

A medium-band-gap polymer based alkoxy-substituted benzoxadiazole moiety for efficient polymer solar cells



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HIGHLIGHTS

- Side-chain engineering promotes benzoxadiazole-based polymer with high M_n and HOMO energy level.
- The efficiency of 8.47% is one highest values for BO-based solar cells.
- The fullerene-based solar cells exhibit weak bimolecular recombination.

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ABSTRACT

A medium-band-gap donor–acceptor (D–A) polymer (PBDTS-DTBO) was designed and synthesized with alkoxy-substituted benzo[*c*][1,2,5]oxadiazole (BO) as A unit and benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT) derivative (BDTTS) as D moiety. The resulting polymer not only possesses a high number-average molecular weight (M_n) of 53.0 kDa, but also exhibits a deep highest occupied molecular orbital (HOMO) energy level of -5.43 eV, which is in favor of a higher V_{oc} of 0.88 V in the photovoltaic devices. Consequently, due to excellent phase separation and weak bimolecular recombination, the efficiency of the fullerene-based solar cells can reach 8.47% with a high current density (J_{sc}) of 14.93 mA cm^{-2} and FF of 0.661, which is one of highest values for currently reported benzoxadiazole-based materials. In addition, considering the polymer also shows a medium optical bandgap of 1.75 eV, which can be well complementary with the classical non-fullerene acceptor ITIC. The best performance device exhibits a good efficiency of 6.45% in fullerene-free devices, which could be ascribed to the serious bimolecular recombination. This work revealed that alkoxy-substituted benzoxadiazole could be a promising moiety to construct efficient light-harvesting polymer.

1. Introduction

Polymer solar cells (PSCs) have attracted considerable attention because of the unique features of light weight, low cost, structure diversity, and large-scale fabrication of flexible devices via solution processing [1–7]. With the great development of molecules innovation and device engineering, the power conversion efficiency (PCE) has been over 11% in the single-junction fullerene-based solar cells and over 13% in the fullerene-free solar cells, demonstrating the promising prospects [8–11]. Donor-Acceptor (D-A) copolymerization has proven

as an efficient strategy to realize high-performance photovoltaic materials with tunable molecular orbital energy level and aggregation state [12–15]. Among various acceptor building blocks, the excellent candidate benzo[*c*][1,2,5]oxadiazole (BO) has attracted our intense attentions [16–21]. In compared with the analogy 2,1,3-benzothiadiazole (BT) unit, due to the oxygen atom with higher electronegativity than sulfur atom, the BO-based polymers generally show decreased highest occupied molecular orbital (HOMO) energy level, and in turn, higher open circuit voltage (V_{oc}) in photovoltaic devices [22,23]. However, the photovoltaic performance of the BO-based polymers

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didn't achieve the expected result with the best PCE around ~7.5%, which could be ascribed to the relatively low molecular weight and poor solubility of the polymer [24–27]. To address this issue, alkoxy groups at the 5- and 6-positions are introduced to enhance the solubility, meanwhile, the non-covalent interaction of the O...S between alkoxy substituents and thiophene rings is also in favor of planar conformation for the polymer backbone. On the other hand, for the donor units, the weak electron donor unit benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT) has been widely used to construct highly efficient conjugated polymers, which usually exhibit excellent properties of broad light absorption, lower HOMO energy levels, enhanced charge mobility, and outstanding photovoltaic performance in PSCs devices [28,29]. Hereinto, side chain appended to the main backbone has occupied an important position in the physicochemical properties, interaction packing of conjugated polymers, as well as the photovoltaic performance. In comparison with alkyl side chain, the alkylthio substituents are more favorable in low steric hindrance and deep frontier orbital energy levels due to the smaller van der Waals radius (~0.18 nm) and the poor overlap of its orbital with the π -system of sulfur atom.

In this work, to excavate benzoxadiazole moiety in the application in PSCs, a new D- π -A copolymer (PBDTS-DTBO) was designed and synthesized, with alkoxy-substituted BO moiety as the acceptor, 2-ethylhexylthiothiophen substituted benzo[1,2-*b*:4,5-*b'*]dithiophene (BDTS) as the donor building block and thiophene as the π bridge. The polymer can well dissolve in hot chlorobenzene and 1,2-dichlorobenzene, although with a relatively higher molecular weight of 53.0 kDa. Meanwhile, it possesses a deeper HOMO energy level of -5.43 eV, which is in favor of a high V_{OC} in the solar cells device. Furthermore, as we expect, it shows a large V_{OC} of 0.88 V in the fullerene-based solar cells. Without any process additives or thermal annealing, the efficiency can reach up to 7.69% ($J_{SC} = 13.61 \text{ mA cm}^{-2}$, and FF = 0.644). After the addition of 1-chloronaphthalene (CN) as the solvent additive, due to the excellent phase separation and low charge recombination, the PCE was enhanced to 8.47% with a simultaneously increased J_{SC} of 14.93 mA cm^{-2} and an FF of 0.661, which is one of highest PCE for currently reported benzoxadiazole-based materials (Table 1). In addition, considering the polymer also shows a medium optical bandgap of 1.75 eV, which can be well complementary with the classical non-fullerene acceptor ITIC. Unfortunately, the best performance device only exhibits a relatively low PCE of 6.45% in fullerene-free devices, although with a higher V_{OC} of 0.91 V, which could be ascribed to the serious bimolecular recombination. This work revealed the significance of the side chain in molecules design.

