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# Two new medium bandgap asymmetric copolymers based on thieno [2,3-*f*]benzofuran for efficient organic solar cells



PIGMENTS

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#### ABSTRACT

Two new medium bandgap, alkoxyphenyl substituted thieno[2,3-*f*]benzofuran (TBFPO) and alkoxyl substituted thieno[2,3-*f*]benzofuran (TBFP)-based polymers were designed, synthesized and applied in polymer solar cells (PSCs), namely, TBFPO-BDD and TBFO-BDD, respectively. Their <u>thermal</u>, optical, electronic properties and photovoltaic performances were systematically investigated. The PSCs prepared using o-dichlorobenzene as solvent, with the single layer device structure of ITO/PEDOT:PSS/TBFPO-BDD:PC<sub>71</sub>BM (1:1; *w/w)*/perylene diimide (PDI) derivative (PDINO)/Al, exhibited a promising power conversion efficiency (PCE) of 6.58% under the illumination of AM 1.5G, 100 mW/cm<sup>2</sup>, without any post-treatment. While the devices based on TBFO-BDD showed an enhanced PCE of 3.07% with 1 vol% 1,8-diodooctane (DIO) as additive. This study demonstrates that TBFPO-BDD is a promising polymer for organic electronics.

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# 1. Introduction

Organic photovoltaics (OPVs) have been considered as one of the most promising candidates for practical photovoltaic applications to solve the increasing energy problems worldwide due to light weight, low-cost, flexible devices through roll-to-roll solution processes and impressive conversion efficiency [1]. Over the past several decades, significant efforts have been made to optimize the performance of OPVs, as a result, the power conversion efficiencies (PCEs) of polymer solar cells (PSCs) have been achieved up to 11.7% [2] using conventional, single-layer bulk heterojunction (BHJ) OPVs and over 12% for tandem cells [3], with the development of photoactive materials, interface engineering and device modification. Although the result is satisfactory, it is still a need to design and synthesize ideal donor materials to improve PCEs by chemical structure modifications and in-depth investigation of the relationship between structure and properties to push this technology toward commercial applications [4–7].

As is well-known, using fusion of aromatic rings, optimization of side chains and extending *p*-conjugation systems could improve PCEs. Side chains in conjugated polymers play a crucial role in

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regulating solubility, electronic and morphological properties [8-11]. Therefore optimizing side chains is considered as an important issue for the molecular design for PSCs [12-16]. Generally, two-dimensional (2D) conjugated polymers not only have broad and strong absorption bands due to extended side chains, but also have larger conjugated planes, better inter-chain overlap and higher charge mobility than one-dimensional conjugated polymers [17]. Benzodichalcogenophene (BDC) derivatives have been widely used in BHJ PSCs and deeply investigated by many groups owing to their lower highest occupied molecular orbital (HOMO) level and stronger absorption, which contributed to obtain high open-circuit voltage ( $V_{oc}$ ) and short circuit current ( $I_{sc}$ ) [18–20]. Many low bandgap benzo[1,2-b:4,5-b']dithiophene (BDT) [21,22] based conjugated polymers with different side chains were studied by several groups. Hou et al. have synthesized 2D-conjugated polymers PBDTTT-E-T and PBDTTT-C-T by introducing conjugated thiophene side chains instead of alkoxy substituents on BDT unit. Hou and Li et al. introduced alkylthiol side chain in PPV to tune the optoelectronic properties of PPV derivatives in 2006 [23]. Later, Li and Huo et al. have reported a series of 2D-BDT conjugated copolymers with the alkylthienyl side chains in comparison to alkyl and alkoxyl group to explore the effects of different side groups on PCEs [24]. Our group has also reported several 2D-conjugated BDT and BDFbased polymers with substituted alkoxyphenyl or alkylthienyl groups as the conjugated side chains, which have shown desirable



