Supporting Information for

Semi-Crystalline Photovoltaic Polymers with Efficiency Exceeding 9% in a ~300 nm Thick Conventional Single-Cell Device

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Synthesis of monomers

The intermediates (**1**~**3**) and monomers (**M1**~**M4**) were prepared by modifying the procedures reported previously.[1-3]

4,7-Bis(5-trimethylstannylthiophen-2-yl)-2,1,3-benzothiadiazole (M1). Yield: 90%. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.17 (d, J=3.45 Hz, 2H), 7.87 (s, 2H), 7.29 (d, J=3.45 Hz, 2H), 0.43 (s, 18H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 152.5, 144.9, 140.3, 136.1, 128.2, 125.8, 125.7, -8.14. HRMS (EI): calcd for $C_{20}H_{24}N_2S_3Sn_2$, m/z (M^+) = 627.9146, found: 627.9138.

4,7-Bis(5-trimethylstannylthiophen-2-yl)-5-fluoro-2,1,3-benzothiadiazole (M2). 5-Fluoro-4,7-dibromo-2,1,3-benzothiadiazole (1.0 g, 3.2 mmol), 2-tributylstannylthiophene (3.0 g, 8.0 mmol), tris(dibenzylideneacetone)dipalladium(0) (4 mol%) and tri(*o*-tolyl)phosphine (8 mol%) were added in a 30 mL microwave vial. The vial was sealed and purged with nitrogen. Chlorobenzene (10 mL) was added to the vial. The reaction mixture was heated at 80 °C for 10 min and at 140 °C for 60 min in a microwave reactor. After the reaction was completed, the solvent was removed under reduced pressure and the compound (**2**), 5-fluoro-4,7-di(thiophen-2-yl)-2,1,3-benzothiadiazole, was purified by column chromatography (eluent: hexane/$CHCl_3$ = 1/1). Yield: 95%. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.25 (d, J=3.90 Hz, 1H), 8.12 (dd, J=3.90 Hz, J=1.20 Hz, 1H), 7.78 (d, J=12.90 Hz, 1H), 7.55 (dd, J =5.10 Hz, J=1.20 Hz, 1H), 7.50 (dd, J=5.10 Hz, J=1.20 Hz, 1H), 7.22 (m, 2H). A solution of **2** (0.6 g, 1.9 mmol) in anhydrous tetrahydrofuran (THF, 20 mL) was cooled down to -78 ^{o}C under nitrogen. A solution of lithium diisopropylamide (LDA) was prepared from the reaction of diisopropylamine (0.76 g, 7.5 mmol) and 1.6 M n-BuLi (4.7 mL, 7.5 mmol) in 2 mL THF, which was added to the above solution dropwise. After stirring for 1 h at -78 ^{o}C, 1 M trimethylstannyl chloride (7.5 mL, 7.5 mmol) was added and reacted for another 1 h. The reaction was quenched by addition of water and the organic layer was extracted with ether, washed with brine and dried over anhydrous $MgSO_4$. After the solvent was removed under reduced pressure, the residue was recrystallized from ethanol to give **M2**. Yield: 85%. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.30 (d, J=2.85 Hz, 1H), 8.19 (d, J=3.30 Hz, 1H), 7.79 (d, J=12.90 Hz, 1H), 7.32 (d, J=2.85 Hz, 1H), 7.29 (d, J=3.30 Hz, 1H), 0.43 (s, 18H). HRMS (EI): calcd for $C_{20}H_{23}F_1N_2S_3Sn_2$, m/z ($M^+$) = 645.9051, found: 645.9046.

4,7-Bis(5-trimethylstannylthiophen-2-yl)-5,6-difluoro-2,1,3-benzothiadiazole (M3). Yield: 96%. ^{1}H

NMR (300 MHz, $CDCl_3$): δ (ppm) 8.33 (d, J=3.15 Hz, 2H), 7.35 (d, J=3.15 Hz, 2H), 0.43 (s, 18H). HRMS (EI): calcd for $C_{20}H_{22}F_2N_2S_3Sn_2$, m/z ($M^+$) = 663.8957, found: 663.8944.

1,4-Dibromo-2,5-bis(2-hexyldecyloxy)benzene (M4). Yield: 80%.^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.06 (s, 2H), 3.80 (d, J=5.70 Hz, 4H), 1.77 (m, 2H), 1.54-1.27 (br, 48H), 0.90 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 150.0, 118.0, 110.9, 72.8, 37.8, 31.9, 31.8, 31.2, 30.0, 29.6, 29.5, 29.3, 26.8, 26.7, 22.7, 14.1.

