Copolymers from benzodithiophene and benzotriazole: synthesis and photovoltaic applications

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Two new alternating low bandgap copolymers from benzodithiophene and benzotriazole units, namely poly{4,8-bis(2-ethylhexyloxy)benzo[1,2-b; 3,4-b]dithiophene-2,6-diyl-*alt*-2-octyl-4,7-di(thiophen-2-yl)-2*H*-benzo[d][1,2,3]triazole-5′,5″-diyl} (**PBDTDTBTz**) and poly{4,8-bis(2-ethylhexyloxy)benzo[1,2-b;3,4-b]dithiophene-2,6-diyl-*alt*-2-dodecylbenzotriazole-4,7-diyl} (**PBDTBTz**), were designed and synthesized by a typical Stille coupling polymerization method. The copolymers were characterized by thermogravimetric analysis, UV-vis absorption and cyclic voltammetry. **PBDTDTBTz** and **PBDTBTz** possess moderate molecular weights and excellent thermal properties with a 5% weight loss temperatures (T_d) around 300 °C. They exhibited good optical absorption, with peaks at 527 nm and 562 nm in the film state, respectively. Photovoltaic properties of the copolymers blended with [6,6]-phenyl-C61-butyric acid methyl ester ($PC_{61}BM$) or [6,6]-phenyl-C71-butyric acid methyl ester ($PC_{71}BM$) as electron acceptors, were investigated. The photovoltaic device with the **PBDTDTBTz**/$PC_{71}BM$ shows a power conversion efficiency of 1.7% with a short circuit current density of 4.5 mA cm^{-2} and a good fill factor of 0.62, while **PBDTBTz** demonstrated a moderate power conversion efficiency of up to 1.4%, under the illumination of AM 1.5, 100 mW cm^{-2} with a device structure of ITO/PEDOT: PSS/polymer: $PC_{71}BM$ (1 : 4)/Ca/Al. All the above information highlighted that this kind of the copolymers is promising for the application of polymer solar cells.

Introduction

Bulk heterojunction (BHJ) polymer solar cells (PSCs) have stimulated broad interest due to their many advantages such as easy fabrication, low cost, light weight, and flexibility.[1] BHJ PSCs involve a thin film blend of the conjugated polymer as the electron donor and a fullerene derivative as the electron acceptor. Among the various types of polymers designed for PSCs, the alternating electron rich and electron deficient units along the polymer backbone have been shown to achieve high power conversion efficiencies (PCEs) through optimizations of their absorption, open circuit voltage and relevant device parameters.[2] During the past two years, benzodithiophene (BDT)-containing conjugated polymers have demonstrated exceptionally excellent photovoltaic properties as electron donors for PSCs. For instance, Yang and co-workers have synthesized a family of BDT based copolymers with optimized electronic and optical properties which led to PCEs as high as 7%.[3] Recently, Leclerc and co-workers reported a new and interesting BDT-based polymer (PBDTTPD) with thienopyrrodione as the new accepting building block exhibiting high PCE up to 5.5% using a large active area of 1 cm^2.[4]

In order to modulate the bandgap and molecular energy levels, new electron accepting units play important role in developing the new D–A copolymers for photovoltaic applications. 2,1,3-Benzothiadiazole (BT) and 4,7-dithienyl-2,1,3-benzothiadiazole (DTBT) units are found to be widely used acceptors for the synthesis of low band gap copolymers.[5] For instance, copolymers of DTBT with fluorene,[5a] silafluorene,[5b] carbazole,[1j] dithienylsilole,[5c] dithienylpyrrole,[5d] were synthesized and applied in PSCs, exhibiting some promising PCEs.

However, 1,2,3-benzotriazole (BTz) which is similar to 2,1,3-benzothidiazole is missing from the chemical inventory. In fact, BTz is a known heteroaromatic compound with a strong electron accepting feature because of two electron withdrawing imine (C = N) nitrogens, furthermore, easy modification of N–H bond of BTz unit can allow tuning of the structural and electronic properties for processable BTz-containing polymers. To the best of our knowledge, BTz based homopolymers and copolymers remain relatively unexplored. Very recently, the polymer from BTz and alkyl-thiophene synthesized using an electrochemical polymerization method has shown some photovoltaic properties for the first time.[6]

Taking all this into consideration, the combination of benzodithiophene and BTz should lead to some interesting features for photovoltaic applications. Herein, we firstly synthesized the copolymer (**PBDTBTz**) of BDT and BTz using a Stille coupling reaction. Furthermore we put thiophene units next to the BTz moiety to minimize the steric hindrance and to lower the band gaps.[7] We synthesized another copolymer (**PBDTDTBTz**) of DBT and dithienyl benzotriazole (DTBTz). The two new

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conjugated polymers exhibit broad absorption, optimized HOMO–LUMO energy levels, efficient photovoltaic properties, together with good thermal stability. The PSC device based on **PBDTDTBTz** as the electron donor and $PC_{71}BM$ as acceptor demonstrated a PCE of 1.7% with a short circuit current density (J_{sc}) of 4.5 mA cm^{-2} and fill factor (*FF*) of 0.62 under the illumination of AM 1.5, 100 mW cm^{-2}. The results indicate that the BTz unit is potentially an interesting building block for polymeric photovoltaic materials.

