Supporting Information

A Ring-Perfluorinated Nonvolatile Additives with a High Dielectric Constant Lead to Highly Efficient and Stable Organic Solar Cells

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Scheme S1. Synthetic routes of PS, PS-\textit{b}-PPFS and PPFS polymer additives.

Fig. S1 $^1$H NMR data of PS-br
Fig. S2 $^1$H NMR data of PS-$b$-PPFS

Fig. S3 $^1$H NMR data of PPFS
Fig. S4 The $J$-$V$ curves for PBDB-TT5:ITIC films with different concentration of each additive: (a) DIO, (b) PS, (c) PS-\textit{b}-PPFS, and (d) PPFS under AM 1.5G simulated solar radiation at 100mW cm$^{-2}$
Table S1. Photovoltaic parameters of NF-OSCs with different concentration of each additive.

<table>
<thead>
<tr>
<th>Additive (v/v)</th>
<th>$V_{OC}$ a) [V]</th>
<th>$J_{SC}$ a) [mA cm$^{-2}$]</th>
<th>FF a)</th>
<th>PCE a) [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1% DIO</td>
<td>0.904 (0.906±0.003)</td>
<td>13.15 (13.09±0.18)</td>
<td>63.55 (62.78±0.80)</td>
<td>7.58 (7.50±0.07)</td>
</tr>
<tr>
<td>2% DIO</td>
<td>0.889 (0.887±0.001)</td>
<td>9.16 (8.98±0.31)</td>
<td>59.69 (59.42±0.28)</td>
<td>4.86 (4.61±0.25)</td>
</tr>
<tr>
<td>3% DIO</td>
<td>0.849 (0.850±0.002)</td>
<td>6.39 (6.16±0.14)</td>
<td>44.09 (44.45±0.38)</td>
<td>2.39 (2.35±0.04)</td>
</tr>
<tr>
<td>1% PS</td>
<td>0.881 (0.882±0.011)</td>
<td>15.02 (14.99±0.15)</td>
<td>63.84 (63.46±0.57)</td>
<td>8.45 (8.39±0.06)</td>
</tr>
<tr>
<td>3% PS</td>
<td>0.894 (0.886±0.008)</td>
<td>14.87 (14.81±0.11)</td>
<td>64.01 (64.46±0.40)</td>
<td>8.51 (8.48±0.02)</td>
</tr>
<tr>
<td>4% PS</td>
<td>0.872 (0.876±0.003)</td>
<td>14.60 (14.83±0.14)</td>
<td>61.51 (60.94±0.56)</td>
<td>8.19 (8.07±0.12)</td>
</tr>
<tr>
<td>5% PS</td>
<td>0.886 (0.885±0.004)</td>
<td>13.37 (13.18±0.21)</td>
<td>50.01 (49.63±0.38)</td>
<td>5.92 (5.87±0.06)</td>
</tr>
<tr>
<td>1% PS-b-PPFS</td>
<td>0.887 (0.884±0.004)</td>
<td>14.46 (14.21±0.19)</td>
<td>67.92 (67.71±0.26)</td>
<td>8.51 (8.45±0.10)</td>
</tr>
<tr>
<td>3% PS-b-PPFS</td>
<td>0.882 (0.877±0.004)</td>
<td>15.00 (14.85±0.15)</td>
<td>64.90 (64.43±0.45)</td>
<td>8.42 (8.39±0.05)</td>
</tr>
<tr>
<td>4% PS-b-PPFS</td>
<td>0.901 (0.879±0.03)</td>
<td>13.62 (13.40±0.22)</td>
<td>69.01 (68.85±0.12)</td>
<td>8.10 (8.09±0.01)</td>
</tr>
<tr>
<td>5% PS-b-PPFS</td>
<td>0.884 (0.881±0.002)</td>
<td>14.77 (14.62±0.11)</td>
<td>63.90 (63.70±0.24)</td>
<td>8.22 (8.07±0.15)</td>
</tr>
<tr>
<td>1% PPFS</td>
<td>0.882 (0.876±0.004)</td>
<td>15.37 (14.88±0.48)</td>
<td>67.20 (66.85±0.37)</td>
<td>8.53 (8.43±0.10)</td>
</tr>
<tr>
<td>3% PPFS</td>
<td>0.894 (0.889±0.005)</td>
<td>15.19 (15.02±0.16)</td>
<td>65.75 (64.88±1.0)</td>
<td>8.87 (8.66±0.22)</td>
</tr>
<tr>
<td>4% PPFS</td>
<td>0.897 (0.886±0.007)</td>
<td>15.10 (14.74±0.34)</td>
<td>68.69 (67.42±0.9)</td>
<td>8.70 (8.53±0.17)</td>
</tr>
<tr>
<td>5% PPFS</td>
<td>0.889 (0.886±0.002)</td>
<td>15.92 (15.73±0.22)</td>
<td>66.02 (66.01±0.12)</td>
<td>8.51 (8.38±0.14)</td>
</tr>
</tbody>
</table>

a) The values in the parentheses are the average values obtained from over 16 devices.
**Fig. S5** *Dark J^{1/2}-V plots* for the (a) electron-only, (b) hole-only devices based on the PBDB-TT5:ITIC blend films.

