Facile Strategy for Reducing Cell-to-Module Efficiency Gap in Organic Solar Cells by Controlling the Preaggregation of Photoactive Solutions

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ABSTRACT: Organic solar cells (OSCS) have recently achieved efficiencies of >20% in single-junction unit cells owing to rapid advancements in materials and device technologies. Large-area OSCs face several challenges that adversely affect their efficiency compared to small unit cells. These challenges include increased resistance loads derived from their larger dimensions, as well as limitations related to morphology, miscibility, and crystallinity. In this study, a preaggregation control technique was employed to develop efficient OSC modules. This was achieved by incorporating a low-concentration D18 solution into a high-performance donor–acceptor combination of PM6 and L8-BO facilitating optimal chain entanglement. As a result, macroscopically clean films and microscopically phase-separated morphologies were obtained. For devices with a small area of 0.04 cm^2 , the device incorporating D18 exhibited a marginally higher power



conversion efficiency (PCE) of 17.82% compared to 17.32% for the device without D18. For devices with significantly larger areas of 4.725 and 30.24 cm², the PCEs increased significantly with the introduction of D18, rising from 14.85 to 15.31% and from 12.77 to 13.49%, respectively. In particular, the module with the largest area of 30.24 cm² demonstrated a significant decrease in load resistance, leading to a substantial reduction in the cell-to-module efficiency gap, which decreased from 26.3 to 24.3%.

KEYWORDS: organic solar cells, morphology, cell-to-module efficiency gap, preaggregation, chain entanglement, large-area module

1. INTRODUCTION

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Organic solar cells (OSCs) have attracted considerable attention as next-generation solar panels for eco-friendly and sustainable energy production.^{1,2} In recent years, advancements in materials and device technologies have significantly contributed to the increase in the power conversion efficiency (PCE) of OSCs. In particular, PCEs approaching 20% have been achieved in single-junction solar cells based on polymeric donors, such as PM6 and D18, and nonfullerene acceptors, such as L8-BO and BTP-eC9.³⁻⁸ The commercial potential of OSCs has been demonstrated through technological advancements that have significantly increased the efficiency of the unit cell. In this context, the development of large-area modules is dynamically underway. Various large-area coating techniques, such as slot-die coating, $^{9-13}$ blade-coating, $^{12,14-22}$ inkjet printing,²³ and spray coating,²⁴ are being investigated for their applicability in roll-to-roll processes from an industrial perspective. Moreover, the fabrication of large-area OSC modules on flexible substrates has been extensively investigated.

Min et al. introduced a small amount of $PM6_L$ (a low-molecular weight version of PM6) into the PM6:Y6 combination. This resulted in a uniform surface morphology

via a high-speed blade-coating process with a speed of 30 m min⁻¹. Consequently, they achieved a PCE of 14.70% in largearea modules with a smooth surface area of 7.5 cm², which were fabricated using high-speed coating technique.¹⁸ Li et al. synthesized BTO-BO by replacing the inner side chain of L8-BO with oligo (ethylene glycol) and subsequently fabricated large-area modules using the PM6:L8-BO:BTO-BO combination; they achieved optimal phase separation in the photoactive layer by employing toluene, a nonhalogenated solvent with a high boiling point, which effectively suppressed excessive aggregation. Consequently, certified PCEs of 19.12% and of 15.97% were achieved in the unit cell and in large-area modules (15.05 cm²), respectively.¹⁹ Yang et al. significantly reduced series resistance and improved performance by implementing ultranarrow interconnections of modules using

Received:September 12, 2024Revised:December 24, 2024Accepted:December 31, 2024Published:January 17, 2025



a nanosecond 355 nm ultraviolet (UV) laser process; they achieved a certified PCE of 15.43% with a geometric fill factor of 98% in large-area modules measuring 11.30 cm^{2.20}These technological advances pave the way for large-scale production and subsequent commercialization of OSCs. However, several factors contributing to the performance disparity between large-area modules and unit cells still remain.

First, the report by Kippelen et al. presents an analysis of resistance generation in large-area indium tin oxide (ITO) layer. This study indicates that power loss density increases with the area of the device, as the photogenerated current travels longer distances within the *x-y* plane of the active area (e.g., the ITO or cathode), resulting in an increase in series resistance. The power loss density ($P_{\rm ITO}$) for the ITO layer is expressed as follow:

$$P_{ITO} = \frac{1}{\alpha} J_{\max}^2 L^2 R_{sheet-ITO}$$
(1)

where $R_{sheet-ITO}$ is the sheet resistance of the ITO, measured in ohms per square (Ω/sq). *L* is the length of the solar cell, and α is determined by the number of interconnect contacts. As a result, numerous researchers have adopted a modular design with elongated stripe-shaped unit cells connected in series, as illustrated in Figure S7. Despite this approach, various types of resistance continue to result in large-area OSCs showing relatively lower PCE values compared to their small-area counterparts.²⁵ Therefore, it is critical to carefully consider cell-to-module (CTM) efficiency gap factors in the module designs. Specifically, optimizing the width of the cells and the spacing between them is essential for minimizing resistance and enhancing the overall module performance. Furthermore, it is imperative to minimize electrical losses, such as increased series resistance and inefficient electrical connections. To achieve these objectives, it is essential to implement efficient device designs that reduce cell-to-cell spacing, as well as highperformance materials that minimize energy losses at the cellto-module interface. By strategically addressing these factors, it will be aided to mitigate the CTM efficiency gaps. The CTM efficiency gap can be quantified using the following equation:

$$CTM \ Gap \ (\%) = \frac{PCE_{Cell} - PCE_{module}}{PCE_{Cell}} \times 100$$
(2)

This equation provides a framework for analyzing the efficiency gap between lab-scale cells and large-area modules, thereby guiding the development of optimized designs and scalable manufacturing processes.^{13,20,26,27}

Second, it is a significant challenge to reach a smooth photoactive layer with uniform thickness and morphology in large-area OSCs. Inadequate film formation in large-area modules can lead to significant leakage current at the interfaces, increased charge recombination, impeded charge extraction, and ultimately reduced efficiency.^{5,27,28}

