Polymer Chemistry

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/polymers

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

High performance polymer solar cells based on a two dimensional conjugated polymer from alkylthienyl-substituted benzodifuran and benzothiadiazole

Bo Liu[‡a,c], Beibei Qiu[‡a], Xuewen Chen[a], Lu Xiao[a], Yongfang Li[b], Yuehui He[c], Lihui Jiang[a], Yingping Zou[a,c,d*]

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

A new low bandgap D-A copolymer **PBDFTDTBT** containing 4,8-bis(2-(2-ethylhexyl)thiophen-2-yl)-benzo[1,2-b;3,4-b']difuran (BDFT) and 4,7-di(thiophen-2-yl)-5,6-dioctyloxybenzo[c][1,2,5]thiadiazole (DTBT) units was synthesized and characterized for the application as donor material in polymer solar cells (PSCs). **PBDFTDTBT** film showed a broad absorption band from 300 nm to around 730 nm in the visible light region and the hole mobility of the blend of **PBDFTDTBT** and $PC_{71}BM$ reached up to 0.36 $cm^2 \cdot V^{-1} \cdot s^{-1}$ by using space charge limited current (SCLC) method. The PSCs based on **PBDFTDTBT**:$PC_{71}BM$ (1:1.5, *w*/*w*) exhibited a promising power conversion efficiency (PCE) of 6.0% under the illumination of AM 1.5G, 100 mW cm^{-2} with a high short circuit current density (J_{sc}) of 12.04 $mA \cdot cm^{-2}$ and an open circuit voltage (V_{oc}) of 0.76 V.

Introduction

During the past several decades, conjugated polymers have attracted significant attention due to their many desirable optoelectronic properties, which have been frequently applied in field effect transistors (FET), photovoltaic cells (PV), light-emitting devices (LED), *etc.*[1-4] Because of their attractive advantages for fabricating light-weight, low-cost, large-area and flexible devices through roll to roll solution processes, considerable efforts have been devoted into bulk heterojunction structures (BHJ) polymer solar cells (PSCs), as a consequence, the power conversion efficiencies (PCEs) have been improved rapidly from below 1% in 1990s to over 10% recently.[5-8] As well known, PSCs are commonly composed of a photoactive blend film of electron-donating conjugated polymers and electron-accepting fullerene derivatives, sandwiched between an ITO positive electrode and a low work function metal negative electrode.[9] Both the innovation of material and the optimization of device structure have played an important role in the exciting progress of PSC.[10-12] Although the present result is fairly satisfactory, it is still necessary to find ideal conjugated polymers combining high PCE with convenient processability in order to meet the requirements of commercialized applications of PSCs.[11] Among the various donor monomers utilised, several benzo[1,2-b:4,5-b']difuran (BDF) based conjugated polymers have exhibited some promising properties in optoelectronic devices in recent years.[13-15] Compared with benzo[1,2-b:4,5-b']dithiophene (BDT), which has been proven to be promising donor unit for high-performance PSC materials, BDF has a similar structure by substituting furan ring with thiophene ring.[12, 16-18] On account of the diameter of oxygen atom is less than sulfur atom, BDF-based copolymers can form promoted stacking and good coplanarity conjugated structure.[15] Besides, 4, 7-dithienyl-2, 1, 3-benzothiadiazole (DTBT), a well-known building block for donor-acceptor (D-A) photovoltaic copolymers, and its derivatives have been widely used as an excellent acceptor unit for highly efficient PSCs.[19-21] Our group previously designed and synthesized a conjugated polymer based on alkoxyl-substituted BDF and DTBT, named PBDFDODTBT, which showed promising photovoltaic properties.[22] Furthermore, the introduction of two-dimensional (2D)-conjugated structure has proven to be an effective way to improve photovoltaic properties, therefore, [23-26] it's worthwhile and meaningful to introduce 2D-conjugated structure into BDF-based polymers.

Taking into account all these reasons discussed above, in order to develop new photovoltaic polymers based on BDF unit and investigate the influence of 2D-conjugated structure on photovoltaic properties of the BDF-based polymer, we substituted alkoxyl for alkylthienyl in BDF unit, hence, a new D-A copolymer was synthesized by a Stille coupling polymerization reaction, named **PBDFTDTBT** in Scheme 1.[22] The hole mobility of the blend of **PBDFTDTBT** and $PC_{71}BM$ reached up to 0.36 $cm^2 \cdot V^{-1} \cdot s^{-1}$, PSC based on **PBDFTDTBT** showed a high PCE of 6.0%, therefore we become more firmly believe that 2D-conjugated BDF unit is also one of promising donor units.

Experimental Section

Materials

Furan-3-carboxylic acid, n-BuLi, $Pd(PPh_3)_4$ and $Sn(CH_3)_3Cl$ were obtained from Acros Organics, and they were used as received.

