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Rhodanine-based nonfullerene acceptors for organic solar cells

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ABSTRACT Significant progress on the development of non-fullerene acceptors (NFAs) for organic solar cells (OSCs) has been made in the past several years, and the power conversion efficiency (PCE) exceeding 17% has been already realized based on a tandem non-fullerene device. To date, NFAs with a linearly fused acceptor-donor-acceptor (A-D-A) structure are of great interest, due to their attracting synthetic flexibility and high photovoltaic performance. Rhodanine is one of the most studied electron-withdrawing moieties to construct such A-D-A type NFAs, and the resulting single-junction OSCs have produced PCEs of ~10%. More interestingly, those rhodanine-based NFAs have demonstrated a particularly excellent compatibility with well-known P3HT donor, enabling respectable PCEs over 7%. Thus in this review, we summarize the important advances on rhodanine-based NFAs with a main focus on discussing the molecular design strategies, providing a better understanding of the structure-property relationship for those rhodanine-based NFAs.

Keywords: organic solar cells, non-fullerene acceptors, rhodanine

INTRODUCTION

Photoinduced charge transfer between p-type and n-type organic semiconductors (donors and acceptors) is the basic process for organic solar cells (OSCs) [1,2]. Since buckminsterfullerene (C₆₀) and its derivatives were introduced as the acceptors to blend with polymer donor MEH-PPV [2], OSCs have been dominated by fullerene acceptors for nearly two decades, such as [6,6]-phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM) and [6,6]-phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM). Currently, the maximum power conversion efficiencies (PCEs) of single-

junction fullerene-based OSCs have been already over 11% [3–6]. Fullerene exhibits a typical ball-like conjugated structure with high electron affinity, which not only enables isotropic electron transfer but also helps to form favorable bulk-heterojunction (BHJ) blend film with nanoscale phase separation for charge separation [7,8]. Nonetheless, the nature of large bandgap absorption for fullerene acceptors and their limited tunability in optical/electronic properties have greatly hindered their development. Besides, most of fullerene-based OSCs generally show a large voltage loss (V_{loss}) of ~0.8 eV [9], thereby limiting the achievement of high efficiency. Fortunately, these challenges that have plagued this field for a long time seem to be solved due to the emergence of a small molecule non-fullerene acceptor (NFA) in 2015, termed as ITIC (Fig. 1a), which was reported by Lin *et al.* [10].

ITIC exhibits a typical acceptor-donor-acceptor (A-D-A) type structure (Fig. 1b), wherein a large fused π -extended core, indacenodithieno[3,2-*b*]-thiophene (IDTT), is end-capped by two strong electron-withdrawing groups, 2-(3-oxo-2,3-dihydroinden-1-ylidene)malononitrile (INCN). In such rigid A-D-A dipolar structure, a strong intramolecular charge transfer (ICT) can be generated to offer a low optical bandgap with a large extinction coefficient ($>10^5 \text{ cm}^{-1}$) [10]. This structure is also beneficial to enhancing the molecular crystallinity of acceptors to realize decent electron mobilities (10^{-4} – $10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) after forming the BHJ blend [10,11]. Moreover, the incorporation of four bulky side-chains at the center of IDTT core plays a critical role in preventing the intermolecular interactions between the donor subunits, and therefore only favors the interactions between the electron-deficient end-capping subunits to

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Figure 1 (a) Chemical structure of ITIC. (b) Cartoon representing a structural template for designing the A-D-A type NFAs. (c) The structures of commonly used electron-donating “D” moieties and electron-withdrawing “A” moieties.

improve the electron transport [10]. Due to these fascinating advantages, ITIC-like NFAs have made significant progress within a short time, and the derived OSCs have afforded impressive PCEs of >15% in the single-junction devices [12–15] and >17% in a tandem device [16], respectively, much higher than those reported in the fullerene-based OSCs.

Nowadays, more and more attentions have been paid to developing new NFAs, given the fact that their excellent synthetic flexibility can make the optical/electronic properties easily tunable to fulfill the device requirements [17]. In such A-D-A type NFAs, there are four sites that can be decorated, including electron-donating cores (D), side-chains, π -conjugated bridges/spacers and electron-withdrawing end-groups (A): (1) the regulation of “D” moieties would tune the optical bandgaps, the highest occupied molecular orbital (HOMO) energy levels and the molecular crystallinity; (2) the modification of side-chains would mainly affect the solubility and the intermolecular π - π stacking behaviors; (3) the introduction of π -conjugated spacers not only extends the conjugation of NFAs but also acts as a second “D” or “A” moiety to modulate the optical/electronic properties; (4) the regulation of “A” moieties would influence the lowest unoccupied molecular orbital (LUMO) energy levels and the

electron transport of NFAs.

So far, most electron-donating “D” moieties (Fig. 1c) used for high-performance NFAs are mainly derived from the large conjugated fused-ring systems such as indacenodithiophene (IDT) [18,19], IDTT [10,20], heptacyclicbenzodi(cyclopentadithiophene) (FBDT) [21,22], etc. While in terms of electron-withdrawing “A” moieties, dye molecules have been often used (Fig. 1c) including 2,3-dihydro-1*H*-indene-1,3-dione (ID) [23,24], INCN [15,25–29], thiobarbituric acid (TBA) [30,31], rhodanine (RD) [9,32], 2-(1,1-dicyanomethylene)rhodanine (RCN) [33,34], etc. Among these dyes, INCN derivatives are the most popular “A” moieties toward high performance NFAs through rational structural modifications. It is worth noting that all the record PCEs reported so far, either in the single-junction devices or in the tandem devices, come from the fluorinated INCN end-capped NFAs [13,16].

In addition to INCN, RD derivatives are another type of widely used “A” moieties toward efficient NFAs. Due to the more electron-deficient property, INCN-based NFAs generally exhibit narrower bandgaps than RD-based NFAs, thereby showing higher short-circuit currents (J_{sc}) beyond 20 mA cm^{-2} [35,36]. By contrast, RD-based NFAs often present high open-circuit voltages (V_{oc}) up to 1.2 V [37–40]. To date, the best PCE from RD-based NFAs has exceeded 12% based on a ternary-blend OSC [41]. Despite the performance of RD-based NFAs is still inferior compared with those outstanding INCN-based NFAs, an attracting feature for some RD-based NFAs is their particularly excellent compatibility with well-known poly(3-hexylthiophene) (P3HT, Scheme 1) donor, due to their well-matched energy levels and optical absorption, favorable phase-segregation film morphology with face-on dominated crystallinity, and suppressed charge recombination [42–48]. Currently, the BHJ blends derived from P3HT donor and RD-based NFAs have produced respectable PCEs over 7% [49], while the P3HT:ITIC blend only delivered a PCE of 1.3%, which could be attributed to the strong geminate and non-geminate charge recombination caused by the almost amorphous blend film [50]. Furthermore, the structure of RD derivatives also can be easily modified to tune their optical/electronic properties as needed. For example, the ketone or thioketone group in the RD unit that endows the electron-withdrawing character can be further substituted by malononitrile, resulting in the RCN unit with much stronger electron-deficient ability. Also, simply altering the imide alkyl chains in the RD unit can regulate the materials’ solubility as well as the intermolecular π - π

Scheme 1 A summary of donors paired with newly-developed RD-based NFAs.

stacking to optimize the blend film and thus to boost the device performance.

In 2011, Li *et al.* [51] first synthesized an RD-based small molecule donor material, DERHD7T, and the resulting fullerene-based OSCs delivered the highest PCE of 6.1% for small-molecule based OSCs at that time. Subsequently, more efforts have been devoted on developing RD-based small molecule donors, of which the PCEs have been yet improved to over 10% with fullerene acceptors [52–54]. In 2014, Kim and coworkers [55] first reported two new RD-based small molecule NFAs, leading to an encouraging PCE of 3.1% with P3HT donor. Soon after, Holliday *et al.* [56] synthesized another new RD-based NFA, FBR, with an A-A'-D-A'-A type structure by incorporating benzothiadiazole (BT) unit as the second

acceptor (A') unit, enabling an enhanced PCE of 4.1% with the same P3HT donor. Since then, RD-based NFAs have been attracted significant interest, and to date, there have been more than 50 research articles reported. Although several recent reviews covering the development of NFAs have been published [17,57–61], the target of this review will particularly focus on discussing the important advances on RD-based NFAs. The discussion will be arranged as follows: (1) A-D-A type one dimensional (1D) RD-based NFAs; (2) A-D-A type three dimensional (3D) RD-based NFAs; (3) other types of RD-based NFAs such as A- π -A structure. Finally, a brief summary and outlook will be provided with some new perspectives for the future molecular design of RD-based NFAs. We aim to provide the readers with a better understanding of the

structure-property relationships for those RD-based NFAs.

A-D-A-TYPE 1D RD-BASED NFAs

So far, most of efficient RD-based NFAs exhibit an A-D-A type 1D structure. In most cases, the second electron-withdrawing units are further introduced to form an A-A'-D-A'-A type structure. Such structural design can broaden and red-shift the absorption and simultaneously reduce the LUMO energy levels, making the derived NFAs more compatible with polymer donors. Moreover, the 1D ladder-type structure would facilitate the intermolecular π - π stacking of resulting molecules to improve the electron transport. Various fused-ring systems such as carbazole, fluorene, IDT and IDTT have been introduced as the electron-rich core. Thus in this section, the content will be organized according to the conjugation length of those fused-core structures.

