Strategies for High Enantioselectivity on Achiral Electrode Surfaces: Implementing Inherent Chirality in Electrode|(Ionic Liquid) Interfaces

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Chiral electroanalysis could be regarded as the highest recognition degree in electrochemical sensing, implying the ability to discriminate between specular images of a given electroactive molecule in terms of significant peak potential difference. Since enantiomers have identical physico-chemical properties, the electron transfer process must take place in asymmetric conditions, exploiting a suitable chiral selector, such as a chiral electrode or a chiral medium. A groundbreaking strategy was recently proposed, based on the use of inherently chiral molecular selectors, either electrode surfaces [1] or media [2]. Inherent chirality implies the chirality source of the chiral selector to be neither localized nor external, but intrinsic to the whole main molecular backbone, featuring a tailored torsion; this can result in outstanding chirality manifestations. Thus, large differences in peak potentials have been observed for the enantiomers of different chiral probes working on achiral electrodes, implementing inherent chirality at their interface with an ionic liquid medium, [2] exploiting the latter's peculiarly high order. To this aim we developed inherently chiral ionic liquids ICILs as double salts of an atropisomeric 3,3′-bipyridine scaffold with long alkyl chains and a suitable anion, resulting in melting points below room temperature. However, we found it even more convenient to employ the new ICILs, as well as other family terms solid at room temperature, as low-concentration chiral additives in commercial achiral ionic liquids: impressive peak potential differences, regularly increasing with additive concentration, have been observed for the enantiomers of different probes on achiral electrodes. Comparable results have also been obtained with other inherently chiral additives (bibenzimidazolium double salts and a thiahelicene derivative). Work is in progress to strengthen and rationalize the recognition mechanism. In this light we have found a strictly connection between our ICILs and liquid crystals; in fact our additives seem to induce a “chiral domino effect” at the electrode interface like the nematic to cholesteric transition in liquid crystals. We have also performed a physico-(electro)chemical characterization of new families of chiral ionic liquids CILs in order to compare their electrochemical properties and enantioselection performance with our ICILs.

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