photovoltaic performance [25–27]. Recently, Huo et al. reported a 2D-conjugated polymer PBDF-T1 delivering a high PCE of 9.43% with additive treatment [28]. However, the asymmetric structure of BDC derivatives, thieno[2,3-*f*]benzofuran (TBF), has not been widely used and explored in PSCs. Some copolymers based on TBF unit have been synthesized and investigated by our group, such as PTBFTDTBT, PTBFP-BT, PTBFP-BO, TBFBT, TBFPF-BT and TBFPF-BO (shown in Fig. S1) with PCEs of 6.40%, 6.02%, 4.41%, 6.10%, 6.80% and 5.98%, respectively [29–31]. Except for the asymmetric structure TBF, the difluoro-benzothiadiazole (DFBT) [32] unit and the dithieno[3,2-b:2',3'-d]pyran (DTPa) building block [33] have been also investigated to explore the effects of asymmetric structure on the photovoltaic performances.

To further explore the copolymers based on TBF unit with or without 2D-cojugated side chains, in this work, two new medium bandgap, alkoxyphenyl and alkoxyl substituted thieno[2,3-*f*] benzofuran (TBF)-based polymers were designed, synthesized and

applied in PSCs, named TBFPO-BDD and TBFO-BDD, as shown in Scheme 1, which possess good solubility, broad absorption in the wavelength range from 300 nm to 700 nm and balanced charge mobility. In order to enhance the photovoltaic performance, we used two type of interlayers, zirconium acetylacetonate (ZrAcac) and perylene diimide (PDI) derivatives (PDINO), shown in Fig. S2. The PSCs with the device structure of ITO/PEDOT:PSS/TBFPO-BDD:PC<sub>71</sub>BM(1:1;*w*/*w*)/PDINO/Al, exhibited a promising PCE of 6.58% without any post-treatment. While the devices based on TBFO-BDD showed an enhanced PCE of 3.07% with 1% 1,8-diodooctane (DIO) as additive.

# 2. Experimental section

#### 2.1. Materials

Pd(PPh<sub>3</sub>)<sub>4</sub>, tetrahydrofuran (THF) and Sn(CH<sub>3</sub>)<sub>3</sub>Cl were obtained



Scheme 1. The Synthetic route of the monomers and polymers.

from J&K and Alfa Asia Chemical Co., and they were used as received. Toluene was dried over Na/benzophenone and freshly distilled prior to use. All other reagents and solvents were purchased commercially as ACS-grade quality and used without further purification.

#### 2.2. Characterization

The polymer structures were confirmed by nuclear magnetic resonance (NMR) spectroscopy which was recorded using a Bruker DMX-400 spectrometer or DMX-500 spectrometer in deuterated chloroform solution at 298 K. Chemical shifts were reported in ppm with tetramethylsilane (TMS) as the internal reference (0.00 ppm). Molecular weight and polydispersity of the polymers were determined by gel permeation chromatography (GPC) analysis with polystyrene as standard. Thermogravimetric analysis (TGA) was conducted on a Perkin-Elmer TGA-7 with a heating rate of 10 K/min under inert atmosphere. UV-Vis absorption spectra were recorded on the Hitachi U-3010 UV-vis spectrophotometer. For the solid state measurements, polymer in chloroform solution was spincoated on quartz plates. Cyclic voltammetry was recorded with a computer controlled Zahner IM6e electrochemical workstation using polymer films on a platinum disk (1.0 cm<sup>2</sup>) as the working electrode, a platinum wire as the counter electrode and Ag/AgCl (0.1 mol/L) as the reference electrode in an anhydrous and argonsaturated solution of 0.1 mol/L tetrabutyl ammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>) in acetonitrile solution at a scan rate of 50 mV/s. Electrochemical onsets were determined at the position where the current starts to differ from the baseline. The morphologies of the polymer/PC71BM blend films were investigated by a SPI 3800N atomic force microscope (AFM) in contacting mode with a 3 mm scanner.