NFAs with a tricyclic electron-rich core

In 2014, Lim and coworkers [55] first synthesized two RD-based NFAs, **Flu-RH** and **Cz-RH** (Scheme 2, Table 1), by using traditional carbazole and fluorene rings as the core structure, respectively. Both NFAs showed a strong absorption in the range of 400–600 nm, indicating a wide bandgap nature. They also had similar HOMO/LUMO energy levels, and the HOMO level of **Cz-RH** was slightly higher than that of **Flu-RH** because of the more electron-donating ability of carbazole. When paired with P3HT donor, the conventional P3HT:**Flu-RH** OSCs afforded an enhanced PCE (3.08%) compared with **Cz-RH**-based devices (2.56%), mainly due to the higher J_{sc} value

of the former. Based on this structure, Holliday *et al.* [56] further synthesized a new acceptor (**FBR**, Scheme 2, Table 1) by replacing the thiophene-bridge in the **Flu-RH** with an electron-withdrawing BT unit. The introduction of BT unit can effectively reduce the HOMO/LUMO energy levels of the derived **FBR**. Moreover, the non-planar molecular structure of **FBR** can not only realize a non-anisotropic electron transport but also prevent the formation of large crystalline domains in the BHJ blend. As a result, despite leading to a reduced V_{oc} , the P3HT:**FBR** blend showed an impressive PCE up to 4.11%, significantly outperforming that of P3HT:PC₆₀BM blend (3.53%). Since then, RD-based NFAs have attracted particular interest in the field of OSCs. In 2016, Baran *et al.* [9] further adopted a low bandgap polymer PffBT4T-2DT (Scheme 1) as the donor to blend with **FBR**, and demonstrated that the synergistic effect of high mobility and low recombination efficiency can efficiently suppress the non-radiative recombination of resulting devices to achieve an extremely low V_{loss} of 0.47 V. Consequently, the as-casted PffBT4T-2DT:**FBR**-based OSCs delivered a high PCE of 7.8% with a large V_{oc} of 1.12 V.

Inspired by these encouraging results, rational structural modifications have been conducted on **FBR** subsequently. For example, by replacing the fluorene core in the **FBR** with carbazole moiety, Ma and coworkers [62] synthesized two new RD-based NFAs, **CzC6C8** and **CzC8** (Scheme 2, Table 1), with branched and linear alkyl side chains, respectively. It was demonstrated that **CzC8** with a linear *n*-octyl chain exhibited a more closely molecular stacking and a more preferred film morphology than **CzC6C8** with a branched 2-hexyldecyl chain, leading to a

Scheme 2 Chemical structures of NFAs with a tricyclic/tetracyclic electron-rich core.

Table 1 Summary of NFAs with a tricyclic/tetracyclic electron-rich core

NFAs	E_{HOMO} (eV)	E_{LUMO} (eV)	$E_{\text{g,opt}}$ (eV)	Donor	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)	Mobility (cm ² V ⁻¹ s ⁻¹)		Ref.
									Electron	Hole	
Cz-RH	-5.53 ^a	-3.50 ^a	2.05	P3HT	1.03	4.69	53	2.56	3.9E-4	8.0E-4	[24,55]
Flu-RH	-5.58 ^a	-3.53 ^a	2.10	P3HT	1.03	5.70	52	3.08	4.6E-4	8.5E-4	[24,55]
FBR	-5.70 ^b	-3.57 ^b	2.14	P3HT	0.82	7.95	63	4.11	2.6E-5	-	[56]
	-5.83 ^c	-3.75 ^a	2.08	PfBT4T-2DT	1.12	11.5	61	7.8	-	-	[9]
CzC6C8	-5.79 ^a	-3.79 ^c	2.00	PBT	0.99	8.24	41	3.30	2.9E-6	1.2E-6	[62]
CzC8	-5.72 ^a	-3.74 ^c	1.98	PBT	1.03	9.00	50	4.64	3.3E-6	2.0E-6	[62]
	-5.72 ^a	-3.74 ^c	1.98	PTB7-Th	0.98	11.24	45	4.91	4.9E-5	4.7E-5	[62]
	-5.72 ^a	-3.74 ^c	1.98	PTFBDT	1.16	7.99	51	4.67	1.6E-6	1.9E-6	[62]
	-5.46 ^a	-3.61 ^a	1.65	J61	1.05	10.92	51	5.81	7.4E-6	2.5E-4	[63]
BAF-4CN	-5.71 ^b	-3.55 ^b	2.16	PfBT4T-2OD	0.77	15.52	71	8.40	4.9E-4	2.9E-4	[64]
FBRCN	-5.84 ^c	-3.77 ^a	2.07	PTB7-Th	1.00	8.1	40	3.3	9.0E-6	-	[65]
FRd ₂	-5.67 ^b	-3.58 ^c	2.09	PTB7-Th	0.83	15.7	72	9.4	4.3E-4	2.4E-4	[66]
FRdCN ₂	-5.88 ^b	-3.81 ^c	2.07	PTB7-Th	0.93	16.0	72	10.7	5.1E-4	3.4E-4	[33]
IBR	-5.64 ^b	-3.41 ^b	-	PBDB-T	1.16	9.6	61	6.66	2.8E-4	8.3E-4	[67]

a) Measured by CV based on films. b) Measured by CV in solutions. c) Calculated by $E_{\text{LUMO}} = E_{\text{HOMO}} + E_{\text{g,opt}}$. “-” indicates that the details were not reported.

better photovoltaic performance (PCE = 4.91%) when paired with one of the state-of-the-art polymer donors, PTB7-Th (Scheme 1). Furthermore, Li *et al.* [63] synthesized another new RD-based acceptor (TP21, Scheme 2, Table 1) containing a thienopyrazine (TP) π -conjugated bridge instead of the commonly used BT unit. Compared with FBR, TP21 showed a decreased optical bandgap of 1.65 eV, but a high-lying LUMO level of -3.61 eV, due to the highly planar and quinoid structure of TP unit that could facilitate the electron delocalization. When blended with another state-of-the-art polymer donor J61 (Scheme 1), the derived OSCs can realize a decent PCE of 5.81% with a high V_{oc} of 1.05 V.

In addition to modifying the core structure and the π -conjugated bridge, the RD end-groups in the FBR can also be replaced by the dicyano-functionalized RCN dye [64]. The obtained RCN-based acceptor, BAF-4CN (Scheme 2, Table 1), possessed similar electrochemical properties with FBR, but much stronger absorption due to the higher electron-withdrawing ability of RCN, and the molar extinction coefficient can be improved from $3.5 \times 10^4 \text{ mol}^{-1} \text{ L}^{-1} \text{ cm}^{-1}$ for FBR to $7.8 \times 10^4 \text{ mol}^{-1} \text{ L}^{-1} \text{ cm}^{-1}$ for BAF-4CN. When blended with a low bandgap polymer donor (PfBT4T-2OD, Scheme 1), a high PCE of 8.40% with a J_{sc} of 15.52 mA cm^{-2} and a fill factor (FF) of 71% was realized. Moreover, in 2018, Radford and co-workers [65] also reported an acceptor FBRCN (Scheme 2, Table 1) with a similar structure as BAF-4CN,

however, containing different alkyl chains at the fluorene and RD units. When blended with the PTB7-Th donor, the FBRCN-based OSCs delivered a moderate PCE of 3.3%.

Furthermore, Suman *et al.* [66] synthesized FRd₂ (Scheme 2, Table 1) by incorporating the furan unit as the second π -spacer between RD and BT units. The furan unit was found to extend the conjugation of the resulting FRd₂ to increase the delocalization of π -electrons, leading to a much higher molar extinction coefficient ($7.8 \times 10^4 \text{ mol}^{-1} \text{ L}^{-1} \text{ cm}^{-1}$) and a slightly red-shifted/broadened absorption. The derived PTB7-Th:FRd₂-based OSCs demonstrated an impressive PCE of 9.4% with a V_{oc} of 0.83 V, a J_{sc} of 15.7 mA cm^{-2} and an FF of 72%. Soon after, they [33] also prepared FRdCN₂ (Scheme 2, Table 1) using RCN as the end-capped groups. As compared with FRd₂ and BAF-4CN, FRdCN₂ exhibited a stronger, broader and red-shifted absorption, as well as a decreased LUMO level of -3.81 eV. With the help of 1-chloronaphthalene (CN) additive and solvent vapor annealing (SVA) treatment, the fabricated PTB7-Th:FRdCN₂ based OSCs produced an excellent PCE of 10.70% with a V_{oc} of 0.93 V, a J_{sc} of 16.0 mA cm^{-2} and an FF of 72%, among the best of the binary-blend single-junction OSCs using RD-based NFAs.

NFAs with a tetracyclic electron-rich core

In 2019, Zulfiqar *et al.* [67] also developed an in-

denoindene-cored small molecule acceptor, **IBR** (Scheme 2, Table 1). Compared with the fluorene-cored **FBR**, **IBR** showed an elevated HOMO energy level and a red-shifted absorption attributed to its stronger electron-donating core. Adopting PBDB-T (Scheme 1) as the donor, the as-cast PBDB-T:**IBR** devices only yielded a poor PCE of 0.68% with a V_{oc} of 0.88 V. While, the optimal OSCs can afford a much higher PCE of 6.66% with an improved V_{oc} of 1.16 V when annealing at 160°C for 10 min. It was shown that the thermal-annealing treatment can diminish the morphological defects to reduce the bimolecular recombination and the saturation dark current density.

NFAs with a pentacyclic electron-rich core

So far, the pentacyclic IDT unit is the most studied electron-rich core for RD-based NFAs. IDT was first reported by Wong *et al.* [68] in 2006. The large and rigid planar conjugated structure of IDT has been demonstrated to facilitate the π -electron delocalization and the intermolecular π - π interaction of the resulting molecules/polymers to promote the charge transport [68]. Initially, IDT was mainly used to construct donor materials in

OSCs [69], and the first A-D-A type IDT-based NFAs, IDT-2DPP, was reported by Bai *et al.* [70] in 2013 by using diketopyrrolopyrrole (DPP) as the end-capped groups for IDT. Later on, numerous high-performance NFAs with IDT and its derivatives as the core have been designed and synthesized using RD and INCN as the end-capped groups.

