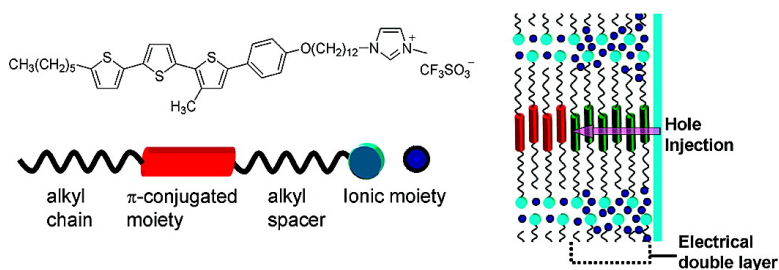


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An Electrochromic Nanostructured Liquid Crystal Consisting of π -Conjugated and Ionic Moieties

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Electroactive nanostructured liquid crystals¹ have attracted attention because self-organized assemblies of π -conjugated molecules² can induce additional enhanced or anisotropic properties such as electric functions.^{3,4} For example, redox-active liquid crystals⁵ are expected to be applied to electrochromic materials,⁶ actuators,⁷ and light-emitting electrochemical cells.⁸ However, the electrochromism of the electroactive liquid crystal materials has been observed only in solutions or in thin films dipped in electrolyte solutions.^{5b,d,e} The reversible electrochromism in the bulk of the liquid-crystalline state should enable realization of single-layer electrochromic devices without electrolyte layers.

For efficient electrochromism, fast formation of an electrical double layer at an electrode surface is essential. Fast electronic charge transfer from the electrode is also required. π -Conjugated polymers bearing ionic moieties have been examined.⁹ However the mobilities of the ionic species are very low in the polymers, and electrical double layers are not formed under the application of the electric field. Therefore electrolyte solutions are essential for the electrochromic devices using π -conjugated polymers.⁹

Our interest is to use nanostructures of liquid crystals that combine an ion-conductive group and a π -conjugated moiety transporting electronic charges for the construction of redox-active anisotropic materials.

Herein, we report on the electrochromism in the bulk liquid-crystalline state without an electrolyte solution. We synthesized liquid crystal **1** consisting of an imidazolium group as an ion-conductive part and phenylterthiophene moiety associated with the electronic charge transport.

Ionic liquid crystals such as imidazolium-based liquid crystals exhibit efficient ion transport in smectic layers or in inner columns.^{4a-f} For π -conjugated liquid crystals, enhanced electronic charge carrier transport has been observed in the smectic phases of oligothiophene derivatives^{3f-1} and the columnar phases of disk-like molecules.^{3a-e} If we use ionic and π -conjugated liquid crystals to obtain electrochromic liquid crystals, ion-conductive and hole-conductive channels should be constructed separately because of the microscopic phase separation^{1e,4a} of these moieties. As shown in Figure 1, the ions would be accumulated on the surface of the electrode forming an electrical double layer when an electric field is applied to the liquid crystal. Subsequently, electronic charges should be injected from the electrode into the π -conjugated systems of the liquid-crystalline molecules and transported between them, leading to electrochromism⁶ or light emission.⁸

As shown in Figure 2, liquid-crystalline molecule **1** has an imidazolium triflate moiety and a 3-methyl-5-phenyl-2,2':5',2''-terthiophene group. For a reference, phenylterthiophene derivative **2** with no ionic moiety was synthesized. Compound **1** exhibits a smectic A phase between 150 and 47 °C on cooling. The layer

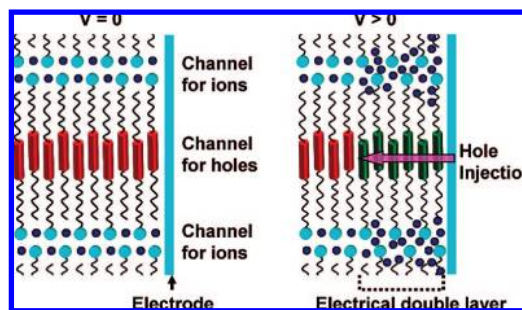


Figure 1. Schematic image of a nanostructured liquid crystal consisting of ionic and π -conjugated moieties. Red cylinders are neutral phenylterthiophene moieties. Dark green cylinders are the oxidized ones. Dark blue spheres and light blue plates are triflate anions and imidazolium moieties, respectively.