#### 2.3. Fabrication and characterization of polymer solar cells

The PSCs were fabricated in the configuration of ITO/PEDOT: PSS (40 nm)/active layer/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, isopropanol and then treated in an ultraviolet-ozone chamber (Jelight Company, 20 min. Then PEDOT:PSS (poly(3,4-ethylen USA) for edioxythiophene):poly(styrene-sulfonate)) (Baytron P VP AI 4083 from H. C. Starck) was filtered through a 0.45 µm poly(tetrafluoroethylene) (PTFE) filter and spin coating at 4000 rpm for 40 s on the ITO substrate. Subsequently, PEDOT: PSS film was baked at 150 °C for 15 min in the air. The polymer and PC<sub>71</sub>BM (10 mg/mL for polymer) were dissolved in ODCB overnight, and spin-cast onto the PEDOT: PSS layer. DIO was added to the blend solutions before spincoating. Then methanol solutions of PDINO and ZrAcac at a concentration of 1.0 mg/mL were then deposited atop the active layer at 3000 rpm for 30 s to afford a thickness of 10 nm. Lately, top Al (~100 nm) electrode was thermally evaporated under a shadow mask with a base pressure of ca.  $10^{-5}$  Pa. The active area of the PSCs is 4.7 mm<sup>2</sup>. Device characterizations were carried out under AM 1.5G irradiation with the intensity of 100 mW/cm<sup>2</sup> by a Newport Oriel 91150V reference cell. J-V curves were recorded on a computer-controlled Keithley 2450 Source-Measure Unit. Oriel Sol3A Class AAA Solar Simulator (model, Newport 94023A) with a 450 W xenon lamp and an air mass (AM) 1.5 filter was used as the light source. The EQE measurements were performed by Solar Cell Spectral Response Measurement System QE-R3-011 (Enli Technology Co., Ltd., Taiwan). The light intensity at each wavelength was calibrated with a standard single-crystal Si photovoltaic cell. The thickness of the interlayer was determined by a profilometer (Ambios Tech. XP-2). All of these fabrications and characterizations after cleaning of ITO substrates were conducted in a glove box.

#### 2.4. Synthesis

2,6-Bis(trimethyltin)-4,8-bis(4-ethylhexyloxy-1-phenyl)thieno-[2,3-*f*]benzofuran (M1) [30] and 2,6-Bis(trimethyltin)-4,8bis(2-ethylhexyloxy)- thieno[2,3-*f*]benzofuran (M2) [34] were synthesized according to our published procedures; 1,3bis(thiophen-2-yl)-5,7-bis(2-ethylhexyl)benzo-[1,2-*c*:4,5-*c*]dithiophene-4,8-dione (M3) [10,14,35,36], was prepared according to the literature procedures. The detailed synthetic route to polymers were shown in Scheme 1. The monomer's detailed synthetic procedures were shown in SI.

#### 2.5. Synthesis of TBFPO-BDD

A solution of M1 (0.136 g, 0.15 mmol), M3 (0.115 g, 0.15 mmol) in dry toluene (10 mL) was put into a two-necked flask. The solution was flushed with argon for 20 min and Pd(PPh<sub>3</sub>)<sub>4</sub> (15 mg) was added into the flask. The solution was flushed with argon again for 20 min. The oil bath was carefully heated to 110 °C and the reactant was stirred for 24 h at this temperature under an argon atmosphere. After the reaction mixture was cooled to room temperature, the mixture was poured into methanol (150 mL) slowly, allowing the crude polymer to precipitate. After filtration, the crude product was subjected to Soxhlet extractions with methanol, hexane and chloroform in sequence. The chloroform fraction was evaporated to dryness and further dried under vacuum for 1 day to get the final product as a blue black solid (150 mg, yield: 81%). Elemental analysis calculated for  $C_{72}H_{82}O_5S_5$ : C, 72.81; H, 6.96; S, 13.50: Actual analysis: C,72.85; H, 6.95, S, 13.51.

GPC (THF):  $M_n = 32$  kDa;  $M_w = 65$  kDa; PDI = 1.83.

#### 2.6. Synthesis of TBFO–BDD

TBFO–BDD was obtained by a similar procedure with the synthesis of TBFPO-BDD starting from M2 (0.114 g, 0.15 mmol) and M3 (0.115 g, 0.15 mmol). The final product was a purple blue solid. (145 mg, yield: 79%). Elemental analysis calculated for C<sub>60</sub>H<sub>74</sub>O<sub>5</sub>S<sub>5</sub>: C, 60.59; H, 7.20; S, 15.48; Actual analysis: C,60.54; H, 7.24; S, 15.42. GPC (THF):  $M_n = 17$  kDa;  $M_w = 36$  kDa; PDI = 1.62.

