# Rational Design of Two Well-Compatible Dimeric Acceptors Through Regulating Chalcogen-Substituted Conjugated Backbone Enable Ternary Organic Solar Cells with 19.4% Efficiency

Wanying Feng, Yuyang Bai, Jia Wang, Yanyi Zhong, Jiaying Wang, Tianqi Chen, Jiangbin Zhang, Kai Han, Xiangjian Wan, Bin Kan,\* and Yongsheng Chen\*

To enhance the performance of dimeric acceptors (DMAs) based organic solar cells (OSCs), two new DMAs, designated as DC9-HD and DYSe-3, are rationally developed and employed to fabricate ternary OSCs. The substitution of the sulfur atom on the outer ring of the fused-ring core of DC9-HD with a selenium atom resultes in the red-shifted DYSe-3. Despite these minor differences, DC9-HD and DYSe-3 possess nearly identical conjugated skeletons, which contribute to their similar packing motifs and crystallinities, ultimately enabling a high degree of miscibility between two DMAs. Upon incorporating DYSe-3 into the host PM6:DC9-HD binary blend, fibril-like morphologies featured with diameters of  $\approx$ 16.9 nm and reduced charge recombination are observed in the PM6:DC9-HD:DYSe-3 ternary blend. More importantly, owing to their long exciton diffusion lengths and low voltage losses, a remarkable power conversion efficiency of 19.4% is achieved for the ternary OSCs, alongside a delicate balance between open-circuit voltage and short-circuit current density. This super result is comparable to the best performance of oligomer acceptor based OSCs reported to date. Furthermore, the proposed ternary strategy, which combines one polymer donor and two well-compatible DMAs, not only retains the advantages of DMAs but also offers a streamlined approach for fabricating high-performance ternary OSCs.

# 1. Introduction

Organic solar cells (OSCs) have garnered significant attention due to their considerable potential for lightweight and largearea device fabrication on flexible substrates utilizing roll-to-roll techniques. This capability opens a wide range of applications in wearable electronics and the Internet of Things.<sup>[1]</sup> Over the past decade, advancements in photovoltaic materials and device engineering,<sup>[2]</sup> particularly the introduction of Y series non-fullerene small-molecular acceptors (SMAs),<sup>[3]</sup> have led to dramatic improvements in the power conversion efficiencies (PCEs) of single-junction OSCs, surpassing 20% to date.<sup>[4]</sup> Furthermore, with mini-module devices achieving PCEs exceeding 17%,<sup>[5]</sup> it is quite exciting to witness the practical application of OSCs in integrated self-power flexible devices. However, due to the undesired open circuit voltage ( $V_{\rm OC}$ ) loss of OSCs, the

W. Feng, Y. Bai, J. Wang, J. Wang, T. Chen, B. Kan School of Materials Science and Engineering National Institute for Advanced Materials Nankai University Tianjin 300350, China E-mail: kanbin04@nankai.edu.cn W. Feng, X. Wan, Y. Chen State Key Laboratory and Institute of Elemento-Organic Chemistry Frontiers Science Center for New Organic Matter The Centre of Nanoscale Science and Technology and Key Laboratory of Functional Polymer Materials Renewable Energy Conversion and Storage Center (RECAST) College of Chemistry Nankai University Tianjin 300071, China E-mail: yschen99@nankai.edu.cn

Y. Zhong, J. Zhang, K. Han College of Advanced Interdisciplinary Studies National University of Defense Technology Changsha 410073, China J. Zhang, K. Han Nanhu Laser Laboratory National University of Defense Technology Changsha 410073, China

D The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/aenm.202404062

#### DOI: 10.1002/aenm.202404062

ADVANCED SCIENCE NEWS \_\_\_\_\_ www.advancedsciencenews.com

current best PCE value remains significantly below the ideal PCEs predicted by the thermodynamic Shockley–Queisser limit theory.<sup>[6]</sup> Consequently, it is imperative to explore novel materials and improve device engineering to further improve the PCEs of OSCs, particularly innovations in material design.<sup>[7]</sup> Additionally, ensuring the long-term stability of OSCs is a vital prerequisite for promoting their future applications.<sup>[1a]</sup>

Based on the superior Y series acceptors, Zou et al. first proposed combining two Y6 monomers into one "quasi-polymer" molecule, which exhibits well-defined chemical structures and excellent film-forming properties, showing great promise in fabricating roll-coated large-area OSCs with low voltage loss and high morphology stability.<sup>[8]</sup> Subsequently, He et al. reported a series of directly linked dimeric acceptors (DMAs), which exhibited higher PCEs and better device stability compared to both small-molecular and polymeric acceptors.<sup>[9]</sup> Following this, a series of oligomerized small molecule acceptors (OSMAs), composed of two or more repeating SMA wings, has been rapidly developed, achieving PCEs surpassing 19%.<sup>[10]</sup> Generally, these state-of-the-art OSMAs combine the advantages of both SMAs and polymerized SMAs, including well-defined molecular structure and batch reproducibility, low organization energy, and low diffusion coefficient.<sup>[11]</sup> Their appealing characteristics position them as important candidates for realizing high-performance and stable OSCs. However, the PCE of the OSMA-based OSCs remains lower than that of traditional SMA-based OSCs, highlighting the urgent need to enhance the potential of OSMAs and improve their device performance through careful material and device optimizations.

