ORIGINAL PAPER

Synthesis of dithieno[2,3-*d*:2',3'-*d*']benzo[1,2-b:4,5-b'] dithiophene -*alt*-isoindigo conjugated polymer and enhancement of photovoltaic property with diphenyl sulfide additives

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Abstract An alternating low band gap conjugated polymer derived from 5.10-di(2-ethylhexyloxy)dithieno[2,3-*d*:2',3'-*d*']benzo[1,2-b:4,5-b']dithiophene (DTBDT) and isoindigo derivative (ID), was synthesized and characterized. The polymer exhibits good solubility in organic solvent and extensive absorption from 350 to 780 nm with the highest occupied molecular orbital (HOMO) level of −5.38 eV and lowest unoccupied molecular orbital (LUMO) level of −3.80 eV. In spite of those, the power conversion efficiency (PCE) of 0.21 % for the photovoltaic cells (PVCs) from the blend of the polymer and [6, 6]-phenyl-C_{71}-butyric acid methyl ester ($PC_{71}BM$) is very low. Interestingly, the performances of the PVCs from the polymer are remarkably increased while a very small amount of diphenyl sulfide (DPS) is used as solvent additives, and the maximal PCE of 4.43 % is achieved in the PVCs from the blend of polymer and $PC_{71}BM$ (W:W, 1:1.5) with DPS as solvent additives under 100 mW/cm^2 illumination (AM 1.5G).

Keywords Conjugated polymer · Dithieno[2,3-*d*:2',3'-*d*']benzo[1,2-*b*:4,5-b']di- thiophene · Isoindigo · Morphology · Synthesis

Introduction

During the past decades, the polymer bulk heterojunction photovoltaic cells (PVCs) have attracted much attention due to the potential application for large area, flexible, and low-cost solar cells [1]. Although the steady improvements have been made and high efficient PVCs with power conversion efficiencies up to 9 % have been demonstrated [2–4], the commercialization is still limited by their low efficiency and short lifetime. For an optimum PVC, low band gap (LBG) conjugated polymers (CPs) with broad absorption spectra, well-matched energy levels and high hole transporting ability, are highly desirable [5–12]. Moreover, the polymers should enable formation of proper morphology with continuous nanostructures of electron donor and electron acceptor materials with large interfacial area in the active layer as the morphology has a profound influence on the excition dissociation, thus improving the performance of the PVCs [1, 13]. To reach the desirable properties, the approach of the combining of electron-rich (D) and electron deficient (A) repeat units to achieve the internal donor-acceptor system has been received significant attention due to the opportunity for tuning the band gaps, energy levels, charge transporting properties and solubility of the CPs through the controlling of the donor and acceptor strength, nature coplanar area and the optimizing of the repeat units solubility [7, 12, 13]. Many promising donor-acceptor (D-A) type LBG CPs have been presented in last decades [14–24]. The most attracting samples are benzo[1,2-b:4,5-b']dithiophene (BDT) derivatives-based D-A type LBG CPs. For instance, Huang and co-workers have reported a new and interesting BDTs-based polymer (PBDT-DTNT) with naphtho[1,2-c:5,6-c]bis[1, 3, 6]thiadiazole as the new electron acceptor moieties exhibiting high PCEs up to 6.0–8.4 % [25, 26]. Hou and Yu et al. have respectively demonstrated a series of D-A type LBG CPs based on BDTs, and the PCEs of 5.63–8.4 % have been achieved in the PVCs from the polymers [27–30].

As a notable aromatic analogue of BDT, DTBDT not only shows a similar HOMO level with BDT, but also holds larger

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coplanar core and extended conjugation length. It was believed to provide advantageous properties for DTBDT-based CPs such as enhanced charge-carrier mobilities, decreased band gaps and facilitated exciton separation into free charge carriers in contrast to BDT-based CPs [31]. In addition, many high performance DTBDTs-based CPs have been presented since Hou et al. firstly introduced the 5,10-di(2-hexyldecyloxy)dithieno[2,3-*d*:2',3'-*d*'-]benzo[1,2-*b*:4,5-*b*']dithiophene to build the D-A type LBG CPs in 2012 [32]. For instance, Yu et al. presented a series of LBG CPs based on 5,10-dialkyl-DTBDT and alkyl 3-fluorothieno[3,4-*b*]thiophene-2-carboxylate (FTT), and the PCE of 7.3 % has been achieved in the PVCs from the CPs in 2013 [33]. Lately, Hou and Kwon et al. respectively presented CPs based on 5,10-di(alkylthieno-2-yl)-DTBDT and 2-(2-hexyldecyl)sulfonylthieno[3,4-*b*]thiophene (S-T) or 2,1,3-benzothiadiazole (BT), and PCEs of 5.1–7.6 % have been achieved in the PVCs from the polymers [34, 35]. More recently, we have provided an effective approach to tune the optoelectronic properties of DTBDTs-based CPs via the changing of substituent groups on the DTBDT, and the PCEs of 1.57–6.39 % have been demonstrated in the PVCs from the CPs derived from DTBDTs and 3,6-bis(thieno-2-yl)-*N*,*N*'-dialkyl-1,4-dioxopyrrolo[3,4-c]pyrrole (DPP) [36]. In spite that PVCs from the D-A type LBG CPs derived from DTBDTs as electron donor units and FTT, S-T, BT and DPP etc. as electron donor units, have shown reasonably high PCEs [33–36], the tailoring and enriching the family of the DTBDT-based D-A type LBG CPs are still promising in the development of new ideal DTBDTs-based CPs for high performance PVCs.

