Dibenzothiophene derivatives as new prototype semiconductors for organic field-effect transistors

Jianhua Gao,[ab] Liqiang Li,[ab] Qing Meng,[ab] Rongjin Li,[ab] Hui Jiang,[ab] Hongxiang Li*[a] and Wenping Hu*[a]

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New prototype semiconductor materials based on dibenzothiophene (DBT) derivatives were successfully synthesized by a convergent approach using palladium catalyzed Stille coupling reactions. Thermogravimetric analysis, UV-vis spectra and electrochemistry results indicated these materials had good thermal and photooxidation stability. X-Ray diffraction measurements of the vacuum-evaporated films showed enhanced crystalline order with increasing substrate deposition temperature. The ordered vacuum-evaporated films with charge carrier mobility as high as 7.7×10^{-2} cm^2 V^{-1} s^{-1} and an on/off ratio of nearly 1×10^7 had been achieved with 3,7-bis(5′-hexyl-thiophen-2′-yl)-dibenzothiophene (3,7-DHTDBTT). These results suggest that the 3,7-substituted DBT system is a good prototype for new type organic semiconductors and will play a more important role in organic semiconductors.

Introduction

Organic field-effect transistors (OFETs) have attracted much attention as an alternative to conventional silicon-based transistors because large areas can be potentially fabricated at low cost, and on flexible substrates.[1–6] To realize these advantages of OFETs in commercial applications, the performance of OFET devices, such as mobility and stability, should be comparable with that of amorphous hydrogenated silicon. Till now, charge mobilities of OFETs in the order of 0.1 cm^2 V^{-1}s^{-1}, similar to those of amorphous silicon transistors, have been achieved.[7–11] However, most of these semiconductor materials have relative high-lying HOMO (highest occupied molecular orbital) levels and narrow band gaps, they are therefore easily photo- and thermally oxidized, leading to degraded OFET performance under ambient conditions.

Currently the research into OFETs mainly focuses on two parts: one is to design and synthesize new types of semiconductors with both high mobility and stability to significantly improve the performance of the devices and to understand the structure–property relationships;[12–18] the second is to optimize the structure of devices by using known semiconductor materials such as pentacene, oligothiophene, phthalocyanine *etc.*, to reveal the intrinsic properties of organic semiconductors and figure out the effect of device structure on device performance.[19–22]

Oligo- and fused-chalcogenophene compounds exhibit high OFET performance,[16,23] and these results suggest that the combination of thiophene (or selenophene) and benzene may be an efficient way to obtain excellent OFET semiconductor materials. However, most of the chalcogenophene compounds suffered tedious synthesis steps and are difficult to purify (due to low solubility in organic solvents). So the design and synthesis of new chalcogenophene units that can form, and be incorporated into, organic semiconductors are desirable and challenging for significant optimization of OFET performances and for a better understanding of the structure–property relationships. Dibenzothiophene (DBT) as a chalcogenophene compound is cheap and commercial available, which has been reported to be one of the most abundant compounds in gas oil.[24] It has a high ionization potential (IP) (low HOMO level) compared with anthracene, fluorene, carbazole normally used in organic semiconductors to improve stability, and a large band gap (no absorption in the visible region). Furthermore, it has a planar structure, which is favorable for intermolecular interaction. Additionally, the S atoms in DBT can enhance intermolecular overlap, which facilitates charge migration. All of these merits indicate that DBT should be an ideal conjugated unit for organic semiconductors, which are cheap and will improve the stability and mobility of materials.

Herein, a new type of organic semiconductor with a dibenzothiophene unit were designed and synthesized (Scheme 1). These DBT derivatives were substituted at different positions so that we could explore the relationship between structure and properties. All compounds exhibited high photooxidation and thermal stability relative to other organic semiconductors as determined by UV-vis spectroscopy, electrochemistry and thermogravimetric analysis (TGA). Surprisingly, we found an alkyl substitution group could largely improve the thermal stability of DBT derivatives, which was obvious from TGA results though the reason was unclear. Thin film devices based on 3,7-DHTDBTT showed mobility up to 7.7×10^{-2} cm^2 V^{-1}s^{-1} and an on/off ratio of nearly 1×10^7. These results suggested that the 3,7-substituted DBT system was a good prototype for a new type of organic semiconductors and would play a more important role in organic semiconductors.

