Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Unveiling Roles of Halogen Ions in Surface Passivation of $CsPbI_3$ Perovskite Solar Cells

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Data availability. All data generated or analyzed during this study are included in this published article (and its Supplementary Information files). All relevant data are available from the authors.

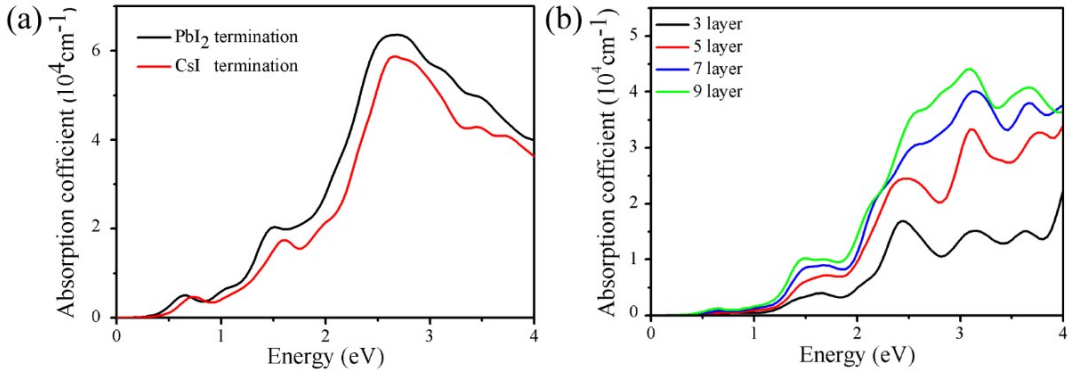

Figure S1. (a). Comparison of absorption spectra for PbI_2 and CsI terminations of perovskites $CsPbI_3$ (001) surface. (b). The absorption spectra of perovskite film (PbI2 terminations) with various slab thicknesses.

To maintain a stable $CsPbI_3$ structure, the chemical potentials of Cs, Pb, and I need

satisfy the thermodynamic equilibrium condition:[1]

$$\Delta\mu_{Cs} + \Delta\mu_{Pb} + 3\Delta\mu_{I} = \Delta H\left(CsPbI_3\right) \quad (1)$$

$$\Delta\mu_{Cs} + \Delta\mu_{I} < \Delta H\left(CsI\right) \quad (2)$$

$$\Delta\mu_{Pb} + 2\Delta\mu_{I} < \Delta H\left(PbI_2\right) \quad (3)$$

where $\Delta H\left(CsPbI_3\right)$, $\Delta H\left(CsI\right)$, $\Delta H\left(PbI_2\right)$ are the formation enthalpy of $CsPbI_3$ CsI and PbI_2, respectively. μ_i represnets the chemical potential of atom i (i=Cs, Pb, I). Here $\mu_i = \mu_i^{bulk} + \Delta\mu_i$, where μ_i^{bulk} is the total energy of corresponding metal or molecule. According to Eqs. (1)-(3), the chemical potential for stabilizing $CsPbI_3$ is determined in yellow area shown as Fig S2. There are three thermodynamic equilibrium conditions (Pb Pb-rich labeled as A, I-rich labeled as B and Moderate labeled as C) for calculating surface energy and formation energy. The used chemical potentials of Cs, Pb, I are shown in Table S2.

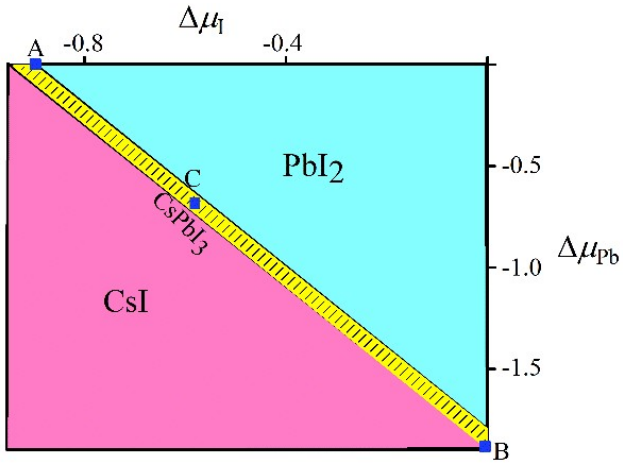

Figure S2. Chemical potential range for stable $CsPbI_3$.