Experimental section

Materials

$Pd(PPh_3)_4$, thiophene-2-boronic acid were obtained from Alfa Asia Chemical Co, and they were used without further purification. Tetrahydrofuran (THF) was dried over Na/benzophenone ketyl and freshly distilled prior to use. Other reagents and solvents were purchased commercially as analytical-grade quality and used without further purification. 2-Octylbenzotriazole (**1**),[8] 4,7-Dibromo-2-octylbenzotriazole (**2**),[8] 2-dodecylbenzotriazole (**5**),[8] 4,7-dibromo-2-dodecylbenzotriazole (**6**),[8] 2,6-bis(trimethyltin)-4,8-bis(2-ethylhexoxy)benzo[1,2-b;3,4-b]dithiophene (**7**)[9] were prepared according to the little modified method based on the reported literature. All the other compounds were synthesized following the procedures described here.

Characterization

^{1}H NMR and ^{13}C NMR spectra were recorded using a Bruker AM-400 spectrometer, with tetramethylsilane (TMS) as the internal reference, chemical shifts were recorded in ppm. Molecular weight and polydispersity of the polymers were determined by gel permeation chromatography (GPC) analysis with polystyrene as standard (Waters 515 HPLC pump, a Waters 2414 differential refractometer, and three Waters Styragel columns (HT2, HT3, and HT4)) using THF (HPLC grade) as eluent at a flow rate of 1.0 mL min^{-1} at 35 °C. Thermogravimetric analysis (TGA) was conducted on a Shimadzu DTG-60 thermogravimetric analyzer with a heating rate of 10 K min^{-1} under a nitrogen atmosphere. The UV-vis absorption spectra were recorded on a JASCO V-570 spectrophotometer. For solid state measurements, polymer solution in chloroform was drop-cast on quartz plates. The optical bandgap was calculated from the onset of the absorption band. The cyclic voltammogram was recorded with a computer controlled Zahner IM6e electrochemical workstation (Germany) using polymer film on platinum disk as the working electrode, platinum wire as the counter electrode and Ag/Ag$^+$ (0.1 M) as the reference electrode in an anhydrous and argon-saturated solution of 0.1 M of tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in acetonitrile. Electrochemical onsets were determined at the position where the current starts to differ from the baseline. The morphology of the polymer/PCBM blend films was investigated by a SPI 3800N atomic force microscope (AFM) in contacting mode with a 1 μm scanner.

Fabrication and characterization of polymer solar cell

The PSCs were fabricated in the configuration of the traditional sandwich structure with an indium tin oxide (ITO) glass positive electrode and a metal negative electrode. Patterned ITO glass with a sheet resistance of 10 Ω/□ was purchased from CSG HOLDING Co., LTD. (China). The ITO glass was cleaned by sequential ultrasonic treatment in detergent, deionized water, acetone, and isopropanol, and then treated in an ultraviolet-ozone chamber (Ultraviolet Ozone Cleaner, Jelight Company, USA) for 20 min. Then PEDOT:PSS (poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate)) (Baytron P 4083, Germany) was filtered through a 0.45 μm filter and spin coated at 2000 rpm for 60 s on the ITO electrode. Subsequently, the PEDOT: PSS film was baked at 150 °C for 15 min in the air to give a thin film with a thickness of 40 nm. A blend of polymer and $PC_{61}BM$ (1 : 3 *w/w*, 10 mg mL^{-1} for polymers) or polymer and $PC_{71}BM$ (1 : 4 *w/w*, 10 mg mL^{-1} for polymers) was dissolved in ortho-dichlorobenzene (ODCB), and spin-cast at 3000 rpm for 45 s onto the PEDOT: PSS layer. The substrates were then dried at 70 °C for 15 min. The thickness of the photoactive layer is in the range 50–70 nm measured by Ambios Technology XP-2 profilometer. A bilayer cathode consisted of Ca (∼20 nm) capped with Al (∼60 nm) was thermal evaporated under a shadow mask in a base pressure of *ca.* 10^{-5} Pa. The device active area of the PSCs is 4 mm². Device characterization was carried out under AM 1.5 G irradiation with the intensity of 100 mW cm^{-2} (Oriel 67005, 500 W) calibrated by a standard silicon cell. *J*–*V* curves were recorded with a Keithley 236 digital source meter. The action spectra of monochromatic incident photo-to-current conversion efficiencies (IPCEs) for the solar cells were also detected with a similar data acquisition system. The calibration of the incident light was performed with monocrystalline silicon diodes.

