

## Supplementary Information

### **Intrinsic Defects at Interface of FAPbI<sub>3</sub>/MAPbI<sub>3</sub> Superlattice: Insight from First-Principles Calculation**

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## Computational methods for properties

The effective masses of the holes and electrons at VBM and CBM, and the reduced effective masses were calculated by Eqs. S1 and 2<sup>1</sup>

$$m^* = \hbar^2 \left( \frac{\partial^2 \varepsilon(k)}{\partial k^2} \right)^{-1} \quad \text{S(1)}$$

$$m_r^* = \frac{m_e^* m_h^*}{m_e^* + m_h^*} \quad \text{S(2)}$$

where  $\varepsilon(k)$  is the band energy of VBM or CBM, and  $k$  is the inverse lattice vector. Wannier exciton model was adopted to calculate the exciton binding energy<sup>2</sup>

$$E_{eb} = \frac{m_r^* e^4}{2\hbar^2 \varepsilon_\infty^2} = 13.6 \frac{m_r^*}{\varepsilon_\infty^2} \quad \text{S(3)}$$

where  $m_r^*$  is the reduced effective mass, and  $\varepsilon_\infty$  is static dielectric constant at zero frequency approximation and it can be calculated by following equation<sup>3</sup>

$$\varepsilon_\infty(\hat{q}, \omega) \approx \lim_{q \rightarrow 0} \varepsilon_{0,0}(\mathbf{q}, \omega) \quad \text{S(4)}$$

where  $\omega$  is the optical frequency and  $q$  is the electron momentum operator.

The linear optical properties<sup>4</sup> of semiconductors can be calculated using the frequency-dependent complex dielectric function  $\varepsilon(\omega)$

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) \quad \text{S(5)}$$

where  $\omega$  is the optical frequency,  $\varepsilon_1$  and  $\varepsilon_2$  are the real and imaginary parts of the dielectric function, respectively. In the one-electron graph, the imaginary part of the dielectric function  $\varepsilon_2(\omega)$  can be obtained from the following equation:

$$\varepsilon_2(\omega) = \frac{4\pi^2 e^2}{\Omega} \lim_{q \rightarrow 0} \frac{1}{q^2} \sum_{c,v,k} 2w_k \delta(E_c - E_v - \omega) |\langle c | \mathbf{e} \cdot \mathbf{q} | v \rangle|^2 \quad \text{S(6)}$$

where  $\langle c | \mathbf{e} \cdot \mathbf{q} | v \rangle$  is the integral optical transition from the valence state ( $v$ ) to the conduction state ( $c$ ),  $e$  denotes the polarization direction of the photon and  $q$  is the electron momentum operator. The integral on  $k$  is the sum of special  $k$  points with weighting factor  $w_k$ . The real part of the dielectric function  $\varepsilon_1(\omega)$  can be gained from the Kramers-Kronig relation<sup>4</sup>

$$\varepsilon_1(\omega) = 1 + \frac{2}{\pi} P \int_0^\infty \frac{\varepsilon_2(\omega') \omega'}{\omega'^2 - \omega^2 + i\eta} d\omega' \quad \text{S(7)}$$

where  $P$  is the principle value and  $\eta$  is the complex shift parameter. The absorption

coefficients can be computed by the following equation<sup>5</sup>:

$$\alpha(\omega) = \sqrt{2\omega} \sqrt{\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} - \varepsilon_1(\omega)} \quad \text{S(8)}$$

Open-circuit voltage  $V_{OC}$ , short-circuit current  $J_{SC}$ , and theoretical power conversion efficiency PCE ( $\eta$ ) were calculated by Eqs. S9-12. The maximum short-circuit current  $J_{SC}$  is calculated on the assumption that all incident photons with energy greater than the superlattice band gap are absorbed,<sup>6</sup>

$$J_{SC} = e \int_{E_g}^{\infty} \frac{S(E)}{E} dE \quad \text{S(9)}$$

where  $e$ ,  $E$ , and  $S(E)$  are the electronic charge, the energy of an incident photon, and the incident spectral power per unit area, respectively. The open circuit voltage  $V_{OC}$  can be estimated by

