Electronic Supporting Information (ESI)

Formation of Highly Luminescent Cesium Bismuth Halide Perovskite Quantum Dots Tuned by Anion Exchange

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Experimental Section

Chemicals. Chemicals used include bismuth tribromide (99%, Alfa Aesar), cesium bromide(99.9%, Meryer), n-octylamine (OA, 99%, Mecklin), n-octane(96%, Mecklin), Ethyl acetate(AR, Sinopharm Chemical Reagent Co., Ltd, China), diethyl ether(≥99.7%, Sinopharm Chemical Reagent Co., Ltd, China), N,N-dimethylformide(AR, Sinopharm Chemical Reagent Co., Ltd, China), ethanol anhydrous (AR, Sinopharm Chemical Reagent Co., Ltd, China), dimethyl sulfoxide (99%, Aladdin), oleic acid (90%, Aladdin), hydrochloric acid (HCl, 37wt% in water, Aladdin), hydroiodic acid (HI, 57wt% in water, Aladdin), and hydrobromic acid (HBr, 48wt% in water, Aladdin). All chemicals were purchased from commercial vendors and utilized as supplied.

Synthesis of octylammonium halide (OA-X, X = Cl, Br or I). The reaction was achieved by reaction of the octylamine with the hydrohalic acid (HBr for instance).[1] 42mmol of n-octylamine was added to 50 ml of ethanol stirred in a single-neck round bottom flask cooled in an ice-bath. And then a slight excess of hydrobromic acid (45mmol) was dropped into the reaction solution using a separating funnel. It was required to proceed for 2 hours at least under ambient conditions with room temperature to achieve a complete reaction. The snow-white octylammonium bromide powder was obtained by the application of rotary evaporation to remove the volatiles from the products. Then the solids were washed with diethyl ether three washing cycles at least and dried under vacuum before being transferred into an argon-filled glovebox for future use.

Fabrication of the $Cs_3Bi_2X_9$ QDs. In order to synthetize the $Cs_3Bi_2Br_9$ QDs，0.2 mmol CsBr was dissolved in 1mL DMSO while 0.13 mmol $BiBr_3$ and 0.25 mmol OA-Br was respectively dissolved in 1 mL ethyl acetate and 1 mL DMF, then the mixture of the three as-prepared solution formed a precursor solution for following synthesis. 0.7 mL precursor solution was injected swiftly into a 50 mL single-neck flask loaded with 5 mL octane and 0.625 mL oleic acid, under vigorous stirring. As a typical collaborative solvent ligand-assisted re-precipitation (Co-LARP) reaction, the reprecipitation strategy was realized by simply injecting the mixture solution into a poor solvent (octane) containing oleic acids at room temperature. It is expected to be characteristic of the ionic metathesis reaction with fast nucleation and growth kinetics.[2] The complete crystallization of the target product can be achieved within a few seconds at room temperature and a pale-yellow colloidal solution was observed. Afterwards, the precipitate was separated by a centrifugation at 6000 rpm for 10 min and a clear light yellow colloidal nanostructures supernatant was obtained for further post-synthesized exchange experiments. The precipitate was washed with octane and centrifuged at 7000 rpm for 10 min to obtain substrate dried in the vacuum oven at 60 °C in the following.

$Cs_3Bi_2Cl_9$ QDs and $Cs_3Bi_2I_9$ QDs were fabricated by anion exchange reaction: 0.25 mmol octylammonium bromide (OA-Br) or octylammonium iodide (OA-I) was dissolved in 2.5 mL DMF, forming a 0.1 M solution, as the halide source for following anion exchange. 650 or 500 μL OA-Cl or OA-I was added into the as-prepared colloidal $Cs_3Bi_2Br_9$ QDs solution to obtain $Cs_3Bi_2Cl_9$ and $Cs_3Bi_2I_9$ QDs. PL spectra can be used to monitor the exchange process and reduced amount of halide source brought alloying $Cs_3Bi_2X_9$ perovskites**.**