Synthesis

The synthetic routes for the monomers and polymers are shown in Scheme 1. The detailed synthetic processes are as follows.

2-Octyl-4,7-di (thiophen-2-yl)-2*H*-benzo[d][1,2,3]triazole (DTBTz) (3)

Compound **2** (3.5 g, 9 mmol) and thiophene-2-boronic acid (3.0 g, 23.4 mmol), and $Pd(PPh_3)_4$ (208 mg, 0.18 mmol) were dissolved in 1,2-dimethoxyethane (80 mL), followed by the addition of aqueous sodium bicarbonate (1.0 M, 90 mL) with the reaction mixture vigorously stirred at 90 °C for 12 h under a nitrogen atmosphere. After cooling, the reaction solution was extracted with methylene chloride, the combined organic layers were washed with 1 M aqueous solution of NaOH and water, dried over anhydrous magnesium sulfate, and then concentrated under reduced pressure. Further purification was performed using silica gel column chromatography (petroleum ether/EtOAc = 50 : 1 as eluent), compound **3** was obtained as yellow-green crystal. The yield was 82%.

^{1}H NMR (400 MHz, CDCl$_3$, ppm): 8.01 (d, 2H), 7.52 (s, 2H), 7.28 (d, 2H), 7.09 (t, 2H), 4.60 (t, 2H), 2.10 (m, 2H), 1.35−1.17 (m, 10H), 0.80 (t, 3H).
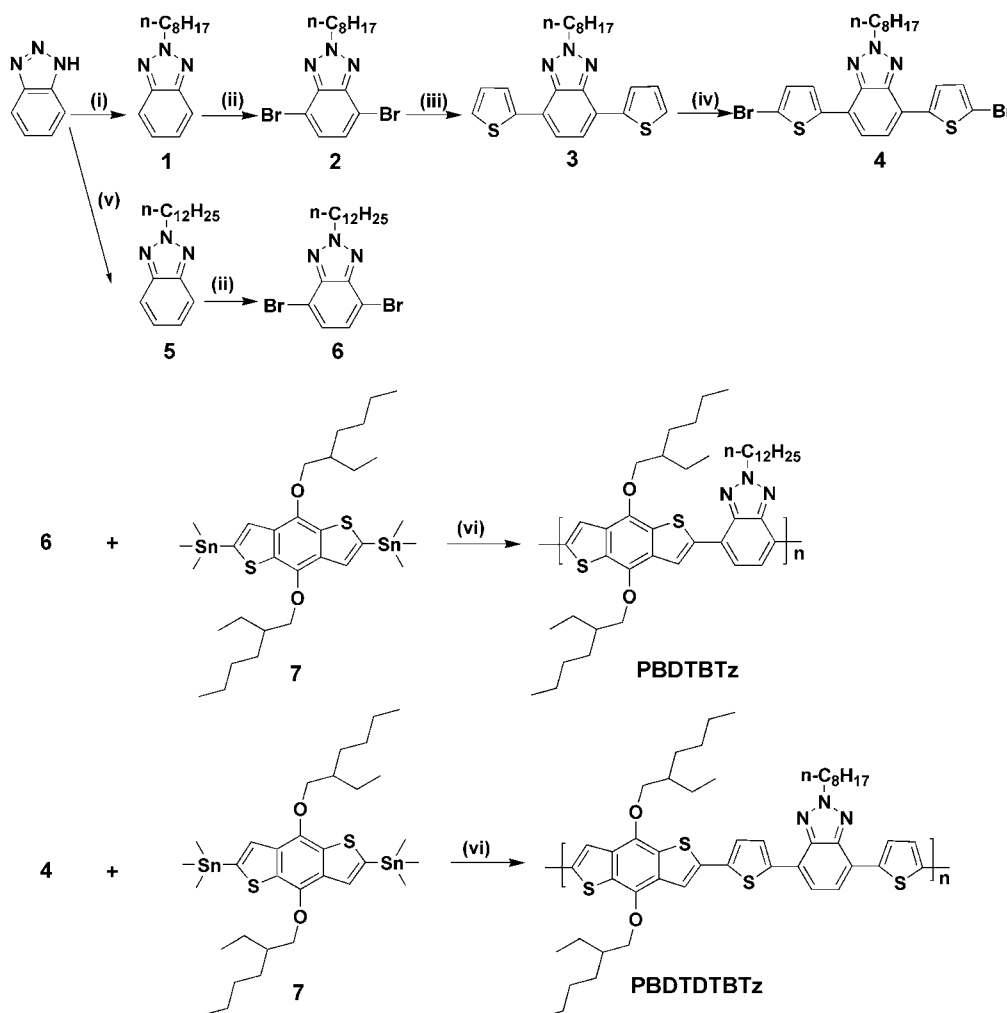
Scheme 1 Synthetic routes of the monomers and polymers. Reagents and conditions: (i) C₈H₁₇Br, KOH, CH₃OH, reflux for 24 h, 30% yield; (ii) Br₂/HBr, 135 °C for 12 h, 75% yield; (iii) thiophene-2-boronic acid, Pd(PPh₃)₄, 1,2-dimethoxyethane (DME), 1 M NaHCO₃, 90 °C for 12 h, 82% yield; (iv) NBS, CHCl₃/HAc, 12 h at ambient temperature, 75% yield; (v) C₁₂H₂₅Br, KOH, CH₃OH, reflux for 24 h, 30% yield; (vi) Pd(PPh₃)₄, toluene, 110 °C for 24 h.

