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Broader context

Dimeric acceptors have emerged as a promising alternative to small-molecular/polymeric acceptor-based OSCs due to their unique advantages such as welldefined structures, batch reproducibility, and excellent stability. Recently, we reported a series of 3D dimeric acceptors and achieved satisfactory PCEs with enhanced thermal/photostabilities for OSCs. However, these newly developed 3D dimeric acceptors exhibited a relatively twisted molecular skeleton and blueshifted absorption leading to undesired J_{sc} and FF in their OSCs. Herein, to overcome these drawbacks, two non-conjugated 3D dimeric acceptors (CH8-6 and CH8-7) were synthesized by linking two independent acceptors with a flexible linker, providing a feasible/effective strategy to preserve the properties of individual molecules as much as possible. As expected, the monomeric acceptor CH8-T and dimeric acceptor CH8-6 exhibited similar molecular properties. Benefiting from the better miscibility between the 3D dimeric acceptors and PM6, OSCs based on CH8-6 achieved a champion PCE of 19.2%, which is the highest value reported for OSCs based on oligomeric acceptors to date. More importantly, the 3D dimeric acceptors with flexible linkers exhibited not only excellent thermal stability but also enhanced mechanical durability. Thus, this study offers a facile and effective approach to develop high-performance, stable, and flexible dimeric acceptors.

^a 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

^b School of Materials Science and Engineering, National Institute for Advanced Materials, Nankai University, Tianjin 300350, China. E-mail: kanbin04@nankai.edu.cn

^c Division of Nano-Devices Research, Suzhou Institute of Nano-Tech and Nano-Bionics, Chinese Academy of Sciences, Suzhou 215123, China

^d School of Materials Science and Engineering, Tianjin Key Laboratory of Molecular Optoelectronic Science, Tianjin University, Tianjin 300072, China

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View Journal | View Rational design of flexible-linked 3D dimeric acceptors for stable organic solar cells

demonstrating 19.2% efficiency[†]

Zhe Zhang,^a Shaohui Yuan,^b Tianqi Chen,^b Jia Wang,^b Yuan-Qiu-Qiang Yi,^c Bin Zhao,^d Miaomiao Li, ^b^d Zhaoyang Yao, ^b^a Chenxi Li,^a Xiangjian Wan, ^b^a Guankui Long, ^b^b Bin Kan*^b and Yongsheng Chen ^b*^a

Despite substantial improvements in the power conversion efficiencies (PCEs) of organic solar cells (OSCs), achieving long-term stability still presents a formidable challenge to their commercial viability. Inspired by the efficient and stable 3D dimeric acceptors of the CH8 series, we developed two dimeric acceptors, CH8-6 and CH8-7, by linking two monomers with flexible alkyl linkers. Interestingly, both the monomeric acceptor CH8-T and dimeric acceptor CH8-6 exhibited similar optical and electronic properties, including molecular absorption, energy levels, packing, and crystallinity, indicating that the incorporated linkers exerted minimal influence on the molecular properties. Such linkers could facilitate morphological optimization, enabling CH8-6- and CH8-7-based binary OSCs to achieve a better PCE than their corresponding mono-like molecules. Furthermore, adding L8-BO to the binary OSCs facilitated appropriate phase separation and order packing, allowing PM6:CH8-6:L8-BO ternary OSCs to achieve a record-high PCE of 19.2% for oligomeric acceptors. Moreover, incorporating a flexible linker suppressed molecular diffusion, stabilizing the active-layer morphology. Consequently, PM6:CH8-6 binary OSCs exhibited excellent thermal stability, while PM6:CH8-6 flexible OSCs also demonstrated remarkable mechanical flexibility, maintaining 96% of their initial PCE even after 1200 bending cycles. Therefore, this study presents a feasible approach to improve the PCE, stability, and flexibility of OSCs simultaneously.

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1. Introduction

In recent decades, organic solar cells (OSCs) have garnered significant research attention as a new form of photovoltaic technology owing to their lightweight, transparency, and potential for large-scale production through roll-to-roll processes.¹⁻⁵ Moreover, the development of non-fullerene small-molecule acceptors (SMAs) with acceptor-donor-acceptor architectures has enabled state-ofthe-art OSCs to achieve power conversion efficiencies (PCEs) exceeding 19% in single-junction devices, approaching the threshold for their commercialization.⁶⁻¹⁰ However, one critical challenge hindering the widespread adoption of OSCs is their long-term stability.11,12 Generally, the deliberately tuned active-layer morphologies of OSCs exist in a thermodynamic non-equilibrium state and may approach thermodynamic equilibrium during long-term operations or at elevated temperatures.¹³ Such degradations are often caused by the demixing and self-aggregation of SMAs with high diffusion coefficients within the blend films.^{14–17} Therefore. improving the long-term stability of OSCs has become the primary focus for advancing their commercial viability.