Characterization. The UV-Vis absorption spectra of the synthesized QDs dispersed in n-octane was carried on a Varian Cary 5000 UV-Vis near infrared (NIR) spectrophotometer. PL measurements were taken using a Fluoromax-4 fluorescence spectrometer (Horiba) at room temperature. The data about crystal structure was examined on a Rigaku Smartlab (3) diffractometer, using a Cu Kα source and operating at 40 kV and 40 mA. Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) images were recorded using a JEM-2100 machine at an acceleration voltage of 200 kV. The FluoroLog-3 TCSPC (Horiba Jobin Yvon Inc) spectrofluorometer was utilized to examine the time resolved photoluminescence decays and photoluminescence quantum yield.

Table S1. Summary of PLQYs and emission peaks for colloidal $Cs_3Bi_2X_9$ QDs with different halide compositions.

QDs	PLQY (%)	PL Peak (nm)	FWHM (nm)
$Cs_3Bi_2Cl_9$	62	380	57
$Cs_3Bi_2Br_9$	22	411	38
$Cs_3Bi_2I_9$	2.3	526	76

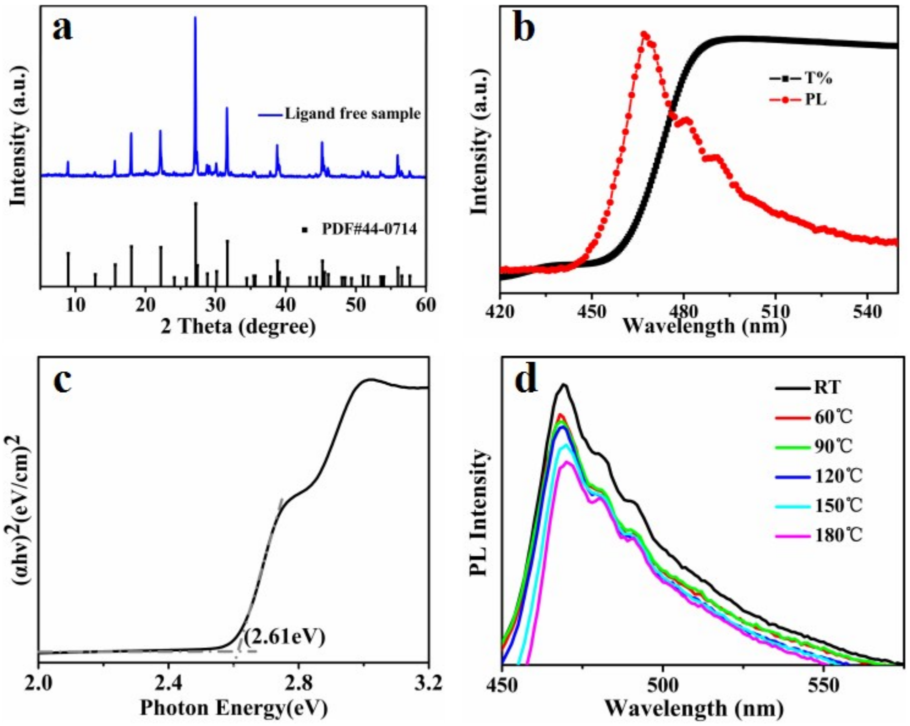

Figure S1. Properties of ligand-free $Cs_3Bi_2Br_9$ sample: (a) Powder XRD spectra. (b) Transmission (black) and PL (red) spectra. (c) Tauc plot (direct; n=2). (d) The fluorescence spectra of ligand-free $Cs_3Bi_2Br_9$ dissolved in isopropanol solution where the powder of $Cs_3Bi_2Br_9$ was heated for 1 h from room temperatures (RT) to 180 °C and then re-dissolved in isopropanol.

