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A medium bandgap dimeric acceptor with a high open-circuit voltage for efficient organic solar cells<sup>†</sup>

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Dimeric acceptors (DMAs) exhibit significant potential for optimizing both the efficiency and stability of organic solar cells (OSCs). However, medium band-gap DMAs with a high open-circuit voltage  $(V_{\rm oc})$  for efficient OSCs remain underexplored. In this study, we designed and synthesized a medium bandgap dimeric acceptor, designated DYO-1, through the strategy of alkoxy side-chain substitutions. The resultant DYO-1 exhibited an upshifted lowest unoccupied molecular orbital (LUMO) level and blue-shifted absorption. Notably, an o-xylene (o-XY) processed OSC with a PM6:DYO-1 binary blend achieved an ultra-high  $V_{\rm oc}$  of 1.022 V and a fill factor (FF) of 73.9%, resulting in a power conversion efficiency (PCE) of 15.1%. To our knowledge, this is the highest PCE reported thus far for dimer-based OSCs with a  $V_{\rm oc}$  exceeding 1.0 V. Furthermore, DYO-1 was incorporated into a PM6:L8-BO-X blend film, effectively reducing excessive aggregation of the host blend film, thus improving the carrier transport efficiency and enhancing both the short-circuit current ( $J_{sc}$ ) and FF. Alongside the improvement in  $V_{ocr}$ the PM6:L8-BO-X:DYO-1 based ternary OSC, which is prepared using an o-XY solvent, achieved a prominent PCE of 19.6%. Additionally, a module device with an effective area of 13.5 cm<sup>2</sup> exhibited a PCE of 15.8%, highlighting the potential for large-area fabrications. Our study unveils the importance of medium bandgap dimeric acceptors in achieving efficient and stable OSCs, providing valuable insights into the design of high-performance electron acceptors.

#### New concepts

By introducing electron-donating alkoxy side chains into the  $\beta$ -position of the thienothiophene unit, in place of alkyl chains, the intramolecular charge transfer (ICT) effect is weakened, leading to the design and synthesis of a medium bandgap dimeric acceptor DYO-1. Notably, the PM6:DYO-1 binary device processed with *o*-xylene (*o*-XY) processing achieves a high open-circuit voltage ( $V_{oc}$ ) of 1.022 V and a power conversion efficiency (PCE) of 15.1%. This represents the highest PCE reported for dimer-based organic solar cells (OSCs) with a  $V_{oc}$  exceeding 1.0 V, elegantly demonstrating the delicate balance between  $V_{oc}$  and PCE. Moreover, DYO-1, serving as a guest component, exhibits modest crystallinity and packing order, which reduces excessive aggregation in the PM6:L8-BO-X blend film, thereby simultaneously enhancing  $V_{oc}$ , short-circuit current ( $J_{sc}$ ), and FF, ultimately achieving a PCE of 19.6% for *o*-XY processed OSCs. These results underscore the pivotal role of medium bandgap dimeric acceptors in the high-performance of OSCs.

#### Introduction

Solution-processed organic solar cells (OSCs) are promising candidates for next-generation photovoltaics due to their considerable upscaling potential, particularly through roll-to-roll and open-air printing.<sup>1–5</sup> The development of non-fullerene acceptors (NFAs), especially Y-series small-molecular acceptors (SMAs), has led to significant improvements in the power

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conversion efficiencies (PCEs) of single-junction OSCs, exceeding 20% to date.<sup>6–8</sup> Despite these advancements in efficiency, concerns regarding device stability persist, as it is mostly linked to the morphology of the active layer. SMAs are prone to molecular diffusion and self-agglomeration, leading to metastable morphologies and thus unsatisfactory device stability under external conditions, such as thermal and photo-stress.<sup>9,10</sup> The development of polymer acceptors with low diffusion rates, which enable the fabrication of all-polymer OSCs, represents a promising strategy for enhancing the long-term stability of OSCs. However, due to the batch-to-batch variations of polymer acceptors, all-polymer OSCs remain heavily reliant on their molecular weights.<sup>11</sup>

It is exciting that recent advancements in dimeric electron acceptors (DMAs) have garnered considerable attention due to their ability to combine the advantages of both small-molecular and polymer materials.<sup>12-14</sup> In general, DMAs with well-defined chemical structures exhibit higher electron mobility than PSMAs because of their regular and relatively tight molecular packing.<sup>15</sup> In addition, the glass transition temperatures  $(T_{os})$ of DMAs are higher than those of SMAs, which can be attributed to their comparatively larger molecular size. These favorable properties resulted in DMA-based OSCs with enhanced thermal and photo-stability, as well as excellent batch-to-batch reproducibility.<sup>16,17</sup> Furthermore, the rational design of DMAs has the great potential to achieve high-efficiency OSCs processed with o-xylene (o-XY) through morphology optimization and crystallization kinetics regulation,<sup>18</sup> thereby providing an effective pathway for fabricating large-area OSCs.

