PAPER

Hyperconjugated side chained benzodithiophene and 4,7-di-2-thienyl-2,1,3-benzothiadiazole based polymer for solar cells

Cite this: *Polym. Chem.*, 2014, 5, 2076Qian Liu,^{ab} Xichang Bao,^a Shuguang Wen,^a Zhengkun Du,^a Liangliang Han,^a Dangqiang Zhu,^a Yanhua Chen,^{ab} Mingliang Sun^{*b} and Renqiang Yang^{*a}

A novel donor–acceptor (D–A) copolymer (P3TBDTDTBT), including hyperconjugated side chained benzodithiophene as a donor and 4,7-di-2-thienyl-2,1,3-benzothiadiazole (DTBT) as an acceptor, was designed and synthesized. Due to the introduction of the hyperconjugated side chain, the resultant polymer exhibited good thermal stability with a high decomposition temperature of 437 °C, a low band-gap of 1.67 eV with an absorption onset of 742 nm in the solid film, and a deep highest occupied molecular orbital (HOMO) energy level of –5.26 eV. Finally, the polymer solar cell (PSC) device based on this polymer and [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) showed the best power conversion efficiency (PCE) of 3.57% with an open-circuit voltage (V_{oc}) of 0.78 V, a short-circuit current density (J_{sc}) of 8.83 mA cm^{–2} and a fill factor (FF) of 53%.

Received 1st November 2013
Accepted 1st December 2013

DOI: 10.1039/c3py01529g

www.rsc.org/polymers

Introduction

Polymer solar cells (PSCs) have recently attracted significant attention as the most promising technique due to their potential advantages such as lightweight, flexible nature and are fabricated by a cost-effective manufacturing process.^{1–7} As a research focus in both industry and academia, the development of PSCs has achieved significant progress recently and a large number of polymers with a high power conversion efficiency (PCE) of 6–9% have been developed.^{8–14} In PSCs, the bulk heterojunction (BHJ) device structure has been proven to be the most successful structure,¹⁵ where the active layer consists of nanoscale bicontinuous phase-separated conjugated polymers and fullerene derivatives. The molecular design of new conjugated polymers is one of the most important, though challenging topics. Most efforts have been focused on conjugated polymers with alternating electron-rich (donor) and electron-deficient (acceptor) units, known as D–A structured polymers.^{16–23}

As the donor unit, the benzodithiophene (BDT) unit has a symmetric and planar conjugated structure, which can easily realize ordered π – π stacking with a large domain size. Since Hou and Yang reported primarily the synthesis and electronic properties of BDT-based copolymers with alkoxy substituents in 2008,²⁴ the BDT unit has become one of the most employed donor moieties for polymers in PSCs.^{25–33} However, in addition to the planar backbone, the BDT core offers the flexibility of

attaching different substitutes onto the central benzene core to fine-tune the energy levels of the polymer. In 2010, the Yang group synthesized a donor–acceptor polymer (PBDTTBT) containing an alkyl substituted thienyl side chained BDT on the copolymer backbone, and the polymer based solar cells exhibited a PCE of 5.66% which was one of the highest values at that time.³⁴ Then the use of a conjugated side chain has been demonstrated to both enhance the solubility of the copolymer and contribute to extending the π -conjugation from the backbone to the lateral substituents, leading to two-dimensional or 2D π -conjugated systems.^{35–46} Thiophene-based π -conjugated side chains, with a high electronic density and a strong tendency to aggregate, are particularly suitable for the described purposes. For example, Huo *et al.*¹¹ have attached different substituents, alkoxy and alkylthienyl, to the benzene core of BDT and exploited the properties of the corresponding polymers. The results show that replacing the alkoxy with alkylthienyl substituents on the BDT core increases the thermal stability, gives broader absorption spectra, lowers the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels, and overall, enhances the photovoltaic properties (PCE up to 7%) of the polymers. In 2012, the Mihaela C. Stefan group extended the π -conjugation of the side chain from a single thiophene unit to two thiophene units, and reported the synthesis and photovoltaic properties of two donor–acceptor polymers containing 3,3',5-trihexylbithienyl substituted benzodithiophene and benzo [c]-[1,2,5]thiadiazole or 5-hexylthieno[3,4-c]pyrrole-4,6-dione as donor and acceptor. The resultant polymers exhibited good solubility and high V_{oc} values of up to 1.04 V because of the low HOMO energy level but a moderate J_{sc} of 5.36 mA cm^{–2} and a FF of 47%.⁴⁷

