Morphology optimization of photoactive layers in organic solar cells

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Abstract

Organic solar cells (OSCs) have unique advantages of light weight, low-cost solution processing, and capability to be fabricated into flexible and semitransparent devices, which are widely recognized as a promising photovoltaic technology. Photoactive layers of the OSCs are composed of a blend of a p-type organic semiconductor as a donor (D) and an n-type organic semiconductor as acceptor (A). The morphology of the active layer with D/A nano-scaled aggregation and face-on π-conjugated packing, and D/A interpenetrating network is crucial for achieving high photovoltaic performance of the OSCs. Therefore, great efforts have been devoted to control and optimize morphology of the active layers. This perspective focuses on the morphological control by solvent/solid processing additives and the morphology optimization by postdeposition treatment with thermal annealing and/or solvent vapor annealing, which have been extensively adopted and exhibit promising positive effect in optimizing the morphology. Representative examples are given and discussed to understand the foundation of the postdeposition treatments on tuning the morphology. Insights into the role of the postdeposition treatments and additive treatments on the morphology optimization will be beneficial to further improvement in morphology optimization for practical organic photovoltaic application.

KEYWORDS

morphology, optimization of photoactive layers, organic solar cells, solvent additive, solvent annealing, thermal annealing

INTRODUCTION

As an emerging photovoltaic technology, organic solar cells (OSCs) have been attracted tremendous research interests because of their unique advantages of the simple device structure, light weight, mechanical flexibility, and transparency. Typical, the device configuration of OSCs (as shown in Figure 1) is sandwich-like with a photoactive layer between a positive electrode and a low work function negative electrode (where at least one of the two electrodes should be transparent), and electron/hole transport materials are widely used as buffer layers for efficient electron/hole collection. Power conversion efficiency (PCE) is the overall parameter to evaluate an OSC device performance, which is directly proportional to open-circuit voltage ($V_{OC}$), short-circuit current density ($J_{SC}$), and fill factor (FF). The photoactive layer is the key component that converts the absorbed photons within its absorption wave-length range into charge carriers. At the early stages of the organic photovoltaic, the photoactive layer of OSC is composed of a single-component organic semiconductor film, which yielded extremely poor photovoltaic performance because of the limited degree of excitons dissociation and charge transport in the single-component organic semiconductors. In 1986, Tang first developed a bi-layer photovoltaic cell with a p-type organic semiconductor layer as a donor and an n-type organic semiconductor layer as an acceptor, which greatly enhances the exciton dissociation efficiency at the p-n junction between the donor and acceptor layers in comparison with the single-component layer, delivering the overall better photovoltaic property with PCE close to 1%. Nevertheless, this kind of device architecture has still confronted the challenge of insufficient exciton dissociation and charge transport due to the limited diffusion length (only ca. 10 nm) of the excitons in the organic semiconductors. These issues can be ideally tackled by forming D-A bulk...
heterojunction (BHJ) film by spin-coating the mixed solution of the donor (D) and acceptor (A), which is developed by Heeger et al. in 1995.[13] The BHJ film can markedly enlarge D/A interfaces for efficient exciton dissociation and potentially provide nanoscale bicontinuous D/A interpenetrating network for charge carriers transport.

In a BHJ OSC, the working mechanism involves the following major procedures (Figure 1):[14, 15] (1) blend active layer absorbs photons to generate excitons; (2) excitons diffuse to D/A interfaces; (3) excitons dissociate into free charge carriers (electrons and holes) at the D/A interfaces driven by the energy difference between the donor and acceptor materials; (4) electrons and holes independently transport along acceptor and donor pathways to the cathode and anode, respectively; (5) extraction and collection of the charge carriers at the electrodes to form photocurrent and photovoltage. The above procedures are closely related to the BHJ morphology of the photoactive layers. Due to the limitation of exciton lifetime, nanoscale domain sizes of ~10 nm that matches the exciton diffusion length are required for efficient diffusion. Besides, nanoscale phase separation associated with the bicontinuous interpenetrating network and ordered face-on molecular packing are desirable for charge separation and transport. In addition, sufficiently high domain purity is essential to suppress bimolecular recombination of free charge carriers. Therefore, the morphology of the photoactive layer is one of the key factors which determine the photovoltaic performance of the OSCs. The realization of optimal morphology is a complicated process that is affected by various factors, such as the solubility, crystallinity, and miscibility of photovoltaic materials, processing solvents, and additives, postdeposition treatments of thermal annealing and solvent annealing, etc. Although some examples are demonstrating that the as-cast blend films can realize optimal morphology,[16–18] proper extra-treatment strategies are extensively required to tune the blend film toward ideal morphology.

In this perspective, we summarize the commonly used strategies for the morphology optimization of the BHJ active layers, including solvent additive, solid additive, thermal annealing, and solvent vapor annealing, aiming to understand how the treatments impact film formation and phase separation to achieve ideal morphology and provide the groundwork to rationally guide further morphology optimization for high-performance and stable OSCs.

