Electronic Supplementary Material (ESI) for Nanoscale.


## Supplementary figures

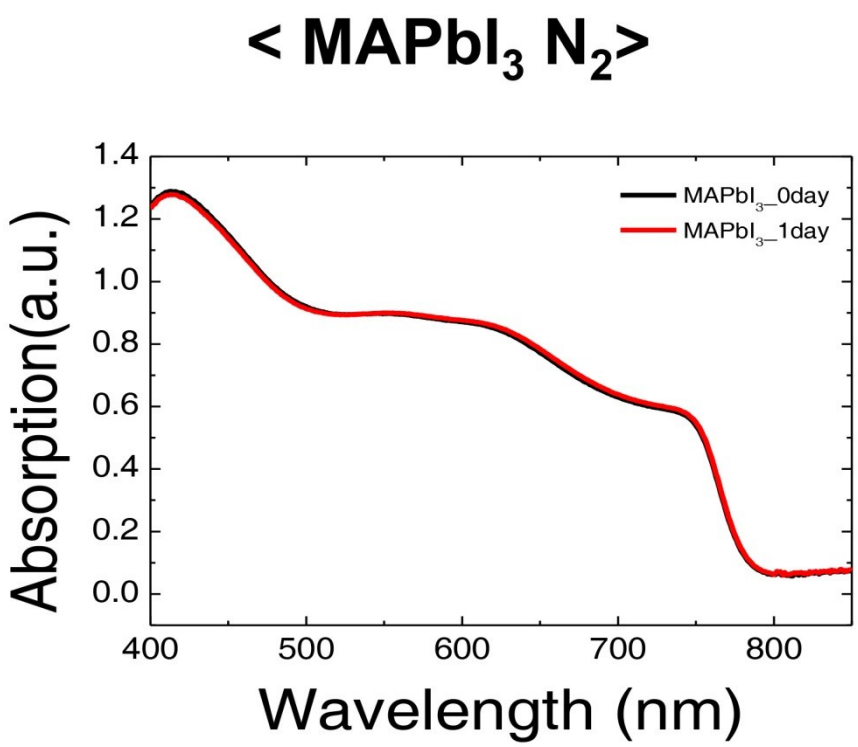


**Figure S1** Absorption spectra of perovskite films aged under 1 Sun of light irradiation in pure nitrogen ambience.

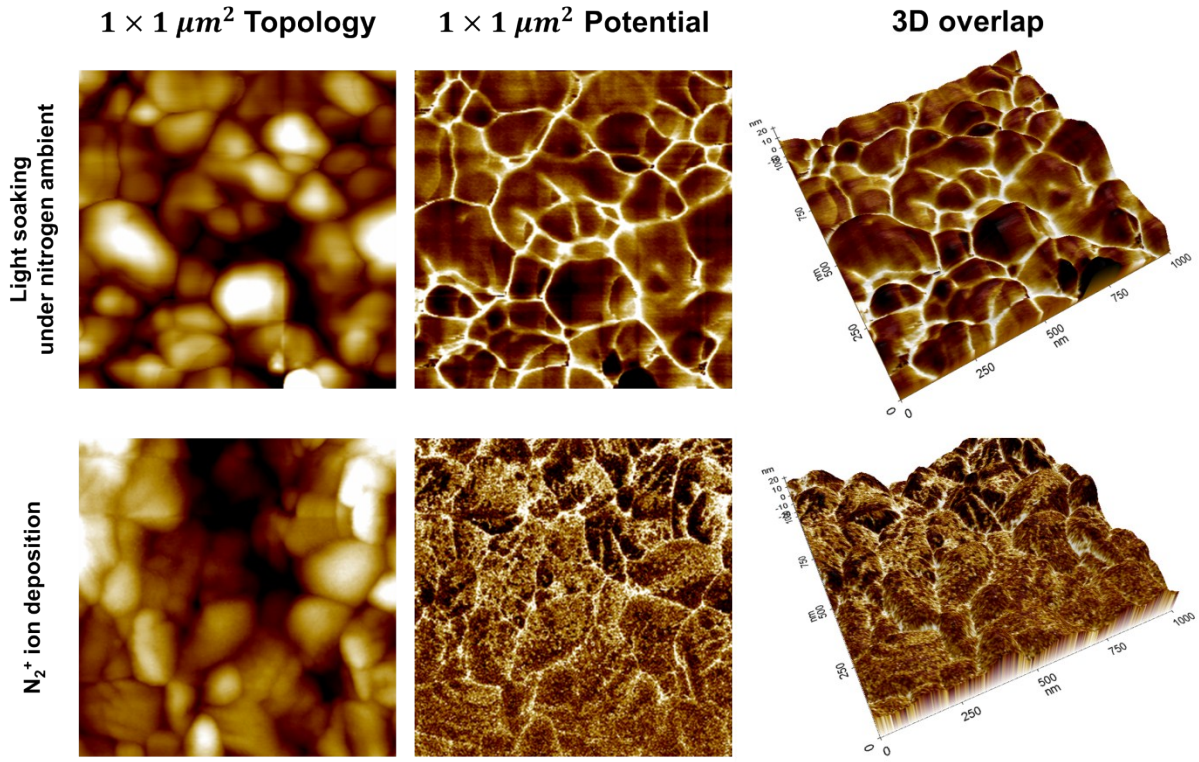


**Figure S2** High-resolution KPFM images of $MAPbI_3$ film after light soaking and nitrogen cation deposition

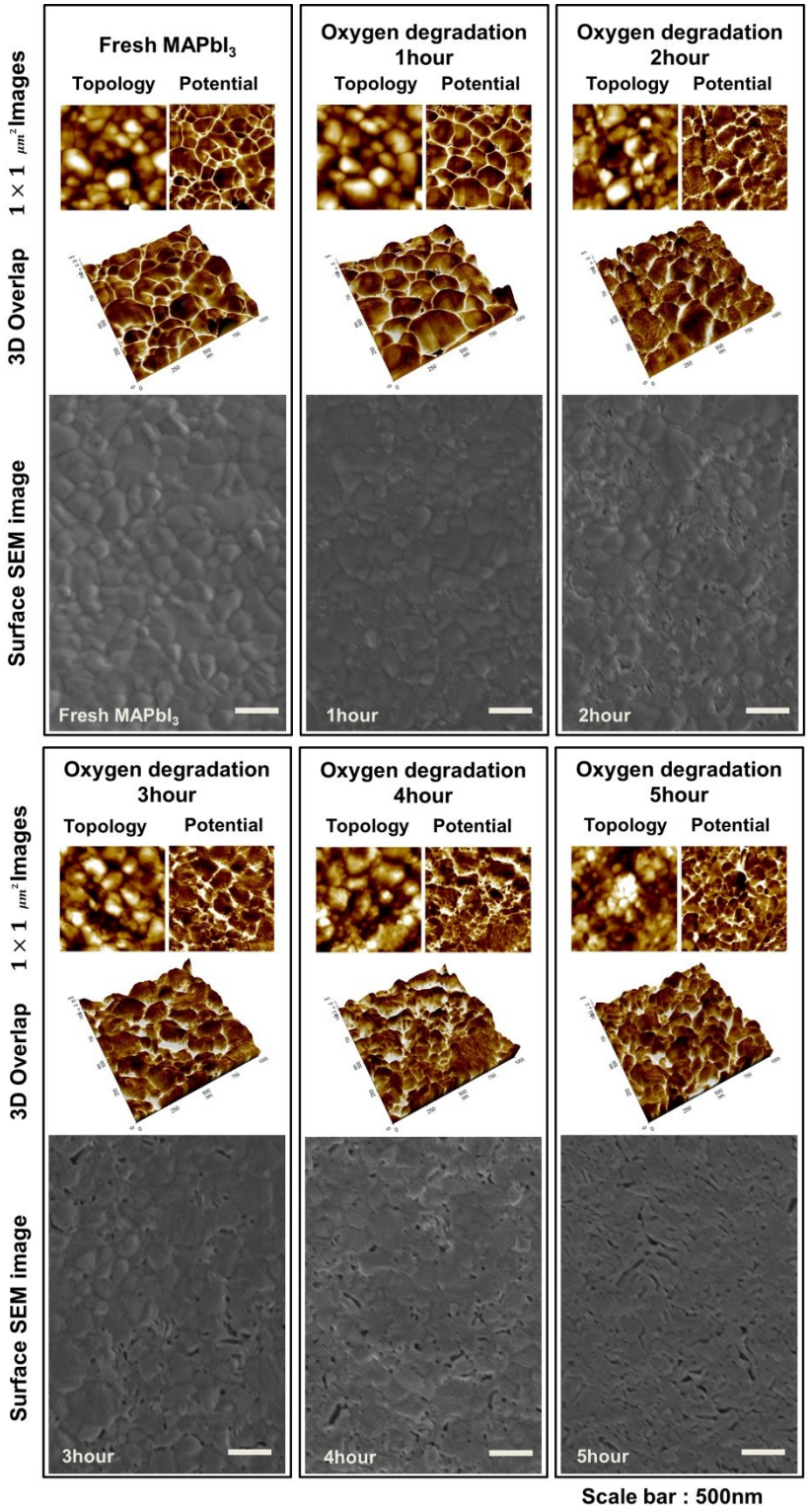


**Figure S3** Time evolution of high-resolution KPFM images and top-view SEM images for the $MAPbI_3$ film. The $MAPbI_3$ films on the $C_{60}$ (35nm)/ITO substrate were degraded under 1 Sun of light irradiation in 100% oxygen ambience.

