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The synthesis of 2,6-dialkylphenyldithieno[3,2-*b*:2′,3′-*d*]thiophene derivatives and their applications in organic field-effect transistors

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ABSTRACT

2,6-Dialkylphenyldithieno[3,2-*b*:2′,3′-*d*]thiophene derivatives (**DPCn–DTT**) were synthesized and characterized. Effect of alkyl groups on optical characteristics, electrochemical properties, film-forming ability, and field-effect performance was studied. The four compounds **DPCn–DTT** show almost the same energy levels of the highest occupied molecular orbits and optical energy gaps, but they exhibit different charge carrier transport characteristics. The thin film transistors based on **DPC1–DTT** with the shortest alkyl groups (methyl groups) show the highest mobility of 0.54 cm^2 V^{-1} s^{-1}. Substrate temperature and surface modification of the SiO_2 insulators have a remarkable effect on field-effect performance. High-quality microribbons of **DPC8–DTT** with octyl groups were prepared by a solution-phase self-assembly process. Single crystal field-effect transistors based on an individual **DPC8–DTT** microribbon exhibit a high mobility of 1.1 cm^2 V^{-1} s^{-1} with a current on/off ratio of 6.5 × 10^4.

1. Introduction

In the last two decades, substantial progress has been made in organic field-effect transistors (OFETs). A large number of organic semiconductors have been developed and investigated owing to their potential applications in low-cost processes. Although preparation technology of the OFET devices is in continuous development to enhance device performance, the key point determining high performance of the OFET devices is still governed by organic semiconductors [1,2] For *p*-channel OFET semiconductors, pentacene derivatives [3–5], fused thiophenes [6,7], and thienoacene derivatives [8] are the major materials which show good performance due to their linear fused rings with CH⋯π interaction, and/or S⋯S interactions, namely, enhanced orbital coupling [9,10]. Organic molecules with long alkyl groups often show the nature of self-organizing which is another effective approach to enhance orbital coupling. Owing to the van der Waals intermolecular interaction between the alkyl groups, or the so-called molecular fastener effect [11,12] where long alkyl groups can act as a driving force for molecular ordering arrangement in the solid state and render semiconducting core to pack tightly, and thereby enhance carrier mobility. This is exemplified by Kazuo Takimiya who has reported a series fused rings with long-chain alkyl moieties (**Cn–DNTT**) as *p*-channel organic semiconductors for vapor-processed OFET devices [13]. The compounds **Cn–DNTT** showed mobilities higher than those of the compound without long-chain alkyl moieties [14]. Moreover, long alkyl groups could also lead a facile formation of micro/nano ribbons and single crystals. One-dimensional micro- and nanostructures from semiconducting materials are promising objects in terms of miniaturizing electronic devices in the field of micro- and nanoelectronics. Organic single-crystal field-effect transistors could offer an opportunity to explore the intrinsic charge transport properties of organic semiconductors. Dithieno[3,2-*b*:2′,3′-*d*]thiophene (**DTT**) is an important building block to synthesize fused thiophene derivatives and π-conjugated polymers which have been widely used as organic-semiconductor materials in OFETs [15–18]. The thin film and micro/nano ribbon OFET devices based on long-chain alkylated **DTT** derivatives were barely reported before.

Based on the above mentioned molecular design strategies for enhancing OFET performance, we designed and synthesized a series of diphenyldithieno[3,2-*b*:2′,3′-*d*]thiophene derivatives with different alkyl groups (**DPCn–DTT**) shown in Scheme 1. We studied optical, electrochemical, and field-effect performance of the compounds **DPCn–DTT** and analyzed the effect of different alkyl groups on these properties. The compound **DPC1–DTT** with methyl groups

