

Supporting Information

Facile synthesis of Mn²⁺ doped ultrathin (n=2) NPLs and their application to anti-counterfeiting

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Experimental section

Chemicals: Cesium carbonate (Cs_2CO_3 , 99.9%) and bromotrimethylsilane (TMSBr, 97%) were purchased from J&K. Lead bromide (PbBr_2 , 99%) and manganese bromide (MnBr_2 , 98%) were purchased from Macklin Inc. Silver acetate (99%) was purchased from Adamas-bate. Oleylamine (OLA, 85%), tetra octyl ammonium bromide (TOAB, 98%), octanoic acid (OTAc, 99%) and dodecylbenzene sulfonic acid (DBSA, 90%) were purchased from Aladdin. Oleic acid (OA, 85%) was purchased from TCI. Toluene was purchased from Kermel. Dimethicone was purchased from Shanghai Lichenkeji. All chemicals were used without further purification.

Preparation of cesium-oleate precursor:

0.0325g Cs_2CO_3 , 0.5 mL OTAc and 9.5 mL toluene were dissolved in a vial.

Preparation of $\text{PbBr}_2/\text{MnBr}_2$ precursor:

0.0458g PbBr_2 , 0.0268g MnBr_2 and 0.2734g TOAB were dissolved in 2.5 mL toluene.

Preparation of Ag precursor:

0.4 mmol silver acetate, 0.3 mL DBSA, 0.5 mL OLA, and 1.5 mL toluene were added into a vial and the mixture was stirred at 40°C until the solution became clear.

Synthesis of Mn^{2+} doped CsPbBr_3 NPLs:

270 μL $\text{PbBr}_2/\text{MnBr}_2$ precursor, 200 μL TMSBr, 100 μL Ag precursor and 1 mL toluene were loaded into a vial. Then 500 μL cesium-oleate precursor solution was injected in the vial swiftly. The whole solution was left to stir for one hour at room temperature.

Synthesis of CsPbBr_3 NPLs (blue):

The CsPbBr_3 NPLs were prepared by an approach reported previously..^[1]

Synthesis of Mn^{2+} doped CsPbBr_3 NPLs@PMMA:

MnBr_2 precursor was prepared by dissolving 0.1mmol MnBr_2 , 30 μL OLA and 30 μL OA into 2mL toluene.

2g PMMA was dissolved in 6mL toluene to prepare PMMA solution.

2mL Mn^{2+} doped CsPbBr_3 NPL crude solution was mixed with 2mL dimethicone. Then, the resulting mixture was centrifuged at 5000rpm. The precipitates were collected and dispersed in 0.1mL MnBr_2 precursor and 0.5mL PMMA solution. Then the solution was spin-coated on the glass slide.

Characterization

The UV-Vis absorption spectra were performed using a MAPADA UV-1800PC UV-

Vis spectrometer. The PL and PLE spectra were conducted by a FLS920P spectrometer. The absolute PLQYs and time-resolved PL decays of the samples were measured by a fluorescence spectrometer (FLS920P, Edinburgh Instruments). The ICP measurements were measured by an ICP Optima 8300. The XRD patterns were measured on a Rigaku Smart Lab 9 kW.

Equation S1.

$$k_{FRET} = \frac{1}{\tau_{DA}} - \frac{1}{\tau_D}$$

where τ_{DA} and τ_D are the exciton lifetime in the presence and absence of Mn^{2+} ions, respectively. For Mn^{2+} doped $CsPbBr_3$ NPLs with Pb:Mn ratio of 1:1, the τ_{DA} is 0.91ns. The τ_D is 2.42ns, which is described as below. According to the above formula, the value of k_{FRET} can be obtained as 68.5%.

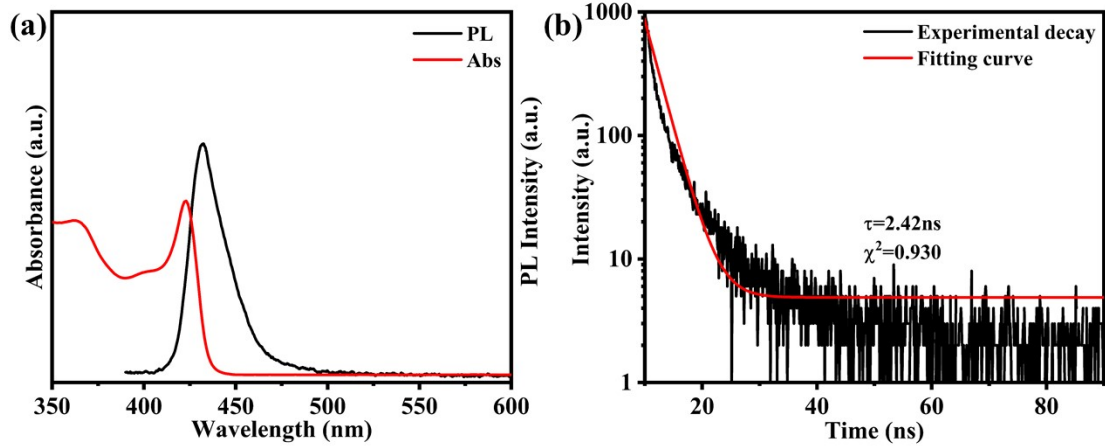


Figure S1. (a) PL and absorption spectra of the sample without $MnBr_2$. (b) PL decay and fitted curve of the peak at 435nm for the sample without $MnBr_2$.

