Contents lists available at ScienceDirect

Organic Electronics

Efficient ternary blend polymer solar cells with a bipolar diketopyrrolopyrrole small molecule as cascade material

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ABSTRACT

We present a ternary strategy to enhance the power conversion efficiency (PCE) of bulk heterojunction polymer solar cells (PSCs) with a bipolar small molecule as cascade material. A bipolar diketopyrrolopyrrole small molecule ($F(DPP)_2B_2$), as the second electron acceptor, was incorporated into poly(3-hexylthiophene) (P3HT): [6,6]-phenyl-C_{61}-butyric-acidmethyl-ester ($PC_{61}BM$) blend to fabricate ternary blend PSCs. The introduction of the bipolar compound $F(DPP)_2B_2$ can not only broaden the light absorption of the active layer because of its absorption in near infrared region but also play a bridging role between P3HT and $PC_{61}BM$ due to the cascaded energy level structure, thus improving the charge separation and transportation. The optimized ternary PSC with 5 wt% $F(DPP)_2B_2$ content delivered a high PCE of 3.92% with a short-circuit current density (J_{sc}) of 9.63 mA cm^{-2}, an open-circuit voltage (V_{oc}) of 0.62 V and a fill factor (FF) of 64.90%, showing an 23% improvement of PCE as compared to the binary systems based on P3HT:$PC_{61}BM$ (3.18%) or P3HT:$F(DPP)_2B_2$ (3.17%). The results indicate that the ternary PSCs with a bipolar compound have the potential to surpass high-performance binary PSCs after carefully device optimization.

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1. Introduction

Bulk heterojunction (BHJ) polymer solar cells (PSCs) have been envisioned to be a promising energy conversion technology which offers the opportunity for cheap, flexible, transparent, lightweight and mass-producible devices to harvest solar energy [1–4]. In recent years, researchers have paid a great deal of attention to the research and development of BHJ PSCs, leading to a considerable progress in power conversion efficiency (PCE) that has exceeded 10% for single-junction cells [5–7]. However, despite the significant breakthrough achieved, further performance enhancement is required to ensure a bright industrial future for BHJ PSCs.

It is generally believed that the photovoltaic performance of BHJ PSCs is still limited by many factors, including low charge carrier mobility and insufficient light absorption. In order to overcome the absorption limitation, various effective strategies have been carried out, such as the development of novel narrow bandgap photoactive materials [8–10], plasmonics based light trapping approaches [11–13] and the innovation of tandem configurations [14–17]. Recently, an elegant alternative strategy named the ternary systems containing two donors and one acceptor (or one donor

and two acceptors) are attracting more and more interests due to their potentials to expand the spectral absorption range of organic semiconductors and improve the photon harvesting, thereby providing an effective route in achieving a higher short-circuit current density (J_{sc}) and thus a higher PCE [18]. Besides, the ternary blend PSCs can maintain the simplicity of the processing conditions used for single active-layer cells rather than the demanding challenging processing of multi-junction solar cells for spectrally broad light harvesting.

Through persistent investigation [19–24], to date, PCEs of exceeding 8% have been achieved for ternary blend PSCs. For instance, Yu et al. reported a ternary blend PSC containing two donor polymers of polythieno[3,4-b]-thiophene/benzodithiophene (PTB7) and poly-3-oxothieno[3,4-d] isothiazole-1,1-dioxide/benzo dithiophene (PID2), and [6,6]-phenyl C71 butyric acid methyl ester ($PC_{71}BM$) as an acceptor with a PCE of 8.22% [25]. Zhan et al. used indene-C_{60} bisadduct (ICBA) as a second electron-cascade acceptor material in PSCs based on the PTB7:$PC_{71}BM$ blend and achieved a best PCE of 8.24% [26]. Wei et al. designed and fabricated a new ternary organic solar cell, which contains a donor–acceptor type polymer and a novel small molecule. The synergistic effect of small molecules and polymers in ternary system led to a maximum PCE of 8.40% at the optimized ratio of ternary blend [27]. These high efficiency records of ternary solar cells are all based on the highly efficient low bandgap polymers as host donors which are

