

Synthesis of a Terpolymer Containing Fluorene, Side Chain Conjugated Thiophene and Benzothiadiazole and Its Applications in Photovoltaic Devices

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ABSTRACT: A terpolymer (POTVTh-8FO-DBT) containing fluorene, side chain conjugated thiophene and 4,7-dithienyl-2,1,3-benzothiadiazole was synthesized by palladium-catalyzed Suzuki coupling method. The polymer is soluble in common organic solvents. The thermal, absorption, and electrochemical properties of the polymer were examined. Photovoltaic properties of POTVTh-8FO-DBT were studied by fabricating the polymer solar cells (PSCs) based on POTVTh-8FO-DBT as donor and [6,6]-phenyl-C61-butyric acid methyl ester (PC₆₁BM) as acceptor. With the weight ratio of POTVTh-8FO-DBT : PC₆₁BM of 1 : 1 and the active layer thickness of 80 nm, the power conversion efficiency (PCE) of the device reached 0.47% with $V_{oc} = 0.61$ V, $J_{sc} = 1.61$ mA/cm², and filled factor (FF) = 0.49 under the illumination of AM 1.5, 100 mW/cm². The results indicated that this polymer was promising donor candidates in the application of PSCs. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: copolymers; optical and photovoltaic applications; synthesis and processing

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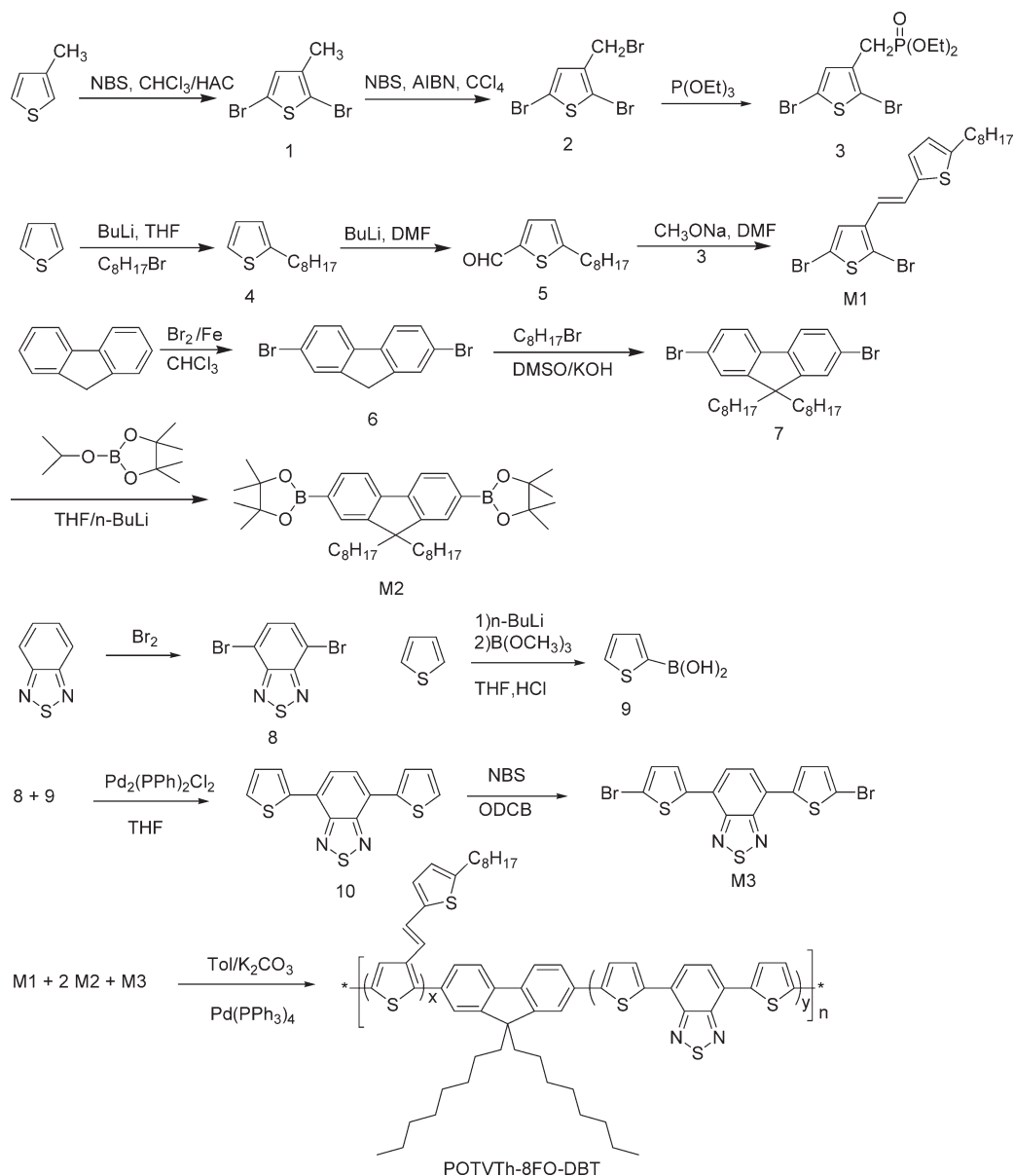
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INTRODUCTION

