

# Highly Enantioselective "Inherently Chiral" Film Electrodes at Work

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The usual approaches to chiral electroactive molecular materials, relying on attaching chiral pendants to an electroactive polyconjugated backbone, generally result in modest chirality manifestations; other approaches, such as chiral templating agents, chiral counteranions, *etc.* actually imply the chirality source to be external to the electroactive material.

Very recently, our research group has unveiled by electrochemical experiments the unprecedented enantioselectivity properties of molecular films based on a new family of "inherently chiral" polyheterocycles, where chirality is not external to the electroactive backbone, but inherent to it, resulting from a tailored torsion produced by the periodical presence of atropisomeric, conjugatively active biheteroaromatic scaffolds (*e.g.* 3,3'-bithiophene [as in the monomers (*R*)- and (*S*)-BT<sub>2</sub>T<sub>4</sub> represented in Figure 1], 2,2'-biindole and 3,3' bithiophene). [1]

The electroactive films obtained by electrooligomerization mostly consist of cyclic electroactive oligomers, constituted by several fully conjugated thiophene units.

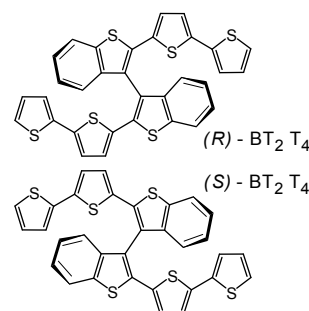
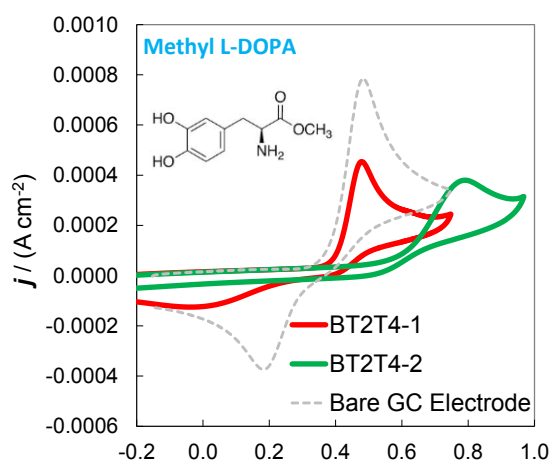


Figure 1



**Figure 2.** An example of the outstanding enantiodiscrimination of the chiral electroactive probe methyl L-DOPA by our chiral antipode electrode surfaces.

These ringlets, which can also be obtained by chemical oligomerization, are endowed with an outstanding pool of attractive properties both as racemates and as enantiopure antipodes. [1,2] The neat peak separation for two enantiomers of electroactive chiral probes (Figure 2) together with the linearity of the peak currents with enantiomer concentration affords estimation of the enantiomeric excess when both enantiomers are present [3].

The new electrodes have been tested with very good results towards several chiral probes, quite different in molecular structure and of applicative interest, on different supports, and in different media. Moreover, we have verified that the same spectacular enantioselectivity is obtained on surfaces prepared starting from monomers designed according to the same structural concept but chemically different, which demonstrates the general validity of the new strategy.

Albeit preliminary, such unprecedented outstanding results open the way to chiral voltammetry.

## References

- [1] F. Sannicolò, S. Arnaboldi, T. Benincori, V. Bonometti, R. Cirilli, L. Dunsch, W. Kutner, G. Longhi, P. R. Mussini, M. Panigati, M. Pierini and S. Rizzo, *Angewandte Chemie Int. Ed.*, 2014, 53, 2623
- [2] F. Sannicolò, P. R. Mussini, T. Benincori, R. Cirilli, S. Abbate, S. Arnaboldi, S. Casolo, E. Castiglioni, G. Longhi, R. Martinazzo, M. Panigati, M. Pappini, E. Quartapelle Procopio and S. Rizzo, *Chemistry-A European Journal*, 2014, 10, 15261
- [3] S. Arnaboldi, P. Mussini, M. Magni, F. Sannicolò, T. Benincori, R. Cirilli, K. Noworyta and W. Kutner, *Chemical Science*, 2015, 6, 1706