Supporting Information for

Switching on near-infrared light in lanthanide-doped CsPbCl$_3$ perovskite nanocrystals

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Table S1 Nominal and actual doping concentrations in CsPbCl$_3$ NCs, determined by XRF measurements. The amount of Pb(CH$_3$CO$_2$)$_2$ is fixed at 0.2 mmol.

Nominal ratio	Starting amounts[a]		Actual amounts		
	Mn(CH$_3$CO$_2$)$_3$ (mmol)	Ln(CH$_3$CO$_2$)$_3$ (mmol)	Pb (%)	Mn (%)	Ln (%)
Mn/Pb = 2.5%	0.005	—	99.42%	0.58%	—
Mn/Pb = 5.0%	0.01	—	98.59%	1.41%	—
Mn/Pb = 10%	0.02	—	97.33%	2.67%	—
Mn/Pb = 15%	0.03	—	96.57%	3.43%	—
Er/Pb = 10%	—	0.02	99.45%	—	0.55%
Ho/Pb = 10%	—	0.02	99.60%	—	0.40%
Nd/Pb = 10%	—	0.02	97.66%	—	2.34%
Mn^{2+}–Er^{3+} (2: 1)	0.01	0.005	98.64%	1.27%	0.09%
Mn^{2+}–Er^{3+} (1: 1)	0.01	0.01	98.69%	1.16%	0.15%
Mn^{2+}–Er^{3+} (1: 2)	0.01	0.02	98.73%	1.03%	0.24%
Mn^{2+}–Er^{3+} (1: 4)	0.01	0.04	98.91%	0.71%	0.38%
Mn^{2+}–Ho^{3+} (1: 2)	0.01	0.02	98.97%	0.86%	0.17%
Mn^{2+}–Nd^{3+} (1: 2)	0.01	0.02	93.88%	1.19%	4.93%

