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New 5-Octyl-thieno[3,4-c]pyrrole-4,6-dione Based Polymers: Synthesis and Photovoltaic Properties

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Two donor-acceptor conjugated polymers, namely poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']difuran-alt-5-octyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione] (PBDFTTPD) and poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-alt-5-octyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione] (PBDTTTPD), were synthesized by Stille coupling polymerization reactions. Their structures were verified by 1H-NMR and elemental analysis, the molecular weights were determined by gel permeation chromatography and the thermal properties were investigated by thermogravimetric analysis. The polymer films exhibited broad absorption bands. The hole mobility of PBDFTTPD:PC71BM (1:2, w/w) blend reached up to 5.5 × 10−2 cm2 V−1 s−1 by the space-charge-current method. Preliminary photovoltaic cells based on the device structure of ITO/PEDOT:PSS/PBDFTTPD:PC71BM (1:2, w/w)/Ca/Al showed a power conversion efficiency of 2.32% with an open-circuit voltage of 0.90 V and a short circuit current of 4.40 mA cm−2.

Keywords: Benzo[1,2-b:4,5-b']difuran, synthesis and processing, device performance

1 Introduction

In the past several decades, polymer solar cells (PSCs) with bulk heterojunction (BHJ) structure have attracted much attention as promising candidates for renewable energy sources because of their many advantages such as low-cost, light-weight and potential for fabrication of flexible devices (1–3). The power conversion efficiency (PCE) of BHJ PSCs based on blends of polymer donors and fullerene acceptors has reached up over 10% in several recently reported devices (4). The factors affecting the PCE of the PSCs include the absorption spectra of conjugated polymers, the charge carrier mobility of polymer photovoltaic materials, etc. Low-band gap conjugated polymers can improve the light harvesting, therefore, they have played an important role in achieving high PCE (5, 6).

Among the various D-A conjugated polymers, benzo[1,2-b:4,5-b']dithiophene (BDT) and its derivatives have been widely used and have been proven to be promising electron donating units for high-performance PSC materials (7). The superiority of BDT include the simple synthetic route, easy modification and planar conjugated structures, moreover, some BDT-based copolymers with different acceptor units have shown high photovoltaic property and high hole mobility (8–10). Furthermore, the fused aromatic structure of benzo[1,2-b:4,5-b']difuran (BDF) is similar with BDT by substituting furan ring for thiophene ring (11). Because the diameter of the oxygen atom is less than the sulfur atom, promoted stacking and well coplanarity conjugated structure can be formed, which is desirable for getting higher charge mobility and smaller energy bandgap of BDF-based copolymers (12–14). Furthermore, 1,3-Dibromo-5-octyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (TPD) is a simple, compact, symmetric and planar electron accepting unit. Consequently, TPD was widely used to synthesize low-band gap conjugated polymers due to the strong electron-withdrawing ability of its imide group (15, 16).
PSCs based on blends of TPD-based copolymers with soluble fullerene derivatives also have exhibited very promising performance (17).

Taking into account all the reasons discussed above and in search of new low-band gap polymers, we were interested in the copolymers of alkylthiophene substituted BDT and BDF derivatives polymerizing TPD derivative. Herein, two copolymers, poly[4,8-bis(2-ethylhexyl)thiophen-2-yl]benzo[1,2-b:4,5-b']difuran-alt-5-octyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (PBDFTTPD) and poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-alt-5-octyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione] (PBDTTTPD), were synthesized by the Stille coupling reaction. The polymers were both soluble in common organic solvents and the polymers film exhibited broad absorption in the wavelength range from 300 nm to 650 nm. What’s more, polymer solar cells with the structure of ITO/PEDOT:PSS/blend:PC71BM (1:2, w/w)/Ca/Al demonstrated a promising PCE of 2.32% under the illumination of AM 1.5G, 100 mW cm\(^{-2}\). Besides, a high hole mobility of 5.5 \(\times\) 10\(^{-2}\) cm\(^2\) V\(^{-1}\) s\(^{-1}\) of PBDFTTPD was obtained in organic field effect transistors (OFETs).

