Polymer 54 (2013) 6150-6157

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Synthesis and photovoltaic properties of D- π -A copolymers based on thieno[3,2-b]thiophene bridge unit

Zhaojun Li ^{a, b, 1}, Lijun Huo ^{b, *}, Xia Guo ^{b, 1}, Weina Yong ^{b, 1}, Shaoqing Zhang ^{a, b, 1}, Huili Fan ^{a, **}

^a University of Science and Technology Beijing, School of Chemistry and Biology, Beijing 100083, China
 ^b State Key Laboratory of Polymer Physics and Chemistry, Beijing National Laboratory for Molecular Sciences Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

ARTICLE INFO

Article history: Received 27 May 2013 Received in revised form 28 August 2013 Accepted 11 September 2013 Available online 18 September 2013

Keywords: Thienothiophene Conjugated polymer Polymer solar cells

ABSTRACT

Three D- π -A copolymers containing thieno[3,2-b]thiophene (TT) bridge and BDT, carbazole, fluorene as D units and benzothiadiazole as A unit were synthesized and characterized. These copolymers of **PBDT-tt-BT** and **PF-tt-BT** exhibited enough high thermal stabilites and good solubilites in chloroform and dichlorobenzene. Among the copolymers, with the increase of the electron-donating abilities of the D units from fluorene to carbazole further to BDT, the absorption spectra of **PF-tt-BT** shows blue shift and that of **PBDT-tt-BT** shows red shift comparing to that of **PC-tt-BT** in their solutions and films. Meanwhile, by electrochemical cyclic voltammetry measurements we found the HOMO levels vary in the same trench according to their electron-donating abilities. Under the illumination of AM 1.5G, 100 mW/cm², power conversion efficiency (*PCE*) of the PSCs based on these copolymers as donors and **PC**-**tt-BT** based devices mostly due to its higher hole mobility and broader absorption range. These results indicate that **PBDT-tt-BT** is a promising photovoltaic polymer donor material for efficient PSCs.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

In the past decade, bulk heterojunction (BHJ) polymer solar cells (PSCs) have attracted extensive scientific attention owing to their distinguished advantages of low cost, lightweight, easy fabrication and flexibility [1–5]. In order to improve the power conversion efficiency (PCE) of PSCs, lots of efforts have been made for chemists in synthesizing new photovoltaic materials. Compared to well-known poly(3-hexylthiophene) (P3HT), low band gap (LBG) polymers match the sunlight spectrum much better and more photons can be absorbed [6]. Thus developing LBG polymers has become an effective strategy to realize highly efficient PSCs. The LBG conjugated polymers can be obtained by copolymerization of electron-donating units (D) and electron-withdrawing units (A) [7–10]. Typical conjugated units such as electron-donating benzodithiophene (BDT),

** Corresponding author.

carbazole, fluorene and electron-withdrawing benzothiadiazole (BT) have been proved to be efficient building blocks in designing photovoltaic materials [11–14].

Recently, according to the some new studies results, it was found that the incorporation of a conjugated π -bridge between an electron-donating unit and an electron-withdrawing unit has an important role in realizing higher PCEs [15–18]. Currently, thiophene, alkylthiophene or furan were mainly adopted as conjugated π -bridge between donor and acceptor segments, which not only increase the effective conjugation of the polymer main chains but also improve the photovoltaic performances [19–22].

In comparison with extensive studies on thiophene or furan as π -bridge, although thieno[3,2-b]thiophene (TT) unit processes larger molecular structure and strengthened conjugated degree, only a few papers reported the new conjugated unit as π -bridge in D- π -A structures. These results show TT has a rigid and coplanar fused ring, which ensures a higher delocalized π -electron system and higher charge mobilities; In addition, as to the introduction of the TT unit as conjugated π bridge, the maximum absorption peak of some polymers hold obvious red shift in comparison with these of polymers containing thiophene as π bridge [23,24]. Based on these considerations, here we synthesized a series of low band gap







^{*} Corresponding author. Tel.: +86 10 82615900.

E-mail addresses: huolijun@iccas.ac.cn (L. Huo), huili.fan@163.com (H. Fan). ¹ Tel.: +86 10 82615900.

^{0032-3861/\$ -} see front matter © 2013 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.polymer.2013.09.021



Scheme 1. Molecular structures of the D- π -A copolymers.

D- π -A copolymers containing TT as π bridge [23,24]. By extending the π -conjugation area in a polymeric backbone through TT unit, it is expected to further explore the optical–electronic properties based on TT unit as π bridge.

In this work, BDT, carbazole and fluorene were adopted as electron-donating unit respectively and BT was selected as electron-withdrawing unit to construct D- π -A copolymers of **PBDT-tt-BT**, **PC-tt-BT** and **PF-tt-BT** (see Sheme 1). The copolymers were characterized by GPC, TGA, UV–Vis absorption and electrochemical cyclic voltammetry. And the photovoltaic properties of the copolymers were studied by fabricating the PSCs based on the copolymer as donors and PC₇₀BM as acceptor.