2. Results and discussion

As shown in Scheme 1, the polymer PBDTS-DTBO was synthesized via the Stille coupling reaction. Soxhlet purification afforded the target polymers PBDTS-DTBO. The details can refer to the description in Experimental Section. The molecular weight of PBDTS-DTBO was

Table 1
Photovoltaic parameters of the reported highly efficient polymers.

Polymer	V_{OC} (V)	J_{SC} (mA/cm^2)	FF (%)	PCE (%)	ref
PBDTT-C-BO	0.74	15.7	64	7.5	[30]
PQcQx-IT	0.78	7.8	59.1	3.6	[31]
PBDTBO	0.86	10.4	64.4	5.7	[32]
PC ₂ DTBF	0.90	7.73	67	5.48	[17]
PBDTPO-DTBO	0.89	11	64	6.2	[33]
PTIPsBDT-DTBO	0.88	10.4	54.8	5.02	[18]
PBDT-DTBO	0.83	10.24	66.3	5.63	[21]
PBDTE-DFBO	0.83	12.7	62	6.5	[20]
PTTTBO	0.85	11.6	54	5.3	[34]
P(BDT-TT-BO)	0.76	13.87	66.6	7.05	[22]
PCySi-TBO	0.64	13.8	57	5.0	[35]
PBDTS-DTBO	0.869	14.93	66.11	8.47	this work

measured by gel permeation chromatography (GPC) using 1,2,4-trichlorobenzene (150 °C) as the eluent, to give a number-average molecular weight (M_n) of 53.0 kDa and a polydispersity index (PDI) is 2.14. In addition, thermogravimetric analyses (TGA) curve in Fig. 1 indicates that the polymer shows excellent thermal stability with the decomposition temperature (T_d , 5% weight loss) located at 304 °C, which is adequate for the fabrication of PSCs and other optoelectronic devices.

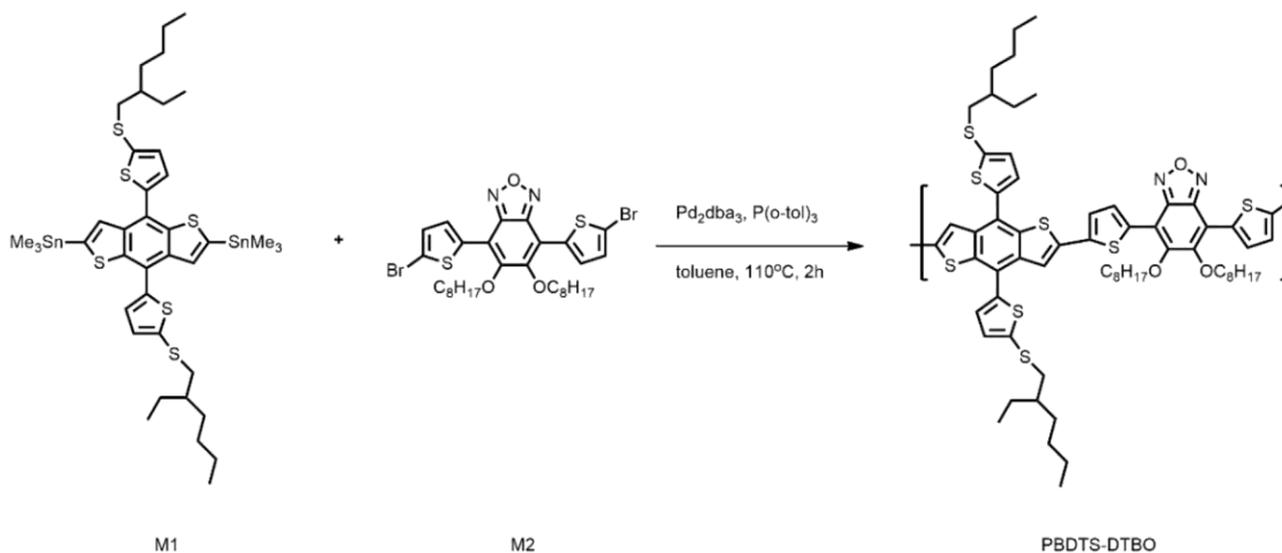
3. Optical and electrochemical properties