2 Experimental

2.1 Materials

Furan-3-carboxylic acid, thiophene-3-carboxylic acid, n-BuLi, Pd(PPh\(_3\))\(_4\) and Sn(CH\(_3\))\(_3\)Cl were obtained from Acros Organics, and they were used as received. PC\(_{71}\)BM (99%) was purchased from American Dye Source, Inc. Toluene was dried over P₂O₅ and freshly distilled prior to use. Tetrahydrofuran (THF) was dried over Na/benzophenone ketyl and freshly distilled prior to use. Other reagents and solvents were purchased commercially as ACS-grade quality and used without further purification. 2,6-Bis(trimethylsilyl)-4,8-bis(5-(2-ethylhexyl)thiophene-2-yl)benzo[1,2-b:4,5-b'] difuran (M1) and 2,6-bis(trimethylsilyl)-4,8-bis(5-(2-ethylhexyl)thiophene-2-yl)benzo[1,2-b:4,5-b']dithiophene (M2) were prepared according to the reported literature (18, 19). 1,3-Dibromo-5-octyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (TPD) was bought from Suna Tech Inc.

2.2 Characterization

\(^1\)H-NMR spectra were obtained on a Varian INOVA-400 Spectrometer, using CDCl\(_3\) as a solvent; TMS was used as an internal standard. All NMR chemical shifts are reported as \(\delta\) values in parts per million (ppm). The splitting pattern abbreviations are as follows: s, singlet; d, doublet; br, broad peak; and m, multiplet. The molecular weights, including number-average (\(M_n\)) and weight-average (\(M_w\)), were measured by gel permeation chromatography (GPC) method, and polystyrene was used as a standard using THF as eluent. Thermogravimetric analysis (TGA) measurements were performed on a Shimadzu DTG-60 with a heating rate of 20 K min\(^{-1}\) under nitrogen atmosphere. UV-Vis absorption spectra were measured on a Shimadzu UV-2450 UV-Vis spectrophotometer. For the solid state measurements, polymer solution in CHCl\(_3\) was cast on quartz plates. Optical bandgap was calculated from the onset of the absorption band. The electrochemical cyclic voltammograms (CV) experiments were conducted on a Zahner IM6e Electrochemical Workstation using platinum disk covered by the polymer film, Pt wire and Ag/AgCl (0.1 M) electrode in an anhydrous and argon-saturated solution. The morphologies of the blend films of polymer/PC\(_{71}\)BM were obtained by using a SPI 3800N atomic force microscopy (AFM) in the tapping mode.

2.3 Fabrication and Characterization of the Polymer Solar Cells

The PSCs were fabricated in the configuration of the traditional sandwich structure with an indium tin oxide (ITO) glass anode and a metal (Ca/Al) cathode. Patterned ITO glass with a sheet resistance of 10 \(\Omega\) \(\square\) was purchased from CSG Holding Co. Ltd. (China). The ITO glass was cleaned by sequential ultrasonic treatment in detergent, deionized water, acetone and isopropanol, and then treated in an ultraviolet-ozone chamber (Ultra Violet Ozone Cleaner, Jelight Company, USA) for 25 min. Then PEDOT:PSS (poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate)) (Baytron P 4083, Germany) was filtered through a 0.45 \(\mu\)m poly(tetrafluoroethylene) (PTFE) filter and spin coated at 2000 rpm for 40 s on the ITO electrode. Subsequently, the PEDOT: PSS film was baked at 150°C for 15 min in the air to give a thin film with a thickness of 40 nm. The polymers and PC\(_{71}\)BM (10 mg mL\(^{-1}\) for polymers) were dissolved in o-dichlorobenzene (o-DCB), and spin-cast at 2000 rpm for 45 s onto the PEDOT:PSS layer. The substrates were then dried at 70°C for 15 min. The thickness of the photoactive layer is about 150 nm measured by an Ambios Technology XP-2 profilometer. A bilayer cathode consisting of Ca (~20 nm) capped with Al (~60 nm) was thermal evaporated under a shadow mask with a base pressure of ca. 10\(^{-5}\) Pa. The active area of the PSCs is 4 mm\(^2\). Device characterization was carried out under AM 1.5G irradiation with the intensity of 100 mW cm\(^{-2}\) (Oriel 67005, 500 W), calibrated by a standard silicon cell. \(J-V\) curves were recorded with a Keithley 236 digital source meter. A xenon lamp with AM1.5 filter was used as the white light source and the optical power was 100 mW cm\(^{-2}\). The external quantum efficiency (EQE) measurements of PSCs were performed by Stanford
Systems model SR830 DSP lock-in amplifier coupled with a WDG3 monochromator and 500 W xenon lamp. A calibrated silicon detector was used to determine the absolute photosensitivity at different wavelengths. All of these fabrications and characterizations after cleaning ITO substrates were conducted in a glove box.

