Programma del

XXVI Congresso Nazionale
della Società Chimica Italiana

Centro Congressi Hotel Ariston
Paestum (SA), 10-14 settembre 2017

➢ Divisione di Chimica Inorganica
XXVI Congresso Nazionale della Società Chimica Italiana

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- Hydrogen Evolution Catalyzed by Cobalt Mimochrome VІ

- Bifunctional triamine Pt(ІІ) complexes containing a DNA intercalating moiety

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- A DFT Rationalization of a Two Metals Strategy to Tune Selectivity in Catalysis

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DIVISIONE DI CHIMICA INORGANICA

Comitato Scientifico

- Adriana Saccone, Università di Genova
- Roberto Gobetto, Università di Torino
- Alberto Credi, Università di Bologna
- Emma Gallo, Università di Milano
- Gaetano Granozzi, Università di Padova
- Alceo Macchioni, Università di Perugia
- Michele Saviano, Consiglio Nazionale delle Ricerche, Bari
- Francesco Paolo Fanizzi, Università del Salento
- Paolo Fornasiero, Università di Trieste

Delegato di Divisione

- Chiara Costabile, Università degli Studi di Salerno
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| **9:00 – 9:45** | **INO-PL01**: J. A. van Bokhoven  
Action at a distance: observing hydrogen spillover |
| **9:45 – 10:15** | **INO-KN01**: M. Chiesa  
Exploring and Engineering Spin-states in Solid State and Surface Chemistry |
| **10:15 – 10:30** | **INO-OR01**: T. Kosmala, L. Calvillo, S. Agnoli, G. Granozzi  
New methods and new catalysts for the oxygen reduction reaction at the cathode of fuel cells: surface science applied to CoO/Pd(100) ultrathin films. |

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| **9:45 – 10:15** | **INO-KN02**: M. Ravera  
Dual-targeting hybrid anticancer platinum(IV) prodrugs for combination therapy. |
| **10:15 – 10:30** | **INO-OR02**: D'Alonso, Linda Leone, Marco Chino, Ornella Maglio, Flavia Nastri, Vincenzo Pavone and Angela Lombardi.  
Control of enzymatic activity in a Mn-containing synthetic metalloenzyme. |
| **10:30 – 11:00** | Coffee Break |

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| **11:00 – 11:30** | **INO-KN03**: R. Zanoni  
Highly delocalized stable systems on semiconductor surfaces |
| **11:30 – 11:45** | **INO-OR03**: D. Cherni, N. Moussa, M. F. Ncib, L. Prati, A. Villa  
Effect of N-doping in the activity of TiO₂ supported catalysts in glycerol oxidation |
| **11:45 – 12:00** | **INO-OR04**: P. Solokha, S. De Negri, A. Saccone  
Long Period Stacking Ordered phases in the Y-Ni-Mg system: experimental and structural studies |
| **12:00 – 12:15** | **INO-OR05**: M. Benedetti, F. De Castro, F. P. Fanizzi  
General cooperative effects of single atom ligands on the ⁷³Ge, ¹¹⁹Sn and ²⁰⁷Pb NMR signals of tetrahedral [MX₄] (M = Ge, Sn, Pb; X₄ = combination of Cl, Br, I) coordination compounds |
| **12:15 – 12:30** | **INO-OR06**: F. Barzagli, C. Giorgi, F. Mani, M. Peruzzini  
CO₂ capture by aqueous Na₂CO₃ combined with the formation of high quality CaCO₃ and the release of pure CO₂ at room conditions |
| **12:30 – 12:45** | **INO-OR07**: M. La Rosa, S. Silvi, G. Jonusauskas, N. D. McClenaghan, A. Credi  
Long-lived luminescent Quantum Dots as result of Reversible Electronic Energy Transfer |
Grafene Functionalization and Tuning of Transport Properties by Plasma Strategies |

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| **11:00 – 11:30** | **INO-KN04**: L. Monsù Scolaro  
On the chirality in porphyrin nanoassemblies. |
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<td>INO-OR10</td>
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<td>Novel strained ruthenium complexes in photodynamic therapy</td>
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### Sessione II
Chairperson: Roberto Gobetto

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<td>Auranoctin, Et₃PAuCl and Et₃PAu exert high in vitro cytotoxic effects toward colorectal cancer cell lines: a comparative chemical, biological and mechanistic study</td>
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<td>Minimizing the release of reactive intermediates in O₂-dependent oxidation by de novo metalloenzymes</td>
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# Martedì 12 Settembre 2017

## Sala Nettuno

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**Chairperson Maurizio Peruzzini**

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<td><strong>INO-MD01</strong>: G. Bertrand, <em>Stable carbenes and related species as powerful tools in inorganic chemistry</em>&lt;br&gt;<strong>Medaglia Sacconi</strong></td>
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<td><strong>INO-PZ01</strong>: G. Ragazzon, S. Silvi, A. Credi, <em>Operating Molecular Machines: Thermodynamic and Kinetic Aspects</em>&lt;br&gt;<strong>Premio miglior tesi di Dottorato</strong></td>
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<td>10:15 – 10:30</td>
<td><strong>INO-IL01</strong>: A. J. T. Shore, <em>Publishing your research in high impact journals</em></td>
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## Sala Puccini (Hotel Savoy)

### Sessione Congiunta Chimica Teorica - Chimica Inorganica

**Chairperson Gianluca Ciancaleoni**

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<td>9:00 – 9:40</td>
<td><strong>TEO/INO-KN01</strong>: B. Civalleri, <em>Ab initio modeling of Metal-Organic Frameworks: from gas adsorption to stimuli responsive properties</em></td>
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<td><strong>TEO/INO-OR01</strong>: A. B. Muñoz-García, M. Pavone, <em>Computational design of Sr$<em>2$Fe$</em>{1.5}$Mo$_{0.5}$O$_6$–δ (SFMO)-based bifunctional electrodes for proton-conducting solid oxide electrochemical cells</em></td>
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<td><strong>TEO/INO-OR02</strong>: M. Cutini, M. Corno, P. Ugliengo, <em>Insight From DFT Simulations On The Collagen/Hydroxyapatite Interface: A Simple Model Based On The Poly-Proline Polymer</em></td>
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<td>10:20 – 10:40</td>
<td><strong>TEO/INO-OR03</strong>: L. Falivene, S. Kozłowski, L. Cavallo, <em>A DFT Rationalization of a Two Metals Strategy to Tune Selectivity in Catalysis</em></td>
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## Sala Nettuno

### Sessione I

**Chairperson Gaetano Granozzi**

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<td><strong>INO-OR32</strong>: F. Tessore, G. Di Carlo, A. Orbelli Birolini, M. Pizzotti, <em>Porphyrin-Sensitized Solar Cells: the challenge of photostability</em></td>
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<td><strong>INO-OR33</strong>: M. Melchionna, F. Paulucci, M. Bonchio, F. Vizza, P. Fornasiero, M. Prato, <em>Hierarchical materials based on carbon nanostructures as advanced catalysts in energy applications</em></td>
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<td>12:15 – 12:30</td>
<td><strong>INO-OR34</strong>: A. Carella, R. Centore, M. Bonomo, D. Dini, A. Di Carlo, <em>Pyran based dyes as photosensitizers for p-type dye-sensitized solar cells</em></td>
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<td>12:30 – 12:45</td>
<td><strong>INO-OR35</strong>: A. G. Marrani, D. Giacco, R. Zanoni, S. Bruttì, <em>Unravelling the surface degradation mechanisms in ether electrolyte based Li-O$_2$ cells</em></td>
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<td>12:45 – 13:00</td>
<td><strong>INO-OR36</strong>: I. Fratoddi, I. Venditti, L. Fontana, C. Sibilia, G. Leahu, A. Belardini, R. Li, L. Voti, C. Battocchio, R. Matassa, G. Familiari, <em>Networks based on functionalized noble metal nanoparticles: advanced materials for optical and electronic applications</em></td>
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### Sessione II

**Chairperson**

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## SOMMARIO – PROGRAMMA – MEDAGLIE E PREMI – PLENARIE - KEYNOTE – ORALI- POSTER - AUTORI

### XXVI Congresso Nazionale della Società Chimica Italiana

#### Chairperson Emma Gallo

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<td>11:00 – 11:30</td>
<td>INO-KN08: C. Tubaro, M. Baron</td>
<td>Selective syntheses of mononuclear vs dinuclear gold(III) complexes with di(N-heterocyclic carbene) ligands</td>
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<td>11:45 – 12:00</td>
<td>INO-OR38: M. Atzori, L. Tesi, E. Morra, M. Chiesa, L. Sorace, R. Sessoli</td>
<td>Synthetic Strategies Towards Quantum Coherence Time Enhancement in Potential Molecular Spin Qubits</td>
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<td>12:00 – 12:15</td>
<td>INO-OR39: F. Grisi, V. Paradiso, C. Costabile, V. Bertolasi</td>
<td>Olefin Metathesis Ruthenium Catalysts Bearing Backbone-Substituted Unsymmetrical NHC Ligands</td>
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<td>12:45 – 13:00</td>
<td>INO-OR42: M. Monticelli, M. Baron, A. Longhi, C. Tubaro, S. Bellemín-Laponnaz, C. Graiff, M. Rancan, G. Bottaro, L. Armelao</td>
<td>Dinuclear $d^{10}$ complexes with nNHC/tzNHC heteroditopic carbene ligands and their luminescence properties</td>
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#### Sessione Congiunta Chimica Teorica - Chimica Inorganica

Chairperson Emilia Sicilia

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<td>11:20 – 12:00</td>
<td>TEO/INO-KN02: I. Tolbatov, C. Coletti, A. Marrone, N. Re</td>
<td>Insight into the Electrochemical Reduction Mechanism of Pt(IV) Anticancer Complexes</td>
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<td>12:00 – 12:20</td>
<td>TEO/INO-OR04: T. Marino, M. Prejanò, P. Piazzetta, N. Russo</td>
<td>The role of metal substitution in the metallo-enzymes: A theoretical point of view</td>
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<td>12:20 – 12:40</td>
<td>TEO/INO-OR05: G. Ciancaleoni, N. Bartalucci, L. Belpassi, F. Marchetti</td>
<td>Back-donation in $d^{0}$ Metal Complexes: Does it Exist? The case of Nb(V)</td>
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<td>12:40 – 13:00</td>
<td>TEO/INO-OR06: G. Mazzone, C. Regina, N. Russo</td>
<td>Combination of Porphyrin and Ruthenium-arene moieties for a Dual Anticancer Function. A Theoretical Investigation</td>
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### Sala Nettuno

#### Sessione Congiunta

Chairperson Adriana Saccone

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<td>INO-PZ02: M. Mannini</td>
<td>Titolo della conferenza Premio Nasini</td>
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15:45 – 16:30  **INO-PZ03**: C. Landis  
*Organotransition Metal Complexes, Catalysis, and Industry*  
*Premio Chini*

16:30 – 17:00  Coffee Break  

**Sala Nettuno**  

**Sessione Congiunta Chimica Organica - Chimica Inorganica (GICO)**  
*Chairperson Fabio Ragaini*

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<td>17:00 – 17:30</td>
<td><strong>ORG/INO-KN02</strong>: L. Zani</td>
<td><em>Conjugated Organic Compounds for Solar Energy Conversion to Electricity and Fuels</em></td>
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<td>17:30 – 18:00</td>
<td><strong>ORG/INO-PZ02</strong>: EurJIC Junior Organometallic Chemist Lecture by M. Bellini</td>
<td><em>Hydrogen and chemicals from renewable alcohols by Organometallic Electro-Reforming (OMER)</em></td>
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<td>18:00 – 18:15</td>
<td><strong>ORG/INO-OR03</strong>: W. Baratta, R. Figliolia, S. Baldino, H. Günter Nedden, A. Zanotti-Gerosa</td>
<td><em>Mild N-Alkylation of Amines with Alcohols Catalyzed by Acetate Ruthenium Complexes</em></td>
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<td>18:15 – 18:30</td>
<td><strong>ORG/INO-OR04</strong>: R. Mazzoni, C. Cesari, A. Cingolani, V. Zanotti, F. Cavani, F. Puzzo, C. Lucarelli, M. Mella, A. Tagliabue, T. Baker</td>
<td><em>The power of ligand combination in redox active ruthenium and iron complexes</em></td>
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<td>18:30 – 18:45</td>
<td><strong>ORG/INO-OR05</strong>: R. Figliolia, S. Baldino, W. Baratta, S. Gibolout, H. Günter Nedden, A. Zanotti-Gerosa</td>
<td><em>Synthesis of New Carbonyl Diphosphane Ruthenium Complexes for Catalytic C-H Bond Activation Reactions</em></td>
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**Sala Mercurio**

**Sessione II**  
*Chairperson Alberto Credi*

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<td>17:00 – 17:15</td>
<td><strong>INO-OR43</strong>: E. Diana, E. Priola, F. Grifasi, R. Gobetto, M. R. Chierotti</td>
<td><em>Symbiotic structural and spectroscopic approach to reticular chemistry: the case study of luminescent Copper(I) cyanide coordination polymers.</em></td>
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<td>17:15 – 17:30</td>
<td><strong>INO-OR44</strong>: S. Pragliola, A. Botta, V. Vendito, A. Velardo, R. Liguori, Alfredo Rubino</td>
<td><em>Polymer Stereoregularity Influence on Optical Properties of Carbazole-based Photoconductor Polymers</em></td>
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<td>17:30 – 17:45</td>
<td><strong>INO-OR45</strong>: C. Daniel, P. Cortelletti, M. Pedroni, G. Antonio D’Amora, G. Guerra, A. Spighini</td>
<td><em>Upconverting polymeric aerogels</em></td>
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<td>17:45 – 18:00</td>
<td><strong>INO-OR46</strong>: C. Crestini, H. Lang, e L. Zongo</td>
<td><em>Coordination Complexes and One Step Assembly of Natural Polyphenols for Versatile Nanocapsule Engineering</em></td>
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<td>18:00 – 18:15</td>
<td><strong>INO-OR47</strong>: V. Nicolini, G. Malavasi, L. Menabue, G. Lusvardi, F. Benedetti, S. Valeri, P. Luches</td>
<td><em>Mesoporous bioactive glasses doped with cerium: investigation of catalase and SOD mimetic activities, and bioactivity</em></td>
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<td>18:15 – 18:30</td>
<td><strong>INO-OR48</strong>: M. Marchini, A. Luisa, G. Bergamini, N. Demitri, M. Baroncini, P. Ceroni, E. Iengo</td>
<td><em>Tetrahedral Arrays of Metallo-porphyrins</em></td>
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Medaglie e Premi della Divisione di Chimica Inorganica

**Medaglia Sacconi:** Prof. Guy Bertrand, University of California San Diego

**Premio miglior Tesi di Dottorato:** Dr. Giulio Ragazzon, Università di Bologna

**Premio Nasini:** Prof. Matteo Mannini, Università di Firenze

**Premio Chini:** Prof. Clark R. Landis, University of Wisconsin-Madison

**Premio under 35 EJOC:** Dr. Valentina Pirovano, Università di Bologna

**Premio under 35 EJIC:** Dr. Marco Bellini, Consiglio Nazionale delle Ricerche
Stable carbenes and related species as powerful tools in inorganic chemistry

Guy BERTRAND

UCSD-CNRS Joint Research Chemistry Laboratory (UMI 3555), Department of Chemistry and Biochemistry, University of California San Diego, La Jolla, CA 92093-0358 (USA)
E-mail: guybertrand@ucsd.edu

It will be shown that the peculiar electronic and steric properties of cyclic (alkyl)(amino)carbenes (CAACs) 1 (1,2) and other stable singlet carbenes allow for the stabilization of unusual diamagnetic and paramagnetic main group element species. As examples, we will describe the preparation of room temperature stable boron, antimony-, and even carbon-centered neutral and cationic radicals. We will also show that CAACs allow for the isolation of catalytically active complexes, which were supposed to be only transient intermediates. Among them, bis(copper) complexes 2 involved in the very popular CuAAC reaction (Click Chemistry) will be discussed (3) We will show that this discovery allows for the development of novel catalytic transformations (4). Another part of the lecture will be devoted to the synthesis, reactivity and coordination behavior of the first stable phosphinidene 3 (5,6,7).

References:
Operating Molecular Machines: Thermodynamic and Kinetic Aspects

Giulio Ragazzon$^{a,b}$, Serena Silvi$^a$, Alberto Credi$^{c,d}$

$^a$ Dipartimento di Chimica “G. Cianiaccian”, Università di Bologna, via Selmi 2, 40126 Bologna; $^b$ Present address: Dipartimento di Scienze Chimiche, Università di Padova, via Marzolo 1, 35131 Padova; $^c$ Dipartimento di Scienze e Tecnologie Agro-alimentari, Università di Bologna, viale Fanin 50, 40127 Bologna; $^d$ Istituto per la Sintesi Organica e la Fotoreattività, Consiglio Nazionale delle Ricerche, via Gobetti 101, 40127 Bologna.

The Nobel Prize in Chemistry 2016 has been awarded “for the design and synthesis of molecular machines”. Despite the incredible progresses of the field, several challenges still require substantial development. These include encoding functionality in simple structures, performing molecular tasks, implementing ratcheting mechanism and developing autonomous systems. In this talk, work aimed at tackling these challenges will be presented. In particular, spectroscopic and electrochemical techniques have been applied to the study of calixarene-based interlocked structures(1,2,3), functional rotaxanes(4,5,6) and pseudorotaxanes(7,8). The most relevant achievement has been the direct observation of a light-driven self-assembling molecular pump operating under nonequilibrium conditions(8).

Figure 1: A rotaxane in which reduction of the secondary station affords a change in pKa at the primary station, due to the ability of the ring to put the two stations in communication (top); molecular components and minimal operation scheme of a light-driven self-assembling pump module (bottom).

Exploring magnetism of molecules at the nanoscale

Matteo Mannini

Laboratory for Molecular Magnetism, Department of Chemistry "Ugo Schiff" & INSTM Research Unit of Firenze, University of Firenze, Sesto Fiorentino (FI), Italy.
matteo.mannini@unifi.it

With their rich and chemically-tuneable properties, molecular materials stand out as a possible solution to the quest for innovative technologies. In particular, magnetic molecules represent a rich playground for chemists and physicists toward the development of novel molecule-based devices, whose functionality can be finely tuned through the rational design and bottom-up assembly of their molecular constituents. This idea explains the huge efforts of molecular magnetism (1) community for exploring the incorporation of magnetic molecules in devices for information and computation technologies, including spintronics and quantum computation.

To achieve this goal it was essential to combine the richness of coordination chemistry with nanostructuration protocols. In particular, the fragility of coordination bonds in metal-based magnetic cores required a careful selection/modification of molecules as well as an attentive tailoring of self-assembly and processing methods. A multi-technique characterization approach (2,3) was also adopted to monitor each step of the nanostructuration process and to evaluate the structural and magnetic integrity of molecules in the environment of a single-molecule-device.

Going beyond a morphological characterization, as provided by scanning probe methods, demands for surface sensitive techniques capable of probing the chemical and electronic properties of surface-supported molecules. A key role is played by investigation tools based on large-scale facilities, which allow to directly access the static and dynamic magnetic properties down to the nanoscale.

Here we will overview our most recent results achieved in the characterization of hybrid nanostructures obtained by assembling magnetic molecules on surfaces. We will follow the path that allowed to demonstrate that three important classes of magnetic molecules retain their peculiar behaviour at the nanoscale. These encompass single molecule magnets, in which classical and quantum magnetic properties may coexist (4,5), spin crossover complexes and redox isomers, which both feature two magnetically inequivalent states accessible by application of an external stimulus (6,7). Such promising results now pave the way for the next ongoing step, namely the realization of innovative multifunctional devices (8).

References:
The rapid growth of organotransition metal chemistry in the last mid-century is tightly coupled with the implementation of organometallics in industrial processes. Prominent examples include alkene polymerization, hydroformylation, alcohol carbonylation, alkene metathesis, hydrogenation, et al. Professor Paolo Chini’s contributions to organometallic chemistry range from producing the first samples of isotactic polypropylene to pioneering the chemistry of metal carbonyls and their clusters. This presentation focuses on two of the major industrial applications of homogeneous, transition metal catalysts: alkene polymerization and hydroformylation. Catalytic polymerization with homogeneous systems enables increasingly sophisticated processes, such as the Dow Chain–Shuttling technology that produces blocky alkene co-polymers with unusual properties on a commodity scale. Ultimately, the composition and structure of such blocky copolymers are kinetically controlled. Key to revealing fundamental kinetic and mechanistic data concerning “Chain–Shuttling” is the development and implementation of a chromophore quench-labeling strategy; such experiments reveal catalyst active site counts and enable detailed extraction of propagation and chain-transfer kinetics from the evolution of polymer molecular weight distributions.

Alkene hydroformylation as catalyzed by metal carbonyls yields nearly 10 million metric tons of linear, achiral aldehyde per annum. New ligands, such as BisDiazaPhospholanes (BDPs), combine with common Rh-precursors to provide high rates, regioselectivity that favors the branched isomer, and high enantioselectivity. These qualities open new possibilities for atom–economical production of complex organic molecules. But what controls the selectivity? Insight results from operando NMR studies in the Wisconsin High Pressure NMR Reactor (WiHP-NMRR). Monitoring catalyst speciation, reaction rates, and reaction selectivity simultaneously, provides quantitative data for detailed kinetic analysis that reveals intimate details of the reaction mechanism and the origins of selectivity under a variety of reaction conditions.
Gold(I)-catalyzed [4+2] cycloaddition reactions of vinylindoles and allenes

Valentina Pirovano, Elisabetta Rossi, Giorgio Abbiati

DiSFarm - Sezione Chimica Generale e Organica "A. Marchesini", Università degli Studi di Milano, Via G. Venezian 21, 20133 Milano, Italy; valentina.pirovano@unimi.it

Carbazole and tetrahydrocarbazole rings are the key structural motif in a great number of biological active molecules, including natural alkaloids and synthetic products. For this reason, strategic syntheses of these indole derivatives are highly required, in particular when based on asymmetric methodologies. In this research field, 2- and 3-vinylindoles have become versatile 4C building blocks for the synthesis of complex tetrahydrocarbazole derivatives by means of [4+2] cycloadditions. Among dienophiles, it has been shown that gold activated allenes could participate in [4+2] processes and we published the first example of gold catalyzed reaction of 2- and 3-vinylindoles with allenamides and allenyl esters. In this latter work we reported also some preliminary investigations on enantioselective synthesis of tetrahydrocarbazoles, by conducting the reaction in the presence of a chiral gold(I) phosphoramidites. Prompted by these results and taking into account the importance of asymmetric tetrahydrocarbazole synthesis, we next explored the reactivity of 3/2-substituted-2/3-vinylindoles with N-allenamides under chiral gold(I) catalysis for the synthesis of a new series of dearomatized indoles bearing a quaternary C4a/C9a stereocenter (Scheme 1). The results obtained in this work will be presented in the context of our investigations on gold(I) catalyzed syntheses of tetrahydrocarbazoles.

Hydrogen and chemicals from renewable alcohols by Organometallic Electro-Reforming (OMER)

Marco Bellini\textsuperscript{a}, Maria V. Pagliaro\textsuperscript{a,b}, Hamish A. Miller\textsuperscript{a}, Werner Oberhauser\textsuperscript{a}, Maria G. Folliero\textsuperscript{a}, Andrea Marchionni\textsuperscript{a}, Jonathan Filippi\textsuperscript{a}, Francesco Vizza\textsuperscript{a} and Hansjörg Grützmacher\textsuperscript{c}.

\textsuperscript{a} Istituto di Chimica dei Composti Organometallici – Consiglio Nazionale delle Ricerche, Via Madonna del Piano 10, 50019, Sesto Fiorentino (Firenze); \textsuperscript{b} Dipartimento di Chimica, Università degli Studi di Siena, Via Aldo Moro 2, 53100 Siena; \textsuperscript{c} Department of Chemistry and Applied Biosciences, ETH Hönggerberg, CH-8093 Zurigo, Svizzera. marco.bellini@iccom.cnr.it

The production of hydrogen by electrolysis of water is a well-established technology but it does not have a significant commercial impact due to its high energy cost. A recent strategy for reducing the energy cost of electrolytic hydrogen production involves the replacement of water oxidation at the anode of the electrolytic cell with the oxidation of a soluble substrate, like a bioalcohol, whose oxidation potential is much lower than that of water. This leads to a significant reduction of the potential required to produce hydrogen (1). The original idea presented here, consists in coupling the partial oxidation of renewable alcohols promoted by an organometallic complex \([\text{Rh(OTf)(trop}_2\text{NH})(\text{P(4-n-butyl-Ph})_3)]\) (trop\textsubscript{2}NH=bis(5-H dibenzo[a,d]cyclohepten-5-yl)-amine; OTf\textsuperscript{-}=CF\textsubscript{3}SO\textsubscript{3}\textsuperscript{-}=triflate; (see 1@C in figure 1 for a structure plot) with the cathodic hydrogen evolution reaction (2). We report an electrolytic device that achieves the simultaneous selective production of carboxylate compounds and high-purity hydrogen gas. This electrolyzer, that we call OrganoMetallic ElectroReformer (OMER), in contrast to electrolysis technologies based on nanoparticles, offers potentially enormous advantages as in principle every single metal atom is catalytically active, thus allowing a vastly reduced metal loading. At the same time, this technology is capable of providing simultaneously high levels of pure hydrogen production and chemicals of industrial importance by the exploitation of bioalcohols. The absence of oxygen production in the anode compartment facilitates the production of hydrogen at elevated pressures. Consequently, we hypothesize the exploitation of bioalcohol electroreforming as an essential component of the biorefinery platform using this new class of electrolyzers based on organometallic complexes.