**THERMAL ANNEALING TREATMENTS**

Thermal annealing is a widely used effective approach to facilitate the molecular packing and formation of crystalline network in the BHJ blend active layers of the OSCs.[19–21] The thermal annealing is performed by heating the active layers prepared on the ITO electrode of the OSCs at a fixed temperature (usually 90–160°C) for some time-period (seconds to minutes). This approach shows a promising positive effect in tuning the domain size and molecular packing of high crystallinity photovoltaic materials. For instance, applying thermal treatment for P3HT:PCBM (Scheme 1) blend can increase P3HT crystallinity and form the polymer matrix and PCBM clusters, leading to ordered nanostructure in the active layer.[22–24] Upon thermal annealing, significant change can be observed in the P3HT:PCBM blend with increasing the annealing time. Kim et al. revealed that the P3HT chains ordering in the P3HT:PCBM blend was greatly enhanced in both out-of-plane and in-plane directions after thermal annealing at 140°C for 2–5 min, while the reversed change was observed by further prolonging the annealing time up to 30 min, and then the P3HT chains ordering was enhanced again and steadily maintained with the annealing time of 30–120 min (Figure 2A).[25] The intermediate stage of molecular packing in the thermal annealing between 5 and 30 min was due to the internal morphological fluctuations by the continuing thermal transition of P3HT chains in the blend film. The crystallites size of P3HT also increased in the presence of fluctuations. The thermal annealing treatments exhibited a slight effect in the $V_{oc}$ and $J_{sc}$, while significantly impacted on the FF, and thus on the PCE of the device (Figure 2A).

In the J71:ITIC (Scheme 1) case, the thermal annealing treatment for the blend film led to higher crystalline characteristics, preferred face-on orientation, and tight π–π stacking of the polymeric backbone compared to the as-cast blend, enabling the higher $J_{sc}$ (from 14.81 to 17.32 mA cm$^{-2}$), improved FF (from 0.636 to 0.698), and thus the higher PCE (from 9.03% to 11.41%, as shown in Table 1).[26]

In many all small molecule OSCs with A-π-D-π-A (A = acceptor unit, D = donor unit, and π = conjugated π-bridge) type organic small molecule as donor and fullerene or nonfullerene narrow bandgap small molecule as acceptor, a thermal annealing treatment is crucial to optimize their morphology.[27–32] Due to the high crystallinity of these small molecules, chloroform which has a relatively
low boiling point is generally employed as processing solvent to shorten the drying dynamic procedure for preventing the over aggregations, and then additional thermal annealing is applied to further manipulate the phase separation and domain sizes. For instance, in the case of DRCN7T:PC71BM and DERHD7T:PC71BM-based blends (Scheme 1), the post-deposition treatment of thermal annealing at 90°C for 10 min can significantly improve their photovoltaic performance compared to the corresponding as-cast blends (as shown in Table 1). Due to the different crystallinity of DRCN7T and DERHD7T (Figure 2B), thermal annealing at 90°C for 10 min led to obviously different phase separation of the DRCN7T:PC71BM and DERHD7T:PC71BM-based blends. According to the transmission electron microscopy (TEM) studies (Figure 2B), the as-cast DRCN7T:PC71BM blend exhibited a well-developed fibrils network which is in favor of charge separation and transport, while a less defined phase separation was observed for the DERHD7T:PC71BM blend. Upon thermal annealing at 90°C for 10 min, the fibrillar network morphology was retained and strengthened for the DRCN7T:PC71BM blend, while the DERHD7T:PC71BM blend showed obvious over aggregation with a large domain size. Thus, the thermal annealing treatment exhibits a more pronounced positive effect in enhancing the PCE of the DRCN7T-based device than the device based on DERHD7T (as shown in Table 1). In the case of nonfullerene acceptor-based all small molecules blend, a thermal annealing treatment is also an effective approach to control their aggregates for achieving optimal morphology. For instance, treating the SM1-series: Y6 blends at 120°C for 10 min effectively regulated their morphology toward more obviously fibrous aggregates compared to their corresponding as-cast blends, resulting in the greatly improved photovoltaic performance (as shown in Figure 2C and Table 1). In comparison with the SM1:Y6 and SM1-S:Y6 blends, SM1-F:Y6 BHJ blend displayed a more favorable fibrous structure with longer and denser aggregates after the thermal annealing, which dramatically elevated the PCE from 1.72% for the device without thermal annealing to 14.07% for the device with the thermal annealing (Table 1).

