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Electronic Supplementary Information (ESI)

Nonvolatile Morphology Regulator for Enhancing Molecular Order in Active Layer and therefore Power Conversion Efficiency of Polymer Solar Cells.

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Experimental Section

Synthesis of PDI-PC61BM



Scheme S1. Synthesis route of PDI-PC₆₁BM.

Compound (2): Compound $\mathbf{1}^{[s1]}$ (4.0 g, 3.76 mmol), cerium (IV) ammonium nitrate (CAN) (2.47g, 4.51 mmol), nitric acid (4.17 g, 66.17mmol) and dichloromethane (150 mL) were mixed and stirred at 25°C under N₂ for 2h. The mixture was neutralized with 10% KOH and extracted with CH₂Cl₂. After the solvent was removed, the crude product was purified by silica gel column chromatography with CH₂Cl₂ eluent to afford product **2** as red solid (3.99 g, 95 %). ¹H-NMR (500 MHz, CDCl₃): δ =8.74 (d, J = 7.5 Hz, 1H), 8.70-8.63 (m, 4H), 8.55 (d, J= 8.0 Hz, 1H), 8.19 (d, J = 8.0 Hz, 1H), 4.11-4.10 (m, 4H), 1.97 (br, 2H), 1.39-1.19 (m, 80H), 0.85-0.81 (m, 12H).

Compound (3) A mixture of compound **2** (2.0 g, 1.8 mmol) and K₂CO₃ (1.24 mg, 9.0 mmol) in chloroform (60 mL) and 1,4-Butanediol (20 mL) was refluxed for 2 days under nitrogen atmosphere. The reaction mixture was allowed to cool to room temperature, and diluted with water (50 mL). The organic layer was washed with brine (2 x 25 mL) and dried over MgSO₄. The organic solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel, eluting with 12-15 % dichloromethane (DCM) in hexane to yield product **3** (0.6 g, 30 %) as a black solid. ¹H-NMR (500 MHz, CDCl₃): δ =9.49 (d, *J* = 8.5 Hz, 1H), 8.55 (d, *J* = 8.0 Hz, 1H), 8.53 (d, *J* = 8.0 Hz, 1H), 8.48 (s, 2H), 8.42 (d, *J*= 8.0 Hz, 1H), 8.34 (s, 1H), 4.52 ((t, *J* = 6.5 Hz, 2H), 4.10 (d, *J* = 6.5 Hz, 4H), 3.88 (t, *J* = 6.0 Hz, 2H), 2.27-2.21 (m, 2H), 1.97-1.92 (m, 4H), 1.31-1.18 (m, 80H), 0.84-0.80 (m, 12H).

PDI-PC₆₁BM: To a mixture of compound **3** (140 mg, 0.122 mmol), compound $4^{[s2]}$ (100 mg, 0.111 mmol), and 4-(Dimethylamino)pyridine (14 mg, 0.111 mmol) in DCM (5.0 mL) was added with 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (25 μ L, 0.133 mmol) at 0 °C. The reaction mixture was stirred at room temperature overnight. Then, solvent was evaporated under reduced pressure. The residue was partitioned

between water (10 mL) and ethyl acetate (20 mL) phases. After separating the organic layer, the aqueous layer was extracted with ethyl acetate (10 mL). The combined organic layer was dried over MgSO₄, and the solvent was removed under reduced pressure. The crude residue was purified by column chromatography on silica gel with 10-20 % ethyl acetate in hexane **PDI-PC₆₁BM** (101 mg, 44 %) as a brown solid. ¹H-NMR (500 MHz, CDCl₃): δ =9.56 (d, *J* = 8.0 Hz, 1H), 8.68-8.65 (m, 3H), 8.64-8.61 (m, 2H), 8.43 (s, 1H), 7.82 (d, *J*= 7.0 Hz, 2H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.41 (t, *J* = 7.2 Hz, 1H), 4.53 (t, *J* = 6.0 Hz, 2H), 4.23 (t, *J* = 6.0 Hz, 2H), 4.12 (d, *J* = 7.5 Hz, 4H), 2.87 (m, 2H), 2.58 ((t, *J* = 7.0 Hz, 2H), 2.18-2.14 (m, 4H), 2.03-1.98 (m, 4H), 1.40-1.19 (m, 80H), 0.85-0.81 (m, 12H).

