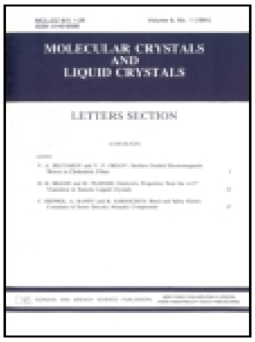

MOLECULAR CRYSTALS AND LIQUID CRYSTALS

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n-Type Columnar Liquid Crystal Combining Ionic and Electronic Functions

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The research in the field of electronic and photonic devices based on ordered organic semiconducting materials has been boosted by the development of new multifunctional materials. The order characterizing liquid crystals has been exploited for improving charge mobility performances. However, while in the last decade much effort has been addressed to the synthesis of hole-conducting materials (p-type), less attention has been paid on the development of electron-conducting ones (n-type). Here we show the bulk multifunctional properties of a π-conjugated thienoviologen ionic liquid crystal which exhibits strong electron acceptor character. Notably, the combination of its optical properties with high ionic conductivities and fast intermolecular electron transport, leads to unique bulk electrochromic functions.

Keywords columnar; ionic conductivity; electrochromism; electrochemistry

1. Introduction

Semiconducting liquid crystals (LCs) are widely recognized as very promising charge-transporting organic materials due to their ability to self-assemble into highly ordered domains in uniform thin films over large areas [1]. These ordered molecular materials have attracted significant attention for their wide range of applications in organic electronic devices such as field-effect transistors [1, 2], solar cells [1, 3] and light emitting diodes [1–3]. Semiconducting organic materials with electron-acceptor and electron transporting character, known as n-type, are still rather scarce compared to their p-type counterparts (hole transporting) [4] because of their often limited ambient stability, poor solubility and synthetic access [5]. p-Type organic semiconductors have seen the most intensive research efforts, which has resulted in comparable hole-mobilities with inorganic materials [6].

Efficient and stable n-type materials are essential for p-n junction diodes, organic photovoltaics (OPV), and complementary organic circuits with greater operation speed and lower power dissipation [7]. Concerning their application in OPV, semiconducting LCs are very promising in bulk heterojunction architecture [8, 9] where p-type and n-type organic

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semiconductors form nanosegregated structures [10], allowing an easy control of the morphology of the photoactive layers. Thus, nowadays one of the most interesting challenge is the design and the synthesis of new n-type LCs that commonly include: sexithiophene [11], phenanthrene [12], perylene [13], anthraquinones [6, 14], viologens [15], hezaazatriphenylene [16] tetraazanaphthacene [17] and heterotriangulenes [18]. Among them, particularly interesting are viologen liquid crystals incorporating a π-conjugated core, known as extended viologens, because of their strong electron-acceptor character and efficient redox activity [19, 20].

Recently, we presented a new class of extended viologen liquid crystals, called thienoviologens, in which a bithiophene group links the two *N,N′*-dialkylated pyridinium units (Figure 1) [21, 22, 23]. The introduction of the bithiophene bridge between the pyridinium rings and of the pro-mesogenic alkyl chains in the *N,N′* positions, leads to compounds that combine the electron acceptor properties typical of viologens salts with new functional properties arising from both the extended π-conjugated core and their liquid crystalline properties [23].

2. Experimental Details

2.1. Polarizing Optical Microscopy

POM images were acquired with a Leitz Laborlux 12 POL polarising optical microscope connected to a Lumix Panasonic DMC-FS42 photocamera.

2.2. Electrochemical and Spectroscopic Measurements in the Bulk Mesophase

Standard cyclic voltammetries were performed with a three-electrode liquid crystal cell (cell gap 40 μm) made of two ITO plates and an Ag wire, placed between them, respectively used as working, counter and reference electrodes. Electronic spectra were acquired in a two-electrode liquid crystal cell with cell gap of 10 μm. ITO cells were placed into a Linkam hot stage (LTS350 stage, TP94 System Controller) with internal electrical contacts for simultaneous temperature and DC voltage control. Spectra were recorded with a Jasco V-550 UV-Vis spectrophotometer and DC voltages were supplied by an Amel 2049 model potentiostat. Electrochemical measurements were performed with an Amel Instruments 7050 model potentiostat.