[a]The starting amount of Ho might be overestimated considering the x-hydrate [Ho(CH$_3$CO$_2$)$_3$·xH$_2$O] formula of the precursor.
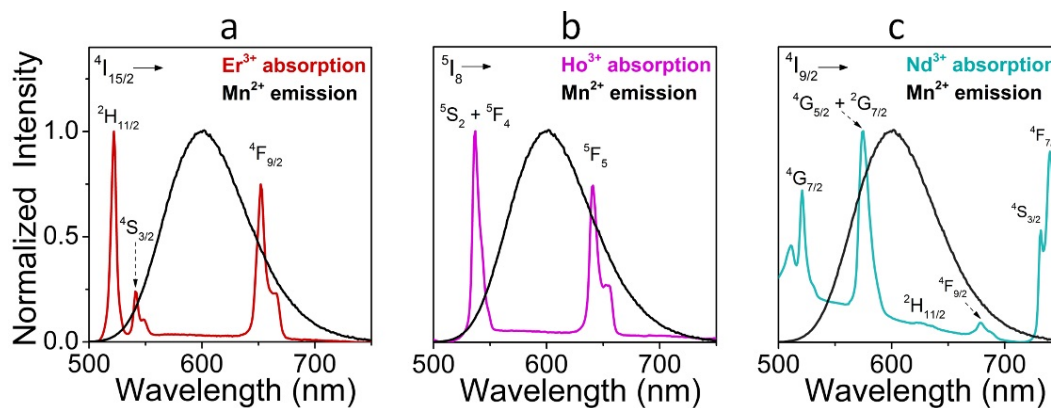
Fig. S1 Spectral overlaps between (a) Mn^{2+} emission and Er^{3+} absorption, (b) Mn^{2+} emission and Ho^{3+} absorption, and (c) Mn^{2+} emission and Nd^{3+} absorption. The Ln^{3+} ions (Er^{3+}, Ho^{3+} and Nd^{3+}) absorption spectra were obtained from 0.05 M lanthanide chloride salts aqueous solution.
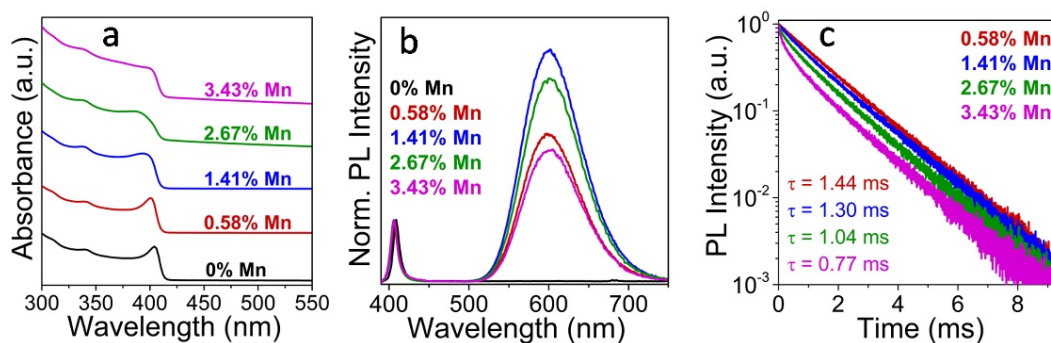
Fig. S2 Optical properties of CsPbCl₃ NCs without and with different doping concentrations of Mn²⁺ ions. (a) Absorption spectra (optical density at first exciton is below 0.3), (b) PL spectra normalized at the band-edge emission, (c) decay curves monitored by the Mn²⁺ $^4T_1 \rightarrow ^6A_1$ transition at 600 nm. The broadening of the band-edge absorption band with increasing Mn²⁺ doping can be attributed to the increased inhomogeneous morphologies of the NCs, as shown in Fig. S3a and b. The decrease in PL intensity and the shortening of the decay dynamics of Mn²⁺ emission in Mn²⁺-doped NCs with increasing Mn²⁺ content (>1.4%) can be attributed to the Mn²⁺–Mn²⁺ coupling interactions and formed defects/traps near the Mn²⁺ ions.[1]
