

## Supporting Information (SI)

### Postsynthesis Doping of Mn and Yb into CsPbX<sub>3</sub> (X = Cl, Br, I) Perovskite Nanocrystals for Downconversion Emission

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#### Chemicals:

Lead bromide (PbBr<sub>2</sub> ,99.999%), lead iodide (PbI<sub>2</sub>, 99.999%), lead chloride (PbCl<sub>2</sub>, 98%), manganese (II) bromide (MnBr<sub>2</sub>, 98%), ytterbium (III) nitrate pentahydrate {Yb(NO<sub>3</sub>)<sub>3</sub>.5H<sub>2</sub>O, 99.99% }, caesium carbonate (Cs<sub>2</sub>CO<sub>3</sub> , 99.9%), oleic acid (OA, 90%), 1-octadecene (ODE, 90%), oleylamine (OLA, 98%), trioctylphosphine (TOP, 90%), methyl acetate (MeOAc, 99.5%), N,N-dimethylformamide (DMF, 99.8%), hydrogen bromide (HBr, 43 wt%, 99.99% ) were purchased from Aldrich and were used without further purification. Acetone (99.0%, SDFCL), Hexane (99.99%, Rankem), Toluene (99.5%, Rankem) solvents are used as obtained.

#### Synthesis:

**Cs-oleate precursor solution:** Prepared by dissolving 350 mg of Cs<sub>2</sub>CO<sub>3</sub> in 20 mL ODE and 1.25 mL OA in inert atmosphere at 150 °C and stored for further use.<sup>1</sup>

### **CsPbBr<sub>3</sub> nanoplatelets:**

Synthesis of CsPbBr<sub>3</sub> nanoplatelets is carried out at room temperature under ambient atmosphere following ref.<sup>1</sup> But reactions are scaled up by 4 times. Typically 5 mL ODE, 0.5 mL OA and 0.5 mL OLA are taken into a 50 mL centrifuge tube followed by addition of 0.5 mL Cs-oleate precursor solution (0.1 M, preheated at 100 °C) under vigorous stirring. After that, 0.8 mL PbBr<sub>2</sub> precursor solution prepared by dissolving 2 mmol (735 mg) PbBr<sub>2</sub> in 5 mL DMF is injected to the reaction mixture. Within ~10 s, slight white turbidity appears and 20 mL acetone is swiftly injected into the reaction mixture to quench the reaction. Then the reaction mixture is centrifuged at 6000 rpm (1-2 mL hexane is added to this crude solution to prevent immiscibility with excess acetone) for 5 minutes. The wet pellet obtained is redispersed in 2-3 mL hexane and washed again by adding methyl acetate (MeOAc) as antisolvent (typically 1 : 2 v/v ratio of hexane : methyl acetate). The resulting turbid solution is centrifuged at 6000 rpm for 5 minutes and pellet obtained is redispersed in hexane for post synthesis doping and characterization. The above procedure results into 5 monolayer (ML) CsPbBr<sub>3</sub> NPLs as desired product.

To control thickness of CsPbBr<sub>3</sub> NPLs to 4 ML and 3 ML, 20 µL and 40 µL HBr are added to the 0.8 mL PbBr<sub>2</sub> precursor solution, respectively. The remaining procedure is same as described for 5 ML NPLs.

### **CsPbBr<sub>3</sub> nanocubes:**

Colloidal CsPbBr<sub>3</sub> nanocubes were synthesized through hot injection synthesis after minor modifications of the protocols reported in ref.<sup>1-2</sup> PbBr<sub>2</sub> (0.5 mmol, 183.5 mg) and 12 mL ODE are loaded into a three neck round bottom flask (RB) connected to schlenk line apparatus. The reaction mixture under continuous stirring was degassed in alternating vacuum and nitrogen at ~100 °C for 30-45 minutes. Then, 1.5 mL OA and 1.5 mL OLA are injected into the reaction mixture under N<sub>2</sub> flow. Again the reaction mixture is degassed in alternating vacuum and N<sub>2</sub> for next half an hour. The temperature of reaction mixture is set to 130 °C under continuous N<sub>2</sub> flow. Once the reaction mixture becomes clear at set temperature 130 °C, 1 mL Cs-oleate from stock solution (0.1 M, pre-heated at ~100 °C) is quickly injected into the reaction mixture. A light green color appears within ~5 s and the reaction is quenched immediately by immersing the flask into liquid nitrogen bath. CsPbBr<sub>3</sub> nanocubes are then precipitated at room temperature by

addition of excess methyl acetate to crude solution of nanocubes till turbidity appears and centrifuged at 6000 rpm for 5 minutes. The obtained pellet is redispersed in 2-3 mL hexane after discarding supernatant. The 2<sup>nd</sup> washing is carried out by adding methyl acetate (~1 : 2 v/v ratio of hexane : methyl acetate) and centrifuging again at 6000 rpm or 5 minutes. The obtained pellet is finally redispersed in hexane and stored for post synthesis doping and further studies.

**CsPbCl<sub>3</sub> nanocubes:** CsPbCl<sub>3</sub> nanocubes are synthesised following same procedure as adapted for CsPbBr<sub>3</sub> nanocubes but with following differences in precursor concentration. For synthesising CsPbCl<sub>3</sub> nanocubes PbCl<sub>2</sub> (0.752 mmol, 209 mg), 20 mL ODE were initially taken in RB and then 2 mL OA, 2 mL OLA, 2 mL TOP are injected at 100 °C after degassing. The reaction in this case is carried out at 160 °C by injecting Cs-oleate 1.4 mL (0.1 M) followed by immediate quenching. **CsPbI<sub>3</sub> nanocubes:** Synthesis and washing procedure are similar for both CsPbI<sub>3</sub> and CsPbBr<sub>3</sub> nanocubes. For synthesis of CsPbI<sub>3</sub> nanocubes, PbI<sub>2</sub> (1 mmol, 461 mg), 20 mL ODE, 2.5 mL OA, 2.5 mL OLA followed by injection of preheated Cs-oleate solution 2 mL (0.1 M) at reaction temperature 120 °C gives desired product.

