Two-Dimensional Conjugation Extended CH-Series Acceptors with a Distinctive A–D–A Character

Zhaoyang Yao, Xiangjian Wan, Chenxi Li, and Yongsheng Chen*





ACCESS

Downloaded via NANKAI UNIV on December 1, 2023 at 15:16:00 (UTC). See https://pubs.acs.org/sharingguidelines for options on how to legitimately share published articles III Metrics & More

CONSPECTUS: As one of the most important indicators for evaluating photovoltaic devices, the power conversion efficiencies (PCEs) for the first-class organic solar cells (OSCs) have reached the level of ~20%, but they still lag far behind that of over 25% for their inorganic counterparts. With the similar if not better fill factor and short-circuit current, this wide gap of PCEs should be fundamentally attributed to the greatly larger nonradiative energy losses in OSCs, which are usually above 0.2 eV for OSCs but only 0.03–0.04 eV for high-performance inorganic solar cells. Note that the stubbornly severe nonradiative recombination in OSCs is associated with multiple characteristics of organic light-harvesting molecules, such as intrinsically large exciton binding energies and small relative dielectric constants, defective intermolecular packing networks, or more crystal defects caused by the flexibility of large organic molecular



Article Recommendations

skeletons, nonideal nanoscale film morphologies, and so on. All the factors above require that rational design of light-harvesting molecules should be carried out not only at single molecule but also at aggregation levels if further dramatic improvement of PCE is to be achieved for OSCs.

In this Account, we will first expound the unique merits of acceptor-donor-acceptor (A-D-A) type light-harvesting materials in frontier orbital distribution, energy level tuning, and intermolecular packings, meanwhile revealing the dominant role of A-D-A type molecules in facilitating charge transfer/transport, suppressing energy loss, and improving photovoltaic performance of OSCs eventually. In light of the conspicuous superiority of A-D-A type molecules, a convincing conclusion can be made that further exploration of novel A-D-A type light-harvesting materials is crucially important to shrink the PCE gap between OSCs and inorganic solar cells. Second, our recent studies for a really exciting A-D-A type molecular platform (CH-series) will be discussed comprehensively, involving various high-performance nonfullerene acceptors (NFAs) with small molecular, dimer-like, and polymerized architectures. Note that the most distinctive feature of CH-series NFAs is two-dimensional (2D) conjugation extension, especially for central units. Therefore, the favorable effects of 2D conjugation extension of these molecules on their fundamental physicochemical properties, intermolecular packing modes, blended film morphologies, photovoltaic parameters, and energy losses of resulting OSCs will be fully discussed. Abiding by the unveiled design rules of high-performance A-D-A type NFAs, the highest PCE of approaching 20% has been achieved for OSCs based on CH-series molecules. The evolution path of previous OSCs is based on traditional materials such as that of PCBM, ITIC, Y6, etc. could be one lesson; CH-series molecules are very likely to offer a great platform capable of achieving record-breaking OSCs along with much decreased energy losses, especially considering their wide and various structural modification possibilities. Finally, despite the rapidly surging PCEs of OSCs, there are still several insurmountable hurdles when attempting to break through bottlenecks existing in OSCs. Therefore, we propose some perspectives that can be further conducted on CH-series NFAs, which may conquer the great challenge of too large energy losses and thus boost OSCs toward commercial applications further.

1. INTRODUCTION

Given its unique advantages of solution processing, economic feasibility, ultra large power-to-weight ratio, and easily achievable flexibility or semitransparency, organic solar cells (OSCs) have emerged as one of the best photovoltaic technologies toward future large-scale applications in multiple scene modes.^{1,2} However, the power conversion efficiency (PCE), which should be the most important parameter for evaluating photovoltaic devices, is only ~20% for the state-of-

 Received:
 May 27, 2023

 Revised:
 July 6, 2023

 Published:
 August 2, 2023



772



Figure 1. (a) A diagram indicating the energy profiles for GS, CT, and LE diabatic states, which evolves from the Mulliken–Hush model to the recently developed "three states" model to describe the inner reason for reduced energy losses in NFAs based OSCs. E_{LE} and E_{CT} are the relaxed excitation energies of LE and CT states, respectively, and their energy offset is represented by ΔE_{LE-CT} ; t_{CT-LE} is used to evaluate the hybridization of CT and LE states; and k_{NR} represents the nonradiative recombination rate of CT states. Adapted with permission from ref 22. Copyright 2022 American Chemical Society. (b) Schematic diagram of typical A–D–A type molecules. (c, d, e) Theoretically calculated charge density difference ΔQ ($\Delta Q = \Psi^2_{LUMO} - \Psi^2_{HOMO}$) along the longest molecular skeletons with A–D–A and D–A–D characters.¹² (c–e) Reproduced with permission from ref 12. Copyright 2020 Royal Society of Chemistry.

the-art OSCs,^{3–5} still lagging far behind that of over 25% for inorganic solar cells.⁶ After analyzing three tangled parameters of open-circuit voltage (V_{OC}), short-circuit current density (J_{SC}), and fill factor (FF) comprehensively and mainly thanks to the rapid development of high performance molecule design recently, it is worth noting that J_{SC} and FF in high-efficiency OSCs are comparable with or even beyond inorganic solar cells, whereas V_{OC} is still significantly lower under similar bandgaps.^{4,7} The deficient V_{OC} in OSCs is largely caused by the large energy losses, especially nonradiative energy losses which are usually above 0.2 eV for OSCs^{8,9} but only 0.03–0.04 eV for high-performance inorganic solar cells.¹⁰ The stubbornly severe nonradiative recombination could be associated with multiple characters of organic molecules and

their solid state, such as intrinsically large Frenkel exciton binding energies and small relative dielectric constants, defective intermolecular packing networks, or more crystal defects caused by the flexibility of large organic molecular skeletons, nonideal nanoscale film morphologies at nanoscale, and so on. In spite of the confronted great challenges for OSCs, what really encourages us is that over 22% PCE could be afforded immediately by OSCs if comparable nonradiative energy losses (like ~0.04 eV) are achieved.^{11,12}

2. ADVANTAGES OF ACCEPTOR MOLECULES WITH A-D-A CHARACTER

In the past few years, OSCs have gone through a rapid development with soaring PCEs, which mainly benefits from



Figure 2. (a) Single crystal structure of ITIC including its dominant intermolecular packing mode ("E/E") and packing network. Adapted with permission from ref 15. Copyright 2019 American Chemical Society. (b) Single crystal structure of Y6 including its main newly emerged intermolecular packing mode ("E/E+C/C") different from ITIC and the resulting 3D packing network. Reproduced with permission from ref 9. Copyright 2022 Royal Society of Chemistry. (c) Schematic diagram illustrating the main structural modifications on typical Y6 molecule.

the huge success of newly developed high performance nonfullerene (NFA) molecules.^{13,14} Compared to traditional fullerene acceptors, NFAs possess much more powerful capacity in harvesting low-energy photons due to the strong intramolecular charge transfer (ICT). More importantly, a unique but superior three-dimensional (3D) molecular packing network could be usually formed by well-designed NFAs,^{15–} thus leading to not only facilitated charge transfer/transport but also significantly suppressed charge recombination in resulting OSCs.^{16,18} In addition, the most concerned nonradiative energy losses ($\Delta E_{\rm loss,nonrad}$) in OSCs could be quantitatively correlated with their external quantum efficiency (EQE_{EL}) of electroluminescence:¹⁹ $\Delta E_{\text{loss,nonrad}} = -k_{\text{B}}T \ln^{-1}$ (EQE_{EL}). Among them, $k_{\rm B}$ and T represent Boltzmann's constant and absolute temperature, respectively. EQE_{EL} can be evaluated by $k_{\rm R}/(k_{\rm R} + k_{\rm NR})$, where $k_{\rm R}$ and $k_{\rm NR}$ indicate the rates of radiative and nonradiative recombination from the charge transfer (CT) state to ground state (GS), respectively. In current high-performance OSCs, $k_{\rm NR}$ is much larger than $k_{\rm R}$ and closely linked to the electron-vibration coupling between CT states and GS²⁰ (Figure 1a). Theoretical studies have also revealed that the CT state of NFA-based systems possess intrinsically weaker electron-vibration coupling with its GS, with respect to that of fullerene-based ones.²⁰ This is likely caused by the effective hybridization of CT and local exciton (LE) states in high-performance NFA systems (Figure 1a).^{19,21,22} In this way, the fluorescence characteristic or EQE_{EL} of CT states can be dramatically enhanced through "intensity borrowing"²³ from high emissive LE states, thus suppressing the nonradiative recombination from CT states greatly.