The un-doped $CsPbBr_3$ NPLs have been synthesized without the addition of $MnBr_2$. As can be seen from Figure S1(a), the both the PL and absorption spectra of un-doped $CsPbBr_3$ NPLs show only one exciton peak, which belong to the $n=2$ phase. Time-resolved PL decays (TRPL) for un-doped $CsPbBr_3$ NPLs are performed. As shown in Figure R1(b), the lifetime of un-doped NPLs is 2.42 ns, which is longer than the Mn-doped one. All of these demonstrate that Mn ions have been successfully doped in the NPLs.

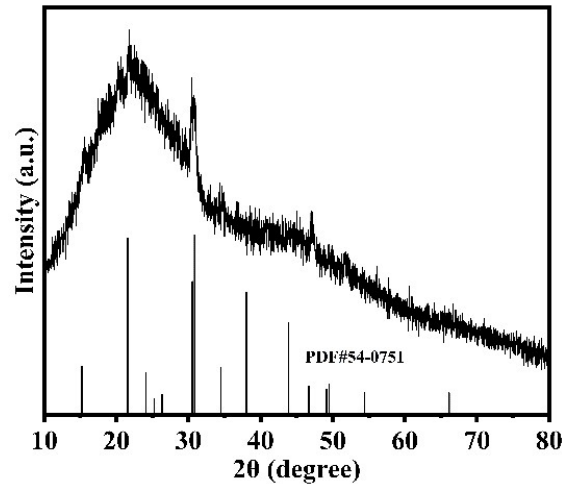


Figure S2. The powder XRD pattern of the sample.

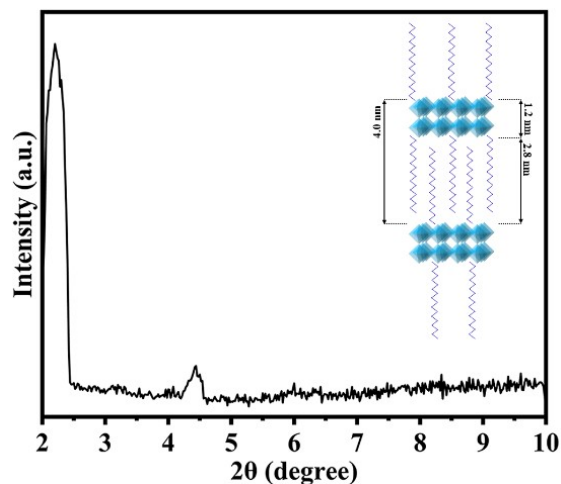


Figure S3. The small angle XRD pattern of the sample (Inset is photograph of the dimensions of the n=2 NPLs).

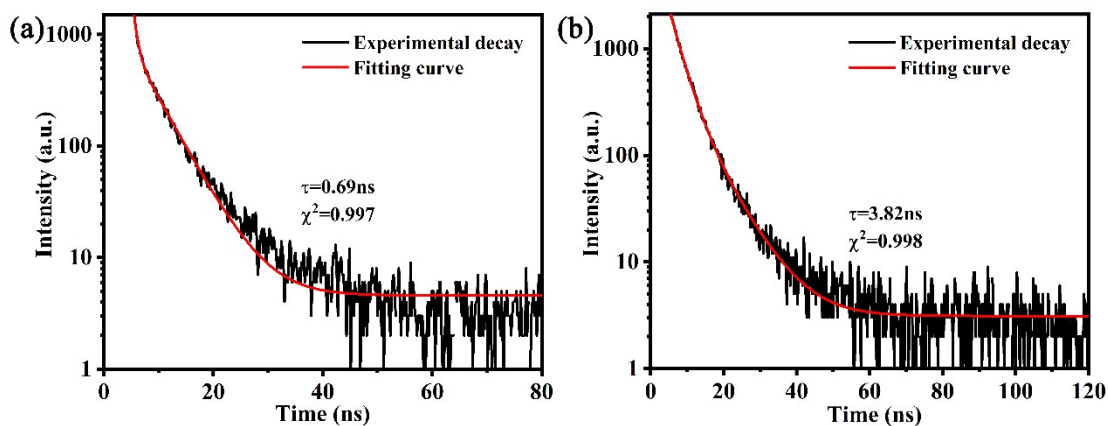


Figure S4. (a) PL decay and fitted curve of the peak (435nm) of the mixture. (b) PL decay and fitted curve of the exciton peak (465nm) of CsPbBr₃ NPLs (n=3)