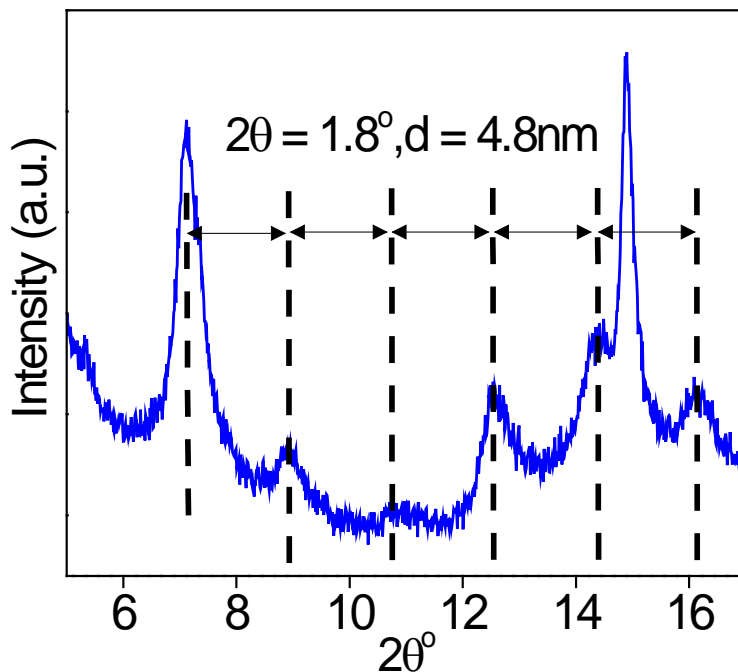
**Doping Mn<sup>2+</sup> or Yb<sup>3+</sup> in CsPbX<sub>3</sub> nanocrystals (NCs, both nanocubes and NPLs):** For efficient and facile postsynthesis doping, the desired CsPbX<sub>3</sub> NCs are washed minimum two times as described above in syntheses procedure of NCs. Our postsynthesis doping is carried out at room temperature and ambient atmosphere. Initially, freshly prepared Mn precursor solution is obtained by sonicating MnBr<sub>2</sub> in a mixture of acetone : toluene solvents with volume ratio of 1 : 3. The volume ratio has been optimized to minimize the polarity of precursor solution detrimental for colloidal stability of CsPbX<sub>3</sub> NCs (see main manuscript for more discussion). Similarly, Yb precursor solution is obtained by dissolving Yb(NO<sub>3</sub>)<sub>3</sub>.5H<sub>2</sub>O in a mixture of methyl acetate : toluene with volume ratio of 1 : 3. Next undoped NCs dispersion obtained after synthesis and washing are divided equally in different vials. Different amounts of dopant precursor solution are then added to the NCs dispersion under continuous stirring for 1 minute to achieve different dopant concentrations. Table S1 and S2 show the relations between amount of dopant ions present in precursor and the product NCs. Once Mn or Yb is doped, the product NCs are then washed using MeOAc as anti-solvent to precipitate the NCs. The wet pellet obtained after centrifugation is redispersed in hexane. In the case of Mn doped CsPbBr<sub>3</sub> NPLs, additional level of purification is achieved by refrigerating the dispersion of Mn doped NPLs in hexane for

2-3 hours to remove unreacted precursors that precipitates out at low temperature. The supernatant is decanted and stored for further studies after discarding any precipitate obtained.

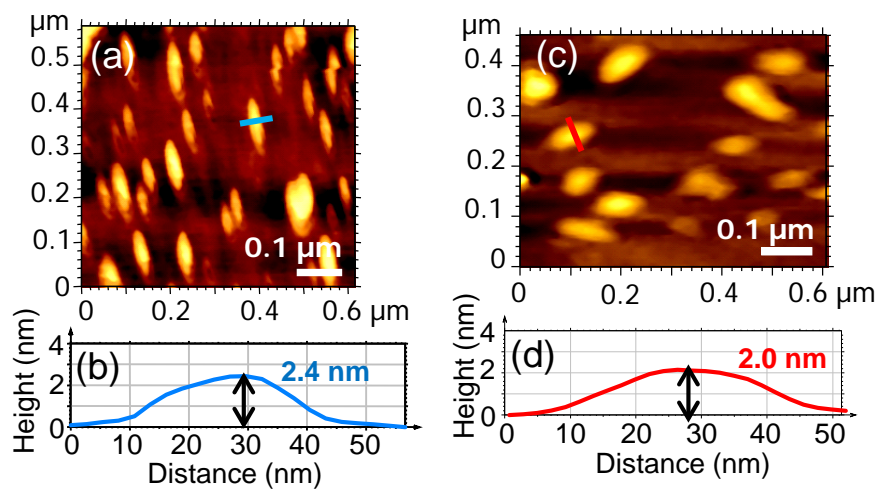
### **Characterization:**

Structural analysis is carried out using a Bruker D8 Advance X-ray diffraction (XRD) machine using Cu K $\alpha$  (1.54 Å) radiation. XRD patterns are recorded after drop casting colloidal NCs on glass slides. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images are collected by using a 200 kV UHR FEG-TEM, JEOL JEM 2100F field emission transmission electron microscope. Atomic force microscopy (AFM) images are captured using Key sight atomic force microscope (AFM 5500) employing tapping mode technique. Dilute dispersions of NCs are drop casted over Si substrate for AFM analysis. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis is carried out using ARCOS simultaneous ICP spectrometer, Analytical Instruments GmbH, Germany. Electron Paramagnetic Resonance (EPR) spectra are collected using a JES- FA200 ESR spectrometer (JEOL, Japan) in X-band frequency range at room temperature and measurements were carried out with powder samples. UV-visible-NIR absorption spectra are recorded using a Perkin Elmer and Lambda-45 UV/Vis/NIR spectrometer. Steady-state photoluminescence (PL) spectra, photoluminescence excitation (PLE) spectra and PL decay dynamics (time-correlated single photon counting) are recorded using FLS 980 spectrophotometer (Edinburgh Instruments). For Mn and Yb PL decay dynamics, microsecond flashlamp is used as excitation source. For excitonic PL decay dynamics, picosecond pulsed diode laser (405 nm) is used as excitation source. Low-temperature PL studies are carried out for NCs films on quartz substrates using a closed cycle cryostat. Reference PL quantum yield of Mn emission were calculated using rhodamine-6G dye dissolved in ethanol as reference standard ( $\Phi = 0.96$ ).

