-nanostructured organic/inorganic material for industrial applications

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The crystallization of biological macromolecules is of great interest in the scientific community. Nevertheless the crystallographic data currently available are often deficient and can represent a serious limit to the progress of molecular biology applications. The development of simple, easily reproducible and economical crystallization techniques also fascinates the biopharmaceutical sector: to date, 80% of the final cost of the biofarm lies in the purification phase, which involves the use of expensive chromatographic separation methods.

In this work the preparation and characterization of a new 3D-nanostructured organic/inorganic material for alternative crystallization of biological compounds is presented.

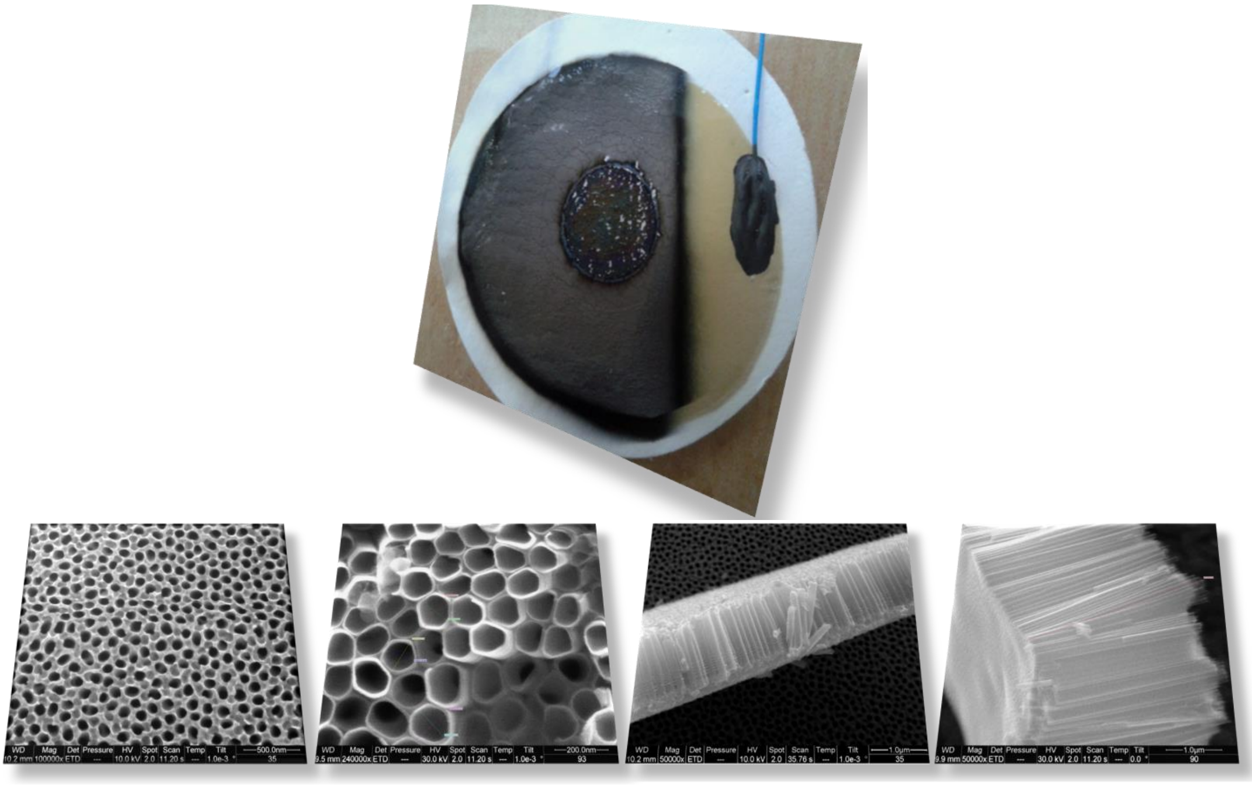

Figure 1. The new 3D-nanostructured organic/inorganic material is formed by titania nanotubes obtained from electrochemical treatment of metal titanium sputtered on porous polymer membranes.

# Effect of $VNbO_x$ on the hydrogen storage properties of $MgH_2$

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Solid state hydrogen storage represents one of the most promising solution for the diffusion of Fuel Cell technology for on- and off-board applications. In the last years several efforts were addressed to find a valid candidate that fits the parameters fixed by the department of energy of US (DOE)(1). In this context, $MgH_2$ has attracted many attentions thanks to its high gravimetric capacity of 7.6 wt% of $H_2$, low cost and availability. But the high desorption temperature (450 °C) and high pressure required for the re-hydrogenation, represents a not yet overcome issue limit for practical applications.(2) In last 20 years various strategies were developed to improve the sorption properties of $MgH_2$. In particular, the addition of V-based and $Nb_2O_5$ compounds allowed to release hydrogen reversibly at 300-350 °C.(2)

Based on this considerations, we investigated, for the first time by our knowledge, the effect of the addition of $VNbO_x$ compound on the sorption properties of $MgH_2$. The sorption measurements showed a significant reduction of the desorption temperature from 330 °C to 230 °C for the doped sample. Interesting, 5 wt% of hydrogen was re-absorbed in 5 minutes at 160 °C under 20 bar of hydrogen pressure and at 275 °C for 70 consecutive cycles. The reduction of the activation energy in the desorption process (98 kJ/mol) confirmed the high performing catalytic activity of dopant.

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# Halloysite Nanotube/Polymer Composites as Sustainable Consolidation and Protection Protocol for Waterlogged Archaeological Wood

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Within the cultural heritage issue, waterlogged archaeological wood plays a relevant role and its conservation is a challenging task (1). In this work, we proposed an innovative consolidation protocol based on Halloysite nanotube dispersions in different polymers. The nanotubes are used like nanocontainers for loading and triggered release of calcium hydroxide.

The incorporation of $Ca(OH)_2$ into the nanotube lumen retards the carbonatation delaying the reaction with $CO_2$ gas. The obtained materials were tested for wood protection and consolidation.

A comprehensive characterization of the materials was carried out through morphology, wettability, thermal degradation and tensile properties. The treatment with pristine halloysite nanotubes does not generated an enhancement of the mechanical performance and did not alter the thermal properties of the woods. The co-presence of polymer and $Ca(OH)_2$ loaded nanoparticles generated a more uniform nanotubes distribution in the lignin channel structures and a significant enhancement of the mechanical properties with respect to the pristine halloysite treatment. Afterwards, the co-presence of the polymer and calcium hydroxide trigger the response to acid exposure minimizing the pH drop-down.

This work proposes the use of halloysite/polymer mixture in a new protocol for waterlogged archaeological wood consolidation and represents a starting point to develop, with a biocompatible approach, smart composite material in which the nanotube cavity is filled with active species for wood protection or active response to external stimuli.

These features are promising for a composite nanoadditive in long-term smart protection of waterlogged archeological woods.

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# ZnO@Ag Patchy Nanostructures for Photo-degradation of Organic Contaminants

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Nowadays, the possibility to tune and to enhance the charge separation at a metal@semiconductor interface for the fabrication of solar energy conversion devices is deeply investigated [review Bari]. Basically, semiconductors, i.e. zinc oxide (ZnO) and titanium dioxide ($TiO_2$), widely employed for Dye Sensitized Solar cells and as photo-catalyst for the removal of environmental pollutants, can be interfaced with noble metals, in particular silver (Ag) or gold (Au) nanoparticles, in order to ensure a photo-induced electrical communication across the nano-junction. Different charge transfer pathways can be (photo)induced depending on the size and geometry of the nanostructures [2]. The fabrication of nanostructures with a semiconductor core (ZnO or $TiO_2$) with a surface decoration obtained by the deposition of Ag or Au nanoparticles was demonstrated to ensure charge transfer from the conduction band of the SC to the Fermi level of the metal, so that reducing the charge recombination and enhancing the photocatalytic performance [3]. In this contribution, a simple synthesis procedure to obtained ZnO@Ag patchy nanostructures ensuring ZnO wurtzite phase was proposed. Morphological and physico-chemical characterizations of such nanojunctions were carried out. Then, the photocatalytic activity of bare ZnO and ZnO@Ag patchy nanostructures was investigated by using methylene blue as standard compound to be degraded. The reaction rate was found to be improved by 212% under 370-800 nm wavelength range illumination in presence of silver. Finally, the degradation of 2,4-Dichlorophenol (as an example of a real contaminant) was followed under sunlight illumination. In this case the reaction rate for ZnO@Ag hybrid nanostructures was improved by 490%.

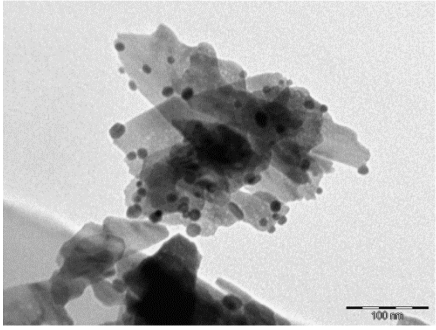

Figure 1: Transmission Electron Microscopy image of the synthetized ZnO@Ag Patchy Nanostructures.

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# Nanomaterials for Enzymatic Immobilization

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In recent years research involving nanoparticles and nanoscale materials has generated a great deal of interest from scientists and engineers of nearly all disciplines. This interest has been motivated to a large extent by reports that a number of physical properties including optical and magnetic properties, specific heats, melting points, and surface reactivity are size-dependent. These size-dependent properties are widely believed to be a result of the high ratio of surface to bulk atoms as well as the bridging state they represent between atomic and bulk materials.

The interest in biocatalysts for chemical production continues to grow because they generally have high stereo-, chemo-, and regioselectivity. The fragile nature, high cost, and high loadings required for commercial production limits the use of free enzymes. Enzyme immobilization is utilized to surmount the stability, recovery, and recyclability disadvantages of using enzymes in solution, making them industrially and commercially viable (1).

Nanomaterials are particularly suitable for enzymatic immobilization.

Among nanomaterials, nanofibers represent one of the most attractive nano-device for the production of high added value products. When the diameters of polymer fiber materials are shrunk from micrometers to sub-microns or nanometers there appear several amazing characteristics such as very large surface area to volume ratio flexibility in surface functionalities, and superior mechanical performance (stiffness and tensile strength) compared with any other known form of the material.

Membranes of electrospun Nylon 6 and polyurethane nanofibers were prepared and functionalized to be used for laccase and lipase immobilization (2).

Other materials like ordered mesoporous silicas (1) or magnetic nanoparticles (3) have been synthesized, functionalized and used for enzymatic immobilization.

The different supporting materials are analyzed and the enzymatic immobilization efficiency has been calculated and compared.

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# Thermal Analysis and Biological Properties of Silica/PEG hybrids synthesized via Sol-Gel methods

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Sol-gel is the method of making glasses and ceramics at low temperature. The low processing temperature combined with the high sol homogeneity make the sol-gel an ideal technology for the fabrication of organic-inorganic hybrid nanocomposites by entrapping various thermolabile organic polymers in a glassy matrix. Moreover, it is found that sol-gel materials exhibit higher bioactivity and biocompatibility (1) than the same materials prepared using other techniques (e.g. melt-quenching technology), due to the hydroxyl groups on their surface, which stimulate hydroxylapatite nucleation, thus promoting the osseointegration. In this work, inorganic/organic hybrid materials containing $SiO_2$ and 60 or 70 wt% of polyethylene glycol (PEG) with average molar mass of 400 g/mol were prepared by means of sol-gel process, using tetraethyl orthosilicate as metal alkoxide precursor of the inorganic phase. PEG, previously dissolved in ethanol, was added to the synthesized silica sol. The thermal behavior of the obtained gels was investigated by simultaneous thermogravimetry/differential thermal analysis (TG/DTA) to establish the best temperatures for their heat treatment. The two materials undergo a two-step dehydration followed by three different exothermic effects in the range 200-400 °C, accompanied by mass losses of about 35 and 58% for the hybrids containing 60 and 70% of PEG, respectively. Moreover, the large mass loss observed indicates that the thermal decomposition of PEG occurred simultaneously in the same temperature range: the higher the mass loss percentage the higher the PEG content in the hybrid gel (4). At temperatures higher than 600°C PEG seems to be completely absent from the material. The chemical structure of the obtained $SiO_2$/PEG 60 and 70wt% was also investigated by FTIR spectroscopy. In the spectra of both samples, all the typical bands of the silica sol-gel materials are present but with a reduced intensity. Moreover, some polymer bands whose intensity increases with the PEG amount are observed. SEM micrographs showed that the materials are homogeneous and no significant differences were present between the two materials. In the SEM images apatite deposition is clearly visible on sample surfaces in recorded after SBF test (3). The EDS confirms that the observed layer is composed of calcium and phosphate. Cytotoxicity assays were performed using a WST-8 assay, a colorimetric test. The NIH-3T3 murine fibroblast cell line (ATCC, USA) were grown in DMEM medium (Gibco, CA, USA) and treated with the extracts of the materials. The results show that in the presence of hybrids, cells are more viable than control cells (2). The best results were obtained for the material with 70wt% of PEG.

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# Novel Approaches To Remove And Recover Tetracycline From Wastewater

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For years, many articles have been reported in literature and related to the presence of new compounds, called "emerging pollutants", in wastewater and aquatic environments. As reported by Deblonde et al. (1) these pollutants are considered new products or chemicals without regulatory status and whose effects on environment and human health are unknown.(1) The number of these chemicals and compounds are increasing due to the development of resources and technologies. As a result, these undesirable compounds are being released, knowingly or unknowingly, into the aquatic environment affecting the whole living organisms. (2) Consequently many efforts and suitable remediation methods have been developed to remove these pollutants from water. In this work due to our expertise in color removal form wastewater using suitable adsorbent materials (3, 4, 5), alginate micro beads wrapped with chitosan were presented removing tetracycline from water (see Figures 1 and 2). Along with the removal of tetracycline from water, the recovery of the pollutant was obtained modifying the ionic strength of the water suspension of alginate beads loaded with tetracycline. However, under these experimental conditions the degradation of beads occurred and for that reason an alternative strategy was proposed. The use of alginate/chitosan beads modified with $TiO_2$ enabled, under UV irradiation, the degradation of the blocked tetracycline inside the beads reusing the adsorbent material for several cycles of adsorption. The use of advanced method of oxidation was also proposed using $H_2O_2$ and $Fe^{2+}/H_2O_2$. As a result the recycle of both the pollutant and the adsorbent material was presented in this work.

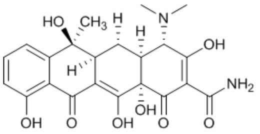

**Figure 1.** Tetracycline

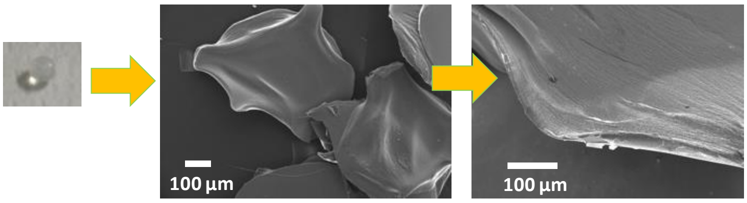

**Figure 2.** Camera Picture of a single Alginate micro bead and the related SEM images

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# An innovative application of polyamidoamine-based hydrogel for removal of blue and red dyes from wastewater

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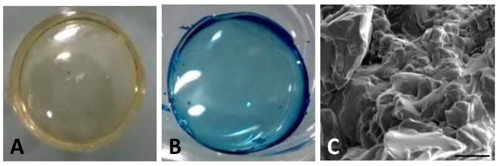
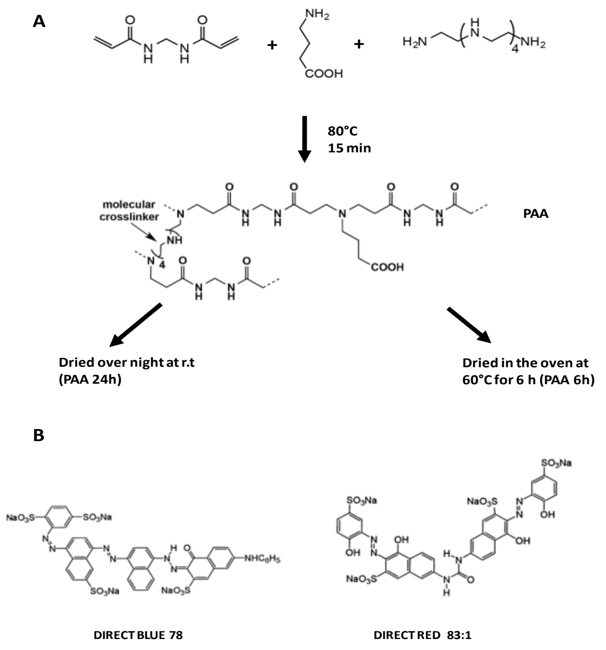


**Figure 1.** Camera pictures of unloaded hydrogel **(A)** and DB dye loaded hydrogel **(B)**; SEM image of hydrogel, scale bar is 50μm **(C)**.

One of the major problems related to the use of dyes in industrial applications is their elimination from the water or the soil and eventually their recovery and reutilization. We report the use of a polyamidoamine-based hydrogel (PAA), prepared by Michael-type polyaddition in water (1), to efficiently adsorb two anionic textile dyes, Direct Red and Direct Blue, from aqueous solutions (Scheme 1 and Figure 1). We have investigated several parameters, such as the pH of solutions containing dyes, the amount of hydrogel and dye, and the effect of the temperature values. The hydrogel can be dried in different conditions and reswollen using water solution containing the dyes. We have observed that the temperature for the dehydration play a major role in determining the subsequent adsorbing behavior. The results showed that the adsorption process could be attributed to a combination of electrostatic attraction and intermolecular interactions between hydrogel functional groups and the dye molecules. Visible absorption spectroscopy and FTIR-ATR were used to support the findings and to determine the rate of the adsorption, which follow a pseudo-second-order kinetics. The excellent ability of PAA to sequester the dyes suggests that such type of hydrogel could be used as a promising adsorbent material for the removal of anionic molecules from wastewater. As an example, in Figure 1, results related to the adsorption of Direct Blue are reported.



**Scheme1. (A)** Steps related to the synthesis of hydrogel: N,N'-methylenebisacrylamide was dissolved and mixed with 4-aminobutyric acid; then pentaethylenehexamine was added and the hydrogel PAA was obtained. PAA was dried for 24h (PAA 24h) and in the oven for 6h (PAA 6h). **(B)** Chemical structures of DB and DR dyes. The color index, as a world identification system of recognition, associated to each dye is also reported.

References: 1. F. Fiorini, E. A. Prasetyanto, F. Taraballi, L. Polfi, F. Monroy, I. López-Montero, E. Tasciotti, L. De Cola, Nanocomposite Hydrogels as Platform for Cells Growth, Proliferation, and Chemotaxis, Small 12(35) (2016) 4881-4893.

# Olive pomace as a wide-ranging bioremediation strategy to adsorb and recover dangerous disperse industrial dyes from wastewater

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In this work industrial dyes, Disperse Blue, Disperse Red and Orange (DB, DR and DO, respectively), were studied as model pollutants to show the excellent performance of olive pomace (OP) to sequester and recover these dangerous dyes from wastewater (Figure 1). (1) Several complementary techniques were adopted to characterize the nature of interaction and the adsorption processes. In batch systems with respect to contact time, pomace dosage, pH and temperature were investigated. SEM, FTIR-ATR, TG and XPS analyses appeared as powerful tools to characterize olive pomace, before and after the adsorption of dyes, while UV-Visible analyses were used to quantify the amount of loaded dyes on adsorbent material. The pseudo-second order kinetic model well fitted the experimental data and described the kinetic of the adsorption processes. The dyes desorption in glacial acetic acid was also obtained enabling the recovery of dyes. The recycle both of adsorbent material and dyes were presented. Five consecutive cycles of adsorption and desorption were performed and the absence of any degradation processes affecting the dyes after the adsorption/desorption cycles were observed. The recorded absorption spectra, in acetic acid solutions, before and after the desorption, confirmed these results. An environmentally friendly and a low cost material is thus presented, showing the excellent olive pomace potential both in disperse dyes adsorption (with an efficiency of around 100%) and desorption (with a mean value of 80% for each cycle). An alternative environmental friendly use of olive oil solid residues is presented.

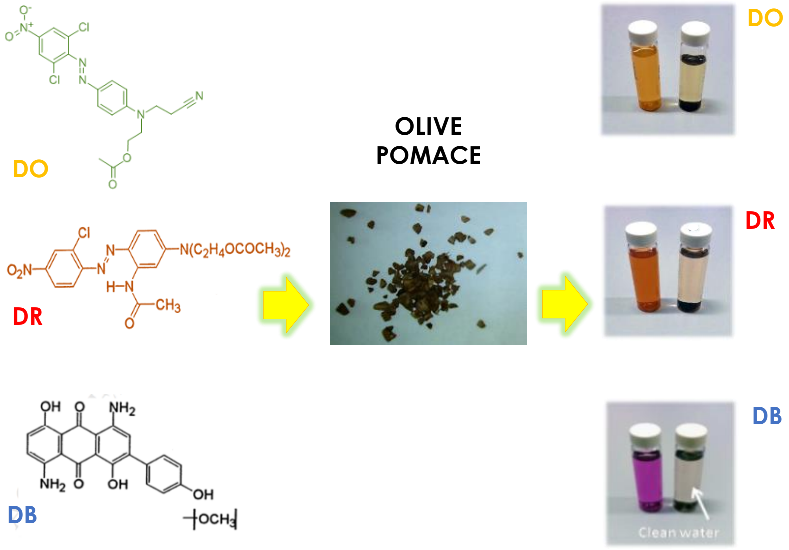

**Figure 1.** Schematic illustration of the adsorption process. The camera pictures of water containing dyes before and after the adsorption process are reported.

References: 1. V. Rizzi, F. D'Agostino, P. Fini, P. Semeraro, P. Cosma. An interesting environmental friendly cleanup: The excellent potential of olive pomace for disperse blue adsorption/desorption from Wastewater, Dyes and Pigments 140 (2017) 480-490

# Electrochemical removal of humic acids from water using aluminum anode

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Humic substances (HS) represent an important fraction of the recalcitrant material to biological treatment of the landfill leachates (1). They are organic macromolecules with high structural complexity, composed of a skeleton of aromatic blocks. They have a significant influence on the efficiency and operation costs of water treatment processes. Several studies have been developed with the aim to remove humic substances from wastewater (2). The most common and economically feasible process is considered to be coagulation/flocculation by using iron, aluminum or calcium ions. In recent years there is an increasing interest on electrochemical processes (EC) as an attractive technique for wastewater treatment (3). Different reactions can occur at the electrodes and in solution. Among the anodic reactions, the oxidation of the metal electrode in its cation and the oxidation of organic pollutants are of particular interest. Using aluminum anodes the following semireaction can occur: $Al \rightarrow Al^{3+}_{(aq)} + 3e^-$. Similar reaction is produced using iron anodes. Moreover, using the appropriate electrodes and the electric potential, oxidation of organic compounds can occur directly on the anode, or in solution via oxidant compounds produced at the anode, such as chlorine from chloride ion : $2Cl^- \rightarrow Cl_2 + 2e^-$. In this communication we report a study on the effect of density current and NaCl concentration on electrochemical removal of humic acids via electrocoaculation and electrooxidation, using aluminum electrodes. The dissolution of these electrodes by oxidation to ions should decrease the electro passivation due to the accumulation of organic compounds at the surface of the **electrodes.** The following figure reports the main result (Figure 1).

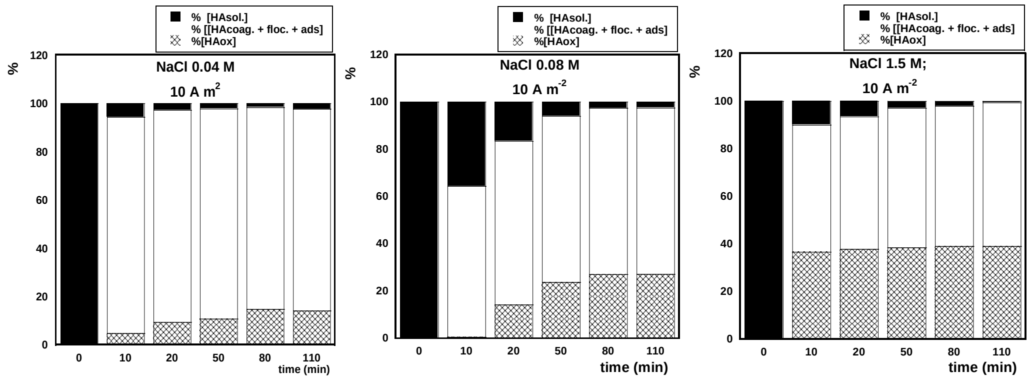

**Fig 1.** time dependence of the % HA removed by precipitation or by oxidation for different NaCl concentrations.

References: 1. Kang, K-H., Shin, H.S., Parka, H., 2002. Characterization of humic substances present in landfill leachates with different landfill ages and its implications. Water Research 36(16), 4023-4032. 2. Leone, V., Canzano, S., Iovino, P., Capasso, S., 2012. Sorption of humic acids by a zeolite-feldspar-bearing tuff in batch and fixed-bed column. J Porous Mater 19, 449-453. 3. Fernandes, A., Pacheco, M.J., Ciríaco, L., Lopes, A., 2015. Review on the electrochemical processes for the treatment of sanitary landfill leachates: Present and future. Applied Catalysis B: Environmental 176-177, 183-200.

# Microstructural and physicochemical characterization of $(AlCl_3)_x$ : (1-ethyl-3-methyl-imidazolium chloride)$_y$ solutions as electrolytes for Aluminium rechargeable batteries

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Al-ion technology is now getting much attention from research on rechargeable batteries, thanks to the huge natural abundance of aluminum and to the potentially high energy density that can be obtained through a 3-electron redox process. In this work, thanks to a multi-technique approach, the ionic liquid composed by aluminum chloride and 1-ethyl-3-methyl-imidazolium chloride is systematically studied, varying the molar ratio of the two components (from 1.1 to 1.7), to find out which is the best composition to be employed in a rechargeable $V_2O_5$-based system. The several employed techniques, ranging from NMR to DSC, from EIS to galvanostatic cycling, show that the 1.2 molar ratio composition is the best compromise among high ionic conductivity, use of low quantity of the highly toxic $AlCl_3$, and consistent presence of $Al_2Cl_7^-$ complex.

# $TiO_2$/$BiVO_4$ Heterojunction for Photoelectrochemical Water Splitting

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Photoelectrochemical (PEC) water splitting is a promising strategy to capture and store solar energy into hydrogen as clean fuel. The $TiO_2$/$BiVO_4$ heterojunction has recently attracted increasing attention, since it allows to exploit the intrinsic properties of the two materials, namely the photoactivity of $BiVO_4$ under visible solar irradiation and the highly negative (respect to RHE) conduction band (CB) position of the $TiO_2$ component (1). Such combination should allow to obtain a stand-alone composite photoanode able to carry out complete water splitting under visible light and without the application of an external bias. Even though the electron transfer from a low-lying CB of $BiVO_4$ to a more negative CB of $TiO_2$ is in principle thermo-dynamically unfavourable (2,3), preliminary evidences of this phenomenon are reported in recent literature (3,4). The injection of visible-light excited high-energy electrons from $BiVO_4$ to $TiO_2$ (Figure 1) can account for the observed hydrogen production through bias-free photocatalytic water splitting (3).

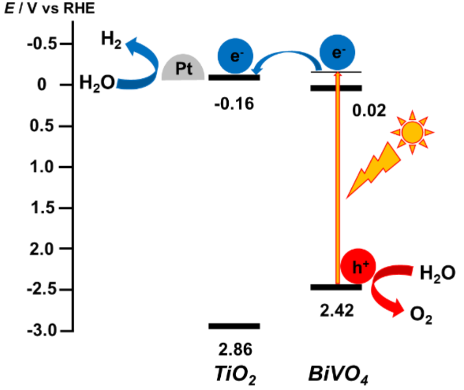

**Figure 1. Proposed electronic interaction mechanism for water splitting with the $TiO_2$/$BiVO_4$ heterojunction.**

Inspired by this counterintuitive electron transfer, we prepared transparent $TiO_2$/$BiVO_4$ heterojunction photoanodes by spin coating onto FTO and characterized the films through PEC measurements. As shown in Figure 2, the coupled system is active at wavelength > 420 (trace a), suggesting that $TiO_2$ gets sensitized $BiVO_4$, while negligible photocurrent response was attained with the $TiO_2$ film (trace c). Back-side irradiation (through FTO, Figure 2 trace a) leads to larger photocurrents respect to front side irradiation (trace b), because of the poor electron transport typical undoped $BiVO_4$. Noteworthy, the heterojunction system produces photocurrent under visible light irradiation even without external bias (inset in Figure 2), supporting highly reducing photoexcited electrons in $BiVO_4$ are able to flow into the $TiO_2$ CB.

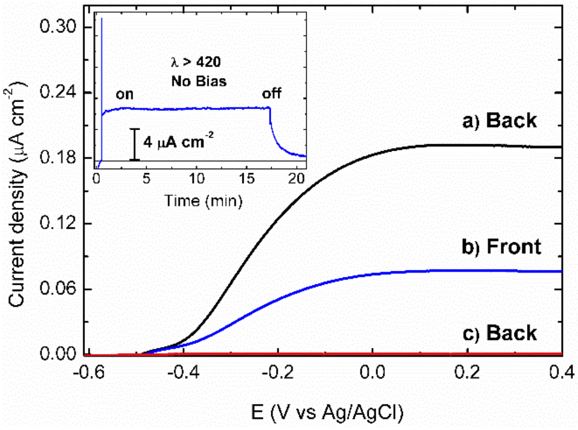

**Figure 2. Visible light (λ > 420 nm) photoelectrochemical analysis in 0.5 M $Na_2SO_3$, 0.5 M potassium phosphate buffer, pH = 7: linear sweep voltammetry analysis of a), b) $TiO_2$/$BiVO_4$ and c) $TiO_2$. Inset: chronoamperometric analysis of $TiO_2$/$BiVO_4$**

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Further evidence of this mechanism is gathered through incident photon to current efficiency measurements, showing that in the coupled system $TiO_2$ is sensitized by $BiVO_4$ up to 490 nm, while $BiVO_4$ alone is active up to 520 nm. This suggests that electrons in $BiVO_4$ need to be excited with a small extra amount of energy in order to be transferred to the $TiO_2$ CB.

References: 1. Dozzi, M. V. et al., *Phys. Chem. Chem. Phys.* **2011**, *13*, 18217. 2. Grigioni, I. et al., *J. Phys. Chem. C* **2015**, *119*, 20792. 3. Xie, M. et al., *Adv. Energy Mater.* **2014**, *4*, 1300995. 4. Resasco, J. et al., *ACS Cent. Sci.* **2016**, *2*, 80.

# Structural and transport properties of $Na_{0.44}MnO_2$, a tunnel oxide cathode material for rechargeable Na-ion batteries

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Nowadays, lithium-ion batteries (LIBs) are considered the best technology for rechargeable energy storage because of their high energy density, high efficiency and long cycle life. However, due to a predicted ever-growing demand of lithium, concerns arise about its future availability and cost, in particular for large-scale energy storage applications. For this reason, research efforts are devoted to find alternative chemistries, based on abundant, cheap and environmentally friendly materials. In this context, sodium-ion rechargeable batteries are acquiring increasing importance.

Among various cathode materials with potential use in Na-ion batteries, one of the most interesting cathode material is $Na_{0.44}MnO_2$. This oxide is characterized by a peculiar crystalline structure, in which Mn (III) ions, in pyramidal coordination, and Mn (IV) ions, in octahedral coordination, are connected to form tunnels running along the *c* crystallographic axis. Within the tunnels, the Na ions are placed on partially occupied crystallographic sites, either within small tunnels (Na1) or larger S-shaped tunnels (Na2 and Na3). This characteristic structure ensures high ion conductivity for the material, especially along the direction of the tunnels, which offers an advantageous path for the intercalation and migration of sodium ions.

In this study we investigate the structural and transport properties of $Na_{0.44}MnO_2$ by means of high temperature neutron diffraction and molecular dynamics simulations, in order to shed light on the intercalation properties of this interesting material.

The evolution of structural parameters along with temperature shows that no phase change is expected in the whole temperature range considered (30-800°C) and that the three sodium ion positions are all partially filled, even at room temperature.

Na-ion migration within the tunnels is clearly visualized through analysis of the Na-ion trajectory plots from molecular dynamics and both intra and inter channel diffusion are investigated. Attention is paid to the potential formation of Na-Mn antisite defects in the structure and their effect on the intercalation mechanism.

# Gellan gum hybrid hydrogels for the cleaning of paper artworks contaminated with Aspergillus versicolor

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The degradation of archive materials is related to irreversible phenomena induced by light, temperature, humidity, air pollution, micro-organisms, and use. Among biological factors, fungi can induce harmful effects in paper artworks. Further forms of damage (e.g. artwork swelling, fibre lifting and sheet delamination) can be caused by water immersion, which is one of the most commonly used methods for cleaning paper. To avoid damage it is necessary to control the amount and absorption rate of water by paper. Recently, gellan gum hydrogels have been proposed as effective tools to allow contaminant removal from paper supports, owing to the controlled water release and adhesive properties of gellan gum. In this study hybrid hydrogels were fabricated by doping gellan gum either with calcium compounds (calcium sulphate, hydroxide, chloride, and acetate) or titanium dioxide nanoparticles in order to evaluate their ability in cleaning different types of paper (1).