Understanding these interdependencies provides valuable insights and practical guidelines for large-area manufacturing, as emphasized by Lin et al. In particular, the preaggregation effect plays a crucial role in facilitating controlled phase separation and precise molecular arrangement, both of which are essential for achieving high performance as the device area increases. A well-balanced preaggregation in the active solutions not only enhances charge generation and transport but also effectively suppresses nonradiative charge recombination losses. Importantly, the preaggregation effect exhibits a

temperature-dependent behavior, whereby the processing temperature significantly influences both the rates of preaggregation and crystallization. These factors, in turn, govern the evolution of the morphology and photo physics of the device during the film formation process, highlighting the preaggregation effect as a pivotal factor in achieving optimized performance.²⁹ Additionally, Ro et al. further highlighted the importance of controlling active layer morphology, emphasizing its critical role in the performance of large-area OSCs. They demonstrated that the morphology of large-area OPVs differs significantly from that of small-area devices. This difference arises primarily from challenges in maintaining uniform film thickness and optimized crystallinity in the process of upscaling.³⁰ Wei et al. observed that the presence of dissolved D18 in the solvent promotes the aggregation of L8-BO, resulting in the formation of a preaggregated structure. During the casting process, as the solvent evaporates, a progressively larger quantity of L8-BO aggregates onto the D18 nanofibers. These preaggregated nanostructures are then dispersed within the amorphous PM6 matrix, resulting in the formation of an interconnected network that enhances charge transport and minimizes recombination. The morphology of this active layer is highly conducive to efficient exciton dissociation and charge transfer, ultimately leading to an enhancement in the shortcircuit current density (J_{SC}) .³¹

A ternary blend strategy has been proposed to solve this issue. The ternary blend strategy enhances the absorption spectrum range of the photoactive layer, facilitating the absorption of a greater number of photons and thereby improving charge generation. Additionally, by combining two types of donor materials alongside one acceptor, or *vice versa*, this approach effectively regulates the miscibility and crystallinity of the components, leading to improved morphology in large-area films. This not only enhances energy level alignment and charge transfer efficiency but also significantly improves the overall performance of the device. Furthermore, the ternary blend strategy is expected to enhance the photostability and thermal stability of the devices by optimizing material interactions and reducing degradation under prolonged light exposure or thermal stress.^{18,32–39}

In this study, efficient OSC modules were developed by inducing the chain entanglement effect. D18 was introduced as a third component to facilitate chain entanglement and improve the morphology of the high-performance photoactive layer combination PM6:L8-BO. Chain entanglement is a phenomenon in which polymer chains become intertwined, resulting in the formation of complex networks that enhance efficient charge transport between PM6 and L8-BO. This enhanced transport leads to more effective exciton diffusion and separation, thereby improving the overall performance and stability of OSCs. Chain entanglement contributes to the uniformity of the active layer nanostructure, optimizes the molecular arrangement, and promotes efficient charge transfer.^{40,41} These results suggest that the effectiveness of this strategy increases with larger areas within the studied material system.

Specifically, we aimed to control chain entanglement via a preaggregation control (PAC) technique. This process involved the presolubilized D18, which has relatively poor solubility, to regulate the preaggregation of the photoactive materials. The PAC technique is based on the high-pressure method by Lu et al., which facilitates the complete dissolution of poorly soluble D18 at the elevated high-temperature (100



Figure 1. (a) Molecular structures of the donor and acceptor materials. Schematic diagrams illustrating the preparation procedures and deposition effects of the photoactive layer solutions based on the (b) PM6:L8-BO and (c) PM6:L8-BO + D18 (PAC technique) blends: optical microscopy images of each 4.725 cm² module device were obtained.

°C) within a sealed vial.⁴² We adapted this approach into the framework of a ternary blend strategy. Preaggregation is known to exhibit temperature-dependent characteristics, which significantly influence the crystallization of the photoactive layer, as reported by Lin et al.²⁹

Herein, we developed a PAC-based ternary blend strategy to enhance the efficiency and viability of OSCs. As shown in Figure S1, when the D18 solution is heated to high temperatures, it becomes a crimson color and low viscosity. Upon cooling to approximately room temperature, the solution transitions to a purple and becomes increased viscosity. Leveraging this temperature-dependent behavior, the PAC technique involves heating the D18 solution in a sealed vial to ensure complete dissolution. Once the solution reaches a lukewarm state (≈60 °C), PM6 and L8-BO are incorporated into the mixture. Upon further cooling to 45 °C, we believe that D18 aggregates may lead to significant chain entanglement with major components (PM6 and L8-BO) among the side chains. These thermal interactions and chain entanglements can facilitate the formation of a uniform layer during film processing, thereby making D18 particularly well-suited for the PAC technique, which will be discussed in further detail later.

The resulting thin film exhibited a more uniform morphology at both the macroscale and microscale compared to films without D18. The uniform morphology enhanced the charge-transport pathways and reduced the extent of charge recombination. The proposed PAC strategy resulted in an increased PCE, with the PCE rising from 17.32% for the control device to 17.82% for the PAC-based ternary device within the unit cell (for the 0.04 cm² device). Moreover, for devices with larger areas (4.725 cm² and 30.24 cm²) compared to the 0.04 cm² unit cell, the difference in PCEs between the control devices and the PAC-based ternary devices was substantial. The PCEs increased from 14.85% to 15.31% for the 4.725 cm² devices and from 12.77% to 13.49% for the 30.24 cm² devices. Consequently, the proposed strategy effectively minimized the CTM efficiency gap by achieving greater efficiency improvements in large-area modules compared to small-area unit cells.

