Control of aggregated structure of photovoltaic polymers for high-efficiency solar cells

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Abstract

Conjugated organic/polymer materials-based solar cells have attracted tremendous research interest in the fields of chemistry, physics, materials science, and energy science. To date, the best-performance polymer solar cells (PSCs) have achieved power conversion efficiencies exceeding 18%, mostly driven by the molecular design and device structure optimization of the photovoltaic materials. This review article provides a comprehensive overview of the key advances and current status in aggregated structure research of PSCs. Here, we start by providing a brief tutorial on the aggregated structure of photovoltaic polymers. The characteristic parameters at different length scales and the associated characterization techniques are overviewed. Subsequently, a variety of effective strategies to control the aggregated structure of photovoltaic polymers are discussed for polymer:fullerene solar cells and polymer:nonfullerene small molecule solar cells. Particularly, the control strategies for achieving record efficiencies in each type of PSCs are highlighted. More importantly, the in-depth structure–performance relationships are demonstrated with selected examples. Finally, future challenges and research prospects on understanding and optimizing the aggregated structure of photovoltaic polymers and their blends are provided.

KEYWORDS

aggregated structure, photovoltaic polymers, polymer solar cells, power conversion efficiency, small molecule acceptors

INTRODUCTION

Organic conjugated polymers have drawn much attention from researchers in many fields, such as polymer solar cells (PSCs), organic field-effect transistors, organic light-emitting diodes, organic photodetectors, and so on.1,2 Because of the ease of structural modification and high carrier mobility, conjugated polymers play a critical role in functionalizing devices.3 In particular, the molecular structure and aggregated structure are modified to meet the performance requirements of optoelectronic devices.4 Further, in order to exploit the full potential of conjugated polymers and to improve performance, structure–performance relationships of conjugated polymers need to be described and clarified in detail.

PSC is an emerging clean energy conversion technology that exhibits many merits including low cost, excellent mechanical flexibility, highly tunable colors, and excellent scalability via industrial roll-to-roll printing.4 Currently, PSCs have achieved power conversion efficiencies (PCEs) in excess of 18%.5–7 To realize such high efficiencies, many approaches such as variation of molecular structures, modification of interfacial contact, and manipulation of film morphology have been highly employed. Excellent reviews and perspectives have been devoted to molecular design,1,8–19 processing methods,20–29 device physics,30–35 morphology characterizations,36–52 stability/degradation,42,53–55 and commercialization paths.56–62 The readers are directed to these reviews for details. The aggregated structure of
Figure 1. Illustration of the correlations between the molecular structure of organic photovoltaic materials, aggregated structure of films, and device performance of PSCs. The characteristic parameters and control methods of the aggregated structure are outlined. Through the modification of molecular structure and aggregated structure of molecules and blends, the photovoltaic properties and stability of PSCs can be manipulated.
### AGGREGATED STRUCTURE OF PHOTOVOLTAIC POLYMERS

The common method for the preparation of PSCs is solution deposition, in particular, spin coating. During this process, the donor and acceptor materials are dissolved and evenly mixed in the solvent and then cast into the film with volatilization of the solvent. In fact, the film-forming process is usually accompanied by chain conformation transformation, polymer aggregation, and liquid–liquid (L–L) separation, and disorder–order transformation, finally forming the BHJ structure. During the film casting, material solubility, solvent volatilization rate, casting conditions, solvent additives, and post-deposition treatments will affect the polymer molecular arrangement and multilevel self-assembly structure in the active layer, including molecular conformation, ordering and orientation, amorphous and crystalline regions, domain purity and size, which are closely related to light-harvesting, exciton generation, exciton dissociation, and charge transport of PSCs.

The morphological optimization of the active layer films in PSCs requires a comprehensive and in-depth understanding of polymer aggregated structure in solution and solid states. According to polymer physics, the aggregated structure of bulk-heterojunction (BHJ) active layer spans multiple length scales and the corresponding structure parameters are illustrated in Figure 2. Understanding the complexity of aggregated structure and associated quantitative parameters of photovoltaic polymers and their blends is important to establish the structure–property relationships in PSCs. We start at describing a single polymer chain structure at the smallest length scale and then expand to the BHJ morphology of PSC devices. Quantitative descriptors of polymer chains include the number of polymerization ($N$), regioregularity ($RR$), persistence length ($L_p$), and radius of gyration ($R_g$). With the length scale increases, molecular aggregates are formed. The highly ordered stacking of polymer molecules often constitutes polymer crystallite. However, due to the semicrystalline properties of the conjugated polymer, the entanglement between molecular chains often results in amorphous region. The aggregated structure of each component and the interaction between components will affect the final morphology. On a larger scale, the miscibility of donor and acceptor materials has a crucial impact on the phase separated structure of blend films. For hyper-miscibility systems, the domain purity is generally low, which results in insufficient exciton dissociation. For hypo-miscibility systems, the acceptor component in the mixed phase is usually quenched to the percolation threshold, where the domain purity is most appropriate for polymer:small molecule blends. By optimizing the vertical phase separation structure of hypo-miscibility systems, the device performance can also be improved.

In this section, we provide a concise overview of the common characteristic parameters for characterizing the aggregated structure of neat polymers and blends in detail and summarize several key techniques that have been employed to characterize nanoscale morphology in polymer photovoltaic blends. The relationship between aggregated structure parameters and device performance is also briefly explained.

![Diagram of aggregated structure with relevant parameters](https://example.com/diagram.png)

**Figure 2** Plot of structural complexity, schematic and relevant structural parameters of aggregated structure in PSCs with the length scale of polymer (blend) structure. The schematic diagram describes the multiscale structure of conjugated polymers, from the simplest single chain structure at the molecular scale, through multiple polymer chains, semicrystalline structure, phase-separated structure, to the most complicated BHJ morphology. The characteristic parameters corresponding to each scale are provided in the text boxes.
**Aggregated structure and the related characteristic parameters**

We first need to comprehensively consider the working mechanism of PSCs in order to better understand the impact of polymer aggregated structure on device performance. Donor and acceptor materials in active layers absorb photons and form closely bound electron-hole pairs (excitons). Subsequently, they diffuse to the D:A interfaces, which provide driving forces for the excitons to dissociate into holes and electrons. Considering the exciton diffusion length of organic conjugated materials is around 5–10 nm,[97,98] the domain size in active layers should be comparable to the exciton diffusion length to maximize the charge generation efficiency. In addition, for improving the charge transport in conjugated polymers, it is necessary to promote intrachain transport, establish intercrystallite connectivity, and enhance interchain coupling.[31] In other words, the pre-aggregation of polymers in solution and the short-range ordered aggregate of molecules in the film are conducive to efficient charge transport.

In conjugated polymers, the charge transport is largely dependent on π-orbital overlap and is fastest along the conjugated polymer backbone due to the large π-conjugated structure.[31,99,100] The molecular spacing, such as π–π stacking distance (d) and lamellar spacing, reflects the information of the molecular packing (as shown in Figure 3A). $L_p$ reflects the size of the ordered (or aggregated) regions.[37] Generally, rDoC and g are the parameters that will come to play for molecular aggregates. The larger rDoC and the smaller g indicate higher molecular order.[81,101] The in-plane and out-of-plane information of molecular self-aggregation to determine the texture orientation, which generally includes three stacking modes according to molecular stacking structure, that is, edge-on, face-on and flat-on. When the π–π stacking is parallel to the substrate and the lamellar stacking is perpendicular to the substrate, the orientation of molecules will be “edge-on.” Although the lamellar stacking is parallel to the substrate and the π–π stacking is perpendicular to the substrate, the orientation of molecules will be “face-on.” The “face-on” molecule order is mostly favorable for PSCs as the efficient charge transport pathway is in the out-of-plane direction, while “edge-on” molecular order is more favorable for field-effect transistors as the efficient pathway is in the in-plane direction.[99,100] In general, the percentage of face-on or edge-on orientation is below 100%. Quantitatively, the orientation distribution of a particular set of crystallographic lattice planes can be described by Herman’s orientational parameter ($S$)[84] and face-on/edge-on ratio.[102]

Due to the miscibility of donor and acceptor, the phase-separated structure of the BHJ becomes more complex in comparison with the structure of neat polymers. For a three-phase system, the phase-separated BHJ film comprises donor domains, acceptor domains, mixed D:A phases, and D:A interfaces.[103] For the mesoscale morphology of blend films, long period ($L$), that is, center-to-center domain spacing is the characteristic parameter describing the length scale of domains in blend films. In addition, the phase purity as represented by root-mean-square variance of the composition ($\sigma$) is an important parameter, which reflects the mixing extent of components.[104,104] Generally, higher phase purity of the blend is beneficial to efficient exciton dissociation and charge transport, reducing carrier recombination probability and improving device performance.[46] In addition, interfacial roughness is another parameter related to the phase-separated structure of the BHJ.[105] Compared with the sharp interfaces, the rougher interfaces reduce the average distance from the photon absorption site to the D:A interaction.
Transmission electron microscopy (TEM), atomic force microscopy (AFM), GISAXS, and phase separated structure

Interfaces, which enhances the exciton dissociation. However, the rougher interfaces will enhance bimolecular recombination.

The aforementioned parameters in solid films \[^{[106–108]}\] are highly correlated with dispersion/aggregation of conjugated molecules in the solution. For instance, molecules entangled in solution to form amorphous aggregates are not conducive to the ordered stacking of molecules in the film formation process, often resulting in low crystallinity. Although the aggregation of molecules in the solution to form crystals can reduce the nucleation barrier during the film formation process and facilitate its crystallization.\[^{[109–112]}\] Therefore, precise control of the solution state is a prerequisite for achieving a controllable active layer structure. The rigidity of a polymer chain is quantified by its persistence length (\(L_p\)), which is an important dimensional characteristic.\[^{[31]}\] Although the Kuhn length (\(L_k\)) is actually a measure of flexibility. As shown in Figure 3C, when the maximum physical extension length of the chain is much larger than \(L_p\), the behavior of polymer is similar to a flexible chain (\(L_k \approx 2L_p\)). When the maximum physical extension length of the chain is much smaller than \(L_p\), the polymer chain is regarded as a rigid rod.\[^{[113,31]}\] In addition, the radius of gyration (\(R_g\)) is also the characteristic parameter of polymer in solution, which is the root mean square distance of the atoms of the chain from the center of gravity of the chain.\[^{[114]}\] In brief, in order to accurately describe the multilevel aggregated structure of polymer and blends, a variety of parameters are needed to be quantitatively analyzed. Next, we will introduce the key techniques to characterize the multilevel aggregated structure.

**Characterization tools of aggregated structures**

The aggregated structure of polymers and polymer blends and the associated characterization techniques are summarized in Table 1. The aggregated structure of neat polymers refers to the arrangement and stacking structure between polymer chains, including amorphous structure, crystalline structure, liquid-crystalline structure, and oriented structure.\[^{[31]}\] The aggregated structure has a multilevel structure, which makes the characterization of the active layer film full of challenges.

Usually, the aggregation behavior of polymers can be inferred by peak shape and shift of the UV-visible (UV-vis) absorption spectrum\[^{[118]}\] or fluorescence (PL) spectrum.\[^{[119]}\] The aggregation of conjugated molecules in solution can be characterized by the peaks of \(\pi-\pi^*\) transition in the UV-vis absorption spectrum. The peak shape of the absorption spectra of conjugated molecules often reflects the changes in their aggregation forms, including single molecules, intramolecular aggregation, and intermolecular aggregation.\[^{[120–123]}\] For instance, when the polythiophene (PT) molecules are completely dissolved in the solution, they present a completely disordered state called coil conformation. When the temperature of the solution decreases gradually, the molecules are precipitated from the solvent and transform disorder to order state. The increase of the conjugate length (\(L_c\)) of the molecular skeleton leads to the red shift of the corresponding absorption peaks and the intermolecular \(\pi-\pi\) stacking forms the microcrystalline absorption peaks.\[^{[124]}\] In addition, the aggregation state of the same polymer in different solutions also causes the shift of UV-vis absorption spectrum.\[^{[125]}\] PL spectroscopy can also be used to characterize the aggregated structure of conjugated polymers in solution. With the increase of solution concentration, the interaction between molecules in the solution leads to PL quenching and a decrease of PL intensity. Besides, due to the \(\pi-\pi\) stacking of molecules to form ordered aggregates, the PL peaks will be red-shifted and even new PL peaks will appear.\[^{[119]}\] PL spectroscopy can also characterize the degree of phase separation of the organic active layer.\[^{[126–128]}\] In the active layer, the charge transfer occurs between the donor and acceptor, causing the excitons to separate at the interfaces of the components so that PL cannot be emitted.

To date, the aggregated structure of the thin film can be characterized by real-space microscopic methods, such as atomic force microscopy (AFM), transmission electron microscopy (TEM), scanning electron microscopy (SEM), which can visualize the surface or bulk morphology of the film. AFM is a very common and useful technique that investigates the surface information of the sample at the micrometer and nanometer scales with high spatial resolution within 10 nm.\[^{[36]}\] Its operating principle is that the probe contacts the sample surface, through the van der Waals interaction between them and the feedback mechanism, the sample surface information (such as height, phase distribution, modulus\[^{[66,129,130]}\]) of the sample can be obtained. Among these, height and phase images in AFM are often used to describe the morphology of thin films. The roughness of the height image is often used to represent the homogeneity of the thin film. It should be noted that the AFM phase image does not represent the real phase separation, but the stiffness of the sample, which is related to the difference between the oscillating of the piezoelectric and the oscillating

| Component          | Aggregated structure                      | Characterization techniques                                                                 |
|--------------------|-------------------------------------------|---------------------------------------------------------------------------------------------|
| Neat polymer       | Amorphous structure                       | Ultraviolet-visible (UV-vis) absorption spectroscopy, fluorescence (PL) spectroscopy, small-angle neutron scattering (SANS), differential scanning calorimetry (DSC), X-ray diffraction (XRD), grazing incidence wide-angle X-ray scattering (GIWAXS), grazing incidence small-angle X-ray scattering (GISAXS), and so on. |
|                    | Crystalline structure                     | XRD, GIWAXS, polarized resonant X-ray scattering (P-SoXS), and so on.                       |
|                    | Oriented structure                        | Polarizing microscope (POM), DSC, and so on.                                                 |
|                    | Liquid–crystalline structure              |                                                                                             |
| Polymer blend      | Phase separated structure                 | Transmission electron microscopy (TEM), atomic force microscopy (AFM), GIWAXS, SANS, resonant soft X-ray scattering (R-SoXS), scanning transmission X-ray microscopy (STXM), optical microscopy (OM), scanning electron microscopy (SEM), time-of-flight secondary ion mass spectrometry (ToF-SIMS), X-ray photoelectron spectroscopy (XPS), and so on. |

**Table 1** The multiscale aggregated structure of neat polymer and polymer blend of PSCs and the relevant characterization techniques
of the AFM probe. Moreover, there are many multifunctional AFM technologies used in the characterization of PSCs, such as the conductive AFM (c-AFM),\textsuperscript{[131–133]} photoconductive AFM (pc-AFM),\textsuperscript{[132,134–136]} photo-induced force microscopy (PiFM),\textsuperscript{[137,138]} and Kelvin probe force microscopy.\textsuperscript{[139–142]} The c-AFM, which was first used by Alexeev et al.,\textsuperscript{[143]} can detect the donor and acceptor region of the film surface by applying an external voltage between the probe and the conductive substrate, and record a surface topography and current image. Therefore, the c-AFM can describe the local electrical property of the blend film. Under positive bias, the bright area in the c-AFM image represents the electron acceptor domain. Although under reverse bias, the bright region is associated with the electron donor domain.\textsuperscript{[134]} Figure 4A shows the AFM image of 1% low $M_w$ fraction PBDB-TF:Y6 blends and the c-AFM image taken at 0 V bias and under white light illumination.\textsuperscript{[144]} Additional information can be obtained by combining Fourier infrared spectroscopy with AFM technique. PiFM,\textsuperscript{[138,145]} the atomic force tip scans the sample while an infrared laser excites the sample to produce contrast for chemical imaging. Bao and colleagues\textsuperscript{[138]} demonstrated the application of PiFM in PSC blends. By adjusting the IR excitation laser to a specific absorption wavelength, the donor and acceptor domains in BHJ can be distinguished, as shown in Figure 4B. PiFM images of all-polymer PII-2T-PS:PPDI-T films with different concentrations of CN additive selectively imaged at the wavelength of 1453 cm$^{-1}$ of donor polymer (bottom). Reprinted from Ref. [138] with permission.
in Figure 4C, the top images show the surface morphology of poly[2-methoxy-5-(3′,7′-dimethoxyloxy)-1,4-phenylenevinylene] (MDMO-PPV):[6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) film with different blending ratios, while the bottom images show the cross-section morphology of the corresponding blending films. The SEM images clearly show that when the blending ratio is 1:3, the large-sized PCBM locates at the surface and inside of the blend films. [146]

TEM is probably the most popular technique in characterizing the morphology of organic semiconductor thin film on the nanometer scale. [147–149] It uses a beam of electrons as the illumination source to create an image with the transmitted electron beam or the diffracted electron beam passing through the sample and then analyzes the internal microstructure of the sample. Precise domain size and the molecule aggregation or the crystallinity of film can be obtained due to the high contrast of a TEM image. [150,151] Therefore, this technology can provide detailed information about a sample with high spatial resolution and ultrasensitive, whereas SEM technique can only be used to scan and obtain the surface information of a sample. As shown in Figure 4D, Janssen and colleagues [148] used the TEM and electron diffraction to investigate the changes in the morphology of P3HT and PCBM derivative blends upon thermal annealing (TA). The images obviously showed that the P3HT crystals were induced to form an ordered stacking structure by TA.