2.4 Synthesis of the Monomers and Polymers

The synthetic routes of the monomers and polymers are shown in Scheme 1. The detailed synthetic procedures for the compounds and polymers are as follows:

Sch. 1. Synthetic route for the monomers and the corresponding polymers.
2.5 2-(2-Ethylhexyl)thiophene (1)

A solution of thiophene (3.78 g, 45 mmol) in dry THF (50 mL) was deoxygenated with argon for 15 min, and 20.8 mL of n-butyllithium (50 mmol, 2.4 mol L \(^{-1}\)) was added dropwise at 0°C. The solution was allowed to be heated to 50°C and stirred for 1.5 h; benzo[1,2-b:4,5-b]dithiophene-4,8-dione (1.76 g, 8 mmol) was added. The mixture was stirred at 50°C for another 1.5 h. The solution was washed with water and then dried over anhydrous MgSO\(_4\). After the solvent was removed under vacuum, the residue was purified by column chromatography (silica gel, PE) to afford pale yellow sticky thickened oil (1.61 g, 35%). \(^1\)H-NMR (400 MHz, CDCl\(_3\)): 7.72 (s, 2H), 7.41 (d, 2H), 6.90 (d, 2H), 2.88 (d, 4H), 1.74 (m, 2H), 1.54-1.33 (br, 16H), 0.95 (m, 12H), 0.47 (s, 18H).

The mixture was poured into 200 mL of cool water and extracted with CH\(_2\)Cl\(_2\). The organic layer was washed with water and then dried over anhydrous MgSO\(_4\). After the solvent was removed under vacuum, the residue was purified by column chromatography (silica gel, PE) to afford pale yellow sticky thickened oil (1.61 g, 35%). \(^1\)H-NMR (400 MHz, CDCl\(_3\)): 7.72 (s, 2H), 7.41 (d, 2H), 6.90 (d, 2H), 2.88 (d, 4H), 1.74 (m, 2H), 1.54-1.33 (br, 16H), 0.95 (m, 12H), 0.47 (s, 18H).

2.6 4,8-Bis(5-(2-ethylhexyl)thiophene-2-yl)benzo[1,2-b:4,5-b'] difuran (2)

A solution of 1 (3.92 g, 20 mmol) in dry THF (120 mL) was deoxygenated with argon for 15 min, and 9.2 mL of n-butyllithium (22 mmol, 2.4 mol L \(^{-1}\)) was added dropwise at 0°C. Then the solution was allowed to heat to 50°C and was stirred for 1.5 h; benzo[1,2-b:4,5-b']difuran-4,8-dione (1.5 g, 8 mmol) was added. The mixture was stirred at 50°C for another 1.5 h. After the reaction mixture was cooled to room temperature, SnCl\(_2\cdot2H_2O\) (14.4 g, 64 mmol) in 25.6 mL of 10% hydrochloric acid was added, and the reaction mixture was stirred for 1.5 h. The mixture was poured into 200 mL of cold water and extracted with CH\(_2\)Cl\(_2\). The organic layer was washed with water and then dried over anhydrous MgSO\(_4\). After the solvent was removed under vacuum, the residue was purified by column chromatography (silica gel, PE) to afford yellow sticky thickened oil (1.61 g, 35%). \(^1\)H-NMR (400 MHz, CDCl\(_3\)): 7.72 (s, 2H), 7.41 (d, 2H), 6.90 (d, 2H), 2.88 (d, 4H), 1.70 (m, 2H), 1.63-1.25 (m, 12H), 0.90 (t, 6H).

