Tuning Morphology of Active Layer by using a Wide Bandgap Oligomer-Like Donor Enables Organic Solar Cells with Over 18% Efficiency

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A wide bandgap oligomer-like donor CNS-6-8 is synthesized and incorporated into the host PM6:Y6:PC₇₁BM system to tune the morphology of the active layer for better device performance. Due to the good miscibility of CNS-6-8 with both host donor (PM6) and acceptors (Y6 and PC₇₁BM), an optimized morphology is achieved with the appropriate phase separation size and enhanced crystallinity, which ultimately leads to more efficient exciton dissociation, charge transport, and lower nonradiative energy loss. As a result, the quaternary device achieves an improved efficiency of 18.07%, with a simultaneously increased open circuit voltage of 0.868 V, fill factor of 78.8%, and the comparable short-circuit current density of 26.43 mA cm⁻². This work indicates that the favorable 3D interpenetrating network morphology of Y6 containing blend films can be optimized by introducing small amount of a specific molecule with high crystallinity, thus providing an effective strategy to achieve better photovoltaic performance for state-of-the-art Y6 analogsbased organic solar cells.

1. Introduction

Organic solar cells (OSCs) are considered as a promising solar energy technology due to the advantages of light weight, flexibility, solution printing preparation, etc.^[1] Presently, it has been a long journey for OSCs from the initial power conversion efficiency (PCE) of 1% to the present level of above 18%,^[2] in which chemists have played a great role by creating new and

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better organic active layer materials, such as those star materials of P3HT (2005 by Kim et al.),^[2c] DR3TBDTT (2013 by Chen et al.),^[2e] ITIC (2015 by Zhan et al.),^[2f] PM6 (2015 by Hou et al.),^[2g] Y6 (2019 by Zou et al.),^[2h] D18 (2018 by Ding et al.).^[2i] Especially in 2019, the rapidly developing OSCs stepped into a new era of PCE exceeding 15% due to the emergence of a super-star acceptor Y6.^[2g] As we all known that two determining factors for PCE of OSCs are the active layer materials and its morphology. Therefore, there have been main two approaches for higher performance, one is to get better molecules, and the latter one is to achieve better morphology. While we are always exploring more efficient active layer materials, the journey has been long and challenging. Therefore, it would be much easier to tune the morphology for better performance

using some existing materials to achieve their best intrinsic performance. Up to now, tremendous efforts in tuning morphology have been made in the **Y6** analogs-based OSCs, such as more suitable coating solvent,^[3] solvent^[4] or low boiling point solid additives,^[5] post treatments of thermal or solvent annealing,^[6] rendering the PCE over 18%.^[7] In spite of the impressive PCE achieved, the continuously increasing performance of **Y6** analogs-based OSCs indicates that the intrinsic best performance might not have been achieved.

The above strategies of morphology regulation, such as more suitable coating solvent, solvent or low boiling point solid additives, post treatments of thermal or solvent annealing, can adapt a favorable morphology upon the quick solvent volatile process or post-treatment process by controlling the crystallization and phase separation process. In addition, a multicomponent strategy, which introduces a guest component into the host systems in OSCs, has been proved as an effective way to further improve the device performance recently.^[7a,8] The application of a multicomponent strategy can break the limits of light absorption of the existing host systems, optimize the morphology and energy level alignment for the active layer, and thus improve the efficiency of OSC devices. Thus, a feasible multicomponent strategy based on a state-of-the-art system is expected to guide superior device performances. In the past decade, the numerous oligomer-like donors-based organic

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photovoltaic (OPV) has stimulated great attention owing to its well-defined structures, easier purification, and less batch to batch variation, compared with the polymer-based OPVs.^[9] Given that the oligomer-like donors are generally advanced in terms of high crystallinity, compatibility with host materials, suitable energy levels, and complementary absorptions, which might play a crucial role to further optimize the 3D interpenetrating network packing morphology and hence approach intrinsic best PCEs of **Y6** analogs-based OSCs if applied as a guest donor properly.

In this work, a new wide bandgap oligomer-like donor CNS-6-8 was designed, synthesized, and incorporated into the state-of-the-art $PM6:Y6:PC_{71}BM$ ternary system^[10] to optimize its active layer morphology with the aim of further improving device performance. Here, multiple factors have been taken into consideration for the rational design. First, CNS-6-8 has the down-shifted highest occupied molecular orbital (HOMO) energy level compared with that of PM6 due to the introduction of highly strong electron-withdrawing cyan (CN) groups. It is conductive to build a tiered energy level alignment in the quaternary blends, to construct cascading charge hopping channels that suppress the current loss by fine-tuning the charge separation and allow manipulation of multiple charge transfer energies to guarantee a high $V_{\rm oc}$.^[8b] Second, CNS-6-8 features a planar conjugated backbone with good crystallinity, which should have the strong π - π packing with both PM6 and Y6, hence be compatible with the host PM6:Y6:PC71BM blends. The combination of above favorable factors affords an optimized morphology with better crystallinity and more suitable domain size, leading to an excellent PCE of 18.07% for the PM6:CNS-6-8:Y6:PC71BM quaternary OSC, better than that of 17.00% for the PM6:Y6:PC71BM ternary OSC. Our success in active layer morphology optimization for achieving its intrinsic performance, by simply introducing small amount of oligomer-like donor with high crystallinity, provides a feasible strategy to approach the intrinsic best performance of Y6 analogs-based OSCs before better active layer materials emerge.

