Supporting Information

Ultrabright Blue Light-emitting Cesium Bromide Quantum Dots for White LEDs

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Experimental Section

Materials

Cesium Bromide (CsBr, 99.99%, from Xi'an Polymer Light Technology Corp.), Oleic acid (OA, 90%, from Alfa Aesar reagent), Oleylamine (OAm, 80–90%, from Aladdin reagent), Hexane (anhydrous, 99.5%).

Synthesis of CsBr QDs

The synthesis procedure of CsBr QDs can be schematically described in Scheme S1. Briefly, ODE (10 mL) and CsBr (55.23 mg) were loaded into a 50 mL three-neck round-bottom flask and heated for 1 h at 120 °C. Dried OAm (1 mL) and OA (1 mL) were injected at 120 °C. The flask was subjected again for 20 min at 120 °C. After the complete dissolution of the CsBr, the temperature was increased to 150 °C or the other temperature for 1.5 h. The solution was immediately cooled down to room temperature by immersing the flask in an ice water bath. The QDs were purified via high-speed centrifugation (at 12 000 rpm for 10 min). Then, the supernatant was discarded and QDs were re-dispersed in hexane for future use.
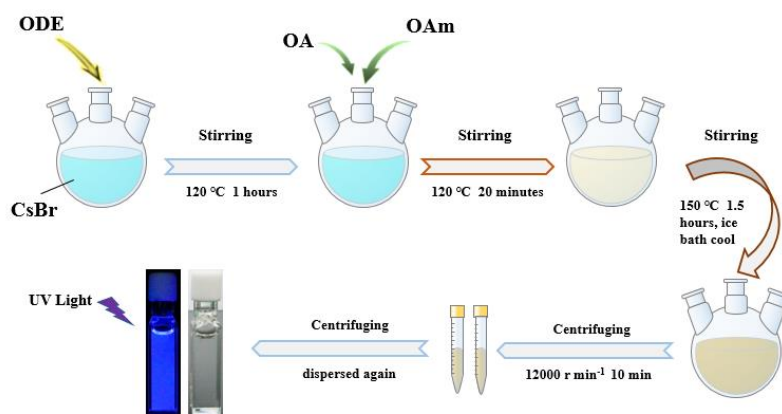
Scheme S1. Schematic diagram for the synthesis of blue-emissive CsBr QDs; the photograph of CsBr QDs solution under UV lamp irradiation.

Characterization

Absorption spectra for CsBr QD solution were recorded using a PerkinElmer Lambda 35 spectrometer with a quartz cell with a 1 cm optical path length. The PL

spectra were recorded at room temperature with a PerkinElmer LS55 fluorescence spectrometer. X-ray diffraction (XRD, DX-2700) with monochromatic Cu Kα irradiation (λ=1.54145 A) was employed to examine the crystalline phase of the CsBr QDs samples (powder) within a test 2θ range of 10-70°. Transmission electron microscopy (TEM) images were taken using a JEM-2100 microscope operating at an acceleration voltage of 200 kV. Samples for TEM measurement were prepared by drop-casting the CsBr QDs dispersion onto a carbon-coated copper grid, followed by evaporation of the solvent at ambient conditions. Fourier transform infrared (FT-IR) spectra were recorded using a PerkinElmer spectrometer (Spectrum One B) in which the CsBr QDs samples were pressed into a tablet. For Time-Correlated Single-Photon Counting (TCSPC) measurements, the samples were excited by a 380 nm wavelength pulse laser (obtained from a BBO nonlinear crystal via an SHG process) from a broadband tunable femtosecond Ti: sapphire pulse laser source (Chameleon Ultra II, Coherent Inc.). The repetition rate of the excitation pulse was controlled by a Pockels cell (Conoptics, Model 305), changing from 1-80 MHz as needed. The TRPL curves were fitted with an exponential function convoluted with the instrumental response function of ~50 ps. X-ray photoelectron spectroscopy (XPS) was conducted on a PHI 5000 Versa Probe delay line detector (DLD) spectrometer equipped with a monochromated Al Kα X-ray source. All the characterization studies were performed at room temperature.

