Supporting Information

Inhibiting the decomposition of methylammonium using the cations with low deprotonation energy

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Table S1. E_{PA} and E'_{PA} are the calculated and experimental proton affinities (eV) of the corresponding molecules, respectively. E_{VD} is the vertical deprotonation energy (eV) of the corresponding cation. Herein, all calculations are implemented using the free energies.

Molecules	Cations	E_{PA} (eV)	E'_{PA} (eV)	E_{VD} (eV)
H_2O	H_3O^+	6.98	6.98[S1]	7.01
$(H_2O)_2$	$H_5O_2^+$	8.16	8.08[S2]	8.99
$NHCHNH_2$	$(NH_2)_2CH^+$	9.73	---	9.95
CH_3NH_2	$CH_3NH_3^+$	9.12	9.34[S3]	9.19
$(CH_3)_3N$	$(CH_3)_3NH^+$	9.65	9.84[S4,S5]	9.75
NH_3	NH_4^+	8.63	8.85[S3]	8.64
HF	H_2F^+	4.92	5.03[S4,5]	4.93
CH_2O	CH_2OH^+	7.24	7.20[S1,4,5]	7.33
CH_3OH	$CH_3OH_2^+$	7.67	7.80[S1,4,5]	7.85
LiOH	$LiOH_2^+$	10.12	10.40[S1]	10.36

To calculate the total free energy of H^+ (E_{H^+}) using the equation of $E_{H^+} = 6.98\ eV + E_{H_3O^+} - E_{H_2O}$, the experimental proton affinity of 6.98 eV of H_2O was employed[S1], where $E_{H_3O^+}$ and E_{H_2O} are the total

free energies of H_3O^+ and H_2O, respectively. The proton affinities of the molecules were estimated by the equation of $E_{PA} = E_{H+} + E_M - E_C$, where E_M and E_C are the total free energies of the corresponding molecules and cations, respectively. As shown in Table S1, the calculation proton affinities are very consistent with the experiment proton affinities. For instance, the proton affinities of 8.16 and 9.12 eV were obtained for $(H_2O)_2$ and CH_3NH_2 molecules, which are in good agreement with the experimental values[S2,3] of 8.08 and 9.28 eV, respectively. The vertical deprotonation energy (E_{VD}) of cations was calculated by the equation of $E_{VD} = E_{H+} + E_{M'} - E_C$, where $E_{M'}$ is the free energy of the structure of the cation without H^+. The structural relaxation from the direct deprotonation structure to the deprotonation molecule structure of the cations can be estimated by comparing E_{VD} with E_{PA}, such as E_{PA} of 8.16 and E_{VD} of 7.01 eV for H_3O^+, suggesting that the H_2O molecule and the H_2O part of H_3O^+ is very similar in structure.

Table S2. Herein, t, $E_{H\text{-}bond}$, E_g, V_{oc}, J_{sc} and η are the tolerance factor, the hydrogen bond energy (eV/a-site-cation), the band gap (eV), the maximum short circuit current density (mA/cm^2), open circuit voltages (V), and the PCE (%), respectively.

Perovskites	t	$E_{H\text{-}bond}$	E_g	V_{oc}	J_{sc}	η
$MAPbI_3$	0.96	0.31	1.60	1.33	25.47	30.58
$MA_{0.9375}(H_5O_2)_{0.0625}PbI_3$	0.95	0.30	1.55	1.28	27.26	31.50
$MA_{0.875}(H_5O_2)_{0.125}PbI_3$	0.94	0.33	1.67	1.39	23.38	29.58
$MA_{0.5}(H_5O_2)_{0.5}PbI_3$	0.90	0.26	1.68	1.40	23.06	29.39
$H_5O_2PbI_3$	0.85	0.22	1.72	1.44	21.91	28.73

