

Hexamethyldisilazane-assisted Mn²⁺ doping of perovskite nanocrystals under ambient conditions

Kaiwen Hu†^a, Yongfei Hu†^a, Tan Li^a, Fen Qiao^b, Yunxia Chen^c, Jianjun Han^{a*}, Lee Li^d, Ghafar Ali^e, Yi Xie^{a*}

^a*State Key Laboratory of Silicate Materials for Architectures, Wuhan University of Technology (WUT), No. 122, Luoshi Road, Wuhan 430070, P. R. China.*

^b*School of Energy and Power Engineering, Jiangsu University, No.301, Xuefu Road, Zhenjiang 212013, P. R. China.*

^c*School of Materials Science and Engineering, Jingdezhen Ceramic University, Jiangxi, P. R. China.*

^d*School of Electrical and Electronic Engineering, Huazhong University of Science and Technology (HUST), Wuhan 430074, P.R. China.*

^e*Nanomaterials Research Group (NRG), Physics Division, PINSTECH, Nilore, Islamabad, Pakistan.*

Email: xiey@whut.edu.cn; hanjj@whut.edu.cn

1. Characterization of the As-synthesized Mn^{2+} -doped LHP Nanocrystals

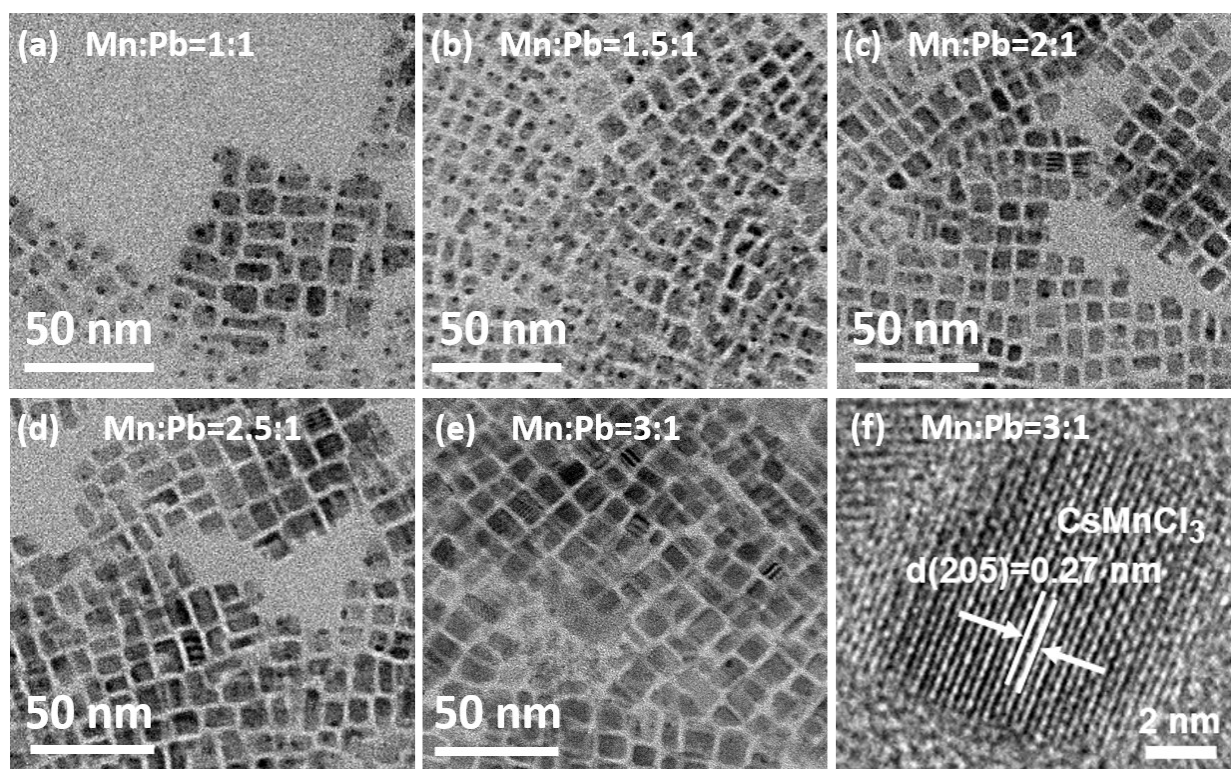


Fig. S1 TEM images of the typical Mn^{2+} -doped CsPbCl_3 NCs achieved in the presence of different amounts of Mn as dictated.

