Supporting Information

Atomic-scale insight into the enhanced surface stability of methylammonium lead iodide perovskite by controlled deposition of lead chloride

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**Supplementary Fig 9.** (a) Ultraviolet photoemission spectroscopy (UPS) spectra corresponding to the secondary electron onset region and valence features and (b) inverse photo emission (IPES) acquired on a pristine MAPbI₃ film (thickness ~4-5 nm) and PbCl₂ (0.75 ML) deposited MAPbI₃ perovskite film (thickness ~4-5 nm) deposited on Au(111). (c,d) Energy diagrams for a pristine MAPbI₃ and PbCl₂ deposited MAPbI₃ film sandwiched between HTL² and ETL¹ as an example of a solar cell architecture.

**Supplementary Fig 10.** UPS and IPES spectra of the pristine MAPbI₃ and Cl-incorporated MAPbI₃ and the VBM and CBM determination considering the intensity in linear and logarithmic scales.
**Supplementary Section 1.** Perovskite surface bandgap combined with the analyses of energy level alignments in a solar cell device
Supplementary Figs (Figs S1-S8)

**Pristine MAPbI₃**

(a) Large area STM image of pristine MAPbI₃ showing the typical grains (Scan area = 300 × 300 nm²; Sample bias voltage = −2.5 V; Tunnelling current = 50 pA).

(b) Large area STM image of Cl incorporated MAPbI₃ showing the typical grains (Scan area = 300 × 300 nm²; Sample bias voltage = −2.5 V; Tunnelling current = 70 pA).

**Fig S1:** (a) Large area STM image of pristine MAPbI₃ showing the typical grains (Scan area = 300 × 300 nm²; Sample bias voltage = −2.5 V; Tunnelling current = 50 pA). (b) Large area STM image of Cl incorporated MAPbI₃ showing the typical grains (Scan area = 300 × 300 nm²; Sample bias voltage = −2.5 V; Tunnelling current = 70 pA).
Fig S2. LT-STM images of the pristine and Cl incorporated MAPbI₃ perovskite thin films deposited on Au (111). (a) High resolution image of iodine dimer (labeled by white dashed ellipse) and iodine zigzag (labeled by white dashed ellipse and black dashed rectangle) structure (Scan area = 4.0 x 4.5 nm², Sample bias voltage = −2.70 V; Tunneling current = 10 pA). Height profiles of the observed domain labeled by red broken lines. (b) LT-STM image of 0.5 ML of PbCl₂ (4 min of deposition) incorporation in the center of a grain of the CH₃NH₃PbI₃ perovskite. Height profiles of observed Cl incorporation in the dimer structures labeled by a black dashed circle (Scan area = 3.7 x 4.8 nm², Sample bias voltage = −2.50V; Tunneling current = 100 pA). (c) Incorporated Cl close to the grain boundary labeled by the black dashed rectangle. Height profile of the observed Cl depression close to the grain boundary labeled by a white dashed circle (Scan area = 4.6 x 5.3 nm², Sample bias voltage = −2.50V; Tunneling current = 100 pA).
Fig S3: Geometrical dimer and zigzag structures of Cl incorporated MAPbI$_3$ (001) surfaces obtained by DFT calculations. (a) The side view, (b) top view of the Cl incorporated dimer structure and Cl-I bond length. (c) Simulated STM image. (d) The side view, (e) top view of the Cl incorporated zigzag structure and Cl-I bond length. (f) Simulated STM image.
Fig S4. XPS spectra and chemical composition determination of the pristine MAPbI$_3$ thin film. The non-monochromatic source related peak is indicated by an arrow in the I 3d core level region.
MAPbI$_3$ Deposition Time MAPb(I$_{1-x}$Cl$_x$)$_3$

<table>
<thead>
<tr>
<th>Deposition Time</th>
<th>[Pb] : [I] : [Cl]</th>
<th>MAPbI$<em>{2.59}$Cl$</em>{0.21}$</th>
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</thead>
<tbody>
<tr>
<td>6 minutes</td>
<td>2.8 : 0.21</td>
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Fig S5. XPS spectra and chemical composition determination of the MAPbI$_3$ thin film after 0.75 ML deposition of PbCl$_2$. 
Fig S6. XPS spectra and chemical composition determination of the MAPbI$_3$ thin film after 1.5 ML deposition of PbCl$_2$. 

