Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Stabilizing Orthorhombic $CsSnI_3$ Perovskites with Optimized Electronic Properties by Surface Ligands with Inter-Molecular Hydrogen Bond

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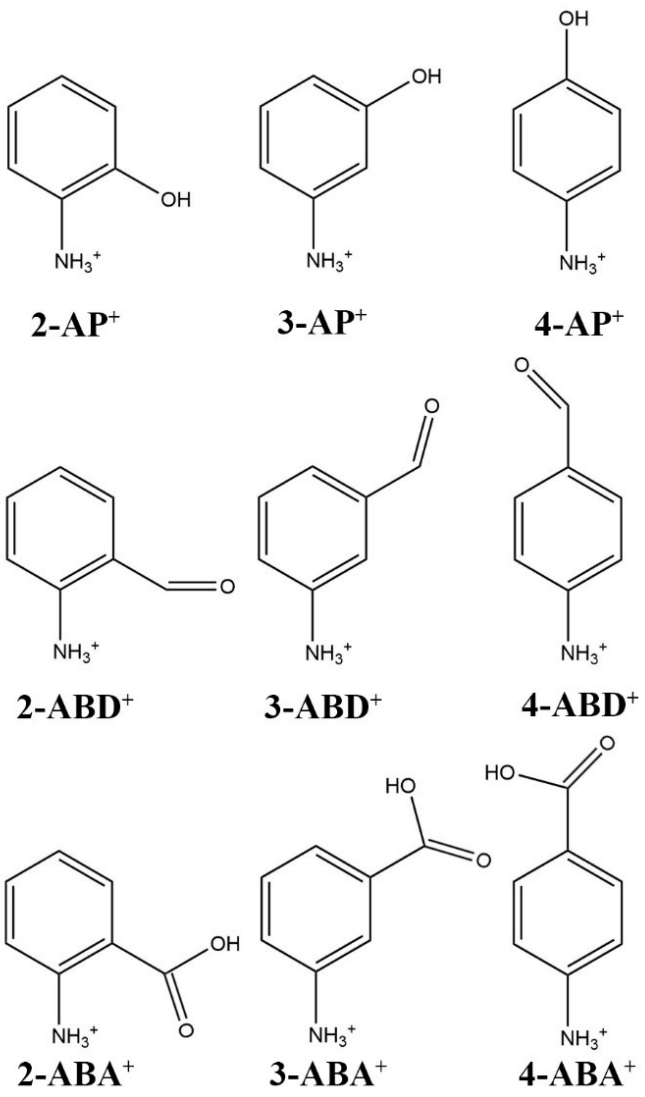

Figure S1. Molecular structures of different ligands.

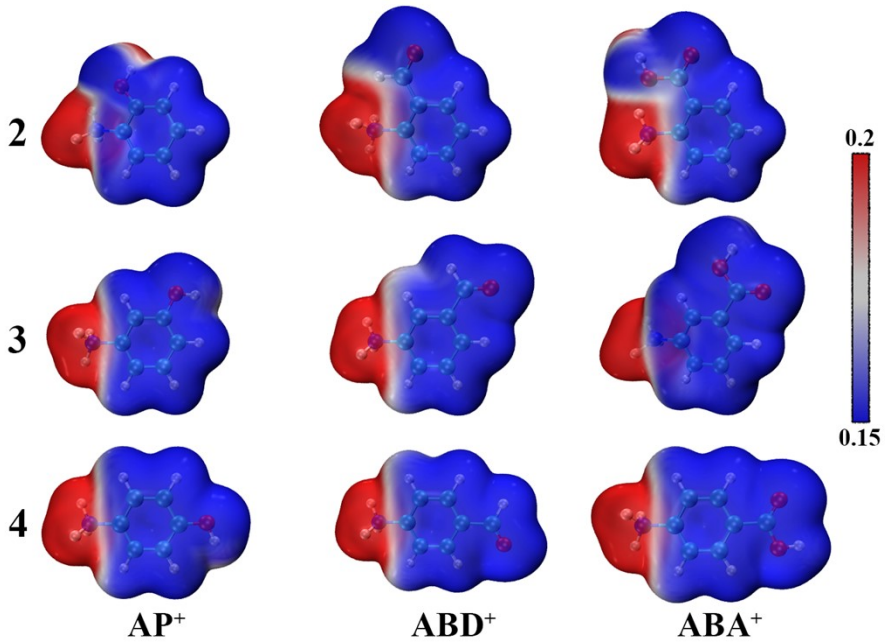

Figure S2. The ESP of different ligands.