Scanning transmission X-ray microscopy (STXM) [149,103,152,153] is also a powerful morphology characterization technique that characterizes the morphology of blend films. Different from the TEM, STXM is a synchrotron-based technique, which utilizes a variable-energy focused X-ray to measure the sample rather than a beam of electron, as displayed in Figure 4E. In PSCs based on fullerene acceptors, [46,94,103] the blends have significant differences in the elemental composition of the donor and acceptor materials, enabling a high contrast signal of characteristic near-edge X-ray absorption fine structure (NEXAFS). Therefore, the chemical composition and morphology of blends can be quantified analysis. In 2010, Ade and colleagues [103] determined the miscibility of P3HT and PCBM by STXM (Figure 4F). They discovered that there was no pure amorphous phase especially after annealing and the two components are miscible at elevated temperatures.

In addition, the morphology parameters can be characterized using reciprocal-space scattering methods, that is, by Fourier transform of the morphology information of the real-space to obtain molecular stacking distance, phase purity, molecular orientation, and so on. Generally, the synchrotron radiation-based scattering techniques [50] may be the most effective method to reveal the molecular packing and multi-level self-assembly structures at the molecular scale, ranging from Ångstrom (Å) to a few nanometers (nm).

Grazing incidence wide-angle X-ray scattering (GIWAXS) [37,38,68,154] applies an incident X-ray in a grazing angle (0.1–1°) to the sample surface and collects scattered X-rays in a reflection direction with high spatial, temporal and energy resolution (as shown in Figure 5A). It is the reciprocal-space technique and it is sensitive to the crystalline parts of the thin film. If the molecules are disordered, the GIWAXS pattern will appear as a diffraction ring. Some key parameters can be used to quantitatively characterize the aggregated structure and morphology of thin films. The molecule spacing, such as π–π stacking distance and lamellar spacing, reflects the information of the molecular packing and crystallinity of the active layer, which is inversely proportional to the diffraction vector in reciprocal (q_{xy} – q_{z}) space, that is, \[ d = 2\pi / q_{c} \] where q_{c} is the center position of a diffraction peak by GIWAXS. The number of repeat units involved in π–π interactions defining the \( L_c \), which reflects the size of the ordered (or aggregated) range, can be obtained using Scherrer’s equation: \[ L_c = 2\pi K / \Delta q_{c} \] where K is the shape factor (~0.9), \( \Delta q_{c} \) is the full width half maximum (FWHM) of the scattering peak. As displayed in Figure 5B, the two-dimensional (2D) pattern of Y6 in chloroform (CF) showed an obvious face-on orientation, indicating that the molecular chain accumulation was more compact, [68] which was conduciive to charge transport among the interchain. However, when chlorobenzene (CB) is used as the processing solvent, a weak diffraction ring appears in the 2D pattern, and its molecular accumulation is much more disordered.

Similar to GIWAXS, grazing incidence small-angle X-ray scattering (GISAXS) also operates in grazing incidence geometry, while GISAXS investigates the structure in a longer scale of films, typically from 10 to 500 nm, due to the longer distance of sample to detector. Therefore, the larger scale features in the film can be characterized by GISAXS, such as the domain size, [155] shape, and aggregation of blend films. [156] The GISAXS profiles of the P3HT:PCBM blends under different annealing conditions are shown in Figure 5C, the structural parameters of the blend can be obtained by fitting the data with the Debye–Anderson–Brumberger equation (DAB model). [157] This can be used to describe the large scale of PCBM distribution around the amorphous or crystalline molecular. In addition, a variety of models are needed to analyze the morphological characteristics, which are beyond the scope of this review. Readers can refer to the literature [157–159] for details.

The formation of domains and bicontinuous structures in the film is important, and these characteristics of morphology can be quantitatively measured by GISAXS and resonant soft X-ray scattering (R-SoXS). [46,160] R-SoXS can obtain additional morphological information, especially the phase purity. R-SoXS is a specialized type of SAXS, which combines the SAXS and NEXAFS spectroscopy. Due to the NEXAFA’s ability to distinguish the different elements of blends, R-SoXS avoids the low scattering contrast of SAXS experiment due to the similarity in the elemental composition of donor and acceptor materials used in PSCs. [46] The scattering signal is the Fourier transform of the real space distribution of a sample in the reciprocal space. Generally, we need to convert the 2D scattering patterns into 1D scattering profiles (I(q) vs. q plots) for quantitative analysis, considering the three-dimensional (3D) anisotropy of the sample, Lorentz correction of the data is required by changing the I(q) versus q plots to the I(q) q^2 versus q plots. In blend films, the long period (L), for example, center-to-center domain spacing can be calculated by using the equation: \( L = 2\pi / q_{peak} \) where q_{peak} is the peak location of the scattering maximum in R-SoXS profiles (see Figure 5D). Domain purity can be expressed by integral scattering intensity (ISI), [46,93] that is,
Figure 5  (A) Schematic for GIWAXS or GISAXS experimental test. The GIWAXS pattern is collected with the area detector being placed close to the sample, whereas the GISAXS pattern is placed further away from the sample. The incident angle, exit angle, and the out-of-plane angle are $\alpha_i$, $\alpha_f$, and $\psi$, respectively. Reprinted from Ref.[50] with permission. Copyright (2014) John Wiley & Sons, Inc. (B) 2D GIWAXS patterns and schematic of molecules arrangement for pure Y6 film processed with CB and CF. Reprinted from Ref. [168] with permission. Copyright (2020) John Wiley & Sons, Inc. (C) GISAXS profiles of the P3HT:PCBM blends under different annealing conditions. Reprinted from Ref.[157] with permission. Copyright (2011) American Chemical Society. (D) Lorentz corrected R-SoXS profiles of various blends of PBPPP-OD and terpolymers. Reprinted from Ref.[161] with permission. Copyright (2017) John Wiley & Sons, Inc. Plot of the $J_{SC}$ versus the respective average long period (E) and FF versus the respective domain purities (F) of PBPPP-based PSCs by R-SoXS. Reprinted from Ref. [161] with permission. Copyright (2017) John Wiley & Sons, Inc. The absolute SANS intensity (G) and Lorentz-corrected scattering pattern (H) of the as-cast and solvent annealed PCPDTBT:PCBM blends. Reprinted from Ref.[164] with permission. Copyright (2014) John Wiley & Sons, Inc. (I) The size distribution of ICBA aggregates in PCPDTBT:ICBA blends with 2-chlorophenol (CP) as the second solvent added to oDCB. Reprinted from Ref. [163] with permission. Copyright (2014) John Wiley & Sons, Inc

\[
\sigma = \sqrt{\frac{1}{II} \int \frac{1}{I(Q)} dQ^2 dq}
\]

As displayed in Figure 5D, Ye et al.[161] characterized the domain spacing and average relative domain purity of blends based on PCBM and a series of DPP-based conjugated polymers with varied side chains by R-SoXS. They observed the linear relationship between $J_{SC}$ and domain spacing (Figure 5E) as well as FF and domain purity (Figure 5F), through R-SoXS characterization and photovoltaic performance characterization, which guided the modification of blend morphology and the improvement of device performance.

Neutron scattering[162–164] has deeper penetration and higher sensitivity, which plays an important role in detecting the internal space structure and dynamic process as well as the aggregated structure in organic semiconductor materials. In the neutron scattering, the scattering intensity $I(Q)$ is proportional to the squares of the difference between the scattering length density of the sample and the scattering length density of the surrounding environment $(b_1 - b_2)^2$ and the form factor $P(Q)$, that is, $I(Q) \sim (b_1 - b_2)^2 P(Q)$. The $P(Q)$ is related to the shape and size of the phase domain, which was commonly modeled by the Schulz sphere model[165–167] or an elliptical cylinder model[165,168,169] in binary blends containing fullerene. Small-angle neutron scattering (SANS) can be used to study the microstructure, especially size, shape and dynamics of their components[114,117,170,171]. Dadmun et al.[164] using the SANS to characterize the morphology and aggregation of the PCPDTBT:PCBM blends in different solvent annealing conditions. Due to the significant differences between PCPDTBT and PCBM in scattering length density, the scattering profile of Figure 5G showed that the scattering strength of as-cast film (AC) is very weak, which suggests that the film is homogeneous and the phase separation is not obvious, while the scattering pattern of the blends with the solvent annealing by oDCB exhibit enhanced scattering, indicating a phase separation of the fullerene and polymer in the blend. Figure 5H is the Lorentz-corrected scattering profile
of Figure 5G, where the q location of the scattering peak can be used to calculate the average distance \((2\pi / Q_{\text{max}})\) between two adjacent phases. In the same year, they also characterized the distribution of indene-C_{50} bisadduct (ICBA) aggregates in the blend region by SANS, as shown in Figure 5I.[163] Pei and colleagues[117] combined SANS and X-ray scattering techniques to characterize the aggregated structure of a conjugated polymer in different solvents. In the good solvent 1,2-dichlorobenzene (oDCB), the polymer displays the worm-like structure, while in the poor solvent toluene, the polymer form 2D ordered structure, which correlated with higher crystallinity.

Apart from the above methods for the characterization of aggregated structure, solid-state NMR (ssNMR), as a powerful probe of the molecular-level characterization technique, has attracted extensive attention in recent years.[144,172,173] The increase in local ordering and \(\pi-\pi\) interactions can be analyzed by the narrower and more resolved peaks from ssNMR.[174,175] In addition, ssNMR can also distinguish which groups of the materials cause the ordered aggregation. Therefore, ssNMR has been valuable in providing detailed information about the molecular interaction and morphological features that are critical in complementing the morphological characterization of PSCs.

Further, film formation kinetics refers to the evolution of the structure in the process of forming a film from a solution. Generally, altering the volatilization process of the solvent can control the self-aggregation of molecules. The film formation process can be detected by combining ellipsometric spectroscopy,[166,176] UV-vis absorption spectroscopy,[109] GIWAXS,[172,177,178] GISAXS, light scattering, and other in situ characterization methods to track changes in film thickness, molecular aggregation, and local order during film formation.

CONTROL OF AGGREGATED STRUCTURE OF PHOTOVOLTAIC POLYMERS IN FULLERENE BASED SOLAR CELLS

Since the emergence of BHJs, researches of PSCs are mainly focused on the blends of polymer donor materials and fullerene-based acceptor materials,[179] affording PCEs up to \(~12\%\).[69] Being beneficial from the unique ball-like fully conjugated skeleton of fullerene, the D:A interface and exciton dissociation are enhanced and isotropic electron-transport properties are provided. Fullerene-based acceptor materials significantly promoted the development of PSCs.[180] In this section, we mainly discuss the influence of the aggregated structure of photovoltaic polymers and blends on device performance in polymer:fullerene blend systems. Among the numerous photovoltaic polymer materials, classical PT and its derivatives, polypyrropyridione (DPP)-based copolymers and polymers with temperature-dependent aggregation are selected as the representatives for discussion.

Polythiophenes

Poly(3-hexyl thiophene) (P3HT) is the most commonly used PT material in OPV research, due to its simple chemical structure, high regioregularity, excellent photoelectric properties, and low cost.[181] The ordered crystal arrangement and intercrystalline link of P3HT provide channels for carrier transport, especially along the direction of the conjugate skeleton and \(\pi-\pi\) stacking direction (Figure 6A). Although the rapid development of PSCs now far exceeds that of P3HT:PCBM blend system,[182,183] the study on the aggregated structure of this classical blend system remains far-reaching influence and reference value. Therefore, we will briefly introduce the optimization of the aggregated structure of the system. Due to the high crystallinity of P3HT, increasing the crystallinity of the polymer is beneficial to carrier transport. In P3HT:PCBM blends, the \(M_w\)[184–187] and \(R^2\)[188,189] of P3HT, composition ratio,[172,190] choice of solvent,[191] the thickness of active layer,[192] and post-deposition treatment[73,74,193–197] can all influence the molecular stacking of P3HT and the aggregation behavior of PCBM. For example, the \(M_w\) affects the semicrystalline structure of P3HT and phase-separated structure[195] of the active layer. Some research groups[184–187] have studied the influence of the \(M_w\) of P3HT on the aggregated structure and device performance of the P3HT:PCBM system. When the \(M_w\) is too low, the poor crystalline link is not conducive to carrier transport. As the \(M_w\) increases, the crystalline link tends to be perfect, which is in favor of carrier transport. However, further increasing \(M_w\) promotes molecular entanglement and leads to a decrease in crystallinity, which limits carrier transport.

Due to the solution processing method, the molecular aggregates in solution strongly depend on the solvent characteristics (e.g., solubility, boiling point,[199] vapor pressure,[159] and polarity, etc.) and the interaction[200] between solvent and D:A components. P3HT in different solutions can exhibit different aggregation behavior (H- or J-aggregate), which can be distinguished by UV-vis absorption spectra.[115] In 2001, the effect of solvents on the aggregated structure and photovoltaic properties of fullerene-based blend films was confirmed by Hummelen et al.[201] In the P3HT:PCBM system, Hansol et al.[202] pointed out that the orientation of P3HT or PCBM has a great influence on the charge generation in PSCs. When spun-cast from the low boiling point solvent CF (61°C), P3HT films with face-on orientation, which can generate charge more efficiently and reduce exciton recombination at the interface, while the edge-on molecule orientation was obtained by spin-coating with high boiling point solvent DCB (182°C; see Figure 6B). Veploogen et al.[199] found that when the solvent CB with high boiling point was selected, the phase separation size of P3HT:PCBM film was larger, which was mainly attributed to the extension of the drying time of the film, providing enough time for the self-aggregation of the P3HT. Selecting suitable solvents for P3HT:PCBM system according to the difference of solubility of materials is a common method to regulate the aggregated structure of blends. Hansen solubility theory can simplify the tedious process of selecting solvents.[203] Taking P3HT:PCBM as an example,[204,205] the ideal morphology is that P3HT is partially self-aggregated in the film to form crystals, while PCBM forms microcrystals uniformly dispersed in the film. Therefore, the best solvent properties should be the poor solvent of P3HT and the good solvent of PCBM. Similarly, the aggregated structure of the blend system can be changed by adding an additive or a cosolvent with selective solubility to a certain component.[182,206]
Adding 1-chloronaphthalene (CN) as a solvent additive to P3HT:ICBA system increases the device efficiency to 7.4%, which is the highest efficiency of photovoltaic devices based on P3HT:fullerene blend system reported so far.

