Recent progress in low-cost noncovalently fused-ring electron acceptors for organic solar cells

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Abstract
The power conversion efficiencies (PCEs) of organic solar cells (OSCs) have improved considerably in recent years with the development of fused-ring electron acceptors (FREAs). Currently, FREAs-based OSCs have achieved high PCEs of over 19% in single-junction OSCs. Whereas the relatively high synthetic complexity and the low yield of FREAs typically result in high production costs, hindering the commercial application of OSCs. In contrast, noncovalently fused-ring electron acceptors (NFREAs) can compensate for the shortcomings of FREAs and facilitate large-scale industrial production by virtue of the simple structure, facile synthesis, high yield, low cost, and reasonable efficiency. At present, OSCs based on NFREAs have exceeded the PCEs of 15% and are expected to reach comparable efficiency as FREAs-based OSCs. Here, recent advances in NFREAs in this review provide insight into improving the performance of OSCs. In particular, this paper focuses on the effect of the chemical structures of NFREAs on the molecule conformation, aggregation, and packing mode. Various molecular design strategies, such as core, side-chain, and terminal group engineering, are presented. In addition, some novel polymer acceptors based on NFREAs for all-polymer OSCs are also introduced. In the end, the paper provides an outlook on developing efficient, stable, and low-cost NFREAs for achieving commercial applications.

KEYWORDS
low cost, noncovalently fused-ring electron acceptors, organic solar cells

INTRODUCTION

Organic solar cells (OSCs) have recently attracted tremendous research attention from the academic and industrial community.¹–⁸ Compared with inorganic solar cells, OSCs have the advantages of low cost, light weight, semitransparency, and flexibility.¹⁹–¹² In general, a typical OSC device consists of a bulk heterojunction active layer (a p-type electron donor and an n-type electron acceptor blend) sandwiched between an anode and a cathode.¹³,¹⁴ Fullerene derivatives have been used as electron acceptors in OSCs for two decades. The ball-like and fully conjugated structures of fullerene derivatives provide strong electron-withdrawing and isotropic electron transport abilities, facilitating electron delocalization at the electron donor:electron acceptor interface. However, the maximum power conversion efficiencies (PCEs) of fullerene-based solar cells are limited to ~12% due to untunable energy levels, weak absorption in the visible region, poor photostability, and other defects of fullerene derivatives.¹⁵–²⁰ In 2015, a fused-ring electron acceptor (FREA) named 3,9-bis(2-methylene-(3-(1,1-dicyanomethylene)-indanone))-5,5,11,11-tetrakis(4-hexylphenyl)-dithieno[2,3-d:2′,3′-d’]-s-indaceno[1,2-b:5,6-b’]dithiophene) (ITIC) with the acceptor-donor-acceptor (A-D-A) type structure reported by Zhan et al. broke through this bottleneck.²¹ FREAs typically...
NFREAs are used in tandem devices within the past 5 years. However, the high cost and poor scalability significantly hinder the industrialization of OSCs. Therefore, there is an urgent need to explore new design strategies to develop molecules with simple structures, easy synthesis, low cost, and high photovoltaic performance. A strategy to construct noncovalently fused-ring electron acceptors (NFREAs) by splitting large fused-ring backbone into small conjugated groups using single bonds has been proposed. This design strategy avoids complex and low-yielding cyclization reactions, thereby simplifying the molecular synthesis steps and reducing the cost of synthesis. The nonfused molecule structure can also enhance intramolecular synthesis steps and reducing the cost of synthesis. The cyclization reactions, thereby simplifying the molecular backbones, the terminal group, and the side-chain. The energy levels and molecular packings of NFREAs can be fine-tuned by selecting the appropriate building blocks, such as cyclopenta[2,1-b:3,4-b]dithiophene (CPDT) and 5,5′-bis(4-hexylphenyl)-5H-dithieno[3,2-b:2′,3′-d]Pyran (DTP). In particular, locking the planar geometries of the molecular backbones through noncovalent interactions induced by heteroatom on the above building blocks such as S⋯O, O⋯H, and F⋯H facilitates forming ordered molecular packing in the solid state and efficient electron transport, leading to highly efficient OSCs. Although great progress has been achieved by NFREAs, they still fall somewhat short of the current PCE record of FREAs. In this regard, this paper reviews recent progress in NFREAs for OSCs. Firstly, we classify NFREAs into two parts, namely A-D-D′-D-A and A-D-A′-D-A type structures, based on the electronic structure of the building blocks. Among them, D and D′ units represent the electron-donating building blocks while A and A′ units represent the electron-withdrawing building blocks. According to the modification of different building blocks, molecular design strategies can be classified into three parts such as core engineering, side-chain engineering, and terminal group engineering. Notably, our review focuses on the effects of changes in the chemical structures of NFREAs on the conformation, aggregation, and arrangement of the molecules. Furthermore, recent new polymer acceptors based on NFREAs for all-polymer OSCs are also presented. This review will provide an outlook on the development of efficient, stable, and low-cost NFREAs for achieving commercial applications.

