Solar Cells

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Complete Peripheral Fluorination of the Small-Molecule Acceptor in Organic Solar Cells Yields Efficiency over 19%

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Abstract: Due to the intrinsically flexible molecular skeletons and loose aggregations, organic semiconductors, like small molecular acceptors (SMAs) in organic solar cells (OSCs), greatly suffer from larger structural/ packing disorders and weaker intermolecular interactions comparing to their inorganic counterparts, further leading to hindered exciton diffusion/dissociation and charge carrier migration in resulting OSCs. To overcome this challenge, complete peripheral fluorination was performed on basis of a two-dimensional (2D) conjugation extended molecular platform of CH-series SMAs, rendering an acceptor of CH8F with eight fluorine atoms surrounding the molecular backbone. Benefitting from the broad 2D backbone, more importantly, strengthened fluorine-induced secondary interactions, CH8F and its D18 blends afford much enhanced and more ordered molecular packings accompanying with enlarged dielectric constants, reduced exciton binding energies and more obvious fibrillary networks comparing to CH6F controls. Consequently, D18:CH8F-based OSCs reached an excellent efficiency of 18.80%, much better than that of 17.91 % for CH6F-based ones. More excitingly, by employing D18-Cl that possesses a highly similar structure to D18 as a third component, the highest efficiency of 19.28 % for CH-series SMAs-based OSCs has been achieved so far. Our work demonstrates the dramatical structural multiformity of CH-series SMAs, meanwhile, their high potential for constructing record-breaking OSCs through peripheral fine-tuning.

Introduction

Organic solar cells (OSCs) have achieved a surging power conversion efficiency (PCE) in the past few years,^[1] whereas the state-of-the-art device still lags far behind its inorganic counterparts (like crystalline silicon, perovskite, etc.).^[2] The inner reason may be attributed to the intrinsically flexible molecular skeletons of organic materials and also quite loose aggregations by means of van der Waals forces, $\pi-\pi$ interactions, halogen bonds, etc. instead of covalent bonds that widely exist in inorganic materials. These characteristics determine that organic light-harvesting materials are confronted with several insurmountable barriers: (1) insufficient intermolecular interaction strength due to inadequate overlap of p-orbital electron clouds; this will generally lead to localized excitons with a very small radius less than 1 nm but relatively large binding energy more than 0.3 eV.^[3] Therefore, the exciton diffusion through Förster or Dexter energy transfers^[4] and even charge carrier migration through a hoping mechanism will be hindered. (2) less molecular packing/crystalline ordering; contrary to the spatial lattice with conspicuous periodicity in inorganic materials, there are lots of crystal defects or amorphous domains hidden in aggregated organic ones, giving rise to plenty of scattering/ recombination sites for excitons and charges.^[5] Therefore, it is plausible to observe reduced carrier mobility by several orders of magnitude in organic materials comparing to that of inorganic ones, whereas the quite opposite is charge recombination rates.^[6] Based on these discussions, strengthening intermolecular packing and also crystalline ordering of light harvesting donors or acceptors could be very crucial if more efficient OSCs are really expected.^[7] In spite of the absence of clear structure-activity relationship currently, a simple but logical pathway to synergistically enhance the multiple forces that bounding organic molecules together

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should be introducing sufficient heteroatoms, especially halogens, on peripheral active sites of molecules, and more important or at least as important is two-dimensional (2D) conjugated extension of molecules' backbone. The former could be favor of constructing multiple secondary or non-covalent interactions through diverse weak bonds of X...H, X...S, X... π , etc. (X represents halogen atoms),^[8] while the latter will contribute to more compact π - π stacking by means of rigid and broad 2D conjugated backbones.^[9] Both of them could work together to strengthen intermolecular interactions greatly and further result in delocalized excitons on neighboring stacked molecules,^[10] constrictive density of states of vibration energy levels,^[11] facilitated carrier migrations and suppressive recombination,^[7b] etc.

Among a series of homomorphic halogen elements, fluorine that featuring with the smallest atomic radius but largest electronegativity, has successfully exerted positive influences on energy levels, absorptions, intermolecular π - π stackings and nanoscale film morphologies of small molecular acceptors (SMAs) without bringing about too much steric hindrance.^[12] In addition, lots of theoretical studies have also manifested that peripheral fluorination is conducive to minimizing the exciton binding energy $(E_{\rm b})$ of SMAs, thus accomplishing highly efficient exciton dissociation even with quite a small driving force.^[13] In light of the huge success in improving performance of OSCs through peripheral fluorination,^[14] much more efficient SMAs can be really expected if more or complete peripheral fluorinations are further implemented. Given the dominant role of electron-withdrawing terminals in effective intermolecular packings for some well-known SMAs like ITIC analogs,^[12a] it is no surprise the fluorination mainly takes place on terminal units (such as 1,1-dicyanomethylene-3-indanone containing two fluorine atoms) at present. However, when endeavoring to further increase fluorine density on terminals, the mismatched energy levels (especially markedly down-shifted lowest unoccupied molecular orbitals, LU-MOs) and thus decreased open circuit voltages (V_{∞}) are usually inevitable.^[15] This should be attributed to the great electron-deficient capacity of fluorine atom that origins from the largest electronegativity and effective $p-\pi$ conjugation with molecular skeletons. However, renewed hope emerges in exploration of high-performance Y-series SMAs.^[1e] These SMAs have not only demonstrated a distinctive molecular packing that involving their central units greatly, but also manifested the dominant role of central units in establishing a desirable three-dimensional (3D) intermolecular packing network.^[16] In a similar fashion, it should be highly possible to further optimize intermolecular packings of SMAs by performing fluorinations on central units of Y-series SMAs more than terminals. Unfortunately, another insurmountable challenge arises from the absence of active sites on central unit (benzothiadiazole) of Y-series SMAs, thus leaving the feasible methodology to increase peripheral fluorine density on molecular backbones still an unaddressed issue.

