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ORIGINAL PAPER

Synthesis and photovoltaic properties of alternative copolymers of benzo[1,2-b:4,5-b′]dithiophene and thiophene

**Jie Min · Bo Peng · Youjun He · Maojie Zhang ·
Zhi-Guo Zhang · Jing Zhang · Xia Guo ·
Chaohua Cui · Dan Deng · Yongfang Li**

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Abstract Two conjugated polymers containing benzodithiophene (BDT) unit and the unit of thiophene or thieno[3,2-b]thiophene, **P(BDT-T)** and **P(BDT-TT)**, were synthesized by Pd-catalyzed Stille coupling method. The UV–Vis absorption, thermal, and electrochemical properties of the two polymers were characterized. Photovoltaic properties of the polymers were studied by using the polymers as donor and PC$_{70}$BM as acceptor with a weight ratio of polymer: PC$_{70}$BM of 1:1.5. The power conversion efficiencies of the PSC devices based on **P(BDT-T)** reached 2.05% with an open-circuit voltage of 0.75 V, a short-circuit current of 4.5 mA cm^{-2}, and a fill factor of 0.61, under the illumination of AM1.5, 100 mW cm^{-2}.

Keywords Benzodithiophene · Conjugated polymers · Polymer solar cells

Introduction

Polymer solar cells (PSCs) have attracted great interests in recent years, due to their advantages of low-cost, light weight, easy fabrication, and large-area processability [1–4]. The photoactive layer of the PSCs is composed of a blend film of conjugated polymer as the electron donor and a soluble fullerene derivative as the electron acceptor [5]. The most representative photoactive system is a blend of regioregular poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C61-butyric acid methyl ester

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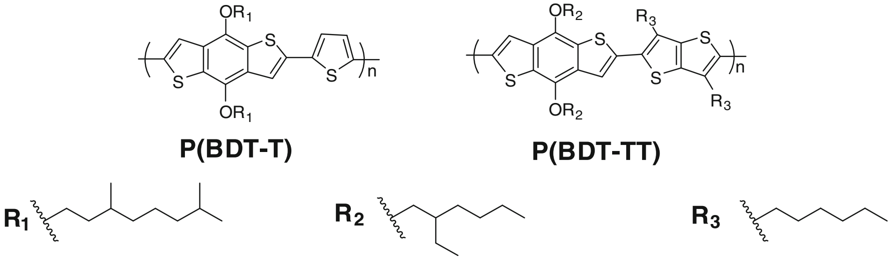
J. Min · B. Peng · Y. He · M. Zhang · Z.-G. Zhang · J. Zhang · X. Guo ·
C. Cui · D. Deng · Y. Li (✉)
Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Organic Solids,
Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China
e-mail: liyf@iccas.ac.cn



Scheme 1 Molecular structures of the BDT-based polymers

($PC_{60}BM$). After extensive optimization, the highest power conversion efficiencies (PCE) of the PSCs based on P3HT/$PC_{60}BM$ has reached over 4% [6, 7].

The photovoltaic performance of the PSCs has been greatly improved in recent 2 years by developing new conjugated polymer donors [8–13] and new fullerene derivative acceptors [14–16]. Among the conjugated polymer donor materials developed in recent years, benzodithiophene (BDT)-based copolymers have drawn great attention [8–11, 17–28]. Hou et al. [17] synthesized the BDT-based copolymers with different alternating units, and effectively tuned the bandgaps and energy levels of the copolymers. Subsequently, the copolymers of BDT and thieno[3,4-b]thiophene demonstrated high PCE of 5–7% [8–11, 18, 19]. Recently, the copolymers of BDT and thieno[3,4-*c*]pyrrole-4,6-dione (TPD) also showed high photovoltaic performance [20–23]. The results indicate that the BDT unit is a promising structural unit for the high efficiency conjugated polymer photovoltaic materials. In addition, thieno[3,2-b]thiophene (TT) and thiophene-based polymers often display high hole mobility and promising photovoltaic performance [29–32].