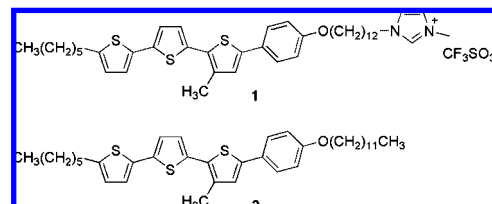


Figure 2. Molecular structures of compound consisting of ionic and π -conjugated moieties **1** and reference compound without an ionic moiety **2**.

spacing of the smectic A phase at 120 °C is 47 Å. Reference compound **2** shows a monotropic smectic A phase between 86 and 82 °C.

We have found that compound **1** exhibits electrochromism in the bulk liquid-crystalline state without a liquid electrolyte layer, unlike conventional redox-active conjugated polymers⁶ and liquid crystals.⁵ Liquid crystal **1** was capillary-filled into a cell consisting of two ITO-coated glass plates. The observation of micrographic texture reveals homogeneous alignment of the liquid-crystalline molecules. When the voltage increases to 5 V, the color of the liquid crystal layer changes from pale yellow to dark blue (Figure 3a). The color is restored to the original state when the voltage is decreased to -1 V (Figure 3b). For a dichloromethane solution of compound **1**, a reversible one-electron oxidation is observed in cyclic voltammetry. This oxidation accompanies a color change due to the formation of the radical cation of the π -conjugated moiety. This observation for the solution state suggests that, for the bulk liquid-crystalline state, the color change should also be attributed to the formation of radical cations of **1**. Such a color change does not occur in the bulk liquid-crystalline states of phenylterthiophene derivative **2** which has no ionic moiety.

The transmittance of the liquid crystal in the cell changes under the bias application, as shown in Figure 4. A He-Ne laser ($\lambda =$

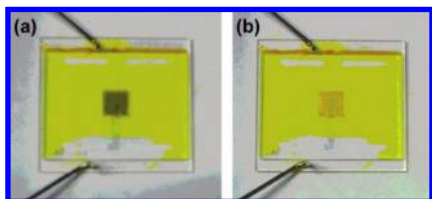


Figure 3. Photographs of the liquid crystal cell heated at 120 °C. After the application of (a) positive bias (5 V) and (b) negative bias (−1 V). The sample thickness is 4 μm.

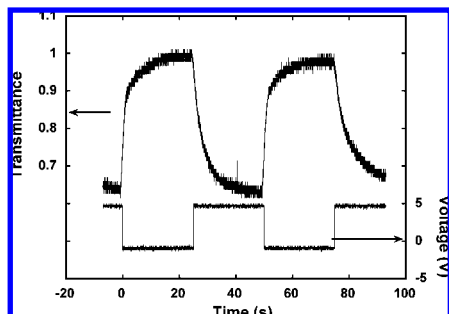


Figure 4. Response of the transmittance on the application of the DC voltage between 5 and −1 V. The sample thickness is 4 μm.

632.8 nm) is illuminated on the liquid crystal cell, and the transmitted light is monitored by a photodiode. When the positive potential of 5 V is applied, the transmittance decreases in several seconds. The transmittance is recovered in several seconds when a negative potential of −1 V is biased. Reference compound **2** does not exhibit such electrochromism in the bulk liquid crystal state in spite of its comparable oxidation potential to that of compound **1**.

Generally, electrochromism based on π -conjugated materials is performed in thin films deposited on electrodes dipped in electrolyte solutions.⁶ Electronic charge injection is assisted by the electrical double layer formed by mobile ions in the electrolyte solution. In contrast, for compound **1**, the ionic and the π -conjugated moieties which are nanosegregated form two-dimensional ion-conductive channels between hole transport layers, as shown in Figure 1. The presence of the mobile ions in the nanosegregated smectic phase leads to the rapid formation of the electrical double layer without the electrolyte solution. Consequently, the holes are injected from the anode and transported into the hole transport layers consisting of phenylterthiophene moieties, resulting in the oxidation of the π -conjugated moieties.

The nanostructured liquid-crystalline materials consisting of the ion-conductive and hole transport layers have been built by the association of π -conjugated molecules having ionic moieties. This liquid crystal can be applied to various electronic devices such as light-emitting electrochemical cells as well as the electrochromic devices.

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Supporting Information Available: Synthesis, polarized optical microscopic images, DSC charts, X-ray diffraction patterns, and electro-

chemical measurements of compound **1**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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