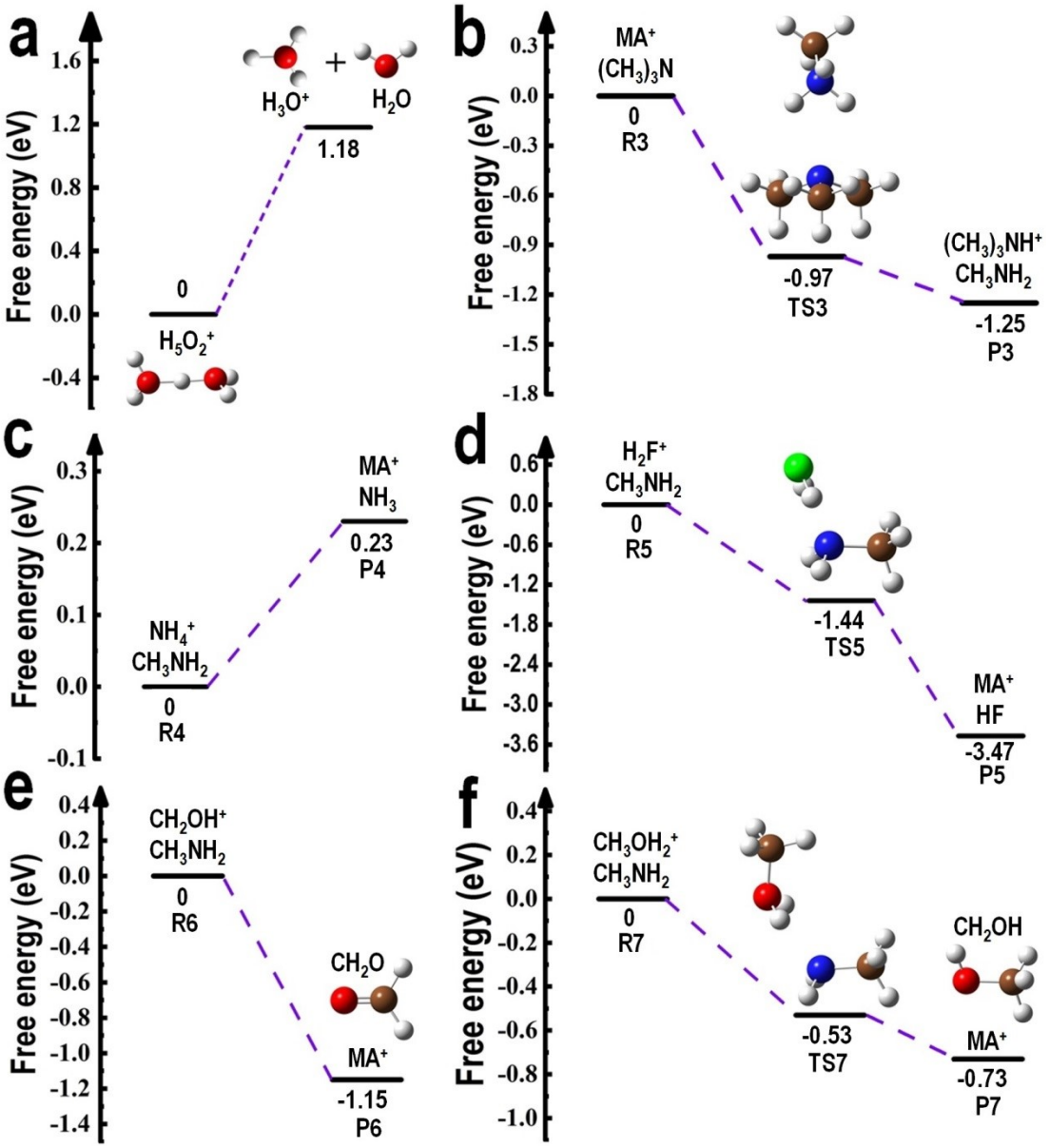

Fig. S1. (a) The free energy of H_2O molecule and H_3O^+ cation, and $H_5O_2^+$ cation, respectively. (b-f) The proton transfer from $(CH_3)_3NH^+$, NH_4^+, H_2F^+, CH_2OH^+, and $CH_3OH_2^+$ cations to CH_3NH_2 molecule to form MA^+ cation, respectively. Atomic colors: H (white), C (coffee), N (blue), O (red) and F (green).

