

Achieving Effective Inherently Chiral Electroanalysis on Chiral and Achiral Electrodes

The usual approaches to chiral electroactive molecular materials, relying on attaching chiral pendants to an electroactive polyconjugated backbone, generally result in modest chirality manifestations; other approaches, such as chiral templating agents, chiral counteranions, *etc.* actually imply the chirality source to be external to the electroactive material. Very recently, we have unveiled by electrochemical experiments the unprecedented enantioselectivity properties of molecular films based on a new family of "inherently 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 [1-2] (*e.g.* 3,3'-bibenzothiophene [as in the antipodal monomers (*R*)- and (*S*)-BT₂-T₄, Fig. 1], 2,2'-biindole and 3,3'-bithiophene). In this way both the stereogenic element responsible for chirality and the electroactivity source coincide with the main molecular backbone; this unique threefold identity enhances the functional properties of the material and connects them together as well. Thus, unprecedented results are being obtained in chiroptical and electroanalytical experiments with inherently chiral electroactive films [1-3]; in particular, inherently chiral electrode surfaces have been proposed as a tool opening the way to chiral voltammetry, especially for enantiodiscrimination and enantiomeric excess quantification of pharmaceutically relevant probes, in aqueous and nonaqueous achiral media [3] (Fig. 2).

By analogy, high enantioselectivity can be expected to be achievable as well by implementing inherent chirality in the working medium. Ionic liquids look ideal for such implementation: for example they are intrinsically much more ordered than organic solvents.

Considering the outstanding enantioselectivity obtained with inherently chiral surfaces, we have started to investigate whether the inherently chiral concept can also yield enantioselectivity when implemented in ionic liquids, supporting electrolytes or even simple additives.

This study is still in its early stage, but preliminary tests carried out on achiral electrodes seem to indicate that, also in this case, huge enantioselectivity could be achieved by applying the inherent chirality concept (Fig. 3).

References

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