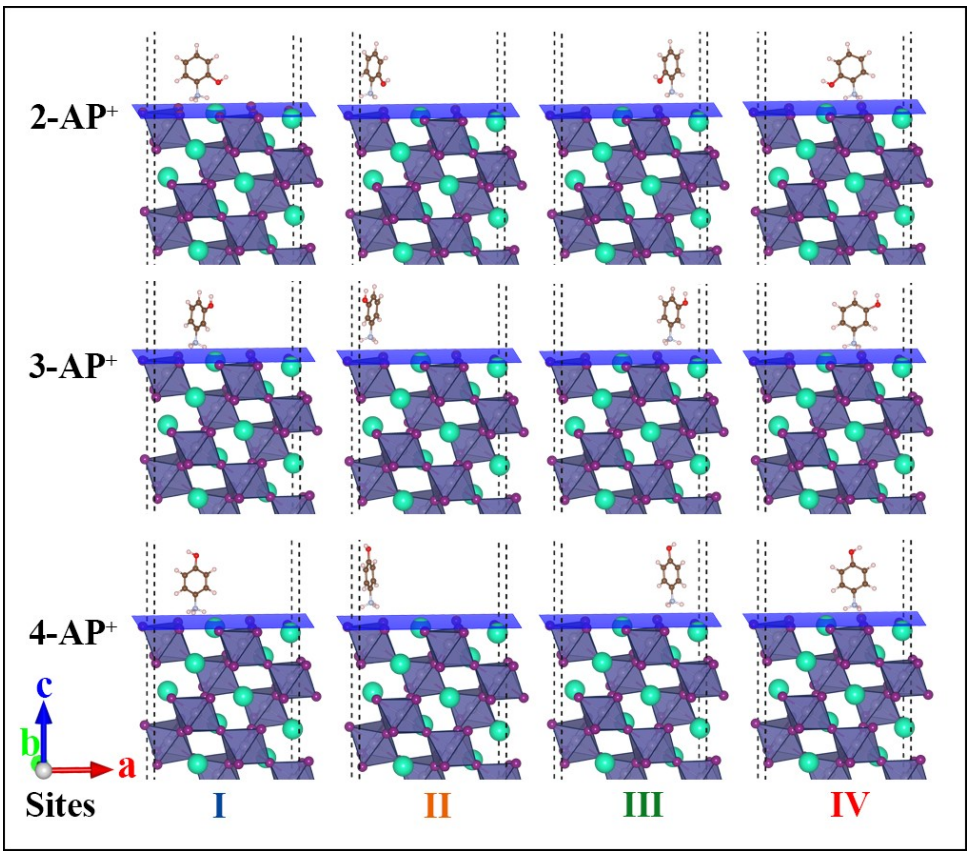

Figure S3. The passivated configurations with one AP^+ ligand situated at adsorption sites I, II, III and IV, respectively.

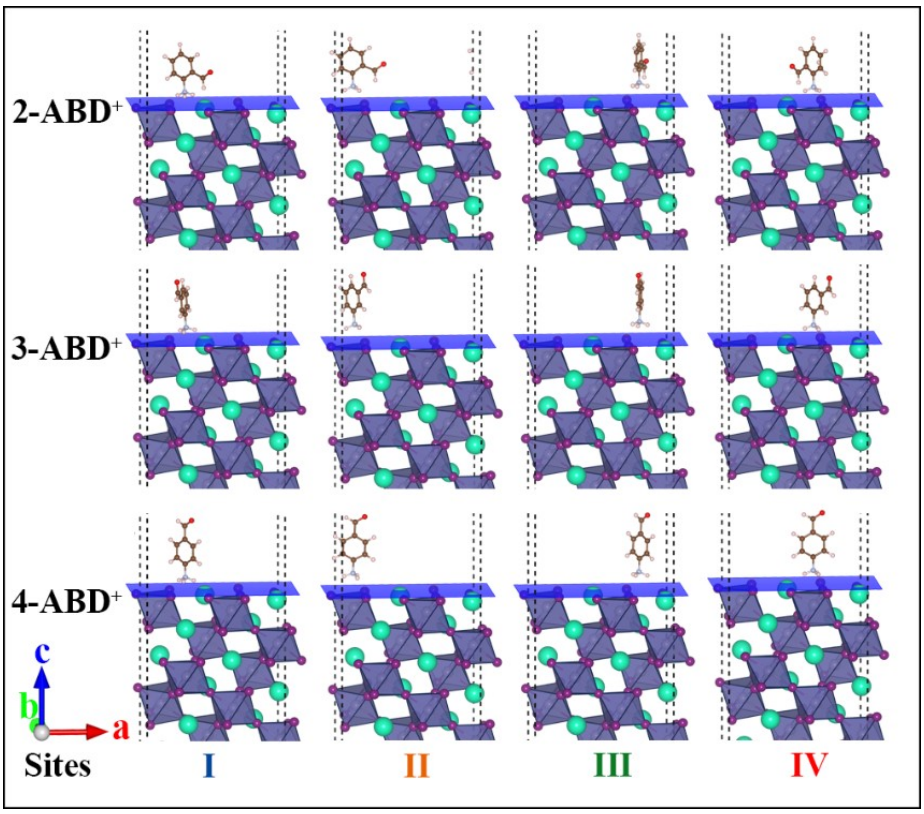

Figure S4. The passivated configurations with one ABD^+ ligand situated at adsorption sites I, II, III and IV, respectively.