In 2015, Wu *et al.* [42] first developed an IDT-RD-based acceptor, **IDT-2BR** (Scheme 3, Table 2), wherein IDT unit was introduced as the core to replace the fluorene unit of **FBR**. Due to the large and planar conjugated structure of IDT, **IDT-2BR** exhibited a lower optical bandgap (1.68 eV), a stronger optical absorption, and a higher electron mobility than **FBR**. Therefore, the P3HT:**IDT-2BR** OSCs showed a higher PCE up to 5.12% due to the simultaneous increase of J_{sc} and FF. Sequentially, they also fabricated a semitransparent all-plastic OSC based on the P3HT:**IDT-2BR** blend to achieve a PCE of 2.88% under an average visible transmittance of ca. 50% [71]. Further fabricating a PTB7-Th:**IDT-2BR** blend, Tang and coworkers [72] reported a significantly enhanced PCE of 8.96% with a high V_{oc} of 1.04 V and a low E_{loss} of 0.55 eV, attributed to the improved solar ab-

Table 2 Summary of NFAs with a pentacyclic electron-rich core

NFAs	E_{HOMO} (eV)	E_{LUMO} (eV)	$E_{\text{g, opt}}$ (eV)	Donor: 2nd component	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)	Mobility (cm ² V ⁻¹ s ⁻¹)		Ref.
									Electron	Hole	
IDT-2BR	-5.52 ^a	-3.69 ^a	1.68	P3HT	0.84	8.91	68	5.12	2.6E-4	2.0E-4	[42]
	-5.52 ^a	-3.69 ^a	1.68	P3HT	0.84	5.93	58	2.88	-	-	[71]
	-5.31 ^a	-3.70 ^a	1.68	PTB7-Th	1.04	13.75	63	8.96	9.1E-5	1.2E-3	[72]
IDT-BT-RO	-5.33 ^a	-3.74 ^a	1.66	PTB7-Th	1.02	13.75	61	8.57	9.1E-5	1.3E-3	[72]
IDT-BT-RF3	-5.35 ^a	-3.78 ^a	1.64	PTB7-Th	0.89	14.74	59	7.75	1.3E-4	1.8E-3	[72]
IDT-BT-RN	-5.26 ^a	-3.62 ^a	1.71	PTB7-Th	1.10	12.04	54	7.09	8.8E-5	1.4E-3	[72]
cis-IDT-BTR	-5.44 ^a	-3.62 ^a	1.64	PTB7-Th	1.08	13.79	58	8.02	1.0E-6	5.9E-4	[73]
trans-IDT-BTR	-5.43 ^a	-3.61 ^a	1.63	PTB7-Th	1.05	15.08	60	9.43	2.2E-6	8.9E-4	[73]
O-IDTBR	-5.51 ^c	-3.88 ^a	1.63	P3HT	0.73	14.1	62	6.4	-	-	[43]
	-5.51 ^c	-3.88 ^a	1.63	P3HT (34 kDa)	0.73	14.6	66	7.0	-	-	[49]
	-5.51 ^c	-3.88 ^a	1.63	PffBT4T-2DT	1.07	15.0	62	9.95	-	-	[9]
	-5.51 ^c	-3.88 ^a	1.63	PffBT2T-TT	1.08	14.32	67	10.4	-	-	[75]
EH-IDTBR	-5.58 ^c	-3.90 ^a	1.68	P3HT	0.77	12.2	62	6.05	-	-	[43]
	-5.58 ^c	-3.90 ^a	1.68	PffBT4T-2OD	1.03	16.1	55	9.1	-	-	[74]
O-IDFBR	-5.75 ^a	-3.70 ^a	2.0	P3HT:O-IDTBR	0.82	14.4	64	7.7	-	-	[32]
	-5.75 ^a	-3.70 ^a	2.0	PTB7-Th: O-IDTBR	1.03	17.2	60	11.0	-	-	[32]
EH-IDFBR	-5.75 ^c	-3.70 ^a		PffBT4T-2DT	1.08	4.4	38	1.75	-	-	[9]
IDT-4CN	-5.45 ^c	-3.95 ^b	1.50	PBDB-T	0.91	14.66	61	8.13	1.9E-4	3.5E-4	[76]
IDT-BT-R-CN	-5.38 ^a	-3.67 ^a	1.63	PTB7-Th	0.88	12.4	50	5.7	8.7E-4	1.3E-3	[77]
ICz-Rd ₂	-5.59 ^b	-3.88 ^c	1.71	P1	1.04	14.04	54	7.88	-	-	[78]
ICz-RdCN ₂	-5.58 ^b	-3.98 ^c	1.61	P1	1.01	15.58	62	9.76	-	-	[78]
IFBR- <i>p</i>	-5.64 ^a	-3.73 ^a	1.67	PTzBI	1.00	11.6	62	7.44	1.5E-4	5.8E-5	[79]
IFBR- <i>d</i>	-5.67 ^a	-3.74 ^a	1.71	PTzBI	0.99	9.4	56	5.28	4.9E-5	5.9E-5	[79]
IfBR	-5.71 ^a	-3.77 ^a	1.71	PBTA-BO	1.013	11.77	52	6.34	-	-	[80]
	-5.71 ^a	-3.77 ^a	1.71	PBTA-BO: PC ₇₁ BM	0.91	14.52	67	9.06	-	-	[80]
BTA1	-5.46 ^a	-3.57 ^a	1.87	J61	1.24	5.21	47	3.02	5.4E-5	1.9E-4	[38]
BTA2	-5.43 ^a	-3.46 ^a	2.00	J61	1.29	0.84	24	0.26	2.4E-5	9.8E-5	[38]
BTA3	-5.49 ^a	-3.61 ^a	1.76	J61	1.15	10.84	66	8.25	2.2E-4	3.3E-4	[38]
	-5.49 ^a	-3.61 ^a	1.76	PE1	1.11	11.95	64	8.43	4.5E-6	2.2E-4	[81]
	-5.49 ^a	-3.61 ^a	1.76	PE2	1.26	8.06	57	5.83	2.4E-6	5.5E-5	[81]
	-5.49 ^a	-3.61 ^a	1.76	J71	1.20	10.39	69	8.60	8.3E-4	4.9E-4	[40]
	-5.49 ^a	-3.61 ^a	1.76	P3HT	0.90	9.64	65	5.64	1.8E-4	1.6E-6	[46]
BTA100	-5.32 ^a	-3.23 ^a	2.05	P3HT	1.34	1.65	47	1.04	6.9E-9	4.4E-8	[39]
BTA101	-5.41 ^a	-3.55 ^a	1.88	P3HT	1.19	5.33	56	3.55	1.4E-7	2.3E-7	[39]
BTA103	-5.37 ^a	-3.64 ^a	1.77	P3HT	0.94	8.56	66	5.31	3.5E-5	1.5E-6	[39]
IDT-DPP-R	-5.39 ^a	-3.55 ^a	1.44	P3HT	0.65	4.07	54	1.46	-	-	[82]
	-5.39 ^a	-3.55 ^a	1.44	P3HT:PC ₆₁ BM	0.62	9.47	65	3.95	-	-	[82]

a) Measured by CV based on films. b) Measured by CV in solutions. c) Calculated by $E_{\text{LUMO}} = E_{\text{HOMO}} + E_{\text{g, opt}}$. “-” indicates that the details were not reported.

sorption and electron transport. In addition, they also prepared another three NFAs, **IDT-BT-RN**, **IDT-BT-RO**, and **IDT-BT-RF3** (Scheme 3, Table 2), by inserting 1-piperidino, methoxymethyl and trifluoroethyl groups into the end-capped RD units, respectively. Compared with the ethyl group, 1-piperidino group can reduce the electron-withdrawing ability of RD units to induce a blue-shifted absorption and an elevated LUMO level for **IDT-BT-RN** due to its electron-donating property. Thus, the PTB7-Th:**IDT-BT-RN** OSCs displayed a higher V_{oc} of 1.10 V with a lower E_{loss} of 0.49 eV. By contrast, the methoxymethyl and trifluoroethyl groups were found to red-shift the absorption and reduce the LUMO levels of the corresponding NFAs. As a result, both PTB7-Th:**IDT-BT-RO** and PTB7-Th:**IDT-BT-RF3** based OSCs showed more efficient charge separation and less monomolecular recombination to enable much higher J_{sc} than that of PTB7-Th:**IDT-2BR** based devices.

Side-chain engineering has been shown as an effective approach to modulate the intermolecular interactions of organic semiconductors. Cao *et al.* [73] reported two new stereoisomers with asymmetrical side chains, namely **cis-IDT-BT-R** and **trans-IDT-BT-R** (Scheme 3, Table 2). Different side-chain configurations negligibly affected the photo-physical and electrochemical properties of the two stereoisomers, however, showed a significant impact on the crystallinity and packing behaviors. Due to the enhanced crystallinity of the centrosymmetric **trans-IDT-BT-R**, the derived OSCs based on PTB7-Th donor demonstrated much better charge transport properties to afford a higher PCE of 9.43% than that of PTB7-Th:**cis-IDT-BT-R** blend.