It is really interesting that nearly all the high-performance NFAs are featured with a distinctive "acceptor–donor– acceptor" (A-D-A) architecture (Figure 1b).¹² Taking two

superstar molecules ITIC¹³ and Y6¹⁴ for examples, an obvious A-D-A character can be easily distinguished according to their peak-valley-peak fluctuant plots of frontier orbital charge density differences (ΔQ) following the conjugated skeletons (Figure 1c,d). In sharp contrast, the plots shape of ΔQ for D-A-D type molecules is valley-peak-valley (Figure 1e), being clearly contrary to that of A–D–A featured ones.¹² It is worth noting that our group first applied the design philosophy of A-D-A architecture on oligomer-like donor molecules and then promoted it toward NFAs. After a longterm molecular exploration and deep understanding of the "chemical structure-device performance" relationship, the main advantages of A-D-A type molecules have been unveiled and concluded in our previous review:¹² (1) Unique and optimal spatial electron distribution at frontier molecular orbitals. To be specific, A-D-A type molecules possess the larger and favorable frontier electron density distribution at the outside terminals rather than middle parts comparing to D-A–D type molecules. (2) Stable and 2D/3D intermolecular networked packings, especially the strong interactions involving both electron-deficient terminals and electrondonating central units among the neighboring molecules in solid state. This is expected to construct sufficient isotropic electron transport channels between adjacent A-D-A type molecules. (3) Facilitated charge generation/transportation and reduced energy losses in resulting OSCs caused by the superior frontier electron density distribution and intermolecular packings as mentioned above. To sum up, in light of so many encouraging advantages, continuous explorations of A-D-A acceptors with innovative chemical structures should likely be the most effective strategy for OSCs, if aiming to further break through the current bottlenecks and achieve comparable or even beyond PCEs with respect to inorganic solar cells.



Reaction Coordinate

Figure 3. (a) Constructing strategy of CH-series NFAs by 2D conjugated extension of central units. The alkyl chains grafted on Y6 and CH-series NFAs were simplified to R to afford a clear structural presentation. R1, R2, R3, and R4 on CH-series NFAs represent the different substituent groups. (b) General synthetic route to central donor of CH-series NFAs. [H] and [O] indicate the reduction and oxidation, respectively. (c) Theoretically calculated charge density distribution ΔQ ($\Delta Q = \Psi^2_{LUMO} - \Psi^2_{HOMO}$) along the longest molecular skeletons of CH-series model compound with a clear A–D–A character. Reproduced with permission from ref 34. Copyright 2022 Wiley. (d) A diagram indicating the energy profiles for GS and CT diabatic states, which mainly displays the effects of molecular optimization, like molecular rigid and conjugated extension, on the energy level of molecules at the vibration state. Adapted with permission from ref 22. Copyright 2022 American Chemical Society.

3. 2D CONJUGATION EXTENDED A-D-A TYPE CH-SERIES ACCEPTORS

3.1. Design Motivation of CH-Series Acceptors

With regard to a successfully designed acceptor molecule, the requirements for matched energy levels, strong light absorption in low energy region of sunlight, and adequate photo/thermal stabilities should be only the most basic prerequisite.²⁴ What is more important, an optimal D/A intermolecular penetrating network at nanoscale should be well established in blended

films, moreover, preferably characteristic of separated 3D packing networks for both donor and acceptor components.⁴ Such an ideal nanoscale morphology has been observed in many high-performance D/A systems^{13,17,25} but possibly proved to be the best for Y6-series molecules,¹⁴ which has rapidly emerged as the most efficient acceptor system thus far.^{7,8,26,27} Comparing to other typical NFAs like ITIC analogues with the dominant "end unit to end unit" intermolecular packing mode ("E/E" mode, Figure 2a),^{15,28} the most striking difference for Y6 is that its central unit

(benzo[c][1,2,5]thiadiazole, BT) participates in molecular packings to the utmost and thus leads to a highly effective nanoscale 3D network (Figure 2b).¹⁸ Lots of investigations have proven that such a 3D intermolecular packing network of Y6 not only boosts the favorable photodynamic but also dramatically suppresses the charge recombination process in blended films, thus contributing most to the excellent PCEs and smaller energy losses (below 0.55 eV) in resulting OSCs.^{4,8} Another exciting finding lies on the decreased exciton binding energy $(E_{\rm b})$ of Y6, which is as low as 0.1–0.15 eV in solid states.²⁹ This really encourages us that efficient charge generation might be realized only with a very small driving force²⁹ or even easily occurs in the bulk of acceptor phase, indicating the great potentials for achieving a comparable energy loss in A-D-A type NFA-based OSCs to that of inorganic solar cells.

Recently, a systemic study has been carried out to clearly reveal the determining role of the central unit in reaching champion PCE and reducing energy losses of OSCs.9,18 For example, two NFAs (namely, CH1 and CH2) were constructed by removing the thiadiazole moiety from Y6, additionally, further grafting two electron deficient fluorine atoms on central benzene to mimic the electron-deficient function of thiadiazole. As a result, the light absorptions of CH1 and CH2 in both solutions and solid states blue-shifted obviously with respect to those of Y6. Finally, CH1 and CH2 based OSCs only afforded a moderate PCE of ~15.5%, much lower than that of $\sim 17\%$ for Y6 under their individual best device fabricating conditions, which further confirms the crucially important role of central units in rendering the state-of-the-art OSCs. However, the majority of structural optimizations on Y6 at the current stage are still focusing on the side group, conjugated bridges, and terminal units;²⁴ very few are performed on the central unit (Figure 2c). This may be induced by the absence of reactive sites on the central unit of BT, more importantly, the great challenges for constructing new central heterocyclic units.^{31–33} All the same, this really surprises us when further considering its dominating role of the central unit in unique 3D intermolecular packings and PCE improvements.

Following the above logic, our initial motivation for developing CH-series acceptors with 2D conjugation extended central units was generated as follows:

- (1) In light of the crucial effect of central units on establishing a unique 3D intermolecular packing network, further chemical innovation on central units, like 2D conjugation extension, could indeed render huge space (or more reactive active sites) for further structural optimization of NFAs (Figure 3a), and then endow resulting OSCs with higher PCEs beyond expectation.
- (2) The ease of synthesis is another important factor to explore central heterocycles. Fortunately, based on the platform of Y6, central donors of CH-series NFAs can be easily constructed through only a two-steps reaction with good yields (Figure 3b).³⁴ Moreover, completely new and feasible synthetic routes might be also possible without using the platform of Y6. Most importantly, the newly constructed molecular backbones still maintain the much-desired A–D–A architecture (Figure 3c).
- (3) With the aim of reducing energy losses of OSCs, weakening the wave function overlap of energy levels between the lower vibrational CT state and high-order

vibrational GS is highly desired,^{20,22} especially for lowenergy-gap NFA systems which are greatly limited by the "Energy Gap Law".³⁵ The 2D conjugation extension of NFAs could give rise to a more rigid molecular skeleton likely with reduced reorganization energies. In this way, the vibration of molecular skeletons can be weakened, thus contributing to the suppressed density of states (DoS) of vibration energy levels (Figure 3d).^{20,22,36} Consequently, energy losses of OSCs are expected to be reduced through weakening the electron–vibration coupling of GS with CT state.

