

Supporting Information

Excellent Long-Term Stability of Power Conversion Efficiency in Non-Fullerene-Based Polymer Solar Cells Bearing Tricyanovinylene-Functionalized n-Type Small Molecules

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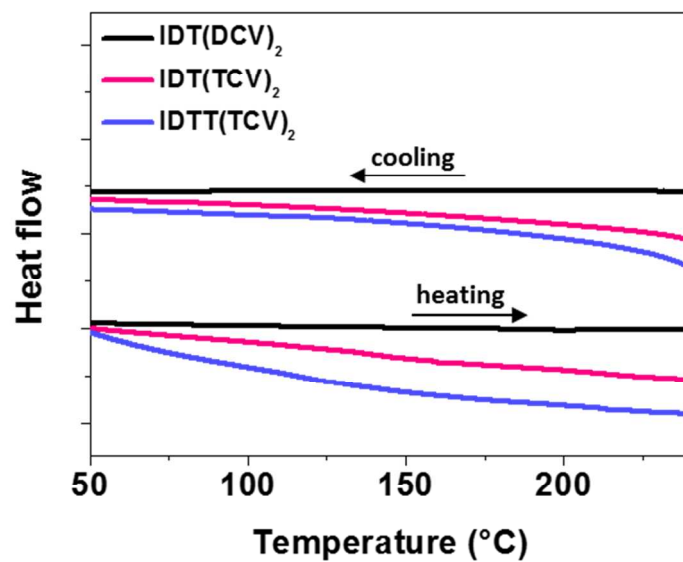


Figure S1. Differential scanning calorimetry (DSC) curves of small molecules.

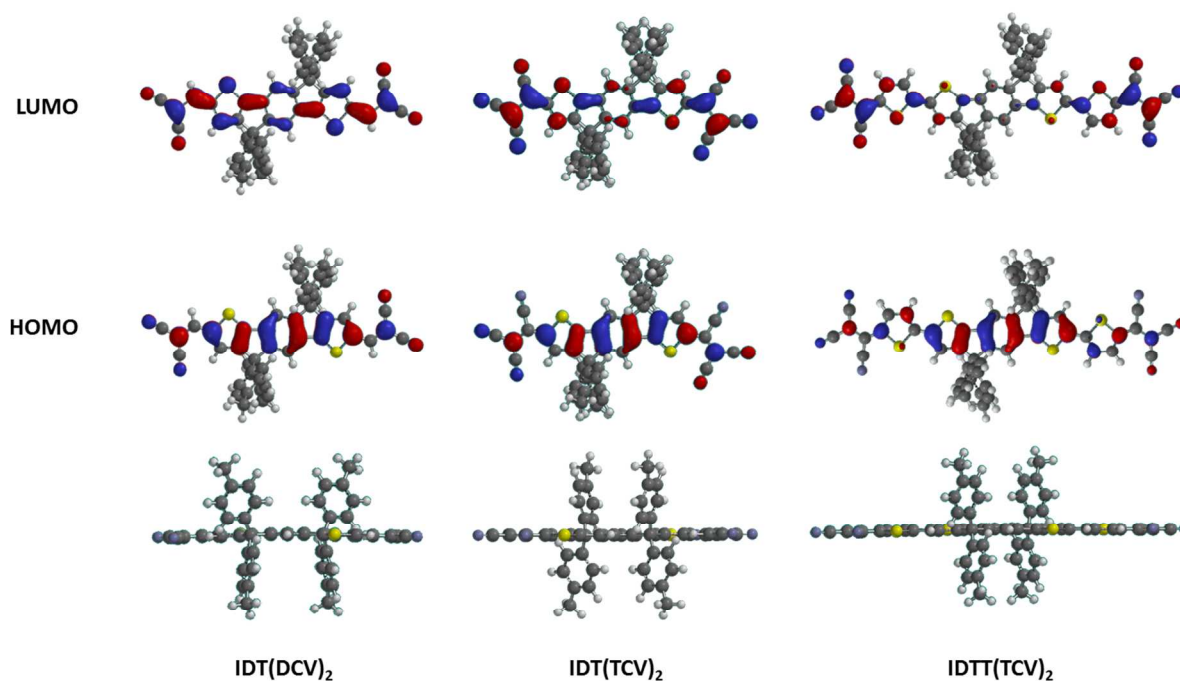


Figure S2. Density functional theory (DFT) calculation of the HOMOs/LUMOs and geometries of small molecules.