The normalized UV-visible absorption spectra of PBDTS-DTBO in solution and as film are shown in Fig. 2 and the data are listed in Table 2. The polymer exhibits a broad absorption region in the range of 350–700 nm with a more red-shifted absorption compared to the analogous polymer based on alkyl-substituted BDT. The absorption peaks at short wavelength (373 nm) could be attributed to the π - π^* transition of the polymer, while the absorption peak at long wavelength (596 nm) is assigned to the strong intramolecular charge transfer (ICT) between the electron-rich BDTST segment and electron-deficient BO unit. Noticeably, the appearance of a distinct shoulder peak at 638 nm indicates PBDST-DTBO has a strong aggregation in solution, which was also confirmed by the almost overlapping absorption profile in the solid film. The temperature-dependent UV-visible absorption spectra were recorded to investigate the stacking and aggregation of the polymer (Fig. 2b). With the temperature increased from 20 to 100 °C, the defined shoulder peak at ~640 nm gradually weakened until disappeared, accompanying with only several nanometers blue-shifted, which implies the intermolecular interactions decreased when continuously heated. The optical band gap (E^{opt}) of the polymer is 1.75 eV estimated from the absorption onset (ca. 708 nm) of the film. In addition, cyclic voltammetry (CV) measurement was carried out to study the electrochemical properties of the polymers. As shown in Fig. 3, the onset oxidation potential of PBDTS-DTBO was 1.03 V vs SCE, corresponding to the HOMO energy level as low as -5.43 eV, which is beneficial to high V_{OC} in the corresponding photovoltaic devices. Moreover, the LUMO energy level calculated by the HOMO and optical band gap is about -3.68 eV, and the LUMO energy level offset between the polymer PBDTS-DTBO and PC₇₁BM or ITIC is about 0.30 eV, which could well realize the exciton dissociation [36,37].

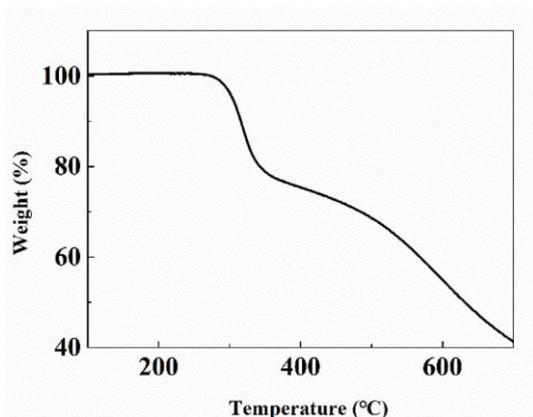
4. Photovoltaic property

Photovoltaic properties of the polymer were investigated with conventional device structures of ITO/PEDOT:PSS/Polymer:PC₇₁BM or ITIC/PFN/Al, and various conditions (different D/A weight ratios, solvent additive) were optimized (Table S1 and S2). Current density-voltage characteristics with the different D/A ratios under AM1.5G illumination are shown in Fig. 5, and corresponding parameters are summarized in Table 3. With PC₇₁BM as the acceptor, all the photovoltaic devices exhibit desirable efficiencies of over 6.7% with different D/A ratios from 1:1 to 1:2. Noticeably, even if without any process additives or post-annealing, the PCE also can reach 7.69% with $V_{OC} = 0.88 \text{ V}$, $J_{SC} = 13.61 \text{ mA cm}^{-2}$, and FF = 0.644. When 1% CN added, a superior efficiency of 8.47% was achieved with a simultaneously enhanced J_{SC} and slightly increased FF, which is the highest value among the BO-based polymers solar cells [38–40]. Furthermore, considering the polymer also shows a medium optical bandgap of 1.75 eV, which can be well complementary with the non-fullerene acceptor ITIC. However, the fullerene-free devices only give the relatively poor photovoltaic performance (PCE = 6.45%) with low FF and J_{SC} , which may be ascribed to the serious molecular recombination discussed below.

The external quantum efficiency (EQE) curves under different conditions are shown in Fig. 4c and d. The PCBM-based devices exhibited broad photo response from 350 to 700 nm, while the ITIC based devices showed a much broader response range from 350 to 800 nm, which well



Scheme 1. Synthetic route and molecular structure of the polymer PBDTS-DTBO.

