

Full-page Abstract Sample (Chirality2017)

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

Serena Arnaboldi¹, Tiziana Benincori², Silvia Cauteruccio¹, Emanuela Licandro¹,
Mariangela Longhi¹, Rocco Martinazzo¹, Simona Rizzo³,
Francesco Sannicolò¹, Patrizia R. Mussini¹

¹Univ. degli Studi di Milano, Dip. di Chimica, Via Golgi 19, 20133 Milano, Italy.

²Univ. degli Studi dell'Insubria, Dip. di Scienza e Alta Tecnologia,
Via Valleggio 11, 22100 Como, Italy

³Istituto di Scienze e tecnologie Molecolari, CNR, via Golgi 19, 20133 Milano, Italy.
patrizia.mussini@unimi.it

Enantioselective electrochemistry, implying the ability to discriminate the *enantiomers* of chiral molecules in terms of electrode potentials (in electroanalysis), or to selectively activate or achieve a given enantiomer of a chiral molecule through the electrode potential (in electrosynthesis), necessarily implies the electron transfer process 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.

The support of Fondazione Cariplo/Regione Lombardia "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) is gratefully acknowledged.

References

1. *Angew Chem. Int. Ed.* **2014**, *53*, 2623-2627.
2. *Chem. Eur. J.* **2014**, *20*, 15298-15302.
3. *Chem. Sci.* **2015**, *6*, 1706-1711.
4. *Anal. Bional. Chem.* **2016**, *408*, 7243-7254.
5. *Chem. Eur. J.* **2016**, *22*, 10839-10847
6. *Angew Chem. Int. Ed.* **2017**, *56*, 2079-2082.