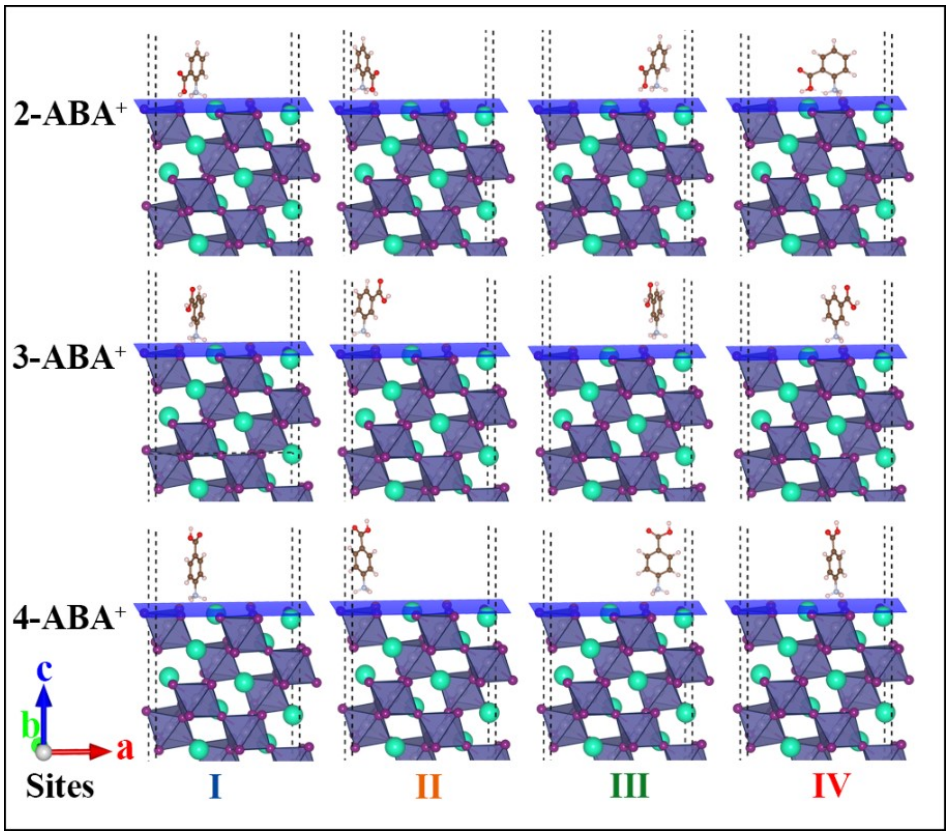

Figure S5. The passivated configurations with one ABA^+ ligand situated at adsorption sites I, II, III and IV, respectively.

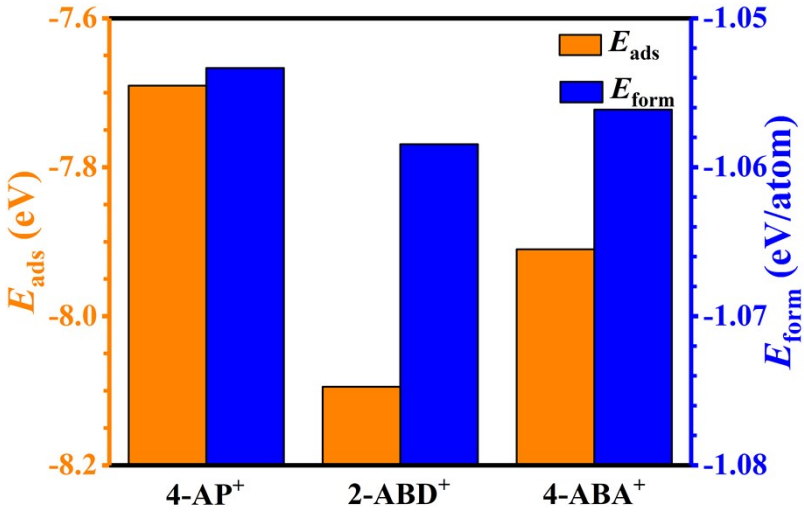

Figure S6. The calculated E_{ads} and E_{form} of 4-AP$^+$, 2-ABD$^+$, 4-ABA$^+$ configurations with 1/2 ML coverage.