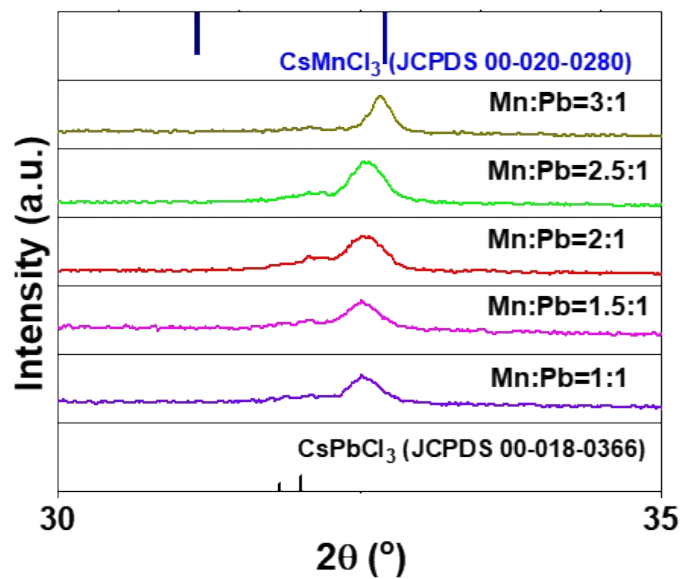


Fig. S2 XRD patterns of Mn²⁺-doped CsPbCl₃ nanocrystals synthesized in the presence of different amounts of Mn²⁺ ions in the precursors (labelled as Mn:Pb).

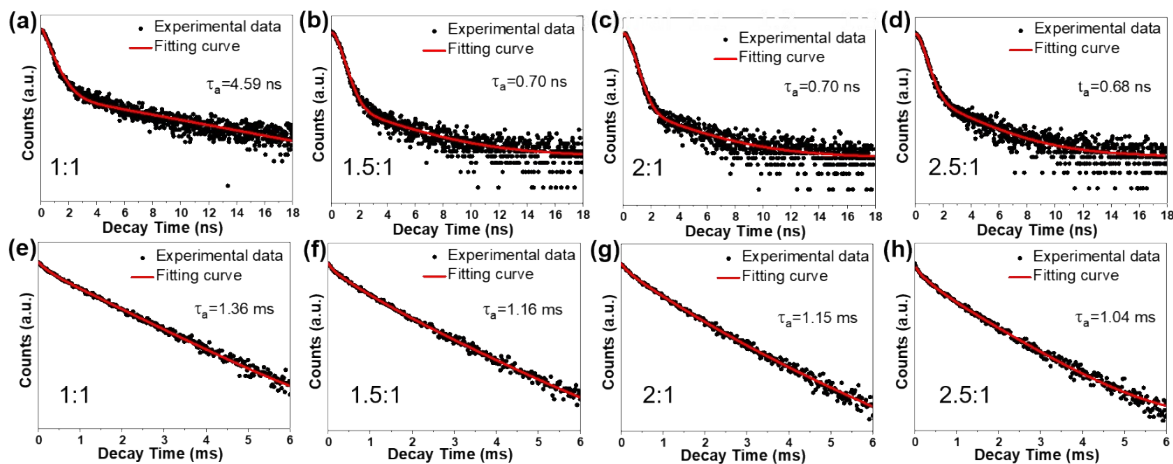


Fig. S3 Time-resolved PL decays and fitting curves of the various Mn^{2+} -doped CsPbCl_3 nanocrystals monitored at 400 nm (a-d) and 600 nm (e-h), respectively. The samples are synthesized in the presence of different feed Mn:Pb ratios as dictated in each panel.