$$V_{OC} = (E_g - E_{loss}) / e \quad \text{S(10)}$$

in which  $E_{loss}$  is the loss-in-potential and 0.5 eV is adopted similar to the previous report.<sup>7</sup> The maximum theoretical PCE ( $\eta$ ) can be obtained by  $J$ ,  $V_{OC}$ , fill factor ( $FF$ ), and the total incident power density ( $P_{sun}$ ).<sup>8</sup>

$$\eta(E_g) = \frac{FF \times J_{SC} \times V_{OC}}{P_{sun}} \quad \text{S(11)}$$

$$P_{sun} = \int_0^{\infty} S(E) dE \quad \text{S(12)}$$

According to the solar spectrum data meter provided by the National Renewable Energy Laboratory<sup>9</sup>, the  $P_{sun}$  is taken as 100 mW/cm<sup>2</sup>. The fill factor  $FF$  is taken as the reported experimental value of 0.731.<sup>9</sup>

Table S1. Calculated band gaps (eV) of MAPbI<sub>3</sub> and FAPbI<sub>3</sub> using PBE, PBE+SOC and HSE06+SOC compared with experimental values (in brackets).

	PBE	PBE+SOC	HSE06+SOC
MAPbI <sub>3</sub>	1.687 (1.61) <sup>11</sup>	0.666	1.575
FAPbI <sub>3</sub>	1.418 (1.43) <sup>12</sup>	0.342	1.320

Table S2. Calculated lattice parameters and average monolayer thickness in perovskites and superlattice.

perovskites	<i>a b c</i> (Å)	$\alpha \beta \gamma$ (degree)	$d_{\text{MAPbI}_3}$ (Å)	$d_{\text{FAPbI}_3}$ (Å)
MAPbI <sub>3</sub>	6.340, 6.330, 6.388 (6.311, 6.311, 6.316) <sup>13</sup>	90.0, 90.8, 89.9	6.340	
FAPbI <sub>3</sub>	6.489, 6.311, 6.396 (6.42 <sup>13</sup> , 6.36 <sup>15</sup> )	90.0, 90.0, 90.0		6.489
(FAPbI <sub>3</sub> ) <sub>2</sub> /(MAPbI <sub>3</sub> ) <sub>2</sub>	25.596, 6.319, 6.388	89.9, 90.1, 90.1	6.447	6.352