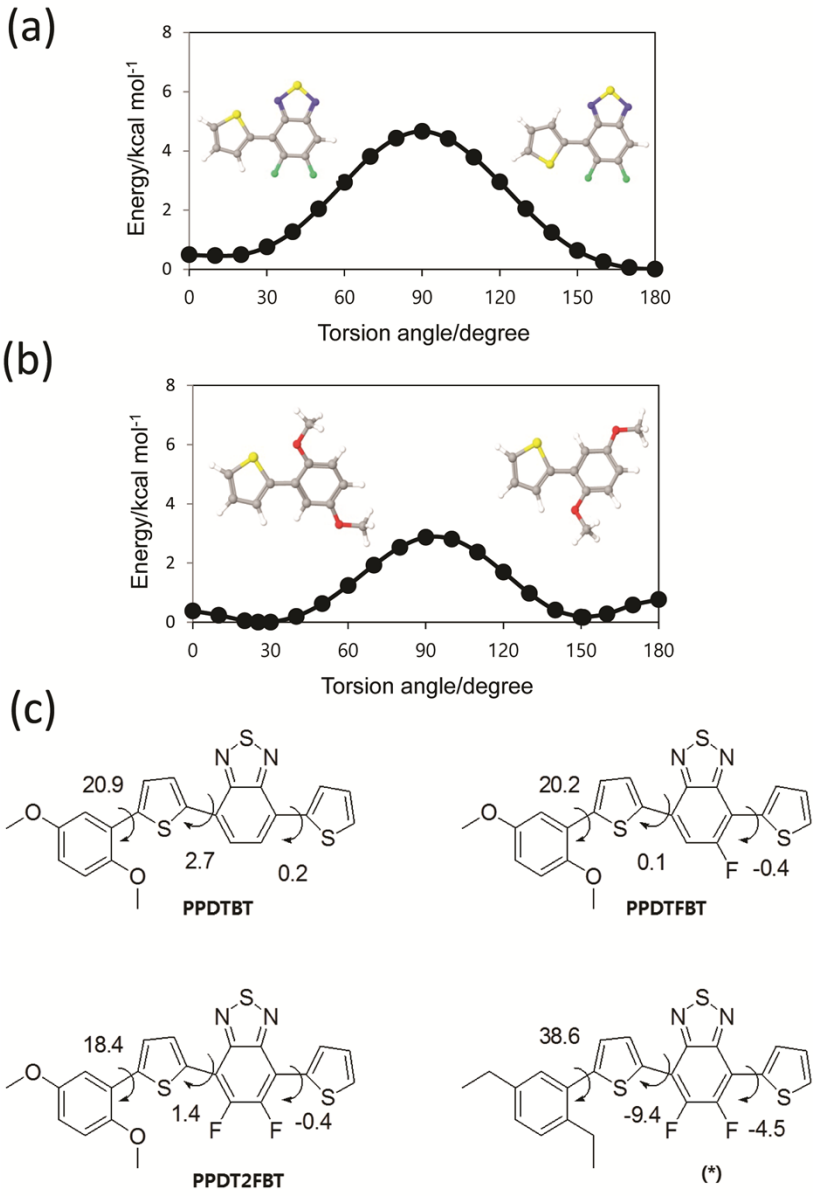

Fig. S1 Torsional profiles for (a) thiophene-difluoro BT and (b) thiophene-dimethoxybenzene (yellow: sulfur, green: fluorine, red: oxygen). (c) The most stable conformation for PPDTBT, PPDTFBT and PPDT2FBT. (*) Methoxy substituents are replaced by ethyl groups in PPDT2FBT.

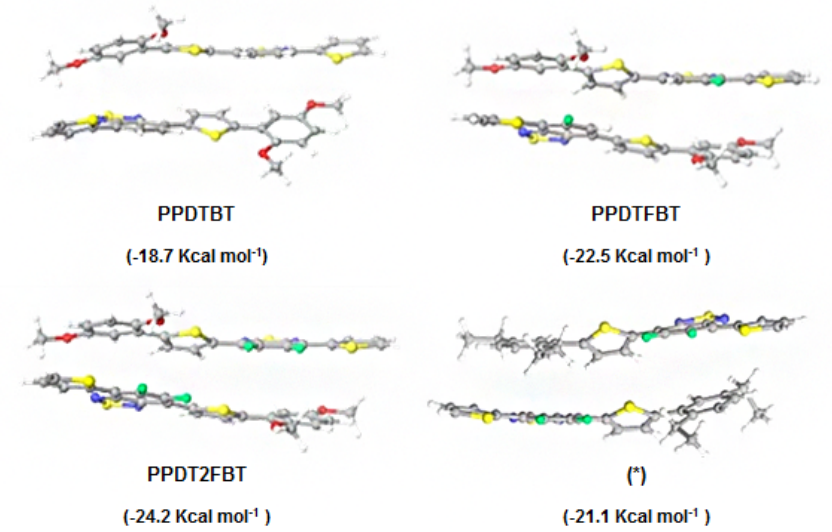

Fig. S2 Calculated binding energies of HT-type cofacial dimeric structures for PPDTBT, PPDTFBT and PPDT2FBT. (*) Methoxy substituents are replaced by ethyl groups in PPDT2FBT. (red: oxygen, yellow: sulfur, green: fluorine)

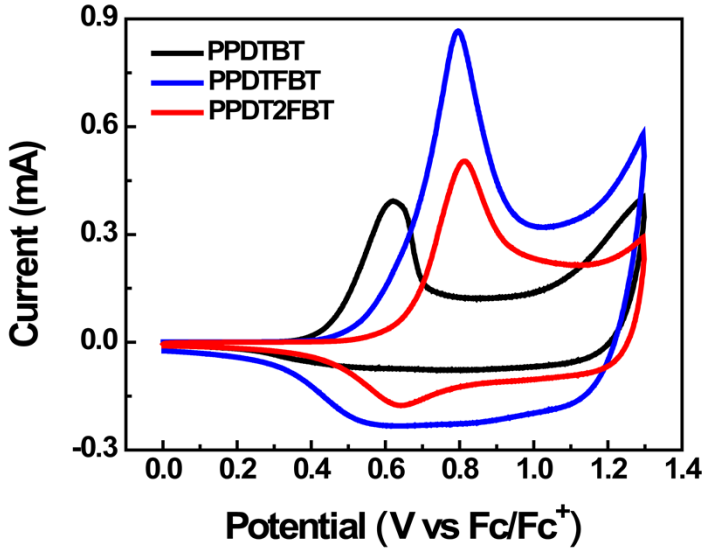

Fig. S3 Cyclic voltammogram of three polymers.