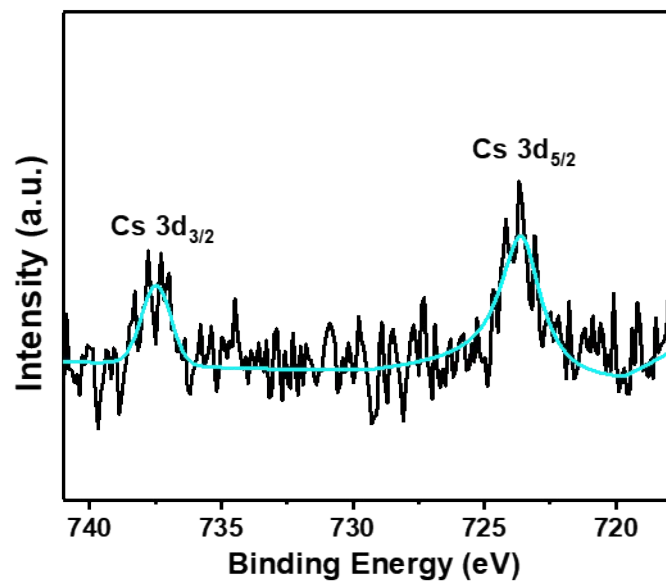


Fig. S4 High-resolution XPS spectrum of Cs 3d of the representative Mn²⁺-doped CsPbCl₃ nanocrystals.

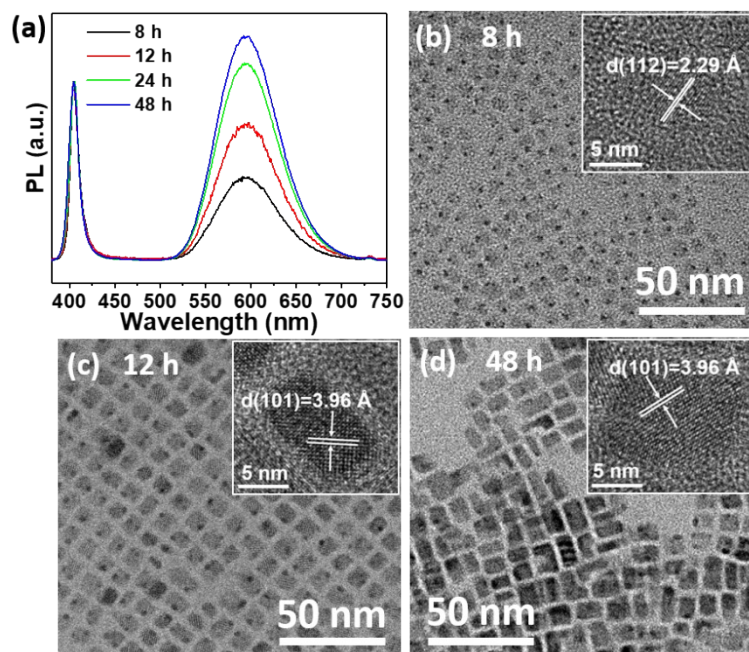


Fig. S5 Experimental PL emission spectra (a) and TEM images (b-d) of the aliquots of the Mn^{2+} -doped CsPbCl_3 nanocrystals collected at different reaction time. The samples are synthesized in the presence of Mn:Pb precursor ratio of 2.5:1 and HMDS of 6 mL.

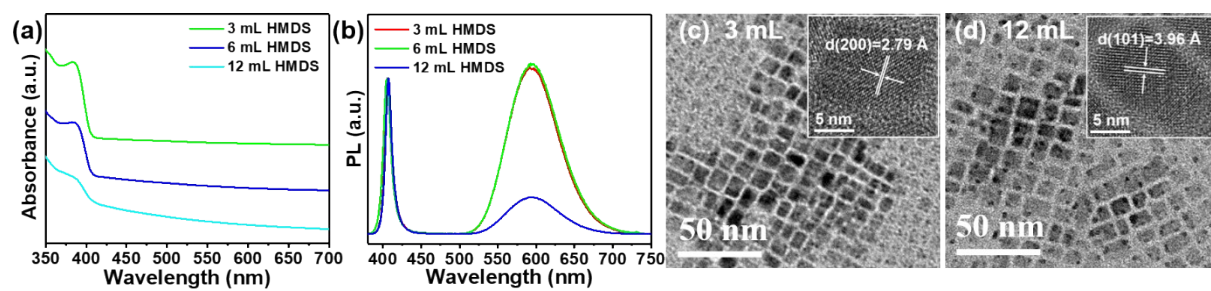


Fig. S6 (a-b) Optical absorbance spectra (a) and PL emissions spectra (b), and (c-d) TEM images of the typical Mn^{2+} -doped CsPbCl_3 NCs achieved in the presence of different amounts of HMDS as dictated.