Moreover, Holliday *et al.* [43] also reported another two IDT-RD-based NFAs, **O-IDTBR** and **EH-IDTBR** (Scheme 3, Table 2), by replacing the bulky 4-hexylphenyl side chains in the **IDT-2BR** with different alkyl side chains. It was found that the alkyl chain substitutions could enable significantly red-shifted absorption in the film state due to the presence of strong intermolecular interactions. Furthermore, the increased crystallinity was found to be beneficial to charge separation/extraction. In detail, **O-IDTBR** with linear *n*-octyl chains was more crystalline and thus displayed a more red-shifted absorption band relative to **EH-IDTBR** with branched 2-ethylhexyl chains, resulting in a higher J_{sc} and PCE (6.4%) with the P3HT donor. More encouragingly, when paired with a 34 kDa P3HT donor, the derived **O-IDTBR**-based OSC can deliver an exceptional PCE over 7.0% due to the optimal BHJ film morphology with suitable donor and acceptor domains [49]. On the other hand, Zhang *et al.*

[74] fabricated an inverted PffBT4T-2OD:**EH-IDTBR** device, which could maintain a high PCE of 9.1% even with an active layer thickness of 300 nm. In this work, they found that the inverted device architecture could overcome the space-charge effects by shortening the transport distance of electrons for efficient charge collection, efficiently reducing the accumulation of electrons at interface in comparison with the conventional device architecture.

Afterwards, Baran *et al.* [32] further developed an inden[1,2-*b*]fluorene-cored acceptor, **O-IDFBR** (Scheme 3, Table 2), showing slightly raised HOMO/LUMO energy levels but similar absorption properties compared with **FBR**. By using **O-IDFBR** as the third component, the derived P3HT:**O-IDTBR**:**O-IDFBR** ternary OSCs offered a very encouraging PCE of 7.8% without any solvent additives [32]. This high device performance could be attributed to the positive micro-structure changes induced by adding **O-IDFBR** as the third component, which could reduce the charge recombination and improve light-harvesting ability across the visible region effectively. More encouragingly, they further found that the storage lifetime and photo-stability of the derived ternary devices can be significantly improved in ambient conditions in comparison with high-efficiency polymer:fullerene solar cells (Fig. 2). Furthermore, they also fabricated the ternary cells by pairing the low-bandgap polymer PTB7-Th with **O-IDTBR** and **O-IDFBR**, and the resulting devices produced a PCE as high as 11.4%, which was almost comparable to those from INCN-based NFAs.

Later on, a low bandgap polymer PffBT4T-2DT (Scheme 1) was also used to pair with **O-IDTBR** [9], and the fabricated OSCs also delivered an encouraging PCE up to 10% with a high V_{oc} of 1.07 V. It is worth noting that a remarkably high EQE value of 75% was achieved in this device. Nonetheless, when blending PffBT4T-2DT with **EH-IDFBR** (Scheme 3, Table 2), the resulting OSCs only showed a poor PCE of 1.75% due to the significant decrease of both J_{sc} and FF. In addition, Chen and co-workers [75] designed and synthesized a new polymer donor, PffBT2T-TT (Scheme 1), with identical bandgaps and energy levels with those of **O-IDTBR**. An impressive PCE of 10.4% was realized with a small V_{loss} of 0.55 V, although the charge driving forces between donor and acceptor were very small.

Yang and coworkers [76] further synthesized an RCN-based acceptor **IDT-4CN** (Scheme 3, Table 2) with deeper HOMO/LUMO energy levels and a smaller optical bandgap of 1.50 eV in comparison with **IDT-2BR**. Con-

Figure 2 Storage lifetime and photo-stability of P3HT:O-IDTBR:O-IDFBR and high-efficiency, low-bandgap polymer:fullerene devices. (a) Shelf storage lifetime (dark, in air, un-encapsulated) comparison of P3HT:O-IDTBR:O-IDFBR device efficiencies with other polymer:fullerene systems. Devices were exposed to ambient conditions over a 1200 h duration or until high devices no longer showed any diode behaviour. (b) Photo-stability of P3HT:O-IDTBR:O-IDFBR device and polymer:fullerene solar cells (in air, un-encapsulated, under AM1.5 illumination at 1 sun) for 90 h. Reprinted with permission from Ref. [32]. Copyright 2017, Nature Publishing Group.

sequently, the IDT-4CN-based OSCs afforded a higher PCE of 8.13% with the medium bandgap polymer donor PBDB-T. Moreover, we have to note that the hexyl analogue IDT-BT-R-CN (Scheme 3, Table 2) yielded an inferior PCE of 5.3% when blended with PTB7-Th [77].

Two new indolo[3,2-*b*]carbazole (ICz) core NFAs (ICz-Rd₂ and ICz-RdCN₂, Scheme 3 and Table 2) recently were reported by Suman *et al.* [78]. The more electron-rich ICz core can result in a more efficient ICT, and thus both molecules showed decreased LUMO levels compared with CzC6C8. In particular, ICz-RdCN₂ had a much lower LUMO level of -3.98 eV than ICz-Rd₂ due to the use of more electron-deficient RCN end-groups. Moreover, both new NFAs showed a strong aggregation in the film state, and particularly for ICz-RdCN₂, a red-shifted absorption up to 60 nm can be observed. With a low bandgap polymer donor P1 (Scheme 1), both ICz-Rd₂ and ICz-RdCN₂ can enable high-performance OSCs with high PCEs of 7.88% and 9.76%, respectively, outperforming that of the reference PC₇₁BM-based one (5.89%).

Based on the IDT-2BR acceptor, Zhong *et al.* [79] studied the effect of fluorination on the BT unit, and synthesized two regioregular NFAs, IFBR-*p* and IFBR-*d* (Scheme 3, Table 2), wherein the orientation of monofluorine substitution on the BT unit was controlled with respect to the IDT core. In spite of having similar optical and electrochemical properties in solutions, the simulated conformational diversity and the electrostatic potential of these two acceptors were quite different with each other. When blended with a wide bandgap polymer donor (PTzBI, Scheme 1), the derived IFBR-*d*-based BHJ blend showed a more pronounced crystallization and a larger

scale phase separation than the IFBR-*p*-based blend. As a result, the PTzBI:IFBR-*p* based OSCs delivered an enhanced PCE of 7.44%.

Meanwhile, the tetrafluorinated IffBR (Scheme 3, Table 2) was also synthesized by Zhong *et al.* [80], with significantly decreased energy levels in comparison with IDT-2BR. IffBR presented a maximum absorption at 658 nm with an optical bandgap of 1.71 eV. With the polymer donor PBTA-BO (Scheme 1), a higher PCE of 6.24% was yielded in comparison with that of IDT-2BR-based control device. Furthermore, through introducing PC₇₁BM as the third component, the photovoltaic performance of the resulting ternary device (PBTA-BO:PC₇₁BM:IffBR) can be further boosted to enable a PCE up to 9.06%, attributed to the broadened absorption, the formation of cascade charge-transfer pathways, the reduced nongeminate recombination and the more favorable BHJ morphology.

On the other hand, benzotriazole (BTA) unit has been also successfully used as the second A' moiety for efficient IDT-RD-based NFAs. The additional N atom in the BTA unit can make it more electron-rich than the BT counterpart. In 2018, Tang *et al.* [38] designed and synthesized three IDT-BTA-RD-based NFAs (BTA1-3, Scheme 3, Table 2) with different substitutions on the 2-position of RD moiety, including oxygen atom, sulfur atom and dicyanomethylene group, respectively. As the electron deficiency of end-groups increases from BTA2, to BTA1 and to BTA3, the resulting NFAs gradually exhibit decreased HOMO/LUMO energy levels and red-shifted absorption. In this material system, the J61:BTA3 devices show a satisfied PCE of 8.25% with a high V_{oc} of 1.15 V, one of the highest V_{oc} reported at that time (Fig. 3), due

Figure 3 Plot of V_{oc} against $E_{opt,min}$ in OSCs with high PCE reported until December 2017. Reprinted with permission from Ref. [38]. Copyright 2018, Wiley-VCH.

to the matched energy levels between donor and acceptor that can provide sufficient driving force for charge separation.

In order to improve the device performance of **BTA3**, different paired polymer donors, like PE1, PE2, J71 and P3HT (Scheme 1), were also investigated. Replacing the thiophene π -bridge of J61 with thieno[3,2-*b*]thiophene (TT) unit can endow the derived PE1 with extended conjugation and more pronounced intermolecular π - π stacking [81]. Further, PE2 with a downshifted HOMO energy level of -5.41 eV was also obtained by introducing fluorine atoms into the thiophene side-chains in PE1 [81]. Both OSCs fabricated from PE1 and PE2 exhibited a high V_{oc} over 1.1 V and the PE1:**BTA3** blend delivered a higher PCE of 8.43% than PE2:**BTA3** (5.83%). However, when blended with another high-performance polymer donor J71 with trimethyl(thiophen-2-yl)silane side-chains, the PCE of derived **BTA3**-based OSCs can be further improved to 8.60% with a V_{oc} as high as 1.2 V [40]. Besides, Xiao *et al.* [46] also fabricated the P3HT:**BTA3** based OSCs, and found that a continuous pathway for electron transport can be resulted for **BTA3** to further strengthen the electron mobility when forming BHJ blend with P3HT, thereby affording an encouraging PCE of 5.64% with a V_{oc} of 0.90 V and an FF of 65%, much higher than the control P3HT:**IDT-4CN** devices (PCE = 2.55%). These above results therefore strongly indicate that BTA is a promising building block toward high-performance RD-based NFAs.

To further study the effects of BTA unit on the RD-

based NFAs, Zhang *et al.* [39] also synthesized **BTA100**, **BTA101** and **BTA103** (Scheme 3, Table 2). It was found that the introduction of electron-donating methoxy groups on BTA units could up-shift the LUMO energy levels of the derived NFAs to provide a possibility of improving the V_{oc} for P3HT-based OSCs. In this work, the RCN-based acceptor **BTA103** showed the best photovoltaic performance with P3HT donor, with a PCE of 5.31% and a V_{oc} of 0.94 V. Note that despite **BTA100** had a very poor PCE of 1.04%, the resulting V_{oc} of 1.34 V could be one of the highest values for P3HT-based solar cells reported thus far.