In recent years, polymer solar cells (PSCs) have attracted great attention as potential large-area, flexible, and low-cost solar cells.^{1–3} Because the discovery of the ultrafast photo-induced charge transfer between conjugated polymers and fullerene in 1995 by Heeger and co-worker, the power conversion efficiency (PCE) of the PSCs has improved obviously.⁴ So far, the PCE of the device based on these conjugated polymers and fullerene derivatives had exceeded 8.0%.^{5,6} To further improve the PCE of PSCs, most of the efforts have been devoted to design and synthesis of novel conjugated polymers with broad absorption in visible region, suitable lowest unoccupied molecular orbital (LUMO), and highest occupied molecular orbital (HOMO) energy levels. Donor-acceptor (D-A) copolymer combined electron-rich (donor) and electron-deficient (acceptor) moiety in the main chain is an efficient approach to obtain good performance for their tunable energy levels and relative narrow bandgap owing to the intermolecular charge transfer from the donor to the acceptor. Several D-A copolymers had already been investigated and good photovoltaic properties had been achieved.^{7–15}

Among various D-A copolymers, polymer based on fluorene as donor and 4,7-dithienyl-2,1,3-benzothiadiazole (DBT) as acceptor have attracted much attention in the PSC field and promising photovoltaic properties have been achieved for this type of polymers.^{16–18} In addition, an alternative way to enhance the absorption property is to increase the conjugated length of the polymer. Side chain conjugated polythiophenes derivatives with two-dimensional conjugated structure were designed and synthesized, which exhibited a broader response range to the solar irradiation spectrum resulting in a 38% improvement of PCE in comparison with poly(3-hexylthiophene) (P3HT).¹⁹ However, D-A type conjugated polymer containing fluorene, 4,7-dithienyl-2,1,3 - benzothiadiazole and side-conjugated thiophene units were seldom studied.²⁰

In this article, a terpolymer containing side chain conjugated thiophene ((5-octyl-thienylene-vinyl)-thiophene), 9,9'-dioctyl-fluorene and DBT units (POTVTh-8FO-DBT) was synthesized. The polymer possesses a low electrochemical bandgap of 1.85 eV and exhibits a PCE of 0.47% when blended with [6,6]-



Scheme 1. Synthetic route of POTVTh-8FO-DBT.

phenyl-C61-butyrac acid methyl ester (PC₆₁BM) with a weight ratio of 1 : 1 under the AM 1.5, 100 mW/cm² condition.

MATERIALS AND METHODS

Materials and Synthesis

All starting materials, unless specified otherwise, were purchased from Aldrich or Alfa Aesar and used without further purification. Some solvents were distilled before use, such as THF, ether. The 2,5-dibromo-3-methylthiophene (**1**), 2,5-dibromo-3-bromomethylthiophene (**2**), (2,5-dibromo-thiophene-3-ylmethyl)phosphonic acid diethyl ester (**3**), 2-octylthiophene (**4**), 5-octylthiophene-2-carbaldehyde (**5**), 2,7-dibromofluorene (**6**), 2,7-dibromo-9,9 - dioctylfluorene (**7**), and 4,7-dibromo-2,1,3-benzothiadiazole (**8**) were synthesized according to the procedures reported in the

literature.^{21–24} The synthetic routes of monomers and the polymer are shown in Scheme 1.

