A new polymer from fluorinated benzothiadiazole and alkoxylphenyl substituted benzo[1,2-b:4,5-b']dithiophene: Synthesis and photovoltaic applications

Lu Xiao a, Jun Yuan a, Yingping Zou a,d,e, Bo Liu b, Jinzhi Jiang a, Yan Wang a, Lihui Jiang a, Yong fang Li c,**

a College of Chemistry and Chemical Engineering, Central South University, Changsha 410083, China
b State key Laboratory for Powder Metallurgy, Central South University, Changsha 410083, China
c Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China
d Key Laboratory of Resources Chemistry of Nonferrous Metals (Central South University), Ministry of Education, Changsha, Hunan 410083, China

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A new donor–acceptor conjugated polymer (PBDTPO-FBT), which consists of a fluorinated benzothiadiazole (FBT) electron-acceptor unit and an electron-donor segment of alkoxylphenyl substituted benzo[1,2-b:4,5-b']dithiophene (BDTPO), was synthesized according to the Stille cross-coupling reaction. The resulting copolymer was characterized by TGA, GPC, UV–vis absorption spectroscopy and cyclic voltammetry measurements. PBDTPO-FBT possesses good thermal stability with 5% weight loss temperature of 410 °C and shows broad absorption at 300–800 nm with an optical bandgap of 1.53 eV. Cyclic voltammetry measurement exhibits HOMO and LUMO energy levels of −5.43 eV and −3.72 eV, respectively. The hole mobility of PBDTPO-FBT:PC71BM (1:1, w/w) reaches up to 3.8 × 10−4 cm2/V/s by the space-charge-limited current (SCLC) method. By using 3% 1,8-diiodooctane (DIO) as the solvent additive, the polymer solar cell with the configuration of ITO/PEDOT-PSS/PBDTPO-FBT:PC71BM (1:1, w/w)/Ca/Al demonstrates a power conversion efficiency of 2.70% with Voc = 0.70 V, Jsc = 7.23 mA/cm2 and FF = 47.08%, under the illumination of AM 1.5 G, 100 mW/cm2.

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1. Introduction

Since the first bulk-heterojunction (BHJ) photovoltaic cell was emerged in 1995 [1], polymer solar cells (PSCs) based on BHJ model which was composed of a polymeric material (donor, such as P3HT) blended with a fullerene derivative (acceptor, such as PCBM) have gained growing interest in academic and industrial laboratories [2]. PSCs possess some unique characteristics over the traditional silicon-based solar cells such as low-cost, easy processing, light-weight, flexibility, solution processability and chemically fine tunability [3]. Although some great success has been achieved up to now [4], there is still a long way for us to meet the demand of commercialization of PSCs.

In order to obtain high PCE, the key point is to design and synthesize high-efficiency conjugated polymer donor and fullerene derivative acceptor photovoltaic materials [5]. In recent years, D–A alternating copolymerization is quite an effective way for tailoring the properties of the promising polymer donors because of fine tuning of the bandgap, absorption spectra, solubility and energy levels [6]. Benzothiadiazole (BT) unit with a strong electron-withdrawing functional substituent (such as fluorine atom) is a typical building block used in low bandgap conjugated polymers for high efficiency PSCs, and many fluorinated BT based conjugated polymers with different electron donor units, such as indacenodithiophene (IDT) [7], pyrroloindacenodithiophene (NDT) [8], cyclopenta[2,1-b:3,4-b']dithiophene (CPDT) [9] and benzo[1,2-b:4,5-b']dithiophene (BDT) [10], were synthesized and showed excellent photovoltaic properties. As well known, BDT has a coplanar geometry and a rigid structure which is good for achieving a high charge mobility [11]. Many research groups including our group have reported polymers containing alkylthienyl substituted benzodithiophene (BDT) unit, and this type of polymer exhibits broad absorption, suitable energy levels, good solubility and a relative high PCE [10c,12]. Last year, Yang and his coworkers reported a new 2-dimensional structure of benzo[1,2-b:4,5-b']dithiophene with two flanking alkylphenyl side group (BDTP) and got a PCE of 6.0% with a solvent additive modification [13]. All of these previous

* Corresponding author at: College of Chemistry and Chemical Engineering, Central South University, Changsha 410083, China.
** Corresponding author.
E-mail addresses: yingpingzou@csu.edu.cn (Y. Zou), liyf@ccas.ac.cn (Y.F. Li).
works have shown that 2-dimensional BDT derivative is a promising electron donor building block.

