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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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A R T I C L E I N F O

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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 $CH\cdots\pi$ interaction, and/or $S\cdots S$ interactions, namely, enhanced orbital coupling [9,10]. Organic molecules with long alkyl groups often show the nature of selforganizing 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

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 cm² V⁻¹ s⁻¹. Substrate temperature and surface modification of the SiO₂ 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 cm² V⁻¹ s⁻¹ with a current on/off ratio of 6.5 × 10⁴.

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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 pchannel 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 cm² V⁻¹ s⁻¹ and a large on/off ratio of up to 2 \times 10⁶. 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 cm² 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 computercontrolled EG&G Potentiostat/Galvanostat5 model 283. Thermogravimetric analysis (TGA) measurements were recorded on a Perkin-Elmer series 7 thermal analysis system under N₂ 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, CD₂Cl₂, ppm) δ : 7.27 (s, 2H). ¹³C NMR (100 MHz, CDCl₃, ppm) δ : 112.32, 123.17, 130.82, 139.05. EI-MS *m*/*z* (M⁺): Calcd. for C₈H₂Br₂S₃, 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 (CH₂Cl₂), the organic layer washed with 70 mL brine and dried with Na₂SO₄ before the solvent was removed. The crude product was purified by column chromatography on silica gel with petroleum ether/CH₂Cl₂ (10:1, v/v) as an eluent to give a white solid (1.1 g, 85% yield). ¹H NMR (400 MHz, CDCl₃, 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). ¹³C NMR (100 MHz, CDCl₃, ppm) δ : 21.72, 24.86, 83.64, 128.55, 134.26, 141.50. EI-MS *m/z* (M⁺): Calcd. for C₁₃H₁₉BO₂, 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, CDCl₃, 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). ¹³C NMR (100 MHz, CDCl₃, 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 C₁₆H₂₅BO₂, 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, CDCl₃) 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). ¹³C NMR (100 MHz, CDCl₃, 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 C₁₈H₂₉BO₂, 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, CDCl₃, 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). ¹³C NMR (100 MHz, CDCl₃, 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 C₂₀H₃₃BO₂, 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/H₂O (3:1, v/v). To the mixture



Fig. 1. UV-vis absorption spectra of DPCn-DTT in (a) CH₂Cl₂ solution (10⁻⁵ M) and (b) thin films. PL spectra of DPCn-DTT in (c) CH₂Cl₂ solution (10⁻⁵ M) and (d) thin films.

was added 164 mg (0.14 mmol) Pd(PPh₃)₄ and then the mixture was stirred for 5 min under argon. Finally, 590 mg (4.28 mmol) K₂CO₃ was added to the mixture. The reaction mixture was refluxed for 36 h under argon. After the reaction solution was cooled down to room temperature, the solution was extracted with CH₂Cl₂. The organic layer was washed with brine and dried with Na₂SO₄. The solvent was evaporated under a reduced pressure and the product was extracted with CH₂Cl₂. The extraction solution was washed with brine and H₂O, and then was dried with anhydrous MgSO₄. The crude product was purified by column chromatography on silica gel using a mixture of petroleum ether/ CH_2Cl_2 (10:1, v/v) as an eluent to provide a yellow solid (410 mg, 77% yield). ¹H NMR (400 MHz, CDCl₃, ppm) δ: 2.39 (s, 6H), 7.22 (d, 4H, *J* = 7.8 Hz), 7.46 (s, 2H), 7.53 (d, 4H, J = 7.8 Hz). ¹³C NMR (100 MHz, CDCl₃, ppm) δ : 21.54, 115.92, 125.51, 129.01, 129.87, 131.91, 141.37, 141.48, 142.83. EI-MS m/z (M⁺): Calcd. for C₂₂H₁₆S₃, 376; found, 376. Elemental analysis (%) calcd for C₂₂H₁₆S₃: C 70.17, H 4.28, S 25.55; found: C 69.90, H 4.27, S 25.65.

