

Supporting Information

Armor-Like Passivated CsPbBr₃ Quantum Dots: Boosted Stability with Hand-in-Hand Ligands and Enhanced Performance of Nuclear Battery

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Experimental part

Materials

Lead (II) bromide (PbBr_2 , 99%), Lead chloride (PbCl_2 , 98%), Lead chloride (PbI_2 , 98%) Cesium carbonate (Cs_2CO_3 , 99.9%), Oleylamine (OAm, 80-90%), Oleic acid (OA, 90%), 4-Dodecyl benzene sulfonic acid (4-DBSA, 95%), Didodecyldimethylammonium bromide (DDAB, 98%) and Didodecyldimethylammonium chloride (DDACl, 98%) were purchased from Aladdin. Undecylamine (98%), Trioctylphosphine oxide (TOPO), Tributylphosphine oxide (TBPO), Triphenylphosphine oxide, 1-octadecene (ODE, 90%), tert-Butylbenzene, Ethyl acetate (EA, AR, 97%), Hexane (anhydrous, 99.5%) and Toluene were bought from Macklin. All chemicals were used without any further purification.

Preparation of Cesium oleate (CsOA) precursors

Cs_2CO_3 (0.36g, 1.1 mmol), octadecene (15 mL) and oleic acid (1.5 mL) were added into 100mL 3-neck flask, exhausted for half an hour at 120 °C, and then heated under Ar to 150 °C until all Cs_2CO_3 reacted with OA. The solution was kept at 120 °C to avoid solidification before injection.

Preparation of Cesium dodecylbenzene sulfonate (CsDBSA) precursors

Cs_2CO_3 (0.36g, 1.1 mmol), octadecene (10 mL) and DBSA (4.5 mmol) were added into 100mL 3-neck flask, exhausted for half an hour at 120 °C until all Cs_2CO_3 reacted with DBSA. The solution was kept at 120 °C to avoid solidification before injection.

Synthesis of OAm-QDs

OAm-QDs were synthesized as described previously. Briefly, PbBr_2 (0.54 mmol, 0.2 g), ODE (15 mL), OA (1.5 mL), and OAm (1.5 mL) were loaded into a 100 mL 3-neck flask and degassed for half an hour at 120 °C under Ar flow. After complete dissolution of PbBr_2 salt, the temperature was increased to 160 °C and then maintained for another 30 min under Ar atmosphere. The preheated Cs-oleate solution was swiftly injected into the transparent precursor solution. After 5 seconds, the reaction mixture was cooled down using a water bath.

Synthesis of CsOA-QDs

PbBr_2 (0.27 mmol, 0.1 g), ODE (8 mL), tert-Butylbenzene (5 mL), DDAB (75 mg), OAm (0.35 mL) and CsOA (0.75 mL) were loaded into a 50 mL Teflon lined autoclave, and then reacted at 150 °C in a rolling oven for 1 h. Ethyl acetate was added into the crude solution with a volume ratio of 1:3 and the mixture were centrifuged for 1 min at 9000 rpm. The purifying procedures were repeated for another one time. The precipitate was dispersed in 2 mL of toluene or to obtain a clear solution.

Ligand Exchange for DP-QDs

The DP-QDs precipitation treated with ethyl acetate was dissolved in toluene solution containing the TOPO ligand (3 mL, 0.037M) and the mixture was vigorously stirred for 30s. and then the DP-QDs was washed by ethyl acetate followed by centrifugation at 9000 rpm for 1 minute and re-dispersion in toluene. The DP-QDs precipitation was dissolved in toluene solution containing the TBPO (3ml, 0.037M) and PhOP (3 mL, 0.037M) in a similar way, respectively. Finally, the TOPO-QDs, TBPO-QDs and PhOP-QDs were obtained to research the surface states of DP-QDs.

Characterization

Powder X-ray diffraction data was recorded on Bruker D8 Advance using Ni-filtered Cu K α radiation ($\lambda = 1.542 \text{ \AA}$). UV-vis spectra were recorded in the range of 300-700 nm by using a UV spectrometer (Shimadzu UV-3600). The photoluminescence (PL) measurements were collected on a Varian Cary Eclipse instrument. Transmission electron microscopy (TEM) images were collected on a TECNAI G2 20 LaB6 instrument at 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were performed using an achromatic Al K α source (148.8 eV) and a double pass cylindrical mirror analyzer (PHI QUANTERA II). FTIR results were measured with a Tensor-27 spectrometer. The absolute PL QY of the solution of QDs was determined using a Quantaaurus-QY absolute photoluminescence quantum yield spectrometer (C11347-11, Hamamatsu Photonics, Japan). The lifetimes of PL were detected by a homemade instrument with a 375 nm picosecond laser. ^1H -NMR spectra were recorded on a Bruker Advance III HD-500 MHz spectrometer equipped with a BBO smart probe.

The performance testing for radioluminescent nuclear Battery

Radiation luminescence imaging uses an electron-multiplying charge-coupled device (EMCCD) camera (Andor iXon Ultra 888, USA) equipped with a Canon EF 24-70 mm f/2.8L II USM zoom lens. The camera lens is $\Phi 82$ mm, and the image resolution is 1024×1024 effective pixels. The excitation source used for radioluminescence is a 50 W Mo X-ray tube (Shanghai KeyWay Electron Company Ltd. KYW900A, China). A dual-channel system source-meter instrument (Keithley 2636A, USA) is used to test the electrical performance of the battery and obtain the volt-ampere characteristic curve. All optical and electrical performance tests are carried out at room temperature of about 298 K and atmospheric pressure of 1 bar, as far as possible to avoid interference caused by external light, electromagnetic and other factors. The physical objects of related equipment are shown in **Fig. S22†**. The radiation source used in the study of the long-term radiation damage effect of the CsPbBr₃ films is the Co-60 source frame with a total activity of 185,000 Curies.

