

Supplementary Materials

Rational design of multifunctional pseudohalide anions for synergistic defect passivation and suppressed ion migration in perovskite solar cells

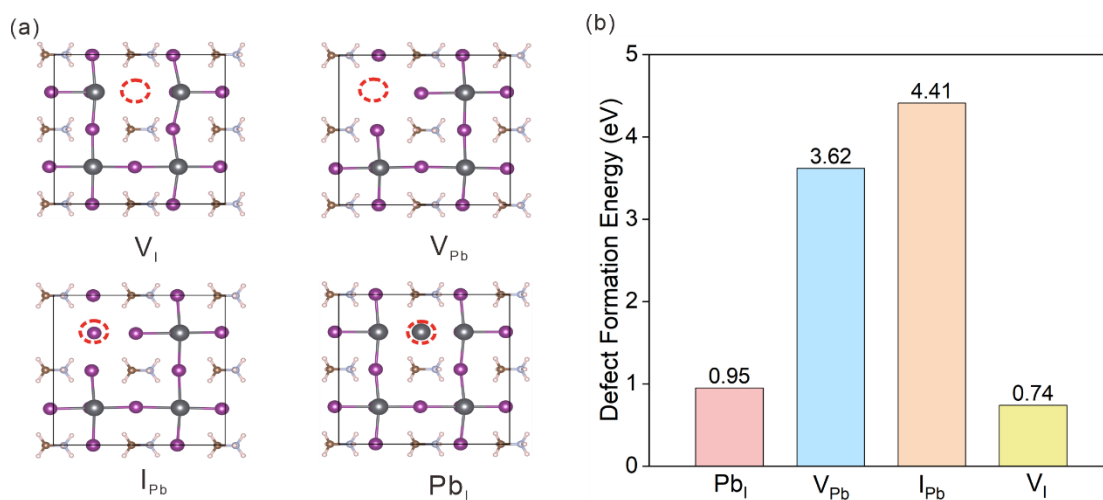
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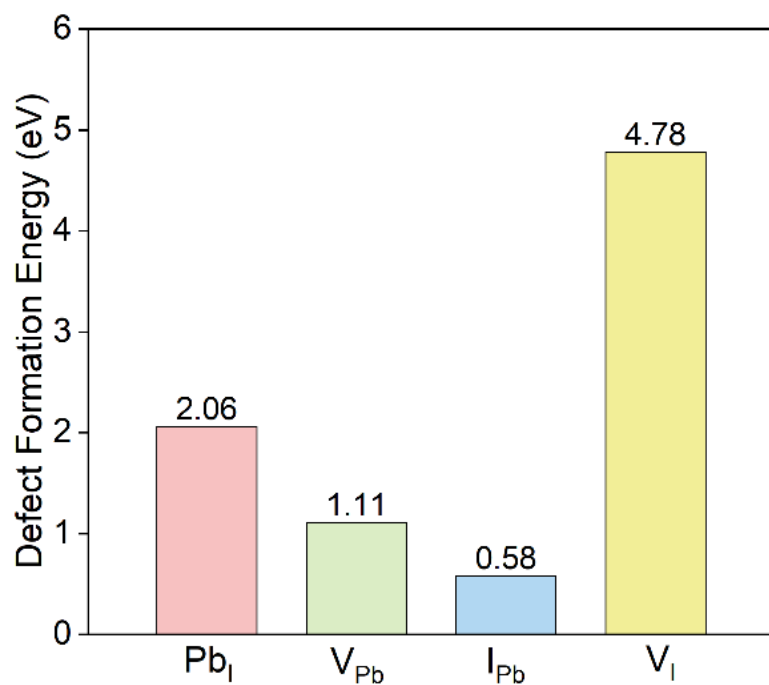
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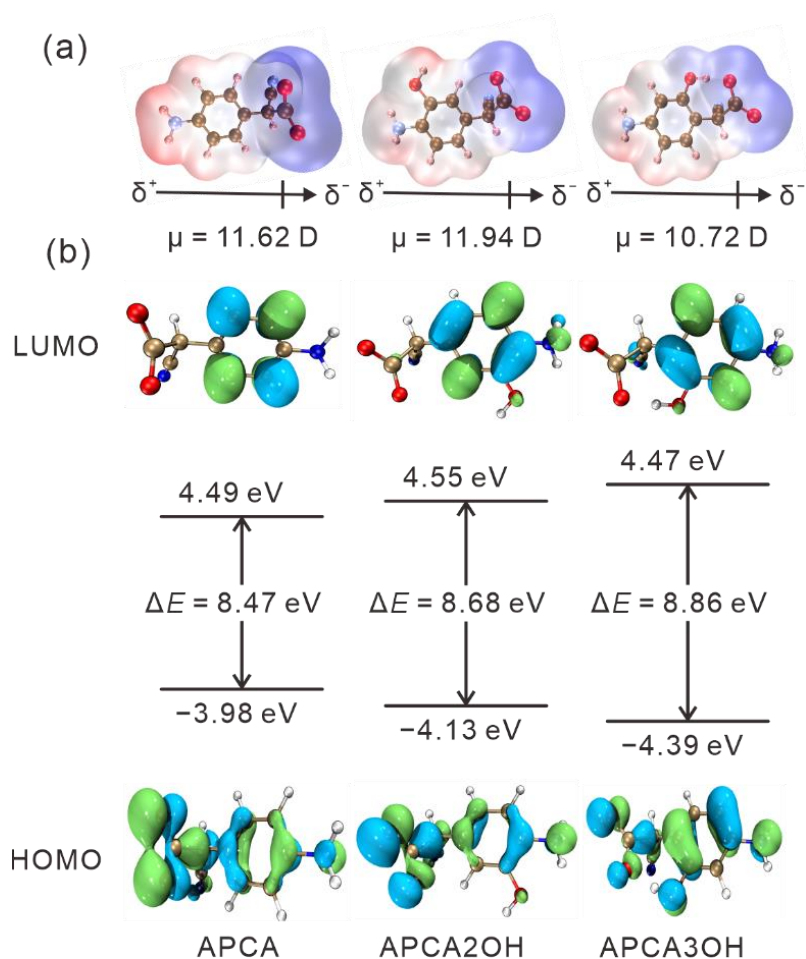
ORCID: Ping-Ping Sun (0000-0002-2772-2631), Chaoyuan Zeng (0000-0001-7032-6004), Qinxì Dong (0009-0005-8425-3404), Weijie Chi (0000-0003-1776-0025)



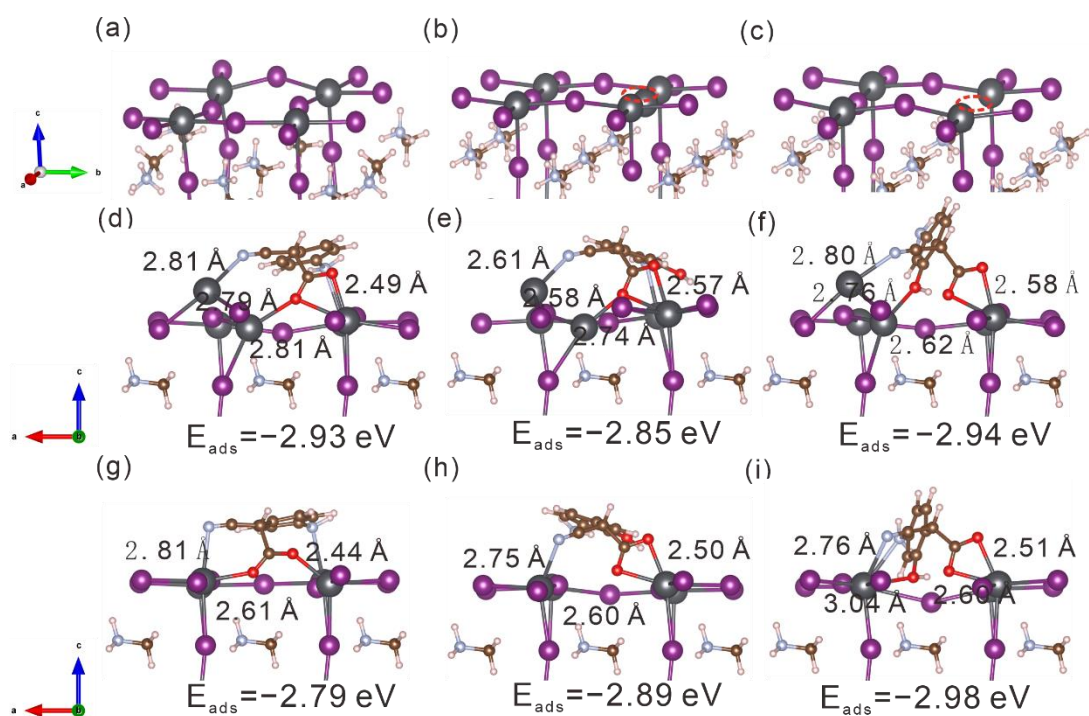
Supplementary Figure 1. (a) Top view of surface-defect identification on perovskite surfaces. The red dotted circles represent the positions of the defects. (b) Surface DFEs of defects at Pb-rich condition.