The drying dynamics of P3HT:PCBM blend film[85,86] plays an important role in the aggregated structure and photovoltaic properties, which is closely related to the self-assembly process of materials from solution state to film state. The aggregated structure and self-organization of crystalline polymers and fullerene could be optimized through regulating film-forming kinetics.[207,208] Yang and colleagues[194] found that controlling the growth rate of the active layer from solution to film by changing the spin-coating environment would increase the hole mobility and balance electron and hole transport, realizing FF up to 0.67. The slow growth will facilitate the formation of a self-organized structure in the P3HT:PCBM blend films and have a high degree of crystallinity of P3HT, which significantly increased hole mobility. Although the fast-grown film has unbalanced electron and hole transport, resulting in the poor FF and photocurrent. In 2011, Benjamin et al.[208] investigated the dynamics of molecular ordering during the film drying process in more detail. The evolution of the (100) diffraction peak of P3HT during the film drying was monitored in real-time by GIWAXS and laser reflectometry. They pointed out that the crystallization of P3HT occurs before the aggregation of PCBM. The strong interactions between P3HT and fullerene suppressed the PCBM crystallization, leading to the formation of electron transport pathway in the blend.

TA[74] is a commonly used method for controlling aggregated structure. The active layer is heated to above the glass transition temperature ($T_g$) of the materials to provide energy for the movement of molecular chains and reduce the free volume of the blend system, making the film more smooth for charge collection and facilitating the charge transport.[72] In addition, with the extension of annealing time or the increase of annealing temperature, phase separation will occur in the blend system, and the blend system moves to the thermodynamic equilibrium state and further promotes the molecular alignment of the crystalline polymer. In 2005, Heeger and colleagues[73] annealed the P3HT:PC60BM active layer at 150°C, the PCE nearly 5% was achieved, and the system exhibited excellent thermal stability. X-ray diffraction (XRD) results demonstrated that the crystallization of P3HT polymer is enhanced, intermolecular spacing is reduced, and molecular stacking is improved after annealing,[193] which are all conducive to the efficient transport of charge carriers (as shown in Figure 6C). This observation was also confirmed in the work of Chirvase et al.[72] The absorption spectra of the blend film show that the absorption peak of P3HT shifts red after annealing, while that of PCBM hardly changes, indicating that the aggregation of the polymer increases. This is related to the change of ordered phase of the polymer. Specifically, the P3HT backbone structure was distorted before annealing because of the aggregation of PCBM, while the P3HT backbone was more planar[74] after TA due to the diffusion of PCBM, which favored charge transport and enhanced PCE. In addition, TA can also improve the contact...
with the electron-collecting electrode\textsuperscript{[73,194]} and facilitate the charge transport for the completed device due to the stronger contacts and increased contact area, as well as the suppressed P3HT:PCBM crystal overgrowth during annealing.

SVA\textsuperscript{[209–211]} is another post-deposition method to adjust the molecular stacking and enhance the crystallinity of P3HT:PCBM active layer since Yang and colleagues first reported this method.\textsuperscript{[194]} Afterward, Yang and colleagues\textsuperscript{[212]} precisely constructed the PCBM aggregates by multistep controlled SVA with tetrahydrofuran (THF) and carbon disulfide (CS\textsubscript{2}) to obtain the appropriate domain size of PCBM aggregates and an improved crystallinity of P3HT (Figure 6D). The THF vapors were absorbed by the active layer and substantially increased the mobility of PCBM, leading to the aggregation of PCBM. Subsequently, The CS\textsubscript{2} vapor with good solubility of P3HT and PCBM was treated, so that P3HT molecules arranged and aggregated as well as the PCBM dispersed in P3HT to form a bicontinuous network in the nanoscale (Figure 6E). Utilizing the difference in solubility of the solvent to the polymer and fullerene to conduct SVA, one can achieve precise control\textsuperscript{[213]} of aggregated structure.

Due to the narrow absorption range and the relatively high-lying HOMO energy levels of P3HT, the P3HT:PCBM system has lower $J_{SC}$ and $V_{OC}$, which results in high energy loss and low device efficiency in solar cells. To overcome this limitation, several PT derivatives have been designed and synthesized by molecular structure modification.\textsuperscript{[214–219]} The molecular structure design of PT derivatives has been introduced in detail in our previous articles.\textsuperscript{[220]} Here, we will focus on the influence of molecular engineering on the aggregated structure. In 2011, Zhang et al.\textsuperscript{[219]} had synthesized PT derivatives with carboxylate substituent. The polymers have stronger absorption and deeper HOMO energy level, exhibiting a relatively high $V_{OC}$ of 0.8 V when matched with PC\textsubscript{71}BM and the suitable phase separation morphology. Afterward, they synthesized a new PT derivative, named poly[2’,5’-bis[(2-butyloctyl)oxy]carbonyl][2,2’,5’,2’’]-quaterthiophene]-5,5’’-diyl (PDCBT),\textsuperscript{[67]} which exhibited the high crystallinity than P3HT. In addition, the smaller $\pi-\pi$ stacking distance of PDCBT is beneficial to the charge transport in the interchain. The device based on PDCBT:PC\textsubscript{71}BM exhibited a PCE of 7.2% with a high $V_{OC}$ of 0.91 V and FF of 0.72. Attaching carboxylate substituents to the side chain is a simple and effective way to enhance molecular stacking with better photovoltaic properties. Huang et al.\textsuperscript{[221]} designed fluorinated PT derivatives with different alkyl side chains to tune the aggregation properties. These polymers show stronger aggregation than P3HT in dilute CB solutions by UV-vis, which indicates the interchain interactions can be tuned by alkyl side chains. In addition, the PT derivative with longer side chain has good solubility, which increases the fiber width in the blend film and is more favorable for exciton dissociation and charge transfer.

In generally, PT has high regioregularity and crystallinity. To improve the carrier transport efficiency of PT blends with fullerene, it is necessary to increase the ordered stacking of polymer. For example, using low boiling point solvent processing probably makes it face-on stacked, while using high boiling point solvent processing tends to former larger domain size due to the strong aggregation tendency of polymer and fullerene. TA can not only reduce the $\pi-\pi$ stacking distance, but also obtain high device stability. Through SVA and solvent additive selectively dissolve the fullerenes, fullerenes can be more evenly dispersed in the nano-network of crystalline polymer to form an ideal film morphology and balance the electron and hole transport for improved performance.

### DPP-based copolymers

DPP-based copolymers are another typical conjugated photovoltaic polymers in addition to PTs. DPP unit has been widely incorporated into conjugated polymers for constructing high-performance PSCs due to its excellent co-planarity and strong electron-withdrawing ability.\textsuperscript{[222–225]} DPP-based copolymers, copolymerizing the DPP unit with the electron-rich unit, often exhibit a broad and tunable optical absorption, energy levels, and high mobilities for holes and electrons, which can easily modify the molecular characterization to match with fullerene acceptors\textsuperscript{[226–229]} (most typically [60]PCBM, or [70]PCBM) and NFA.\textsuperscript{[230–232]} DPP-based conjugated polymers were not extensively used in the PSCs field until 2008 when Janssen and colleagues\textsuperscript{[233]} blended the DPP-based donor materials with fullerene acceptors to form BHJ active layers. After that, the rapid development of DPP-based polymers:fullerene solar cells was witnessed in the following decade.\textsuperscript{[167,172–176]} In this part, we will introduce the aggregated structure and device performance of the DPP-based conjugated polymer:fullerene blend systems.

The influence of the molecular structure of polymer\textsuperscript{[222,226,228,234–238]} on its aggregation in solution and film cannot be ignored. This influence is mainly through improving the solubility and molecular arrangement of the polymer. In 2013, McCulloch et al.\textsuperscript{[237]} systematically investigated the effect of the alkyl-side chain branching position (as shown in Figure 7A) on the molecular stacking characteristics and photovoltaic properties of DPP-based polymers. As the alkyl-side chain branching position is far away from the DPP core, stronger molecular aggregation of DPP polymers occurred in solution, which is consistent with the results evidenced by GIWAXS (Figure 7B). By adjusting the branched sites of alkyl-side chains on the DPP core to enhance $\pi-\pi$ electron transport, more than 7% efficiency is achieved in DPP-based polymer:fullerene solar cells without the use of processing additives. There are many related studies,\textsuperscript{[235]} such as adjusting the length of DPP polymer fiber by changing the $\pi$-conjugated segment (thienothiophene, dibenzothiophene, and bithiophene) copolymerized with DPP unit\textsuperscript{[223]} or the length of alkyl side chain\textsuperscript{[239]} to achieve enhanced exciton dissociation efficiency and charge transport, so that the efficiency of DPP-based conjugated polymers:PCBM is close to 8%. In addition, Ye et al.\textsuperscript{[161]} designed random copolymers based on DPP-based polymer using side-chain engineering method, which precisely modified the energy level and mesoscale morphology of the polymer. By increasing the proportion of short side-chain in the terpolymers, the $\pi-\pi$ stacking of blends in the out of plane is more compact and the domain size is smaller. By employing the alkylthio-substituted terpolymer, the DPP-based polymer:fullerene binary systems realized more than
8% device performance. Based on R-SoXS characterizations, they found that the FF of the device exhibited a linear correlation with the phase purity, which can be used as a guide to the optimization of device performance.

With the emergence of a large number of DPP-based conjugated polymers, Hou and colleagues invented a new DPP-based polymer P266 (utilizing BDD and DPP units as the backbone framework, Figure 7C) in 2017. The newly developed DPP-based polymer showed pronounced temperature-dependent aggregation in the solution state. By taking advantage of this temperature-dependent aggregation characteristic of the polymer, the P266:PCBM device performance was improved from 7.37% to 9.18% by altering the solution processing protocol. In their study, the donor material and the acceptor material were dissolved separately and then mixed together at low temperature. Compared with the method of dissolving together at high temperature, the donor material tends to aggregate in the solution to obtain higher phase purity (see Figure 7D), which reduced the charge recombination.

The dynamics of solvent evaporation and the aggregation of polymer in solution govern the final structure of blends. For some DPP-based polymer:fullerene blends, using cosolvent (mixed solvent) or adding solvent additive is an efficient method to improve the aggregated structure and device performance. The cosolvent or adding solvent additive, which is quite different from the primary solvent, can avoid the formation of large fullerene aggregation and the oversized domain in solution-processed blend films. Janssen et al. conducted a real-time study on polymer aggregation and phase separation during solvent evaporation by using optical techniques. They observed that the cosolvent could prolong the film-forming time and make the polymer aggregate early in the solution to form a continuous network. After that, the L–L separation occurred and PCBM was dispersed in the polymer
network, which inhibited the aggregation of PCBM and the formation of large PCBM-rich domains. Therefore, in the PDPP5T:PC71BM systems, the PCE of the system is less than 2% without cosolvent, while the PCE can be up to 8% with cosolvent oDCB present (as shown in Figure 7E and F). The performance difference was attributed to the suppressed PCBM aggegate and smaller domain size. The influence of solvent additives on the aggregated structure of DPP-based polymer:PCBM system was also investigated by Russell and colleagues.\[251\] GIWAXS results showed that the addition of solvent additives enhances the (010) diffraction peak of the DPP-based polymer and increases the persistence length of the polymer, which was beneficial to the formation of fiber networks. As a result, a fivefold increase in J_{SC} was achieved in the device processed with solvent additive, compared with a single solvent. With the presence of a selective solvent additive, the film-drying process and the crystallization of polymers are altered, leading to the ordered crystal arrangement, reduced phase area size, and uniform distribution of PCBM in the polymer fiber network.

In all, the length and width of the fibers in the blends can be carefully adjusted by optimizing the π-conjugated segment and side chain of DPP-based conjugated polymer. In addition, a remarkable feature of DPP-based conjugated polymer:fullerene systems is that fullerenes aggregate seriously in the blend.\[250,251\] which leads to the formation of large domain size. For this feature of DPP-based polymer:fullerene system, the use of solvent additives, cosolvent, and control of film drying time are particularly conducive to optimizing the morphology of the blends. Therefore, it is necessary to understand the forming process of the aggregated structure of the blends in detail and select the appropriate solvent processing conditions that are beneficial to obtain the targeted aggregated structure of polymer and phase separation structure of the blend film. Using Flory-Huggins theory, Janssen and colleagues\[250\] established a theoretical model of multicomponent system to describe the phase separation process. They showed that the spinodal L–L phase separation during the drying process is responsible for the larger PCBM aggregates, and the model predicted that the aggregate size of fullerene in the polymer matrix increases with the drying time. Toney and colleagues\[249\] also explained why the use of solvent additives in DPP-based polymers could improve the efficiency by SAXS. Compared with single solvent, adding solvent additive in polymer solution can make polymer aggregate and form short-range lamellar order (Figure 7G). These structures are regarded as seed crystallites (nuclei), and the increased nucleation density promotes orderly crystallization and jagged interface in the film formation process, which is conducive to charge dissociation and transport.

Conjugated polymers with temperature-dependent aggregation

For solution-processed PSCs, the conformation and aggregated structures of polymers in solution, the vitrification of molecular conformation during solvent volatilization and the post-deposition treatment after film formation have significant effects on charge transport and device performance.\[252\] In many conditions of solution processing, temperature as one of the important factors has been extensively studied by researchers, such as the solution temperature\[71,106,123,162,253–259\] casting temperature,\[255,260\] substrate temperature,\[261,262\] film annealing temperature, and post-annealing temperature. Among them, it has been mentioned above that the film aggregated structure and device performance are adjusted by annealing on the film. This section will focus on how to control the aggregated structure and device performance of conjugated polymers with temperature-dependent aggregation in solution and its film formation.

A typical characteristic of conjugated polymers with temperature-dependent aggregation is that the polymers can disaggregate and easily dissolve in solution at high temperatures, and they are strongly aggregated and arranged in order when the solution cooled down\[71\] (Figure 8A). The aggregation feature can be visually characterized by UV-vis absorption spectrum, GIWAXS, and light scattering, and so on. For example, the absorption spectra of poly[(5,6-difluoro-2,1,3-benzothiadiazol-4,7-diyl)-alt-(3,3′′-di(2-octyldodecyl)-2,2′,5′,2′′-terthiophen-5,5′′-diyl)] (PfBT4T-2OD), a typical polymer with temperature-dependent aggregation in dilute oDCB solution at various temperatures (Figure 8B), indicates that the polymer solution under the high temperature of 85°C shows only one absorption peak at 530 nm. With the decrease of solution temperature, the absorption spectrum gradually red-shifts; when the temperature drops to 25°C, the absorption spectrum is identical to that of thin film.\[261\] This indicates that with the decrease of solution temperature, conjugated polymers undergo disordered-ordered transition, and the planarity of molecular chains increases, which are conducive to form strong intermolecular attraction and effective charge transfer.