Stimulated by the good photovoltaic performance of the BDT-based copolymers and the TT- and thiophene-based polymers, here we synthesized two copolymers of BDT and thiophene, poly{4,8-di(3,7-dimethyloctaneoxy)benzo[1,2-b;3,4-b]dithiophene-alt-thiophene} (**P(BDT-T)**), and BDT and TT, poly{4,8-di(2-ethylhexyloxy)-benzo[1,2-b;3,4-b]dithiophene-alt-3,6-dihexyl-thieno[3,2-b]thiophene} (**P(BDT-TT)**), as shown in Scheme 1. The two polymers have good solubility in toluene, chloroform, and THF. The PCE of the PSCs based on **P(BDT-T)** as donor and $PC_{70}BM$ as acceptor reached 2.05% with $V_{oc} = 0.75$ V, $J_{sc} = 4.5$ mA cm^{-2}, and FF = 0.61.

Experimental section

Materials

All of the chemicals were purchased from Aldrich and used as received, unless otherwise stated. 1,5-bibromo-4,8-di(2-ethylhexyloxy)benzo[1,2-b:4,5-b′]dithiophene [33–35], benzo[1,2-b:4,5-b′b′]dithiophene-4,8-dione [17], 2,5-dibromo-3,6-dihexyl-thieno[3,2-b] thiophene [33–36], and 2,5-bis(trimethyltin)thiophene [37] were synthesized according to the procedures reported in the literatures. The other materials were common commercial level and used as received.

Measurements and characterization

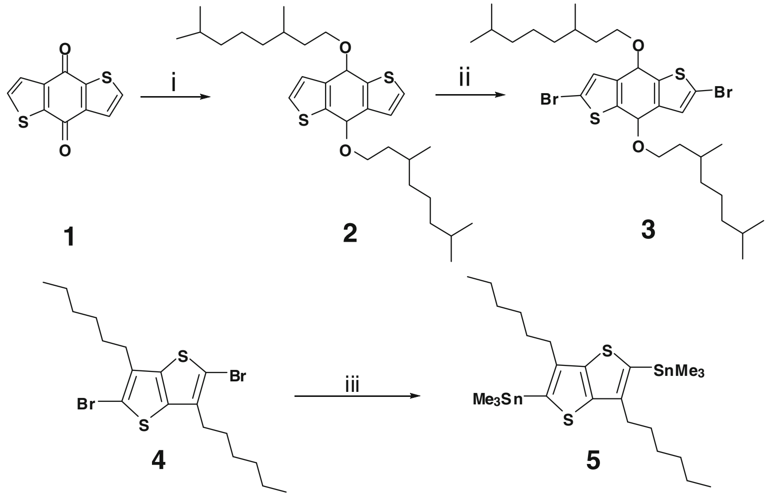
^{1}H NMR spectra were measured on a Bruker DMX-400 spectrometer. Chemical shifts of the ^{1}H NMR were reported in ppm relative to the singlet of $CDCl_3$ at 7.26 ppm. Splitting patterns were designated as s (singlet), d (doublet), t (triplet), m (multiplet), and br (broaden). Absorption spectra were taken on a Hitachi U-3010 UV–Vis spectrophotometer. Molecular weight of the polymers was measured by GPC method and polystyrene was used as a standard. TGA measurement was performed on a Perkin-Elmer TGA-7. The electrochemical cyclic voltammetry was conducted on a Zahner IM6e 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 $L-^1$ tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) acetonitrile solution. Polymer thin films were formed by dropcasting 1 μL of the polymer solutions in chloroform (analytical reagent, 1 mg mL^{-1}) onto the working electrode, and then dried in the air.

