

Review

Morphology Optimization in Ternary Organic Solar Cells*

Lin Zhang and Wei Ma**

State Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University, Xi'an 710049, China

Abstract Ternary organic solar cells have drawn great attention because the highest power conversion efficiencies have reached ~12%, showing a promising prospect for the future applications. However, most reported ternary solar cells focus on the increase of light absorption and the optimization of energy alignment, but ignore the importance of morphology. Herein, we summarize the morphology optimization on the ternary blends with different structural aspects, such as controlling crystallinity, crystal orientation, domain size, and domain purity. Furthermore, the fundamental mechanism of ternary solar cells which is related to the morphology has been described. The efforts here will provide a guiding role for the morphology optimization on the ternary solar cells in the future.

Keywords Ternary organic solar cells; Morphology; Crystallization; Phase separation

INTRODUCTION

Harvesting and using clean energy is one of the important projects for scientific research. The solar cell is a clean energy technology that transforms the solar energy into electricity. It is of great significance to alleviate the current energy crisis and environmental pollution. At present, novel photovoltaic technologies, including inorganic thin film solar cells (such as polycrystalline silicon solar cells, monocrystalline silicon solar cells, cadmium telluride solar cells, dye-sensitized solar cells) and organic solar cells have attracted much attention worldwide^[1–4]. The organic solar cells can be categorized as polymer solar cells and small-molecule solar cells based on their molecular weight. Currently, several inorganic semiconductor solar cells have been initially commercialized, but the wide applications for these solar cells are limited because of their high cost, high energy consumption and complex manufacturing process. In particular, organic solar cells with bulk-heterojunction (BHJ) are prepared by blending organic materials with fullerene derivatives in a proper proportion^[5–7]. BHJ has drawn significant attention in the past decades due to their light weight, low-temperature solution-processing, good mechanical flexibility, and large area manufacturing^[7–18].

The working principle and device structure of organic solar cells with BHJ are shown in Fig. 1. The active layer containing donor material and acceptor material absorbs photons from sunlight and generates excitons. When the exciton binding energy is less than the energy level difference of electron donor and acceptor, the exciton separates into hole and electron at the interface between donors and acceptors. Then, the hole transmits to anode along the donor domains, and the electron transmits to cathode along the acceptor domains. Finally,

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** Corresponding author: Wei Ma (马伟), E-mail: msewma@xjtu.edu.cn

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holes are collected by anode and electrons are collected by cathode, resulting in the generation of photocurrent and photo-voltage.

Due to the intrinsic narrow absorption window of organic conjugated polymers, the power conversion efficiency (PCE) of organic solar cells is much lower than its inorganic counterpart. However, polymers with different bandgaps and absorption ranges can be coupled to enlarge the absorption window. The concept of tandem solar cell is a successful example, in which two or more sub-cells are linked either in series or parallel to absorb photons in different ranges of solar spectrum^[19–21]. The individual sub-cells work separately in a single BHJ cell configuration. However, tandem design has the major drawback of fabrication complexities. Ternary blend BHJ solar cells (Fig. 1c) are made from the blends of two donors (D) and one acceptor (A) or two acceptors and one donor in order to enlarge the absorption window. As the fundamental device configuration of ternary blend, BHJ is identical to the binary solar cell with the simple fabrication process.

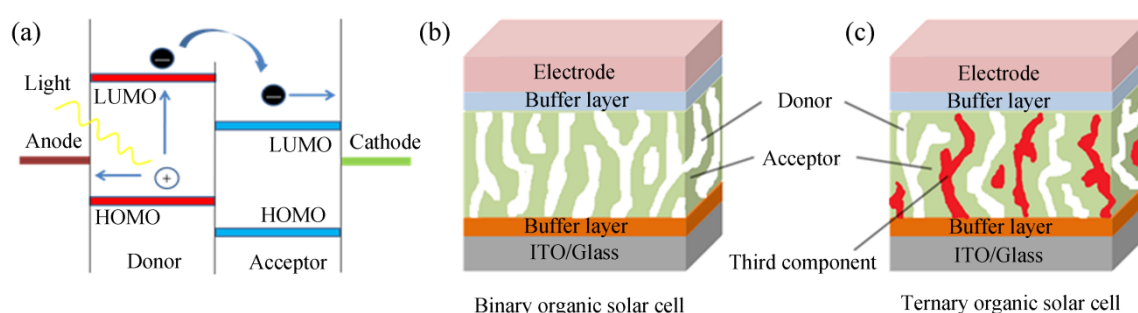


Fig. 1 (a) Working mechanism; (b) Binary device structure and (c) ternary device structure of organic solar cells

The prerequisite of improving photocurrent by using the ternary components strategy is to keep the efficient charge separation and transport properties of single layer devices. Recently, a very interesting result reports that the added third component not only maintains the efficient optoelectronic process, but also improves the efficiency of initial binary blend *via* optimizing the morphology. That is due to the fact that the third component induces the crystallinity of polymer, tune the crystal orientation and optimize the phase separation (domain size and domain purity).

In order to achieve high PCE, the morphology of active layer is required to possess special properties. Firstly, the phase separation size between donor and acceptor domain should be confined because the exciton diffusion length is usually only about 10 nm. If the phase separation size is too large, the exciton will recombine before diffusion and have no effect on photocurrent. Small phase separation offers sufficient D/A interfaces for the exciton dissociation. Secondly, the formation of bicontinuous interpenetrating network structure provides efficient transmission channels for holes and electrons, which in turn increase the charge transfer efficiency^[22–26]. The ideal morphology of active layer for BHJ organic solar cells consists of an interpenetrating network structure (≈ 10 nm lateral dimensions) of electron donor and acceptor materials. It exhibits large interfacial area where excitons generated by photons can split into holes and electrons that are subsequently transported to electrodes^[27, 28]. This scale structure is an essential issue to increase the photovoltaic performance according to the working principle of BHJ organic solar cells. In actual cases, the morphology of BHJ organic solar cell is very complicated. Besides the phase separation size, domain purity is another crucial factor which is critical for the photovoltaic performance. The high domain purity possesses excellent connectivity between donor/acceptor domain and anode/cathode, which exhibits expedite transmission channel and high transfer efficiency for charge carriers. On the contrary, low domain purity resulting in poor connectivity not only hinders the charge transmission but also decreases the transfer efficiency due to the increased recombination rate of charge carriers. Meanwhile, the domain purity is highly related to the crystallization^[25, 29, 30].