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In this paper, we further extended the π -conjugation by attaching a hyperconjugated side chain to the BDT unit and synthesized the polymer P3TBDTDTBT. In this polymer, four dodecyl chains were selected to guarantee that the high molecular weight polymer would be soluble in organic solvents and no side-chained DTBT was chosen to lower the band-gap and reduce the steric repulsion between the adjacent monomer units, which would assist the polymer backbone to adopt a more planar conformation. The polymer exhibited a high decomposition temperature of 437 °C, a broad absorption in the range of 300–742 nm, and a low-lying HOMO energy level of -5.26 eV. The best PSC device based on this polymer and PCBM showed a PCE of 3.57% with a V_{oc} of 0.78 V, a J_{sc} of 8.83 mA cm^{-2} and a FF of 52%.

Experimental section

Materials

Unless otherwise stated, all reagents and starting materials were used as commercially purchased without further purification. All air and water sensitive reactions were performed under an argon atmosphere. Toluene or tetrahydrofuran (THF) were distilled from sodium with benzophenone as an indicator and *N,N*-dimethylformamide (DMF) was distilled from CaH_2 under an argon atmosphere before use. Compounds 3TC12 (ref. 48) and BDT-Dio²⁴ were synthesized according to the corresponding literature.

Characterization

^1H and ^{13}C NMR (Nuclear magnetic resonance) spectra were recorded on a Bruker Advance III 600 (600 MHz). High resolution mass spectra (MS) were recorded in APCI mode on a Bruker Maxis UHR TOF spectrometer. The melting point was tested using an X-4 digital display micro-melting point apparatus. The molecular weight and polydispersity were determined by gel permeation chromatography (GPC) analysis using an ELEOS System. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were performed using a TA-Q600 analyzer with a heating rate of $10^\circ\text{C min}^{-1}$ under a nitrogen atmosphere. The Ultraviolet-visible (UV-vis) absorption spectra were recorded using an Hitachi U-4100 spectrophotometer. Cyclic voltammetry (CV) measurements were performed on a CHI660D electrochemical workstation with a glassy carbon working electrode, a platinum wire counter electrode and an Ag/AgCl reference electrode. The CV of P3TBDTDTBT was carried out under an argon atmosphere in a solution of Bu_4NPF_6 (0.1 M) in acetonitrile at a scan rate of 50 mV s^{-1} at ambient temperature. Atomic Force Microscope (AFM) images were acquired with an Agilent-5400 scanning probe microscope with a Nanodrive controller in tapping mode with MikroMasch NSC-15 AFM tips with resonant frequencies of $\sim 300 \text{ kHz}$.

Device fabrication

Photovoltaic devices were fabricated on $15 \text{ mm} \times 15 \text{ mm}$ patterned indium tin oxide (ITO) coated glass substrates with a

layered structure of ITO/PEDOT:PSS/P3TBDTDTBT:PCBM blend/Ca (10 nm)/Al (100 nm). The ITO coated glass substrates were cleaned in an ultrasonic bath with acetone, toluene, methanol and isopropyl alcohol sequentially. The substrates were then oxygen plasma treated for 20 min, spin coated with PEDOT:PSS at 5000 rpm, and dried under argon at 120°C for 20 min. P3TBDTDTBT and PCBM were dissolved in deoxygenated anhydrous *o*-dichlorobenzene in the weight ratios from 2 : 1, 1.5 : 1, 1 : 1, 1 : 1.5, 1 : 2 respectively and stirred overnight in an MBraun glovebox. An active layer consisting of the blend of P3TBDTDTBT and PCBM was then spin coated on PEDOT:PSS with a thickness of $\sim 80 \text{ nm}$. A typical concentration of the P3TBDTDTBT/PCBM blending solution was 24 mg mL^{-1} . Subsequently Ca (10 nm) and Al (100 nm) were thermally evaporated in a vacuum of $\sim 2 \times 10^{-4} \text{ Pa}$ on top of the active layer as a cathode. Photovoltaic performance was characterized under illumination with an AM1.5 (100 mW cm^{-2}) in a nitrogen atmosphere ($<0.1 \text{ ppm H}_2\text{O}$ and O_2), and the current-voltage curves were recorded using a Keithley 2400 source meter.