Additionally, DPP unit has been also introduced as the second A' moiety between IDT and RD units, affording a new acceptor, **IDT-DPP-R** (Scheme 3, Table 2) [82]. Since DPP is more electron-deficient than both BT and BTA units, the resulting HOMO/LUMO energy levels as well as absorption band of **IDT-DPP-R** were significantly reduced. Nonetheless, the fabricated P3HT:**IDT-DPP-R** OSCs only delivered a PCE of 1.42%. Fortunately, when used as the third component in the ternary devices, **IDT-DPP-R** not only extended the active layer absorption to near infrared ray (NIR) region to improve the J_{sc} , but also increased the V_{oc} due to its higher LUMO energy level relative to PC₆₁BM. Finally, the derived ternary devices with 20% content of **IDT-DPP-R** yielded an average PCE of 3.84%, outperforming the binary P3HT:PC₆₁BM devices (3.30%).

In addition to incorporating the second A' moiety between IDT core and RD/RCN units, thiophene derivatives have been used as the π -conjugated bridge to tune the optical and electronic properties of the resulting NFAs. For example, Jiang and coworkers [41] synthesized a new acceptor, **ITCN** (Scheme 4, Table 3), wherein 2-hexylthienyl substituted IDT-core was linked with two hexyl-substituted RCN units *via* a 3-(2-ethylhexyl)thiophene bridge. Compared with **IDT-4CN**, **ITCN** had a higher-lying LUMO energy level and a blue-shifted absorption due to the electron-donating property of thiophene bridges. However, the thiophene bridges in the **ITCN** can effectively reduce its molecular planarity to prevent aggregation and phase separation in the BHJ blend. Therefore, although the binary PBDB-T:**ITCN**-based OSCs only afforded a low PCE of 2.21%, the ternary OSCs can achieve an impressive PCE of 12.16% with a V_{oc} of 0.95 V using **ITCN** as the third component. It was shown that in the ternary blend of PBDB-T:IT-M:**ITCN**, **ITCN** not only provided a complementary optical absorption, but also enabled a more effective exciton diffusion.

Scheme 4 Chemical structures of NFAs with a pentacyclic/hexacyclic electron-rich core.

Table 3 Summary of NFAs with a pentacyclic/hexacyclic electron-rich core

Acceptor	E_{HOMO} (eV)	E_{LUMO} (eV)	$E_{\text{g,opt}}$ (eV)	Donor	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)	Mobility (cm ² V ⁻¹ s ⁻¹)		Ref.
									Electron	Hole	
ITCN	-5.40 ^a	-3.62 ^a	-	PBDB-T	1.17	4.97	37	2.21	-	-	[41]
	-5.40 ^a	-3.62 ^a	-	PBDBT: IT-M	0.95	17.67	71	12.16	-	-	[41]
ORCN	-5.37 ^a	-3.56 ^a	1.64	P3HT	0.87	11.50	62	6.55	1.8E-4	1.0E-4	[45]
ERCN	-5.50 ^a	-3.59 ^a	1.82	P3HT	0.90	5.87	50	2.77	2.7E-5	2.3E-4	[45]
IDTzCR	-5.67 ^a	-3.77 ^a	1.79	PTB7-Th	1.04	13.80	61	8.71	1.6E-5	3.1E-4	[83]
IDTCR	-5.46 ^a	-3.67 ^a	1.76	PTB7-Th	1.11	11.01	50	6.10	5.9E-6	5.6E-4	[83]
H-IDTzR	-5.31 ^c	-3.44 ^a	1.87	P3HT	1.04	6.67	53	3.53	1.8E-6	1.0E-4	[48]
P-IDTzR	-5.31 ^c	-3.42 ^a	1.89	P3HT	1.02	9.00	55	5.01	7.1E-6	9.0E-5	[48]
ATT-1	-5.50 ^b	-3.63 ^b	1.54	PTB7-Th	0.87	16.48	70	10.07	2.4E-4	5.1E-4	[35]
ATT-3	-5.32 ^b	-3.40 ^b	1.61	P3HT	0.93	10.81	59	5.89	5.1E-7	1.0E-5	[44]
ATT-8	-5.46 ^a	-3.71 ^a	1.55	PBDB-T	0.80	13.90	65	7.31	1.9E-5	2.6E-4	[86]
A1	-5.66 ^a	-3.70 ^a	1.40	PTB7-Th	0.89	12.54	52	5.79	6.3E-5	6.1E-4	[87]
A2	-5.70 ^a	-3.78 ^a	1.36	PTB7-Th	0.71	20.33	63	9.07	2.3E-4	1.0E-3	[87]
DTNR	-5.67 ^a	-3.75 ^a	1.72	PTB7-Th	1.08	15.72	56	9.51	2.5E-5	1.8E-5	[88]

a) Measured by CV based on films. b) Measured by CV in solutions. c) Calculated by $E_{\text{LUMO}} = E_{\text{HOMO}} + E_{\text{g,opt}}$. “-” indicates that the details were not reported.

Later on, Wu and coworkers [45] synthesized two thiophene-bridged NFAs, **ERCN** and **ORCN** (Scheme 4, Table 3), to study the effect of different types of alkyl chains in the thiophene bridges. In comparison with **ERCN**, the introduction of alkoxy chain in the **ORCN** was shown to enable strong S...O noncovalent conformational locks (NCLs) that can efficiently increase the

planarity and rigidity of the backbone (Fig. 4c). Therefore, **ORCN** showed a significantly red-shifted absorption in the film state (Fig. 4a) due to the aggregation effect and increased HOMO/LUMO energy levels (Fig. 4b) compared with **ERCN**. Furthermore, such noncovalent interactions could optimize the BHJ film morphology to improve the charge transport mobility in the BHJ blend.

Figure 4 (a) UV-vis absorption spectra for the films of ERCN, ORCN, and P3HT. (b) Energy levels of P3HT, ORCN, and ERCN. (c) Molecular geometries of ORCN and ERCN obtained by DFT calculation. Reprinted with permission from Ref. [45]. Copyright 2018, Wiley-VCH.

As a result, the fabricated P3HT:ORCN OSCs demonstrated an impressive PCE of 6.6%, attributed to the simultaneous enhancement of all device parameters compared with those of control ERCN-based device.

To further study the effect of NCLs, they further introduced thiazole (Tz) as the π -conjugated bridge between IDT core and RD units to yield a new acceptor IDTzCR (Scheme 4, Table 3) [83]. In respect to the thiophene-bridged analogue IDTCR (Scheme 4, Table 3), the electron-withdrawing thiazole units can effectively lower the HOMO/LUMO energy levels and also increase the maximum absorption coefficient of IDTzCR. Moreover, due to the existence of S...N NCLs, the planarity/rigidity of IDTzCR can also be increased to elevate the electron mobility and thus achieve more balanced electron/hole mobility in the BHJ blend. Through blending with PTB7-Th, the PCEs of derived OSCs were significantly improved from 6.10% (IDTCR) to 8.71%

(IDTzCR). Recently, two new Tz-bridged small molecule NFAs, H-IDTzR and P-IDTzR (Scheme 4, Table 3), were also reported by integrating design strategy of NCLs with side-chain engineering [48]. Similarly, the S...N NCLs were found to enable good planar configuration in both acceptors, while the change of side-chains can affect the interchain π - π stacking to tune the crystallinity. In comparison with H-IDTzR with *n*-hexyl side chains, P-IDTzR with bulky 4-hexylphenyl side chains exhibited more suitable crystallinity to match with P3HT donor. As a result, a more optimal BHJ morphology can be realized in the P3HT:P-IDTzR blend to afford a higher PCE of 5.01%.

Ester-substituted thieno[3,4-*b*]thiophene (TbT) unit is one of the most successful electron-withdrawing building blocks toward high-performance D-A type polymer donors such as PTB7-Th [84]. TbT unit typically exhibits a fully delocalized conjugation with a pronounced quinoid-

enhancing effect, and its electron-withdrawing ester substitution can lower the HOMO/LUMO energy levels to improve the stability against oxidation [4,85]. Recently, ester-substituted *TbT* unit has been also used to construct efficient RD-based NFAs as the π -conjugated bridge and second A' moiety simultaneously. In 2016, Liu *et al.* [35] reported a new *TbT*-bridged acceptor **ATT-1** (Scheme 4, Table 3) with IDT as the core and RCN as the end-groups, showing a low optical bandgap of 1.54 eV. The as-cast PTB7-Th:**ATT-1** OSCs showed an impressive PCE up to 10.07% due to its proper energy level alignment, excellent carrier transport property and favorable BHJ film morphology. Soon after, they further synthesized **ATT-3** (Scheme 4, Table 3) based on RD units [44]. **ATT-3** exhibited a complementary absorption and well-matched HOMO/LUMO energy levels with P3HT donor. Thus, the resulting P3HT:**ATT-3** based OSCs showed a comparable PCE of 6.26% to the P3HT:**O-IDTBR** blend, due to the achievement of a higher V_{oc} of 0.93 V and a smaller E_{loss} of 0.68 eV. Very recently, another acceptor **ATT-8** was also obtained based on the electron-withdrawing 2-(trifluoromethyl)thieno[3,4-*b*]thiophene unit (Scheme 4, Table 3), and the optimized OSCs based on the PBDB-T:**ATT-8** blend afforded a high PCE to 7.31% with a V_{oc} of 0.80 V and an FF of 65% [86].

Similarly, Xu and coworkers [87] recently reported two new NFAs, **A1** and **A2** (Scheme 4, Table 3), with low optical bandgaps below 1.40 eV, wherein ester-substituted benzothiadiazole (BTT) was used as the π -spacer. Compared with the BT-based analogous (**IDT-2BR**), the fused thiophene ring in the BTT unit can extend the conjugation length effectively to increase the quinoid population. Moreover, the ester substitution can also make the spacer electron-deficient, thereby forming the A-A'-D-A'-A structure. These two structural changes can enable a more effective ICT effect to broaden the absorption and reduce the optical bandgap. Both NFAs realized good photovoltaic performance, and due to the enhanced light absorption resulted from RCN units, the corresponding **A2**-based devices delivered a higher PCE of 9.07% than that of **A1**-based one (5.79%), with the same polymer donor PTB7-Th.