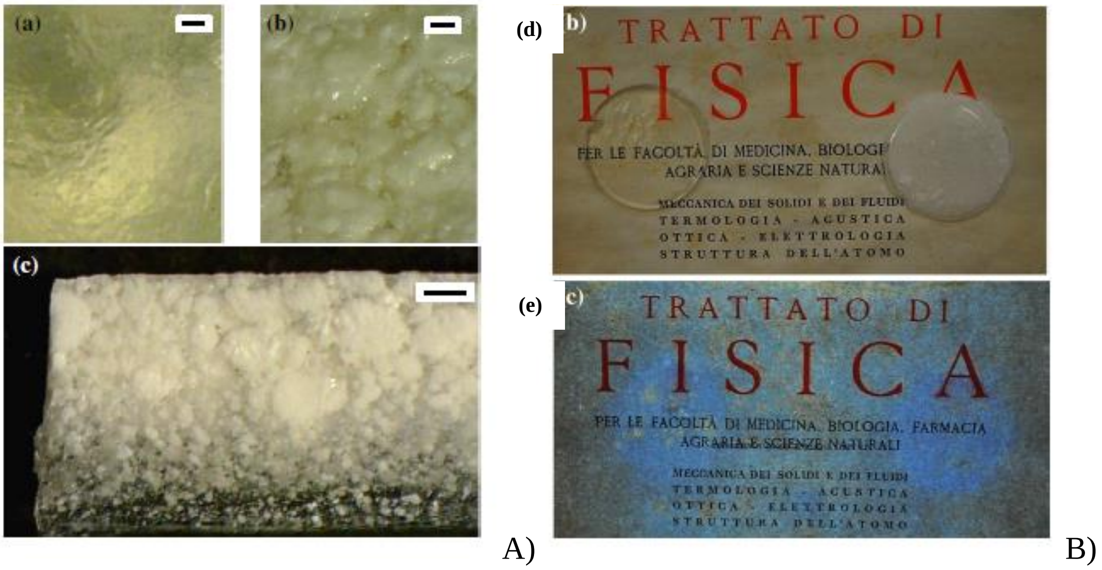

Figure 1. A) on the left: a) Top view of a gellan gum hydrogel; b) top view and c) cross section of a gellan gum hydrogel loaded with titanium dioxide nanoparticles. B) on the right: Cleaning, decolouring action, and biostatic/biocidal activity by gellan gum/calcium acetate/$TiO_2$ nanoparticle hybrid hydrogels d) during the treatment, and e) after a further 15 days in a climatic chamber under a Wood's lamp.

References: 1. Giovanni De Filpo, Anna Maria Palermo, Riccardo Tolmino, Patrizia Formoso and Fiore Pasquale Nicoletta, 2016 Cellulose, 23:3265–3279.

# Wild-type, Nickel-substituted and mutated (N47S/M121L, HPAz) Azurin DFT models: Structures and Redox Potentials

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Azurin (Az) from *Pseudomonas aeruginosa* is a blue copper protein belonging to the family of cupredoxins (1,2). The T1 copper active site consists of a trigonal bipyramidal coordination geometry where the copper ion is coordinated by a cysteine (Cys112) thiolate group and two histidine (His46 and His117) nitrogen atoms. The thioether group from a Met residue (Met121) and the backbone amide oxygen of a glycine (Gly45) constitute axial ligands. Cupredoxins span a wide range of reduction potentials ($E^0$) going from stellacyanin having the lowest potential of ca. 184 mV to rusticyanin showing the higher potential of ca. 680 mV. Several works have been devoted to the understanding of the factors influencing $E^0$ by changing primary coordination sphere ligands or exploring secondary coordination sphere mutations. To this goal, a series of Az mutants have been designed and showed that $E^0$ could be tuned over a very broad range (between 90 mV and 640 mV) without significantly perturbing the metal binding site. Among these mutants, the HPAz variant (containing the mutations: Met44Phe, Asn47Ser, Phe114Asn, Gly116Phe and Met121Leu) (3) showed the highest $E^0$ value (970 mV) ever reported for Az while a significant lowering of E° value (-590 mV) has been reached in a Ni-substituted Az (4).
In the present work, DFT models were used to evaluate the $E^0$ of wild-type Az, Ni-subst Az and two mutants (N47S/M121L and HPAz) of protein Az. The active site models were constructed including the copper or nickel ion and the coordinated residues (Cys112, His46, His117, Met121 and Gly45). The Met44, Asn47, Phe114 and Gly116 residues relevant for this study were also included. The computed structures for the oxidized and reduced forms of wild-type Az, N47S/M121L and HPAz mutants nicely reproduce the geometrical features of T1 copper sites. Moreover, the DFT models revealed the expected hydrogen bonding patterns within secondary coordination spheres. B3LYP energies and Gibbs free energies computed on the optimized structures of the oxidized and reduced species were combined to evaluate $E^0$. All calculations were performed using the ORCA program package (5). The results show that the implemented strategy is able to reproduce the experimental lowering or increasing of $E^0$ among the studied Az proteins.

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# Elettropolymerization of push-pull copolymer for flexible optoelettronic device

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Push-pull polymer systems containing naphthalenediimide (acceptor) and thiophene (donor) derivatives exhibit high air-stability, good processability, low band gap and large electron mobilities, principally due to their substantial crystalline structure or ordered supramolecular packing (1,2). In addition, recent reports demonstrated the capability of new symmetric naphthalenediimidequaterthiophene (s-NDI2ODT4) systems to electropolymerize alone or with EDOT, yielding polymers with controlled donor/acceptor monomer ratios along with low band gaps, a wide optical absorption range extending to the near IR region, tuned electrical properties, tunable thin-film surface morphology and hydrophilicity as well as high coloration efficiency in electrochromic devices (3). Moreover, fulleropyrrolidine derivatives tailored with thiophene substituents have been succesfully employed as electron acceptors especially for the fabrication of organic heterojunction solar cells (4).

Herein, copolymers of new bithiophene fulleropyrrolidine bisadducts (bis-C60Bi) systems and s-NDI2ODT4 have been successfully obtained by anodic oxidation of the monomers on flexible ITO/PET electrodes. XPS and UV-VIS spectroscopy as well as cyclic voltammetry have been employed for characterizing the thin film chemical features, the band gap and the HOMO and LUMO levels. The electronic transfer data show that both the homopolymers and the copolymer behave as acceptor at the interface with P3HT and also an intramolecular charge transfer in the copolymer, confirmed by DFT data. This class of copolymers showed interesting physico-chemical properties and applications including efficient plastic photovoltaic and sensor devices will be shown.

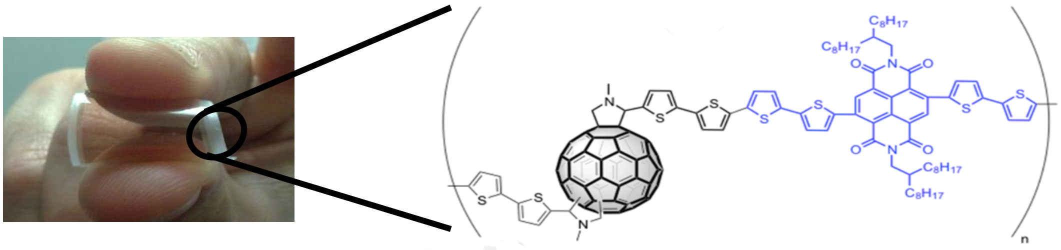

**Figure 1: Structure of the new copolymer deposited in thin film for plastic devices.**

References: 1. H. Yan, Z. Chen, Y. Zheng, C. Newman, J. R. Quinn, F. Dotz, M. Kastler, A. Facchetti, *Nature*, **2009**, *457*, 679. 2. S. Fabiano, Z. Chen, S. Vahedi, A. Facchetti, B. Pignataro, M. A. Loi. *J. Mater. Chem*. **2011**, *21*, 5891. 3. V. Figà, C. Chiappara, F. Ferrante, M. P. Casaletto, F. Principato, S. Cataldo, Z. Chen, H. Usta, A. Facchetti, B. Pignataro. *J. Mater. Chem. C* **2015**, *3,* 5985-5994. 4. K. M. Kaunisto, N. K. Subbaiyan, C. B. K.C. ,V. I. K. M. Kaunisto, N. K. Subbaiyan, C. B. K.C. ,V. I. Chukharev, H. M. Hakola, T. K. Vuorinen, V. M. Manninen, N. V. Tkachenko, H. J. Lemmetyinen, F. D'Souza , *Synth. Met.* 2014, **195**, 193–200.

# Fluorescent discrimination of amine compounds in aqueous matrices

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Detection of amines is very important for monitoring industrial and environmental pollution, checking the quality of food products and medical diagnosis of certain diseases. Moreover, aliphatic amines are found in waste water effluents from pharmaceutical industries, agriculture, and food processing units. Biogenic amines are biomarkers for certain types of diseases such as lung cancer, uremia and hyperammonemia.[1] Several amines affect nervous system, cause abnormalities of blood vessels and cell membranes permeability, induce liver dysfunctions and dystrophy [2]. Therefore, the researchers focused their attention on the development of systems for the detection and removal of these organic compounds from different aqueous matrices [3]. In this work, a highly sensitive «ON–OFF» fluorescent amines trace amounts sensor has been proposed based on a perylene derivative compound.

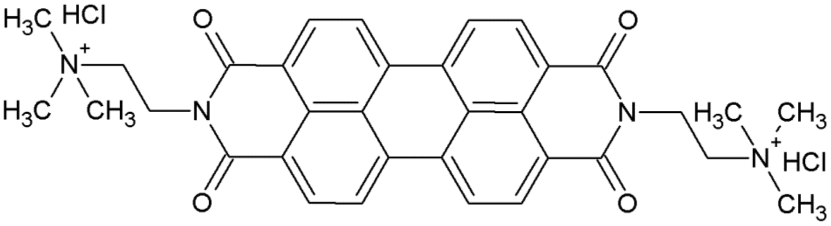

*Figure1: Chemical structure of perylene derivative (FR80).*

Different class of organic amines, aliphatic, heterocyclic and aromatic ones, were tested and a different electronic communication among amines and the perylene derivative was demonstrated to be the key mechanism for the selective discrimination in aqueous matrices down to $10^{-9}$ M aromatic amine.

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# A multi-analytical non-invasive and micro-invasive approach to oil paintings on canvas or wood. General considerations from some specific cases

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The investigation of artwork to understand story, state of conservation and to know about the composing materials is an issue that is getting growing attention in specialized literature. From a methodological point of view the scientific community is trying to reach a common proposal that could contribute to define a Standard Operating Procedure (SOP) for the application of portable non-invasive and microinvasive techniques for in-situ analyses.

In this work the oil painting on canvas "St. Girolamo nello studio" by Nicolò Buttafoco (1), the oil painting on canvas S. Maria delle Grazie of Cappella Palatina in Palermo, four painted slabs, called "Tavolette fuori posto" (Slabs out of place), of Galleria Interdisciplinare Regionale della Sicilia — Palazzo Abatellis (Palermo, Italy) and two painted slabs belonging to the decoration of the wooden ceiling of the "Hall of Barons" of the Palazzo Chiaramonte, said Steri, in Palermo (Italy) (2,3), were investigated to known the materials and techniques used by the artist as well as to evaluate its preservation status.

The survey has been conducted by applying in situ non-destructive techniques. Depending on specific questions arising during the survey, microsamples were taken and analyzed by micro-destructive techniques. The applied methodology to the specific painting can be considered an application of best practices useful to define the SOP. The obtained information were preparatory to the restoration work and have been used to plan and direct the relative choices.

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*This work is part of the project "Development and Application of Innovative Materials and processes for the diagnosis and restoration of Cultural Heritage - DELIAS" - PON03PE_00214_2 (Programma Operativo Nazionale Ricerca e Competitività 2007-2013).*

# A physical-chemical approach to the investigation of Objects of artistic and archeological interest

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The scientific approach for the Diagnostic of Cultural Heritage allows the knowledge of the constituent materials of an artifact, observing their distribution, studying the phenomena occurring at the interface with the environment, interpreting the changes due to the time and to natural or accidental events, to the understanding the technique used by the artists, and the conservative history of the object.

Sometimes, a specific questions of archeologists and of conservators need a precise answer. The identification of the materials provides a decisive contribution to the correct historical and artistic placement of an artefact or to the history of an archeological object. In addition, the identification of materials allows to trace the cause of any problem, identifying the formed products generated by the transformation of the original materials, the presence of foreign materials to the original work and provide a support for an appropriate project of restoration work.

Generally, a correct protocol of investigation involves a first screening by non-invasive techniques. Only, if necessary and possible, in a second step, the micro-sampling can be done and the samples analyzed in laboratory using micro-destructive techniques.

In this work, some examples of a physical-chemical approach applied to several kind of opera and objects, of archeological and artistic interest, are presented.

*This work is part of the project "Development and Application of Innovative Materials and processes for the diagnosis and restoration of Cultural Heritage - DELIAS" - PON03PE_00214_2 (Programma Operativo Nazionale Ricerca e Competitività 2007-2013).*

# A Ni-Bisdipyrrin Metalloligand as Sensitizer Inserted Into a Zr-based Framework

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As a derivative of the dipyrrins, bisdipyrrin can be regarded as a parent structure of corroles (1). This class of molecules, exhibiting wide visible light absorption, has been described long ago (2), but its use has been limited to the preparation of helicate complexes (3,4), though appearing attractive as sensitizers for solar light capture and optoelectronic applications.

Thus, we synthesized a Ni-based 2,2'-bisdipyrrin complex (Ni-bisdpmCOOH) with absorption extending up to the NIR region (Figure 1). Through electrochemical tests, we found that such molecule has an extremely high LUMO energy, which can potentially allow sensitization of thermodynamically uphill reactions, such as proton and carbon dioxide photoreduction. Therefore, a photo-anode was prepared by absorbing Ni-bisdpmCOOH onto a $TiO_2$ film, to verify its ability to inject electrons into the $TiO_2$ conduction band.

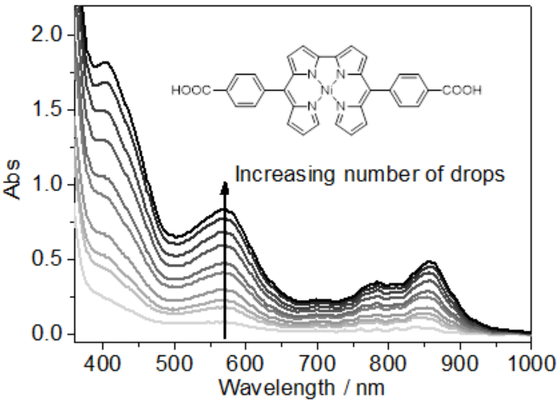

Figure 1. UV-Vis-NIR absorption spectrum of Ni-bisdpmCOOH adsorbed onto a $TiO_2$ film through drop/drying cycles.

The incident photon to current efficiency (IPCE) measured at 0.61 V vs RHE reported in Figure 2 shows that the sensitized electrode generates photocurrent also under visible light irradiation, which confirms that electronically excited Ni-bisdpmCOOH is effectively able to inject electrons into the conduction band of $TiO_2$.

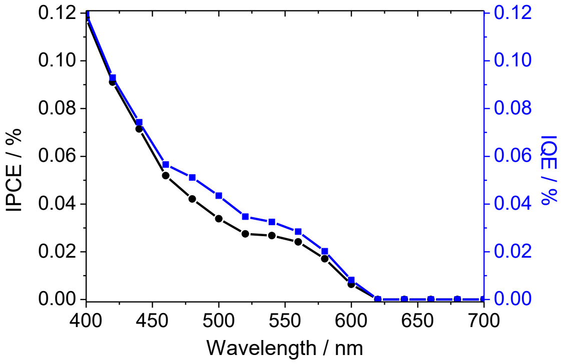

Figure 2. IPCE analysis of Ni-bisdpmCOOH adsorbed onto $TiO_2$.

Furthermore, aiming at obtaining a material that combines the visible light activity of Ni-bisdpmCOOH with the high chemical stability of metal organic frameworks (MOFs), we succeeded in incorporating this complex into the Zr-containing UiO-66 MOF through the one-pot mixed-ligand approach (5), despite the length of the Ni-bisdpmCOOH molecule largely exceeds that of the primary ligand (terephthalic acid).

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# Visible light active self-cleaning materials based on porphyrin-sensitised titanium dioxide

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Starting from second half of last century, nanostructured semiconductors have had a crucial function in the material science because of their wide application field going from renewable energy to organic/hybrid electronics up to photocatalysis.

Among those materials, titanium dioxide is probably the most used because of some important characteristics like the chemical/mechanical stability, environmental sustainability, its low cost and versatility. Indeed, it has been successfully employed as photo- and electro-active component in electronic devices as well as photocatalytic agent[1] in water de-pollution application. Interestingly and importantly together, titanium dioxide may also be applied in the protection of cultural heritages[2] by using its photocatalytic properties to prepare self-cleaning materials able to passivate the manufact surfaces and degrade organic pollution, in this way limiting blackening and reducing maintenance costs.

Unluckily, the photoactivity of $TiO_2$ under the natural sunlight exposition or artificial illumination is greatly reduced because its low absorption in the Vis range. Hence, in order to improve the material performance under the environmental illumination conditions, the extension of the absorption range in the visible region is crucial.[3]

To this end, we prepared novel $TiO_2$-based photocatalysts functionalized *in-bulk* with *meso*-tetra(carboxyphenyl)-porphyrin (TCPP) and its metal complex (Me-TCPP) working as visible-light antennas. The peculiar sol-gel synthesis used for the preparation allows porphyrin dye to be bonded inside the $TiO_2$ structure rather than being easily adsorbed onto the outer surface due to the *in situ* incorporation of the dye during the synthesis of the $TiO_2$.[3,4] The material structure, composition and electronic properties were investigated by Raman, diffuse reflectance spectroscopy and photoelectron spectroscopy while photocatalytic properties were studied by following the degradation kinetic of carminic acid by UV-Vis spectrophotometry under both UV and visible light.

The sensitised materials showed an enhanced photocatalytic activity in the visible range compared to commercial titanium dioxide under different illumination conditions, indicating that *in-bulk* dye sensitisation is a valuable strategy for effective visible-light $TiO_2$ photocatalysts.

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# 2DES reveals ultrafast energy transfer in an organic-biological hybrid made of a synthetic antenna and the reaction center of photosynthetic bacteria

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The photosynthetic Reaction Center (RC) from purple bacterium *Rb Sphaeroides* has unique photoconversion capabilities that can be ideally used to build up bio-hybrid devices for solar energy conversion. Recently, an efficient covalent functionalization of the bacterial RC with an '*ad-hoc*' synthetized organic chromophore has been successfully implemented (1-3). Heptamethyne Cyanine dyes were purposely synthesized to acts as a light harvesting antennas in the visible spectral range, leading to a robust increase in ability of energy photoconversion compared to the pristine native system. We have characterized the dynamics of energy and charge transfer in this bio-conjugated RC employing 2D electronic spectroscopy (2DES). This technique has specific abilities to reveal complex patterns of energy migration and couplings among interconnected chromophores with femtosecond time resolution. Our results reveal the occurrence of ultrafast energy transfer from the artificial light harvesting chromophore towards the monomer bacterio-chlorophyll located in the active branch of the photosynthetic RC.

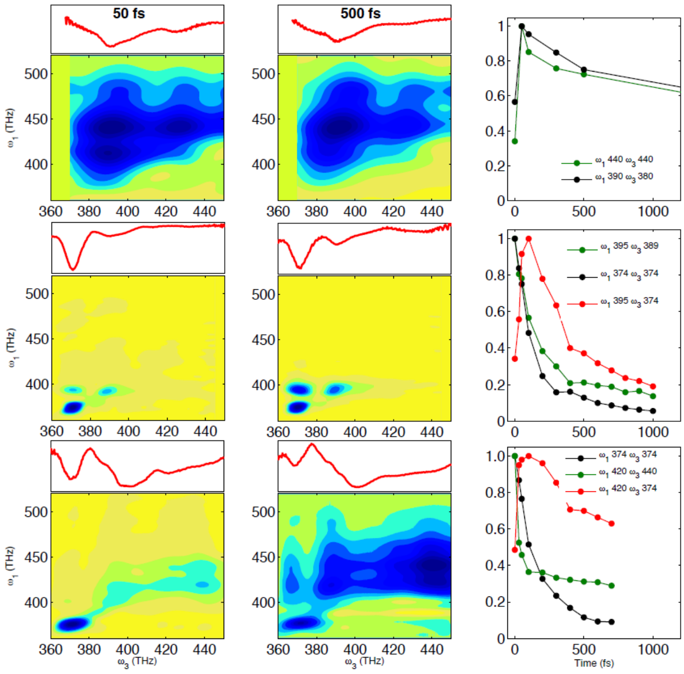

Figure: 2DES Spectra of Heptamethyne Cyanine dye (Top Panel); Bacterial RC (Middle Panel) and Bio-Conjugate RC (Bottom Panel)

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# “Active” drop-like particle-based modelfor living cells dynamics

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Liquid droplets and biological cells share some morphological features and mechanical properties. Here, we propose a drop-like, particle-based model to describe the process of cell adhesion onto materials surfaces. The cell is made of “parcel of fluids” or beads and is treated as an active mechanical object that is able to generate adhesion forces. The beads are described by few quantities/parameters related to fundamental chemical forces such as hydrophilicity and lipophilicity that represent an average of the properties of a patch of material or an area of the cells surface. The simulations are able to describe with a single model different cell features and properties, such as adhesion dynamics, motility, shape deformation, and multiple cell organizations onto homogeneous and chemically patterned surfaces.

# Langmuir-Schäfer Transfer of Nanocellulose Crystals (NCCs)/Cationic Fullerene dyads onto Solid Substrates

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Nanocellulose crystals (NCCs), bearing sulfate moieties arising from the preparation procedure, are negatively charged and form stable aqueous dispersions; this prevents their assembly at the air-water interface for subsequent transfer onto solid substrates by means of Langmuir-Blodgett methods. An approach that can be employed to allow the assembling of organized NCCs Langmuir films at the air-water interface is the deposition of floating films of suitable amphiphilic substances, able to bind NCCs dissolved in the aqueous sub-phase. The choice of the proper amphiphilic compound has a key role, since chemical or physical interactions among these species and those dissolved in the sub-phase drive the assembly of the hybrid film. A similar approach was employed to realize hybrid films containing both water soluble molecules and amphiphilic compounds (1).

More in detail, in this work, two cationic fullerene derivatives (fulleropyrrolidines), bearing one and two positive charges, were used as amphiphilic compounds to assist the assembly of NCCs at the air-water interface, by exploiting the electrostatic interactions among the positive charges of fullerene derivatives and the negative charges of the sulfate groups present on the NCCs. Subsequently, the transfer of these hybrid layers onto solid substrates was achieved by Langmuir-Schäfer method (2). It was found that NCCs, dispersed in the water sub-phase, could interact with fullerene derivatives floating films, leading to modifications on Langmuir isotherms, yielding to a marked shift towards higher limiting area values. Moreover, the presence of NCCs promoted a decrease of amount and size of fullerene aggregates in floating layers at the air-water interface, as revealed by Brewster angle microscopy. The floating layers were transferred onto ITO/glass substrates and the NCCs presence in the hybrid films was confirmed by multireflection FT-IR spectroscopy with bands at 3340 cm$^{-1}$ (O–H stretching) and at 2850 cm$^{-1}$ (C–H symmetric stretching). Increasing the NCCs concentration in the sub-phase results in a higher NCCs amount in the hybrid film. In addition, the efficiency of Langmuir-Schäfer transfer was confirmed by a linear dependence of infrared absorbance on the number of transferred layers. The typical morphology of NCCs interacting with fullerene films was highlighted by Atomic force microscopy.

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# Tracing the geographical origin of lentils by infrared spectroscopy and chemometrics

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Lentil (*Lens culinaris* Medik.) is the fourth most important pulse crop in the world after bean (*Phaseolus vulgaris* L.), pea (*Pisum sativum* L.), and chickpea (*Cicer arietinum* L.). Canada is the world's largest exporter of lentils, while in Italy lentils are a minor legume and can be found in restricted areas. However, Italian lentils present unique and characteristic qualities giving them a higher value, so that many of them have obtained international and national marks linked to their geographical origins, such as "protected geographical indication" (PGI), "traditional food products" (PAT) and Slow Food Presidium. For these reasons, there is a growing demand for analytical methods able to certify the declared lentil geographical origin, in order to protect consumers and producers from fraud and unfair competition.

In this work, the potential of infrared spectroscopic fingerprinting technique for the geographical origin traceability of lentils was investigated. In particular, lentil samples from two different countries, i.e. Italy and Canada, were collected and analysed by Fourier transform near- and mid-infrared spectroscopy (FT-NIR, FT-MIR). Linear Discriminant Analysis (LDA) was used examining the FT-NIR and FT-MIR fingerprints separately and in combination in order to evaluate the spectral range mostly influenced by geographical origin. The LDA classification results were expressed in terms of recognition and prediction abilities (cross validation and external validation). Good classification results were obtained for both FT-NIR and FT-MIR ranges with FT-MIR one giving better prediction abilities, i.e. 95% and 92% for cross and external validation, respectively. The combination of the FT-MIR and F-NIR did not improve the model performances. These findings demonstrated the suitability of the developed methods to discriminate geographical origin of lentils and confirmed the applicability of the infrared spectroscopy, in combination with chemometrics, to solve geographic origin issues of foodstuffs.

# Elenco degli Autori

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| Montoya Noemì | ABC/ANA/FISOR05 |
| Morresi Assunta | FIS OR15 |
| Moscatelli Riccardo | FIS OR27 |
| Muas Gabriele | FIS PO28 |
| Murgia Sergio | FIS OR65 |
| Musiani Marco* | ELE OR20 |
| Mustarelli Piercarlo | FIS PO39 |
| Mustarelli Piercarlo* | FIS OR53 |
| Naldoni Alberto | ELE OR24 |
| Nasillo Giorgio | FIS PO45 |
| Nicoletta Fiore Pasquale | FIS OR13 |
| | FIS PO27 |
| | FIS PO40 |
| Nicolotti Orazio | FIS PO12 |
| Noel Yves | TEO OR01 |
| Notomista Eugenio | FIS OR69 |
| Novellino Ettore | FIS PO12 |
| Núñez Estrella | FIS OR43 |
| Oliva Rosario* | FIS OR69 |
| Olivares Maitane | ABC/ANA/FISKN02 |
| Oliveri Paolo | ABC/ANA/FISKN01 |
| Ortica Fausto* | FIS OR02 |
| Paduano Luigi | FIS OR10 |
| Paganini Maria Cristina | FIS OR24 |
| Pagano Rosanna | FIS PO30 |
| Pagano Rosanna* | FIS PO43 |
| Paiano Aurora | FIS PO08 |
| Painelli Anna | FIS OR61 |
| Painelli Anna* | FIS OR07 |
| Palermo Anna Maria | FIS PO40 |
| Palleschi Antonio | FIS OR37 |
| | FIS PO23 |
| | FIS PO24 |
| Palumbo Giuseppe | FIS OR44 |
| Pane Katia | FIS OR69 |
| Panero Stefania | FIS OR55 |

# DIVISIONE DI CHIMICA TEORICA E COMPUTAZIONALE

## Comitato Scientifico

- **Vincenzo Barone**, Scuola Normale Superiore di Pisa
- **Benedetta Mennucci**, Università degli Studi di Pisa
- **Carlo Adamo**, ENSCP - Chimie ParisTech
- **Maria Cristina Menziani**, Università di Modena e Reggio
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- **Mauro Stener**, Università degli Studi di Trieste
- **Cristina Puzzarini**, Università degli Studi di Bologna

**Delegato di Divisione**

- **Nadia Rega**, Università degli Studi di Napoli "Federico II"

# Programma Scientifico

## Divisione di Chimica Teorica e Computazionale

## Lunedì 11 Settembre 2017

| | |
|---|---|
| ***Hotel Savoy Sala Puccini*** | |
| ***Sessione DCTC*** | |
| ***Chairperson: Mauro Stener*** | |
| 9.00 – 9.40 | TEO KN01: Massimiliano Aschi<br>*Toward a Computational Modelling of Charge-Transfer Reactions in Condensed Phase: from Ultrafast Photo-Induced to Slow Thermal Processes* |
| 9.40 – 10.00 | TEO OR01: Cristina Puzzarini, Alessio Melli, Nicola Tasinato, Julien Bloino, Vincenzo Barone<br>*Astrochemistry: A Computational Spectroscopy's View* |
| 10.00 – 10.20 | TEO OR02: Alessandro Landi, Raffaele Borrelli, Andrea Peluso<br>*Modeling Charge Transport in Organic Materials* |
| 10.20 – 10.40 | TEO OR03: Umberto Raucci, Nadia Rega<br>*Ab Initio Molecular Dynamics to Simulate Excited State Proton Transfer to Solvent: the Strange Case of a Super Photoacid in Water and Methanol Solutions* |
| 10.40 – 11.10 | Coffee Break |
| ***Sessione DCTC*** | |
| ***Chairperson: Maria Cristina Menziani*** | |
| 11.10 – 11.30 | TEO OR04: Silvio Pipolo, Roberto Cammi, Stefano Corni<br>*Real-Time Coupling between Molecules and a Continuum Environment* |
| 11.30 – 11.50 | TEO OR05: Oscar Baseggio, Mauro Stener, Giovanna Fronzoni, Daniele Toffoli, Alessandro Fortunelli, Stan van Gisbergen, Erik van Lenthe<br>*A New Efficient Time Dependent Density Functional Algorithm for Large Systems: Theoretical Study and Applications to Plasmonic Systems* |
| 11.50 – 12.10 | TEO OR06: M. Gabriella Chiariello, Nadia Rega<br>*Exploring Nuclear Photorelaxation and Photoreactivity by Excited State Ab-Initio Dynamics and Time Resolved Vibrational Analysis* |
| 12.10 – 12.30 | TEO OR07: Alessandra Serva, Valentina Migliorati, Francesco Sessa, Paola D'Angelo<br>*Lanthanoid(III) Ions: Transferable Lennard-Jones and Buckingham Pair Potentials from Aqueous to Complex Media* |
| 12.30 – 12.50 | TEO OR08: Marco Fusè, Julien Bloino, Franco Egidi, Alberto Baiardi, Vincenzo Barone<br>*Unraveling Chiral Properties of Metal Complexes Through Computational Vibrational Spectroscopy* |
| 12.50 – 13.10 | TEO OR09: Francesco Tavanti, Erika Ferrari, Alfonso Pedone Maria Cristina Menziani<br>*Computational Study of Curcumin-derivatives for Alzheimer's Disease Treatment* |

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| 13.10 - 14.00 | Intervallo Pranzo |

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| ***Sala Paestum B*** | |
| 14:00 – 15:00 | ***Sessione Poster 1 (TEO PO01 – TEO PO11)*** |

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|---|---|
| ***Hotel Savoy Sala Puccini*** | |
| ***Sessione DCTC*** | |
| ***Chairperson: Carlo Adamo*** | |
| 15.00 – 15.40 | TEO KN02: Giuseppe B. Suffritti, Pierfranco Demontis<br>*Reverse Mössbauer Effect as a Source of "Hot" Protons in Hydrogen Absorbing Metals* |

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|---|---|
| 15.40 – 16.00 | TEO OR10: Eduardo Schiavo, Ana B. Muñoz-García, Michele Pavone<br>*First-Principles Design of P-Type Semiconductor Oxides as Alternative to NiO in P-Type Dye-Sensitized Solar Cells* |
| 16.00 – 16.20 | TEO OR11: Marco Dalla Tiezza, Laura Orian<br>*Toward a Rational Design of Half-Sandwich Group 9 Catalysts for [2+2+2] Alkynes Cycloadditions* |
| 16.20 – 16.40 | TEO OR12: Stefano Piotto, Anna Montano, Simona Concilio, Lucia Sessa, Pio Iannelli, Barbara Panunzi, Rosita Diana<br>*Ramachandran Energy Approach for Protein Folding* |
| 16.40 – 17.10 | Coffee Break |
| ***Sessione DCTC*** | |
| ***Chairperson: Cristina Puzzarini*** | |
| 17.10 – 17.30 | TEO PZ01: Julien Bloino<br>*Accurate Spectra of Medium-Large Molecules: Recent Developments and New Challenges* |
| 17.30 – 17.50 | TEO PZ02: Alfonso Pedone<br>*From First-Principle Chemical Shift and EFG Tensors Calculations to Solid-State 1D and 2D NMR Spectra Simulations of Complex Systems* |
| 17.50 – 18.10 | TEO PZ03: Franco Egidi<br>*Development of Theoretical and Computational Models for the Calculation of Spectroscopic Properties of Molecules in the Gas Phase and in Solution* |
| 18.10 – 18.20 | TEO PZ04: Greta Donati, Alessio Petrone, Nadia Rega<br>*Wavelet Analysis for Non-Equilibrium Processes in Chemistry* |
| 18.20 – 18.25 | TEO PZ05: Marco Mendolicchio, Nicola Tasinato, Vincenzo Barone<br>*New Models and Computational Strategies for Molecular Structure Prediction* |
| 18.25 – 18.30 | TEO-PZ06: Sergio Rampino, Marco Fusè, Andrea Salvadori, Giordano Mancini, Vincenzo Barone<br>*Chemical bonding and spectroscopic observables in coordination complexes: analysis techniques and applications* |
| | ***Hotel Ariston Sala Mercurio*** |
| 18.30 – 20.00 | *Assemblea dei Soci della Divisione di Chimica Teorica e Computazionale* |