2.3. Dynamic Ionic Conductivity Measurement

Ionic conductivity measurements were performed with an Amel model 7200 frequency response analyzer in the frequency range 1 MHz-0.1 Hz at an applied voltage of 0.3 V. Measurements were performed in the temperature range 160–100°C on cooling from the isotropic liquid state. Two relaxation processes were generally found. The high frequency process was used to fit the bulk electrical resistance of the material (R_b). The low frequency process was ascribed to the charge transfer resistance of the interface between sample and electrode [24, 25]. Ionic conductivity (σ) was calculated by the equation:

$$\sigma = K_{cell}/R_b$$

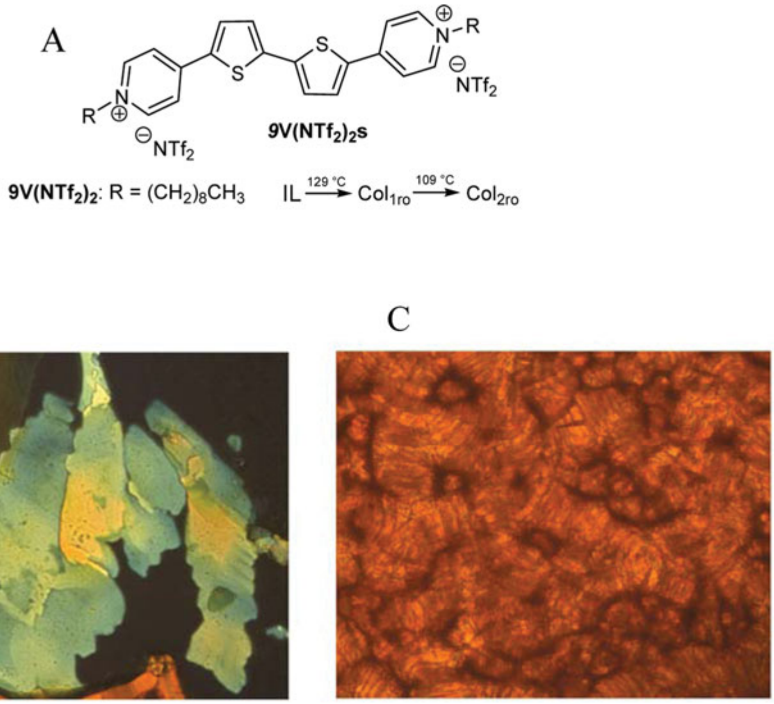

Figure 1. Chemical structure of the columnar thienoviologen investigated and its mesophase behavior (A). POM image acquired at 126°C (B) showing the coexistence of dendritic and mosaic textures typical of the rectangular columnar assembling, Col_{1ro}. POM image acquired at 90°C (C), on further cooling, showing the more ordered columnar phase, Col_{2ro}.

where, K_{cell} is the cell constant given by the ratio between cell gap and electrode area [24, 25]. R_b was obtained from the semicircle diameter on the real axis (Z') by fitting the experimental spectral points with a single RC circuit.

2.4. Electrochromic Switching Study

The transmittance of the liquid crystal cell was measured with an optical line equipped with a He-Ne laser source (Melles Griot 05 LHR 106) generating a light with wavelength 632.8 nm that passes through a chopper, whose rotation frequency controls the reference signal of the lock-in. The light leaves the chopper through a slit which avoids any reflection. The presence of a beam-expander, increasing the size of the beam, and a slit, reducing the size of the beam, produces a perfectly collimated beam of light, which reaches the liquid crystal cell located within a hot stage (Linkam LTS350 stage, TP94 System Controller). The light leaving the sample impinges on a photodiode (detector) that collects light and converts it into an electrical signal. The signal is then directed to a lock-in amplifier, sent to a reader, digital oscilloscope (Hewlett Packard 546001) and recorded on a PC. The software for recording and processing the optical data has been home made.

The measurements were carried out under atmospheric conditions. The liquid crystal cells comprised two glass plates coated with indium tin oxide (ITO) (the area of the electrode was 4 mm × 4 mm). The thickness of the cell was set at 5 μm by means of glass-spheres. The liquid crystals were capillary-filled into the cells in the isotropic states. The

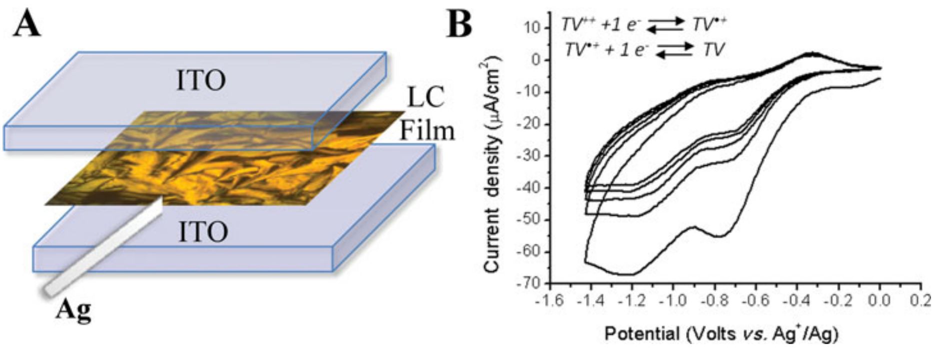

Figure 2. ITO/ITO/Ag three-electrodes liquid crystalline cell (A). Cyclic voltammograms of compound $9V(NTf_2)_2$ in the Col_{1ro} phase at 120°C (B). The inset shows the redox reactions of the thienoviologen dication (TV^{++}).

transmittance curves were detected under application of potential steps modulated by the function generator (Amel 568 model programmable function generator). The transmittance was determined as the ratio of the intensity of the transmitted light through the liquid crystal cell during the measurement to the intensity before the potential application.

