Molecular engineering of Y-series acceptors for nonfullerene organic solar cells

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Abstract
The power conversion efficiencies (PCEs) of single-junction organic solar cells (OSCs) have surpassed 19%, owing to the emerging Y-series nonfullerene acceptors (NFAs). Undoubtedly, the power and flexibility of chemical design has been a strong driver for this rapid efficiency improvement in the OSC field. Over the course of the past 3 years, a variety of modifications have been made to the structure of the Y6 acceptor, and a large number of Y-series NFAs have been reported to further improve performance. Herein, we present our insights into the rationale behind the Y6 acceptor and discuss the design principles toward high-performance Y-series NFAs. It is clear that structural modifications through choice of heteroatom, soluble chains, π spacers, central cores, and end groups alter the material characteristics and properties, contributing to distinctive photovoltaic performance. Subsequently, we analyze various design strategies of Y-series-containing materials, including polymerized small-molecule acceptors (PSMA), non-fused-ring acceptors (NFRA), and all-fused-ring acceptors (AFRA). This review is expected to be of value in providing effective molecular design strategies for high-performance NFAs in future innovations.

KEYWORDS
molecular engineering, narrow bandgap, nonfullerene, organic solar cell, Y-series acceptor

1 | INTRODUCTION

Organic solar cells (OSCs) have recently emerged as one of the most promising photovoltaic technologies that can be a potential cost-effective solution for the current energy and environmental crisis. The power conversion efficiencies (PCEs) of single-junction OSCs have been boosted to over 19%, thanks to the continuing development of new photovoltaic materials. Materials in the photoactive layer consist of electron donors and electron acceptors, where these two types of materials cooperate to realize the absorption and conversion of sunlight. The PCE trend in Figure 1 shows that the efficiency of OSC devices was initially 2.5% with the P3HT:PC61BM system in 2001, where P3HT acted as the donor and PC61BM, a classic fullerene, acted as the acceptor. The efficiencies of OSCs gradually improved with the design of new donor materials to match with the energy levels of fullerene acceptors. However, the best efficiencies of the donor:PCBM system saturated around ~10%. Since 2015, the development
of nonfullerene acceptors (NFAs) has resulted in further efficiency improvements. Compared to fullerenes, NFAs have superior chemical flexibility to manipulate and tune both optical band gap and overall molecular energy levels. Continuing material design and engineering to develop innovative NFAs has enabled the PCEs of OSC devices to recently exceed 19%.1,2,12–19

One milestone in the OSC field was the development of a class of new NFA in 2015, namely ITIC,20 with a record PCE at that time of 6.8% when blended with PTB7-Th as the donor. This report by the Zhan group demonstrated the potential of employing new NFAs to replace the dominating but already problematic fullerenes in practical applications of OSCs. Following this work, the PCE of ITIC-based OSCs was enhanced to over 11% with new donor materials.21,22 The structure of ITIC is shown in Figure 2, and consists of an electron-rich indacenodithienothiophene (IDTT) core with two electron-deficient 3-dicyanomethylene-1-indanone (IC) terminals. By extending the absorption into the near-infrared (NIR) region and adjusting the energy levels and molecular packing properties, the ITIC-series acceptors, typically containing an electron-rich core flanked with two electron-deficient end groups, have advanced the efficiencies of OSCs to 13%–15%.23–26

Another milestone was achieved in 2019 with the report of a new class of Y-series NFA, Y6, by Yuan et al.27 The structure of Y6 is shown in Figure 2, and while it still retains an electron-rich core flanked by two electron acceptors, the central core contains an electron-deficient benzothiadiazole (BT) unit, which is flanked by two alkylated thienothiophene groups. Different to ITIC, the solubilizing groups are not attached via sp3-hybridized carbon atoms but instead via electron-donating sp2-hybridized nitrogen atoms, which led to extended NIR absorption, high electron mobility, and low energy loss (Eloss). A highly impressive PCE of 15.7% was attained and from then on, these Y-series NFAs began to promote the progress of OSC research with high PCEs, which remain as the best-performing NFAs to date.28,29

In this review, we will first compare the chemical structures and relevant optical/electrical properties of ITIC and Y6 and highlight the structural property improvement from ITIC-series to Y-series NFAs. We will elucidate the structure–performance relationship and point out the unique features of Y6 from its superior device performance and single crystal results. The design principles relating to Y-series NFAs will be summarized in order to achieve further breakthroughs in OSCs. Taking advantage of the Y-series NFAs with strong NIR absorption and excellent photovoltaic performance, other Y-series-containing materials will be briefly described; for example, polymerized small-molecule acceptors (PSMAs), nonfused-ring acceptors (NFRAs) and all-fused-ring acceptors (AFRAs).

