Inherently Chiral, Highly Electroactive Macrocyclic Oligothiophenes: A New Class with a "*Portfolio*" of Outstanding Potentialities

Patrizia R. Mussini*[1], Francesco Sannicolò[1], Serena Arnaboldi[1], Tiziana Benincori[2],
Sephira Riva[1], Elisa Lo Bello[1], Valentina Marino[1], Mirko Magni[1]
[1]Dip.di Chimica, Univ. degli Studi di Milano, Via Golgi 19, 20133 Milano, Italia.
[2]Dip. di Scienza e Alta Tecnologia, Univ. degli Studi dell'Insubria,
via Valleggio 11, 22100 Como, Italia
patrizia.mussini@unimi.it

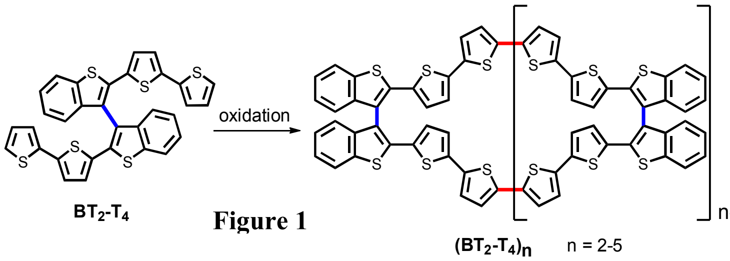


Figure 1

We have recently introduced[1,2,3] an entirely new class of chiral oligothiophene macrocycles, easily accessible by either chemical or electrochemical oxidation of monomers, like the BT$_2$-T$_4$ one in Figure 1 (*taken from ref. 3*), endowed with "inherent chirality". Such property stems from a tailored torsion in the main conducting backbone,[1,2] corresponding to a high rotational energy barrier. Thus the monomer can be separated into stable enantiopure antipodes, whose chirality is entirely transferred to the corresponding cyclic oligomers.

The new molecules possess an uncommon pool of outstanding properties even as racemates. For example:

- they idealize conducting polymers without end, that is, without defectivity connected with free terminals;
- in CV and EIS experiments they exhibit very fast and reversible electron transfer and charge transport;
- their HOMO and LUMO levels, which are modulable with the multiplicity and length of the monomer units in the cyclic oligomer, appear convenient for application in devices like bulk heterojunction solar cells;
- they are electrochromic;
- they exhibit (negative) photocurrent activity.

Most impressive, however, are the properties as enantiopure antipodes, possibly as a consequence of the unique coincidence of the source of both chirality and electroactivity with the entire main conducting backbone, which affords *inter alia* to reversibly modulate chiroptical properties by electrochemical polarization.

The enantiopure oligomers exhibit:

- impressive optical rotatory power;

- impressive circular dichroism signals, which can be finely and reversibly modulated by the electrical potential ("breathing chirality");
- remarkable circularly polarized luminescence (CPL);
- outstanding enantiorecognition ability.

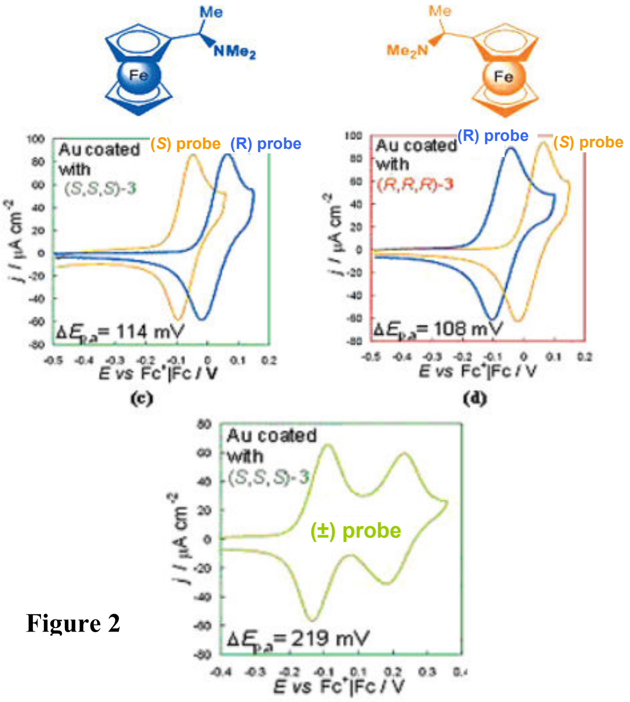
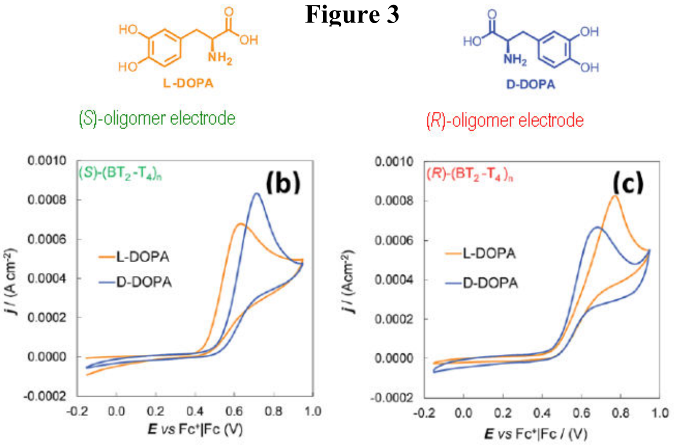


Figure 2

In particular, we have recently highlighted[3] their applicative potentialities as low-cost and easy-to-prepare artificial enantiopure electrode surfaces, which display an unprecedented ability to pronouncedly separate voltammetry peaks of enantiomers of quite different chiral probes, including the model ferrocenyl one in Figure 2 (*adapted from ref. 2, and where 3 stays for the BT_2-T_4 cyclic trimer*), or of applicative interest (*e.g.* pharmaceutical ones like DOPA, *Figure 3 from ref. 3*), concurrently with linear dynamic ranges for peak currents, affording enantiomer excess determination, particularly on disposable SPEs, testing small drops of enantiomer solutions.

Figure 3



It is also remarkable that, while usual chiral recognition methods are based on selectors of natural origin and therefore available as a single enantiomer, this approach offers availability of both selector enantiomers.

Thus inherently chiral enantiopure electrodes can indeed be regarded as a key to chiral voltammetry.

With the contribution of Fondazione Cariplo, grant no.2011-0417
Patent deposited MI2014A000948-23/05/2014

References:

[1] F. Sannicolò, P.R. Mussini, T. Benincori, S. Arnaboldi, M. Panigati, E. Quartapelle Procopio *et al.*, *Chem. Eur. J.* 2014, 20, 15298 – 15302.

[2] F. Sannicolò, S. Arnaboldi, T. Benincori, P.R. Mussini, M. Panigati *et al.*, *Angew. Chem. Int. Ed.* 2014, 53, 2623 –2627.

[3] S. Arnaboldi, T. Benincori, R. Cirilli, W. Kutner, M. Magni, P.R. Mussini, K. Noworyta, F. Sannicolò, *Chemical Science*, 2015, 6, 1706–1711.