## Martedì 12 Settembre 2017

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|---|---|
| | ***Hotel Savoy Sala Puccini*** |
| ***Sessione congiunta DCTC-INO*** | |
| ***Chairperson: Gianluca Ciancaleoni*** | |
| 9.00 – 9.40 | TEO/INO KN01: Bartolomeo Civalleri<br>*Ab Initio Modeling of Metal-Organic Frameworks: from Gas Adsorption to Stimuli Responsive Properties* |
| 9.40 – 10.00 | TEO/INO OR01: Ana B. Muñoz-García, Michele Pavone<br>*Computational Design of* $Sr_2Fe_{1.5}Mo_{0.5}O_{6-\Delta}$ *(SFMO)-based Bifunctional Electrodes for Proton-Conducting Solid Oxide Electrochemical Cells* |
| 10.00 – 10.20 | TEO/INO OR02: Cutini Michele, Marta Corno, Piero Ugliengo<br>*Insight from DFT Simulations on the Collagen/Hydroxyapatite Interface: a Simple Model Based on the Poly-Proline Polymer* |
| 10.20 – 10.40 | TEO/INO OR03: Laura Falivene, Sergey Kozlov, Luigi Cavallo<br>*A DFT Rationalization of a Two Metals Strategy to Tune* Selectivity in Catalysis |
| 10.40 – 11.10 | Coffee Break |
| ***Sessione congiunta DCTC-INO*** | |
| ***Chairperson: Emilia Sicilia*** | |
| 11.20 – 12.00 | TEO/INO KN02: Iogann Tolbatov, Cecilia Coletti, Alessandro Marrone, Nazzareno Re<br>*Insight into the Electrochemical Reduction Mechanism of Pt(IV) Anticancer Complexes* |

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| 12.00 – 12.20 | TEO/INO OR04: Tiziana Marino, Mario Prejano, Paolo Piazzetta, Nino Russo<br>*The Role of Metal Substitution in the Metallo-Enzymes: a Theoretical Point of View* |
| 12.20 – 12.40 | TEO/INO OR05: Gianluca Ciancaleoni, Niccolò Bartalucci, Leonardo Belpassi, Fabio Marchetti<br>*Back-Donation in $d^0$ Metal Complexes: Does it Exist? The case of Nb(V)* |
| 12.40 – 13.00 | TEO/INO OR06: Gloria Mazzone, Claudia Regina, Nino Russo<br>*Combination of Porphyrin and Ruthenium-arene Moieties for a Dual Anticancer Function. A Theoretical Investigation* |
| 13.00 - 14.00 | Intervallo Pranzo |

## Mercoledì 13 Settembre

<table>
<tr><td colspan="2" align="right"><b><i>Hotel Savoy Sala Puccini</i></b></td></tr>
<tr><td colspan="2" align="center"><b><i>Sessione congiunta DCTC-FIS</i></b></td></tr>
<tr><td colspan="2" align="center"><b><i>Chairperson: Michele Pavone</i></b></td></tr>
<tr><td>15.00 – 15.40</td><td>TEO/FIS KN01: Chiara Cappelli<br><i>A Fully Polarizable Embedding Model for Molecular Spectroscopy of Aqueous Solutions</i></td></tr>
<tr><td>15.40 – 16.00</td><td>TEO/FIS OR01: Roberto Dovesi, Simone Salustro, Francesco Gentile, Yves Noel<br><i>Hydrogen defects in Diamond. A quantum mechanical approach</i></td></tr>
<tr><td>16.00 – 16.15</td><td>TEO/FIS OR02: Lorenzo Zamirri, Marta Corno, Albert Rimola, Piero Ugliengo<br><i>Forsterite Surfaces as Models of Interstellar Core Dust Grains: Computational Study of Carbon Monoxide Adsorption</i></td></tr>
<tr><td>16.15 – 16.30</td><td>TEO/FIS OR03: Mattia Melosso, Claudio Degli Esposti, Luca Dore, Cristina Puzzarini, Lorenzo Spada<br><i>Prebiotic Molecules in Interstellar Space: Aminoacetonitrile and C-Cyanomethanimine</i></td></tr>
<tr><td>16.30 – 17.00</td><td align="center">Coffee Break</td></tr>
<tr><td colspan="2" align="center"><b><i>Sessione congiunta DCTC-FIS</i></b></td></tr>
<tr><td colspan="2" align="center"><b><i>Chairperson: Ludovico Valli</i></b></td></tr>
<tr><td>17.00 – 17.15</td><td>TEO/FIS OR04: M. Vincenzo La Rocca, Lorella Izzo, Simona Losio, Massimo Mella<br><i>Should we Introduce Pre-Equilibria into Markov Models for Homogeneously Catalyzed Copolymerization?</i></td></tr>
<tr><td>17.15 – 17.30</td><td>TEO/FIS OR05: Francesco Di Maiolo, Carlotta Pieroni, Anna Painelli<br><i>Intermolecular Energy Transfer in Real Time</i></td></tr>
<tr><td>17.30 – 17.50</td><td>TEO/FIS OR06: Enrico Bodo, Andrea Le Donne<br><i>Proton Mobility in Protic Ionic Liquids: New Results from Theoretical Calculations</i></td></tr>
<tr><td>17.50 – 18.10</td><td>TEO/FIS OR07: Nicola Tasinato, Lorenzo Spada, Cristina Puzzarini, Vincenzo Barone<br><i>Computational Tools for the Interpretation of Rotational Spectra within the Virtual Multifrequency Spectrometer</i></td></tr>
<tr><td>18.10 – 18.25</td><td>TEO/FIS OR08: Alessandro Mariani, Ruggero Caminiti, Lorenzo Gontrani<br><i>A Spotlight on The Complex Hierarchical Structure of Some Ionic Liquid-Molecular Liquid Binary Mixtures</i></td></tr>
<tr><td>18.25 – 18.40</td><td>TEO/FIS OR09: Olga Russina, Ruggero Caminiti<br><i>Fluorous Mesoscopic Domains in Room Temperature Ionic Liquids</i></td></tr>
<tr><td>18.40 – 18.55</td><td>TEO/FIS OR10: Ettore Fois, Rossella Arletti, Lara Gigli, Giovanna Vezzalini, Simona Quartieri, Gloria Tabacchi<br><i>Supramolecular Organization of Water–Ethanol Solution in Ferrierite under Pressure</i></td></tr>
</table>

# Premi alla ricerca

### ***Premio Roetti***

Dott. **Julien Bloino**, *Consiglio Nazionale delle Ricerche, Istituto di Chimica dei Composti OrganoMetallici*

### ***Premio Roetti***

Prof. **Alfonso Pedone**, *Università degli Studi di Modena e Reggio Emilia*

### ***Premio Scrocco***

Dott. **Franco Egidi**, *Scuola Normale Superiore di Pisa*

### ***Premio del Re***

Dott.ssa **Greta Donati**, *Università degli Studi di Napoli* "Federico II"

### ***Premio Nordio***

Dott. **Marco Mendolicchio**, *Scuola Normale Superiore di Pisa*

### ***Finalista Premio Levi***

Dott. **Sergio Rampino**, *Scuola Normale Superiore di Pisa*

# Premio Roetti
# Accurate Spectra of Medium-Large Molecules: Recent Developments and New Challenges

*Julien Bloino*[a]

[a]*Consiglio Nazionale delle Ricerche, Istituto di Chimica dei Composti OrganoMetallici (ICCOM-CNR),*
*UOS di Pisa, Via G. Moruzzi 1, 56124 Pisa, Italy;*
*e-mail: julien.bloino@pi.iccom.cnr.it*

Computational spectroscopy is nowadays routinely used as a predictive and interpretative tool to complement and support experimental results, providing insights of the underlying elementary phenomena responsible for the overall band-shape. However, its reliability is strongly correlated to the underlying models, which affect the level of accuracy of the calculated results. This aspect can be especially critical in some fields of applications like chiropticalanalysis or astrochemistry for instance. Such considerations emphasize the need of carefully setting up computational protocols, in particular by selecting the most appropriate level of theory available. For medium-to-large molecular systems with possible environmental effects, a trade-off is indeed necessary between accuracy and feasibility, and several strategies can be devised, with suitability varying depending on the cases.

To facilitate the setup of the most efficient and reliable route for the simulation of accurate spectra, we have been developing a versatile and modular platform, called virtual spectrometer.(1) A primary objective in its design has been its simplicity of use and its computational efficiency. The spectrometer has currently two major modules. The first one (2,3) aims at simulating vibrational spectra beyond the harmonic approximation, using second-order perturbation level of theory (VPT2) to compute both transition energies and intensities. The second module (4,5) adds vibrational contributions to electronic spectra.

In this presentation, I will describe some key features of the virtual spectrometer and discuss the theoretical frameworks used for the simulation of anharmonic vibrational and vibronic spectra. The simplicity of use of the tool is strongly conditioned by its capability to identify and possibly overcome the shortcomings in the approximations adopted by the basic models on which it relies. The potential impact of such issues, like resonances in VPT2 calculations or molecular deformations and mode mixing upon electronic transition, and strategies to ensure the reliability and accuracy of the results will be discussed. Those aspects, as well as current projects, will be illustrated with different case studies.

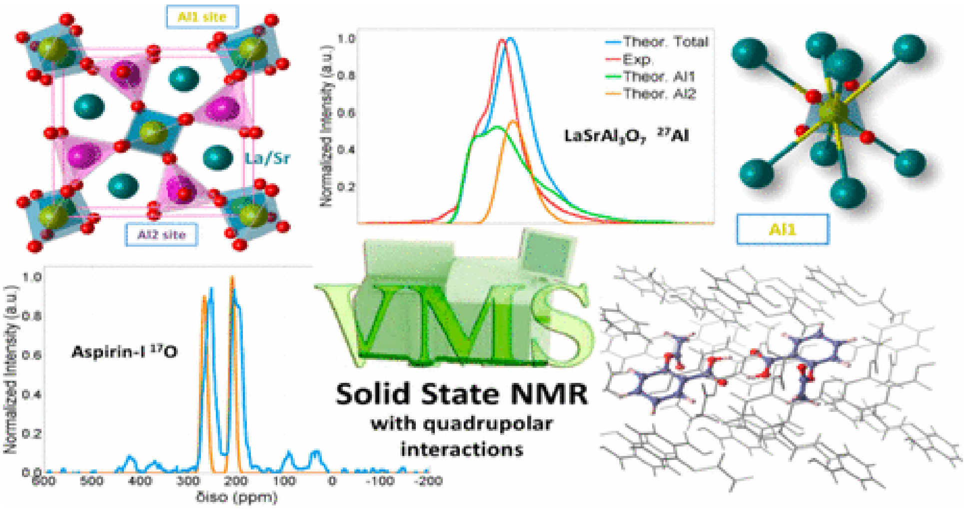
References: 1. J. Bloino et al., Int. J. Quantum Chem. 116, 1543 (2016). 2. J. Bloino et al., J. Chem. Phys. 136, 124108 (2012). 3. J. Bloino et al., J. Phys. Chem. A 119, 11862 (2015). 4. J. Bloino et al., J. Chem. Theory Comput. 6, 1256 (2010). 5A. Baiardi et al., J. Chem. TheoryComput. 9, 4097 (2013).

# Premio Roetti
# From First-Principle Chemical Shift and EFG Tensors Calculations to Solid-State 1D and 2D NMR Spectra Simulations of Complex Systems.

*Alfonso Pedone*[a]

[a]*Department of Chemical and Geological Sciences, University of Modena and Reggio Emilia, via G. Campi 103, 41058, Modena*

In the last decades, NMR spectroscopy has arisen as one of the most powerful techniques to probe the atomic level structure of polycrystalline or disordered systems for which XRD techniques can provide only an average vision of the structure.
Although, several high-resolution 1D and 2D NMR experiments have been devised for the solid state such as Magic Angle Spinning (MAS), Variable Angle Spinning (VAS), Dynamic Angle Spinning (DAS) and Multi-Quantum MAS (MQMAS), their interpretation remains difficult in most cases. This is often because in disordered systems the continuous distribution of structural parameters and topological environments leads to a continuous distribution of NMR parameters and thus broad spectra with peaks in most cases strongly overlapped are observed. It is thus necessary to have a deep knowledge of the correlation between the NMR parameters and the local structure. In the past this was pursued empirically by referencing to known crystalline structures but the development of cost-effective quantum mechanical methods like DFT and the implementation of methods and algorithms to compute NMR parameters for periodic systems has allowed gain more reliable insights on the atomic structure theoretically.(1)
In this communication, I will show the recent advances achieved in the computation of ab initio NMR parameters of spin active nuclei in several complex systems and present a new software tool (SoSNMR) developed in our group to simulate several 1D and 2D solid state NMR spectra of half-integer and quadrupolar nuclei.(2)
The SoSNMR module, also implemented in the graphical user interface of VMS (VMS-Draw),(3)can work under both periodic and non-periodic conditions. Therefore, it can simulate spectra resulting from NMR calculations by some popular quantum chemistry codes, namely Gaussian09/16, Castep, and Quantum Espresso.



References: 1. Charpentier, T.; Menziani, M.C.; Pedone, A. RSC Advances, 2013, 3 (27), 10550-10578.
2. Presti, D.; Pedone, A.; Licari, D.; Barone, V. J. Chem. Theor. Comp. 2017, 13(5), 2215-2229.
3. Licari et al., J. Comput. Chem. 2015, 36, 321-334

# Premio Scrocco
# Development of Theoretical and Computational Models for the Calculation of Spectroscopic Properties of Molecules in the Gas Phase and in Solution

*Franco Egidi*[a,b,c]

[a]*Scuola Normale Superiore, Piazza dei Cavalieri 7, 56126 Pisa, Italy;* [b]*Gaussian Inc., 340 Quinnipiac St, Bldg 40, Wallingford, Connecticut 06492, USA;* [c]*Department of Chemistry, University of Washington, Seattle, WA 98195, USA.*
*e-mail: franco.egidi@sns.it*

The accurate simulation of spectroscopic properties requires the inclusion of multiple effects into the theoretical model. Both the electronic and vibrational degrees of freedom need to be treated with sufficient accuracy to be able to reproduce experimental findings. This means choosing an appropriate electronic structure model, whether wave function theoryor DFT based, and going beyond the harmonic approximation for the vibrational component. In addition, since most experiments are carried out on solvated samples, an accurate treatment of the effect of solvation on a molecule's spectroscopic properties is crucial (1). We show that by carefully combining vibrational effects with either continuous and discrete solvation models, it is possible to simulate a wide variety of spectra that can be directly compared with experimental measurements, provided the solvation model also takes into accounts effects due to solvation dynamics and the screening of the electromagnetic radiation caused by the solvent (2-8). All such effects can be effectively combined with a description of the molecular vibrations that goes beyond the harmonic approximation (3-7).This framework can be applied to all kinds of properties, whether purely vibrational, vibronic, and involving both electric and magnetic perturbations (2-7). The developed methods are both accurate and easy to use, allowing these methods to be used by non-specialists as well as expert theoreticians, thus bridging the gap between theory and experiment in a synergistic way. The research leading to some of these results has been performed in the framework of the ERC Advanced Grant Project DREAMS "Development of a Research Environment for Advanced Modelling of Soft Matter", GA No. 320951.

References:1. F. Egidi, C. Cappelli, *Reference Module in Chemistry, Molecular Sciences and Chemical Engineering* (2015) Elsevier 2. F. Lipparini et al, *J. Chem. Theory Comput.*9 (2013) 234303.3. F. Egidi et al, *Chirality* 25 (2013) 701. 4. F. Egidi et al, *J. Chem. Theory Comput.*8 (2012) 585. 5. F. Egidi et al, *Mol. Phys.* 111 (2013) 1345. 6. F. Egidi et al, *J. Chem. Theory Comput.*10 (2014) 2456. 7. F. Egidi et al, *J. Phys. Chem. A* 119 (2015) 5396. 8. F. Egidi et al, *J. Chem. Theory Comput.* 10 (2014) 346

# Premio del Re
# Wavelet Analysis for Non-Equilibrium Processes in Chemistry

*Greta Donati*[a], *AlessioPetrone*[a], *Nadia Rega*[a,b]

[a] *Department of Chemical Sciences, University of Napoli Federico II, Napoli, 80126, Italy;*[b] *Italian Institute of Technology, IIT@CRIB Center for Advanced Biomaterials for Healthcare, Napoli, 80126, Italy;* ¶ *Current address: Department of Chemistry, University of Washington, Seattle, WA, 98195.*
*e-mail: greta.donati@unina.it*

New and sophisticated computational tools represent the *conditio sine qua non* information provided by simulation techniques in the field of theoretical modeling of molecules, such as molecular dynamics, can be extracted in the most efficient way.

Nowadays, excited state ab-initio molecular dynamics (AIMD) in Born-Oppenheimer approximation(1) can be also employed for the simulation of molecular systems with huge number of degrees of freedom (such as biomolecules) in non-equilibrium conditions (i.e. after interaction with light). But nevertheless, this method still represents a non-conventional approach because of the huge computational cost.

This work represents a challenge not only because excited state AIMD simulations were employed for studying the photo-induced proton transfer of the Green Fluorescent Protein(2), but also because we employed for the first time a multiresolution and time-resolved vibrational analysis, the continuous Wavelet transform (3,4), to investigate the protein conformational rearrangements favouring the reaction event and the reaction mechanism itself. The Wavelet analysis allowed to perform a reciprocal-space domain based analysis of structural properties extracted from the excited state AIMD simulations. The extracted time-evolving vibrational bands revealed that the protein active site undergoes an important rearrangement to reach the best conformation to start the reaction. We found that the main molecular motions involved in this step were collective low frequency in nature, involving not only the chromophore but also other residues sometimes not *directly* involved in the active site.

The Wavelet based approach gave access to thereal time evolution of the molecule rearrangements immediately after the excitation and so to obtain a clear and complete picture of the non-equilibrium events. Moreover, the capability to disentangle in a more accurate way the different frequency range contributions (because of the multiresolution nature of the transform) allowed for a more accurate description of the vibrational bands. Last but not least, we found excellent agreement with time-resolved spectroscopic experiments.

On the basis of this work an innovative, not molecule dependent and efficient protocol is established for the investigation of photo-induced chemical processes.

References: 1. T.Helgaker, E.Uggerud, H.J A.Jensen, Chem.Phys.Lett. 173, 145 (1990).2.P.J.Tonge, S.R.MeechJ.Photoch.Photobio.A 205, 1 (2009).3.R.Carmona, W.L.Hwang, B.Torresani, *Practical time-frequency analysis* (Academic Press, San Diego. 1998).4.A.Petrone, G.Donati, P.Caruso, N.Rega JACS 136, 14866 (2014).

# Premio Nordio
# New Models and Computational Strategies for Molecular Structure Prediction

*Marco Mendolicchio*[a], *Nicola Tasinato*[a], *Vincenzo Barone*[a]

[a] *Scuola Normale Superiore, Pisa, I-56126, Italy.*
*e-mail: marco.mendolicchio@sns.it*

The knowledge of the equilibrium structures of isolated molecular systems of chemical and biological interest is of fundamental relevance to gain detailed information on many chemical-physical processes, in the framework of the so-called structure-property relationships. Moreover, accurate equilibrium geometries serve as benchmarks in the development of new computational strategies. Molecular structures obtained through isotopic substitution are subject to vibrational average, nevertheless vibrational effects are often not explicitly considered during the inversion of the spectroscopic data. Hence, the resulting structures strongly depend on the isotopic species under investigation. From this point of view, the determination of the equilibrium structure, i.e. the geometry associated with the Born-Oppenheimer (B-O) potential energy surface minimum, is the most appealing alternative (1). While this type of structure is more challenging to be inferred at the experimental level, its determination allows the inclusion of vibrational effects and, within the B-O approximation, it is isotopic substitution independent. Furthermore, such structures are directly comparable with theoretical results. In this contribution we present the new program MSR (Molecular Structure Refinement) (2), specifically devised for computing equilibrium structures by means of the semi-experimental approach (3,4). The program includes a large panel of optimization algorithms and an extended error analysis (5). Particular attention has been devoted to the definition of the internal coordinates to be employed in the refinement. The most widespread set of internal coordinates used in this context, defined in terms of the so called Z-matrix, has proven to be often problematic when complex molecular topologies are faced, not to speak about their intrinsic user-dependency. In order to overcome these issues, a different procedure is proposed, based on the identification of all the $A_1$ coordinates belonging to a set of non-redundant internal symmetry coordinates, which can be, in turn, derived from the redundant set formed by all the bond lengths, valence, and dihedral angles. This approach, which is particularly advantageous when symmetric molecules are studied, is implemented as a completely automatic black-box procedure. The MSR program is also equipped with the possibility of including predicate observations in the fit (6). By means of this method, the set of input data (i.e. the rotational constants of different isotopologues) can be augmented by estimates of structural parameters obtained, for example, through quantum-chemical calculations. In this contribution, the underlying theory and the organization of our implementation are presented in some detail. The reliability of the new code is proven by applications of $A_1$ coordinates and predicate observations to the determination of the equilibrium structure of medium-size organic and biological molecules.

References: 1. J. Demaison, J. Boggs, J. Császár, *Equilibrium Molecular Structures: From Spectroscopy to Quantum Chemistry*, edited by J. Demaison (CRC Press, 2011). 2. M. Mendolicchio, E. Penocchio, D. Licari, N. Tasinato, V. Barone, *J. Chem. Theory Comp.* (2017) DOI: 10.1021/acs.jctc.7b00279. 3. P. Pulay, W. Meyer and J. Boggs, J. Chem. Phys. 68. (1978). 5077. 4. J. Demaison, Mol. Phys. 105. (2007). 3109. 5. E. Penocchio, M. Mendolicchio, N. Tasinato, V. Barone, Can. J. Chem. 94. (2016). 12. 6. L. Bartell, D. Romenesko, T. Wong, G. Sims, L. Sutton, *Chemical Society Specialist Periodical Report No. 20: Molecular Structure by Diffraction Methods*. 3. (1975). 72.

# Finalista Premio Levi
# Chemical Bonding and Spectroscopic Observables in Coordination Complexes: Analysis Techniques and Applications

*Sergio Rampino*[a], *Marco Fusè*[a], *Andrea Salvadori*[a], *Giordano Mancini*[a], *Vincenzo Barone*[a]

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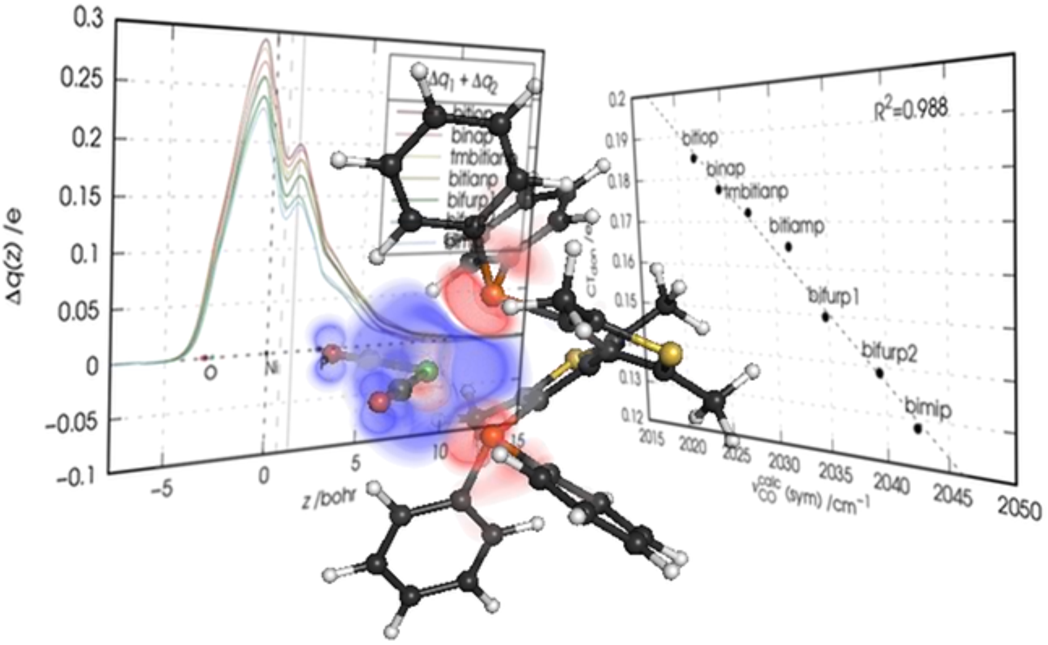
The relation between spectroscopic observables and the detailed metal–ligand bonding features in coordination complexes is addressed. A theoretical scheme based on a double analysis in orbital space and real space is shown to provide a detailed, quantitative description of the several charge fluxes following the metal–ligand bond formation, whence clear-cut estimates of donation and back-donation charge transfers can be extracted (1). Through two case studies on metal-carbonyl complexes (2,3), we elucidate the role of the metal–ligand bond components in altering the distance and stretching frequency of the carobnyl group and provide the framework in which spectroscopic data on coordinated CO can be used to extract quantitative information on the donor/acceptor porperties of the metal–ligand moieties. The porting of the discussed bond-analysis tools in a virtual laboratory exploiting immersive virtual reality (IVR) through the Caffeine project (4) and combining the immediacy of an IVR experience with quantitative numerical analysis will also be discussed.



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# Keynote

- TEO KN01: Massimiliano Aschi, Università degli Studi dell’Aquila
- TEO KN02: Giuseppe B. Suffritti, Università degli Studi di Sassari
- TEO/INO KN01: Bartolomeo Civalleri, Università degli Studi di Torino
- TEO/INO KN02: Nazzareno Re, Università degli Studi di Chieti-Pescara "G. d'Annunzio"
- TEO/FIS KN01: Chiara Cappelli, Scuola Normale Superiore di Pisa

# Toward a Computational Modelling of Charge-Transfer Reactions in Condensed Phase: from Ultrafast Photo-Induced to Slow Thermal Processes.

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During the last five years we have been focusing much of our efforts for developing and testing a theoretical-computational approach, based on Molecular Dynamics simulations and basic Statistical Mechanics, for modelling the kinetics of charge-transfer and spin-transfer reactions in condensed phase. The method, based on arguments extremely different (and somewhat complementary to) the Marcus model, has been tested on a number of processes ranging from the ultrafast photo-induced charge-transfer reactions to slow bimolecular thermal processes. In this talk I will present the basic underlying theory, the results from a number of selected examples and the limitations still present in our model.

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# Reverse Mössbauer Effect as a Source of "Hot" Protons in Hydrogen Absorbing Metals

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As an attempt to explain some of the many anomalies and unresolved problems, which have been reported about the dynamic behavior of particles and molecules absorbed in crystalline solids, in a recent paper (1) we derived an extension of the Bragg – von Laue scattering law to high-energy colliding particles, which is related also to the Mössbauer effect (2), and was referred to as "reverse Mössbauer effect" (RME). In particular, we proposed an explanation of a specific and well characterized anomalous behavior found in neutron inelastic-scattering spectra (recoiled bands) of methane adsorbed in a zeolite (3).

According to RME, a particle in non-equilibrium state with respect to a crystal (colliding with the crystal or adsorbed/absorbed in it, and, set *out of thermal equilibrium* with the crystal by some external cause), can be scattered by the whole crystal with momentum proportional to a vector representing a reciprocal lattice point. The scattering is expected to occur with a well-defined probability and the momentum transferable to the particle is expected to follow a predictable distribution.

As hydrogen is lighter than methane and is adsorbed not only in nanoporous materials, but also is absorbed in a number of metals, we wondered if RME could be present also in H-metal systems and could be detected through some anomalous behavior. RME is essentially a non-equilibrium phenomenon occurring in crystals. Therefore, it could be detected, in principle, by looking for behaviors, which for similar systems differ whether the systems are or not in equilibrium, as well as whether they are crystalline or amorphous.

Enhanced diffusion of H under irradiation by ions and electrons (4,5) was observed. Enhanced diffusion was even reported for hydrogen atoms absorbed in bulk Pd in low-temperature scanning tunneling microscopy(6). In a recent paper (7), the interpretation of the anisotropic diffusion of hydrogen in Nickel required unexpectedly high fitting parameters, at least one order of magnitude larger than the values derived from experimental and *ab initio* studies.

The consideration of all these phenomena encouraged us to study the features of the RME for H absorbed in metals, and, as some examples, we evaluated its general features for H absorbed in Ni, Nb, Pd and Ti, because they are among the most frequently studied systems.

It was then applied to explain, at least in part, the above reported anomalies.

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# Ab Initio Modeling of Metal-Organic Frameworks: from Gas Adsorption to Stimuli Responsive Properties

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Metal-organic frameworks (MOFs) are amongst the most extensively studied hybrid framework materials and they have garnered major developments in the last decade mainly because of their nanoporous architectures and tunable physical and chemical properties (1). They are comprised of an inorganic part, usually formed by either metal ions or small clusters (e.g. metal-oxide) that acts as a node in a network, and an organic ligand that operates as a linker, or a spacer, among the nodes to form the framework through metal-ligand coordination bonds. In addition, they have a porous (and in most cases crystalline) structure that is architecturally stable with a high and ultra-high porosity. Traditionally, this has lead to applications such as gas storage and separation, catalysis and drug delivery (2). Nevertheless, the incredibly rich structural diversity and chemical versatility of such materials can lead to the emergence of many unique and novel properties that opens access to a wide spectrum of multifunctionalities not present in traditional materials (3). The exploration of structure-function relationships has then attracted considerable interests in broadening the combination of chemically bound organic and inorganic building blocks. Therefore, other promising technological applications have emerged, in particular, for electronics and opto-electronics, sensors and nonlinear optics (4).

Here, we give an overview of our recent results on a throughout theoretical characterization and prediction of adsorption properties of different MOFs from small to giant frameworks (5), structural flexibility and framework dynamics (6), as well as tunable electronic and dielectric properties in response to diverse physical and chemical stimuli (7).

The combined use of ab initio modeling in conjunction with experimental techniques (e.g. neutron and synchrotron spectroscopy or infrared and Raman spectroscopy) will be also highlighted.

All results have been obtained through a fully periodic ab-initio approach with the CRYSTAL program (8).

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# Insight into the Electrochemical Reduction Mechanism of Pt(IV) Anticancer Complexes

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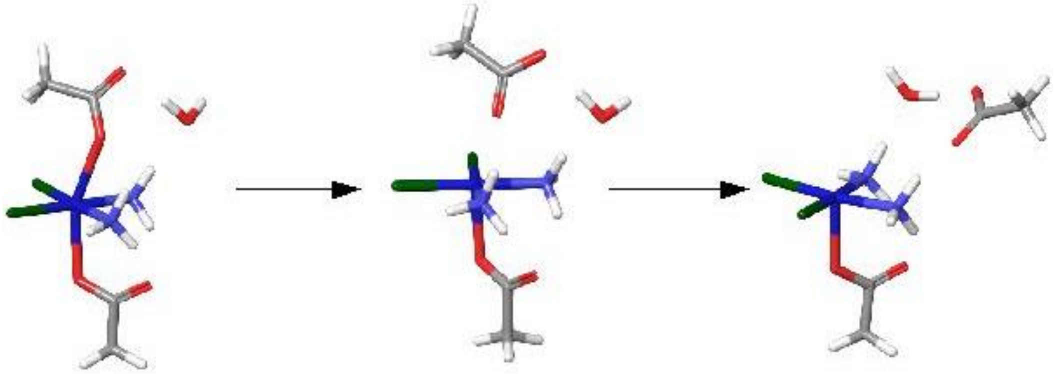
A theoretical study was carried out on the mechanism of electrochemical reduction of the prototypical platinum(IV) anticancer complex $[Pt(NH_3)_2(CH_3COO)_2Cl_2]$ to the corresponding platinum(II) $[Pt(NH_3)_2(CH_3COO)_2]$ derivative.

Energies and geometric structures of the original Pt(IV) complex and all possible Pt(III) and Pt(II) intermediates and transition states during the reduction process have been calculated using several levels of theory, and allowed to formulate a detailed mechanism for the two-electron reduction of the $[Pt(NH_3)_2(CH_3COO)_2Cl_2]$ complex. Solvation was accounted for both by a continuum solvent model and through the inclusion of an increasing number of explicit water molecules.



The results show that, in agreement with the experimental evidence from cyclic voltammetry, the initial one electron reduction of the $[Pt^{IV}(NH_3)_2(CH_3COO)_2Cl_2]$ complex occurs through a stepwise mechanism via a metastable hexacoordinated platinum(III) $[Pt^{III}(NH_3)_2(CH_3COO)_2Cl_2]^-$ intermediate and a subsequent acetate ligand detachment with a low but significant activation free energy. On the other hand, the second electron reduction of the resulting pentacoordinated $[Pt^{III}(NH_3)_2(CH_3COO)Cl_2]$ species occurs through a barrierless concerted process to the final $[Pt^{II}(NH_3)_2(CH_3COO)_2]$ derivative. Accurate values for the redox potential were obtained in good agreement with the experimental data.

A deeper insight into the dependence of the mechanism of reduction of Pt(IV) complexes would be very important to understand its mechanism of action *in vivo* and may be useful to design new and more potent platinum(IV) anticancer drugs.

