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A redox-active columnar metallomesogen and its cyclic voltammetric responses[†]

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We demonstrate a strategy that appears particularly well suited for the design of redox-active liquid crystals and also constitutes the first demonstration of cyclic voltammetric responses of a metallomesogen in the columnar liquid crystalline phase.

Liquid crystals (LCs) have anisotropic structures with an enormous variety of functional properties. The self-assembly of mesogenic units into ordered materials has thus been a useful technique in materials science. More recently, new molecular components are being designed that readily form ordered supramolecular LC assemblies.1 Here we note that in addition to the presence of periodic order in LCs, flexibility in physical structure, correlated with changes in electronic structure, seems to be regarded as a desirable property. Changes in electronic structure may be associated with an electron transfer process occurring at a redox-active functionality of the mesogen. LCs with redox-active groups have been reported,² however, studies on their electrochemical activity have only been carried out in solution where there is little or no periodic order.³ To develop this field, (1) a proper design of a LC consisting of redox-active molecular units having a melting point (the temperature for the crystal-to-liquid crystal phase transition) around room temperature and (2) a proper electrochemical methodology are needed as important initial steps. Thereby, it would be possible to better understand the correlation between redox-induced changes in electronic structure with the macroscopic change in physical structure that would occur within the ordered assembly. In this communication, we report a first synthesis and electrochemical properties of a metallomesogen containing dioxylene ligands, which shows reversible redox steps between o-benzoquinone (BQ), o-semiquinonate (SQ^{•-}), and catecholate (Cat²⁻) electronic forms.⁴

Our design and synthesis of a redox-active metallomesogen started with a complex of Pt(II) with 2,2'-dipyridyl ligands substituted by two branched 3-octyltridecyl groups (C8,10bpy) at the 4,4'-positions (Scheme 1). Subsequent reaction with catechol (CatH₂) and [PtCl₂(C8,10bpy)] afforded violet-colored [Pt(Cat)(C8,10bpy)] (1). Differential scanning calorimetry (DSC) and X-ray diffraction (XRD) measurements‡ revealed that a

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Scheme 1

sample of **1** prepared by methods reported in the ESI[†] transformed to an isotropic liquid (Iso) at 189 °C, and successive cooling initiated the growth of a dendritic texture with sixfold symmetry at 180 °C, shown in Fig. 1a. Complex **1** manifests itself through the XRD pattern shown in Fig. 1a obtained at 30 °C. In the low angle region, up to five sharp Bragg reflections appear, with reciprocal spacings in the ratio of $1 : (1/3)^{1/2} : 1/2 : (1/7)^{1/2} : 1/3$



Fig. 1 a) XRD pattern of **1** at 30 °C and optical polarizing micrographic texture of a thin film of **1** between two glass slides at 180 °C under crossed polarizers. The crossed arrows indicate the orientation of the polarization filters in the microscope. b) The assembled structure of the Col_{ho} phase; top view of the column (left) and the hexagonal packing of the columns (right). The red and blue circles illustrate the domains shared by the mesogenic core and the molten alkyl chains, respectively.

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a)

0.03

in agreement with Miller indices (10), (11), (20), (21), and (30), respectively, for a hexagonal lattice. In addition, a broad reflection centered at 20.7° with a *d*-spacing of 4.3 Å appears, indicative of the molten alkyl chains. Of particular interest was a reflection centered at 26.4° with a d-spacing of 3.4 Å, demonstrating a weakly ordered structure. All these features support the conclusion that complex 1 forms a hexagonal columnar ordered LC phase (Col_{ho}),³ as schematically illustrated in Fig. 1b. Inter- and intracolumnar distances were estimated to be 22.5 Å (a_{bex}) and 3.4 Å (001), respectively, which can be reproduced by assuming a one-dimensional column constructed from the molecules aligned in an antiparallel fashion. Because the size of the mesogenic core of 1 was estimated to be about 11 Å,5[†] the antiparallel alignment is reasonable, not only from the size balance between the observed $a_{\rm hex}$ and the mesogenic core (11 Å), but also from consideration of the asymmetric dipolar alignment of the cores.

Further analyses of the variable temperature XRD and DSC data have revealed that the thermal annealing of the supercooled Col_{ho} phase at 0 °C for 5 h leads to the formation of an unidentified phase (X), which is characterized by a hexagonal lattice with an expanded lattice constant of $a_{hex(X)} = 27.1$ Å, together with four new reflections at 5.96, 15.1, 23.9, and 27.2°, instead of the (001) reflection.† Upon cooling, the X phase transforms into a glassy phase (G_X) at -62 °C keeping its symmetry, and a subsequent second heating process proved the sequence of phase changes summarized as follows: G_X -62 °C X 31 °C (3.9 kJ mol⁻¹) Col_{ho} 192 °C (1.3 kJ mol⁻¹) Iso. The Col_{ho} phase appears over the relatively wide temperature range of 161 °C.

