Benzo[1,2-b:4,5-b′]dithiophene-dioxopyrrolothiophen copolymers for high performance solar cells†

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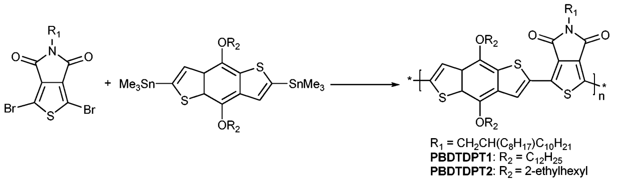
New donor/acceptor polymers PBDTDPT1 and PBDTDPT2 with alternating benzodithiophene and *N*-alkylated dioxopyrrolothiophene were synthesized. The new polymers had deep HOMO levels of −5.42 and −5.44 eV for PBDTDPT1 and PBDTDPT2, respectively. A PBDTDPT2 based BHJ solar cell device achieved a PCE of 4.79% and V_{oc} of 0.91 V.

Research on polymeric solar cells (PSCs) has been intensified in recent years because PSCs have a potential to generate electricity from sunlight at low cost.[1] Bulk heterojunction (BHJ), based on blending of electron-donating conjugated polymers and high-electron-affinity fullerene derivatives such as PCBM, has become the most successful device structure for organic photovoltaics (OPVs).[2] In the past few years, encouraging progress has been made both in new polymer materials[3] and methods to optimize the morphology of BHJ composites.[4] Although the power conversion efficiency (PCE) of OPVs has exceeded 6%, substantial improvements on efficiency and device lifetime are needed for possible commercialization.[5] Power conversion efficiency is the product of the short-circuit current density (J_{sc}), open circuit voltage (V_{oc}) and fill factor (FF) divided by the incoming light power density. Many examples of low band gap polymers, absorbing the visible and near-IR part of the solar spectrum, have been developed for maximizing solar photon harvest, thereby increasing J_{sc} and PCE. However, the efficiency of solar cells based on those low band gap polymers is often limited by the low V_{oc}.[6] The V_{oc} of BHJ device with PCBM as acceptor is determined by the HOMO level of the donor and the LUMO level of the PCBM molecule. Systematic studies on matching the energy levels of donor polymer with those of PCBM have been carried out.[3f,6,7] Reducing the band gap of polymers without sacrificing efficient charge separation and raising the HOMO level of the donor polymer will result in high J_{sc} and V_{oc}, thereby maximizing PCE.

Recently, low band gap copolymers based on benzo[1,2-b:4,5-b′]dithiophene (**BDT**) and thieno[3,4-b]thiophene (**TT**) have exhibited very promising performance in PSC applications.[9] As reported, gradually introducing electron withdrawing groups on the thieno[3,4-b]thiophene repeating units reduced the HOMO level of **PBDTTT** copolymer while keeping the band gap unchanged. The devices showed an increased open circuit voltage (0.79 eV) and high PCE (6.77%).[8] However, synthesis of copolymer **PBDTTT** is nontrivial because thieno[3,4-b]thiophene monomers are quite tedious to make. We seek to develop new low band gap conjugated polymers with facile monomers and to achieve a lower HOMO level thereby increasing the open circuit voltage (V_{oc}) and PCE. Here we report efficient synthesis of new conjugated copolymers **PBDTDPT1** and **PBDTDPT2** (Scheme 1), based on alternating benzo[1,2-b:4,5-b′]dithiophene (**BDT**) and *N*-alkylated dioxopyrrolothiophene (**DPT**) monomers. PSC device studies on copolymer **PBDTDPT2** showed a high open circuit voltage of 0.91 V and power conversion efficiency of 4.79%.

Dioxopyrrolothiophene (**DPT**) monomer was synthesized before by us.[10] The monomer is electron deficient due to the imide group and it maintains a symmetrical structure after attachment of a solubilizing side chain.[11] Copolymers **PBDTDPT1** and **PBDTDPT2** were synthesized by Stille coupling reaction of 1,3-dibromo-5-alkyl-thieno[3,4-c]pyrrole-4,6-dione with a bis(stannyl) derivative of benzo[1,2-b:4,5-b]-dithiophene (Scheme 1). Both polymers showed good solubility in common organic solvents such as chloroform, THF and chlorobenzene. The number-average molecular weights were 43.5 kDa and 91.1 kDa, and the polydispersity indexes were 3.62 and 6.59 for **PBDTDPT1** and **PBDTDPT2**, respectively.

Differential scanning calorimetry (DSC) analysis showed that neither polymer displayed noticeable glass transition. Absorption spectra of both copolymers in chloroform solutions and as thin films on glass slides were shown in Fig. 1. Like other benzo[1,2-b:4,5-b′]dithiophene (**BDT**) containing polymers, a distinct shoulder peak next to the absorption maximum appeared in both solution and solid state spectra.[9] The absorption maxima of the solid films were red-shifted about 20 and 8 nm for **PBDTDPT1** and **PBDTDPT2**, respectively, compared to those of the solutions (Table S1 in ESI†). The optical band gaps were calculated from the absorption edges of the film absorption spectra.