To further enhance the performance of dimeric acceptor-based OSCs, the ternary strategy, which is widely used in SMA-based OSCs, could be directly employed. <sup>[12]</sup> For instance, Huang et al. incorporated a SMA (Y6) as the third component in the D18:DYF-TF dimeric binary system, resulting in an increase in PCE from 18.26% for a binary device to 18.73% for the ternary device.<sup>[13]</sup> Besides, Sun et al. introduced a small portion of a trimeric acceptor to the PM6:L8-BO-X binary blend, achieving efficiencies approaching 20% for the ternary devices.<sup>[14]</sup> Despite these advancements, the fabrication of ternary devices that combine one electron donor with two OSMAs could fully leverage their potential, including benefits such as red-shifted absorption, reduced  $V_{OC}$  loss, and improved device stability. However, this simplified strategy for enhancing the performance of OSMA-based OSCs has been less investigated to date.

In this study, we presented a new dimeric acceptor DC9-HD, which is derived from reported material DC9 by shortening the alkyl chains on pyrrole units from 2-octyldodecyl to 2-hexyldecyl.<sup>[15]</sup> When paired with the wide bandgap polymer donor PM6, the DC9-HD based binary OSCs achieved a promising PCE of 18.7%, along with a high fill factor (*FF*) of ≈80%. Meanwhile, based on the multi-selenophene substituted dimeric acceptor DYSe-1, we replaced the undecyl side chains on the outer ring of DYSe-1 with the nonyl side-chains, resulting in a red-shifted dimeric acceptor designated as DYSe-3.<sup>[16]</sup> As a result, the PM6:DYSe-3 binary OSCs achieved a super  $J_{SC}$  of 27.5 mA cm<sup>-2</sup>. Notably, DYSe-3 possesses a similar conjugated skeleton and demonstrates well compatibility with DC9-HD. We subsequently fabricated a ternary OSC using DYSe-3 as the third component. On the one hand, it is essential for the third component to exhibit good compatibility when blended with the host binary blend to optimize the morphology and enhancing the charge transport properties. On the other hand, a third component with red-shifted near-infrared absorption is necessary to broaden light absorption and increase the  $J_{\rm SC}$ .<sup>[17]</sup> Consequently, the ternary device achieved a maximum PCE of 19.4% with a ratio of 1:1:0.2 of PM6:DC9-HD:DYSe-3. According to charge dynamics analysis and characterization of the morphology, improved morphological features and optimized charge dynamics were observed in the corresponding PM6:DC9-HD:DYSe-3 ternary blend, ultimately resulting in a highly efficient OSCs based on DMAs. Our work advances the development of DMA-based OSCs and provides a straightforward pathway to fabricate high-performance ternary devices by utilizing two well-compatible DMAs.

# 2. Results and Discussion

#### 2.1. Materials and Properties

The chemical structures of DC9-HD and DYSe-3 are illustrated in Figure 1a, while the detailed synthetic routes are presented in Scheme S1 in the Supporting Information. DC9-HD and DYSe-3 exhibit nearly identical conjugated skeletons, with two A-D-A monomers linked by a thiophene unit at the terminal group. In contrast to the 3-nonylthieno[3,2-b]thiophene fragment present in DC9-HD, the compound 6-nonylselenopheno[3,2b]thiophene, which incorporates a selenium atom, was utilized to construct DYSe-3. The multi-selenophene strategy is expected to enhance the inter-molecular charge transfer (ICT) process in DYSe-3, thereby enabling its red-shifted features.<sup>[18]</sup> Density functional theory (DFT) calculations were performed to assess the molecular conformations of DC9-HD and DYSe-3. As depicted in Figure 1a, both molecules exhibit spiral-like molecular structures, and the dihedral angles between two independent monomer wings are 22.9° for DC9-HD and 27.1° for DYSe-3, respectively. Herein, different molecular stacking motifs and interactions might exist in these two dimers, which will affect the active layer morphology.

The UV-Vis-NIR absorption spectra of DC9-HD and DYSe-3 are presented in Figure 1b. The maximum absorption peak  $(l_{max})$ of DC9-HD and DYSe-3 in dilute chloroform solution is located at 746 and 764 nm, which are shifted to 812 and 842 nm in their neat films, respectively (Table S1, Supporting Information). In comparison to DC9-HD, DYSe-3 exhibits a red-shifted absorption spectrum, which can broaden the light-harvesting window and enhance the  $I_{sc}$  in photovoltaic devices. The energy levels of both molecules were assessed by cyclic voltammetry (CV), as illustrated in Figure S1 (Supporting Information), with the relevant data summarized in Table S1 (Supporting Information). As shown in Figure 1c, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels are -5.63 and -3.67 eV for DC9-HD, and -5.66 and -3.82 eV for DYSe-3, respectively. Besides, under the same measure conditions, the HOMO and LUMO energy levels of PM6 are determined to be -5.53 and -3.55 eV, respectively. The well-aligned energy levels between donor and acceptor might facilitate charge transport in solar cell devices.<sup>[19]</sup> In addition, temperature-dependent photoluminescence (PL) measurements were conducted to investigate the exciton dissociation kinetics of ADVANCED SCIENCE NEWS \_\_\_\_\_



**Figure 1.** a) Chemical structures and the illustration of the dihedral angle of DC9-HD and DYSe-3, respectively; b) Normalized absorption spectra of DC9-HD and DYSe-3 in diluted chloroform solution and in neat film; c) Energy levels of PM6, DC9-HD, and DYSe-3 in their film state; d) Fitting results of the calculated energy barriers for DC9-HD and DYSe-3 from temperature-dependent photoluminescence measurements.