Synthesis of 3TC12BDT

Under the protection of argon, *n*-butyllithium (8.8 mL, 2.5 M) was added to 3TC12 (11.7 g, 20 mmol) in THF (30 mL) at 0°C ; then the mixture was warmed to 50°C and stirred for 2 h. Subsequently, BDT-Dio (1.54 g, 7 mmol) was added and the mixture was stirred at 50°C for 1.5 h. After cooling down to 0°C , SnCl_2 (5.31 g, 28 mmol) in 10% HCl (20 mL) was added and the mixture was warmed to 50°C again. After being stirred for 2 h, the mixture was poured into ice water and was extracted by diethyl ether. The ether layer was dried over anhydrous MgSO_4 . After removing the solvent, the crude product was purified *via* silica gel column chromatography using petroleum ether as the eluent. 3TC12BDT was obtained as a yellow solid (5.15 g, yield 54.24%).

^1H NMR (CDCl_3 , 600 MHz), δ (ppm): 7.76 (d, $J = 6.0 \text{ Hz}$, 2H), 7.51 (d, $J = 4.8 \text{ Hz}$, 4H), 7.05 (d, $J = 3.6 \text{ Hz}$, 2H), 6.98 (d, $J = 3.0 \text{ Hz}$, 2H), 6.72 (d, $J = 3.6 \text{ Hz}$, 2H), 6.70 (d, $J = 3.6 \text{ Hz}$, 2H), 2.80 (m, 8H), 1.68 (m, 8H), 1.38–1.26 (m, 72H), 0.88 (m, 12H).

Synthesis of 3TC12BDTBr

Under the protection of argon, *n*-butyllithium (1.76 mL, 2.5 M) was added dropwise to 3TC12BDT (2.71 g, 2 mmol) in THF (50 mL) at 0°C and stirred for 2 h. Then, CBr_4 (1.66 g, 5 mmol) was added in one portion. After stirring at 0°C for 2 h, the mixture was warmed to ambient temperature and stirred overnight. Then, the reactant was poured into ice water and extracted by diethyl ether. The ether layer was dried over anhydrous MgSO_4 . After removing the solvent, the crude product was purified *via* silica gel column chromatography using petroleum ether as the eluent. 3TC12BDTBr was obtained as a yellow solid (2.10 g, yield 69.35%).

Melting point: 90°C . ^1H NMR (CDCl_3 , 600 MHz), δ (ppm): 7.70 (s, 2H), 7.42 (s, 2H), 7.04 (d, $J = 3.6 \text{ Hz}$, 2H), 6.97 (d, $J = 3.6 \text{ Hz}$, 2H), 6.72 (d, $J = 3.6 \text{ Hz}$, 2H), 6.70 (d, $J = 3.6 \text{ Hz}$, 2H), 2.80 (m, 8H), 1.68 (m, 8H), 1.38–1.26 (m, 72H), 0.88 (m, 12H). ^{13}C NMR (CDCl_3 , 150 MHz), δ (ppm): 148.13, 146.60, 140.21, 136.42,

135.95, 134.32, 132.94, 132.38, 131.57, 130.61, 128.00, 126.52, 125.91, 124.36, 124.16, 121.64, 117.36, 31.93, 31.66, 31.59, 30.22, 30.16, 29.70, 29.68, 29.66, 29.60, 29.40, 29.39, 29.37, 29.15, 29.12, 22.70, 14.13. HRMS (APCI): m/z found: 1510.4907; calcd for $C_{82}H_{112}Br_2S_8$: 1510.4896.

