Strong violet emission from ultra-stable strontium-doped $CsPbCl_3$ superlattices

Yongqiang Ji[a, b], Minqiang Wang*[a], Zhi Yang[a], Hao Wang[a], Muhammad Amin Padhiar[a], Hengwei Qiu[a, c], Jialin Dang[a], Yinru Miao[a], Yun Zhou[a], Arshad Saleem Bhatti[d]

[a]Electronic Materials Research Laboratory, Key Laboratory of the Ministry of Education International Center for Dielectric Research&Shannxi Engineering Research Center of Advanced Energy Materials and Devices, Xi'an Jiaotong University, 710049 Xi'an, China.

[b]State Key Laboratory for Artifcial Microstructure and Mesoscopic Physics, School of Physics, Peking University, Beijing, 100871, China

[c]Department of Chemistry, Key Laboratory of Bioorganic Phosphorus Chemistry & Chemical Biology, Tsinghua University, Beijing 100084, China.

[d]Centre for Micro and Nano Devices, Department of Physics, COMSATS Institute of Information Technology, Islamabad, 44500, Pakistan

Corresponding Author: E-mail: mqwang@xjtu.edu.cn

Experimental section

Materials and chemicals

The cesium carbonate (Cs_2CO_3, 99.99%), oleic acid (OA, 85%), oleylamine (OLA, 80-90%), strontium chloride hexahydra ($SrCl_2 \cdot 6H_2O$, 99.995%), tri-n-octylphosphine (TOP, 90%), 1-octadecene (ODE, 90%), and lead(II) chloride ($PbCl_2$, 99.99%) were purchased from Aladdin. The hexane, and ethyl acetate purchased from Shanghai Chemical Industrial Company. All the reagents were used without further purification.

Preparation of Cs-OA Precursor

In the Cs-OA precursor, a 100 mL 3-neck flask containing 0.4 g Cs_2CO_3, 15 mL ODE, 1.25 mL OA were dried for 1 h at 120 °C under N_2. After that, with the protection of N_2, the temperature was increased to 150 °C until Cs_2CO_3 had reacted with OA sufficiently.

Synthesis of $CsPbCl_3$ PQDs.

104 mg $PbCl_2$ and 10 mL ODE were loaded into a 100 mL three neck flask, and dried under N_2 for 1 h at 120 °C. Then, 1.2 mL OLA, 1.2 mL OA and 2 mL TOP were injected to the flask at this temperature. After the solution became clear, the temperature was raised to 180 °C and kept at this temperature for 5 min, followed by a quick injection of 0.8 mL of CsOA precursor. and 60 s later the reaction mixture was cooled by an ice-water bath.

Synthesis of $CsSr_xPb_{1-x}Cl_3$ (x = 0.05 to x = 0.5) PQDs.

For a typical synthesis of $CsSr_{0.1}Pb_{0.9}Cl_3$ PQDs. $PbCl_2$ (104 mg), dried $SrCl_2 \cdot 6H_2O$ (11.2 mg), ODE (10 mL), OAm (1.2 mL), OA (1.2 mL), and TOP (2 mL) were added

into a 100 mL three-neck round-bottomed flask, dried under vacuum for 1 h at 120 °C, and then heated under N_2 at 120 °C. After 10 min, the temperature was raised to 180 °C and kept at this temperature for 5 min. Then, 0.1 mL Cs-oleate solution was quickly injected, and 60 s later the reaction mixture was cooled by an ice-water bath. Note that $SrCl_2 \cdot 6H_2O$ was dried under vacuum for 12 h at 100 °C to remove water. The different doping concentrations $CsSr_xPb_{1-x}Cl_3$ (x = 0 to x = 0.5) PQDs were accomplished by tuning the feeding ratio of $PbCl_2$ and $SrCl_2 \cdot 6H_2O$, while keeping all the other parameters unchanged. Similarly, the different sized $CsSr_{0.1}Pb_{0.9}Cl_3$ PSCs were synthesized by increasing the concentration of the precursor in equal proportion.