In general, conjugated donor polymers possess crystallinity with the main chains arranged regularly in a particular direction. The length of the arranged polymer can reach dozens of nanometer in three-dimensional

space. Crystallinity is one of important parameters in the morphological research of organic solar cells because highly crystalline polymers present many advantages, such as excellent charge mobility and high domain purity. As a more recent concept in the structure of organic solar cells, crystal orientation has been proved to be an important factor that influences the device performance^[30, 31]. A face-on orientation of donor materials is better for charge transport in perpendicular direction to the substrate than edge-on orientation due to the enhanced electronic overlapping of π - π stacking^[24, 32].

Hence, the regulating crystallization, crystal orientation, phase separation size and domain purity are of great significance for optimizing the morphology of active layer and improving the device performance^[6, 24, 33–37]. In recent years, many efforts have been contributed to the processing methods for the morphology optimization of the active layer. The pristine active layer prepared by spin coating method could not reach the thermodynamic equilibrium state. However, many methods exploited by the pioneers provided useful ways to achieve an optimal morphology, such as choosing an appropriate solvent, thermal annealing, solvent annealing, with solvent additives or a third component, and so on^[34, 38–45]. Among them, the morphology optimization by adding a third component into binary blends has not been systematically reported because such a method usually is used to improve the light absorption and alignment of ternary energy level. In this review, we present the morphology optimization by adding a third component into binary system from the morphology point of view. Unfortunately, traditional characterization approaches, such as AFM, SEM, TEM, cannot well characterize the morphology of active layers, especially for the ternary system with an additional component, which is due to the lower contrast of organic materials with similar element composition and electronic cloud density, compared to the inorganic materials. Inspiringly, resonant soft X-ray scattering (R-SoXS) provides a convenient route to observe enhanced scattering contrast and chemical differentiation by tuning the incident X-ray energy to a desired near-edge resonance, without the need for deuteration. It can overcome the drawbacks, such as low contrast between/among different organic components and the lack of three-dimensional (3D) information. It is an important mean to obtain the phase separation information in the active layer of solar cells, and facilitates to understand the microstructure and to establish the relationship between morphology and photoelectric conversion process. In addition, grazing incidence wide-angle X-ray scattering (GIWAXS) is a refined 2D X-ray diffraction (XRD), which can give the in-plane information and out-of-plane information to provide more detailed and more accurate information of the crystallinity and crystal orientation as compared to the XRD. Therefore, the GIWAXS and R-SoXS measurements develop rapidly in recent years for the characterization of internal morphology. By combining the traditional microtechniques of AFM and TEM, GIWAXS and R-SoXS measurements may afford the useful information for analyzing the morphologies and clarify the relationship between the morphology and device performance.

Many morphological characterizations have been discussed in the organic solar cells, but the crystallization, molecular orientation and phase separation are the notable problems that widely exist in the organic solar cells^[23, 27, 28, 46–49]. Therefore, we discuss and summarize the morphology optimization on ternary solar cells by adding a third component.

MORPHOLOGY OPTIMIZATION BY ADDING A THIRD COMPONENT

Crystallization

High crystallinity of polymers (Figs. 2a and 2b) is always desired in organic solar cells to improve the charge transfer and photovoltaic performance. Thus, the crystallinity is one of the most important characters in the morphology optimization, which involves the morphology characterization and the crystallinity of donor materials. High crystallinity of donor materials exhibits regular molecular arrangement, which is beneficial for the fast charge transformation. Moreover, high crystallinity facilitates the formation of bicontinuous interpenetrating network structure and can improve the domain purity in most cases.

For conjugated polymers, the crystallinity of them is usually low due to the high molecular weight (M_w) and dispersity, which is unfavorable to improve PCE of the organic solar cells. The addition of a third component with high crystallinity or as a crystallization nucleating agent into the binary system has been proved to be

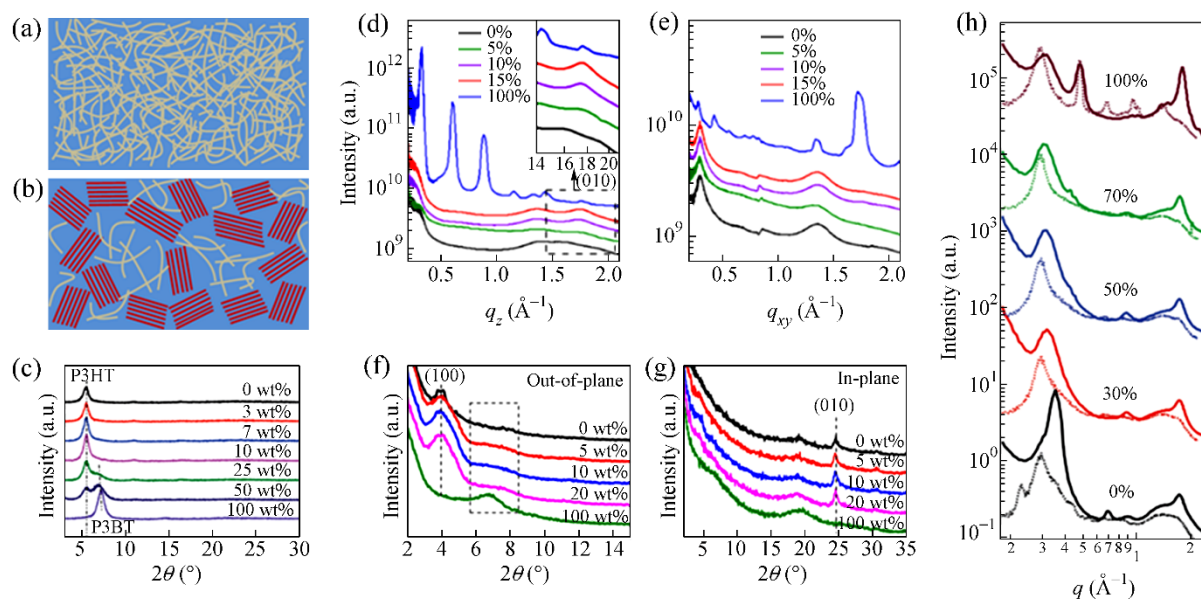


Fig. 2 The diagram of (a) amorphous polymers and (b) high crystallinity polymers; (c) X-ray diffraction patterns of P3HT:P3BT-nw blends at different weight percentages of P3BT-nws (Reprinted from Ref. [52] with permission from The Royal Society of Chemistry); The out-of-plane (d) and in-plane (e) cuts of GIWAXS patterns for the PTB7-Th:*p*-DTS(FBTTH₂)₂:PC₇₁BM film at the different ratio of *p*-DTS(FBTTH₂)₂ ((010) diffraction peak is enlarged in the inset profile) (Reprinted with permission from Ref. [58]; Copyright (2015) American Chemical Society); (f) Out-of-plane and (g) in-plane GIXRD profiles for *p*-DTS(FBTTH₂)₂:P3BT:PC₇₁BM films at different weight ratios of P3BT (Reprinted with permission from Ref. [62]; Copyright (2015) American Chemical Society); (h) The out-of-plane (solid line) and in-plane (dotted line) line-cut profiles of GIWAXS patterns for the PDBT-T1:SdiPBI-Se:ITIC-Th ternary films with different ITIC-Th contents (Reprinted with permission from Ref. [65]; Copyright (2016) American Chemical Society)

