From Alloy-Like to Cascade Blended Structure: Designing High-Performance All-Small-Molecule Ternary Solar Cells

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ABSTRACT: Ternary blending strategy has been used to design and fabricate efficient organic solar cells by enhancing the short-circuit current density and the fill factor. In this manuscript, we report all-small-molecule ternary solar cells consisting of two compatible small molecules DR3TBDTT (M1) and DR3TBDTT-E (M2) as donors and PC71BM as acceptor. A transformation from an alloy-like model to a cascade model are first realized by designing a novel molecule M2. It is observed that after thermal and solvent vapor annealing M2 shifts from the mixed region to donor–acceptor (D–A) interfaces which ameliorates the charge transfer and recombination processes. The optimal ternary solar cells with 10% M2 exhibited a power conversion efficiency of 8.48% in the alloy-like model and 10.26% in the cascade model. The proposed working mechanisms are fully characterized and further supported by the density functional theory and atomistic molecular dynamics simulations. This provides an important strategy to design high-performance ternary solar cells which contains one molecule not only is compatible with the main donor molecule but also performs a preference to appear at the D–A interfaces hence builds cascade energy levels.

INTRODUCTION

Organic solar cells (OSCs) have been extensively investigated because of several advantages, including low cost, light weight, easy processing, and flexibility.1–3 Designing novel molecules and tuning bulk heterojunctions (BHJs) of active layers have contributed to the improvement of the performance of OSCs. The power conversion efficiencies (PCEs) of OSCs for polymers and small molecules have respectively exceeded over 13 and 11% by designing appropriate molecules and optimizing the morphological characteristics of BHJs.4,5 To overcome the light harvest shortage of solar light, researchers fabricated ternary blend solar cells consisting of two electron-donating materials with different structures and one electron-withdrawing acceptor or one donor and two acceptors.6–8 Ternary blends have been demonstrated as efficient strategy to increase the light-harvesting efficiency and tune the morphological characteristics of BHJs.9

With the development of ternary OSCs, different models and mechanisms have been proposed to guide the design of ternary blends. You et al. reported a parallel-like model for ternary OSCs by applying two conjugated polymers as donors, which form bicontinuous interpenetrating networks with a fullerene phase.9 Thompson et al. proposed an alloy model for OSCs by studying the origin of the tunable open-circuit voltage ($V_{OC}$) of a series of ternary BHJ solar cells.10 In the alloy model, two donor molecules with a small Flory–Huggins interaction parameter are properly mixed, and they consequently form alloy-like domains, which exhibit the proportionally highest occupied molecular orbital (HOMO) level; thus, ternary solar cells yield a tunable $V_{OC}$ as the ratio of these donors varies.13 Yang et al. suggested that two donors with similar chemical and physical properties should be selected because unfavorable interactions among three components may function as morphological traps and recombination centers.14 Our group investigated the synergistic effect of a polymer and a small molecule with a similar chemical backbone in ternary blends and revealed that an optimal alloy-like structure of the small molecule and the polymer can induce the crystallinity of polymer domains and result in the formation of favorable nanostructures, which can simultaneously increase the short-circuit current density ($J_{SC}$) and fill factor (FF).15,16 The third component can generally extend the absorption of the solar...
spectrum or optimize the morphological characteristics of OSCs.\textsuperscript{6−8,17,18} In addition to molecule and BHJ mesophase optimization, exciton separation and charge transport for BHJ organic solar cells are facilitated by donor−acceptor (D−A) interfaces.\textsuperscript{19−21} McGehee et al. proposed that mixed regions exist at D−A interfaces in polymer:fullerene binary solar cells, and low charge carrier recombination and high internal quantum efficiency can be accomplished by carefully modifying the mixed regions.\textsuperscript{19,20} A ternary strategy, especially for three components with cascade energy levels, provides a potential mechanism to optimize D−A interfaces.\textsuperscript{22,23} The cascade energy levels of ternary blends are beneficial to charge transfer, while charge recombination is minimized.\textsuperscript{24−29} Ameri et al. presented strategies based on a cascade model to decrease charge carrier recombination at D−A interfaces by employing third compounds.\textsuperscript{30,31} In a PTB7:sensitizer:fullerene ternary system, an effective charge transfer occurs from a disordered host system to a highly ordered sensitizer, which effectively avoids traps of host matrices and features an almost ideal recombination behavior.\textsuperscript{31} Thus, designing a ternary OSC system containing one molecule not only exhibits compatibility with the main donor molecule but also preferably appears at D−A interfaces and hence builds cascade energy levels will be much likely to enhance the performance of OSCs.\textsuperscript{32−34} Herein, strengthening the interaction between the third component and 6,6-phenyl-C\textsubscript{71}-butyric acid methyl ester (PC\textsubscript{71}BM) is proposed to reach the aforementioned goal in a PC\textsubscript{71}BM-containing ternary system, which can be realized by introducing an ester functional group to electron-donating molecules. In accordance with this guideline, all-small-molecule ternary OSCs consisting of two compatible small molecules, namely, DR3TBDTT (M\textsubscript{1})\textsuperscript{32} and DR3TBDTT-E (M\textsubscript{2}), as donors and PC\textsubscript{71}BM as an acceptor are designed and fabricated. M\textsubscript{2} is a key novel small molecule that contains thiophene-substituted benzo[1,2-b:4,5-b′]dithiophene (BDT) with ester-anchored alkyl side chains as a donor moiety and 3-ethylrhodanine (RHD) as acceptors connected with terthiophene π-conjugated bridges (Scheme S1). The chemical structures of M\textsubscript{1}, M\textsubscript{2}, and PC\textsubscript{71}BM are shown in Figure 1a.

