Supporting Information

Enhancing the Stability of Orthorhombic $CsSnI_3$ Perovskite *via* Oriented π -Conjugated Ligand Passivation

Yapeng Zheng,^{a,b} Zhi Fang,^{a,b} Ming-Hui Shang,^{b,*} Zhentao Du,^b Zuobao Yang,^b Kuo-Chih Chou,^a Weiyou Yang,^b Shihao Wei,^c and Xinmei Hou^{a,*}

^a Collaborative Innovation Center of Steel Technology, University of Science and

Technology Beijing, Beijing 100083, P. R. China.

^b Institute of Materials, Ningbo University of Technology, Ningbo City 315211, P. R.

China.

^c Faculty of Science, Ningbo University, 818 Fenghua Rd., Jiangbei, Ningbo City 315211,

P. R. China.

*To whom correspondence should be addressed: Email: shangminghui@nbut.edu.cn (M.-H. Shang), houxinmeiustb@ustb.edu.cn (X. Hou).



Figure S1. (a-b) Energies of $B\gamma$ -CsSnI₃ slab plotted as a function of thickness of vacuum layer and atomic layers of the slab model, respectively. (c) Pristine $B\gamma$ -CsSnI₃ slabs with Sn and Cs-I terminal ions. (d) The molecular structure of PEA⁺ ligand.

Convergence test on the thickness of vacuum layer and the slab are both performed and plotted in the Figure S1(a,b). The convergence tolerance of thickness of vacuum layer is empirically determined as 10^{-3} eV/atom. Moreover, the size of PEA⁺ molecule is the other factor influencing thickness of vacuum layer, and the size of PEA⁺ molecule along *z* axis is ~8 Å. To meet the convergence tolerance of energy and avoid the interaction between slab models, the thickness of vacuum layer is set as 16 Å. The convergence tolerance of number of atomic layers is larger than that of thickness of vacuum layer and determined as 2×10^{-2} eV/atom (green line in Figure S1 b). The energy differences ΔE between neighbor models are also calculated and plotted as shown yellow line in Figure S1 b. The slab with 15 atomic layers satisfied the convergence tolerance. Hence, the number of atomic layer is set as 15 in consideration of computational cost.



Figure S2. Schematic diagram of surface and bulky components in the slab.



Figure S3. Optimized configurations of 1/2 ML coverage.



Figure S4. The CDD between Model VI and pristine $B\gamma$ -CsSnI₃ slab. Yellow and blue isosurfaces indicate charge accumulation and charge depletion regions, respectively. The isosurfaces were set as 0.003 e/a₀³.



Figure S5. The top view of pristine slab.



Figure S6. (a-c) Orbital-resolved COHPs of H1-I1, H2-I2 and H3-I3 of Model VI, respectively. Positive (negative) sign indicates bonding (anti-bonding) character. The fermi energy level was set as zero.



Figure S7. (a) Initial and optimized configurations of 1 ML coverage. (b) Top view of 2×2 supercells of 1 ML coverage.

According to the top view of 2×2 supercells, two PEA⁺ ligands could passivate all the six I⁻ on the surface of slab, namely, the coverage reaches 100%.



Figure S8. Schematic diagram of atomic layers of slab.



Figure S9. (a-c) Snapshots at 0 ps and 5 ps of AIMD simulations of bulk $B\gamma$ -CsSnI₃, bulk Y-CsSnI₃ and 1 ML coverage at 300 K, respectively. (d) The energy fluctuations in respect to time at 300 K.

The stability of crystal structure could be judged by structure distortion and energy fluctuation after AIMD simulation. The obviously structure distortion and larger energy fluctuation of bulk $B\gamma$ -CsSnI₃ confirm its poor stability at 300 K. The stable structure and slight energy fluctuation of Y-CsSnI₃ indicate the good stability of Y-CsSnI₃. The stable structure and negligible energy fluctuation of 1 ML coverage demonstrate the improved stability after surface passivation by PEA⁺ ligands.