In this paper, a new DTBDT-based D-A type LBG conjugated polymer with 5,10-di(2-ethylhexyloxy)dithieno[2,3-*d*:2',3'-*d*']benzo[1,2-*b*:4,5-*b*']dithiophene as electron donor moieties and *N*,*N*-di(2-hexyldecyl)-isoindigo as electron acceptor moieties, was synthesized through the palladium-catalyzed Stille coupling reaction under mono-microwave heating condition, and named as PDTBDT-ID. The chemical structure, optoelectronic property, thermal stability and electrochemical property of PDTBDT-ID were characterized. In spite that the polymer exhibits appropriate energy levels and extensive absorption from 350 to 780 nm, the power conversion efficiency (PCEs) of 0.21 % for the PVCs from the blend of the PDTBDT-ID and PC$_{71}$BM is very low. It was founded that the performances of the PVCs from the PDTBDT-ID/PC$_{71}$BM were remarkably increased while a very small amount of 1,8-diiodooctane (DIO) or DPS was used as solvent additives in the fabrication of the PVCs. And the maximal PCEs of 2.54 and 4.43 % were respectively achieved in the PVCs from the blend of PDTBDT-ID and PC$_{71}$BM (W:W, 1:1.5) with DIO and/or DPS as solvent additives under 100 mW/cm^2 illumination (AM 1.5G).

Experiment section

Materials

All reagents, unless otherwise specified, were obtained from Aldrich, Acros and TCI Chemical Co., and used as received. All the solvents were further purified under a nitrogen flow. Dithieno[2,3-*d*:2',3'-*d*']benzo[1,2-*b*:4,5-*b*']dithiophene-5,10-diketone (I) [35] and *N*,*N*-di(2-hexyldecyl)-6,6'-dibromo-isoindigo (ID) [24] were synthesized as the procedure reported in the references, and characterized by ^{1}H NMR before use.

General methods

^{1}H NMR spectra were recorded on a Brucker DRX 400 spectrometer operating at 400 MHz and were referred to tetramethylsilane. FAB-MS were obtained on VG ZAB-HS. The polymerization reaction was carried on a mono-microwave system (NOVA, PreeKem Scientific Instruments Co.). Analytical GPC was performed using a Waters GPC 2410 in tetrahydrofuran (THF) relative to polystyrene standards. Elemental analyses were performed on a Vario EL Elemental Analysis Instrument (Elementar Co.). Thermal gravimetric analysis (TGA) was conducted on a TGA 2050 (TA instruments) thermal analysis system under a heating rate of 10 °C/min and a nitrogen flow rate of 20 mL/min. UV-visible absorption spectra were measured on a UV-2550 spectrophotometer (Shimadzu Co.). The cyclic voltammetry (CV) of the polymer was measured on CHI 660 electrochemical workstation (Shanghai Chenhua Co.) at a scan rate of 50 mV/s with a nitrogen-saturated solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu$_4$NPF$_6$) in acetonitrile with glass carbon and Ag/AgCl electrode as the working and reference electrode, respectively. Tapping-mode atomic force microscopy (AFM) images were obtained using a NanoScope NS3A system (Digital Instrument).

Preparation and characterization of the photovoltaic solar cells

A patterned indium tin oxide (ITO) coated glass with a sheet resistance of 10–15 Ω/square was cleaned by a surfactant scrub, followed by a wet-cleaning process inside an ultrasonic bath, beginning with de-ionized water, followed by acetone and iso-propanol. After oxygen plasma cleaning for 5 min, a 40 nm thick poly(3,4- ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) (Bayer Baytron 4083) anode buffer layer was spin-casted onto the ITO substrate and then dried by baking in a vacuum oven at 80 °C overnight. The active layer, with a thickness in the 80–90 nm range, was then deposited on top of the PEDOT:PSS layer by spin-casting from the toluene solution containing PDTBDT-ID/PC$_{71}$BM (W:W, 1:1, 1:1.5 and 1:2) with or without DPS or DIO as solvent additives. Then a 8 nm calcium and a 100 nm aluminum layer were

evaporated with a shadow mask under vacuum of $(1-5) \times 10^{-5}$ Pa. The overlapping area between the cathode and anode defined a pixel size of device of 0.1 cm^2. The thickness of the evaporated cathode was monitored by a quartz crystal thickness/ratio monitor (SI-TM206, Shenyang Sciens Co.). Except for the deposition of the PEDOT:PSS layers, all the fabrication processes were carried out inside a controlled atmosphere in a nitrogen drybox (Etelux Co.) containing less than 1 ppm oxygen and moisture. The power conversion efficiencies (PCEs) of the resulting polymer solar cells were measured under 1 sun, AM 1.5G (Air mass 1.5 global) condition using a solar simulator (XES-70S1, San-EI Electric Co.) with irradiation of 100 mW/cm^2. The current density-voltage (*J-V*) characteristics were recorded with a Keithley 2400 source-measurement unit. The spectral responses of the devices were measured with a commercial EQE/incident photon to charge carrier efficiency (IPCE) setup (7-SCSpecIII, Bejing 7-star Opt. In. Co.). A calibrated silicon detector was used to determine the absolute photosensitivity.

