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 blends 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:PC\(_{71}\)BM 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:PC\(_{71}\)BM 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:PC\(_{71}\)BM based OSCs without and with \( H\)-P(NDI2OD-T2) additive of 0.8 wt\%.

Fig. S8. 2D GIWAXD characterizations of PTB7:PC\(_{71}\)BM 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:PC\(_{71}\)BM without \( H\)-P(NDI2OD-T2) additive exposed to various temperatures (30 and 120 °C).

Fig. S10. Histogram of PTB7:PC\(_{71}\)BM and PTB7-Th:PC\(_{71}\)BM 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:PC\(_{71}\)BM with \( H\)-P(NDI2OD-T2) of 0.8 wt\%.

Table S3. Device performance parameters of PTB7-Th:PC\(_{71}\)BM 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:PC$_{71}$BM blends 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:PC$_{71}$BM 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:PC$_{71}$BM 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:PC$_{71}$BM based OSCs without and with H-P(NDI2OD-T2) additive of 0.8 wt%.

Fig. S8 2D GIWAXD characterizations of PTB7:PC$_{71}$BM 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:PC_{71}BM 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:PC_{71}BM and PTB7-Th:PC_{71}BM 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 $\times$ 15 mm which contains 4 individual cells, and the device (i.e., cell) area for glass/ITO based OSCs is 13 mm$^2$ (6.5 mm $\times$ 2 mm) and shadow mask size is also 13 mm$^2$ (6.5 mm $\times$ 2 mm).

Table S1. Summary of physical properties of $L$-P(NDI2OD-T2), $I$-P(NDI2OD-T2), and $H$-P(NDI2OD-T2).
<table>
<thead>
<tr>
<th>n-type polymer</th>
<th>LUMO (eV)(^a)</th>
<th>HOMO (eV)(^c)</th>
<th>Bandgap (E_{\text{opt}}) (eV)(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(H)-P(NDI2OD-T2)</td>
<td>-3.88</td>
<td>-5.37</td>
<td>1.49</td>
</tr>
<tr>
<td>(I)-P(NDI2OD-T2)</td>
<td>-3.88</td>
<td>-5.37</td>
<td>1.49</td>
</tr>
<tr>
<td>(L)-P(NDI2OD-T2)</td>
<td>-3.87</td>
<td>-5.36</td>
<td>1.49</td>
</tr>
</tbody>
</table>

\(^a\)Cyclic voltammetry determined with \(\text{Fc/Fc}^+\) (\(\Delta\text{HOMO} = - 4.80\) eV) as the internal reference.
\(^b\)Determined by subtracting the optical bandgap from reduction potential. \(^c\)Determined from the onset of the absorption of the thin film.

**Table S2.** Device performance parameters of PTB7-Th:PC\(_{71}\)BM with \(H\)-P(NDI2OD-T2) of 0.8 wt%.

<table>
<thead>
<tr>
<th>P(NDI2OD-T2) (wt%)</th>
<th>(J_{\text{sc}}) (mA cm(^{-2}))</th>
<th>(V_{\text{oc}}) (V)</th>
<th>(FF) (%)</th>
<th>PCE (%) max./avg.</th>
</tr>
</thead>
<tbody>
<tr>
<td>w/o</td>
<td>19.2±0.5</td>
<td>0.78±0.02</td>
<td>61±2</td>
<td>9.86/9.62</td>
</tr>
<tr>
<td>0.8 wt%</td>
<td>23.0±0.5</td>
<td>0.81±0.01</td>
<td>61±1</td>
<td>11.60/11.25</td>
</tr>
</tbody>
</table>

**Table S3.** Device performance parameters of PTB7-Th:PC\(_{71}\)BM with \(H\)-P(NDI2OD-T2) of 0.8 wt% on ITO-free substrate.

<table>
<thead>
<tr>
<th>P(NDI2OD-T2) (wt%)</th>
<th>(J_{\text{sc}}) (mA cm(^{-2}))</th>
<th>(V_{\text{oc}}) (V)</th>
<th>(FF) (%)</th>
<th>PCE (%) max./avg.</th>
</tr>
</thead>
<tbody>
<tr>
<td>w/o</td>
<td>14.1±0.2</td>
<td>0.61±0.02</td>
<td>35±2</td>
<td>3.18/2.92</td>
</tr>
<tr>
<td>0.8 wt%</td>
<td>15.1±0.5</td>
<td>0.78±0.02</td>
<td>48±1</td>
<td>5.66/5.24</td>
</tr>
</tbody>
</table>