Supporting Information

Dopant-Driven 0D-to-3D Phase Transition in Perovskite Nanocrystals via Interfacial Ligand Shuttling

Yi Wei,[a] Yongfei Li,[a] Liang Li,[b] Zhaohui Liu*[a] and Ke Xin Yao*[a]

[a] School of Chemistry and Chemical Engineering, Chongqing University, Chongqing 400044, China. Email: zhaohui.liu@cqu.edu.cn and kexinyao@cqu.edu.cn

[b] Department of Sciences and Engineering, Sorbonne University Abu Dhabi, PO Box 38044, Abu Dhabi, UAE

*Corresponding author E-mail: zhaohui.liu@cqu.edu.cn and kexinyao@cqu.edu.cn

Materials and Methods

I. Chemicals.

Cesium acetate (Cs_2CO_3, 99.99%), oleic acid (OA, AR), oleylamine (OAm, 80-90%), Octadecene (ODE, 90%), $PbBr_2$ (99.999%), $PbCl_2$ (99.999%), hydrobromic acid (HBr, 48%), $MnCl_2$•$4H_2O$ (99.99%), $MnBr_2$•$4H_2O$ (98%), 1-Butylamine (≥99%), 1-Octylamine (99%), 1-Dodecanamine (98%) and 3-Aminopentane (≥98%) were purchased from Aladdin. Aniline (≥99.5%) were purchased from Macklin. N,N-dimethylformamide (DMF, 99.5%) was purchased from Chengdu Kelong Chemical Co., Ltd. (Chengdu, China). n-Hexane (97%) and hydrochloric acid (HCl, 36-38%) were purchased from Chuandong Chemical Co., Ltd. (Chongqing, China). All chemicals were directly used without further purification.

II. Synthesis of precursor.

Cs-cleate (Cs-OA) stock solution: 0.45 g of Cs_2CO_3 was mixed with 4.3 mL of OA and degassed by stirring under vacuum at 100°C for 1 h to generate a yellowish stock of Cs-OA precursor. The Cs-OA was stored at room temperature.

$PbBr_2$ stock solution: A mixture of 0.011 g $PbBr_2$, 1 mL DMF, 15 μL HBr, 0.1 mL OA, and 0.05 mL OAm was set aside.

$PbCl_2$ stock solution: A mixture of 0.0083 g $PbCl_2$, 1 mL DMF, 15 μL HCl, 0.1 mL OA, and 0.05 mL OAm was set aside.

Cs_4PbBr_6 NCs: Firstly, 0.2 mL of Cs-OA precursor, 5 mL of OA were loaded into a 50 mL three-neck flask, which was degassed and purged with nitrogen at room temperature, and then 10 mL of hexane was added. Subsequently, the $PbBr_2$ precursor was rapidly injected into the flask with vigorous stirring for 10 min. The synthesized NCs were centrifuged at 8000 rpm for 3 min and then dispersed in 8 mL of hexane.

Cs_4PbCl_6 NCs: $PbBr_2$ was replaced by an equimolar amount of $PbCl_2$ in the above-described Cs_4PbBr_6 NCs synthesis, with all other conditions kept the same.

Saturated aqueous solution of $MnCl_2$: Dissolve 1.1622 g of $MnCl_2$•$4H_2O$ in 1 mL of deionized water and store at room temperature.

Saturated aqueous solution of $MnBr_2$: Dissolve 1.9503 g of $MnBr_2$•$4H_2O$ in 1 mL of deionized water and store at room temperature.

Saturated aqueous solution of $PbCl_2$: Dissolve 0.0100 g of $PbCl_2$ in 1 mL of deionized water and store at room temperature.

III. Post-synthetic ion exchange reaction

Mn^{2+} treated Cs_4PbBr_6 NCs: In the first step, 50 μL of a saturated aqueous solution of manganese salts (MnX_2, X=Br, Cl) was added to 2 mL of hexane containing OAm. The mixed solution was shaken for 30 s and then the hexane solution of the upper phase was centrifuged in a tube at 9000 rpm for 5 min. The hexane solution of the upper phase containing MnX_2 was retained for further use and the precipitate was discarded. Then, 1 mL of hexane containing MnX_2 prepared in the first step was mixed with 1 mL of prepared Cs_4PbBr_6 NCs and stirred.

Mn^{2+} treated Cs_4PbCl_6 NCs: The same doping method described above was applied, except that Cs_4PbCl_6 NCs was used in place of Cs_4PbBr_6 NCs.

