

Electronic Supplementary Information for:

**Nonfullerene acceptors based on extended fused rings flanked with
benzothiadiazolymethylenemalononitrile for polymer solar cells**

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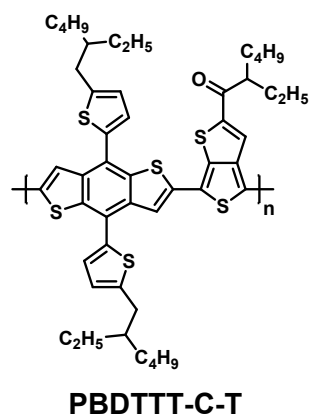


Fig. S1 Chemical structure of PBDTTT-C-T.

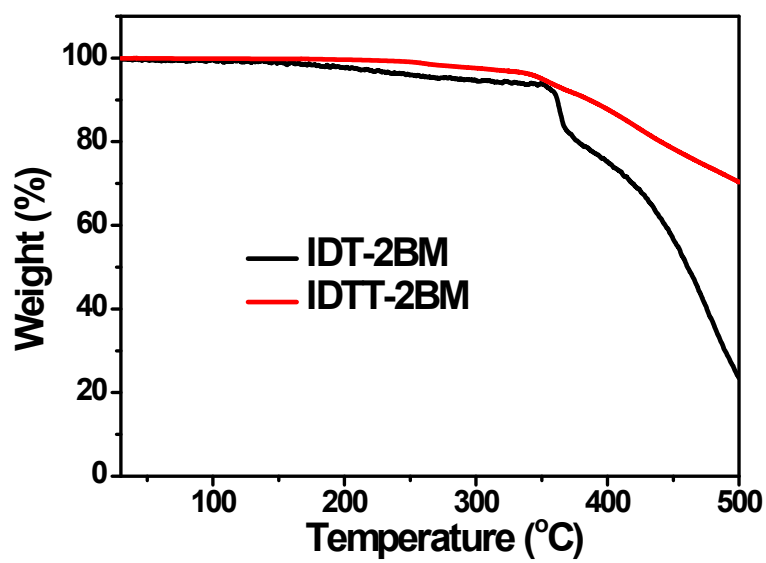


Fig. S2 TGA curves of IDT-2BM and IDTT-2BM.

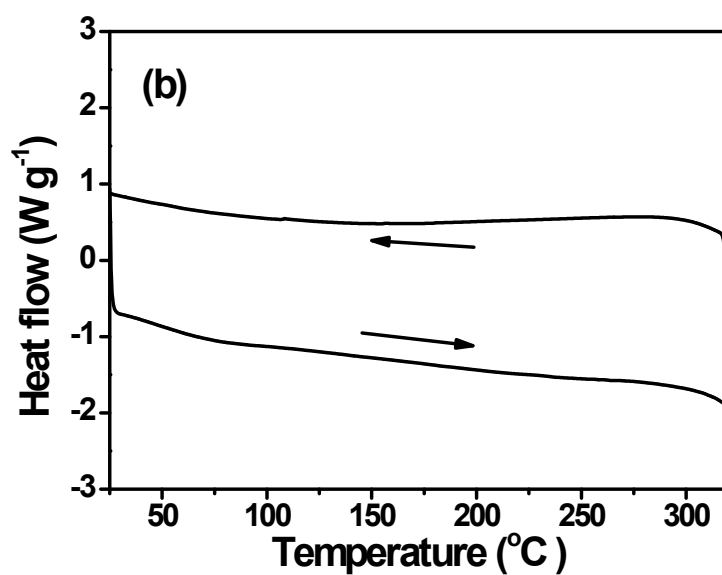
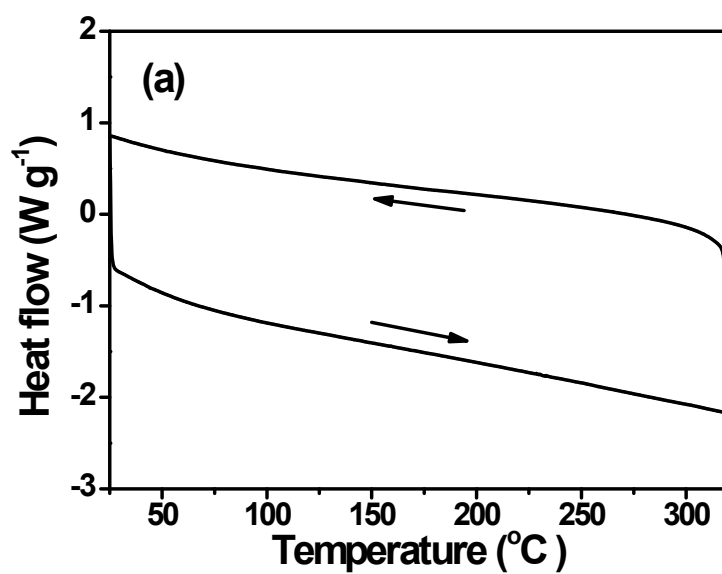


Fig. S3 DSC curves of (a) IDT-2BM and (b) IDTT-2BM.