an effective strategy and shows great potential to improve the crystallization of the donor in organic solar cells. Poly(3-hexylthiophene):[6,6]-phenyl-C₆₁-butyric acid methyl ester (P3HT:PC₆₁BM)-based organic solar cells were widely studied in the past decades. However, the crystallinity of P3HT is low before thermal annealing. In 2008, a copolymer including thieno-thiophene units (DHPT³) was used as a crystallization nucleating agent in the active layer of P3HT:PC₆₁BM solar cells. The device performance was significantly improved due to the enhanced crystallinity of P3HT^[50]. Similarly, the incorporation of a low bandgap oligomer, oligo(benzo[1,2,5]thiadiazole-*alt*-3,3'-dihexylquaterthiophene) (BT4T) into the P3HT:PC₆₁BM solar cells was also demonstrated to increase the crystallinity of P3HT^[51]. In order to improve the crystallization of P3HT, highly crystalline poly(3-butylthiophene) nanowires (P3BT-nws) were incorporated into the P3HT:PC₆₁BM BHJ solar cell^[52]. The addition of P3BT-nws was found to play the role of nucleating agents to induce the crystallization of P3HT molecules and increase the crystallinity of P3HT, which was evidenced by the analysis of XRD, GIXRD, DSC and TEM. As shown in Fig. 2(c), the specimen with 7 wt% P3BT-nws presents a stronger and more remarkable diffraction peak of P3HT than that of the specimen without P3BT-nws, demonstrating the effect of increased crystallinity of P3HT. Thus, the device with 7 wt% of P3BT-nws exhibited the highest PCE of 4.2%, representing an approximate 40% increase relative to the reference cell without additives, which proved that the crystallization could increase the hole mobility, resulting in more balanced charge transport. Russell *et al.*^[53] added a narrow bandgap polymer of poly[2,6-(4,4-bis-(2-ethylhexyl)-4*H*-cyclopenta[2,1-*b*;3,4-*b'*]-dithiophene)-*alt*-4,7-(2,1,3-enzothiadiazole)] (PCPDTBT) into P3HT:PC₆₁BM blends and studied its influence on the morphology of the active layer. It presented that the addition of PCPDTBT increased the crystallinity of P3HT and phase separation of amorphous PCPDTBT and P3HT, and guided the formation of P3HT fibrils, showing a unique multi-length-scale morphology. The blend consisted of a network

from bundles of well-defined P3HT fibrils, which imbedded in an amorphous mixture of PCBM, PCPDTBT and P3HT. This multi-length-scale morphology was related to the improved device performance of P3HT:PCPDTBT:PC₆₁BM and photophysics of the active layer.

Poly(thieno[3,4-b]-thiophene-*co*-benzodithiophene) (PTB7)^[54] is a narrow bandgap polymer widely used in organic photovoltaic cells. However, the crystallinity of PTB7 is poor and cannot achieve an optimal morphology in the PTB7:PC₇₁BM system. In many cases, the improved photovoltaic performance of PTB7:PC₇₁BM BHJ solar cell is related to the increased crystallinity of PTB7. Zhang *et al.*^[55] reported a ternary solar cell based on PTB7:PC₇₁BM blends. Poly[2,7-(5,5-bis-(3,7-dimethyloctyl)-5*H*-dithieno[3,2-b:2',3'-d]pyran)-*alt*-4,7-(5,6-difluoro-2,1,3-benzothiadiazole) (PDTP-DFBT) with a lower bandgap than PTB7 was demonstrated to improve the crystallinity of PTB7, yielding an increased PCE from 8.08% to 8.60%.

Lu *et al.*^[56] synthesized a polymer of poly(3-oxothieno[3,4-d]isothiazole-1,1-dioxide/benzodithiophene) (PID2), with the similar chemical structure as that of PTB7, and incorporated it into the active layer based on PTB7:PC₇₁BM blends. It was found that PID2 played the role of template for the formation of fibrous structure in PTB7, and improved the crystallinity of PTB7, so as to increase the charge transport and device performance. In addition, the PID2 was incorporated into PTB7-Th:PC₇₁BM system which was another important and widely used narrow bandgap material with poor crystallinity. The PCE of 9.20% for the ternary system was realized as compared to PCE of 7.88% for its binary system^[57].

Besides the high crystallinity conjugated polymer, organic small molecule is also chosen to be a third component to improve the photovoltaic performance due to the excellent crystallization of them with uniform chemical structure. Wei's group and our group^[58] designed a ternary organic solar cell system by combining the characteristics of polymers with an poor crystallinity and small molecules with a high crystallinity. As shown in Figs. 2(d) and 2(e), the (010) peak of PTB7-Th at $q \approx 1.73 \text{ \AA}^{-1}$ in the out-of-plane was enhanced as the 7,7-(4,4-bis(2-ethylhexyl)-4*H*-silolo[3,2-b:4,5-b']dithiophene-2,6-diyl)bis(6-fluoro-4-(5'-hexyl-[2,2'-bithiophen]-5-yl)benzo-[c][1,2,5]thiadiazole) (*p*-DTS(FBTTh₂)₂) small molecules were added into PTB7-Th:PC₇₁BM blends. It indicated that the incorporation of *p*-DTS(FBTTh₂)₂ could improve the crystallization of PTB7-Th, due to the formation of organic alloy as described below. Similarly, because the crystallinity of the D-A polymer containing benzo[1,2-b:4,5-b'] dithiophene and thieno[3,4-c]pyrrole-4,6-dione groups (named as PBDTPD-HT) was insufficient to obtain the interconnecting bicontinuous nanomorphology, a high crystallinity small molecule of BDT-3T-CNCOO was added into PBDTPD-HT:PC₇₁BM blends to promote the crystallization of polymer and tune the crystalline domain size by the same group^[59]. In addition, it facilitated the formation of interpenetrating network structure for high-efficiency charge generation and transport.

