

Electronic Supporting Information

Chlorine-Additives-Promoted Incorporation of Mn^{2+} Dopants in CsPbCl_3 Perovskite Nanocrystals

Su Zhou^a, Yiwen Zhu^a, Jiasong Zhong^{a,*}, Feifan Tian^{b,c}, Hai Huang^{b,c}, Jiangkun Chen^{b,c}, Daqin Chen^{a,b,c,*}

^aCollege of Materials & Environmental Engineering, Hangzhou Dianzi University, Hangzhou, Zhejiang, 310018, P. R. China

^bCollege of Physics and Energy, Fujian Normal University, Fuzhou, Fujian 350117, China

^cFujian Provincial Collaborative Innovation Center for Optoelectronic Semiconductors and Efficient Devices, Xiamen, Fujian, 361005, China

Corresponding Authors

*E-Mail: jiasongzhong@hdu.edu.cn (J. S. Zhong); dqchen@fjnu.edu.cn (D. Q. Chen)

Experimental Section

Materials.

Cs₂CO₃ (Aladdin, 99.9%), octadecene (ODE, Aladdin, 90%), oleic acid (OA, Aldrich, 90%), oleylamine (OM, Aladdin, 80-90%), tri-n-octylphosphine (TOP, Macklin, 90%) PbCl₂ (Macklin, 99.9%), manganese acetate (Mn(Ac)₂, Macklin, 99%), MnCl₂ (Aladdin, 99%), NiCl₂·6H₂O (Macklin 99%), CuCl₂ (Macklin 99%), ZnCl₂ (Macklin 99%), trimethylchlorosilane (TMS-Cl, Macklin 99%), hexane (Aladdin, 99%) . All chemicals were directly used without further purification.

Preparation of Cs-oleate

Cs₂CO₃ (0.407 g, 1.25 mmol) was loaded into a 50 mL 3-neck flask along with ODE (18 mL) and OA (1.74 mL), heated for 1 h at 120 °C to remove water, and then heated under N₂ to 150°C until all Cs₂CO₃ were dissolved. The solution was preheated to 100 °C before injection.

Preparation of OM-Cl

10 mL OM and 1 mL hydrohalic acid (HCl) were loaded in 25 mL three-neck flask and heated under N₂ at 120 °C for at least 2 h. Then temperature was elevated to 150 °C for 1 hour. The prepared OM-Cl was preheated to 100°C for further usage.

Synthesis of Mn²⁺-doped CsPbCl₃ NCs

PbCl₂ (0.1mmol, 0.0278g), Mn(Ac)₂ (0.1mmol, 0.0245g), ODE (10 mL), OA (2 mL), OM (2 mL), and different amount of TMS-Cl (0~3 mmol) were added into a 50 mL three-neck flask heated under N₂ at 120 °C for at least 1 h to dissolve the precursors and remove water. Then, temperature was raised to 170 °C and kept at this temperature for 5 min. Then, the prepared Cs-oleate solution (0.4 mL) was quickly injected and reacted for 1 min. The mixture was finally cooled by an ice-water bath to room temperature. The procedure is similar when MnCl₂ was used as Mn²⁺ source or OM-Cl was employed as Cl⁻ source.

Synthesis of TM-doped CsPbCl₃ NCs

For the synthesis of TM-doped CsPbCl₃ NCs, PbCl₂ (0.1mmol, 0.0278g), TMCl₂ (TM=Mn, Ni, Cu, Zn) (0.1mmol), ODE (10 mL), OA (2 mL), OM (2 mL), and different amount of TMS-Cl (0.5 mol, 1 mmol) were added into a 50 mL three-neck flask 1 mL TOP was further added to promote dissolving. The mixture was heated under N₂ at 120 °C for at least 1 h to dissolve the precursors and remove water. Then, temperature was raised to 170 °C and kept at this temperature for 5 min. Then, the prepared Cs-oleate solution (0.4 mL) was quickly injected and reacted for 1 min. Finally, the reaction mixture was cooled by an ice-water bath.

Cation exchange

- (a) Cation exchange at 170°C. 0.5 mmol MnCl₂ was dissolved in 5 mL OED, 1 mL OA and 1 mL OM at 150 °C for further using. The prepared MnCl₂ ODE/OA/OM solution was injected into three-necked flask immediately after Cs-OA has been injected.
- (b) Cation exchange at room temperature. Prepared CsPbCl₃ NCs were dispersed in toluene and MnCl₂ solution (dissolved in ODE/OA/OM or 3 mL DMF) was injected.

Purification

Mn-doped CsPbCl₃ NCs and TM-doped CsPbCl₃ NCs were extracted from the crude solution by centrifuging at 8000 rpm for 5 min to discard the supernatant containing unreacted precursor. Then, 1 mL hexane was added into the precipitates to disperse, and centrifuged at 10000 rpm for 5 min and the supernatant was discarded. This step must be repeated at least twice. After centrifugation, the supernatant was discarded and the precipitates were re-dispersed in hexane for further characterization.

