

Electronic Supplementary Information

Supplementary Materials for Synthesis of CsPbBr₃ Perovskite
Nanocrystals by Sole Ligand of Protonated (3-aminopropyl)
Triethoxysilane

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Materials

Cesium bromide (99.99 %, Macklin), Lead bromide (99.99 %, Adamas), Cesium bromide (99.99 %, Adamas), Hydrobromic acid (40 %, Aladdin), (3-aminopropyl)triethoxysilane (98 %, APS, Aladdin), Toluene (99.8 %, Alfa), Oleyl amine (90 %, OAm, innochem), Oleic acid (90 %, OA, innochem), N,N-Dimethylformamide (99.5 %, DMF, Macklin), Dimethyl sulfoxide (≥ 99 %, DMSO, Aladdin), 1-Octadecene (90%, ODE, Aldrich). All reagents were used as received without further purification.

Experimental Section

Synthesis of a cesium precursor

ODE (15 mL), OA (0.5 mL) and CsOAc (0.292 g, 1.5 mmol) were loaded in a 50 mL three-necked round bottom flask and dried under vacuum for 1 h at 150 °C along with mild magnetic stirring followed by purging with N₂ for 30 min.

Synthesis of CsPbBr₃ nanocrystals

ODE (20 mL) and PbBr₂ (0.1835 g, 0.5 mmol) were taken in a 50 mL three-necked round bottom flask and then the mixture were degassed (under alternate vacuum and nitrogen) at 120 °C for 1 h along with magnetic stirring. OA and OAm, each 0.5 mL, were loaded in the mixture at 120 °C under a N₂ flow. After 30 minutes, the temperature was increased to 180 °C. The prepared cesium precursor (CsOAc, 0.1 M, 1 mL) was swiftly injected into the reaction mixture. After 10 seconds, the reaction mixture were

cooled by an ice-water bath. The crude solution was centrifuged at 8000 rpm for 10 minutes. Finally, the precipitate was re-dispersed in toluene for characterization.

Synthesis of CsPbBr₃ with ligand of APS

In a typical synthesis of perovskite quantum dots using 20 μL HBr, the stock solution consisted of a stoichiometric mixture of CsBr and PbBr₂ dissolved in 10 mL volume of DMSO or DMF (0.04 M) stirred at room temperature. After filtering through a nylon membrane with an average pore diameter of 220 nm, 20 μL of HBr and 600 μL of APS was added into the stock solution. Afterwards, cautiously, 300 μL of the stock solution was added, dropwise, into toluene (5 mL) under vigorous stirring. After 30 minutes, the nanocrystals were precipitated by centrifuged at 13000 rpm for 10 minutes. The obtained precipitated nanocrystals were re-dispersed in 10 mL of toluene mixed with 2 mL of DMF by sonicating for 30 minutes.

Fabrication of PQDs films

Slide (1 \times 2 cm²) was cleaned by sonicating sequentially in alcohol and deionized water, each for 5 minutes. The slide was placed inside a 10 mL centrifuge tube and followed by addition of 6 mL PQDs. It should be noted that a 75-degree inclination was needed. This tube was centrifuged at 10000 rpm for 10 minutes to form the films of PQDs. Finally, the films were dried under vacuum at room temperature overnight.

Fabrication of down-converted LEDs

The down-converted LEDs is fabricated by covering as-synthesized APS⁺-PQDs on LEDs chips (365nm).

Characterization

The high-resolution transmission electron microscope (HR-TEM) images were obtained with a JEM-2100F TEM operated at an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were recorded on a Thermo Fisher ESCALAB 250 Xi spectrometer. The samples were powder PQDs obtained by centrifuged at 8000 rpm. Powder diffraction patterns were collected on a Rigaku Corporation max 2550 VB Rotating Anode X-ray Powder Diffractometer with Cu K α radiation ($\lambda = 1.54060 \text{ \AA}$). The measurements were done in the Bragg-Brentano geometry from $2\theta = 10$ to 80 . The samples were prepared by dropping solutions on quartz substrates. Zeta potentials of as synthesized PQDs were measured using an Anton Paar GMBH Surpass Instrument. The samples were dispersed in ethanol under ultrasonication for 10 minutes. Fourier Transform Infrared (FRIT) Spectrometer spectra in the region of $400\sim 4000 \text{ cm}^{-1}$ were recorded on a Thermo Fisher Scientific Nicolet 6700 Spectrometer. The absorption spectra were recorded on a Perkin Elmer Lambda 950 UV/Vis Spectrophotometer. In a routine measurement, the colloidal perovskite quantum dots were kept in quartz cuvettes and the spectra were measured from 300-800 nm. Photoluminescence and photoluminescence excitation spectra were obtained by using a Shimadzu RF-6000 with a Xe lamp. The photoluminescence spectra of multiple below-band-gap photons were recorded on a Perkin Elmer LS-55 and it should be noted that the light source was a pulse Xenon lamp (8.3 KW 50 Hz) equipped with an additional UV filter (cut-off 380 nm). Absolute values of Photoluminescence quantum yield (PLQY) were measured using a Horiba Fluorolog system equipped with

