ADVANCED FUNCTIONAL MATERIALS

A Densely and Uniformly Packed Organic Semiconductor Based on Annelated β-Trithiophenes for High-Performance Thin Film Transistors

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A novel semiconductor based on annelated β-trithiophenes is presented, possessing an extraordinary compressed packing mode combining edge-to-face π–π interactions and S...S interactions in single crystals, which is favorable for more effective charge transporting. Accordingly, the device incorporating this semiconductor shows remarkably high charge carrier mobility, as high as 0.89 $cm^2\,V^{-1}\,s^{-1}$, and an on/off ratio of 4.6 × 10^7 for vacuum-deposited thin films.

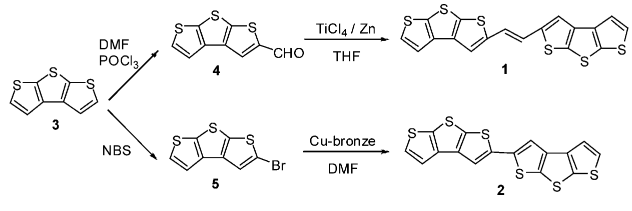
1. Introduction

Organic field-effect transistors (OFETs) have attracted particular attention recently because of their potential applications in flexible, large-area, and low-cost electronic circuits.[1] Significant progress has been made in this field.[2] Some OFETs even exhibit performance over their inorganic counterparts (amorphous silicon devices).[3] However, a detailed understanding of the relationship between the electronic structure, the crystal packing, and device performance is still a significant challenge.[4]

Oligothiophenes are among the most versatile and effective molecular scaffolds for organic functional materials.[5] It has already been shown that quasi-linearly annelated α-oligothiophenes provide materials with significantly improved optical and electronic properties.[6] However, it is surprising that annelated β-oligothiophenes are usually chosen as building blocks for helicene,[7] while organic semiconductors based on annelated β-oligothiophenes are rarely investigated. Recently, we reported that the integration of S atoms into the perylene skeleton induces an extraordinary solid-state packing arrangement with the likelihood of double-channel superstructure, which is responsible for effective intermolecular hole transport.[8] In this contribution, we present our studies of a novel high performance organic semiconductor based on β-trithiophenes units, namely *trans*-1,2- (dithieno[2,3-*b*:3′,2′-*d*]thiophene)ethene (**1**). To our surprise, the molecules adopt a compressed herringbone arrangement with marked multiple S...S close contacts (as short as 3.34 Å) in single crystals, which is favorable for more effective charge transporting. Accordingly, the device incorporating this semiconductor shows remarkable high charge carrier mobility, as high as 0.89 $cm^2\,V^{-1}\,s^{-1}$ for vacuum deposited thin films.

2. Results and Discussion

Scheme 1 illustrates the approach to the new semiconducting molecules based on annelated β-trithiophenes units. Inspired from unusual π-stacked structure of the dimer of fused α-trithiophenes, α,α'-bis(dithieno[3,2-*b*:2′,3′-*d*]thiophene) (BDT)[4a,9] and bis(benzodithiophene) (BBT),[10] we choose the dimer of fused β-trithiophenes, α,α'-bis(dithieno[2,3-*b*:3′,2′-*d*]thiophene) as the first target molecule. The building block **3** was prepared according to procedures described elsewhere.[7] Ullmann coupling reaction of mono-brominated fused trithiophenes (**5**) afforded desired product **2**, while the general approach (lithiation and subsequent oxidative coupling reaction of **3**) did not work. To further investigate the structure/property relationship of this new molecular scaffold, fused β-trithiophenes with vinyl linkage were also prepared in two steps. The aldehyde functionality of fused trithiophenes was easily converted into a C=C double bond via the low-valence titanium-mediated McMurry coupling to afford **1** in moderate yield. The absorption spectrum of compound **1** in tetrahydrofuran acid (THF) shows a maximum at 379 nm, which is bathochromically shifted



Scheme 1. Synthetic route to 1 and 2.