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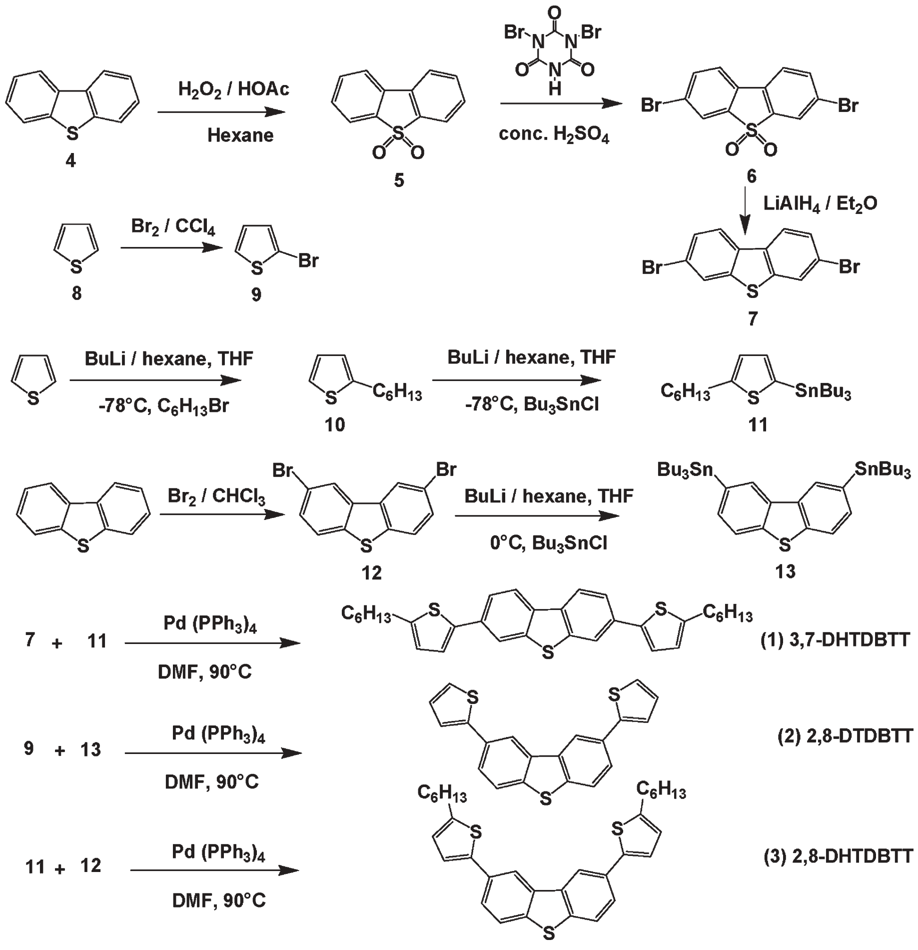
[a] *Beijing National Laboratory for Molecular Sciences (BNLMS), Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing, China, 100080. E-mail: lhx@iccas.ac.cn; Fax: +86 10 6252 7295; Tel: +86 10 8261 5030*
[b] *Graduate School of Chinese Academy of Sciences, Beijing, China, 10039*



Scheme 1 Synthetic scheme for compounds **1–3**.

Experimental

Materials and general methods

All the reactions were done under nitrogen unless otherwise stated. ^{1}H-NMR spectra were recorded on a Varian 400 MHz and 300 MHz spectrometer in deuterated chloroform with tetramethylsilane as an internal reference. 2,8-dibromodibenzothiophene was obtained by brominating DBT directly,[25] while 3,7-dibromodibenzothiophene was synthesized through oxidation, bromination and reduction steps.[23] The reagents 2-bromothiophene,[26] and 5-hexyl-2-tributylstannylthiophene were prepared according to known procedures. Other reagents and chemicals were obtained from commercial sources and used without further purification. Et_2O, THF, DMF were all dried and distilled before being used for reaction solvents. UV-vis spectra were obtained on a JASCO V-570 UV-vis spectrometer. Cyclic voltammetry (CV) was run on a CHI660C electrochemistry station in CH_2Cl_2 solution using tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) as an electrolyte at a scan rate of 100 mV s^{-1}. Thermogravimetric analysis (TGA) was carried out on a PERKIN ELMER TGA7.