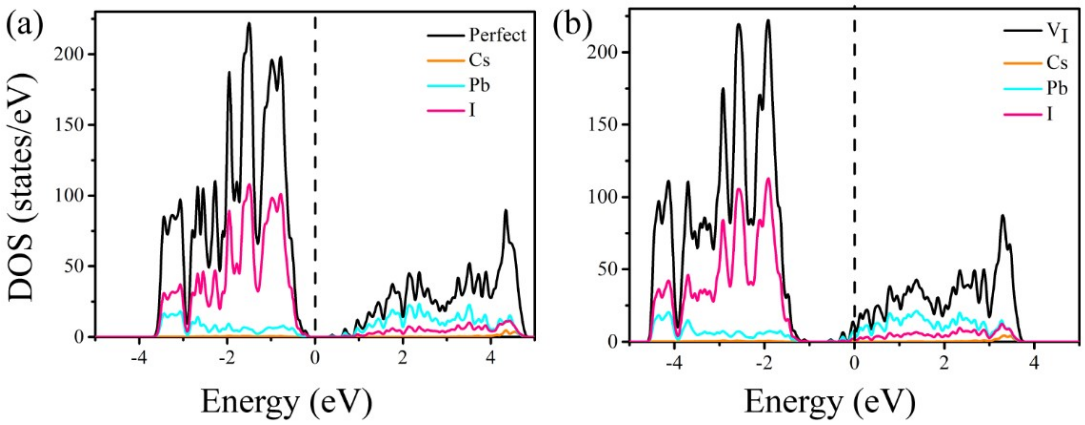

Figure S3. Enlarged DOSs of defect-free (a) and defective (b) $CsPbI_3$ films.

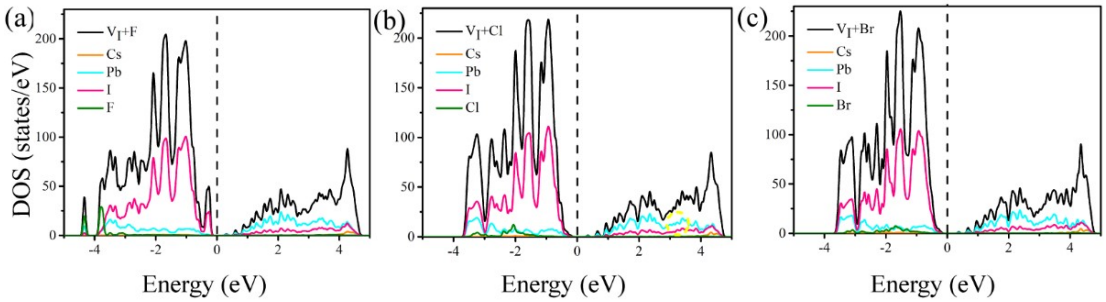

Figure S4. Enlarged DOSs of defective $CsPbI_3$ films passivated by halogen ions F^- (a), Cl^- (b), and Br^- (c).