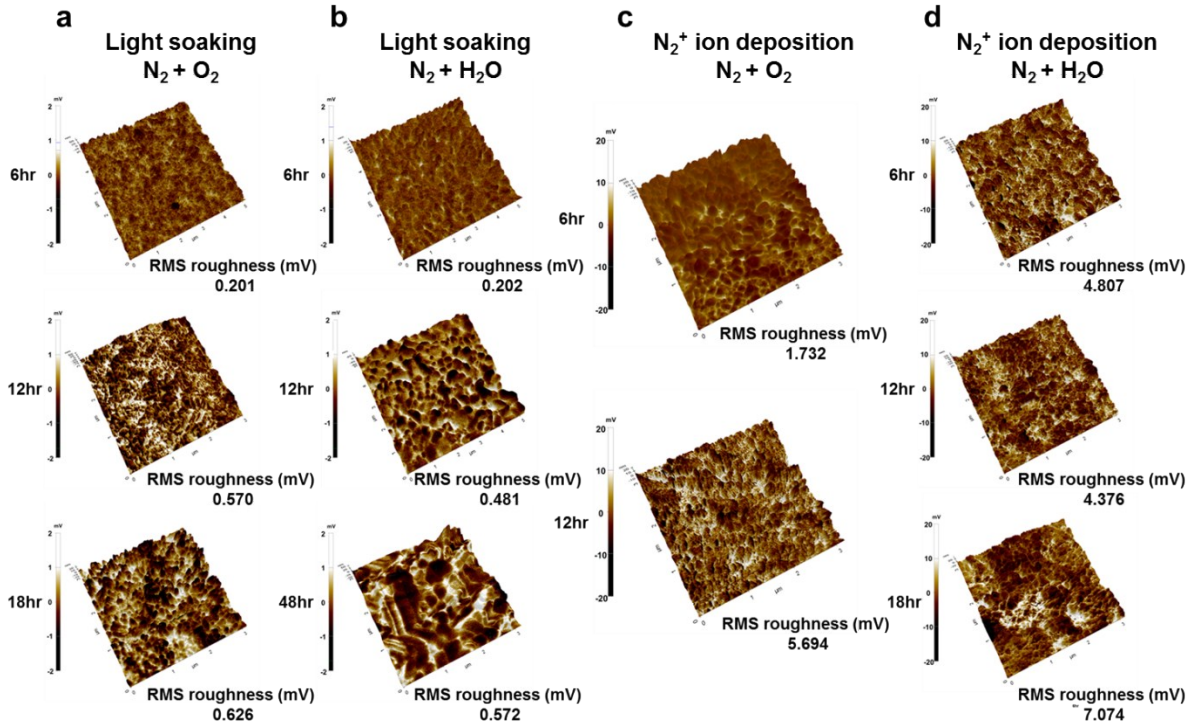


**Figure S4** Time evolution of KPFM images for $MAPbI_3$ films degraded under different charge generation conditions in humidified nitrogen or dry air. (RMS roughness is defined by $RMS\ roughness = \sqrt{\frac{1}{N}\sum_{i=1}^{N} V_i^2}$ where $V_i$ is a potential difference of pixel i and N is the total number of pixels of the measured area)

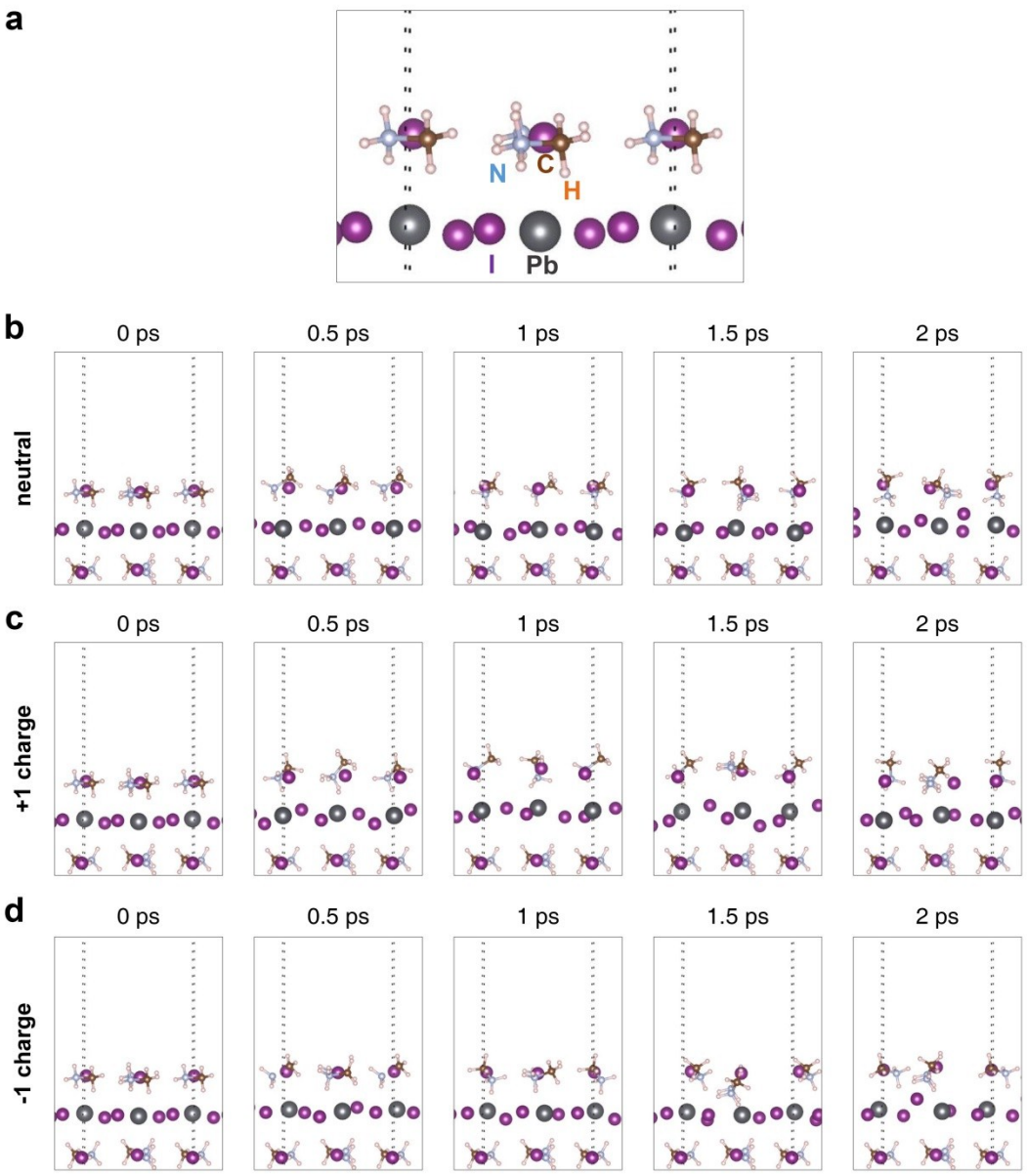


**Figure S5 a,** Expanded view for the initial geometry of pure $MAPbI_3$ surface. **b-d,** Temporal snapshots of the AIMD simulated atomic trajectories of $MAPbI_3$ crystal with a charge of **b,** 0, **c,** +1, and **d,** −1. All simulations start with the same initial geometry at 0 ps shown in **a**. Dotted vertical lines represent the boundaries of actual simulation space, beyond which repeated images of atoms are shown because of the periodic boundary condition.

