

"Inherently Chiral" Electrode Surfaces and Media: Attractive Alternative Approaches to Enantioselective Electroanalysis

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Enantioselective electroanalysis, implying the ability to discriminate the enantiomers of chiral molecules in terms of electrode potentials, necessarily implies the electron transfer process on which the recognition is based to take place in asymmetric conditions. This can be achieved by the use of either a chiral electrode surface or a chiral medium. Among the many approaches so far proposed, a groundbreaking strategy was recently introduced [1], based on the use of "inherently chiral" molecular materials, either as electrode surfaces [2-5] or as media [6]. The peculiarity of inherently chiral molecular materials is that the same element endows the molecule with both its key functional property and with chirality, coinciding with the main molecular backbone, featuring a tailored torsion; this results in outstanding chirality manifestations.

Thus, electrooligomerization of enantiopure inherently chiral electroactive monomers, based either on biheteroaromatic atropisomeric cores combined with thiophene-based wings or on thiahelicene scaffolds, yields enantiopure inherently chiral electrode surfaces, on which impressive peak potential differences are observed in voltammetric experiments for the antipodes of chiral probes, even quite different in structure and electrochemical activity, and of pharmaceutical interest.[1-5]

Large differences in peak potentials can also be achieved for the enantiomers of different chiral probes working on achiral electrodes, but in suitable inherently chiral media. For instance, inherently chiral ionic liquids ICILs have been prepared from atropisomeric 3,3'-bicollidine, resolved into antipodes without chiral HPLC and converted into long-chain dialkyl salts with melting points below room temperature. Both the new ICILs and shorter family terms that are solid at room temperature, employed as low-concentration additives in achiral ionic liquids, result in impressive peak potential differences, regularly increasing with additive concentration, for the enantiomers of different probes on achiral electrodes. [6]

Work is in progress to strengthen and rationalize the first proofs of concepts by developing, characterizing and testing a wider variety of inherently chiral inductors (both monomers for electrode surface preparation and ionic liquids/additives) with different chiral probes.

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