The mixture was poured into 200 mL of cool water and extracted with CH\(_2\)Cl\(_2\). The organic layer was washed with water and then dried over anhydrous MgSO\(_4\). After the solvent was removed under vacuum, the residue was purified by column chromatography (silica gel, PE) to afford pale yellow sticky thickened oil (1.61 g, 35%). \(^1\)H-NMR (400 MHz, CDCl\(_3\)): 7.72 (s, 2H), 7.41 (d, 2H), 6.90 (d, 2H), 2.88 (d, 4H), 1.70 (m, 2H), 1.63-1.25 (m, 12H), 0.90 (t, 6H).

2.7 4,8-Bis(5-(2-ethylhexyl)thiophene-2-yl)benzo[1,2-b:4,5-b'] dithiophene (3)

A solution of 1 (3.92 g, 20 mmol) in dry THF (120 mL) was deoxygenated with argon for 15 min, and 9.2 mL of n-butyllithium (22 mmol, 2.4 mol L \(^{-1}\)) was added dropwise at 0°C. Then the solution was allowed to be heated to 50°C and stirred for 1.5 h; benzo[1,2-b:4,5-b']dithiophene-4,8-dione (1.76 g, 8 mmol) was added. The mixture was stirred at 50°C for another 1.5 h. After the reaction mixture was cooled to room temperature, SnCl\(_2\cdot2H_2O\) (14.4 g, 64 mmol) in 25.6 mL of 10% hydrochloric acid was added, and the reaction mixture was stirred for 1.5 h.

The mixture was poured into 200 mL of cool water and extracted with CH\(_2\)Cl\(_2\). The organic layer was washed with water and then dried over anhydrous MgSO\(_4\). After the solvent was removed under vacuum, the residue was purified by column chromatography (silica gel, PE) to afford pale yellow sticky thickened oil (1.61 g, 35%). \(^1\)H-NMR (400 MHz, CDCl\(_3\)): 7.72 (s, 2H), 7.41 (d, 2H), 6.90 (d, 2H), 2.88 (d, 4H), 1.70 (m, 2H), 1.63-1.25 (m, 12H), 0.90 (t, 6H).

2.8 2,6-Bis(trimethyltin)-4,8-bis(5-(2-ethylhexyl)thiophene-2-yl)benzo[1,2-b:3,4-b'] difuran (M1)

A solution of 2 (0.76 g, 1.4 mmol) in dry THF (30 mL) was deoxygenated with argon for 15 min, and 2.0 mL of n-butyllithium (4.8 mmol, 2.4 mol L \(^{-1}\)) was added dropwise at −78°C and was stirred for another 1 h. Then the reaction was stirred at room temperature for 1 h. After that, 5.5 mL of trimethyltin chloride (5.5 mmol, 1 mol L \(^{-1}\)) was added at −78°C again. After stirring at room temperature overnight, the mixture was washed with water and extracted with CH\(_2\)Cl\(_2\). The organic phase was evaporated, and the residue was recrystallized from isopropanol to afford pale yellow crystals (0.64 g, 54%). \(^1\)H-NMR (400 MHz, CDCl\(_3\)): 7.72 (s, 2H), 7.41 (d, 2H), 6.90 (d, 2H), 2.88 (d, 4H), 1.74 (m, 2H), 1.54-1.33 (br, 16H), 0.95 (m, 12H), 0.47 (s, 18H).

