Electronic Supplementary Information

Highly efficient self-trapped exciton emission in a one-dimensional face-shared hybrid lead bromide

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1. Experimental section

1.1 Synthesis of (2cepiH)PbBr₃ (1). All chemicals were analytically pure and commercially available, which were directly used without any further purification. The mixture of 3.7933 g (10 mmol) Pb(CH₃COO)₂ 3H₂O and 1.8411 g (10 mmol) 1-(2-Chloroethyl)-piperidine hydrochloride ((2cepiH)Cl) was dissolved in 20 mL HBr (48%) and stirred for 30 min at 80 °C. The bulk crystals of **1** (Fig. S1) were obtained by slowly evaporating the synthesized clear aqueous solution at room temperature after a few days. Thermogravimetric analysis (TGA) demonstrates that **1** has high thermal stability up to 523 K (Fig. S14).

1.2 X-ray Crystallographic Study. Single-crystal X-ray diffraction data of 1 were collected using an Xcalibur, Eos, Gemini EOS diffractometer with Mo K α radiation ($\lambda = 0.71073$ Å) at 293 K. The program SAINT was used for integration of the diffraction profiles. The structure was solved by direct methods and refined by full-matrix least-squares methods minimization on F^2 (SHELXL-97). All non-hydrogen atoms were refined anisotropically. All hydrogen atoms of organic molecules were generated theoretically onto the specific carbon and nitrogen atoms and refined isotropically with fixed thermal factors. Crystallographic data and structure refinements of 1 are summarized in Table S1, and the selected Pb-Br bond distances and angles are listed in Table S2.

1.3 Photoluminescence measurements. The photoluminescence (PL) measurements of **1**, involving excitation spectrum, temperature-dependent PL spectra, and time-resolved decay data, were performed on an Edinburgh FLS920 fluorescence

spectrometer with a picosecond pulsed diode laser. For the variable temperature PL measurements, the temperature firstly was lowered to 5 K, which was realized by the compressor equipped with liquid helium. Then, the PL spectra from 5 K to 300 K were collected, during which the slit widths keep constant. PLQY was also achieved using FLS920 spectrofluorometer equipped with an integrating sphere. The equation: $\eta_{\text{QE}} = I_{\text{S}}/(E_{\text{R}} - E_{\text{S}})$ was used to calculate PLQY, where I_{S} stands for the emission spectra of the compound, E_{R} is the spectra of the excitation light of the empty integrated sphere, and E_{S} is the excitation spectra of the excited sample. The CIE chromaticity coordinates, CCT, and CRI were calculated using the CIE calculator software based on the emission spectra.

1.4 Absorption spectral measurements. TU-1901 Ultraviolet spectrometer was used to record the UV-vis absorption curves of **1** at ambient condition, where the standard reference was BaSO₄. The corresponding optical band gap was evaluated as a function of the Kubelka–Munk equation: $\alpha/S = (1 - R)^2/2R$.

1.5 Powder X-ray diffraction. Powder X-ray diffraction (XRD) measurements were measured at 40 kV and 100 mA on a Rigaku D/Max-2500 diffractometer with Cu K α radiation, and the powder diffraction patterns were collected in the 2θ range of 4° to 50° with a step size of 0.02 min⁻¹.

1.6 Characterization. Digital microscope (HiROX RH-2000, Japan) was used to acquire photograph of (2cepiH)PbBr₃ crystals. The morphology of the powder samples (Fig. S5) was observed by scanning electron microscopy (JEOL-JSM-7001F) at an acceleration voltage of 10 kV. Fourier transform infrared (FT-IR) spectrum of **1** in Fig.

S3 was recorded from KBr pellets in range 400-4000 cm⁻¹ on a Nicolet iS50 spectrometer. TGA measurement was carried out on a NETZSCH STA 449F3 thermal analyzer under N₂ at a heating rate of 10 °C/min. Raman spectra of the bulk crystal of 1 in the range of 100-3000 cm⁻¹ were measured using Renishaw inVia spectrometer with a 785 nm laser and 50 × objective lens.

1.7 Computational methodology. First-principles calculations were performed using the density-functional theory, as implemented in the Vienna *ab-initio* simulation package (VASP, version 5.4) ^[1, 2] in MedeA platform ^[3]. The all-electron information was reconstructed using projector augmented wave (PAW) pseudopotentials ^[4]. The exchange-correlation energy was treated by the local density approximation (LDA) formulation ^[5]. The valence electron configurations applied in this work were Pb ($6s^{2}6p^{2}$), Br ($4s^{2}4p^{5}$), C ($2s^{2}2p^{2}$), N ($2s^{2}2p^{3}$), and H ($1s^{1}$). The kinetic energy cutoff was determined to be 400 eV in all cases. Gaussian smearing method ^[6] with a value of 0.1 eV was adopted to describe the electronic occupancies. The convergence thresholds for the electronic and ionic relaxations were chosen as 10^{-7} eV and 0.005 eV/Å, respectively. The standard Monkhorst-Pack ^[7] special k-point meshes with densities of 0.2 Å⁻¹ were employed for Brillouin zone sampling.

2. Supporting figures



Fig. S1 Photograph of bulk crystals of 1.



Fig. S2 Experimental and simulated PXRD data of 1.



Fig. S3 FT-IR spectrum of **1**. The infrared characteristic peak of the C–Cl bond from (2cepiH)⁺ cation was clearly shown at around 670 cm⁻¹, marked by the red circle.



