

Supporting Information

Reverse Synthesis of $\text{CsPb}_x\text{Mn}_{1-x}(\text{Cl}/\text{Br})_3$ Perovskite Quantum Dots from CsMnCl_3 Precursor through Cation Exchange

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Table S1 Tabulation of Cs, Pb, Mn and Cl mole contents from EDX data for CsMnCl₃ precursor NCs and the prepared PQDs with Mn-to-Pb feeding ratio of 1:4 for different reaction times.

Element Sample	Cs	Pb	Mn	Cl
CsMnCl ₃	0.333		0.284	1.143
5 min	0.313	0.106	0.109	0.856
10 min	0.345	0.233	0.071	1.099
30 min	0.322	0.256	0.018	0.979
60 min	0.339	0.277	0.004	0.993

Table S2 Tabulation of Mn: Pb mole ratio from ICP data for CsMnCl₃ precursor NCs and the prepared PQDs with Mn-to-Pb feeding ratio of 1:4 for different reaction times.

Element Sample	Mn (mmol/L)	Pb (mmol/L)	Mn: Pb
CsMnCl ₃	0.556		
5 min	0.413	0.159	0.72:0.28
10 min	0.251	0.313	0.45:0.55
30 min	0.021	0.527	0.04:0.96
60 min	0.007	0.559	0.01:0.99

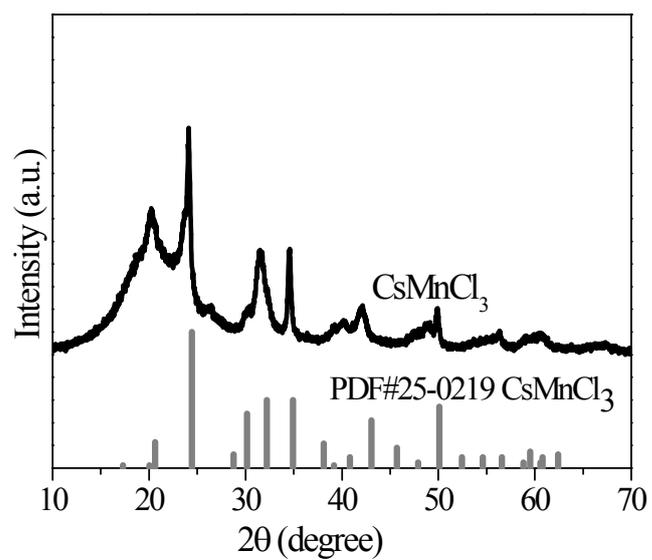


Figure S1 XRD pattern of CsMnCl₃ precursor nanocrystals via a hot injection method.

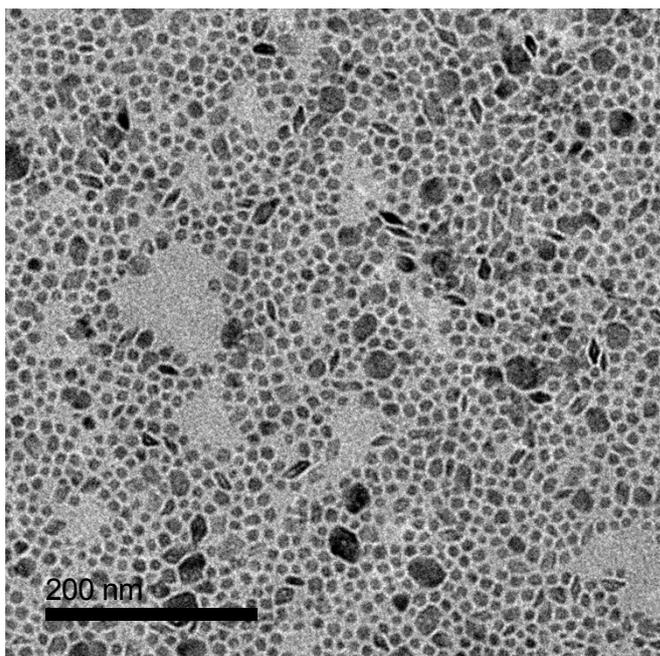


Figure S2 TEM image of CsMnCl_3 precursor nanocrystals via a hot injection method.