**RESULTS AND DISCUSSION**

**Molecular Energy Levels and UV−Vis Absorption Spectra.** The electrochemical HOMO/lowest unoccupied molecular orbital (LUMO) levels of M\textsubscript{1} and M\textsubscript{2} are approximately −5.02/−3.27 eV and −5.22/−3.36 eV, respectively. The cyclic voltammogram of the M\textsubscript{2} thin film is shown in Figure S1. The optical and electrochemical data of these two small molecules are listed in Table S1. The energy levels for M\textsubscript{2} are lowered by introducing ester functions to side chains, and energy cascades are formed in the LUMO and HOMO levels of
Table 1. Summary of the Photovoltaic Parameters of Solar Cells with Different M1:M2 Ratios without Post Treatment

<table>
<thead>
<tr>
<th>M1:M2:PC71BM</th>
<th>V\textsubscript{OC} (V)</th>
<th>J\textsubscript{SC} (mA/cm\textsuperscript{2})</th>
<th>FF (%)</th>
<th>PCE\textsubscript{ave} (%)</th>
<th>PCE\textsubscript{max} (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:0:0.8</td>
<td>0.906 ± 0.002</td>
<td>12.73 ± 0.37</td>
<td>65.8 ± 1.4</td>
<td>7.50 ± 0.09</td>
<td>7.59</td>
</tr>
<tr>
<td>0.9:0.1:0.8</td>
<td>0.931 ± 0.002</td>
<td>12.82 ± 0.25</td>
<td>71.1 ± 0.4</td>
<td>8.30 ± 0.16</td>
<td>8.48</td>
</tr>
<tr>
<td>0.8:0.2:0.8</td>
<td>0.936 ± 0.001</td>
<td>12.00 ± 0.05</td>
<td>66.5 ± 0.8</td>
<td>7.43 ± 0.06</td>
<td>7.47</td>
</tr>
<tr>
<td>0.6:0.4:0.8</td>
<td>0.943 ± 0.001</td>
<td>11.87 ± 0.04</td>
<td>61.5 ± 0.7</td>
<td>6.82 ± 0.07</td>
<td>6.88</td>
</tr>
<tr>
<td>0.4:0.6:0.8</td>
<td>0.957 ± 0.004</td>
<td>11.21 ± 0.14</td>
<td>59.2 ± 0.8</td>
<td>6.29 ± 0.05</td>
<td>6.35</td>
</tr>
<tr>
<td>0.2:0.8:0.8</td>
<td>0.970 ± 0.006</td>
<td>10.32 ± 0.03</td>
<td>55.9 ± 0.6</td>
<td>5.54 ± 0.08</td>
<td>5.60</td>
</tr>
<tr>
<td>0:1:0.8</td>
<td>1.002 ± 0.003</td>
<td>8.37 ± 0.18</td>
<td>48.1 ± 1.5</td>
<td>3.89 ± 0.11</td>
<td>4.04</td>
</tr>
</tbody>
</table>

