

Donor–Acceptor–Donor-Type Liquid Crystal with a Pyridazine Core

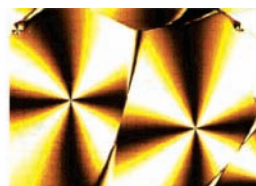
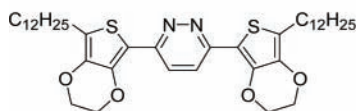
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Received July 12, 2006

ABSTRACT



A new liquid crystalline material having an ethylenedioxythiophene–pyridazine–ethylenedioxythiophene (EDOT–PDZ–EDOT) core with two peripheral long alkyl chains was prepared. The designated donor–acceptor–donor (D–A–D)-type core structure induced a distinct smectic liquid crystalline phase due to the strong intermolecular interaction. The photophysical property and the layer structure of the liquid crystal were investigated by differential scanning calorimetry, polarized light microscopy, X-ray diffraction, and cyclic voltammetry.

The π -conjugated organic materials have been the subject of recent research work in relation to their optical and electronic properties as well as their electronic applications in many fields such as electroluminescent diodes (OLED),¹ thin-film organic field-effect transistors (OFET),² photovoltaic cells, sensors, semiconductors, and displays.³ If one introduces a π -conjugated moiety into a liquid crystalline system, the resulting material can have many advantages

arising from the inherent self-assembling propensity.⁴ In the past few years, considerable efforts have been made to design, synthesize, and characterize various π -conjugated liquid crystalline materials. In particular, smectic liquid crystals have been a promising alternative approach to organic semiconductors because of their spontaneous alignment behavior and good solubility.⁵

We have been focusing on new π -conjugated materials with a donor–acceptor–donor (D–A–D) system containing electron-rich 3,4-ethylenedioxythiophene (EDOT) and electron-deficient pyridazine and found that this system shows strong intermolecular interaction.⁶ Although many nitrogen-containing heteroaromatic rings such as pyridine,⁷ pyrazine,⁸ and pyrimidine⁹ have been employed as an electron acceptor, the use of a pyridazine ring as an acceptor in a conjugated system has not been studied until Yamamoto and co-workers reported thiophene–pyridazine–thiophene D–A–D conju-

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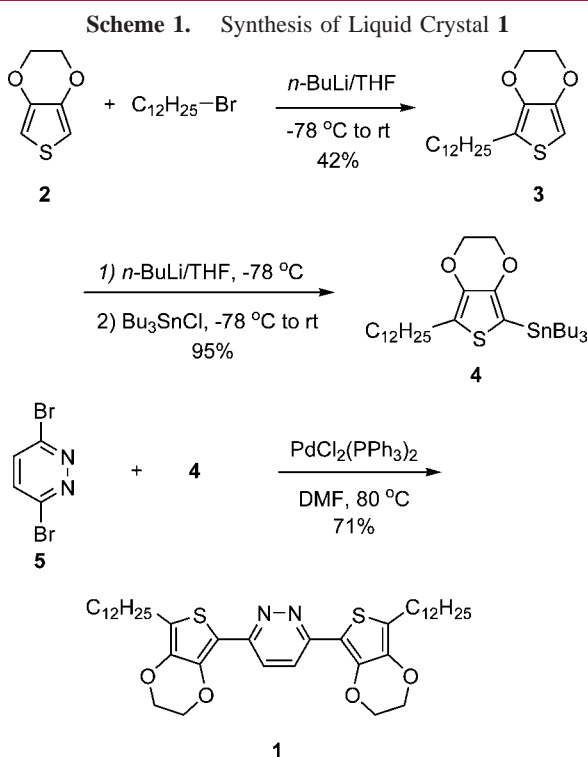
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(6) We have synthesized 3,6-bis(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)pyridazine (EDOT–pyridazine–EDOT) and found that this compound is very insoluble in any solvent once it forms a solid upon concentration. It is presumed that the lattice energy of this material is substantially high.

gated polymers in 2005.¹⁰ In their report, they have shown that the thiophene–pyridazine–thiophene D–A–D repeat unit allows compact packing arising from the strong intermolecular interaction resulting in good charge mobility for OFET applications. In addition, although EDOT has been widely used as a building block for many functional π -conjugated systems,¹¹ reports on liquid crystalline compounds containing EDOT can rarely be found except for a few studies on EDOT oligomers containing short alkyl chains.¹²

To understand this strong intermolecular interaction further, we have synthesized pyridazine and the EDOT-containing D–A–D-type liquid crystal, 3,6-bis(5-dodecyl-2,3-dihydrothieno[3,4-*b*][1,4]dioxin-7-yl)pyridazine (**1**) (Scheme 1), and studied its photophysical and liquid crystalline properties.



EDOT (**2**) was treated with *n*-BuLi at $-78\text{ }^{\circ}\text{C}$ in THF, and the resulting lithiated EDOT was alkylated with dodecyl

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bromide to give 2-dodecyl-3,4-ethylenedioxythiophene (**3**) in 42% yield. Then, **3** was converted to stannyl derivative **4** by treatment with *n*-BuLi followed by Bu₃SnCl. The resulting stannane **4** was subjected to the Stille coupling reaction¹³ with 3,6-dibromopyridazine (**5**) in DMF using PdCl₂(PPh₃)₂ as a catalyst to give the desired product **1** in 71% isolated yield. The structure of **1** was confirmed by ¹H NMR and ¹³C NMR spectroscopy and mass spectrometry.

The UV absorption and fluorescence emission spectra of **1** are given in Figure 1. The absorption spectrum of **1** in

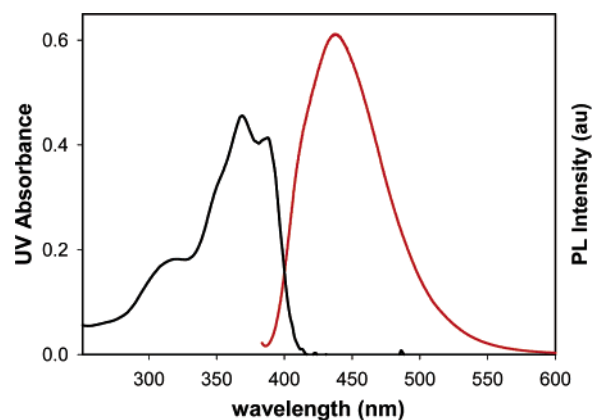


Figure 1. UV–vis absorption (black) and PL spectra (red) of **1** (excitation $\lambda = 386\text{ nm}$) in CHCl₃ ($1 \times 10^{-5}\text{ M}$).

chloroform shows a well-resolved vibronic structure with two distinct maxima at 369 ($\epsilon = 33\,400\text{ M}^{-1}\text{ cm}^{-1}$) and 388 nm ($\epsilon = 30\,300\text{ M}^{-1}\text{ cm}^{-1}$), which infers the rigidity of the core structure. On the other hand, the fluorescence spectrum of **1** shows a structureless blue emission at 432 nm. The relative fluorescence quantum yield (Φ_F) of **1** was measured to be 0.045 using quinine sulfate as a standard.¹⁴

Thermotropic and liquid crystalline behaviors of **1** were evaluated by means of differential scanning calorimetry (DSC) and polarized-light optical microscopy (POM). DSC measurement of **1** exhibited two endothermic peaks at 58 and 108 $^{\circ}\text{C}$ at a heating rate of 1 $^{\circ}\text{C}/\text{min}$ (Figure 2a). It seems that the peak at 58 $^{\circ}\text{C}$ with a small ΔH is due to the crystal phase–smectic phase transition, and another peak at 108 $^{\circ}\text{C}$ with a larger ΔH is due to the smectic phase–isotropic phase transition, suggesting a higher-order mesophase such as a smectic phase. The mesophase has also been identified by polarized-light optical microscopy (POM): slow cooling of the sample from the isotropic liquid revealed the formation of a small focal conics which is the typical fingerprint of a smectic phase (Figure 2b).

To investigate the molecular packing structure of **1**, we performed a powder X-ray diffraction (XRD) experiment at room temperature (Figure 3a). The liquid crystal displayed a strong Bragg reflection. In the small-angle region, a sharp

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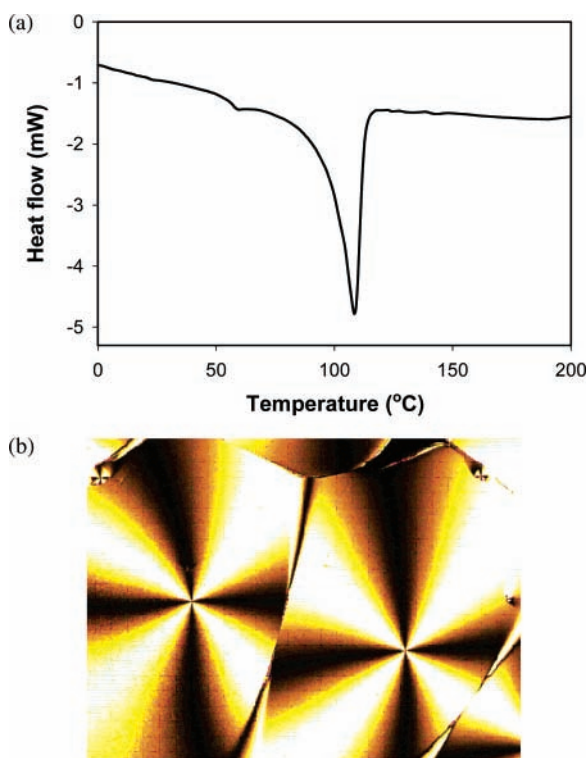


Figure 2. (a) DSC thermogram of **1**. (b) Texture of the liquid crystalline mesophase of **1** as observed by polarization microscopy ($\times 100$).

reflection peak at $2\theta = 3.65^\circ$ was detected, from which a d -spacing of 24.2 \AA was estimated. This value corresponds to the spacing between the layer planes. Its second-, third-, and fourth-order reflections ($24.2/n$; $n = 2, 3$, and 4) appeared at 12.1 , 8.1 , and 6.1 \AA , respectively. The several signals detected in the wide-angle region ($2\theta = 20\text{--}25^\circ$) indicate the intermolecular distances of the face-to-face π - π interaction in the crystalline structure. This result indicates that **1** self-assembles with high ordering via strong π - π stacking of D-A-D cores. Considering the estimated molecular length of **1** (41 \AA) and the XRD data, the liquid crystal seems to have the interdigitated molecular arrangement as shown in Figure 3b via strong π - π stacking of D-A-D cores and hydrophobic interaction of side chains.

The redox behavior of **1** was also investigated by cyclic voltammetry. The cyclic voltammogram of **1** (0.5 mM in MeCN with $0.1 \text{ M Bu}_4\text{NPF}_6$) was obtained in the region between $+0.7$ and -2.3 V vs Ag/Ag^+ at a sweeping rate of 50 mV/s . As shown in Figure 4, the CV of **1** showed a quasi-reversible oxidation wave at $+0.55 \text{ V}$ corresponding to oxidation of the EDOT unit and a reversible reduction wave with $E_{1/2} = -2.02 \text{ V}$ corresponding to one-electron reduction

(15) The difference in potential between the anodic peak ($E_a = -2.06 \text{ V}$) and the cathodic peak ($E_c = -1.99 \text{ V}$) in the negative potential region is 70 mV . The number of electrons (n) involved in the half reaction is calculated to be 0.8 at 25°C (see: Vassos, B. H.; Ewing, G. W. *Electroanalytical Chemistry*; John Wiley & Sons: New York, 1983; pp 124–126). This value closely corresponds to one electron half reaction.

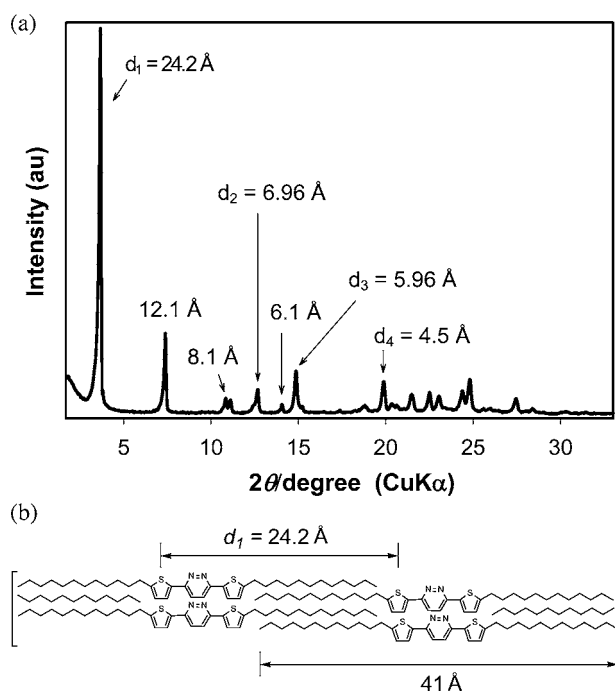


Figure 3. (a) Powder X-ray diffraction pattern of **1** at room temperature. (b) A proposed molecular arrangement of the liquid crystal.

of the pyridazine unit.¹⁵ Thereby, this material is expected to find a potential application as a hole-transporting (p -type) and electron-transporting (n -type) liquid crystalline semiconductor.

In summary, we have synthesized a new donor–acceptor–donor-type liquid crystalline material **1** that contains a pyridazine and two EDOT units using the Stille coupling reaction. This molecule showed a highly ordered smectic phase via strong π - π stacking of the D-A-D cores.

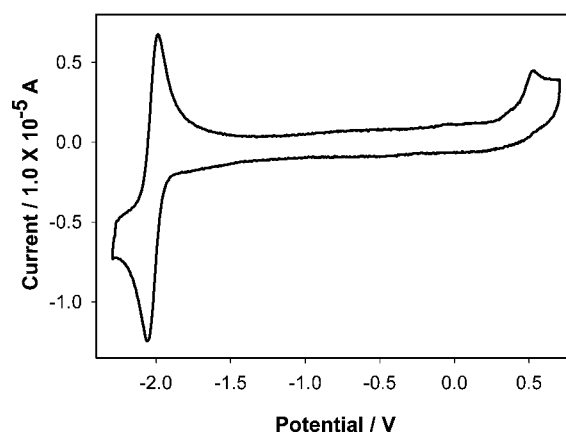


Figure 4. Cyclic voltammogram of **1** (0.5 mM) in $0.1 \text{ M Bu}_4\text{NPF}_6\text{-MeCN}$, with a GC electrode at a scan rate of 50 mV/s . A Pt electrode and a Ag/Ag^+ electrode were used as the reference and the counter electrode, respectively.

Electrochemical study of this molecule also showed a reversible reduction peak at -2.02 V vs Ag/Ag⁺ and a quasi-reversible oxidation peak at $+0.55$ V vs Ag/Ag⁺. We expect that this material can find a useful application in organic thin-film transistors.

Acknowledgment. This work was supported by Korea Research Foundation Grant (KRF-2006-005-J02101). This work was also partially supported by Sogang University Research Fund 2005. We are grateful to Dr. Jin Seok Lee

(Sogang University) for taking XRD of **1** and to Mr. Semin Lee (Sogang University) for measuring the fluorescence quantum yield of **1**.

Supporting Information Available: Synthetic procedures and characterization data for all new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OL061711Q