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Synthesis and Photovoltaic Properties of Low Band Gap Polymers Containing Benzo[1,2-*b*:4,5-*c*′]dithiophene-4,8-dione

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S *Supporting Information*

As the energy crisis is becoming a serious problem all over the world, cheap production of electricity from solar energy has attracted more and more attention. Among all the photovoltaic devices, polymer bulk heterojunction solar cells (PSCs) have shown many advantages, such as low fabrication cost, excellent mechanical flexibility and lightweight. The active layer of PSCs is based on the blend of a conjugated polymer as the electron donor and a fullerene derivative as the electron acceptor.[1] Up to now, poly(3-hexylthiophene) (P3HT) is one of the best commercialized donor materials. P3HT/PC$_{61}$BM-based PSCs have achieved power conversion efficiencies (PCE) up to ∼4−5%.[2] However, P3HT only absorbs part of the solar emission (300−600 nm) and its high-lying HOMO energy level (−4.76 eV)[3] limits the open circuit voltage (V_{oc}) of the solar cells. Therefore, design and synthesis of new conjugated polymers with deep HOMO levels for high V_{oc} and low bandgaps for broad absorption, as well as high mobilities and good solubilities, are essential for obtaining high performance PSCs.[4]

A recent strategy to satisfy these requirements above is to design conjugated copolymer containing alternating donor and acceptor units in the polymer backbone. Yu et al. reported the D−A polymers based on poly(benzo-[1,2-*b*:4,5-*b*′]-dithiophene)-*alt*-(thieno[3,4-*b*]thiophene) (PBDTTT) with efficiency up to 7.73%.[5] However, the synthesis of the monomer thieno[3,4-*b*]thiophene in PBDTTT is very tedious and with low yield. Li et al. reported a new strong electron-withdrawing unit naphtho[2,3-*c*]thiophene-4,9-dione (NTDO), which was synthesized in short route and with high yield. The copolymer with NTDO as acceptor unit has relatively lower HOMO (−5.52 eV) and gives a high PCE of 5.21%.[6] Inspired by Li's work, we designed a new acceptor unit benzo[1,2-*b*:4,5-*c*′]-dithiophene-4,8-dione (BDTD) by replacing the benzene ring of NTDO with thiophene ring because the fused thiophene ring systems are well-known to stabilize the quinoidal structure and can efficiently reduce the bandgap (Scheme 1).[7] Furthermore, BDTD unit possesses the similar structure as thieno[3,4-*b*]thiophene but more electron deficient. In this work, we synthesized two low-bandgap polymers **P1** and **P2** by copolymerization of BDTD with benzo-[1,2-*b*:4,5-*b*′]dithiophene (BDT) and dithieno[3,2-*b*:2′,3′-*d*]silole (DTS), respectively. Both **P1** and **P2** exhibit low-lying HOMO and good light-absorption properties. We further demonstrated that **P1** and **P2** are good donor materials in PSCs. Solar cells based on **P2**/PC$_{61}$BM blend afforded a PCE of 4.33% with an impressively high V_{oc}, 0.93 V.

The synthetic routes for monomers and polymers were illustrated in Scheme 1. Thiophene-3,4-dicarboxylic was brominated by bromine in acetic acid to give 2,5-dibromothiophene-3,4-dicarboxylic acid in 50% yield. Treating 2,5-dibromothiophene-3,4-dicarboxylic acid with oxalyl chloride afforded the intermediate 2,5-dibromothiophene-3,4-dicarbonyl dichloride. The 2,5-dibromothiophene-3,4-dicarbonyl dichloride was then treated with 2-hexylthiophene in presence of $AlCl_3$ to obtain monomer BDTD in 12% yield. Monomers BDT and DTS were prepared according to the literature methods.[8,9] **P1** and **P2** were both synthesized by the Stille reaction using $Pd(PPh_3)_4$ as the catalyst. The crude products were precipitated in methanol. The impurities in the products were successively removed by methanol and hexane in a Soxhlet extractor 24 h each. Finally, the polymers were extracted with chloroform and reprecipitated in methanol and dried under vacuum. **P1** and **P2** have good solubilities in common organic solvents such as chloroform and toluene. The molecular weights of **P1** and **P2** were determined by gel permeation chromatography (GPC) against polystyrene standards in THF eluent, and the data are listed in Table 1.