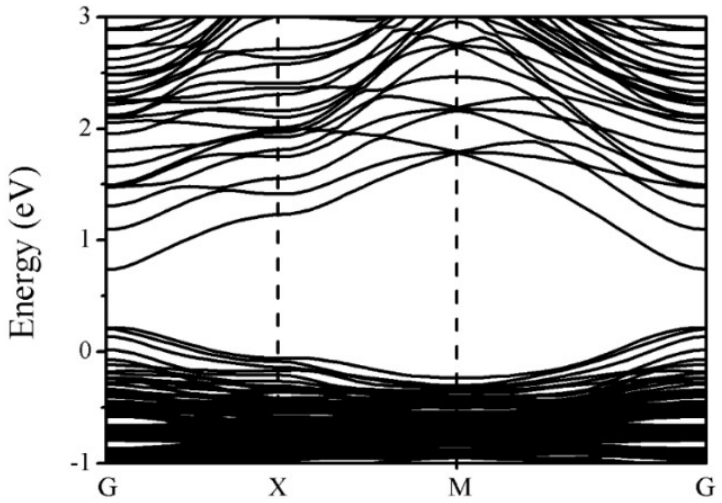

Figure S5. Electronic band structures of uncoordinated Pb^{2+} passivated by F^{-}.

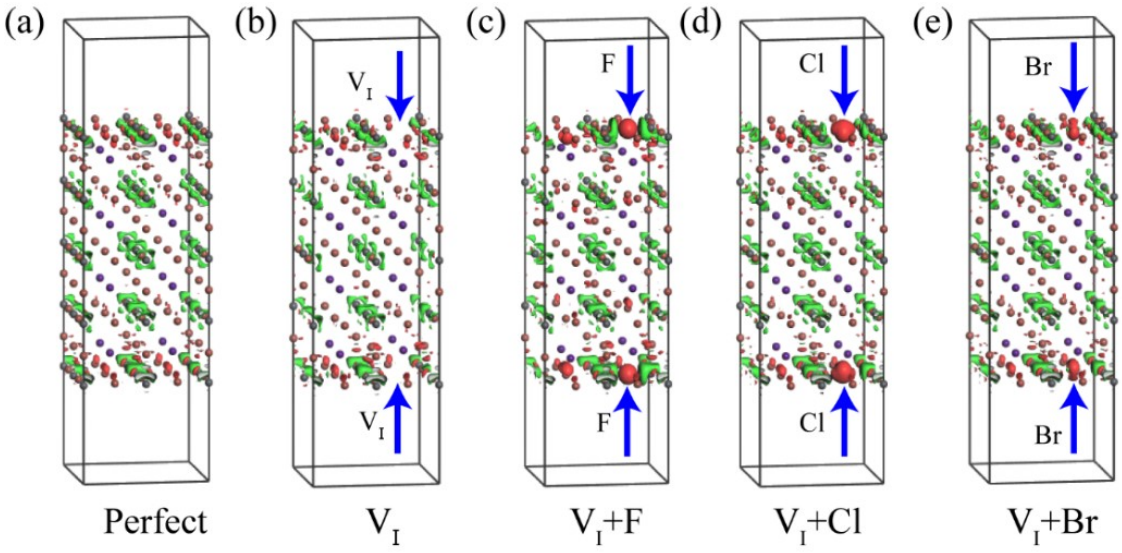

Figure S6. Difference charge density of perfect, defective and passivated systems. Isosurface level is 0.00385 e/bohr^3.

Table S1. The Value of Chemical Potential in Different Conditions.

Conditions	μ_{Cs} (eV)	μ_{Pb} (eV)	μ_{I} (eV)
A (Pb-rich)	-3.14	-3.91	-2.60
B (I-rich)	-4.05	-5.79	-1.67
C (Moderate)	-3.26	-4.18	-2.47

Table S2. Comparison between Experimental Data and the Calculated Effective Masses of Electrons and Holes, Reduced Mass, Static Dielectric Constant and Exciton Binding Energy of bulk $CsPbI_3$.

	PBE+SOC	Exp.[2,3]	Theory[4]	
			GGA	LDA
$m_e^*(m_0)$	0.144		0.219	0.188
$m_h^*(m_0)$	0.186		0.190	0.138
$\mu(m_0)$	0.081	0.014-0.214		
ε_{eff}	9.820	10		
E_b(meV)	11.440	14-16, 21.2		

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