# 3. Results and discussion

#### 3.1. Thermal stability and polymerization result

The thermal stability of the polymers were investigated by TGA in an inert atmosphere, and the TGA plots of the two polymers are shown in Fig. S2. The TGA profiles reveal that two polymers possess similar thermal stabilities. Although the onset points of the 5% weight loss ( $T_d$ ) of the polymers are under 300 °C, the thermal stability of TBFPO-BDD and TBFO-BDD is still good enough for PSCs. Molecular weights determined by GPC using THF as eluent were 32 kDa ( $M_n$ ) and 65 kDa ( $M_w$ ) for TBFPO-BDD and 17 kDa ( $M_n$ ) and 36 kDa ( $M_w$ ) for TBFO-BDD with corresponding polydispersity indices (PDI) of 1.83 and 1.62, respectively. The TGA and GPC data are shown in Table 1.

#### 3.2. Optical properties

The spectral absorption of two polymers could reflect their ability to utilize solar spectrum, which usually have a direct impact on  $J_{sc}$ . Fig. 1a shows the UV–Vis absorption spectra of the conjugated polymers in chloroform solution and as a thin film on a

#### Table 1

Molecular weights and thermal properties of the polymers.

Polymers	$M_{\rm w}^{\rm a}$ (KDa)	$M_{\rm n}^{\rm a}$ (KDa)	PDI <sup>a</sup>	$T_d{}^b(^\circ C)$
TBFPO-BDD	65	32	1.83	287
TBFO-BDD	36	17	1.62	255

<sup>a</sup>  $M_{\rm n}$ ,  $M_{\rm w}$  and PDI of the polymers were determined by GPC using polystyrene standard in THF.

The 5% weight-loss temperatures under inert atmosphere.



Fig. 1. (a) UV-Vis absorption spectra of two polymers in solution and film states; (b) Absorption coefficient spectra of the pure polymer film and polymer:PC71BM blend film.

quartz substrate cast from chloroform solution, the related absorption data are listed in Table 2 for comparison. As expected, the introduction of a conjugated benzene ring on TBF moiety from

Table 2	
The data of absorption spectra and cy	clic voltammetry.



Fig. 2. (a) Cyclic voltammograms of polymer films on a glassy carbon electrode in 0.1 M Bu<sub>4</sub>NPF<sub>6</sub>, CH<sub>3</sub>CN solution. (b) The energy diagram of the materials involved in PSCs.

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TBFPO-BDD caused red shifts in absorption maximum in the solution compared to that of TBFO-BDD, and similar phenomenon was observed in the solid films. For example, the TBFPO-BDD solution exhibited the broader absorption with the red shifted absorption peak at 581 nm which contributed to higher Jsc compared with TBFO-BDD peaking at 550 nm. Moreover, the film spectra exhibited broad absorption over the range from 300 to 750 nm and had two strong absorption peaks [37]. From Fig. 1b, the pure TBFPO-BDD  $(6.17 \times 10^4)$  and the blend film  $(4.01 \times 10^4)$  have higher absorption coefficient than the TBFO-BDD ( $5.61 \times 10^4$ ) and the TBFO-BDD/ PC<sub>71</sub>BM blend  $(3.51 \times 10^4)$  in the maximum absorption wavelength.

Polymers	Absorption spect	Absorption spectra			Cyclic voltammetry	ry	
	Solutiona <sup>a</sup>	Film <sup>b</sup>	Film <sup>b</sup>		p-doping	n-doping	
	$\lambda_{\max}$ (nm)	$\lambda_{\max}$ (nm)	$\lambda_{edge} (nm)$	$E_g^{opt}$	$\overline{E_{ox}/\text{HOMO}^{d}(V)/(eV)}$	E <sub>red</sub> /LUMO (V)/(eV)	
TBFPO-BDD TBFO-BDD	581 550	628 607	706 683	1.76 <sup>c</sup> 1.80 <sup>c</sup>	0.89/-5.30 0.86/-5.27	-0.76/-3.65 -0.95/-3.46	

<sup>a</sup> Measured in chloroform solution. <sup>b</sup> Cast from chloroform solution.