Measurement and characterization

The morphology and chemical compositions of the as-synthesized PQDs were recorded using a transmission electron microscope (JEOL JEM-F200) and EDS detector (Oxford X-Max 65) attached to a transmission electron microscope operating at an accelerating voltage of 200 kV. TEM samples were prepared by drop-casting a dilute toluene solution of the NCs on a carbon coated copper grid and was dried under vacuum overnight. EDS spectra of powder samples were investigated by field emission scanning electron microscopy (SEM, FEI Quatan FEG 250) equipped with an energy dispersive spectrometer. The size distribution histograms were measured by Zetasizer Nano ZSE. The photoluminescence (PL) spectra, PL quantum yields (PLQYs) and time-resolved PL (TRPL) decay curves were recorded on an Edinburgh Instruments FLS9 spectrometer. Absorbance spectra of the samples were obtained using a Jasco V-570 UV/vis/NIR spectrophotometer, which has a wavelength ranging from 190 to 2500

nm. For solution absorption and PL measurements, $CsSr_xPb_{1-x}Cl_3$ nanocrystals solution was diluted so that optical density at the excitation wavelength of 365 nm was lower than 0.1. To determine the PLQYs, the samples were placed in an integrating sphere, using a 150 W xenon lamp coupled to a spectrometer as an excitation source. Laser strobe technique was used for time-resolved PL (TRPL) measurements, and the samples were excited by 366 nm dye laser with pulse width of 0.8 ns and equivalent power of about 1 mW. Powder X-ray diffraction (XRD) patterns were measured using a D/Max 2400 X-ray diffraction meter with Cu Ka (40 kV, 100 mA) irradiation (λ=1.5406 Å). In all cases, a concentrated colloidal solution of the nanocrystals was drop-casted on a thin quartz glass plate and were dried under vacuum overnight. X-ray photoelectron spectroscopy (XPS) spectra were measured by a Thermo Fisher ESCALA670B Xi^+. An optimum concentration of the NCs was drop-casted onto a quartz substrate for the XPS measurements.

Introduce and discuss bi-exponential fitting function, which can be written as

$$I = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right)$$

Where A_1 and A_2 are constants, t is time, and τ_1, τ_2 represent the decay lifetimes. The average lifetime (τ_{ave}) can be calculated as follows

$$\tau_{avu} = \frac{A_1\tau_1^2 + A_2\tau_2^2}{A_1\tau_1 + A_2\tau_2}$$

Table S1. The tri-exponential fitting parameters of time-resolved PL decay curves for $CsSr_xPb_{1-x}Cl_3$ (x = 0 to x = 0.5) PQDs.

	A_1(%)	τ_1(ns)	A_2(%)	τ_2(ns)	τ_{avg}(ns)
x=0	49.47	12.69	50.03	51.51	32.04
x=0.01	48.01	13.19	59.56	51.99	37.29
x=0.05	38.54	4.38	61.46	62.45	40.02
x=0.1	17.44	5.86	82.56	146.49	121.96
x=0.2	37.72	12.42	67.28	101.84	73.20
x=0.5	32.48	3.97	65.72	78.63	52.96

Table S2. The bi-exponential fitting parameters of time-resolved PL decay curves for $CsSr_{0.1}Pb_{0.9}Cl_3$ PSCs.

	A_1(%)	τ_1(ns)	A_2(%)	τ_2(ns)	τ_{avg}(ns)
1-fold	17.44	5.86	82.56	146.49	121.96
2-fold	13.58	12.42	86,42	178.35	151.81
5-fold	10.17	15.34	89.83	193.56	175.43

Table S3. Percentage of each elemental atom of the energy spectrum of different samples for SEM-EDS.