Most small molecules in organic solar cells possess high crystallinity, but their crystallinity is dramatically decreased when blending with fullerene derivative in the BHJ organic solar cells. For instance, the crystallinity of pristine *p*-DTS(FBTTh₂)₂ is high, but it decreases remarkably when blending with the acceptor materials of PC₇₁BM. Hence, diiodooctane (DIO) as a solvent additive was widely used in the organic solar cells to solve this problem and improve the donor crystallinity^[60, 61]. Unfortunately, DIO causes the device with lower stability because it is a high boiling point solvent and is not easily to be removed from the film. Considering the circumstances, we propose a simple but effective approach to improve crystallization of small molecular donor without the addition of DIO. A high crystalline conjugated polymer P3BT was incorporated into the *p*-DTS(FBTTh₂)₂:PC₇₁BM system^[62]. It was revealed that the addition of P3BT increased the crystallinity of *p*-DTS(FBTTh₂)₂ by the GIXRD (Figs. 2f and 2g), and P3BT served as the heterogeneous nucleating agent, which induced the crystallization of *p*-DTS(FBTTh₂)₂ to form the interconnected nanofibers throughout the whole film, so as to improve the charge carrier mobility. Moreover, Bazan^[63] found that the addition of a high-molecular-weight insulating polymers of polystyrene (PS) into *p*-DTS(FBTTh₂)₂:PC₇₁BM blends could also increase the crystallinity of small molecule and promote the formation of nanofibers. It is due to the entanglement of the very long PS chains and the interactions between PS and solvent. The interactions result in a longer retention time of solvent, such to improve the crystallization of *p*-DTS(FBTTh₂)₂ and facilitate the evolution of respective *p*-DTS(FBTTh₂)₂ phase and PC₇₁BM phase. The crystallinity is further improved by the

solvent additive of DIO. Polydimethylsiloxane (PDMS) is another widely used insulating polymer. Interestingly, PDMS was added into small molecular solar cells to serve as an additive by Reynolds^[64]. The PDMS increased the nucleating density of small molecules as a role of nucleating agent. Therefore, the crystal size decreased, but the crystallinity increased due to the formation of more crystals with smaller grain size.

Increased crystallinity of donor materials by adding a third component often exhibits a better photovoltaic performance with enhanced short-circuit current density (J_{sc}) and fill factor (FF), because of the higher exciton dissociation efficiency and charge transfer rate. However, in some cases, the reduction of the crystallization could increase the device performance, although it occurred rarely in the field of organic solar cells. Recently, Sun and coworkers^[65] reported a non-fullerene ternary solar cell with a conjugated polymer donor (PDBT-T1) and two non-fullerene acceptors (SdiPBI-Se and ITIC-Th). As shown in Fig. 2(h), the scattering peak of the ternary film with 50% ITIC-Th became weaker than that of the film without ITIC-Th. It is indicated that the addition of ITIC-Th into the PDBT-T1:SdiPBI-Se blends reduced the crystallinity due to the miscible interaction of ITIC-Th and SdiPBI-Se. A high efficiency of 10.3% was achieved at the ITIC-Th ratio of 50% in acceptor. It was one of the highest values in the reported non-fullerene organic solar cells.

Crystal Orientation

Crystal orientation can often be seen in the morphological studies of BHJ organic solar cells and is of great importance for high charge transport efficiency. Three different orientations are shown in Figs. 3(a), 3(b) and 3(c). “End-on” orientation will not be discussed in this article as it is extremely difficult to be achieved in organic solar cells. A face-on orientation with respect to the substrate is considered to be more beneficial to improve charge transport efficiency than edge-on orientation^[31]. In ternary solar cells, the addition of a third component into a binary system could regulate the crystal orientation of active layer. As aforementioned, the crystallization of PTB7-Th is poor, but the PTB7-Th molecules have a preferential face-on orientation with respect to the substrate. For the PTB7:PDTP-DFBT:PC₇₁BM system^[55], the crystal orientation was investigated by GIXRD. As shown in Figs. 3(d), 3(e) and 3(f), the (010) diffraction peaks at $q_z \approx 1.65 \text{ \AA}^{-1}$ in the out-of-plane corresponding to π - π stacking were observed. Meanwhile, the (010) peak of the PTB7:PDTP-DFBT film is stronger and more remarkable than the film without PDTP-DFBT, suggesting that the addition of PDTP-DFBT can improve the molecular ordering and enhance the face-on orientation of PTB7, giving a better device performance.

In the PTB7-Th:*p*-DTS(FBTTH₂)₂:PC₇₁BM ternary solar cell^[58], the 2D GIWAXS images are shown in Figs. 3(g), 3(h) and 3(i). A broad arc-like scattering ($q \approx 1.73 \text{ \AA}^{-1}$) is observed, which arises from the Bragg diffraction of periodic PTB7-Th in the out-of-plane direction corresponding to the π - π stacking peak. There is almost no peak at $q \approx 1.73 \text{ \AA}^{-1}$ in the in-plane direction, indicating that PTB7-Th molecules have a preferred face-on orientation with respect to substrate. However, the *p*-DTS(FBTTH₂)₂ molecules prefer to have an edge-on orientation, due to the obvious (100), (200) and (300) scattering peaks in the out-of-plane and the strong (010) peak in the in-plane direction. Interestingly, the ternary film with 15% *p*-DTS(FBTTH₂)₂ shows a strong and remarkable (010) scattering peak for the polymers at $q \approx 1.73 \text{ \AA}^{-1}$ and almost no (100), (200), (300) scattering peak for small molecules in the out-of-plane direction, indicating that the ternary film has an improved face-on orientation. It leads to the ternary film with a better charge transfer efficiency than both the binary films of PTB7-Th:PC₇₁BM and *p*-DTS(FBTTH₂)₂:PC₇₁BM. Eventually, the device with 15 wt% *p*-DTS(FBTTH₂)₂ achieves the highest PCE of 10.5%.

Recently, we^[66] studied the crystal orientation of the PBDTPD-HT:BDT-3T-CNCOO:PC₇₁BM ternary blends. As shown in Figs. 3(j), 3(k) and 3(l), the PBDTPD-HT:PC₇₁BM specimen has no obvious scattering peak, and the BDT-3T-CNCOO:PC₇₁BM specimen has remarkable (100), (200) and (300) scattering peaks in the out-of-plane direction and (010) in-plane scattering peak, indicating the BDT-3T-CNCOO prefers to have edge-on orientation. However, the film with 40% BDT-3T-CNCOO shows an obvious (010) scattering peak at $q \approx 1.75 \text{ \AA}^{-1}$ in the out-of-plane direction, hinting a face-on orientation. These results reveal the transformation from edge-on to face-on orientation for the BDT-3T-CNCOO small molecules. This orientation manipulation increases the solar cell efficiency from 6.85% to 8.40%.