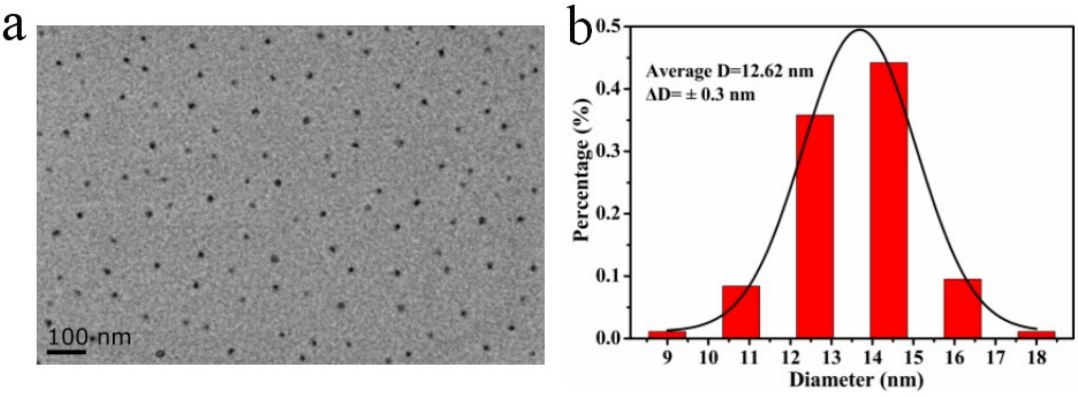

Figure S2. TEM image (a) and the corresponding size distribution histogram (b) of the $Cs_3Bi_2Br_9$ samples without ligands.

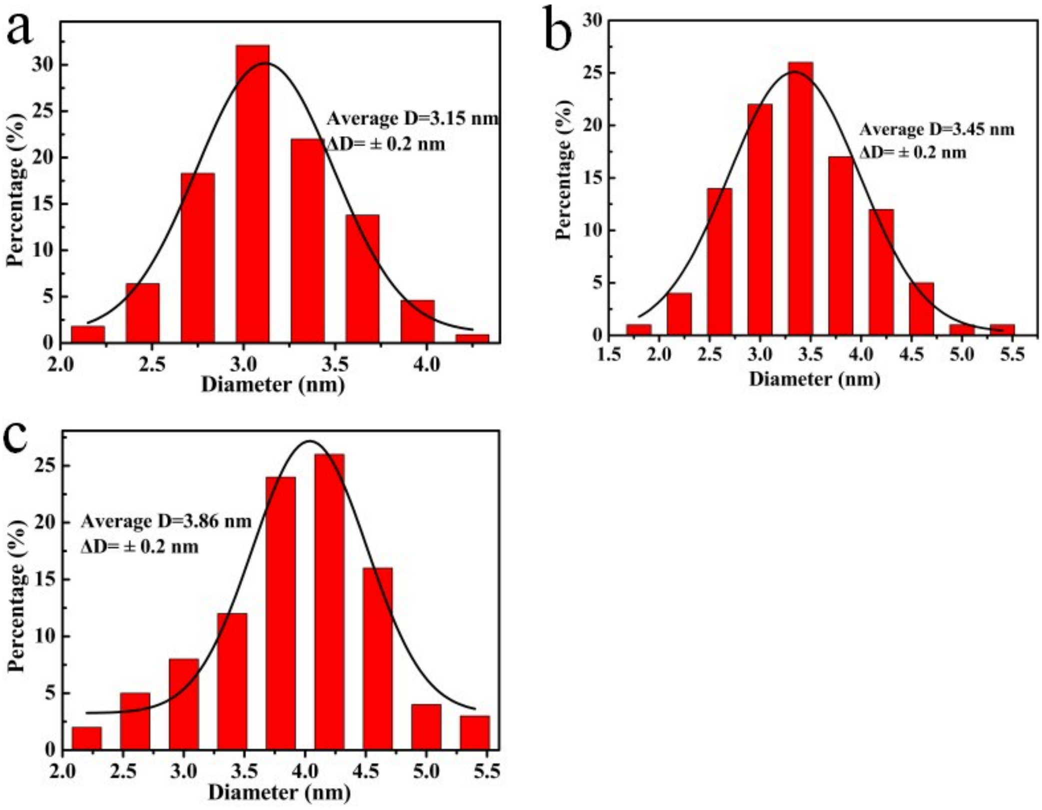

Figure S3. The corresponding size distribution histograms of the post-synthesized $Cs_3Bi_2Cl_9$ (a), as-synthesized $Cs_3Bi_2Br_9$ QDs (b), and the post-synthesized $Cs_3Bi_2I_9$ QDs (c).

