

Supplementary Information

Simultaneous 100% PLQY of Mn²⁺ Emission and High Pb Substitution via Sr²⁺ Doping in Mn-CsPbCl₃ Nanocrystals

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Experimental and characterization

2.1 Materials

Lead (II) chloride (PbCl_2 , 99.99%), manganese chloride (MnCl_2 , 99.99%), strontium chloride (SrCl_2 , 99.99%), cesium carbonate (Cs_2CO_3 , 99.9%) were purchased from Macklin, oleylamine (OLA, 85%), oleic acid (OA, 85%), 1-octadecene (ODE, 90%), n-hexane (99.9%), ethyl acetate (99.9%), Methyl methacrylate (PMMA, 99%) were purchased from Aladdin.

2.2. Preparation of the Cs-OA precursor

This synthetic method has been reported in our previous work.¹ A mixture of 0.814 g Cs_2CO_3 , 30 mL ODE, and 3 mL OA was added to a 100 mL three-necked flask. The entire reaction was carried out under constant stirring in a nitrogen atmosphere. The solution was heated from 20 °C to 120 °C and held at that temperature for 60 minutes to remove residual water and oxygen. Subsequently, the temperature was increased to 150 °C and maintained for 30 minutes. A transparent-to-pale yellow color change indicated the successful formation of the precursor solution.

2.3. Synthesis of Mn-CsPbCl₃ NCs

This synthetic method has been reported in our previous work.¹ A mixture of 0.6 mmol of $\text{MnCl}_2/\text{PbCl}_2$ (The molar ratio of MnCl_2 to PbCl_2 was between 3:7 and 8:2), 10 mL of ODE, 1.5 mL OA and 1.5 mL OLA was added to a 100 mL three-neck flask. The reaction solution was maintained at 80 °C, 100 °C, and 120 °C for 20 minutes at each temperature. Then, three evacuation-nitrogen purge cycles were performed to ensure an inert atmosphere. Finally, the solution was heated to the target reaction temperature (170 - 200 °C), followed by rapid injection of 1.2 mL of Cs-oleate solution preheated to 150 °C. After reacting for 5 seconds, the mixture was immediately cooled using an ice-water bath to quench the reaction.

2.4. Synthesis of Mn/Sr-CsPbCl₃ NCs

Similar to the above process, to investigate the effect of the Sr/Pb feeding ratio on $\text{Mn}^{2+}/\text{Sr}^{2+}$ co-doped CsPbCl_3 NCs, the molar ratio of MnCl_2 to PbCl_2 was maintained at a constant 6:4, while a strontium source (SrCl_2) was introduced into the three-neck flask at $\text{SrCl}_2/\text{PbCl}_2$ molar ratios ranging from 10% to 60%. To investigate the effect of the Mn/Pb feeding ratio on $\text{Mn}^{2+}/\text{Sr}^{2+}$ co-doped CsPbCl_3 NCs, the $\text{SrCl}_2/\text{PbCl}_2$ molar ratio was maintained at a constant 30%, while the $\text{MnCl}_2/\text{PbCl}_2$ molar ratio was varied between 3:7 and 8:2.

2.5. Purification of NCs

The crude solution was transferred to a centrifuge tube. Then, 10 mL n-hexane and 20 mL ethyl acetate were added to induce precipitation. The mixture was centrifuged at 8000 rpm for 3 min to removed unreacted precursors. The resulting precipitate was redispersed in 10 mL of n-hexane, forming a stable colloidal solution for subsequent characterization.

2.6. Fabrication of the WLED device

0.5 g of PMMA was dissolved in 2 mL of toluene. 2000 μL of the Mn/Sr-CsPbCl₃ NCs toluene dispersion solution was added to PMMA/ toluene solution, and the mixture was blade-coated uniformly at a controlled thickness of 1000 μm , then dried in an oven at 60 °C for 3 hours, yielding a Mn²⁺/Sr²⁺ co-doped CsPbCl₃ NC-PMMA composite film. The preparation process of CsPb(Cl,Br)₃ and CsPbBr₃ NC-PMMA composite films were similar to the above process. Finally, these films were applied onto a commercial 365 nm UV-LED chip, WLED devices were fabricated.