With the enhanced crystallinities of the small molecules, the positive effect of the thermal annealing is more pronounced. Wei et al. modulated the side chains branching position of the small molecules (ZR2-C1, ZR2-C2, and ZR2-C3, as shown in Figure 3A) to tune their crystallinity. The π-π stacking interactions of the three molecules are
increased with the branching position of side-chains moving away from a conjugated core moiety, which is in favor of regulating nano-scale phase separation morphology due to the match of crystallinities between donor and acceptor materials. As a result, the nanofibers morphologies of ZR2-C2:Y6 and ZR2-C3:Y6 are more pronounced compared to the ZR2-C1:Y6 blend after thermal annealing, relative to their corresponding as-cast blend (Figure 3B). Such morphological difference of the blend films apparently resulted in the different photovoltaic performance for the three molecules-based all small-molecule OSCs (as shown in Table 1). Regarding the liquid-crystalline small molecules, thermal annealing treatment also effectively regulated their morphology toward optimized phase separation, delivering to the significantly improved PCEs.[29, 34] These results provide examples of building state-of-the-art OSCs by taking a comprehensive account of merits of photovoltaic materials and post-deposition treatment.

Generally, morphology optimization enabled by thermal annealing treatments ascribes to the change of crystallinity, phase separation, and domain sizes, etc. In the case of PM6:Y6 (Scheme 1) blend, Marks et al. found that the thermal annealing under 110°C for 3 min barely change the molecular orientations, crystallinity, domain size scales, and phase separation, while forcing Y6 vertical migration toward the top surface of blend film, that changes the PM6:Y6 vertical-phase separation and intermixing, and reduces the bottom surface roughness.[35] These morphology changes aroused by thermal annealing treatment significantly increase hole charge mobility (at least two fold), but accelerate bimolecular recombination and lower the free photo-generated free charge yield. However, the effect of increased mobility dominates the overall device behavior, resulting in the improved photovoltaic performance (see Table 1).

It should be noted that the treatment for the morphology of blend film is sensitive to the host processing solvents, which is ascribed to their different volatility and diverse solubility to photovoltaic materials. Liu et al. demonstrated that Y6 film processed by chloroform trended to form polymer-like extended crystal transport channels, while Y6 in chlorobenzene processed film exhibited small and discrete oriented crystallities.[36] Such morphology difference significantly impacts the charge transport and an ultrafast hole and electron transfer, resulting in the much different photovoltaic
### TABLE 1  Photovoltaic performance of the OSCs without/with thermal annealing treatment

| Active layer   | Thermal annealing                  | $V_{oc}$ [V] | $J_{sc}$ [mA cm$^{-2}$] | FF  | PCE [%] | Ref. |
|----------------|------------------------------------|--------------|-------------------------|-----|---------|------|
| J71:ITIC       | N/A                                | 0.96         | 14.18                   | 0.636 | 9.03    | 26   |
| J71:ITIC       | 150°C for 10 min                   | 0.94         | 17.32                   | 0.698 | 11.41   | 26   |
| DRCN7T:PC71BM  | N/A                                | 0.91         | 14.87                   | 0.687 | 9.30    | 27   |
| DRCN7T:PC71BM  | 90°C for 10 min                    | 0.93         | 8.28                    | 0.340 | 2.62    | 27   |
| DRCN7T:PC71BM  | 90°C for 10 min                    | 0.89         | 9.49                    | 0.516 | 4.35    | 27   |
| SM1:Y6         | N/A                                | 0.897        | 2.70                    | 0.219 | 0.53    | 30   |
| SM1:Y6         | 120°C for 10 min                   | 0.805        | 23.59                   | 0.670 | 12.72   | 30   |
| SM1-S:Y6       | N/A                                | 0.921        | 1.26                    | 0.202 | 0.23    | 30   |
| SM1-S:Y6       | 120°C for 10 min                   | 0.825        | 23.23                   | 0.677 | 12.94   | 30   |
| SM1-F:Y6       | N/A                                | 0.936        | 7.46                    | 0.246 | 1.72    | 30   |
| SM1-F:Y6       | 120°C for 10 min                   | 0.866        | 23.25                   | 0.699 | 14.07   | 30   |
| ZR2-C1:Y6      | 120°C for 10 min                   | 0.848        | 21.35                   | 0.651 | 11.79   | 33   |
| ZR2-C2:Y6      | 120°C for 10 min                   | 0.852        | 23.03                   | 0.654 | 12.84   | 33   |
| ZR2-C3:Y6      | 120°C for 10 min                   | 0.854        | 24.69                   | 0.701 | 14.78   | 33   |
| PM6:Y6         | N/A                                | 0.826        | 24.35                   | 0.690 | 13.88   | 35   |
| PM6:Y6         | 110°C for 3 min                    | 0.815        | 26.04                   | 0.705 | 14.97   | 35   |

**FIGURE 3**  (Left) Chemical structures of ZR2-C1, ZR2-C2, and ZR2-C3. (Right) TEM images of the blend films without/with thermal annealing. Reproduced with permission[33]

Performance between the chlorobenzene ($V_{oc} = 0.796$ V, $J_{sc} = 21.16$ mA cm$^{-2}$, FF = 0.7215, and PCE = 12.15%) and the chloroform-processed ($V_{oc} = 0.835$ V, $J_{sc} = 26.52$ mA cm$^{-2}$, FF = 0.7621, and PCE = 16.88%) OSCs based on PM6:Y6.

