Electronic Supplemental Information for

Successive surface engineering of TiO$_2$ compact layer via dual modification of fullerene derivatives affording hysteresis-suppressed high-performance perovskite solar cells

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S1. UV-vis absorption and XPS spectra of PC₆₁BM and C₆₀-ETA films before and after DMSO washing.

After fabricating the PC₆₁BM layer on FTO/TiO₂ substrate, pure DMSO solvent was spin-coated onto the PC₆₁BM layer at 4000 rpm for 30 s (exactly identical to the condition used for spin-coating PbI₂/DMSO solution during device fabrication). According to the comparison of the UV-vis spectra of PC₆₁BM film before and after DMSO washing, all characteristic absorption peaks are clearly observed despite of the small decreases of the intensities of several peaks (see Fig. S1). This indicates that PC₆₁BM layer may be partially washed out by DMSO, while most materials in the PC₆₁BM layer still remains on the substrate.
Figure S2. XPS spectra of PC$_{61}$BM/C$_{60}$-ETA film before and after DMSO washing in comparison with that of PC$_{61}$BM film.

C$_{60}$-ETA layer was spin-coated onto the PC$_{61}$BM layer on FTO/TiO$_2$ substrate, and DMSO solvent treatment was carried out by spin-coating pure DMSO solvent onto the PC$_{61}$BM/C$_{60}$-ETA film at 4000 rpm for 30 s. According to the comparison of the XPS survey spectra of PC$_{61}$BM/C$_{60}$-ETA film before and after DMSO washing (see Fig. S2), the N1s signal detected for the pristine PC$_{61}$BM/C$_{60}$-ETA film (curve b) is still detected in the XPS survey spectrum of the film after DMSO washing (curve c). Since C$_{60}$-ETA is the only source of N element (which is absent in the spectrum of PC$_{61}$BM film, curve a), these results confirm that C$_{60}$-ETA layer remains on PC$_{61}$BM layer after DMSO washing.
S2. Estimated void ratios of CH$_3$NH$_3$PbI$_3$ films fabricated on different substrates.

![Image](Figure S3. The pixels of whole area (A) and the pinhole area (B) of CH$_3$NH$_3$PbI$_3$ films fabricated on TiO$_2$ (a, b), TiO$_2$/C$_{60}$-ETA (c, d), TiO$_2$/PC$_{61}$BM (e, f) and TiO$_2$/PC$_{61}$BM/C$_{60}$-ETA (g, h) ETLs.)

Table S1. The estimated void ratios of CH$_3$NH$_3$PbI$_3$ films fabricated on different ETLs.

<table>
<thead>
<tr>
<th>ETL</th>
<th>Total pixels of the pinhole areas</th>
<th>Total pixels of the whole area</th>
<th>Void (pinhole) ratio $^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>12155</td>
<td>302016</td>
<td>4.02%</td>
</tr>
<tr>
<td>TiO$<em>2$/C$</em>{60}$-ETA</td>
<td>10647</td>
<td>311622</td>
<td>3.42%</td>
</tr>
<tr>
<td>TiO$<em>2$/PC$</em>{61}$BM</td>
<td>43931</td>
<td>302500</td>
<td>14.52%</td>
</tr>
<tr>
<td>TiO$<em>2$/PC$</em>{61}$BM/C$_{60}$-ETA</td>
<td>3771</td>
<td>301532</td>
<td>1.25%</td>
</tr>
</tbody>
</table>

$^a$ Void (pinhole) ratio = Total pixels of the pinhole areas / Total pixels of the whole area.
S3. AFM images of different substrates.

Figure S4. AFM phase (A) and the corresponding height (B) images of pristine TiO$_2$ (a, b), TiO$_2$/C$_{60}$-ETA (c, d), TiO$_2$/PC$_{61}$BM (e, f) and TiO$_2$/PC$_{61}$BM/C$_{60}$-ETA (g, h) films.

S4. UV-vis absorption spectra of different substrates and the corresponding perovskite films.

Figure S5. UV-vis absorption spectra of different substrates (a) and the corresponding perovskite films (b).
S5. Estimation of the energy levels of C$_{60}$-ETA.

Figure S6. (a) Cyclic voltammogram of C$_{60}$-ETA in DMSO solution with ferrocene (Fc) as the internal standard. Scan rate: 100 mV/s, TBAPF$_6$ as supporting electrolyte. The asterisk labels the oxidation peak of ferrocene. (b) Tauc’s law plot of the absorption coefficient of C$_{60}$-ETA deposited on a glass substrate.

The lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) of C$_{60}$-ETA was determined by cyclic voltammetric study and diffuse reflectance spectroscopy. The cyclic voltammetric study was performed on a CHI 660D potentiostat (CHI Instrument, USA) in dimethyl sulfoxide (DMSO) with tetrabutylammonium hexafluorophosphate (TBAPF$_6$, Puriss. electrochemical grade, Fluka) as supporting electrolyte. A standard three-electrode arrangement of a platinum (Pt) wire as working electrode, a platinum coil as counter electrode, and a silver wire as a pseudo-reference electrode was used. In comparison, ferrocene (Fc) was added as the internal standard and all potentials are referred to Fe/Fc$^+$ couple which owes an absolute energy level of -4.8 eV to vacuum. As depicted in Figure S6a, the onset reduction potentials ($E_{\text{red onset}}$) of C$_{60}$-ETA was estimated to be -1.08 V vs Fe$^+/Fc$ (which has a half-wave oxidation potential ($E_{1/2}$) at 0.70 V vs Ag$^+/Ag$). Hence the LUMO energy level of C$_{60}$-ETA is -3.72 eV calculated by $E_{\text{LUMO}}=-e(E_{\text{red onset}} + 4.8)$. S1,S2

As is seen in Fig. S6a, there is no oxidation peak was observed in the cyclic voltammogram of C$_{60}$-ETA, so the HOMO energy level of C$_{60}$-ETA is calculated by $E_{\text{HOMO}}=E_{g}^{\text{opt}} - E_{\text{LUMO}}$, and $E_{g}^{\text{opt}}$ is the optical bandgap. The bandgap ($E_{g}^{\text{opt}}$) is estimated...
by diffuse reflectance spectroscopy (Figure S6b), the conventional Tauc's law $(\alpha h\nu)^2$ as a function of the photon energy $h\nu$. The $E_g$ of C$_{60}$-ETA is estimated to be 1.88 eV according to the extrapolation of the linear part of this curve.\textsuperscript{S3} Thus HOMO energy level of C$_{60}$-ETA is estimated to be -5.60 eV calculated by $E_{HOMO}=E_g - E_{LUMO}$.

**S6. Determination of the thickness of the C$_{60}$-ETA.**

![Figure S7](image)

**Figure S7.** Surface profile of C$_{60}$-ETA measured on KLA-Tencor P6 surface profilometer. The thickness of C$_{60}$-ETA layer is ~6.3 nm.

**S7. Box plots of photovoltaic parameters.**

![Box plots](image)

**Figure S8.** Photovoltaic parameters extracted from current-voltage measurements of devices A, B, C, and D.
S8. PCE histograms of devices A and D.

![Figure S9. PCE histograms of devices A and D.](image)

S9. Stabilized current density and power output of device D.

![Figure S10. Stabilized photocurrent density and power output measured at the maximum power point (0.82 V) for device D.](image)
S10. Photovoltaic parameters of forward and reverse scans.

Table S2. Photovoltaic parameters of forward and reverse scans with 0.1 V/s scan rate for devices A and D.

<table>
<thead>
<tr>
<th>Device</th>
<th>Scan direction</th>
<th>Voc (V)</th>
<th>Jsc (mA/cm²)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>Hysteresis of PCE a</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Reverse</td>
<td>1.07</td>
<td>18.16</td>
<td>69.31</td>
<td>13.49</td>
<td>29.4%</td>
</tr>
<tr>
<td></td>
<td>Forward</td>
<td>1.05</td>
<td>18.35</td>
<td>49.36</td>
<td>9.53</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>Reverse</td>
<td>1.06</td>
<td>23.73</td>
<td>66.53</td>
<td>16.91</td>
<td>6.8%</td>
</tr>
<tr>
<td></td>
<td>Forward</td>
<td>1.05</td>
<td>23.54</td>
<td>63.73</td>
<td>15.75</td>
<td></td>
</tr>
</tbody>
</table>

a Hysteresis of PCE = (PCE(reverse) - PCE(forward))/PCE(reverse)

S11. Fitting parameters for EIS data.

Table S3. Parameters employed for the fitting of the impedance spectra of devices A, B, C and D.

<table>
<thead>
<tr>
<th>Device</th>
<th>Rs (Ω·cm²)</th>
<th>Rse (Ω·cm²)</th>
<th>Rrec (Ω·cm²)</th>
<th>CPE1 (F/cm²)</th>
<th>CPE2 (F/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>16.22</td>
<td>3289</td>
<td>9784</td>
<td>5.21E-8</td>
<td>2.95E-7</td>
</tr>
<tr>
<td>B</td>
<td>14.75</td>
<td>2343</td>
<td>15636</td>
<td>6.98E-8</td>
<td>9.86E-7</td>
</tr>
<tr>
<td>C</td>
<td>12.62</td>
<td>2540</td>
<td>17530</td>
<td>3.48E-7</td>
<td>2.51E-6</td>
</tr>
<tr>
<td>D</td>
<td>8.52</td>
<td>303</td>
<td>26373</td>
<td>2.60E-6</td>
<td>3.89E-6</td>
</tr>
</tbody>
</table>
S12. J-V curves and photovoltaic parameters of inverted perovskite solar cells based on different ETLs.

Figure S11. J–V curves of inverted perovskite solar cells containing different ETLs measured under illumination of an AM 1.5 solar simulator (100 mW·cm⁻²) in air. The inset shows the schematic structure of the device based on PC₆₁BM/C₆₀-ETA ETL.

Table S4. Photovoltaic parameters of inverted perovskite solar cells containing PC₆₁BM or PC₆₁BM/C₆₀-ETA layer as ETL.

<table>
<thead>
<tr>
<th>ETL</th>
<th>V_{oc} (V)</th>
<th>J_{sc} (mA/cm²)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>R_s (Ω·cm²)</th>
<th>R_{sh} (Ω·cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC₆₁BM</td>
<td>0.88</td>
<td>15.82</td>
<td>64.80</td>
<td>9.05</td>
<td>7.6</td>
<td>494.5</td>
</tr>
<tr>
<td>PC₆₁BM/C₆₀-ETA</td>
<td>0.92</td>
<td>17.74</td>
<td>72.23</td>
<td>11.70</td>
<td>3.9</td>
<td>1573.3</td>
</tr>
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</table>
References:

