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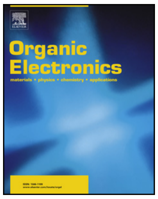

Influence of side chains on low optical bandgap copolymers based on 2,1,3-benzoxadiazole for polymer solar cells

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ABSTRACT

Two copolymers based on 2,1,3-benzoxadiazole (BO) as the acceptor unit and quaterthiophene as the donor unit, which possess different steric hindrance in the backbone, were designed and synthesized. The backbone conformations and electronic structures as well as the theoretically optimal structures of both copolymers were calculated. The influences of steric hindrance on photophysical and electrochemical properties of the polymers were investigated. With the steric hindrance of the polymers decreased, the optical bandgaps were decreased, and the HOMO levels upshifted while the LUMO levels downshifted. The weight ratio and annealing temperature on the performances of the polymer-based devices were evaluated in detail. The best device based on the polymer exhibited a moderate power conversion efficiency of 4.44%.

1. Introduction

In the past decade, polymer solar cells (PSCs) have been extensively studied due to their virtues of low cost, light weight, flexibility and facile solution processibility [1–4]. To date, the power conversion efficiencies (PCEs) of bulk-heterojunction (BHJ) PSCs based on a conjugated polymer as electron donor and a fullerene derivative as electron acceptor have surpassed 10% [5–10]. Recently, several new polymer donor materials, such as J71 [11,12] and PBDB-T [13,14] which have medium optical bandgaps and deep highest occupied molecular orbital (HOMO) levels, have been developed. The PCEs of single-junction solar cells based on these polymers have broken 12% by blending with nonfullerene acceptors [15], such as 3,9-bis(2-methylene-(3-(1,1-dicyanomethylene)-indanone))-5,5,11,11-tetrakis (4-hexylphenyl)-dithieno [2,3-*d*:2′,3′-*d*']-*s*-indaceno [1,2-*b*:5,6-*b*']dithiophene (ITIC) [16], further paving the way for commercialization. In fact, the breakthrough of the PCEs are originated from the synergistic effects of the progress of electron donors and electron acceptors. Therefore, the exploration of new polymer donors is still of great significance in view of further improving the PCE of PSCs.

Narrow-bandgap polymers have attracted much attention because of their absorption spectra in the visible and near-infrared region. Such polymer donors provide more complementary absorptions with fullerene and perylenediimide derivatives acceptors than wide-bandgap polymers [17]. Typically, narrow-bandgap polymers are generally obtained by the polymerization of electron-rich (D) and electron-deficient (A) units [18]. This strategy will increase electron delocalization along the polymer backbone through D-A hybridization, which lead to the decrease of the optical bandgap [19]. Additionally, the molecular energy levels of polymers can be modulated by choosing different donor and acceptor units. Due to its highly electron-withdrawing nature and good coplanarity, it is expected that 2,1,3-benzoxadiazole (BO) is a candidate of acceptor units in the synthesis of narrow-bandgap polymers for PSCs. The polymers based on BO can obtain low optical bandgaps, deep HOMO levels as well as high hole mobilities [20], which are beneficial to obtain high open circuit voltage (V_{oc}), short circuit current density (J_{sc}) and fill factor (FF), thus delivering high PCE [21]. These characteristics make it a potential unit in view of designing high-performance PSC materials [22–27]. For example, Bazan et al. reported a BO-based copolymer (SDTBO), which exhibited broad optical absorption spectra and favorable frontier molecular orbital levels, and obtained a PCE of above 5% in solar cell device [28]. Recently, Yan

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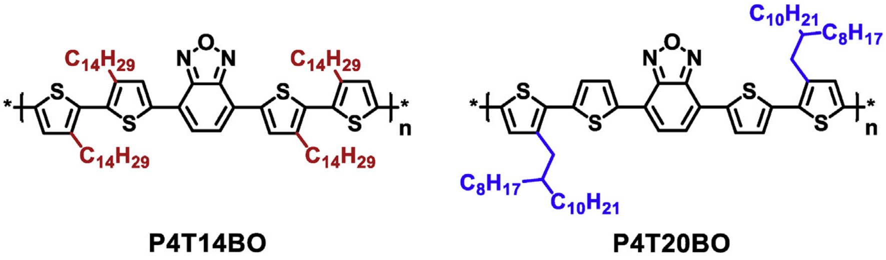


Fig. 1. Molecular structures of **P4T14BO** and **P4T20BO**.

el al. reported a copolymer (PffBX4T-2DT) with the fluorinated benzoxadiazole as the electron-withdrawing unit, demonstrating a high PCE of 9.4% [29]. However, BO has not been widely studied in solar energy materials compared with other famous electron-deficient units such as 2,1,3-benzothiadiazole (BT) [30] and diketopyrrolopyrrole (DPP) [31,32], which have attracted a tremendous attention. Thus, it is interesting to explore more BO-based polymers.