Tetrahydrofuran (THF) and toluene were dried over Na/benzophenone ketyl and freshly distilled prior to use. All of other reagents and solvents were purchased commercially as ACS-grade quality and used without further purification. 2, 6-Bis (trimethyltin)-4, 8-bis (2-(2-ethylhexyl)thiophen-2-yl)-benzo[1,2-b;3,4-b']difuran (M1) and 4,7-di(5-bromothiophen-2-yl)-5,6-dioctyloxybenzo[c][1,2,5]thiadiazole (M2) and were prepared according to the literature procedures.[27, 28]

Measurements and instrumentations

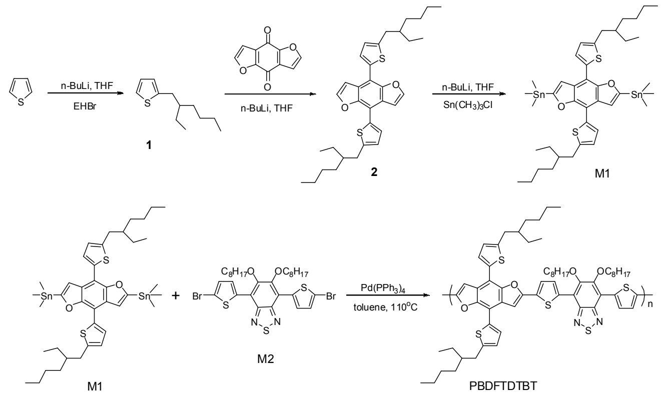
^{1}H NMR spectra were recorded using a Bruker DMX-400 spectrometer in $CDCl_3$ at 293 K, chemical shifts were reported as δ values (ppm) relative to an internal tetramethylsilane (TMS) standard. The Number-average (M_n) and weight-average (M_w) of the polymer were measured by gel permeation chromatograph (GPC) method, wherein polystyrene was used as a standard by using chloroform as eluent. TGA was performed on a PE TGA-7 at a heating rate of 20 K/min under nitrogen atmosphere. UV-vis absorption spectra were measured on a Hitachi U-3010 UV-Vis spectrophotometer. For solid state measurements, polymer solution in chloroform was cast on quartz plates. Optical bandgap was calculated from the onset of the absorption band. The cyclic voltammetric (CV) experiments were conducted on a Zahner IM6e electrochemical workstation using a platinum disk covered by the polymer film, Pt wire and a Ag/AgCl (0.1 M of AgCl in acetonitrile) electrode in an anhydrous and argon-saturated solution as working electrode, counter electrode and reference electrode respectively in a 0.1 mol/L tetrabutyl ammonium hexafluorophosphate (Bu_4NPF_6) acetonitrile solution at a scan rate of 50 mV/s. The morphologies of the blend films of polymer/$PC_{71}BM$ were obtained by using a Veeco's Dimension V atomic force microscopic (AFM) in the tapping mode.

Fabrication and characterization of the polymer solar cells

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, then treated in an ultraviolet-ozone chamber (Ultraviolet Ozone Cleaner, Jelight Company, USA) for 20 min. The 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 3000 rpm for 460 s on the ITO electrode. Subsequently, the PEDOT:PSS film was baked at 120 ºC for 20 min in the air to give a thin film with a thickness of 30 nm. A blend of the polymer and $PC_{71}BM$ was dissolved in orth-dichlorobenzene (*o*-DCB), and spin-cast at 3000 rpm for 45 s onto the PEDOT: PSS layer. The substrates were then dried at 70 ºC for 15 min. The thickness of the photoactive layer is in the range of 70-100 nm measured by Ambios Technology XP-2 profilometer. A bilayer cathode consisting of Ca (~20 nm) capped with Al (~100 nm) was thermal evaporated under a shadow mask with a base pressure of ca. 10^{-5} Pa. The active area of the PSCs is 4 mm^2. Device characterization was carried out under AM 1.5G 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.

Synthesis of the monomers and polymers

The synthetic routes of the monomer and polymer are shown in Scheme 1. The detailed synthetic procedures are as follows.



Scheme 1 Synthesis and structures of the BDFT monomer and the copolymer **PBDFTDTBT**.