Recently, great efforts have been devoted to developing narrow-bandgap DMAs with film absorption extending beyond 900 nm, with the aim of further improving the photo-harvesting ability.<sup>9,10</sup> As a matter of fact, the design of medium bandgap DMAs, characterized by bandgaps in the range of approximately 1.5 eV to 1.7 eV, is also critical for enhancing the open-circuit voltage (Voc) in both binary and ternary OSCs, while maintaining a high fill factor (FF) and short-circuit current  $(J_{sc})$  value, thereby boosting the PCEs.<sup>19-21</sup> Particularly for ternary OSCs, this approach serves the dual purpose of optimizing the utilization of photons and the thin-film morphology, both of which contribute to enhanced photovoltaic performance. The alkoxy substitution on the side chain has been proven to be an effective strategy for developing medium bandgap acceptors. For instance, Yan et al. introduced asymmetric alkoxy and alkyl substitution on Y6, yielding a molecule named Y6-1O that can maintain the positive effect of Voc improvement and achieve reasonably good solubility, resulting in OSCs with a higher PCE than the Y6-based device.<sup>22</sup> However, studies specifically targeting medium bandgap DSMAs remain limited to date.

Herein, a medium bandgap alkoxy-substituted dimer, DYO-1, was designed and synthesized for the fabrication of efficient and stable OSCs processed from a non-halogenated solvent. The binary OSC based on PM6:DYO-1 showed a high  $V_{\rm oc}$  of 1.022 V and a PCE of 15.1%, representing the best results of the binary OSCs with a  $V_{\rm oc}$  exceeding 1.0 V. More importantly, DYO-1 exhibited modest crystallinity and packing order, rendering it suitable as the extra component to prevent the excessive aggregation of small-molecular materials, thereby optimizing the morphological features of the corresponding blend films. In this work, DYO-1 was introduced into the PM6:L8-BO-X binary blend. Due to the optimized morphologies and the related charge dynamics, simultaneous improvements in  $V_{\rm oc}$ , FF, and  $J_{\rm sc}$  were observed for the PM6:L8-BO-X:DYO-1-based ternary OSC. As a result, the optimized PM6:L8-BO-X:DYO-1-based ternary OSC achieved a PCE of 19.6%, surpassing the 17.6% of its PM6:L8-BO-X based binary counterpart. Moreover, a module device based on an optimal ternary OSC with an area of 13.5 cm<sup>2</sup> achieved a PCE of 15.8%, which shows the potential for fabrication in a large area. Our study highlights the importance of manipulating the bandgap in molecular design and offers a highly efficient third component for ternary OSCs.

#### Results and discussion

DYO-1 was synthesized as described in Scheme S1 (ESI<sup>+</sup>), with its chemical structure illustrated in Fig. 1a. The optical properties of PM6, L8-BO-X, and DYO-1 were determined using ultravioletvisible-near infrared (UV-vis-NIR) absorption spectroscopy. As shown in Fig. 1b and Table S1 (ESI†), the absorption peak of DYO-1 in chloroform solution is observed at 713 nm, which redshifts to 755 nm in its neat film. In comparison with typical dimeric acceptors,  $^{23,24}$  DYO-1 exhibited a slight redshift (~42 nm) from the solution to the thin-film state, indicating the relatively weak molecule crystallinity and packing ordering,<sup>20</sup> which may mitigate excessive aggregation in the active layer. Furthermore, the optical absorption profile of the DYO-1 film is situated between those of the PM6 and L8-BO-X films, indicating the potential for the fabrication of highly efficient ternary devices through the optimization of the dimer acceptor content in the active layer. The energy levels of PM6, L8-BO-X, and DYO-1 in the solid state were assessed using cyclic voltammetry under consistent conditions (Fig. S1, ESI<sup>†</sup>). As illustrated in Fig. 1c, the lowest unoccupied molecular orbital (LUMO) levels of PM6, DYO-1, and L8-BO-X are estimated to be -3.60, -3.64, and -3.88 eV, respectively. The cascade energy level diagram from PM6 to DYO-1 to L8-BO-X is believed to facilitate exciton dissociation and charge transfer in the corresponding ternary blend film.<sup>25</sup> Meanwhile, we calculated the frontier molecular orbitals (FMOs) and the energy levels using density functional theory (DFT) with the Gaussian 16 package at the B3LYP/ 6-31G(d) level. The electron densities of the highest occupied molecular orbitals (HOMOs) and the LUMOs are uniformly distributed across two monomers of the dimers, as illustrated in Fig. S2 (ESI<sup>†</sup>). Furthermore, the calculated HOMO/LUMO energy levels are -5.49/-3.38 eV, which are generally consistent with the CV test results (Fig. 1c). Additionally, the upshifted LUMO level of DYO-1, compared to that of the host L8-BO-X acceptor, would facilitate achieving a higher Voc in the corresponding ternary device.14,26