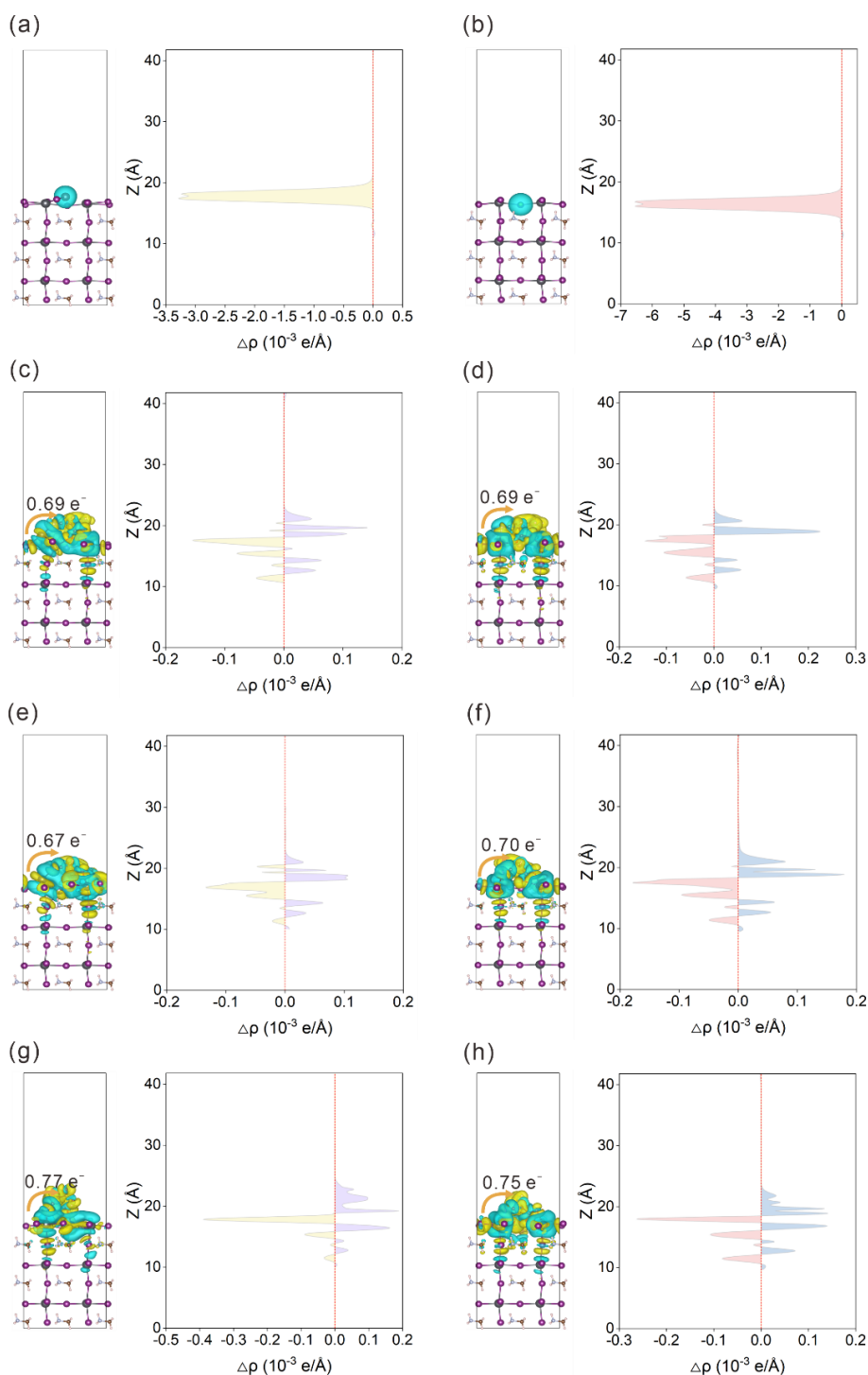
Supplementary Figure 2. Surface DFEs of defects at I-rich condition.



Supplementary Figure 3. Molecular dipole moments and frontier molecular orbital (HOMO and LUMO) distributions of APCA, APCA2OH, and APCA3OH (from left to right). (a) ESP and the corresponding calculated dipole moments (μ). (b) Spatial distributions of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), along with their respective energy levels and energy gaps (ΔE).



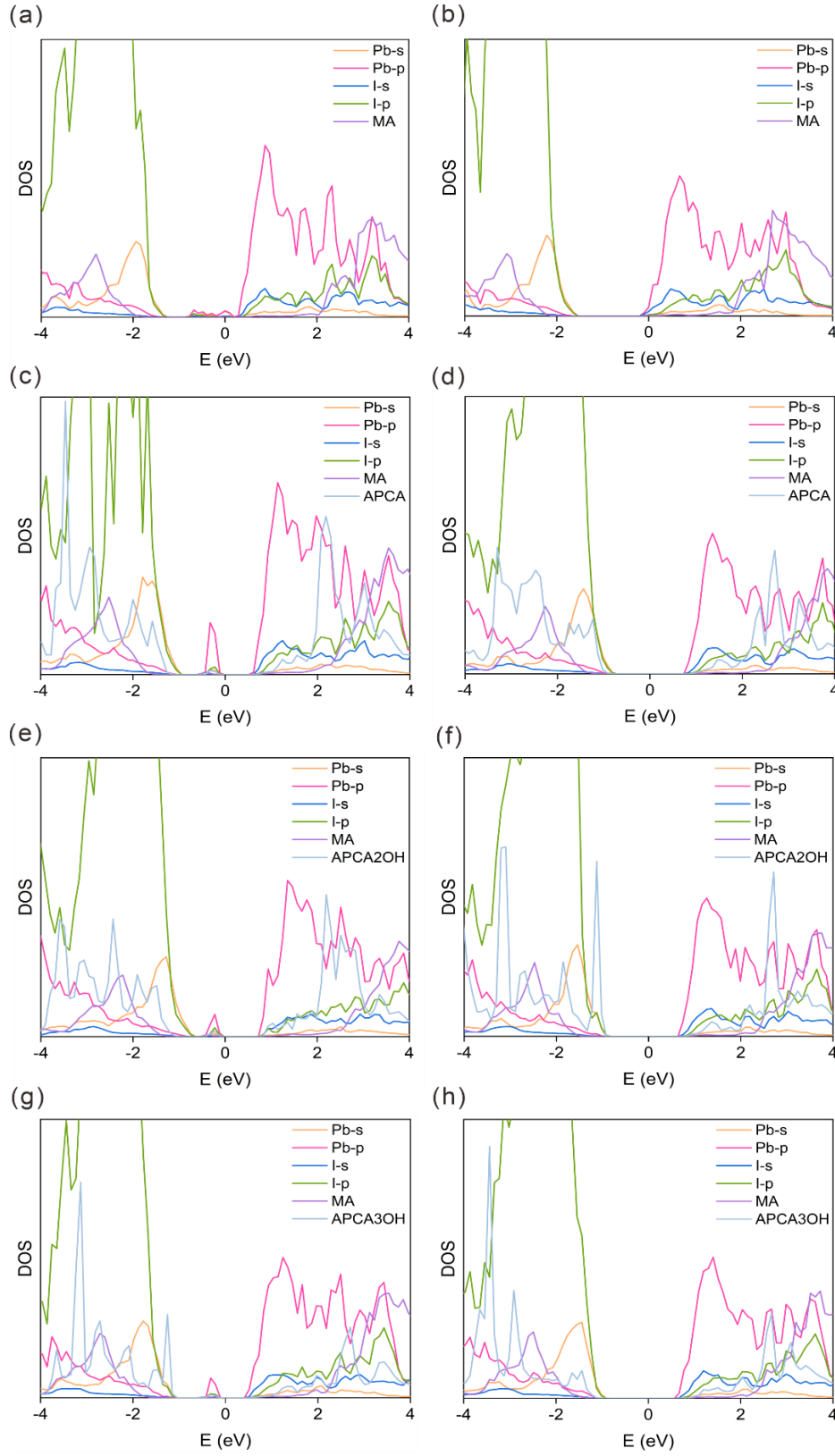
Supplementary Figure 4. Stable structures of (a) MAPbI₃, (b) PbI₂-MAPbI₃, (c) V₂O₅-MAPbI₃, (d) APCA@PbI₂-MAPbI₃, (e) APCA2OH@PbI₂-MAPbI₃, (f) APCA3OH@PbI₂-MAPbI₃, (g) APCA@V₂O₅-MAPbI₃, (h) APCA2OH@V₂O₅-MAPbI₃, (i) APCA3OH@V₂O₅-MAPbI₃. (Pb: dark gray, I: purple, C: brown, N: blue, O: red, H: white).



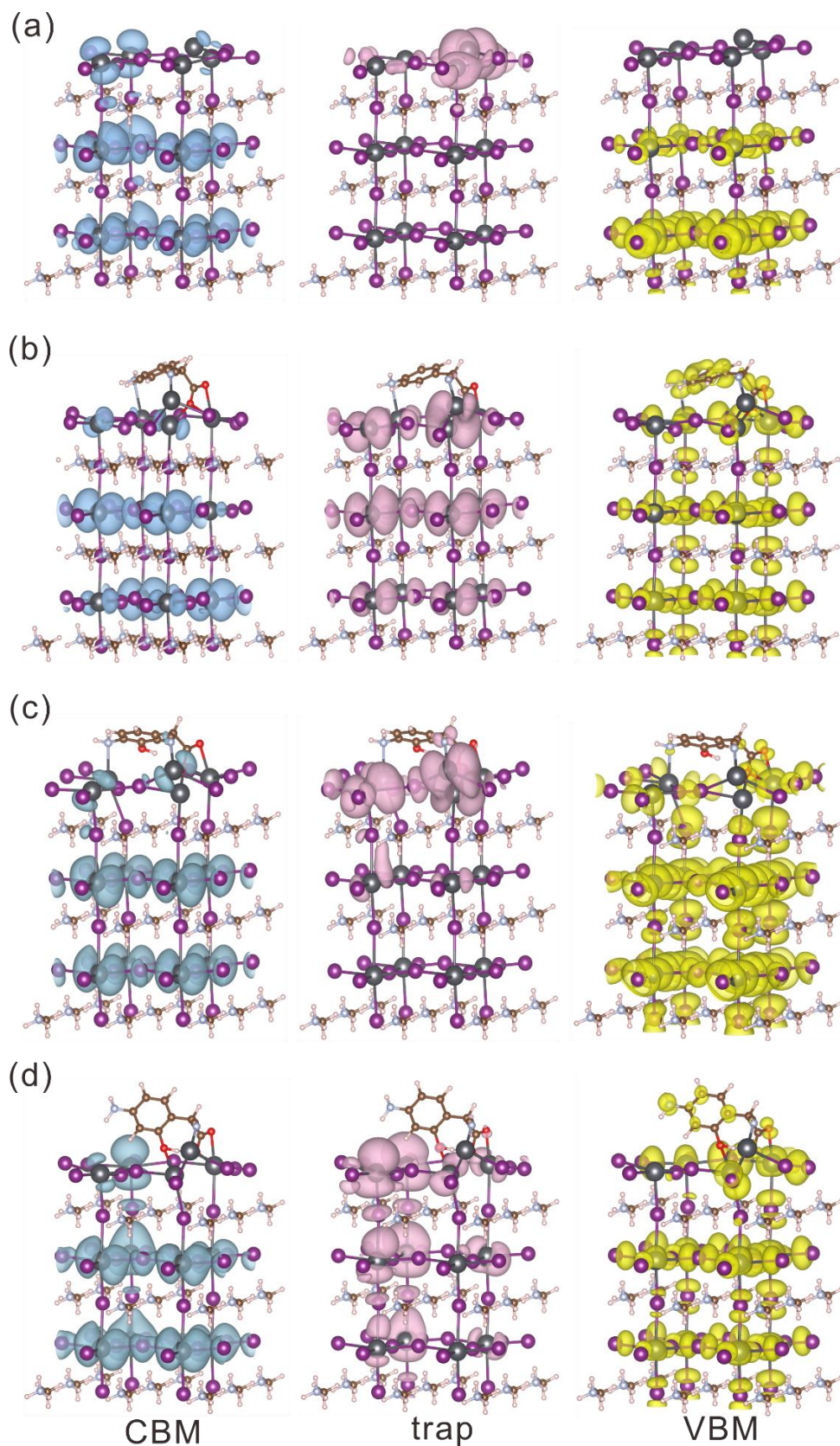
Supplementary Figure 5. Charge density difference and plane-averaged charge density difference for the (a) PbI_MAPbI_3 , (b) V_I_MAPbI_3 , (c) APCA@PbI_MAPbI_3 , (d) APCA@V_I_MAPbI_3 , (e) $\text{APCA2OH@PbI_MAPbI}_3$, (f) $\text{APCA2OH@V_I_MAPbI}_3$, (g) $\text{APCA3OH@PbI_MAPbI}_3$, (h) $\text{APCA3OH@V_I_MAPbI}_3$. Positive values (upper region of the vertical axis) indicate charge accumulation, while negative values (area below the vertical axis) indicate charge depletion.