Taking all of these into account, we attached 2-ethylhexoxyphenyl group to the phenyl rings of BDT to afford a more electron-rich donor. In this work, we synthesized a new D–A copolymer (PBDTPO-FBT) (see Fig. 1) from alklyoxyphenyl substituted BDT-derivative (BDTPO) and a fluorinated benzothiadiazole electron-acceptor unit (FBT) (as shown in Scheme 1). PBDTPO-FBT was designed and synthesized toward photovoltaic applications. The polymer was soluble in the common organic solvents and exhibited a broad absorption from 300 nm to 800 nm in the film state. From their absorption spectra, we can see that the absorption edge of the polymer film is located at 808 nm. Furthermore, the film of PBDTPO-FBT blended with PC71BM shows a hole mobility of $3.8 \times 10^{-3}$ cm$^2$/Vs using SCLC method. Polymer solar cells with the configuration of ITO/PEDOT:PSS/PBDTPO-FBT:PC71BM (1:1, w/w)/Ca/Al and 1,8-diodooctane (DIO, 3 vol%) as an additive demonstrated a promising power conversion efficiency of 2.70% with a $V_{oc}$ of 0.79 V, a $J_{sc}$ of 7.23 mA/cm$^2$ and a $FF$ of 47.08%, under the illumination of AM 1.5, 100 mW/cm$^2$.

2. Experimental parts

2.1. Materials

p-Bromophenol (1), n-BuLi, Pd(PPh$_3$)$_4$, tetrahydrofuran (THF) and Sn(CH$_3$)$_2$Cl were purchased from Aladdin and Alfa Asia Chemical Co., and they were used as received without further purification. Toluene was dried over molecular sieves and freshly distilled prior to use. The other chemical reagents and solvents were obtained commercially as analytical-grade quality and used without further purification. Column chromatography was carried out on silica gel (size: 200–300 mesh).

1H NMR spectra were recorded using a Bruker DMX-400 spectrometer in deuterated chloroform solution at 298 K, unless specified otherwise. Chemical shifts were reported as $\delta$ values (ppm) relative to an internal tetramethylsilane (TMS) standard. Number-average ($M_n$) and weight-average ($M_w$) molecular weights were determined by gel permeation chromatography (GPC) analysis using polystyrene calibration as a standard (Waters 515 HPLC pump, a Waters 2414 differential refractometer, and three Waters Styragel columns (HT2, HT3, and HT4)) using THF (HPLC grade) as eluent at a flow rate of 1.0 mL/min at 35 °C. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TGA-7 at a heating rate of 20 K/min under nitrogen atmosphere. UV–vis absorption spectra were taken using a Hitachi U-3010 UV–vis spectrophotometer. For the solid state measurements, polymer solution in chloroform was spin-coated on quartz plates. Optical bandgap was calculated from the onset of the absorption band. Cyclic voltammograms (CV) were recorded on a Zahner IM6e Electrochemical Workstation using platinum disk coated with the polymer film on carbon electrode (1.0 cm$^2$) as the working electrode, Pt wire as the counter electrode and a Ag/AgCl (0.1 M) as the reference electrode in an anhydrous and argon-saturated solution of a 0.1 M tetrabutylammonium hexafluorophosphate (Bu$_4$NPF$_6$) in acetonitrile solution at a scan rate of 50 mV/s. The HOMO energy level was determined from the oxidation onset of the CV spectra; LUMO energy level was estimated from the reduction onset of the CV spectra. Electrochemical onsets were determined at the position where the current starts to differ from the baseline. AFM images were investigated by a SPI 3800N atomic force microscope (AFM) in contacting mode with a 3 μm scanner.

