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A copolymer based on benzo[1,2-b:4,5-b']dithiophene and quinoxaline derivative for photovoltaic application

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1. Introduction

Polymer bulk-heterojunction (BHJ) solar cells with an increasing demand on cheap renewable energy source have drawn broad attention in recent years, owing to their advantages of light weight, low cost, easy fabrication and large-area devices through roll to roll printing [1–5]. In this type of device, a phase separated blend of electron-accepting material and electron-donating material is used as the active layer. [6,6]-phenyl-C-61-butyric acid methyl ester (PC₆₁BM) is the common-used acceptor material and poly(3-hexylthiophene) (P3HT) [6–8] is a representative conjugated donor material. However the shortcoming of P3HT is the quite large band gap and high HOMO level, which may limit the absorption from the solar spectrum and reduce the value of V_{oc} , respectively. The power conversion efficiency (PCE) of polymer solar cells (PSCs) based on the thin film blended with PC₆₁BM is limited to 4–5% [9].

To achieve high performance BHJ polymer solar cells, one efficient way is to design alternating donor–acceptor–donor (D–A–D) copolymers combined electron-rich (donor) and electron-deficient (acceptor) moieties, which can modulate the energy

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ABSTRACT

A D–A–D copolymer (PBDTQx) with a bandgap of 1.78 eV, containing alkoxy-substituted benzo[1,2-b:4,5-b']dithiophene (BDT) as donor and quinoxaline derivative (Qx) as acceptor, was synthesized by Stille coupling reaction. In order to study the photovoltaic property of PBDTQx, polymer solar cells (PSCs) were fabricated with PBDTQx as the electron donor blended with [6,6]-phenyl-C61-butyric acid methyl ester (PC₆₁BM) as the electron acceptor. The power conversion efficiency (PCE) of PSC was 1.01% for an optimized PBDTQx: PC₆₁BM ratio of 11:5, under the illumination of AM 1.5, 100 mW/cm². The results indicated that PBDTQx was a promising donor candidate in the application of polymer solar cells.

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levels and absorption properties by controlling the intermolecular charge transferring from the donor to the acceptor. Recently, many kinds of D–A–D copolymers have been developed and excellent photovoltaic properties with PCE as high as 3–8% have been achieved [10]. Among these conjugated copolymers, polymers based on benzo[1,2-b:4,5-b']dithiophene (BDT) units as electron donors and electron-deficient units like thieno[3,4-b]thiophene (TT) [11,12], N-alkylthieno[3,4-c]pyrrole-4,6-dione (TPD) [13], and 4,7-dithiophene-2-yl-2,1,3-benzothia-diazole (DTBT) [14], have attracted much attention in the PSC field and promising photovoltaic properties have been achieved for this type of polymers.

Meanwhile, as a type of acceptors, quinoxaline can effectively tune the band gap and energy levels due to the electron-deficient N-heterocycle. For example, APFO-15-based device had a low HOMO of -5.36 eV and a high V_{oc} of 1.0 V [15], quinoxaline-based copolymer TQ1 exhibited a V_{oc} of 0.9 V and a very low-lying HOMO of -5.7 eV [16], and PECz–DTQx showed a high PCE of 6.07% with PFN as the cathode interlayer [17]. Although copolymers based on BDT or quinoxaline exhibited promising photovoltaic performance [18], the copolymers based on BDT and quinoxaline is less reported in photovoltaic fields to the best of our knowledge.

In this work, we synthesized a copolymer (PBDTQx) using BDT as electron-donating moiety and quinoxaline as electron-accepting moiety, respectively. The photovoltaic performance under AM1.5 conditions with a V_{oc} of 0.80 V, J_{sc} of 2.67 mA/cm², a fill factor

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(FF) of 0.47, and a power conversion efficiency (PCE) of 1.01% was achieved by the copolymer (PBDTQx:PC₆₁BM, 1:5 w/w, in chlorobenzene solution) due to its interpenetrating network morphology of PBDTQx:PC₆₁BM blend film.

