Supporting Information

## Charge Localization Control of Electron–Hole Recombination in Multilayer Two–Dimensional Dion–Jacobson Hybrid Perovskites

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## **Computational details:**

Density functional theory (DFT) calculations of the linear optical absorption for the optimized (3AMP)(MA)Pb<sub>2</sub>I<sub>7</sub> and (4AMP)(MA)Pb<sub>2</sub>I<sub>7</sub> were performed using the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional<sup>1</sup> and projector-augmented wave pseudopotential,<sup>2</sup> implemented within Vienna ab initio simulation package (VASP).<sup>3</sup> The frequency–dependent complex dielectric function  $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ , including both real and imaginary parts, are obtained by VASP calculations. Based on the dielectric function, the linear absorption coefficient  $I(\omega)$  can be given by the equation:<sup>4</sup>

$$I(\omega) = \frac{\sqrt{2\omega}}{c} \left\{ \left[ \varepsilon_1^2(\omega) + \varepsilon_2^2(\omega) \right]^{1/2} - \varepsilon_1(\omega) \right\}^{1/2} \right\}$$

where the imaginary part  $\varepsilon_{2}^{\partial\beta}(\omega)$  is determined by a summation over empty states using the equation:<sup>4</sup>

$$\varepsilon_{2}^{\partial\beta}(\omega) = \frac{2\pi_{e}^{2}}{\Omega\varepsilon_{0}} \sum_{k,\nu,c} \delta\left(E_{k}^{c} - E_{k}^{\nu} - \hbar\omega\right) \left|\left\langle\Psi_{k}^{c}|u \cdot r|\Psi_{k}^{\nu}\right\rangle\right|^{2},$$

where  $\varepsilon_0$  is the vacuum dielectric constant,  $\Omega$  is the volume, v and c represent the valence and conduction bands respectively,  $\hbar\omega$  is the energy of the incident phonon, u is the vector defining the polarization of the incident electric field,  $u \cdot r$  is the momentum operator, and  $\Psi_k^c$  and  $\Psi_k^v$  are the wave functions of the conduction and valence bands at the k point, respectively.

The real part of the dielectric tensor  $\varepsilon_1^{\partial\beta}(\omega)$  is obtained by the usual Kramers–Kronig transformation:

$$\varepsilon_{1}^{\partial\beta}(\omega) = 1 + \frac{2}{\pi} P \int_{0}^{\infty} \frac{\varepsilon_{2}^{a\beta}(\omega')\omega'}{\omega'^{2} - \omega^{2} + \hbar\eta} d\omega'$$

where P denotes the principal value. The method is explained in detail in Ref<sup>4</sup>. The complex shift  $\eta$  is determined by the parameter CSHIFT.

## **Radiative electron-hole recombination:**

In order to estimate the radiative decay process, we calculated the radiative lifetimes for both the (3AMP)(MA)Pb<sub>2</sub>I<sub>7</sub> and (4AMP)(MA)Pb<sub>2</sub>I<sub>7</sub>. The Einstein coefficient for spontaneous emission,  $A_{21}$ , between states 1 and 2 relates the oscillator strength,  $f_{12}$ , and the lifetime,  $\tau_{21}$ , of the specified transition:

$$A_{21} = \frac{8\pi^2 v_{21}^2 e^2 g_1}{\varepsilon_0 m_e c^3 g_2} f_{12},$$

Here, v is the transition frequency, e,  $\varepsilon_0$ ,  $m_e$ , and c are the fundamental constants, and  $g_i$  is degeneracy of state *i*. The state degeneracies are  $g_1 = g_2 = 1$  in the current systems because the two systems have no symmetry due to thermal atomic fluctuations. The lifetime of the emission is inverse of the Einstein coefficient:

$$\tau_{21} = [A_{21}]^{-1} = \frac{\varepsilon_0 m_e c^3 g_2 1}{8\pi^2 v_{21}^2 e^2 g_1 f_{12}} = \frac{\varepsilon_0 m_e c^3 1}{16\pi^2 v_{21}^2 e^2 f_{12}}$$

The calculated radiative recombination lifetimes for the  $(3AMP)(MA)Pb_2I_7$  and  $(4AMP)(MA)Pb_2I_7$  perovskites are 0.36 and 0.17 ns, respectively, which are longer than the nonradiative electron-hole recombination times, Table 1, indicative of that nonradiative electron-hole recombination constitutes the main process responsible for luminescence decay, in accordance with the experimental observation.<sup>5</sup>



**Figure S1.** The geometric structures of (a)  $(3AMP)(MA)Pb_2I_7$  and (b)  $(4AMP)(MA)Pb_2I_7$  are obtained by averaging overall the molecular dynamics trajectories at 300K. The right-hand-side panels of (a) and (b) show the schematic diagram (middle panel) reflects the extent of octahedral tilting. The hydrogen bonding is marked by red dashed line, and the equatorial Pb–I–Pb angle is marked by blue curve. The average Pb-I bond length and Pb–I–Pb angle are 3.253 Å and 138.16° in the  $(3AMP)(MA)Pb_2I_7$ , and 3.281 Å and 130.27° in the  $(4AMP)(MA)Pb_2I_7$ . The pronounced octahedral tilting in  $(4AMP)(MA)Pb_2I_7$  is caused by shorter average hydrogen bond distance (3.276 Å) than that (3.592 Å) in  $(3AMP)(MA)Pb_2I_7$ . The results are consistent with the analysis of the chosen MD snapshot as mentioned in the main text.



**Figure S2.** The calculated linear optical absorption spectra of the (3AMP)(MA)Pb<sub>2</sub>I<sub>7</sub> and (4AMP)(MA)Pb<sub>2</sub>I<sub>7</sub>. The yellow shaded area shows the visible light wavelength range from 400 to 760 nm. The (3AMP)(MA)Pb<sub>2</sub>I<sub>7</sub> absorption edge is about 0.15 eV lower than that in the (4AMP)(MA)Pb<sub>2</sub>I<sub>7</sub>, agreeing with the bandgap difference reported in Figure 2 in the main text. Higher intensity of the absorption peak together with smaller bandgap in the (3AMP)(MA)Pb<sub>2</sub>I<sub>7</sub> compared to 4AMP(MA)Pb<sub>2</sub>I<sub>7</sub> suggest that the former perovskite should be a better choice for photovoltaic device.



**Figure S3.** Schematic diagram showing the orbital interactions between the Pb and I atoms in (3AMP)(MA)Pb<sub>2</sub>I<sub>7</sub> and (4AMP)(MA)Pb<sub>2</sub>I<sub>7</sub> systems. The strong anti–bonding interaction between I 5p and Pb 6s orbitals in the 3AMP perovskite pushes up the VBM (valence band maximum), resulting in a reduced bandgap compared to that of 4AMP–based counterparts.

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## References

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