Characterization

X-ray diffraction (XRD) analysis was carried out to identify perovskite phase structures using a powder diffractometer (MiniFlex600 RIGAKU) with Cu K_α radiation ($\lambda= 0.154$ nm) operating at 40 kV. Microstructure observations of Mn-doped CsPbCl₃ perovskite NCs were carried out on a JEOL JEM-2010 transmission electron microscopy (TEM) operated at 200 kV accelerating

voltage. The actual chemical compositions were determined by inductively coupled plasma mass spectroscopy (ICP-MS) technique using a Perkin-Elmer Optima 3300DV spectrometer. Electron paramagnetic resonance (EPR) spectra were recorded by an E-580 Bruker Elexsys X-band EPR spectrometer. Mn 2p X-ray photoelectron spectroscopy (XPS) was determined using a VG Scientific ESCA Lab Mark II spectrometer equipped with two ultra-high-vacuum 6 chambers. Absorption, photoluminescence (PL) spectra and Mn²⁺ decay curves were recorded on an Edinburgh Instruments FS5 spectrofluorometer equipped with 150 W xenon lamps and 60 W pulse xenon lamps as the excitation sources. Time-resolved spectra for exciton recombination were detected on a fluorescent lifetime spectrometer (Edinburgh Instruments, LifeSpec-II) based on a time correlated single photon counting technique under the excitation of 375 nm picosecond laser. The decay lifetimes are determined via the equation of $\tau = \int I(t)dt / I_0$, where $I(t)$ is the time-related luminescence intensity and I_0 is the peak intensity. PL quantum yield (PLQY), defined as the ratio of emitted photons to absorbed ones, was determined by a spectra fluorometer (FS5) equipped with the xenon lamp as the excitation source and a 15 cm integrating sphere. Temperature-dependent PL spectra were measured on an Edinburgh Instruments FLS980 spectrofluoremeter equipped with a Linkam THMS600 temperature controlling stage.

Table S1 ICP-MS results of Mn-doped CsPbCl₃ NCs prepared with the addition of different TMS-Cl concentrations.

Mn(Ac) ₂ content (mmol)	Mn-to-Pb feeding molar ratio	TMS-Cl content (mmol)	measured Mn-to-Pb molar ratio
0	0:1	0	0:1
0.1	1:1	0	0.007:1
0.1	1:1	0.5	0.032:1
0.1	1:1	1	0.056:1
0.1	1:1	1.5	0.066:1
0.1	1:1	2	0.078:1
0.1	1:1	3	0.103:1

Table S2 ICP-MS results of TM-doped (TM=Mn, Ni, Cu, Zn) CsPbCl₃ NCs prepared with the addition of different TMS-Cl concentrations.

	Mn-to-Pb molar ratio	Ni-to-Pb molar ratio	Cu-to-Pb molar ratio	Zn-to-Pb molar ratio
0.5mmol TMS-Cl	0.032:1	0.033:1	0.041:1	0.027:1
1.0 mmol TMS-Cl	0.056:1	0.053:1	0.057:1	0.049:1

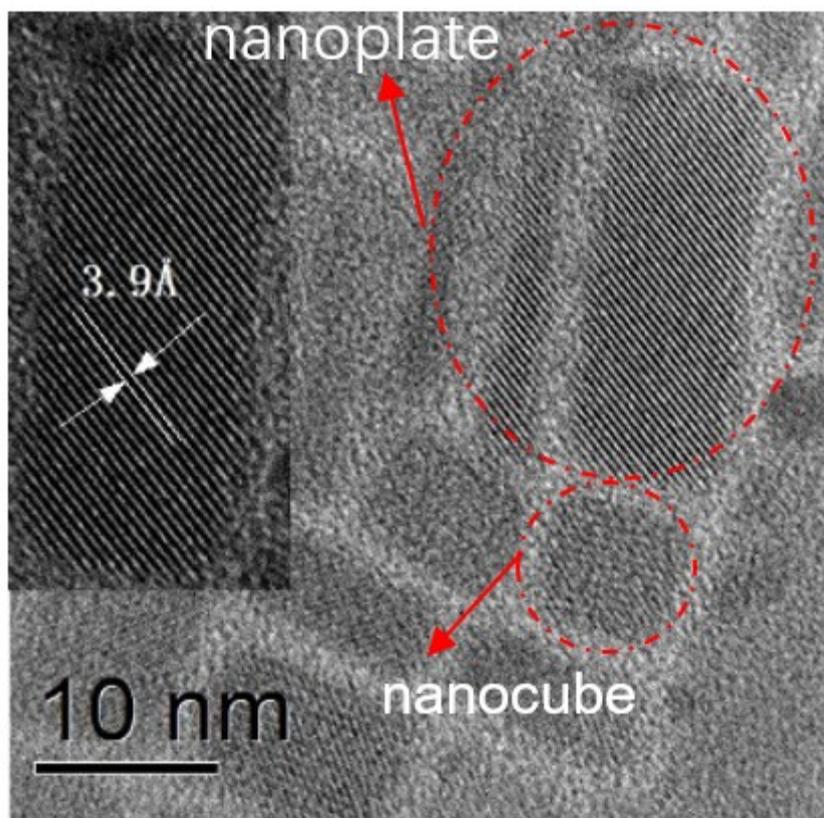


Figure S1 HRTEM micrograph of Mn-doped CsPbCl₃ prepared with the addition of 3 mmol TMS-Cl. Two morphologies of nanoplatelet and nanocube are clearly discerned.