Synthesis of P3TBDTDTBT

3TC12BDTBr (303 mg, 0.2 mmol) and DTBTsn (125 mg, 0.2 mmol) were dissolved in 8 mL toluene and 2 mL DMF. The mixture was purged with argon for 30 min, then $Pd_2(dba)_3$ (4 mg) and $P(o\text{-tol})_3$ (9 mg) were added. After being purged with argon for another 30 min, the reaction mixture was heated to 100 °C and stirred for 12 h under an argon atmosphere. Then, the mixture was cooled down to ambient temperature and the polymer was precipitated by the addition of 150 mL methanol and filtered through a Soxhlet thimble, which was then subjected to Soxhlet extraction with methanol, hexane, and chloroform. The polymer recovered from chloroform was purified by preparative gel permeation chromatography. Then the product was dried under vacuum for 1 day to recover the target polymer P3TBDTDTBT as a dark solid. (270 mg, yield 81.6%, M_n = 23.1 kDa, PDI = 1.9).

1H NMR ($CDCl_3$, 600 MHz), δ (ppm): 7.67–6.47 (br, 18H), 2.84 (br, 8H), 1.55–1.16 (br, 80H), 0.87 (br, 12H).

Results and discussion

Synthesis and characterization

The synthetic routes to obtain the monomers and the polymer are outlined in Scheme 1. The 3TC12 group was introduced to the BDT core as the hyperconjugated side chain to form a two-dimensional system. 3TC12BDTBr was prepared by the bromination of 3TC12BDT with *n*-butyllithium and CBr_4 . DTBTsn was purchased directly. Finally, the D–A structured polymer was synthesized *via* Stille coupling polymerization between 3TC12BDTBr and DTBTsn in the presence of $Pd_2(dba)_3$ catalyst and tri(*o*-tolyl)phosphine ligand with a yield of 81.6%. The structure of the synthesized polymer was characterized by 1H NMR and the number-average molecular weight (M_n) was determined by GPC to be 23.1 kDa with a polydispersity index (PDI) of 1.9.

Thermal stability

The thermal properties of the polymer P3TBDTDTBT were measured by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). As can be seen from Fig. 1, TGA indicates that P3TBDTDTBT exhibits high thermal stability and the decomposition temperature (T_d) at 5% weight loss is about 437 °C. This high decomposition temperature prevents the deformation of the polymer morphology and the degradation of the polymeric active layer under applied electric fields in solar cell devices. DSC reveals that there is no obvious glass transition for the polymer before 437 °C.

Optical properties

Fig. 2 shows the normalized UV-vis absorption spectra of P3TBDTDTBT in dilute chloroform solution and in the thin solid film. The absorption peak wavelengths are (λ_{max}) 628 nm and 656 nm in the solution and thin film, while the absorption onset wavelengths (λ_{onset}) are 730 nm and 742 nm. The polymer shows broad absorption from 300 to 742 nm, covering the whole visible spectrum, with two distinct absorption bands at around 392 nm and 628 nm in solution. The peak at 392 nm is corresponding to the π – π^* transition of the conjugated polymer backbone and the peak at 628 nm is attributed to a strong intermolecular charge transfer (ICT) between the electron-donating BDT and the electron-accepting DTBT units in the main chain. In the solid film, the absorption spectrum become broader and show a 28 nm red-shift in comparison with their

Fig. 1 TGA and DSC curves of P3TBDTDTBT.

Scheme 1 Synthetic route of P3TBDTDTBT.

Fig. 2 Normalized UV-vis absorption spectra of P3TBDTDTBT in chloroform solution and in the thin solid film.

solution absorption, which indicates a planar polymer chain structure and effective interchain π - π stacking in the solid state. Very interestingly, the solid absorption spectrum demonstrates a more pronounced shoulder peak at approximately 615 nm, which can be attributed to the slightly increased interchain π - π stacking and the extension of the conjugation of two dimensional structures in the solid state.⁴⁹ The optical band-gap of P3TBDTDTBT is 1.67 eV determined from the onset of the UV-vis absorption in the thin solid film.