2.2. Measurements

2.3. Fabrication and characterization of PSCs

The PSCs were fabricated in the configuration of the traditional sandwich structure with an indium tin oxide (ITO) glass positive electrode and a metal negative electrode (Ca/Al). Patterned ITO glass with a sheet resistance of 15–20 Ω/cm$^2$ was purchased from CSFHOLDING 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 (Ultraviolet Oxygen Cleaner, Jelight Company, USA) for 25 min. The PEDOT:PSS (poly[(3,4-ethylenedioxythiophene):poly(styrene sulfonate)] (Baytron P, PVP 4083, Germany) was filtered through a 0.45 μm poly(tetrafluoroethylene) (PTFE) filter and spin coated at 2000 rpm for 40 s on the ITO glass. 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. A blend of the polymer and PCBM (10 mg/mL for polymer) was dissolved in o-dichlorobenzene (ODCB) overnight, and spin-cast at 2000 rpm for 45 s onto the PEDOT:PSS layer. The thickness of the photoactive layer is in the range of 100–120 nm measured by Ambios Technology XP-2 profilometer. A bilayer cathode consisting of Ca (~20 nm) capped with Al (~40 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 1.5 G irradiation with the intensity of 100 mW/cm$^2$ (Oriel 6700S, 500 W) calibrated by a standard silicon cell. $J$–$V$ curves were recorded with a Keithley 236 digital source meter. A xenon lamp with AM 1.5 filter was used as the white light source and the optical power was 100 mW/cm$^2$. The EQE measurements of PSCs were performed by Stanford Systems model SR830 DSP lock-in amplifier coupled with 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 of ITO substrates were conducted in a glove box.

2.4. Synthesis

4,7-Bis(5-bromo-4-dodecylthiophen-2-yl)-5-fluorobenzof[c][1,2,5]thiadiazole (M2) has been synthesized according to our group before [14]. Benzo[1,2-b:4,5-b']dithiophene-4,8-dione (3) was prepared according to the previous reported literature [15]. The general synthetic strategy for the monomer and polymer is outlined in Scheme 1. All of the other compounds were prepared following the synthetic procedures described herein.

2.4.1. 1-Bromo-4-(2'-ethylhexyloxy)benzene (2)

4-Bromophenol (1) (8.6 g, 50 mmol), K$_2$CO$_3$ (8.3 g, 60 mmol) and DMF (200 mL) were put into a three-neck round-bottom flask. Under the argon atmosphere, 1-bromo-2-ethylhexane (9.5 g, 50 mmol) was added dropwisely via a syringe. The mixture was heated to 150 °C overnight in the dark. And then cooled to room temperature and the reaction mixture was poured into 200 mL water and then extracted three times with chloroform. The organic extraction was washed successively with saturated potassium hydroxide and water for twice, respectively. The combined organic phases were dried over magnesium sulfate. After filtration, the solvents were evaporated in vacuum and the crude product was purified on a silica gel column eluting with petroleum ether. Brown oil was obtained (10.3 g, 73% yield).

MS: $m/z = 284$ (M$^+$). $^1$H NMR (400 MHz, CDCl$_3$, ppm): $\delta$: 7.36 (d, 2H); 6.80 (d, 2H); 3.97 (d, 2H); 1.79 (m, 1H); 154–1.36 (m, 8H); 0.96 (s, 6H).

2.4.2. 4,8-Bis(4-ethylhexyloxy-1-phenyl)-benzo[1,2-b:4,5-b']-dithiophene (4)

Under vigorous stirring, 1-bromo-4-(2-ethylhexyloxy)benzene (7.87 g, 27.6 mmol) was added dropwise to magnesium turnings (0.797 g, 33.2 mmol) in anhydrous THF (35 mL) which was protected by argon. During the process, I$_2$ (10 mg) was added as catalyst in the reaction. The solution was refluxed for 5 h until the magnesium was consumed. The mixture was refluxed one more hour and then was cooled down. The solution was added slowly to benzo[1,2-b:4,5-b']dithiophene-4,8-dione (2.03 g, 9.22 mmol) dispersed in 40 mL THF. SnCl$_2$ (13.3 g) was dissolved in 10% aqueous HCl (18.6 mL) and then added dropwisely. The solution was stirred for another 1 h at 50 °C. After cooling to room temperature, the mixture was poured into water and extracted with dichloromethane, the organic extraction was washed successively with water and sodium bicarbonate solution twice and the combined organic phase was dried over magnesium sulfate and evaporated to afford the crude product. The crude product was purified on a silica gel column, eluting with pure hexane. White crystals were obtained (1.7 g, 31% yield).