Figure 1: proposed mechanism for the reactions occurring on the anode coated with 1@C.
Conferenze Plenarie

- **INO PL01**: Jeroen A. van Bokhoven, Institute for Chemical and Bioengineering, ETH Zurich and Laboratory for Catalysis and Sustainable Chemistry, ENE Division, Paul Scherrer Institute, Villigen

- **INO PL02**: Paolo Carloni, Forschungszentrum Jülich, Jülich, Germany and Department of Physics, RWTH-Aachen University, Aachen, Germany
Action at a distance: observing hydrogen spillover

Jeroen A. van Bokhoven

Institute for Chemical and Bioengineering, ETH Zurich and Laboratory for Catalysis and Sustainable Chemistry, ENE Division, Paul Scherrer Institute, Villigen; j.a.vanbokhoven@chem.ethz.ch, jeroenvanbokhoven@psi.ch

Depending on the nature of the support, hydrogen spillover may occur in hydrogen-catalyzed reactions. Evidence of its occurrence on non-reducible supports, such as alumina, is disputed while its occurrence on reducible supports like titania is generally accepted. [1] Direct experimental proof of its existence does not exist due to the lack of well-defined model systems and the inability to observe the effect directly. We employ enhanced precision of top-down nanofabrication [2-4] and single-particle in-situ X-ray absorption spectromicroscopy [3,4] to visualize hydrogen spillover. For the first time, distance dependence of hydrogen spillover has been experimentally visualized [4], and the hydrogen diffusion and migration mechanisms are elucidated by DFT calculations. We develop a novel model surface with precision in particle size and its positioning. Multiple pairs of nano-sized iron oxide and platinum particles, at varying distances from each other starting at 0 nm to 45 nm, are positioned on the same support with an accuracy of one nanometer. X-ray photoemission electron microscope (XPEEM) at the Swiss Light Source (SLS) enables in-situ structural analysis on individual iron oxide particles to visualize chemical reduction by hydrogen spillover at different distances [4]. We find that spillover on alumina support depends on distance from the catalyst and is relevant only at distances below 15 nm, occurring on three-coordinate aluminum sites. Spillover on titania support occurs via coupled electron-proton transfer and is uniform all over the support irrespective of distance.

Multiscale simulation-based structural predictions of metalloproteins of pharmacological relevance.

Paolo Carloni,

Forschungszentrum Jülich, Jülich, Germany and Department of Physics, RWTH-Aachen University, Aachen, Germany
p.carloni@fz-juelich.de

I will present recent hybrid Quantum Mechanics/Molecular Mechanics (QM/MM) - based investigations of the structural determinants of the drug cisplatin in complex with some of its cellular targets. This information may be of help in counteracting drug’s resistance, which limits greatly drug’s efficacy after repeated administrations. The talk will close with a QM/MM study on a bioinorganic system of possible neuropharmacological interest, copper binding to the human alpha synuclein protein.

Funding: HPC-Leap, BioExel, Human Brain Project, DFG.
Keynote e Conferenze su invito

- **INO KN 01**: M. Chiesa, Università di Torino
- **INO KN 02**: M. Ravera, Università del Piemonte Orientale
- **INO KN 03**: R. Zanoni, Università degli Studi di Roma "La Sapienza"
- **INO KN 04**: L. Monsù, Università di Messina
- **INO KN 05**: L. Zaccaro, CNR, Napoli - Università di Napoli “Federico II”
- **INO KN 06**: F. Ragaini, Università degli Studi di Milano
- **INO KN 07**: D. Armentano, Università della Calabria
- **INO KN 08**: C. Tubaro, Università degli Studi di Padova
- **ORG/INO KN 01**: A. Caselli, Università degli Studi di Milano - ISTM-CNR, Milano
- **ORG/INO KN 02**: Lorenzo Zani, CNR, Sesto Fiorentino (Fi)
- **INO IL 01**: Andrew J. T. Shore-Royal Society of Chemistry, Cambridge (UK)
- **TEO/INO KN 01**: B. Civalleri, Università di Torino
- **TEO/INO KN 02**: N. Re, Università “G. D’Annunzio” Chieti-Pescara
Exploring and Engineering Spin-states in Solid State and Surface Chemistry

Mario Chiesa

Dipartimento di Chimica Università di Torino, Via Giuria 7, 10125 Torino E-mail mario.chiesa@unito.it

Spin is a fundamental property of elements and molecules, which originates from the presence of unpaired electrons. Spin states constitute thus a fundamental aspect of the electronic structure, which concur to determine the electronic, magnetic and chemical properties of matter. Moreover, the possibility to control the spin-dependent electronic structure of molecular-scale architectures is essential for the development of solid-state devices and the implementation of future devices based on quantum states. The determination and control of spin states is thus an important - and often not properly discussed – issue in the context of understanding many aspects of chemical reactivity and materials science. Electron Paramagnetic Resonance (EPR) spectroscopy is the technique of election for this task, allowing for a molecular level description of the structure and reactivity of paramagnetic species. In this contribution, an overview of the wealth and breadth of information that can be obtained from EPR in the characterization of paramagnetic species in the bulk or at the surface of solid-state systems will be provided. Attention will be paid to illustrate the advantages offered by modern pulsed EPR methodologies in determining the spin state and monitoring the elementary processes occurring within the coordination sphere of paramagnetic species, with emphasis on transition-metal ions (TMI). Specific cases involving TMI acting as spin bearing units will be presented, trying to outline the methodological approaches, which characterize the application of advanced EPR techniques and the questions that can be answered and addressed in connection to the chemical reactivity and magnetic properties of solid state systems.

References:
Dual-targeting hybrid anticancer platinum(IV) prodrugs for combination therapy

Mauro Ravera

Dipartimento di Scienze e Innovazione Tecnologica, Università del Piemonte Orientale, Viale T. Michel 11, 15121 Alessandria, Italy; mauro.ravera@uniupo.it.

Despite the use of cisplatin (CDDP) and its Pt(II) congeners in several chemotherapeutic regimes, the associated heavy side effects and the intrinsic/acquired chemoresistance have prompted inorganic medicinal chemists to design, inter alia, alternative Pt(IV) derivatives. These antitumor complexes are considered prodrugs, since they can be selectively reduced in the hypoxic and acidic intracellular milieu of the tumor cells to the corresponding cytotoxic Pt(II) metabolite with the usual loss of their two axial ligands (activation by reduction, Figure 1).

Figure 1

The saturated six-coordinated octahedral geometry of the low spin d⁶ Pt(IV) is characterized by a high kinetic inertness that minimizes off-target effects, thus improving the therapeutic index and, furthermore, allowing oral administration. Their axial ligands affect the cellular accumulation of Pt(IV) compounds due to their enhanced lipophilicity (the influx occurs mainly by passive diffusion). Moreover, these axial ligands can be biologically active vectors towards tumor tissue or adjuvant (synergistic) drugs. Indeed, clinicians usually combine the approved Pt(II) drugs with other therapeutics to potentiate their efficacy. The bifunctional (dual action) Pt(IV) derivatives, where one/two synergistic drug molecules are conjugated to Pt(IV) in the axial position/s, represent an efficient tool to realize such a combination therapy (Figure 2) (1).

Figure 2

Several examples will be described. In particular, there is a growing interest in the co-administration of DNA-damaging drugs (including CDDP) with Histone DeACetylase inhibitors (HDACi) as auxiliary agents. The naïve rationale for such a combination is that the inhibition of HDAC results in the hyperacetylation of lysines in nucleosomal histones that no longer associate with the nuclear DNA. This increases the accessibility of nucleobases to the DNA-damaging agents, as CDDP (2–4).

References:
Highly delocalized stable systems on semiconductor surfaces

Robertino Zanoni

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The quest for systems able to bring the field of molecular-scale electronics into true applicability has started since few decades now, but the challenging key issue of their stability still requires continuous effort. (1) The exciting electronic, mechanical, thermal, and optical properties of graphene have switched on areas of basic and applied research in many fields worldwide. (2) The relatively recent progresses in the characterization of true graphene deposits have allowed a much better interpretation of results in the field, also allowing for a comparison between the outcomes of distinct synthetic strategies. (3) A notable goal in view of studies and applications of graphene is the obtainment of handy forms of this material, allowing for developments in real conditions. To achieve applications, a large-scale production of high quality graphene sheets in an efficient and effective way is required. (4)

In this lecture, very recent results will be discussed coming from research done at the Department of Chemistry, La Sapienza, which stem from an international collaboration work with E.A. Dalquiele (Univ. of Montevideo), R. Schrebler (Univ. Valparaiso), A.G. Marrani (Un. La Sapienza). (5) Novel experimental approaches to produce graphene/silicon interface will be reported, which consist of an electrochemical reduction of graphene oxide (GO) directly in contact with Si(111) wafers. Such modified surface was utilized as a working electrode in an electrochemical cell, and characterized also by means of field-emission scanning electron microscopy, and Raman and X-ray photoelectron spectroscopies. The transformation of GO into electrochemically reduced graphene oxide (ERGO) over the silicon surface was fully demonstrated. Parallel research studies on the functionalization of graphene nanoplatelets (GNP) with substituted porphyrins in a collaboration with P. Tagliatesta (Univ. Tor Vergata) and S. Bellucci (INFN) will be also reported. These outcomes are new and a step forward in the direction of an easy procedure to high quality graphene interfaces.

On the chirality in porphyrin nanoassemblies

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Observation of optical activity for assemblies of achiral entities in the absence or in the presence of chiral templates has attracted attention of many researchers, due to the potential implications with the ubiquitous homochirality in our universe. Some porphyrins have been of quite considerable importance for such studies due to their ability to self-assemble into chiral supramolecular structures. In this contribution, a series of examples will be reported on cationic and anionic water soluble porphyrins.

Under moderate ionic strength conditions, a copper(II) metal complex of a cationic porphyrin (t-CuPagg) extensively self-aggregates forming large mesoscopic clusters that bind avidly polyanionic substrates such as poly-glutamate (PGA). This interaction leads to large enhancement of the induced circular dichroism signals in the absorption region of the porphyrin, through a specific chirality transfer mechanism.(1) Such an effect could be exploited as chiroptical probe towards simple chiral substrates (carbohydrates or nucleotides) and biopolymers such as human serum albumin, poly(adenylic acid), calf-thymus DNA and alginate.(2)

Under proper conditions, an anionic porphyrin (TPPS) self-assembles into nanotubes, that in the absence of any added chiral templating agent, show an unpredictable chirality. We provided evidence that the rate of aggregation plays an important role on the final observed optical activity.(3) The supramolecular aggregation processes are based on thermodynamically- and kinetically-controlled paths related to medium properties and experimental conditions such as concentration, pH and ionic strength. Also the important role of mixing protocol, counter-anions(4) and isotopic substitution(5) on kinetics and chirality will be discussed. In the presence of chiral templating reagents, such as tartaric acid, distinct kinetic patterns and a corresponding variance in the amplification of chirality has been also observed for the two enantiomers.(6) The resulting chiral nanoaggregates have been efficiently transferred onto solid substrates by soft lithography.(7)

Quite recently, control of the handedness of chiral J-aggregates obtained from such achiral compounds has been achieved by applying rotational, gravitational and orienting forces at the beginning of the assembly process.(8)

RGDechi chimeric peptide as new scaffold for gaining insight into structural features of integrins selectivity for theranostics.

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Over the last three decades intensive efforts have been devoted to elucidate the structural features that govern integrin-specific interactions. Given the involvement of integrins in the regulation of physiological processes (1), as well as of pathological ones, the development of integrin subtype-exclusive antagonists is highly desirable. Integrins \(\alpha\beta_3\), \(\alpha\beta_5\) and \(\alpha_5\beta_1\), key mediators of cell adhesion, differentiation, proliferation, angiogenesis and tumor growth, have been considered very promising targets for theranostic application. Due to the similarity of the RGD binding regions in these integrins, the development of small synthetic molecules with high activity and selectivity for the different subtypes is a tricky goal to pursue. The majority of the ligands described so far as integrin subtype-selective have in fact residual, yet significant, affinity for the other integrins, thus stimulating extensive research to develop novel integrin specific molecules.

In the last decade we designed and characterized the peptide RGDechi, a chimeric molecule encompassing a cyclic portion containing the RGD triade for integrin binding and a linear sequence derived from the C-terminal fragment of the echistatin protein to confer specificity for \(\beta_3\) subunit (2). We demonstrated anti-adhesive and proapoptotic effects on tumor cells and antiangiogenic activity in vivo (3,4,5). More, SPECT and PET imaging studies with \(^{111}\)In and \(^{18}\)F-labelled RGDechi in a xenograft model confirmed the ability of peptide to selectively visualize this integrin. Recently NMR and computational analyses on cell membranes allowed a detailed understanding of \(\alpha_5\beta_3\)/RGDechi recognition mechanism (6). On the basis of the identified molecular determinants, we used RGDechi as scaffold peptide gaining from its chimeric nature to shift the selectivity towards \(\alpha\beta_3\) or \(\alpha_5\beta_1\) integrins.

In conclusion our studies, providing an improved understanding of ligand–integrin interactions, pave the way for the design of novel peptides selective for the different integrins to use in theranostics.

Schiff Bases of the BIAN Family: from Symmetrical Biaryl Derivatives to Mixed, Alkyl, Chiral or Reduced Ligands and Heterogeneous Catalysts.

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The number of applications of bis-imines as ligands in homogeneous catalysis has much increased in recent years. Derivatives of acenaphthenequinone (R-BIANs) are especially useful to this purpose because the rigidity of the acenaphthene skeleton strengthen coordination to a metal and add stability against the rupture of the central C-C bond of the diimine moiety. During the years, we have expanded the available range of Ar-BIANs to ligands where the aryl group bears strongly electron withdrawing substituents (1), two different aryl groups are present (2), and first prepared usually unstable Alkyl-BIAN compounds (3,4). The key principles which allowed these products to be obtained will be illustrated. Solubility of the products and the right control of ring strain for alkyl derivatives are essential points. The coordinating strength of a series of Ar-BIAN ligands to several palladium complexes has been measured and varies linearly with the log of Hammett σ constant. The slope of the correlation (ρ) depends on the metal complex and can be regarded as measure of its Lewis acidity (5). The family of R-BIAN ligands was then further expanded to chiral derivatives (6) (Figure 1) and finally to reduced ligands, Ar-BIANH₂ (7) (Figure 2). The latter are air sensitive compounds, but are stable under in the solid state an inert atmosphere and can be employed to synthesize catalytically active complexes without resorting to the use of reduced metal precursors or alkaline-metal reduced intermediates (8). At the end of this evolution, the last application was to decompose the coordinated ligand at high temperatures to generate heterogeneous nitrogen-enriched graphitic cobalt catalysts, effective in hydrogenation reactions for which traditional cobalt catalysts are inactive (9).

References:
Synthesis and X-ray Snapshots of Ultrasmall Metallic Clusters within Metal-Organic Frameworks for High Performance in Catalysis.

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Cluster catalysis may represent a major technological step forward in a similar way to that metal nanoparticles did, in view of the extremely high catalytic performance of metal clusters below the nanometer. However, much effort is still needed in terms of synthesis, stabilization and characterization of such small entities in order to design precisely novel catalysts bearing such active sites. Ultrasmall metal nanoclusters (NCs), consisting of aggregations of less than 10 atoms with a high percentage of them exposed to the external environment, have emerged as formidable catalysts capable to surpass the state-of-the-art catalysts in organic reactions of industrial interest, being thus capable to make feasible certain reactions which are currently financially prohibitive. Such small NCs, that may give rise to a technological leap in a similar way as the irruption of metal nanoparticles (NPs) did, still show important weaknesses regarding the synthetic control of their shape and nuclearity as well as their lack of stability.

Supporting these clusters within a type of porous materials named metal-organic frameworks (MOFs) is a very promising strategy. Metal-Organic Frameworks (MOFs), a type of porous materials possessing regular and well-defined channels and exhibiting a fascinating host-guest chemistry, are, in principle, the perfect platforms to synthesize, in a controlled manner, metal clusters below the nanometer allowing to gain information about their nature by means of X–ray crystallography, thus illustrating every single step during their synthetic route. Here we report on the MOF-mediated chemical synthesis of structurally and electronically well–defined ultrasmall Pt\textsubscript{2}\textsuperscript{0} clusters, grown within the functional channels of MOFs specifically designed for this purpose. The functional pores, a metal controlled stoichiometry and a highly homogeneous distribution of the metal ions results in such controlled chemical synthesis. Reactions in which the resulting [Pd\textsubscript{4}\textsuperscript{2+}–Pt\textsubscript{2}–MOF hybrid material outperform state–of–the–art metal catalysts will be illustrated.

Fig. 1. Crystal structures of the Pt\textsuperscript{11}@MOF (a) and Pt\textsubscript{2}\textsuperscript{0}@MOF (b). c. Perspective view, in detail, of a channel of Pt\textsubscript{2}\textsuperscript{0}@MOF along the c axis. Cyan and blue polyhedral for Copper and calcium atoms, respectively, sticks for organic ligands. Dashed lines represent the Pt···S interactions.

Selective syntheses of mononuclear vs dinuclear gold(III) complexes with di(N-heterocyclic carbene) ligands

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N-heterocyclic carbene-gold species represent one of the most recent and appealing class of organometallic complexes, in view of their wide range of applications. Limiting the attention to di(N-heterocyclic carbene) ligands, the synthesis of gold(I) complexes is quite straightforward and usually involves i) transmetalation of the carbene ligand from the corresponding silver(I) complex or ii) deprotonation of an azolium salt in the presence of a gold(I) species like AuCl(SMe₂). By contrast, due to the instability of gold(III) towards reduction, deprotonation of an azolium salt in the presence of gold(III) precursors generally gives the corresponding gold(I) complex, so that transmetalation of the diNHC ligand remains the only viable synthetic procedure for diNHC-gold(III) species. In this way mononuclear tricationic complexes are obtained with two diNHC ligands coordinated in a chelating fashion. Alternatively, bridged dinuclear gold(III) complexes can be prepared via oxidative addition of halogen X₂ (X=Cl, Br, I) to the pristine dinuclear gold(I) complexes.

In this contribution, the different strategies for the synthesis of mononuclear or dinuclear gold(III) complexes with diNHC ligands will be illustrated and critically evaluated. The different applications of the synthesized complexes will also be discussed.

References:
Catalytic Applications of Pyridine-Containing Macrocyclic Complexes

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Polyazamacrocycles are a common class of macrocyclic compounds, utilized across a number of fields, including, but not limited to, catalysis, selective metal recovery and recycling, therapy and diagnosis, and materials and sensors. Worth of note is their ability to form stable complexes with a plethora of both transition, especially late, and lanthanide metal cations. Deviation of the macrocycle donor atoms from planarity often leads to rather uncommon oxidation states. Both the thermodynamic properties and the complexation kinetics are strongly affected by the introduction of a pyridine moiety into the skeleton of polyazamacrocycles by increasing the conformational rigidity and tuning the basicity. Pyridine-containing ligands engender great interest due to various potential field of applications. They have been successfully employed in biology, Magnetic Resonance Imaging, molecular recognition, supramolecular chemistry and self-assembly, molecular machines and mechanically interlocked architectures. In this lecture, I will provide a perspective on the catalytic applications of metal complexes of pyridine-containing macrocyclic ligands (Pc-L’s) which have been studied in our group (Figure), with a focus interest on the structural features relevant to catalysis. The increased conformational rigidity imposed by the pyridine ring allowed for the isolation and characterization of metal complexes which showed a rich coordination chemistry. The very different conformations accessible upon coordination and the easy tuneable synthesis of the macrocyclic ligands have been exploited in stereoselective syntheses.

Figure. Metal complexes of Pc-L’s and X-ray structure of a Cu(I) complex with a rare $\eta^2$-naphtyl moiety coordinated to the metal center.

Key words: macrocyclic ligands, homogeneous catalysis, copper, silver, C-C and C-O bond forming reactions.

References:
Conjugated Organic Compounds for Solar Energy Conversion to Electricity and Fuels

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Over the years, conjugated organic compounds have been extensively employed in devices for solar energy exploitation, both as light-harvesting materials and semiconductors with high charge carrier mobility: relevant examples include sensitizers for dye-sensitized solar cells (DSSC) (1) and hydrogen photocatalytic production (2), small-molecule donor materials in organic solar cells (3) and hole-conductive materials for perovskite solar cells (4).

In this communication, we will provide an overview of our group’s recent activity in the design, synthesis and application of donor-acceptor conjugated compounds for solar energy conversion (5-9). Compounds containing different heterocyclic rings (Figure 1) were assembled by means of typical organometallic and transition metal-catalyzed transformations, such as halogen-lithium exchange and Pd- or Cu-mediated coupling reactions, and were characterized using various spectroscopic and electrochemical techniques. The influence of their optical and redox properties on the efficiency of solar energy conversion devices will be discussed, together with the role of charge transfer processes taking place between them and other device components (such as inorganic semiconductors, electrolytes, sacrificial electron donors).

Figure 1. Examples of conjugated organic compounds employed in devices for solar energy exploitation.

Publishing your research in high impact journals

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As Editor of *Dalton Transactions*, the Royal Society of Chemistry’s flagship inorganic chemistry journal, I will present an overview on how to get your research published in high impact journals. I will also offer my personal hints and tips as an editor to guide you through the publication process and to be a successful published author. I will highlight the importance of publication ethics and the open access initiatives at the Royal Society of Chemistry.
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 optoelectronics, 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).

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$_3$COO)$_2$Cl$_2$] to the corresponding platinum(II) [Pt(NH$_3$)$_2$(CH$_3$COO)$_2$] 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$_3$COO)$_2$Cl$_2$] 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$_3$COO)$_2$Cl$_2$] complex occurs through a stepwise mechanism via a metastable hexacoordinated platinum(III) [Pt$^{III}$(NH$_3$)$_2$(CH$_3$COO)$_2$Cl] 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$_3$COO)Cl$_2$] species occurs through a barrierless concerted process to the final [Pt$^{II}$(NH$_3$)$_2$(CH$_3$COO)$_2$] 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.

Comunicazioni Orali
New methods and new catalysts for the oxygen reduction reaction at the cathode of fuel cells: surface science applied to CoO\textsubscript{x}/Pd(100) ultrathin films

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A great deal of efforts is currently taken for the development of innovative electroactive materials. A little travelled road envisages the use of ultrathin metal oxide films supported on metal substrate. As a matter of fact, these hybrid systems exhibit unprecedented structural and chemical properties and a wide gamut of special phenomena such as interfacial electronic hybridization and easy electron tunneling that can be exploited for a rational design of highly active catalysts. However, the subtle physics and chemistry ruling these systems require a sophisticated methodological approach for their study. With this aim, a rather unique home-lab set-up (see Fig.1), which allows combining X-ray photoelectron spectroscopy (XPS) and electrochemical measurements, has been used. We have prepared highly controlled CoO\textsubscript{x}/Pd(100) model systems in UHV conditions (1), with atomic scale precision in order to study the activity of different prototypical cobalt oxide nanostructures (CoO and Co\textsubscript{3}O\textsubscript{4} from nm to bulk dimension) and the influence of the Pd substrate on their chemical properties. Composition/structure/activity relationships have been established through a systematic study of their electrochemical behavior and the chemical/structural changes induced under working conditions. The combination of cobalt oxide with palladium allowed to obtain a very active material, with comparable activity with respect to pure palladium, but maintaining a higher poisoning tolerance due to the presence of the oxide. Moreover, thanks to the exploitation of an in situ technique we were able to identify the real active phase involved in ORR conditions. Such study demonstrates how the use of ultrathin hybrid films and in situ techniques can pave the way toward the development and comprehension of radically new electroc materials.

Figure 1: Experimental set-up for the in situ combined XPS and electrochemical measurements (left); LSV in O\textsubscript{2}-saturated 0.1M KOH and number of transferred electrons for the CoO\textsubscript{x}/Pd(100) systems studied (middle); and Co 2p\textsubscript{1/2} region for the CoO and Co\textsubscript{3}O\textsubscript{4} systems at different potentials in O\textsubscript{2}-saturated 0.1M KOH.

References:
Control of enzymatic activity in a Mn-containing synthetic metalloenzyme

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Over the last decades, the search for cost-effective, highly efficient and chemically stable catalysts has inspired the development of synthetic metalloproteins. The aim is to reproduce the catalytic activity of natural enzymes while displaying a higher chemical stability (1). In this area, our interest is currently focused on the development of a new class of protein models, named Mimochromes (Figure 1). Mimochromes are composed of a deuteroporphyrin core, which is covalently linked to two peptide chains with a well-defined helical conformation, covering both planes of the heme and resulting in a helix-heme-helix sandwich structure. These enzymes are promising catalysts, exhibiting in many cases efficient peroxidase-like activity (2).

To further expand the repertoire of artificial metalloenzymes with catalytic potential, we have herein studied the properties of the last-generation Mimochrome VI\textsubscript{a}, bearing Mn(III) as the metal ion. This was driven by the expected higher versatility of Mn-containing catalysts compared to the corresponding Fe(III) congeners, due to the higher number of accessible oxidation states (3).

Figure 1. Fe- and Mn-containing protein models (Mimochromes).

Spectroscopic studies of the synthetic enzyme have enabled to detect a peculiar catalytic behavior, due to its ability to selectively work as a peroxidase (using an organic substrate as reducing agent) or as a catalase/dismutase (using the oxidizing agent as substrate). Interestingly, the control of the enzymatic activity is achieved by suitably varying the pH conditions. The analysis of the catalytic properties of the enzyme in model oxidation reactions has also been performed. In both cases, notable results have been obtained concerning both the conversion of the substrates and the selectivity of the transformations.

References:

Effect of N-doping in the activity of TiO\(_2\) supported catalysts in glycerol oxidation

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Glycerol constitutes an important renewable feedstock and its valorization greatly contributes to the economy of some processes mainly in the field of biofuels. Glycerol oxidation can produce a large amount of useful products and this research focuses on the effect of N-doping of the support (TiO\(_2\)) on the catalytic activity of AuPt catalysts in the selective glycerol oxidation for skipping the use of an external base. In fact, Au based catalysts have been shown to be active and selective in glycerol oxidation but it presents the drawback to be active only in the presence of an external base. It has been recently demonstrated that the addition of Pt allows the reaction to proceed under neutral conditions (1, 2) even the influence of the support is fundamental. In this work, we prepared N-doped TiO\(_2\) via facile sol-gel method using different N-doping precursors during the synthesis [4-fluorobenzylamin (TNF), urea (TN) and chitosan (TNC)]. These materials were used for supporting preformed bimetallic AuPt nanoparticles. This preparation method allowed obtaining nanoparticles with comparable size and dispersion thus allowing studying the real influence of the support modification in the catalytic reaction.