Complex 1 undergoes a quasi-reversible one electron oxidation and reduction at -0.01 V and -1.87 V versus Fc/Fc⁺, respectively, in CH₂Cl₂ solution (Fig. 2a). These electrochemical couples correspond to ligand-based processes:⁶ the oxidation process could provide a mono-cationic [Pt^{II}(SQ⁺)(C8,10bpy)]⁺ species, while a low-lying π^* orbital of the C8,10bpy could accept an electron to produce a mono-anionic [Pt^{II}(Cat)(C8,10bpy⁺)]⁻ species (Fig. 2b).

Fig. 2 a) CV in CH₂Cl₂ solution at 25 °C (1 mM, 0.1 M *n*-Bu₄NClO₄, N₂, 100 mV s⁻¹) and b) the redox scheme for 1.



Fig. 3 a) A photograph of 1 spin-coated on an ITO electrode (0.8 cm \times 5 cm) at 25 °C. b) An atomic force microscopy image of a spin-coated film on an ITO electrode. c) The XRD patterns of 1 spin-coated on an ITO electrode (red line) at 25 °C and the bulk sample of 1 at 30 °C (black line). A diffraction peak at 21.3° (red line) is that of an ITO electrode.

To establish the direct electrochemical activity of 1 in the LC phase, we mounted 1 on an indium tin oxide (ITO) electrode by a spin coating method or gradual cooling method from the Iso phase.^{†7} A photograph and an AFM image of the spin-coated film prepared at 4000 rpm for 30 s are shown in Fig. 3a and b, respectively. The AFM data collection was performed in a tapping mode under air. The film is very flat, and has a thickness of 50 nm (a part of the film was removed using hexane before the AFM measurement to expose the bare ITO surface. This procedure formed a film with thick edges). The XRD diffraction pattern of the film shows that two sharp diffractions of at $2\theta = 4.42^{\circ}$ and 8.84° can be indexed as (10) and (20), respectively, indicating the formation of the Col_{ho} phase on the electrode (Fig. 3c). The film was then immersed in a DMSO solution containing 0.1 M n-Bu₄NClO₄ at 25 °C. Since the Col_{ho} phase is insoluble in DMSO, the film of 1 was not removed via dissolution. Fig. 4a shows a plot of the peak current (I_p) in cyclic voltammetry at 2 V s^{-1} as a function of the number of potential scans. Here, the peak current decreases relatively rapidly, then remains almost unchanged after several scans, indicating a pseudo-steady state was reached. The transient decrease in current during several of the initial scans may be due to dissolution or exfoliation of the oxidized molecules that is the result of neutral molecules attached metastably onto the ITO electrode. In the pseudo-steady state region (after the twentieth cycle), the film shows a quasi-reversible CV response against repetitive scans (Fig. 4b), demonstrating the formation of an oxidized species and the reformation of the initial species within the electrochemically generated thin regions. The slight decrease in current on cycling is due to the dissolution of the



Fig. 4 a) Anodic (blue line) and cathodic (red line) peak currents as a function of the number of potential scans and b) repetitive CVs after the twentieth cycle for a spin-coated film of **1** on an ITO electrode.

oxidized species into the electrolyte solution.⁸ The observed I-V curve is characterized by diffusion tails with a peak separation of 0.21 V (the twentieth scan), suggesting a diffusion-controlled electron transfer process. The $E_{\rm mid}$ values are linearly dependent on the logarithm of the concentration of *n*-Bu₄NClO₄,† suggesting anion insertion/expulsion processes upon oxidation and reduction accompanied by the redox processes described in eqn (1).⁸

$$\mathbf{1}_{\text{Colho}} + \text{ClO}_{4}^{-}_{\text{DMSO}} \rightleftharpoons \mathbf{1}^{+} \cdot \text{ClO}_{4}^{-}_{\text{ITO}} + e^{-} \qquad (1)$$

In summary, we demonstrate a strategy for the design of electrochemically active LC materials. A significant stabilization of the Col_{ho} phase is brought out by the interplay of the branched alkyl chains and the stacking interactions of the central planar core comprised of the asymmetric mixed ligands. The results reported here also characterize the electrochemical activity of a metallomesogen, promising to provide significant insight into the electronic functions of LC materials. Further work is in progress to control both molecular properties and macroscopic bulk phases of liquid crystalline compounds by means of electrochemical stimulus.

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Notes and references

‡ XRD measurements were carried out with Cu Kα radiation equipped with a Rigaku RINT-2000 diffractometer using Al sample pans. Differential scanning calorimetry measurements were performed on a METTLER DSC822e. Electrochemical measurements were carried out with an ALS model 650A electrochemical analyzer. A standard threeelectrode system (a glassy carbon working electrode, platinum-wire counter electrode, and Ag/Ag⁺/CH₃CN electrode as reference) was used for CV studies in solution. Liquid crystalline 1 was spin-coated (4000 rpm, 30 s) from 100 µl of a 10 mM toluene solution on an indium tin oxide electrode purchased from Sanyo Vacuum Industries Co. Ltd. (5.7 Ω \square^{-1} , A =2.4 cm²). The AFM image was taken with a NANOSCALE hybrid microscope VN-8000 series (Keyence) in a tapping mode.

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