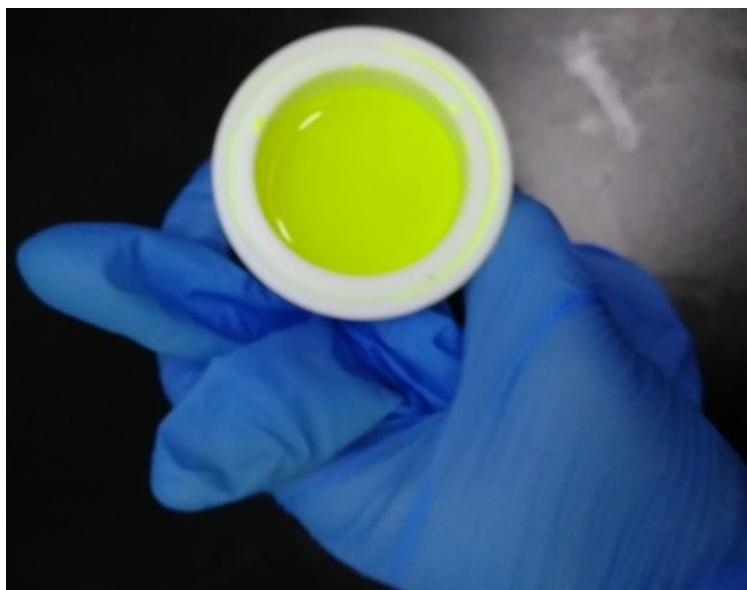


Fig. S1 Photo of the DP-CsPbBr₃ solution under natural light.

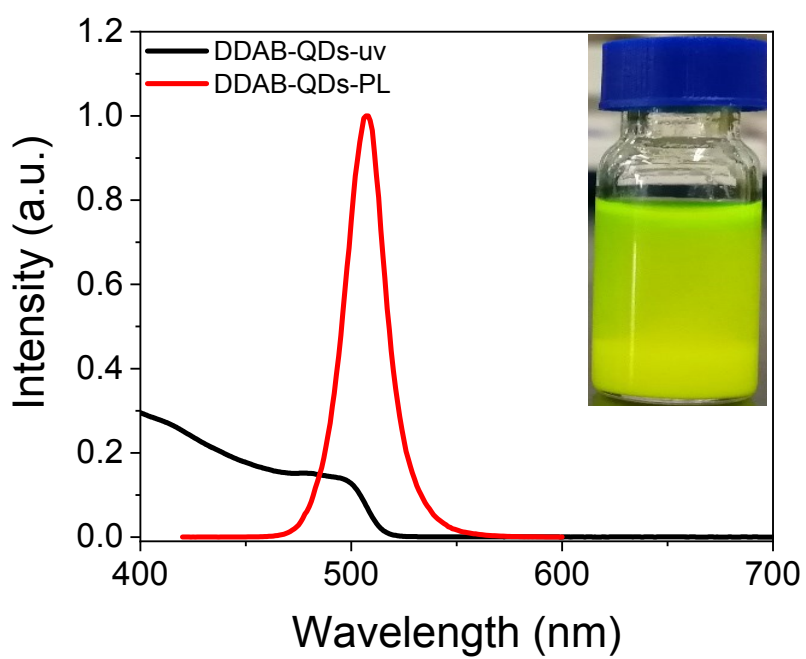


Fig. S2 Absorbance and PL spectra of DDAB-QDs dispersions in hexane.

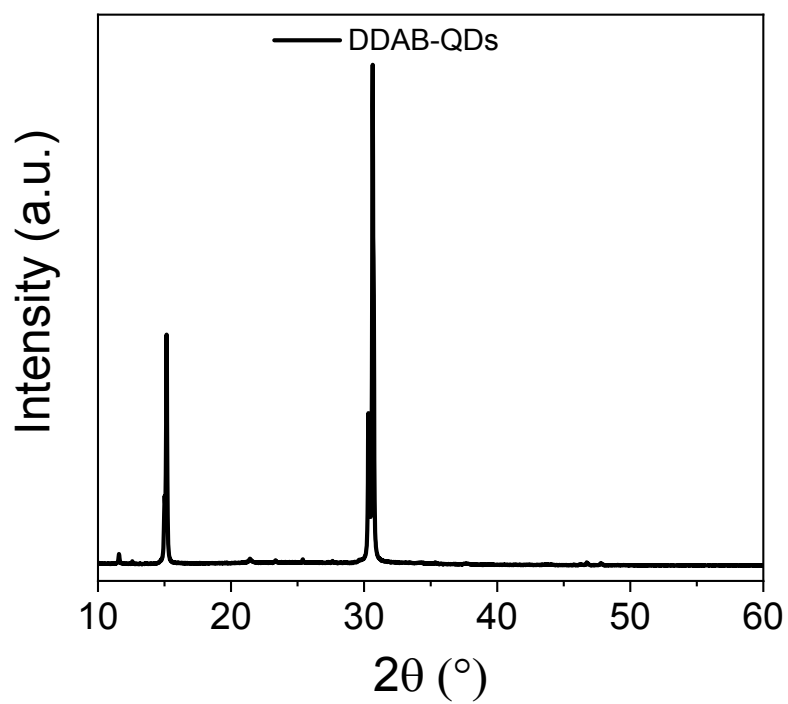


Fig. S3 XRD pattern of DDAB-QDs.