Table 2. Summary of the Photovoltaic Parameters of Solar Cells with Different M1:M2 Ratios with TSA

<table>
<thead>
<tr>
<th>M1:M2:PC71BM</th>
<th>V\textsubscript{OC} (V)</th>
<th>J\textsubscript{SC} (mA/cm\textsuperscript{2})</th>
<th>FF (%)</th>
<th>PCE\textsubscript{ave} (%)</th>
<th>PCE\textsubscript{max} (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:0:0.8</td>
<td>0.880 ± 0.004</td>
<td>13.52 ± 0.06</td>
<td>74.9 ± 0.3</td>
<td>8.83 ± 0.06</td>
<td>8.90</td>
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<tr>
<td>0.9:0.1:0.8</td>
<td>0.896 ± 0.006</td>
<td>14.97 ± 0.20</td>
<td>76.5 ± 1.2</td>
<td>10.02 ± 0.12</td>
<td>10.26</td>
</tr>
<tr>
<td>0.8:0.2:0.8</td>
<td>0.901 ± 0.003</td>
<td>12.67 ± 0.10</td>
<td>74.7 ± 0.5</td>
<td>8.44 ± 0.07</td>
<td>8.52</td>
</tr>
<tr>
<td>0.6:0.4:0.8</td>
<td>0.895 ± 0.002</td>
<td>12.56 ± 0.14</td>
<td>61.5 ± 0.3</td>
<td>6.89 ± 0.03</td>
<td>6.92</td>
</tr>
<tr>
<td>0.4:0.6:0.8</td>
<td>0.902 ± 0.003</td>
<td>12.38 ± 0.08</td>
<td>58.4 ± 0.5</td>
<td>6.51 ± 0.01</td>
<td>6.52</td>
</tr>
<tr>
<td>0.2:0.8:0.8</td>
<td>0.920 ± 0.002</td>
<td>11.24 ± 0.09</td>
<td>54.7 ± 1.4</td>
<td>5.47 ± 0.19</td>
<td>5.66</td>
</tr>
<tr>
<td>0:1:0.8</td>
<td>0.944 ± 0.005</td>
<td>10.85 ± 0.27</td>
<td>68.2 ± 1.1</td>
<td>6.94 ± 0.04</td>
<td>6.99</td>
</tr>
</tbody>
</table>

Figure 2. (a) J−V curves of OSCs with M1:M2:PC\textsubscript{71}BM ratios of 1:0:0.8, 0.9:0.1:0.8, and 0:1:0.8 with and without TSA. (b) EQE curves of the OSCs that correspond to the devices in panel a. (c) Dependence of J\textsubscript{SC} on the light intensity for the OSCs that correspond to the devices in panel a. (d) V\textsubscript{OC}’s of OSCs with different M1:M2 weight ratios with and without TSA. (e–f) Calculated HOMO as a function of the M1:M2 ratios of complexes with alloy-like (e) and cascade (f) packing patterns.
the three compounds (Figure 1b). The UV–vis absorption spectra of the ternary and binary systems were examined (see Figure 1d) to determine the photochemical effect of doping M2 into M1:PC71BM blends. The M1:PC71BM binary films exhibit more red-shifted absorption edge than the M2:PC71BM films before and after TSA. However, the M2:PC71BM binary films showed stronger absorption intensities in the range of 300–550 nm. At the optimized ratio of M1:M2 (0.9:0.1), the absorption intensities are enhanced in the range of 300–550 nm compared with the M1:PC71BM films. The absorption band edge is comparable with the M1:PC71BM films. Thus, the induction of M2 can enhance the absorption ability in the range of 300–550 nm.