2. RESULTS AND DISCUSSION

A ternary blend comprising PM6 and L8-BO with a small amount of D18 (Figure 1a) was used as the photoactive layer to develop efficient OSC modules. The optical and electrochemical characteristics of the photoactive layer materials used in this study are presented in the Supporting Information (Figure S2). Initially, we fabricated the devices by preparing ternary blend solutions based on typical methods as reported in the literature.^{4,6,7,35,43,44}

The optimized PCE of the ternary OSC devices based on the PM6:D18:L8-BO = 0.8:0.2:1.2 blend was found to be approximately 0.06% higher than that of the control device (Table S1). However, the efficiency and reproducibility of the typical ternary blend strategy were significantly low, as achieving consistent film uniformity and coverage proved challenging. This difficulty may be attributed to the low solubility and strong aggregation of D18. Hence, the typical ternary blend strategy was unsuitable for application in largearea modules. To address this issue, we developed a ternary blend strategy by preparing fully dissolved D18 solutions at various ratios. This approach is based on the aforementioned PAC technique. Based on this strategy, the devices were subsequently fabricated by coating the photoactive layer films at low temperatures using fully dissolved D18 solutions with PM6 and L8-BO. A schematic diagram of the proposed strategy is shown in Figures 1b and 1c.



Figure 2. (a) Device architecture of the conventional structure used in this study. (b) J-V characteristic and (c) EQE curves (absorbance spectra of blended films), and (d) dark current density-V curves of optimized binary and PAC-based ternary devices.

Table 1. Photovoltaic Parameters of Optimized Binary and PAC-based Ternary OSCs

active layer	$J_{\rm SC} [{\rm mA \ cm^{-2}}]$	$\int_{cal}^{a} [mA cm^{-2}]$	$V_{\rm OC}$ [V]	FF [%]	$PCE_{max} (PCE_{avg})^{b}$ [%]	$R_{ m series}$ [Ω]	$R_{\rm shunt} \left[\Omega\right]$
PM6:L8-BO	$25.21 \ (25.09 \pm 0.25)$	23.46	$0.871~(0.867~\pm~0.005)$	$78.95 (79.13 \pm 0.54)$	17.32 (17.21 \pm 0.10)	80.67	48986.48
PM6:L8-BO + D18	$25.88 \ (25.24 \pm 0.34)$	23.67	$0.868~(0.873~\pm~0.002)$	$79.36~(79.69~\pm~0.53)$	17.82 (17.57 \pm 0.12)	73.53	57829.41
^{<i>a</i>} J _{cal} values obtained	l from the EQE curves.	^b Average PC	E values calculated for	10 independent devic	ces.		

All experimental results related to device optimization are summarized in Table S1. Ternary OSC devices developed using the proposed PAC strategy were optimized at a ratio of the PM6:D18:L8-BO = 1.0:0.2:1.2 blend, resulting in 0.5% increase in efficiency compared with the control device. More importantly, the issues of uniformity and coverage in ternary blend films, which are commonly observed in conventional ternary blend devices, were fully resolved. These findings can be attributed to the formation of relatively uniform films that exhibit superior quality compared to the PM6:L8-BO-based control device. These results suggest that efficient large-area modules can be developed by controlling the preaggregation of photoactive layer materials through the pretreatment of D18 in solution.

All OSC devices were fabricated with a conventional structure: ITO glass/poly(3,4-ethlyenedioxythiophene): polystyrenesulfonate (PEDOT:PSS)/active layer/PDINN/Ag (Figure 2a). The current density–voltage (J-V) curves for the optimized control (PM6:L8-BO) and PAC-based ternary (PM6:L8-BO + D18) devices are presented in Figure 2b. The photovoltaic parameters are presented in Table 1. The control device exhibited a maximum PCE of 17.32%, with a J_{SC} of 25.21 mA cm⁻², an open-circuit voltage (V_{OC}) of 0.874 V, and a fill factor (FF) of 78.95%. In contrast, the PAC-based ternary device exhibited a slightly higher PCE of 17.82%, with a J_{SC} of 25.88 mA cm⁻², $V_{\rm OC}$ of 0.868 V, and FF of 79.36%. The observed increase in PCE is attributed to the enhancements in both $J_{\rm SC}$ and FF.

The external quantum efficiency (EQE) curves and absorbance spectra (Figure 2c) were examined to elucidate these results. Notably, the absorbance spectrum of the PAC-based ternary blend device showed stronger peaks in the range of 300–640 nm, which corresponds to the absorption region of pristine D18 (Figure S2).

The PAC-based ternary device exhibited an increased calculated photocurrent density (J_{cal}) compared to the binary blend-based control device, showing a trend similar to the improvement observed in the ternary blend.³⁶ The increase in J_{cal} can be attributed to the incorporation of D18, which improved light absorption in the range of 300–640 nm, thereby increasing the number of photons collected for charge generation. These results clarify the reasons for the improvement in J_{SC} of the ternary device.

Next, the J-V characteristics were measured under dark conditions. As shown in Figure 2d, the PAC-based ternary device exhibited a lower leakage current compared to the control device. Leakage currents can be caused by defects in the morphology of the active layer, such as pinholes or trapped charges. A high leakage current results in charge recombina-

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Figure 3. (a) $J_{ph}-V_{eff}$ (b) $J_{SC}-P_{light}$ and (c) $V_{OC}-P_{light}$ curves of optimized binary and PAC-based ternary OSCs: light intensities were controlled within the range of 110 to 10 mW/cm².



Figure 4. (a, d) Optical microscopy, (b, e) AFM, and (c, f) TEM images of optimized (a, b, c) PM6:L8-BO and (d, e, f) PM6:L8-BO + D18 blend films.

tion, which hinders efficient charge collection and thereby reduces the FF. 26,45

To gain a deeper understanding of the exciton and charge carrier dynamics underlying the improved performance of the PAC-based ternary device, we measured the photocurrent $(J_{\rm ph})$ against the effective applied voltage $(V_{\rm eff})$ of the corresponding devices. $J_{\rm ph}$ and $V_{\rm eff}$ are defined as follow:

$$J_{ph} = J_L - J_D, \ V_{eff} = V_0 - V \tag{3}$$

where current densities under illumination (J_L) and in darkness (J_D) . In addition, V_0 is the voltage at which $J_{\rm ph} = 0.46$ As shown in Figure 3a, the PAC-based ternary device exhibits a high $J_{\rm ph}$ and a rapid saturation current density $(J_{\rm sat})$ when $V_{\rm eff}$ exceeds 0.5 V, compared to the control device. From the derived $J_{\rm sat}$, we estimate the maximum exciton generation rate $(G_{\rm max})$ from the equation as follow:

$$J_{sat} = eG_{\max}L \tag{4}$$

where *e* is the electric charge and *L* is the thickness of the active layer.⁴⁷ The $G_{\rm max}$ value was obtained 1.619 × 10²⁸ m⁻³ s⁻¹ in PAC-based ternary device, indicating better exciton generation compared to the control device (1.609 × 10²⁸ m⁻³ s⁻¹). In addition, we calculated the values of the exciton dissociation probability ($P_{\rm diss}$) and charge collection efficiency ($P_{\rm coll}$) under short-circuit conditions.

