

SYNTHESIS, CHARACTERIZATION AND SOLAR CELL APPLICATION OF A D-A COPOLYMER WITH CYCLOPENTADITHIOPHENE AND FLUORENE AS DONOR UNITS*

Hai-yang Song^{a,b}, Hui Tong^{a**}, Zhi-yuan Xie^a, Li-xiang Wang^{a**} and Fo-song Wang^a

^a State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China

^b Graduate University of Chinese Academy of Sciences, Beijing 100039, China

Abstract In this paper, a new D-A copolymer, PFDBCPDT, which consists of benzo-2,1,3-thiadiazole as acceptor units and cyclopentadithiophene and fluorene as donor units, was synthesized. The thermal, electrochemical, photophysical and photovoltaic properties of PFDBCPDT were studied. PFDBCPDT showed a low optical band gap of 1.84 eV, and relatively low HOMO level of –5.69 eV. The best device performance was obtained by PFDBCPDT/PC₆₁BM (1:3) with 0.5 vol% DIO. The device exhibited a power conversion efficiency of 3.06%, with a relatively high open circuit voltage of 0.87 eV.

Keywords: Polymer solar cell; Copolymerization; Fluorene; Cyclopentadithiophene; Conjugated polymers.

INTRODUCTION

Thin film polymer solar cells (PSCs) have become a promising option for low cost renewable energy production. Most solar cells are fabricated based on blends of conjugated polymers as p-type materials and fullerene derivatives (PCBMs) as n-type materials^[1–4]. To achieve good device performance, conjugated polymers are required to have low optical band gaps, which determine the light harvest ability of the blend films. Therefore, most researches were focused on design and synthesis of new low band gap polymer materials^[5–12]. In recent years, a popular approach to low band gap polymers is to synthesize copolymers containing alternating electron-donor units (D) and electron-acceptor units (A) on the conjugated polymer backbones, which are known as the D-A copolymers^[13–25]. Through varying chemical structures of donor units and acceptor units, optical, electrochemical and photovoltaic properties of D-A copolymers can be easily manipulated.

Cyclopentadithiophene (CPDT) based conjugated copolymers have been proved to be one of the most promising D-A copolymers for bulk heterojunction (BHJ) solar cells^[26–38]. In 2006, Brabec *et al.* reported the first high efficiency CPDT-based D-A conjugated copolymers (PCPDTBT) with 4,7-(2,1,3-benzothiadiazole) (BT) as the acceptor unit. With a rather low V_{oc} (ca. 0.65 V), PSCs of this copolymer showed the power conversion efficiency (PCE) of 2.67% with PC₆₁BM and 3.16% with PC₇₁BM, respectively^[26]. Since then, many CPDT-based copolymers were further explored as low band gap polymers^[27–34]. However, most of these

* This work was financially supported by the 973 Project (Nos. 2009CB623601 and 2009CB930603), the Science Fund for Creative Research Groups (No. 20921061), and the National Natural Science Foundation of China (Nos. 51173179, 20904055 and 21074130).

** Corresponding authors: Hui Tong (童辉), E-mail: chemtonghui@ciac.jl.cn

Li-xiang Wang (王利祥), E-mail: lixiang@ciac.jl.cn

Received September 18, 2012; Revised October 30, 2012; Accepted November 26, 2012

doi: 10.1007/s10118-013-1302-z

copolymers showed similar low V_{oc} (0.47–0.65 eV). Because PCE is determined by open circuit voltage (V_{oc}), short circuit current (J_{sc}) and fill factor (FF), it is necessary to improve V_{oc} of CPDT-based copolymer devices for high efficiency PSCs. It has been reported that tuning the chemical structure of acceptor units in D-A copolymers could lower HOMO levels of copolymers, leading to higher V_{oc} of devices^[39]. Polymer solar cells based on CPDT-based copolymers with different acceptor units such as dibenzothiadiazole, tetrazine or fluorinated benzothiadiazole *etc.* showed relatively higher V_{oc} of 0.74–0.83 V^[35–38]. In our previous work, we have reported efficient V_{oc} enhancement (*ca.* 0.3 V) for dithieno[3,2-b:2',3'-d]pyrrole (DTP) based D-A copolymer by simply introducing a fluorene unit as an additional donor unit^[40], instead of the design and synthesis of novel acceptors. The new copolymer, PDTPDBF, showed a V_{oc} of 0.84 V due to its low lying HOMO level relative to other DTP-based copolymers. In this paper, the similar strategy was applied to obtain a new CPDT-based copolymer, PFDBCPDT, containing both the fluorene unit and the CPDT unit as donor units and benzo-2,1,3-thiadiazole (BT) unit as the acceptor unit. Compared to the well-known PCPDTBT, we expected the simple introduction of the fluorene unit could also bring a lower HOMO level, leading to a higher V_{oc} and good device performance. Another copolymer, PFDBDT, which has similar backbone structure to PFDBCPDT but without the fuse ring structure in the dithiophene unit, was also prepared as a reference polymer.

EXPERIMENTAL

Measurements

¹H spectra were recorded at 298 K with a Bruker Avance 300 NMR spectrometer. Number-average (M_n) and weight-average (M_w) molecular weights were determined by GPC on a Waters 410 instrument with polystyrene as standards and THF as eluent. MALDI-TOF was measured by a Bruker Daltonics Flex analysis system. UV-Vis absorption spectra were recorded by a Perkin-Elmer Lambda35 UV-Vis spectrometer. Mass spectra were obtained with an LDI-1700 MALDI-TOF mass spectroscope. Thermogravimetric analysis (TGA) was carried on a Perkin-Elmer TGA-7 instrument. Cyclic voltammetry (CV) was used to determine the highest occupied orbitals (HOMO) and the lowest unoccupied orbitals (LUMO) energy levels of copolymers with a Pt counter electrode and Ag/Ag⁺ reference electrode in 0.1 mol/L Bu₄NClO₄ in acetonitrile at a scan rate of 50 mV s⁻¹ at room temperature under argon. A glass carbon electrode coated with a thin polymer film was used as the working electrode. Transmission electron microscopy (TEM) was performed on a JEM-1011 transmission electron microscope with 100 keV accelerating voltage. Samples for the TEM analysis were prepared by spin-casting from polymer and PCBM mix solution onto a PEDOT:PSS/glass substrate. The films were then floated onto water and placed on a 200-mesh copper TEM grid (Agar Sci. Inc.)

