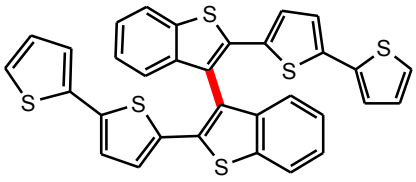
Enantiorecognition performances of "inherently chiral" film electrodes: a successful first example with planar-chirality probes

Patrizia Mussini,[a] Serena Arnaboldi,[a]Giorgio Tomboni,[a] Mirko Magni?,[a] Francesco Sannicolò[a]
Heinrich Lang,[b] Marcus Korb[b],Tiziana Benincori[c]

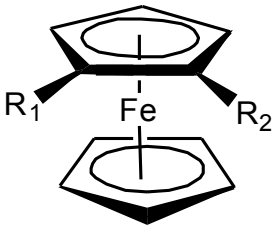
[a]*Università degli Studi di Milano, Dipartimento di Chimica,Via Golgi 19,20133 Milano,*
[b]*Technische Universität Chemnitz, Straße der Nationen 62, 09111 Chemnitz, Germany*
[c]*Univ. degli Studi dell'Insubria, Dip. di Scienza e Alta Tecnologia, Via Valleggio 11, 22100 Como, Italy*
patrizia.mussini@unimi.it

Enantiorecognition in voltammetry is a quite attractive target, implying a superior selectivity degree, which necessarily requires the electron transfer to take place in a chiral interphase environment, exploiting a chiral electrode surfaces or a chiral medium. Many approaches have been proposed, but unfortunately however most of them suffer from some drawback, like complex preparation, high cost and/or lack of robustness...., but above all, in most cases, they result in current differences between the two enantiomer of chiral probes, while a difference in peak potentials would be the desirable feature for enantiorecognition purposes.[1,2]

In this context, we have recently reported the outstanding performances of "inherently chiral" electrodes prepared by fast and reproducible electrodeposition of a thin film of thiophene-based oligomers from "inherently chiral" monomers like BT_2T_4 (right) [3-6]. "Inherent chirality" implies that chirality and key functional properties originate from the same structural element; in the cited monomer cases, this is obtained by a tailored torsion in the conjugated electroactive system, with an energy barrier too high to be overcome at room *T*, so that the monomer exists in two stable enantiomers. Upon electrooligomerization of the (*R*)- or (*S*)- enantiomer, electroactive oligomer films are obtained, including linear and cyclic terms of different dimensions, and fully retaining the monomer configuration. Testing such electrode surfaces in chiral CV experiments with chiral probes, neat differences in peak potentials are observed for the enantiomers of chiral probes even of significantly different structure, specular upon inverting the film or probe configuration. The property appears to be of general character, testing a first small series of probes of different structures, even of pharmaceutical interest [3-6] (and also working on achiral electrodes in inherently chiral ionic-liquid based media[7,8]).



Of course, it is important to widen the range of investigated cases. One issue concerns testing probes having *other stereogenic elements than stereogenic centres* (which is the most current occurence, as in our first tested cases), considering for instance axial chirality, helical chirality, and planar chirality.



In this presentation we will focus on the latter case, for which convenient, electrochemically reversible model probes are provided by disubstituted ferrocene scaffolds like the one shown on the left (with $R_1 \neq R_2$).

Successful and reproducible chiral voltammetry tests with a first couple of such planar chirality examples on oligo BT_2T_4 films nicely confirm the general character of the successful inherent chirality electrode strategy.

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References: 1. *Curr.Op.* 2018, 7, 188-199 2 *Curr. Op.* 2018, 8, 60-72 3. *Angew. Chem. Int. Ed.* 2014, 53, 2623. 4. *Chem. Eur. J.* 2014, 20, 15298. 5. *Chem. Sci.* 2015, 6,1706. 6. *Chem. Eur.*2016 , 22,10839. 7. *Anal. Bioanal. Chem.* 2016, 408, 7243. 8. *Angew Chem.*2017 9. *Electrochem. Comm*. 2018, 89, 57-61

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