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Semiconductive Polymers Containing Dithieno[3,2-*b*:2′,3′-*d*]pyrrole for Organic Thin-Film Transistors

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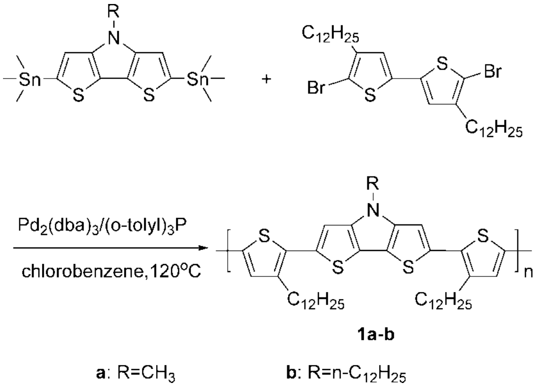
Organic thin-film transistors have attracted intense research interest in recent years as a promising alternative to amorphous silicon transistors for applications in flexible, large area electronics devices such as bendable displays, electronic paper, ID tags, and sensors.[1−6] To enable low-cost manufacturing, fabrication using simple solution techniques under ambient or nonsterile conditions is highly desirable. Polymer semiconductors generally display lower mobility, but their easy solution processability and good film-forming property offer excellent opportunities for use in fabricating low-cost OTFTs.[7,8] Although considerable efforts have been taken in the development of new polymer semiconductors, to date the known polymer semiconductors are still limited, and only a few can truly present the high mobilities required for organic circuits.[9−12] Therefore, design and synthesis of new conjugated polymer semiconductors are of great interest.

Dithieno[3,2-*b*:2′,3′-*d*]pyrrole (DTP) has received much interest as a new unit in conjugated polymers due to its good molecular planarity and N−H bond which can be easily substituted by functional groups.[13,14] The literatures are mainly focused on the optical property of DTP homopolymers. To the best of our knowledge, there are few reports concerning the potential application in OTFTs of DTP-containing polymers. Very recently, McCullough et al. reported DTP-based highly disordered copolymers and their properties in OTFT applications.[15] In this independent work, a new kind of DTP-containing copolymers—poly(2,6-bis(3-dodecylthiophen-2-yl)-*N*-alkyldithieno[3,2-*b*:2′,3′-*d*]pyrrole), is synthesized, and their application in OTFTs is explored.

Scheme 1. General Synthetic Route for the Copolymers 1



Copolymers **1a** and **1b** were prepared by Stille coupling polymerization of 2,6-bis(trimethylstannanyl)-*N*-alkyldithieno[3,2-*b*:2′,3′-*d*]pyrrole with 5,5-dibromo-4,4-bis(dodecyl)-2,2-bithiophene in good yield (see Scheme 1) and purified by sequential Soxhlet extraction with ethanol and then hexane (see Supporting Information). They exhibit good solubility in normal solvent such as THF, $CHCl_3$, chlorobenzene, and so forth. Molecular weights were determined by gel-permeation chromatography (GPC) with polystyrene as a standard and THF as solvent. **1a** and **1b** show a number-average molecular weight of 17 400 and 29 700, respectively (see Supporting Information). The differential scanning calorimetry (DSC) thermogram of **1a** does not reveal any obvious phase transitions between 25 and 300 °C. However, a glass transition temperature (T_g) of 126 °C appears in the case of **1b**, where the longer side chain in N atom may play an important role for the thermal behavior (see Figure S1 in the Supporting Information). Both of the polymers present good thermal stability with high decomposition tem-

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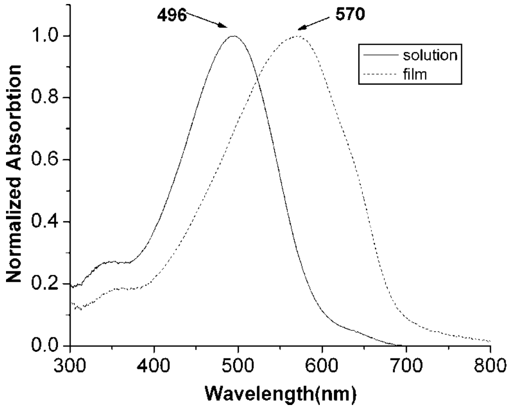

Figure 1. UV−vis absorption spectra of **1a** both in chlorobenzene solution and in the thin film.

peratures (T_d) over 400 °C in the thermogravimetric analysis (TGA).