Fig. 1. TGA curve of PBDTS-DTBO with a heating rate of 10 °C/min under inert N₂ atmosphere.

agreed with the corresponding absorption spectra. Meanwhile, it is obvious that high EQE value can reach 80% in fullerene solar cell. The J_{SC} values of 14.73 mA cm⁻² integrated from the EQE curves are consistent with the values obtained by $J-V$ measurements (14.93 mA cm⁻²). The hole mobilities of the polymers were investigated by the space charge limited current (SCLC) in optimized BHJs, the relationship between current density and voltage in the hole-

only devices is shown in Fig. 5. The hole mobilities of the blend films of PBDTS-DTBO/PC₇₁BM, or PBDTS-DTBO/ITIC, are on the same order of magnitude (10⁻⁴ cm² V⁻¹ s⁻¹). High mobility could guarantee effective charge carrier transport to the electrodes and reduce the photocurrent loss in photovoltaic devices. The hole mobility PBDTS-DTBO/PC₇₁BM is 3.2 × 10⁻⁴ cm² V⁻¹ s⁻¹, and PBDTS-DTBO/ITIC is 1.4 × 10⁻⁴ cm² V⁻¹ s⁻¹.

What's more, the V_{OC} and J_{SC} under different light intensity were recorded to analyze the charge recombination characteristics in the active layers (Fig. 6). From V_{OC} - P_{light} curves in Fig. 6a, the slope of V_{OC} versus $\ln(P_{light})$ is close to nkT/q (k_B is Boltzmann's constant, T is temperature and q is elementary charge). Herein, it can be found that the slopes yielded 1.05 kT/q and 1.18 kT/q for PCBM and ITIC-based devices, respectively, indicating a weaker trap-assisted recombination in fullerene devices. Furthermore, the relationship between J_{SC} and light intensity follows the following formula: $J_{SC} \propto (P_{light})^S$, and the fitting slope S value is closer to 1, implying weak bimolecular recombination. As shown in Fig. 6b, in the optimal devices, the higher S value for PCBM-based device, implies that the bimolecular recombination is more suppressed and charge transport and extraction

could be highly efficient. It could be the main reason why fullerene-free devices enable poor photovoltaic performance.

To investigate the exciton-dissociation and charge transfer behavior in the active layers, the photoluminescence (PL) quenching experiments were carried out. As shown in Fig. 7, in comparison with the pure

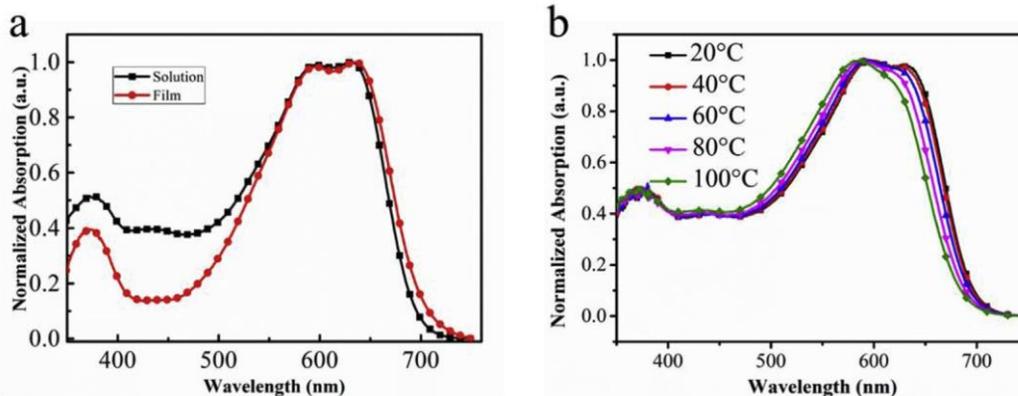


Fig. 2. (a) UV-vis absorption spectra of the polymer PBDTS-DTBO in solution and as solid film; (b) Temperature-dependent optical spectra from 20 to 100 °C in 1,2-dichlorobenzene solution.

Table 2
The absorption properties and energy values of PBDTS-DTBO.