<sup>c</sup> Bandgap estimated from the onset of the optical absorption.

<sup>d</sup> HOMO =  $-e(E_{ox} + 4.41)$  (eV); LUMO =  $-e(E_{red} + 4.41)$  (eV).

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**Fig. 3.** (a) The hole and electron mobilities of the TBFPO-BDD:PC<sub>71</sub>BM (b) The hole and electron mobilities of the TBFO-BDD:PC<sub>71</sub>BM.

The optical band gaps ( $E_g^{opt}$ ) estimated from the UV–Vis absorption onsets in solid state of TBFPO-BDD and TBFO-BDD are determined to be 1.76 eV, 1.81 eV, respectively.

## 3.3. Electrochemical properties

Cvclic voltammetry is used to measure the HOMO and LUMO energy levels of the polymers, which were calculated from the onset oxidation and reduction potentials. As shown in Fig. 2a and b, the onset reduction potentials  $(E_{red})$  of TBFPO-BDD and TBFO-BDD are -0.76 V and -0.95 V, while the onset oxidation potentials ( $E_{ox}$ ) are 0.89 V and 0.86 V, respectively. It is well known that the HOMO and LUMO levels of the polymers were calculated according to the equations, HOMO =  $-e(E_{ox} + 4.41)$  (eV); LUMO =  $-e(E_{red} + 4.41)$ (eV), where the unit of  $E_{ox}$  and  $E_{red}$  is in V vs. Ag/AgCl. The HOMO and LUMO levels of TBFPO-BDD and TBFO-BDD are -5.30 eV/ -3.65 eV and -5.27 eV/-3.46 eV, respectively. The investigation shows that the two polymers possess low lying HOMO level, which offers the potential to obtain high  $V_{oc}$  [38]. Moreover, their LUMO energy level offset from PCBM acceptor is enough for charge transfer and separation [39]. The related CV data are summarized in Table 2.



**Fig. 4.** (a) Current density–voltage (*J*–V) characteristics; (b) External quantum efficiency (EQE) spectra of TBFPO–BDD and TBFO–BDD based solar cells; (c) Light intensity dependence of the short-circuit current density.

#### 3.4. Mobility measurements

The charge mobility has an important impact upon the PCE. Charge mobilities were measured by space-charge-limited current (SCLC) method with a structure of ITO/PEDOT: PSS/polymer:

#### Table 3

Summary of the photovoltaic characteristics of the polymer:PC<sub>71</sub>BM blend films.

	Ratio	$V_{\rm oc}\left({\sf V}\right)$	$J_{\rm sc}~({\rm mA/cm^2})$	FF (%)	PCE <sub>max</sub> (%)	PCE <sub>avg</sub> <sup>d</sup> (%)	$R_s^e (\Omega \ cm^2)$
TBFPO-BDD:PC71BM	1:1 <sup>a</sup>	0.82	12.81	62	6.58	6.32	11.29
	1:1 <sup>b</sup>	0.82	12.10	63	6.26	6.14	11.70
	1:2 <sup>b</sup>	0.84	8.59	68	4.87	4.76	13.85
	1:1 <sup>a,c</sup>	0.79	12.07	65	6.22	6.20	11.43
	1:1 <sup>b,c</sup>	0.80	11.56	67	6.21	6.18	11.77
TBFO-BDD:PC71BM	1:1 <sup>a</sup>	0.83	5.36	51	2.29	2.23	52.58
	1:1 <sup>b</sup>	0.83	5.41	49	2.18	2.15	55.94
	1:2 <sup>b</sup>	0.84	3.63	56	1.71	1.70	59.03
	1:1 <sup>a,c</sup>	0.81	8.52	46	3.21	3.07	31.32
	1:1 <sup>b,c</sup>	0.79	8.28	46	3.05	3.02	33.49

<sup>a</sup> Device structure of ITO/PEDOT:PSS/polymer:PC71BM/PDINO/Al.

<sup>b</sup> Device structure of ITO/PEDOT:PSS/polymerPC<sub>71</sub>BM/ZrAcac/Al.