Scheme 1 The synthesis and structure of **PBDTDPT1** and **PBDTDPT2**. Reaction conditions: $Pd_2(dba)_3$, $AsPh_3$, toluene, 115 °C, 24 h.

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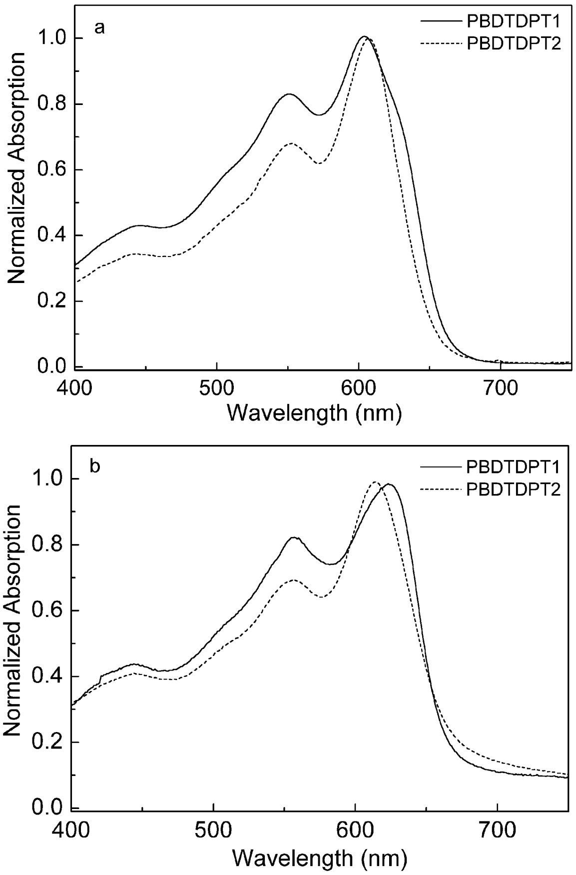

Fig. 1 Normalized UV-vis spectra of **PBDTDPT1** and **PBDTDPT2** (a) in chloroform solution, (b) as thin films.

PBDTDPT1 and **PBDTDPT2** had equivalent optical band gaps of 1.84 eV. Cyclic voltammetry (CV) was carried out on these two polymers to determine their HOMO and LUMO positions. The HOMO energy levels of **PBDTDPT1** and **PBDTDPT2** were calculated to be −5.42 eV and −5.44 eV from onset oxidation potential by using ferrocence as an internal standard (which had an absolute energy level of −4.8 eV).[12] The LUMO levels of **PBDTDPT1** and **PBDTDPT2** were −3.60 and −3.58 eV which were calculated from the optical band gap and HOMO energy levels of the polymers. Two polymers exhibited similar HOMO and LUMO energy levels due to the same polymer main chain structure.

The photovoltaic properties of polymers **PBDTDPT1** and **PBDTDPT2** were evaluated in BHJ solar cell devices (Table 1). The polymers were used as donor and $PC_{71}BM$ was used as electron acceptor. The device structures were ITO/PEDOT:PSS/polymer:PCBM (1 : 2, w/w)/LiF/Al. Solar cells were characterized under AM 1.5G illumination at 100 mW cm^{-2} from a solar simulator. Detailed device fabrication and characterization were described in the ESI.† The thickness of thin films and weight ratio of polymer to PCBM were adjusted to optimize the PV performance. The high open circuit voltage (V_{oc}) of 0.97 V and 0.91 V was obtained for **PBDTDPT1** and **PBDTDPT2**, respectively. These results demonstrated that the dioxopyrrolothiophene (**DPT**) units have a critical role in lowering the HOMO level of the polymers. The optimized **PBDTDPT1** device had a thickness of 85 nm, a J_{sc} value of 3.25 mA cm^{-2}, a fill factor of 0.62, and a V_{oc} value of 0.97 V to give a power conversion efficiency (PCE) of 1.95%. The optimized **PBDTDPT2** device had a thickness of 100 nm, a J_{sc} value of 2.85 mA cm^{-2}, a fill factor of 0.57, and a V_{oc} value of 0.91 V to yield a PCE of 1.49%. The structure difference between polymer **PBDTDPT1** and **PBDTDPT2** is on the side chain of the benzo[1,2-b:4,5-b′]-dithiophene (**BDT**) units. **PBDTDPT1** had a straight dodecyl chain and **PBDTDPT2** had a branched ethylhexyl chain. The different side chains might affect solubility, degree of polymerization, and packing of polymer chains in the solid state, and thereby result in the difference of the PSC performance.