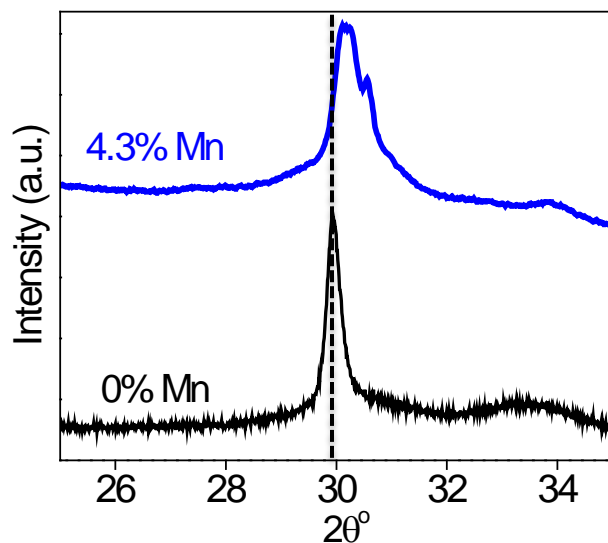
Supporting Figures:



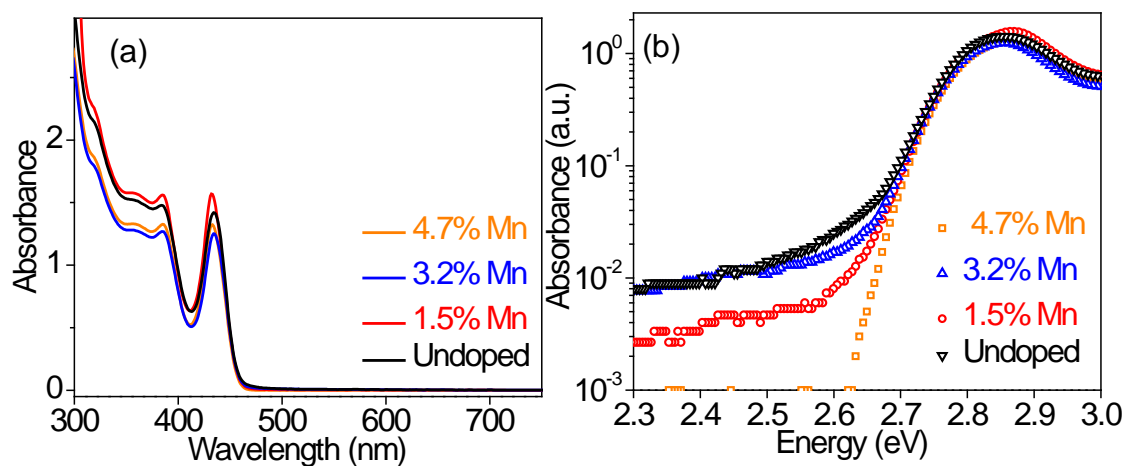
**Figure S1.** XRD pattern in the range  $2\theta = 5^\circ$  to  $17^\circ$  of self stacked 5 ML  $\text{CsPbBr}_3$  NPLs displaying interlayer spacing of 4.8 nm.



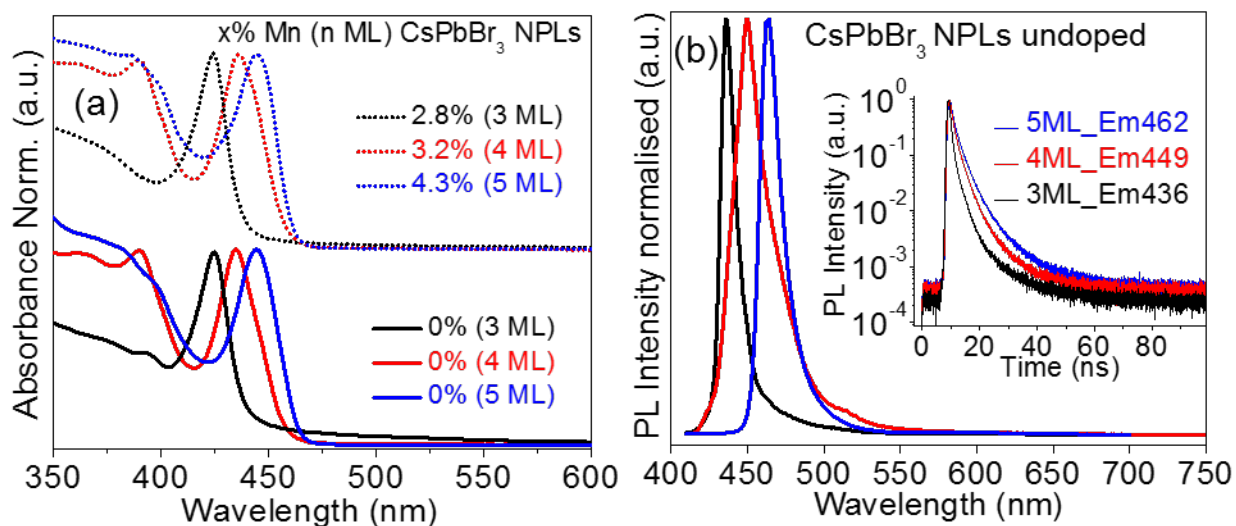
**Figure S2.** AFM images and respective height profile of Mn-doped  $\text{CsPbBr}_3$  NPLs. (a) and (b) corresponds to Mn-doped 4 ML with thickness  $\sim 2.4$  nm, (c) and (d) belong to 3 ML with thickness  $\sim 2$  nm.