To suppress the molecular diffusion of SMAs, Li et al.18 proposed a strategy involving polymerized small-molecule acceptors (PSMAs) synthesized by copolymerizing SMAs with different linkage units. While these PSMAs exhibit excellent mechanical flexibility, photostability, and thermal stability compared to SMAs, they are inevitably prone to structural defects and batch-to-batch variations,¹⁹⁻²¹ limiting their potential utility in OSCs. Consequently, new oligomeric acceptors have been developed recently as viable alternatives. These oligomeric acceptors combine the advantages of SMAs, such as well-defined molecular structures and good repeatability, with those of polymers, such as low diffusion coefficients and excellent stability.²² Furthermore, as alternatives to oligomeric acceptors with linear molecular skeletons, we have introduced a series of three-dimensional (3D) dimeric acceptors extending their linear skeletons into three dimensions.^{23,24} Interestingly, these 3D dimeric acceptors demonstrate extremely low reorganization energies, fibrillar-network film morphologies, and versatile processability. By exploiting these attributes of 3D dimeric acceptors, devices processed using both halogen and non-halogen solvents have demonstrated notable PCEs. More importantly, OSCs employing 3D dimeric acceptors with low molecular diffusion coefficients have exhibited satisfactory thermal and photostability. These promising outcomes suggest that 3D dimeric acceptors present feasible routes to simultaneously improve the efficiency and stability of OSCs.

However, conventional linkage units such as thiophene, selenophene, and benzodithiophene can lead to relatively larger dihedral angles between the independent wings and linkage units, further inducing intramolecular twisting.^{25,26} The resulting twisted conjugated backbones of oligomeric acceptors can disrupt the ordered intermolecular packing, consequently affecting the charge-transport properties and overall PCEs.^{27,28} Meanwhile, oligomeric acceptors that link SMAs with conjugated units are known to exhibit strong π - π interactions, leading to reduced solubilities to some extent. To ensure adequate solubilities of oligomeric acceptors, researchers often lengthen the alkyl chains

on their molecular backbones, ultimately deteriorating molecular packing and charge-transport behaviors.²² Owing to these issues, the PCEs of oligomeric acceptors are generally lower than those of SMAs. Remarkably, the incorporation of flexible alkyl linkage units into oligomeric acceptors effectively tunes the molecular conformation, crystallinity, and miscibility between oligomeric acceptors and polymer donors.^{29,30} This is because the flexible alkyl linkage units reduce the rigidity of the molecular backbone. weaken the strong intermolecular interactions, enhance solubility, and improve the miscibility between polymer donors and acceptors.³¹ Moreover, enhanced solubility promotes the shortening of other excessively long alkyl chains on the molecular backbone, thus improving the charge-transport properties.^{31,32} Furthermore, organic photovoltaic materials linked by flexible alkyl linkage units typically exhibit excellent mechanical properties due to the flexibility of the alkyl chains.^{33,34} As these flexible alkyl linkage units restrict the motion of SMAs, polymers and oligomeric acceptors with such units demonstrate enhanced longterm stability in devices.^{35–38} These observations prompted the incorporation of flexible alkyl linkage units into our newly developed 3D dimeric acceptors.

Thus, herein, we developed two 3D dimeric acceptors, CH8-6 and CH8-7, by introducing a flexible alkyl linker between the acceptors. To investigate the impact of the flexible alkyl linker on the molecular properties, the corresponding monomer, CH8-T, was also synthesized. Interestingly, CH8-6 and its monomer precursor CH8-T exhibited similar photoelectric properties, including molecular absorption, energy levels, packing, and crystallinity, indicating that the flexible linker minimally affected the molecular properties of the monomers. However, the linker enhanced the miscibility between the acceptors and PM6, allowing PM6:CH8-6 blend films to achieve a more uniform phase separation featuring a distinct bicontinuous network. Consequently, OSCs based on the two 3D dimeric acceptors achieved higher PCEs than those based on the monomers. Particularly, owing to efficient charge carrier transport and reduced recombination losses, PM6:CH8-6 binary devices achieved a champion PCE of 18.2%, with a J_{sc} of 26.23 mA cm⁻². Conversely, PM6:CH8-7 binary devices achieved a PCE of 17.7% with a lower $J_{\rm sc}$ of 24.97 mA cm⁻², owing to the narrow absorption range of CH8-7. To further improve the photovoltaic performance, L8-BO, featuring high crystallinity, was added to tune the aggregation behavior of the PM6:CH8-6 blend film, improving its active-layer morphology. The resulting PM6:CH8-6:L8-BO ternary devices achieved an enhanced PCE of 19.2%, the highest value reported for OSCs based on dimeric acceptors. Moreover, PM6:CH8-6 binary OSCs not only exhibited excellent thermal stability but also enhanced mechanical durability owing to the incorporation of a flexible linker. Consequently, the PM6:CH8-6-based flexible device retained 96% of its initial PCE even after 1200 bending cycles, showcasing superior performance compared to monomer-based flexible devices. Thus, this study offers a straightforward and efficient approach to develop 3D dimeric acceptors for constructing high-performance, stable, and flexible OSCs.