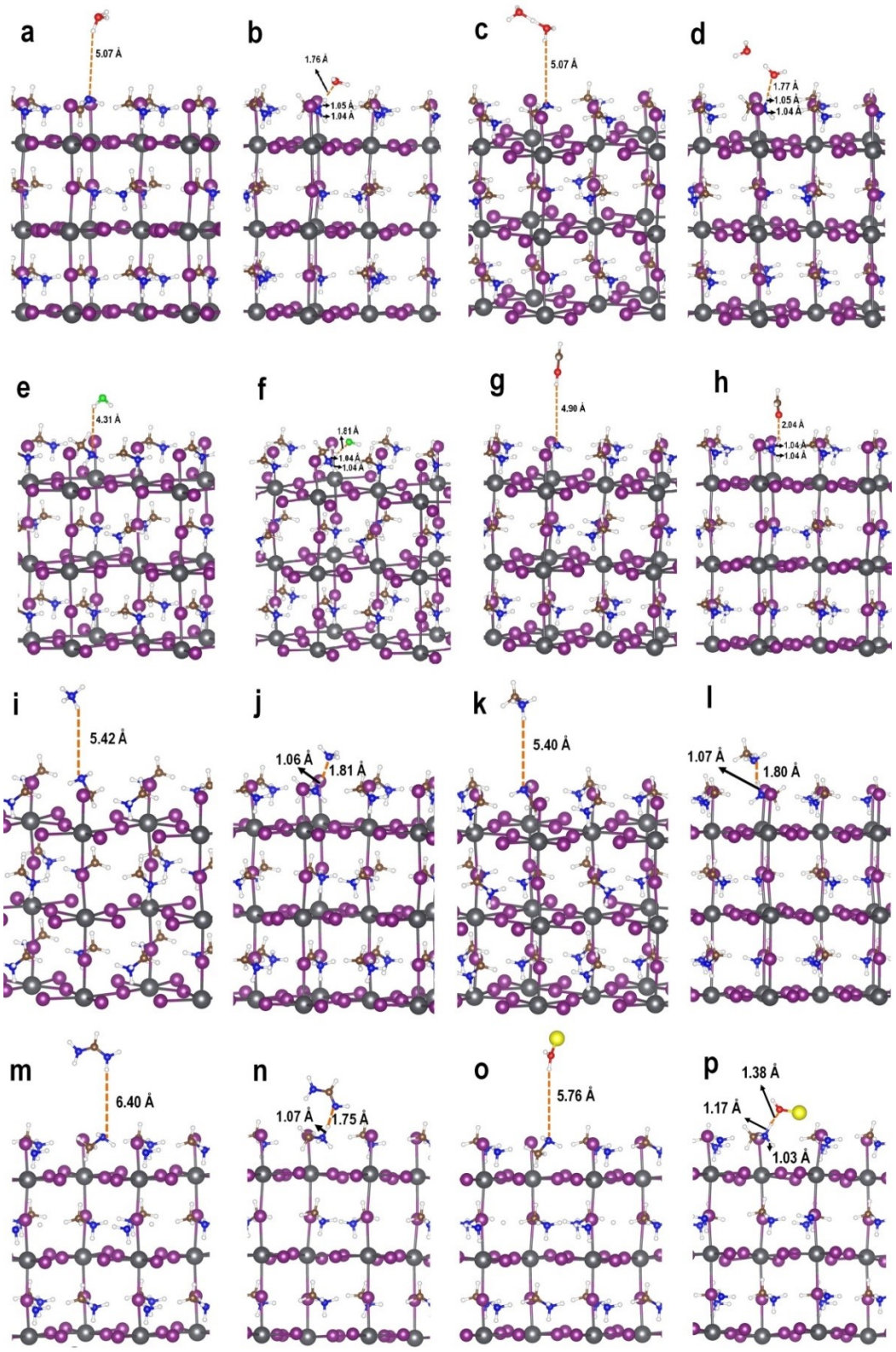

Fig. S2. The initial and optimal structures for the (001) MAI plane of the $MAPbI_3$ perovskite with H_3O^+ (a) and (b), $H_5O_2^+$ (c) and (d), H_2F^+ (e) and (f), CH_2OH^+ (g) and (h), NH_4^+ (i) and (j), MA^+ (k) and (l), FA^+ (m) and (n), and H_2OLi^+ (o) and (p) cations, respectively. Atomic colors: H (white), Li (yellow), C (coffee), N (blue), O (red), F (green), I (violet) and Pb (grey).