Fabrication of polymer solar cells

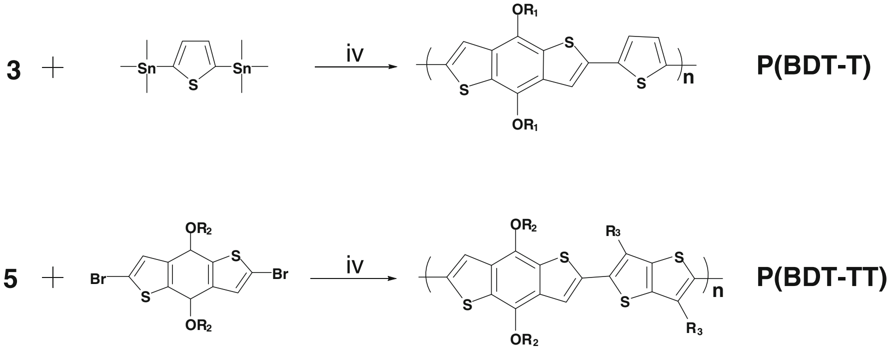
The PSCs were fabricated in the configuration of the traditional sandwich structure with ITO positive electrode and metal negative electrode. The ITO glass was cleaned by sequential ultrasonic treatment in detergent, deionized water, acetone, and isopropanol, and then treated in an ultraviolet–ozone chamber (Ultraviolet Ozone Cleaner, Jelight Company, USA) for 20 min. A thin layer of poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) (Baytron, PVP 4083, Germany) was spin-coated on the ITO glass and dried in vacuum oven at 150 °C for 15 min. The thickness of the PEDOT:PSS layer was ca. 70 nm. Subsequently, the active layer was prepared by spin-coating the *o*-dichlorobenzene solution of polymers P(BDT-T) or P(BDT-TT):$PC_{70}BM$ (1:1.5, w/w) with the polymer concentration of 20 mg mL^{-1} on the top of the PEDOT:PSS layer. The devices were completed by evaporating Ca/Al metal electrodes defined by mask. The Ca (10 nm) capped with Al (80 nm) was thermally deposited on the active layer at a pressure of 3×10^{-5} Pa, The active area of a device was 4 mm^2. The current–voltage (*I*–*V*) measurement of the PSCs was conducted on a computer-controlled Keithley 236 source measure unit. A Xenon lamp with AM1.5 filter was used as a white-light source and the optical power was 100 mW cm^{-2}. All the measurements were controlled by a computer system, and performed under ambient atmosphere at room temperature.

Synthesis of monomers and polymers

The synthetic routes of the monomers and polymers are shown in Schemes 2 and 3. The detailed synthetic processes are as follows.



Scheme 2 Synthesis of Monomers. (*i*) Zn, NaOH, H_2O, reflux for 3 h; then $C_{10}H_{21}Br$, TBAB, reflux for 6 h; (*ii*) Br_2, methylene chloride, ambient temperature, 4–6 h; (*iii*) *n*-butyllithium, THF, −78 °C, 1 h, argon; then $(CH_3)_3SnCl$, ambient temperature, 2 h



Scheme 3 Synthetic routes of **P(BDT-T)** and **P(BDT-TT)**. (*iv*) $Pd(PPh_3)_4$, toluene, 120 °C, 12 h, argon

*4,8-Di(3,7-dimethyloctaneoxy)benzo[1,2-b;3,4-b]dithiophene (**2**)*

Compound **1** (17.6 g, 80 mmol), zinc powder (10.92 g, 168 mmol), and 200 mL of water were put into a 500 mL flask; then, 48 g of NaOH was added into the mixture. The mixture was well stirred and heated to reflux for 3 h. Then, 1-bromo-3,7-dimethyloctane (53.04 g, 240 mmol) and a catalytic amount of tetrabutylammonium bromide were added into the flask. After being refluxed for 6 h, the reactant was poured into cold water and extracted by diethyl ether for three times. The ether layer was dried over anhydrous $MgSO_4$. After removing solvent, the crude product was re-adsorbed in silica gel and purified by silica gel chromatography using hexane as eluent. 24.9 g of Compound **2** (50 mmol, yield 62.5%) was obtained as light yellow oil. ^1H NMR ($CDCl_3$, 400 MHz), δ(ppm) = 7.45 (s, 2H), 7.35 (s, 2H), 4.37 (t, 4H), 1.93 (quintuple, 4H), 1.69 (m, 4H), 1.56–1.29 (m, 18H), 0.87 (t, 12H). Elemental analysis: Calculated for $C_{30}H_{46}O_2S_2$: C 71.71, H 9.16; found: C 71.46, H 9.07.