Domain Size and Domain Purity

Phase separation is an essential problem, not ignorable while optimizing the morphology of organic solar cells. As mentioned above, the optimal phase separation of donor and acceptor is about 10–20 nm. However, most binary blends could not reach this scale structure (Figs. 4a and 4b), so optimizing the phase separation size to

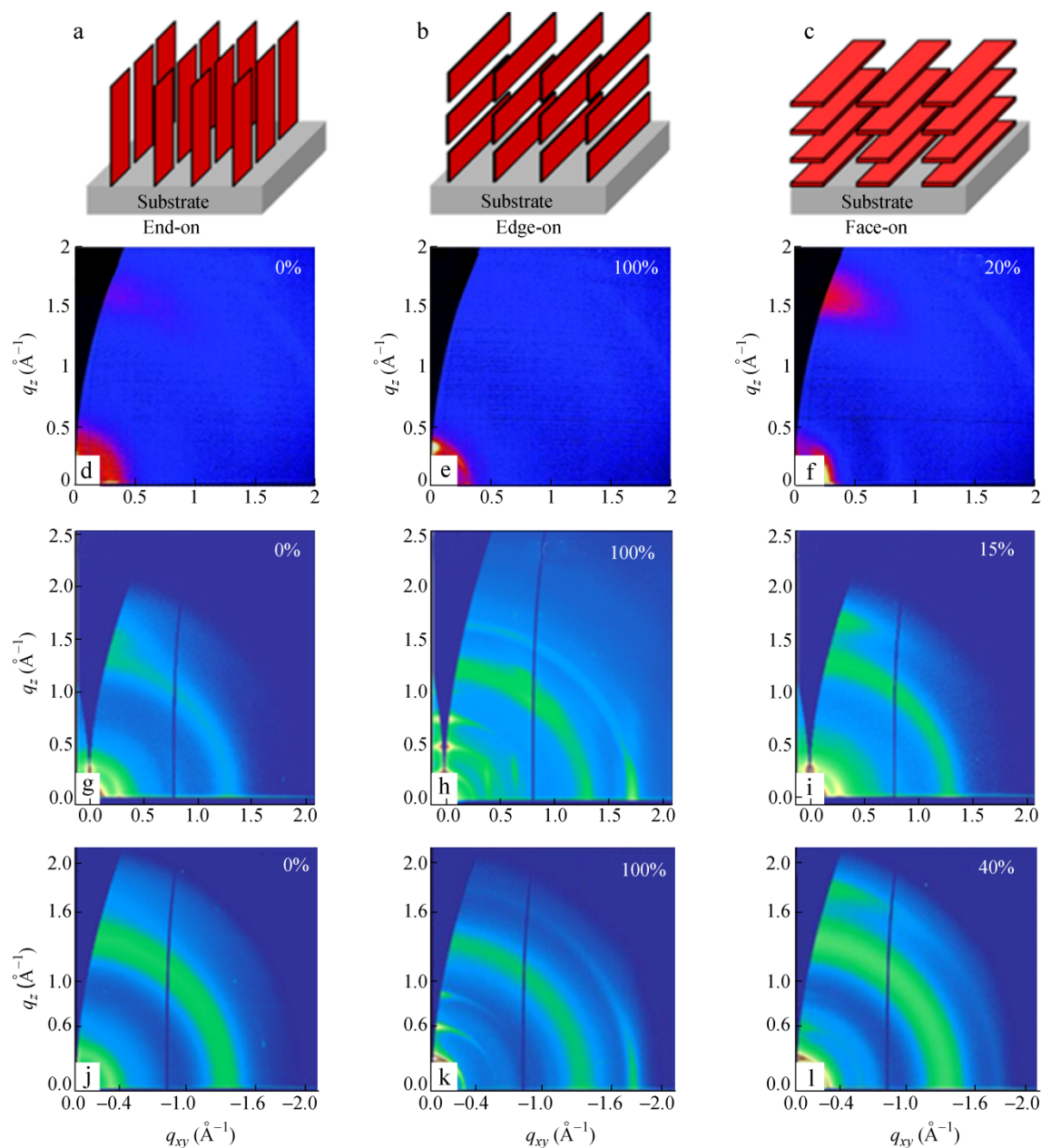


Fig. 3 The diagram of (a) end-on orientation, (b) edge-on orientation and (c) face-on orientation with respect to the substrate; 2D-GIXRD patterns of pure (d) PTB7, (e) PDTP-DFBT and (f) blend PTB7:PDTP-DFBT (0.8:0.2) solid films (Reprinted from Ref. [55] with permission from The Royal Society of Chemistry); Two-dimensional GIWAXS patterns of (g) PTB7-Th:PC₇₁BM film, (h) *p*-DTS(FBTTH₂)₂:PC₇₁BM and (i) PTB7-Th:*p*-DTS(FBTTH₂)₂:PC₇₁BM film at the *p*-DTS(FBTTH₂)₂ weight ratio of 15% (Reprinted with permission from Ref. [58]; Copyright (2015) American Chemical Society); 2D-GIXRD patterns of (j) PBDTPD-HT:PC₇₁BM, (k) BDT-3T-CNCOO:PC₇₁BM and (l) PBDTPD-HT:40% BDT-3T-CNCOO:PC₇₁BM films (Reprinted with permission from Ref. [66]; Copyright (2016) Wiley-VCH)

this scale is particularly important. In addition, the domain purity should be high enough to offer rapidly transport channels to increase charge carrier mobility. In the ternary solar cells, adding a third component into binary blends would influence the phase separation size and domain purity.

