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Vinylene- and ethynylene-bridged perylene diimide dimers as nonfullerene acceptors for polymer solar cells

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ABSTRACT

Vinylene (**V**)- and ethynylene (**E**)-bridged perylene diimide dimers (**PDI-V** and **PDI-E**) were designed, synthesized and used as nonfullerene acceptors for polymer solar cells. Our researches revealed that the linkage between two **PDI** units has a great impact on the molecular geometry, the optical properties, the blend film morphology, the molecular packing orientation, and the photovoltaic performance. Computational calculations via density functional theory (DFT) showed that **PDI-E** and **PDI-V** possessed planar and twisted geometric structures, respectively. TEM investigations showed that **PTB7-Th**:**PDI-V** based blend film exhibited a uniform morphology with small domain size and **PTB7-Th**:**PDI-E** based one showed apparent phase separation with large domain size. GIWAXS results revealed that the **PDI-V** can influence **PTB7-Th** to take on a face-on orientation, which is beneficial for vertical charge transport to increase J_{sc}. A PCE of 4.51% with a V_{oc} of 0.76 V, a J_{sc} of 10.03 mA cm^{-2}, and an *FF* of 0.59 was obtained for PSCs based on **PTB7-Th**:**PDI-V**, which is almost two times higher than that of **PTB7-Th**:**PDI-E** based devices, which showed a PCE of 2.66%, a V_{oc} of 0.66 V, a J_{sc} of 7.33 mA cm^{-2}, and an *FF* of 0.55. These results help to gain deeper insight into the design of new nonfullerene small molecular acceptors for high efficiency PSCs.

1. Introduction

Bulk heterojunction polymer solar cells (BHJ PSCs) with the active layer composed of a blend of a semiconducting polymer donor and a fullerene derivative acceptor ($PC_{61}BM$, $PC_{71}BM$, etc.) have attracted considerable attention due to their solution-processability, low-cost and light-weight and flexibility [1–6]. Fullerene derivatives have been widely used as the dominant electron acceptors in BHJ PSCs due to their high electron mobility, high electron affinity and isotropic charge transport properties [7,8]. Power conversion efficiencies (PCEs) of fullerene-based BHJ PSCs have reached 10% in single-junction devices [9,10]. However, the intrinsic drawbacks of fullerene derivatives such as expensive, difficult chemical modification, weak absorption in the visible spectral region and limited energy level variability could not be ignored [11–13]. Thus, the newly emerging nonfullerene (NF) acceptors become more and more attractive due to their advantages such as tunable molecular energy levels, excellent optical absorption properties, easy purification and low cost production processes [14,15]. Recently, some outstanding nonfullerene acceptors, such as **ITIC** [15–21], naphthalene diimide (**NDI**) derivatives [22–26], perylene diimide (**PDI**) derivatives [27–45], etc. have been developed and PCEs over 12% have been achieved [46–48].

Perylene diimide (**PDI**) derivatives have captured particular attention because of their several appealing merits including excellent photochemical stability, broad optical absorption range, high electron mobility, and tunable electronic structures and properties [29,43]. However, due to their highly planar and rigid structure, most mono-**PDI** derivatives are prone to self-aggregate in the solid state to form large domains that are detrimental to exciton separation and give low efficiency [30,41]. Linking two **PDI** units at the bay position with an appropriate spacer such as phenylene, thiophene, spirobifluorene, etc. has been proved to be an effective way to obtain dimers with nonplanar conformations, which can

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suppress the strong π-π aggregation of **PDI** units and prevent them from forming large aggregates in the blend films [30–34].

To investigate the influence of linker between two **PDI** units, we designed and synthesized two **PDI** based acceptors, vinylene (**V**) and ethynylene (**E**) -bridged **PDI** dimers as presented in Fig. 1, and used them as electron acceptors for the fabrication of nonfullerene PSCs. Our studies have revealed that the linker has a great influence on the optical properties, molecular geometry, molecular packing, blend film morphology, transport properties of blend film, and photovoltaic properties of devices. **PDI-V** exhibits a slightly twisted conformation; whereas **PDI-E** takes on a planar conformation. **PDI-V** both in solution and as film shows a featureless broad absorption with higher molar extinction efficiency; whereas **PDI-E** presents a broad absorption with fine structures and lower molar extinction efficiency. To investigate the photovoltaic performance, **PTB7-Th** (Poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b; 4,5-b'] dithiophene-2,6-diyl-alt-(4-(2-ethylhexyl)-3-fluorothieno [3,4-b] thiophene-)-2-carboxylate-2-6-diyl)]) was chosed as donor. Due to its slightly twisted conformation, the **PTB7-Th**:**PDI-V** based blend films showed a smooth morphology without large phase separation; whereas for the planar **PDI-E**, its blend films with **PTB7-Th** showed an apparent phase separation with a large domain size. In addition, **PTB7-Th**:**PDI-V** based blend films also exhibit higher and more balanced charge carrier mobility. Finally, **PTB7-Th**:**PDI-V** based PSCs gave a PCE of 4.51% with a V_{oc} of 0.76 V, a J_{sc} of 10.03 mA cm^{-2}, and an *FF* of 0.59; whereas **PTB7-Th**:**PDI-E** based PSCs only gave a PCE of 2.66% with a V_{oc} of 0.66 V, a J_{sc} of 7.33 mA cm^{-2}, and an *FF* of 0.55.

