



Liquid crystalline dialkyl-substituted thienylethenyl [1] benzothieno[3,2-b] benzothiophene derivatives for organic thin film transistors

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ABSTRACT

New benzothieno[3,2-b]benzothiophene (BTBT)-based soluble semiconducting molecules have been synthesized through Horner–Emmons coupling reactions using 5-alkylthiophene-2-carbaldehyde and BTBT-diethylphosphonate. The only difference between the two molecules is the length of alkyl chains as a substituent. The molecules are intrinsically thermotropic liquid crystalline (LC) and exhibit good solubility in common organic solvents. The semiconducting properties of the two LC molecules were evaluated in organic thin film transistors (OTFTs). After annealing the samples at the temperature at which liquid crystallinity appears, the TFT device performance improved significantly. The two conjugated molecules **4** and **5** exhibited fairly high charge carrier mobilities of $0.020 \text{ cm}^2/(\text{Vs})$ ($V_{\text{th}} = -14.5 \text{ V}$, $I_{\text{ON/OFF}} = 1.42 \times 10^5$) and $0.023 \text{ cm}^2/(\text{Vs})$ ($V_{\text{th}} = -2.0 \text{ V}$, $I_{\text{ON/OFF}} = 1.20 \times 10^6$), respectively.

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1. Introduction

With the recent rapid progress in the development of novel p-type organic semiconductors, high-performance organic thin film transistors (OTFTs) with high hole mobilities of the order of $1 \text{ cm}^2/(\text{Vs})$ have been realized [1–9]. Most p-channel OTFTs with very high mobility reported thus far have been fabricated using only the vacuum deposition method.

Organic semiconductors that are soluble in organic solvents can be employed for the fabrication of TFT devices via conventional low-cost spin coating or drop-casting techniques. [10–14] As compared to vacuum-processed TFT devices, solution-processed OTFTs usually show much poor properties and device performance. This is mainly due to the difficulty in the formation of high-quality films with

a desirable crystalline anisotropic molecular arrangement from a solution. Therefore, the development of solution-processable p-type semiconducting materials is an important issue in the further development of OTFTs.

Special attention should be paid to highly soluble conjugated molecules, which are highly promising materials. These molecules are strongly expected to show good solubility and good TFT device performance due to their favorable anisotropic molecular arrangement. The fused benzothieno[3,2-b]benzothiophene (BTBT) structure inherently shows rigid and flat π -conjugated molecular frameworks. It has been reported that dialkyl-substituted BTBT molecules can be employed to prepare TFT devices with very high hole mobilities [15–17]. Although they have relatively short conjugation lengths and large bandgap energies, the molecular order as evidenced by X-ray diffraction (XRD) shows outstanding carrier transport properties. However, the low molecular weight and large bandgap energies of the reported molecules are still disadvantageous

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for fabricating practical large-scale devices. We are interested in BTBT moieties that contain large number of heteroatomic groups and superior molecular order. Molecules with high formula weights have been designed to realize liquid crystalline behavior at moderately high temperatures.

In this paper, we present two LC semiconducting molecules bearing thienylethenyl [1] BTBT with two different alkyl end groups. We investigated the optical, thermal, electrochemical, and photophysical properties of the new conjugated molecules. We used these solution-processable LC molecules to fabricate OTFTs and investigate their device performance. The two molecules incorporating a BTBT moiety not only offer high carrier mobility of the order of $10^{-2} \text{ cm}^2/(\text{Vs})$ but also a high current on/off ratio, which we attributed to the annealing effect due to liquid crystalline behavior.

2. Experiment

2.1. Synthesis

All commercially available starting materials and solvents were purchased from Aldrich, TCI, and Acros Co. Compounds **1**, **2**, and **3** were synthesized following the method in the literature and a slightly modified method. [18–21]

2.1.1. 2,7-Bis((E)-2-(5-hexylthiophen-2-yl)vinyl)[1]benzothieno[3,2-b]benzothiophene (**4**)

100 mL of oven-dried, magnetically stirred RBF was charged with a solution of **1** (0.7 g, 1.29 mmol) and 5-hexylthiophene-2-carbaldehyde, with **2** (0.63 g, 3.24 mmol) in 20 mL of freshly distilled tetrahydrofuran (THF). The reaction was allowed to stand for 0.5 h, and then, potassium *tert*-butoxide (0.36 g, 3.24 mmol) was added to it. After the reaction was complete, the solution was poured into ethanol to collect the precipitates. The product was obtained after column chromatography using toluene as an eluent. Yield: 84%, 0.68 g of yellow powder. $^1\text{H NMR}$ (300 MHz, CDCl_3): δ (ppm) 7.95 (s, 2H), 7.83 (d, $J = 8.2$ Hz, 2H), 7.58 (d, $J = 8.5$ Hz, 2H), 7.30 (d, $J = 3.8$ Hz, 2H), 6.93 (d, $J = 3.8$ Hz, 2H), 6.88 (d, $J = 3.6$ Hz, 2H), 6.71 (d, $J = 3.6$ Hz, 2H), 2.83 (t, 4H), 1.71~1.55 (m, 4H), 1.44~1.28 (m, 12H), 0.92 (t, 6H).

Anal. calcd. for $\text{C}_{38}\text{H}_{40}\text{S}_4$: C, 73.03; H, 6.45; S, 20.52. Found: C, 73.02; H, 6.43; S, 20.55.

2.1.2. 2,7-Bis((E)-2-(5-octylthiophen-2-yl)vinyl)[1]benzothieno[3,2-b]benzothiophene (**5**)

The preparation method was identical to that for **4**. Instead of 5-hexylthiophene-2-carbaldehyde, 5-octylthiophene-2-carbaldehyde was employed. After completing the reaction, the solution was poured into methanol to collect the precipitates. The product was obtained after column chromatography using toluene as an eluent. Yield: 74%, 0.65 g of yellow powder. $^1\text{H NMR}$ (300 MHz, CDCl_3): δ (ppm) 7.95 (s, 2H), 7.83 (d, $J = 8.2$ Hz, 2H), 7.59 (d, $J = 8.5$ Hz, 2H), 7.31 (d, $J = 3.8$ Hz, 2H), 6.93 (d, $J = 3.8$ Hz, 2H), 6.88 (d, $J = 3.6$ Hz, 2H), 6.71 (d, $J = 3.6$ Hz, 2H), 2.83 (t, 4H), 1.71~1.54 (m, 4H), 1.33~1.28 (m, 20H), 0.90 (t, 6H).

Anal. calcd. for $\text{C}_{42}\text{H}_{48}\text{S}_4$: C, 74.06; H, 7.10; S, 18.83. Found: C, 74.04; H, 7.09; S, 18.78.

2.2. Instrumental analysis

$^1\text{H NMR}$ spectra were recorded on a Varian Mercury NMR 400-Hz spectrometer using deuterated chloroform (Cambridge Isotope Laboratories, Inc.). Elemental analyses were performed using an EA1112 elemental analyzer (Thermo Electron Corp.). The optimized molecular geometry was calculated employing the density functional theory (DFT) using Spartan'06.

Thermal properties were studied under a nitrogen atmosphere by differential scanning calorimetry (DSC) using a Mettler DSC 821e instrument. Thermogravimetric analysis (TGA) was conducted on a Mettler TGA50 (temperature rate of $10^\circ\text{C}/\text{min}$ under N_2). Phase transition behaviors of the liquid crystals were observed in micrographic optical textures under a polarized light microscope (Olympus BH-2) with a hot stage (Mettler Toledo 90/F82HT hot stage).

The redox properties of the two molecules were examined by using cyclic voltammetry (Model: EA161 eDAQ). The electrolyte solution employed was 0.10 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in freshly dried methylenechloride (MC). Ag/AgCl and Pt wire (diameter: 0.5 mm) electrodes were utilized as reference and counter electrodes, respectively. The scan rate was 50 mV/s.

X-ray diffraction (XRD) experiment was performed at varying temperatures using the synchrotron radiation (wavelength: $\sim 1.54 \text{ \AA}$) of the 3C2 beam line at the Pohang Synchrotron Laboratory, Pohang, Korea. Grazing incidence XRD (GI-XRD) measurements were performed at the 10C1 beamline (wavelength: $\sim 1.54 \text{ \AA}$) at the same laboratory. The measurements were obtained using scanning intervals of 2θ between 2.5° and 32° . The film samples were fabricated by drop-casting on a silicon wafer followed by drying at 70°C under vacuum (solvent: chloroform, conc. of the solution: 10 mg/mL).

Atomic force microscopy (Digital Instruments Multi-mode equipped with a Nanoscope IIIa controller) operating in tapping mode with a silicon cantilever was used to characterize the surface morphologies of the samples. The film samples were fabricated by spin coating (1500 rpm) on a silicon wafer followed by drying at 70°C under vacuum (solvent: chloroform, conc. of the solution: 10 mg/mL).

2.3. UV-Vis absorption and photoluminescence (PL) spectroscopy

Absorption spectra of samples in a solution state (chloroform, conc.: $1 \times 10^{-6} \text{ mol/L}$) were obtained using a UV-VIS spectrometer (HP 8453, photodiode array type) in the wavelength range of 190–1100 nm. PL spectra of the solutions at room temperature were acquired using a Hitachi F-7000 FL spectrophotometer.

2.4. OTFT fabrication

To characterize the TFT performance, a bottom-gate top-contact device geometry was employed. Spin-coated

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