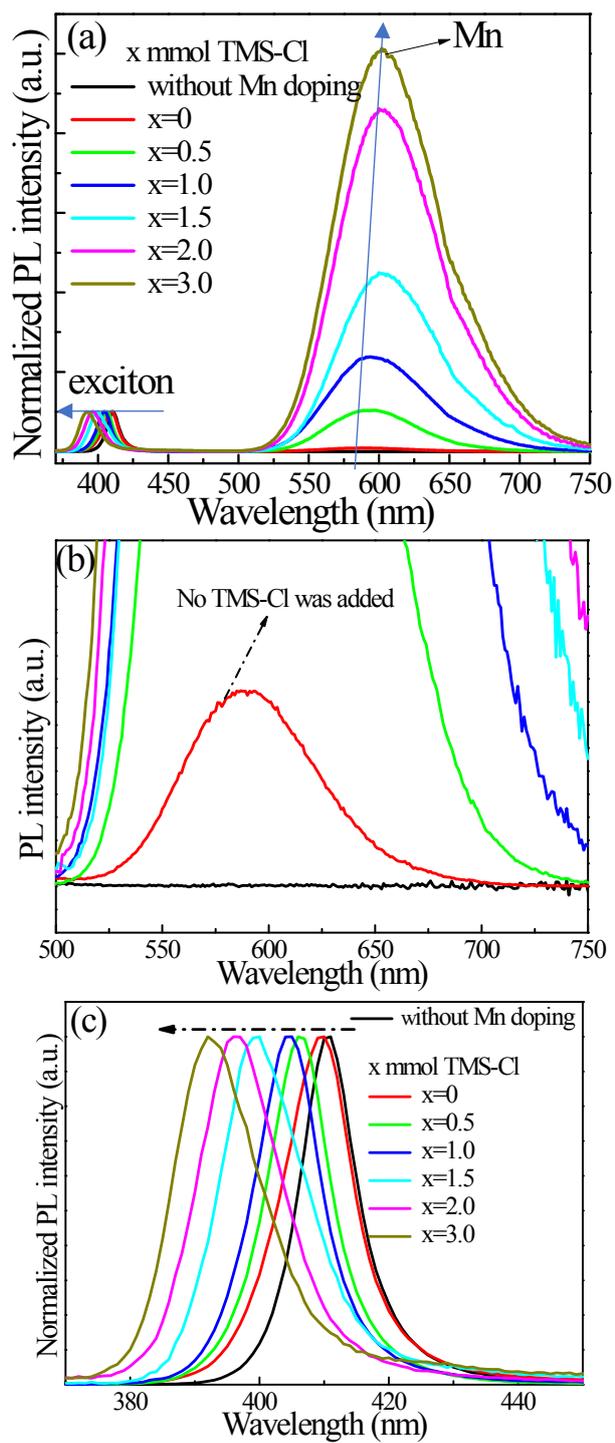


Figure S2 (a) PL spectra of Mn-doped CsPbCl₃ NCs, and enlarged PL spectra of (b) Mn²⁺ dopants and (c) CsPbCl₃ host NCs with increase of TMS-Cl content.

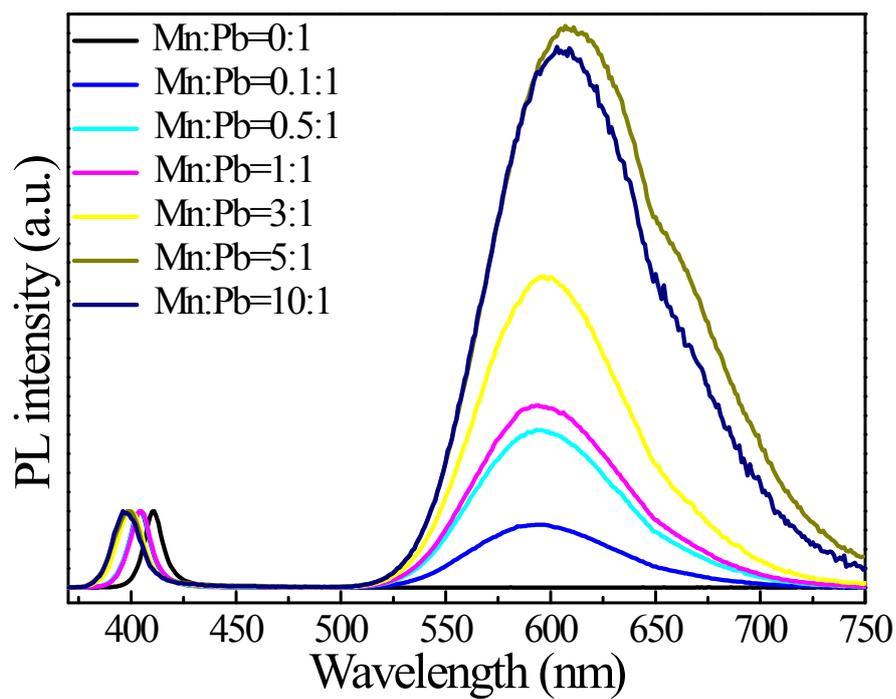


Figure S3 PL spectra of Mn-doped CsPbCl₃ perovskite NCs prepared with fixed TMS-Cl content (1mmol) and increased Mn-to-Pb feeding ratio from 0:1 to 10:1.