The truly turning moment lies on the high-performance CH-series SMAs explored by our group recently (Figure S1).^[7b,9a, 14a] These featured SMAs have demonstrated

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their dramatical structural multiformity, especially sufficient peripheral active sites for chemical modifications on their central units. Note that the 2D conjugation extended backbones of CH-series SMAs well meet the criterion to strength intermolecular π - π stacking (discussed above) and have manifested their great effectiveness in reducing $E_{\rm b}$, facilitating charge migration and suppressing recombination dynamics, etc.^[17] However, what really excites us is that the intermolecular packing modes and strengths could be easily tuned through even a quite minor structural adjustment on central units, for example, employing different halogens.^[14b] This unique feature of CH-series SMAs allows us to maximize the advantages of peripheral fluorination while circumventing its weaknesses on energy level, if introducing much more peripheral fluorine on central units (even complete fluorination) not merely on terminals. Bearing these thoughts in mind, on basis of a 2D conjugation extended molecular platform of CH-series SMAs, complete fluorination on peripheral active sites was performed, rendering an acceptor of CH8F (Figure 1a) with eight fluorine atoms surrounding the molecular backbone. Benefitting from the broad 2D molecular backbone, more importantly, strengthened fluorine-induced secondary interactions, CH8F affords much enhanced and more ordered molecular packings accompanying with enlarged dielectric constants (ε_r), reduced E_b and facilitated charge migration comparing to its CH6F controls (Figure 1a). When employing D18 as the donor part, more obvious fibrillary network can be observed in blends of D18:CH8F. This renders more favorable photodynamic and thus an excellent PCE of 18.80%, much better than that of 17.91% for D18:CH6Fbased one. More excitingly, by adopting D18-Cl that possesses a highly similar structure to D18 as a third component, the highest efficiency of 19.28 % for CH-series SMAs-based OSCs has been achieved so far along with an encouraging long-term stability. This work further manifested the huge potential of CH-series SMAs for constructing record-breaking OSCs by means of peripheral microstructural adjustments.

Results and Discussion

The influence of complete peripheral fluorination on frontier molecular orbitals was firstly unveiled by density functional theory (DFT) calculations. As illustrated in Figure 1b and S2, CH6F and CH8F both displayed a relatively planar geometry but quite different dipole moments (1.34 Debye for CH6F and 2.67 Debye for CH8F). The large dipole moment of CH8F is expected to induce more compact stacking of adjacent molecules, thus in favor of more efficient charge migration and improved fill factor (FF) of OSCs.^[1k] In addition, the polarizability of complete fluorinated phenazine (150.87 Bohr³) is comparable but slightly larger than that of its difluorinated analog (149.15 Bohr³). The enlarged polarizability will contribute to an increased ε_r and electron mobility of CH8F in theory (see detailed discussions below).^[17] The highest occupied molecular orbitals (HOMOs) and LUMOs mainly locate along

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Figure 1. (a) Chemical structures of CH6F and CH8F. (b) Molecular frontier orbital distributions. The HOMO and LUMO energy levels were illustrated for a clear comparison. (c) Electrostatic surface potential (ESP) maps. (d) Theoretical density difference $\triangle Q$ ($\triangle Q = \Psi^2_{LUMO} - \Psi^2_{HOMO}$) along molecular backbones.

molecular backbones, with the most distribution on central donors and electron-deficient terminals, respectively, suggesting an effective intramolecular charge transfer (ICT).^[18] As it can be expected that the HOMO and LUMO energy levels downshifted by 50 and 30 meV, respectively, varying from CH6F to CH8F. This should be attributed to the decreasing of electron-donating ability of CH8F, especially on its phenazine central unit, which can be confirmed by electrostatic surface potential (ESP) maps shown in Figure 1c. In spite of four electron-withdrawing fluorine atoms assembling on central unit of CH8F, an obvious A-D-A architecture can be still observed with the characteristic peak-valley-peak shape of frontier orbital charge density differences (ΔQ) (Figure 1d and S3). Such an A-D-A feature could endow with SMAs favorable molecular stacking, better photodynamic, decreased energy losses and eventually improved device performance with respect to some other types of SMAs.^[19] Notably, as we have discussed above, the degree of LUMO down-shifting is quite small (only $\approx 30 \text{ meV}$) for complete peripheral fluorination on central units of CH-series SMAs rather than the conventional fluorination on end groups ($\approx 150 \text{ meV}$).^[15] In this way, the advantages of peripheral fluorination over molecular packings, exciton dissociations, charge migrations, etc. can be really maximized whilst circumventing its weaknesses on LUMO energy levels and device V_{oc} .

The synthetic route to CH8F was described in Scheme S1 and the prepared details including characterized

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data/spectra were illustrated in Supporting Information. Both molecules exhibit a comparable but high decomposition temperature (T_d) of 324 degree for CH6F and 326 degree for CH8F (Figure S4). The HOMO/LUMO energy levels of CH6F and CH8F derived from cyclic voltammetry (CV) measurements are -5.74/-3.77 eV and -5.78/-3.80 eV, respectively (Figure 2a and S5), which roughly agree with the theoretically calculated results. The energy gaps can be rendered as 1.97 eV for CH6F and 1.98 eV for CH8F, thus resulting in blue-shifted absorptions of CH8F in both solutions and solid states (Figure 2b). Additionally, the enlarged molar extinction coefficients for CH8F could be observed in both solid films $(1.52 \times 10^5 \text{ cm}^{-1})$ and solutions $(1.84 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1})$, comparing to that of CH6F with 1.37×10^5 cm⁻¹ in films and 1.41×10^5 M⁻¹ cm⁻¹ in solutions (Figure S6), demonstrating the enhanced light harvesting capacity of CH8F with complete peripheral fluorination. More peripheral fluorination on SMAs is also expected to improve their electron-transporting ability that could be regarded as one of the most crucial indicators for material evaluations. Therefore, the electron mobility (μ_e) of CH6F and CH8F neat films were measured by applying the spacecharge limited current (SCLC) method (Figure S7). A statistically larger μ_e can be achieved by CH8F comparing to that of CH6F (Figure 2c), demonstrating its superiority of CH8F as electron-transporting acceptors. Note that the enlarged μ_e should be greatly determined by the more favorable molecular packing behaviors of CH8F. Hence, we

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Figure 2. (a) Energy levels derived from CV measurements. (b) UV/Vis spectra in solutions and solid films. (c) Electron mobility of neat films. (d, e) 2D GIWAXS patterns of neat films, respectively. (f) Line-cut profiles of CH6F and CH8F neat films. (g) Time-resolved photoluminescence (PL) decay traces. (h) E_b derived from temperature-dependent PL spectra. (i) ε , as a function of frequency measured by impedance spectroscopy.