Synthesis of compound 2

A solution of 2-(2-ethylhexyl)thiophene (1) (2.36 g, 12 mmol) in dry THF (50 mL) was deoxygenated with argon for 15 min, and then n-butyllithium (8.0 mL, 2.4 mol L^{-1}) was added dropwise at 0 ºC. After that, the mixture was warmed up to 55 °C and stirred for 2 h. Subsequently, 4, 8-dehydrobenzo [l, 2-b: 4, 5-b′]difuran-4,8-dione (0.76 g, 4 mmol) was added, and the mixture was stirred for 2 h at 55 °C. After the reaction mixture was cooled down to room temperature, a solution of $SnCl_2{\cdot}2H_2O$ (9.0 g, 40 mmol) in 10% HCl (15 mL) was added, and the reaction mixture was stirred for an additional 2 h and then poured into ice water. The mixture was extracted by CH_2Cl_2, washed by water two times, then dried by anhydrous $MgSO_4$. After the solvent was removed under vacuum, the residue was purified by column chromatography (silica gel, PE) to afford a yellow oil (1.02 g, yield 54%). 1H NMR ($CDCl_3$, 400 MHz, ppm): 7.74 (d, 2H), 7.67 (d, 2H), 7.35 (d, 2H), 6.83 (d, 2H), 2.80 (d, 4H), 1.72 (m, 2H), 1.42-1.24 (br, 16H), 0.92-0.88 (m, 12H). GC-MS: *m/z* =547.

Synthesis of compound M1

Compound 2 (1.09 g, 2 mmol) and 30 mL of dry THF were added into a flask under an inert atmosphere. The solution was cooled down to -78 °C and 3.0 mL of n-butyllithium (7.0 mmol, 2.4 mol L^{-1}) was added dropwisely. After being stirred at -78 °C for 1 h, 8 mL of trimethyltin chloride (8.0 mmol, 1 mol L^{-1}) was added in one portion. The cooling bath was removed and the reactant was stirred at room temperature overnight. Finally, it was poured into 100 mL of iced water and extracted by CH_2Cl_2. The organic layer was washed by water two times, and then dried by anhydrous $MgSO_4$. The organic phase was evaporated, and the residue was recrystallized from isopropanol to give the target monomer M1 as a yellow powder (1.1 g, yield 63%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.70 (d, 2H), 7.46 (s, 2H), 6.86 (d, 2H), 2.84 (d, 4H), 1.79-1.29 (m, 18H), 0.88 (t, 12H), 0.47 (s, 18H). GC-MS: *m/z* =872.

Synthesis of PBDFTDTBT

M1 (0.174 g, 0.2 mmol), M2 (0.143 g, 0.2 mmol) and 12 mL of dry toluene were put into a two-necked flask. The solution was flushed with N_2 for 10 min, then $Pd(PPh_3)_4$ (10 mg) was added into the flask. The solution was flushed with N_2 again for 20 min. The oil bath was heated to 115°C carefully, and the reactant was stirred for 24 h at this temperature under N_2 atmosphere. Then the reaction mixture was cooled to room temperature, the polymer was precipitated by the addition of 100 mL of methanol and filtered through a Soxhlet thimble, which was then subjected to Soxhlet extractions with methanol, hexanes and chloroform. The polymer was recovered as a solid from the chloroform fraction by rotary evaporation. Finally, the blue solid was obtained (0.122 g, yield 68%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.75-7.32(br, 6H), 7.13-6.73(br, 4H), 4.41-4.00(br, 4H), 3.31-2.76(br, 6H), 2.20-0.63(br, 58H). Anal. Calcd for $(C_{66}H_{84}N_2O_4S_5)_n$ (%): C, 70.17; H, 7.49; N, 2.48. Found (%): C, 70.21; H, 7.43; N, 2.49.

Results and discussion

Polymerization results

The polymer **PBDFTDTBT** was synthesized from M1 and M2 by using a typical Stille coupling polymerization reaction. The polymer was purified by continuous extractions with methanol, hexanes and chloroform, the chloroform fraction was recovered. Gel permeation chromatography (GPC) results (using polystyrene as the standard and THF as eluent) have shown that **PBDFTDTBT** has a number-average molecular weight (M_n) of 12.5 kDa with a polydispersity index (PDI) of 1.27. The GPC data of the copolymer is shown in Table 1.

Thermal Stability

Thermal stability of the polymer was investigated by thermogravimetric analysis (TGA) in the inert atmosphere. Fig.1 displays the TGA thermogram of **PBDFTDTBT**. The thermal data of the copolymer is also summarized in Table 1. The TGA analysis reveals that, under the protection of an inert atmosphere, the onset point of the weight loss (5%) of **PBDFTDTBT** is *ca.* 315 °C. Good thermal stability of the resulting copolymer prevents the deformation of the copolymer morphology and the degradation of the polymeric active layer at the resulting device operating temperature under applied electric field.

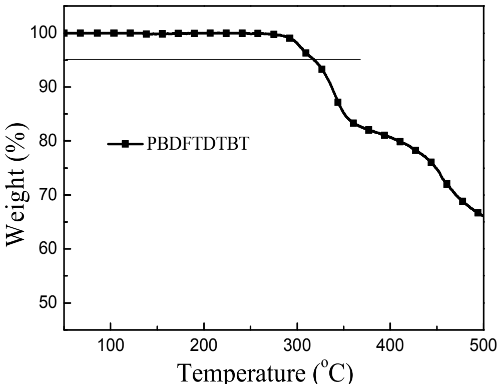


Fig. 1 TGA plot of **PBDFTDTBT** with a heating rate of 20 K/min under the inert atmosphere.

