Thermotropic properties of new electrochromic viologen-based ionic liquid crystals

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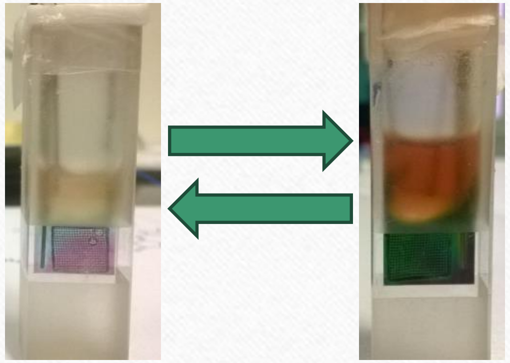
Vis Electrochromism: solution and solid state



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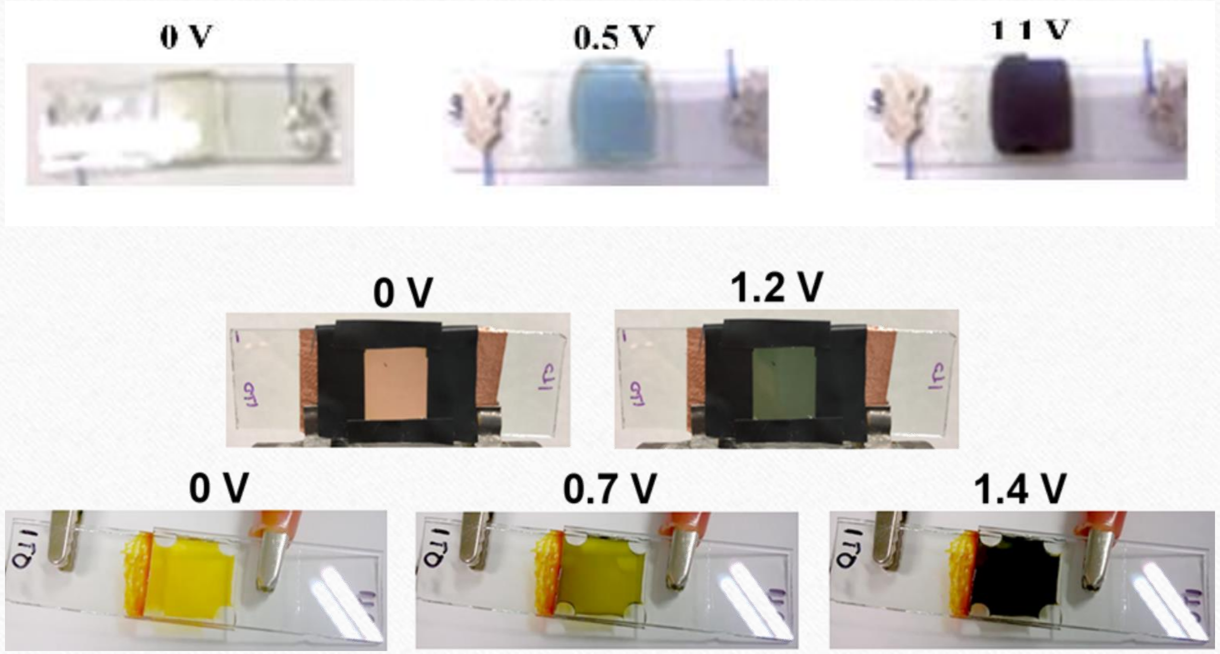
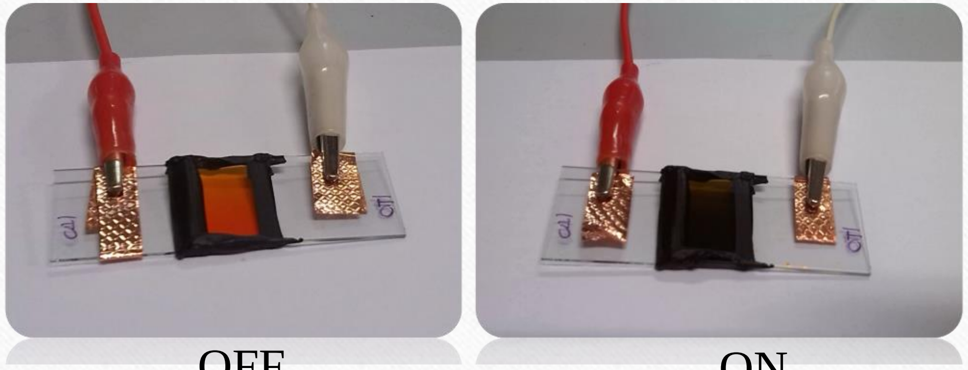
- ➢ **Multiple redox states**
- ➢ **Many hues**
- ➢ **Low potentials**