expensive and frequently complex to scale up. On the other hand, poly(3-hexylthiophene) (P3HT), as the most-studied and most-used donor material for PSCs, possess many advantages such as high crystallinity, relatively good charge-transport properties, defined quality and reasonable price [28]. More importantly, BHJ PSCs based on blend of P3HT and PCBM can be easily processed and made relatively thick (~300 nm) film, which are important for fabrication of large area flexible solar modules [29–31]. Due to all these advantages, further improving P3HT-based solar cells by ternary concept has continued to an area of immense interests. So far, various types of materials such as low bandgap polymers, small molecules, dyes or nanoparticles have been utilized as a third component in ternary P3HT-based solar cells with PCEs of 3–5% [32–35]. Despite of the considerable efforts devoted to the ternary blend PSCs, there are rather a limited number of material systems that have been shown to deliver an enhanced PCE. Moreover, the third components added were commonly functioned as the additional donor material for extending the light harvesting in the solar spectrum rather than the acceptor. The effect of acceptors, especially bipolar materials, as the third component in ternary blend PSCs on photovoltaic performance is still not fully understood.

Recently, we designed and synthesized a new diketopyrrolopyrrole small molecule (F(DPP)$_2$B$_2$) with bipolar charge-transporting property [36]. This molecule shows intense absorption in the range of 550–700 nm which is complement well with that of P3HT and exhibits suitable the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels matching perfectly those of PCBM and P3HT. Furthermore, when it is used as either an acceptor blended with P3HT or a donor blended with PCBM, the resulting organic solar cells demonstrate good PCEs over 3% [36].

In this work, F(DPP)$_2$B$_2$ was introduced as a cascade material into P3HT:[6,6]-phenyl-C$_{61}$-butyric-acidmethyl-ester (PC$_{61}$BM) based PSCs to form a ternary system. Due to its high absorption coefficient and intense absorption in the near infrared range, F(DPP)$_2$B$_2$ can compensate the light harvesting of P3HT in the solar spectrum for an improved J_{sc}. On the other hand, the open-circuit voltage (V_{oc}) can be increased by the addition of F(DPP)$_2$B$_2$ because of its higher LUMO energy levels relative to PC$_{61}$BM. Meanwhile, the cascaded energy level structure of P3HT:F(DPP)$_2$B$_2$:PC$_{61}$BM can also enhance the exciton dissociation and the charge carrier transportation. As a result, the obtained optimal ternary PSC with 5 wt% content of F(DPP)$_2$B$_2$ exhibits a high PCE of 3.92%, which is ~23% improvement of efficiency as compared to that of 3.18% for the binary P3HT:PC$_{61}$BM devices. We demonstrated, for the first time, efficient ternary PSCs with a bipolar small molecule as the cascade material and we attributed the enhanced performance of the ternary PSCs to a synergistic effect of both the improved light absorption and the better charge separation and transportation induced by the third bipolar component.

2. Experimental

2.1. Materials

P3HT with a molecular weight (Mn) of 40,000 Da was obtained from Rieke Metals. PC$_{60}$BM was purchased from 1-material. F(DPP)$_2$B$_2$ was synthesized in our laboratory according to our previous reported procedure [36]. All the solvents were commercially available and used as received.

