

Electronic Supplementary Information (ESI)

Luminescence Tuning and Exciton Dynamics of Mn-doped CsPbCl₃ Nanocrystals

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List of contents:

1. Experimental Section: S1 (p: S2-S3).
2. Transmission Electron Microscope (TEM) images and Tolerance and octahedral factor for different samples Figure S1, S2 (p: S4).
3. UV-Vis absorption spectra of all NCs: Figure S3 (p: S5).
4. (a) Tauc plot, (b) Excitation spectra of 12% Mn:CsPbCl₃: Figure S4 (p: S5).
5. (a)-(d) TA spectra and (e) Comparison of bleach recovery kinetics: Figure S5 (p: S6).
6. PL and TA spectra of Br⁻ exchanged undoped and 12% Mn doped CsPbCl₃ NCs: Figure S6 (p: 76).
7. Relative Mn content estimated from ICP-OES: Table S1 (p: S8)
8. Mn PL lifetime decay parameters of different samples: Table S2 (p: S8).

S1. Experimental Section:

S1.1 Characterization:

Transmission electron microscopy (TEM) images were recorded by using a transmission electron microscope, TECNAI FE12, JEOL, Japan having a 120 kV electron source. Powdered X-ray diffraction (PXRD) patterns were recorded on Bruker D8 Advance diffractometer (Bruker-AXS, Karlsruhe, Germany) using Cu-K α X-radiation ($\lambda = 1.5406 \text{ \AA}$) at 40 kV and 30 mA power. Room temperature X-band EPR measurements were performed by using JEOL JES-FA200 spectrometer. The elemental ratio was determined by Varian 720-ES, inductively coupled plasma optical emission spectrometer (ICP-OES). UV-Vis absorption and emission spectra were recorded by Cary100, Varian spectrophotometer and FlouroLog-3, Horiba Jobin Yvon spectrofluorimeter, respectively.

Transient Measurement: Details of the femtosecond transient absorption setup used in this study has been described elsewhere.¹ Briefly, the setup consisted of a mode-locked Ti:sapphire seed laser (Mai-Tai, Spectra Physics) with 80 MHz repetition rate having center wavelength 801 nm. A part of its output was directed to the regenerative amplifier (Spitfire Ace, Spectra Physics) which was pumped by an output of 527 nm of a frequency doubled Nd:YLF laser (Empower, Spectra Physics). The amplified output of 801 nm (4.2 W), operating at a repetition rate of 1 kHz were divided into two parts. One part was directed to an optical parametric amplifier (TOPAS-Prime, Spectra Physics) to generate excitation pulse at 330 nm and second part was passed through a 4 ns delay unit followed by a CaF₂ crystal to generate white light continuum. The white light was split by a beam splitter to generate a signal and a reference beam. Both the beams were directed to the

detector (photodiode array) to record the pump induced changes at different time delay of probe beam. All the spectra were chirp-corrected for group velocity dispersion of white light continuum. The instrument resolution was ~ 120 fs.

S1.2 QY Measurement:

The excitonic and Mn PL QY were measured using quinine sulphate in 1.0 N aqueous H_2SO_4 solution (QY= 0.546)² and rhodamine-6G³ in aqueous medium (QY= 0.95) as reference standard, respectively.