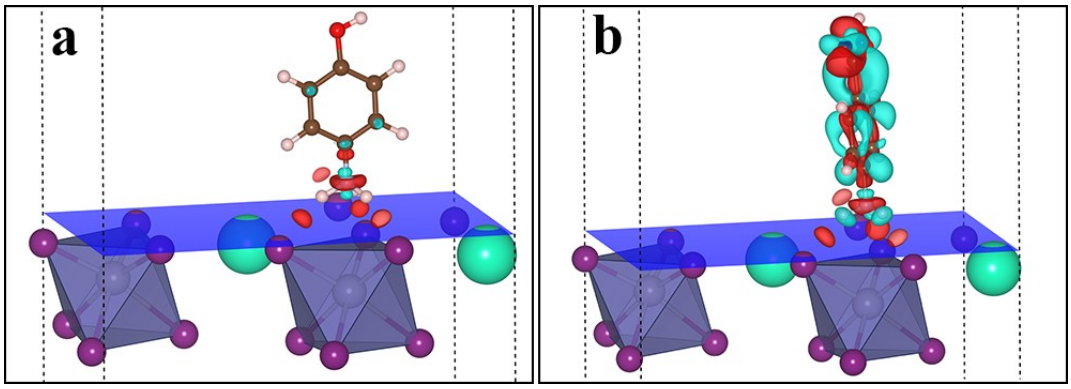

Figure S7. (a-b) The CDD between 4-AP^{+}, 4-ABA^{+} configurations with 1/2 ML coverage and pristine slab, respectively. The red and cyan isosurfaces set as 0.004 e/a_0^3 indicate the charge accumulation and depletion region, respectively.

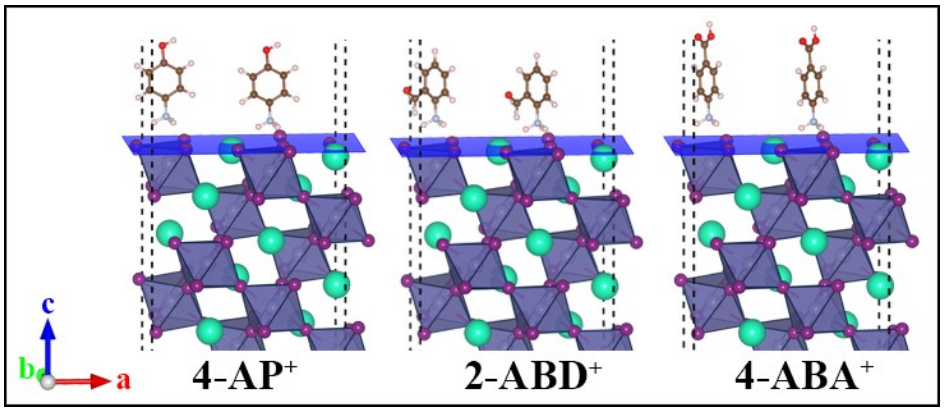

Figure S8. Structures of 4-AP$^+$, 2-ABD$^+$, 4-ABA$^+$ configurations with 1 ML coverage.

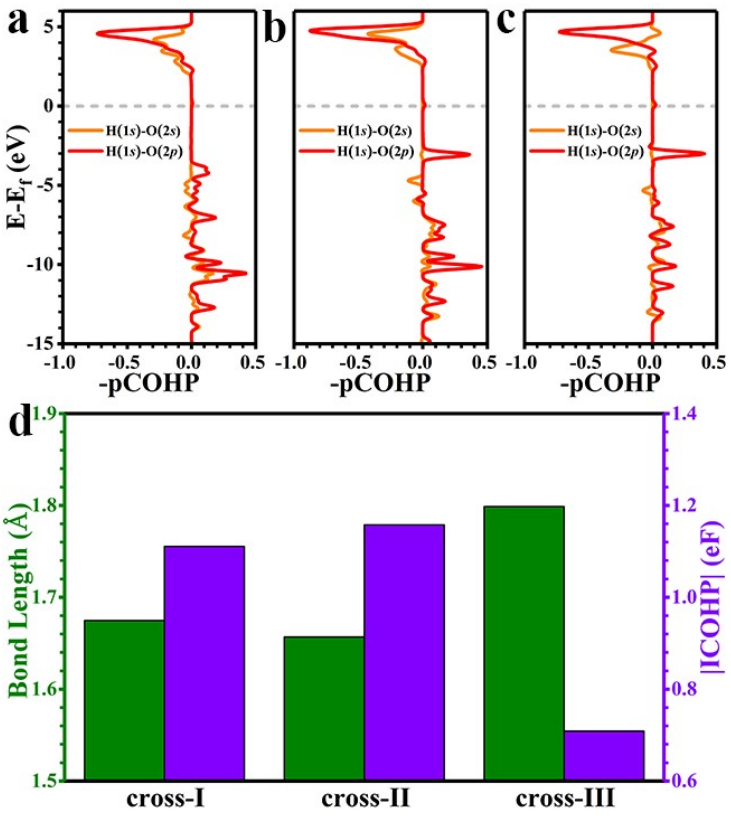

Figure S9. (a-c) Orbital-resolved COHP of inter-molecular hydrogen bond of cross-I, II and III configurations, respectively. The fermi energy level was set as zero. (b) The bond length and absolute value of ICOHP of inter-molecular hydrogen bond for cross-I, II and III configurations.