**Photovoltaic Properties.** Binary and ternary solar cells were then fabricated with conventional device structures of indium tin oxide (ITO)/PEDOT:PSS/active layer/Ca/Al. The experimental details can be referenced in the Supporting Information. The performances of the solar cells are listed in Tables 1 and 2, and the J–V curves under AM 1.5 G illuminations at 100 mW cm\(^{-2}\) are shown in Figure 2a. Active layers for binary and ternary blends performed thin thicknesses of 80–90 nm. Without any post treatment, the M1:PC71BM-based devices exhibit an efficiency level of 7.59% with a VOC of 0.906 V, JSC of 12.73 mA cm\(^{-2}\), and FF of 65.8%, whereas the M2:PC71BM-based solar cells show a lower PCE of 4.04% with a VOC of 1.002 V, JSC of 8.37 mA cm\(^{-2}\), and FF of 48.1%. The ternary solar cells at the optimized ratio of M1:M2 (0.9:0.1) yield an increased PCE of 8.48% with a VOC of 0.931 V, JSC of 12.82 mA cm\(^{-2}\), and FF of 71.1%. After carefully controlled thermal annealing at 70 °C for 5 min and solvent vapor annealing in chloroform vapor at room temperature for 60 s, the performances of the binary and ternary solar cells with M1:M2:PC71BM ratios of 0.9:0.1:0.8 and 0.8:0.2:0.8 are significantly enhanced. The M1:PC71BM-based devices exhibit an PCE of 8.90% with a VOC of 0.880 V, JSC of 13.52 mA cm\(^{-2}\), and FF of 74.9%, whereas the M2:PC71BM-based solar cells perform a lower PCE of 6.99% with a VOC of 0.944 V, JSC of 10.85 mA cm\(^{-2}\), and FF of 68.2%. A remarkable PCE of 10.26% with a VOC of 0.896 V, JSC of 14.97 mA cm\(^{-2}\), and FF of 76.5% is attained by the optimal ternary OSCs. The J–V curves show that the indenecce of 10% (weight ratio) of the M2 to M1:PC71BM system does increase the JSC and FF of the devices. The external quantum efficiency (EQE) results (Figure 2b) are consistent with the JSC values of the corresponding OSCs. The deviations between the integral current densities and JSC read from the J–V measurements are under 3%, which indicate a suitable consistency of the photovoltaic results. The enhanced EQE for the ternary system surely does not originate from the sum of M1 and M2 because it is higher than either of the two small molecules. A new photophysical mechanism should be proposed for the optimal ternary solar cells.

**Bimolecular Recombination Analysis.** Bimolecular recombination is studied by mapping JSC as a function of the incident light intensity of the selected systems (Figure 2c). The JSC follows the power–law dependence on light intensity, which can be expressed as JSC \(\propto P_{\text{light}}^{0.534}\). In this case, P_{\text{light}} is the light intensity, and \(\alpha\) is the exponential factor. Weak bimolecular recombination in the device would result in a linear dependence of JSC on the light intensity with \(\alpha\) value close to 1.\(^{55}\) The exponential factors for M1:PC71BM-, M1:M2:PC71BM (0.9:0.1:0.8)-, and M2:PC71BM-based solar cells before TSA are 0.964, 0.972, and 0.950, respectively, whereas those after TSA are 0.983, 0.994, and 0.958, respectively. We can conclude that the ternary blending and TSA treatment lower the bimolecular recombination in solar cells. In the optimized ternary solar cells, the lowest bimolecular recombination results in a high JSC and subsequently high PCE.

**Open-Circuit Voltage Evolution.** The VOC’s evolution with different M1:M2 ratios, as well as before and after thermal and solvent vapor treatment, are investigated. The statistical summary of the change in VOC’s is shown in Figure 2d. The VOC’s before TSA are higher and exhibit a tendency of quasi-linear change along with the M2 weight ratio increase in the ternary blends. The highest VOC of 1.002 V is obtained by the M2:PC71BM-based solar cells, which prove a deeper HOMO level of M2. VOC’s after TSA showed a subtle varying trend. In particular, VOC is approximately 0.90 V with an M2 ratio between 10 and 60%, whereas the VOC’s changed accordingly with an M2 ratio of below 10% or above 80%. Different models for ternary blend solar cells could help us understand the subtle differences in VOC changing tendencies before and after TSA. The alloy-like model can explain the tunable VOC’s of ternary systems without any post treatment. The cascade model could be employed to explain the pinned VOC of ternary solar cells with a M2 ratio of 10% to 60% after TSA. With a very small amount (e.g., less than 10% weight ratio), and even after TSA, the third component will most likely be embedded in the host phases, in which case the chemical and photophysical properties of the third component maybe disregarded. By contrast, with a M2 ratio of 10–60%, the third component is supposed to locate at the D–A interfaces and serve as a sensitizer to form a cascade energy level. When the M2 ratio is higher than 60% and after TSA treatment, the M1 is embedded in the M2 host phases and acts as an alloy-like phase separation, which also shows a quasi-linear change for VOC. Thus, we can assume a transformation from an alloy-like model to a cascade model (Figure 1c) occurred for the optimized ternary solar cells, especially at the M2 ratio of 10–60%, in which M2 shifts from the mixed region to D–A interface as a result of TSA.