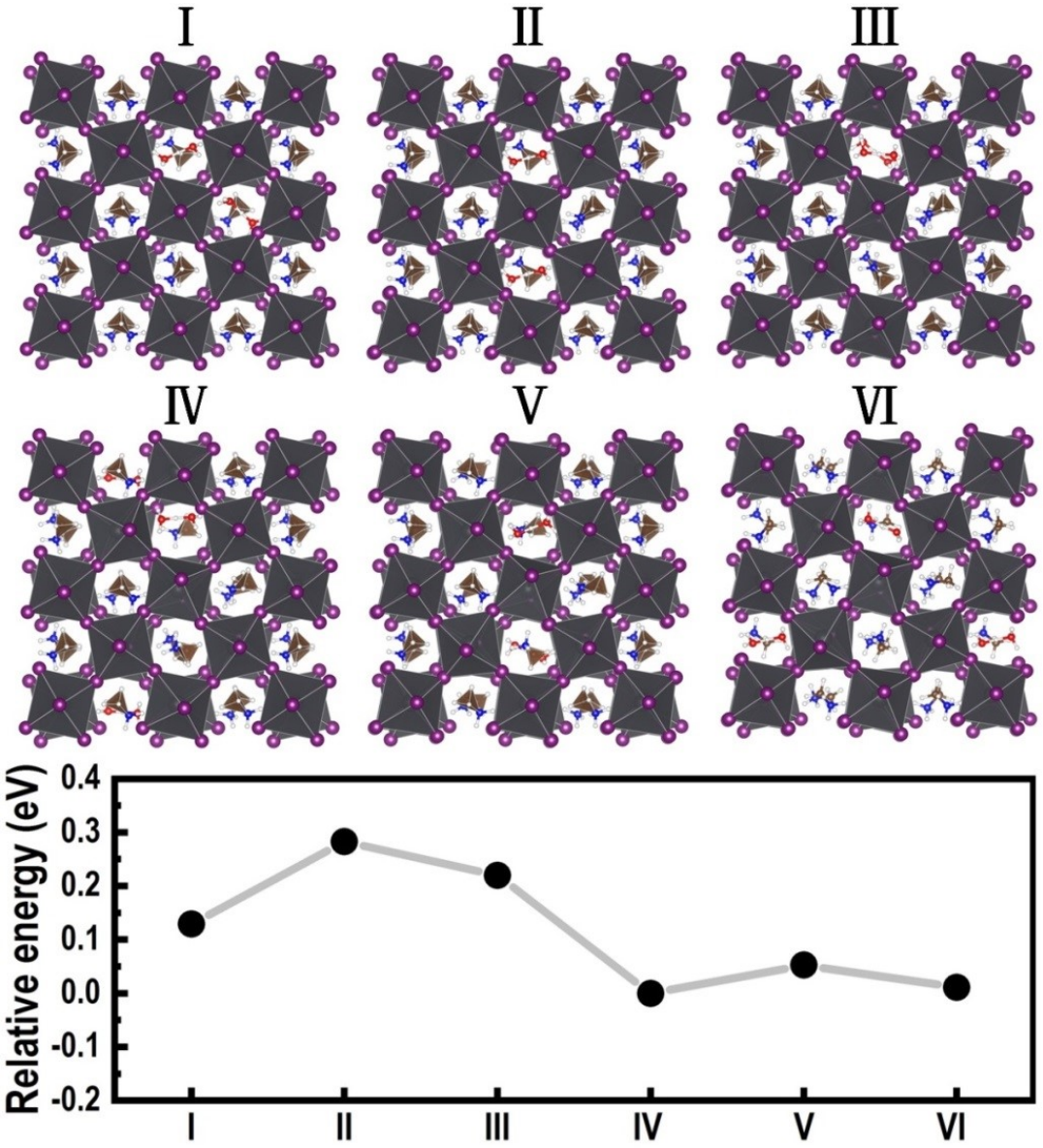

Fig. S3. Six possible structures of the $MA_{0.875}(H_5O_2)_{0.125}PbI_3$ perovskite with a tetragonal crystal structure and 2×2×1 supercell. Their relative energies (E_R) are obtained by the equation of $E_R = E_X - E_{IV}$, where E_X and E_{IV} represent the total energies of X (X = I, II, III, IV, V, or VI) and IV structures. Atomic colors: H (white), C (coffee), N (blue), O (red), I (violet) and Pb (grey).