Materials

Unless otherwise specified, all chemicals and reagents were purchased from commercial suppliers and used without further purification. Toluene was distilled over sodium prior to use. 4H-cyclopenta [2,1-b;3,4-b']-dithiophene and 2,7-bis(trimethyleneboronate)-9,9-dioctylfluorene (**6**) were synthesized according to the literature^[26, 41].

Monomers

Synthesis of 4,4-bis(hexyl)-4H-cyclopenta [2,1-b;3,4-b']-dithiophene (**1**)

Under the argon atmosphere, a mixture of 4H-cyclopenta [2,1-b;3,4-b']-dithiophene (0.8 g, 4.49 mmol), 1-bromohexane (1.48 g, 8.98 mol), KOH (0.76 g, 13.5 mmol), KI (20 mg) and DMSO (30 mL) was stirred at room temperature overnight. Then the mixture was washed by water three times. The organic layer was separated and dried over anhydrous Na₂SO₄ and evaporated to dryness. The residue was chromatographically purified on silica gel column eluting with petroleum ether to afford 4,4-bis(hexyl)-4H-cyclopenta [2,1-b;3,4-b']-dithiophene (**1**) as light yellow liquid (1.15 g, 74%). ¹H-NMR (300 MHz, CDCl₃, δ): 7.14 (d, J = 4.8 Hz, 2H), 6.92 (d, J = 4.8 Hz, 2H), 1.84–1.79 (m, 4H), 1.22–1.14 (m, 4H), 1.14–1.10 (m, 8H), 0.98–0.90 (m, 4H), 0.81 (t, J = 7.2 Hz, 6H).

Synthesis of 4,4-bis(hexyl-2,6-bis(trimethylstannyl)-4H-cyclopenta[2,1-b:3,4-b']-dithiophene (2)

Into a mixture of 4,4-bis(hexyl-4H-cyclopenta [2,1-b:3,4-b']-dithiophene (1) (1.15 g, 3.33 mmol) and THF (30 mL) was added *n*-BuLi (2.5 mol/L, 3 mL, 7.32 mmol) dropwise at -78°C . The mixture was stirred at this temperature for 1 h, and warmed to room temperature for 1 h. SnMe_3Cl was added into the mixture at -78°C . The mixture was warmed to room temperature overnight after stirred at -78°C for 1 h. The mixture was washed by saturated KF aqueous solution three times and by water three times. Then the organic layer was separated and dried over anhydrous Na_2SO_4 and evaporated to dryness. The residue was not further purified and used directly in the next step.

Synthesis of 7,7'-(4,4'-dihexyl-4H-cyclopenta[2,1-b:3,4-b']-dithiophene-2,6'-diyl)bis(4-bromobenzo[c][1,2,5]thiadiazole) (3)

A mixture of 4,4-bis(hexyl-2,6-bis(trimethylstannyl)-4H-cyclopenta[2,1-b:3,4-b']-dithiophene (2), 4,7-dibromobenzo[c][1,2,5]thiadiazole (3 g, 10.1 mmol), $\text{Pd}(\text{PPh}_3)_4$ (370 mg), CuI (121 mg) was deaerated three times with argon, and added with toluene (150 mL). The mixture was stirred at 100°C overnight, then cooled to room temperature. The mixture was washed by saturated KF aqueous solution three times and by water three times. Then the organic layer was separated and dried over anhydrous Na_2SO_4 and evaporated to dryness. The residue was chromatographically purified on silica gel column eluting with petroleum ether/ CH_2Cl_2 (4:1, *V/V*) to afford **3** as black crystals in a yield of 31% (0.8 g). $^1\text{H-NMR}$ (300 MHz, CDCl_3 , δ): 8.06 (s, 2H), 7.84 (d, $J = 7.8$ Hz, 2H), 7.73 (d, $J = 7.8$ Hz, 2H), 2.10–1.90 (m, 4H), 1.30–1.00 (m, 16H), 0.85–0.70 (m, 6H). $^{13}\text{C-NMR}$ (101 MHz, CDCl_3 , δ): 159.88, 153.87, 151.52, 139.83, 138.96, 132.32, 127.81, 124.24, 122.64, 111.33, 54.39, 37.84, 31.59, 29.70, 24.65, 22.59, 14.01. MALDI-TOF MS: Calcd. for: $\text{C}_{33}\text{H}_{32}\text{Br}_2\text{N}_4\text{S}_4$: 772.70; Found: 772.0 $[\text{M}^+]$.

Synthesis of 3-hexylthiophene (4)

A mixture of Mg (5.83 g, 240 mmol) and a grain of I_2 was deaerated three times with argon, and then a solution of 1-bromohexane in ethyl ester (200 mL) was added drop wise at 0°C . The mixture was stirred at 0°C until the drop wise adding was finished, then warmed to room temperature and heated to reflux for 2 h. The mixture was added drop wise to a solution of 3-bromothiophene (32.6 g, 200 mmol) and $\text{Ni}(\text{dppp})\text{Cl}_2$ (0.542 g, 1 mmol) in ethyl ester (100 mL) at room temperature. Then the mixture was heated to reflux overnight. After being cooled to room temperature, the mixture was washed by saturated NH_4Cl aqueous solution one time, by saturated Na_2CO_3 aqueous solution two times and by water three times. The organic layer was separated and dried over anhydrous Na_2SO_4 and evaporated to dryness. The residue was distilled at reduced pressure to afford 3-hexylthiophene (4) as colorless liquid (31 g, 91%). $^1\text{H-NMR}$ (300 MHz, CDCl_3 , δ): 7.22 (dd, $J = 3.0$ Hz, 1H), 6.95–6.88 (m, 2H), 2.61 (t, $J = 7.5$ Hz, 2H), 1.70–1.50 (m, 2H), 1.40–1.20 (m, 6H), 0.90–0.83 (m, 3H).