**Charge Transport Processes.** The femtosecond transient absorption spectra (fs-TAS) measurements were performed to figure out the charge transport processes in the binary and ternary blend films. As is shown in Figure S2a–c, without TSA, the M1:PC71BM-based film shows three absorption peaks of 482, 582, and 683 nm, and the M2:PC71BM-based film only shows two peaks of 570 and 626 nm. As for the ternary blend film, three distinguished peaks are located, and the one of 480 nm is slightly enhanced. Therefore, the decays of the photoluminescence probed at 480 nm were measured. As can be seen in Figure S2d and Table S2, the charge carrier life times (\(\tau_1\), \(\tau_2\), and \(\tau_3\)) are lengthened, and the data of films with TSA exhibits the very similar phenomenon (Figure S3 and Table S3). We conclude that there are charge transport processes from M2 to M1 both in the alloy-like model and the cascade model. The different is that in the cascade model excitons generated by the M2 can split with the PC71BM to generate charge carriers and then transport via the M1 and PC71BM. In the alloy-like model, the charge separation and transport processes are likely similar as in the conventional BHJ structures, but the donor phase is M1:M2 alloy.

**Density Functional Theory Simulations.** To enhance our understanding of the origin of VOC changes in the alloy-like and cascade blending structures, density functional theory (DFT) calculations are performed using long-range corrected functional oB97X with 6–31G (\(d_p\)) basis set. The computational details can be referenced in SI. Two different types of
complexes are constructed to model the alloy-like and cascade packing patterns based on the optimized M1 and M2 monomers (see Figures S4 and S6 in SI). The M1 and M2 molecules in alloy-like model are combined along the stacking direction (M1-M2-M1...), whereas those in the cascade model form adjacent separated stacks (...M1-M1-M1... and ...M2-M2-M2...). The intermolecular distances along the stacking direction are maintained at 3.6 Å in all cases. Figure S5 shows that for the alloy-like model complexes, the HOMO orbitals are delocalized on the M1 molecule and varied with the increase in the number of M2 molecule. As expected, an approximately linear relationship is noted between the HOMO energy of the complexes and ratio of M1:M2 (Figure 2e). This condition is consistent with the findings of Thompson et al. in the alloy-like model. However, the HOMO orbitals (Figure S7) in the cascade model complexes are localized on the M1 molecules, and the HOMO energy is independent of the increase in the number of the M2 molecule (Figure 2f). Thus, our calculations fully support the experimentally observed transformation from alloy-like to cascade packing in the blended structure.

Theoretical simulations are also performed to calculate the binding energies of M1-PC71BM, M2-PC71BM, and M1-M2. The geometries of the complex structures are optimized with DFT methods with the long-range corrected functional CAMB3LYP and 6-31G (d,p) basis set, shown in Figure S8. Results show that the M1-M2 complex has a binding energy (−10.0 kcal mol⁻¹) larger than those of other two complexes (−3.8 kcal mol⁻¹ for M1-PC71BM and −5.0 kcal mol⁻¹ for M2-PC71BM, respectively), which indicates that these two molecules have suitable compatibility. A stronger intermolecular interaction was also observed for the M2-PC71BM complex than M1-PC71BM complex, which means a larger probability for M2 to appear at donor–PC71BM interfaces. Ester side chains with withdrawing ability can also modify the energy level of M2, which can benefit the formation of the cascade blending structure in ternary systems.