a single grating and a Quanta-Phil integration sphere coupled to the Fluorolog system at room temperature. Photoluminescence decays were measured on a time-resolved single photon counting using a Hamamatsu C11367-32 Quantaaurus-Tau spectrometer in solvent mode at room temperature.

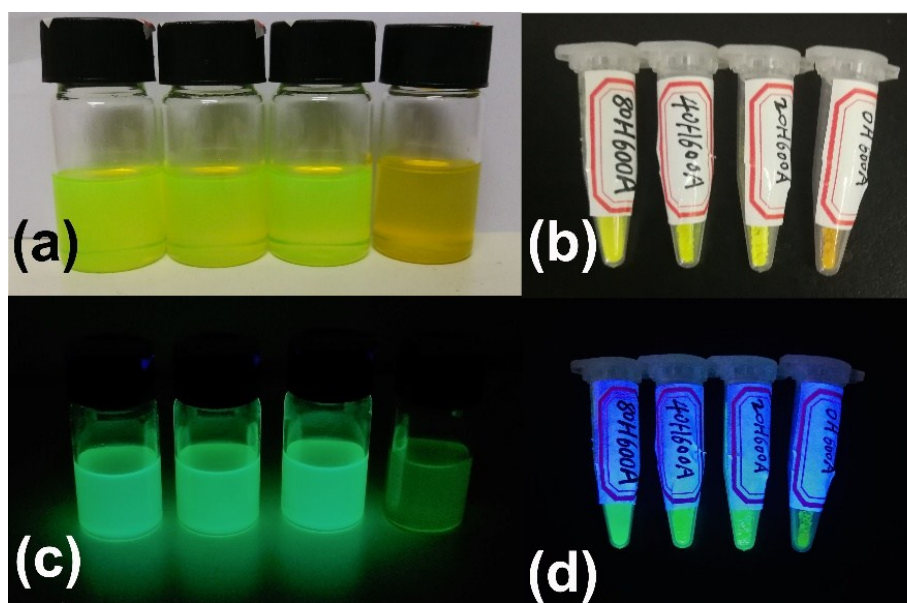


Figure S1. Images of colloidal perovskite quantum dots using APS as ligands with HBr acid varying from 0 to 80 μL (named APS⁺-PQDs) (a) under ambient light and (c) under 365 nm UV irradiation. Images of powder APS⁺-PQDs (b) under ambient light and (d) under 365 nm UV irradiation.

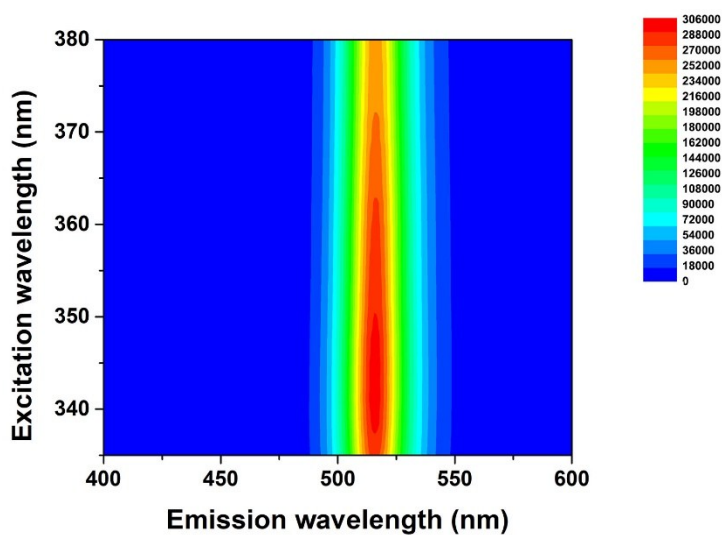


Figure S2. Two-dimensional photoluminescence excitation (2D PLE) spectra of APS⁺-PQDs with 20 μL of HBr. The PL intensity was represented by colors.