2. Results and discussion

2.1. Thermal stability

The synthetic routes of the monomers and the corresponding copolymers were shown in Scheme 2 and Scheme 3, respectively. All copolymers show good solubilities in chloroform and *ortho*-dichlorobenzene (*o*-ODCB). The weight-average molecular weight (M_w) and polydispersity index (PDI) were measured by gel permeation chromatography (GPC) using polystyrene standards in CHCl₃, and **PBDT-tt-BT**, **PC-tt-BT**, and **PF-tt-BT** show higher M_w (64 K–91 K) and moderate PDI values. The results were listed in Table 1.

Thermal stability of the copolymers was investigated with thermogravimetric analysis (TGA), as shown in Fig. 1. The TGA analysis results reveal that the onset temperatures with 5% weightloss (T_d) of **PBDT-tt-BT**, **PC-tt-BT**, and **PF-tt-BT** are 351, 352, and 417 °C, respectively, which indicate that the thermal stabilities of these copolymers are good enough for the applications in PSCs. Meanwhile, it was noted that PF-tt-Bt exhibits obvious decompose from 200 to 300 °C. This could be attributed to the presence of the stronger steric hindrance of fluorene moieties with the polymeric main chains, which are not fully coplanar with the main chains and could cause unstable.

2.2. Optical properties

The normalized ultraviolet-visible (UV-vis) absorption spectra of PBDT-tt-BT, PC-tt-BT and PF-tt-BT, in diluted chloroform solutions and films spin-coated on guartz substrates are shown in Fig. 2. The detailed absorption data, including absorption maximum wavelength of solutions and films, the optical band gap estimated from the absorption edges are summarized in Table 2. As shown in Fig. 2a, the absorption spectra of the three copolymers in solution all show typical absorption bands at the shorter wavelength and the longer wavelength. For PBDT-tt-BT and PC-tt-BT the three absorption peaks, from short to long wavelength, are attributed to the intrinsic absorption of the BDT and carzole moiety, the $\pi - \pi^*$ transition band and the intramolecular change transfer (ICT) between donor and acceptor monomers, respectively. The absorption spectra of these copolymers films, as shown in Fig. 2b, are all redshifted in comparison with those of the copolymers in diluted solutions, which imply more aggregated configurations are formed for these copolymers in the films than in the solutions. Meanwhile, one shorter absorption peak both in the PBDT-tt-BT and PC-tt-BT films diminished may due to the stronger coplanarity of BDT and carzole moiety in film state, which lead to diminish their absorption peaks. The absorption maxima (λ_{max}) locations of the films are 630 nm, 589 nm, 569 nm for PBDT-tt-BT, PC-tt-BT and PF-tt-BT, respectively. Among the main peaks in films, **PBDT-tt-BT** processes the longest absorption peaks than these of **PC-tt-BT** and **PF-tt-BT**. Meanwhile, in **PBDT-tt-BT** film a broad vibronic shoulder peak appears at 650 nm but in PC-tt-BT and PF-tt-BT films the weaker vibronic shoulder peak were observed. These results imply that PBDT-tt-BT not only has the lowest band gap due to the strongest electron-donating ability of BDT unit than carbazole and fluorene units, but also has the strongest interchain interactions. For PC-tt-BT and PF-tt-BT, the latter exhibits the shorter main absorption peak than that of the former mostly due to the relatively weaker electron-donating abilities of fluorene than carbazole. The absorption edges of the three copolymers films are 767 nm, 714 nm, 670 nm for PBDT-tt-BT, PC-tt-BT and PF-tt-BT, respectively, from



Scheme 2. Synthetic routes of the acceptor monomer containing TT unit.



Scheme 3. Synthetic routes of the D- π -A copolymers.

which the optical band gaps (E_g^{opt}) of the copolymers could be calculated according to $E_g^{opt} = 1240/\lambda_{onset}$ and the results are listed in Table 2. In addition, as to the introduction of the TT unit as conjugated π bridge, the λ_{max} of the **PBDT-tt-BT**, **PC-tt-BT** and **PF**tt-BT hold obvious red shift in comparison with these of PBDT-t-BT. **PC-t-BT** and **PF-t-BT** containing thiophene as π bridge [25–27].

2.3. Electrochemical properties

Electrochemical cyclic voltammetry was employed to investigate the redox behavior of these copolymers and to estimate their HOMO and LUMO levels. Fig. 3 shows the cyclic voltammograms of PBDT-tt-BT, PC-tt-BT and PF-tt-BT films on a Pt electrode in a 0.1 mol/L Bu₄NPF₆ acetonitrile solution. It can be seen from Fig. 3 that **PBDT-tt-BT** exhibits irreversible *n*-doping/dedoping (reduction/reoxidation) processes at negative potential range and reversible p-doping/dedoping (oxidation/re-reduction) process at positive potential range. However, there are reversible both at negative and positive regions for PC-tt-BT and PF-tt-BT. The onset reduction potentials (*E^{red}*_{onset}) of **PBDT-tt-BT**, **PC-tt-BT** and **PF-tt-BT** are -1.05 eV, -1.21 eV, and -1.14 eV vs. Fc/Fc⁺, respectively, meanwhile the onset oxidation potentials (E_{onset}^{ox}) are 1.62 eV, 1.74 eV and 1.85 eV vs. Fc/Fc⁺, respectively.