Synthesis of the monomers and the polymer

*5,10-Di(2-ethylhexyloxy)dithieno[2,3-d:2',3'-d']
benzo[1,2-b:4,5-b']dithiophene (II)* [34]

In a 50 mL flask, the diketone of I (0.5 g, 1.5 mmol), zinc powder (0.39 g, 6 mmol), and 15 mL distilled water were added. After the mixture was stirred for 15 min, 3 g of NaOH was added, and the solution was refluxed for 1 h. Then, 2-ethylhexyl bromide (3.48 g, 18 mmol) and a catalytic amount of tetrabutylammonium bromide (Bu$_4$NBr) were added, and the solution was refluxed overnight. After the reaction mixture was cooled to ambient temperature, the resulted solution was poured into cold water and hydrochloric acid (20 mL) was added to the mixture for adjusting the pH (~3). The mixture was extracted with chloroform and the organic phase was dried over anhydrous Na$_2$SO$_4$. After removing solvent under reduced pressure, the crude product was purified over a silica gel column. Compound II (0.62 g, yield 73.9 %) was obtained as white powder. M.p.: 49–51 °C. ^{1}H NMR (CDCl$_3$, 400 MHz), δ (ppm): 7.56 (d, J=5.2 Hz, 2H), 7.32 (d, 3 J= 5.2 Hz, 2H), 4.23 (d, J=4.8 Hz, 4H), 2.06–2.01 (m, 2H), 1.78–1.56 (m, 8H), 1.47–1.37 (m, 8H), 1.05 (t, J=7.2 Hz, 6H), 0.94 (t, J=6.8 Hz, 6H). Elemental analysis: Calculated for C$_{30}$H$_{38}$O$_2$S$_4$: C, 64.47; H, 6.85. Found: C, 64.38; H, 6.79.

*2,7-Di(trimethylstannyl)-5,10-bis(2-ethylhexyloxy)
dithieno[2,3-d:2',3'-d']- benzo [1,2-b:4,5-b']dithiophene (III)*

Compound II (1.12 g, 2 mmol) was dissolved in 40 mL of anhydrous THF and cooled in an ice bath under nitrogen atmosphere. 1.2 mL *n*-butyllithium solution (2.5 M in hexanes) was added dropwise. And the solution was kept in the

dry ice bath for 0.5 h and ambient temperature for another 0.5 h under vigorous stirring. The mixture was cooled in an ice bath again and trimethyltin chloride solution (0.61 g, 3.1 mmol) was added in one portion. Then the solution was stirred at ambient temperature overnight. The mixture was quenched with 20 mL water and extracted with hexanes. The organic extraction was dried with anhydrous sodium sulfate and the solvent was removed under reduced pressure. The resulted solid was recrystallized into *iso*-propanol to yield III as colorless needles (1.1 g, yield, 62.2 %). ^{1}H NMR (CDCl$_3$, 400 MHz), δ (ppm): 7.45 (s, 2H), 4.22 (d, J=6.0 Hz, 4H), 2.01–2.07 (m, 2H), 1.62–1.69 (m,16H), 1.06 (t, 6H), 0.9 (t, 6H). 0.49 (s, 18H). FAB-MS, 884.

Synthesis of PDTBDT-ID

A mixture of toluene (6 mL) and *N,N*-dimethylformamide (DMF, 0.5 mL) was added to a 55 mL microwave tube containing III (265.3 mg, 0.3 mmol), *N,N*-di(2-hexyldecyl)-6,6'-dibromo-isoindigo (ID) (260.7 mg, 0.3 mmol) and Pd(PPh$_3$)$_4$ (4.0 mg) in a glove box with moisture and oxygen under 1 ppm. Then the tube was subjected to the following reaction conditions in a microwave reactor: 120 °C for 5 min, 140 °C for 5 min and 160 °C for 20 min. At the end of polymerization, the polymer was end-capped with 2-tributylstannylthiophene and 2-bromothiophene to remove bromo and trimethystannyl end groups. The mixture was then poured into methanol. The precipitated material was collected, and extracted with ethanol, acetone, hexane and toluene in a Soxhlet extractor. The solution of the copolymer in toluene was condensed to 20 mL and then poured into methanol (500 mL). The precipitation was collected and dried under vacuum overnight (yield: 75 %). $M_n=$ 14,650 g/mol with a polydisperse index (PDI) of 1.76. ^{1}H NMR (CDCl$_3$, 400 MHz), δ (ppm): 9.08 (br, 2H), 7.50 (br, m 2H), 7.18–6.98 (m, br, 4H), 4.22 (br, 2H), 3.65 (br, 2H), 2.03–0.84 (m, br, 96H).