Thermogravimetric analyses of **P1** and **P2** are shown in Figure 1. The temperature of 5% weight-loss was selected as the onset point of decomposition (T_d). The T_d values of **P1** and **P2** are 329 and 346 °C, respectively, indicating that they are thermally stable for organic photovoltaic applications.

The absorption spectra of the polymers in chloroform and films are shown in Figure 2. The optical properties of **P1** and **P2** are summarized in Table 2. Both polymers show strong absorption in the range of 500−650 nm. The absorption maxima of the polymers in solution are located at 551 and 586 nm for **P1** and **P2**, respectively. **P2** shows stronger absorption at the long wavelength region than **P1**, while **P1** exhibits a broader spectrum, especially in the 400−500 nm region. In solid films, both **P1** and **P2** show red shifts at the absorption maxima (576 nm for **P1** and 626 nm for **P2**), indicating the enhanced interchain $\pi-\pi$ stacking in the solid state. The optical band gaps were calculated to be 1.78 eV for **P1** and 1.63 eV for **P2**.

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Scheme 1. Synthesis of P1 and P2

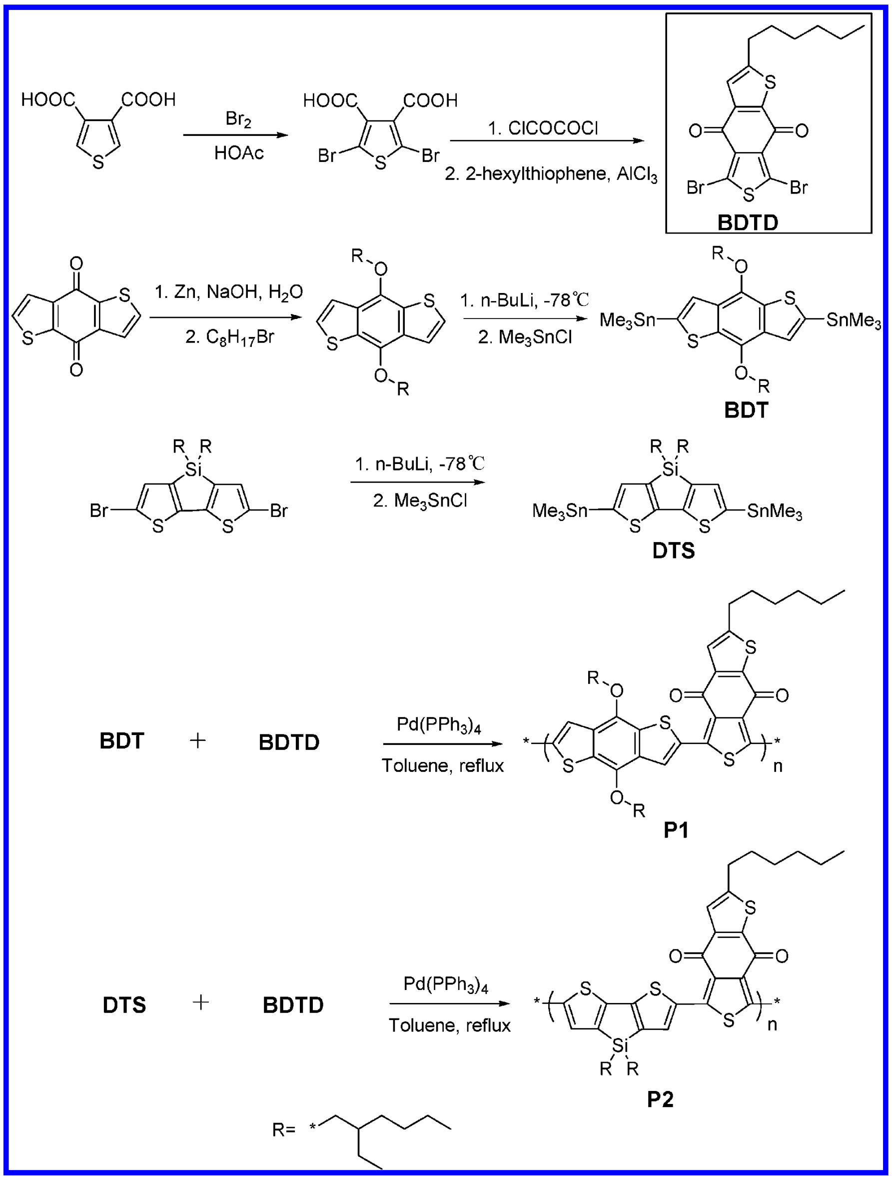

Table 1. Molecular Weights and Thermal Properties of Polymers

polymers	M_n[a]	M_w[a]	PDI[a]	T_d (°C)[b]
P1	11 490	39 382	3.43	329
P2	7037	13 384	1.90	346

[a] M_n, M_w, and PDI were determined by GPC using polystyrene standards with THF as eluent. [b] The temperature at 5% weight-loss under nitrogen.