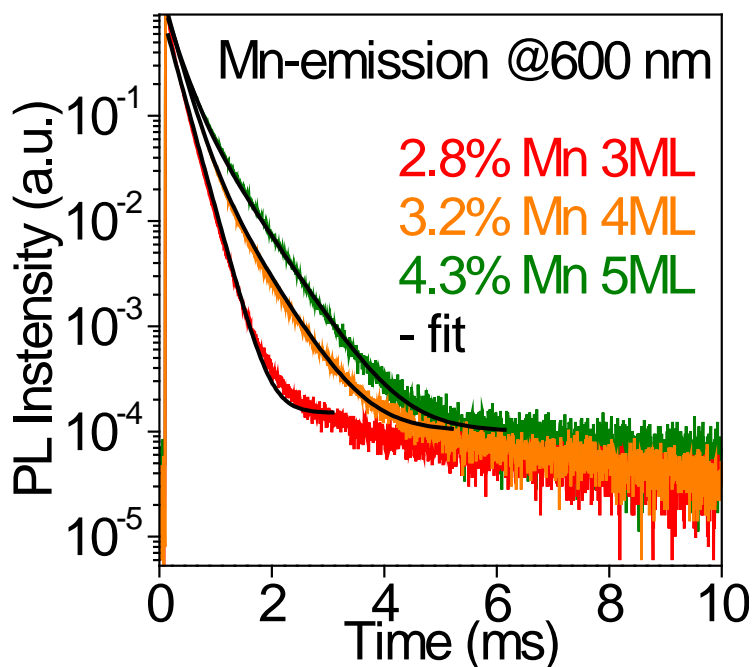
**Figure S3.** Magnified view of most intense XRD peak ( $2\theta = 30^\circ$ ) for undoped and 4.3% Mn doped CsPbBr<sub>3</sub> 5 ML NPLs. Compared to 0% Mn, the XRD peak in 4.3% Mn sample is slightly shifted towards higher  $2\theta$  due to partial 4.3% substitution of Pb<sup>2+</sup> by smaller Mn<sup>2+</sup> ions in CsPbBr<sub>3</sub> crystal lattice.



**Figure S4.** (a) Optical absorption and (b) Urbach tail for different dopant concentrations of Mn-doped in CsPbBr<sub>3</sub> NPLs (4 ML). Increase in Mn doping from 1.5% to 4.7% leads to systematic reduction of Urbach tail.

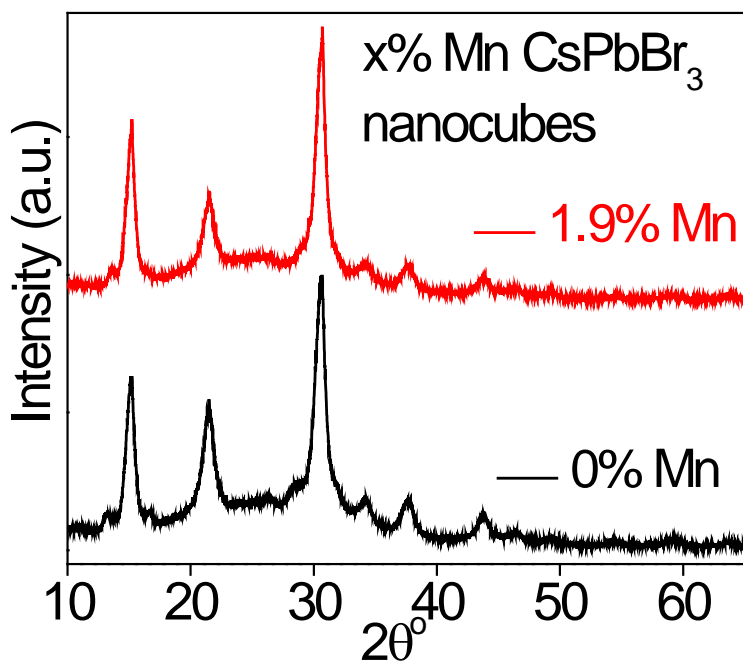


**Figure S5.** (a) Optical absorption for undoped and Mn-doped CsPbBr<sub>3</sub> NPLs with 3 ML, 4 ML and 5 ML thicknesses. (b) PL spectra and PL decay dynamics (shown in the inset) for excitonic emission in case of undoped 3 ML, 4 ML and 5 ML CsPbBr<sub>3</sub> NPLs. PL spectra and PL decay dynamics for Mn-doped samples are shown in Figure 4 of the manuscript and Figure S6 of SI respectively.