Calculated for $C_{22}H_{25}N_3S_2$: C, 66.80; H, 6.37; N, 10.62; found: C, 66.78; H, 6.31; N, 10.58.

2-Octyl-4, 7-di(5-bromo-thiophen-2-yl)-2H-benzo[d] [1, 2, 3]triazole (4)

Under the darkness, compound **3** (2.37 g, 6 mmol) was dissolved in the mixture of CHCl₃ (60 mL) and HOAc (60 mL), after cooling the mixture to 0 °C, NBS (2.35 g, 13.2 mmol) was added in portions. After 12 h, the reaction mixture was extracted with CH₂Cl₂ and washed by water twice, and then combined organic extractions were dried over anhydrous Na₂SO₄. The organic solvent was evaporated. The crude product was purified by recrystallization using dimethyl formide (DMF), yellow crystals were obtained with 75% yield.

¹H NMR (400 MHz, CDCl₃, ppm): 7.79 (d, 2H), 7.51 (s, 2H), 7.13 (d, 2H), 4.80 (t, 2H), 2.18 (m, 2H), 1.41–1.27 (m, 10H), 0.87 (t, 3H).

¹³C NMR(100 MHz, CDCl₃, ppm): 141.69, 141.23, 130.86, 126.93, 122.98, 122.16, 113.16, 59.91, 31.75, 30.03, 29.10, 28.97, 26.58, 22.62, 14.07.

Calculated for $C_{22}H_{23}N_3S_2Br_2$: C, 47.75; H, 4.19; N, 7.59; found: C, 47.72; H, 4.23; N, 7.62.

Synthesis of PBDTBTz

2,6-Bis(trimethyltin)-4,8-bis-ethylhexyloxy-benzo[1,2-b:4,5-b′]di-thiophene (231.6 mg, 0.3 mmol), 4,7-dibromo-2-dodecylbenzo-triazole (133.5 mg, 0.3 mmol), and 10 mL of toluene were put into a two necked flask. The solution was flushed with argon for 20 min, and then 17 mg of Pd(PPh₃)₄ was added into the flask. The solution was flushed again for 10 min. The oil bath was heated to 100 °C carefully, and the reactant was stirred for 24 h at this temperature under an argon atmosphere. Then, the reactant was cooled to room temperature, and the polymer was precipitated by the addition of 50 mL of methanol and filtered through a Soxhlet thimble, which was then subjected to Soxhlet extraction with methanol, hexane, and chloroform. The polymer was recovered from the chloroform fraction by rotary evaporation. The red solid was dried under vacuum at 50 °C overnight to get the final product. (170 mg, 78%).

¹H NMR (400 MHz, CDCl₃, ppm): 7.74 (br, 2H), 7.49 (br, 2H), 4.90 (br, 2H), 3.53 (br, 4H), 2.28 (br, 4H), 1.53–1.10 (br, 34H), 0.87 (br, 15H).

Synthesis of PBDTDTBTz

PBDTDTBTz was synthesized with a similar procedure to **PBDTBTz** from monomer **7** (231.6 mg, 0.3 mmol) and monomer **4** (165.9 mg 0.3mmol), giving a red dark solid of 34 mg. Yield: 14%.

