

Supporting Information

Unveiling Mn²⁺ Dopant States in Two-Dimensional Halide Perovskite toward Highly Efficient Photoluminescence

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EXPERIMENTAL DETAILS

Materials. PbBr₂ (Lead(II) bromide, Aladdin, 99.9 %), HBr (hydrobromic acid, Aladdin, 48 wt% in water), C₈H₁₈N₂ (1,3-Cyclohexanebis(methylamine) 99.9 %, Aladdin), MnBr₂•5H₂O (99.5 %, Aladdin), C₂H₅OH (Ethanol 99.8%, Aladdin). All reagents and solvents were used without any purifications.

Synthesis of (C₈H₂₀N₂)PbBr₄ and (C₈H₂₀N₂)Pb_{1-x}Mn_xBr₄ samples. 0.002 mol PbBr₂ (1.8967 g) was dissolved in 15 ml 48% HBr solution and dropwise add of 0.002 mol (0.5811 g) 1,3-Cyclohexanebis(methylamine) at 110 °C to form a clear solution. Upon cooling to room temperature, the white powder was separate out, the supernatant liquids were removed and the polycrystalline samples were repeatedly washed using ethanol. Then the samples were filtered and dried under vacuum at 70 °C overnight. Mn²⁺ doped (C₈H₂₀N₂)PbBr₄ samples were synthesized by substituting PbBr₂ for MnBr₂ partially with corresponding stoichiometric ratio.

Synthesis of (C₈H₂₀N₂)PbBr₄ single crystal sample. Temperature-lowering method was employed to grow single crystals of (C₈H₂₀N₂)PbBr₄. Firstly, 0.002 mol PbBr₂ (99.9 %, Aladdin) (1.8967 g) was dissolved in 15 ml 48% HBr solution at 110 °C for 5 min, followed by dropwise add of 0.002 mol (0.5811 g) 1,3-Cyclohexanebis(methylamine) to form a clear solution. Subsequently, the hot solution was transferred into a preheated Teflon autoclave and then sealed in a stainless-steel Parr autoclave, which was subsequently placed in a drying oven and kept at 110 °C for 30 min, then the temperature was lowered with a rate of 5.0 °C/day, colorless transparent sheet crystals of (C₈H₂₀N₂)PbBr₄ were obtained about two weeks. Finally, the obtained white crystals were filtered out, washed with ethanol and dried at 60 °C overnight.

Characterization. Single-crystal X-ray diffraction was conducted on a SMART APEX II X-ray single crystal diffractometers (Bruker AXS, analytical equipment of Krasnoyarsk Center of collective use of SB RAS) equipped with a CCD-detector, graphite monochromator and Mo K α radiation ($\lambda = 1.5406 \text{ \AA}$) at 296 K. The absorption corrections were applied using the SADABS program. The structures were solved by the direct methods using package SHELXS and refined using the SHELXL program. All the hydrogen atoms of the C₈H₂₀N₂ ligand were positioned geometrically as riding on their parent atoms with $d(\text{C-H}) = 0.97 \text{ \AA}$ for the C-H bonds and $d(\text{N-H}) = 0.89 \text{ \AA}$ for all other N-H bonds and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C,N})$. The structural tests for the presence of missing symmetry elements and possible voids were produced using the PLATON program. Powder X-ray diffraction (PXR) measurement was performed on a Aeris powder X-ray diffraction (XRD) diffractometer (PANalytical Corporation, Netherlands) operating at 40 kV and 15 mA with monochromatized Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). The data used for Rietveld analysis (2θ range 5-120°) was collected in a step-scanning mode with a step size of 0.01° and 10 s counting time per step. Electron paramagnetic resonance (EPR) spectroscopy were recorded by an electron paramagnetic resonance EPR spectrometer (Bruker, A300). The absorption spectra was collected by SolidSpec-3700 Shimadzu UV-vis-NIR spectra photometer at room temperature, in which BaSO₄ was used as the reference standard. The photoluminescence (PL), photoluminescence excitation (PLE) spectra were performed on an FLS1000

fluorescence spectrophotometer (Edinburgh Instruments Ltd., U. K.) The photoluminescence quantum yields (PLQYs) was recorded by sphere, which was attached in the FLS1000 spectrofluorometer. The PLQYs was calculated based on the equation: $\eta_{QE} = I_S/(E_R - E_S)$, in which I_S is the luminescence emission spectra of the sample, E_R represents the spectra of the excitation light of the empty integrated sphere, and E_S is the excitation spectra of the excited sample. The lifetimes were measured on an Edinburgh FLS1000 fluorescence spectrometer using a picosecond pulsed diode lasers. The dynamics of emission decay were monitored by using the FLS1000's time-correlated single-photon counting capability (1,024 channels; 1 μ s window) with data collection for 5000 counts in the maximum channel.

