A New Dibenzoquinoxalineimide-Based Wide-Bandgap Polymer Donor for Polymer Solar Cells

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Abstract: The molecular design of a wide-bandgap polymer donor is critical to achieve high-performance organic photovoltaic devices. Herein, a new dibenzo-fused quinoxalineimide (BPQI) is successfully synthesized as an electron-deficient building block to construct donor–acceptor (D–A)-type polymers, namely P(BPQI-BDT) and P(BPQI-BDTT), using benzodithiophene and its derivative, which bears different side chains, as the copolymerization units. These two polymers are used as a donor, and the narrow bandgap (2,20-((2Z,20Z)-((12,13-bis(2-ethylhexyl)-3,9-diundecyl-12,13-dihydro-[1,2,5]thiadiazolo[3,4-e]thieno[2,3-c:4,5]thieno[2,3-b]indole-2,10 diyl)bis(methanylylidene))dimalononitrile) Y6 is used as an acceptor to fabricate bulk heterojunction polymer solar cell devices. Y6, as a non-fullerene receptor (NFA), has excellent electrochemical and optical properties, as well as a high efficiency of over 18%. The device, based on P(BPQI-BDTT):Y6, showed power conversion efficiencies (PCEs) of 6.31% with a $J_{SC}$ of 17.09 mA cm$^{-2}$, an open-circuit voltage ($V_{OC}$) of 0.82 V, and an FF of 44.78%. This study demonstrates that dibenzo-fused quinoxalineimide is a promising building block for developing wide-bandgap polymer donors.

Keywords: wide bandgap; donor–acceptor; imide; polymer solar cells

1. Introduction

Organic solar cells (OSCs) have attracted a lot of attention from both academia and industry due to their versatile advantages, such as their light weight, stretchability, and solution processability [1–6]. Following great efforts in recent years, power conversion efficiencies (PCEs) were achieved in the range of 18–19% [7–9]. The remarkable progress in organic photovoltaics (OPVs) mainly depends on the development of new polymer donors and non-fullerene small molecule electron acceptors (NFSMEAs) [10–15]. Recently, various narrow-bandgap NFSMEAs have been designed and have achieved excellent performances in OPVs when paired with wide-bandgap polymer donors. Most NFSMEAs show intense absorption in the visible and near-infrared (NIR) region (650–950 nm) for enhancing the light-harvesting ability [16–18]. Compared to NFSMEAs, the development of wide-bandgap (WBG) polymer donors is still limited; only a few donor–acceptor (D–A)-type WBG polymer donors have been reported, such as PM6 and D18 [19–21]. Therefore, it is imperative to design novel WBG polymer donors, which absorb the solar energy in the wavelength...
range of 300–650 nm to further improve the OPV’s performances [22–25]. Simultaneously, polymers can also be a carrier transport layer in perovskite solar cells [26,27]. Specially, the polymer donors of organic solar cells are often used as the hole transport layers in the perovskite solar cells due to their extraordinary p-type characteristics.

The ideal WBG polymer donors can be synthesized following the donor–acceptor strategy, where benzodithiophene (BDT) [28–30] and its derivatives are usually used as the donor units, and some electron-deficient moieties, such as quinoxaline [31–33], benzothiadiazole, benzotriazole, and imide, are used as the acceptor co-units [34–36]. In addition to these acceptor units, quinoxaline-based polymers have some characteristics that are useful for constructing WBG polymer donors: (1) quinoxaline derivatives possess strong electron-withdrawing properties that can adjust the energy levels; (2) the quinoxaline moiety can be easily modified by introducing sidechains and other functional groups to modulate the physical, chemical, and electronic properties; and (3) quinoxaline has a rigid and large planar structure that favors close \( \pi-\pi \) stacking. Li et al. [12], reported a low cost quinoxaline-based D–A-type polymer donor, PTQ10, that contains an alkoxy-substituted difluoro quinoxaline acceptor unit and thiophene donor unit on the backbone; when blended with IDIC, a PCE value of 12.7% was achieved for PSCs. Recently, Hou and coworkers reported a WBG polymer donor, PBQx-TCl, based on the thiophene-fused quinoxaline acceptor unit DTQx; the device based on PBQx-TCl:BTP-eC9 exhibited a PCE of 16.0% [14]. Therefore, quinoxaline is a promising building block for constructing high-performance WBG polymer donors in OPVs.

