Perylene diimide-benzodithiophene D-A copolymers as acceptor in all-polymer solar cells

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ABSTRACT

Two n-type conjugated D-A copolymers with perylene diimide (PDI) as acceptor unit and benzodithiophene (BDT) as donor unit, **P(PDI-BDT-Ph)** and **P(PDI-BDT-Th)**, were synthesized and applied as electron acceptor in all-polymer solar cells (all-PSCs). **P(PDI-BDT-Ph)** and **P(PDI-BDT-Th)** films exhibit similar absorption spectra in the visible region with optical bandgap (E_g) of 1.65 eV and 1.55 eV respectively, and the identical LUMO level of −3.89 eV. The all-PSCs based on **P(PDI-BDT-Ph)** as acceptor and PTB7-Th as donor demonstrated a power conversion efficiency (PCE) of 4.31% with a short-circuit current density (J_{sc}) of 11.94 mA cm^{-2}, an open-circuit voltage (V_{oc}) of 0.81 V, and a fill factor (FF) of 44.49%. By contrast, the corresponding all-PSCs with **P(PDI-BDT-Th)** as acceptor showed a relative lower PCE of 3.58% with a J_{sc} of 11.36 mA cm^{-2}, V_{oc} of 0.79 V, and FF of 40.00%.

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1. Introduction

All-polymer solar cells (all-PSCs) with n-type conjugated polymer as acceptor have developed rapidly in recent years due to the potential advantages of easy-tuning absorption spectra and molecular energy levels as well as better flexibility of the polymer acceptor over the traditional fullerene derivative acceptor PCBM [1—16]. However, the power conversion efficiencies (PCEs) of the all-PSCs are still lag behind those of the polymer:fullerene PSCs. Thus, it is crucial to design and synthesize more suitable n-type conjugated polymer acceptors for improving the photovoltaic performance of the all-PSCs [17—19].

Perylene diimides (PDIs)-based D-A copolymers possess higher electron mobility and suitable LUMO energy levels for the application as acceptor in the all-PSCs. In 2007, Zhan et al. synthesized a PDI-based D-A copolymer with PDI as acceptor unit and dithieno [3,2-b:2,3-d]thiophene as donor unit, and the all-PSCs with the polymer as acceptor and a two-dimension (2D)-conjugated polythiophene derivative as donor displayed a PCE of ca. 1% [20]. Then the PCE was further improved to ca. 1.5% by the molecular structural modification of the polymer donor and polymer acceptor [21]. Subsequently, a series of n-type PDI-based conjugated copolymers were designed and synthesized by Zhou et al. and the PCE of the all-PSCs with the PDI-based polymer as acceptor reached over 2% by using a 2D-conjugated polythiophene derivative as donor [3]. Bao et al. achieved a higher PCE of 4.4% in 2014 for the all-PSCs with the PDI-based polymer as acceptor and the isoindigo-containing polymer as donor [22].

In the past few years, 2D-conjugated polymers based on benzodithiophene (BDT) unit with conjugated side chains play an important role in the application as polymer donor in high performance PSCs [23—32]. Recently, we applied the 2D-conjugation concept to n-type conjugated polymers and synthesized a 2D-conjugated D-A copolymer P(PDI-BDT-T) with alkylthienyl substituted benzodithiophene (BDT) as donor unit and PDI as acceptor unit, and the all-PSCs with P(PDI-BDT-T) as polymer acceptor demonstrated a PCE of 4.71% [33]. In order to extend the family of the n-type 2D-conjugated polymers, herein we

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synthesized two new n-type 2D-conjugated D-A alternative co-polymers **P(PDI-BDT-Th)** and **P(PDI-BDT-Ph)** with alkoxy-thienyl or alkoxy-phenyl substituted BDT as donor unit and PDI as acceptor unit (Scheme 1), and compared their physicochemical and photovoltaic properties in the all-PSCs with the polymers as acceptor and a narrow bandgap polymer PTB7-Th as donor.

2. Experimental section

2.1. General procedure for the polymerization

Monomers 2Br-PDI [34−38], BDT-Th-Sn [39,40] and BDT-Ph-Sn [41,42] were prepared by using experimental procedures reported in literatures.

2Br-PDI (0.30 mmol), BDT-Th-Sn or BDT-Ph-Sn (0.30 mmol) were dissolved into 10 mL of toluene in a flask under nitrogen. The flask equipped with a return pipe was then degassed and filled with argon for three times. $Pd(PPh_3)_4$ (18 mg) was added into the flask. Then, the reaction mixture was treated for 18−24 h at 110 °C. After the reaction mixture was cooled to room temperature, the polymer was precipitated in 150 mL of methanol. Subsequently, the crude product was collected by filtration, dried in vacuum drying oven, and then purified by Soxhlet extraction with methanol, acetone, and hexane.