Optical Properties

Fig. 2 shows the UV-visible absorption spectra of **PBDFTDTBT** in $CHCl_3$ solution and in the thin film on quartz, and Table 2 lists the related absorption data for comparison. **PBDFTDTBT** exhibited favorable optical absorption properties in terms of harvesting visible solar photos. In solution, **PBDFTDTBT** shows two broad absorption bands with a high energy absorption from 300 nm to 500 nm and a low energy absorption from 500 nm to 700 nm. The absorption band from 300 nm to 500 nm can be ascribed to the π-π* transition of their main chain units, and the absorption band from 500 nm to 700 nm can be attributed to the intermolecular charge transfer (ICT) absorption of the polymer main chains.[29, 30]

Table 1 Polymerization results and thermal data of **PBDFTDTBT**.

polymer	M_n (kDa)	M_w (kDa)	PDI	yield (%)	T_d (°C)
PBDFTDTBT	12.5	15.9	1.27	68	315

Compared to its absorption in the solution, the maximal absorption peak of polymer film shows a little red-shift, indicating the polymer chains have stronger intermolecular interactions in the polymer film than those in solution, because the polymer chains adopt a planar geometry and pack closely in the solid state. The edge of the absorption band for **PBDFTDTBT** is 730 nm, and the optical bandgap (E_g^{opt}) estimated from the UV-vis absorption onset is 1.70 eV.

Electrochemical Properties

We studied the electrochemical properties of **PBDFTDTBT** by electrochemical cyclic voltammetry (CV), which has been widely employed in investigating the electrochemical behavior of the conjugated polymers and estimate their HOMO and LUMO energy levels. The onset oxidation and reduction potentials obtained from the cyclic voltammogram correspond to the HOMO and LUMO energy levels, respectively. We calculated the HOMO and LUMO energy levels of the **PBDFTDTBT** according to the equations: HOMO=-e(E_{on}^{ox} +4.4) (eV) and LUMO=-e(E_{on}^{red} +4.4) (eV), where the units of E_{on}^{ox} and E_{on}^{red} are V *vs*. Ag/AgCl. As shown in the cyclic voltammogram of **PBDFTDTBT** in Fig.3, the onset reduction and oxidation potentials *vs* Ag/AgCl of **PBDFTDTBT** are -1.29 eV and 0.81 eV, respectively. Hence, the LUMO and HOMO energy levels as well as the electrochemical band gap (E_g^{EC}) are -3.11 eV, -5.21 eV and 2.10 eV, respectively. According to Bittner and co-workers, the band offset determined by the LUMO of the donor and the LUMO of the acceptor must be greater than the exciton binding energy.[31] The energy offset between **PBDFTDTBT** and $PC_{71}BM$ is about 0.8 eV which is much larger than 0.4 eV, apparently, it is sufficient to drive charge separation for polymer **PBDFTDTBT** and it could ensure energetically favorable electron transfer.[32-35] The related CV data (E_{on}^{ox} / E_{on}^{red} , HOMO and LUMO energy levels, E_g^{EC}) are summarized in Table 2. Electrochemical bandgap is larger than optical bandgap, this discrepancy might have been induced by the presence of an energy barrier at the interface between the polymer film and the electrode surface.[36]

Hole mobility

Besides the absorption and energy levels, the charge carrier transport abilities of conjugated polymers also have great effects on the resulting performance, especially on short circuit current

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Table2 Optical and electrochemical properties of **PBDFTDTBT**.

Polymer	Absorption spectra				Cyclic voltammetry (*vs* Ag/AgCl)		
	Solution[a]	Film[b]			p-doping	n-doping	
	λ_{max} (nm)	λ_{max} (nm)	λ_{onset} (nm)	E_g^{opt} [c] (eV)	E_{on}^{ox} /HOMO[d] (V)/(eV)	E_{on}^{red} /LUMO[d] (V)/(eV)	E_g^{EC} (eV)
PBDFTDTBT	577	599	730	1.70	0.81/-5.21	-1.29/-3.11	2.10

[a] Measured in chloroform solution. [b] Cast from chloroform solution. [c] Bandgap estimated from the onset wavelength of the optical absorption. [d] HOMO= -e(E_{on}^{ox} +4.4) (eV); LUMO= -e(E_{on}^{red} +4.4) (eV) using Ag/AgCl as the reference electrode.