Herein, we design and synthesize a new dibenzo-fused quinoxalineimide (BPQI) building block, which has a rigid and planar structure. By using BDT as the copolymerization unit with BPQI, two new polymer donors, P(BPQI-BDT) and P(BPQI-BDTT), were synthesized. Both polymer donors possess wide bandgaps and deep highest occupied molecular orbital (HOMO) levels, due to the strong electron-withdrawing ability of the BPQI moiety, and have a good compatibility with the Y6 acceptor. As a result, the optimized P(BPQI-BDTT):Y6 device delivers a higher PCE of 6.31% with a \( J_{SC} \) of 17.09 mA cm\(^{-2} \), a \( V_{OC} \) of 0.82 V, and an FF of 44.78%, compared with the P(BPQI-BDT):Y6 system (PCE of 1.48% with a \( J_{SC} \) of 6.23 mA cm\(^{-2} \), a \( V_{OC} \) of 0.68 V, and an FF of 34.61%).

2. Results and Discussion

2.1. Materials Synthesis and Characterization

The synthetic routes to the monomer BPQI and polymers are displayed in Scheme 1. The detailed synthetic procedures are shown in the Supplementary Materials (Figures S1 and S2). Both polymers P(BPQI-BDT) and P(BPQI-BDTT) are obtained by polymerization of BPQI and the co-monomer BDT derivative. The resulting polymers were purified by Soxhlet extraction with methanol, acetone, hexane, and dichloromethane to remove the catalyst and low molecular weight fractions. The final chloroform fractions were collected and used to test the device’s performance. The numerical average molecular weights (\( M_n \)) and polydispersity indices (PDIs) of P(BPQI-BDT) and P(BPQI-BDTT) were determined by using high-temperature gel permeation chromatography (HT-GPC) at 150 °C with 1,2,4-trichlorobenzene as the eluent. The GPC results are summarized in Table 1: P(BPQI-BDT) has an \( M_n \) of 24 kDa with a PDI of 2.2, and P(BPQI-BDTT) shows an \( M_n \) of 37 kDa with a PDI of 2.0. The thermal properties of P(BPQI-BDT) and P(BPQI-BDTT) were characterized using thermogravimetric analyses (TGA) and differential scanning calorimetry (DSC). Both polymers exhibit excellent thermal stability (5% weight loss) over 300 °C, which indicates good thermal stability for PSC fabrication. Based on the DSC thermograms, no obvious exotherm or endotherm peaks were observed for both polymers P(BPQI-BDT) and P(BPQI-BDTT) in the temperature range from 50 to 300 °C, which likely indicates a low degree of crystallinity in both polymers.
Table 1. Molecular Weights and Optical and Electrochemical Properties of Polymers.

| Polymer           | $M_n$ (kDa)$^a$ | PDI$^a$ | $\lambda_{onset}^{film}$ (nm)$^b$ | $E_g^{opt}$ (eV)$^c$ | HOMO (eV)$^d$ | LUMO (eV)$^c$ |
|-------------------|-----------------|--------|---------------------------------|----------------------|--------------|--------------|
| P(BPQI-BDT)       | 24              | 2.2    | 584                             | 2.12                 | -5.41        | -3.29        |
| P(BPQI-BDTT)      | 37              | 2.0    | 588                             | 2.10                 | -5.51        | -3.41        |

$^a$ Measured from GPC versus polystyrene standard; trichlorobenzene as the eluent at 150 °C.$^b$ Absorption spectra of the pristine film from chloroform solution. $^c$ Optical bandgap estimated from the absorption onset of the as-cast polymer film using the equation: $E_g^{opt} = 1240/\lambda_{onset}$ (eV). $^d$ $E_{HOMO} = -e(E_{ox}^{onset} + 4.80)$ eV.

2.2. Optical and Electrochemical Properties

The UV-vis absorption spectra of P(BPQI-BDT) and P(BPQI-BDTT) in a chloroform solution and as thin films were shown in Figure 1a, and the corresponding data are summarized in Table 1. In solution, both polymers show two absorption shoulder peaks in the range of 350–500 nm, and the absorption maxima ($\lambda_{max}$) of P(BPQI-BDT) and P(BPQI-BDTT) in chloroform solution are located at 393 and 432 nm, respectively. In the thin film state, the similar absorption with a slightly red-shifted absorption peak was observed for both polymers, which should be due to close packing in the solid state. The optical bandgaps of P(BPQI-BDT) and P(BPQI-BDTT) are 2.12 and 2.10 eV, respectively, according to the absorption onsets of the polymer thin films.
The electrochemical properties of P(BPQI-BDT) and P(BPQI-BDTT) were characterized by cyclic voltammetry. As shown in Figure 1b, the HOMO energy levels of P(BPQI-BDT) and P(BPQI-BDTT) were calculated from the onset potential of the oxidation peak, which are −5.41 and −5.51 eV (Table 1), respectively. By using the equation of $E_{\text{LUMO}} = (E_{\text{HOMO}} + E_g)$ eV, the LUMO energy levels of P(BPQI-BDT) and P(BPQI-BDTT) were found to be −3.29 and −3.41 eV, respectively. The $E_{\text{HOMO}}/E_{\text{LUMO}}$ of both polymers match well with acceptor Y6, indicating that these two polymers can be used as polymer donor in PSCs.