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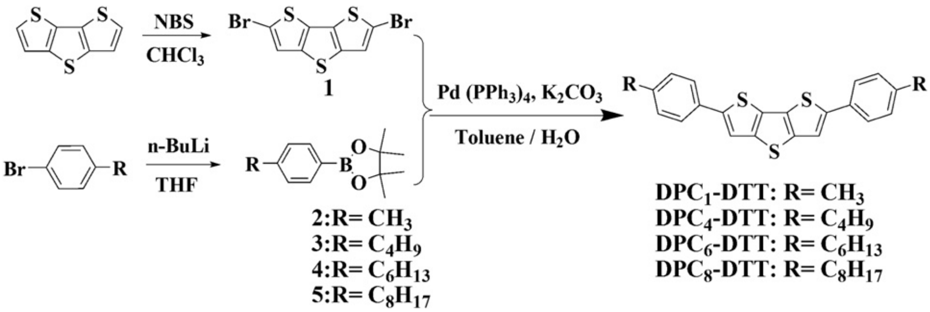

Scheme 1. Synthetic routes of the **DPCn−DTT**.

exhibits an excellent field-effect performance with a high mobility of 0.54 $cm^2\ V^{-1}\ s^{-1}$ and a large on/off ratio of up to 2×10^6. Furthermore, we prepared micro/nano ribbons of the compound **DPC8−DTT** with two octyl groups by solvent diffusion method. The single crystal transistor based on the individual **DPC8−DTT** microribbon shows a maximum mobility of 1.1 $cm^2\ V^{-1}\ s^{-1}$.

2. Experimental section

2.1. Characterization of materials

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 400 spectrometer. Chemical shifts were reported as *d* values [ppm] relative to internal tetramethylsilane (TMS). Elemental analyses were carried out using a Carlo Erba model 1160 elemental analyzer. Electron-impact mass spectra (EI-MS) were collected on a GCI−MS micromass (UK) spectrometer. UV−vis absorption spectra were measured on a Hitachi U-3010 spectrophotometer. Cyclic voltammetric measurements were performed using a computer-controlled EG&G Potentiostat/Galvanostat5 model 283. Thermogravimetric analysis (TGA) measurements were recorded on a Perkin−Elmer series 7 thermal analysis system under N_2 at a heating rate of 10 °C min^{-1}. Atomic force microscopy (AFM) measurements were carried out with a Nanoscope V instrument. X-ray diffraction (XRD) of thin films was performed in the reflection mode at 40 kV and 200 mA with CuKa radiation using a 2 kW Rigaku X-ray diffractometer. The scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images were recorded on a Hitachi S−4800 SEM and a TETEM Tecnai G2 F20 U−TWIN, respectively.

2.2. Synthesis of materials

All chemicals and solvents are of reagent grade unless otherwise indicated. Tetrahydrofuran (THF) was purified with a standard distillation procedure prior to use. Dithieno[3,2-*b*:2′,3′-*d*]thiophene was synthesized as previously reported [17].

2.2.1. 2,6-Dibromodithieno[3,2-b:2′,3′-d]thiophene (1)

Dithieno[3,2-*b*:2′,3′-*d*]thiophene (0.98 g, 5.0 mmol) in chloroform (20 mL) was reacted with *N*-bromosuccinimide (NBS, 2.0 g, 11.2 mmol) at room temperature overnight. Batch-wise addition of NBS is necessary. The light yellow suspension was treated with water and filtered off. After silica column chromatography with petroleum ether, pale needle crystals were obtained (1.8 g, 90% yield). ^1H NMR (400 MHz, CD_2Cl_2, ppm) δ: 7.27 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 112.32, 123.17, 130.82, 139.05. EI-MS *m*/*z* (M^+): Calcd. for $C_8H_2Br_2S_3$, 352; found, 352.