<table>
<thead>
<tr>
<th>Deposition Time</th>
<th>MAPbI$_3$</th>
<th>Pb 4f, I 3d, Cl 2p ratio</th>
<th>MAPb(I$_{1-x}$Cl$_x$)$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>12 minutes</td>
<td>[Pb] : [I] : [Cl] = 1 : 3.5 : 0.8</td>
<td>MAPbI$<em>{2.7}$Cl$</em>{0.8}$</td>
<td></td>
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</table>
**Fig S7**: Possible configurations of (a,b) one Cl-Cl pair and (c,d) two Cl-I pairs appearing in the dimer structure predicted by DFT calculations. $E_t = \text{total energy.}$
**Fig S8:** Possible configurations of two Cl-I pairs appearing in the zigzag structure predicted by DFT calculations. $E_s =$ surface energy.
Supplementary Section 1. Perovskite surface bandgap combined with the analyses of energy level alignments in a perovskite solar cell device

To evaluate the effects of surface bandgap increase from 1.13 eV (pristine MAPbI$_3$) to 1.62 eV (Cl-incorporated MAPbI$_3$) on the device performance, the energy level alignments at the perovskite/ETL and perovskite/HTL interfaces were analysed (ETL = electron transport layer and HTL = hole transport layer). As an example for the analyses, we considered a well-established regular device structure composed of TiO$_2$ as ETL and 2,2',7,7'-Tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene (spiro-MeOTAD) as HTL$^{1,2,3}$. The valence band maximum (VBM) values for the pristine MAPbI$_3$ and the Cl-incorporated MAPbI$_3$ were determined by UPS measurements (Figures S9(a) and S10(a-d)) and the conduction band minimum (CBM) values were determined by IPES measurements (Figures S9(b) and S10(e-h)). The energy diagrams considering pristine MAPbI$_3$ and Cl-incorporated MAPbI$_3$ sandwiched by ETL and HTL are illustrated in Figures S9(c,d), respectively. The VBM and CBM values were referenced with respect to (w.r.t.) the Fermi level (0 eV). The difference in the energy barrier between the CBM values of pristine MAPbI$_3$ and TiO$_2$ reduces from $\sim$0.15 eV (Figure S9(c)) down to $\sim$0.03 eV (Figure S9(d)) when Cl is incorporated on the MAPbI$_3$ surface, suggesting the enhancement in open-circuit voltage (Voc) of the device. Furthermore, because the Cl-incorporated MAPbI$_3$ still shows a small barrier for electron extraction (i.e., less driving force for electron extraction from the perovskite to TiO$_2$ ETL), the current density (Jsc) is expected to be not optimal$^1$. A similar analysis is performed on the perovskite/HTL side. The energy difference between VBM of the pristine MAPbI$_3$ perovskite and the highest occupied molecular orbital (HOMO) of spiro-MeOTAD increases from $\sim$0.11 eV (Figure S9(c)) to $\sim$0.48 eV (Figure S9(c)) when Cl is incorporated on MAPbI$_3$ surface,
which leads to decrease in the overall Voc of the device. The driving force for the hole extraction is enhanced for the Cl-incorporated MAPbI₃, but further enhancement in Jsc of this device may not be expected as Jsc is limited by the small energy barrier differences at the perovskite/ETL interface. Therefore, in terms of Voc, Cl-incorporated MAPbI₃ surface would be beneficial at the interface formed with the TiO₂ ETL, but detrimental at the interface formed with the spiro-MeOTAD HTL. Cl-incorporated perovskites are also advantageous in tandem solar cells. For single-junction cells, the bandgap from 1.3 eV to 1.4 eV is ideal. But for two-junction tandem solar cells, the larger bandgap is desirable. Thus, bandgap tuning by Cl incorporation in the MAPbI₃ can make it a better choice as the top cell in a tandem solar cell. However, it is important to note that in this study, Cl incorporation mainly occurs at the surface and thus such a bandgap increase effect is only valid for the surface.
**Fig S9:** (a) Ultraviolet photoemission spectroscopy (UPS) spectra corresponding to the secondary electron onset region and valence features and (b) inverse photo emission spectroscopy (IPES) measurement results acquired on the pristine MAPbI$_3$, film (thickness ~ 4-5 nm) and PbCl$_2$ (0.75 ML) deposited MAPbI$_3$ perovskite film (thickness ~ 4-5 nm) deposited on Au(111). (c-d) Energy diagrams with respect to (w.r.t.) the Fermi level ($E_F$) for the pristine MAPbI$_3$ and PbCl$_2$ deposited MAPbI$_3$ film sandwiched between spiro-MeOTAD HTL$^2$ and TiO$_2$ ETL$^1$ as an example of a solar cell architecture.
**Fig S10:** (a-d) UPS and (e-h) IPES spectra of the pristine MAPbI$_3$ and Cl-incorporated MAPbI$_3$ and the VBM and CBM determination considering the intensity in (a,c,e,g) linear and (b,d,f,h) logarithmic scales.
References:


