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Correlation between polymer molecular weight and optimal fullerene content in efficient polymer solar cells

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In this contribution, a donor-acceptor (D-A) copolymer PTP8, consisting of alternating benzodithiophene and thienopyrroledione with conjugated side-chains on both donor and acceptor units, was sucessfully prepared. We further investigated the effect of polymer molecular weight on polymer physicochemical properties, solar cell device performance, polymer-PCBM blend morphology, and, most importantly, polymer/PCBM blend ratio. We found that increasing the molecular weight of the donor polymer can both effectively improve the device performance and simultaneously stabilize solar cell efficiency over a wide range of polymer/PCBM blend ratios (from 1:0.5 to 1:1.0), which may lead to more thermally stable and cost-effective devices. Through intensive morphological investigation, we propose a sound morphological evolution for PTP8/PCBM blends with different molecular weights at low fullerene content.

1. Introduction

Organic semiconducting materials, especially conjugated polymers, have been incorporated into a variety of electronic applications including light-emitting diodes (LEDs), photovoltaic cells (PVs), thermoelectrics and thin-film transistors (TFTs) [1]. Both polymer and fullerene can be readily formulated into printable inks, which make them viable for large scale solution deposition processing techniques. Typical polymer solar cell (PSC) devices are normally composed of a low band-gap conjugated polymer and a fullerene derivative such as phenyl-C61-butyric acid methyl ester ($PC_{61}BM$) with an optimized weight ratio. During the past decade, a great amount of progress has been achieved in bulk hetero-junction (BHJ) PSCs, including improved molecular design and synthesis, device processing, and morphology refinement, which leads to an improved power conversion efficiency (PCE) of ~12% [2]. However, the performance of polymer PVs is still limited by the exciton dissociation and charge transport process, which is strongly affected by the polymer/PCBM blend morphology [3]. Therefore, a better understanding of the key factors driving blend morphology is crucial to further improve the performance of PSCs.

In high-efficiency polymer solar cells, the optimal polymer/PCBM weight ratio typically ranges from 1/1 to 1/4 in order to provide favourable phase separation and promote a percolated network for efficient charge transport [4]. As it is well-understood, PCBM exhibits weaker extinction coefficients and a narrower absorption than conjugated polymers. As the ratio of fullerene is increased, the thickness of the active layer will grow, further promoting increased recombination and degradation of the fill factor (FF) [5]. Recently, many reports have demonstrated the correlation between polymer structure and an optimized blend weight ratio [6], and by introducing the conjugated side-chains into polymer backbone and PCBM, we have successfully fabricated efficient polymer solar cells with a low PCBM content [7].

Despite the high PCEs achieved for polymer BHJ solar cells, one finds that for a given polymer structure, batch-to-batch variations in molecular weight and polydispersity can lead to different processing properties and performance. Multiple reports have revealed that the polymer molecular weight greatly affects the molecular packing, carrier mobility, and blend morphology [8]. For example, in 2010 a novel donor-acceptor (D-A) copolymer PBDTTPD was independently synthesized by four groups with PCEs ranging from 4.2 to 6.6% [9], highlighting great potential for applications in tandem solar cells due to its wide band-gap. However, the optimal blend ratio was also notably different, even for the same material. To the best of our knowledge, few efforts have been

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dedicated to the investigation of molecular weight effect upon the optimal polymer/fullerene weight ratio.

In this contribution, we synthesized a D-A copolymer PTP8 consisting of conjugated side-chain modified benzodithiophene(BDT) and thienopyrroledione (TPD) moieties. By controlling the polymerization reaction time, we successfully prepared PTP8 with a defined molecular weight to further investigate its influence on device performance and polymer/fullerene blend ratio. PTP8 with a higher molecular weight exhibits narrower optical bandgap, enhanced intermolecular π-π stacking, and slightly modified energy levels. As a result of improved light absorption, charge transport and polymer-fullerene blend morphology, the high molecular weight version polymer exhibit improved FF, J_{sc}, and PCE in solar cell devices. By fabricating solar cells over a wide range of polymer/fullerene blend ratios, as well as carrying out morphological characterization, including atomic force microscopy (AFM), transmission electron microscope (TEM), and 2-dimension grazing incidence wide X-ray scattering (2d-GIWAXS), we thoroughly investigated the effect of molecular weight. Preliminary results have demonstrated that the higher molecular weight can serve not only to improve the device performance, but can also serve to improve the device stability over a wide range of polymer/PCBM blend ratios (from 1:0.5 to 1:1.0), which may lead to more thermally stable and cost-effective devices.

2. Experimental section

2.1. Materials and instruments

All chemicals were purchased from J&K and Sigma-Aldrich and used as received. UV–vis–NIR spectra were recorded on a Perkin Elmer model Lambda 750 instrument. Tapping-mode atomic force microscopy (AFM) images were obtained with a Veeco Multimode V instrument using Standard Silicon Cantilever AFM tips from OLYMPUS company with a radius of 10 nm. 2D Grazing Incidence X-Ray Diffraction (2D GIXD) experiments were conducted at Shanghai Synchrotron Radiation Facility (*SSRF*) on diffraction beamline (BL14B1) at incident angles of 0.12°.