NFAs with a hexacyclic electron-rich core

Unlike the pentacyclic core, the hexacyclic core has been less studied for RD-based NFAs thus far. Given that the fused rings with angular shapes would lead to higher-lying LUMO energy levels than the linear-shaped counterparts, Ma *et al.* [88] developed a new acceptor **DTNR** (Scheme 4, Table 3) based on a ladder-type angular-

shaped dithienonaphthalene (DTN). **DTNR** had a higher-lying LUMO energy level and an enhanced electron mobility compared with **EH-IDTBR**. Although the LUMO energy level offset between donor and acceptor was only 0.13 eV, the derived PTB7-Th:**DTNR** blend still showed a high PCE of 9.51% with a large V_{oc} of 1.08 V and a low E_{loss} of 0.50 eV, attributed to the efficient photoinduced charge separation.

NFAs with a heptacyclic electron-rich core

Replacing two thiophene rings in the IDT with TT units can afford a novel heptacyclic IDTT donor. This structural modification can significantly improve the charge mobility of the resulting IDTT-based molecules/polymers due to the extended effective conjugation length and enhanced intermolecular interactions [89]. Since the first demonstration of ITIC [10], IDTT has become the most studied core structure for A-D-A type NFAs [90]. Qu and coworkers [91] reported the synthesis of a series of new IDTT-RCN-based NFAs (**ITBTR-C2**, **ITBTR-C4**, **ITBTR-C6**, and **ITBTRC8**) (Scheme 5, Table 4) by tuning the side-chains in the RCN units including ethyl-, butyl-, hexyl-, and octyl- chains, respectively. Although all molecules exhibit similar absorption and HOMO/LUMO energy levels, distinct photovoltaic performance has been realized with the same polymer donor PBDB-T, and in particular, the PBDB-T:**ITBTR-C6** devices deliver the highest PCE of 8.26%, attributed to its higher electron mobility and better phase separation morphology. Furthermore, by SVA, this PCE can be further increased to 9.29% due to both enhancements of J_{sc} and FF. The results thus highlight the importance of introducing appropriate alkyl chains in the end-groups.

Further integrating IDTT core with BTA unit, Tang *et al.* [37] synthesized **BTA13** (Scheme 5, Table 4), showing a larger maximum molar extinction coefficient, a red-shifted optical absorption and elevated energy levels in comparison with the analogue **BTA3**. Paired with three BTA-based polymer donors (J52, J52-F and J52-FS, Scheme 1), the device performance of derived **BTA13**-based OSCs was carefully optimized, and when blended with the fluorinated polymer donor J52-F, a highest PCE of 8.36% was demonstrated, benefited from the simultaneously achievement of high V_{oc} and J_{sc} . Song *et al.* [92] also reported another new NFA, **DTFBR** (Scheme 5, Table 4), by adopting fluorene-based heptacyclic donor as the core. When blended with P3HT, the derived OSCs showed a PCE of 3.68%. Interestingly, blended with the fullerene acceptor PC₇₁BM, **DTFBR** can also work as a donor to deliver a PCE of 2.50%, suggesting **DTFBR** is a

Scheme 5 Chemical structures of NFAs with a heptacyclic electron-rich core, and other type 1D NFAs.

Table 4 Summary of NFAs with a heptacyclic electron-rich core, and other type 1D NFAs

NFAs	E_{HOMO} (eV)	E_{LUMO} (eV)	$E_{\text{g,opt}}$ (eV)	Donor	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)	Mobility (cm ² V ⁻¹ s ⁻¹)		Ref.
									Electron	Hole	
ITBTR-C2	-5.30 ^a	-3.70 ^a	1.52	PBDB-T	0.89	13.47	59	7.04	8.6E-6	3.2E-6	[91]
ITBTR-C4	-5.30 ^a	-3.71 ^a	1.52	PBDB-T	0.90	14.94	55	7.43	2.4E-5	1.9E-5	[91]
ITBTR-C6	-5.30 ^a	-3.71 ^a	1.52	PBDB-T	0.88	16.30	64	9.29	6.6E-5	6.0E-5	[91]
ITBTR-C8	-5.28 ^a	-3.70 ^a	1.49	PBDB-T	0.90	14.88	59	7.93	3.4E-5	2.8E-5	[91]
BTA13	-5.34 ^a	-3.62 ^c	1.72	J52	1.05	12.70	59	7.82	2.8E-4	5.9E-4	[37]
	-5.34 ^a	-3.62 ^c	1.72	J52-F	1.18	11.55	61	8.36	6.2E-5	3.9E-4	[37]
	-5.34 ^a	-3.62 ^c	1.72	J52-FS	1.24	6.74	46	3.84	1.7E-5	1.4E-4	[37]
DTFBR	-5.54 ^a	-3.68 ^a	1.74	P3HT	0.71	8.15	62	3.68	-	-	[92]
ITBR	-5.55 ^a	-3.71 ^a	1.71	PTB7-Th	1.02	14.46	51	7.49	1.5E-5	-	[93]
ITBRC	-5.60 ^a	-3.82 ^a	1.63	PTB7-Th	0.91	9.21	51	4.26	1.3E-5	-	[93]
TIDT-BT-R2	-5.25 ^a	-3.65 ^a	1.68	PTB7-Th	1.04	13.10	64	8.70	2.5E-4	2.7E-4	[94]
TIDT-BT-R6	-5.28 ^a	-3.67 ^a	1.70	PTB7-Th	1.03	10.30	52	5.60	7.4E-5	1.4E-4	[94]
DFPCBR	-5.12 ^b	-3.59 ^b	1.59	P3HT	0.80	10.39	64	5.34	1.0E-5	8.6E-5	[47]

a) Measured by CV based on films. b) Measured by CV in solutions. c) Calculated by $E_{\text{LUMO}} = E_{\text{HOMO}} + E_{\text{g,opt}}$. “-” indicates that the details were not reported.

bipolar charge transport molecule.

Other A-D-A type 1D NFAs

In addition to these large fused-ring systems, a particular attention has been paid to designing core structure with single bonds interconnected aromatic rings, due to the low synthetic complexity. In 2017, Tang *et al.* [93] took advantage of the asymmetric thiophene-indenothiophene

(TIDT) unit as the core toward two new BT-bridged NFAs, **ITBR** and **ITBRC** (Scheme 5, Table 4), with RD and RCN as the end-groups, respectively. Inverted OSCs based on PTB7-Th:**ITBR** blend afforded a higher PCE of 7.49% with a lower E_{loss} of 0.59 eV than those based on PTB7-Th:**ITBRC** blend, due to its higher electron mobility and more suitable BHJ morphology. Later on, Bai and coworkers [94] also used the same core to synthesize

TIDT-BT-R2 and **TIDT-BTR6** (Scheme 5, Table 4), possessing complementary absorption and well-matched energy levels with PTB7-Th. Compared with **TIDTBT-R6**, **TIDT-BT-R2** with shorter ethyl side-chains showed better crystallinity and higher charge carrier mobilities in the BHJ blend. As a result, the PTB7-Th:**TIDT-BT-R2** OSCs demonstrated much higher exciton dissociation efficiency and lower charge recombination, resulting in higher J_{sc} and FF to achieve a PCE up to 8.7%.

Moreover, Wang and coworkers [47] recently reported a new RD-based NFA (**DFPCBR**, Scheme 5, Table 4) based on another non-fused core structure. In this molecule, the core structure was designed by linking two electron-rich cyclopentadithiophene (CPDT) units with a 2,5-difluorobenzene (DFB) ring. Due to the F...H non-covalent interactions between CPDT and DFB units, the core conformation can be locked effectively to form a largely planar geometry. **DFPCBR** exhibited a red-shifted absorption and higher-lying energy levels than **EH-IDTBR**, which would enhance the light-harvesting ability and mitigate the energy loss of the resulting OSCs. Due to proper device optimizations, the P3HT:**DFPCBR** OSCs produced a decent PCE of 5.34%. More encouragingly, it was found that almost 80% of the initial PCE can be remained even if the active layer thickness reached 320 nm.

A-D-A-TYPE 3D RD-BASED NFAs

3D structure design has been shown to enhance the

compatibility of resulting NFAs with polymer donors desirably [95–97]. Besides, the acceptor aggregation in the BHJ blend can be also well-controlled through this molecular design. These two advantages thus would help to achieve preferred BHJ film morphology for charge separation/transport. So far, two major building blocks, spirofluorene and truxene, have been successfully developed as the core structure for constructing 3D RD-based NFAs.

In 2012, Ma *et al.* [98] first reported a spirofluorene-cored 3D small molecule donor (SF8TBT). Compared with the linear analogue molecule (LF8TBT), the designed spirofluorene structure can enable optimized intermolecular stacking to increase the FF. Consequently, the SF8TBT:PC₇₁BM devices showed a dramatically increased PCE of 4.82% with an FF of 56%. Until 2016, Qiu *et al.* [99] first used spirobifluorene as the central core to develop two 3D RD-based NFAs, **SF-OR** and **SF-ORCN** (Scheme 6, Table 5). Grazing-incidence X-ray diffraction (GIXD) measurements showed that such 3D conformation can effectively reduce the overall crystal packing in the BHJ blend with P3HT donor and endow the derived blends with suitable phase separation to improve the device performance. In comparison with the corresponding linear molecule **Flu-RH**, **SF-OR** based OSCs afforded a higher PCE of 4.66% with an enhanced FF of 65%. On the other hand, although the RCN end-groups can improve the light absorption, the derived **SF-ORCN**-based devices delivered a slightly decreased PCE of 4.48%

Scheme 6 Chemical structures of A-D-A-type 3D RD-based NFAs.