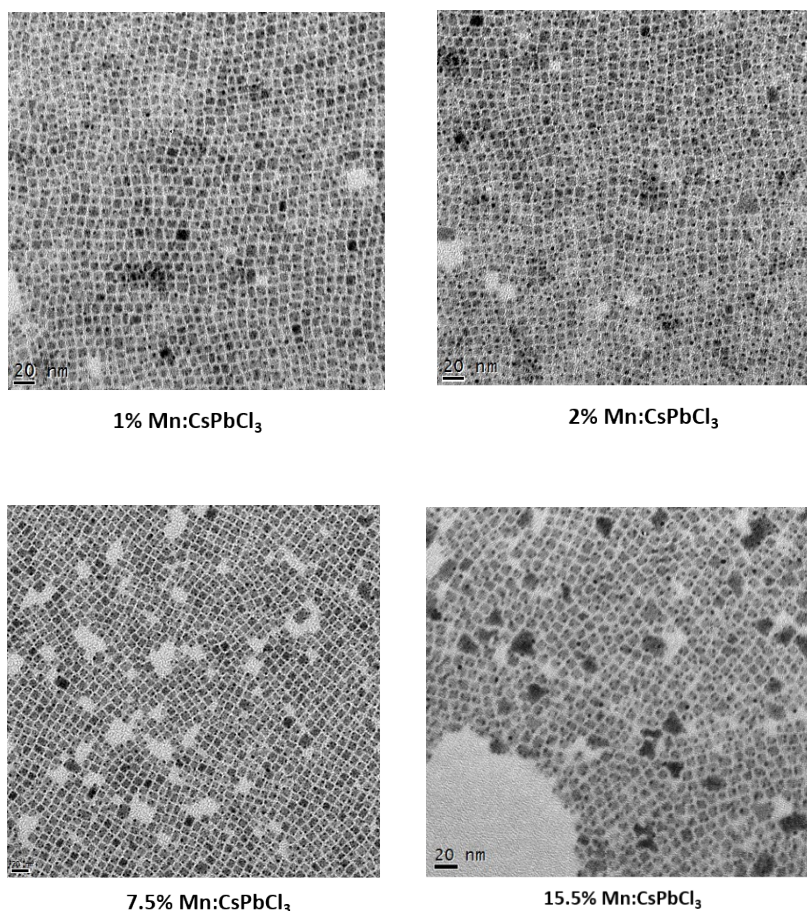


Figure S1. TEM images of different samples showing uniform size distribution. Scale bar shown here is of 20 nm.

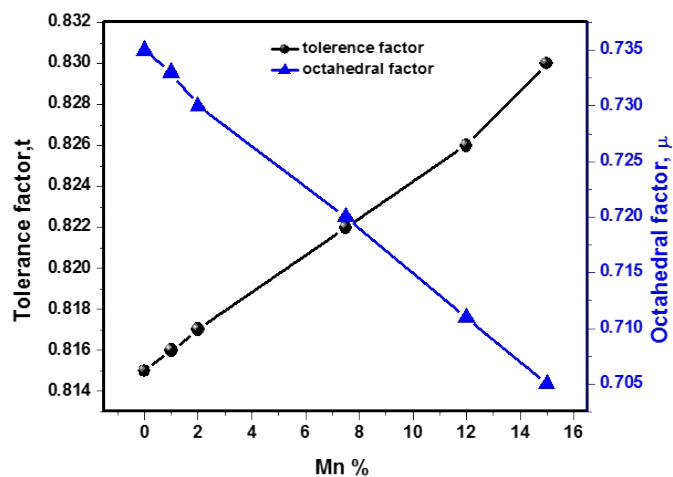


Figure S2. Tolerance factor and octahedral factor of different sets of synthesized materials.

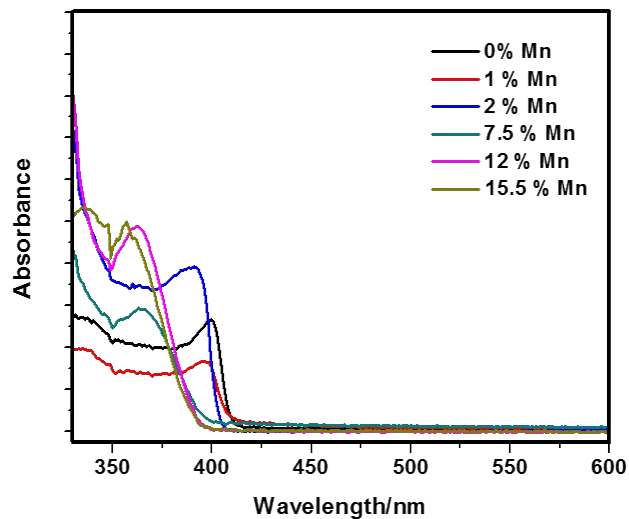


Figure S3. UV-Vis absorption spectra of undoped and doped CsPbCl₃ NCs.