Fig. S4 Asymmetric unit of **1** containing one protonated (2cepiH)⁺ cation, one Pb(II) atom, and three Br atoms.



Fig. S5 SEM image of powder sample of 1.



Fig. S6 Emission spectra of 1 for mm-sized bulk crystals and powder sample.



Fig. S7 CIE coordinate of 1.



Fig. S8 Emission spectra of 1 before (black line) and after (red line) about two months.



Fig. S9 Diffuse reflectance spectrum of 1.



Fig. S10 (a) Temperature-dependent steady state PL spectra of **1**. (b) Emission bands of the marked areas in panel a.



Fig. S11 PL intensity of the STE emission as a function of 1/T in the range of 100 - 300 K, where the red line shows the fitting data according to the Arrhenius equation.



Fig. S12 Bandwidth of the STE emission as a function of 1/T in the range of 5 - 300 K, in which the red line indicates the fitting data.



Fig. S13 Raman spectra of (2cepiH)Cl and (2cepiH)PbBr₃. The green circle unravels the Raman stretching mode of Pb–Br bonds in metal halide octahedral framework. The red curves shows pure vibrational modes of the organic molecules, while the black arrows indicate new active modes of (2cepiH)⁺ embedded in the metal halide framework. This result proves the presence of a great intermolecular interaction between organic and inorganic parts, which probably leads to the ultrahigh structural distortion of inorganic octahedral units.



3. Supporting tables

Table S1 Crystal data of 1

	Т / К			
	293	120	100	80
Formula	C7H15NClBr3Pb	C7H15NClBr3Pb	C7H15NClBr3Pb	C ₇ H ₁₅ NClBr ₃ Pb
Mr	595.57	595.57	595.57	595.57
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_{1}/c$	$P2_{1}/c$	$P2_{1}/c$	$P2_{1}/c$
Ζ	4	4	4	4
a/Å	10.9554(13)	10.9752(3)	10.9690(3)	10.9594(3)
b/Å	16.2655(17)	16.0374(3)	16.0026(4)	15.9764(3)
$c/{ m \AA}$	7.9831(8)	7.9786(2)	7.9735(2)	7.9680(2)
$eta / ^{\circ}$	109.324(12)	109.744(3)	109.755(3)	109.805(3)
$V/\text{\AA}^3$	1342.4(3)	1321.80(6)	1317.23(6)	1312.60(6)
$ ho_{ m calc}/ m gcm^{-3}$	2.947	2.993	3.003	3.014
μ/mm^{-1}	21.659	21.997	22.073	22.151
<i>F</i> (000)	1072.0	1072.0	1072.0	1072.0
Size/mm ³	0.5×0.3×0.2	0.5×0.3×0.2	0.5×0.3×0.2	0.5×0.3×0.2
S	1.059	1.052	1.085	1.073
R_{int}/R_{sigma}	0.0955/0.1336	0.1363/0.0514	0.1598/0.0669	0.1378/0.0686
Reflections	7907/3698	17235/2328	16595/2328	16802/2852
Data/Para.	2287/118	2124/118	2114/118	2524/118
$R_1^{a}, wR_2^{b}[I \ge 2\sigma(I)]$	0.1128/0.2531	0.0373/0.0953	0.0500/0.1257	0.0537/0.1322
R_1^{a} , w R_2^{b} (all data)	0.1724/0.3068	0.0408/0.0974	0.0539/0.1282	0.0583/0.1353
$\Delta ho_{ m max}/\Delta ho_{ m min}$ / e Å ⁻³	3.98/-7.00	3.75/-2.84	4.15/-4.17	6.05/-5.87

^a $R_1 = \sum ||F_0| - |F_c|| / \sum |F_0|$. ^b $wR_2 = [w(F_0^2 - F_c^2)^2 / w(F_0^2)^2]^{1/2}$

Atom-Atom	Length / Å	Atom–Atom	Length / Å
Pb1…Pb1b	3.992(4)	Pb1–Br3	2.827(2)
Pb1–Br1a	2.961(2)	Pb1–Br3a	3.330(2)
Pb1–Br1	3.213(2)	Br1–Pb1b	2.961(2)
Pb1–Br2a	2.931(2)	Br2–Pb1b	2.931(2)
Pb1–Br2	3.079(2)	Br3–Pb1b	3.330(2)
Atom–Atom–Atom	Angle / °	Atom–Atom–Atom	Angle / °
Br1a–Pb1–Br1	95.39(8)	Br3–Pb1–Br2a	91.71(7)
Br1a–Pb1–Br2	173.64(7)	Br3a–Pb1–Br3	167.44(2)
Br2a–Pb1–Br1a	86.50(7)	Br3a–Pb1–Br1	105.93(2)
Br2a–Pb1–Br1	176.24(6)	Br3a–Pb1–Br2	104.37(2)
Br2–Pb1–Br1	79.79(6)	Br3a–Pb1–Br1a	80.86(2)
Br2a–Pb1–Br2	98.08(8)	Br3a–Pb1–Br2a	77.56(2)
Br3–Pb1–Br1	84.97(7)	Pb1b–Br1–Pb1	80.44(6)
Br3–Pb1–Br1a	92.10(6)	Pb1b–Br2–Pb1	83.20(6)
Br3–Pb1–Br2	83.39(6)	Pb1b–Br3–Pb1	80.37(2)

 Table S2 Selective bond lengths and bond angles.

Symmetric code: (a) +x, 1/2-y, 1/2+z; (b) +x, 1/2-y, -1/2+z

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