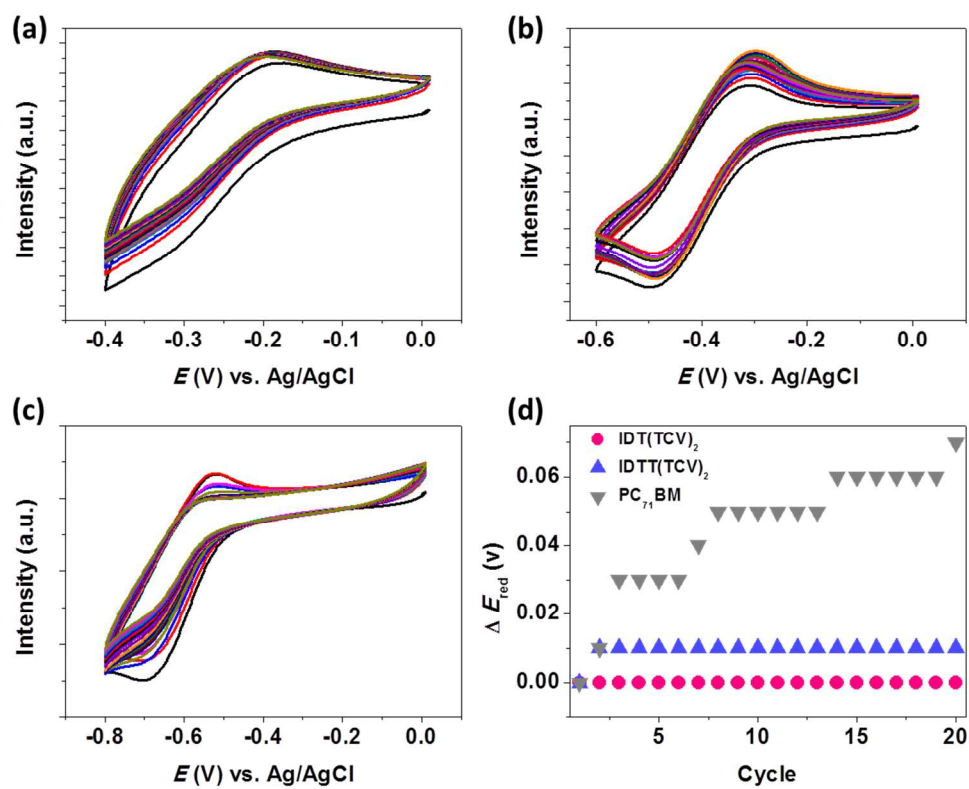


Figure S3. Solutions-state cyclic voltammograms of (a) IDT(TCV)₂, (b) IDTT(TCV)₂, and (c) PC₇₁BM for 20 cycles. (d) The change of E_{red} upon cycling.

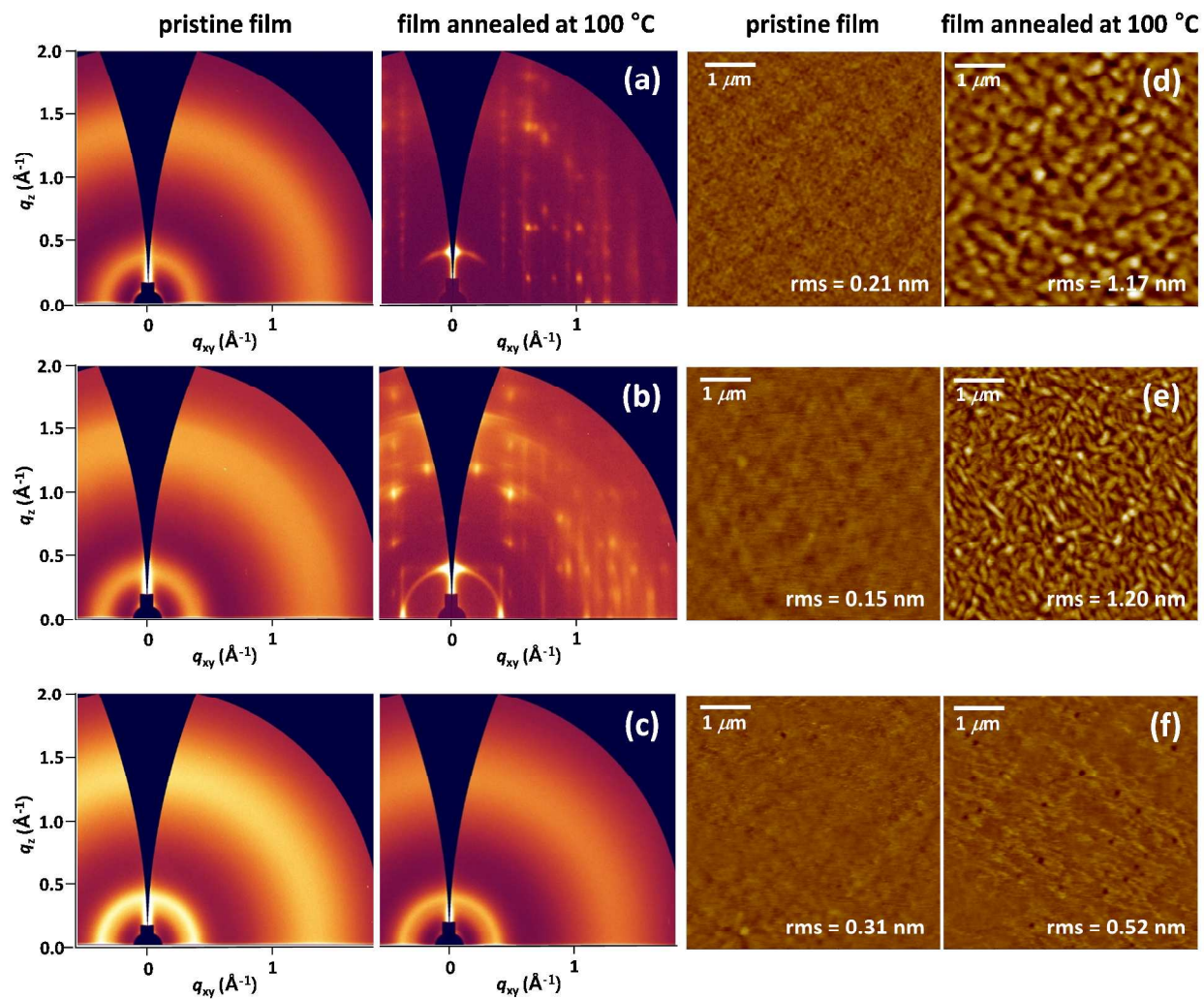


Figure S4. 2D-GIWAXS patterns (a, b, c) and AFM images (d, e, f) of small molecule films. (a, d) IDT(DCV)₂, (b, e) IDT(TCV)₂, and (c, f) IDTT(TCV)₂.