All the catalysts appeared active in the selective oxidation of glycerol (Table 1) showing conversions in the range 53-92% after six hours of reaction with high selectivity to glyceric acid (74\% -79\%). Comparing the results using N-doped versus bare TiO\(_2\) (entry 1, Table 1) we can conclude that the introduction of N-groups have a beneficial effect on the catalyst performance. Surprisingly, the most active catalyst is the one synthetized with chitosan, which presents the lowest N content. Most probably this results is correlated with the higher surface area observed in TiO\(_2\) after the addition of chitosan.

Table 1. Glycerol oxidation in the presence of 1\%wt AuPt/N-TiO\(_2\)

<table>
<thead>
<tr>
<th>AuPt/TiO(_2) +modifier</th>
<th>%at N ([\text{XPS}])</th>
<th>%wt N ([\text{bulk}])</th>
<th>Conv. (%)</th>
<th>Selectivity (%)</th>
<th>Mass balance (%)</th>
</tr>
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<tr>
<td>-</td>
<td>-</td>
<td>-</td>
<td>67.6</td>
<td>2.5</td>
<td>75.2</td>
</tr>
<tr>
<td>TN</td>
<td>0.6</td>
<td>46.5</td>
<td>78.4</td>
<td>2.3</td>
<td>77.7</td>
</tr>
<tr>
<td>TNF</td>
<td>0.6</td>
<td>11.2</td>
<td>73.4</td>
<td>2.4</td>
<td>74.9</td>
</tr>
<tr>
<td>TNC</td>
<td>0.0</td>
<td>8.7</td>
<td>92.1</td>
<td>2.6</td>
<td>79.9</td>
</tr>
</tbody>
</table>

Metal/Glycerol = 1/500; Glycerol = 0.3M; T\(^{\circ}\) = 100\(^{\circ}\)C; O\(_2\) = 3atm; time = 6h

References:
Long Period Stacking Ordered phases in the Y-Ni-Mg system: experimental and structural studies

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Long Period Stacking Ordered (LPSO) phases form a continuously growing family of compounds, whose peculiar structures are related to exceptional mechanical properties, such as high strength coupled with high ductility (1, 2). So far, LPSO phases were exclusively found in R-T-Mg (R = rare earth metal; T = transition element) systems and they are characterized by a magnesium content higher than 50 at.%; in fact, their crystal structures can be qualitatively described as composed of hcp Mg blocks of different thicknesses alternated with R_xT_yMg_z slabs. Nevertheless, an accurate description of these phases is challenging, and complete structural models are rarely proposed. This is due both to their intrinsic structural complexity and to experimental problems related also to their mechanical properties (e.g. intricate microstructures, difficulties in single crystal selection and fine powder preparation).

In the framework of our studies on the constitutional properties of the Y-Ni-Mg system, numerous LPSO phases were detected, densely distributed along the 4:3 (Y:Ni) compositional line, the major part of which were not previously reported/described.

In this work, results on our studies on these compounds are presented, targeting different goals:
- Achievement of samples with more easily interpretable microstructures, in order to better distinguish between different, compositionally closed, LPSO phases and successively submit them to further analyses, such as transmission electron microscopy (TEM). For this purpose, diffusion couple experiments were designed and realized. Magnesium and Y-Ni binary alloys were chosen as end-members of the tested couples, which were successful to obtain well resolved layers of LPSO compounds (see figure).
- Generation of different structural models, to complement TEM-characterization results in order to fully describe the studied phases. For this purpose, an automated procedure is proposed, based on a joint application of the graph and group theories.

General cooperative effects of single atom ligands on the $^{73}$Ge, $^{119}$Sn and $^{207}$Pb NMR signals of tetrahedral $[MX_4]$ ($M = Ge, Sn, Pb; X_4 =$ combination of Cl, Br, I) coordination compounds

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The relation between atomic substituents, bonded to a central element, and the NMR chemical shift variations, observed on a central atom, is strongly debated. (1) We found that the $^{73}$Ge, $^{119}$Sn and $^{207}$Pb NMR chemical shifts, and the halido ligands ionic radii overall sum, $\Sigma(r_h)$, are related by straight linear correlations in the tetrahedral $[MX_4]$ ($M = Ge, Sn, Pb; X_4 =$ combination of four Cl, Br, I) coordination compounds. This finding is well consistent with analogue linear relations, previously reported for series of octahedral, pentacoordinate, and square-planar Pt(II) and Pt(IV) complexes, see Figure. (2-4) Therefore, the analyzed $^{73}$Ge, $^{119}$Sn, and $^{207}$Pb spectroscopic NMR data, confirm that even in $[MX_4]$ tetrahedral complexes, the coordinated halido ligands could act on the central metal as shielding conducting rings. (5) Notwithstanding such general straight linear dependences found in the halide complexes of heavy metals $\{[MX_4], [PtX_4]^{2-} \text{ and } [PtX_6]^{2-} \}$ ($X_6 =$ combination of six F, Cl, Br and I), Ge(IV), Sn(IV), Pb(IV), Pt(II) and Pt(IV) heavy metal complexes) (1-5), as those here analyzed, many other halido derivatives seem to follow partially different behaviors. This suggests that the interactions defining the relations between the experimental NMR chemical shift of a central atom and the $\Sigma(r_h)$, need to be better understood. For this reason, a further work is in progress in order to clarify the factors, which are determining such altered correlations between experimental NMR chemical shifts of central atoms and the ionic radii overall sum of bonded halides, sometimes observed in $[MX_n]$ derivatives.

CO₂ capture by aqueous Na₂CO₃ combined with the formation of high quality CaCO₃ and the release of pure CO₂ at room conditions

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The reduction of anthropogenic CO₂ emissions is an urgent challenge, and strategies must be adopted to improve the efficiency of CO₂ capture and to reduce the costs of this technique. As an alternative to traditional processes, in our laboratory has been developed a new concept of CO₂ capture technology which combines the CO₂ abatement with the production of commercially valuable products (1,2,3). This unconventional approach has the potential of circumventing the main drawbacks of the traditional processes of CO₂ capture (the energy penalties of absorbent regeneration, CO₂ compression and its disposal underground) by virtue of the formation of valuable commercial products.

Now we present the results of an alternative procedure of CO₂ capture by dilute aqueous solutions of Na₂CO₃ combined with the formation of high quality CaCO₃ and the release of pure CO₂ at room temperature and pressure.

CaCO₃ has an important market, estimated 74 million tonnes in 2011, and it is used in a wide range of applications in rubbers, paints, coatings, in cement industry and as a filler in the manufacture of paper and plastics.

The proposed process can be divided into two parts: i) the efficient CO₂ capture from a gas mixture by using the worldwide naturally available and cheap Na₂CO₃; ii) the production of CaCO₃ and the release of CO₂ at room temperature and pressure by reacting the CO₂ loaded solution with aqueous CaCl₂, an inexpensive by-product of the Solvay process and of potassium chlorate manufacture.

A continuous ¹³C NMR spectroscopic investigation has enabled us to identify and quantify the species occurring in every step of the CO₂ capture process. The accurate study of the composition of CO₂ loaded solutions is crucial for the development of the more performing solutions in term of high efficiency of CO₂ capture and high degree of conversion into calcium carbonate.

Long-lived luminescent Quantum Dots as result of Reversible Electronic Energy Transfer

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Electronic energy transfer is normally considered a unidirectional process from the donor to a suitable acceptor. However, if the excited states involved in such a process are sufficiently energetically close one to another, then the forward energy transfer can be followed by the back transfer from the acceptor to the donor, giving rise to the reversible electronic energy transfer (REET), and consequently establishing an equilibration between states. This process has been generalised in a range of molecule-based bichromophore systems, including molecular dyads (1) and non-covalent assemblies(2,3). However, to the best of our knowledge there is no example reported in literature concerning REET occurring in Quantum Dot (QD)-based (nano)systems. The QDs have the enormous advantage that their emitting state can be tuned by manipulating their size, thus providing a significant accuracy in projecting and developing of REET-based systems. Here we reported the first evidence of REET involving QDs and suitable chromophoric ligands attached to their surface. In our system the emitting state of a QD undergoes an equilibration with the long-lived triplet states of the chromophoric unit, thus resulting in the elongation of the lifetime of the QD by several orders of magnitude. Strong experimental evidence of such a process have been observed. Moreover, the effect of the oxygen, as well as of the size of the QDs have been also investigated.

References:
Grafene Functionalization and Tuning of Transport Properties by Plasma Strategies

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The outstanding physical properties of graphene (ambipolar field effects, high room temperature mobility, optical transparency, etc) make this material promising for a number of applications in several fields (electronics, photonics, photovoltaics, etc.). Indeed, electrical, optical and chemical properties of graphene, which range from doping type, and surface wettability up to optical gap opening and modulation, should be carefully controlled and designed to satisfy specific requirements for practical device applications. To this aim, several theoretical and experimental works have investigated the chemical modifications of graphene as a mean for tuning the intrinsic material properties or for the introduction of new ones: opening of a band gap; improving wettability toward other materials of technological interest, providing selective interactions with analytes, etc.. Since graphene is characterized by a high chemical inertness, its functionalization typically involves the exploitation of free radicals addition reactions. Several strategies have been investigated for providing the generation of radical species in a controlled way including thermal, photochemical, and plasma processes. In particular, plasma chemistry offers a high potential in terms of process scalability but it often resulted in a low control of the functionalization processes as well as in the structural damaging of the materials.

In this contribution, we present mild modulated plasma processes for tailoring transport properties of large area chemical vapor deposition (CVD) graphene by functionalization with hydrogen (1), fluorine (2, 3) and oxygen species (4). The functionalization processes have been developed and optimized with the twofold aim: the fine control of graphene functionalization kinetics while minimizing the induced structural damage. This, together with the real time monitoring of graphene optical properties by spectroscopic ellipsometry, allows for an unprecedented control over the degree of functionalization.

The suitability of our functionalized graphene with engineered transport properties for applications in optics, optoelectronics and photovoltaics is experimentally demonstrated.

References:

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Drug delivery systems: hydrophilic gold nanoparticles for controlled drug loading and release

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Drug delivery systems based on gold nanoparticles (AuNPs) are being widely applied, due to their unique chemical and physical properties, biocompatibility, and well-established strategies for surface modification.\textsuperscript{(1-4)} In this framework we report studies about drug delivery systems based on gold nanoparticles stabilized by sodium 3-mercaptop-1-propane sulfonate (Au-3MPS NPs) used as carrier for different drugs: the dexamethasone, DXM and copper complexes, Cu(I)R, based drugs. The drug loading and release were optimized for each delivery system and the bioconjugates were characterized by means of several technique, (Uv-visible, FTIR, XPS, DLS, FESEM, AFM). After optimization studies the best loading for Au-3MPS NPs @DXM have efficiency 80\% , for Au-3MPS NPs @Cu(PTA)\textsubscript{4} have efficiency 78\%. Studies regarding the release were performed in the range 1-14 days, showing at the end a drug release around 85\% for each systems. The stability (see Fig.1) and citotoxicity studies on AuNPs confirm the biocompatibility of the drug delivery systems and open new exciting perspectives in the field in vitro and in vivo studies.\textsuperscript{(5,6)}

Fig.1. DLS data: \textless 2R_{H}\textgreater show the stability of Au-3MPS NPs in different media (H\textsubscript{2}O, HEPES, RPMI, complete RPMI, FBS, HS) and at different temperatures (25°C ■; 37°C ○).

Novel strained ruthenium complexes in photodynamic therapy

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Photodynamic therapy (PDT) is a field of growing interest in chemistry, which can be successfully employed in medicine for the treatment of a wide variety of skin diseases, bacterial infections and cancers. (1,2) It consists in the use of specific molecules (photosensitizer agents PS) which can be triggered by low energy light, leading to the production of active cytotoxic species (as reactive oxygen species ROS), which are in turn, able to bring serious damages to the biological environment, as DNA of cancer cells. (3) One of the main advantages of the PDT consists in the possibility to achieve a temporal and spatial control of the drug-activation, ensuring a discrimination between malignant and surrounding healthy tissues, and allowing to obtain a strong reduction of the dose-limiting side effects, commonly incurred with standard chemotherapies.

Many ruthenium polypyridyl complexes have been exploited in the PDT field since they have tunable absorption properties and induce 1O2-mediated DNA photocleavage when exposed to visible light. However, in the case of hypoxic tumors, the reliance on molecular oxygen might preclude their application. For this reason it has been recently studied a new class of ruthenium polypyridyl complexes, characterized by the presence of a distortion feature in their octahedral geometry. The enhanced strain lowers the triplet metal-centered state (3MC), allowing for thermal population from the triplet metal to ligand charge transfer state (3MLCT), bringing to the loss of one or more ligands. (4) The resulting active species are then capable of forming covalent adducts with DNA, more difficult to repair respect on single strand breaks caused by 1O2.

In this context we present a series of novel ruthenium (II) polypyridyl complexes (figure), containing 1,10-phenanthroline (phen) (L1) or 2,9-dimethyl-1,10-phenanthroline (dmphen) (L2) or 2,2’ biquinoline (biq) (L3) as ligands, and featuring the macrocycle 4,4’-(2,5,8,11,14-pentaaza[15])-2,2’-bipyridilophane (L’). From our studies emerges that these complexes are able both to produce oxygen singlet (L1) or release a ligand unit (L2, L3) upon photo-activation. In particular, L2 and L3 exhibit fast kinetics of the ligand photo-ejection processes, even by employing radiations within the therapeutic window. Furthermore, the introduction of the polyamine macrocycle L’, able to strongly bind copper ion in physiological media, (5) makes possible to add the injury due to the Fenton reaction in the presence of a co-reactant (H2O2) to the damage provoked through photo-activation of such systems. These types of damage were evaluated towards pUC-19 plasmid by means of gel electrophoresis analysis. Finally, investigations on the cytotoxic abilities of such potential drugs were performed towards selected cell lines.

References:
Fluorescent solvatochromic molecules as probes for lipid bilayers

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In recent years, the study of cell membranes has been the subject of a great interest in biological research. Lipid bilayers are made up of numerous phospholipids, which, according to their structure, charge, and interaction with membrane proteins and cytoskeletal proteins, spontaneously organize in aggregates having different fluidity (e.g. liquid ordered, L\textsubscript{o} and liquid disordered, L\textsubscript{d}). Among the techniques for membrane characterization, fluorescence microscopy is the most common used and one of the less invasive for the cell (1). The red edge excitation shift (REES) of a fluorophore depends on the slow solvent reorientation around a fluorophore in the excited state. REES can be used to monitor the environment and dynamics around it in an organized molecular assembly (2,3). Different fluorescent probes, with a different charge, polarity, and magnitude, have been developed containing lipid chains of various lengths (4). In spite of the large number of available probes, it often remains the problem of membrane perturbation, which the probe itself causes when inserted.

The aim of this work is the design and the synthesis of new fluorescent solvatochromic probes containing a fluorophore and characterized by an inverted phospholipid structure, able to interact with the heads of the phospholipids of a membrane and not fully internalized in the lipid bilayer (Fig. 1).

Figure 1 – chemical structure of some of the synthesized probes

In particular, NBD group possesses some of the most desirable solvatochromic properties to serve as an excellent probe for both spectroscopic and microscopic applications, since fluorescence lifetime of the NBD group exhibits sensitivity to environmental polarity (5). The fluorescence behavior of these probes has been characterized both in organic solvents and in model membranes. Computational methods have been used to evaluate the metal binding and the interaction of probes with model membranes.

References:
Platinum(II) complexes of ligands containing OH functional groups: synthesis, reactivity and antiproliferative properties

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Following the discovery of the anticancer properties of cisplatin(1), hundreds of new platinum(II) complexes are prepared and tested every year. Although different mechanisms of action can be involved, it is generally accepted that the main target of these bioactive molecules is DNA. The platination of DNA generally involves the coordination of purine bases to activated, hydrolyzed forms of the metal complexes and can be greatly helped by additional interactions such as hydrogen bonding. As a matter of fact, good results have been described for some platinum complexes characterized by the presence of OH groups on coordinated ligands(2). Indeed, among the non-conventional, \textit{trans} triphenylphosphino complexes [PtCl\(_2\)(PPh\(_3\))(R\(_2\)NH)] recently prepared by us(3), promising \textit{in vitro} data were observed for R = CH\(_2\)CH\(_2\)OH(3e).

In this contribution we report:

\textit{i)} the preparation and the characterization of Pt(II) complexes containing, besides PPh\(_3\), a monodentate and/or bidentate arylaldoxime ligand (complexes a and b, respectively) and

\textit{ii)} the synthesis of pyridinimino (c) and pyridinamino (d) complexes, bearing a terminal hydroxyl group.

Complexes a and b are reactive under basic conditions, due to the enhanced acidity of OH oxime group upon complexation to the metal, allowing the preparation of some rare dinuclear derivatives as well as the functionalization of OH oxime group. Complexes b were tested in \textit{in vitro} against some human cancer cell lines and preliminary data show an interesting antiproliferative activity (IC\(_{50}\) \textasciitilde 1-10 \textmu M).

Complexes c and d show enhanced affinity towards water and are good candidates as antiproliferative agents. Moreover, their further functionalization is possible, exploiting the known reactivity of hydroxyl group.

References:

Killing bacteria via ion-complexing polymeric materials

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New copolymers containing either MMA and 18C6 crown ether pedants, or PEG, MMA, and 18C6 crown ether pedants were synthesized via uncontrolled radical polymerization or ATRP to test the idea that sequestering structural alkali-earth ions from bacterial Outer Membrane (OM) may lead to bacterial death. ATRP allowed to produce Y-like architecture to investigate structural effects already evidenced for copolymers containing DMAEMA rather than 18C6 pedants (1,2). It was found that copolymer plaques were able to complex Mg(II)/Ca(II) ions and also showed antimicrobial activity when placed in pure water \textit{E. coli} suspensions, albeit with different efficiencies (Figure 1).

![Figure 1](image)

**Figure 1.** \textit{E. coli} % survival vs time for 18C6-containing polymers. A(BC)\textsubscript{2} is a copolymer containing DMAEMA instead of 18C6, and linear mPEG-b-PMMA copolymer is used as the control.

Different plaque porosities and surface morphology, as evidenced by both TGA-determined water adsorption and direct visualization with FE-SEM, were considered as responsible for the differences in antimicrobial efficiency.

The role of the 18C6 was elucidated by pre-saturating plaques with Mg/Ca ions obtaining a marked reduction in antimicrobial efficiency in the first 5 h of contact with bacteria. The latter finding indicated that the plaque complexation ability is a key ingredient in bacterial killing at short contact time (< 5h). At longer times, the mode of action is instead related to the polycationic nature acquired by the plaque due to ions sequestering.(3)

References:
Novel gold(I) and silver(I) metal complexes as promising antibacterial candidates

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Several metals and metal-based compounds have been used for centuries as anti-infective agents on a simple empirical basis, with some appreciable result. For instance, the complex dicyanoaurate(I) was proposed and used by Koch as an antitubercular agent in the pioneering times of modern pharmacology, while several bismuth, antimony and mercury compounds have been extensively employed to fight various bacterial and parasitic diseases.(1-4) Yet, more recently, due to the advent of the golden era of antibiotics and to grounded concerns on their conspicuous systemic toxicity, metal-based agents were gradually abandoned. However, during the last two decades, the so called “antibiotic resistance crisis”, arising from the emergence of bacterial strains with multidrug-resistant (MDR) and extensively drug-resistant (XDR) phenotypes, and from the simultaneous decline in the discovery rate of new and effective antibiotic molecules, has posed the dramatic problem of finding out new substances capable of fighting life-threatening infections caused by these pathogens.(5,6) Metal-based compounds were thus reconsidered as a rich source of antimicrobial agents often endowed with innovative modes of action. In this context auranofin (AF), an antiarthritic agent still sporadically used to treat some severe forms of rheumatoid arthritis, has been extensively revisited within new drug repurposing strategies with promising results. Indeed, remarkable antimicrobial and antiparasitic properties were disclosed for this oral gold(I) drug, that has become the reference compound even for the development and the studies of novel gold-based antibacterial agents or specific inhibitors of important enzymes.(6,7) Yet, the precise mechanisms of the antimicrobial action of AF and the respective biomolecular targets are not known. The promising antibacterial properties detected for AF prompted us to expand this kind of investigations even further, working not only with AF but also with a series of silver(I) and gold(I) analogues with general structure Et\textsubscript{3}PMX that were recently prepared in our laboratory. Comparative analysis of the results allowed us to define some remarkable structure activity relationships in this series of linear metal complexes as detailed below:

1. The thiosugar ligand is not essential for the antimicrobial activity of AF.
2. The nature of the X group in the Et\textsubscript{3}PAuX series is not relevant for the activity.
3. Altogether, the above results point to the [AuPEt\textsubscript{3}]\textsuperscript{+} moiety as the true pharmacophore in this series of metal complexes; their antimicrobial activity probably arises from gold coordination to appropriate targets upon ligand exchange.
4. Unexpectedly, replacement of gold with silver causes a net reduction in activity. Thus the presence of the gold(I) center is a major determinant of the antimicrobial properties.

Overall, we have shown here that selective modifications of the Auranofin scaffold may be conveniently exploited to modulate the antimicrobial profiles; important insight is gained into structure-activity relationships inherent to this class of metal compounds. The comparative analysis of the respective antimicrobial profiles is a valid tool to select the “best performers” to be further evaluated as innovative and more efficient antimicrobial metal-based drugs. Hints are obtained to design better metal based antimicrobial agents.

The inorganic side of neurotrophins: metal coordination and new therapeutic perspectives

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Neurotrophins (NTs) are secreted proteins essential for development, maintenance and survival of central and peripheral nervous systems. The main NTs are the nerve growth factor (NGF) and the brain derived neurotrophic factor (BDNF), which play an essential role in neuroplasticity, memory, learning in the adult nervous system and their impairment may be involved in several degenerative disorders, including Alzheimer’s Disease (AD). According to the metal hypothesis some d-block metal ions play a crucial role in AD, and neurotrophins perform their activity in the same brain areas affected by metal dyshomeostasis in pathological conditions. Thus, it is conceivable that transition metal ions could play selective physiological/pathological roles by modulating NTs activity. High concentrations of Zn\textsuperscript{2+} and Cu\textsuperscript{2+} have been shown to modulate the \textit{in vitro} effects of NGF and BDNF. Taking into account the essential role played by NTs in the presence of metal ions, they have been considered for the treatment of neurodegenerative diseases, to induce spinal cord repair and neurogenesis. A promising strategy to overcome current limits in their effective therapeutic application (such as poor plasma stability, side effects due to concomitant binding to multiple receptor, pain, poor penetration in the blood brain barrier (BBB) involves the use of peptides retaining the most essential elements of neurotrophic action. The N-terminal region of NGF and BDNF as well as of other NTs is critical for the binding selectivity and activation of their specific Trk receptors.

We studied the Cu\textsuperscript{2+} and Zn\textsuperscript{2+} complexes with neurotrophins’ N-terminal domain by means of potentiometric and spectroscopic (UV/Vis, CD, NMR and EPR) techniques and DFT calculations. The coordination features of single point mutated peptides were also characterized to better define the metal coordination environment and the involvement of the N-terminal amino group in metal binding. Metal binding to these peptides modulate their proliferative activity similar to that observed with the whole protein. The peptide NGF(1-14) partly exerts an effective and specific NGF-like action on some crucial NGF intracellular targets such as cAMP-response element binding protein (CREB), able to induce dendritic spine growth, morphology change, synaptic plasticity, and long-term memory.\textsuperscript{(1)} Finally, live cell imaging experiments of PC12 treatment with fluorescent labelled peptide NGF(1-14)FAM, show that the peptide is able to pass cellular membrane and acts as a ionophore, increasing the intracellular amount of copper.

Homogenous and Heterogeneous Transition Metal Catalysts for CO$_2$ Reduction

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The catalytic conversion of the extremely stable CO$_2$ molecule to usable fuels or chemical products is a critical goal that would positively impact the global environment, hopefully helping in overcoming some of the problems of energy crisis. (1) Valuable products, such as carbon monoxide, formic acid and high molecular-weight polymers, obtained from the electrochemical conversion of CO$_2$, have been indicated as chemicals that can store intermittent energy source like the solar light, thus balancing power supply, energy demand and environmental concerns of greenhouse gas emissions. A possible approach to reduce the large overpotentials required for this multi-electron process is the use of organometal molecular compounds, able to catalyze CO$_2$ reduction through proton-assisted processes. (2,3) In this presentation an overview of our recent advances in the use of organometallic complexes as catalysts for electrochemical CO$_2$ reduction will be illustrated. Enhanced catalytic activity and clear mechanistic pathway will be discussed. Analogies and differences among several transition metal complexes will be outlined, including the better known mechanism based on Re(bpy) complexes, the effect of local proton sources on the Mn(bpy) complexes [4] as well as some outline on the use of earth-abundant transition metal complexes (Mo and W) [5] employed as redox catalysts for CO$_2$ electrochemical reduction.

Relatively few studies were focused on the heterogeneous electrochemical catalysis despite the large number of potential advantages such as easier recovery of products and catalysts, small amounts of catalyst necessary for efficient electrolysis, deactivation pathways often hindered or suppressed and elimination of solubility problems. Furthermore, in a heterogeneous system the electron transfer will be more efficient to the attached or bonded catalyst compared with that in solution, lowering the limitation of the electron transfer in the catalytic cycle. Transition metal complexes immobilized on electrode surfaces can represent promising catalysts to be utilized in a large-scale process for CO$_2$ reduction, particularly if non-precious metals like cobalt, iron, nickel, copper, and zinc are involved. We very recently exploited the electropolymerization properties of Re(bpy) complexes containing the thiophene moiety that have the advantage to produce an electron-conducting film, with interesting results. (6,7)

A new series of Ag and Au carbene complexes with interesting anticancer properties

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Elemental silver and its salts have long been known for their antimicrobial properties, predominantly against chronic ulcers, extensive burns and wounds.\textsuperscript{(1)} Gold and its complexes like aurothiomalate, aurothiosulfate or auranofin were recognized to be effective drugs for the treatment of rheumatoid arthritis. The research on potential utilization in medicinal chemistry of new complexes of both metals has experienced a renaissance over the last decades.\textsuperscript{(2)} Silver (I) and gold (I) N-heterocyclic carbene (NHC) complexes have emerged as a new generation of potential anticancer agents due to their high cytotoxicity and stability. Metal N-heterocyclic carbene complexes readily fit the requirements for an efficient drug design and fast optimization.\textsuperscript{(3)}

Recently, we have reported the synthesis and the anticancer properties of three new silver and three new gold NHCs complexes, having a methyl group and an alkyl ß-hydroxy derivative as N,N’-substituents (Fig. 1). The most active antitumor compounds were holding a lipophilic structure and they did not affect the proliferation of nontumorigenic epithelial breast cells.\textsuperscript{(4)}

In the literature, 4,5-dichloro-1H-imidazole complexes (5,6) are promising molecules with antibacterial and anti-tumor activity.