both acceptors in neat films. As shown in Figure 1d and Figure S2 (Supporting Information), a decrease in temperature resulted in an increase in the PL intensity of all acceptors, indicating that lower temperatures enhance the recombination of charge carriers back into emissive excitons.<sup>[20]</sup> The energy barrier ( $E_a$ ) for exciton dissociation into charge carriers was calculated to be 44.7 meV for DC9-HD and 86.5 meV for DYSe-3, suggesting a more efficient exciton dissociation and charge generation could be occurred in DC9-HD based film, which may positively influence the  $J_{SC}$  of the OSCs.<sup>[21]</sup> In addition, the electron mobilities of DC9-HD and DYSe-3 in the neat films, measured by the space-charge-limited current (SCLC) method (Figure S3, Supporting Informa-

tion), are 6.61  $\times$  10<sup>-4</sup> and 5.69  $\times$  10<sup>-4</sup> cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, respectively, suggesting their satisfactory charge transport ability.

The packing motifs of both molecules in neat films were investigated using grazing-incidence wide-angle X-ray scattering (GIWAXS) measurements.<sup>[22]</sup> As illustrated in **Figure 2a**, the diffraction patterns of DC9-HD and DYSe-3 exhibited an obvious (010) peak, indicative of the  $\pi$ - $\pi$  stacking, in the out-of-plane (OOP) direction, and a (100) peak, associated with the alkyl-to-alkyl stacking motif, in the in-plane (IP) direction. This observation suggests their preferred face-on molecular orientations within the films. By analyzing their line-cut profiles presented in Figure S4 (Supporting Information), the  $\pi$ - $\pi$ 



Height Sensor 400.0 nm Height Sensor 400.0 nm Height Sensor 400.0 nm

Figure 2. a) GIWAXS images, and b) AFM height images of DC9-HD, DYSe-3, and DC9-HD:DYSe-3 (10:2) based films, respectively.

alkyl-to-alkyl stacking distances, along with the corresponding coherence lengths (CLs), were extracted and summarized in Table S2 (Supporting Information). Although the alkyl-to-alkyl stacking distance of DYSe-3 (17.54 Å) is slightly larger than that of DC9-HD (17.20 Å), their CLs for the (010) peak in OOP and (100) peak in IP are quite similar. Furthermore, when blending

-3.9 nm

DC9-HD and DYSe-3 at the weight ratio of 10:2, a merged (010) peak in OOP, together with a (100) peak in IP, was observed in the resulting film. Additionally, atomic force microscopy (AFM) height images (Figure 2b) revealed no significant molecular over-aggregation or isolated domains in the DC9-HD:DYSe-3 film. Subsequently, the contact angle measurements (Figure S5,



**Figure 3.** a) *J*–*V* curves and b) EQE spectra for devices based on PM6:DC9-HD, PM6:DYSe-3, and PM6:DC9-HD:DYSe-3. c) A summary of highperformance dimeric acceptor-based devices. d) Voltage loss distributions for devices based on PM6:DC9-HD, PM6:DYSe-3, and PM6:DC9-HD:DYSe-3. e) *J*-*V* curve of large-area device based on PM6:DC9-HD:DYSe-3. f) Thermal stabilities of devices based on PM6:DC9-HD, PM6:DYSe-3, and PM6:DC9-HD:DYSe-3. HD:DYSe-3.

ĹS

www.advenergymat.de

#### **ADVANCED** SCIENCE NEWS \_\_

www.advancedsciencenews.com

#### ENERGY MATERIALS www.advenergymat.de

 Table 1. Optimal photovoltaic parameters for devices based on PM6:DC9-HD, PM6:DYSe-3, and PM6:DC9-HD:DYSe-3. The average values in the parentheses were obtained from ten independent devices.

Active layer	V <sub>oc</sub> [V]	$J_{\rm SC}[{\rm mA~cm^{-2}}]$	$J_{\rm SC, CAL}[\rm mA~cm^{-2}]$	FF%	PCE%	V <sub>loss</sub> [V])
PM6:DC9-HD	0.900	26.2	25.7	79.3	18.7	0.533
	$(0.897 \pm 0.003)$	$(26.3 \pm 0.2)$		(78.9 ± 0.7)	(18.6 ± 0.1)	
PM6:DYSe-3	0.864	27.5	26.8	78.3	18.6	0.523
	$(0.859 \pm 0.003)$	(27.5 ± 0.2)		(77.7 ± 0.3)	(18.3 ± 0.1)	
PM6:DC9-HD:DYSe-3	0.898	27.4	26.5	78.7	19.4	0.526
	(0.898 ± 0.002)	$(27.2 \pm 0.2)$		(78.6 ± 0.2)	$(19.2 \pm 0.1)$	

Supporting Information) revealed that these two acceptors exhibited relatively low Flory–Huggins interaction parameter ( $\chi$ ) values of 0.04 K, which is substantially lower than the values observed for the donor–acceptor pairs (Table S3, Supporting Information).<sup>[23]</sup> Collectively, these findings confirm the excellent miscibility between DC9-HD and DYSe-3, highlighting their potentials for forming alloy acceptors. Notably, the PM6:DC9-HD pair showed a consistent  $\chi$  value of 0.26 K, similar to that of PM6:DC9-HD:DYSe-3 pair, further substantiating the compatibility between DC9-HD and DYSe-3. The various compatibility between the active layer materials has a significant influence on the resulting blend nanomorphology and thus device performance.