Synthesis of 4,4'-dihexyl-2,2'-bithiophene (5)

Under the argon atmosphere, *n*-BuLi (2.5 mol/L, 13.1 mL, 32.68 mmol) was added dropwise into a mixture of 2,2,6,6-tetramethylpiperidine (TEMP, 5.03 g, 35.65 mmol) and ethyl ester (150 mL) at -78°C . The mixture was stirred at this temperature for 1 h. 3-hexylthiophene (4) (5 g, 29.71 mmol) was added drop wise to the mixture. Then the mixture was warmed to room temperature, and heated to reflux for 1 h. After cooling to -78°C , CuCl_2 (5.2 g, 38.62 mmol) was added into the mixture at once and the mixture was stirred overnight. The mixture was washed by water three times. The organic layer was separated and dried over anhydrous Na_2SO_4 and evaporated to dryness. The residue was purified by recrystallization from *n*-hexane to afford 4,4'-dihexyl-2,2'-bithiophene (5) as yellow solid (2 g, 40%). $^1\text{H-NMR}$ (300 MHz, CDCl_3 , δ): 7.00 (s, 2H), 6.79 (s, 2H), 2.59 (t, $J = 7.5$ Hz, 4H), 1.70–1.50 (m, 4H), 1.40–1.20 (m, 12H), 0.90–0.83 (m, 6H).

Synthesis of (4,4'-dihexyl-2,2'-bithiophene-5,5'-diyl)bis(tributylstannane) (6)

Into a solution of 4,4'-dihexyl-2,2'-bithiophene (5) (1.87 g, 5.6 mmol) in THF (40 mL) was added *n*-BuLi (2.5 mol/L, 5.4 mL, 13.5 mmol) at -78°C . The mixture was stirred at this temperature for 1 h, and SnBu_3Cl (4.56 g, 14 mmol) was added. The mixture was stirred at -78°C for 1 h, and warmed to room temperature for

1 h, then washed by saturated KF aqueous solution three times and by water three times. The organic phase was separated and dried over anhydrous Na_2SO_4 and evaporated to dryness. The residue was not further purified and directly used in the next step.

Synthesis of 7,7'-(4,4'-dihexyl-2,2'-bithiophene-5,5'-diyl)bis(4-bromobenzo[c][1,2,5]thiadiazole) (7)

Compound **7** was synthesized following the procedure for preparation of **3** as red crystals in a yield of 31% (1.3 g). $^1\text{H-NMR}$ (300 MHz, CDCl_3 , δ): 7.92 (d, $J = 7.5$ Hz, 2H), 7.51 (d, $J = 7.2$ Hz, 2H), 7.21 (s, 2H), 2.61 (t, $J = 7.8$ Hz, 4H), 1.80–1.50 (m, 4H), 1.40–1.20 (m, 12H), 0.85–0.70 (m, 6H). $^{13}\text{C-NMR}$ (101 MHz, CDCl_3 , δ): 153.53, 153.45, 142.86, 137.67, 131.95, 130.63, 130.14, 127.31, 126.19, 113.50, 31.51, 30.51, 29.53, 29.09, 22.50, 13.99. MALDI-TOF MS: Calcd for: $\text{C}_{32}\text{H}_{32}\text{Br}_2\text{N}_4\text{S}_4$: 760.69. Found: 760.0 $[\text{M}^+]$.

Copolymers

Synthesis of PFDBCPDT

Polymerization of PFDBCPDT was performed by Suzuki coupling reaction. 7,7'-(4,4'-Dihexyl-4H-cyclopenta[2,1-b:3,4-b']-dithiophene-2,6'-diyl)bis(4-bromobenzo[c][1,2,5]thiadiazole) (**3**) (154.5 mg, 0.2 mmol), 2,7-bis(trimethyleneboronate)-9,9-dioctylfluorene (**8**, 111.7 mg, 0.2 mmol), $\text{Pd}(\text{PPh}_3)_4$ (2 mg) and one drop Aliquat 336 were all added in the reaction bulb. Toluene (6 mL) and K_2CO_3 aqueous solution (2 mol/L, 2 mL) were added under the argon atmosphere. The solution was heated to 105 °C and stirred for 7 h. Then phenylboronic acid (0.1 mol/L, 2 mL) was added 3 h earlier before bromobenzene (0.5 mL). 5 h later, the solution was cooled down to the room temperature, and added with CHCl_3 (100 mL). The organic solution was washed by water for three times, and dried by anhydrous Na_2SO_4 . The polymer was precipitated into 200 mL methanol from a concentrated solution. After this, the precipitated solid were collected and vacuum dried overnight to get PFDBCPDT as black solid in a yield of 90% (180 mg). $^1\text{H-NMR}$ (300 MHz, CDCl_3 , δ): 8.20–8.10 (m, 2H), 8.10–7.95 (m, 6H), 7.95–7.90 (m, 2H), 7.90–7.80 (m, 2H), 2.20–2.00 (m, 8H), 1.30–0.60 (m, 52H). $M_n = 6.9$ kDa, PDI = 2.46.

Synthesis of PFDBDT

Copolymer PFDBDT was synthesized following the procedure for preparation of PFDBCPDT as red solid in a yield of 92% (182 mg). $^1\text{H-NMR}$ (300 MHz, CDCl_3 , δ): 8.20–8.10 (m, 2H), 8.10–7.95 (m, 6H), 7.95–7.90 (m, 2H), 7.90–7.80 (m, 2H), 2.30–2.00 (m, 8H), 1.30–0.60 (m, 52H). $M_n = 16.8$ kDa, PDI = 2.28.