OFET devices were fabricated by the top contact geometry configuration. Thin films were deposited under vacuum deposition on octyltrichlorosilane (OTS) modified silicon oxide layers. Gold electrodes were deposited by using shadow masks with *W*/*L* of *ca.* 48.2/1. Organic semiconductors were deposited at a 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 65 nm determined by a quartz crystal monitor. OFET characteristics were obtained at room temperature in air by a Keithley 4200 SCS and Micromanipulator 6150 probe station. X-Ray diffraction measurements were performed in reflection mode at 40 kV and 200 mA with Cu Kα radiation using a 2 kW Rigaku D/max-2500 X-ray diffractometer.

Materials synthesis

2,8-Bis(tributylstannyl)dibenzothiophene 13. BuLi (2.6 ml, 6.5 mmol) in hexane was added to a solution of 2,8-dibromodibenzothiophene (1.05 g, 3 mmol) in Et_2O under nitrogen at 0 °C. The reaction was kept at 0 °C for 1 h, then tributyltin chloride (2.05 g, 1.71 mmol) was added. The reaction mixture was allowed to warm to room temperature and stood overnight. Then it was quenched by ice water and extracted with ether, the organic layer was washed with water and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography on alumina with petroleum ether. The product was obtained as a colorless liquid and used without further purification, yield 2.1 g (91%). MS (EI): *m*/*z* 762 (M+).

3,7-Bis(5′-hexyl-thiophen-2′-yl)-dibenzothiophene (3,7-DHTDBTT) 1. A three-neck flask equipped with a condenser was charged with 5-hexyl-2-tributylstannylthiophene (2.75 g, 6 mmol), 3,7-dibromodibenzothiophene (0.85 g, 2.5 mmol), $Pd(PPh_3)_4$ (288 mg, 0.25 mmol) and DMF (25 ml). The reaction mixture was heated to 90 °C and stirred at this temperature for 20 h. Then it was cooled to room temperature, and the solvent was removed under vacuum. Then the product was purified by column chromatography on silica gel using petroleum ether as eluent and further recrystallized in CH_2Cl_2 and *n*-hexane respectively. Yield, 0.72 g (56%). Mp, 250 °C. ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): 8.06 (d, 2H), 8.00 (s, 2H), 7.65 (d, 2H), 7.22 (d, 2H), 6.78 (d, 2H), 2.84 (t, 4H), 1.72 (m, 4H), 1.35 (m, 12H), 0.90 (t, 6H). MS (EI): *m*/*z* 516 (M+). Elemental analysis calculated for $C_{32}H_{36}S_3$: C, 74.41; H, 6.97. Found: C, 74.19; H, 7.06.

2,8-Bis(thiophen-2′-yl)-dibenzothiophene (2,8-DTDBTT) 2. A three-neck flask equipped with a condenser was charged with 2,8-ditributylstannyldibenzothiophene (1.02 g, 3 mmol), 2-bromothiophene (3.37 g, 9 mmol), $Pd(PPh_3)_4$ (207 mg, 0.18 mmol) and DMF (30 ml). The reaction mixture was heated to 80–90 °C and stirred at this temperature for 20 h. After the mixture was cooled to room temperature, the solvent was removed under vacuum, the residue was purified by silica gel column chromatography using petroleum ether : CH_2Cl_2 9 : 1 as eluent, affording product as a colorless solid, yield, 0.51 g (49%). Mp, 184–185 °C. ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): 8.40 (s, 2H), 7.85 (d, 2H), 7.74 (d, 2H), 7.45 (d, 2H), 7.34 (d, 2H), 7.15 (t, 2H). MS (EI): *m*/*z* 348 (M+). Elemental analysis calculated for $C_{20}H_{12}S_3$: C, 68.97; H, 3.45. Found: C, 68.78; H, 3.51.