2. Materials and methods

2.1. Synthesis of the polymer

All chemicals and reagents are obtained from Aldrich and Alfa Aesar. THF is dried over Na/benzophenone ketyl and freshly distilled prior to use. The synthetic routes of monomers and copolymer are shown in Scheme 1. Monomers of 3,6-dibromo-1,2phenylenediamine (2) and 1,2-bis(3-(octyloxy)phenyl)ethane-1,2dione (5) were prepared according to the published literature [15] and dissolved in acetic acid to obtain 5,8-dibromo-2,3-bis(3-(octyloxy)phenyl)- quinoxaline (9) in high yield of 97%. 2,6-Bis(trimethyltin)-4,8-bis(2-ethylhexyl)benzo[1,2-b:3,4-b']dithiophene

was adopted as a electron donor and prepared according to the literature [19]. PBDTQx was synthesized by Stille polycondensation of monomer 8 and 9. The molecular weight and polydispersity index of the resulting polymer were recorded by GPC analysis, which shows a large number-average molecular weight (M_n) of 192.86 kDa, with the corresponding polydispersity index (PDI) of 2.88.

2.1.1. 3,6-Dibromo-1,2-phenylenediamine (2)

4,7-Dibromo-2,1,3-benzothiadiazole (1) (8.82 g, 0.03 mol) was dissolved in ethanol (190 ml), to the suspension was added portionwise sodium borohydride (21 g, 0.55 mol) at 0 °C, and the mixture was stirred for 20 h at room temperature. Then evaporation of the solvent, 200 ml water was added, and the mixture was extracted with ethyl acetate. The extract was washed with brine and dried over anhydrous magnesium sulfate. After evaporation of the solvent, the residue was purified by column chromatography on silica gel using hexane/ethyl acetate (25:1) as eluent to afford 3,6-dibromo-1,2-phenylenediamine (5.01 g) as a pale solid in 63% yield. ¹H NMR (CDCl₃, 500 MHz) δ (ppm): 6.80(s,2H), 3.60(s,4H). ¹³C NMR (CDCl₃, 500 MHz) δ (ppm): 133.85, 123.08, 109.66. GC-MS: *m/z* = 263.

2.1.2. 1,2-Bis(3-(octyloxy)phenyl)ethane-1,2-dione (5)

A THF solution of anhydrous LiBr (3.19 g, 36.8 mmol, 15 ml) was added to a suspension of CuBr (2.64 g, 18.4 mmol) in THF (15 ml) under nitrogen. The mixture was stirred at room temperature until it became homogeneous and was then cooled to 0 °C in an icewater bath. A freshly prepared solution of 3-octyloxybenzene magnesium bromide in THF (5.23 g, 18.4 mmol, 20 ml) was added dropwise to the mixture. After 10 min, oxalyl chloride (1.04 g, 8.22 mmol) was added and the mixture was stirred at 0 °C for 20 min, Then the reaction was quenched with saturated aqueous NH₄Cl and extracted with ethyl acetate, the combined organic



Scheme 1. Synthesis routes of the copolymer PBDTQx.

layer was washed with brine and dried over anhydrous magnesium sulfate. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel using hexane/ethyl acetate (100:1) as eluent to afford compound 5 (2.03 g) as a white solid in yield 53%. ¹H NMR (CDCl₃, 500 MHz) δ (ppm):7.51(s,2H), 7.45(m,2H), 7.38(t,2H, *J* = 8 Hz), 7.19(ddd,2H, *J* = 5 Hz), 4.00(t,4H, *J* = 6.5 Hz), 1.79(m,4H), 1.46(m,4H), 1.33(m,16H), 0.89(t,6H, *J* = 5 Hz). ¹³C NMR (CDCl₃, 500 MHz) δ (ppm): 194.56, 158.36, 133.91, 129.88, 122.80, 122.15, 113.72, 68.39, 31.81, 29.33, 29.23, 29.13, 26.01, 22.67, 14.11. GC–MS: *m*/*z* = 466.

2.1.3. 2,6-Bis(trimethyltin)-4,8-bis(2-ethylhexyl)benzo[1,2-b:3,4-b']dithiophene (8)