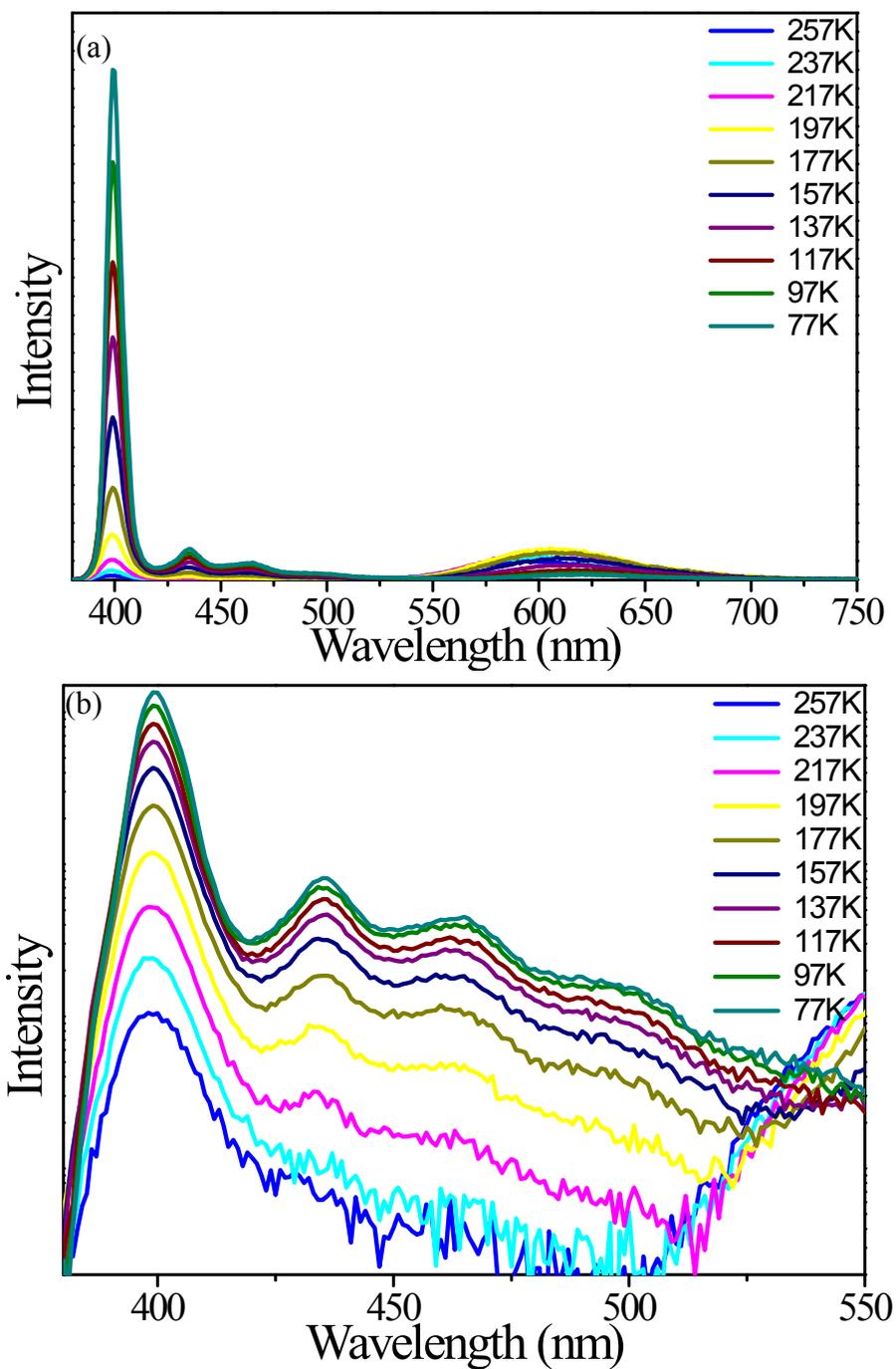


Figure S4 (a) Temperature evolution for PL spectra of Mn-doped CsPbCl₃ NCs prepared with 3 mmol TMS-Cl. (b) Logarithm plot of PL spectra in the range from 390nm to 550nm.