Supplementary Table 1. Bandgap (in eV) of PbI₂/MAPbI₃, APCA@PbI₂/MAPbI₃, APCA2OH@PbI₂/MAPbI₃, APCA3OH@PbI₂/MAPbI₃, V₂O₅/MAPbI₃, APCA@V₂O₅/MAPbI₃, APCA2OH@V₂O₅/MAPbI₃ and APCA3OH@V₂O₅/MAPbI₃ systems

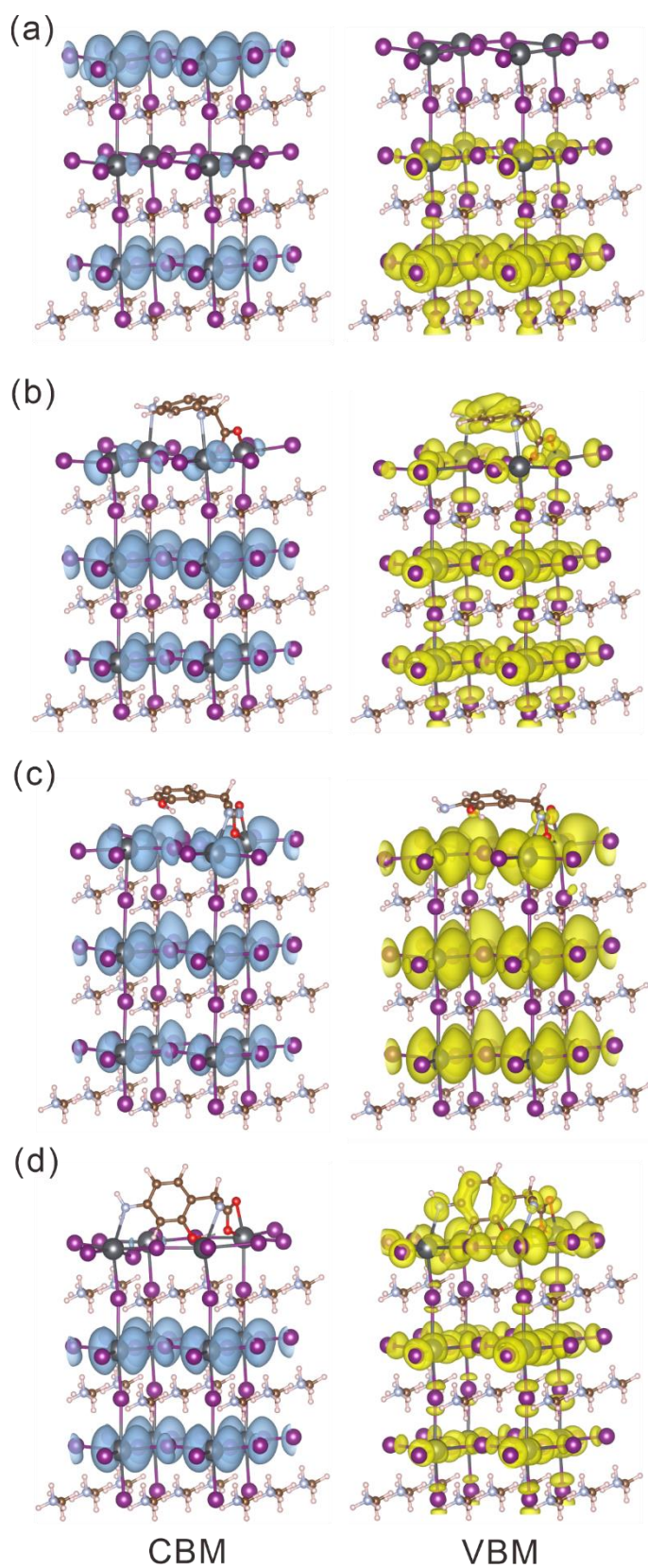
System	Bandgap (eV)
PbI ₂ /MAPbI ₃	1.74
APCA@PbI ₂ /MAPbI ₃	1.76
APCA2OH@PbI ₂ /MAPbI ₃	1.62
APCA3OH@PbI ₂ /MAPbI ₃	1.73
V ₂ O ₅ /MAPbI ₃	1.55
APCA@V ₂ O ₅ /MAPbI ₃	1.72
APCA2OH@V ₂ O ₅ /MAPbI ₃	1.73
APCA3OH@V ₂ O ₅ /MAPbI ₃	1.75



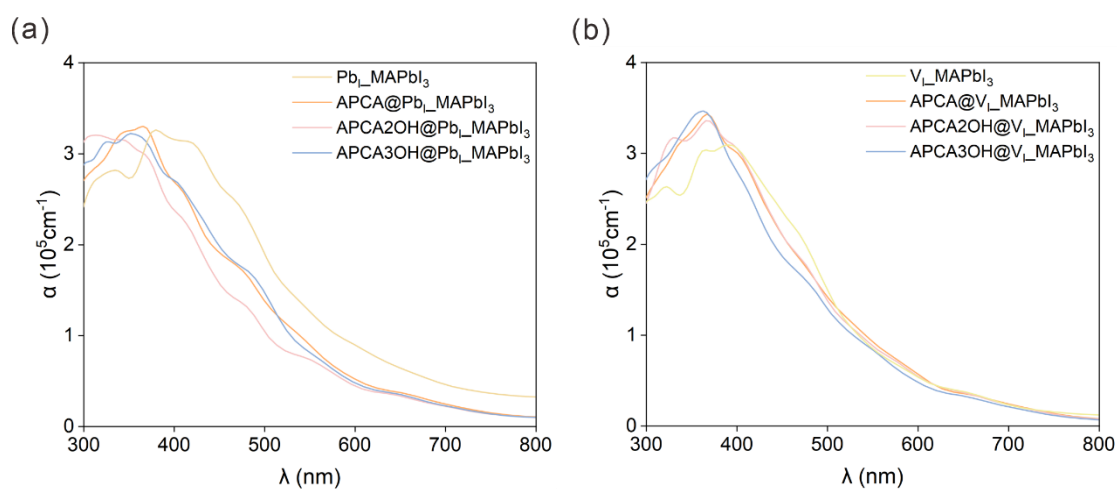
Supplementary Figure 6. Projected density of states (PDOS) for (a) PbI_MAPbI_3 , (b) V1_MAPbI_3 , (c) APCA@PbI_MAPbI_3 , (d) APCA@V1_MAPbI_3 , (e) $\text{APCA2OH@PbI_MAPbI}_3$, (f) $\text{APCA2OH@V1_MAPbI}_3$, (g) $\text{APCA3OH@PbI_MAPbI}_3$, and (h) $\text{APCA3OH@V1_MAPbI}_3$.



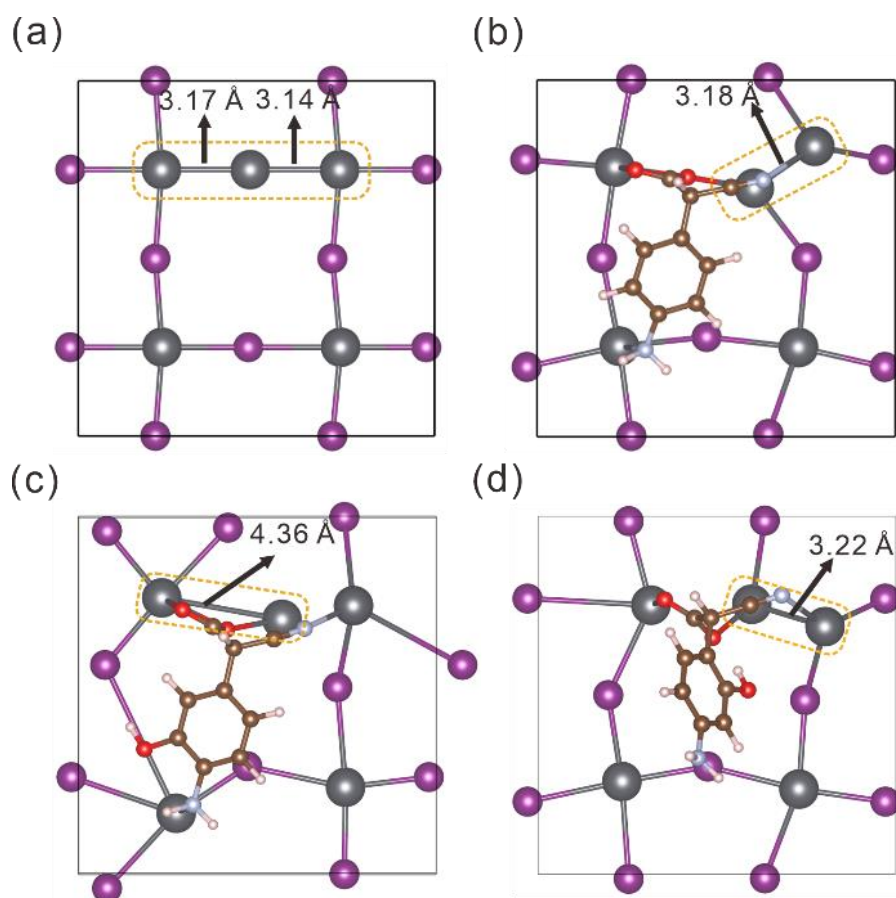
Supplementary Figure 7. Contour plots of CBM (blue), trap (pink) and VBM (yellow) states of (a) PbI_MAPbI_3 , (b) APCA@PbI_MAPbI_3 , (c) $\text{APCA2OH@PbI_MAPbI}_3$, (d) $\text{APCA3OH@PbI_MAPbI}_3$.



