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Letter

Novel N-heteroacene small molecules as electron donors for organic bulk heterojunction photovoltaics

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ABSTRACT

Two N-heteroacene small molecules, P2BT and P2B2 T, with 2,1,3-benzodiathiazole end-capped N-heteroacene unit as the central building block have been designed and synthesized for bulk-heterojunction solar cells. Single-junction devices based on P2B2 T:$PC_{71}BM$ have achieved an impressive power conversion efficiency of 7.16% without any special treatment, which is the record efficiency among the N-heteroacene-based photovoltaics.

1. Introduction

Solution-processed small-molecule (SM) solar cells based on bulk heterojunction (BHJ) structure composed of SM donors and fullerene derivative acceptors have attracted intensive research attention over the last few years owing to their light weight, mechanical flexibility, large area and low-cost device fabrication [1–8]. To date, considerable research effort has been devoted to develop high-performance BHJ SM solar cells, and power conversion efficiencies (PCEs) of over 10% have been realized mainly due to remarkable development of novel p-type conjugated small molecules [9–12]. However, these results are still far away from the theoretical efficiency (20–24%) [6,13], clearly indicating that there is still much room for improving the photovoltaic performance of BHJ solar cells by designing and synthesizing novel SM donors.

N-heteroacenes are derivatives of acenes in which one or more CH groups are substituted by electronegative nitrogen atoms [14–17]. Theoretically, they have a great potential of application as electron donors in BHJ solar cells, owing to their superior hole transporting mobility, good stability, and tunable optical and electrochemical properties [18,19], but the related research is still rare. Recently, we have reported a series of all-thiophene-substituted N-heteroacene small molecules [20]. The introduction of thiophene units endowed N-heteroacenes with high solubility and thermostability, favorable light absorption and hole mobility, low-lying highest occupied molecular orbital (HOMO) levels, as well as suitable intermolecular packing. As a result, PCEs of more than 5% have been obtained by utilizing them as electron donors in BHJ SM solar cells with $PC_{71}BM$ as electron acceptor. The findings demonstrate that our strategy is effective, and it provides an opportunity to realize the high-efficiency application of N-heteroacenes in solar cells. On the other hand, though with high open-circuit voltage (V_{oc}) (greater than 1.00 V) and relatively good fill factor (FF) (about 0.55), the devices based on our previously synthesized N-heteroacene donors exhibited relatively low short-circuit current (J_{sc}) (8–10 mA cm^{-2}). As is well recognized, photoelectric properties of organic materials can be finely tuned through judicious molecular structure modification [21,22]. It is thus expected that better photovoltaic performance could be achieved if careful molecule design can be carried out by using more optimized building units.

As reported before, due to the highly rigid molecular structure and strong electron-withdrawing ability, end capping with 2,1,3-benzodiathiazole (BT) unit could further improve the overall planarity, reduce the bandgap and widen the light absorption region, and thus enhance the J_{sc} values of the resultant devices [23,24]. Therefore, if taking advantages of these merits and our recent results together, the new BT end-capped N-heteroacene small molecules could be expected to have a higher J_{sc} value, and also combine the good V_{oc} and FF from the previous materials. Based on this, two small molecules, P2BT and P2B2 T, with a BT end-capped N-heteroacene unit as the central building block and with 2-octylthiophene and 5-octyl-2,2′-bithiophene as different

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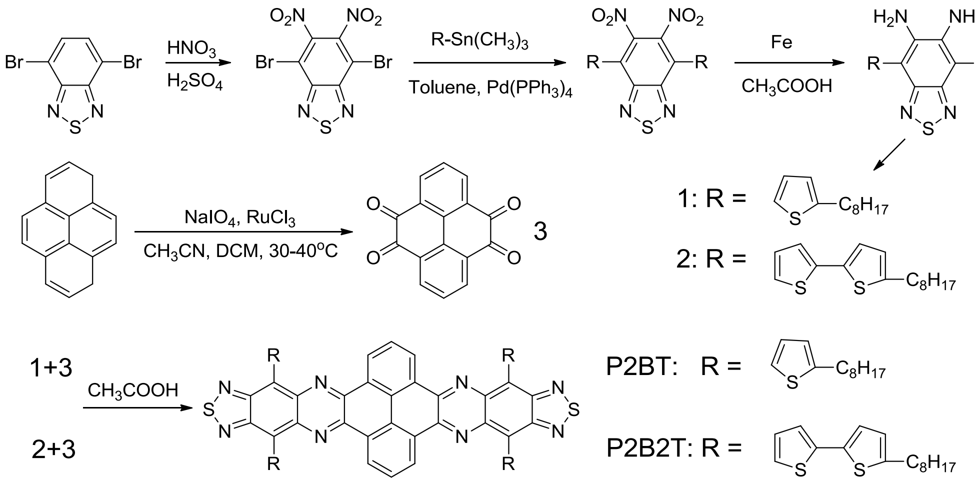

Scheme 1. Synthesis of P2BT and P2B2 T.

substituents have been designed and synthesized, as shown in Scheme 1. Their thermal, optical, electrochemical and photovoltaic properties have been carefully characterized and compared. As expected, these materials exhibited broader absorption spectra, and a higher PCE of 7.16% was achieved based on P2B2 T and $PC_{71}BM$, with significantly enhanced J_{sc} of 12.89 mA cm^{-2}, comparable V_{oc} of 1.01 V and FF of 0.55.