From E_{onset}^{ox} and E_{onset}^{red} of the copolymers, HOMO, LUMO levels and the electrochemical energy gap (E_g^{ec}) of the copolymers could be calculated according to the following equations, [28]

 $HOMO = -e(E_{ox} + 4.80)(eV)$

 $LUMO = -e(E_{red} + 4.80)(eV)$

$$Eg^{ec} = e(E_{ox} - E_{red})(eV)$$

Table 1

14010 1								
Molecular	weights and	thermog	ravimetric	temper	atures of	these of	copoly	mers

Copolymers	M_w^a	M_n^a	$PDI^{a}(M_{w}/M_{n})$	$T_d(^{\circ}C)^b$
PBDT-tt-BT	64 kDa	20 kDa	3.2	351
PC-tt-BT	72 kDa	51 kDa	1.4	352
PF-tt-BT	91 kDa	46 kDa	2.0	417

^a M_n , M_w , and PDI of the polymers were determined by gel permeation chromatography (GPC) using polystyrene standards in CHCl₃.

The 5% weight-loss temperatures under inert atmosphere.

The LUMO levels of PBDT-tt-BT, PC-tt-BT and PF-tt-BT are -3.78 eV, -3.59 eV and -3.66 eV, respectively. The HOMO energy levels of PBDT-tt-BT. PC-tt-BT and PF-tt-BT are -5.21 eV. -5.32 eV and -5.43 eV, respectively. With the increase of electron-donating abilities of polymers, their HOMO Levels are enhanced. It's not hard to find that the HOMO levels of the three copolymers rise from PFtt-BT to PC-tt-BT and to PBDT-tt-BT, with the increase of the electron-donating abilities of fluorene to carbazole and to BDT. Meanwhile, in comparison with the HOMO levels of PBDT-t-BT, PC**t-BT** and **PF-t-BT** containing thiophene as π bridge [25–27], the HOMO levels of PBDT-tt-BT, PC-tt-BT and PF-tt-BT all rise in different degree, which demonstrates that the TT unit as π bridge in D- π -A copolymers improve the corresponding HOMO levels. In addition, the electrochemical band gaps of the three copolymers were well matched with their optical band gaps within the experimental errors.

The wave functions of the frontier molecular orbital which were obtained through the density functional theory (DFT) at the B3LYP/ 6-31G(d,p) level are depicted in Fig. 4. To simplify the calculations, only two repeating units of each polymer were subject to simulation, with alkyl chains replaced by CH₃ groups. As can be observed, the HOMO is delocalized along the whole π -conjugated backbone while the LUMO is mostly concentrated on the benzothiadiazolebased acceptor groups, except for the PBDT-tt-BT. Although



Fig. 1. TGA plots of PBDT-tt-BT, PC-tt-BT, and PF-tt-BT with a heating rate of 10 °C/ min in the inert atmosphere.

discrepancies exist between the calculation and experimental results, the trends of variation in the energy gaps are similar.

As one of very important tool to detect the nanomorphology of these polymeric films, X-ray diffraction (XRD) was adopted to gain insight into the intermolecular interactions. As shown in Fig. 5, **PBDT-tt-BT** exhibited sharp diffraction peaks at 4.1°, while **PC-tt-BT** and **PF-tt-BT** neither showed diffraction peaks. Since the value corresponds to the distance between polymeric backbones, which is determined by the alkyl side chains. From the XRD patterns of the three polymers it clearly indicate that a more ordered structure can be formed in the film of **PBDT-tt-BT**, which is in agreement with the phenomena observed in UV–vis absorption measurements.

2.4. Hole mobility

The hole mobilities of copolymers were measured by the space charge limited current (SCLC) method using a device structure of ITO/PEDOT:PSS/polymer/Au. For the hole-only devices, SCLC can be approximated by the Mott–Gurney equation [29]:

$$J \cong (9/8)\varepsilon\varepsilon_0\mu_0 V^2 \exp\left(0.89\sqrt{V/E_0L}\right) / L^3$$
(1)

where *J* is the current density, ε is the dielectric constant of the polymer, ε_0 is the permittivity of the vacuum, μ_0 is the charge



Fig. 2. Normalized UV–vis absorption spectra of **PBDT-tt-BT**, **PC-tt-BT** and **PF-tt-BT**: (a) in chloroform solutions (b) thin films on quartz substrate casted from diluted chloroform solutions.