2. Results and Discussions

2.1. Material Synthesis and Characterization

The synthetic route to **CNS-6-8** is displayed in Scheme S1 in the Supporting Information and the detailed synthetic processes are described in the Supporting Information. Generally, **CNS-6-8** was successfully synthesized within four steps and with good yields. First, compound 1 featuring one cyan group was afforded by treating 3-bromo-2-((2-ethylhexyl)thio)thiophene with CuCN in a good yield of $\approx 85\%$. Thereafter, a carbonyl addition reaction of benzo[1,2-*b*:4,5-*b*]dithiophene-4,8-dione with compound 1 in the presence of *n*-butyllithium was implemented and followed by a reduction reaction using SnCl₂ to yield compound **2** in one pot. Then compound **2** further underwent a lithium-hydrogen exchange with lithium diisopropylamide at a cryogenic temperature and then transformed into its derived distannane, which was subsequently cross-coupled with 5"-bromo-3',3"-dihexyl-[2,2':5',2"-terthiophene]-5-carbaldehyde

via the Stille-coupling reaction to generate compound **3** in a good yield. Eventually, the target **CNS-6-8** was afforded through a reaction of Knoevenagel condensation with 3-octyl-2-thiox-othiazolidin-4-one. The molecular structures of key intermediates and target molecules were confirmed by ¹H NMR, ¹³C NMR, and high-resolution mass spectrometry, and the corresponding spectra are presented in the Supporting Information (Figure S10–S17).

2.2. Optical and Electrochemical Properties

The chemical structures of the two donors PM6, CNS-6-8, and the two acceptors Y6, PC₇₁BM are present in Figure 1a. Figure 1b shows the UV-vis absorption spectra of their pristine films. CNS-6-8 has a light absorption in the range of 400-650 nm and thus is well complemented with Y6 (600-950 nm), while overlapping with the absorption of the host donor, PM6. It is known that the well alignment of energy levels between donors and acceptors should facilitate the efficient energy/ charge transfer at D/A interface and thus enhance device performance.^[8b] Hence, electrochemical cyclic voltammetry is performed to measure the energy levels of the donors and acceptors (Figure S1, Supporting Information). As indicated in Figure 1c, a cascade energy alignment is formed between the HOMO and the lowest unoccupied molecular orbital energy levels of these active layer components. The cascade energy level is beneficial to reduce charge transfer barrier as well as facilitate charge transport and collection for better device performance.^[8b]

2.3. Photovoltaic Performances

To investigate the effect of CNS-6-8 as a donor guest on device photovoltaic performance, both the ternary and quaternary OPV devices were fabricated with the conventional structure of ITO (indium tin oxide)/PEDOT:PSS (poly(3,4-ethyl enedioxythiophene):polystyrene sulfonate)/active layer/perylene diimide functionalized with amino N-oxide/Ag. For the PM6:Y6:PC71BM ternary blend film, a mixing ratio of 1:1.1:0.2 (D1:A1:A2) was found to be optimal, while a mixing ratio of 0.8:0.2:1.1:0.2 (D1:D2:A1:A2) yielded optimum performance for the PM6:CNS-6-8:Y6:PC71BM guaternary blend film. The corresponding current density versus voltage (J-V) characteristics and photovoltaic performance parameters under simulated AM 1.5 G illumination at 100 mW cm⁻² are presented in Figure 2a and Table 1, respectively. The optimal PM6:Y6:PC71BM ternary OSC exhibits an open-circuit voltage (V_{oc}) of 0.849 V, a I_{sc} of 26.37 mA cm⁻², and an FF of 76.0%, yielding a PCE of 17.00%, in line with the previous report.^[10] After a series of optimization with different CNS-6-8 ratios (Table S1, Supporting Information), when introducing 20% CNS-6-8 (in donors w/w) into the host PM6:Y6:PC71BM blend film, the resulting quaternary OSC affords an excellent PCE of 18.07%, accompanied with a comparable J_{sc} of 26.43 mA cm⁻², but significantly enhanced V_{oc} of 0.868 V and FF of 78.8%, which is one of the best efficiencies for the quaternary OSCs reported to date.^[8b,11] Figure 2b displays the external quantum efficiency (EQE) spectra of the optimized

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Figure 1. a) Chemical structures; b) normalized absorption; and c) energy levels of PM6, Y6, PC₇BM, and CNS-6-8 pristine films (as cast).