2.7 Characterization

The absorption of NCs was done by a SHIMADZU UV3600 UV-vis-NIR spectrophotometer. Photoluminescence (PL) spectra and photoluminescence excitation (PLE) spectra were acquired using an Agilent Cary Eclipse fluorescence spectrophotometer. The photoluminescence quantum yield (PLQY) was determined with a Hamamatsu Quantaurus-QY C11347-11 integrated fluorescence quantum yield measurement system featuring an integrating sphere. X-ray diffraction (XRD) patterns were collected over by a Bruker D8 Advance X-ray diffractometer. Elemental composition and chemical states were analyzed by X-ray photoelectron spectroscopy (XPS) on a ULVAC-PHI instrument. The transmission electron microscopy (TEM), high-resolution TEM (HR-TEM), and energy-dispersive X-ray spectroscopy (EDS) analysis were performed on a JEOL JEM-2100F microscope. Time-resolved photoluminescence (TRPL) decays were recorded on a Horiba FluoroMax system configured for high/low-temperature transient fluorescence and absorption measurements. The relative proportions of B-site ions were quantified by inductively coupled plasma optical emission spectrometry (ICP-OES) on a Thermo Scientific iCAP Pro series instrument. The optoelectronic characteristics of the resulting LEDs were evaluated using an OLED-1000 comprehensive photoelectric measurement system.

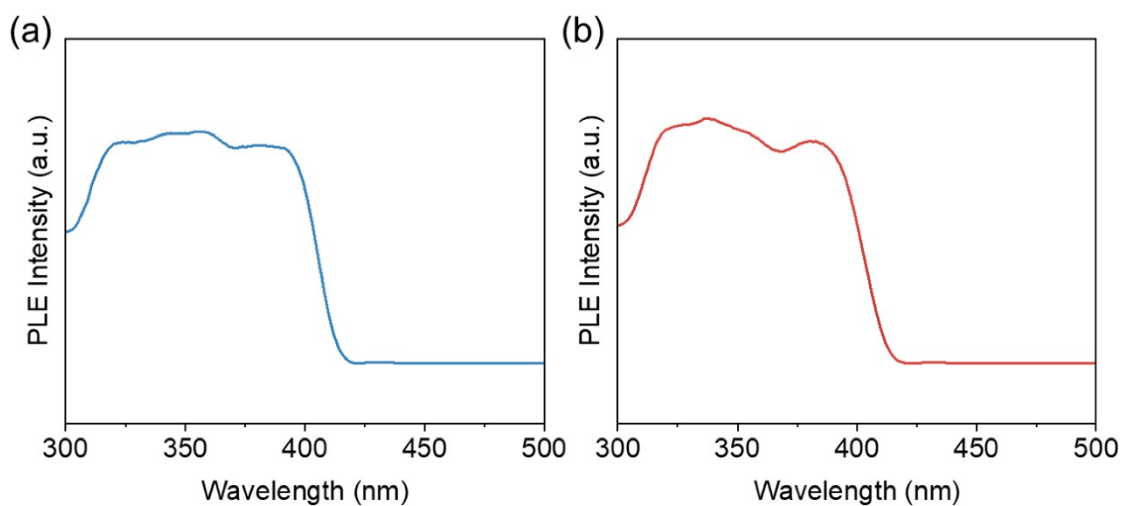


Fig. S1 PLE ($\lambda_{em} = 600$ nm) spectra of (a) Mn-CspbCl₃ NCs and (b) Mn/Sr-CspbCl₃ NCs.