2,5-Dibromo-3-(5-Octyl-Thienylene-Vinyl)-Thiophene (M1)

Compound **5** (6.7 g, 0.03 mol) was dissolved in 30 ml DMF. Under an ice-water bath, NaOCH₃ (3 g in 20 ml DMF) was added into the solution. Then compound **3** (11.8 g, 0.03 mol) was added dropwise to the solution. The reaction was remained at 0°C for 2 h, and then the solution was poured into cold water and extracted with ether. The combined organic fractions were washed with water and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure. Purification was carried out via silica gel column chromatography, using hexane as the eluent. Compound **M1** was obtained as pale yellow oil (7.29 g, yield:52.6%). ¹H-NMR (500 MHz, CDCl₃,

ppm): δ 7.15(s, 2 H); 6.95(d,1 H); 6.89(d, 1 H); 6.70(s, 1 H), 6.69(d,1 H), 6.67(d,1 H), 2.80(t,2 H); 1.71(m,2 H); 1.29–1.4(m,8 H); 0.98(t,3 H).

2,7-bis(4,4,5,5-Tetramethyl-1,3,2-Dioxaborolan-2-yl)-9,9-Diethylfluorene(M2). Compound 7 (5 g, 9.1 mmol) was dissolved in 70 ml THF in a flask protected by nitrogen and cooled down to -78°C by a liquid nitrogen/ethanol bath. Then 8.7 ml (19.1 mmol) of *n*-butyllithium (2.2 M in hexane) was added by syringe. The mixture was warmed to 0°C for 15 min and cooled again at -78°C for 15 min. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4.2 g, 21.7 mmol, 96%) was added rapidly to the solution and the resulting mixture was warmed to room temperature and stirred for 24 h. The mixture was poured into water and extracted with ether. The organic extracts were washed with brine and dried over anhydrous magnesium sulfate. The solvent was removed by rotary evaporation, and the residue was purified by recrystallization in THF/methanol(ca. 1 : 1) to obtain M2 as a white solid (3.1 g, yield:53%). $^1\text{H-NMR}$ (500 MHz, CDCl_3 , ppm): δ 7.84 (d, 2 H);7.78 (s, 2 H);7.75 (d, 2 H.); 2.03 (m, 4 H); 1.43(s, 24 H); 1.26–1.04 (m, 20 H); 0.83 (t, 6 H); 0.58 (m, 4 H).

2-Thiopheneboronic Acid(9). In a 250 ml three-necked flask, thiophene (11.7 g, 139.3 mmol) and 90 ml THF were added. The solution was cooled to -35°C and 57.4 ml (126.3 mmol) of *n*-butyllithium (2.2 M in hexane) was added dropwise to the solution. The reaction was remained at -35°C for 3 h and then trimethyl borate (14.4 g, 138.5 mmol) was added dropwise to the solution. The reaction was remained at -35°C for 1 h. The reactant was warmed to room temperature and quenched by the addition of dilute hydrochloric acid. This mixture was extracted with ether and was washed with water and dried over anhydrous magnesium sulfate. Removal of solvent gave a crude product, which was purified by crystallization in water/petroleum ether to obtain compound 9 as a white solid (7.4 g, yield: 45.7%).

4,7-Dithienyl-2,1,3-Benzothiadiazole(10). In a 250 ml three-necked flask, compound 9 (7.8 g, 60.9 mmol), compound 8 (6.6 g,22.4 mmol), 62 mg of PPh_3 , 80 ml THF, and 49 ml 2 mol/L Na_2CO_3 solution were added. The flask was purged with nitrogen for 30 min and then 25.6 mg of palladium acetate was added. The resulting solution was heated to reflux for 5 h. Then the reactant was cooled to room temperature and added into toluene. The organic layer was washed with water and dried over anhydrous magnesium sulfate. Removal of solvent gave a crude product, which was purified by recrystallization in toluene/ethanol (ca. 1 : 2) to obtain compound 10 as a red solid (6.2 g, yield:92.3%). $^1\text{H-NMR}$ (500 MHz, CDCl_3 , ppm): δ 8.12–8.13 (d, 2 H); 7.88 (s, 2 H);7.46–7.47(d, 2 H);7.21–7.26(m,2 H).