Results and discussion

Monomers and polymers synthesis

The synthetic routes of the monomers and polymers are shown in Scheme 1. The comonomer **4**, was synthesized as the following process. Starting from 1,2,3-benzotriazole, an alkylation reaction was performed to get 2-octylbenzotriazole (compound **2**) with a similar yield,[8] by using KOH as base instead of t-BuOK reported in the literature. Because of the two possible alkylation sites of the benzotriazole, the desired isomer was isolated in 30% yield in the first step of the reaction sequence. However, this reaction stands as a practical step with relatively cheap starting materials and reagents; hence it can be performed in quite large scales. This step was then followed by a dibromination reaction using Br₂/HBr system to yield compound **2** with 75% yield. Compound **2** took a Suzuki coupling reaction with 2-thiophene boronic acid to obtain the compound **3**, this step revealed a quite satisfactory yield. A dibromination step of compound **3** using NBS as brominating agent to get comonomer **4** in 75% yield. The synthetic procedure for compound **6** was similar to that for compound **2**. Compound **7** copolymerized with compound **4** or compound **6** through Stille coupling reactions to afford the target polymers (**PBDTDTBTz** and **PBDTBTz**), respectively,[10] and the polymers were purified by sequential Soxhlet extraction with methanol, hexane and CHCl₃. The CHCl₃ fraction was then reduced in volume, precipitated into methanol, and collected by filtration yielding a dark red or red solid. The monomers and **PBDTBTz** were verified by ¹H NMR spectra. However, we can't obtain the NMR of **PBDTDTBTz** because of its limited solubility. The copolymer **PBDTBTz** exhibits excellent solubility in
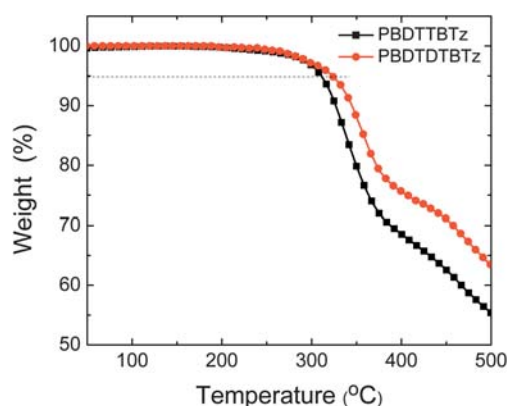

Fig. 1 TGA plots of **PBDTBTz** and **PBDTDTBTz** with a heating rate of 10 °C min⁻¹.

common solvents such as THF, CHCl₃, dichlorobenzene, and so forth, and **PBDTDTBTz** has limited solubility in the solvents. The number average molecular weight (M_n) of **PBDTDTBTz** and **PBDTBTz** is 9276 and 12387, with a PDI of 2.0 and 1.6, respectively.

Thermal stability

The thermal stability of the two polymers was investigated with thermogravimetric analysis as shown in Fig. 1. The TGA analysis reveals that the 5% weight loss temperatures (T_d) of the **PBDTBTz** and **PBDTDTBTz** are 310 and 324 °C, respectively, maybe due to the removal of the alkoxyl groups. The glass transition temperature (T_g) of the polymers was not observed from DSC measurements. The thermal stability of two polymers is favorable for their applications in PSCs and other optoelectronic devices.

Absorption spectra of the polymers

The photophysical characteristics of the copolymers were investigated by ultraviolet-visible (UV-vis) absorption spectra in diluted chloroform solutions and in solid films drop-cast on a quartz substrate. Fig. 2 depicts the absorption spectra of the polymer solutions and films, the optical data of the polymers are
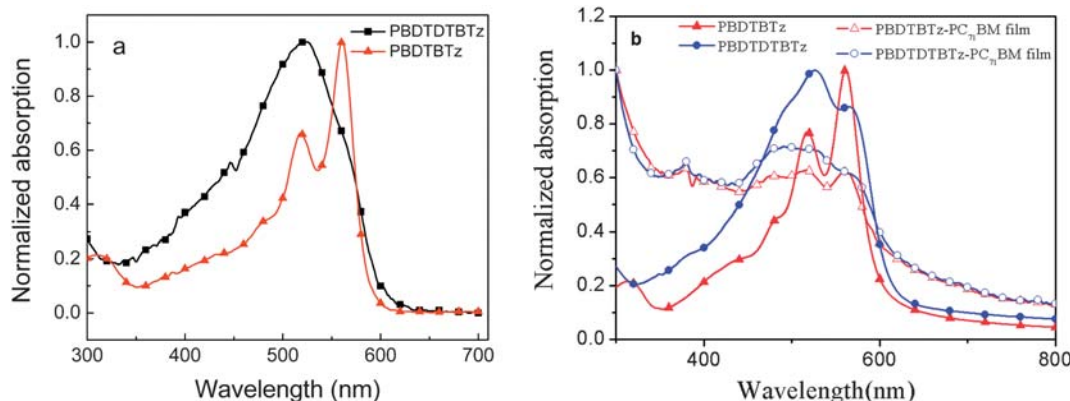

Fig. 2 UV-vis absorption spectra of **PBDTDTBTz** and **PBDTBTz**: (a) solution in diluted CHCl₃ at room temperature; (b) polymer films and polymer/PC₇₁BM (1/4) blend on quartz.

Table 1 The optical and electrochemical properties of the polymers

Polymers	UV-vis-NIR absorption spectra				Cyclic voltammetry (vs Ag/Ag+)	
	Solution[a] λ_{max}/nm	Film[b] λ_{max}/nm	λ_{onset}/nm	$E_g^{opt\,c}$/eV	p-doping E_{on}^{ox} (V)/HOMO[d] (eV)	n-doping LUMO[e]/eV
PBDTDTBTz	524	527	635	1.95	0.35/−5.06	−3.11
PBDTBTz	561	562	620	2.0	0.33/−5.04	−3.04

[a] Measured in chloroform solution. [b] Cast from chloroform solution. [c] Bandgap estimated from the onset wavelength of the optical absorption.[12] [d] HOMO= −e(E_{on}^{ox} + 4.71) (eV).[13] [e] LUMO = E_g^{opt} + HOMO.