**Table S2.** The $P(E, T)$ values at short-circuit condition and maximum power output condition.

<table>
<thead>
<tr>
<th>Devices</th>
<th>$P(E, T)$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>At short-circuit</td>
</tr>
<tr>
<td>w/o additive</td>
<td>92.3</td>
</tr>
<tr>
<td>0.5% DIO</td>
<td>93.5</td>
</tr>
<tr>
<td>2% PS</td>
<td>95.2</td>
</tr>
<tr>
<td>2% PS-b-PPFS</td>
<td>94.6</td>
</tr>
<tr>
<td>2% PPFS</td>
<td>95.8</td>
</tr>
</tbody>
</table>
Table S3. The GIWAX parameters of out-of-plane and in-plane.

<table>
<thead>
<tr>
<th>Additive</th>
<th>Out-of-Plane</th>
<th>In-Plane</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>π-π stacking cell axis (010)</td>
<td>Unit cell long axis (100)</td>
</tr>
<tr>
<td></td>
<td>$q$ (Å$^{-1}$)</td>
<td>d-spacing (Å)</td>
</tr>
<tr>
<td>w/o additive</td>
<td>1.685</td>
<td>3.723</td>
</tr>
<tr>
<td>0.5% DIO</td>
<td>1.692</td>
<td>3.713</td>
</tr>
<tr>
<td>2% PS</td>
<td>1.695</td>
<td>3.707</td>
</tr>
<tr>
<td>2% PS-b-PPFS</td>
<td>1.692</td>
<td>3.714</td>
</tr>
<tr>
<td>2% PPFS</td>
<td>1.696</td>
<td>3.704</td>
</tr>
</tbody>
</table>

Fig. S6 The AFM height images in 4μm x 4μm (top) and TEM images of the blend film (bottom): (i) w/o additive, (ii) DIO, (iii) PS, (iv) PS-b-PPFS, and (v) PPFS.
Fig. S7 Device stability of the different processing additive contained films under different conditions: (a), (b) annealing-temperature stability in the N$_2$-filled glovebox; (c),(d) thermal-time stability at 150 °C; (e), (f) in the N$_2$-filled glovebox without capsulation of the long-term stability.
**Fig. S8** Frequency dependence of the (a) capacitance and (b) dielectric constant in the blend system.

**Fig. S9** Chemical structures of donors and acceptors used in other host systems.
**Fig. S10** The $J-V$ curves with optimal concentration additive (a) J71:ITIC, (b) PTB7-Th:PC$_{71}$BM, and (c) PTB7-Th:PNDI-T10.
Table S4. Photovoltaic parameters having different types of active layers with and without additives.

<table>
<thead>
<tr>
<th>Devices</th>
<th>Additive</th>
<th>$V_{oc}$(^{a)}) [V]</th>
<th>$J_{sc}$(^{a)}) [mA/cm(^2)]</th>
<th>FF (^{a)})</th>
<th>PCE (^{a)}) [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>J71:ITIC</td>
<td>X</td>
<td>0.919 (0.913±0.003)</td>
<td>17.15 (17.01±0.14)</td>
<td>61.30 (61.08±0.20)</td>
<td>9.68 (9.52±0.12)</td>
</tr>
<tr>
<td></td>
<td>0.5% DIO</td>
<td>0.922 (0.919±0.007)</td>
<td>15.38 (15.38±0.13)</td>
<td>56.01</td>
<td>7.96 (7.79±0.19)</td>
</tr>
<tr>
<td></td>
<td>1% PPFS</td>
<td>0.924 (0.927±0.006)</td>
<td>17.38 (17.08±0.40)</td>
<td>66.20</td>
<td>10.70 (10.45±0.23)</td>
</tr>
<tr>
<td>PTB7-Th:PC(_{71})BM</td>
<td>X</td>
<td>0.785 (0.792±0.006)</td>
<td>15.60 (15.28±0.38)</td>
<td>67.64</td>
<td>8.29 (8.05±0.24)</td>
</tr>
<tr>
<td></td>
<td>3% DIO</td>
<td>0.792 (0.793±0.003)</td>
<td>17.69 (17.45±0.25)</td>
<td>69.21</td>
<td>9.40 (9.21±0.20)</td>
</tr>
<tr>
<td></td>
<td>2% PPFS</td>
<td>0.805 (0.804±0.008)</td>
<td>15.49 (15.76±0.26)</td>
<td>69.67</td>
<td>8.70 (8.58±0.06)</td>
</tr>
<tr>
<td>PTB7-Th:PNDI-T10</td>
<td>X</td>
<td>0.793 (0.803±0.004)</td>
<td>12.74 (12.49±0.24)</td>
<td>56.21</td>
<td>5.68 (5.60±0.14)</td>
</tr>
<tr>
<td></td>
<td>1% DIO</td>
<td>0.782 (0.786±0.012)</td>
<td>12.44 (12.09±0.58)</td>
<td>46.51</td>
<td>4.52 (4.15±0.60)</td>
</tr>
<tr>
<td></td>
<td>2% PPFS</td>
<td>0.795 (0.799±0.003)</td>
<td>13.69 (13.52±0.17)</td>
<td>56.10</td>
<td>6.10 (6.01±0.12)</td>
</tr>
</tbody>
</table>

\(^{a)}\) The values in the parentheses are the average values obtained from over 16 devices.