Results and discussion

Synthesis and characterization

The general synthetic route toward the monomers and polymer is outlined in Scheme 1. 5,10-Di(2-ethylhexyloxy)dithieno[2,3-*d*:2',3'-*d*']benzo[1,2-*b*:4,5-*b*'-]dithiophene (II) was synthesized as the following procedure: the diketone (I) was successively treated with zinc powder under the presence of NaOH aqueous solution and 2-ethylhexyl bromide with catalytic amount of tetrabutylammonium bromide to lead 5,10-di(2-ethylhexyloxy)dithieno[2,3-*d*:2',3'-*d*']benzo[1,2-*b*:4,5-

Scheme 1 Synthetic route of the monomers and polymer
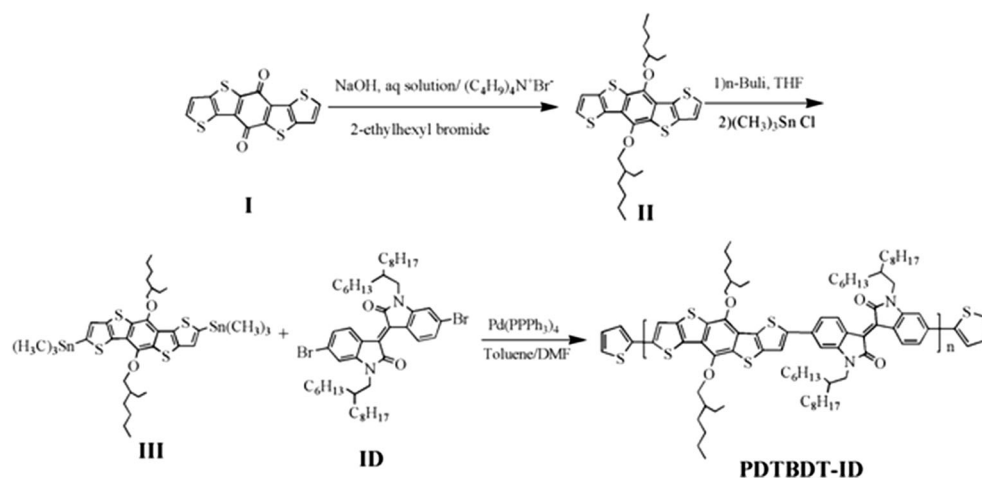
b']dithiophene (II) [34]. The 2,7-Di(trimethylstannyl)-5,10-bis(2-ethylhexyloxy)-DTBDT (III), was synthesized as the following procedure: the II was firstly reacted with n-BuLi in anhydrous THF at 0 °C, then the solution of trimethylstannyl chloride in anhydrous THF was added in one portion to lead compound III with yield of 62.2 %. The structures of the compounds were confirmed by ^{1}H NMR and elemental analyses. The alternating conjugated copolymer (PDTBDT-ID) was synthesized with III and *N,N*-di(2-hexyldocyl)-6,6'-dibromo-isoindigo (ID) through the palladium-catalyzed Stille coupling reaction under mono-microwave heating condition. Subsequently, the polymer was end-capped with 2-tributylstannylthiophene and 2-bromothiophene to remove bromo and trimethystannyl end groups. The ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of the copolymer exhibited broad NMR signals at ca. 9.05, 7.50, 7.18–6.98, 4.22, 3.65 and 2.02–0.84 ppm. The peaks at 9.05 and 7.18–6.98 ppm were presented the H atoms of ID rings in the copolymer, and one at 7.50 ppm was presented H atoms of DTBDT rings. We also monitored the NMR signal at 4.22 and 3.65 ppm which was respectively presented the α-H atoms of 2-ethylhexyl and 2-hexyldecyl in the di(2-ethylhexyloxy)-DTBDT units and ID units. And the NMR signals ranging from 2.02 ppm to 0.84 ppm were presented the other H atoms of the alkyl on the di(2-ethylhexyloxy)-DTBDT units and ID units. ^{1}H NMR spectrum of the copolymer confirmed that the copolymer is right on target alternating molecular structures containing di(2-ethylhexyloxy)-DTBDT and di(2-hexyldecyl)-isoindigo units. The number-average molecular weights of the resulting polymer determined by GPC in tetrahydrofuran (THF) with polystyrene standards, is about to 14,650 g/mol with a polydisperse index (PDI) of 1.76. The decomposed temperature (T_d, 5 % weight-loss) of the polymers is about 367.0 °C (Fig. 1).

Optoelectronic properties of the polymer

The UV–vis absorption spectra of PDTBDT-ID in chloroform solution and solid thin film were monitored on a UV-2550 spectrophotometer, and presented in Fig. 2. As shown in Fig. 2, the PDTBDT-ID exhibited two absorption peaks at 402 and 648 nm with a shoulder absorption peak at around 702 nm in chloroform solution. The PDTBDT-ID in solid thin film exhibited two absorption peaks at 409 and 710 nm with shoulder absorption at around 648 nm. The PDTBDT-ID in chloroform solution and solid thin film showed extensive light absorption ranging from 330 to 782 nm, and the optical band gap (E_g) of PDTBDT-ID estimated from the onset of absorption edge in solid thin film is about 1.58 eV.