Figure S10. Structure of Y-CsSnI₃ slab passivated by one PEA⁺ ligand.



Figure S11. 3D band structure of bulk $B\gamma$ -CsSnI₃. The VBM was set as zero.



Figure S12. Calculated partial charge densities of VBM and CBM of bulk $B\gamma$ -CsSnI₃. The isosurfaces were set as 0.002 e/a_0^3 .



Figure S13. (a) Orbital-resolved COHP. Positive (negative) sign indicates bonding (anti-bonding) character. (b) Schematic energy level diagram extracted from the COHP analysis. Bonding interactions were shaded in yellow, and anti-bonding interactions were in blue. The fermi energy level was set as zero.



Figure S14. (a-b) The detailed distribution of atomic orbitals of PEA⁺ ligands on the surface of Model VI and 1 ML coverage, respectively. The VBM was set as zero.



Figure S15. Calculated partial charge densities of CBM and VBM of pristine slab (a and d), Model VI (b and e) and 1 ML coverage (c and f), respectively. The isosurfaces were set as 0.0005 e/a_0^3 .



Figure S16. Schematic diagram of apical direction.

- 1 - 2 - 2 - 2 - 2 - 2 - 2 - 2 - 2 - 2			
	a	b	С
experimental	8.6885	8.6384	12.3775
DFT-D2	8.2519	8.4966	12.2094
zero damping DFT-D3	8.7495	8.6854	12.4754
BJ-damping DFT-D3	8.5917	8.7211	12.4498

Table S1. Experimental and calculated lattice constants considering DFT-D2 and DFT-D3 of bulk $B\gamma$ -CsSnI₃.

Table S2. The main X-ray diffraction peaks of bulk $B\gamma$ -CsSnI ₃ .					
Main Diffraction Peaks	Refs.				
(202) (220/002) (400)	1				
(202) (220/002) (020)	2				
(101) (121/200) (202 /040)	3				
(220) (202) (242)	4				
(202) (200) (400)	5				
(202) (220) (242)	6				

Table S3. Surface energies of pristine slab with Sn and Cs-I terminal ions.

Termination	Surface Energies (meV/Å ²)
Sn	23.1
Cs-I	2.6

Table S4. Bader charges of the upper 2 atomic layers of pristine slab, Model VI and 1 ML coverage.

	I1	I2	13	I4	15	16	Sn1	Sn2	Cs1	Cs2
Slab	7.5242	7.5299	7.5306	7.5369	7.5258	7.5278	13.0809	13.0837	8.124	8.1257
Model VI	7.6377	7.613	7.6021	7.5826	7.5726	7.5659	13.0831	13.099	8.1437	8.1485
1 ML	7.6978	7.6304	7.6329	7.6743	7.6248	7.612	13.0763	13.0783	8.1543	8.1574

Table S5. Adsorption energies, formation energies and VDW energies of bulk $B\gamma$ -CsSnI₃, bulk Y-CsSnI₃, pristine $B\gamma$ -CsSnI₃ slab, Model VI and 1 ML coverage, respectively.

r essing, pristine B7 essing shas, frieder vi una r frib es verage, respectively.						
	E_{ads} (eV/atom)	$E_{form} \left(\mathrm{eV} \right)$	E_{VDW} (eV/atom)			
Bγ-CsSnI ₃	-	-0.408	-			
Y-CsSnI ₃	-	-0.425	-			
Pristine slab	-	-0.318	-			
Y-CsSnI ₃ with one PEA ⁺	-	-0.452	-			
Model VI	-0.078	-0.87	-0.01			
1 ML	-0.126	-1.4396	-0.005			

The E_{form} of bulk By and Y-CsSnI₃ are calculated by:

$$E_{form} = E_{CsSnI_3} - E_{CsI} - E_{SnI_2} \tag{1}$$

where E_{CsSnI_3} is the energy of B γ or Y-CsSnI₃ unit cell, E_{CsI} is the energy of CsI bulk phase and E_{SnI_2} is the energy of SnI₂ bulk phase, respectively. The calculated E_{form} of B γ and Y-CsSnI₃ unit cell are -0.408 and -0.425 eV, respectively. The VDW energy represents the VDW energy of ligands contributing to the E_{ads} and is calculated by

$$E_{VDW} = \frac{E_{VDW/mod} - E_{VDW/slab}}{n}$$
(2)

where $E_{VDW/mod}$ is the VDW energy of passivated configurations, $E_{VDW/slab}$ is the energy of pristine slab and *n* is number of atoms within passivated models, respectively.