Polymer	λ_{abs} (nm)Solution	λ_{abs} (nm) film	λ_{onset} (nm) films	$E_{\text{g}}^{\text{opt}}$ (eV)	HOMO (eV)	LUMO (eV)
PBDTS-DTBO	373, 596, 638	374, 597, 640	708	1.75	-5.43	-3.68

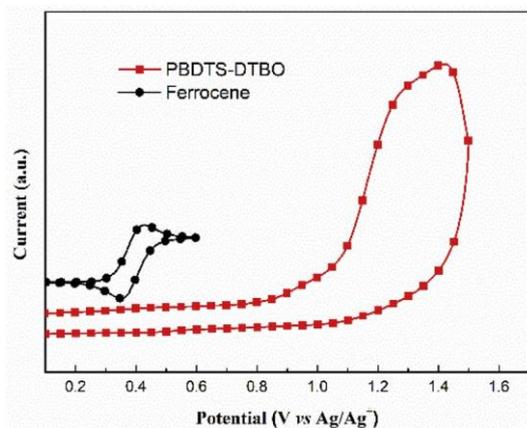


Fig. 3. CV curve of the as casted film vs. the SCE in 0.1 M Bu_4NPF_6 /acetonitrile solution.

PBDTS-DTBO film, the emission of PBDTS-DTBO:PCBM blend film was quenched 99%, which is obviously higher than that of PBDTS-DTBO:ITIC (80%), suggesting that more effective electron transfer from the polymer to PCBM acceptor, which is a prerequisite for achieving high photovoltaic performance.

In order to investigate the morphology of the active layers, atomic force microscopy (AFM) and transmission electron microscopy (TEM) measurements were carried out. As shown in Fig. 8, the PBDTS-DTBO:ITIC film showed a similar rough surface than PBDTS-DTBO:PC₇₁BM films. The root-mean-square (RMS) surface roughness values were 0.761 nm for PBDTS-DTBO:PC₇₁BM and 0.740 nm for PBDTS-DTBO:PC₇₁BM with 1% CN, respectively and the ITIC device performs similar with the RMS 0.945 nm, so the blend film of PCBM device with 1% CN additive exhibited a more smooth surface than the others, which is favorable to charge carrier transport and separation [39–42]. Meanwhile, TEM images clearly showed that the phase separation of PBDTS-DTBO:ITIC was aggregated seriously. As the exciton diffusion length is only 10–20 nm, the large phase separation is detrimental to the separation of exciton. In contrast, PBDTS-DTBO:PC₇₁BM, PBDTS-DTBO:PC₇₁BM with 1% CN both showed a much smaller phase separation with nanoscale domains than PBDTS-DTBO/ITIC blend film. The difference of morphology could be another factor to give different photovoltaic performance in the fullerene and fullerene-free devices.

5. Conclusions

In summary, a new BDT-based polymer (PBDTS-DTBO) was

Table 3
Photovoltaic parameters of polymer solar cells based on PBDTS-DTBO and PC₇₁BM.

Devices		Additive (CN)	V_{oc} (V)	J_{sc} (mAcm^{-2})	FF (%)	PCE^{max} (%)	PCE^{ave} (%) ^a
PBDTS-DTBO:PC ₇₁ BM	1:1	0	0.873	12.54	61.22	6.70	6.57
	1:1.5	0	0.878	13.61	64.37	7.69	7.59
	1:2	0	0.830	12.09	67.50	6.77	6.67
	1:1.5	1%	0.869	14.93	66.11	8.47	8.39
PBDTS-DTBO:ITIC	1.5:1	0	0.888	13.44	39.26	4.69	4.52
	1:1	0	0.911	13.57	52.19	6.45	6.39
	1:1.5	0	0.879	14.57	48.80	6.25	6.14

^a The average PCE was obtained from over 10 devices.

successfully synthesized. The polymer exhibits good solubility, although with a relatively larger molecular weight of 53.0 kDa. Meanwhile, it possesses a deeper HOMO energy level of -5.43 eV, lead to a high V_{OC} of 0.88 V in the solar cells. Even if without any process additives or thermal annealing, the efficiency also can reach 7.69%. Moreover, due to excellent phase separation and low charge recombination, a superior PCE of 8.47% was obtained with a desirable J_{SC} of 14.93 mA cm^{-2} , which is one of highest efficiency for currently reported benzoxadiazole-based materials. In addition, considering the polymer also shows a medium optical bandgap of 1.75 eV, which can be well complementary with the classical non-fullerene acceptor ITIC. In fullerene-free devices, the active layer presented serious bimolecular recombination, resulting in a poor photovoltaic performance with a relatively low PCE of 6.45%.

6. Experimental Section

6.1. Polymer synthesis

Compounds M1 (139.7 mg, 0.2 mmol), M2 (193.7 mg, 0.2 mmol), Pd₂dba₃ (1.8 mg, 0.002 mmol), and P(o-tol)₃ (3.6 mg, 0.012 mmol) were added into a 25 mL flask. The flask was subjected to three successive cycles of vacuum followed by refilling with argon, and then 5 mL of dry toluene was added. The reaction mixture was heated to 110 °C for 2 h under argon protection. Then the mixture was cooled to room temperature, and the polymer was precipitated into 100 mL methanol, filtered, and purified by Soxhlet extraction with methanol, chloroform, and o-dichlorobenzene (o-DCB), respectively. The o-DCB solution was concentrated by evaporation and then precipitated into methanol. The black-blue solid was filtered to yield the desired polymer (153.4 mg, 65% yield).

