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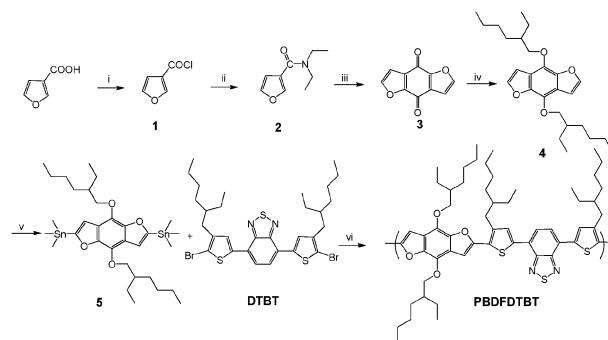
Synthesis of a 4,8-dialkoxy-benzo[1,2-*b*:4,5-*b'*]difuran unit and its application in photovoltaic polymer†Lijun Huo,^a Ye Huang,^a Benhu Fan,^a Xia Guo,^a Yan Jing,^a Maojie Zhang,^a Yongfang Li^{*b} and Jianhui Hou^{*a}

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A new building block of benzo[1,2-*b*:4,5-*b'*]difuran (BDF) was firstly designed and synthesized. The newly designed unit was applied for constructing a new photovoltaic low band gap polymer, PBDFDTBT, which exhibited promising power conversion efficiency of 5.0%.

Tremendous progresses have been made in polymer solar cells (PSCs) over the past decade, and the applications of new active layer materials are some of the main driving forces to promote the field.¹ At the early stage, PPV derivatives, like MEH-PPV and MDMO-PPV, were broadly used as electron donors in bulk heterojunction PSCs,² and power conversion efficiencies (PCEs) of around 2% were obtained.³ In order to make better use of the sunlight, a derivative of polythiophene, P3HT, was applied to PSCs as electron donor, and thereby >4% PCE was realized in P3HT-based PSCs in 2005.⁴ After that, more and more new conjugated polymers built by different conjugated components were developed and applied in PSCs, and currently over 7% PCEs have been reported by several groups.⁵ The application of new conjugated building blocks is of great importance to molecular design of photovoltaic polymers. For example, a benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT) unit was firstly introduced into photovoltaic materials in 2008.⁶ Although the initial photovoltaic properties of the BDT-based polymers were below 2%, the BDT unit exhibited potential properties as a building block, like tunable band gaps and molecular energy levels and high hole mobilities.^{1/6} Therefore, the BDT unit attracted much attention and more and more BDT-based polymers were designed and applied in PSCs. Currently, PCE of ~8% has been achieved by using BDT-based polymer as electron donor.⁷ Therefore, based on the reported works, it can be concluded that the progresses of PSCs are closely related to the applications of new building blocks.



Scheme 1 Synthetic route and molecular structure of PBDFDTBT. (i) Oxalyl chloride, room temperature, 12 h; (ii) diethylamine, methylene chloride, room temperature, 40 min; (iii) 0 °C, THF, *n*-butyllithium, then room temperature, 15 h, then HCl; (iv) 0 °C, ethanol, sodium borohydride, 3 h, HCl; then 2-ethylhexyl bromide, 150 °C, 15 h; (v) THF, *n*-butyllithium, room temperature, 1 h, then chlorotrimethylstannane, 30 min; (vi) toluene, Pd(PPh₃)₄, 110 °C, 16 h.

In this work, benzo[1,2-*b*:4,5-*b'*]difuran (BDF) was used as a new building block to design a photovoltaic conjugated polymer, named PBDFDTBT (Scheme 1), and its photovoltaic properties were investigated initially. As a furan-containing fused aromatic unit, BDF possesses unique properties. As reported, in comparison with thiophene, the five-member ring of furan shows weaker steric hindrance to adjacent units, because the diameter of the oxygen atom is smaller than that of the sulfur atom.⁸ Therefore, when BDF is copolymerized with other conjugated components, planar structure and thus a well conjugated backbone will be formed. Consequently, smaller band gap and better mobility can be expected from BDF-based conjugated polymers. On the other hand, furan-based compounds show feasibilities in making biodegradable and biorenewable materials,⁹ which might be a potential property of BDF-based polymers. In this first BDF-based photovoltaic polymer, 4,7-dithienyl-2,1,3-benzothiadiazole (DTBT) was selected as an electron withdrawing block to build a D–A backbone. As is known, DTBT and its derivatives have been broadly used as building blocks in photovoltaic materials. Several important polymers like PFDTBT,¹⁰ PCDTBT,¹¹ PDTSDTBT¹² and PBDDTDTBT¹³ have been developed and fully studied in the past several years, and PCEs of ~4–7% have been achieved by using those polymers as electron donors in PSCs. Since the chemical,

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physical and photovoltaic properties of these four polymers with DTBT segments have been well reported, the comparison between PDBFDTBT and the reported polymers will provide a general guide to molecular design of BDF-based polymers.