2. Results and discussion

Fig. 1a depicts the molecular structures of the newly developed 3D dimeric acceptors and the SMA, and Scheme S1 (ESI) displays the corresponding synthetic routes. Notably, following our previously reported procedure,^{23,24} both the dimeric acceptors (CH8-6 and CH8-7) and the SMA (CH8-T) were obtained in satisfactory yields. Furthermore, upon introducing a flexible alkyl linker, both the 3D dimeric acceptors demonstrated good solubility in organic solvents conventionally used for device processing. These 3D dimeric acceptors with enhanced solubility facilitated greater reduction in the lengths of alkyl chains on the N atom compared to other previously reported 3D dimeric acceptors.^{23,24,39,40} The chemical structures of these compounds were characterized by nuclear magnetic resonance spectroscopy and matrix-assisted laser desorption/ionization-time-of-flight mass spectrometry. Additionally, density functional theory calculations were performed on CH8-6, CH8-7, and CH8-T to elucidate the influence of the flexible alkyl linkers on the molecular geometry. As depicted in Fig. S1 (ESI[†]), the two monomers linked to the flexible alkyl linker in CH8-6 are almost perpendicular to each other, whereas those in CH8-7 are almost parallel. Meanwhile, both dimeric acceptors exhibit 3D structures, which are essentially the extensions of conventional linear molecular skeletons into three dimensions. Theoretically, such 3D molecules are expected to exhibit strong light-harvesting capabilities and superior charge recombination dynamics owing to their expanded conjugation planes.^{23,40,41} Notably, for CH8-6, CH8-7, and CH8-T, the dihedral angles between the thiophene and the central core were 18.49° , 27.79° , and 17.97° , respectively. Here, the planar molecular conformations observed for CH8-6 and CH8-T originate from the progressive strengthening of the non-covalent conformational locks induced by F–S secondary interactions.²³

Additionally, to evaluate the light-harvesting capacities of CH8-6, CH8-7, and CH8-T, their absorption spectra were recorded both in solution and as neat films, as presented in Fig. 1b and Fig. S2 (ESI⁺). In solution, the maximum absorption peaks of CH8-6, CH8-7, and CH8-T appeared at 774 nm, 767 nm, and 763 nm, respectively. A much higher molar extinction coefficient of \sim 3 \times 10⁵ M⁻¹ cm⁻¹ is achieved by CH8-6 and CH8-7 when compared to that of $\sim 2 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ for CH8-T. Evidently, both the 3D dimeric acceptors exhibited a red shift compared to CH8-T, potentially owing to pre-aggregation induced by the flexible alkyl linker.31,36 CH8-6, with its planar molecular conformation, exhibited a more pronounced red shift in its absorption than CH8-7 in solution. In the film form, CH8-6, CH8-7, and CH8-T displayed maximum absorption peaks at 817 nm, 806 nm, and 825 nm, respectively. Particularly, CH8-T exhibited the largest redshift $(\Delta \lambda)$ of 61 nm when transitioning from a solution to a film, indicating strong π - π stacking interactions and aggregation.⁴² Based on the film absorption edges of CH8-6, CH8-7, and CH8-T measured at 909, 895, and 919 nm, their corresponding optical bandgaps were found to be 1.36 eV, 1.39 eV, and 1.35 eV, respectively. In particular, CH8-6 and CH8-7 with flexible alkyl linkers demonstrated the most red-shifted absorption among previously reported 3D dimeric acceptors, thus enhancing their photon-



Fig. 1 (a) The molecular structures of CH8-6, CH8-7 and CH8-T, respectively; (b) the normalized absorption spectra of CH8-6, CH8-7 and CH8-T in the neat film; and (c) the energy level diagrams of PM6, CH8-6, CH8-7 and CH8-T. (d) Evolution of PL intensity as a function of temperature for CH8-6, CH8-7 and CH8-T films; and (e)–(g) the temperature-dependent PL spectra of CH8-6, CH8-7 and CH8-T films.

Table 1 Summary of physicochemical data of CH8-6, CH8-7 and CH8-T

Comp.	$\lambda_{\max}^{ m sol}$ (nm)	$\lambda_{\max}^{\mathrm{film}}$ (nm)	$\lambda_{ m edge}^{ m film}$ (nm)	$E_{\rm g}^{\rm onset}$ (eV)	HOMO (eV)	LUMO (eV)	E _a (meV)
CH8-6	774	817	909	1.36	-5.64	-3.85	86
CH8-7	767	806	895	1.39	-5.70	-3.83	96
CH8-T	763	825	919	1.35	-5.63	-3.83	69

collection efficiency.^{23,24} Notably, the optical bandgaps of these acceptors well satisfied the fundamental requirements for highperformance OSCs according to our previously proposed semiempirical model.⁴³ Particularly, CH8-7 demonstrated the most blue-shifted absorption among all acceptors, indicating weaker molecular interactions and aggregation, likely attributed to its less planar molecular structure.^{44,45}

