

Supporting Information

For

Long-term stable electrochemiluminescence of perovskite quantum dots in aqueous media

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Experimental Section

Materials: Cesium bromide (CsBr, Aladdin, 99.0%), lead bromide (PbBr₂, Aladdin, 99.99%), oleic acid (OA, Aladdin, 85%), oleyl amine (OAm, Macklin, 80 - 90.0%), polyethylene glycol-600 (PEG-600, Solarbio, 100%), N,N-dimethylacetamide (DMA, Sinopharm, AR), 2-methylimidazole (2-Met, Macklin, 98%), ethyl acetate (EA, Sinopharm, AR), potassium persulfate (K₂S₂O₈, Sinopharm, AR), tripropylamine (TPrA, Sinopharm, AR) and tris(2,2'-bipyridine)dichlororuthenium(II) hexahydrate (Ru(bpy)₃²⁺, Sigma-Aldrich, 98%) were used directly without further purifications.

Ultrapure water (~18.2 MΩ cm) was obtained using a Millipore Integral Water Purification System (Sichuan, China), and was used to prepare all the aqueous solutions required during experimentation.

Apparatus: The fluorescence (FL) spectra were measured on a F-7000 FL (Hitachi Ltd., Japan). And ultraviolet-visible (UV-vis) absorption spectra were collected by using a Shimadzu UV-2550 spectrophotometer (Tokyo, Japan). Fourier transform infrared (FT-IR) spectrum was recorded on a Nicolet 5700-IR spectrometer (USA). X-ray photoelectron spectroscopy (XPS) analysis were performed on a Thermo ESCALAB 250XI X-ray photoelectron spectrometer (USA). X-ray diffraction (XRD) analysis were performed on a Bruker (Karlsruhe, Germany) D8 Advance X-ray diffractometer monitored at scanning steps of 0.02° in the 2θ ranging from 10° to 50° with graphite monochromatized Cu-Kα radiation ($\lambda = 0.15418$ nm). Transmission electron microscopy (TEM) image was conducted on a JEM-2100 microscope equipped with a thermionic gun operated at an acceleration voltage of 200 kV (JEOL Ltd, Japan). The luminescence decay curve was measured on a FLS980 spectrofluorometer with the excitation at 365 nm (Edinburgh Instruments Ltd., UK). Electrochemical experiments were performed on a CHI 660B electrochemical workstation (CH Instruments Inc., China). The electrochemiluminescence (ECL) signals were captured by an MPI-E multifunctional ECL analyzer (Xienan Rimax Electronics Co. Ltd, China) with a three-electrode system where a modified glassy carbon electrode (GCE) was used as the working electrode, a Pt wire as the counter electrode, and Ag/AgCl as the reference electrode.

Synthesis of aqueous-based $C_2P_3B_8$ AQDs: In a typical synthesis of $C_2P_3B_8$ AQDs, 146.8 mg $PbBr_2$, 85.1 mg CsBr and 8.2 mg 2-Met were added to a three-necked flask with 10 mL DMA solution and the mixed materials were heated to 60 °C and kept magnetically stirring for 60 min. Subsequently, 200 μL OA (stock solution), 200 μL PEG-600 (stock solution) and 500 μL OAm (stock solution) were heated to 60 °C and successively injected to the above solution swiftly. For the sake of making the ligands react fully, this reaction system was kept on stirring for 30 min at 60 °C. Then, 1.0 mL of the above mixed precursor solution was quickly injected into 10 mL of EA (stock solution) and stirred for around 2 min. Next, the above mixed solution was kept at 60 °C for 60 min to ensure sufficient crystallization of AQDs. The reaction mixture was then centrifuged at 8000 rpm for 15 min and the yellow precipitate solid in the bottom of the centrifugal tube was reserved, and immediately add into 20 mL deionized water, followed by ultrasonication processing for dissolving

the AQDs in water solution. Finally, the chartreuse and totally aqueous C₂P₃B₈ AQDs solution (1.8 mg/mL) was obtained and kept at 4 °C refrigerator for further use. The AQDs without PEG protection were prepared under the same condition, except that PEG was not involved in the reaction.

Electrochemical and ECL measurements: A GCE (3 mm diameter, CH Instruments, Inc.) was wet polished carefully with 0.3 and 0.05 μm alumina slurry, followed by thorough washing with ultrapure water. The electrode was then successively sonicated in 1:1 nitric acid, ethanol and doubly distilled water, and then allowed to dry at room temperature. 6 μL of the C₂P₃B₈ AQDs solution (0.18 mg/mL) was then dripped onto the surface of the GCE and dried in air at room temperature, obtained C₂P₃B₈ AQDs modified GCE electrode.