2.3. Theoretical Calculations

Theoretical computation on the backbone geometry of P(BPQI-BDT) and P(BPQI-BDTT) were performed by density functional theory (DFT) using the B3LYP/6-31G level method (Figure 2). The long side chains on the BPQI and BDT were replaced by a methyl group for simplifying the computations, respectively. The DFT-calculated HOMO/LUMO are −4.76/−2.50 and −5.13/−2.56 eV for P(BPQI-BDT) and P(BPQI-BDTT), respectively. The trend of the HOMO/LUMO energy level from the theoretical energy levels are in good agreement with the values obtained by CV measurements.

Figure 2. Chemical structures and FMO energy levels of (a) P(BPQI-BDT) and (b) P(BPQI-BDTT).

2.4. Photovoltaic Properties

To investigate the photovoltaic properties of P(BPQI-BDT) and P(BPQI-BDTT) in PSCs, the conventional device structure indium tin oxide (ITO)/poly(3,4-ethyl-enedioxythiophene):
poly(styrene sulfonic acid) (PEDOT:PSS)/active layer/silver(Ag)/gold(Au) was fabricated. Y6 was chosen as the acceptor due to its excellent performance in the field of OSCs, and the device architecture is shown in Figure 3a. The molecular energy levels of P(BPQI-BDT) and P(BPQI-BDTT) are shown in Figure 3b. The active layer was deposited by spin-coating the P(BPQI-BDT)/P(BPQI-BDTT):Y6 mixed solution in chloroform at a D/A weight ratio of 1/1, and the solution concentration is 10 mg mL\(^{-1}\). The current density–applied voltage (\(J–V\)) curves are shown in Figure 3c, and the corresponding parameters are summarized in Table 2. As shown in Figure 3c, the optimized P(BPQI-BDTT):Y6-based device delivers a PCE of 6.31\% with a \(J_{SC}\) of 17.09 mA cm\(^{-2}\), a \(V_{OC}\) of 0.82 V, and an FF of 44.78\%. whereas the optimized P(BPQI-BDT):Y6-based device displays a low PCE of 1.48\% with a \(J_{SC}\) of 6.23 mA cm\(^{-2}\), a \(V_{OC}\) of 0.68 V, and an FF of 34.61\%. The increased \(V_{OC}\) for the P(BPQI-BDTT)-based PSC is due to the deep-positioned HOMO energy level, since the \(V_{OC}\) is determined by the HOMO of a donor’s and the LUMO of an acceptor’s energy offset. The external quantum efficiency (EQE) spectra are shown in Figure 3d: the larger \(J_{SC}\) of the P(BPQI-BDTT):Y6 devices is ascribed to the higher EQE response in the wavelength range from 400 to 850 nm. In contrast, the EQE value of the P(BPQI-BDTT):Y6 cells is lower than 25\% in this range, resulting in a smaller \(J_{SC}\). The relationship between \(J_{SC}\) and the light intensity is revealed in Figure S3a: the \(\alpha\) values of the P(BPQI-BDTT):Y6 and P(BPQI-BDTT):Y6 devices are 0.92 and 0.974, respectively, which reflects that the P(BPQI-BDTT):Y6 based devices have a smaller bimolecular recombination effect. Figure S3b shows the light-intensity dependence of \(V_{OC}\). The \(\eta\) values of P(BPQI-BDTT):Y6 and P(BPQI-BDTT):Y6 are 2.37 and 1.78, respectively. It is shown that the device structure of P(BPQI-BDTT):Y6 produces fewer trap-assisted recombination centers, which are responsible for facilitating charge extraction and improving the PV performance. In order to investigate the device properties of the polymers in more depth, we constructed P(BPQI-BDTT):Y6 devices with a surface area of 1 cm\(^2\), shown in Figure 3e, and the corresponding parameters are shown in Table 3. The PCE of large device is 5\%, with a \(V_{OC}\) of 0.8 V, a \(J_{SC}\) of 13.92 mA cm\(^{-2}\), and an FF of 44.77\%. It demonstrated that polymers have the prospect of large-area applications in devices. The commercially polymer PTB7-Th was selected to compare the new polymer P(BPQI-BDTT). The photovoltaic performances of two devices are shown in Figure S4 and Table S1. In Figure S5, we demonstrate the performance of the device in the dark; the variations in the \(J_{SC}\) and \(V_{OC}\) are slight, thus showing the stability of the device’s performance in a dark environment.