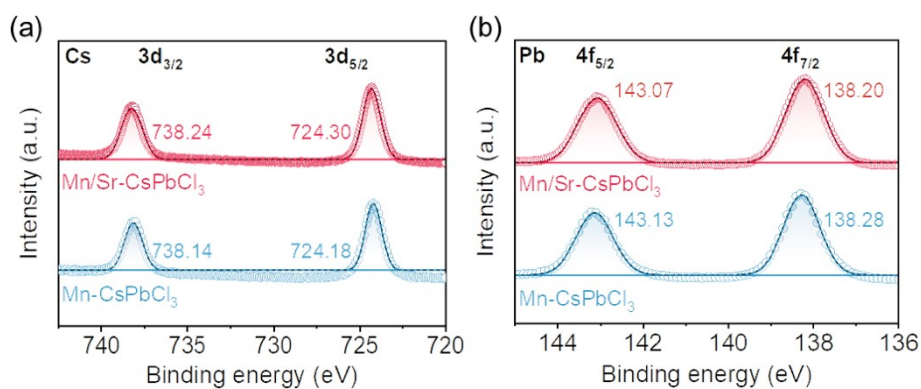


Fig. S2 High-resolution XPS spectra of Mn-CspbCl₃ and Mn/Sr-CspbCl₃ for (a) Cs and (b) Pb, respectively.

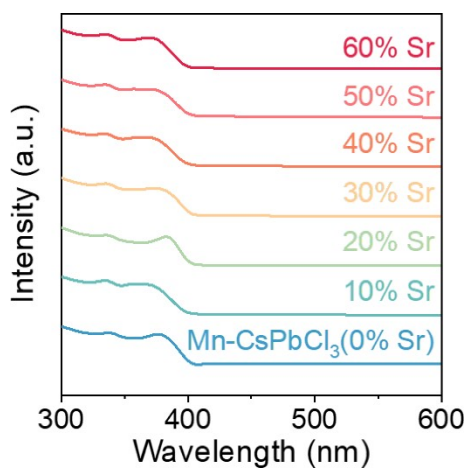


Fig. S3 Absorption spectra of Mn/Sr-CspbCl₃ NCs synthesized with different Sr/Pb feed ratios.

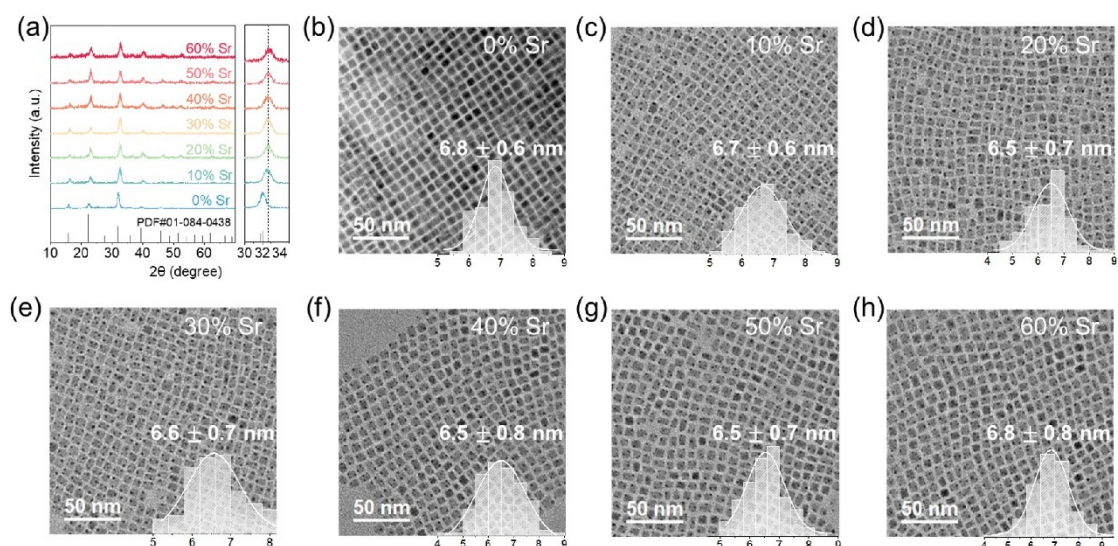


Fig. S4 (a) XRD patterns, (b)-(h)TEM images and corresponding size distribution histograms of Mn/Sr-CsPbCl₃ NCs prepared with different Sr/Pb feed ratios.

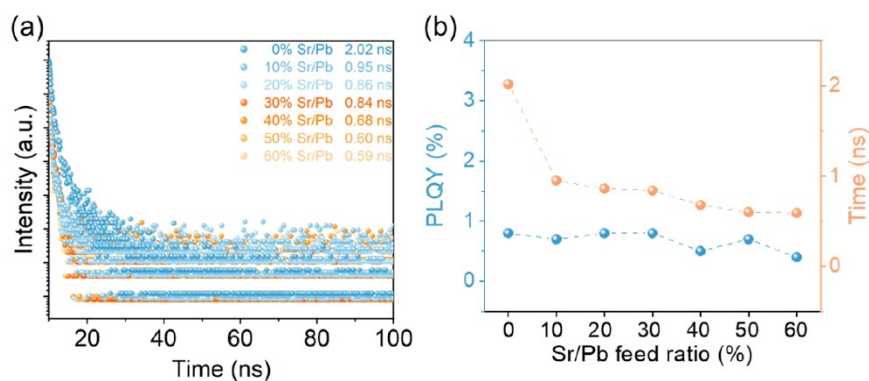


Fig. S5 (a) TRPL decays of excitonic emission, (b) excitonic emission PLQY and average lifetime as a function of Sr/Pb feed ratio (0% - 60%).

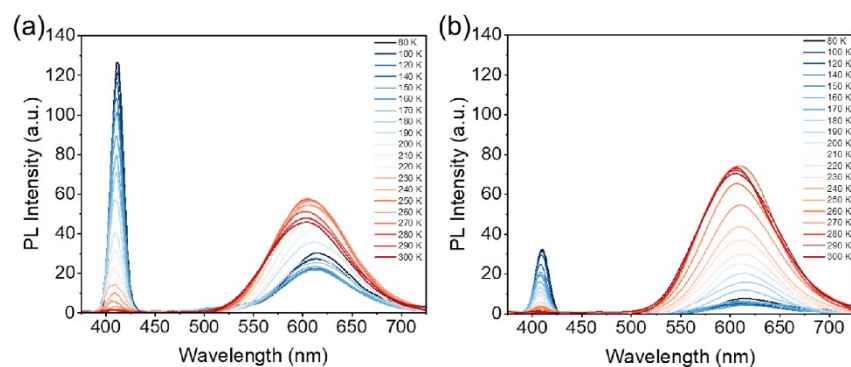


Fig. S6 Temperature-dependent PL spectra of (a) Mn -CsPbCl₃ NCs and (b) Mn/Sr-CsPbCl₃ NCs.

