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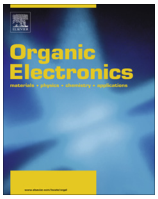

Control over fibril width via different solubility additives for diketopyrrolopyrrole-based photovoltaic devices

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ABSTRACT

Control over polymeric bulk heterojunction (BHJ) morphology is one of the key factors in obtaining high-efficiency devices. The domain size influence on device performance is widely considered critical. In this paper, the fibril width of 3,6-bis-(thiophen-2-yl)-N,N′-bis(2-octyl-1-dodecyl)-1,4-dioxo-pyrrolo[3,4-c]pyrrole and thieno[3,2-b]thiophene (PDBT-TT):[6,6]-phenyl-C_{71}-butyric acid methyl ester ($PC_{71}BM$) blend thin film was adjusted by different processing additives. By decreasing the solubility of PDBT-TT in different additives, the fibril width can be decreased from 65.7 nm to 14.8 nm. It is possible that the PDBT-TT seed-crystallite nuclei concentration is higher in the relatively low solubility solvents than that in the relatively high solubility solvents, thus leading to the formation of narrower fibrils. The PDBT-TT/PC71BM narrow fibrillar interpenetrating network structure was beneficial to exciton separation and charge transport processes. As a result, the solar cell with the narrowest fibril width has a higher short circuit current (J_{sc}) and fill factor (FF), thus achieving optimized device performance from less than 1% to 4.75%.

1. Introduction

Polymer solar cells (PSCs) based on bulk heterojunction (BHJ) materials comprising conjugated polymers as electron donor and fullerene derivatives as electron acceptor are currently regarded as the most promising organic photovoltaic (OPV) devices. To achieve high device performance, an interpenetrating networks structure with length scale of 10–20 nm should be formed by donor and acceptor components [1,2]. To achieve this morphology, approaches including thermal annealing [3] and solvent annealing [4–6], the use of different solvents [7,8] and the use of additives [9–12] have been adopted.

In recent years, low bandgap diketopyrrolopyrrole (DPP)-based polymers have achieved success in OPVs [13,14]. Considering that low band gap DPP-based polymers could absorb over a large range of solar spectrum, and their high charge carrier mobility would decrease the recombination of the holes and electrons [14–16], they are excellent donor materials in OPVs. For the as-cast blend films, DPP-based polymers and [6,6]-phenyl-C71-butyric acid methyl ester ($PC_{71}BM$) tend to form large size aggregates, thus the device performance of these polymers strongly depends on the processing conditions [17–20]. Russell et al. cast a copolymer of diketopyrrolopyrrole and quaterthiophene (pDPP):PC71BM blends from a DCB/$CHCl_3$ solvent mixture. They found that a nanofibrillar structure was formed and they demonstrated that pDPP initially crystallized into a fibrous network surrounded by a continuous matrix containing pDPP and $PC_{71}BM$ [21]. By processing additives or solvent mixture, fibrillar network structure can be obtained in general [22–24]. What's more, the fibrillar microstructure including fibril length, fibril width, domain purity and domain size has a great effect on the performance of the solar cells [25,26]. Among them, the fibril width is particularly important in promoting the separation of excitons [27]. Janssen et al. studied six different DPP-based polymers and concluded that the width of the DPP-based polymer fibrils was an important factor contributing to the efficiency of charge generation. They thought the width was controlled by the solubility of the polymer in the host solvent [28]. Therefore, synthetic methods such as changing the molecular main chain or side chain could adjust the width of the fibrils. However, compared to the complex synthetic methods, the use of physical means to control the fibril width of DPP-based polymer:$PC_{71}BM$ system is more convenient, and the physical means of quantitative regulation of fibril width rarely reported.

Herein, we adjusted the width of 3,6-bis-(thiophen-2-yl)-N,N′-bis(2-octyl-1-dodecyl)-1,4-dioxo-pyrrolo[3,4-c]pyrroleandthieno

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[3,2-b]thiophene (PDBT-TT) fibrils in blend films by processing selective additives. It is generally believed that additives should selective dissolve the fullerene component. However, how the solubility of polymers in additives effect on the morphology of blend films is unclear. Here we show the width of the fibrils can be adjusted by changing the solubility of PDBT-TT in the additives. A lower solubility resulted in much narrower fibrils. Narrower fibrils showed smaller phase separation size and led to better separation efficiency of excitons. A higher fill factor (FF) and an increased short circuit current (J_{sc}) were obtained with the additives with the lower solubility of PDBT-TT. Consequently, the BHJ solar cells with a power conversion efficiency (PCE) of 4.75% was obtained, with a great improvement compared with the reference device (PCE = 0.66%).