PLQY measurement

The PLQY measurements of CsBr QDs were performed using a relative method with quinine sulfate as the standard sample at room temperature. The standard sample is quinine sulfate, with 57.7% PLQY in 0.1 mol/L H_2SO_4 under 355 nm excitation source while the cuvette is 10 mm. The refractive index of 0.1 mol/L H_2SO_4 was 1.3443 and that of 1.3981 for octane at 355 nm were applied, respectively.[1] According to the following formula, PLQY of CsBr QDs were obtained,

$$\Phi_1/\Phi_2=F_1/F_2*A_2/A_1*(n_1/n_2)^2$$

where Φ_1 and Φ_2 are the quantum yields of the standard and sample, respectively. A_1

and A_2 are the absorbances of the standard and sample at the excitation wavelength; F_1 and F_2 are the integrated emission intensity of the standard and sample; n_1 and n_2 are the refractive indexes of the standard solution and sample solution.

**Transient absorption measurement**

Transient absorption spectroscopy measurements were performed on a commercial femtosecond TA spectrometer (HELIOS, Ultrafast Systems). The excited pulse at 380 nm was obtained from an optical parametric amplifier (TOPAS) pumped by an 800 nm pulse from a femtosecond amplifier laser system (Astrella Vitara-S, Coherent) with the pulse width of 110 fs, centered at 800 nm, and repetition rate of 1 kHz. A small fraction of the 800 nm beam was focused on a CaF_2 crystal in the HELIOS to generate broadband white-light continuum pulses as probe pulses. Both pump and probe beams were focused onto the sample, and the time delay was controlled by a motorized delay stage. After passing through the sample, the excitation-induced transmission change of the probe light was collected by a fiber-coupled spectrometer with CMOS sensors. All measured temporal evolution of the excitation-induced transmission/absorption change $A(t)$ can be well fitted by a two-exponential function convoluted with the instrumental response function (IRF) of ~200 fs, i.e., $A(t) = [A_1\exp(-t/\tau_1) + A_2\exp(-t/\tau_2)]\otimes i(t)$, where $\otimes$ represents the convolution, τ_1, τ_2 are time constants, A_1, A_2 are the corresponding amplitudes of two lifetimes.

Fabrication of White WLEDs

Commercially available GaN LED chips without phosphor coating were purchased from Shenzhen looking long technology co., LTD. The prepared CsBr QDs in hexane (1 mL) were added into the mixture of silica gel ET-821 A and B, and the weight ratio of ET-821 A and B was kept at 4:1. Then the mixture was stirred for 15 min to fully mix the CsBr QDs with silica gel. The S550 phosphor and silica gel mixture was prepared with a similar process. After that, the CsBr QDs mixture was coated onto the LED chip, and then a desired amount of S550 phosphor mixture was added onto the chip surface.

Table S1. Optical properties comparison of CsBr-based QDs.

QDs	Emission peak (nm)	PLQY (%)	FWHM (nm)	Refs
CsBr	428	92.0	/	This work
CsBr: Eu^{2+}	440	32.8	31	2
CsBr: Ca^{2+}, Eu^{2+}	440	23.3	29	2
CsBr: Zn^{2+}	415 &438	79.05	47	3
Cs_2ZnBr_4: Cu^+	465	65.3	/	4
Cs_2ZnX_4	391	51.93	/	5
$CsPb(Br_{1-x}Cl_x)_3$	463	85	/	6
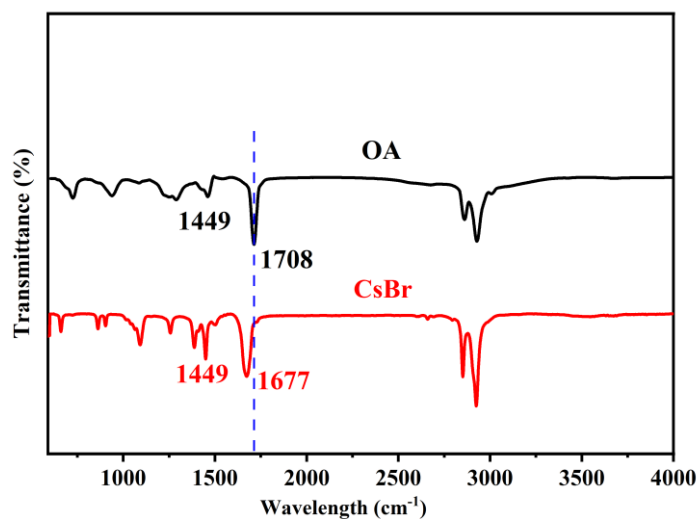
Fig. S1. FT-IR spectra of free OA (black line) and CsBr QDs (red line).