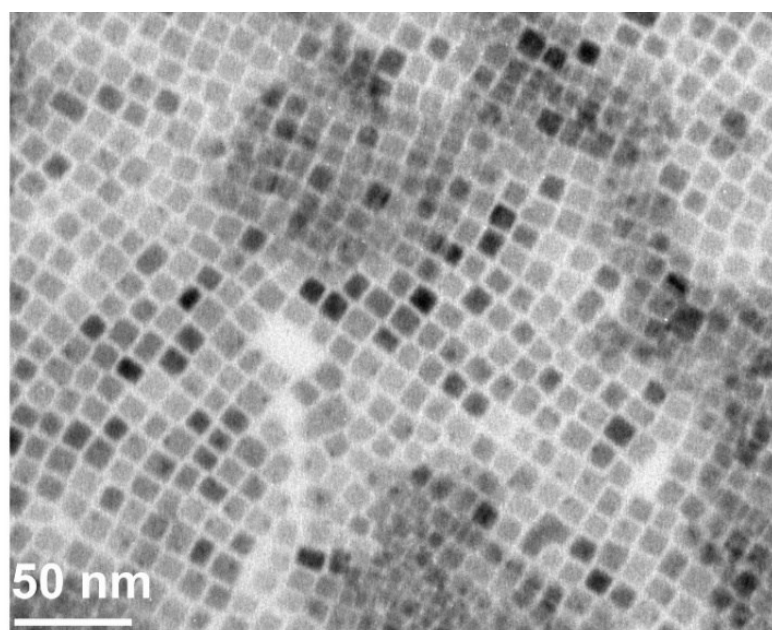


Fig. S4 TEM image of CsOA-QDs.

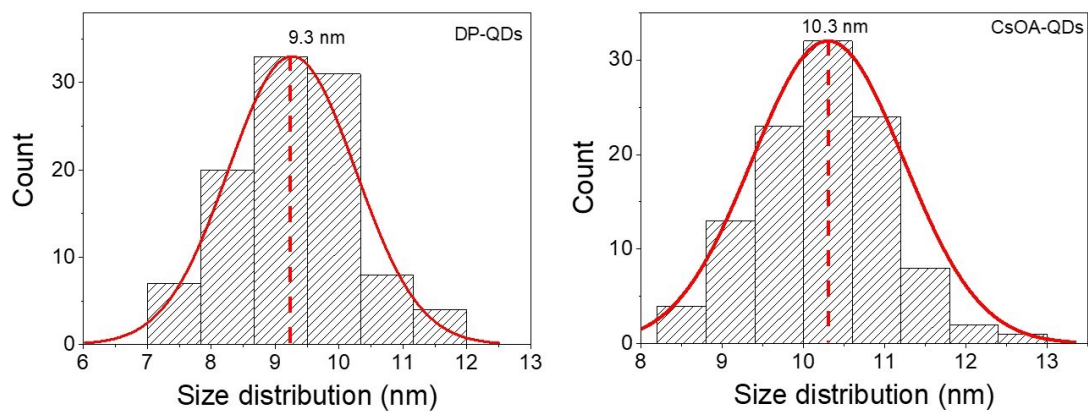


Fig. S5 Size distribution of DP-QDs (left) and CsOA-QDs (right).

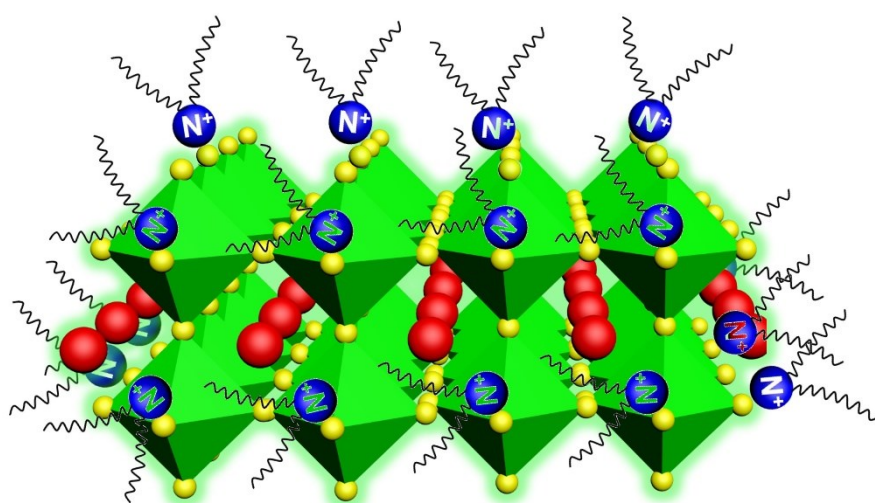


Fig. S6 Structure schematic diagram of DDAB-QDs.

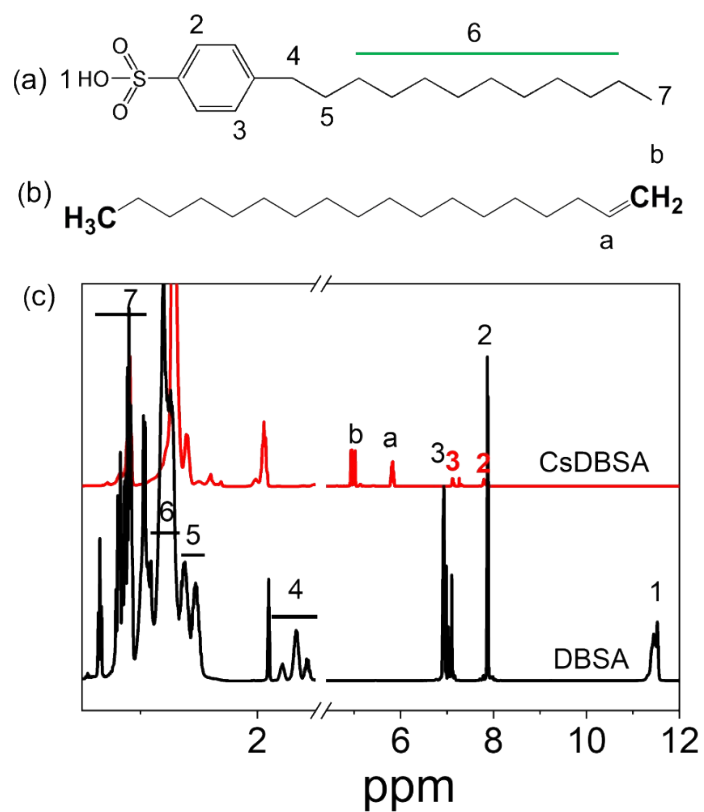


Fig. S7 Molecular structural formula and location number of (a) DBSA and (b) ODE; (c) the ¹H NMR patterns of DBSA and CsDBSA.