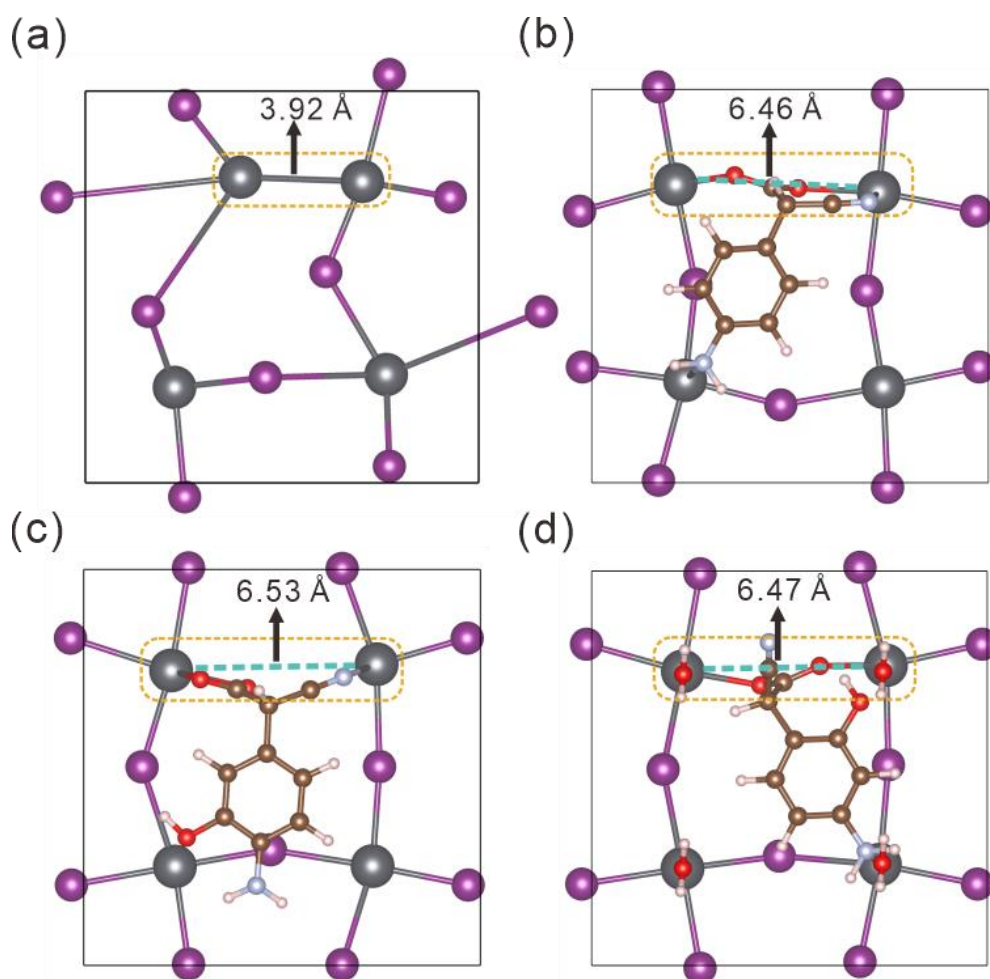
Supplementary Figure 8. Contour plots of CBM (blue) and VBM (yellow) states of (a) $V_I_MAPbI_3$, (b) $APCA@V_I_MAPbI_3$, (c) $APCA2OH@V_I_MAPbI_3$, (d) $APCA3OH@V_I_MAPbI_3$.



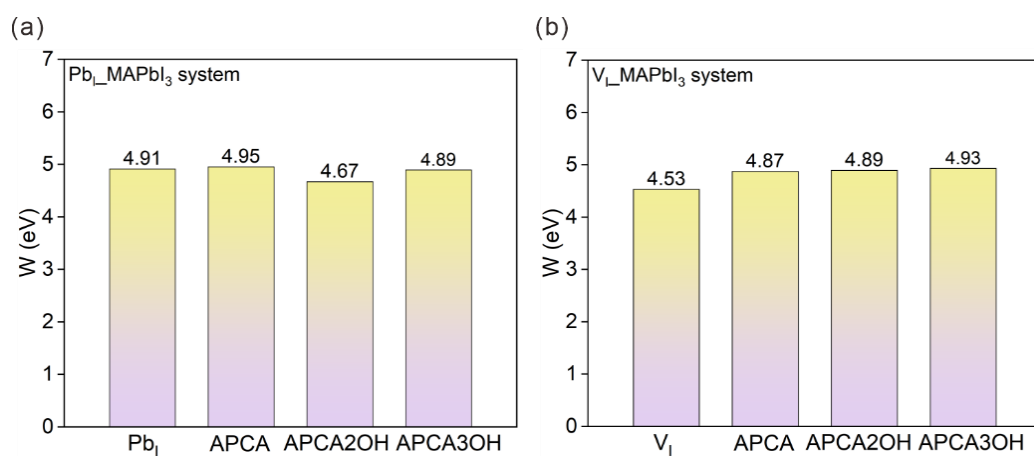
Supplementary Figure 9. Absorption spectra of defected and passivated (a) PbI_MAPbI_3 systems and (b) V_I_MAPbI_3 systems.



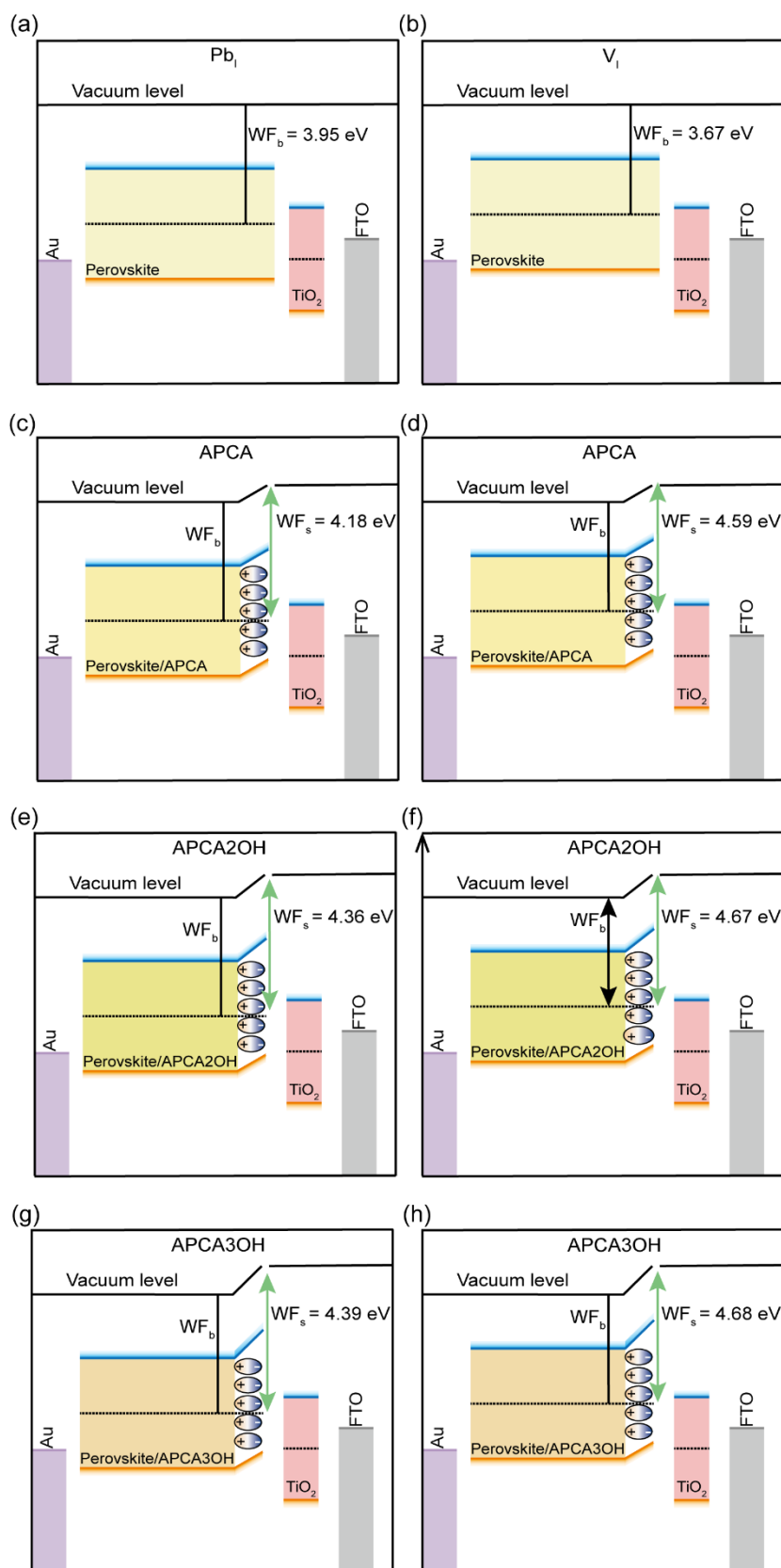
Supplementary Figure 10. (a) Pb_3 trimer formed in PbI_MAPbI_3 , and Pb_2 dimer formed in (b) APCA@PbI_MAPbI_3 , (c) $\text{APCA2OH@PbI_MAPbI}_3$ and (d) $\text{APCA3OH@PbI_MAPbI}_3$.



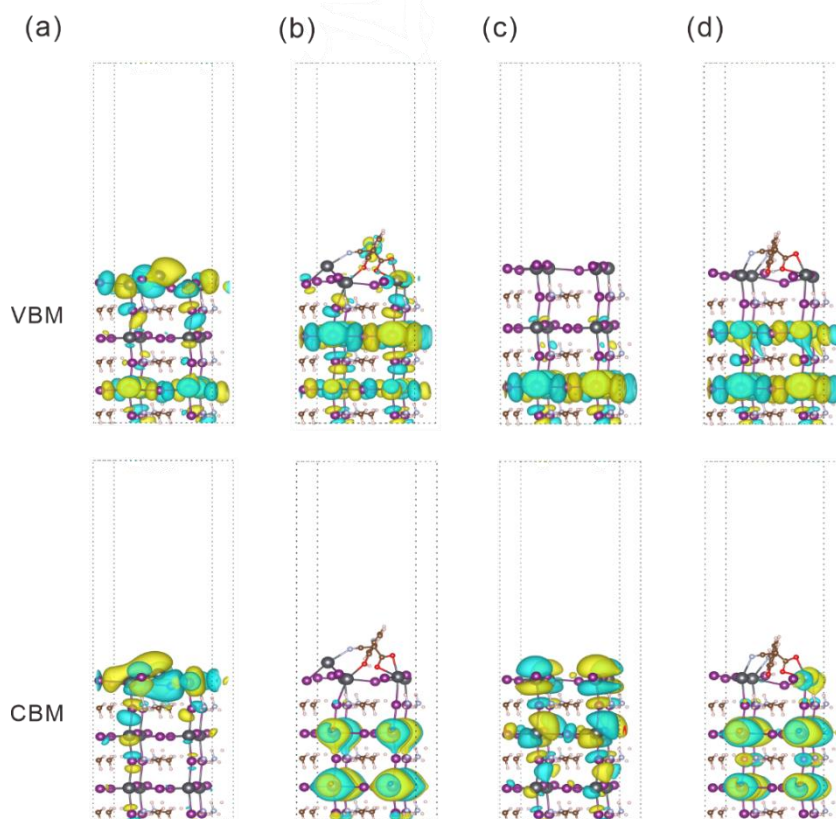
Supplementary Figure 11. (a) Pb_2 dimer formed in V_I -MAPbI₃, adjacent Pb–Pb distance around iodine vacancy in (b) APCA@ V_I -MAPbI₃, (c) APCA2OH@ V_I -MAPbI₃, and (d) APCA3OH@ V_I -MAPbI₃.