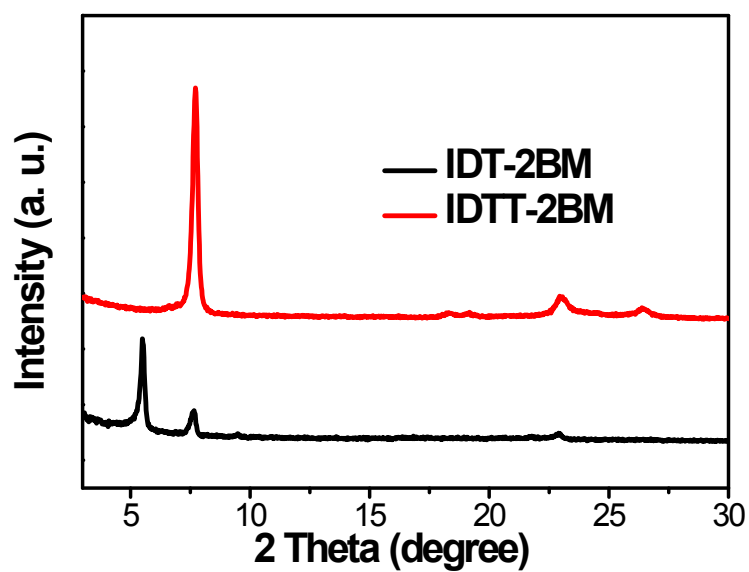


Fig. S4 XRD patterns of pristine IDT-2BM and IDTT-2BM films on SiO₂/Si substrate.

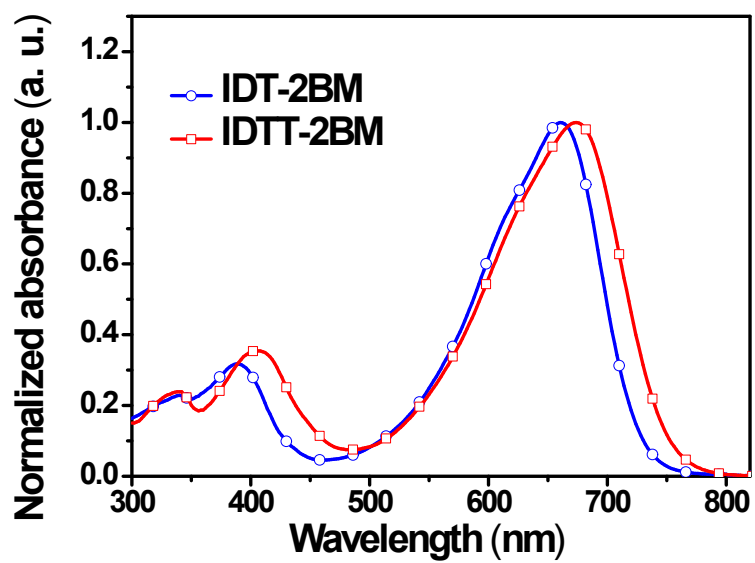


Fig. S5 Absorption spectra of IDT-2BM and IDTT-2BM in chloroform solution.