Therefore, the photovoltaic performance of DYO-1, serving as the acceptor and the guest component in conventional OSCs, was evaluated and optimized, utilizing PM6:DYO-1 and



**Fig. 1** (a) Chemical structure of DYO-1. (b) Normalized UV-Vis absorption spectra and (c) energy level diagram of PM6, L8-BO-X and DYO-1. (d) J-V characteristics and (e) EQE spectra and the corresponding integrated current density of devices based on PM6:DYO-1, PM6:L8-BO-X, and PM6:L8-BO-X:DYO-1 blends. (f) J-V curves and output power density of 13.5 cm<sup>2</sup> modules based on PM6:L8-BO-X:DYO-1 BHJ. The inset shows a photograph of the module device. (g) Deviation metric of absorption spectra under different thermal annealing temperatures for DYO-1, L8-BO-X, and L8-BO-X:DYO-1 blends. (h) Thermal stability of devices stored in a dark glove box filled with nitrogen.

PM6:L8-BO-X:DYO-1 as the active layers. Detailed device fabrication procedures and the device parameters (Tables S2–S4, ESI†) are provided in the ESI.† The current density–voltage (J–V) curves of all the optimal devices are depicted in Fig. 1d, with the corresponding photovoltaic parameters summarized in Table 1. As expected, the binary OSC based on PM6:DYO-1 exhibits a PCE of 15.1% with a notably high  $V_{oc}$  of 1.022 V. To the best of our knowledge, this represents the highest PCE obtained for a polymeric donor:dimeric acceptor system with a  $V_{oc}$  exceeding 1.0 V (Table S5, ESI†). Furthermore, DYO-1 was introduced into PM6:L8-BO-X to explore its effect as a guest component on photovoltaic performance. The binary OSC based on PM6:L8-BO-X delivers a modest PCE of 17.6%, attributed to the limited  $V_{oc}$  of 0.863 V and  $J_{sc}$  of 26.1 mA cm<sup>-2</sup>. Upon the introduction of 10% DYO-1, significant enhancements in  $V_{oc}$  and  $J_{sc}$  were achieved while maintaining a high FF, resulting in a PCE of 19.6% for the device based on PM6:L8-BO-X:DYO-1. This achievement represents one of the highest efficiencies reported to date for OSCs processed from non-halogenated solvents.<sup>18,26</sup>

ВНЈ	$V_{ m oc}$ (V)	FF (%)	$J_{ m sc}~({ m mA~cm^{-2}})$	$J_{ m sc}^{ m cal}~({ m mA~cm^{-2}})$	$PCE^{a}$ (%)
PM6:DYO-1	$1.022~(1.017\pm0.002)$	73.9 (73.8 $\pm$ 0.2)	19.8 (19.7 $\pm$ 0.2)	19.0	$15.1~(15.0\pm0.1)$
PM6:L8-BO-X	$0.863~(0.860\pm0.002)$	$78.6(78.1\pm0.4)$	$26.1~(25.9\pm0.3)$	25.2	$17.6(17.4 \pm 0.2)$
PM6:L8-BO-X:DYO-1	$0.882(0.879 \pm 0.002)$	$79.8(79.6\pm0.2)$	$27.8(27.7\pm0.1)$	27.1	$19.6(19.5 \pm 0.1)$
PM6:L8-BO-X:DYO-1 <sup>b</sup>	5.220	72.7	4.2	—	15.8

<sup>*a*</sup> The average parameters were calculated from 10 independent devices, and the active layer thickness of all devices is approximately 100 nm. <sup>*b*</sup> 13.5 cm<sup>2</sup> module device consisting of 6 series-connected sub-cells prepared by the spin-coating method in the glove box.