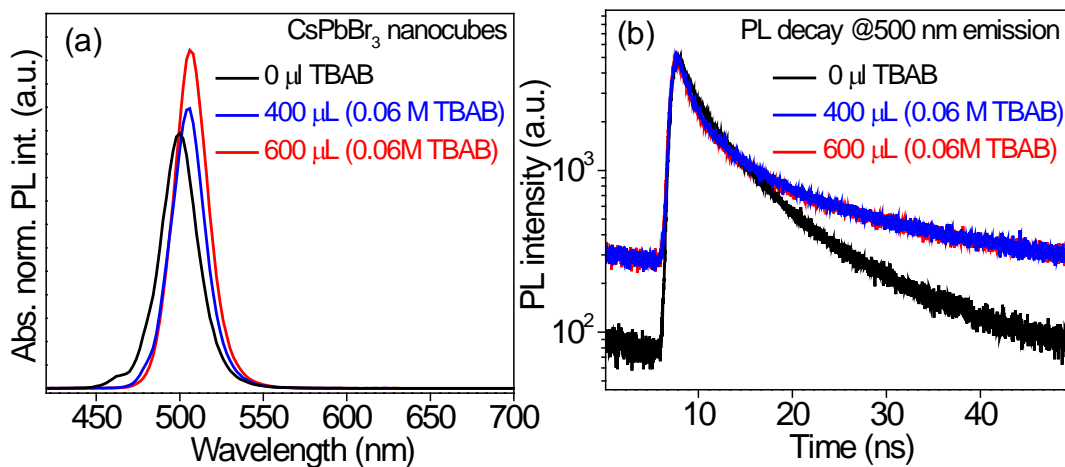
**Figure S6.** PL decay dynamics of Mn emission collected at 600 nm for x% Mn-doped CsPbBr<sub>3</sub> NPLs with different thicknesses. In case of Mn-doped 3 ML sample, the experimental data is

fitted with single exponential decay function that yielded a lifetime of 222  $\mu\text{s}$  attributed to Mn present on surface or subsurface region. While as for Mn-doped 4 ML and 5 ML sample, bi-exponential decay function is used to fit the data. The decay parameters obtained with respective contributions for 4 ML sample are  $\tau_1 = 210 \mu\text{s}$  (93%),  $\tau_2 = 510 \mu\text{s}$  (7%) and for 5 ML case  $\tau_1 = 220 \mu\text{s}$  (83%),  $\tau_2 = 550 \mu\text{s}$  (17%).  $\tau_1$  in both 4 ML and 5 ML comes from surface bound Mn matching with lifetime for 3 ML sample, whereas,  $\tau_2 \sim 550 \mu\text{s}$  is attributed to Mn present in bulk of  $\text{CsPbBr}_3$  crystal lattice.

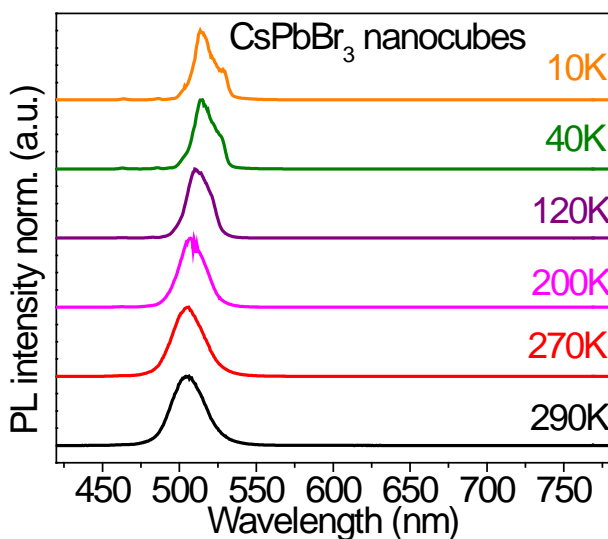


**Figure S7.** Comparison of XRD pattern of undoped and 1.9% Mn-doped  $\text{CsPbBr}_3$  nanocubes with no additional impurity arising after post synthesis Mn doping.

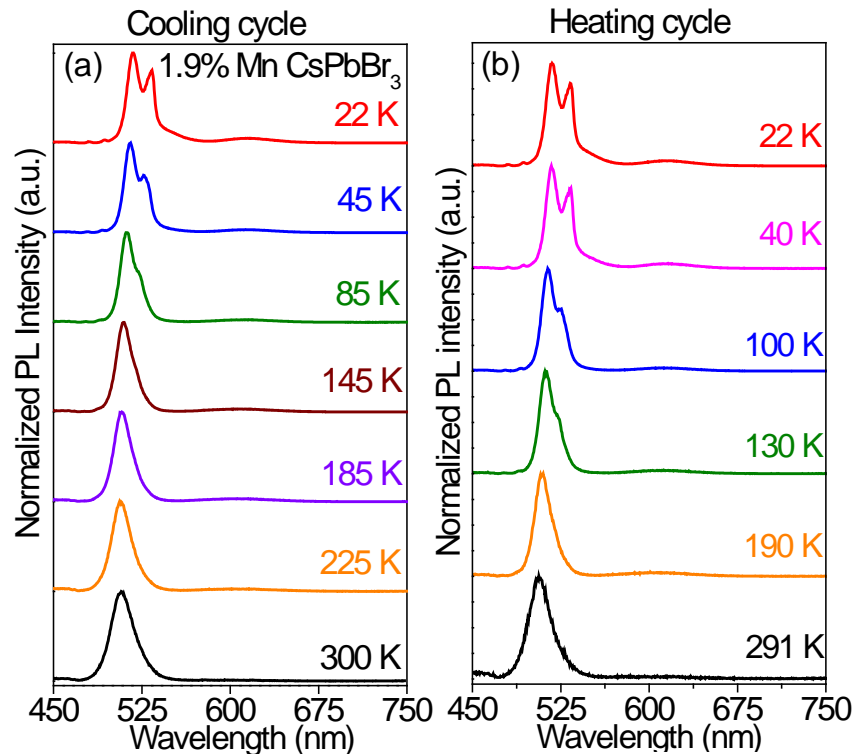




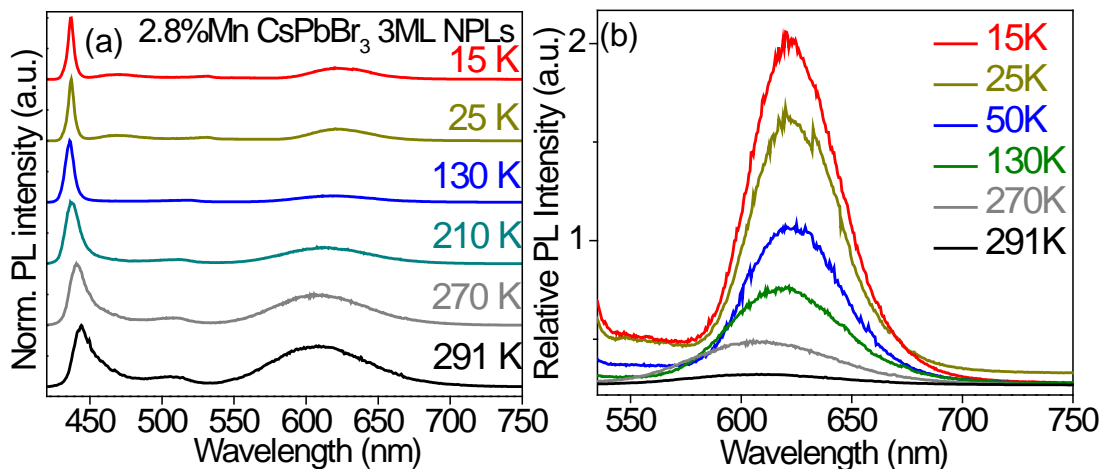
**Figure S8.** (a) PL spectra normalized with absorbance at excitation wavelength and (b) corresponding PL decay dynamics at the emission maximum of CsPbBr<sub>3</sub> nanocubes (~100 mg dispersed in 2 ml toluene) before and after treatment with tetrabutylammonium bromide (TBAB) 0.06 M. On addition of TBAB to CsPbBr<sub>3</sub> nanocubes both excitonic emission and PL decay lifetime enhances compared to untreated nanocubes. These results suggest the passivation of surface defects by addition of TBAB.



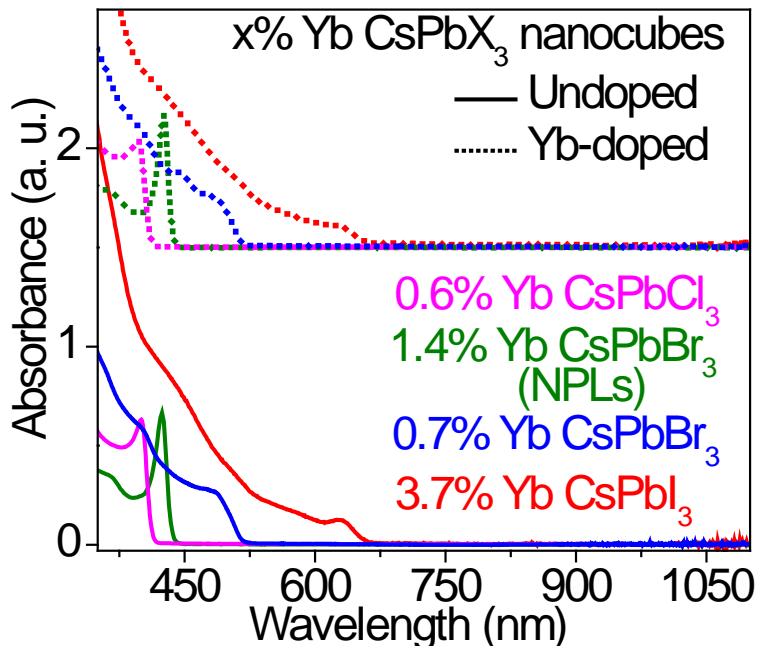
**Figure S9.** Temperature dependent PL spectra of undoped CsPbBr<sub>3</sub> nanocubes. The spectra's are normalized and shifted upwards for clarity in presentation.



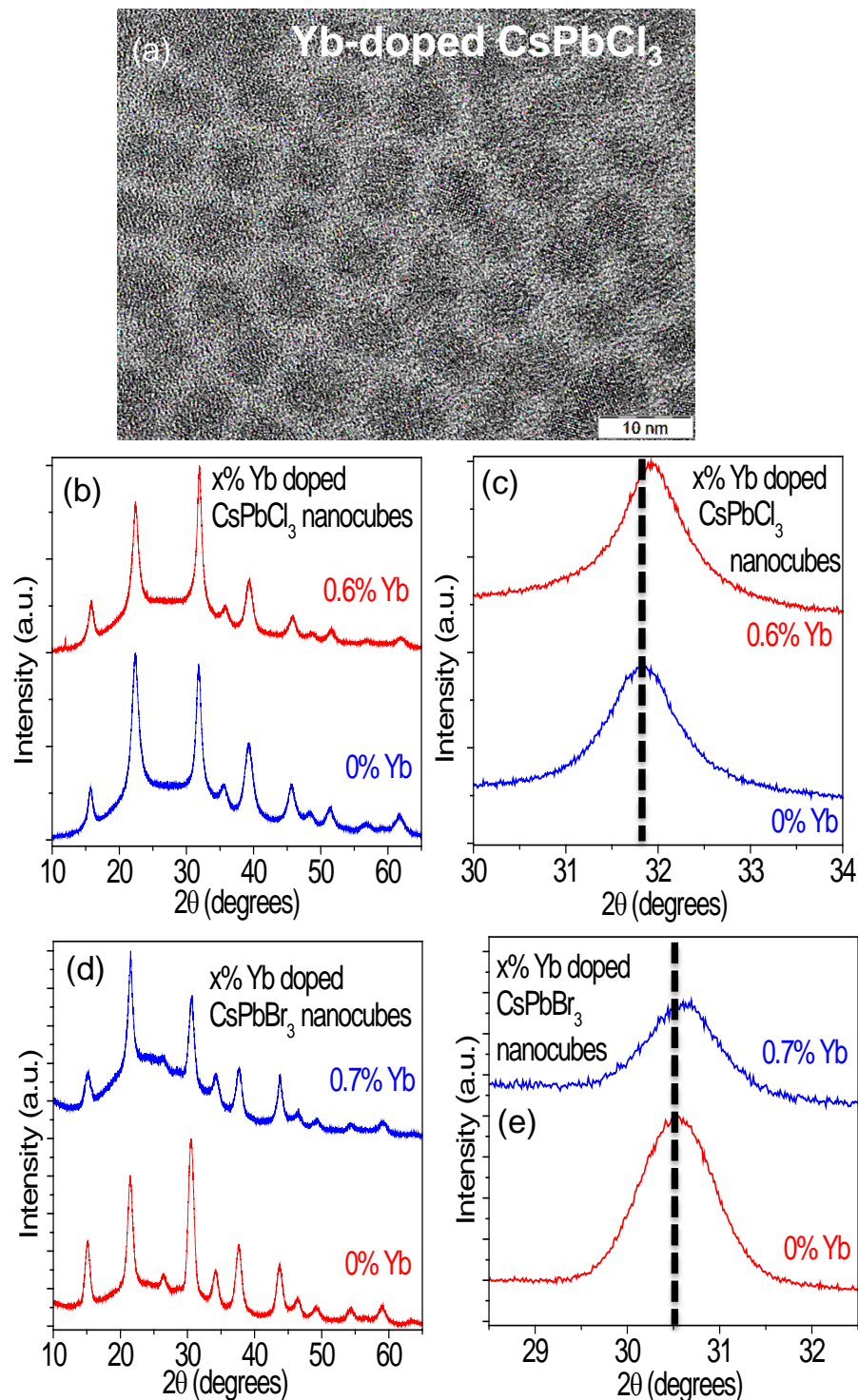
**Figure S10.** Temperature dependent PL spectra of 1.9% Mn-doped CsPbBr<sub>3</sub> nanocubes during (a) cooling cycle and (b) heating cycle. Initially, Mn-emission is not observed at room temperature and starts appearing below 225 K.