MS: $m/z = 598$ (M$^+$). $^1$H NMR (400 Hz, CDCl$_3$, ppm): $\delta$: 7.63 (d, 4H), 7.36 (m, 4H), 7.09 (d, 4H), 3.95 (d, 4H), 1.80 (m, 2H), 1.56–1.38 (br, 16H), 0.97 (m, 12H).

2.4.3. 2,6-Bis(trimethyltin)-4,8-bis(4-ethylhexyloxy-1-phenyl)-benzo[1,2-b:4,5-b']-dithiophene (M1)

A solution of compound 4 (0.9 g 1.5 mmol) in dry THF (30 mL) was deoxygenated with argon for 30 min, and then 2.4 M n-butyllithium solution in n-hexane (1.8 mL, 4.32 mmol) was added.
dropwise at 0 °C. Then the solution was allowed to warm up to 50 °C for 1 h, and 1.0 M trimethyltin chloride solution in THF (10 mL, 10 mmol) was added. Then the mixture was poured into water and extracted with dichloromethane. The organic phase was evaporated, and the residue was recrystallized from 20 mL acetone to afford the pale yellow solid (0.75 g, 55%).

MS: m/z = 924 (M⁺). 1H NMR (400 MHz, CDCl₃, ppm): δ: 7.65 (d, 4H), 7.38 (s, 2H), 7.11 (d, 4H), 3.96 (d, 4H), 1.80 (m, 2H), 1.58 (br, 16H), 0.97 (m, 12H), 0.35 (t, 18H).

2.4.4. Synthesis of PBDTPO-FBT
2.6-Bis(trimethylstannyl)-4,8-bis(4-ethylhexyloxy-1-phenyl)-benzo[1,2-b;4,5-b′]-dithiophene (M1) (182.1 mg, 0.2 mmol) and 4,7-bis(5-bromo-4-dodecylthiophen-2-yl)-5-fluorobenzothiadiazole (M2) (162.6 mg, 0.2 mmol) were dissolved in 12 mL of dry toluene. The solution was flushed with argon for 20 min. And then Pd(PPh₃)₄ (20 mg, 0.016 mmol) was added into the flask. The flask was purged three times with successive vacuum and argon filling cycles. And then the oil bath was heated to 110 °C carefully, and the mixture was stirred for 48 h at this temperature under the argon atmosphere. Then the reaction mixture was cooled to room temperature and then poured into 100 mL methanol very slowly. The resulting precipitate was filtered through a Soxhlet thimble, which was then subjected to Soxhlet extractions with methanol, hexane and chloroform, successively. Finally the polymer was recovered as a solid from the chloroform fraction by rotary evaporation. The brown solid was dried under vacuum at 40 °C overnight (127 mg, yield: 37%).

3. Results and discussion

3.1. Synthesis and structural characterization

The general synthetic route of the monomer and polymer is sketched in Scheme 1. Compound M2 was copolymerized with the ditin derivative (M1) through Stille coupling reactions to obtain the target polymer PBDTPO-FBT. The polymer was purified by continuous Soxhlet extractions with methanol, hexane and CHCl₃. And then the CHCl₃ fraction was reduced in volume, precipitated into methanol and collected by filtration, to yield a tan solid. The molecular weight of the polymer was determined by gel-permeation chromatography (GPC) using THF as eluent and polystyrene as the standard. The number average molecular weight (Mₐ) of PBDTPO-FBT is 3.4 kDa, with a PDI of 2.0. The related data are summarized in Table 1. Given the low molecular weight of the polymer, it is believed that the photovoltaic performance of this kind of polymers can be further improved from the material aspect, such as optimizing the polymerization conditions to increase the molecular weight and improving the polymer purity. The polymer PBDTPO-FBT was readily soluble by common organic solvents such as chloroform, chlorobenzene, and dichlorobenzene. Thin film of the polymer was easily fabricated from the solution in α-dichlorobenzene (α-DCB) by spin-coating.