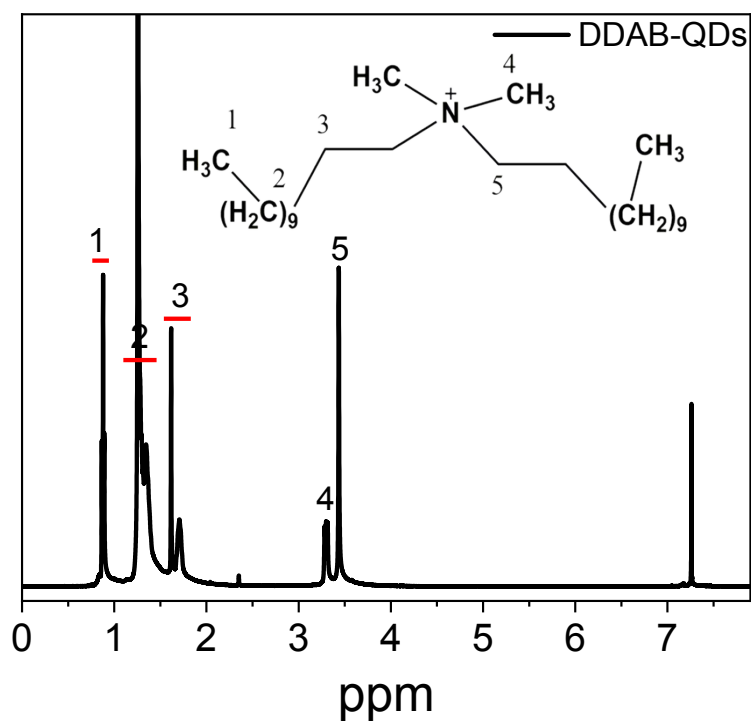


Fig. S8 The ¹H NMR pattern of DDAB-QDs and Molecular structural formula and location number of DDAB.

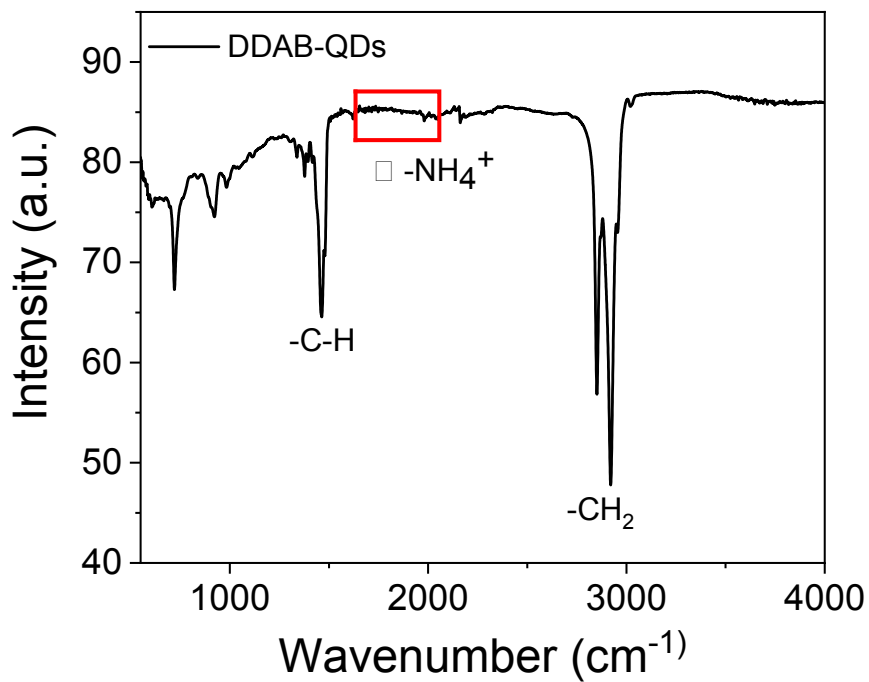


Fig. S9 The FT-IR pattern of DDAB-QDs.

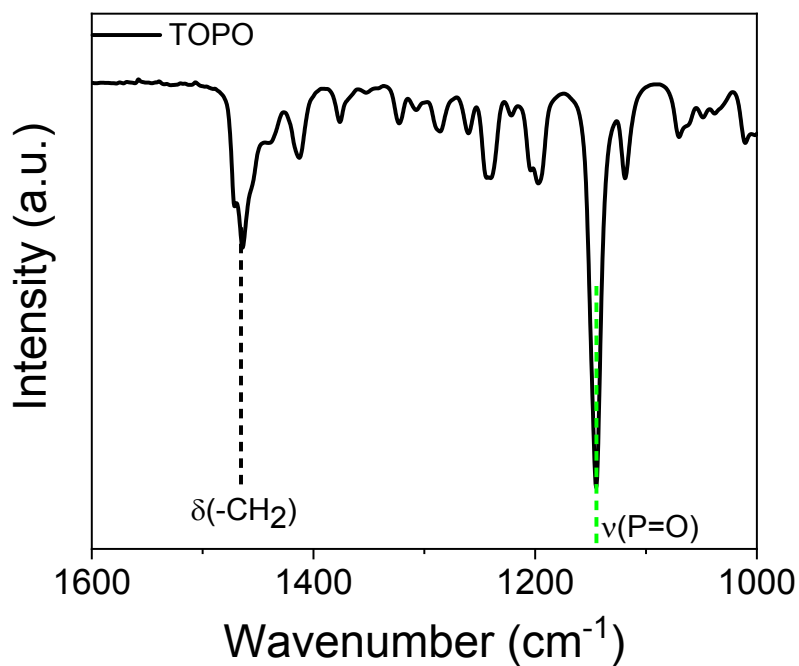


Fig. S10 The FTIR pattern of TOPO ligand.