6.2. Instrumentation

Thermogravimetric analysis (TGA) was recorded on a PerkinElmer Pyris under nitrogen atmosphere at a heating rate of 10 °C/min. A Hitachi U-4100 UV-vis-NIR scanning spectrophotometer was employed to measure absorption spectra. Atomic force microscopy (AFM) measurements of film morphology were imaged by an Agilent 5400 with tapping mode. Transmission electron microscopy (TEM) images were obtained on a Hitachi H-7650 transmission electron microscope at an accelerating voltage of 100 kV. Cyclic voltammetry (CV) measurements were taken on a CHI660D electrochemical workstation. The CV experiments were carried out at room temperature with a conventional three-electrode system using a glassy carbon electrode as working electrode, Pt wire as the counter electrode, and saturated calomel

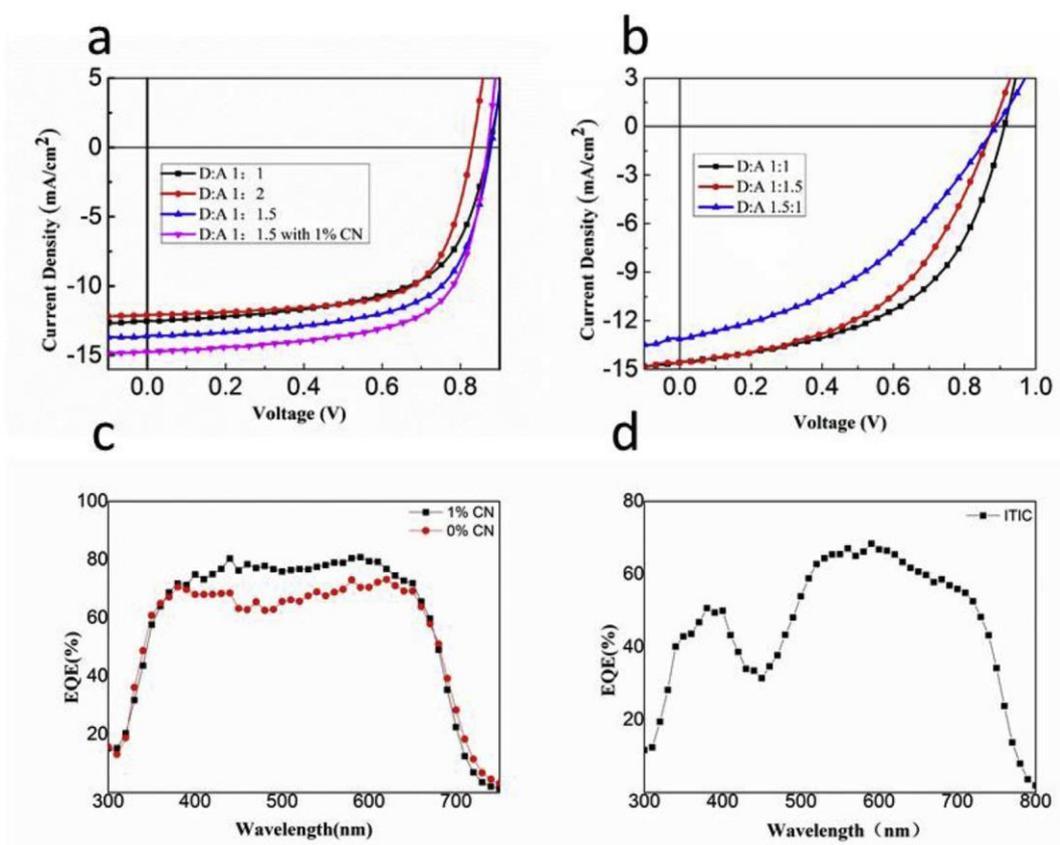


Fig. 4. J - V curves under different fabrication conditions. (a) PBDTS-DTBO/PCBM; (b) PBDTS-DTBO/ITIC; EQE curves of solar cells fabricated under different conditions; (c) PBDTS-DTBO/PCBM without or with additive; (d) PBDTS-DTBO/ITIC.