2. Results and discussion

2.1. Synthesis

The synthesis of P2BT and P2B2 T are shown in Scheme 1. The detailed synthetic procedures and characterization data are provided in the Supporting Information (SI). Both the target materials can be dissolved in common solvents, such as chloroform, chlorobenzene and *o*-dichlorobenzene, which guaranteed their applications in solution-processed solar cells. The results of thermogravimetric analysis suggest that the small molecules have excellent thermostability with high decomposition temperatures (T_d, 5% weight loss) above 400 °C, as shown in Fig. S1 (SI). Moreover, no obvious endothermic or exothermic peaks were observed in the differential scanning calorimetry thermogram of P2BT and P2B2 T (Fig. S2).

2.2. Optical and electrochemical properties

The absorption spectra of the new designed donors in dichloromethane solution and in thin film are shown in Fig. 1. In dilute dichloromethane, P2BT shows two feature absorption bands, ranging from 350 to 460 nm and 460–670 nm, which can be assigned to the π-π* transition and the intramolecular charge transfer, respectively. After prolonging the thiophene chains, the P2B2 T solution exhibits a similar absorption spectrum with a bathochromic absorption maximum at 580 nm. Compared with their absorptions in solutions, the peak values of P2BT and P2B2 T films are red-shifted to 588 and 604 nm by 30 and 24 nm, respectively. Furthermore, no shoulder peaks appear at the longer wavelength, indicating the relatively weak intermolecular packing in their solid state [25,26], which could be attributed to the twisted molecular structure induced by the thiophene substituents [20], as confirmed by the density functional theory calculations (Fig. S3). The optical band gaps determined from the absorption onset of the films are 1.86 and 1.78 eV, respectively.

Cyclic voltammetry was used to investigate the electrochemical properties of the small molecules, as shown in Table 1. The HOMO and lowest unoccupied molecular orbital (LUMO) energy levels of P2BT and P2B2 T, calculated from the onset oxidation and reduction potential are −5.44 and −3.59 eV, −5.39 and −3.58 eV, respectively. Their electrochemical band gaps are estimated to be 1.85 and 1.81 eV, respectively, which is consistent with the optical band gaps. The HOMO and LUMO levels of the small molecules obtained from DFT calculations are also listed in Table 1, and the change in the trend of the energy levels is consistent with that of the energy levels obtained from CV measurements. Notably, when compared with our previously reported N-heteroacene small molecules [20], the introduction of the BT unit could effectively lower the band gap and broaden the light absorption spectrum as expected, indicating that they would absorb and harvest

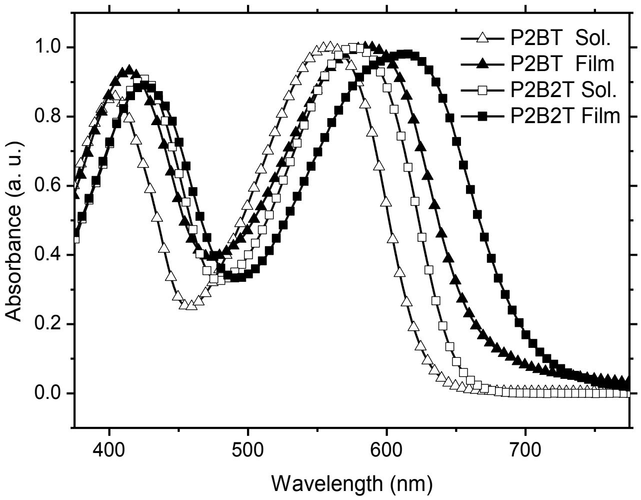

Fig. 1. Absorption spectra in dichloromethane solution and thin film for P2BT and P2B2 T.

Table 1
Optical and redox parameters of P2BT and P2B2 T.

	λ_{max}[a] (nm)	λ_{max}[b] (nm)	HOMO[c] (eV)	LUMO[c] (eV)	HOMO[d] (eV)	LUMO[d] (eV)	E_g[e] (eV)	E_g[f] (eV)
P2BT	558	588	−5.44	−3.59	−5.91	−3.80	1.85	1.86
P2B2 T	580	604	−5.39	−3.58	−5.83	−3.78	1.81	1.78

[a] The absorption maximum in dichloromethane.
[b] The absorption maximum in thin film.
[c] From the onset of the first reduction or oxidation waves in CV.
[d] From the DFT calculation.
[e] Band gap from CV (E_{LUMO}-E_{HOMO}).
[f] Optical energy gap determined from the onset position of the absorption band (1240/λ_{onset}).