4,7-di(2'-Bromothien-5'-yl)-2,1,3-Benzothiadiazole(M3). In a 250 ml three-necked flask, compound 11 (5.5 g,18.3 mmol), NBS (6.24 g, 35.1 mmol), and 11 ml *o*-dichlorobenzene were added. The reaction mixture was heated to 55°C . After 3 h at 55°C , the reaction mixture was heated to 150°C and was cooled to room temperature. The resultant compound was collected by filtration. The solid was washed with *o*-dichlorobenzene and ethanol/water (ca. 1 : 1). The crude product was purified by recrystallization in *o*-dichlorobenzene to obtain M3 as an orange solid (6.9 g, yield:

85.8%). $^1\text{H-NMR}$ (500 MHz, CDCl_3 , ppm): δ 7.81 (d, 2 H); 7.79 (s, 2 H); 7.16 (d, 2 H).

Polymer Synthesis

In a 50 ml three-necked flask, M2 (0.65 g, 1 mmol), M1 (0.23 g, 0.5 mmol), M3 (0.229 g,0.5 mmol), 4 ml 2 mol/L K_2CO_3 solution, 46.4 mg Aliquant 336, and 20 ml degassed toluene were added. The flask was purged with nitrogen for 30 min and then 22 mg of $\text{Pd}(\text{PPh}_3)_4$ was added. After another purged with nitrogen for 30 min, the resulting solution was heated to reflux for 24 h. Then the reactant was cooled to room temperature and precipitated into methanol. The resultant polymer was collected by filtration, dried, and extracted successively with methanol, hexanes, and chloroform using a Soxhlet apparatus. The chloroform fraction was evaporated under reduced pressure and then precipitated with methanol. After filtrated and dried, 0.28 g of the polymer was given, yield 41%. The molecular weight was decided by GPC as $M_n = 32,536$, $M_w = 85,895$, polydispersity index (PDI) = 2.64. Elemental analyses, found C:77.73;H: 2.29;N: 2.61;S: 12.31. From the date of elemental analysis, it can be decided that the conjugated polymer containing 36% unit of side chain conjugated thiophene and 64% unit of benzothiadiazole.

Characterization

$^1\text{H-NMR}$ spectra was measured on a Bruker Advance 500 spectrometer at 500 MHz with deuterated CDCl_3 as solvent, and the chemical shifts were reported as δ values (ppm) relative to an internal tetramethylsilane (TMS) standard. Elemental analysis was carried out by a Vario EL III elemental analyzer. The molecular weight and PDI of the polymer were determined by PL-GPC50 with THF as eluent and polystyrene as standard. Differential scanning calorimetry (DSC) measurement was performed on a TA DSC Q20 instrument at a heating rate of $10^{\circ}\text{C}/\text{min}$ under nitrogen. Thermogravimetric analysis (TGA) was performed on Hi-Res TGA 2950, with a heating rate of $10^{\circ}\text{C}/\text{min}$ under nitrogen. Absorption spectra were recorded on a Unico UV-2102PCS spectrophotometer. The electrochemical cyclic voltammetry (CV) was carried out on a CHI 660D electrochemical workstation with a platinum disk coated with the polymer film, platinum wire, and Ag^+/AgCl electrode as working electrode, counter electrode, and reference electrode respectively, with a solution of 0.1 mol/L tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in acetonitrile solution with a scan rate as 50 mV/s.

Fabrication and Characterization of PSCs

The PSCs were fabricated in the traditional sandwich structure with indium tin oxide (ITO) glass as an anode, Al as a cathode and the blend film of POTVTh-8FO-DBT : PC_{61}BM as a photosensitive layer. A thin layer of PEDOT : PSS was spin-coated from a PEDOT:PSS aqueous solution (Bayer) on a pre-cleaned and modified ITO glass, giving the thickness of the PEDOT : PSS layer was about 40 nm. The photosensitive blend layer was prepared by spin-coating a blend solution of the polymer and PC_{61}BM (1 : 1 w/w, *o*-dichlorobenzene solution, 30 mg/ml) on top the of ITO/PEDOT : PSS electrode. The thickness of the active layer is about 80 nm. Finally, 0.5 nm thick of LiF layer and 85 nm thick of Al layer were evaporated in sequence under the vacuum of 3×10^{-6} Torr. The active area of the device was measured to be 0.1 cm^2 .