3. Results and Discussion

3.1. Bulk Electrochemistry in the Columnar Phase

The electrochemical properties of compound $\mathbf{9V(NTf_2)_2}$ in the bulk liquid crystalline phase were studied with the three electrode cell schematized in Figure 2A. The two ITO plates served as working and counter electrodes and the Ag wire was used as pseudo reference electrode. The material was capillary filled into the liquid crystalline cell in the isotropic liquid state and then it was cooled in order to enter into the columnar phase. The cyclic voltammetry of the Col_{1ro} phase is reported in Figure 2B. It shows two distinct one-electron reduction steps during which the thienoviologen dication (TV^{++}) transforms into the radical-cation species ($TV^{\cdot +}$), which in turn is further reduced to the neutral species (TV). The low reduction potentials of this compound, indicates that the electrons can be easily injected into the material from the electrode.

3.2 Bulk Electronic Properties

The strong n-type character of compound $\mathbf{9V(NTf_2)_2}$ in the Col_{1r0} phase, is evidenced by its HOMO/LUMO energy level values which were estimated from the electronic spectrum and the electrochemical properties. Figure 3 shows the optical absorption spectra of $\mathbf{9V(NTf_2)_2}$ in the Col_{1r0} phase at 120°C. According to its red-orange color this material exhibits an intense and broad band in the low wavelength region with a tail that extends up to about 550 nm and no absorption bands in the remaining part of the visible spectrum. The LUMO energy value was determined by calibrating the first reduction peak with the ferrocene-ferrocenium couple (Fc/Fc^{+}). Taking the value of 4.8 eV for the HOMO level of ferrocene, a LUMO level of −4.3 eV results. The optical band-gap, estimated from the edges of the absorption spectrum of the thin columnar film, was found to be 1.9 eV and consequently, a HOMO energy value of −6.2 eV, was estimated.

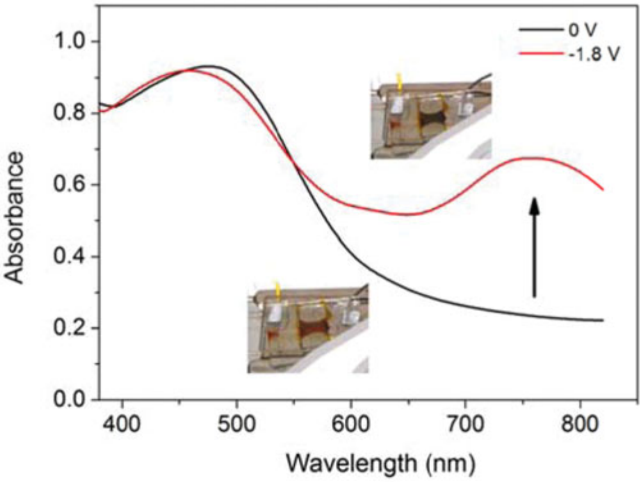

Figure 3. Electrochromic response of the Col_{1ro} phase at 120°C measured by its optical absorption spectra at 0 V and at −1.8 V. Data acquired on a thin film of the material (15 μm thick).

Notably, a clear electrochromic response was found upon reduction of the columnar film during which it changed colour from red to almost dark. This was due to the formation of a new absorption band in the 600-850 nm range (Figure 3).

When the electrochromic process was monitored under a polarized light microscope, we observed that the mesophase texture of the Col_{1ro} phase was not altered during material reduction, indicating that the nanostructured liquid-crystalline organization was preserved.

The electrochromic response was quantitatively monitored by measuring the cell transmittance at 632.8 nm under the application of a double potential step sequence. This experiment was carried out in strictly controlled temperature conditions by introducing the samples into a Linkam with internal electric contacts. Figure 4 shows the transmittance