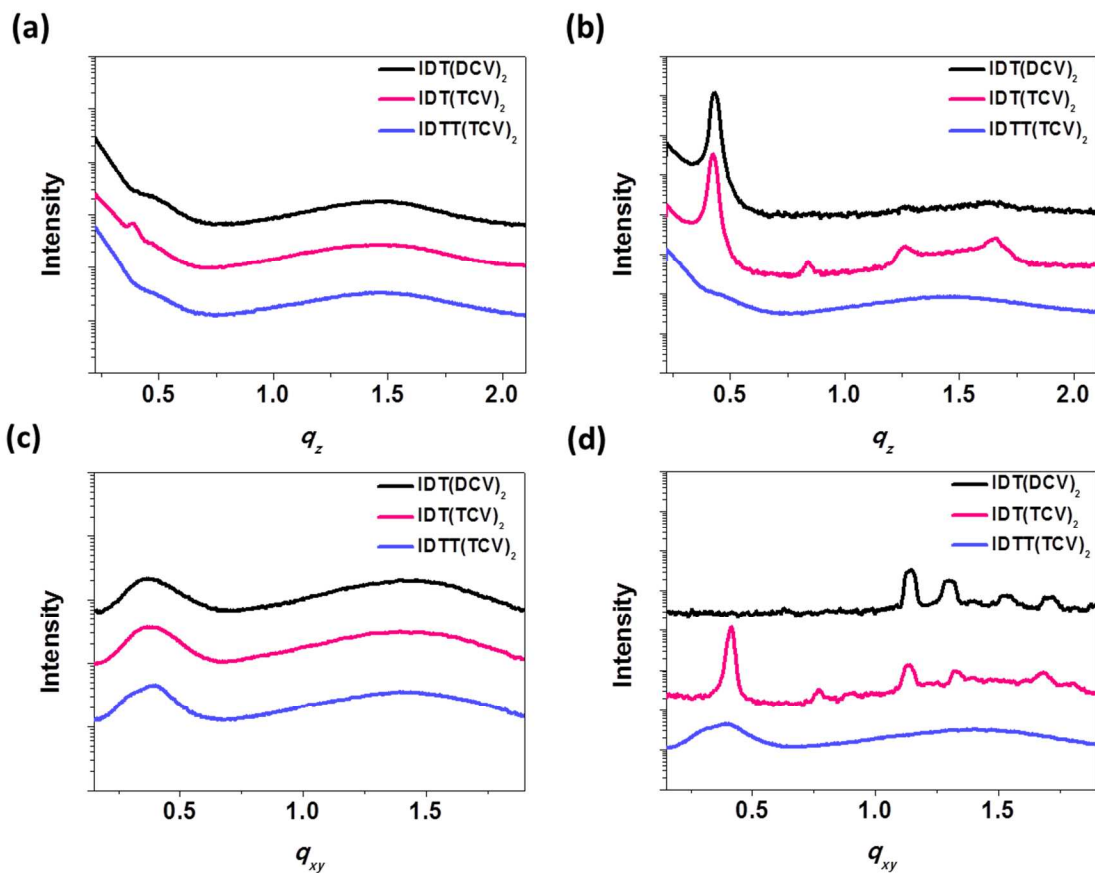


Figure S5. GIWAXS spectra of small molecules. (a, c) Pristine state, (b, d) films annealed at 100 °C. (a, b) Out-of-plane, (c, d) in-plane.

Table S1. TFT characteristics of IDT(TCV)₂ and IDTT(TCV)₂.

Small molecules	$T_{\text{annealing}}$ (°C)	V_{th} (V)	$I_{\text{on}}/I_{\text{off}}$	μ (cm ² V ⁻¹ s ⁻¹)
IDT(TCV) ₂	pristine	6.86	10 ²	4.36 × 10 ⁻⁵
	100	14.3	10 ⁵	9.58 × 10 ⁻³
IDTT(TCV) ₂	pristine	32.4	10 ²	6.56 × 10 ⁻⁵
	100	14.9	10 ²	1.99 × 10 ⁻⁵

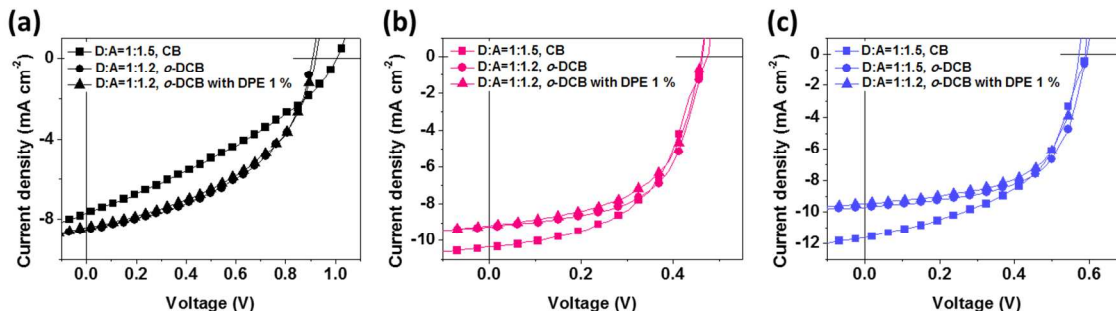


Figure S6. J - V characteristics of BHJ PSCs for different D:A ratios. (a) IDT(DCV)₂, (b) IDT(TCV)₂, and (c) IDTT(TCV)₂.