As an important driving force for morphological rearrangement, thermal annealing treatment plays an essential role in optimizing the phase separation of blend films for improving the efficiency of the OSCs. This postdeposition treatment is widely and synergistically used to remove the additives and further tune the morphology of the blend film. Nevertheless, the high temperature (>120°C) of thermal annealing for some state-of-the-art photovoltaic material systems limited their application in flexible OSCs.

**SOLVENT VAPOR ANNEALING**

Solvent vapor annealing (SVA) is another effective way to control the molecules’ rearrangement in the active layer for morphology optimization. Under the SVA treatment, the active layer was immediately kept in a covered petri dish with a small amount of solvent after the spin-coating (Figure 4(f)). Due to the different crystallinity and solubility of...
TABLE 2 Photovoltaic performance of the OSCs processed without/with SVA treatment

| Active layer       | SVA treatment | $V_{oc}$ [V] | $J_{sc}$ [mA cm$^{-2}$] | FF  | PCE [%] | Ref. |
|--------------------|---------------|--------------|--------------------------|-----|---------|------|
| DR3TBDTT:PC$_{71}$BM | N/A           | 0.918        | 12.95                    | 0.667 | 7.92%  | 38   |
| THF for 60 s       | 0.893         | 13.38        | 0.693                    | 8.28 | 38      |
| CH$_2$Cl$_2$ for 60 s | 0.889     | 13.55        | 0.717                    | 8.66 | 38      |
| CHCl$_3$ for 60 s  | 0.881         | 13.84        | 0.748                    | 9.12 | 38      |
| CS$_2$ for 60 s    | 0.886         | 14.21        | 0.761                    | 9.58 | 38      |
| DRTB-T:IC-C$_{6}$$i$DT-IC | N/A     | 1.05         | 11.37                    | 0.42 | 5.03%  | 39   |
| CH$_2$Cl$_2$ for 30 s | 1.02       | 14.17        | 0.52                     | 7.47 | 39      |
| CH$_2$Cl$_2$ for 60 s | 0.98       | 14.25        | 0.65                     | 9.08 | 39      |
| CH$_2$Cl$_2$ for 90 s | 0.97       | 13.49        | 0.63                     | 8.25 | 39      |

FIGURE 4 (I) Schematic diagram of the solvent vapor annealing treatment. (II) Detailed crystal information of DR3T-BDTT:PC$_{71}$BM blend films with different SVA treatments accessed by fitting the OOP (100) peak and IP (010) peak. A) The (100) relative crystallinity of DR3TBDTT in the blend films. B) (100) d-spacing and the estimated (100) crystal size of DR3TBDTT in the blend films. C) The (010) relative crystallinity of DRT3BDTT in the blend films. D) (010) d-spacing and the estimated (010) crystal size of DR3TBDTT in the blend films. Reproduced with permission[37]

donor and acceptor materials, their aggregations are separately controlled by the vapor annealing solvent toward optimized phase separation. Yang et al. firstly developed this treatment method to control the growth rate of P3HT in the P3HT:PCBM active layer[22] By using 1,2-dichlorobenzene as vapor solvent, the crystal growth of P3HT and PCBM is effectively controlled and thus leads to the enhanced photovoltaic performance of the OSCs. The selection of vapor solvent plays a critical role in controlling the morphology. Dadmun et al. demonstrated that the aggregation behavior of the active layer is dominated by the donor or acceptor photovoltaic material with better solubility in the vapor solvent.[37] Using bromobenzene possessing preferable solubility for the polymer donor PCPDTBT as vapor solvent, the solvent molecules insert into the PCPDTBT:ICBA blend film and drive the aggregation of polymer PCPDTBT chains. While using o-dichlorobenzene with similar solubility for PCPDTBT donor and ICBA acceptor as annealing solvent, the aggregations of donor and acceptor are both enhanced, which results in the large phase separation. In addition, due to the higher solubility of PCBM in chlorophenol, enhanced aggregations of PCBM in the PCPDTBT:PCBM blend film are obtained.[37] In addition to the solubility, solvent vapor pressure and solvent-molecular interaction should also be considered. Chen et al. found that the vapor pressures and solubility of the solvents for the photovoltaic materials show a critical effect in controlling the aggregates of the BHJ blend (Figure 4(II)).[38] Tetrahydrofuran (THF) solvent annealing has less effect in crystalline content and phase separation for the DR3TBDTT (Scheme 1) and PC$_{71}$BM blend because of its poor solubility and limitation in driving the aggregation of molecules, and therefore only a slightly higher PCE of 8.28% is obtained for the device with THF SVA for 60 seconds compared to the as-cast device with PCE of 7.92% (Table 2). In the case of using dichloromethane as vapor solvent, although it possesses lower boiling point and poorer solubility, larger crystal of both DR3TBDTT and PC$_{71}$BM and a higher domain sizes purity are realized due to the fact that dichloromethane molecules can permeate into the BHJ thin films for enhancing the intermolecular interaction, which benefits for the charge transport and collection. Thus, the PCE of the device can be improved to 8.66% after processed with dichloromethane SVA treatment for 60 seconds. By using chloroform or carbon disulfide which has high vapor pressures and good solubility for the donor material DR3TBDTT as annealing solvent, the aggregation of DR3TBDTT is readily enhanced to increase the length scale of phase separation, contributing to both enhanced $J_{sc}$ and FF, and therefore an enhanced PCE[38] (Table 2).