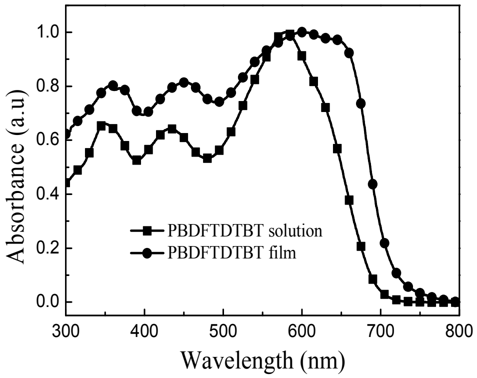


Fig. 2 UV-vis absorption spectra of **PBDFTDTBT** in dilute $CHCl_3$ solution and in the film state.

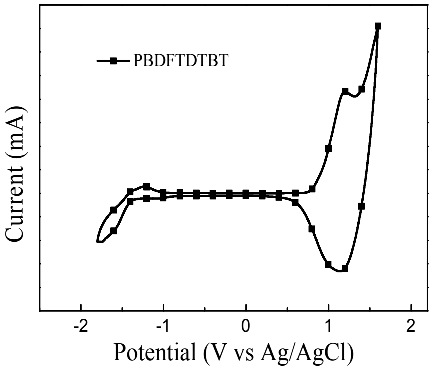


Fig. 3 Cyclic voltammogram of **PBDFTDTBT** film cast on platinum disk in 0.1 M Bu_4NPF_6 /CH_3CN solution at 50 mV/s.

density (J_{sc}) and fill factor (FF) of BHJ solar cells.[37] We measured the hole mobility of **PBDFTDTBT** blended with $PC_{71}BM$ by space charge limited current (SCLC) method which is based on Poole–Frenkel Law with a device structure of ITO/PEDOT:PSS/polymer:$PC_{71}BM$(1:1.5, *w/w*)/Au. SCLC is described by

$$J_{SCLC}=\frac{9}{8}\varepsilon_0\varepsilon_r\mu_0\frac{(V-V_{bi})^2}{d^3}\exp\left[0.89\gamma\sqrt{\frac{V-V_{bi}}{d}}\right] \qquad (1)$$

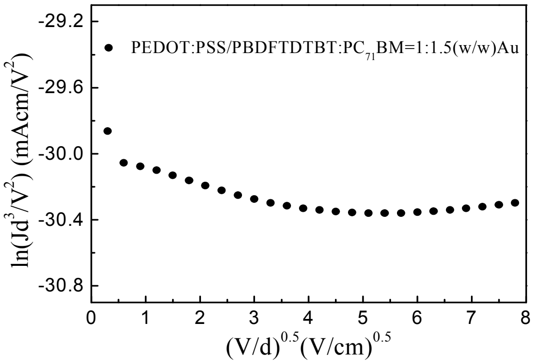


Fig. 4 $\ln(Jd^3/V^2)$ *vs* $(V/d)^{0.5}$ plot of the blend of **PBDFTDTBT** and $PC_{71}BM$ for the measurement of the hole mobility by SCLC method.

The results are plotted as $\ln(Jd^3/V^2)\ vs\ (V/d)^{0.5}$, as shown in Fig.4. Here, *J* stands for current density, *d* is the thickness of the device, $V= V_{appl}-V_{bi}$, where V_{appl} is the applied potential and V_{bi} is the built-in potential. According to Equation (1), the hole mobility of the blend of **PBDFTDTBT** and $PC_{71}BM$ is as high as 0.36 $cm^2 \cdot V^{-1} \cdot s^{-1}$, which implies that the relatively high J_{sc} and FF could be obtained in the PSCs that will be discussed later. Compared to the corresponding BDT or BDF based copolymers with alkoxyl groups, this kind of BDFT based polymer demonstrated at least one order of magnitude higher hole mobility, which may be due to the introduction of 2D-conjugated structure.[38, 39]

Photovoltaic properties

To investigate the photovoltaic properties of the polymer, the BHJ PSCs were fabricated with a device structure of ITO/PEDOT:PSS/polymer:$PC_{71}BM$/Ca/Al. Fig.5 shows the typical *J-V* curves of the devices under the illumination of AM 1.5G, 100 mW/cm^2 and the corresponding open-circuit voltage (V_{oc}), short circuit current (J_{sc}), fill factor (FF), power conversion

Dynamic Article Links ►

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Table 3 Photovoltaic properties of PSCs based on **PBDFTDTBT**:$PC_{71}BM$.