Cyclic voltammetry was employed to estimate the energy levels of all acceptors and assess their electrochemical properties (Fig. S3, ESI⁺). Fig. 1c displays the energy level diagrams of PM6 and the acceptors. The lowest unoccupied molecular orbital and highest occupied molecular orbital energy levels of CH8-6, CH8-7, and CH8-T were determined to be -3.85 eV/-5.64 eV, -3.83 eV/-5.70 eV, and -3.83 eV/-5.63 eV, respectively (Table 1). Evidently, the energy levels of all acceptors exhibited only slight differences, implying that the flexible alkyl linker exerted a minimal impact on the energy. Generally, the energy offsets between polymer donors and acceptors range from 0.15 to 0.25 eV, providing adequate driving forces for charge separation. Next, temperature-dependent photoluminescence (PL) measurements were conducted to investigate the exciton dissociation kinetics of all acceptors in neat films⁴⁶ (Fig. 1e-g). As illustrated in Fig. 1d, decreasing the temperature increased the PL intensity of all acceptors, indicating that the decrease in temperature enhanced the recombination of charge carriers back to emissive excitons, leading to an increase in the PL intensity. Notably, for CH8-6, CH8-7, and CH8-T, the energy barrier $(E_{\rm a})$ for exciton dissociation into charge carriers was calculated by fitting the temperature dependence of the PL intensity using the equation

 $I(T) = I_0 / [1 + A \exp(-E_a / k_B T)],$

where I_0 is the intensity at 0 K, k_B represents the Boltzmann constant, and *T* denotes the temperature.⁴⁶ The E_a values for CH8-6, CH8-7, and CH8-T were estimated to be 86, 96, and 69 meV, respectively. Thus, CH8-6 and CH8-T possess similar E_a values, suggesting that vertically linking two SMAs with a flexible alkyl block does not significantly affect exciton dissociation. The slightly large E_a value of CH8-7 suggests hindrances in the exciton dissociation process, potentially impacting the J_{sc} of OSCs.

To investigate the effect of the flexible alkyl linker on the photovoltaic performance, we fabricated devices with conventional ITO/PEDOT:PSS/PM6:acceptors/PNDIT-F3N/Ag architectures. Fig. 2a and Table 2, respectively, present the corresponding current density *versus* voltage (J-V) curves of the PM6:acceptors and the photovoltaic parameters of the optimized devices. Detailed device parameters under various conditions are summarized in Tables S1–S7 (ESI†). As a result, control devices based on the monomer CH8-T exhibited a typical PCE of 17.0%, with an open-circuit voltage (V_{oc}) of 0.869 V, a J_{sc} of 25.92 mA cm⁻², and a fill factor (FF) of 75.4%. Compared to these CH8-T-based devices, both devices utilizing 3D dimeric acceptors linked by flexible alkyl linkers presented higher PCEs. The PM6:CH8-6-based devices achieved a notable PCE of 18.2%, along with an enhanced V_{oc} of 0.891 V, a high J_{sc} of 26.23 mA cm⁻², and an FF of 77.8%. For devices based on its isomer counterpart, CH8-7, a low J_{sc} of 24.97 mA cm⁻² contributed to a slightly lower PCE of 17.7%, despite the higher V_{oc} and FF values of 0.904 V and 78.3%, respectively.

To further investigate the disparities in the current densities of OSCs, their external quantum efficiency (EOE) spectra were recorded. As illustrated in Fig. 2b, the CH8-6-, CH8-7-, and CH8-T-based devices exhibited distinct photoelectric conversion ranges. Among these devices, those based on CH8-7 exhibited the narrowest photoelectric conversion range with a photoresponse of 300 to 900 nm, accounting for their lowest Jsc. Notably, for the CH8-7-based devices, the value of J_{sc} integrated from the EQE values was only 24.43 mA cm⁻². Devices based on CH8-T displayed a broader but lower photoresponse range from 300 to 1000 nm, whereas those based on CH8-6 presented a higher photoresponse from 300 to 950 nm. Hence, CH8-T- and CH8-6-based devices exhibited similar integrated J_{sc} values of 25.30 and 25.44 mA cm^{-2} , respectively. The integrated photocurrent densities for all devices aligned well with the J_{sc} values obtained from the J-V curves, supporting their differences in the $J_{\rm sc}$ values.

To investigate the effect of the flexible linkers on stability, the thermal stability of the devices based on the monomer or dimer was evaluated (Fig. 2c). For this, the unencapsulated devices were subjected to thermal stress under continuous heating at 65 °C in a nitrogen-filled glovebox. Under these conditions, the PM6:CH8-6-based devices could maintain approximately 88% of their initial PCEs after 500 h. Conversely, devices based on their corresponding monomer (CH8-T) underwent rapid degradation under the same conditions. This difference could be attributed to the immobilization effect induced by the dimer, which suppressed the diffusion of molecules to maintain the morphology of the active layer^{31,36,38} Meanwhile, energy-loss analysis was conducted to examine the influence of the flexible alkyl linker on Voc. As depicted in Fig. 2d and Table S8 (ESI†), although devices based on CH8-7 exhibited a high V_{oc} , they presented the highest total energy loss (ΔE) of 0.518 eV, primarily owing to a substantial non-radiative energy loss (ΔE_3) of 0.202 eV. In contrast, the devices based on CH8-6 presented the smallest ΔE_3 of 0.187 V, resulting in a low energy loss of 0.508 eV. This reduced non-radiative recombination energy loss (ΔE_3) observed in CH8-6-based devices may be attributed to their unique 3D structures elucidated in our previous reports.23,40