2.9 2,6-Bis(trimethyltin)-4,8-bis(5-(2-ethylhexyl)thiophene-2-yl)benzo[1,2-b:3,4-b'] dithiophene (M2)

A solution of 3 (0.81 g, 1.4 mmol) in dry THF (30 mL) was deoxygenated with argon for 15 min, and 2.0 mL of n-butyllithium (4.8 mmol, 2.4 mol L \(^{-1}\)) was added dropwise at −78°C and was stirred for another 1 h. Then the reaction was stirred at room temperature for 1 h. After that, 5.5 mL of trimethyltin chloride (5.5 mmol, 1 mol L \(^{-1}\)) was added at −78°C again. After stirring at room temperature overnight, the mixture was washed with water and extracted with CH\(_2\)Cl\(_2\). The organic phase was evaporated, and the residue was recrystallized from isopropanol to afford pale yellow solid (0.83 g, 65%). \(^1\)H-NMR (400 MHz, CDCl\(_3\)): 7.70 (s, 2H), 7.34 (d, 2H), 6.92 (d, 2H), 2.89 (d, 4H), 1.74 (m, 2H), 1.55-1.32 (br, 16H), 0.93 (m, 12H), 0.42 (s, 18H).

2.10 Synthesis of PBDFTPD

M1 (0.1745 g, 0.2 mmol), TPD (0.0846 g, 0.2 mmol) and 15 mL of dry toluene were put into a two-necked flask. The solution was flushed with argon for 20 min, then Pd (PPH\(_3\)H\(_4\)) (15 mg) was added into the flask and then the solution was flushed with argon for another 25 min. The oil bath was heated to 110°C carefully, and the reactant was stirred for 48 h at this temperature under argon
atmosphere. Then the reaction mixture was cooled to room temperature and then slowly poured into methanol (100 mL). The resulting precipitation was filtered through a Soxhlet thimble, which was then subjected to Soxhlet extraction with methanol, hexane and CHCl₃. The polymer was recovered as a solid from the CHCl₃ fraction by rotary evaporation. The purple solid was dried under vacuum overnight (0.066 g, 41%). ¹H-NMR (500 MHz, CDCl₃): 8.25 (s, 1H), 7.61 (s, 1H), 6.72 (s, 1H), 3.91 (br, 1H), 3.02(br, 2H), 1.89 (br, 6H), 1.4-1.8 (br, 16H), 0.90-1.3 (br, 12H), 0.30-0.55 (br, 17H).

2.11 Synthesis of PBDTTTPD

PBDTTTPD was obtained by a similar procedure to the synthesis of PBDFTTPD starting from M2 (0.1809 g, 0.2 mmol) and TPD (0.0846 g, 0.2 mmol). Finally, the purple solid was obtained (0.073 g, 43%).

3 Results and Discussion

3.1 Polymer Synthesis

As shown in Scheme 1, the polymers were synthesized with the ditin derivatives (M1 and M2) in the presence of TPD using Stille coupling reactions. The synthesized polymers were purified by continuous extractions with methanol, hexane, and CHCl₃, and the CHCl₃ fractions were recovered. The weight-average molecular weight (M_w) of PBDFTTPD and PBDTTTPD, were measured by using GPC results, they were found to be 12.1 kDa (PDI=3.69) and 62.3 kDa (PDI=2.32), respectively. The obtained copolymers from CHCl₃ fractions are readily dissolved in common organic solvents such as chlorobenzene, THF and dichlorobenzene, etc. Table 1 lists the polymerization results and thermal data of the polymers.

3.2 Thermal Stability

Thermal stability of the polymer is an important factor for device fabrication. The TGA analysis reveals that, under the protection of an inert atmosphere, the decomposition temperature (Td) of 5% weight loss of PBDFTTPD and PBDTTTPD are ca. 378°C and 364°C, respectively (Fig. 1). Good thermal stability of the copolymer prevents the deformation of copolymer morphology and the degradation of polymeric active layer under an applied electric field.