2,8-Bis(5′-hexyl-thiophen-2′-yl)-dibenzothiophene (2,8-DHTDBTT) 3. 2,8-DHTDBTT was synthesized by using the same procedure as 2,8-DTDBTT. Yield, 63%. Mp, 75 °C. ^{1}H-NMR (400 MHz, d^6-DMSO, ppm): 8.74 (s, 2H), 8.03 (d, 2H), 7.75 (d, 2H), 7.56 (d, 2H), 6.92 (d, 2H), 2.85 (t, 4H), 1.68 (m, 4H), 1.37 (m, 12H),0.89 (t, 6H). MS (EI): *m*/*z* 516 (M+). Elemental analysis calculated for $C_{32}H_{36}S_3$: C, 74.42; H, 6.98. Found: C, 73.99; H, 6.88.

Results and discussion

Synthesis

The syntheses of compounds **1–3** are outlined in Scheme 1. All of the compounds were started from commercially available DBT. 2,8-Dibromodibenzothiophene was obtained by direct bromination of DBT, the preparation of 3,7-dibromodibenzothiophene was carried out through oxidation and reduction steps due to the electron donating properties of sulfur in DBT. Then compounds **1–3** were synthesized by Stille coupling reactions.[27] Two approaches were tested in Stille coupling reactions, one was using stannyldibenzothiophene and bromothiophene, the other was reacting stannylthiophene with bromodibenzothiophene. We found the second approach was a better way to prepare DBT derivatives with improved yield and easy purification. All the compounds were quite soluble in normal organic solvents such as CH_2Cl_2, $CHCl_3$, THF and totally characterized by ^{1}H-NMR, MS and elementary analysis.

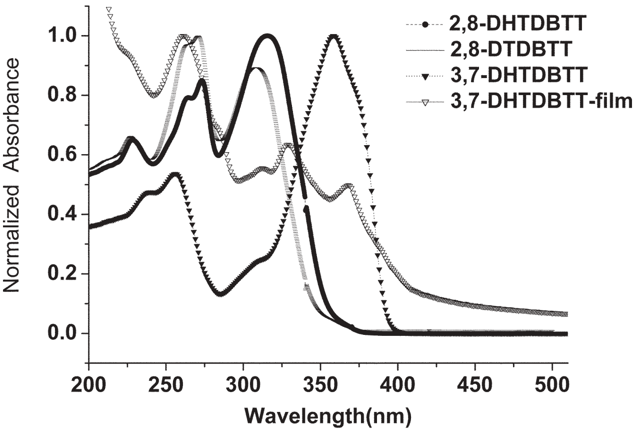


Fig. 1 UV-vis absorption spectra of compounds **1–3** in CH_2Cl_2 solution and on thin films.

Optical, electrochemical and thermal properties

The UV-vis spectra of compounds **1–3** in CH_2Cl_2 solution are shown in Fig. 1. Compound **1** showed three absorption peaks at 358, 257, and 240 nm. The absorption at 358 nm corresponds to the π–π* transition band of the conjugated compound, and the peaks at 240 nm and 257 nm were due to the electronic transition of the individual thiophene and dibenzothiophene units respectively. Compounds **2** and **3** showed similar absorption to **1**, but their maximum absorptions were blue-shifted compared with **1**, which indicated that the conjugated length of molecules at 2,8-disubstitution was shorter than that of 3,7-disubstitution. The band gaps of compounds **1–3** estimated from UV-vis absorption spectra were in the range 3.1–3.4 eV (Table 1), larger than most of the semiconductors used in OFETs, indicating their high photostability.