listed in Table 1. The absorption maxima peaks of **PBDTDTBTz** and **PBDTBTz** films are *ca.* 527 nm and 562 nm, respectively (see Fig. 2b), which is a little red-shifted in comparison with those of the polymer solutions (the absorption peaks of **PBDTDTBTz** and **PBDTBTz** solutions are located at 524 nm and 561 nm, respectively). This phenomena indicates that the conformation changed little from the solution to the film sate. The absorption of two polymer films exhibit well defined vibronic splitting peak at 524 nm and 566 nm for **PBDTDTBTz** and peaks at 517 nm and 561 nm for **PBDTBTz**, respectively, which reflects the high structural organization of the molecules in the films.[11] The absorption edge of **PBDTBTz** and **PBDTDTBTz** are at 625 nm and 635 nm, corresponding to the energy gap of 2.0 eV and 1.95 eV, respectively. The absorption of the polymer and $PC_{71}BM$ (ratio of 1 : 4) blend films was observed. The blend films show similar broader absorption from 300–650 nm than those of pure polymer films due to the strong absorption of $PC_{71}BM$ between 400–530 nm.[15]

Electrochemical properties

In order to investigate the electrochemical properties of **PBDTBTz** and **PBDTDTBTz** and estimate their the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels, cyclic voltammetry (CV) was carried out in a 0.1 M solution of Bu_4NPF_6 in acetonitrile at room temperature under argon with a scan rate of 50 mV s^{-1}.[13] All potentials are reported *vs.* Ag/Ag$^+$ with the ferrocene/ferrocenium couple used as an internal standard. CV curves of **PBDTBTz** and **PBDTDTBTz** are displayed in Fig. 3. The related electrochemical data are listed in Table 1. **PBDTDTBTz** exhibits one reversible oxidation peak while **PBDTBTz** shows a quasi-reversible oxidation peak. No reduction peak in the n-doping region is observed for these two polymers. In a positive potential region, the onset oxidation potential (E_{on}^{ox}) is 0.33 V *vs.* Ag/Ag$^+$ for **PBDTBTz**. For **PBDTDTBTz**, E_{on}^{ox} is 0.35 V *vs.* Ag/Ag$^+$.

From E_{on}^{ox} of the polymers, we calculated the HOMO and LUMO energy levels of the polymer according to the equation:[13]

$$E_{HOMO} = -e(E_{on}^{ox} + 4.71)\ (eV)$$

We obtained E_{LUMO} from the E_{Eg}^{opt} and E_{HOMO}. The E_{LUMO} and E_{HOMO} values of **PBDTBTz** are −3.04 eV and −5.04 eV, respectively. The E_{LUMO} and E_{HOMO} values of **PBDTDTBTz** are −3.11 eV and −5.06 eV, respectively, the HOMO level of
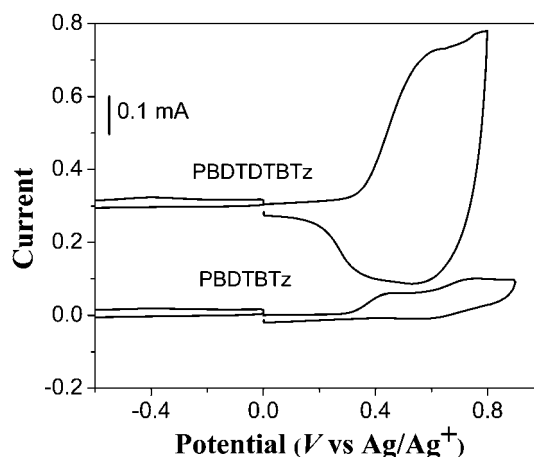

Fig. 3 Cyclic voltammograms of **PBDTBTz** and **PBDTDTBTz** films on platinum electrode in 0.1 mol L^{-1} Bu_4NPF_6, CH_3CN solution.

PBDTBTz is very similar to that of **PBDTDTBTz**. The electrochemical results show that the two copolymers exhibit similar energy level.

Photovoltaic devices

To explore the potentials for solar cells, the photovoltaic properties of the copolymers were investigated in two composites (with either $PC_{61}BM$ or $PC_{71}BM$) with the structure of ITO/PEDOT:PSS (40 nm)/polymer:fullerenes/Ca (20 nm)/Al (60 nm). Fig. 4a shows the J–V curves of the polymer solar cells with a polymer: $PC_{61}BM$ 1 : 3 weight ratio. The active layer thickness is about 50–60 nm. The relationship between the thickness of the active layer and PCE was investigated by controlling the spinning speed during the spin coating process. We found that the thickness is increased, the J_{sc} decreased slightly, while the V_{oc} and FF seemed the same. This phenomenon indicates that the photovoltaic properties of the polymers may be limited by the poor charge transporting properties of the blend film.[14] The optimized **PBDTDTBTz** device had a thickness of 60 nm, a J_{sc} value of 4.4 mA cm^{-2}, and a relatively high FF of 0.55, combined with a V_{oc} value of 0.61 V to give an efficiency of 1.5%. However for **PBDTBTz**, due to the relatively low FF and J_{sc}, the PCE of **PBDTBTz** was only 0.7%.