Device Fabrication and Characterization

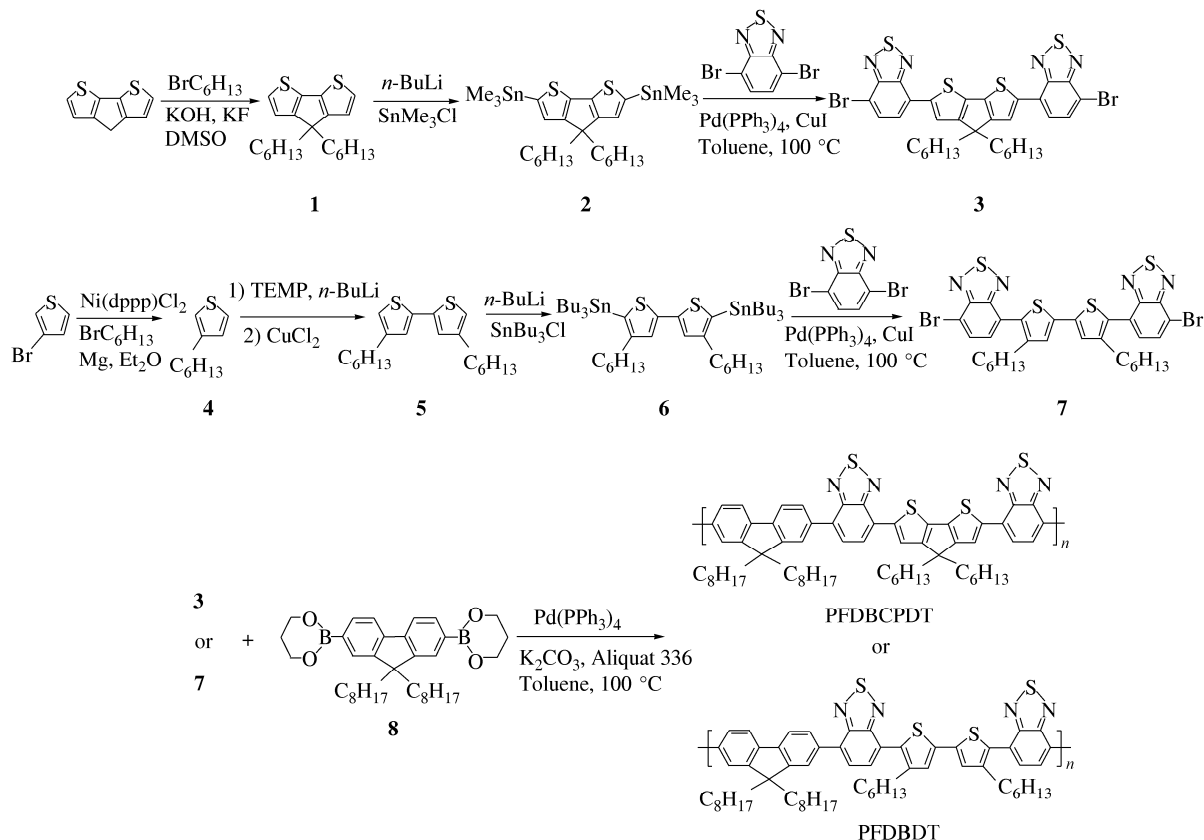
BHJ solar cell devices were fabricated with a structure of indium oxide (ITO)/poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS)/copolymer:PCBM/LiF/Al. The ITO glass was pre-cleaned and modified by a 45–50 nm PEDOT:PSS (Baytron P4083) layer which was spin-coated from a PEDOT:PSS aqueous solution on the ITO substrate, and was dried subsequently at 120 °C for 30 min. Then a chlorobenzene solution of a blend of polymer/PCBM was spin-coated on the surface of the PEDOT:PSS layer to form a photosensitive layer. The LiF/Al cathode was deposited at a vacuum level of 4×10^{-4} Pa. The thicknesses of the LiF and Al layers are 1 and 100 nm, respectively. The effective area of the unit cell is 12 mm². The current-voltage (I - V) measurement of the devices was conducted on a computer-controlled Keithley 236 Source Measure Unit. A xenon lamp (500 W) was used as the light source, and the optical power at the sample was 100 mW cm⁻². The external quantum efficiency (EQE) was measured using a Model SR830 DSP Lock-in Amplifier coupled with a SBP500 monochromator, a DSC102 data acquisition system and a Model SR540 chopper controller. The light intensity at each wavelength was calibrated with standard single-crystal Si photodiode.

RESULTS AND DISCUSSION

Synthesis and Characterization

Scheme 1 shows the synthetic route of the monomers and copolymers. Copolymer PFDBCPDT and PFDBDT were prepared *via* Suzuki polymerization. PFDBCPDT was black solid with a yield of 90% and PFDBDT turned

to be orange red solid with a yield of 92%. PFDBCPDT and PFDBDT are soluble in common solvents, such as THF, CHCl_3 and chlorobenzene. Gel permeation chromatography (GPC) analysis results exhibited that the molecular weight of PFDBCPDT and PFDBDT was 6.9 kDa and 16.8 kDa, respectively. Figure 1 gives the thermogravimetric analysis (TGA) results of PFDBCPDT and PFDBDT. Both PFDBCPDT and PFDBDT showed good thermal stability with the decomposition temperature of 356 °C and 326 °C (5% weight loss) for PFDBCPDT and PFDBDT, respectively.