3.3 Optical Properties

The absorption spectra of PBDFTTPD and PBDTTTPD in dilute CHCl₃ and the film state coating on a quartz substrate are shown in Figure 2. The optical data including the absorption peak wavelength, absorption onset wavelength and the optical bandgap are listed in Table 2. As shown in Figure 2, two polymers display a broad absorption plateau in the dilute CHCl₃ solution and films on quartz cast from CHCl₃ solution. Meanwhile, in the film state, the absorbance maximum of PBDFTTPD and PBDTTTPD were 630 nm and 611 nm, with 12 nm and 6 nm red shift relative to those in solution, respectively, suggesting the strong interchain interaction. The optical bandgaps of polymers estimated from the absorption edge of thin film were 1.51 eV (λ_onset=823 nm) and 1.83 eV (λ_onset=679 nm), respectively.

3.4 Electrochemical Properties

To investigate the electrochemical properties of PBDFTTPD and PBDTTTPD, and estimate the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels, cyclic voltammetry (CV) was carried out in a 0.1 M Bu₄NPF₆-acetonitrile solution at room temperature under argon at a scanning rate of 50 mV s⁻¹. The HOMO and LUMO values of two polymers were measured from the onset oxidation and reduction potentials, and the CV curves of the two polymers are shown in Figure 3. From E^ox and E^red of the

Table 1. Polymerization results and thermal data of PBDFTTPD and PBDTTTPD

<table>
<thead>
<tr>
<th>Polymers</th>
<th>M_n (kDa)</th>
<th>M_w (kDa)</th>
<th>PDI</th>
<th>Yield (%)</th>
<th>T_d (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBDFTTPD</td>
<td>3.3</td>
<td>12.1</td>
<td>3.69</td>
<td>41</td>
<td>378</td>
</tr>
<tr>
<td>PBDTTTPD</td>
<td>22.3</td>
<td>61.3</td>
<td>2.32</td>
<td>43</td>
<td>364</td>
</tr>
</tbody>
</table>
copolymers, we calculated the HOMO and LUMO energy levels of the polymers according to the equation:

\[
\text{HOMO} = -e(E_{\text{on}}^{\text{ox}} + 4.4) \text{ (eV)}
\]

\[
\text{LUMO} = -e(E_{\text{on}}^{\text{red}} + 4.4) \text{ (eV)}
\]

Using Ag/AgCl as the reference electrode, the oxidation potential of Fe/Fe\textsuperscript{2+} is 0.4 V. Due to the electron-withdrawing TPD unit, the HOMO energy levels of two polymers were relatively low (≈5.48 eV and ≈5.37 eV, respectively for PBDFTTPD and PBDTTTPD), which could be expected to afford higher Voc in the applications of PSCs (11, 20). Accordingly, the LUMO levels of PBDFTTPD and PBDTTTPD were ≈3.77 eV and ≈3.57 eV, respectively. The optical and electronic energy level data of the polymers are summarized in Table 2 for comparison.

### 3.5 Hole Mobility

As another important factor of conjugated polymers, hole mobility plays a direct effect on the charge transport in PSCs. Therefore, we investigated the hole mobilities of PBDFTTPD and PBDTTTPD, with the space-charge-limited current (SCLC) model based on the Poole-Frenkel Law by fabricating a device structure of ITO/PEDOT:PSS/polymer:PC\textsubscript{71}BM (1:2, w/w)/Au (21). The results are

![Fig. 2. UV-Vis absorption spectra of PBDFTTPD and PBDTTTPD: (a) solutions in dilute CHCl\textsubscript{3} and (b) films on quartz cast from CHCl\textsubscript{3} solution.](image)

![Fig. 3. Cyclic voltammograms of PBDFTTPD and PBDTTTPD films cast on platinum wire in 0.1 M Bu\textsubscript{4}NPF\textsubscript{6}/CH\textsubscript{3}CN solution at a scan rate of 50 mV s\textsuperscript{-1}.](image)