In our previous work, we have reported two polymers based on quaterthiophene, which achieved high organic field-effect transistor (OFET) and organic photovoltaic (OPV) performances [33]. Here, we combined the BO unit with quaterthiophene to construct a new polymer, namely, **P4T20BO** (Fig. 1). In addition, in order to investigate the influence of the position of alkyl chains on the photophysical properties of polymers [34], we synthesized **P4T14BO** as the control polymer, as shown in Fig. 1. The optical absorption and cyclic voltammetry revealed evident differences in the absorption and energy levels of the polymers with different alkyl chains. **P4T20BO** showed the best PCE of 4.44% in the PSC device with the conventional structure.

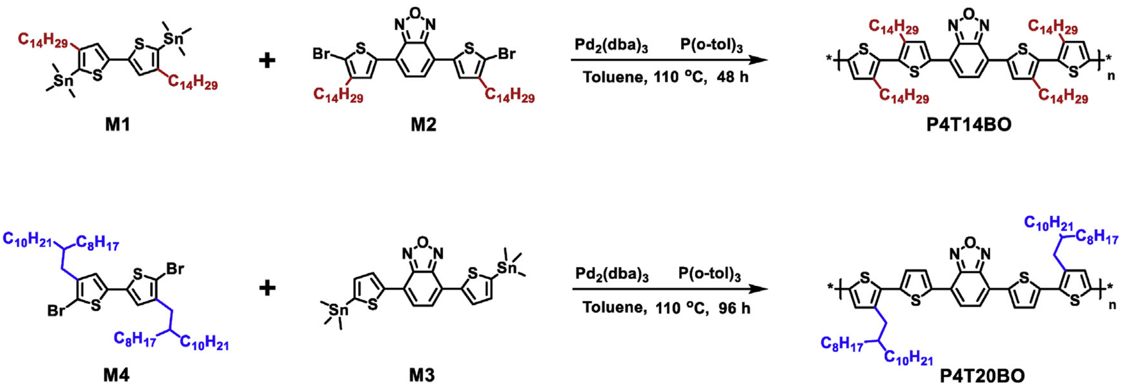
2. Results and discussion

2.1. Synthesis and characterization

The synthesis of the two polymers required four monomers **M1-M4**. **M1-M3** were synthesized according to the routes depicted in Scheme S1 and the detailed synthetic procedures are described in the Supporting Information. **M1** was prepared by stannylation of compound **3**, using a palladium-catalyzed homocoupling method reported in the literature [35]. **M2** was synthesized by a *Suzuki* coupling reaction between compound **5** and 2-(4-tetradecylthiophen-2-yl)-4′,4′,5′,5′-tetramethyl-1,3,2-dioxaborolane, followed by a stannylation reaction. **M3** was synthesized by the *Stille* coupling reaction between compound **5** and 2-(tributylstannyl)thiophene, followed by a stannylation reaction. **M4** was synthesized according to the literature methods [33]. The chemical structures of the monomers were verified by ^{1}H and ^{13}C NMR spectroscopies as well as mass spectrometry. The target polymers were synthesized by a *Stille* reaction (Scheme 1). The crude polymers were precipitated into methanol and filtered, followed by sequential Soxhlet extraction with acetone, hexane, and chloroform. The two polymers were collected from the chloroform extracts with moderate yields. The molecular weights of **P4T14BO** and **P4T20BO** were measured by gel permeation chromatography with tetrahydrofuran as an eluent and polystyrene as standards at room temperature. The number-average molecular weights (M_n) of **P4T14BO** and **P4T20BO** were 11.0 and 14.7 kDa, respectively. The polydispersity indices ($Đ$) of **P4T14BO** and **P4T20BO** were 1.37 and 1.74, respectively. The thermal properties of **P4T14BO** and **P4T20BO** were then characterized by thermogravimetric analysis (TGA) (Fig. S1). Under nitrogen atmosphere, the thermal decomposition temperature (T_d) of **P4T14BO** and **P4T20BO** are about 393 and 383 °C, respectively, indicating that they both have good thermal stability. The similar T_d of the two polymers indicated that different alkyl chains have little effect on the thermal properties of polymers.

2.2. Theoretical calculations

To investigate the backbone conformations and electronic structures of the polymers, the theoretically optimal structures of both **P4T14BO** and **P4T20BO** trimer were calculated at the B3LYP/6-31G* level. It was found that the distributions of the frontier orbitals of the two trimers are similar (Fig. S2). The results of the calculation reveal that the HOMOs of **P4T14BO**/**P4T20BO** are well delocalized along the backbones. The lowest unoccupied molecular orbital (LUMO) of **P4T14BO** is mainly localized on the BO moieities, suggesting that the planar conformation is interrupted by the alkyl chains, whereas the LUMO of **P4T20BO** is well delocalized along the backbone (Fig. S2). It is interesting to note that the **P4T14BO** trimer exhibits a rather twisted structure, while the **P4T20BO** trimer displays a more planar structure. The S–C–C–S dihedral angle of **P4T14BO** between the two thiophenes with alkyl chains head-to-tail is 53° (Fig. S3), which is the main origins of the twisted structure. The S–C–C–S dihedral angle of **P4T20BO** between the two thiophenes is 13° (Fig. S3). This result reveals a more coplanar structure of **P4T20BO**, which is likely beneficial for charge transport [36].



Scheme 1. Synthesis of polymers.