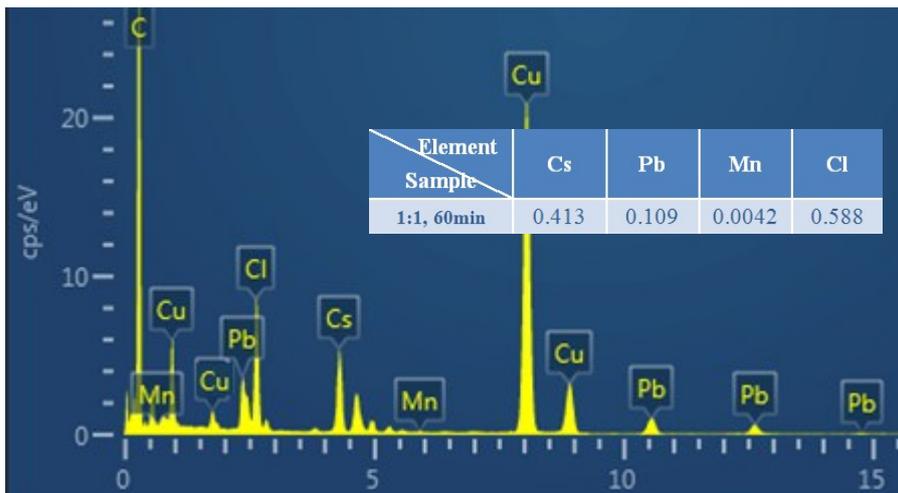


Figure S3 EDX spectrum of $\text{Cs}_4\text{Pb}_x\text{Mn}_{1-x}\text{Cl}_6$ sample with reaction time of 60 min, showing the existence of Cs, Pb, Cl and Mn elemental signals. Inset is the calculated elemental contents with Cs: (Pb+Mn): Cl ratio being close to 4:1:6.

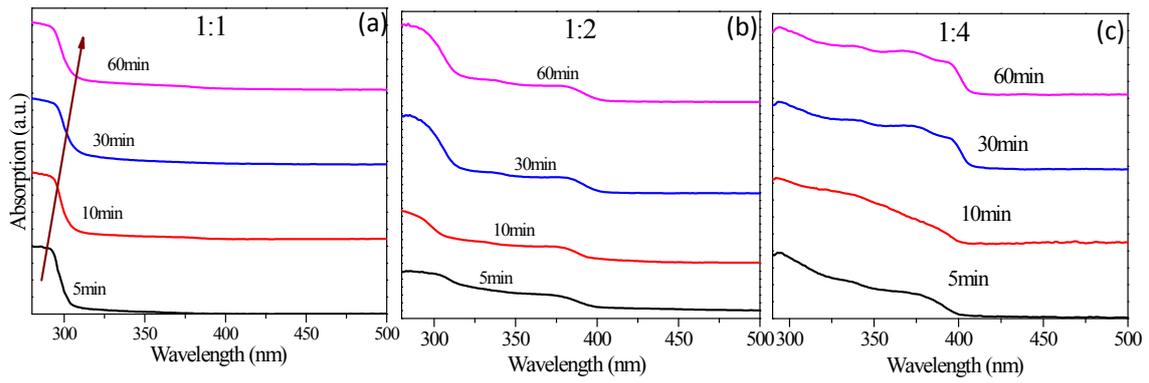


Figure S4 Absorption spectra of the as-prepared products with different Mn-to-Pb feeding ratios for reaction time of 5, 10, 30, 60 min using PbCl_2 as the source for cation exchange: (a) 1:1, (b) 1:2 and (c) 1:4.