The external quantum efficiency (EQE) spectra of these devices reveal substantial differences in response in the medium-long wavelength region (Fig. 1e). The PM6:L8-BO-X:DYO-1 ternary device shows a considerably higher EQE than the binary control device in the 540–870 nm region, resulting in an integrated  $J_{sc}$ higher by 1.9 mA  $cm^{-2}$ , which is consistent with the increased  $J_{\rm sc}$  observed from the J-V curves. Additionally, the ternary device also exhibits a flatter EQE band compared to the control device in the 570-780 nm region. Given that the absorption spectrum of DYO-1 is mainly located between those of PM6 and L8-BO-X (Fig. 1b), we inferred that the increased EQE of the ternary device is partially contributed by the absorption and morphology regulation effects of DYO-1. The current densities calculated from EQEs are 19.0 mA cm<sup>-2</sup> for PM6:DYO-1, 25.2 mA cm<sup>-2</sup> for PM6:L8-BO-X, and 27.1 mA cm<sup>-2</sup> for PM6:L8-BO-X:DYO-1 devices, respectively. These results verified the Jsc values extracted from J-V characteristics, indicating the reliability of our results (Table 1).

To demonstrate the feasibility of the devices for large-scale manufacturing, a module based on an optimal ternary blend consisting of six sub-cells connected in series was fabricated as presented in Fig. 1f, which exhibits a superior PCE of 15.8%. Both small- and large-area devices based on the ternary blend film demonstrated outstanding performance, highlighting the potential of DYO-1-based OSCs for future applications. Furthermore, device stability is a crucial factor for the commercialization of OSCs. The construction of dimeric acceptors has been shown to increase the  $T_{\rm g}$ , thereby diminishing molecular diffusion and enhancing device stability.<sup>27</sup> Therefore, the UV-vis absorption spectra of the films at various post-treatment temperatures were recorded to determine the  $T_{\rm g}$  values.<sup>28</sup> As plotted in Fig. 1g, the  $T_{\rm g}$ s of DYO-1, L8-BO-X, and the

L8-BO-X:DYO-1 blend film were estimated to be 107, 77, and 83 °C, respectively. Afterwards, the thermal stability tests were conducted on unencapsulated devices at 65 °C, as illustrated in Fig. 1h, and the PM6:DYO-1-based device maintains 89% of its initial PCE after more than 1000 h of heating, indicating its exceptional thermal stability. Besides the PM6:L8-BO-X:DYO-1 device retains 84% of the initial PCE, while the PM6:L8-BO-X binary cell retains 81%, indicating that the introduction of DYO-1 definitely enhanced the thermal stability of the device.

To gain insight into the high  $V_{oc}$  observed in the ternary device, a detailed  $E_{loss}$  analysis was conducted (Fig. 2a and b), with relevant data summarized in Table S6 (ESI<sup>†</sup>). The overall  $E_{\rm loss}$  values were calculated to be 0.541, 0.560, and 0.545 eV for the PM6:DYO-1, PM6:L8-BO-X, and PM6:L8-BO-X:DYO-1 devices, respectively. According to the detailed-balance theory,<sup>29</sup>  $E_{\text{loss}}$  can be divided into three parts:  $E_{\text{loss}} = \Delta E_1 + \Delta E_2 + \Delta E_3$ . Here,  $\Delta E_1$  is the radiative loss above the bandgap derived from the S–Q limit, and  $\Delta E_2$  and  $\Delta E_3$  are the radiative and non-radiative energy losses below the bandgap, respectively.  $\Delta E_1$  is inevitable for any kind of photovoltaics, determined only by the bandgap (Fig. S3, ESI<sup>†</sup>).<sup>17</sup> The introduction of DYO-1 into PM6:L8-BO-X led to a slight decrease in  $\Delta E_2$  (from 0.063 to 0.061 eV), implying that DYO-1 can improve molecular ordering, thereby reducing the energetic disorder of band tail states in the ternary blend.<sup>29</sup> Further analysis is presented in the morphological characterization below. Given the rapid non-radiative decay rate during the exciton relaxation process, minimizing  $\Delta E_3$  has been regarded as a key and challenging issue in reducing the total  $E_{\text{loss}}$ . The low  $\Delta E_3$  values (0.207 eV) of the PM6:DYO-1 binary device allow the PM6:L8-BO-X:DYO-1 ternary device to demonstrate a decreased  $\Delta E_3$  value (0.219 eV) compared to PM6:L8-BO-X (0.232 eV), which reveals that the introduction of



Fig. 2 (a) Detailed  $E_{\text{loss}}$  of binary and ternary devices. (b) EQE<sub>EL</sub> spectra. (c) Plots of the  $V_{\text{oc}}$  versus PCE of the dimer-based binary OSCs with high  $V_{\text{oc}}$  reported in the literature. (d)  $J_{\text{ph}}$  versus  $V_{\text{eff}}$  curves. (e)  $J_{\text{sc}}$  versus light intensity. (f) Hole and electron mobilities of devices.