## 2 NFREAs WITH A-D-D′-D-A STRUCTURE

The chemical structures of recently reported A-D-D′-D-A type NFREAs are shown in Figure 2. CPDT is a common electron-donating building block for organic optoelectronic materials, which is composed of a thiophene dimer bridged at the 3,3′-position with a nonconjugated carbon atom. Due to the electron-donating characteristics of CPDT, organic semiconductors based on CPDT possess narrow bandgaps and strong intramolecular charge transfer (ICT) effects. In 2018, Li et al. reported the first NFREA called 2,2′-(2Z,2′Z)-((2,5-difluoro-1,4-phenylene)bis(4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b′]dithiophene-6,2-diyl)bis(methanylylidene))bis(3-oxo-2,3-dihydro-1H-indene-2,1-diyldiene)dimalononitrile (DF-PCIC) (Figure 2), which consists of 2,5-difluorobenzene as the core and two CPDT as D units. Due to the F⋯H noncovalent interactions, DF-PCIC formed a nearly planar molecule conformation (Figure 3A). The bulky substituents attached to the sp3 carbon atoms of the CPDT unit could inhibit the intramolecular aggregation, resulting in appropriate phase separation in the blends. Compared with the benchmark FREA ITIC, DF-PCIC is more...
FIGURE 2  Chemical structures of A-D-D'-D-A type noncovalently fused-ring electron acceptors (NFREAs)
accessible to synthesis with the equivalent light absorption range (Figure 3B) and energy levels, PBDB-T:DF-PCIC-based OSC ultimately obtained a PCE of 10.14% with a short circuit current ($J_{SC}$) of 15.66 mA/cm$^2$. To further improve the $J_{SC}$ of devices, Chen et al. synthesized 2,2′-((2Z,2′Z)-(((2,5-difluoro-1,4-phenylene)bis(4,4-bis(2-ethylhexyl)-4H-cyclopenta[1,2-b:3,4-b′]dithiophene-6,2-diyl))bis(methanylylidene))bis(5,6-difluoro-3-oxo-2,3-dihydro-1H-indene-2,1-diylidene))dimalononitrile (HF-PCIC)$^{[63]}$ and HC-PCIC$^{[64]}$ (Figure 2) by attaching four fluorine or chlorine atoms to the terminal groups of DF-PCIC. Due to the electronegativity of fluorine and chlorine atoms, HF-PCIC and HC-PCIC showed more red-shifted absorption than DF-PCIC. As a result, HF-PCIC and HC-PCIC-based OSCs achieved the PCEs of 11.49% with the $J_{SC}$ of 17.81 mA/cm$^2$ and 11.75% with the $J_{SC}$ of 18.13 mA/cm$^2$, respectively. Although the F⋯H noncovalent interactions favored the formation of the planar conformation of DF-PCIC, HF-PCIC and HC-PCIC, the introduction of strong electron-withdrawing fluorine atoms suppressed the electron-donating ability of D′ units. Thus, it weakened the ICT from D to A units, leading to a narrowing of the absorption spectrum. Accordingly, Huang et al. developed DOC-series NFREAs consisting of 2,5-bis(alkyloxy)phenylene unit as the core and two CPDT blocks as D units (Figure 2).$^{[65]}$ Due to the S⋯O noncovalent interactions between the core and D units, a ladder-like structure was formed, which effectively inhibited the free rotation of the molecular backbone. Furthermore, the resulting planar conformation (Figure 3C) enhanced the $\pi$–$\pi$ stacking interactions between the terminal groups in the films and broadened the absorption to the NIR region (800 nm). Among DOC-series NFREAs, the optimizing OSC based on DOC2C6-2F (Figure 2) presented the highest PCE of 13.24%, with a $J_{SC}$ of 21.35 mA/cm$^2$ and low non-radiative energy losses of 0.27 eV. Inspired by these, Feng et al. designed and synthesized three novel NFREAs with asymmetric cores (FOC6-IC, FOC6-FIC, and FOC2C6-2FIC) (Figure 2) by simultaneously introducing the S⋯O and S⋯F conformation locks. Due to the noncovalent intramolecular interaction, the fluorinated NFREAs FOC6-IC and FOC2C6-2FIC showed a planar backbone. Compared with DOC2C6-IC, FOC6-IC with replacing an alkyl side-chain with a fluorine atom in the core exhibited a narrow absorption spectrum, increased optical bandgap ($E_{g,opt}$), and elevated energy level, resulting in a relatively low $J_{SC}$ of 17.64 mA/cm$^2$ while a high $V_{OC}$ of 0.93 V. In addition, FOC6-FIC and FOC2C6-2FIC with fluorinated terminal groups exhibited red-shifted absorption, decreased $E_{g,opt}$, and down-shifted energy level. With the increasing fluorination of the terminal groups, the $J_{SC}$ of FOC2C6-2FIC slightly increased from 19.18 (FOC6-FIC) to 19.66 mA/cm$^2$ with the decreased $V_{OC}$ from 0.89 (FOC6-FIC) to 0.87 V. Resultantly, the OSC based on FOC2C6-2FIC yielded a PCE of 12.36%, higher than that (10.80%) of FOC6-IC-based OSC.$^{[66]}$ The regioisomeric effects of the cores also have significantly impact opto-electronic properties and intermolecular packing behaviors.$^{[67]}$ For instance, Hou et al. developed two iso-mericized NFREAs, p-DOC6-2F and o-DOC6-2F (Figure 2), by tailoring the position of alkyl chains on the core.$^{[68]}$ The $C_{2v}$ symmetric $o$-DOC6-2F exhibited a higher solubility, larger dipole moment, and wider bandgap than $C_{2h}$ symmetric $p$-DOC6-2F. When blended with polymer donor PBDB-T, the $o$-DOC6-2F-based OSC yielded a higher PCE of 11.87% than that (9.23%) of $p$-DOC6-2F-based OSC.
Recently, Zhang et al.\cite{69} designed and synthesized three NFREAs, NOF-1, NOF-2, and NOF-3 (Figure 2), which comprised different alkoxy-substituted naphthalene (2,6-\(\alpha\), 1,5-\(\beta\), and 3,7-\(\beta\)) as the core, respectively. Among them, NOF-1 presented a distorted structure due to the strong steric repulsion between \(\alpha\)-hydrogen on the naphthalene and the CPDT unit, while NOF-3 exhibited a more planar molecular structure than the other isomers due to S-O noncovalent interactions. The OSC based on PBDB-T:NOF-3 exhibited a PCE of 11.58\%, higher than NOF1 (6.01\%) and NOF2 (10.67\%). Compared with CPDT, DTP with an oxygen atom possesses a stronger electron-donating capacity and thus can be employed to develop NFREAs to enhance the ICT effects and extend the absorption range.\cite{70,71} For instance, Zhao et al. developed two NFREAs, DTP-in-F and DTP-out-F (Figure 2), consisting of 2,5-difluorophenylene as the core flanked by DTP blocks and end-capped by 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (IC-2F) terminal groups.\cite{55} Both DTP-in-F and DTP-out-F displayed good absorption and narrow \(E_g^{opt}\) below 1.50 eV. Due to the asymmetric property of the DTP block, the structural isomers DTP-in-F and DTP-out-F were obtained by linking the 2-position and 7-position of DTP to 2,5-DFB, respectively. Compared with DTP-out-F, DTP-in-F tended to form J-aggregation and face-on \(\pi-\pi\) packing, which promoted absorption of long wavelength and offered extended crystal transport channels like polymers for improved charge transport. Consequently, DTP-in-F-based OSC achieved an improved PCE of 10.66\%, much higher than that (3.97\%) of DTP-out-F-based OSC. Except as a bridge D unit, the CPDT unit can also serve as the core for constructing NFREAs. For example, DTC-BO-4F (Figure 2) with CPDT as the core was designed and synthesized,\cite{72} which showed stronger red-shifted absorption and more ordered molecular packing than DTP-BO-4F and DTS-BO-4F with nitrogen and silicon atoms on the central bridge, respectively. The DTC-BO-4F-based blend film showed ideal nanoscale phase separation, and then the corresponding device obtained a higher PCE of 13.26\% than those (2.65\% and 11.40\%) of DTP-BO-4F and DTS-BO-4F-based devices.