In general, the incorporation of a highly crystalline third component increases the phase separation size of active layer because the crystallization is a driving force of phase separation. As aforementioned, a high crystallinity small molecule BDT-3T-CNCOO was incorporated into the PBDTTPD-HT:PC₇₁BM blends by Wei's group^[59]. The addition of BDT-3T-CNCOO not only promotes the crystallization of polymers, but also increases the domain size. As shown in Figs. 4(c), 4(d) and 4(e), pristine PBDTTPD-HT:PC₇₁BM film presents a homogeneous morphology with small phase separation size. However, an increased phase separation size of ternary film with 40 wt% BDT-3T-CNCOO is observed. The optimal phase size is sufficiently large for an effective bicontinuous interpenetrating structure, but it is small to match the short exciton diffusion distance. Hence, a high crystallinity of donor material and an appropriate phase separation size were achieved by adding small molecules. In addition, the BDT-3T-CNCOO small molecules were added into PBDTTT-C-T:PC₇₁BM blends by Wei's group and our group^[67]. As shown in Fig. 4(f), the R-SoXS profiles give the information of domain size and relative domain purity. The phase separation size of the ternary films was increased by adding the BDT-3T-CNCOO small molecules. Domain purity for PBDTTT-C-T:PC₇₁BM and BDT-3T-CNCOO:PC₇₁BM were increased with the loading of BDT-3T-CNCOO small molecules. However, the blends without polymer (100%) tend to form a relative mixed domain. All of the ternary blends exhibit purer PBDTTT-C-T:PC₇₁BM and BDT-3T-CNCOO:PC₇₁BM domains than the corresponding binary blends. Higher domain purity results in a decreased bimolecular recombination. Compared to the binary systems of PBDTTT-C-T:PC₇₁BM (PCE 7.60%) and BDT-3T-CNCOO:PC₇₁BM (PCE 4.98%), the PCE of this ternary system reached 8.37% when adding 50% of BDT-3T-CNCOO in the blend.

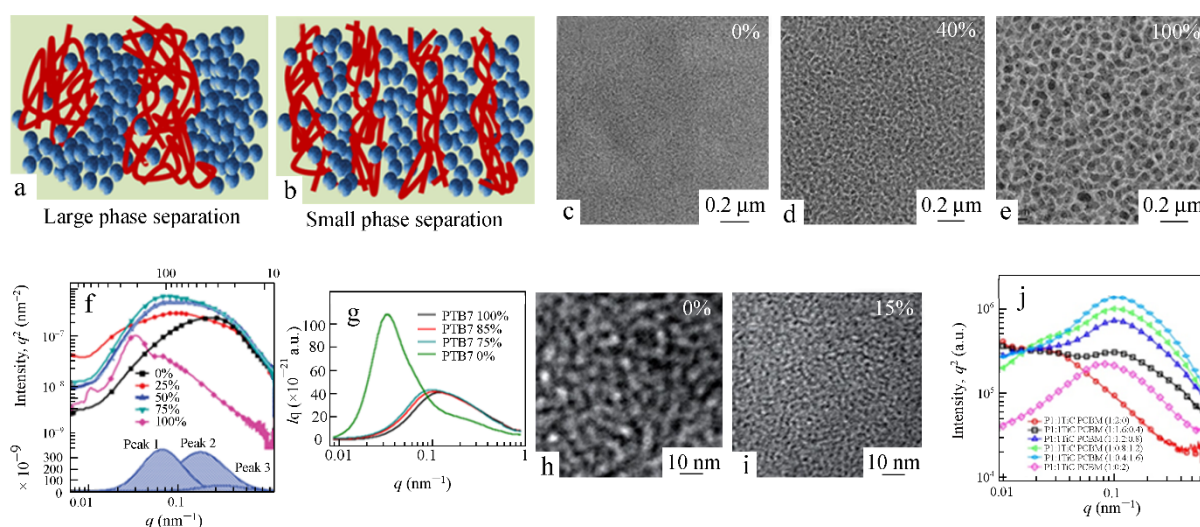


Fig. 4 The diagram of (a) large phase separation and (b) small phase separation; TEM images of (c) PBDTTPD-HT:PC₇₁BM binary film, (d) PBDTTPD-HT:40 wt% BDT-3T-CNCOO:PC₇₁BM ternary film and (e) BDT-3T-CNCOO:PC₇₁BM binary film (Reprinted with permission from Ref. [59]; Copyright (2015) Wiley-VCH); (f) R-SoXS scattering profiles at 284.2 eV of PBDTTT-C-T:BDT-3T-CNCOO:PC₇₁BM ternary and binary blends with different small molecular ratios (Reprinted with permission from Ref. [67]; Copyright (2015) Wiley-VCH); (g) Lorentz-corrected and normalized R-SoXS profiles for PTB7:PC₇₁BM, PTB7:Si-PCPDTBT:PC₇₁BM (0.85:0.15:1.5), PTB7:Si-PCPDTBT:PC₇₁BM (0.75:0.25:1.5) and Si-PCPDTBT:PC₇₁BM films under 284.2 eV (Reprinted with permission from Ref. [68]; Copyright (2016) Nature Publishing Group); TEM images of (h) BDT6T:PC₇₁BM binary film and (i) BDT6T:15% ICBA:PC₇₁BM ternary film (Reprinted from Ref. [75] with permission from The Royal Society of Chemistry); (j) R-SoXS information of blend films based on PPBDTBT:ITIC:PC₇₁BM with different ITIC:PC₇₁BM ratios (Reprinted with permission from Ref. [78]; Copyright (2016) Wiley-VCH)

Recently, a highly crystalline polymer poly[(4,4'-bis(2-ethylhexyl)dithieno[3,2-b:2',3'-d]silole)-2,6-diyl-*alt*-(4,7-bis(2-thienyl)-2,1,3-benzothiadiazole)-5,5'-diyl] (Si-PCPDTBT) was incorporated into PTB7:PC₇₁BM solar cells by Gasparini to attain a high performance^[68]. The phase separation was characterized by R-SoXS. As shown in Fig. 4(g), the scattering profile of Si-PCPDTBT:PC₇₁BM is significantly different from other specimens. It was found that the median length scale of PTB7:Si-PCPDTBT:PC₇₁BM ternary blends enlarged as the Si-PCPDTBT content increased, suggesting an improved phase separation with the addition of Si-PCPDTBT. In addition, Huang *et al.*^[69] found that the addition of 2,4-bis[4-(*N,N*-diisobutylamino)-2,6-dihydroxyphenyl] squaraine (SQ) small molecule into P3HT:PC₆₁BM blends could increase the phase separation size. In 2013, a small amount of P3HT was incorporated into PCPDTBT:PC₆₁BM solar cells by Chen's group^[70]. It was found that π - π stacking of PCPDTBT and the aggregation of PC₆₁BM were increased to form extended bicontinuous domains for efficient charge transport.

However, many binary solar cells possess a serious phase separation with large aggregation. In order to obtain an optimal morphology and a high device performance, it is of great importance to suppress the phase separation at a proper scale. Interestingly, the separation size could also be reduced by adding a third component into the binary system^[71–78]. In 2009, small amount of amorphous region-random P3HT were incorporated into the P3HT (rr-P3HT):PC₆₁BM blends^[71]. It restrained the phase separation with decreased PC₆₁BM domain size and crystallites size of rr-P3HT due to the dilute matrix. In 2015, An *et al.*^[72] reported a ternary solar cell based on SMPV1:DIB-SQ:PC₇₁BM by only adjusting the DIB-SQ doping ratio in donors without any treatment on the blend solutions or active layers. The pristine SMPV1:PC₇₁BM film presented large SMPV1 domains, and the phase separation size decreased to an appropriate value when 10 wt% DIB-SQ was added into the blends, resulting in the champion photovoltaic performance of ternary solar cells.