Table S1. The crystal structure parameters of (C₈H₂₀N₂)PbBr₄

Chemical formula	C ₈ H ₂₀ Br ₄ N ₂ Pb
Molecular weight	671.09
Temperature (K)	150
Space group, <i>Z</i>	<i>Pnma</i> , 4
<i>a</i> (Å)	8.4804 (2)
<i>b</i> (Å)	24.4406 (6)
<i>c</i> (Å)	7.9107 (2)
<i>V</i> (Å ³)	1639.62 (7)
ρ_{calc} (g/cm ³)	2.719
μ (mm ⁻¹)	31.246
Reflections measured	5438
Reflections independent	1669
Reflections with $F > 4\sigma(F)$	1659
$2\theta_{\text{max}}$ (°)	73.52
<i>h, k, l</i> - limits	$-10 \leq h \leq 10$; $-27 \leq k \leq 29$; $-9 \leq l \leq 9$
R_{int}	0.0286
<i>Refinement results</i>	
The weighed refinement of F^2	$w=1/[\sigma^2(F_o^2)+(0.0557P)^2+6.8973P]$ where $P=\max(F_o^2+2F_c^2)/3$
Number of refinement parameters	74
$R1 [F_o > 4\sigma(F_o)]$	0.0299
$wR2$	0.0861
<i>Goof</i>	1.095
$\Delta\rho_{\text{max}}$ (e/Å ³)	2.37
$\Delta\rho_{\text{min}}$ (e/Å ³)	-1.1
$(\Delta/\sigma)_{\text{max}}$	<0.001
Extinction coefficient (SHELXL 2014/7)	0.0067 (4)

Table S2. Fractional atomic coordinates and isotropic or equivalent isotropic

displacement parameters (\AA^2)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Pb	0.5000	0.5000	0.0000	0.01308 (16)
Br1	0.29761 (5)	0.47551 (2)	0.30453 (6)	0.01853 (18)
Br2	0.46438 (6)	0.38267 (2)	-0.09048 (6)	0.02187 (18)
C1	0.5829 (7)	0.35239 (19)	0.3942 (6)	0.0225 (10)
H1A	0.6895	0.3469	0.3533	0.027*
H1B	0.5151	0.3583	0.2972	0.027*
C2	0.5820 (9)	0.2500	0.3954 (9)	0.0189 (13)
H2A	0.5382	0.2500	0.2821	0.023*
H2B	0.6961	0.2500	0.3858	0.023*
C3	0.3491 (6)	0.3013 (2)	0.5147 (6)	0.0202 (11)
H3A	0.3185	0.3333	0.5794	0.024*
H3B	0.2970	0.3031	0.4057	0.024*
C4	0.2963 (8)	0.2500	0.6074 (10)	0.0237 (15)
H4A	0.3402	0.2500	0.7206	0.028*
H4B	0.1823	0.2500	0.6171	0.028*
C5	0.5286 (8)	0.3015 (3)	0.4888 (6)	0.0163 (11)
H5A	0.5787	0.3016	0.6005	0.020*
N1	0.5784 (6)	0.40140 (18)	0.5057 (5)	0.0212 (10)
H0A	0.6105	0.4306	0.4479	0.025*
H0B	0.4802	0.4068	0.5419	0.025*
H0C	0.6417	0.3962	0.5939	0.025*

Table S3. The main bond lengths (Å) of compound (C₈H₂₀N₂)PbBr₄

Pb—Br ²ⁱ	2.9710 (5)	C1—N1	1.488 (6)
Pb—Br ²	2.9710 (5)	C1—C5	1.522 (8)
Pb—Br ¹ⁱ	3.0179 (5)	C2—C5	1.529 (7)
Pb—Br ¹	3.0179 (5)	C3—C4	1.520 (6)
Pb—Br ¹ⁱⁱ	3.0198 (4)	C3—C5	1.536 (8)
Pb—Br ¹ⁱⁱⁱ	3.0198 (4)	C4—C ^{3iv}	1.520 (6)

Symmetry codes: (i) -x+1, -y+1, -z; (ii) -x+1/2, -y+1, z-1/2; (iii) x+1/2, y, -z+1/2; (iv) x, -y+1/2, z.