General Instrumentations

The thicknesses of the active layers were measured by Tencor P-10 Surface Profiler. UV-vis spectra were measured using a Perkin-Elmer (Lambda 19) UV-vis spectrometer. The current-voltage (*J-V*) curves were measured under nitrogen atmosphere using a Keithley 2400 source-measure unit and an AM 1.5G solar simulator (SAN-EI XES-40S2-CE, 150 W). Illumination intensity of 100 mW/cm² irradiation was calibrated using a standard monocrystal Si reference cell (Oriel 91150V from Newport) for accurate light source intensity. The external quantum efficiency (EQE) data were measured in ambient environment, based on a system (model QE-R) of Enli Technology Co, with a light source from a filtered 150 W xenon lamp (Oriel, U.S.A.); EQE (λ) = 12400 (*J*_{sc}/ $\lambda \phi$) was normalized by the incident radiative flux ϕ (mW/cm²). GIWAXS was measured at the BL 17A endstation of the National Synchrotron Radiation Research Center, Taiwan. AFM topography images were measured by the scanning probe microscopy (Digital Instrument Nanoscope V). Contact angle with water was measured using contact angle meter (GBX DIGIDROP).

Cyclic voltammetry (CV)

Cyclic voltammetry (CV) of thin films of IT-DM coated on the ITO glass electrode by spin-cast from its solution in chlorobenzene was conducted in an electrolyte of 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) dissolved in acetonitrile using ferrocene as the calibration standard.^[S3] The HOMO/LUMO levels of IT-DM and PDI-PC₆₁BM were determined by cyclic voltammetry (CV) and calibrated with the ferrocene along with absorption onset are -5.47 eV/-3.78 eV and -5.88 eV/-3.86 eV for IT-DM and PDI-PC₆₁BM, respectively. For PDI-PC₆₁BM, the oxidation onset of PDI^[S4] and PC₆₁BM^[S5] are very closed, therefore, it is hard to distinguish the oxidation peak individually on PDI-PC₆₁BM.



Figure S1. Cyclic voltammetry measurement of thin films of (a) IT-DM and (b) $PDI-PC_{61}BM$.

Device fabrication

For the device fabrication, ITO glass was cleaned sequentially with detergent aqueous solution, deionized water, acetone and isopropyl alcohol, followed by treatment with oxygen plasma at a pressure of 1.93*10⁻¹ torr for 5 minutes. A layer of PEDOT:PSS (25 nm) (Clevios AI4083, 1.5 wt% in water) was spin-cast on the treated ITO, and dried for 10 minutes at 140 °C. We use different high boiling point additives

for adjusting the miscibility of PBDB-T and IT-DM, namely, 1-Chloronaphthalene 1-Naphthalenethiol (SH-na),^[S7] (Me-na),^[S8] (Cl-na).^[S6] 1-Methylnaphthalene 1,8-diiodooctane (DIO)^[S9] and diphenyl ether (DPE).^[S10] The device based on DPE additive shows the best PCE. Active layers (about 100 nm) were spin-cast from the blend solutions of PBDB-T:IT-DM (1.5:1 w/w, 20 mg/ml) in chlorobenzene with 0.5 vol% DPE additive onto the PEDOT: PSS layer. The active layers were annealed at 160°C under vacuum (10^{-2} torr) for ten minutes. After cooling, the active layers were treated with methanol vapor annealing for one minute. The PFN-Br (0.5mg/ml) was dissolved in methanol and spin coated on top of the active layer as electron transport layer. Aluminum (100 nm) as the cathode was deposited on the active layer in vacuum thermal evaporator (through a shadow mask and a vacuum pressure lower than $2*10^{-6}$ torr; the active area of a typical device was about 3 mm². After ITO cleaning and PEDOT:PSS spin-casting, devices were fabricated in a glovebox under nitrogen atmosphere.

Experimental data



J–V Characteristics of PBDB-T:IT-DM based Polymer Solar Cells

Figure S2. The *J-V* curve of PBDB-T:IT-DM active layer adding (a) different additives;(b) different volumn ratio of DPE additive.



Figure S3. *J-V* curve of PBDB-T:IT-DM (0.5 vol% DPE) adding different weight ratio of (a) PDI;(b) PC₆₁BM.



