Thermotropic properties of new electrochromic viologen-based ionic liquid crystals

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Vis Electrochromism: solution and solid state

- Multiple redox states
- Many hues
- Low potentials

Applications of electrochromic devices

- E-papers
- Optical switching devices
- Smart windows: light control
- Camouflage materials
- Optical communication
- Data storage
- Smart windows: thermal control
Electrochromic Devices and Properties

Over the electro-active, -chromic species

✓ high ionic conductivity,
✓ ideal zero electronic conductivity,
✓ large electrochemical windows,
✓ fast ion mobility during redox events,
✓ low volatility,
✓ thermal and environmental stability
LCs are characterized by the integration of ionic and electronic functions.

Ion conduction can be obtained by doping the LC or by covalent attachment to LC mesomorphic salts where, in most cases, the mesogenic part exists as an organic cation (substituted pyridinium, bipyridinium, imidazolium, phosphonium, etc.). Bulk ion conductivity in these materials, which can be as high as $10^{-2}$ S cm$^{-1}$, is due to the nanosegregation between insulating layers made of long promesogenic alkyl chains and conducting layers bearing the ionic moiety.
Viologen as electrochromic ILCs

\[
\begin{align*}
R\text{-N} & \quad \text{Anion} & \quad \text{Solvent} & \quad \text{Colour} \\
\text{Methyl} & \quad \text{Cl}^- & \quad \text{H}_2\text{O} & \quad \text{Blue} \\
\text{Octyl} & \quad \text{Br}^- & \quad \text{H}_2\text{O} & \quad \text{Crimson} \\
\text{Benzyl} & \quad \text{Cl}^- & \quad \text{H}_2\text{O} & \quad \text{Mauve} \\
\text{4-Cyanophenyl} & \quad \text{BF}_4^- & \quad \text{PC} & \quad \text{Green/black}
\end{align*}
\]

Extended viologen as electrochromic ILCs

New electrochromic viologen-based ionic liquid crystals

Mono-substituted viologen

Bis-substituted viologen

$X^- = \text{NTf}_2$

Alkylphenyl moiety

Affects the thermotropic behavior

Bulk electrochemical properties
POM investigation

Cooling 101 °C
Cooling 68 °C
Cooling 49 °C

Cooling 82 °C
Cooling 47 °C

Cooling 63 °C
Cooling 42 °C
## Transition temperatures

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature (°C) of transition</th>
<th>$T_{\text{clearing}}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M 8-NTf$_2$</td>
<td>108-72</td>
<td>130</td>
</tr>
<tr>
<td>M 10-NTf$_2$</td>
<td>101-68</td>
<td>117</td>
</tr>
<tr>
<td>M 12-NTf$_2$</td>
<td>84-63</td>
<td>119</td>
</tr>
<tr>
<td>M 14-NTf$_2$</td>
<td>84-67</td>
<td>116</td>
</tr>
<tr>
<td>D 8-NTf$_2$</td>
<td>66-17</td>
<td>194</td>
</tr>
<tr>
<td>D 10-NTf$_2$</td>
<td>83-61</td>
<td>175</td>
</tr>
<tr>
<td>D 12-NTf$_2$</td>
<td>273-74</td>
<td>293</td>
</tr>
<tr>
<td>D 14-NTf$_2$</td>
<td>310-80</td>
<td>314</td>
</tr>
</tbody>
</table>
POM investigation

Cooling 170 °C

Cooling 66 °C

Cooling 74 °C

Cooling 47 °C

Cooling 296 °C

Cooling 122 °C

Cooling 73 °C

Cooling 273 °C
Electrochemical and spectroelectrochemical analysis

Cyclic voltammetry of 8-NTf₂ as representative redox behaviour of alkyl-based phenyl-viologens in PC/TBAPF₆ (0.1 M) at 1000 mV/s.

The redox processes occur at more positive potentials with respect to classic viologens.

Spectroelectrochemistry of the compound 14-NTf₂ with potential referred to Ag/AgCl. The inset, zooming the range 600-800 nm, show the viologen absorption bands.
Bulk electrochromic properties

POM images of a thin film (5 μm) of 8-NTf₂ sandwiched in a liquid crystalline cell, acquired during the reduction process as a function of the applied voltage difference.

Conclusions

✓ Two new sets of mono- and di-substituted viologens having electrochromic and electron accepting properties have been successfully characterized.

✓ All the viologens exhibit a liquid-crystalline phase. Many of them show low crystal-to-smectic phase transition under 100°C while almost all have a wide range of LC phase.

✓ These characteristics make such materials suitable for the development of new high performance devices (opto-electronic devices), since they exhibit LC mesophases with a good reversibility and with an high fluidity.
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