 Table S6. Hole and electron effective masses of bulk Bγ-CsSnI₃.

 G-X
 G-Y
 G-Z

 me*
 0.413
 0.413
 0.011

 mh*
 -0.048
 -0.048
 -0.017

Table S7. Averaged Sn-I bond lengths of bulky and surface components of pristine $B\gamma$ -CsSnI₃ slab, Model VI and 1 ML coverage, respectively.

	Dullay	Surface			
	Bulky	slab	Model VI	1 ML	
Bond Length (Å)	3.169	3.115	3.157	3.173	

Table S8. Hole and electron effective masses of pristine $B\gamma$ -CsSnI₃ slab, Model VI and 1 ML coverage, respectively.

	me*			m _h *		
	slab	Model VI	1 ML	slab	Model VI	1 ML
G-X	0.05	0.063	0.211	-0.036	-0.037	-0.057
G-Y	0.464	0.512	0.353	-0.114	-0.113	-0.162

REFERENCES

Wu, B.; Zhou, Y.; Xing, G.; Xu, Q.; Garces, H. F.; Solanki, A.; Goh, T. W.; Padture, N. P.; Sum,
 T. C. Long Minority-Carrier Diffusion Length and Low Surface-Recombination Velocity in Inorganic
 Lead-Free CsSnI₃ Perovskite Crystal for Solar Cells. *Adv. Funct. Mater.* 2017, *27*, 1604818-1-10.

(2) Heo, J. H.; Kim, J.; Kim, H.; Moon, S. H.; Im, S. H.; Hong, K.-H. Roles of SnX₂ (X=F, Cl, Br)
Additives in Tin-Based Halide Perovskites Towards Highly Efficient and Stable Lead-Free Perovskite
Solar Cells. J. Phys. Chem. Lett. 2018, 9, 6024-6031.

(3) Liu, F.; Ding, C.; Zhang, Y.; Ripolles, T. S.; Kamisaka, T.; Toyoda, T.; Hayase, S.; Minemoto, T.;
Yoshino, K.; Dai, S. Colloidal Synthesis of Air-Stable Alloyed CsSn_{1-x}Pb_xI₃ Perovskite Nanocrystals
for Use in Solar Cells. *J. Am. Chem. Soc.* 2017, *139*, 16708-16719.

(4) Chen, L.-J.; Lee, C.-R.; Chuang, Y.-J.; Wu, Z.-H.; Chen, C. Synthesis and Optical Properties of Lead-Free Cesium Tin Halide Perovskite Quantum Rods with High-Performance Solar Cell Application. *J. Phys. Chem. Lett.* **2016**, *7*, 5028-5035.

(5) Hong, W.-L.; Huang, Y.-C.; Chang, C.-Y.; Zhang, Z.-C.; Tsai, H.-R.; Chang, N.-Y.; Chao, Y.-C. Efficient Low-Temperature Solution-Processed Lead-Free Perovskite Infrared Light-Emitting Diodes. *Adv. Mater.* 2016, 28, 8029-8036.

(6) Jellicoe, T. C.; Richter, J. M.; Glass, H. F. J.; Tabachnyk, M.; Brady, R.; Dutton, S. E.; Rao, A.; Friend, R. H.; Credgington, D.; Greenham, N. C.; Böhm, M. L. Synthesis and Optical Properties of Lead-Free Cesium Tin Halide Perovskite Nanocrystals. *J. Am. Chem. Soc.* **2016**, *138*, 2941-2944.