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# A Fully Polarizable Embedding Model for Molecular Spectroscopy of Aqueous Solutions

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The computational modeling of molecular spectra of aqueous solutions is particulary challenging. In fact, it requires at the same time an accurate modeling of the response of the solute to the external radiation field and a reliable account of the effects of the surrounding environment, which can hugely modify the solute's spectral features as a result of specific/directional interactions (1).

A recently developed Quantum-Mechanical (QM)/polarizable molecular mechanics (MM)/polarizable continuum model (PCM) (2) embedding approach has shown extraordinary capabilities, yielding calculated spectra in excellent agreement with experiments.

An overview of the the theoretical fundamentals of this methods, which combines a fluctuating charge (FQ) approach to the MM polarization with the PCM is given, and specific issues related to the calculation of spectral responses (3) are discussed in the context of selected applications (4).

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# Contributi Orali

# Astrochemistry: a Computational Spectroscopy's View

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For many years, the interstellar medium (ISM) was considered too hostile an environment for organic molecules. This paradigm of thought began to deteriorate roughly forty years ago with the discovery of molecules containing carbon chains and rings. As time has gone on, the pace of molecular discovery has accelerated, and the detection in the last decade of molecules showing some significant complexity (for example, glycolaldehyde, acetamide and methyl acetate), has served to completely erase the original point of view. Indeed, the detection of almost two hundred molecules in space suggests that the ISM is characterized by a rich chemistry. Among the "complex" organic molecules detected, "prebiotic" molecules – those similar to, or the same as, molecules involved in the biochemistry of Earth – have attracted particular interest. Debate on the origin of the biomolecular building blocks has been further stimulated by the discovery of nucleobases and amino acids in meteorites and other space environments. Understanding the chemical evolution of the universe is one of the main aims of astrochemistry. The starting point for the development of astrochemical models is the knowledge of whether a particular molecule is present in the astronomical environment and, if so, its abundance. In this scenario, molecular spectroscopy plays a critical role since it provides the information needed to make definitive astronomical searches. Increasingly, these astrochemical-spectroscopic investigations areassisted by quantum-chemical calculations of structures as well as spectroscopic and thermodynamic properties, such astransition frequencies and reaction enthalpies, to guide and support observations, line assignments, and data analysis in these newand chemically complicated situations (1).In this contribution, the state-of-the-art computational approaches purposely set up in our research groups are presented through the discussion of selected and exemplificative examples. Starting from the accurate spectroscopic characterization of oxirane - a potential prebiotic species in Titan's atmosphere - as a test case (2), the small prebiotic molecules under investigation in the frame of the "STARS in the CAOS (Simulation Tools for Astrochemical Reactivity and Spectroscopy in the Cyberinfrastructure for Astrochemical Organic Species)" PRIN 2015 project and the challenge of the spectroscopy of building blocks of polycyclic aromatic hydrocarbons (PAHs), like the phenalenyl radical, are addressed.Emphasis will be also given to the powerful support provided by the Virtual Multi-frequency Spectrometer, VMS (3), and in particular by the newborn rotational module VMS-ROT (4) – those that are interested are referred to the dedicated contribution. VMS is intimately related to theoretical calculations, to be used as a starting point for guiding experiments and spectral interpretations, and also features VMS-Draw, a multiplatform graphical user interface (GUI).

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# Modeling Charge Transport in Organic Materials

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Understanding charge transport in molecular systems is of paramount importance, both for designing new molecular materials for modern optoelectronic devices (1), such as organic light emitting diodes, bulk heterojunction solar cells, and field effect transistors, and for understanding important biochemical processes (2), such as photosynthesis, respiration, and DNA oxidative damage.

Herein, we discuss different theoretical approaches for treating charge transport between molecular blocks at full quantum mechanical level: Fermi's Golden Rule, second order cumulant approximation of Liouville equation (3), and the numerical solution of the time dependent Schrödinger equation (4), focusing attention on charge transport in DNA oligomers and charge transport in organic semiconductor.

As concerns hole transfer in DNA, we analyze the rates of hole transfer between guanines separated by up to five adenines or thymines, exploring both the coherent single step superexchange mechanism and the incoherent multi step hopping. Theoretical simulations show that in short oligomers, consisting of two guanines separated by a high energy bridge of up to threethymine bases, hole tunnelling between guanines can occur on picosecond timescales, about three order of magnitude faster than hole hopping. However, tunnelling becomes extremely slow in longer oligomers, containing more trap sites, where charge can bounce among them. Our results are able to reconcile conflicting experimental results (5,6), showing the great complexity of charge transport in molecular systems.

As concerns charge transport in organic semiconductors, we will show that Fermi's golden rule can be inadequate for systems exhibiting ultrafast hole hopping rates, while cumulant second order approximation is extremely more accurate in those cases.

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# Ab Initio Molecular Dynamics to Simulate Excited State Proton Transfer to Solvent: the Strange Case of a Super Photoacid in Water and Methanol Solutions

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Light irradiation adds new dimensions to the conventional ground state chemistry. Basically, the strongly perturbed electronic structure, reached when molecules get excited, leads to a reactive behavior that ground state chemistry cannot achieve. In this way weak acids in the ground state can turn theirself in very strong photoacids upon the electronical excitation.(1) Unveiling at molecular level the complex aspects of Excited State Proton Transfer (ESPT) reactions, with solvent molecules acting as proton acceptor, is extremely difficult.Indeed, a wide range of time scales affects the ESPT kinetics, going from the femtosecond (electron density redistribution of the chromophore) to the nanosecond (diffusion process after the reaction) scale.(1) Furthermore the reaction phase space is very complex, involving both the photoacid and solvent degrees of freedom.(1,2)The exploration of different time scales in a very complex reaction space represents the main challenge for the theoretical simulation of ESPT processes. What is more, theoretical approaches are called to handle at the same time both the electronic redistribution of the chromophore and the solvent relaxation around the proton transferring complex, finely modulating the kinetics and thermodynamics of the reaction.(3)In this contribution we took up this challenge, investigating the mechanism and driving forces of ESPT reactions by means of Time-Dependent Density Functional Theory based ab-initio molecular dynamics simulations. An effective hybrid implicit/explicit model of solvation, was adopted to consider in an explicit way the solvent coordinate in the ESPT process.(4) The solvation and photoreactivity of a super photoacid, named QCy9, was investigated in water and methanol solution, both in the ground and the excited state. More closely, QCy9 is a super photoacid, which exhibits a very large ESPT rate constant, $k_{PT} = 1 \times 10^{13}\ s^{-1}$, the largest value reported in the literature so far. This constant is the same independently on the nature of the solvent (water or methanol).(1)The solvent configuration space at the ground electronic state was deeply investigated analyzing the hydrogen bond network around the acid group and the proton acceptor solvent molecule.Several configurations in the Franck-Condon region, describing an average solvation, were then chosen as starting points for the excited state dynamics. In any case the excited state evolution spontaneously leads to the proton transfer event, whose rate is strongly dependent from the hydrogen bond network around the proton acceptor solvent molecule. This is true both in water and methanol solution. Our calculations revealed that the explicit and polarizable representation at least of three solvation shells around the proton acceptor molecule is necessary to stabilize the solvated proton and allow its diffusion across the solution. Moreover the analysis of the solvent molecules motions in proximity of the reaction site confirmed that the ESPT event between the donor and the acceptor molecules is actually assisted by the oscillations of solvent molecules belonging to the first and second solvation shell of the accepting molecule.

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# Real-Time Coupling between Molecules and a Continuum Environment

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We have recently developed a real-time approach for including the non-equilibrium response of a continuum environment in the propagation of the wavefunction (1,2) or the electronic density (3) of a molecule, respectively described with the Real-Time TDCI and TDDFT.

The molecule-environment interaction is treated with the Boundary Element Method (BEM), that we reformulated using a diagonal representation for the frequency-dependent response matrices. Our *diagonal BEM* formulation is equivalent (i) to the Polarizable Continuum Model (PCM) (4) when the space is occupied by a polarizable continuum medium and the molecule is placed in a vacuum cavity created within such medium, and (ii) to the approach, analogous to PCM, developed to describe the enhancement induced by plasmonic excitations in metallic nanoparticles surrounding the molecule on its spectroscopic properties (5); but it clearly highlights the connection between BEM-based and multipolar-based description of the molecule-environment interaction potential (3). Moreover, in the time-domain, our approach provides *equations of motion* for the fictitious degrees of freedom (polarization charges) generating the time-dependent interaction potential, that we derived both for a Debye (solvent) and a Drude-Lorentz (nanoparticle) response (1,2).

As a result we detail the effects of the environment polarization on the population of the molecular excited states, induced by an external electric-field short pulse, and on linear and non-linear spectroscopic properties of the molecule.

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# A New Efficient Time Dependent Density Functional Algorithm for Large Systems: Theoretical Study and Applications to Plasmonic Systems

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A new algorithm to solve the TDDFT equations in the space of the density fitting auxiliary basis set has been developed and implemented in ADF.[1]In particular, the method extracts the spectrum from the imaginary part of the polarizability at any given photon energy, avoiding the bottleneck of Davidson diagonalization in Casida formulation. The original idea consists in the simplification of the double sum over occupied-virtual pairs in the definition of the complex dynamical polarizability, allowing an easy calculation of such matrix as a linear combination of constant matrices with photon energy dependent coefficients. This makes the present scheme very efficient. The method has been applied to very different systems in nature and size (from $H_2$ to $[Au_{309}]^-$)[2,3]. In all cases, the maximum deviations found for the excitation energies with respect to Casida approach are below 0.2 eV. The new algorithm has the merit to calculate the spectrum at whichever photon energy but also to allow a deep analysis of the results, in terms of Transition Contribution Maps,[4] plasmon scaling factor analysis[5], induced density analysis, and with a fragment projection analysis[6]. Circular Dichroism of large systems becomes also affordable.[7]

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# Exploring Nuclear Photorelaxation and Photoreactivity by Excited State Ab-Initio Dynamics and Time Resolved Vibrational Analysis.

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Understanding at atomistic level the mechanism of photoinduced chemical reactions in terms of electronic/nuclear motions responding to the external perturbation is a challenging task from both experimental and theoretical point of view. Time resolved vibrational spectroscopies, such as femtosecond stimulated Raman spectroscopy (FSRS) (1), were shown to be a very powerful tool to investigate and follow in real time the nuclear motion of photoexcited chromophores. The interpretation of the often complex experimental spectra can benefit from the employment of a theoretical-computational approach. In particular, ab-initio molecular dynamics methods allow to simulate and accurately reproduce the behaviour of chromophore in solution in both equilibrium and far for equilibrium regime, i.e. after the interaction with light (2,3). The analysis of the signals extracted from dynamics allows to create a direct link electronic/nuclear structure and spectroscopic properties (2). The present contribution is focused on the photoreactivity of pyranine [ 8-hydroxypyrene-1,3,6-trisulfonic acid] in water solution (4). Pyranine is a popular photoacid molecule, upon irradiation with light an excited state proton transfer reaction (ESPT) takes place. We are interested in ultrafast reactivity, namely that occurring in the femtosecond to picosecond time scale. During this time pyranine shows a characteristic activation of low frequencies skeleton modes upon excitation that precedes the ESPT event (5). We adopted an integrated computational approach including ab-initio molecular dynamics and time resolved vibrational analysis based on Wavelet Transform (2). This latter allows us to localize any signal extracted from excited state trajectory in both time and frequency domain. In this way, we can follow the activation and relaxation of the key normal modes of the photoexcited pyranine, and to reproduce the reaction pathway before the reactive event itself.

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# Lanthanoid(III) Ions: Transferable Lennard-Jones and Buckingham Pair Potentials from Aqueous to Complex Media

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Lanthanoid(III) ions, which are commonly denoted as Ln(III), represent the most extended series of chemically similar metal ions. The solvation properties of Ln(III) ions in solvents with different polarity are of special interest due to the huge number of possible applications, including industrial processes, separation in nuclear power technology, waste management, and liquid-liquid extraction processes. (1,2) Understanding the coordination properties of Ln(III) ions in different solvents and sheding light into the molecular interactions taking place in these solutions is therefore important to select the best performing solvents.

Here, for the first time, new sets of Lennard-Jones and Buckingham potentials have been developed for the whole lanthanoid series in water, by directly comparing the structural hydration properties obtained from classical Molecular Dynamics (MD) simulations and the extended X-ray absorption fine structure (EXAFS) experimental data. This joint MD-EXAFS approach is a powerful tool to assess the capability of the employed force field to correctly describe the structural properties of the investigated systems. (3,4) Starting from these sets of Ln-water parameters we have extrapolated generic Ln-Ln pair potentials to be used in combination with force fields available in the literature for studying the coordination of Ln(III) ions in different disordered systems, going from inorganic to bio-inorganic to organic systems.

The importance of developing a new set of Lennard-Jones parameters for Ln(III) ions is due to the fact that they are computationally efficient interaction potentials that can be readily used to perform classical MD simulations without explicit polarization. However, the transferability of a given potential to systems different from those for which they have been developed has to be verify case by case. To this end we will show examples of MD simulations of Ln(III)-containing systems, carried out using our developed Lennard-Jones parameters. In particular, we have investigated Ln(III) ions in water and acetonitrile, but in the presence of their counteranions, such as nitrate, triflate or bis(trifluoromethylsulfonil)imide ions. Finally, we will show the possibility of using the Ln-Ln Lennard-Jones pair potentials in MD simulations of a more complex and disordered Ln(III)-containing system: a diluted solution of $Ce(NO_3)_3$ in the protic ionic liquid (IL) ethylammonium nitrate. ILs may be ideal alternatives to standard solvents due to their excellent chemical and thermal stability, non-volatility and favorable solvating properties for a range of polar and non-polar compounds. In this case, for the first time polarizable effects have been included in the MD force field to describe a heavy metal ion in a protic IL, but they were found to be unessential.

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# Unraveling Chiral Properties of Metal Complexes through Computational Vibrational Spectroscopy

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Transition metal complexes play a key role in asymmetric synthesis of fine chemicals and in the last year have drawn attention for their potential use as antitumoral agents. However, applying them for pharmaceutical purposes requires a correct and extensive characterization of their properties. In this respect, chiroptical methodologies are the only experimental techniques capable of directly probing the molecular chirality. In tangled systems like metal complexes, several stereogenic units can be present and it is often useful to find some features in the spectrum that could be referred to the specific contribution of each one of them. However, experimental spectra can seldom be interpreted on the basis of classical or phenomenological models and an accurate theoretical treatment is mandatory. In particular, vibrational analysis supported by Density Functional Theory (DFT) calculations have had considerable successes in assigning the absolute configuration (AC) and evaluating the conformational properties of many molecular systems. Nevertheless, the harmonic approximation, which is commonly used to simulate spectra, may be insufficient due to limitations in the accuracy and lack of features caused by the missing contributions from overtones and combinations. Thanks to the recent developments done in our group, it is now possible to simulate full anharmonic spectra with correction to both energies and intensities. In this contribution, we will show examples of accurate simulation of IR and vibrational circular dichroism (VCD) spectra beyond the harmonic approximation (1). Furthermore, a toolbox aimed at analyzing and interpreting the different features in the spectra will be presented. Due to the computational cost, full anharmonic calculations in systems of medium-to-large size can be very challenging. Therefore, an appealing alternative is to reduce the dimension of the system to a set of normal modes directly involved in the studied feature of the spectrum. Helped by user-friendly interfaces, a careful definition of the reduced dimensionality (RD) scheme can lead to very good results in target portions of the spectrum (2), at a fraction of the computational cost of the full calculations. Moreover, computations can provide extensive analysis on the origin of the band-shape and employing graphical tools can significantly aid the understanding of these phenomena. For example, transition current density (TCD) (3) maps, which allow an evaluation of the electron flow associated to the molecular vibration, provide insights in the origin of the intensities, that are generally lost when only numerical values are considered. All these aspects will be illustrated through a series of chiral ruthenium cyclopentadienyl carbonyl complexes, for which the carbonyl stretching has been recently proposed as probe of the chirality at the metal center (4). The relation between the chirality at the metal center and CO stretching will be deeper investigated with the presented ad hoc tools.

The research leading to these results has been performed in the framework of the ERC Advanced Grant Project DREAMS "Development of a Research Environment for Advanced Modelling of Soft Matter", GA No. 320951.

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# Computational Study of Curcumin-Derivatives for Alzheimer's Disease Treatment

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The Alzheimer's disease (AD) is responsible of 60% of memory loss and cognitive disorders in people over their 65 due to the formation of amyloid plaques in the brain that modify or block nervous impulses. Amyloid plaques are made by the aggregation of amyloid-β fibrils that stack together through their β-sheets(1). Curcumin is used in traditional medicine in India and China due to its anti-inflammatory, anti-oxidants, chemopreventive and chemotherapeutic properties(2). In recent years, curcumin has been tested as an amyloid inhibitor finding that it is able to bind to small amyloid-fibrils and to block the aggregation and formation of fibrils *in vitro* and *in vivo*(3). In order to find curcumin-derivativeswith improved inhibition characteristics with respect to the Aβ(1-40) fibril aggregation, we have performed molecular docking(4) of curcumin-derivatives over full-length Aβ(1-40) fibrils obtaining for each compound 4 binding regions mainly located in the correspondence of the β-sheets. Then, each Aβ(1-40) fibril—curcumin configuration has been simulated by means of classical molecular dynamics in order to study the dynamics of the interaction and obtain the binding energies(5). This last step is of crucial importance to reproduce the fibril flexibility not taken into account in the docking procedure. From both computational approaches, we obtained an affinity ranking based on the binding energy of that molecule on each fibril region where the basic form of curcumin is used as a reference for others compounds. Data have been found to be in good agreement with experimental dissociation constants (DC50) of compounds on mature Aβ(1-40) fibrils measured in our lab.

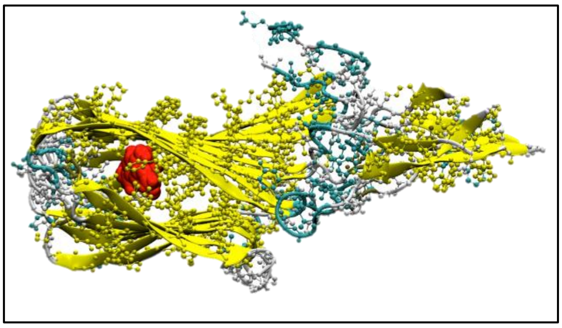

**Figure 4:** Docking of Curcumin to an Aβ(1-40) fibril.

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# First-Principles Design of P-Type Semiconductor Oxides as Alternative to NiO in P-Type Dye-Sensitized Solar Cells

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Tandem Dye Sensitized Solar Cells (t-DSSCs), consisting of a n-type DSSC photoanode coupled with a p-type DSSC photocathode, have brought a lot of attention in the solar energy conversion scenario since they are capable to break the theoretical performance limits of the single devices. (1)Actually, tandem cells with a $V_{oc}$ equal to the sum of that from the separate p and n devices have been reported. (2) The main limitation in this scheme is that p-DSSCs are underdeveloped with respect to their n-type counterparts. (3) This is in large part due to the choice of the semiconductor. Currently, the most efficient semiconductor in p-DSSCs is NiO, but presents several drawbacks: low electrical conductivity and redox potential, high visible light absorption and low hole mobility. Delafossites, showing a high p-type conductivity and a wide band gap around 3.6 eV, are a possible alternative to NiO for p-DSSCs. (4,5) Since the discovery of p-type conductivity in $CuAlO_2$ (6), many experimental and theoretical studies have focused on materials with delafossite-type structures, suggesting that these materials could outperform NiO as photocathodes. (7) The role of divalent cations (expecially $Mg^{2+}$) substitutions in the B site has been studied both theoretically and experimentally. (8) It is suggested that this kind of substitution reinforces the $Cu^{+}/Cu^{2+}$ mixed valence and enhances the p-type conductivity by increasing the charge carrier concentration. (9) However, there are no studies that demonstrate the electronic and structural effects of Mg dopants on the delafossite bulk properties. Thus, here we report a first-principles investigation on the $CuBO_2$ (B = Al, Ga and Cr) delafossite oxides. $CuAlO_2$, $CuGaO_2$ and $CuCrO_2$ are among the most studied and synthesized delafossites, and record conductivities have been measured with p-doping on these materials. We investigated at the PBE+U and HSE06 levels of theory both the pristine materials and the p-type derivative with 8.3% of Mg doping. Our electronic structure and charge distribution analyses show that Mg doping creates Cu(II) acceptor states inside the band gap that can interfere the photoconversion process. Moreover, we also aimedat establishing the feasibility of $CuBO_2$ for DSSC devices. To this end, wepredicted the $V_{oc}$ with respect to some of the most commonly used redox couples: we evaluated the absolute position of the valence band edges modelling the stoichiometric (100) orthorhombic surfaces and calculating the relative work-function ($\phi$). From these results, we established the most convenient element at the B site to be exploited for p-type DSSCs.

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# Toward a Rational Design of Half-Sandwich Group 9 Catalysts for [2+2+2] Alkynes Cycloadditions

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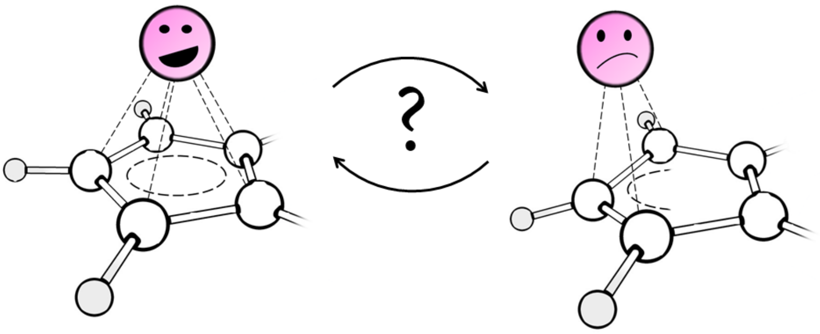
Filling the gap between molecular structure and reactivity is a well-known challenging task in chemistry. The rational design of catalysts may greatly benefit of computational aid, provided state-of-the-art methodologies are employed. The case of metal catalyzed [2+2+2] cycloaddition of alkynes/alkynes-nitriles to benzene/pyridine is investigated in detail, due to the paramount importance of these reactions for the synthesis of cyclic and polycyclic organic compounds.(1) Catalysts of general formula Cp'M are considered, where Cp' is the cyclopentadienyl anion or the cyclopentadienyl moiety of larger polycyclic aromatic/heteroaromatic ligands, and M=Co, Rh, Ir. Energy profiles of the whole cycles with a number of intermediates ranging from 5 to 9 connected by the corresponding transition states are computed and the catalyst performance is evaluated based on its turnover frequency (TOF), by implementing the equations of the energy span model.(2) TOF values are related to peculiar structural features of the Cp'M fragment, i.e. to the M-Cp' bonding mode which results in slippage phenomena during the catalytic cycle. In fact, the metal is never coordinated to the five carbon atoms ring in highly symmetric fashion ($\eta^5$), but is *slipped* and the amount of this distortion changes during the various steps of the catalysis.(3,4) This fluxionality is found to affect importantly the efficiency of the catalyst.



Scalar ZORA relativistic density functional methods are employed and activation strain analysis (5) is systematically performed to gain insight on the factors controlling the height of the relevant energy barriers.

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# Ramachandran Energy Approach for Protein Folding

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Despite a tremendous effort to develop reliable models for the prediction of protein folding, and in spite of the results obtained so far, the quality of the geometry prediction remains quite poor for peptides longer than 60-80 residues (1). There are mainly two kinds of approaches: the *ab initio*, which relies simply on the amino acids sequence and on chemical-physical principles, and the homology, in which one starts from proteins with similar structure found in nature. In the present work, we will summarize the advances in the peptide folding research and we will offer a new approach that is promising to sensational results (2). The approach, falling in the realm of *ab initio* simulations, is largely inspired by biological and biochemical mechanisms (3). We have added two new terms to the Amber force field to drive the minimization toward the proper region in the Ramachandran plot (see Fig. 1). The method, entitled Ramachandran folding as a tribute to the great Indian biochemist, is capable to suggest the most realistic folding mechanism so far described.

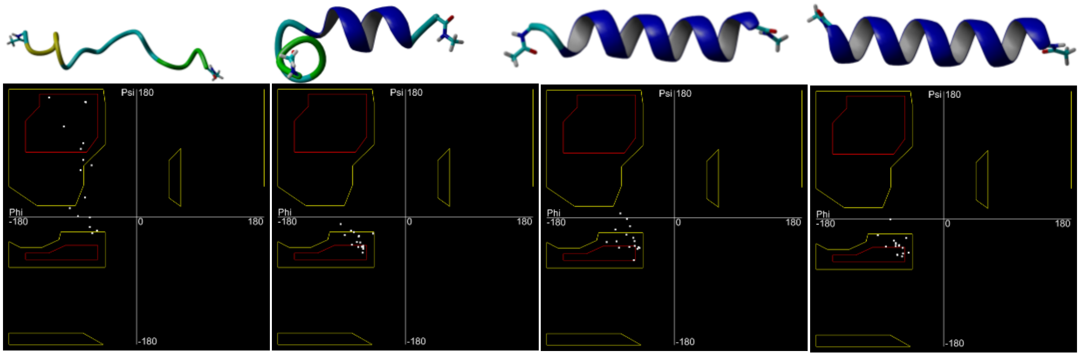

Figure 1 – Protein folding evolution in a Ramachandran plot

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# Computational Design of $Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$ (SFMO)-based Bifunctional Electrodes for Proton-Conducting Solid Oxide Electrochemical Cells

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Double perovskite $Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$ (SFMO) has attracted interest in the last few years as cathode material in intermediate temperature oxide-conducting (OC) solid oxide fuel cells (SOFCs) due to its good electrochemical activity, chemical stability in red-ox conditions, and resistance to coking and sulfur poisoning.(1) By means of state-of-the art first-principles calculations, we have unveiled SFMO structural, electronic, defect and catalytic properties and propose SFMO derivatives with promising performance also in proton-conducting (PC) SOFCs. SFMO excellent performance in the OC regime can be ascribed to the easy formation of oxygen vacancies and extraordinary low oxide migration barrier heights.(2)SFMO inherent non-stoichiometry(3) turns it into a good candidate for proton conduction provided that oxygen vacancies allow the incorporation of protons into the lattice via water dissociation.Our calculations show that aliovalent doping enables convenient hydration and effective proton transport in bulk SFMO, which opens the route toward new promising triple-conducting (proton/oxide/electron) oxides for use as single-phase electrodes in PC-SOFCs.(4) Moreover, we have analyzed different reaction pathways for the performance-limiting oxygen evolution and reduction reactions (OER/ORR) and evaluated the corresponding overpotentialswithin the theoretical standard hydrogen electrode (TSHE) framework.(5)Beyond discussion of specific SFMO applications, we use these results on SFMO and related systems within a general framework to discuss key structural and electronic properties/processes and easily-computable descriptors that can help to design new perovskite-based electrodes for OC- and PC-SOFCs.

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# Insight From DFT Simulations on the Collagen/Hydroxyapatite Interface: a Simple Model Based on the Poly-Proline Polymer

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Collagen protein (COL) is one of the most abundant protein in mammals. Its structural peculiarity is the geometrical motif in which three parallel polypeptides strands, in a poly-proline type II (PPII) fashion, coil about each other to form a triple helix (1). COL is also the main component of bone where is in strict interaction with the hydroxyapatite mineral (HAP). Large amount of Proline (PRO) and derivatives are found in COLs. It is known that the side chain conformations of PROs have a huge role in COL features. Conformational changes between PRO puckers can lead to the COL triple helix unfolding (2). Moreover, PRO side chain mobility induces structural flexibility to the COL protein (3). In our work, we focused on the very delicate conformations of the PRO ring embedded in the COL protein. We carried out the investigations by means of accurate *ab initio* calculations by employing a very simple COL model, e.g the PPII polymer (4-5). We characterized the free PPII polymer and we simulated its adsorption on the HAP surface. We computed the relative stabilities of the PPII as free and on the HAP surface. The comparison reveals that HAP adhesion guides the formation of puckering conformers which are un-accessible by the free polymer alone.

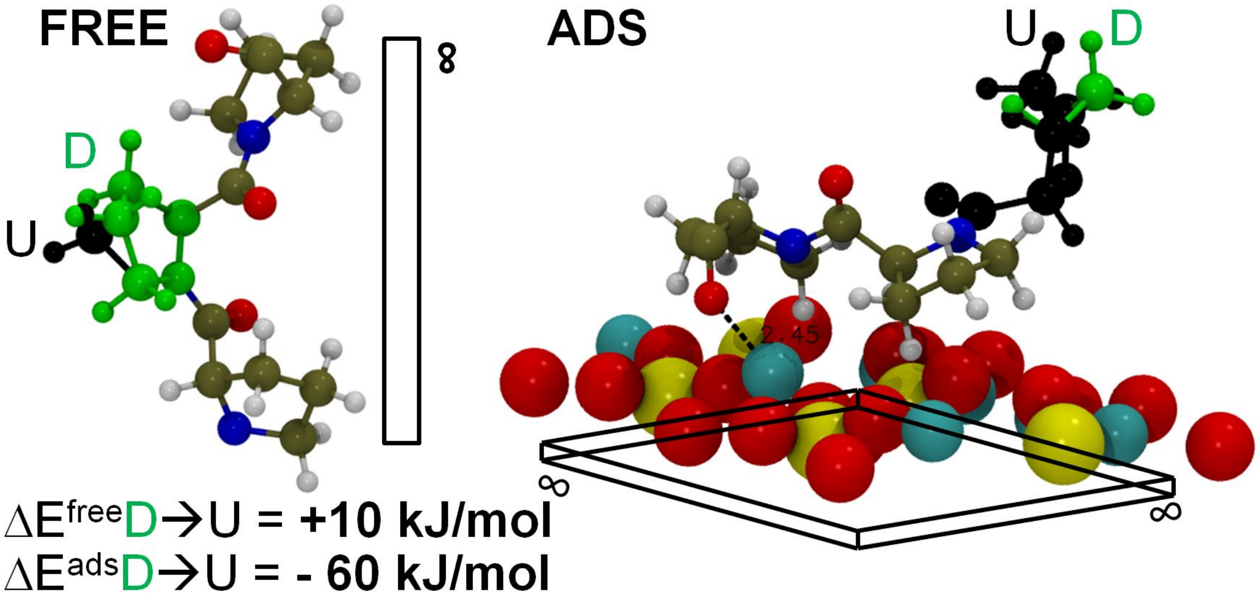

*Figure* **3.** *Difference in the relative stability for the U and D PPII conformers as free (FREE) and as adsorbed (ADS) on the HAP surface (by C=O···Ca electrostatic interaction).*

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# A DFT Rationalization of a Two Metals Strategy to Tune Selectivity in Catalysis

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Selectivity is among the most important properties of an effective catalyst. In homogeneous transition metals catalysis this can be achieved by appropriate design of the ligand wrapped around the metal. In heterogeneous catalysis this is a more complex issue, since selectivity is often associated with different reactivity at different surfaces of the catalyst, as well as at steps, edges, and any type of defects that almost inevitably are present in any heterogeneous catalyst. Indeed, the less selective sites on a metallic catalyst are usually associated with low coordinated metals, such as those of rugged surfaces or defects, since these sites are considered as the most reactive. Under these conditions, a promising strategy to improve the selectivity of a metallic catalyst is alloying a second metal, less reactive and capable to occupy preferentially sites corresponding to low coordinated metals.(1) In this communication we will present some DFT insights in the dry reforming of methane promoted by Ni/Co catalysts.(2) In details, we performed DFT simulations aimed to elucidate the availability of the different active sites on the surface of the reduced CoNi particles to supplement the experimental techniques used that lack of atomic resolution.

Moreover, calculations allowed to rationalize the catalytic behavior of the alloy showing that the CoNi metal surface has an intermediate energy of oxygen chemisorption, between those of monometallic Co and Ni (see Chart 1).