Table S2. PSC characteristics of IDT(DCV)₂, IDT(TCV)₂, IDTT(TCV)₂, and PC₇₁BM under various conditions.

	D:A	rpm/s	solvent	condition	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF	PCE ^a (%)
IDT(DCV) ₂	1:1.5	2000/30	CB	-	1.00	7.70	0.34	2.59 (2.45)
	1:1.2	1000/40	<i>o</i> -DCB	-	0.91	8.51	0.47	3.63 (3.20)
	1:1.2	1000/40	<i>o</i> -DCB	1000 h	0.83	4.56	0.38	1.43 (1.28)
	1:1.2	1000/40	<i>o</i> -DCB	DPE ^b 1 %	0.92	8.41	0.45	3.53 (3.35)
IDT(TCV) ₂	1:1.5	2000/30	CB	-	0.49	11.02	0.53	2.84 (2.61)
	1:1.5	2000/30	CB	1000 h	0.49	10.39	0.50	2.57 (2.43)
	1:1.2	1000/40	<i>o</i> -DCB	-	0.46	9.21	0.60	2.54 (2.41)
	1:1.2	1000/40	<i>o</i> -DCB	DPE ^b 1 %	0.46	9.15	0.56	2.35 (2.27)
IDTT(TCV) ₂	1:1.5	2000/30	CB	-	0.60	11.98	0.50	3.57 (3.42)
	1:1.5	2000/30	CB	1000 h	0.59	10.64	0.51	3.25 (3.10)
	1:1.2	1000/40	<i>o</i> -DCB	-	0.60	9.66	0.59	3.46 (3.43)
	1:1.2	1000/40	<i>o</i> -DCB	DPE ^b 1 %	0.59	9.45	0.58	3.28 (3.24)
PC ₇₁ BM	1:1.5	2000/30	CB	-	0.82	14.19	0.53	6.25 (6.23)
	1:1.5	2000/30	CB	1000 h	0.82	12.45	0.38	3.83 (3.75)

^a Average power conversion efficiencies are given in parenthesis; ^b DPE: diphenyl ether

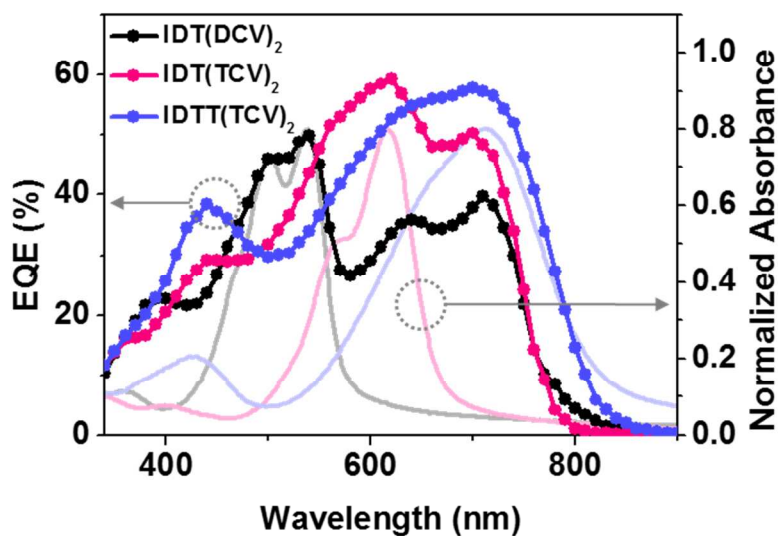


Figure S7. EQE of PTB7-Th:IDT(DCV)₂, PTB7-Th:IDT(TCV)₂, and PTB7-Th:IDTT(TCV)₂ blend films and corresponding UV-Vis absorption spectra of small molecules.

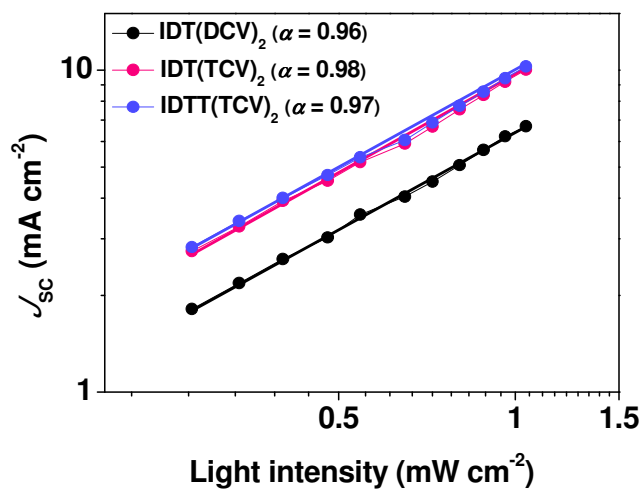


Figure S8. Plot of photocurrent density vs. light intensity for PTB7-Th:IDT(DCV)₂, PTB7-Th:IDT(TCV)₂, and PTB7-Th:IDTT(TCV)₂ blend films.