Table S4. Main parameters of processing and refinement of the (C₈H₂₀N₂)PbBr₄: xMn²⁺

samples

Number of samples	x(Mn)	Space Group	Cell parameters (Å), Cell Volume (Å ³)	R _{wp} , R _p , R _B , χ ²
HPB-0	0	<i>Pnma</i>	<i>a</i> = 8.55288 (13), <i>b</i> = 24.5694 (4), <i>c</i> = 7.94449 (12), <i>V</i> = 1669.45 (4)	3.37, 2.55, 0.11, 1.66
HPB-2	0.10	<i>Pnma</i>	<i>a</i> = 8.55282 (11), <i>b</i> = 24.5659 (3), <i>c</i> = 7.94441 (11), <i>V</i> = 1669.18 (4)	3.17, 2.44, 0.08, 1.55
HPB-4	0.40	<i>Pnma</i>	<i>a</i> = 8.55372(11), <i>b</i> = 24.5624 (3), <i>c</i> = 7.94226 (10), <i>V</i> = 1668.67 (4)	4.36, 3.25, 0.30, 2.15
HPB-5	0.60	<i>Pnma</i>	<i>a</i> = 8.55268 (13), <i>b</i> = 24.5674 (4), <i>c</i> = 7.94265 (13), <i>V</i> = 1668.88 (5)	3.23, 2.52, 0.10, 1.56
HPB-6	0.80	<i>Pnma</i>	<i>a</i> = 8.555117 (10), <i>b</i> = 24.5687 (3), <i>c</i> = 7.94088 (10), <i>V</i> = 1668.31 (4)	3.16, 2.42, 0.09, 1.52

Table S5. The inductively coupled plasma optical emission spectroscopy (ICP-OES)

analyses of $(C_8H_{20}N_2)PbBr_4: xMn^{2+}$ samples

Number of samples	$x(Mn^{2+})$	The tested Mn content
HPB-1	0.05	0.006 at %
HPB-3	0.20	0.019 at %
HPB-4	0.40	0.051 at %
HPB-5	0.60	0.385 at %
HPB-6	0.80	0.476 at %

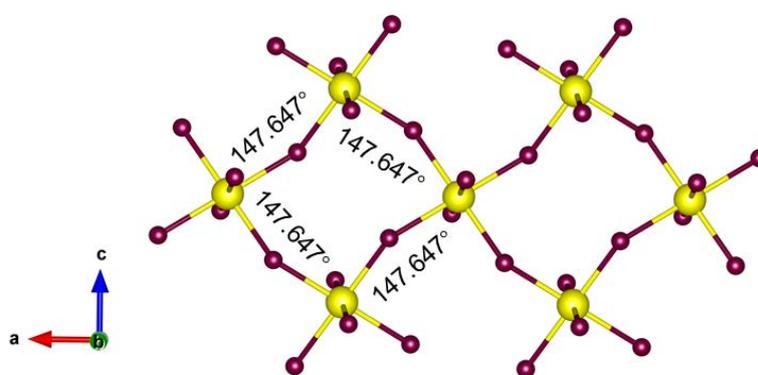


Figure S1. The distorted angle of inorganic layer of $(C_8H_{20}N_2)PbBr_4$ in ac plane.

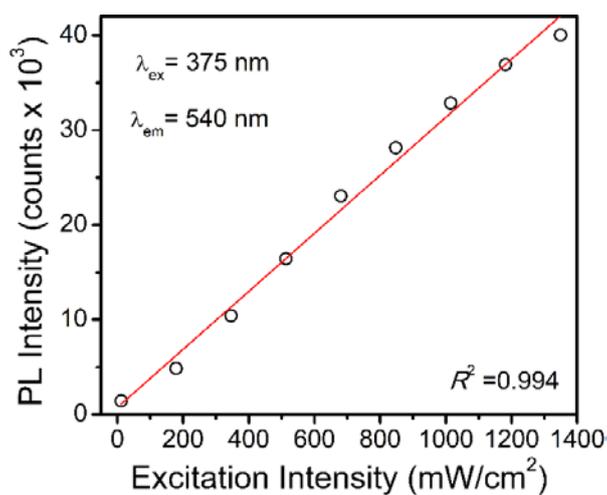


Figure S2. Variation of the emission intensities of STE of $(C_8H_{20}N_2)PbBr_4$ crystal excited at 375 nm as a function of the excitation power density.