Figure 1 depicts the UV−vis spectrum of **1a** in dilute chlorobenzene solution and in thin film. **1a** shows an absorption maximum at 496 nm in solution while exhibiting a strong red shift in the film with absorption peak at 570 nm, reflecting a higher structural ordering in thin film. It is also found that the spectrum of **1b** is the same as **1a**, indicating that the length of the alkyl chains attached to the N atom does not affect the optical properties of the polymers.

Cyclic voltammetric measurements were conducted in a 0.1 M solution of Bu_4NPF_6 in acetonitrile at room temperature under argon with a scan rate of 100 mV/s. For the comparison, cyclic voltammetric measurements of regioregular poly(3-hexylthiuophene) (HT-P3HT) and PQT-12^{9} were also taken under identical conditions. **1a** and **1b** show quasi-reversible reduction and oxidation processes (see Figure S2 in the Supporting Information). It is found that **1a** and **1b** exhibit the almost same HOMO level, which is just a little lower than the one of HT-P3HT but higher than the one of PQT-12, hinting that the HOMO level of **1** is not low enough that **1** could possibly be oxidatively doped when the OFET is measured in ambient conditions. It may be ascribed to the electron-rich character of DTP units in the polymer backbone.

The X-ray diffraction (XRD) patterns of **1** under various processing conditions are shown in Figure 2. A powdered sample of **1a** exhibits two diffractions at $2\theta = 4.3°$ and 25.3°,

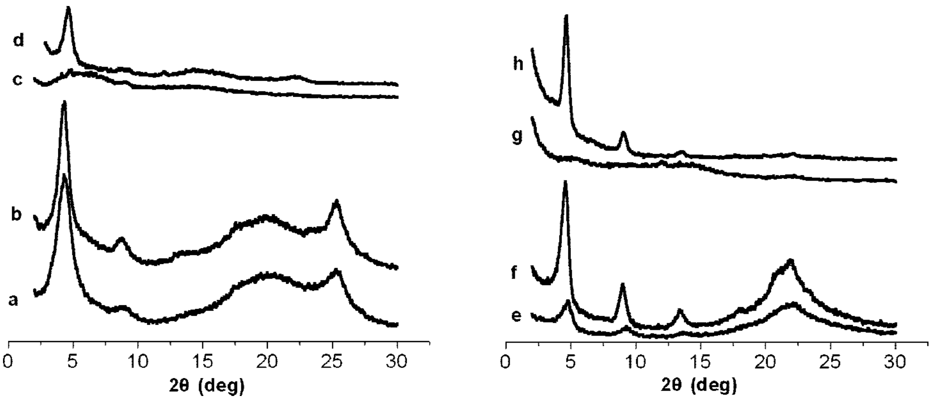

Figure 2. XRD spectra of **1**: (a) powder pellet of **1a** at room temperature; (b) powder pellet of **1a** after annealed at 130 °C; (c) thin film of **1a** at room temperature; (d) thin film of **1a** after annealed at 130 °C; (e) powder pellet of **1b** at room temperature; (f) powder pellet of **1b** after annealed at 130 °C; (g) thin film of **1b** at room temperature; (h) thin film of **1b** after annealed at 130 °C.