### Figure 1
Development trend of OSC efficiencies

**2 | DIFFERENCES BETWEEN ITIC AND Y6**

Relative to the ITIC-series NFAs, the prominent structural differences of Y6 are the introduction of an electron-deficient BT core, replacement of the cyclopentadienyls with pyrrole rings, and end group fluorination (Figure 2). The absorption onset (λonset) for Y6 is located at 931 nm, corresponding to an optical bandgap (Egopt) of 1.33 eV with a film absorption coefficient (ε) of 1.07 × 10^5 cm\(^{-1}\). With the same number of fused rings, it harvests more near-infrared light than ITIC (λonset = 780 nm, Egopt = 1.59 eV, and ε = 1.01 × 10^5 cm\(^{-1}\) for ITIC).27 Compared to their respective solution absorption spectra, an important bathochromic shift of 90 nm is observed in the thin film of Y6, indicating stronger aggregation of the molecular backbone and π–π interactions in the solid state than those of ITIC (bathochromic shift of 38 nm). Here, it is noteworthy that even nonfluorinated BZIC, a Y-series NFA with five fused ladder-type rings, exhibits a more red-shifted absorption than ITIC.30,31 However, according to energy levels measured by cyclic voltammetry, the HOMO and LUMO levels of Y6 are estimated to be at −5.65 and −4.10 eV, downshifted from those of ITIC, which is unfavorable for open-circuit voltage (VOC) in the OSC devices. This reduction in VOC is compensated by the enhancement in JSC from the broadened optical spectra in Y6-based blend films, in order to yield overall higher PCEs. Fluorination has demonstrated its positive effects on favorable molecular packing and optimal nanoscale morphology in...
FIGURE 2 Chemical structures of ITIC, BZIC, IT-4F, and Y6, with characteristics comparison of “landmark nonfullerene acceptor” ITIC and Y6. Normalized absorption spectra in chloroform solution and spun-cast thin film. Energy levels estimated by cyclic voltammograms

many studies.\textsuperscript{16,31,32} For example, both fluorinated ITIC-4F and Y6 exhibited better OSC efficiencies than nonfluorinated ITIC and BZIC.\textsuperscript{30,31} The red-shifted absorption and lower bandgap of Y6 can be attributed to the fluorinated electron-deficient end groups,\textsuperscript{16} the enhanced intramolecular electronic interactions induced by electron-deficient BT, and electron-donating pyrrole rings.\textsuperscript{33}

Both conventional and inverted OSC devices based on the as-cast PM6:Y6 blend achieved an impressive PCE of 15.7\%, and the best current density versus voltage ($J$–$V$) curve is shown in Figure 3A. From the figure, the optimal device based on the PM6:Y6 blend had a $V_{OC}$ of 0.86 eV, lower than that (1.04 eV) of PM6:ITIC,\textsuperscript{34} which can be well explained from the low-lying LUMO energy level of Y6. A short-circuit current ($J_{SC}$) of 25.3 mA cm$^{-2}$ was obtained for Y6-based devices, significantly larger than that (16 mA cm$^{-2}$) of ITIC-based devices due to its intensive NIR-absorbing spectrum, high electron mobility, broad internal quantum efficiency in the range from 450 to 860 nm, and nano-segregated structure with preferred orientation. The balanced charge carrier mobilities and ideal blend morphology also lead to higher fill factor (FF = 0.75) in Y6-based devices. More importantly, the Y6-based solar cells maintained high PCEs of 14.1\% and 13.6\% with thicker active layers of 250 and 300 nm respectively, which exhibited its compatibility with the roll-to-roll large-area printing process toward commercialization.\textsuperscript{35}

Figure 3B shows the theoretical 3D structure of Y6 based on the density functional theory (DFT) calculations, where -C$_{11}$H$_{23}$ side chains on the thiophene units were replaced by -CH$_{3}$ groups but the 2-ethylhexyl side chains on the nitrogen atoms were maintained. Influenced by the alkyl groups attached to the nitrogen atoms, the Y6 acceptor consists of two planar units, with a twist in the center. The dihedral angle for the twisted planar units is ca. 17.5°, with the 2-ethylhexyl side chains on the nitrogen atoms predicted to be orthogonal to the main plane. From the literature,\textsuperscript{27} there are three possible arrangements of the N-alkyl 2-ethylhexyl side chains, with the lowest energy predicted to be that with the two hexyl side chains directed toward the central core. There is a C2 axis of symmetry through the core of Y6, and a degenerate structure exists with the central core twisted in the opposite manner. From the chemical structure point of view, the presence of the alkyl side chains on the pyrrolic nitrogen atoms prevent overaggregation of the electron-deficient core through steric effects and also maintains an efficient intramolecular charge transport channel.\textsuperscript{36}
The single crystal of the Y6 molecule has been analyzed to deepen the understanding of its molecular packing behavior (Figure 3C). The alkyl side chains onto the N-atoms can greatly influence the stacking of adjacent molecules. As seen from the main view and side view, the curve-shape molecular geometry forms a twisted 1D transport channel and slipped packing motif, agreeing with the planar structure from DFT calculations. The zigzag polymer-like conjugated backbone with π–π stacking between end groups is the major driving force for such morphology. The electron-deficient BT core also interacts with the end-group terminals to some extent. In view of the dimerization in a crystal unit cell, the other set of Y6 molecules could form another 1D transport channel, which is strikingly dissimilar from the ITIC-series molecules, resulting in a multidimensional interpenetrating network and transport channels. Single-crystal structures of related Y-series NFAs have also been obtained. A Y-series NFA with trifluoromethyls attached at the terminals exhibited both traditional J-aggregation caused by the π–π stacking between end groups and H-aggregation caused by the π–π stacking between electron-deficient cores. This 3D interpenetrating network should provide more electron-hopping channels to improve the charge transport in multiple directions. Certainly, the special molecular design of Y-series NFAs, different from anterior ITIC-series, has led to different molecular packing behaviors, resulting in different blend morphologies and OSC performances. The following discussion will focus on chemical synthesis as a powerful tool in the development of new...
Y-series acceptors. For in-depth information relating to the physical mechanisms of Y-series nonfullerene acceptors, readers are referred to other existing works. 45–47