The difference of **P1** and **P2** in optical properties reflects the different electron donating strength of their donor units (BDT and DTS).

The electrochemical properties of polymers were investigated by cyclic voltammetry (CV) method. Figure 3 shows the cyclic voltammograms of **P1** and **P2** films on glassy-carbon electrode in CH_3CN solution containing 0.1 mol/L Bu_4NPF_6. The CV data are summarized in Table 3. The onset oxidation potentials (E_{ox}) of **P1** and **P2** are 0.69 and 0.53 V, respectively, while the onset reduction potentials (E_{red}) of **P1** and **P2** are −1.27 and −1.33 V, respectively. The energy level of polymers were calculated according to the following equation: HOMO or LUMO = $-(E_{ox}$ or $E_{red} + 4.8)$ eV. As a result, the HOMO energy levels of **P1** and **P2** are −5.49 and −5.33 eV, respectively, which are significantly deeper than that of P3HT (−4.76 eV) and close to ideal HOMO energy level (−5.4 eV).[10] Deep HOMO should render these polymers good stability against oxidization. The LUMO energy levels of **P1** and **P2** are −3.53 and −3.47 eV, respectively, and the electrochemical bandgaps of **P1** and **P2** are 1.96 and 1.86 eV, respectively. The electrochemical bandgaps of the polymers are ~0.2 eV higher than the optical bandgaps, which might result from the interface barrier between the polymer film and the electrode surface.[11]

Solar cells with a configuration of ITO/PEDOT:PSS/polymer:$PC_{61}BM$/Ca/Al were fabricated and tested under simulated AM1.5G irradiation (86 mW/cm^2). The weight ratios of polymer to $PC_{61}BM$ for **P1** and **P2** cells were optimized from 1:1 to 1:2. *J*–*V* curves for **P1** and **P2** are shown in Figure 4. The corresponding open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), fill factor (FF), and power conversion efficiency (PCE) of the cells are listed in Table 4.

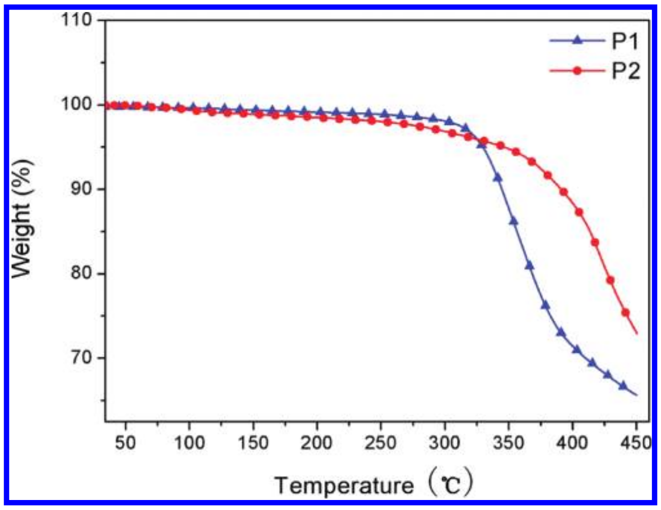

Figure 1. TGA plots of **P1** and **P2** with a heating rate of 10 °C/min under nitrogen.