2.2.7. 2,6-Bis(4-butylphenyl)dithieno[3,2-b:2',3'-d]thiophene (**DPC4–DTT**)

The compound **DPC4–DTT** was synthesized according to the procedure described for **DPC1–DTT** using **3**, **1**, K₂CO₃, and Pd(PPh₃)₄. The crude product was purified by column chromatography on silica gel using a mixture of petroleum ether/CH₂Cl₂ (10:1, v/v) as an eluent to provide a yellow solid in 66% yield. ¹H NMR (400 MHz, CDCl₃, ppm) δ : 0.95 (t, 6H, *J* = 7.3 Hz), 1.39 (m, 4H), 1.63 (m, 4H), 2.64 (t, 4H, *J* = 7.6 Hz), 7.22 (d, 4H, *J* = 7.8 Hz), 7.46 (s, 2H), 7.55 (d, 4H, *J* = 7.8 Hz); ¹³C NMR (100 MHz, CDCl₃, ppm) δ : 13.98, 22.37, 33.55, 35.82, 116.02, 125.61, 129.12, 129.98, 132.00, 141.48, 141.59, 142.93. EI-MS *m/z* (M⁺): Calcd. for C₂₈H₂₈S₃, 460; found,

460. Elemental analysis (%) Calcd for C₂₈H₂₈S₃: C 72.99, H 6.13, S 20.88; found: C 72.85, H 6.01, S 21.06.

2.2.8. 2,6-Bis(4-hexylphenyl)dithieno[3,2-b:2',3'-d]thiophene (**DPC6–DTT**)

The compound **DPC6–DTT** was synthesized according to the procedure described for **DPC1–DTT** using **4**, **1**, K_2CO_3 , and Pd(PPh₃)₄. The crude product was purified by column chromatography on silica gel using a mixture of petroleum ether/CH₂Cl₂



Fig. 2. Cyclic voltammograms of the DPCn–DTT thin films (Scan rate: 0.1 V/s).



Fig. 3. (a) Output and (b) transfer curves of the DPC1–DTT based OFETs on bare SiO₂ insulator deposited at substrate temperature of 100 $^\circ$ C.

(10:1, v/v) as an eluent to provide a yellow solid in 72% yield. ¹H NMR (400 MHz, CDCl₃, ppm) δ : 0.89 (t, 6H, *J* = 6.4 Hz), 1.30–1.35 (m, 12H), 1.64 (m, 4H), 2.64 (t, 4H, *J* = 7.8 Hz), 7.22 (d, 4H, *J* = 7.8 Hz), 7.46 (s, 2H), 7.55 (d, 4H, *J* = 7.8 Hz). ¹³C NMR (100 MHz, CDCl₃, ppm) δ : 14.25, 22.77, 29.14, 31.51, 31.88, 35.84, 116.15, 125.75, 129.24, 130.12, 132.13, 141.63, 143.11, 145.34. EI-MS *m*/*z* (M⁺): Calcd. for C₃₂H₃₆S₃, 516; found, 516. Elemental analysis (%) calcd for C₃₂H₃₆S₃: C 74.37, H 7.02, S 18.61; found: C 74.03, H 6.96, S 18.95.

2.2.9. 2,6-Bis(4-octylphenyl)dithieno[3,2-b:2',3'-d]thiophene (**DPC8–DIT**)

The compound **DPC8–DTT** was synthesized according to the procedure described for **DPC1–DTT** using **5**, **1**, K_2CO_3 , and Pd(PPh_3)_4. The crude product was purified by column chromatography on silica gel using a mixture of petroleum ether/CH₂Cl₂ (10:1, v/v) as an eluent to provide a yellow solid in 78% yield. ¹H

Table 1	l
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The device characteristics of OFETs i	fabricated at various	substrate temperatures
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NMR (400 MHz, CDCl₃, ppm) δ : 0.86 (t, 6H, J = 6.8 Hz), 1.26–1.30 (m, 16H), 1.64 (m, 4H), 2.63 (t, 4H, J = 8.0 Hz), 7.22 (d, 4H, J = 7.8 Hz), 7.46 (s, 2H), 7.55 (d, 4H, J = 7.8 Hz). ¹³C NMR (100 MHz, CDCl₃, ppm) δ : 14.28, 22.79, 29.17, 31.11, 31.61, 31.90, 32.15, 35.84, 116.16, 126.00, 129.35, 130.21, 132.33, 141.95, 143.30, 145.51. EI-MS m/z (M⁺): Calcd. For C₃₆H₄₄S₃, 572; found, 572. Elemental analysis (%) calcd for C₃₆H₄₄S₃: C 75.47, H 7.74, S 16.79; found: C 75.42, H 7.56, S 16.97.