<sup>c</sup> With 1% DIO as additive.

<sup>d</sup> PCEavg is the data obtained from 20 devices.

<sup>e</sup> Calculated from the inverse slope at V = 0 in *J*-*V* curves under illumination.

PC<sub>71</sub>BM (1:1; w/w) with or without 1% DIO/Au for holes and Al/ polymer: PC<sub>71</sub>BM (1:1; w/w) with or without 1% DIO/Al for electrons. The results are plotted as  $J^{1/2} \sim (V_{appl} - V_{bi})$ , as shown in Fig. 3a and b, the hole and electron mobilities are calculated by MOTT-Gurney equation [40,41]. The SCLC is described by

$$J_{\rm SCLC} = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu \frac{V^2}{d^3}$$

where I is the current density, d stands for the thickness of the device,  $\varepsilon_r$  is the relative dielectric constant of active layer material usually 2-4 for organic semiconductor, herein we use a relative dielectric constant of 4,  $\varepsilon_0$  is the permittivity of empty space,  $\mu$  is the mobility of hole or electron, V is the internal voltage in the device, and  $V = V_{appl} - V_{bi}$ , where  $V_{appl}$  is the applied potential and  $V_{bi}$  is the built-in potential (in the hole-only and the electron-only devices,  $V_{\rm bi}$  values are 0.2 V and 0 V, respectively). The hole and electron mobilities of the TBFPO-BDD/PC71BM blend without any treatment can be calculated to be  $1.84 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , and  $1.21 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , respectively, while  $5.10 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ,  $4.17 \times 10^{-5}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> with 1% DIO treatment. This result suggests DIO may suppress exciton separation and transport in TBFPO-BDD/ PC71BM blend system However, the hole and electron mobilities of the TBFO-BDD/PC71BM blend with 1% DIO as additive, which is conducive to form the interpenetrating networks to realize the separation and transport of exciton, are 2.62  $\times$  10<sup>-5</sup> cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>,  $3.86 \times 10^{-5}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, respectively, higher than  $1.19 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and  $0.20 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  without 1% DIO.

#### 3.5. Photovoltaic properties

In order to investigate the photovoltaic properties of two different polymers, PSC devices with a configuration of ITO/ PEDOT:PSS/polymer:PC<sub>71</sub>BM/PDINO(ZrAcac)/Al were prepared and measured by blending with PC<sub>71</sub>BM in ODCB at different weight ratios (*w*/*w*; 1:1 and 1:2), DIO as additive. Fig. 4a shows the typical current density-voltage (*J*-V) curves under the illumination of AM 1.5G, 100 mW/cm<sup>2</sup> and the corresponding device performance including  $V_{oc}$ ,  $J_{sc}$ . FF and PCE at different fabrication conditions is also summarized in Table 3. The highest PCE of TBFPO-BDD up to 6.58% was obtained at a weight ratio of 1:1 without any treatment, while the PCE of TBFO-BDD at 1:1 wt ratio was increased from 2.29% to 3.21% with the addition of 1% DIO. Using ZrAcac and PDINO as the different cathode buffer layer, the data of photovoltaic performances are shown in Table 3. The different PCEs of TBFPO-BDD and TBFO-BDD are mainly originated from  $J_{sc}$  and FF. Also the