**Table 2. Optical and electrochemical properties of PBDFTTPD and PBDTTTPD**

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Absorption spectra</th>
<th>Cyclic voltammetry (vs. Ag/AgCl)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Solution\textsuperscript{a}</td>
<td>Film\textsuperscript{b}</td>
</tr>
<tr>
<td></td>
<td>(\lambda_{\text{max}}) (nm)</td>
<td>(\lambda_{\text{onset}}) (nm)</td>
</tr>
<tr>
<td>PBDFTTPD</td>
<td>618</td>
<td>630</td>
</tr>
<tr>
<td>PBDTTTPD</td>
<td>605</td>
<td>611</td>
</tr>
</tbody>
</table>

\(\text{a)}\) Measured in CHCl\textsubscript{3} solution;  
\(\text{b)}\) Spin-coated from CHCl\textsubscript{3} solution;  
\(\text{c)}\) Bandgap estimated from the onset wavelength of the optical absorption;  
\(\text{d)}\) HOMO = −e(\(E_{\text{on}}^{\text{OX}}\) + 4.71); LUMO = −e(\(E_{\text{on}}^{\text{RED}}\) + 4.71)
plotted as $\ln(Jd^3/V^2)$ vs. $(V/d)^{0.5}$, as shown in Figure 4, and SCLC model can be described by the following equation:

$$J_{\text{SCLC}} = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu \frac{(V - V_{\text{bi}})^2}{d^3} \exp\left[0.89 \sqrt{\frac{V - V_{\text{bi}}}{d}}\right]$$

Figure 4. $\ln(Jd^3/V^2)$ vs. $(V/d)^{0.5}$ plots of the blends of PBDFTTPD and PBDTTTPD and PC$_{71}$BM for measurement of the hole mobilities by SCLC method.

Herein, $J$ is current density, $d$ stands for the thickness of the device, and $V = V_{\text{appl}} - V_{\text{bi}}$, where $V_{\text{appl}}$ is the applied potential and $V_{\text{bi}}$ is the build-in potential. According to the Equation 1 and Figure 4, the hole mobilities of PBDFTTPD and PBDTTTPD are calculated to be $5.5 \times 10^{-2}$ cm$^2$ V$^{-1}$ s$^{-1}$ and $8.25 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$, respectively. The results show that the hole mobility of PBDFTTPD/PC$_{71}$BM blend is two orders of magnitude higher than that of PBDTTTPD/PC$_{71}$BM blend under the same conditions, which may come from the good planarity and close $\pi-\pi$ stacking of PBDFTTPD, which are beneficial for obtaining higher mobility (22).

3.6 Photovoltaic Properties

In order to investigate and compare the photovoltaic properties of PBDFTTPD and PBDTTTPD, PSCs with a single layer sandwich configuration of ITO/PEDOT: PSS/ polymer:PC$_{71}$BM/Ca/Al were fabricated. The polymer active layers were spin-coated from $o$-DCB solution with different concentrations (polymer: PC$_{71}$BM=1:1 and 1:2; w/w). Figure 5 shows the typical current-density-voltage ($J-V$) curves of the PSCs based on polymers: PC$_{71}$BM blend under the illumination of AM 1.5G, 100 mW cm$^{-2}$. The corresponding results of the devices are listed in Table 3. $J_{\text{sc}}$, $V_{\text{oc}}$ and FF have shown a little difference between PBDFTTPD-based and PBDTTTPD-based solar cells, high $J_{\text{sc}}$ comes from strong absorbance and good charge transport in the active layer. The resulting PCE of PBDFTTPD: PC$_{71}$BM(1:2, w/w) reached up to 2.32% without annealing or any additives, which is better than that of PBDTTTPD: PC$_{71}$BM(1:2, w/w)(2.04%) in the same conditions, which may result from the larger $V_{\text{oc}}$ and FF of PBDFTTPD-based PSCs than those of PBDTTTPD.