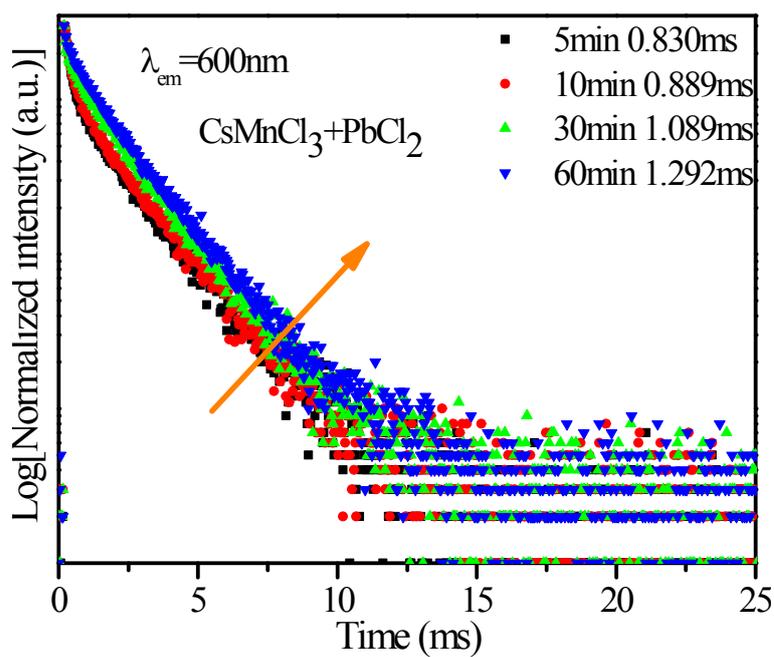


Figure S5 PL decay curves of Mn^{2+} luminescence ($\lambda_{em} = 600\text{ nm}$, assigned to $\text{Mn}^{2+}: {}^4\text{T}_1 \rightarrow {}^6\text{A}_1$ transition) in the $\text{CsPb}_x\text{Mn}_{1-x}\text{Cl}_3$ PQDs synthesized with Mn-to-Pb feeding ratio of 1:2. Evidently, with increase of reaction time, the lifetime of $\text{Mn}^{2+}: {}^4\text{T}_1$ emitting state increases from 0.830 ms to 1.292 ms.

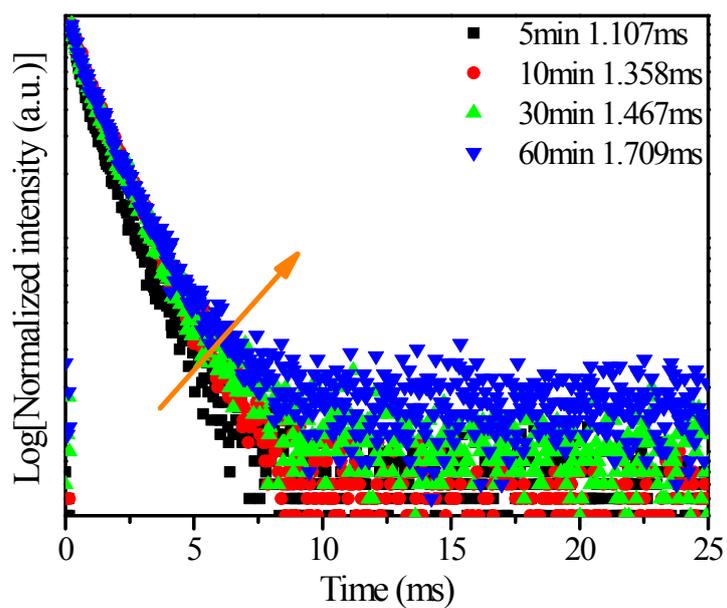


Figure S6 PL decay curves of Mn^{2+} luminescence ($\lambda_{\text{em}}=600$ nm, assigned to $\text{Mn}^{2+}: {}^4\text{T}_1 \rightarrow {}^6\text{A}_1$ transition) in the $\text{CsPb}_x\text{Mn}_{1-x}\text{Cl}_3$ PQDs synthesized with Mn-to-Pb feeding ratio of 1:4. Evidently, with increase of reaction time, the lifetime of $\text{Mn}^{2+}: {}^4\text{T}_1$ emitting state increases from 1.107 ms to 1.709 ms.

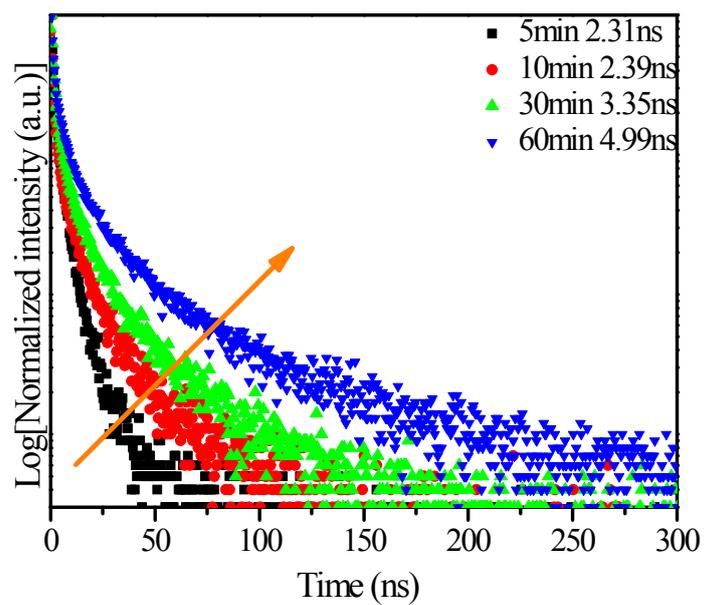


Figure S7 PL decay curves of exciton recombination for CsPb_xMn_{1-x}Cl₃ PQDs synthesized with Mn-to-Pb feeding ratio of 1:4, showing gradual increase of lifetime for PQDs with increase of cation exchange time.