2.3. Fabrication of organic thin film transistor devices and measurement

Prior to the deposition of organic thin films, all compounds **DPCn–DTT** were purified twice by vacuum sublimation ($<10^{-3}$ Pa). Top-contact bottom gate OFET devices were fabricated by vacuum deposition on bare or octadecyltrichlorosilane (OTS)-treated SiO₂/Si substrates at preset substrate temperatures (T_{sub}). Organic semiconductors were deposited 10 nm at a rate of 5 Å/min, then deposited 30 nm at the rate of 30 Å/min. Gold source and drain contacts were patterned 50 nm by thermal evaporation using shadow masks. The channel length (L) and width (W) were 80 and 8800 µm, respectively. The characteristics of the OFET devices were determined using a Keithley 4200 SCS semiconductor parameter analyzer at room temperature in air. The mobility of the devices was calculated in the saturation regime. The equation is listed as follows:

$$I_{\rm DS} = (W/2L)C_i\mu(V_{\rm GS} - V_{\rm th})^2$$

where W/L is the channel width/length, C_i is the insulator capacitance per unit area, and V_{GS} and V_{th} are the gate voltage and threshold voltage, respectively.

2.4. Preparation of micro/nano ribbons and their OFET devices

Into a 5 mL cylinder bottle was added 1 mL solution of **DPC8**– **DTT** in CHCl₃ (10⁻⁴ mol/L), and then 12.5 mL ethanol was slowly dropped along the walls of bottle into the solution. After standing for about 6 days, micro/nano ribbons were formed and suspended in the mixed solvent. OFET devices with a top-contact/bottom-gate configuration were fabricated using an individual **DPC8–DTT** microribbon precipitated from chloroform/alcohol solution. A heavily doped *n*-type Si substrate and a 300 nm SiO₂ layer with a capacitance per unit area of 11.5 nF cm⁻² were used as a gate electrode and gate dielectric layer, respectively. The microribbon was transferred onto an OTS-treated SiO₂/Si substrate. Then Gold shadow masks were used to deposit the gold source/drain electrodes. For the top-contact/bottom-gate configuration, the

Compound	T _{sub} (°C)	Bare SiO ₂			OTS-treated SiO ₂		
		$\mu (cm^2 V^{-1} s^{-1})$	I _{on} /I _{off}	$V_{\rm th}$ (V)	$\mu (cm^2 V^{-1} s^{-1})$	I _{on} /I _{off}	$V_{\mathrm{th}}\left(V\right)$
DPC1-DTT	25	0.20	7.8×10^{3}	0	0.15	7.3×10^4	-9
	70	0.21	$1.4 imes 10^6$	8	0.20	$2.5 imes 10^6$	2
	100	0.54	$2.2 imes 10^6$	16	0.16	$1.1 imes 10^6$	3
DPC4-DTT	25	0.25	$8.3 imes 10^5$	1	0.15	$3.5 imes 10^6$	-11
	70	0.12	$1.0 imes 10^6$	5	0.08	$3.5 imes 10^5$	-8
	100	0.10	$1.5 imes 10^5$	9	0.05	4.4×10^5	-7
DPC6-DTT	25	0.14	$2.8 imes 10^5$	-17	0.08	1.6×10^5	-7
	70	0.09	2.8×10^4	-22	0.12	1.3×10^5	-14
	100	0.12	5.2×10^4	-16	0.18	$1.1 imes 10^4$	-22
DPC8-DTT	25	0.12	4.2×10^3	3	0.10	$5.1 imes 10^4$	-16
	70	0.11	$5.5 imes 10^5$	-1	0.08	$5.5 imes 10^4$	6
	100	0.08	1.5×10^5	16	0.06	6.6×10^3	-3



