Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supporting Information for

Promote doping efficiency and photoluminescence quantum yield of Mn-doped perovskite nanocrystals *via* two-step hot-injection

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EXPERIMENTAL SECTION

Chemicals. Cesium carbonate (Cs_2CO_3, 99%), Lead acetate trihydrate ($PbAc_2{\cdot}3H_2O$, 99.5%), Manganese acetate tetrahydrate ($MnAc_2{\cdot}4H_2O$, 99.0%), 1-octadecene (ODE, 90%), Oleic acid (OA, 85%), Oleylamine (OLA, 90%), Hydrochloric acid (HCl, 36%), Hydrobromic acid (HBr, 48%) and toluene were purchased from Aldrich. All chemicals were used without further purification.

Two-step hot-injection synthesis of Mn-doped $CsPbCl_3$ NCs. Typically, x mmol $MnAc_2{\cdot}4H_2O$ (x=0.1, 0.3, 0.5, 0.7, 0.9), 1-x mmol $PbAc_2{\cdot}3H_2O$, 5 mL OA and 40 mL ODE were added to a 100 mL three neck round bottom flask and degassed 1 hour at 120 °C. The temperature was increased to 180-210 °C under N_2 atmosphere and 4 mL oleylammonium halide (OLA-HX) precursors (pre-prepared by the same protocol reported by Pradhan et al. *Angew. Chem., Int. Ed.*, 2019, 58 , 5552) was injected immediately. Then injecting 6 mL Cs-oleate (pre-prepared by the same protocol reported by Protesescu et al. *Nano Lett*. 2015, 15, 3692) after 30 second, the flash was cooled to room temperature naturally. The NCs were collected by 8000 r/min centrifugation for 5 minutes and then dispersed in toluene. The gram-scale Mn-doped $CsPbCl_3$ NCs were synthesized by enlarging all the reaction precursors 10 times. Mn-doped $CsPb(Cl/Br)_3$ NCs were synthesized by injecting the mixture of OLA-HBr and OLA-HCl at a volume ratio of 0.6 to 1.

Fabrication of LEDs. Mn-doped $CsPbCl_3$ NCs were well mixed with 25% polystyrene (PS)-toluene solution, respectively. Then the mixture was coated on a 375nm LED chip and dried 1 h in the air to obtain an orange LED. White LED was constructed by the same process with Mn-doped $CsPb(Cl/Br)_3$ NCs.

Characterization. Powder X-ray diffraction (XRD) was carried out by a Bruker AXS D8 X-ray diffractometer equipped with monochromatized Cu Kα radiation (λ = 1.5418 Å). The diffraction pattern was scanned over the angular range of 10-60 degrees (2θ) with a step size of 0.05. Transmission electron microscopy (TEM) was obtained by using a FEI Tecnai G2 F20

electron microscope operating at 200 kV. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) were performed on a JEOL JSM-7800F at 10 kV. Inductively coupled plasma optical emission spectrometry (ICP-OES) was performed with an OPTIMA 3300 DV analyzer (PerkinElmer). X-band electron paramagnetic resonance measurements were performed on Bruker EMX PLUS(PPMS) with microwave frequency 9.85 GHz at room temperature. Ultraviolet and visible absorption (UV−vis) spectra were measured by a Shimadzu UV-3600 plus spectrophotometer. Photoluminescence (PL) and the absolute photoluminescence quantum yields (PLQYs) were measured using a Horiba PTI Quanta Master 400 steady-state fluorescence system with an integrated sphere and double checked with a Hamamatsu Photonics Quantaurus-QY (model:C11347-11) under ambient conditions. Time-Resolved Photoluminescence Lifetime was detected by Edinburgh FLS920 at room temperature.