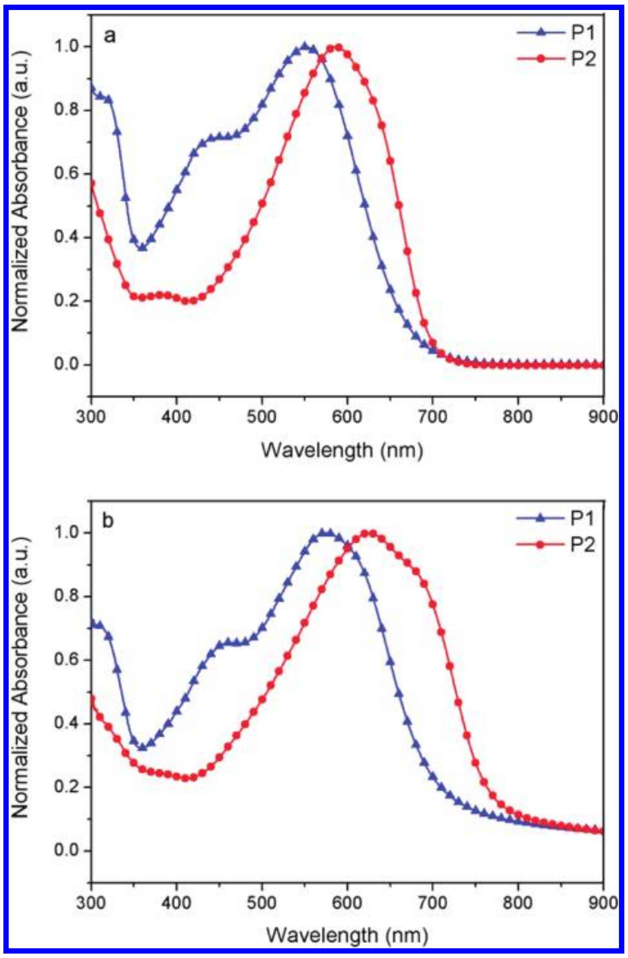

Figure 2. Normalized UV−vis absorption spectra of **P1** and **P2**: (a) in chloroform; (b) as thin film.

Table 2. Optical Properties of P1 and P2

	λ_{max} (nm)		λ_{onset} (nm)	
	solution	film	film	E_g^{opt} (eV)^a
P1	551	576	697	1.78
P2	586	626	762	1.63

^{a}Calculated from the absorption band edge of the films, $E_g = 1240/\lambda_{onset}$.

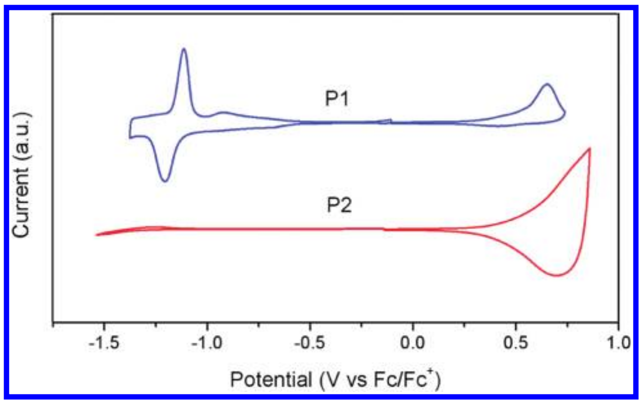

Figure 3. Cyclic voltammograms of **P1** and **P2** films in CH_3CN containing 0.1 mol/L Bu_4NPF_6.

Table 3. Electrochemical Properties of P1 and P2

	E_{ox}^{on} (V)	E_{red}^{on} (V)	HOMO (eV)	LUMO (eV)	E_g^{ec} (eV)^a
P1	0.69	−1.27	−5.49	−3.53	1.96
P2	0.53	−1.33	−5.33	−3.47	1.86

^{a}Calculated from $E_g = e(E_{ox}^{on} - E_{red}^{on})$.

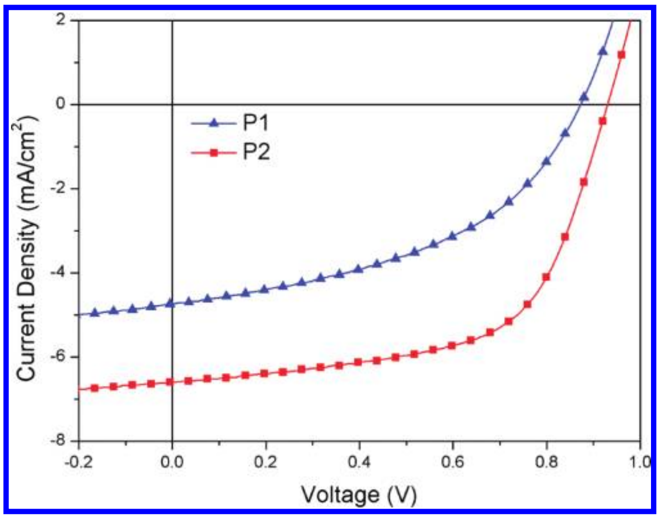

Figure 4. *J*−*V* curves for the polymer solar cells based on **P1** and **P2** under the illumination of AM1.5G, 86 mW/cm^2.