*2,6-Dibromo-4,8-di(3,7-dimethyloctaneoxy)benzo[1,2-b;3,4-b]dithiophene (**3**)*

Compound **2** (20.08 g, 40 mmol) was dissolved into 500 mL of methylene chloride in a 1,000 mL flask. Bromine (13.44 g, 84 mmol) was dissolved into 100 mL of methylene chloride in a funnel and slowly dropped into the flask under an ice-water bath, and then the reactant was stirred for 20 h at room temperature. After removing solvent, the crude product was re-adsorbed in silica gel and purified by silica gel chromatography using hexane as eluent. 21.12 g of Compound **3** (32 mmol, yield 80%) was obtained as a light yellow oil. ^1H NMR ($CDCl_3$, 400 MHz), δ(ppm) = 7.43 (s, 2H), 4.17 (t, 4H), 1.88 (m,4H), 1.55–1.18 (m, 28H), 0.89 (t, 6H). Elemental analysis: Calculated for $C_{30}H_{44}Br_2O_2S_2$: C 54.55, H 6.67; found: C 52.40, H 6.45.

*2,5-Di(trimethyltin)-3,6-dihexyl-thieno[3,2-b]thiophene (**5**)*

Compound **4** (9.36 g, 20 mmol) and 100 mL of THF were added into a flask under an inert atmosphere. The solution was cooled down to −78 °C by a liquid nitrogen–acetone bath, and 17.60 mL of *n*-butyllithium (44 mmol, 2.5 M in *n*-hexane) was added dropwise. After being stirred at −78 °C for 3 h, a great deal of white solid precipitate appeared in the flask. Then, 44 mmol of trimethyltin chloride was added quickly in one portion. The cooling bath was removed, and the reactant was stirred at ambient temperature for 12 h. Then, it was poured into 500 mL of cool water and extracted by ether three times. The organic layer was washed by water two times, and then dried by anhydrous $MgSO_4$. After removing solvent under vacuum, the residue was recrystallized by ethyl alcohol two times. 10.11 g of Compound **5** (16 mmol, yield 80%) was obtained as colorless needle crystal. ^1H NMR ($CDCl_3$, 400 MHz), δ(ppm) = 2.70 (t, 4H), 1.72 (m, 4H), 1.38–1.27 (m, 12H), 0.89 (t, 6H). Elemental analysis: Calculated for $C_{24}H_{44}S_2Sn_2$: C 45.57, H 6.96%; found: C 45.32, H 6.63.

Poly{4,8-di(3,7-dimethyloctaneoxy)benzo[1,2-b;3,4-b]dithiophene-alt-thiophene} ***P(BDT-T)***

Under nitrogen, 1.0 mmol of the monomer **3** was dissolved in 15 mL dried toluene, 2,5-bis(trimethyltin)thiophene (1 mmol) was added to the mixture. The solution was flushed with argon for 10 min, and then 25 mg of $Pd(PPh_3)_4$ were added. After another flushing with argon for 20 min, the reactant was heated to reflux for 12 h. The reaction solution was cooled to room temperature, the reaction mixture was added dropwise to 200 mL methanol, and then filtered through a Soxhlet thimble, which was then subjected to Soxhlet extraction with methanol, hexane, and chloroform. Polymer was recovered from the chloroform fraction by rotary evaporation as solid. The polymer was purified with bio-beads S-1 column chromatography eluted with THF, the solvent was removed in vacuum, and the solid was dried under vacuum for 1 day to get **P(BDT-T)**. The yield of the polymerization reaction was about 45%. GPC: $M_w = 13.1$ kg mol^{-1}, $M_n = 6.7$ kg mol^{-1}, $M_w/M_n = 1.96$. ^{1}H NMR (400 MHz, CDCl$_3$), δ(ppm) = 7.52–6.95 (br, 4H), 4.27(m, 4H), 1.99–0.67 (m, 42H). Elemental analysis for $(C_{34}H_{46}S_3O_2)_n$. Calculated: C 70.10, H 7.90, S 16.49; found: C 71.07, H 7.95, S 17.08.