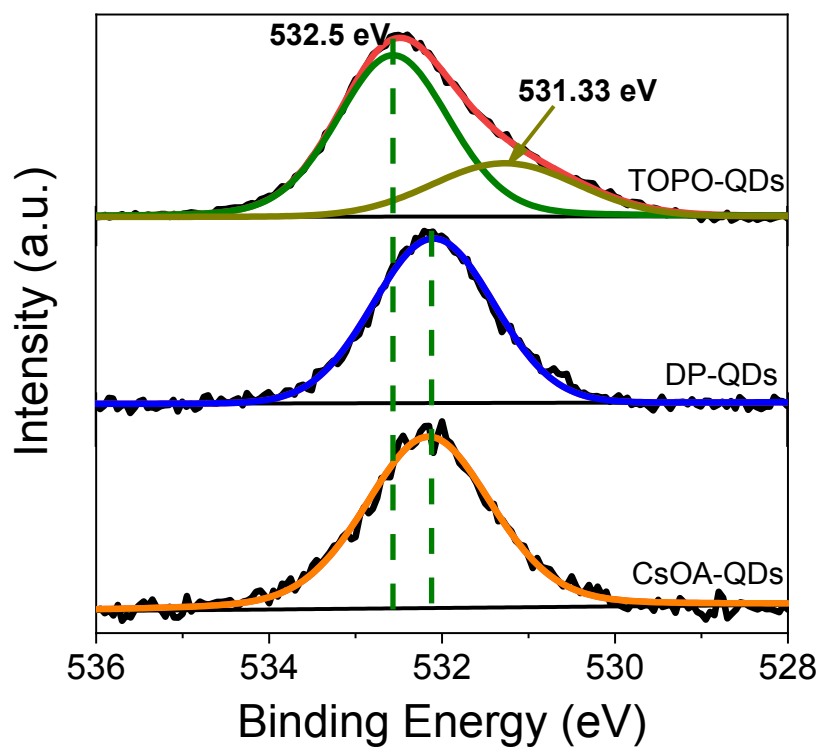


Fig. S11 The XPS spectra of O1s for CsOA-QDs, DP-QDs and TOPO-QDs.

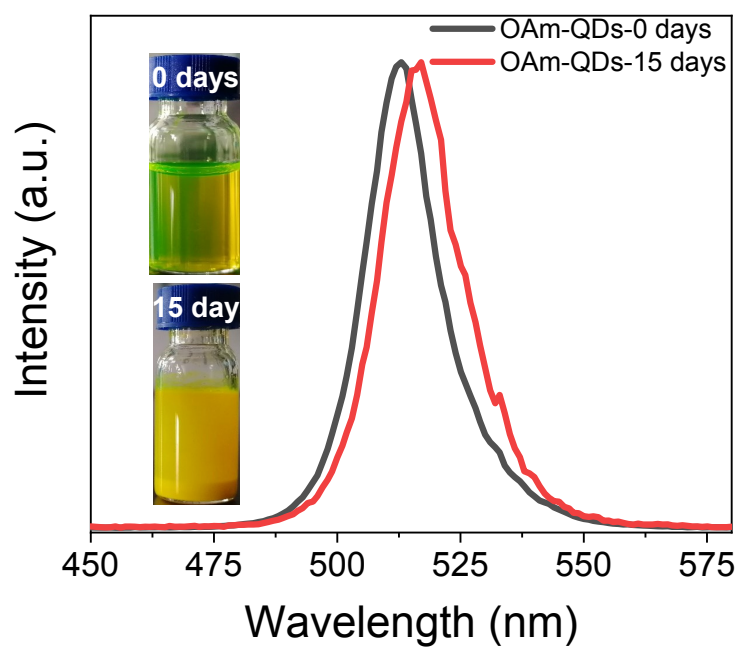


Fig. S12 PL spectra and photos of OAm-QDs at 0 days and 15 days.

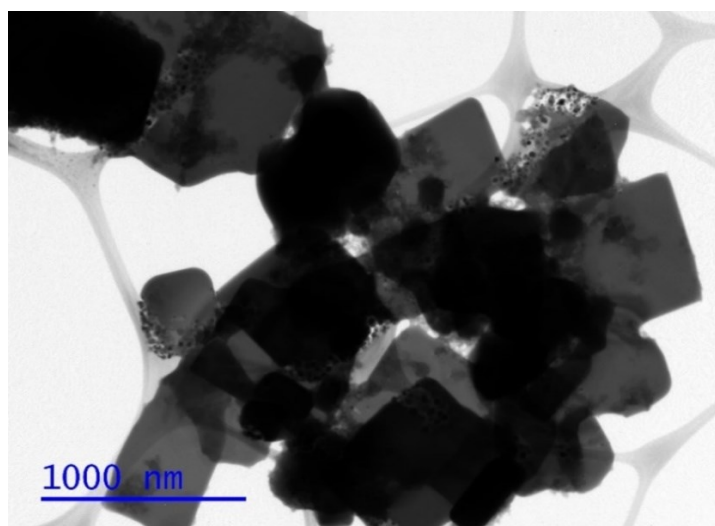


Fig. S13 TEM image of OAm-QDs after 15 days.

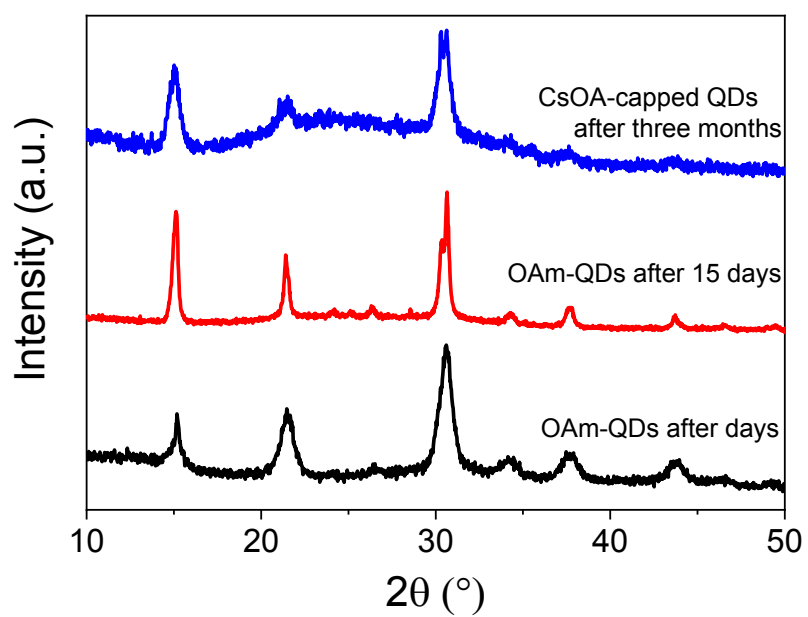


Fig. S14 PXRD patterns of OAm-QDs after 0 (black line) and 15 days (red line) and CsOA-QDs (blue line) after three months.