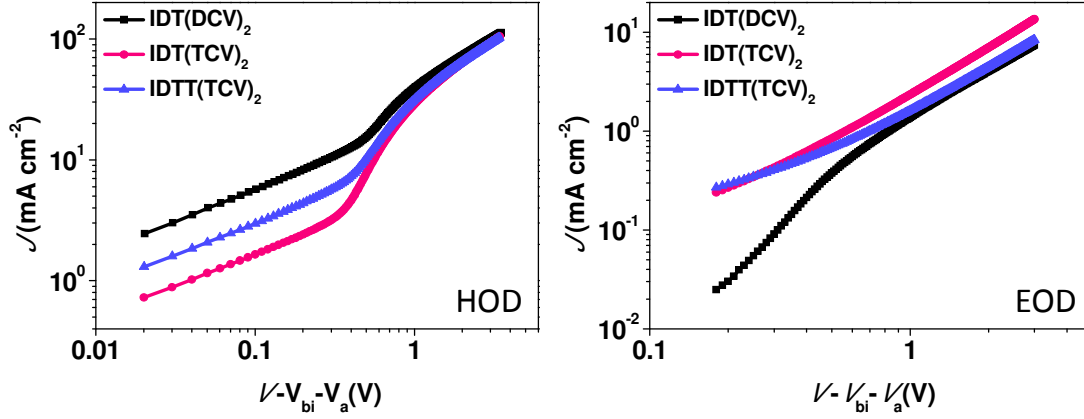


Figure S9. Measured space-charge-limited J - V characteristics under dark condition for hole-only devices (HODs) and electron-only devices (EODs).

Table S3. Measured hole and electron mobilities of SCLC devices.

	μ_h [$\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$]	μ_e [$\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$]	μ_h / μ_e
PTB7-Th:IDT(DCV) ₂	1.41×10^{-5}	1.58×10^{-6}	8.92
PTB7-Th:IDT(TCV) ₂	1.12×10^{-5}	2.45×10^{-6}	4.57
PTB7-Th:IDTT(TCV) ₂	1.15×10^{-5}	1.69×10^{-6}	6.80

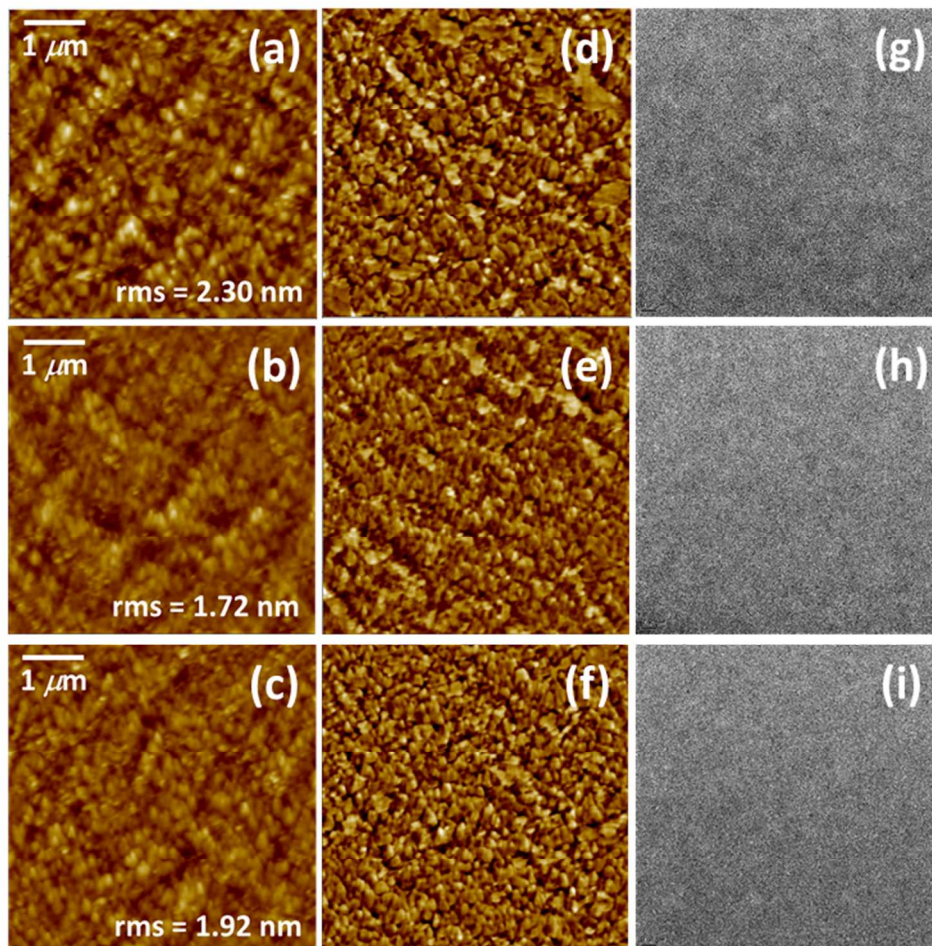


Figure S10. AFM height images ($5\ \mu\text{m} \times 5\ \mu\text{m}$) of the blend films. Topography images of (a) PTB7-Th:IDT(DCV)₂ (1:1.2 w/w), (b) PTB7-Th:IDT(TCV)₂ (1:1.5 w/w) and (c) PTB7-Th:IDTT(TCV)₂ (1:1.5 w/w) blend films, and phase images of (d) PTB7-Th:IDT(DCV)₂, (e) PTB7-Th:IDT(TCV)₂, and (f) PTB7-Th:IDTT(TCV)₂ blend films. TEM images of (g) PTB7-Th:IDT(DCV)₂, (h) PTB7-Th:IDT(TCV)₂, and (i) PTB7-Th: IDTT(TCV)₂ blend films.