In addition to CPDT and its derivative, dithieno[3,2-b:2′,3′-d]pyrrole is another attractive D unit for NFREAs. It possesses the strong electron-donating ability, and the resulting NFREAs exhibit a low bandgap and broad absorption range due to the electron-rich nitrogen atom.\cite{73} Based on dithieno[3,2-b:2′,3′-d]pyrrole, Cao et al. designed and synthesized DBT-4F and DBD-4F, respectively (Figure 2).\cite{74} Both of them showed strong absorption from visible to NIR region, resulting in the narrow \(E_g^{opt}\) below 1.45 eV. Asymmetric DBT-4F displayed a more planar molecular backbone than DBD-4F. The high planarity was conducive to intramolecular \(\pi-\pi\) stacking, thereby forming effective charge transport. As a result, the resultant DBT-4F-based OSC delivered a PCE of 12.14\%, much higher than that (8.34\%) of DBD-4F-based OSCs. Cao et al. further screened 2-(4-(thiophen-2-yl)phenyl)ithieno[3,2-b:2′,3′-d]pyrrole-derived NFREAs and developed three new asymmetric NFREAs (DBT-EH, DBT-BO, and DBT-HD) (Figure 2) by modulating side-chains on the core.\cite{75} All three NFREAs presented similar strong absorption (600–800 nm) and narrow \(E_g^{opt}\). Among them, the 2-hexyldecyl substituted DBT-HD-based blend film exhibited nanoscale phase separation and strong \(\pi-\pi\) stacking, conducive to more efficient exciton dissociation, and effective charge transport in OSCs.\cite{76,77} As a result, a high PCE of 13.57\% was obtained for PBDB-T:DBT-HD-based OSCs.

Thiophene fused oligomers-based organic semiconductors have shown considerable mobility and vacant outer \(\beta\)-positions for achieving further structural modification. Triarylamine (TAA) has a three-dimensional molecular configuration and a strong electron-donating feature, which can suppress molecular aggregation and enhance the ICT effect to widen the absorption.\cite{78} Combining with the advantages of thiophene-fused oligomers and TAA building blocks, Bo and coworker developed four NFREAs by using thieno[3,2-b]-bithiophene (TT) as the core and the diphenylamine units as the flanking groups.\cite{79} The electron-donating dipheny lamino substituents on the TT block enhanced the ICT effect and extended absorption to the NIR region. Among them, CH3-2F (Figure 2) with methyl substituent on the phenyl unit exhibited an obvious face-on molecular orientation and more ordered molecular stacking, obtaining the highest PCE of 12.28\%. Recently, the same group designed 2BTh-2F by extending the D units (Figure 2).\cite{80} 2BTh-2F with two 3-oxothieno[3,2-b]-bithiophene as the D units can form a more planar molecular backbone than 2TH-2F analog. The grazing-incidence wide-angle X-ray scattering (GIWAXS) measurements demonstrated that 2BTh-2F (Figure 2) tended to form tighter molecular stacking with the smallest \(\pi-\pi\) stacking distance. More importantly, the single-crystal analysis revealed that 2TH-2F and 2BTh-2F have two-dimensional grid-like and three-dimensional network packing models, respectively. The three-dimensional network packing structure of 2BTh-2F was favorable for the charge transport. Resultantly, 2BTh-2F-based OSC achieved a champion PCE of 15.44\%, which is one of the current PCE records of NFREAs. Very recently, Bo group introduced 3,4-bis(octyloxy)-thiophene as D units to construct NFREAs, named BTH-OC8-2F and DTh-OC8-2F (Figure 2).\cite{80} Compared with BTh-OC8-2F with a linear molecular backbone and trans-arranged side-chains, DTh-OC8-2F with a C-shaped molecular shape and cis-arranged side-chains showed more appropriate molecular crystallinity. Therefore, the blend films based on DTh-OC8-2F displayed better nanoscale phase separation, more suppressed charge recombination, more efficient exciton dissociation, and lower nonradiative energy loss than BTh-OC8-2F. As a result, DTh-OC8-2F-based OSC delivered a PCE of 14.13\% higher than that (11.95\%) of BTh-OC8-2F. Furthermore, a series of NFREAs based on TT with varied substituents as the core to tune molecular geometry, such as TT6, TT-C8T, TT-TC8,\cite{81} Isopropyl-0F, and Isopropyl-2F\cite{82} were developed (Figure 2). These works pave a new way to design high-performance NFREAs with reasonable utilization of the steric hindrance effect. Besides the above-mentioned building blocks, fluorene (F8IDT-Br),\cite{83} carbazole (C8IDT-Br),\cite{83} 7H-dibenzo[c,g]carbazole (DBC-4F),\cite{84} and cyclopenta-dithiophene (CTIC-4F)\cite{85} and BDTC-4Cl\cite{86} have been employed to develop NFREAs as D units. The device parameters related to the above A-D-D′-D-A type NFREAs are listed in Table 1.

Apart from the bridge D and the core D′ units, terminal A units also play a key role in fine-tuning molecular packing. For example, DF-PCNC (Figure 2) obtained by
TABLE 1  Device performance of organic solar cells (OSCs) based on representative A-D-D'-D-A type noncovalently fused-ring electron acceptors (NFREAs)