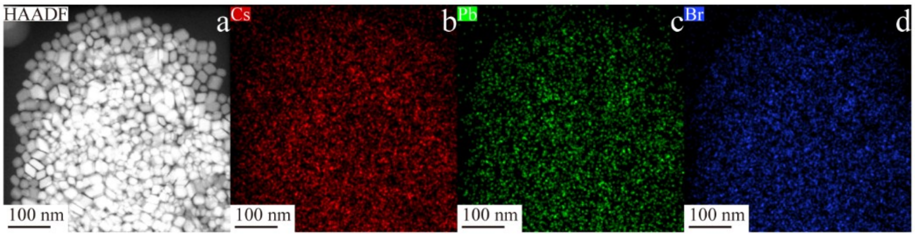
Pb^{2+} treated Cs_4PbBr_6 NCs: The same doping method described above was applied, except that the saturated aqueous solution of manganese salt (MnX_2, X = Br, Cl) was replaced by the saturated aqueous solution of $PbCl_2$.

IV. Synthesis of $CsPbBr_3$ NCs

In a typical synthesis[1], 5 mL of ODE and 0.069 g of $PbBr_2$ were loaded into a 25 mL three-necked flask. The mixture was dried under vacuum for 1 hour at 120 °C. Subsequently, 0.5 mL of OAm and 0.5 mL of OA were injected at 120 °C under N_2. After complete solubilisation of $PbBr_2$, the temperature was raised to 160 °C, followed by the quickly injection of 0.4 mL of a Cs-oleate precursor solution. This precursor was prepared by dissolving 0.814 g of Cs_2CO_3 and 2.5 mL of OA in 40 mL of ODE, followed by vacuum drying. The reaction was allowed to proceed for 5 s before being cooled by the ice-water bath. The as-synthesized NCs were collected by centrifugation at 6000 rpm for 5 minutes and subsequently dispersed in hexane.

V. Materials Characterization.

Transmission electron microscopy (TEM) images were obtained with a Talos F200S operated at 200 kV. Specimens for the TEM images were prepared by dropping a drop of diluted dispersed solution of nanocrystals in hexane on a carbon-coated copper grid or Nano-Chip. Patterns of nanocrystal samples were obtained using a PANalytical Instrument with Cu Kα. All XRD samples were prepared by drop casting a concentrated solution on a zero diffraction silicon wafer. Ultraviolet visible (UV-vis) absorption spectra were taken by using a UV-vis spectrophotometer (UV-3600, Shimadzu). Photoluminescence (PL) spectra were measured with a fluorescence spectrophotometer (RF-6000). TRPL spectra were collected by Edinburgh fluorescence spectroscopy (FLS1000) with an EPL-375 light source. For UV-vis absorption, PL and PL lifetime measurements, the sample was dispersed in hexane and taken in a cuvette. Elemental analysis was used to determine the elemental contents of Mn and Pb using a Thermo ICAP PRO inductively coupled plasma-optical emission spectrometer (ICP-OES). Fourier transform infrared spectroscopy (FTIR) measurements were performed on Fourier Transform Infrared Spectrometer (Nicolet iS50) with an ATR attachment.



Supporting Figures

Fig. S1 (a) HAADF-STEM image of original Cs_4PbBr_6 NCs and the corresponding elemental mappings of (b) Cs, (c) Pb and (d) Br.

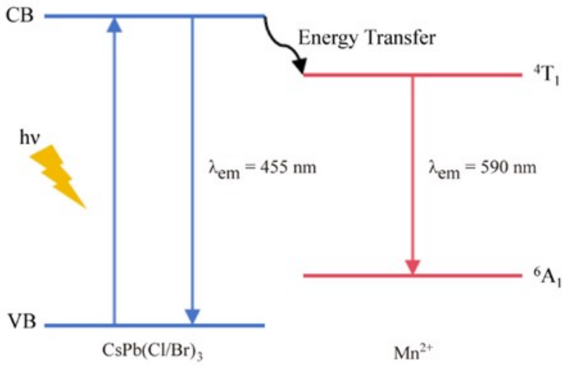


Fig. S2 Energy level diagram of the NCs following Mn^{2+} doping.