The electrochemical behavior of the polymer in solid state was investigated by CV in a nitrogen-saturated solution of 0.1 M tetrabutylammonium hexafluorophosphate in
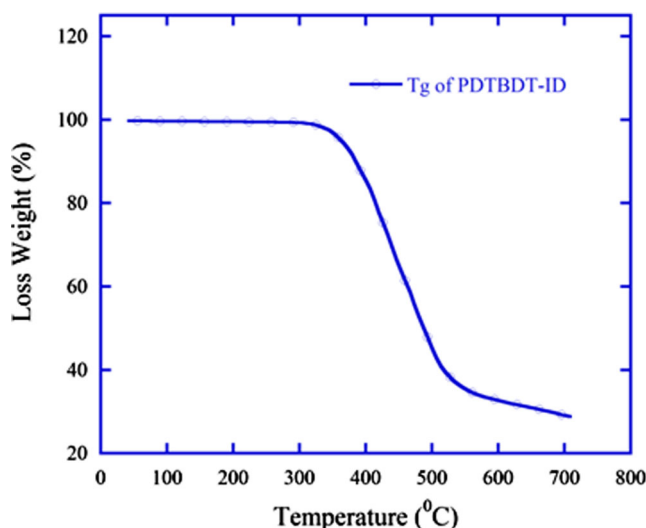
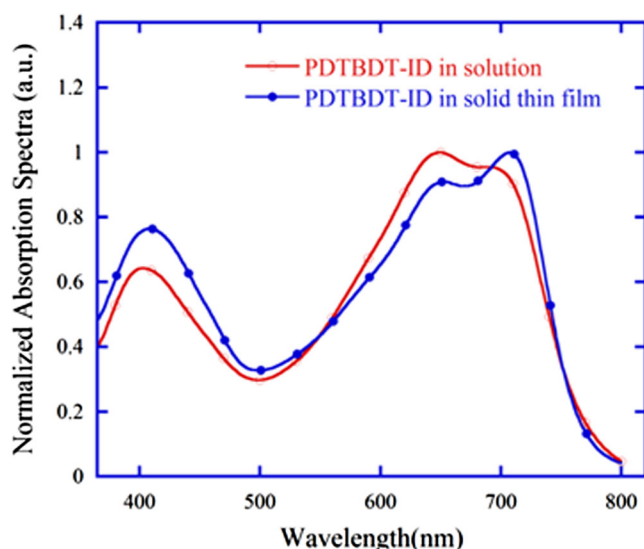**Fig. 1** TG curve of PDTBDT-ID

Fig. 2 Normalized absorption spectra of PDTBDT-ID in solid thin film and chloroform solution

acetonitrile with glass carbon and Ag/AgCl electrode as the working and reference electrode, respectively. The oxidation potential of PDTBDT-ID was observed at around 0.92 eV (Fig. 3). The redox potential of Fc/Fc$^+$ in the above-mentioned condition is +0.34 V, which is assumed to have an absolute energy level of −4.8 eV to vacuum for calibration [36]. The HOMO and LUMO levels of the PDTBDT-ID calculated by empirical formulas ($E_{HOMO}=-(E_{ox}+4.46)$ (eV), and $E_{LUMO}=(E_{HOMO}+E_g)$ (eV) [35]) were −5.38 and −3.80 eV, respectively.

Photovoltaic property of the polymer

Photovoltaic property of the PDTBDT-ID was investigated by fabricating PVCs with a configuration of ITO/PEDOT:PSS/
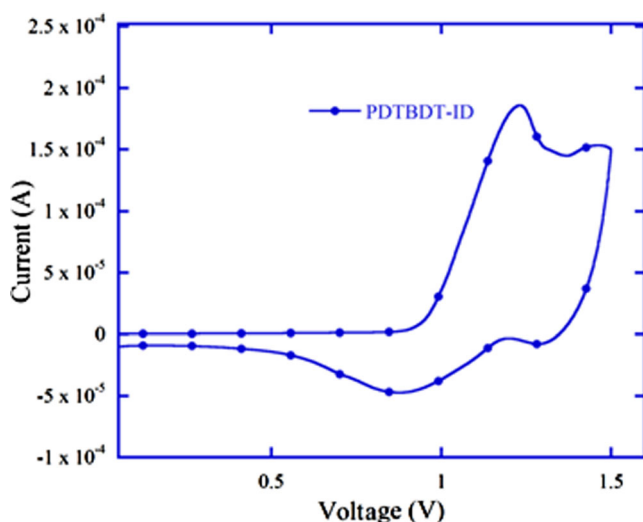
polymer:PC$_{71}$BM/Ca/Al. Initially, the *o*-dichlorobenzene (ODCB) was used as the solvent for the fabrication of PVCs based on PDTBDT-ID/PC$_{71}$BM. Unfortunately, the thickness (20–30 nm) of the blend film of PDTBDT-ID/PC$_{71}$BM with weight ration of 1:1 is not enough to fabricate the PVCs. Then, we used toluene as the solvent in the fabrication of PVCs. Although the film with thickness of 80–200 nm can be prepared through the spin-coating of the solution PDTBDT-ID/PC$_{71}$BM in toluene, there are many pin-holes in the blend film of PDTBDT-ID/PC$_{71}$BM, and a low PCE of 0.21 % with open circuit voltage (V_{oc}) of 0.75 V, short circuit current density (J_{sc}) of 0.86 mA/cm^2 and fill factor (*FF*) of 0.33 % under AM 1.5 G with irradiation of 100 mW/cm^2 was obtained in the PVCs from the blend film of PDTBDT-ID/PC$_{71}$BM with weight ratio of 1:1 (Table 1 and Fig. 4a). As the PDTBDT-ID exhibited extensive absorption from 350 to 780 nm and appropriate energy levels (Figs. 2 and 3), the low PCE of
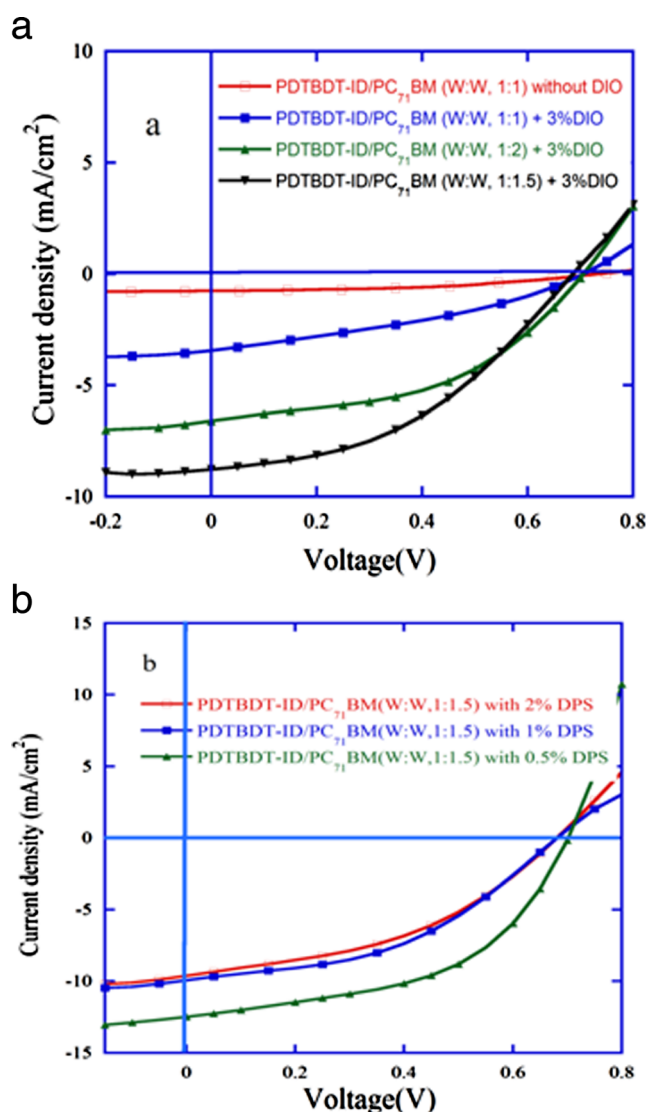
a