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DOI: 10.1002/adfm.200800933

34 nm compared to the dimer **2** (345 nm) and consistent with a more extended π-system as expected. Optical HOMO–LUMO (HOMO: highest occupied molecular orbit; LUMO: lowest unoccupied molecular orbit) energy gaps obtained from the absorption onset are 2.91 and 3.15 eV for compounds **1** and **2**, respectively, which are wider than that of BDT. The HOMO levels of compounds **1** and **2** are estimated from the oxidation onsets (0.99 eV for compound **1** and 1.09 eV for compound **2**) to be 5.39 and 5.49 eV by cyclic voltammetry, which are much higher than that of pentacene (5.14 eV), implying good environmental stability of the compounds.

Crystals suitable for single-crystal X-ray diffraction structure analysis were obtained by slow evaporation of solution of **1** and **2** in toluene/THF mixed solvents at room temperature. The crystal structure of **2** shows a nearly planar conformation with a sandwich-herringbone arrangement (Fig. 1a). The two fused β-trithiophenes units adopt an anti conformation with a torsion of 4.7° and the π-stacked dimers are separated by 3.48 Å. However, the crystal structure of **1** is considerably different from that of **2**. As shown in Figure 1b and c, the molecular packing of **1** is characteristic of condensed herringbone mode with unique S…S interaction networks. Distances of 3.56 and 3.34 Å, which are smaller than twice the Van der Waals radius of S atoms (3.70 Å), are observed between the central S atom of fused trithiophenes units along the short molecular axis and the outmost S atoms along the long molecular axis of neighboring molecules, respectively. It should be noted that this extremely short S…S distance (3.34 Å) is one of the shortest S…S distances existing in sulfur-decorated organic semiconductors.[11] Although it is assumed that cofacial π-stacking would facilitate the charge transport,[12] our extraordinary 3D network combining edge-to-face π–π interactions and S…S interactions is expected to provide new a packing mode for charge transport.

Thin film OFETs were fabricated with "top contact" geometry as reported previously.[13] Briefly, semiconductors were evaporated onto a SiO_2 (500 nm)/n-doped Si substrate, which had been treated with octadecyltrichlorosilane (OTS). Gold was evaporated as the source/drain electrodes. At room temperature, the mobility of **2** was 0.005 $cm^2\,V^{-1}\,s^{-1}$, the on/off ratio was 3.9×10^5, and the threshold voltage was −40 V. The mobility of **1** was as high as 0.47 $cm^2\,V^{-1}\,s^{-1}$, the on/off ratio was 1.2×10^7, and the threshold voltage was −32 V. The device performance of **1** was obviously much better than that of **2**, probably due to the molecular arrangement of **1**, which was favorable for carrier transport with uniform intermolecular orbital overlap. Moreover, the device performance of compound **1** could be further optimized. The thin films of compound **1** were evaporated at different substrate temperatures. As a preliminary result, it was found that the mobility and on/off ratio of **1** OFETs were improved by optimizing the film deposition conditions, e.g., by using a two-stage film deposition process to prepare the film.[14] Firstly, a 20-nm film was evaporated on substrate under high substrate temperature (100 °C) to form large-size grains on substrate,and then the cracks and voids between grains were further filled with a second 40-nm deposition at lower substrate temperature (27 °C). Devices made by this two-stage deposition process exhibited OFET performance with mobility as high as 0.89 $cm^2\,V^{-1}\,s^{-1}$ and on/off ratio 4.6×10^7 (Table 1).

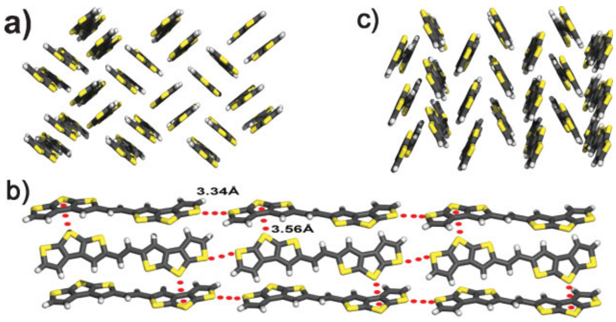

Figure 1. Crystal packing of **1** and **2**: a) sandwich-herringbone arrangement of **2**; b) herringbone arrangement of **1**; c) multiple S…S interaction of **1**.

