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Synthesis and Characterization of Near-Infrared Absorbing and Fluorescent Liquid-Crystal Chromophores

Xianzhen Li,[†] Anhua Liu,[‡] Shidi Xun,[†] Wenqiang Qiao,[†] Xinhua Wan,[‡] and Zhi Yuan Wang*[,†,‡]

Department of Chemistry, Carleton University, 1125 Colonel By Drive, Ottawa, Ontario, Canada K1S 5B6, and Department of Polymer Science and Engineering, College of Chemistry and Molecular Engineering, Peking University, 202 Chengfu Road, Beijing 100871, People's Republic of China

wayne_wang@carleton.ca

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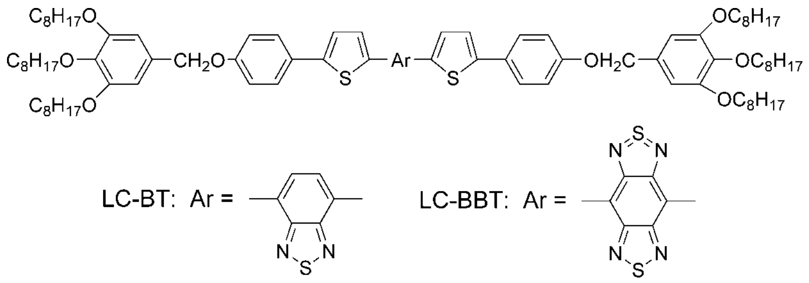
ABSTRACT



This work demonstrates that the donor−acceptor−donor charge-transfer chromophores can be tailor-made to be near-infrared absorbing and fluorescent, as well as being liquid crystals. The chromophore containing an extremely strong acceptor of benzo[1,2-*c*:4,5-*c*′]bis([1,2,5]thiadiazole) can form a columnar mesophase that absorbs at 890 nm and emits at 1160 nm in the solid state. These chromophores are readily soluble in common organic solvents and can form thin films by casting or spin coating, making them suitable for further device applications.

Recently, columnar mesophase liquid crystals (LC) have attracted considerable academic and commercial interests because of their unique structures and properties in organic semiconductors.[1−4] The planar uniaxial alignment with edge-on orientation of the molecules and columns parallel to the substrate is needed for field effect transistors (FET) to ensure the charge migration between the source and the drain, while the homeotropic alignment with a face-on orientation of the discs and the columnar axes perpendicular to the substrate is expected to be beneficial for the performance in photovoltaic cells (PVC) and light-emitting diodes (LED).[1,5−7] Generally, columnar mesophases are generated from discotic LC molecules. A large number of discotic LCs are known and derived from more than 50 different mesogens,[2] typically being a polyaromatic core such as triphenylene, phthalocyanine, and hexabenzocoronene (HBC).[8,9] For example, a p/n-type PVC containing a discotic LC HBC

[†] Carleton University.

[‡] Peking University.

(1) Sergeyev, S.; Pisula, W.; Geerts, Y. H. *Chem. Soc. Rev.* **2007**, *36*, 1902–1929.

(2) Kumar, S. *Chem. Soc. Rev.* **2006**, *35*, 83–109.

(3) 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*, 4832–4887.

(4) Tant, J.; et al. *J. Phys. Chem. B* **2005**, *109*, 20315–20323.

(5) Pisula, W.; Menon, A.; Setpputat, M.; Lieberwirth, I.; Kolh, U.; Tracz, A.; Sirringhaus, H.; Pakula, T.; Müllen, K. *Adv. Mater.* **2005**, *17*, 684–689.

(6) Zucchi, G.; Donnio, B.; Geerts, Y. H. *Chem. Mater.* **2005**, *17*, 4273–4277.

(7) Stapff, I. H.; Stumpflen, V.; Wendorff, J. H.; Spohn, D. B.; Mobius, D. *Liq. Cryst.* **1997**, *23*, 613–617.

(8) Herwig, P.; Kayser, C. W.; Müllen, K.; Spiess, H. W. *Adv. Mater.* **1996**, *8*, 510–513.