In addition, P3HT\[54,106,162,260,263,264\] and poly[(2,6-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)-benzo[1,2-b:4,5-b′]dithiophene)-alt-(5,5-(1′,3′-di-2-thienyl-5′,5′-bis(2-ethylhexyl)benzo[1′,2′:4′,5′-c′]dithiophene-4,8-dione)] (PBDB-T\[107,265\]) are also the conjugated polymers with temperature-dependent aggregation. Understanding the temperature dependence of aggregation behavior in solution and film forming process is a prerequisite for controlling the aggregated structure of thin films. Taking P3HT for example, by using dynamic light scattering and static light scattering characterization, Han et al.\[106,162\] discovered that the radius of a single P3HT chain is ~4 nm, and the radius of the formed loose aggregates gradually increased at room temperature. Jeong et al.\[260\] observed that the color of P3HT polymer solution varies significantly with temperature. When the temperature drops from 40°C to ~20°C, the solution color changes from orange to purple and then to dark purple along with decreased solubility. The corresponding AFM images are shown in Figure 8C. Oh et al.\[262\] significantly improved the PCE of the P3HT:PCBM film coating on the cold poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) substrate compared with the spin coating at room temperature. At lower temperature, P3HT was aggregated and highly ordered (Figure 8D), which inhibited the aggregation of PCBM and the excessive domain size. After annealing, the blend film presented a sharp interface between the polymer and PCBM phase, promoting efficient exciton dissociation and charge transport. In addition, the limited solvability of P3HT at low temperature enables it to accumulate in the active layer and
Moreover, star donor polymer PBDB-T \cite{265} is also a well-known polymer with strong temperature-dependent aggregation behavior in solution state. For example, Hou and colleagues \cite{107} observed that the aggregation behavior of PBDB-T showed strong temperature dependence in solution state, it has obvious aggregation effect at room temperature and the aggregation can be eliminated at \(\sim 110^\circ C\), which was proved by UV-vis absorption spectra and temperature-dependent photoluminescence spectra. To investigate the influence of temperature on the aggregated structure of PBDB-T and the blend film with PCBM, they compared the device performance of the cyclically heated cooling solution and the device performance prepared at room temperature (Figure 8E). The morphologic results showed that the blend film exhibited continuous network structure and moderate phase scale at low temperature, leading to the 6.67\% PCE with an outstanding FF as high as 0.72. Instead, a larger scale of phase separation was observed after cyclic heating and cooling (Figure 8F), resulting from the polymer disaggregated at high temperature, and the subsequent cooling caused the isolated molecular chains to rearrange and form larger fiber, and higher purer polymer domains, which limited the charge transport, resulting in lower \(J_{SC}\) and FF. The larger conjugate skeleton of PBDB-T polymer enhances the interaction between molecular chains and the \(\pi-\pi\) stacking, which promotes the aggregation of polymer in solution.

PffBT4T is an important class of polymers with strong temperature dependence of aggregation behaviors, which exhibits a highly crystalline and easily adjustable aggregation behavior. \cite{259} In 2014, Yan and colleagues \cite{255} reported that the PffBT4T-2OD:PCBM system exhibits a high PCE up to 10.8\% and FF up to 0.77, which were attributed to the proper aggregation control of PffBT4T-2OD. When the PffBT4T-2OD:PCBM blend film was cast on a hot substrate, the UV-vis absorption spectra showed a decrease in the 0–0 transition peaks and the blend film exhibited disorder, which was consistent with the effect of high spin rates. \cite{256} On the hot substrate, the polymer is in disaggregated state, and the rapid drying of the film does not allow enough time for rearrangement, forming a more disordered molecular ordering with low phase purity, which significantly affects the hole transport.
With the decreasing spin speed and solution temperature, the polymer chains of PFBT4T-2OD can be aggregated. The orientation of PFBT4T-2OD switched significantly from edge-on to face-on and the $L_d$ increased gradually in the GIWAXS profiles, which greatly facilitated the hole mobility in the blend film and increased the $J_{SC}$ and FF. In addition, the ordered molecular arrangement in the blend film is conducive to obtaining higher $V_{OC}$, which is mainly attributed to the aggregation of PFBT4T-2OD at low temperature causing the absorption spectra blue shift and the larger band gap of the polymer film. Yan and colleagues investigated the influence of alkyl side chains on the temperature-dependent aggregation of the polymer. As the PFBT4T-2OD with second-position branched alkyl chain has strong aggregation characteristics, its temperature dependence is more obvious than that of the third-position branched alkyl side chain (PFBT4T-3OT), so that the aggregated structure and device performance could be adjusted by simply controlling the processing temperature.

For the conjugated polymers with temperature-dependent aggregation, controlling the temperature is the most direct method to modify the aggregated structure of polymer and blend morphology. The polymer is easy to self-aggregate and orderly accumulate at low temperature, which is helpful to inhibit the serious aggregation tendency of fullerenes and avoid the formation of large domain size. According to the characteristics of polymer aggregated structure changing with temperature, by precisely adjusting the processing methods to realize more compact and face-on stacking, the carrier transport can be greatly facilitated.

Other polymers

Benzo[1,2-b:4,5-b′]dithiophene (BDT) and thieno[3,2-b]thiophene (TT)-based conjugated polymers have been extensively used in the field of fullerene-based PSCs due to their large aromatic structure, which facilitates the formation of ordered π–π stacking. Poly[4,8-bis(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b′]dithiophene-2,6-diyl][3-fluoro-2-(2-ethylhexyl)carbonyl]thieno[3,4-b][thiophenediyl]] (PTB7):PCBM blend system is a potential fullerene-based solar cell with an efficiency of 7.4% at that time. DeLongchamp et al. quantitatively analyzed the characteristics of molecular orientation and accumulation of PTB7. The XRD results showed that PTB7 was very poor in crystallinity and the ordered phase domain only accounted for a small part of about 20% after blending with PCBM. In 2011, Darling and colleagues optimized the nanoscale aggregated structure of the blend films by using solvent additives. The results of GIWAXS confirmed that the use of solvent additive DIO could enhance the crystallinity of the blend system, which was mainly caused by the increase in the number of PTB7 and fullerenes nanocrystals. Moreover, R-SoXS showed that after DIO is added into the blend system, the phase size decreases significantly, which was verified with TEM results in real space. In 2013, Collins et al. further used STXM and R-SoXS to characterize the morphology and composition of the blend of PTB7:PCBM. After adding DIO, the crystallinity of the blend system was almost unchanged, while the domain size of PCBM agglomerate was significantly reduced, from 117 to 34 nm. The reduced domain size is more conducive to exciton dissociation at the interface of PTB7 and PCBM, thus significantly increasing the $J_{SC}$ of the device.

CONTROL OF AGGREGATED STRUCTURE OF PHOTOVOLTAIC POLYMERS IN NONFULLERENE SMALL MOLECULE BASED SOLAR CELLS

The BHJs based on polymer:nonfullerene (NF) small molecule blend are widely employed in NF-PSCs. The well-performed polymer:NFA blends have been reported in numerous literature and make a breakthrough of the NF-PSC efficiency over 18%.[5–7] To further enhance PSCs performance, it is crucial to understand and effectively modulate the aggregated structure, crystallization behavior, intermolecular interaction and miscibility of polymer:NFA blends. In this section, we will discuss the high-performance NF-PSCs tracing different polymer donors in recent years. Crucially, we summarize the control strategies of the aggregated structure of polymer:NFA blends and the relationship between aggregation properties and device performance.

Aggregated structure control of PTs

As the representative PT donors, P3HT is one of the most promising donor materials, featuring simple structure and low synthesis cost. The P3HT:fullerene-based PSCs have been extensively studied in the past decades. We have discussed in detail the effect of conjugated molecular structure on the aggregation behavior and the common methods for controlling the morphology of P3HT-PCBM system in the prior section. However, the limited absorption for visible light and high HOMO energy level of P3HT:fullerene blends cause a low $J_{SC}$ and $V_{OC}$ and therefore greatly restrict the PCE of P3HT-based PSCs. Although the performance of NF-PSCs has been increasing rapidly with the development of NFAs, the application of P3HT in NF-PSCs is limited in a way by narrow absorption range and unfavorable miscibility with many NFAs, which demands special structure design of donor and acceptor molecules and simultaneously the improvement of process techniques. For example, Peng et al. designed and synthesized a new NFA called 2,7,12-tris((3-oxo-2,3-dihydroinden-1-ylidene)malononitrile-7-benzothiadiazole-2-yl)truxene (TrBTIC), which matched P3HT well and achieved a high PCE of 8.25% by optimizing the fabrication process, namely solution aging. Remarkably, Hou and colleagues designed a new NFA called 2,2′-(12,13-bis(2-butyldecyl)-3,9-diundecyl-12,13-dihydro-[1,2,5]-thiaziazolo[3,4-ε]thieno[2′,3′,4′,5′]thieno[2′,3′,4′,5]pyrrolo[3,2-g]thieno[2′,3′,4,5]thieno[3,2-b]indole-2,10-dyli (bis(methane-ylidyne))bis (5,6-dichloro-1H-indene-1,3(2H)-dione) (ZY-4C1) to modulate the miscibility between P3HT and NFA. The NF-PSCs with P3HT:ZY-4C1 photoactive layer achieved the record PCE of 9.46% among P3HT-based NF-PSCs. Thus, in order to enhance the PT-based NF-PSCs performance, it is essential to modulate the aggregation and crystallization of PT donors and their miscibility with NFA.

The molecule design strategies attract much attention to control the aggregated structure of PT donors, which have been extensively studied in the past decades. We have discussed in detail the effect of conjugated molecular structure on the aggregation behavior and the common methods for controlling the morphology of P3HT-PCBM system in the prior section. However, the limited absorption for visible light and high HOMO energy level of P3HT:fullerene blends cause a low $J_{SC}$ and $V_{OC}$ and therefore greatly restrict the PCE of P3HT-based PSCs. Although the performance of NF-PSCs has been increasing rapidly with the development of NFAs, the application of P3HT in NF-PSCs is limited in a way by narrow absorption range and unfavorable miscibility with many NFAs, which demands special structure design of donor and acceptor molecules and simultaneously the improvement of process techniques. For example, Peng et al. designed and synthesized a new NFA called 2,7,12-tris((3-oxo-2,3-dihydroinden-1-ylidene)malononitrile-7-benzothiadiazole-2-yl)truxene (TrBTIC), which matched P3HT well and achieved a high PCE of 8.25% by optimizing the fabrication process, namely solution aging. Remarkably, Hou and colleagues designed a new NFA called 2,2′-(12,13-bis(2-butyldecyl)-3,9-diundecyl-12,13-dihydro-[1,2,5]-thiaziazolo[3,4-ε]thieno[2′,3′,4′,5′]thieno[2′,3′,4′,5]pyrrolo[3,2-g]thieno[2′,3′,4,5]thieno[3,2-b]indole-2,10-dyli (bis(methane-ylidyne))bis (5,6-dichloro-1H-indene-1,3(2H)-dione) (ZY-4C1) to modulate the miscibility between P3HT and NFA. The NF-PSCs with P3HT:ZY-4C1 photoactive layer achieved the record PCE of 9.46% among P3HT-based NF-PSCs. Thus, in order to enhance the PT-based NF-PSCs performance, it is essential to modulate the aggregation and crystallization of PT donors and their miscibility with NFA.

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in which copolymerization is an efficient method. For instance, the PFTBT blocks incorporated into copolymer poly(3-hexylthiophene-2,5-diyl)-block-poly[(9,9-dioctylfluorene-2,7-diyl)-alt-(4,7-di(thiophene-2-yl)-2,1,3-benzothiadiazole)-5',5'-diyl)] (P3HT-b-PFTBT) could suppress the strong crystallization of P3HT blocks caused by the molecular ordering during casting.\cite{154,289} The suppressed crystallization of P3HT formed a favorable microphase structure during TA in 195°C. Through the copolymerization strategy and annealing, the P3HT-b-PFTBT-based single component PSCs obtained a promising PCE of 3.2%. Notably, Ye et al.\cite{290} applied the group contribution calculation to assist the molecule design of PT and finely modulated the miscibility of PT:NFA blend. Based on the Flory–Huggins interaction parameter $\chi_{aa}$, replacing alkyl chain on PDCBT-Cl with siloxane-terminated group could effectively reduce the miscibility between PDCBT-Cl and 3,9-bis(2-methylene-((3-(1,1-dicyanomethylene)-6-difluoro-indanone))-5,5,11,11tetakis(5-hexylthienyl)dithieno[2,3-d:2',3'-d']-s-indaceno[1,2-b:5,6-b']dithiophene (ITIC-Th1). The miscibility decreased with the increase of siloxane-terminated group (Figure 9A and B). When alkyl chain was substituted by 5% siloxane-terminated group, the formed PDCBT-Cl-Si5:ITIC-Th1 produced favorable phase separation and domain properties (as shown in Figure 9C) and contributed to an impressive PCE of 12.85%.

Moreover, the halogenation on the PT backbone is effective to optimize the crystallization behavior and enhance the performance of PSCs. Take fluorinated PT as an example. As the fluorine content increased, the fluorinated PT exhibited larger $L_c$ values indicating obvious lamellar $\pi-\pi$ stacking and higher crystallinity, which increased charge mobility of P6T-Fx:EH-IDTBR blends (Figure 9E and F).\cite{291} Especially, the highly fluorinated P6T-F100 showed both face-on and
edge-on molecular orientation simultaneously and improved the miscibility with EH-IDTBR. Therefore, the P6T-F100:EH-IDTBR blend provided efficient phase separation for charge generation and enhanced the PCE of NF-PSCs to 7.3%.

Apart from the structure of PT donors, the molecular structure of NFAs has a significant influence on the crystallinity and aggregated structure of blend films. The properties determined by NFAs structure can provide different crystallization degrees, domain size, and phase purity, which affects the exciton transport and dissociation. On the one hand, the conformational lock[292] and side chain strategy[293] are widely adopted to modulate the crystallinity and aggregation behaviors of P3HT. By introducing oxygen atoms to the side chain of thiophene in ERCN, O⊂S interaction formed between side chain and adjacent thiophene in newly formed 2,2’-(5Z,5’S)-(((4,4,9,9-tetakis(4-hexylphenyl)-4,9-dihydro-s-indaceno[1,2-b:5,6-b]dithiophene-2,7-diyli)b(is(4(octyloxy)thiophene-5,2-diyl))bis(methanlylidene))bis(3-ethyl-4-oxothiazolidine-5,2-diyliidene))dimalononitrile (ORCN). This conformational lock increased the planarity of ORCN and resulted in higher crystallization and similar molecule orientation with P3HT, which produced suitable miscibility between P3HT and ORCN. Therefore, the PCE of P3HT:ORCN-based NF-PSCs increased from 2.64% to 6.6%. Nevertheless, the conformational locks may overly reinforce the crystallinity and aggregation. For example, N⊂S conformational locks in IDTzR caused strong self-aggregation and therefore produced overlapped domain size.[294] By introducing bulky hexylphenyl side chain IDTzR, the optimized P3HT:(5,5’S)-5,5’-’-(((4,4,9,9-tetakis(4-hexylphenyl)-4,9-dihydro-s-indaceno[1,2-b:5,6-b]dithiophene-2,7-diyli)b(is(thiazole-2,5-diyl))bis(methanlylidene))bis(3-ethyl-2-thioxothiazolidin-4-one) (P-IDTzR) exhibited favorable phase separation and small domain size, which contributed to an improved $J_{SC}$ and PCE (5.01%).