Figure S4. (a) The transmittance of different thickness of ITO glass. (b) The J-V curve of PBDB-T:IT-DM (DPE) (2% PDI-PC₆₁BM) fabricated with different thickness of ITO glass.



Table S1. Performance characteristic values of PBDB-T:ITIC (10mg/10mg, 0.5 vol% DIO) with adding different amount of PDI-PC₆₁BM and active layer annealed at 140°C for 10min.

PDI-PC ₆₁ BM	Voc	Jsc	ББ	PCE ^{max}
(wt%)	(V)	(mA/cm^2)	ГГ	(%)
-	0.89	14.32	0.64	8.16
1% PDI-PC ₆₁ BM	0.90	14.73	0.67	8.87
2% PDI-PC ₆₁ BM	0.90	14.76	0.68	8.95
3% PDI-PC ₆₁ BM	0.90	14.43	0.67	8.68



 Table S2. Photovoltaic performances of PBDB-T:IT-DM adding different additives.

Additives	Voc	Jsc	PP	PCE ^{max}	PCE ^{ave}	Rs	Rsh
(1 vol%)	(V)	(mA/cm^2)	ГГ	(%)	(%)	(Ωcm^2)	(Ωcm^2)
-	0.95	15.25	0.66	9.56	9.42	5.37	578
Cl-na	0.94	15.82	0.67	9.96	9.79	4.39	565
SH-na	0.95	15.76	0.65	9.73	9.54	5.46	523
Me-na	0.94	15.83	0.66	9.82	9.65	7.24	992
DIO	0.95	15.94	0.68	10.29	10.02	4.86	645
DPE	0.95	16.18	0.68	10.45	10.32	4.34	626

Additives	Voc	Jsc	PP	PCE ^{max}	PCE ^{ave}	Rs	Rsh
(vol%)	(V)	(mA/cm^2)	FF	(%)	(%)	(Ωcm^2)	(Ωcm^2)
-	0.95	15.25	0.66	9.56	9.42	5.37	578
0.25% DPE	0.95	16.02	0.68	10.35	10.13	6.31	1377
0.5% DPE	0.95	16.23	0.69	10.63	10.41	5.23	1113
1% DPE	0.95	16.18	0.68	10.45	10.32	4.34	626

 Table S3. Photovoltaic performances of PBDB-T:IT-DM adding different volume

 ratio of PDI.

Table S4. Performance characteristic values of PBDB-T:IT-DM (0.5 vol% DPE) with adding different amount of PDI-PC₆₁BM.

PDI-PC ₆₁ BM	Voc	Jsc	EE	PCE ^{max}	PCE ^{ave}	Rs	Rsh
(wt%)	(V)	(mA/cm ²)	ГГ	(%)	(%)	(Ωcm^2)	(Ωcm^2)
-	0.95	16.23	0.69	10.63	10.41	5.23	1113
1% PDI-PC ₆₁ BM	0.95	16.92	0.72	11.57	11.38	4.18	1592
2% PDI-PC ₆₁ BM	0.95	17.11	0.74	12.02	11.62	4.26	2522
3% PDI-PC ₆₁ BM	0.94	16.81	0.71	11.22	10.97	4.32	1060

 Table S5. Photovoltaic performances of PBDB-T:IT-DM (0.5% DPE) adding different

Ternary blend	Voc	Jsc	EE	PCE ^{max}	PCE ^{ave}	Rs	Rsh
(wt%)	(V)	(mA/cm^2)	ГГ	(%)	(%)	(Ωcm^2)	(Ωcm^2)
-	0.95	16.23	0.69	10.63	10.41	5.23	1113
0.5% PDI	0.95	16.63	0.70	11.06	10.82	3.71	944
1% PDI	0.95	16.82	0.71	11.35	11.04	3.79	1126
2% PDI	0.95	16.46	0.69	10.79	10.57	4.81	895

weight ratio of PDI.