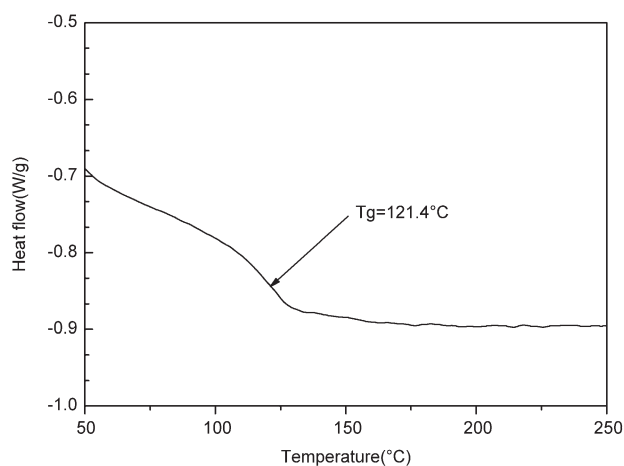


Figure 1. DSC plot of POTVTh-8FO-DBT with a heating rate of 10°C/min in nitrogen.

This experiment was carried out in a nitrogen-filled glove box. The current density-voltage (J-V) curves were obtained using a Keithley 2611 source-measure unit. The photocurrent was measured with a solar simulator (Newport Thermal Oriol 6911 300 W, 4 in.×4 in.beam size) with AM 1.5 G illumination at 100 mW/cm². A calibrated mono silicon diode is used as a reference.

RESULTS AND DISCUSSION

Thermal Properties

The thermal properties of POTVTh-8FO-DBT were determined by differential scanning calorimetry (DSC) and TGA. As shown in Figure 1, the glass transition temperature (T_g) of POTVTh-8FO-DBT was observed to be 121.4°C. Figure 2 shows the TGA plots of POTVTh-8FO-DBT. The polymer possess excellent thermal stability with decomposition temperatures (T_d) (5% weight loss) over 451°C. The thermal stability is adequate for the application of the polymer in polymer optoelectronic devices.

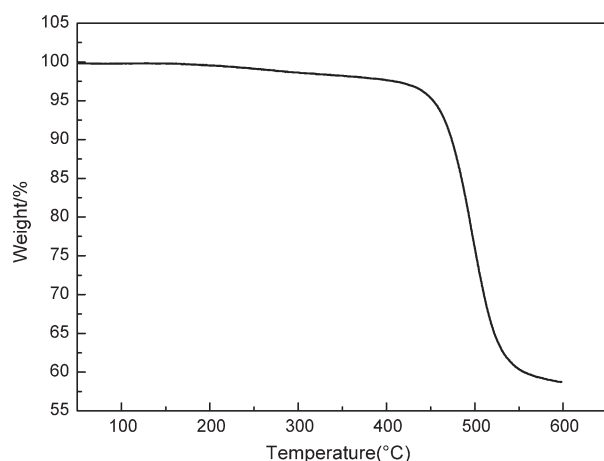


Figure 2. TGA plot of POTVTh-8FO-DBT with a heating rate of 10°C/min in nitrogen.

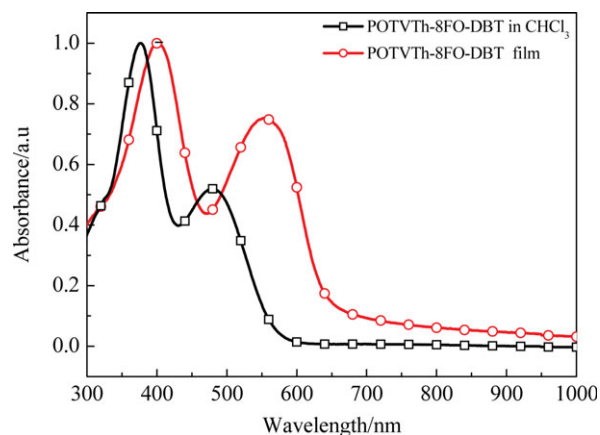


Figure 3. Absorption spectra of POTVTh-8FO-DBT. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Absorption Properties