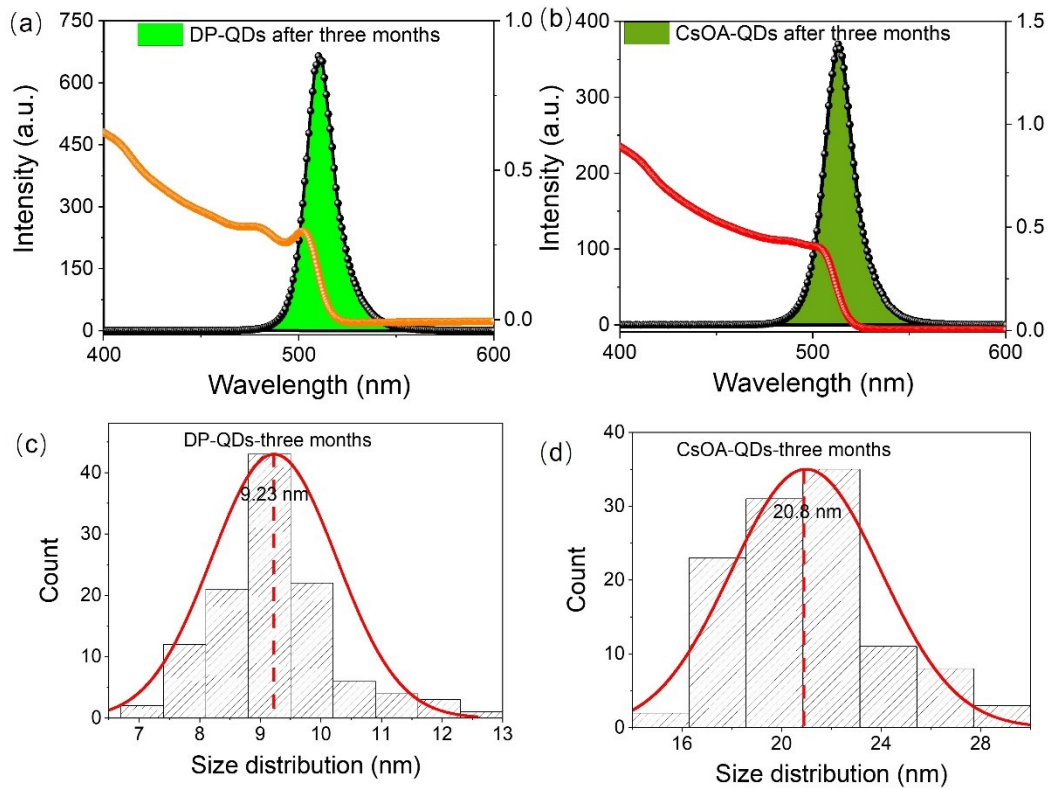


Fig. S15 Absorption and PL spectra of (a)DP-QDs and (b) CsOA-QDs after three months under air in closed vials. The size distribution of (c)DP-QDs and (d) CsOA-QDs after three months.

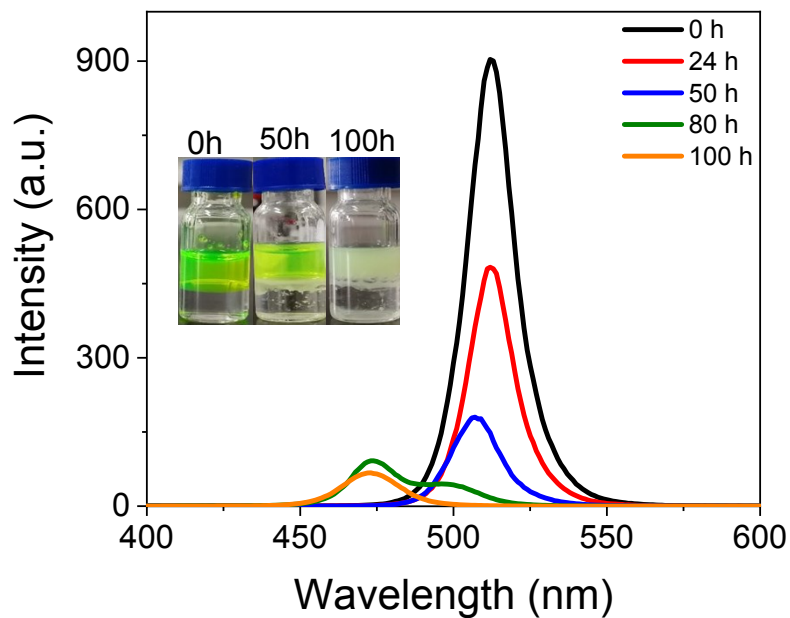


Fig. S16 PL emission spectra at different time points in the continuous water treatment process of OAm-QDs.