(9) Iyer, V. S.; Wehmeier, M.; Brand, J. D.; Keegstra, M. A.; Müllen, K. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1604–1607.

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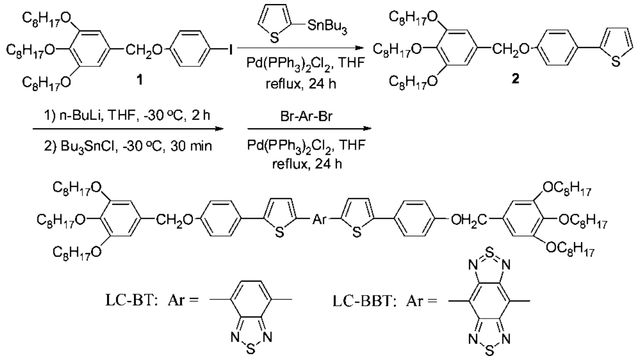
derivative and a perylene diimide derivative exhibited an external quantum efficiency of more than 34% near 490 nm and power efficiency of up to 2%.[10] To capture the infrared energy, low band gap or NIR-absorbing organic columnar mesophase LC semiconductors are urgently needed for PVCs. NIR materials have potential applications for telecommunications, thermal imaging, and biological imaging. The NIR light enables a deeper depth (5 cm) of detection than the visible light in tissue imaging and reduces the autofluorescence and absorption of biological species and water.[11] All the known columnar mesophase LC compounds absorb and emit light strongly only in the visible spectral region.[4]

Herein, we report the design and synthesis of low band gap donor−acceptor−donor (D-A-D) charge-transfer (CT) LC chromophores (Scheme 1). Among many low band gap organic compounds, the D-A type of chromophores are particularly useful as a potential NIR chromophore, because their band gap levels and other properties can be readily tuned by using a variety of donors and acceptors.[12−14] Thus, in our design for low band gap LC chromophores, a strong electron-withdrawing heterocyclic quinoid, benzo[1,2-*c*:4,5-*c′*]bis([1,2,5]thiadiazole) (BBT), is selected as an acceptor. A relatively less powerful electron-withdrawing acceptor, benzo[*c*][1,2,5]thiadiazole (BT), was also selected for comparison. The BBT-type unit is known to possess a substantial quinoidal character, allowing for greater electron delocalization and thus lowering the bandgap.[15−18] The two alkoxyphenyl donors are linked to the acceptor via a thiophene spacer, in order to facilitate a stronger intramolecular charge transfer and thus lower the band gap energy.

Scheme 1. Synthesis of LC-BT and LC-BBT Chromophores



Considering the molecular geometry, most of discotic LC molecules typically consist of a large disk-like core that is surrounded by several flexible peripheral chains. However, a long rod-like rigid core with two or three paraffinic chains at both ends is also known to generate columnar mesophases by assembling into groups of 3−4 molecules that generate one slice in a columnar stack.[19,20] Thus, in our design, the rigid rod-like D-A-D moiety is deemed to be a suitable mesogen and is attached with three long aliphatic tails at each side.

LC-BT and LC-BBT were synthesized by the Stille coupling reaction of the dibromo-BT and dibromo-BBT with the tributyltin derivative of **2**, respectively (Scheme 1). The reaction of **1** with tributyl(2-thienyl)stannane gave **2** in 97% yield (see the Supporting Information). Compound **2** was first converted to the tributyltin intermediate that was then used without further purification in the Stille coupling reactions for making LC-BT and LC-BBT. Both final products are characterized by spectroscopic means and their structures are consistent with the spectral data. They are found to be quite soluble in common organic solvents such as chloroform, tetrahydrofuran, toluene, and xylene. Thermogravimetric analysis indicates that the onset temperatures for 5% weight loss in air are 327 and 336 °C for LC-BT and LC-BBT, respectively (Figures S9 and S10, Supporting Information).