On the other hand, the backbone and end group of NFAs affect the aggregation properties as well. Chen et al.[295] synthesized two NFAs called JC1 and JC2 based on benzothiadiazole and benzoazirrole π-riges, respectively. The JC2 based on alkyl benzoazirrole unit exhibited less backbone twist compared to JC1. Therefore, the P3HT:JC2 blend showed small domain size and improved phase separation according to AFM images, realizing a considerable PCE of 6.24% in NF-PSCs. For end group of NFAs, a notable example is a comparative study by Hou et al.[285] ZY-4Cl exhibited decreased miscibility with P3HT compared to the overmixed P3HT:BTP-4Cl. Hence, the P3HT:ZY-4Cl exhibited favorable crystallization and obvious phase separation. The improved morphology enhanced the exciton dissociation and charge transport, which realized the highest PCE of 9.46% in P3HT-based PSCs. Particularly, they demonstrated a consistent conclusion in 3,9-bis (2-methylene-(3-(1,1-dicyanomethylene))-indane)-5,5,11,11-tetrakis(4-hexylphenyl)-dithieno[2,3-d:2’,3’-d’]-s-indaceno[1:2-b:5,6-b’]dithiophene (ITIC) and 3,9-bis(2-methylene-(3-(1,1-dicyanomethylene)-6,7-dichloro)-indane)-5,5,11,11-tetrakis(4-hexylphenyl)-dithieno[2,3-d:2’,3’-d’]-s-indaceno[1:2-b:5,6-b’]dithiophene (IT-4Cl) systems. Ye et al.[200,287] systematically studied the relationship of the miscibility, morphology and the device performance based on PDCBT-Cl and different NFAs. The five NFAs containing different end groups or cores presented varied miscibility with PDCBT-Cl, tuning the crystallization and phase domain properties. The low miscibility between PDCBT-Cl:2,2’-(2Z,2’Z)-(4,4,4,9,9-tetrahexyl-4,9-dihydro-s-indaceno[1,2-b:5,6-b’]dithiophene-2,7-diyli)b(is(methanlylidene))bis(3-oxo-2,3-dihydro-1H-indene-2,1-diyliidene))dimalononitrile (IDIC) ($\chi_{sa} = 1.75$) produced large phase separation that caused relatively low device performance, while high miscibility between PDCBT-Cl:2,2’-(2Z,2’Z)-(12,13-bis(2-ethylhexyl)-3,9-dimidecyl-12,13-dihydro-[1,2,5]thiadiazolo[3,4-c][thieno[2’,3’,4’,5’]thieno[2’,3’,4’,5][thieno[2’,3’-b]indole-2,10-diyli)b(is(methanlylidene))bis(5,6-difluoro-3-oxo-2,3-dihydro-1H-indene-2,1-diyliidene))dimalononitrile (Y6) ($\chi_{sa} = 0.19$) produced extremely small phase separation resulting in low performance as well. In contrast, suitable miscibility between PDCBT-Cl:ITIC-Th1 contributed to favorable phase separation and domain purity and therefore resulted in the best PCE of 12.11%.

In addition, improving the solution processes plays a crucial role to modulate the aggregated structure and morphology of PT: NFAs blend films. The strategies mainly include additive, solvent and annealing. The four additives, namely DIO, 1,6-diodohexane (DH), CN, and diphenyl ether (DPE), produced different morphology evolution of polymer donor films due to the interaction between additive and materials.[296] In contrast to CN and DPE, the polymer donor P3HT by DIO and DH based solution process exhibited longer morphology evolution in timescale range (Figure 10) because the dominated interaction between additive and material was on side chains. This allowed polymer could complete crystallization and microstructure during post-treatment. 1-Methylanthalene (MN) was also utilized as additive for the fabrication of P3HT:(5,5’S)-5,5’-’-((7,7’-(4,4,9,9-tetraoctyl-4,9-dihydro-s-indaceno[1,2-b:5,6-b’]dithiophene-2,7-diyli)b(is(benzoc[c][1,2,5][thiazadizole-7,4-diyli)b(is(methanlylidene))bis(3-ethyl-2-thioxothiazolidin-4-one) (O-IDTBR) based NF-PSCs with 2-methylnano (ο-MA) as solvent.[297] In o-MA solvent, P3HT tended to form crystalline fibrils and face-on orientation, which benefited charge transport. Meanwhile, MN caused an obvious phase domain of the P3HT-O-IDTBR blend. The NF-PSCs fabricated with o-MA/MN reached a high PCE of 7.1%. In addition, Hou et al.[298] demonstrated that P3HT showed strong aggregation in anisole solvent in contrast to indistinct aggregation in CF. The aggregation behaviors in two solvents, respectively, resulted in a large and small phase separation degree of P3HT:IEICO blend. Therefore, with a mixed CF/anisole/DIO solvent, the P3HT:IEICO-based NF-PSCs obtained an optimized PCE of 4.91%.

Finally, some special processed technique was utilized to modulate the crystallization and aggregation process. Spin-coating polymer donors on nanostructured template confined the evaporation of solvent.[299] These polymers were confined to form regular nanostructures and improved face-on stacking, which provided the capability to tune the aggregated structure in NF-PSCs.

In brief, the strong crystallinity of PT and excessive miscibility with many NFAs inhibit the improvement of PT-based NF-PSCs performance. Aiming to enhance the NF-PSCs performance, copolymerization enables tuning the aggregation
behavior in some way, while it causes a relatively complex synthesis route. Fluorination on PT backbone can increase the crystallinity effectively. For NFAs, the conformational lock between heteroatoms is an efficient strategy to increase crystallinity, decrease miscibility and optimize the aggregated structure of PT:NFA blends. Moreover, the modification of side chain, backbone, and end groups play an important role in tuning the miscibility of PT:NFAs. For instance, enlarging the steric hindrance on side chain can suppress the strong self-aggregation of NFAs and provide a favorable aggregated structure of PT:NFA blends. Finally, the solution processes affect the morphology evolution and aggregated structure of PT:NFA blends.

Aggregated structure control of BDT-based polymers

Combination of BDT-based polymer donor and NFAs, such as poly[(2,6-(4,8-bis(5-(2-ethylhexyl)-3-fluorothiophen-2-yl)-benzo[1,2-b:4,5-b'][dithiophene])-alt-(5,5-(1',3'-di-2-thienyl-5',7'-bis(2-ethylhexyl)benzo[1',2'-c:4',5'-c'][dithiophene-4,8-dione]) (PBDB-TF):Y6, PBDB-TF:3,9-bis(2-methylene-(3-(1,1-dicyanomethylene)-6,7-difluoro)-indanone))-5,5,11,11-tetrakis(4-hexylphenyl)-dithieno[2,3-d:2',3',4',5'-c']-s-indaceno[1,2-b:5,6-b']dithiophene (IT-4F) and poly[4,8-bis(5-2-ethylhexyl)thiophene-2-yl]benzo[1,2-b;4,5-b']dithiophene-2,6-diy-alt-(4-(2-ethylthyl)-3-fluorothieno[3,4-b][thiophene]-2-carboxylate-2-6-diy)] (PTB7-Th):2,2'-(2Z,2'Z)-((4,4,9,9-tetrakis(4-hexylphenyl)-4,9-dihydro-sindaceno[1,2-b;5,6-b']dithiophene-2,7-diy)bis(4-((2-ethylhexyl)oxy)thiophene-5,2-diyl))bis(methanylylidene)]bis(5,6-difluoro-3-oxo-2,3-dihydro-1H-indene-2,1-diylidene)dimalononitrile (IEICO-4F), has significantly improved the performance of PSCs in recent years and been widely investigated in PSCs with different device structures. In contrast to PT donors, typical BDT-based polymer donors contain alternant electron donor units and electron acceptor units, providing tunable chemical structures with many modifiable sites. Furthermore, the changes of chemical structure provide tunable light absorption range, energy level, crystallinity, aggregation properties, miscibility with solvent and acceptors, which promote the understanding of the structure–property relationships. Benefiting from the development of NFAs, diverse BDT-based polymer:NFAs are used as photoactive layer in NF-PSCS and improve the device performance continuously. Zou et al.[300] designed and synthesized a high-performance NFA with benzothiadiazole core named Y6 and the PBDB-TF:Y6-based NF-PSCS achieved a record PCE of 15.7% among binary single-junction PSCs. Hou et al.[301] modulated the substituent groups of Y6 and synthesized BTP-eC9, which realized a promising PCE of 17.8% in corresponding PBDB-TF-based NF-PSCS. In 2020, Ding et al.[15] reported a new polymer donor D18 including BDT donor unit and dithieno[3',2',3,4':5,6']benzo[1,2-c][1,2,5]thiadiazole (DTBT) acceptor unit. The device based on D18:Y6 blend achieved a record PCE of 18.22% for single-junction PSCS. Although the PSCs performance developed rapidly, the morphology and aggregated features of BDT-based polymer donor are discussed, respectively, less. To emphasize the understanding of the aggregated structure of BDT-based polymer donor and increase the efficiency of NF-PSCS, some reports have focused on the modulation of aggregation properties of polymers or polymer:NFAs blends.[302,303]

Aggregated structure control of PTB7

The structure of PTB7-based polymer decides its crystallinity and aggregation properties. Compared to PTB7, PTB7-Th contains thiophene groups on BDT units replacing the oxygen atoms in PTB7, which causes an increasing
The polymer structure was shown to affect the thermal transition and morphology of polymer films.\[304\] The polymer with a large side chain, like PTB7 and PTB7-Th, was found to exhibit a strong sub-$T_g$ transition and weak $T_g$ transition behaviors, relating to their crystallinity. Furthermore, the hairy morphology formed in these polymer films. Chen et al.\[305\] reported a series of PTB7-Th based polymer donors using siloxane-terminated side chain to replace the alkyl side chain of BDT unit. In contrast to alkyl side chain, siloxane-terminated side chain could decrease the surface energy of polymer donors and caused lower miscibility with IEICO-4F with the increase of the content of siloxane-terminated side chains, providing a finely tunable driving force for phase separation. The device containing PTBSi100 (100% siloxane-terminated side chains) and IEICO-4F presented excessive phase separation, whereas the device based on PTBSi25:IEICO-4F presented optimized phase separation and the best PCE of 12.61%.

The effect of diverse NFAs is also investigated in PTB7:NFAs or PTB7-Th:NFA blends. The extensive fused core in NFAs greatly affected the molecular stacking.\[306,307\] For example, less fused ring in COixDFIC like COi5DFIC and COi6DFIC caused edge-on stacking, which was unmatched with the face-on stacking of PTB7-Th and therefore resulted in low performance. On the contrary, the PTB7-Th:COi8DFIC showed favorable face-on stacking and phase separation after hot spin-coating, contributing to an improved PCE of 13.1%. Moreover, side chain strategy is widely adopted to modulate the aggregation and phase features. NFA 3TT-OCIC was designed by introducing octyl to the thiophene of 3TT-CIC.\[308\] The octyl side chain produced larger $\pi-\pi$ stacking distance of 3TT-OCIC than that of 3TT-CIC. This increased the domain purity and decreased the miscibility of PTB7-Th:3TT-OCIC blend suggested by the higher $\chi$ value of PTB7-Th:3TT-OCIC blend.

Steric hindrance and molecule interaction between donor and acceptor are important for aggregation control. As a promising acceptor block, perylene diimide (PDI) exhibits good planarity and high charge mobility, while its excessive aggregation and strong crystallinity limit the performance of polymer donor:PDI-based acceptor blends. Constructing twisted backbone for PDI-based NFAs\[309\] can effectively suppress the crystallization behavior and optimize the aggregated structure of BHJs. For instance, introducing multiple PDI units to phenyl core extended the steric hindrance between PDI units that resulted in a twisted structure (Figure 11A–C) and suppressed the crystallinity of blend films.\[310,311\] These BHJs based on PTB7-Th:B(PDI)$_3$ or PTB7-Th:HPB-PDI$_6$ produced improved PCE (5.65% and 6.63%, respectively) in PSCs. However, overtwisted structure can reduce the charge mobility and efficiency of NF-PSCs. Zheng et al.\[312\] reported that twisted $\pi$-bridge was utilized to connect two PDI unit to suppress the aggregation of corresponding NFAs. In contrast to PDI-2Th-PDI, the spatial geometry of PDI-ThFTh-PDI was more twisted and caused lower crystallinity and unfavorable phase separation (Figure 11D–H). Therefore, the PCE of PTB7-Th:PDI-ThFTh-PDI based PSCs was lower than PTB7-Th:PDI-2Th-PDI based PSCs by half.

Moreover, the ternary NF-PSCs are a crucial strategy to improve the PSC performance by adding a third component into BHJs.\[313,314\] The effect of a third component mainly
depends on the property difference and interaction between each component. The reported third component mixed with PTB7:NFAs blend mainly contains fullerenes, other NFAs, and donors. First, PC71BM as the third component mainly mixed with PTB7-Th, while it could diffuse into IEICO-4F domain.\textsuperscript{[315]} 15 wt% PC71BM could effectively suppress the crystallization behavior of IEICO-4F and produced favorable domain size in BHJs due to suitable miscibility with PTB7-Th and IEICO-4F. Thus, the PSCs based on PTB7-Th:IEICO-4F:15 wt% PC71BM reached an improved PCE of 12.0%. With regard to NFAs, Liang et al.\textsuperscript{[316]} investigated the effect of ITIC as a third component on the crystallinity and phase separation of PTB7-Th:PDI blend in detail. The addition of ITIC distinctly suppressed the crystallization of PDI and produced a smoother film with smaller phase separation. As the content of ITIC increased, the BHJ first showed suppressed phase separation and then obvious phase separation (Figure 12B–D) due to the low miscibility between donor and acceptors. When the content of ITIC reached 70 wt%, the BHJ showed favorable phase separation because ITIC dominated in this composition. Nevertheless, ITIC exhibited a contrasting impact on the aggregation of PTB7-Th:IEICO-4F blend due to higher crystallinity of ITIC than IEICO-4F (Figure 12I).\textsuperscript{[317]} Small amount of ITIC increased the crystallinity and domain size of PTB7-Th:IEICO-4F:ITIC, which contributed to efficient charge transport and 10.2% PCE of ternary PSCs. Finally, introducing other polymer donors affects the aggregated structure of both donor and acceptor. The quaternary PSCs were fabricated by introducing PBDB-T and ITIC into the PTB7-Th:FOIC (FOIC is based on 3TT unit and uses 2-(5/6-fluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)-malononitrile as end groups) blend.\textsuperscript{[318]} PBDB-T increased the face-on stacking of PTB7-Th and the crystallization of FOIC that was indicated by increased $L_c$ up to 21 nm, while ITIC provided suitable phase separation with FOIC and decreased the domain size due to a smaller $\chi$ of ITIC and FOIC than that (0.39) of ITIC and PTB7-Th. For these improved factors, the addition of PBDB-T and ITIC provided an increased PCE of 12.04% in quaternary PSCs.

As a key parameter for PCE improvement, the finely tuned ratio of D:A improves the aggregated structure of polymer:NFA blends. Trimmel et al.\textsuperscript{[319]} analyzed the phase separation of PTB7-Th:O-IDTBR films with different composition ratio. With the increase of O-IDTBR content, BHJ film exhibited extensive phase separation degree and domain size. When the D:A ratio was 1:1.5, favorable phase separation was observed and this ensured efficient charge dissociation and transport, which resulted in a maximum PCE of 9.42%.

In addition, well-controlled solution process is of great significance to modulate the aggregated structure of
PTB7-based BHJs. The solvent and additive with high boiling point allow longer morphology evolution time during casting and annealing, which may cause increasing crystallization and domain size and modulate the molecular stacking. Wang et al. demonstrated the effect difference of DIO, DPE, and CN additives on the aggregation of PTB7-Th:CoI8DFIC blend film. Compared to DPE and CN, the addition of 0.5 vol% DIO was more effective to produce favorable J-aggregation of the blend, contributing to a highly improved PCE of 12.9%. In addition, the effect of DIO additive on morphology was investigated for PTB7-Th:ITIC using CB or CF solvent. Note that 0.6 vol% DIO showed negligible effect on phase separation of BHJ blend using CB solvent, while DIO enhanced phase separation degree and face-on stacking orientation of blend using CF solvent by increasing the crystallinity of ITIC. Consistent with morphology features, the performance of PSCs showed similar variation trend and obtained a higher PCE (5.81%) in CF/DIO than that (3.19%) in neat CF. Moreover, SVA using nonvolatile and well-soluble solvent is commonly used to rearrange molecule order and improve the morphology of polymer:NFAs blend film. Wang et al. reported the CS2: SVA of PTB7-Th:ITIC blend. The SVA in CS2 for 60 s distinctly increased the phase separation and produced larger PTB7-Th and ITIC domain by GIWAXS patterns. In addition, CS2 SVA enhanced π–π stacking of PTB7-Th and ultimately improved the PSCs PCE to 7.9%.