Supplementary Figure 12. Electron-hole creation energies of (a) Pb_I and (b) V_I defective surfaces before and after PH anions passivation.



Supplementary Figure 13. Work function of Pb_I and V_I defective surfaces before and after PH anions passivation. (a, b) Pristine perovskite films with Pb_I and V_I defects. (c–h) Perovskite passivated by APCA, APCA2OH and APCA3OH.



Supplementary Figure 14. Calculated VBM and CBM isosurfaces for (a) PbI_MAPbI₃, (b) APCA3OH@PbI_MAPbI₃, (c) VI_MAPbI₃ and (d) APCA3OH@VI_MAPbI₃.

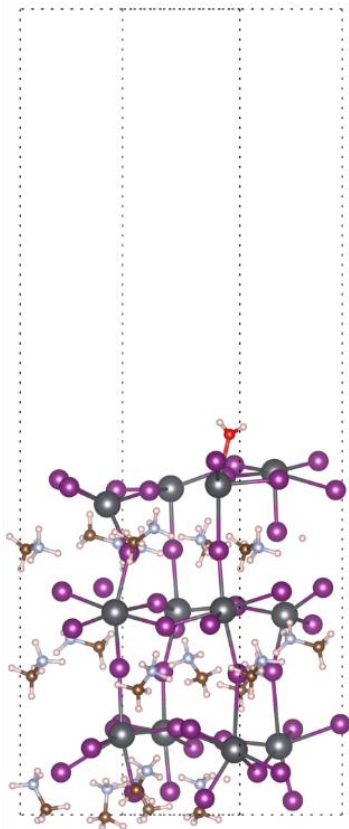
Supplementary Table 2. Hole-electron distribution overlap function (S_m), electron-hole centroid distance (D_{ij} , in Å), hole delocalization index (HDI) and electron delocalization index (EDI) of the selected excited states (S_n) for PbI_MAPbI₃, APCA3OH@PbI_MAPbI₃, VI_MAPbI₃ and APCA3OH@VI_MAPbI₃ systems

System	Excitation state	S_m	D_{ij} (Å)	HDI	EDI
PbI_MAPbI ₃	$S_0 \rightarrow S_{15}$	0.52	5.82	3.98	3.72
APCA3OH@PbI_MAPbI ₃	$S_0 \rightarrow S_{16}$	0.24	7.23	2.81	2.74
VI_MAPbI ₃	$S_0 \rightarrow S_{18}$	0.31	1.71	2.83	2.50
APCA3OH@VI_MAPbI ₃	$S_0 \rightarrow S_{16}$	0.26	2.66	2.75	2.43

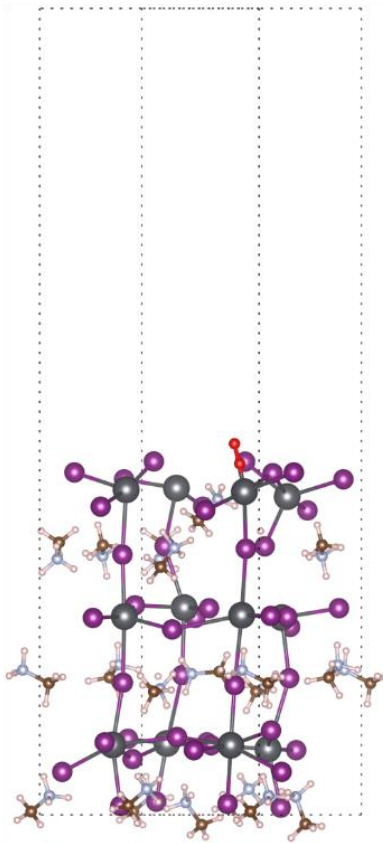
Supplementary Table 3. Activation energies (E_a) and migration rate constants (κ) for the migration of I ions on the $V_I_MAPbI_3$ surfaces and APCA, APCA2OH and APCA3OH passivated systems

System	E_a (eV)	κ (s ⁻¹)
$V_I_MAPbI_3$	0.49	2.30×10^5
APCA@ $V_I_MAPbI_3$	5.40	7.55×10^{-78}
APCA2OH@ $V_I_MAPbI_3$	5.80	1.44×10^{-84}
APCA3OH @ $V_I_MAPbI_3$	10.72	3.21×10^{-167}

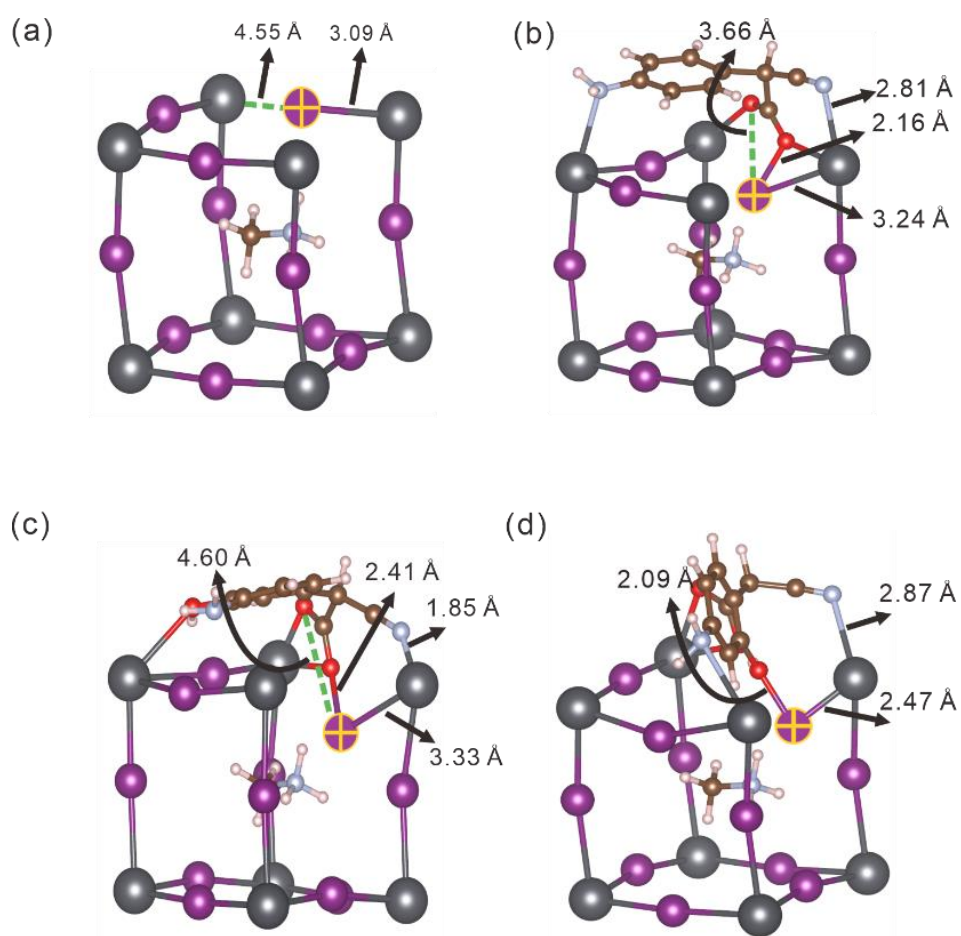
(a)



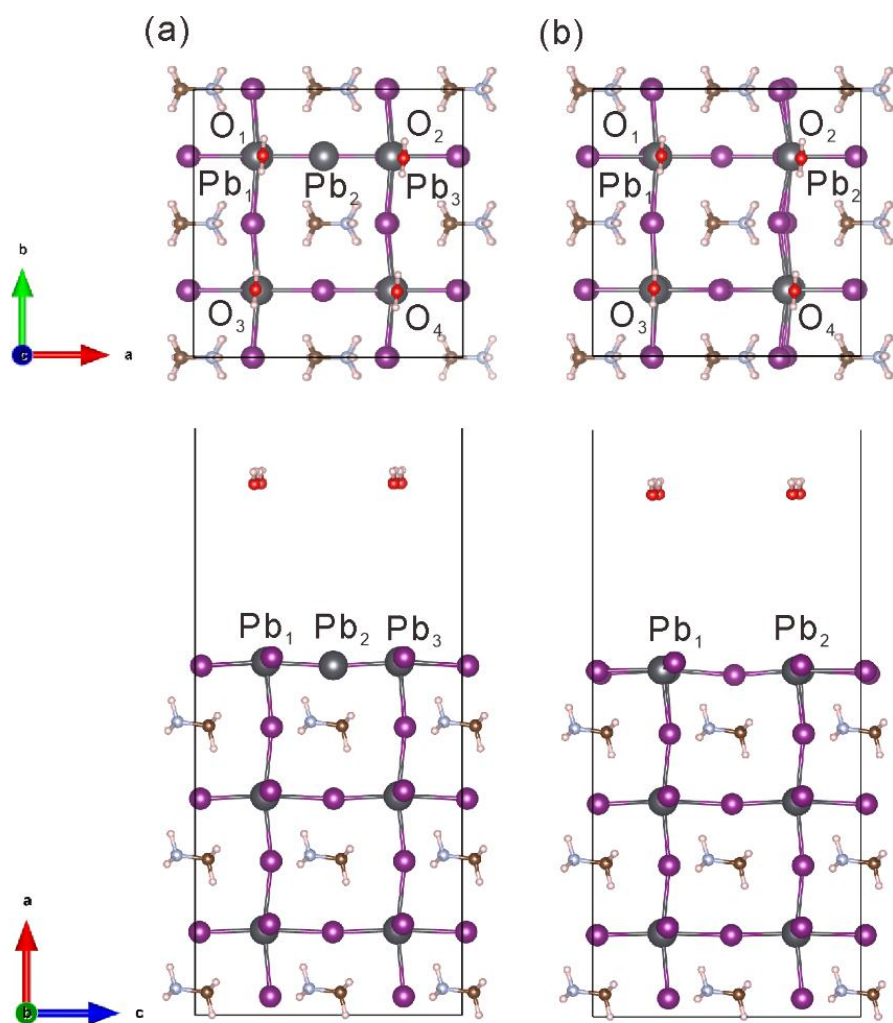
(b)



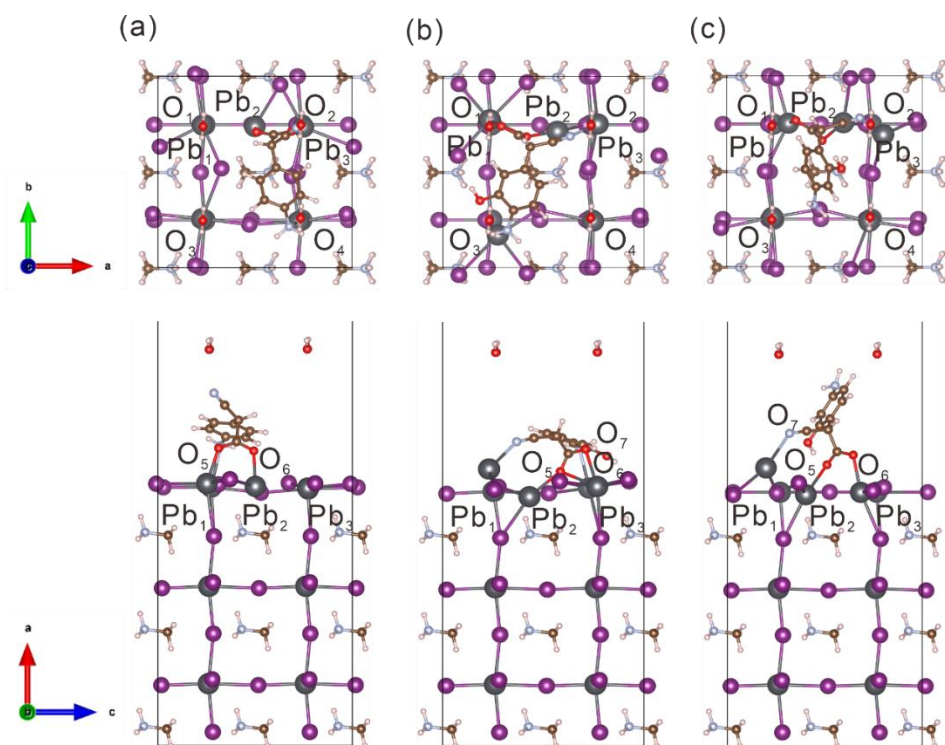
Supplementary Figure 15. (a) Configuration of H₂O adsorbed on $V_I_MAPbI_3$, (b) configuration of O₂ adsorbed on $V_I_MAPbI_3$.



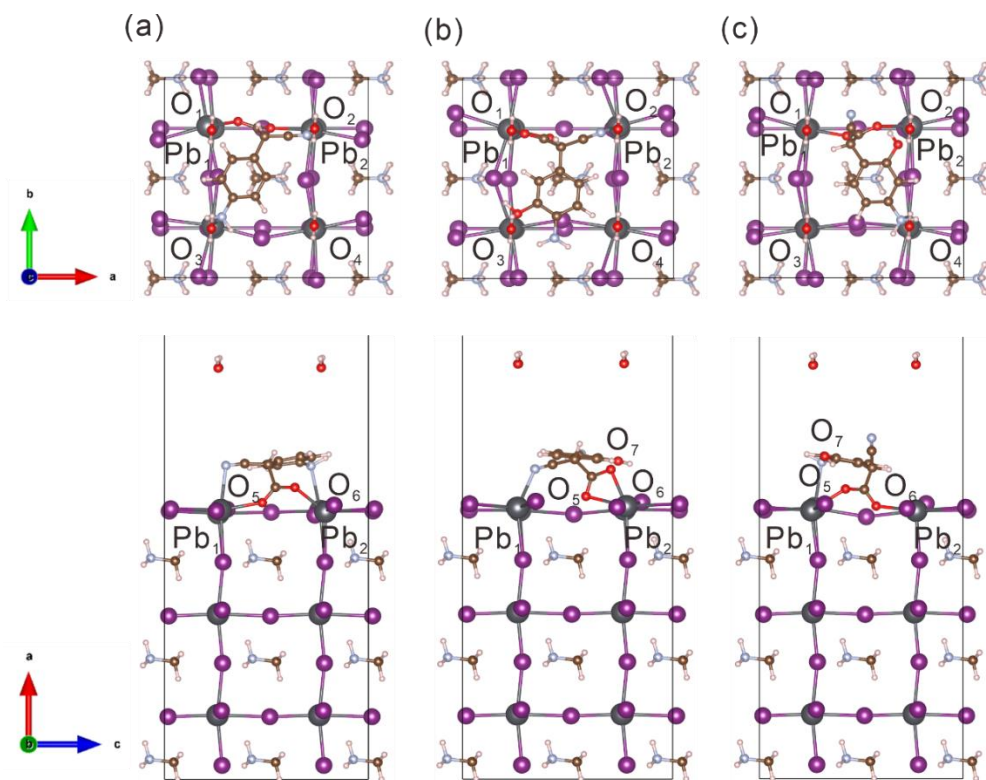
Supplementary Figure 16. Configurations of the transition states in iodine ion migration pathways. (a) $V_I_MAPbI_3$, (b) $APCA@V_I_MAPbI_3$, (c) $APCA2OH@V_I_MAPbI_3$, and (d) $APCA3OH@V_I_MAPbI_3$. The migrating iodine ions in transition states are highlighted.



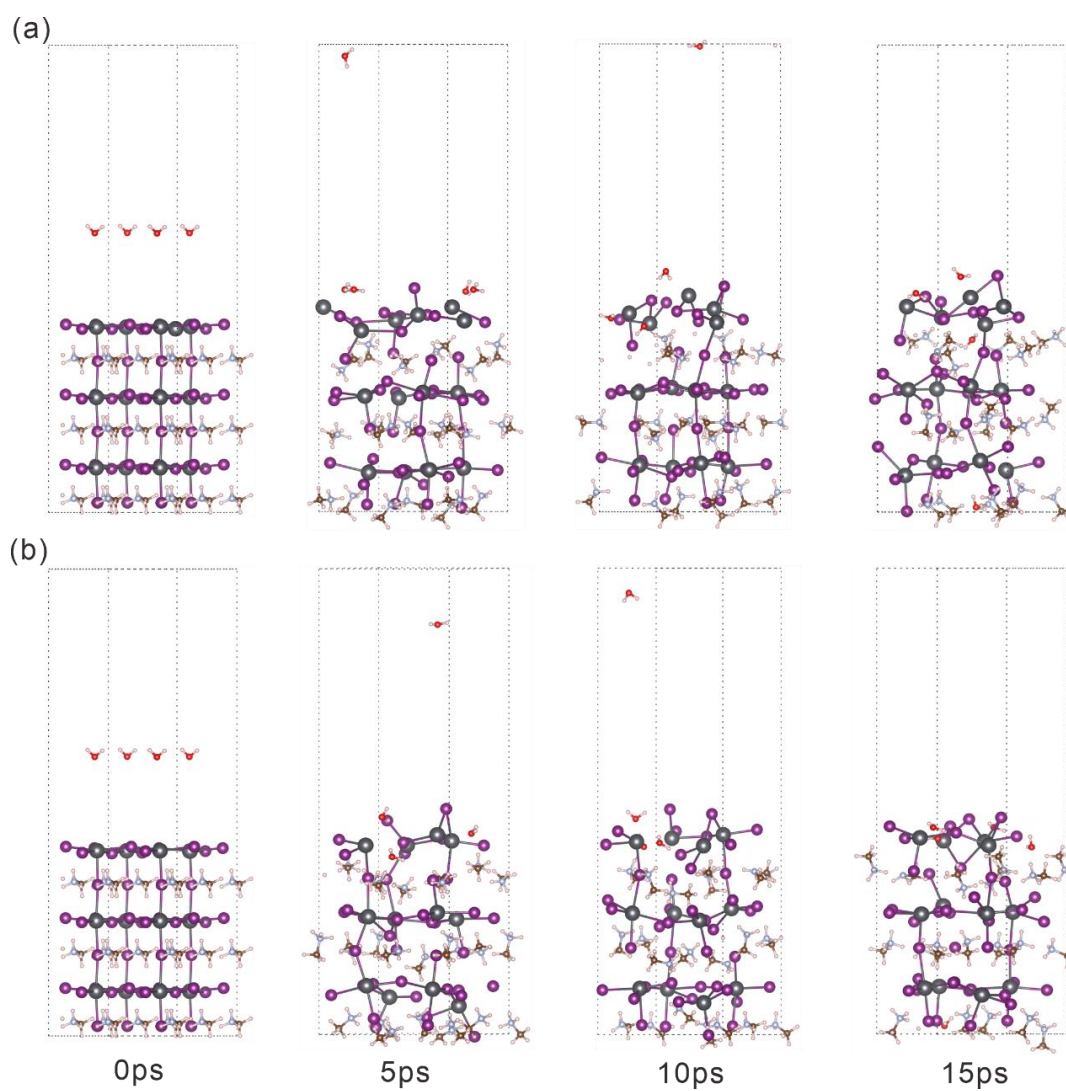
Supplementary Figure 17. Top (up layer) and side views (second layer) of the optimized configurations of H₂O molecules on (a) PbI-MAPbI_3 surfaces, (b) VI-MAPbI_3 surfaces.



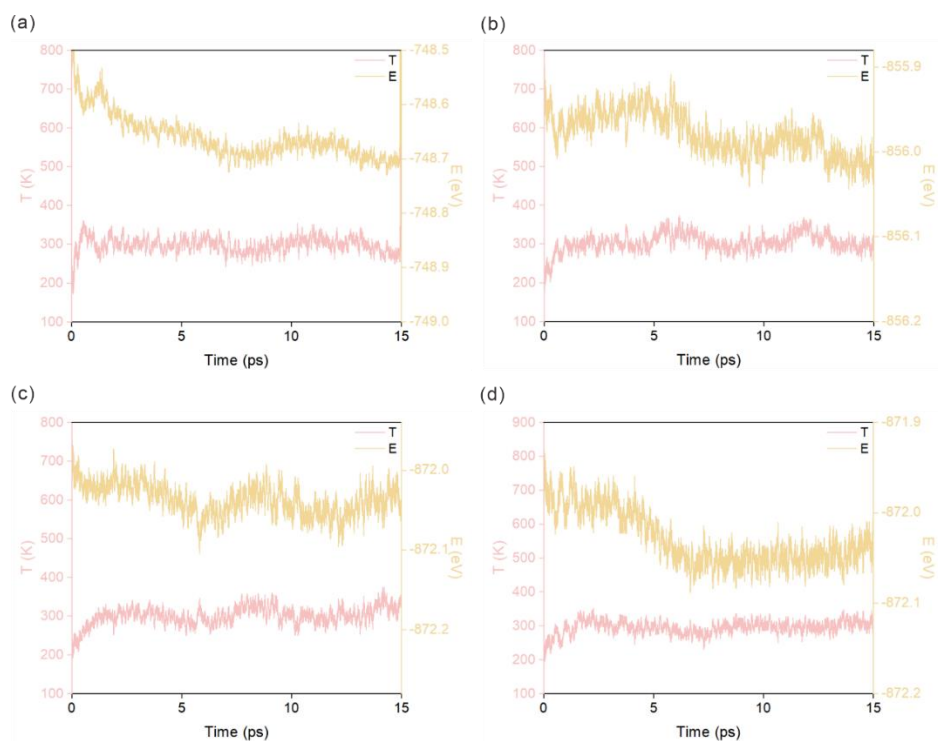
Supplementary Figure 18. Top (upper layer) and side views (second layer) of the optimized configurations of H₂O molecules on (a) APCA@PbI₁-MAPbI₃, (b) APCA2OH@PbI₁-MAPbI₃, (c) APCA3OH@PbI₁-MAPbI₃.