resorted to grazing-incidence wide-angle X-ray scattering (GIWAXS) to unveil the effects of complete peripheral fluorination on molecular packing strength and ordering (Figure 2d and 2e).^[20] As plotted line-cut profiles in Figure 2f and summarized parameters in Table S1, both CH6F and CH8F demonstrated a favorable face-on packing orientation, indicated by the strong (010) peaks in the outof-plane (OOP) direction. Interestingly, CH8F possesses a smaller intermolecular π - π stacking distance of 3.72 Å than that of 3.79 Å for CH6F, meanwhile, enlarged crystal coherence lengths (CCLs) in both OOP and in-plane (IP) directions (Table S1). This suggests the generally enhanced molecular packing and ordering for CH8F, which should account for the improved electron transportation of CH8F films and further manifest the advantages of more fluorine on central unit of CH-series SMAs. Moreover, the quadrupole moment components of CH6F and CH8F in three spatial dimensions were also calculated. As illustrated in Figure S8, the quadrupole moment of CH8F in each dimension $(Q_{xx} = -680.46, Q_{yy} = -479.12, Q_{zz} = -441.00 \text{ D})$ is stronger than that of CH6F $(Q_{xx} = -672.34, Q_{yy} = -462.79,$ $Q_{zz} = -434.10$ D), which should be partially responsible for the preferable intermolecular packing and charge carrier dynamic of CH8F.^[21] As we have discussed above, the

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compact and ordered molecular packings could efficaciously delocalize the vibrational relaxation of photogenerated excitons on adjacent tacked molecules,^[10] thus contributing to shrunken density of states (DoS) of excited molecular vibrations, prolonged exciton lifetimes (τ) and reduced $E_{\rm b}$.^[9a] It is thus plausible to observe that CH8F affords a slightly larger τ of 1.8 ns than that of 1.7 ns for CH6F (Figure 2g), meanwhile, a much reduced E_b of 16.5 meV comparing to that of 54.2 meV for CH6F (Figure 2h and S9). It is interesting that the $E_{\rm b}$ s of isolated CH8F is 1.639 eV, slightly larger than that of 1.630 eV for CH6F (Table S2). Therefore, the greatly decreased $E_{\rm b}$ for CH8F in solid films comparing to CH6F should be attributed to the enhanced intermolecular interactions of CH8F after complete peripheral fluorination. Note that such a favorable feature of photogenerated excitons could facilitate efficient exciton dissociation with a really small driving force, moreover, suppressed nonradiative recombination of charge transfer (CT) states.[11a,22] Moreover, CH8F-based neat films achieve a slightly larger ε_r than that of CH6F-based ones (Figure 2i and S10), agreeing well with the larger dipole moment and stronger intermolecular interaction of CH8F. Meanwhile, a much larger ε_r of \approx 5.0 can be afforded by D18:CH8F blends comparing to that of ≈ 3.2 for D18:CH6F, which could be conducive to improved charge generation/migration in theory and endow with D18:CH8F-based OSCs a better FF and short-circuit current density (J_{sc}) .

Our previous works have highlighted the great effectiveness in optimizing intermolecular packing modes of CHseries SMAs just by a minor structural modification on central units.^[14] In addition, the more compact and ordered molecular packings for CH8F unveiled by GIWAXS have already implied its quite different molecular packing modes from CH6F. Therefore, single-crystal X-ray diffraction measurements were carried out to shed light on the variations of molecular packing modes after complete peripheral fluorination.^[23] As illustrated in Figure S11, both SMAs of CH6F and CH8F afford a featured banana-shape and helical geometry. The N–S distances between nitrogen on phenazine and sulfur on adjacent thiophene are ranging from 3.2 to 3.4 Å, slightly smaller than the van der Waals radii (≈ 3.55 Å) of nitrogen and sulfur. The existing N–S noncovalent interactions could further rigidify the planar molecular skeletons of CH-series SMAs, thus leading to smaller reorganization energies with respect to other type of SMAs.^[17] Both single crystals of CH6F and CH8F could be classified as triclinic systems (see Table S3 for details). More importantly, the distinctive and highly desirable 3D molecular packing networks were well formed (Figure 3a), which have been proven to facilitate charge migration in resulting OSCs greatly.^[9a,16,24] Although the rectangle-shaped voids were observed for both CH6F and CH8F, the size of voids for CH8F could be estimated as $\approx 18.4 \times 17.6$ Å, generally smaller than that of $\approx 24.9 \times 15.1$ Å for CH6F. This may contribute to an enlarged molecular packing density and



Figure 3. (a) Single-crystal packing topological structures of CH6F and CH8F on the top view. (b) Intermolecular packing modes. E, b and C represent end, bridge and central units, respectively. (c) π - π stacking distances of interlayer including all the main molecular packing modes.

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 ε_r ,^[25] agreeing well with the discussions above (Figure 2f and 2i).

Notably, the formed 3D molecular packing networks are extensively involved with both central and end units, thus the complete peripheral fluorination on central unit should give rise to much different intermolecular packing modes. As illustrated in Figure 3b, four main packing modes can be observed for CH6F including dual end to bridge mode (dual E/b), end to end and central to central mode (E/E + C/C)and two types of end to end modes (E/E), which have been fully discussed in our previous work.^[14b] As regards to CH8F with complete peripheral fluorination, three packing modes were afforded, being dual end to central mode (dual E/C), dual central to bridge mode (dual C/b) and only one type of "E/E" mode. The less intermolecular packing modes for CH8F comparing to CH6F may decrease the disorder of molecular packing and be conducive to more favorable charge transportation/recombination dynamic. Among them, "dual E/C" for CH8F and "dual E/b" for CH6F with relatively large intermolecular packing potentials over 150 kJ/mol (Table S4) were widely observed in CH-series SMAs but merely existing in some other materials. More interestingly, all the three intermolecular packing modes for CH8F demonstrate the overall reduced π - π stacking distances ("E/E" mode: 3.36 Å, "dual E/C" mode: 3.35 Å, "dual C/b" mode: 3.37 Å) than that of CH6F ("E/E-1" mode: 3.47 Å, "E/E-2" mode: 3.45 Å, "dual E/b" mode: 3.50 Å, "E/E + C/C" mode: 3.43 Å). This should be ascribed to the stronger secondary interactions induced by more peripheral fluorination on CH8F. The smaller π - π stacking distance in CH8F crystals is in good accordance with GIWAXS results and accounts for its improved electron mobility. The conclusion of fluorine-induced reduction of π - π stacking distances can be further confirmed by CH7F molecules that containing seven fluorine atoms surrounding molecular backbones (Figure S12). As displayed in Figure S13, CH7F possesses much more intermolecular packing modes due to its unsymmetrical structure. The general π - π stacking distances for CH7F fall in between CH8F and CH6F, manifesting the dominant role of fluorine in strengthening intermolecular packing of SMAs.