b

Fig. 4 *J/V* characteristics of PVCs based on PDTBDT-ID and PC$_{71}$BM

Fig. 3 Electrochemical curve of PDTBDT-ID

Table 1 Photovoltaic parameters of PVCs from PDTBDT-ID and $PC_{71}BM$

Blend	Additives (%)	V_{oc} (V)	J_{sc} (mA/cm^2)	J^{interg}_{sc} (mA/cm^2)	FF(%)	η (%)
PDTBDT-ID:/PC$_{71}$BM (W:W, 1:1)	0	0.75	0.86	0.54	0.33	0.21
PDTBDT-ID:/PC$_{71}$BM (W:W, 1:1)	3[a]	0.69	6.60	–	46.29	2.10
PDTBDT-ID:/PC$_{71}$BM (W:W, 1:1.5)	3[a]	0.70	8.86	8.93	40.88	2.54
PDTBDT-ID:/PC$_{71}$BM (W:W, 1:2)	3[a]	0.71	3.43	–	34.87	0.84
PDTBDT-ID:/PC$_{71}$BM (W:W, 1:1.5)	0.5[b]	0.70	12.58	13.20	50.28	4.43
PDTBDT-ID:/PC$_{71}$BM (W:W, 1:1.5)	1[b]	0.68	10.04	–	43.71	2.98
PDTBDT-ID:/PC$_{71}$BM (W:W, 1:1.5)	2[b]	0.68	9.75	–	41.31	2.74

[a] DIO was used as solvent additive

[b] DPS was used as solvent additive

PVCs from PDTBDT-ID/PC$_{71}$BM should be attributed to the poor property and morphology of blend film from PDTBDT-ID/PC$_{71}$BM.

Solvent additives, like DIO, played an important role in optimizing photovoltaic performance of PVCs [7, 12, 13, 37–41]. Similar to the results in the reported works [37–41], the PCEs of PVCs from PDTBDT-ID and PC$_{71}$BM were clearly increased as 3 % (V_{DIO}:$V_{toluene}$) of DIO was added to the solution of PDTBDT-ID/PC$_{71}$BM in toluene. And PVCs with PCEs of 0.21–2.54 %, V_{oc} of 0.75–0.70 V, J_{sc} of 0.86–8.86 mA/cm^2 and FF of 0.33–40.88 % were achieved from the blend film of PDTBDT-ID and PC$_{71}$BM (Table 1, Fig. 4a). The maximal PCE of 2.54 % has been achieved in the PVCs from PDTBDT-ID and PC$_{71}$BM with the weight ratio of 1:1.5.