devices and the calculated integrated Jsc values agree well with the current densities from J-V curves (within a 2% deviation range), as listed in Table 1. Note that the smaller extinction coefficients of CNS-6-8 in both solution (5.67 \times 10³ L g⁻¹ m⁻¹) and solid film $(6.11 \times 10^4 \text{ cm}^{-1})$ can be observed comparing to those of 6.16×10^3 L g⁻¹ m⁻¹ and 7.56×10^4 cm⁻¹ for **PM6** (Figure S2, Supporting Information), which should result in inferior light harvest of PM6:CNS-6-8:Y6:PC71BM blend film (Figure 2c). However, the obtained comparable J_{sc} for both systems indicate that there are similar but optimal charge dynamics for the OSCs with CNS-6-8. The improved V_{oc} and FF should be attributed to multiple factors, such as improved morphology of blend film and reduced energy losses (E_{loss}) of OSC, which will be discussed below in detail. Figure 2d shows the distribution of PCEs for both the systems with 15 devices, confirming the reliability of this high photovoltaic performance. The distributions of the V_{oc} , J_{sc} , and FF are shown in Figure S3 in the Supporting Information.

2.4. Morphology Investigation

In order to better determine the difference of device performance caused by introduction of CNS-6-8, atomic force microscopy (AFM) was carried out to characterize the surface topographies, while transmission electron microscopy (TEM) was applied to investigate internal morphologies of the ternary and quaternary blends.^[12] As depicted in Figure 3, a fibrillar network morphology was observed in both the blend films, which is favorable for efficient charge transport in the blend films.^[13] Furthermore, the AFM images of PM6, Y6 pristine films, PM6:CNS-6-8 (0.8:0.2) and CNS-6-8:Y6 (0.2:1.1) blend films were measured to investigate the impact of the incorporation of CNS-6-8 on PM6 and Y6 domains morphology (Figure S4, Supporting Information). Height and phase images of PM6 with or without CNS-6-8 exhibited negligible variations, while the morphology of Y6 with and without CNS-6-8 demonstrates significant difference. This result indicates that www.advancedsciencenews.com



Figure 2. a) J-V characteristics for optimized OSCs; b) EQE spectra (solid lines) and integrated current densities (dashed lines) for optimized OSCs; c) absorption of **PM6:Y6:PC₇₁BM** and **PM6:CNS-6-8:Y6:PC₇₁BM** blend films under the optimized condition of thermal annealing (TA) at 90 °C for 10 min; d) PCE distribution for optimized OSCs (AM 1.5 G, 100 mW cm⁻²).

CNS-6-8 has more profound influence on the **Y6** domains in quaternary blends, which is also reflected in the TEM images. As shown in Figure 3c, the ternary blends are intimately mixed, resulting in smaller domains, which may limit the extension of the perfect 3D interpenetrating network of **Y6**-based blend films and thus suffer from higher geminate recombination and reduced charge photogeneration yields.^[14] However, after introducing **CNS-6-8** into the ternary blends, the quaternary blends with **CNS-6-8** exhibit an enlarged domain size, resulting the optimized phase separation morphology (Figure 3f). This may enable better exciton dissociation and charge transport, affording an improved FF and comparable J_{sc} .

Furthermore, the 2D grazing incidence wide angle X-ray scattering (2D GIWAXS) measurement was carried out to investigate the effect of **CNS-6-8** on molecular packing orientation and crystallinity.^[15] The 2D GIWAXS patterns and corresponding scattering profiles of **PM6**, **Y6** and **CNS-6-8** pristine films in the out-of-plane (OOP, q_z) and in-plane (IP, q_{xy}) directions are shown in Figures S5 and S6 in the Supporting Information, respectively. The detailed parameters of corresponding 2D GIWAXS are summarized in Table S2 in the Sup-

porting Information. Clearly, PM6 and Y6 exhibit preferential face-on orientation and strong π - π stacking diffraction peak with $q_z = 1.63$ Å⁻¹ and $q_z = 1.72$ Å⁻¹, respectively. The **CNS-6-8** pristine film exhibits noticeable edge-on orientation and multiple (100) diffraction peaks, demonstrating much better crystallinity comparing with PM6 and Y6. As shown in Figure 4, both PM6:Y6:PC71BM (1:1.1:0.2) and PM6:CNS-6-8:Y6:PC71BM (0.8:0.2:1.1:0.2) blend films exhibited preferential face-on orientation on the substrate. As summarized in Table 2, in the OOP direction, the (010) diffraction peaks of PM6:CNS-6-8:Y6:PC71BM (0.8:0.2:1.1:0.2) blend slightly shifted to a higher q region (1.72 Å⁻¹) compared to that of 1.71 Å⁻¹ for **PM6:Y6:PC₇₁BM** blend film, indicating a smaller π - π stacking distance (d, 3.65 Å) than that of the ternary blends (3.67 Å), but same π - π stacking distance with Y6 pristine film (3.65 Å). This result should indicate that the acceptor morphology of quaternary blends is closer to that of Y6 pristine due to the incorporation of CNS-6-8. The crystal coherence lengths (CCL) were calculated by full-width at half-maxima (FWHM) according to the Scherrer equation (Table 2). The CCL of PM6:CNS-6-8:Y6:PC71BM (21.41 Å) is larger than that

Table 1. Summary of photovoltaic parameters of the optimized OSCs under the illumination of AM 1.5G (100 mW cm⁻²).