3 | MOLECULAR DESIGN OF Y-SERIES NONFULLERENE ACCEPTORS

The general synthesis of Y-series molecules is relatively complex, and more efficient routes are desirable for large-scale preparations. Figure 4A,D shows that 11 synthetic steps are involved to prepare the original molecule of Y6 and more steps are required for other Y-series NFAs, such as benzotriazole (BTz) (Figure 4B), benzoselenadiazole (Figure 4C), and quinoxaline as the electron-deficient cores. 48–50 From the reported routes, all the Y-series derivatives are prepared following a synthetic process of Stille coupling, double intramolecular Cadogan reductive cyclization, N-alkylation, formylation reaction, and Knoevenagel condensation. Ideally any commercially viable NFA would be readily synthesized in steps avoiding the use of toxic reagents or extremes of temperature. This can be potentially realized by NFRAs with ordered molecular packing through noncovalent interaction, which significantly addresses the synthetic complexity, vide infra.

In general, there are five possible modifications that can be made to the structure of Y6: (i) variation of side chains on the nitrogen atoms of pyrrole rings or thiophene \( \beta \)-sites; (ii) alteration of the electron-rich thienothiophene units; (iii) modification of electron-deficient central core and end groups; (iv) extension of the \( \pi \)-conjugated backbone by inserting \( \pi \) spacers; and (v) replacement of the sp\(^2\)-hybridized nitrogen atoms. 59,60 These modifications are illustrated in Figure 5.

3.1 | Side chain

Side-chain engineering will affect the solubility of target Y-series molecules but is also critical for molecular packing and self-assembly properties, which will determine the morphologies of the photovoltaic materials. Side chains on the pyrrole rings and the \( \beta \) position of thiophene are tailorable to induce changes to the molecular assembly and influence on photovoltaic properties of Y-series NFAs.

To ensure the good solubility of Y6, alkyl chains are introduced at the \( \beta \) position of the outermost thiophene rings of the central core. These alkyl chains on both sides are also favorable for conformational locking to achieve less energetic disorder. For example, Kong et al. reported two isomeric Y-series NFAs with thienyl outer side chains attaching a 2-ethylhexyl substituent at the \( \alpha \)-or \( \beta \)-position (named \( o \)-TEH and \( m \)-TEH, respectively, Figure 6). 51 They found that the substitution position on the thienyl outer side chains influenced the molecular geometry, molecular aggregation, and photovoltaic performance of the NFAs significantly. These bulky thienyl chains can bring steric hindrance effect and force end groups to form a locked conformation with O\( \cdots \)S interaction. \( m \)-TEH exhibited stronger and more ordered intermolecular packing than \( o \)-THE from DFT calculation and morphology analysis, which could facilitate the charge transport. By using the wide-bandgap quinoxaline-based copolymer PBQ6 as the donor, \( m \)-TEH-based binary OSCs demonstrated an
impressive PCE of 18.51%, with a $V_{OC}$ of 0.880 V, a $J_{SC}$ of 26.61 mA cm$^{-2}$, and a FF of 0.79, while $o$-THE-based devices showed a moderate PCE of 16.22%. The outermost alkyl chains are reported to be beneficial to a low degree of energetic disorder and reduced energy loss, caused by the torsion-free molecular conformation. Besides, linear rather than branched side chains are preferred on the outermost sites, as the branched alkyl chains may affect the intermolecular terminal packing and would be harmful to the device performance. The length of alkyl
chains is another consideration for optimization to further adjust the material properties, including terminal packing strength and absorption.