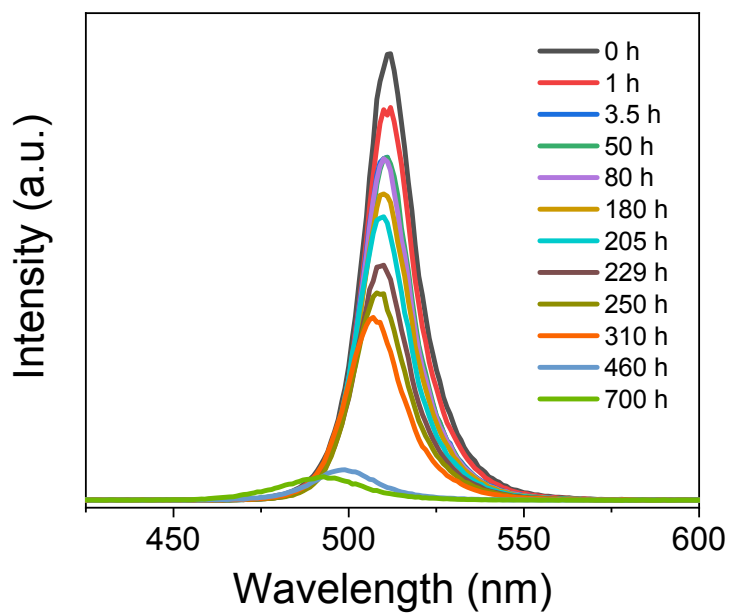


Fig. S17 PL emission spectra at different time points in the continuous water treatment process of CsOA-QDs.

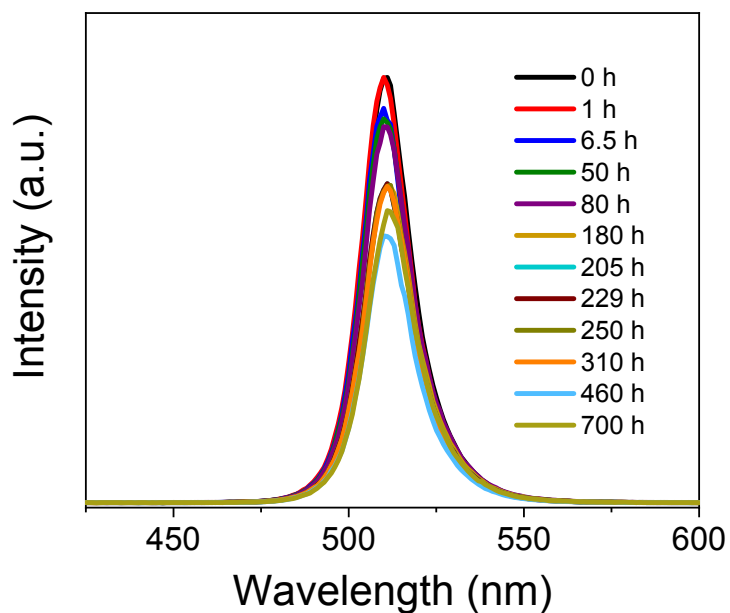


Fig. S18 PL emission spectra at different time points in the continuous water treatment process of DP-capped QDs.

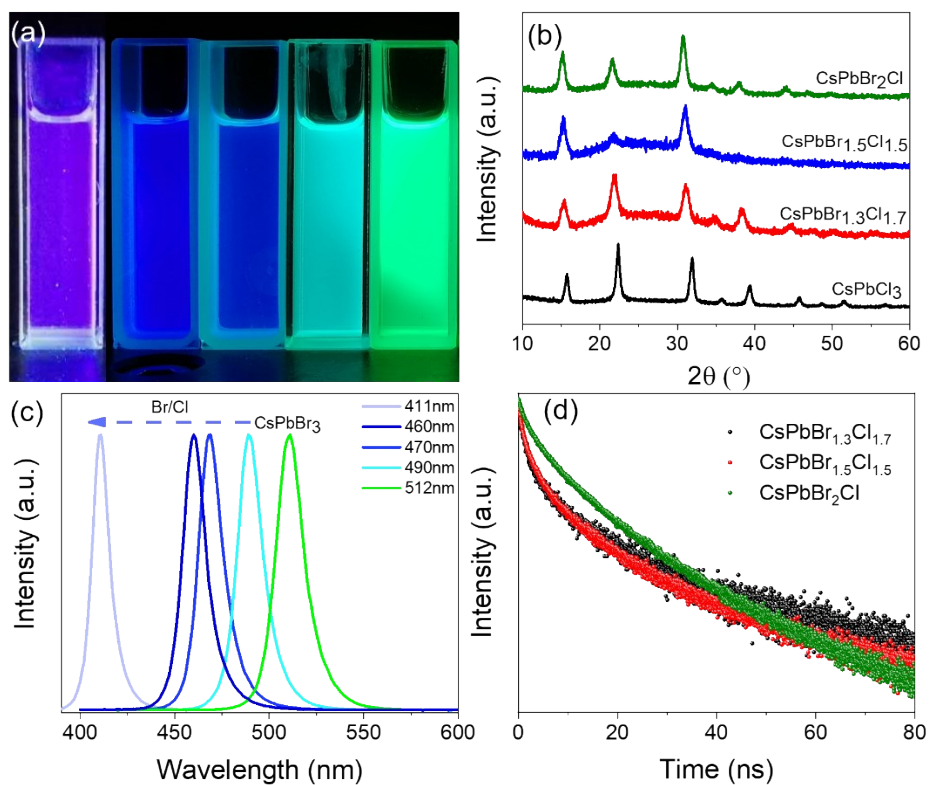


Fig. S19 (a) The fluorescence photos under the 365nm UV light illumination, (b) PXRD patterns, (c) PL emission and (d) decay lifetimes of CsPbX₃ QDs.