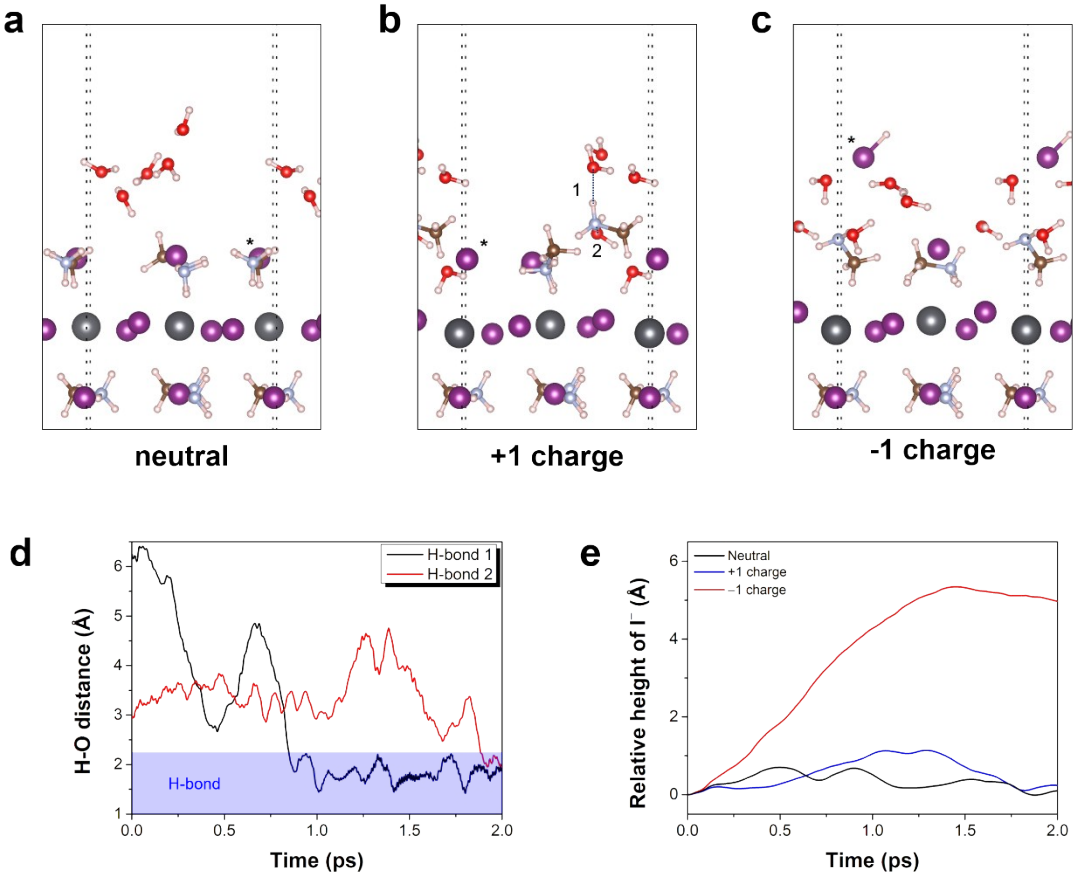


**Figure S6 a-c,** Snapshots at 2 ps of the AIMD simulations of Fig. 2 with a charge of **a,** 0, **b,** +1, and **c,** −1. **d,** Temporal change in the distances between the adjacent hydrogen and oxygen atoms of **b** (dotted navy lines). **e,** Temporal change in the relative height of $I^-$ marked by asterisk in **a**, **b**, and **c** compared to the initial height.

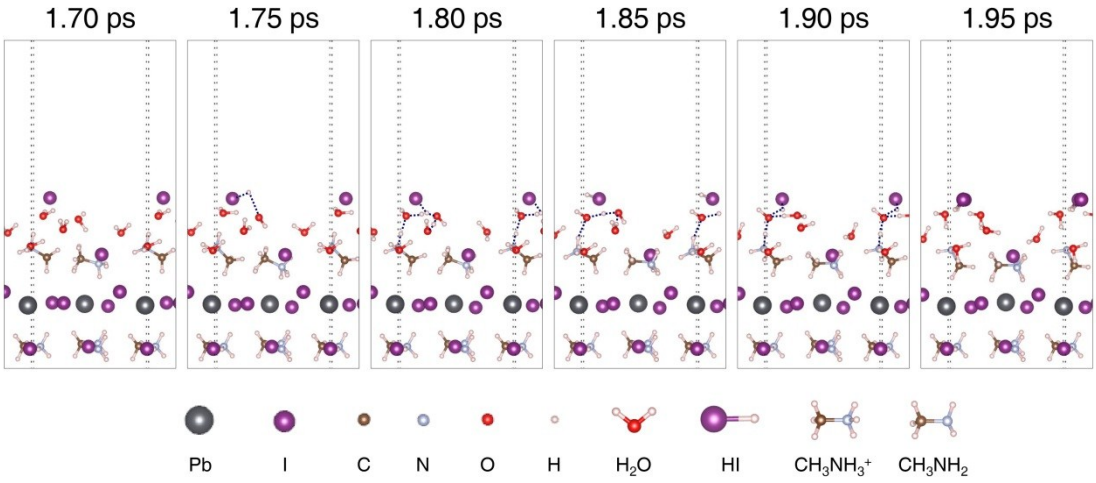


**Figure S7** Temporal snapshots of the AIMD simulated atomic trajectories of 5 $H_2O$-covered $MAPbI_3$ crystal with a charge of −1 during the proton transfer. Hydrogen bonds that form proton wires are shown by dotted navy lines. Dotted vertical lines represent the boundaries of actual simulation space, beyond which repeated images of atoms are shown because of the periodic boundary condition.