2.2. General procedure for the synthesis of PTP8

In a 50 mL reaction tube, 2,6-Bis(trimethyltin)-4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)-benzo[1,2-b:4,5b']dithiophene (0.22 g, 0.24 mmol),1,3-dibromo-5-(4-octylphenyl)- 5H-thieno[3,4-c]pyrrole-4,6-dione (0.12 g, 0.24 mmol) tri(*o*-tolyl)phosphine (0.02 g, 0.08 mmol), and $Pd_2(dba)_3$(0.01 g, 0.01 mmol) were dissolved in 5 mL dry toluene under argon. After stirred at 110 °C for different time (20 h for LW, 32 h for MW and 48 h for HW), the mixture was cooled to room temperatures and precipitated in methanol (80 mL). The precipitate was filtered and washed with methanol (24 h) and hexane (24 h) successively in a Soxhlet apparatus to remove oligomers and catalyst residue. Finally, the polymer was extracted with chloroform. The chloroform fraction was concentrated and precipitated in methanol. The precipitate was filtered and dried in vacuum at 80 °C overnight. **PTP8**: obtain as dark purple solid, GPC: M_w = 10.0 kg mol^{-1}, PDI = 1.88 (LW); M_w = 16.3 kg mol^{-1}, PDI = 1.80 (MW) and M_w = 26.1 kg mol^{-1}, PDI = 2.08 (HW).

2.3. Fabrication and characterization of polymer solar cells

Polymer solar cells were fabricated with a general structure of ITO/PEDOT-PSS (40 nm)/polymer:PCBM/LiF/Al. Patterned ITO glass substrates were cleaned by sequential ultrasonic treatment in detergent, acetone, deionized water and isopropyl alcohol. The organic residue was further removed by treating with UV-ozone for 10 min. A thin film of PEDOT: PSS (~40 nm) was spin-coated on ITO substrates and dried at 150 °C for 10 min. A blend of PBDT-T-TPDs and PCBM with different ratios was dissolved in chloroform containing 0–2% (v/v) diiodooctane, a fixed polymer concentration of 8 mg/mL was adopted for different D/A ratios solutions, DIO content was optimized as 0.5% for D/A weight ratio of 1/0.3 and 1/0.5, 1.0% for 1/0.6 and 1/0.7, 1.5% for 1/0.8 and 2.0% for 1/1.0, filtered through a 0.45 μm poly(tetrafluoroethylene) (PTFE) filter, spin-coated at 1500 rpm for 40 s, 0.6 nm of LiF (0.2A/s) and 100 nm Al (2A/s) layers were then thermally evaporated on the active layer at a pressure of 1.0×10^{-6} mbar through a shadow mask (active area 7.25 mm^2). The current density–voltage characteristics of the photovoltaic cells were measured using a Keithely 2400 (*I–V*) digital source meter under a simulated AM 1.5G solar irradiation at 100 mW/cm^2 (Newport, Class AAA solar simulator, 94023A-U). The light intensity is calibrated by a certified Oriel Reference Cell (91150V) and verified with a NREL calibrated Hamamatsu S1787-04 diode.

3. Results and discussions

3.1. Synthesis of the polymers

The selected polymer, PTP8, was synthesized across a selection of different molecular weights as described in Scheme 1. It was synthesized via Stille polymerization between di-stannylated BDT monomer and di-brominated TPD monomer. In the same manner as our previous report [7a], the materials can be easily optimized by changing the reaction time. Soxhlet extraction was introduced to remove the impurities and oligomers using methanol and hexane. The remaining crude product in the thimble was then extracted with chloroform and precipitated into methanol. The weight average molecular weights were determined using gel permeation chromatography (GPC) at 150 °C in 1,2,4-trichlorobenzene against polystyrene standards. Results are shown in Fig. S3, with the corresponding data listed in Table 1. Each of these results confirms that we have successfully controlled the polymer molecular weight and achieved a similar polydispersity index (PDI).

3.2. Optical and electrochemical properties

UV–vis absorption spectra of polymer solutions and solid films are shown in Fig. 1, with the corresponding data listed in Table 1. All samples were evaluated under the same conditions. Both polymer solutions and films displayed broad absorptions from 400 to 700 nm. Previous reports showed that the optical band-gaps slightly decreased when increasing the molecular weight [8c,10]. Herein, both MW (medium molecular weight) polymer and HW (high molecular weight) polymer exhibit a sharp absorption peak at ~650 nm, indicating stronger intermolecular contact compared to that in LW (low molecular weight) polymer. We also found that the HW and MW polymers exhibit red-shifted absorption edges relative to the LW polymer, which may be also attributed to enhanced molecular interaction [10]. Similarly, as thin films, the absorption coefficients gradually increase when increasing the polymer molecular weight. The MW and HW polymers show an indistinguishable E_g value of approximately 1.78 eV, as determined by the onset of absorption, and a narrower optical band gap relative to the LW polymer (1.85 eV). However, the main difference is found within in the 550–650 nm absorption spectrum, both in solution and film, with the increased conjugation lengths of polymer backbone further strengthening intermolecular π-π interaction and hence resulting in increased light absorption. Molecular energy levels are also slightly modified by the polymer molecular weight. As measured by cyclic voltammetry [11] (CV, Fig. S4), the HOMO