Active layer ^{a)}	V _{oc} [V]	FF [%]	$J_{\rm sc}$ [mA cm ⁻²]	J ^{cal} [mA cm ^{−2}]	PCE [%]
PM6:Y6:PC ₇₁ BM (1:1.1:0.2)	$0.849~(0.847\pm 0.002)$	76.0 (75.6 \pm 0.5)	26.37 (26.23 ± 0.12)	25.92	17.00 (16.83 \pm 0.16)
PM6:CNS-6-8:Y6:PC ₇₁ BM (0.8:0.2:1.1:0.2)	$0.868~(0.867\pm0.001)$	78.8 (77.8 \pm 0.4)	26.43 (26.36 \pm 0.14)	26.12	18.07 (17.80 ± 0.11)

^{a)}The average parameters included in the brackets were calculated from 15 devices.



C) PM6:Y6:PC₇₁BM а) _{РМ6:Y6:PC₇₁BM} b) PM6:Y6:PC71BM 2.5 nm 5.000 -2.5 nm -5.000 200 nm RMS=0.694 nm Height Sensor 400.0 nm Phase 400.0 nm d) PM6:CNS-6-8:Y6:PC₇₁BM e) PM6:CNS-6-8:Y6:PC₇₁BM f) PM6:CNS-6-8: 2.5 nm 5.000 -2.5 nm -5.000 00 nm RMS=0.729 nm Height Sensor 400.0 nm Phase 400.0 nm

Figure 3. a,d) AFM height images, b,e) AFM phase images, and c,f) TEM images of PM6:Y6:PC7BM and PM6:CNS-6-8:Y6:PC7BM (TA: 90 °C for 10 min).



Figure 4. 2D GIWAXS patterns of a) PM6:Y6:PC₇₁BM (1:1.1:0.2) and b) PM6:CNS-6-8:Y6:PC₇₁BM (0.8:0.2:1.1:0.2) blend films under the optimal conditions (TA: 90 °C for 10 mins); c) scattering profiles of the corresponding films.

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Table 2. The detailed	parameters of	corresponding	2D GIWAXS
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	(010) diffraction peak				(100) diffraction peak			
_	Q [Å ⁻¹]	D [Å]	FWHM [Å ⁻¹]	CCL [Å]	Q [Å ⁻¹]	D [Å]	FWHM [Å ⁻¹]	CCL [Å]
PM6:Y6:PC ₇₁ BM	1.71	3.67	0.293	19.29	0.29	21.66	0.061	92.70
PM6:CNS-6-8:Y6:PC ₇₁ BM	1.72	3.65	0.264	21.41	0.30	20.94	0.060	94.24

of **PM6:Y6:PC**₇₁**BM** (19.29 Å). Thus, the reduced π – π stacking distance and increased CCL with 20% **CNS-6-8** incorporation should indicate that a more ideal acceptor phase morphologies with higher crystallinity is achieved. The above changes for the morphology based on both different systems conform to the device performance trend, therefore showing that the quaternary OSCs with the optimal morphology exhibited the improved FF and comparable $J_{\rm sc}$. In addition, a space-charge-limited current method was used to evaluate electron transport in the blend films, as shown in Figure S7 and Table S3 in the Supporting Information. **PM6:CNS-6-8:Y6:PC**₇₁**BM** (0.8:0.2:1.1:0.2) exhibits higher electron mobility (2.07 × 10⁻³ cm² V⁻¹ s⁻¹) than that of the ternary counterpart (1.57 × 10⁻³ cm² V⁻¹ s⁻¹), which is in good accordance with the GIWAXS results above.

The difference in surface energy (γ) has been reported to be one of the driving forces for the phase-separation in blend films.^[16] Results of the aforementioned morphology characteristics aroused our interest to further investigate the difference in surface energy of PM6, CNS-6-8, PC₇₁BM, Y6 pure films and Y6:PC₇₁BM(1.1:0.2) blend film. The surface tension value ($\gamma_{sv} = \gamma_s^d + \gamma_s^p$) can be estimated from the contact angle (θ) according to the Owens–Wendt–Kaelble's model^[17]

$$\gamma_{\rm LV} \left(1 + \cos\theta\right) = 2 \left(\sqrt{\gamma_{\rm S}^{\rm p} \gamma_{\rm L}^{\rm p}} + \sqrt{\gamma_{\rm S}^{\rm d} \gamma_{\rm L}^{\rm d}}\right) \tag{1.1}$$

