

Supplementary Material

First-principles study of exciton self-trapping and electric polarization in one-dimensional organic lead halide perovskites

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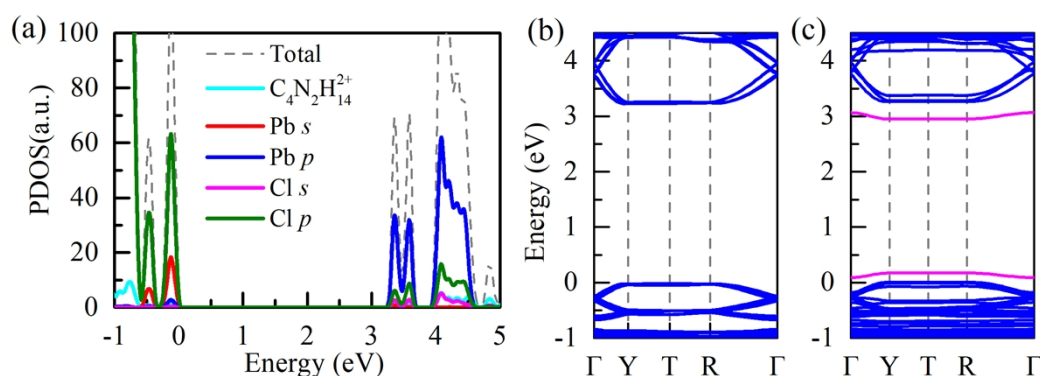


Figure S1. (a) Calculated partial density of states (PDOS) for ground states 1D- $C_4N_2H_{14}PbCl_4$. (b) and (c) Calculated energy band structure of the ground state (pristine structure) and excited state (distorted structure), respectively.

As shown in Fig. S1 (a), to reveal the orbitals contribute near the fermi level, we further project the density of states (PDOS) of ground states. The valence band maximum (VBM) is mainly composed of Cl 3p orbitals and hybridized with Pb 6s orbitals, while the conduction band minimum (CBM) is mainly contributed by the Pb 6p orbitals, which indicates that the inorganic $[PbCl_6]$ octahedron is responsible for

band-edge. As shown in Fig. S1 (b) and (c), compared with the pristine structure, the self-trapped excitons create a defect-like energy level in bandgap by structural distortion, where the local energy levels near VBM and CBM come from the trapped holes and electrons, respectively.

Table. S1. The equilibrium lattice constants and band gap of 1D-C₄N₂H₁₄PbCl₄ are obtained by different vdW dispersion method.

	a (Å)	b (Å)	c (Å)	lattice deviation	gap (eV)	gap deviation
Experiment ¹	14.14	5.80	14.22	/	4.05	/
DFT-D2 (vdW)	14.21	5.78	14.02	0.34%-1.41%	3.98	1.7%
DFT-D3 (vdW)	14.09	5.78	13.73	0.34%-3.45%	4.52	11.6%
optB86b-vdW	14.09	5.80	13.89	0.00%-2.32%	4.65	14.8%
optB88-vdW	16.30	6.82	15.88	11.67%-17.59%	2.46	39.3%

In the manuscript, we have carefully considered the influence of dispersion forces on the lattice and band gap of 1D-C₄N₂H₁₄PbCl₄. We found that the results obtained by DFT-D2 are good agreement with the experimental lattice constants and band gaps (the deviation range is 0.34%-1.41%), while other vdW methods have large deviations, which are summarized in Table S1. Therefore, HSE06+DFT-D2 method is adopted in all our theoretical simulations.

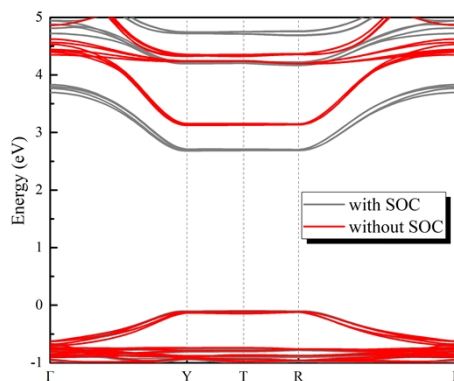


Figure S2. Band structures of 1D-C₄N₂H₁₄PbCl₄, the gray line and the red line are the results of with and without spin orbital coupling (SOC), respectively.

As shown in Fig. S2, after considering SOC effect the band gap of 1D- $C_4N_2H_{14}PbCl_4$ decreases by 0.35 eV, while the band edge shape hardly changes. Yan and co-workers² confirmed that the effective mass was very important for the self-trapping of carriers, while the SOC effect nearly no change for the 1D perovskite. Since the SOC induced effective mass change is minor, the effect on the self-trapping is expected to be small. Therefore, we ignore the influence of SOC on STEs formation. In order to ensure the accuracy of our simulation results, HSE06 hybrid functional and DFT-D2 method are used in all our calculations.

Table. S2. The space group and equilibrium lattice constants of 1D- $C_4N_2H_{14}PbX_4$ (X= Cl, Br and I).

