

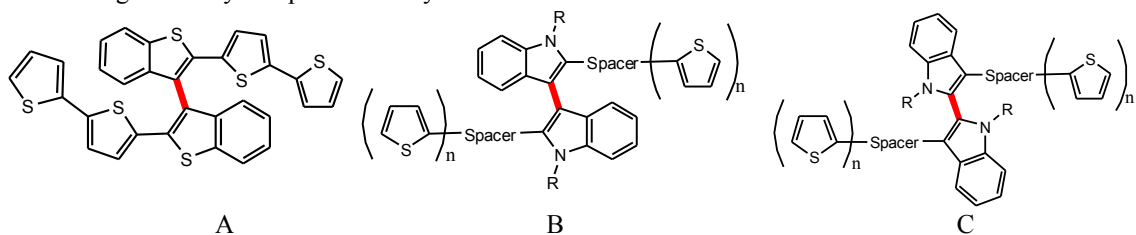
**Electrochemistry of inherently chiral molecular materials  
with bisindole atropisomeric cores:  
interacting equivalent redox sites, configurational stability,  
and enantioselection ability for different chiral probes**

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In "inherently chiral" molecules chirality and key functional properties originate from the same structural element, and are thus strictly linked together. In the case of poly(hetero)aromatic electroactive molecules, this can be achieved by inserting in the main conjugated backbone a tailored torsion with an energy barrier too high to be overcome at room temperature, while not entirely hampering conjugation. This strategy results in outstanding chirality manifestations, including *e.g.* circularly polarized luminescence as well as outstanding enantioselective ability in CV experiments. For instance, large peak potential differences were observed for the enantiomers of different chiral probes on electroactive surfaces obtained by electrooligomerization of inherently chiral monomers having atropisomeric (= with hindered rotation between two moieties) bibenzothiofene (Fig 1A) or bithiophene cores. [1-4]. An interesting option is also to change the thiophene-based atropisomeric cores with 2,2'-bisindole and 3,3'-bisindole ones (Fig 1B and 1C), on account of the easy functionalization of the core *e.g.* with long alkyl chains, modulating solubility and processability.



**Figure 1** R = H or C<sub>1</sub>-C<sub>6</sub> alkyl chains; Spacer = phenyl or nothing (oligothiophene wing attached to core)

The change also leads to quite interesting modifications in the electrochemical activity. Since indole is electron richer than thiophene, the first two oxidations take place at significantly less positive potentials than in the former cases, and are localized on the two interacting moieties of the bisindole core rather than on the terminal wings; thus, they are chemically reversible (oligomerization can be achieved cycling around the third oxidation peak). A peculiar attractive feature concerns the interaction between the two equivalent redox centers in the biindole core, which can be evaluated from the potential difference between the corresponding oxidation peak: it can be shown that it can account for the atropisomeric energy barrier (depending on the 2,2' or 3,3' connectivity and on the N-alkyl substituents), and is also modulated by temperature and the solvent polarity. Thus electrochemistry can provide information on the torsional energy barrier and on the enantiomer stability, as confirmed by other approaches.

Besides the intrinsic interest of these inherently chiral families, they are also quite attractive from the applicative point of view, since enantioselective test on films obtained by electrooligomerization of the more stable 2,2' monomers yield large potential differences for the antipodes of very different chiral probes, also of pharmaceutical interest.

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