Electronic Supplementary Information (ESI) for

Solvothermal synthesis of Mn-doped CsPbCl₃ perovskite nanocrystals with tunable morphology and their sizedependent optical properties

Chang Liu,^{a, b} Jing Lin, *, ^{a, b} Wei Zhai,^{a, b} Zhikai Wen,^{a, b} Xin He,^{a, b} Mengmeng Yu,^{a, b} Yang Huang, *, ^{a, b} Zhonglu Guo,^{a, b} Chao Yu, *, ^{a, b} and Chengchun Tang^{a, b}

^a School of Materials Science and Engineering, Hebei University of Technology, Tianjin 300130, P. R. China

^b Hebei Key Laboratory of Boron Nitride Micro and Nano Materials, Hebei University of Technology, Tianjin 300130, P. R. China

*To whom correspondence should be addressed: *E-mail: <u>linjing@hebut.edu.cn</u> (J. Lin)*, *huangyang@hebut.edu.cn* (Y. Huang), <u>yuchao20130426@126.com (</u>C. Yu)



Fig. S1 EDX spectra of Mn-doped CsPbCl₃ QDs prepared with different Mn-to-Pb molar feed ratios: (a) 5:1, (b) 7.5:1, and (c) 10:1. The compositions are $CsPb_{0.94}Mn_{0.06}Cl_3$, $CsPb_{0.85}Mn_{0.15}Cl_3$ and $CsPb_{0.75}Mn_{0.25}Cl_3$, respectively.



Fig. S2 (a) Normalized PL spectra, (b) exciton PL lifetime and (c) Mn^{2+} luminescence lifetime of Mn-doped CsPbCl₃ QDs prepared under different reaction times (with a same Mn-to-Pb molar feed ratio of 5:1 at 120 °C).

Method for the calculation of average lifetime: To reveal the mechanism of luminescence and energy transfer process in Mn-doped CsPbCl₃ NCs, the time-resolved PL spectrum was investigated. As observed in both Mn-doped CsPbCl₃ QDs and NPLs, the lifetimes of Mn²⁺ emission can be fitted by single-exponential relation: $I(t)=A+B*exp(-i/\tau_1)$

while the lifetimes of exciton emission can be fitted well by double-exponential relation: $I(t)=A+B_1*exp(-i/\tau_1)+B_2*exp(-i/\tau_2)$

Thus, the average lifetime of exciton emission τ_{ave} can be calculated as follows:

$$\tau_{ave} = \Sigma_i^n B_i T_i = \Sigma_i^n \frac{B_i}{\sum_{i=1}^n B_i} T_i$$

in which B_i are amplitudes of each components, and τ_1 , τ_2 are the corresponding lifetime constants.¹

Table S1. Summary of PLQYs and PL lifetimes of Mn-doped CsPbCl₃ QDs prepared under different reaction times (with a same Mn-to-Pb molar feed ratio of 5:1 at 120 °C).

Reaction time	PLQY	Exciton avg. lifetime	Mn ²⁺ avg. lifetime
3 h	6%	2.32 ns	1.77 ms
6 h	4.8%	1.66 ns	1.38 ms
9 h	5.9%	2.23 ns	1.44 ms

Table S2. Detailed amplitude and corresponding lifetime data for exciton emission decay curves.

Reaction time	B_1	τ_1 (ns)	B_2	τ_2 (ns)	τ_{ex} (ns)
3 h	0.68	0.58	0.32	6.02	2.32
6 h	0.77	0.44	0.23	5.65	1.66
9 h	0.69	0.55	0.31	5.93	2.23



Fig. S3 (a) TEM and (b) HRTEM image of $CsMnCl_3$ NCs formed by a spinodal decomposition process. The $CsMnCl_3$ NCs exhibit hexagon morphology with sizes of 16-32 nm. The interplanar lattice distance of 3.64 Å corresponds to the (104) plane of h-CsMnCl₃ or the (110) plane of r-CsMnCl₃.



Fig. S4 XRD pattern of the sample prepared after a prolonged reaction time over 12 h (with a Mn-to-Pb molar feed ratio of 10:1), indicating that the host CsPbCl₃ structure was nearly destroyed and phase of CsMnCl₃ was precipitated instead.



Fig. S5 Photographs of Mn-doped CsPbCl₃ QDs prepared with different Mn-to-Pb molar feed ratios (under a 365 nm UV light).



Fig. S6 EDX spectrum of Mn-doped $CsPbCl_3$ NPLs prepared under a solvothermal reaction time of 4.5 h (with Mn-to-Pb feed ratio of 5:1).



Fig. S7 (a) TEM and (b) HRTEM image of ultrathin Mn-doped CsPbCl₃ NPLs with a thickness of 2 nm (using 3 mL of OA and OLA).

Reference

1 A. Sillen, and Y. Engelborghs, Photochem. Photobio., 1998, 67, 475-486.