Supplementary Information

Incredible PCE Enhancement Induced by Damaged Perovskite Layers: Deeply Understanding the Working Principle of Additives in Bulk Heterojunction Perovskite Solar Cells

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Fig. S1. J-V curves of the champion M-PSCs and M-BHJ-PSCs with 0.01 wt% Spiro-OMeTAD additive.
The crystallization of perovskite layer was deterred by Spiro-OMeTAD additive, even an extremely low concentration (0.01 wt%), which could be observed from XRD results shown as Fig. S3 and Table 2. With more Spiro-OMeTAD additive, the full width of peaks at half maxima (FWHM) of the perovskite crystal in XRD increased. From equation of Debye-Scherrer:

\[ D = \frac{K \lambda}{B \cos \theta} \]

Where D is size of perovskite crystal, K is constant of Scherrer, B is FWHM, \( \theta \) is angle of diffraction. Therefore, the Spiro-OMeTAD additive shows a negative role in the crystallization of perovskite film, because the size of perovskite layer decreased with FWHM increasing.

Table 2 XRD parameter full width of peaks at half maxima (FWHM) of perovskite layer in M-PSCs and M-BHJ-PSCs with different Spiro-OMeTAD additive.

<table>
<thead>
<tr>
<th>Spiro-OMeTAD additive (wt%)</th>
<th>FWHM( ( 2\theta=14.1^\circ ))</th>
<th>FWHM( ( 2\theta=28.4^\circ ))</th>
<th>FWHM( ( 2\theta=31.8^\circ ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.178</td>
<td>0.170</td>
<td>0.186</td>
</tr>
</tbody>
</table>
Fig. S4 (a) J-V curves of the champion planar PSCs (MAPbI$_3$) and planar BHJ-PSCs (MAPbI$_3$) with 0.01 wt% Spiro-OMeTAD additive measured under simulated AM 1.5G (100 mW cm$^{-2}$) illumination and dark with a reverse voltage scanning mode; (b) IPCE curves of the champion planar PSCs (MAPbI$_3$) and planar BHJ-PSCs (MAPbI$_3$) with 0.01 wt% Spiro-OMeTAD additive.

Fig. S5 J-V curves of the champion planar PSCs (MAPbI$_3$) and planar BHJ-PSCs (MAPbI$_3$) with 0.01 wt% Spiro-OMeTAD additive.

Fig. S6 Steady-state efficiencies measurements in planar PSCs (MAPbI$_3$) and planar BHJ-PSCs (MAPbI$_3$).
Table 3. Photovoltaic parameters based on planar BHJ-PSCs (MAPbI$_3$) with different Spiro-OMeTAD additive.

<table>
<thead>
<tr>
<th>Spiro-OMeTAD additive</th>
<th>Voc [V]</th>
<th>Jsc [mA cm$^{-2}$]</th>
<th>FF</th>
<th>PCE [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 wt%</td>
<td>Average</td>
<td>0.83±0.03</td>
<td>14.54±1.27</td>
<td>0.68±0.05</td>
</tr>
<tr>
<td></td>
<td>Champion</td>
<td>0.85</td>
<td>14.98</td>
<td>0.71</td>
</tr>
<tr>
<td>0.01 wt%</td>
<td>Average</td>
<td>0.87±0.04</td>
<td>16.68±1.19</td>
<td>0.71±0.03</td>
</tr>
<tr>
<td></td>
<td>Champion</td>
<td>0.91</td>
<td>16.28</td>
<td>0.74</td>
</tr>
<tr>
<td>0.03 wt%</td>
<td>Average</td>
<td>0.83±0.03</td>
<td>14.50±1.88</td>
<td>0.69±0.04</td>
</tr>
<tr>
<td></td>
<td>Champion</td>
<td>0.87</td>
<td>14.59</td>
<td>0.70</td>
</tr>
<tr>
<td>0.05 wt%</td>
<td>Average</td>
<td>0.83±0.03</td>
<td>10.59±2.08</td>
<td>0.68±0.09</td>
</tr>
<tr>
<td></td>
<td>Champion</td>
<td>0.84</td>
<td>12.02</td>
<td>0.69</td>
</tr>
<tr>
<td>0.1 wt%</td>
<td>Average</td>
<td>0.78±0.05</td>
<td>7.77±2.67</td>
<td>0.67±0.06</td>
</tr>
<tr>
<td></td>
<td>Champion</td>
<td>0.81</td>
<td>8.89</td>
<td>0.69</td>
</tr>
</tbody>
</table>

Data in parentheses are the average values of the fabricated 30 PSCs.

Fig. S7. J-V curves of the champion planar PSCs and planar BHJ-PSCs (MAPbI$_{3-x}$Cl$_x$) with 0.01 wt% Spiro-OMeTAD additive.

Table 4 Photovoltaic parameters based on planar BHJ-PSCs with different Spiro-OMeTAD additive.

<table>
<thead>
<tr>
<th>Spiro-OMeTAD additive</th>
<th>Voc [V]</th>
<th>Jsc [mA cm$^{-2}$]</th>
<th>FF</th>
<th>PCE [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 wt%</td>
<td>Average</td>
<td>0.94±0.02</td>
<td>20.39±0.79</td>
<td>0.73±0.01</td>
</tr>
<tr>
<td></td>
<td>Champion</td>
<td>0.95</td>
<td>21.72</td>
<td>0.74</td>
</tr>
<tr>
<td>0.01 wt%</td>
<td>Average</td>
<td>0.91±0.02</td>
<td>18.28±0.89</td>
<td>0.73±0.02</td>
</tr>
<tr>
<td></td>
<td>Champion</td>
<td>0.93</td>
<td>20.54</td>
<td>0.73</td>
</tr>
<tr>
<td>0.03 wt%</td>
<td>Average</td>
<td>0.89±0.04</td>
<td>16.76±1.29</td>
<td>0.73±0.01</td>
</tr>
<tr>
<td></td>
<td>Champion</td>
<td>0.91</td>
<td>19.16</td>
<td>0.74</td>
</tr>
<tr>
<td>0.05 wt%</td>
<td>Average</td>
<td>0.87±0.03</td>
<td>15.38±0.91</td>
<td>0.73±0.01</td>
</tr>
<tr>
<td></td>
<td>Champion</td>
<td>0.93</td>
<td>16.89</td>
<td>0.71</td>
</tr>
<tr>
<td>0.1 wt%</td>
<td>Average</td>
<td>0.86±0.03</td>
<td>14.35±1.22</td>
<td>0.73±0.02</td>
</tr>
<tr>
<td></td>
<td>Champion</td>
<td>0.90</td>
<td>15.81</td>
<td>0.72</td>
</tr>
</tbody>
</table>

Data in parentheses are the average values of the fabricated 50 PSCs.
Fig. S7. Jsc, Voc, FF and PCE values versus different percentages by weight of Spiro-OMeTAD additive to mixed halide perovskite (MAPbI$_{3-x}$Cl$_x$) in planar BHJ-PSCs.

Fig. S8. Steady-state efficiencies measurements in planar PSCs (MAPbI$_{3-x}$Cl$_x$) and planar BHJ-PSCs (MAPbI$_{3-x}$Cl$_x$).
Fig. S9. (a-c) Sequence of Nyquist plot of PSCs based on planar BHJ-PSCs (MAPbI$_{3-x}$Cl$_x$ light absorber) with different ratio of Spiro-OMeTAD additive in dark at 0.6 V, (d) was the equivalent circuit.