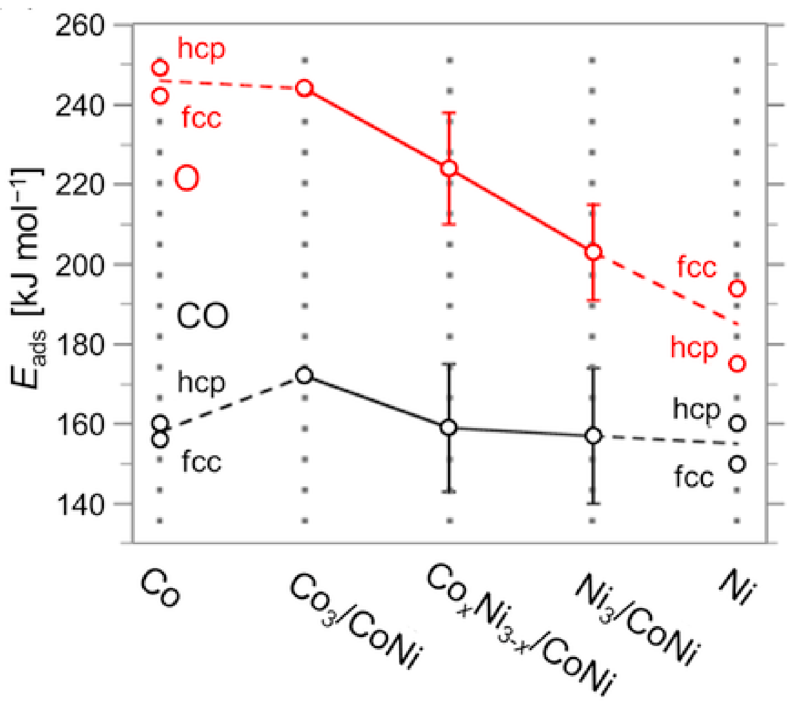

**Chart 1.**

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# The Role of Metal Substitution in the Metallo-Enzymes: a Theoretical Point of View

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Quantum mechanical (QM) cluster model and quantum mechanical/molecular mechanical (QM/MM) calculations were performed on some metalloenzymes belonging to different classes. Insight is gained into the enzymatic activity upon metal-ion substitution.
The examined cases:

-Carbonic anhydrase (CA): Zn-, Co-, Cd-CA hydrating $CO_2$;(1,2)Rh-CA hydrogenating $CO_2$ to formic acid. (3)

-Methanol dehydrogenase (MDH)**:** Ce(III)-MDH versus Ca(II)-MDH. (4)

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# Back-Donation in $d^0$ Metal Complexes: does it Exist? The Case of Nb(V)

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Since the introduction of the Dewar-Chatt-Duncanson (DCD) model, which almost 70 years ago proposed an elegant framework to rationalize the coordination of an olefin to a transition metal, inorganic chemists expanded its use to the coordination of every ligands, including carbon monoxide, phosphines and carbenes, demonstrating its general applicability.

Particularly interesting is the bonding in $d^0$ metal complexes: in the simplest sense, they should not be able to back-donate electronic density to the ligand because their *d* orbitals are formally empty, but, obviously, things are more complex than this.For example, $[Cp^*_2M(H)_2CO]$ complexes (M = Zr, Hf) exhibit a classical behavior ($\upsilon_{CO}$ = 2044 and 2036 $cm^{-1}$ for Zr(IV) and Hf(IV), respectively) (1) and it has been proposed that "back-donation" could come from a M-H orbital of appropriate symmetry.

Recently, various Nb(V)-carbene complexes have been structurally characterized(2) and all of them exhibit a peculiar metal arrangement: the halides *cis* to the carbene that lie almost perpendicular to the plane of the carbene are slightly bent toward the carbene itself. According to some authors, this is an evidence of Cl → carbene back-donation, but according to others, the Nb-carbene bond is a pure σ bond.

In this contribution, we shed some light on this controversial topic through a combined experimental/theoretical approach, studying complexes with appropriate ligands and analyzing their Nb-L bond by means of the Charge Displacement analysis, which recently demonstrated its potential in the detailed and quantitative characterization of coordinative bonds.(3)

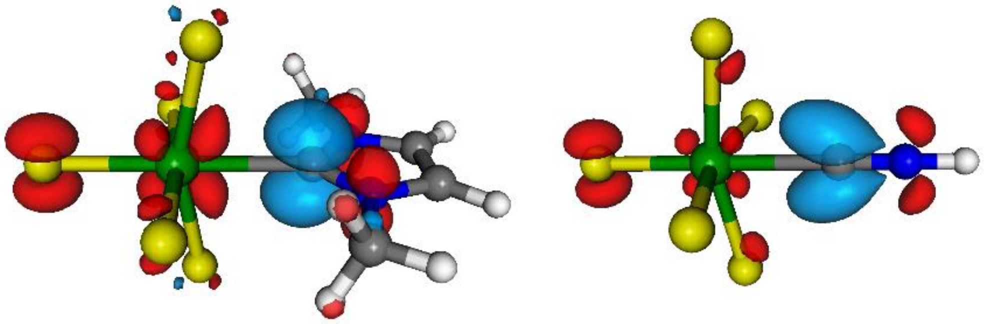

Figure: Isodensity surfaces (±0.001 e/a.u.) for the B1 component of the density deformation function upon the formation of the $[NbCl_5]$-L bond (L = 1,3-dimethyl-imidazol-2-ylidene, hydrogen isocyanate).

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# Combination of Porphyrin and Ruthenium-arene Moieties for a Dual Anticancer Function. A Theoretical Investigation.

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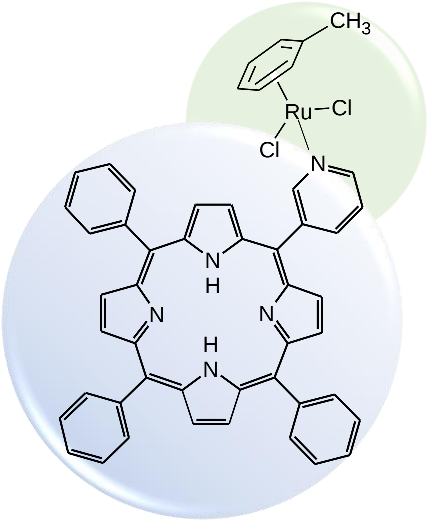
Combining therapies for the treatment of diseases has become a worthwhile strategy to improve efficiency and decrease side effects. In particular against cancer, a combination of chemotherapeutics with radiation is recently appeared as a common form of treatment. It requires the photosensitizing action of a molecule able to absorb a radiation with appropriate wavelength and a metal complex demanded to exert the chemotherapeutic function.



As regards the metal complex, several efforts have been devoted in the last years to find an alternative to cisplatin anticancer, whose clinical effectiveness has been greatly limited by drug resistance and significant side effects. In the search for new metal based anticancer agents ruthenium complexes have raised great interest, and their antitumor potential has been established over two decades ago. Thus, a huge variety of plausible complexes able to inhibit tumor cells growth have been proposed, some of them are under clinical trials.[1]

From the other hand, photosensitizers currently approved for clinical use in photodynamic therapy belong to the porphyrin-like class of molecules thanks to their low dark toxicity, thermodynamic stability, absorption properties in the Q band that can be modulated by varying $\pi$ electrons and facility to form metal complexes or to include in their structures heavy atoms.

Recently some Ru-based complexes, as that depicted in figure, have been suggested as drug candidatestoward human melanoma cancer cells, due to their dual synergistic effect of thearene ruthenium chemotherapeutics and the porphyrinphotosensitizer.[2]

Previous studies have largely demonstrated that theoretical computationsbased on first-principles methods can reliably predict orreproduce and rationalize electronic transitions,[3-8] as well as can give further insight into the mechanisms involved in the drug action.[9,10]

Density Functional Theory and its time-dependent formulation (TD-DFT) have been used to shed light on the mechanism of action of these compounds, exploring their photophysical properties and the mechanistic features.

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# Hydrogen Defects in Diamond. A Quantum Mechanical Approach

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The investigation of native and radiation-induced point-defects in diamond (as well as in other semiconductors) has attracted large theoretical and experimental interest. Diamond is a wide-bandgap material characterized by well-known extreme physical properties (high Young's modulus and thermal conductivity, broad transparency range, high carriers mobility, etc.) with attractive applications in different fields, ranging from microelectromechanical systems to heatsinks, laser windows, particle detectors, etc (1). Hydrogen, with nitrogen, is the most important impurity in diamond. It is included during the growth of natural diamond as well as in chemical vapour deposition (CVD) processes. It is certainly present at the surfaces; a non minor fraction, however, is also thought to be incorporated in the bulk. H atoms are supposed to be involved in several defects combining vacancies and nitrogen aggregates(2). It is identified through its infrared(IR) active modes (stretching and bending), although probably not all hydrogen atoms present in diamond are IR active. Thesharp vibrational peaks at 3107 and 1405 $cm^{-1}$ that appear in most natural diamonds (3) have been attributed in the past to various H containing defects. Experimental evidence suggest that His strongly bonded to a carbon atom, with weak perturbations due to nitrogen atoms (3).

Various H containing defects, in particular $VN_3H$ (a vacancy surrounded by three N and one C atom, the latter being saturated with H), have been considered by using a quantum mechanical approach, a local gaussian-type basis set, hybrid functionals, the supercell scheme and the CRYSTAL code (4). The same scheme has recently been used for describing the vacancy (5) and interstitial (6). Various properties (structural, electronic vibrational) have been used for a complete identification of the defect. The Infrared spectra (wavenumbers and intensities, evaluated analytically through the Coupled Perturbed Hartree-Fock method) aregenerated and compared with experiments.

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# Forsterite Surfaces as Models of Interstellar Core Dust Grains: Computational Study of Carbon Monoxide Adsorption

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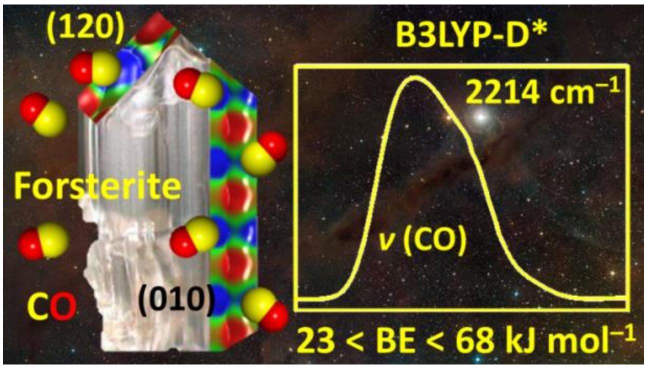
Carbon monoxide (CO) is thesecond most abundant gas-phase molecule (after hydrogen) of the Interstellar Medium (ISM) (1). In Molecular Clouds (MCs), regions of the ISM where star-forming processes occur, it adsorbs at the surface of grain cores – typically partially crystalline Mg/Fe silicates – or within the icy grain mantle and originate other molecular species through the catalytic power of surface active sites. More than 200 molecular species in the MCs have been observedso far by means of rotational spectroscopic, partly derived from reactions among molecules entrapped at the grains surfaces, while the presence of Mg-silicates has been inferred by IR spectroscopy (1,2,3). Laboratory studies can only partially reproduce the harsh conditions of the ISM (4), thus computational modeling can play a major role in the understanding of the chemical network charactering MCs. In this work, we performed and accurate analysis of the energetic and structural features of CO adsorption on different crystalline forsterite (Fo, $Mg_2SiO_4$) surfaces by means of DFT techniques. Data indicate that CO exclusively physisorbs on Mg exposed cations of Fo surfaces, with binding energies in the 23-68 kJ mol$^{-1}$ range. Not only simple charge-dipole forces are involved, but also quadrupolar and dispersive ones are responsible of the CO adsorption. We also performed a full thermodynamic treatment of the CO adsorption at the very low temperatures and pressures typical of the MCs together with a full spectroscopic characterization of the CO stretching frequency. We proved the CO stretching frequency value to be extremely sensitive to the local nature of the surface active site of adsorption and showed results at variance with what is known about CO adsorbed on flat oxide surfaces due to the complex electrostatic and structural morphologies of the Fo surfaces.The detailed kinetic analysis of CO desorption at different low temperaturessuggested that desorption times are higher than the typical evolution times of the ISM, at least until 100 K when they become comparable.Our computed data could be incorporated in the various astrochemical models of interstellar grains developed so far and thus contribute to improve the description of the complex chemical network occurring at their surfaces.



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# Prebiotic Molecules in Interstellar Space: Aminoacetonitrile and C-Cyanomethanimine

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The attempts to detect amino acids in the interstellar medium were so far unsuccessful even for its simplest form, glycine, despite that decades-long efforts have been devoted by many observational studies. From a chemical point of view, it is therefore important to identify the possible precursors of amino acids as well as the astronomical sources where they are abundant. Aminoacetonitrile ($NH_2CH_2CN$) is one of the possible precursors of glycine in the production process known as Strecker reaction, whose synthetic route is shown below:
$NH_3 + H_2C{=}O \rightarrow HN{=}CH_2 + H_2O$
$HN{=}CH_2 + HCN \rightarrow NH_2CH_2CN$
$NH_2CH_2CN + H_2O \rightarrow NH_2CH_2CONH_2$
$NH_2CH_2CONH_2 + H_2O \rightarrow NH_2CH_2COOH + NH_3$
Aminoacetonitrile has been already detected toward the giant molecular cloud Sagittarius B2 (1). Its vibrational ground-state rotational spectrum has been characterized in the laboratory up to 1.3 THz (2). Aminoacetonitrile has a few low-lying (below 400 $cm^{-1}$) vibrational excited states (3) and rotational transitions within these states may be observed in hot cores and circumstellar shells. In this study (4), the pure rotational transitions in the 3 lowest vibrational states have been assigned and analyzed in the range 80-450 GHz. It was found very important to include Coriolis coupling between the two lowest vibrational fundamentals, while the other one resulted unperturbed. The spectral data of these vibrational excited states are essential for future observations of the molecule in relatively high kinetic temperature conditions.
Another molecule of astrochemical interest is the dimerization product of hydrogen cyanide, C-Cyanomethanimine (HN=CHCN), that is thought to play an important role as intermediate in the prebiotic formation of purines and proteins. In fact, hydrogen cyanide tends to polymerize, giving biologically important molecules such as adenine (pentamer of HCN) (5). C-Cyanomethanimine exists in two isomeric forms, *Z* and *E*. Although the (*E*)-C-cyanomethanimine is about 210 $cm^{-1}$ less stable than the (*Z*)-C-Cyanomethanimine (6), the former has been detected through radio-astronomical observation (7) in the star-forming region (Sgr)B2(N), while no detection for the latter has been claimed so far. For its astrophysical interest and because its rotational spectrum has been investigated only below 100 GHz, the study of this molecule is being extended to higher frequency (millimeter and sub-millimeter wave regions) in order to facilitate astronomical detection. The sextic centrifugal distortion constants for both isomers of C-Cyanomethanimine were evaluated by means of highly accurate *ab initio* calculations (8). Therefore, the assignment of the rotational spectrum above 200 GHz can rely on accurate predictions.

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# Should we Introduce Pre-equilibria into Markov Models for Homogeneously Catalyzed Copolymerization?

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Polyolefin elastomers based on ethene and propene are important players in the field of synthetic rubbers and the molecular features that control bulk properties are strictly related to the monomer distributions along the chains (1). Usually, the chemical reactivity of a propagating chain is considered to depend only on the identity of monomer units at the growing end. Two reactivity ratios, $r_1$and $r_2$, were thus defined starting from the kinetic expressions for the uncontrolled radical mechanism in order to describe the radical copolymer micro-structure; mathematical models (e.g. Mayo-Lewis, Fineman-Ross and Kelen-Tudos) derived from such approach have also been exploited to characterize homogeneous catalyzed copolymers despite the latters could present a more complicated mechanism, involving coordination pre-equilibria (2,3).
In this study, we describe a theoretical study of E/P copolymerization by a $C_2$-symmetric metallocene catalyst, *rac*-$Me_2C$-$Ind_2ZrCl_2$ via a synergic DFT/kMC approach offering a robust alternative interpretation of homogeneously catalyzed copolymer process: the mechanism consists of at least two steps, equally important, namely coordination and insertion. If this holds, the application of Markovian models to copolymerization induced by homogeneous catalyst might request extreme care, as they hinge on the mechanism proposed for uncontrolled radical polymerization, which neglects coordination and pre-equilibria.

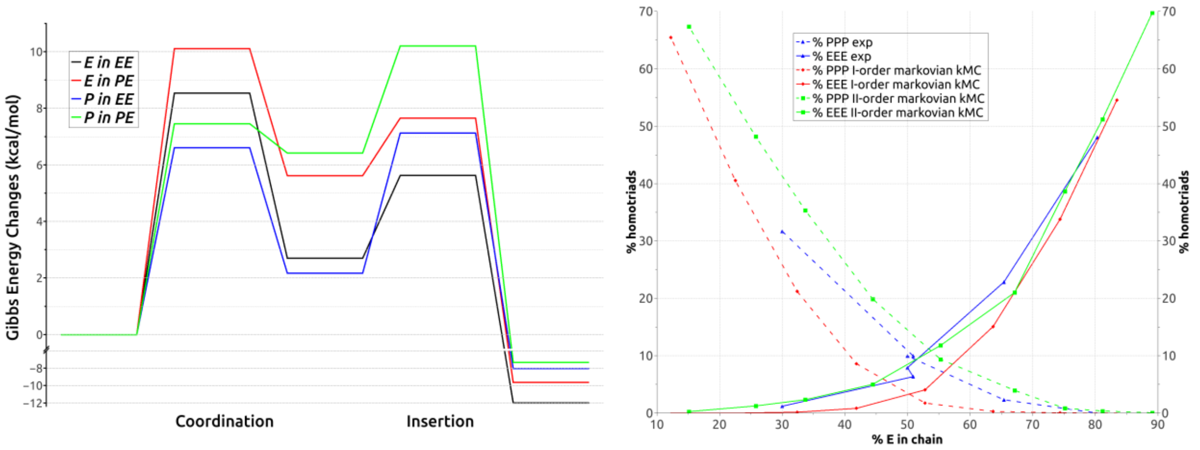

Figure 1. Left, a typical reaction pathway composed of coordination and insertion; right, comparison of experimental and kMC-simulated EEE and PPP triads.

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# Intermolecular Energy Transfer in Real Time

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Essential state models (ESM) have been successfully used to describe low-energy optical properties (1,2,3) of different classes of charge-transfer (CT) chromophores, namely dipolar (D-A, where D=donor and A=acceptor of electrons), quadrupolar (D-A-D or A-D-A) and octupolar (A(-D)3 or D(-A)3) chromophores.

Here we introduce a truly dynamical and non-adiabatic model for resonant energy transfer (RET). More precisely, we consider two different dipolar chromophores, an energy donor ($\mathcal{D}$) and an energy acceptor ($\mathcal{A}$), their main resonating structures being used as electronic basis states and introducing the coupling to one effective molecular vibration per chromophore.

By means of a non-adiabatic dynamical calculation also accounting for energy dissipation, we follow in real time the complete $\mathcal{D}$-to-$\mathcal{A}$ energy transfer process (fig.1, panel a). Coherent oscillations of $\mathcal{D}*$ as induced by an ultrashort light pulse are washed-out in the few hundred femtoseconds by fast intramolecular energy dissipation, while the $\mathcal{D}*$-to-$\mathcal{A}$ energy transfer process takes place in the following few picoseconds (fig.1, panel b). The whole process is followed through time-dependent fluorescence spectra (fig.1, panel c).

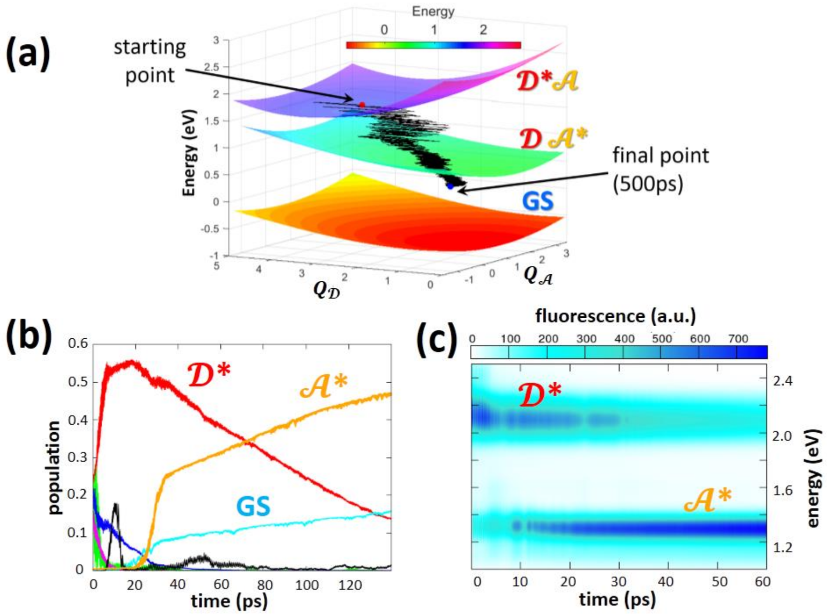

Fig. 1. Energy transfer in real time. Panel a: non-adiabatic $\mathcal{D}\mathcal{A}$ dynamics following impulsive excitation of $\mathcal{D}$; to help the eye, relevant adiabatic energy surfaces are also shown. Panel b: population time-dependence plotted for some relevant $\mathcal{D}\mathcal{A}$states. Panel c: time-dependent fluorescence spectra for the $\mathcal{D}\mathcal{A}$ system.

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# Proton Mobility in Protic Ionic Liquids: New Results from Theoretical Calculations

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Ionic liquids (ILs) are salts made by bulky, sterically mismatched molecular ions that possess a low melting point because the electrostatic interactions are weakened by charge delocalization and lattice formation frustrated by geometric effects. In contrast to traditional organic solvents, ILs possess negligible flammability and volatility and represent a new class of "green" solvents that are inherently safer than conventional solvents. A Protic Ionic Liquid (PIL) is formed through an acid base reaction. When the difference of pKa between the acid and the conjugate acid of the base is large (>10 pKa units) the ensuing liquid is completely ionized. In this case, the acidic proton is transferred quantitatively from the acid to the base during the synthesis reaction and turns out to be strongly bound to the latter. Subsequent proton transfer is therefore not possible. Conduction in these liquids is therefore due to ion drift (Walden mechanism) and inversely proportional to the liquid viscosity. In order to have a larger conductivity one has to find a way to promote the formation of different charge carriers. One possibility is to have proton transfer from one molecular ion to another. Compounds where amino acids in their deprotonated (anionic) form are combined with inorganic cations such as [Ch][Asp] and [Ch][Cys] might have these features. The former has a weak acid terminal, while the latter has a weak basic proton attached to the sulphur atom. We will show evidences of a non-ordinary behavior of these two materials that have been obtained by carefully validated ab-initio and classical molecular dynamics simulations [1].

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# Computational Tools for the Interpretation of Rotational Spectra within the Virtual Multifrequency Spectrometer

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Spectroscopic techniques provide a wealth of qualitative and quantitative information on the chemical and physical-chemical properties of molecular systems, in a variety of environments. However, the interpretation of experimental data is often a difficult task mainly because the observed spectroscopic properties depend on the subtle interplay of different effects, whose specific impact on the overall behavior is difficult to address. From this point of view, theoretical approaches are invaluable tools for guiding andcomplementing experiment as well as supporting the interpretation of spectra. For this reason, measurements are increasingly supported by theoretical studies, and computational spectroscopic techniques have become essential tools for understanding spectra in terms of basic physical-chemical process. The widespread use of computational spectroscopy has prompted the development of a virtual multifrequency spectrometer (VMS), which gives access to the latest developments in the field of computational spectroscopy also to non-specialists (1-4). In addition to the computational module (VMS-Comp), which provides the support for a wide range of spectroscopic techniques, it features VMS-Draw. This is a multiplatform graphical user interface (GUI), which offers to the user a powerful integrated environment for processing the outcomes of quantum-chemical calculations and visualizing the relevant information in an intuitive way. In addition, VMS-Draw includes a panel of advanced tools for the comparison of theoretical and experimental spectra, thus assisting their interpretation. In this contribution, we present VMS with particular attention to its newborn rotational spectroscopy module, VMS-Rot. VMS-Rot has been specifically designed for guiding the assignment and interpretation of rotational spectra: from the assignment of the observed transitions to a set of quantum numbers, as well as their fitting with a given model Hamiltonian, to the prediction and simulation of the whole spectrum. Given the general philosophy of VMS and the leading role played by quantum-chemical calculations in modern rotational spectroscopy, unlike other software supporting the analysis of MW spectra, VMS-Rot is intimately related to theoretical calculations, to be used as a starting point for guiding experiments and spectral interpretations. VMS-Rot is composed of four closely related modules, namely (i) the computational engine that allows spectroscopic parameters to be computed from first principles; (ii) the fitting-prediction engine that allows the refinement of the spectroscopic parameters, based on the assigned transitions, and the calculation of the simulated spectrum. (iii) the GUI that allows the comparison between theoretical and experimental spectra, aided by a number of advanced features for spectra manipulation and (iv) the assignment tool that takes care of the assignment of the rotational spectrum recorded experimentally by comparison with the simulated one. An overview of the range of applicability of VMS-Rot is given in order to demonstrate how this module of VMS represents a one-pot solution for the analysis of rotational spectra based on the interpretation of experimental measurements supported byquantum chemical simulations.

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# A Spotlight on the Complex Hierarchical Structure of Some Ionic Liquid-Molecular Liquid Binary Mixtures

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Ionic Liquids (salts with melting point below 373K) are a class of compounds that are being intensively studied because of their peculiar properties(1). Being neat ions in the liquid phase, they exhibit almost zero vapour pressure, high viscosity, high conductivity, wide electrochemical window and low flammability. While it is possible to find a relatively wide literature for these neat chemicals, works on their mixtures are just about 14% of the total and only ~1% concerning structural properties. These mixtures are innovative materials that are recently reported as even more versatile and cheap than pure ILs. The structure of many neat ILs consists of two segregated micro-domains percolating each other: one is polar and the other is non-polar. This organization, often called "sponge like", is at the basis of the characteristic low-q peak in the SAXS patterns (~2-7 $nm^{-1}$) (2). Adding a second substance into the IL forces some rearrangement in its structure, affecting the domains, for example water enlarges the polar domain, while hexane does so in the apolar. The recent discovery (3) of a more complex structure hierarchy in some ethylammonium nitrate (EAN) + methanol mixtures, opened a new debate on the properties of ILs and the potential applications of such mixtures. A cluster-like organization was suggested then, while almost at the same time Atkin et al. (4) observed the same odd feature in other IL mixtures with longer n-alcohols. They interpreted the "Low q Excess" (LqE) as the fingerprint of self-assembled structures. Recently wehave shown that the LqE can be found not only when the co-solvent is amphiphilic (as reported so far), but also when it is highly symmetrical, regardless if the compound is polar or almost apolar. We had the experimental evidence of LqE in EAN+1,4-diaminobutane and EAN+1,2- dimetoxyethane mixtures(5). These molecules cannot self-assembly, thus confuting the hypothesis from Atkin et al. The results collected using synchrotron radiation together with MD calculations enable us to state that the LqE arise when the mixture is preparing to demix, and is undergoing strong density fluctuations. This appears to be a general behaviour, and not strictly linked to the polar/apolar nature of the co-solvent. Our models are suggesting that some supramolecular structures can be found in the samples showing the LqE.The understanding of the driving force behind this large-scale hierarchical organization could open new landscapes for ionic liquids applications.

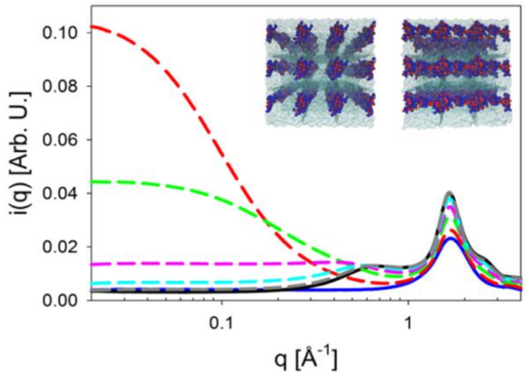

Figure 1: **SAXS patterns for ethylammonium nitrate+acetonitrile mixtures. In the inset two snapshots of the simulation box for the mixture with the highest "Low q Excess".**

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# Fluorous Mesoscopic Domains in Room Temperature Ionic Liquids.

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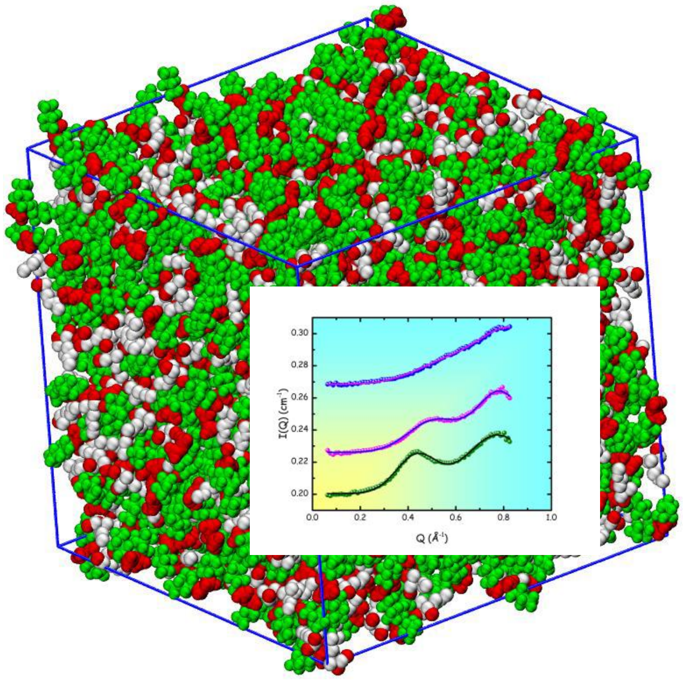
Room temperature ionic liquids (RTILs) are compounds composed solely of ionic species. Recently attention is focusing on the interesting properties of fluorinated RTILs that find application in separation, pharmacology, catalysis etc and show an appealing blending of ionic liquid specific properties and fluorous moieties induced features. Among the relevant properties highlighted in FRTILs, the possibility that fluorous moieties might segregate analogously to their alkyl counterparts in conventional RTILs has been proposed in the past [1–6]. So far however, no direct experimental evidence for such a behavior has been provided.

Here we provide the first direct experimental evidence that RTILs bearing a long enough side fluorous chain are characterized by the occurrence of a well-defined mesoscopic organization, consistent with the segregation of the fluorous tails. [7] By exploiting the synergy between x-ray and neutron scattering coupled with state of the art Molecular Dynamics simulations, we will discuss several consistent examples where such a phenomenology has been observed. We envisage an important role played by these self-aggregating domains of fluorous moieties in determining specific performances in the fields of separation, catalysis and related fields.



Simulation box of fluorinated RTILs, highlighting the different alkyl, fluorous and charged moieties.The inset data sets refer to neutron scattering data set collected as a function of the fluorous tail length. [Adapted from Ref. 7 with permission from the PCCP Owner Societies. ]

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# Supramolecular Organization of Water–Ethanol Solution in Ferrierite under Pressure

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Turning disorder into organization is a key issue in science. In particular, supramolecular organization induced by external stimuli has opened new paths for the bottom-up fabrication of nanostructures. By using a combined strategy based on the synergy of X-ray powder diffraction experiments and modeling studies (1), we showed that high pressure - in combination with the shape and space constraints of a hydrophobic all-silica zeolite - separate an ethanol–water liquid mixture into ethanol dimer wires and water tetramer squares (Figure 1).

Separation of ethanol from water was accomplished in an all-silica ferrierite (Si-FER), by using as pressure transmitting medium a mixture of (1:3) ethanol and water in the 0.20 to 1.34 GPa pressure range. The system was studied in situ by high-pressure synchrotron X-ray powder diffraction at BM01 beamline at ESRF and refined via first principles modeling.

Upon separation, the confined supramolecular blocks alternate in a binary two-dimensional architecture that remains stable upon complete pressure release. These results support the combined use of high pressures and porous networks as a viable strategy for driving the organization of molecules or nano-objects towards complex, pre-defined patterns relevant for the realization of novel functional nanocomposites and highlight the need of appropriate modeling for an atomistic level understanding of complex phenomena.

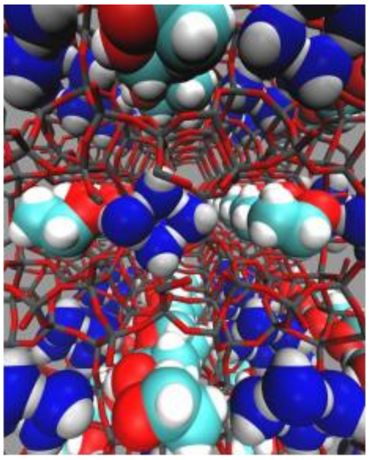

Figure 1.

