Electronic supplementary information

Ladder-Type Dithienocyclopentadibenzothiophene-Cored Wide-Bandgap Polymers for Efficient Non-Fullerene Solar Cells with Large Open-Circuit Voltages

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Table S1 Photovoltaic parameters of PSCs based on **PSS2**/EH-IDTBR (1:2.5, *w/w*), under the illumination of AM 1.5G (100 mW/cm^2)

DPE Additive (*v/v*)	Annealing temperature [^{o}C]	V_{OC} [V]	J_{SC} [mA cm^{-2}]	FF [%]	PCE [%][a]
0	None	1.042	11.96	55.2	6.88 (6.61±0.17)
1%	None	1.051	13.72	53.0	7.64 (7.44±0.15)
0	120	1.049	12.35	56.2	7.28 (7.17±0.10)
1%[b]	None	1.053	13.16	53.6	7.43 (7.35±0.05)

[a] In parentheses are averaged values based on 8 devices. [b] The devices were quenched with methanol at room temperature.

Table S2 Hole and electron mobilities of the PSCs based on polymer:EH-IDTBR (1:2.5, *w/w*)

Active layer	μ_h (cm^2 V^{-1}s^{-1})	μ_e (cm^2 V^{-1}s^{-1})	μ_h/μ_e ratio
PSS2:EH-IDTBR[a]	6.60×10^{-6}	1.10×10^{-5}	0.60
PSS2:EH-IDTBR[b]	2.85×10^{-5}	2.10×10^{-5}	1.36
PSS3:EH-IDTBR[b]	1.34×10^{-5}	4.52×10^{-5}	0.30

[a] Calculated by using the SCLC model from the as-cast blend film. [b] Calculated by using the SCLC model from blends with quenching treatment (120 ^{o}C).

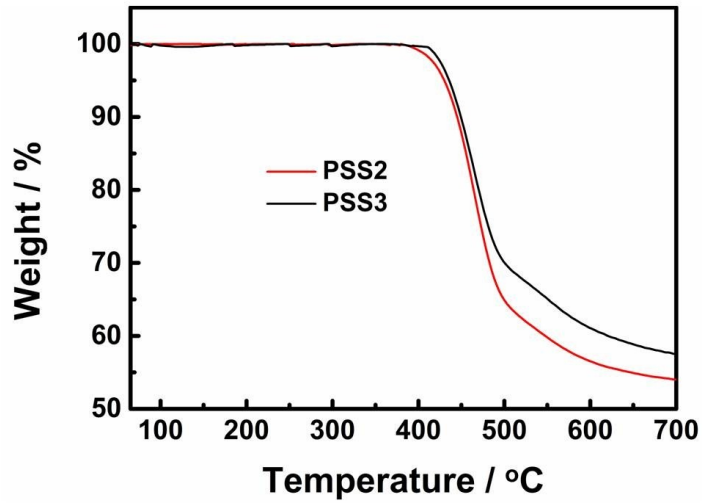

Fig. S1 TGA curves of copolymers with a heating rate of 10 °C/min under N_2 atmosphere.

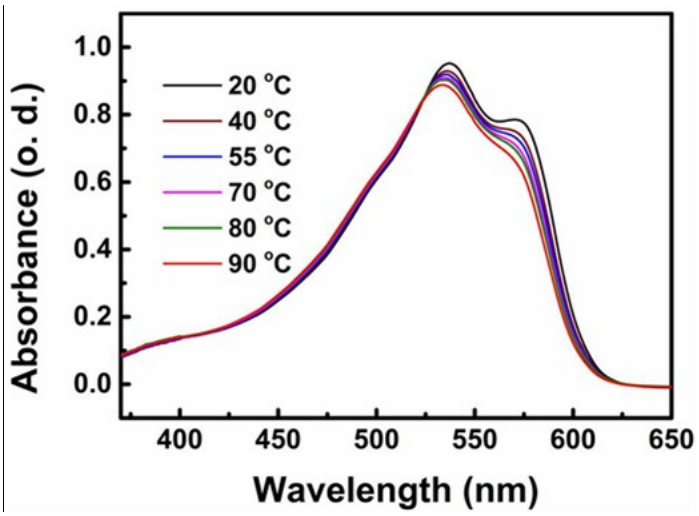

Fig. S2 Temperature-dependent absorption spectra of **PSS2** in CB solution (1×10^{-5} M).

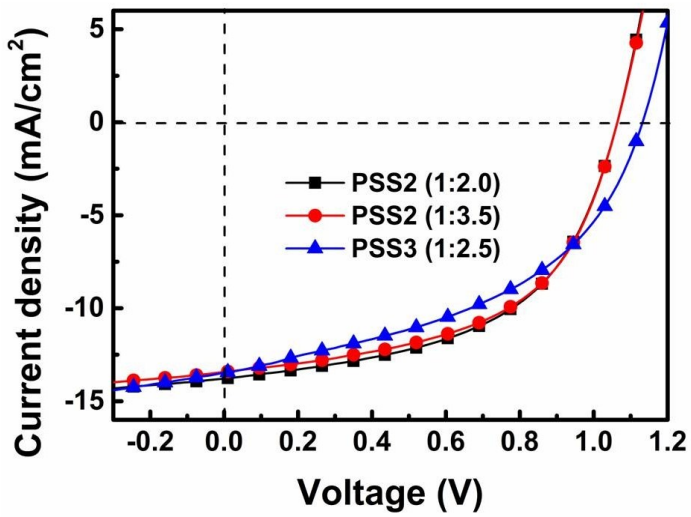

Fig. S3 *J-V* characteristics of the devices based on polymer:EH-IDTBR with different blend ratios.