| Acceptor | Donor | $V_{OC}$ (V) | $J_{SC}$ (mA/cm²) | FF (%) | PCE (%) | Year | Ref. |
|----------|-------|--------------|-------------------|--------|---------|------|------|
| DF-PCIC  | PBDB-T | 0.91         | 15.66             | 0.72   | 10.14   | 2017 | [51] |
| OF-PCIC(CB) | PBDB-TF | 0.91         | 13.76             | 73.37  | 9.09    | 2018 | [63] |
| HF-PCIC(CB) | PBDB-TF | 0.92         | 16.01             | 72.42  | 10.97   | 2018 | [63] |
| HF-PCIC(CF) | PBDB-TF | 0.91         | 17.81             | 70.77  | 11.49   | 2018 | [63] |
| HC-PCIC  | PBDB-TF | 0.89         | 18.13             | 72.06  | 11.75   | 2018 | [64] |
| DOC2C6-2F | PBDB-TF | 0.85         | 21.35             | 73.15  | 13.24   | 2019 | [65] |
| HF-PCIC(CF) | PBDB-TF | 0.91         | 17.89             | 70.77  | 11.49   | 2018 | [63] |
| HC-PCIC  | PBDB-TF | 0.89         | 18.13             | 72.06  | 11.75   | 2018 | [64] |
| DOC2C6-2F | PBDB-TF | 0.85         | 21.35             | 73.15  | 13.24   | 2019 | [65] |
| HF-PCIC(CF) | PBDB-TF | 0.91         | 17.89             | 70.77  | 11.49   | 2018 | [63] |
| HC-PCIC  | PBDB-TF | 0.89         | 18.13             | 72.06  | 11.75   | 2018 | [64] |
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| HF-PCIC(CF) | PBDB-TF | 0.91         | 17.89             | 70.77  | 11.49   | 2018 | [63] |
| HC-PCIC  | PBDB-TF | 0.89         | 18.13             | 72.06  | 11.75   | 2018 | [64] |
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| HC-PCIC  | PBDB-TF | 0.89         | 18.13             | 72.06  | 11.75   | 2018 | [64] |
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| HC-PCIC  | PBDB-TF | 0.89         | 18.13             | 72.06  | 11.75   | 2018 | [64] |
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| HF-PCIC(CF) | PBDB-TF | 0.91         | 17.89             | 70.77  | 11.49   | 2018 | [63] |
| HC-PCIC  | PBDB-TF | 0.89         | 18.13             | 72.06  | 11.75   | 2018 | [64] |
| DOC2C6-2F | PBDB-TF | 0.85         | 21.35             | 73.15  | 13.24   | 2019 | [65] |
| HF-PCIC(CF) | PBDB-TF | 0.91         | 17.89             | 70.77  | 11.49   | 2018 | [63] |
| HC-PCIC  | PBDB-TF | 0.89         | 18.13             | 72.06  | 11.75   | 2018 | [64] |
| DOC2C6-2F | PBDB-TF | 0.85         | 21.35             | 73.15  | 13.24   | 2019 | [65] |
extending one phenyl at the 1,1-dicyanomethyl-3-indanone (IC) terminal groups showed more red-shifted absorption and more ordered intermolecular \( \pi-\pi \) stacking than DF-PCIC, facilitating charge generation and transfer. Ultimately, PBDB-T:DF-PCNC-based OSC yielded a PCE of 11.63\% with a \( J_{SC} \) of 18.16 mA/cm\(^2\), which was higher than that (10.14\%) of DF-PCIC-based OSC. Recently, integrating the strategies of \( \pi \)–extended terminal group engineering and noncovalent conformational locks, Zhang et al. developed a series of NFREAs BN-nF (\( n = 0, 2, 4 \)) (Figure 2) [88] BN-2F with the fluorinated \( \pi \)–extended terminal groups exhibited more red-shifted absorption, higher electron mobility, and less recombination loss than BN-0F, resulting in the increased value of \( V_{OC} \) from 21.91 of BN-0F to 25.25 mA/cm\(^2\) of BN-2F. While the value of \( V_{OC} \) slightly decreased from 0.835 to 0.813 V due to the down-shifted lowest unoccupied molecular orbital (LUMO) energy level. As increased electron-withdrawing fluorine atoms attached to the terminal groups, the \( J_{SC} \) of BN-4F slightly increased to 25.76 mA/cm\(^2\), while the \( V_{OC} \) further decreased from 0.813 (BN-2F) to 0.792 V. Hence, fine-tuning the degree of multifluorination on the \( \pi \)–extended terminal groups allows for well modulating the light-harvesting capabilities, energy levels, charge transport properties, and film morphology than the widely used IC terminal group, thereby facilitating high-performance OSCs. Resultantly, OSCs based on JS2:BN-2F exhibited the champion PCEs of 14.53\% (certified PCE of 13.8\%), higher than those (11.00\% and 13.24\%) of BN-0F, and BN-4F-based OSCs.

### 3 | NFREAs WITH A-D-A’-D-A STRUCTURE

Unlike the electron-donating core used above (such as benzene and thiophene) to develop NFREAs, the electron-deficient building blocks as the core to design A-D-A’-D-A type NFREAs have drawn significant attention because such molecule architecture can maintain relatively deep energy levels with narrow \( E_g^{opt} \). Among them, BT has been widely adopted as electron-deficient core (A’) to construct NFREAs for their unique merits: (1) The free 5- and 6- positions of BT can be substituted by electron-donating or electron-withdrawing substituents, such as halogen atoms or alkoxy groups, which help to regulate the frontier molecular orbitals of the resulting molecule. (2) The noncovalent interactions induced by between the BT core and adjacent unit are beneficial for improving molecular planarity and thus enhancing carrier mobility. In 2020, Duan and Chen groups independently developed A-D-A’-D-A type NFREAs consisting of the electron-deficient BT as the core with fluorinated or chlorinated terminal groups. [89] Benefitting from the quinoidal character of the BT unit, the absorption of BTCIC-4Cl was thus enhanced to the NIR region with the \( E_g^{opt} \) of 1.31 eV, thus enhancing the ICT effect. [89] OSC based on PBDB-T:BTCIC-4Cl blend achieved an impressive PCE of 10.2\% with a \( V_{OC} \) of 0.75 V and a \( J_{SC} \) of 21.0 mA/cm\(^2\) (Figure 4A and Table 2). Despite this, the introduction of the BT unit significantly down-shifted the LUMO energy level of BTCIC-4Cl, leading to a relatively small \( V_{OC} \). To this end, the alkoxy group-functionalized BT unit is utilized as the core to maintain the LUMO energy level when bonded with the CPDT bridge and halogenated terminal groups to construct the ICT effect for absorption extension. Compared with its fluorinated counterpart BCDT-4F, the chlorinated NFREA BCDT-4Cl (Figure 4A) presented closer intermolecular packing and stronger J-aggregation, which facilitated the formation of more suitable phase separation in blends. [90] As a result, OSC based on BCDT-4Cl obtained a PCE of 12.10\%, much higher than that (9.65\%) of the BCDT-4F-based OSC. Based on these results, Wang et al. systematically studied the impacts of H (BT-IC4F), F (BT2F-IC4F), and alkoxy chains (BTOR-IC4F) at the 5,6 positions of the BT core on the molecule structure and device properties. [91] According to density functional theory (DFT) calculations, BT-IC4F, BT2F-IC4F, and BTOR-IC4F presented the ladder-like molecular configuration due to the intramolecular S⋯N, F⋯S, and S⋯O interactions. Due to the effect of alkoxy chains at the 5,6 positions of the BT, BTOR-IC4F exhibited higher solubility and elevated LUMO energy level than BT-IC4F and BT2F-IC4F. As a result, OSC based on PBDB-T:BTOR-IC4F obtained the highest PCE of 11.48\% with a relatively high \( V_{OC} \) of 0.80 V.

