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Viologen-Based Redox-Active Ionic Liquid Crystals Forming Columnar Phases

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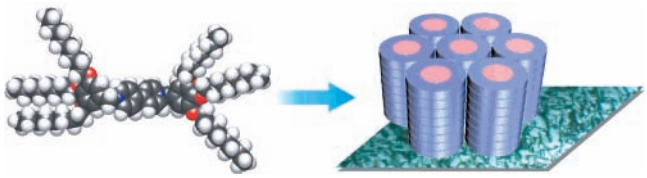
ABSTRACT



Viologens possessing three alkoxy chains at each terminal self-organize into columnar liquid-crystalline phases through nanophase segregation and electrostatic interactions. These viologens are redox-active and susceptible to two consecutive electrochemical reductions.

Liquid-crystalline (LC) molecular assemblies can be used for preparing a variety of dynamically functional materials.[1,2] Columnar liquid crystals exhibiting ion- and electron-active functions have received significant attention because they can act as one-dimensional (1D) transporters.[2a,3,4] We have recently reported that fan-shaped imidazolium salts bearing alkoxy chains form columnar LC phases and serve as anisotropic ion-conductors.[3a,b]

Our intention here is to incorporate a redox-active functional unit into dynamically ordered LC structures.[5] If redox-active materials form columnar assemblies, 1D pseudo "core−shell" structures that have anisotropic electrical and electrochemical functions could be obtained in the LC states. In this regard, we have designed new viologen-based molecules having three alkoxy chains at each terminal (Figure 1), which can promote self-organization into columnar LC structures. Viologens are an important class of

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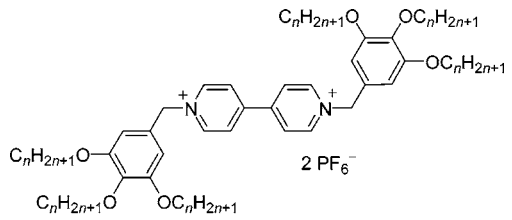

1 (n = 8)
2 (n = 12)
3 (n = 16)
4 (n = 1)

Figure 1. Molecular structures of liquid-crystalline viologens **1**−**3** and their model compound **4**.

materials that show interesting properties such as electrochromism and electrical conductivity,[6] and are also employed as components of supramolecular architectures.[7−9] For further applications of viologens, the introduction of ordered self-organized structures as well as the control of intermolecular interactions in the condensed state should be of great importance.

Herein we report on a new series of redox-active liquid crystals **1**−**3** based on viologens that form columnar assemblies. To date, a few thermotropic LC viologens exhibiting smectic and/or nematic phases have been reported.[10] To our knowledge, however, there is no precedent of viologens which are capable of forming columnar LC phases.

New viologens **1**−**4** (Figure 1) were prepared via the quaternization reaction of 4,4′-bipyridyl with 2 equiv of the corresponding trialkoxy-substituted benzyl bromide, followed by the counterion exchange. All these compounds were characterized by ^{1}H and ^{13}C NMR spectroscopy, MALDI-TOF mass spectrometry, and elemental analysis (see the Supporting Information).

The LC properties of viologens **1**−**3** are summarized in Table 1 (see also the Supporting Information). Viologen **1** bearing six octyloxy chains shows a hexagonal columnar (Col_h) phase, whereas viologens **2** and **3** form rectangular columnar (Col_r) phases. The crystalline (Cr)-Col_h phase transition for **1** is observed at −15 °C and the Col_h phase is stable up to 160 °C. At 160 °C, the compound starts to decompose gradually. The transition temperatures of crystal-to-liquid crystal increase with the increase of the alkoxy chain length.

Table 1. Liquid-Crystalline Properties of Viologens **1**−**3**

compd	n	phase transition[a]	lattice parameter[b] (Å)
1	8	Cr −15 (5.1) Col_h[c]	a = 33.7
2	12	Cr 47 (43.2) Col_r[c]	a = 69.5, b = 34.4
3	16	Cr 64 (98.2) Col_r[c]	a = 74.9, b = 39.1

[a] Transition temperatures (°C) and enthalpies (kJ mol^{-1}, in parentheses) determined by DSC on the second heating at 10 °C min^{-1}. Cr: crystalline. Col_h: hexagonal columnar. Col_r: rectangular columnar. [b] Determined by XRD data in the Col_h phase for **1** and in the Col_r phases for **2** and **3** at 100 °C. [c] The isotropization temperatures could not be determined because thermal degradation occurred above 160 °C before reaching the isotropic state.