(4) The planar and rigid molecular framework of 2D lightharvesting materials, along with compact and ordered intermolecular packing, could effectively delocalize the vibrational relaxation of photogenerated excitons to several adjacent molecules in aggregated states, thus weakening the vibrational coupling of LE and GS and increasing the photoluminescence quantum yield of molecules.^{37,38} Based on the proposed model of describing energy losses with three states (Figure 1a),^{19,21,39} an effective orbital hybridization occurs between CT and LE states. If NFA molecules have high fluorescence characteristics (that is, the LE state is highly emissive), the nonradiative transition of CT states should be effectively suppressed.

In short, the chemical innovation on central units of NFAs, especially 2D conjugation extension, brings forth not only favorable intrinsic molecular properties (like small reorganization energy and high fluorescence quantum yield) but also superior 3D intermolecular packing network, with the hope of addressing the issue of too large energy losses in OSCs. It is worth noting that we have developed a series of NFAs with such an excellent molecular platform, contributing to OSCs with the highest PCE already approaching 20%. The detailed discussion will be carried out below.

3.2. High-Performance CH-Series Acceptors with A–D–A Characters

3.2.1. Small Molecular CH Acceptors. A series of CH acceptors have been developed by our group through central unit innovations very recently.^{9,18,34,40–44} The great structural tuning space, especially on the newly emerged central unit, endows CH acceptors with the remarkable facility of finely optimizing energy levels, absorption, intermolecular packing, and photodynamic in OSCs. As a result, the champion PCE of over 19% and energy loss as low as ~0.48 eV have been rendered thus far, demonstrating great potential of CH acceptors for breaking current bottlenecks confronted by OSCs. In the following, the recent progress about CH-series acceptors will be introduced briefly at three aspects.

3.2.1.1. 2D Conjugated Extension and Halogenation Effect on Central Unit. CH4 was first synthesized through the general route illustrated in Figure 3b,³⁴ which possesses comparable absorption and energy level distribution to that of Y6.¹⁴ Finally, CH4-based OSCs give rise to a good PCE of 16.49% (Figure 4a) with respect to that of 16.27% for Y6 under their individual best device conditions in our lab. The limited factor for CH4-based OSCs is its moderate FF (71.1%), far from the best level of over 80% for the state-of-the-art OSCs.⁴ Halogenation has been proven as the highly effective strategy to optimize film morphology, facilitate photodynamic and improve FFs of OSCs.^{24,44–48} In light of the dominant "E/E" molecular packing mode for NFAs like



Figure 4. (a) J-V curves of OSCs based on PM6:CH4 and PM6:CH6 blends. The PCEs and FFs are listed for a clear comparison. (b) Atomic force microscopy (AFM) phase image of CH6-based blended film. (c) Energy loss analysis of OSCs based on PM6:CH4 and PM6:CH6 blends. $\Delta E_{\rm CT}$ is determined by the energetic difference between the CT and singlet excited states. $q\Delta V_{\rm r}$ and $q\Delta V_{\rm nr}$ indicate the energy losses of radiative and nonradiative recombination, respectively. Reproduced with permission from ref 34. Copyright 2022 Wiley.

ITIC¹⁵ or F²⁵ analogues, it is understandable that halogenation is mostly implemented on end units to make the utmost of advantages. In sharp contrast, central units significantly participate in intermolecular packings in current best Y-series NFAs (Figure 2b) and usually result in an excellent 3D molecular packing network.¹⁶ In a similar fashion, further improvement of OSCs is really expected if suitable halogenations are implemented on the central unit of highefficiency Y-series molecules. However, very few investigations are involved with central unit halogenation at present, which may be ascribed to two hurdles: (i) the lack of reaction active sites on the BT unit in Y-series molecules; (ii) more importantly, the exploration of new central heterocyclic unit is always faced with huge synthetic challenges.

Herein, based on the molecular platform of CH4 with multiple active sites on central units, fluorination was first performed to afford a new NFA of CH6.³⁴ It is worth noting that CH6-based OSC reaches a much enlarged PCE of 18.33% along with a greatly improved FF of 78.4% compared to that of CH4, which mainly benefits from its superior fibrillar network film morphology (Figure 4b). Moreover, OSCs with 1 cm² active area also afford a good PCE of 16.52%, suggesting the great prospects of CH-series NFAs in large-area productions. Note that a relatively small energy loss of about 0.53 eV for

both OSCs can be achieved (Figure 4c). A systematic study has disclosed the vital role of fluorination on central units in (I) enhancing molecular $\pi - \pi$ interaction, improving intermolecular packing order, and increasing material crystallinity; (II) constructing favorable fibrillar network film morphologies with a lower energy disorder; (III) facilitating photoinduced charge carrier dynamic in bulk heterojunction films; and(IV) getting a better trade-off between tangled J_{SC} and V_{OC} to reach a small energy loss.

This work first demonstrated an excellent CH molecular platform with 2D conjugated extension of central unit and unveiled the favorable achievements of fluorination on central units. More importantly, the sufficient reaction active sites on newly formed central units offer huge opportunities for further structural optimization with the aim of achieving recordbreaking OSCs.

3.2.1.2. Molecular Packing and Device Performance Optimization by Peripheral Halogenations. Peripheral halogenation tuning on NFAs has been regarded as a feasible strategy to boost PCEs of OSCs.²⁴ Especially, our recent research on CH4 and CH6 has fully manifested the crucially important role of central unit halogenation in optimizing nanoscale film morphology and PCE of OSCs.³⁴ However, the lack of systematic study renders the bridge between peripheral halogenation of NFAs and their intermolecular packing, film morphology, photodynamics, and photovoltaic parameters still an unaddressed issue.

Owing to the sufficient halogenation sites on molecular backbones of CH-series NFAs, four NFAs of CH-6F, CH-4Cl, CH-6Cl, and CH23 were well designed and synthesized, characteristic of different peripheral halogenations (Figure 5a). A comprehensive study has unveiled that even such a small structural modification just through a peripheral halogenation swap could result in totally different crystal systems and featured intermolecular packing modes (Figure 5b). For example, CH-6F possesses nearly the same intermolecular packing modes with those of Y6 based on the detailed crystallographic analysis, demonstrating the "E/E+C/C" mode as the most dominant one. However, CH-4Cl, CH-6Cl, and CH23 display several exotic packing modes of "dual E/C" or "dual C/b", which are unobserved in other material systems.¹⁶ More importantly, these unique and favorable molecular packing behaviors could contribute to optimized nanoscale film morphologies with low energy disorders, more effective hybridization of CT and LE states and thus a suppressed nonradiative recombination process in blended films.^{19,21} As a result, a series of high-performance OSCs have been rendered along with PCEs over 18% and relatively small nonradiative energy losses about 0.2 eV. Among them, the best PCE of 18.77% was afforded by CH23-based OSCs due to the enlarged molecular packing density and relative dielectric constant.⁴² Recently, we further replaced chlorine atoms on the central unit of CH23 with bromines to afford a new NFA of CH22. Finally, over 19% PCE has been obtained by OSCs based on such a rare case of brominated NFA. Our results above clearly indicate that the delicate regulating halogen formulas on newly explored CH-series NFAs may pave a new way for reaching record-breaking OSCs.

3.2.1.3. Reducing Energy Losses by Multiple Conjugation Extension of NFAs. In order to achieve more compact and ordered intermolecular packing, a new A–D–A type NFA of CH17 was further constructed (Figure 6a), which is featured



Figure 5. (a) Chemical structures of CH-6F, CH-4Cl, CH-6Cl and CH23 with the same molecular framework but different peripheral halogenations. R represents the 2 hexyldecyl alkyl chain. (b) 3D intermolecular packing networks along with the most distinctive packing modes extracted from single crystals. Reproduced with permission from refs 9 and 42. Copyright 2022 Royal Society of Chemistry and 2023 Wiley.