Scheme 1 Synthetic route of PFDBCPDT and PFDBDT

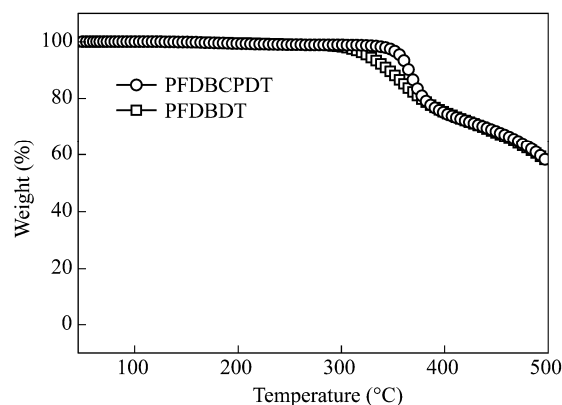


Fig. 1 TGA curves of PFDBCPDT and PFDBDT

Optical and Electrochemical Properties

As shown in Fig. 2, the optical properties of PFDBCPDT and PFDBDT were investigated in their chlorobenzene (CB) solutions (1×10^{-5} mol/L) and as thin films. PFDBCPDT exhibited absorption maximum of 602 nm in the CB solution. In thin films, absorption maximum of PFDBCPDT was red shifted by 2 nm to 604 nm. Compared with the absorption in the solution, the absorption spectra of PFDBCPDT in thin films became broader, and the absorption edge of PFDBCPDT was red shifted by 22 nm to 673 nm, suggesting good aggregation formed in the solid state^[42]. The optical band gap ($E_{g,opt}$) of PFDBCPDT determined by the onset of the absorption in solid films was 1.84 eV. On the other hand, PFDBDT showed a relatively large optical band gap of 2.20 eV. The absorption maxima of PFDBDT in CB solution and in thin films were only 476 and 478 nm, respectively. The poor absorption and large optical band gap of PFDBDT limit its light capture ability, suggesting its poor performance in solar devices.

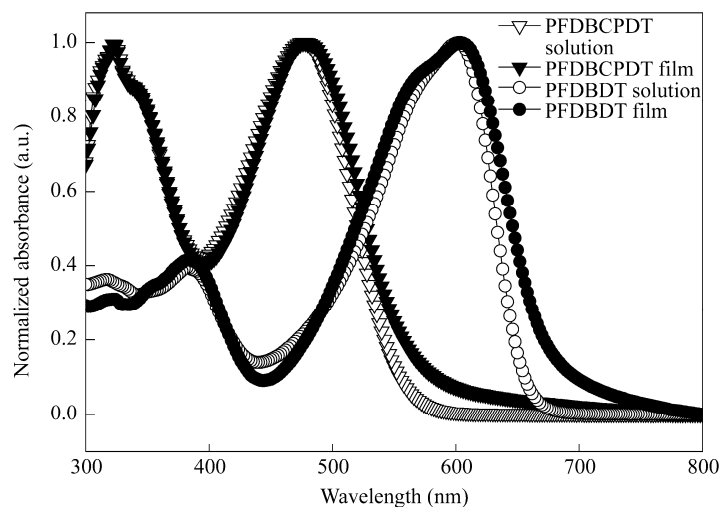


Fig. 2 Normalized UV-Vis spectra of PFDBCPDT and PFDBDT in 1×10^{-5} mol L⁻¹ chlorobenzene solution and thin films deposited on glass

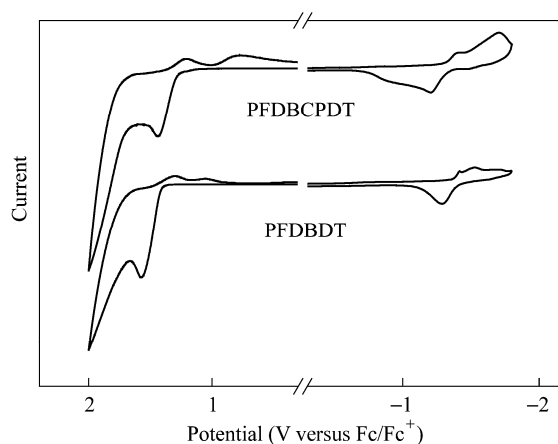


Fig. 3 Cyclic voltammogram of PFDBCPDT and PFDBDT films on a glass carbon electrode measured in 0.1 mol/L Bu₄NClO₄ acetonitrile solution at a scan rate of 50 mV s⁻¹

Table 1. Molecular weight, thermal and electrochemical properties of the copolymers

Copolymers	M_n (kDa)	PDI	T_d (°C)	E_{HOMO} (eV)	E_{LUMO} (eV)
PFDBCPDT	6.9	2.46	356	-5.69	-3.12
PFDBDT	16.8	2.28	326	-5.82	-3.04

The electrochemical properties of PFDBCPDT and PFDBDT films were given in Fig. 3 which were studied in a three-electrode electrochemical cell in 0.1 mol/L Bu₄NClO₄ acetonitrile solution and Ag/AgCl as reference electrode. The HOMO and the LUMO energy levels were determined according to the empirical formula $E_{\text{HOMO}} = -[4.8 - E_{\text{FOC}} + E_{\text{onset}}^{\text{ox}}]$ and $E_{\text{LUMO}} = -[4.8 - E_{\text{FOC}} + E_{\text{onset}}^{\text{red}}]$ ^[43]. The E_{FOC} is the half-wave potential of ferrocene (the standard). The LUMO and the HOMO levels of PFDBCPDT were determined to be -3.12 and -5.69 eV, respectively (Table 1). Compared to HOMO levels of typical CPDT-based copolymer (5.35 – 5.55 eV)^[27–34], PFDBCPDT exhibited a lower HOMO level, suggesting a relatively high V_{oc} in the solar devices. Moreover, the HOMO level of PFDBDT (-5.82 eV) was much lower than that of PFDBCPDT, while the two LUMO levels of PFDBDT and PFDBCPDT were very close (-3.04 eV for PFDBDT), which is consistent with the large band gap of PFDBDT.