2. Results and discussion

2.1. Material synthesis and characterization

The synthetic routes of **PDI-V** and **PDI-E** are outlined in Scheme 1. Compound **1** was prepared according to the previous literature procedure [42]. Pd-catalyzed Stille coupling of **1** with *trans*-1,2-bis(tri-*n*-butylstannyl)ethylene and bis(trimethylstannyl) acetylene afforded **PDI-V** and **PDI-E** in yields of 77% and 70%, respectively. **PDI-V** and **PDI-E** are of good solubility in common organic solvents, such as dichloromethane, chloroform, *o*-dichlorobenzene (DCB), chlorobenzene (CB), etc. at room temperature. Thermogravimetric analysis (TGA) indicated that the two small acceptors have excellent thermal stability with the 5%-decomposition temperature up to 433 °C for **PDI-V**, and 442 °C for **PDI-E** (Fig. S1). In the range of 50–250 °C, no obvious melting peak or glass transition was observed for **PDI-V** in differential scanning calorimetry (DSC) curves under N_2 atmosphere at a heating rate of 10 °C/min; while a clear melting peak at about 200 °C and a crystallization peak at about 150 °C were detected for **PDI-E** (Fig. S2). The above results indicated that **PDI-V** could form amorphous film; whereas **PDI-E** are prone to form crystalline one.

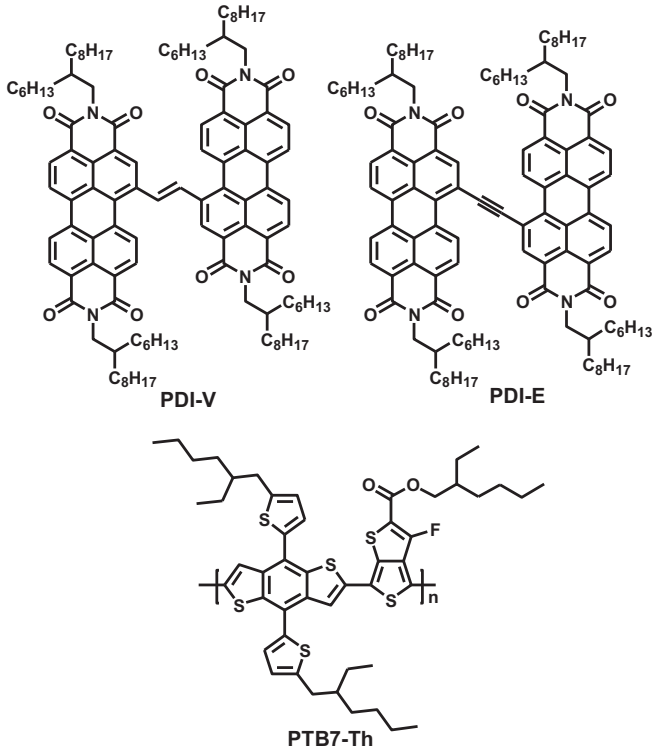

Fig. 1. Molecular structures of **PDI-V**, **PDI-E** and donor **PTB7-Th**.

2.2. Optical properties

UV–vis absorption spectra of **PDI-V**, **PDI-E** and **PTB7-Th** in DCB solutions and as films are depicted in Fig. 2. Different from mono-**PDI** derivatives, **PDI-V** in DCB solutions displayed a broad absorption ranging from 350 to 650 nm with three peaks at 448, 517 and 554 nm; whereas **PDI-E** in DCB solutions exhibited a well-resolved absorption spectrum in the same range with four peaks located at 450, 515, 546 and 590 nm. The molar extinction efficiency for the main absorption peak of each molecule is 5.46×10^4 $M^{-1}cm^{-1}$ for **PDI-V** and 5.08×10^4 $M^{-1}cm^{-1}$ for **PDI-E**. In going from solutions to films, the absorption spectrum of **PDI-V** became broader and the maximum absorption peak slightly red-shifted from 554 to 558 nm, indicating the formation of weak aggregation in the solid state. As film, **PDI-E** exhibited a broad and well resolved absorption spectrum with all peaks red-shifted in comparison with their solution ones. The red-shifted and enhanced 0-0 absorption peak in the film spectrum indicated that **PDI-E** formed stronger aggregation in the solid state due to its much planar molecular geometry (vide infra). The absorption spectra of **PTB7-Th**:**PDI-V** and **PTB7-Th**:**PDI-E** blend films are showed in Fig. S3, **PDI-V** and **PDI-E** have complement absorption spectra with that of **PTB7-Th**, which will be beneficial for more efficient use of the solar radiation. Determined from the onset absorption of films, band gaps of **PDI-V** and **PDI-E** were calculated to be 1.88 and 1.85 eV, respectively. The related data are also summarized in Table 1.

2.3. DFT calculations

To investigate the structural properties of two compounds, density functional theory (DFT) calculations at the B3LYP/6-31G(d) level were performed to evaluate the molecular geometries of **PDI-V** and **PDI-E**. The alkyl chains were simplified as methyl groups to facilitate the calculation. The optimized molecular geometries of **PDI-V** and **PDI-E** are shown in Table 2. The dihedral angles between the vinylene unit and two PDI units are 18.1° and 15.5°, resulting in a twisted geometry for **PDI-V**. The slightly twisted geometry of **PDI-V** might be attributed to the steric hindrance of the hydrogen atoms at the bay region of **PDI** and at the vinylene group. Unlike **PDI-V**, **PDI-E** displays a completely planar conformation in the optimized geometry.

To better understand the absorption properties of **PDI-V** and **PDI-E**, the peaks were assigned by calculations at the CASPT2//CASSCF(10e/8o)/6-31G level and the results are summarized in Table 3. The schematic frontier molecular orbitals are shown in Fig. S4. The computational results showed good agreement with the experimental data. Transitions of HOMO→LUMO, HOMO−1→LUMO and HOMO−2→LUMO+1 of **PDI-V** and **PDI-E**