2.2.2. 2-(4-Tolyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2)

1-Bromo-4-methylbenzene (1.0 g, 5.88 mmol) was dissolved in 30 mL anhydrous THF under argon. The solution was cooled to −78 °C before solution of *n*-BuLi (2.4 M) in hexane (3.4 mL, 8.16 mmol) was added dropwise. The reaction mixture was stirred for 10 min at −78 °C. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.9 g, 10.2 mmol) was added then. The reaction mixture was allowed to warm up to room temperature and stirred overnight before it was poured into ice water. The solution was extracted with 100 mL dichloromethane (CH_2Cl_2), the organic layer washed with 70 mL brine and dried with Na_2SO_4 before the solvent was removed. The crude product was purified by column chromatography on silica gel with petroleum ether/CH_2Cl_2 (10:1, v/v) as an eluent to give a white solid (1.1 g, 85% yield). ^1H NMR (400 MHz, $CDCl_3$, ppm) δ: 1.32 (s, 12H), 2.36 (s, 3H), 7.20 (d, 2H, $J = 7.6$ Hz), 7.73 (d, 2H, $J = 7.6$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 21.72, 24.86, 83.64, 128.55, 134.26, 141.50. EI-MS *m*/*z* (M^+): Calcd. for $C_{13}H_{19}BO_2$, 218; found, 218.

2.2.3. 2-(4-Butylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3)

The compound **3** was synthesized according to the procedure described for **2** using 1-bromo-4-butylbenzene and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. A white production was obtained with a yield of 90%. ^1H NMR (400 MHz, $CDCl_3$, ppm) δ: 0.88 (t, 3H, $J = 7.0$ Hz), 1.18−1.26 (m, 4H), 1.31 (s, 12H), 1.65(m, 2H), 2.62 (t, 2H, $J = 7.6$ Hz), 7.22 (d, 2H, $J = 7.6$ Hz), 7.75 (d, 2H, $J = 7.6$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 14.11, 22.58, 24.90, 34.51, 35.84, 83.56, 128.16, 134.20, 144.54. EI-MS *m*/*z* (M^+): Calcd. for $C_{16}H_{25}BO_2$, 260; found, 260.

2.2.4. 2-(4-Hexylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4)

The compound **4** was synthesized according to the procedure described for **2** using 1-bromo-4-hexylbenzene and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. A white product was obtained with a yield of 83%. ^1H NMR (400 MHz, $CDCl_3$) δ: d (ppm): 0.86 (t, 3H, $J = 7.6$ Hz), 1.18−1.26 (m, 8H), 1.33 (s, 12H), 1.67 (m, 2H), 2.62 (t, 2H, $J = 7.8$ Hz), 7.20 (d, 2H, $J = 7.8$ Hz), 7.73 (d, 2H, $J = 7.8$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 14.09, 22.65, 25.06, 29.11, 31.88, 34.51, 35.94, 83.62, 128.26, 134.61, 144.83. EI-MS *m*/*z* (M^+): Calcd. for $C_{18}H_{29}BO_2$, 288; found, 288.

2.2.5. 2-(4-Octylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5)

The compound **5** was synthesized according to the procedure described for **2** using 1-bromo-4-octylbenzene and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. A white product was obtained with a yield of 93%. ^1H NMR (400 MHz, $CDCl_3$, ppm) δ: 0.89 (t, 3H), 1.18−1.26 (m, 10H), 1.33 (s, 12H), 21.67(m, 2H), 2.62 (t, 2H), 7.21 (d, 2H, $J = 8.0$ Hz), 7.74 (d, 2H, $J = 8.0$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 14.23, 22.80, 24.99, 29.40, 29.45, 29.61, 29.86, 31.49, 32.02, 36.34, 83.69, 128.01, 134.95, 146.52. EI-MS *m*/*z* (M^+): Calcd. for $C_{20}H_{33}BO_2$, 316; Found, 316.

2.2.6. 2,6-Bis(4-tolyl)dithieno[3,2-b:2′,3′-d]thiophene (DPC1−DTT)

The compounds **1** (500 mg, 1.42 mmol) and **2** (774 mg, 3.55 mmol) were dissolved in toluene/H_2O (3:1, v/v). To the mixture