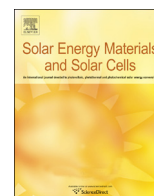




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Enhanced performance of polymer solar cells through sensitization by a narrow band gap polymer

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ABSTRACT

The performance of polymer solar cells (PSCs), based on poly(3-hexylthiophene) (P3HT) and [6,6]phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM), were improved by adding poly[(4,8-bis-(2-ethylhexyloxy)-benzo[1,2-b:4,5-b']dithiophene)-2,6-diyl-alt-(4-(2-ethylhexanoyl)-thieno[3,4-b]thiophene)-2,6-diyl] (PBDTTT-C). The absorption region of the ternary blend films is extended into near infrared region (NIR). Power conversion efficiency (PCE) of the ternary blend PSCs is improved to 2.48% with 6% PBDTTT-C, which is 27% higher than the binary blend PSCs. The dominant mechanism for the PCE improvement could be attributed to the well balance between photon harvest and charge carrier transport by doping proper concentration PBDTTT-C. The energy transfer or charge carrier transfer directly between P3HT and PBDTTT-C was investigated, which are found to be positive for the performance improvement of ternary blend PSCs.

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1. Introduction

Polymer solar cells (PSCs) have attracted more and more attention due to its beneficial features, such as low fabrication cost, environmental friendly, flexibility, easy large size fabrication and so on [1–3]. The power conversion efficiency (PCE) of bulk heterojunction (BHJ) PSCs with poly(3-hexylthiophene) (P3HT): fullerene derivative [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) has been improved to 4–5%, the PCE of PSCs with novel narrow band gap polymer as donor arrives to about 10% [4–7]. However, there is still a plenty of room to develop high performance and long lifetime PSCs for satisfying even-increasing market demand. Krebs et al. have done a series investigation and put forward the key 10–10 targets (10% PCE and 10 years of life cycle) about utilizing PSCs to solve energy crisis, such as life cycle assessment methodologies, large scale fabrication [8–10]. A series of research works on promoting efficiency and lifetime of the PSCs were carried out from cell's configuration, such as the inverted configuration, tandem configuration and BHJ ternary blend PSCs [11–13]. Minnaert et al. reported that the PCE of PSCs

could be boosted up 35% by expanding the absorption window from realistic width of 200 nm to an optimistic width of 400 nm [14]. Ternary blend BHJ and tandem configuration cells are considered as the efficient ways for expanding the absorption spectrum of active layers. However, the ternary blend BHJ cells have superiority of low cost, easy fabrication technology compared to the tandem configuration cells. Three key parameters must be optimized to improve the performance of tandem configuration cells, such as active layer thickness of each subcell, transmission and charge carrier collection ability of intermediate cathode and the complementarities of active layer absorption spectra in each subcell [15–17]. For optimization the PCE of tandem configuration PSCs, the tradeoff between fill factor (FF) and short circuit current (J_{sc}) must be balanced, while the open circuit voltage (V_{oc}) is constant. Therefore, several technological challenges must be accurately controlled to fabricate high performance tandem configuration cells.

Another promising strategy for the enhancement photon harvest of PSCs, the ternary blend BHJ configuration has attracted more and more attention [18–20]. The ternary blend BHJ PSCs could be clarified as two types: “two donors/one acceptor” or “one donor/two acceptors”, either two donors or two acceptors component consist of absorption spectral complementary materials [21–23]. The photovoltaic dynamic process of PSCs with P3HT: PCBM as the active layer has been well investigated, which favor

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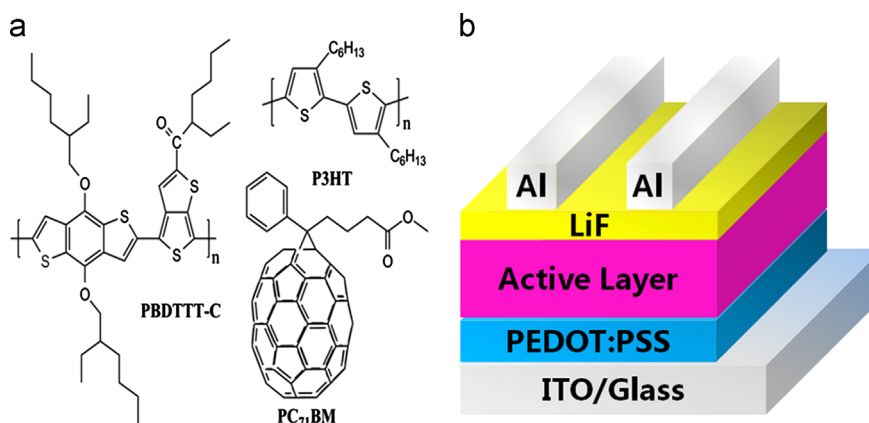


Fig. 1. (a) Chemical structures of used materials PBDTTT-C, P3HT, and PC₇₁BM; and (b) schematic structure of binary (P3HT:PC₇₁BM) and ternary (P3HT:PBDTTT-C:PC₇₁BM) blend PSCs.