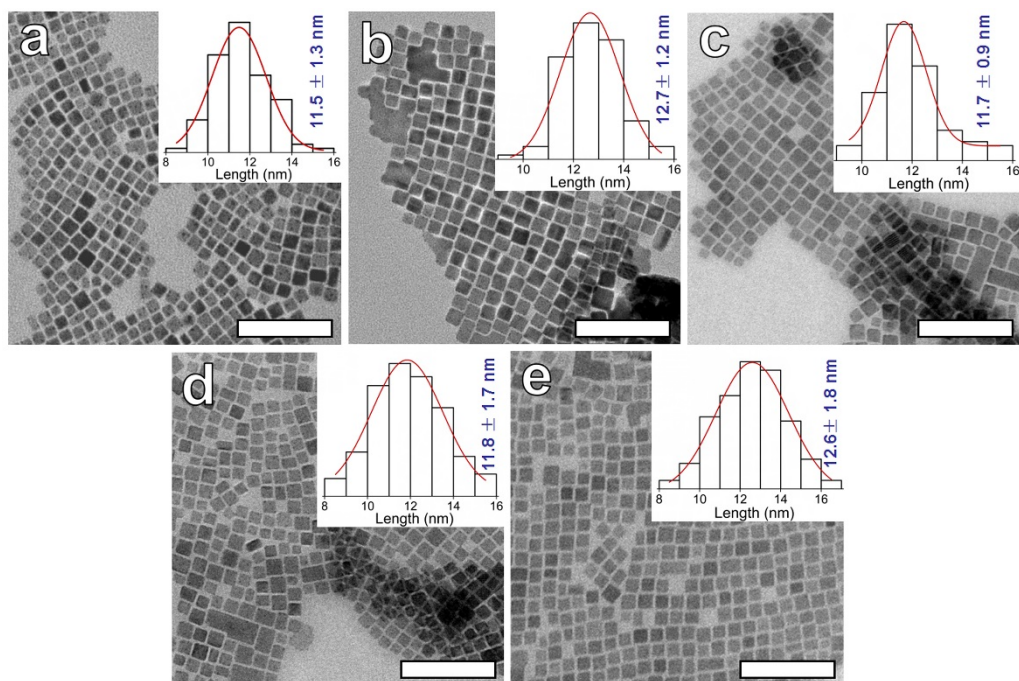
Fig. S3 TEM images of (a) undoped CsPbCl$_3$ NCs, (b) 1.41% Mn^{2+}, (c) 1.03% Mn^{2+}–0.24% Er^{3+}, (d) 0.86% Mn^{2+}–0.17% Ho^{3+}, and (e) 1.19% Mn^{2+}–4.93% Nd^{3+} codoped CsPbCl$_3$ NCs together with the corresponding size distribution histograms. The scale bars are 100 nm.
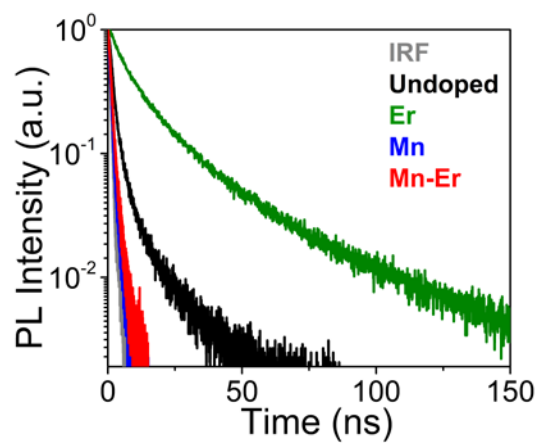
Fig. S4 PL decay curves of undoped and doped $CsPbCl_3$ NCs collected by monitoring the band-edge emission of the $CsPbCl_3$ host (λ_{ex} = 350 nm). The instrumental response function (IRF) was determined to be approximately 0.8 ns by measuring the scattering of a Ludox solution. The BE emission lifetimes of undoped and Er^{3+}-doped NCs are ~2.4 and 12.3 ns, respectively.
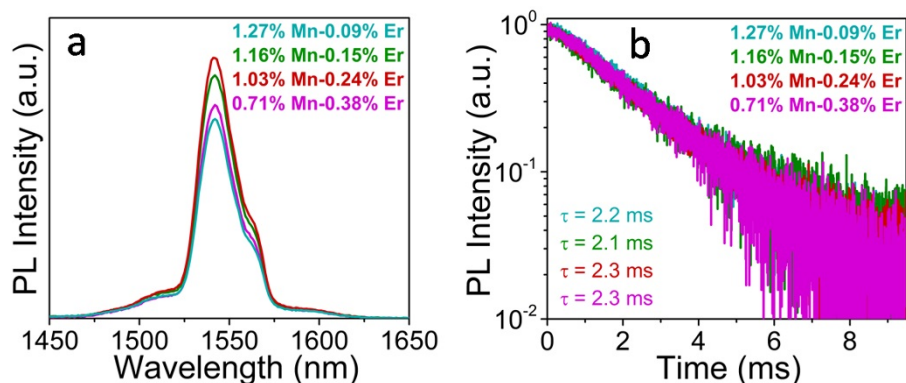
Fig. S5 (a) PL spectra of Mn^{2+}–Er^{3+} codoped $CsPbCl_3$ NCs with different doping concentrations under excitation at 365 nm. It is worth noting that, while maintaining the same nominal amount, the actual Mn^{2+} concentration decreases as the Er^{3+} loading is increased, likely indicating a competition of the two ions for the doping sites. (b) Corresponding PL decay curves collected by monitoring Er^{3+} emission at 1542 nm.