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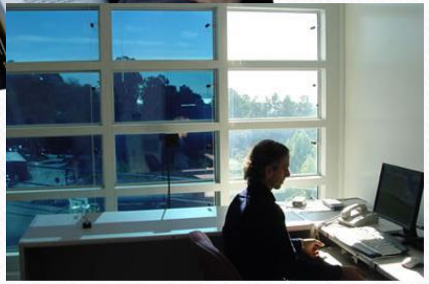
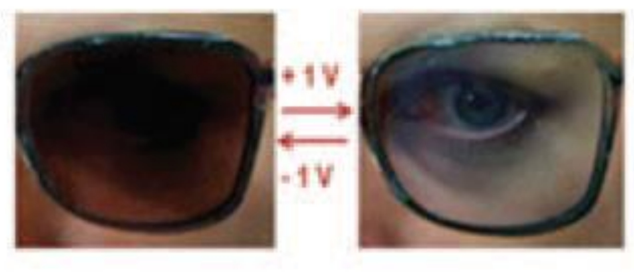
Corrente, et al. Colorless to All-Black Full-NIR High-Contrast Switching in Solid Electrochromic Films Prepared with Organic Mixed Valence Systems Based on Dibenzofulvene Derivatives. Chem. Mater. 2018, 30, 5610-5610.

Applications of electrochromic devices

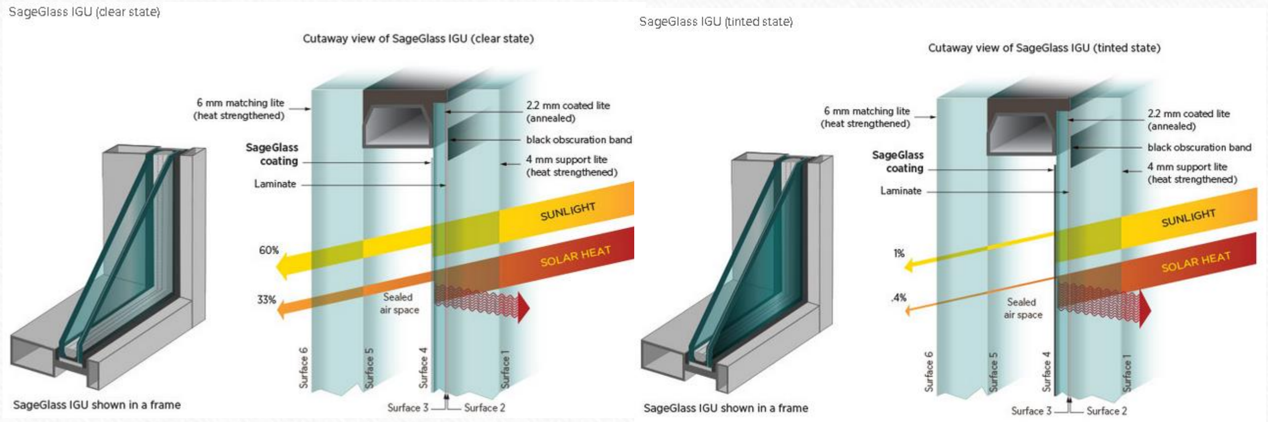
- E-papers
- Optical switching devices
- Smart windows: light control
- Camouflage materials



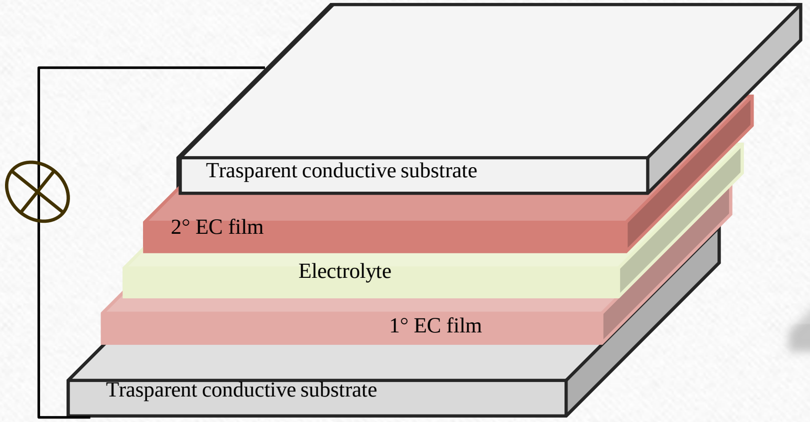
- Optical communication
- Data storage
- Smart windows: thermal control



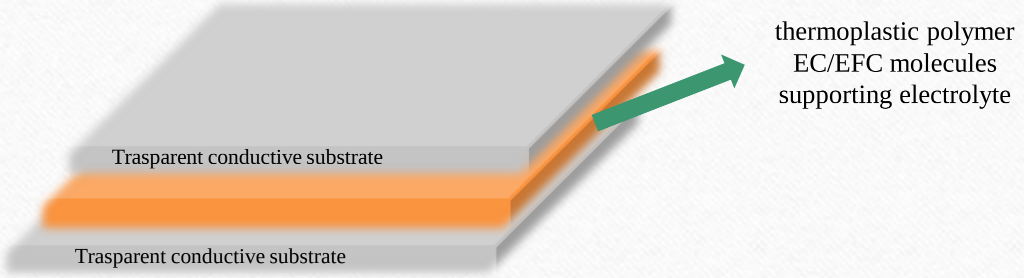
Electrochromic windows



Electrochromic Devices and Properties



Multilayer architecture of ECD



Single-layer architecture of ECD

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

Materials with advanced properties: LCs and ILCs

REDOX ACTIVE LIQUID CRYSTALS (LCs)