Regarding the side chains on the pyrrole rings, Hong et al. tuned the 2-ethylhexyl chains on Y6 to 2-butyloctyl chains, and the resultant molecule, BTP-4F-12, showed better processability and enhanced π–π stacking, yielding an improved PCE of 16.4%, superior to that of Y6 (15.7%). Because of the improved solubility, various kinds of greener solvents can be used to fabricate the OSC devices with over 14% PCEs, and THF-processed OSCs could reach a high PCE of 16.1%, demonstrating the benefits of simple alkyl chain modification.52 Other systematic alkyl chain modifications on the pyrrole rings have also demonstrated that the alkyl chain’s length and branched positions will have effects on the molecular geometries and the OSC device performance.38,61

3.2 | Electron-rich core

Structural modification of the fused-ring cores has a significant influence on the molecular properties and photovoltaic performance for ITIC- and Y-series molecules. Adjustment of the conjugation length of the electron-rich units and the introduction of heteroatoms are among the most popular design approaches to construct new cores.62,63 To study the conformation effects of electron-rich units on molecular properties and device performance of Y6, three Y-series NFAs were designed and synthesized by Gao et al., employing asymmetric molecular design strategies through regulating the lateral thiophene orientation of the fused core.53 BP5T-4F is an asymmetric NFA that extends the π-conjugation length of Y6 by fusing one more thiophene onto one side of the thienothiophene unit, leading to a Z-shaped conformation. With this asymmetric design, the PM6:BP5T-4F device showed a suppressed nonradiative $E_{\text{loss}}$ (0.242 eV) and a high $V_{\text{OC}}$ (0.89 V). The best PCE for BP5T-4F-based devices was further increased from 16.7% to 17.2% by employing a ternary OSC device with another NFA, CH1007, as the complementary third component.

Asymmetric design strategies have been applied to modify each part of Y6 and its derivatives, such as the backbone,64,65 side chains,66,67 and end groups,68,69 possibly inspired by the asymmetry of fullerene acceptors, PC$_{61}$BM and PC$_{71}$BM. First, the design of asymmetric central cores may endow the resultant NFAs with larger dipole moment and stronger intermolecular binding energy than their symmetric counterparts.53 This would be favorable to reinforce intermolecular interaction/stacking and increase charge carrier mobility. Second, the LUMO level of the NFAs and the morphology in blend films can also be finely tuned, contributing to an increase of all four key parameters ($V_{\text{OC}}$, $J_{\text{SC}}$, FF, and PCE) in OSCs.65 Third, different functional groups may be substituted onto each side of the NFAs, which can have a synergistic regulation effect on the physicochemical properties, molecular packing, and photovoltaic performance of Y-series variants.64,65 Likewise, the substitution of asymmetric side chains (vide supra) has shown great potential to minimize the trade-off between $V_{\text{OC}}$ and $J_{\text{SC}}$ and obtain appropriate morphology.66,67

CH1007 was designed as a selenium analog of Y6 to study the effect of chalcogen substitution.54,55 Selenium atom is more polarizable than sulfur due to its larger size.70 Replacing sulfur with selenium can also enhance the intra- and intermolecular interactions, allowing refinement of molecular properties to a subtle extent.71 The more electron-rich and polarizable selenophene can also enhance the quinoidal character of the corresponding NFAs, resulting in decreased optical band gaps. The single crystal results of CH1007 showed that the conjugated backbone became more coplanar, with less π-core torsion and smaller dihedral angles, presumably due to incorporation of the larger selenium atoms, forming longer C–Se bonds. Benefitting from the red-shifted optical absorption via selenium substitution, the CH1007-based photovoltaic devices yielded best PCE of 15.96% when blended with PM6 as the donor. OSC devices were also further fabricated with a PM6:CH1007:PC$_{71}$BM ternary blend, which delivered an exceptionally high $J_{\text{SC}}$ of 27.48 mA cm$^{-2}$ and a PCE of 17.08%.54

3.3 | Electron-deficient unit

The 3D molecular packing of Y6 appears to result from its unique π-core interactions owing to the S–N interactions between BT moieties, which facilitates further development of its molecular packing to construct 3D networks. Electron-deficient core engineering plays a key role in the photovoltaic properties of Y-series NFAs. In contrast to the benzene core in ITIC, the electronegative fused-ring core in Y-series NFAs helps to enhance the intramolecular electronic interactions, which results in lower bandgap.

Compared to Y6, the replacement of sulfur with nitrogen atom in the central electron-deficient unit can serve as a new bridge for covalent planarization,50 which provides stronger electron-donating character and thus increases the HOMO energy levels. Prior to Y6, Y1 and Y2 were synthesized by Yuan et al., where benzotriazole (BTz) unit was used as the molecular core.50 Both Y1 and Y2 possessed low nonradiative recombination losses of ~0.25 eV, owing to the reduced $E_{\text{loss}}$ by enhancing the electroluminescence efficiency of these NFAs. Y11 is another NFA based on the BTz unit.56 An $E_{\text{loss}}$ of just 0.17 eV and a high PCE of up
to 16.54% was reported for the Y11-based single-junction OSCs.

It is vital to develop the electron-deficient cores to construct new Y-series NFAs because the variation of electron-deficient cores will greatly influence the energy levels and molecular packing. For example, the BT unit enables high electron mobility for charge transport, while the BTz unit has an extra electron-donating nitrogen atom, leading to higher energy levels than BT and quinoxaline units. Though, the quinoxaline unit has more possibility for structural modifications. Exploring new electron-deficient cores to achieve better photovoltaic performances is a development trend of Y-series NFAs. However, there are limitations due to the synthetic difficulty of the Cadogan reaction.