The cyclic voltammetry of compounds **1–3** was done in CH_2Cl_2 by using glass carbon as the working electrode and Ag/AgCl as the reference (Fig. 2). **1** showed two irreversible

Table 1 Optical properties, energy band gaps and thermal stability of compounds **1–3**

	E_{pa}[a] (Oxidation)/V	E_{onset} (Oxidation)/V	HOMO[b]/eV	LUMO/eV	λ_{max}/nm	E_g[c]/eV	T_{dec}[d]/°C
3,7-DHTDBTT	1.24, 1.38	1.07	−5.57	−2.44	358	3.13	352
2,8-DTDBTT	1.33	1.23	−5.73	−2.43	315	3.30	283
2,8-DHTDBTT	1.40	1.24	−5.74	−2.39	308	3.35	346

[a] Peak potentials of anodic peak. [b] The HOMO levels of the compounds determined by using the onset positions of the oxidation according to literature.[28] [c] E_g values were determined from UV-vis absorption spectra in solution with CH_2Cl_2. [d] Decomposition temperature observed from TGA corresponding to 5% weight loss at 10 °C min^{-1} under nitrogen.

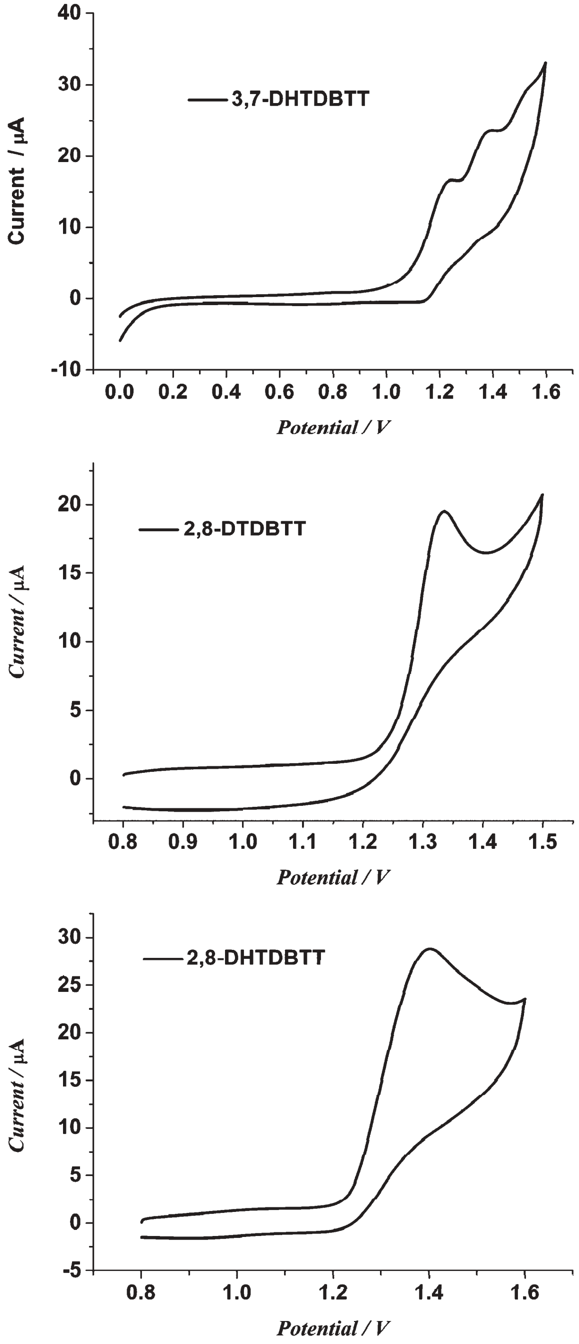


Fig. 2 Cyclic voltammograms of compounds **1–3**.

oxidation waves (1.24 V, 1.38 V), while the others had only one wave at more positive potentials (**2**: 1.33 V; **3**: 1.40 V). The lowest oxidation potential of **1** among the three DBT derivatives indicated that it had longest conjugation length, which was consistent with the UV-vis absorption results. The HOMO levels of the compounds determined by using the onset positions of the oxidation according to literature[28] (Table 1) were −5.57, −5.53 and −5.54 eV respectively. The low-lying HOMO levels confirmed the high oxidation stability of compounds **1–3**.

The thermal properties of the dibenzothiophene derivatives were investigated by thermogravimetric analysis (TGA) as illustrated in Fig. 3. TGA results showed that compounds **1** and **3** had good thermal stability and did not decompose until 340 °C under nitrogen atmosphere. However, compound **2** decomposed at 283 °C under the same conditions. Since the difference between **2** and **3** was only the hexyl substitution group, there is no doubt that the alkyl substitution group improved the thermal stability of the DBT derivative, though the reason was unclear.