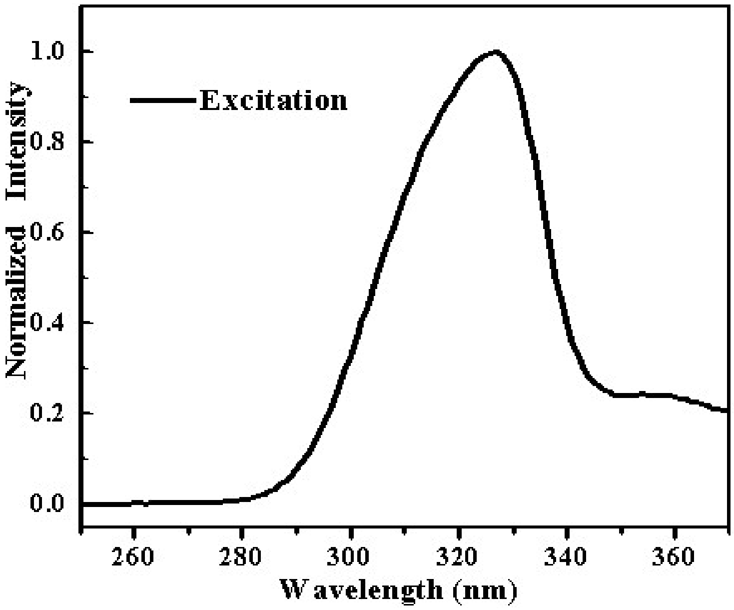

Figure S4. Excitation spectrum of as-synthesized $Cs_3Bi_2Br_9$ QDs.