The synthetic route of PBDFDTBT is shown in Scheme 1. Furan-3-carbonyl chloride, compound **1**, was readily prepared from furan-3-carboxylic acid by reacting with an excess amount of oxalyl chloride; after removing the remaining oxalyl chloride under vacuum, the product was used without further purification. Then, compound **2** was obtained with a yield of ~90%. Benzo[1,2-*b*:4,5-*b'*]difuran-4,8-dione (compound **3**) was synthesized by the same method used for benzo[1,2-*b*:4,5-*b'*]dithiophene-4,8-dione.⁶ Subsequently, compound **3** was reduced to 4,8-dihydrobenzofuro[5,6-*b*]furan-4,8-diol by sodium borohydride in ethanol under 0 °C, and the diol was separated by acidification with hydrochloric acid. Subsequently, the diol was mixed with potassium carbonate and 2-ethylhexyl bromide in DMF and then refluxed for 15 h under inert atmosphere. 4,8-Bis-ethylhexyloxy-benzo[1,2-*b*:4,5-*b'*]difuran, compound **4**, was synthesized and purified by using chromatographic column with hexane. The DTBT monomer was prepared through the reported method.¹⁴ A typical Stille coupling reaction was employed to produce the polymer, and the final product shows good solubility in chloroform and dichlorobenzene. The molecular weight of PBDFDTBT was measured through Gel Permeation Chromatography (GPC) by using polystyrene as standard and THF as eluent; a molecular weight of 10 K (M_w) and a poly-dispersity index (PDI) of 1.6 were recorded, respectively. This polymer exhibits good thermal stability below 360 °C under the inert atmosphere.

The absorption spectra of PBDFDTBT in solution and solid film are shown in Fig. 1a). In dilute chloroform solution, PBDFDTBT shows two absorption peaks at 398 nm and 563 nm, respectively. In solid film, the main absorption peak is *ca.* 50 nm red-shifted compared to its absorption in solution, which indicates that this polymer exhibits longer effective conjugation length in solid state than in solution. In solid film, the absorption edge is at ~775 nm, corresponding to a band gap (E_g) of 1.60 eV. The strong and broad absorption band of PBDFDTBT's film matches well with the solar irradiation spectrum, which indicates that this polymer should be an excellent absorber of the sunlight.⁶ Electrochemical cyclic voltammetry (CV) was employed to determine its oxidation/reduction potentials. From the cyclic voltammogram of PBDFDTBT as shown in Fig. 1b), it can be seen that both p- and n-doping processes are quasi-reversible, and the oxidation (p-doping) onset point is 0.30 V and the reduction (n-doping)

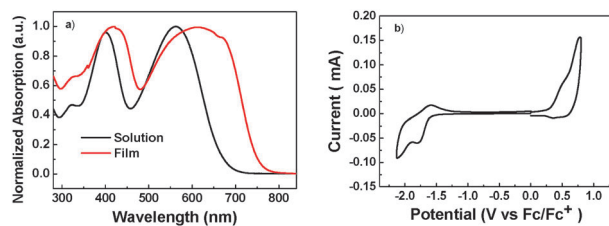


Fig. 1 (a) Absorption spectra of PBDFDTBT in chloroform solution and in solid film on quartz; (b) cyclic voltammogram curve of PBDFDTBT film on platinum electrode in acetonitrile containing 0.1 mol L⁻¹ Bu₄NPF₆ at a scan rate of 20 mV s⁻¹.

Table 1 Absorption and molecular energy level data of PBDFDTBT and the other four polymers with similar backbones

	λ peak/ nm	E_g opt/ eV	HOMO/ eV	LUMO/ eV	PCE (%)	Ref.
PBDFDTBT	613	1.60	-5.10	-3.24	5.0	This work
PBDTDTBT	596	1.75	-5.31	-3.44	5.6	13
PFDTBT	550	1.90	-5.52	-3.50	4.5	10
PCDTBT	576	1.88	-5.45	-3.60	3.6	11
PSiDTBT	644	1.53	-4.99	-3.17	3.4	12

onset point is -1.56 V vs. Fc/Fc⁺. Accordingly, the HOMO and LUMO levels of the polymer are -5.10 eV and -3.24 eV, respectively, which were calculated according to the reported method.¹⁵ In order to make comparison, band gaps, HOMO and LUMO levels of PFDTBT, PCDTBT, PDSiDTBT and PBDTDTBT are also listed in Table 1. It can be seen that PBDFDTBT has relatively smaller band gap and moderate HOMO and LUMO levels compared to the other four polymers.¹⁰⁻¹³ These basic properties of PBDFDTBT indicate that BDF should be a potential building block for photovoltaic donor materials.