To further evaluate the influence of flexible alkyl linkers on exciton dissociation and carrier generation, we evaluated the dependence of the photocurrent density $(J_{\rm ph})$ on the effective voltage $(V_{\rm eff})$,⁴⁷ and the corresponding results are depicted in Fig. 2e. The exciton dissociation probability $(\eta_{\rm diss})$ was calculated using $\eta_{\rm diss} = J_{\rm sc}/J_{\rm sat}$, and the charge collection efficiency

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Fig. 2 (a) J-V curves of PM6:CH8-6, PM6:CH8-7 and PM6:CH8-T based OSCs; (b) EQE spectra of PM6:CH8-6, PM6:CH8-7- and PM6:CH8-T based OSCs; (c) thermal stability of PM6:CH8-6- and PM6:CH8-T based OSCs without encapsulation in a nitrogen-filled glove box at 65 °C; (d) E_{loss} and three detailed parts of ΔE_1 , ΔE_2 and ΔE_3 values of OSCs; (e) $J_{\text{ph}}-V_{\text{eff}}$ curves of OSCs; (f) J_{sc} vs. light intensity of OSCs; (g) V_{oc} vs. light intensity of OSCs; (h) transient photocurrent measurements of OSCs; (i) hole and electron mobilities of OSCs.

Table 2 Summary of optimal photovoltaic parameters of OSCs with conventional device structures. The average parameters in parentheses were calculated from at least 10 independent devices

Active layer	$V_{\rm oc}$ (V)	$J_{\rm sc}~({ m mA~cm^{-2}})$	$J_{\rm sc}^{\rm EQE}$ (mA cm ⁻²)	FF (%)	PCE (%)
PM6:CH8-6	$0.891~(0.887\pm0.002)$	$26.23~(26.26\pm0.16)$	25.44	77.8 (76.6 \pm 0.7)	$18.2~(17.8\pm0.2)$
PM6:CH8-7	$0.904~(0.899\pm0.004)$	$24.97(24.93 \pm 0.21)$	24.43	78.3 (77.7 \pm 0.7)	$17.7(17.4 \pm 0.2)$
PM6:CH8-T	$0.869(0.859 \pm 0.005)$	$25.92(25.86 \pm 0.29)$	25.30	$75.4(74.6 \pm 0.5)$	$17.0(16.6 \pm 0.3)$
PM6:L8-BO	$0.872(0.873 \pm 0.002)$	$26.66(26.43 \pm 0.18)$	25.61	$80.1(79.9 \pm 0.3)$	$18.6(18.4 \pm 0.1)$
PM6:CH8-6:L8-BO	$0.884~(0.884\pm 0.002)$	$27.46~(27.46\pm0.22)$	26.72	78.6 (78.4 \pm 0.3)	$19.2~(19.0\pm0.2)$

 $(\eta_{\rm coll})$ was determined from the ratio $\eta_{\rm coll} = J_{\rm ph}/J_{\rm sat}$, where $J_{\rm sat}$ denotes the saturated photocurrent density, and $J_{\rm ph}$ represents the photocurrent density at the maximum power output point. The $\eta_{\rm diss}/\eta_{\rm coll}$ values for the CH8-6-, CH8-7-, and CH8-T-based devices were found to be 0.98/0.87, 0.97/0.87, and 0.96/0.86, respectively. The highest $\eta_{\rm diss}/\eta_{\rm coll}$ value for the CH8-6-based device suggests efficient charge generation and exciton dissociation, leading to high $J_{\rm sc}$ values. Notably, the monomeric CH8-T-based devices demonstrated the lowest $\eta_{\rm diss}/\eta_{\rm coll}$ values, explaining their low EQE response values. To probe the charge recombination behavior of these devices, the dependence of $J_{\rm sc}$ on the light intensity ($P_{\rm light}$)⁴⁸ was tested (Fig. 2f). The $J_{\rm sc}$ versus $P_{\rm light}$ dependency curves of all devices presented slopes close to

unity, indicating negligible and minimal bimolecular recombination in the devices. Next, we tested the dependence of $V_{\rm oc}$ on the light intensity $(P_{\rm light})^{48}$ for all devices (Fig. 2g). In this regard, the PM6:CH8-6-based devices presented a lower slope value (n = 1.01) compared to the PM6:CH8-7- (1.04) and PM6:CH8-T- (1.09) based devices. This indicates that the PM6:CH8-6-based devices demonstrate lower trap-assisted charge recombination, which potentially contributes to their superior photovoltaic performances. Furthermore, transient photocurrent methods were employed to investigate the charge extraction processes of the OSCs.⁴⁹ Fig. 2h shows that the PM6:CH8-6-based devices exhibited a shorter charge extraction time (0.19 µs) compared to the PM6:CH8-7- (0.28 µs) and

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PM6:CH8-T- $(0.29 \ \mu s)$ based devices, suggesting that the PM6:CH8-6-based devices feature enhanced exciton dissociation, favorable charge carrier transport, and lower trap recombination losses.