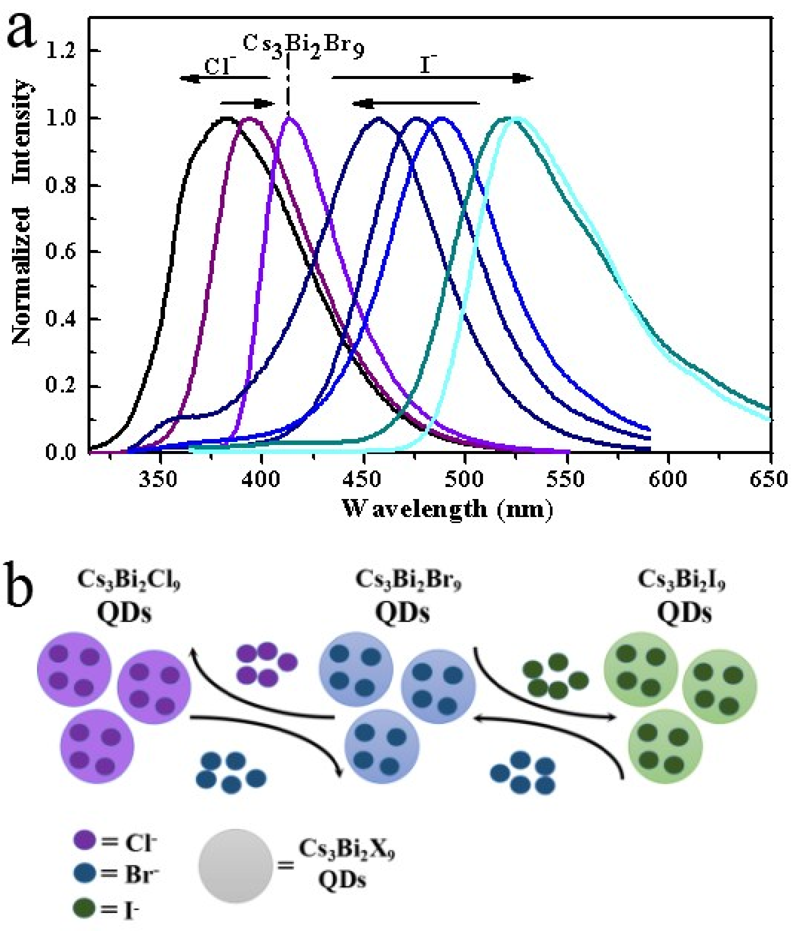

Figure S5. (a) Reversible fluorescence regulation of $Cs_3Bi_2X_9$ QDs from anion exchange reaction. (b) Sketch of the anion exchange between the $Cs_3Bi_2X_9$ QDs.

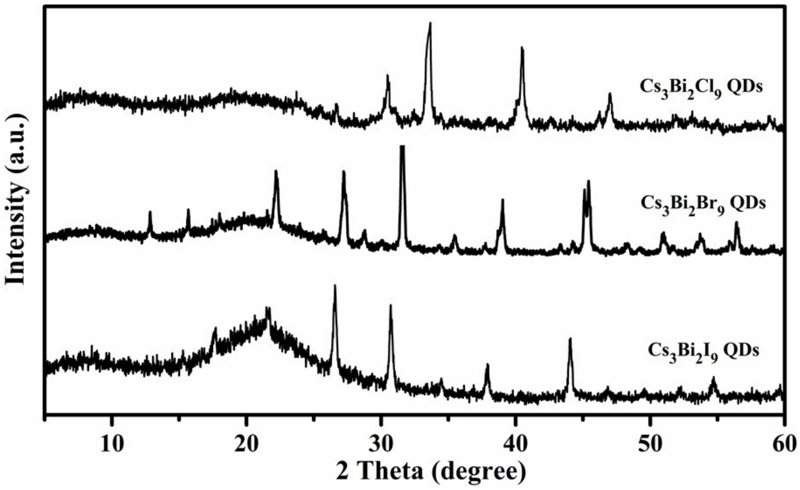

Figure S6. The XRD patterns of pristine $Cs_3Bi_2Br_9$ QDs (middle pattern) as well as the anion exchanged $Cs_3Bi_2Cl_9$ (top) and $Cs_3Bi_2I_9$ (bottom) QDs.

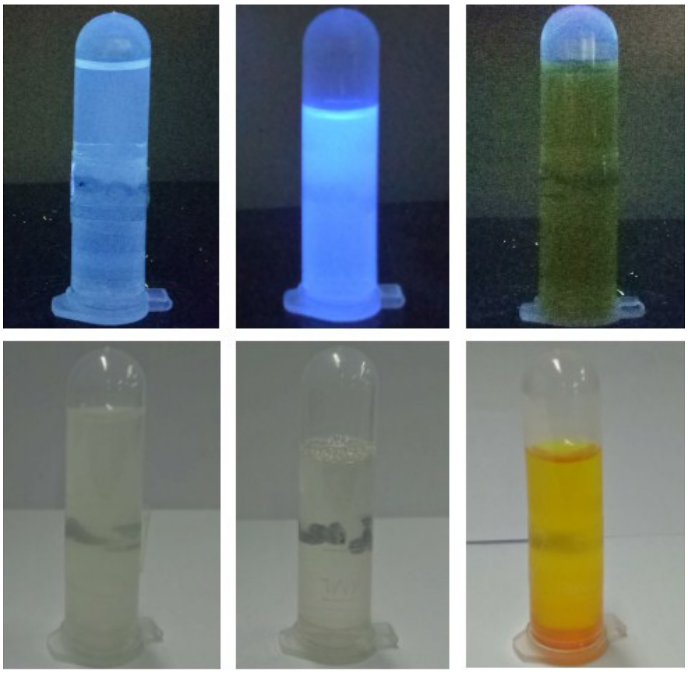

Figure S7. Photographs of the $Cs_3Bi_2X_9$ QDs without (a-c) and with (d-f) 365 nm UV light excitation, from the left to right: X=Cl, Br and I.