(1)Arletti, R., Fois, E., Gigli, L., Vezzalini, G., Quartieri, S., Tabacchi, G. (2017) Angew. Chem. Int. Ed. 56, 2105,DOI: 10.1002/anie.201700219

# Contributi Poster

# Methods for Time-Resolved Vibrational Analysis from Ab-Initio Molecular Dynamics Simulations

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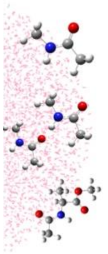
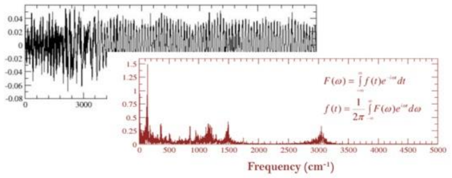
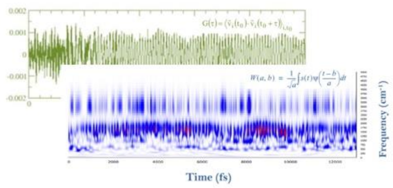
Advanced time resolved and non-linear vibrational spectroscopic techniques, such as time-resolved Fourier Transform Infrared, two-dimensional Infrared and Femtosecond Stimulated Raman Spectroscopy,(1,2) are powerful tools to characterize in detail the structure and the dynamics of molecular systems in condensed phase. Plenty of information is provided by interpreting trends in the time of vibrational features, which are subtle probes of structural motifs and reaction mechanisms. Indeed, the connection of the spectroscopic data with the structural and the dynamical features is far to be an easy task. The computational vibrational spectroscopy can provide a valuable support due to its predictive-interpretative character. However, standard techniques are aimed at the solution of the quantum vibrational problem, as alternative, very promising are those computational protocols based on the analysis of molecular dynamics simulations of large molecules in condensed phase and at finite temperature. In this contribution we present the development and the validation of a novel theoretical-computational method to perform time-resolved vibrational analysis on peptide benchmarks in aqueous solution. This method(3) is based on the Wavelet Transform(4) of suitable time dependent signals obtained through ab-initio molecular dynamics.(3,4) The Wavelet protocol, unlike the Fourier Transform, allows for the accurate localization in the time domain of a given vibrational band, thus monitoring frequency fluctuations, anharmonicity and vibrational modes coupling. We focused on three models presenting several vibrational fingerprints of peptides: the Methyl-2-Acetamidopropanoate,the trans-N-MethylAcetamide and the non-covalent dimer in both gas and explicit water phase.(5-9) Once sampled the AIMD trajectories in ground electronic state,(10,11) the time dependent signals were then Wavelet transformed to get generalized normal-modes and time-resolved vibrational spectra directly comparable to those provided from modern vibrational spectroscopies.(12,13) We were able to reproduce accurately many vibrational signatures of the systems (fundamental, overtone and combination bands), including the vibrational frequencies, the qualitative vibrational coupling, reproducing also the characteristic solvent-induced frequency shift and line broadenings. Importantly, we were able to interpret these features in terms of a clear correlation between structure and spectroscopic behavior. In conclusion, we obtained a very good agreement with both the experimental results and the data that is possible to calculate with standard approaches.(5-9)







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# Experimental and Theoretical Investigation on the Catalytic Generation of Environmentally Persistent Free Radicals from Benzene

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Environmentally Persistent Free Radicals (EPFRs) are toxic products deriving from incomplete combustion processes and are able to generate DNA damage and pulmonary dysfunction. They are formed on particulate matter through interaction with aromatic hydrocarbons, catalyzed by transition metal oxides, and produce reactive oxygen species (ROS) in aquatic media. The processes are already described for substituted aromatic molecules, e.g. phenol (1), not for unsubstituted aromatic systems, such as benzene.

Here we present an experimental and computational investigation, based on cluster and periodic computational models, of the reaction of benzene with molecular oxygen in the presence of $Cu_xO/SiO_2$ (2).

The computational study was performed, at the Density Functional Theory (DFT) level with the hybrid functional B3-LYP, on a cluster model consisting in a Cu(I) center embedded in the silica matrix that mimics the case of totally dispersed metal centers on silica; the periodic calculations, performed at the DFT level with the PBE exchange-correlation density functional,investigated the reactivity of a whole crystalline surface of $Cu_2O$. Both approaches converge to the same picture of the reaction mechanism: the activation of $O_2$ by interaction with silica–coordinated Cu(I) centers leads to a peroxy species that yields the phenoxy radical upon reaction with benzene;dissociation of OH• radical eventually allows for the recovery of the catalyst.

The experimental characterization of the $Cu_xO/SiO_2$ catalyst regarded morphology, crystal structure, copper electronic state, and crystal field around Cu(II). Electron paramagnetic resonance (EPR) spectroscopy revealed the formation of phenoxy radical entrapped in the catalyst upon reaction between benzene and $Cu_xO/SiO_2$. Moreover, ESR investigation of ROS in aqueous solution evidenced the generation of OH• radicals by benzene–contacted $Cu_xO/SiO_2$. All the experimental results nicely fit the outcomes of the computational models.

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# Hyperbranched Ethylene Oligomers by K2-(N,O)-Salicylaldiminato Ni(II) Complexes: DFT Investigation of Role of Remote Substituents

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Beyond the extensively studied high molecular weight polyethylenes, ethylene oligomers are also of practical importance. Recently, neutral κ2-(N,O)-salicylaldiminato Ni(II) complexes showed to be promising candidates.(1,2) These Ni(II) catalysts convert ethylene to highly branched, low molecular weight oligomers. The microstructure of the polymer showed to be dependent on the catalyst structure and, in particular, on the size and on the nature of the ligand substituents (see Chart 1).(3)

**1a**
76 branches /1000 C; Mn = 1.1 × $10^3$ g/mol

**1b**
10 branches /1000 C ; Mn =1.6 × $10^4$ g/mol

**Chart 1.**

To clarify the role of the -CF3 groups, linear propagation, termination and branches formation mechanisms were studied theoretically.(4)

The results showed that the linear propagation and termination/branches formation mechanisms overlap until the ethylene coordinates with the chain in cis to the oxygen ligand. Then, the reaction proceed toward the new insertion or a monomer de-coordination. The de-coordination is the key step for a) B-H elimination and 2,1 re-insertion or b) chain transfer reaction. In the de-coordination transition state, the ethylene is replaced by η2 coordination of the ligand aromatic ring. Since the strength of the interaction between Ni and the aromatic ring strongly depends on the remote substituents of the ligand, by tuning these effects the structure of the polyethylene can be regulate.

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# In Silico Identification of New Potential Antitubercular Drugs by The Multi-Target Approach

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The World Health Organization (WHO) reported that tuberculosis (TB) is one of the top 10 causes of death worldwide. In 2015 there were 10.4 million new TB cases, including 1.2 million among human immunodeficiency virus (HIV) positive people, and 1.4 million of deaths (1). The current therapy used to treat drug-susceptible *Mycobacterium tuberculosis* (Mtb) infection requires 2-month intensive phase of a four-drug cocktail containing rifampicin (RIF), isoniazid (INH), pyrazinamide (PZA) and ethambutol (EMB), followed by a longer continuation phase of RIF and INH. Infections with resistance to the two most efficacious frontline agents, RIF and INH, were classified as multidrug-resistant tuberculosis (MDR-TB) while the extensively drug-resistant tuberculosis (XDR-TB) is a form of TB which is resistant to at least four of the core anti-TB drugs. MDR-TB and XDR-TB require the use of second-line anti-TB drugs, which are more expensive and have more side-effects than the first-line drugs used for drug-susceptible TB. Moreover, a very common and deadly complication of TB is coinfection with HIV because RIF is a potent inducer of drug-metabolizing enzymes (e.g. CYP3A4) and patients are often forced to complete TB treatment before beginning HIV treatment (2).

It is evident the importance to discover and develop new antitubercular agents with novel mechanisms of action and a polypharmacological profile. *In silico* methods represent an alternative and innovative strategy to early identify new potential hit compounds. In particular, considering new promising antitubercular molecules under preclinical and clinical studies, a structure based virtual screening (SBVS) was performed using the most selective targets of Mtb deposited in the Protein Data Bank (3) with co-crystallized inhibitors. In order to discover new multi-target ligands (MuTaLig) the chemoinformatics platform of the homonymous European project (4) was taken into account for building the ligands library of the SBVS study. In addition, a database of FDA approved drugs was also screened, not excluding a possibility of discovering new antitubercular agents by a repurposing approach (**Figure 1**). For the promising hit compounds identified *in silico*, theoretical data of the binding affinity will be confirmed by enzymatic assays and *in vitro* test against Mtb models in order to confirm the ability to exert the predicted biological activity.

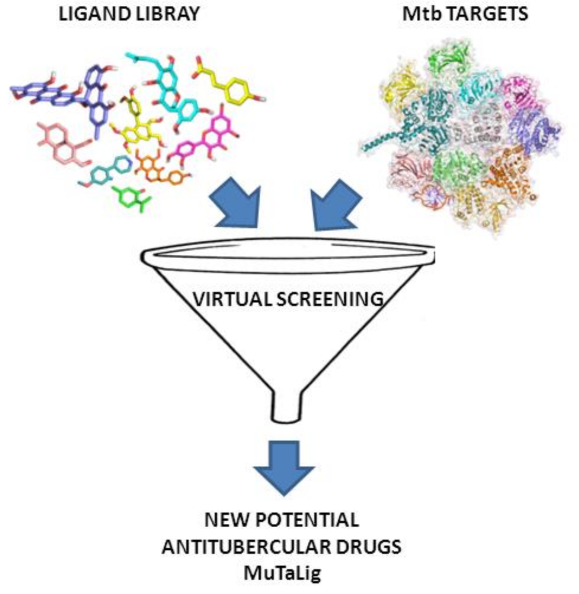

**Figure 1**. workflow of the *in silico* virtual screening study

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# To Swell or to Shrink? Alkylammonium Alkanoates plus Molecular Solvents

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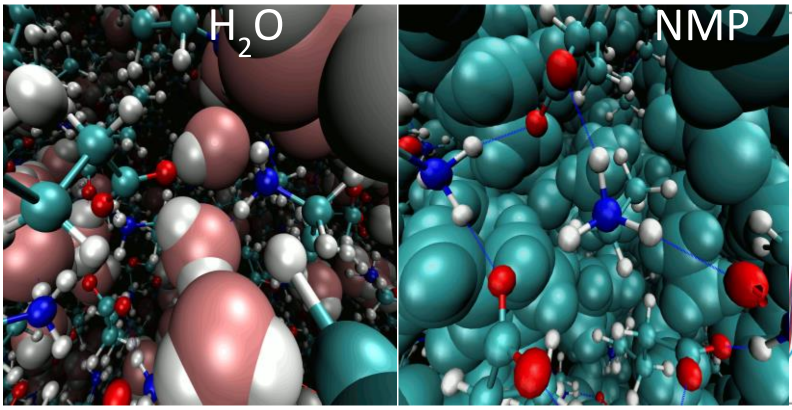
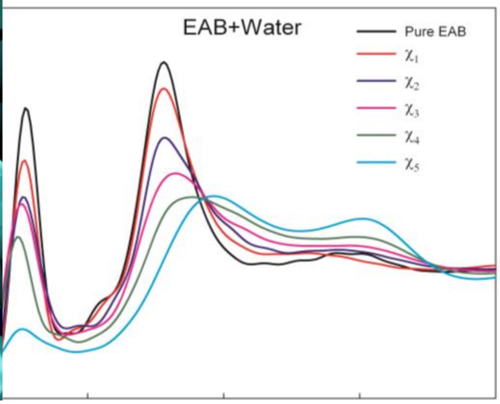
Aggregation in ILs is a phenomenon by which either or both the cations and anions interact with each other in solution to form local, highly charged phases. Most of the ionic liquids exhibit an intermediate range order ofsegregated polar and nonpolar domains, similar to surfactantaggregation, which can be pointed out in small-angle X-Ray scattering (SAXS)or neutron scattering (SANS) patterns in the form of pre-peaks. The scattering intensity of the pre-peak depends on the polarity alternation and is high when either cations or anions bear long alkyl chains, and becomes stronger when the alkyl chains are present on both ions. It has been noticed in **alkylammonium alkanoate**ionic liquids ($[N000_n][C_mCO_2]$) that ***mesoscopic*** order can be observed in the system when the alkyl chain ofcation and anion contains at least two or more carbon atoms (1).Theeffect of water and othercosolvents on ionic liquid structure has already been reported for 1,3-dialkylimidazolium ionic liquids (2), showing, for instance, that the liquid phase aggregates can be disrupted or broken at high shear rates orat high concentrations of water, that viscosity falls down very rapidly, and that the Newtonian behavior is recovered, showing that no aggregates are present. Recently, we have also shown that, at given concentration ratio, in the ethylammonium nitrate-DME solutions the peculiar critical phenomenon of "low-Q excess" shows up (3,4), indicating that the behavior of these systems is hardly predictable.





In this communication, we concentrate on the X-Ray properties of water solutions of different alkylammonium alkanoate liquids (n=3,4; m=2,3), that were compared with the nitrate analogous, and with the solutions of Ethylammonium butanoate ($[N_{0002}][C_3CO_2]$) with water and another polar solvent, N-methylpyrrolidone. In the first case, we show that: the scattering pattern is independent of the m-n sequence (4+3=3+4), and that the dilution of the alkanoate solution gives a marked system swelling, while a compaction is observed using the nitrate anion; in the second case, we point out how the different behavior of water vs NMP: water causes the swelling of the system (indicated by the shift of pre-peak towards lower Q values), NMP gives the opposite effect, signaling that the excluded volume of the big NMP molecule leads to the segregation of the ions.

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# Can Ionic Liquids Support Grotthuss-like Proton Transfer? A Preliminary Study

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Ionic liquids (ILs) represent an interesting new type of solvents and have been the subject of a large number of studies in the last decade. The fact of being pure liquid electrolytes at room temperature gives them unique characteristics: thermal stability, negligible vapor pressure, hygroscopicity, extreme viscosity and low thermal and electric conductivity.

Various classes of ILs have been studied but we focus on a special subset of these compounds consisting of choline [Ch+] and anionic amino acids [AA-]. Some of these ILs showed an intriguing possibility that consists in the ability to transfer a proton between two anions (1). A condition is required: the side chain of AAs must have an "acid" proton (like Cys and Asp) to allow the proton transfer (PT) to take place.

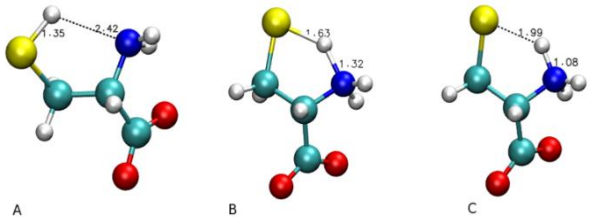

Figure 4.Example of structures for anion [Cys$^-$]. The Structure A represents the anionic form, B the transition state and C the final product (a zwitterionic anion).

The presence of this phenomenon suggested the possibility for an IL to improve its typical low conductivity through a controlled and concerted proton migration. In order to provide robust evidence for this behavior, we studied the physical condition under which the PT can take place. In this work, we focused on the study of stable geometries and energy barriers for an intramolecular and intermolecular PT. The starting molecules are the AAs with acid side chain (Cys, Sec, HomoCys, Asp and Glu). These type of calculations have been carried out at MP2 and B3LYP level (see Figure 1). The most promising results arise from Asp and Glu, where the transition state energy is only few kcal/mol.

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# First-Principles Study of Co and Cu-based Electrolytesfor Dye-Sensitised Solar Cells

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Since the pioneering work by 'O Regan and Grätzel (1), dye–sensitized solar cells (DSSC) have attracted great academic and industrial interests as promising technology in solar energy conversion thanks to low manufactural costs, eco-friendly materials and high efficiency under diffuse light conditions. The chemical complexity of these devices, which is inherent to the electronic processes involved at semiconductor/dye/electrolyte interfaces, represents a great challengefor the effective design and engineering of DSSC devices with high photo-conversion efficiency (PCE) (2).
State-of-the-art devices have PCE at ~14% with metal-organic dyes on mesoporous ZnO or $TiO_2$ n-type semiconductor, but there is still room for improvement. Beside the optimization of the dye-electrode interface, several research groups are addressing the role of the electrolyte and possible alternatives to the most exploited $I_3^-/I^-$ redox couple:latest efforts have focused on one-electron redox systems based on metal-organic complexes with Co(II/III) and more recently with Cu(I/II), which can overcome the problems of the twoelectron process of the triiodide/iodide: corrosiveness, competitive light absorption and large internal potential losses (3).
The aim of this work is providestructural and electronic insights at the dye–electrolyte interfacein DSSCs. We characterizedwith first-principles methods the new organometallic complexes as possible one-electron redox mediators (4) and their interactions with push–pull organic dyes. In particular, we investigated the structural and electronic features of several cobalt-based complexes(5) andcopper-based complexes, which have recently shown to outperform Co-based ones due to a minimum steric hindrance that avoids mass-transport limitations (6). Here wereport the computed redox potentials and reorganization energies for each Co(II/III) and Cu(I/II) couple in order to understand how the ligands can tune these important parameters for the electron transfer processes. These results are discussed together with the electronic properties of the push-pull dyes used in n-type and p-type DSSCs in order to predict and assess the most promising combinations of dye-electrolyte couple for the foreseen development of tandem-DSSCs.

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# Molecular Dynamics Simulations of Amyloid-beta Fibrils for Alzheimer's Theranostic Applications

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Alzheimer's disease (AD) affects tens millions of people only in the US after their 65 causing to patients a progressive memory loss, cognitive deprivation and death(1). Extracellular proteic plaques formation on brain is the typical hallmarks of AD mainly made by amyloid-β (Aβ) fibrils. Aβ fibrils are peptides with a length from 39 to 43 amino acids and appear in two major isoforms that differ only for two amino acids on the C-terminus: Aβ40 and Aβ42(2). A single fibril monomer is structurally a region of amorphous residues followed by a β-sheet stretch, called "beta-1", an elbow and a second β-sheet called "beta-2" anti-parallel to beta-1 (obtaining an U-shape monomer), which is stabilized by a salt bridge between D23 and K28(3).The fibril is made by parallel β-strands where β-sheets are perpendicular to the fibril axis and adjacent monomers are stabilized by hydrogen bonds(4). Fibrillar amyloid-β structures grow in two distinct way: a growth along the fibrillar axis is obtained adding Aβ monomers to the ends(elongation) and the lateral binding of two fibrils along the fibril axis (thickening), which brings to a close packed fibril(4). However, other mechanisms have been found and a deep understanding of the tertiary fibrillar structure is still lacking(5).
We used classical Molecular Dynamics simulations to study how coated-nanoparticles and small molecules interact with long Aβ fibrils in order to gaining insight for the design of new agents for early diagnosis and therapeutic applications. The results obtained showthat their ability of binding to the β-sheets regions and to inhibit fibrillation depending on the coating, nanoparticle dimensions and the small molecules substituents.

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# Vibrational Fingerprints of a Promising Mimic of the Oxygen Evolving Complex

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FTIR spectroscopy has been widely applied to the mechanistic characterization of both the Photosystem II (PSII) oxygen evolving complex (OEC) and the Mn-based water oxidations catalysts (WOCs) employed in artificial photosynthetic devices. In particular, the low-frequency (< 1000 $cm^{-1}$) region is able to provide direct electronic and structural information about WOCs Mn clusters, because it includes many Mn-ligand and Mn-substrate bands which are sensitive to cluster geometry and to the oxidation state of Mn metal centers. (1,2)

The spectroscopic characterization of the oxidized $S_n$ intermediates (n = 2, 3, 4) of natural and artificial WOCs catalytic cycles has been proved quite challenging so far, due to the difficulty in obtaining and stabilising such states. Moreover, the assignment of the IR bands often turned out to be not simple. Therefore, a theoretical approach based on the simulation of IR spectra can be useful to support bands assignments and to validate the structures proposed for the $S_n$ intermediates. In this work we have simulated the low-frequency IR spectrum of a synthetic calcium-tetramanganese $[CaMn_4O_4(t\text{-}BuCOO)_8(t\text{-}BuCOOH)_2(py)]$ complex (t-Bu: tert-butyl, py: pyridine) developed by Zhang and co-workers, characterized by a cubane-like $[CaMn_4O_4]$ cluster. (3) Beside the striking structural similarity with the native PSII OEC, also the main electronic features of the OEC reactivity appear to be well reproduced by this system, as shown by previous theoretical studies. (4)

A good reproduction of the experimental IR spectrum has been achieved, allowing a straightforward assignment of the observed low-frequency IR bands. In particular, in the 400-750 $cm^{-1}$ spectral region, as expected, $[CaMn_4O_4]$ cluster vibrational modes have been observed, together with $t\text{-}BuCOO^-$ and py bending modes.

The evolution of $[CaMn_4O_4]$ cluster and Mn-ligand modes along the catalytic cycle has been then evaluated. IR spectra have been computed for every $S_n$ intermediate (n = -1, 0, 1, 2, 3) in its high-spin state. The comparison of calculated spectra has shown that the position and intensity of most low-frequency IR bands are sensible to the oxidation state of the Mn metal centers. Moreover, IR bands active only for specific $S_n$states and so having a potential diagnostic relevance have been identified. The insights given by our theoretical approach suggest a structural flexibility of $[CaMn_4O_4]$ cluster along the OEC catalytic cycle and provide spectroscopic fingerprints of the different $S_n$intermediates, which can support the interpretation of experimental spectra.

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# Brominated BODIPY as Possible Photosensitizers in Photodynamic Therapy

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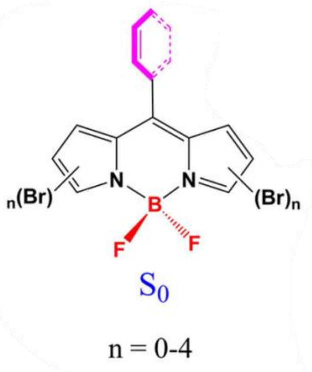
Photodynamic therapy (PDT) is an anti-cancer treatment modality, clinically approved, based on the interaction of light, a photosensitizing drug, and oxygen. PDT is commonly practiced in the treatment of a number of cancers (neck, lungs, bladder, and particular skin cancers) and is more selective (the drug can be given directly into the organ). Upon irradiation, the photosensitizer becomes excited and this energy is transferred to ground-state triplet oxygen ($^3O_2$). If the amount of transferred energy is higher than 0.98eV, highly reactive singlet oxygen ($^1O_2$) is formed, leading to cell death (referred to as Type II PDT mechanism). Different compounds are now used as photosensitizers, including phthalocyanine, chlorin, bacteriochlorin, porphyrin derivatives etc. A potential candidate induces light sensitivity in the region of 600-900 nm, the so called "therapeutic window", produces a good singlet oxygen quantum yield ($\Phi_\Delta$) and therefore a high intersystem spin crossing probability between the excited $S_1$ and the $T_1$ electronic states.In recent years, new sensitizers have been studied such as boron-dipyrromethane complexes (BODIPY) and their aza derivatives and, in order to enhance spin-orbit coupling, heavy atoms, as Br (1)andI, have been incorporated. In this study the role that can be played by heavy atoms (Br) in influencing the photosensitizing properties of BODIPY dye8-phenyl boron-dipyrromethane (Scheme) hasbeen investigated by means of density functional theory (DFT) and its time-dependent formulation (TDDFT).



**Scheme**

References: 1. Xian-Fu Zhang,Xudong Yang, J. Phys. Chem. B 2013, 117, 5533−5539.

# Unveiling the Adsorption Interaction of Glycolaldehyde on $TiO_2$ - Anatase (1 0 1) by Quantum Chemical Calculations

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The knowledge of the chemical species that are present in the Universe and in the interstellar medium (ISM), as well as of the reactions involving them, is of fundamental importance for understanding the elementary reactive steps toward chemical evolution. Among the 200 molecules discovered up to now in interstellar and circumstellar shells, Glycolaldehyde (GA) is the smallest monosaccharide detected in the ISM. GA is an important prebiotic molecule, since it is an intermediate in the formose reaction that leads to the synthesis of sugars up to ribose, the principal constituent of RNA. Understanding how simple organic molecules may evolve toward the biochemical building blocks of life in space or in a primeval Earth is one of the main concerns of astrochemistry. For this purpose, it has been recognized that mineral surfaces play an important role in the synthesis of more complex molecules starting from simple precursors (1,2) and $TiO_2$ represents a catalytic substrate where these processes can take place (3).

In the present work, the adsorption of GA over the surface of $TiO_2$ - anatase (1 0 1) is deeply investigated from both theoretical and experimental points of view. Theoretically, six adsorption configurations are modeled by periodic density functional theory (DFT) calculations, and for each of them, structural, energetic and vibrational properties are calculated. The proposed configurations differ for both the orientation of the GA molecule with respect to the anatase (10 1 ) and for the atoms involved in the adsorbate – substrate interaction. Experimentally, infrared spectra of GA adsorbed on $TiO_2$ are recorded by Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectroscopy coupled to the use of a properly suited environmental chamber for *in situ* operations (4). Theoretical simulations are compared with experimental observations in order to get insights into the mechanism of GA adsorption on the $TiO_2$ surface. The interplay between theory and experiment shows that the interaction between GA and $TiO_2$ takes place provided that both carboxylic and hydroxyl groups of the molecule are involved in the anchoring to the $TiO_2$ - anatase (1 0 1) surface. Further, quantum mechanical simulations suggest GA activation through the formation of highly reactive species on the solid surface.

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# First-Principles Study of the Lanthanum Ferrite Surface Chemistry Toward Oxygen Evolution/Reduction Reactions

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Perovskite oxides are object of considerable interests by academic and industrial research groups, especially those that show mixed ion-electron conductor properties (MIEC) (1) and can be used as air-electrode in intermediate-temperature solid oxide fuel/electrolyzer cells (SOFC/ECs) (2).
Here we present an *ab initio* study of the oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) at the (001) surface of the Fe-based perovskite $LaFeO_3$. In particular, we used density functional theory plus U (DFT+U) to analyze the factors governing the OER/ORR potential determining steps. We characterized the minimum-energy geometries of OER/ORR reactants, intermediates and products on the $FeO_2$-terminated $LaFeO_3$ (001) surface. Furthermore, we evaluated the role on OER/ORR catalytic mechanism of oxygen vacancies in the topmost layer of the $LaFeO_3$ (001) slab. To model the electrocatalytic reaction pathways, we considered proton-coupled electron transfer steps, according to the simple and effective approach based on the theoretical standard hydrogen electrode as proposed by Nørskov and co-workers.(3) With our *ab initio* results we have thus assessed the best model for the prototypical $LaFeO_3$ (001) surface.
In conclusion, we performed first-principles periodic DFT+U calculations to analyze the physic-chemical properties of a prototypical airelectrode. Our results pave the route toward the development and rational design of new Fe-based perovskite oxides for application as electrocatalysts for solid oxide electrochemical cells.

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# Elenco degli Autori

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| Melosso Mattia* | TEO/FIS OR03 |
| Mendolicchio Marco* | TEO PZ05 |
| Menziani Maria Cristina* | TEO PO08 |
| Menziani Maria Cristina | TEO OR09 |
| Migliorati Valentina | TEO OR07 |
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| Muñoz-García Ana Belén | TEO PO02 |
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## Divisione Didattica

## Lunedì 11 Settembre 2017

| | |
|---|---|
| | ***Sala Medusa*** |
| ***Sessione di apertura*** | |
| ***Chairperson: Giovanni Villani*** | |
| 8:30 – 9:00 | *Registrazione Partecipanti* |
| 9:00 – 9:15 | *Saluti* |
| 9:15 – 10:00 | DID-PL01: Margherita Venturi.<br>*Chimica e creatività* |
| 10:00 - 10:30 | DID-KN01: Eleonora Aquilini.<br>*Formazione Iniziale degli insegnanti: Legge aprile 2017* |
| 10:30 – 11:00 | Coffee Break |
| ***Sessione: Insegnare Chimica, che cosa e a chi*** | |
| ***Chairperson: Maria Funicello*** | |
| 11:00 – 11:20 | DID-OR01: Anna Madaio, Giuseppina Andreotti, Massimo Poletto, Renzo Stio<br>*Insieme nel Reale e nel Virtuale per la chimica sostenibile – Progetto per le Scuole Secondarie di I grado* |
| 11:20 – 11:40 | DID-OR02: Patrick Marcantelli, Giovanni Villani, Silvana Saiello, Cecilia Giordano, Fabiana Tescione<br>*Un approccio didattico alle Trasformazioni fisiche e chimiche della materia* |
| 11:40 – 12:00 | DID-OR03: Elena Lenci<br>*La Chimica per la Luce: un percorso didattico attraverso la storia delle reazioni chimiche sfruttate dall'uomo per ottenere luce* |
| 12:00 – 12:20 | DID-OR04: Marilena Muraglia, Teresa Turi, Graziano De Scisciolo, Ivana Defrenza, Filomena Corbo, Maria Lisa Clodoveo, Franchini Carlo<br>*Teknologhia: A novel Project Based Learning (PBL) laboratory education program between Highschool and R&D* |
| 12:20 – 12:40 | DID-OR05: Francesca Vergine, Liberato Cardellini<br>*La Chimica al Liceo – Il sogno di Giovanni* |
| 12:40 – 13:00 | DID-OR06: Enrico Mansueti, Liberato Cardellini<br>*L'inclusione degli alunni con BES attraverso la realtà compensativa* |

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| 13:00 - 14:00 | Intervallo Pranzo |

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| | ***Sala Paestum B*** |
| 14:00 – 15:00 | *Sessione poster 1 (DID PO01 – DID PO12)* |

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| | ***Sala Medusa*** |
| ***Sessione: Metodi e approcci all'insegnamento scientifico*** | |
| ***Chairperson: Anna Caronia*** | |
| 15:00 – 15:20 | DID-OR07: Laura Orian, Camilla Ferrante<br>*Interdisciplinarietà, Co-progettazione e altro ancora nel PLS* |
| 15:20 – 15:40 | DID-OR08: Simonetta Antonaroli, Gabriella Bandini, Alessandra D'Epifanio, Mariano Venanzi<br>*Chimica ed Energia: dalle parole ai fatti* |
| 15:40 – 16:00 | DID-OR09: Luca Scalzullo, Francesco Piero Paolicelli, Domenico Aprile, Rosanna Dell'Università, Daniele Sofia, Massimo Poletto<br>*Un progetto civico per una centralina a basso costo per il monitoraggio delle polveri sottili* |

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| 16:30 – 17:00 | Coffee Break |
| ***Sessione Tavola Rotonda*** | |
| ***Chairperson: Giovanni Villani*** | |
| 17:00 – 18:30 | Angela Agostiano, Ugo Cosentino, Antonio Floriano, Maria Rosaria Tinè<br>*Corsi e Dottorati in Didattica della Chimica/Scienze* |
| 18:30 – 20:00 | *Riunione Consiglio Direttivo e Assemblea dei Soci della Divisione di Didattica.* |

## Martedì 12 Settembre 2017

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| | ***Sala Medusa*** |
| ***Sessione Tavola Rotonda*** | |
| 9:00 – 10:30 | Le associazioni AIF-ANISN-DDSCI-SIRD<br>*Le competenze per insegnare* |
| 10:30 – 11:00 | Coffee Break |
| ***Sessione: Il Chimico verso il lavoro: esperienze formative*** | |
| ***Chairperson: Silvana Saiello*** | |
| 11:00 – 11:30 | DID-KN02: Damiano Manigrassi<br>*Titolo della conferenza da definire* |
| 11:30 – 11:50 | DID-OR10: Martino Di Serio<br>*Il Chimico nell'Industria: le competenze richieste* |
| 11:50 – 12:10 | DID-OR11: Maria Funicello<br>*L'Università come luogo di lavoro per i giovani* |
| 12:10 – 12:30 | DID-OR12: Anna Caronia<br>*Valutare l'alternanza per competenze* |

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|---|---|
| 13:00 - 14:00 | Intervallo Pranzo |

## Mercoledì 13 Settembre 2017

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| | ***Sala Medusa*** |
| ***Sessione: Comunicare la Chimica: a chi e per che cosa*** | |
| ***Chairperson: Federica Bella*** | |
| 15:00 – 15:30 | DID-KN03: Sara Tortorella<br>*Research at 360°: the novel mission of dissemination* |
| 15:30 – 16:00 | DID-KN04: Valentina Domenici<br>*Perception of Chemistry and its relationship with Teaching and Communicating Chemistry* |
| 16:00 – 16:20 | DID-OR13: Cristina Lazzerini, Valentina Domenici<br>*"Chemistry of Soap": an example of vertical curriculum developed in collaboration with a Science Museum* |
| 16:20 – 16:40 | DID-OR14: Alice Soldà<br>*A European Video Contest to promote Chemistry among High Schools* |
| 16:40 – 17:00 | Coffee Break |
| ***Sessione Tavola rotonda*** | |
| ***Chairperson: Pietro Greco*** | |
| 17:00 – 18:30 | Luciano D'Alessio, Luigi Campanella, Luigi Amodio, Valentina Dominici<br>*Comunicare le Scienze (e la Chimica) al grande pubblico* |

# Conferenze Plenarie

- DID PL01: Margherita Venturi, Dipartimento di Chimica “G. Ciamician” dell’Università di Bologna

# Chimica e Creatività

*Margherita Venturi*

*Dipartimento di Chimica "G. Ciamician" dell'Università di Bologna*
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Per i "non addetti ai lavori" associare Chimica e creatività potrebbe sembrare arduo, se non addirittura impossibile. La creatività, infatti, è da sempre legata a ciò che di più elevato la mente umana è capace di produrre come la poesia, la pittura, la musica, mentre la Chimica nell'immaginario comune è considerata quasi una parolaccia e, comunque, qualcosa di brutto e sporco da cui stare alla larga.

Nel seminario verrà invece mostrato come la Chimica, oltre ad essere importante e utile, sia una disciplina bella e soprattutto connotata da una grande creatività, cosa che emerge molto chiaramente analizzando in che cosa consiste e come sia cambiato con il passare del tempo il lavoro del chimico. Raccontare infatti questa storia significa a tutti gli effetti intraprendere un meraviglioso viaggio fra Chimica e creatività.

# Keynote

- ORG KN 01: Eleonora Aquilini, Liceo Artistico F. Russoli,- Pisa
- ORG KN 02: Damiano Manigrassi, Consiglio Nazionale dei Chimici, vicepresidente
- ORG KN 03: Sara Tortorella, Molecular Horizon - Perugia
- ORG KN 04: Valentina Domenici, Dipartimento di Chimica e Chimica Industriale, Università di Pisa

# Formazione iniziale degli insegnanti: Legge Delega 13/4/2017

*Eleonora Aquilini*

*Liceo Artistico F. Russoli,Via San Frediano 13 Pisa*

Il modello triennale di formazione e inserimento alla professione docente con procedura concorsuale e periodo di formazione e tirocinio è da considerarsi positivamente. Tale modello si inserisce in un contesto di esperienze (SSIS e TFA) e con il modello che da quasi venti anni forma efficacemente gli insegnanti della scuola primaria e dell'infanzia.