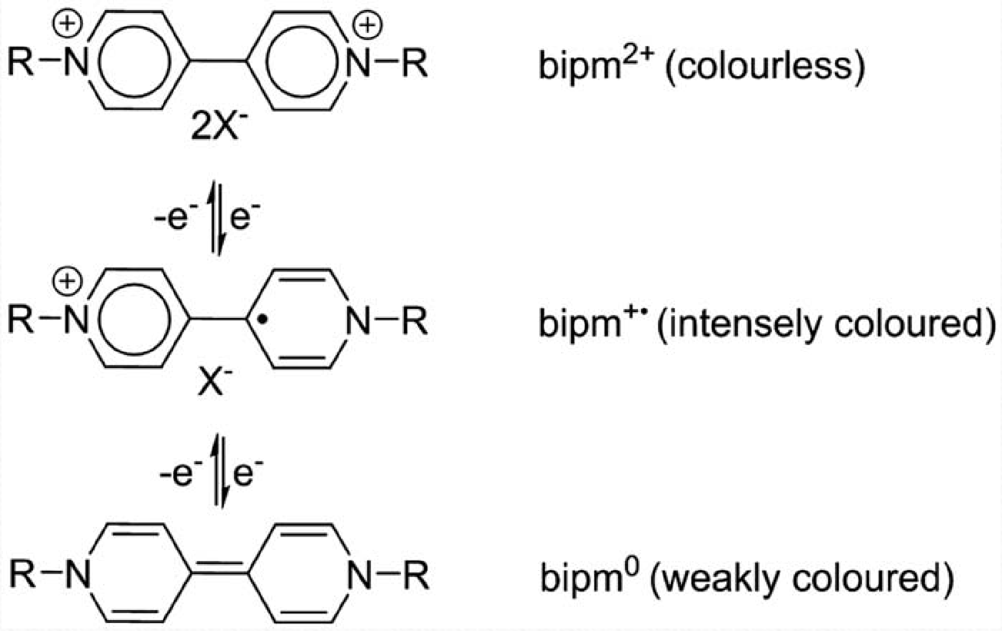
LCs are characterized by the integration of ionic and electronic functions.

Ion conduction can be obtained by doping the LC or by covalent attachment to LC →

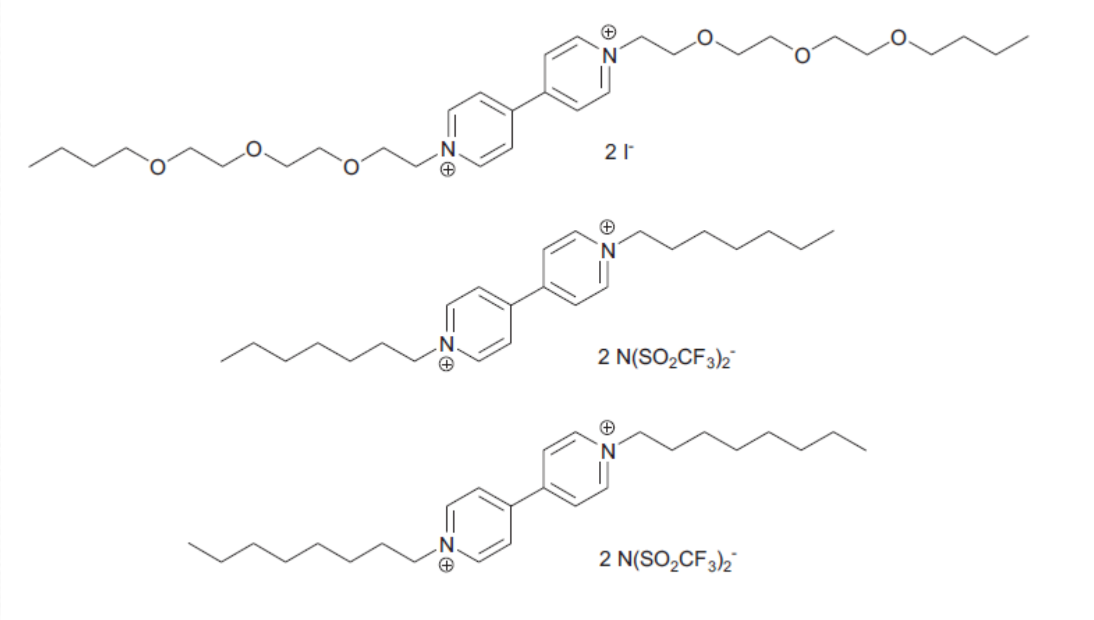
IONIC LIQUID CRYSTALS (ILCs)