Table S2 Decay parameters of the Mn^{2+} emission at 600 nm in Mn^{2+}-doped, Mn^{2+}–Er^{3+}, Mn^{2+}–Ho^{3+} and Mn^{2+}–Nd^{3+} codoped $CsPbCl_3$ NCs. Average lifetimes: $\tau = \Sigma A_i\tau_i/\Sigma A_{i,}$, where A_i and τ_i represent the amplitude and the lifetime component of the multiple exponential functions by fitting the PL decay curve, respectively; energy transfer efficiency: $\eta = 1\text{-}\tau_{Mn-Ln}/\tau_{Mn}$, where τ_{Mn-Ln} and τ_{Mn} are the lifetimes of Mn^{2+} emission in the presence and absence of Ln^{3+}, respectively.

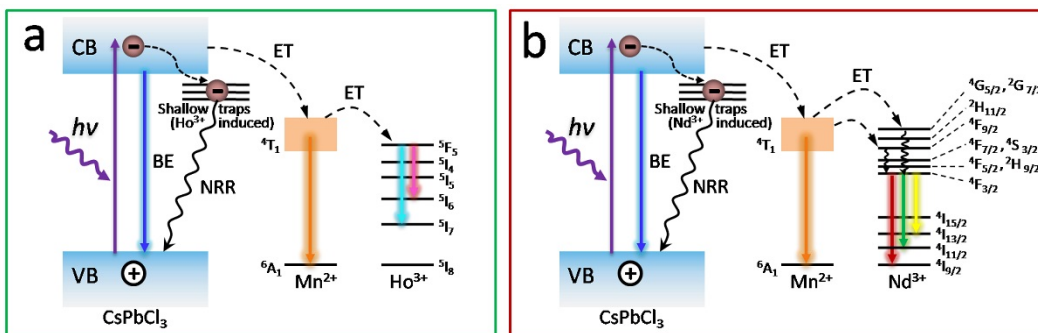| Sample	τ_1 (ms) (A_1)	τ_2 (ms) (A_2)	τ (ms)	η
Mn^{2+}		1.30	1.30	
Mn^{2+}–Er^{3+}	0.27 (0.43)	1.19 (0.57)	0.79	39.2%
Mn^{2+}–Ho^{3+}	0.23 (0.37)	1.21 (0.63)	0.85	34.6%
Mn^{2+}–Nd^{3+}	0.12 (0.65)	0.88 (0.35)	0.39	70.0%

Fig. S6 Schematic energy-level diagram illustrating the possible energy-transfer mechanism in (a) Mn^{2+}–Ho^{3+} codoped $CsPbCl_3$ NCs and (b) Mn^{2+}–Nd^{3+} codoped $CsPbCl_3$ NCs. The vertical blue arrow represents the host band-edge (BE) emission, the vertical orange arrow corresponds to the Mn^{2+} d–d transition, the vertical colorful arrow to the f–f transition of Ho^{3+} and Nd^{3+}, and the zigzag black arrow depicts the nonradiative recombination (NRR). Energy transfer (ET) processes are indicated by dashed black arrows.

Fig. S6 depicts the proposed energy-transfer mechanism in Mn^{2+}–Ho^{3+} and Mn^{2+}–Nd^{3+} codoped $CsPbCl_3$ NCs. The energy-transfer processes from the $CsPbCl_3$ host to the Mn^{2+} ions in both cases are similar. For Mn^{2+}–Ho^{3+} codoped $CsPbCl_3$ NCs, energy is first transferred from Mn^{2+} to the $^5F_5$ excited state of Ho^{3+} and then radiative decay to the $^5I_6$ and $^5I_7$ energy levels occurs giving rise to emission at wavelengths of 986 nm and 1484 nm. For Mn^{2+}–Nd^{3+} codoped $CsPbCl_3$ NCs, the obtained energy in the $^4T_1$ d-state of Mn^{2+} is transferred to the lower $^4G_{5/2}$ and $^4F_{9/2}$ receiving energy levels of Nd^{3+} and then experiences nonradiative relaxation to the $^4F_{3/2}$ emitting level, followed by the radiative emissions at 888 nm, 1064 nm and 1340 nm.

REFERENCES

1 K. Xing, X. Yuan, Y. Wang, J. Li, Y. Wang, Y. Fan, L. Yuan, K. Li, Z. Wu, H. Li and J. Zhao, *J. Phys. Chem. Lett.*, 2019, **10**, 4177-4184.