Compared with BT, BTz has a unique triazole structure with relatively weak electron-withdrawing ability, which is beneficial to further enhancing the \( V_{OC} \) of NFREAs. Lv et al. reported the first NFREA (NTTI) (Figure 4A) with fluorinated BTz as the core. [92] Nevertheless, due to the existence of strong electron-withdrawing fluorine atoms, the NTTI exhibited similar \( V_{OC} \) (0.80 V) values as BTOR-IC4F. Then, Liu et al. developed a novel NFREA (BTzO-4F) (Figure 4A) by employing an alkoxy-substituted BTz unit as the core for enhancing the LUMO energy level. [93] Resultantly, OSC based on PBDB-T:BTzO-4F delivered a PCE of 13.80\% with a high \( V_{OC} \) of 0.84 V. On the basis of BTzO-4F (here renamed NoCA-1), Zhang et al. designed a new NFREA (NoCA-5) (Figure 4A) by attaching the side-chains to the terminal \( \beta \)-position of the CPDT unit. [94] Compared with the counterpart (BTzO-4F), NoCA-5 presented a higher LUMO energy level, improved molecular rigidity, and reorganization energy due to the incorporation of weak electron-donating terminal side-chains. As shown in Figure 3D, NoCA-5 tended to form face-on orientation and higher crystallinity than BTzO-4F, facilitating charge transport and fill factors (FF). Resultantly, the JS2:NoCA-5-based OSC exhibited an excellent PCE of 14.82\% with a \( V_{OC} \) of 0.81 V. This work demonstrated that terminal side-chain engineering has great potential for obtaining high-performance NFREAs. The benzo-[1,2-c:4,5-c’]diphenoephene-4,8-dione (BDD) is a popular electron-deficient building block extensively employed to design high-performance polymer donors, such as PBDB-T and PM6. Inspired by this, a series of NFREAs based on the BDD unit as the core has recently been reported. For example, Wu et al. developed two NFREAs, BDDEH-4F and BDDBO-4F (Figure 4A), consisting of BDD units with different side-chains as the core. [95-97] The PM6:BDDEH-4F-based OSC exhibited a PCE of 12.59\% with a \( J_{SC} \) of 22.57 mA/cm\(^2\) higher than that (9.80\%) of BDDBO-4F-based OSC, which attributed to the more balanced carrier mobilities and appropriate phase separation in the PM6:BDDEH-4F blends. On this basis, a novel NFREA BDIC2F was developed by replacing CPDT with dithieno[3,2-b:2’3’-d]pyrrole as the D unit. [98] The PBDB-T:BDIC2F blend exhibited a considerable fraction of disordered local crystalline
FIGURE 4 Chemical structures of (A) A-D-A'-D-A type noncovalently fused-ring electron acceptors (NFREAs) and (B) completely nonfused electron acceptors (CNFEAs)
TABLE 2 Device performance of organic solar cells (OSCs) based on representative A-D-A’-D-A type noncovalently fused-ring electron acceptors (NFREAs)

| Acceptor       | Donor        | $V_{OC}$ (V) | $J_{SC}$ (mA/cm²) | FF (%) | PCE (%) | Year | Ref. |
|----------------|--------------|--------------|-------------------|--------|---------|------|------|
| BTCIC          | PBDB-T       | 0.79         | 18.60             | 63.00  | 9.30    | 2020 | [89] |
| BTCIC          | PBDB-T-2Cl   | 0.83         | 5.40              | 62.00  | 2.80    | 2020 | [89] |
| BTCIC-4Cl      | PBDB-T       | 0.63         | 23.20             | 69.00  | 10.20   | 2020 | [89] |
| BTCIC-4Cl      | PBDB-T-2Cl   | 0.75         | 21.00             | 66.00  | 10.50   | 2020 | [89] |
| BCDT-4Cl       | PBDB-T       | 0.76         | 23.77             | 67.00  | 12.10   | 2020 | [90] |
| BCT-IC4F       | PBDB-T       | 0.69         | 21.40             | 66.40  | 9.83    | 2020 | [91] |
| BT2F-IC4F      | PBDB-T       | 0.67         | 19.43             | 64.70  | 8.45    | 2020 | [91] |
| BTOR-IC4F      | PBDB-T       | 0.80         | 20.57             | 69.60  | 11.48   | 2020 | [91] |
| NTTI           | PBDB-T       | 0.80         | 17.08             | 63.00  | 8.61    | 2020 | [92] |
| BTzO-4F        | PBDB-T       | 0.80         | 23.28             | 66.00  | 9.65    | 2020 | [92] |
| TPDCIC         | PBDB-T       | 0.80         | 17.40             | 67.00  | 12.10   | 2020 | [93] |
| TPDCNC         | PBDB-T       | 0.80         | 26.02             | 69.96  | 14.82   | 2020 | [94] |
| BDDBO-4F       | PM6          | 0.87         | 19.09             | 58.96  | 9.80    | 2021 | [95] |
| BDDDEH-4F      | PM6          | 0.88         | 22.57             | 63.38  | 12.59   | 2021 | [97] |
| TPDCIC         | PBDB-T       | 0.80         | 18.16             | 67.14  | 10.12   | 2019 | [100]|
| TPDCNC         | PBDB-T       | 0.80         | 17.40             | 70.40  | 9.80    | 2019 | [100]|
| TCIC2F         | PBDB-T       | 0.71         | 19.10             | 64.60  | 8.80    | 2021 | [98] |
| TPDC-4F        | PM6          | 0.85         | 22.19             | 70.60  | 13.35   | 2022 | [101]|
| C8C8-4Cl       | PM6          | 0.82         | 24.01             | 71.10  | 13.96   | 2022 | [102]|
| BDC-4F-C8      | PM6          | 0.90         | 21.40             | 63.42  | 12.14   | 2022 | [102]|
| C8C8-4Cl: BDC-4F-C8 | PM6 | 0.83         | 24.56             | 73.41  | 15.01   | 2022 | [102]|
| BTIC-4F        | PM6          | 0.89         | 20.50             | 65.70  | 12.04   | 2021 | [101]|
| X-PCIC         | PBDB-T       | 0.84         | 21.80             | 62.51  | 11.50   | 2019 | [91] |
| 2T2Csi-4F      | PBDB-T       | 0.84         | 19.50             | 61.29  | 10.04   | 2022 | [103]|
| 4T2Csi-4F      | PBDB-T       | 0.82         | 8.46              | 52.32  | 3.63    | 2022 | [103]|
| QCIC1          | PBDB-T       | 0.82         | 18.81             | 55.50  | 8.58    | 2021 | [104]|
| QCIC2          | PBDB-T       | 0.81         | 18.65             | 60.30  | 9.09    | 2021 | [104]|
| QCIC3          | PBDB-T       | 0.82         | 19.39             | 66.90  | 10.55   | 2021 | [104]|
| QCIC4          | PBDB-T       | 0.78         | 19.16             | 63.80  | 9.53    | 2021 | [104]|
| QOC6-4H        | PBDB-T       | 0.86         | 16.19             | 56.64  | 7.90    | 2022 | [123]|
| OC6-4Cl        | PBDB-T       | 0.78         | 22.91             | 69.01  | 12.32   | 2022 | [123]|
| Y6:BDC4F-C8    | PBDB-T       | 0.84         | 26.37             | 76.54  | 17.02   | 2022 | [124]|

Lattice. This unfavorable crystallization pattern led to extremely bimolecular and trap-assisted recombination, thereby resulting in a low $J_{SC}$ of 9.90 mA/cm² and thus a suboptimal PCE of 3.01%.