Optimized processed techniques provide beneficial microstructures of PTB7-Th-based BHJs, resulting in higher PSCs performance. By spin-coating on hot substrate, the molecular stacking of NFA CoI8DFIC could transfer from flat-on and edge-on to face-on π–π stacking. The transformation of CoI8DFIC stacking type suppressed CoI8DFIC crystallization and the phase separation of PTB7-Th:CoI8DFIC. In addition, sequential blade coating could produce effective vertical phase separation and distribution of donor and acceptor, which formed a vertical microstructure of photoactive layer. By sequential blade coating FOIC:poly[N,N-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl-alt-5,5′-(2,2′-bithiophene)] (N2200) and PTB7-Th, the photoactive layer exhibited increasing crystallinity, favorable vertical phase separation and improved stability. N2200 was introduced as the third component to increase the crystallinity of FOIC and improve the stability by forming continuous network. Through the combined strategies, the sequential blade coated PSCs based on PTB7-Th:FOIC:N2200 achieved the maximum PCE of 12.27%.

Aggregation structure control of PBDB-T

As famous BDT-based polymer donors, PBDB-T and PBDB-TF (or so-called PM6) are commonly used in high-efficiency NF-PSCs. As discussed before, the molecular structure is an essential factor for the aggregation control of PBDB-T based polymer donors. Modification of polymer backbone by copolymerizing disparate units can combine the features of copolymeric units to modulate the aggregation properties. Copolymer ES1 was synthesized by introducing fluorine and ester substituted thiophene unit (FE-T). Compared to PBDB-TF, the introduction of FE-T enhanced face-on π–π stacking through S···O and S···F interaction and therefore resulted in fibril nanostructure of ES1:Y6 film. The ES1:Y6-based PSCs with optimized morphology reached a considerable PCE of 16.4%. Chen et al. introduced benzotriazole unit into PBDB-T, forming PBDB-TAZ20 and PBDB-TAZ40. PBDB-TAZ20 exhibited improved miscibility with ITIC and the blend film exhibited weaker phase separation than PBDB-T:ITIC. The improved phase separation and favorable microstructure contributed to a higher PCE of 12.34%.

Moreover, the tuning of side chain of polymer donors has a great impact on the morphology of BHJs blend. The influence of conjugated size of side chain on morphology was investigated in detail. Comparing phenyl, naphthyl, and biphenyl side chain on BDT unit, naphthyl side chain enhanced the crystallinity of polymer and produced favorable aggregation of PBDB-Na, while small-size phenyl caused excessive aggregation and large-size biphenyl caused less fibril nanostructure. In consistent with the morphology of three polymers, the PSCs based on PBDB-Na:ITCPTC achieved the best PCE of 12.52%. Meanwhile, fluorination on phenyl side chain enabled to induce crystallization of acceptor through F···F interaction between side chain of donor and end group of acceptor. For example, PBDB-PSF could induce the crystallization of IT-4F and provided favorable phase separation of BHJs, which resulted in 13.63% PCE in PBDB-PSF:IT-4F-based PSCs. The substituted position of side chain affects the aggregation properties and morphology of BHJs blend films. Huo et al. demonstrated that the substituted position of alkylthio on phenyl side chain affected the aggregated structure of PTBB (Figure 13A). From ortho-position to meta-position to para-position, PTBB exhibited gradually increasing crystallinity and aggregation properties (Figure 13B and C), which provided different miscibility with ITCPTC and carrier transport properties. The PTBB-m:ITCPTC PSCs reached an enhanced PCE of 12.22% due to the moderate crystallinity and aggregation of PTBB-m. The influence of alkyl substituted position in the NTD unit was investigated on the aggregation properties of PBTN. Comparing phenyl, naphthyl, and biphenyl side chain on BDT unit, naphthyl side chain enhanced the crystallinity of acceptor and optimizes the aggregation properties, which provided disparate aggregated structure of BHJs blend film. By replacing thiophene core with TT core, the axysymmetric FTBT transformed to centrosymmetric FTTBT, which reduced the crystallinity of acceptor and optimized its stacking features. The centrosymmetric molecular geometry having lower miscibility with PBDB-TF enhanced the phase separation and the face-on orientation of PBDB-TF:FTTBT film. With the optimized morphology, the PSCs obtained higher PCE of 9.79% and doubled J_sc of 16.0 mAcm-2. Additionally, three twisted core, namely benzene, biphenyl, and spiro-bifluorene were investigated for PDI-based NFAs. Blending with PBDB-T, the Ph-PDI4 exhibited excessive aggregation ascribing gear-like aggregation behavior, and the SF-PDI3 based acceptor...
exhibited a larger domain size. In contrast, the PBDB-T:BP-PDI4 exhibited favorable aggregation and suitable phase separation degree, which contributed to the highest PCE of 7.0% among these three NFAs.

The position variation of NFAs side chain changes the aggregation properties and crystallization behaviors by tuning molecular geometry. For example, o-4TBC-2F with ortho-substituted phenyl side chain exhibited a planar backbone than m-4TBC-2F with meta-substitution by DFT calculation. The planar structure of o-4TBC-2F provided increasing crystallinity and J-type aggregation of PBDB-T:o-4TBC-2F blend, which was further enhanced by TA. These improved aggregation behaviors produced a favorable microstructure of the blend film and resulted in a greatly increased PCE of 10.26%. Yang et al. reported an interesting method to balance the crystallinity and miscibility of NFAs, that was introducing phenyl to the end of alkyl side chain. Compared to IDIC (hexyl side chain) and IDIC-PhC6 (hexylphenyl side chain), IDIC-C4Ph exhibited moderated crystallinity and dislocated packing in contrast to IDT-2O and IDT-2B. The features of IDT-OB resulted in suitable phase separation and domain size of PBDB-T:IDT-OB blend film, which presented face-on stacking and fibril nanostructure (Figure 14E), proved to be a favorable morphology. The PSCs based on PBDB-T:IDT-OB obtained a PCE of 10.12%.

The conjugated size and halogenation of the end group of NFAs can be utilized to modulate the aggregation behaviors and phase separation of BHJs. Hou et al. demonstrated that newly formed IDTN with an extensive conjugation of end group presented enhanced aggregation properties and ordered face-on stacking, which provided higher electron mobility than IDTI. Meanwhile, the PBDB-T:IDTN blend film acquired enhanced crystallinity and aggregation and showed an ordered nanostructure, contributed to an increased PCE of 12.2% in PSCs. In addition, the chlorination and fluorination of end group generally produced enhanced crystallinity and weakened

**Figure 13** (A) Chemical structure of PTBB-o, PTBB-m, PTBB-p and ITCPTC. (B) The GIWAXS patterns and line profiles of PTBB-o, PTBB-m, PTBB-p neat films. (C) The GIWAXS patterns and line profiles of corresponding blend films with ITCPTC. (D) Chemical structure of PBTN-o, PBTN-p and BO-4Cl. (E) The GIWAXS patterns and line profiles of PBTN-o, PBTN-p neat films and corresponding blend films with BO-4Cl. (F) The curves of relative aggregation strength versus solution temperature. Reprinted from Ref. [332] with permission. Copyright (2020) Royal Society of Chemistry.
FIGURE 14  (A) Chemical structure of BTP-eC9 based on the modification of Y6. (B) Absorption spectra of BTP-based NFAs. (C) The line profiles of GIWAXS patterns of BTP-based NFAs.301 Reprinted from Ref. [301] with permission. Copyright (2020) John Wiley & Sons, Inc. (D) Chemical structures of PBDB-T and IDT-2B, IDT-OB, IDT-2O. (E) TEM images of PBDB-T:IDT-2O, PBDB-T:IDT-OB, and PBDB-T:IDT-2B blend films, respectively.343 Reprinted from Ref. [343] with permission. Copyright (2017) John Wiley & Sons, Inc.

the miscibility with PBDB-T based polymer donor, which enhanced the phase separation and face-on stacking orientation.[349–351] For example, poly[(2,6-(4,8-bis(5-(2-ethylhexyl-3-chlorothiophen-2-yl)-benzo[1,2-b:4,5-b’]dithiophene))-alt-(5,5-(1’,3’-di-2-thienyl-5’,7’-bis(2-ethylhexyl)benzo[1’,2’-c:4’,5’-c’][dithiophene-4,8-dione)]) (PM7): TPIC-4F and PM7:TPIC-4Cl exhibited relatively large phase separation degrees and PM7:TPIC-4Cl-based PSCs obtained a higher PCE of 15.4% resulting from favorable aggregated structure.[350] This improvement was also demonstrated in ITIC and BTP based systems. On the contrary, the poor performance of PSCs containing BDT-based polymer and NFAs without halogenation was ascribed to weak crystallinity and excessive miscibility.

The incorporation of third components, such as structurally similar polymer donor,[352] fullerene[353,354] and NFAs,[355–359] provides extra disturbance and obviously modulates the aggregated structure. A ternary OSC was fabricated by introducing poly[(2,6-(4,8-bis(5-(2-ethylhexylthio)-4-fluorothiophen-2-yl)-benzo[1,2-b:4,5-b’][dithiophene])-alt-(5,5-(1’,3’-di-2-thienyl-5’,7’-bis(2-ethylhexyl)benzo[1’,2’-c:4’,5’-c’][dithiophene-4,8-dione]) (PBDB-T-SF) to the PBDB-TF:Y6 blend.[352] The ternary blend film presented weakened crystallinity and mesoscale morphology with enlarged domain size, which was ascribed to the frustrated stack order by different orientations of the polymer side chain. With the improved aggregated structure, the ternary PSCs achieved a high PCE of 16.42% and an increased FF of 0.76. In addition, a special morphology transformation was observed when using small molecule donor benzodithiophene terthiophene rhodamine derivative (BTR) as the third component for the PBDB-TF:Y6 blend.[356] The incorporation of BTR increased the crystallinity of BHJs and simultaneously decreased the phase separation degree. Thus, this special morphology improvement resulted in an increased PCE of 16.6% and FF of 0.77.
The incorporation of fullerene additives can also modulate the crystallinity, aggregation behaviors and phase domain of BHJ blends by dispersing into acceptors. Both PCBM and ICBA in low content were used to enhance the crystallinity and domain purity of BHJs based on PBDB-T series donors by distributing into acceptor domain and mixing with original acceptor.[360,361] Nevertheless, PCBM or ICBA might form its own phase in high content and therefore reduced the crystallinity of BHJ blends and destroyed the previous aggregated structure. Moreover, the incorporation of PCBM or ICBA could improve the vertical phase separation.[354,362] Especially, Chen et al.[362] fabricated PBDB-TF:IT-4F based PSCs by sequential blade coating and utilized ICBA as the third component. ICBA induced the crystallization of PBDB-TF according to GIWAXS analysis and improved the vertical distribution of PBDB-TF and IT-4F, which contributed to more favorable vertical phase separation and produced an enhanced PCE of 14.25% for 1.05 cm² ternary PSCs.

The aggregated structure and crystallinity of BHJ blends can be optimized by using NFAs as the third component. For example, with the addition of COi8DFIC, the ternary blend containing PBDB-TF:IT-4F:COi8DFIC exhibited generally enhanced crystallinity and domain size because COi8DFIC had stronger aggregation properties than IT-4F.[363] Wang et al.[364] used 3,9-bis(2-methylene) (3-(1,1-dicyanomethylene)-6(7-methyl)-indenone))-5,5,11,11-tetrakis(4-hexylphenyl)-dithieno[2,3-d:2',3'-d']-s-indaceno[1,2-b:5,6-b']dithiophene (IT-M) as the third component in the PBDB-T:IT-M-INPOIC blend. The addition of 10 wt% IT-M distinctly increased the phase separation degree and domain size of the ternary blend, and balanced the charge mobility of the blend. The optimized morphology and electric properties produced a higher PCE of 13.9% in ternary PSCs. Tao et al.[365] introduced a small molecule DIBC as the third component to form hydrogen-bond with NFA IEICO-4F. The formed interaction between DIBC and IEICO-4F suppressed the aggregation and crystallization behavior of the PTB7-Th:IEICO-4F blend and therefore contributed to an increased PCE (13.53%) and FF (0.71). The DIBC-based ternary structure also produced a positive impact on PBDB-TF:Y6-based PSCs, which achieved a considerable PCE of 16.41%. Notably, Liu et al. [6] reported a quaternary PSC by blending PM7 and PC71BM with PBDB-TF:Y6. According to GIWAXS profiles, PBDB-TF and PM7 formed a homogeneous polymer-enrichment phase, which resulted in optimized crystallinity and morphological quality. Meanwhile, Y6 and PC71BM formed a well-mixed phase without disturbing the network between PBDB-TF and Y6. Therefore, the addition of PM7 and PC71BM provided double carrier transport pathways and the corresponding quaternary PSCs achieved a remarkable PCE of over 18%.

Solvent additive is the significant factor to modulate the aggregated structure and crystallinity of PBDB-T series polymer donor and NFAs acceptor. As the most common additive, the incorporation of DIO generally enhances the crystallization and reduces the domain size of PBDB-T:NFA blends at proper concentration, while excessive DIO may cause unfavorable morphology and poor PSCs performance.[366] A strategy based on binary additives, for instance, DIO and 2,6-dimethoxynaphthalene (DMON) was utilized to modulate the aggregation and crystallization behaviors combining the unique properties of both additives.[367] DIO was added to enhance the crystallinity and molecular stacking order and DMON was added to suppress the aggregation and crystallization of PBDB-T:TTC8-O1-4F blend. The combination of DIO and DMON contributed to a prominent fibril nanostructure and resulted in a higher PCE of 13.22% than those with a single additive. Moreover, some novel solid additives were designed to tune the morphology of BHJs and increase the PSCs performance effectively.[368–372] Jiu et al.[368] designed and synthesized a graphdiyne derivative additive called GCl, which featured a large conjugated structure. Compared to CN additive, the addition of GCl resulted in a higher phase separation degree and crystallinity of the PBDB-TF:Y6 blend, producing an efficient charge transport path. This new additive also improved the photoelectric properties of PBDB-TF:Y6 blend film, resulting in a highly increased PCE of 17.3%. Wang et al.[369] designed three solid additives with disparate numbers of fluorine, namely INB-1F, INB-3F, INB-5F, which had similar structure with the end group of BTP-4F. The incorporation of these additives promoted the aggregation and π–π stacking of BTP-4F in PBDB-TF-BTP-4F blend due to strong interaction between BTP-4F and additives. With addition of INB-5F, the best PCE of 16.5% was obtained in PBDB-TF:BTP-4F based PSCs.

In addition, the aggregation and crystallization behaviors of BHJs can be modulated through solvents with disparate boiling points.[68,73] Y6 was demonstrated to form the polymer-like conjugated backbone in J-aggregation type by utilizing CF as solvent.[68] Due to fast evaporation process of CF, this optimized J-aggregation provided 2D transport network that benefitted charge transport and therefore the PBDB-TF:Y6 based PSCs achieved a higher PCE of 16.88%.

Importantly, the well-control of solution processes has a great impact on the aggregated structure and morphology features of PBDB-T based BHJ blends.[374] As reported by Qin et al.[375] a double annealing treatment at 80°C and 120°C was utilized for PBDB-TF:N3:PC71BM ternary blend during spin coating, based on that N3 showed low transition temperature at 82°C. The double annealing treatment was demonstrated to enhance the molecular stacking on a small length scale at low temperature and increased the phase separation and domain purity at high temperature. These improvements are attributed to double annealing treatment increased the PCE of PBDB-TF:N3:PC71BM based PSCs to 17.6% and was also feasible in PBDB-TF:Y6 based PSCs.