Poly{4,8-di(2-ethylhexyloxy)benzo[1,2-b;3,4-b]dithiophene-alt-3,6-dihexyl-thieno[3,2-b]thiophene} ***P(BDT-TT)***

The synthesis process of **P(BDT-TT)** is similar with that in the synthesis of **P(BDT-T)**, except using 2,5-di(trimethyltin)-3,6-dihexyl-thieno[3,2-b]thiophene instead of thiophene, and 1,5-bibromo-4,8-di(2-ethylhexyloxy)benzo [1,2-b:4,5-b′]dithiophene instead of 2,6-dibromo-4,8-di(3,7-dimethyloctaneoxy) benzo[1,2-b;3,4-b]dithiophene (Yield: 42%). GPC: $M_w = 18.3$ kg mol^{-1}, $M_n = 6.9$ kg mol^{-1}, $M_w/M_n = 2.65$. ^{1}H NMR (400 MHz, CDCl$_3$), δ(ppm) = 7.55–7.01 (br, 2H), 4.25(m, 4H), 3.05–2.74(t, 4H), 1.87–0.91 (m, 52H). Elemental analysis for $(C_{44}H_{62}S_4O_2)_n$. Calculated: C 70.40, H 8.27, S 17.07; found: C 70.97, H 8.95, S 16.68.

Results and discussion

Synthesis and structural characterization of the polymers

The general synthetic strategy for the monomers and polymers is outlined in Schemes 2 and 3, respectively. Monomer **1** was prepared according to reported literature method [17]. Monomer **1** was reduced by zinc dust in aqueous sodium hydroxide solution for 3 h. Subsequently, 1-bromo-3,7-dimethyloctane and a catalytic amount of tetrabutylammonium bromide were added. After being refluxed for 12 h, monomer **2** was obtained with a yield of 62.5%. Bromination of **2** using Br_2 provided monomer **3** in 80% yield. Monomer **5** was synthesized with a similar method reported in the literature [38]. By Stille coupling reaction in toluene using $Pd(PPh_3)_4$ as catalyst at 120 °C for 12 h, the polymers **P(BDT-T)** and **P(BDT-TT)** were obtained with a yield of 40–45%. All the polymers are soluble in chloroform, toluene, and THF at room temperature, and can readily be processed from solution. The weight-average molecular weights (M_w) of **P(BDT-T)** and **P(BDT-TT)** are 13.1 and 18.3 K, respectively. Meanwhile, the polydispersity index (PDI) of the polymers was estimated to be 1.96 and 2.65 for **P(BDT-T)** and **P(BDT-TT)**, respectively, using gel permeation chromatography (GPC) against polystyrene standards.

Thermal analysis

Thermal stability of the polymers was investigated with thermogravimetric analysis (TGA), as shown in Fig. 1. The TGA reveals that, in the inert nitrogen atmosphere, the onset points of the weight loss with 5% weight-loss temperature (T_d) of

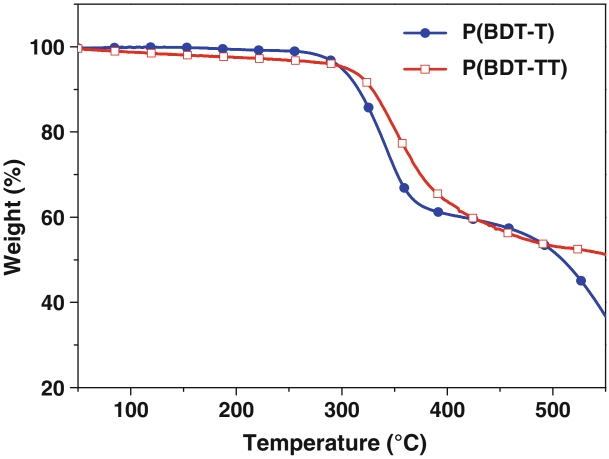


Fig. 1 TGA plots of the polymers with a heating rate of 10 °C min^{-1} under inert atmosphere

P(BDT-T) and **P(BDT-TT)** are 302 and 305 °C, respectively. The results indicate that the two polymers have good thermal stability, which is stable enough for the application in polymer optoelectronic devices.