The ECL curves were obtained by potential scanning from 0 to -2.0 V in 0.1 M PBS (pH 7.4) containing 0.1 mM K₂S₂O₈ as co-reactant. Where the stability of ECL intensity of AQDs were conducted with 10-fold diluted AQDs stock solution. Unless otherwise stated, the ECL window was placed in front of the photomultiplier tube (PMT) biased at 450 V with a scan rate of 100 mV s⁻¹. ECL spectra were recorded on a homemade ECL spectrum analyzer consisting of a Princeton Acton P-2300 monochromator, a liquid N₂ cooled Princeton PyLoN digital charge-coupled device (CCD) detector, and a CHI-660D electrochemical workstation.

ECL Efficiency of C₂P₃B₈/GCE: The ECL efficiency of the C₂P₃B₈/GCE system was calculated relative to Ru(bpy)₃²⁺ solution system. The relative ECL efficiency was calculated applying the relation below:¹

$$\Phi_x = \Phi_{st} \left(\frac{\int_0^t I dt}{\int_0^t i dt} \right)_x / \left(\frac{\int_0^t I dt}{\int_0^t i dt} \right)_{st} = \Phi_{st} \left(\frac{\int_a^b I dv}{\int_a^b i dv} \right)_x / \left(\frac{\int_a^b I dv}{\int_a^b i dv} \right)_{st} \quad (\text{Eq. S1})$$

Here, Φ_{st} is the ECL efficiency of 1.0 mM Ru(bpy)₃²⁺/(0.1 M K₂S₂O₈ in 0.1 M PBS with pH 7.4), where the Φ_{st} value is recognized as 100%; i is current value; I is ECL intensity; and x was the sample.

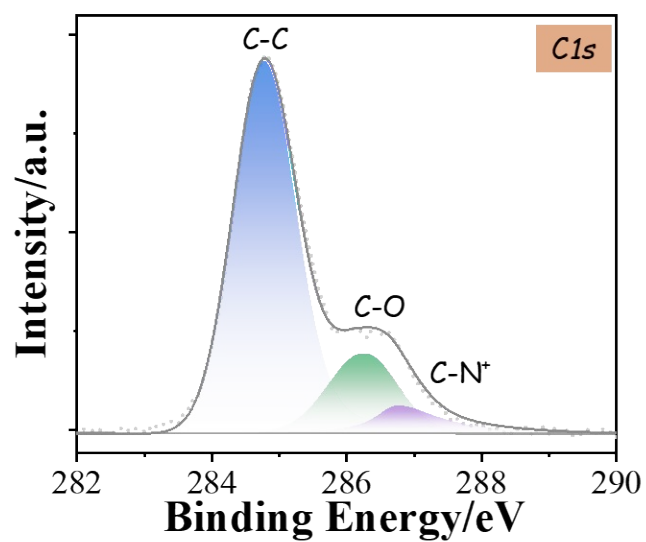


Fig. S1 High-resolution XPS spectra of C1s of $C_2P_3B_8$ AQDs.

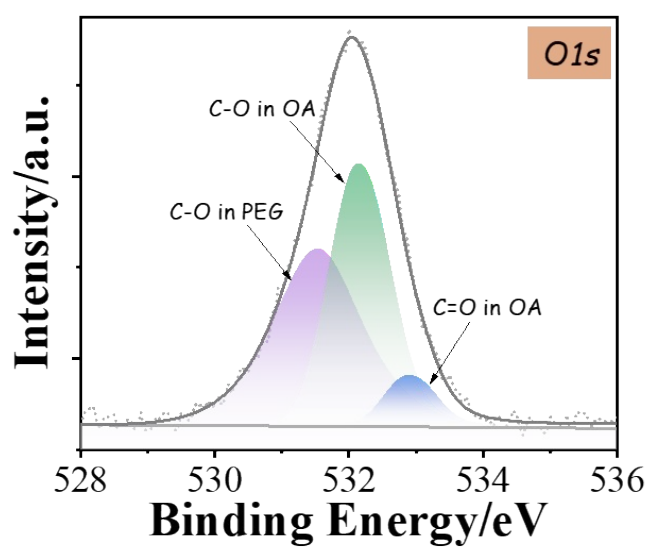


Fig. S2 High-resolution XPS spectra of O1s of $C_2P_3B_8$ AQDs.