where $\gamma_{\rm LV}$ is the surface tension of the liquid in equilibrium with its vapor and $\gamma_{\rm SV}$ is that of the solid. The measured contact angle data are listed in Figure S8 in the Supporting Information. The degree of molecular miscibility can be evaluated by Flory–Huggins interaction parameter χ , calculated by formula^[18]

$$\chi_{A:B} = K \left(\sqrt{\gamma_A} - \sqrt{\gamma_B} \right)^2 \tag{1.2}$$

The location of compound in ternary or quaternary blends was predicted by calculating the wetting coefficient (ω) following the Young's equation and Neumann's equation^[19]

$$\omega_{\rm C} = (\gamma_{\rm C:B} - \gamma_{\rm C:A}) / \gamma_{\rm A:B} \tag{1.3}$$

where $\gamma_{A:B}$ represents the interfacial surface energy between two components of A and B (If the wetting coefficient is larger than unity, namely, $\omega_{\rm C} > 1$, the material C should be located in the domain A. If $\omega_{\rm C} < -1$, C should be distributed in the domain B. If $-1 < \omega_{\rm C} < 1$, C should be located at the interface between A and B). The interfacial surface energy can be calculated by Neumann's equation as follow^[18,19]

$$\gamma_{A:B} = \gamma_A + \gamma_B - 2e^{\left[-\beta(\gamma_A - \gamma_B)\right]} \sqrt{\gamma_A \gamma_B}$$
(1.4)

where $\beta = 0.000115 \text{ m}^4 \text{ mJ}^{-2}$.

As listed in Table S4 in the Supporting Information, the reckoned $\gamma_{PM6:Y6}$ is 0.86, while the $\gamma_{PC_{71}BM:Y6}$, $\gamma_{PC_{71}BM:PM6}$ are only 0.38 and 0.11, respectively. The wetting coefficient $\omega_{PC_{2}BM}$ was calculated to be 0.314. Thus, PC71BM should be located at the interface between PM6 and Y6 in the PM6:Y6:PC71BM ternary blend film. In the PM6:CNS-6-8:Y6:PC71BM quaternary blend film, we studied the two acceptors of Y6 and PC₇₁BM as a whole (Table 3). The reckoned χ between PM6 and Y6:PC₇₁BM(1.1:0.2) blend film is 0.74, while the χ between PM6 and CNS-6-8, Y6:PC71BM(1.1:0.2) and CNS-6-8 is only 0.22 and 0.15, respectively, suggesting that both CNS-6-8:PM6 and CNS-6-8:Blend A (the acceptors of Y6 and PC71BM were studied as a whole Y6:PC₇₁BM(1.1:0.2), which is considered as **Blend** A) show better miscibility, compared to the miscibility between PM6 and Blend A. Thus, CNS-6-8 should be prone to locate at the interface between donor (PM6) and acceptors (Y6 and PC₇₁BM) in the quaternary system, which will reduce the miscibility of donor and acceptor and increase their individual domain sizes. The wetting coefficient of $\omega_{\text{CNS-6-8}}$ was calculated to be -0.157 when we studied the two acceptors of Y6 and PC71BM as a whole in the PM6:CNS-6-8:Y6:PC71BM quaternary blend film, demonstrating CNS-6-8 should be located at the interface between PM6 and Y6:PC71BM(1.1:0.2) blend film in the PM6:CNS-6-8:Y6:PC71BM quaternary system. Based on the above results, the introduction of CNS-6-8 with

Table 3. The detailed parameters about surface energies of PM6, CNS-6-8 pure films, and Y6:PC₇₁BM(1.1:0.2) blend film under the condition of thermal annealing at 90 °C for 10 min.

	γ ^d [mN m ^{−1}]	γ^{p}_{S} [mN m ⁻¹]	γ _{SV} [mN m ⁻¹]	<i>Х</i> РМ6: А ^{а)} [К]	<i>Х</i> РС ₇₁ ВМ:В [К]	γ _{PM6: A} ^{b)} [mJ m ⁻²]	γ _{PC₇₁BM:B} [mJ m ⁻²]
PM6	0.48	17.70	18.18	-	0.22	-	0.24
Y6:PC71BM (Blend A)	0.37	25.86	26.23	0.74	0.15	0.70	0.13
CNS-6-8	0.55	21.87	22.42	-	_	-	-

^{a)} $\chi_{PM6:A}$ represents the Flory–Huggins interaction parameter between compound PM6 and compound A (or blend A); ^{b)} $\gamma_{PM6:A}$ represents the interfacial surface energy between compound PM6 and compound A (or blend A). Using the interfacial surface energy (γ) values, we can estimate the relative the wetting coefficient (ω) following the Young's equation and Neumann's equation: $\omega_{C} = (\gamma_{C:B} - \gamma_{C:A})/\gamma_{A:B}$, $\omega_{CNS-6-8} = (\gamma_{CNS-6-8} = (-\gamma_{CNS-6:B-M6})/\gamma_{PM6:blend} = -0.157$.