Photovoltaic Properties

A device structure of ITO/PEDOT:PSS/copolymer:PC₆₁BM/LiF/Al was used to investigate the photovoltaic properties of PFDBCPDT. The active layer was made by spin coating the CB solutions of copolymers and PC₆₁BM. Current density-voltage curves of PFDBCPDT with different PC₆₁BM contents are shown in Fig. 4. All device results were summarized in Table 2. As we expected, the solar devices of PFDBCPDT with PC₆₁BM showed V_{oc} of 0.83 – 0.87 V, which were relatively high for CPDT-based copolymers. In the meanwhile, the device results also exhibited rather large J_{sc} (> 6 mA cm⁻²) at the copolymer:PCBM blend ratio of $1:2$ – $1:3$. The FF of devices remained similar (0.43 – 0.46) at different copolymer:PCBM blend ratio of $1:2$ – $1:4$. The best device performance of PFDBCPDT and PC₆₁BM was realized at blend ratio of $1:3$ with PCE of 2.59% . While for PFDBDT, a high V_{oc} of 0.86 – 0.95 V was observed. However, J_{sc} and FF of the devices were below 2 mA cm⁻² and 0.30 , respectively, resulting in very poor photovoltaic performance (PCE $< 0.5\%$). These results also demonstrated the importance of the CPDT donor structure.

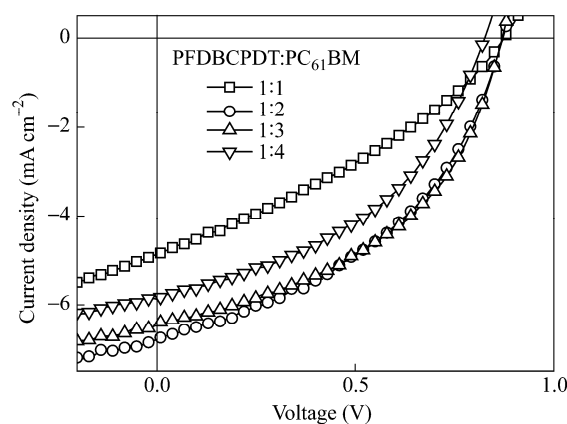


Fig. 4 Current density-voltage characteristics of PFDBCPDT:PC₆₁BM with blend ratio of $1:1$, $1:2$, $1:3$ and $1:4$ under illumination of AM 1.5 at 100 mW cm⁻²

Table 2. Photovoltaic results of PSCs based on PFDBCPDT:PC₆₁BM blends

	DIO	Blend ratio	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF	PCE (%)
PFDBCPDT:PC ₆₁ BM		1:1	0.87	4.88	0.33	1.41
		1:2	0.87	6.79	0.43	2.55
		1:3	0.87	6.46	0.46	2.59
		1:4	0.83	5.87	0.43	2.12
	0.5	1:3	0.87	7.65	0.46	3.06
	1.0	1:3	0.86	6.92	0.43	2.54
	2.0	1:3	0.87	6.91	0.41	2.48

It has been testified that addition of 1,8-diiodooctane (DIO) could improve the device performance by modifying the blend film morphology of CPDT-copolymers and PCBM^[44, 45]. To investigate the DIO effect on the device performance of PFDBCPDT, PSC devices fabricated by the solution of PFDBCPDT:PC₆₁BM (1:3) with different DIO contents were studied (as shown in Fig. 5). According to Table 2, V_{oc} of PSC devices remained around 0.87 V, while J_{sc} increased to *ca.* 7 mA cm⁻² upon the addition of DIO. At 0.5 vol% DIO, both J_{sc} and FF reached the highest results of 7.65 mA cm⁻² and 0.46, respectively, which declined upon the further increasing of DIO content. According to Fig. 6, PFDBCPDT with 0.5 vol% DIO yield IPCE up to 45% at 604 nm, which was slightly higher than that without DIO. Thus, the optimum photovoltaic performance with the maximum PCE of 3.06% was obtained from the blend solution containing 0.5 vol% DIO.

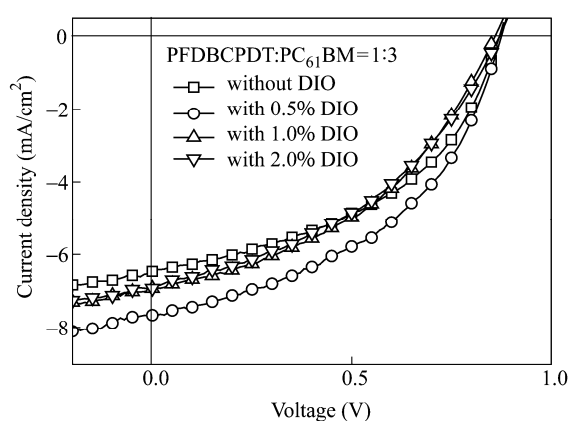


Fig. 5 Current density-voltage characteristics of PFDBCPDT:PC₆₁BM with different DIO contents

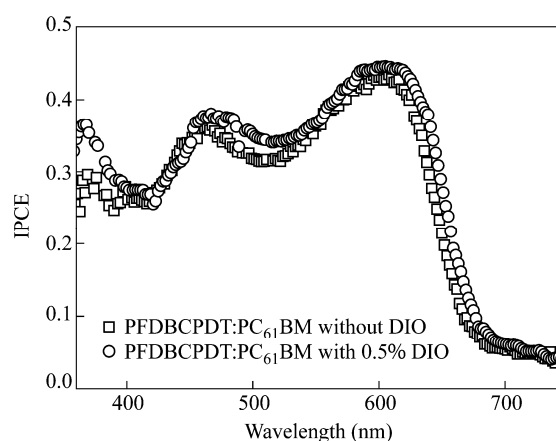


Fig. 6 IPCE spectra of PFDBCPDT:PC₆₁BM (1:3) without DIO and with 0.5 vol% DIO

To investigate the device performance enhancement brought by DIO, transmission electron microscopy (TEM) was used to study the blend film morphology of PFDBCPDT:PC₆₁BM without and with 0.5 vol% DIO (Fig. 7). As shown in Fig. 7(a), large fibrillar structure could be found obviously in the blend film of PFDBCPDT:PC₆₁BM without DIO. Compared with the blend films without DIO, much smaller fibrillar structure in the blend film emerged upon the addition of the small amount DIO (Fig. 7b), suggesting the formation of better nanoscale phase separation. It is believed that too large or too small phase separation will be detrimental to the performance of PSCs^[44, 45]. According to device performance, the introduction of DIO can improve the blend film morphology by increasing interfacial area between PFDBCPDT and PC₆₁BM, resulting in the larger J_{sc} .