$$P_{diss} = \frac{J_{ph}}{J_{sat}}, P_{coll} = \frac{J_{mp}}{J_{sat}}$$
(5)

where $J_{\rm mp}$ represents the current density at maximum power. The $P_{\rm diss}/P_{\rm coll}$ of the PAC-based ternary device (97.99%/ 94.52%) is relatively higher than the control device (96.16%/ 92.82%). This indicates more effective exciton dissociation and charge collection, as well as a reduction in germinate recombination. In this context, the superior $J_{\rm ph}-V_{\rm eff}$ characteristics of the PAC-based ternary device support its higher photovoltaic performance compared to the control device. This observation is consistent with the enhanced FF and $J_{\rm SC}$.⁴⁸⁻⁵⁰ The photovoltaic parameters related to $J_{\rm ph}-V_{\rm eff}$ characteristics are presented in Table S2.

Furthermore, electron-only and hole-only devices were fabricated for space-charge-limited current (SCLC) measurements, which were used to calculate the mobility of the charge carriers. As shown in Figure S3 and Table S3, the PAC-based ternary device exhibited an improvement in the balance between electron mobility ($\mu_{\rm e}$) and hole mobility ($\mu_{\rm h}$) compared to the control device.

In addition, the dependence of J_{SC} and V_{OC} on light intensity $(J_{SC}-P_{light} \text{ and } V_{OC}-P_{light})$ was investigated ranging from 110 to 10 mW cm⁻² to assess the recombination tendency in the devices (Figures 3b and 3c). The $J_{SC}-P_{light}$ relationship can be expressed as follows:

$$J_{SC} \propto \left(P_{light}\right)^{\mu} \tag{6}$$

An α value closer to 1 corresponds to more effective suppression of bimolecular combination in OSCs.⁵¹ The α value of the PAC-based ternary device (1.032) was smaller than that of the control device (1.034); this suggests that the bimolecular recombination was relatively inhibited in the PAC-based device.

Furthermore, the $V_{\rm OC}-P_{\rm light}$ relationship can be expressed as follows:

$$V_{OC} \propto n \left(\frac{k_{\rm B}T}{q} \right) \ln(P_{light})$$
 (7)

where k_B denotes the Boltzmann constant, T represents the temperature, and q represents the elementary charge. A slope of Equation 7 that approaches 1 corresponds to a lower probability of trap-assisted recombination, and thereby suggesting more effective inhibition of nonradiative recombination.^{4,52} The slope of the PAC-based ternary device (1.077 k_BT/q) was smaller than that of the control device (1.086 k_BT/q); thus, trap-assisted recombination was more effectively inhibited in the PAC-based device.

The morphology of the active layer significantly affects the OSC device performance with regard to the photovoltaic properties.³⁹ As mentioned earlier, the PAC-based ternary strategy improved the surface morphology compared to the binary blend. These aspects were further examined at the microscale and nanoscale using optical microscopy, atomic force microscopy (AFM), and transmission electron microscopy (TEM) (Figure 4). Figures 4a and 4d present optical microscopy images of the film surfaces, with dimensions of 673 μ m (width) and 505 μ m (height), magnified by a factor of 20. In large-area processes, the likelihood of defects that can significantly affect charge mobility increases, highlighting the need for advanced techniques to control these issues. Zhang et al. previously addressed the challenges associated with thickness and phase imbalances that can occur during the blade coating process through a reversible sequential layer-bylayer deposition technique. This approach involves sequential forward and reverse blade coating for the donor materials, followed by a single coating for the acceptor, ensuring uniform thickness and phase distribution. Their study demonstrated the effectiveness of this approach, achieving smoother surfaces and consistent film quality, indicating the critical role of precise deposition techniques in large-area applications.¹⁴

In this context, the differences in surface morphology between binary and ternary blend films are particularly noteworthy. As shown in Figure 4a, the binary blend film based on PM6:L8-BO displays a "spider web" pattern, indicating a relatively nonuniform thin film. This nonuniformity in the binary blend film can lead to localized thickness variations, which may result in inefficient charge transport and increased recombination, ultimately hindering device performance in large-area applications.

In contrast, the ternary blend film based on PM6:L8-BO + D18 (Figure 4d) exhibits a highly uniform and smooth surface morphology. The incorporation of D18 to the PM6:L8-BO blend improves miscibility and phase distribution, thereby suppressing the formation of defects, such as spider web patterns. This uniform surface morphology not only reduces charge recombination but also promotes more efficient charge transport across the active layer, which is essential for maintaining high performance in large-area OSCs. These findings underscore the importance of optimizing surface morphology in large-area devices. The distinct contrast between the spider web patterns in the binary blend film and the smooth surface of the ternary blend film highlights the advantages of adopting a ternary strategy to achieve uniform thin films and enhanced performance in large-area OSCs.

To further examine the morphology, AFM topographic images with a scale of 5 μ m × 5 μ m were obtained, as shown in Figures 4b and 4e. The microscale observations indicated that both films consisted of interpenetrating D-A networks, which facilitate efficient charge transport. The root-mean-square (RMS) roughness value of the binary blend film was measured at 1.151 nm, whereas the ternary blend film exhibited a lower RMS value of 1.025 nm. This indicates that, despite the incorporation of D18-which is characterized by poor solubility and strong aggregation-the PAC-based ternary blend film demonstrated significantly reduced roughness; this improves the interfacial contact and contributes to the inhibition of recombination.³⁸ When the AFM topographic images obtained at the 5- μ m scale were cropped to a 1- μ m scale, larger aggregates were observed in the ternary blend film compared to the binary blend film (Figure S4). This trend was also observed in the AFM phase images obtained at the 5- μ m scale, where phase separation in ternary blend films was more pronounced than in binary blend films (Figure S5). These observations suggest that the presence of relatively large aggregates and distinct phase separation in the nanoscale region, provided that there is sufficient distance for exciton generation and dissociation, may contribute to the enhancement of $J_{\rm SC}$.