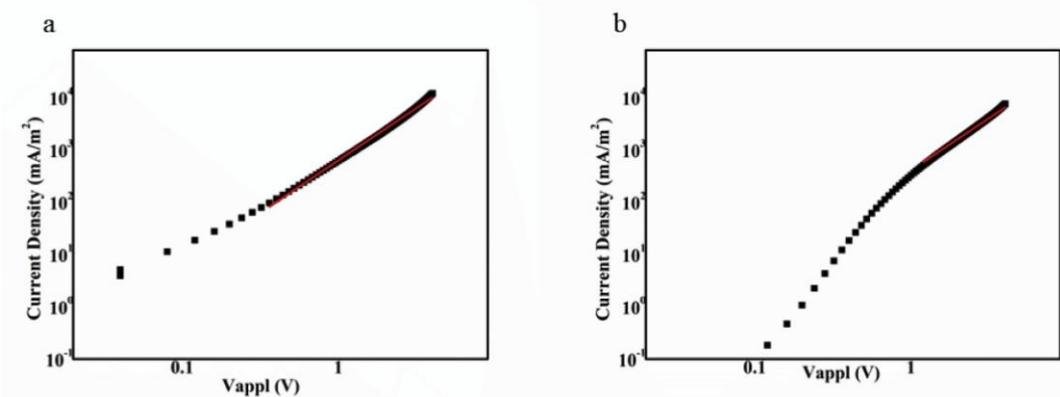


Fig. 5. Hole mobility characteristics of (a) PBDTS-DTBO/PC₇₁BM (1:1.5 with 1% CN) and (b) PBDTS-DTBO/ITIC.

electrode as the reference electrode. Tetrabutylammonium phosphorus hexafluoride (Bu₄NPF₆, 0.1 M) in acetonitrile solution was used as the supporting electrolyte, and the scan rate was 100 mV s⁻¹. Ferrocene/ferrocenium (Fc/Fc⁺) was used as the internal standard and their energy levels are assumed at -4.8 eV relative to vacuum. The potential of this internal standard under the same condition was 0.40 V versus saturated calomel electrode. Gel permeation chromatography (GPC) was performed with trichlorobenzene (TCB) as eluent at 150 °C and polystyrene was used as the standard.

6.3. Fabrication and characterization of devices

Polymer solar cells were prepared with the device structure ITO/PEDOT:PSS/polymer:acceptor/PFN/Al. Patterned ITO-coated glasses

were ultrasonically cleaned sequentially with ITO detergent, deionized water, acetone and isopropanol for 20 min each time, and then treated with oxygen plasma for 6 min. ITO-coated glass substrates were modified with PEDOT:PSS (Baytron PVP Al 4083) about 35 nm thickness. Subsequently, the substrates were transferred to a glove box filled with N₂. The *o*-DCB solutions of PBDTS-DTBO with PC₇₁BM (6 mg/mL for polymer) with different ratio were stirred at 100 °C for 4 h. The solutions were spin-coated to prepare the active layer (ca. 100 nm) at 1250 rpm for 90s on PEDOT:PSS modified ITO coated glass. And then PFN solution was spin-coated on the active layers with speed of 2000 rpm. The spin-coating was operated in a glove box. Finally, after the samples were transferred to a vacuum chamber, Al (100 nm) were deposited in high vacuum via a mask to define the active area of 0.10 cm². Over 10 devices were fabricated under the same condition.

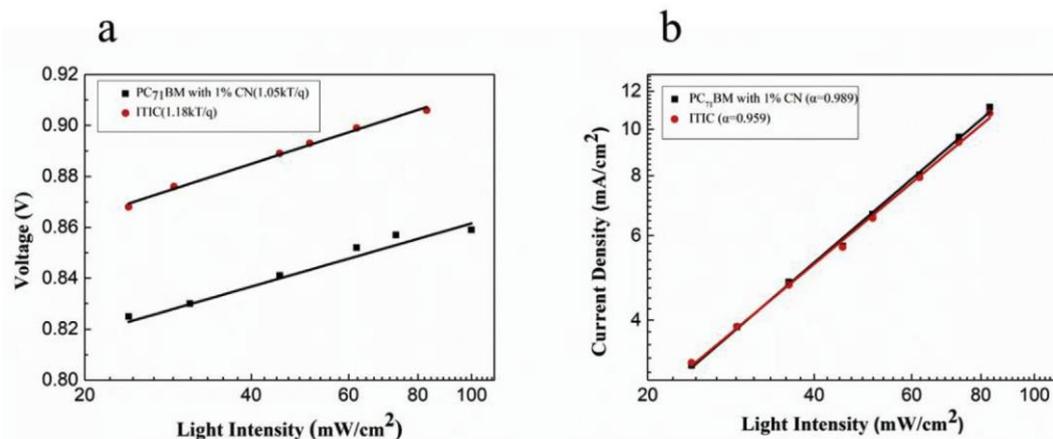


Fig. 6. (a) V_{OC} , and (b) J_{SC} versus light intensity (symbols) with linear fits to the data (solid lines) for the optimal devices based on PBDTS-DTBO.