Active layer	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	*PCE*
PBDFTDTBT:$PC_{71}BM$=1:1	0.77	10.67	64.7	5.3
PBDFTDTBT:$PC_{71}BM$=1:1.5	0.76	12.04	65.0	6.0
PBDFTDTBT:$PC_{71}BM$=1:2	0.75	10.69	63.4	5.1

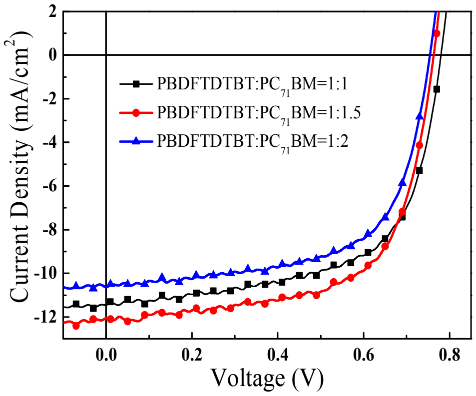


Fig. 5 *J-V* curves of the PSCs based on **PBDFTDTBT**/$PC_{71}BM$ with different ratios under illumination of AM1.5G, 100 mW/cm^2.

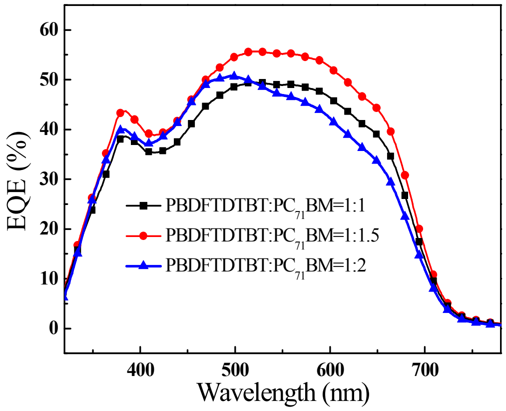


Fig. 6 The *EQE* curves of the PSCs based on **PBDFTDTBT**:$PC_{71}BM$ with different ratios in *o*-DCB.

efficiency (PCE) are also summarized in Table 3. The blends of the polymer and $PC_{71}BM$ at different weight ratios of 1:1, 1:1.5, 1:2 were used to optimize the device performances. For each ratio, we have fabricated five devices with little variations, therefore, herein, we chose the medium values as listed in Table 3. We can see that these BHJ devices with three ratios all show commendable performance, FF of them were all greater than 0.60, the J_{sc} were higher than 10 mA·cm^{-2}, and V_{oc} of them were similar and all above 0.75 V. The optimized blend ratio is 1:1.5 between the donor polymer and $PC_{71}BM$ while fabricating BHJ PSCs, which exhibited a promising PCE of 6.0%. The *EQE* values are above 40% from 450 nm to 650 nm of **PBDFTDTBT** and the maximum *EQE* plateau reached 55% between 500 nm and 600 nm, which led to higher J_{sc} up to 12.04 mA·cm^{-2}.

Morphology

Besides absorption, energy levels and charge mobility, the morphology of the active layer is also very important for PSCs. To better explain different photovoltaic properties and determine if the devices were fully optimized, we investigated the morphologies of **PBDFTDTBT** and $PC_{71}BM$ blend spin-coating from their *o*-DCB solutions by using tapping-mode atomic-force microscopy (AFM). Fig.7 shows the height and phase images of **PBDFTDTBT**:$PC_{71}BM$ (1:1.5, *w/w*) films.

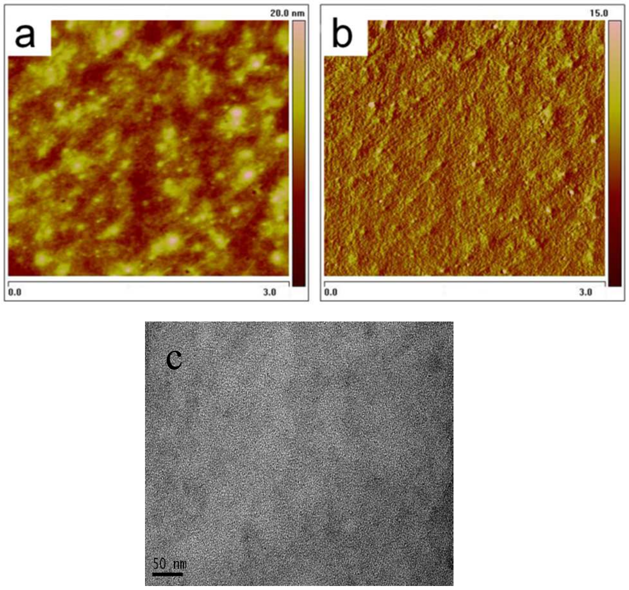


Fig.7 AFM and TEM images of **PBDFTDTBT**:$PC_{71}BM$ (1:1.5) in *o*-DCB: (a) height image; (b) phase image; (c) TEM image.

From the height image (Fig. 7a), the root-mean-square (RMS) surface roughness value of the blend film is 0.89 nm. The blend forms very smooth high quality film when spinning-cast from *o*-DCB solutions. The film is very homogenous with little apparent phase separation and low surface roughness. From the phase image of **PBDFTDTBT** and PC$_{71}$BM blend (Fig. 7b), the connectivity is sensitive to the structures of the polymers. For BHJ PSCs, nanoscale phase separation is a practical way to form bicontinuous donor-acceptor network. AFM images indicate that the **PBDFTDTBT**/PC$_{71}$BM possesses good morphology for PSCs. From the TEM (Fig. 7c) of the blend, nanoscale phase separation could be well formed.