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



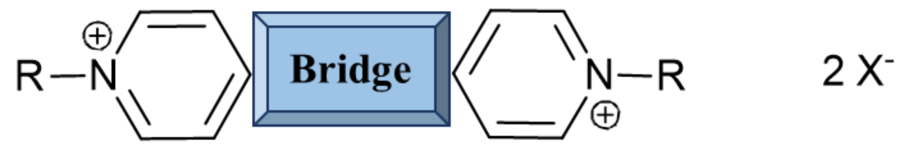
R	Anion	Solvent	Colour
Methyl	Cl^-	H_2O	Blue
Octyl	Br^-	H_2O	Crimson
Benzyl	Cl^-	H_2O	Mauve
4-Cyanophenyl	BF_4^-	PC	Green/black

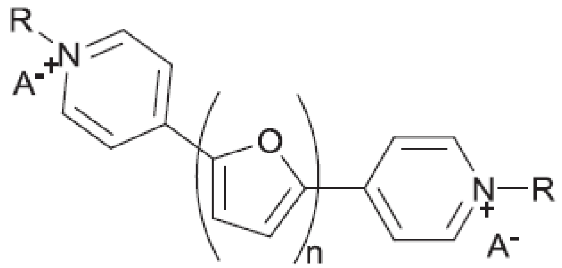


VIOLOGENs showing LC properties

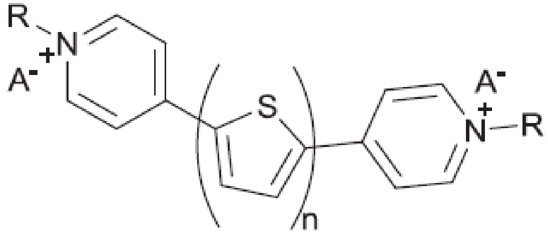
Neo, W.T.; Chua, M.H.; Xu, J.W. Fundamentals of Electrochromic Materials and Devices in Electrochromic Smart Material; Fabrication And Application 2019. Hatazawa, et al. Microelectrode Voltammetry and Electron Transport in an Undiluted Room Temperature Melt of an Oligo(ethylene glycol)-Tailed Viologen, Anal. Chem., 1996, 68, 597

Extended viologen as electrochromic ILCs

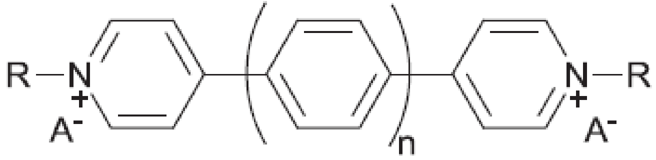




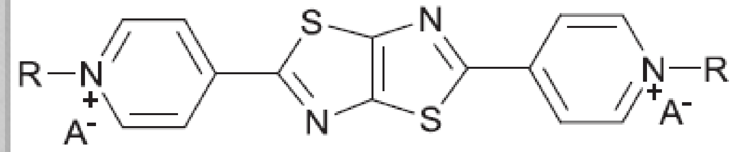
n = 1,2



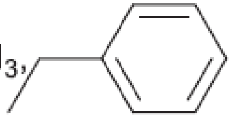
n = 1; R = $-CH_3$
n = 2; R = $-C_mH_{2m+1}$
m = 8, 9, 10, 11, 12