Optical properties of the polymers

Figure 2 shows the UV–Vis absorption spectra of the polymers in chloroform solutions and films spin-coated on quartz substrates. The absorption of **P(BDT-T)** in chloroform solutions (see Fig. 2a) agrees with that reported by Hou et al. [17] for the similar polymers. It is noted that **P(BDT-T)** exhibits an absorption maxima at 500 nm, while **P(BDT-TT)** displays a blue-shifted absorption with the absorption maxima at 478 nm. Figure 2b shows the absorption of the polymer films.

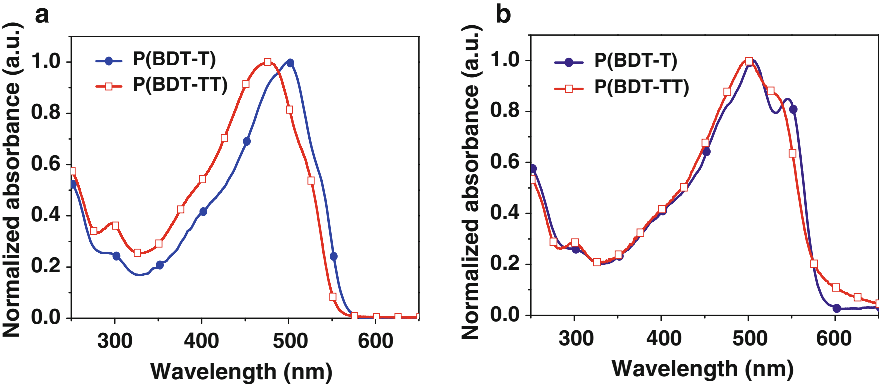


Fig. 2 UV–Vis absorption spectra of the copolymers in **a** chloroform solution and **b** film

Table 1 Optical and electrochemical properties of the polymers

Polymers	UV–Vis absorption spectra				Cyclic voltammetry		
	Solution[a]		Film[b]		p-doping	n-doping	
	λ_{max} (nm)	λ_{max} (nm)	λ_{onset} (nm)	E_g^{opt} (eV)[c]	φ_{ox}/HOMO (V)/(eV)	φ_{red} /LUMO (V)/(eV)	E_g^{EC} (eV)
P(BDT-T)	500	506	587	2.11	0.36/−5.07	−1.98/−2.73	2.34
P(BDT-TT)	472	500	604	2.05	0.34/−5.05	−1.91/−2.80	2.25
H6 [17]				2.06	0.33/−5.05	−2.07/−2.69	2.36

[a] Measured in chloroform solution

[b] Cast from chloroform solution

[c] Bandgap estimated from the onset wavelength (λ_{edge}) of the optical absorption: $E_g^{opt} = 1240/\lambda_{edge}$

The absorption peaks of the polymer films are more or less red-shifted in comparison with those of their corresponding solutions, which results from the intermolecular interaction of the conjugated polymers in the solid state. Among the two polymers, the absorption maximum of **P(BDT-TT)** film is red-shifted by 28 nm compared with that of its solution, which indicates that there is strong intermolecular interactions in the **P(BDT-TT)** films. The detailed absorption data, including absorption maximum wavelength of solutions and films, the absorption edge (onset wavelength of the absorption peak, λ_{onset}) of the polymer films, and the optical bandgap deduced from the absorption edges, are summarized in Table 1.

Electrochemical properties

The electrochemical cyclic voltammetry has been widely used to measure the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) of the conjugated polymers [39–41]. And the LUMO and HOMO energy levels are key parameters for the application of the conjugated polymers in PSCs. Therefore, we measured the LUMO and HOMO energy levels of the two copolymers by cyclic voltammetry.