Ternary blend	Voc	Jsc		PCE ^{max}	PCE ^{ave}	Rs	Rsh
(wt%)	(V)	(mA/cm ²)	FF	(%)	(%)	(Ωcm^2)	(Ωcm^2)
-	0.95	16.23	0.69	10.63	10.41	5.23	1113
0.5% PC ₆₁ BM	0.94	16.52	0.71	11.03	10.86	4.81	1172
1% PC ₆₁ BM	0.94	16.73	0.71	11.16	10.97	4.54	1274
2% PC ₆₁ BM	0.93	16.56	0.70	10.78	10.63	5.32	1481

Table S6. Photovoltaic performances of PBDB-T:IT-DM (0.5% DPE) adding different weight ratio of $PC_{61}BM$.

Table S7. Photovoltaic performances of PBDB-T:IT-DM (0.5% DPE) with the addition of PDI&PC₆₁BM and PDI-PC₆₁BM.

blend (wt%)	Voc (V)	Jsc (mA/cm ²)	FF	PCE ^{max} (%)	PCE ^{ave} (%)	Rs (Ωcm ²)	Rsh (Ωcm^2)
1% PDI + 1% PCBM	0.95	16.88	0.72	11.55	11.27	3.95	1837
2% PDI-PCBM	0.95	17.11	0.74	12.02	11.62	4.26	2522

Table S8. Photovoltaic performances of PBDB-T:IT-DM (DPE)(2% PDI-PC₆₁BM)fabricated with different thickness of ITO glass.

ITO	Voc (V)	Jsc (mA/cm ²)	FF	PCE ^{max} (%)	PCE ^{ave} (%)
320 nm	0.95	17.11	0.74	12.02	11.62
75 nm	0.95	17.63	0.73	12.23	11.88

Photoluminescence (PL) spectra



Figure S5. The PL spectra of PBDB-T, IT-DM, PBDB-T:IT-DM (0.5 vol% DPE) and PBDB-T:IT-DM (0.5 vol% DPE + 2 wt% PDI-PC₆₁BM).

GIWAXS Measurements

For GIWAXS measurements, the active layers were spin-cast on silicon wafers pre-coated with PEDOT:PSS (also by spin-casting). GIWAXS measurements were performed at the 17A endstation of the National Synchrotron Radiation Research Center (NSRRC) in Taiwan, using MARCCD for GIWAXS area detector. The 10 keV X-ray beam of 0.2 mm diameter was used with a sample incident angle 0.2°; the sample-to-detector distances were 25 cm for GIWAXS.

The two dimensional (2D) GIWAXS patterns shown in **Figure S6** are the PBDB-T:IT-DM active layers processed with different addition of materials (PDI, PC₆₁BM, PDI&PC₆₁BM, PDI-PC₆₁BM). The corresponding correlation lengths (referred as grain sizes for simplicity) were extracted from the peak widths using the Sherrer equation, and summarized in **Table S7**. Scherrer equation^[S11] is $L_{hkl} = 0.9\lambda/(B_{hkl}\cos\theta)$, where L_{hkl} is the correlation length along the (hkl) direction, λ is the wavelength of incident x-ray, B_{hkl} is the full width at half maximum (FWHM) of (hkl) diffraction peak, and $\theta = \sin^{-1}(q\lambda/4\pi)$.



Figure S6. The GIWAXS two dimensional patterns of (a) PBDB-T;(b) ITDM;(c) PBDB-T:IT-DM;(d) PBDB-T:IT-DM (DPE);(e) PBDB-T:IT-DM (DPE) (PDI);(f) PBDB-T:IT-DM (DPE)(PC₆₁BM);(g) PBDB-T:IT-DM (DPE)(PDI&PC₆₁BM);(h) PBDB-T:IT-DM (DPE)(PDI-PC₆₁BM).



Figure S7. GIWAXS one-dimension profiles of PBDB-T:IT-DM adding different materials along (a) in-plane direction; (b) out-of-plane direction; (c) in-plane direction zoomed from q_z =0.22 Å⁻¹ to 1 Å⁻¹;(d) out-of-plane direction zoomed from q_z =0.22 Å⁻¹





Figure S8. The GIWAXS profiles through deconvolution of π - π stacking scattering $(q_z=1.1-2.2 \text{ Å}^{-1})$ of (a) PBDB-T:IT-DM, (b) PBDB-T:IT-DM (DPE), (c) PBDB-T:IT-DM (DPE)(PDI), (d) PBDB-T:IT-DM $(DPE)(PC_{61}BM),$ (e) PBDB-T:IT-DM (DPE)(PDI&PC₆₁BM) (f) PBDB-T:IT-DM and (DPE)(PDI-PC₆₁BM).