Electrochemical properties

Cyclic voltammetry (CV) was performed to investigate the redox behavior of the polymer and also to determine the HOMO and LUMO energy levels of the polymer.⁵⁰ The HOMO and LUMO energy levels were determined by measuring the onset oxidation potential ($E_{\text{onset}}^{\text{ox}}$) and reduction potential ($E_{\text{onset}}^{\text{re}}$) of the polymer film. To obtain the oxidation and reduction potentials of the polymer film, the reference electrode was calibrated using ferrocene/ferrocenium (Fc/Fc^+), which had a redox potential with an absolute energy level of -4.80 eV in a vacuum; the potential of this external standard under the same conditions was 0.44 V versus Ag/Ag^+ . As shown in Fig. 3, the polymer showed an $E_{\text{onset}}^{\text{ox}}$ at 0.90 V and an $E_{\text{onset}}^{\text{re}}$ at -0.80 V. Accordingly, the HOMO and LUMO energy values (E_{HOMO} and E_{LUMO}) were calculated using the following equation: $E_{\text{HOMO}} = -(E_{\text{onset}}^{\text{ox}} + 4.36)$ eV; $E_{\text{LUMO}} = -(E_{\text{onset}}^{\text{re}} + 4.36)$ eV.⁵⁰ The corresponding HOMO and LUMO energy levels were estimated to be -5.26 eV and -3.56 eV respectively. The energy band-gap calculated from

Fig. 3 Cyclic voltammogram of P3TBDTDTBT.

the HOMO and LUMO energy levels is 1.70 eV which is consistent with the optical band-gap (1.67 eV) estimated from absorption onset in the thin solid film.

Polymer solar cell performance

The bulk heterojunction solar cells were fabricated using the resultant polymer as the donor and PCBM as the acceptor to investigate the photovoltaic properties of the polymer. The device structure used in this work was ITO/PEDOT:PSS/P3TBDTDTBT:PCBM/Ca/Al. The J - V curves for P3TBDTDTBT:PCBM devices with different D/A ratios are shown in Fig. 4a, and the key photovoltaic parameters are listed in Table 1. When the ratio of PCBM and P3TBDTDTBT increased from $1:2$ to $1:1.5$, $1:1$, $1.5:1$ and then to $2:1$, although both the open-circuit voltage (V_{oc}) and fill factor (FF) of the devices improved gradually, the device showed the highest short circuit current density (J_{sc}) value at $1:1$, and therefore, the PCE of the device reached 2.80% .

Fig. 4 J - V characteristics of PSCs based on the P3TBDTDTBT/PCBM blend with different ratios (a) and different annealing temperatures (b).

Table 1 Photovoltaic properties of the PSCs based on the blend of P3TBDTDTBT and PCBM

Ratio (A : D)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE _{max} /PCE _{ave} (%)
1 : 2	0.81	5.28	29	1.26/1.21 $\pm$ 0.04
1 : 1.5	0.81	5.60	29	1.32/1.24 $\pm$ 0.05
1 : 1	0.83	7.38	46	2.80/2.72 $\pm$ 0.07
1.5 : 1	0.83	7.17	46	2.73/2.66 $\pm$ 0.06
2 : 1	0.83	6.31	50	2.65/2.60 $\pm$ 0.06
1 : 1 (90 °C, 10 min)	0.78	8.83	52	3.57/3.51 $\pm$ 0.06
1 : 1 (120 °C, 10 min)	0.74	7.96	56	3.33/3.27 $\pm$ 0.05

Fig. 5 EQE of devices based on P3TBDTDTBT/PCBM (1 : 1, w/w) before and after thermal annealing at 90 °C for 10 min.

Fig. 6 Hole mobility characteristics of P3TBDTDTBT and PCBM (1 : 1) before and after annealing.

