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Supporting Information

How Organic Ligands Affect the Phase Transition and Fluorescent

Stability of Perovskite Nanocrystals

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Experiment Section

Chemicals.

All chemicals, including Cs_2CO_3 (Aladdin, 99.9%), PbBr₂ (Aladdin, 99%), oleylamine (OAm) (Aladdin, 80-90%), oleic acid (OA, Aladdin, AR), octadecene (ODE, Aladdin, 90%), and toluene (Sinopharm, AR) were commercially available and used as received without further purification.

Preparation of Cs-oleate solution.

To obtain Cs-oleate solution, 0.326 g of Cs₂CO₃, 2 mL of OA, and 18 mL of ODE were loaded in a 50 mL 3-neck flask and heated to 150 °C under nitrogen flow until all the powder was dissolved absolutely.

Synthesis of perovskite NCs.

We adopted a synthetic method reported by Protesescu et al. with some modifications.^{S1} 0.147 g of PbBr₂ (0.4 mmol), different feeding volume ratios of OA and OAm (8:1, 4:1, 2:1, 1:1, 1:2, 1:4, 1:8) and 10 mL of ODE were loaded in a 50 mL 3-neck flask. The mixture was heated to 120 °C until all the powder was dissolved absolutely under nitrogen atmosphere, then the temperature of the solution was increased to 160 °C, and 1 mL of Cs-oleate solution was swiftly injected into the optically transparent precursor solution. After 0.5 h from the injection, the heating mantle was removed and the flask was rapidly cooled down in a water bath. Other preparation processes mentioned in other sections of the text are similar to the above description, just one or several conditions changed.

Purification of NCs.

After the reaction, crude reaction solution was centrifuged for 3 min at 8000 rpm. After the centrifugation, the supernatant was discarded and the precipitates were redispersed in 10 mL of toluene. After the NCs were completely dispersed in toluene, the solution was centrifuged for 5 min at 10000 rpm. After that, the supernatant was discarded and the NC precipitates were redispersed in 10 mL toluene, which was used for further characterization.

Characterization.

The Photoluminescence (PL) and Ultraviolet and visible absorption (UV-vis) spectra were recorded

using a Shimadzu RF-5301PC fluoremeter (Japan) and a Biomate 3S spectrophotometer (Thermo Fisher, USA), respectively. The transmission electron microscope (TEM) images and high-resolution TEM (HRTEM) data were acquired with a JEM-2100 TEM (JEOL, Japan). The scanning electron microscope (SEM) images and energy dispersive spectrometer (EDS) were measured by a Zeiss Ultra Plus SEM (Zeiss, Germany). Powder X-ray diffraction (XRD) patterns were recorded with a D8-ADVANCE diffractometer (Cu Ka radiation; 40 kV, 60 mA). Fourier transform infrared spectroscopy (FTIR) was performed using a Thermo scientific Nicolet iS5 FT-IR spectrometer. ¹H NMR spectra were recorded on a Bruker Avance III HD 600 MHz NMR spectrometer operating at a ¹H frequency of 600 MHz and equipped with a CP/MAS probe. The relative PLQY of greenemitting NCs was estimated by using quinine sulfate as standard reference according to the literature.^{\$2}



Figure S1. SEM images of perovskite NCs prepared with volume ratios of OA and OAm 4:1 (a), 2:1 (b); TEM images of the perovskite NCs prepared with volume ratios of OA and OAm 1:2 (c); 1:4 (d).



Figure S2. SEM images of NCs prepared with the ratio of OA and OAm 8:1 at 120 °C for 4 h (a); the ratio of OA and OAm 8:1 at 140 °C for 2 h (b); the ratio of OA and OAm 4:1 at 160 °C for 1 h (c); the ratio of OA and OAm 1:1 at 180 °C for 1 h (c);



Figure S3 The XRD patterns of generated NCs with different ratio of OA and OAm: (a) CsPbCl₃ NCs; (b) CsPbI₃ NCs.



Figure S4. The SEM images of NCs prepared with different ratios of OA and OAm, stored in the crude solutions for one month: fresh NCs of 8:1 (a), 4:1 (c), 1:1 (e), 1:4 (g), 1:8 (h); after stored NCs of 4:1 (d), after stored NCs of 8:1 (b), 4:1 (d), 1:1 (f), 1:4 (h), 1:8 (j); the corresponding photos of NCs' solution under UV light were inserted.



Figure S5 XRD pattern of the decomposed NCs induced by excess OAm.



Figure S6. PL intensity changes of reheated NCs with different temperatures (a) and reaction times (b).



Figure S7. Photos of solution containing PbBr₂ and organic ligands in ODE at 120 °C for 40 min: only OA (a), only OAm (b), mixture of OA and OAm (c); SEM image (d) and EDS (e) of the products of OAm and PbBr₂ reacted for 40 min.

OA/OAm	Cs (%)	Pb (%)	Br (%)
8:1	11.8	23.7	64.5
4:1	12.8	22.8	64.4
2:1	15.2	20.0	64.8
1:1	14.9	16.9	68.2
1:2	17.0	18.2	66.0
1:4	16.8	19.2	64.0
1:8	16.5	19.6	63.9

Table S1. Atomic ratios of NCs with different ratio of OA/OAm

Table S2. EDS of NCs prepared with the ratio of OA and OAm 1:8

	Cs (%)	Pb (%)	Br (%)
Fresh	16.5	19.6	63.9
After one month	11.8	29.2	59.0
Reheated	19.6	18.8	61.6

Table S3. The effect of temperature to the reaction of OAm with PbBr₂

ODE	OAm	PbBr ₂	Time	Temp.	Atomic ratio of Pb	Atomic ratio of Br
(mL)	(mL)	(mmol)	(min)	(°C)	(%)	(%)
10	1	0.2	40	40	37.8	62.2
10	1	0.2	40	80	25.0	75.0
10	1	0.2	40	120	46.0	54.0
10	1	0.2	40	160	31.2	68.8

References

- S1 Protesescu, L.; Yakunin, S.; Bodnarchuk, M. I.; Krieg, F.; Caputo, R.; Hendon, C. H.; Yang, R. X.; Walsh, A.;
 Kovalenko, M. V., Nanocrystals of Cesium Lead Halide Perovskites (CsPbX₃, X = Cl, Br, and I): Novel
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- S2 Rao, L.; Tang, Y.; Yan, C.; Li, J.; Zhong, G.; Tang, K.; Yu, B.; Li, Z.; Zhang, J. Z., Tuning the emission spectrum of highly stable cesium lead halide perovskite nanocrystals through poly(lactic acid)-assisted anion-exchange reactions. *Journal of Materials Chemistry C* **2018**, *6*, 5375-5383.