Figures 4c and 4f present TEM images that illustrate the surface morphology of the binary and PAC-based ternary blend films, respectively, with 100 nm scale bars. A detailed comparison of these surface morphologies reveals significant differences between the two blend systems. In the binary blend film (Figure 4c), fibril-like aggregation is observed, characterized by elongated and interconnected structures. This morphology suggests strong phase separation between the donor and acceptor materials, which are typical in PM6:L8-BO systems.⁵⁴ While these fibrils indicate a certain degree of phase separation, they lack the uniformity necessary for optimal charge transport pathways across the active layer. In contrast, the PAC-based ternary blend film incorporating D18 (Figure 4f) displays coin- and/or fibril-like aggregation, characterized by well-dispersed and robust aggregates at the nanoscale. The incorporation of D18 appears to facilitate more pronounced phase separation between the donor and acceptor components,

resulting in a well-distributed film morphology. This improved dispersion of nanosized large aggregates enhances interfacial charge transport by providing well-defined pathways for charge carriers to move efficiently through the active layer.⁵⁵ These results can promote exciton dissociation and charge transport, thereby improving the J_{SC} and FF.⁵⁶ Such morphological improvements in the PAC-based ternary blend film can directly contribute to enhanced photovoltaic performance, including higher J_{SC} and EQE-calculated currents, reduced leakage current as indicated by dark current measurements, and enhanced suppression of recombination as demonstrated by light-dependent measurements. Comprehensively, we demonstrated that the incorporation of D18 through the PAC technique enhances the macroscopic film surface morphology, ensures efficient phase separation at the microscale by controlling the chain entanglement between PM6 and L8-BO, and consequently improves the performance of OSCs.

The contact angles of pristine PM6, D18, and L8-BO films for water and diiodomethane (DIM) were measured to assess the compatibility between the materials in the photoactive layer. The results are shown in Figure 5. The surface energies



Figure 5. Contact angle images of water and DIM on pristine PM6, D18, and L8-BO films.

(γ) of the PM6, D18, and L8-BO films, calculated using the Wu model,⁵⁷ were found to be 33.71, 33.91, and 49.52 mN m⁻¹, respectively. The difference in surface energies of PM6 and D18 was minimal with 0.2 mN m⁻¹, which indicates a high level of miscibility between the two substances.^{35,58} Furthermore, the Flory–Huggins interaction parameter (χ) was calculated based on the results of the surface energy measurements:

$$\chi_{AB} \propto \left(\sqrt{\gamma_A} - \sqrt{\gamma_B}\right)^2 \tag{8}$$

A smaller χ value corresponds to a higher level of compatibility between two substances.⁵⁹ The calculated χ values for PM6:L8-BO and D18:L8-BO were 1.513 and 1.466, respectively. These results suggest that the introduction of D18, which exhibits good compatibility with L8-BO, through the PAC technique leads to a relatively uniform surface morphology of ternary blend film. This is attributed to the high compatibility between the photoactive materials. The parameters related to the contact angle measurements are presented in Table S4.

The crystallinity and molecular arrangement characteristics of the photoactive layers fabricated with and without via the PAC technique were examined via two-dimensional grazing-incidence wide-angle X-ray scattering (2D-GIWAXS) measurements.⁶⁰ The 2D-GIWAXS patterns and 1D-line cut profiles of the optimized blend films (PM6:L8-BO and PM6:L8-BO +

D18) are shown in Figure 6. All line-cut data were collected from the out-of-plane (OOP) direction. The detailed results are presented in Table 2. To better understand the blend film results, the neat films of PM6, D18, and L8-BO, processed using the same method with fabricated devices, were systematically characterized, as shown in Figure S6 and Table S5. For donor polymers, the apparent face-on to edgeon orientation ratio (A_{xy}/A_z) results indicate that the PM6 film, with an A_{xy}/A_z value of 0.64, exhibited a predominantly edge-on orientation. In contrast, the D18 film, with an A_{xy}/A_z value of 4.87, demonstrated a predominantly face-on structure. The L8-BO film, utilized as an acceptor in the device, displays a preferred face-on orientation, characterized by an A_{yy}/A_{z} value of 1.66. Therefore, we can expect that the PM6 may provide balanced face-on and edge-on orientation when blended with L8-BO, compared to that of the D18, and the D18-incorporation suggests the enhanced intermolecular stacking the PM6:L8-BO system.^{37,61} As shown in Figures 6a and 6b, both blend films of PM6:L8-BO and PM6:L8-BO + D18 demonstrate pronounced $\pi - \pi$ stacking and lamellar stacking characteristics, which are advantageous for charge transport within the device. However, the binary and ternary films exhibit a notable difference in their diffraction *q*-vector values, as illustrated in Figure 6c. The PAC-based incorporation of D18 into the PM6:D18 blend phase simultaneously enhanced the lamellar packing structures in both the (100) and (200) planes of the ternary blend film, compared to those observed in the binary blend film. However, the (300) peak near 0.93 $Å^{-1}$ observed in the neat PM6 film has disappeared, which may be attributed to the hindrance caused by D18 that disrupts the close packing of PM6 molecules. Nevertheless, the spacing and the crystal coherence length (CCL) between (100) planes of the PM6:L8-BO + D18 blend film were found to be 21.25 and 62.87 Å, respectively, in contrast to 21.89 and 57.60 Å for the PM6:L8-BO blend film. In addition, in the ternary blend film, the $\pi - \pi$ (010) stacking distance $(d_{(010)})$ decreased to 3.69 Å, while the CCL (010) increased to 28.28 Å, in comparison to the binary blend film $(d_{(010)}$: 3.70 Å; CCL (010): 28.41 Å). More importantly, as illustrated in Figure 6d, A_{xy}/A_z value of the ternary blend film significantly increased to 1.40, compared to a value of 0.80 for the binary blend film. These findings can facilitate the charge transport in the ternary blend device, thereby contributing to the increased J_{SC} and FF observed in the corresponding OSCs.^{62,63}