### Table 1
Molecular weights and thermal properties of PBDTPO-FBT.

<table>
<thead>
<tr>
<th>Polymers</th>
<th>Mₐ (kDa)</th>
<th>Mₙ (kDa)</th>
<th>PDI</th>
<th>T_d (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBDTPO-FBT</td>
<td>6.8</td>
<td>3.4</td>
<td>2.0</td>
<td>410</td>
</tr>
</tbody>
</table>

a. Mₙ, Mₐ, and PDI of the polymer was determined by GPC using polystyrene standards in THF.
b. T_d is the 5% weight-loss temperatures of the polymer under inert atmosphere.

3.2. Thermal stability of the polymer

The thermal stability of polymer is an important parameter for the device application. The thermal stability of the copolymer was determined from thermogravimetric analysis (TGA). The TGA curve of PBDTPO-FBT was shown in Fig. 2 and the related data were summarized in Table 1. TGA measurement displays that the 5% weight-loss temperature (T_d) of PBDTPO-FBT was 410 °C under an inert atmosphere. The thermal stability of the resulting copolymer is favorable for its application in PSCs and other optoelectronic devices.

3.3. Optical properties of the polymer

The photophysical characteristics of PBDTPO-FBT were investigated by UV–vis absorption spectra in dilute CHCl₃ solution and in a thin film spin-coated on a quartz substrate. Fig. 3 shows the normalized UV–vis absorption spectra of the copolymer and the related absorption data are summarized in Table 2. From Fig. 3, we can see that there are three absorption bands in the range of 300–700 nm for the solution and thin film. The absorption maxima of the copolymer in solution locate at 320 nm, 400 nm and 550 nm, while those of thin film are at 330 nm, 430 nm and 620 nm, respectively. The peak in the long wavelength should result from an intramolecular charge transfer (ICT) between the donor unit and the acceptor unit. The other two bands could be assigned to π–π*
transition. Compared to the solution absorption, the absorption in thin film gets broaden and red-shifted about 70 nm, indicating that a higher structural organization and stronger intermolecular interactions in solid state [16]. The optical band gap calculated from the film absorption edge is 1.53 eV.

### 3.4. Electrochemical properties of the polymer

Cyclic voltammetry (CV) is widely used to estimate the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels of the copolymers [17]. Fig. 4 shows the CV curve of PBDTPO-FBT film on a Pt electrode with 0.1 mol/L Bu4NPF6/CH3CN as the electrolyte at room temperature under argon with a scanning rate of 50 mV/s. From Fig. 4, we can see that in a positive potential region, the oxidation is quasi-reversible; the onset oxidation potential \( E_{ox}^{on} \) is 1.08 V vs Ag/AgCl, and the onset reduction potential \( E_{red}^{on} \) is −0.68 V vs Ag/AgCl. From \( E_{ox}^{on} \) and \( E_{red}^{on} \) of the copolymer, the HOMO and LUMO energy levels of PBDTPO-FBT were calculated according to the equation below [18].

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

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

The HOMO energy level of PBDTPO-FBT is −5.48 eV, which was lower than that of the air oxidation threshold (ca. −5.27 eV or 0.57 V vs SCE), indicating higher stability against oxidation [19]. As well known, the deeper HOMO level of PBDTPO-FBT is beneficial for obtaining higher \( V_ba \) when using PCBM as the acceptor. Accordingly, the LUMO level is −3.72 eV for PBDTPO-FBT. The electrochemical bandgap of 1.76 eV deducing from the electrochemical measurement is relatively higher than the optical bandgap due probably to the interface barrier for the charge injection from electrochemical measurement [20]. The related CV data are summarized in Table 2.