X-ray diffraction (XRD) of the film of compound **1** deposited by the two-stage (100/27 °C) process showed a series of sharply resolved peaks (Fig. 3a) assignable to multiple (h00) reflection, indicating that the film has highly ordered structures on the substrate. The XRD profile indicates that the first diffraction peak is at $2\theta = 9.46°$, corresponding to a d-spacing of 9.39 Å. This value is about half the value of the molecule length. Based on the X-ray crystallographic analysis, the molecular of compound **1** is nearly orthogonally oriented onto the substrate. The molecular assembly of the compact thin film (Fig. 3b) is basically the same as that of bulk crystals. As expected, the device made from this film exhibits excellent OFET performance.

Further theoretical simulations can help to understand the different charge transport properties between these two compounds more clearly. Usually, there are two kinds of charge transport models in organic systems: the band model and the hopping model.[12] Due to the large reorganization energy and relatively small transfer integrals (see Table S1 and S2 of the Supporting Information), the charge transport in the two compounds here can be well described by the latter: a diffusion process. Namely, the charge is assumed to be localized in one molecule, instead of spreading over several molecules. The charge transfer rate from one molecule to another is described by the Fermi golden rule, namely, a quantum version of charge transfer:[15]

$$k_{\mathrm{CT}} = \frac{1}{\hbar^2}|V|^2 \int_{-\infty}^{\infty} \mathrm{d}t \exp\Big\{ -\sum_j S_j[(2\bar{n}_j + 1) - \bar{n}_j e^{-it\omega_j} - (\bar{n}_j + 1)e^{it\omega_j}] \Big\} \tag{1}$$

Table 1. FET characteristics of devices fabricated under different substrate temperatures.

Compound	T [°C]	Mobility [$cm^2\,V^{-1}\,s^{-1}$]	On/off ratio
1	27	0.47–0.32	10^7
	40	0.45–0.26	10^6
	60	0.15–0.06	10^6
	100/27	0.89–0.50	10^7
2	27	0.005–0.002	10^5

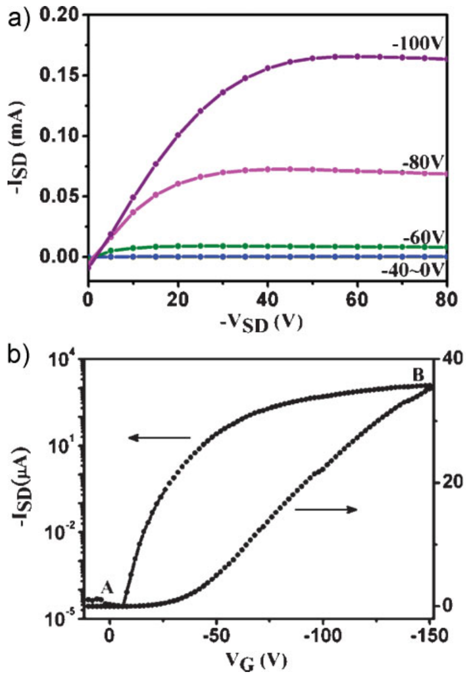

Figure 2. a) Output and b) transfer characteristics of thin film OFETs of compound **1** with mobility at 0.89 $cm^2 V^{-1} s^{-1}$ and on/off ratio of 4.6×10^7 fabricated by using a two-stage film deposition process.