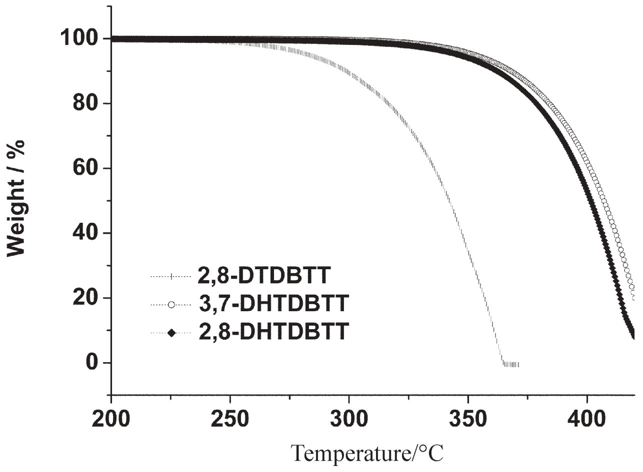


Fig. 3 TGA results of compounds **1–3**.

Thin films

In order to study the aggregation behavior of molecules in the solid state, the UV-vis spectrum of a vacuum-evaporated thin film of compound **1** was investigated (Fig. 1). Compared with the absorption of **1** in solution, the π–π* transition absorption peak in the thin film was blue-shifted about 20 nm, which indicated H-aggregation.[29] The optical absorption maximum at around 366 nm was attributed to vibronic progression according to the conventionally accepted conception.[30,31] This vibronic mode with the longest wavelength presents the lowest-allowed transition in molecules in the solid state. It could not be observed in solution, because the well-defined molecular alignment which was responsible for the vibronic absorption was broken in the solution.

The X-ray diffraction of vacuum-evaporated thin films of **1** at different substrate temperatures is shown in Fig. 4. At low substrate temperature, a dominant peak at 26.3 Å and a very weak signal in the 3–5 Å region was observed. Since the length of compound **1** was 29 Å (Fig. 5), the dominant peak at 26.3 Å suggested that **1** exhibited end-to-end packing on the substrate, which means an almost orthogonal alignment of molecules onto the substrate plane was formed upon deposition. However, some slight chain tilting against the substrate must be presented since the observed *d* spacing (26.3 Å) was smaller than the corresponding extended chain length. The weak reflection peak at 4.2 Å was caused by some parallel alignment from side-by-side packing rather than multiple orders of the primary 26.3 Å peak. When the film was deposited at higher temperature (T_{sub} = 60 °C), the peak in the 3–5 Å region disappeared, which means high crystallinity and a perfectly orientated film was formed. For further increases of substrate