X-ray diffraction (XRD) measurements were conducted for viologens **1**−**3**. The XRD pattern of **1** taken at 100 °C (Figure 2a) clearly shows three reflection peaks in the small-angle region with the reciprocal d-spacing ratio of $1:\sqrt{3}:2$, characteristic of a Col_h structure. In addition, a diffuse halo around 4.5 Å arising from the conformationally disordered alkoxy chains is observed, whereas no distinct peaks corresponding to the stacking periodicity could be detected in the wide-angle region. The intercolumnar distance (a) of **1** in the Col_h phase is calculated to be 33.7 Å from the XRD data (Table 1). This value agrees with the fully extended molecular length of ca. 36 Å for **1** (Supporting Information).

Meanwhile, there are obvious differences in the XRD patterns as well as the columnar structures as for **2** and **3**. As shown in Figure 2b, the XRD pattern of **2** at 100 °C gives two intense peaks at 34.0 and 30.4 Å with a set of smaller peaks in the small-angle region. This pattern is consistent with a Col_r phase with $c2mm$ symmetry.[11] This structural difference in the Col_h and Col_r phases can be explained in terms of the aspect ratio for respective viologen

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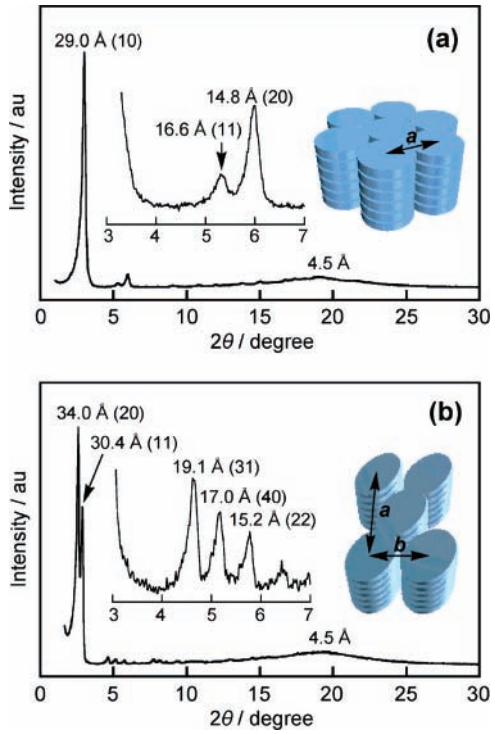

Figure 2. X-ray diffraction patterns of (a) **1** in the Col_h phase at 100 °C and (b) **2** in the Col_r phase at 100 °C. Insets show schematic representations of the proposed structures of the columnar phases.

molecules. Viologens **2** and **3** with elongated terminal alkoxy chains should have more elliptical molecular structures compared to **1**, so that they may prefer to form the Col_r phases. The phase behavior of viologens **1**−**3** is different from that of previously reported oligothiophenes having two trialkoxy benzoyl moieties at their extremities,[4g] in which Col_h phases are exclusively observed regardless of the terminal chain length.

It is noteworthy that in spite of the bent structure of the attached benzyl groups that prevent planarity of the molecule, the mesomorphism for viologens **1**−**3** is not disturbed. The nanosegregation of the ionic bipyridinium cores and the surrounding lipophilic parts will facilitate the organization of such viologen molecules into the columnar assemblies. Such nanosegregation behavior was observed for thermotropic ionic liquid crystals based on ammonium, pyridinium, and imidazolium salts.[3a,b,12] For viologens **1**−**3**, it can be assumed that approximately 2−3 molecules[13] self-assemble to form an overall disk-like object in a similar way as in polycatenar mesogens.[4g,14]

To obtain further structural insight, X-ray crystallographic analysis was performed for nonmesomorphic homologue **4**.[15] Figure 3 depicts the projection of the packing structure for

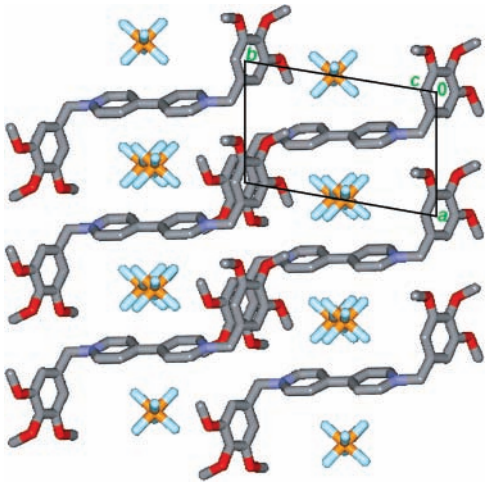

Figure 3. Crystal packing diagram of **4** (as the PF_6 salt) along the *c* lattice direction: N blue, O red, P orange, and F light-blue. Hydrogen atoms and solvent molecules (acetone) are omitted for clarity.

4. The bipyridinium central core adopts a nearly planar conformation with the dihedral angle between two rings of 0.7°, supporting delocalization of the positive charges along the conjugated bipyridinium fragment. Furthermore, the viologen molecules are arranged in a parallel manner through electrostatic interactions with PF_6^- counterions, giving rise to a columnar structure with segregation between the ionic bipyridinium and the lipophilic benzyl moieties. This result supports the foregoing notion that viologens **1**−**3** preferably form columnar assemblies in their LC states.