The electron-deficient end groups function as the channels for electron transport via \( \pi-\pi \) stacking, in addition to modulating the absorption and energy levels. Compared to alkyl chain and core engineering, end group engineering has been more extensively investigated. Partly this is due to the improved synthetic accessibility, with attachment via Knoevenagel condensation to the respective donor core. Halogenation and conjugation extension of the acceptor end group have been the most common strategies.\(^{72,73}\) Wang et al. synthesized an array of Y-series NFAs with hetero-dihalogenated electron-deficient end groups.\(^{56}\) The Y-BO-FCl NFA exhibited a slightly lower energy level, the most planar molecular geometry, the shortest intermolecular packing distance, and largest \( \pi-\pi \) electronic coupling compared to the other two synthesized NFAs with -FBr and -ClBr terminals. Moreover, the PM6:Y-BO-FCl blend films presented a more ordered face-on orientation crystallinity and more suitable fiber-like phase separation, resulting in a remarkable PCE of 17.52%. Many achievements in the PCEs of OSCs demonstrated that altering the electron-deficient end groups is an effective way to design new NFAs.\(^{74-76}\) Here, we note that molecular engineering of Y-series NFAs with asymmetric end groups can provide diverse structural variants and create a platform to investigate the structure–property–performance relationship.\(^{68,69}\) Compared to asymmetric electron-rich core and peripheral side chains, asymmetric end groups have many attractive advantages. Asymmetric Y-NFAs can be readily prepared, as connecting end groups with the backbone via the Knoevenagel condensation is the last reaction step. Moreover, high efficiency and high luminescence can exist simultaneously, which is conducive to regulating the energy loss. Besides, as molecular packing is a stark difference between ITIC and Y6, the intermolecular interaction between the three electron-deficient units (BT core and two different IC end groups) can be adopted to align crystal packings.

### 3.4 \( \pi \)-Conjugated spacer

The use of \( \pi \)-spacers was a common strategy in the ITIC-series NFAs, but few studies have reported the influence of \( \pi \)-spacers on Y-series NFAs.\(^{77}\) Hai et al. designed two ultra-narrow bandgap acceptors by introducing a vinylene \( \pi \)-bridge into the Y-series NFAs.\(^{57}\) BTP-2V-2F, with two vinylene \( \pi \)-bridges on each backbone terminal, only exhibited a moderate PCE of 11%, despite its absorption being extended to the NIR range \((E_g = 1.22 \text{ eV})\). Through decreasing the number of vinylene \( \pi \)-bridges, BTP-1V-2F, with an asymmetric backbone, also exhibited NIR absorption and low-lying energy levels. Benefiting from the higher \( V_{OC} \) and \( FF \), a superior efficiency of 14.24% was achieved, which was one of the highest values for single-junction OSCs based on ultra-narrow bandgap NFAs \((E_g < 1.29 \text{ eV})\). Another set of NIR Y-series NFAs was reported by conjugating the central core to end groups through alkyl thiophene bridges.\(^{58}\) Chen et al. found that the alkyl chains on the thiophene bridges played a decisive role in regulating the optoelectronic properties of Y-series NFAs and optimizing the device performance. The acceptor H3 with outward alkyl chains had clear advantages to achieve a higher PCE (13.75%) over those with either inward or branched side chains. As low-bandgap NFAs are of great potential for applications in ternary,\(^{4,78}\) tandem,\(^{79}\) semitransparent\(^{80,81}\) OSCs, and organic–inorganic hybrid solar cells, it is worth exploring new \( \pi \)-conjugated spacers to construct NIR NFAs with a photosresponse beyond 1000 nm.

### 3.5 Bridging atom

The synthetic route toward the donor core (Figure 4) relies upon the Cardogan reaction for ring-closing, and as such the bridging atom in Y6 is nitrogen; this leaves limited room for replacement with new bridging atoms. However, the importance of bridging atoms in ladder-type materials cannot be underestimated.\(^{82}\) To the best of our knowledge, all reports of Y-series NFAs utilize a bridging nitrogen atom in OSCs. However, structurally similar ladder-type materials with a benzothiadiazole/benzotriazole central unit and adjacent sulfur bridges have been successfully synthesized. Additional benzodithiophene-containing side chains were fused to the core to increase the whole conjugation length and solubility. These materials were investigated for two-photon absorption\(^{59}\) and single-molecular conductance\(^{60}\) rather than OSCs however. Whether it is alkyl chain engineering, core engineering, or end group engineering, any modifications on the Y-series molecules might lead to changes in
molecular packing behaviors, film morphology, and device performance.

4 | DEVELOPMENT OF Y-SERIES-CONTAINING ACCEPTORS

With the emergence of Y6, many efforts have been taken to further develop Y-series NFAs to achieve new improvements in the PCEs of OSCs. However, these small-molecule NFA-based OSCs tend to have shorter operational lifetime due to their poor morphological and device stabilities under mechanical and thermal stresses compared to all-polymer-based OSCs. Although, the PCEs of all-polymer-based OSCs lag behind due to the lack of high-performance polymer acceptors. To broaden the library of polymer acceptors, polymerized small molecular acceptors (PSMAs) are proposed to provide a new way to develop efficient polymer acceptors.