The corresponding incident-photon-to current efficiency (IPCE) from polymer/$PC_{61}BM$ BHJ solar cells is shown in Fig. 4b. From their EQE curves of the polymers, it can be seen
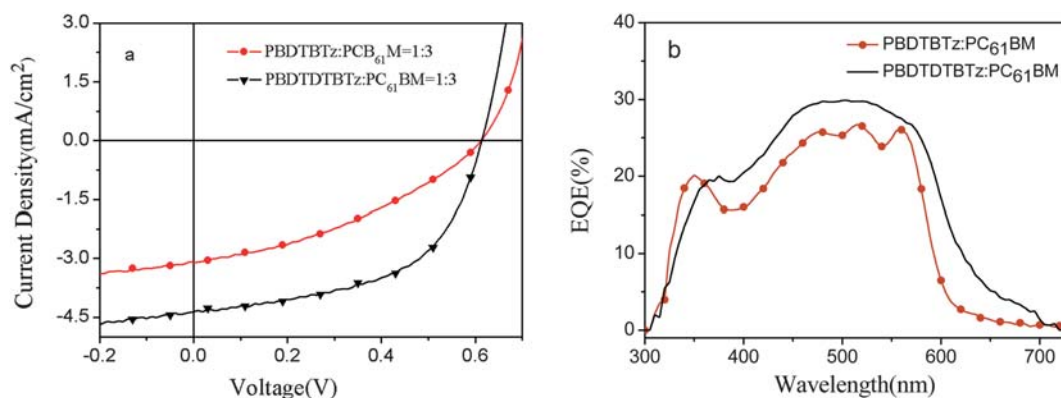
Fig. 4 (a) J–V curves of polymer : $PC_{61}BM$ (1 : 3) based solar cell devices under illumination of AM 1.5G, 100 mW cm^{-2}; (b) IPCE curves of the polymer : $PC_{61}BM$ (1 : 3) based device.
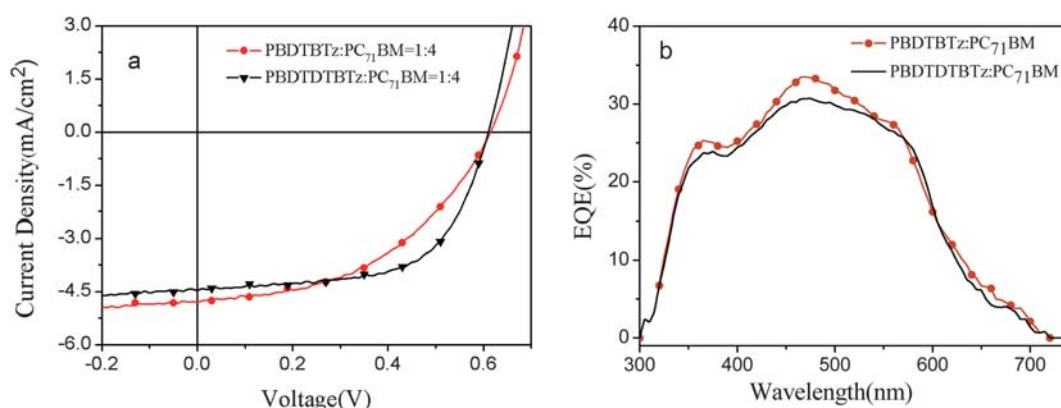

Fig. 5 (a) J–V curves of polymer/$PC_{71}BM$ (1 : 4) based solar cell devices under illumination of AM 1.5G, 100 mW cm^{-2}; (b) IPCE curves of the polymer/$PC_{71}BM$ (1 : 4) based device.

that the response range of **PBDTDTBTz** based device is relatively broader than that of **PBDTBTz** based device, in the range from 350 nm to 750 nm, **PBDTDTBTz** based devices also exhibit higher EQE values with a maximum plateau external quantum efficiency of 30% from 465 nm to 530 nm than those of **PBDTBTz** based devices, so J_{sc} of the **PBDTDTBTz** (4.4 mA cm^{-2}) based devices is higher than that of **PBDTBTz** (3.1 mA cm^{-2}).