Molecular Dynamics Simulations. To obtain insights into the molecular packing in the mixed regions in binary and optimized ternary blends, atomistic molecular dynamics (MD) simulations were performed using the GROMACS 4.6.7 software suite. The computational details can be referenced in the Supporting Information, and the results are shown in Figure 3a–c. Figure 3b shows that M2 tends to locate at the interfaces between M1 and PC71BM in the mixed regions of the ternary system, which indicates that M2 has a stronger interaction with PC71BM than M1. This condition is consistent with our earlier DFT calculations. Moreover, the radial distribution functions (RDFs) among three individual chemical groups in the donor molecules (i.e., BDT, second thiophene unit of the terthiophene bridge (Th2), and RHD) and center-of-mass (COM) of C70 are analyzed for each system. RDF is the probability of finding other particles near around by drawing a series of circles about one certain particle. A diagrammatic sketch of RDF can be found in Figure S9. The results are shown in Figure 3d–f. In the case of the binary system, C70 is close to the BDT moieties in the M1:PC71BM system. In the case of the M2:PC71BM system, C70 is close to the bridge of Th2 due to the stronger steric effects of the longer side chains for the M2 molecule. However, when 10% M2 molecules are added to the M1:PC71BM binary blend, the RDF peak of RHD-C70 in the ternary system becomes the strongest.
This scenario implies that the probability of finding the PC71BM molecules close to the RHD moiety increased and results in the lesser extent of charge recombination. It is also consistent with recent experimental results by Graham et al. that pointed to the high efficiency of the polymer:fullerene system being obtained when the fullerene is generally docked with the electron-accepting moiety of the polymer.37

**Morphology.** The molecular stacking and orientation of the active layers was investigated by grazing incidence wide-angle X-ray scattering (GIWAXS).38 Figure 4a–f presents the 2D GIWAXS patterns of selected binary and ternary blends. 2D GIWAXS patterns of other ternary systems are shown in Figure S10. In the in-plane direction, the π−π stacking peaks (010) are located at \( q = 1.71 - 1.74 \) Å\(^{-1}\), whereas the π−π stacking peak is absent in the out-of-plane direction. The results indicate that the two π-conjugated small molecules and ternary blend have a preferred edge-on packing orientation with respect to the substrate. The corresponding in-plane cuts for all systems without and with TSA are shown in Figure 4g,h, respectively, to quantify the scattering data. The in-plane 1D profiles show that the (010) peaks of the M1:PC71BM and M2:PC71BM systems before TSA are located at \( q = 1.735 \) and \( 1.716 \) Å\(^{-1}\), respectively, whereas the peaks after TSA are located at \( q = 1.742 \) and 1.720 Å\(^{-1}\), respectively. The (010) locations of the ternary blends vary between the largest \( q \) of M1 and smallest \( q \) of M2 (Figure S11). The results indicate that M2 has a larger π−π stacking distance than M1. For all systems, the crystallinity is enhanced by TSA treatment because the coherence lengths of (010) peaks increase after TSA, which are shown in Figure 4i. The increased coherence length of the blends with an M2 ratio of 10–20% can explain the enhancement in the FF of the corresponding devices. For the blends with an M2 ratio of 40–80%, the device performance does not significantly change even with the larger coherence lengths. This scenario can be related to the large π−π stacking distance. The (010) locations and coherence lengths were calculated by using the Scherrer analysis,39 in which the full width at half-maximum were extracted by fitting the in-plane cuts with the Gaussian equation.

To deeply understand the morphological change introduced by TSA treatment, we performed the Gaussian fitting analysis for all (010) peaks of in-plane 1D cuts. According to the (010) peak locations of M1 and M2 in their binary blend films, we tried to divide the (010) peaks of ternary blend films into two peaks corresponding to M1 and M2, respectively. As is shown in Figure S12, for data of films without TSA, it is quite difficult to obtain the distinguished two peaks, more precisely, the peaks that correspond to M2. When it comes to data of films with TSA, we can easily divide the (010) peaks into two fitting peaks correspond to M1 and M2 respectively (Figure S13), and the intensities of the fitted peaks are interestingly consistence with the M1:M2 ratios in the ternary blend films. This could be an...
evidence to the transformation from alloy-like model to cascade model for \( \pi-\pi \) stacking is a significant factor of molecular assembly.