Table	2
Ontic	1

ptical absorption and electrochemica	l properties of	f the copolymers.
--------------------------------------	-----------------	-------------------

Copolymers	$\frac{\lambda_{\max}}{\text{Sol.}}$	nm) Film	E_g^{opt} (eV)	Oxidation potentials/ HOMO (eV)	Reduction potentials/ LUMO (eV)	E_g^{elec} (eV)
PBDT-tt-TBT	617	630	1.62	1.62/-5.21	-1.05/-3.78	1.46
PC-tt-BT	577	589	1.74	1.74/-5.32	-1.21/-3.59	1.73
PF-tt-BT	554	569	1.85	1.85/-5.43	-1.14/-3.66	1.77

mobility at zero field, $V = V_{appl} - V_{bi}$, V_{appl} is the applied potential, and $V_{\rm bi}$ is the built-in potential which results from the difference in the work function of the anode and the cathode (in this device structure, $V_{bi} = 0.2$ V), *L* is the thickness of the blended films layer. Fig. 6 displays $\ln(JL^3/V^2)$ versus $(V/L)^{0.5}$ plots for the measurement of the hole mobility of the conjugated polymers by the SCLC method. According to eq (1), the hole mobilities of the copolymers are $1.7 \times 10^{-4} \text{ cm}^2/\text{Vs}$, $2.2 \times 10^{-6} \text{ cm}^2/\text{Vs}$, $2.9 \times 10^{-5} \text{ cm}^2/\text{Vs}$, for **PBDT**tt-BT, PC-tt-BT and PF-tt-BT, respectively. It is obvious that the mobility of **PBDT-tt-BT** is higher by one order than these of **PC-tt-**BT and PF-tt-BT, which could be attributed to more ordered molecular structure of PBDT-tt-BT film. In both of PC-tt-BT and PF-tt-**BT**, because the steric hindrances between the TT bridge unit and six-ring aromatic units such as fluorene and carbazole are larger than that between the TT unit and five-ring aromatic unit such as BDT

2.5. Photovoltaic properties

To investigate the photovoltaic properties of the three copolymers, PSCs were fabricated with a typical configuration of ITO/ PEDOT:PSS/polymer:PC₇₀BM/Ca/Al. The I-V curves of the PSCs under the illumination of AM 1.5, 100 mW/cm² are shown in Fig. 7, meanwhile V_{oc} , J_{sc} , FF, and PCE of the PSCs are listed in Table 3.

When these copolymers are blended with PC₇₀BM as active layers, different weight ratios (polymer vs PC₇₀BM) were firstly scanned and we found for all devices, all the optimized results were obtained from the same 1:1 weight ratio. Therefore, we will focus on discussing 1:1 weight ratio devices results. The **PBDT-tt-BT**/PC₇₀BM (1:1 w/w) based devices gave a J_{sc} of 10.58 mA/cm², a V_{oc} of 0.73 V and a *FF* of 63.6%, and lead to a high *PCE* of 4.91%. In



Fig. 3. Cyclic voltammogram spectra of PBDT-tt-BT, PC-tt-BT, and PF-tt-BT films on a platinum plate in an acetonitrile solution of 0.1 mol/L Bu₄NPF₆ at a scan rate of 100 mV/s.



Fig. 4. The frontier molecular orbital of LUMO(a) and HOMO(b) obtained from DFT calculations on the polymers with a chain length n = 1.

comparison with **PBDT-tt-BT** based photovoltaic devices, however, both of PSCs devices based on PC-tt-BT and PF-tt-BT exhibited lower I_{sc} of 3.96 mA/cm², 4.66 mA/cm², and lower Fill Factors (FF) of 45.9 and 47.5, respectively. Although PF-tt-BT and PC-tt-BT based devices own higher V_{oc} of 0.83 V and 0.78 V respectively than **PBDT**tt-BT based devices, the lower PCEs of PF-tt-BT and PC-tt-BT than that of PBDT-tt-BT show PBDT-tt-BT have more potential in realizing higher efficiency. For the obvious improvement of J_{sc} of **PBDT**tt-BT based devices than these of PF-tt-BT and PC-tt-BT based devices, the reasonable reasons are following: are smaller steric hindrances between TT bridge unit and five-ring aromatic units such as BDT comparing to six-ring fluorene and carbazole units, which is favorable to form better molecular planarity and better interchain interactions; In the meantime, PBDT-tt-BT exhibited the red shifted absorption compared with other polymers and could enhance light absorption. Both of two reasons contributed to a much higher short-circuit current density for PBDT-tt-BT based devices than other two polymers based devices. For the lower FF of PC-tt-BT and PF-tt-BT comparing to that of PBDT-tt-BT, It is proposed that there are bigger steric hindrances between TT bridge unit and six-ring aromatic units such as fluorene and carbazole comparing to five-ring BDT unit and therefore the bigger steric hindrances lower the mobilities and caused their low FF. [30,31,32]

The external quantum efficiencies (*EQE*) based on **PBDT-tt-BT**, **PC-tt-BT** and **PF-tt-BT**/PC₇₀BM blend are shown in Fig. 8. The *EQE* curves of the blend films all cover a broad wavelength from 350 to 700 nm and exhibit maxima *EQE* values of 56.07% at ~537 nm, 24.39% at ~523 nm, and 33.9% at ~484 nm for the PSCs based on



Fig. 5. X-ray diffraction patterns: the pristine PBDT-tt-BT, PC-tt-BT and PF-tt-BT films casted from *o*-DCB onto a Si substrate.