Conclusions

In summary, a new D-A copolymer based on BDFT donor unit and DTBT acceptor unit, **PBDFTDTBT**, was synthesized by a Stille coupling polymerization reaction and used as the donor material in PSCs. The polymer film showed a broad absorption band from 300 nm to around 730 nm in the visible light region, with an optical bandgap of 1.70 eV and a medium electrochemical bandgap of 2.10 eV. Besides, the hole mobility of the blend of **PBDFTDTBT** and PC$_{71}$BM (1:1.5, *w/w*) is 0.36 cm^{2}·V^{-1}·s^{-1} by using SCLC method, which may one of the main motivations of getting relatively high J_{sc} and FF. The PSCs based on **PBDFTDTBT**:PC$_{71}$BM (1:1.5, *w/w*) exhibited a promising PCE of 6.0% with a V_{oc} of 0.76 V, a high J_{sc} of 12.04 mA·cm^{-2} and a FF of 0.65, without any device modifications or post treatment. These results indicate that 2D-conjugated **PBDFTDTBT** is a promising candidate for high-efficiency polymer solar cells.

Acknowledgments

This work was supported by NSFC (Nos. 51173206, 21161160443), National High Technology Research and Development Program (NO. 2011AA050523) and Central South University.

Notes and references

a. College of Chemistry and Chemical Engineering, Central South University, Changsha 410083, China. E-mail: yingpingzou@ csu.edu.cn(Y.Zou)
b. Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China.
c. State key Laboratory for Powder Metallurgy, Central South University, Changsha 410083, China.
d. Institute of Super-microstructure and Ultrafast Process in Advanced Materials,, Central South University, Changsha 410083,China.
‡ B.Liu and B.Qiu contributed this work equally.