2. Experimental section

2.1. Materials

PDBT-TT (M_n = 29 K, PDI = 3.9) was purchased from Solarmer Inc. $PC_{71}BM$ was purchased from American Dye Source. The chemical structures of them are shown in Fig. 1(a). Chlorobenzene (CB), 1,2-dichlorobenzene (ODCB), 1-chloronaphthalene (CN) and 1,8-diiodooctane (DIO) were purchased from Sigma Aldrich. 1-Benzothiophene (BT) and 3,4-dimethylanisole (DMA) were purchased from Alfa Aesar. 1,2-Dimethoxybenzene (ODAB) was purchased from Acros Organics. 1,2,4-Trimethoxybenzene (TAB) was purchased from TCI Shanghai. 1,2,4-Trichlorobenzene (TCB) was purchased from Sinopharm Chemical Reagent Co., Ltd., China. The chemical structures of these solvents are shown in Fig. 1(b). All of the solvents are used without further purification.

2.2. Sample preparation

The pristine solution was get by dissolving 6 mg PDBT-TT and 18 mg $PC_{71}BM$ in 1 ml CB at 70 °C for 2 h. After stirring overnight, 1%, 3%, 5%, 10%, 25% (v/v) DMA were added to get the solutions with different volumes of DMA. The poly(ethylenedioxythio phene):poly(styrenesulfonate) (PEDOT:PSS) layer with a thickness of 25 nm was spin-coated on cleaned glass substrates and dried at 140 °C in a vacuum for 30 min. Then, solutions without or with different volumes of DMA were spin-coated. After stand for 20 min, all the films were annealed at 100 °C for 10 min to get rid of the additives, then we got blend films prepared from different volumes of DMA. Blend films prepared from 5% different additives were gotten in the same way.

2.3. Characterization

We used transmission electron microscopy (TEM) and atom force microscopy (AFM) to characterize the morphology of the active layer. TEM experiments were performed on a TEM-1011 (JEOL Co., Japan) with an accelerating voltage of 100 kv. The samples were made by floating the film on the water and then transferring onto a copper grid. AFM images were obtained using a SPI3800N AFM (Seiko Instruments Inc., Japan) with a si tip with a spring constant of 2 N m^{-1}.

Photoluminescence (PL) spectra obtained from a Labram HR800 spectrometer (Horiba Jobin Yvon) equipped with an Olympus BX41 microscope in the backscattering geometry was used to assess the extent of phase separation. The confocal hole and the slit width were fixed at 200 μm. We used a 632.8 nm He–Ne laser to excite the films.

The UV–vis absorption spectroscopy was measured by a Lambda 750 spectrometer (Perkin-Elmer, Wellesley, MA).

To study the crystallinity of the blend films, out-of-plane grazing incidence X-ray diffraction (GIXD) using a Bruker D8 Discover reflector with an X-ray generation power of 40 kV tube voltage and 40 mA tube current was carried out. The films were measured at a step-scan rate of 0.05° per 5 s with the scattering angle 2θ ranging from 2° to 30°. The sizes of the samples for GIXD were

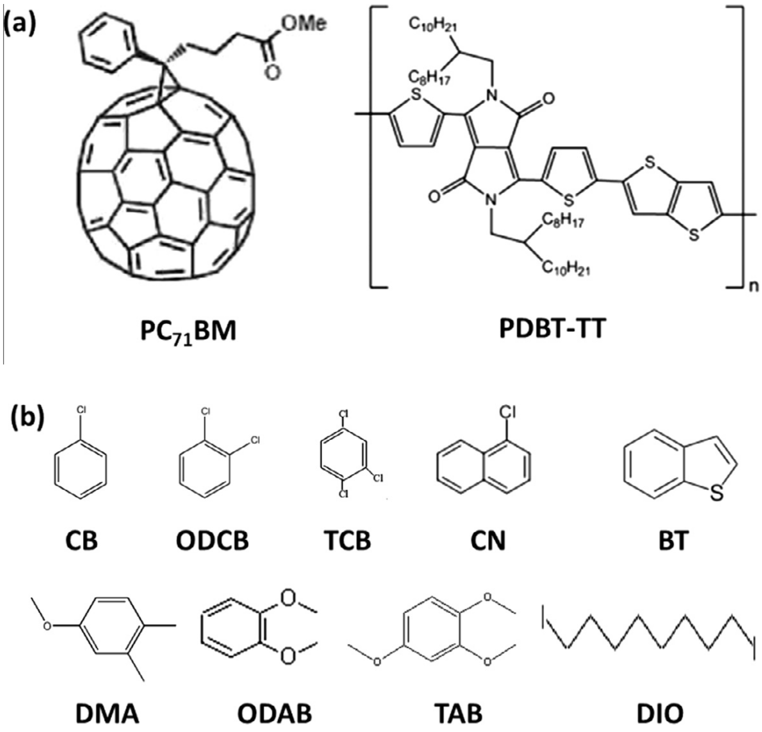

Fig. 1. (a) Chemical structures of $PC_{71}BM$ (left) and PDBT-TT (right), (b) chemical structures of the host solvent CB and the additives ODCB, TCB, CN, BT, DMA, ODAB, TAB and DIO.