PBDT-tt-BT, **PC-tt-BT** and **PF-tt-BT**, respectively. The PSC device based on **PBDT-tt-BT** show more efficient quantum efficiency (QE) in the whole response range, agreeing with the highest J_{sc} of the corresponding devices.

2.6. Film morphology

Considering the morphology of the photoactive layers is rather sensitive to the photovoltaic performances of the PSCs [33], the morphologies of the blend films of polymer/PC₇₀BM were analyzed by tapping mode atom force microscopy (AFM) measurements. As shown in Fig. 9, there is more like crystallized aggregations in **PBDT-tt-BT** blend in comparison with more amorphous morphologies in **PC-tt-BT** and **PF-tt-BT** blend films. At the same time, the roughness of the **PBDT-tt-BT**, **PC-tt-BT** and **PF-tt-BT** based blends is 0.45, 0.2, and 0.24, respectively. From AFM images it is concluded that better nanoscale phase separation is realized in ordered morphologies of **PBDT-tt-BT**, which is consistent with the higher photovoltaic performance of **PBDT-tt-BT** based PSCs.

3. Conclusion

In conclusion, we have successfully synthesized a series of D- π -A copolymers containing fused thienothiopene (TT) as π bride and BDT, carbazole, fluorene as D units and benzothiadiazole as A unit. Among the copolymers, **PF-tt-BT** has the lowest HOMO level at ca. -5.43 eV mostly due to the highest oxidation potential of



Fig. 6. $\ln(JL^3/V^2)$ versus $(V/L)^{0.5}$ plots of polymers/PC₇₀BM for the measurement of the hole mobility by the SCLC method.



Fig. 7. *J*–*V* curves of the polymer solar cells based on **PBDT-tt-BT**, **PC-tt-BT** and **PF-tt-BT** with PC₇₀BM as acceptor under the illumination of AM 1.5G, 100 Mw/cm².

Fluorene unit. Meanwhile, **PBDT-tt-BT** exhibited an higher hole mobility by one order than that of **PF-tt-BT** and **PC-tt-BT**, which is proposed that there are bigger steric hindrances between TT bridge unit and six-ring aromatic units such as fluorene and carbazole comparing to five-ring BDT unit and therefore the bigger steric hindrances lower the mobilities. Accordingly, when these copolymers are applied in PSCs as donor materials, a highest *PCE* of the PSCs based on **PBDT-tt-BT**/PC₇₀BM (1:1 w/w) reached 4.91% under the illumination of AM 1.5G, 100 mW/cm². These results indicate that the D- π -A copolymers based on the TT bridge unit are potential promising polymer donor materials for efficient PSCs.

4. Experimental section

4.1. Materials

3-Bromothiophene, ethyl 2-mercaptoacetate, Pd(PPh₃)₄ was purchased from Sigma—Aldrich Chemical Co., dodecanoyl chloride, 4,7-dibromo[2,1,3]benzothiadiazole were purchased from Acros Chemical Co., and they were used as received without further purification. Hexane and THF were dried over Na/benzophenone ketyl and freshly distilled prior to use. The other materials were commercial grade and used as received.

4.2. Instruments and measurements

The molecular weight of polymers was measured by GPC method with polystyrene as the standard and chloroform as the eluent. Thermogravimetric analysis (TGA) was performed on a TA Instruments, Inc., TGA-2050 under a nitrogen atmosphere. All new compounds were characterized by ¹H nuclear magnetic resonance (¹H NMR) and ¹³C NMR spectra carried out on a Bruker DMX-400 spectrometer. UV–visible absorption spectroscopy measurements were recorded by a Hitachi U-3100 UV–vis spectrophotometer.

Table 3

Photovoltaic properties of the PSCs based on polymers/PC₇₀BM under illumination of AM 1.5 G, 100 mW/cm².

Copolymer: PC ₇₀ BM(w/w)	$V_{oc}\left(V\right)$	J_{sc} (mA/cm ²)	FF (%)	PCE (%)	μ (cm ² /(Vs))
PBDT-tt-BT(1:1)	0.73	10.58	63.6	4.91	$\begin{array}{c} 1.7\times 10^{-4}\\ 2.2\times 10^{-6}\\ 2.9\times 10^{-5} \end{array}$
PC-tt-BT(1:1)	0.78	3.96	45.9	1.42	
PF-tt-BT(1:1)	0.83	4.66	47.5	1.84	



Fig. 8. EQE of the PSCs based on PBDT-tt-BT, PC-tt-BT and PF-tt-BT with $\mathsf{PC}_{70}\mathsf{BM}$ (1:1, w/w).