It is worth noting that reduced phase separation size of active layer often occurs in the double-acceptor ternary solar cells^[73]. Due to the easily aggregated fullerene or fullerene derivative, another acceptor material as a third component in the ternary solar cells is usually used to suppress the aggregation of fullerene acceptor. Zhan and coworkers^[74] employed double-acceptors of PC₇₁BM and ICBA in the ternary solar cells with five classical donors, PTB7, PBDTTT-C-T, PTB7-Th, PDBT-T1 and PThBDTP. It was found that the PC₇₁BM and ICBA form acceptor alloy (be described below) in the ternary blends. The film of PTB7-Th:alloy acceptor preferred to form relatively dense and continuous polymer networks than the film of PTB7-Th:PC₇₁BM, suggesting that the incorporation of ICBA into PTB7-Th:PC₇₁BM blends could suppress the aggregation of fullerene derivative. They further proved it by R-SoXS and concluded that the addition of ICBA into PTB7-Th:PC₇₁BM blends could decrease the phase separation size. In addition, the ICBA was also incorporated into all-small-molecular solar cells based on (2Z,20'E)-dioctyl 3,3'-(5'',5''''-(4,8-bis(5-octylthiophen-2-yl)benzo[1,2-b:5,4-b']dithiophene-2,6-diyl)bis(3,4',4''-trioctyl-[2,2':5',2''-terthiophene]-5'',5-diyl))bis(2-cyanoacrylate) (BDT6T) and PC₇₁BM by Huang^[75]. As shown in Figs. 4(h) and 4(i), the TEM image of ternary film with 15% ICBA exhibits smaller domain size than that of the film without ICBA. The small domains of ternary film at this scale improve the excitons dissociation, and enhanced PCE.

A di-substituted fullerene (bis-PCBM) serving as an additive was added into P3HT:PCBM solar cells by Wang^[76]. It was demonstrated that the phase separation size decreased when 8.3 wt% of bis-PCBM was added in the system, and the formation of bicontinuous networks was promoted due to the second substituent in bis-PCBM. It further hindered the close contract of C₆₀ cores to form large clusters, prevented the diverse molecular geometry of regioisomers of di-substituted fullerene to form the ordered molecular packing, and increased interface area. This approach exhibited a highly stable morphology in high-temperature environment because of the inhibition of fullerene aggregation. Moreover, Chen^[77] reported that all conjugated C₆₀-containing block copolymer (C₆₀-BCPs) with self-assembled fiber-like structures was incorporated into P3HT:C₆₀ blends to induce the formation of a self-organization nanostructure, and enhanced the phase separation and interchain interaction of P3HT domain because of the self-assembled behavior interplay between π - π^* stacking. The C₆₀-BCPs played a role of compatibilizer among the active layer and facilitated the formation of interpenetrating network structure

with smaller fullerene aggregation clusters.

Recently, Bo's group and our group^[78] report a ternary polymer solar cell by combining fullerene and non-fullerene acceptors to synergistically boost the photovoltaic performance with the optimal morphology. As shown in R-SoXS profiles (Fig. 4j), the scattering peak of ternary films shifts to a large q value as the PC₇₁BM content increased, indicating that the incorporation of PC₇₁BM results in a decreased phase separation size. The domain purity of blends is also increased with the loading of PC₇₁BM. The decreased domain size and improved domain purity increase PCE to 10.41%. The added third component is of great influence on the phase separation, including domain size and domain purity. In summary, the domain size and domain purity can be improved by adding a highly crystalline third component in most of the cases. Moreover, adding another acceptor with good miscibility and compatibility of the pristine fullerene derivative often inhibits the aggregation of acceptor materials, showing a decreased phase separation size.

FUNDAMENTAL MECHANISM OF TERNARY SOLAR CELLS IN MORPHOLOGICAL RESEARCH

Since the ternary solar cell contains three components in the active layer, it makes the morphology of active layer more complicated than that of binary solar cell. Four different locations of the third component in the blends of donor and acceptor are proposed^[28, 48, 79]. The third component could: (i) form its own channel, (ii) form a mixed phase with donor or acceptor, (iii) embed in one phase, or (iv) locate at interfaces. The interactions of three components and the fundamental mechanism of ternary solar cells are related to the location of third component (the morphology of ternary blends). The mechanism that governs the photovoltaic process in ternary solar cells is different from binary solar cells. Therefore, some different mechanisms base-on different morphology in ternary solar cells are established and shown in the following section^[28, 48, 79].

Parallel-like Model

The parallel-like model (Fig. 5a) is an important mechanism, greatly related to the morphology. For the D₁:D₂:A ternary solar cells in this mechanism, excitons generated in the individual donor domains can diffuse to the respective interface of donor and acceptor domain, and then dissociate into holes and electrons. After that, holes (electrons) transport along the donor (acceptor) channels and are collected by the anode (cathode). However, in the D:A₁:A₂ ternary solar cells of parallel-like mechanism, excitons generated in the donor domain diffuse to the D/A₁ interface or D/A₂ interface and then dissociate into holes and electrons in the corroding interfaces. Subsequently, holes transport to anode through the sole donor channel and electrons transport to the cathode by the two parallel acceptor channels. This parallel-like model is dependent on the morphology of ternary active layer which requires two parallel donor channels with one acceptor channel, or two parallel acceptor channels with one donor channel. Therefore, the morphology of ternary active layer is required to form two continuous donor networks for the D₁:D₂:A system or two continuous acceptor networks for the D:A₁:A₂ system. That is to say, the additional third component should form its own network structures independently. The parallel-like ternary solar cell was firstly reported by You's group^[80]. They fabricated two groups ternary solar cells of TAZ:DTBT:PC₆₁BM system and DTfBT:DTPyT:PC₆₁BM system, and proposed that ternary solar cell could be considered as two individual sub-cells. In 2015, the parallel-like model was demonstrated to exist in the PTB7:PBDT-TS1:PC₇₁BM ternary solar cell by Zhang's group^[81]. The improved device performance is well explained by the parallel-like model, suggesting that the respective network structures of PTB7 and PBDT-TS1 are formed in the ternary blends.