As the next step, photostability tests were performed to evaluate the durability of small devices based on binary and PAC-based ternary OSCs. The results provide a comprehensive understanding of the impact of device structure and material properties on stability performance. As a result, PACbased ternary device demonstrated slightly enhanced stability compared to the control device. The PAC-based ternary device retained 80% of their initial PCE for 210 h under continuous AM 1.5G illumination (100 mW/cm^2), while the control device maintained this level for only approximately 129 h (Figure S8). This improved photostability can be attributed to the role of D18 in enhancing the morphological and structural stability of the active layer. The PAC technique promotes improved chain entanglement and molecular arrangement of the active materials, effectively reducing charge recombination and enhancing overall device durability. These findings underscore the potential of the PAC strategy to improve the operational lifetime of OSC devices under prolonged light exposure.



Figure 6. (a, b) 2D-GIWAXS patterns, (c) 1D-line-cut profiles (in the out-of-plane (OOP) and in-plane (IP) directions), and (d) azimuthal pole figures (extracted from the $0-180^{\circ}$ of the (100) lamellar diffraction) of the optimized blend films based on the PM6:L8-BO and PM6:L8-BO + D18 blends.

Table 2. 2D-GIWAXS Results of the Optimized Blend Films Based on the PM6:L8-BO and PM6:L8-BO + D18 Blends in the IP and OOP Directions

	$d_{(100)}{}^{a} \begin{bmatrix} \text{\AA} \\ \text{\AA}^{-1} \end{bmatrix}$ at (100)	$\stackrel{\text{fwhm (100)}^{b}}{[\text{\AA}^{-1}]}$	CCL (100) ^c [Å]	$d_{(010)}^{a} \begin{bmatrix} A \\ A^{-1} \end{bmatrix}$ at (010)	$\stackrel{\text{fwhm (010)}^{b}}{[\text{\AA}^{-1}]}$	CCL (010) ^c [Å]	$\begin{array}{c} A_{xy} / \\ A_z^{'d} \end{array}$
PM6:L8-BO	21.89 at 0.303	0.098	57.60	3.70 at 1.696	0.211	26.74	0.80
PM6:L8-BO + D18	21.25 at 0.309	0.090	62.87	3.69 at 1.702	0.200	28.28	1.40

 ${}^{a}q_{xy}$ (or q_{z}) = $2\pi/d_{(100)}$ (or $d_{(010)}$); ^bfwhm (Δq) is the full width at half-maximum of the corresponding peaks; ^cCCL (100 or 010) (Scherrer equation: CCL = $2\pi K/(\Delta q)$ where K is a shape factor, 0.9) is a crystal coherence length (CCL) of the corresponding crystallite; ^dRatio of face-on to edge-on orientation determined by the pole figure analysis, where A_{xy} and A_z correspond to the face-on and edge-on fractions (A_{xy} and A_z were extracted as average values from the (100) lamellar diffraction pattern within the 0–180° range), respectively.



Figure 7. PCE distribution for (a) 0.04 cm² unit cells, (b) 4.725 cm² small modules, and (c) 30.24 cm² large modules based on binary and PACbased ternary blends.

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active layer	area [cm ²]	I _{SC} [mA]	$J_{\rm SC} [{ m mA}~{ m cm}^{-2}]$	$V_{\rm OC}$ [V]	FF [%]	$\frac{\text{PCE}_{\text{max}}}{(\text{PCE}_{\text{avg}})^{\alpha}}[\%]$	P_{max} [mW]	$R_{ m series}$ [Ω]	$R_{\rm shunt} \left[\Omega \right]$	CTM gaj [%]
PM6:L8-BO	4.725	36.89	$7.807 \\ (7.623 \pm 0.124)$	$2.630 \\ (2.632 \pm 0.024)$	$72.31 \\ (71.93 \pm 0.29)$	14.85 (14.43 ± 0.26)	70.41	11.24	3437.80	14.3
	30.24	77.51	$2.638 \\ (2.625 \pm 0.029)$	$7.094 \\ (7.037 \pm 0.069)$	$\begin{array}{c} 68.22 \\ (68.21 \pm 0.37) \end{array}$	$\begin{array}{c} 12.77 \\ (12.52 \pm 0.232 \end{array}$	367.1	15.38	3105.23	26.3
PM6:L8-BO + D18	4.725	37.71	$7.946 \\ (7.937 \pm 0.032)$	$2.659 \\ (2.668 \pm 0.007)$	$72.47 \\ (72.23 \pm 0.17)$	$\begin{array}{c} 15.31 \\ (15.29 \pm 0.07) \end{array}$	72.34	11.33	4640.31	13.3
	30.24	82.76	2.737	7.137	69.08	13.49	408.0	13.98	4571.07	24.3

Table 3. Photovoltaic Parameters of Optimized Binary and PAC-based Ternary OSC Modules with Different Photoactive Areas

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^{*a*}Average PCE values were calculated for 4 independent devices with an area of 4.725 cm² and 3 independent devices with an area of 30.24 cm², respectively.