3.6 Photovoltaic Properties

Table 3. Photovoltaic properties of PSCs based on polymers: PC$_{71}$BM

<table>
<thead>
<tr>
<th>Active layer</th>
<th>$V_{\text{oc}}$ (V)</th>
<th>$J_{\text{sc}}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBDFTTPD:PC$_{71}$BM=1:1</td>
<td>0.78</td>
<td>4.35</td>
<td>43.7</td>
<td>1.48</td>
</tr>
<tr>
<td>PBDFTTPD:PC$_{71}$BM=1:2</td>
<td>0.79</td>
<td>5.10</td>
<td>50.8</td>
<td>2.04</td>
</tr>
<tr>
<td>PBDTTTPD:PC$_{71}$BM=1:1</td>
<td>0.87</td>
<td>3.79</td>
<td>53.2</td>
<td>1.75</td>
</tr>
<tr>
<td>PBDTTTPD:PC$_{71}$BM=1:2</td>
<td>0.90</td>
<td>4.40</td>
<td>58.6</td>
<td>2.32</td>
</tr>
</tbody>
</table>

Fig. 5. $J-V$ curves of the PSCs based on polymers/PC$_{71}$BM with different ratios under illumination of AM1.5G, 100 mW cm$^{-2}$.

Table 3. Photovoltaic properties of PSCs based on polymers: PC$_{71}$BM

<table>
<thead>
<tr>
<th>Active layer</th>
<th>$V_{\text{oc}}$ (V)</th>
<th>$J_{\text{sc}}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
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</tr>
</tbody>
</table>

Fig. 6. The EQE curves of the PSCs based on polymers:PC$_{71}$BM with different ratios in $o$-DCB.
based PSCs. From Table 3, devices with a donor:acceptor weight ratio of 1:2 showed the best performance than 1:1, which may be related with the increasing ratio of PC71BM. From Figure 6, the complementary absorbance of PC71BM and polymers gives a relatively high photo-conversion efficiency over the wavelength range of 370 nm to 620 nm, with monochromatic EQE values close or above 20% for both polymers. It is worth noting that the $J_{sc}$ calculated by integrating the $EQE$ curve with an AM 1.5G reference spectrum matches well with the $J_{sc}$ value obtained from the $J-V$ measurements.

3.7 Morphology

In addition to absorption, energy level and charge mobility, the morphology of the photoactive layer is also an important factor of organic PSCs (23). Hence, we investigated the surface morphology of the active layer by spin-coating blends on an ITO glass by using AFM. The height and phase images of the blend films are shown in Figure 7. The surface RMS (root mean-square) roughness of the polymer:PC71BM films (1:2, w/w) are 0.42 nm and 0.70 nm for PBDTTTPD and PBDFTTTPD, respectively. From the height images Figure 7(A and B), the PBDFTTTPD/PC71BM blend show rough surfaces with relatively large aggregates, which may be compact chain packing and aggregates crystallization, beneficial for obtaining high hole mobility. As shown in the corresponding phase image Figure 7(b), pronounced nanophase separation and nano fibril were formed, which to some extent explains the relatively high photovoltaic properties of the PBDFTTTPD/PC71BM blend.

4 Conclusions

In summary, we have designed and synthesized two D-A copolymers, PBDTTTPD and PBDFTTTPD. They have been well characterized by GPC, TGA, UV-Vis absorption and CV. The relationship between the structures and properties was investigated in detail. A high mobility of $5.5 \times 10^{-2}$ cm$^2$ V$^{-1}$ s$^{-1}$ was obtained from the
PBDFTPD and PC_{71}BM blend by SCLC model. A PCE of 2.32% from PBDFTPD-based polymer solar cells with $V_{oc}=0.90$ V, $J_{sc}=4.4$ mA cm$^{-2}$ and FF=58.6% was recorded without any device modifications. Those results indicate that PBDFTPD is a promising candidate for polymer solar cells.

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**References**