Figure 6. (a) Constructing strategy of CH17 by multiple conjugated extensions of both central and terminal units. The molecular reorganization energies, the calculated largest electron transfer integrals of packing modes, and energy losses in resulting OSCs were also listed. The alkyl chains grafted on Y6 and CH17 were simplified as R for a better structural presentation. (b) 3D intermolecular packing networks for both Y6 and CH17 derived from their single crystals. (c) AFM phase images of blended films. (d) Time-resolution photoluminescence (TRPL) spectra of Y6 and CH17-based pristine films. (e) Photoluminescence quantum yields (PLQY) of Y6 and CH17-based pristine films. (b and c) Reproduced with permission from ref 18. Copyright 2022 Science China Press and Springer-Verlag GmbH Germany.

with multiple conjugation extensions on both central and end units comparing to Y6 series.¹⁸

Such a multiple conjugation extension endows CH17 with a

more compact 3D molecular packing network with respect to

that of Y6 based on X-ray single crystal results (Figure 6b).¹⁸ Moreover, the superior nanoscale film morphology could also be formed by PM6:CH17 blends with more obvious fibrillar networks (Figure 6c). Benefiting from the reduced molecular



Figure 7. Three potential ways ("Terminal coupling, Central ring fusing, and Central ring coupling") to construct dimerized acceptors by taking CH-D1, CH8 and CH8-1 for examples. The alkyl chains grafted on CH-D1, CH8 and CH8-1 were simplified as R for a clearer presentation.

reorganization energy, enlarged electron transfer integrals and more favorable blended film morphology for CH17, facilitated charge generation/transport and reduced energetic disorders can be rendered. Therefore, CH17-based OSCs finally lead to an excellent PCE of 18.13% accompanied by a markedly decreased energy loss of 0.49 eV. What is more interesting, both the exciton lifetime (~830 ps) and PLQY (~5.6) for CH17 pristine film are larger than those of ~678 ps and 4.8 for Y6, respectively (Figure 6d,e). Note that the enlarged exciton lifetime and PLQY of CH17 are favorable for achieving a much lower energy loss in resulting OSCs due to the potentially effective hybridization of CT and LE states.^{19,21}

3.2.2. Dimer-like CH Acceptors. Recently, dimer-like acceptors have gained lots of attention owing to their powerful ability in maintaining both the good efficiency and long-term stability of devices. 49-51 In our view, the PCE for OSCs based on dimer-like acceptors may be not as high as their monomer acceptors ultimately because of the intrinsically less ordered molecular packing structures for dimer acceptors than that of their monomer counterparts. However, the long-term stability of OSCs is expected to get a striking improvement due to greatly suppressed molecular diffusion in blended films.⁴⁹ Note that the most conventional way to build dimer acceptors is "terminal coupling" through end units (brominated 2-(3-oxo-2,3-dihydro-1*H*-inden-1-ylidene)malononitrile groups) of small molecular acceptors at present, just like plenty of dimer acceptors based on Y-series molecular backbones⁴⁹⁻⁵¹ or CH-D1⁵² in Figure 7. However, this strategy to construct dimer acceptors will bring about several unavoidable shortcomings: (1) Inferior intermolecular packings, especially for the "E/E" mode.¹⁸ Note that a relatively twist backbone will be formed due to the relatively large dihedral angles between two

monomers.⁵⁰ Therefore, the already perfect molecular packings for planar monomers may be broken. In particular, the effective "E/E" intermolecular packing for two end units that work as connection sites (light blue color filled area) should be greatly damaged, because of the much changed chemical structure, electron-deficient property, and steric hindrance. (2) Reduced halogen density on molecular backbones. The connection through end units will consume at least two halogen atoms on molecular backbones. However, the halogen atom has been proven to be in favor of getting optimized molecular packings and facilitated photodynamic for efficient OSCs.^{24,44-48} (iii) Regionally isomeric problems. Presently, the widely employed end units of NFAs are based on 1,1-dicyanomethylene-3indanone (IC).⁵³ In order to carry out "terminal coupling" successfully, brominating on IC is usually indispensable. However, the separation of two isomers of brominated IC is usually very difficult;⁵⁴ meanwhile, the regionally isomeric issue will remained in dimer-like acceptors if just leaving the brominated IC unpurified.

In order to liberate more end units for efficient molecular stackings as well as address the disadvantages mentioned above, two exotic pathways to build dimer-like acceptors were explored on CH-series molecules. As displayed in Figure 7, CH8 was constructed by the way of "Central ring fusing", which has provided a highly symmetrical, planar, and rigid backbone leaving four fluorinated end units outside.⁴⁰ Although OSCs based on the CH8 acceptor were not excellent enough, only affording a PCE of 9.37%, its great application in light-driven hydrogen evolutions has become more and more concerned.⁵⁵ Furthermore, after side chain optimization on CH8, ternary OSCs based on the newly constructed 4A-DFIC afforded an encouraging PCE of 18.6%,⁵⁶ demonstrating the



Figure 8. (a) Constructing strategy of dimerized acceptors through the "Central ring coupling" method and molecular structures of CH8-0, CH8-1, and CH8-2. (b) Side view of ground-state geometries provided by DFT calculations with the dihedral angles between two monomer planes being marked. (c) AFM phase images and statistical distributions of fibril width for blended films. Reprinted with permission from ref 41. Copyright 2023 Royal Society of Chemistry.

huge PCE potentials for this type of dimer-like acceptors. Another more feasible method to easily synthesize dimer-like acceptors can be classified as "Central ring coupling". The sufficient reaction active sites on the 2D conjugated central unit of CH-series NFAs make the ease construction of dimerlike acceptors highly possible by directly connecting two CH small molecular acceptors with a bridged building block (like the red color filled area in CH8-1, Figure 7). As follows, we will take CH8 series for examples.⁴¹

Recently, the 2D conjugation extension of central unit for CH-series NFAs has not only rendered much improved photovoltaic performance of OSCs but also provided the huge space for further structural optimizations.⁹ Our success in CHseries NFAs encourages us to extend the linear molecular skeletons toward three dimensions, for example, developing



Figure 9. (a) Chemical structures of polymerized acceptors of PZC16 and PZC17. (b) J-V curves of PZC17-based OSCs with a 1 cm² active area. Reprinted with permission from ref 43. Copyright 2023 Wiley. (c) Chemical structures of TZ1 and TZ2. (d) TEM images of PM6:TZ1 and PM6:TZ2. Reprinted with permission from ref 61. Copyright 2023 Elsevier B.V.

dimer-like acceptors by directly coupling two CH-series NFAs through the "Central ring coupling" strategy (Figure 8a). Such an exotic connection could (1) assemble four end units into a dimer-like acceptor and thus enhance the intermolecular $\pi - \pi$ stacking, especially when taking the amazingly vital effect of end units on more compact molecular packings; (2) easily tune the molecular configurations of dimer-like acceptor and nanoscale morphologies of active layers through the selection of bridged units (Figure 8a). Bearing these thoughts in mind, three dimer-like acceptors, namely, CH8-0, CH8-1 and CH8-2, were developed.⁴¹ Despite the intrinsically lower electron reorganization energy of dimer-like acceptors,⁴⁰ a comprehensive investigation has also disclosed that the dihedral angles between two planes of monomer gradually decreased from CH8-0 to CH8-2 (Figure 8b). This is caused by the different strengths of noncovalently conformational locks (F-S/F-H secondary interactions)57 established between central and bridged units, which also contributes to the stepwise enlarged width of D/A fibril (Figure 8c). Finally, OSCs with the highest PCE of 17.05% were fabricated on the basis of CH8-1. More excitingly, CH8-0 (1, 2)-series molecule-based OSCs could remain above 90% or even 95% PCE after 2700 h at room temperature and over 80% after 360 h with heat treatments at 65 °C with respect to their original PCEs, demonstrating a really good long-term stability as expected.

In short, based on such an outstanding constructing platform of CH-series molecules, we have not only developed two exotic but feasible pathways to build dimer-like acceptors but also manifested the tremendous possibilities of assembling high efficiency and excellent long-term stability into one OSC.

3.2.3. Polymerized CH Acceptors. All-polymer solar cells (all-PSCs) have attracted tremendous attention in view of the extra merit of outstanding stability with respect to small molecular acceptor based OSCs.⁵⁸ Thus, far, all-PSCs have gone through a great improvement and achieved an excellent PCE surpassing 18%,^{59,60} mainly benefiting from the state-of-the-art Y6-based polymerized acceptors. However, PCEs of all-PSCs still lag behind those of OSCs employing small molecular

acceptors. In light of the crucial role of polymerized acceptors in all-PSCs, it is quite pivotal to further explore novel polymerized acceptors.