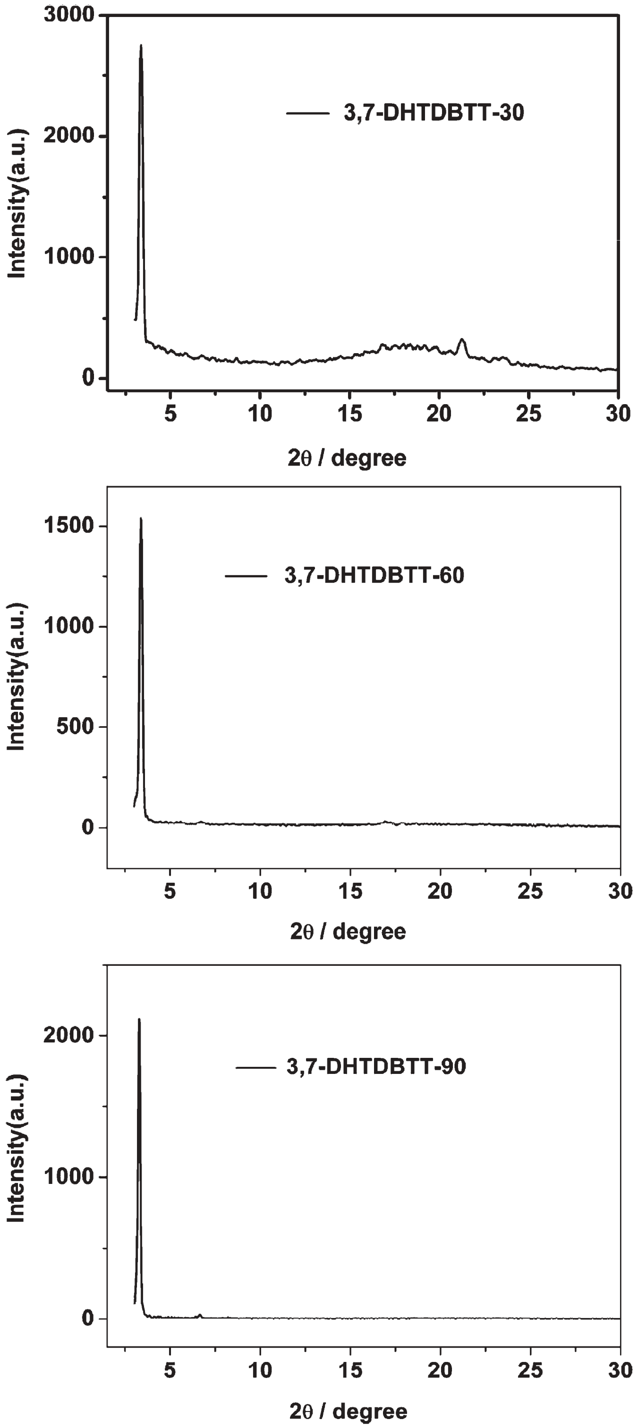


Fig. 4 X-Ray diffraction of 3,7-DHTDBTT film deposited at different temperatures; the numbers at the end of the compound names correspond to the deposition temperature.

temperature (T_{sub} = 90 °C), no significant improvement over the already excellent orientation could be observed.

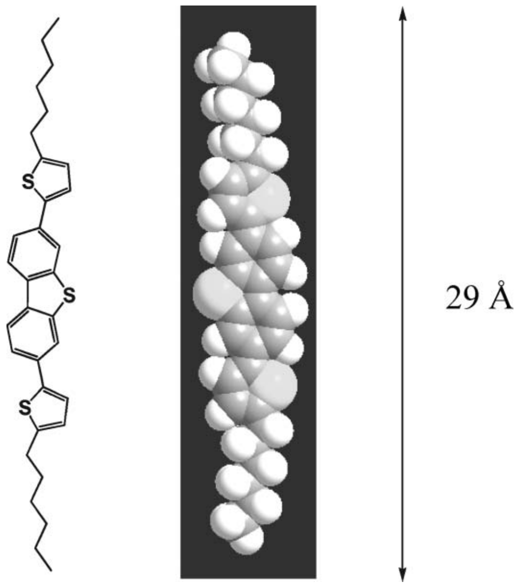


Fig. 5 Molecular model of 3,7-DHTDBTT.

FET device performance

The transistor behavior of compounds **1** and **2** was studied using the top contact device structure on an OTS modified Si/SiO_2 substrate. Due to the low melt point, **3** could not be deposited under vacuum. Field-effect mobility was estimated in the saturated regime using eqn 1

$$I_{DS} = \mu C_i (V_G - V_T)^2 W/2L \tag{1}$$

Where, W is the channel width, L is the channel length, C_i is the capacitance per unit area of the SiO_2 layer (7.5 nF cm^{-2}), V_G is the gate voltage, V_T is the threshold voltage, and I_{DS} is the source–drain current. Both compounds displayed p-type accumulation FET behavior when they were used as channel semiconductors in OTFTs.

