



GS 2015

in memoria di Marco Mascini

Sensori e biosensori: stato dell'arte e nuove prospettive

BOOK OF ABSTRACTS

Parma, 15-17 giugno 2015

"INHERENTLY CHIRAL" ELECTRODES: TOOLS FOR CHIRAL VOLTAMMETRY AND ENANTIOMERIC EXCESS EVALUATION

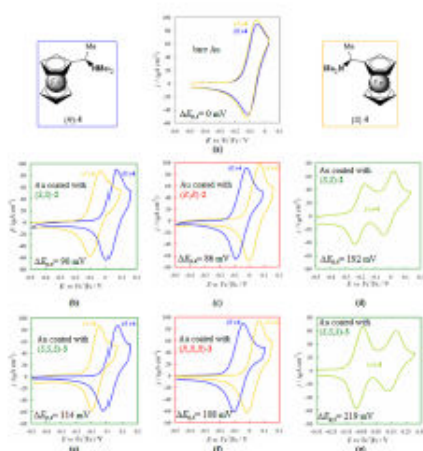
Patrizia R. Mussini¹, Serena Arnaboldi¹, Francesco Sannicolò¹,
Rocco Martinazzo¹, Tiziana Benincori², Roberto Cirilli³

¹Dip. di Chimica, Università degli Studi di Milano, Via Golgi 19, 20133 Milano, patrizia.mussini@unimi.it

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

³Dip. del Farmaco, Istituto Superiore di Sanità, Via Regina Elena 299, 00161 Roma

The development of artificial "intelligent" electrodes, capable to discriminate and quantify the enantiomers of chiral analytes, particularly of biological and pharmaceutical interest, is a quite attractive issue in electroanalysis. Obviously, selectivity towards specular molecules can only be achieved on enantiopure chiral electrodes. For this aim, many approaches have been proposed in the last years. However, even the most successful attempts at chiral discrimination almost invariably resulted in the detection of a difference in current intensity between the signals of the two antipodes of a chiral probe, without differentiation of their redox potentials; the chiral enantioselective layer is in many instances not of general use, but tailored for a given probe; many preparation procedures are very sophisticated and/or the active films fragile. A winning solution comes from a new class, which we have recently presented¹⁻³ and patented⁴, of "inherently chiral" molecular semiconductors, whose stereogenic element is a tailored torsion in the electroactive conductive backbone. The coincidence of the element granting both electroactivity and chirality with the entire molecular backbone results in extraordinary chirality manifestations (such as circularly polarized luminescence), that can be finely and reversibly tuned by the electric potential. Above all, enantiopure electrode surfaces can be easily prepared e.g. by fast electrooligomerization, mostly consisting of cyclic oligomers, highly electroactive and chiral, idealizing conducting polymers



without ends and of high complexing ability; they are able to discriminate enantiomers of chiral molecules in terms of large peak potential differences (80-200 mV and more), with linear dynamic ranges for peak currents, thus affording enantiomeric ratio evaluation. The same spectacular enantioselectivity is obtained on chemically different surfaces of the same structural concept, which demonstrates the general validity of our proposed strategy. A simple reconditioning protocol affords performing more experiments on a single electrode.

The new electrodes have been tested with very good results on chiral probes even very different and of applicative interest³ (Dopa and methyl-Dopa [see our parallel presentation] ofloxacin, norepinephrine, tyrosine, naproxen, catechines, ascorbic acid...), on different supports, including commercial screen printed ones, and in different media (aqueous and nonaqueous ones, as well as small ionic liquid drops on SPEs).

This work was supported by Fondazione Cariplo (Grant no. 2011-0417)

References

1. F. Sannicolò, S. Arnaboldi, T. Benincori, V. Bonometti, R. Cirilli, L. Dunsch, W. Kutner, G. Longhi, P.R. Mussini, M. Panigati, M. Pierino, S. Rizzo, *Angew. Chem. 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, S. Rizzo, *Chem. Eur. J.* 2014, 20, 15296..
3. S. Arnaboldi, T. Benincori, R. Cirilli, W. Kutner, M. Magni, P.R. Mussini, K. Noworyta, F. Sannicolò, *Chemical Science*, 2015, 6, 2041.
4. F. Sannicolò, P.R. Mussini, S. Arnaboldi, T. Benincori, R. Cirilli et al., Patent appl. MI2014A000948 (2014)