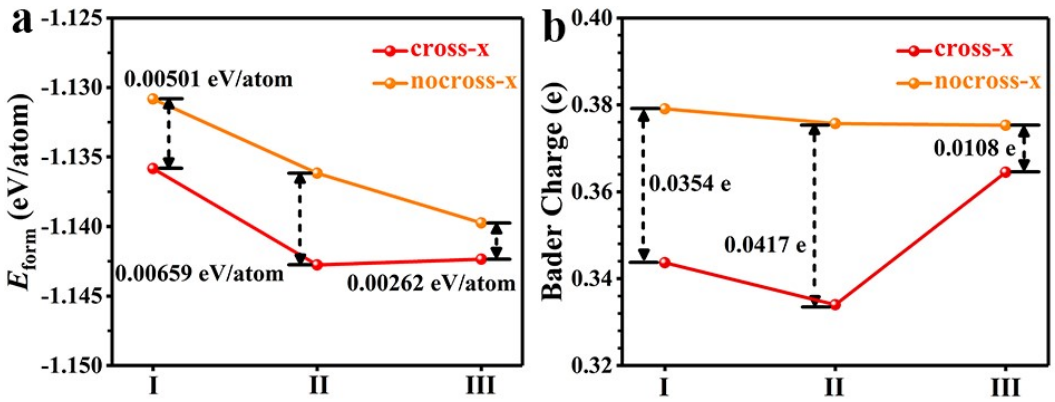

Figure S10. (a) The calculated E_{form} of cross-x and nocross-x configurations. (b) The calculated Bader charges of H atoms linking with adjacent O atoms for cross-x and nocross-x configurations.

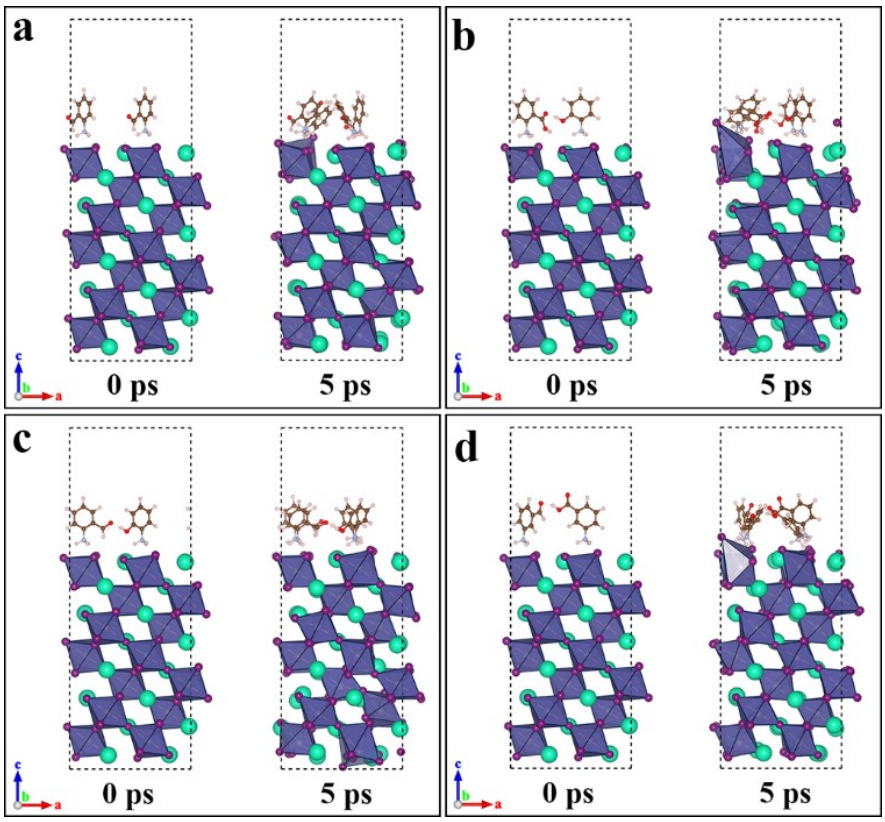

Figure S11. (a-d) Snapshots recorded at 0 and 5 ps of AIMD simulations for 2-ABD^{+} configuration with 1 ML coverage, cross-I, II and III configurations at 300 K, respectively.

