Supporting Information

High-Efficiency Ternary Nonfullerene Polymer Solar Cells with Reduced Nonradiative Energy Loss and Increased Phase Purity

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Experimental Section

Materials and Instruments: PBDB-T and IDT-EDOT were synthesized following the methods in our previous work, The ZnO solution was used to make the cathode butter layers. $PC_{71}BM$ was purchased from Solarmer Materials Inc. Unless otherwise stated, all the chemicals were commercially available products and were used as received. UV-visible absorption spectra were obtained on a PerkinElmer UV-vis spectrometer model Lambda 750. Atomic force microscopy (AFM) measurements were performed under ambient conditions using a Digital Instrument Multimode Nanoscope IIIA in the tapping mode. Transmission electron microscopy (TEM) images were obtained with a FEI Technai TF20 (Philip) transmission electron microscopy. The thickness of the blend films was determined by a Dektak 6 M surface profilometer.

Fabrication and Characterization of PSCs: The device architecture was ITO/ZnO (30 nm)/active layer (100 nm)/MoO_3 (85 Å)/Ag (100 nm) for solar cells. Precleaned ITO substrates were treated by UV-ozone for 30 min. A thin layer of ZnO was spin-

coated on top of the precleaned ITO substrates at 3500 rpm for 15 s and annealed at 200 °C for 20 min on a hotplate before being transferred into a glove box. The binary and ternary blend films keep the same optimal donor/receptor weight ratio of 1:1.2 (the two acceptors were mixed with different ratios to fabricate the ternary PSCs) with polymer concentration of 5 mg/mL in the 1,2-dichlorobenzene solution (without any additives), then spin-coated at 1500 rpm for 40 s to obtain a film thickness of 100 nm on the top of ITO/ZnO layer. Finally, to complete the devices, the top electrode was thermally evaporated with an 8.5 nm MoO_3 layer and followed by a 100 nm Ag film at a vacuum pressure below 10^{-7} Torr. Cells were fabricated on the substrate with an effective area of 0.04 cm^2. The measurement of the devices was conducted in a glove box without encapsulation. The temperature while measuring the *J–V* curves was approximately 25 °C. The characteristics of the solar cells were statistically analysed by testing over 6 cells. J_{sc} values integrated from the EQE curves agreed well with those obtained from *J–V* tests (within 5% mismatch). The *J–V* curves were measured under AM 1.5G illumination at 100 mW cm^{-2} using an class AAA solar simulator (XES-70S1, SAN-EI Electric Co., Ltd) calibrated with a standard photovoltaic cell equipped with a KG5 filter (certificated by the National Institute of Metrology) and a Keithley 2400 source-measure unit. The EQE data were obtained using a solar cell spectral response measurement system (QER3011, Enli Technology Co. Ltd), and the intensity was calibrated with a standard single-crystal Si photovoltaic cell.

Grazing Incidence Wide-Angle X-ray Scattering (GIWAXS) Characterization: GIWAXS measurements were performed at beamline 7.3.3 at the Advanced Light Source. Samples were prepared on Si substrates using identical blend solutions as those used in devices. The 10 keV X-ray beam was incident at a grazing angle of 0.12°-0.16°, selected to maximize the scattering intensity from the samples. The scattered x-rays were detected using a Dectris Pilatus 2M photon counting detector.

Resonant Soft X-ray Scattering (RSoXS): RSoXS transmission measurements were

performed at beamline 11.0.1.2 at the Advanced Light Source (ALS). Samples for R-SoXS measurements were prepared on a PSS modified Si substrate under the same conditions as those used for device fabrication, and then transferred by floating in water to a 1.5 mm × 1.5 mm, 100 nm thick Si_3N_4 membrane supported by a 5 mm × 5 mm, 200 μm thick Si frame (Norcada Inc.). 2-D scattering patterns were collected on an in-vacuum CCD camera (Princeton Instrument PI-MTE). The sample detector distance was calibrated from diffraction peaks of a triblock copolymer poly(isoprene-b-styrene-b-2-vinyl pyridine), which has a known spacing of 391 Å. The beam size at the sample is approximately 100 μm by 200 μm.