Next, to elucidate the influence of the flexible alkyl linker on the charge-transport properties, we employed the space-chargelimited current method to measure the carrier mobilities of the blend films. As depicted in Fig. 2i, both the electron (μ_e) and hole (μ_h) mobilities of the PM6:CH8-6-based blend films $(4.38 \times 10^{-4} \text{ and } 5.22 \times 10^{-4} \text{ cm}^{-2} \text{ V}^{-1} \text{ S}^{-1}$, respectively) surpassed those of the PM6:CH8-7-based (3.91 \times 10⁻⁴ and $4.41 \times 10^{-4} \text{ cm}^{-2} \text{ V}^{-1} \text{ S}^{-1}$, respectively) and PM6:CH8-T-based blend films (3.02 \times 10^{-4} and 3.83 \times 10^{-4} cm^{-2} V^{-1} $S^{-1},$ respectively), which is conducive to swifter charge extraction and reduced charge accumulation, leading to improved photovoltaic performance. The corresponding $\mu_{\rm h}/\mu_{\rm e}$ ratios were 1.20, 1.13, and 1.27 for the PM6:CH8-6-, PM6:CH8-7-, and PM6:CH8-Tbased blend films, respectively. The more balanced charge transport observed for the PM6:CH8-7-based blend film may account for its higher FF.50 Importantly, both the dimeric acceptors, as well as the monomeric acceptors, exhibit comparable mobilities, suggesting that dimeric acceptors incorporating a flexible alkyl linker can retain the charge-transport capacities of monomers to the greatest extent.

Furthermore, to probe the effect of the flexible alkyl linker on the molecular packing behaviors of neat and blend films, grazing-incidence wide-angle X-ray scattering (GIWAXS) analysis was conducted.^{51,52} Fig. S4 and Table S9 (ESI[†]), respectively, display the 2D patterns of the films and the corresponding 1D line-cut profiles of the neat films. Evidently, all neat films exhibit a dominant face-on orientation, as evidenced by the prominent (010) diffraction peak in the out-of-plane (OOP) direction, as well as sharp (100) diffraction peaks in the inplane (IP) direction. The *d*-spacings and coherence lengths (CLs) of the (100) peaks along the IP direction were measured to be 19.94 and 27.32 Å, 20.46 and 36.02 Å, and 19.93 and 19.57 Å for the CH8-6, CH8-7, and CH8-T neat films, respectively (Fig. S10, ESI[†]). The larger d-spacings and CLs in the CH8-7 films could be attributed to the longer alkyl chains on the N atom in CH8-7. Additionally, for the CH8-6, CH8-7, and CH8-T neat films, the *d*-spacings and CLs of the (010) peaks along the OOP direction were 3.72 and 16.30 Å, 3.75 and 15.88 Å, and 3.66 and 16.73 Å, respectively. Thus, both dimeric acceptors exhibited slightly larger *d*-spacings than the monomeric acceptors.



Fig. 3 (a)–(c) 2D GIWAXS patterns of the optimized blend films of PM6:CH8-6, PM6:CH8-7 and PM6:CH8-T; (d) line cuts of GIWAXS images of the blend films in the out-of-plane (OOP) direction; (e) the *d*-spacing and coherence length of (010) in the OOP direction for PM6:CH8-6, PM6:CH8-7 and PM6:CH8-7 blend films; (f) Statistical distribution of the fiber diameters for PM6:CH8-6, PM6:CH8-7 and PM6:CH8-T blend films; and (g)–(i) AFM phase images of PM6:CH8-6, PM6:CH8-7, and PM6:CH8-7

The similar CLs of the CH8-6 and CH8-T films suggest that incorporating the alkyl chain linker does not significantly influence molecular stacking.

After blending with PM6, all blend films still maintained a clear face-on orientation (Fig. 3a–c). As depicted in Fig. 3d and Table S9 (ESI†), for the PM6:CH8-6, PM6:CH8-7, and PM6:CH8-T blend films, the *d*-spacings and CLs of the (010) peaks along the OOP direction were 3.65 and 18.98 Å, 3.70 and 17.14 Å, and 3.63 and 19.77 Å, respectively. Compared with the PM6:CH8-7 blend films, those containing PM6:CH8-6 featured a shorter *d*-spacing and larger CL of the (010) peak, indicating higher crystallinity and tighter π – π packing, thus resulting in superior photovoltaic performance (Fig. 3e). Notably, both the PM6:CH8-6 and PM6:CH8-T blend films demonstrated similar *d*-spacings and CLs of the (010) peaks, and hence, the dimers and monomers presented very similar charge-transport properties.