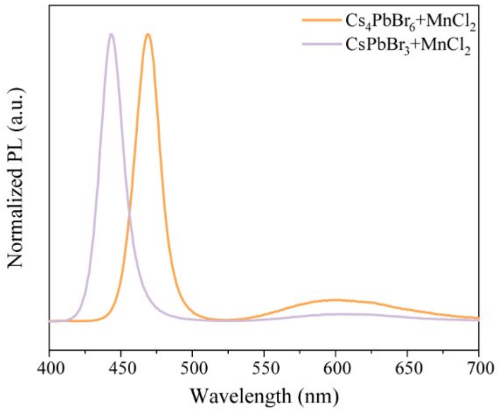


Fig. S3 The PL spectra of $MnCl_2$-treated Cs_4PbBr_6 NCs and $CsPbBr_3$ NCs were measured after a post-treatment reaction time of 10 min.

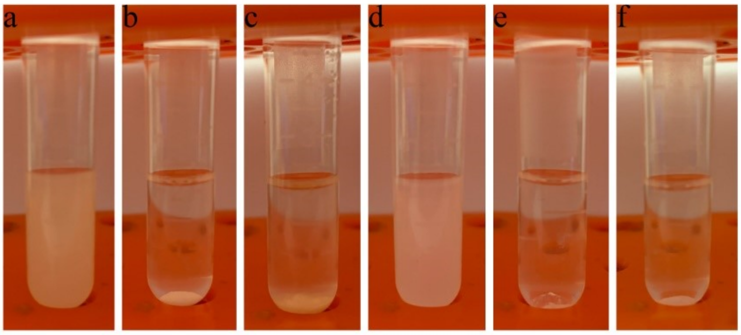


Fig. S4 Photographs of doped precursors prepared using different kinds of amines, including (a) OAm, (b) 1-Butylamine, (c) 1-Octylamine, (d) 1-Dodecanamin, (e) Aniline, (f) 3-Aminopentane.

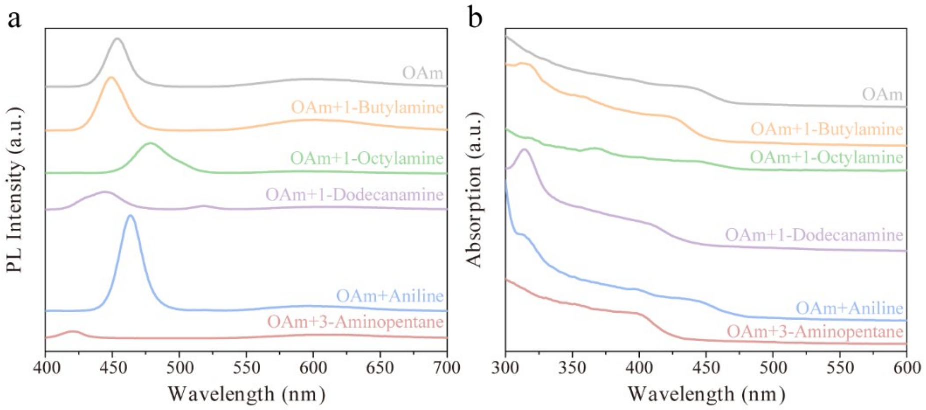


Fig. S5 (a) PL and (b) UV-Vis spectra of the post-synthetic samples after using both OAm and another amine in the preparation of the doped precursors.

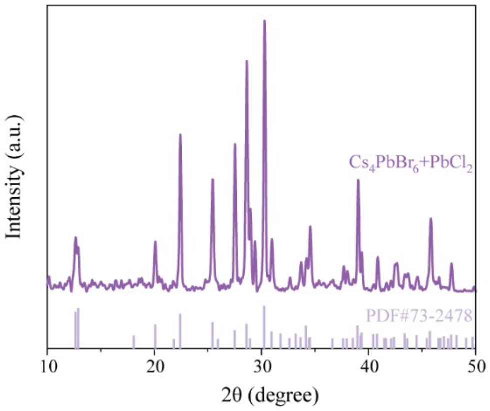


Fig. S6 XRD spectrum of $PbCl_2$ treated Cs_4PbBr_6 NCs.