In a flask, 4.8-dihvdrobenzo[1.2-b:4.5-b']dithiophen-4.8-dione (6) (6.6 g, 30 mmol) and zinc powder (4.29 g, 66 mmol) were added to 90 ml of water, then 18 g of NaOH was added into the mixture. After the solution was refluxed for 1 h, 1-bromo-2-ethylhexane (17.4 g, 90 mmol) and a catalytic amount of tetrabutylammonium bromide were added and heated to reflux for another 6 h. Then, cold water (300 ml) was added and the mixture was extracted with ethyl acetate, the extract was dried over anhydrous magnesium sulfate, the residue was purified by column chromatography on silica gel to obtain 4,8-bis(2-ethylhexyloxy)benzo[1,2-b:3,4-b]dithiophene (7) in a 65% yield. Compound 7 (6.1 g, 13.6 mmol) was added into THF (200 ml) under nitrogen, n-butyllithium (36.3 mmol, 2.2 M) was added dropwise to the mixture at -80 °C and stirred for 1 h, the cooling bath was removed, and the reactant was stirred at ambient temperature for another 1 h. Trimethyltin chloride (8 g, 40.4 mmol) was added in one portion at -80 °C and the reactant was stirred at ambient temperature overnight. After 200 ml cold water was added and the mixture was extracted with hexane, the organic layer was dried over anhydrous magnesium sulfate, after the evaporation of solvent, the residue was recrystallized by ethyl alcohol and obtained 2,6-bis(trimethyltin)-4,8-bis(2-ethylhexyl)benzo[1,2-b:3,4-b']dithiophene 8 (6.15 g, 7.96 mmol) in a 58.3% vield. ¹H NMR (CDCl₃, 500 MHz) δ (ppm): 7.52 (s.2H), 4.23 (d.4H, I = 10 Hz), 1.79(m.2H), 1.54–1.36 (m.16H), 1.06 (t,6H, J = 7.5 Hz), 0.96 (t,6H, J = 7.5 Hz), 0.40(s,18H). ¹³C NMR (CDCl₃, 500 MHz) δ (ppm): 143.41, 140.41, 133.91, 132.89, 128.03, 40.73, 30.60, 29.30, 23.97, 23.23, 14.24, 11.41, -6.97, -8.32, -9.95.

2.1.4. 5,8-Dibromo-2,3-bis(3-(octyloxy)phenyl)quinoxaline (9)

A mixture of compound 2 (2.28 g, 8.58 mmol) and compound 5 (4 g, 8.58 mmol) were added into the acetic acid (70 ml), the mixture was briefly warmed to 60 °C, and then the solution was stirred at room temperature for another 2 h. The precipitate was collected by filtration, washed with ethanol, and dried to afford 5,8-dibromo-2,3-bis(3-(octyloxy)phenyl)quinoxaline 9 (5.69 g) as a white solide in yield 97%. ¹H NMR (CDCl₃, 500 MHz) δ (ppm): 7.91(s,2H), 7.23(d,4H, *J* = 10 Hz), 7.18(d,2H, *J* = 10 Hz), 6.94(d,2H, *J* = 10 Hz), 3.87(t,4H, *J* = 6.5 Hz), 1.75(q,4H), 1.25–1.52(m,20H), 0.91(t,6H, *J* = 5.5 Hz). ¹³C NMR (CDCl₃, 500 MHz) δ (ppm): 159.07, 154.05, 139.31, 139.14,133.09, 129.33, 123.72, 122.56, 116.57, 115.77, 68.12, 31.85, 29.36, 29.29, 29.13, 26.04, 22.70, 14.13.

2.1.5. Synthesis of PBDTQx

In a 50 ml dry flask, monomer 8 (231.6 mg, 0.3 mmol) and 9 (209 mg, 0.3 mmol) were dissolved in degassed toluene (10 ml), the mixture was flushed with nitrogen for 30 min, tris(dibenzylideneacetone)dipalladium(0) $(Pd_2(dba)_3)$ (5.5 mg) and tri(otolyl)phosphine (P(o-Tol)_3) (7.3 mg) were added, and flushed with nitrogen for another 30 min. Then the mixture was vigorously stirred at 100 °C for 24 h under nitrogen. After cooling down, the solution was poured into methanol. The polymer was collected by

filtration and was Soxhlet-extracted in order with methanol, hexane, and then with chloroform. The chloroform solution was concentrated to a small volume, and the polymer was precipitated by pouring this solution into methanol. Finally, the polymer was collected by filtration, dried under vacuum at 50 °C overnight and afforded PBDTQx (247 mg) as a deep-blue solid in yield 84.3%. ¹H NMR (CDCl₃, 500 MHz) δ (ppm): 7.68(m,2H), 7.40(br,4H), 7.15(br,2H), 7.01(br,4H), 3.77(m,8H). GPC (tetrahydrofuran, polystyrene standard): M_n = 192.86 kDa, M_w = 556.36 kDa, PDI = 2.88. Anal. Calcd for ($C_{62}H_{80}N_2O_4S_2$)_n (%): C 75.87, H 8.22, N 2.85. Found (%):C75.28, H 8.13, N 2.90.