#### 3.5. Hole mobility

Hole mobility plays a direct effect on the charge transport in PSCs. Therefore, we measured the hole mobility of PBDTPO-FBT with a typical device structure of ITO/PEDOT:PSS/polymer:PC71BM (1:1, w/w)/Au via the space–charge–limited current (SCLC) model which is based on Poole–Frenkel Law [21]. The typical result is plotted as \( \ln(\text{Jd}^3/\text{V}^2) \) vs \( (\text{Vd})^{1/2} \), as shown in Fig. 5. Herein, \( J \) refers to current density, \( d \) stands for the thickness of the device, and \( V = V_{appl} - V_ba \), where \( V_{appl} \) is the applied potential and \( V_ba \) is the built-in potential. SCLC current can be determined by the following equation:

\[
J_{SCLC} = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu_o \left( \frac{V - V_ba}{d} \right)^2 \exp \left[ \frac{0.89}{\varepsilon_0 \varepsilon_r \mu_o} \left( \frac{V - V_ba}{d} \right)^{1/2} \right]
\]

According to Eq. (1) and Fig. 5, the average hole mobility of PBDTPO-FBT is evaluated to be \( 3.8 \times 10^{-3} \text{ cm}^2/\text{V/s} \) among the four devices. The results show that the PBDTPO-FBT/PCBM blend

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**Table 2**

Optical and electrochemical properties of the conjugated copolymer PBDTPO-FBT.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Absorption spectra</th>
<th>Cyclic voltammetry</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Solution(^a)</td>
<td>Film(^b)</td>
</tr>
<tr>
<td></td>
<td>( \lambda_{max} ) (nm)</td>
<td>( \lambda_{max} ) (nm)</td>
</tr>
<tr>
<td>PBDTPO-FBT</td>
<td>550</td>
<td>620</td>
</tr>
</tbody>
</table>

\(^a\) Measured in chloroform solution.

\(^b\) Cast from chloroform solution.

\(^c\) Bandgap estimated from the onset wavelength of the optical absorption.

\(^d\) HOMO = \(-eE_{ox}^{on} + 4.4\) (eV); LUMO = \(-eE_{red}^{on} + 4.4\) (eV) using Ag/AgCl as the reference electrode.
obtained a high mobility, which may be from the larger planar structure and close π–π stacking of copolymer.

3.6. Photovoltaic properties

In order to investigate the photovoltaic properties of the copolymer, PSCs with a sandwich structure of ITO/PEDOT:PSS/polymer:PC71BM/Ca/Al were fabricated. The PSC devices were tested under simulated 100 mW/cm², AM 1.5 G illumination. The photovoltaic performance of the polymer was firstly measured by blending with PC71BM in ODCB at different weight ratios (1:1, 1:1.5 and 1:2), 1,8-diiodooctane (DIO) was added as a processing additive. The photovoltaic curves are demonstrated in Fig. 6 and corresponding photovoltaic data are listed in Table 3. The best performance of PBDTPO-FBT was obtained at a weight ratio of 1:1, while PBDTPO-FBT:PC71BM = 1:1, the PCE is 1.96% with VOC = 0.82, JSC = 5.62 mA/cm² and FF = 42.48%. The PBDTPO-FBT based device was further investigated by adding DIO. As shown in Fig. 6(a), with 3% DIO addition, the PCE of 1:1, 1:1.5 and 1:2 weight ratios were increased to 2.70%, 2.22% and 1.95%, respectively. The improvements may originate from the rise of JSC and FF. Compared to the similar backbone polymer [10c], PBDTPO-FBT has relatively lower PCE which originated from lower FF and JSC. For this kind of polymer, an appropriate structure is still needed to obtain a higher JSC and FF. And also the photovoltaic properties can be further improved by higher molecular weight by optimizing the polymerization conditions and different processing conditions such as thermal annealing and different additive.

From Fig. 6(b), the complementary absorbance of PC71BM and polymer gives relatively high photo-conversion efficiency over the wavelength range of 350–620 nm, with monochromatic EQE values above 25%. It is worth noting that the JSC value calculated from the integration of the EQE curve closely matches with the JSC value obtained from the J–V measurements under an AM 1.5 G reference spectrum. When adding 3% DIO, it is obvious that the EQE has an increase at each weight ratio, which indicates DIO additive has an effect on PBDTPO-FBT based photovoltaic devices.

