Electronic Supplemental Information for

**Pyridine-functionalized Fullerene Additive Enabling Coordination Interactions with CH$_3$NH$_3$PbI$_3$ Perovskite towards Highly Efficient Bulk Heterojunction Solar Cells**

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S1. $^1$H NMR and $^{13}$C NMR spectrum of C$_{60}$-PyP.

**Figure S1.** $^1$H NMR spectrum of C$_{60}$-PyP in CS$_2$/d-acetone solution.

**Figure S2.** $^{13}$C NMR spectrum of C$_{60}$-PyP in CS$_2$/d-acetone solution.
S2. Mass spectrum of C\textsubscript{60}-PyP.

![Mass spectrum of C\textsubscript{60}-PyP](image)

**Figure S3.** MALDI-TOF Mass spectra of C\textsubscript{60}-PyP.

S3. Estimation of the energy levels of C\textsubscript{60}-PyP.

**Table S1.** Electrochemical data of C\textsubscript{60}-PyP and PCBM.

<table>
<thead>
<tr>
<th></th>
<th>λ\textsubscript{onset}\textsuperscript{a} (nm)</th>
<th>E\textsubscript{g, opt}\textsuperscript{b} (eV)</th>
<th>E\textsubscript{red, onset}\textsuperscript{c} (eV)</th>
<th>E\textsubscript{LUMO}\textsuperscript{d} (eV)</th>
<th>E\textsubscript{HOMO}\textsuperscript{e} (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C\textsubscript{60}-PyP</td>
<td>723</td>
<td>1.72</td>
<td>-0.94</td>
<td>-3.89</td>
<td>-5.61</td>
</tr>
<tr>
<td>C\textsubscript{60}-MPy</td>
<td>724</td>
<td>1.71</td>
<td>-1.00</td>
<td>-3.80</td>
<td>-5.51</td>
</tr>
<tr>
<td>C\textsubscript{60}-Bpy</td>
<td>724</td>
<td>1.71</td>
<td>-0.99</td>
<td>-3.81</td>
<td>-5.52</td>
</tr>
<tr>
<td>C\textsubscript{60}-HPy</td>
<td>724</td>
<td>1.71</td>
<td>-0.97</td>
<td>-3.83</td>
<td>-5.54</td>
</tr>
<tr>
<td>PCBM</td>
<td>725</td>
<td>1.71</td>
<td>-0.98</td>
<td>-3.82</td>
<td>-5.53</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Attained from UV-vis spectrum; \textsuperscript{b} E\textsubscript{g, opt}=1240/λ\textsubscript{onset}; \textsuperscript{c} Referred to the half wave potential of ferrocene; \textsuperscript{d} E\textsubscript{LUMO}=−e(E\textsubscript{red, onset} +4.8 V); \textsuperscript{e} E\textsubscript{HOMO}=E\textsubscript{LUMO}−E\textsubscript{g, opt}
The structure of PCBM and C_{60}-Py.

The energy levels of the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) of the fullerene derivatives were estimated by a cyclic voltammetry study in combination with UV-Vis absorption spectroscopy. Cyclic voltammetry study was performed in o-dichlorobenzene with a CHI 630D potentiostat (CHI Instrument, U.S.A.) at room temperature. The supporting electrolyte was tetrabutylammonium perchlorate (TBPA, electrochemical grade, Fluka). A standard three-electrode arrangement of a platinum (Pt) wire as counter electrode, a platinum coil as working electrode, and a saturated calomel electrode as a pseudo-reference electrode was used. In a comparison experiment, ferrocene (Fc) was added as the internal standard and all potentials are referred to the Fc^+/Fc couple.