Atom Force Microscopy (AFM) was performed to characterize the surface morphology of the films on a Nanoscope III A (Vecco) AFM by the tapping mode. The electrochemical cyclic voltammetry (CV) was carried out on a CHI650D Electrochemical Workstation with Pt disk, Pt plate, and Fc/Fc⁺ electrode as working electrode, counter electrode and reference electrode, respectively, in a 0.1 mol/L tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) acetonitrile solution. The current density-voltage (J-V) characteristics were recorded on an Agilent B2912A Precision Source/Measure unit. The power conversion efficiency (PCE) of the polymer solar cells was measured under 1 sun, AM 1.5G (air mass 1.5 global) spectrum from a solar simulator (100 mW/cm²) using a XES-70S1 (SAN-EI ELEC-TRIC CO., LTD.) solar simulator (AAA grade, 70 mm \times 70 mm photobeam size). The external quantum efficiency (EQE) was measured by Solar Cell Spectral Response Measurement System QE-R3011 (Enli Technology Co., Ltd.).

4.3. Fabrication of polymer solar cells

PSCs with the structure of ITO/PEDOT-PSS/Polvmers:PC71BM/Ca (20 nm)/Al (80 nm) were fabricated under conditions as follows: The ITO glass was cleaned by a surfactant scrub and then underwent a wet-cleaning process inside an ultrasonic bath, beginning with deionized water followed by acetone and isopropanol. After oxygen plasma cleaning for 10 min, the ITO glass was modified by a 40 nm poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) thick (PEDOT:PSS) (Bayer Baytron 4083) anode buffer layer, which was spin-cast from a PEDOT:PSS aqueous solution onto the ITO substrate. Then the active layer was then deposited on top of the PEDOT:PSS layer by casting from a 10 mg/ml o-DCB solution. Finally, Ca (20 nm)/Al (80 nm) layer was successively deposited in vacuum onto the photosensitive layer at a pressure of ca. 4×10^{-4} Pa. The effective area of one cell defined a pixel size of 4 mm². Except for the deposition of the PEDOT:PSS layers, all the fabrication processes were carried out under nitrogen atmosphere.

4.4. Synthesis of monomers

4.4.1. 3-Undecylthieno[3,2-b]thiophene (4)

Compound **4** was synthesized according to related reference [34]. It's purified by chromatographic column using petroleum ether as eluent to get the pure product (29.28 g, yield 42%).



Fig. 9. AFM topography images (a, c, e, g) and phase contrast images (b, d, f, h) of PBDT-tt-BT/PC71BM (a, b), PC-tt-BT/PC71BM(c, d), and PF-tt-BT/PC71BM (e, f).

¹H NMR (CDCl₃, 400 MHz), δ (ppm): δ 7.39 (d, J = 2.6 Hz, 1H), 7.28 (d, J = 2.6 Hz, 1H), 7.03 (s, 1H), 2.79 (t, J = 4.1 Hz 2H), 1.79 (m, 2H), 1.44–1.21 (br, 16H), 0.95 (m, 3H). ¹³C NMR (CDCl₃, 100 MHz), δ (ppm): δ 140.02, 138.77, 134.93, 126.60, 121.79, 119.96, 31.97, 29.98, 29.73, 29.70, 29.64, 29.49, 29.46, 29.39, 28.70, 22.74, 14.15. MS: m/z = 294.

4.4.2. 4,7-Bis(6-undecylthieno[3,2-b]thiophen-2-yl) benzothiadiazole (**5**)

In a 250 ml argon purged round flask, n-BuLi (2.88 M, 18.89 ml) was injected slowly by a syringe into a solution of compound **4** (16.0 g, 54.4 mmol) in THF (100 ml) at 0 $^{\circ}$ C, and then the mixture was stirred at this temperature for 1.5 h. Subsequently,

chlorotrimethylstannane (1.0 M, 54.4 ml) was added at 0 °C and heated to room temperature for 6 h, then 4,7-dibromobenzothiadiazole (6.76 g, 23 mmol) and Pd(PPh₃)₄ (2.65 g, 2.3 mmol) were added together into the solution and the mixture was refluxed for 12 h. After cooled to room temperature, water (100 ml) was added to the solution and extracted by chloroform twice, then the combined organic phase was concentrated. The residue was purified by chromatographic column using dichloromethane (10:1) as eluent to obtain compound **5** as deep red power (7.79 g, yield 47%).