Fig. 4. AFM topography (5 \times 5 $\mu m) of the DPC1–DTT films.$

thickness of Au is about 40 nm. SEM measurements of an individual **DPC8–DTT** microribbon and Au electrodes for the OFET devices based on the individual **DPC8–DTT** microribbon were performed on a Hitachi S-4800 SEM.

maximum absorption of **DPC1–DTT** appears in longer wavelength than those of the other three compounds. Additionally, the **DPC1–DTT** thin film has a red shift of 5 nm compared with the **DP–DTT** (363 nm) [18], suggesting a stronger intermolecular interaction in the **DPC1–DTT** thin film. Optical band gaps (E_{gap}) of **DPCn–DTT** were estimated from the absorption edges of the absorption

3. Results and discussion

3.1. Synthesis of materials

The synthetic routes of the compounds **DPCn – DTT** are shown in Scheme 1. The synthesis of dithieno[3,2-b:2',3'-d]thiophene was carried out as previously reported [17]. Dithieno[3,2-b:2',3'-d] thiophene reacts with NBS to give the compound 1 with a high yield of 90%. The lithiation of 1-bromo-4-methylbenzene with an excess amount of *n*-BuLi at -78 °C, followed by treatment with 2-isopropoxy-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane, gave the boronic ester **2**. Compounds **3**–**5** were synthesized in a similar way. The Pd catalyzed Suzuki coupling reaction of compound 1 with the boronic ester 2 was performed to obtain the compound DPC1-DTT with a 77% yield. The obtained diboromo derivative 1 treated with the boronic esters 3-5, respectively, gives the corresponding products DPC4–DTT, DPC6–DTT, and DPC8–DTT in modest yields (66–78%) by a similar coupling reaction. All the synthesized compounds were further purified twice by vacuum sublimations, whose chemical structures were determined by ¹H NMR, ¹³C NMR, EI-MS, and elemental analysis. The compound **DPCn-DTT** exhibits good solubility in common organic solvents such as CH₂Cl₂, THF, and o-dichlorobenzene.

3.2. Optical and electrochemical properties

Fig. 1 shows absorption and photoluminescent (PL) spectra of the four compounds **DPCn–DTT** in CH₂Cl₂ solution and thin films. All compounds exhibit absorption maxima (λ_{max}) at 360–372 nm both in solution and thin films. In CH₂Cl₂ solution, the four compounds exhibit similar absorption spectra. **DPC1–DTT** in solution has a 4 nm blue shift compared with those of the other three compounds which show almost the same absorption maxima. **DPC1–DTT** exhibits the same λ_{max} in solution and thin film as well. However, different results are obtained for the compounds **DPC4– DTT**, **DPC6–DTT**, and **DPC8–DTT**. The absorption peaks of the three compounds in thin films demonstrate a blue shift of 8–12 nm compared with those in solutions. The modest blue-shifts in solid state could be attributed to H-aggregates [19]. In the film state, the alkyl groups have an obvious effect on absorption peak. The



Fig. 5. (a) XRD of the **DPCn–DTT** thin films on the bare SiO₂ insulators deposited at 100 °C and (b) XRD of **DPC1–DTT** on the bare SiO₂ insulators at different deposited temperature.

spectra in thin films. E_{gap} is larger than 3.0 eV for the four compounds. The **DPCn–DTT** thin films emit blue-greenish light with an emission peak at 480–540 nm. The PL spectra in thin films shift to longer wavelength compared with those in solution. A large red shift of 70 nm was observed, which can contribute to the molecular vibration and/or stronger intermolecular interaction [20].

Cvclic voltammetry measurements were conducted using an Ag/AgCl reference and a glassy carbon working electrode with 0.1 M [n-Bu₄N][PF₆] as a supporting electrolyte, in degassed CH₂Cl₂ solution purged with nitrogen. Fig. 2 shows cyclic voltammograms of the compounds **DPCn–DTT**. The four compounds show fully reversible oxidation behavior with two oxidation peaks. No obvious difference exists for the onset oxidation potentials (E_{ox}^{onset}) of the compounds DPCn-DTT. The similar energy levels of the highest occupied molecular orbits (HOMO) for the four compounds were evaluated to be -5.5 eV, according to the equation $E_{\text{HOMO}} = -(E_{\text{ox}}^{\text{onset}} + 4.4)$ eV. The energy levels of the lowest unoccupied molecular orbits (LUMO) were estimated as -2.5 eV by combining the HOMO energy level with the E_{gap} . The thermal properties of the compounds **DPCn**–**DTT** investigated by means of thermal gravimetric analysis show that the four compounds exhibit very good thermal stabilities. The decomposition temperatures with 5% weight loss are 318, 336, 340, and 350 °C for the DPC1–DTT, DPC4–DTT, DPC6–DTT, and DPC8–DTT, respectively.