Nel merito si intendono sottolineare alcuni punti che possono costituire un reale miglioramento dell'offerta formativa fornita ai futuri insegnanti. E' positivo che si prevedano tre figure di riferimento per la formazione degli insegnanti: il tutor accademico, il tutor coordinatore e il tutor dei tirocinanti. Si auspica che si abbia un'effettiva collaborazione strutturata fra scuola e università. Ciò si potrà concretizzare assicurando un accesso regolato dal possesso delle competenze necessarie per gli incarichi da attribuire ai diversi soggetti coinvolti nel nuovo percorso iniziale di formazione iniziale e tirocinio. In particolare è da ritenere che gli insegnamenti relativi alle didattiche disciplinari e ai laboratori di didattica vengano attribuiti a chi ha un curriculum che ne certifichi la preparazione. Tali competenze vengono spesso attribuite automaticamente all'università anche quando non esiste, all'interno del dipartimento disciplinare, un ambito di ricerca specifico per la didattica. E' importante che, a partire dall'esigenza di integrazione fra le competenze indispensabili per l'insegnamento, nascano centri di ricerca didattica che siano punti d'incontro fra competenze disciplinari, didattiche e psicopedagogiche. Tali centri dovrebbero essere costituiti da esperti della scuola e dell'università. Potranno essere luoghi di formazione per le tipologie di tutor previste nella legge delega in questione. In generale è necessaria l'esistenza di gruppi di lavoro permanenti per la strutturazione e la valutazione di percorsi didattici efficaci nell'insegnamento.

Bibliografia

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2. http://www.anfis.eu/documenti/Rapporti_ANFIS_TFA/RA_TFA_2013/Rapporto_ANFIS_sul_TFA-primo_ciclo_2013-1_settembre_2013.pdf
3. http://www.cidi.it/articoli/primo-piano/legge-107-delega-formazione

# Research at 360°: the novel mission of dissemination.

*Sara Tortorella*

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Communication, dissemination and exploitation are three key activities increasingly required to researchers when presenting their projects for grant applications (e.g., Horizon2020 (1)).
These requirements include not only traditional publications in peer-reviewed journals or attendance at national and international conferences, but also innovative way of disseminating research including social media, websites, video, conferences, event, and even exhibitions.
As a consequence, researchers are required to prove additional skills that are, however, usually poorly taught during traditional undergraduate and postgraduate programs. Moreover, such activities take time away from busy research careers.

In light of this, different questions arise:

- Why should we do that?
- To whom are we really talking?
- How and where can we acquire such communication skills?

Trying to address these issues, general guidelines for an effective dissemination strategy will be proposed (1, 2).
Special consideration will be given to young researchers and novel tools - such as social media - and contexts - such as science festivals - to communicate their research activities, and advises and warnings to improve the success rate will be discussed.
Finally, examples and inspirations on how to integrate the mission of dissemination into a researcher' everyday life will be presented, with the aim of demonstrating that it can turn out to be a unique opportunity to ultimately complete our mission as scientists.

References:
1. "Communicating EU research and innovation", European Commission, *Horiz. 2020*, 2014, 1–13.
2. D. M. Eagleman, *J. Neurosci.*, 2013, 33, 12147–12149.

# Perception of Chemistry and its relationship with Teaching and Communicating Chemistry

*Valentina Domenici*

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Perception of Chemistry in the Society is an important issue for Chemists, since it is related to the awareness and understanding of their role in the Society and in the everyday life [1]. Most of chemists agree with the idea that people have a negative feeling towards Chemistry and a specific term was coined to describe such feeling: *chemophobia* (defined from IUPAC: an "irrational fear of chemicals"). As suggested by M. Francl [2], the main problem connected to *chemophobia* is that it concerns the whole Society and not just single persons, giving rise to potential negative decisions for the future of our Society.

In the recent years, several efforts have been spent in the systematic and detailed study of the perception of Chemistry in the public [3-6]. For instance, in 2015 the Royal Society of Chemistry sponsored a huge study [4] through people leaving in UK about their perception of Chemistry, reaching very interesting results. The general attitude of people towards Chemistry is not negative, as most of Chemists think, and this result is in agreement with an almost simultaneous study on the Italian youth [5-7]. Instead of hating Chemistry, most of the people involved in the surveys [4,5] think that Chemistry is fundamental in their life and beneficial for the Society. However, they don't feel comfortable with topics related to Chemistry and with chemicals, due to their poor knowledge of Chemistry and to their 'negative' experiences at school. In this sense, the perception of Chemistry in the general public seems to be most connected with the diffuse idea of Chemistry as a "difficult" subject [8,9].

Another important aspect underlined by these researches [3-7] is the role of Communication [10]. Interestingly, one of the main outcomes of the study performed in UK [4] was the preparation of the "toolkit" for a better communication of Chemistry.

In this seminar, the role of teaching Chemistry and communicating Chemistry in the creation of a new image of Chemistry and Chemists in the Society will be discussed.

References:
1. V. Domenici, LA CHIMICA NELLA SCUOLA, **2016**, 2:25.
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3. V. Domenici, JOURNAL OF CHEMICAL EDUCATION, **2008**, 85:1365.
4. Public attitude to Chemistry Technical report June 2015, Royal Society of Chemistry, 2015. Web-site: http://www.rsc.org/campaigning-outreach/campaigning/public-attitudes-chemistry/
5. G. Chiocca, "*A study of the perception of Chemistry in young generations and of their chemical/scientific knowledge*", Master Thesis, Università di Pisa (Italy): **2015**.
6. G. Chiocca & V. Domenici, LA CHIMICA NELLA SCUOLA, **2015**, 5:55.
7. G. Chioccca & V. Domenici, submitted manuscript.
8. G. R. Silberman, JOURNAL OF CHEMICAL EDUCATION, **1981**, 58:1036.
9. A. H. Johnstone, JOURNAL OF COMPUTER ASSISTED LEARNING, **1991**, 7:75.
10. M. R. Hartings & D. Fahy, NATURE CHEMISTRY, **2011**, 3:674.

# Comunicazioni Orali

# Insieme nel Reale e nel Virtuale per la Chimica Sostenibile
## Progetto congiunto destinato alle Scuole secondarie di primo grado per la diffusione della Chimica Sostenibile e per l'Innovazione Didattica

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Il Progetto “Insieme nel Reale e nel Virtuale per la Chimica Sostenibile**”** (1), realizzato grazie al bando 2015 per la promozione della Diffusione della Cultura Scientifica (legge n. 113/1991; L. n. 6/2000), è destinato ai docenti di Scienze e di Tecnologia delle Scuole secondarie di primo grado. Le attività di orientamento in ingresso e di divulgazione scientifica sviluppate dall’ITT Focaccia hanno evidenziato che la chimica, come disciplina, non sempre viene adeguatamente trattata nei programmi delle scuole medie di primo grado, essendo alcune volte relegata a ruoli marginali della formazione e altre volte illustrata con metodologie tradizionali, in genere scarsamente efficaci nel suscitare interesse e nel raggiungere obiettivi minimi di apprendimento. A riguardo, i docenti spesso lamentano mancanza di competenze specifiche e di mezzi necessari allo sviluppo di metodi d’insegnamento basati sulla didattica laboratoriale e sull’utilizzo di strumenti didattici innovativi e stimolanti. Il risultato è che, frequentemente, gli alunni considerano la chimica una disciplina di difficile comprensione e lontana dalla realtà quotidiana, percependola anche con il senso negativo convogliato dall’opinione pubblica e facilmente supportato dai casi della cronaca . Il risultato è un circolo vizioso che alimenta e giustifica la mancanza di vocazione e di interesse verso la disciplina. Con il Progetto si intende promuovere la cultura tecnico-scientifica nelle scuole secondarie di primo grado incentrandola su tematiche della Chimica per lo Sviluppo Sostenibile e riguardanti l’ambiente, l’agricoltura, la salute, l’energia, i materiali, con lo scopo di sottolineare il ruolo chiave che la chimica, e la ricerca scientifica in chimica e nelle sue tecnologie, riveste per il benessere e lo sviluppo economico e tecnologico del Paese. Durante il Progetto i docenti delle scuole secondarie di primo grado sono stati formati ed informati su nuovi contenuti tecnico-scientifici, sull’utilizzo di attività laboratoriali e strumenti didattici innovativi, quali la didattica immersiva nei mondi virtuali. Il Progetto ha fornito ai docenti spunti metodologici e didattici per orientare gli alunni verso le discipline scientifiche, per far sviluppare competenze di cittadinanza attiva e responsabile e per far acquisire comportamenti improntati al rispetto della sostenibilità ambientale, economica e sociale. Il Progetto è stato strutturato in tre fasi, per un totale di 40 ore di formazione: una fase seminariale, una fase laboratoriale e un evento di divulgazione finale, aperto anche al pubblico esterno, avente come principali protagonisti gli alunni dei docenti corsisti, i quali hanno mostrato al pubblico le attività svolte in classe sulle tematiche della Chimica Sostenibile, sviluppate dai propri docenti in seguito alla formazione ricevuta, e presentate tramite elaborati multimediali, poster, exhibit, esperimenti, ambienti immersivi 3D. L’evento divulgativo è stato arricchito da spettacoli scientifici, talk, talk-show ed esposizioni a cura dei diversi soggetti coinvolti, tra cui anche gli studenti del triennio dell’indirizzo Chimica e Materiali dell’ITT “B. Focaccia”, e si è rivelato una vera kermesse della chimica che ha coinvolto un ampio numero di studenti, docenti e pubblico esterno.

**Figura 5. Realizzazione di un ambiente interattivo per la didattico immersiva nei Mondi Virtuali**

References: 1. Sito web del Progetto http://dinagaldi.wixsite.com/chimicasostenibile

# Trasformazioni fisiche e chimiche della materia
# Un approccio didattico ai livelli macroscopico, submicroscopico e simbolico

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Sia in ambito scientifico sia in quello didattico viene generalmente operata una netta distinzione tra le trasformazioni fisiche e quelle chimiche. In questo lavoro ci si pone la domanda se tale distinzione sia utile ed efficace a tutti i livelli scolari.

La possibilità di identificare una variazione della materia è funzione della dimensione alla quale conduciamo l'osservazione/riflessione, in quanto ciò che può risultare invariato a un livello (per esempio quello macroscopico) può invece risultare variato ad altri livelli (microscopico, submicroscopico e/o elettronico).

In ambito didattico, quindi, per una migliore comprensione di alcuni concetti di base legati alle trasformazioni della materia da parte dello studente, gli autori propongono di utilizzare una metodologia che, esplicitando il *soggetto* e la sua *forma* (quello che resta invariato e quello che si modifica nella trasformazione) consenta di analizzare le trasformazioni ai diversi livelli di dimensione/concettualizzazione con l'obiettivo di evidenziare i punti di forza e di debolezza di queste analisi.

Riferimenti: (1) G. Villani "La trasformazione della materia. L'approccio chimico", Nuova Secondaria, 2016, 1, 102-105.

# La Chimica per la Luce: un percorso didattico attraverso la storia delle reazioni chimiche sfruttate dall'uomo per ottenere luce

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Oggi è normale pensare di poter ottenere luce semplicemente premendo un interruttore. Tuttavia, prima dell'invenzione della lampadina elettrica, l'unico modo per "fare luce" era attraverso lo sfruttamento di reazioni chimiche.

Questo percorso didattico è stato progettato durante un'esperienza di Tirocinio Formativo Attivo in una classe quarta di un istituto tecnico tecnologico (ad indirizzo Chimica, Materiali e Biotecnologie) nel 2015 (Anno Internazionale della Luce) con l'intento di far apprezzare agli studenti quanto la chimica sia stata importante prima dell'avvento della lampadina elettrica, e quanto ancora svolga un ruolo centrale nel campo dell'illuminazione e nella vita di tutti i giorni.

Sfruttando la strategia pedagogica della lezione narrativa (strategia sempre più consigliata anche nella didattica delle scienze, alla luce della valorizzazione che il pensiero narrativo ha ricevuto da autori come Bruner e Schank)[1] e seguendo un percorso storico che va dalle lampade ad olio dei romani fino alla moderna chemiluminescenza, gli studenti sono stati stimolati a ragionare su concetti chiave delle varie aree disciplinari della chimica, riflettendo in particolare su come l'energia chimica sia collegata alla struttura molecolare di una sostanza e su come questa possa essere liberata generando luce e calore.

Particolare enfasi è stata data alla reazione di combustione di diversi composti organici, seguendo il percorso con cui Michael Faraday,[2] circa un secolo e mezzo fa, condusse per mano il suo pubblico a interrogarsi sui fenomeni legati allo sviluppo della luce di una candela, l'incandescenza e la chemiluminescenza. Attività di laboratorio, e video,[3] hanno inoltre permesso di mostrare come le reazioni di ossidazione di metalli e di non metalli siano state sfruttate fino a inizio novecento per l'illuminazione a teatro o nel mondo della fotografia. Infine, i principi alla base della bio- e della chemiluminescenza sono stati esposti agli studenti e un'attività conclusiva di laboratorio riguardante la reazione di ossidazione del Luminol ha permesso loro di capire come questa reazione venga sfruttata in analisi forensi per la rilevazione di tracce di sangue.

Riferimenti: 1. Jerome Bruner, "La fabbrica delle storie", Laterza, 2002; 2. Michael Faraday, "La storia chimica di una candela", Istituto dell'Enciclopedia Italiana Treccani, 1982; 3. Peter Wothers, "The Chemistry of Light": http://sms.cam.ac.uk/media/1183061.

# *Tekhnologhia*: a novel Project Based Learning (PBL) laboratory education program between Highschool and R&D.

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Here we propose a novel PBL laboratory approach aimed to high school chemistry course pupils.(1) Specifically, in this work a combined university laboratory research lead the students to use ultrasound-assisted extraction (USAE) as an environmentally friendly extraction method, for grape pomace phenolic derivatives.(2) Currently there are evidences that support the potential antimicrobial, anti-inflammatory, antioxidant and anticancer properties of phenolic derivatives as well as their beneficial in the cardiovascular protection.(3) Since collected experimental data revealed an enhancement of extraction yield in shorter time, of grapes phenolic derivatives with USAE compared to the traditional methods, the latter is an excellent and promising choice for an eco-friendly extraction method potentially useful in foods and nutritional field.

The proposed pedagogical approach gives the opportunity to teach to the students, all aspects of chemical research through a problem solving approach. The lab activities offer numerous teaching moments as group discussion, small group activities and peer review. Furthermore, the pitfalls of a research program as well as development opportunities for student teamwork skills encourage a scientific mindset.

Since we received student positive feedback about this learning approach we propose it as a valuable education component to learn chemistry.

More details about the academic laboratory program and pedagogical approach will be illustrated and discussed.

1. Robinson, J. K. Project-based Learning: improving student engagement and performance in the laboratory. *Anal. Bioanal. Chem.* **2013**, 405, 7−13.
2. Carrera, C.; Ruiz-Rodriguez, A.; Palma, M.; Barroso, C. G. Ultrasound assisted extraction of phenolic compounds from grapes. *Analytica Chimica Acta*, **2012**, 732, 100-104.
3. Moss, J. W. E.; Ramji, D. P. Nutraceutical theraphies of atherosclerosis. *Nature Review-Cardiology. Advance research on line*. **2016**, 1.

# Chimica al Liceo: Il sogno di Giovanni

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Una parte degli studenti prova una delusione quando giunge alle scuole superiori perché scopre che l'impegno profuso negli studi non è sufficiente per raggiungere gli stessi risultati delle scuole precedenti. Inoltre, i nostri studenti hanno molti interessi fuori dalla scuola ed è sempre più difficile coinvolgerli in processi significativi di apprendimento. Viene riportata un'esperienza di insegnamento che in modo molto positivo ha coinvolto gli studenti in un processo entusiasmante di apprendimento. Il progetto didattico è stato sviluppato per una quarta classe del Liceo Scientifico Statale "G. Galilei" di Perugia, composta da 24 studenti. Il tema del modulo didattico utilizzato è stato sviluppato dall'insegnante insieme agli studenti ed è inserito nella tematica dell'inquinamento. Il contenuto stato preceduto e seguito da altri moduli, come il pH, le teorie acido-base e le titolazioni.

## Una classe speciale

Questi studenti, per i risultati raggiunti e se confrontati con molti altri, possono essere considerati una classe sotto molti aspetti speciale. Ma non è stato sempre così. Al primo anno del Liceo sono risultati essere studenti problematici e all'inizio del secondo anno, d'accordo con la Dirigente e tutti gli insegnanti si è deciso di invitare i genitori a partecipare ad una assemblea con questi studenti. L'atteggiamento delle famiglie è stato molto positivo e collaborativo verso la scuola e praticamente tutti hanno mostrato interesse e di avere a cuore la preparazione dei propri figli. L'insegnante ha mostrato interesse ed entusiasmo per la Chimica e per l'insegnamento e gli studenti sono cresciuti in un ambiente di apprendimento cooperativo (1) e motivante.

Gli studenti conoscono e frequentano il lago Trasimeno. Qualche settimana prima della presentazione del progetto, l'insegnante ha stimolato la curiosità della classe alludendo e poi chiedendo l'aiuto degli studenti per risolvere un problema piuttosto delicato e complesso; quello che poi è diventato "il problema di Giovanni". La famiglia di Giovanni vive in una grande città e sogna di investire i risparmi nella casa del nonno, vicino al lago Trasimeno e di godere la vita all'aperto allevando trote. Dai giornali scopre che il lago ha problemi di inquinamento, così per assicurarsi di investire bene i loro risparmi, Giovanni e sua moglie si rivolgono ad un'agenzia di ricerca ambientale per un parere tecnico. Il compito degli studenti era quello di fare il lavoro dell'agenzia per arrivare se fosse stato possibile, al progetto finale.

Con gli studenti sono stati formati quattro gruppi cooperativi; ciascuno degli studenti aveva un ruolo e delle responsabilità. Dopo una sessione di brainstorming iniziale per definire il problema, il lavoro degli studenti e dell'insegnante è avvenuto soprattutto all'interno dei gruppi. Gli studenti hanno affrontato in modo entusiastico un periodo di grandi attività: ricerche bibliografiche, incontri con esperti dell'Università di Perugia, analisi di campioni dell'acqua del lago in laboratorio, confronto dei dati ottenuti con quelli dell'Agenzia Regionale Per la protezione ambientale dell'Umbria, documentazione circa i costi di un impianto di fitodepurazione delle acque del lago prospicienti la proprietà del sig. Giovanni, identificare la specie ittica più adeguata per l'allevamento, valutare la redditività di un allevamento per le carni o per la pesca sportiva, presentazione e discussione del lavoro svolto e dei risultati ottenuti, preparazione della relazione finale come risposta al problema.

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# L'inclusione degli alunni con Bisogni educativi speciali attraverso la realtà compensativa: mediatori concreti in un caso di autismo

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Nel 1978 il rapporto Warnock in Gran Bretagna introduce l'acronimo SEN, (Special Educational Needs, in italiano BES), suggerendo la necessità di integrare gli alunni tradizionalmente diversi attraverso un approccio inclusivo che si basi sull'individuazione di obiettivi educativi comuni a tutti gli alunni, indipendentemente dalle loro abilità e difficoltà. (1) In Italia a partire dal 1977 (legge 517) gli allievi con disabilità sono stati progressivamente inseriti nelle classi frequentate dal resto degli studenti. (2)

Dal 2012 con l'introduzione dei Bisogni educativi speciali la scuola italiana dedica una maggiore attenzione alle cause dello scarso rendimento scolastico: accanto ai deficit cognitivi propriamente detti si considerano ora anche situazioni di svantaggio sociale e culturale, disturbi specifici di apprendimento, problemi comportamentali, disturbi evolutivi specifici, difficoltà derivanti dalla non conoscenza della lingua e della cultura italiana. Nella diversità delle situazioni c'è purtroppo una tendenza generalizzata per cui non pochi docenti, diuturnamente attenti al rapporto programma ministeriale da svolgere/tempo tentano di aggirare gli ostacoli cognitivi spalmando atarassicamente la didattica sui supporti multimediali convinti di trovare conforto nelle indicazioni dei documenti ufficiali.

Nel campo delle difficoltà di apprendimento l'utilizzo massivo delle tecnologie può invece paradossalmente tradursi in una sorta di pericoloso disimpegno educativo; l'uso di certi strumenti può infatti esporre a una medicalizzazione della didattica, col rischio che i supporti multimediali e le fonti informative della rete (con le sue piattaforme comunicative), da stimolo intellettivo possano trasformarsi in sorgenti di conoscenza di dubbia attendibilità, o addirittura in rifugio e ostacolo per forme di interazione sociali più sane. La proposta di esperienze didattiche riconoscibili e riproducibili in maniera autonoma (ad esempio incoraggiando la sperimentazione a casa di compiti di realtà in didattica capovolta) può indirizzare lo studente nella costruzione di competenze suggerendogli un senso, un'utilità e un possibile proseguimento-approfondimento dell'apprendimento scolastico. È opportuno perciò concentrarsi sui vantaggi di quegli approcci didattici che rendono riconoscibile il compito proposto, tale da renderlo utile agli occhi del proprio vissuto personale.

L'autismo è caratterizzato dalla tendenza all'isolamento e alla chiusura sociale, dall'apparente indifferenza emotiva agli stimoli, e dalla difficoltà ad instaurare un contatto visivo. Compromissione e atipicità del linguaggio e della comunicazione (verbale e non-verbale), insieme alla reattività abnorme ai cambiamenti dell'ambiente esterno e della routine quotidiana, ci sono sembrate caratteristiche adatte per l'applicazione di mediatori concreti. Verrà riportata un'esperienza significativa attuata all'interno di un Istituto Alberghiero: i risultati mostrano che la realtà prossimale può essere sia un mediatore didattico fondamentale per accorciare la distanza tra scienza e realtà (efficace per stimolare la motivazione), sia un ponte che permette di superare le difficoltà che compromettono le interazioni sociali dirette (impossibili da superare con l'approccio tecnologico-multimediale).

References: 1. H. M. Warnock, (1978). Special Educational Needs. Report of the Committee of Enquiry into the Education of Handicapped Children and Young People. Online at: http://www.educationengland.org.uk/documents/warnock/warnock1978.html. 2. R. Vianello, S. Lanfranchi. In R. Vianello, S. Di Nuovo (A cura di), *Quale scuola inclusiva in Italia? Oltre le posizioni ideologiche: risultati della ricerca* (pp. 35-56), Erickson, Trento, 2015.

# Interdisciplinarietà, co-progettazione ed altro ancora nel PLS: verso un'efficace sincronizzazione tra la scuola secondaria e l'università

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Il Piano Lauree Scientifiche (PLS) attraverso le sue quattro linee di azione principali (laboratori, autovalutazione-orientamento, formazione insegnanti, riduzione del tasso di abbandono fra il primo e il secondo anno di università) è potenzialmente uno strumento efficace per sincronizzare la scuola secondaria e l'università. Al fine di favorire nei giovani la maturazione di una scelta di un corso di laurea chimico consapevole, condizione essenziale per una carriera di studi di successo, è necessario uno sforzo congiunto dei docenti della scuola e dell'università, che può concretizzarsi proprio nella pluralità di attività del PLS Chimica.

L'esperienza di questi due anni a Padova, che si innesta in una tradizione consolidata del PLS nel nostro dipartimento e ha beneficiato negli ultimi anni di un efficiente coordinamento a livello nazionale, sta dimostrando che interdisciplinarietà e co-progettazione sono elementi coesivi alla base del successo dei nuovi progetti realizzati. Cosa può nascere dall'incontro di matematica, geologia e chimica? Cosa succede se 25 insegnanti di scuole diverse sono coinvolti nella realizzazione di un gioco da tavolo didattico? Insegnare chimica con passione! non è uno slogan, ma il nome del convegno autunnale degli insegnanti delle scuole secondarie del Veneto che presentano e condividono le loro esperienze didattiche in classe.

Queste e altre attività sono illustrate focalizzando sui prodotti, condivisi nel portale PLS Chimica della Scuola di Scienze patavina, (1) sulla rete regionale di collaborazione scuola-università che si è stabilita e continua ad espandersi e sul livello di soddisfazione riscontrato negli studenti, principali destinatari delle azioni intraprese.

References: 1. Sito web: pls.scienze.unipd.it/chimica Ultimo accesso: 8 maggio 2017.

# Laboratorio PLS-Chimica: Chimica ed Energia, *dalle parole ai fatti*. Preparazione di Biodiesel da Olii Esausti

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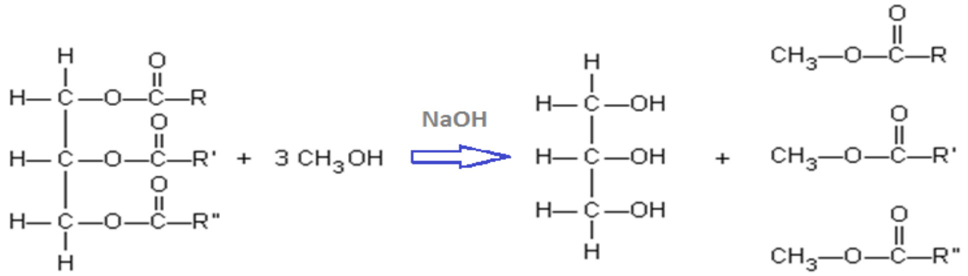
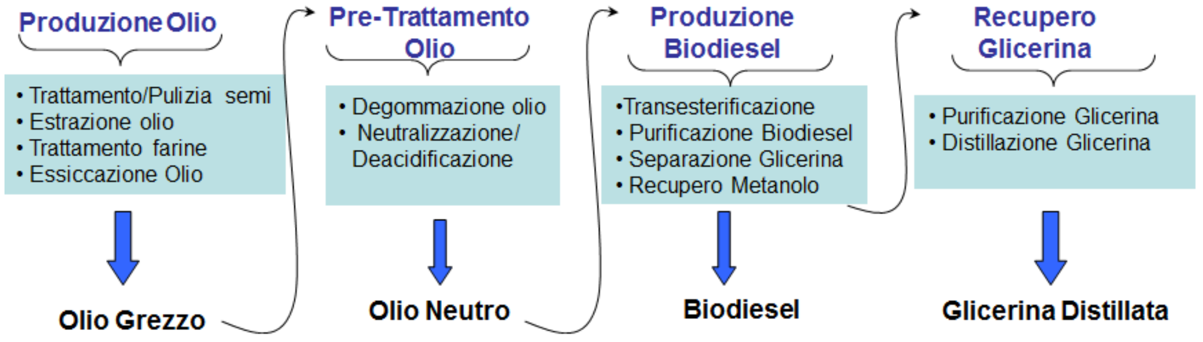
Viene descritta l'esperienza effettuata nell'ambito del Piano Lauree Scientifiche-Chimica dell'Università di Roma "Tor Vergata", che ha visto coinvolti Licei ed ITIS di Roma e Frascati.

Le esperienze sono rivolte agli studenti del triennio della scuola superiore ed hanno come scopo prioritario l'approfondimento delle conoscenze di base sulla produzione di energia. Per un'adeguata comprensione ed acquisizione dei concetti teorici legati allo sviluppo di Energia sostenibile e alle caratteristiche dei biocombustibili, si è messo a punto un laboratorio PLS dedicato alla sintesi del biodiesel da olii esausti e commerciali.

La reazione di transesterificazione degli olii in ambiente basico



diventa uno strumento per:
- divulgare la cultura di riciclo (cittadino consapevole)
- presentare le biomasse, le loro caratteristiche ed i processi termochimici e biochimici.



L'esperienza in laboratorio può essere un'opportunità per definire:
- le composizioni e le caratteristiche degli olii (titolazione dei diversi olii, studio dei componenti , aspetti organolettici e caratteristiche nelle applicazioni alimentari);
- affrontare aspetti termodinamici e cinetici delle reazioni chimiche;
- descrivere processi di distillazione ed apprezzare l'utilizzo di strumentazione di laboratorio (bilance, rotavapor, agitatori magnetici, GC);
- effettuare semplici calcoli stechiometrici.

In fase di verifica si valuteranno le competenze acquisite in relazione alle attività logico-formali connesse all'espressione verbale o scritta e a quelle connesse alla risoluzione di problemi ed alle pratiche di laboratorio.

# Un progetto civico per una centralina a basso costo per il monitoraggio delle polveri sottili.

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Le principali fonti di polveri sottili (PM10 e PM2,5) sono sorgenti legate all'attività dell'uomo come processi di combustione, usura di pneumatici, freni ed asfalto, combustione di biomasse legnose. Inoltre, una parte rilevante di polveri sottili presente in atmosfera deriva dalla trasformazione in particelle liquide o solide di alcuni gas (composti dell'*azoto* e dello *zolfo*) emessi da attività umane.

La tutela dell'ambiente, dunque, è argomento di stringente attualità e noi docenti abbiamo l'obbligo morale di portarlo nelle scuole, di parlarne con le nuove generazioni generando riflessioni che restino nel bagaglio culturale dei nostri ragazzi. L'idea, nata durante un corso di formazione, spinge proprio in questa direzione valutando la possibilità di superare i muri delle singole discipline e i confini stessi territoriali unendo i partecipanti in una rete civica di controllo ambientale (1, 2, 3). Illustreremo nell'articolo la costruzione di una centralina a basso costo utile per il monitoraggio ambientale di tali polveri, mediate l'uso di sensori basati su ARDUINO.

L'attività didattica è ad ampio raggio. I ragazzi dovranno essere impegnati non solo alla progettazione e alla realizzazione della centralina utilizzando tecniche di prototipazione rapida e progettazione 3D, ma dovranno anche essere in grado di inviare online i dati rilevati su piattaforme Open Data IoT, mappandoli su sistemi OPEN DATA con possibilità di interrogare ogni centralina in tempo reale utilizzando comuni programmi di chat come TELEGRAM.

Il progetto si adatta a ragazzi dell'ultimo anno di una scuola secondaria di I grado e ai ragazzi di scuola superiore in una formulazione che ha carattere di *verticalità* unendo ragazzi con formazione ed età diverse e di *multidisciplinarietà* raccordando conoscenze di diverse discipline.

La metodologia utilizzata è quella dell'IBSE (Inquiry-Based Science Education) e PBL (problem Based Learning) in un nuovo approccio pedagogico centrato sugli studenti che utilizza l'analisi di un dato problema quale scenario di partenza per l'acquisizione di nuove conoscenze (4, 5).

Obiettivo finale del progetto è, dal punto di vista scientifico la validazione di una centralina a basso costo per il monitoraggio delle polveri sottili, mentre dal punto di vista didattico lo sviluppo di competenze secondo il quadro europeo delle competenze chiave. Per come è concepito il progetto mira a sviluppare *competenze scientifiche, tecnologiche e matematiche*, ingenerate dalla progettazione della centralina stessa, dalla lettura e dalla validazione dei dati. I ragazzi dovranno essere in grado di leggere i dati quantitativi restituiti dalla centralina, analizzarne gli andamenti e ricavarne relazioni anche rispetto alle attività antropiche. Potranno in questa maniera maturare una attenta consapevolezza chimico-fisico-matematica delle problematiche ambientali del loro stesso territorio. Da non trascurare lo sviluppo di *competenze digitali*. Le metodologie didattiche descritte mirano a sviluppare la capacità di *imparare ad imparare*, ingenerando, in tema di salvaguardia ambientale, una coscienza civica e la consapevolezza di poter adoperarsi per cambiare le cose (*competenze sociali e civiche, spirito di iniziativa ed imprenditorialità*).

References: 1. http://www.camera.it/parlam/leggi/deleghe/10155dl.htm 2. Council Directive 1996/62/EC of 27 September 1996. On ambient air quality assessment and monitoring. 3. European Standard EN 12341. Final draft July 1998. Air Quality ñ Determination of the PM10 fraction of suspended particulate matter ñ Reference method and field test procedure to demonstrate reference equivalence of measurement methods. 4.. http://www.scuolavalore.indire.it/nuove_risorse/linquiry-based-science-education-ibse-nella-formazione-docenti-e-nella-pratica-didattica/ 5. http://didamatica2016.uniud.it/proceedings/dati/articoli/paper_101.pdf

# L'Università come luogo di lavoro per i giovani

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La Legge 107/2015 "Buona Scuola" ha rivoluzionato il Sistema Scolastico in vari ambiti, compreso quello dell'estensione a tutte le tipologie di scuola dell'Alternanza Scuola Lavoro (ASL), diventata obbligatoria con un monte ore pari a 200 per il triennio nei Licei e a 400 negli istituti tecnici.

Le Università sono spesso considerate come sedi per lo svolgimento delle attività di ASL, soprattutto nell'Italia centro-meridionale dove c'è poca disponibilità di aziende private. Inoltre, visto che tra gli obiettivi dell'Alternanza c'è l'orientamento consapevole agli studi successivi, l'attività ASL nelle Università è stata facilmente collegata al Piano Lauree Scientifiche.

In molte sedi universitarie si svolgono attività ASL sia di Ateneo che collegate ai laboratori PLS e la figura lavorativa di riferimento è sia quella del ricercatore che quella del divulgatore scientifico.

I problemi sono molti ma ci sono anche delle opportunità e si intende affrontare sia un aspetto che l'altro attraverso l'esperienza dell'Università della Basilicata.

