Enantioselective voltammetry on achiral electrodes

Serena Arnaboldi,[a] Patrizia Mussini,[a] Sara Grecchi, [a] Mirko Magni,[a] Francesco Sannicolò,[a] Silvia Cauteruccio[a], and Simona Rizzo[c]

[a] *Dipartimento di Chimica, Università degli Studi di Milano, Via Golgi 19, 20133 Milano, Italy*
[b] *Istituto di Scienze e Tecnologie Molecolari, CNR, via Golgi 19, 20133 Milano, Italy*
serena.arnaboldi@unimi.it

An attractive target in electroanalysis is the availability of chiral media affording enantioselection in terms of significant peak potential difference between the antipodes of chiral probes in voltammetry experiments on achiral electrodes.

Previous literature attempts pointed to enantioselectivity increasing with the structural order of the chiral medium; on the other hand, outstanding enantioselection performance has been recently observed working on electrode surfaces consisting in "inherently chiral" oligomer films [1-2].

Combining both strategies, we have recently developed two inherently chiral ionic liquids, ICILs, consisting of dialkylated bicollidinium salts, with an atropoisomeric bipyridinium cation featuring at least one octyl chain and bistrifilimide counteranions. They showed high enantioselectivity when tested even as low concentration additives in commercial achiral ionic liquid media [3] and also as chiral bulk media.

Importantly, similar ability was also shown by other terms of the same family, having shorter alkyl chains and/or different counteranions, solid at room temperature but of easier synthesis. As a first tentative explanation we are considering the high supramolecular order of even simple ionic liquids at the interphase with a charged surface. A chiral additive could result in chiral reorganization of this peculiar interphase, as in the case of nematic-to-cholesteric transitions induced by chiral dopants in liquid crystals.

This allowed us to include in our chiral voltammetry experiments a quite larger number of inherently chiral selectors based on different stereogenic elements, *i.e.*, the bicollidine and bibenzimidazole atropoisomeric scaffolds and the tetrathielicene helicoidal scaffold. They all proved successful.

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.

[1] F. Sannicolò, S. Arnaboldi, T. Benincori, V. Bonometti, R. Cirilli, L. Dunsch, W. Kutner, G. Longhi, P. R. Mussini, M. Panigati, M. Pierini, S. Rizzo, *Angew. Chem. Int. Ed.* **53** (2014) 2623
[2] S. Arnaboldi, P. Mussini, M. Magni, F. Sannicolò, T. Benincori, R. Cirilli, K. Noworyta, W. Kutner*, Chem. Sci*. **6** (2015) 1706
[3] S. Rizzo, S. Arnaboldi, V. Mihali, R. Cirilli, A. Forni, A. Gennaro, A. A. Isse, M. Pierini, P. R. Mussini, F. Sannicolò, *Angew. Chem. Int. Ed* **56** (2017) 2079