A critical factor for improving the efficiency of photovoltaic devices is to match the absorption spectra of the photovoltaic materials with the solar spectrum with a maximum photon flux around 700 nm. Thus, conjugated polymers with broad absorption band, in addition to narrow bandgap, are desirable for PSCs. Figure 3 shows the absorption spectra of POTVTh-8FO-DBT solution in chloroform and film on quartz plate. There are two absorption peaks both in chloroform solution and in film. The absorption peaks of POTVTh-8FO-DBT are located at 480 nm in chloroform and 553 nm in film, respectively. The absorption peak of the film is red-shifted 73 nm in compared with that in solution, which can be attributed to the aggregation of the polymer chains in the solid state. The absorption edge of POTVTh-8FO-DBT film is at about 651 nm. The optical bandgap (E_g^{opt}) of POTVTh-8FO-DBT is 1.91 eV, which was calculated by the formula [$E_g^{\text{opt}} = 1240/\lambda_{\text{maxonse}}$ (eV)].

Electrochemical Properties

The electrochemical property is one of the most important properties of conjugated polymers, which was studied by CV.

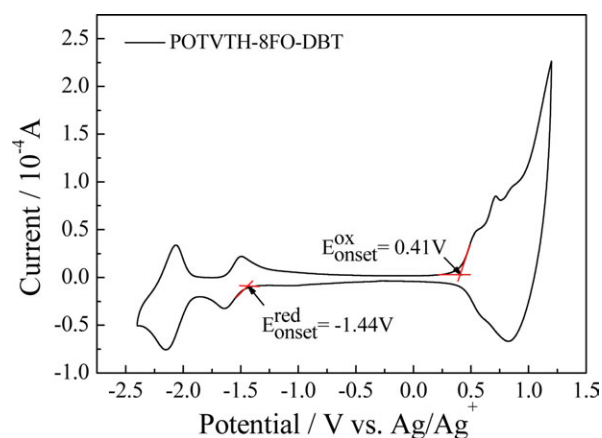


Figure 4. CV of POTVTh-8FO-DBT film on Pt electrode in 0.1 mol/L Bu₄NPF₆-CH₃CN solution at a scan rate of 50 mV/s. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. Electrochemical Parameters of P3HT and POTVTh-8FO-DBT

Polymer	E_{ox} (V)	E_{red} (V)	E_{HOMO} (eV)	E_{LUMO} (eV)	E_g^{elec} (eV)	E_g^{opt} (eV)
P3HT ²⁶	0.12	-2.13	-4.84	-2.59	2.25	1.91
POTVTh-8FO-DBT	0.41	-1.44	-5.13	-3.28	1.85	1.91

Figure 4 shows the CV of POTVTh-8FO-DBT film on Pt electrode. From the onset oxidation potential ($\varphi_{ox} = 0.41$ V) and the onset reduction potential ($\varphi_{red} = -1.44$ V) of the polymer, the HOMO and the LUMO levels were calculated according to equations to be -5.13 eV and -3.28 eV, respectively. The calculating equations are as follows²⁵:

$$E_{HOMO} = -e(\varphi_{ox} + 4.72) \text{ (eV)};$$

$$E_{LUMO} = -e(\varphi_{red} + 4.72) \text{ (eV)};$$

$$E_g^{ec} = e(\varphi_{ox} - \varphi_{red}) \text{ (eV)}$$

Table I shows the electrochemical parameters of P3HT and POTVTh-8FO-DBT. Figure 5 shows the energy levels of the P3HT, the polymer, and PC₆₁BM, respectively. According to Table I and Figure 5, the HOMO energy level of POTVTh-8FO-DBT (-5.13 eV) was lower than that of P3HT (-4.84 eV).²⁶ The relative lower HOMO energy level of the polymer is desirable for obtaining high open-circuit voltage when used in PSCs. In addition, the LUMO energy level was calculated as -3.28 eV, which was high enough to match the LUMO energy level of PC₆₁BM (-3.91 eV)²⁷ for efficient charge transfer and separation at the interface between the donor and acceptor.