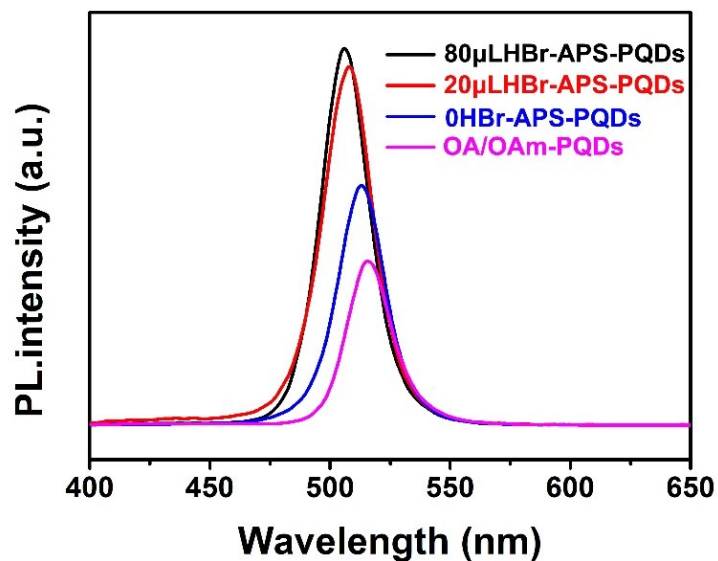


Figure S3. PL emission spectra of APS⁺-PQDs under 700 nm excitation light in comparison to spectrum of OA/OAm-PQDs under 700 nm excitation light. The concentrations of all samples are consistent (0.004 M).

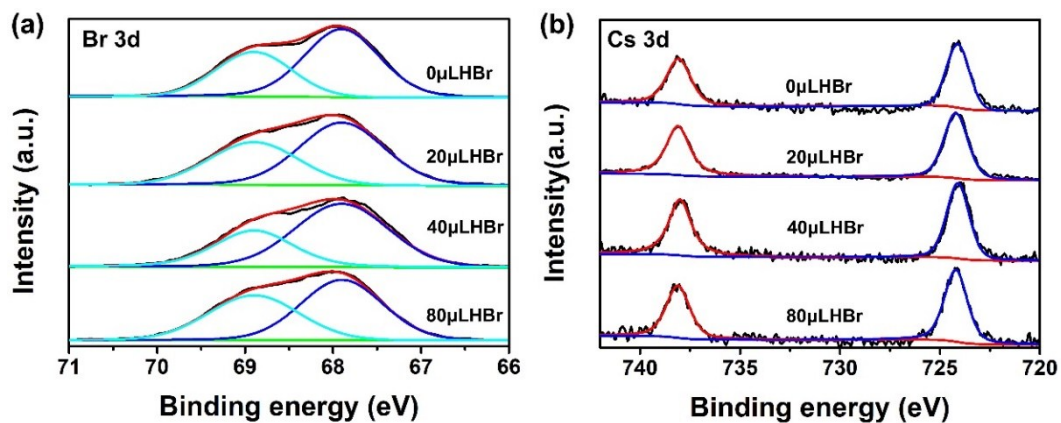


Figure S4. XPS spectra of Cs 3d (a) and Br 3d (b) of perovskite synthesized by varying aqueous hydrobromic acid from 0 to 80 μ L.

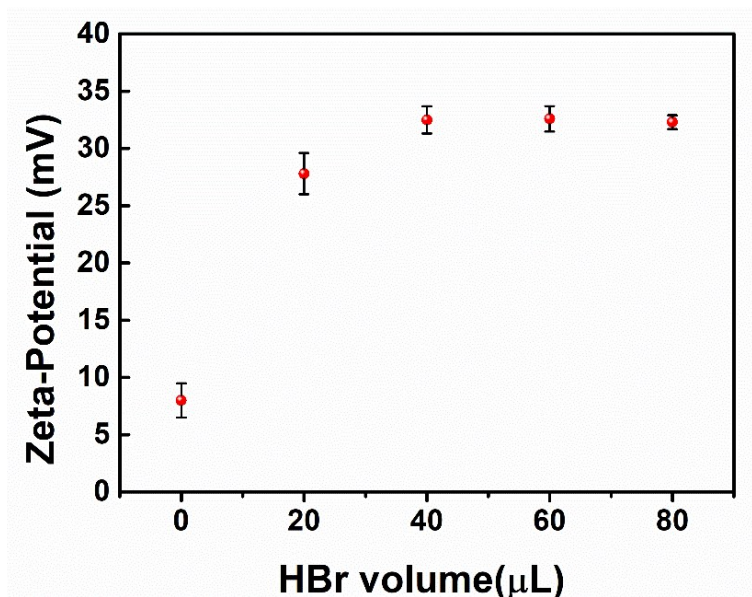


Figure S5. Zeta-potential of as synthesized PQDs.