## 2.2. Photovoltaic Performance

To boost the photovoltaic potential of DC9-HD and DYSe-3, polymer PM6 was selected as the electron donor to deliver complementary absorption and matched energy levels for the OSCs. The detailed device optimizations, including the donor: acceptor ratio and post-treatment, are summarized in Tables S4-S7 (Supporting Information). The optimal PCE values for PM6:DC9-HD and PM6:DYSe-3 binary devices were 18.7% and 18.6%, respectively (Figure 3a and Table 1). In contrast, the dimeric acceptor DC9, which possesses a longer alkyl chain, achieved a maximum power conversion efficiency (PCE) of 18.1% when blended with PM6 (see Tables S8 and S9, Supporting Information). This efficiency is lower than that of the PM6:DC9-HD device (refer to Figure S6, Supporting Information), indicating the effectiveness of the design strategy employed for DC9-HD. Compared to the PM6:DC9-HD device, the PM6:DYSe-3 device achieved a higher  $J_{SC}$  of 27.5 mA cm<sup>-2</sup>, which can be attributed to a its red-shifted absorption range, as further evidenced by its broaden external quantum efficiency (EQE) spectra (Figure 3b). Due to the high-lying LUMO energy level of DC9-HD, the PM6:DC9-HD device demonstrated a higher  $V_{\rm OC}$  of 0.900 V, surpassing the  $V_{\rm OC}$  value observed in the PM6:DYSe-3 device (0.864 V). This phenomenon inspired us to combine DYSe-3 with DC9-HD to construct ternary devices, thereby achieving the desired  $V_{\rm OC}$  and  $J_{\rm SC}$ . Notably, after optimizing the ratio of DYSe-3 to the PM6:DC9-HD host binary (Table S6, Supporting Information), the  $J_{SC}$  value was significantly improved from 26.2 mA cm<sup>-2</sup> for the PM6:DC9-HD device to 27.4 mA cm<sup>-2</sup> for the ternary device. Meanwhile, the satisfactory  $V_{\rm OC}$  of 0.898 V and FF near 79% contribute to a maximum PCE of 19.4% for the PM6:DC9-HD:DYSe-3 ternary device at the weight ratio of 1:1:0.2. It is noteworthy that the PCE of 19.4%

represents the highest ever reported for single-junction dimeric acceptors-based OSCs, as illustrated in Figure 3c and Table S10 (Supporting Information). According to their corresponding EQE response spectra, the PM6:DC9-HD:DYSe-3 ternary device displayed a broader absorption range and enhanced EQE values across the 600–800 nm range, contributing to the increased  $J_{SC}$  when compared with the PM6:DC9-HD binary device. The integrated  $J_{SC}$  value of the ternary device was 26.5 mA cm<sup>-2</sup>, which is 0.8 mA cm<sup>-2</sup> higher than that of PM6:DC9-HD binary device (25.7 mA cm<sup>-2</sup>). These results verify their different  $J_{SC}$  values obtained from J-V curves. Generally, the improved EQE response spectra of the ternary blend are correlated with more efficient charge generation, transport and collection properties, which will be discussed in detail.

Apart from the super  $J_{SC}$  of ternary device, a  $V_{OC}$  of 0.898 V also played a vital role in realizing its high PCE. Thus, to gain insight into the high  $V_{\rm OC}$  observed in the ternary device, a detailed  $V_{\rm loss}$  analysis was conducted (Figure 3d; Figure S7, Supporting Information), with relevant data are summarized in Table S11 (Supporting Information).<sup>[24]</sup> According to the detailed-balance theory,<sup>[25]</sup>  $V_{\text{loss}}$  can be divided into three parts:  $V_{\text{loss}} = \Delta V_1 +$  $\Delta V_2 + \Delta V_3$ . Here,  $\Delta V_1$  is the radiative loss above the bandgap derived from the S-Q limit, and  $\Delta V_2$  and  $\Delta V_3$  are the radiative and non-radiative energy losses below the bandgap, respectively.  $\Delta V_1$  is inevitable for any kind of photovoltaics, determined only by the bandgap. The ternary device exhibited the lowest  $\Delta V_2$  values of 0.050 V, whereas PM6:DC9-HD-based and PM6:DYSe-3based binary OSCs present a  $\Delta V_2$  value of 0.052 and 0.054 V, respectively. These results can be ascribed to the decreased energetic disorder of band tail states. As shown in Figure S7 (Supporting Information), the PM6:DC9-HD:DYSe-3 blend displayed the lowest Urbach energy  $(E_{\rm U})$  value of 22.5 meV, indicating that the introduction of DYSe-3 into PM6:DC9-HD can effectively reduce energetic disorder.<sup>[26]</sup> This not only contributes to a reduction in  $V_{\rm loss}$  but also aids in suppressing charge recombination, as discussed in the subsequent charge dynamic section. Given the rapid non-radiative decay rate during the exciton relaxation process, minimizing  $\Delta V_3$  has been regarded as a key and challenging issue in reducing the total  $V_{\rm loss}$ . Thanks to the low  $\Delta V_3$  values (0.207 V) of PM6:DYSe-3 binary device, the PM6:DC9-HD:DYSe-3 ternary device demonstrates an intermediate  $\Delta V_3$  value of 0.211 V, contributing to its relatively high  $V_{\rm oc} \approx 0.90$  V.