Charge Mobility Measurements:

Space-charge-limited-current (SCLC) measurements were carried out using a Keithley 236 source/measure unit. Electron-only devices were constructed in the architecture ITO/ZnO/active layer/Al, while hole-only devices were constructed in the architecture ITO/PEDOT:PSS/active layer/Ag. A numerical solver was used fit the data using the drift-diffusion model. Trap densities, characteristic trap energies, mobility and injection barriers were allowed to vary. Active layer thicknesses were measured using a Dektak profilometer, and were found to be 100 nm for PBDB-T:IDT-EDOT, PBDB-T:IDT-EDOT:$PC_{71}BM$ and PBDB-T:$PC_{71}BM$ for electron-only and hole-only measurements.

Table S1 Photovoltaic parameters of the OSCs with PBDB-T:IDT-EDOT=1:0.5/1:0.8/1:1.2/1:1.5/1:2.

PBDB-T:IDT-EDOT	V_{oc}(V)	J_{sc}(mA/cm^2)	FF(%)	PCE (%)
1:0.5	0.91	15.12	50.95	7.02
1:0.8	0.89	15.80	56.54	8.01

1:1.2	0.87	18.42	62.34	9.93
1:1.5	0.87	18.91	58.74	9.67
1:2	0.87	17.73	56.82	8.75

Table S2 Photovoltaic parameter of PBDB-T:IDT-EDOT:$PC_{71}BM$=1:0.6:0.6 based devices with DIO additives.

Additive (DIO%)	V_{oc}(V)	J_{sc}(mA/cm^2)	FF(%)	PCE (%)
0.1	0.86	19.55	62.33	10.60
0.2	0.87	19.00	66.80	11.08
0.3	0.86	19.66	62.15	10.51
0.4	0.87	18.74	63.56	10.36
0.5	0.85	18.33	51.87	8.10

Table S3 Photovoltaic parameter of PBDB-T:IDT-EDOT:$PC_{71}BM$=1:0.6:0.6 based devices with o-chlorobenzaldehyde (CBA) additives.

Additive (CBA%)	V_{oc}(V)	J_{sc}(mA/cm^2)	FF(%)	PCE (%)
0.1	0.86	18.60	59.45	9.53
0.2	0.86	20.73	65.46	11.72
0.3	0.86	20.13	66.48	11.48
0.4	0.86	19.65	65.32	11.10
0.5	0.86	19.36	64.82	10.82

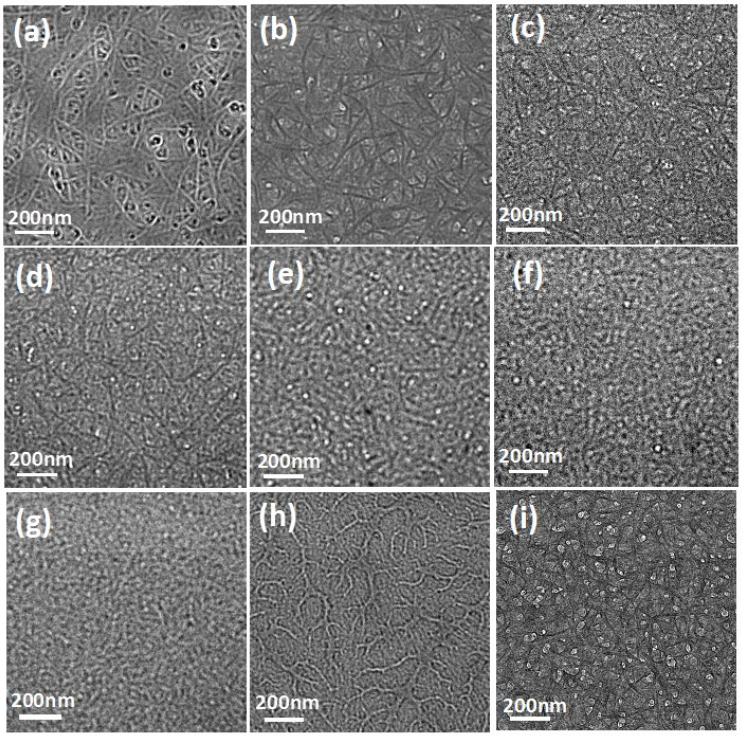
Table S4 The photovoltaic parameters of the PBDB-T:IDT-EDOT:$PC_{71}BM$=1:0.6:0.6 based devices with different active-layer rotate speed.