XPS analysis of CsBr QDs

High-resolution, core-level X-ray photoelectron spectroscopy (XPS) spectra of CsBr QDs are presented in Fig. S2. The XPS spectra exhibit the characteristic peaks of cesium (Cs), bromine (Br), and a little oxygen (O), suggesting the existence of O on

CsBr QDs. The Cs 3d spectrum exhibits two prominent peaks located at 724-728 eV and 738-742 eV, corresponding to the Cs3d$_{5/2}$ and Cs 3d$_{3/2}$ levels, respectively. Each main peak corresponding to cesium can be fitted into two sub-peaks, which implies that cesium exists in two chemical states. According to previous reports [7] and the NIST XPS Database, the signal of Cs 3d$_{5/2}$ near 725.5 eV belongs to the cesium ion, and the other signals near 727.3 eV can be assigned to CsOH on the surface of CsBr QDs, originated from the reaction of cesium and the hydroxyl or carbonate groups of OA. The decomposed two prominent peaks at 66.9 eV and 67.9 eV are attributed to Br 3d$_{5/2}$ and 3d$_{3/2}$, respectively, which are in well-agreement with previous reports.[2] In Fig. S2d two peaks (labeled peak 1 and peak 2) can be observed. The low binding energy peak of O could be originated from the O^{2-} ions, while the high energy peak at 530.8 eV could be assigned to the low coordination surface oxygen species.
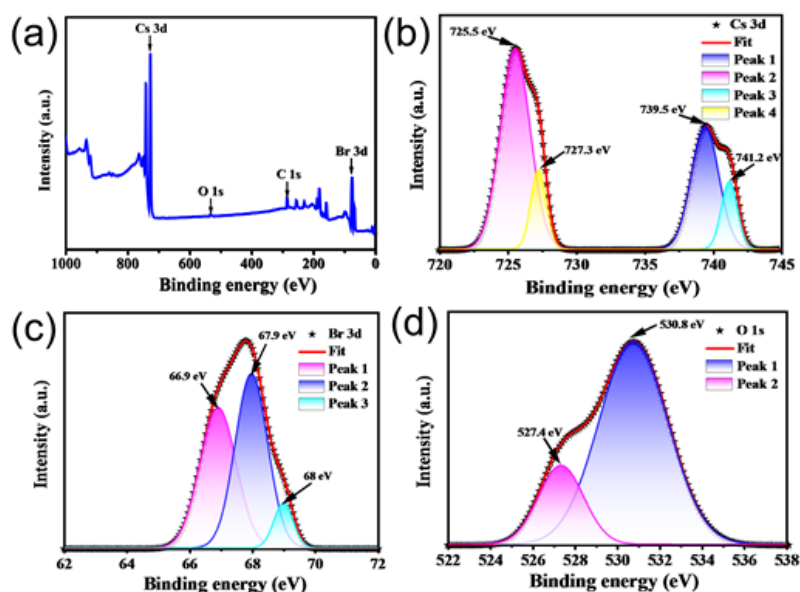