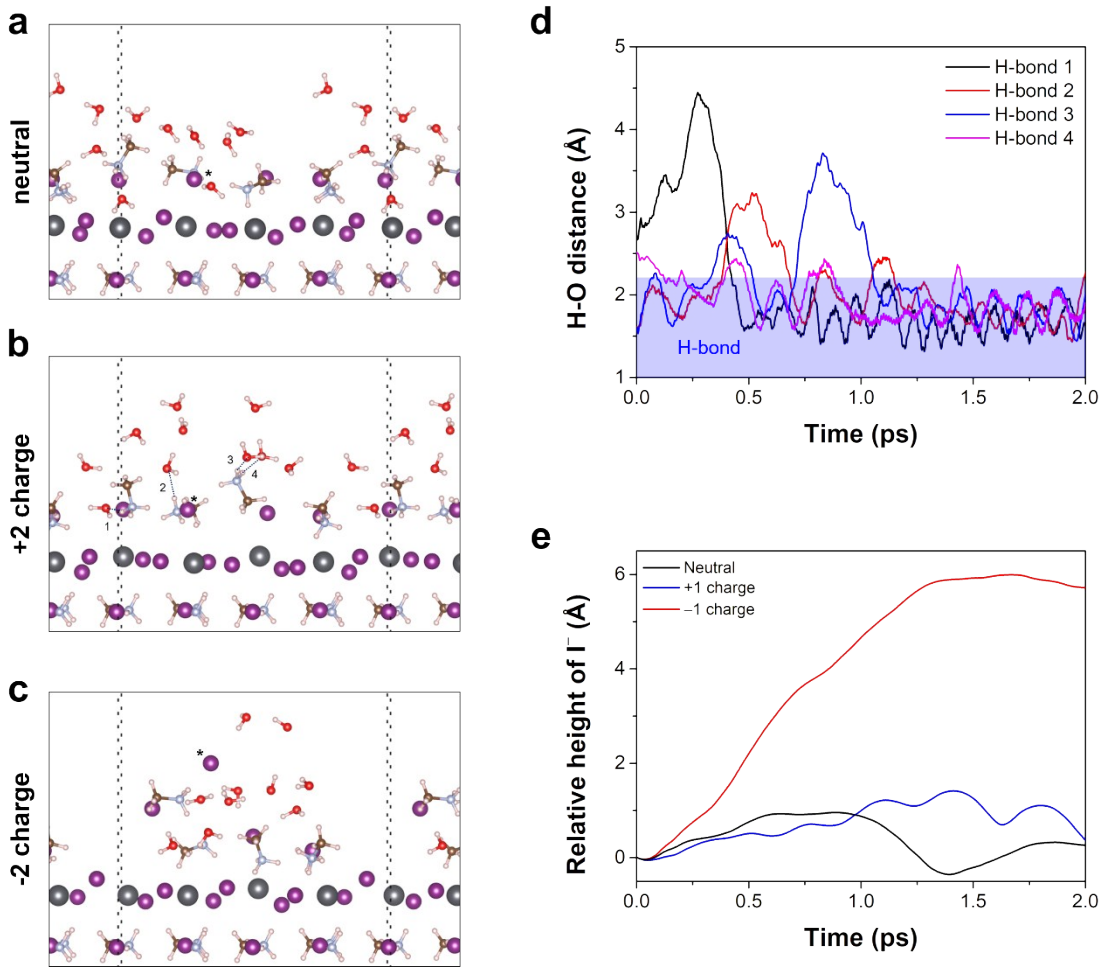


**Figure S8 a-c,** Snapshots at 2 ps of the AIMD simulations of the 2 × 1 supercell of Fig. 2a with a charge of **a,** 0, **b,** +2, and **c,** −2. **d,** Temporal change in the distances between the adjacent hydrogen and oxygen atoms of **b** (dotted navy lines). **e,** Temporal change in the relative height of $I^-$ marked by asterisk in **a**, **b**, and **c** compared to the initial height.