2.2. Measurement and characterization

All compounds were characterized by nuclear magnetic resonance spectra (NMR) recorded on a Bruker AV 500 spectrometer in CDCl₃ at room temperature. Molecular weights and distributions of the copolymer were determined using GPC, THF as eluent and polystyrene as standard. The absorption spectra were taken by a Unico UV-2102 scanning spectrophotometer. Thermogravimetric analysis (TGA) of the polymer was recorded on a Universal V2.6D TA instruments. The electrochemical cyclic voltammetry was conducted on a CHI 660D Electrochemical Workstation with Pt disk, Pt plate, and Ag/Ag⁺ electrode as working electrode, counter electrode, and reference electrode respectively in a 0.1 mol/L tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) acetonitrile solution. Polymer thin films were formed by drop-casting chloroform solution (analytical reagent, 1 mg/mL) onto the working electrode, and then dried in the air. Atomic force microscopy (AFM) images were collected in air under ambient conditions using the MultiMode scanning probe microscope (Agilent Technologies 5500).

2.3. Solar cell device fabrication and characterization

The organic photovoltaic cells were fabricated with ITO glass as the anode, Al as the cathode and the blend films of PBDTQx: PC₆₁-BM as the photosensitive layer. The ITO glass was pre-cleaned and modified by a thin layer of PEDOT:PSS which was spin-coated from a PEDOT:PSS aqueous solution (Bayer), and the thickness of the PEDOT:PSS layer was about 40 nm. The photosensitive layer was prepared by spin-coating a blend solution of the PBDTQx and PC₆₁₋ BM in chlorobenzene (CB) with the concentration of 30 mg/ml on top of ITO/PEDOT:PSS substrate and the thickness of the active layer was about 80 nm. Then the blend system was put in glove box overnight, Finally, 0.5-nm thick LiF layer and 85-nm thick Al laver were evaporated in sequence under the vaccum of 3×10^{-6} -Torr. The effective area of the device was 0.0314 cm². The current density-voltage (I-V) curves were obtained using a Keithley 2611 source-measure unit. The photocurrent was measured with a solar simulator (Newport Thermal Oriel 69911 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.

3. Results and discussion

3.1. Thermal properties

The thermal properties of PBDTQx were determined by TGA (Fig. 1). The copolymer exhibited a reasonable thermal stability with 5% weight-loss temperature (T_d) of 310 °C. Obviously, the thermal property of PBDTQx is adequate for further application in photovoltaic solar cells and other optoelectronic devices.



Fig. 1. Thermogravimetric analysis plot of PBDTQx.



Fig. 2. Absorption spectra of PBDTQx solution and film.

3.2. Absorption properties

The absorption properties of PBDTOx were investigated both in CHCl₃ solution and film as shown in Fig. 2. The copolymer showed two main absorption peaks at 378 and 598 nm in UV-vis spectra. The absorption peak at 378 nm could be assigned to the π - π * transition of their conjugated backbone, while the other peak at 598 nm could be ascribed to the strong intermolecular charge transfer between BDT donor and quinoxaline acceptor. The absorption edge of the polymer film was 696 nm, about 22 nm red¹ shift in comparison with that of the polymer solution as seen in Fig. 2, which implied that π stacked structure in the solid state might be formed. The optical bandgap of copolymer can be calculated to be 1.78 eV from the absorption onset of the film. It is strange that the absorption maximum of the polymer film is less than that of its chloroform solution. The derivation of the absorption maximum for film and for solution may result from the big steric hindrance caused by the two octyloxyl group in the donor (BDT) and in the acceptor (quinoxaline), which may even affect the aggregation state properties of the polymer.