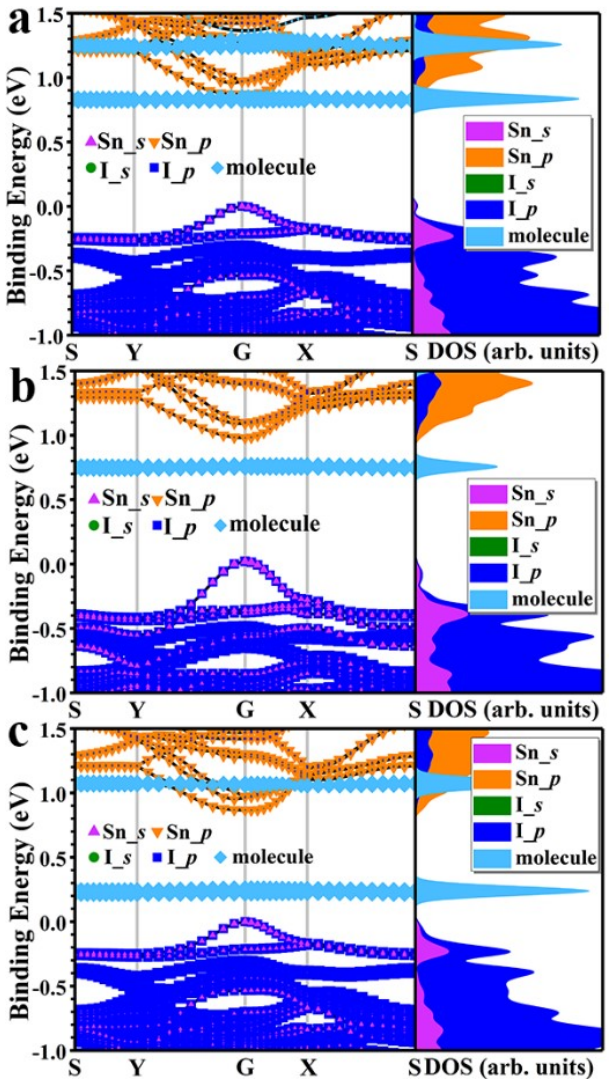

Figure S12. (a-c) The fat-band and PDOS of 4-AP^{+} configuration with 1/2 ML coverage, 4-ABA^{+} configurations with 1/2 and 1 ML coverages, respectively.

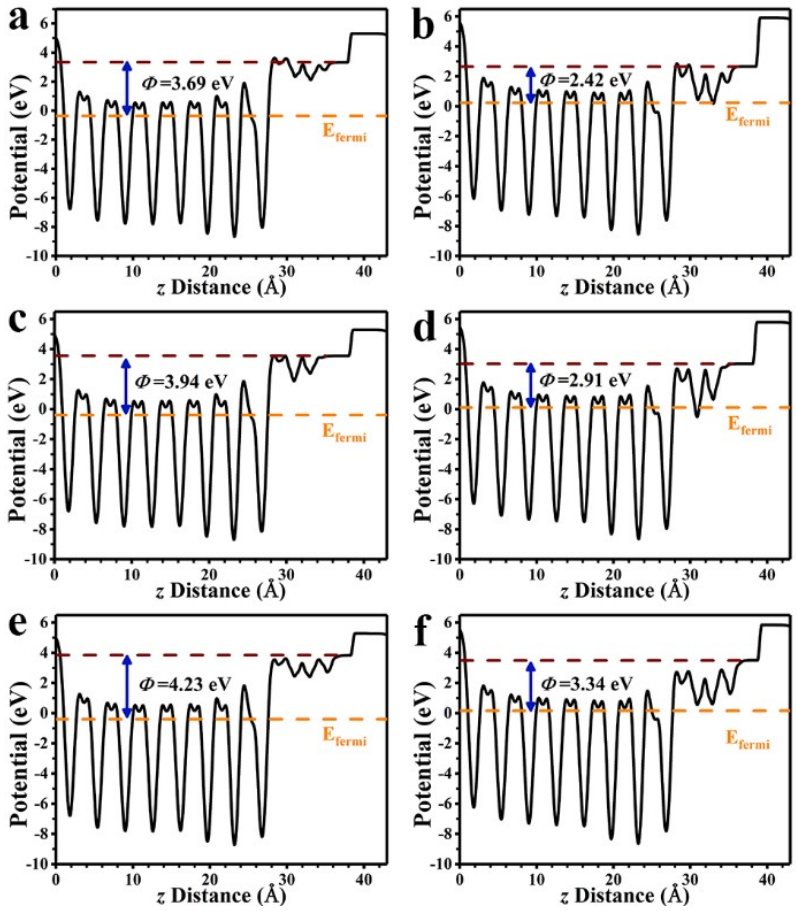

Figure S13. (a-b) The averaged planar electrostatic potentials along *z* axis of 4-AP$^+$ configurations with 1/2 and 1 ML coverages, respectively. (c-d) The averaged planar electrostatic potentials along *z* axis of 2-ABD$^+$ configurations with 1/2 and 1 ML coverages, respectively. (e-f) The averaged planar electrostatic potentials along *z* axis of 4-ABA$^+$ configurations with 1/2 and 1 ML coverages, respectively.