The sequential deposition techniques, such as sequential blade coating[376,377] and sequential spin coating[7,378,379] are promising methods to increase the crystallization of materials and provide favorable vertical phase distribution and separation degree. Ma et al.[376] investigated the formation of the aggregated structure and morphology of photoactive layers during sequential blade coating. PBDB-T:IT-M and PBDB-T:FOIC (Figure 15) were sequentially blade coated on substrate to form the PSCs with double BHJ layers. During the deposition process, the previously formed PBDB-T:IT-M film provided numerous nucleated sites, which resulted in higher crystallization of latter PBDB-T and therefore suppressed the excessive aggregation of FOIC. Therefore, the sequential blade coating improved the vertical distribution and phase separation of the blend, contributing to an increased PCE of 11.9%. Moreover, the sequential spin coating was utilized to sequentially deposit PT2 and Y6.[379] First deposited PT2 formed a fibril-like network,
while later deposited Y6 dispersed into PT2 network, which produced a favorable aggregated structure with suitable vertical phase separation and slightly increased crystallization. The corresponding PSCs were optimized to achieve a high PCE of 16.5%. Recently, Chen et al. [7] fabricated a ternary PSC based on PBDB-TF:BO-4Cl:BTP-S2 system through sequential spin coating, where PBDB-TF and BO-4Cl:BTP-S2 were sequentially coated on the substrate. In contrast to the PBDB-TF:BO-4Cl binary system, the addition of BTP-S2 efficiently promoted vertical phase separation during sequential processing. Donors tended to be enriched at the anode, while acceptors were enriched at the cathode to form a vertical morphology that caused less charge recombination. The PBDB-TF:BO-4Cl:BTP-S2 based devices fabricated by sequentially spin coating achieved a remarkable PCE of 18.16%, which was certified as 17.8%.

Aggregationed structure control of other BDT-based polymer donors

Many other polymer donors consisting of BDT unit and other acceptor unit are utilized in high-performance NF-PSCs, such as poly[[5, 6-difluoro-2-(2-hexyldecyl)-2H-benzotriazole-4,7-diyl]-2,5-thiophenediyl][4,8-bis[5-(tripropylysilyl)-2-thienyl]benzo][1,2-b:4,5-b′:2′,5′-dithiophene-2,6-diyl]-2,5-thiophenediyl] (J71), J52 and the copolymer that consists of alternating units of benzodithiophene (BnDT) and fluorinated benzotriazole (FTAZ), PBNrDT-FTAZ (abbreviated as FTAZ). In this section, we summarize some representative modulation strategies for the aggregated structure of these polymer donors, mainly focusing on the chemical structure of materials and the component of BHJs blend.
The tuning of the polymer backbone is important to determine the aggregation properties of polymer donors. Polymer PBDE-DFTD was synthesized by introducing fluorinated bithiophene to replace TT group in PBDE-TT. PBDE-DFTD presented an increased aggregated trend in solution and ordered stacking in neat film than PBDE-TT resulting from the F--S conformational locks on the backbone that was indicated by the larger $L_c$ of PBDT-DFTD. Meanwhile, the PBDE-DFTD:IT-4F blend also exhibited favorable $\pi-\pi$ stacking and higher face-on stacking ratio, which contributed to a higher PCE of 14.16% than 11.10% of PBDE-TT:IT-4F based PSCs. On the contrary to noncovalent conformational locks, Peng et al. proposed a novel method to control the aggregation properties of PSFTZ by creating coordinated locks using a Pt-based complex. Due to the large steric hindrance of the Pt-based complex, the newly formed Pt-PSFTZ exhibited suppressed aggregation and crystallinity causing a relatively weak phase separation of the Pt-PSFTZ-Y6 blend. When 10% coordination blocks existed, corresponding PSCs achieved a record PCE of 16.35% at that time.

The influence of side chain on the aggregated structure is widely investigated in different polymer:NFAs blend. The length, substituted position and steric hindrance of side chain were demonstrated to have a distinct influence on the aggregation, crystallinity, and domain features of BHJs blend. Especally, the halogenation on the side chain of BDT unit was demonstrated to enhance the crystallinity and aggregated order effectively. For instance, PBDT-Cl and PBDT-F exhibited stronger crystallinity than nonhalogenated PBDT-H. Interestingly, PBDT-Cl has a smaller $\pi-\pi$ stacking distance and larger $L_c$ than that of PBDF-T and PBDF-H. Meanwhile, the PBDT-Cl:Y6 blend exhibited the most compact $\pi-\pi$ stacking and strongest crystallinity that contributed to favorable order and domain purity. Thus, the PBDT-Cl:Y6 based PSCs obtained an improved PCE of 15.63% compared to PBDT-H and PBDF-F systems.

Apart from side chain of polymer donor, the side chain of acceptor affects the aggregation behaviors and morphology characteristics of polymer:NFA pairs. Chen et al. thoroughly studied the aggregation properties and stacking features of blends containing J52 and NFAs with the same backbone and disperse side chain. Compared to methyl, isopropyl, and isobutyl, the NFAs with large side chain like octyl and ethylhexyl produced better performance in J52-based PSCs. UF-EH-2F resulted in distinct phase separation and fibril-like nanostructure when blending with J52, which benefited the dissociation and transport of charge. With the optimized morphology among these NFAs, the J52:UF-EH-2F based PSCs reached the highest PCE of 13.56% and the highest $J_{SC}$ of 24.87 mA cm$^{-2}$.

Zhan et al. systematically investigated the effect of fluorination and fluorine number of NFAs on the crystallinity and device performance in FTAGZ-based blend films. In consistent with PBDB-T or PBDB-TF based BHJs, the fluorination of NFAs enhanced the crystallinity of respective blend films. By controlling fluorine number on end group, INIC3 substituted by four fluorine atoms produced an increased PCE of 11.5% in FTAZ:INIC3 based PSCs.

Moreover, the interaction between blend components can produce different aggregated behaviors and morphology features. For example, the incorporation of tetraphenylethylene (TPE), an aggregation-induced emission material, enhanced the crystallinity of J71:ITIC blend, which further increased with the content of TPE. Due to the high compatibility of J71 and TPE, TPE replaced ITIC to enter J71 domain and resulted in ITIC concentrated at the bottom of the device, which produced a higher domain purity and vertical phase separation (Figure 16). For this improvement, the J71:ITIC:TPE ternary PSCs obtained a higher PCE of 12.16% with an increased FF value when adding 15 wt% TPE.

The incorporation of additives produces varied intermolecular interaction, resulting in changes of aggregated structure and crystallization behaviors of polymer:NFA blend films. Hou et al. used TCNQ as the additive in J52:IEICO-based PSCs to modulate the morphology of J52:IEICO blend. The J52:IEICO blend exhibited increased crystallinity with 12 wt% TCNQ added, resulting from strong interaction between TCNQ and IEICO. Removing TCNQ by TA, the film presented optimized phase separation that produced a higher PCE of 8.2% than the PSCs without TCNQ added. Moreover, the synergistic effect of binary additives, ODT:DIO, was investigated in detail for FTAZ:ITIC-Th-based PSCs. By adjusting the content of two additives, both ODT and DIO were found to enhance the crystallinity of the blend, while the binary additives cause similar morphology features with only DIO. With respect to this phenomenon, Ma et al. demonstrated that ODT worked at the beginning stage of morphology evolution due to low boiling point and DIO worked at the later stage due to high boiling point. With the synergistic process of nucleation and phase growth, the FTAZ:ITIC-Th blend with 0.375%:0.125% ODT:DIO binary additives exhibited balanced domain size and purity, which contributed to an improved PCE of 10.93%.

Ye et al. reported an eco-compatible solvent pair of (R)-(+)-limonene (LM) and 2-methyltetrahydrofuran (MeTHF), which were, respectively, used in two steps of sequential spin-coating. As the periodic (h00) peak in 1D GIWAXS line profiles and long period in R-SoXS presented, solvent LM effectively enhanced the stacking and molecular order of FTAGZ and provided large domain spacing. Thus, the sequentially deposited PSCs based on LM processed FTAGZ and MeTHF processed IT-M achieved an increased PCE of 12.2%. More importantly, they suggested that the polymer:solvent interaction parameter $\chi$ is correlated with the domain spacing of these sequentially coated PSCs, benefiting from the modulation of the aggregated structure of polymer:NFA blend.

In brief, in order to improve the aggregated structure of BDT-based polymer donors, strategies for polymeric structure mainly include backbone tuning and sidechain tuning. It is an efficient method to change the substituted position and length of the side chain. In particular, halogenation and larger conjugated scale generally enhance the crystallinity and aggregation of polymer donors. As for NFAs, the tuning of the end group also has an important effect on the aggregation of polymer:NFA blends apart from backbone and sidechain. Halogenation on end groups and the length of the side chain and conjugated backbone are precisely controlled for a well-performed NFA. Notably, asymmetric molecular structure generally presents moderated aggregation behavior, providing a feasible method for tuning aggregated structure. Moreover, modifying the composition of polymer:NFA...
blends, especially adding a third component, has a great influence on the aggregated structure. The selection of third component (polymer or small molecule donors and acceptors), additives and solvents are nonnegligible factors to obtain a favorable morphology. Finally, the control of solution-processing techniques is also a key method to improve the aggregated structure, which includes the selection of processing solvents, TA, SVA, modulation of solution and substrate temperatures.

**Aggregated structure control of polymer donors with temperature-dependent aggregation behaviors**

Other polymer donors that consist of thiophene unit and benzothiadiazole unit or benzotriazole unit, such as PffBT4T-2OD, PTFB-O, P3TEA, present strong temperature-dependent aggregation behavior and therefore attract extensive attention in NF-PSCs researches.\(^{[71,396]}\) That means these polymer donors present increasing aggregation and crystallization degree and ordered molecular stacking with the decrease of temperature. Therefore, these polymer donors provide efficient charge transport paths and high hole mobility, which is favorable to achieve prominent performance for PSCs, especially thick-film PSCs. In this section, we mainly summarize the molecular design and blend composition of temperature-dependent aggregated polymer and NFAs for modulating the aggregated structure of corresponding BHJs blend films.

The chemical structure of polymer donor has a crucial impact on the aggregation features and crystallization behaviors. Yan et al.\(^{[71,397–399]}\) discussed the structure–aggregation properties relationship in detail. On the one hand, the fluorination on the backbone is important to increase the crystallinity and \(\pi-\pi\) stacking of polymer to produce temperature-dependent aggregation feature. On the other hand, the 2-position alkyl substitution introduced steric hindrance and caused obvious geometric transformation relevant to temperature that resulted in changes of aggregation state. Nevertheless, due to strong aggregation and crystallization, some temperature-dependent aggregation polymers showed unsatisfying performance when blending with NFAs.\(^{[71]}\) This demanded weaker aggregation behaviors of polymer donors to produce a suitable phase domain. For example, PTFB-O containing benzotriazole unit exhibited relatively weak aggregation and resulted in increased PCE of 10.9% in PTFB-O:ITIC-Th based PSCs. Yan and colleagues\(^{[397]}\) also demonstrated the regiochemistry of alkyl side chains produced different aggregated structure of polymer:NFAs. PBTAZ with alkyl substitution on thiophene adjoining benzothiazole exhibited a less-twisted backbone, which resulted in excessive aggregation and large domain size of the PBTAZ:O-IDTBR blend. In contrast, PBTAZS with alkyl substitution on thiophene adjoining benzothiazole exhibited twisted backbone and reduced crystallinity and aggregation properties (Figure 17). The improved PBTAZS-O-IDTBR PSCs obtained higher PCE (10.4%) and \(J_{SC} \) (16.4 mA cm\(^{-2}\)) than PBTAZ-based PSCs. Similar regulation was also observed in PTFB-P and PTFB-PS, which produced better performance than PTFB-P. In addition, the modulation on polymer backbone can improve the aggregated structure and crystallization behavior of BHJs blend. The copolymerization of PffBT4T-2OD with T3T unit suppressed the aggregation and crystallization of polymer and the aggregation decreased with the increase of T3T unit content.\(^{[400]}\) The formed PffBT4T\(_{90}\)-co-T3T\(_{10}\) exhibited improved aggregation properties and miscibility blending with IDTBR, contributing to a relatively higher PCE of 8.7% than PffBT4T-2OD:IDTBR-based PSCs.

The changes of crystallinity and aggregation properties of NFAs affect the aggregated features of BHJs blend, in which the chemical structure of NFAs plays a key role. For instance, TPE-PDI possesses a largely twisted molecular structure causing unideal stacking features when blending with P3TEA.\(^{[401]}\) BF-PDI using bifluorenylidene core to replace former TPE core had smaller twist and balanced the self-aggregation and weak molecular stacking. Thus, the
compact stacking and favorable morphology resulted in an improved PCE of 8.05% in P3TEA:BF-PDI based PSCs.

The third component introduced to binary PSCs enables to influence the aggregated structure and crystallinity of BHJs blend, while the temperature-dependent aggregated polymer donor may maintain their own aggregation properties during film forming. Based on PTFB-O:ITIC-Th:IEIC-Th blend, PTFB-O first aggregated and formed donor phase due to its temperature-dependent aggregation when NFAs was still dissolved, formed morphology of which presented the aggregation features of PTFB-O (Figure 18).[78] Moreover, the similar interfacial tension of ITIC-Th and IEIC-Th was crucial to form a compatible acceptor phase, which produced a binary-like blend. As a result, the choice and combination of polymer and NFAs was demonstrated to efficiently control the morphology and phase features. The PTFB-O:ITIC-Th:IEIC-Th base ternary PSCs obtained an optimized FF of 0.72 and the PCE of 11.2%. On the other hand, the ratio of the introduced third component obviously affected the aggregation of BHJs blend. PC71BM could be introduced to PBTTFB:ITIC blend to suppress the aggregation of ITIC.[402] As the content of PC71BM increased, ITIC exhibited weakened aggregation and produced smoother film morphology. When the ratio of ITIC:PC71BM was 1:9, the PCE of corresponding PSCs was increased to 9.73%.

FIGURE 17 (A) Chemical structure of PIBTAZ, PIBTAZS, O-IDTBR, and molecule geometry of PIBTAZ and PIBTAZS. (B) GIWAXS patterns of PIBTAZ and PIBTAZS neat films and the corresponding blend films with O-IDTBR. (C) Line profiles of neat films and blend films. Reprinted from Ref. [397] with permission. Copyright (2018) John Wiley & Sons, Inc
acceptor modulates the aggregated structure by changing the dominated morphology evolution mechanism.

CONCLUSION AND FUTURE PERSPECTIVES

In summary, we have discussed the recent advances in achieving efficiency breakthroughs in PSCs by controlling the aggregated structure of photovoltaic polymers. The case studies of polymer:fullerene systems were first reviewed. We focused on the classic polymer:fullerene blend system and summarized the methods of adjusting the aggregated structure and optimizing the film morphology of the blend system. For highly crystalline PT systems, post-treatment through TA or SVA is conducive to the regular arrangement of molecular segments. In the DPP-based conjugated polymer:fullerene systems, the use of solvent additives or cosolvents to fine-tune the kinetics of the film formation process is beneficial to inhibit the aggregation of fullerene and form a bicontinuous network. Additionally, systematically adjusting the aggregated structure of the conjugated polymers with temperature-dependent aggregation can finely optimize the device performance. As for polymer:NFA systems, the tunable molecular structures of polymer and NFAs provide more approaches to finely tune the aggregated structure of BHJ blends. The control strategies of NF-PSCs employing PM6 and PTs are discussed in detail. The crystallinity and aggregation behavior can be efficiently tuned by modifying the backbone and side chain of polymer donors, such as halogenation, copolymerization and substituting position of side chains. In addition, the backbone, side chain, and end group of NFAs have profound effects on the aggregated structure. More specifically, the strategies based on conformational locks, conjugated length, halogenation on end groups, length and substituted position of side chains, and so on, can
contribute to the improved aggregated structure, leading to increased device performance. Moreover, the selection of third components and additives affects the aggregated structure of BHJ blends by changing intermolecular interaction and morphology evolution. As the aggregation behaviors of polymer chains in solution are often temperature-dependent, tuning the solution preparation protocols (solution temperature, substrate temperature, annealing time, dissolving methods, etc.) should be feasible approaches to control the aggregated structure of photovoltaic polymer blend films.

