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A Highly π-Stacked Organic Semiconductor for Thin Film Transistors Based on Fused Thiophenes

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Organic semiconductors that consist of conjugated oligomers or polymers are the subject of considerable current research interest, owing to their fundamental optoelectronic properties and their potential applications ranging from photodiodes[1] to light-emitting devices (LEDs)[2] and thin film transistors (TFTs).[3] Oligomers of thiophenes, typically the hexamer of thiophene (sexithiophene, α-6T) or its derivatives, have dominated as the active organic materials for TFTs[4−6] and exhibit high field-effect charge mobility (0.02 cm^2/V s for α-6T and 0.05 cm^2/V s for α,ω-dihexyl-6T, respectively). High on/off ratios up to 10^6 have been achieved in these systems. Recently, record high mobilities of 0.3−0.7 cm^2/V s have been reported for films of commercially available pentacene by successfully controlling the morphology during fabrication,[7,8] although a lower mobility of 10^{-6} to 10^{-3} cm^2/V s had been previously recorded.[9−11] The high mobility has been associated with both the π-stacking and the macroscopic highly ordered pentacene films which exhibit essentially "single crystal like" morphology.[12] Realizing the importance of π-stacking, Katz and co-workers[13] have recently successfully synthesized a new high mobility (0.04 cm^2/V s) organic TFT material, bis-(benzodithiophene). Here, we report another approach to the design and synthesis of new organic semiconductors for TFT application, using the fused thiophene derivative, dithieno[3,2-*b*:2′,3′-*d*]thiophene (**2a**) as a building block. The dimer of the fused thiophene, α,α′-bis(dithieno[3,2-*b*:2′,3′-*d*]thiophene) (BDT) (**3**), was found to have an unusual π-stacked structure, a high mobility (up to 0.05 cm^2/V s), and a very high On/Off ratio (up to 10^8) in the best present device evaluations.

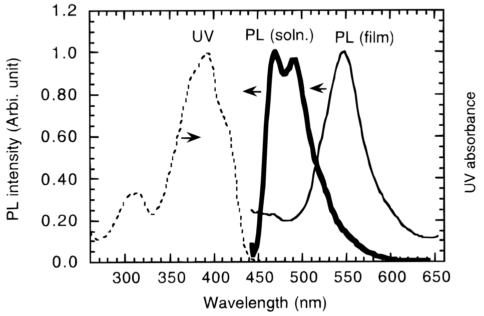
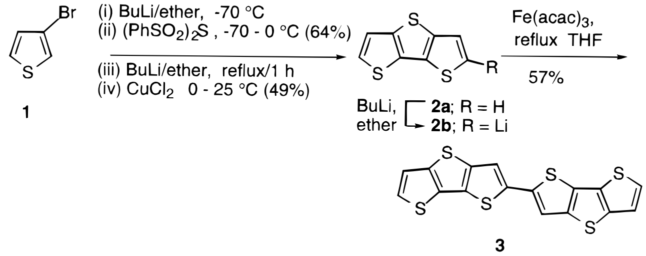


Figure 1. The absorption and emission spectra of BDT (**3**). UV−vis was measured in dilute chloroform solution. The solution PL was excited at 390 nm, and the solid-state PL was at 340 nm.

Scheme 1



The building block **2**[14] was prepared from 3-bromothiophene (**1**) (Scheme 1). The "dimerization" was carried out through a coupling reaction of the lithiated monomer **2b** using ferric acetylacetonate as the oxidative coupling reagent.[15] BDT (**3**) was sufficiently soluble in boiling toluene or hot DMF to allow recrystallization and was slightly soluble in warm THF (2 g/L) for characterization by ^{1}H NMR. The microcrystalline powder thus obtained has a gold-like luster and shows no chemical change when stored under ambient conditions over several months.

Although the monomer **2** melts at 67 °C, its "dimer" BDT (**3**) melts at 316 °C, as revealed from hot-stage microscopic observation under polarized light and differential scanning calorimetry (DSC) measurement, which implies the presence of very strong intermolecular interactions. After melting, BDT begins to sublime and is chemically stable below 350 °C, as suggested from thermogravimetric analysis (TGA) in nitrogen. It sublimed in vacuo (10^{-4} to 10^{-5} Torr) at 200 °C, allowing further purification to meet the stringent requirement for application in TFTs.

BDT (**3**) exhibits orange fluorescence in the solid state and a blue emission when irradiated in dilute solution with UV light. A HOMO−LUMO gap of 2.8 eV in dilute chloroform solution was observed from the absorption edge (440 nm), and a 2.3 eV energy gap was obtained from the emission peak (547 nm) of a thin film (Figure 1).

The cyclic voltammetry of a BDT film on Au-coated glass is shown in Figure 2. A distinct color change from yellow → brown → yellow was observed upon oxidative sweeping from 0 → +0.9

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(1) Halls, J. J. M.; Walsh, C. A.; Greenham, N. C.; Marseglia, E. A.; Friend, R. H.; Moratti, S. C.; Holmes, A. B. *Nature* **1995**, *376*, 498−500.