The redox behavior of viologens **1**−**3** was examined by cyclic voltammetry (CV). A representative voltammogram for **1** in CH_2Cl_2 is displayed in Figure 4a. Two consecutive reversible one-electron reductions take place at the half-wave potentials ($E_{1/2}$) of −0.58 and −1.03 V vs Ag^+/Ag, which are assignable to the formation of the radical cation and the neutral species, respectively (Scheme 1).[6] The first and second reduction potentials of **1** are comparable to those of

(11) In the XRD patterns of viologens **2** and **3**, all the (*hk*) reflections satisfy the condition of $h + k = 2n$. On the basis of these results, the type of symmetry of the Col_r phase can be identified as *c*2*mm*: Laschat, S.; Baro, A.; Steinke, N.; Giesselmann, F.; Hägele, C.; Scalia, G.; Judele, R.; Kapatsina, E.; Sauer, S.; Schreivogel, A.; Tosoni, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 4832.

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(13) The average number of molecules in a column stratum (μ) was estimated according to the following equation: $\mu = (N_A Sc\rho)/M$, where N_A is Avogadro's number, S is the cross-section area of each column ($S = a^2\sqrt{3}/2$ for a Col_h phase and $S = ab/2$ for Col_r phases), c is the thickness (estimated as ca. 6.3 Å based on the X-ray crystal structure of **4**), ρ is the density (assumed to be 1 g cm^{-3}), and M is the molecular weight of the compound.

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(15) Single crystals of **4** suitable for X-ray crystallography were obtained by slow diffusion of methanol into a solution of **4** in acetone. The data (CIF) are given in the Supporting Information.

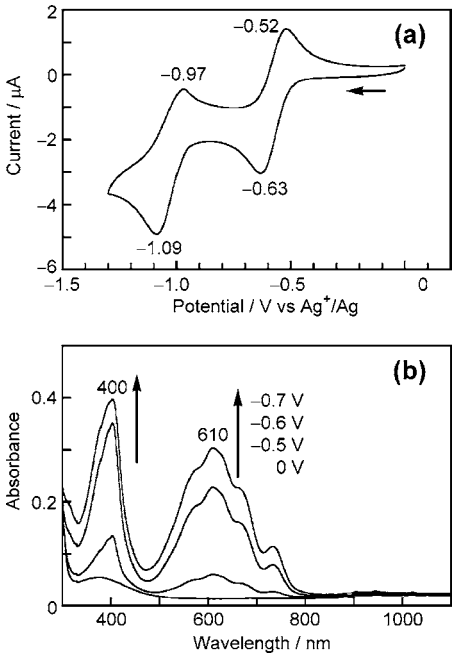
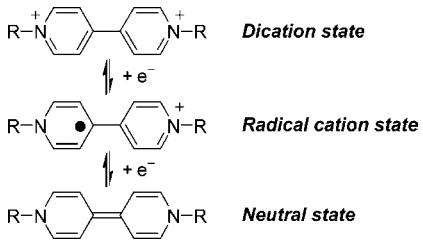


Figure 4. (a) Cyclic voltammogram of **1** (1.0 mM) recorded in a CH_2Cl_2 solution of Bu_4NClO_4 (0.10 M) with a Pt working electrode. The sweep rate is 100 mV s^{-1}. (b) UV-vis-NIR spectra of **1** observed during the first reduction in the same solution. Arrows indicate the direction of spectral changes.

1,1′-dioctyl-4,4′-bipyridinium in CH_2Cl_2 ($E_{1/2} = -0.58$ and -1.06 V vs Ag^+/Ag).

The absorption spectra of **1** at different reduction states are shown in Figure 4b. When the potential is negatively increased from 0 to −0.7 V, new absorption bands centered at 400 and 610 nm appear, which would originate from the radical cation state (Scheme 1). This reduction process is accompanied by an obvious color change from light-yellow to dark-blue in the solution. Upon application of further negative potentials up to −1.3 V, the visible absorption in the range of 500−800 nm becomes weaker again (Supporting Information), suggesting the transformation into the neutral state. The redox processes of **1** remain stable after continuous cycling.

Scheme 1. Structural Changes in Viologens by Electrochemical Reduction (R = 3,4,5-trialkoxybenzyl)



In summary, we have described the first example of columnar liquid crystals incorporating a redox-active viologen unit. These viologens were found to form columnar assemblies through nanosegregation and electrostatic interactions. The obtained results may offer new prospects for developing redox-active liquid crystals as bulk materials.

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Supporting Information Available: Synthetic procedures and characterization data for **1**−**4** and crystallographic information file (CIF) for **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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