Here, $\bar{n}_j = 1/(e^{\hbar\omega_j/k_BT} - 1)$ denotes the population of the *j*th normal mode. ω_j is its frequency. $S_j = (1/2)\hbar^{-1}\omega_j(\Delta Q_j)^2 \equiv \lambda_j/\hbar\omega_j$ is the Huang–Rhys factor, measuring the charge-vibration coupling strength. λ_j is the reorganization energy of the *j*th mode. In the strong coupling $\left(\sum_j S_j \gg 1\right)$ and high temperature limits ($\hbar\omega_j/k_BT \ll 1$, $\bar{n}_j \approx k_BT/\hbar\omega_j$, the classical limit), where the short time approximation can be applied, it can be shown that Equation 1 goes to the Marcus formula:

$$k_{CT} = \frac{|V|^2}{\hbar}\left(\frac{\pi}{\lambda k_B T}\right)^{1/2} \exp\left(-\frac{\lambda}{4k_B T}\right) \tag{2}$$

where $\lambda = \sum_j \lambda_j = \sum_j S_j\hbar\omega_j$ is the total reorganization energy. Equation 2 has been often used to describe charge transport in organic materials.[16]

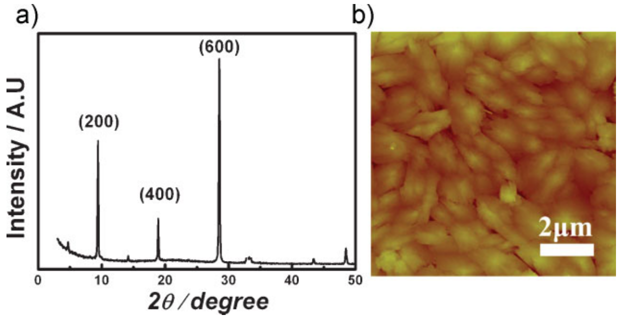

Figure 3. a) XRD pattern of an evaporated thin film of compound **1**; b) atomic-force microscopy image of a thin film of compound **1** deposited on an OTS-treated SiO_2 substrate.

With the quantum CT rates at hand, the charge mobility is obtained through the Einstein formula $\mu = eD/k_BT$ by assuming a diffusion process. The isotropic charge diffusion constant *D* is simulated by random walk. We take the molecular crystal as a structure reference and choose one molecule as the initial charge center. The charge is only allowed to hop between nearest neighbor molecules with a probability $p_\alpha = k_{CT}^\alpha / \sum_\alpha k_{CT}^\alpha$, where α indicates the hopping path. The hopping time is $1/k_{CT}^\alpha$ and the hopping distance is taken to be the molecular center–center distance. At each step, a random number *r* uniformly distributed between 0 and 1 is generated. If $\sum_{\alpha=1}^{j-1} p_\alpha < r \le \sum_{\alpha=1}^{j} p_\alpha$ (accumulated probability), then the charge is allowed to go along the *j*th direction. The typical time is from a few tens to a few hundred microseconds for each simulation. Then the diffusion constant is obtained as: $D = \lim_{t\to\infty}(l(t)^2/6t)$where $l(t)^2$ is the mean squared displacement. In order to get a converged diffusion constant, namely a linear relationship between the square of the diffusion distance and the diffusion time, two thousand diffusion processes are simulated. A typical simulation is shown in Figure 4. We note that it is impossible to reach a linear behavior. However, after 2000 simulations, the averaged squared displacement becomes linear with respect to time.

The random walk simulation coupled with quantum chemical calculations indicate that the RT hole mobility of **1** is 48 times as large as that of **2**, because the crystal packing of the former is much more uniform than the latter, even though the intermolecular electron couplings and molecular reorganization energies are similar for **2** and **1**. This agrees with experiment, indicating charge transfer rate only is not enough to describe charge transport behavior in bulk materials (see the Supporting Information).

In summary, we have presented a novel semiconductor based on annelated β-trithiophenes, which possesses an extraordinarily compressed packing mode combining edge-to-face π–π interactions and S…S interactions. It has exhibited excellent OFET performance as films with mobility up to 0.89 $cm^2 V^{-1} s^{-1}$ and on/off ratio of 4.6×10^7. Further investigations on modifications of the molecule to better understand the structure/property relationships are currently underway.