	Cs (Atom%)	Pb (Atom%)	Sr (Atom%)	Cl (Atom%)
$CsPbCl_3$ PQDs	24.45	19.32	0	56.23
$CsSr_{0.1}Pb_{0.9}Cl_3$ PQDs	19.57	19.03	1.98	60.42

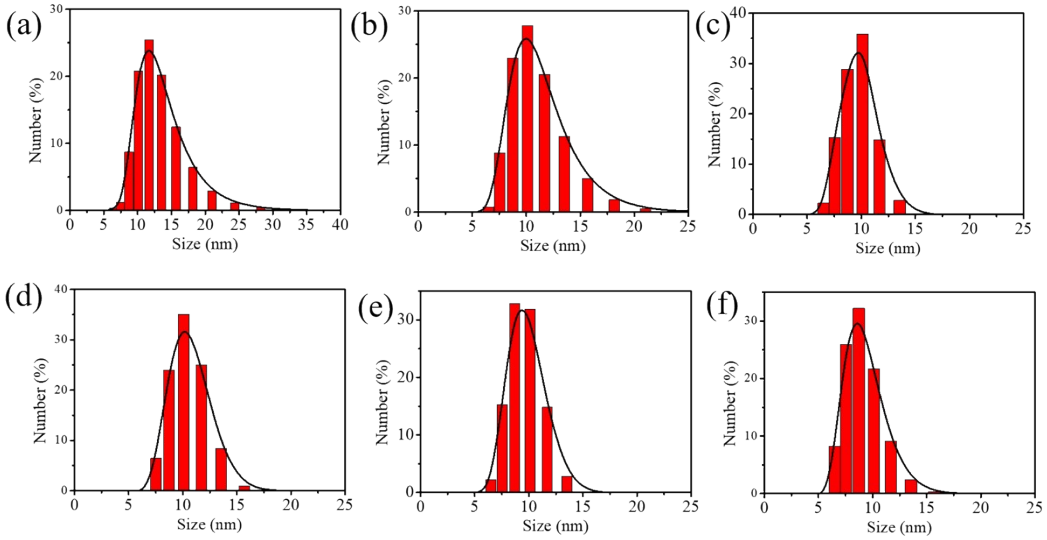
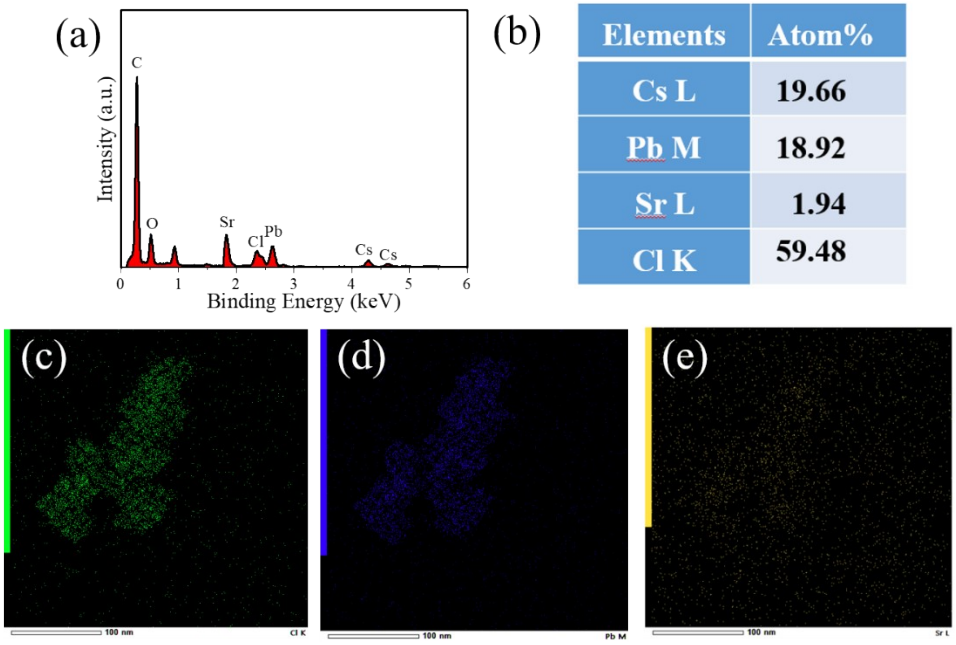


Fig. S1 The size distribution histogram of $CsSr_xPb_{1-x}Cl_3$ PQDs (x = 0 to x = 0.5) (a) x=0. (b) x= 0.01. (c) x=0.05. (d) x=0.1. (e) x=0.2. (f) x= 0.5.