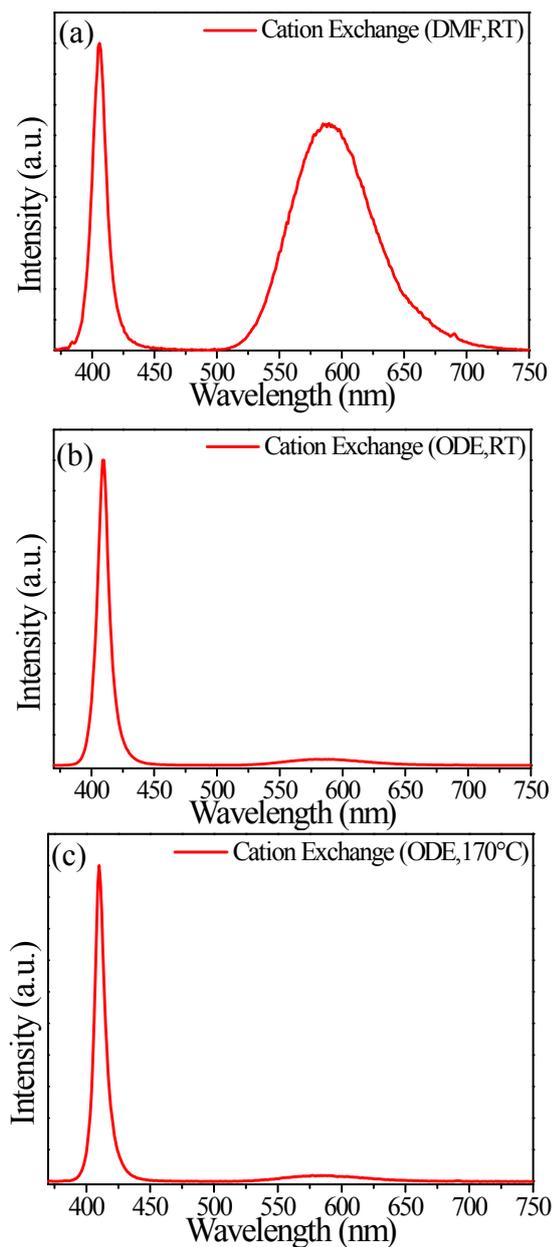


Figure S5 PL spectra of Mn-doped CsPbCl₃ perovskite NCs synthesized via a cation exchange route in three conditions.

(a) MnCl₂ was dissolved in DMF solution and mixed with preformed CsPbCl₃ NCs (in toluene) to carry out cation exchange at room temperature.

(b) MnCl₂ was dissolved in ODE/OA/OM solution and mixed with preformed CsPbCl₃ NCs (in toluene) to carry out cation exchange at room temperature.

(c) MnCl₂ is dissolved in ODE/OA/OM and mixed with preformed CsPbCl₃ NCs (in ODE/OA/OM) to carry out cation exchange at 170°C.

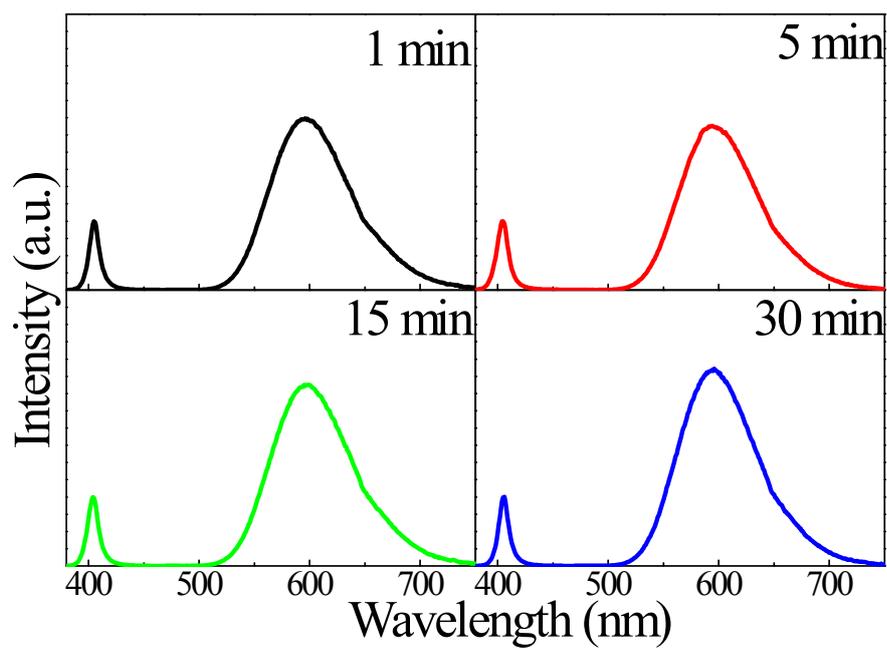


Figure S6 PL spectra of Mn-doped CsPbCl₃ perovskite NCs synthesized by reaction at 170 °C for different durations (1 min, 5 min, 15 min and 30 min).