Figure 3 shows the cyclic voltammograms (CVs) of the polymer films on Pt electrode in a 0.1 mol/L Bu_4NPF_6–acetonitrile solution. From the onset oxidation potentials (φ_{ox}) and the onset reduction potentials (φ_{red}) of the polymers, the HOMO and LUMO energy levels as well as the energy gap (E_g^{EC}) of the polymers were calculated according to the equations [40, 41]:

$$\begin{aligned} E_{\mathrm{HOMO}} &= -\mathrm{e}\ (\varphi_{ox} + 4.71)\ (\mathrm{eV}); \\ E_{\mathrm{LUMO}} &= -\mathrm{e}\ (\varphi_{red} + 4.71)\ (\mathrm{eV}); \\ E_g^{EC} &= \ \mathrm{e}\ (\varphi_{ox} - \varphi_{red})\ (\mathrm{eV}) \end{aligned}$$

where the units of φ_{ox} and φ_{red} are V versus Ag/Ag^+. The results of the electrochemical measurements are listed in Table 1. It can be seen that the HOMO energy level of **P(BDT-T)** has a lower value of −5.07 eV relative to that of **P(BDT-TT)**

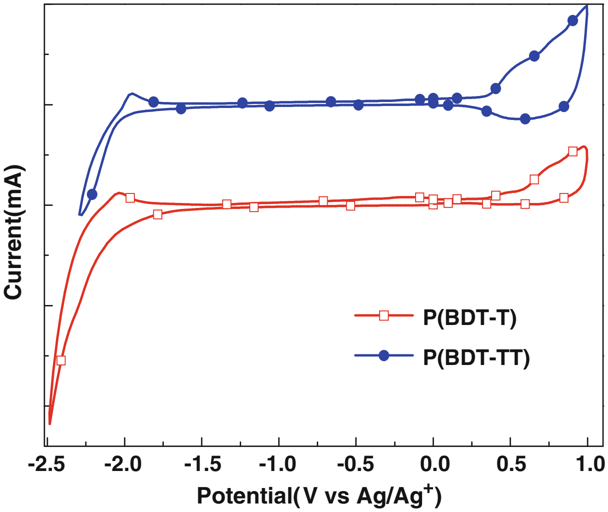


Fig. 3 CVs of the polymer films on Pt electrode in 0.1 mol L^{-1} Bu_4NPF_6, CH_3CN solution with a scan rate of 100 mV s^{-1}

(−5.05 eV). Correspondingly, the LUMO energy level of **P(BDT-T)** and **P(BDT-TT)** are −2.73 and −2.80 eV, respectively. The electrochemical bandgaps are 2.34 and 2.25 eV for **P(BDT-T)** and **P(BDT-TT)**, respectively.

In order to make a clear comparison, properties of a similar BDT-based polymer H6 (with different alkoxyl side chains on BDT unit) reported in Ref [17] were also listed in Table 1. The bandgap as well as the molecular energy level of **P(BDT-T)** is similar with that of H6, the results indicated that different alkoxyl chains on the BDT unit influence the energy bandgap of polymers very little. The electrochemical bandgap of **P(BDT-T)** and **P(BDT-TT)** is a little higher than that of the optical bandgap aforementioned, which is a common phenomenon for the conjugated polymers [42, 43].

Photovoltaic properties

To explore the photovoltaic properties of the two copolymers, the bulk heterojunction PSCs were fabricated with a structure of ITO/PEDOT:PSS/polymer:$PC_{70}BM$ (1:1.5 w/w)/Ca/Al, where the two BDT-based polymers was used as donor and the fullerene derivative $PC_{70}BM$ was used as acceptor. The polymer active layers were spin-coated from a dichlorobenzene solution. Figure 4 shows the *J*–*V* curves of the devices, and Table 2 lists the corresponding V_{oc}, J_{sc}, FF, and PCE of the devices under the illumination of AM 1.5G, 100 mW cm^{-2}. The two polymers have the similar V_{oc} which is from the deep-lying HOMO level. PCE of **P(BDT-T)** reached 2.05%,which is better than that of **P(BDT-TT)** (0.54%). The difference of PCEs results from the different J_{sc} and FF of the polymers as shown in the *J*–*V* curves. In comparison with the photovoltaic performance ($V_{oc} = 0.75$ V, $J_{sc} = 3.78$ mA/cm^2,