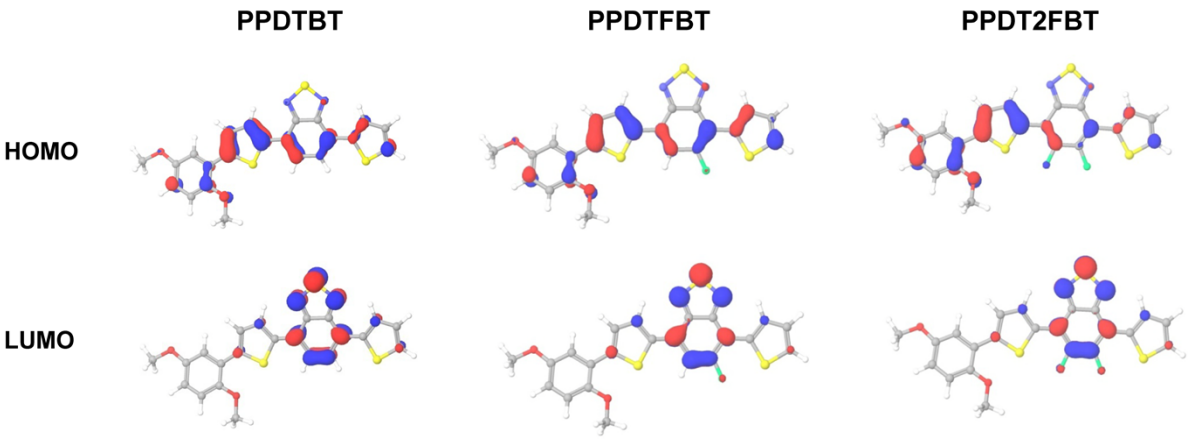

Fig. S4 Calculated electronic structure of frontier orbitals.

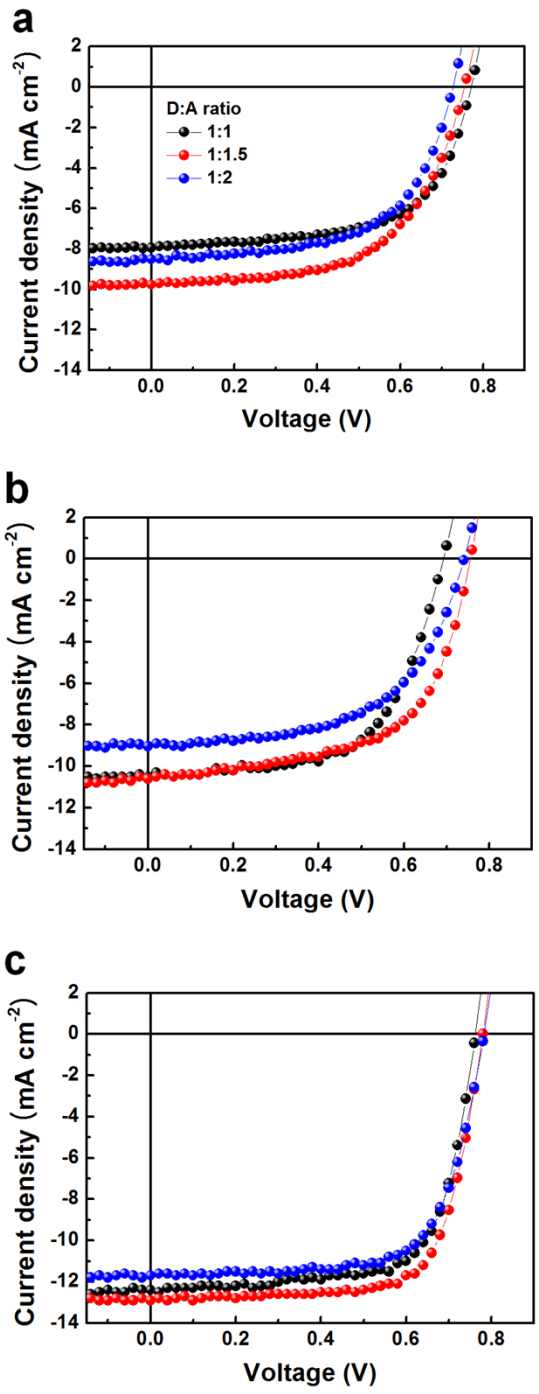

Fig. S5 *J-V* characteristics of (a) PPDTBT, (b) PPDTFBT and (c) PPDT2FBT based PSCs with different polymer:$PC_{70}BM$ blend ratios (solvent: o-dichlorobenzene).