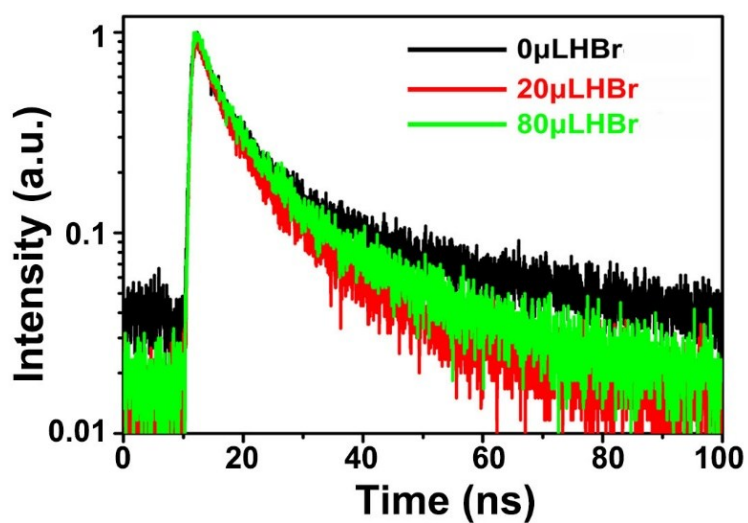


Figure S6. Time-resolved PL decays spectra of APS-PQDs with 0 μL of HBr (black line), APS⁺-PQDs with 20 μL of HBr (red line) and APS⁺-PQDs with 80 μL of HBr (green line)

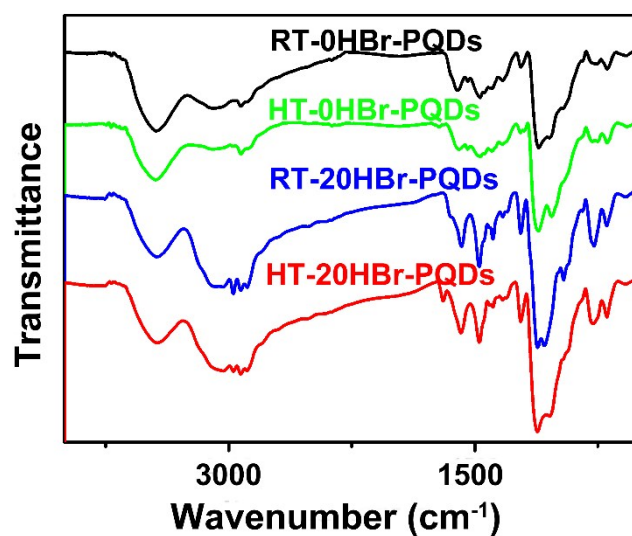


Figure S7. FTIR spectra of as synthesized PQDs without annealing (RT-xHBr-PQDs) in comparison to spectra of that with annealing (HT-xHBr-PQDs).

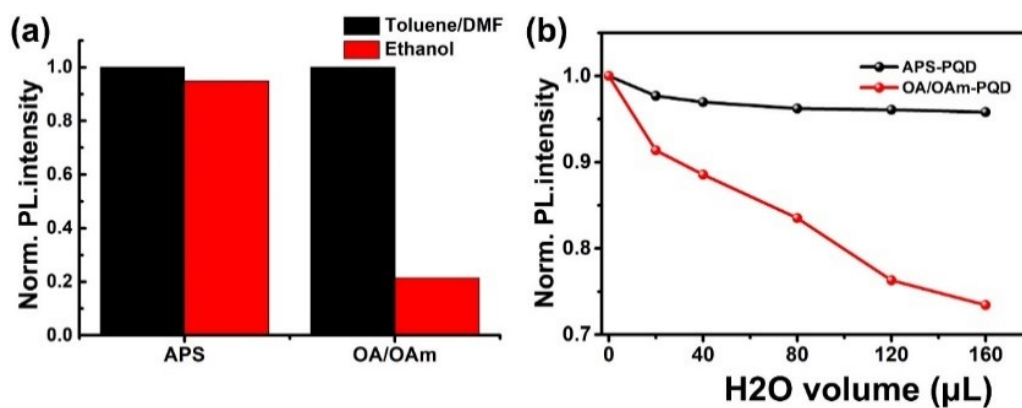


Figure S8. (a) PL intensity of APS-PQDs (synthesized with 20 μ L of hydrobromic acid) and OA/OAm-PQDs in different solvents. (b) PL intensity of APS-PQDs (black) and OA/OAm-PQDs (red) in 10 mL of ethanol mixed with different quantities of deionized water ranging from 0 to 160 μ L.