It has been reported that $PC_{71}BM$ has similar electronic properties as $PC_{61}BM$, but a higher absorption coefficient from 400–530 nm.[15] The active layer was then further modified with the weight ratio of polymer: $PC_{71}BM$ at 1 : 4 and identical thickness of around 50– 60 nm. For the devices with $PC_{71}BM$, the optimized weight ratio is 1 : 4. J-V curves and IPCE of the polymer/$PC_{71}BM$ (1 : 4) based solar cell devices are shown in Fig. 5. The effect of the polymer: PCBM weight ratio on the photovoltaic performance can be explained as following. There is a balance between the absorbance and the charge transporting network of the active layer in the PSC devices. Too low content of PCBM will limit the electron transporting ability, while too high content of PCBM will decrease the absorbance and enhance the electron transporting ability of the active layer. The different optimized weight ratios for $PC_{61}BM$ and $PC_{71}BM$ could be due to their different electron transport and absorption properties.

Table 2 Photovoltaic performances of polymer solar cells based on the copolymers

Polymers : PCBM ratio	Thickness	V_{oc}/V	I_{sc}/mA cm^{-2}	FF (%)	PCE (%)
PBDTDTBTz : $PC_{61}BM$ (1 : 3)	60 nm	0.61	4.4	55	1.5
PBDTDTBTz : $PC_{71}BM$ (1 : 4)	58 nm	0.61	4.5	62	1.7
PBDTBTz : $PC_{61}BM$ (1 : 3)	56 nm	0.61	3.1	37	0.7
PBDTBTz : $PC_{71}BM$ (1 : 4)	57 nm	0.61	4.8	47	1.4

From the data listed in Table 2, it can be seen the main difference between the photovoltaic performances of the polymers at different device conditions appeared in the J_{sc} and FF while the V_{oc} remained constant. Compared to the polymer/$PC_{61}BM$ system, the FF improved which is indicative of better charge mobility balance in the polymer/$PC_{71}BM$ blend. Higher J_{sc} values were observed which may be the higher absorption coefficient of $PC_{71}BM$ in the visible region. For **PBDTBTz**, J_{sc} increased from 3.1 mA cm^{-2} to 4.8 mA cm^{-2}, which is even higher than that of **PBDTDTBTz**, probably because the $PC_{71}BM$ can greatly compensate for the low absorption of **PBDTBTz** from 400– 530 nm. However, when **PBDTDTBTz** mixed with $PC_{71}BM$, the device demonstrated a very high FF of 0.62, J_{sc} of 4.5 mA cm^{-2} with the device PCE of 1.7%. For **PBDTBTz**/$PC_{71}BM$ BHJ solar
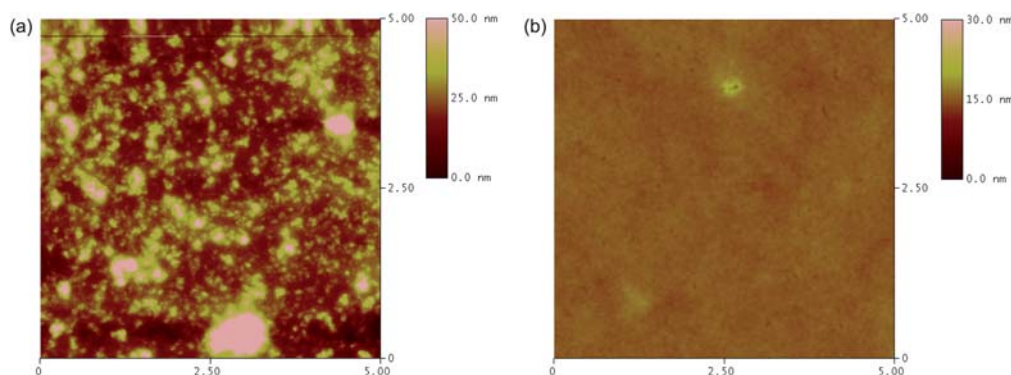
Fig. 6 AFM (5μm × μm) topography images of (a) **PBDTBTz** : PC$_{71}$BM (1 : 4); (b) **PBDTDTBTz** : PC$_{71}$BM (1 : 4) blend films.

cells, with the increased J_{sc} and *FF*, the PCE of **PBDTBTz** increased from 0.7% to 1.4%. Compared to **PBDTBTz**-based photovoltaic cells, the **PBDTDTBTz** possesses higher *FF*, which is probably due to the smoother morphology and better inter-penetrating network in the **PBDTDTBTz**/PCBM blend (the morphology of the blend is as shown in Fig. 6).

Conclusions

Two new benzotriazole-based polymers, **PBDTDTBTz** and **PBDTBTz**, were designed and synthesized through the typical Stille coupling polycondensation reactions. The polymers combine good thermal stability and broad absorption. The photovoltaic devices demonstrated a power conversion efficiency of up to 1.7% and 1.4%, respectively for **PBDTDTBTz** and **PBDTBTz**, under the illumination of AM 1.5, 100 mW cm^{-2} with a device structure of ITO/PEDOT:PSS/polymer:PC$_{71}$BM (1 : 4)/Ca/Al. The results indicate that the BTz-based copolymers are promising for application in PSCs. We believe that with further structural and device optimizations, increased power efficiencies are possible in the future.

Acknowledgements

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