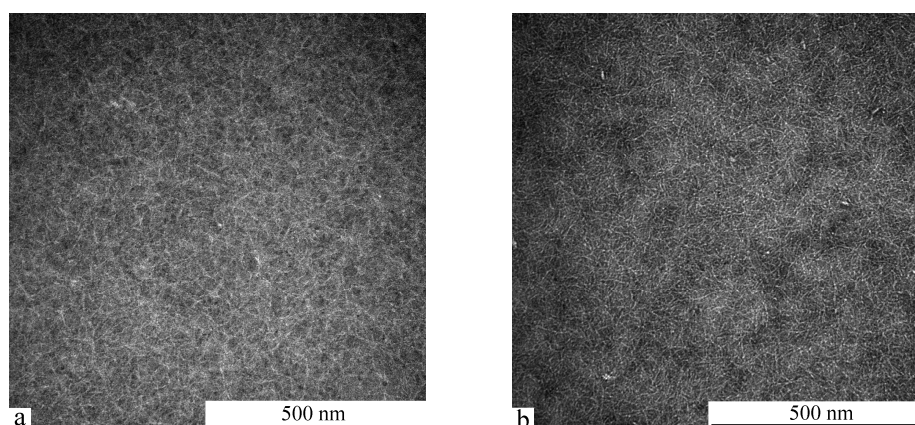


Fig. 7 TEM images of (a) PFDBCPDT:PC₆₁BM (1:3) without DIO and (b) PFDBCPDT:PC₆₁BM (1:3) with 0.5 vol% DIO films

CONCLUSIONS

In summary, we have designed and synthesized a new cyclopentadithiophene based D-A copolymer (PFDBCPDT) with the fluorene unit as an additional donor unit and benzo-2,1,3-thiadiazole as the acceptor unit for polymer solar cells. PFDBCPDT showed a small optical band gap (1.84 eV) and a low lying HOMO level of -5.69 eV, leading to a relatively high V_{oc} (ca. 0.87 V) for CPDT-based copolymers. The devices of PFDBCPDT and PC₆₁BM with 0.5 vol% DIO can achieve the PCE of 3.06% with V_{oc} of 0.87 eV, J_{sc} of 7.65 mA cm⁻² and FF of 0.46. While for the reference polymer PFDBDT, only poor photovoltaic performance was observed.

REFERENCES

- 1 Thompson, B.C. and Fréchet, J.M., *Angew. Chem. Int. Ed.*, 2008, 47: 58
- 2 Heremans, P., Cheyns, D. and Rand, B., *Acc. Chem. Res.*, 2009, 42: 1740
- 3 Peet, J., Heeger, A.J. and Bazan, G.C., *Acc. Chem. Res.*, 2009, 42: 1700
- 4 Helgesen, M., Søndergaard, R. and Krebs, F.C., *J. Mater. Chem.*, 2010, 20: 36
- 5 Nguyen, L.H., Hoppe, H., Erb, T., Guenes, S., Gobsch, G. and Sariciftci, N.S., *Adv. Func. Mater.*, 2007, 17: 1071
- 6 Shi, C., Yao, Y., Yang, Y. and Pei, Q., *J. Am. Chem. Soc.*, 2006, 128: 8980
- 7 Chen, J. and Cao, Y., *Acc. Chem. Res.*, 2009, 42: 1709
- 8 Cheng, Y., Yang, S. and Hsu, C., *Chem. Rev.*, 2009, 109: 5868
- 9 Beaujuge, P.M., Subbiah, J., Choudhury, K.R., Ellinger, S., McCarley, T.D., So, F. and Reynolds, J.R., *Chem. Mater.*, 2010, 22: 2093
- 10 Li, S., He, Z., Yu, J., Chen, S., Zhong, A., Tang, R., Wu, H., Qin, J. and Li, Z., *J. Mater. Chem.*, 2012, 22: 12523
- 11 Wang, M., Hu, X., Liu, P., Li, W., Gong, X., Huang, F. and Cao, Y., *J. Am. Chem. Soc.*, 2011, 133: 9638
- 12 Duan, R., Ye, L., Guo, X., Huang, Y., Wang, P., Zhang, S., Zhang, J., Huo, L. and Hou, J., *Macromolecules*, 2012, 45: 3032
- 13 Liang, Y., Xu, Z., Xia, J., Tsai, S. T., Wu, Y., Li, G., Ray, C. and Yu, L., *Adv. Mater.*, 2010, 22: E135
- 14 Chu, T.Y., Lu, J., Beaupre, S., Zhang, Y., Pouliot, J.R., Wakim, S., Zhou, J., Leclerc, M., Li, Z., Ding, J. and Tao, Y., *J. Am. Chem. Soc.*, 2011, 133: 4250
- 15 Price, S.C., Stuart, A.C., Yang, L., Zhou, H. and You, W., *J. Am. Chem. Soc.*, 2011, 133: 4625
- 16 Park, S.H., Roy, A., Beaupre, S., Cho, S., Coates, N., Moon, J.S., Moses, D., Leclerc, M., Lee, K. and Heeger, A.J., *Nat. Photon.*, 2009, 3: 297
- 17 Patil, A.V., Lee, W.H., Lee, E., Kim, K., Kang, I.N. and Lee, S.H., *Macromolecules*, 2011, 44: 1238
- 18 Wang, E., Ma, Z., Zhang, Z., Henriksson, P., Inganäs, O., Zhang, F. and Andersson, M.R., *Chem. Comm.*, 2011, 47: 4908
- 19 Bijleveld, J.C., Verstrijden, R.A.M., Wienk, M.M., Janssen, R.A.J., *J. Mater. Chem.*, 2011, 21: 9224
- 20 Bronstein, H., Chen, Z., Ashraf, R.S., Zhang, W., Du, J., Durrant, J.R., Tuladhar, P.S., Song, K., Watkins, S.E., Geerts, Y., Wienk, M.M., Janssen, R.A.J., Anthopoulos, T., Sirringhaus, H., Heeney, M. and McCulloch, I., *J. Am. Chem. Soc.*, 2011, 133: 3272
- 21 Zhang, Y., Zou, J., Yip, H.L., Chen, K.S., Zeigler, D.F., Sun, Y. and Jen, A.K.Y., *Chem. Mater.*, 2011, 23: 2289
- 22 Zhang, Y., Zou, J., Yip, H.L., Chen, K.S., Zeigler, D.F., Sun, Y. and Jen, A.K.Y., *Macromolecules*, 2011, 44: 4752
- 23 Yue, W., Zhao, Y., Tian, H., Song, D., Xie, Z., Yan, D., Geng, Y. and Wang, F., *Macromolecules*, 2009, 42: 6510
- 24 Wang, Z., Meng, K.G., Zhang, W., Yang, X.J., Deng, S.W. and Li, Y., *Chinese J. Polym. Sci.*, 2010, 28(6): 931
- 25 Yang, S., Zhang, W., Shen, X.X., Liu, Y., Du, X.Y., Chen, S., Xiao, Z., Yang, Z.Y., Zuo, Q.Q. and Ding, L.M., *Acta Polym. Sin. (in Chinese)*, 2012, (8): 838
- 26 Mühlbacher, D., Scharber, M., Morana, M., Zhu, Z., Waller, D., Gaudiana, R. and Brabec, C., *Adv. Mater.*, 2006, 18: 2884