3.3. Electrochemical properties

Fig. 3 showed the cyclic volatmmogram of PBDTQx film on Pt electrode. It could be seen that there were p-doping/dedoping (oxidation/re-reduction) processes at positive potential range and n-doping/dedoping(reduction/oxidation) processes at negative



Fig. 3. Electrochemical cyclic voltammetry curves of PBDTQx.

potential range. The HOMO and LUMO energy levels of the polymer were calculated from the onset oxidation potentials (E_{ox}) and the onset reduction potentials (E_{red}) and by assuming the energy level of ferrocene/ferrocenium (Fc/Fc⁺) to be -4.72 eV below the vacuum level. The formal potential of Fc/Fc⁺ was measured as 0.09 eV against Ag/Ag⁺. The energy gap (E_g^{ec}) of the polymer was calculated from the HOMO and LUMO energy levels. The calculating equations are as follows:

$$E_{\rm HOMO} = -e(E_{\rm ox} + 4.72) \tag{1}$$

$$E_{\text{LUMO}} = -e(E_{\text{red}} + 4.72) \tag{2}$$

$$E_{g}^{ec} = e(E_{ox} - E_{red}) \tag{3}$$

where the units of $E_{\rm red}$ and $E_{\rm ox}$ are V vs Ag/Ag⁺. The electrochemical potentials and energy levels of PBDTQx are shown in Table 1. The $E_{\rm ox}$ is 0.54 V and the $E_{\rm red}$ is -1.56 V. The HOMO and LUMO energy levels of PBDTQx are -5.26 and -3.16 eV, respectively. The electrochemical energy bandgap is 2.1 eV, which is somewhat larger than the optical bandgap estimated from UV-vis spectra (1.78 eV). The higher electrochemical bandgap than optical bandgap is common phenomenon for the conjugated polymers because of the energy barriers of the charge transfer at electrodes during the electrochemical measurement. It is worthy to note that the HOMO of PBDTQx is relatively low, which indicates that the polymer should have good air stability for its HOMO energy level being below the air oxidation threshold (-5.2 eV). Meanwhile, this low energy level might be benefited to the photovoltaic performance of the polymer solar cells because HOMO energy level of donor and LUMO of acceptor have direct relation with the $V_{\rm oc}$ of device. In addition, the LUMO energy level of PBDTQx is significantly higher than that of PC₆₁BM (-3.91 eV, as shown in Fig. 4), it facilitate electron transferring from the excitons of PBDTQx to the LUMO of PC₆₁BM at the interface of the donor/acceptor.

3.4. Photovoltaic properties

In order to investigate the photovoltaic properties of the copolymer, the photovoltaic cells were fabricated with a typical configuration of ITO/PEDOT:PSS/polymer:PC₆₁BM/LiF/Al, in which PBDTQx was used as donor, PC₆₁BM as acceptor. The active layer of the device was fabricated with chlorobenzene (CB) solution of copolymer and PC₆₁BM by spincoating technique. The concentration of blend solution of the polymer and PC₆₁BM in CB was 30 mg/ml. Weight ratios of the donor and acceptor varied from 1:2 to 1:6. The *J*–*V* curves of the PBDTQx-based PSC with different D/A ratios under illumination of AM1.5G (100 mW/cm²) were shown in Fig. 5. As

¹ For interpretation of color in Figs. 2–8, the reader is referred to the web version of this article.

Table 1

Electrochemical and optical properties of the PBDTQx.

Polymer	$E_{\mathrm{ox}}\left(V\right)$	$E_{\rm red}\left(V\right)$	$E_{\rm HOMO}~({\rm eV})$	E_{LUMO} (eV)	$E_{\rm g}^{\rm ec}~({\rm eV})$	$E_{\rm g}^{\rm opt}({\rm eV})^{\rm a}$	
PBDTQx	0.54	1.56	-5.26	-3.16	2.1	1.78	

^a Optical band gaps determined from the onset of electronic absorption of the polymer films $(E_{i}^{opt} = 1240/\lambda (nm))$.



Fig. 4. Energy level diagrams for PBDTQx and PC₆₁BM.



Fig. 5. *J*–*V* curves of the PSCs based on PBDTQx: $PC_{61}BM$ with different donor/acceptor ratios (1:2,1:3,1:4,1:5 and 1:6), under illumination of AM1.5G, 100 mW/ cm².

Table 2	
Photovoltaic results of the PSCs based on PBDTQx and PC61BM with different weig	h
ratio under the illumination of AM1.5G (100 mW/cm^2) .	

D/A ratio	$V_{\rm oc}$ (V)	$J_{\rm sc}~({\rm mA/cm}^2)$	FF	PCE (%)
1:2	0.77	0.82	0.35	0.22
1:3	0.65	1.72	0.43	0.48
1:4	0.73	1.45	0.49	0.52
1:5	0.79	1.44	0.45	0.51
1:6	0.70	1.07	0.50	0.37

listed in Table 2, the optimized performance was achieved with the weight ratio of polymer: $PC_{61}BM$ being 1:4, which was slight higher than that of 1:5-device.