In recently, we chanced on an interesting phenomenon that the addition of small amount of DPS could remarkably improve blend film properties from the solution of PDTBDT-ID and PC$_{71}$BM in toluene. It should give the chance to further modify the performance of PVCs based on PDTBDT-ID and PC$_{71}$BM. To further modify the performance of PVCs from PDTBDT-ID, the volume ratios of DPS (V/V, DPS/toluene) with 0.5 %, 1 % and 2 % were employed to find the optimal composition of the processing solvent, and the weight ratios of PDTBDT-ID and PC$_{71}$BM was fixed at 1:1.5 (Table 1, Fig. 4b). As shown in Table 1, the values of J_{sc} for the PVCs based on PDTBDT-ID/PC$_{71}$BM (W:W, 1:1.5) were decreased from 12.58 to 10.04 mA/cm^2, and then dropped to 9.75 mA/cm^2 and V_{oc} were fluctuated between 0.68 and 0.70 V while the volume content of DPS were varied from 0.5 % and 1 % to 2 %, The maximal PCEs of 4.43 % with Voc of 0.70 V, J_{sc} of 12.58 mA/cm^2 and FF of 50.28 %, could be obtained in the PVCs from the blend film of PDTBDT-ID/PC$_{71}$BM with the weight ratio of 1:1.5 while 0.5 % of DPS was used as solvent additives (Table 1, Fig. 4b).

The incident photon to charge carrier efficiency (IPCE) curves of the PVCs from PDTBDT-ID/PC$_{71}$BM are presented in Fig. 5. All of PVCs based on PDTBDT-ID and PC$_{71}$BM

exhibited photo-response ranging from 330 to 780 nm except that the photo-response intensities of PVCs were varied as the solvent additives and weight ratio of PDTBDT-ID and PC$_{71}$BM were changed. According to the IPCEs of the PVCs, the integral current density values of the PVCs based on optimal weight ratio of PDTBDT-ID/PC$_{71}$BM with DIO and DPS as solvent additives were 8.93 and 13.20 mA/cm^2, respectively. The mismatch between the integral current densities and the J_{sc} values of the PVCs obtained from J-V measurement is within 5 % (Table 1). It indicated that J_{sc} obtained from J-V measurements in this study are reliable.

To verify the modification of morphologies and properties of the blend films from PDTBDT-ID and PC$_{71}$BM through the addition of the solvent additives such as DIO and DPS, thus improving the performance, especially improving the J_{sc} of the PVCs from PDTBDT-ID and PC$_{71}$BM, the topography images of the composite films prepared by the PDTBDT-ID/PC$_{71}$BM (W:W, 1:1.5) in toluene with different solvent additives were monitored (Fig. 6). Study of the film morphology by atomic force microscopy (AFM) showed that there were
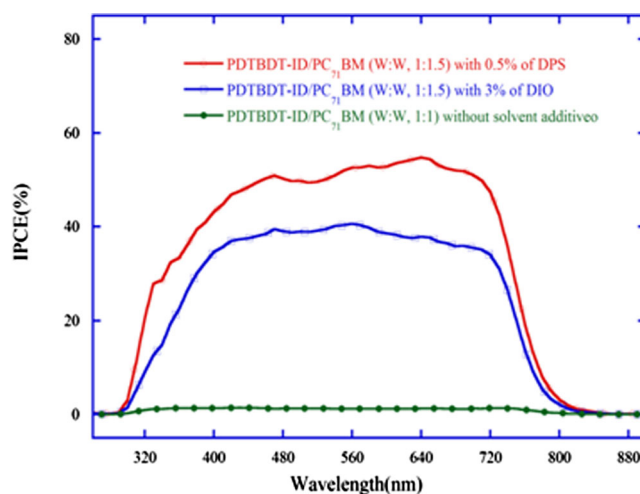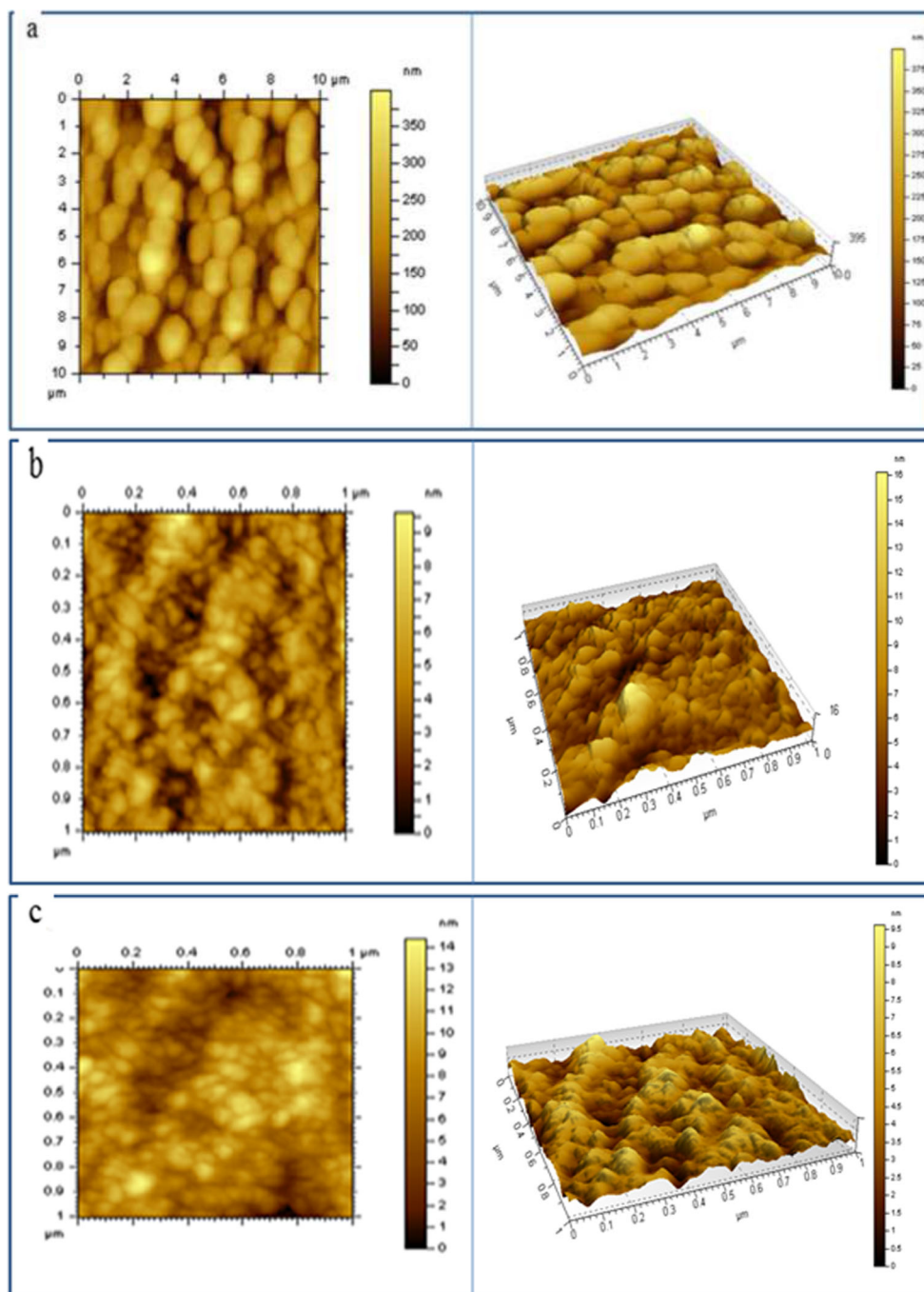