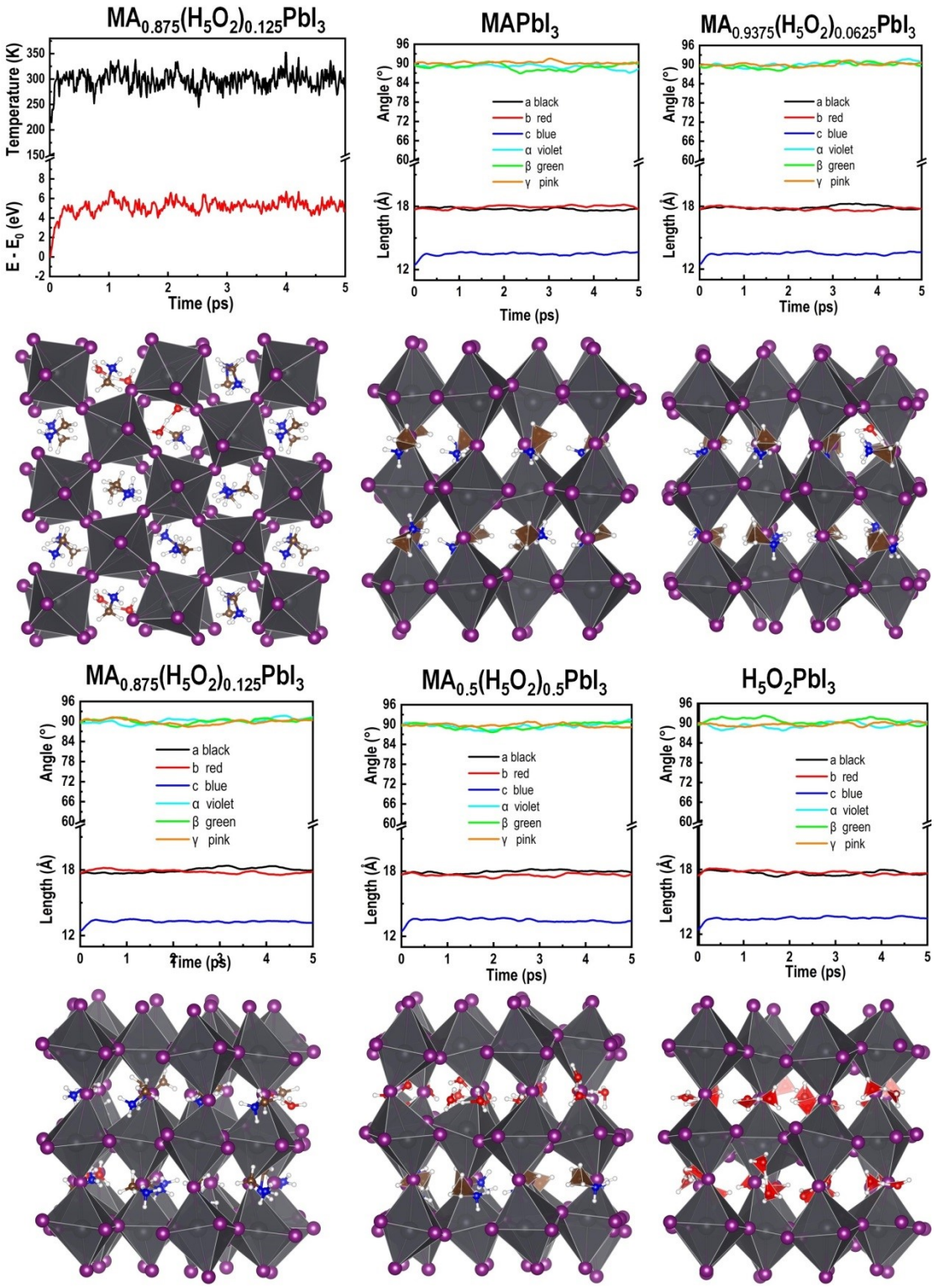

Fig. S4. Ab initio molecular dynamics (AIMD) simulation for the energy, temperature, lattice parameters and structure of the $MA_{1-x}(H_5O_2)_xPbI_3$ (x = 0, 1/16, 1/8, 1/2, or 1) perovskites with a tetragonal crystal structure and 2×2×1 supercell under 300 K, 10^5 Pa and AIMD simulation of 5 ps, respectively. Atomic colors: H (white), C (coffee), N (blue), O (red), I (violet) and Pb (grey).