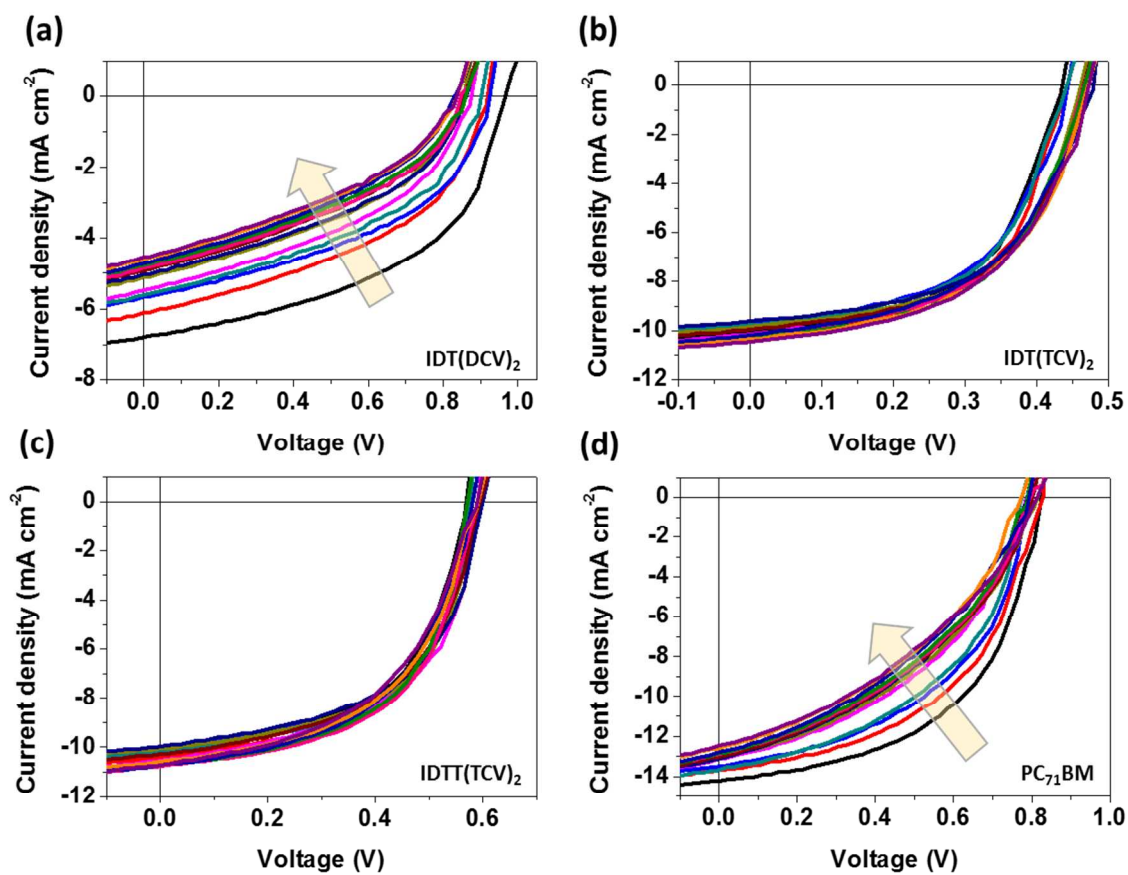


Figure S11. J - V characteristics of BHJ PSCs based on (a) IDT(DCV)₂, (b) IDT(TCV)₂, (c) IDTT(TCV)₂, and (d) PC₇₁BM during the 1000-h test.