Herein, on the basis of CH-series NFAs, two polymerized acceptors, PZC16 and PZC17,⁴³ were constructed by use of nonaromatic conjugated linkers (ethynyl for PZC16 and vinylene for PZC17) to avoid the twist of polymeric backbones (Figure 9a). The number-average molecular weights were estimated to be 12.0 and 7.8 kDa for PZC16 and PZC17, respectively. Finally, the PM6:PZC17 blended film displays a distinctive bicontinuous D/A network, affording all-PSCs with a satisfactory PCE of 16.33%, additionally an impressive PCE of 15.14% for large area device (ca. 1 cm² active area) (Figure 9b).

As is well-known, the compact molecular packing plays a vital role in reaching efficient charge transport in OSCs. In view of the sufficient reaction active sites on the central unit of CH-series NFAs, we proposed a new strategy to construct nonlinear polymerized acceptors by use of both central and end units as connection sites. By selecting different linkers, two novel nonlinear polymerized acceptors (TZ1 and TZ2) were successfully established (Figure 9c), providing a quite rare case of nonlinear π -conjugated polymerized acceptors.⁶¹ Finally, TZ2-based all-PSC only achieved an unsatisfied PCE of 7.41% mainly due to its inferior nanoscale film morphology (Figure 9d), especially compared to the bundlelike nanofiber networks widely observed in high-performance OSCs currently. In spite of unsatisfied PCEs, this work indeed paved a new pathway to construct nonlinear polymerized acceptors and also excavated the possibility to get highly efficient all-PSCs when considering the diverse structures of both linkers and central units.

4. SUMMARY AND PERSPECTIVES

With the aim of addressing large energy losses and further boosting efficiencies of OSCs, we developed an excellent CH molecular platform for NFAs through 2D conjugated extension of central units. Then, a series of novel CH acceptors, including small molecular, dimer-like, and polymerized accept-

pubs.acs.org/amrcda



Figure 10. (a) Schematic diagram showing the potential for more chemical modifications on CH-series NFAs. (b) Exciton binding energies of NFAs in pristine films measured by temperature dependent photoluminescence. Predicted PCEs vs E_{loss} and onset absorption of active layers for single junction (c) and tandem OSCs (d). Note that the average EQE of 80% and FF of 0.80 are assumed. Reprinted with permission from ref 12. Copyright 2020 Royal Society of Chemistry.

ors, were further constructed, featuring multiple reaction active sites on central units. The intrinsic physicochemical characteristics, molecular packing behaviors, charge transfer/transport dynamics, and ultimate photovoltaic parameters of OSCs have been greatly optimized by performing diverse substitutions on central units. Eventually, OSCs based on CH-series NFAs reached the highest PCE of approaching 20% with relatively small energy losses below 0.5 eV and excellent long-term stabilities. If the history of the evolution of previous star molecules such as PCBM, ITIC, and Y6 could be a mirror, it is quite possible that CH-series NFAs may have even greater potential for achieving record-breaking OSCs when taking the extra and huge space offered by this molecular platform for further structural modifications into account. The following are several perspectives that may lead to further molecular design for better OSCs with CH molecules:

- Standing on chemical innovations of NFAs with a clear A-D-A characteristic. As mentioned above, OSCs based on A-D-A type molecules usually exhibit superior photovoltaic performances with facilitated photodynamic and smaller energy losses.
- (2) Developing NFAs with low molecular reorganization energies and high fluorescence properties to achieve facilitated charge transport and suppressed nonradiative recombination. At the single molecule level, introducing more 2D conjugated moieties with unique structures on central units should be very promising, for example, replacing the benzene on the central unit of CH-series NFAs with other polycyclic aromatic hydrocarbons or heterocycles that featured intrinsically high fluorescent quantum yields and long exciton lifetimes (Figure 10a). At the level of aggregates, tuning the molecular size of

central units or substitutions to induce a more compact and ordered intermolecular packing is really essential.

- (3) Reducing exciton binding energies (E_b) of NFAs. Lots of theoretical studies have revealed that E_b of NFAs could be greatly reduced if suitable molecular packing networks with stronger intermolecular coupling are established. Fortunately, molecular packing modes of CH-series NFAs can be fully optimized even by a quite minor structural modification on central units, which have already led to markedly decreased E_b (Figure 10b). Therefore, further deep investigations should be carried out to disclose the relationship between molecular packings and E_b . In this way, E_b may further decrease (even close to that of inorganic semiconductors) with delicate optimization of both molecular structures and packing mode control.
- (4) Exploring NFAs with smaller energy gaps than the state-of-the-art NFAs. Based on the semiempirical model and analysis we developed before, the predicted PCEs could be over 20% for single junction OSCs (Figure 10c) and 28% for 2-terminal tandem OSCs (Figure 10d) under a specified condition, if the onset absorption up to ~950 nm and 1050–1150 nm can be achieved, respectively.^{11,12} Given that the onset absorptions for the state-of-the-art NFAs are still below 950 nm, further extensive exploration of NFAs with smaller energy gaps should be carried out urgently.

Anyway, the large energy losses existing in OSCs should still be the greatest impediment for achieving comparable PCEs with the best inorganic solar cells. Note that the origin of energy losses in OSCs is really complicated, but it should be strongly correlated with the intrinsically large exciton binding

Accounts of Materials Research

applications.

functional material design and synthesis.

ACKNOWLEDGMENTS

energies and small relative dielectric constants of organic materials, defective intermolecular packing networks caused by flexibility of molecular skeletons, nonideal nanoscale film morphologies, more crystal defects of these organic materials, and so on. The markedly improved photovoltaic performance for CH-series acceptors caused by 2D conjugation extension suggests that there is still huge space to boost PCEs of OSCs by addressing the most concerned issue, i.e, how to get a much smaller energy losses, through performing molecular optimizations at both single molecule and aggregation levels.

AUTHOR INFORMATION

Corresponding Author

Yongsheng Chen – State Key Laboratory and Institute of Elemento-Organic Chemistry, 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; ◎ orcid.org/0000-0003-1448-8177; Email: yschen99@nankai.edu.cn

Authors

- Zhaoyang Yao State Key Laboratory and Institute of Elemento-Organic Chemistry, 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; orcid.org/0000-0003-1384-183X
- Xiangjian Wan State Key Laboratory and Institute of Elemento-Organic Chemistry, 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; Orcid.org/0000-0001-5266-8510
- Chenxi Li State Key Laboratory and Institute of Elemento-Organic Chemistry, 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

Complete contact information is available at: https://pubs.acs.org/10.1021/accountsmr.3c00093

Notes

The authors declare no competing financial interest.

Biographies

Zhaoyang Yao received his PhD degree from University of Chinese Academy of Science in 2017. Currently, he is a distinguished researcher in Nankai University. His research focuses on polycyclic aromatic hydrocarbons-based photoelectric materials.

Xiangjian Wan received his PhD degree in Organic Chemistry from Nankai University, China, in 2006. Currently, he is a professor of Chemistry, Nankai University. His research interests focus on organic functional material design and application, especially on OPV material design and device optimization.

Chenxi Li received his PhD degree in Organic Chemistry from Nankai University, China, in 1990. Currently, he is a professor of

Science Foundation of China (21935007, 52025033,

51873089), Tianjin city (20JCZDJC00740, 22JCQNJC00530), 111 Project (B12015) and Haihe Laboratory of Sustainable Chemical Transformations.

Chemistry, Nankai University. His research interests focus on organic

Yongsheng Chen received his PhD in Chemistry from the University

of Victoria in 1997. Since 2003, he has been a Chair Professor at

Nankai University. His main research interests focus on carbon-based

nanomaterials and organic functional materials for green energy

The authors gratefully acknowledge the financial support from Ministry of Science and Technology of the People's Republic

of China (National Key R&D Program of China,

2022YFB4200400, 2019YFA0705900) and National Natural

REFERENCES

(1) Yu, G.; Gao, J.; Hummelen, J. C.; Wudl, F.; Heeger, A. J. Polymer Photovoltaic Cells: Enhanced Efficiencies via a Network of Internal Donor-Acceptor Heterojunctions. *Science* **1995**, 270 (5243), 1789–1791.

