

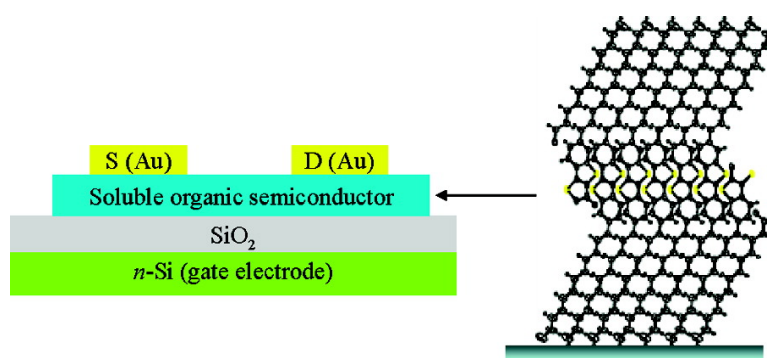
Communication

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## Highly Soluble [1]Benzothieno[3,2-*b*]benzothiophene (BTBT) Derivatives for High-Performance, Solution-Processed Organic Field-Effect Transistors

Hideaki Ebata,<sup>†</sup> Takafumi Izawa,<sup>†</sup> Eigo Miyazaki,<sup>†</sup> Kazuo Takimiya,<sup>\*,†,‡</sup> Masaaki Ikeda,<sup>§</sup> Hirokazu Kuwabara,<sup>§</sup> and Tatsuto Yui<sup>§</sup>

Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan, Institute for Advanced Materials Research, Hiroshima University, Higashi-Hiroshima 739-8530, Japan, and Functional Chemicals R&D Laboratories Nippon Kayaku Co., Ltd., 3-31-12 Shimo, Kita-ku, Tokyo 115-8588, Japan

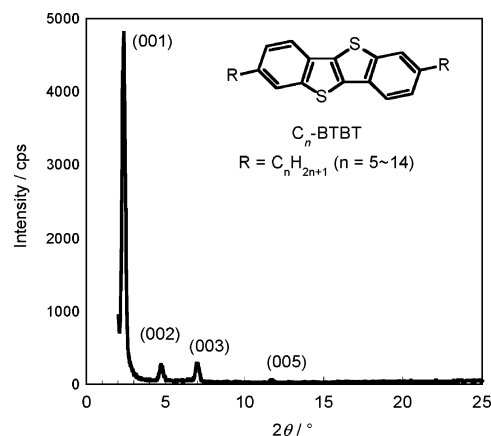
Received July 2, 2007; E-mail: ktakimi@hiroshima-u.ac.jp

$\pi$ -Conjugated polymers with aromatic and/or heteroaromatic backbones, represented by poly(3-hexylthiophene) (P3HT), have been widely investigated as soluble organic semiconductors for solution-processed organic field-effect transistors (OFETs).<sup>1</sup> Recently, the very high field-effect mobility ( $\mu_{\text{FET}}$ ) of 0.7 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> was reported for solution-processed OFETs possessing the thieno[3,2-*b*]thiophene–thiophene copolymer-based active semiconducting channel.<sup>2</sup> For further improvement of device performance, however, polymer materials may have disadvantages owing to the statistical distribution of molecular size and structural defects caused by mislinkage of monomers, which may act as carrier traps in the semiconducting channel.

In this regard, molecular materials are advantageous in terms of their well-defined structure, ease of purification, and controllable properties.<sup>3</sup> In fact, a recent impressive example of molecular-based solution-processed OFETs showing  $\mu_{\text{FET}}$  higher than 1.0 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> was reported using soluble pentacene derivatives, in which bulky 2-(trialkylsilyl)ethynyl substituents at the peri position (the molecular *short-axis* direction) act as solubilizing groups.<sup>4</sup> Owing to the presence of substituents that hinder intermolecular CH- $\pi$  interaction in the lateral direction, these pentacene derivatives take the two-dimensional (2D)  $\pi$ -stack structure, not the herringbone-type packing, a typical solid-state structure for molecular organic semiconductors such as pentacene.

Recently, we developed several high-performance, air-stable, molecular semiconductors for vacuum-processed OFETs.<sup>5</sup> In the course of our studies, we found that [1]benzothieno[3,2-*b*][1]benzothiophene (BTBT) is a promising core structure for air-stable organic semiconductors. As solution-processible organic semiconductors based on the BTBT core structure, we focused on 2,7-dialkyl derivatives ( $C_n$ -BTBT, Figure 1 inset),<sup>6</sup> in which two solubilizing long alkyl groups are introduced in the molecular *long-axis* direction of the core to facilitate lateral intermolecular interaction.<sup>7</sup> We here report the syntheses and characterization of a series of  $C_n$ -BTBTs and their application to an active semiconducting channel in solution-processed OFETs.

A series of  $C_n$ -BTBTs were synthesized via two reaction steps, namely, Friedel–Crafts acylation and Wolff–Kishner reduction, using parent BTBT as starting material,<sup>6</sup> or via the palladium-catalyzed Sonogashira coupling of 2,7-diiodo-BTBT with 1-alkynes, followed by catalytic hydrogenation (see Supporting Information). Thus synthesized  $C_n$ -BTBTs are quite soluble in common organic solvents; their solubilities in chloroform at room temperature are listed in Table 1. Derivatives with C<sub>5</sub>H<sub>11</sub>–C<sub>9</sub>H<sub>19</sub> groups are almost



**Figure 1.** Structure of 2,7-dialkyl[1]benzothieno[3,2-*b*][1]benzothiophenes (inset) and XRD pattern of spin-coated thin film of  $C_{12}$ -BTBT. Calculated *d*-spacing is 37.5 Å.

**Table 1.** FET Characteristics of  $C_n$ -BTBT Devices Fabricated on Si/SiO<sub>2</sub> Substrates

<i>n</i>	solubility <sup>a</sup> (g L <sup>-1</sup> )	<i>d</i> -spacing (Å)	$\mu_{\text{FET}}^b$ (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	$I_{\text{on}}/I_{\text{off}}^b$	$V_{\text{th}}^b$ (V)
5	>60	22.8	0.16–0.43	10 <sup>8</sup>	–21
6	70	24.5	0.36–0.45	10 <sup>8</sup>	–25
7	70	27.1	0.52–0.84	10 <sup>7</sup>	–29
8	80	29.0	0.46–1.80	10 <sup>7</sup>	–17
9	90	31.6	0.23–0.61	10 <sup>8</sup>	–21
10	24	33.3	0.28–0.86	10 <sup>8</sup>	–23
11	13	35.9	0.73–1.76	10 <sup>7</sup>	–20
12	8.6	37.5	0.44–1.71	10 <sup>8</sup>	–20
13	5.0	40.2	1.20–2.75	10 <sup>7</sup>	–27
14	2.3	41.8	0.19–0.72	10 <sup>8</sup>	–18

<sup>a</sup> Concentration of saturated solution in chloroform at room temperature.

<sup>b</sup> Typical device characteristics obtained from more than 10 devices.

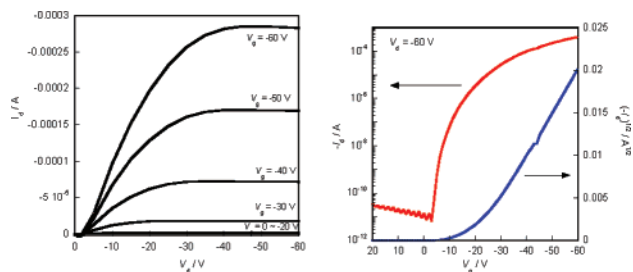
freely soluble, while those with alkyl groups longer than the C<sub>12</sub>H<sub>25</sub> group showed reduced solubilities.

Homogeneous thin films were deposited on a Si/SiO<sub>2</sub> substrate by spin coating using a 0.4 wt % solution of  $C_n$ -BTBT in chloroform at 3000–4000 rpm for 30 s. The spin-coated thin films have well-ordered structure as indicated by X-ray diffraction (XRD) measurements: as a representative, an XRD pattern of  $C_{12}$ -BTBT thin film is shown in Figure 1, where a series of peaks assignable to (00 $l$ ) reflections were clearly observed, and the interlayer distance (*d*-spacing) calculated from these reflections is 37.5 Å. *d*-Spacings of the other derivatives depended on the length of the alkyl groups: with longer alkyl groups, larger *d*-spacings were obtained (Table 1), indicating that all the derivatives take similar molecular packing structures.

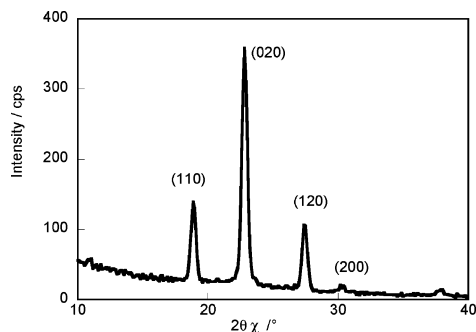
<sup>†</sup> Graduate School of Engineering, Hiroshima University.

<sup>‡</sup> Institute for Advanced Materials Research, Hiroshima University.

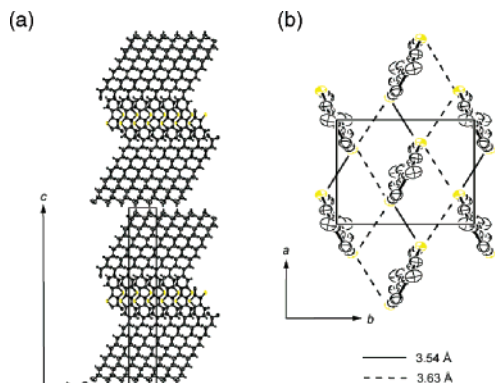
<sup>§</sup> Nippon Kayaku Co., Ltd.



**Figure 2.** FET characteristics of  $C_{12}$ -BTBT-based OFET: output characteristics (left) and transfer characteristics at  $V_d = -60$  V (right).



**Figure 3.** In-plane XRD ( $2\theta$   $\chi/\phi$  scan) of a spin-coated thin-film of  $C_{12}$ -BTBT on Si/SiO<sub>2</sub> substrate (incident angle, 0.19°). All the peaks are assignable with the structural data from the single-crystal X-ray analysis of  $C_{12}$ -BTBT.



**Figure 4.** Crystal structure of  $C_{12}$ -BTBT: (a)  $b$ -axis projection representing a lamella structure and (b) molecular arrangement in the BTBT layer. For clarity, alkyl groups are omitted.

Gold source and drain electrodes (80 nm) were vapor-deposited on top of the thin films ( $\sim 100$  nm) through a shadow mask to complete fabrication of OFET devices with channel length and width of 50  $\mu\text{m}$  and 1.5 mm, respectively. Table 1 summarizes the FET characteristics of the devices evaluated under ambient conditions without any precautions to eliminate air and moisture. Regardless of the length of the alkyl groups, thin films of  $C_n$ -BTBT derivatives acted as a superior semiconducting channel (Figure 2, Table 1), and  $\mu_{\text{FET}}$  of the devices was higher than  $10^{-1}$   $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ .

To understand the high performance of  $C_n$ -BTBT-based FET devices, we carried out in-plane XRD analysis of the thin film and single-crystal X-ray structural analysis for  $C_{12}$ -BTBT. As shown in Figure 3, clear diffractions are observed in the in-plane XRD measurement, indicating that the film has a crystalline order in the in-plane direction. Since all the observed peaks are assigned well by the single-crystal lattice, the structure in the thin film is identical with that in the single crystal. Figure 4 shows the single-crystal structure of  $C_{12}$ -BTBT. The crystal assumes a “layer-by-layer” structure consisting of alternately stacked aliphatic layers and BTBT

core layers (Figure 4a). In the BTBT core layer, the molecules take herringbone packing (Figure 4b) to facilitate 2D carrier transport property. In addition, a network of intermolecular interactions through short S–S contacts (3.54 and 3.63 Å) exists. These structural aspects can be related to the high mobility of  $C_n$ -BTBT-based FET devices, since the existence of 2D semiconducting layers with strong intermolecular overlap is considered to be one of the prerequisites to realizing high-performance OFET devices.<sup>8</sup>

In summary, we have successfully developed a series of highly soluble molecular semiconductors, 2,7-dialkyl[1]benzothieno[3,2-*b*]benzothiophenes, and tested their utility as active layers for solution-processed OFETs. The OFET devices showed typical p-channel FET responses with field-effect mobility higher than 1.0  $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$  and  $I_{\text{on}}/I_{\text{off}}$  of  $\sim 10^7$ . These results indicate that small molecules possessing an extended aromatic core and solubilizing long aliphatic chains are promising candidates for solution-processible organic semiconductors.

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**Supporting Information Available:** Experimental details for the syntheses, characterization and device fabrication of  $C_n$ -BTBTs, Crystallographic information file (CIF) and in-plane XRD for  $C_{12}$ -BTBT. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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