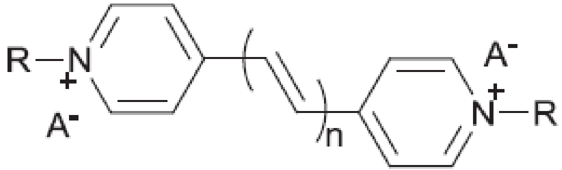


R = $-CH_3$, $-CH_2(CH_2)_6CH_3$



R = $-CH_3$, $-CH_2(CH_2)_6CH_3$,





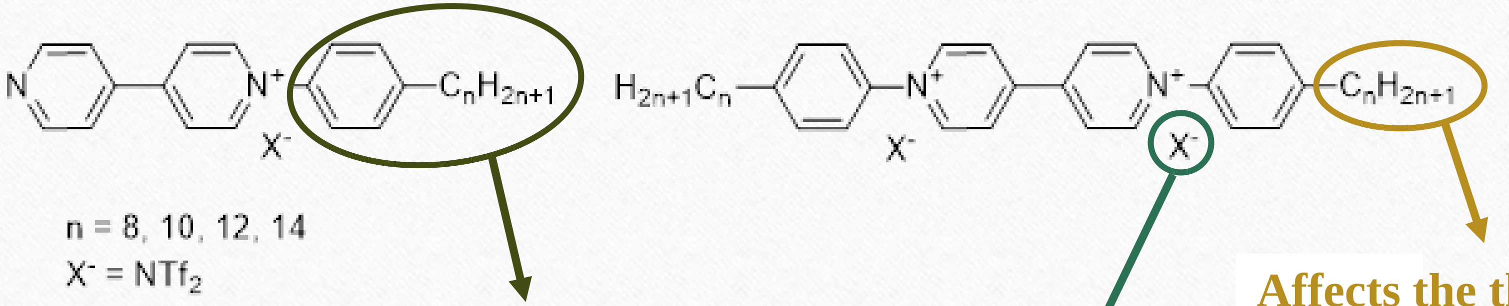
n = 1 - 9

Beneduci, et al. Electrochomic and Electrofluorescence Liquid Crystals. In Electrochromic Smart Materials: Fabrication and Application 2019. Pibiri, et al. Mesomorphic and electrooptical properties of viologens based on non-symmetric alkyl/polyfluoroalkyl functionalization and on an oxadiazolyl-extended bent core. *J. Mater. Chem. C* **2019**, *7*, 7974-7983. Beneduci, et al. Electrofluorochromism in π-conjugated ionic liquid crystals. Nat. Commun. 2014, 5, 3105.