To sum up, the main advantage of complete peripheral fluorination, especially on central units not merely end units, could be concluded as followings: (1) only slightly down-shifted LUMO energy levels of SMAs, thus avoiding the significantly decreased $V_{\rm oc}$ in resulting OSCs; (2) enlarged

dipole moment and greatly enhanced molecular packing strength/ordering, which could contribute to a large ε_r and further facilitated charge migrations; (3) prolonged exciton lifetime and reduced E_b that are conducive to achieving efficient exciton dissociation with a small driving force and suppressing non-radiative recombination of CT states.

Given that complete peripheral fluorination has been proved to possess so many advantages, an excellent device performance is really expected for OSCs based on CH8F. When blending with a well-matched polymer donor D18 (Figure S14),^[26] D18:CH6F-based OSCs afforded a good PCE of 17.91 %, accompanied by a $V_{\rm oc}$ of 0.895 V, a $J_{\rm sc}$ of $26.02\;\text{mA}\,\text{cm}^{-2}$ and an FF of 76.89% (Table 1). As regards to D18:CH8F-based OSCs, the comparable $V_{\rm oc}$ (0.899 V) and $J_{\rm sc}$ (26.01 mA cm⁻²), however, greatly superior FF (80.38%) and PCE (18.80%) can be observed comparing to D18:CH6F-based ones. More excitingly, the best PCE of 19.28% is further rendered by introducing D18-Cl (Figure S14),^[27] which has a highly similar structure to D18 but downshifted HOMO energy level, as the third component. Note that the 19.28 % PCE has reached the best value for CH-series SMAs-based OSCs thus far and also ranked among the first-class OSCs currently. In addition, we also evaluated the photovoltaic performance of D18:CH7F-based OSCs, which afford an excellent PCE of 18.43 % accompanied by a $V_{\rm oc}$ of 0.896 V, a $J_{\rm sc}$ of 26.08 mA cm⁻² and an FF of 78.85% (Figure S15 and Table S5). For D18-Cl:CH8F-based binary OSCs, a PCE of 17.85 % with a V_{oc} of 0.922 V, a J_{sc} of 25.07 mA cm^{-2} and an FF of 77.21 % is delivered (Figure S16 and Table S5). The detailed device fabrication and optimization data were presented in Supporting Information (Table S5–S13), and the best current density-voltage (J-V)curves of CH6F- and CH8F-based OSCs were shown in Figure 4a. The obvious enlarged FF for CH8F-based OSCs should be attributed to their improved charge migration, which caused by more compact and ordered packings of CH8F. The external quantum efficiencies (EQEs) were recorded and displayed in Figure 4b. The integrated $J_{sc}s$ were calculated as 25.01, 25.24 and 25.93 mA cm⁻² for D18: CH6F-, D18:CH8F- and D18:D18-Cl:CH8F-based OSCs, respectively, matching well with their J-V tests. Despite of the blue-shifted absorption of CH8F comparing to CH6F, the overall improved EQEs for CH8F-based OSCs still contributed to a larger integrated J_{sc} . Note that EQEs are usually determined by multiple factors, such as light harvesting, charge generation/transport/recombination, etc. Consid-

Table 1: Summary of photovoltaic parameters for OSCs.[a]

Active layers	V _{oc} (V)	J _{sc} (mA cm ⁻²)	Cal. $J_{sc}^{[b]}$ (mA cm ⁻²)	FF (%)	PCE (%)
D18:CH6F	0.895	26.02	25.01	76.89	17.91
	(0.887±0.005)	(26.25±0.31)		(75.61±1.07)	(17.61±0.18)
D18:CH8F	0.899	26.01	25.24	80.38	18.80
	(0.898±0.002)	(25.94±0.11)		(80.31±0.17)	(18.70±0.07)
D18:D18-Cl:CH8F	0.909	26.81	25.93	79.10	19.28
	(0.908 ± 0.004)	(26.72 ± 0.16)		(78.78 ± 0.21)	(19.12 ± 0.09)

[a] Average parameters derived from 15 independent OSCs (Table S9–S13). [b] Current densities by integrating EQE plots.

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Figure 4. (a) J-V curves for OSCs. (b) EQE plots and integrated J_{sc} curves. (c) PL spectra of neat and blend films indicating efficiencies of PL quenching. (d) J_{ph} versus V_{eff} curves indicating η_{diss} and η_{coll} . (e) Light intensity (P_{light}) dependence of V_{oc} . (f) EQE_{EL} plots of OSCs.

ering their comparable ability of light harvesting, the facilitated photodynamic should be responsible for the enlarged EQEs and improved PCEs for CH8F-based OSCs (see the detailed discussions below). Moreover, the PCEs of both D18:CH8F- and D18:D18-Cl:CH8F-based OSCs could be retained over 90% with respect to their initial values after \approx 1500 h at room temperature and \approx 500 h at 65 °C (Figure S17). The excellent storage and thermal stabilities of CH8F-based OSCs along with their remarkable PCEs provide the great potentials for large scale production.