Based on the above results, a device with an effective area of 1 cm<sup>2</sup> was fabricated using PM6:DC9-HD:DYSe-3 ternary blend. Figure 3e shows the corresponding J–V curve, and the







**Figure 4.** a,b) Dynamics of the singlet excitons measured with 800 nm pump excitation at different densities in DC9-HD film and DYSe-3 film, respectively. c)  $J_{ph}$  versus  $V_{eff}$ , d) current density versus light intensity, and e) transient photocurrent measurements for devices based on PM6:DC9-HD, PM6:DYSe-3, and PM6:DC9-HD:DYSe-3. f) Histograms of electron mobility ( $\mu_e$ ) and hole mobility ( $\mu_h$ ).

resultant device yielded a desirable PCE of 16.4%, highlighting the potential of such combinations in the fabrication of largearea devices. Meanwhile, thermal stability tests were performed for all binary and ternary OSCs. As shown in Figure 3f, after  $\approx$ 800 h of thermal-aging of storage at 65 °C in a glove box, all investigated binary and ternary OSCs retained 80% of their original efficiency, indicating that the dimeric acceptor-based OSCs have good thermal stability. Besides, the PCEs of PM6:DC9-HD, PM6:DYSe-3, and PM6:DC9-HD:DYSe-3 based devices maintained 70%, 63%, and 71% of their original PCEs after 200 h of light aging under max power point (MPP) tracking in a nitrogen-filled glovebox (Figure S8, Supporting Information), respectively.

#### 2.3. Charge Dynamics

To gain a deeper understanding of the enhanced device performance in PM6:DC9-HD:DYSe-3 ternary blend, it is essential to investigate the charge dynamic process, including exciton dissociation, charge transport and collection properties. First, the exciton diffusion length  $L_D$  in the DC9-HD film and DYSe-3 film were estimated by the exciton-exciton annihilation method via pump-fluence-dependent transient absorption spectroscopy (Table S12, Supporting Information).<sup>[27]</sup> The extracted  $L_D$  value of DC9-HD film is greater than that of DYSe-3 (46.4 nm vs 38.2 nm), which might induce faster exciton diffusion and exciton dissociation in DC9-HD based devices compared with those of DYSe-3 based device (Figure 4a,b). Then, the charge dissociation probability ( $P_{diss}$ ) and charge collection probability ( $P_{\rm coll}$ ) for all devices were calculated from their photo-induced current density against effective voltage plots (Figure 4c).<sup>[28]</sup> Compared with the PM6:DYSe binary device, the PM6:DC9-HD binary device and PM6:DC9-HD:DYSe-3 ternary device exhibit slightly higher  $P_{\rm diss}$  values of 98%, and  $P_{\rm coll}$  values of 90% and 89%, respectively. These findings are consistent with the longer  $L_{\rm D}$  values of DC9-HD, and verify the higher EQE response in DC9-HD-based binary and ternary devices.

Furthermore, the relationship between  $J_{SC}$  and  $P_{light}$  can be described as a power-law dependence equation of  $J_{SC}$  versus  $P_{\text{light}}^{\alpha}$ , where  $\alpha$  is close to unity, suggesting the minimal bimolecular recombination.<sup>[29]</sup> As shown in Figure 4d, the PM6:DC9-HD:DYSe-3 ternary device exhibits the highest  $\alpha$  values of 0.99, indicating a restrained bimolecular recombination, which favors the result of  $V_{loss}$  analysis. Besides, transient photocurrent (TPC) measurements were carried out to evaluate the charge extraction time of three devices (Figure 4e).<sup>[30]</sup> The charge extraction times of the PM6:DC9-HD, PM6:DYSe-3, and PM6:DC9-HD:DYSe-3 devices are 0.28, 0.25, and 0.22 µs, respectively. The shortest charge extraction time suggests that carriers are extracted more efficiently in the PM6:DC9-HD:DYSe-3 ternary device. Subsequently, the charge transport properties were evaluated through the SCLC method (Figure S9, Supporting Information), and the calculated hole and electron mobilities are depicted in Figure 4f. The ternary device received the highest hole and electron mobilities, along with balanced charge transport, which can reduce the likelihood of both bimolecular and trap-assisted recombination. These observations demonstrated that the fabrication



www.advancedsciencenews.com



Figure 5. a) AFM height images and b) GIWAXS images of the PM6:DC9-HD, PM6:DYSe-3, and PM6:DC9-HD:DYSe-3 blend films. c) Fibril diameter distributions obtained from AFM phase images of the PM6:DC9-HD, PM6:DYSe-3, and PM6:DC9-HD:DYSe-3 blend films. d) In-plane line-cuts of the GIWAXS images. e) Coherence length of the (100) along in-plane direction of the PM6:DC9-HD and PM6:DC9-HD:DYSe-3 blend films.

of PM6:DC9-HD:DYSe-3 ternary device effectively mitigates the geminate recombination and promotes efficient charge generation, resulting in increased EQE response values and reduced  $V_{\rm OC}$  loss, thereby maximizing the  $J_{\rm SC} \times V_{\rm OC}$  value in the corresponding device.