- 27 Zhu, Z., Waller, D., Gaudiana, R., Morana, M., Muhlbacher, D., Scharber, M. and Brabec, C., *Macromolecules*, 2007, 40: 1981
- 28 Moule', A., Tsami, A., Bünnagel, T., Forster, M., Kronenberg, N., Scharber, M., Koppe, M., Morana, M., Brabec, C., Meerholz, K. and Scherf, U., *Chem. Mater.*, 2008, 20: 4045
- 29 Xiao, S., Zhou, H. and You, W., *Macromolecules*, 2008, 41: 5688
- 30 Hou, J., Chen, T., Zhang, S., Chen, H. and Yang, Y., *J. Phys. Chem. C*, 2009, 113: 1601
- 31 Helgesen, M. and Krebs, F., *Macromolecules*, 2010, 43: 1253
- 32 Chen, G., Chiang, C., Kekuda, D., Lan, S., Chu, C. and Wei, K., *J. Polym. Sci. Part A: Polym. Chem.*, 2010, 48: 1669
- 33 Jung, I., Yu, J., Jeong, E., Kim, J., Kwon, S., Kong, H., Lee, K., Woo, H. and Shim, H., *Chem. Eur. J.*, 2010, 16: 3743
- 34 Li, K., Huang, J., Hsu, Y., Huang, P., Chu, C., Lin, J., Ho, K., Wei, K. and Lin, H.C., *Macromolecules*, 2009, 42: 3681
- 35 Bijleveld, J., Shahid, M., Gilot, J., Wienk, M. and Janssen, R., *Adv. Funct. Mater.*, 2009, 19: 3262
- 36 Li, Z., Ding, J., Song, N., Lu, J. and Tao, Y., *J. Am. Chem. Soc.*, 2010, 132: 13160
- 37 Li, Z., Ding, J., Song, N., Du, X., Zhou, J., Lu, J. and Tao, Y., *Chem. Mater.*, 2011, 23: 1977
- 38 Albrecht, S., Janietz, S., Schindler, W., Frisch, J., Kurpiers, J., Kniepert, J., Inal, S., Pingel, P., Fostiropoulos, K., Koch, N. and Neher, D., *J. Am. Chem. Soc.*, 2012, 134: 14932
- 39 Blouin, N., Michaud, A., Gendron, D., Wakim, S., Blair, E., Neagu-Plesu, R., Belletete, M., Durocher, G., Tao, Y. and Leclerc, M., *J. Am. Chem. Soc.*, 2008, 130: 732
- 40 Song, H.Y., Tong, H., Xie, Z.Y., Wang, L.X. and Wang, F.S., *Polymer*, 2012, 53: 5103
- 41 Liu, J., Zhou, Q.G., Cheng, Y.X., Geng, Y.H., Wang, L.X., Ma, D.G., Jing, X.B. and Wang, F.S., *Adv. Funct. Mater.*, 2006, 16: 957
- 42 Zhou H.X., Yang L.Q., Xiao S.Q., Liu S.B. and You W., *Macromolecules*, 2010, 43: 811
- 43 Jiang, Z., Zhang, W., Yao, H., Yang, C., Cao, Y., Qin, J., Yu, G. and Liu, Y., *J. Polym. Sci., Part A: Polym. Chem.*, 2009, 47: 3651
- 44 Peet, J., Kim, J., Coates, N., Ma, W., Moses, D., Heeger, A. and Bazan, G., *Nat. Mater.*, 2007, 6: 497
- 45 Lee, J., Ma, W., Brabec, C., Yuen, J., Moon, J., Kim, J., Lee, K., Bazan, G. and Heeger, A., *J. Am. Chem. Soc.*, 2008, 130: 3619