Electronic Supplementary Information

The use of *n*-type macromolecular additive as a simple yet effective tool for improving and stabilizing the performance of organic solar cells

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Characterizations

Fig. S1. Cyclic voltammetry of *L*-P(NDI2OD-T2), *I*-P(NDI2OD-T2), and *H*-P(NDI2OD-T2). **Fig. S2.** GIWAXD images of *L*-P(NDI2OD-T2), *I*-P(NDI2OD-T2), and *H*-P(NDI2OD-T2) polymer films with different molecular weights.

Fig. S3. Conventional device structure.

Fig. S4. Hole and electron mobilities of electron- and hole-only devices of $PTB7:PC_{71}BM$ blneds with different amounts of the *H*-P(NDI2OD-T2) additive by a space-charge-limited current (SCLC) method.

Fig. S5. Light intensity dependence of J_{SC} on PTB7:PC₇₁BM based device with different amounts of *H*-P(NDI2OD-T2) polymer (0, 0.4, 0.8, 1.2, 1.6, and 2.0 *wt*%).

Fig. S6. *J-V* characteristics of PTB7:PC₇₁BM based OSCs without and with *H*-P(NDI2OD-T2) additive (0.8 *wt*%) to exposure at different temperatures (30, 60, 80, 100, and 120 °C).

Fig. S7. Long-term stability of PTB7:PC₇₁BM based OSCs without and with *H*-P(NDI2OD-T2) additive of 0.8 wt%.

Fig. S8. 2D GIWAXD characterizations of PTB7:PC₇₁BM with 0.8 *wt*% *H*-P(NDI2OD-T2) additive exposed to various temperatures (60, 80, 100, and 120 °C).

Fig. S9. 2D GIWAXD characterizations of PTB7:PC₇₁BM without *H*-P(NDI2OD-T2) additive exposed to various temperatures (30 and 120 $^{\circ}$ C).

Fig. S10. Histogram of PTB7:PC₇₁BM and PTB7-Th:PC₇₁BM based OSCs without and with H-P(NDI2OD-T2) additive tested in this study.

Fig. S11. ITO-free device structure.

Fig. S12. Device measurement set-up and *J-V* characteristics with and without the shadow mask.

Table S1. Summary of electrochemical properties of *L*-P(NDI2OD-T2), *I*- P(NDI2OD-T2), and *H*-P(NDI2OD-T2).

Table S2. Device performance parameters of PTB7-Th:PC₇₁BM with *H*-P(NDI2OD-T2) of 0.8 wt%.

Table S3. Device performance parameters of PTB7-Th:PC₇₁BM with *H*-P(NDI2OD-T2) of 0.8 wt% on ITO-free substrate.



Fig. S1 Cyclic voltammetry of L-P(NDI2OD-T2), I-P(NDI2OD-T2), and H-P(NDI2OD-T2).



Fig. S2 GIWAXD images of *L*-P(NDI2OD-T2), *I*-P(NDI2OD-T2), and *H*-P(NDI2OD-T2) polymer films with different molecular weights.



Fig. S3 Conventional device structure.



Fig. S4 Hole and electron mobilities of electron- and hole-only devices of PTB7:PC₇₁BM blneds with different amounts of the H-P(NDI2OD-T2) additive by a space-charge-limited current (SCLC) method.



Fig. S5 Light intensity dependence of J_{SC} on PTB7:PC₇₁BM based device with different amounts of *H*-P(NDI2OD-T2) polymer (0, 0.4, 0.8, 1.2, 1.6, and 2.0 *wt*%).



Fig. S6 *J-V* characteristics of PTB7:PC₇₁BM based OSCs without and with *H*-P(NDI2OD-T2) additive (0.8 *wt*%) to exposure at different temperatures (30, 60, 80, 100, and 120 °C).



Fig. S7 Long-term stability of PTB7:PC₇₁BM based OSCs without and with *H*-P(NDI2OD-T2) additive of 0.8 *wt*%.



Fig. S8 2D GIWAXD characterizations of PTB7:PC₇₁BM with 0.8 *wt*% *H*-P(NDI2OD-T2) additive exposed to various temperatures (60, 80, 100, and 120 °C). a, GIWAXD images. b, in-plane profile. c, out-of-plane profile.



Fig. S9 2D GIWAXD characterizations of PTB7:PC₇₁BM without *H*-P(NDI2OD-T2) additive exposed to various temperatures (30 and 120 °C). a, GIWAXD images. b, in-plane profile. c, out-of-plane profile.



Fig. S10 Histogram of PTB7:PC₇₁BM and PTB7-Th:PC₇₁BM based OSCs without and with *H*-P(NDI2OD-T2) additive tested in this study.



Fig. S11 ITO-free device structure.



Fig. S12 Device measurement set-up and *J-V* characteristics with and without the shadow mask. a, Digital image of the test jig and shadow mask. b, PTB7- and c, PTB7-Th-based organic solar cells with 0.8 *wt*% P(NDI2OD-T2) additive: The substrate size is 15 mm × 15 mm which contains 4 individual cells, and the device (i.e., cell) area for glass/ITO based OSCs is 13 mm² (6.5 mm × 2 mm) and shadow mask size is also 13 mm² (6.5 mm × 2 mm).

Table S1. Summary of physical properties of *L*-P(NDI2OD-T2), *I*- P(NDI2OD-T2), and *H*-P(NDI2OD-T2).

<i>n</i> -type polymer	LUMO (eV) ^a	HOMO (eV) ^c	Bandgap E _{opt} (eV) ^b
H-P(NDI2OD-T2)	-3.88	-5.37	1.49
I-P(NDI2OD-T2)	-3.88	-5.37	1.49
L-P(NDI2OD-T2)	-3.87	-5.36	1.49

^aCyclic voltammetry determined with Fc/Fc⁺ (*E*HOMO = - 4.80 eV) as the internal reference. ^cDetermined by subtracting the optical bandgap from reduction potential. ^bDetermined from the onset of the absorption of the thin film.

Table S2. Device performance parameters of PTB7-Th:PC₇₁BM with *H*-P(NDI2OD-T2) of

0.8 *wt*%.

P(NDI2OD-T2) (<i>wt%</i>)	$J_{ m SC}$	V _{OC}	FF	PCE (%)
	(mA cm ⁻²)	(V)	(%)	max./avg.
w/o	19.2±0.5	0.78±0.02	61±2	9.86/9.62
0.8 <i>wt%</i>	23.0±0.5	0.81±0.01	61±1	11.60/11.25

Table S3. Device performance parameters of PTB7-Th:PC₇₁BM with *H*-P(NDI2OD-T2) of

0.8 *wt*% on ITO-free substrate.

P(NDI2OD-T2) (<i>wt</i> %)	J _{SC} (mA cm ⁻²)	V _{OC} (V)	FF (%)	PCE (%) max./avg.
w/o	14.1±0.2	0.61±0.02	35±2	3.18/2.92
0.8 wt%	15.1±0.5	0.78±0.02	48±1	5.66/5.24