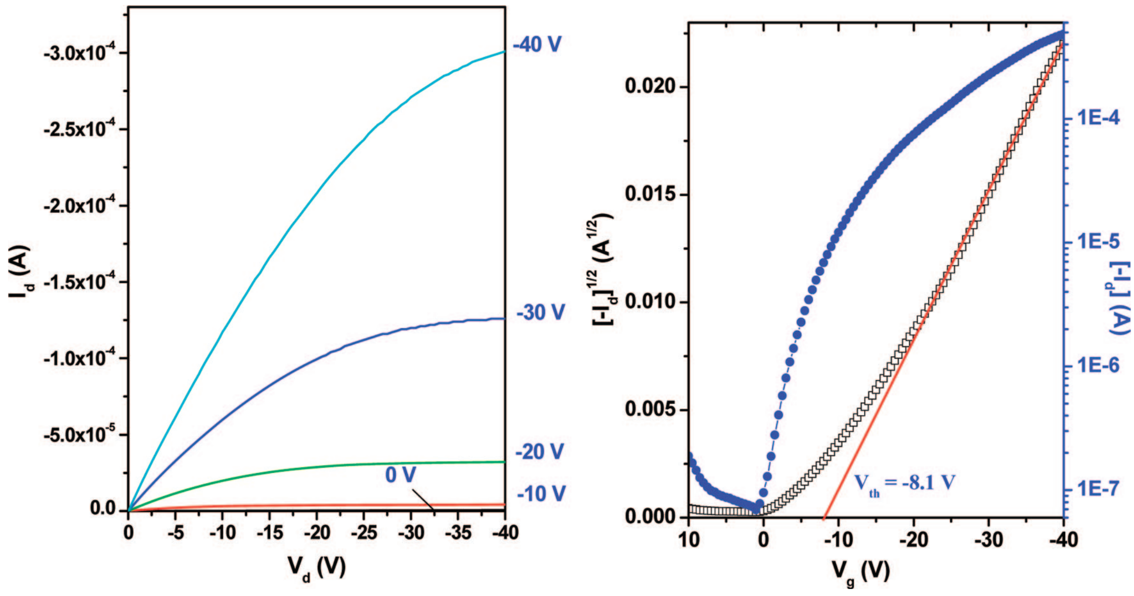

Figure 3. *I*−*V* characteristics of an illustrative TFT device using **1b** as semiconductive layer: (a) output curves at different gate voltages; (b) transfer curve in saturated regime at constant source-drain voltage of −40 V and square root of the absolute value of the drain current as a function of gate voltage.

corresponding respectively to an interchain *d*-spacing of 20.5 Å and a $\pi-\pi$ stacking distance of 3.5 Å, and the XRD pattern does not change much after the powdered sample was annealed at 130 °C. However, the XRD pattern of a solution-cast thin film of **1a** in chlorobenzene on an octyltrichlorosilane-modified silicon wafer substrate is featureless until annealing at 130 °C. The annealed thin film shows crystalline characteristic with a strong primary diffraction peak at $2\theta = 4.6°$, which corresponds to an interchain distance of 19.2 Å. Because of the introduction of the longer alkyl chain into the N atom, **1b** exhibits a little different XRD patterns as compared to **1a**. A powdered sample of **1b** shows distinctive diffraction peaks at $2\theta = 4.6°$ (100), 9.2° (200), and 13.8° (300), corresponding to *d*-spacing of 19.2 Å for the interchain distance between two neighboring polymer chains. It also presents another diffraction at $2\theta = 22.1°$ which is ascribed to a $\pi-\pi$ stacking distance of 4.0 Å. When the powdered sample is annealed at 130 °C, a more distinctive, highly crystalline XRD pattern is observed. Meanwhile, after annealing at 130 °C, the XRD pattern of a solution-cast thin film of **1b** also exhibits high crystallinity with strong diffraction peaks at $2\theta = 4.5°$ (100), 9.0° (200), and 13.5° (300), with respect to an interchain *d*-spacing of 19.6 Å. For both of the polymers, conspicuously absent in the annealed thin film is the prominent $\pi-\pi$ stacking peak of the annealed powdered sample. This demonstrates that annealing leads to formation of lamellar $\pi-\pi$ stacks which are oriented normal to the substrate.[9]

The fabrication and characterization of OTFT devices were carried out under ambient conditions without any precautionary measures being taken to isolate the material and devices from exposure to ambient oxygen, moisture, or light. Bottom-gate, bottom-contact TFT devices were fabricated on an n-doped silicon wafer with octyltrichlorosilane-modified SiO_2 gate dielectric and octylthiol-modified gold source/drain electrodes. And then the semiconductor layer was deposited on the substrate by drop-casting a 0.5 wt % solution of **1** in chlorobenzene and vacuum-dried. Figure 3 exhibits a characteristic p-type FET behavior of a representative OTFT device with **1b** after annealing at 130 °C. The output characteristics display very good saturation behavior with no obvious contact resistance. The transfer characteristics show a near-zero turn-on voltage and a threshold voltage of −8.1 V. The mobility extracted from the saturated regimes is as high as 0.11 $cm^2\ V^{-1}\ s^{-1}$, with a current on/off ratio close to 10^4. Without annealing, the mobility and on\off ratio are 0.062 $cm^2\ V^{-1}\ s^{-1}$ and 170, respectively, which are worse than the annealed materials. The relative low on/off ratio is a result of large leakage current (ca. 7×10^{-8} A) under ambient conditions, which indicates the polymers are oxidatively doped in air to some extent as that reported.[15] The device with **1a** also presents the same performance with a mobility of 0.08 $cm^2\ V^{-1}\ s^{-1}$ and a current on/off ratio of 10^3. As compared with **1a**, the longer alkyl chain in the N atom is believed to facilitate the ordered aggregation in film of **1b** and then enhance the mobility of the device.