Table S1 Device characteristics of polymer:$PC_{70}BM$ PSCs with different D:A blend ratios (solvent: o-dichlorobenzene).

Polymer	D:A ratio	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF	PCE (%)
PPDTBT	1:1	7.94	0.77	0.62	3.77
	1:1.5	9.77	0.76	0.58	4.27
	1:2	8.50	0.73	0.59	3.63
PPDTFBT	1:1	10.5	0.69	0.60	4.38
	1:1.5	10.6	0.76	0.59	4.72
	1:2	9.03	0.74	0.57	3.80
PPDT2FBT	1:1	12.5	0.79	0.71	6.94
	1:1.5	12.9	0.78	0.71	7.18
	1:2	11.7	0.78	0.69	6.34

Table S2 Comparison of photovoltaic characteristics and device stability.

Active layer	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF	Initial PCE (%)	TA time[a] (h)	Final PCE after TA (%)	PCE decrement after TA (%)	Ref.
P3HT:$PC_{60}BM$	8.93	0.54	0.65	3.11	10	1.00	67	[4]
P3HNT:$PC_{60}BM$	7.55	0.64	0.63	3.03	10	1.74	43	[4]
TPD-Br16:$PC_{70}BM$	11.70	0.73	0.66	5.60	72	4.00	26	[5]
P3HT:$NC_{70}BA$	10.73	0.83	0.66	5.88	20	4.89	17	[6]
PPDT2FBT:$PC_{70}BM$[b]	12.9	0.78	0.71	7.18	200	6.25	13	Current work

[a] TA: Thermal annealing at 130 °C. [b]Device was prepared using a o-dichlorobenzene solvent.

Table S2-1 Thermal cycling test protocol.

		ISOS-T-1 (thermal cycling)
Testing setup	Test environment	Dark
	Load	Open circuit
	Storage temperature	Cycle between RT and 130°C by cycling on/off hot plate
	Storage R.H.	Nitrogen-filled glove box
	Characterization light source	Solar simulation
Testing protocol	Temperature	130°C
	JV measurement	Intermediate procedure
	Min. measurement interval	Gradually increased annealing time (See Table R1)
	Characterization temperature	Room temperature
	Characterization irradiation level	Monitor
	IPCE	None
Output	Time	200 hours
	Characterization light source	AM 1.5G (100 mW/cm^2)
	Instantaneous performance parameters	PCE
	Stability performance parameters	See Fig. 2b
	Storage temperature/R.H.	Thermal annealing at 130°C and measurement at RT under nitrogen atmosphere
	IPCE	None
	Description of measurement protocol and setup	See experimental section 4.3 for detailed description
Required equipment	Characterization light source	AM 1.5G reference spectral irradiation
	Temperature	RTD
	R.H. monitoring	Nitrogen
	Storage	Hot plate with capability to cycle between RT and 130°C
	JV measuring setup	Intermediate procedure
	IPCE measuring system	None

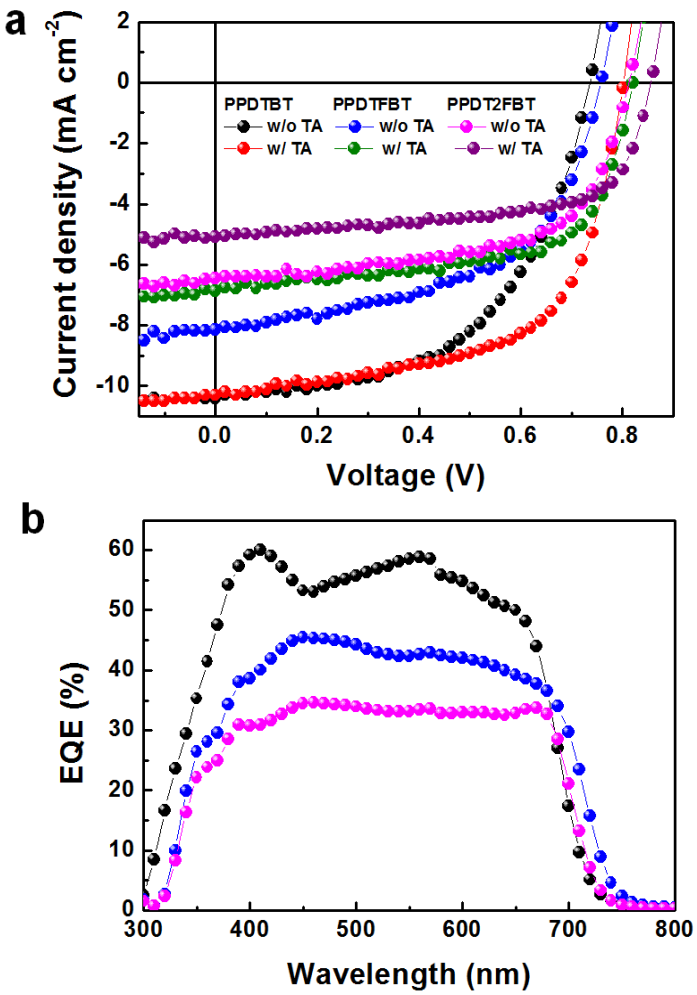

Fig. S6 (a) *J-V* characteristics (w/o TA: without thermal annealing, w/ TA: with thermal annealing) and (b) EQE of polymer:$PC_{70}BM$ PSCs prepared from a chlorobenzene solution without processing additives.