1,8-Diiodooctane (DIO) is one of processing solvent additives, which can improve the morphology of the active layer [20,21], DIO doping ratio was controlled to be 2.5% (v/v) in the film deposition, and the device performance could be improved accord-



Fig. 6. *J*-*V* curves of the PSCs based on PBDTQx: PC₆₁BM in CB with and without 2.5 vol.% DIO under illumination of AM1.5G, 100 mW/cm².

Table 3 Photovoltaic results of the PSCs based on PBDTQx:PC₆₁BM with and without DIO under the illumination of AM1.5G (100 mW/cm²).

D/A ratio	Solvent	$V_{\rm oc}\left({\sf V}\right)$	$J_{\rm sc}$ (mA/cm ²)	FF	PCE (%)
1:4	CB	0.73	1.45	0.49	0.52
	CB + 2.5%DIO	0.84	1.90	0.43	0.68
1:5	CB	0.79	1.44	0.45	0.51
	CB + 2.5%DIO	0.80	2.67	0.47	1.01

ingly. The PCE of 1:4-device and 1:5-device was gauged to be 0.68% and 1.01%, respectively. The J-V curves of the PBDTQx-based solar cells (1:4,1:5) with and without DIO were shown in Fig. 6 and summarized in Table 3. Both V_{oc} and J_{sc} were optimized with the addition of DIO, and J_{sc} of 1:4-device and 1:5-device was increased by 31% and 84% compared with that of devices without DIO doping.

To investigate the surface morphology of the blend polymer:PC₆₁BM = 1:4 and 1:5 with and without the additive DIO, atomic force microscopy (AFM) studies had been carried out (Figs. 7 and 8). It can be seen that evident aggregation of the blend films and the poor miscibility between polymer and PC₆₁BM (Fig. 7a and c). After the addition of DIO, the resulting blend films showed a more uniform and finer domain structure (Fig. 7b and d) and an average domain size of 1:4-device and 1:5-device was 30-50 nm and 20-30 nm (Fig. 8), respectively, the latter is closed to ideal domain size and favorable for efficient exciton dissociation and charge transport. As a result, the J_{sc} increased from 1.44 to 2.67 mA/cm², and the V_{oc} and FF are all increased, above-mentioned factors made the device performance was greatly improved and reached 1.01%. Although the PBDTQx-based photovoltaic device showed low J_{sc} of 2.67 mA/cm², it had a reasonable FF of 0.47 and a high $V_{\rm oc}$ of 0.80 V. If the morphology of blend film can be optimized by thermal annealing or solvent annealing, the improved photovoltaic performance is prospective.

4. Conclusion

A copolymer (PBDTQx) based on BDT and quinoxaline was synthesized by stille coupling reaction. PBDTQx had a narrow bandgap of 1.78 eV and a low HOMO level of -5.26 eV, which facilitated high V_{oc} of PBDTQx-based PSCs. With the concentration being 30 mg/ml, the highest PCE of 1.01% was obtained when the blending ratio of PBDTQx and PC₆₁BM reached 1:5 and DIO doping ratio was 2.5%. Although the copolymer PBDTQx-based photovoltaic device showed relatively low J_{sc} , it had a reasonable high V_{oc} of 0.80 V. If the morphology of blend film can be further optimized, the improved photovoltaic performance is prospective.



Fig. 7. AFM images for polymer: $PC_{61}BM$ films (1:4,1:5) prepared without and with DIO (2.5 vol.%) (5 μ m × 5 μ m). (a–d). The topography of each film is showed in the left panels, and the corresponding phase images in the right panels.



Fig. 8. AFM images for polymer: $PC_{61}BM$ films (1:4, 1:5) prepared with DIO (2.5 vol.%) (0.5 μ m × 0.5 μ m). (a and b). The topography of each film is showed in the left panels, and the corresponding phase images in the right panels.

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Appendix A. Supplementary material

¹H NMR,¹³C NMR spectra of 2, 5, 8, 9 and ¹HNMR of PBDTQx. This material is available free of charge via the Internet at http:// www.sciencedirect.com. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/ 10.1016/j.reactfunctpolym.2012.07.006.

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