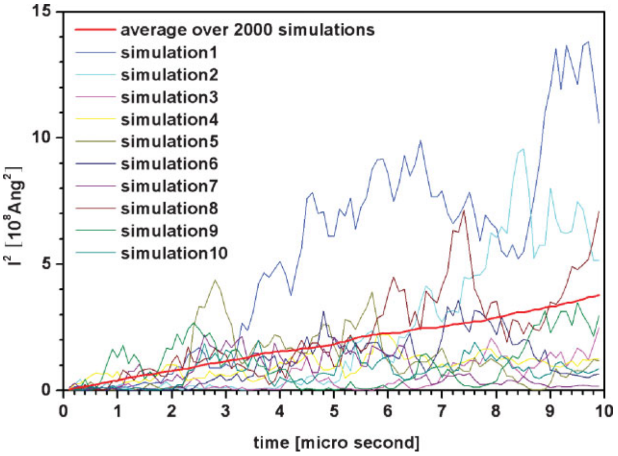

Figure 4. The squared displacement versus simulation time.

3. Experimental

5-Bromodithieno[2,3-b:3′,2′-d]thiophene (Compound **5***)*: To a solution of dithieno[2,3-*b*:3′,2′-*d*]thiophene (1 g, 5.1 mmol) in chloroform/AcOH (1:1 50 mL), *N*-bromosuccinimide (NBS) (1 g, 5.6 mmol) was added at room temperature. The mixture was stirred under argon for 2 h at room temperature, and then quenched with water, and the aqueous layer was extracted with chloroform several times. The combined organic phase was washed with saturated brine, dried over magnesium sulfate, and purified by chromatography (petroleum ether as eluent) to give white crystals (1.30 g, 93%). Mp: 118–120 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, 1H, $J = 5.2$ Hz), 7.39 (s, 1H), 7.31 (d, 1H, $J = 5.2$ Hz); ^{13}C NMR (600 MHz, $CDCl_3$) δ 137.6, 137.1, 136.7, 136.1, 126.9, 121.5, 117.7, 111.7; MS (EI) *m*/*z* = 275 (M^+). Anal. calcd for $C_8H_3BrS_3$: C 34.91%; H 1.10%; found: C 34.56%, H 1.32%.

Dithieno[2,3-b:3′,2′-d]thiophene-5-carbaldehyde (Compound **4***)*: To a solution of dithieno[2,3-*b*:3′,2′-*d*]thiophene (4 g, 20.4 mmol) in *N, N*-dimethylformamide (DMF) (100 mL), $POCl_3$ (7.80 g, 4.8 mL) was added at 0 °C. The mixture was stirred at 0 °C for 1 h and then at room temperature for 24 h. The resulting suspension was stirred at 50 °C for 5 h and cooled to room temperature. The mixture was poured into ice water and saturated sodium acetate was added until a pH of approximately 5 was achieved; the mixture was then stirred for another 3 h. The resulting solid was filtered and washed with water. The crude product was dried and purified by chromatography using petroleum/dichloromethane (1:1) as eluent to give a pale yellow crystal.(3.9 g, 85%). Mp: 169–170 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.93 (s, 1H), 8.00 (s, 1H), 7.47 (d, 1H, $J = 5.3$ Hz), 7.42 (d, 1H, $J = 5.3$ Hz); ^{13}C NMR (600 MHz, $CDCl_3$) δ 182.8, 149.0, 146.3, 140.1, 138.4, 128.9, 127.7, 118.9; MS (EI) *m*/*z* = 224 (M^+). Anal. calcd for $C_9H_4OS_3$: C 48.19%, H 1.80%; found: C 48.14%, H 1.84%.

a,a′-Bis(dithieno[2,3-b:3′,2′-d]thiophene) (Compound **2***)*: 5-Bromodithieno[2,3-*b*:3′,2′-*d*]thiophene (0.7 g, 2.5 mmol) and Cu (0.2 g, 3.1 mmol) in dry DMF (50 mL) was stirred at 130 °C under argon for 12 h. The resulting mixture was filtered, purified by a short column (petroleum/dichloromethane 3:1) to afford a pale yellow crystal (0.21 g, 43%). Mp: 254–256 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (s, 2H), 7.42 (d, 2H, $J = 5.3$ Hz), 7.38 (d, 2H, $J = 5.3$ Hz); MS (MALDI-TOF) 390.1. Calcd for $C_{16}H_6S_6$: C 49.20%, H 1.55%; found: C 48.64%, H 1.55%.