(2) Tang, C. W. Two-Layer Organic Photovoltaic Cell. Appl. Phys. Lett. **1986**, 48 (2), 183–185.

(3) Zheng, Z.; Wang, J.; Bi, P.; Ren, J.; Wang, Y.; Yang, Y.; Liu, X.; Zhang, S.; Hou, J. Tandem Organic Solar Cell with 20.2% Efficiency. *Joule* **2022**, *6* (1), 171–184.

(4) Zhu, L.; Zhang, M.; Xu, J.; Li, C.; Yan, J.; Zhou, G.; Zhong, W.; Hao, T.; Song, J.; Xue, X.; Zhou, Z.; Zeng, R.; Zhu, H.; Chen, C.-C.; MacKenzie, R. C. I.; Zou, Y.; Nelson, J.; Zhang, Y.; Sun, Y.; Liu, F. Single-Junction Organic Solar Cells with Over 19% Efficiency Enabled by a Refined Double-Fibril Network Morphology. *Nat. Mater.* **2022**, *21* (6), 656–663.

(5) Pang, B.; Liao, C.; Xu, X.; Yu, L.; Li, R.; Peng, Q. Benzo[d]thiazole Based Wide Bandgap Donor Polymers Enable 19.54% Efficiency Organic Solar Cells Along with Desirable Batch-to-Batch Reproducibility and General Applicability. *Adv. Mater.* **2023**, 35, 2300631.

(6) NREL Best Research-cell Efficiencies Chart; https://www.nrel.gov/pv/cell-efficiency.html.

(7) Jiang, K.; Zhang, J.; Zhong, C.; Lin, F. R.; Qi, F.; Li, Q.; Peng, Z.; Kaminsky, W.; Jang, S.-H.; Yu, J.; Deng, X.; Hu, H.; Shen, D.; Gao, F.; Ade, H.; Xiao, M.; Zhang, C.; Jen, A. K. Y. Suppressed Recombination Loss in Organic Photovoltaics Adopting a Planar–Mixed Heterojunction Architecture. *Nat. Energy* **2022**, 7 (11), 1076–1086.

(8) Li, C.; Zhou, J.; Song, J.; Xu, J.; Zhang, H.; Zhang, X.; Guo, J.; Zhu, L.; Wei, D.; Han, G.; Min, J.; Zhang, Y.; Xie, Z.; Yi, Y.; Yan, H.; Gao, F.; Liu, F.; Sun, Y. Non-Fullerene Acceptors with Branched Side Chains and Improved Molecular Packing to Exceed 18% Efficiency in Organic Solar Cells. *Nat. Energy* **2021**, *6* (6), 605–613.

(9) Zou, Y.; Chen, H.; Bi, X.; Xu, X.; Wang, H.; Lin, M.; Ma, Z.; Zhang, M.; Li, C.; Wan, X.; Long, G.; Zhaoyang, Y.; Chen, Y. Peripheral Halogenation Engineering Controls Molecular Stacking to Enable Highly Efficient Organic Solar Cells. *Energy Environ. Sci.* **2022**, *15* (8), 3519–3533.

(10) Green, M. A. Radiative Efficiency of State-of-the-Art Photo-voltaic Cells. *Prog. Photovoltaics* **2012**, *20* (4), 472–476.

(11) Meng, L.; Zhang, Y.; Wan, X.; Li, C.; Zhang, X.; Wang, Y.; Ke, X.; Xiao, Z.; Ding, L.; Xia, R.; Yip, H.-L.; Cao, Y.; Chen, Y. Organic and Solution-Processed Tandem Solar Cells with 17.3% Efficiency. *Science* **2018**, *361* (6407), 1094–1098.

(12) Wan, X.; Li, C.; Zhang, M.; Chen, Y. Acceptor–Donor– Acceptor Type Molecules for High Performance Organic Photovoltaics–Chemistry and Mechanism. *Chem. Soc. Rev.* **2020**, *49* (9), 2828–2842. (13) Lin, Y.; Wang, J.; Zhang, Z.-G.; Bai, H.; Li, Y.; Zhu, D.; Zhan, X. An Electron Acceptor Challenging Fullerenes for Efficient Polymer Solar Cells. *Adv. Mater.* **2015**, *27* (7), 1170–1174.

(14) Yuan, J.; Zhang, Y.; Zhou, L.; Zhang, G.; Yip, H.-L.; Lau, T.-K.; Lu, X.; Zhu, C.; Peng, H.; Johnson, P. A.; Leclerc, M.; Cao, Y.; Ulanski, J.; Li, Y.; Zou, Y. Single-Junction Organic Solar Cell with over 15% Efficiency Using Fused-Ring Acceptor with Electron-Deficient Core. *Joule* **2019**, 3 (4), 1140–1151.

(15) Aldrich, T. J.; Matta, M.; Zhu, W.; Swick, S. M.; Stern, C. L.; Schatz, G. C.; Facchetti, A.; Melkonyan, F. S.; Marks, T. J. Fluorination Effects on Indacenodithienothiophene Acceptor Packing and Electronic Structure, End-Group Redistribution, and Solar Cell Photovoltaic Response. J. Am. Chem. Soc. **2019**, *141* (7), 3274–3287.

(16) Zhu, W.; Spencer, A. P.; Mukherjee, S.; Alzola, J. M.; Sangwan, V. K.; Amsterdam, S. H.; Swick, S. M.; Jones, L. O.; Heiber, M. C.; Herzing, A. A.; Li, G.; Stern, C. L.; DeLongchamp, D. M.; Kohlstedt, K. L.; Hersam, M. C.; Schatz, G. C.; Wasielewski, M. R.; Chen, L. X.; Facchetti, A.; Marks, T. J. Crystallography, Morphology, Electronic Structure, and Transport in Non-Fullerene/Non-Indacenodithieno-thiophene Polymer:Y6 Solar Cells. J. Am. Chem. Soc. 2020, 142 (34), 14532–14547.

(17) Shi, X.; Chen, J.; Gao, K.; Zuo, L.; Yao, Z.; Liu, F.; Tang, J.; Jen, A. K.-Y. Terthieno[3,2-b]Thiophene (6T) Based Low Bandgap Fused-Ring Electron Acceptor for Highly Efficient Solar Cells with a High Short-Circuit Current Density and Low Open-Circuit Voltage Loss. *Adv. Energy Mater.* **2018**, *8* (12), 1702831.

(18) Chen, H. B.; Zou, Y. L.; Liang, H. Z.; He, T. F.; Xu, X. Y.; Zhang, Y. X.; Ma, Z. F.; Wang, J.; Zhang, M. T.; Li, Q. W.; Li, C. X.; Long, G. K.; Wan, X. J.; Yao, Z. Y.; Chen, Y. S. Lowing the Energy Loss of Organic Solar Cells by Molecular Packing Engineering via Multiple Molecular Conjugation Extension. *Sci. China Chem.* **2022**, 65 (7), 1362–1373.

(19) Chen, X.-K.; Qian, D.; Wang, Y.; Kirchartz, T.; Tress, W.; Yao, H.; Yuan, J.; Hülsbeck, M.; Zhang, M.; Zou, Y.; Sun, Y.; Li, Y.; Hou, J.; Inganäs, O.; Coropceanu, V.; Bredas, J.-L.; Gao, F. A Unified Description of Non-Radiative Voltage Losses in Organic Solar Cells. *Nat. Energy* **2021**, *6* (8), 799–806.

(20) Benduhn, J.; Tvingstedt, K.; Piersimoni, F.; Ullbrich, S.; Fan, Y.; Tropiano, M.; McGarry, K. A.; Zeika, O.; Riede, M. K.; Douglas, C. J.; Barlow, S.; Marder, S. R.; Neher, D.; Spoltore, D.; Vandewal, K. Intrinsic Non-Radiative Voltage Losses in Fullerene-Based Organic Solar Cells. *Nat. Energy* **2017**, *2* (6), 17053.