Thus, we have synthesized and tested anticancer activity of two carbene complexes of silver and gold, derived from 4,5-dichloro-1H-imidazole having a methyl group and an alkyl ß-hydroxy derivative as N,N’-substituents and in order to increase the lipophilicity of these compounds, we have synthesized also the complexes having in the position 4,5 of the imidazole ring two phenyl groups (Fig. 2). The complexes were characterized by NMR and mass-spectroscopy and by elemental analysis. The biologic action of these complexes was tested in vitro against two cancer cell lines MCF-7 and Hela, showing an interesting antiproliferative activity.

Fig. 1 Silver and gold NHCs complexes

Fig. 2 New silver and gold NHCs complexes

NMR studies on copper transport proteins interacting with silver nanoparticles

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Despite the widespread use of silver nanoparticles, little is known about the potential risks arising from the silver nanoparticles (AgNPs) themselves and from the silver ions released from them. Since Ag(I) or Cu(I) have similar coordination properties, an impact on copper metabolism is expected. Cells utilize several pathways to ensure uptake, storage and export of copper. In humans, the Cu chaperone Atox1 delivers Cu(I) to the metal-binding domains (MBDs) of two P1B-type ATPases: the Menkes (Atp7a) and Wilson (Atp7b) disease proteins.\cite{1,2} Both Atox1 and the first MBD of Menkes (Mnk1) bind one Cu(I) through two Cys residues located in a conserved CXXC motif.\cite{3} Thus, the aim of our work has been to gain direct evidence by NMR of the interaction of Atox1 and Mnk1 with Ag(I) or AgNPs. Although the two proteins have quite similar structure, their behaviors is substantially different. AgNPs are also characterized by a remarkable antibacterial effect, thus monitoring the interactions of AgNPs with bacterial cells can be crucial for elucidating the origin of the bactericidal activity and for expanding their biomedical and environmental applications. Therefore, we have investigated the Ag metabolism in gram-negative bacteria, by a forefront technique called in-cell NMR.\cite{4} E. coli cells overexpressing Atox1 were treated with Ag salts. In-cell NMR revealed that, within treated cells, Atox1 undergoes only minor changes. In contrast, after the lysis of the cells, the protein appears to be bound to the metal. From these data, it can be inferred that the scarce reactivity of Atox1 with Ag(I) inside the cell can be due to compartmentalization (e.g. in the periplasm) and/or sequestration of the metal ion. Further studies are ongoing to trace the fate of Ag(I) ions within E. coli cells and to unravel the mechanisms used by gram-negative bacteria to become resistant to xenobiotics. This latter is a particularly hot issue, especially after the recent discovery of an E. coli strain resistant to the last-resort antibiotic Colistin.\cite{5}

Acknowledgment

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New Differently Sized Neutral and Octacationic Porphyrazines. Physicochemical Properties and Potentialities as Anticancer Drugs.

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As part of our recent studies on porphyrazine compounds, UV-visible solution studies in DMF proved that a progressive extension of the central tetrapyrrolic $\pi$-electron delocalized system for the triad of externally octapyridinated Mg\textsuperscript{II} porphyrazine complexes [Py\textsubscript{8}PzMg(H\textsubscript{2}O)], [Py\textsubscript{8}TPyzPzMg(H\textsubscript{2}O)], and [Py\textsubscript{8}QxPzMg(H\textsubscript{2}O)] (Scheme 1; M = Mg\textsuperscript{II}(H\textsubscript{2}O)), sensibly moves the Q-band maximum toward the red; the observed spectral changes were adequately interpreted by DFT/TDDFT calculations (1).

The spectroscopic and electrochemical properties of the newly synthesized smaller macrocycles, i.e. the unmetalated species [Py\textsubscript{8}PzH\textsubscript{2}] and the metal derivatives [Py\textsubscript{8}PzM] with M = Co\textsuperscript{II}, Cu\textsuperscript{II}, Zn\textsuperscript{II}, and Mg\textsuperscript{II} included, were also examined and the data compared with those of the related more expanded macrocycles [Py\textsubscript{8}TPyzPzM] (Scheme 1B) and [Py\textsubscript{8}QxPzM] (Scheme 1C). The photosensitizer activity for the generation of singlet oxygen, $^1$O\textsubscript{2}, was explored for the neutral species [Py\textsubscript{8}PzM] (M = Mg\textsuperscript{II}(H\textsubscript{2}O), Zn\textsuperscript{II}) in DMF, with found $\Phi_\Delta$ values 0.42 and 0.64, respectively (2).

The related water soluble octacations [(2-Mepy)\textsubscript{8}PzM]\textsuperscript{8+} (M = Mg\textsuperscript{II}(H\textsubscript{2}O), Zn\textsuperscript{II}), carrying externally N-methylated 2-pyridyl rings, isolated as iodide salts, are present in H\textsubscript{2}O/SDS solution exclusively in their monomeric form. Both species exhibit $\Phi_\Delta$ values 2.3-2.5 higher than the value measured for the standard PcAlS\textsubscript{mix}, a very promising response in view of their potential application as anticancer drugs in photodynamic therapy (PDT). Studies on the differently sized Zn\textsuperscript{II} octacations [(2-Mepy)\textsubscript{8}PzZn]\textsuperscript{8+}, [(2-Mepy)\textsubscript{8}TPyzPzZn]\textsuperscript{8+} and [(2-Mepy)\textsubscript{8}QxPzZn]\textsuperscript{8+} as to their possible interaction with a G-quadruplex structure and ds DNA are in due course (3).

Auranofin, Et₃PAuCl and Et₃PAuI exert high in vitro cytotoxic effects toward colorectal cancer cell lines: a comparative chemical, biological and mechanistic study

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Auranofin [2,3,4,6-tetra-o-acetyl-L-thio-β-D-glyco-pyranosyl-sato-S-(triethyl-phosphine)-gold(I)] (AF) is a clinically established oral chrysotherapeutic agent that is used for the treatment of some severe forms of rheumatoid arthritis (1). During the last few years, this drug, has attracted renewed attention in the medicinal chemistry scientific community as a prospective anticancer and antimicrobial agent according to innovative drug repurposing strategies (2-4). In particular, AF has been, or still is, the object of clinical trials in the US as an anticancer agent (5,6). We thought that selective and limited chemical modifications of AF might lead to a modulation and hopefully an improvement of its pharmacological profile. The solution behavior of Et₃PAuI, Et₃PAuCl and Auranofin, as well as their interactions with a hen egg white lysozyme and a standard single strand oligonucleotide, were comparatively analyzed through NMR spectroscopy and ESI-MS. Binding ability of the three complexes toward ds-DNA was also assessed by ethidium bromide displacement and viscometric tests. The cytotoxic effects toward two representative colorectal cancer cell lines were found to be strong and similar in the three cases and a good correlation could be established between the cytotoxicity and the ability to inhibit thioredoxin reductase. Remarkably, no cytotoxic effect was found on normal cell lines. Overall, a very similar profile emerges for Et₃PAuI and Et₃PAuCl, that retain the potent cytotoxic effects of Auranofin, while showing some peculiar features. These results demonstrate that the presence of the thiosugar moiety is not mandatory for the pharmacological action, suggesting that the tuning of some relevant chemical properties such as lipophilicity could be exploited to improve bioavailability, with no loss of the pharmacological effects.

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Hydrogen Evolution Catalyzed by Cobalt Mimochrome VIa

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Molecular hydrogen is an energy-dense fuel that has collected significant interest as alternative to fossil fuels (1). In order to be sustainable, hydrogen must be produced from water electrolysis utilizing carbon free energy and using catalysts based on earth-abundant elements (2). Natural hydrogenases evolve H\textsubscript{2} from neutral water with high efficiency and activity, but oxygen sensitivity of many hydrogenases and their difficulty to be handled render them unsuitable candidates for industrial applications (3). Nowadays there is an increasing demand in developing molecular functional hydrogenase mimics, as they are more amenable to detailed manipulation and study.

Cobalt-porphyrin-containing biomolecular catalysts have shown their capability in reducing proton to molecular hydrogen in neutral water (4), therefore, they represent valid noble-metal free catalysts for such reaction. For example, cobalt-microperoxidase 11, a cobalt-porphyrin-peptide complex, is an efficient catalyst for hydrogen evolution from neutral water in the presence of oxygen (4). Stimulated by these findings, we have studied Cobalt-Mimochrome VIa (CoMC6a) as a robust and water soluble catalyst for hydrogen evolution. CoMC6a comprises the deuteroporphyrin core, covalently linked to two peptide chains in helical conformation, covering both porphyrin faces. It presents a helix-porphyrin-helix sandwich structure and a penta-coordinated metal site (Figure 1).

CoMC6a shows hydrogenase activity in water solution at neutral pH under aerobic conditions. It works as molecular electrocatalyst for hydrogen evolution with near quantitative Faradaic efficiency, an overpotential value of 850mV, a TOF of 4.7s\textsuperscript{-1}. Remarkably, CoMC6a exhibits a TON of 3x10\textsuperscript{5}, which is one order of magnitude higher compared to the other cobalt porphyrins (4). These results suggest that the “sandwich” structure surrounding the porphyrin moiety may play a protective role from bleaching.

CoMC6a is an interesting model that can help us to understand the structural requirements needed to enhance hydrogen evolution reactions. In this context, our future efforts will be aimed at modifying the peptide scaffold, to develop novel enzymes with lower overpotential values, and, consequently, more competitive respect to the currently catalysts.

References:
Bifunctional triamine Pt(II) complexes containing a DNA intercalating moiety

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Different strategies can be exploited to improve the activity of Pt-based antitumor drugs and the design of bifunctional drugs is one of the most intriguing one since synergistic effects of the two parts are expected. In particular, in this work alkylating Pt(II) complexes have been combined to DNA intercalators. Monochlorido Pt(II) complexes with tridentate pyrazolyl-diamine ligands are able to form only monofunctional adducts with DNA, being generally less active than cisplatin. However, the incorporation into such Pt complexes of a functional group, able to interact with or intercalate into DNA, such as anthracene or acridine orange (1 and 2), increased their activity (1,2).

The in vitro evaluation of these complexes comprised: \textit{i}) cytotoxicity against ovarian carcinoma A2780 and A2780cisR cell lines; \textit{ii}) interaction with supercoiled DNA; \textit{iii}) cellular and nuclear uptake. The anthracenyl-containing complex 1 displayed a covalent type of binding with DNA, whereas the acridine orange counterpart 2 showed a combination of intercalative and covalent binding modes with a strong contribution from the former. Complex 1 showed a very strong antiproliferative activity on cell lines A2780 and A2780cisR and both 1 and 2 were able to significantly overcome cisplatin cross-resistance. The encouraging results on the antitumor activity of Pt(II) complexes 1 and 2 led to an extension of the study to related Pt(II) complexes with anthracenyl-containing terpyridine ligands (3 and 4). These derivatives showed affinity for quadruple-stranded DNA (G-quadruplex) with a good selectivity over duplex DNA, whereas the free ligands did not have significant affinity for any DNA sequences, indicating that the presence of the metal is essential for high affinity and selectivity. Moreover, the presence of a longer linker between the Pt core and the anthracene moiety enhances the interaction with G-quadruplex (3).

References:
Minimizing the release of reactive intermediates in O₂-dependent oxidation by de novo metalloenzymes

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Dioxygen activation and its transformations are key reactions both in chemistry and biology. In biological systems, these reactions are often catalyzed by transition metal cofactors. The desire to develop catalysts that match or even exceed the performance of natural enzymes has stimulated researchers towards the construction of functional metal sites into peptide/protein-based architectures by protein design (1,2,3,4). Successful examples of de novo designed oxygen-activating metalloproteins are the DF (Due Ferro) proteins, which fold into a four-helix-bundle structure. These catalysts oxidize quinols to corresponding quinones (5,6) upon O₂ reduction, while cycling between di-Fe(II) and di-Fe(III) states.

One of the key questions in protein design is to understand how different protein environments influence the properties of the bound cofactor or substrate. Starting from the DF protein scaffold, we used a recently developed design protocol (7) for constructing a heterodimeric four-helix bundle by covalent ligation of two α₂ chains through click chemistry. By modulating the substrate interactions within the active site, we designed an artificial metalloenzyme, DF-Click1, that catalyzes a net four-electron O₂ reduction in two consecutive two-electron steps inside the protein. Differently from earlier DFs, DF-Click1 catalyzes the oxidation of 4-aminophenol (4AP) without releasing H₂O₂ or other reactive species. This catalyst further promotes an oxidative coupling between one molecule of oxidized and reduced 4AP at the active site. The diiron site of DF-Click1 is able to perform O₂-dependent phenol-oxidase activity preventing the reactive intermediates from diffusing in solution, filling a gap between de novo designed and natural proteins.

References:
Biosourced Polymers from Stereoregular Polymerization of Monoterpenes in the Presence of Homogeneous Titanium Catalysts.

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The shift from conventional, fossil chemical feedstock to renewable resources is one of the main objectives of the chemical industry in recent decades. In this context many efforts have been devoted to synthesis of polymers by renewable resources. In particular carbohydrates, fatty acid and lignin have been intensively studied as possible starting materials. (1) Conversely, in spite of their widespread presence in natural products such as essential oils, terpenes have received little attention as viable candidate for the synthesis of polymers from biomasses. Regardless of their structural diversity they can be viewed as hydrocarbons consisting of the repetition of isoprene units (C₅). The acyclic simplest monoterpenes (C₁₀) due to their structural features can give rise to a chemistry very close to that of 1,3 alldienes deriving from fossil sources. In particular β-myrcene obtained in large scale from turpetine, has showed to be an excellent starting material for the synthesis of a wide range of useful chemicals. (2) More recently the stereoregular polymerization of β-myrcene and its isomer β-octymene has been reported to be promoted by catalysts based on lanthanides. (3) Among the possible microstructures both the 1,4-trans-polymyrcene and 1,4-cis-polymyrcene have been obtained. Cui and coworkers also reported the isoselective synthesis of 3,4-polymyrcene in the presence of a lutetium bearing a NSN-type ligand. (4) Titanium is the second most abundant transition metal on the earth-crust, therefore the development of catalytic systems based on this metal is advantageous from both the environmental and economical points of view. It is worth noting that notwithstanding the central role played by titanium in polymerization catalysis there are no examples to date of titanium based catalysts able to efficiently promote the polymerization of these monoterpenes to stereoregular polymers.

In this contribution we report on the synthesis of stereoregular polymers of β-myrcene and β-octymene and their copolymers with styrene by using the homogeneous titanium catalysts the [OSSO]-type complexes 1 and 2 and monocyclopentadienyl Ti(η⁵-C₅H₅)-(κ²-MBMP)Cl (3) (MBMP = 2,2’-methylenebis(6-tert-butyl-4-methylphenoxy) complex that have already shown to be active and versatile catalysts, when activated by methylaluminoxane (MAO), for the stereoregular polymerization of various 1,3-alkadienes and their copolymerization with styrene. (5)

Sustainable synthesis of aziridines: versatile precursors of fine chemicals

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The scientific community is greatly interested in the development of new methodologies to synthesise aziridines due to their pharmaceutical and biological properties (1). The use of atom efficient nitrene precursors, such as organic azides (RN₃), and efficient catalysts, such as metal porphyrins, could be an answer to society’s demand for a more sustainable chemistry. For example, the activation of RN₃ by a metal catalyst forms the reactive fragment “RN” as well as N₂ as the only stoichiometric by-product (2).

In our group, porphyrin complexes have been extensively employed in batch conditions (3) to catalyse the synthesis of aziridines (A) and vinylaziridines (B), starting from alkenes and dienes, respectively. Considering that one of the main drawbacks of classic homogeneous catalysis is the catalyst recycling, we investigated the use of either catalytic membrane reactors (CMR) (4) or mesoreactors under continuous flow conditions (5) to increase the procedure sustainability.

When the aziridination was performed in CMR, aziridines were formed in very good yields and in several cases the membrane was reused with a low catalyst leaking and no decrease in reaction selectivities. By using continuous flow conditions, yields and selectivities of ruthenium porphyrin-catalysed aziridinations were comparable to those achieved in batch conditions, while better performances and shorter reaction times were observed by using cobalt porphyrin catalysts. The flow system process was also successful in performing a two-step procedure in a single reactor where anilines were first transformed into aryl azides (Sandmeyer reaction) and then their reaction with styrenes yielded desired aziridines (5).

The study of the chemical reactivity of aziridines revealed that they are suitable starting materials for interesting fine chemicals such as benzoazepines (6) and oxazolidinones, which were obtained by aza-[3,3]-Claisen rearrangement of N-aryl-2-vinylaziridines and CO₂ cycloaddition reaction to aziridines, respectively.

References:
Aspects of the Functionalization of the Phosphorene Surface

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Phosphorene, a 2D material derived from the exfoliation of layered black phosphorus, is appealing for potential applications and it is often compared to graphene in spite of quite different electronic properties.\textsuperscript{(1)} Phosphorene is already a topic of great interest, although its functionalization is still scarcely proved experimentally, especially with transition metals.\textsuperscript{(2)} The many P-lone pairs on the surface may imply high donor power toward unsaturated metals having mono- or poly-functional acceptor character. On the other hand, they are tilted by 30° out the perpendicular axis to the surface, requiring metal fragments having suitable empty σ hybrids. Nonetheless, mono-metallic species of formula \(L_nM\) (\(n = 1, 2\) and 3 and \(M = d^{10}, d^8\) and \(d^6\), respectively) can be locally added to form an uncharged system with small \(L\) (e.g., Cl or CO). The \(η^1\), \(η^2\) and \(η^3\) coordination type were optimized at both molecular and periodic levels, as shown in Figure 1a-c, respectively. Remarkably, larger coligands determine hindrance problems for equivalent acceptor functionality of the metal. For instance, for \(L=PPh_3\) the species with \(n= 2\) or 3 cannot be formed because some bulky phenyl group are too close to the phosphorene’s surface. Also, not all the metal fragments are equally suitable in spite of having equivalent acceptor capabilities. The systems have been analyzed also in terms of energy, including those of the interactions between two or more P\(_n\) layers to estimate the role of the dispersion forces in the assembly. Remarkably, the band gap increases on exfoliating the black phosphorus with some justification for its electronic underpinnings. Additionally, the behavior of DMSO as an exfoliating agent of black phosphorus has been explored with evidence of oxygen atom transfers to the surface. Analogously, other elements or groups (S or NR imido) similarly transfer from species such as Cl\(_3\)PS, S\(_8\) or organic azides. Finally, also the behavior of I\(_2\) has been monitored from the electronic and energy viewpoints in parallel with the different behavior of the diatomic toward the P\(_4\) cage, which is fully demolished.

Figure 1. Functionalized phosphorene with metal fragments in: a) \(η^1\), b) \(η^2\) and c)\(η^3\) coordination, respectively.

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Polyesters from the Alternating Copolymerization of Epoxides and Cyclic Anhydrides

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Polyesters are amongst the most widely applied oxygenated polymers. They can be broadly divided into semiaromatic and aliphatic polyesters. Semiaromatic polyesters found application for the production of fibers, rigid plastics and engineering materials. Aliphatic polyesters, because of their biodegradability and biocompatibility, are the potentially sustainable alternatives to polymers derived from fossil sources and they find large application in biomedical field.

An efficient route for the syntheses of aliphatic polyesters is the ring-opening polymerization (ROP) of cyclic esters. (1) This method consents a punctual control of the microstructural parameters of the polymers allowing the synthesis of sophisticated macromolecular architectures (2, 3).

A more versatile way to produce polyesters, both aliphatic and semiaromatic, is the ring-opening copolymerization (ROCOP) of epoxides with cyclic anhydrides (4, 5). This method allows the access to a wide range of diverse polymer structures, thanks the availability to the two large distinct sets of monomers (3).

The most common catalysts described for this reaction generally feature a Lewis acid metal center penta-coordinated with salen or porphyrin ligands (4, 5). For all these catalysts, a complete selectivity of the process is reached only in the presence of a nucleophilic species that acts as co-catalyst.

Currently, the precise role of the co-catalyst remains rather obscure, but it is generally proposed that it coordinates to the metal center, promoting a dissociative mechanism resulting in the labilizing of the propagating polymer chain and accelerating polymerization.

We speculated that reactive aluminum centers with lower coordination, permitting the simultaneous coordination of the nucleophilic cocatalyst and the incoming monomer, could promote more the reaction rate (6 and 7). Thus, we decided to investigate the catalytic behavior in the copolymerization of epoxides with cyclic anhydrides of different tetra-coordinated aluminum complexes supported by phenoxy-imine and phenoxy-amine ligands.

For all complexes, we observed catalytic activities much higher than those reported for the related penta-coordinated aluminum complexes. The structure-activity relationship of diverse monometallic hemi-salen complexes was also rationalized.

Subsequently, the structure of the ancillary phenoxy-imine ligand was modify by introducing an additional pendant donor able to simulate the function of the co-catalyst. This complex was able to promote perfectly selective polymerization without the addition of a hexogen co-catalyst. This complex represents the first example of bifunctional aluminum catalyst for the selective copolymerization of epoxides and anhydrides.

References:
Water Oxidation catalyzed by Ir(III) and Ru(III)-doped hydrotalcite-like compounds

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Water oxidation (WO) is considered the bottleneck for the development of an artificial photosynthetic apparatus aimed at the green production of renewable fuels(1). Over the last few years, many molecular(2), heterogeneous(3) and heterogenized(4) catalysts have been reported. Furthermore, we demonstrated that a ternary system constituted by an Ir(III)-doped ZnAl hydrotalcite-like compound (HTlc) is an efficient and recyclable heterogeneous WO catalyst(5). Particularly, we showed that $\text{[Zn}_{0.667}\text{Al}_{0.306}\text{Ir}_{0.027} \text{(OH)}_{2}\text{]}\text{Cl}_{0.333} \cdot 0.4\text{H}_{2}\text{O}$ is capable of catalyzing WO with top performance both in terms of TOF (up to 113 min$^{-1}$) and TON (> 11900), in the presence of NaIO$_4$ as the sacrificial oxidant(5). Herein, we show that both Ir(III) and Ru(III)-doped HTlc's are efficient and robust heterogeneous catalysts for water oxidation also in electrocatalytic experiments. The HTlc's presented here have zinc or magnesium as the bivalent cation and aluminum as the trivalent one. Two of them were doped with Ir(III) and one with Ru(III) ions, via an isomorphic replacement of Al(III) ions. Their chemical formulas, determined by ICP-OES analysis, are:

- $\text{[Zn}_{0.647}\text{Al}_{0.349}\text{Ir}_{0.004} \text{(OH)}_{2}\text{]}\text{Cl}_{0.353} \cdot x\text{H}_{2}\text{O}$ (1),
- $\text{[Mg}_{0.647}\text{Al}_{0.349}\text{Ir}_{0.004} \text{(OH)}_{2}\text{]}\text{(CO}_{3}\text{)}_{0.177} \cdot x\text{H}_{2}\text{O}$ (2),
- $\text{[Zn}_{0.650}\text{Al}_{0.330}\text{Ru}_{0.020} \text{(OH)}_{2}\text{]}\text{Cl}_{0.350} \cdot x\text{H}_{2}\text{O}$ (3).

The brucitic structure is retained after the incorporation of the noble metal that was found to be homogeneously distributed throughout the sample, as confirmed by X-ray diffraction patterns and SEM-EDX images. The performances of the HTlc's toward water oxidation have been evaluated in a standard three electrode-apparatus (KOH 1M), immobilizing the catalysts in carbon paste electrodes. Interestingly, 1 and 3 show a lower overpotential (352mV vs 388mV at 10mA/cm$^2$) and twice as high current density with respect to IrO$_2$ (2.1 vs 1.2 mA/cm$^2$ at 280mV), used as benchmark (Fig.1). Instead, 2 shows a current density comparable to that of IrO$_2$. In addition, long-term stability tests, such as chronoamperometry and chronopotentiometry, show that these catalysts are not only stable under the catalytic conditions used, but also their performances increase over time.

New Self-Assembling Luminescent Materials from Pyridyl Oxadiazole Zn(II) Complexes

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In the last years, a large number of papers have been published from our laboratories on zinc complexes from polydentate ligands, their interest due both to their fascinating structural topologies and the potential applications in sensing, photoluminescence and optoelectronic (1,2). In some cases, the assembling of suitable ligands and/or preformed polymeric chains with Zn(II) proved to be an efficient route for the formation of metallated polymeric materials whose photoluminescence properties were examined in correlation with structural data (3,4). In particular, self-assembling of small building blocks by coordination to the metal centers can generate polymers or networks. Recently, interest has increased on self-assembling metal containing structures where weak metal-ligand interactions easily allow to obtain materials with specific desirable properties, offering a convenient alternative to the conventional preparation of macromolecules by covalent bond formation (5,6).

We now report the synthesis of zinc-mediated self-assembling luminescent materials from pyridyl oxadiazol 2-phenol ligands (Figure 1).

As expected, ligands act as mononegative chelates in mononuclear Zn(II) tetracoordinated complexes. The presence of the pyridyl moiety produces an additional potential coordination site whose role can be tuned by changing position of the nitrogen in the ring.