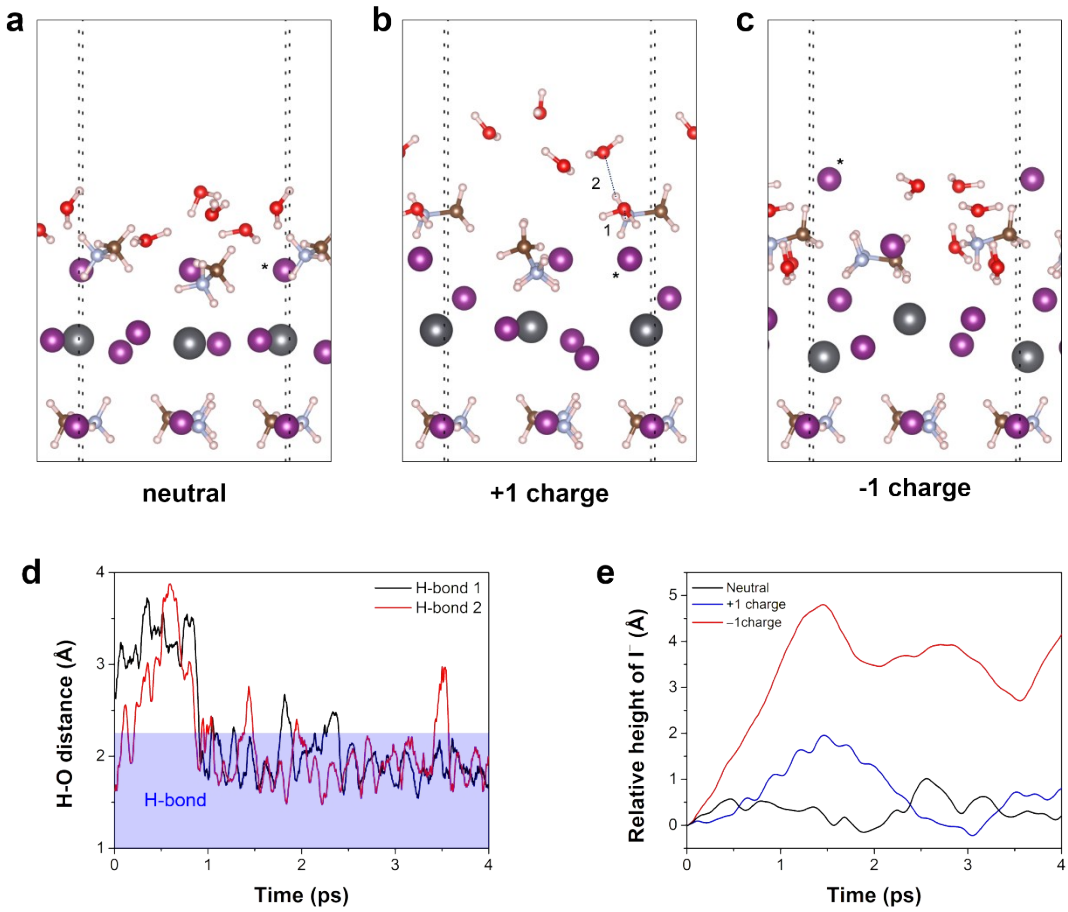


**Figure S9 a-c,** Snapshots at 4 ps of AIMD simulations with a charge of **a,** 0, **b,** +1, and **c,** −1 using 1.5 fs time-step whose initial geometries are the same as in Fig. 2a. **d,** Temporal change in the distances between the adjacent hydrogen and oxygen atoms of **b** (dotted navy lines). **e,** Temporal change in the relative height of $I^-$ marked by asterisk in **a**, **b**, and **c** compared to the initial height.

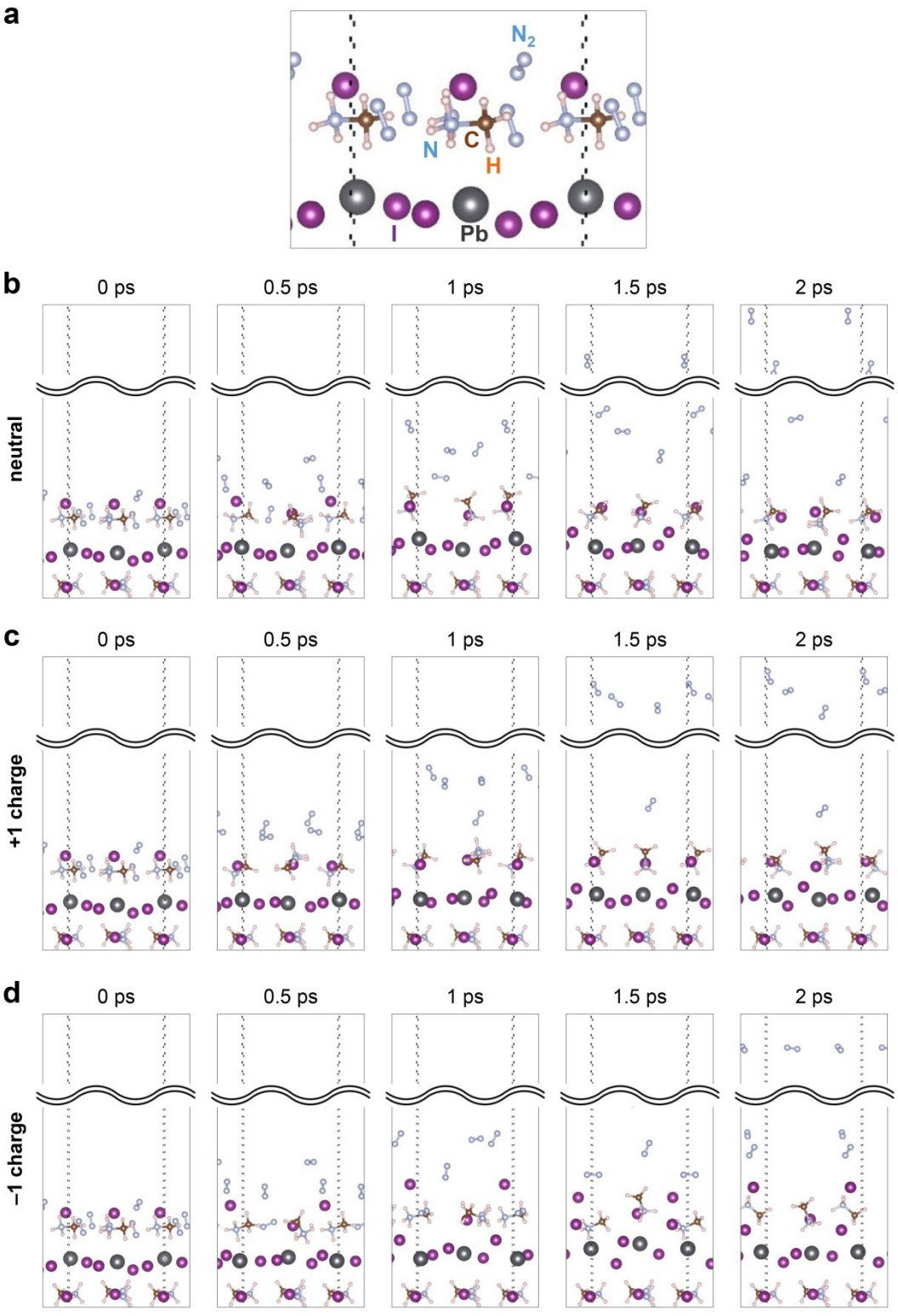
a
$N_2$
N
C
H
I
Pb
b
0 ps
0.5 ps
1 ps
1.5 ps
2 ps
neutral
c
0 ps
0.5 ps
1 ps
1.5 ps
2 ps
+1 charge
d
0 ps
0.5 ps
1 ps
1.5 ps
2 ps
–1 charge