(21) Qian, D.; Zheng, Z.; Yao, H.; Tress, W.; Hopper, T. R.; Chen, S.; Li, S.; Liu, J.; Chen, S.; Zhang, J.; Liu, X.-K.; Gao, B.; Ouyang, L.; Jin, Y.; Pozina, G.; Buyanova, I. A.; Chen, W. M.; Inganäs, O.; Coropceanu, V.; Bredas, J.-L.; Yan, H.; Hou, J.; Zhang, F.; Bakulin, A. A.; Gao, F. Design Rules for Minimizing Voltage Losses in High-Efficiency Organic Solar Cells. *Nat. Mater.* **2018**, *17* (8), 703–709.

(22) Huang, F.; He, T.; Li, M.; Meng, L.; Feng, W.; Liang, H.; Zhou, Y.; Wan, X.; Li, C.; Long, G.; Yao, Z.; Chen, Y. Can Isotope Effects Enable Organic Solar Cells to Achieve Smaller Non-Radiative Energy Losses and Why? *Chem. Mater.* **2022**, *34* (13), 6009–6025.

(23) Bixon, M.; Jortner, J.; Verhoeven, J. W. Lifetimes for Radiative Charge Recombination in Donor-Acceptor Molecules. J. Am. Chem. Soc. **1994**, 116 (16), 7349–7355.

(24) Duan, C.; Ding, L. The New Era for Organic Solar Cells: Non-Fullerene Small Molecular Acceptors. *Science Bulletin* **2020**, *65* (15), 1231–1233.

(25) Ke, X.; Meng, L.; Wan, X.; Li, M.; Sun, Y.; Guo, Z.; Wu, S.; Zhang, H.; Li, C.; Chen, Y. The Rational and Effective Design of Nonfullerene Acceptors Guided by a Semi-Empirical Model for an Organic Solar Cell with an Efficiency over 15%. *J. Mater. Chem. A* **2020**, *8* (19), 9726–9732.

(26) Jia, Z.; Qin, S.; Meng, L.; Ma, Q.; Angunawela, I.; Zhang, J.; Li, X.; He, Y.; Lai, W.; Li, N.; Ade, H.; Brabec, C. J.; Li, Y. High Performance Tandem Organic Solar Cells via a Strongly Infrared-Absorbing Narrow Bandgap Acceptor. *Nat. Commun.* **2021**, *12* (1), 178.

(27) Shi, Y.; Chang, Y.; Lu, K.; Chen, Z.; Zhang, J.; Yan, Y.; Qiu, D.; Liu, Y.; Adil, M. A.; Ma, W.; Hao, X.; Zhu, L.; Wei, Z. Small Reorganization Energy Acceptors Enable Low Energy Losses in Non-Fullerene Organic Solar Cells. *Nat. Commun.* **2022**, *13* (1), 3256.

(28) Zhu, L.; Tu, Z.; Yi, Y.; Wei, Z. Achieving Small Exciton Binding Energies in Small Molecule Acceptors for Organic Solar Cells: Effect of Molecular Packing. *J. Phys. Chem. Lett.* **2019**, *10* (17), 4888–4894.

(29) Zhu, L.; Zhang, J.; Guo, Y.; Yang, C.; Yi, Y.; Wei, Z. Small Exciton Binding Energies Enabling Direct Charge Photogeneration Towards Low-Driving-Force Organic Solar Cells. *Angew. Chem., Int. Ed.* **2021**, *60* (28), 15348–15353.

(30) Xu, J.; Jo, S. B.; Chen, X.; Zhou, G.; Zhang, M.; Shi, X.; Lin, F.; Zhu, L.; Hao, T.; Gao, K.; Zou, Y.; Su, X.; Feng, W.; Jen, A. K.-Y.; Zhang, Y.; Liu, F. The Molecular Ordering and Double-Channel Carrier Generation of Nonfullerene Photovoltaics within Multi-Length-Scale Morphology. *Adv. Mater.* **2022**, *34* (16), 2108317.

(31) Zhou, Z.; Liu, W.; Zhou, G.; Zhang, M.; Qian, D.; Zhang, J.; Chen, S.; Xu, S.; Yang, C.; Gao, F.; Zhu, H.; Liu, F.; Zhu, X. Subtle Molecular Tailoring Induces Significant Morphology Optimization Enabling over 16% Efficiency Organic Solar Cells with Efficient Charge Generation. *Adv. Mater.* **2020**, *32* (4), 1906324.

(32) Liu, S.; Yuan, J.; Deng, W.; Luo, M.; Xie, Y.; Liang, Q.; Zou, Y.; He, Z.; Wu, H.; Cao, Y. High-Efficiency Organic Solar Cells with Low Non-Radiative Recombination Loss and Low Energetic Disorder. *Nat. Photonics* **2020**, *14* (5), 300–305.

(33) Zhu, C.; An, K.; Zhong, W.; Li, Z.; Qian, Y.; Su, X.; Ying, L. Design and Synthesis of Non-Fullerene Acceptors based on a Quinoxalineimide Moiety as the Central Building Block for Organic Solar Cells. *Chem. Commun.* **2020**, *56* (34), 4700–4703.

(34) Chen, H.; Liang, H.; Guo, Z.; Zhu, Y.; Zhang, Z.; Li, Z.; Cao, X.; Wang, H.; Feng, W.; Zou, Y.; Meng, L.; Xu, X.; Kan, B.; Li, C.; Yao, Z.; Wan, X.; Ma, Z.; Chen, Y. Central Unit Fluorination of Non-Fullerene Acceptors Enables Highly Efficient Organic Solar Cells with Over 18% Efficiency. *Angew. Chem., Int. Ed.* **2022**, *61* (41), No. e202209580.

(35) Englman, R.; Jortner, J. The Energy Gap Law for Radiationless Transitions in Large Molecules. *Mol. Phys.* **1970**, *18* (2), 145–164.

(36) Chandrabose, S.; Chen, K.; Barker, A. J.; Sutton, J. J.; Prasad, S. K. K.; Zhu, J.; Zhou, J.; Gordon, K. C.; Xie, Z.; Zhan, X.; Hodgkiss, J. M. High Exciton Diffusion Coefficients in Fused Ring Electron Acceptor Films. J. Am. Chem. Soc. **2019**, 141 (17), 6922–6929.

(37) Wei, Y.-C.; Wang, S. F.; Hu, Y.; Liao, L.-S.; Chen, D.-G.; Chang, K.-H.; Wang, C.-W.; Liu, S.-H.; Chan, W.-H.; Liao, J.-L.; Hung, W.-Y.; Wang, T.-H.; Chen, P.-T.; Hsu, H.-F.; Chi, Y.; Chou, P.-T. Overcoming the Energy Gap Law in Near-Infrared OLEDs by Exciton–Vibration Decoupling. *Nat. Photonics* **2020**, *14* (9), 570– 577.

(38) Lin, C.; Kim, T.; Schultz, J. D.; Young, R. M.; Wasielewski, M. R. Accelerating Symmetry-Breaking Charge Separation in a Perylenediimide Trimer through a Vibronically Coherent Dimer Intermediate. *Nat. Chem.* **2022**, *14* (7), 786–793.

(39) Eisner, F. D.; Azzouzi, M.; Fei, Z.; Hou, X.; Anthopoulos, T. D.; Dennis, T. J. S.; Heeney, M.; Nelson, J. Hybridization of Local Exciton and Charge-Transfer States Reduces Nonradiative Voltage Losses in Organic Solar Cells. *J. Am. Chem. Soc.* **2019**, *141* (15), 6362–6374.

(40) Chen, H.; Cao, X.; Xu, X.; Li, C.; Wan, X.; Yao, Z.; Chen, Y. A Low Reorganization Energy and Two-Dimensional Acceptor with Four End Units for Organic Solar Cells with Low Eloss. *Chin. J. Polym. Sci.* **2022**, 40 (8), 921–927.