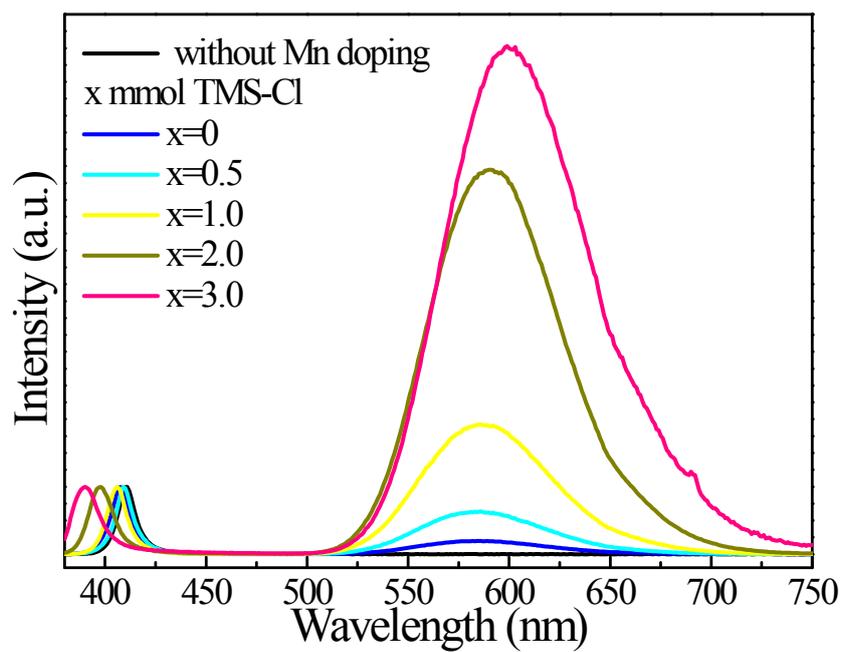


Figure S7 Normalized PL spectra of Mn-doped CsPbCl₃ NCs prepared by using MnCl₂ precursor as Mn²⁺ source and TMS-Cl as extra Cl⁻ source. The Mn-to-Pb feeding ratio was fixed to 1:1 for all the samples.

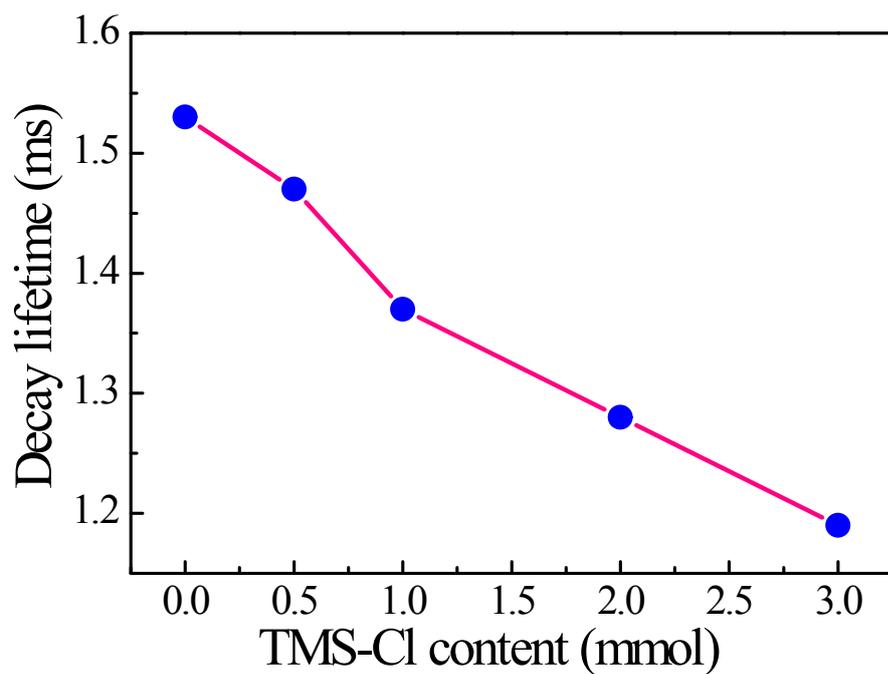


Figure S8 Decay lifetime of Mn^{2+} dopants in CsPbCl_3 NCs versus TMS-Cl content.

The Mn-doped CsPbCl_3 NCs were prepared using MnCl_2 precursor as Mn^{2+} source and TMS-Cl as extra Cl^- source. The Mn-to-Pb feeding ratio was fixed to 1:1 for all the samples.

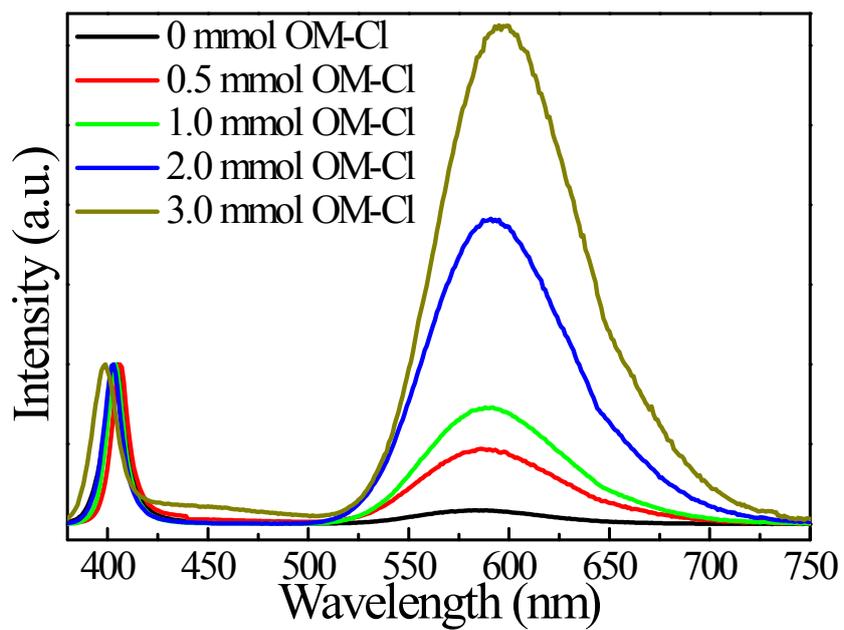


Figure S9 Normalized PL spectra of Mn-doped CsPbCl₃ NCs prepared by using Mn(Ac)₂ precursor as Mn²⁺ source and OM-Cl as extra Cl⁻ source. The Mn-to-Pb feeding ratio was fixed to 1:1 for all the samples.