Elements	Atom%
Cs L	19.66
Pb M	18.92
Sr L	1.94
Cl K	59.48

Fig. S2 (a, b) STEM-EDS spectra of the Cs $Sr_{0.1}Pb_{0.9}Cl_3$ from Fig. 1g. (c-e) Raw data of Cl, Pb, and Sr enrichment.

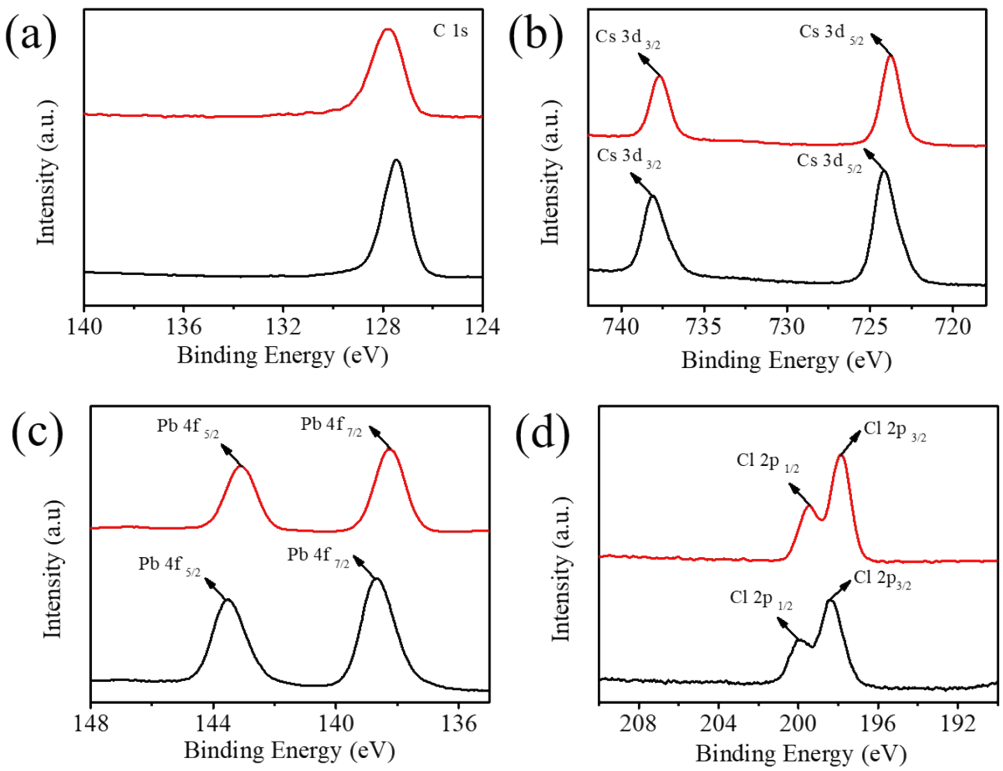


Fig. S3. Comparison of $CsPbCl_3$ and $CsSr_{0.1}Pb_{0.9}Cl_3$ PQDs. (a) High resolution XPS of C 1s. (b) High resolution XPS of Cs 3d. (c) High resolution XPS of Pb 4f. (d) High resolution XPS of Cl 2p.