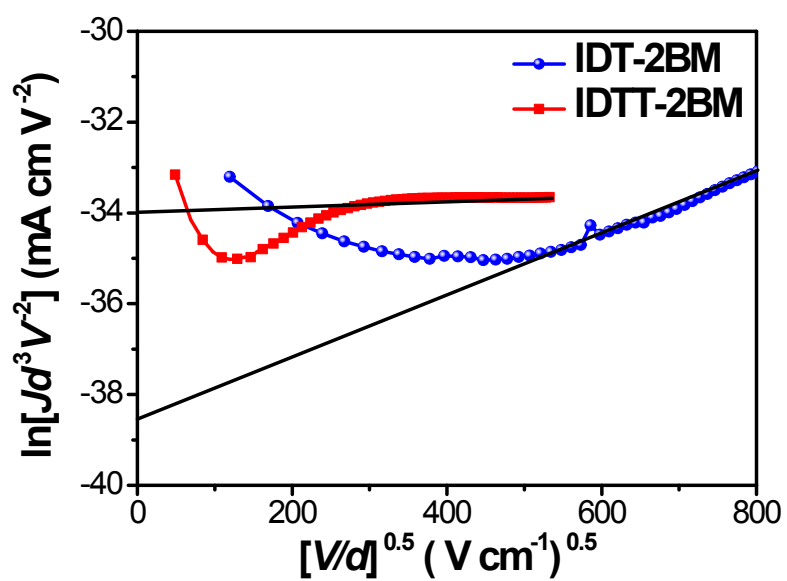


Fig. S6 J - V characteristics for electron-only devices based on pristine IDT-2BM and IDTT-2BM films.

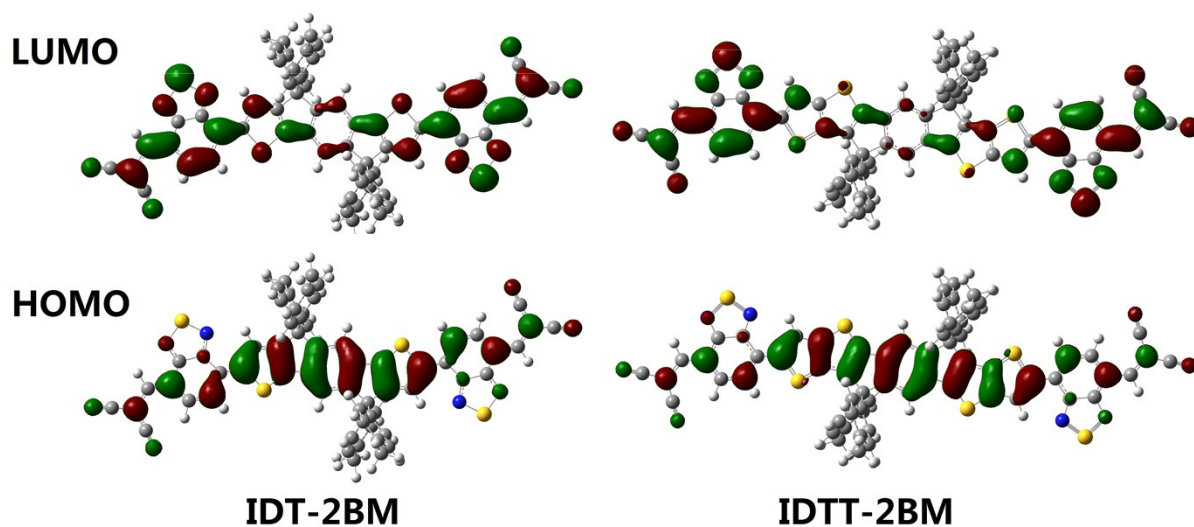


Fig. S7 Theoretically calculated molecular orbitals of IDT-2BM and IDTT-2BM. The alkyl chains are replaced with methyl groups for computational simplicity.

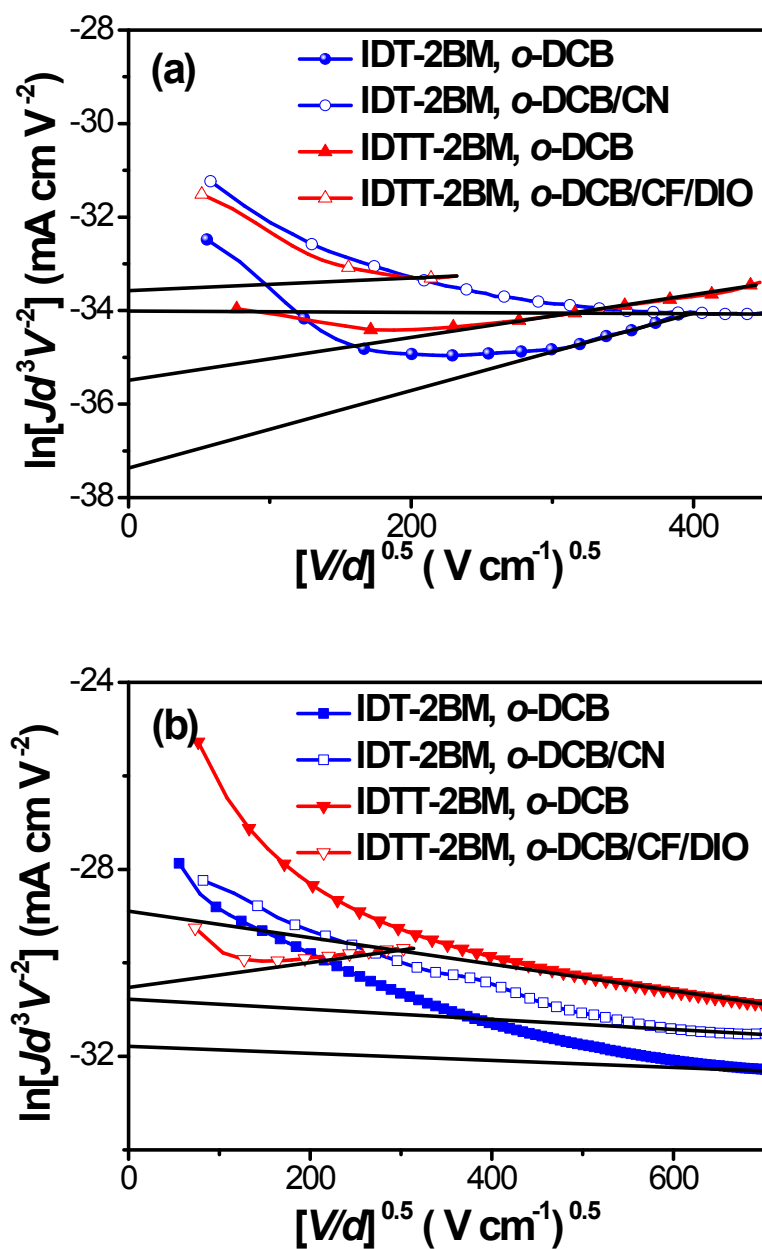


Fig. S8 J - V characteristics for (a) electron-only and (b) hole-only devices based on PBDTTT-C-T: IDT-2BM or IDTT-2BM (1.5: 1, w/w) blend films prepared with different conditions.

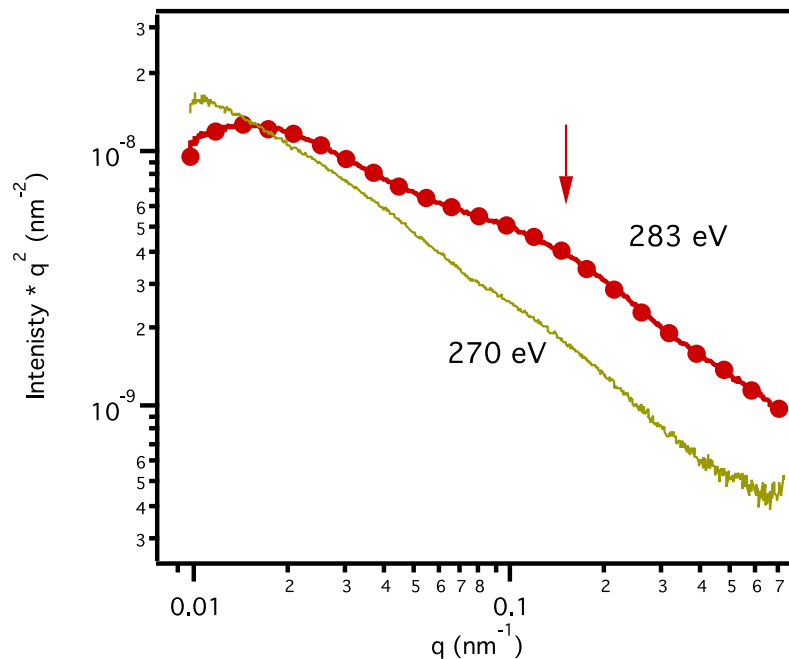


Fig. S9 R-SoXS profiles of PBDTTT-C-T: IDTT-2BM processed with *o*-DCB/CF/DIO with the energy of 270 and 283 eV. Before the absorption edge 270 eV, the mass-contrast dominates the scattering. At 283 eV, the contrast between PBDTTT-C-T and IDTT-2BM is enhanced and the phase separation is detected with peak near $q=0.1-0.2 \text{ nm}^{-1}$.