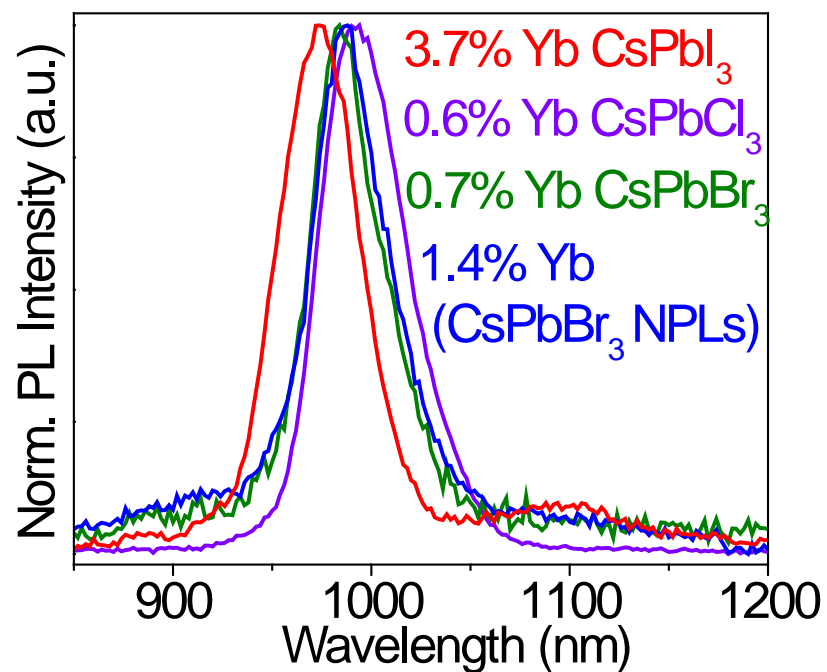
**Figure S11.** (a) Temperature dependent normalized PL spectra of 2.8% Mn-doped CsPbBr<sub>3</sub> NPLs (3 ML). Spectra are shifted upwards for clarity in presentation. (b) Temperature dependent relative PL intensity of Mn emission of corresponding PL spectra shown in (a).



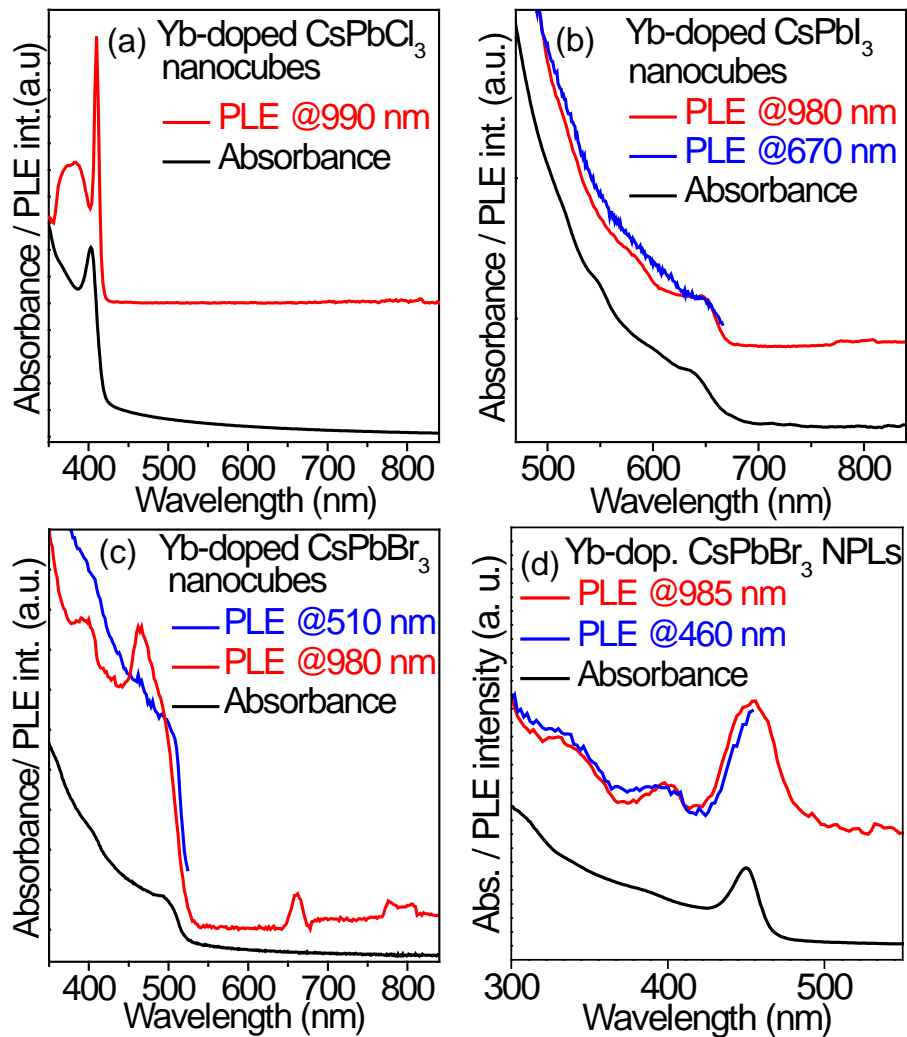
**Figure S12.** UV-visible-NIR absorption plots of undoped (solid lines) and Yb-doped (dashed lines) CsPbX<sub>3</sub> nanocubes and CsPbBr<sub>3</sub> NPLs. The corresponding Yb-doped CsPbX<sub>3</sub> spectra are vertically shifted by adding constant 1.5 for clarity in presentation. Optical band gap remains unshifted before and after doping Yb into the CsPbX<sub>3</sub> NCs.



**Figure S13.** (a) TEM image of 0.6% Yb-doped CsPbCl<sub>3</sub> nanocubes. (b) XRD patterns and (c) magnified view of the patterns showing the most intense peak at  $2\theta \sim 31.8^\circ$  for undoped and 0.6% Yb-doped CsPbCl<sub>3</sub> nanocubes. (d) XRD patterns and (e) shows magnified view of the most intense peak at  $2\theta \sim 30.6^\circ$  for undoped and 0.7% Yb-doped CsPbBr<sub>3</sub> nanocubes.



**Figure S14.** Normalized PL spectra of dopant emission in Yb-doped CsPbX<sub>3</sub> (X = Cl, Br, I) nanocubes and CsPbBr<sub>3</sub> NPLs. This Yb-emission undergoes blue shift ~20 nm as the halide composition is varied from Cl to Br to I of host CsPbX<sub>3</sub> nanocubes.



**Figure S15.** Comparison of absorbance spectra and PLE spectra collected at both excitonic emission and Yb-emission in case of Yb-doped in  $\text{CsPbX}_3$  ( $X = \text{Cl}, \text{Br}, \text{I}$ ) nanocubes and  $\text{CsPbBr}_3$  NPLs. Resemblance of PLE spectra Yb-emission with that that of excitonic emission and corresponding absorbance spectra of host, suggests that the host absorbs excitation light which then excites dopant through energy transfer. Finally dopant shows emission in NIR region. These PLE spectra suggest incorporation Yb into the  $\text{CsPbX}_3$  NCs.

**Table S1.** Comparison of amount of Mn (atomic %, with respect to Pb) taken as precursor for postsynthesis doping, with that obtained in the product NCs measured using ICP-AES.

Mn-doped CsPbBr <sub>3</sub> NCs	
%Mn Precursor taken	%Mn from (ICP-AES)
CsPbBr <sub>3</sub> 5ML NPLs	
6	0.6
13	1.6
22	4.3
30	6.5
CsPbBr <sub>3</sub> 4ML NPLs	
6	1.5
13	3.2
22	4.7
30	8
CsPbBr <sub>3</sub> 3ML NPLs	
6	2.8
CsPbBr <sub>3</sub> nanocubes	
22	1.9
30	3.9

**Table S2.** Comparison of amount of Yb (atomic %, with respect to Pb) taken as precursor for postsynthesis doping, with that obtained in the product NCs measured using ICP-AES.

Yb-doped CsPbX <sub>3</sub> nanocubes		
Sample	%Yb Precursor taken	%Yb from (ICP-AES)
CsPbCl <sub>3</sub>	4	0.6
CsPbBr <sub>3</sub>	7	0.7
CsPbI <sub>3</sub>	9	3.7

**Table S3.** Best fit parameters of excitonic PL decay of Mn-doped 5 ML CsPbBr<sub>3</sub> NPLs, corresponding to data shown in Figure 3c. The experimental data are fitted using bi-exponential decay fit:  $I(t) = I(0) + (a_1 \exp^{-\frac{t}{\tau_1}} + a_2 \exp^{-\frac{t}{\tau_2}})$ , where  $I(t)$  and  $I(0)$  are PL intensities at time ‘t’ and  $t = 0$  s respectively,  $a_1$  and  $a_2$  are amplitudes of lifetime components  $\tau_1$  and  $\tau_2$  respectively.

x% Mn-doped CsPbBr <sub>3</sub> NPLs	$\tau_1$ (ns)	$\tau_2$ (ns)	$a_1$ (%)	$a_2$ (%)
0	1.0	4.7	99	1
1.5	1.4	4.9	98.5	1.4
4.3	1.5	5.5	98	2
6.5	1.6	6.0	98	2

## References:

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2. Swarnkar, A.; Marshall, A. R.; Sanehira, E. M.; Chernomordik, B. D.; Moore, D. T.; Christians, J. A.; Chakrabarti, T.; Luther, J. M. Quantum dot-induced phase stabilization of  $\alpha$ -CsPbI<sub>3</sub> perovskite for high-efficiency photovoltaics. *Science* **2016**, *354*, 92-95.