Solvent vapor annealing treatments are also applied to optimize the morphology of nonfullerene-based blend films. For instance, Hou et al. employed dichloromethane vapor annealing treatment to fine-tune the molecular packing and phase separation in the DRTB-T:IC-C$_{6}$$i$DT-IC (Scheme 1) system.[39] Relative to the as-cast DRTB-T:IC-C$_{6}$$i$DT-IC blend, the scattering intensity, crystal coherence length (CCL), and domain sizes of the blend film were gradually increased with increasing the annealing time of the dichloromethane vapor annealing (Figure 5), indicating that the crystallization is significantly increased after solvent vapor annealing. As a result, the PCE of 5.03% for the as-cast device is distinctly enhanced to 7.47% for the device processed by SVA treatment for 30 s and is further improved to the champion PCE of 9.08% after being treated for 60 s (as shown in Table 2), whereas the values are slightly decreased when the SVA treatment time is further increased to 90 s. Relative to the as-cast device, the enhanced PCEs of the devices with SVA treatment of 30–60 s are mainly ascribed
to the increased $J_{sc}$ and FF (Table 2). It is well known that the extremely small domain sizes impede the charge transport, while the large domain sizes are harmful for exciton dissociation. Apparently, the appropriate domain sizes in the DRTB-T:IC-C6IDT-IC blend controlled by the solvent vapor annealing treatment lead to the better device performance.

Although the solvent vapor annealing has been widely used as an important strategy to control the aggregations of the photovoltaic materials, this postdeposition treatment confronts the operational complexity and reproducibility issues in the application considering the fact that the solvent vapors and exposure time significantly affect the morphology quality of the blend active layers of the OSCs.

**SOLVENT ADDITIVES**

Adding appropriate solvent as an additive in host solvent is the most widely used strategy to tune the BHJ morphology for enhancing PCE of the OSCs. By adding a trace amount of higher vapor pressure solvent (compared to host solvent), which has selective solubility to one of the donor and acceptor photovoltaic materials, into the host solution, additive solvent remains in the film after the host solvent was evaporated. The remaining additive molecules offer a feasible opportunity to tune the aggregations and phase separations of the blend films.

Generally, choosing solvent additives to tune the morphology should meet the following criteria: (1) solvent additives have selective solubility to the donor or acceptor material in the blend film, and (2) solvent additives have higher boiling points with lower volatile compared to the host solvent. Solvent additive treatments exhibit great impact on enhancing the crystallinity, favoring molecular packing towards face-on orientation and appropriate phase separation domains, which is critical for efficient exciton dissociation and charge transport. In the case of PBTTPD:PC$_71$BM blend film, Wei et al. found that using 1,6-diiodohexane (D IH) as a solvent additive can feature smaller and better dispersed PC$_71$BM domains with smaller fractal cluster sizes ($\xi$) and can enhance the PBTTPD crystallinity in both the out-of-plane and in-plane directions to form superior pathways for charge carrier transport, leading to the improved photovoltaic performance (Figure 6(I)). Ade et al. demonstrated that the additive plays a critical influence on the nanoscale phase separation in the PTB7:PC$_71$BM blend film. Due to the selected affinity toward fullerene derivatives, the solvent additive 1,8-diiodooctane (DIO) significantly reduced the domain size of PC$_71$BM agglomerates which can be embedded in a polymer-rich matrix, resulting in a significant increase in exciton dissociation efficiency from the fullerene phase. As depicted in Figure 6(II), the positive effect of 3% DIO additive in improving the morphology is that it improves the fullerene agglomerates along with an increase of

