Supporting Information

1. Synthetic Complexity

Table S1 Summary of the synthetic details of the various fluorene and carbazole based NFAs.

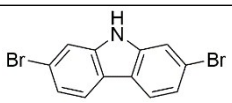
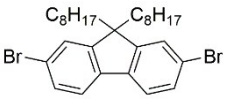
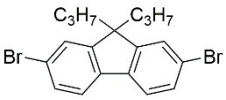
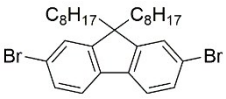
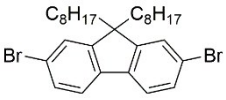
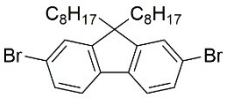
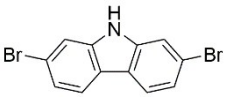
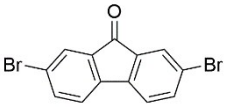
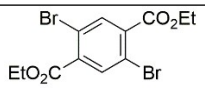
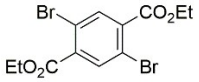
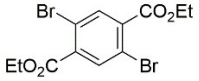
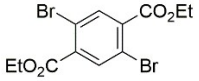
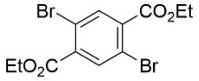
Acceptor	Commercially available starting material of acceptor core	NSS	Ref.
Cz-RH		4	36
Flu-RH		3	36
F(DPP)$_2$B$_2$		2	37
FBR		3	38
DICTF		4	40
FDICTF		8	41
CBM		6	42
SF-OR		3	43
H1		2	44

Table S2 Summary of the synthetic details of the various IDT and IDTT based NFAs.

Acceptor	Commercially available starting material of acceptor core	NSS	Ref.
IEIC		6	45,46
IEICO		6	47
IDSe-T-IC		6	48
O-IDTBR		10	49, 50
EH-IDTBR		10	49,51

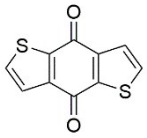
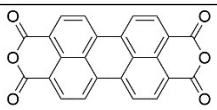
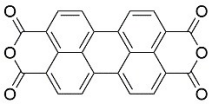
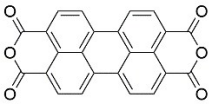
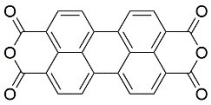
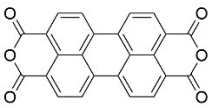
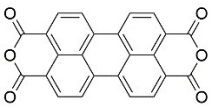
IDT-2BR		6	52,53
IDT-2BR1		10	54
ATT-1		10	55
ITIC		5	56,57,62
ITIC-Th		5	58,60
IC-C6IDT-IC		7	61
IT-M		5	62
IT-DM		5	62
IT-4F		5	64
m-ITIC		5	66
BT-IC		7	67

Table S3 Summary of the synthetic details of the various monomeric and dimeric PDI NFAs.

Acceptor	Commercially available starting material of acceptor core	NSS	Ref.
PDI		1	73,74
TP		4	75
H-di-PDI		4	76
s-diPBI		3	77-79
SdiPBI-S		5	80
SdiPBI-Se		5	81

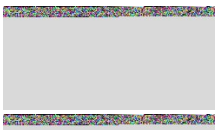
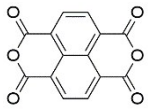
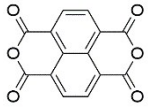
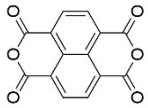
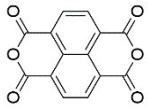
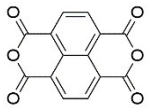
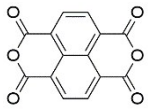
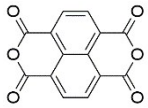
Helical PDI 1		4	82
Bis-PDI-T-EG		4	83-85
Bis-PDI-T-BuO		4	86
FPDI-T		4	87
FITP		4	88
SF-PDI$_2$		3	89,90

Table S4 Summary of the synthetic details of the various trimeric and tetrameric PDI NFAs.

Acceptor	Commercially available starting material of acceptor core	NSS	Ref.
S(TPA-PDI)		4	91
B(PDI)$_3$		3	92
TPH		4	93
TPH-Se		6	93
Ta-PDI		4	94
H-tri-PDI		4	95
hPDI3		7	96
TPE-PDI$_4$		3	97
TPPz-PDI$_4$		3	98

TPB		3	99

Table S5 Summary of the synthetic details of the various polymeric NFAs.

