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Improve exciton generation and dissociation by increasing fullerene content in the mixed phase of P3HT/fullerene

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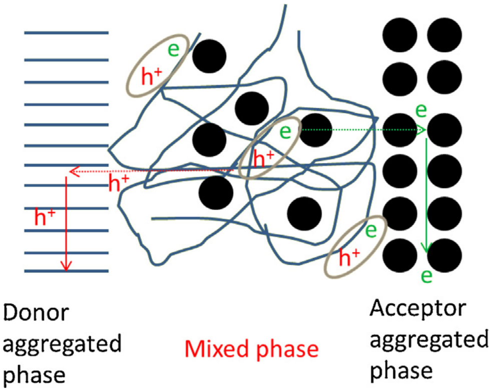
HIGHLIGHTS

- Different amount of fullerene in the mixed phase of P3HT/fullerene was achieved.
- More fullerenes in the mixed phase induced more interface, bigger ΔE value and higher local carrier mobility.
- More fullerenes in the mixed phase were beneficial to the exciton generation and dissociation.
- Donor and acceptor should have good miscibility to increase the fullerene content in mixed phase.

GRAPHICAL ABSTRACT

Different amount of fullerene in the mixed phase of poly(3-hexylthiophene) (P3HT)/fullerene was achieved by changing the ratio of two fullerenes ([6,6]-phenyl-C71-butyric acid methyl ester ($PC_{71}BM$) and its bisadduct bis-$PC_{71}BM$), which have different miscibility with P3HT. When the content of $PC_{71}BM$ increasing from 0% to about 60%, the mixed phase containing more fullerenes. Higher content of fullerenes in the mixed phase was beneficial to the exciton generation and dissociation due to the enlarged donor/acceptor (D/A) interface, increased ΔE value and higher local charge carrier mobility.



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ABSTRACT

Designing polymeric bulk heterojunction (BHJ) morphology with good exciton separation efficiency is one of the key factors in obtaining high-efficiency polymer solar cells (PSCs). Cascaded energy formed by the energy level difference (ΔE) between aggregated phase and the mixed phase is thought to encourage spatial separation of the geminate charge pair. However, how the composition of the mixed phase affects the exciton generation and dissociation process is still unknown. In this paper, different amount of fullerene in the mixed phase of poly(3-hexylthiophene) (P3HT)/fullerene was achieved by changing the ratio of two fullerenes ([6,6]-phenyl-C71-butyric acid methyl ester ($PC_{71}BM$) and its bisadduct bis-$PC_{71}BM$), which have different miscibility with P3HT. When the content of $PC_{71}BM$ increasing from 0% to about 60%, the mixed phase containing more fullerenes. More donor/acceptor (D/A) interface was formed, and the

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ΔE value also increased from 0.19 eV to 0.23 eV. As a result, the maximum exciton generation rate (G_{max}) increased from 5.36×10^{27} m^{-3}/s to 6.48×10^{27} m^{-3}/s, and the exciton dissociation probabilities increased from 47% to 81%. Thus, perfect three-phase morphology for high performance solar cells was proposed, in which not only the donor and acceptor have good crystallinity to form interpenetrating network but also have good miscibility with each other to increase the fullerene content in mixed phase.

1. Introduction

The process of charge photogeneration in polymer/fullerene blend films for polymer solar cells (PSCs) can be summarized in four steps: the forming of exciton by exciting an electron from the donor HOMO to its LUMO through photoabsorption, exciton diffuse to a donor/acceptor (D/A) interface, the electron transfer to the LUMO of the acceptor material and form a charge transfer (CT) state, and the dissociated charges transport to the electrodes [1,2]. To improve the efficiency of exciton dissociation, the length scale for self-assembly must be of order 10–20 nm to allow the excitons to reach the interface [3,4] and the energy offset should be greater than the Coulomb binding energy of the exciton ($E_B{}^{exc}$) to form the CT states [1,5]. However, as the donor and acceptor molecules are physically adjacent at the charge separation interface, the electron and hole in the initial electron transfer step are very close to each other (0.5–1 nm). Thus, the electron and hole still exhibit a significant Coulomb attraction. This Coulomb attraction is referred as the charge-transfer-state binding energy ($E_B{}^{CT}$) and estimated to be in the range 0.1–0.5 eV. The $E_B{}^{CT}$ is hard to overcome by the thermal energy (0.025 eV) and represents a large energetic barrier to charge photogeneration at D/A interfaces [1,6].