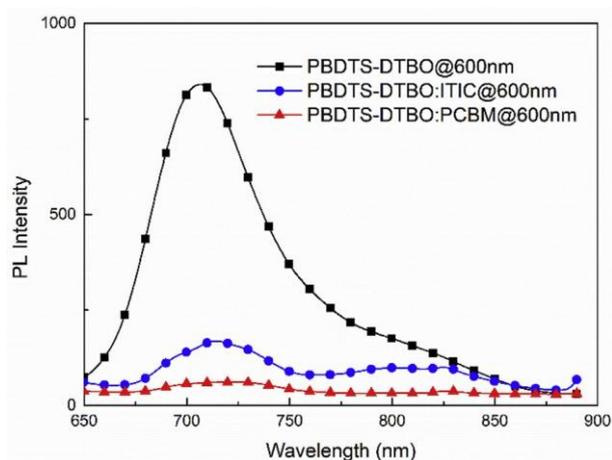


Fig. 7. Photoluminescence spectra of pure PBDTS-DTBO and the blend films of PBDTS-DTBO:PCBM, PBDTS-DTBO: ITIC (the excited wavelength is at 600 nm).

PCE was calculated from current density-voltage (J - V) curves recorded by a Keithley 2420 source meter under illumination with an intensity of 100 mW cm^{-2} (AM1.5G). A standard silicon photodiode is used for calibrating the light intensity. External quantum efficiencies (EQEs) of solar cells were analyzed using a certified Newport incident photon conversion efficiency (IPCE) measurement system.

The hole only mobilities of the blend films were measured with a device structure of ITO/PEDOT: PSS/ Polymer: PC₇₁BM (100 nm)/Au. The SCLC model is described by

$$J_{SCLC} = \frac{9}{8} \epsilon_0 \epsilon_r \mu \frac{V^2}{L^3} \quad (1)$$

Here, J stands for current density, ϵ_0 is the permittivity of free space, ϵ_r is the relative dielectric constant of the transport medium, μ is the hole mobility, V is the internal potential in the device and L is the thickness of the active layer. The internal potential V is obtained by subtracting the built-in voltage (V_{bi}) and the voltage drop (V_s) from the series resistance of the substrate from the applied voltage (V_{appl}), accordingly: $V = V_{appl} - V_{bi} - V_s$.

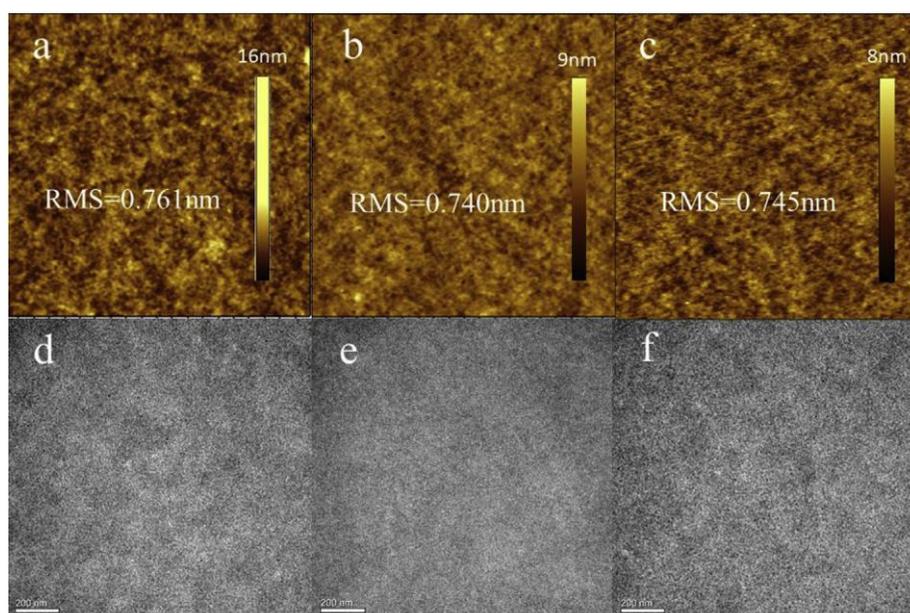


Fig. 8. AFM height and TEM images of PBDTS-DTBO/PC₇₁BM blend film (a, d), PBDTS-DTBO/PC₇₁BM blend film with 1% CN (b, e), PBDTS-DTBO/ITIC (1:1) blend films (c, f).

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.polymer.2019.01.087>.

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