Table S3 Device characteristics of polymer:$PC_{70}BM$ PSCs (solvent: chlorobenzene).

	Thermal annealing[a]	J_{sc} (mA/cm²)	V_{oc} (V)	FF	PCE (%)
PPDTBT	No	10.40	0.74	0.54	4.13
	Yes	10.30	0.80	0.61	5.02
PPDTFBT	No	8.14	0.76	0.55	3.36
	Yes	6.87	0.82	0.64	3.58
PPDT2FBT	No	6.46	0.81	0.61	3.22
	Yes	5.08	0.86	0.64	2.78

[a] Thermal annealing at 130 °C for 10 min

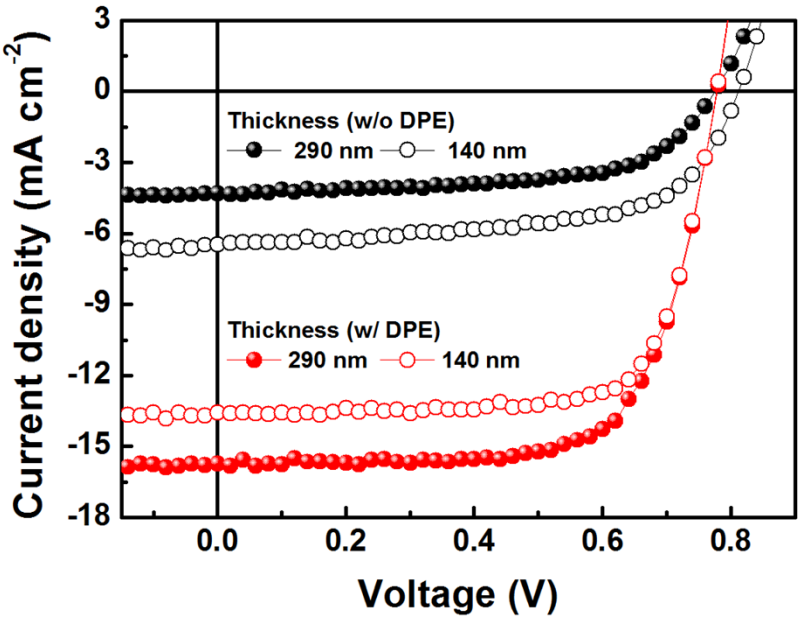

Fig. S7 *J-V* characteristics of PPDT2FBT:$PC_{70}BM$ PSCs with variable film thickness.

Table S4 Device characteristics of PPDT2FBT:$PC_{70}BM$ PSCs with variable film thickness.

Polymer	DPE	Thickness of active layer (nm)	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF	PCE (%)
PPDT2FBT	No	290	4.30	0.78	0.26	2.07
		140	6.46	0.81	0.61	3.22
	Yes	290	15.73	0.78	0.71	8.64
		140	13.57	0.78	0.74	7.79