Table 1 Device performance of photovoltaic cells based on new polymers

	PBDTDPT1:$PC_{71}BM$		**PBDTDPT2**:$PC_{71}BM$	
	No DIO	2% DIO	No DIO	2% DIO
J_{sc} (mA cm^{-2})	3.25	6.58	2.85	10.34
V_{oc}/V	0.97	0.93	0.91	0.91
FF	0.62	0.56	0.57	0.51
PCE (%)	1.95	3.42	1.49	4.79

Control over the morphology is crucial for the performance of bulk heterojunction solar cells. Several techniques can be used for morphology optimization.[4] Addition of a small amount of diiodooctane (DIO) (2% by volume) to the blend before spin-coating significantly improved the efficiency of the resulting organic solar cells. The current density-voltage (*J-V*) curves of the devices based on the polymers:$PC_{71}BM$ blend with additive (DIO, 2% by volume) were presented in Fig. 2a. With addition of processing additive, the **PBDTDPT2** based device had an average PCE of 4.79%, a V_{oc} of 0.91 V, a J_{sc} of 10.34 mA cm^{-2}, and a FF of 0.51. The enhanced J_{sc} and PCE value were observed in both **PBDTDPT1** and **PBDTDPT2** based devices with processing additive. This significant increasing of performance was attributed to the improvement of charge separation in BHJ. The external quantum efficiencies (EQE) of devices with additive were shown in Fig. 2b. **PBDTDPT2** showed very efficient photo-conversion efficiency in the range 445–562 nm, with the EQE values over 50%. The J_{sc} and PCE values can be calculated by integrating the EQE data with an AM 1.5G reference spectrum. For the **PBDTDPT2** based device with processing additive system, which has the highest PCE value in this work, the calculated J_{sc} was 8.89 mA cm^{-2} and the calculated PCE was 4.12% using the V_{oc} and FF values obtained from *J-V* measurements. The J_{sc} and PCE obtained from *J-V* measurements were 10.34 mA cm^{-2} and 4.79%. The relatively large difference between those values can be attributed to the starting point of integration of the EQE curve. The EQE curve was integrated from 350 nm to 800 nm. As a result, the photocurrent generated below 350 nm was not included in the calculated J_{sc} value.

The effect of additive on morphology was studied by atomic force microscopy (AFM) and transmission electron microscopy (TEM). AFM topography and phase image were measured on film cast from **PBDTDPT2**:$PC_{71}BM$ blend with or without processing additive. The film processed with DIO

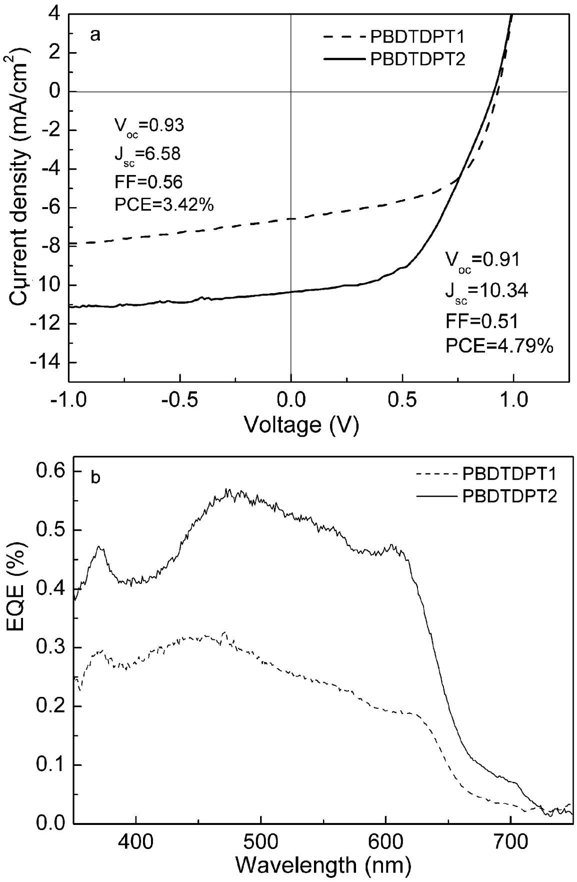

Fig. 2 (a) Current–voltage curves of **PBDTDPT1**:PC$_{71}$BM and **PBDTDPT2**:PC$_{71}$BM solar cells under AM 1.5 G irradiation. (b) External quantum efficiency of **PBDTDPT1**:PC$_{71}$BM and **PBDTDPT2**:PC$_{71}$BM.

exhibited fine domains compared to the film processed without DIO. TEM image showed the morphology of film cast from **PBDTDPT2**:PC$_{71}$BM blend. Nanofiber-like domains were observed over the entire area in the sample processed with additive (Fig S12, S13 in ESI†). Film processed with addition of DIO additive showed better interconnected regions than film processed without using additive.

In conclusion, we have successfully synthesized two new low band gap polymers. The new polymers had a low HOMO level and resulted in higher open circuit voltages in PCS devices based on these polymers. The morphologies of polymer:PC$_{71}$BM composite can be effectively optimized by addition of diiodooctane. The polymer **PBDTDPT2** based device achieved a PCE of 4.79% and V_{oc} of 0.91 V. The open circuit voltage is very high compared to other related low band gap polymers, making this new polymer a good candidate for OPV applications.

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