Fig. 5 IPCE characteristics of PVCs based on PDTBDT-ID and PC$_{71}$BM

Fig. 6 Tapping mode AFM topography images of the 1: 1.5 (weight ratio) composite films of **a** PDTBDT-ID/PC$_{71}$BM without additives, **b** PDTBDT-ID/PC$_{71}$BM with 3 % DIO additives, **c** PDTBDT-ID/PC$_{71}$BM with 0.5 % DIO additives

many large isolated domains (~2 μm diameters) in the blend film prepared without using solvents. And the root-mean-square (rms) of the surface roughness of the blend films prepared by PDTBDT-ID/PC$_{71}$BM in toluene was 65.1 nm (Fig. 6a). When DIO (3 % by volume) was added to the solution, the uniform and domain structure of the resulting blend film from PDTBDT-ID/PC$_{71}$BM was clearly modified, and the rms of the surface roughness was dramatically decreased to 1.88 nm (Fig. 6b). When DPS (0.5 % by volume) was added to the solution, the uniform and domain structure of

the resulting blend film from PDTBDT-ID/PC$_{71}$BM were further improved, and the rms of the surface roughness was decreased to 1.38 nm (Fig. 6c). It indicated that improvements of the PCEs and J_{sc} for the PVCs should be attributed to the improvements of uniform and domain structure of blend film from PDTBDT-ID/PC$_{71}$BM with solvent additives, such as DIO and DPS. These results also implied that the DPS may be a promising candidate for the notable DIO which was used as solvent additives to modify the morphologies and properties of the blend films from CPs and fullerene derivatives.

Conclusions

In this paper, an alternating low band gap conjugated polymer derived from 5,10-di(2-ethylhexyloxy)dithieno[2,3-*d*:2',3'-*d*']-benzo[1,2-*b*:4,5-*b*']dithiophene and *N*,*N*-di(2-hexyldecyl)isoindigo, was synthesized and named as PDTBDT-ID. The chemical structure, optoelectronic, thermal stability and electrochemical property of PDTBDT-ID were characterized. The polymer exhibited extensive absorption from 350 and 780 nm with the HOMO energy level of −5.38 eV and the LUMO energy level of −3.80 eV. The photovoltaic properties of PDTBDT-ID were also investigated. The power conversion efficiency of 0.21 % for PVCs from the blend of the PDTBDT-ID and PC$_{71}$BM is very low. The uniform and domain structure of the resulting blend film from PDTBDT-ID and PC$_{71}$BM (W:W, 1:1.5) could be remarkably modified while a very small amount of DPS or DIO was used as solvent additives in the fabrication of the films. And the maximal PCE of 2.54 and 4.43 % were respectively achieved in the PVCs from the blend of PDTBDT-ID and PC$_{71}$BM (W:W, 1:1.5) with DIO and/or DPS as solvent additives under 100 mW/cm^2 illumination (AM 1.5G). It could be found that, the PCEs of PVCs from the PDTBDT-ID and PC$_{71}$BM (W:W, 1:1.5) with DPS as solvent additives were increased 74 % as compared with that for the PVCs from the PDTBDT-ID and PC$_{71}$BM (W:W, 1:1.5) with DIO as the solvent additives. These results implied that the DPS may be a promising candidate for the notable DIO which was used as solvent additives to modify the morphologies and properties of the blend films from CPs and fullerene derivatives.

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