rotate speed	V_{oc}(V)	J_{sc}(mA/cm^2)	FF(%)	PCE (%)
900	0.85	18.44	60.08	9.45
1100	0.85	19.40	63.17	10.53
1300	0.86	20.09	64.69	11.23
1500	0.88	20.84	66.7	12.07

1700	0.87	20.18	65.01	11.36
1900	0.86	19.80	65.49	11.20
2100	0.86	19.75	66.20	11.36
2300	0.87	19.73	65.63	11.29
2500	0.87	18.51	66.37	10.65

Table S5. Photovoltaic parameters of the OSCs with different weight ratio of $PC_{61}BM$.

PBDB-T:A1:A2	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
1:1.2:0	0.87	18.42	62.34	9.93
1:1:0.2	0.89	17.35	59.54	9.22
1:0.8:0.4	0.89	17.20	58.78	9.07
1:0.6:0.6	0.90	16.55	61.23	9.12
1:0.4:0.8	0.91	15.63	60.18	8.53
1:0.2:1	0.91	14.21	63.79	8.23
1:0:1.2	0.88	10.88	67.34	6.50



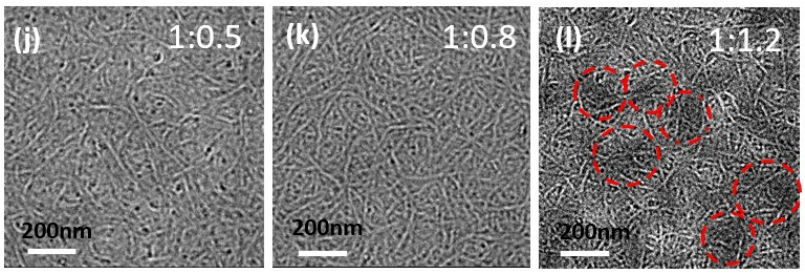


Fig. S1 (a)-(g) TEM images of the devices in D/A ratio of 1:1.2 (w/w) with different proportions of $PC_{71}BM$; (h) the pristine PBDB-T film; (i) the bottom panels of PBDB-T:IDT-EDOT blend film by washing with dichloromethane, (j)-(m) (f) blend film with PBDB-T:IDT-EDOT=1:0.2/1:0.5/1:0.8/1:1.2, respectively.

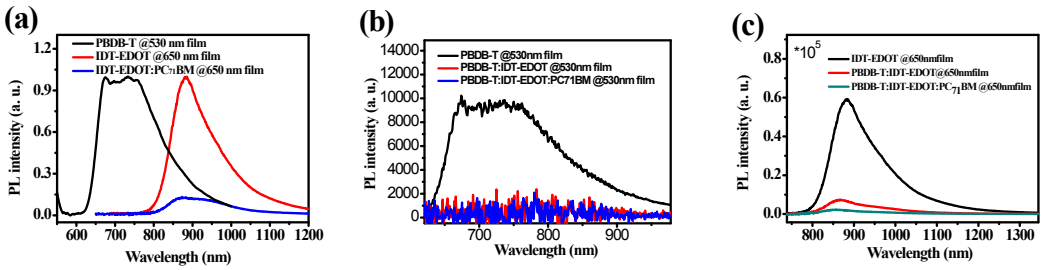


Fig. S2 (a) PL spectra of the neat PBDB-T and IDT-EDOT films and the IDT-EDOT:$PC_{71}BM$ blend film. (b) and (c) Photoluminescence spectra of neat acceptor IDT-EDOT and blend film PBDB-T:IDT-EDOT and PBDB-T:IDT-EDOT:$PC_{71}BM$ excitation at 530 nm and excitation at 650 nm.

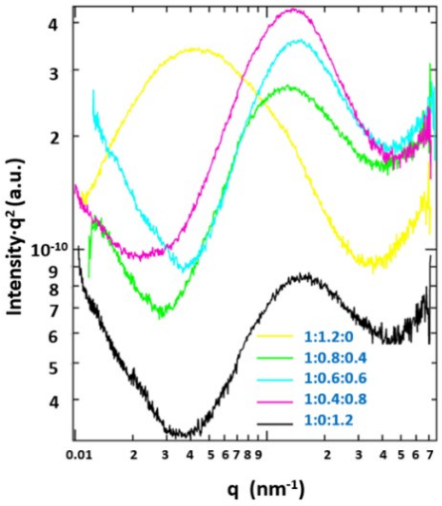


Fig. S3 R-SoXS profiles of blend films based on PBDB-T:IDT-EDOT:$PC_{71}BM$ with different ratios of IDT-EDOT:$PC_{71}BM$.

Table S6 Summary of the crystal coherence length of neat polymer films

PBDB-T:IDT-EDOT:$PC_{71}BM$	d-spacing(100)	FWHM	CCL (nm)
1:1.2:0	21.53	0.034	16.76
1:1:0.2:	21.47	0.038	14.90
1:0.8:0.4	21.47	0.035	15.93
1:0.6:0.6	21.39	0.036	15.51
1:0.4:0.8	21.30	0.037	15.40
1:0.2:1	21.01	0.041	13.69
1:0:1.2	20.75	0.040	14.15
1:0:0	21.37	0.049	11.45
0:1:0	19.93	0.035	16.23

Table S7 Summary of the domain size and domain purity

PBDB-T:IDT-EDOT:$PC_{71}BM$	domain size (Å)	domain purity
1:1.2:0	74.41	0.77
1:0.8:0.4	24.19	0.90
1:0.6:0.6	21.63	1.00
1:0.4:0.8	23.54	1.00
1:0:1.2	20.27	0.52

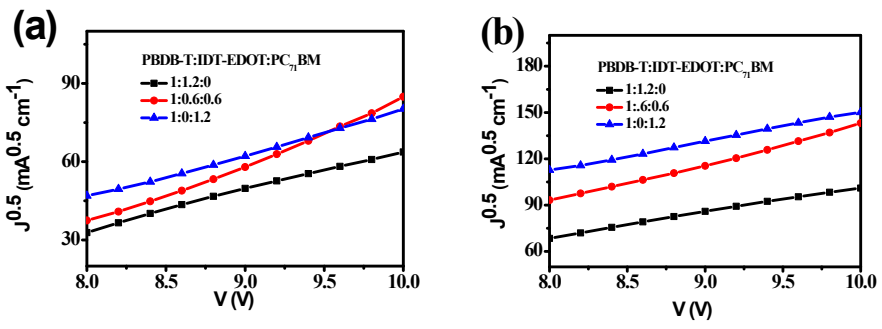


Fig S4 SCLC method for determine electron and hole mobilities based on electron-only (a) and hole-only (b) devices using PBDB-T:IDT-EDOT:$PC_{71}BM$ as the active layer with various IDT-EDOT:$PC_{71}BM$ ratios.

Table S8 Hole and electron mobilities of devices.

PBDB-T:IDT-EDOT:$PC_{71}BM$	μ_e[cm^2 $V^{-1}s^{-1}$]	μ_h[cm^2 $V^{-1}s^{-1}$]	μ_h/μ_e
1:1.2:0	7.77×10^{-5}	9.00×10^{-5}	1.16
1:0.6:0.6	1.18×10^{-4}	2.05×10^{-4}	1.06
1:0:1.2	9.46×10^{-5}	1.25×10^{-4}	1.32