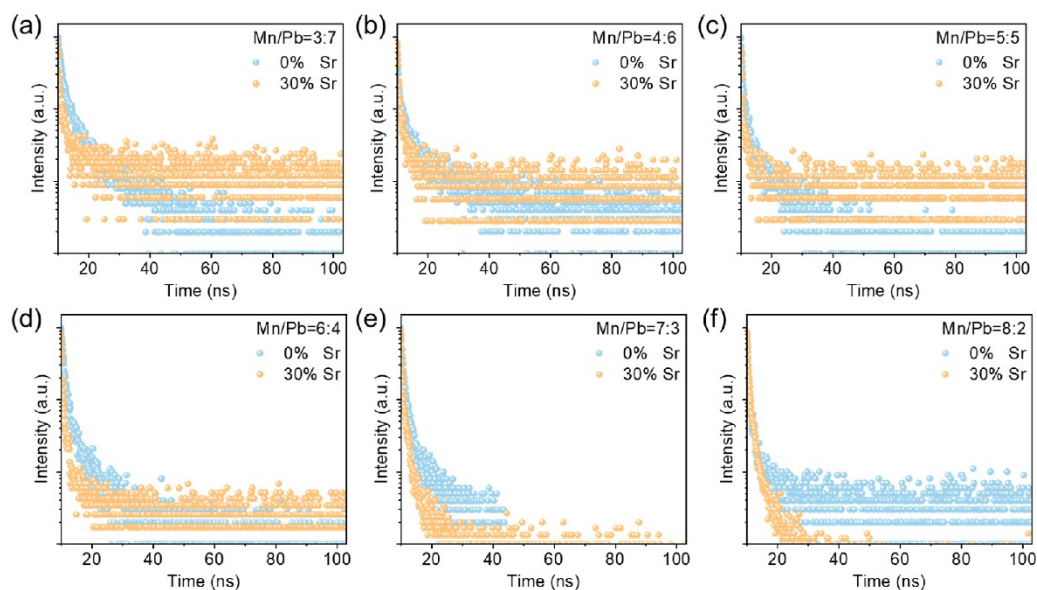


Fig. S7 Comparative TRPL decays of excitonic emission from Mn-CsPbCl₃ NCs and Mn/Sr-CsPbCl₃ NCs (30% Sr/Pb feed ratio) at different Mn/Pb feed ratios: (a) 3:7, (b) 4:6, (c) 5:5, (d) 6:4, (e) 7:3, (f) 8:2.

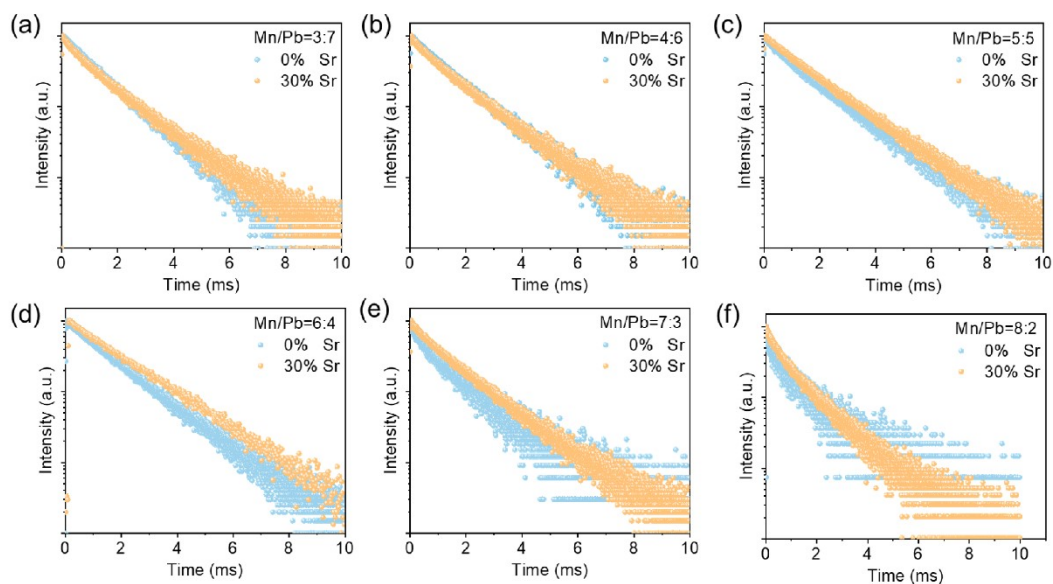


Fig. S8 Comparative TRPL decays of Mn²⁺ emission from Mn-CsPbCl₃ NCs and Mn/Sr-CsPbCl₃ NCs (30% Sr/Pb feed ratio) at different Mn/Pb feed ratios: (a) 3:7, (b) 4:6, (c) 5:5, (d) 6:4, (e) 7:3, (f) 8:2.