Photovoltaic Properties

To investigate the photovoltaic performance of the POTVTh-8FO-DBT, PSCs with a structure of ITO/PEDOT : PSS/POTVTh-8FO-DBT : PC₆₁BM/LiF/Al was fabricated. Figure 6 shows current density–voltage curve of the device with the structure of ITO/PEDOT : PSS/ POTVTh-8FO-DBT : PC₆₁BM (1 : 1, w/w)/LiF/Al under illumination of simulated AM 1.5 at

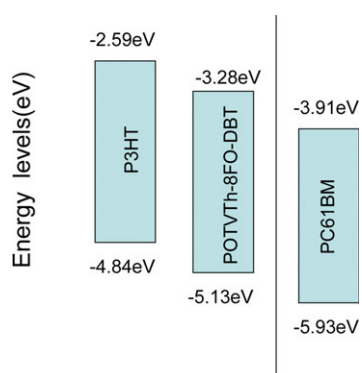


Figure 5. The energy levels of the P3HT, POTVTh-8FO-DBT, and PC₆₁BM. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

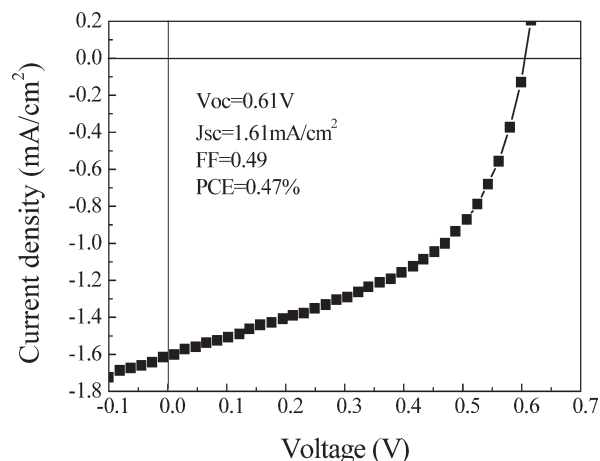


Figure 6. I–V curve of the PSCs based on POTVTh-8FO-DBT and PC₆₁BM (1 : 1, by weight) under AM1.5 G, 100 mW/cm².

100 mW/cm². The PSCs device exhibited the performance with V_{oc} of 0.61 V, J_{sc} of 1.61 mA/cm², filled factor (FF) of 0.49, and a PCE of 0.47%. In addition, it is found that the V_{oc} of POTVTh-8FO-DBT-based PSCs is only 0.61 V, which is lower than expected (about 0.90 eV estimated by the difference between the HOMO of the polymer and the LUMO of PC₆₁BM), indicated bad charge transport properties, as revealed also in the low FF.

Based on the above experimental results, it is revealed that the novel terpolymer POTVTh-8FO-DBT based on fluorene, side chain conjugated thiophene, and DBT showed promise as organic photovoltaic materials. However, more work is needed to do, such as prepare high quality polymer with good ratio of donor and acceptor in main chain, optimize the solar cell structure (for example, blend ratio, film thickness, or electrode materials), processing conditions (for example, thermal or solvent annealing), or the surface morphology of the active layer so as to substantially improve the solar cell performance.²⁸

CONCLUSION

A novel terpolymer (POTVTh-8FO-DBT) based on fluorene, side chain conjugated thiophene, and DBT was synthesized by palladium-catalyzed Suzuki coupling method. POTVTh-8FO-DBT shows high molecular weight and good thermal stability. The polymer exhibits strong absorption in the visible with a band gap of 1.91 eV. PSC was fabricated based on the blend of the polymer and PC₆₁BM, V_{oc} of 0.61 V, J_{sc} of 1.61 mA/cm², FF of 0.49, and PCE of 0.47% were achieved under AM 1.5, 100 mW/cm² using polymer : PC₆₁BM (1 : 1, w/w) as active layer without annealing. The results indicated that this polymer was promising donor candidates in the application of PSCs. More work is needed to do, such as preparing high quality polymer, adjusting the ratio of the various units, optimizing the solar cell structure, controlling the surface morphology of the active layer by thermal annealed, and solvent annealed, so as to enhance the photovoltaic performance of the terpolymer.

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