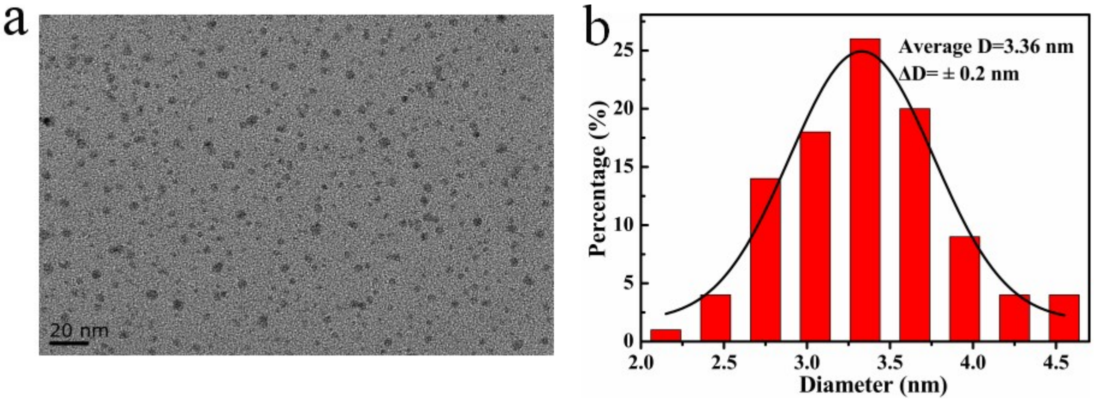

Figure S8. TEM image (a) and the corresponding size distribution histogram (b) of the $Cs_3Bi_2Br_9$ QDs reprecipitation at 90 °C.

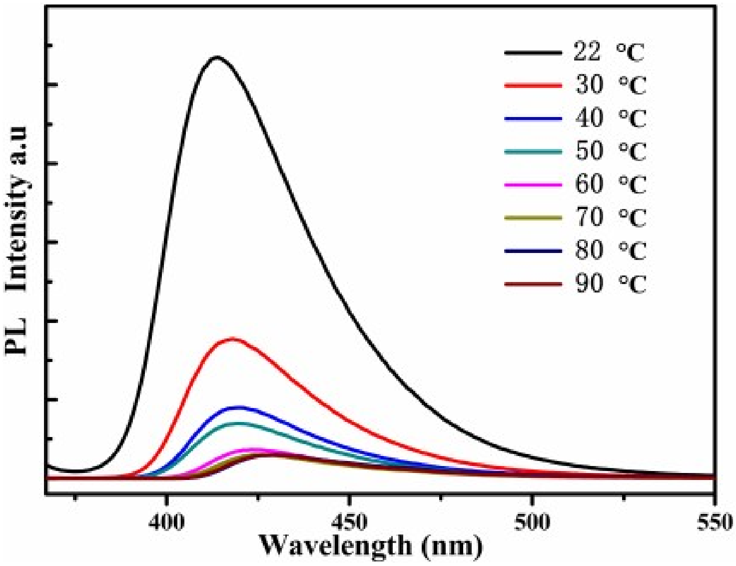

Figure S9. Temperature-dependent PL spectra: intensity changes of fluorescence of as-synthesized $Cs_3Bi_2Br_9$ QDs at different reprecipitation temperature.

References

1. M. C. Weidman, M. Seitz, S. D. Stranks and W. A. Tisdale, *ACS Nano*, 2016, **10**, 7830-7839.
2. J. Song, J. Li, X. Li, L. Xu, Y. Dong and H. Zeng, *Adv. Mater.*, 2015, **27**, 7162-7167.