to develop ternary blend BHJ PSCs [24,25]. The efficiency of P3HT:PCBM based solar cells is limited due to the following factors: (i) limited light harvest by P3HT due to a relatively high band gap (1.9 eV); (ii) low V_{oc} of approximately 0.6 V that is attributed to the small energy difference between the highest occupied molecular orbital (HOMO) of P3HT and the lowest unoccupied molecular orbital (LUMO) of PCBM [26]. The narrow band gap materials are considered as the best candidate materials to compensate the lower energy photon harvest [27–29]. The selection of narrow band gap material for PCE improvement of BHJ PSCs based P3HT:PCBM should meet the following rules: (i) narrow band gap material has high carrier mobility; (ii) the HOMO and LUMO of narrow band gap material should locate at between the corresponding values of P3HT and LUMO of PCBM, which could enhance the efficiency of charge transfer between two donors and exciton dissociation [30–33]. Recently, Hou et al. reported a narrow band gap polymer poly[(4,8-bis-(2-ethylhexyloxy)-benzo[1,2-b:4,5-b']dithiophene)-2,6-diyl-alt-(4-(2-ethylhexanoyl)-thieno[3,4-b]thiophene)-2,6-diyl] (PBDTTT-C), which has the HOMO and LUMO levels of -5.12 eV and -3.55 eV [34–36]. Polymer PBDTTT-C has a strong absorption in the range of 650–800 nm, is considered as a promising candidate second donor for P3HT:PCBM system. In our knowledge, the research on ternary blend BHJ PSCs based P3HT:PBDTTT-C:PCBM as the active layer has rarely reported. In the paper, the PCE of the ternary blend BHJ PSCs has been improved to 2.48%, with 27% improvement compared with the binary blend P3HT:PCBM BHJ PSCs.

2. Experimental section

The indium tin oxide (ITO) glass substrates (sheet resistance $15 \Omega/\square$) were cleaned consecutively in ultrasonic baths containing acetone, ethanol and de-ionized water and dried by high pure nitrogen gas. The pre-cleaned ITO substrates were then treated by UV-ozone for 10 min in order to further clean the substrates and improve the work function of ITO substrates. An ultrathin layer of poly-(3,4-ethylenedioxythiophene)-poly-(styrenesulfonate) (PEDOT:PSS) (purchased from H.C. Starck Co. Ltd.) was spin-coated on the ITO substrates under 3000 rpm for 40 s. Then PEDOT:PSS coated ITO substrates were dried in air at 120°C for 10 min. The polymer materials PBDTTT-C, P3HT and [6,6]-phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM) were dissolved in chlorobenzene with a concentration 20 mg/ml, respectively. The doping ratio of donor materials P3HT and PBDTTT-C to acceptor material PC₇₁BM was kept 1:1, and the content of PBDTTT-C in the donor materials were increased from 0 to 30%. The addition of the 3 vol%

1,8-diiodooctane (DIO) was doped into mixed solutions, then they were used to spin-coat the active layers at rates of 1400 rounds per minute (RPM). The active layer was pre-annealed at 70°C for 10 min in a high nitrogen glove box. The 0.8 nm interfacial layer LiF was deposited under 10^{-4} Pa vacuum conditions, which was monitored by a quartz crystal microbalance. An aluminum cathode layer of about 100 nm was deposited on the active layer under 10^{-4} Pa vacuum conditions. The active area is about 9 mm^2 , which is defined by the vertical overlap of ITO anode and Al cathode.

The absorption spectra of films were measured with a Shimadzu UV-3101 PC spectrometer. The current–voltage characteristics of PSCs were measured using a Keithley 4200 semiconductor characterization system and ABET Sun 2000 solar simulator. Photoluminescence spectra were measured by a Perkin Elmer LS-55 spectrophotometer. The external quantum efficiency (EQE) spectra were measured on Zolix Solar Cell Scan 100. The morphology of films was investigated by atomic force microscopy (AFM) using a multimode Nanoscope IIIa operated in tapping mode. The chemical structures of used materials and schematic diagram of cell configuration are shown in Fig. 1.

3. Results and discussion

The absorption spectra of pristine of P3HT, PBDTTT-C, PC₇₁BM and ternary blend films with different PBDTTT-C proportions were measured. The normalized absorption spectra of P3HT, PBDTTT-C and PC₇₁BM are shown in Fig. 2a. PC₇₁BM has two apparent absorption peaks at 375 nm and 480 nm, which widens the active layer absorption in the shorter wavelength range. The absorption spectra of the two polymers show an apparent complementary absorption in the range from 400 nm to 800 nm, which are ideal constituent for ternary BHJ PSCs. In order to confirm the widen absorption range into near infrared region (NIR) induced by doping PBDTTT-C, absorption spectra of ternary blend films with different PBDTTT-C proportions were measured and are shown in Fig. 2b. It is obvious that the relative absorption intensity in the region of 650–800 nm was increased along with the increase of PBDTTT-C proportion in donors. It is interesting that an obvious rise of absorption intensity in whole absorption range is observed when the proportion of PBDTTT-C in donors reaches to 6%. Meanwhile, the relative absorption intensity of P3HT molecules does not significantly change with PBDTTT-C proportion in donors from 9% to 15%, but sharply decrease when proportion of PBDTTT-C in donors exceeds 18%. The decreased absorption intensity of P3HT molecules should be attributed to the disordered molecular arrangement and the relative decrease of P3HT proportion induced by the

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