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high crystallization should be conducive to the ordered accumulation of acceptors, especially for the host acceptor of Y6, enhancing the crystallinity of acceptor phase, and further improving the phase separation morphology between the PM6 and Y6. This is consistent with the above AFM, TEM, and GIWAXS data analyses.

2.5. Charge Dynamics

In order to study the effects of **CNS-6-8** incorporation on charge generation and extraction kinetics in detail, we first measured the exciton dissociation probabilities P(E, T) of both ternary and quaternary devices following the procedure in previous literature.^[20] The photocurrent density (J_{ph}) versus effective voltage (V_{eff}) curves are shown in **Figure 5**a. Under the short-circuit condition, the calculated P(E, T) values were 97.80% and 98.17% for ternary and quaternary devices, respectively, indicating the similar but slightly improved exciton dissociation due to the optimized morphology of **PM6:CNS-6-8:Y6:PC**₇₁**BM** blend film.

Bimolecular recombination can be a serious problem for bulk heterojunction devices due to the intimate mixing of p-type and n-type semiconductors. In order to analyze charge carrier losses due to bimolecular recombination, intensity (P_{light}) dependent photocurrent (J_{sc}) measurements have been performed (Figure 5b).^[20] Note that the intensity-dependent measurements were conducted under white light from the solar simulator, thus probing the rate for bimolecular recombination within the full spectrum. The relationship between J_{sc} and P_{light} can be described as power-law dependence equation of $J_{\rm sc}$ versus $P_{\rm light}^{\alpha}$, where α is close to unity, suggesting the minimal bimolecular recombination. The PM6:Y6:PC71BM ternary device showed an α value of 0.987 while CNS-6-8-based quaternary device showed that of 0.988, implying negligible bimolecular recombination in both devices. The degree of trap-assisted in devices can be determined by the slope of $V_{\rm oc}$ versus ln P_{light} (Figure 5c).^[21] Basically, a slope close to kT/qindicates devices are dominated by bimolecular recombination and close to 2 kT/q suggests trap-assisted recombination is the dominating mechanism (where k is the Boltzmann's constant, T is the absolute temperature, and q is the elementary charge). The slopes of PM6:Y6:PC71BM device and CNS-6-8-based quaternary device are 1.24 and 1.20 kT/q, respectively. This is consistent with the better crystallinity of PM6:CNS-6-8:Y6:PC₇₁BM, which may reduce the corresponding spatial disorder and trap states concentration, thus suppresses trapassisted recombination.

Complementing our analyses of charge transport process, we adopted the transient photovoltage (TPV) and transient photocurrent (TPC) measurements to obtain the carrier lifetime and charge extraction time.^[22] The carrier lifetime (τ) under open-circuit condition (Figure 5d) was derived from the TPV decay dynamics under dark condition by employing a mono-exponential fitting. The fitting of the TPV signal follows the equation: $y = A * e^{(-\chi/\tau_c)}$, and the carrier lifetime of 39.5 and 64.8 µs were obtained for the ternary and quaternary devices, respectively. It should be noted that the incorporation of **CNS-6-8** leads to a longer carrier lifetime as compared to the control **PM6:Y6:PC**₇₁**BM** device, implying the suppressed charge recombination in the quaternary device. Figure 5e shows the charge extraction rate at short-circuit condition



Figure 5. a) The $J_{ph}-V_{eff}$ curves; dependences of b) J_{sc} on P_{light} and c) V_{oc} on P_{light} ; d) transient photovoltage and e) transient photocurrent measurements for optimized OSCs.



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Figure 6. Optical bandgap determination of a) PM6:Y6:PC₇BM blend film and b) PM6:CNS-6-8:Y6:PC₇BM on the basis of the derivatives of the sensitive EQE spectra (*d*EQE/*dE*, black curves) for optimized OSCs; c) the corresponding EQE_{EL} spectra for optimized OSCs.

measured by TPC measurements. The extraction time of the corresponding devices is $\tau_c = 1.10 \ \mu s$ for PM6:Y6:PC₇₁BM and $\tau_c = 0.39 \ \mu s$ for PM6:CNS-6-8:Y6:PC₇₁BM, respectively. The shorter charge extraction time suggests that carriers are extracted more efficiently in the quaternary devices than the control device.