Acceptor	Commercially available starting material of acceptor core	NSS	Ref.
P(NDI2OD-T2)		3	102-107
P(NDI2HD-T2)		3	108
P(NDI2TOD-T2)		3	109
P(NDI2DT-FT2)		3	110
P(NDI2HD-T)		3	111
PNDIS-HD		3	112,113
P(IDT-NDI)		3	114
P(TP)		3	115
PPDIODT		3	116
PDI-V		3	117
NDP-V		6	118
PFPDI-2T		6	119

PFPDI-2FT		6	119
PNDI-T10		3	120,121

2. OPV Performance Comparison between the Highest Performing Donor:NFA and Donor:Fullerene Blends

Table S6 Summary of the J-V characteristics of the highest performing donor:NFA and donor:fullerene blends employing different donors in bulk heterojunction solar cells.

Acceptor	Donor	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF	PCE (%)[c]	Ref.
O-IDTBR	P3HT	0.73	14.10	0.62	6.38	49
$PC_{70}BM$	P3HT	0.61	10.6	0.61	4.37	S1
ATT-1	PTB7-Th	0.87	16.48	0.70	10.07	55
$PC_{70}BM$	PTB7-Th	0.82	19.1	0.69	10.8	S2
EH-IDTBR	Pff4TBT-2DT	1.02	17.20	0.63	11.09	51
$PC_{60}BM$	Pff4TBT-2DT	0.76	16.0	0.62	7.50	S3
30PDI	PBDTTT-C-T	0.79	18.55	0.45	6.29	122
$PC_{70}BM$	PBDTTT-C-T	0.77	17.7	0.67	9.13	S4
ITIC-Th	PDBT-T1	0.88	16.24	0.67	9.60	58
$PC_{70}BM$	PDBT-T1	0.92	14.1	0.75	9.7	S5
IT-M	PBDB-T	0.94	17.44	0.74	12.05	62
$PC_{70}BM$	PBDB-T	0.84	14.19	0.66	7.86	S6
IDSe-T-IC	J51	0.91	15.20	0.62	8.58	48
$PC_{70}BM$	J51	0.75	11.90	0.67	6.00	S7

To exemplify the great strides made by NFAs, eventually leading to them overtaking the best performing fullerene devices, the PCEs of the best performing donor:NFA devices were compared with the corresponding fullerene blends where possible, as displayed in table S6. In more than half of the cases presented, the donor:acceptor blends employing an NFA as the electron acceptor outperformed the fullerene analogue by >40%. Unsurprisingly, in the majority of these cases the polymer donor used was either a medium or wide bandgap material (1.8-2.0 eV), thereby allowing for a greater spectral coverage with the low bandgap NFAs (1.52-1.68 eV). This in turn was reflected by the superior J_{SC} of these devices compared to the fullerene ones. Nonetheless, as shown by the example of Pff4TBT-2DT:**EH-IDTBR** *c.f.* Pff4TBT-2DT:**$PC_{70}BM$**, NFAs can also afford improved PCEs, compared tofullerenes, when blended with a low-bandgap polymer donor (E_g PffBT4T-2DT = 1.65 eV). NFAs thus offer a greater flexibility and can be paired with a greater range of donor polymers than fullerenes, which generally require a low bandgap donor to compensate for their poor optical properties. In the few cases were fullerene-containing devices able to achieve superior PCEs than their NFA counterparts, the fullerene acceptors were only able to significantly (>10%) outperform their NFA counterpart once, thus suggesting that the NFA molecular engineering advances over the past decade ultimately led to a scenario where fullerenes are no longer the state-of-the-art electron acceptors. Another interesting finding in table S6 was that out of the seven highest donor:NFA cases reported, six utilised a NFA based on either an IDT or IDTT core therefore highlighting the relative superiority of these NFAs, in comparison to other classes of acceptors. The pre-eminence of this NFA class is perhaps all the more surprising, considering the relative novelty of the IDT/IDTT core in NFAs, with the first report of an IDT acceptor dating back to 2015. The prospect for even higher efficiencies seems inevitable as more research groups are devoted towards expanding the library of IDT based NFAs, though as pointed out above, addressing issues of stability and industrial viability must be addressed in addition to chasing greater PCE values.

3. References

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