Another challenge for developing new NFAs is to address the trade-off between their high performance and synthetic complexity. As seen from the structures of ITIC and Y6 (Figure 2), a multiple-fused ring serves as the central core, which is always associated with multiple-step synthesis and purification, hampering their large-scale production and potentially limiting the commercialization of OSCs. Recent research has demonstrated that NFRAFs are structurally simpler and may offer a route to a better cost-efficiency balance. Instead of chemically fusing the adjacent aromatics with covalent bonds, noncovalent interactions of NFRAFs are employed as conformational locks to mediate the coplanarity of the π-conjugated skeleton. Moreover, the exocyclic double bonds in the ITIC- and Y6-series NFAs, formed by the kinetically reversible Knoevenagel condensation reaction, have been proven highly labile upon photo-oxidation, ZnO-catalyzed photodegradation, and base-induced decomposition. To improve the stability of the NFAs, increasing the steric hindrance of the exocyclic double bonds by incorporation of side alkyl chains or developing a ring-locked double bond have been reported as effective strategies. Recently, AFRAs, with a rigid and planar ladder-type structure, have been proposed to reduce reorganization energy and achieve both high PCEs and stability.

4.1 | Polymerized small molecular acceptors

A strategy of polymerizing small-molecule acceptors (SMA) to construct new polymer acceptors has been proposed to take advantage of the optoelectronic properties of the NFAs, as all-polymer solar cells have inherent merits of facile film formation, stable morphology, and mechanical flexibility. Most studies have used a conjugated linkage to design PSMAs while nonconjugated linkages have also realized a promising PCE for its OSC devices, along with good thermal stability. Y-series-containing PSMAs are developed to take advantage of the Y-series small molecule acceptors with strong NIR absorption and excellent photovoltaic performance.

Thiophene and selenophene are among the widely used electron-rich linkages. Fan et al. developed a series of multiselenophene-containing PSMA by varying the numbers of selenophene in the NFA and π-conjugated linkage (Figure 7). Compared to the selenophene-free analog PFY-0Se, PFY-3Se exhibited a red-shifted absorption spectrum, closer π–π stacking, and increased electron mobility. The all-polymer solar cells derived from PFY-3Se yielded a highest PCE of 15.1%, much better than that of PFY-0Se (PCE = 13.0%). Furthermore, PFY-3Se maintained good batch-to-batch properties for realizing reproducible device performance and showed a low dependence of photovoltaic performance on device area (0.045–1.0 cm²) and active layer thickness (110–250 nm), indicating that PFY-3Se is a potential candidate for efficient all-polymer solar cells toward practical applications.

By copolymerizing with a bithiophene imide as an electron-deficient linkage, Sun et al. reported the development of a narrow-bandgap n-type polymer L14 with an acceptor–acceptor backbone (Figure 7). L14 showed a narrow bandgap, high absorption coefficient, and low-lying frontier molecular orbital levels. Luckily, open-circuit voltage \( V_{OC} \) was not sacrificed, attributed to a small nonradiative recombination \( E_{loss} \) of 0.22 eV. An excellent PCE of 14.3% with a high \( V_{OC} \) of 0.96 V was achieved for the PM6:L14-based OSCs. Later, they designed a regioregular analog L15, which had a higher absorption coefficient as well as higher electron mobilities compared to those of L14. The regioregular backbone endowed L15 to have superior backbone ordering and form more optimal blend morphology with PM6 compared to those achieved by L14, leading to a higher PCE of 15.2%.

Constructing PSMAs with regioregular backbone is a promising method for improving the OSC performance. Fu et al. also developed a regioregular PSMA PZT-γ to achieve higher regiospecificity and superior backbone ordering for avoiding the formation of isomers during polymerization (Figure 7). The less electron-deficient BTz, relative to BT, endowed PZT-γ with a red-shifted absorption and upshifted LUMO level. Consequently, PZT-γ-based OSCs showed simultaneously enhanced \( V_{OC} \) and \( J_{SC} \) along with a small nonradiative recombination \( E_{loss} \) (0.51 eV), affording a high PCE of 15.8%, which highlighted the importance of regulating the fused electron-deficient core...
FIGURE 7  Chemical structures of the Y-series-containing polymerized small molecular acceptors (PSMAs).

and controlling backbone regioregularity for achieving high-performance OSCs.

A random ternary copolymerization strategy was adopted by Du et al. to develop new PSMAs (Figure 7).\textsuperscript{102} By random copolymerization of Y6-like units, thiophene $\pi$-linkage units, and 3-ethylesterthiophene units, a series of PSMAs PTPBT-ET$_x$ with controlled molar ratios of 3-ethylesterthiophene were synthesized. Compared to PTPBT with only Y6-like units and thiophene units, PTPBT-ET$_x$ with an incorporated 3-ethylesterthiophene unit in the ternary copolymers showed upshifted LUMO energy levels, increased electron mobilities, and improved blend morphologies. With a gradual increase of the 3-ethylesterthiophene molar ratio in the PSMAs, the PTPBT-ET$_0.3$-based OSCs showed progressively increased $V_{OC}$. Highest PCE of 12.52% with a long-term photostability of over 300 h was obtained with PTPBT-ET$_{0.3}$ as the acceptor and PBDB-T as the donor, which indicated that random ternary copolymerization is another effective strategy for the construction of high-performance PSMAs.