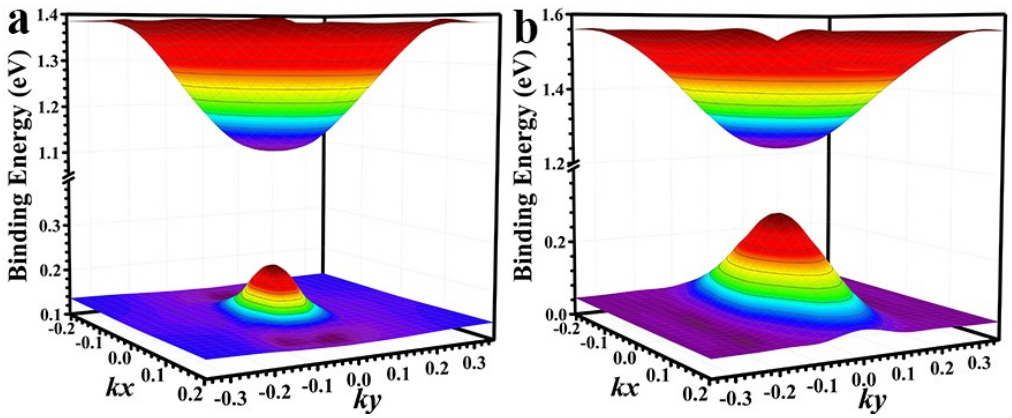

Figure S14. (a-b) The 3D band of 2-ABD^{+} configuration with 1 ML coverage and cross-II configuration, respectively.

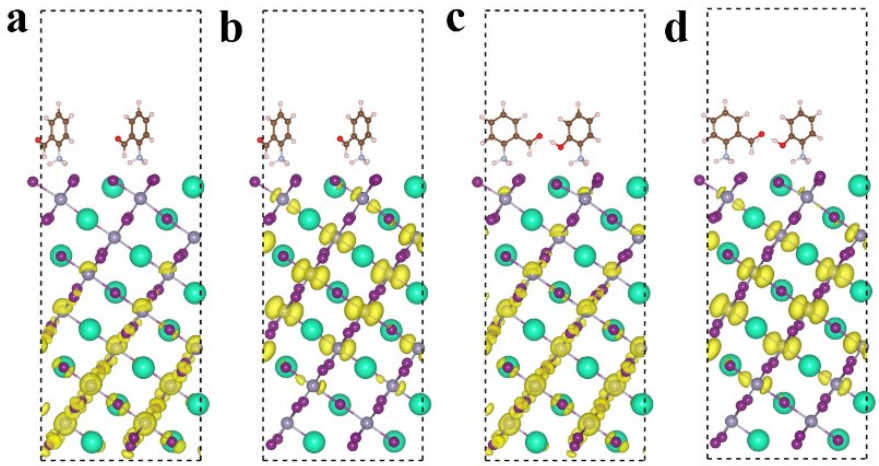

Figure S15. (a-b) The charge densities of VBM and CBM for 2-ABD$^+$ configuration with 1 ML coverage, respectively. (c-d) The charge densities of VBM and CBM for cross-II configuration, respectively. The isosurfaces are set as 0.0008 e/a_0^3.

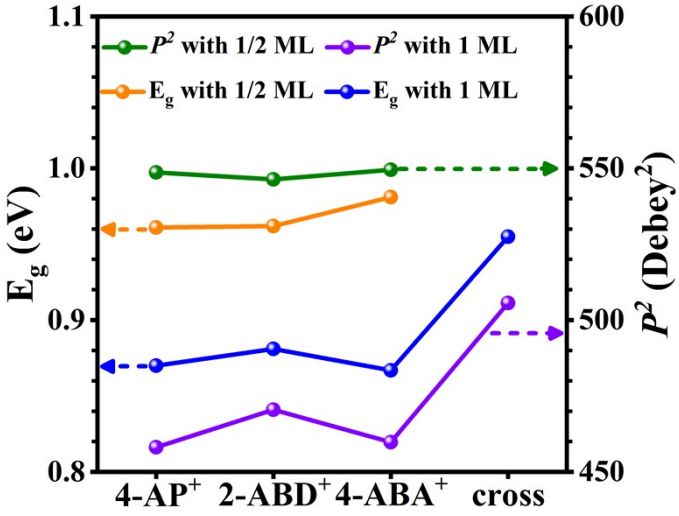

Figure S16. The band gap and the corresponding P^2 at gamma point of passivated configurations extracted from Figure 4a.