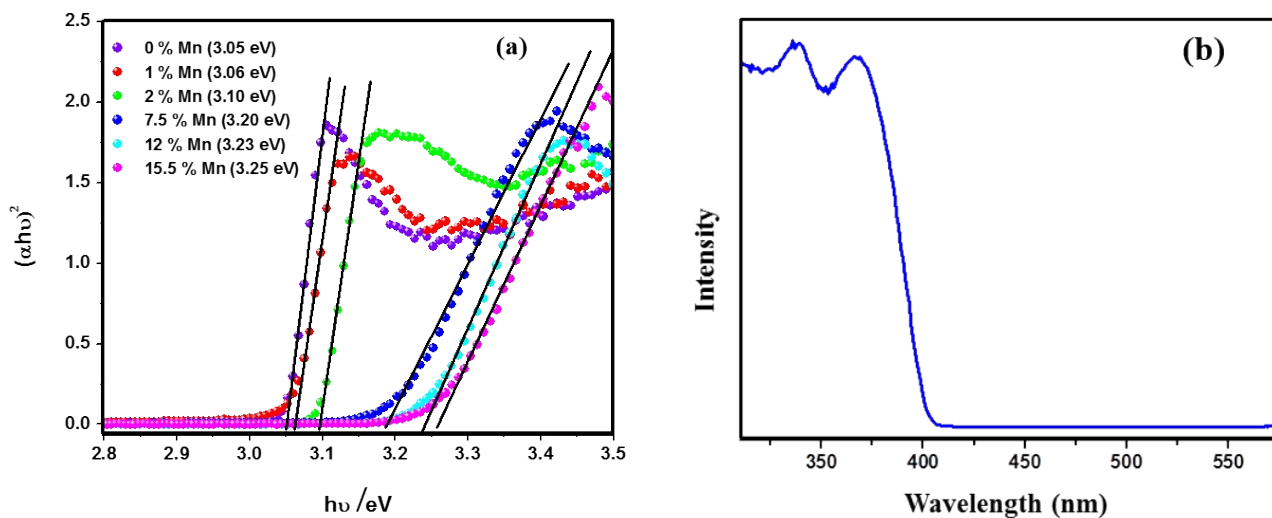


Figure S4. (a) Tauc plot of undoped and doped nanocrystals. Estimated band gaps are given in brackets. (b) Excitation spectra of 12% Mn:CsPbCl₃ recorded by monitoring at 604 nm.