4.2  Non-fused-ring acceptors

The high-performance ITIC- and Y-series NFAs consist of a multiple-fused ring framework in their central cores, resulting in an elevated synthetic cost. Designing NFRAs is an effective strategy to break the fused structures and reduce the number of synthetic steps (Figure 8A).

Yu et al. have developed a series of NFAs with unfused backbones, that is, PTICH, PTIC, and PTICO, by utilizing noncovalent O--H interactions.\textsuperscript{103} These NFRAs were synthesized from simple aromatic units with reduced reaction steps. Decent PCEs of 10.27% and 13.97% were achieved...
in single and tandem OSCs, which exhibited better thermal and light stabilities than their fused counterpart-based devices. At the same time, Huang et al. reported a series of low-cost noncovalently bound NFRAs, which consisted of a ladder-like core locked by noncovalent S⋯O interactions. These NFRAs had optical absorption broadened to the NIR region, high electron mobilities, small nondiabetic recombination \( E_{\text{loss}} \) loss, and displayed an outstanding efficiency of 13.24%.\(^{104} \) Other intramolecular interactions, such as F⋯H and S⋯N, have also been utilized to construct NFRAs. Recently, the PCEs of NFR-based OSCs have been pushed to 15.2% by a completely non-fused molecule A4T-16, realizing their great potential to achieve low-cost high-performance OSCs.\(^{105} \)

For the Y-series NFAs, design ideas, like using a strong electron-deficient core, introducing nitrogen atoms, or using alkyl chains, should be further explored to improve molecular ordering.\(^{106} \) A Y-series NFA NoCA-5 with a benzotriazole core has a promising PCE of 14.82%.\(^{106} \) There are several merits of NFRAs.\(^{107} \) By deploying noncovalent interactions and steric hindrance, rigid and coplanar structures can be realized in NFRAs, which lead to ordered molecular packing and high electron mobility. Besides, numerous building blocks can be utilized to readily modify the chemical structures of NFRAs. Moreover, NFRs have exhibited higher photostability and device stability than the fused-ring NFAs. Due to their inferior efficiencies when compared to fused-ring NFAs, it is urgent to develop new NFRAs to achieve a better efficiency–stability–cost balance.

### 4.3 All-fused-ring acceptors

Designing new NFAs with the all-fused-ring strategy is still at the initial stage. With the all-fused-ring design, AFRAs are expected to have low reorganization energy, favorable aggregation, and high electron mobility, attributed to their rigid and planar structures. Similarly, AFRA-based OSCs tend to have high thermal, chemical, and photochemical stability. For example, three AFRAs, namely ITYM, F11 and F13(Figure 6 and 8(B)), were reported by Zhu and coworkers, which exhibited extraordinary thermal, chemical, and photochemical stability.\(^{86,90} \) Confirmed by the single-crystal X-ray analysis, ITYM, an ITIC-series NFA, formed a strong \( \pi–\pi \) stacking along the end groups, which could facilitate 1D charge transport. In contrast, electron-deficient BT unit was introduced in the central core to construct F11 and F13. These Y-series-containing AFRAs had a more red-shifted absorption, more favorable J-aggregation, and a 3D network packing structure. A high PCE of 13% was achieved for the D18:F13-based devices (9.51% for D18:ITYM and 11.2% for D18:F11), demonstrating that constructing AFRAs is a promising strategy for high-performance OSCs with high stability. The optoelectronic properties of the AFRAs can be further tuned by incorporation of other electron-rich or electron-deficient cores, side chain modification, or end group modification.

### 5 CONCLUSIONS AND PERSPECTIVES

The recent development of high-performance Y-series NFAs has contributed immensely to the PCE increase for single-junction OSCs, and PCEs of over 20% are expected soon. In this review, the structural comparison between ITIC and Y6 has been provided, and it is clear that the markedly different molecular packing and NIR absorption have a great impact on their respective optoelectronic properties. As BT-based conjugated polymers have demonstrated great importance in organic transistors, fusion of the electron-deficient BT unit into the central backbone of nonfullerene acceptors can contribute to high electron mobility with enhanced delocalization of \( \pi \) electrons.\(^{49} \) Compared to ITIC-type acceptors with predominately linear stacking, 3D network structures are found in most Y-series small molecule acceptors, due to the multiple noncovalent interactions between central cores and terminal groups.\(^{34} \) The absorption of Y6 has been extended further in the NIR region, which is beneficial to harvest more photons in the blends and a prerequisite for high-efficiency OSCs.\(^{46} \)