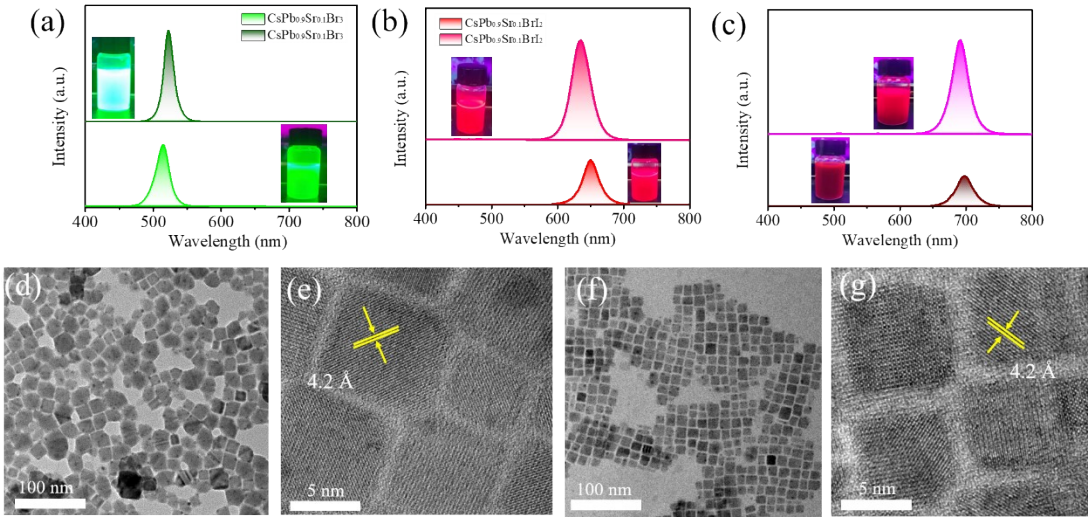


Fig. S4. PL spectra of pristine (bottom) and Sr doped (up) $CsPbX_3$ QDs. Images for the QDs solutions are also shown for comparison. (a) $CsPbBr_3$. (b) $CsPbBrI_2$. (c) $CsPbBrI_3$. TEM images of pristine (d, e) and Sr doped (f, g) $CsPbI_3$ PQDs.

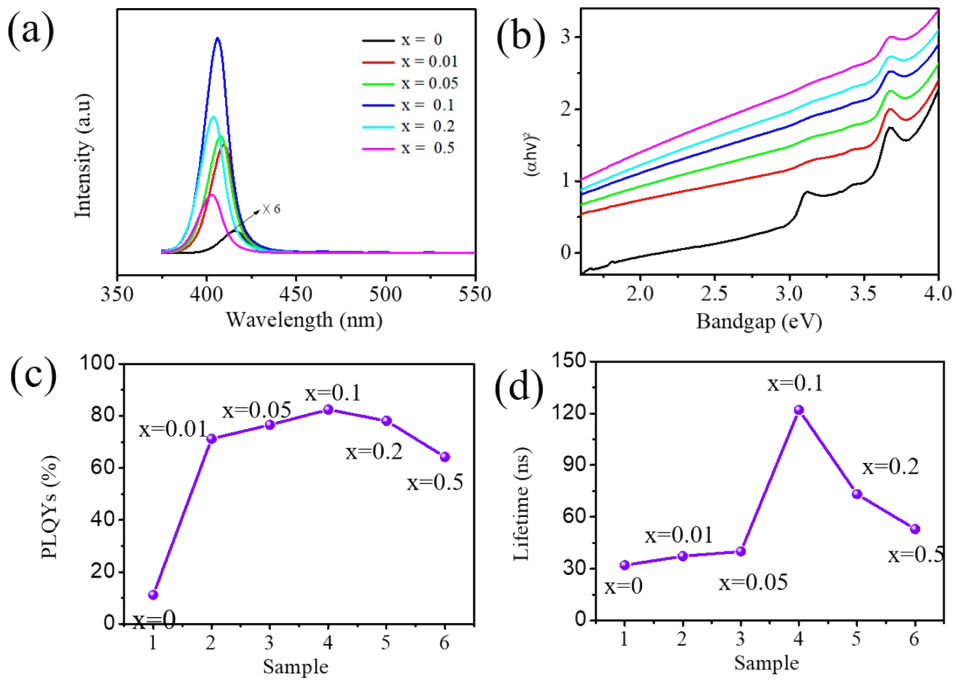


Fig. S5. (a) PL, (b) Bandgap, (c) PLQYs, (d) Lifetime of $CsSr_xPb_{1-x}Cl_3$ (x = 0 to x = 0.5) PQDs.

