Supporting Information - Potassium Doping-induced Variations on Geometric and Photoelectric Properties of MAPbI$_3$ Perovskite and MAPbI$_3$/TiO$_2$ Junction†

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Fig. S1 Optimized structures of SD-MAPbI\textsubscript{3} slabs: a) two K\textsuperscript{+} located well separately (isolated), b) common-vertexed (vertical), c) common-edged (coplanar) and d) directly face-to-face adjacent

Table 1 Band gaps and conduction band offsets (in eV) for bulk MAPbI\textsubscript{3}, TiO\textsubscript{2} and the junction with K\textsuperscript{+} doped inside perovskite layers

<table>
<thead>
<tr>
<th>Dopants</th>
<th>$E_{\text{cb},\text{don}}$</th>
<th>$E_{\text{cb},\text{acc}}$</th>
<th>$\Delta V_{\text{mix}}$</th>
<th>$E_{\text{cb}-\text{don}}$</th>
<th>$E_{\text{cb}-\text{acc}}$</th>
<th>Band Offset</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inside K</td>
<td>0.932</td>
<td>0.763</td>
<td>8.096</td>
<td>11.621</td>
<td>19.476</td>
<td>0.242</td>
</tr>
</tbody>
</table>
Fig. S 2 Optimized structures of ID-MAPbI$_3$ slabs: a) two K$^+$ located well separately (isolated), b) common-vertexed (vertical), c) common-edged (coplanar) and d) directly face-to-face adjacent.
**Fig. S 3** The *a*) topological structure and its *b*) three views that make two K⁺ doped Pb-I cube neither adjacent directly nor coplanar.

**Fig. S 4** Schematic diagram of MAPbI₃/TiO₂ heterojunction with different doping manners.
Fig. S 5 Geometric structure for ID-K\(^+\) set far from MAPbI\(_3\)/TiO\(_2\) junction. The purple arrow represents the direction of movement of K\(^+\) ions during the lattice relaxation.
Fig. S 6 Geometric structure for SD-K near or far from the MAPbI\textsubscript{3}/TiO\textsubscript{2} junction.
Fig. S 7 Schematic diagram a) and optimized geometric structure b) of ID-K⁺ in PbI₂-terminated MAPbI₃/TiO₂ junction.
Fig. S 8 Plane-average potentials of pristine and interstitially doped MAPbl$_3$/TiO$_2$ heterojunction.
Fig. S 9 Calculated absorption spectra of MAPbI$_3$/TiO$_2$ junction with and without ID-K$^+$. The bulk-like MAPbI$_3$ and anatase TiO$_2$ are shown for reference.
Fig. S 10 pDOSs of a)pristine TiO$_2$ and b)trivalent TiO$_2^-$ by PBE+SOC.
Fig. S 11 pDOS for interfacial Ti cations with a) and without b) interfacial ID of K⁺ in PbI₂-terminated MAPbI₃/TiO₂ junction in PBE+SOC.