(2) Greenham, N. C.; Moratti, S. C.; Bradley, D. D. C.; Friend, R. H.; Holmes, A. B. *Nature* **1993**, *365*, 628−630.

(3) Garnier, F.; Hajlaoui, R.; Yassar, A.; Srivastava, P. *Science* **1994**, *265*, 1684−1686.

(4) Horowitz, G.; Fichou, D.; Peng, X. Z.; Xu, Z. G.; Garnier, F. *Solid State Commun.* **1989**, *72*, 381−384.

(5) Garnier, F. *Pure Appl. Chem.* **1996**, *68*, 1455−1462.

(6) Katz, H. E. *J. Mater. Chem.* **1997**, *7*, 369−376.

(7) Gundlach, D. J.; Lin, Y. Y.; Jackson, T. N.; Nelson, S. F.; Schlom, D. G. *IEEE Electron Device Lett.* **1997**, *18*, 87−89.

(8) Lin, Y. Y.; Gundlach, D. J.; Jackson, T. N. *54th Ann. Device Res. Conf. Digest* **1996**, 80. See also: *Science* **1996**, *273*, 879.

(9) Horowitz, G.; Fichou, D.; Peng, X.; Garnier, F. *Synth. Met.* **1991**, *41−43*, 1127−1130.

(10) Brown, A. R.; Pomp, A.; Hart, C. M.; de Leeuw, D. M. *Science* **1995**, *270*, 972−974.

(11) Brown, A. R.; Pomp, A.; De Leuw, D. M.; Klaassen, D. B. M.; Havinga, E. E.; Herwig, P.; Müllen, K. *J. Appl. Phys.* **1996**, *79*, 2136−2138.

(12) Laquindanum, J. G.; Katz, H. E.; Lovinger, A. J.; Dodabalapur, A. *Chem. Mater.* **1996**, *8*, 2542−2544.

(13) Laquindanum, J. G.; Katz, H. E.; Lovinger, A. J.; Dodabalapur, A. *Adv. Mater.* **1997**, *9*, 36−39.

(14) Jong, F.; Janssen, M. J. *J. Org. Chem.* **1971**, *36*, 1645−1648.

(15) Katz, H. E.; Dodabalapur, A.; Torsi, L.; Elder, D. *Chem. Mater.* **1995**, *7*, 2238−2240.

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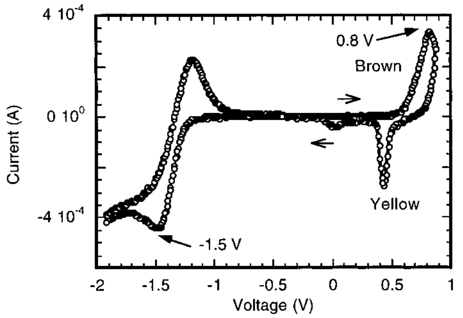

Figure 2. Cyclic voltammogram of BDT film on Au-coated glass at a full sweep from 0 → +0.9 → 0 → −1.7 → 0 V at 20 mV/s [0.1 M Et_4NBF_4 in CH_3CN as electrolyte, a platinum gauze as counter electrode, a Ag wire as quasi-reference, and referenced against the Fc/Fc^+ redox couple ($E° = 0.42$ V)].

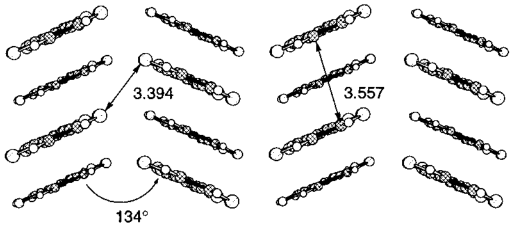

Figure 3. Packing view of a BDT single crystal perpendicular to the *bc* plane.

→ 0 V [(vs ferrocene/ferrocenium (Fc/Fc^+)], indicating a quasi-reversible p-doping (or hole injection) process that is probably related to the formation of a radical cation.[16] The reduction sweep showed a reversible n-doping (or electron injection) with no change in color. The electrochemically determined HOMO−LUMO gap of 2.3 eV is in good agreement with that measured from the emission spectrum of the film. When the oxidation potential was larger than 1.2 V, the color changed to dark green, indicating the possible formation of a dication which is also quite common for conjugated polymers.[16,17]

Slow cooling of a saturated solution of BDT in hot toluene afforded small crystals, which were too small for standard laboratory X-ray diffractometry. To determine the structure, it was necessary to exploit the high intensity of a synchrotron radiation source. Hence, using a crystal of volume 500−1000 times smaller than a typical single crystal necessary for laboratory X-ray analysis, we were able to determine (with synchrotron radiation microcrystal diffraction facilities) an extremely high quality crystal structure.[18] The crystal structure of BDT revealed a completely coplanar conformation with a unique $\pi-\pi$ stacking feature (Figure 3) which is significantly different from the herringbone packing found in sexithiophene[19] and pentacene.[20] The shortest distance between carbon atoms in two face-to-face molecules is 3.557 Å (3.394 Å for sulfur atoms in two adjacent molecules), indicating a very compressed molecular packing and strong intermolecular interactions.