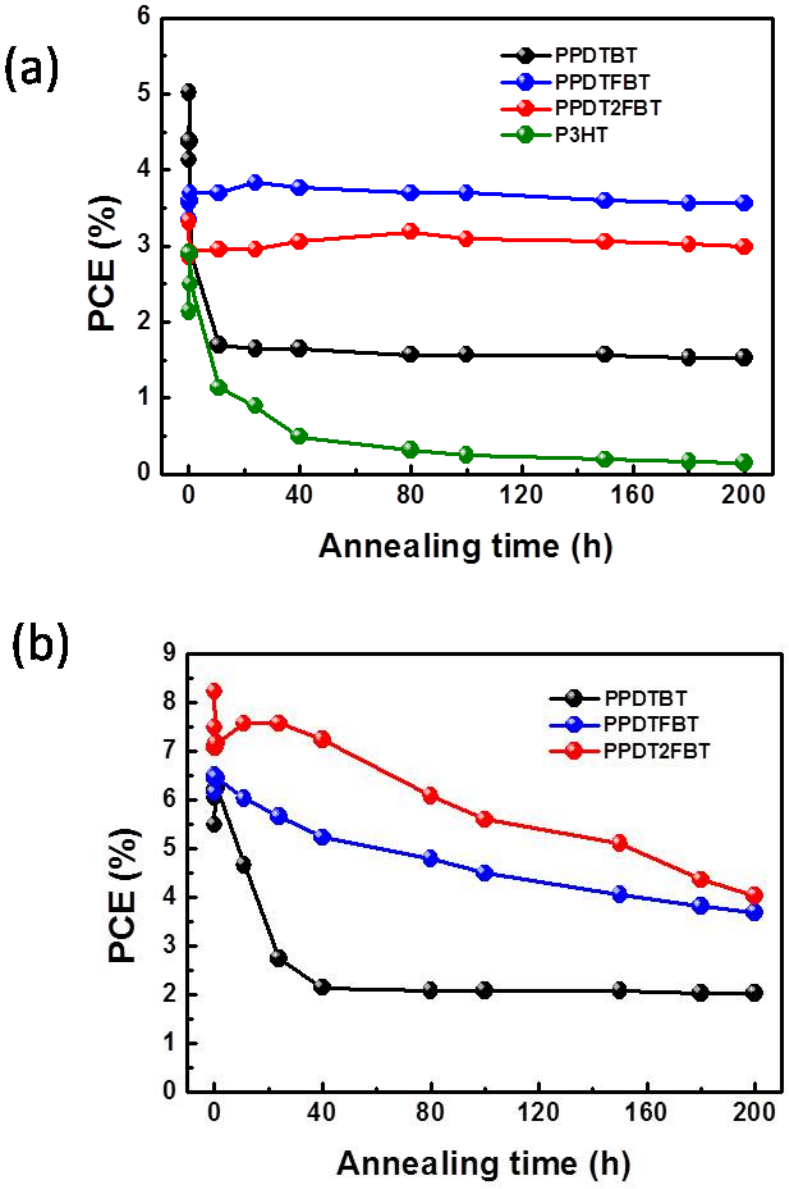

Fig. S8 Temporal stability of polymer:$PC_{70}BM$ PSCs (a) without and (b) with DPE at an annealing temperature of 130 °C for 200 h (P3HT-based device for comparison). All devices were prepared from chlorobenzene.

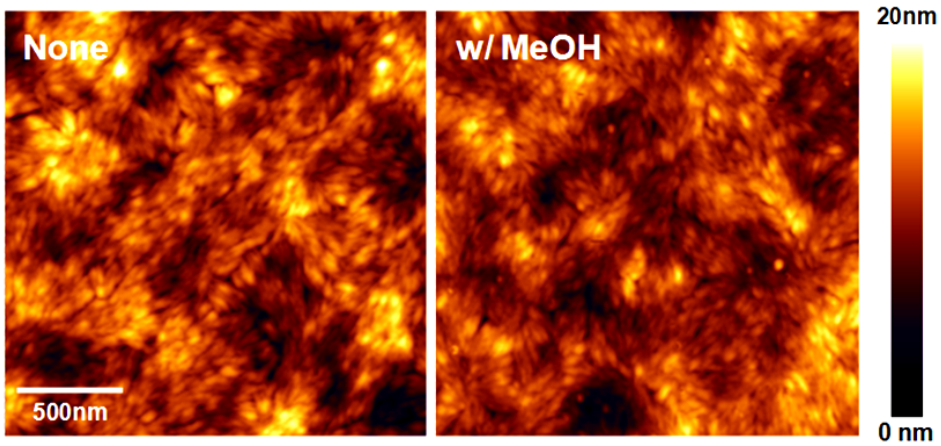

Fig. S9 AFM topography images of PPDT2FBT:$PC_{70}BM$ without (left) and with (right) MeOH treatments. (solvent: CB:DPE, 98:2 vol%).