In all cases, by spectroscopic studies, no interactions were detected in solution, making the system soluble and processable. On the other hand, in the solid state N-Zn weak interactions cause the assembling of the isolated complexes in a non-structured network. Strong and stable glasses were obtained by spin-coating or casting of complex solutions, giving in some cases highly luminescent films. PLQY values measurements and theoretical analysis complete the study of this systems.

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Luminescent complexes and their bright ligands

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Luminescent transition metal complexes are of great interest for the development of probes, sensors, electroluminescent materials, light-harvesting materials, photocatalysts, and so on. Their electronic absorption and luminescence properties can, in principle, be fine-tuned by an appropriate choice of the central metal and of the coordinated ligands, however rationalizing the structure-property relationships is not straightforward. This contribution provides a brief overview on the photophysical features of a series of transition metal complexes containing as ligands organic molecules that are themselves luminescent. In particular, the attention is focused on the use of pyridinylimidazo[1,5-a]pyridine derivatives, a class of aromatic heterocyclic compounds widely reported in literature for its optical properties (1,2). Adopted with the aim of obtaining highly emitting complexes, the coupling of pyridinylimidazo[1,5-a]pyridines and transition metals such as Cu, Re Ir resulted in complexes displaying unconventional and counterintuitive emission properties (3,4,5,6) that can be somewhat rationalized recalling the intersystem crossing between low-lying singlet and triplet excited states localized at the bidentate ligand bound directly to a heavy metal atom (7).

Layer by layer order of molecular thin films detected by Torque Magnetometry

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Thin layers composed by magnetic molecules, have attracted considerable interest in the scientific community for application in the fields of quantum computation (1), information storage (2) and spintronics (3). However, before proceeding with any kind of application, a detailed knowledge of the molecular order is mandatory. The technique that are commonly used to obtain this information are however often limited by the penetration length of the radiation used as a probe (usually few nm), or are only able to deliver an average orientation of the film.

To overcome this limitation, we exploited the peculiar sensitivity of Cantilever Torque Magnetometry to magnetic anisotropy (4). Indeed, we measured several samples composed by LnPc\textsubscript{2} (Bis-phthalocyaninato neutral complex, where Ln=Tb or Y) molecules evaporated on three different substrates (glass, gold and perylene-3,4,9,10-tetracarboxylic dihanidride, PTCDA). Since YPc\textsubscript{2} is diamagnetic and isotropic, CTM is able to selectively detect the order of the TbPc\textsubscript{2} molecules that were evaporated at different distance from the substrate. Collecting information of four different samples, we were able to precisely reconstruct the packing of molecules from the first layers up to hundreds of nanometers. To reproduce the experimental points, we developed a code that is able to include a Gaussian molecular distribution centred on the most probable orientation. On glass, the molecules assumed a standing configuration (Pc rings perpendicular to the surface) while on PTCDA a lying configuration (Pc rings parallel to the surface) was imposed by the strong interaction between the highly-conjugated substrate and the Pc rings. The case of the gold substrate was more complex: the first layer assumed a lying configuration that rapidly turned into a standing configuration due to the competing effect between favorable interaction with the substrate and π−π interactions. This study opens the possibility to use anisotropic molecules as local probes to detect order in surface or buried layers of molecular thin films (5). References: 1. Ladd T.L. \textit{et al.}, Nature, 2010, 464, 7285 2. Mannini M. \textit{et al.}, Nature Materials, 2009, 8, 194 3. Bogani L. \textit{et al.}, Nature Materials, 2008, 7, 179 4. Perfetti M. \textit{et al.}, Chem. Eur. J. 2014, 20, 14051. 5. Perfetti M. \textit{et al.}, Adv. Mater. 2016, 28, 6946.
Porphyrid-Sensitized Solar Cells: the challenge of photostability

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Dye-sensitized solar cells (DSSC) are a highly promising alternative to conventional photovoltaic silicon-based devices (1). A key-role is played by the dye and porphyrin sensitizers have drawn great interest because of their excellent light-harvesting properties mimicking photosynthesis (2, 3). In 2014 a device based on a D-π-A ZnII porphyrin with a [Co(bpy)3]2+/3+ redox couple attained an unprecedented photon-to-current conversion efficiency (PCE) of 13.0% (4), higher than that reported for the best Ru(II)-based dyes traditionally employed in DSSC. However, a still quite unexplored topic is the stability towards photodegradation of Porphyrin Sensitized Solar Cells (2), an issue of outstanding importance for their potential application in Building Integrated Photovoltaics (BIPV), for which the greenish color displayed by porphyrin complexes could be very appealing (5).

Therefore two β-substituted ZnII-tetraarylporphyrins, bearing hexyloxy chains (–OC6H13) in the ortho-position of each aryl ring (so to prevent detrimental π-π aggregation) and a carboxylic or a cyanoacetic acceptor group (to be anchored to TiO2 surface) have been synthesized. Thanks to the facilities of the SmartMatLab Centre hosted by the Department of Chemistry of the Università degli Studi di Milano (6), prototype solar cells of both dyes have been assembled on FTO glasses (1.25x2.0 cm, with an active area of 0.196 cm²) coated with a 6 μm thick transparent TiO2 layer (20 nm nanoparticles), in air or under nitrogen atmosphere, uptaking the dye by two different solvent mixtures (EtOH:THF = 9:1 or EtOH:toluene=1:1), and using a I-/I3 redox couple. Some cells have been coated also with a UV filter adhesive film purchased by Solaronix. The photostability of the devices has been evaluated through UV-Vis spectroscopy after radiation of the solar cells with a Solar Simulator (under 1 sun illumination through an AM 1.5G filter), monitoring the changes in absorption maximum and intensity of the Q bands of the dye after regular time intervals (0’, 90’,180’, 240’, 300’, 360’, 540’, 720’, 900’, 1080’, 1260’, 1440’, 1620’ and 1800’). Moreover, the starting PCE of the cells have been compared to that after 1800’ irradiation.

Hierarchical materials based on carbon nanostructures as advanced catalysts in energy applications

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Carbon nanostructures (CNSs) have emerged as unique building blocks in the assembly of complex functional materials. Heterogeneous catalysis is one particular field where the intriguing properties of CNSs can be fruitfully exploited (1). This contribution provides a glimpse of the results of the last 3 years within our group on the synthesis of new hierarchical materials based on CNSs and their application in modern key energy processes. In particular, two types of nanomaterials are discussed, one featuring a hierarchical ternary nanohybrid integrating CNSs (carbon nanotubes, nanohorns and nanocones), Pd nanoparticles and TiO\textsubscript{2}, and the other consisting of a metal free hierarchical carbon material appropriately doped with N atoms. The fully characterized materials have shown excellent performance in photocatalytic H\textsubscript{2} production (2,3), as well as in the electrocatalytic hydrogen evolution reaction (4), CO\textsubscript{2} reduction (5) and selective oxygen reduction to hydrogen peroxide (6).

References:
Pyran based dyes as photosensitizers for p-type dye-sensitized solar cells

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The heart of a dyes-sensitized DSSC device is a wide bandgap semiconductor oxide, sensitized with a photoactive dye able to inject, upon photoexcitation, electrons (n-type) or holes (p-type) in the semiconductor substrate (1). While n-type DSSC have been thoroughly investigated and a power conversion efficiency (PCE, \( \eta \)) exceeding 14% have been reached (2), the number of studies regarding p-type DSSCs is significantly lower; it is anyway increasing in the last years because these kinds of devices open the way to the realization of tandem DSSC device based on the connection of a p-type photoelectrode with a n-type photoelectrode, each contributing to the total photovoltage generated by the cell (3). So far, the performances of p-DSSCs remain a way lower (4) than the n-type counterparts and a great work of optimization of different is still required. For what concerns the sensitizers different requirements as absorption in a broad range of the solar spectrum along with high molar extinction coefficients are needed. Moreover, it is essential that, upon photoexcitation, electron density moves away from the anchoring points on semiconductor oxide surface so that charge recombination occurs at lower rate. In this context, we investigated the properties of pyran based dyes, featuring, as shown in Figure 1, a similar molecular structure: the dyes are based on a pyran core functionalized with electron acceptor groups of different strengths and symmetrically coupled to carbazole or phenothiazine donor branches. Donor branches are functionalized with carboxylic group to allow a firm adhesion on the semiconductor oxide surface in the device assembling. Optical properties of the dyes are deeply influenced by the nature of the electron-acceptor group, so that the overall absorption of the reported dyes covers most of the visible spectrum. The properties of devices based on the NiO electrodes sensitized with the investigated dyes were evaluated under simulated solar radiation: the larger short circuit current density exceeded 1 mA/cm\(^2\) and power conversion efficiency as high as 0.07% could be recorded.

Figure 1. Molecular structure scheme of the reported dyes

Unravelling the surface degradation mechanisms in ether electrolyte based Li-O₂ cells

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Li-air cells are at the cutting edge among the devices for energy storage (1-3). The electrode reactions, called Oxygen Reduction Reaction (ORR) and Oxygen Evolution Reaction (OER), occur on discharge and charge at the triple interface O₂/cathode/electrolyte. The use of a stable lithium salt (e.g. lithium bis(trifluoromethane sulfonyl) imide, LiTFSI) dissolved in an ethereal solvent (e.g. tetraethylene glycol dimethyl ether, TEGDME) as aprotic electrolyte leads to the reversible formation of lithium peroxide (Li₂O₂) as main discharge product (1-3).

A carbon paper has usually been used as cathode material for Li-air cells due to its favorable matching with various desired characteristics (high porosity and surface area, high anodic stability, lightness, availability, low cost etc.). However, carbon has shown low inertness to chemical oxidative attacks from reduced forms of oxygen (O₂⁻, O₂²⁻, LiO₂, Li₂O₂). We have recently reported about the long-term fading of performance of Li-air cells assembled with a carbon cathode and an ether-based electrolyte due to the carbon paper and/or the TEGDME chemical instability (4,5).

In the search for a stable cathode material for Li-air cells, our experimental activity is now focused on carbon-free electrodes. Within this family, NiCo₂O₄ is well known for its bifunctional electrocatalytic activity towards the ORR and the OER (6,7).

Networks based on functionalized noble metal nanoparticles: advanced materials for optical and electronic applications

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A wide range of advanced applications are based on noble metal nanoparticles (MNPs), because of their unique chemical and physical properties and versatile synthesis, that allows to functionalized metal surface with optically active organic or organometallic molecules.\textsuperscript{(1,2)} In particular, the research in biomedicine, catalysis, energy conversion and sensors are strongly influenced by these materials \textsuperscript{(3,4)}. The colloidal MNPs can be manipulated to induce self-assembly into complex structures, 2D or 3D networks that show collective properties \textsuperscript{(5)}. In this work platinum, palladium, gold and silver nanoparticles (PtNPs, PdNPs, AuNPs, AgNPs) have been synthesized in the presence of different bifunctional thiols; the prepared MNPs have been characterized with spectroscopic and morphological techniques and by means optical and electrical conductivity measurements. In particular, the obtained AuNPs have shown a diameter of about 5-10 nm and a spherical shape (see Fig.1), showing the typical Surface Plasmon Resonance (SPR) of the system that was found at 520 nm. For AgNPs dimension are around 3-5 nm, with SPR at 430 nm. The MNPs showed interesting results regarding the electrical conductivity measurements, carried out at room temperature, in dark conditions and under visible light: the AuNPs showed a nonohmic behavior whereas the AgNPs an ohmic one.

Fig.1. MNPs based network; TEM image and electrical characterization.

New examples of interstitial Bismuth atoms in icosahedral rhodium cages

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The chemistry of homo-metallic carbonyl clusters of rhodium has been widely investigated over the last four decades. (1, 2) The capability of rhodium compounds to interstitially host light $p$ elements, such as C and N, gave rise to the fruitful chemistry of carbide and nitride Rh clusters. (3) However, less has been achieved when moving to heavier post-transition elements, and only a few examples are known so far, among which $[\text{Sb}@\text{Rh}_{12}(\text{CO})_{27}]^{3−}$ (4, 5) and $[\text{Sn}@\text{Rh}_{12}(\text{CO})_{27}]^{4+}$. (6) In order to widen the chemistry of rhodium compounds containing post-transition elements, we investigated the chemistry of hetero-metallic Rh-Bi carbonyl clusters. The reaction of $[\text{Rh}_{7}(\text{CO})_{16}]^{3−}$ with $\text{BiCl}_3$ under $\text{N}_2$ and at room temperature results in the formation of the new hetero-metallic $[\text{Bi}@\text{Rh}_{12}(\text{CO})_{27}]^{3−}$ cluster in high yields. Further controlled addition of $\text{BiCl}_3$ leads firstly to the formation of the dimeric $[(\text{Bi}@\text{Rh}_{12}(\text{CO})_{26})_{2}\text{Bi}]^{5−}$ and the closo-$[\text{Bi}@\text{Rh}_{14}(\text{CO})_{27}\text{Bi}_2]^{3−}$ species in low yields, and finally, to the $[\text{Bi}@\text{Rh}_{17}(\text{CO})_{33}\text{Bi}_2]^{4−}$ cluster. All clusters have been spectroscopically characterized by IR and ESI-MS spectrometry, and their molecular structures fully determined by X-ray diffraction studies. Notably, they represent the first examples of Bi atoms interstitially lodged in metallic cages that, in this specific case, are all based on an icosahedral geometry. Moreover, $[\text{Bi}@\text{Rh}_{14}(\text{CO})_{27}\text{Bi}_2]^{3−}$ forms an exceptional network of infinite zig-zag chains in the solid state, thanks to intermolecular Bi-Bi distances.

Synthetic Strategies Towards Quantum Coherence Time Enhancement in Potential Molecular Spin Qubits

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The preparation and characterization of magnetic molecules that behave as potential molecular spin qubits represent a fundamental step to evaluate the viability of such systems in the field of quantum information processing (1,2). In this regard, mononuclear vanadium(IV) complexes have been identified among the best performing molecular candidates (3,4).

Aim of this communication is to provide an overview of the most recent results obtained by our group in the development of potential spin qubits, in their multitechnique investigation through alternate current susceptometry and pulsed electron paramagnetic resonance spectroscopy, and in the identification and understanding of the molecular parameters which affect the spin dynamics. In this context, three recently reported systems will be presented and discussed.

The investigation of the quantum coherence and the magnetization dynamics of vanadyl phthalocyanine, VOPc, an easily-processable semiconducting molecular material in its pure form, and its crystalline dispersions in the isostructural diamagnetic host TiOPc at different percentages, VOPc:TiOPc 1:10, and VOPc:TiOPc 1:1000, allowed coherent spin manipulation at room-temperature (5).

A comparative study of two vanadium(IV) based systems in which the introduction of a unique structural difference, i.e. an oxovanadium(IV) in a square pyramidal versus a vanadium(IV) in an octahedral environment featuring the same coordinating ligand, allowed to identify in electronic and vibrational features of the vanadyl moiety the source of the enhancement of quantum coherence up to room temperature (6).

Finally, a detailed investigation of the magnetization dynamics by ac susceptometry of a vanadyl complex with diethyldithiocarbamate ligands, which showed an anomalous and unprecedentedly observed field dependence of the relaxation time, revealed important insights on the role of low energy vibrations, experimentally detected by THz spectroscopy, on the spin dynamics [7].

These fundamental studies represent a step towards the identification of optimized molecular building blocks for the preparation of more complex molecular architectures with long-life quantum coherence that can be exploited as molecular quantum gates for quantum computation.

Olefin Metathesis Ruthenium Catalysts Bearing Backbone-Substituted Unsymmetrical NHC Ligands

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N-heterocyclic carbenes (NHCs) have gained increasingly importance in modern chemistry as excellent ancillary ligands for metal catalysts. Due to their unique steric and electronic properties, efficient catalysts for a huge number of academically and industrially important processes have been found.(1,2) One of the most important and extensively studied transformations mediated by NHC-metal complexes is ruthenium-catalyzed olefin metathesis.(3,4,5) The fine tuning of steric and electronic properties of the NHC ligand can strongly influences catalytic behavior of the resulting ruthenium complexes. In this context, the development of unsymmetrical NHCs (uNHCs), able to differentiate steric bulkiness in proximity of the ruthenium center, has led to important effects on reactivity and selectivity of the resulting catalysts.(6) Recently, we investigated the impact of differently oriented substituents on the backbone of uNHCs as an effective means to modulate the catalytic properties of the resulting complexes.(7,8) The catalytic behavior of new uNHCs combining different backbone configurations with \(N\)-alkyl/\(N\)-aryl substituents of variable bulkiness on catalyst properties will be discussed.

![Figure 1](image_url). New Grubbs’ and Hoveyda-Grubbs’ second generation catalysts with uNHCs.

References:
4,4’ bipyridine monoxide (bipyMO): a simple heterotopic divergent ligand

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Although 4,4’ bipyridine (bipy) can be considered a classical connector since it has been used to prepare a huge number of metal coordination polymers (1) and the oxidized 4,4’ bipyridine dioxide (bipyDO) has been largely chosen to prepare examples with the oxophilic lanthanides (2), 4,4’ bipyridine monoxide (bipyMO) has been mostly neglected and only a few examples of metal complexes have been reported so far. In most of them bipyMO is coordinated as a terminal ligand through the nitrogen or the oxygen donor atom in dependence of the nature of the metal (3) while only rarely bipyMO is a divergent ligand acting as a bridge in homo-metallic derivatives. (4) Examples where the ligand bridges two different metals are missing in the literature.

In this contribution, a few homo and hetero-metallic complexes of bipyMO for d and f transition metals are reported. Isostructural homo-metallic coordination polymers [M(hfac)\textsubscript{2}(bipyMO)]\textsubscript{n} (M = Zn, Cu, Co, Mn; hfac = hexafluoroacetylacetonate) have been prepared. Every bipyMO ligand bridges two metal centers forming a monodimensional metal-bipyMO network with two different metal coordination polyhedrons, M(hfac)\textsubscript{2}N\textsubscript{2} and M(hfac)\textsubscript{2}O\textsubscript{2}. In the former two bipyMO ligands are coordinated through their N-donor atoms while in the latter through their O-donor atoms. Such a result opened the way to the synthesis of hetero-bimetallic chains with exactly alternated metal centres showing a sufficiently different affinity for nitrogen and oxygen donor ligands. Monodimensional coordination polymers alternating either two different d transition ions, [Mn(hfac)\textsubscript{2}(bipyMO)Cu(hfac)\textsubscript{2}(bipyMO)]\textsubscript{n} or d and f transition metals [M(hfac)\textsubscript{2}(bipyMO)Ln(hfac)\textsubscript{3}(bipyMO)]\textsubscript{n}, where M/Ln are Cu/Eu, Zn/Eu, or Co/Dy, were prepared and structurally characterized. Luminescence studies on the europium containing samples have been carried out.

Molecular compounds containing the terminal ipodentate ligand have been obtained for metals showing a high preference between the two donor atoms. A mononuclear platinum complex cis-PtCl\textsubscript{2}(PPh\textsubscript{3})(bipyMO) where the ligand is bonded through the nitrogen atom and the dinuclear [Eu\textsubscript{2}(hfac)\textsubscript{6}(μ-bipyMO)]\textsubscript{3} where the ligand is bonded through the oxygen atom have been structurally characterized. These complexes can behave as ligands as exemplified by the synthesis of the trinuclear [trans-PtCl\textsubscript{2}PPh\textsubscript{3}bipyMO]\textsubscript{2}Zn(hfac)\textsubscript{2}.

References:
Catalysis by Group IV Amido-Pyridinate Complexes for the Reduction of Carbon Dioxide to Methane

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A highly attractive renewable energy technology involves the transformation of CO₂ into fuel. Indeed, CO₂ has not to be regarded as a waste product from the combustion of fossil fuel but rather as a chemical resource to be harvested and recycled into products of added value using the assistance of a catalyst. The metal-mediated CO₂ reduction with silanes (hydrosilylation) is a thermodynamically favored chemical process and it can be conveniently applied to the transformation of this feedstock.

Early transition-metal complexes stabilized by nitrogen-containing ligands have been identified as valuable candidates for a number of highly efficient and selective catalytic transformations (1). In particular, amidopyridinate Group-IV organometallics have shown excellent performance as catalysts precursors in olefins oligomerization, polymerization, and copolymerization (1,2) as well as in the intramolecular hydroamination of primary and secondary aminoalkenes (3).

In search for catalytic applications in the renewable energy field, we have focused on a new class of neutral dibenzyl ZrIV and HfIV complexes stabilized by a tridentate dianionic benzoimidazolyl-amidopyridinate ligand [(N,N,N′)MIVBn₂, M = Zr, Hf] as pre-catalysts for the CO₂ hydrosilylation reaction.(4) In this study, we have demonstrated that their in-situ activation with an equimolar amount of B(C₆F₅)₃ leads to the generation of cationic monoalkyl species (Figure 1). In the presence of silanes, these cations promote the CO₂ reduction to methane under mild reaction conditions (room temperature and 1 atm of CO₂). ¹³C- and ¹/C{¹H}-NMR experiments with isotopically enriched ¹³CO₂ have been conducted to check the reaction course through the generation and conversion of all the reduction intermediates. A full account of the catalytic performance of these Group IV amido-pyridinate complexes in the reduction of carbon dioxide with various hydrosilanes will be discussed.


References:

Dinuclear d^{10} complexes with nNHC/tzNHC heteroditopic carbene ligands and their luminescence properties

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Homoleptic gold complexes with N-heterocyclic carbene (NHC) ligands are nowadays studied for a multitude of applications.(1) This type of organometallic complexes, in which all the coordination sites on the gold center are occupied by carbene donors, are characterized by a high stability, due to the strength and inertness of the gold-NHC bond, which can be further enhanced by using multidentate NHC ligands.(2) As a consequence, this family of compounds is scarcely appealing for catalytic applications but earns success in other areas such as luminescent materials,(3) medicinal chemistry,(4) and more recently also molecular recognition and sensing.(5) We are interested since few years in the study of the luminescence properties of dinuclear gold(I) diNHC complexes of general formula \([\text{Au}_2(\mu-\text{diNHC})_2]\)(PF_6)_2. The photoemission in these systems arises from the so-called “aurophilicity”, a dispersive interaction between the gold centers, whose presence is usually accompanied by high quality emission.(3) Our efforts to understand the different factors affecting the luminescence properties of the complexes have been focused up to now in modifying the bridging group between the carbene units. We identified the trimethylene group (-CH_2-CH_2-CH_2-) as a privileged linker because it presents the right length and flexibility for allowing the interaction between the two gold centers. In this contribution, we present our recent results on the study of asymmetric bidentate ligands bearing a nNHC (normal N-heterocyclic carbene) and a tzNHC (1,2,3-triazole N-heterocyclic carbene) linked by a trimethylene bridge. Synthesis, structural characterization and emission properties of the novel gold(I) complexes will be presented and compared to those of the corresponding silver(I) complexes. Preliminary results on the synthesis of heterobimetallic Ag(I)/Au(I) complexes with this type of ligands will be also illustrated.

References:
Symbiotic structural and spectroscopic approach to reticular chemistry: the case study of luminescent Copper(I) cyanide coordination polymers.

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The reticular description of coordination polymers in recent years attracted a great interest for its easiness and compactness. (1) The use of the graph formalism to characterize complex structures by considering only the connection between nodes and a simplified description of the non-bridging fragments is a powerful tool both in a predictive and a comparative point of view. (2) However, this theory has usually been limited only to the structure description, without considering the effect of net structure on the spectroscopic behavior of the different materials. The connection of topological invariants typical of a specific family of coordination polymers with some characteristics NMR or vibrational pattern could be useful when is difficult to obtain single crystals, and can be a powerful aid to the structure resolution by means of powder X-ray diffraction of complex structures. However, this correlation is often not so clear: spectra signals of complex molecules usually don’t reflect the long range spatial disposition, but only the local environment, that is only partially correlated to the overall topology. In other cases, the coupling between signals, especially in the case of simple bridging molecules, is very informative. This is the case of cyanide; this bridging anion has a prominent role in the reticular chemistry, and despite the common simple linear coordination geometry, demonstrated to be a powerful tecton to construct a multitude of different coordination polymer topologies, by choosing different metal nodes. (3) An interesting system is done by the copper (I) cyanide: the non-obvious preference of copper (I) for a specific coordination geometry and the different bridging possibilities shown by the cyanide ligand, make very difficult to predict the reticular chemistry of copper cyanide coordination polymers, that possess a peculiar emissive behavior that make these systems interesting for LED applications and sensoristics. (4) We reported the synthesis and characterization of 12 new compounds of copper cyanide with different geometries and arrangements of the ligands, with very different topologies. These topologies are connected by the presence of some typical topological invariants build up by cyanide and metal centers, like rings of different dimensions and chains. After a comment on the possibility to control the topology of the compound by a judicious choice of the ligand and by a different synthetic approach, it will be analyzed the correlation of vibrational and NMR analysis and the topological connectivity of the specific fragments, demonstrating that in some cases this correlation can be rationalized.

References:
Polymer Stereoregularity Influence on Optical Properties of Carbazole-based Photoconductor Polymers

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Carbazole-based compounds have gained in importance in the last few decades because of their use as organic photoconductor, photorefractive and light-emitting materials etc.\textsuperscript{(1)}. From the structural point of view, carbazole containing polymers can be divided into two groups: polymers with in-chain isolated carbazole groups and polymers with pendant carbazole groups, like poly(N-vinylcarbazole) (PVK) the first to be synthesized. Despite its low electrical conductivity, PVK has been largely used in combination with other layers in the fabrication of organic light emitting diodes (OLEDs) \textsuperscript{(1)}. As for the PVK homologues, it is generally accepted that photoconductivity is affected by the chemical nature of the spacer linking the carbazole chromophore to the main chain as well as the stereochemical configuration of the polymer chain.\textsuperscript{(1-5)}.

In this contribution, the synthesis and physical properties of stereoregular poly(carbazole)s presenting different spacers linking pendant carbazole groups to the polymer main chain are reported.