In order to unveil the inner reasons of better EQEs and FFs for CH8F-based OSCs, a comprehensive investigation has been performed. Firstly, exciton dissociation efficiency (P_{diss}) was roughly estimated by measuring the PL quenching of blended films (Figure 4c). The excellent P_{diss} s of ≈ 98 % were achieved by CH8F-based devices, however, only \approx 94% for CH6F-based ones. Then, $P_{\rm diss}$ and charge collection efficiency (P_{coll}) were further evaluated by plots of photocurrent density $(J_{\rm ph})$ versus effective voltage $(V_{\rm eff})$ (Figure 4d). The derived P_{diss} keep the same tendency to that afforded by PL measurements. Meanwhile, slightly improved P_{coll} s of $\approx 89\%$ can be also rendered by CH8Fbased OSCs, comparing to that of ≈ 87 % for CH6F-based ones. In light of the comparable ability in light harvesting (Figure S18), the enlarged EQEs for CH8F-based OSCs should mainly attributed to the facilitated charge generation/collection dynamics. On one hand, the better P_{diss} for CH8F-based OSCs can be ascribed to two aspects: (1) the downshifted HOMO of CH8F, which provides a larger driving force for exciton dissociation in theory; (2) the reduced $E_{\rm b}$ and prolonged exciton lifetime that caused by its favorable molecular packing behaviors. On the other hand, the larger charge mobility for CH8F blends (Figure S19) should account for the improved P_{coll} for CH8F-based OSCs and also be mainly responsible for their improved FFs comparing to that of CH6F. Additionally, by measuring the

The improved device performances for CH8F-based OSCs should be closely associated to their better nanoscale morphology of blended films. Therefore, atomic force microscopy (AFM) and transmission electron microscopy (TEM) were further employed to monitor the film morphology. Both blended films of D18:CH6F and D18:CH8F were featured with a uniform and relatively smooth surface (Figure S21). Meanwhile, obvious nanoscale fibrillary networks can be also afforded (Figure 5a), which has been proven to facilitate charge migration and suppress charge recombination effectively. By performing a statistical analysis of nanofiber size (Figure S22), a gradually enlarged fiber size can be observed as 14.8 and 16.8 nm for D18:CH6F and D18:CH8F, respectively, suggesting the enhanced molecular crystallinity for D18:CH8F. The TEM images in Figure S23 further confirmed the fibrillar network structures in all blended films.

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dependence of V_{oc} and J_{sc} on light intensity (Figure 4e and S20), S/(kT/q) for D18:CH6F-, D18:CH8F- and D18:D18-Cl: CH8F-based OSCs were rendered as 1.27, 1.23 and 1.18, respectively, suggesting stepwise suppressed trap-assisted charge recombination.^[28] Whereas the very similar α values closing to unit were observed for all three OSCs, indicating the negligible bimolecular recombination.^[29] The EQEs of electroluminescence (EQE_{EL}) for D18:CH6F-, D18:CH8Fand D18:D18-Cl:CH8F-based devices were displayed in Figure 4f and the non-radiative energy losses of OSCs could be estimated as 0.195, 0.177 and 0.174 eV, respectively (see Supporting Information for the calculation details).^[22a] The decreased non-radiative energy losses for CH8F-based OSCs should be attributed to multiple factors including the larger $\varepsilon_{\rm r}$, reduced $E_{\rm b}$, and more importantly, better molecular packing and nanoscale film morphology. All of them highlight the superiority of complete peripheral fluorination on SMAs.

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Figure 5. (a) AFM phase images of blended films. (b) Statistical distribution of fibril diameters. (c) 2D GIWAXS patterns of blended films. (d) Extracted line-cut profiles from 2D GIWAXS patterns of blended films.

When considering the selection of third component, the extra induction that does not greatly change the already perfect micromorphology should be crucially important. Therefore, besides the fine-tuning energy levels, the molecules with similar structure and good miscibility to the existing components in blends should be really promising. As shown in Figure S24 and Table S14, an excellent miscibility between D18 and D18-Cl can be indicated by a very small Flory-Huggins interaction parameters (γ) of 0.03.^[30] Therefore, it is reasonable to observe the similar fibrillary networks and fiber size (17.3 nm) between D18: D18-Cl:CH8F and D18:CH8F (Figure 5a and 5b). In addition, $\chi_{D:A}$ for D18:CH8F (0.23) is larger than that of 0.17 for D18:CH6F, indicating less D/A miscibility after complete peripheral fluorination. This may be ascribed to the stronger secondary interactions between neighboring SMAs caused by sufficient fluorine atoms on molecular backbone of CH8F and also agrees well with the enlarged fiber size in D18:CH8F blends.

The molecular packing behaviors in blended films were further investigated by measuring their GIWAXS patterns (Figure 5c). All the blended films exhibited a pronounced (010) diffraction peaks at 1.64 Å⁻¹ for D18:CH6F, 1.66 Å⁻¹ for D18:CH8F and 1.67 Å⁻¹ for D18:D18-CI:CH8F in OOP directions and sharp (100) diffraction peaks locating at ≈ 0.30 Å⁻¹ in IP directions (Figure 5d), demonstrating the preferential face-on molecular stacking orientation with respect to substrates. The smaller π - π stacking distance of ≈ 3.76 Å for CH8F-based blends can be afforded comparing to that of 3.83 Å for CH6F-based one. Moreover, the slightly larger CCLs for D18:CH8F (31.42 Å) and D18:D18-CI:

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CH8F (33.26 Å) can be also observed than that of 29.76 Å for D18:CH6F (Table S15), indicating more ordered molecular packings in CH8F-based blends. The slightly larger CCL for D18:D18-Cl:CH8F comparing to D18:CH8F may be ascribed to the relatively better crystallinity of D18-Cl, which was suggested by the more obvious change of the maximum absorption peaks from high temperature to low (Figure 6a and S25).^[31] Generally, the more compact molecular π - π stacking and improved packing ordering for CH8F-based blends should response for their facilitated charge migration and much better FFs in resulting OSCs.