 (67.33 ± 1.24)

 (13.32 ± 0.21)

 (7.108 ± 0.041)

To investigate whether the PAC-induced performance enhancement observed in small-area unit cells could be replicated in module devices comprising large-area cells connected in series, we fabricated module devices with active areas of 4.725 and 30.24 cm². The photovoltaic results of all OSC devices are presented in Figure 7, Table 3, and Figure S9. Figure 7 and Figure S9 depict the distribution of the device performance characterization counts for both control and PAC-based ternary devices, each fabricated in three different areas: 10 devices with an area of 0.04 cm², 4 devices with an area of 4.725 cm², and 3 devices with an area of 30.24 cm². The corresponding values are presented in relation to the cell-tomodule size. A comparison of the 4.725 cm² module devices indicated that the PM6:L8-BO blend achieved a PCE of 14.85%, with a $J_{\rm SC}$ of 7.807 mA cm⁻², a $V_{\rm OC}$ of 2.630 V, and a FF of 72.31%. In contrast, the PM6:L8-BO + D18 blend achieved an enhanced PCE of 15.31%, with a J_{SC} of 7.946 mA cm^{-2} , a V_{OC} of 2.659 V, and a FF of 72.47%. The improvements in all parameters of the PAC-based ternary module device were observed, similar to the performance enhancement trends observed for the 0.04 cm² unit cell (Table 1). In particular, the CTM efficiency gap between the control OSCs to PAC-based ternary OSCs, when comparing the 0.04 cm² unit cells to the 4.725 cm² module devices, decreased from 14.3% to 13.3%. The incorporation of D18 through the PAC technique led to a significant performance improvement in the module device with a larger photoactive area of 4.725 cm², compared to the unit cell with a smaller photoactive area of 0.04 cm^2 .

 (2.784 ± 0.037)

The module device with a photoactive area of 30.24 cm^2 based on the PM6:L8-BO blend achieved a $J_{\rm SC}$ of 2.638 mA cm^{-2} , a V_{OC} of 7.094 V, a FF of 68.22%, and an overall PCE of 12.77%. In contrast, the module device with a photoactive area of 30.24 cm² based on the PM6:L8-BO + D18 blend achieved an enhanced PCE of 13.49%, with a J_{SC} of 2.737 mA cm⁻², a $V_{\rm OC}$ of 7.137 V, and a FF of 69.08%. The introduction of D18 into the PM6:L8-BO blend using the PAC technique effectively reduced the CTM efficiency gap, when comparing the 0.04 cm^2 unit cells to the 30.24 cm^2 module devices, decreasing the gap from 26.3% to 24.3%. This case study highlights the potential of the PAC technique to mitigate CTM efficiency losses in large-area devices. Figure 8 shows photographs of large module devices with an area of 30.24 cm². The improvement in the morphology of the PAC-based ternary module device is clearly observable with the naked eye, compared to the control module device. On the other hand, all parameters of the PAC-based ternary module device, despite its significantly larger size with an area of 30.24 cm^2 , exhibited



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Figure 8. Photographs of 30.24 cm^2 module devices based on the (a) PM6:L8-BO and (b) PM6:L8-BO + D18 blend films.

substantial improvement compared to the 0.04 cm^2 unit cell device (Table 1). This result contributed to a reduction in the CTM efficiency gap for large-area modules.

The measured series (R_{series}) and shunt resistances (R_{shunt}) of all module devices are presented in Table 3. The results indicate a trend of increased R_{shunt} values in the PAC-based ternary module devices, as confirmed by the smooth surface morphology observed through AFM measurements.^{26,27,64} These results are consistent with the decrease in leakage current, as confirmed by the dark J-V curve, and align well with the R_{shunt} of the 0.04 cm² cell presented in Table 1. As a result, the incorporation of D18 through the PAC technique is essential for accelerating the industrialization of large-area modules by improving their morphology and reducing resistance load. We emphasize that the performance distribution of 0.04 cm² unit cells, 4.725 cm² small modules, and 30.24 cm² large modules is depicted in Figure 7 and Figure S9.

To verify the universality of the PAC technique, we fabricated OSCs using various active layers, such as PM6:Y6, PM6:BO-4Cl, and PM6:BTP-eC9 combinations with D18 as the PAC agent. As shown in Table S6, the PM6:BO-4Cl, and PM6:BTP-eC9 blends exhibited improved PCEs, when D18 PAC agents were introduced, which can be ascribed to enhanced J_{SC} and V_{OC} . This enhancement agreed well with the results from PM6:L8-BO + D18-based OSCs. However, PM6:Y6-based OSCs showed rather lower performance when D18 was added. This may be attributed to the different chainchain interaction effects between the side chains of the polymers and NFAs. The side chains of D18 are expected to entangle with other side chains of NFAs during the preaggregation process. While D18, L8-BO, BO-4Cl, and BTP-eC9 all have 2-butyloctyl chains in their molecular structures, Y6 features shorter 2-ethylhexyl chains. This difference in alkyl chain lengths of NFAs may contribute to

their varying performances. As a result, Y6-based OSCs showed lower performance despite the increase in J_{SC} when D18 was added. Consequently, in BO-4Cl, and BTP-eC9-based systems, the trends in the performance improvements are consistent with those observed in the PM6:L8-BO system, indicating that the PAC technique may serve as a universal method across various NFAs-based systems.

To further investigate the universality of PAC technique, PM6:L8-BO-based OSCs were fabricated with D18, D18-Cl, and PM7 as the PAC agent, respectively. As shown in Table S7, the PAC effect of the PM6:L8-BO + PM7-based device was the lowest with a PCE of 17.37% when compared to those of PM6:L8-BO + D18 (PCE = 17.82%) and PM6:L8-BO + D18-Cl (PCE = 17.52%)-based devices. This finding may be attributed to the influence of the relatively shorter side chains of the PM7 backbone in comparison to those of D18 and D18-Cl, as discussed above.⁶⁵ Among the PAC agents, a significant enhancement in J_{SC} were observed upon the introduction of D18-Cl, which can be attributed to its suitable energy levels and molecular packing behavior.⁶⁶ Among the three PAC agents, D18 exhibited relatively high aggregation properties and crystallinity, which contributed to the highest FF compared to the other PAC agents, leading to the most significant performance improvement. Consequently, D18 was identified as the most suitable PAC agent among three polymer donors.