New electrochromic viologen-based ionic liquid crystals

Mono-substituted viologen

Bis-substituted viologen



Alkylphenyl moiety

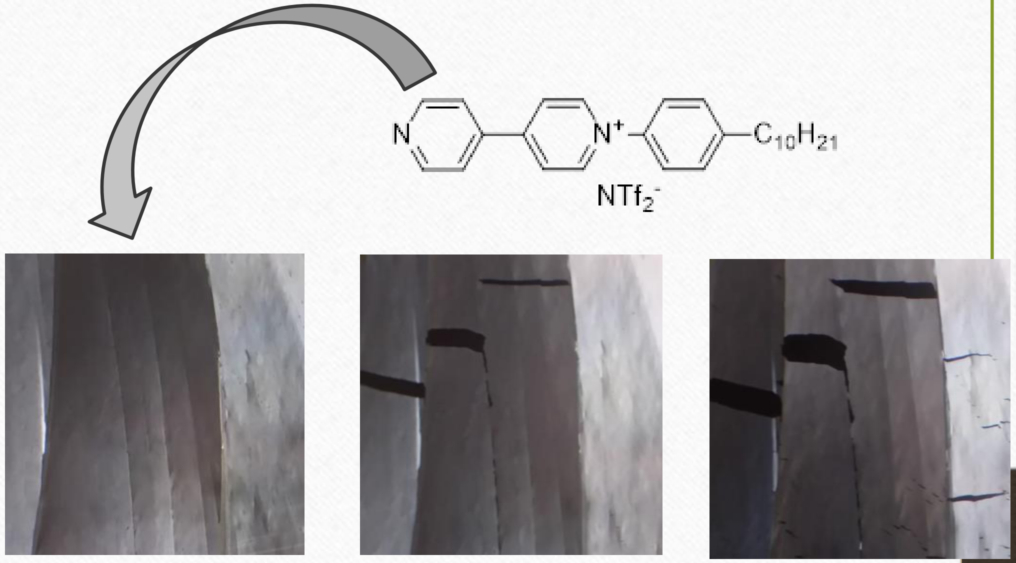
Affects the thermotropic behavior

Affects the thermotropic behavior
Bulk electrochemical properties

POM investigation

Cooling 76 °C

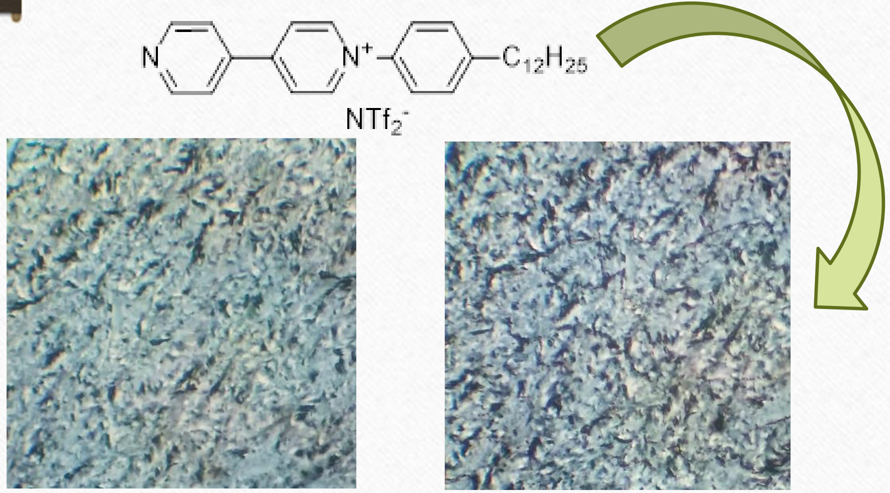
Cooling 70 °C



Cooling 101 °C

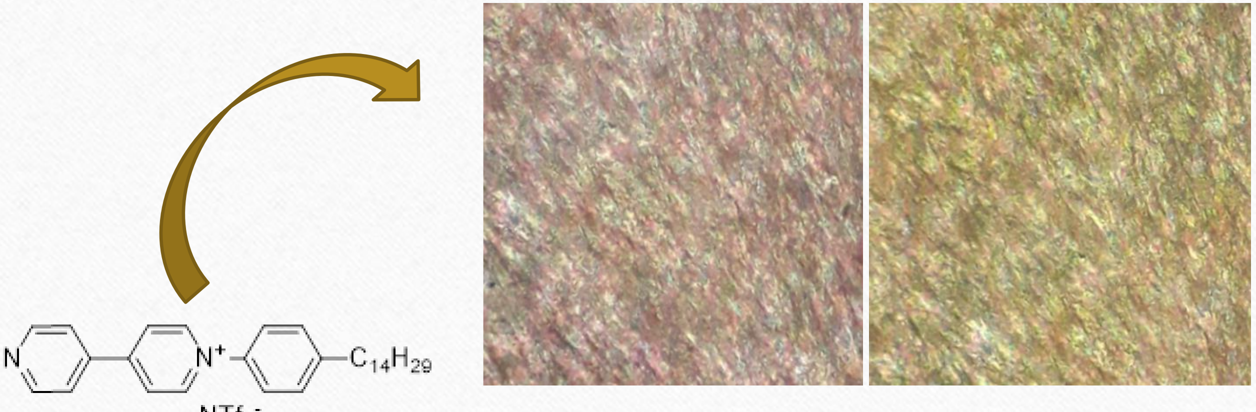
Cooling 68 °C