Atomic force microscopy (AFM) was subsequently employed to measure the phase separations of the PM6:CH8-6-, PM6:CH8-7-, and PM6:CH8-T blend films, and the corresponding AFM phase images are presented in Fig. 3g-i. As evident, the blend films displayed distinct and uniform phase separation with bundle-like fibrous aggregates. Notably, the expected domain size of the phase separation ranged between 10 and 20 nm, which could be advantageous for exciton dissociation and charge transportation and lead to enhanced photovoltaic performance of OSCs.⁵³ Subsequently, the diameters of the nanofibers were estimated using the AFM phase images. As presented in Fig. S6 and S7 (ESI[†]) and Fig. 3f, the nanofiber diameters for the PM6:CH8-6, PM6:CH8-7, and PM6:CH8-T blend films were estimated to be 11.7 \pm 3.2, 14.3 \pm 6.6, and 14.9 \pm 5.9 nm, respectively. The relatively smaller phase separation observed in the PM6:CH8-6 blend films could result in closer contact between the donor/acceptor (D/A) interface, thus facilitating exciton dissociation and leading to a high J_{sc} . To understand the impact of the flexible alkyl linker on the phase separation size within the active layer, we assessed the surface tension (γ) and miscibility between PM6 and acceptors by measuring the contact angles of the materials (Fig. S8, ESI⁺). The miscibility between the donor and acceptor was assessed using the Flory-Huggins interaction parameter (γ). Here, a low γ indicated better miscibility between the donor and acceptor, resulting in small phase separation and an increased density of D/A interfaces within the blend films.⁵⁴ Specifically, the χ values for the PM6:CH8-6, PM6:CH8-7, and PM6:CH8-T blend films were 0.213, 0.271, and 0.348 K, respectively (Table S11, ESI⁺). Notably, the enhanced miscibility between PM6 and CH8-6 could lead to smaller phase separation. The observations outlined above indicate that incorporating a flexible alkyl linker could effectively tune the crystalline behavior, enhance the miscibility between the donor and acceptor, and improve the morphology of the active layer, ultimately leading to improved performance.

Given that flexible linkers can improve the mechanical durability of devices, the mechanical robustness of the blend films was tested using the film-on-elastomer method.^{55–57} Fig. 4a depicts the shapes and propagation patterns of cracks in the three blend films. As displayed in Fig. 4b, the crack onset strains (COSs) on the PM6:CH8-6, PM6:CH8-7, and PM6:CH8-T blend films were 40.2%, 41.9%, and 28.3%, respectively. The higher COS value observed for the dimeric acceptors underscores the advantages of flexible linkers in improving the mechanical properties of devices. Subsequently, flexible devices with a PEN/ITO/PEDOT:PSS/active layer/PNDIT-F3N/Ag configuration were fabricated. Fig. 4c displays the *J*–V curves of these flexible devices, while Table S12 (ESI†) provides detailed

Fig. 4 (a) Optical micrographs of the formed cracks of PM6:CH8-6, PM6:CH8-7 and PM6:CH8-T blend films by stretching on PDMS substrates at their respective crack-onset strains; (b) histograms of crack-onset strain (COS) of three blend films; (c) *J*–*V* curves of PM6:CH8-6-, PM6:CH8-7- and PM6:CH8-T-based flexible devices; and (d) normalized PCE value for the flexible all-PSC as a function of bending cycles with a radius of 5 mm.



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photovoltaic parameters. The PM6:CH8-6-based flexible device exhibited a PCE of 16.2%, higher than those of the PM6:CH8-7based (15.8%) and PM6:CH8-T-based (15.9%) devices. Following this, the flexible devices were subjected to bending tests with a bending radius of 5 mm to investigate their mechanical stability. As depicted in Fig. 4d, both the CH8-6- and CH8-7based flexible devices maintained over 96% of their initial PCEs after 1200 consecutive bending cycles. However, the CH8-Tbased flexible devices could only retain approximately 92% of their initial PCEs after 600 bending cycles. This diminished performance can be attributed to the pronounced phase separation between the rigid polymer donor and the monomer under external stress. For the CH8-6- and CH8-7-based flexible devices, the flexible linker could impart some flexibility, thereby alleviating the stress induced during bending and resulting in a stable morphology with PCE retention.³¹

To further enhance the $J_{\rm sc}$ and FF values of CH8-6-based devices, L8-BO was introduced as a guest component into the PM6:CH8-6 host active layer. As depicted in Fig. 5a, the performance of the ternary OSCs initially improved but later deteriorated with increasing L8-BO content. The ratio of CH8-6:L8-BO

was optimized to 10:3. As presented in Fig. 5b and Table 2, the ternary devices achieved an impressive PCE of 19.2%, along with an enhanced $J_{\rm sc}$ of 27.63 mA cm⁻² and FF of 78.6%. Remarkably, this PCE of 19.2% represents the highest value reported for OSCs based on oligomeric acceptors (Fig. 5c and Table S13, ESI†). Compared with the PM6:CH8-6 binary devices, the PM6:CH8-6:L8-BO ternary devices exhibited a greater photoresponse from 700 to 850 nm, along with a higher integrated $J_{\rm sc}$ of 26.72 mA cm⁻², which was presumed to be the major factor contributing to the significantly improved performance of the ternary devices (Fig. 5d).