Among various effective electron-deficient building blocks, imide-functionalized arenes have been widely employed in a large number of high-performance polymer donors and acceptors due to their strong electron-withdrawing property, good planarity, and excellent solubility enabled by an alkyl group on the nitrogen position.[99] These merits triggered researcher to use imide-functionalized arenes to construct NFREAs. For instance, Chen and coworker firstly reported two new A-D-A’-D-A type NFREAs, called TPDCIC and TPDCNC with the thieno[3,4-c]pyrrole-4,6-dione (TPD) as the core (Figure 4A).[100] Due to strong electronegativity of fluorine atoms, TPDC-4F showed more red-shifted absorption than TPDCIC. Subsequently, TPDC-4F-based OSC delivered a PCE of 13.35% with a $J_{SC}$ of 22.19 mA/cm². To further improve the $J_{SC}$ of devices, Luo et al. designed and synthesized a new NFREA TPDC-4F (Figure 4A) by attaching four fluorine atoms to the terminal groups of TPDCIC.[101] Due to strong electronegativity of fluorine atoms, TPDC-4F showed more red-shifted absorption than TPDCIC. Subsequently, TPDC-4F-based OSC delivered a PCE of 13.35% with a $J_{SC}$ of 22.19 mA/cm². Then, side-chain and terminal group engineering were carried out for TPDC-4F, a NFREA C8C8-4Cl was synthesized by the same group.[102] The OSC based on PM6:C8C8-4Cl yielded a PCE of 13.96% due to the improved charge transport, suppressed charge recombination, and optimal blend morphology. They also tried to design a NFREA with BTI as the core. Although a relatively large $V_{OC}$ showed higher crystallinity and smaller phase-separation domains than that of PBDB-T:TPDCNC blend film, which was beneficial to obtain larger $J_{SC}$ for the resulting OSCs. Resultantly, OSC based on PBDB-T:TPDCIC delivered a PCE of 10.12% with a large $J_{SC}$ of 18.16 mA/cm². To further improve the $J_{SC}$ of devices, Luo et al. designed and synthesized a new NFREA TPDC-4F (Figure 4A) by attaching four fluorine atoms to the terminal groups of TPDCIC.[101]
Table 3

| Acceptor | Donor   | $V_{OC}$ (V) | $J_{SC}$ (mA/cm$^2$) | FF (%) | PCE (%) | Year | Ref. |
|----------|---------|--------------|----------------------|--------|---------|------|------|
| ICTP     | PBDB-T  | 0.97         | 8.29                 | 55.00  | 4.43    | 2019 | [105]|
| PTICH    | PBDB-TF | 0.92         | 8.22                 | 54.00  | 4.28    | 2019 | [60] |
| PTIC     | PBDB-TF | 0.93         | 16.73                | 66.00  | 10.27   | 2019 | [60] |
| PTICO    | PBDB-TF | 1.01         | 12.60                | 52.00  | 6.62    | 2019 | [60] |
| PTB4f    | PBDB-TF | 0.94         | 19.01                | 72.17  | 12.76   | 2021 | [58] |
| PTB4Cl   | PBDB-TF | 0.93         | 20.71                | 54.46  | 9.69    | 2022 | [58] |
| PhO4T-1  | PBDB-T  | 0.86         | 21.49                | 65.91  | 11.91   | 2022 | [52] |
| PhO4T-2  | PBDB-T  | 0.84         | 22.78                | 72.17  | 10.26   | 2020 | [106]|
| PhO4T-3  | PBDB-T  | 0.85         | 23.03                | 71.21  | 13.76   | 2022 | [52] |

was obtained, suboptimal efficiency of 12.04% was achieved due to low electron mobility and reduced molecular packing order.[101] Several other A-D-A’-D-A type NFREAs, such as (X-PCIC,[91] bis-ester thieno[3,2-b]thiophene [2T2CSi-4F and 4T2CSi-4F],[103] QCIC-series[104]) are also summarized in Figure 4A, and the associated device parameters are listed in Table 2.

4 COMPLETELY NON-FUSED ELECTRON ACCEPTORS

Although the above NFREAs simplify the synthetic route to a certain degree, some building blocks of the NFREAs, such as the CPDT unit, still consist of fused-ring structures that require the cost of multistep synthesis. Therefore, to further reduce the material costs and simplify the molecule structures, completely nonfused electron acceptors (CNFEAs) have been developed. Figure 4B summarizes the chemical structures of some representative CNFEAs, as mentioned in the review. Table 3 lists the device parameters based on CNFEAs. Li, Chen, and coworkers pioneering reported that a CNFEA ICTP (Figure 4B) consists of one alkoxy benzene core flanked with two thiophenes and end-capped with IC terminal group,[105] which can be synthesized in three feasible steps with high yields. The H⋯O noncovalent interaction locked the space configuration and led to good planarity. The PBDB-T:ICTP-based OSC yielded a PCE of 4.43%. To further improve the efficiencies, they developed another CNFEA PTICH (Figure 5A,B) by attaching fluorine atoms to the IC terminal groups to extend the light absorption range and strengthen charge transfer.[60] On the basis of PTICH molecules, 2,2′-(((2,5-bis(2-hexyldodecyl)oxy)-1,4-phenylene)bis(3-hexylthiophene-5,2-diyl))bis(methaneyllidene))bis(5,6-difluoro-3-oxo-2,3-dihydro-1H-indene-2,1-diylidene)dimalononitrile (PTIC) and PTICO (Figure 4B) were further synthesized by introducing 3-hexyl or 3-hexyloxy side-chains to improve the solubility of molecules.[60] The introduction of alkyl chains also locked the orientation of IC terminal groups, thereby enhancing the molecular ordering in the film. As a result, PBDB-TF:PTIC-based OSC delivered the highest PCE of 10.27%. This work made it feasible to design effective NFREAs with simple benzene and thiophene rings. To further optimize the molecular packing and orientation of PTIC, the same group developed a CNFEA PTB4Cl by attaching two-dimensional phenyl side-chains to the β-position of thiophene rings (Figures 4B and 5C).[58] GIWAX measurements showed that PTB4Cl exhibited bimodal face-on and edge-on orientations, while PTIC exhibited an edge-on dominant orientation, indicating that the introduction of two-dimensional phenyl chains had been favorable in optimizing the orientation of NFREAs. As a result, PBDB-TF: PTB4Cl-based OSC yielded a higher PCE of 12.76%, which was significantly higher than that (7.04%) of its fluorine-substituted counterpart. To further improve the $J_{SC}$ of devices, Li et al. developed a set of NFREAs (PhO4T-1, PhO4T-2, and PhO4T-3) (Figure 4B).[152] With the extension of terminal substitutes, the absorption peaks were gradually red-shifted from 709 (PhO4T-1) to 724 (PhO4T-2), then to 746 nm (PhO4T-3) due to the different electron-deficient properties of the three terminal groups. All three NFREAs
displayed broad and significant red-shifted absorption peaks in the films relative to solutions, indicating the formation of π-π stacking. Finally, a high PCE of 13.76% was obtained for PhO4T-3-based OSC with a high $J_{SC}$ of 23.03 mA/cm$^2$, much higher than that (9.69% and 11.91%) of the PhO4T-1 and PhO4T-2-based OSCs, respectively.