As we have mentioned above, D18 and D18-Cl demonstrate a very good miscibility due to their highly similar molecular structures. This makes the already perfect micromorphology for D18:CH8F blend was maintained to the maximum extent after introduction of D18-Cl. Another interesting point is that a slightly enlarged fiber size of 16.6 nm can be observed for D18:D18-Cl blend with respect to that of ≈ 15.5 nm for both D18 and D18-Cl (Figure 6b and S26), demonstrating the overall enhanced molecular crystalline after introducing D18-Cl. The featured lattices for D18 and D18-Cl with a spacing of ≈ 0.24 and 0.21 nm, respectively, disappeared in D18:D18-Cl blend and a newly lattice spacing of ≈ 0.38 nm emerged (Figure 6c). This suggests that D18 and D18-Cl seem to stack with each other evenly and thus form a well-mixed phase in resulting OSCs. Moreover, the enhanced intermolecular packing with a π - π stacking distance of 3.88 Å can be also rendered by wellmixed D18:D18-Cl phase, comparing to individual D18 and D18-Cl with comparable π - π stacking distances of 3.95 and 3.93 Å, respectively (Figure 6d and S27, Table S16). This

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Figure 6. (a) Temperature-dependent UV/Vis spectra of D18, D18-Cl and D18:D18-Cl solutions at a range of 500–600 nm. (b) Statistical distribution of fibril diameters for D18, D18-Cl and D18:D18-Cl blend. (c) High resolution transmission electron microscopy images with the roughly estimated lattice spacings. (d) Extracted line-cut profiles of from 2D GIWAXS patterns of D18, D18-Cl and D18:D18-Cl films. (e) Fibril diameter analysis based on AFM images of D18:D18-Cl blends with different ratios. (f) Variation of π - π stacking distances and CCLs for (010) peaks in OOP directions.

rational combination of D18/D18-Cl could also be applied in other high-performance systems and has the huge potential for yielding record-breaking OSCs. In addition, the blended ratios of D18 and D18-Cl have also been screened systemically. Figure 6e demonstrates the fiber sizes variation for D18:D18-Cl:CH8F blends with different D18/D18-Cl ratios and the statistically largest fiber size can be achieved at a D18/D18-Cl ratio of 0.6/0.4 (see Figure S28 for details). Furthermore, the smallest π - π stacking distance and the largest CCL were also achieved at the same ratio of 0.6/0.4 (Figure 6f and S29, Table S17). All the results above agree with the best composition of D18/D18-Cl that has provided the champion PCE of 19.28 % in this work.

Conclusion

In order to conquer the great challenges of insufficient intermolecular packings and less crystalline ordering of SMAs, complete fluorination on peripheral active sites was performed on basis of a 2D conjugation extended molecular platform of CH-series SMAs, rendering an acceptor of CH8F with eight fluorine atoms surrounding the molecular backbone. As unveiled by both single crystal and GIWAXS analysis, CH8F possesses the much enhanced and more ordered molecular packings comparing to its CH6F control, which are mainly benefitting from the broad 2D conjugated backbone, more importantly, strengthened fluorine-induced secondary interactions and larger dipole moment. This favorable molecular packing behavior of CH8F gives rise to the enlarged dielectric constant, prolonged exciton lifetime and reduced exciton binding energy. All of these advantages could contribute to facilitated charge generation/migration and suppressed charge recombination in theory. When blending with a matched donor D18, the favorable molecular packing features of CH8F can be remained, thus providing more obvious fibrillary networks with relatively larger fiber size than that of CH6F blends. Consequently, D18:CH8F-based OSCs reached an excellent efficiency of 18.80%, much better than that of 17.91% for CH6F-based one. More excitingly, by employing D18-Cl that possesses a highly similar structure to D18 as a third component, the highest efficiency of 19.28% for CH-series SMAs-based OSCs has been achieved so far. Furthermore, a comprehensive investigation of nanoscale morphology has suggested that D18 and D18-Cl seem to stack with each other evenly and thus form a well-mixed phase with enhanced intermolecular π - π stacking and crystalline ordering in resulting blends, which mainly accounts for the improved PCE of ternary OSCs. Our work demonstrates the great potentials of CH-series SMAs for constructing record-breaking OSCs through peripheral adjustments, at the same time, will stimulate more innovative explorations in light of the dramatical structural multiformity.

Supporting Information

The Supporting Information is available free of charge, including materials synthesis, device characterization and stability measurements, charge mobility, CV, UV/Vis spectra, NMR and HR-MS spectra (Figure S30–S43), additional tables, *etc.*

Author Contributions

Z. Y., X. C. and X. B. contributed equally to this work. The synthetic works were carried out by X. B.; the device optimizations and measurements were carried out by X. C.; T. H. and G. L. performed the DFT calculations. Y. C. and Z. Y. conceived and directed the study, wrote the manuscript. Y. L., X. J., H. L., B. K., X. W., C. L. et al. helped to analyze the data and commented on the manuscript.

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Conflict of Interest

The authors declare no competing interests.

