

Chiral Electrochemistry

Introducing the Inherent Chirality Concept in Ionic Liquids

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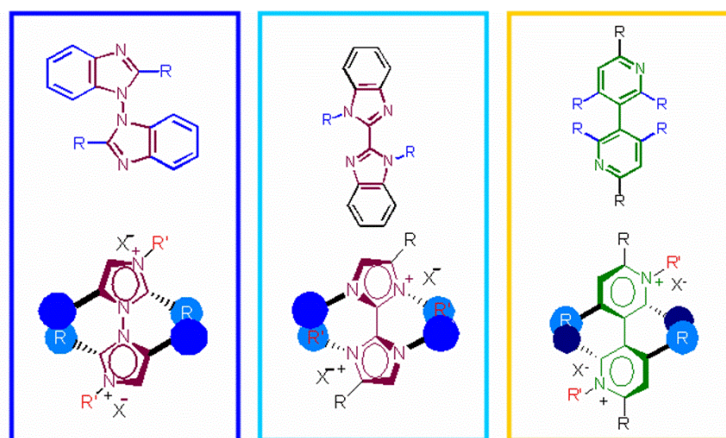
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The typical design of chiral electroactive materials involves attaching chiral pendants to an electroactive polyconjugated backbone and generally results in modest chirality manifestations. In this frame we have proposed our innovative approach based on the concept of "inherent chirality" implying a stereogenic element not external to, but coinciding with, the whole electroactive backbone, derived from a tailored torsion originating in the molecule by the insertion of atropisomeric scaffolds. Therefore both chirality and electroactivity are strictly connected, deriving from the same element, which constitutes the main part of the molecule. Such property is fully transmitted from inherently chiral monomers to the oligomers obtained by their electrooxidation. Thus, the inherent chirality concept has turned out to afford molecular materials endowed with powerful chirality manifestations plus an unprecedented pool of other outstanding properties [1,2,3].

Besides extending such exciting study, we are now trying to apply the same "inherent chirality" approach to the development of inherently chiral ionic liquids (ICILs), hopefully endowed with high enantioselectivity. The new molecules are based on cations including different atropisomeric bis-benzimidazolium and bis-collidinium groups acting as the stereogenic element, responsible for both the molecular chirality and the IL properties of the material, modulated by number, position and length of alkyl chain substituents.



An overview will be given of the first structures obtained and of their electrochemical properties compared with those of the corresponding scaffolds.

Results emerging from the comparison of the cyclic voltammetry patterns of each scaffold family are here summarized.

1,1'-bis-benzimidazoles [4] display a racemization barrier of $\sim 40 \text{ kcal mol}^{-1}$.

First reduction and first oxidation peaks are close to the boundaries of the available potential windows, consistent with very low effective conjugation deriving from the high energy barrier. The effect of alkyl chain length is very slight.

2,2'-bis-benzimidazoles exhibit the narrowest potential window of all scaffold families: both first reduction and first oxidation peaks are significantly shifted to less extreme potentials, pointing to higher effective conjugation between the two equal scaffold moieties, which is in accordance with the much lower computed racemization barriers. Actually the scaffolds are in this case nearly planar, and their reduction CV pattern, featuring two reversible monoelectronic peaks, is consistent with two reciprocally interacting equivalent redox centers.

It is worthwhile noticing that bridging alkyl substituents result in a different reduction mechanism with respect to simple alkyl chains and appear to destabilize the first ET product, which reacts much more rapidly. Moreover, the 3-term bridge results in a significantly lower E_{gap} with respect to the 4-term one, consistently with its lower calculated racemization barrier.

3,3'-bis-collidines have the highest computed racemization barrier ($42.5 \text{ kcal mol}^{-1}$) and yield the largest potential window in CV experiments ($E_{\text{gap}} \sim 4.8 \text{ eV}$). First reduction and oxidation are in this case barely perceivable as background shoulders, coherently with very low effective conjugation.

These inherently chiral scaffolds can be employed, even without salification, as chirality inductors in stereoselective processes, either dissolved in achiral commercial ionic liquid media or, together with a supporting electrolyte, in traditional solvents.

When mono- or di-alkylation occurs the quaternarization of the imidazole and pyridine rings results in a huge positive shift of the first reduction potentials.

The **1,1'-bis-benzimidazolium di- (or mono-) alkyl salt family** [4] shows a very high racemization barrier; thus enantiomers can be separated by preparative HPLC, stored and characterized.

Unfortunately such salts are solid or wax-like at room temperature, since so far double alkylation has succeeded only when either R or R' chains were short.

However, they could be used as chiral supporting electrolytes or even, at lower concentration, as chirality inductors (see below).

The **2,2'-bis-benzimidazolium mono-alkyl salt family** are waxes or oils at room temperature. Unfortunately, however, in this case the low barrier and easy rotation between the two equal halves, which results in high effective conjugation, also makes it impossible to separate stable enantiomers.

The **3,3'-bis-collidinium di- (or mono-) alkyl salt family** is the most promising one displaying the highest racemization barrier in the three families as the corresponding scaffold; moreover, alkylation with long chains has been successfully achieved, finally affording, with proper counteranion choice, low melting points.

Products are synthesized from inexpensive starting reagents; the scaffold enantiomers can be separated by fractional crystallization of diastereomeric salts with *o,o*-dibenzoyltartaric acids, and also the mono- and dialkylated salts can be isolated by a convenient protocol; thus low-cost synthesis is possible, avoiding the necessity of preparative chiral HPLC. In view of testing the new ICILs as media for electrooligomerizations a first proof was carried out using a 3,3'-bis-collidinium salt as supporting electrolyte evidencing the powerful influence of the anion choice in the oligomerization process. The anion choice is also very important for obtaining the desired melting points.

Finally, very promising appear the preliminary enantioselectivity tests (figure below) using 1,1'-bibenzimidazolium enantiopure salts as additives, even in small amount, in the electrooligomerization of our inherently chiral monomer [4].

We are now looking forward to testing as supporting electrolytes and/or ionic liquids the newly achieved low-melting 3,3'-bis-collidinium salts, which look the most promising family, being low-cost, having the highest racemization barriers, the largest potential windows, as well as reaching low melting points.

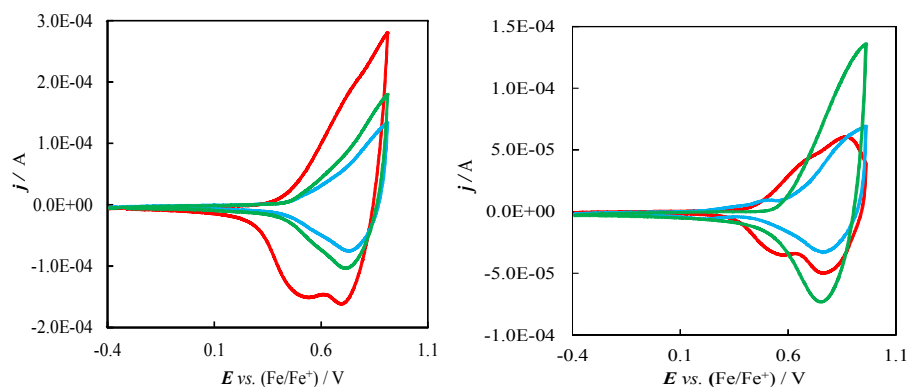


Figure. Electrooligomerization tests of racemic (left) or enantiopure (right) inherently chiral monomer (parent BT₂T₄) in the absence (red) or in the presence of 2:1 enantiopure (*R*)- (blue) or (*S*)- (green) 1,1'-bis-benzimidazolium based salt.

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