Polymerizations were performed by using homogeneous Ziegler-Natta catalytic systems. Polymers have been fully characterized by NMR, X-ray diffraction, thermal analysis, FT-IR and UV-Vis as well as photoluminescence analysis. Moreover, the influence of the polymer stereoregularity on the optical properties of achieved poly(carbazole)s has been also investigated. The optical analysis of all polymer film samples reveals the presence of two different excimers arising from a fully (“sandwich-like”, low energy excimer) or partially (higher energy excimer) overlapping of two carbazole groups. In detail, the isotactic polymers show a higher emission intensity ratio between “sandwich-like” and “partially overlapping” excimers respect to syndiotactic ones. Thin polymer films have been tested as single emissive layers of OLEDs. A blue light is obtained from all the devices, except for the isotactic poly(N-pentenylcarbazole)-based OLED with an optimized architecture that emits a white light.

References:
Upconverting polymeric aerogels

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Aerogels constitute an important class of highly porous materials and their unique properties make them interesting for many technological applications such as thermal and acoustic insulation, catalysts/catalyst supports, water/air purification and airborne particle filtration.¹

Upconverting lanthanide doped alkaline-earth fluoride nanoparticles (e.g. SrF₂ or CaF₂ doped with Yb³⁺ and Er³⁺ ions) with typical particle size of 20 nm were prepared by a facile, environmental friendly hydrothermal technique, using oleate group as a capping agent².

The nanoparticles (NPs) have been then incorporated in syndiotactic polystyrene (s-PS) aerogels polymer. The monolithic s-PS/NP aerogels with NPs amount up to 50 wt% have been prepared by a sol-gel process followed by solvent extraction with supercritical CO₂. These composite NP/s-PS aerogels are characterized by an apparent porosity up to 98% and surface area up to 300 m²/g. The SEM analysis have also shown that the aerogels display a fibrillar morphology with the dispersion of NPs within the aerogel macropores.

Spectroscopic properties have been investigated using a 980 nm laser as the excitation source. An evident upconversion emission of the Er³⁺ ions in the visible and near infrared range, in particular in the green and red regions, has been observed and investigated.

Mechanism for the upconversion emission under 980 nm excitation

References:

Coordination Complexes and One Step Assembly of Natural Polyphenols for Versatile Nanocapsule Engineering

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Nanoencapsulation of active substances with controlled release in harmless matrices has been the subject of numerous scientific efforts mainly due to the significant biomedical potential of such endeavors. Lignin, the environmentally sustainable by-product of the pulp and paper industry, contains a multitude of phenolic hydroxyl groups, some of which are known to readily and strongly chelate with iron ions. In this effort we demonstrated that the concerted use of chelation chemistry, oil in water emulsion principles and low energy sonication, offers a facile, one pot strategy to assemble lignin nanocapsules (LNCs) of a controlled architecture. Under these conditions capsules are shown to rapidly assemble utilizing two driving forces, the π-stacking propensity of lignin and its metal chelating ability at alkaline pH. Detailed size exclusion chromatographic evidence validates that the formation of capsules is driven mainly by the enumerated physical interactions with no significant chemical modification of the lignin. The developed process was systematically optimized so as to create the foundations for the morphology and the yield of the capsules being modulated as a function of sonication time, power and surface contact area. Both pure LNCs and Fe-LNCs were synthesized in high yields with size distributions varying from 0.3 to 5 μm and their release efficiencies evaluated in detail. As anticipated, the complexation effects of the phenolic OH groups offered to the Fe-LNCs, increased stability, reduced shell thickness (allowing for greater loading efficiencies) and lower release kinetics, compared to LNCs.

References
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Mesoporous bioactive glasses doped with cerium: investigation of catalase and SOD mimetic activities, and bioactivity

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We investigate the ability of mesoporous bioactive glasses doped with cerium ions (Ce\textsuperscript{3+}/Ce\textsuperscript{4+}) to act as catalase and superoxide dismutase (SOD) mimic materials. Our aim is to synthesize a material able to show both bioactivity and antioxidant properties. Bioactive Ce-doped glasses synthesized via melting technique (molten glasses) have shown good catalytic properties, but low bioactivity (formation of hydroxyapatite); thus we decided to modify with cerium oxide a class of glasses that has already demonstrated to have better bioactivity properties than the classical molten glasses. This class is constituted of mesoporous bioactive glasses synthesized through the EISA (Evaporation-Induced Self-Assembly) method and have a very high surface area. Because of this, their reactivity is increased with respect to the molten glasses, and they show the formation of hydroxyapatite over the surface at a shorter times as compared to the molten bioactive glass 45S5 Bioglass\textsuperscript{®}. The XPS data collected in previous studies on the valence state of cerium in the molten bioactive glasses highlighted that on the surface of the samples there were both Ce\textsuperscript{3+} and Ce\textsuperscript{4+} ions and that during the catalase tests their ratio changed (1-3) as it happens in nanoceria. (4) Moreover, the Ce\textsuperscript{3+}/Ce\textsuperscript{4+} ratio on the glass surface was shown to depend on the glass composition: the presence of phosphate in the molten bioactive composition favors the increase of Ce\textsuperscript{3+} amount and in the same time decrease of the catalase mimetic activity.

Starting from this state of the art, we have decided to study Ce-mesoporous glasses: i) with different compositions in order to verify how the glass composition affects the catalase-like activity; ii) with both good bioactivity and good antioxidant properties. We have tested the SOD and the catalase mimic activities on glasses with different Ce\textsuperscript{3+}/Ce\textsuperscript{4+} ratio (range 3.9-0.7) in order to find the better synthesis conditions.

The catalase and SOD mimic activity tests have revealed that the Ce-mesoporous glasses are able to act as mimic materials for the two enzymes. In addition, the FT-IR and XRD analysis have confirmed that in several samples the hydroxyapatite is present, even if, increasing the content of cerium oxide, the intensity of the characteristic peaks of hydroxyapatite decreases. These results highlight that it is possible to obtain a glass with both antioxidant properties and bioactivity.

Tetrahedral Arrays of Metallo-porphyrins

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Artificial photosystems mimicking the natural occurring ones (1) play a prominent role in the contemporary research (2). In particular, the study of multichromophoric systems with a shape-persistent arrangement of the chromophores has gained increasing relevance since new properties may emerge from the interaction between the spatially organized units. In this context, we studied a supramolecular system constituted by four ruthenium porphyrins and a tetramer based on pyridylypyridium units.

The ruthenium porphyrin was synthesized in Prof. Elisabetta Iengo’s group (University of Trieste), whereas the pyridylypyridium derivatives (3) were synthesized in our laboratory in Bologna.

By NMR and spectrophotometric experiments it was possible to estimate the stoichiometry of the supramolecular complex: 1:1 in the case of pyridylypyridium monomer model and 1:4 for the tetramer.

The tetramer is a good water-soluble chromophore (40% quantum yield), and we were able to follow the complexation also by looking at the changes in the tetramer fluorescence and porphyrin phosphorescence. The final complex, in fact, is not emissive because of the formation of a low lying charge transfer state.

The crystal structures of the complexes have been fully resolved by X-ray measurements performed at the ELETTRA Synchrotron in Trieste.

Figure 2 Crystal structure of ruthenium porphyrins-tetramer array (a) and ruthenium porphyrin-monomer array (b).

References:
Plasmonics Applied to a Nanotheranostic System: Synthesis, Photophysical Properties and Anticancer Activity of Silica/Gold Nanoparticles

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Gold-silica nanoparticles (Ir$_1$-AuSiO$_2$) embedding a luminescent water soluble cyclometalated Ir(III) compound, Ir$_1$, with formula [(ppy)$_2$Ir(en)]CH$_3$COO (where ppy= 2-phenylpyridine and en= ethylenediamine), were synthesized (1,2) and used to promote photodynamic and photothermal action on human glioblastoma cells (U87MG). Multifunctionality of this system is the result of three contributes: i) the heavy atom promotes, through excited triplet state formation, an energy transfer process towards molecular oxygen, with generation of $^1$O$_2$, that is responsible for the photodynamic effect; ii) the overlap of the Ir(III) complex emission with gold plasmonic band (3), that allows an energy transfer towards the nanoparticles metallic core, increasing the photothermal effect; iii) the photophysical peculiarities of the Ir(III) complex, allowing an excellent emission simultaneously to the transfer processes, make the system an excellent luminescent bioprobe. Obtained results were compared with those of nanoparticles synthesized without gold core (Ir$_1$-SiO$_2$): in-vitro cell assays show a good cytotoxic effect and, when observed by confocal fluorescent microscope, an optimal resolution of this nanostructured material into cells, demonstrating that the presented approach can be successfully used in fluorescence imaging as well as a very promising biocompatible platform for the photogeneration of singlet oxygen and photothermal catalysis, achieving an all-in-one nanotheranostic system.

Fig. 1 Ir$_1$-AuSiO$_2$: a) TEM image; b) confocal image; c)thermal image

Functionalized triazolylidenes as versatile mesoionic carbenes: metal complexes for catalysis and luminescent materials

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1,2,3-Triazol-5-ylidene derivatives have recently emerged as a new class of so-called mesoionic (MICs) carbenes,\textsuperscript{(1)} and have found a wide range of applications as ligands in metal complexes.\textsuperscript{(2)} The success of this class of ligands is based on a combination of favorable features, as a result of their strong donor character and the easy preparation of the triazole precursors through the regioselective copper(I) catalyzed ‘click’ cycloaddition of alkynes with azides (CuAAC).\textsuperscript{(3)} Subsequent N-alkylation and deprotonation of the readily obtained 1,2,3-triazoles afford the desired mesoionic carbene ligands.\textsuperscript{(4)} The presence of a heteroatom in a suitable position of a substituent of the triazolylidene can lead to a bis-chelating ligand or to a ligand carrying an activating functionality. We exploited such triazolylidene mesoionic carbenes to obtain a wide set of both positive and neutral Ir(III)-complexes,\textsuperscript{(5,6)} with good luminescent performances, and neutral Ru(0)-complexes, used as active catalysts in hydrogenation reactions.\textsuperscript{(6,7)}

Copper complexes with biomimetic antioxidant activity

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The anomalous production of reactive oxygen species (ROS), generated as by-products of normal cellular metabolism, is responsible for an enhanced oxidative stress, which is ultimately associated with several disorders, chronic diseases and ageing. A major defense strategy of living systems against the ROS is represented by the antioxidant enzymes (1). These primarily belong to the superoxide dismutase (SOD) family, whose task is the disproportionation of O$_2^-$ into O$_2$ and H$_2$O$_2$. This latter oxidant is then detoxified by catalase (CAT) enzymes upon conversion into O$_2$ and H$_2$O. The active sites of the antioxidant enzymes contain metal ions as Cu(II) and Mn(III), coordinated by a set of N and O donor atoms. Despite the large availability of metal complexes showing a similar coordination environment, the efficient mimicking of the enzymatic redox activity still represents a challenging goal (2,3).

In this communication, the use of tetradentate N$_3$O tripodal ligands, for the preparation of antioxidant synthetic enzymes, will be presented. In particular, mononuclear and dinuclear copper complexes have been prepared and tested under physiological-like conditions, in order to assess their structure-dependent catalytic behavior towards SOD-like and CAT-like reactions, showing in some cases an interesting dual activity.

Moreover, since free Cu(II) ions may also be responsible for an enhanced ROS production, the ligands have been tested to scavenge these ions from an aqueous solution, in order to convert their harmful reactivity into a benign antioxidant activity, while the peroxidase-like reactivity of the resulting complexes has been evaluated in the presence of different substrates. The speciation and the stability of the complexes will be also discussed.

Mild N-Alkylation of Amines with Alcohols Catalyzed by Acetate Ruthenium Complexes

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The formation of C-N bonds for the preparation of amines compounds is a reaction of high relevance for the synthesis of bulk and fine chemicals (1). The preparation of several drug molecules involves N-substitution transformations that are usually performed by reaction of amines with alkylating agents or via reductive amination. In this context, the catalytic N-alkylation of amines using environmentally friendly alcohols as alkylating reagents and affording water as only byproduct, is an attractive atom-economic way for the C-N bond formation (2,3).

We report here the straightforward synthesis of the carboxylate ruthenium complexes of formula Ru(OAc)2(diphosphane)(CO)n (n = 0, 1). These compounds are efficient catalysts for the N-alkylation of amines using primary alcohols under mild reaction conditions, with an alcohol / amine molar ratio of 10-100. Evidence has been provided that in catalysis a monohydride species is formed through an equilibrium reaction.

![Chemical reaction diagram](image)

R = alkyl, aryl; R1 = H, alkyl
R2 = alkyl

References:
The power of ligand combination in redox active ruthenium and iron complexes.

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In recent years, cyclopentadienone complexes have drawn attention due to their air-water stability, availability from cheap starting materials, and unique catalytic features arising from the presence of a non-innocent ligand.\textsuperscript{(1)} In the meantime N-heterocyclic carbenes increased their ubiquity as ancillary ligands in catalysis and other fields due to their great potential for both easy synthesis and functionalization.\textsuperscript{(2)} Our recent research interest has been thus devoted to the development of novel ruthenium and iron based complexes combining carbonyls, cyclopentadienones and variously functionalized N-heterocyclic carbenes.\textsuperscript{(3)} These complexes can be rapidly protonated on cyclopentadienone by strong acid (e.g. HOTf) giving rise, in the case of ruthenium, to active precursors for bifunctional hydrogenation and dehydrogenation catalysis.\textsuperscript{(4)}

The straightforward synthetic method allowed the design of complexes containing hydroxyl, amino and pyridine functionalized NHC directed to the improvement of their catalytic activity, to the development of supported materials and to the preparation of water-soluble complexes. Herein, we report on the chemistry of the ruthenium complexes as bifunctional catalysts in hydrogenation and dehydrogenation with particular emphasis on the peculiar role that a basic nitrogen on the late ral chain of NHC can play on the mechanism investigated by \textit{in situ} IR and DFT calculations. Joy and pain of the shift to earth abundant iron congeners will be then described. Finally the potential of these ligand-metal combinations in biphasic catalysis, bio-derived substrate transformations, electrochemistry and bio-inorganic chemistry will be also outlined.

Synthesis of New Carbonyl Diphosphane Ruthenium Complexes for Catalytic C-H Bond Activation Reactions

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Homogeneous catalysis plays a key role in development of new chemo- and enantio-selective syntheses that point to efficiency and low environmental impact. For this purpose, great concern has been devoted to processes that employ non-toxic reagents / solvents and that can be carried out under mild reaction conditions, using low quantities of catalysts. As regards the reduction of carbonyl compounds, ketones and aldehydes are generally converted to alcohols with strongly reducing agents, namely NaBH₄ and LiAlH₄. In addition, dihydrogen at high pressure (HY) has been widely used with ruthenium based catalysts. Milder reaction conditions associated with low risks can be achieved via transfer hydrogenation (TH) using 2-propanol catalyzed by efficient ruthenium catalysts.

We report here a straightforward procedure for the preparation of a class of ruthenium carbonyl compounds RuX₂(PP)(CO)ₙ (X = Cl, OCOCH₃, OCOCF₃) (n = 0 - 2) bearing aryl and alkyl diphosphane ligands. Ruthenium hydride complexes are formed by reaction with H₂ via dihydrogen splitting or with hydrogen donor molecules. These derivatives easily react with nitrogen ligands affording efficient catalytic species for the hydrogenation and transfer hydrogenation of carbonyl compounds and other hydrogen borrowing reactions.

References:
Computational design of Sr$_2$Fe$_{1.5}$Mo$_{0.5}$O$_{6-\delta}$ (SFMO)-based bifunctional electrodes for proton-conducting solid oxide electrochemical cells

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Double perovskite Sr$_2$Fe$_{1.5}$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 overpotentials within 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.

References
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 \textit{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.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{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).}
\end{figure}

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).

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 CO₂;(1,2) Rh-CA hydrogenating CO₂ to formic acid. (3)

- Methanol dehydrogenase (MDH): Ce(III)-MDH versus Ca(II)-MDH. (4)

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*$^2$M(H)$_2$CO] complexes (M = Zr, Hf) exhibit a classical behavior ($\nu_{CO} = 2044$ and $2036 \text{ cm}^{-1}$ 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 $\rightarrow$ carbene back-donation, but according to others, the Nb-carbene bond is a pure $\sigma$ 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 ($\pm0.001$ 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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2. (a) Bortoluzzi, M.; Ferretti, E.; Marchetti, F.; Pampaloni, G.; Zacchini, S. Chem. Commun. 2014, 4472; (b) Bortoluzzi, M.; Ferretti, E.; Marchetti, F.; Pampaloni, G.; Zacchini, S. Dalton Trans. 2016, 6939.
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 candidates toward human melanoma cancer cells, due to their dual synergistic effect of the arene ruthenium chemotherapeutics and the porphyrin photosensitizer.\(^2\)

Previous studies have largely demonstrated that theoretical computations based on first-principles methods can reliably predict or reproduce 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.

References:
Comunicazioni Poster
In vitro Anticancer Activity of Diiron Vinyliminium Complexes

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Vinyliminium ligands, bridging coordinated in diiron carbonyl complexes (1,2), can undergo a variety of functionalization reactions driven by the cooperative effects of the two adjacent metal centres (Scheme)\textsuperscript{1}. The antiproliferative activity of a number of air and water stable derivatives has been assessed towards the cisplatin sensitive A2780 and the cisplatin resistant A2780cisR human ovarian carcinoma cell lines. The results will be discussed with reference to possible structure-activity relationship; in particular, those compounds containing a N-bound xylyl substituent exhibit considerable cytotoxicity.

Self-assembling peptides for regenerative medicine: structural characterization and biological properties.

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The main object of regenerative medicine is to develop novel therapies to replace or restore function to tissues and organs within the human body [1]. In this context, self-assembling peptides (SAPs) are an appealing class of materials, due to their ability to organize in nanostructures that can be successfully anchored to appropriate substrates or directly injected into a lesion [2]. SAPs are able to mimic the structure of the extra-cellular matrix (ECM), offering tridimensional support for cell growth [3,4]. Indeed, these nanomaterials, eventually functionalized with signaling biomolecules (growth factors, small adhesive peptidic sequences, glycans) may constitute a biomimetic matrix with the ability of surrounding cells and promoting specific interactions with them, in order to control and conduct their behavior by mimicking their native environment. The ideal matrix must have a 3D geometry similar to the extracellular matrix and must be able to promote cell adhesion, proliferation, infiltration and differentiation aimed at new tissue formation [4]. The realization of self-assembling peptides must include a first step of chemical and structural characterization, to check the stability of the molecular structure following the scaffold’s development. In the present study we have chemically characterized different type of peptides using X-ray photoelectron spectroscopy (XPS), Near Edge X-ray Absorption Fine Structure (NEXAFS) also in angular-dependent mode, Fourier Transform Infrared Spectroscopy (FT-IR) both in transmission and total reflection mode (IRRAS) with the aim to probe the chemical composition, molecular structure and conformation of the proposed materials. The second step of this work consists in an accurate investigation of the biological properties of SAPs and their interaction with cells. For this reason cells were cultured in the presence of the SAPs in order to assess if peptides exert cytotoxic effect and to evaluate biocompatibility, cellular adhesion and proliferation.

![Chemical structure of a self-assembling peptide](image)

References:
Thiosemicarbazones and their copper complexes: evaluation of antifungal and anti-aflatoxin activity for the development of novel plant protection products

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Food security and preservation is an ongoing major concern. It is estimated that about 40\% of the food produced worldwide is lost or spoiled. One of the most important cause of food spoilage is related to the presence of fungi, in particular of Aspergillus, Penicillium, Fusarium and Alternaria genera (1). These fungi are the principal producers of aflatoxins (AF), secondary metabolites with a severe toxic and carcinogenic potential. Concerns on food safety and environmental health, combined with the issue of emerging resistant pest strains, make urgent to develop novel crop-protective agents. Some studies suggested that metal ions can influence the growth and the mycotoxin production of the toxigenic fungi and that this effect can be related to the ability of metal ions to intervene on the pattern of gene expressions of \textit{A. flavus} (2). Metal chelation could improve lipophilicity, facilitating the penetration of the complexes into lipid membranes, and should restrict proliferation of the microorganisms. Thiosemicarbazones represent a very attractive class of metal-chelating ligand for their coordinating versatility and their known antifungal activity (3). Here the evaluation of the antifungal and anti-aflatoxin activity towards \textit{A. flavus} of some thiosemicarbazones ligands, derived from the vanillin scaffold, and of their metal complexes are presented. The metal complexes were studied both in solution and at the solid state (the complex in figure is the product of the cyclic oxidation of the ligand during the reaction with CuCl\textsubscript{2}). Tests to assess cyto- and geno-toxic effects on human cells were performed on the most active compounds. Best hits were also evaluated for their toxic and mutagenic activities on bacteria and plants cells.

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References:
De novo design of a dinuclear copper protein with diphenolase activity

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The type III copper center (T3) consists of a binuclear copper site; its main role in biology is the binding of molecular oxygen and, eventually, its subsequent activation (1).

The metal site is characterized by two magnetically coupled copper ions that bind dioxygen in a symmetric, side on ($\mu$-$\eta^2$:$\eta^2$) fashion, which exhibits unique spectral features. Each copper ion is bound in a nearly planar trigonal geometry by three histidine residues, provided by an antiparallel $\alpha$-helix pair.

Several synthetic compounds, bearing the side-on peroxo-Cu(II)$_2$ (Cu$_2$O$_2$) core, confirmed its capability to perform an electrophilic $\sigma^*$ attack to a properly oriented aromatic ring (2). Stack and coworkers have managed to recreate the core through the self-assembly of monodentate imidazole ligands and to prove its innate ability to hydroxylate phenolic substrates (3). However, the Cu$_2$O$_2$ core has not yet been reported in water under mild conditions.

To shed light on the obstacles that Nature faced in stabilizing and tuning the metal core under physiological conditions, a model peptide was designed using a de novo approach. The previously designed DFs (Due Ferro), a series of artificial proteins inspired to natural di-iron proteins, have been exploited as starting scaffold. DFs self-assemble into an antiparallel four-helix bundle dimer and bind two iron ions in the protein core (4).

The coordinating and the second sphere residues were modeled in an attempt to reconstruct a type III copper center. The final model was evaluated through MD simulations, leading to the DR1 (Due Rame) sequence.

DR1 is a dimer in the apo-form, and binds two copper ions as expected. More importantly, DR1 catalyzes the oxidation of 3,5-di-tert-butyl catechol to the corresponding o-quinone, cycling between Cu(I) and Cu(II) under mild conditions. Nevertheless, further effort should be paid for a finer positioning of the two copper ions to obtain the Cu$_2$O$_2$ core.

In perspective, the diphenolase activity of DR1 paves the way for numerous biotechnological applications in environmental technology and in pharmaceutical industries (5).

Structural characterization and reactivity of bare cis- and transplatin hydrolysis products

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Cisplatin (cis-[PtCl\textsubscript{2}(NH\textsubscript{3}\textsubscript{2}]) is a widely used antineoplastic drug, particularly effective in the treatment of lung and prostate solid tumors. Its activity relies on the interaction with the nucleobases of DNA, in particular adenine and guanine, leading to inhibition of transcription and eventually cell death.\textsuperscript{(1-3)} However, the actual active species are recognized to be the products of cisplatin aquation (substitution of Cl\textsuperscript{−} with H\textsubscript{2}O), making a matter of great interest the understanding of the reactivity of these aquated complexes.\textsuperscript{(4)} In this context, the use of a solvent-free environment permits to obtain an unambiguous characterization of these ions, while prototropic equilibria and the formation of hydroxo-bridged polinuclear complexes make hard to achieve the same result in water solution.

In this contribution we present a thorough characterization of the geometrical features of cisplatin and its geometrical isomer transplatin hydrolysis products, obtained using IR multiple photon dissociation spectroscopy in the X-H (X = C, N, O) stretch region (3000-3700 cm\textsuperscript{-1}) and quantum mechanics calculations.\textsuperscript{(5,6)} Moreover, cis- and transplatin aquated and diaquated species were mass-selected and allowed to interact with several neutral molecules in the cell of an FT-ICR mass spectrometer to obtain kinetic information about gas-phase reactivity. Chosen molecules were representatives of cisplatin binding motifs with biological targets, e.g. pyridine for nucleotides, thioanisole and dimethylsulfide for thiol-containing amino-acid residues and trimethylphosphate for ubiquitous inorganic phosphates as well as for phosphate groups present in the backbone of nucleic acids. The kinetic data showed a consistently higher reactivity for the primary aquation product of both cis- and transplatin ([PtCl(NH\textsubscript{3}\textsubscript{2})(H\textsubscript{2}O)]\textsuperscript{+}) compared with the complexes that have experienced a second hydrolysis process ([Pt(OH)(NH\textsubscript{3}\textsubscript{2})(H\textsubscript{2}O)]\textsuperscript{+}). Differences in reactivity between the cis and trans isomers are also critically discussed comparing geometrical features and employing potential energy surface calculations.

[Pt(O,O′-acac)(γ-acac)(DMS)] antitumour activity on epithelial ovarian carcinoma cells resistant to cisplatin: ¹H NMR metabolomic study

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Epithelial ovarian carcinoma (EOC) is the principal cause of death among women (1). Actually, the treatment of advanced ovarian cancer consists of combinations of a maximal surgical effort together with chemotherapeutic approaches based on the synergistic action of taxanes and various platinating agents. Unfortunately, notwithstanding such new therapeutic approaches the overall 5-year survival still remains unsatisfying, being of about 44% (2). The main problems in the treatment of EOC are the necessity of an early diagnose, together with the ability to circumvent the acquired on intrinsic resistance of some EOC tumours. For this reason, it is very important the research of valid alternatives to currently used chemotherapeutic approaches. The [Pt(O,O′-acac)(γ-acac)(DMS)], I, is a recently synthesized compound (3) containing two acetylacetonates and one dimethylsulphide (DMS) ligands in the metal coordination sphere. This complex demonstrated interesting biological activities, produced by the capability to cross efficiently the plasma cell membranes. Consistently, it was measured a cytotoxicity level more than 10 times higher than that of cisplatin. This was recognized in several cell types (4–6) where, differently from cisplatin, the involvement of non genomic targets was also identified. It clearly indicates the existence of mechanisms of action different from that of cisplatin (6). In this work, we evaluated the activity of complex I on the Skov-3 cells being an EOC cell line resistant to cisplatin. At this regard, we first made MTT assays, to evaluate the antitumour efficacy of complex I on the Skov-3 cells. Then, we examined cellular extracts and culture media, by using a ¹H NMR based metabolomic approaches, see Figure. In this way, we could identify the metabolic variations, induced by complex I on the Skov-3 cells, which show the possible pathways involved in the antitumour activity.