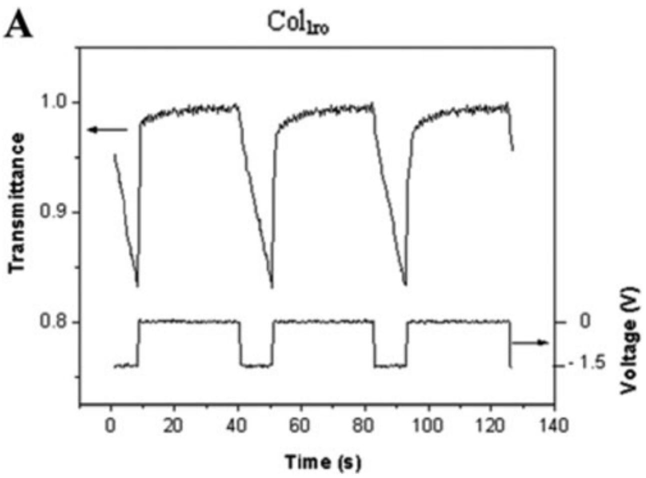

Figure 4. Bulk electrochromism for compound $9V(NTf_2)_2$ in the Col_{1ro} phase at 120°C.

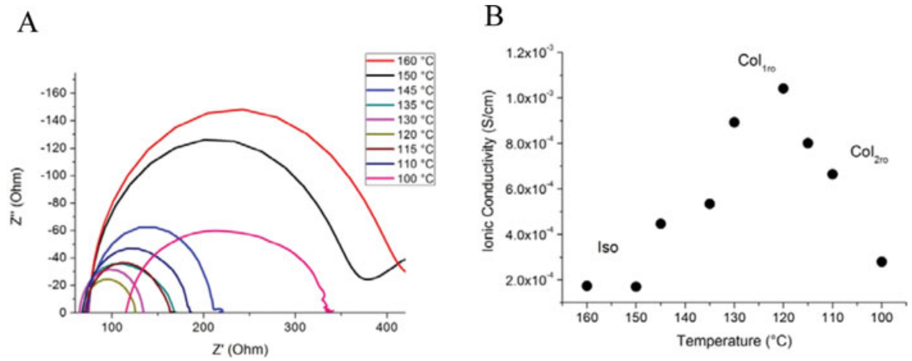

Figure 5. Electrochemical impedance spectra as a function of temperature measured on a thin film of the LC material with a two ITO electrodes cell (cell gap 10 μm; active electrode area 0.16 cm^2) (A). Ion conductivity of the LC material as a function of temperature (B).

response of the material at 120°C in the Col$_{1ro}$ phase. Under a DC bias, the normalized transmittance suddenly decreases and is completely recovered at zero voltage in a few seconds, clearly showing the reversibility of the electrochromic response accompanied by a discoloration of the LC film.

An efficient electrochromic response can be achieved in electroactive LCs if two conditions are respected: (i) fast formation of an electrical double layer at the electrode surface and (ii) fast electronic transfer through the overlapped LUMO orbitals of the large π-conjugated system [1–3]. The first condition can be provided by an electrolyte solution because its ions prevent electrode polarization that otherwise limits the electronic charge injection. Electrolyte solution can be avoided if the semiconducting liquid crystals incorporate ionic groups [25], because an electrical double layer can be rapidly generated by the fast moving counterions, under an electric field. Bulk electrochromism was indeed observed for the first time by Kato et al. on a series of π-coniugated smectic A ionic LCs in which hole transport and ionic transport occurred through preferential channels within the nanosegregated strutture of the SmA phase [25].

Here we showed for the first time the bulk electrochromic switching in the columnar rectangular phase of an n-type semiconducting ionic liquid crystal, the thienoviologen **9V(NTf$_2$)$_2$**. In this case, electrochromism is achieved by easy electron injection at the cathode. Electrons are then transported within the LC film through the highly delocalizated π-system of the thienoviologen, by a hopping mechanism. At the same time, the triflimide counterions migrate toward the anode in order to prevent electrode polarization. Anion migration should be fast indicating the high ionic conductivity of the material.

This was measured as a function of the temperature by impedance spectroscopy (Figure 5). Figure 5A reports the impedance spectra as a function of the temperature in the range 160–100°C. The complete semicircle, occurring at high frequency, was used to fit the conductivity of the material, which is shown in Figure 5B. It can be seen that the conductivity of the LC material increases by approximately one order of magnitude when going from the isotropic liquid state to the Col$_{1ro}$ phase, where it exhibits values as high as 10^{-3} S/cm. Upon further cooling in the Col$_{2ro}$ phase, the conductivity decreases, but it is still very high. These data show that when the material is structured into the columnar rectangular assembling, active transporting channels are created that allow an efficient bistriflimide ion migration.

4. Conclusions

Here we showed for the first time an electrochromic device based on a rectangular columnar ionic liquid crystal with strong n-type behavior. The electrochromic response is reversible as shown by both cyclic voltammetry and electrochromic switching studies. Electrochromism, consisting in a color change from red to dark of the thin liquid crystalline film, is due to the combination of fast electronic and ionic conductivities arising from the anisotropic functional organization of the columnar phase.

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