**Figure S10 a,** Expanded view for the initial geometry of 4 $N_2$-covered $MAPbI_3$ surface. **b-d,** Temporal snapshots of the AIMD simulated atomic trajectories of 4 $N_2$-covered $MAPbI_3$ crystal with a charge of **b,** 0, **c,** +1, and **d,** −1. All simulations start with the same initial geometry at 0 ps shown in **a**. Dotted vertical lines represent the boundaries of actual simulation space, beyond which repeated images of atoms are shown because of the periodic boundary condition.

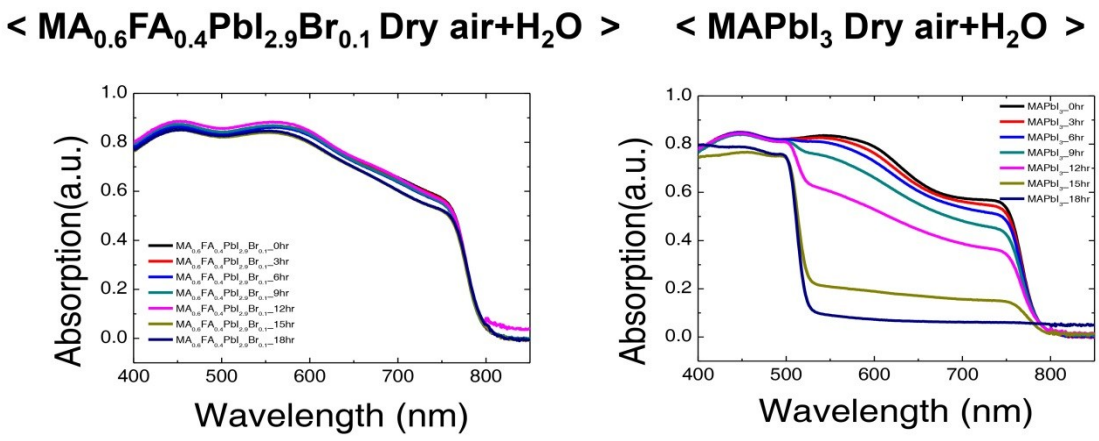


**Figure S11** Time evolution of the absorption spectra of $MA_{0.6}FA_{0.4}PbI_{2.9}Br_{0.1}$ (left) and $MAPbI_3$ (right) films aged under 1 Sun of light irradiation in humidified dry air for 18 hours.

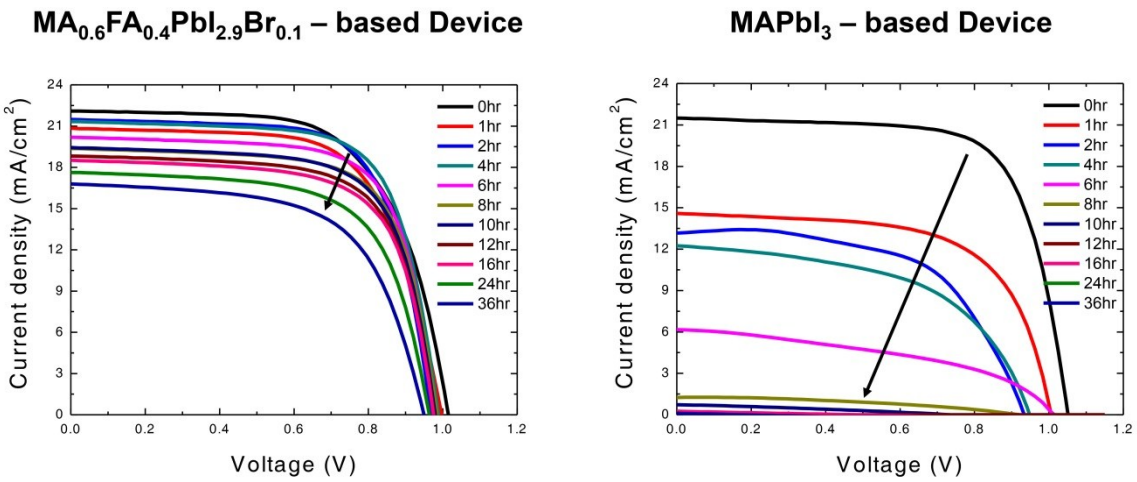


**Figure S12** Time evolution of the J-V curve for the devices containing $MA_{0.6}FA_{0.4}PbI_{2.9}Br_{0.1}$ (left) and $MAPbI_3$ (right) films aged under 1 Sun of light irradiation in 100% oxygen ambience for 36 hours.