Birefractive phenomena were obviously observed for LC-BT by polarized optical microscopy (POM) when cooling to 103 °C from its isotropic phase, but no clear changes of the textures appeared when further cooling to room temperature (Figure S11, Supporting Information). The mesophase transition of LC-BT could not detected by differential scanning calorimetry (DSC) (Figure S16 and Table S2, Supporting Information) and X-ray diffraction (Figure S17, Supporting Information) at a heating or cooling rate of 5 deg/min. Thus, although LC-BT seems to a liquid crystal, its liquid crystal behavior is not very obvious, which may be due to the small molecular size and low structural symmetry of the benzothiadiazole core.

LC-BBT was then subjected to studies by DSC (Figure 1 and Table S2 in the Supporting Information) and POM (Figure 2). During the cooling run, DSC reveals two transitions: One takes place from isotropic to liquid crystal phase at 163.5 °C and another from liquid crystal phase to another phase at 138.5 °C. In the heating process two transitions occur at 158.3 and 165.7 °C. Upon cooling, fluid and birefringent phases are observed below 168 °C by POM (Figure S12, Supporting Information). Figure 2, taken from POM at 160 °C on cooling from the isotropic phase, shows clearly a pseudo-focal-conic texture, typical of a columnar mesophase. At temperature below 140 °C a large change in the optical texture took place (Figure S13, Supporting

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(10) Schmidt-Mende, L.; Fechtenkötter, A.; Müllen, K.; Moons, E.; Friend, R. H.; MacKenzie, J. D. *Science* **2001**, *293*, 1119–1122.

(11) Wang, S.; Li, X.; Xun, S.; Wan, X.; Wang, Z. Y. *Macromolecules* **2006**, *39*, 7502–7507.

(12) Roncali, J. *Chem. Rev.* **1997**, *97*, 173–206.

(13) van Mullekom, H. A. M.; Vekemans, J. A. J. M.; Havinga, E. E.; Meijer, E. W. *Mater. Sci. Eng., R* **2001**, *32*, 1–40.

(14) Wudl, F.; Kobayashi, M.; Heeger, A. J. *J. Org. Chem.* **1984**, *49*, 3382–3384.

(15) Ono, K.; Tanaka, S.; Yamashita, Y. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1977–1979.

(16) Karikomi, M.; Kitamura, C.; Tanaka, S.; Yamashita, Y. *J. Am. Chem. Soc.* **1995**, *117*, 6791–6792.

(17) Kitamura, C.; Tanaka, S.; Yamashita, Y. *Chem. Mater.* **1996**, *8*, 570–578.

(18) Yamashita, Y.; Ono, K.; Tomura, M.; Tanaka, S. *Tetrahedron* **1997**, *53*, 10169–10178.

(19) Ribeiro, A. C.; Heinrich, B.; Cruz, C.; Nguyen, H. T.; Diele, S.; Schröder, M. W.; Guillon, D. *Eur. Phys. J. E* **2003**, *10*, 143–151.

(20) Lincker, F.; Bourgun, P.; Masson, P.; Didier, P.; Guidoni, L.; Bigot, J.-Y.; Nicoud, J.-F.; Donnio, B.; Guillon, D. *Org. Lett.* **2005**, *7*, 1505–1508.

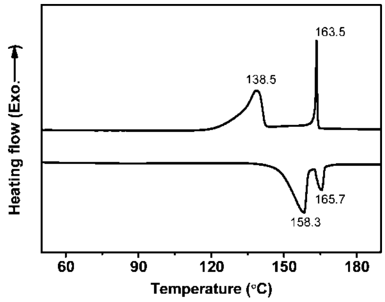

Figure 1. DSC of LC-BBT (heating/cooling rate: 5 deg/min).

Information) and so we could not confirm whether or not LC-BBT was in the solid crystalline phase.

On the basis of X-ray diffraction analysis (Figure 2), the mesogen is in the isotropic phase at 170 °C. When cooling to 160 and 150 °C, two diffraction peaks appear at $2\theta = 25°$ and 2.44°. Together with POM analysis, it can be confirmed that the mesophase is columnar. The wide-angle diffraction data are consistent with intercolumnar distance ($l = 3.4$ nm) and cofacial distance ($d_c = 3.5$ Å). With further cooling to 140 °C, two sharp peaks at $2\theta = 2.49°$ and 6.75° appeared. The *d*-spacing ratio of the two diffractions was about $1{:}1/\sqrt{7}$, while in the wide angle region, only a scattering peak was present, indicating a hexagonal columnar mesophase ($\mathrm{Col_h}$) arrangement of the molecules. The polycatenar calamitic molecules, such as LC-BBT, are able to develop columnar mesophase by having several calamitic rigid cores disposed side by side and surrounded by the corresponding disorganized aliphatic end chains.[19,20]

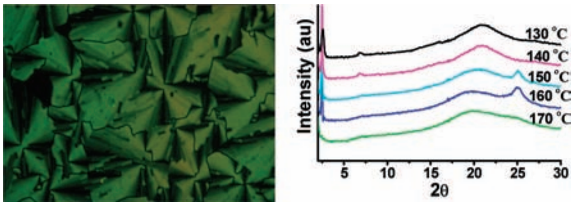

Figure 2. Focal-conic texture (left) at 160 °C and X-ray diffraction patterns (right) of LC-BBT at different temperatures on cooling from the isotropic phase.

The electrochemical behavior of LC-BBT was investigated with cyclic voltammetry (Figure S14, Supporting Information). One quasireversible oxidation/reduction process was found for LC-BBT, with the oxidation onset at 0.62 V and the reduction onset at −0.44 V. Thus, the E_{HOMO} and E_{LUMO} are calculated [$E_{\mathrm{HOMO}} = -e(E_{\mathrm{ox}} + 4.4)$ (eV) and $E_{\mathrm{LUMO}} = -e(E_{\mathrm{red}} + 4.4)$ (eV)] to be −5.02 and −3.96 eV, respectively. In comparison, LC-BBT has a much lower band gap (1.06 eV) than LC-BT (2.02 eV), representing the lowest band gap LC chromophore reported to date.

LC-BBT is strongly NIR-absorbing with peaks at 836 nm in solution and at 890 nm in film (Figure 3), which fills up the NIR spectral gap (e.g., 700−900 nm) left by most organic PVCs. The optical band gap deducted from the absorption onset for LC-BT and LC-BBT films is 1.95 and 1.09 eV, respectively. Thus, PL of LC-BBT is expected to be in the NIR region as well, as is evident from the emission peaks at 1060 nm in solution and 1160 nm in film (Figure 3). In comparison, LC-BT film has a maximum absorption at 533 nm and emits a deep red color at 665 nm (Figure S15, Supporting Information).

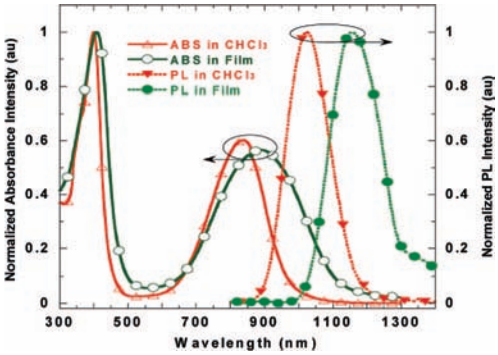

Figure 3. Normalized absorption and PL spectra (excited at 780 nm) of LC-BBT in $\mathrm{CHCl_3}$ (10^{-5} M) and in film.

In summary, a NIR-absorbing and fluorescent columnar mesophase LC chromophore has been successfully designed and obtained. This work implies that a variety of low band gap columnar mesophase LC having a rigid D-A-D core can be realized. LC-BBT should be useful for exploration in tandem solar cells and NIR LC display.

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Supporting Information Available: Experimental procedures; ^{1}H and ^{13}C NMR spectra of **1**, **2**, LC-BT, and LC-BBT; CV, optical textures and thermal behaviors of LC-BT and LC-BBT; absorption and PL spectra; DSC trace; and variable-temperature X-ray diffraction patterns of LC-BT. This material is available free of charge via the Internet at http://pubs.acs.org.

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