	PBI	DB-T	IT-DM		
PDDB-1:11-DM	L(100)(nm)	L(010)(nm)	L(100)(nm)	L(010)(nm)	
Without additive	11.81	1.62	9.46	1.98	
DPE additive	12.62	1.81	10.34	2.08	
DPE + 1% PDI	11.53	1.50	6.19	1.88	
DPE + 1% PCBM	12.51	1.92	12.02	2.13	
DPE + 1% PDI & 1% PCBM	11.08	1.58	8.66	1.93	
DPE + 2%PDI-PCBM	13.91	1.98	12.91	2.37	

Table S9. The correlation length of face-on orientation molecule arrangement ofPBDB-T and IT-DM in the active layer added with different materials.

Contact Angle Measurements



Figure S9. The water contact angle of (a) PBDB-T;(b) IT-DM;(c) PBDB-T:IT:DM (DPE);(d) PBDB-T:IT:DM (DPE)(PDI);(e) PBDB-T:IT:DM (DPE)(PC₆₁BM);(f) PBDB-T:IT:DM (DPE)(PDI&PC₆₁BM);(g) PBDB-T:IT:DM (DPE)(PDI-PC₆₁BM).

Atomic Force Microscopy (AFM) images



Figure S10. AFM tapping mode topological and phase contrast images of PBDB-T:IT-DM (DPE) active layers added with different materials: (a,f) without, (b,g) PDI, (c,h) PC₆₁BM, (d,i) PDI&PC₆₁BM, and (e,j) PDI-PC₆₁BM.

Single Carrier Device with SCLC Analysis

We fabricated the hole-only device with the configuration ITO/PEDOT:PSS/active layer/MoO₃/Al and electron-only device with the configuration ITO/Al/active layer/Al to measure the hole and electron mobilities, respectively. Data are analyzed using the single carrier space-charge-limited-current (SCLC) equation for extracting the related charge mobilities, where SCLC follows the Mott–Gurney Law^[s12] : $J=9\varepsilon\varepsilon0\mu(V-Vbi)^2/8L^3$, where ε_0 is the permittivity of free space, ε is the dielectric constant of the polymer (the dielectric constant ε is taken as 3, which is a typical value for conjugated polymers^[s13]) μ is the carrier mobility, *V* is the applied voltage across device, V_{bi} is the built-in voltage and is taken as zero, and *L* is the thickness of the film.



Figure S11. Current density versus bias voltage with semi-log and double-log scale of (a,c) hole-only devices; (b,d) electron-only devices.

PBDB-T:IT-DM	$\frac{\mu_{hole}}{(cm^2V^{-1}s^{-1})}$	$\mu_{electron}$ (cm ² V ⁻¹ s ⁻¹)	R_{μ} (µelectron/µhole)
0.5 vol% DPE	2.31×10 ⁻⁴	4.01×10 ⁻⁵	0.17
0.5 vol% DPE +2 wt% PDI-PC ₆₁ BM	2.62×10 ⁻⁴	6.57×10 ⁻⁵	0.25

Table S10. The hole and electron mobilities and their ratio $R\mu$ of the active layer PBDB-T:IT-DM (DPE) with the addition of PDI-PC₆₁BM.

J-V Characteristics of PBDB-T:IT-DM PSCs under Various Light Intensities

The fitting of *Jsc* versus *I* with the power law relationship^[S12-13]: *Jsc* $\propto I^{\alpha}$, where $\alpha(\leq 1)$ is ideality factor. This power law relationship describes the charge recombination kinetics at short circuit condition (V=0); as $\alpha=1$, no recombination occurs, and deviation from 1 indicates an extent of charge recombination. For the devices with the PBDB-T:IT-DM (DPE) and PBDB-T:IT-DM (DPE)(PDI-PC₆₁BM), the α values are 0.96 and 0.975, respectively.



Figure S12. The *J-V* curve of (a) PBDB-T:IT-DM and (b) PBDB-T:IT-DM (PDI-PC₆₁BM) as the active layer of the PSC devices measured under different light intensity (from 100 mW/cm² to 2.8 mW/cm²). (c) log-log plot of current density versus irradiation light intensity.

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