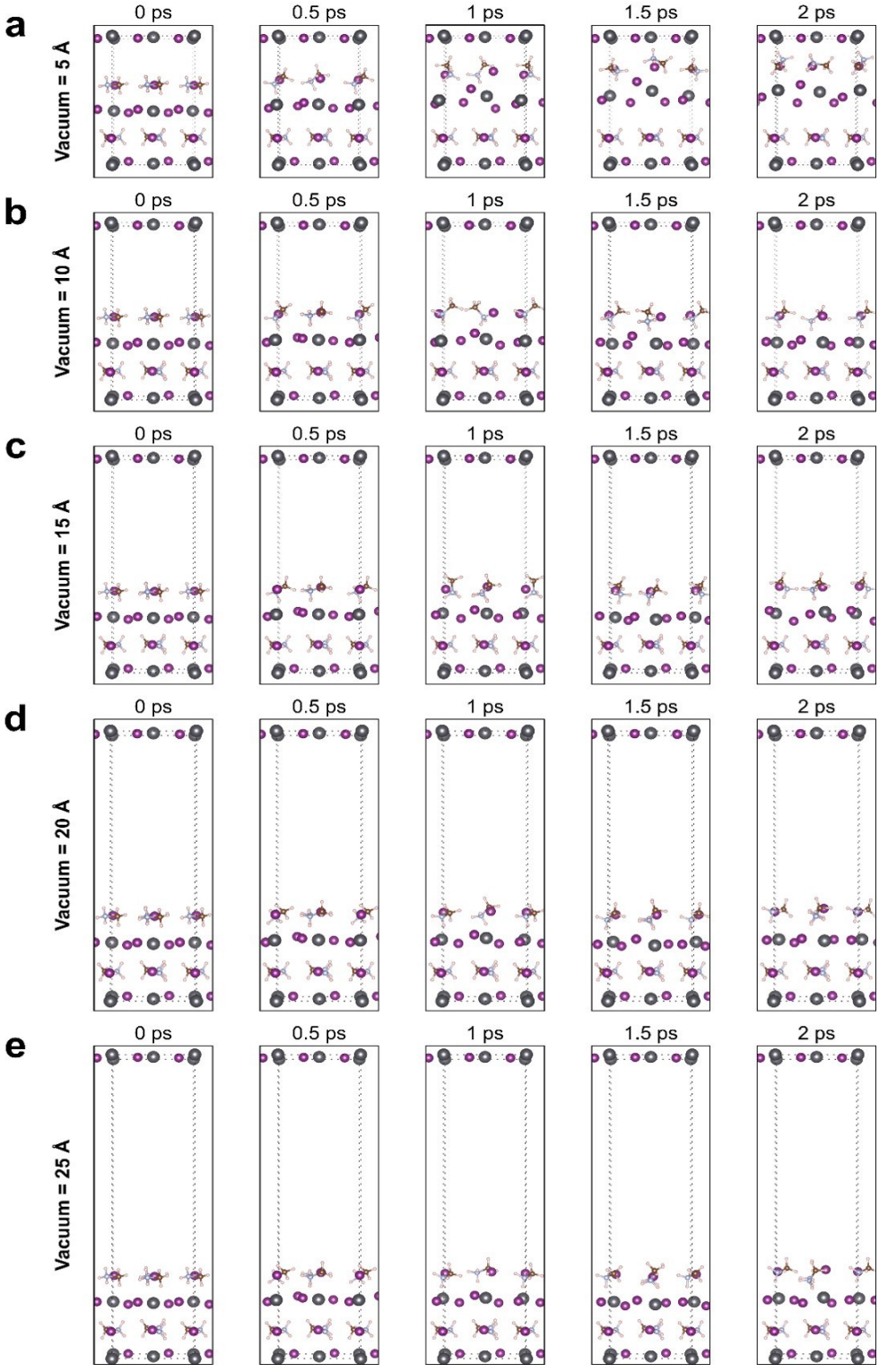


**Figure S13** Temporal snapshots of the AIMD simulated atomic trajectories of $MAPbI_3$ crystal with no net charge with a vacuum thickness of **a,** 5 Å, **b,** 10 Å, **c,** 15 Å, **d,** 20 Å, and **e,** 25 Å.

## Supplementary Table

| Net charge | | Oxygen | | | |
|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 |
| 0 | status | nonbonded | nonbonded | nonbonded | nonbonded |
| | charge | −0.42 | −0.38 | −0.19 | −0.02 |
| +1 | status | bonded | nonbonded | nonbonded | nonbonded |
| | charge | −0.94 | −0.08 | +0.01 | +0.19 |
| −1 | status | bonded | bonded | nonbonded | nonbonded |
| | charge | −1.04 | −0.98 | −0.55 | −0.13 |

**Table S1.** Bonding status of $O_2$ molecules with perovskite (top entry) and their calculated electrostatic charge (bottom entry in number) for the geometry at 2 ps snapshot of Figure 3.

## Video

**Video 1.** AIMD simulation of neutral $MAPbI_3$ surface without any adsorbate.

**Video 2.** AIMD simulation of positively charged $MAPbI_3$ surface without any adsorbate.

**Video 3.** AIMD simulation of negatively charged $MAPbI_3$ surface without any adsorbate.

**Video 4.** AIMD simulation of neutral $MAPbI_3$ surface with 5 $H_2O$ molecules.

**Video 5.** AIMD simulation of positively charged $MAPbI_3$ with 5 $H_2O$ molecules.

**Video 6.** AIMD simulation of negatively charged $MAPbI_3$ with 5 $H_2O$ molecules.

**Video 7.** AIMD simulation of neutral $MAPbI_3$ surface with 4 $N_2$ molecules.

**Video 8.** AIMD simulation of positively charged $MAPbI_3$ with 4 $N_2$ molecules.

**Video 9.** AIMD simulation of negatively charged $MAPbI_3$ with 4 $N_2$ molecules.

**Video 10.** AIMD simulation of neutral $MAPbI_3$ surface with 4 $O_2$ molecules.

**Video 11.** AIMD simulation of positively charged $MAPbI_3$ with 4 $O_2$ molecules.

**Video 12.** AIMD simulation of negatively charged $MAPbI_3$ with 4 $O_2$ molecules.