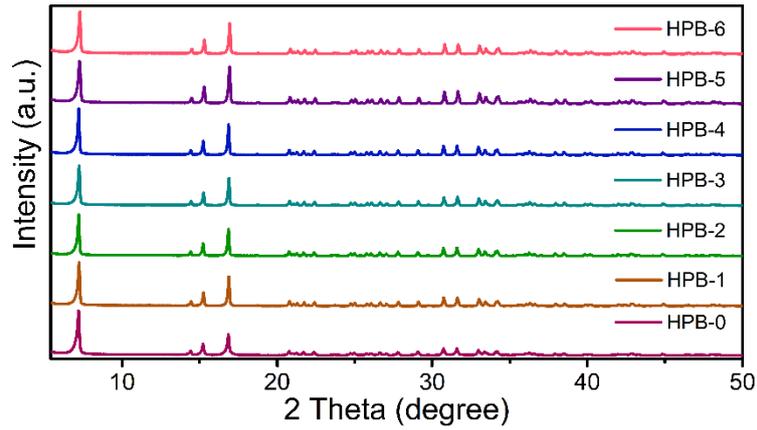


Figure 3. XRD patterns of Mn^{2+} doped $(\text{C}_8\text{H}_{20}\text{N}_2)\text{PbBr}_4$ with different Mn^{2+} concentration.