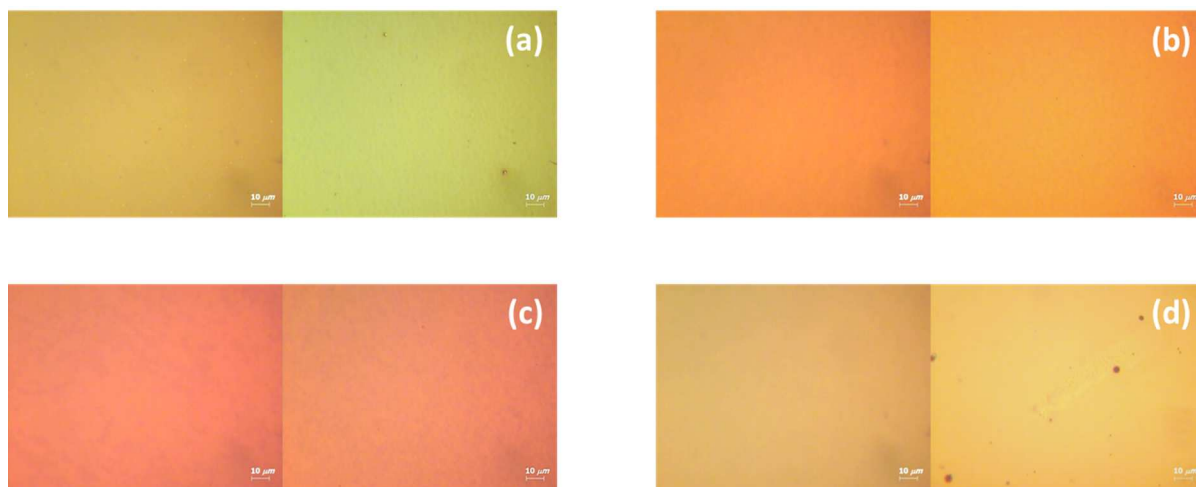


Figure S12. Optical microscopic images of the blend films on ITO/ZnO substrates before aging (left) and after storage in air for 1000 h (right) for (a) IDT(DCV)₂, (b) IDT(TCV)₂, (c) IDTT(TCV)₂, and (d) PC₇₁BM blend films with PTB7-Th.

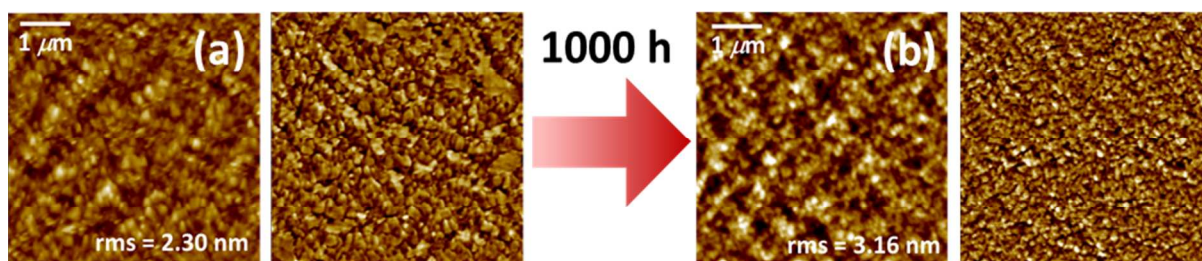


Figure S13. AFM height images (5 μm x 5 μm) of blend film. Topography images (left) and phase images (right) of PTB7-Th:IDT(DCV)₂ (1:1.2 w/w) blend film. (a) Pristine film and (b) film after 1000 h.

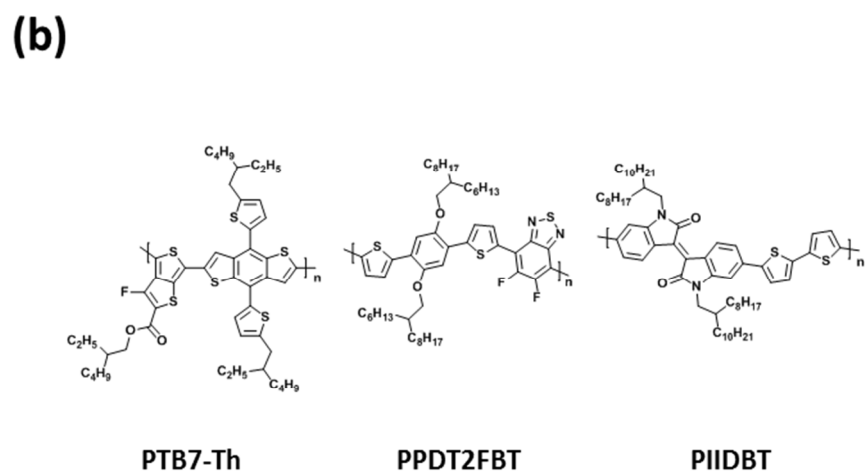
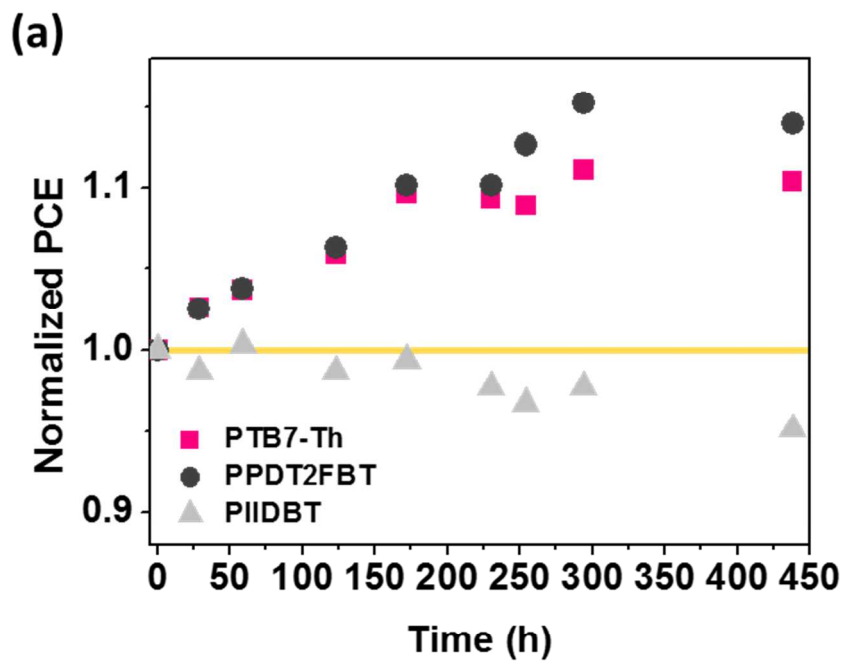


Figure S14. Stability of BHJ PSCs under ambient conditions: (a) p-type polymer:IDT(TCV)₂ blend PSCs and the structures of (b) p-type polymers.