Trials were also made to do the same peak function fit analysis for the (100) peaks of 1D profiles because the (100) peaks directly reflect the molecular crystallization. However, due to the very similar chemical structures, the difference between the peak locations corresponding to M1 and M2 is negligible.

Therefore, another small molecule with longer BDT substitutional side chains, named C6C8-M1 (chemical structure is shown in Figure S14) was synthesized. Binary blend films and ternary blend films with C6C8-M1:PC71BM ratio of 0.9:0.1:0.8 were made, and GIWAXS data were collected to analyze the influence introduced by TSA. The 2D patterns are shown in Figure S15, showing that after TSA treatment the crystallinity was enhanced, and more importantly, the (100) peak locations of 1D profiles along out-of-plane direction for ternary blend films show an obvious difference before and after TSA. As is shown in Figure S16, before TSA, the C6C8-M1:PC71BM film shows a (100) peak location of 0.29 Å\(^{-1}\), M2:PC71BM film shows a (100) peak location of 0.34 Å\(^{-1}\), and the ternary blend film gives a (100) peak location of 0.31 Å\(^{-1}\). After TSA, both the C6C8-M1:PC71BM binary and the ternary blend film show (100) peak locations of around 0.30 Å\(^{-1}\). This can be attributed to the fact that without TSA treatment C6C8-M1 and M2 mix very well in the ternary blend films and the existence of small amount of M2 influences the aggregation of C6C8-M1 causing a (100) peak shift. After TSA, M2 shifts out from the mixed region to D–A interfaces showing little crystallization. Performance of devices based on C6C8-M1:PC71BM was also found to be enhanced after the inducement of 10% M2 (as is shown in Table S4).

Transmission electron microscopy (TEM) was also performed to investigate the effect of morphological characteristics by adding M2 to the host system. Figure S17 shows that the bright and dark regions in the TEM images correspond to the donors and PC71BM-rich domains, respectively.40,41 These images reveal that all systems show fibrous features with domain sizes of 15–20 nm, which benefit the exciton separation and charge transport.42 The dark–bright contrast ratio of the M1:PC71BM and ternary blend images become higher after TSA, which imply a higher purity of domains introduced by annealing. As for the M2:PC71BM system, the domain size becomes slightly smaller after annealing.

Polymer:Small Molecule:Fullerene Solar Cells. To verify the effect of the interfacial optimization for ternary systems introduced by M2, another ternary solar cell based on the PTB7-Th:M2:PC71BM system is fabricated. With conventional device structures, the PTB7-Th:PC71BM-based solar cells exhibit a PCE of 8.76% with a \( V_{OC} \) of 0.786 V, \( J_{SC} \) of 16.62 mA cm\(^{-2}\), and FF of 67.5%. The PTB7-Th:M2:PC71BM-based solar cells yield a high PCE of 9.44% with a \( V_{OC} \) of 0.786 V, \( J_{SC} \) of 16.77 mA cm\(^{-2}\), and FF of 71.5%. A summary of the solar cells performance is listed in Table S5. In the all-small-molecule ternary solar cells, a molecule that performs high interactions with PC71BM could serve as an interfacial sensitizer in polymer:small molecule:fullerene solar cells.

## CONCLUSION

In conclusion, all-small-molecule ternary solar cells based on DR3TBDTT:DR3TBDTT-E:PC71BM have been designed and fabricated. In these cells, the new small molecule DR3TBDTT-E exhibits low HOMO and LUMO levels induced by ester-anchored side chains. A high PCE of 10.26% is achieved by the optimal ternary solar cells. It is believed that the ternary solar cells are correspond to an alloy-like model without thermal and solvent vapor annealing. However, a cascade model is formed after annealing because DR3TBDTT-E shifts from the mixed region to D–A interfaces and serves as a sensitizer, which is beneficial to charge separation process. PCE is also improved in the polymer:small molecule:fullerene ternary solar cells, and this finding indicates a universality of the interfacial optimizing function of DR3TBDTT-E. This transformation from an alloy-like level to a cascade level may provide useful information to fabricate high-performance OSCs.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b13054.

Details for synthetic procedures, characterization of the materials, solar cells fabrication and measurement, fs-TAS measurements, DFT calculations, MD simulations, GIWAXS and TEM characterizations (PDF)

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### Notes

The authors declare no competing financial interest.

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