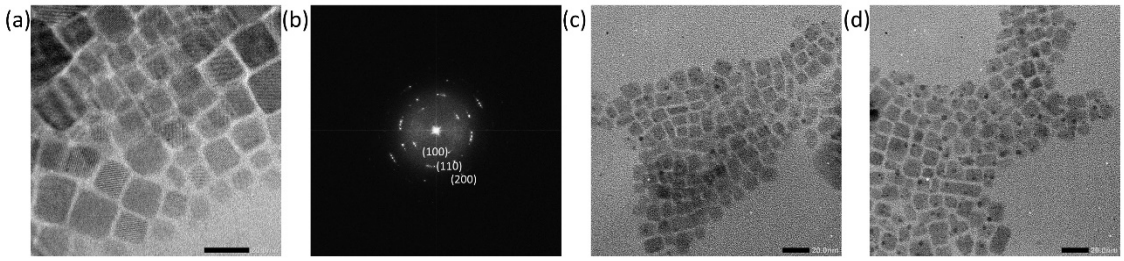

Fig. S1 a, b) HRTEM image and its FFT pattern of $CsPb_{1-x}Mn_xCl_3$ NCs with nominal Mn content of 10 mol%. c, d) HRTEN images of $CsPb_{1-x}Mn_xCl_3$ NCs with nominal Mn content of 90 mol%. The black particles around the edges and corners of NCs been Pb^0 caused by electron beam damage (ACS Nano 2017, 11, 2, 2124–2132; Chem. Mater. 2020, 32, 5410-5423).

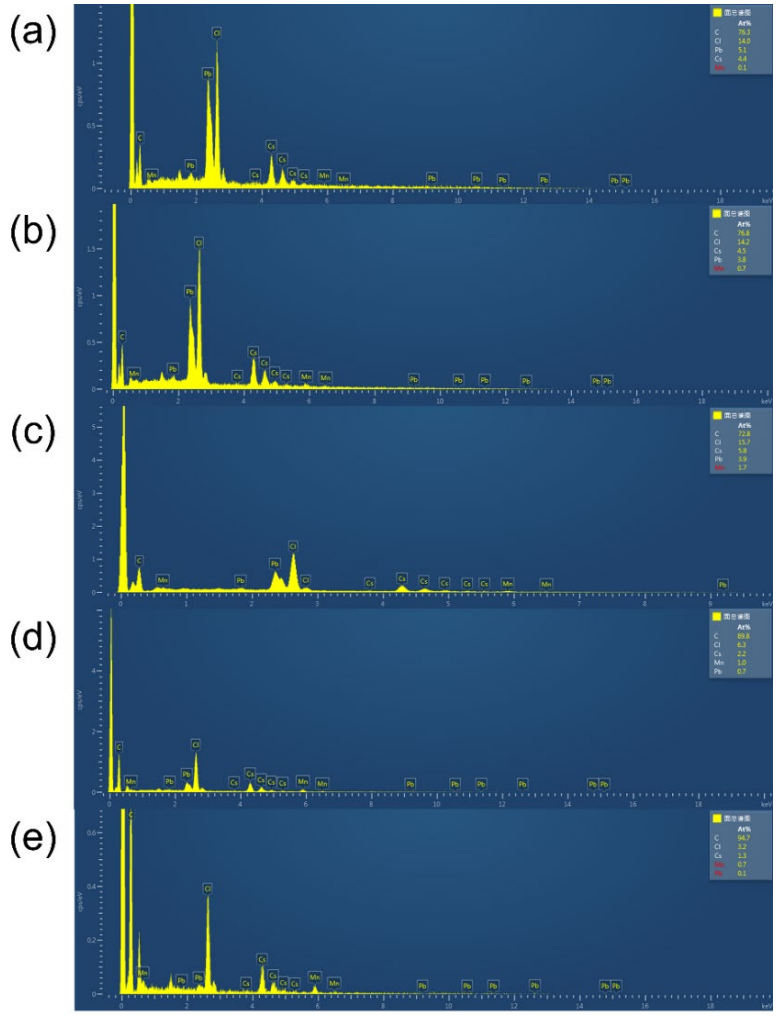

Fig. S2 Energy dispersive X-ray (EDX) spectra of the $CsPb_{1-x}Mn_xCl_3$ NCs synthesized with $MnAc_2$:$PbAc_2$ molar feed ratios of (a) 0.1: 0.9 (b) 0.3: 0.7 (c) 0.5: 0.5 (d) 0.7: 0.3 (e) 0.9: 0.1.