¹H NMR (CDCl₃, 400 MHz), δ (ppm): δ 8.39 (s, 2H), 7.78 (s, 2H), 7.04 (s, 2H), 2.75 (t, *J* = 6.9 Hz, 4H), 1.78 (m, 4H), 1.51–1.14 (br, 32H), 0.88 (m, 6H). ¹³C NMR (CDCl₃, 100 MHz), δ (ppm): δ 152.48, 140.50, 140.18, 139.68, 135.17, 126.35, 125.36, 122.95, 121.00, 31.95, 29.97, 29.70, 29.67, 29.63, 29.46, 29.44, 29.39, 28.67, 22.72, 14.15. MS: *m*/*z* = 721.

4.4.3. 4,7-Bis(5-bromo-6-undecylthieno[3,2-b]thiophen-2-yl) benzothiadiazole (tt-BT)

Compound **5** (0.95 g, 1.32 mmol) was dissolved into a solution of DMF (50 ml) and N-bromosuccinimide (0.52 g, 2.9 mmol) was added one portion and stirred for 12 h at room temperature. Then the mixture was washed by water several times and extracted by chloroform twice. The combined organic phase was concentrated and the residue was recrystallized from DMF to obtain compound **6** as deep red power (1.0 g, yield 86%).

¹H NMR (CDCl₃, 400 MHz), δ (ppm): δ 8.15 (s, 2H), 7.55 (s, 2H), 2.68 (t, *J* = 3.9 Hz, 4H), 1.74 (m, 4H), 1.58–1.13 (br, 32H), 0.88 (m, 6H). ¹³C NMR (CDCl₃, 100 MHz), δ (ppm): δ 151.96, 139.60, 138.60, 137.89, 134.20, 125.62, 124.75, 120.14, 111.66, 31.97, 29.98, 29.73, 29.70, 29.64, 29.44, 29.41, 29.14, 28.07, 22.74, 14.17. MS: m/z = 878.

General method of polymerization by Stille or Suzuki coupling reaction for the copolymers. The tt-BT monomer (0.5 mmol) and the monomer of 6 (0.5 mmol) were mixed in 10 ml of toluene and 2 ml of DMF. After being purged by argon for 5 min, 30 mg of $Pd(PPh_3)_4$ was added as catalyst, and then the mixture was purged by argon for 25 min. The reactant was stirred and heated to reflux for 16 h. Similarly, The tt-BT monomer (0.5 mmol) and the monomer of 7 or 8 (0.5 mmol) were mixed in 10 ml of toluene and 2 ml of K₂CO₃ (2 M). After being purged by argon for 5 min, 30 mg of Pd(PPh₃)₄ was added as catalyst, and then the mixture was purged by argon for 25 min. The reactant was stirred and heated to reflux for 16 h. Then the reactant was cooled to room temperature, and all the copolymers were precipitated by addition of 50 ml methanol, and then filtered through a Soxhlet thimble, which were then subjected to Soxhlet extraction with methanol, hexane, and chloroform. The copolymers were recovered as solid from the chloroform fraction by precipitation from methanol. The solid powders were dried under vacuum. The yields and molecular weight results of the polymers are as follows:

PBDT-tt-BT: Yield: 64%. $M_w = 64$ kDa, $M_n = 20$ kDa, PDI = 3.2. **PC-tt-BT**: Yield: 49%. $M_w = 72$ kDa, $M_n = 51$ kDa, PDI = 1.4. **PF-tt-BT**: Yield: 55%. $M_w = 91$ kDa, $M_n = 46$ kDa, PDI = 2.0.

Acknowledgment

This work was supported by National Natural Science Foundation of China (NSFC) (No. 21104088, 51173189, 51273203, 51261160496).

References

- [1] Yu G, Gao J, Hummelen JC, Wudl F, Heeger AJ. Science 1995;270:1789.
- [2] Peet J, Kim JY, Coates NE, Ma WL, Moses D, Heeger AJ, et al. Nat Mater 2007;6:497.
 [3] [a] Thompson BC, Frechet JM. J Angew Chem Int Ed 2008;47:58;
- [b] Chen H-Y, Hou JH, Zhang SQ, Liang YY, Yang GW, Yang Y, et al. Nat Photonics 2009;3:649.
- [4] [a] Wang M, Hu X, Liu P, Li W, Gong X, Huang F, et al. J Am Chem Soc 2011;133:9638;
 - [b] He ZC, Zhang C, Xu XF, Zhang LJ, Huang L, Chen JW, et al. Adv Mater 2011;23:3086;

[c] Huo LJ, Huang Y, Fan BH, Guo X, Jing Y, Zhang MJ, et al. Chem Commun 2012;48:3318.