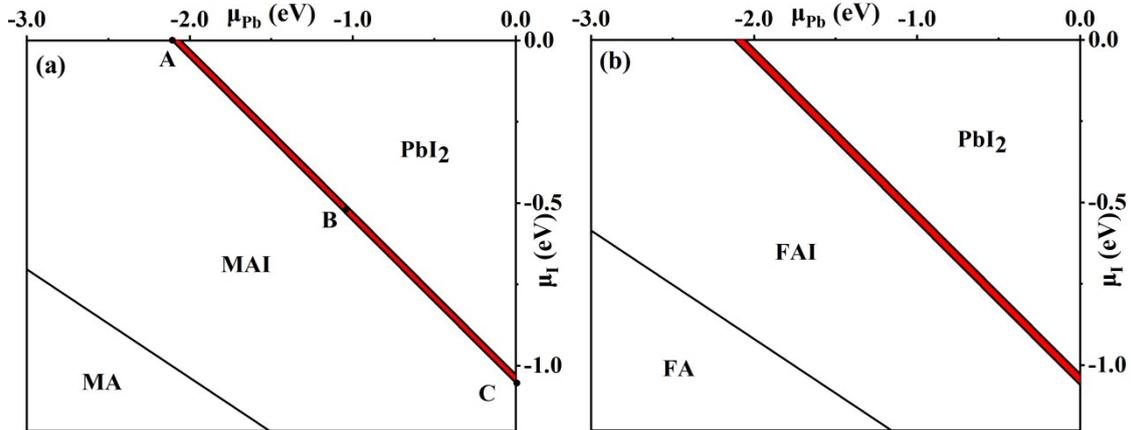
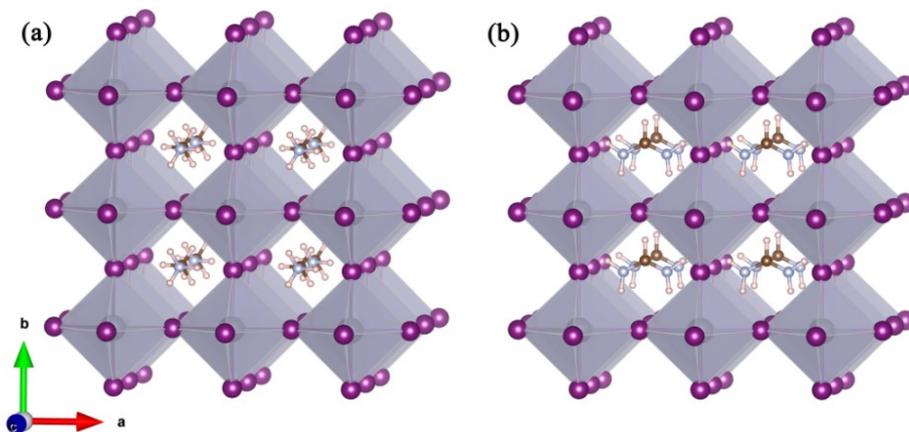
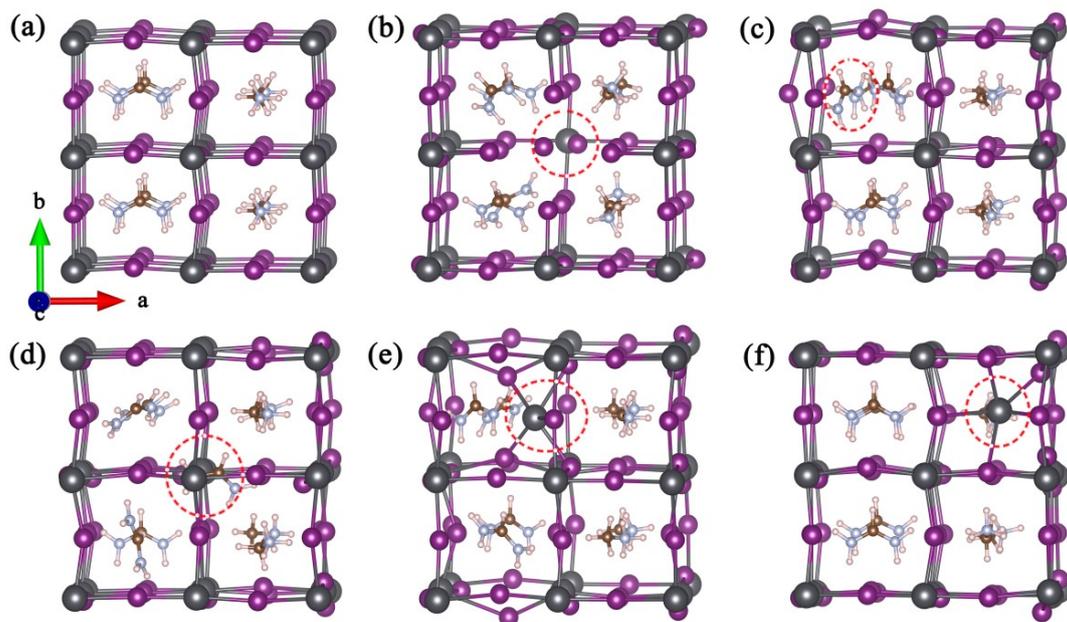