Table 5 Summary of A-D-A-type 3D RD-based NFAs

NFAs	E_{HOMO} (eV)	E_{LUMO} (eV)	$E_{\text{g, opt}}$ (eV)	Donor: 2nd com- ponent	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)	Mobility (cm ² V ⁻¹ s ⁻¹)		Ref.
									Electron	Hole	
SF-OR	-5.50 ^b	-3.25 ^b	2.15	P3HT	0.96	7.44	65	4.66	6.7E-6	8.5E-5	[99]
SF-ORCN	-5.55 ^b	-3.29 ^b	2.08	P3HT	0.91	7.54	65	4.48	1.0E-4	1.6E-4	[99]
SF(BR) ₄	-5.78 ^a	-3.73 ^a	2.10	PffBT4T-2OD	0.95	12.27	53	6.15	7.8E-5	5.6E-4	[100]
XFBRCN	-5.89 ^c	-3.77 ^a	2.12	PTB7-Th	0.91	4.60	34	1.42	3.0E-6	-	[65]
SFBRCN	-5.93 ^a	-3.86 ^a	2.05	PTB7	0.85	14.00	61	7.63	1.2E-4	5.5E-5	[101]
	-5.93 ^a	-3.86 ^a	2.05	PTB7-Th	0.90	17.80	64	10.26	2.2E-4	1.5E-4	[101]
	-5.93 ^a	-3.86 ^a	2.05	PBDB-T:PTB7-Th	0.93	17.86	74	12.27	2.4E-4	2.3E-4	[102]
BTA21	-5.76 ^a	-3.56 ^a	2.19	P3HT	1.02	5.45	59	3.28	2.5E-6	7.0E-6	[103]
BTA23	-5.70 ^a	-3.64 ^a	2.15	P3HT	0.90	3.98	52	1.86	1.0E-6	1.2E-7	[103]
para-TrBRCN	-5.98 ^a	-3.71 ^a	2.19	PTB7-Th	0.95	13.75	64	8.29	1.2E-4	6.5E-5	[34]
meta-TrBRCN	-5.95 ^a	-3.72 ^a	2.10	PTB7-Th	0.94	16.75	65	10.15	2.0E-4	1.3E-4	[34]
	-5.95 ^a	-3.72 ^a	2.10	PDTF-TZNT:IT-M	0.82	18.54	76	11.48	-	-	[105]
Tr(Hex)6-3BR	-5.79 ^a	-3.74 ^a	2.15	PTB7-Th	1.02	5.92	33	2.10	1.5E-5	1.5E-3	[104]
RhBT-Por	-5.48 ^a	-3.55 ^a	1.45	PDPP5T	0.54	7.40	47	1.9	2.6E-5	5.0E-5	[106]

a) Measured by CV based on films. b) Measured by CV in solutions. c) Calculated by $E_{\text{LUMO}} = E_{\text{HOMO}} + E_{\text{g, opt}}$. “-” indicates that the details were not reported.

mainly due to the inferior V_{oc} .

Later on, Tan and coworkers [100] further reported **SF(BR)₄** (Scheme 6, Table 5) by introducing four BT units between the spirobifluorene core and the RD end-groups. **SF(BR)₄** exhibited significantly downshifted HOMO/LUMO energy levels in comparison with **SF-OR**, making it more compatible with low-bandgap polymer donor, PffBT4T-2OD. Furthermore, the 3D molecular geometry of **SF(BR)₄** was found to suppress the strong intermolecular aggregation efficiently after forming a PffBT4T-2OD:**SF(BR)₄** blend. As a result, a respectable PCE of 6.15% can be achieved. Meanwhile, a new RCN-based 3D acceptor **XFBRCN** was also synthesized by Radford *et al.* [65] (Scheme 6, Table 5). Time-dependent density functional theory (TDDFT) showed that the dynamic torsion of spirobifluorene core could lead to a small amount of exciton coupling at room temperature. **XFBRCN** had a broader absorption, a higher extinction coefficient and a higher permittivity than the linear analogue fluorene-cored **FBRCN** (Scheme 2, Table 1), but showed an inferior PCE of 1.42% compared with that of latter (3.3%). Further mechanism studies showed that the long alkyl chain substitutions on the fluorene core of **FBRCN** not only facilitated the intermolecular packing in the solid-state to improve the electron mobility, but also

provided more miscibility with polymer donors to ensure well-defined domain size in the blend, both of which therefore can effectively reduce the non-geminate recombination of the derived PTB7-Th:**FBRCN** blend to improve the J_{sc} .

In addition, several 3D NFAs were also designed by end-capping RD units only onto two sides of spirofluorene. In 2017, Zhang and coworkers [101] adopted an alkoxy-substituted spirofluorene as the core to synthesize a wide bandgap NFA, **SFBRCN** (Scheme 6, Table 5). In the **SFBRCN**, a planar conjugated backbone can help to realize high charge mobility, while the 3D spirobifluorene core can reduce its self-aggregation tendency to induce an optimal domain size in the BHJ blend. Furthermore, the deep HOMO (-5.93 eV) and LUMO (-3.86 eV) levels of **SFBRCN** can match well with both polymer donors of PTB7 and PTB7-Th, and the resulting PTB7-Th:**SFBRCN**-based PSCs realized a higher PCE of 10.12%. Later on, they also fabricated PBDB-T:PTB7-Th:**SFBRCN** based ternary OSCs, showing an impressive PCE of 12.27% [102]. Based on this, Wen *et al.* [103] prepared two BTA-bridged 3D acceptors, **BTA21** and **BTA23** (Scheme 6, Table 5), having wide optical bandgaps of 2.19 and 2.15 eV, respectively. Compared with **BTA23**, the resulting **BTA21** based OSCs showed a better PCE of

3.28% with a high V_{oc} of 1.02 V due to its more compatible energy levels and absorption with respect to P3HT.

Using the weak electron-donating truxene as the central core, Wu and coworkers [34] further designed and synthesized two RCN-based isomeric 3D NFAs, **para-TrBRCN** and **meta-TrBRCN** (Scheme 6, Table 5). These two star-shaped acceptors exhibited a nonplanar structure due to the large dihedral angles between the truxene skeleton and the connecting BT units (Fig. 5), which was shown to prevent the excessive aggregation of acceptor molecules in the BHJ blend to realize optimized film morphology and ideal domain size. Compared with that of **para-TrBRCN**, the smaller structure distortion of **meta-TrBRCN** can enhance the intermolecular π - π stacking to improve the charge transfer. Therefore, when blended with the same donor PTB7-Th, **meta-TrBRCN**-based OSCs delivered a higher PCE compared with the **para-TrBRCN**-based devices (10.15% vs. 8.28%). By contrast, Lin *et al.* [104] also reported an RD-based analogue **Tr(Hex)6-3BR** (Scheme 6, Table 5), which, however, only showed a PCE of 2.10%, attributed to low electron mobility, serious charge recombination and unfavorable BHJ film morphology. Soon after, Tang *et al.* [105] further introduced **meta-TrBRCN** as the second acceptor to fabricate the PDTF-TZNT:IT-M:**meta-TrBRCN** ternary OSCs. It was found that in the formed ternary blend, **meta-TrBRCN** not only expanded the absorption range, but also finely tuned the blend morphology. Thus, when adding 20% content of **meta-TrBRCN**, the PCE can be improved from 10.05% to 11.48%.

Moreover, Guo *et al.* [106] adopted the zinc-coordinated porphyrin molecule as the electron-rich core to develop a new star-shaped RD-based NFA, **RhBT-Por** (Scheme 6, Table 5), possessing three distinct absorption regions due to the Soret and Q-bands of the porphyrin and the ICT between the porphyrin core and the RD end-

groups. A very broad photo-response from 300 to 850 nm can be achieved when blended with a DPP-based conjugated polymer donor, PDPP5T (Scheme 1); however a low PCE of 1.9% was yielded possibly due to the unideal BHJ morphology.

OTHER-TYPE RD-BASED NFAs

Recently, Lee and coworkers [107] reported a simple RD-based NFA, **T2-ORH** (Scheme 7, Table 6), wherein a bithiophene core was end-capped by two octyl-substituted RD units. In addition to the previously discussed A-D-A or A-A'-D-A'-A type structure, **T2-ORH** could be regarded as an A- π -A type structure with a very short π -conjugation length. **T2-ORH** exhibited a wide bandgap, and a blue-shifted absorption can be observed in the pristine film state due to the formation of H-like aggregation. Interestingly, during device fabrication, thermal annealing (TA) or SVA was found to enable **T2-ORH** to form a J-like aggregation in the BHJ film, accompanied with a red-shifted absorption. As a result, the derived PTB7-Th:**T2-ORH** blend films can feature both vertical and parallel charge transport channels to improve the device performance, and the corresponding additive-free OSCs delivered an impressive PCE of 9.33% with a low E_{loss} of 0.51 eV.

Besides, a new A-A'-A type acceptor, **ISDT-RH** (Scheme 7, Table 6) with an electro-deficient isoindigo core was reported by Kim and coworkers in 2016 [108]. The pristine **ISDT-RH** film showed a strong absorption in a range of 350–650 nm with a maximal extinction coefficient of $8.0 \times 10^4 \text{ cm}^{-1}$ at 465 nm. The HOMO and LUMO energy levels of **ISDT-RH** were determined to be -5.59 and -3.82 eV, respectively. Unfortunately, the fabricated P3HT:**ISDT-RH** devices only gave a PCE as low as 0.42%.