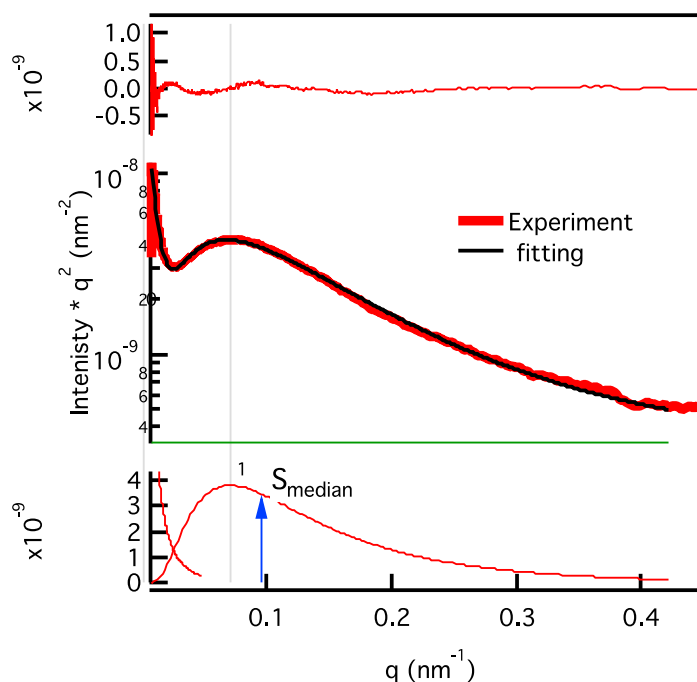


Fig. S10 The fitting of the R-SoXS (PBDTTT-C-T: IDT-2BM processed with CN) with log-normal distribution.

Table S1. Photovoltaic parameters of the OSCs (processed with *o*-DCB solution) based on PBDTTT-C-T: acceptor with different weight ratios under the illumination of AM1.5G, 100 mW cm⁻².

acceptor	D/A ratio (w/w)	V_{oc}^a (V)	J_{sc}^a (mA cm ⁻²)	FF ^a (%)	PCE ^a (%)
IDT-2BM	1: 1.5	0.765 ± 0.003	8.80 ± 0.15	45.5 ± 0.4	3.07 ± 0.08
		(0.769)	(8.97)	(46.0)	(3.17)
	1: 1	0.764 ± 0.003	9.18 ± 0.17	45.7 ± 0.4	3.29 ± 0.09
		(0.768)	(9.38)	(47.2)	(3.40)
	1.5: 1	0.762 ± 0.003	10.63 ± 0.18	45.2 ± 0.4	3.67 ± 0.12
		(0.766)	(10.85)	(45.6)	(3.79)
IDTT-2BM	2: 1	0.766 ± 0.004	7.86 ± 0.18	31.4 ± 0.2	1.89 ± 0.07
		(0.771)	(8.08)	(31.6)	(1.97)
	1.5: 1	0.771 ± 0.002	6.92 ± 0.09	38.1 ± 0.2	2.01 ± 0.06
		(0.773)	(7.03)	(38.5)	(2.09)
	1: 1	0.738 ± 0.006	4.77 ± 0.06	33.9 ± 0.2	1.20 ± 0.03
		(0.747)	(4.83)	(34.1)	(1.23)
	1: 1.5	0.751 ± 0.005	3.77 ± 0.04	34.5 ± 0.2	0.95 ± 0.04
		(0.758)	(3.82)	(34.5)	(1.00)

^a The performance of the best device is given in parentheses and the average PCE was obtained from over 20 devices.

Table S2. SCLC data of hole-only and electron-only devices based on PBDTTT-C-T: acceptor (1.5: 1, w/w) blended films.

acceptor	solution	μ_h ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$) ^c	μ_e ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$) ^c	μ_h/μ_e
IDT-2BM	<i>o</i> -DCB	$(8.3 \pm 0.4) \times 10^{-5}$	$(5.0 \pm 0.2) \times 10^{-7}$	166
	<i>o</i> -DCB/CN ^a	$(2.5 \pm 0.1) \times 10^{-4}$	$(1.0 \pm 0.1) \times 10^{-5}$	25
IDTT-2BM	<i>o</i> -DCB	$(1.7 \pm 0.1) \times 10^{-3}$	$(2.8 \pm 0.1) \times 10^{-6}$	607
	<i>o</i> -DCB/CF/DIO ^b	$(4.1 \pm 0.2) \times 10^{-4}$	$(1.3 \pm 0.1) \times 10^{-5}$	32

^a *o*-DCB/CN = 100: 6 (v/v); ^b *o*-DCB/CF/DIO = 60: 40: 3 (v/v). ^c These mobilities were obtained from over 10 devices.