Table S1. Summary of key performance parameters of the Mn²⁺ co-doped CsPbCl₃ NCs with different metal ions in previous studies.

Metal ion	PLQY for Mn ²⁺ ions (%)	Pb substitution level (%)	Synthesis Method	Reference
Sr²⁺	100	18.58	Hot-injection	This work
Sr ²⁺	49.1	0.26	Hot-injection	Ref 2
Sr ²⁺	72.83	2.96	Hot-injection	Ref 3
Mg ²⁺	61.14	7.04	Hot-injection	Ref 3
Ca ²⁺	57.80	3.18	Hot-injection	Ref 3
Ba ²⁺	40.38	2.21	Hot-injection	Ref 3
Fe ²⁺	27	-	Hot-injection	Ref 4
Ni ²⁺	70	5.15	Hot-injection	Ref 5
Cu ²⁺	63	5.24	Hot-injection	Ref 6
Zn ²⁺	51.2	-	Ultrasonic	Ref 7
Co ²⁺	30	4.9	Hot-injection	Ref 8

Table S2. The TRPL fitting parameters of exciton emission of Mn/Sr-CsPbCl₃ NCs.

Sample	$\tau_{1/ns}$	$\tau_{2/ns}$	A ₁	A ₂	τ/ns	w ₁ %	w ₂ %	PLQY
CsPbCl ₃	2.924	12.009	796.544	153.248	6.93	55.86	44.14	0.5%
Mn-doped	0.796	5.269	1186	68.116	2.02	72.45	27.55	0.8%
10% Sr	0.417	4.134	1661.4	28.186	0.95	85.60	14.40	0.7%
20% Sr	0.420	3.838	1709.79	27.466	0.86	87.20	12.80	0.8%
30% Sr	0.494	3.292	1705.45	36.1397	0.84	87.63	12.37	0.8%
40% Sr	0.381	2.424	1717.76	46.955	0.68	85.19	14.81	0.5%
50% Sr	0.398	1.891	1821.55	59.258	0.60	86.61	13.39	0.7
60% Sr	0.384	2.093	1731.97	44.114	0.59	87.81	12.19	0.4

Table S3. The TRPL fitting parameters of Mn emission of Mn/Sr-CsPbCl₃ NCs.

Sample	τ_1/ms	τ_2/ms	A ₁	A ₂	τ/ms	w ₁ %	w ₂ %	PLQY
0% Sr	0.668	1.492	270.005	1697.057	1.44	6.65	93.35	85.8%
10% Sr	0.784	1.463	149.161	1383.994	1.43	5.46	94.54	96.6%
20% Sr	0.360	1.494	277.595	1226.541	1.44	5.18	94.82	93.4%
30% Sr	0.472	1.759	270.836	2691.539	1.73	2.63	97.37	100%
40% Sr	0.548	1.721	393.499	2652.896	1.67	4.51	95.49	100%
50% Sr	0.581	1.658	279.481	1630.806	1.60	5.67	94.33	100%
60% Sr	0.369	1.648	375.489	1548.684	1.58	5.15	94.85	92.5%

Lattice strain of the NCs was calculated via the Williamson-Hall (W-H) method (Equation (S1)), with results listed in Table S3.

$$\beta \cos \theta = \frac{kD}{\lambda} + 4\epsilon \sin \theta \quad (\text{S1})$$

Specifically, D, λ , β , θ , and the constant k (k=0.9) correspond to crystallite size, radiation wavelength, FWHM, peak position, and a constant, respectively, while ϵ represents the lattice microstrain.⁹

Table S4. Calculated microstrain (ϵ) and linear fit parameters of NCs from W-H plots.

