Strategies for High Enantioselectivity in Electroanalysis: Implementing Inherently Chiral Selectors as Electrode Surfaces or at Electrode|Ionic Liquid Interfaces

Patrizia R. Mussini,*[1] Serena Arnaboldi[1], Mirko Magni[1], Sara Grecchi[1], Tiziana Benincori[2], Simona Rizzo[3], Emanuela Licandro[1], Silvia Cauteruccio[1], Francesco Sannicolò[1]

[1]Università degli Studi di Milano, Dip. di Chimica, Via Golgi 19, 20133 Milano, Italy,
[2] Università degli Studi dell'Insubria, Dip. di Scienza e Alta Tecnologia, Como, Italy
[3] Istituto di Scienze e Tecnologie Molecolari, CNR, Milano, Italy
E-mail: patrizia.mussini@unimi.it

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.

A groundbreaking strategy was recently proposed, based on the use of "inherently chiral" molecular selectors, *i.e.* with chirality and key functional properties originating from the same structural element. Large differences in peak potentials have been observed for the enantiomers of different chiral probes:

(a) working on inherently chiral electrode surfaces consisting of thin electroactive oligomer films[1] (often including macrocycle terms) electrodeposited from enantiopure inherently chiral monomers with atropisomeric or helical scaffolds;

(b) working on achiral electrodes, implementing inherent chirality in their interphase with an ionic liquid medium[2] exploiting the latter's peculiarly high order. Inherently chiral ionic liquids ICILs were developed as double salts of an atropisomeric 3,3′-bipyridine scaffold with long alkyl chains and a suitable anion, Even more convenient, the new ICILs as well as other family terms solid at room temperature but of easier synthesis, or other inherently chiral salts, can be efficiently applied as low-concentration chiral additives in commercial achiral ionic liquids: large peak potential differences, regularly increasing with additive concentration, have been observed for the enantiomers of different probes on achiral electrodes.

Work is in progress to strengthen and rationalize the first proofs of concepts by developing, characterizing and testing a wider variety of inherently chiral selectors with different chiral probes, particularly of pharmaceutical interest, with more optimized and detailed protocols, and with the support of other techniques, particularly aiming to the recognition mechanism elucidation..

The inherent chirality research is currently supported by Regione Lombardia and Fondazione Cariplo (Avviso congiunto per l'incremento dell'attrattività del sistema di ricerca lombardo e della competitività dei ricercatori candidati su strumenti ERC-edizione 2016, Project 2016-0923).

1 *Angew. Chem.*, **2014**, 53, 2623. *Chem. Eur J.* **2014**, 20, 15298; *Chem. Sci.* **2015**, 6, 1706; *Anal. Bional. Chem.* **2016**, 408, 7243; *Chem. Eur J.* **2016**, 22, 10839
2 *Angew. Chem.* **2017**, 56, 2079; *Electrochem. Comm.* **2018**, 89, 57.