To delineate the differences between the charge carrier dynamics of binary and ternary devices, we assessed the dependencies of $J_{\rm ph}$ on $V_{\rm eff}$ and $J_{\rm sc}$ on $P_{\rm light}$. As presented in Fig. 5e and f, the CH8-6-based devices demonstrated efficient charge generation, exciton dissociation, and reduced charge recombination, all of which contributed to a high $J_{\rm sc}$ and FF. Furthermore, to elucidate the effect of L8-BO on the molecular packing, aggregation, and crystallization behaviors of the blend films, GIWAXS analysis was also conducted. Fig. 5g and Fig. S9 (ESI[†]) display the 2D patterns and 1D extracted profiles of the



Fig. 5 (a) PCEs of PM6:CH8-6:L8-BO ternary devices with different amounts of L8-BO; (b) J-V spectra of PM6:CH8-6:L8-BO based OSCs; (c) statistical PCE vs. J_{sc} of the OSCs based on oligomeric acceptors; (d) EQE spectra of PM6:CH8-6:L8-BO-based OSCs; (e) $J_{ph}-V_{eff}$ curves of PM6:CH8-6:L8-BO based OSCs; (f) J_{sc} vs. light intensity of PM6:CH8-6:L8-BO based OSCs; (g) 2D GIWAXS patterns of the optimized blend film of PM6:CH8-6:L8-BO; (h) AFM phase image of the PM6:CH8-6:L8-BO blend film; (i) statistical distribution of the fiber diameter for the PM6:CH8-6:L8-BO blend film.

blend films. As depicted, the PM6:CH8-6:L8-BO films displayed clear (010) peaks along the OOP direction and (100) diffraction peaks along the IP direction, indicating good retention of the preferred face-on orientation of the PM6:CH8-6:L8-BO blend film. As summarized in Table S9 (ESI[†]), the PM6:CH8-6:L8-BO blend film exhibited a shorter π - π stacking distance and an improved π - π coherence length compared to the PM6:CH8-6 blend film, both of which are conducive to charge transport and reduced charge recombination in the ternary devices. Additionally, the morphologies of the PM6:CH8-6:L8-BO ternary blend films were characterized by AFM (Fig. S10, ESI[†] and Fig. 5h). As depicted in Fig. 5i, for the PM6:CH8-6:L8-BO ternary blend films, the diameter of the nanofibers was 12.3 \pm 3.3 nm. The larger sizes of the nanofibers observed in the PM6:CH8-6:L8-BO ternary blend films compared to those in the PM6:CH8-6 films can be attributed to the enhanced crystallinity of L8-BO. These relatively larger nanofibers in PM6:CH8-6:L8-BO can facilitate charge transport and retard charge recombination, ultimately leading to improved J_{sc} and FF values for the PM6:CH8-6:L8-BO ternary devices.23

3. Conclusions

Thus, in this study, two non-fully conjugated dimeric acceptors (CH8-6 and CH8-7) were developed by linking two monomers with a flexible alkyl linker. Interestingly, the monomeric acceptor CH8-T and dimeric acceptor CH8-6 exhibited similar molecular absorption, energy levels, energy barriers (E_a) , molecular packing and crystallinity behaviors, implying that incorporation of non-conjugate linkers exerts minimal effects on the molecular properties. Notably, the flexible alkyl linkage units in CH8-6 enhance its miscibility with PM6, creating a uniform phase separation morphology with a distinct bi-continuous network in the blend film. Consequently, the PM6:CH8-6based binary device achieved a high PCE of 18.2%, along with a $V_{\rm oc}$ of 0.891 V, a high $J_{\rm sc}$ of 26.23 mA cm⁻², and an FF of 77.8%. Adding L8-BO as the third component further optimized the molecular packing and crystallinity, leading to more suitable phase separation and improved device performance. Ultimately, the resulting PM6:CH8-6:L8-BO-based ternary devices achieved a record-high PCE of 19.2%. Devices based on the CH8-6 dimeric acceptor also presented excellent thermal stability owing to inhibited molecular diffusion. Moreover, incorporating the flexible linker provided some flexibility to the dimeric acceptors, potentially alleviating mechanical stress and enhancing mechanical durability. Finally, flexible photovoltaic devices based on PM6:CH8-6 exhibited a notable PCE of 16.2% and maintained 96% of its initial PCE even after 1200 bending cycles. Thus, this study offers a facile and effective approach to develop high-performance, stable, and flexible dimeric acceptors.

Author contributions

Z. Zhang and B. Kan designed the work plan for this research; Z. Zhang and S. Yuan carried out the synthetic works; B. Kan carried out most of the device fabrication and measurements. Z. Zhang and S. Yuan performed UV-Vis, CV, and contact angle measurements; T. Chen and B. Kan performed charge recombination, TPC and SCLC measurements; T. Chen and J. Wang performed the EL, EQE_{EL} and sEQE experiments and analyzed the data. G. Long carried out the theoretical computation of the three acceptors. Y. Yi performed GIWAXS characterization and analyzed the data. B. Zhao and M. Li performed mechanical characterization and analysis; B. Kan, Z. Yao, C. Li, and X. Wan supervised and directed this project; Z. Zhang and B. Kan wrote the draft manuscript. All authors discussed the results and commented on the manuscript. Y. Chen mentored the other authors throughout the whole research.

Data availability

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

Conflicts of interest

The authors declare no conflict of interest.

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