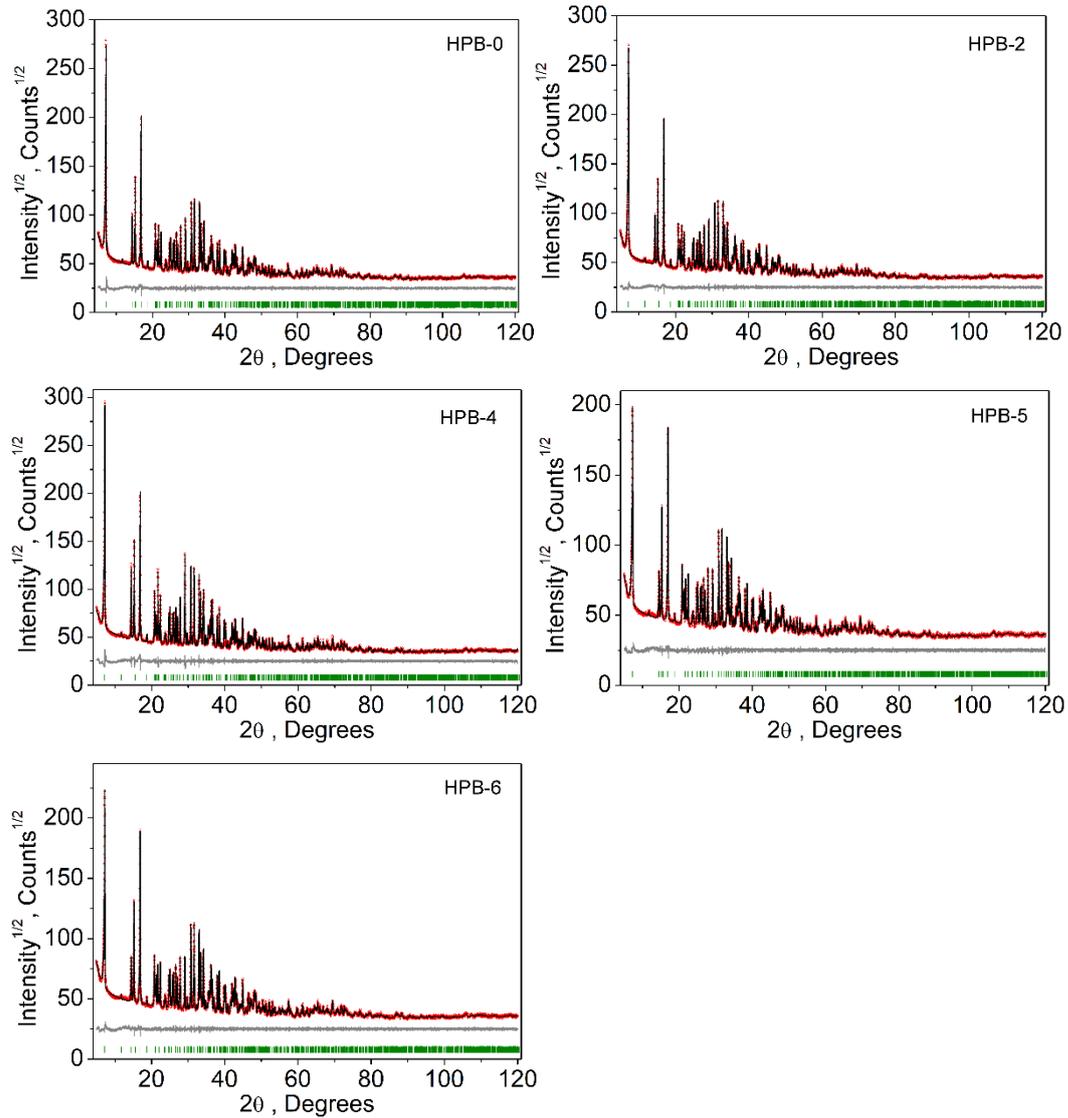


Figure S4. Rietveld refinement patterns of Mn^{2+} doped $(\text{C}_8\text{H}_{20}\text{N}_2)\text{PbBr}_4$ with different Mn^{2+} concentration.

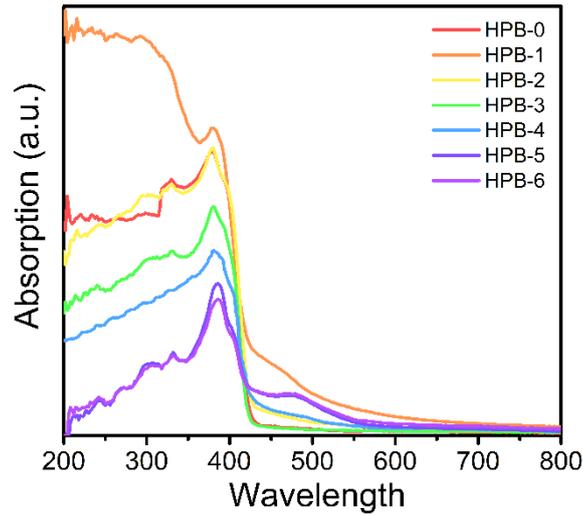


Figure S5. The absorption spectra of Mn^{2+} doped $(\text{C}_8\text{H}_{20}\text{N}_2)\text{PbBr}_4$ with different Mn^{2+} concentration.

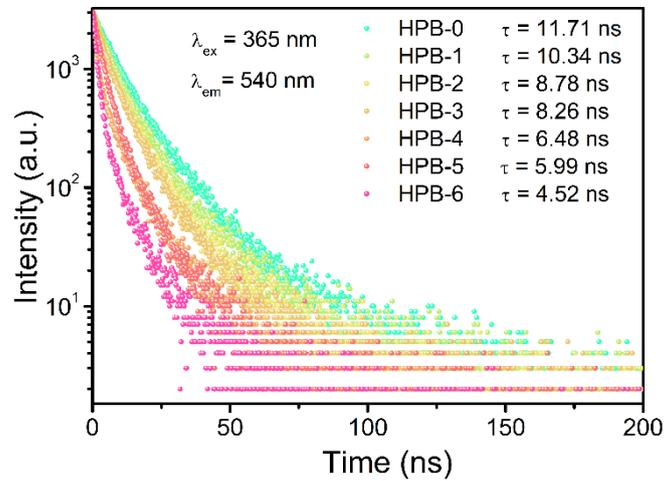


Figure S6. Time-resolved PL decay of STEs emission of Mn^{2+} doped $(\text{C}_8\text{H}_{20}\text{N}_2)\text{PbBr}_4$ with different Mn^{2+} concentration at room temperature under 365 nm irradiation.

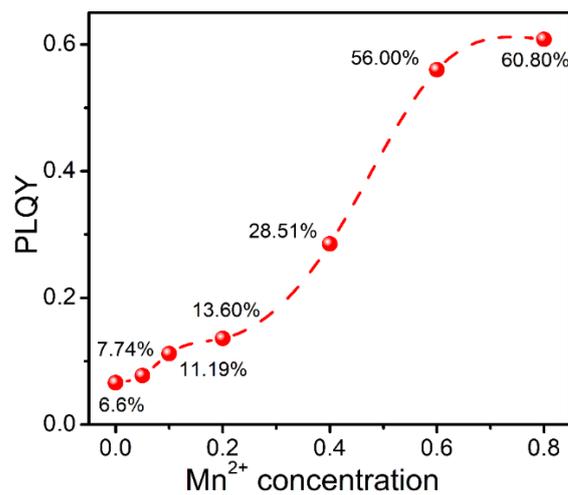


Figure S7. The PLQYs of different Mn^{2+} doped $(\text{C}_8\text{H}_{20}\text{N}_2)\text{PbBr}_4$, corresponding to HPB- x ($x = 0, 1, 2, 3, 4, 5, 6$) samples respectively, under the 365 nm excitation at room temperature.

References

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