Azahelicenes: an Attractive Family of Inherently Chiral Electroactive Molecular Tools

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Achieving enantiodiscrimination in analytical, preparative or smart device experiments with chiral electroactive molecules at the electrochemical interphase requires the local presence of a suitable chiral selector, which can be implemented at the electrode surface or in the medium [1-4]. Outstanding performances can be achieved exploiting *inherently chiral* molecules, in which both chirality and key functional properties originate from the same element, corresponding to the main molecular backbone, featuring a tailored torsion with a racemization energy barrier too high to be overcome at room temperature. Inherently chiral selectors of *axial* stereogenicity, based on atropisomeric biheteroaromatic cores, have been very successfully applied in many enantiodiscrimination experiments, to prepare chiral surfaces (*e.g.* [5,6]), chiral devices (*e.g.* [4,7]) as well as chiral media (*e.g.* [8]). Inherently chiral selectors of *helical* stereogenicity also look quite attractive; for example, successful enantiodiscrimination has been obtained on electrodes modified with enantiopure films electrodeposited from tetrathiahelicene, a helical conjugated molecule consisting of condensed thiophene and benzene rings with thiophene terminals [9].
In this context very promising are also azahelicenes, a family of electroactive helical molecules consisting of condensed benzene and (at least one) pyridine rings [10,11]. They are attractive not only in themselves, but also as they can be converted by N alkylation into molecular salts, the melting point of which can be remarkably lowered by suitable alkyl chain length and counter anion choice, which is very interesting in the perspective of new inherently chiral ionic liquid media and/or additives. We will discuss the electrochemistry of a group of mono and diazahelicenes, as a function of the condensed ring number, of the number and positions of the nitrogen atoms, and of the partial or total alkylation of the nitrogen sites. We will also present and discuss voltammetry enantiodiscrimination experiments with different chiral probes, based on azahelicene selectors implemented as chiral additives in achiral ionic liquid media.

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