1. C. Wang, H. Dong, W. Hu, Y. Liu and D. Zhu, *Chemical reviews*, 2012, **112**, 2208.
2. C. Zhong, C. Duan, F. Huang, H. Wu and Y. Cao, *Chemistry of Materials*, 2011, **23**, 326.
3. P. M. Beaujuge and J. R. Reynolds, *Chemical reviews*, 2010, **110**, 268-320.
4. Y. Li, *Accounts of Chemical Research*, 2012, **45**, 723.
5. G. Yu, J. Gao, J. Hummelen, F. Wudl and A. Heeger, *Science-AAAS-Weekly Paper Edition*, 1995, **270**, 1789.
6. Y. Zou, A. Najari, P. Berrouard, S. Beaupré, B. Réda Aïch, Y. Tao and M. Leclerc, *Journal of the American Chemical Society*, 2010, **132**, 5330.
7. J. You, L. Dou, K. Yoshimura, T. Kato, K. Ohya, T. Moriarty, K. Emery, C.-C. Chen, J. Gao, G. Li and Y. Yang, *Nature Communications*, 2013, **4**, 1446.
8. J. Min, Z.-G. Zhang, S. Zhang and Y. Li, *Chemistry of Materials*, 2012, **24**, 3247.
9. Y. Li and Y. Zou, *Advanced Materials*, 2008, **20**, 2952.
10. J. F. Jheng, Y. Y. Lai, J. S. Wu, Y. H. Chao, C. L. Wang and C. S. Hsu, *Advanced Materials*, 2013. **25**, 2445.
11. N. Li, D. Baran, K. Forberich, F. Machui, T. Ameri, M. Turbiez, M. Carrasco-Orozco, M. Drees, A. Facchetti, F. C. Krebs and C. J. Brabec, *Energy & Environmental Science*, 2013, **6**, 3407.
12. C. Cabanetos, A. El Labban, J. A. Bartelt, J. D. Douglas, W. R. Mateker, J. M. J. Fréchet, M. D. McGehee and P. M. Beaujuge, *Journal of the American Chemical Society*, 2013, **135**, 4656.
13. L. Huo, Z. Li, X. Guo, Y. Wu, M. Zhang, L. Ye, S. Zhang and J. Hou, *Polymer Chemistry*, 2013, **4**, 3047.
14. X. Chen, B. Liu, Y. Zou, L. Xiao, X. Guo, Y. He and Y. Li, *Journal of Materials Chemistry*, 2012, **22**, 17724.
15. L. Huo, L. Ye, Y. Wu, Z. Li, X. Guo, M. Zhang, S. Zhang and J. Hou, *Macromolecules*, 2012, **45**, 6923.
16. J. Yuan, L. Xiao, B. Liu, Y. Li, Y. He, C. Pan and Y. Zou, *Journal of Materials Chemistry A*, 2013, **1**, 10639.
17. B. Liu, X. Chen, Y. He, Y. Li, X. Xu, L. Xiao, L. Li and Y. Zou, *Journal of Materials Chemistry A*, 2013, **1**, 570.
18. A. Najari, S. Beaupré, P. Berrouard, Y. Zou, J.-R. Pouliot, C. Lepage-Pérusse and M. Leclerc, *Advanced Functional Materials*, 2011, **21**, 718.
19. N. Wang, Z. Chen, W. Wei and Z. Jiang, *Journal of the American Chemical Society*, 2013, **135**, 17060.
20. J. Zhou, S. Xie, E. F. Amond and M. L. Becker, *Macromolecules*, 2013, **46**, 3391.
21. K. Wang, Y. Zhao, W. Tang, Z.-G. Zhang, Q. Fu and Y. Li, *Organic Electronics*, 2014, **15**, 818.
22. B. Liu, X. Chen, Y. Zou, L. Xiao, X. Xu, Y. He, L. Li and Y. Li, *Macromolecules*, 2012, **45**, 6898.
23. L. Huo, S. Zhang, X. Guo, F. Xu, Y. Li and J. Hou, *Angewandte Chemie International Edition*, 2011, **50**, 9697.
24. X. Guo, M. Zhang, J. Tan, S. Zhang, L. Huo, W. Hu, Y. Li and J. Hou, *Advanced Materials*, 2012, **24**, 6536.
25. M. Zhang, Y. Gu, X. Guo, F. Liu, S. Zhang, L. Huo, T. P. Russell and J. Hou, *Adv Mater*, 2013, **25**, 4944.
26. M. Zhang, X. Guo, S. Zhang and J. Hou, *Adv Mater*, 2014, **26**, 1118.
27. P. Ding, C.-C. Chu, B. Liu, B. Peng, Y. Zou, Y. He, K. Zhou and C.-S. Hsu, *Macromolecular Chemistry and Physics*, 2010, **211**, 2555.
28. B. Liu, X. Chen, Y. Zou, Y. He, L. Xiao, X. Xu, L. Li and Y. Li, *Polymer Chemistry*, 2013, **4**, 470.
29. F. Huang, K.-S. Chen, H.-L. Yip, S. K. Hau, O. Acton, Y. Zhang, J. Luo and A. K.-Y. Jen, *Journal of the American Chemical Society*, 2009, **131**, 13886.
30. C. Duan, K.-S. Chen, F. Huang, H.-L. Yip, S. Liu, J. Zhang, A. K.-Y. Jen and Y. Cao, *Chemistry of Materials*, 2010, **22**, 6444.
31. E. R. Bittner, J. G. Ramon and S. Karabunarliev, *The Journal of chemical physics*, 2005, **122**, 214719.
32. B. Carsten, J. M. Szarko, H. J. Son, W. Wang, L. Lu, F. He, B. S. Rolczynski, S. J. Lou, L. X. Chen and L. Yu, *J Am Chem Soc*, 2011, **133**, 20468.
33. M. C. Scharber, D. Mühlbacher, M. Koppe, P. Denk, C. Waldauf, A. J. Heeger and C. J. Brabec, *Advanced Materials*, 2006, **18**, 789-794.
34. B. Kraabel, D. McBranch, N. Sariciftci, D. Moses and A. Heeger, *Physical Review B*, 1994, **50**, 18543.
35. N. Sariciftci, L. Smilowitz, A. J. Heeger and F. Wudl, *Science*, 1992, **258**, 1474.
36. Y. Li, Y. Cao, J. Gao, D. Wang, G. Yu and A. J. Heeger, *Synthetic Metals*, 1999, **99**, 243.
37. P. W. M. Blom, V. D. Mihailetchi, L. J. A. Koster and D. E. Markov, *Advanced Materials*, 2007, **19**, 1551.
38. P. Ding, C. Zhong, Y. Zou, C. Pan, H. Wu and Y. Cao, *The Journal of Physical Chemistry C*, 2011, **115**, 16211.
39. Z. Zhang, B. Peng, B. Liu, C. Pan, Y. Li, Y. He, K. Zhou and Y. Zou, *Polymer Chemistry*, 2010, **1**, 1441.

High performance polymer solar cells based on a two dimensional conjugated polymer from alkylthienyl-substituted benzodifuran and benzothiadiazole

Bo Liu‡[a,c], Beibei Qiu‡[a], Xuewen Chen[a], Lu Xiao[a], Yongfang Li[b], Yuehui He[c], Lihui Jiang[a],Yingping Zou[a,c,d*]

A new copolymer PBDFTDTBT was synthesized and applied in PSCs. PBDFTDTBTdemonstrates a power conversion efficiency of 6.0% with high J_{sc} and FF.