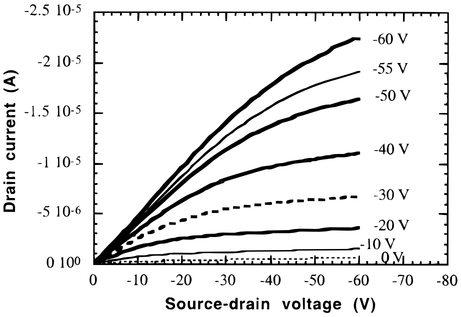

Figure 4. Source−drain current vs voltage characteristics of BDT TFTs (top-contact configuration) at different gate voltages. BDT was sublimed at ca. 200 °C onto a substrate maintained at room temperature.

Field-effect measurements were carried out on TFTs using vacuum-sublimed BDT (**3**) as the active layer. Top-contact TFTs and bottom contact TFTs have been fabricated.[21] Distinct field effects using BDT as the active layer were observed for TFTs in both configurations. The negative signs of both gate voltage (V_G) and source−drain current (I_{DS}) indicate that BDT is a typical p-type semiconductor (Figure 4). The field-effect mobilities measured in the saturation regime ($V_{DS} > V_{GS}$) were 0.02−0.05 cm^2/V s for top contact TFTs, which is slightly higher than the best values recorded for α-6T and bis(benzodithiophene) TFTs.[13] Similar mobilities were also achieved for bottom-contact TFTs in which the BDT film was vacuum-deposited on silicon wafer substrates at 100 °C to achieve a better ordered film. Exceptionally high on/off ratios (up to 10^8) with sharp turn-on characteristics comparable to that of amorphous silicon TFTs were achieved (subthreshold slope $S = 0.6$ V/decade) for the bottom-contact TFTs. The X-ray diffraction data of the sublimed BDT films together with the device characteristics indicate that the high mobility is along the $\pi-\pi$ stacking direction, and it is presumed that the mobility is lower along the molecular axis.[22]

In summary, it is considered that the high mobility and high on/off ratio for BDT-based TFTs are attributed to the closely packed face-to-face stacking and the wide HOMO−LUMO gap of the material. We expect that higher mobilities may be possible for BDT by increasing the granular size of the polycrystalline film.

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Supporting Information Available: Experimental procedures for the synthesis and characterization of **2** and **3**; TGA and DSC traces for BDT **3**; details of the X-ray structure determination, tables of atomic coordinates, isotropic displacement parameters, anisotropic displacement parameters, bond lengths, and bond angles for BDT (**3**) (10 pages). These data have been deposited with the Cambridge Crystallographic Database. An X-ray crystallographic file, in CIF format, is available through the Web only. See any current masthead page for ordering information and Web access instructions.

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[16] Helbig, M.; Hörhold, H.-H. *Makromol. Chem.* **1993**, *194*, 1607−1618.

[17] Cervini, R.; Li, X. C.; Spencer, G. W. C.; Holmes, A. B.; Moratti, S. C.; Friend, R. H. *Synth. Met.* **1997**, *84*, 359−360.

[18] Crystal data for **3**: yellow microcrystals, mp 316 °C; monoclinic, space group *C*2/*c*; crystal dimensions 0.07 × 0.02 × 0.02 mm; $a = 33.689(2)$ Å, $b = 3.883(4)$ Å, $c = 11.1055(5)$ Å; $\beta = 101.093(2)°$; $V = 1425.75(13)$ Å^3; $Z = 4$; R1 [$I > 2\sigma(I)$] = 0.0478; GOF = 1.112.

[19] Horowitz, G.; Bachet, B.; Yassar, A.; Lang, P.; Demanze, F.; Fave, J.-L.; Garnier, F. *Chem. Mater.* **1995**, *7*, 1337−1341.

[20] Campbell, R. B.; Robertson, J. M.; Trotter, J. *Acta Crystallogr.* **1961**, *14*, 705−711.

[21] For bottom-contact TFTs (with channel length of 20 μm, channel width of 1 cm), a highly doped silicon wafer was used as gate electrode, SiO_2 as dielectric insulator layer (capacitance of 16 nF/cm^2) on which BDT (**3**) was vacuum-deposited (500−1500 Å) at a rate of 1−5 Å/s at a substrate temperature of *ca.* 100 °C, and gold as source and drain electrodes. For top contact TFTs (with channel length of 50 μm and width of 1.5 mm), an aluminum layer was the gate, poly(methyl methacrylate) (PMMA) (capacitance of 5 nF/cm^2) layer was the dielectric insulator on which BDT **3** was deposited (200−1000 Å) at 25 °C at a rate of 1−5 Å/s, and two gold strips (500−1500 Å) were vacuum-deposited on BDT layer as source and drain electrode, respectively. Mobility measurements can vary by a factor of 2 in different laboratories according to the method of sample preparation.

[22] Sirringhaus, H.; Friend, R. H.; Li, X. C.; Moratti, S. C.; Holmes, A. B.; Feeder, N. *Appl. Phys. Lett.* **1997**, *71*, 3871−3873.