Cooling 49 °C



Cooling 82 °C

Cooling 47 °C



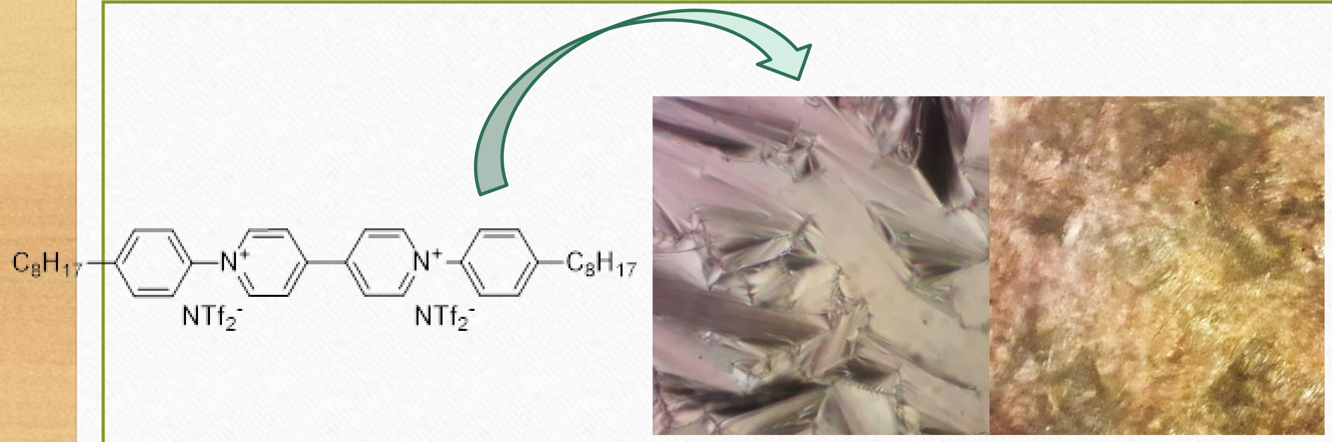
Cooling 63 °C

Cooling 42 °C

Transition temperatures

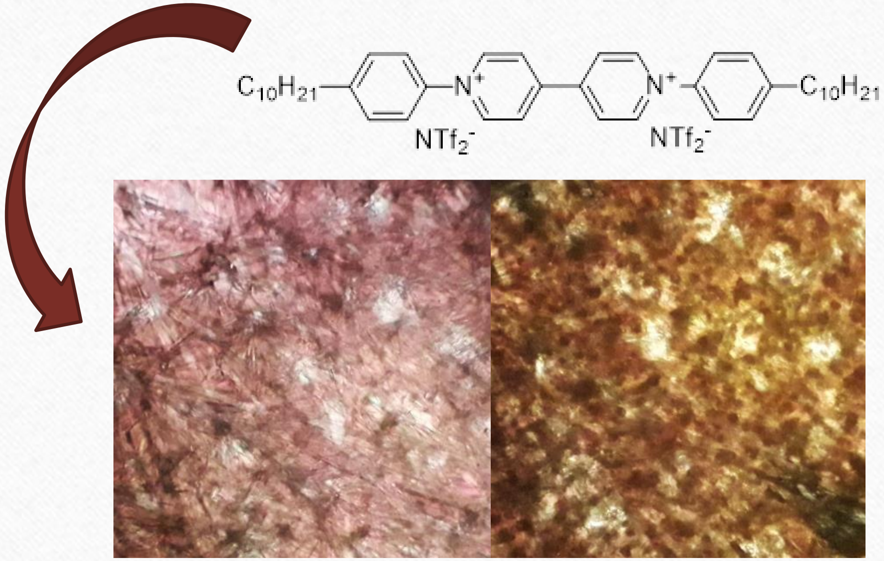
Sample	Temperature (°C) of transition	$T_{clearing}$ (°C)
M 8-NTf_2	108-72	130
M 10-NTf_2	101-68	117
M 12-NTf_2	84-63	119
M 14-NTf_2	84-67 67-40	116
D 8-NTf_2	66-17	194
D 10-NTf_2	83-61	175
D 12-NTf_2	273-74 74-54	293
D 14-NTf_2	310-80	314