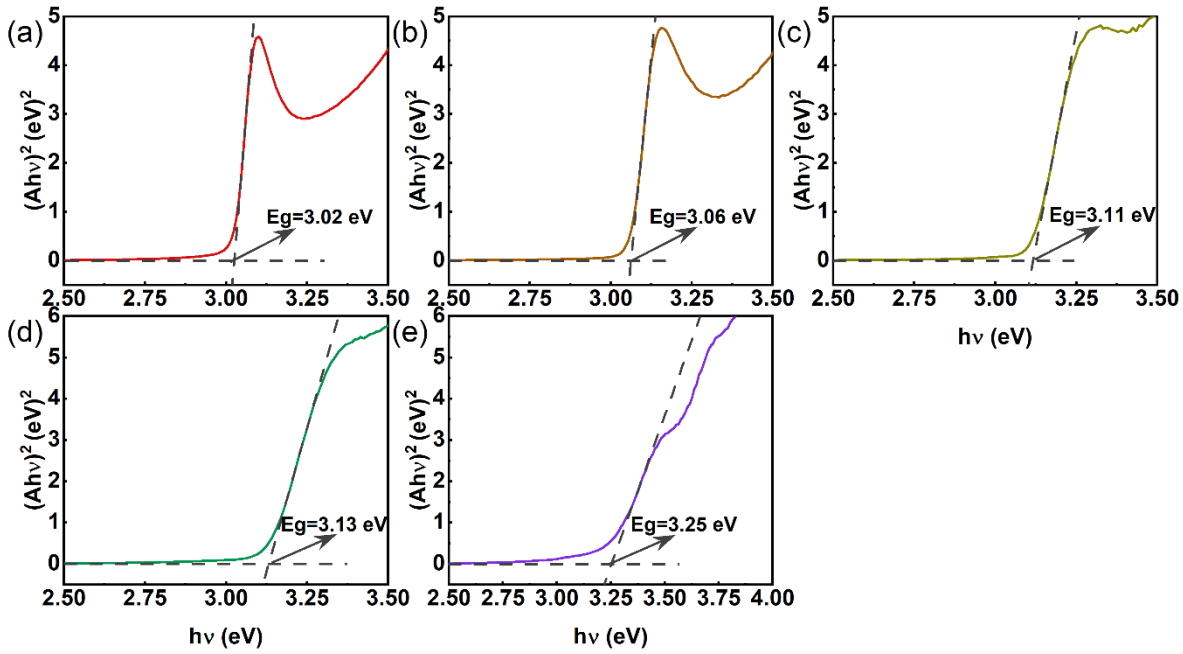

Fig. S3 Plots of $(Ahu)^2$ vs photon energy (hu) of the $CsPb_{1-x}Mn_xCl_3$ NCs synthesized with $MnAc_2$:$PbAc_2$ molar feed ratios of (a)0.1:0.9 (b) 0.3:0.7 (c) 0.5:0.5 (d)0.7:0.3 (e)0.9:0.1.