(41) Chen, H.; Zhang, Z.; Wang, P.; Zhang, Y.; Ma, K.; Lin, Y.; Duan, T.; He, T.; Ma, Z.; Long, G.; Li, C.; Kan, B.; Yao, Z.; Wan, X.; Chen, Y. 3D Acceptors with Multiple A–D–A Architectures for Highly Efficient Organic Solar Cells. *Energy Environ. Sci.* **2023**, *16* (4), 1773–1782.

(42) Liang, H.; Chen, H.; Wang, P.; Zhu, Y.; Zhang, Y.; Feng, W.; Ma, K.; Lin, Y.; Ma, Z.; Long, G.; Li, C.; Kan, B.; Yao, Z.; Zhang, H.; Wan, X.; Chen, Y. Molecular Packing and Dielectric Property Optimization through Peripheral Halogen Swapping Enables Binary Organic Solar Cells with an Efficiency of 18.77%. *Adv. Funct. Mater.* **2023**, DOI: 10.1002/adfm.202301573.

(43) Zhang, Z.; Li, Z.; Wang, P.; Chen, H.; Ma, K.; Zhang, Y.; Duan, T.; Li, C.; Yao, Z.; Kan, B.; Wan, X.; Chen, Y. New Polymerized Small Molecular Acceptors with Non-Aromatic π -Conjugated Linkers for Efficient All-Polymer Solar Cells. *Adv. Funct. Mater.* **2023**, *33*, 2214248.

(44) Liao, Q.; Kang, Q.; Yang, Y.; An, C.; Xu, B.; Hou, J. Tailoring and Modifying an Organic Electron Acceptor toward the Cathode Interlayer for Highly Efficient Organic Solar Cells. *Adv. Mater.* **2020**, 32 (7), 1906557.

(45) Benatto, L.; Koehler, M. Effects of Fluorination on Exciton Binding Energy and Charge Transport of π -Conjugated Donor Polymers and the ITIC Molecular Acceptor: A Theoretical Study. *J. Phys. Chem. C* **2019**, *123* (11), 6395–6406.

(46) Han, G.; Yi, Y. Molecular Insight into Efficient Charge Generation in Low-Driving-Force Nonfullerene Organic Solar Cells. *Acc. Chem. Res.* **2022**, 55 (6), 869–877.

(47) Meng, D.; Zheng, R.; Zhao, Y.; Zhang, E.; Dou, L.; Yang, Y. Near-Infrared Materials: The Turning Point of Organic Photovoltaics. *Adv. Mater.* **2022**, *34* (10), 2107330.

(48) Zhu, W.; Alzola, J. M.; Aldrich, T. J.; Kohlstedt, K. L.; Zheng, D.; Hartnett, P. E.; Eastham, N. D.; Huang, W.; Wang, G.; Young, R. M.; Schatz, G. C.; Wasielewski, M. R.; Facchetti, A.; Melkonyan, F. S.; Marks, T. J. Fluorine Tuning of Morphology, Energy Loss, and Carrier Dynamics in Perylenediimide Polymer Solar Cells. *ACS Energy Lett.* **2019**, *4* (11), 2695–2702.

(49) Liang, Y.; Zhang, D.; Wu, Z.; Jia, T.; Lüer, L.; Tang, H.; Hong, L.; Zhang, J.; Zhang, K.; Brabec, C. J.; Li, N.; Huang, F. Organic Solar Cells Using Oligomer Acceptors for Improved Stability and Efficiency. *Nat. Energy* **2022**, *7* (12), 1180–1190.

(50) Wang, H.; Cao, C.; Chen, H.; Lai, H.; Ke, C.; Zhu, Y.; Li, H.; He, F. Oligomeric Acceptor: A "Two-in-One" Strategy to Bridge Small Molecules and Polymers for Stable Solar Devices. *Angew. Chem., Int. Ed.* **2022**, *61* (23), No. e202201844.

(51) Sun, C.; Lee, J. W.; Lee, C. Y.; Lee, D. C.; Cho, S. N.; Kwon, S. K.; Kim, B. J.; Kim, Y. H. Dimerized Small-Molecule Acceptors Enable Efficient and Stable Organic Solar Cells. *Joule* **2023**, 7 (2), 416–430.

(52) Li, Z.; Zhang, Z.; Chen, H.; Zhang, Y.; Yi, Y.-Q.-Q.; Liang, Z.; Zhao, B.; Li, M.; Li, C.; Yao, Z.; Wan, X.; Kan, B.; Chen, Y. Oligomeric Acceptor Enables High-Performance and Robust All-Polymer Solar Cells with 17.4% Efficiency. *Adv. Energy Mater.* **2023**, *13*, 2300301.

(53) Liu, F.; Hou, T.; Xu, X.; Sun, L.; Zhou, J.; Zhao, X.; Zhang, S. Recent Advances in Nonfullerene Acceptors for Organic Solar Cells. *Macromol. Rapid Commun.* **2018**, *39* (3), 1700555.

(54) Luo, Z.; Liu, T.; Ma, R.; Xiao, Y.; Zhan, L.; Zhang, G.; Sun, H.; Ni, F.; Chai, G.; Wang, J.; Zhong, C.; Zou, Y.; Guo, X.; Lu, X.; Chen, H.; Yan, H.; Yang, C. Precisely Controlling the Position of Bromine on the End Group Enables Well-Regular Polymer Acceptors for All-Polymer Solar Cells with Efficiencies over 15%. *Adv. Mater.* **2020**, 32 (48), 2005942.

(55) Zhang, Z.; Si, W.; Wu, B.; Wang, W.; Li, Y.; Ma, W.; Lin, Y. Two-Dimensional Polycyclic Photovoltaic Molecule with Low Trap Density for High-Performance Photocatalytic Hydrogen Evolution. *Angew. Chem., Int. Ed.* **2022**, *61* (10), No. e202114234.

(56) Meng, X.; Li, M.; Jin, K.; Zhang, L.; Sun, J.; Zhang, W.; Yi, C.; Yang, J.; Hao, F.; Wang, G.-W.; Xiao, Z.; Ding, L. A 4-Arm Small Molecule Acceptor with High Photovoltaic Performance. *Angew. Chem., Int. Ed.* **2022**, *61* (38), No. e202207762.

(57) Shen, Q.; He, C.; Li, S.; Zuo, L.; Shi, M.; Chen, H. Design of Non-Fused Ring Acceptors toward High-Performance, Stable, and Low-Cost Organic Photovoltaics. *Acc. Mater. Res.* **2022**, *3* (6), 644–657.

(58) Zhang, Z.-G.; Li, Y. Polymerized Small-Molecule Acceptors for High-Performance All-Polymer Solar Cells. *Angew. Chem., Int. Ed.* **2021**, 60 (9), 4422–4433. (59) Ma, R.; Fan, Q.; Dela Peña, T. A.; Wu, B.; Liu, H.; Wu, Q.; Wei, Q.; Wu, J.; Lu, X.; Li, M.; Ma, W.; Li, G. Unveiling the Morphological and Physical Mechanism of Burn-in Loss Alleviation by Ternary Matrix Toward Stable and Efficient All-Polymer Solar Cells. *Adv. Mater.* **2023**, *35* (18), 2212275.

(60) Yang, X.; Sun, R.; Wang, Y.; Chen, M.; Xia, X.; Lu, X.; Lu, G.; Min, J. Ternary All-Polymer Solar Cells with Efficiency up to 18.14% Employing a Two-Step Sequential Deposition. *Adv. Mater.* **2023**, 35 (7), 2209350.

(61) Zhang, Z.; Chen, H.; Xiao, Z.; Zhu, Y.; Wang, P.; Zhang, Y.; Kan, B.; Li, C.; Chen, Y. Two Nonlinear π -Conjugated Polymerized Small Molecular Acceptors Containing Thiophene or 3,4-Difluor-othiophene Linkage Unit for All-Polymer Solar Cells. *Org. Electron.* **2023**, *114*, 106735.