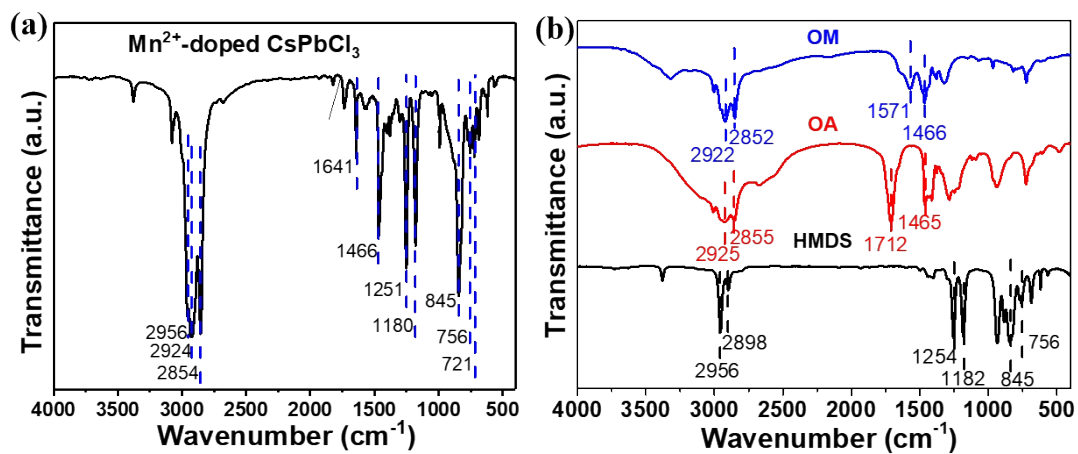


Fig. S7 FTIR spectra of the representative Mn²⁺-doped CsPbCl₃ nanocrystals (a) and the pure oleylamine (OM), oleic acid (OA) and hexamethyl disilazane (HMDS) as dictated (b), respectively.

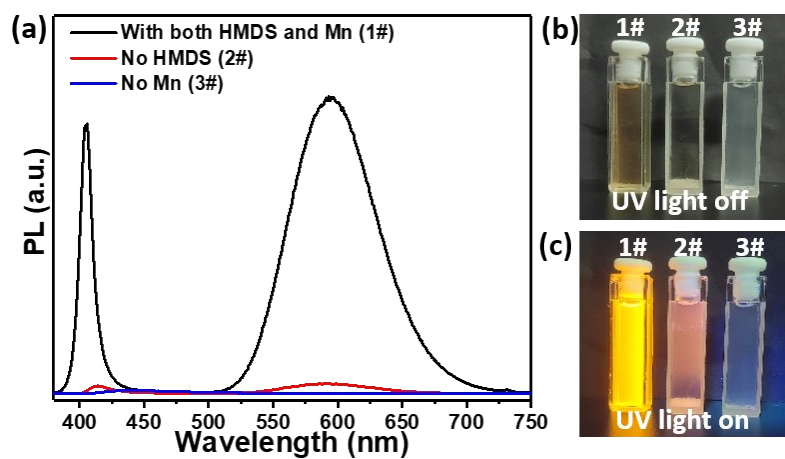


Fig. S8 Experimental PL emission spectra of typical products collected in the presence of both Mn^{2+} and HMDS, no HMDS and no Mn^{2+} ions, respectively (a), and digital photographs of the corresponding dispersions under UV light off (b) and on (c), respectively.