# Valutare l'alternanza per competenze

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L’alternanza scuola-lavoro venne introdotta nel sistema scolastico italiano con la Legge 53/2003 (1), voluta dall’allora Ministro Moratti; si trattava di una sperimentazione che è rimasta tale fino a luglio 2015, quando il Parlamento italiano ha approvato la Legge 107/2015 (2) , la così detta “Buona scuola”, con cui di fatto termina la fase di sperimentazione e l’alternanza scuola-lavoro diviene ordinamento. Nello specifico, è previsto un obbligo di alternanza di 200 ore per gli studenti dei licei e di 400 ore per gli studenti di istituti tecnici e professionali. L’alternanza scuola-lavoro è intesa, con l’entrata in vigore della “Buona scuola” una metodologia didattica e pertanto gli obiettivi individuati sono anche disciplinari, è necessario, quindi, puntare al raggiungimento di alcune conoscenze, abilità e competenze individuate nelle “Linee guida” (3) previste dalla normativa riguardanti le singole discipline e lo specifico profilo in uscita. E’ compito del consiglio di classe, tenuto conto delle informazioni fornite dal tutor aziendale, procedere alla valutazione dell’esperienza di alternanza scuola lavoro; e procedere alla certificazione delle competenze acquisite dallo studente. Il presente lavoro ha lo scopo di evidenziare le problematiche connesse al processo di valutazione dell’alternanza scuola lavoro.

Riferimenti: 1. http://archivio.pubblica.istruzione.it/normativa/2004/legge53.shtml,
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3. http://www.indire.it/lucabas/lkmw_file/nuovi_tecnici/INDIC/_LINEE_GUIDA_TECNICI_.pdf

# "*Chemistry of Soap*": an example of vertical curriculum developed in collaboration with a Science Museum

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Didactic activities based on laboratory and interactive experiences represent an exceptional occasion to teach Chemistry in a more effective way [1-3]. Moreover, learning Science in "out of school" environments, such as science centers and museums, is more attracting and stimulating even for students who normally experience difficulties at school [4-7].

In this presentation, a new project of structured didactic activities was developed and realized concerning the theme "*Chemistry of Soap*". The project was planned at three levels of schools as a vertical curriculum, involving primary schools (8-9 years old students), intermediate schools (13-14 years old students) and high schools (17-19 years old students). The idea was to develop different activities for the three grades of school, with an increasing level of deepness of the chemical topics and required skills and competences. The activities covered within this project were planned to answer to the following questions: "What is soap?", "Why do we use soap to clean ourselves?", "What is the impact of using soap on the environment?", "Can we prepare soap by ourselves"? The didactic activities were performed in the "science museum" and at school. The main results of the project in terms of achieved skills and competences will be presented and discussed.

*Figure 1. Example of activities related to the project "Chemistry of Soap" in a Primary School (February 2017).*

Acknowledgments:
The project was funded by the "Rotary Club Rosignano Solvay" and it was supported by the staff of the "*Museo di Storia Naturale*" in Rosignano Solvay (Italy).

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6. H. Itzek-Greulich, B. Flunger, C. Vollmer, B. Nagengast, M. Rehm, U. Trautwein, "*Effects of a science center outreach lab on school students' achievement e Are student lab visits needed when they teach what students can learn at school?*" Learning and Instruction, *38,* 43, **2015**.
7. C. Faria, E. Guilherme, R. Gaspar, D. Boaventura, "*History of Science and Science Museums. An Enriching Partnership for Elementary School Science*", Science & Education, *24,* 983, **2015**.

# A European Video Contest to promote Chemistry among High Schools.

*Alice Soldà*

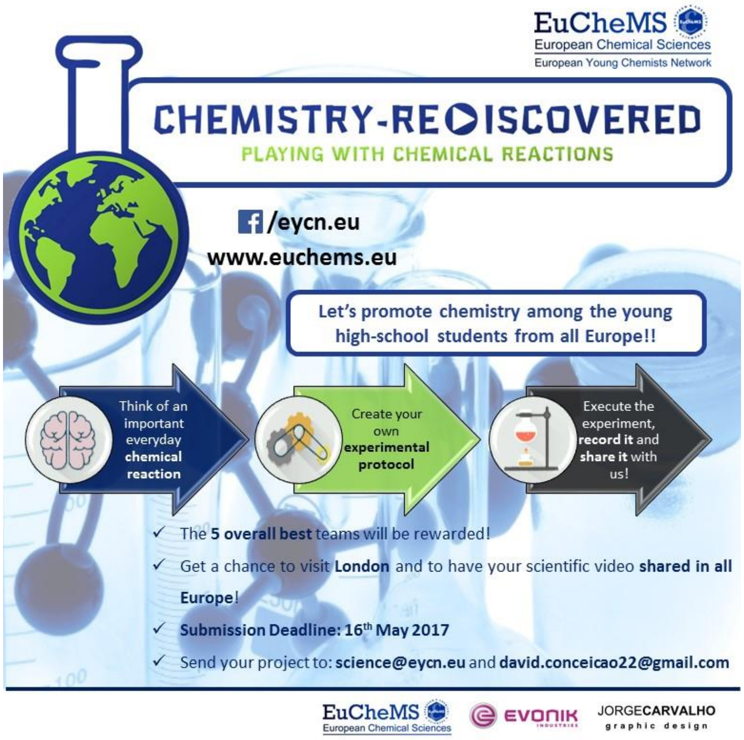
*Chair of EYCN (European Young Chemists' Network), Division of EuCheMS (European Association for Chemical and Molecular Science).*
*e-mail: chair@eycn.eu; Website: www.eycn.eu*

EYCN's goal is to promote Chemistry all around Europe, as well as to give new educational and networking opportunities to students and professionals. We promote several awards in different conferences, organize career days to improve soft-skills and collaborate in a variety of exchange programs to promote the mobility of our members. To do all this, we partner with powerful industries as well as with other young scientific societies around the world (ACS-YCC, IYCN).

The Video Contest ***Chemistry Rediscovered - Playing with chemical reactions*** was an educational project organized by us, in collaboration with EVONIK Industries, to promote chemistry among the young high-school students from all around Europe. This was achieved with the help of teachers, who developed scientific projects for their students and encourage them to present their findings. The contest initially started on a national level, and the Young Group of SCI fully supported the Italian high schools' participation, but the final goal was to present the projects from the young participants, seen as future chemists, in a European context.

In total, more than 100 high schools participated at the contest at national level, coming from 8 different participant countries: Italy, Portugal, Germany, Greece, Belgium, France, Romania, and Sweden. Only the best 15 videos and related experimental protocols gained the finals, and the quality and originality of all projects exceeded all expectations for this inaugural edition. All the projects were evaluated considering: *i)* the relevance and originality of the experiment, from the scientific and pedagogic point of view; *ii)* the quality and originality of the submitted video; *iii)* the scientific accuracy and rigor of the concepts presented in the experiment; *iv)* the reproducibility of the experiment, taking in account the details presented in both the experimental protocol and the video.

On behalf of EYCN and Young Group of SCI, we are pleased to announce that ***"Test-Tube Silver&Gold"*** directed and produced by ***Zero Karat*** group under the supervision of Prof. Cecilia Giordano, from IIS "G. Peano" (Turin) has been evaluated and considered to be the **1st best** at Italian level and the **2nd best**, on equal terms with two other teams, at European Level.



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- ✓ **Submission Deadline: 16th May 2017**
- ✓ Send your project to: **science@eycn.eu** and **david.conceicao22@gmail.com**

EuCheMS European Chemical Sciences
EVONIK INDUSTRIES
JORGECARVALHO graphic design

# Comunicazioni Poster

# Morphological and electrical properties of composites filled with carbon nanotubes functionalized with 1-Pyrene-butyric acid

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Composite materials with carbon nanotubes (CNT) as a filler are suitable for replacing many existing materials in different engineering fields due to their superior thermal, mechanical and electrical properties (1). However, the development of such added-value polymer-based composite materials with specific functionalities and tailored performances, still presents several critical issues. In particular the carbon nanotubes dispersed in the polymer matrix tend to form aggregates, thus reducing the performance obtainable by homogeneous dispersion of the CNT within the matrix, which improves the electrical and mechanical properties of the resulting composites–Chemical modification of nano-particles can prevent agglomeration during dispersion processes, preserving the electronic properties of the nanofillers and thus extending their potential applications. Covalent modifications, as well as the insertion of ionic groups on the surface of CNTs, produces hybridized $sp^3$ carbon, resulting in loss of electrical conductivity of the nanofillers. Instead, non-covalent modifications do not alter the characteristics of the nanofiller (2, 3, 4, 5). In this work we report a non-covalent functionalization of Multi-wall carbon nanotubes by π – stacking interaction with 1-pyrene-butyric acid in order to preserve the $sp^2$ hybridization of carbon atoms. A preliminary morphological and thermogravimetric characterization of both pristine and functionalized fillers is carried out in order to highlight the presence of eventual significant differences.

This functionalization of MWCNTs prevents the agglomeration during the filler dispersion within composite, thus optimizing the manufacturing process, which in turns improve the electrical properties of the resulting materials.

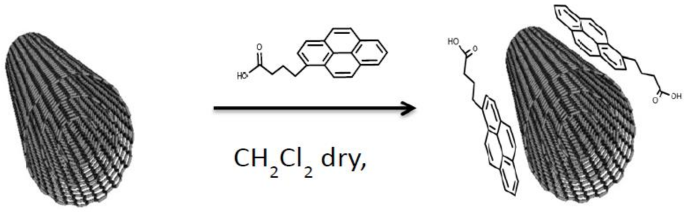

Figure 6: Preparation of MWCNT (3100) – pyrene butyric acid

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# Materials science as a tools to teach chemistry at secondary school: the experience of PLS Material Science National Project

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The Piano Lauree Scientifiche (PLS) - Scienza dei Materiali, was born in 2004 as result of collaboration of MIUR, CON.Scienze and Confindustria, with the aim to contribute to solve the crisis of the scientific vocations in the young people. Since then, moving from guidance programmes concerning themes and problems of scientific knowledge through practical activities, the current project is following new national guidelines (1,2,3) to further strengthen the teacher training program together with a constant attention to the educational path of the student at the scholastic and academic level. It is noteworthy that the large number of actions proposed by the project in turn will be stimulating challenges for the involved professors.

Currently the national project on material science involves nine Universities in different regions of Italy. One of the reached goal has been to raise interest in Material Science through laboratory activities addressed to a great number of students of the secondary schools. The experiments were chosen to show how Material Science research can help to solve contemporary problems and to understand what is behind the technological objects of our everyday life. Many of these experiments dealt with subjects not present in the standard secondary school programs, but strictly related to front line research problems. Some more the students put their hands on real chemistry related matters, which aroused a great interest, because they were deeply involved in the experimental work, thus appreciating the opportunity of preparing materials in very simple manner.

The involved chemistry professors, authors of this works, not only propose various theoretical and laboratory activities destined to the students of the upper secondary school triennium but also pay special attention to the formation of teachers through educational laboratories and experimental activities integrated with other disciplines (like physics). A national website (3) has been developed in which teaching materials and laboratory experience guidelines have been reported and classified. Each secondary school teacher can register and free download documents to be directly used in their classes.

Various collaborations (4) at local level with companies, research entities and administrations allowed to implement many satellite activities that greatly increased the participation of students and teachers as well as provided different perspectives for learning and teaching the discipline of material science as well at school. The good feedback, the encouraging results of self-evaluation and the active participation of teachers confirm the fundamental importance of promoting and implementing such projects. In this work some of the most significant and successful experiences on how to teach and learn chemistry through Material Science will be presented and discussed.

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# Pratica intenzionale e *gifted children*

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I cosiddetti gifted children sono i bambini ad alto potenziale cognitivo che spesso subiscono con sofferenza la normale attività didattica, manifestando noia, disinteresse, irrequietezza e mancanza di partecipazione. Altrettanto frequentemente, le particolari capacità cognitive che li caratterizzano creano loro difficoltà di inserimento sociale. Questi loro atteggiamenti non "omologati" sono spesso fonte di fraintendimento da parte degli insegnanti che, non riconoscendo le loro particolari capacità, li etichettano di conseguenza come portatori di deficit di attenzione e di iperattività.

Da tempo la scuola italiana, giustamente, presta particolare attenzione ai ragazzi meno dotati e affetti da difficoltà (BES e DSA). In questa sicuramente condivisibile azione vi è tuttavia il rischio di un livellamento verso il basso che penalizzi proprio gli allievi maggiormente forniti di capacità cognitive. Al contrario tali capacità devono essere opportunamente valorizzate e coltivate, potendo rappresentare vere e proprie eccellenze. Questo richiede nuove competenze professionali perché "La scuola è chiamata a gestire l'eterogeneità delle classi e a condurre contemporaneamente didattiche differenziate per andare incontro alle esigenze dei singoli, promuovendone il riconoscimento e la valorizzazione delle identità." (1, p. 141)

Altri paesi investono in programmi che favoriscono le esigenze sociali e affettive di questi studenti attraverso uno sviluppo professionale mirato dei docenti in modo che gli studenti si sentano a proprio agio nell'ambiente scolastico. "Finland has established its strength in supporting academic and creative talent through gifted programs and special schools." (2, p. 9) Recenti ricerche hanno dimostrato che non esistono abilità predefinite e il potenziale degli individui può essere sviluppato: il cervello è adattabile e l'addestramento può aumentare le abilità. Secondo Anders Ericsson, le prestazioni eccezionali sono il prodotto della pratica intenzionale (Deliberate practice) e del coaching. (3,4) La pratica intenzionale può essere definita come "goal-directed activities designed to improve specific aspects of performance through gradual improvements by repetition on the tasks with diagnostic feedback and opportunities for reflection." (3,4, p. 410)

Con l'intento di far sperimentare agli studenti delle abilità cognitive nuove, agli studenti di chimica di corsi di ingegneria vengono proposte delle sfide e richiesto di risolvere problemi impegnativi di logica e di chimica. Verranno riportate soluzioni creative trovate dagli studenti al problema: Un miscuglio di $CH_4O$, $C_6H_6$ e $C_7H_6O$ del peso di 44,37 g dà all'analisi elementare: C = 68,74%; H = 8,905% ed il resto ossigeno. Calcolare i grammi di $C_6H_6$ nel miscuglio. Le 'regole del gioco' chiedono di risolvere il problema usando un ragionamento. L'uso di equazioni, incognite o sistemi di equazioni non è ammesso.

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# Chimica, preziosa Chimica! Estraiamo oro dai rifiuti RAEE

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L'apprendimento esperienziale costituisce un modello di apprendimento basato sull'esperienza e che coinvolge gli studenti in modo attivo, le loro idee e la loro conoscenza. "Experiential learning is a process of constructing knowledge that involves a creative tension among the four learning modes. experiencing, reflecting, thinking, and acting–in a recursive process that is responsive to the learning situation and what is being learned." (1) Abbiamo considerato un problema complesso: il recupero di metalli preziosi dai rifiuti RAEE.

La direttiva europea sui rifiuti RAEE (apparecchiature elettriche ed elettroniche) 2012/19/EU permette un circolo virtuoso nel settore hi-tech. Il recupero di metalli preziosi offre una soluzione sia al difficile approvvigionamento di materie prime che alla necessità di smaltimento. Le procedure classiche per il preventivo allontanamento dei metalli diversi dall'oro con acido nitrico non si inquadrano in un'ottica environmentally friendly che costituisce la Vision del nostro Dipartimento di Chimica. La Chimica sostenibile che viene insegnata al Montani non poteva non cercare l'approccio più ecologico possibile alla valorizzazione dei rifiuti hi-tech.

Sfruttando le nostre competenze chimiche, abbiamo cercato un reattivo non pericoloso per l'ambiente e che potesse fungere da ossidante per i metalli diversi dall'oro senza rilasciare fumi tossici. Il cloruro ferrico soddisfa questi prerequisiti. L'ambiente acido per HCl ne potenzia il potere ossidante: abbiamo messo a punto una nostra procedura innovativa per l'allontanamento dei metalli diversi dall'oro.

Siamo partiti da RAM, CPU, schede madri, PIN schede audio, schede video, connettori. Sono state fatte delle prove con l'allontanamento dei metalli diversi dell'oro con $FeCl_3/HCl$, filtrazione, dissoluzione dell'oro con acqua regia e suo recupero riduttivo con metabisolfito, fusione. Nelle discussioni, ci è sembrato questo un metodo parecchio inquinante e ci siamo chiesti se non si potesse raggiungere lo stesso risultato con un numero minore di passaggi. Ne è risultata una nuova procedura con l'allontanamento dei metalli diversi dell'oro con $FeCl_3/HCl$, suo recupero per semplice filtrazione, fusione. Certamente un procedimento più semplice, meno inquinante, più rapido e meno costoso.

Una miniera in città: Un computer contiene 1 g di Ag, 200 mg di Au, 80 mg di Pd, 500 g di Cu. La batteria contiene circa 65 g di Co. Se recuperassimo tutto il venduto annuo in Italia e recuperassimo tutti i metalli preziosi e le terre rare il valore economico potrebbe ammontare a 141 milioni di euro!

La nostra scuola vuol essere un punto di riferimento per il tessuto culturale e imprenditoriale del territorio. La nostra mission è "preparare tecnici per lavori che ancora non esistono!". Ciò significa che non intendiamo solo ripetere ma puntiamo ad accrescere il sapere! L'esperienza dell'alternanza scuola-lavoro a tal fine risulta essere preziosa perché ci porta a conoscenza delle tante esigenze di innovazione che provengono da un'imprenditorialità creativa, che non si rassegna al pessimismo, ma intende puntare lo sguardo oltre l'orizzonte.

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# A Transformational Approach to the Teaching of Analytical Chemistry

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Analytical chemistry is an important part in the formation of students and in the chemical profession. (1) The teaching of analytical chemistry to students aged 16 in a vocational school is an engaging challenge. Despite the fact that in the workplace much analysis is simply a routine matter of running many samples through the appropriate apparatus and reading off the appropriate numbers, we believe that the training of students consists primarily in the development of cognitive skills by becoming familiar with the way of thinking of chemists. Also, laboratory work is indispensable because learning the methodology is considered to be valuable in training a student in accurate and precise analytical procedures. Courses that require laboratory work are expensive to run in terms of time, equipment, special accommodation, chemicals, and a greater demand for staff. So, it is necessary that they are effective for the training of students and useful for their professional training. Our teaching goal is to provide the best possible preparation for students for their future professional life. Examining students' difficulties together with our experience, we have developed a teaching method that aims to achieve this purpose, i.e., to make learning a meaningful experience for our students in order to make them autonomous in the practices of the laboratory.

Two teachers share the same approach and philosophy in the classroom and in the laboratory. Several objectives are pursued with an active involvement of the students to acquire these skills: solving stoichiometric problems connected with laboratory work; following the instructions in a critical way and sticking to a methodology; interpreting the results obtained; processing the experimental data; knowing how to work in cooperative groups; using digital technologies to produce a report and making a presentation; designing and implementing experimental activities in safety and respecting the environment; becoming autonomous and developing skills to find a solution to a new (and unknown) lab problem.

Much emphasis and time is devoted to problem solving. For many students, it comes to acquiring new skills and it takes much time and effort to learn to think in the same way a chemist thinks. On the chalkboard, problems are solved with the students who are asked to specify whether it refers to a solute, solvent or solution. While solving the problem, students are asked to specify whether they are talking about mass, volume or density. Students then solve the same problem in groups by commenting and discussing/exchanging views on the problem-solving steps and making their reasoning visible.

After acquiring the necessary knowledge of theory, students go to the lab to acquire the skills necessary to carry out a volumetric analysis. We used the prelab exercises which are very beneficial for students. (2) Since "Lab should be a puzzle to be solved" (3), students will have to wait for the surprise analysis. Towards the end of the course, students perform the analysis of a commercial vinegar with partial instructions. Then, they have to perform the analysis of the acidity of the milk without any hint from the teachers, find the method, discuss it and perform a titration. More than 85% of the students liked this approach.

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# A software tool for a better visualization and understanding of the particulate nature of matter

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Among all scientific concepts, the concept of ‘matter’ plays one of the most central roles for scientific literacy, however, studies about the students’ understanding of matter have shown that students fail to obtain a deeper understanding of the particle nature of matter [1]. To this aim, several studies have been recently devoted to the investigation of students’ misconceptions [2], the development of new drawing and visualization tools [3,4], the implementation of new teaching strategies, including inquiry-based activities [5].

As reported in a recent review [1], the main difficulties experienced by students related to the concept of “matter” are: *(1)* chemical reactions, *(2)* physical states and their changes, *(3)* atoms, molecules and particle systems and *(4)* conservation of matter.

In the present work, we focused our attention on the topic *(2)* and, partially, topic *(3)*. In particular, a new software tool was developed [6] to better visualize the particulate nature of matter of several substances in their different states of matter (see *Figure 1*). The novelty of the tool is related to its “dynamic” and “interactive” features.

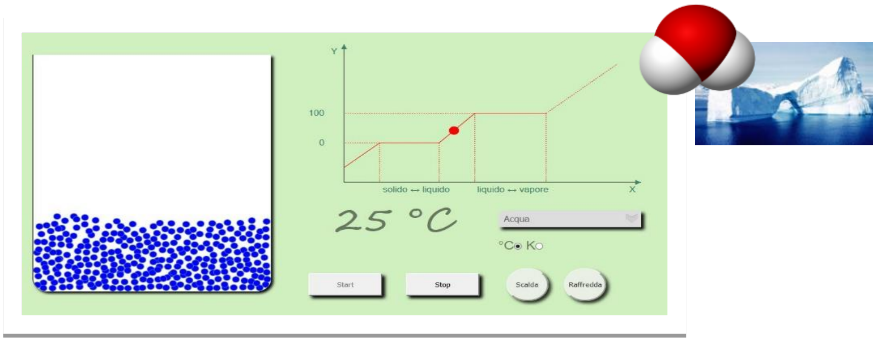

*Figure 1*. Snapshot of the software on the page dedicated to “water”. Several interactive buttons help students to visualize the particulate nature of water at different temperatures, in different states of matter, with the possibility to virtually heat or cool the ideal sample of water.

The software was intended for students of the second and third classes of the intermediate schools (*Scuole Superiori di Primo Grado*), where the *particulate model* is normally introduced to describe matter at a (sub-)microscopic level. A ‘pilot project’ about the use of the new software tool is described and preliminary results will be discussed.

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# Il Festival della Chimica in Basilicata: Esperimenti di Comunicazione

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Nel 2009, in occasione del primo centenario della Società Chimica Italiana, nasce a Potenza il Festival della Chimica, un nuovo modo di divulgare questa disciplina spesso considerata ostica e responsabile dei mali ambientali. Lo slogan della manifestazione era, e lo è tutt'oggi, quello di "portare la chimica alla gente".

La prima edizione del festival è stata un evento colossale: per la prima volta nella storia della Basilicata, la chimica è scesa in piazza e per un'intera settimana ha riempito teatri, musei e sale conferenze della città. Nel catalogo del festival, un volume di sessanta pagine, erano riportati oltre ai programmi delle attività anche articoli divulgativi e due "Crucichem" per testare con i cruciverba le proprie competenze.

In un percorso lungo quasi 10 anni é stato sperimentato un modo diverso per parlare di chimica. Sono stati mostrati i collegamenti della chimica con le altre discipline, non soltanto scientifiche ma anche umanistiche come la letteratura, la storia, la filosofia, la musica, il canto, le arti figurative.

Insomma la chimica come gioco, non con la pretesa di educare ma solo quella di divertirsi e di incuriosire: sono stati organizzati spettacoli, mostre, conferenze, dibattiti, esperimenti, in cui la chimica protagonista velata della manifestazione appariva sempre in maniera sfumata ma determinante.

All'interno del festival è stato dato spazio anche ad aspetti più tradizionali, come la discussione delle attività di ricerca dei dottorandi, la presentazione delle esperienze di studio e professionali dei laureati e lo spettacolo degli esperimenti svolti dagli alunni delle scuole superiori della regione.

Ogni anno il festival si arricchisce di nuovi contenuti e nuove idee e nella comunicazione saranno presentate alcune immagini, tra le più rilevanti, per illustrare le molteplici attività svolte.

# “Investigatori per caso”: spunti di attività attraverso il Laboratorio PLS

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Il Piano Lauree Scientifiche prevede nei suoi obiettivi sia la formazione degli insegnanti in servizio sia l’orientamento alla scelta del percorso di studi universitari più consapevole da parte degli studenti ai quali è diretto, cioè studenti di quarto-quinto anno di scuola superiore.

In particolare, è dedicato a ciò il “Laboratorio delle Scienze di base”, attività che può essere svolta come mini-laboratori, come stage e/o come Laboratorio PLS se è organizzato in 10-15 ore, direttamente presso le scuole, con solo 2-4 ore massimo di lezioni teoriche.

La sede PLS-Basilicata propone ogni anno una diversa scheda di lavoro, in generale su argomenti di chimica organica che trovano poco spazio nei programmi in particolare dei licei. Quest’anno 2016/17 è stata proposta, invece, la chimica forense attraverso una serie di esperimenti:

a) Funzionamento dell’etilometro (determinazione tasso alcolico)
b) Ricerca tracce di sangue (esperimento di chemiluminescenza)
c) Ricerca sostanze di abuso (oppioidi, cannabinoidi e alcaloidi dell’ergot)
d) Estrazione della nicotina

Hanno partecipato 11 istituti scolastici di cui 7 licei e 4 istituti tecnici disseminati in diverse zone della regione. L’attività svolta sarà illustrata attraverso la scheda degli esperimenti e le immagini e i commenti dalle diverse sedi.

# Un approccio integrato Flipped Classroom- Inquiry-Based in un percorso di ricerca-azione sulla reattività dei metalli.

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Nell'ambito del Piano Nazionale Lauree Scientifiche, il corso di laurea in Chimica dell'Università di Camerino organizza attività di formazione sulla didattica sperimentale della Chimica (1) per i docenti di Scienze dei Licei della Regione Marche, con incontri in presenza e formazione online su piattaforma Moodle dedicata. A completamento della formazione, due docenti di Chimica del Liceo "Galilei" di Ancona hanno intrapreso una sperimentazione di ricerca-azione sull'apprendimento di alcuni aspetti delle reazioni chimiche in due classi terze del Liceo scientifico opzione scienze applicate. In questa sperimentazione sono state applicate due metodologie didattiche: la *Flipped Classroom* (2) e l'approccio IBSE (*Inquiry Based Science Education*), basato sul *Learning cycle delle 5E* (3). La *Flipped Classroom* è una metodologia in cui si favorisce la fruizione di contenuti al di fuori della scuola da parte dello studente. L'allievo può così personalizzare tempi e ritmi di apprendimento, attuando poi, con la guida del docente, la fase di approfondimento e rielaborazione. Alla metodologia della *Flipped Classroom*, è stato affiancato l'approccio IBSE semistrutturato (4) che si adatta ai tempi stretti del curricolo di Chimica. Dopo la formazione online sulla piattaforma Moodle di UNICAM, i docenti hanno sperimentato con gli alunni una serie di attività sulla reattività dei metalli, strutturate nelle cinque fasi *Engage, Explore, Explain, Elaborate, Evaluate*, utilizzando nella fase di *Explain* una classe virtuale. In quest'ultimo contesto sono state inserite sia risorse digitali interattive reperite in rete, in particolare un laboratorio virtuale (5) per testare la reattività dei metalli, che materiale originale elaborato dai docenti di UNICAM. Nella fase di *Elaborate*, gli studenti hanno eseguito l'attività di laboratorio con l'approccio IBSE semistrutturato, progettando autonomamente alcuni step. Il monitoraggio e la valutazione della sperimentazione sono stati effettuati con questionari somministrati a docenti ed alunni e test finali di valutazione delle conoscenze e competenze, correlati sia all'attività nella classe virtuale che alla progettazione ed esecuzione dell'esperimento in laboratorio. L'analisi dei risultati mostra un generale vantaggio, sia in termini di competenze degli alunni che di acquisizione da parte dei docenti della nuova prassi didattica, con evidenti ricadute sulla motivazione allo studio della Chimica e alla pratica laboratoriale.

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# Niccolo: a free software for chemistry laboratories management

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Niccolo is a multiusers chemicals database, furthermore, it helps you in the laboratory safety and waste management. The database allows you to manage a theorically infinite number of chemicals or mixtures to which can be associated many safety data (MSDS, H and P Phrases, GHS pictograms and so on) and that you can safely storage avoiding chemical incompatibilities(1). It is possible to federate many laboratories and sharing their databases to avoid useless redundancies. A Chemical Risk Assestement, both for hazardous and carcinogenics compounds, is embedded in the software(2). As for anything else it comes a time when your chemicals become wastes, Niccolo allows you to manage them using a SISTRI(3) like database. Many others features are already in the software: compounds searching by structure, 2D code for safety storage, internal messaging system (for example for important deadlines) and many more are going to be implemented in the next future, we will surely appreciate your contribution.

References: 1. J. J. M. Wiener and C. A. Grice, "Practical Segregation of Incompatible Reagents in the Organic Chemistry Laboratory", *Organic Process Research & Development*, vol. 13, pp. 1395–1400, 2009. 2. ISPRA e ARPA Sicilia,"Linee guida per la valutazione del rischio da esposizione ad Agenti Chimici Pericolosi e ad Agenti Cancergoeni e Mutageni – Centro Interagenziale Igiene e Sicurezza del Lavoro -. 73/2011", ISBN 978-88-448-0504-3. 3. WWW.SISTRI.IT.

# Disclosing the thermodynamic and kinetic aspects of a chemical reaction: A PLS experiment

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One of the major sources of confusion and misunderstanding among non trained students is the distinction between the thermodynamic and kinetic aspects of a chemical reaction. In particular, the difference between kinetic rate constants and thermodynamic (equilibrium) constant is rarely fully understood by high-school students and sometimes even by undergraduates.

In the proposed experiments the reaction between Ferrimyoglobin and fluoride ion is studied by UV-Vis absorption measurements, determining the forward and reverse rate constants. The equilibrium rate constant can be obtained by the ratio of the two rate constants (kinetic approach), and from the absorption data at equilibrium.[1]

In this manner, one can compare the thermodynamic results of equilibrium measurements with the corresponding quantities that are obtained from a kinetic study of the same chemical reaction under pseudo-first order conditions (Figure 1).

We use this reaction for implementing a PLS activity articulated in a preliminary group-working stage carried out by a team comprising four high-school teachers and two professors from the academy. After a thorough discussion of the theoretical and pedagogical aspects of the experiment in the group, the school teachers prepared a selected group of students, illustrating the objectives and the content of the experiment. The experiments were therefore carried out at the Laboratory of Physical Chemistry of the University of 'Rome' Tor Vergata. The students participated actively to the treatment of the experimental data (log linearization, fitting and plotting of the data).

The impact of this experience on the chemical knowledge of the students and on their understanding of the thermodynamic and kinetic features of a chemical reaction was verified by multiple-choice and open answer tests.

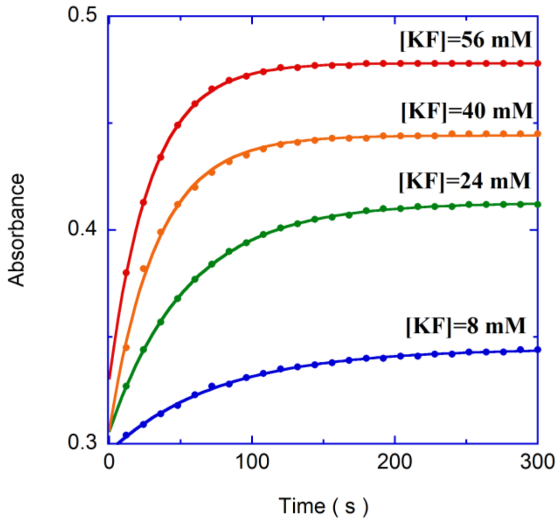

Figure 1 – Time dependence of UV-Vis absorption of the Ferrimyoglobine-fluoride complex for different initial concentrations of KF.

References: 1. S.O. Russo and G.L.H. Hanania, J. Chem. Ed. (1990) 67, 352.

# Nanotechnology for Solar Energy Conversion

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Nel presente lavoro è descritto un modulo didattico sviluppato, nell'ambito del progetto europeo IRRESISTIBLE, dall'unità di Palermo sul tema dell'applicazione delle nanoscienze allo sfruttamento dell'energia solare. L'attività è stata rivolta ad alunni del biennio dell'Istituto Tecnico, nell'ambito delle discipline Scienze Chimiche Integrate e Scienze e Tecnologie Applicate Chimca e ad alunni dell'ultimo anno del Liceo Scientifico, nell'ambito della disciplina Fisica. Tra le varie attività, anche sperimentali, è stata realizzata una cella DSSC che, insieme ad altro materiale di comunicazione preparato dagli stessi studenti, è stata presentata alla mostra scientifica Esperienza inSegna e al meeting finale del progetto, che si è svolto a Kiel in Germania. Alla fine del modulo gli studenti hanno dimostrato di aver acquisito, oltre alle necessarie competenze chimiche, anche una notevole sensibilità nei riguardi del rapporto tra scienza e società con particolare riferimento nei confronti della ricerca e della innovazione responsabili. Il progetto europeo IRRESISTIBLE ha affrontato i problemi inerenti la formazione scientifica e ha avuto lo scopo di diffondere la consapevolezza delle tematiche di Ricerca e Innovazione Responsabili (RRI), promuovendo attività di formazione degli insegnanti da sperimentare in classe con l'ausilio della metodologia Inquiry-based Science Education (IBSE).

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