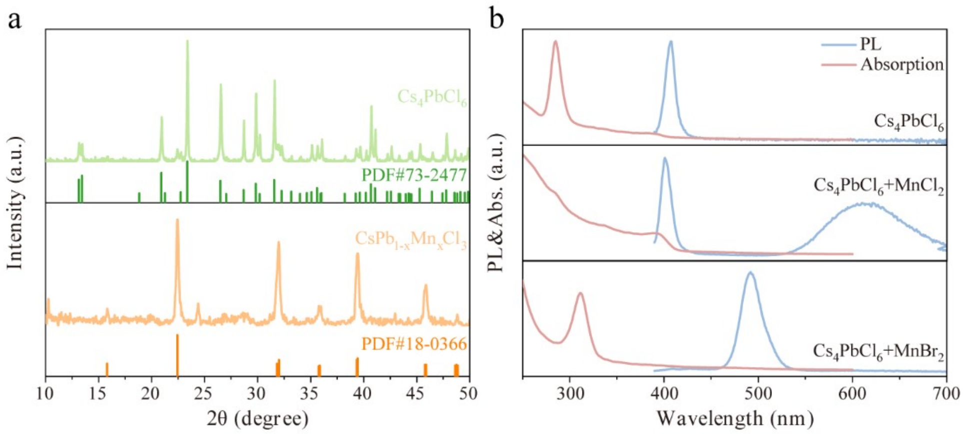


Fig. S7 (a) XRD spectra of Cs_4PbCl_6 NCs before (green) and after (orange) Mn^{2+} doping. (b) PL and UV-Vis spectra of original Cs_4PbCl_6 NCs, $MnCl_2$ treated Cs_4PbCl_6 NCs and $MnBr_2$ treated Cs_4PbCl_6 NCs.

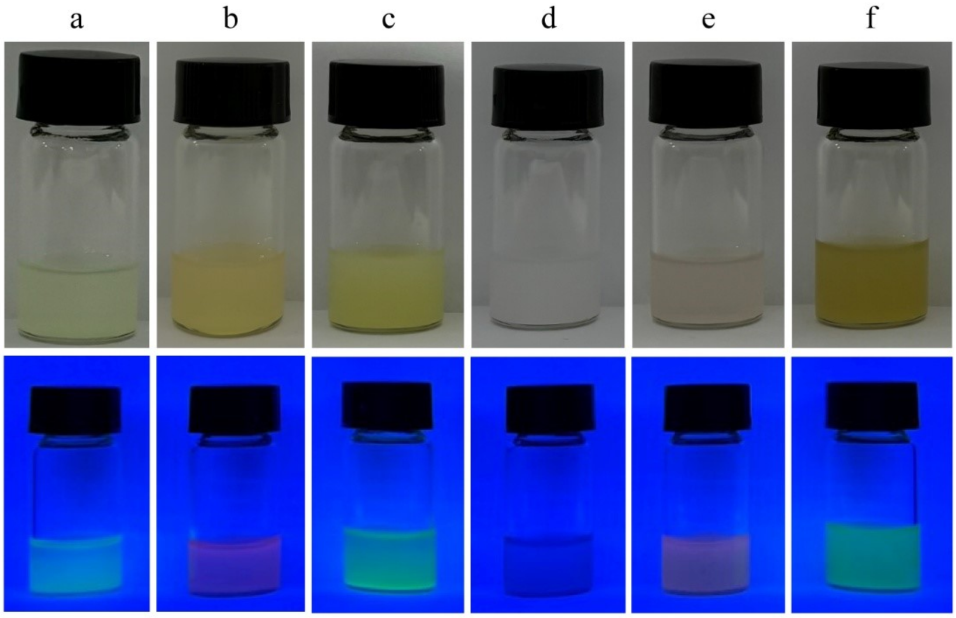


Fig. S8 Photographs of the samples under irradiation with and without UV lamps, the upper picture is without UV lamps and the lower picture is under UV lamps with a wavelength of 395 nm for (a) original Cs_4PbBr_6 NCs, (b) $MnCl_2$ treated Cs_4PbBr_6 NCs, (c) $MnBr_2$ treated Cs_4PbBr_6 NCs, (d) original Cs_4PbCl_6 NCs, (e) $MnCl_2$ treated Cs_4PbCl_6 NCs, (f) $MnBr_2$ treated Cs_4PbCl_6 NCs.

Table S1. Fitted parameters of the PL decay curves.

Sample Name	Emission Wavelength	A_1	τ_1	A_2	τ_2	τ_{ave}
Cs_4PbBr_6 NCs	λ_{em}=515 nm	154089.219	3.876 ns	811.974	22.740 ns	4.44 ns
$CsPb_{1-x}Mn_x(Cl/Br)_3$ NCs	λ_{em}=455 nm	2000.133	11.334 ns	2.284×10^7	2.035 ns	2.04 ns
	λ_{em}=590 nm	556.343	0.196 ms	815.700	0.694 ms	0.61 ms

Notes and references

1 L. Protesescu, S. Yakunin, M. I. Bodnarchuk, F. Krieg, R. Caputo, C. H. Hendon, R. X. Yang, A. Walsh and M. V. Kovalenko, *Nano Lett.*, 2015, **15**, 3692-3696.