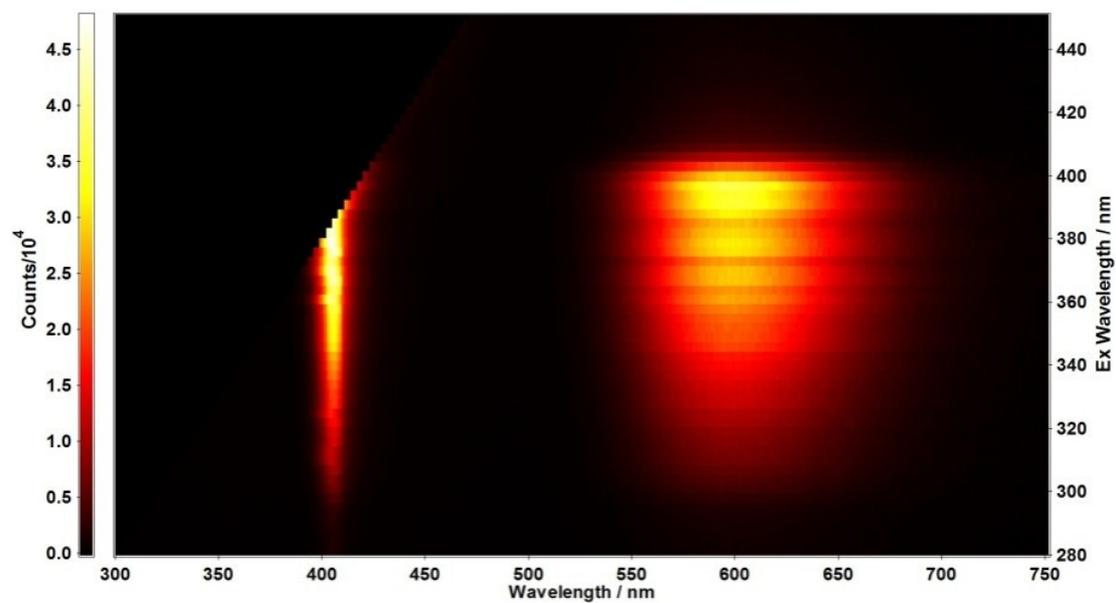


Figure S8 Excitation-emission mapping for the as-prepared CsPb_xMn_{1-x}Cl₃ PQDs with Mn-to-Pb feeding ratio of 1:4 and reaction time of 60 min, showing the excitation wavelength independent emissions for both CsPbCl₃ QDs and Mn²⁺ ions.

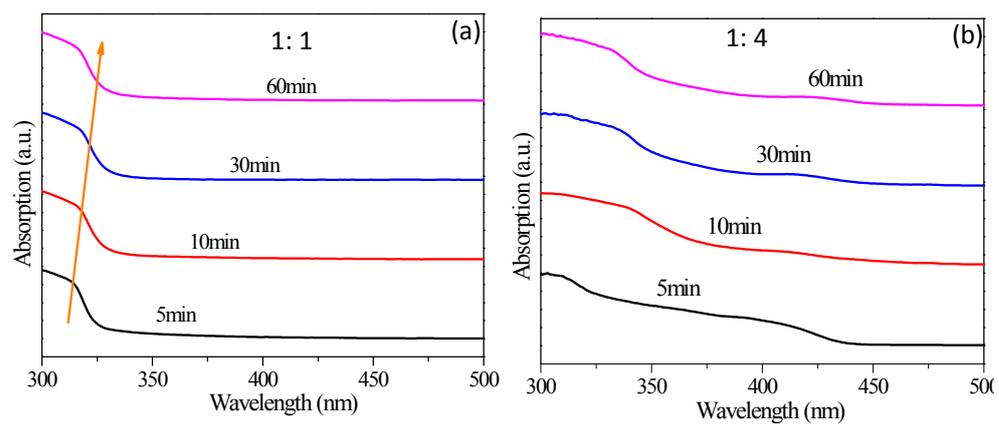


Figure S9 Absorption spectra of the as-prepared products with different Mn-to-Pb feeding ratios for reaction time of 5, 10, 30, 60 min using PbBr_2 as the source for cation exchange: (a) 1:1, (b) 1:4.