Passive and Active Bone-Targeting of the Pt-based Antitumor Drug Kiteplatin.

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Platinum-based antitumor drugs, such as cisplatin carboplatin, and oxaliplatin, have poor pharmacokinetic profile and their un-specific distribution in the body leads to systemic toxicity. Therefore, it is highly desirable to develop antitumor Pt-complexes with ligands specific to target the tumor site. In addition, nanoparticle formulations allow the preferential delivery of drugs to the tumor site since they can take advantage of the leaky vasculature surrounding the malignant tissue (Enhanced Permeability and Retention effect).

We have been involved in the preparation of bone-targeted platinum-bisphosphonate anticancer drugs and their subsequent loading onto inorganic silica xerogels or hydroxyapatite (HA) nanocrystals with the aim of using these matrices for the local treatment of bone tumors.(1) In the present study, we have investigated the adsorption on and the release from biomimetic HA nanocrystals of kiteplatin [PtCl\(_2\)(cis-1,4-DACH)] (DACH = diaminocyclohexane) and of its 1,1-cyclobutanedicarboxylate derivative [Pt(CBDCA)(cis-1,4-DACH)]. The release has been investigated as a function of pH to mimic the different physiological environments of healthy (including blood) and tumor tissues and the in vitro cytotoxicity of the releasates from the HA matrices has been assessed against various human cancer cell lines.(2) Moreover, active targeting of kiteplatin towards bone tumors has been pursued by preparing two new pyrophosphate derivatives that resulted to be activated at acidic pH and hence at the hypoxic and low-pH environment surrounding a tumor mass. The two kiteplatin-pyrophosphate derivatives have also been tested in vitro to assess their cytotoxicity against a panel of human tumor cell lines.(3)

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References
Valproic acid and cisplatin: comparison among different ways to combine them

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Malignant pleural mesothelioma (MPM) is an aggressive tumor of the mesothelial cells that line the pleural cavity and is associated to the exposure to asbestos fibers. The Food and Drug Administration accepted the combination of cisplatin and pemetrexed as a treatment which only partially extends the mean survival. Since epigenetic modifications play a significant role in neoplastic progression, the research aims to co-administer a drug with this function, with another chemotherapeutic. One of the epigenetic modifications is the acetylation of histones (structural components of chromatin), controlled by histone acetyltransferases and histone deacetylases (HDAC). HDAC remove the acetyl groups from the histone, increasing its association with DNA. For this reason, HDAC inhibitors can favor the binding of a drug to its DNA target. Moreover, the acetylated histones can activate the transcription of some genes with following inhibition of tumor growth and apoptosis (1).

Even though cisplatin and its analogues are important antitumor drugs, many side effects and deactivation processes occur. To overcome these limits, the higher inertness of the Pt(IV) complexes can be exploited. They are reduced to their corresponding Pt(II) active metabolite in the hypoxic and reducing tumor milieu: for this reason, they are considered produgs. Furthermore, passive Drug Targeting and Delivery (DTD) strategies can be developed to improve the selective accumulation of such species. The increased vascular permeability of the tumor tissue and the reduced drainage of the lymphatic system allow macromolecules (e.g. nanoparticles, liposomes, etc.) to extravasate and to be retained for long time. Therefore, nanosized carriers can be used as carriers of drugs towards the tumor tissue.

This work aims to combine cisplatin and valproic acid, a HDAC inhibitor. In particular, cationic liposomes containing cisplatin, valproate or the 1:2 combination of both drugs were synthesized and tested on tumor cells to evaluate if the co-administration of the two species encapsulated either into the same liposome or into separated lipid vectors allows to obtain the same antiproliferative effect of a Pt(IV) complex, containing valproates as axial ligands (Pt(IV)-diVPA in Figure). This latter proved to have a high cytotoxic activity on several tumor cell lines, higher than cisplatin(3).

References:
Anti-proliferative effects of copper(II) complexes with tridentate thiosemicarbazone ligands

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The therapeutic use of cisplatin, the drug actually employed against various types of cancer, is hampered by the presence of adverse effects and the occurrence of resistance (1,2). These reasons have stimulated extensive research towards other metal-based anti-tumor compounds with improved pharmacological properties. In this context, the use of essential metals such as copper can lead to the development of less toxic and more effective drugs (3). Thiosemicarbazones (TSCs) are a class of compounds that have been studied for a long time due to their biological properties (4). TSCs can lead to interesting compounds with potent cytotoxicity towards cancer cells and low toxicity for healthy cells, as demonstrated by the studies on Triapine\textsuperscript{TM} (3-aminopyridine-2-carboxyaldehyde-TSC), that entered phase II of clinical trials against many types of cancer (5).

Here we report the synthesis and characterization, both in solution and at the solid state, of novel copper(II) complexes of O,N,S-tridentate TSC ligands (the X-ray structure of one of them is reported in figure below). The antiproliferative activity of the complexes has been studied in two-dimensional and three-dimensional cell cultures. Cytotoxicity tests were conducted against a large panel of human tumor cell lines of different histology. The obtained data allowed to formulate some preliminary structure-activity relationships. In order to correlate the cytotoxic effect promoted by the compounds under investigation with their intracellular accumulation, cell uptake experiments were also conducted. Furthermore, we investigated the mechanism of action at the base of their anti-tumor activity in vitro by appropriate biochemical and microscopy tests.

References:
Curcumin-based Bifunctional chelators as new diagnostic tools in early diagnosis of Alzheimer’s disease.

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Alzheimer's disease (AD) is the most common form of dementia and is characterized by the formation of amyloid plaques, neurofibrillary tangles, and neurotransmitter deficits. Since age, it is the most important risk factor for AD, the rapidly aging population will further increase the number of AD patients, which will have a tremendous impact on society and the medical systems. Although several radio-tracers, especially for positron emission tomography (PET), were developed to study AD \textit{in vivo} (1), the understanding of this disease is far from complete. The accumulation of Aβ aggregates as soluble oligomers and senile plaques in the brain are key indicators of AD, hence, their presence can be exploited as a selective target for diagnostic drugs. Recently, Curcumin has shown to possess \textit{in vitro} and \textit{in vivo} high affinity for Aβ-amyloid plaques (Fig. 1) (2), and anti-AD properties due to its ability to bind and subsequently disrupt the aggregation of amyloid peptide and already formed fibrils (3).

Radiolabeled curcuminoids could be potential biomarkers for AD by means of nuclear medicine imaging techniques. In the present study, new curcumin derivatives are synthesized and completely characterized. In view of potential medical applications, their disaggregating ability for Aβ fibrillar aggregates was tested, and the most promising compounds were connected through a spacer to a polydentate macrocycle to give new curcumin based bifunctional chelators, to be used as chelating agents to bind radionuclides suitable for nuclear medicine applications. If compared with fluorine-18 and technetium-99m, gallium-68 exhibits advantageous features, being a generator produced positron emitter radionuclide with characteristics suitable for diagnostic nuclear medicine and direct labelling of biomolecules (89% β\textsuperscript{-}, maximum energy = 1.92 MeV; T\textsubscript{1/2} = 67.7 min). The new chelators were bound to nat\textsuperscript{68}Ga, complexing and labelling conditions were optimized, and complex stability was performed by means of trans-chelation and trans-metallation assays. The results will give insight into the possibility to employ these compounds as radiotracer for monitoring the presence of Aβ-amyloid plaques \textit{in vivo} by positron emission tomography.

Synthetic peroxidases for enhancing sensitivity in glucose biosensors

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In the last decades, research has been focusing on the development of biosensors, based on Glucose oxidase (GOx), for selectively monitoring blood glucose in daily management of diabetes \cite{1}. Among active nanomaterials, gold nanoparticles (AuNPs) have been extensively investigated for biosensor application due to their unique physicochemical properties. They indeed represent an efficient loading platform for immobilization of biomolecules (such as proteins, enzymes or DNA). Several studies demonstrated that AuNP-bioconjugates enhance sensitivity and selectivity of optical and electrochemical sensors \cite{2}.

Last generation glucose biosensors usually consist in bienzimatic systems, made up of GOx and Horseradish Peroxidase (HRP) as reporter enzyme. GOx oxidizes glucose and produce hydrogen peroxide, which in turn undergoes an HRP-mediated reduction, easily detectable electrochemically.

Small-sized synthetic heme-peroxidases represent valuable candidates in biosensor construction. Replacement of HRP (42 kDa) with smaller mimics may enable high sensitivity detection of analytes in samples of different nature, offering economic benefits and high efficiency.

Fe(III)-Mimochrome VIa (3.5 kDa), recently developed by us as HRP mimic, shows higher performances, in terms of reactivity and turnover number respect to the natural enzyme \cite{4}.

Here we report the development of a fast and efficient conjugation protocol of GOx and Fe(III)-Mimochrome VIa onto gold surface.

A bioorthogonal approach (Strain Promoted alkyne-azide click chemistry SPAAC) has been selected to ensure fast and quantitative conjugations \cite{5}. Preliminary catalytic and quantitative analysis demonstrated that SPAAC-mediated conjugation is more convenient respect to direct enzyme chemisorption onto AuNPs surface. In particular, higher conjugation enzyme/AuNP ratios and initial rate \((v_0)\) were observed. Protocol optimization for the co-immobilization of both enzymes on AuNPs surface is currently being evaluated.

References

Metal N-heterocyclic carbenes (NHCs) as antitumor drugs: synthesis and biological activity tests

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Cisplatin and other platinum drugs currently used in the treatment of cancer may have many drawbacks such as systemic toxicity, related resistance and tolerance mechanisms. Therefore, many efforts are being spent in the development of new metal based antitumor drugs. Among these, metal N-heterocyclic carbenes (NHCs) turned out to be particularly promising.\cite{1} NHCs manifest similar donor properties to phosphines, thus affording very stable complexes. In addition, the imidazolium salt precursors are more easily synthesized than similarly functionalized phosphines. Herein, we present the synthesis of a series of gold-NHCs and of silver precursor. These complexes are commonly known to target proteins,\cite{2} yet more recent studies also consider the interaction of gold compounds with dsDNA or G-quadruplexes.\cite{3,4} In particular, our designed complexes aim at combining gold or silver inhibition of TrxR with the intercalating activity of the NHC ligand.\cite{5,6} In this frame, the novel compounds were chemically characterized and different biochemical, biophysical and spectroscopical methods were used to characterize their interaction with target proteins, an oligonucleotide and CT-DNA. Furthermore, preliminary \textit{in vitro} studies on solid tumor cell lines were performed.

Nanostructured materials have a strong impact on nanomedicine and have attracted more scientific effort due to its scientific and social impact,(1-4) and in particular in nuclear medicine and radiation oncology, both in diagnostic and therapeutic approaches, shows new challenges with new nanomaterials. In fact, radiolabeled nanoparticles are promising tools in cancer diagnosis and therapy.(5-7) Moreover, yttrium-90 ($^{90}$Y) is a good candidate as suitable β- emitting radioisotope for a new approach to radio-guided surgery (RGS) proposed by some researchers of our group.(8) In this framework, a novel composite nanomaterials, based on poly(methylmethacrylate-co-acrylic acid), P(MMA-co-AA), embedded with yttrium ion ($^{89}$Y$^{3+}$), were developed as a first step for future production of $^{90}$Y$^{3+}$ based nanocomposites. The nanoparticles were synthesized by emulsion polymerization technique in the presence of KPS as radical initiator, using different MMA/AA molar ratio in the range 1-20%, DTPA/$^{89}$Y$^{3+}$ molar ratio 2/1, and different MMA/$^{89}$Y$^{3+}$ molar ratios, in the range 1-20%. Yttrium doped polymeric nanoparticles were characterized by means of FTIR spectroscopy, DLS and Z-potential measurements, SEM-EDX and AFM (see Fig.1). The DTPA and Y$^{3+}$ influence on morphology and dimension of composite nanoparticles were investigated, and monodispersed nanoparticles with diameters above 30-50 nm were obtained.

Coating with Poly (ε-Caprolactone)-based Hybrid Nanocomposites Synthesized Via Sol-Gel for Improvement of the Titanium Implant Biological Properties

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In the field of biomaterials, surface modifications of bioinert implants aim to improve their properties (1,2,3). The functional coatings are used to overcome early fail of the metallic implants. The aim of the present study has been to synthesize bioactive and biocompatible silica- and zirconia-based hybrid materials containing poly-ε-caprolactone (PCL) via sol-gel and use these materials to dip coat substrates of commercially pure titanium grade 4 (CP Ti gr. 4) in order to improve their biological properties. ZrO₂/PCL and SiO₂/PCL inorganic/organic hybrid materials (PCL=6, 12, 24 and 50wt%) were prepared by sol-gel process, using the zirconium propoxide and the titanium butoxide as precursor of ZrO₂ and TiO₂, respectively. Finally, a solution of Poly-ε-caprolactone (PCL) (Mw = 65000) in chloroform was added to the inorganic sol. The materials obtained, in sol phase, were used to coat CP Ti gr.4 substrates by means of the dip coating technique. The ATR-FTIR analysis has been used to study the chemical composition of the obtained coatings. Each spectrum has confirmed the formation of hydrogen bonds between the organic and inorganic phases. SEM micrographs of all coatings has shown the cracks formation, that decreased when polymer was added to the matrix and crack-free films were obtained using high PCL amounts (Figure 1(b, d)). Moreover, the apatite deposition on sample surfaces is clearly visible in SEM images recorded after SBF test. Irrespective of the matrix and PCL amount, the whole surface of all coated samples is covered by a globular precipitate and the EDS confirms that the observed layer is composed of calcium and phosphate. On the contrary, fewer globules are visible on the surface of the uncoated sample. WST-8 assay shows that the highest values of cell viability were obtained using coatings PCL-free or containing PCL 6wt%. This result can be explained by the hydrophobic nature of PCL which inhibits cells adhesion and consequently causes a decrease of cells vitality. In conclusion, the coating presence improves the bioactivity and biocompatibility of the CP Ti grade 4, especially if low amount of PCL are contained in a silica matrix. However, the PCL is necessary to obtain crack-free coatings.

FIGURE 1. SEM of (a) SiO₂, (b) SiO₂+50%PCL (c) ZrO₂ and (d) ZrO₂+50%PCL hybrid coatings

Fixation of Carbon Dioxide in Organic Carbonates Catalyzed by Bimetallic Complexes

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Carbon dioxide is an attractive, renewable one-carbon source: it is non toxic, highly abundant, relatively inexpensive, however its thermodynamic stability is the major impediment to its utilization. For this reason feasible reactions, in combination with the CO$_2$, involve highly reactive chemicals, such as epoxides (1). In particular, the transformation of epoxides and carbon dioxide into either aliphatic polycarbonates or cyclic carbonates is of commercial importance. Aliphatic polycarbonates produced by these reactions have been commercialized as adhesive, binders and coatings (2). In the same way, cyclic carbonates have numerous and interesting applications since they can be used as polar aprotic solvents, electrolytes in lithium ion batteries and intermediates in organic synthesis (3). Several metal-based catalytic systems for this reaction have been developed and in most cases dinuclear catalysts show enhanced performances compared to their related mononuclear analogues (4). For this reason in this work we decided to prepare new hexadentate dianionic ligands which will be able to host two different metallic centres (Figure 1). The new ligands scaffold allows to vary the nature of the nitrogen donors atoms (amine and imine), the substituents on the aromatic rings, and to modulate the length of the bridge in order to find the optimal distance for the cooperation between the two metallic centers. We concentrate on common metals which are either non-toxic, inexpensive, earth-crust abundant, such as iron, zinc and magnesium. The new bimetallic complexes have been employed as catalysts for CO$_2$/epoxide reactions, evaluating the effect of the reaction conditions (nature of epoxide, temperature, pressure of CO$_2$) on the productivity and selectivity of the catalytic systems.

Figure 1. Bimetallic complexes bearing new hexadentate dianionic ligands.

Autonomous supramolecular pumps fueled by light

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The bottom-up design, preparation and characterization of chemical systems that behave as molecular-scale machines and motors is a stimulating challenge of nanoscience (1). The interest on this kind of systems arises from their ability to perform a (useful) function in response to chemical and/or physical signals. In this context, the use of light stimulation has several advantages, primarily because photons can be used to supply energy to the system (i.e., write) and to gain information about its state (i.e., read) (2).

Here we will describe investigations undertaken in our laboratories aimed at photo-inducing and controlling large-amplitude molecular motions, both under thermodynamic and kinetic viewpoints, in threaded and interlocked multicomponent (supramolecular) species that comprise photoreactive units (3,4,5,6,7). This work has culminated with the design, construction and operation of a system in which light irradiation causes the relative unidirectional transit of a nonsymmetric molecular axle through a macrocycle (see Figure) (8).

As a matter of fact, this is the first example of a photochemically driven artificial molecular pump (9,10). Systems of this kind can not only lead to radically new approaches in catalysis, materials science and medicine, but also disclose unconventional routes for the conversion of light energy into chemical energy. Such applications are being investigated in the frame of the project LEAPS-Light effected autonomous molecular pumps: towards molecular transporters and actuating materials, funded by the European Research Council (Advanced Grant n. 692981).

Reaction of CO\textsubscript{2} with Epoxides Promoted by [OSSO]-type Fe(III) Complexes

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The suppression of carbon dioxide emission from anthropic activities is a hard, but mandatory, objective to reach worldwide. The reuse of carbon dioxide itself for the synthesis of chemicals, represent a valid strategy for the reduction of its concentration in the atmosphere.\textsuperscript{(1)} One of the most interesting processes studied for this purpose is the reaction of CO\textsubscript{2} with epoxides for the synthesis of cyclic organic carbonates (COCs) and polycarbonates (PCs).\textsuperscript{(2)} Recently we reported on a series of dinuclear Fe(III) complexes, based on thioeter-tri-phenolate ligands, that resulted to be efficient catalysts for the selective synthesis of COCs.\textsuperscript{(3)} To better understand the effect of nuclearity on the catalytic activity, saving the presence of sulfur neutral donor in the coordination sphere of the iron centre, we prepared a group of [OSSO]-type Fe(III) mononuclear complexes (Figure 1).

![Figure 3. [OSSO]-type Fe(III) complexes 1-4.](image)

The use of complexes 1-4, in the presence of a suitable co-catalyst, under mild reaction conditions is described in this contribution. In particular the binary catalytic system is able to selectively produce COCs when the starting reactant is an acyclic epoxide while PC is obtained if the starting epoxide is cyclohexene oxide. A DFT study was carried out to better understand the role of the metal centre in the reaction pathway.

Synthesis and thermal behavior of Sn-based lead-free nanosolders

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The potential applications of nanoalloys in different fields originates the interest in obtaining reliable thermodynamic data necessary to determine the stability of the nanoalloy systems, to develop materials property databases, as well as to carry out theoretical calculations to substantiate experimental work (1, 2). The resolution to ban the use of solders containing Pb in all new electronic devices raised considerable interest in the field of low temperature interconnect technologies and materials, mainly based on Sn incorporating Ag, Cu and sometimes Bi, Zn and other metals in varying amounts (3). The melting point of most lead-free solders is higher than the widely Sn-Pb solder (melting point 183°C) adopted in electronic devices in the past. Owing to the large surface to volume ratio and size effect, in particular concerning the melting point depression, the metallic nanoparticles (NPs), have gained an increasing attention for their application in the field of the lead-free solders (4).

In the present study AgSn and SnAgCu (SAC) nanoparticles at the eutectic composition have been successfully synthesized by a low temperature chemical reduction method. The thermodynamic characteristics of the nanocrystals have been investigated by means of differential scanning calorimetry (DSC). X-ray Diffraction (XRD) analysis and Scanning Electron Microscopy (SEM and FE-SEM) have been employed to study the morphology, microstructure and phase evolution of the as-synthesized particles before and after heating process. The formation of the phases pertaining to the binary and ternary eutectics has been confirmed by XRD analysis, and a depression melting temperature of 7-10°C was observed for both systems. The experimental results will be discussed and compared with the corresponding literature data.

Energy efficient production of hydrocarbons and formate by depolarized-anode CO$_2$ electroreduction on tailored copper nanostructures

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The electroreduction of carbon dioxide is a promising candidate for promoting high energy density storage processes and providing alternative preparation routes for fuels, energy vectors, and chemicals. On the other hand, the electrochemical reduction of CO$_2$ is an energy-intensive process, both on thermodynamic and kinetic point of view, requiring extensive studies on electrocatalytic structures. Copper-based electrocatalysts have the almost unique characteristic to reduce carbon dioxide to C1-C3 hydrocarbons and alcohols but the activities and stabilities are rather low (1). Modifications of the copper surface as well as alloying can potentially improve the electrocatalytic performance; furthermore the face index of the electrocatalyst have a huge effect on selectivity (2,3). In this study, plain metallic copper is modified by additive (copper electrodeposition) and subtractive (electrochemical faceting) roughening and structure and performance of those materials is evaluated by material investigation and product analysis in a alkaline membrane electrolizer, demonstrating the possibility of driving the selectivity towards hydrocarbons or formate depending on the type of electrochemical roughening treatment applied. In particular, it was observed that the electrochemical faceting on copper drove the selectivity towards methane while increasing the total faradaic efficiency compared to plain polycrystalline copper surface. The electrodeposited copper sample maintained almost the same selectivity of the plain copper, instead, but with higher total faradaic efficiency. In addition the electrochemical reduction of carbon dioxide at the cathode is coupled with (bio)alcohol selective (4) partial oxidation at the anode, leading to a reduction of the electrical requirements of the reaction and opening a route for the production of acetate from ethanol (4). The total cell potentials for carbon dioxide electrolysis when using sacrificial (bio)ethanol ranges from 1.6 to 1.8V, compared to almost 4V when a state-of-the-art water-splitting anode is employed. The energy consumption of the entire system, assessing the ethanol energy cost at an EROEI (Energy Return on Energy Invested) value of 8 is almost half of the traditional CO$_2$ electrolysis cell with a total energy efficiency of 50%.

![Figure 1: left: SEM micrographs of Cu electrodeposits generated by EP process on a Cu foil surface and right: SEM micrographs of surface defects generated by ECF on a Cu foil surface (Conditions: f=0.25 Hz; 15 h)](image)

Preparation of novel hydrophobic cellulosic composites containing Silver (I) acylpyrazolonato

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The surface modification of cellulose is central for a fast growing area of applications, since most vegetable-derived natural polymers are renewable materials, some of them displaying properties comparable to those of petroleum derived products. (1) The preparation of highly hydrophobic cellulose based materials is particularly important in the field of food packaging. Most materials used for food packaging applications are still produced from fossil fuels, so non-renewable and also nearly non-biodegradable, therefore representing an environmental problem. (2) In order to prepare hydrophobic cellulose, the hydroxyl groups are chemically modified, due to their reactive nature compared to the rest of the molecule. To date, fluorochemicals are usually employed for this purpose. These compounds impart not only hydrophobicity, but also oil and stain repellency. (3) However, longer fluoroalkyl chains have bio-accumulative potential in living organisms since their tendency to oxidation towards highly persistent pollutants. (4) For this reason, in this work, an alternative to the already existing processes for the preparation of hydrophobic cellulose is provided. Novel composite materials based on cellulose and Silver(I) acylpirazolonato complexes have been prepared for this aim. Since Silver (I)-based compounds are highly toxic to microorganisms, as proved recently by a class of new complexes based on acylpyrazolone synthesized and tested on some antibacterial family. (5) In this work, pure and functionalized cellulose are used as substrate for the deposition of silver complexes obtained through coordination with different acylpirazolonato ligands able to promote both covalent chemical bonds and/or van der Waals interactions with the substrate. These ligands are chosen in order to facilitate the interaction of the resulting complexes with the hydroxyl groups on the cellulose surface. Once the cellulose composites containing Silver(I) acylpyrazolonato are obtained, the hydrophobicity of this modified cellulose is going to be evaluated by many different methodologies, also addressed to control the stability, biodegradability and biocompatibility of the new synthesized silver-based composites.

Improved size-tunable synthesis of gold nanorods and surface functionalization strategies for biomedical applications

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Gold nanorods (AuNRs) are attracting interest for biomedical applications due to their unique optical and electronic properties which are dependent on their shape and size. Compared to spherical nanoparticles, AuNRs possess a strong adsorption band in the near-infrared region of the electromagnetic spectrum. Since biological tissues show minimal light adsorption in this spectral region, AuNRs may additionally allow the investigation of nanoparticle targeting\textsuperscript{(1)} and biodistribution via tissue imaging\textsuperscript{(2)} using near-infrared light. The most common method to produce AuNRs is seed-mediated synthesis involving the use of cetyltrimethylammonium bromide (CTAB) to control aspect ratio.\textsuperscript{(3)} Nevertheless, CTAB is known to be highly cytotoxic.\textsuperscript{(4)} It tightly adsorbs on the AuNR surface and it is difficult to be removed without causing aggregation. Yet, the ability to completely remove CTAB while maintaining colloidal stability are key requirements for AuNR application in vivo.

\textbf{Figure:} SEM micrograph of PEGylated AuNRs

In this contribution, we describe the improved synthesis of monodisperse AuNRs with different aspect ratio and the optimization of surface functionalization strategies to replace CTAB with biocompatible surface modifiers such as ω-functionalized PEG-thiols developed in our group.\textsuperscript{(5)} We report the physicochemical characterization of these systems and demonstrate that the PEG-based passivation layer allows to fully abolish cytotoxicity. We finally show that mixed self-assembled monolayers of ω-functionalized PEG-thiols can be exploited for simple conjugation of a precise number of biologically active molecules onto the AuNRs. We envision a great potential for these functionalized AuNRs as safe nanomaterials for biomedical applications.