3.7. Morphology

Besides absorption, thermal stability, energy level and mobility, the nanoscale morphology of the photoactive layer is also a very vital factor for device fabrication, and in some cases the performance of the device depends strongly on its morphological characteristics [22]. Proper morphology is an important role for exciton dissociation and charge transport [23]. Here, we use AFM to investigate the morphology of the PBDTPO-FBT/PC71BM (1:1, w/w) blend films. Fig. 7 shows the height and phase images the optimized ratio (1:1) and PBDTPO-FBT:PC71BM (1:1) with 3% DIO. From the height images (Fig. 7A and B), the surface RMS (root mean-square) roughness values of the blend films for PBDTPO-FBT:PC71BM and PBDTPO-FBT:PC71BM with 3% DIO are 2.61 nm and 0.85 nm, respectively. From the phase images (Fig. 7a and b), PBDTPO-FBT:PC71BM (1:1) with 3% DIO blend showed clearer nanoscale separation morphology, which may account for higher PCE compared to the blend with PBDTPO-FBT:PC71BM (1:1) without DIO. As a result, JSC of device with 3% DIO was increased due to the more efficient charge generation and transport.

**Table 3**

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Active layer</th>
<th>Voc (V)</th>
<th>Jsc (mA/cm²)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
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</thead>
<tbody>
<tr>
<td>In ODCB drop-coating</td>
<td>PBDTPO-FBT:PC71BM = 1:1</td>
<td>0.82</td>
<td>5.62</td>
<td>42.48</td>
<td>1.96</td>
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<tr>
<td></td>
<td>PBDTPO-FBT:PC71BM = 1:1.5</td>
<td>0.81</td>
<td>5.80</td>
<td>40.29</td>
<td>1.89</td>
</tr>
<tr>
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<td>PBDTPO-FBT:PC71BM = 1:2</td>
<td>0.77</td>
<td>5.63</td>
<td>36.64</td>
<td>1.59</td>
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<tr>
<td>In ODCB with DIO</td>
<td></td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td>with DIO drop-coating</td>
<td>5% PBDTPO-FBT:PC71BM = 1:1</td>
<td>0.81</td>
<td>6.72</td>
<td>45.72</td>
<td>2.49</td>
</tr>
<tr>
<td></td>
<td>3% PBDTPO-FBT:PC71BM = 1:1</td>
<td>0.79</td>
<td>7.23</td>
<td>47.08</td>
<td>2.70</td>
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<tr>
<td></td>
<td>5% PBDTPO-FBT:PC71BM = 1:1.5</td>
<td>0.80</td>
<td>6.48</td>
<td>42.72</td>
<td>2.22</td>
</tr>
<tr>
<td></td>
<td>3% PBDTPO-FBT:PC71BM = 1:2</td>
<td>0.76</td>
<td>6.40</td>
<td>40.13</td>
<td>1.95</td>
</tr>
</tbody>
</table>

Fig. 6. (a) J–V curves of the PSCs based on PBDTPO-FBT:PC71BM (1:1, 1:1.5 and 1:2, w/w) or with 3% DIO, under illumination of AM 1.5, 100 mW/cm². (b) EQE spectra of PSCs based on PBDTPO-FBT:PC71BM (1:1, 1:1.5 and 1:2, w/w) or with 3% DIO.
4. Conclusion

In summary, we have synthesized a new D–A conjugated polymer based on fluorinated benzothiadiazole (FBT) unit and alkyl-oxyphenyl substituted benz[1,2-b:4,5-b′]dithiophene (BDTPO) unit. The polymer PBDTPO-FBT shows good absorption in the visible region and moderate hole mobility. When blended with PC71BM in PSCs processed without additive, the low PCE is limited by a low $J_{sc}$ and $FF$. When 3% DIO was used as an additive, the value of $J_{sc}$ and $FF$ had increased and we obtained an increasing PCE up to 2.70% from 1.96%, accountable to improved film morphology for exciton generation and charge transportation.

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