![Figure 5](image-url)
FIGURE 6  (I) Schematic representations of mesograins in PBTTPD:PC$_{71}$BM films processed in the (left) absence and (right) presence of an additive. In the presence of the additive, the mesoscale grains dissolved into smaller fractal clusters; the additive also intercalated with the PBTTPD lamellar nanodomains. The fractal-like PC$_{71}$BM clusters were circular objects filled with interconnected PC$_{71}$BM units. Reproduced with permission.[47] (II) Morphological and operational schematic of the PTB7:PC$_{71}$BM film (A) without or (B) with DIO. The red region represents the pure PC$_{71}$BM agglomerate phase and the blue region is the mixed matrix phase. IE and IIE represent the most efficient photovoltaic effect regions. ID represents the dead region and IIR indicates the dead region. (C) Molecular view at an interface between Regions I and II. Red circles are PC$_{71}$BM molecules and blue lines represent PTB7 chains. Yellow dots are excitons while purple and green dots are separated electrons and holes, respectively. Excitons created in the darker regions lie outside the efficient zone and will either relax back to the ground state or recombine geminately. Reproduced with permission[48]

TABLE 3  Photovoltaic performance of the OSCs without/with solvent additive treatment

| Active layer | Additive treatment | $V_{oc}$ [V] | $J_{sc}$ [mA cm$^{-2}$] | FF | PCE [%] | Ref. |
|--------------|--------------------|--------------|--------------------------|----|--------|-----|
| PTB7:PC$_{71}$BM | N/A | 0.78 | 7.2 | 0.43 | 2.4 | 48 |
| PTB7:PC$_{71}$BM | 3% DIO | 0.74 | 14.1 | 0.51 | 5.3 | 48 |
| PTB7:PC$_{71}$BM | N/A | 0.70 | 11.43 | 0.46 | 3.99 | 49 |
| PTB7:PC$_{71}$BM | 3% DIO | 0.72 | 14.36 | 0.64 | 6.73 | 49 |
| PTB7:PC$_{71}$BM | 3% SH-na | 0.78 | 13.97 | 0.66 | 7.30 | 49 |
| PTB7:PC$_{71}$BM | 3% SH-na(a) | 0.79 | 15.67 | 0.70 | 8.75 | 49 |
| PffBT4T-C$_9$C$_{13}$:PC$_{71}$BM | N/A(b) | 0.773 | 13.2 | 0.55 | 6.4 | 62 |
| PffBT4T-C$_9$C$_{13}$:PC$_{71}$BM | 2.5% PN(b) | 0.784 | 19.8 | 0.73 | 11.7 | 62 |
| PffBT4T-C$_9$C$_{13}$:PC$_{71}$BM | 2.5% DIO(c) | 0.767 | 18.3 | 0.66 | 9.6 | 62 |

Table 3

Interfacial area between the two phases, delivering a higher PCE of 5.3% (as shown in Table 3).

(a) The active layers were dipped in a methanol solution containing 4.5% SH-na for 3 s followed by spinning off residual solution. The processing solvent is (b) 1,2,4-trimethylbenzene and (c) chloroform.

The various solvent additives lead to different morphological features of the BHJ blend film. Jeng et al. compared the morphology of PTB7:PC$_{71}$BM blend processed with the additive of DIO or 1-naphthalenethiol (SH-na).[49] Differing from the DIO additive that has selected solubility toward PC$_{71}$BM, SH-na facilitates both the crystallization of PTB7 and PC$_{71}$BM. As depicted in Figure 7, in comparison with the active layer without additive, which shows large and discrete PC$_{71}$BM-rich domains (Figure 7A), using DIO as additive significantly restricts the aggregation of PC$_{71}$BM, and therefore PTB7 and PC$_{71}$BM are well dispersed in the blend film (Figure 7B), which effectively improved the PCE from 3.99% to 6.73% (Table 3). When processing the PTB7:PC$_{71}$BM blend film with SH-na as a solvent additive, the polymer crystalline domains exhibit better growth within the fractal PC$_{71}$BM networks, thereby well-developed interpenetrating networks with the formation of appropriate polymer and PC$_{71}$BM aggregation domains (Figure 7C), resulting in the further enhanced PCE of 7.30%. The additional treatment by dipping the active layer with a methanol solution containing 4.5% SH-na can further enrich the film surface with PC$_{71}$BM (Figure 7D), enabling the champion PCE of 8.75% (Table 3).
The solvent additives developed for the fullerene derivatives-based OSCs also exhibit a positive effect in controlling the morphology of the nonfullerene acceptors-based systems. For instance, in 2011 Jenekhe et al. found that a very low concentration of 0.2% DIO showed a positive effect in optimizing the nanomorphology of the nonfullerene acceptor-based system of P3HT:NDI-3TH (Scheme 1) to enhance the performance of OSCs. While the increment of DIO concentration (>0.5%) significantly increased the NDI-3TH domains from the nanoscale to the micrometer scale, resulting in poorer photovoltaic performance. Apparently, such a low optimum concentration of DIO additive for the nonfullerene system is much less than that for the polymer/fullerene systems. DIO was also employed to optimize the BHJ morphology in the PBDB-T:ITIC and PBDB-T-SF:IT-4F blends. The morphology of the PM6:Y6 blend is effectively optimized by 1-chloronaphthalene additive to achieve higher efficiency compared to the device prepared without the additives.