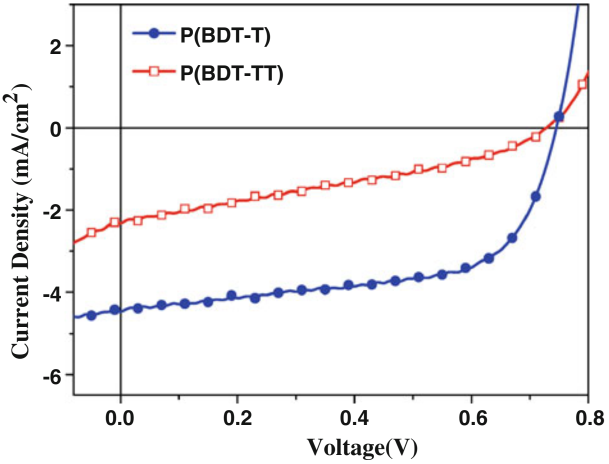


Fig. 4 *I–V* curves of the PSCs based on the BDT-based polymers under AM 1.5 illumination (100 mW cm^{-2})

Table 2 Photovoltaic parameters of the PSCs based on copolymer/PC$_{70}$BM (1:1.5, w/w)

Polymers	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	PCE (%)	Thickness (nm)
P(BDT-T)	0.750	4.50	0.608	2.05	63
P(BDT-TT)	0.730	2.22	0.330	0.54	70

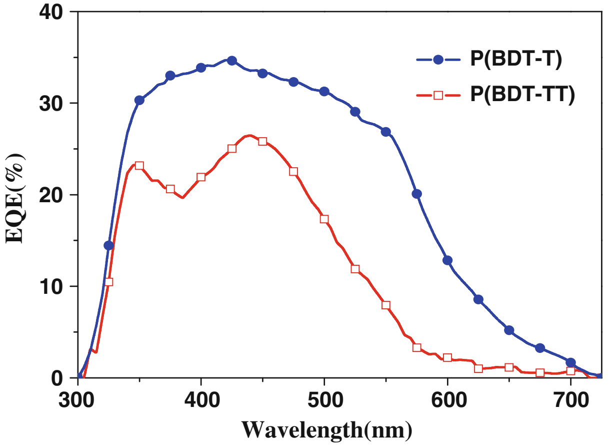


Fig. 5 EQE of PSCs based on BDT-containing polymers with PC$_{70}$BM

FF = 0.56, and PCE = 1.60%) of H6 with linear alkyl chains on BDT unit [17], **P(BDT-T)** with the branched alkylside chains shows higher power conversion efficiency with higher J_{sc} and FF values.

Figure 5 shows the external quantum efficiency (EQE) of the optimized PSC device with the BDT-based polymers: $PC_{70}BM$ weight ratio of 1:1.5 and an active layer thickness of 67 and 60 nm, respectively. The EQE values agree with the short-circuit current very well for the two devices. Comparing the EQE of the devices in Fig. 5 and the absorption of the polymers in Fig. 2, we can see that $PC_{70}BM$ absorption contributes substantially to the photocurrent in the wavelength range from 350 to 400 nm.

Conclusion

Two BDT-based conjugated polymers, **P(BDT-T)** and **P(BDT-TT)**, were designed and synthesized by Pd-catalyzed Stille coupling method. The PSC device based on a blend of **P(BDT-T)**:$PC_{70}BM$ gives a PCE of 2.05% with $V_{oc} = 0.75$ V, $J_{sc} = 4.50$ mA cm^{-2} and FF = 0.608 under the illumination of AM 1.5G, 100 mW cm^{-2}. The EQE values of the PSCs based on **P(BDT-T)**:$PC_{70}BM$ blends extend to above 35%. These results indicate that the copolymer of BDT unit and thiophene is a promising conjugated polymer donor material for the application in PSCs.

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