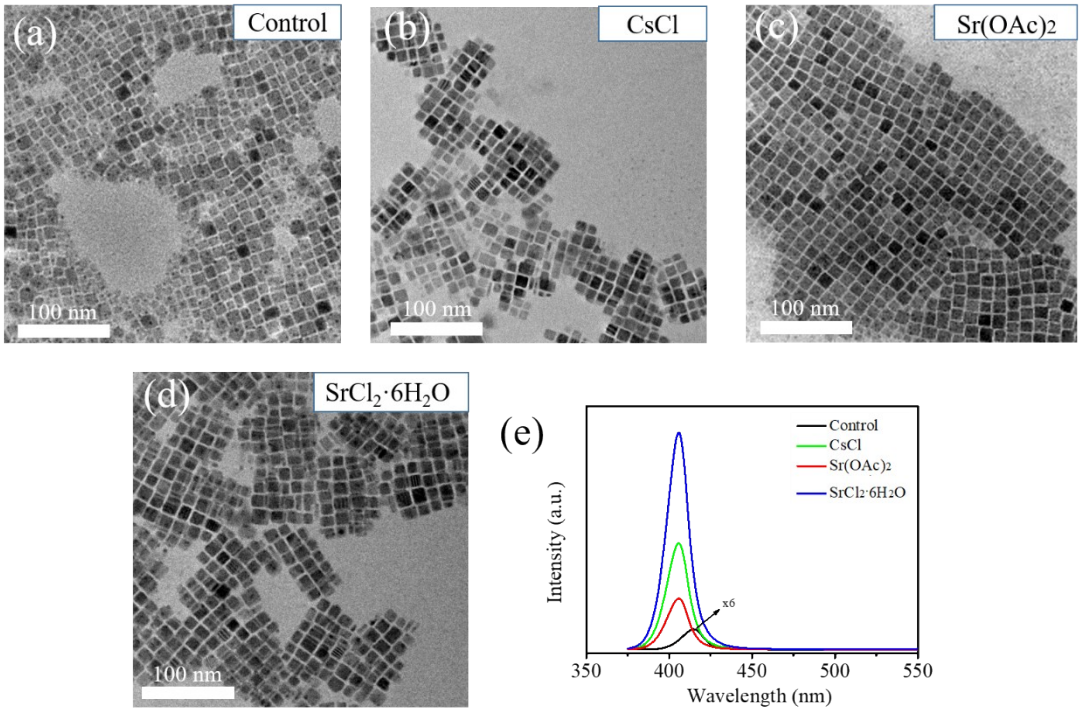


Fig. S6 (a-d) TEM images of the $CsSr_xPb_{1-x}Cl_3$ PQDs for different additives. (e) PL spectra of the $CsSr_xPb_{1-x}Cl_3$ PQDs for different additives，