Currently, many widely used solvent additives have high boiling points and they are difficult to be completely removed after the formation of the film. In many cases, the additive residue has been proven to be unfavorable for the stability and reproducibility of the devices. For instance, the widely used solvent additive DIO could act as the photo-acid under the UV light exposure, that the UV irradiation can decompose the DIO residual in the active layer, arousing the morphology traps which hinders the charge transport. A feasible approach to tackle this issue is the development of a low boiling point solvent additive for morphology controlling. For instance, Li et al. applied 1,4-Difluorobenzene, which has a relatively low boiling point of 361.95 K, as an additive to tune the morphology of the J71-m-ITIC blend. 1,4-Difluorobenzene exhibits a positive effect in optimizing the molecular packing and aggregation of the blend film and can be easily removed, facilitating the enhanced efficiency and stability of the device.

Considering the environmental friendliness issue, it is critical to exploit nonhalogen additive to tune the morphology of nonhalogen solvent-processed blend film. Yan et al. applied 1-phenyl naphthalene (PN) as an additive in a hydrocarbon solvent-based processing system to realize better BHJ blend film morphology and photovoltaic performance as compared to that obtained from conventional halogenated solvents (Table 3). The PN additive played a critical role in promoting face-on polymer backbone orientation, reducing domain size, and increasing domain purity of PffBT4T-C9C13:PC71BM blend, which enhanced the PCE of 1,2,4-trimethylbenzene-processed OSCs from 6.4% to 11.70% (Table 3).

**FIGURE 7** Schematic diagrams (cross-sections of the active layers) illustrate the feature dispersions of PC71BM and PTB7 crystalline domains in the PTB7:PC71BM active layers processed with the different routes indicated. Note the PC71BM-enriched surface layer in panel (D) with the dipping treatment. Reproduced with permission.

**SOLID ADDITIVES**

Applying appropriate solid materials as additives is also an effective approach to control the morphology of blend film toward enhancing the efficiency of the OSCs. This treatment can be classified as a ternary strategy if the solid additives remain in the blend film after processing. The ternary strategy is an important approach to manipulate the absorption features, energy levels, and morphology, which have been reviewed by many comprehensive review papers. In the
following discussions, we will focus on the volatilizable solid additives used for morphology optimization.

The selection of solid materials, which can effectively control morphology and can be easily volatilized at relatively low thermal annealing temperature, is the key issue for this treatment method. A pioneering work reported by Hou et al. used a molecular segment of nonfullerene acceptor as the volatilizable solid additives to enhance the intermolecular packing of nonfullerene acceptors\textsuperscript{[71]} This concept originated from the fact that the electron-deficient end-capping units of the fused-ring nonfullerene acceptors form π–π interactions for efficient intermolecular charge transport.\textsuperscript{[4]} The molecular segment SA-1 (Figure 8), which has a similar chemical structure to that of the end-groups of IT-4F, was designed as a solid additive to control the morphology of PM6 (PBDB-TF):IT-4F blend. As illuminated in Figure 8B, SA-1 can be well mixed with IT-4F and may act as a packing template to enhance the π–π stacking of IT-4F during the spin-coating process; once SA-1 is removed from the blend film by thermal annealing at 140°C, the leaving room is in favor of self-assembly and forms a more condensed and ordered molecular arrangement of IT-4F. As a result, using 17.3% SA-1 as a solid additive to process the PM6:IT-4F blend effectively enhanced the PCE from 12.2% to 13.8%, which is comparable to that of the DIO additive-processed devices (as shown in Table 4).\textsuperscript{[71]} Importantly, the device processed by SA-1 additive showed better stability (under illumination in the air) and reproducibility compared with the device processed by DIO (Figure 8C). Additionally, SA-1 can be applied as a solid additive to optimize the morphology of other blend films to obtain better photovoltaic performance compared to the devices processed without any additives (as shown in Table 4). Similar solid additives have been developed and proven to achieve ideal morphology to enhance the PCEs.\textsuperscript{[72, 73]} By using 1,4-diiodotetrafluorobenzene as a volatile solid additive for the PM6:Y6 blend, the synergetic halogen interactions between 1,4-diiodotetrafluorobenzene and BHJ blend film matrix contribute to more condensed and ordered molecular arrangement in the favorable interpenetrating donor/acceptor domains, enabling the significantly enhanced efficiency for the device.\textsuperscript{[74]}

This solid additive strategy opens a feasible and promising way to regulate the morphology correlated with better photovoltaic performance and device stability. The substituents on the solid additives affect the physicochemical properties and thus the outcome of blend film morphology, leaving the challenge of designing solid additives. Due to the variation of molecular structures, the challenge of developing...
versatile solid additives limits the application of volatilizable solid additive treatments.