	Space group	a (Å)	b (Å)	c (Å)
1D- $C_4N_2H_{14}PbCl_4$	<i>Imma</i> (# 74)	14.21	5.78	14.02
1D- $C_4N_2H_{14}PbBr_4$	<i>Imma</i> (# 74)	14.59	6.05	14.34
1D- $C_4N_2H_{14}PbI_4$	<i>Imma</i> (# 74)	15.07	6.37	14.67

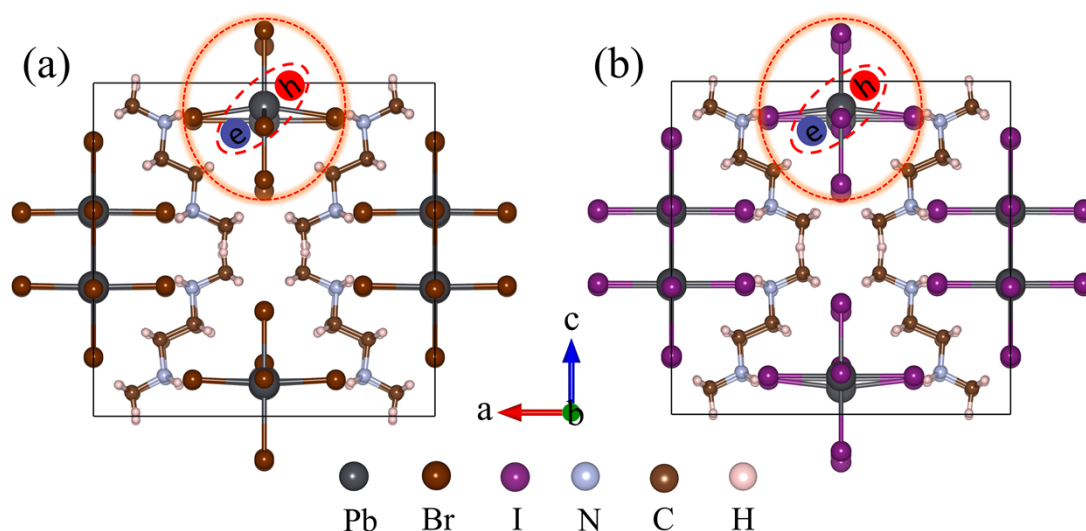


Figure S3. (a) and (b) are the self-trapping structures of 1D- $C_4N_2H_{14}PbBr_4$ and 1D- $C_4N_2H_{14}PbI_4$, respectively. A trapped configuration with local distortion (highlighted circle) can be obtained after sufficient relaxation of the free excited state structure. The gray, purple, purple, blue, brown, and pink balls present Pb, Br, I, N, C, and H atoms, respectively.

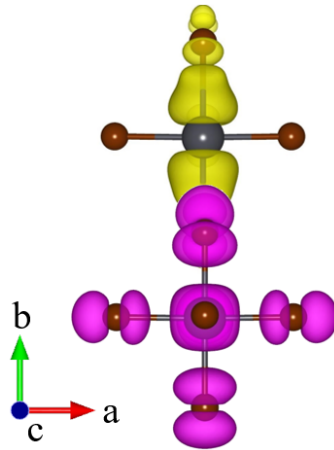


Figure S4. The localized orbital density contours of the hole (red) and electron (yellow) for the exciton in 1D-C₄N₂H₁₄PbBr₄. The isosurface value was set to 0.002 eÅ⁻³.

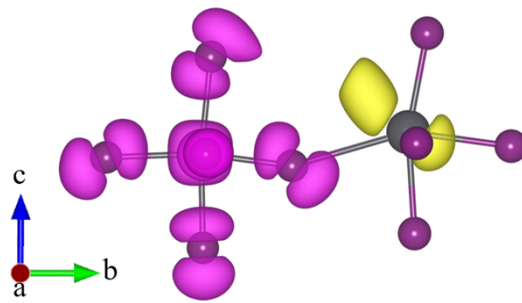


Figure S5. The localized orbital density contours of the hole (red) and electron (yellow) for the exciton in 1D-C₄N₂H₁₄PbI₄. The isosurface value was set to 0.002 eÅ⁻³.

Table. S3. Electronic and optical properties of self-trapped excitons in 1D-C₄N₂H₁₄PbX₄ (X= Cl, Br and I). Δd , E_g , E_{ST} , E_{PL} and E_d are the magnitude of structural distortion, band gap, self-trapping energy, emission energy, and lattice-deformation energy, respectively.

	Δd	E_g (eV)	E_{ST} (eV)	E_{PL} (eV)	E_d (eV)
1D-C ₄ N ₂ H ₁₄ PbCl ₄	38.3×10^{-4}	3.98	0.31	2.40	1.27
1D-C ₄ N ₂ H ₁₄ PbBr ₄	15.6×10^{-4}	3.73	0.27	2.34	1.12
1D-C ₄ N ₂ H ₁₄ PbI ₄	6.2×10^{-4}	3.68	0.25	2.33	1.10

Table. S4. The electric polarization ($\mu\text{ C/cm}^2$) of 1D-C₄N₂H₁₄PbX₄ (X= Cl, Br and I).

	<i>a</i> -axis	<i>b</i> -axis	<i>c</i> -axis	total
1D-C ₄ N ₂ H ₁₄ PbCl ₄	0.00	0.47	0.75	0.89
1D-C ₄ N ₂ H ₁₄ PbBr ₄	0.00	0.26	0.44	0.51
1D-C ₄ N ₂ H ₁₄ PbI ₄	0.00	0.71	0.12	0.72

Reference:

- [1] G. Wu, C. Zhou, W. Ming, D. Han, S. Chen, D. Yang, T. Besara, J. Neu, T. Siegrist, M.-H. Du, B. Ma, and A. Dong, *ACS Energy Lett*, 2018, **3**, 1443-1449.
- [2] X. Wang, W. Meng, W. Liao, J. Wang, R.-G. Xiong, and Y. Yan, *J. Phys. Chem. Lett*, 2019, **10**, 50-506.