photovoltaic properties can be further improved via higher molecular weight by optimizing the polymerization conditions and different processing conditions such as thermal annealing and different additives. Recently, non-fullerene n-type organic semiconductors consists of n-type polymers and small molecules [42–45] have attracted extensive attention, especially n-type small acceptor ITIC [46], in this work, we also fabricated the nonfullerene devices based on TBFPO-BDD/ITIC and TBFO-BDD/ITIC. The result indicates that when TBFPO-BDD blending with ITIC (with or without DIO), there is no any improvement of the photovoltaic performance than those of PC<sub>71</sub>BM (6.58%). However, compared with the TBFPO-BDD:PC<sub>71</sub>BM, the PCEs of devices based on TBFO-BDD: ITIC (with and without DIO) both have lager improvement as shown in Table S1. EQEs of PSCs under the best condition with PDINO as cathode layer for TBFPO-BDD:PC71BM without any treatment and TBFPO-BDD: PC71BM with 1% DIO as solvent additive are shown in Fig. 4b. The EQE curves are essentially in accordance with the absorption wavelength range from Fig. 1, BHJ solar cells exhibit a spectral response from 300 nm to 700 nm with a broad and flat peak value around 60%-70% at approximately 350-650 nm for TBFPO-BDD and 30%-40% at approximately 370-650 nm for TBFO-BDD without any treatment, respectively. Additionally, a less than 5% deviation between J<sub>sc</sub> and the integral of the EQE is observed. Moreover, light-intensity dependence of photovoltaic performance with the optimized condition is further used to investigate the charge recombination behavior in the devices, which is regarded as one of the determining factors to affect the value of  $J_{sc}$  [47]. Generally,  $J_{sc}$  follows a power-law dependence on  $P_{\text{light}}$  ( $J_{\text{sc}} \propto \text{Plight } \alpha$ ), where power-law component ( $\alpha$ ) should be 1 when the bimolecular recombination of the charge carriers is weak. As shown in Fig. 4c, the  $\alpha$  value of the TBFO-BDD as donor material is 0.93, while the  $\alpha$  value of the TBFPO-BDD is 0.97, which suggests that the TBFPO-BDD as donor material in PSCs can suppress the bimolecular recombination well in correlation well with the higher charge carrier mobilities of the devices mentioned above.

# 3.6. Morphology

The nanoscale morphology of the photoactive layer is also important for device performances compared with absorption, energy level and mobility, which is related to exciton dissociation and charge transport. Therefore, we investigated the surface morphology of the active layer by AFM (shown in Fig. 5a–h). The surface roughness (RMS, root-mean-square) of TBFPO-BDD:PC<sub>71</sub>BM (1:1) blend (without or with 1% DIO as additive) decreases from 1.23 nm (Fig. 5a) to 0.60 nm (Fig. 5c). Moreover, comparing with 1%



Fig. 5. Tapping mode AFM height images: (a) TBFPO-BDD without DIO, (c) TBFPO-BDD with DIO, (e) TBFO-BDD without DIO, (g) TBFO-BDD with DIO and phase images: (b) TBFPO-BDD without DIO, (d) TBFPO-BDD with DIO, (f) TBFO-BDD without DIO, (h) TBFO-BDD with DIO of the surface of the blend of polymer with  $PC_{71}BM$  (1:1) (size:  $3 \times 3 \mu m^2$ ). Root-mean-square (RMS) roughness values are given to describe the smoothness of the morphology.

DIO treatment, the phase images (Fig. 5b without DIO treatment) shows better crystalline grains. Together with the photovoltaic data in Table 3, the addition of DIO has decreased PCE of TBFPO-BDD. By contrast, the TBFO-BDD has the opposite results, the RMS of TBFPO-BDD:  $PC_{71}BM(1:1)$  (without or with 1% DIO as solvent additive) increases from 0.63 nm to 0.93 nm from Fig. 5e and h. The blend with 1% DIO as shown in Fig. 5h has more surface aggregates with no large phase separation, the addition of DIO can improve PCE from 2.15% to 3.07% for of TBFO-BDD/PC<sub>71</sub>BM blend.

#### 4. Conclusion

In summary, we have designed and synthesized two new medium bandgap alkoxyphenyl and alkoxyl substituted thieno[2,3-*f*] benzofuran (TBF)-based polymers to further explore the copolymers without or with 2D-cojugated side chains. The 2D-cojugated polymer, TBFPO-BDD, with a single layer device structure of ITO/PEDOT:PSS/TBFPO-BDD:PC71BM(1:1; *w/w*)/PDINO/Al, exhibited a promising PCE of 6.58% under the illumination of AM 1.5G, 100 mW/cm<sup>2</sup>, without any post-treatment, with higher  $J_{sc}$  and FF compared to those of TBFO-BDD, which exhibited a PCE of 3.07% with 1% DIO as additive. This investigation demonstrates that 2Dcojugated polymer with an asymmetric structure is promising for organic electronics.

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# Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2017.01.058.

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