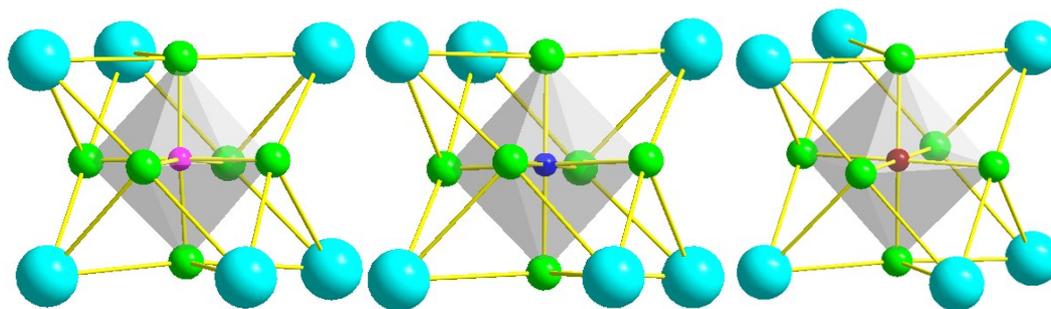


Figure S10 Schematic illustrations of CsTMCl₃ crystal structures (from left to right: TM=Ni, Cu, Zn). All the crystals possess similar [TMCl₆]⁴⁻ octahedral structure units.

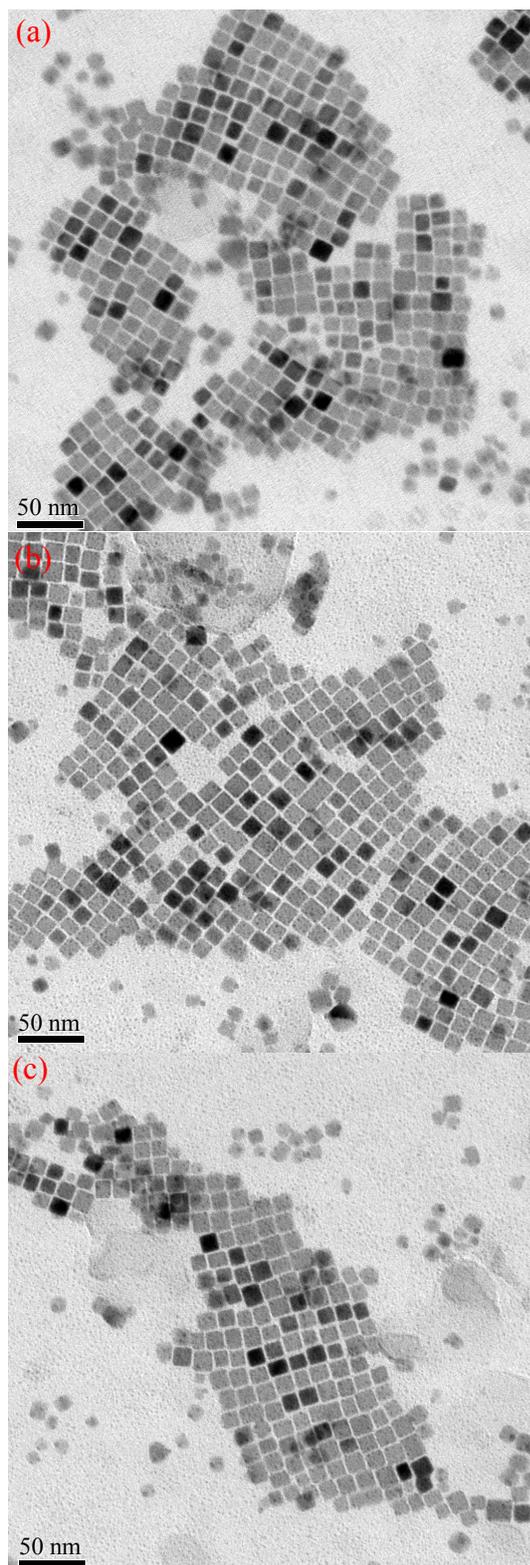


Figure S11 TEM images of TM-doped (TM=Ni, Cu, Zn) CsPbCl₃ perovskite NCs: (a) Ni, (b) Cu, (c) Zn. All the samples were prepared by using TMCl₂ precursor as TM²⁺ source and TMS-Cl (1 mmol) as extra Cl⁻ source. The TM-to-Pb feeding ratio was fixed to 1:1 for all the samples. The bar represent 50 nm.