2.6. Energy Loss Analysis

To investigate the impact of **CNS-6-8** on quaternary device E_{loss} . The detailed E_{loss} of the ternary and quaternary OSCs were investigated. The total E_{loss} can be divided into three parts by applying the detailed balance theory, as follows^[23]

$$E_{\text{loss}} = E_{\text{g}}^{\text{PV}} - qV_{\text{oc}} = \left(E_{\text{g}}^{\text{PV}} - qV_{\text{oc}}^{\text{SQ}}\right) + \left(qV_{\text{oc}}^{\text{SQ}} - qV_{\text{oc}}^{\text{rad}}\right) \\ + \left(qV_{\text{oc}}^{\text{rad}} - qV_{\text{oc}}\right) = \Delta E_{1} + \Delta E_{2} + \Delta E_{3}$$
(1.5)

where the E_g^{PV} of all the blend films have been estimated via the derivatives of the sensitive EQE (EQE_{PV}) spectra (P(E) = dEQE/dE)^[23,24]

$$E_{\rm g}^{\rm PV} = \frac{\int\limits_{a}^{b} E_{\rm g} P(E_{\rm g}) dE_{\rm g}}{\int\limits_{a}^{b} P(E_{\rm g}) dE_{\rm g}}$$
(1.6)

where the integration limits *a* and *b* are chosen as the energy where $P(E_g)$ is equal to 50% of its maximum, $P(a) = P(b) = \max P(E_g)/2$ as exemplarily depicted in **Figure 6**a,b. The quaternary blend film exhibits same E_g^{PV} in comparison to that of **PM6:Y6:PC₇₁BM** ternary blend film in the optimized quaternary OSCs (**Table 4**). In Equation (1.5), the first term $\Delta E_1 = E_g - q V_{oc}^{SQ}$ represents the unavoidable radiative loss originating from absorption above the bandgap. The V_{oc}^{SQ} is the maximum voltage based on the Shockley–Queisser (SQ) limit^[24]

$$V_{\rm oc}^{\rm SQ} = \frac{kT}{q} \ln\left(\frac{J_{\rm sc}^{\rm SQ}}{J_{\rm 0}^{\rm SQ}} + 1\right) \cong \frac{kT}{q} \ln\left(\frac{q \cdot \int_{E_g}^{+\infty} \phi_{\rm AM1.5G}(E) \, dE}{q \cdot \int_{E_g}^{+\infty} \phi_{\rm BB}(E) \, dE}\right)$$
(1.7)

The second-term $\Delta E_2 = qV_{oc}^{SQ} - qV_{oc}^{rad}$ can be regarded as radiative loss caused by absorption below the bandgap, where

the $V_{\rm oc}^{\rm rad}$ is the open circuit voltage when there is only radiative recombination. The radiative recombination limit for the saturation current ($J_0^{\rm rad}$) is also calculated from the EQE spectrum using the detailed balance theory^[23,25]

$$V_{\rm oc}^{\rm rad} = \frac{kT}{q} \ln\left(\frac{J_{\rm sc}}{J_0^{\rm rad}} + 1\right) \cong \frac{kT}{q} \ln\left(\frac{q \cdot \int_0^{+\infty} EQE(E)\phi_{\rm AM1.5G}(E) dE}{q \cdot \int_0^{+\infty} EQE(E)\phi_{\rm BB}(E) dE}\right) (1.8)$$

where *q* is the elementary charge and ϕ_{BB} is the black body spectrum at 300 K. The calculated values of V_{or}^{rad} are listed in Table 4, and ^{a)} ΔE_3 calculated from $V_{\rm oc}^{\rm rad}$ (^{a)} $\Delta E_3 = qV_{\rm oc}^{\rm rad} - qV_{\rm oc}$). The ^b ΔE_3 is also confirmed by directly measuring the external quantum efficiency of electroluminescence (EQE_{FI}) of the solar cell through the equation of ${}^{b)}\Delta E_3 = -kT \ln (EQE_{FL})$ (Figure 6c).^[26] Moreover, the ΔE_3 values calculated from two different methods show similar variation tendency for the ternary and quaternary OSCs. As summarized in Table 4. It is apparent that the incorporation of **CNS-6-8** has little impact on ΔE_1 and ΔE_2 values in the two optimized devices. Thus, the differences in Eloss between the PM6:Y6:PC71BM-based ternary and optimized quaternary OSCs mainly should originate from the changes in ΔE_3 . As plotted in Figure 6c, a higher EQE_{FL} of 1.08×10^{-4} than that of **PM6:Y6:PC**₇₁**BM** (7.27×10^{-5}) host system was yielded by the quaternary device, which leads to a lower ${}^{b}\Delta E_{3}$ of 0.230 eV. Finally, the total energy loss can be obtained, which are 0.562 and 0.543 eV in PM6:Y6:PC71BM and PM6:CNS-6-8:Y6:PC71BM quaternary devices, respectively. The optimal quaternary device afforded a reduced $V_{\rm loss}$, and therefore gives rise to the higher $V_{\rm oc}$ (0.868 V) of the corresponding device. It is noticeable that the great enhancement of Voc in CNS-6-8-based quaternary device compared to the PM6:Y6:PC71BM ternary system mainly originates from the reduced nonradiative energy losses.