2.2. Device fabrication

The devices were fabricated on commercially available indium tin oxide (ITO)-coated glass substrates. Glass/ITO substrates were pre-cleaned with a detergent, ultrasonicated in deionized water, acetone and isopropyl alcohol consecutively every 15 min, and then dried in an oven. After treatment in an ultraviolet ozone generator for 15 min on the substrates, a thin layer of 40 nm PEDOT:PSS was spin-coated on the substrates at 3000 rpm for 40 s and baked at 140 °C for 10 min. The ternary blends of P3HT, PC$_{61}$BM, and F(DPP)$_2$B$_2$ with different ratios were dissolved in chlorobenzene with a total concentration of 40 mg ml^{-1} and stirred for 12 h before use. The weight ratio of F(DPP)$_2$B$_2$ in electron acceptors (PC$_{61}$BM and F(DPP)$_2$B$_2$) is 0, 2.5, 5, 10, 15, 20, or 30 wt%, and the weight ratio of the donor to the acceptor was kept the constant as 1:0.8. The ternary blend solution was spin-coated at 1000 rpm for 60 s in a nitrogen glovebox to form a photoactive layer. Subsequently, a 100 nm thick aluminum layer was evaporated through a shadow mask to define the active layer area of the devices (~5.4 mm^2) and form the top cathode. Finally, all the devices were treated with post-annealing at 200 °C for 5 min before testing.

2.3. Film and device characterizations

The absorption spectra were recorded on a UV-Visible spectrophotometer (UV-2450, Shimadzu Corporation, Japan). The AFM images were taken by a Veeco Multimode atomic force microscopy in the tapping mode. The steady-state PL spectra were taken on a FluoroMax-4 HORIBA Jobin Yvon spectrofluorometer. The X-ray diffraction patterns were recorded at a scan rate of 2 deg/min on the Rigaku D/max-2550PC X-ray diffractometer with Cu Kα radiation (1.5406 nm). The J–V curves were measured with Keithley 236 measurement source units at room temperature in air. The photocurrent was measured under a calibrated solar simulator (Abet 300W) at 100 mW cm^{-2}, and the light intensity was calibrated with a standard Si photovoltaic reference cell. External quantum efficiency (EQE) spectrum was measured with Stanford lock-in amplifier 8300 unit.

3. Results and discussion

The chemical structures of P3HT, F(DPP)$_2$B$_2$ and PC$_{61}$BM are shown in Fig. 1a. The cascade energy levels of the three materials are presented in Fig. 1b. We first fabricated the ternary blend BHJ solar cells based on the mixtures of P3HT:F(DPP)$_2$B$_2$:PC$_{61}$BM and the control binary P3HT:PC$_{61}$BM based BHJ solar cell under the same conditions with a conventional structure of ITO/PEDOT: PSS/Active layer/Al (as illustrated in Fig. 1c). The overall donor to acceptor ratio was kept at 1:0.8 in this work. Fig. 1d shows the typical current density versus voltage (J–V) characteristics of the binary and ternary PSCs under AM 1.5 G illumination at 100 mW cm^{-2} and the related photovoltaic parameters are summarized in Table 1. The reference device based on P3HT:PC$_{61}$BM exhibited an average PCE of 3.18% with an open-circuit voltage (V_{oc}) of 0.62 V, a J_{sc} of 8.27 mA cm^{-2} and a fill factor (FF) of 61.95%. As described in Fig. 1d, it is apparent that the V_{oc}, J_{sc}, and FF of the ternary PSCs are significantly affected by the weight ratio (2.5, 5, 10, 15, 20 and 30 wt%) of F(DPP)$_2$B$_2$ in electron acceptor. The V_{oc} increased slightly with increasing F(DPP)$_2$B$_2$ content due to the higher LUMO energy level of F(DPP)$_2$B$_2$ relative to that of PC$_{61}$BM. The J_{sc} was increased in the beginning with the increase of F(DPP)$_2$B$_2$ ratio (≤20 wt%) in acceptors and then decreased as the F(DPP)$_2$B$_2$ ratio exceed 20 wt%. Meanwhile, the FF and PCE were also increased first and then decreased with increasing the F(DPP)$_2$B$_2$ content. A best PCE of 3.92% was achieved for the ternary PSCs with 5 wt% F(DPP)$_2$B$_2$ content in the acceptor, which is attributed to the simultaneous enhancement of J_{sc} (9.63 vs 8.27 mA cm^{-2}) and FF (64.90% vs 61.95%) compared with the