Owing to the systematic control of aggregated structures, the PCEs of most efficient PSCs based on polymer:small molecule blends are approaching 19% or above. Despite the rapid progress in the last decade, some open questions remain to be addressed. Here, we outline five urgent challenges and possible paths to address them.

**Aggregated structure of conjugated polymers in solution**

The self-aggregated structure of conjugated polymer solution will directly affect the morphology of films. Therefore, controlling the solution aggregation behavior of conjugated polymers can achieve a microstructure that is more conducive to charge transport. However, the characterization and control methods of polymer solution aggregation are still lacking. It is necessary to systematically study the aggregated structure of conjugated polymers in solution and then comprehensively establish the relationship between molecular structure, solution aggregated structure, film microstructure, and electrical properties. It provides further guidance for the design of high-performance conjugated polymers and the optimization of device performance.

**Morphology control strategies for complex material systems**

The control of aggregated structure of the polymer acceptors double-cable polymers and multicomponent polymer blends remains a critical hurdle. These complex material systems may exhibit different aggregation behaviors, remaining challenges for controlling the aggregated structure of corresponding systems. In addition, materials with simple molecular structure and synthetic routes show practical potential in commercialization.
despite the relatively low efficiency for the moment. However, the aggregated structure and the control strategies of these materials are still less explored. To efficiently tuning the aggregated structure of these systems and fully establish the structure–property relationships, precise modulation of molecular structure, processing techniques and parameters can be further studied.

New characterization tools for the aggregated structure of conjugated polymers

Present understanding of the aggregated structure greatly benefits from the advances in characterization tools of soft matters.\textsuperscript{45,47,416} For instance, R-SoXS has been a very powerful tool to analyze the structural parameters (domain size,\textsuperscript{417,418} domain purity,\textsuperscript{419} type and degree of orientation\textsuperscript{420,421}) of polymers blends in solid films. Use of other techniques (e.g., in situ neutron scattering\textsuperscript{422} and cryo-TEM\textsuperscript{423}) will help to understand how the aggregated structure forms in solution state. In particular, cryo-TEM\textsuperscript{423,424} has been proven a powerful tool to in situ visualize the solution structures of conjugated polymers in real-space.

Thermodynamic descriptions of less studied polymer blends

Although the miscibility of polymer donor: (fullerene/NF) small molecule acceptor systems has been extensively studied,\textsuperscript{94,103,425} miscibility of all-polymer blends, small molecule donor:polymer acceptor blends are much less explored. Recent studies hold promises that applying a thermodynamic quantity, that is, Flory–Huggins interaction parameter, might aid the understanding of mixing behaviors of these blends.\textsuperscript{93}

Full structure–property relationships for polymer blend films

The aggregated structure of conjugated polymers not only affects the photovoltaic properties of the polymer blend films, but also impacts other properties that are also critical to practical applications. The relationship between aggregated structure and intrinsic mechanical properties of photovoltaic polymer blends remains poorly understood.\textsuperscript{130,426} Furthermore, it is time to focus on the link between aggregated structures and device stability.\textsuperscript{427}

Looking to the future, a more complete understanding of the above questions will be of great significance for the commercialization of high-efficiency PSCs.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

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REFERENCES

1. K. Wang, X. Feng, Z. An, C. Cai, H. Chen, H. Chen, Y. Dong, X. Feng, W. Fu, J. Gu, Y. Han, D. Hu, R. Hu, D. Huang, F. Huang, F. Huang, Y. Huang, J. Jin, X. Jin, Q. Li, T. Li, Z. Li, Z. Li, J. Liu, J. Liu, S. Liu, H. Peng, A. Qin, X. Qinq, Y. Shen, J. Shi, X. Sun, B. Tong, B. Wang, H. Wang, L. Wang, S. Wang, Z. Wei, T. Xie, C. Xu, H. Xu, Z.-K. Xu, B. Yang, Y. Yu, X. Zeng, X. Zhan, G. Zhang, J. Zhang, M. Q. Zhang, X.-Z. Zhang, X. Zhang, Y. Zhang, Y. Zhang, C. Zhao, W. Zhao, X. Zhou, Z. Zhou, J. Zhu, X. Zhu, B. Z. Tang, Mater. Chem. Front. 2020, 4, 1803.
2. F. Huang, Z.-s., Bo, Y.-h., Geng, X.-h., Wang, L.-x., Wang, Y.-g., Ma, J.-h., Hou, W.-p., Hu, J. Pei, H.-l., Dong, S. Wang, Z. Li, Z.-g., Shuai, Y.-f., Li, Y. Cao, Acta Polym. Sinica 2019, 50, 988.
3. S. Fratini, M. Nikolova, A. Salileo, G. Schweitzer, H. Sirringhaus, Nat. Mater. 2020, 19, 491.
4. L. Ma, S. Zhang, J. Wang, Y. Xu, J. Hou, Chem. Commun. 2020, 56, 14337.
5. Q. Liu, Y. Jiang, K. Jin, J. Qin, J. Xu, W. Li, J. Xiong, J. Liu, X. Xiao, K. Sun, S. Yang, X. Zhang, L. Ding, Sci. Bull. 2020, 65, 272.
6. M. Zhang, L. Zhu, G. Zhou, T. Hao, C. Qiu, Z. Zhao, Q. Hu, B. W. Larson, H. Zhu, Z. Ma, Z. Tang, W. Feng, Y. Zhang, T. P. Russell, F. Liu, Nat. Commun. 2021, 12, 309.
7. L. Zhan, S. Li, X. Xia, Y. Li, X. Lu, L. Zuo, M. Shi, H. Chen, Adv. Mater. 2021, 33, 2007231.
8. J. Chen, Y. Cao, Acc. Chem. Res. 2009, 42, 1709.
9. J. Zhang, H. Tan, X. Guo, A. Facchetti, H. Yan, Nat. Energy 2018, 3, 720.
10. Z. A. Li, C. C. Chueh, A. K. Y. Jen, Prog. Polym. Sci. 2019, 99, 101175.
11. L. Lu, M. A. Kelly, W. You, L. Yu, Nat. Photonics 2015, 9, 491.
12. J. Hou, O. Inganas, R. H. Friend, F. Gao, Nat. Mater. 2018, 17, 119.
13. G. Li, R. Zhu, Y. Yang, Nat. Photonics 2012, 6, 153.
14. A. Wadsworth, M. Moser, A. Marks, M. S. Little, N. Gasparini, C. J. Brabc, D. Baran, I. McCulloch, Chem. Soc. Rev. 2019, 48, 1596.
15. L. Lu, T. Zheng, Q. Wu, A. M. Schneider, D. Zhao, L. Yu, Chem. Rev. 2015, 115, 12666.
16. H. X. Zhou, L. Q. Yang, W. You, Macromolecules 2012, 45, 607.
17. P. M. Beaunege, J. M. J. Fruchot, J. Am. Chem. Soc. 2011, 133, 20009.
18. L. Ye, S. Zhang, L. Hao, M. Zhang, J. Hou, Acc. Chem. Res. 2014, 47, 1595.
19. S. Zhang, L. Ye, H. Zhang, J. Hou, Mater. Today 2016, 19, 533.
20. X. Gu, L. Shaw, K. Gu, M. F. Toney, Z. Bao, Nat. Commun. 2018, 9, 534.
21. Y. Diao, L. Shaw, Z. A. Bao, S. C. B. Mannsfeld, Energy Environ. Sci. 2014, 7, 2145.
22. N. D. Treat, P. Westacott, N. Stingelin, Annu. Rev. Mater. Res. 2015, 45, 459.
23. H. Lee, C. Park, D. H. Sin, J. H. Park, K. Cho, Adv. Mater. 2018, 30, 1800453.
24. X. Yang, J. Loos, Macromolecules 2007, 40, 1353.
25. C. J. Brabc, M. Heeney, I. McCulloch, J. Nelson, Chem. Soc. Rev. 2011, 40, 1185.
26. S. Zhang, L. Ye, J. Hou, Adv. Energy Mater. 2016, 6, 1502529.
27. G. Wang, M. A. Adil, J. Zhang, Z. Wei, Adv. Mater. 2019, 31, 1805089.
28. Y. Lin, F. Zhao, S. K. K., Prasad, J. D. Chen, W. Cai, Q. Zhang, K. Chen, Y. Wu, W. Ma, F. Gao, J. X. Tang, C. Wang, W. You, J. M. Hodgkiss, X. Zhan, Adv. Mater. 2018, 30, 1706363.
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380. H. Zhao, H. B. Naveed, B. Lin, X. Zhou, J. Yuan, K. Zhou, H. Wu, R. Guo, M. A. Scheel, A. Chumakov, S. V. Roth, Z. Tang, P. Müller-Buschbaum, W. Ma, Adv. Mater. 2020, 32, 2002302.

381. B. Lin, X. Zhou, H. Zhao, J. Yuan, K. Zhou, K. Chen, H. Wu, R. Guo, M. A. Scheel, A. Chumakov, S. V. Roth, Y. Mao, L. Wang, Z. Tang, P. Müller-Buschbaum, W. Ma, Energy Environ. Sci. 2020, 13, 2467.

382. S. Li, W. Zhao, J. Xiong, X. Liu, Z. Zheng, C. He, B. Xu, Z. Wei, J. Hou, Chem. Mater. 2020, 32, 1993.

383. X. Xu, K. Feng, Z. Bi, W. Ma, G. Zhang, Q. Peng, Adv. Mater. 2019, 31, 1901872.

384. Y.-C. Lin, Y.-J. Lu, C.-S. Tsao, A. Saeki, J.-X. Li, C.-H. Chen, H.-C. Wang, H.-C. Chen, D. Meng, K.-H. Wu, Y. Yang, K.-H. Wei, J. Mater. Chem. A 2019, 7, 5072.

385. Q. Wang, M. Li, Y. Liu, Z. Wang, Z. Liang, Y. Geng, J. Mater. Chem. C 2019, 7, 9581.

386. W. Chen, G. Huang, X. Li, Y. Li, H. Wang, H. Jiang, Z. Zhao, D. Yu, E. Wang, R. Yang, ACS Appl. Interfaces 2019, 11, 33137.

387. S. Wen, Y. Li, N. Zheng, I. O. Raji, C. Yang, X. Bao, J. Mater. Chem. A 2020, 8, 13671.

388. J. S. Park, G. U. Kim, D. Lee, S. Lee, B. Ma, S. Cho, B. J. Kim, Adv. Funct. Mater. 2020, 30, 2005787.

389. M. Chang, L. Meng, Y. Wang, X. Ke, Y.-Q. Qi, Y. Ni, Z. Zheng, W. Zheng, Z. Xie, M. Zhang, Y. Yi, H. Zhang, X. Wan, CL. Li, Y. Chen, Chem. Mater. 2020, 32, 2593.

390. S. Dai, F. Zhao, Q. Zhang, T.-K. Lau, T. Li, K. Liu, Q. Ling, C. Wang, X. Lu, W. You, X. Zhan, J. Am. Chem. Soc. 2017, 139, 1336.

391. M. A. Adil, J. Zhang, Y. Wang, J. Yu, C. Yang, G. Lu, Z. Wei, Nano Energy 2020, 68, 104271.

392. Y. Xiong, L. Ye, A. Gadissa, Q. Zhang, J. Rech, W. You, H. Ade, Adv. Energy Mater. 2019, 9, 1806262.

393. B. Yu, H. Yao, L. Hong, M. Gao, L. Ye, J. Hou, J. Mater. Chem. C 2020, 8, 44.

394. J. Chen, Z. Bi, X. Xu, Q. Zhang, S. Yang, S. Guo, H. Yan, W. You, W. Ma, Adv. Sci. 2019, 6, 1801560.

395. L. Ye, Y. Xiong, Z. Chen, Q. Zhang, Z. Fei, R. Henry, M. Heeney, B. T. O’Connor, W. You, H. Ade, Adv. Energy Mater. 2019, 9, 1808153.

396. A. Ashokan, T. Wang, M. K. Ravva, J.-L. Brédas, J. Mater. Chem. C 2018, 6, 13162.

397. S. Chen, L. Zhang, C. Ma, D. Meng, J. Zhang, G. Zhang, Z. Li, P. C. Y. Chow, W. Ma, Z. Wang, K. S. Wong, H. Ade, H. Yan, Adv. Energy Mater. 2018, 8, 1702427.

398. H. Hu, K. Jiang, P. C. Y. Chow, L. Ye, G. Zhang, Z. Li, J. H. Carpenter, H. Ade, H. Yan, Adv. Energy Mater. 2018, 8, 1701674.

399. Z. Li, K. Jiang, G. Yang, J. Y. L. Lai, T. Ma, J. Zhao, W. Ma, H. Yan, Nat. Commun. 2016, 7, 1038.

400. X. Yi, Z. Peng, B. Xu, D. Seyiltiyesi, C. H. Y. Ho, E. O. Danilov, T. Kim, J. R. Reynolds, A. Amassian, K. Gundogdu, H. Ade, F. So, Adv. Energy Mater. 2020, 10, 1902430.

401. H. Han, L.-K. Ma, L. Zhang, Y. Guo, L. Yi, H. Hu, W. Ma, H. Yan, D. Zhao, ACS Appl. Mater. Interfaces 2019, 11, 6970.

402. T. Kim, J. Jeo, J. Y. Lee, Y. J. Yoon, T. H. Lee, Y. S. Shin, I.-S. Kim, H. Kim, M. S. Jeong, I.-W. Hwang, B. Walker, P. S. Jo, B. Lim, J. Y. Kim, Adv. Energy Mater. 2019, 11, 7208.

403. Z. Hamid, A. Wadsworth, E. Rezasoltani, S. Holliday, M. Azzouzi, M. Neophytou, A. A. Y. Guibert, Y. Dong, M. S. Little, S. Mukherjee, A. A. Herzing, H. Bristow, R. J. Kline, D. M. DeLongchamp, A. A. Bakulin, J. R. Durrant, J. Nelson, I. McCulloch, Adv. Energy Mater. 2020, 10, 1903248.

404. Y. Jiang, L. Ning, C. Liu, Y. Sun, J. Li, L. Liu, Y. Yi, D. Qiu, C. He, Y. Guo, W. Hu, H. Liu, Chem 2021. https://doi.org/10.1002/chem.202101016.

405. T. Jia, J. Zhang, W. Zhong, Y. Liang, K. Zhang, S. Dong, L. Ying, F. Liu, X. Wang, F. Huang, Y. Cao, Nano Energy 2020, 72, 104718.

406. Q. Fan, Q. An, Y. Lin, Y. Xia, Q. Li, M. Zhang, W. Su, W. Peng, C. Zhang, F. Liu, L. Hou, W. Zhu, D. Yu, M. Xiao, E. Moons, F. Zhang, T. D. Anthopoulos, O. Inganäs, E. Wang, Energy Environ. Sci. 2020, 13, 5017.

407. H. Sun, H. Yu, Y. Shi, J. Yu, Z. Peng, X. Zhang, B. Liu, J. Wang, R. Singh, J. Lee, Y. Li, Z. Wei, Q. Liao, Z. Kan, L. Ye, H. Yan, F. Gao, X. Guo, Adv. Mater. 2020, 32, 2004183.

408. F. Peng, K. An, W. Zhong, Z. Li, L. Ying, N. Li, Z. Huang, C. Zha, B. Fan, F. Huang, Y. Cao, ACS Energy Lett. 2020, 5, 3702.
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