References:
Functional dipyrrins for a multi-purpose task: chemical sensing and energy transfer investigations

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The synthesis of multifunctional π-electron systems with specific photophysical properties represents a goal for researchers both in synthetic chemistry and materials science. In this framework, opportunely functionalized chromophores like porphyrins or bodipys can be considered high versatile tools for multifunctional applications such as artificial light harvesting supramolecular architectures or as chemical sensors for the detection of contaminants in solution. Despite many reports dealing with the use of porphyrin or bodipy systems, their subunits such as dipyrrin are only rarely used for photometric metal detection (1). Indeed, these classes of molecules due to their photophysical properties and for their high coordination constants with metal ions and then their optical feedback upon coordination, are excellent candidate for achieving new fast, cheap and sensitive chemical sensors. Based on these considerations, recently we focused our attention on the synthesis of new molecules opportunely functionalized with uracil and/or the acetylated diamino pyridine moieties for detection of contaminant such as melamine and/or metal ions in solution. The spectroscopic investigation has been carried out using a combination of UV/Vis absorption, static and time-resolved fluorescence, and 1H-NMR. Furthermore, in the case of bodipy molecules, the presence of the two complementary groups able to interact by hydrogen bonding allow the formation of an heterodimer that could be an interesting system to investigate the role and the mechanism of long-lived quantum coherence phenomenon in electronic energy transfer (EET) in artificial photosynthetic light harvesting systems (LHs) (2, 3,4).

Ring Opening Metathesis Polymerization promoted by ruthenium benzylidene complexes with unsymmetrical NHC ligands

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Olefin Metathesis is one of the most important catalytic transformations for the formation of carbon-carbon double bonds.(1) The metathesis reaction involving the polymerization of cyclic unsaturated monomers is known as ROMP (Ring Opening Metathesis Polymerization) and is nowadays implicated in the production of several industrially important polymers, such as Norsorex and Vestenamer.(2)

Due to their non-symmetric nature, Grubbs second generation catalysts bearing unsymmetrical N-heterocycle carbene (u-NHC) ligands are particularly efficient in the copolymerization of norbornene (NBE) with cys-cyclooctene (COE) and cyclopentene (CPE).(3) Recently in our group new u-NHC ruthenium catalysts 1 and 2 have been synthesized (figure 1). These catalysts, bearing two phenyl groups with syn or anti configuration on backbone positions, have been investigated in several metathesis transformations, showing valuable activity and selectivity.(4) Moreover these two isomers have exhibited a very different catalytic behavior, thus demonstrating the important role of backbone configuration also for u-NHC ruthenium catalysts, according to the literature regarding other families of metathesis catalysts.(5)

![Figure 1: Ruthenium catalysts with backbone substituted u-NHC ligands](image)

In this contribution we discuss the reactivity of 1 and 2 in the copolymerization of NBE with CPE and COE. This represents nowadays a very challenging scope, being the copolymerization promoted by backbone substituted u-NHC catalysts still totally unexplored.

References:
Laser treatment of tattoo pigment PG-36

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Worldwide, tattooed population has been significantly increasing for a long time, especially among young people (1). To date, because of an improved self-image or social stigmatization, we simultaneously observe the opposite tendency: many tattooed individuals undergo a therapy of tattoo removal, the most common removal pathway being treatment with Q-Switch laser. In spite of this, few though remarkable investigations have been carried out aimed at understanding the tattoo inks decomposition patterns (2-3). Inks are typically made of two components: the pigment and the vehicle. In the present study, we investigate the chemical processes, and the morphological changes following the laser and ultrasound treatment of the pigment commercially known as PG36, a fully halogenated copper-phtalocyanate, with formula C$_{32}$H$_{16}$Br$_6$Cl$_{10}$N$_8$Cu (Fig. 1a) which imparts yellowish green color to some of the most common inks on the market. Laser treatments were carried out with a Nd:YAG laser, operating at 532 nm, with a fluence of 50 mJ/mm$^2$, on two different dispersions of the pigment, i.e. in isopropanol and in water. The decomposition fragments were, then, analyzed by GC-mass. The morphology variations were monitored by Scanning Electron Microscopy. In Fig. 1b) and c) the SEM micrographs are reported before and after 30 minutes sonication of the pigment with

![Fig.1](image)

The ultrasound treatment, change the morphology from the typical $\beta$ arrangement of the phthalocyanine aggregates to roundish agglomerates. The rearranged compound still contain Br and Cl, though it cannot be inferred whether a fragmentation occurred.

We found out that the laser treatment yields very complex fragmentation patterns, which include the generation of toxic fragments such as BrCN and ClCN, regardless of the dispersion solvent.

References:
Analysis of molecular structure, spectroscopic properties (FT-IR, micro-Raman and UV–vis) and quantum chemical calculations of free and ligand 4 amino pyridine acid in metal halides (Zn, Hg and Cd)

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Organic-inorganic hybrid compounds have paid more and more attention in the solid-state materials chemistry due to their significant applications in the field of optics, ionics, mechanics, energy, environment, biology and medicine. Those applications include a new generation of photovoltaic and fuel cells, photo-catalysts, sensors, functional smart coatings, smart membranes and separation devices, micro-optical and photonic components. Especially the materials based to halogenated metals such as Zn, Hg, and Cd, etc... present very interesting physical properties (1,2,3) and these materials show good results due to their electronic properties and extended structure, with strong interaction between the atoms, ions or molecules which occur throughout the lattice system.

In this study we report the synthesis of a series of novel organic inorganic hybrid compound (C₅H₇N₂)₂MCl₄ (M = Zn, Hg, Cd). The crystal structure, vibrational, and optical properties were characterized by X-ray diffraction (XRD), Raman and infrared spectroscopy, UV–vis absorption studies, the structural properties and vibrational frequencies have been investigated extensively using density functional theory (DFT). We will explain more about crystal packing and hydrogen bonds in these compounds in details.

References

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Cyclopropane containing compounds represent a class of very active molecules which often display biological and pharmaceutical characteristics (1,2). One of the most sustainable and atom-efficient methodologies to synthesise cyclopropanes is the one pot reaction of diazo compounds with alkenes forming N\textsubscript{2} as the only stoichiometric by-product (Scheme 1).

![Scheme 1. General scheme of cyclopropanations.](image)

Amongst all the applied catalysts, iron porphyrins, which show a cheap, eco-friendly and very active metal centre, have recently received a lot of attention also because they mimic the catalytic activity of enzymes containing an iron-heme unit.

We recently reported on the catalytic activity of C\textsubscript{2}-symmetrical Fe\textsuperscript{III}(1)OMe complex which was efficient in promoting cyclopropanations with excellent diastereoselectivity and enantioselectivities (3,4).

In order to increase the bio-compatibility of iron porphyrin-catalysed cyclopropanations, the binaphthyl chiral unit of 1 was replaced by an amino ester functionality. The three new C\textsubscript{2}-symmetrical iron porphyrin amino ester conjugates 2-5 were synthesised and fully characterised including the X-ray crystallographic analysis of 5 (Scheme 2) (5).

Fe\textsuperscript{III}(porphyrin)(OMe) complexes were tested in the reaction of \(\alpha\)-methylstyrene with different diazo compounds, which afforded corresponding cyclopropanes with an excellent diastereoselectivity (trans/cis ratio up to 93:7) but with modest enantioselectivity. The DFT study, which was carried out to rationalise the lack of the reaction enantiocontrol, indicated that chiral amino acid residues were not effective to select an enantiomeric pathway because they were too far from the catalytic active metal centre.

![Scheme 2. Synthesis of porphyrins 3, 4 and 5.](image)

References:

Selective oxidation of alkenes by H$_2$O$_2$ catalysed by well-defined [Iron(III)(Pyridine-Containing Ligand)] complexes

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The introduction of a pyridine moiety into the skeleton of a polyazamacrocyclic ligand affects both thermodynamic properties and coordination kinetics of the resulting metal complexes (1). These features have engendered a great interest of the scientific community in recent years. The applications of pyridine-containing macrocyclic ligands ranges from biology to supramolecular chemistry, encompassing MRI, molecular recognitions, materials and catalysis. Much of the efforts in the use of macrocyclic pyridine containing ligands have been devoted to the study of catalytic oxidation reactions. We report here the synthesis and characterization of [Fe(III)Pc-L’s] complexes (Pc-L = Pyridine-Containing Ligand) and their catalytic applications in alkene epoxidation or cis-dihydroxylation reactions using H$_2$O$_2$ as the terminal oxidant under mild conditions (Figure). Depending on the anion employed for the synthesis of the iron(III) metal complex, we observed a completely reversed selectivity. When $X = $ OTf, a selective cis-dihydroxylation reaction was observed. On the other hand, employing $X = $ Cl, we obtained the epoxide as the major product (traces of aldehyde were observed at very high conversions). It should be pointed out that under otherwise identical reaction conditions, using FeCl$_3$·6H$_2$O as catalyst in the absence of the ligand, no reaction was observed.

![Figure](image)

**Figure** Selective epoxidation or cis-dihydroxylation of alkenes catalysed by well-defined [Iron(III)(Pyridine-Containing Ligand)] complexes.

**Key words:** macrocyclic ligands, homogeneous catalysis, iron, oxidation reactions.

References:
New quinoline-based chiral ligands and their Eu(III) complexes

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Luminescent complexes of Eu(III) and Tb(III) soluble in alcohol and water have been extensively exploited in biomedical field, as their excited states (in particular the ones of Tb(III) ion) are less sensitive to non-radiative vibrational quenching caused by high energy oscillators (such as OH) (1). This behaviour gives rise to reasonable values of the luminescence quantum yield. In addition, when a lanthanide complex is designed for biomedical applications, a strong overall luminosity or Brightness (B) is required, \( B = \varepsilon \cdot \phi \), where \( \varepsilon \) is the molar absorption coefficient and \( \phi \) the luminescence quantum yield. B can be increased if the ligand is capable to strongly absorb the exciting light and efficiently transfer the excitation energy to the lanthanide ion (\textit{antenna effect}). In the presence of a chiral Ln(III) environment, the metal may also display circularly polarized luminescence (CPL), a chiroptical phenomenon, which has found interesting applications such as chirality sensing (2,3) and medical imaging techniques (4).

In this contribution we focus our attention on the synthesis and the characterization of new chiral ligands containing the quinoline fragment (Figure 1) and their Eu(III) complexes. We also discuss in detail, the luminescence spectroscopy of this complexes in the solid state and in solution of alcohol and water.

\textbf{Figure 1.} Molecular structure of the ligand discussed in the present contribution

Stacking motives and solid state interactions of methylene blue cation in three unreported chloromercurate salts

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Methylene blue (MB) is a renowned organic cation whose properties find application in a remarkably high number of science branches. The molecule, mostly used as chloride salt, whose formula structure is reported in Fig. 1 (left), features three condensed aromatic rings and two terminal dimethylamine groups, and its +1 charge is delocalized on the whole structure, with the only exception of the terminal methyl groups. This peculiar electronic panorama has important consequences on the physical and chemical properties of the molecule.

Fig. 1. (Left) Formula structure of MBCl. (Right) Ortep view of (MB)CuCl₂ compound.

Aside from the many applications of MB in solutions, its properties in the solid state are less investigated. We recently reported (1) the first evidence of its coordinative capability by describing two crystalline phases in which MB is coordinated, together with two Cl atoms, by a Cu and an Ag metal centers respectively, resulting in two (MB)MCl₂ complexes (M= Cu, Ag). (See Fig. 1 (right)). This capability is due to the presence, on the middle aromatic N atom, of a localized partial negative charge which confers to the nitrogen lone pair a crucial Lewis basicity. Remarkably, we showed how this behavior is observed only in the solid state, sustained by supramolecular packing effects. Along with this recently discovered feature, actually, MB showed interesting supramolecular behaviors, since its arrangement in solid phases can vary depending on the other surrounding species.

Here we report studies on the behavior of MB towards mercury chlorometallates, undertaken to gain information regarding the MB-anion interactions, the overall packing features and how these influence the properties of the observed crystals. Three different compounds involving MB and [HgCl₃]⁻, [HgCl₄]²⁻ and [HgCl₃]ₙ⁻ chains respectively as anionic counterparts, have been synthesized by solid state reactions and structurally characterized by single crystal X-Ray diffraction. Remarkably, in the crystal packing of the three compounds, MB shows completely different stacking arrangements depending on the geometrical features and hindrance of the inorganic moiety. In the first case the π-stacking of the MB molecules is organized in a head-to-tail fashion. This is likely to be the most stabilizing geometrical configuration between different MB, because it allows the best match between the most positively and negatively charged part of the molecule (the S and the middle N atoms respectively). In the second case, the π-stacking is limited to MB dimers, arranged in a head to tail fashion as in the previous case. Dimers are packed together in a zig-zag fashion, and different MB pillars form square-shaped channels where the anions are accommodated. In the third case, MB arranges in head-to-head stacking, since the S atoms are oriented in the same direction. MB forms infinite pillars, each pillar being separated from the others by [HgCl₃]ₙ⁻ polymeric chains and nitromethane molecules.

References:
Chemical and electrochemical water oxidation catalyzed by iridium complexes

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Water oxidation to molecular oxygen is a key half reaction in natural photosynthesis because it provides protons and electrons that can be exploited for the reduction of carbon dioxide to carbohydrates. Inspired by this natural process, people are intensely interested in water splitting using sunlight to convert and store solar energy into chemical energy (1). However, the efficiency of an artificial photosynthetic apparatus seems to be limited by the still unsatisfactory performance of the water oxidation catalytic pool. In our efforts to develop efficient water oxidation catalysts (WOCs), we recently reported hydroxy-pyridine-carboxylate iridium complexes (Figure 1) that exhibit remarkable activity in WO, when CAN (2) and NaIO\textsubscript{4} (3) were used as sacrificial oxidants.

Figure 4. Water oxidation catalysts

Particularly, OH-containing complexes showed a similar TOF (23−28 \text{ min}^{-1}), which was more than two times greater than that of pic (complex without OH), with CAN. Whereas the catalytic activity strongly depended on the position of the OH-substituent in the pyridine ring and pH with NaIO\textsubscript{4}. The highest catalytic activity was observed for pic, which, at pH 7, showed a record TOF of 458 \text{ min}^{-1} (3). More recently we found that complexes reported in Figure 1 are also active in electrocatalytic water oxidation. Also in this case, their performances were affected by the “oxidant” nature. When an ITO working electrode was used, catalytic activity was dramatically influenced by the position of the OH group substituent; on the contrary similar performances were obtained with a gold electrode.

Syntheses, Structural characterization and chromotropism study of mono and dinuclear copper(II) complexes containing chelating ligand of 2-methyl-N-(pyridine-2-yl-methyl) propane-2-amine

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Chromotropism is defined as a reversible color change of the materials caused by the surrounding chemical or physical stimulus; the stimuli could be solvent (solvatochromism), temperature (thermochromism), pressure (piezochromism), light (photochromism), pH (halochromism), ion (ionochromism) or electrons (electrochromism). Chromotropism has attracted much attention because of the wide variety of potential applications as thermosensitive materials, imaging, photoswitching materials, sensor materials, molecular switches, pollutant sensors and Lewis-acid-base color indicators. A combination of metal-ion recognition moieties with appropriate ligands has been reported to afford metal-ion responsive chromotropic molecules. Among chromotropic metal complexes, copper (II) ion with a combination of chelate ligands have been recognized as the most promising candidates for practical applications due to their high thermodynamic stabilities, accessibility of other oxidation states and also existence of simple and regular changes in their electronic spectra according to the strength of the stress imposed to the system (1,2,3). Here, a series of mono and dinuclear copper(II) complexes with chelating ligand of 2-methyl-N-(pyridine-2-yl-methyl)propane-2-amine, in which demonstrated distinctive solvato- and thermom- iono and halochromism properties is presented. The mechanism of the chromotropism in these compounds is discussed in detail.

References
Dependence of the second order NLO response of 5,15 *meso* push-pull Zn$^{II}$ diarylporphyrins on complex aggregation phenomena

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A series of 5,15 *meso* push-pull Zn$^{II}$ diarylporphyrins, carrying one or two –COOH or –COOCH$_3$ acceptor groups and a –OCH$_3$ or a –N(CH$_3$)$_2$ donor group (Figure 1) show in both DMF and CHCl$_3$ solution a negative and solvent dependent second order NLO response measured by the EFISH technique (1), different from the structurally related Zn$^{II}$ porphyrins carrying a –N(CH$_3$)$_2$ donor and a –NO$_2$ acceptor group, for which a still solvent dependent, but positive EFISH second order response was previously reported (2). Moreover, when a –N(CH$_3$)$_2$ donor group and a –COOH acceptor group are part of a sterically hindered 2,12 push-pull β-pyrrolic substituted Zn$^{II}$ tetraaryl porphyrin, the EFISH response is positive and solvent independent. In order to rationalize these rather intriguing series of observations, EFISH measurements have been integrated by electronic absorption and infrared spectroscopic investigations and by DFT and CP-DFT theoretical and $^1$H PGSE NMR investigations, which prompt that the significant concentration effects and the strong influence of the solvent nature on the NLO response are originated by a complex variety of aggregation processes induced by the –COOH group (Figure 2).

Gold(III) bis-di(N-heterocyclic carbene) square planar trications as receptors towards halogen anions

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NHC gold complexes are attractive for several applications, like for example catalysis, medicinal chemistry or material science. In this regard, while the examples of di(NHC) ligands coordinated to gold(I) centers are frequent, the number of gold(III) complexes remains still limited. We report here on the synthesis of mononuclear tricationic bis-di(NHC) gold(III) complexes, isolated by transmetalation of the ligand from the corresponding silver(I) complex to KAuBr\textsubscript{4}. The counteranion of the gold(III) cationic complex depends on the adopted synthetic procedure. In the solid state, these complexes present interactions between the gold center and the halides of the counteranions, so that the geometry around gold is distorted pseudo-octahedral. Most interesting this interaction is maintained also in solution, thus suggesting the application of these compounds in anion sensing.\textsuperscript{(1,2)} Titration studies with halides and DFT calculations clarified the formed species and the nature of the Au···X interaction.

References:
Globular molecular platinum carbonyl nanoclusters

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Homoleptic Pt-CO clusters can be grouped into two main categories depending of their CO content: (a) CO-rich clusters, the so called Chini clusters; (b) CO-poorer species, which can be referred as globular molecular platinum carbonyl nanoclusters or "platinum browns" (1). Globular platinum carbonyl clusters with almost regular structures may be viewed as molecular models of ultra-small metal nanoparticles (2). When defects are introduced, these respond with localized deformations which tend to eliminate and repair such defects (3). In addition, high-nuclearity platinum carbonyl clusters exhibit a rich redox chemistry: they undergo several reversible one-electron oxidation and reduction processes affording relatively stable species. In this respect, they may be viewed as molecular nanocapacitors and electron sinks (4).

Two general strategies are known for the preparation of globular Pt carbonyl nanoclusters: (a) thermal decomposition of \([\text{Pt}_{3n}(\text{CO})_{6n}]^2− (n = 2-8)\) Chini clusters; (b) oxidation/reduction of preformed platinum browns (5). Herein, we report the synthesis and structural characterization of globular molecular platinum nanoclusters with nuclearities ranging from 14 up to 44 Pt atoms. Their metal cores may adopt \textit{pp} (pentagonal prismatic), \textit{bcc}, \textit{ccp}, \textit{hcp} or twinned \textit{hcp/ccp} structures. Indeed, at these sub-nanometric length-scales there is not a clear structure/size relationship, being the overall structure the result of the balance of M-M and M-ligand interactions (6).

Salts and cocrystals assembled from noncovalent associations between carboxylic acids and bases containing aromatic and aliphatic polyamine

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Multicomponent crystals and organic acid-base complexes have received considerable attention over the past few years (1). The design and construction of multicomponent supramolecular arrays utilizing noncovalent bonding is a rapidly developing area in supramolecular synthesis. Thus, the supramolecular synthesis successfully employs hydrogen-bonding, halogen-bonding and the other types of noncovalent interactions, in building supramolecular systems (2,3). In the course of a wide-ranging study concerning the solid state aggregation of polyarboxylic acids and polyamines at different solvothermal conditions and under pH control, we obtained several supramolecular complexes with total partial or without proton transfer depending on $\Delta pK_a$ values. We will present a series of supramolecular structures and some associate ab-initio calculations.


Antitumor activity of [Pt(O,O'-acac)(γ-acac)(DMS)] in MG-63 human osteosarcoma cells

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Osteosarcoma (OS) is the most common malignant mesenchymal neoplasm amongst adolescents. Today, the regimen of methotrexate, adriamycin, and cisplatin (MAP) has become standard in North America and Europe. Despite this, an important number of patients will still develop fatal metastatic disease or serious complications of treatment, emphasizing the need for further clinical advancements.

In the present study, we investigated the potential citotoxicity of [Pt(O,O'-acac)(γ-acac)(DMS)] (Ptac2S), a Pt(II) drug having non genomic targets, on the MG-63 human osteosarcoma cell line. Ptac2S been tested in various cancer cells in opposition to cisplatin and results affirm that it induces fast and strong apoptosis death of cancer cells (1-3).

MG-63 cell were treated with various concentrations of Ptac2S and cisplatin and then cytotoxicities were assessed by using an 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenol tetrazolium bromide (MTT) assay. The citotoxicity of Ptac2S is approximately twelvefold greater than that observed for cisplatin (with IC50 of 4.5 ± 0.8 µM and 46.1 ± 3.2 µM for Ptac2S and cisplatin, respectively). Subsequent experiments, aimed at understanding the mechanisms of cell death triggered by Ptac2S, were made using a single concentration of Ptac2S (5 µM) and cisplatin (50 µM). It was found that Ptac2S provoked the activation of caspase-9 and -7 after 6 h treatment, whilst cisplatin provoked the activation of caspase 3 and -7 after 24 h treatment.

In conclusion, this study show that also in OS cells Ptac2S is far more citotoxic than cisplatin and that meanwhile both compounds provoked apoptosis, the activated caspases are different and the Ptac2S-provoked process is much more rapid.

References


Apoptosis by [Pt(O,O'-acac)(γ-acac)(DMS)] requires p53 activation in Malignant Pleural Mesothelioma

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Mesothelium cancer cells have epithelioid or sarcomatoid morphology. The worst prognosis is associated with sarcomatoid phenotype and resistance to therapy is affected by cells heterogeneity. We recently showed that in ZL55 mesothelioma cell line of epithelioid origin [Pt(O,O'-acac)(γ-acac)(DMS)] (Ptac2S) has an antiproliferative effect in vitro and in vivo. Aim of this work was to extend the study on the effects of Ptac2S on ZL34 cell line, representative of sarcomatoid mesothelioma. ZL34 cells were used to assay in vivo the antitumor activity of Ptac2S in a mouse xenograft model and, in vitro, the involvement of p53 protein in (a) the processes underlying the sensitivity to chemotherapy and (b) the activation of various transduction proteins involved in apoptosis/survival processes. Ptac2S increases ZL34 cell death in vivo compared with cisplatin and, in vitro, Ptac2S was more efficacious than cisplatin in inducing apoptosis (Figure). In Ptac2S-treated ZL34 cells, p53 regulated gene products of apoptotic BAX and anti-apoptotic Bcl-2 proteins via transcriptional activation (1).

Results confirm that Ptac2S is a promising therapeutic agent for malignant mesothelioma (2), giving a substantial starting point for its further validation.

References
Ruthenium(III) complexes entrapped in liposomes with enhanced cytotoxic and anti-metastatic properties

D. Tesauro\textsuperscript{a}, M. E. Cucciolito,\textsuperscript{b} R. Iannitti,\textsuperscript{c} R. Palumbo,\textsuperscript{c} G. Morelli,\textsuperscript{a} F. Ruffo,\textsuperscript{b} A. D'Amora\textsuperscript{b}

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Metal-based anticancer drugs are pivotal in the fight against cancer pathologies. Since 1978 cis-platin was licensed for medical treatment of a wide number of tumor pathologies (1). However its chemotherapeutic use is strongly limited by many and severe side effects and acquired tumor resistance. Since these limitations could be overcome by other metal complexes, in the last thirty years ruthenium compounds have been tested showing a remarkable antitumoral and antimetastatic activity associated with a lower toxicity. A hexacoordinate Ru(III) complex (NAMI-A) is currently undergoing advanced clinical evaluation (2). All data indicate that NAMI-A acts as a pro-drug, but the integrity of ruthenium complexes is essential to store the cytotoxic activity. In this scenario the condition of administration of ruthenium drugs are crucial to exploit their anticancer activity (3). In the last years innovative strategies have been produced to vehicle ruthenium ions in tumor cells like aggregates. This study aims to incorporate the ruthenium complexes in the inner aqueous compartment of liposomes and to test biological properties of two NAMI-A like pyridine derivatives. Specifically, we have investigated the pyridine derivatives of the sodium-compensated analogue of NAMI-A, Na[\textit{trans}-RuCl\textsubscript{4}(pyridine)(DMSO)] (NAMI-Pyr) and Na[\textit{trans}-RuCl\textsubscript{4}(Pytri)(DMSO)] (NAMI-Pytri). In the latter complex the pyridine ligand is functionalized with a sugar moiety so as to increase biocompatibility and the ability to cross the cell membrane. The stability of the complexes was studied and compared in solution at different pH following UV-VIS spectra. Lipid formulations based on Egg PC were prepared adding Cholesterol, DSPE-PEG\textsubscript{2000} joining molar ratio 57/38/5\% w/w respectively in MeOH/CHCl\textsubscript{3} (50/50 v/v) mixture and hydrated with 0.9\% w/w of NaCl. This composition was selected to reproduce analog supramolecular aggregates in clinical use to vehicle doxorubicin (Doxil). Ruthenium complexes were loaded into liposomes using the passive equilibration loading method. Full drug containing liposomes were structurally characterized by dynamic light scattering (DLS) measurements. Data indicate the formation of stable aggregates with size and shape in the right range for \textit{in vivo} applications. The amount of encapsulated ruthenium complexes was quantified by means of ICP-AES. Stability and drug release properties of ruthenium containing liposomes were confirmed in buffer. The growth inhibitory effects of both liposomal and free complexes drug were tested on prostate cancer cells (PC3). Preliminary results show high cytotoxic effect of ruthenium complexes delivered by supramolecular aggregates with respect to free complexes drug.

References:
# Elenco degli Autori

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