Data Availability Statement

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

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- [1] a) C. W. Tang, Appl. Phys. Lett. 1986, 48, 183-185; b) G. Yu, J. Gao, J. C. Hummelen, F. Wudl, A. J. Heeger, Science 1995, 270, 1789-1791; c) Y. Lin, J. Wang, Z.-G. Zhang, H. Bai, Y. Li, D. Zhu, X. Zhan, Adv. Mater. 2015, 27, 1170-1174; d) L. Meng, Y. Zhang, X. Wan, C. Li, X. Zhang, Y. Wang, X. Ke, Z. Xiao, L. Ding, R. Xia, H.-L. Yip, Y. Cao, Y. Chen, Science 2018, 361, 1094-1098; e) J. Yuan, Y. Zhang, L. Zhou, G. Zhang, H.-L. Yip, T.-K. Lau, X. Lu, C. Zhu, H. Peng, P. A. Johnson, M. Leclerc, Y. Cao, J. Ulanski, Y. Li, Y. Zou, Joule 2019, 3, 1140-1151; f) 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, 656-663; g) K. Jiang, J. Zhang, C. Zhong, F. R. Lin, F. Qi, Q. Li, Z. Peng, W. Kaminsky, S.-H. Jang, J. Yu, X. Deng, H. Hu, D. Shen, F. Gao, H. Ade, M. Xiao, C. Zhang, A. K. Y. Jen, Nat. Energy 2022, 7, 1076-1086; h) C. Duan, L. Ding, Sci. Bull. 2020, 65, 1231-1233; i) Z. Zheng, J. Wang, P. Bi, J. Ren, Y. Wang, Y. Yang, X. Liu, S. Zhang, J. Hou, Joule 2022, 6, 171-184; j) C. Dou, X. Long, Z. Ding, Z. Xie, J. Liu, L. Wang, Angew. Chem. Int. Ed. 2016, 55, 1436-1440; k) S. Li, C. He, T. Chen, J. Zheng, R. Sun, J. Fang, Y. Chen, Y. Pan, K. Yan, C.-Z. Li, M. Shi, L. Zuo, C.-Q. Ma, J. Min, Y. Liu, H. Chen, Energy Environ. Sci. 2023, 16, 2262-2273; l) Y. Ma, M. Zhang, S. Wan, P. Yin, P. Wang, D. Cai, F. Liu, Q. Zheng, Joule 2021, 5, 197–209; m) K. Chong, X. Xu, H. Meng, J. Xue, L. Yu, W. Ma, Q. Peng, Adv. Mater. 2022, 34, 2109516; n) Y. Liu, Z. Zhang, S. Feng, M. Li, L. Wu, R. Hou, X. Xu, X. Chen, Z. Bo, J. Am. Chem. Soc. 2017, 139, 3356-3359; o) 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, 1180-1190; p) H. Wang, C. Cao, H. Chen, H. Lai, C. Ke, Y. Zhu, H. Li, F. He, Angew. Chem. Int. Ed. 2022, 61, e202201844; q) H. Sun, B. Liu, Y. Ma, J.-W. Lee, J. Yang, J. Wang, Y. Li, B. Li, K. Feng, Y. Shi, B. Zhang, D. Han, H. Meng, L. Niu, B. J. Kim, Q. Zheng, X. Guo, Adv. Mater. 2021, 33, 2102635.
- [2] S. Zhang, F. Ye, X. Wang, R. Chen, H. Zhang, L. Zhan, X. Jiang, Y. Li, X. Ji, S. Liu, M. Yu, F. Yu, Y. Zhang, R. Wu, Z. Liu, Z. Ning, D. Neher, L. Han, Y. Lin, H. Tian, W. Chen, M. Stolterfoht, L. Zhang, W.-H. Zhu, Y. Wu, *Science* 2023, 380, 404–409.
- [3] D. Beljonne, G. Pourtois, C. Silva, E. Hennebicq, L. M. Herz, R. H. Friend, G. D. Scholes, S. Setayesh, K. Müllen, J. L. Brédas, *Proc. Natl. Acad. Sci. USA* **2002**, *99*, 10982–10987.
- [4] K. Feron, X. Zhou, W. J. Belcher, P. C. Dastoor, J. Appl. Phys. 2012, 111, 044510.
- [5] N. F. Mott, Trans. Faraday Soc. 1938, 34, 500-506.
- [6] I. Ramirez, M. Causa', Y. Zhong, N. Banerji, M. Riede, Adv. Energy Mater. 2018, 8, 1703551.
- [7] a) H. Chen, H. Lai, Z. Chen, Y. Zhu, H. Wang, L. Han, Y. Zhang, F. He, Angew. Chem. Int. Ed. 2021, 60, 3238–3246;

5213773, 2023, 44, Downloaded from https://onlinelibrary.wiley.com/doi/10.1002/anie.202312630 by Nankai University, Wiley Online Library on [25/11/2023]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

Angew. Chem. Int. Ed. 2023, 62, e202312630 (10 of 11)

b) H. Chen, Y. Zou, H. Liang, T. He, X. Xu, Y. Zhang, Z. Ma, J. Wang, M. Zhang, Q. Li, C. Li, G. Long, X. Wan, Z. Yao, Y. Chen, *Sci. China Chem.* **2022**, *65*, 1362–1373.

- [8] a) L. Yan, H. Zhang, Q. An, M. Jiang, A. Mahmood, M. H. Jee, H.-R. Bai, H.-F. Zhi, S. Zhang, H. Y. Woo, J.-L. Wang, Angew. Chem. Int. Ed. 2022, 61, e202209454; b) Z. Zhang, Y. Li, G. Cai, Y. Zhang, X. Lu, Y. Lin, J. Am. Chem. Soc. 2020, 142, 18741–18745; c) Z. Luo, T. Liu, R. Ma, Y. Xiao, L. Zhan, G. Zhang, H. Sun, F. Ni, G. Chai, J. Wang, C. Zhong, Y. Zou, X. Guo, X. Lu, H. Chen, H. Yan, C. Yang, Adv. Mater. 2020, 32, 2005942.
- [9] a) Z. Yao, X. Wan, C. Li, Y. Chen, Acc. Mater. Res. 2023, 10.1021/accountsmr.1023c00093; b) Y. Shi, Y. Chang, K. Lu, Z. Chen, J. Zhang, Y. Yan, D. Qiu, Y. Liu, M. A. Adil, W. Ma, X. Hao, L. Zhu, Z. Wei, Nat. Commun. 2022, 13, 3256.
- [10] G. Zhang, X.-K. Chen, J. Xiao, P. C. Y. Chow, M. Ren, G. Kupgan, X. Jiao, C. C. S. Chan, X. Du, R. Xia, Z. Chen, J. Yuan, Y. Zhang, S. Zhang, Y. Liu, Y. Zou, H. Yan, K. S. Wong, V. Coropceanu, N. Li, C. J. Brabec, J.-L. Bredas, H.-L. Yip, Y. Cao, *Nat. Commun.* **2020**, *11*, 3943.
- [11] a) J. Benduhn, K. Tvingstedt, F. Piersimoni, S. Ullbrich, Y. Fan, M. Tropiano, K. A. McGarry, O. Zeika, M. K. Riede, C. J. Douglas, S. Barlow, S. R. Marder, D. Neher, D. Spoltore, K. Vandewal, *Nat. Energy* **2017**, *2*, 17053; b) F. Huang, T. He, M. Li, L. Meng, W. Feng, H. Liang, Y. Zhou, X. Wan, C. Li, G. Long, Z. Yao, Y. Chen, *Chem. Mater.* **2022**, *34*, 6009–6025.
- [12] a) T. J. Aldrich, M. Matta, W. Zhu, S. M. Swick, C. L. Stern, G. C. Schatz, A. Facchetti, F. S. Melkonyan, T. J. Marks, J. Am. Chem. Soc. 2019, 141, 3274–3287; b) W. Zhu, J. M. Alzola, T. J. Aldrich, K. L. Kohlstedt, D. Zheng, P. E. Hartnett, N. D. Eastham, W. Huang, G. Wang, R. M. Young, G. C. Schatz, M. R. Wasielewski, A. Facchetti, F. S. Melkonyan, T. J. Marks, ACS Energy Lett. 2019, 4, 2695–2702; c) H. Yu, Z. Qi, J. Yu, Y. Xiao, R. Sun, Z. Luo, A. M. H. Cheung, J. Zhang, H. Sun, W. Zhou, S. Chen, X. Guo, X. Lu, F. Gao, J. Min, H. Yan, Adv. Energy Mater. 2021, 11, 2003171.
- [13] a) A. Ashokan, T. Wang, M. K. Ravva, J.-L. Brédas, J. Mater. Chem. C 2018, 6, 13162–13170; b) L. Zhu, J. Zhang, Y. Guo, C. Yang, Y. Yi, Z. Wei, Angew. Chem. Int. Ed. 2021, 60, 15348– 15353.
- [14] a) H. Chen, H. Liang, Z. Guo, Y. Zhu, Z. Zhang, Z. Li, X. Cao, H. Wang, W. Feng, Y. Zou, L. Meng, X. Xu, B. Kan, C. Li, Z. Yao, X. Wan, Z. Ma, Y. Chen, *Angew. Chem. Int. Ed.* **2022**, *61*, e202209580; b) Y. Zou, H. Chen, X. Bi, X. Xu, H. Wang, M. Lin, Z. Ma, M. Zhang, C. Li, X. Wan, G. Long, Y. Zhaoyang, Y. Chen, *Energy Environ. Sci.* **2022**, *15*, 3519–3533.
- [15] Z. Yao, X. Liao, K. Gao, F. Lin, X. Xu, X. Shi, L. Zuo, F. Liu, Y. Chen, A. K. Y. Jen, J. Am. Chem. Soc. 2018, 140, 2054– 2057.
- [16] W. Zhu, A. P. Spencer, S. Mukherjee, J. M. Alzola, V. K. Sangwan, S. H. Amsterdam, S. M. Swick, L. O. Jones, M. C. Heiber, A. A. Herzing, G. Li, C. L. Stern, D. M. DeLong-champ, K. L. Kohlstedt, M. C. Hersam, G. C. Schatz, M. R.

