Caso 1: studio voltammetrico di oligotiofeni “spider like”

“Spider-like” oligothiophenes

TN\_10 series: bi thiophenyl pendants, $n = 3$ nodes

TN\_10 series: thiophene pendants, $n = 3$ nodes
Effective conjugation in branched oligothiophenes

Electrochemical properties

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_{p,a}$ (V(SCE))</th>
<th>$E_{p,c}$ (V(SCE))</th>
<th>$E_{onset,a}$ (V(SCE))</th>
<th>$E_{onset,c}$ (V(SCE))</th>
<th>$\lambda_{abs}$ (nm)</th>
<th>$\lambda_{em}$ (nm)</th>
<th>$E_{g,a}$ (eV)</th>
<th>$E_{g,c}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T14a</td>
<td>1.08</td>
<td>-1.46</td>
<td>2.74</td>
<td>-0.95</td>
<td>420</td>
<td>2.96</td>
<td>515</td>
<td>2.41</td>
</tr>
<tr>
<td>T14b</td>
<td>1.11</td>
<td>-1.97</td>
<td>3.08</td>
<td>-0.97</td>
<td>370</td>
<td>3.38</td>
<td>500</td>
<td>2.48</td>
</tr>
</tbody>
</table>

The term from the “BT” series, having the lower node density, has

- Less positive $E_{p,a}$
- Less negative $E_{p,c}$
- Significantly lower $E_g$ both electrochemical and spectroscopic

“Spider-like” oligothiophenes

TN$_n$ series: bithiophenyl pendants, $n_a = 3$ nodes

TN$_n$ series: thiophene pendants, $n_a = 3$ nodes
Polymerization ability in branched oligothiophenes

0.0005 M oligomer in CH$_2$Cl$_2$ +0.1 M TBAP

Fast polymer deposition

Two merging reversible peaks

A single reversible monoelectronic peak accounting for 2 electrons per oligomer

Caso 2: studio voltammetrico di complessi “kiss lock”
Caso 3: studio voltammetrico, EIS e spettrooelettrochimico di un "charm-bracelet conducting polymer"
“Charm bracelet”

electroactive polymer with
diRhenium complex pendants

A: Quasi reversible monoelectronic reduction of the pyridazine group;
B: Oxidation of the thiophene group(s), resulting in radical cation formation in α-thiophene position and therefore affording polymerization
C: Oxidation of the two Rh centers, taking place at a more positive potential than in the reference complex since the bridging ligands are on the whole less electron attracting

By comparison with free HOOC-Cpdt ligand and the 3-Me-pyridazine complex without cpdt, the CV peaks of the new conjugate can be assigned as follows:

Redox processes of monomer
Cycling around peak B, the conjugate affords efficient electrochemical polymerization on GC, Pt, and ITO electrodes:

The resulting polymer
- is stable in a monomer free solution;
- exhibits two subsequent reversible oxidation peaks, whose relative charge ratio is regularly depending on the potential scan rate (possibly, on account of different rates of the counter ion ingress/egress)

Stability and charge trapping in the resulting film

The polymer also exhibits charge-trapping features which strongly depend on the potential scan rate, strongly affecting the negative charging of the polymer (possibly, again on account of different rates of the counter ion ingress/egress)
Spectroelectrochemistry on the resulting film

Upon polymer charging the UV-vis characteristics radically changes (electrochromic effect)
Chiral molecular recognition, of outstanding importance in biological and pharmaceutical fields, is the highest form of the molecular recognition, implying to measure energetic differences often very small between diastereoisomeric complexes.

In particular, chiral sensing is much more critical than chiral separations, since in direct chiral sensing devices there is only one single unitary process of separation corresponding to one theoretical plate in chromatographic separations.

Chiral molecular recognition depends on difference in stability constants of diastereoisomeric complexes with applied selectors

*Natural selectors*: proteins, polysaccharides, cyclodextrins, macrocyclic glycopeptides, alkaloids…

*Synthetic selectors*: ligand exchangers, ligands forming $\pi,\pi$ complexes, molecularly imprinted polymers, chiral crown ethers, polymers…

Already widely applied with separation and spectroscopic techniques

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**Chiral electroanalytical sensors**

Many efforts have been devoted to achieve chiral electroanalytical sensors based on artificial selectors, following many strategies, such as
- electrodes modified with chiral SAMs, chiral sylane derivatives, adsorbed chiral reagents
- electrodes modified with polymers with “external” stereocentres
- electrodes molecularly imprinted with chiral templates
- electrodes modified with molecular layers asymmetrically grown by magnetopolarization
- chiral metal surfaces
- chiral organic thin-film transistors

However,
- in many cases poor or labile enantioselectivity is observed using of electrode materials with a chirality source localized or external respect to the bulk material
- even the most successful attempts almost invariably resulted in the detection of a difference in current intensity between the signals of the two antipodes;
- the chiral enantioselective layer is in many instances not of general use, but tailored for a given probe;
- many preparation procedures are very sophisticated/expensive…
- … and/or the active films fragile.
A recent breakthrough: “inherently chiral” electrodes, effective tools for chiral voltammetry

The stereogenic element coincides with the whole main molecular backbone

The electroactive oligomer films exhibit outstanding enantioselection properties towards many chiral analytes, opening the way to effective chiral voltammetry.

An alternative strategy to achieve chiral electroanalysis: working on achiral electrodes in chiral working media

As an alternative strategy, chiral electroanalysis might also be achieved working on an achiral electrode in a chiral medium.

Possibilities:
- Chiral organic solvents
- Chiral supporting electrolytes
- Chiral ionic liquids (CILs)
With chiral ionic liquids (CILs), such a high degree of supramolecular organization can induce a significant chirality transfer from the solvent to the dissolved species. Analogously with the electrode case, this attitude could be maximized by the “inherent chirality” strategy, that is, working in “inherently chiral” ionic liquids ICILs.

### Ionic liquids, Chiral ionic liquids, Inherently chiral ionic liquids

ILs have an intrinsically high supramolecular order; they are assumed to display a behavior similar to highly organized liquid polymers.

C.P. Frizzo, M.A.P. Martins et al., CrystEngComm. 2015, 17, 2996

### Implementing the inherent chirality concept in ionic liquids: the rationale

Most ionic liquids have N-heteroaromatic cations with long alkyl substituents (to lower their melting point)

**bi-N-heteroaromatic cations with a rotational barrier arising from sterical hindrance between alkyl substituents** could yield inherently chiral ionic liquids ICILs.

<table>
<thead>
<tr>
<th>1,1'-bibenzimidazole</th>
<th>1,1'-bibenzimidazolium salts</th>
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<tbody>
<tr>
<td>Atropoisomeric scaffolds</td>
<td></td>
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<table>
<thead>
<tr>
<th>3,3'-bicollidine</th>
<th>3,3'-bicollidinium salts</th>
</tr>
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</table>

**Homotopic moieties** → higher intermolecular organization and easier supramolecular interactions then common CILs.
The enantiomer discrimination capability also holds changing the achiral ionic liquid medium and is modulated by the nature of the available counteranions. Moreover, it increases with additive concentration.

Enantiopure probes

A linear trend is observed of $\Delta E_p$ vs $\log c_{\text{additive}}$, reminding of the classical Kolthoff and Lingane equation of redox processes with complex formation.

Using the same diethyl additive in BMIMPF$_6$ achiral IL

(R) and (S) enantiomers of BT$_4$T$_4$ inherently chiral monomer

L- and D-DOPA methylester