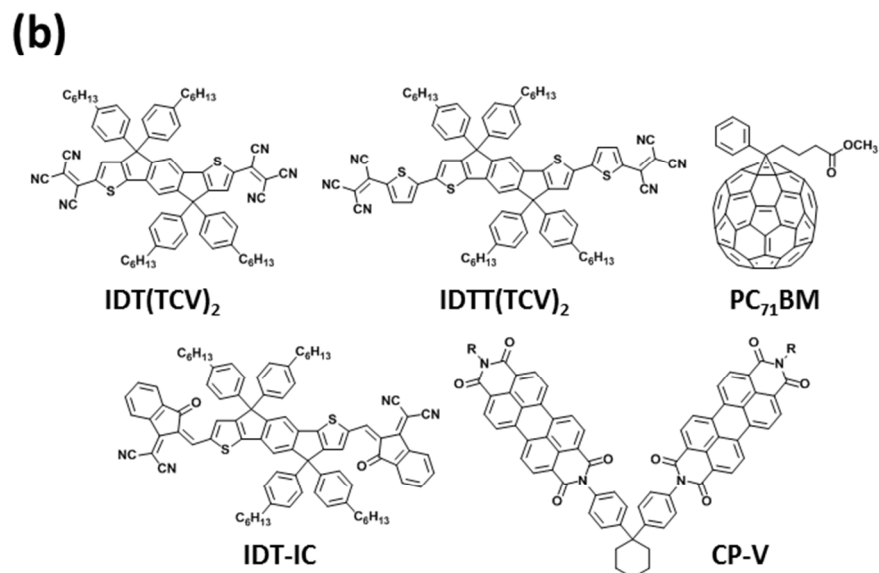
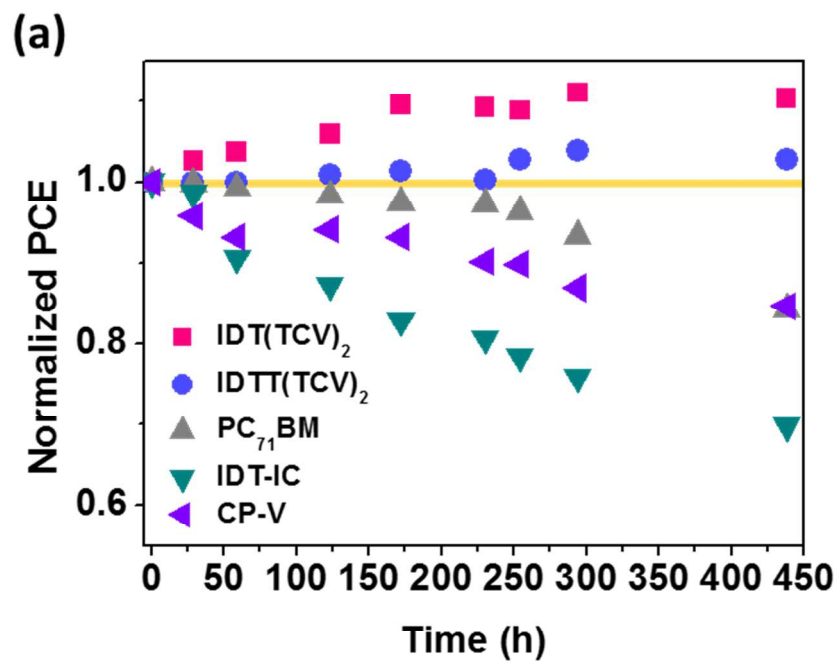


Figure S15. Stability of BHJ PSCs under ambient conditions: (a) PTB7-Th:n-type small molecule blend PSCs and the structures of (b) n-type small molecules.

Table S4. PSC characteristics of p-type polymer:IDT(TCV)₂ blend, PTB7-Th:n-type small molecule blend.

p-type polymer	n-type small molecule	condition	V _{oc} (V)	J _{sc} (mA cm ⁻²)	FF	PCE (%)
PTB7-Th	IDT(TCV) ₂	-	0.47	9.98	0.58	2.70
		440 h	0.48	10.03	0.61	2.98
PPDT2FBT	IDT(TCV) ₂	-	0.40	3.81	0.51	0.79
		440 h	0.42	3.87	0.55	0.89
PIIDBT	IDT(TCV) ₂	-	0.70	8.97	0.49	3.11
		440 h	0.70	9.06	0.47	2.96
PTB7-Th	IDTT(TCV) ₂	-	0.60	11.27	0.52	3.52
		440 h	0.61	10.87	0.54	3.62
PTB7-Th	PC ₇₁ BM	-	0.82	13.37	0.51	5.55
		440 h	0.79	12.67	0.46	4.67
PTB7-Th	IDT-IC	-	0.83	8.39	0.52	3.61
		440 h	0.82	6.81	0.45	2.52
PTB7-Th	CP-V	-	0.77	9.56	0.42	3.06
		440 h	0.75	8.78	0.39	2.59

ITO/ZnO/2 wt% CB solution, p-type polymer:n-type small molecule = 1:1.5 w/w/MoO₃/Ag.