Apart from alkoxy-substituted benzene counterparts, Bo group reported two CNFEAs (o-4TBC-2F and m-4TBC-2F) with ortho- and meta-hexyloxy substituted phenyl groups on bithiophene core, respectively (Figure 4B).

It was found that the molecule geometry can be fine-tuned by modulating the position of the hexyloxy chains on the phenyl substituents. According to DFT calculations, o-4TBC-2F showed a large dihedral angle (74°) between the molecule backbone and peripheral phenyl, thereby showing a planar backbone (Figure 5D). Whereas m-4TBC-2F generated a smaller dihedral angle (46°), thus presenting a twisted backbone conformation due to the steric hindrance effect (Figure 4B). Moreover, o-4TBC-2F preferentially formed $J$-aggregations with ca. 144 nm of absorption red-shift after thermal annealing. Upon optimizing, PBDB-T-o-4TBC-2F-based OSC yielded a PCE of 10.26%, much higher than m-4TBC-2F-based OSC (2.63%). Bo and coworkers developed a set of tetrathiophene-based CNFEAs (4T-1, 4T-2, 4T-3, and 4T-4) (Figure 4B).

They used side-chain engineering to regulate the solubility, absorption, and film morphology. It is found that the incorporation of 2-ethylhexyl side-chains can effectively improve the compatibility with different electron donors. Among them, OSCs based on D18:4T-3 achieved the champion PCEs of 12.04%. Very recently, two isomeric CNFEAs, LW-out-2F and LW-in-2F, have been designed and synthesized by the
same group (Figure 4B); they feature two diphenylamine side-chains at the outside and inside positions of the bithiophene core, respectively.\textsuperscript{[107]} GIWAXS measurements demonstrated that LW-out-2F tended to form face-on orientation and closer molecular stacking with the short $\pi-\pi$ stacking distance. However, LW-in-2F showed a random molecular orientation. The PBDB-T:LW-out-2F blend films exhibited better crystalline quality than PBDB-T:LW-in-2F, which facilitated the charge transfer. Consequently, the OSC based on PBDB-T:LW-out-2F showed a good PCE of 12.83\%, much higher than those based on LW-in-2F (0.43\%).

Referring to the above works, it is found that the functional groups are necessary for the formation of noncovalent intramolecular interactions (such as S⋯O and S⋯F) to reduce the rotation of the C–C single bond and improve the conformational stability of the NFREAs. However, such noncovalent intramolecular interaction is difficult to provide the high steric hindrance like the alkyls in the fused-ring units. To this end, Hou and coworkers designed and synthesized a new bithiophene-based building block (TT-Pi), which features good planarity, high conformational stability, and bulky steric hindrance. A new full NFREA named A4T-16 was developed with TT-Pi as the core (Figure 4B).\textsuperscript{[154]} According to DFT calculations, the steric hindrance caused by the bulky substituents firmly locked the molecular conformations of bithiophene units, thus enhancing the high planarity and high conformation stability in TT-Pi. This approach is not only more effective than noncovalent conformational locks (e.g., S⋯O and S⋯F) for enhancing the conformation stability of the planar architecture, but also affords the high steric hindrance to induce favorable intermolecular packing mode for A-D-A-structured NFREAs. The single-crystal X-ray diffraction (XRD) results reveal that A4T-16 can form a three-dimensional interpenetrated network through the $\pi-\pi$ interaction of its terminal groups, which facilitates electron transport (Figure 5E). The A4T-16-based cells yielded an outstanding PCE of 15.2\%, which is one of the highest values among the OSCs based on the NFREAs and comparable with FREAs.

Compared with sulfur-based building blocks, selenium (Se)-based analogues have drawn tremendous interest in the design of organic photovoltaic materials. Li group developed a CNFEA (2T2Se-F) using selenophene as a bridge D unit, which is the first study of how the presence of selenophene impacts the photovoltaic performance of NFREAs (Figure 4B).\textsuperscript{[108]} The incorporation of Se atoms led to the red-shifted absorption and elevated energy levels. The crystal structure showed that 2T2Se-F was conducive to strong intramolecular and intermolecular interactions. Finally, OSC based on PM6:2T2Se-F yielded a good PCE of 12.17\%. The above results demonstrated that CNFEAs can also show excellent performance, and further improved performance is expected by modulating the molecules.

5 | NFREAs FOR VERSATILE PHOTOVOLTAIC APPLICATIONS

Compared with narrow-bandgap electron acceptors, wide-bandgap (WBG) electron acceptors play an important role for indoor and tandem organic photovoltaic applications. However, most of them feature fused-ring structures, which are unfavorable for commercial applications. Very recently, Bi et al.\textsuperscript{[56]} designed and synthesized three novel WBG NFREAs, GS-OEH, GS-OC6 and GS-ISO, consisting of bithiophene units with bulky substituents as D units and cyano-rhodanine-modified BTz units as terminal A units (Figure 5F). Due to the intramolecular noncovalent interactions and high steric hindrance effect, these three acceptors featured high planar molecule conformations. Their $E_g$\textsuperscript{opt}s are ca. 1.70 eV, ideal candidates for indoor photovoltaic applications\textsuperscript{[77]} and the front subcells in the tandem OSCs. Ultimately, OSC based on PBDB-TF:GS-ISO yielded a PCE of 11.62\%. In addition, GS-ISO-based OSC with a 1.0 cm$^2$ effective area demonstrated a PCE of 28.37\% under 500 lux, and the OSC with a 10.0 cm$^2$ effective area remained a PCE of 25.74\%. In addition, the tandem OSC with PBDB-TF:GS-ISO-based cell as the front subcell yielded a PCE of 19.10\%. These results demonstrated that WBG NFREAs are promising electron acceptors for versatile photovoltaic applications.