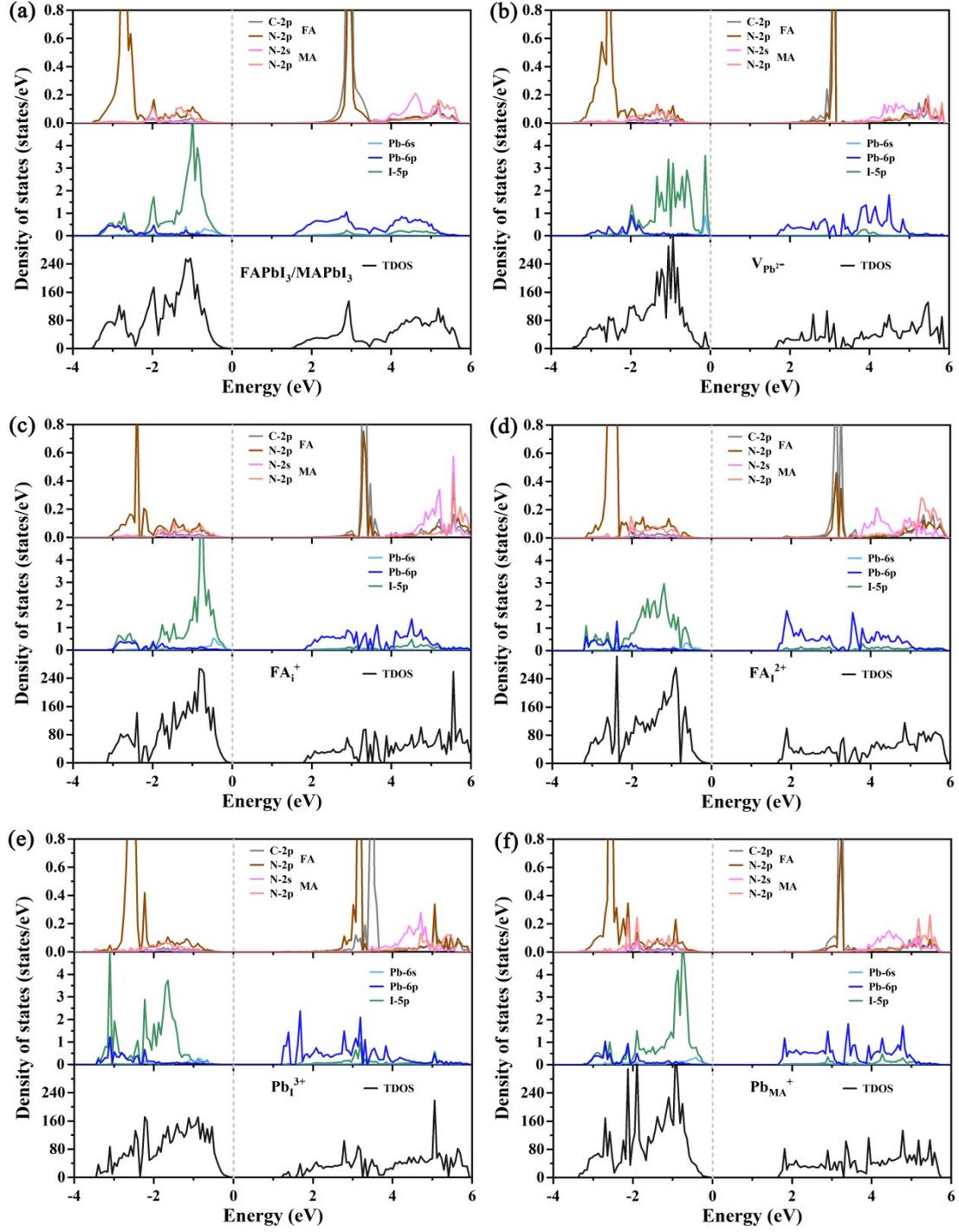
Fig. S1. Chemical potential region for the thermal equilibrium growth of (a) MAPbI<sub>3</sub> and (b) FAPbI<sub>3</sub> crystal.