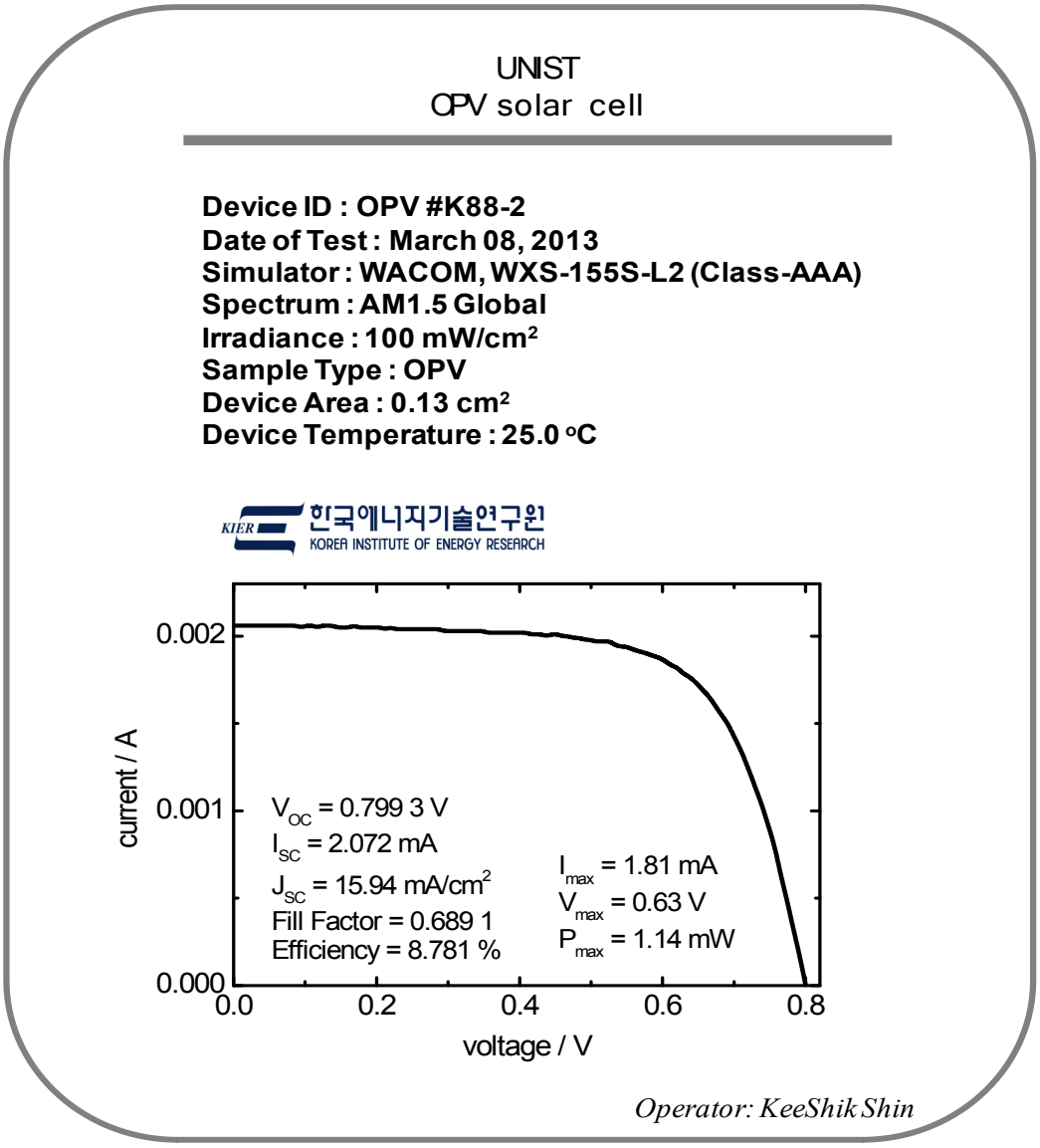

Fig. S10 Photovoltaic data of PPDT2FBT:$PC_{70}BM$-based PSCs certified by KIER (solvent: CB:DPE (98:2 vol%), MeOH treatment on top of the active layer).

Table S5 Comparison of photovoltaic characteristics with previously reported high-efficiency PSCs.

Solvent (additive)[a]	Active layer	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF	Best EQE (%)	Best PCE (%)	Ref.
CB (DIO)	PBDTTT-CF:$PC_{70}BM$	15.20	0.76	0.67	69	7.73	[7]
CB (DIO)	PTB7:$PC_{70}BM$	14.5	0.74	0.69	68	7.40	[8]
DCB (DIO)	PBDTTT-C-T:$PC_{70}BM$	17.48	0.74	0.59	75	7.59	[9]
CB (DIO)	PTDBD2:$PC_{70}BM$	13.0	0.89	0.65	N/A	7.60	[10]
DCB (DIO)	PBDTTT-ST:$PC_{70}BM$	16.35	0.69	0.66	75	7.81	[11]
DCB (DIO)	PBDT-TFQ:$PC_{70}BM$	17.90	0.76	0.58	86	8.00	[12]
CB (CN)	PBDTTPD: $PC_{70}BM$	12.60	0.97	0.70	N/A	8.50	[13]
CB (DPE)	PPDT2FBT:$PC_{70}BM$	15.73	0.78	0.71	82	8.64 9.39 (MeOH treatment)	Current work

[a]CB: chlorobenzene; DCB: *o*-dichlorobenzene; DIO: 1,8-diiodooctane; CN: 1-chloronaphthalene; DPE: diphenyl ether.

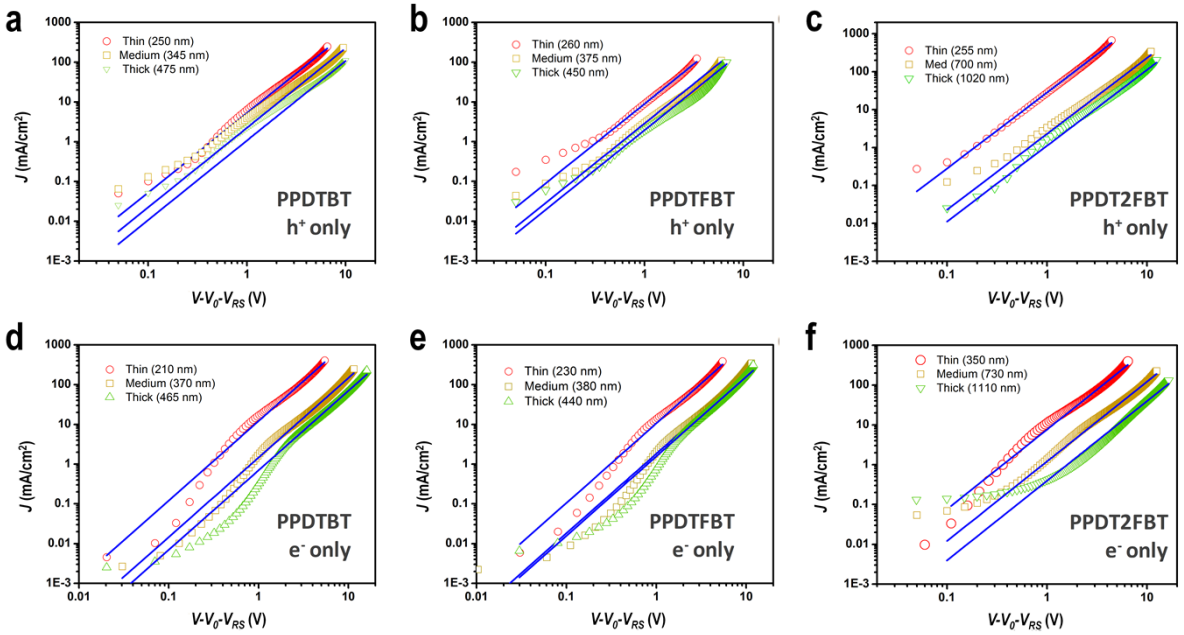

Fig. S11 J-V characteristics of (a)~(c) hole-only and (d)~(f) electron-only devices based on polymer:$PC_{70}BM$ blend films with various film thickness (solvent: CB:DPE = 98:2 vol%). Blue lines represent fits of the curves using the Mott-Gurney relationship.