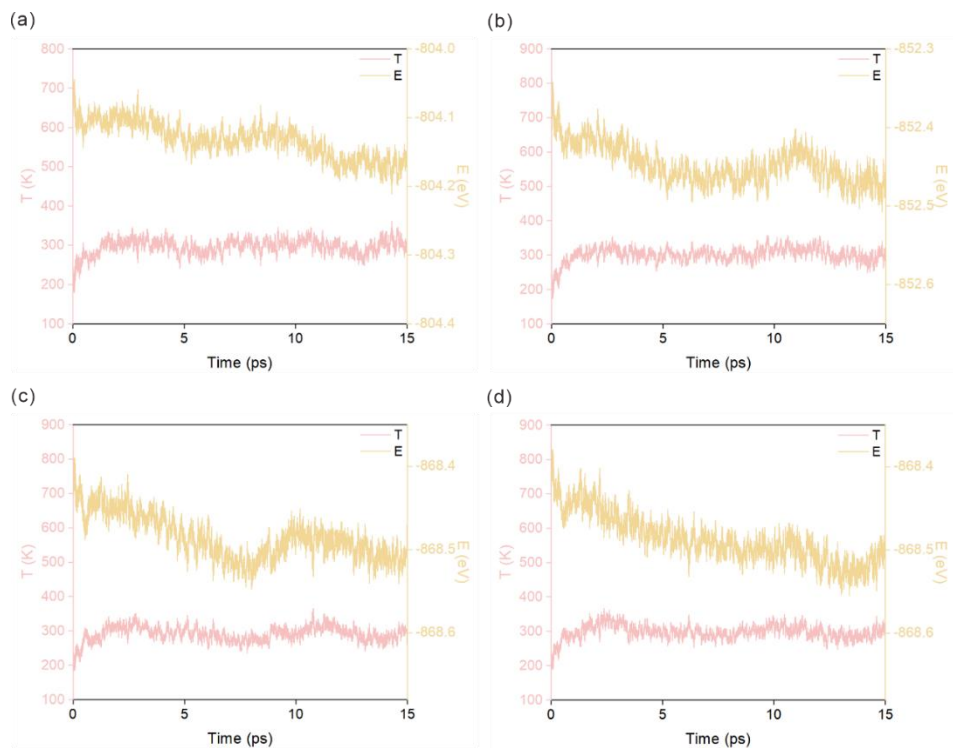
Supplementary Figure 19. Top (upper layer) and side views (second layer) of the optimized configurations of H₂O molecules on (a) APCA@V₁-MAPbI₃, (b) APCA2OH@V₁-MAPbI₃ and (c) APCA3OH@V₁-MAPbI₃.



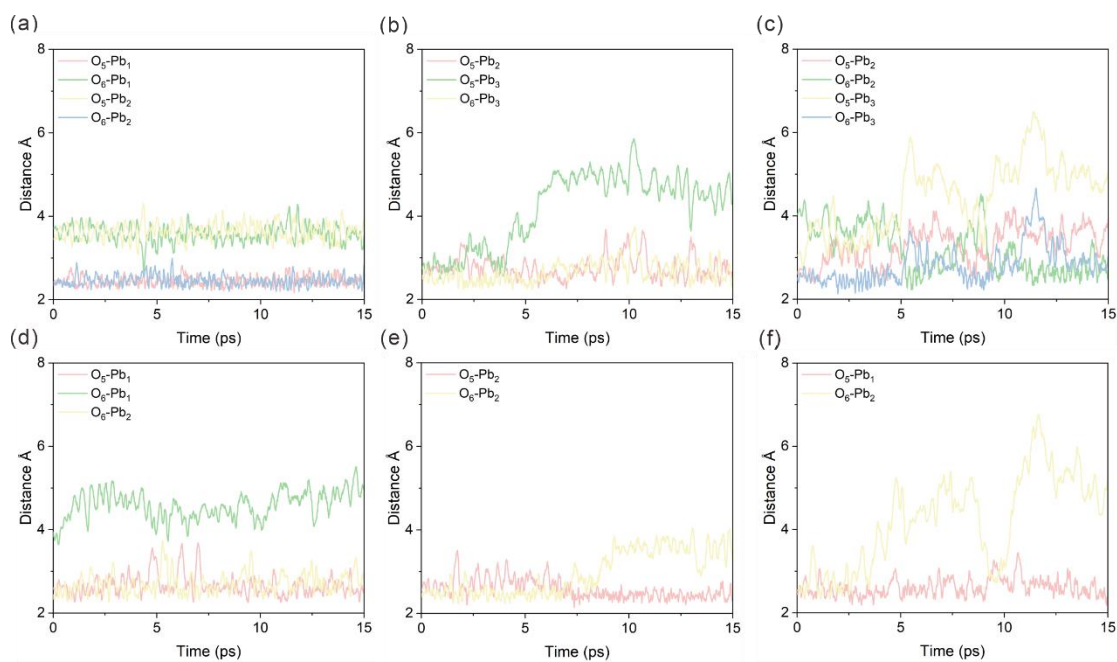
Supplementary Figure 20. Trajectory snapshots of H₂O on (a) PbI₁-MAPbI₃ surfaces, (b) V₁-MAPbI₃ surfaces.



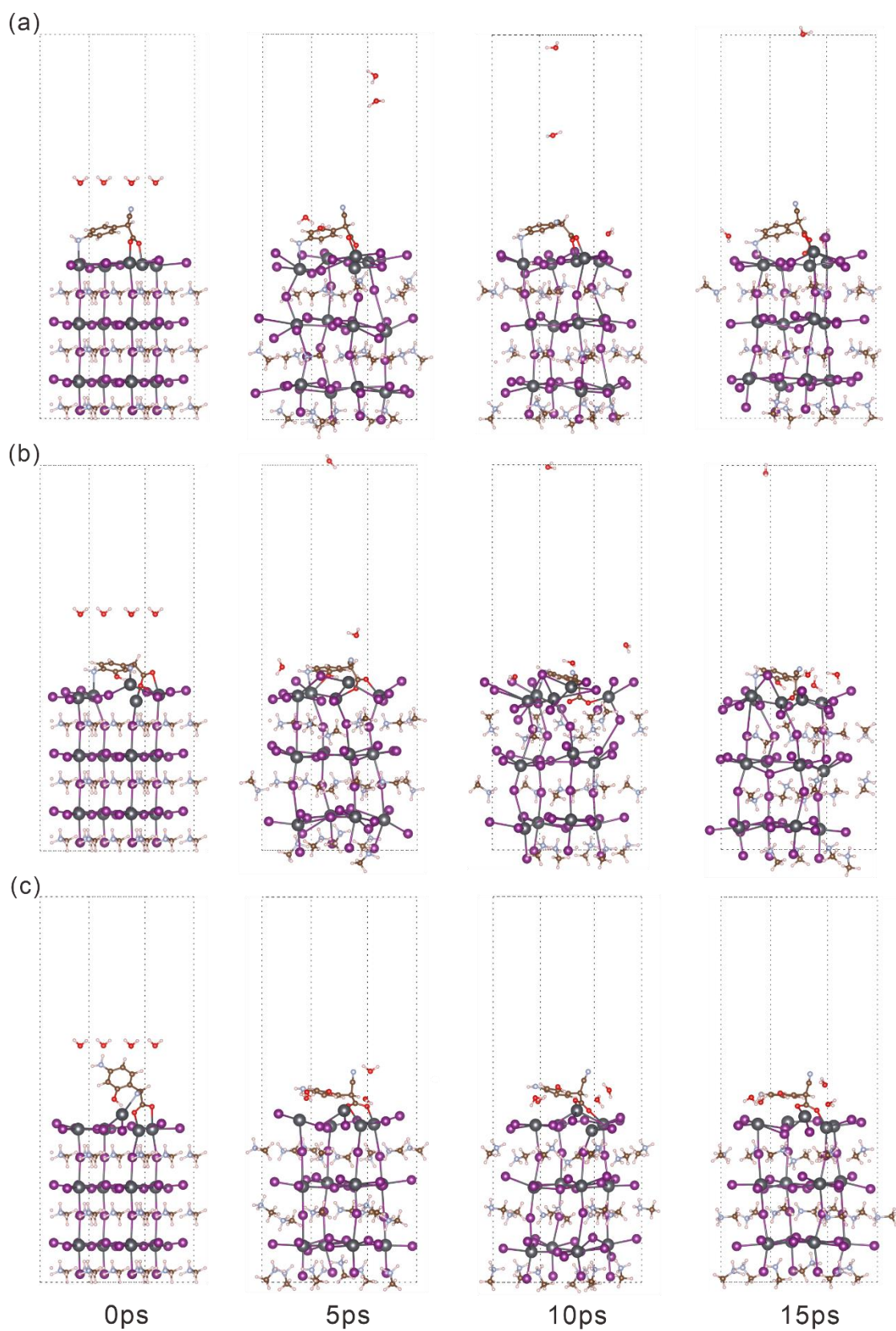
Supplementary Figure 21. Evolution of energy and temperature fluctuations for (a) $\text{PbI}_2/\text{MAPbI}_3$, (b) $\text{APCA}/\text{PbI}_2/\text{MAPbI}_3$, (c) $\text{APCA2OH}/\text{PbI}_2/\text{MAPbI}_3$, (d) $\text{APCA3OH}/\text{PbI}_2/\text{MAPbI}_3$.