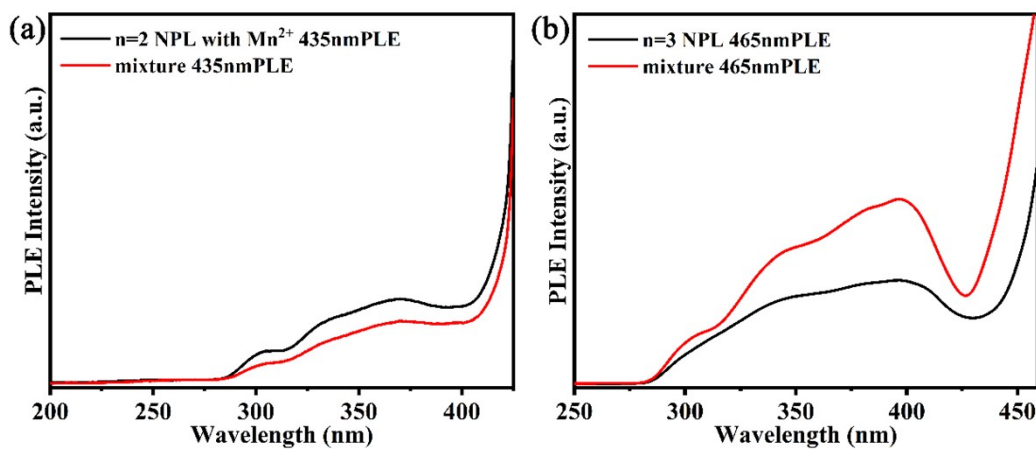


Figure S5. (a) PLE spectra of Mn²⁺ doped CsPbBr₃ NPLs and the mixture monitored at 435 nm. (b) PLE spectra of CsPbBr₃ NPLs and the mixture monitored at 465 nm.

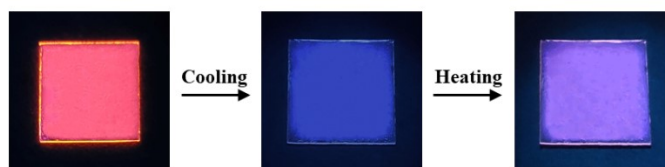


Figure S6. Stimuli-responsive progress of Mn^{2+} doped CsPbBr_3 NPLs@PMMA without MnBr_2 precursor (heating and cooling represent that the conditions are 100°C and 25°C , respectively).

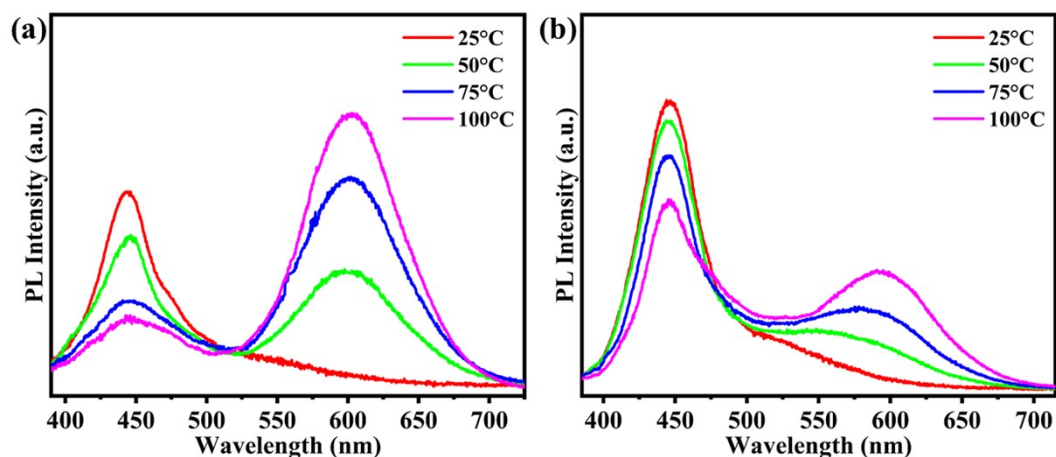


Figure S7. The temperature-dependence PL spectra of the films prepared from (a) the solution with MnBr_2 precursor and (b) the pristine solution.

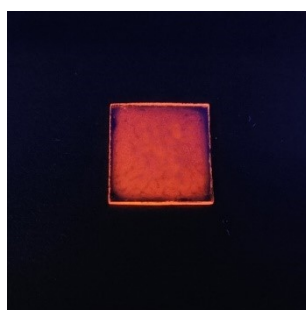


Figure S8. The film of Mn^{2+} doped CsPbBr_3 NPLs at elevated temperature after being placed in the air for ten days.

Table S1. The actual doping ratio of Pb:Mn obtained from ICP.

the nominal ratio of Pb:Mn	the doping ratio of Pb:Mn from ICP	the doping level of Mn from ICP
1:0.5	1:0.38	27.5%
1:1	1:0.63	38.6%
1:2	1:1.14	53.3%

REFERENCES

- [1] S. Su, J. Tao, C. Sun, D. Xu, H. Zhang, T. Wei, Z.-H. Zhang, Z. Wang, C. Fan, W. Bi, Chem. Eng. J. 2021, 419, 129612.