Alloy Model

Alloy model is proposed by Thompson *et al.* (Fig. 5b) in the discussion of the open circuit voltage for the ternary solar cells^[82–86]. Instead of forming independent charge transport channels for each component in the parallel-like model, the third component formed a mixed phase with the pristine donor material or acceptor material for the alloy model. The physical and chemical performances mainly depend on the average content of the two components in alloy model, such as open circuit voltage and energy level. For the ternary solar cells of alloy

model, two electronically similar components, either two donors or two acceptors, should form an electronic alloy. It requires that the two components possess excellent miscibility and compatibility to ensure the formation of the mixed phase. Recently, the alloy structure was demonstrated to exist in many ternary solar cells. It can be roughly divided into two groups (donor alloy and acceptor alloy). As aforementioned, for the PTB7-Th:*p*-DTS(FBTTH₂)₂:PC₇₁BM ternary solar cell^[58], the increased device performance is attributed to the formation of alloy with two miscible donors which enhances the crystallization and face-on orientation of PTB7-Th. Sun *et al.*^[87] proposed that the polymer PDBT-T1 and PTB7-Th could form alloy donor with mixed polymer domain. Besides, the acceptor alloy with PC₆₁BM and ICBA or PC₇₁BM and ICBA was demonstrated to exist in many ternary systems due to electronic structure similarity and good miscibility which led to the formation of a mixed acceptor phase in the ternary active layer. In 2015, Krebs and coworkers confirmed the alloy formation between PC₆₁BM and ICBA using solid state cross-polarization magic-angle-spinning (CP MAS) NMR spectroscopy^[88]. Furthermore, the alloy acceptor of PC₇₁BM and ICBA combining with different donor materials was demonstrated to improve the device performance remarkably by Zhan's group and our group^[74].

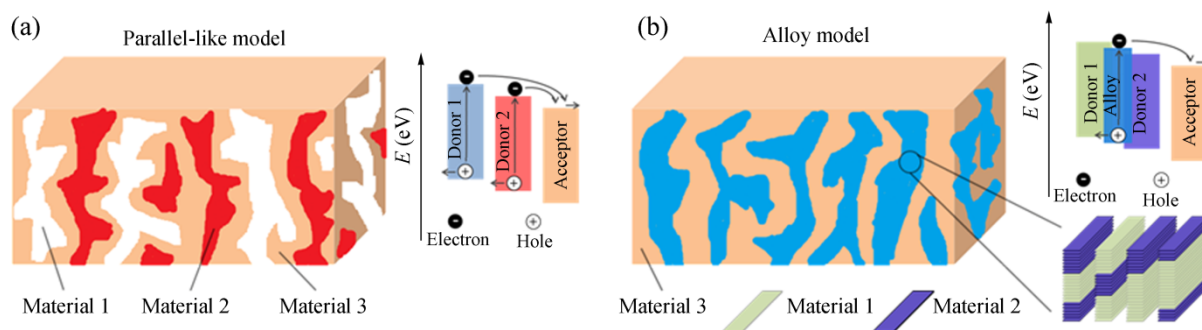


Fig. 5 The schematic of (a) parallel-like mechanism and (b) alloy mechanism

Other Mechanisms

Besides the parallel-like mechanism and alloy mechanism, there are two other different mechanisms of charge transfer and energy transfer for the ternary solar cells. For the charge transfer mechanism, the third component should possess an appropriate energy level and bandgap to achieve a cascade energy level alignment for an effective charge transfer and charge transport, so the third component needs to locate at the interface of pristine donor domain and acceptor domain. That is to say, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels of the third component approximately locate between that of donor and acceptor^[73, 89]. However, in the case of energy transfer mechanism^[57, 69], the excited sensitizer transfers energy to either donor or acceptor through the Dexter or Förster resonance energy transfer (FRET) mechanism. This requires that the emission spectrum of one material and the absorption spectrum of another material must overlap for efficient energy transfer. The third component could act as “energy donor” or “energy acceptor” in the ternary solar cells depending on their bandgap. The exciton energy generated in large bandgap materials transferred to narrow bandgap materials, and then excitons dissociated at the interface of narrow bandgap donor domains and acceptor domains.

As discussed above, the mechanisms of parallel-like model, alloy model, charge transfer and energy transfer for ternary solar cells are obviously different from each other, but one or more mechanisms may exist in one ternary solar cell^[28, 48]. For instance, we have demonstrated that the parallel-like mechanism and the so-called alloy model can coexist in the PBDTTPD-HT:BDT-3T-CNCOO:PC₇₁BM solar cells which are depended on the ratio of BDT-3T-CNCOO small molecules^[66]. When the BDT-3T-CNCOO content is low, both the parallel-like model and alloy model exist, but only alloy model exists in the ternary blends when BDT-3T-CNCOO small molecules are in majority. Every mechanism has its own special requirements for the materials. The parallel-like mechanism requests the additional component to form its own channel for charge transport. For the alloy

mechanism, the excellent miscibility and high compatibility between the third component and the pristine donor material or the pristine acceptor material are needed to achieve a well mixed phase. The charge transfer mechanism requires a suitable energy level and bandgap, as well as the location of third component at the D/A interfaces. However, energy transfer mechanism needs that the emission spectrum of one material and the absorption spectrum of another material must overlap to perform the Förster effect. In order to achieve a high device performance, the optimization and balance of these mechanisms should be carefully considered.

CONCLUSIONS

The incorporation of a third component into the binary organic solar cells certainly affects the morphology of active layer as well as the fundamental mechanism relative to the morphology. These morphological changes of active layer exhibit in many aspects, such as crystallization, crystal orientation and phase separation. Some important results are obtained from the discussions above on the ternary solar cells from the view of the morphology. Firstly, the crystallinity should be high enough to achieve an interpenetrating network structure, and it can be increased by adding a high crystallinity third component or introducing the crystallization nucleating agents. Secondly, the enhanced face-on orientation with respect to the substrate by adding a third component is beneficial for the charge transport and device performance, attributing to the strong π - π stacking. Thirdly, the phase separation size should be controlled at an appropriate value (10–20 nm) and the domain purity should be high. Usually, adding a high crystallinity third component increases the phase separation size, and the addition of a second fullerene derivative mainly inhibits the aggregation of fullerene molecules to achieve a better morphology with small phase separation and better device stability. Moreover, we discussed the fundamental mechanism of the ternary system according to the previous reports in the literature. The discussions on the morphology optimization and fundamental mechanisms will provide a convenience way to understand the ternary solar cells clearly and have a guiding role for the optimized morphology study on the ternary solar cells. Nowadays, organic solar cells develop rapidly, especially for the ternary solar cells, and we believe that they have a bright prospect for a significant breakthrough in future.

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