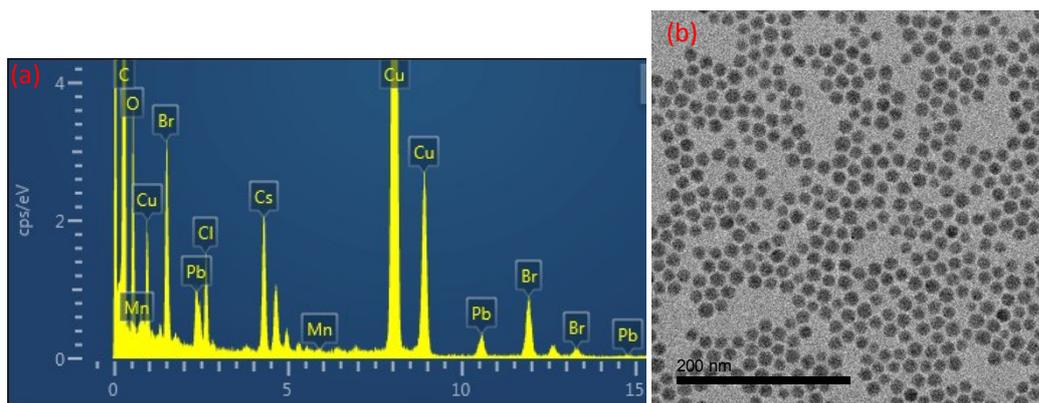


Figure S10 (a) EDX spectrum of $\text{Cs}_4\text{Pb}_x\text{Mn}_{1-x}(\text{Cl}/\text{Br})_6$ sample with Mn-to-Pb feeding ratio of 1:1, Cl-to-Br ratio of 3:2 and reaction time of 60 min, showing the existence of Cs, Pb, Cl, Br and Mn elemental signals. (b) TEM image of $\text{Cs}_4\text{Pb}_x\text{Mn}_{1-x}(\text{Cl}/\text{Br})_6$ sample, exhibiting spherical shape with homogeneous size distribution.

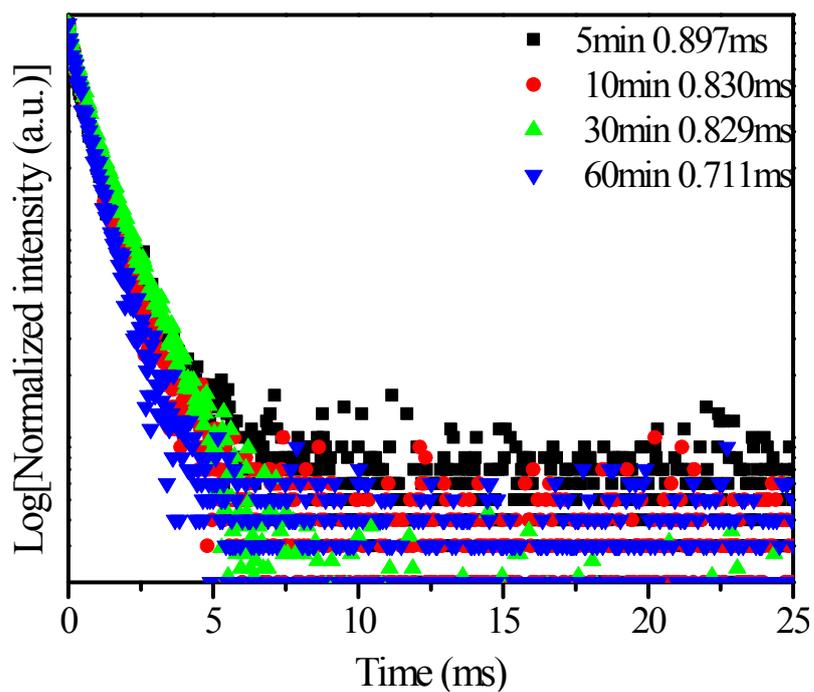


Figure S11 PL decay curves of Mn^{2+} luminescence ($\lambda_{\text{em}}=600$ nm, assigned to $\text{Mn}^{2+}: {}^4\text{T}_1 \rightarrow {}^6\text{A}_1$ transition) in the $\text{CsPb}_x\text{Mn}_{1-x}(\text{Cl}/\text{Br})_3$ PQDs synthesized with Mn-to-Pb feeding ratio of 1:4 using PbBr_2 as the source for cation exchange. Evidently, with increase of reaction time, the lifetime of $\text{Mn}^{2+}: {}^4\text{T}_1$ emitting state decreases from 0.897 ms to 0.711 ms ascribing to gradual change of Mn^{2+} ligand-field from Cl^- octahedron to Br^- dominant one.