DYO-1 can restrain the non-radiative recombination energy loss, thus resulting in an elevated  $V_{\rm oc}$  (0.882 V) in the ternary device in comparison with the PM6:L8-BO-X binary device (0.863 V).

As illustrated in Fig. 2c, the PM6:DYO-1 BHJ-based binary OSC exhibited an ultra-high  $V_{\rm oc}$  of 1.022 V, while maintaining the highest PCE of 15.1% (among the dimeric acceptor-based OSCs with  $V_{\rm oc} > 1.0$  V). Furthermore, the binary OSCs based on D18:DYO-1 and D18-Cl:DYO-1 blends showcased higher  $V_{\rm oc}$  values of 1.042 V and 1.067 V with  $E_{\rm loss}$  values of 0.523 eV and 0.496 eV (Tables S6 and S7, ESI†), respectively. These results confirm the success of the strategy of designing medium bandgap dimer acceptors for the enhancement of the  $V_{\rm oc}$  of OSCs.

To elucidate the role of DYO-1 in exciton dissociation and charge collection within the ternary device, the photogenerated current density  $(J_{\rm ph})$  versus effective voltage  $(V_{\rm eff})$  relationship was assessed. As displayed in Fig. 2d, both the binary and ternary devices exhibit a rapid increase in  $J_{\rm ph}$  with  $V_{\rm eff}$  at low voltage bias, saturating at  $V_{\rm eff} \sim 2$  V. The probabilities of exciton dissociation/charge collection  $(P_{\rm diss}/P_{\rm coll})$  were calculated to be 0.959/0.829, 0.982/0.917, and 0.981/0.924 for the PM6:DYO-1, PM6:L8-BO-X, and PM6:L8-BO-X:DYO-1 devices, respectively. The higher  $P_{\rm coll}$  of the ternary device indicates that the incorporation of DYO-1 promotes charge collection. To investigate the charge recombination in these devices, we measured the variation in  $J_{\rm sc}$  and  $V_{\rm oc}$  with light intensity  $(P_{\rm in})$ . As shown in Fig. 2e, the variation in  $J_{\rm sc}$  with  $P_{\rm in}$  follows the

power law  $J_{sc} \propto (P_{in})^{\alpha}$ , where  $\alpha$  approaching unity implies negligible bimolecular recombination. The PM6:L8-BO-X:DYO-1 ternary device exhibits the highest  $\alpha$  value of 0.992, denoting restrained bimolecular recombination.<sup>30</sup> The degree of trapassisted recombination was assessed by fitting the slope of  $V_{oc}$ *versus* the natural logarithm of  $P_{in}$ . As shown in Fig. S4 (ESI†), the calculated slopes (*n*) for the PM6:DYO-1, PM6:L8-BO-X and PM6:L8-BO-X:DYO-1 devices are 1.32, 1.17 and 1.12, respectively, suggesting that the trap-assisted recombination is effectively suppressed in the ternary device.<sup>31</sup>

Moreover, the PM6:L8-BO-X:DYO-1 based OSC features a shorter charge extraction time (0.33 µs) than the PM6:L8-BO-X based OSC (0.39  $\mu$ s), as observed in the transient photocurrent (TPC) decay curves (Fig. S5, ESI<sup>+</sup>). The shorter charge extraction time suggests that carriers are extracted more efficiently in the PM6:L8-BO-X:DYO-1 ternary device.<sup>32</sup> The charge transport properties of the binary and ternary devices were studied using the space-charge-limit current method (Fig. S6 and Table S8, ESI<sup>†</sup>). As shown in Fig. 2f, the addition of DYO-1 to the host system increased both the  $\mu_{\rm h}$  and  $\mu_{\rm e}$  from 7.12 imes 10<sup>-4</sup> cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> and 3.98  $\times$   $10^{-4}~\text{cm}^2~\text{V}^{-1}~\text{s}^{-1}$  in the PM6:L8-BO-X device to  $7.64 \times 10^{-4} \mbox{ cm}^2 \mbox{ V}^{-1} \mbox{ s}^{-1}$  and  $4.72 \times 10^{-4} \mbox{ cm}^2 \mbox{ V}^{-1} \mbox{ s}^{-1}$  in the PM6:L8-BO-X:DYO-1 device, respectively. Moreover, the ternary device exhibited a more balanced  $\mu_{\rm h}/\mu_{\rm e}$  ratio of 1.62 than the binary device, thus improving the  $J_{sc}$  and FF of the ternary devices.16



Fig. 3 Transient absorption spectra of PM6:DYO-1, PM6:L8-BO-X and PM6:L8-BO-X:DYO-1 blend films pumped with 800 nm. (a)–(c) 2D TAS images. (d)–(f) Corresponding TA spectra at different probe delay times. Normalized TAS dynamic curves probed (g) at 930 nm, (h) at 1030 nm, and (i) at 630 nm of PM6:L8-BO-X and PM6:L8-BO-X:DYO-1 blend films.