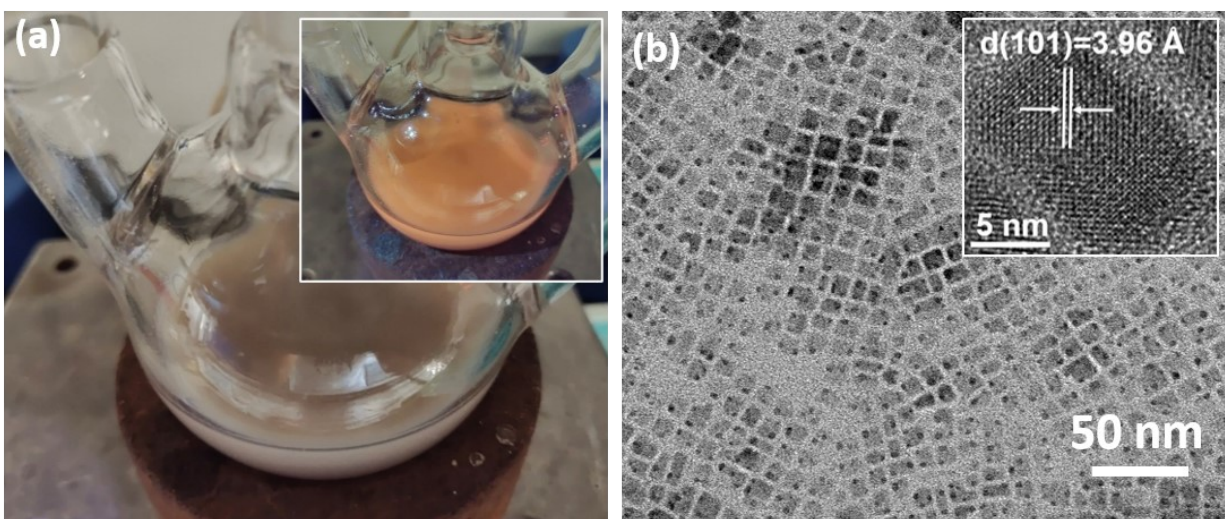


Fig. S9 (a) Digital photograph of Mn²⁺-doped CsPbCl₃ dispersion under normal indoor light and UV illumination (inset), and (b) TEM image and HRTEM image (inset) of the large-scaled synthesized Mn²⁺-doped CsPbCl₃ nanocrystals. The lattice spacing of 0.39 nm marked in HRTEM image displays the (101) crystal plane of tetragonal phase of CsPbCl₃.

Table S1 *The summarization on the optical characterization of the Mn²⁺-doped CsPbCl₃ nanocrystals achieved in the presence of different Mn:Pb precursor ratios.*

Mn:Pb	PL peak positions (nm)	Mn:(Mn+Pb) in the final NCs (%) ^a	PLQY (%)	Lifetimes monitored at 400 nm (ns)	Lifetimes monitored at 600 nm (ms)
1:1	406/591	33	18.3	4.59	1.36
1.5:1	406/592	39	18.6	0.70	1.16
2:1	406/592	43	18.9	0.70	1.15
2.5:1	406/593	51	39.6	0.68	1.04

^a Analyzed by using Inductively coupled plasma-optical emission spectroscopy (ICP-OES) test.

Table S2 The summarization on the optical characterization of the Mn^{2+} -doped $CsPbBr_xCl_{3-x}$ nanocrystals achieved in the presence of different Br:Cl precursor ratios.

Br:Cl	Absorption peak (nm)	PL Peak (nm)	FWHM (nm)	Relative intensity (peak2/peak1)
0:1	384	406/594	5/38	1.1
1:1	419	425/593	10/39	0.45
2:1	431	440/591	14/55	0.3
3:1	442	462/	15/-	0

2. Characterization of Anion-exchanged Mn-doped LHP Nanocrystals

Preparation of PbBr₂ and PbI₂ Stock Solution for Anion Exchange. Typically, 69 mg (i.e., 0.188 mmol) of PbBr₂, 10 ml of ODE, 1 ml of OM and 0.5 ml of OA were loaded into a 50 mL three-neck flask. The temperature was then raised to 100 °C under vacuum and kept stirring for 60 min. The system was then filled with Ar gas and the reaction was continued at 120°C for additional 60 min. The resulting PbBr₂ stock solution was cooled to room temperature, transferred to a vial and stored in the glove box for subsequent anion exchange. The preparation process for the PbI₂ stock solution was the same as above except that PbI₂ (87 mg) instead of PbBr₂ was used.