Wasielewski, L. X. Chen, A. Facchetti, T. J. Marks, J. Am. Chem. Soc. 2020, 142, 14532–14547.

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- [17] H. Liang, X. Bi, H. Chen, T. He, Y. Lin, Y. Zhang, K. Ma, W. Feng, Z. Ma, G. Long, C. Li, B. Kan, H. Zhang, O. A. Rakitin, X. Wan, Z. Yao, Y. Chen, *Nat. Commun.* **2023**, *14*, 4707.
- [18] Z. Jia, S. Qin, L. Meng, Q. Ma, I. Angunawela, J. Zhang, X. Li, Y. He, W. Lai, N. Li, H. Ade, C. J. Brabec, Y. Li, *Nat. Commun.* **2021**, *12*, 178.
- [19] X. Wan, C. Li, M. Zhang, Y. Chen, Chem. Soc. Rev. 2020, 49, 2828–2842.
- [20] P. Müller-Buschbaum, Adv. Mater. 2014, 26, 7692–7709.
- [21] R. Yu, H. Yao, Y. Xu, J. Li, L. Hong, T. Zhang, Y. Cui, Z. Peng, M. Gao, L. Ye, Z. a. Tan, J. Hou, *Adv. Funct. Mater.* 2021, *31*, 2010535.
- [22] a) X.-K. Chen, D. Qian, Y. Wang, T. Kirchartz, W. Tress, H. Yao, J. Yuan, M. Hülsbeck, M. Zhang, Y. Zou, Y. Sun, Y. Li, J. Hou, O. Inganäs, V. Coropceanu, J.-L. Bredas, F. Gao, *Nat. Energy* **2021**, *6*, 799–806; b) F. D. Eisner, M. Azzouzi, Z. Fei, X. Hou, T. D. Anthopoulos, T. J. S. Dennis, M. Heeney, J. Nelson, J. Am. Chem. Soc. **2019**, *141*, 6362–6374.
- [23] Deposition numbers 2272098 for CH7F and 2272092 for CH8F contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.
- [24] M. Zhang, L. Zhu, G. Zhou, T. Hao, C. Qiu, Z. Zhao, Q. Hu, B. W. Larson, H. Zhu, Z. Ma, Z. Tang, W. Feng, Y. Zhang, T. P. Russell, F. Liu, *Nat. Commun.* **2021**, *12*, 309.
- [25] X. Zhang, C. Li, J. Xu, R. Wang, J. Song, H. Zhang, Y. Li, Y.-N. Jing, S. Li, G. Wu, J. Zhou, X. Li, Y. Zhang, X. Li, J. Zhang, C. Zhang, H. Zhou, Y. Sun, Y. Zhang, *Joule* **2022**, *6*, 444–457.
- [26] Q. Liu, Y. Jiang, K. Jin, J. Qin, J. Xu, W. Li, J. Xiong, J. Liu, Z. Xiao, K. Sun, S. Yang, X. Zhang, L. Ding, *Sci. Bull.* 2020, 65, 272–275.
- [27] A. Zeng, X. Ma, M. Pan, Y. Chen, R. Ma, H. Zhao, J. Zhang, H. K. Kim, A. Shang, S. Luo, I. C. Angunawela, Y. Chang, Z. Qi, H. Sun, J. Y. L. Lai, H. Ade, W. Ma, F. Zhang, H. Yan, *Adv. Funct. Mater.* **2021**, *31*, 2102413.
- [28] L. J. A. Koster, V. D. Mihailetchi, R. Ramaker, P. W. M. Blom, *Appl. Phys. Lett.* **2005**, *86*, 123509.
- [29] M. Lenes, M. Morana, C. J. Brabec, P. W. M. Blom, Adv. Funct. Mater. 2009, 19, 1106–1111.
- [30] S. Nilsson, A. Bernasik, A. Budkowski, E. Moons, *Macro-molecules* 2007, 40, 8291–8301.
- [31] a) F. Panzer, H. Bässler, A. Köhler, J. Phys. Chem. Lett. 2017, 8, 114–125; b) M. Más-Montoya, R. A. J. Janssen, Adv. Funct. Mater. 2017, 27, 1605779.

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