To further elucidate the impact of DYO-1 on the photophysical properties, we investigated the charge generation and recombination processes in the binary and ternary films using femtosecond transient absorption spectroscopy (fs-TAS).<sup>30</sup> An 800-nm laser was used to excite the neat films and blends. The 2D color transient absorption plots for the binary and ternary blend films are illustrated in Fig. 3a-c, and the corresponding TA spectra recorded at different probe delay times are displayed in Fig. 3d-f. The corresponding data for the neat films are depicted in Fig. S7 (ESI<sup>†</sup>). For the neat DYO-1 film and PM6:DYO-1 blend, as shown in Fig. S7a and Fig. 3a (ESI<sup>+</sup>), at early times, the positive near-infrared band peaking at 900 nm was assigned to the photo-induced absorption (PIA) of singlet excitons while the negative broadband in the 600-800 nm region was ascribed to ground state bleaching (GSB). For the neat L8-BO-X film and PM6:L8-BO-X blend (Fig. S7b and Fig. 3b, ESI<sup>†</sup>), at early times, the PIA of excitons is observed at 930 nm, and the GSB-induced bleaching zone at 600-900 nm. Different from the neat film, the charge transfer process from the acceptor to PM6 is indicated by a signal of PM6 GSB at 630 nm in the PM6:DYO-1 and PM6:L8-BO-X blends.33

Considering that the singlet exciton and polaron features partially overlap, we chose the signal at 1030 nm in the

PM6:L8-BO-X blend to represent polarons. Because of the relatively low content of DYO-1 in the PM6:L8-BO-X:DYO-1 ternary blend, we mainly discuss the excitation of PM6 and L8-BO-X. First, excitons of L8-BO-X show a longer lifetime in L8-BO-X:DYO-1 (Fig. S8, ESI<sup>+</sup>) than in L8-BO-X. Additionally, we compared the exciton dissociation rates in binary (PM6:L8-BO-X) and ternary (PM6:L8-BO-X:DYO-1) blends, as depicted in Fig. 3g. The ternary blend exhibits faster exciton dissociation before 10 ps, while a slower decay rate at the time scale of 10-1000 ps, possibly because of the polaron signal formed in DYO-1. Moreover, with the rising process of the polaron signal observed in Fig. 3h and Table S9 (ESI<sup>+</sup>), the ternary blend showed a faster charge generation rate ( $\tau_{avg}$  = 7.18 ps) than the binary blend ( $\tau_{avg}$  = 8.30 ps), possibly attributed to the optimization of phase separation and morphology after the introduction of DYO-1. We further studied the charge recombination process by observing the long-time GSB of PM6 as shown in Fig. 3i. At 2500 ps after excitation, the ternary blend maintains 80% of the peak value, whereas the binary blend maintains 71%. This observation largely indicates that there is less charge recombination and better charge transfer in the ternary blend.34

To further investigate the molecular orientation and packing motifs, the grazing-incidence wide-angle X-ray scattering (GIWAXS)



Fig. 4 (a)–(c) 2D GIWAXS patterns and (d) the corresponding OOP and IP line-cut profiles. (e)  $\pi$ – $\pi$  stacking distances and CL results in the OOP direction for the three blend films. (f) Statistical particle size distribution diagrams. (g)–(i) AFM-IR images of the three blend films.

signals of blend films were recorded in Fig. 4a-c, with the corresponding line-cut profiles presented in Fig. 4d. As shown in Fig. 4a-c, all blend films display a distinct (100) diffraction peak in the in-plane (IP) direction and a prominent (010) diffraction peak in the out-of-plane (OOP) direction, indicating a favorable face-on orientation of the molecular packing, which is beneficial for efficient charge transport along the vertical direction of the devices.<sup>20</sup> Additionally, in the OOP direction, the (010) peaks for PM6:DYO-1, PM6:L8-BO-X, and PM6:L8-BO-X:DYO-1 blends are located at 1.56, 1.65, and 1.62 Å<sup>-1</sup> (Table S10, ESI<sup> $\dagger$ </sup>), respectively, corresponding to the  $\pi$ - $\pi$  stacking distances (d-spacing) of 4.04, 3.81, and 3.87 Å (Fig. 4e), respectively. In comparison with the PM6:L8-BO-X binary blend film, the ternary blend film displays an increased *d*-spacing due to the incorporation of the dimeric acceptor DYO-1. However, the ternary blend film exhibits an elevated (010) crystallite coherence length (CL) value of 34.27 Å, compared to the PM6:L8-BO-X binary blend film, which has a CL of 31.95 Å along (010) in the OOP direction. This increased CL enhances charge transport and effectively reduces charge recombination within the ternary blend film, ultimately leading to a significant improvement in the device performance.<sup>29</sup>