As discussed in recent studies,^[27] the nonradiative recombination is correlated to the energetic disorder of blend films, which is closely involved with the Urbach tail states below the band edge.^[28] The exponential part along the absorption coefficient curve and near the optical band edge is regarded as the Urbach tail. This exponential tail generally exits in some poor crystalline, disordered, and amorphous materials because of the localized states which extended in the band gap. The Urbach empirical rule can be described as the spectral dependence of the absorption coefficient (α) and photon energy (*E*) in the low photon energy range, which follows the below equation^[28b]

 Table 4. The detailed parameters of energy losses for optimized OSCs.

Active layer	E ^{PV} [eV]	V_oc ^{SQ [V]}	$\Delta E_1 [\text{eV}]$	V_{oc}^{rad} [V]	$\Delta E_2 [{\rm eV}]$	$\Delta E_3^{a)}$ [eV]	$\Delta E_3^{\rm b)}$ [eV]	V _{oc} [V]	E _{loss} [eV]
PM6:Y6:PC71BM	1.411	1.147	0.264	1.089	0.058	0.240	0.245	0.849	0.562
PM6:CNS-6-	1.411	1.147	0.264	1.087	0.060	0.219	0.230	0.868	0.543
8:Y6:PC ₇₁ BM									

 $^{a)}\Delta E_{3}$ is calculated from V_{oc}^{ad} through the equation of $^{a)}\Delta E_{3} = qV_{oc}^{ad} - qV_{oc}^{*,b}\Delta E_{3}$ is calculated from the EQE_{EL} through the equation of $^{b)}\Delta E_{3} = -kT$ in (EQE_{EL}).

$$\alpha(E) = \alpha_0 \exp\left(\frac{E - E_g}{E_U}\right) \tag{1.9}$$

where $E_{\rm g}$ represents the energy at the peak of the exponential part and $E_{\rm U}$ is the energy of the band tail, namely, Urbach energy, which is often interpreted as an indicator of the degree of disorder for low crystalline materials. Generally, a smaller Urbach energy indicates a smaller degree of energy disorder and nonradiative energy loss in OSCs.^[27b] Finally, the Urbach energy ($E_{\rm U}$) can be calculated from the slope of the straight line by plotting ln (α) against the incident photon energy (E), which follows the straight line equation below

$$\ln\alpha(E) = \ln\alpha_0 + \frac{E}{E_U} - \frac{E_g}{E_U}$$
(1.10)

To assess the degree of energetic disorder in the photon active layers, we performed the Fourier transform photocurrent spectroscopy-external quantum efficiency (FTPS-EQE) to quantificationally evaluate the Urbach energy. According to the exponential fitting of the sub-band-gap FTPS-EQE spectra (Figure S9, Supporting Information), the PM6:CNS-6-8:Y6:PC₇₁BM blend exhibits relatively lower energy disorder with an E_U of 23.44 meV compared to that of 24.39 meV for PM6:Y6:PC₇₁BM blend, indicating that PM6:CNS-6-8:Y6:PC₇₁BM film exhibits a reduced energy disorder with respect to its counterpart. This should be beneficial for a lower nonradiative recombination loss, which confirms the energy loss analysis above.

In summary, the incorporation of **CNS-6-8** into **PM6:Y6:PC₇₁BM** blends formed a better morphology with good crystallinity and appropriate domain size, which affords the more efficient exciton dissociation, charge transport and extraction, thus reducing the energy losses and improving device performance with respect to that of **PM6:Y6:PC₇₁BM** blend.

3. Conclusion

To summarize, a high crystallinity and wide bandgap oligomerlike donor, **CNS-6-8** was synthesized and incorporated into the state-of-the-art system of **PM6:Y6:PC₇₁BM** to tune its active layer morphology. The optimal quaternary device possessed an enhanced V_{oc} of 0.868 V and FF of 78.8%, and a comparable J_{sc} of 26.43 mA cm⁻², eventually reaching an impressive PCE of 18.07%. Through the contact angle measurements and the calculation of wetting coefficient, **CNS-6-8** was presumed to preferably locate at the interface of host donor (**PM6**) and acceptors (**Y6** and **PC**₇₁**BM**). This could enhance the phase separation between donors and acceptors, affording a better morphology with good crystallinity and suitable domain size, thus enhancing charge transport, suppressing recombination, and further improving the device photovoltaic performance. Our success by incorporating highly ordered oligomer-like donor guest to construct highly efficient multicomponent systems demonstrates that would be an effective and feasible strategy. Thus, much higher efficiency of OSCs might be further achieved if applying the more suitable oligomer-like donors with complementary light absorption and stronger extinction coefficient into the current host system or those with high efficiencies.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

W.F. and S.W. contributed equally to this work. Y.C. and Z.Y. conceived and directed the study. W.F. fabricated and characterized the photovoltaic devices. S.W. and H.C. synthesized the **CNS-6-8**. The manuscript was mainly prepared by Y.C., W.F., Z.Y. and all authors participated in the manuscript preparation and commented on the manuscript.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

active layer morphology, miscibility, multicomponent strategy, oligomerlike donors, organic solar cells

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