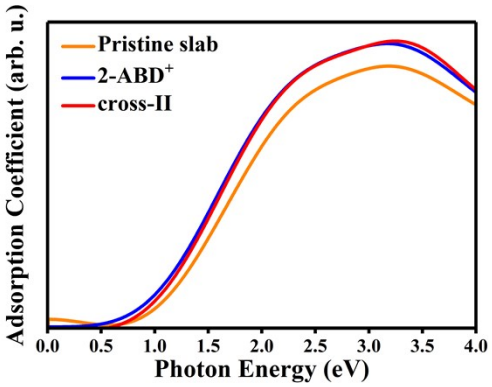

Figure S17. Calculated optical adsorption spectra of pristine slab, 2-ABD$^+$ configuration with 1 ML coverage and cross-II configuration.

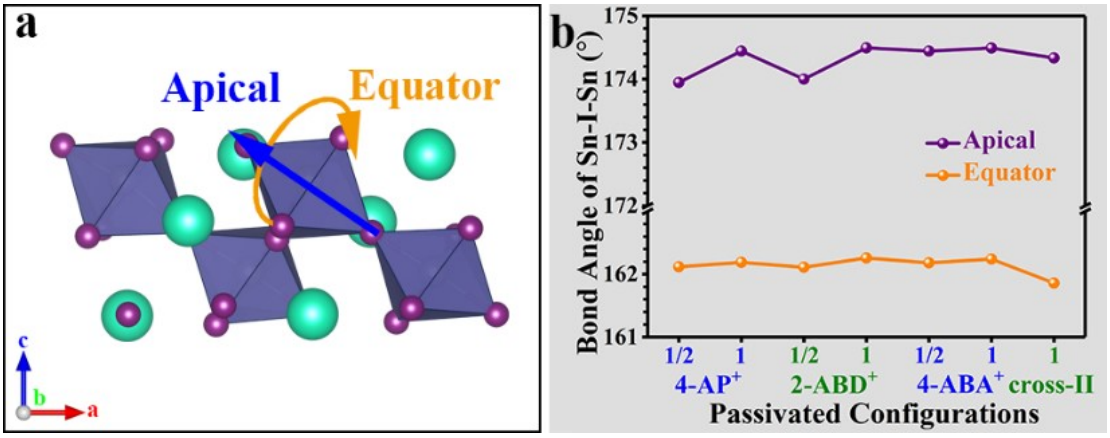

Figure S18. (a) Schematic diagram on the apical and equator directions. (b) The average bond angle of Sn-I-Sn along apical and equator directions for passivated configurations.

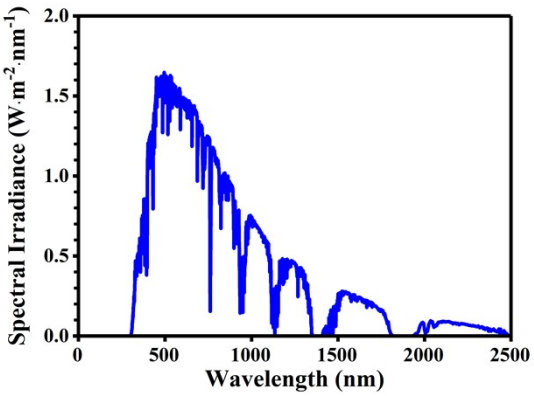

Figure S19. The solar irradiance spectrum.

Table S1. The calculated RMSDs of total passivated configurations, ligands and slab for 2-ABD^+ configuration with 1 ML coverage and cross-II configuration.

	Total (Å)	Ligands (Å)	Slab (Å)
2-ABD^+	1.59	2.73	0.62
cross-II	1.13	1.94	0.48

Table S2. The average I-Sn-I angle, Sn-I-Sn angle and Sn-I bond length for 2-ABD^+ configuration with 1 ML coverage and cross-II configuration after AIMD simulations and bulk γ-$CsSnI_3$.

	I-Sn-I (°)	Sn-I-Sn (°)	Sn-I (Å)
Bulk	179.98	170.12	3.118
2-ABD^+	168.34	165.34	3.169
cross-II	170.51	167.39	3.166

Table S3. Calculated *FF*, J_{sc}, V_{oc} and η of pristine slab and passivated configurations.

	V_{oc} (V)	*FF*	J_{sc} (mA/cm^2)	η (%)
Pristine Slab	0.474	0.796	35.72	13.5
2-ABD$^+$	0.426	0.78	44.46	14.8
cross-II	0.667	0.84	35.35	19.8