Figure 3. (a) Structure of P(BPQI-BDT) or P(BPQI-BDTT) as the polymer donor and Y6 as the acceptor; (b) the molecular energy levels of BPQI-BDT, BPQI-BDTT, and Y6; (c) current density–applied voltage (\(J–V\)); (d) external quantum efficiency (EQE) curves of P(BPQI-BDTT):Y6 or P(BPQI-BDTT):Y6 devices; (e) P(BPQI-BDTT):Y6 (\(J–V\)) curve when active area is 1 cm\(^2\).
Table 2. Photovoltaic parameters of OSCs based on P(BPQI-BDT):Y6’s and P(BPQI-BDTT):Y6’s active layer. \(^a\) Average data from 10 independent devices.

| Active Layer     | \(V_{OC}\) (V) | \(J_{SC}\) (mA cm\(^{-2}\)) | \(J_{cal}\) (mA cm\(^{-2}\)) | FF (%)   | \(PCE_{max}/PCE_{ave}\) \(^a\) (%) |
|------------------|-----------------|-----------------------------|-----------------------------|---------|-----------------------------------|
| P(BPQI-BDT):Y6   | 0.68            | 6.23                        | 6.71                        | 34.61   | 1.48/1.35 ± 0.10                  |
| P(BPQI-BDTT):Y6  | 0.82            | 17.09                       | 17.00                       | 44.78   | 6.31/5.97 ± 0.29                  |

Table 3. Photovoltaic parameters of OSCs based on P(BPQI-BDTT):Y6’s active layer with its surface area of 1 cm\(^2\).

| Active Layer      | \(V_{OC}\) (V) | \(J_{SC}\) (mA cm\(^{-2}\)) | FF (%) | PCE (%) |
|-------------------|-----------------|-----------------------------|--------|---------|
| P(BPQI-BDTT):Y6   | 0.80            | 13.92                       | 44.77  | 5.00    |

2.5. Polymer Film Morphology

Atomic force microscopy (AFM) measurements were taken to study the surface and phase separation morphology of the blend films. As shown in Figure 4, both P(BPQI-BDT):Y6 and P(BPQI-BDTT):Y6 have a relatively smooth surface. The root mean square (RMS) values of roughness for both the P(BPQI-BDT):Y6 and P(BPQI-BDTT):Y6 blend films were 1.28 and 0.9 nm, respectively. It is clear that the P(BPQI-BDT):Y6 blend film has a higher roughness than the P(BPQI-BDTT):Y6 blend, indicating that the P(BPQI-BDT):Y6 blend film enhances the aggregation and phase separation. The P(BPQI-BDTT):Y6 blend has minimal roughness, which is beneficial for charge carrier transportation, charge collection, and less charge recombination, leading to the enhancement of the FF and PCE in OPVs. X-ray diffraction (XRD) was applied to investigate the crystalline properties of these polymers. As shown in Figure S6, the two polymers show wide diffraction and high peaks located at \(2\theta = 37.32^\circ\) and \(2\theta = 43.62^\circ\), which should derive from the two polymers exhibiting similar crystalline surfaces and analogous crystal structures. To further investigate the film morphologies of the polymers, SEM was used to study the surface of the P(BPQI-BDT):Y6 and P(BPQI-BDTT):Y6 films. As shown in Figure S7, it can be seen that these two polymers are irregularly flat films, while P(BPQI-BDTT):Y6 has a more uniform surface morphology, which is favorable for its charge transfer and suppresses charge recombination, effectively improving its device performance.

Figure 4. AFM phase images of (a) P(BPQI-BDT) and (b) P(BPQI-BDTT) blend films, respectively.

3. Conclusions

In summary, a new dibenzo-fused quinoxalineimide (BPQI) is successfully synthesized as an electron-deficient building block to construct donor–acceptor (D–A)-type polymers, namely P(BPQI-BDT) and P(BPQI-BDTT). Both polymers possess deep HOMO energy levels and wide bandgaps. These two polymers were used as donor materials for polymer
solar cells. The PSC based on the P(BPQI-BDTT):Y6 blend showed a higher PCE (6.31%) with a $V_{OC}$ of 0.82 V, a $J_{SC}$ of 17.09 mA cm$^{-2}$, and an FF of 44.78% as compared to P(BPQI-BDT):Y6 (1.48%) with a $V_{OC}$ of 0.68 V, a $J_{SC}$ of 6.23 mA cm$^{-2}$, and an FF of 34.61%. The higher PCE is mainly attributed to improvements in the $J_{SC}$ and FF. These results demonstrate that BPQI is a promising building block for developing a wide-bandgap polymer donor in OPVs. In addition, the acceptor BPQI can also be applied to other organic opto-electronic devices, such as organic field effect transistors (OFET) and perovskite solar cells (PSCs), due to its large conjugated backbone and electron-deficient characteristics. In future work, a series of quinoxalineimide electron-deficient units will be synthesized, and we believe that quinoxalineimides will become a promising building block for constructing organic semiconductors.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/polym14173590/s1

Table S1: Photovoltaic parameters of OSCs based on P(BPQI-BDTT):Y6 and P(BPQI-BDT):Y6.

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