In conclusion, we prepared two new polymer semiconductors containing DTP and bithiophene units for OFETs. Both of them showed good solubility in common organic solvents and high thermal stability. The FET devices made from them with a bottom contact geometry exhibited good performance under ambient conditions with the mobility up to 0.11 $cm^2\ V^{-1}\ s^{-1}$ and the current on/off ratio close to 10^4. These results show that the polymers containing DTP and bithiophene units are a new class of solution processable semiconductors potentially for printed electronics.

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Supporting Information Available: Experimental procedures, the data of the characterizations, and detailed information about the fabrication and measurement of TFTs. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Sirringhaus, H.; Tessler, N.; Friend, R. H. *Science* **1998**, *280*, 1741–1744.

(2) Sirringhaus, H.; Kawase, T.; Friend, R. H.; Shimoda, T.; Inbasekaran, M.; Wu, W.; Woo, E. P. *Science* **2000**, *290*, 2123–2126.

(3) Huitema, H. E. A.; Gelinck, G. H.; van der Putten, J. B. P. H.; Kuijk, K. E.; Hart, C. M.; Cantatore, E.; Herwig, P. T.; van Breemen, A. J. J. M.; de Leeuw, D. M. *Nature (London)* **2001**, *414*, 599.

(4) Baude, P. F.; Ender, D. A.; Haase, M. A.; Kelley, T. W.; Muyres, D. V.; Theiss, S. D. *Appl. Phys. Lett.* **2003**, *82*, 3964–3966.

(5) Mabeck, J. T.; Malliaras, G. G. *Anal. Bioanal. Chem.* **2006**, *384*, 343–353.

(6) Dodabalapur, A. *Mater. Today* **2006**, *9*, 24–30.

(7) Dimitrakopoulos, C. D.; Malenfant, P. R. L. *Adv. Mater.* **2002**, *14*, 99–117.

(8) Ling, M. M.; Bao, Z. *Chem. Mater.* **2004**, *16*, 4824–4840.

(9) Ong, B. S.; Wu, Y.; Liu, P.; Gardner, S. *J. Am. Chem. Soc.* **2004**, *126*, 3378–3379.

(10) Mcculloch, I.; Heeney, M.; Bailey, C.; Genevicius, K.; Macdonald, I.; Shkunov, M.; Sparrowe, D.; Tierney, S.; Wagner, R.; Zhang, W.; Chabinyc, M. L.; Kline, R. J.; Mcgehee, M. D.; Toney, M. F. *Nat. Mater.* **2006**, *5*, 328–333.

(11) Pan, H.; Li, Y.; Wu, Y.; Liu, P.; Ong, B. S.; Zhu, S.; Xu, G. *J. Am. Chem. Soc.* **2007**, *129*, 4112–4113.

(12) Li, J.; Qin, F.; Li, C. M.; Bao, Q.; Chan-Park, M. B.; Zhang, W.; Qin, J.; Ong, B. S. *Chem. Mater.* **2008**, *20*, 2057–2059.

(13) Ogawa, K.; Rasmussen, S. C. *Macromolecules* **2006**, *39*, 1771–1778.

(14) Koeckelberghs, G.; De Cremer, L.; Persoons, A.; Verbiest, T. *Macromolecules* **2007**, *40*, 4173–4181.

(15) Liu, J.; Zhang, R.; Sauvé, G.; Kowalewski, T.; McCullough, R. D. *J. Am. Chem. Soc.* **2008**, *130*, 13167–13176.

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