3. CONCLUSIONS

This study focused on analyzing how improvements in active layer morphology enhance the performance of OSCs. The PAC technique, which combines PM6 and L8-BO with a small amount of D18, was used to mitigate the low solubility and strong aggregation tendencies of D18. The technique effectively addressed the issues of uniformity and coverage of the films, and the effects of the PAC technique were comprehensively examined. The results suggested that the incorporation of D18 could strengthen chain the entanglement between PM6 and L8-BO, leading to the formation of a more uniform and smooth surface structure. As a result, the charge mobility was improved, and recombination was effectively suppressed. GIWAXS measurements confirmed that the incorporation of D18 enhanced the crystallinity and molecular arrangement characteristics of the PM6:L8-BO combination: The D18 introduction reinforced the face-on orientation, which is favorable for charge transport, and increased the crystallinity in the (100) and (010) planes, significantly improving the charge transfer properties. The improvement in molecular stacking resulted in an increase in the J_{SC} . In conclusion, the OSCs of the PM6:L8-BO + D18 blend, achieved through the PAC technique, demonstrated superior performance compared to the PM6:L8-BO blend, particularly in terms of charge mobility, efficiency, and CTM efficiency loss. The incorporation of D18 resulted in both macroscopic and microscopic improvements in morphology, which played a crucial role in enhancing the performance of large-area organic solar modules. These findings are expected to contribute to the commercialization of large-area OSC modules and are anticipated to be applicable to mass production through continuous printing processes in the future.

4. EXPERIMENTAL SECTION

Unit Cell Device Fabrication (Control Devices). The unit cell devices had a conventional ITO/PEDOT:PSS/active layer/PDINN/

Ag structure. ITO glasses were cleaned by ultrasonication in Alconox solution, isopropyl alcohol, and deionized water in a sequence for 15 min each. The substrates were heat-treated on a hot plate at 100 °C to remove residual moisture, followed by UV-ozone treatment (Ahtech LTS AH 1700) for 15 min. PEDOT:PSS (Heraeus, AI4083) was filtered through 0.45 μ m PTFE filter, spin-coated at 4000 rpm for 30 s onto ITO substrates, and annealed at 110 °C for 10 min. For the photoactive blend, the PM6:L8-BO was dissolved in CF:DIO (99.75:0.25, volume ratio) with a total concentration of 14.3 mg/ mL. The weight ratio of donor to acceptor was 1:1.2 (w/w). (Figure 1b). All prepared solutions were preheated to a moderate temperature of 45 °C and stirred for 10 min at 250 rpm using a magnetic bar. The active blend solution was then spin-coated onto PEDOT:PSS surface to form 100 nm of photoactive layer. One mg/mL PDINN in methanol was coated onto the photoactive layer via spin coating at 3000 rpm for 30 s. Additional heat treatment was not conducted. Finally, a 100 nm-thick layer of Ag was deposited under a high vacuum (at 10^{-7} Torr).

Unit Cell Device Fabrication (PAC Devices). PAC active solution was prepared by completely dissolving D18 at a concentration of 1.3 mg/mL in a CF:DIO (99.75:0.25, volume ratio) solution. The solution was then added to a vial containing PM6 and L8-BO for blending. To ensure proper mixing, the blend solution was heated to 60 °C and stirred with a magnetic bar at 250 rpm for 4 h. Just before spin coating, the solution temperature was reduced to 45 °C and preheated at 250 rpm for 10 min (Figure 1c). All other processes are the same as control devices.

Module-Device Fabrication. The fabrication process of the module devices was largely similar to that of the unit cells. As shown in Figure S7, P1 was custom-made to be included in the ITO glass that was fabricated according to a predesigned layout (AMG). After cleaning, the PEDOT:PSS, active layer, and electron-transport layer PDINN were fabricated via a procedure identical to that described above. P2 was patterned using a cotton bar. Finally, a 100 nm-thick Ag layer was deposited using a premade mask under a high vacuum (under 10^{-7} Torr).

ASSOCIATED CONTENT

③ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.4c15679.

1. Materials Description of the materials used, including PM6, PM7, D18, D18-Cl, Y6, BO-4Cl, L8-BO, BTPeC9, solvents, and substrates. 2. Instruments and Characterizations Detailed descriptions of the instruments and methods used for characterization: Optical microscopy, AFM, TEM, GIWAXS, UV-Vis spectroscopy, cyclic voltammetry, and contact angle measurements. 3. Space Charge-Limited Current (SCLC) Measurements Explanation of SCLC measurements for charge carrier mobility in electron-only and holeonly devices. 4. Figures and Tables Figure S1: D18 solution images in heated and cooled states. Figure S2: CV curves, UV-Vis spectra, and energy levels of PM6, D18, and L8-BO. Table S1: Photovoltaic parameters for different blend ratios. Table S2: Photovoltaic parameters calculated from the J_{ph} - V_{eff} . Figure S3: Electron and hole mobilities. Table S3: Charge carrier mobility results. Figures S4: AFM topography images of blended films Figures S5: AFM phase images of blended films. Table S4: Contact angle measurements for PM6, D18, and L8-BO. Figure S6: 2D-GIWAXS patterns and 1D line-cut profiles. Table S5: 2D-GIWAXS results. Figure S7: OSC module details (ITO-patterned substrates and aperture masks). Figure S8: Stability test curves (photostability for PCE, V_{OC} , J_{SC} , FF). Figure S9:

Distribution of photovoltaic parameters (J_{SC} , V_{OC} , FF, PCE) for unit cells and modules. **Table S6**: Photovoltaic parameters for universality tests with various NFAs. **Table S7**: Photovoltaic parameters for universality tests with polymer donors (DOCX)

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Author Contributions

Y. C. K. for drafting the manuscript, conducting the experiments, performing measurements and analyses, and contributing to the discussions. S. J. J. supported the original draft and reviewed/edited the draft paper. S. J. J. measured/ analyzed the 2D-GIWAX. N. G. Y. conducted universality tests and reviewed/edited the draft paper. J. Y. K. contributed to the universality tests/exciton dissociation and charge collection measurements and dark current characteristic analysis. Y. W. H. designed the module devices. D. K. M. reviewed and edited the manuscript, and also planned and led the entire project.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This paper was written as part of Konkuk University's research support program for its faculty on sabbatical leave in 2022. This work also was supported in part by Human Resources Development Program of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant funded by the Ministry of Trade, Industry and Energy, Republic of Korea (No. RS-2023-00237035), and the Commercializations Promotion Agency for R&D Outcomes (COMPA) grant funded by the Korea government (MSIT) (No. RS-2023-00304788).

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