A number of modifications to the structure of Y6 have been explored in order to elucidate effective molecular design strategies to attain high-performance OSCs. Such
modifications are shown to influence material properties (e.g., energy levels, absorption, molecular packing), resulting in different OSC performances. Variation of side chains on the nitrogen atoms of pyrrole rings or thiophene \( \beta \)-sites mainly influences the solubility of Y-series acceptors, molecular crystallization, and film morphology in blends.\(^{14,57,58} \) Alteration of the electron-rich thienothiophene units can greatly impact the light-absorbing capability and intermolecular charge transport of the resultant molecules.\(^{53,54} \) The main feature in Y-series acceptors is the incorporation of an electron-deficient unit into the central core, which induces multiple interlocked interactions and forms favorable 3D electronic transport channels. From the reported single crystal results, fluorine, bromine, chlorine, or trifluoromethyl substituted end groups do not affect the formation of 3D stacking in Y-series acceptors. End groups functionalization is essential to adjust optical bandgaps, energy levels and finely construct 3D network packing for more effective electron transport.\(^{55,56} \) Extension of the \( \pi \)-conjugated backbone by inserting \( \pi \) spacers has been widely used in ITIC-series acceptors to obtain narrow bandgap absorption, but comparatively its application in Y-series acceptors does not yield high-efficiency devices.\(^{57,58} \) Most Y-series acceptors contain sp\(^2\) hybridized nitrogen atoms, and replacement of these bridging atoms can provide more structural flexibility for new class of NFAs.\(^{59,60} \)

Other Y-series-containing acceptors, such as PSMAs, NFRAs, and AFRAs, are reviewed. These are promising candidates to tackle the serious issues of mechanical processability, synthetic complexity, and device stability in ITIC- and Y-series-based devices. All-polymer solar cells have very promising applications in wearable electronics due to their good morphological and mechanical stabilities. N2200 is a well-studied n-type polymer and, because of its suitable energy levels and high electron mobility, N2200-based all-polymer solar cells have exhibited PCEs of \( \sim \)12\%. The limiting factor is its weak absorption, therefore developing narrow-bandgap polymer acceptors is critical to achieve high photocurrent generation and device efficiency.\(^{91} \) The chemical strategy by polymerizing Y-series small-molecule acceptors to construct new polymer acceptors is impressively successful in achieving high PCEs, because these PSMAs possess a narrow bandgap and a broad absorption in the NIR region. NFRAs can also be a good candidate as electron acceptors. With this chemical strategy, complex synthetic steps (Figure 4) can be avoided.\(^{55,105,107} \) The \( \pi-\pi \) interaction and intermolecular charge transfer can be enhanced by noncovalent interactions or steric hindrance that lock the molecular geometry and thus maintain conformational unicity. Alternatively, the arrangement of electron-deficient end groups, electron-rich bridge, and central core can be used to the same effect. Construction of a 3D network packing as in fused Y6 molecules is an effective approach to further improve the PCEs of NFA-based OSCs. The concept of AFRAs was proposed last year to synergistically achieve high stability, low cost, and good efficiency OSCs.\(^{86,90} \) This class of nonfullerene acceptors possess low molecular reorganization energy and excellent chemical, photochemical, and thermal stability. All-fused Y-series acceptors F11 and F13 (Figure 6) exhibit NIR response, and the 3D honeycomb stacking structure enables efficient charge transport. Therefore, AFRAs are a class of high-performance NFAs without the traditional IC terminals.

Although Y-series NFAs have made exciting breakthroughs in OSC efficiencies, there are some continuing challenges for material chemists. For instance, currently most Y-series NFA-based OSCs have yielded low \( V_{OC} \) (<1.0 V)\(^{68,108} \) Innovation in molecular design is thus crucial to upshift their LUMO levels and reduce \( E_{loss} \) for further boosting device performance. Different to their inorganic and perovskite counterparts, flexibility and semitransparency are superior features for OSCs. However, the absorption edge of Y-series NFAs is mainly located at \( \sim \)930 nm, which is not optimal for constructing semitransparent devices. Developing new Y-series NFAs with absorption extended over 1000 nm will be beneficial for achieving high-performance semitransparent OSCs. A third component has been utilized in the fabrication of ternary OSCs, as the additional photovoltaic material can function as an optical complement to enhance light harvesting, an energetic agent to promote charge generation and transport, a morphology regulator to finely tune the microstructures in the blends, and a stabilizer to suppress phase separation during the device aging process.\(^{47,78} \) Developing ratio-insensitive ternary OSCs with improved reproducibility needs to be explored. Furthermore, the development of new donor materials that are well matched with Y-series acceptors can further enhance efficiency. Molecular design of new donors and acceptors remains a prerequisite for the evolution of high-efficiency low-cost good-stability devices in the OSC research. The stability issue is a crucial gap existing between high efficiency and real commercialization in OSCs.\(^{18,88,105} \) Exploration of new organic molecules is perhaps the most powerful way to target stability, such as the benzothiadiazole-rhodanine terminated nonfullerene acceptors and the emerging classes of NFRAs and AFRAs. In addition, an in-depth understanding of OSCs device limitations and degradation mechanisms can provide crucial insights for the design of new robust NFAs.

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**CONFLICT OF INTEREST**
The authors declare no conflict of interest.

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