Atomic force microscopy (AFM) was conducted to analyze the morphological differences between the binary and ternary blends. As presented in Fig. S9a–c (ESI<sup>†</sup>), PM6:DYO-1 exhibits the largest root-mean-square roughness ( $R_q$ ) of 1.37 nm. Both the PM6:L8-BO-X binary blend and the PM6:L8-BO-X:DYO-1 ternary blend exhibited smooth surfaces and successive phase separations with small R<sub>q</sub> values in the range of 0.90–1.00 nm, which benefited the establishment of efficient ohmic contacts with the electron transport layer (PNDIT-F3N).<sup>18</sup> Notably, the PM6:L8-BO-X:DYO-1 film exhibits a slightly increased nanofiber diameter (11.5 nm) than the PM6:L8-BO-X film (11.0 nm) as shown in Fig. 4f and Fig. S10 (ESI<sup>+</sup>), which provided effective pathways for exciton separation and charge generation in blend films,<sup>35</sup> where the sampled segments are from the phase diagrams shown in Fig. S9d-f (ESI<sup>†</sup>). We further employed AFM-based infrared (AFM-IR) spectroscopy to examine the fibril structures. The AFM-IR images revealed the donor (PM6) and acceptor distributions, as well as the fiber morphology by analyzing the infrared absorption peak at 2216 cm<sup>-1</sup> which is unique to the cyano ( $C \equiv N$ ) group in the acceptors (Fig. 4g-i, blue and red regions identified as PM6 and the acceptor, respectively). As shown in Fig. 4i, we note the PM6:L8-BO-X:DYO-1 blends exhibited a typical co-continuous interpenetrating network, facilitating exciton dissociation and charge transport. For the PM6:L8-BO-X binary film (Fig. 4h), the polymer donor was found to be dispersed into very small domains and enveloped by the acceptor domains, likely due to the excessive crystallinity of L8-BO-X. This resulted in a lack of sufficient donor/acceptor interfaces and continuous channels for efficient charge transport, leading to an inferior  $J_{sc}$ . As depicted in Fig. S11 (ESI<sup>†</sup>), by calculating the standard deviation, the average size of donor: acceptor domains for the binary and ternary blend films was found to be 78  $\pm$  38 nm and 38  $\pm$  20 nm, respectively. The results further demonstrated that the ternary blend films, upon



Fig. 5 (a)–(c) MD simulations of the structure of PM6:DYO-1, PM6:L8-BO-X, and PM6:L8-BO-X:DYO-1 systems. (d) Total stacking and face-on stacking counts per unit volume comparison for PM6:DYO-1, PM6:L8-BO-X, and PM6:L8-BO-X:DYO-1 systems.

the introduction of DYO-1, formed a better nanofiber interpenetrating network compared to their binary counterparts. The favorable morphology mediation induced by DYO-1 was primarily attributed to its good non-halogenated solvent processability and superior compatibility with the host L8-BO-X, enabling DYO-1 to disrupt the excessive aggregation of L8-BO-X and improve its morphology, thus favoring the enhancement of FF and  $J_{sc}$ .<sup>26</sup>

To conduct a more systematic study of molecular stacking, we performed molecular dynamics simulations on all the systems (Fig. 5a-c). We have divided donor PM6 into two segments, labeled C and E. The acceptor L8-BO-X has been divided into three segments, labeled A, D, and A', while the dimeric acceptor DYO-1 was divided into four segments, labeled F, A, D, and A' (Fig. S12, ESI<sup>†</sup>). Eight distinct packing conditions were identified. To illustrate the molecular packing scenarios, radial distribution functions (RDFs) between PM6 and acceptors were calculated.<sup>18</sup> The RDFs measure the probability of finding a particle some distance away from a reference particle, with a higher RDF peak pointing to a larger packing density. As shown in Fig. S13 (ESI<sup>+</sup>), all conditions demonstrated significant increases in the range of 3.8-4.0 Å, corresponding to the  $\pi$ - $\pi$  packing distances determined through GIWAXS analysis. This agreement between observed and measured packing distances confirms the accuracy of the computational models. Furthermore, it is worth noting that the RDF peaks (the first peak) of CD, CA' and EA' stacking in the PM6:L8-BO-X:DYO-1 ternary blend (blue solid lines) are markedly elevated in comparison with those observed in the PM6:L8-BO-X binary blend (blue dashed lines). According to relevant reports,<sup>18,36</sup> these results indicating a significant degree of  $\pi$ - $\pi$  interaction suggest that the addition of DYO-1 leads to enhanced structural ordering in the system.