The PSC devices with a structure of ITO/PEDOT:PSS/PBDFDTBT:PC₇₀BM/Ca/Al were fabricated to investigate photovoltaic properties of PBDFDTBT (see Fig. 2). First, chlorobenzene (CB) and *o*-dichlorobenzene (ODCB) were used to make the solution of active layer for spin-coating, and we found that the device made from ODCB solution exhibited better performance compared to the device made from CB solution. Subsequently, different D/A (polymer/PC₇₀BM) ratios, from 1:0.5 to 1:2, were investigated to optimize the device performance, and the detailed results are listed in Table 2. Very interestingly, the photovoltaic properties of PBDFDTBT-based devices are almost independent of the D/A ratio of the devices. For example, the open circuit voltage (V_{oc}) of all the devices is around 0.77 V; the fill factor (FF) is around 0.6; and the short circuit current density (J_{sc}) is around 9 mA cm⁻². As a result, PCE values of the devices are 4.3 ± 0.3%. Since PCE of the device with a D/A ratio of 1:1.5 is slightly higher than that of the others, the devices with 1:1.5 D/A ratio were further optimized by using 1,8-diiodooctane (DIO) as additive¹⁶ and by using thermal annealing treatment⁴ according to the reported works. We found that photovoltaic performance of the device had little change after adding DIO; however, performance of the device was slightly increased after thermal annealing treatment (90 °C for 10 min), the J_{sc} and the FF varied within 10.5–12.1 mA cm⁻² and 55–63% for a 1:1.5 weight ratio, respectively. The highest PCE of 5.0% was recorded among 40 devices.

Table 2 Photovoltaic results of the PSCs based on PBDFDTBT/PC₇₀BM under the illumination of AM 1.5G 100 mW cm⁻²

D/A ratio	Film thickness/nm	V_{oc} /V	J_{sc} /mA cm ⁻²	FF	PCE (%)
1:0.5	95	0.79	8.71	0.587	4.04
1:0.8	90	0.78	9.10	0.606	4.30
1:1	80	0.75	8.79	0.617	4.07
1:1.5	80	0.78	10.00	0.598	4.66
1:1.5 ^a	80	0.78	11.77	0.546	5.01
1:2	70	0.77	8.80	0.578	3.92

^a Annealed at 90 °C for 10 min.

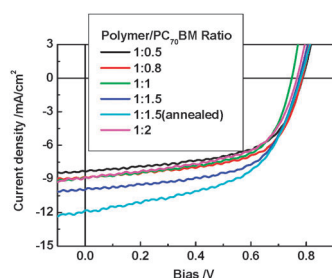


Fig. 2 J - V curves of the PSCs based on PBDFDTBT/PC₇₀BM with different donor/acceptor ratios (1:0.5, 1:0.8, 1:1, 1:1.5, 1:2 and 1:1.5 annealing treatment) under illumination of AM 1.5G, 100 mW cm⁻².

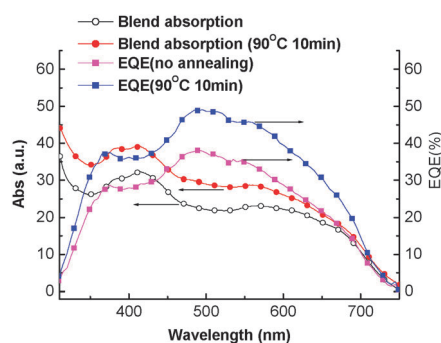


Fig. 3 The blend absorption and external quantum efficiency (EQE) curves of PBDFDTBT-based PSCs before and after thermal annealing with a D/A ratio of 1:1.5.

Charge carrier mobility is another important parameter for conjugated polymers. The hole mobility of the PBDFDTBT/PCBM blend (w/w, 1:1.5) was measured by the space-charge-limited current (SCLC) method which is based on field-dependent Poole-Frenkel Law¹⁷ with a device structure of ITO/PEDOT:PSS/polymer:PC₇₀BM/Au, and a hole mobility of 8.96×10^{-4} cm² V⁻¹ s⁻¹ was recorded. The atomic force microscope (AFM) images of the active layers before and after thermal annealing treatments are shown in the ESI.† It can be seen that the blend film (w/w, 1:1.5) became smoother after annealing.

The external quantum efficiency (EQE) curves of the devices before/after annealing treatment (D/A ratio, 1:1.5) are shown in Fig. 3. In comparison with the device before annealing, EQE of the annealed device increased obviously. The variation between the calculated J_{sc} from the EQE curve and the J_{sc} from J - V measurement is within 8%. Furthermore, based on the standard spectrum of the solar irradiation (AM 1.5G) and the response range of the device, we tried to calculate the theoretical maximum of the current density, and we found that a J_{sc} of 17 mA cm⁻² should be achievable if the EQE of the device could reach 70%.

In conclusion, a furan-based conjugated component, BDF, was firstly used as a building block, and a new polymer, named PBDFDTBT, was designed, synthesized and applied in PSCs. The band gap, HOMO and LUMO levels of this new polymer are -1.6 eV, -5.10 eV and -3.24 eV, respectively. In comparison with the other four representative polymers

with commonly used building blocks, like fluorene, carbazole, dithieno[3,2-*b*:2',3'-*d*]silole and BDT, this new polymer exhibits smaller band gap and moderate HOMO and LUMO levels. A PCE of 5% has been achieved by using this polymer as electron donor in a PSC device. Considering the broad response range and the high V_{oc} of the PBDFDTBT-based PSC device, PBDFDTBT should be a potential photovoltaic material. More importantly, these results indicate that BDF would be a promising building block for highly efficient and biodegradable photovoltaic materials.

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