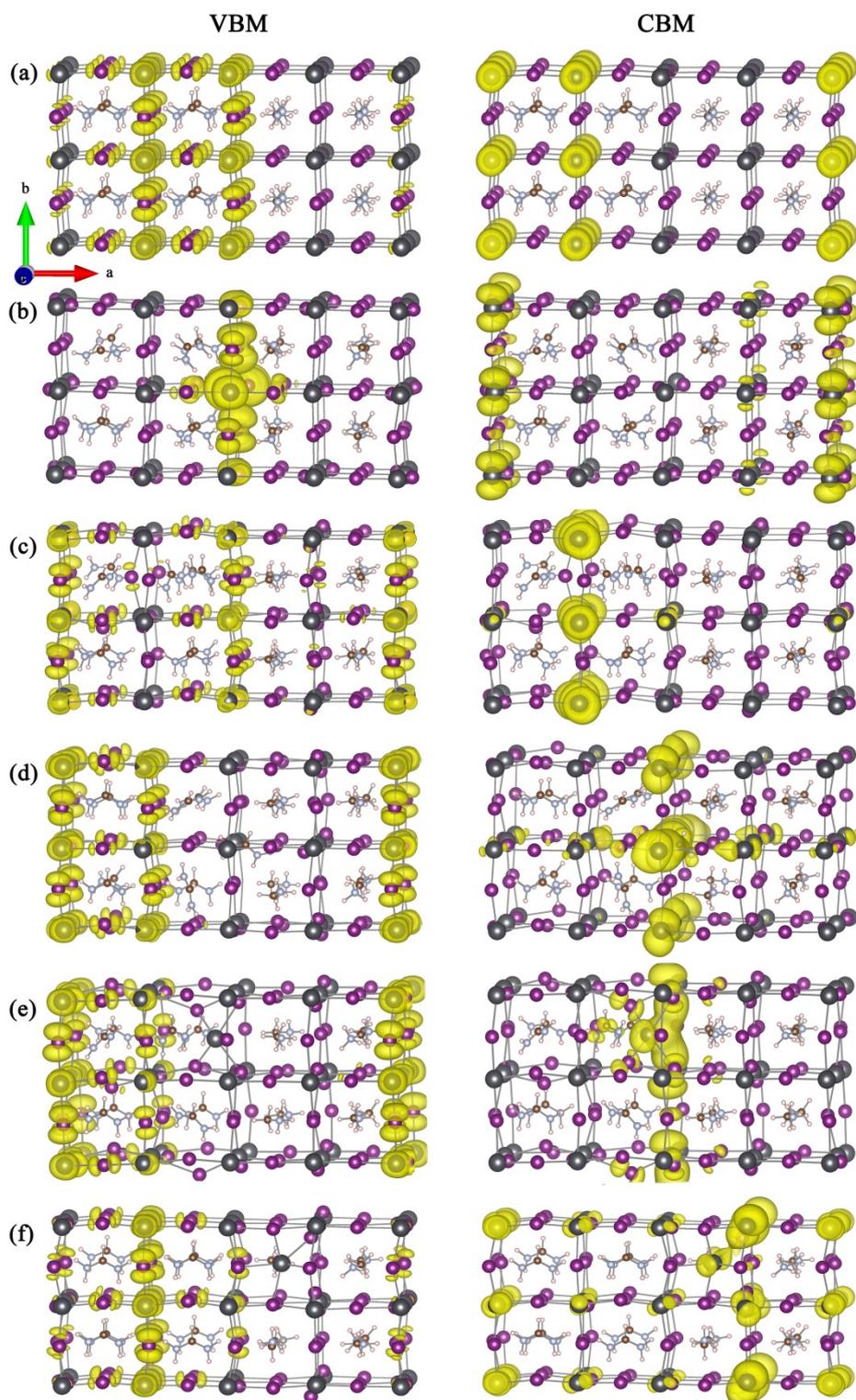
**Fig. S2.** The bulk models of  $2 \times 2 \times 2$  supercell used to calculate electrostatic potentials for MAPbI<sub>3</sub> and FAPbI<sub>3</sub>.



**Fig. S3.** Local structures of FAPbI<sub>3</sub>/MAPbI<sub>3</sub> superlattice with (a) defect free, (b) V<sub>Pb</sub><sup>2-</sup>, (c) FA<sub>i</sub><sup>+</sup>, (d) FA<sub>I</sub><sup>2+</sup>, (e) Pb<sub>I</sub><sup>3+</sup>, (f) Pb<sub>MA</sub><sup>+</sup>.



**Fig. S4.** TDOS and PDOS of superlattice with (a) defect free, (b)  $V_{\text{Pb}^{2-}}$ , (c)  $\text{FA}_i^+$ , (d)  $\text{FA}_I^{2+}$ , (e)  $\text{Pb}_I^{3+}$ , (f)  $\text{Pb}_{\text{MA}}^+$ . The Fermi level is set to zero (the gray dotted line).



**Fig. S5.** Band decomposed charge densities distributions of VBM (with an isosurface value of  $0.0001 \text{ e}\text{\AA}^{-3}$ ) and CBM (with an isosurface value of  $0.0002 \text{ e}\text{\AA}^{-3}$ ) for the superlattices with and without defects. (a) perfect, (b)  $\text{V}_{\text{pb}}^{2-}$ , (c)  $\text{FA}_{\text{I}}^{+}$ , (d)  $\text{FA}_{\text{I}}^{2+}$ , (e)  $\text{Pb}_{\text{I}}^{3+}$ , (f)  $\text{Pb}_{\text{MA}}^{+}$ .

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