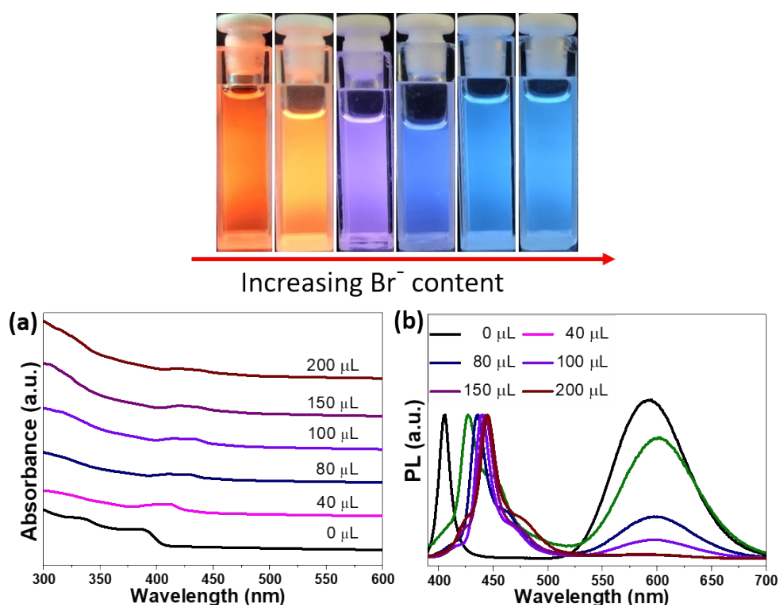


Fig. S10 (a) Optical absorbance spectra and (b) PL spectra of the various Mn-doped CsPbBr_xCl_{3-x} nanocrystals achieved by anion exchange of the as-synthesized Mn-doped CsPbCl₃ in the presence of different amounts of Br⁻ ions as dictated. The top panel presents the digital photographs of corresponding nanocrystals dispersed in hexane under UV light illumination (365 nm excitation wavelength).

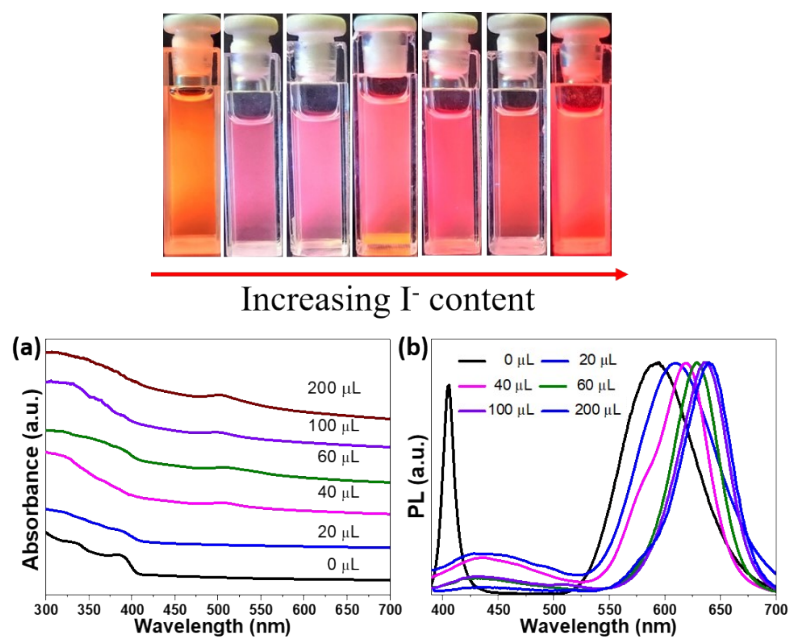


Fig. S11 (a) Optical absorbance spectra and (b) PL spectra of the various Mn-doped $\text{CsPbI}_x\text{Cl}_{3-x}$ nanocrystals achieved by anion exchange of the as-synthesized Mn-doped CsPbCl_3 in the presence of different amounts of I^- ions as dictated. The top panel presents the digital photographs of corresponding nanocrystals dispersed in hexane under UV light illumination (365 nm excitation wavelength).