Supplementary materials

Improving the stability and performance of perovskite solar cells via off-the-shelf post-device ligand treatment

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**Fig. S1** Zoom-in on the onset of absorption in Fig. 1b.

**Fig. S2** Top-view SEM image of the perovskite materials in the lateral region after PDL treatment.

**Fig. S3** Cross-sectional SEM image of the PVSCs after PDL treatment.
**Fig. S4** XPS peak of C 1s, N 1s, Pb 4f, and I 3d spectra obtained from the surface of as-prepared perovskite film (blue color) and perovskite removal by tape and chlorobenzene washing (red color).

**Fig. S5** XPS peak of Pb 4f obtained from the surface of control perovskite film without any treatment and the covered (active-region) perovskite with PDL treatment.
**Fig. S6** XPS peak of N 1s obtained from the surface and 10 nm depth of control perovskite film without any treatment and the covered (active-region) perovskite with PDL treatment.

**Fig. S7** Photovoltaic metrics of devices plotted as a function of duration of PDL treatment (37 cells were fabricated and tested).
**Fig. S8.** J-V curves of the PVSC (device A) measured under different scan directions.

**Table S1.** Photovoltaic parameters of PVSCs (device A) measured under different scan directions.

<table>
<thead>
<tr>
<th>PDL treatment</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
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<tbody>
<tr>
<td>Before (F)</td>
<td>22.12</td>
<td>1.06</td>
<td>79.6</td>
<td>18.67</td>
</tr>
<tr>
<td>Before (S)</td>
<td>22.03</td>
<td>1.03</td>
<td>76.9</td>
<td>17.44</td>
</tr>
<tr>
<td>After (F)</td>
<td>23.47</td>
<td>1.08</td>
<td>79.4</td>
<td>20.13</td>
</tr>
<tr>
<td>After (S)</td>
<td>23.35</td>
<td>1.06</td>
<td>78.5</td>
<td>19.44</td>
</tr>
</tbody>
</table>
Fig. S9 (a) Photovoltaic metrics of $\text{Cs}_5(\text{MA}_{0.17}\text{FA}_{0.83})_{95}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3$ PVSCs plotted as a function of duration of PDL treatment. (b) $J-V$ curves and (c) the relevant steady-state PCE of a typical $\text{Cs}_5(\text{MA}_{0.17}\text{FA}_{0.83})_{95}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3$ PVSCs without and with PDL treatment. The scan rate is 0.1V/s. 15 cells were fabricated and tested.
**Fig. S10** $J$-$V$ curves of some typical PVSCs (device A to D) in Fig. S6.

**Fig. S11** Top-view SEM images of perovskite film in a ‘poor’ PVSC (a) without (b) with LPD modification. The produced \( \text{CH}_3\text{NH}_2 \) gas during PDL treatment process can heal the defects (or pin-holes) of active region through the following reaction:

\[
\begin{align*}
\text{CH}_3\text{NH}_3\text{PbI}_3(s) + \text{CH}_3\text{NH}_2(g) & \rightarrow \text{CH}_3\text{NH}_3\text{PbI}_3-x\text{CH}_3\text{NH}_2(l)(s) & 25^\circ\text{C} \\
\text{PCE enhancement} & \approx 84\%
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3\text{NH}_3\text{PbI}_3(s) + \text{CH}_3\text{NH}_2(g) & \rightarrow \text{CH}_3\text{NH}_3\text{PbI}_3(s) + \text{CH}_3\text{NH}_2(g) & 25^\circ\text{C} \\
\text{PCE enhancement} & \approx 335\%
\end{align*}
\]
Fig. S12 Trap states density of perovskite films as determined by space-charge-limited current (SCLC) method using the electron-only device with the configuration of ITO/SnO$_2$/CH$_3$NH$_3$PbI$_3$(Cl)/C$_6$0/BCP/Ag. The trap density $N_{\text{trap}}$ is determined by the equation: $V_{\text{TFL}} = eN_{\text{trap}}L^2/(2\varepsilon\varepsilon_0)$, where $V_{\text{TFL}}$ is the trap-filed limit voltage; $L$ is the thickness of perovskite; $\varepsilon$ is the relative dielectric constant of perovskite; $\varepsilon_0$ is the vacuum permittivity.

Notes for DFT calculations

We did not consider the MAI termination since previous reports from both experiments and theories had indications that PbI$_2$-terminated [001] surface is more stable. For examples, in experiment, Lindblad et al\cite{lindblad2012} reported that a small understoichiometry in I and N atoms for the two-step synthesis of the TiO$_2$/MAPbI$_3$ interface, which indicates that surface is CH$_3$NH$_3$-poor. In theory, Haruyama et al\cite{haruyama2014} pointed out that (001) surface of tetragonal surface are flat nonpolar surface, which consists of alternate stacking of the neutral [MAI]$^0$ and [PbI$_2$]$^0$ planes. The (100) surface is constructed with stacking of the [MAPbI]$^{2+}$ and [I$_2$]$^{2-}$ layers, while the [MAI$_3$]$^{2-}$ and [Pb]$^{2+}$ layers compose the (101) surface. The calculations on surface energy show that nonpolar surface is much more stable than nonpolar surface. In conclusion, we choose PbI$_2$-tementated (001) surface since it is the most stable and common surface for MAPbI$_3$ from both experiment and theory.

The contributions of density of states of MAPbI$_3$ surface have been extensively studied in Haruyama et al\'s work. Basically, the surface states are within the band gap, which is benign for carrier recombination. However, the bandgap at surface area will be enlarged. The effect of DETA is to passivate surface by reducing its bandgap (see Fig. S14a,b).
Defect calculations on bulk MAPbI$_3$\cite{3} show that the dominating defects are Pb vacancy and MA interstitial while MA vacancy has much larger formation energy. Considering that PbI$_2$-terminated surface is intrinsically MA poor, we choose Pb vacancy for the study. We double checked the formation energies of Pb and MA vacancies on PbI$_2$-terminated (001) surface and found that the Pb vacancy are still dominating defects on surface. As shown in Fig. S14c, DETA passivation can reduce the trap states near band edge.

**Fig. S13** Calculated band structure of PbI$_2$-terminated MAPbI$_3$ (a) without (b) with DETA passivation. (c) Projected density of states show the formation of trap states in the case of PbI$_2$-termination and an absence of trap states in the case of DETA passivated PbI$_2$-termination.
**Fig. S14** Bode plot to the circuit shown in Fig. 4e.

**Fig. S15** Ultraviolet photoelectron spectra (UPS) of the control and PDL treated perovskite films.
**Fig. S16** Theoretically fitted and experimentally measured $J$-$V$ characteristics for device A and device B.

**Fig. S17** Absorption spectra of (a) unencapsulated control device, (b) unencapsulated PDL treated device, (c) encapsulated control device, and (d) encapsulated PDL treated device with time. The devices were stored in ambient environment. The humidity and temperature are 50±5 % and 25±1 degC, respectively. The encapsulated devices were sealed by commercial epoxy glue.
**Fig. S18** Real photographs of PVSCs with and without PDL treatment after MPP tracking. The electrode is silver in the picture.

**References:**