Fig. S2. (a) Survey XPS spectra of CsBr QDs; (b-d) high-resolution Cs 3d, Br 3d and O 1s spectra of CsBr QDs
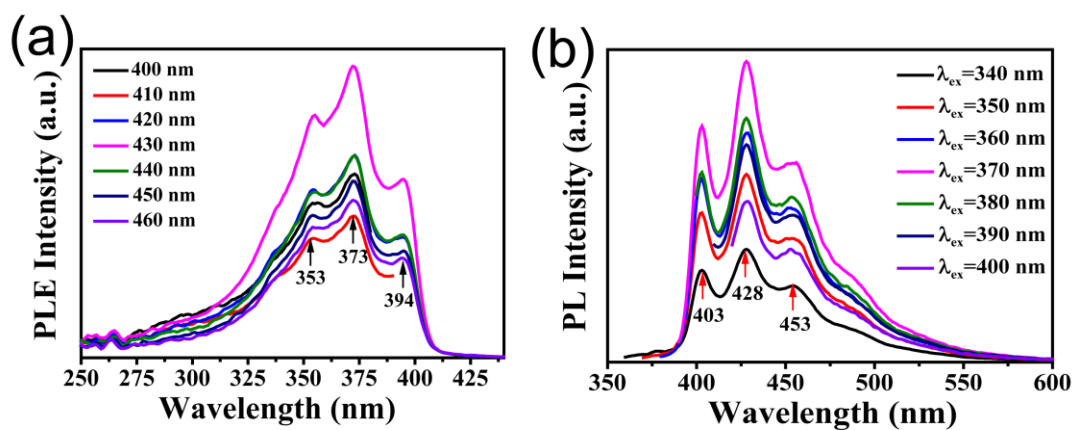
Fig. S3. (a) PL excitation (PLE) spectra of CsBr QDs at different emission wavelengths. (b) PL spectra of CsBr QDs under different excitation wavelengths.
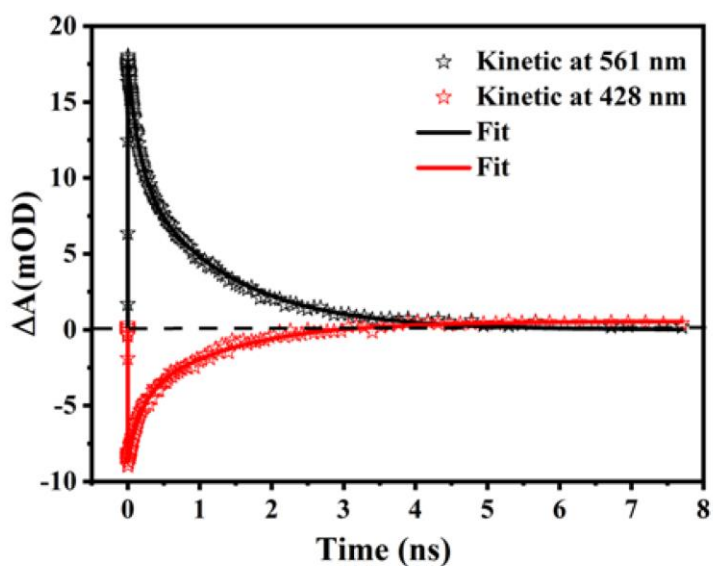

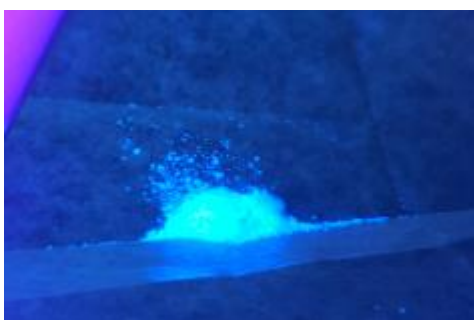**Fig. S4.** TA kinetics of CsBr QDs at 428 and 561 nm.

Fig. S5. CsBr QDs powder under 365 nm UV lamp.

References

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