The onset reduction potentials (E_{red, onset}) of C_{60}-PyP, C_{60}-BPy was estimated to be -0.94 V vs Fc^+/Fc. Thus, the LUMO energy levels of C_{60}-PyP was calculated by E_{LUMO} = -e(E_{red, onset} + 4.8). The HOMO energy level of C_{60}-PyP was calculated by E_{HOMO} = E_{g, opt} - E_{LUMO}, where E_{g, opt} is the optical bandgap. Based on the onset (λ_{onset}) of UV-vis absorption spectrum of C_{60}-PyP (~723 nm, see Fig. 2b), E_{g, opt} is estimated to be ~ 1.72 eV, according to the equation: E_{g, opt} = 1240/λ_{onset}. Therefore, the HOMO energy levels of C_{60}-PyP was estimated to be -5.61 eV. The data of PCBM and C_{60}-Py are quoted from Ref. S2.
S4. TGA analysis of C$_{60}$-PyP.

![TGA Curve](image)

**Figure S4.** TGA curve (solid line) and differential thermo-gravimetric (DTG) curve (dashed line) of C$_{60}$-PyP.

S5. UV-vis spectra of the MAPbI$_3$ perovskite with varying C$_{60}$-PyP concentration.

![UV-vis Spectra](image)

**Figure S5.** UV-vis spectra of the MAPbI$_3$ perovskite with varying C$_{60}$-PyP concentration.

S6. PCE histograms of the control and 0.13 wt% devices.
Figure S6. PCE histograms of the control and 0.13 wt% devices.

S7. Photovoltaic parameters box plots of devices with varying C$_{60}$-PyP concentration.

Figure S7. Box plots of $V_{oc}$ (a), $J_{sc}$ (b), FF (c) and PCE (d) for PSC devices with varying C$_{60}$-PyP concentration.

S8. Hysteresis characterization of devices with and without 0.13 wt% C$_{60}$-PyP.

Table S2. Photovoltaic parameters of the devices in different scan directions with 0.1 V/s scan rate.
Hysteresis Factor = \[\frac{\text{PCE (reverse)} - \text{PCE (forward)}}{\text{PCE (reverse)}}\]

Table S3. Photovoltaic parameters of the control and 0.13 wt% PSC devices with different scan rates.

<table>
<thead>
<tr>
<th>Device</th>
<th>Scan Rate</th>
<th>(V_{oc}) (V)</th>
<th>(J_{sc}) (mA/cm(^2))</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>(R_s) ((\Omega\cdot\text{cm}^2))</th>
<th>(R_{sh}) ((\Omega\cdot\text{cm}^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>0.01 V/s</td>
<td>1.031</td>
<td>20.40</td>
<td>70.20</td>
<td>14.77</td>
<td>13.43</td>
<td>1556.63</td>
</tr>
<tr>
<td></td>
<td>0.1 V/s</td>
<td>1.082</td>
<td>21.01</td>
<td>73.65</td>
<td>16.74</td>
<td>13.35</td>
<td>1170.35</td>
</tr>
<tr>
<td></td>
<td>1 V/s</td>
<td>1.084</td>
<td>21.60</td>
<td>72.50</td>
<td>16.98</td>
<td>5.43</td>
<td>1208.30</td>
</tr>
<tr>
<td>0.13 wt%</td>
<td>0.01 V/s</td>
<td>1.087</td>
<td>21.10</td>
<td>77.65</td>
<td>17.81</td>
<td>4.68</td>
<td>7201.70</td>
</tr>
<tr>
<td></td>
<td>0.1 V/s</td>
<td>1.092</td>
<td>22.25</td>
<td>77.26</td>
<td>18.77</td>
<td>4.41</td>
<td>3584.64</td>
</tr>
<tr>
<td></td>
<td>1 V/s</td>
<td>1.093</td>
<td>22.50</td>
<td>77.50</td>
<td>19.05</td>
<td>4.46</td>
<td>3991.21</td>
</tr>
</tbody>
</table>

S9. Histograms of grain size distributions of the MAPbI\(_3\) perovskite film with varying C\(_{60}\)-PyP concentration.
Figure S9. Histograms of grain size distributions of the MAPbI$_3$ perovskite film with varying C$_{60}$-PyP concentration.

S10. XPS profile of I 3d of the CH$_3$NH$_3$PbI$_3$ perovskite films without and with 1.0 wt% C$_{60}$-PyP doping.

Figure S10. I 3d XPS spectra of the CH$_3$NH$_3$PbI$_3$ perovskite films without and with 1.0 wt% C$_{60}$-PyP doping.

S11. Analysis of time-resolved photoluminescence (TRPL) spectra of the perovskite films with or without C$_{60}$-PyP.

The excitation source was a 543 nm picosecond laser pulse which was filtered from a super continuum generation. The TRPL spectrum can be fitted by a single-exponential decay function as shown in equation (S1):$^{[3-5]}

$$f(t) = A \cdot \exp\left(-\frac{t}{\tau}\right) + B \quad (S1)$$

Where A, $\tau$ and B are the decay amplitude, the decay lifetime, and a constant for the baseline offset, respectively. The pristine MAPbI$_3$ perovskite film shows a lifetime of
\( \tau = 39.41 \text{ ns}, \) which is similar to those reported values for perovskite film fabricated under similar conditions. After the addition of \( \text{C}_{60}\)-PyP, the \( \tau \) value dramatically increases to 8.82.

**S12. Fitted EIS data for Control and 0.13 wt% devices.**

From the Nyquist plot (Figure 5f), the impedance spectra were fitted with one R-CPE arcs, which a resistor \( R_s \) (series resistance) and parallel with an R-CPE elements. \( R_s \) is determined by the starting point at the real part of the Nyquist plot. The \( R_{ct} \) (charge transfer resistance) is related to the charge transfer dynamics of devices, CPE is the non-ideal chemical capacitances.

**Table S4.** Fitted EIS data for Control and 0.13 wt% devices.

<table>
<thead>
<tr>
<th>Device</th>
<th>( R_s ) (( \Omega \cdot \text{cm}^2 ))</th>
<th>( R_{ct} ) (( \Omega \cdot \text{cm}^2 ))</th>
<th>CPE-T (( \text{F/cm}^2 ))</th>
<th>CPE-P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>2.802</td>
<td>32.45</td>
<td>3.12E-07</td>
<td>0.993</td>
</tr>
<tr>
<td>0.13wt%</td>
<td>1.385</td>
<td>23.71</td>
<td>3.24E-07</td>
<td>0.989</td>
</tr>
</tbody>
</table>

**S13. J-V curves and the stabilized photocurrent densities and power outputs measured at the maximum power.**
Figure S11. J-V curves (a-b) and the stabilized photocurrent densities and power outputs (c-d) measured at the maximum power points (labelled in curves a-b) of the control and 0.13 wt% devices. For J-V curve measurements, the scanning direction is from open-circuit voltage to short circuit (reverse) and the measurements were carried out with 0.1 V/s scan rate.

Table S5. Photovoltaic parameters of the Control and 0.13 wt% devices

<table>
<thead>
<tr>
<th>Device</th>
<th>V_{oc} (V)</th>
<th>J_{sc} (mA/cm²)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>Maximum power point (V)</th>
<th>Stabilized J (mA/cm²)</th>
<th>Stabilized PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>1.079</td>
<td>21.03</td>
<td>75.14</td>
<td>17.05</td>
<td>0.892</td>
<td>17.50</td>
<td>15.61</td>
</tr>
<tr>
<td>0.13 wt%</td>
<td>1.098</td>
<td>22.47</td>
<td>78.84</td>
<td>19.45</td>
<td>0.913</td>
<td>20.40</td>
<td>18.63</td>
</tr>
</tbody>
</table>

S14. Ambient stabilities of the control and C_{60}-PyP doped perovskite films.
Figure S12. XRD patterns of the control and 0.13 wt% perovskite films before and after ambient storage for 30 days.

Figure S13. Surface topographic SEM of the MAPbI₃ perovskite film with varying C₆₀-Pyridine concentration after storage for 24h at 80% humidity. (a) Pristine film without C₆₀-PyP, (b) with 0.13 wt% C₆₀-PyP, and (c) with 1 wt% C₆₀-PyP.

Reference:

