ENANTIOSELECTIVE ELECTRODES
BASED ON INHERENTLY CHIRAL MOLECULAR MATERIALS

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The availability of materials coupling electroactivity with enantiorecognition capability is an attractive objective in materials research. The usual strategy, hinging on attaching chiral pendants to an electroactive polyconjugated backbone, generally results in modest chirality manifestations. We have thus designed electroactive chiral polyheterocycles, where chirality is not external to the electroactive backbone, but inherent to it, resulting from a tailored torsion produced by the periodical presence of atropisomeric, conjugatively active biheteroaromatic scaffolds. This affords enantiopure electroactive films of impressive chiroptical activity; moreover, since the stereogenic element coincides with the electroactive site, chirality manifestations can be finely and reversibly tuned by the electric potential, since progressive injection of positive charges forces the atropisomeric scaffold angle to regularly decrease to favour delocalization. Such deformations are elastic and reversible (CD spectroelectrochemistry).

In order to test the enantiorecognition ability of the new enantiomeric electrodes, we have in the last months developed a protocol in ionic liquid medium affording preparation of very reproducible electrode surfaces on screen printed electrode supports. The resulting specular R and S electrodes have been tested in the presence of (R)-(+) and S-(−)-N,N-dimethyl-1-ferrocenylethylamine specular probes. The response is highly and reproducibly enantioselective (with even more than 100 mV separation between R and S probes, either with single enantiomers and with the racemate), specular for R vs S surfaces with respect to S and R probes, and reversible in repeated alternating sequences of S and R probe sensing on a single electrode.