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K13b. Inherently chiral electrodes, the effective tool for chiral voltammetry

Patrizia Romana Mussini, *a Serena Arnaboldi, a Francesco Sannicolò, b Tiziana Benincori, bWłodzimierz Kutner, c and Krzysztof Noworyta

^a Dip. di Chimica, Università degli Studi di Milano, Via Golgi 19, Milano, 20133, Italia b Dip. di Scienza e Alta Tecnologia, Università degli Studi dell'Insubria, via Valleggio 11, 22100 Como, Italy c Institute of Physical Chemistry, Polish Academy of Sciences (IPC PAS), Kasprzaka 44/52, 01-224 Warsaw, Poland

*patrizia.mussini@unimi.it

An attractive issue in electroanalysis is the development of artificial "intelligent" electrodes, capable to discriminate as well as quantify the enantiomers of chiral analytes, particularly of biological and pharmaceutical interest. 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 presented and patented, of "inherently chiral" molecular semiconductors, in which the coincidence of the element granting both electroactivity and chirality with the entire molecular backbone results in extraordinary chiroptical manifestations, which can be finely and reversibly tuned by the electric potential. Above all, enantiopure electrode surfaces can be easily prepared e.g. by electrooligomerization; they mostly consist of cyclic oligomers, highly electroactive and chiral, idealizing conducting polymers without ends and of high complexing ability.

Such electrode surfaces 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 interest² (Dopa, methyl-Dopa, 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).

As an interesting alternative strategy to effective enantiodiscrimination, preliminary results about inherently chiral ionic liquid media applied on achiral electrodes will be also presented.

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References

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