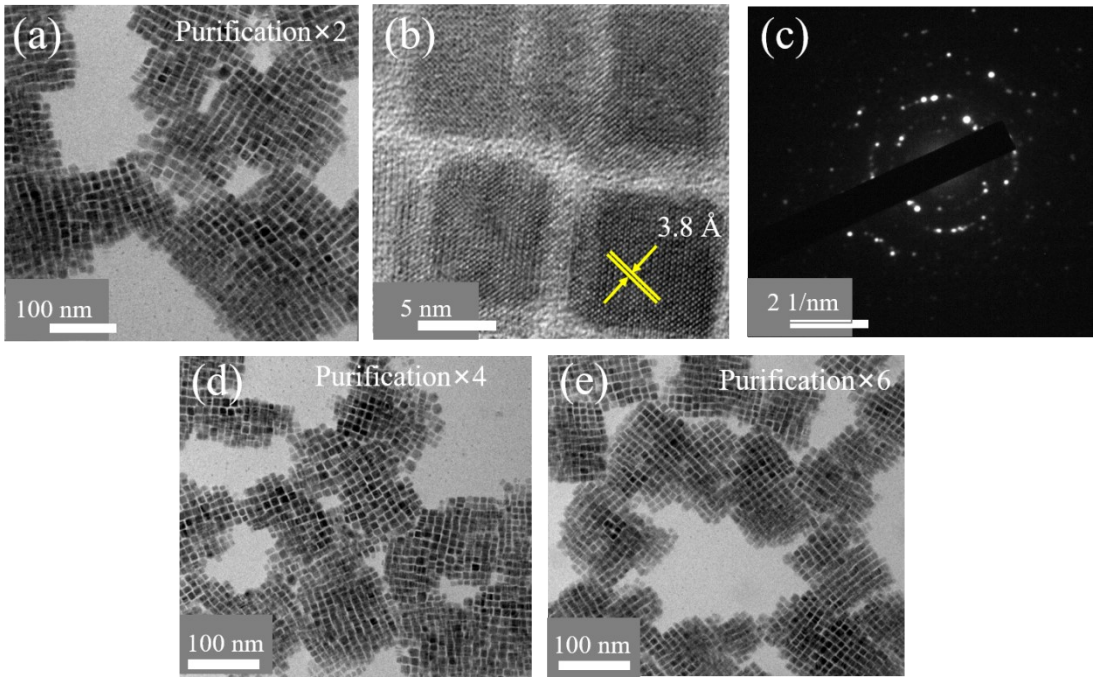


Fig. S7. (a-c) TEM, HRTEM, SAED images of $CsSr_{0.1}Pb_{0.9}Cl_3$ PSCs. (d, e) TEM images of the $CsSr_{0.1}Pb_{0.9}Cl_3$ PSCs after 4, 6 cycles of purification.