trans-1,2-[Dithieno(2,3-b:3′2′-d)thiophene]ethene (Compound **1***)*: To a suspension of zinc power (2.6 g, 41 mmol) in THF (60 ml), titanium tetrachloride (2.2 mL) was slowly added, and then refluxed for 3 h. A solution of dithieno[2,3-*b*:3′,2′-*d*]thiophene-5-carbaldehyde (0.9 g, 4.1 mmol) and pyridine (3.5 g) in THF (30 mL) was slowly added to the mixture and the mixture was refluxed for 5 h. After cooling to room temperature, the mixture was diluted with saturated sodium hydrogen carbonate (500 mL) and stirred for 3 h. The solid was filtered and washed with diluted HCl, water, acetone, and dried. The crude product was sublimated twice to give bright yellow crystals (0.32 g, 38%). Mp: 337–339 °C; MS (MALDI-TOF) 415.8. Calcd for $C_{18}H_8S_6$: C 51.89%, H 1.94%; found: C 52.35%, H 1.72%.

Single crystals of compounds **1** and **2** were obtained by slow evaporation of toluene/THF solution at room temperature. The X-ray crystal structure analyses were made on a Bruker SMART CCD diffractometer, using graphite-monochromated MoKα radiation (λ) 0.7107 Å. The data were collected at 113 K and the structures were refined by full-matrix least-square on F^2. The computations were performed with SHELXL-97 program. All hydrogen atoms were refined anisotropically. **1**. Crystal size: $0.12 \times 0.10 \times 0.04$ mm^3; $Z = 4$; cell dimensions: $a = 16.329(17)$Å; $b = 11.539(12)$Å; $c = 8.163(8)$Å; $\alpha = 90.00°$; $\beta = 101.201$; $\gamma = 90.00°$; $V = 1509(3)$Å^3; $\rho = 1.719$ mg cm^{-3}. Of 19 092 reflections, 2966 were unique ($R_{int} = 0.0454$); GOF = 1.168; 200 parameters; RI = 0.0522; $wR_2 = 0.1148$; **2**. Crystal size: $0.12 \times 0.16 \times 0.02$ mm^3; $Z = 2$; monoclinic; P121/C1; cell dimensions: $a = 18.800(19)$Å; $b = 7.622(8)$Å; $c = 5.742(7)$Å; $\alpha = 90.00°$; $\beta = 92.791°$; $\gamma = 90.00°$; $V = 829.90(16)$Å^3; $\rho = 1.638$ mg cm^{-3}; $2\theta_{max} = 27.88$; Of 9518 reflections, 1965 were unique ($R_{int} = 0.0442$); GOF = 1.226; 110 parameters; RI = 0.0667; $wR_2 = 0.1551$; CCDC 6 80 797 (**2**) CCDC 680 798 (**1**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Device Fabrication: FET devices were fabricated in the top contact geometry configuration. Thin films were deposited under vacuum on OTS-modified silicon oxide layers. Gold electrodes were deposited using shadow masks with length-to-width ratio (L/W) of ca. 48.2/1. Organic semiconductors were deposited at an initial rate of 0.1 Å s^{-1} then increasing to 0.4–0.6 Å s^{-1} gradually under a pressure of about 4.0×10^{-6} Torr to a final thickness of 60 nm determined by a quartz crystal monitor. FET characteristics were obtained at room temperature in air on a Keithley 4200 SCS and Micromanipulator 6150 probe station

Acknowledgements

The authors would like to acknowledge financial support from NSFC (20772131, 20721061, 50725311), 973 Program (2006CB932100, 2006CB806200), and Chinese Academy of Science. Supporting Information is available online from Wiley InterScience or from the author.

Received: July 7, 2008

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