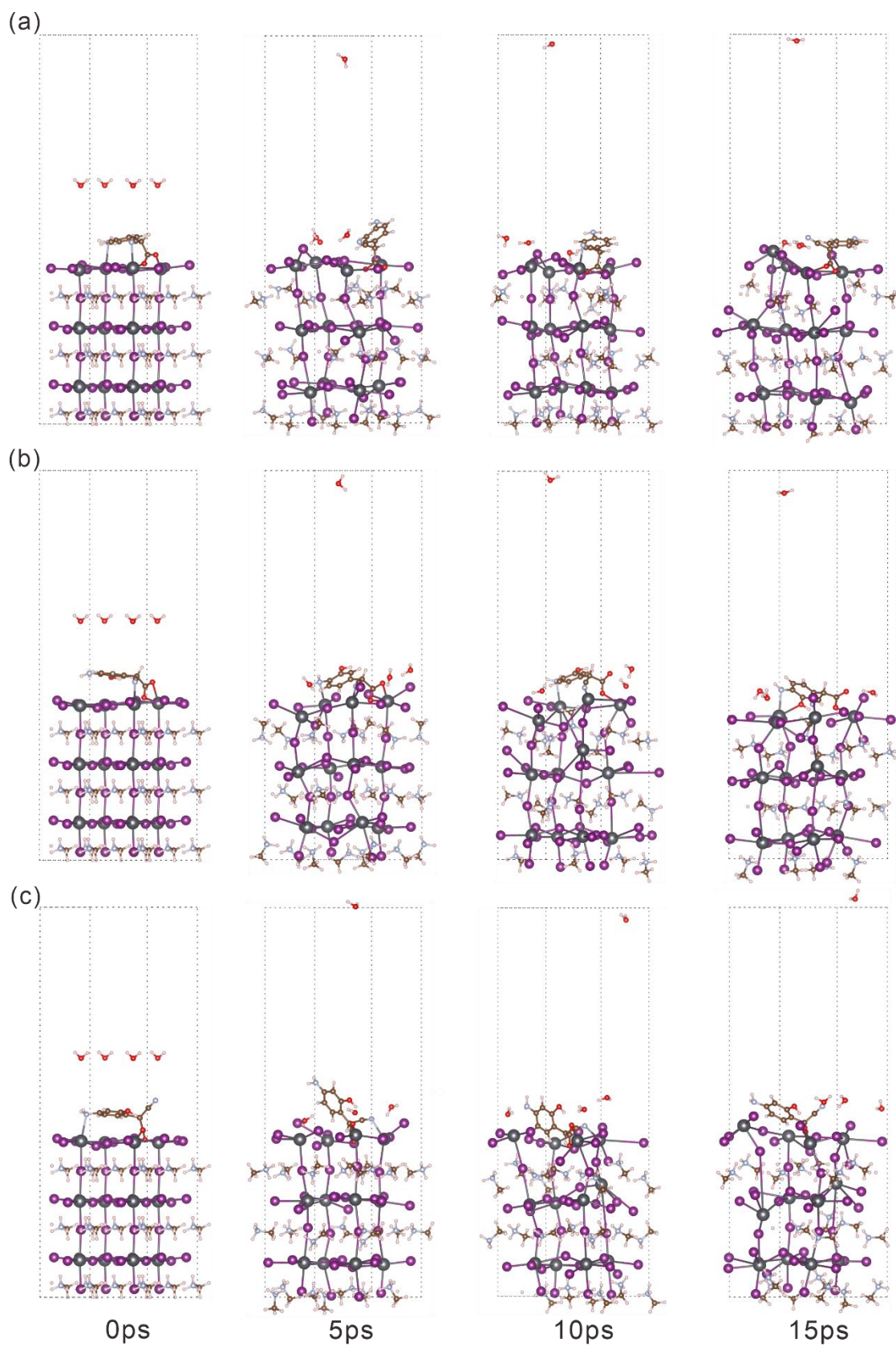
Supplementary Figure 22. Evolution of energy and temperature fluctuations for (a) $\text{V}_2\text{I}_6/\text{MAPbI}_3$, (b) $\text{APCA}/\text{V}_2\text{I}_6/\text{MAPbI}_3$, (c) $\text{APCA2OH}/\text{V}_2\text{I}_6/\text{MAPbI}_3$, (d) $\text{APCA3OH}/\text{V}_2\text{I}_6/\text{MAPbI}_3$.



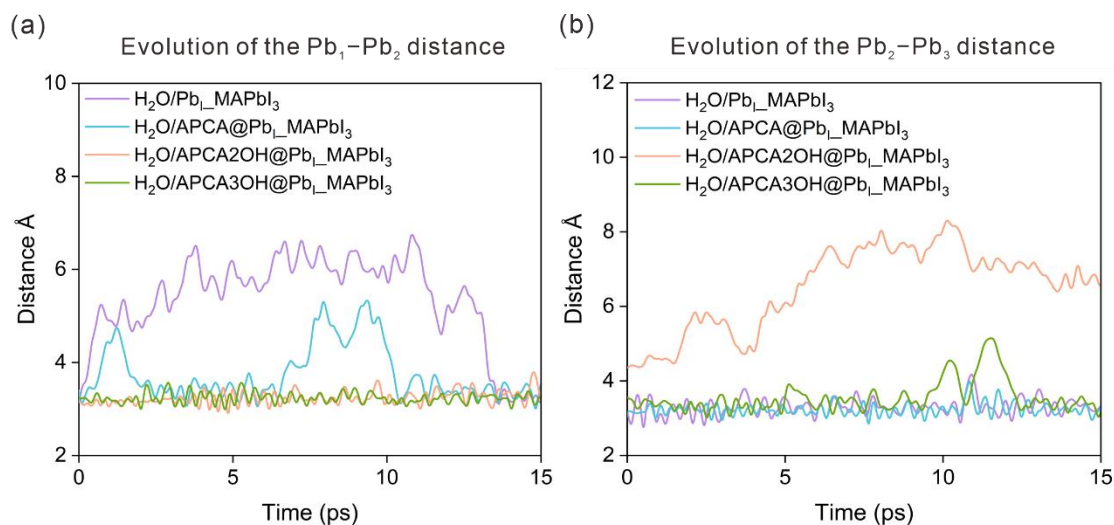
Supplementary Figure 23. Evolution of the Pb–O distances with PH anion in (a) APCA@Pb_I_MAPbI₃, (b) APCA2OH@Pb_I_MAPbI₃, (c) APCA3OH@Pb_I_MAPbI₃, (d) APCA@V_I_MAPbI₃, (e) APCA2OH@V_I_MAPbI₃, (f) APCA3OH@V_I_MAPbI₃.



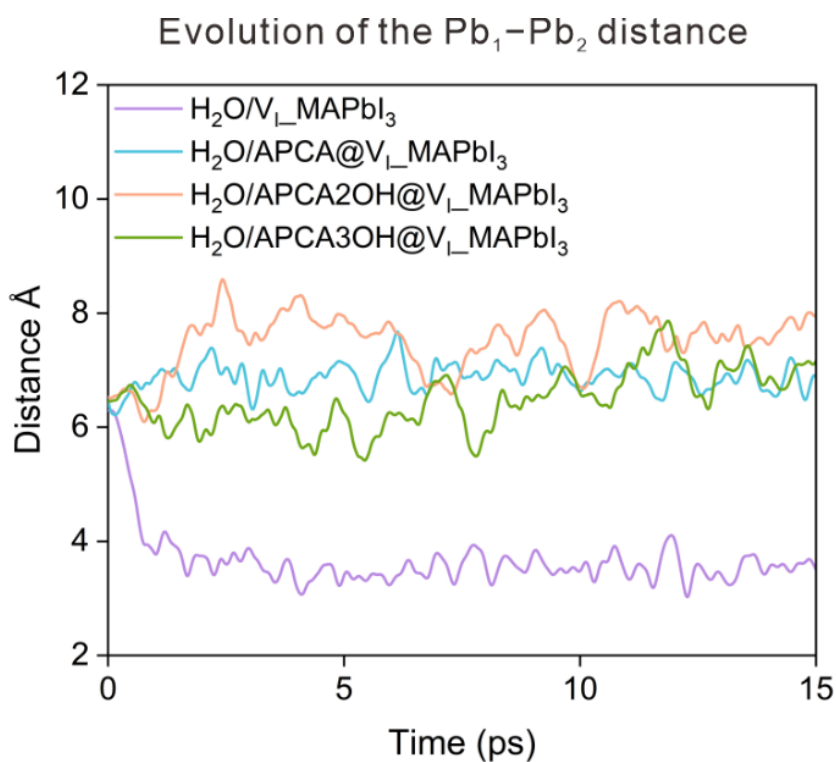
Supplementary Figure 24. Trajectory snapshots of H₂O on (a) APCA@PbI₁-MAPbI₃, (b) APCA2OH@PbI₁-MAPbI₃, (c) APCA3OH@PbI₁-MAPbI₃ systems described by the AIMD simulations.



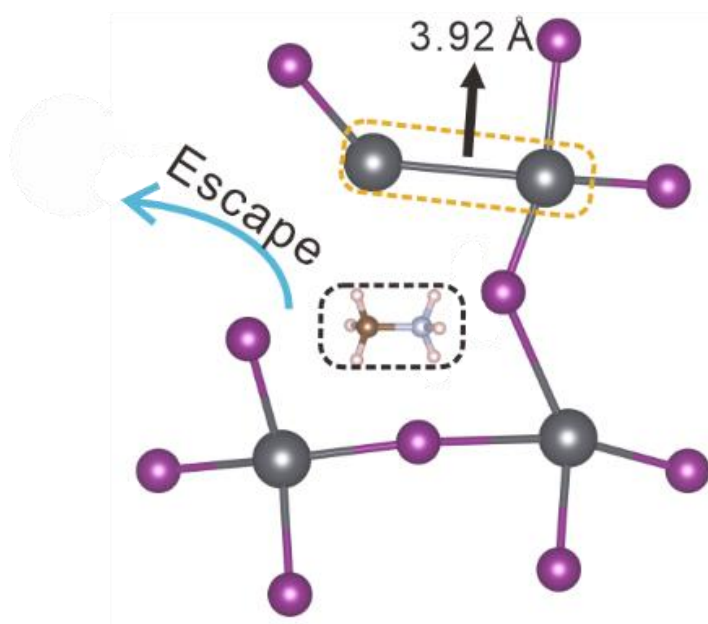
Supplementary Figure 25. Trajectory snapshots of H₂O on (a) APCA@V_I-MAPbI₃, (b) APCA2OH@V_I-MAPbI₃, (c) APCA3OH@V_I-MAPbI₃ systems described by the AIMD simulations.



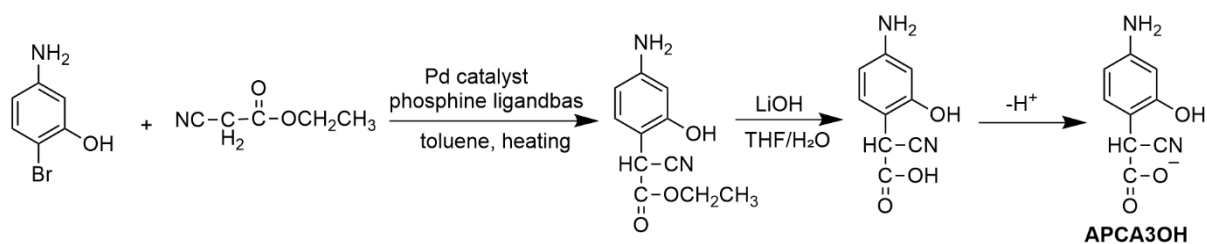
Supplementary Figure 26. Evolution of the (a) $\text{Pb}_1\text{-Pb}_2$ and (b) $\text{Pb}_2\text{-Pb}_3$ distances around the anti-sites for PbI-MAPbI_3 systems.



Supplementary Figure 27. Evolution of the $\text{Pb}_1\text{-Pb}_2$ distances around the vacancy sites for VI-MAPbI_3 systems.



Supplementary Figure 28. Schematic diagram of MA^+ cations escape from the defective MAPbI_3 surface.



Supplementary Figure 29. Synthetic route of APCA3OH.