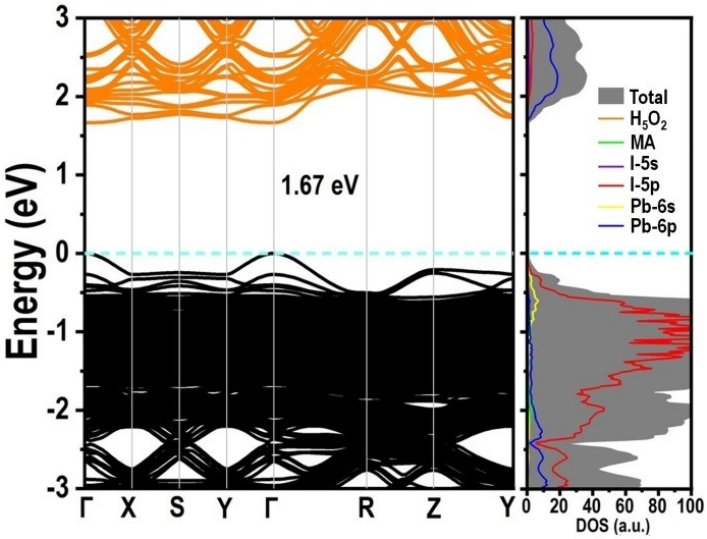

Fig. S5. The calculated band structures, and total/partial DOSs for the $MA_{0.875}(H_5O_2)_{0.125}PbI_3$ perovskite with a tetragonal crystal structure and 2×2×1 supercell. The dotted line is Fermi level.

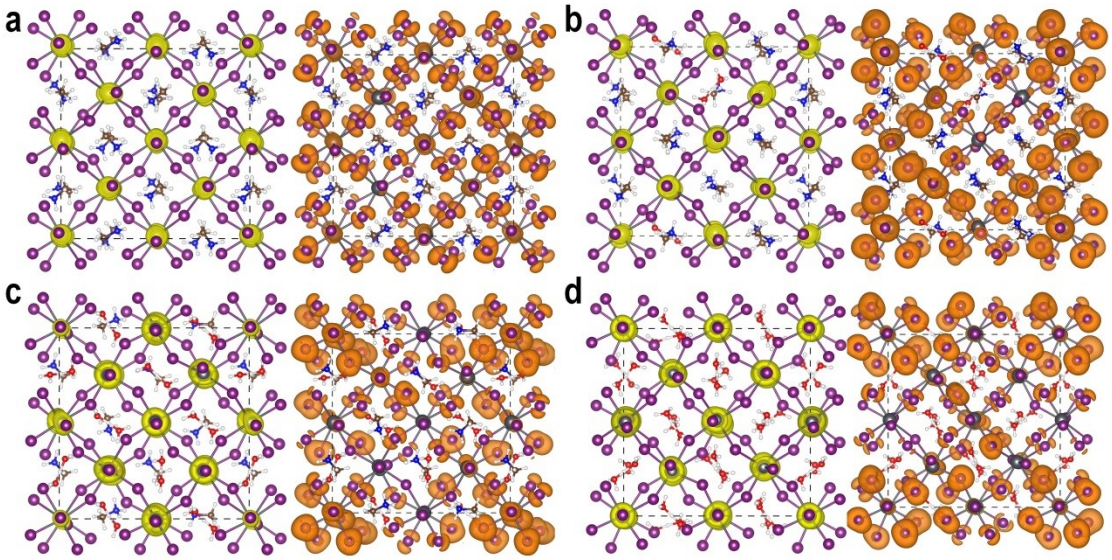

Fig. S6. The partial charge density of the CBM (yellow) and VBM (orange) states (isovalue = 0.002 e/Å^3) for the $MA_{1-x}(H_5O_2)_xPbI_3$ perovskites with a tetragonal crystal structure and 2×2×1 supercell, (a) x = 0, (b) 1/8, (c) 1/2 and (d) 1, respectively. Atomic colors: H (white), C (coffee), N (blue), O (red), I (violet) and Pb (grey).

References

S1 E. P. Hunter and S. G. Lias, J. Phys. Chem. Ref. Data 1998, **27**, 413-656.

S2 D. J. Goebbert and P. G. Wenthold, Eur. J. Mass Spectrom. 2004, **10**, 837-845.

S3 J. E. Szulejko and T. B. McMahon, J. Am. Chem. Soc. 1993, **115**, 7839-7848.

S4 J. L. Beauchamp, Annu. Rev. Phys. Chem. 1971, **22**, 527-561.

S5 P. Kollman and S. Rothenberg, J. Am. Chem. Soc. 1977, **99**, 1333-1342.