## Supporting information

Non-fullerene acceptors based on fused-ring oligomers for efficient polymer solar cells *via* complementary lightabsorption

Renlong Li, Gongchu Liu, Manjun Xiao, Xiye Yang, Xiang Liu, Zhenfeng Wang, Lei Ying\*, Fei Huang\* and Yong Cao Institute of Polymer Optoelectronic Materials and Devices, State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou 510640, P. R. China. \*E-mail: <u>msleiying@scut.edu.cn</u>, E-mail: <u>msfhuang@scut.edu.cn</u>



Fig. S1 The TG curve of the two acceptors IDT-N and IDT-T-N.



**Fig. S2** UV-vis absorption spectra of the acceptors (IDT-N and IDT-T-N) and donors (PTB7-Th and PBDB-T) in the film states.



**Fig. S3** UV-vis absorption coefficient spectra of the two acceptors in chloroform solution (a) and in the film state (b).

Acceptors	Solution $\lambda_{\text{max}}$ (nm)	ε (10 <sup>5</sup> M <sup>-1</sup> cm <sup>-1</sup> )	Film $\lambda_{max}$ (nm)	ε (10 <sup>5</sup> cm <sup>-1</sup> )
IDT-N	687	1.53	727	1.49
IDT-T-N	734	1.03	755	0.76

**Table. S1**UV-vis absorption coefficient of the two acceptors in chloroform solution and in thefilm state.



Fig. S4 UV-vis absorption coefficient spectra of the four acceptors in the film state

Acceptors	Film $\lambda_{max}$ (nm)	ε (10 <sup>5</sup> cm <sup>-1</sup> )
IDT-N	727	1.49
IDT-T-N	755	0.76
IDT-IC	684	1.01
IEIC	715	0.62

**Table. S2**UV-vis absorption coefficient of the four acceptors in the film state.



**Fig. S5**  $J^{1/2}$ -V characteristics of electron only for IDT-N and IDT-T-N neat films from SCLC.

**Table S3** Photovoltaic properties of the PSCs based on PTB7-Th or PBDB-T as donors and IDT-Nas the acceptor under AM 1.5 G at 100 mW cm $^{-2}$ .

Active layer	D:A (w/w)	Additive (v/v)	V <sub>oc</sub> (V)	<i>J<sub>sc</sub></i> (mA cm <sup>-2</sup> )	FF (%)	PCE (%)
PTB7-Th:IDT-N	1:1	w/o	0.73	13.02	57.70	5.45
PBDB-T:IDT-N	1:1	w/o	0.78	14.89	59.12	6.88
PBDB-T:IDT-N	1:1	0.25 % DIO	0.71	15.91	73.42	8.25
PBDB-T:IDT-N	1:1	0.5 % DIO	0.75	10.49	66.46	5.21
PBDB-T:IDT-N	1:1.5	0.25 % DIO	0.71	14.58	70.54	7.31
PBDB-T:IDT-N	1.5:1	0.25 % DIO	0.72	16.50	70.37	8.42
PBDB-T:IDT-N	2:1	0.25 % DIO	0.72	16.83	69.38	8.46
PBDB-T:IDT-N	1:1	0.25 % CN	0.79	15.88	71.91	8.99
PBDB-T:IDT-N	2:1	0.25 % CN	0.78	16.00	69.49	8.70
PBDB-T:IDT-N	1:1	0.5 % CN	0.80	13.03	68.1	7.64

Active layer	D:A (w/w)	CN additive	$V_{OC}$ (V)	<i>J<sub>sc</sub></i> (mA cm <sup>-2</sup> )	FF (%)	PCE (%)
PTB7-Th:IDT-T-	1:1	w/o	0.84	12.75	38.99	4.18
Ν						
PTB7-Th:IDT-T-	1:1	2 %	0.87	14.67	51.38	6.55
Ν						
PBDB-T:IDT-T-N	1:1	w/o	0.92	12.97	44.79	5.35
PBDB-T:IDT-T-N	1:1	1 %	0.92	14.08	48.30	6.28
PBDB-T:IDT-T-N	1:1	2 %	0.94	14.03	56.11	7.42
PBDB-T:IDT-T-N	1:1	2.5 %	0.95	13.67	50.83	6.60
PBDB-T:IDT-T-N	2:1	2 %	0.97	10.37	46.76	4.70
PBDB-T:IDT-T-N	1:2	2 %	0.93	10.31	40.81	3.91

**Table S4**Photovoltaic properties of the PSCs based on PTB7-Th or PBDB-T as donors and IDT-T-N as the acceptor under AM 1.5 G at 100 mW cm $^{-2}$ .

**Table S5**Photovoltaic parameters of the PSCs based on PBDB-T as donor and IDT-IC or IEIC asacceptors under AM 1.5 G illumination at 100 mW cm<sup>-2</sup>.

Active layer	D:A (w/w)	CN additive	V <sub>oc</sub> (V)	J <sub>sc</sub> (mA cm⁻²)	FF (%)	PCE (%)
PBDB-T:IDT-IC	1:1	w/o	0.82	11.88	58.39	5.7
PBDB-T:IDT-IC	1:1	0.25 %	0.83	12.41	65.41	6.8
PBDB-T:IEIC	1:1	w/o	0.95	11.31	36.44	3.9
PBDB-T:IEIC	1:1	2 %	1.00	12.76	54.18	6.9



**Fig. S6** AFM height images  $(1 \times 1 \mu m)$  of PBDB-T:IDT-N (a, without CN; c, with 0.25% CN) and PBDB-T:IDT-T-N (b, without CN; d, with 2% CN) blend films.



**Fig. S7** TEM images of PBDB-T:IDT-N (a, without CN; c, with 0.25% CN) and PBDB-T:IDT-T-N (b, without CN; d, with 2% CN).



**Fig. S8** (a–f) 2D-GIWAXS patterns and (g) line-cut profiles of the in-plane (dash line) and out-ofplane (solid line) direction of neat IDT-N, IDT-T-N, and PBDB-T/IDT-N, PBDB-T/IDT-T-N blend films with and without CN additives.



Fig. S9 <sup>1</sup>H NMR spectrum of 2 solution in CDCl<sub>3</sub>.



Fig. S10 <sup>13</sup>C NMR spectrum of 2 solution in CDCl<sub>3</sub>.



Fig. S11 <sup>1</sup>H NMR spectrum of N solution in CDCl<sub>3</sub>.



Fig. S12 <sup>13</sup>C NMR spectrum of N solution in DMSO.



Fig. S13 <sup>1</sup>H NMR spectrum of IDT-N solution in CDCl<sub>3</sub>.



Fig. S14 <sup>13</sup>C NMR spectrum of IDT-N solution in CDCl<sub>3</sub>.



Fig. S15 Mass (MALDI-TOF) spectrum of IDT-N.



Fig. S16 <sup>1</sup>H NMR spectrum of IDT-T-N solution in CDCl<sub>3</sub>.



Fig. S17 <sup>13</sup>C NMR spectrum of IDT-T-N solution in CDCl<sub>3</sub>.



Fig. S18 Mass (MALDI-TOF) spectrum of IDT-T-N.