**CONCLUSIONS AND OUTLOOK**

The outstanding photovoltaic performance of the OSCs is closely related to the BHJ morphology of its donor:acceptor blend active layers, because the aggregates, molecular packing, and the domain size have a critical influence on the exciton dissociation and charge transport. The morphology of the blend film is determined by the inherent properties of the photovoltaic materials and the film formation processing. In most cases, additives treatment and extra postdeposition treatments are performed to achieve optimal nanoscale phase separation, vertical composition distribution, and face-on π-conjugation orientations in the blend film. In this perspective, we provide an overview of the effect of the commonly used postdeposition treatments of thermal/solvent vapor annealing and the solvent/solid additives treatment on controlling morphology for improving PCEs of the OSCs. The examples demonstrated herein offer a rational guide to understand the foundation of these postdeposition treatments and additive processing on tuning the BHJ morphology of blend films.

Presently, nonfullerene acceptors-based OSCs dominate the development of OSCs. The morphology optimization of the nonfullerene-based blend films empirically follows the postdeposition treatments originally developed in the fullerene-based blends. Considering the easier manipulation of nonfullerene acceptors over the fullerene derivatives, morphology optimization should take comprehensive attention to the active layers of the photovoltaic materials, and rational morphology control treatments should be developed toward the combination of improved efficiency and increased stability. Additionally, new treatment methods are highly demanded to meet the requirement for practical application of OSCs, such as the fabrication of large-area and flexible OSCs. We envisage that exploiting solid additives (volatilized under relatively lower temperature or functionalize as guest materials) that can induce the molecular packing of photovoltaic materials toward face-on orientation and restrict the over aggregates of nonfullerene acceptors with high crystallinity should be a feasible strategy. Developing non-halogenated processing solvent with the treatment of non-halogenated additives should be taken into account to fabricate OSCs with green solvent for their future application.

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**TABLE 4** Photovoltaic performance of the OSCs without/with solid additive treatment

| Active layer | Solid additive treatment | $V_{oc} \text{ [V]}$ | $J_{sc} \text{ [mA cm}^{-2}\text{]}$ | FF | PCE [%] | Ref. |
|--------------|-------------------------|----------------------|---------------------------------|----|--------|-----|
| PM6:IT-4F    | N/A                     | 0.89                 | 18.8                            | 0.71 | 12.2   | 71  |
| PM6:IT-4F    | 17.3% SA-1              | 0.86                 | 20.2                            | 0.76 | 13.8   | 71  |
| PBDB-TCl:IT-4F | N/A                 | 0.90                 | 19.0                            | 0.71 | 12.8   | 71  |
| PBDB-TCl:IT-4F | 17.3% SA-1            | 0.86                 | 21.1                            | 0.75 | 14.2   | 71  |
| PM6:IT-2F    | N/A                     | 0.94                 | 18.2                            | 0.72 | 12.7   | 71  |
| PM6:IT-2F    | 17.8% SA-1              | 0.92                 | 19.2                            | 0.76 | 13.7   | 71  |
| PBTA-TF:IT-M | N/A                     | 0.95                 | 19.2                            | 0.66 | 11.8   | 71  |
| PBTA-TF:IT-M | 17.5% SA-1              | 0.94                 | 19.0                            | 0.70 | 12.8   | 71  |
| PBDB-T:ITIC  | N/A                     | 0.89                 | 16.2                            | 0.63 | 9.4    | 71  |
| PBDB-T:ITIC  | 17.8% SA-1              | 0.87                 | 17.1                            | 0.69 | 10.4   | 71  |
| PBDB-T:ITCC  | N/A                     | 0.98                 | 15.2                            | 0.63 | 9.7    | 71  |
| PBDB-T:ITCC  | 18.2% SA-1              | 0.97                 | 15.6                            | 0.70 | 10.6   | 71  |
| J52:IEICO    | N/A                     | 0.86                 | 13.4                            | 0.51 | 6.2    | 71  |
| J52:IEICO    | 14.9% SA-1              | 0.86                 | 14.5                            | 0.57 | 7.3    | 71  |
Yongfang Li is a professor at the Institute of Chemistry, Chinese Academy of Sciences (ICCAS), and in Soochow University. He received his PhD. degree from the Department of Chemistry, Fudan University in 1986, then did his postdoctoral research at ICCAS from 1986 to 1988. He became a staff in 1988 and was promoted to professor in 1993 in ICCAS. He was elected as a member of the Chinese Academy of Sciences in 2013. His present research field is photovoltaic materials and devices for polymer solar cells.

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