In recent years, people have turned attentions to the efficacy of ubiquitous molecular mixing between fullerenes and polymers (form the mixed phase) and crystallization on the exciton dissociation progress. Many groups have shown that the crystallization of fullerene or polymer could be a driver of charge separation [7–9]. PSCs with polymer and fullerene aggregated phase as well as the mixed phase can achieve good performance [10,11]. This results may due to the fact that the mixed phase has been reported to have energy levels that are shifted with respect to the aggregated phases, forming an energy cascade that assists the generation of free charge [7,12,13]. Groves used the Kinetic Monte Carlo (KMC) model to simulate the cascaded energy heterojunction (the cascade could be the mixed phase or a third component), and found that cascaded heterojunction encouraged spatial separation of the geminate charge pair. The HOMO edge offset and the thickness of the cascade layer (<10 nm) had a big effect on the charge separation efficiency [12]. McGehee et al. also studied the role of the mixed phase in assisting geminate splitting by using KMC simulations of idealized trilayer (pure donor/mixed region/pure acceptor) morphologies. They demonstrated that a 200 meV energetic offset between the mixed and pure regions in the simulated trilayer devices greatly decreased the local mobilities and CT state lifetimes required for efficient charge generation [14]. To design cascaded PSCs, one should think about the ratio of aggregated and cascade phase to control the thickness of the cascade layer, as well as the difference of HOMO (LUMO) value (ΔE) between donor (acceptor) and cascade material. The ratio of aggregated phase and cascade phase may be changed by control the crystallinity of the donor [15,16], the miscibility and ratio of D/A [9,17,18]. While the ΔE value could be obtained by adding a third component with suitable energy level [19–21]. However, how the composition of the mixed phase affects the exciton generation and dissociation process is still unknown, and establishing the relationship between the mixed phase composition and exciton dissociation process is necessary to further improve the device performance.

In this paper, we studied the effect of the composition of the mixed phase on charge generation and dissociation process. The composition of the mixed phase was adjusted by changing the ratio of [6,6]-phenyl-C71-butyric acid methyl ester ($PC_{71}BM$) and its bisadduct bis$PC_{71}BM$ in poly(3-hexylthiophene) (P3HT)/bis-$PC_{71}BM$/$PC_{71}BM$ system. The amount of aggregated P3HT phase were controlled the same by processing additives [22]. Our results show that higher amount of fullerene in the mixed phase could achieve higher exciton generation rate and better exciton dissociation probabilities.

2. Experimental section

2.1. Materials

Regioregular HT-HT P3HT (>98.5%; HT: head-to-tail; $M_w = 68$ kDa) was purchased from Nichem Fine Technology Co. Ltd. $PC_{71}BM$ was purchased from American Dye Source. Bis-$PC_{71}BM$ was purchased from 1-Material Inc. The chemical structures of them are shown in Fig. 1. 1,2-Dichlorobenzene (ODCB) and 1-chloronaphthalene (CN) were purchased from Sigma Aldrich. All of the solvents are used without further purification.

2.2. Sample preparation

The solutions of P3HT/bis-$PC_{71}BM$ (P3HT/$PC_{71}BM$) were got by dissolving the same amount of P3HT and bis-$PC_{71}BM$ ($PC_{71}BM$) in ODCB with or without 3% (v/v) CN at 70 °C for 2 h. The concentration of P3HT was 10 mg/ml. After stirring overnight, solutions of P3HT/bis-$PC_{71}BM$/$PC_{71}BM$ with different ratio of bis-$PC_{71}BM$ and $PC_{71}BM$ were got by mixing the P3HT/bis-$PC_{71}BM$ and P3HT/$PC_{71}BM$ solutions (ODCB + 3% CN as the solvent) at different ratio. These solutions were heated under stirring at 70 °C for 30 min before used. The poly(ethylenedioxythiophene):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, blend films were got by spin-coating the solutions on the PEDOT:PSS layer.

2.3. Characterization

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 1.5 cm × 1.5 cm cut from the middle of 2.5 cm × 2.5 cm blend films. All the samples had almost the same thickness.

We used transmission electron microscopy (TEM) and atom force microscopy (AFM) to characterize the morphology of the active layer. AFM images were obtained by using a SPI3800N AFM