Later on, Privado *et al.* [109–111] successfully synthesized three new DPP-cored acceptors with A-A'-A type structure, **MPU1-3** (Scheme 7, Table 6). **MPU1** exhibited a narrow optical bandgap (1.48 eV) and a low-lying LUMO level of -3.99 eV. When blended with a medium bandgap D-A copolymer donor P2 (1.75 eV), the derived **MPU1**-based OSCs showed a broad photo response covering from 400 to 850 nm to enable an impressive PCE of 7.5%, much higher than that of P3HT:**MPU1**-based devices (2.16%) under similar fabrication conditions. Moreover, the RCN-capped **MPU2** presented a broad absorption with a reduced optical energy gap of 1.41 eV, and a lower-lying LUMO level of -4.15 eV compared with **MPU1**. The higher electron withdrawing ability of RCN can endow a higher electron mobility for

Figure 5 Optimized molecular geometries of **para-TrBRCN** (a) and **meta-TrBRCN** (b). Reprinted with permission from Ref. [34]. Copyright 2018, Wiley-VCH.

Scheme 7 Chemical structures of other-type RD-based NFAs.

Table 6 Summary of other-type RD-based NFAs

NFAs	E_{HOMO} (eV)	E_{LUMO} (eV)	$E_{\text{g,opt}}$ (eV)	Donor	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)	Mobility ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)		Ref.
									Electron	Hole	
T2-ORH	−5.89 ^a	−3.64 ^a	2.03	PTB7-Th	1.07	14.72	59	9.33	9.0E-4	2.1E-3	[107]
ISDT-RH	−5.59 ^a	−3.82 ^a	1.77	P3HT	0.58	1.77	–	0.42	–	–	[108]
ISDT-ECA	−5.56 ^a	−3.61 ^a	1.95	P3HT	0.68	1.47	–	0.53	–	–	[108]
MPU1	−5.81 ^b	−3.99 ^b	1.48	P2	0.98	12.37	62	7.52	–	–	[109]
	−5.81 ^b	−3.99 ^b	1.48	P3HT	0.60	6.54	55	2.16	–	–	[109]
	−5.81 ^b	−3.99 ^b	1.48	DTS (QxHTh ₂) ₂	1.02	11.04	62	6.98	–	–	[110]
MPU2	−5.72 ^b	−4.15 ^b	1.41	DTS (QxHTh ₂) ₂	0.94	12.15	68	7.76	7.1E-5	1.2E-4	[110]
MPU3	−5.61 ^b	−3.74 ^b	1.52	p-DINI-(FBTTTH ₃) ₂	0.98	13.72	67	9.14	7.9E-5	1.2E-4	[111]
TTz2	−5.50 ^a	−3.80 ^a	1.61	J71	0.92	12.75	54	6.30	8.7E-5	2.9E-4	[112]
PDIBDT-RDN	−5.86 ^a	−3.81 ^a	1.64	PTB7-Th	0.76	9.28	47	3.34	2.9E-5	1.5E-3	[113]
PNDI-2T-TR (5)	−5.91 ^a	−3.91 ^a	1.48	PBDB-T	0.85	14.83	64	8.13	3.9E-4	6.5E-4	[116]
PNDI-2TTR (10)	−5.92 ^a	−3.93 ^a	1.50	PBDB-T	0.80	11.36	54	4.89	1.2E-4	8.5E-4	[116]

a) Measured by CV based on films. b) Measured by CV in solutions. “–” indicates that the details were not reported.

MPU2. Consequently, when paired with a small molecular donor DTS(QxHTh₂)₂ (Scheme 1), the vacuum-processing MPU2-based OSCs delivered a higher PCE of

7.76% than that of the control MPU1-based devices (6.28%).

Further introduction of hexyl-substituted thienylethy-

nyl group between the DPP core and the RCN units as the π -conjugated bridge afforded a new A- π -A'- π -A type acceptor, **MPU3**. In comparison with **MPU2**, the additional thienylethynyl bridge can broaden the ICT band, accompanied with a higher molar extinction coefficient. Nonetheless, **MPU3** exhibited a larger optical bandgap of 1.52 eV than **MPU1-2**. The **MPU3**-based OSCs delivered an impressive PCE of 9.05% with a small molecule donor p-DINI-(FBTTh₃)₂ (Scheme 1), greatly outperforming the p-DINI-(FBTTh₃)₂:PC₇₁BM (5.80%) devices, mainly due to that **MPU3**-based devices showed a much lower E_{loss} of 0.54 eV by comparison with the PC₇₁BM-based counterpart (1.02 eV) as a result of the significantly decreased LUMO offset between p-DINI-(FBTTh₃)₂ and **MPU3**.

In 2018, Peng and coworkers [112] also synthesized a medium bandgap RD-based A- π -A'- π -A type NFA, **TTz2** (Scheme 7, Table 6), using a weakly electron-deficient thiazolothiazole (TTz) unit as the core. The HOMO/LUMO energy levels of **TTz2** were very compatible with those of polymer donor J71, and thus the fabricated devices exhibited a good PCE of 6.30%.

Recently, Liu *et al.* [113] developed an interesting cross-conjugated NFA based on a BDT core, **PDIBDT-RDN** (Scheme 7, Table 6). In this structure, the BDT unit was flanked by two different kinds of electron-withdrawing moieties (perylene diimides and 3-ethylrhodanine units). **PDIBDT-RDN** presented low-lying HOMO/LUMO energy levels and a broad absorption band ranging from 300 to 700 nm. With the polymer donor PTB7-Th, the derived **PDIBDT-RDN**-based OSCs delivered a PCE of 3.34%, which was mainly limited by the low J_{sc} and FF.

Naphthalene diimide (NDI)-based polymer acceptors, such as N2200 [114,115], has been widely used in all-polymer solar cells (all-PSCs); however, their low light absorption, suboptimal energy levels and strong self-aggregation have retarded the further elevation of device performance. To resolve this problem, Chen *et al.* [116] introduced a RD-based dye molecule into the NDI-based polymer acceptor through a simple random copolymerization. The new NDI-based polymer acceptors (**PNDI-2TTR(x)**, ($x = 5$ and 10, Scheme 7, Table 6), with a dye of content of 5% and 10%, respectively, showed enhanced light absorption, up-shifted LUMO levels and reduced crystallization in comparison with N2200. In addition, the bimolecular and monomolecular recombination can be suppressed substantially in the **PNDI-2TTR(5)**-based devices. As a result, a high PCE of 8.13% was achieved from the additive-free PBDB-T:**PNDI-2T-TR(5)** based OSCs, much higher than that of N2200-based devices.

Unfortunately, the PBDB-T:**PNDI-2T-TR(10)**-based OSCs only showed a PCE of ~5% due to the unfavorable blend morphology caused by disordered molecular packing. These results therefore suggest that the polymer structure from such random polymerization strategy needs to be controlled carefully.

SUMMARY AND PERSPECTIVE

In summary, RD dye and its derivatives have been successfully used as the electron-withdrawing moieties to construct high-performance A-D-A type NFAs. When blended with well-known narrow bandgap polymer donor PTB7-Th and medium bandgap polymer donor PffBT2T-TT, the derived binary OSCs based on RD-based NFAs both have shown encouraging PCEs over 10% [33,75]. Although the device performance is still lower than that of other state-of-the-art INCN-based NFAs, RD-based NFAs have demonstrated a particularly excellent compatibility with well-known P3HT donor. The optimized P3HT:O-IDTBR OSCs have achieved a record PCE of 7.0% in single-junction binary devices [49]. So far, P3HT has always been considered as one of the few feasible polymer donors suitable for large-scale commercialization of OSCs, due to its simple synthesis and monomer availability. In this context, more novel molecular designs of RD-based NFAs with suitable energy levels, complementary absorption and favorable molecular crystallinity should be continuously developed.

Recently, a new D-A-D type fused core structure was designed to construct NFAs, affording very exciting PCEs up to 16% [13–15]. These encouraging results manifest that the core structure engineering can provide an ample room to further boost the performance of NFAs. Indeed, both non-fused and simple A- π -A-type RD-based NFAs have been reported with very good performance. Furthermore, other suitable structural modifications, like side-chain engineering and introduction of the second acceptor units, need to be taken into account carefully in parallel with the development of new core structure. For RD itself, it is worthwhile to mention that its 2-position can be further functionalized by different aromatic rings, which may provide a new approach to tune the optical/electronic properties and the intermolecular stacking behaviors of the resulting NFAs. We believe that through a rational molecular design, PCEs over 10% could be achieved for RD-based NFAs with the P3HT donor in the near future.

On the other hand, the properties related to absorption and energy levels of RD-based NFAs also make them a class of potential third component materials in the tern-

ary OSCs. Besides, the OSCs derived from RD-based NFAs always exhibit a high V_{oc} over 1.0 V, suggesting that they could be suitable material candidates for fabricating high-performance tandem OSCs. From these points of view, we have to also pay particular attention to exploring new design strategies of RD-based NFAs to fulfill the requirements of these advanced devices.

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基于饶丹宁的有机太阳能电池非富勒烯受体

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摘要 近年来, 有机太阳能电池非富勒烯受体(NFAs)的研究取得了重大进展, 且在叠层器件中实现了超过17%的光电转换效率(PCE). 目前, 具有线型稠合受体-供体-受体(A-D-A)结构的NFAs因其优异的合成灵活性和高光伏性能而受到了广泛关注. 其中, 饶丹宁染料是构建这类A-D-A型NFAs的最为常见的吸电子受体单元, 且所得单结太阳能电池的PCE已超过10%. 尤为重要的是, 饶丹宁受体与众所周知的P3HT供体结合时表现出十分优异的相容性, 进而获得了7%的PCE. 因此, 本文总结了饶丹宁非富勒烯受体材料的研究进展, 侧重于讨论其分子设计策略, 旨在帮助读者更好的理解这类非富勒烯受体的构性关系.