3.3. OFET performance and film morphology

OFET devices were fabricated in a top-contact/bottom gate configuration with **DPCn–DTT** thin films deposited onto bare SiO₂/Si or OTS-treated SiO₂/Si substrates as active semiconductor layers. All the OFET devices exhibit *p*-channel transistor characteristics in ambient conditions. Fig. 3 shows output and transfer characteristics

of the **DPC1–DTT** based OFET devices fabricated on the bare SiO₂ insulators. Device characteristics of OTFTs based on the DPCn-DTT thin films prepared at different substrate temperature (T_{sub}) are summarized in Table 1. For the bare SiO2 insulator and at $T_{sub} = 25 \text{ °C}$, the OFET devices based on **DPC1–DTT** or **DPC4–DTT** exhibit relatively high mobilities of 0.17–0.18 cm² V⁻¹ s⁻¹ which are about twice higher than those of the corresponding devices based on the compound **DPC6–DTT** or **DPC8–DTT**. T_{sub} has an obvious effect on carrier charge mobility. On the bare SiO₂ insulator, only **DPC1–DTT** shows raised performance along with T_{sub} rising from 30 to 100 °C. The highest mobility of 0.54 cm² V⁻¹ s⁻¹ was obtained at $T_{sub} = 100$ °C. An opposite effect of T_{sub} on field-effect performance was obtained for the other three compounds. Increasing T_{sub} value decreases their mobilities. Highest mobility was obtained at $T_{sub} = 25 \circ C$ for the compounds **DPC4–DTT**, **DPC6–** DTT, or DPC8-DTT, respectively. For the OFETs based on the OTStreated SiO₂ insulators, we found that OTS-treatment on the SiO₂ surface does not enhance device characteristics. For the OTStreated SiO₂ insulator and at $T_{sub} = 25$ °C, the **DPC1–DTT** based OFETs exhibit a mobility of 0.14 cm² V⁻¹ s⁻¹, which is higher than those of the corresponding devices based on the compound DPC4-DTT, DPC6–DTT, or DPC8–DTT. The OFETs based on the DPC1–DTT thin films deposited on the OTS-treated SiO₂/Si substrates at different T_{sub} values from 25 to 100 °C show almost the same mobilities of 0.12–0.20 $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ with the current on/off ratios of 10⁴-10⁶. For the **DPC4-DTT** or **DPC8-DTT** based OFET devices fabricated on the OTS-treated SiO₂ insulators, mobility decreases with increase of the T_{sub} value and the highest mobility was obtained at 25 °C. However, different result was observed for the DPC6-DTT based OFET devices fabricated on the OTS-treated SiO₂ insulators and the highest mobility 0.13 cm² V⁻¹ s⁻¹ was obtained at 100 °C.



Fig. 6. (a), (b) SEM images, (c) TEM image, and (d) corresponding SAED pattern of a DPC8-DTT microribbon.