It has been well-recognized that thermal annealing may be helpful in optimizing the nano-scaled phase separation of the DA blends,⁵¹ and therefore, when the ratio of the polymer and PCBM is 1 : 1, different thermal annealing conditions were used to further improve the PCE of the devices. The J - V curves are shown in Fig. 4b. After annealing, the J_{sc} and FF values increase while the V_{oc} value drops, which may be attributed to the interfacial effects, in particular at the BHJ and Ca interface, which has been proved by Heeger and Bazan,⁵² and a similar phenomenon can be observed in the reported literature.⁵³ When the device is annealed at 90 °C for 10 min, the highest PCE value of 3.57% is achieved. For all the optimized conditions, we have averaged the performance over 6 devices and the data are given in Table 1. The addition of additive such as 1,8-diiodooctane (Dio) does not contribute to performance of the solar cells.

The external quantum efficiencies (EQEs) of devices based on the polymer and PCBM (1 : 1, w/w) blend film before and after thermal annealing at 90 °C are measured and are shown in Fig. 5. Both the devices show efficient photoelectronic conversions between 300 and 742 nm with the EQE value as high as 55%. The J_{sc} value (8.74 mA cm^{-2}) calculated from the integration of the EQEs agrees well with the J_{sc} value (8.83 mA cm^{-2}) obtained from the J - V measurements.

Hole mobility

The hole mobility of the P3TBDTDTBT and PCBM blend film (1 : 1) has been measured using the space-charge-limited current (SCLC) method and the curves before and after annealing are plotted in Fig. 6. The calculated mobility values of

Fig. 7 AFM topography (A and B) and phase images (C and D) of the P3TBDTDTBT/PCBM (1 : 1, w/w) film before (A and C) and after (B and D) annealing at 90 °C for 10 min (scan size: $5 \mu\text{m} \times 5 \mu\text{m}$).

the polymer are 7.61×10^{-5} and $2.27 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ before and after annealing. The higher hole mobility after annealing can well explain the improvement of PCE in solar cells.

Atomic force microscopy (AFM) images

Tapping mode atomic force microscopy (AFM) measurements are carried out to demonstrate the morphology of the blend films of P3TBDTDTBT/PCBM (1 : 1, w/w) before and after thermal annealing at 90 °C for 10 min and the images are shown in Fig. 7. Both the blend films before and after thermal annealing exhibit a uniform and smooth surface and the root mean square roughnesses are 1.41 and 1.49 nm respectively. The smooth surface of the blend film ensures a better contact with the Ca/Al electrode, which is helpful in the increase of the charge collection efficiency. The donor and acceptor distribution and interpenetrating network structure can be seen from the AFM phase image. As shown in Fig. 7C and D, the phase images reveal two distinct feature types in the interpenetrating network, which are assigned to the acceptor PCBM-rich and the donor-rich domains, indicating that the donor materials have a good miscibility with the PCBM molecule in the blend films.

Conclusions

In summary, a donor-acceptor copolymer, P3TBDTDTBT, was synthesized, in which the BDT unit with a hyperconjugated side chain was selected as the donor and the DTBT unit was chosen as the acceptor. The copolymer exhibited good solubility in organic solvents, a high decomposition temperature of 437 °C, broad absorption in the range of 300–742 nm, a low-lying HOMO energy level of -5.26 eV . The best PSC device based on the copolymer and PCBM showed a PCE value of 3.57% with $V_{oc} = 0.78 \text{ V}$, $J_{sc} = 8.83 \text{ mA cm}^{-2}$, and $FF = 52\%$. Our preliminary results show that BDT with a hyperconjugated side chain is a promising donor unit, and when it is combined with a suitable building block, the resultant polymer would give high photovoltaic performance.

Acknowledgements

The authors are deeply grateful to the National Natural Science Foundation of China (Project no. 21274134, 21202181, 51173199, 61107090), the Ministry of Science and Technology of China (2010DFA52310), New Century Excellent Talents in University (NCET-11-0473), Department of Science and Technology of Shandong Province (2010GGC10345), and Qingdao Municipal Science and Technology Program (11-2-4-22-hz, 13-1-4-200-jch) for financial support.

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