Fig. 6 shows typical FET characteristics of compound **1** at T_{sub} = 30 °C. The I–V characteristics showed standard linear and saturation regions. The FET performance of compounds **1** and **2** obtained at different substrate temperatures is summarized in Table 2. From Table 2, we can see that with the increase of substrate temperature, the mobility of compound **1** increased and a high mobility of up to 7.7×10^{-2} cm^2 V^{-1} s^{-1} with an on/off ratio of nearly 1×10^7 was obtained at T_{sub} = 60 °C. This was because at this temperature, a more ordered thin film was formed which was evidenced by X-ray diffraction. The decrease in mobility at T_{sub} = 90 °C was possibly due to the increase in the distance between grains at the semiconductor–dielectric interface,[19,32] since the X-ray diffraction of the film at T_{sub} = 90 °C was same as the one at T_{sub} = 60 °C. The FET performance of compound **2** was worse than that of **1**, this was not surprising because 3,7-disubstitution of DBT could provide longer conjugated length than that of 2,8-disubstitution which was evidenced by UV-vis spectra and electrochemistry.

Though the mobilities of DBT derivatives **1** and **2** were not very high compared with pentacene, considering the merits of DBT derivatives: low HOMO level, large bandgap, none tedious synthesis and easy purification, undoubtedly DBT is a promising candidate unit for OFET semiconductor materials.

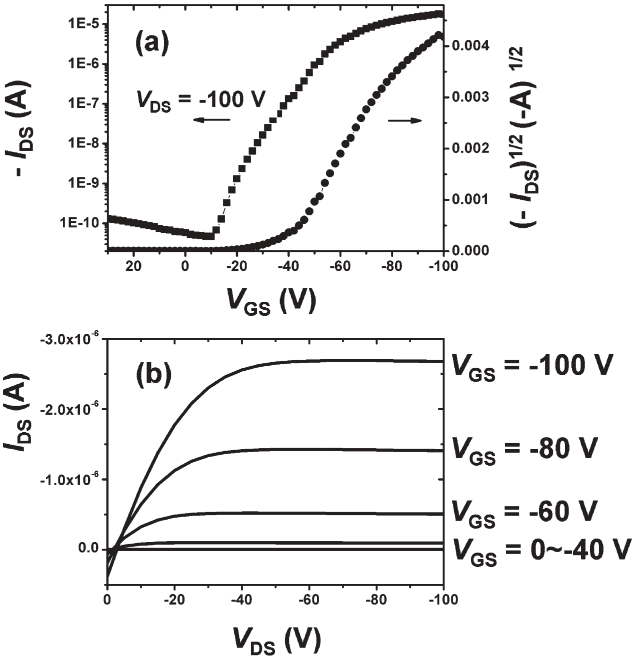


Fig. 6 OFET characteristics of an exemplary device with vacuum-deposited 3,7-DHTDBTT (substrate temperature, 30 °C; channel length, 0.11 mm; channel width, 5.3 mm): (a) the transfer curve in the saturated regime at a constant source–drain voltage of −100 V and square root of the absolute value of the current as a function of the gate voltage and (b) output curves at different gate voltages.

Table 2 OFET characteristics of compounds **1** and **2** deposited at different substrate temperatures

Material	T_{sub}/°C	μ/cm^2 V^{-1} s^{-1}	I_{on}/I_{off}	V_t/V
3,7-DHTDBTT	30	5.0×10^{-2}	4.2×10^5	−40.2
	60	7.7×10^{-2}	9.2×10^6	−53.3
	90	5.5×10^{-2}	8.0×10^5	−38.2
2,8-DTDBTT	30	6.3×10^{-4}	6.0×10^4	−49.9

[a] All films were deposited on OTS modified silicon oxide layers.

Conclusions

In summary, organic semiconductors based on dibenzothiophene derivatives were designed and synthesized through a Stille reaction. All of the materials had good solubility in normal organic solvents. UV-vis spectra, electrochemistry and TGA results showed these materials had low-lying HOMO levels, large HOMO–LUMO band gaps and good thermal stability. TGA results also suggested that alkyl substitution could improve the thermal stability of DBT derivatives though the reason was unclear. Mobility up to 7.7×10^{-2} cm^2 V^{-1} s^{-1} and an on/off ratio of nearly 1×10^7 was achieved for 3,7-DHTDBTT at T_{sub} = 60 °C. These results indicate that 3, 7-disubstituted DBT is a promising candidate for organic semiconductors with high mobility and stability, and will play more roles in organic semiconductors.

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