POM investigation



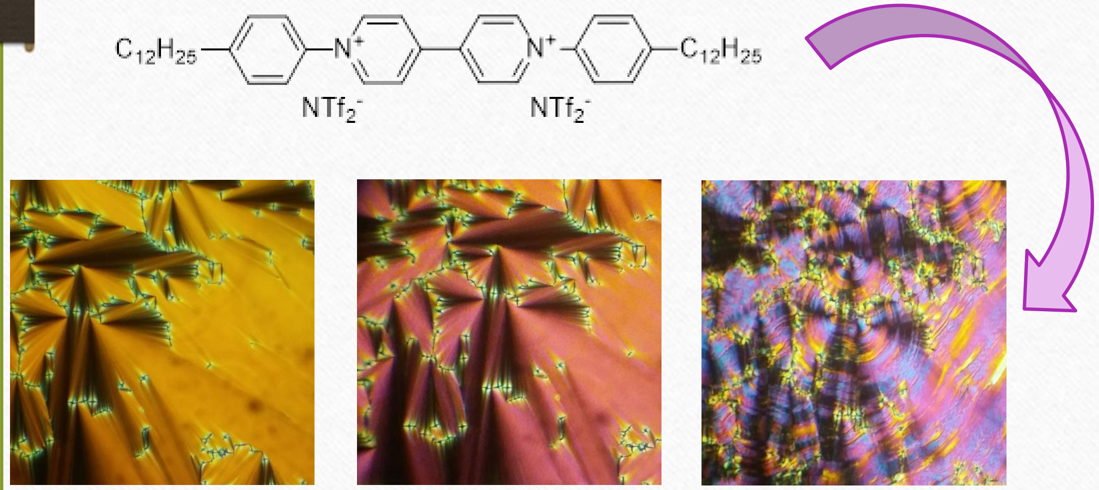
Cooling 170 °C

Cooling 66 °C



Cooling 74 °C

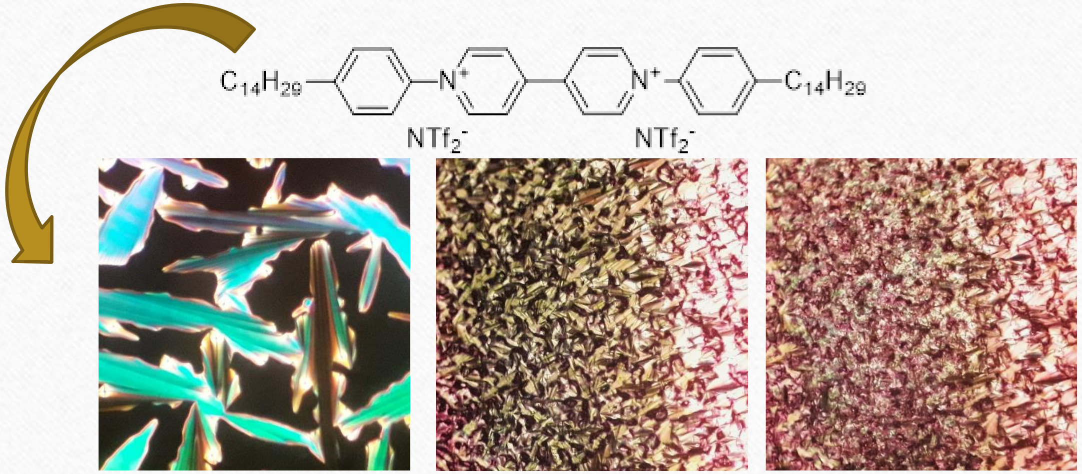
Cooling 47 °C



Cooling 273 °C

Cooling 74 °C

Cooling 54 °C

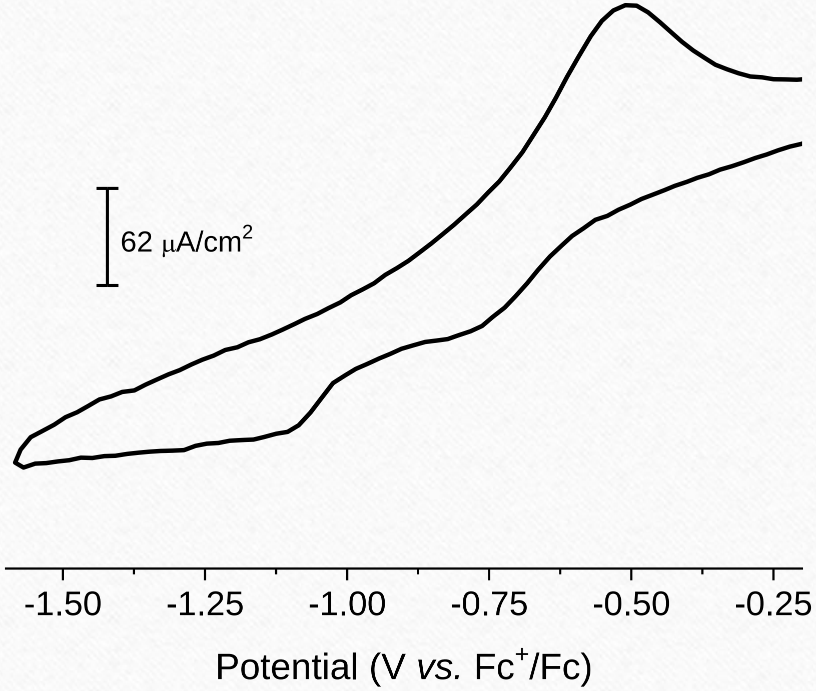


Cooling 296 °C

Cooling 122 °C

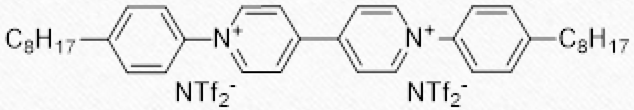
Cooling 73 °C

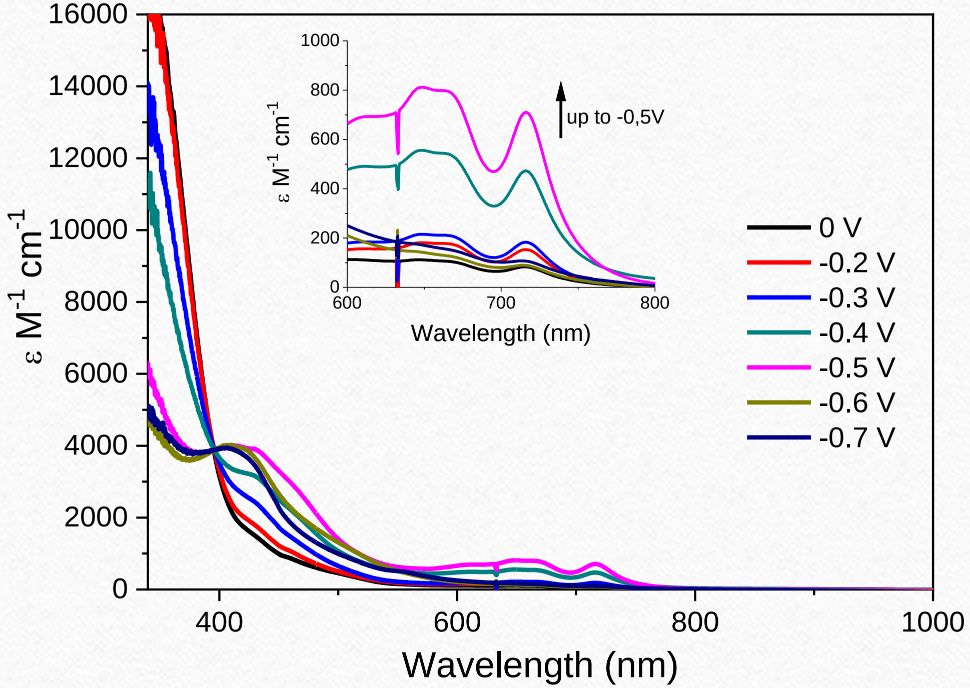
Electrochemical and spectroelectrochemical analysis



Cyclic voltammetry of 8-NTf_2 as representative redox behaviour of alkyl-based phenyl-viologens in PC/$TBAPF_6$ (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-NTf_2 with potential referred to Ag/AgCl. The inset, zooming the range 600-800 nm, show the viologen absorbtion bands.

Bulk electrochromic properties

POM images of a thin film (5 μm) of 8-NTf_2 sandwiched in a liquid crystalline cell, acquired during the reduction process as a function of the applied voltage difference

Veltri et al. Synthesis and thermotropic properties of new green electrochromic ionic liquid crystals, New Journal of Chemistry, **2019**, 43, 18285-18293.

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.

THANK YOU FOR YOUR KIND ATTENTION