P(PDI-BDT-Th) (364 mg, 77%): M_n = 25.1 KDa, PDI = 1.95, Anal. Calcd for $C_{96}H_{126}N_2O_6S_4$ (%): C 75.25, H 8.29, N 1.83; found (%): C 74.92, H 8.07, N 1.64; ^1H NMR (400 MHz, $CDCl_3$) δ 8.82 (d, 1H), 8.55−8.26 (m, 2H), 8.18−7.87 (m, 1H), 7.20−6.97 (m, 1H), 6.35−6.10 (m, 1H), 4.39−3.76 (m, 4H), 1.95 (d, 1H), 1.70 (d, 1H), 1.27 (m, 39H), 1.00−0.72 (m, 13H).

P(PDI-BDT-Ph) (374 mg, 80%): M_n = 27.8 KDa, PDI = 1.67, Anal. Calcd for $C_{102}H_{134}N_2O_6S_2$ (%): C 79.13, H 8.72, N 1.81; found (%): C 79.25, H 8.57, N 1.75; ^1H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, 1H), 8.52−8.19 (m, 2H), 7.64 (s, 3H), 7.00 (s, 3H), 3.99 (d, 4H), 2.00 (s, 1H), 1.68 (d, 1H), 1.28 (m, 40H), 0.91−0.76 (m, 12H).

2.2. Instruments and measurements

UV−vis absorption spectra were taken on an Agilent Technologies Cary Series UV−Vis−NIR Spectrophotometer in chloroform solution and in thin film. The electrochemical cyclic voltammetry (CV) was performed on a Zahner Ennium Electrochemical Workstation with glassy carbon disk, Pt wire, and Ag/Ag^+ electrode as working electrode, counter electrode, and reference electrode respectively, in a 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) acetonitrile electrolyte solution. Atomic force microscopy (AFM) measurements were carried out on a Dimension 3100 (Veeco) Atomic Force Microscope in the tapping mode. Transmission electron microscopy (TEM) was performed using a JEOL 2200FS instrument at 160 kV accelerating voltage. X-ray diffraction (XRD) measurement was performed using a Bruker D8 Advance Instrument at 40 kV voltage and 200 mA current with Cu Kα radiation.

### 2.3. Charge carrier mobility measurement

The charge carrier mobility was measured by the space charge limited current (SCLC) method with the hole-only device of ITO/PEDOT:PSS/Active layer/MoO_3/Al for the hole mobility measurement or with the electron-only device of ITO/ZnO/Active layer/Ca/Al for the electron mobility measurement. After measurements of the J-V curves of the devices, the hole mobilities and the electron mobilities were calculated according to the following equation,

$$J = \frac{8}{9}\varepsilon_r\varepsilon_0\mu\frac{V^2}{L^3}$$

where ε_r is the dielectric constant of the polymer, ε_0 is the permittivity of the vacuum, μ_0 is the zero-field mobility, J is the current density, L is the thickness of the blend films, $V = V_{appl} - V_{bi}$, V_{appl} is the applied potential, and V_{bi} is the built-in potential from the difference in the work function of the anode and the cathode (in the hole-only and electron-only device, V_{bi} value is 0.2 V and 0 V, respectively).

2.4. Device fabrication and characterization

The ITO-coated glass substrate was cleaned in an ultrasonic bath with deionized water, acetone, and isopropanol, each process was approximately 15 min, and then dried under a stream of dry nitrogen. Subsequently, the ITO-coated glass substrate was treated by UV-ozone for 15 min. PEDOT:PSS (Clevios P VP AI 4083, H.C. Starck) solution was then spin-coated onto the pre-cleaned ITO coated glass substrates, and thermal-treated at 150 °C for 15 min to get the
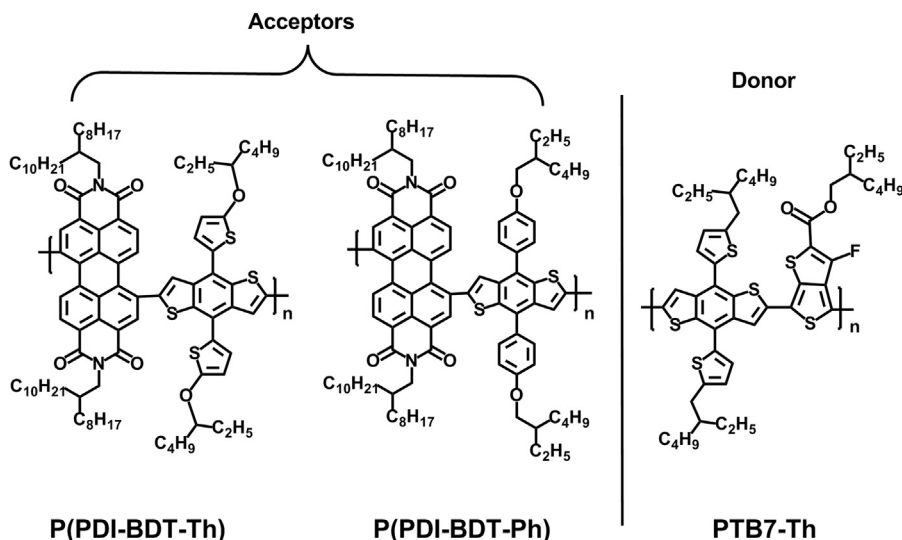
Scheme 1. Molecular structures of polymer donor PTBT-Th, and polymer acceptors **P(PDI-BDT-Th)** and **P(PDI-BDT-Ph)**.