In fact, AFM images (Fig. 4) of the evaporated thin films support the OFET measurements. When deposited at 100 °C on the bare SiO₂ insulators (Fig. 4c), the **DPC1–DTT** thin films show a better uniformity than those deposited at other temperatures. While with the OTS-treated SiO₂ substrates, the grain size of the DPC1-DTT films becomes larger as the T_{sub} increases, as generally observed for films of organic semiconductor materials [21]. When the DPC1-**DTT** thin film was deposited at the same temperature, the grain boundary is deeper on the OTS-treated SiO₂ insulator than that on the bare SiO₂ insulator, leading to a decreased mobility. The X-ray diffraction (XRD) (Fig. 5) of the **DPCn-DTT** thin films also coincides with the OFET test. The DPC1-DTT thin films deposited at 100 °C on the bare SiO₂ insulators show high order Bragg peaks indicating excellent crystalline ordering in films [22], which corresponds to the highest mobility. At different substrate temperatures, the **DPC1–DTT** thin films on the bare SiO₂ insulators exhibit the same XRD peaks order with different intensity, which represents the same crystal arrangement but different degrees of crystallinity. Along with the shortening of alkyl chain, compounds **DPCn–DTT** on the bare SiO₂ insulators at 100 °C exhibit stronger XRD peak intensities and multiple reflections, consistent with raising of fieldeffect mobility. According Bragg equation $2d\sin\theta = \lambda$, the d space was 22.82 and 26.30 Å for compound DPC1–DTT and DPC4–DTT, respectively. The diffraction peaks around 21.2 and 23.6° reflect the intermolecular $\pi - \pi$ and S/S interactions, respectively. It is also found that mobilities are relatively higher on the bare SiO₂ insulators than those on the OTS-treated SiO₂ insulators. The AFM images reveal much smaller crystallite grains compared to the untreated substrates, which would suggest more grain boundaries. heterogeneity, and more electron trapping states for the thin film on OTS-treated substrate [23,24].

3.4. DPC8-DTT micro/nano ribbons and their OFET devices

The **DPC8**–**DTT** micro/nano ribbons were prepared by a solventdiffusion method in solution phase. Ethanol is slowly injected into chloroform solution of DPC8-DTT and the mixed solution sits to form micro/nano structures. The DPC8-DTT molecules readily selfassemble into micro/nano ribbons because long alkyl groups could act as a driving force for molecular ordering in the solid state and render semiconducting core to pack tightly. As shown in scanning electron microscope (SEM) (Fig. 6a and b), micro/nano structure based on **DPC8–DTT** exhibits a good linearity. The length of the micro/nano ribbon ranged from 150 µm to 0.5 mm with a high aspect ratio. Transmission electron microscopy (TEM) images and the corresponding selected area electron diffraction (SAED) patterns were collected from an individual micro/nano ribbon (Fig. 6c and d). The TEM image of the DPC8-DTT micro/nano ribbons shows very orderly diffraction point. Moreover, no difference was observed in different areas of the individual micro/nano ribbon, indicating that the whole ribbon is a single crystal. After an individual DPC8-DTT microribbon was transferred onto the OTStreated SiO₂/Si substrate, the gold source/drain electrodes were prepared using a gold silk as a shadow mask. Device structure and SEM image of single crystal OFETs based on an individual DPC8-DTT microribbon are showed in Fig. 7a and b. Fig. 7c and d shows the output and transfer characteristics of the single crystal OFET devices. The transistors exhibit a *p*-channel behavior with a highest



Fig. 7. Field-effect characteristics of single crystal OFETs based on an individual **DPC8–DTT** microribbon. (a) Device structure. (b) SEM image of the OFET devices. (c) Output and (d) transfer characteristics.

mobility of 1.1 cm² V⁻¹ s⁻¹ estimated from the saturation current, threshold voltage of -8 V, and current on/off ratio 6.5 × 10⁴.

4. Conclusions

We designed and synthesized a series of organic semiconductors **DPCn–DTT** containing a phenyldithieno[3,2-*b*:2',3'-*d*] thiophene core and different alkyl groups. Although these compounds show almost the same optical energy gaps (2.5 eV), LUMO (-3.0 eV), and HOMO energy level (-5.5 eV), the alkyl groups have an obvious effect on device characteristics of the thin film transistors because of different film forming ability and crystallinity. Among the four organic semiconductors, **DPC1–DTT** with the shortest alkyl groups (methyl groups) exhibits an excellent fieldeffect performance with the highest mobility of 0.54 cm² V⁻¹ s⁻¹ and an on/off current ratio of up to 2.2 × 10⁶. Furthermore, the individual **DPC8–DTT** single crystal microribbon prepared from a solution-phase self-assembly process shows more outstanding field-effect characteristics with the mobility of 1.1 cm² V⁻¹ s⁻¹.

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