Sample	Strain, ϵ	Standard error, E	R value	Adj R ²	R ² (COD)	Root MSE (SD)
Mn/Sr-CsPbCl ₃	0.00808	0.000902	0.96818	0.90607	0.93738	0.000636
Mn-CsPbCl ₃	0.01204	0.001646	0.93944	0.82384	0.88256	0.001164

Table S5. The TRPL fitting parameters of exciton emission of Mn-CsPbCl₃ NCs with different Mn/Pb feed ratios.

Sample	τ_1/ns	τ_2/ns	A_1	A_2	τ/ns	$w_1\%$	$w_2\%$	PLQY
3:7	1.181	8.057	1116.98	115.226	4.02	58.69	41.31	0.8%
4:6	0.544	7.910	1216.640	66.111	3.79	55.86	44.14	0.7%
5:5	0.592	6.460	1282.240	52.840	2.41	68.98	31.02	0.4%
6:4	0.796	5.269	1186	68.116	2.02	72.45	27.55	0.8%
7:3	0.582	3.198	1080.540	108.164	1.51	64.51	35.49	0.5%
8:2	0.467	5.444	1394.1	30.227	1.47	79.82	20.18	0.3%

Table S6. The TRPL fitting parameters of exciton emission of Mn/Sr-CsPbCl₃ NCs with different Mn/Pb feed ratios (30 % Sr/Pb feed ratio).

Sample	τ_1/ns	τ_2/ns	A_1	A_2	τ/ns	$w_1\%$	$w_2\%$	PLQY
3:7+Sr	0.557	5.120	433.530	18.177	1.83	72.19	27.81	0.8%
4:6+Sr	0.493	3.489	517.518	25.547	1.27	74.12	25.88	0.6%
5:5+Sr	0.388	2.171	512.889	20.202	0.71	81.93	18.07	0.4%
6:4+Sr	0.494	3.292	1705.45	36.1397	0.84	87.63	12.37	0.8%
7:3+Sr	0.512	3.142	4238.660	99.271	0.84	87.43	12.57	0.5%
8:2+Sr	0.527	2.989	6263.580	246.948	0.84	81.72	18.28	0.6%

Table S7. The TRPL fitting parameters of Mn emission of Mn-CsPbCl₃ NCs with different Mn/Pb feed ratios.

Sample	τ_1/ms	τ_2/ms	A_1	A_2	τ/ms	$w_1\%$	$w_2\%$	PLQY
3:7	0.736	1.308	513.161	1427.152	1.21	16.83	83.17	0.7%
4:6	0.616	1.432	419.640	1463.871	1.34	10.98	89.02	22.3%
5:5	0.522	1.545	489.458	1348.956	1.43	10.92	89.08	30.6%
6:4	0.668	1.492	270.005	1697.057	1.44	6.65	93.35	85.8%
7:3	0.180	1.266	142.378	194.748	1.16	9.42	90.58	63.8%
8:2	0.002	1.012	3125.675	71.679	0.93	7.93	92.07	59.3%

Table S8. The TRPL fitting parameters of Mn emission of Mn/Sr-CsPbCl₃ NCs with different Mn/Pb feed ratios (30 % Sr/Pb feed ratio).

Sample	τ_1/ms	τ_2/ms	A_1	A_2	τ/ms	$w_1\%$	$w_2\%$	PLQY
3:7+Sr	0.539	1.512	657.743	1186.230	1.25	16.51	83.49	15.2%
4:6+Sr	0.474	1.472	461.464	1376.766	1.38	9.74	90.26	49.2%
5:5+Sr	0.431	1.561	431.443	1199.628	1.46	8.56	91.43	58.1%
6:4+Sr	0.472	1.759	270.836	2691.539	1.73	2.63	97.37	100%
7:3+Sr	0.452	1.432	721.722	1145.318	1.27	16.57	83.43	77.5%
8:2+Sr	0.376	1.265	404.672	472.154	1.08	20.31	79.69	70.9%

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