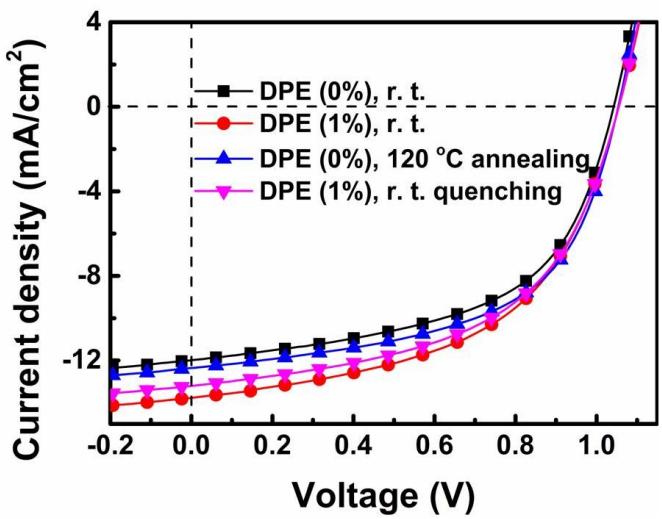

Fig. S4 *J-V* characteristics of **PSS2-**based devices under different processing conditions.

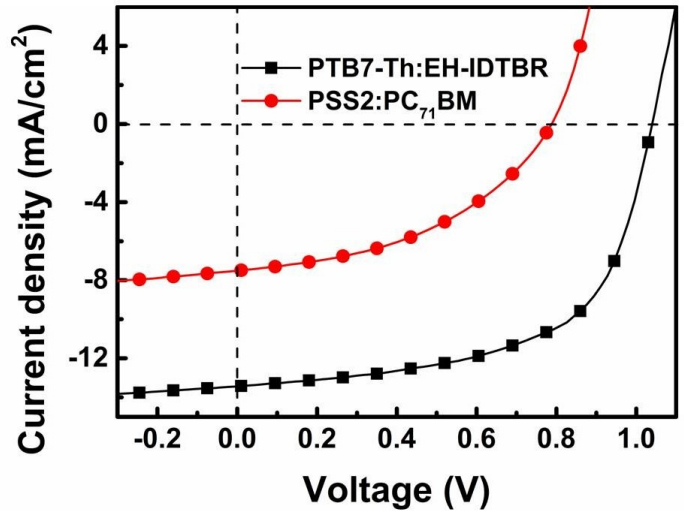

Fig. S5 *J-V* characteristics of devices based on **PSS2:**$PC_{71}BM$ and PTB7-Th:EH-IDTBR.

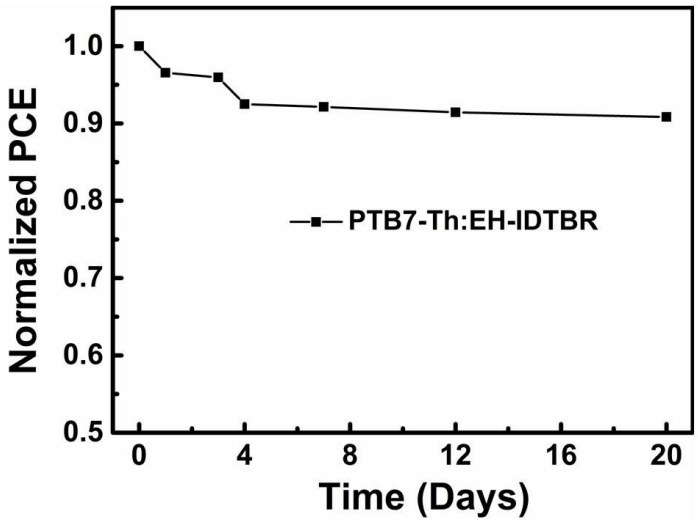

Fig. S6 Shelf stability of the best-performance PSC based on PTB7-Th:EH-IDTBR.

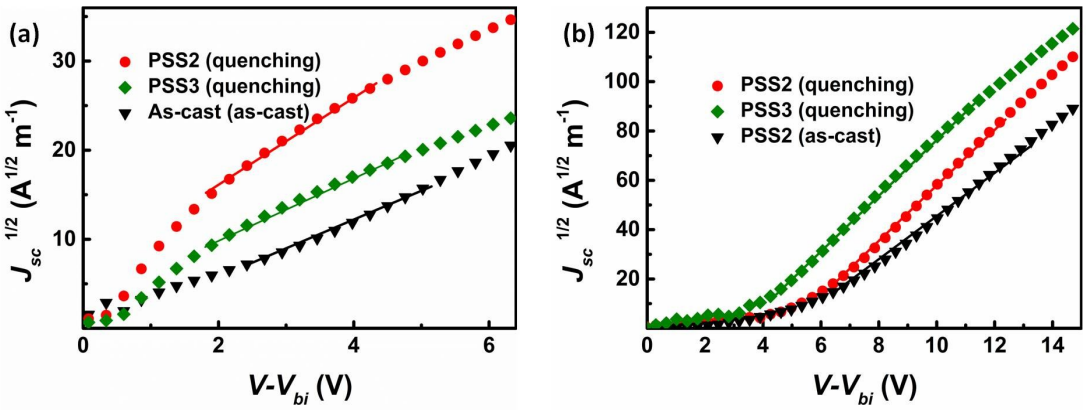

Fig. S7 $J^{1/2}$-V characteristics of (a) hole- and (b) electron-only devices based on the polymer blends.