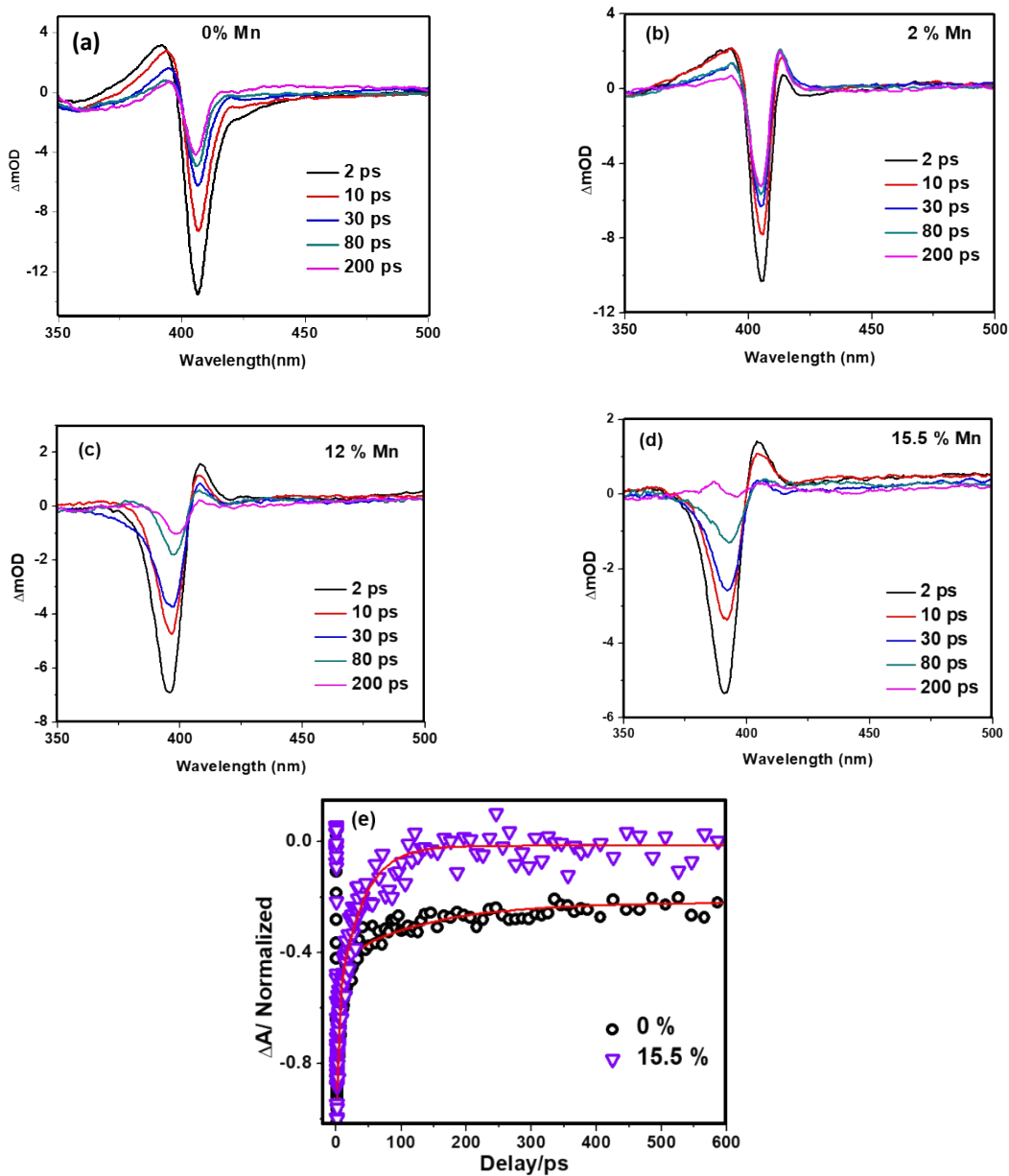


Figure S5. TA spectra of (a) undoped, (b) 2% Mn, (c) 12% Mn and (d) 15.5% Mn doped CsPbCl₃ NCs in toluene at 330 nm excitation (E) Comparison of bleach recovery kinetics of 0% and 15.5% Mn-doped CsPbCl₃ NCs.

