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

Ran Shi, ${ }^{1}$ Zhaosheng Zhang, ${ }^{1,2}$ Wei-Hai Fang, ${ }^{1}$ and Run Long ${ }^{1 *}$<br>${ }^{1}$ College of Chemistry, Key Laboratory of Theoretical \& Computational

Photochemistry of Ministry of Education, Beijing Normal University, Beijing, 100875,
People's Republic of China
${ }^{2}$ College of Chemistry \& Environmental Science, Hebei University, Baoding, 071002, People's Republic of China

## Computational details:

Density functional theory (DFT) calculations of the linear optical absorption for the optimized (3AMP)(MA) $\mathrm{Pb}_{2} \mathrm{I}_{7}$ and (4AMP)(MA) $\mathrm{Pb}_{2} \mathrm{I}_{7}$ were performed using the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional ${ }^{1}$ and projectoraugmented wave pseudopotential, ${ }^{2}$ implemented within Vienna ab initio simulation package (VASP). ${ }^{3}$ The frequency-dependent complex dielectric function $\varepsilon(\omega)=\varepsilon_{1}(\omega)+\pi \varepsilon_{2}(\omega)$, 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: ${ }^{4}$

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

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

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

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:

$$
\varepsilon_{1}^{\partial \beta}(\omega)=1+\frac{2}{\pi} P \int_{0}^{\infty} \frac{\varepsilon_{2}^{a \beta}\left(\omega^{\prime}\right) \omega^{\prime}}{\omega^{\prime 2}-\omega^{2}+\mathbb{\square} \eta} d \| \omega^{\prime}
$$

where $P$ denotes the principal value. The method is explained in detail in Ref ${ }^{4}$. 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) $\mathrm{Pb}_{2} \mathrm{I}_{7}$ and (4AMP)(MA) $\mathrm{Pb}_{2} \mathrm{I}_{7}$. 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 $g_{l}=g_{2}=1$ 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:

$$
\tau_{21}=\left[A_{21}\right]^{-1}=\frac{\varepsilon_{0} m_{e} c^{3} g_{2} 1}{8 \pi^{2} v_{21}^{2} e^{2} g_{1} f_{12}}=\frac{\varepsilon_{0} m_{e} c^{3}}{16 \pi^{2} v_{21}^{2} e^{2} f_{12}}
$$

The calculated radiative recombination lifetimes for the (3AMP)(MA) $\mathrm{Pb}_{2} \mathrm{I}_{7}$ and (4AMP)(MA) $\mathrm{Pb}_{2} \mathrm{I}_{7}$ 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. ${ }^{5}$

## (a) (3AMP)(MA) $\mathrm{Pb}_{2} \mathrm{I}_{7}$ <br> (b) (4AMP)(MA) $\mathrm{Pb}_{2} \mathrm{I}_{7}$



Figure S1. The geometric structures of (a) (3AMP)(MA) $\mathrm{Pb}_{2} \mathrm{I}_{7}$ and (b) $(4 \mathrm{AMP})(\mathrm{MA}) \mathrm{Pb}_{2} \mathrm{I}_{7}$ are obtained by averaging overall the molecular dynamics trajectories at 300 K . 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 $\mathrm{Pb}-\mathrm{I}-\mathrm{Pb}$ angle is marked by blue curve. The average $\mathrm{Pb}-\mathrm{I}$ bond length and $\mathrm{Pb}-\mathrm{I}-\mathrm{Pb}$ angle are $3.253 \AA$ and $138.16^{\circ}$ in the (3AMP)(MA) $\mathrm{Pb}_{2} \mathrm{I}_{7}$, and $3.281 \AA$ and $130.27^{\circ}$ in the (4AMP)(MA) $\mathrm{Pb}_{2} \mathrm{I}_{7}$. The pronounced octahedral titling in (4AMP)(MA) $\mathrm{Pb}_{2} \mathrm{I}_{7}$ is caused by shorter average hydrogen bond distance $\left(3.276 \AA\right.$ ) than that $(3.592 \AA)$ in $(3 A M P)(M A) \mathrm{Pb}_{2} \mathrm{I}_{7}$. 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) $\mathrm{Pb}_{2} \mathrm{I}_{7}$ and (4AMP)(MA) $\mathrm{Pb}_{2} \mathrm{I}_{7}$. The yellow shaded area shows the visible light wavelength range from 400 to 760 nm . The (3AMP)(MA) $\mathrm{Pb}_{2} \mathrm{I}_{7}$ absorption edge is about 0.15 eV lower than that in the (4AMP)(MA) $\mathrm{Pb}_{2} \mathrm{I}_{7}$, 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 ( 3 AMP )(MA) $\mathrm{Pb}_{2} \mathrm{I}_{7}$ compared to $4 \mathrm{AMP}(\mathrm{MA}) \mathrm{Pb}_{2} \mathrm{I}_{7}$ 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) $\mathrm{Pb}_{2} \mathrm{I}_{7}$ and (4AMP)(MA) $\mathrm{Pb}_{2} \mathrm{I}_{7}$ systems. The strong anti-bonding interaction between I 5 p and Pb 6 s orbitals in the 3AMP perovskite pushes up the VBM (valence band maximum), resulting in a reduced bandgap compared to that of 4AMP-based counterparts.

## References

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