To obtain a more detailed analysis of the amorphous forms studied in the present work, we characterized the dimer configurations arising from adjacent molecules. Specifically, we defined a dimer as a pair of molecules where the distance between the closest neighboring atoms is less than 5 Å. This characterization was based on two key parameters: the distance between the centers of mass (COM) of the molecular backbones (d), and the dihedral angle ( $\varphi$ ) between the planes of the two molecules. An arrangement is classified as a face-on orientation when the dihedral angle  $\varphi$  is less than 30° and the COM distance d is less than 0.8 nm. Typically, a face-on orientation promotes the most robust parallel  $\pi$ - $\pi$  stacking interactions, resulting in enhanced electronic coupling, which is indicative of an improved charge transfer rate. Fig. 5d and Tables S11 and S12 (ESI<sup>†</sup>) show the total stacking and face-on stacking counts per unit volume for each blend system. In the PM6:L8-BO-X system, the total stacking number is 201.84 per unit volume, whereas for the PM6:L8-BO-X:DYO-1 system, it is 152.96 per unit volume. Regarding face-on stacking, the PM6:L8-BO-X system has a stacking number of 36.43 per unit volume, while the PM6:L8-BO-X:DYO-1 system has a stacking number of 26.97 per unit volume. Although both the total stacking number and the face-on stacking number are slightly lower in the PM6:L8-BO-X:DYO-1 system compared to the PM6:L8-BO-X system, this reduction is an unavoidable consequence of the improved structural ordering in the PM6:L8-BO-X:DYO-1

system. It is reasonable to speculate that the incorporation of DYO-1 decreases the stacking density and improves the structural order, favoring the device performance.<sup>18,36</sup>

#### Conclusion

To summarize, we reported a medium bandgap dimeric acceptor DYO-1 by introducing electron-donating alkoxy side chains into the  $\beta$ -position of the thienothiophene unit to replace the alkyl chains for weakening the intramolecular charge transfer effect. DYO-1 showed an upshifted LUMO level and modest crystallinity, which translated to an impressive  $V_{\rm oc}$  of 1.022 V based on the PM6:DYO-1 blend film processed in an o-XY solvent while maintaining a satisfactory PCE of 15.1%, denoting the highest PCE reported to date for dimer-based OSCs with  $V_{\rm oc} > 1.0$  V. To fully harness the advantages of DYO-1, it was incorporated into the PM6:L8-BO-X host blend film as the third component. The results from UV-vis absorption, GIWAXS, AFM-IR, and molecular dynamics simulations indicate that DYO-1 effectively mitigates the excessive aggregation of small-molecule materials within the active layer, enabling morphological regulation, while simultaneously forming complementary absorption with the host blend film. Multidimensional enhancements in  $V_{\rm oc}$ , FF, and  $J_{\rm sc}$  caused by the above results support that the PM6:L8-BO-X:DYO-1 ternary OSC achieved an outstanding PCE of 19.6%, coupled with improved thermal stability. Additionally, a module device with an effective area of 13.5 cm<sup>2</sup>, processed using o-XY solvent spin-coating, achieved a PCE of 15.8%, showcasing its promising potential for large-area fabrication. This work underscores the transformative potential of medium bandgap dimeric acceptors in advancing high-performance and stable OSCs, highlighting the urgent demand for continued research and development to expedite the commercialization of OSCs.

#### Author contributions

B. Kan and Y. Chen designed the work plan for this research; B. Lan fabricated and optimized the devices with the help of J. Wang; S. Yuan synthesized the dimeric acceptor materials; W. Zhao performed the DFT calculation and MD simulation under the supervision of G. Long; W. Shi conducted the measurement of GIWAXS; Y. Zhong, J. Zhang, and K. Han performed and analyzed the femtosecond transient absorption spectroscopy measurements; O. A. Rakitin contributed to the material synthesis; and B. Lan wrote the draft manuscript. All the authors contributed to the revision of the manuscript.

#### Data availability

The data that support the findings of this study are available in the ESI† of this article.

#### Conflicts of interest

The authors declare no competing interests.

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