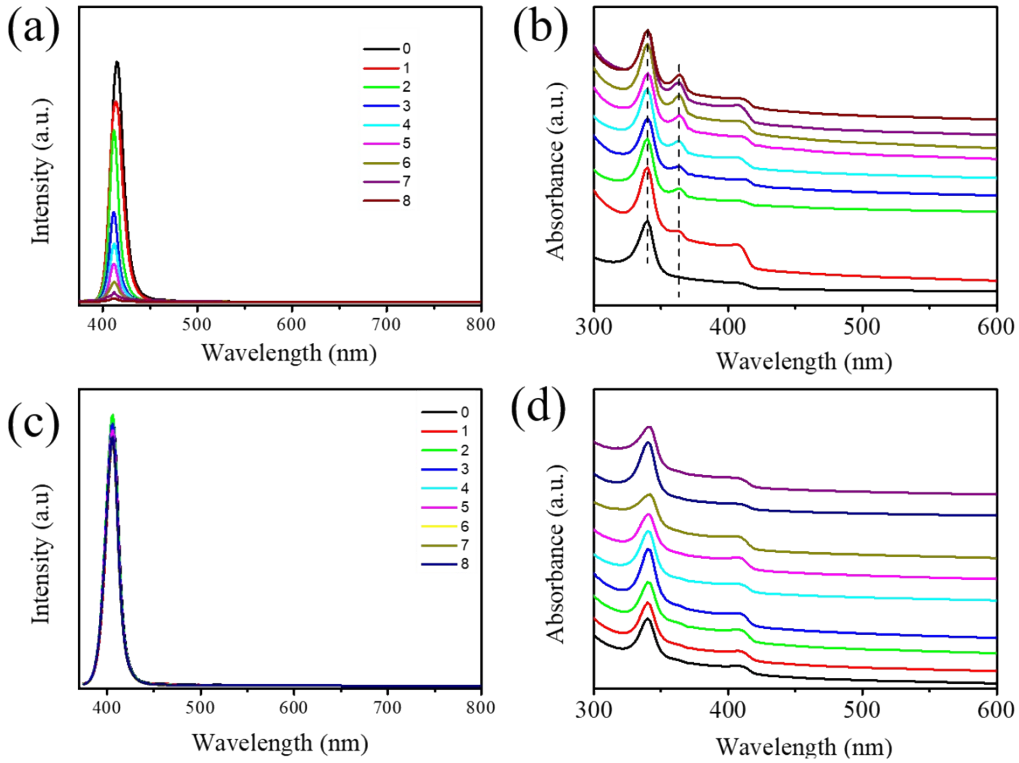


Fig. S8. Absorption and PL spectra of the (a, b) $CsSr_{0.1}Pb_{0.9}Cl_3$ PQDs, (c, d) $CsSr_{0.1}Pb_{0.9}Cl_3$ PSCs before and after different cycles of purifications with anti-solvent.

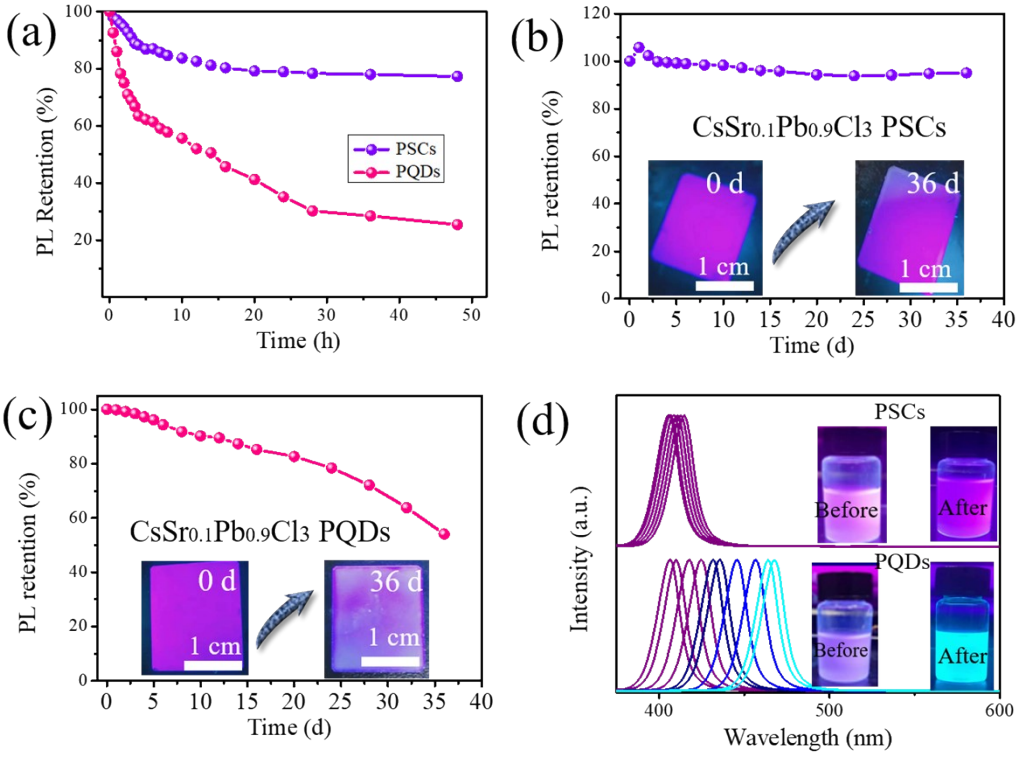


Fig. S9. (a) UV illumination stability test. (b, c) Storage stability. (d) Anion exchange stability test.