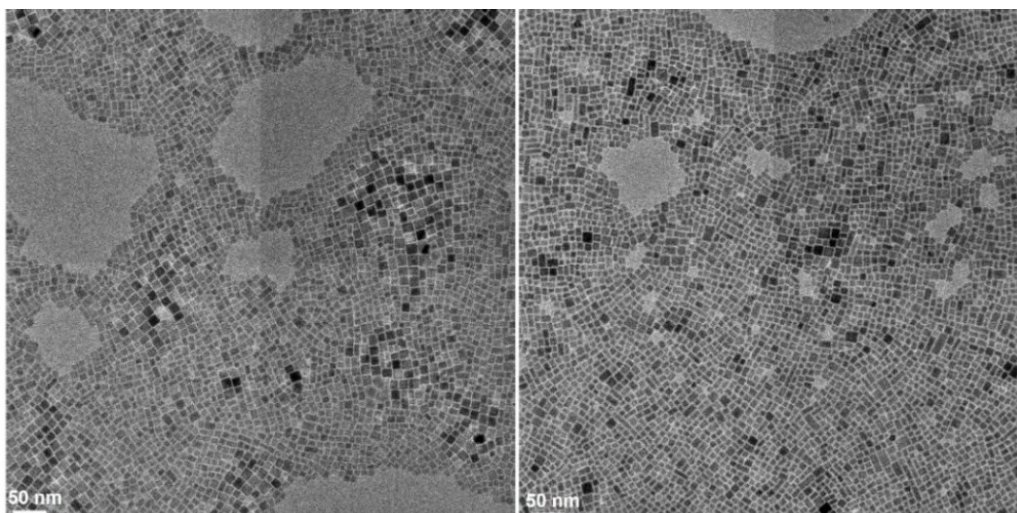


Fig. S20 TEM images of CsPbBr₂Cl QDs (left) and CsPbBr_{1.3}Cl_{1.7} QDs (right).

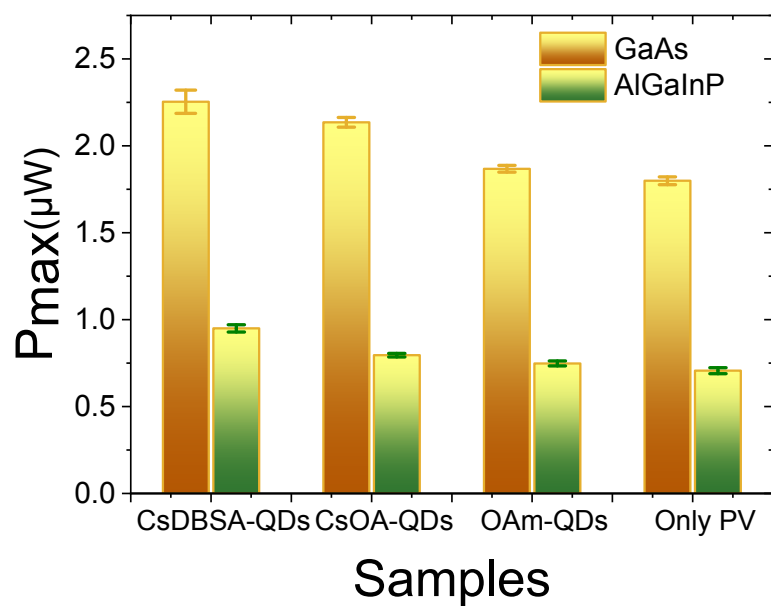


Fig. S21 Comparison of maximum output power values of different combinations of batteries

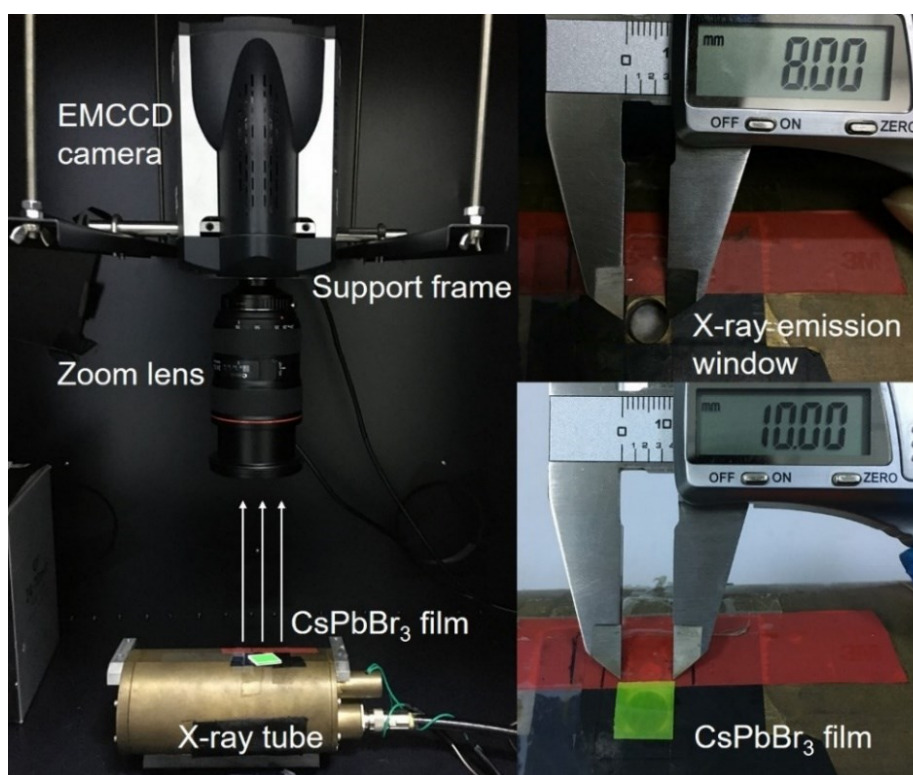


Fig. S22 Perovskite films radioluminescence test platform and imaging system.

Table S1 The optical properties of CsOA-capped, DP-QDs and CsPbX₃ QDs.

Materials (QDs)	Peak (nm)	FWHM (nm)	PLQY (%)	τ (ns)	τ_1 (ns)	τ_2 (ns)
CsOA	513	17	69	6.93	1.8	8.4
DP	513	17	97+/-3	7.58	2.58	7.9
CsPbBr _{1.3} Cl _{1.7}	460	15	45	11.84	1.2	13.9
CsPbBr _{1.5} Cl _{1.5}	470	15	60	10.55	1.3	12.5
CsPbBr ₂ Cl	490	16	90	12.35	2.4	14