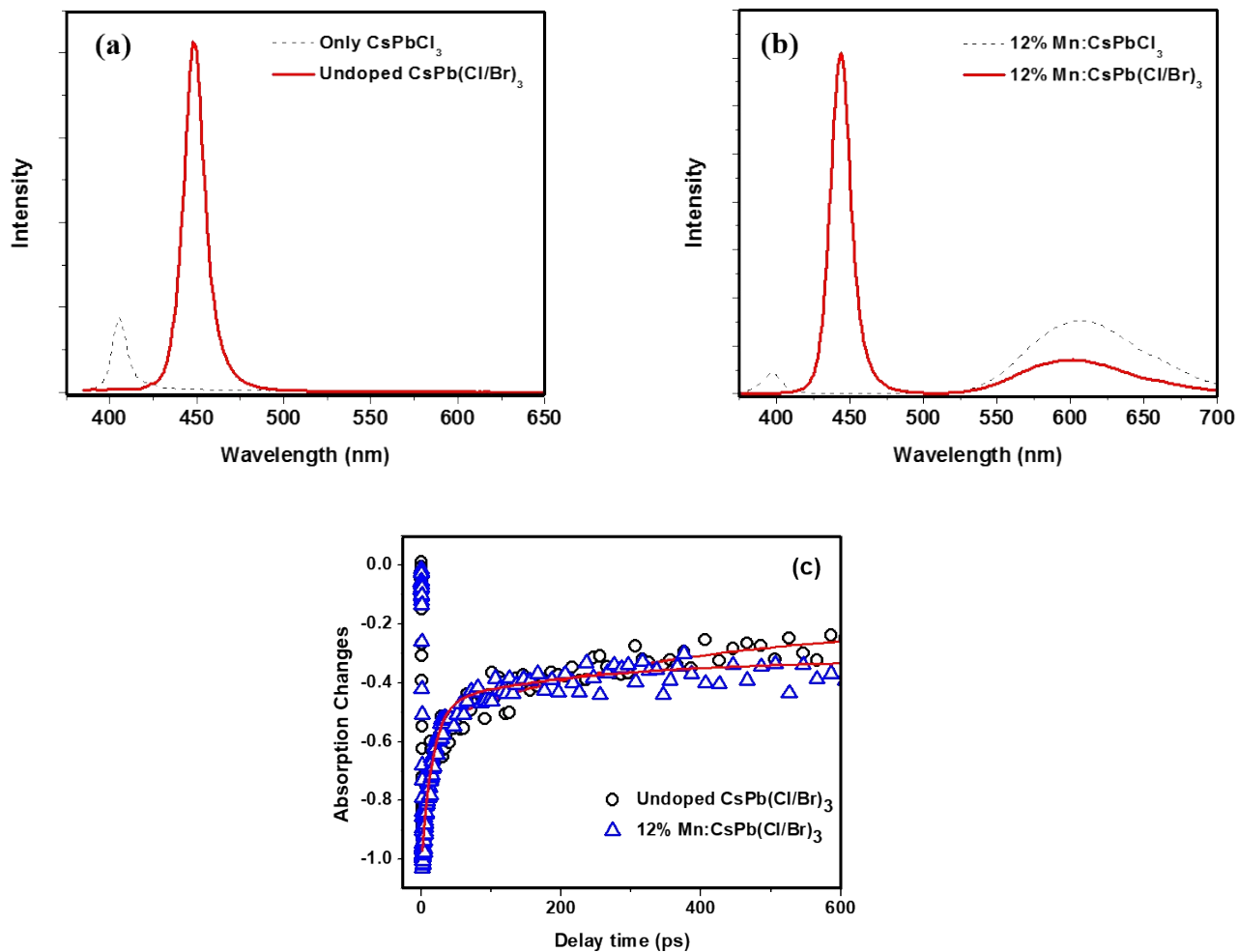


Figure S6. Dotted lines represent PL spectra of (a) Undoped CsPbCl₃ NCs (b) 12% Mn doped CsPbCl₃ NCs. Solid lines are for Br⁻ exchanged NCs for both cases. Halide (Br⁻) exchange was performed by adding freshly prepared CsPbBr₃ NCs solution dispersed in toluene into the sample of interest. (c) Comparison of bleach recovery dynamics between undoped and 12% Mn doped CsPb(Cl/Br)₃ NCs.

Table S1. Relative Mn content estimated from ICP-OES against the precursor used during synthesis.

Precursor ratio % (Mn/Pb)	ICP ratio % (Mn/Pb)
10	1
20	2
30	7.5
40	12
50	15.5

Table S2. Mn PL decay parameters of different samples by monitoring at their respective peak position.

Sample	t_1 (b_1) [ms]	t_2 (b_2) [ms]	$\langle t_{int} \rangle$ [ms]
1% Mn:CsPbCl ₃	1.3 ± 0.03	-----	1.30
2% Mn:CsPbCl ₃	1.24 ± 0.05	-----	1.24
7.5% Mn:CsPbCl ₃	$0.70 \pm 0.01(0.79)$	$0.18 \pm 0.01 (0.21)$	0.66
12% Mn:CsPbCl ₃	$0.64 \pm 0.03 (0.86)$	$0.10 \pm 0.03 (0.14)$	0.51
15.5% Mn:CsPbCl ₃	$0.45 \pm 0.02 (0.82)$	$0.1 \pm 0.01 (0.18)$	0.43

1. N. Mondal and A. Samanta, *J. Phys. Chem. C*, 2016, **120**, 650-658.
2. W. H. Melhuish, *J. Phys. Chem.* 1961, **65**, 229.
3. R. F. Kubin and A. N. Fletcher, *JOL*, 1982, **27**, 455