Cells based on **P1**/PC$_{61}$BM and **P2**/PC$_{61}$BM both show high V_{oc} (~0.9 V), due to the quite low HOMO levels of **P1** and **P2**. The optimized weight ratios (polymer/PC$_{61}$BM) for **P1** and **P2** both are 1:1.5. As shown in Table 4, **P2** exhibits the best PCE of 4.33% with a V_{oc} of 0.93 V, a J_{sc} of 6.66 mA/cm^2 and a FF of 60% in comparison with the best PCE of 2.18% for **P1** with a V_{oc} of 0.87 V, a J_{sc} of 4.75 mA/cm^2 and a FF of 45%. The higher performance of **P2** results from its higher J_{sc} and FF, which is probably due to its better absorption at the long wavelength region. The good hole mobility of silole moiety may account for the high J_{sc}.[12] The AFM images (tapping mode) (see Figure S1, Supporting Information) show the morphology change for the polymer/PC$_{61}$BM composite films. The rms roughness for **P1**/PC$_{61}$BM film decreased from 6.94 to 0.47 nm,

Table 4. Photovoltaic Properties of the Solar Cells Based on P1 and P2

polymer	polymer:$PC_{61}BM$	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)
P1	1:1	0.91	4.03	42	1.79
	1:1.5	0.87	4.75	45	2.18
	1:2	0.89	5.23	37	1.99
P2	1:1	0.95	6.64	55	4.02
	1:1.5	0.93	6.66	60	4.33
	1:2	0.92	6.56	59	4.04

while for **P2**/$PC_{61}BM$ film from 3.85 to 2.48 nm, indicating the film morphology for **P1**/$PC_{61}BM$ film is more sensitive to thermal treatment. The molecular weight difference and structure difference could be responsible for this.

Figure 5 shows external quantum efficiency (EQE) curves for the solar cells based on **P1** and **P2**. **P1** device shows two maxima at 400 and 560 nm, respectively, and **P2** device shows two maxima at 380 and 580 nm, respectively. **P2** device exhibits higher EQE than that of **P1**, which is due to stronger sunlight absorption of **P2** film (see Figure 2b).

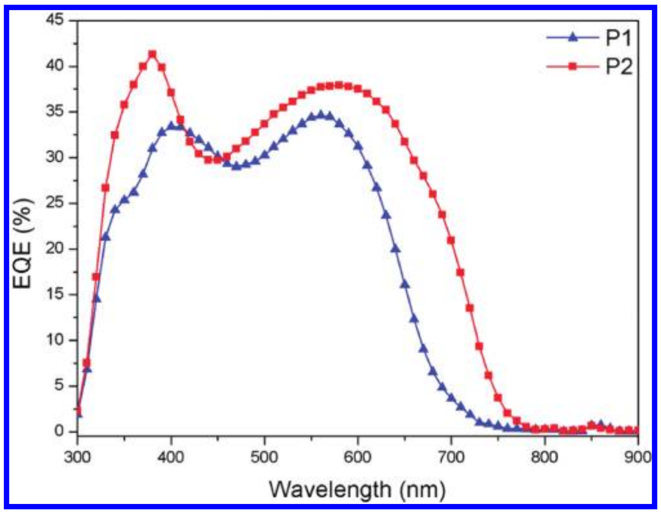

Figure 5. EQE curves for the devices based on **P1** and **P2**.

In summary, we have synthesized two new low bandgap D−A copolymers with benzo[1,2-*b*:4,5-*c*′]dithiophene-4,8-dione as the acceptor unit. The polymers possess good light-absorption properties, thermal stability, and deep HOMO levels (−5.49 eV and −5.33 eV) due to the strong electron-withdrawing effect of BDTD unit. Solar cells based on these polymers give good PCEs and high V_{oc} indicating that BDTD is a potential building block for conjugated polymer donors. Further modification of the chemical structure of the polymer to redshift the light-absorption is currently underway.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthetic procedures, NMR spectra, and AFM images. This material is available free of charge via the Internet at http://pubs.acs.org/.

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Notes

The authors declare no competing financial interest.

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