#### 2.4. Morphology Analysis

The aggregation behaviors of photovoltaic materials in the blend films are of vital importance for achieving high photovoltaic performance in OSCs, and thus the nanomorphology of all blend films was systematically investigated. The surface morphology of all binary and ternary blends was evaluated by atomic force microscopy (AFM) as displayed in **Figure 5**a. In general, all blend films exhibit smooth surfaces with root-mean-square surface roughness ( $R_0$ ) values of  $\approx 1$  nm. While, a relatively obvious fiber structure is observable in the corresponding phase images (Figure S10, Supporting Information). The fibril diameters could be estimated from the line profiles across the phase images according to reported methods.<sup>[27]</sup> As a result, the fibril diameters of 14.6  $\pm$  3.8 nm, 13.2  $\pm$  2.8 nm, and 16.9  $\pm$  3.7 nm are received for PM6:DC9-HD film, for PM6:DYSe-3 film, and for PM6:DC9-HD:DYSe-3 film, respectively (Figure 5c). Among them, the PM6:DYSe-3 binary film exhibits smaller fibril diameters due to the high miscibility between PM6 and DYSe-3 (as evidenced by its small  $\chi$  value of 0.09 K in Table S3, Supporting Information). Despite the larger fibril diameters observed in PM6:DC9-HD and PM6:DC9-HD:DYSe-3 blend films compared to those of the PM6:DYSe-3 blend film, the larger LD of DC9-HD could facilitate effective exciton dissociation in the corresponding blend films.

GIWAXS measurements were conducted to elucidate the molecular stacking and crystallinity of three blend films, with



the corresponding diffraction images presented in Figure 5b. Notably, the PM6 neat films exhibited a (100) diffraction peak at  $q_{xy} = 0.29$  Å<sup>-1</sup> and a (010) diffraction peak at  $q_z = 1.67$ Å<sup>-1</sup> (Figure S11, Supporting Information), indicating its preferred face-on molecular packing motifs. The combination of the polymer donor PM6 with these acceptors contributes to the emerged (010) diffraction peak located at  $\approx$ 1.60 Å<sup>-1</sup>in the OOP direction (Figure S12, Supporting Information), indicating that the preferred face-on molecular orientations of PM6, DC9-HD, and DYSe-3 are well-maintained in three blend films. In the IP direction (Figure 5d), the (100) diffraction peaks at  $\approx 0.30$  Å<sup>-1</sup> and 0.37 Å<sup>-1</sup> (Figure S13, Supporting Information), attributed to the (100) diffraction of PM6 and dimeric acceptors, respectively, are observed in the DC9-HD-based binary and ternary blends. While, an emerged (100) diffraction peak is identified in the PM6:DYSe-3 binary film, which arises from the favorable miscibility between PM6 and DYSe-3, as discussed previously. Importantly, the larger CLs of the (100) diffraction peaks at  $\approx 0.30$  and  $\approx 0.37$  Å<sup>-1</sup> in the ternary blend indicate a simultaneous enhancement in the crystallinity of both donor and acceptors (Figure 5e). This enhanced crystallinity in PM6:DC9-HD:DYSe-3-based blend contributes to improved charge transport properties, which aligns with their enhanced charge dynamics and ultimately benefits the enhancement of EQE response.

## 3. Conclusions

In summary, two highly compatible dimeric acceptors, DC9-HD and DYSe-3, were designed and synthesized. Benefitting from their low  $V_{OC}$  loss and long exciton diffusion length, both DC9-HD and DYSe-3 based binary OSCs achieved PCEs over 18.5%. Notably, the incorporation of DYSe-3 as the third component into PM6:DC9-HD blend could optimize the photon-utilization range and improve the morphological characters, thereby facilitating charge generation and reducing charge combination in the ternary blend. This optimization led to the simultaneous achievement of ideal  $V_{\rm OC}$  of 0.898 V,  $J_{\rm SC}$  of 27.4 mA cm<sup>-2</sup> and FF near 79% for the ternary OSCs, resulting in a remarkable PCE of 19.4% for the dimeric acceptors-based single junction OSCs. To our knowledge, this result ranks the best performance of OSMA-based devices to date. In addition, all binary and ternary OSCs retained over 80% of their original efficiency after  $\approx$ 800 h of thermal-aging at 65 °C in a glove box, indicating that the OSMA-based OSCs possess excellent thermal stability. These findings underscore the significant potential of OSMAbased OSCs for achieving highly efficient and stable devices, warranting increased attention to accelerate the development of OSCs.

# **Supporting Information**

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

# Acknowledgements

W.F. and Y.B. contributed equally to this work. The authors gratefully acknowledge the financial support from Ministry of Science and Technology of the People's Republic of China (2022YFB4200400, 2019YFA0705900, and 2023YFE0210400), National Natural Science Foundation of China (52303237, 21935007, 52025033, and 22361132530), the Fundamental Research Funds for the Central Universities, Nankai University (023-632343116), and the Science and Technology Innovation Program of Hunan Province (2021RC3083).

## **Conflict of Interest**

The authors declare no conflict of interest.

## **Data Availability Statement**

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

## Keywords

dimeric acceptors, high-performance, organic solar cells, ternary devices

Received: September 5, 2024 Revised: October 31, 2024 Published online:

- a) P. Ding, D. Yang, S. Yang, Z. Ge, *Chem. Soc. Rev.* 2024, *53*, 2350;
   b) H. Yu, J. Wang, Q. Zhou, J. Qin, Y. Wang, X. Lu, P. Cheng, *Chem. Soc. Rev.* 2023, *52*, 4132; c) G. Zhang, F. R. Lin, F. Qi, T. Heumüller, A. Distler, H.-J. Egelhaaf, N. Li, P. C. Y. Chow, C. J. Brabec, A. K. Y. Jen, H.-L. Yip, *Chem. Rev.* 2022, *122*, 14180; d) J. Jing, Y. Dou, S. Chen, K. Zhang, F. Huang, *eScience* 2023, *3*, 100142.
- [2] a) Y. Liu, B. Liu, C. Ma, F. Huang, G. Feng, H. Chen, J. Hou, L. Yan, Q. Wei, Q. Luo, Q. Bao, W. Ma, W. Liu, W. Li, X. Wan, X. Hu, Y. Han, Y. Li, Y. Zhou, Y. Zou, Y. Chen, Y. Liu, L. Meng, Y. Li, Y. Chen, Z. Tang, Z. Hu, Z. Zhang, Z. Bo, *Sci. China Chem.* **2022**, *65*, 1457; b) X. Li, X. Kong, G. Sun, Y. Li, *eScience* **2023**, *3*, 100171.
- [3] Q. Wei, J. Yuan, Y. Yi, C. Zhang, Y. Zou, Natl. Sci. Rev. 2021, 8, nwab121.
- [4] a) Y. Jiang, S. Sun, R. Xu, F. Liu, X. Miao, G. Ran, K. Liu, Y. Yi, W. Zhang, X. Zhu, *Nat. Energy* 2024, *9*, 975; b) S. Guan, Y. Li, C. Xu, N. Yin, C. Xu, C. Wang, M. Wang, Y. Xu, Q. Chen, D. Wang, L. Zuo, H. Chen, *Adv. Mater.* 2024, *36*, 2400342; c) C. Chen, L. Wang, W. Xia, K. Qiu, C. Guo, Z. Gan, J. Zhou, Y. Sun, D. Liu, W. Li, T. Wang, *Nat. Commun.* 2024, *15*, 6865; d) Z. Chen, J. Ge, W. Song, X. Tong, H. Liu, X. Yu, J. Li, J. Shi, L. Xie, C. Han, Q. Liu, Z. Ge, *Adv. Mater.* 2024, *36*, 2406690.
- [5] L. Zhu, M. Zhang, G. Zhou, Z. Wang, W. Zhong, J. Zhuang, Z. Zhou, X. Gao, L. Kan, B. Hao, F. Han, R. Zeng, X. Xue, S. Xu, H. Jing, B. Xiao, H. Zhu, Y. Zhang, F. Liu, *Joule* **2024**, https://doi.org/10.1016/j.joule. 2024.08.001.
- [6] a) K. Wang, L. Y. Zheng, Y. C. Hou, A. Nozariasbmarz, B. Poudel, J. Yoon, T. Ye, D. Yang, A. Pogrebnyakov, V. Gopalan, S. Priya, *Joule* 2022, 6, 756; b) Z. L. Guo, A. K. Jena, G. M. Kim, T. Miyasaka, *Energy Environ. Sci.* 2022, 15, 3171.
- [7] H. F. Yao, J. H. Hou, Angew. Chem., Int. Ed. 2022, 61, 202209021.
- [8] J. Yuan, H. Zhang, R. Zhang, Y. Wang, J. Hou, M. Leclerc, X. Zhan, F. Huang, F. Gao, Y. Zou, Y. Li, *Chem* **2020**, *6*, 2147.
- [9] H. Wang, C. Cao, H. Chen, H. Lai, C. Ke, Y. Zhu, H. Li, F. He, Angew. Chem., Int. Ed. 2022, 61, 202201844.
- a) M. Lv, Q. Wang, J. Zhang, Y. Wang, Z.-G. Zhang, T. Wang, H. Zhang,
   K. Lu, Z. Wei, D. Deng, *Adv. Mater.* **2024**, *36*, 2310046; b) X. Gu, X.
   Zhang, H. Huang, *Angew. Chem.*, *Int. Ed.* **2023**, *62*, 202308496; c) S.

ADVANCED ENERGY MATERIALS

## www.advenergymat.de

Li, R. Zhang, M. Zhang, J. Yao, Z. Peng, Q. Chen, C. Zhang, B. Chang, Y. Bai, H. Fu, Y. Ouyang, C. Zhang, J. A. Steele, T. Alshahrani, M. B. J. Roeffaers, E. Solano, L. Meng, F. Gao, Y. Li, Z.-G. Zhang, *Adv. Mater.* **2023**, *35*, 2206563; d) W. Liu, J. Yuan, C. Zhu, Q. Wei, S. Liang, H. Zhang, G. Zheng, Y. Hu, L. Meng, F. Gao, Y. Li, Y. Zou, *Sci. China Chem.* **2022**, *65*, 1374; e) H. Chen, B. Kan, P. Wang, W. Feng, L. Li, S. Zhang, T. Chen, Y. Yang, T. Duan, Z. Yao, C. Li, X. Wan, Y. Chen, *Angew. Chem., Int. Ed.* **2023**, *62*, 202307962.