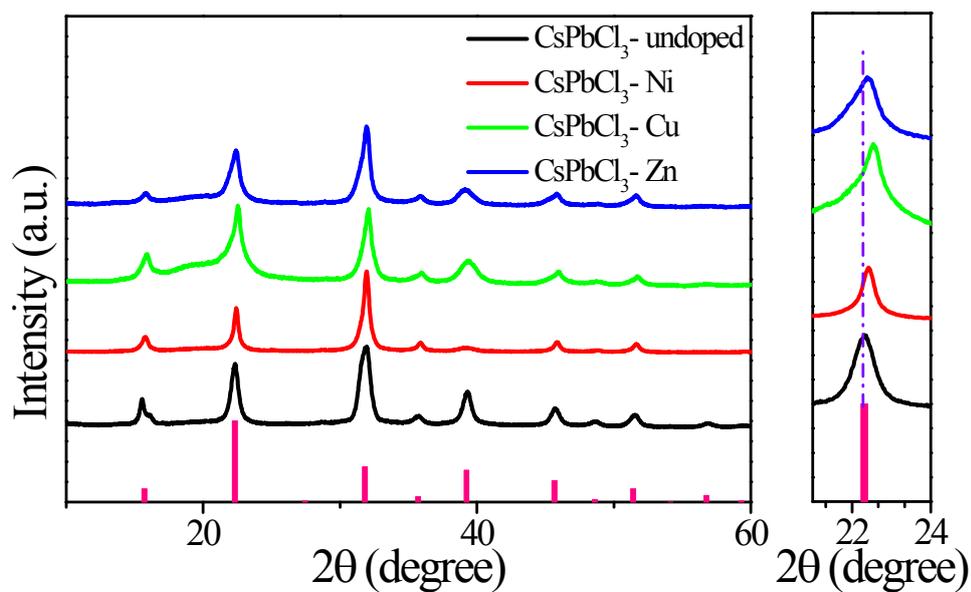


Figure S12 XRD patterns of TM-doped (TM=Ni, Cu, Zn) CsPbCl₃ perovskite NCs prepared by using TMCl₂ precursor as TM²⁺ source and TMS-Cl (1 mmol) as extra Cl⁻ source. The TM-to-Pb feeding ratio was fixed to 1:1 for all the samples.

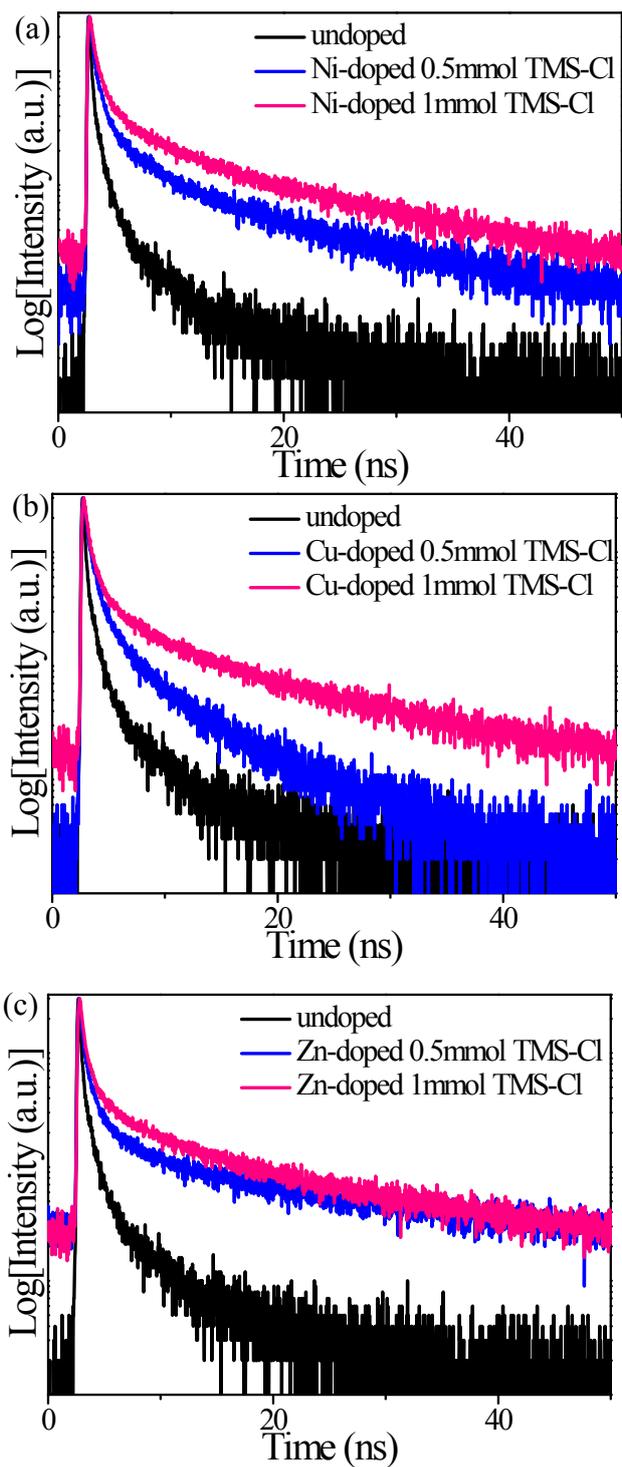


Figure S13 Time-resolved PL spectra by monitoring exciton recombination ($\lambda_{em}=400$ nm) for the TM-doped CsPbCl₃ perovskite NCs: (a) TM=Ni, (b) TM=Cu, (c) TM=Zn.