[5] [a] Wu Y, Li ZJ, Ma W, Huang Y, Huo LJ, Guo X, et al. Adv Mater 2013;35:3449;
[b] Peet J, Heeger AJ, Bazan GC. Acc Chem Res 2009;42:1700;
[c] Wu Y, Li ZJ, Guo X, Fan HL, Huo LJ, Hou JH. J Mater Chem 2012;22:21362;
[d] Liang YY, Xu Z, Xia J, Tsai ST, Wu Y, Li G, et al. Adv Mater 2010;22:E135;
[e] Huo LJ, Li ZJ, Guo X, Wu Y, Zhang MJ, Ye L, et al. Polym Chem 2013;4:3047;
[f] Huo LJ, Ye L, Wu Y, Li ZJ, Guo X, Zhang MJ, et al. Macromolecules 2012;45: 6923;
[c] Genetics MC, Michlenders D, Korner M, Deck D, Malders G, Hanner AL, et al.

[g] Scharber MC, Muhlbacher D, Koppe M, Denk P, Waldauf C, Heeger AJ, et al. Adv Mater 2006;18:789;

- [h] Zhou H, Yang L, You W. Macromolecules 2012;45:607
- [6] Thompson BC, Frechet JMJ. Angew Chem Int Ed 2008;47:58.
- [7] Bundgaard E, Krebs FC. Sol En Mater Solar Cells 2007;9:954.
- [8] Hou JH, Chen HY, Zhang S, Li G, Yang YJ. Am Chem Soc 2008;130:16144.
- [9] [a] Chen CP, Chen YC, Yu CY. Polym Chem 2013;4:1161;
 [b] Kularatne RS, Magurudeniya HD, Sista P, Biewer MC, Stefan MC. J Polym Sci Part A: Polym Chem 2013;51:743.
- [10] Blouin N, Michaud A, Gendron D, Wakim S, Blair E, Plesu NR, et al. J Am Chem Soc 2008;13:732.
- [11] Inganas O, Svensson M, Zhang F, Gadisa A, Persson NK, Wang X, et al. Appl Phys A: Mater Sci Process 2004;79:31.
- [12] Helgesen M, Gevorgyan SA, Krebs FC, Janssen RA. J Chem Mater 2009;21:4669.
- [13] [a] Li Y, Chen Y, Liu X, Wang Z, Yang X, Tu Y, et al. Macromolecules 2011;44:6370;
 [b] Price SC, Stuart AC, You W. Macromolecules 2010;43:4609.
- [14] Peet J, Heeger AJ, Bazan GC. Acc Chem Res 2009;42:1700.
- [15] Roncali J. Chem Rev 1997;97:173.
- [16] Zhu Z, Waller D, Gaudiana R, Morana M, Mu D, Scharber M, et al. Macromolecules 1981;2007:40.
- [17] Zhou H, Yang L, Stoneking S, You W. ACS App Mater Interfaces 2010;2:1377.
- [18] Wang XC, Chen S, Sun YP, Zhang MJ, Li YF, Li XY, et al. Polym Chem 2011;2: 2872
- [19] Zhang MJ, Guo X, Li YF. Macromolecules 2011;44:8798.
- [20] Woo CH, Beaujuge PM, Holcombe TW, Lee OP, Frechet JMJ. J Am Chem Soc 2010;132:15547.
- [21] Ku J, Kim D, Ryu T, Jung E, Lansac Y, Jang YH. Bull Korean Chem Soc 2012;33:1029.
 [22] [a] Wang XC, Sun YP, Chen S, Guo X, Zhang MJ, Li XY, et al. Macromolecules 2012;45:1208;
 - [b] McCulloch I, Heeney M, Bailey C, Genevicius K, Macdonald I, Shkunov M, et al. Nature Mater 2006;5:328.
- [23] Guo X, Zhang MJ, Huo LJ, Xu F, Wu Y, Hou JH. J Mater Chem 2012;22:21024.
- [24] Hou JH, Chen HY, Zhang S, Yang Y. J Phys Chem C 2009;113:21202.
- [25] Blouin N, Michaud A, Leclerc M. Adv Mater 2007;19:2295.
- [26] Li W, Qin R, Zhou Y, Andersson M, Li F, Zhang C, et al. Polymer 2010;51:3031.
- [27] Hou JH, Tan ZA, Yan Y, He YJ, Yang CH, Li YF. J Am Chem Soc 2006;128:4911.
- [28] Malliaras GG, Salem JR, Brock PJ, Scott C. Phys Rev B 1998;58:13411.
- [29] Yuan MC, Chou YJ, Chen CM, Hsu CL, Wei KH. Polymer 2011;52:2792
- [30] Guo XG, Zhou NJ, Lou SJ, Smith J, Tice DB, Hennek JW. Nat Photon 2013. <u>http:// dx.doi.org/10.1038/nphoton.2013.207</u>.
- [31] Chang YT, Hsu SL, Su MH, Wei KH. Adv Mater 2009;21:2093.
- [32] Wan MJ, Zhu HB, Deng HQ, J L, Guo J, Huang YL. J Polym Sci Part A: Polym Chem 2013:51:3477.
- [33] Zheng Q, Jung BJ, Sun J, Katz HE. J Am Chem Soc 2010;132:5394.
- [34] He M, Zhang F. J Org Chem 2007;7:442.