6 | NFREAs-BASED ALL-POLYMER OSCs

All-polymer OSCs have great potential for application in flexible large-scale devices due to their superior photochemical, thermal, and mechanical stability.\textsuperscript{[109]} FREA polymerization was invented by Li et al., which incorporates FREAs as A units to construct D–A polymers, leading to significantly improved light harvesting ability for the resulting polymer acceptors.\textsuperscript{[110]} Recently, the PCEs of all-polymer OSCs have been increased to over 17\%, mainly benefitting from the optimization of FREA structures.\textsuperscript{[111–116]} Inspired by this, the polymerization of NFREAs may offer an excellent platform for reducing the cost of all-polymer OSCs, which is important for the industrialization of all-polymer OSCs technology. Very recently, Huang and Duan groups independently carried out the NFREA polymerization strategy.\textsuperscript{[117]} As shown in Figure 6, PFBTz-TT and PBTz-TT employed A-D-A′-D-A type NFREAs as the electron-deficient building blocks and TT as the linking unit. Both polymers exhibited narrow $E_g$\textsuperscript{opt} and intense light absorption. PFBTz-TT exhibited a more coplanar structure, higher absorption coefficient, stronger interchain interaction, and higher electron mobility than its nonfluorinated analogue PBTz-TT. All-polymer OSCs based on PBDB-T:PFBTz-TT yielded a PCE of 10.14\%\textsuperscript{[117]} using the layer-by-layer deposition technique.\textsuperscript{[118]} It is found that the alkoxy group-functionialized BT unit is utilized as the core to further enhance $V_{OC}$ without sacrificing $J_{SC}$ in NFREAs mentioned above. Gu et al. reported two novel polymer acceptors (PBTZO and PBTZO-2F) (Figure 6) based on the NFREA BTzo-O-4F (Figure 4) with an alkoxy-substituted BTz unit.\textsuperscript{[119]} Compared with PFBTz-TT, PBTZO-2F exhibited an elevated LUMO energy level due to the alkoxy-substituted groups. Resultantly, the PBTZO-2F-based all-polymer OSC obtained an impressive PCE of 11.04\% with a higher $V_{OC}$ of 0.897 V than that (0.85 V) of PFBTz-TT-based OSC. Very recently, CNFEAs were also incorporated into the polymer backbone for developing new polymer acceptors. Li et al. reported three new polymeric NFREAs PBTI-H, PBTI-F,
and PBTI-Cl (Figure 6). They exhibited much higher figure of merit (FOM) values than the fused-ring-based counterparts contributed by their completely nonfused core. Among them, the PBTI-Cl-based all-polymer OSCs yielded the highest PCE of 8.80% thanks to its better charge transport characteristics and morphological properties. This work highlighted that polymerizing CNFEAs is an effective strategy to develop low-cost polymer acceptors for high-performance all-polymer OSCs. Table 4 lists the device parameters of NFREAs-based all-polymer OSCs.

### Table 4: Device performance of noncovalently fused-ring electron acceptors (NFREAs)-based all-polymer organic solar cells (OSCs)

| Acceptor | Donor  | $V_{OC}$ (V) | $J_{SC}$ (mA/cm²) | FF (%) | PCE (%) | Year | Ref. |
|----------|--------|--------------|-------------------|--------|---------|------|------|
| PBTz-TT  | PBDB-T | 0.84         | 16.01             | 51.00  | 6.85    | 2022 | [117]|
| PFBTz-TT | PBDB-T | 0.85         | 18.95             | 63.00  | 10.14   | 2022 | [117]|
| PBTzO    | PBDB-T | 0.89         | 2.90              | 41.74  | 1.08    | 2022 | [119]|
| PBTzO-2F | PBDB-T | 0.90         | 18.27             | 67.37  | 11.04   | 2022 | [119]|
| PBTI-H   | PBDB-T | 0.94         | 13.67             | 64.60  | 8.27    | 2022 | [120]|
| PBTI-F   | PBDB-T | 0.93         | 12.40             | 54.00  | 6.20    | 2022 | [120]|
| PBTI-Cl  | PBDB-T | 0.93         | 13.98             | 67.90  | 8.80    | 2022 | [120]|

### 7 | MATERIAL COST ANALYSIS

More endeavors are urgently needed on material cost, such as cost, which must be addressed for commercial applications of OSCs. The cost of an active material is proportional to its SC, which can be evaluated by considering five parameters: (1) the number of synthetic steps (NSS), (2) the reciprocity yields (RY), (3) the number of chromatographic purifications (NCC), (4) the number of unit operations (NUO), and (5) the number of hazardous chemicals (NHC), which can be summarized by the following equation:[121,122]

$$SC = \frac{35NSS}{NSS_{max}} + \frac{25\log (RY)}{\log (RY_{max})} + \frac{15NCC}{NCC_{max}} + \frac{15NUO}{NUO_{max}} + \frac{10NHC}{NHC_{max}}$$

Integrated SC and PCE, we can calculate a FOM value (FOM = SC/PCE) to represent the cost-efficiency balance for a given acceptor material. For instance, Li et al. have evaluated the SC and FOM values of five representative FREAs (COi8DFIC, Y6, IT-4F, CH1007, and M34) and NFREA PhO4T-3.[52] Among them, PhO4T-3 possessed the highest FOM value of 133.45, much higher than those (e.g., 30.76 for Y6, 37.47 for IT-4F) of FREAs. This result demonstrated that the simple-structured NFREAs are promising candidates for low-cost OSCs. Hence, simplifying the molecular structure, cutting down the number of synthesis steps, and increasing the overall yield are deemed to be the most efficient strategies.

In detail, FREAs generally suffer from multiple synthesis steps, low yields, and high synthetic costs due to the architecture of the highly conjugated fused-ring core, such as the star
FREA Y6 in Figure 7A, which consists of approximately 10 steps, while the initially reported yield was only 64% at the milligram-scale and currently costs $\approx US$2000 per gram.

Regarding the synthesis of NFREAs, taking NFREA DF-PCIC as an example, the synthetic route of DF-PCIC is depicted in Figure 7B. Following the linkage of the alkyl chain to the CPDT unit to obtain intermediate 2, the benzene ring is then linked to intermediate 2 by Stille coupling reaction. After introducing aldehyde groups on both sides of intermediate 4, the terminals are linked by Knoevenagel condensation to obtain the target product. To further simplify the synthesis steps, the same group developed novel NFREAs (PTICH, PTIC, and PTICO) in only two steps. 5,5′-(2,5-bis((2-hexyldecyl)oxy)-1,4-phenylene)bis(3-substituent-2-thenaldehyde) (PT-CHO) is first constructed from C–H activated coupling reactions between 1,4-dibromo-2,5-bis((2-hexyldecyl)oxy)benzene and thiophene-2-carbaldehydes catalyzed by Palladium(II). Target molecules are ultimately obtained from Knoevenagel condensation of PT-CHOs and terminals. Notably, NFREAs are purified by recrystallization without silica gel column, featuring a simple and scalable posttreatment process.

Accordingly, the typical synthesis process of NFREA generally can be summarized as follows: Firstly, the core is
linked to the π–bridge unit by the Stille coupling reaction or the C–H activation reaction, then the aldehyde groups on both sides of the π–bridge unit are linked by the Vilsmeier-Haack reaction. Finally, D units at the end of aldehyde groups are connected with activated methylene-based end-capping A groups, such as IC and its derivatives, through a conventional pyridine-catalyzed Knoevenagel condensation reaction. The synthetic approach of NFREAs offers facile and low-cost access to photovoltaic materials and opens up the possibility of large-scale commercial application of OSCs.

(4) Considering that NFREAs are easily synthesized, recent results demonstrate that polymerizing NFREAs is an effective strategy to develop high-performance and low-cost polymer acceptors for all-polymer OSCs.

We expect that this review will be valuable for comprehensively understanding the development of NFREAs and addressing the longstanding challenges, thereby facilitating the practical application of NFREAs for OSCs.

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CONFLICT OF INTEREST
The authors declare no conflict of interest.

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