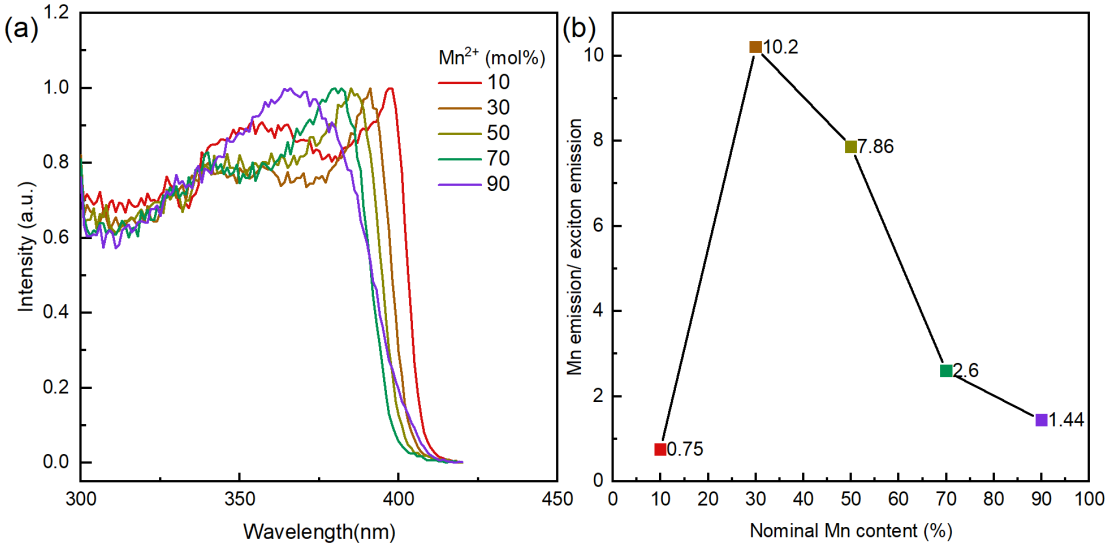

Figure S4. (a) Excitation spectrum and (b) Mn emission intensity relative to exciton emission intensity of the $CsPb_{1-x}Mn_xCl_3$ NCs with different nominal Mn content (mol%).

Fig. S5 Gram-scale $CsPb_{1-x}Mn_xCl_3$ NCs synthesized with $MnAc_2$:$PbAc_2$ molar feed ratios of 3:7.

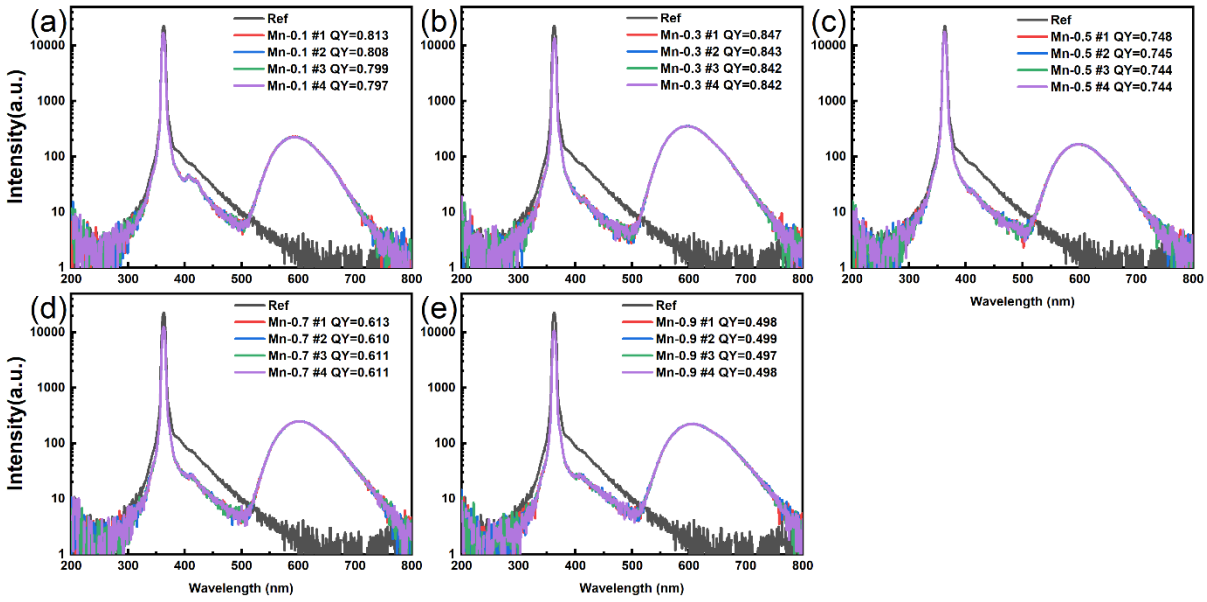

Fig. S6 PLQYs of $CsPb_{1-x}Mn_xCl_3$ NCs synthesized with $MnAc_2$:$PbAc_2$ molar feed ratios of (a)0.1:0.9 (b) 0.3:0.7 (c) 0.5:0.5 (d)0.7:0.3 (e)0.9:0.1. Each sample was repeated four times, and PLQYs were calculated the average of four times tests.

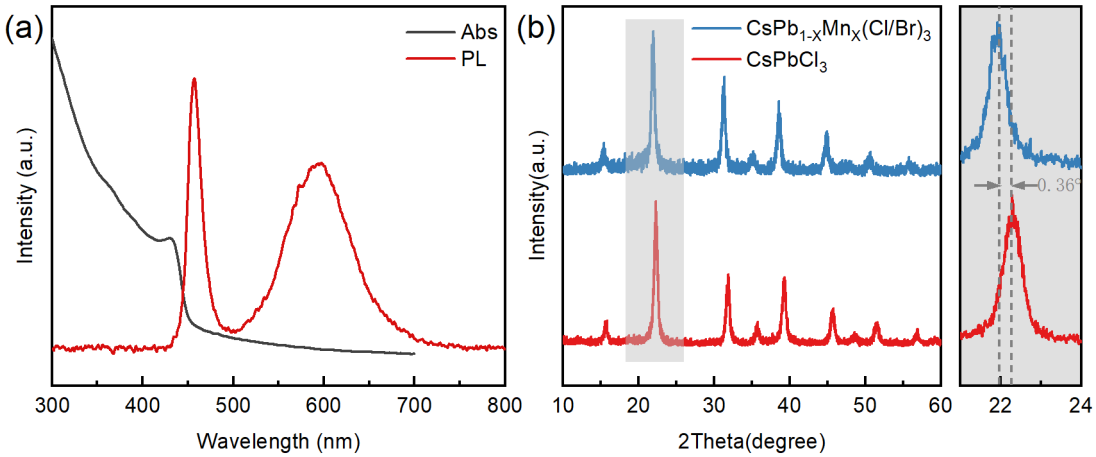

Fig. S7 (a) UV-vis absorption and PL spectra and (b) Powder XRD patterns of Mn-doped $CsPb(Cl/Br)_3$ NCs.

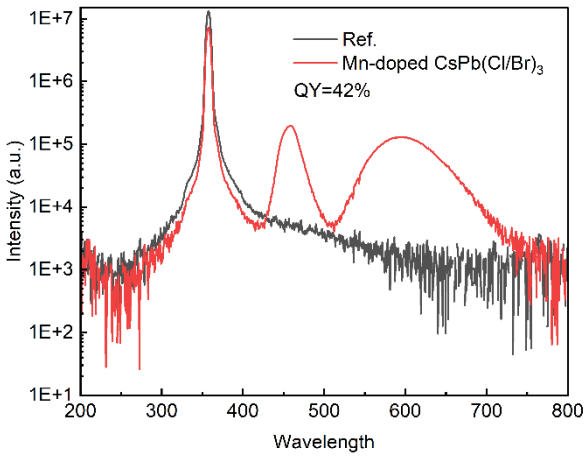

Fig. S8 PLQY of Mn-doped $CsPb(Cl/Br)_3$ NCs.

Tab. S1 The PL decay curves of Mn^{2+} related emission from $CsPb_{1-x}Mn_xCl_3$ NCs were fitted by double exponential function (eqs 1):

$$A(t) = A_0 + A_1\exp(-t/\tau_1) + A_2\exp-(t/\tau_2) \quad \text{(eqs 1)}$$

The average lifetimes (τ_{ave}) were calculated by eqs 2:

$$\tau_{ave} = (A_1\tau_1^2 + A_2\tau_2^2)/ (A_1\tau_1 + A_2\tau_2) \quad \text{(eqs 2)}$$

The fitting results were as follows:

Pb to Mn molar feed ratio	A_1	τ_1 (ns)	A_2	τ_2 (ns)	τ_{ave} (ms)	R^2
0.9:0.1	691.06	423815.16	5364.93	1155975.66	1.12	0.9996
0.7:0.3	969.24	304296.67	5081.68	1072498.28	1.03	0.9996
0.5:0.5	1320.19	389006.18	4611.50	1075653.64	1.01	0.9996
0.3:0.7	2094.22	231726.21	3876.48	905463.16	0.82	0.9995
0.1:0.9	2429.65	215203.00	3511.11	903338.72	0.80	0.9995

Tab. S2 EDS elements analysis results of $CsPb_{1-x}Mn_xCl_3$ NCs synthesized with different $MnAc_2$: $PbAc_2$ molar feed ratios.

Mn to Pb molar feed ratio	Cs: Pb : Mn: Cl	Mn/ (Mn+ Pb)
0.1: 0.9	1: 1.16: 0.02: 3.18	0.017
0.3: 0.7	1: 0.84: 0.16: 3.15	0.160
0.5: 0.5	1: 0.67: 0.29: 2.71	0.302
0.7: 0.3	1: 0.32: 0.45: 2.86	0.584
0.9: 0.1	1: 0.07: 0.54: 2.46	0.885