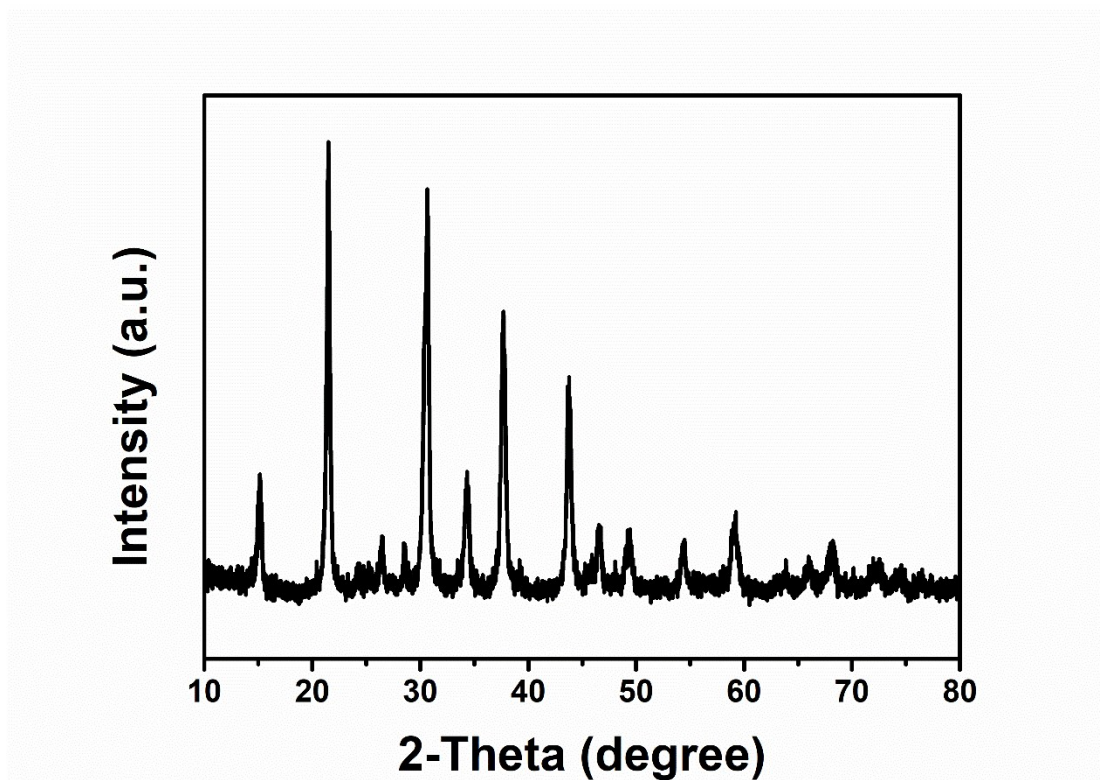


Figure S9. XRD patterns of the CsPbBr₃ nanocrystals with OA/OAm.

Table S1. Br/Pb ratios Feed, Br/Pb ratios measured by XPS.

Samples	Br/Pb ratios Feed	Br/Pb ratios XPS
0 μ L HBr-APS-PQDs	3	3.01
20 μ L HBr-APS ⁺ -PQDs	3.92	4.54
80 μ L HBr-APS ⁺ -PQDs	6.68	5.35

Table S2. Fitting parameters for the bi-exponential decay plot in **Figure S6** (τ_i : component lifetime, ϕ_i : relative amplitude, τ_{ave} : average luminescent lifetime).

Sample	ϕ_1 (%)	τ_1 (ns)	ϕ_2 (%)	τ_2 (ns)	τ_{ave} (ns)
0 μ L HBr-APS-PQDs	35.03	4.216	64.97	20.94	15.01
20 μ L HBr-APS ⁺ -PQDs	46.88	4.473	53.12	18.01	11.66
80 μ L HBr-APS ⁺ -PQDs	40.66	4.510	59.34	19.46	13.84

Table S3. Urbach energy of PQDs and PQDs films.

Sample	OA/OAm						APS		APS ⁺	
	25 mM	10 mM	5 mM	2.5 mM	1 mM	PQDs film	PQDs	PQDs film	PQDs	PQDs film
Urbach energy (meV)	44.33	45.65	46.08	45.64	44.23	48.87	14.32	5.605	40.39	41.19

Urbach energy were calculated according to absorption spectra of our products.

$$E_U = \frac{\hbar}{\frac{d(\ln\alpha(\omega))}{d\omega}}$$

Where E_U is Urbach energy, \hbar is reduced Planck constant, $\alpha(\omega)$ is absorptance and ω is frequency.