- [11] a) J.-W. Lee, J. S. Park, H. Jeon, S. Lee, D. Jeong, C. Lee, Y.-H. Kim, B. J. Kim, Chem. Soc. Rev. 2024, 53, 4674; b) Y. Liang, D. Zhang, Z. Wu, T. Jia, L. Lüer, H. Tang, L. Hong, J. Zhang, K. Zhang, C. J. Brabec, N. Li, F. Huang, Nat. Energy 2022, 7, 1180; c) H. Yu, M. Pan, R. Sun, I. Agunawela, J. Zhang, Y. Li, Z. Qi, H. Han, X. Zou, W. Zhou, S. Chen, J. Y. L. Lai, S. Luo, Z. Luo, D. Zhao, X. Lu, H. Ade, F. Huang, J. Min, H. Yan, Angew. Chem., Int. Ed. 2021, 60, 10137; d) H. Yu, Y. Wang, H. K. Kim, X. Wu, Y. Li, Z. Yao, M. Pan, X. Zou, J. Zhang, S. Chen, D. Zhao, F. Huang, X. Lu, Z. Zhu, H. Yan, Adv. Mater. 2022, 34, 2200361; e) W. Liu, H. Yu, B. Liu, Y. Wang, H. Hu, H. M. Ng, C. H. Kwok, J. Yi, C. Zhang, F. Huang, Z. Zhu, H. Yan, Adv. Funct. Mater. 2024, 34, 2400131; f) H. Yu, Y. Wang, C. H. Kwok, R. Zhou, Z. Yao, S. Mukherjee, A. Sergeev, H. Hu, Y. Fu, H. M. Ng, L. Chen, D. Zhao, Z. Zheng, X. Lu, H. Yin, K. S. Wong, H. Ade, C. Zhang, Z. Zhu, H. Yan, Joule 2024, 8, 2304.
- [12] M. Günther, N. Kazerouni, D. Blätte, J. D. Perea, B. C. Thompson, T. Ameri, Nat. Rev. Mater. 2023, 8, 456.
- [13] X. Gu, Y. Wei, N. Yu, J. Qiao, Z. Han, Q. Lin, X. Han, J. Gao, C. Li, J. Zhang, X. Hao, Z. Wei, Z. Tang, Y. Cai, X. Zhang, H. Huang, CCS *Chem* **2023**, *5*, 2576.
- [14] J. Song, C. Zhang, C. Li, J. Qiao, J. Yu, J. Gao, X. Wang, X. Hao, Z. Tang, G. Lu, R. Yang, H. Yan, Y. Sun, *Angew. Chem.*, Int. Ed. **2024**, 63, 202404297.
- [15] W. Feng, Y. Bai, J. Wang, S. Yuan, X. Wan, Y. Chen, B. Kan, Y. Chen, *Chin. J. Chem.* **2024**, 42, 3075.

- [16] Y. Bai, T. Chen, X. Ji, J. Wang, W. Zhao, S. Yuan, Y. Zhang, G. Long, Z. Zhang, X. Wan, B. Kan, Y. Chen, *Adv. Energy Mater.* **2024**, *14*, 2400938.
- [17] a) X. P. Xu, Y. Li, Q. Peng, Adv. Mater. 2022, 34, 2107476; b) C. He, Q. Shen, B. Wu, Y. Gao, S. Li, J. Min, W. Ma, L. Zuo, H. Chen, Adv. Energy Mater. 2023, 13, 2204154.
- [18] F. Lin, K. Jiang, W. Kaminsky, Z. Zhu, A. K. Y. Jen, J. Am. Chem. Soc. 2020, 142, 15246.
- [19] Z. Zheng, O. M. Awartani, B. Gautam, D. L. Liu, Y. P. Qin, W. N. Li, A. Bataller, K. Gundogdu, H. Ade, J. H. Hou, *Adv. Mater.* **2017**, *29*, 1604241.
- [20] J. Ji, L. Zhu, X. Xiong, F. Liu, Z. Liang, Sci. Adv. 2022, 9, 2200864.
- [21] L. Zhu, J. Zhang, Y. Guo, C. Yang, Y. Yi, Z. Wei, Angew. Chem., Int. Ed. 2021, 60, 15348.
- [22] J. Rivnay, S. C. B. Mannsfeld, C. E. Miller, A. Salleo, M. F. Toney, *Chem. Rev.* 2012, 112, 5488.
- [23] S. Honda, H. Ohkita, H. Benten, S. Ito, Adv. Energy Mater. 2011, 1, 588.
- [24] Y. Wang, D. Qian, Y. Cui, H. Zhang, J. Hou, K. Vandewal, T. Kirchartz, F. Gao, Adv. Energy Mater. 2018, 8, 1801352.
- [25] U. Rau, Phys. Rev. B 2007, 76, 085303.
- [26] a) S. S. Liu, J. Yuan, W. Deng, M. Luo, Y. Xie, Q. Liang, Y. Zou, Z. He,
   H. Wu, Y. Cao, *Nat. Photo.* **2020**, *14*, 300; b) Z. Zhang, Y. Li, G. Cai, Y.
   Zhang, X. Lu, Y. Lin, *J. Am. Chem. Soc.* **2020**, *142*, 18741.
- [27] L. Zhu, M. Zhang, J. Xu, C. Li, J. Yan, G. Zhou, W. Zhong, T. Hao, J. Song, X. Xue, Z. Zhou, R. Zeng, H. Zhu, C.-C. Chen, R. C. I. MacKenzie, Y. Zou, J. Nelson, Y. Zhang, Y. Sun, F. Liu, *Nat. Mater.* 2022, 21, 656.
- [28] A. K. K. Kyaw, D. H. Wang, V. Gupta, W. L. Leong, L. Ke, G. C. Bazan, A. J. Heeger, ACS Nano 2013, 7, 4569.
- [29] P. Schilinsky, C. Waldauf, J. Hauch, C. J. Brabec, J. Appl. Phys. 2004, 95, 2816.
- [30] S. Wood, D. O'Connor, C. W. Jones, J. D. Claverley, J. C. Blakesley, C. Giusca, F. A. Castro, Sol.Energy Mater. Solar Cells 2017, 161, 89.

lcense