Table S6 Electron and hole mobilities of electron- and hole-only devices based on polymer:$PC_{70}BM$ films measured using a space-charge-limited current method.

Material	Hole-Only		Electron-Only		μ_h/μ_e
	Film Thickness (nm)	μ_h[a] (cm^2/Vs)	Film Thickness (nm)	μ_e[b] (cm^2/Vs)	
PPDTBT	250	2.7×10^{-4}	210	3.7×10^{-4}	0.7
	345	3.1×10^{-4}	370	2.4×10^{-4}	1.3
	475	3.8×10^{-4}	465	2.4×10^{-4}	1.6
PPDTFBT	260	5.4×10^{-4}	230	4.3×10^{-4}	1.3
	375	5.1×10^{-4}	380	3.7×10^{-4}	1.4
	450	6.0×10^{-4}	440	4.5×10^{-4}	1.3
PPDT2FBT	255	2.3×10^{-3}	350	1.1×10^{-3}	2.1
	700	2.6×10^{-3}	730	1.6×10^{-3}	1.6
	1020	4.0×10^{-3}	1110	1.8×10^{-3}	2.2

[a] Hole mobility, [b] Electron mobility.

Table S7 Packing parameters derived from GIWAXS measurements.

Films	Polymers	Additive (DPE)	Crystallographic parameters			
			Lamellar spacing		π-π stack	
			q_z (Å^{-1})	*d*-spacing (Å)	q_z (Å^{-1})	*d*-spacing (Å)
Pristine polymer	PPDTBT	No	0.3324	18.9	-	-
		Yes	0.3312	19.0	-	-
	PPDTFBT	No	0.3035	20.7	1.6614	3.78
		Yes	0.3036	20.7	1.6706	3.76
	PPDT2FBT	No	0.3036	20.7	1.6873	3.72
		Yes	0.3000	20.9	1.6901	3.72
Polymer:$PC_{70}BM$ blend	PPDTBT	No	0.3297	19.1	-	-
		Yes	0.3332	18.9	-	-
	PPDTFBT	No	0.3182	19.7	1.6925	3.71
		Yes	0.3178	19.8	1.7590	3.57
	PPDT2FBT	No	0.3164	19.9	1.7089	3.68
		Yes	0.3133	20.1	1.7514	3.59

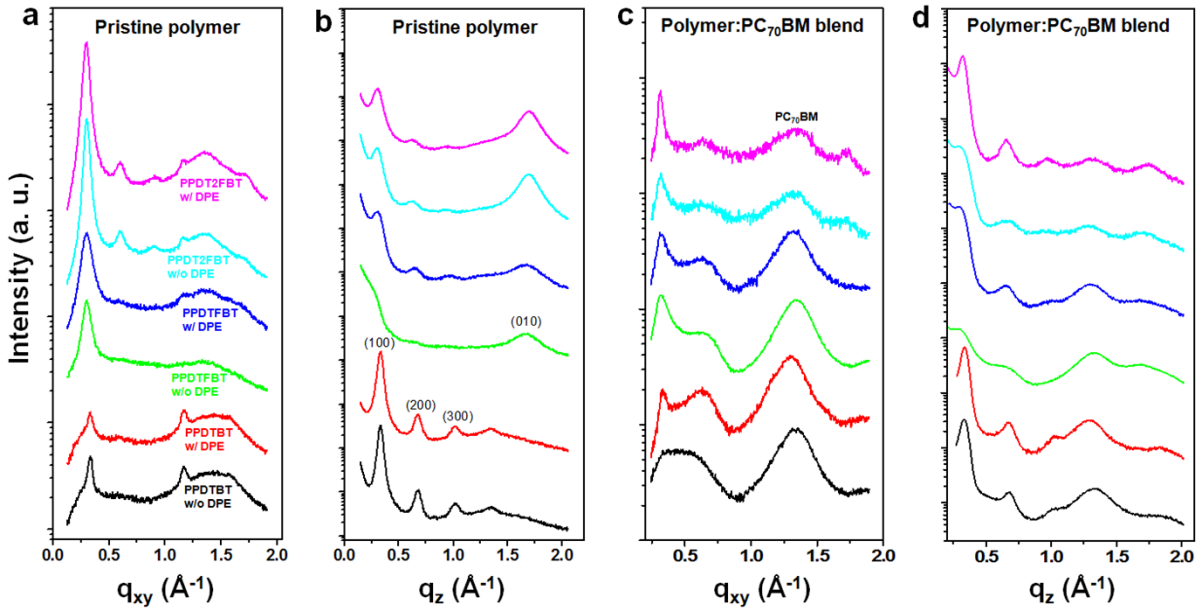

Fig. S12 In-plane (a and c) and out-of-plane (b and d) GIWAXS data for pristine polymers (a and b) and polymer:$PC_{70}BM$ (c and d) films with and without DPE.

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