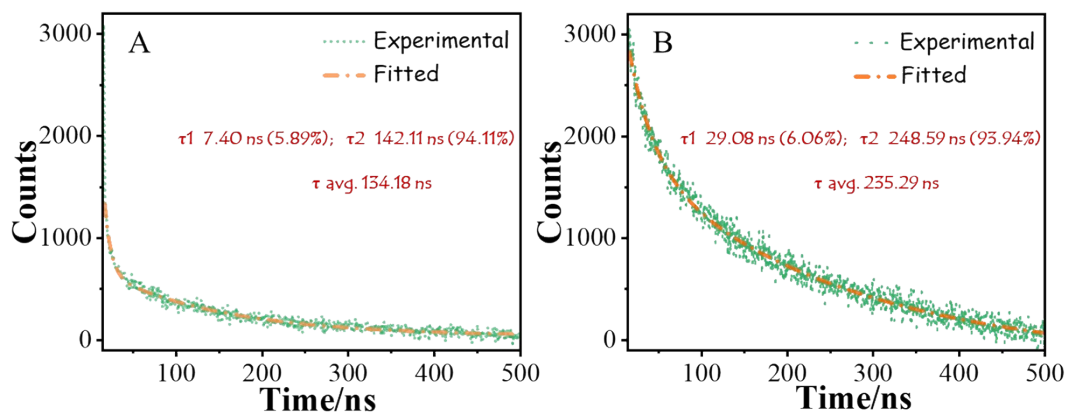


Fig. S3 The FL decay curves of the AQDs without PEG protection (A) and aqueous-based $C_2P_3B_8$ AQDs with PEG protection (B). Excitation at 365 nm.

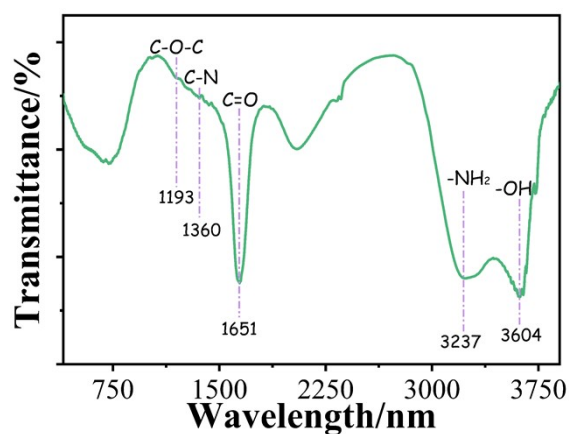


Fig. S4 FT-IR spectrum of $C_2P_3B_8$ AQDs.

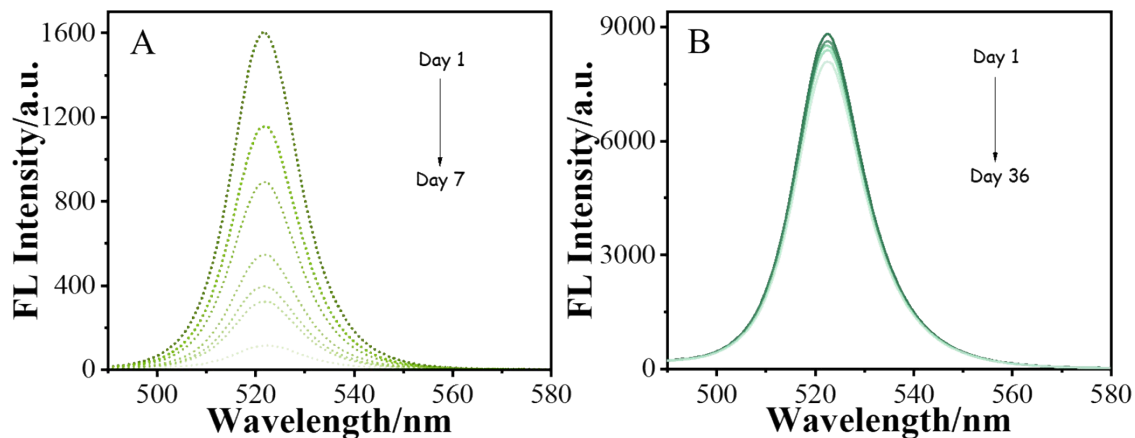


Fig. S5 The FL emission spectra of AQDs without PEG protection (A) and $C_2P_3B_8$ AQDs with PEG protection (B) as time goes. Excitation is set at 365 nm, and emission wavelength scans from 490 to 580 nm. Both the excitation and emission slit widths are set at 5 nm.



Fig. S6 Photographs of $C_2P_3B_8$ AQDs with PEG protection under natural (up) and UV light irradiation at 365 nm excitation (down) with time goes.

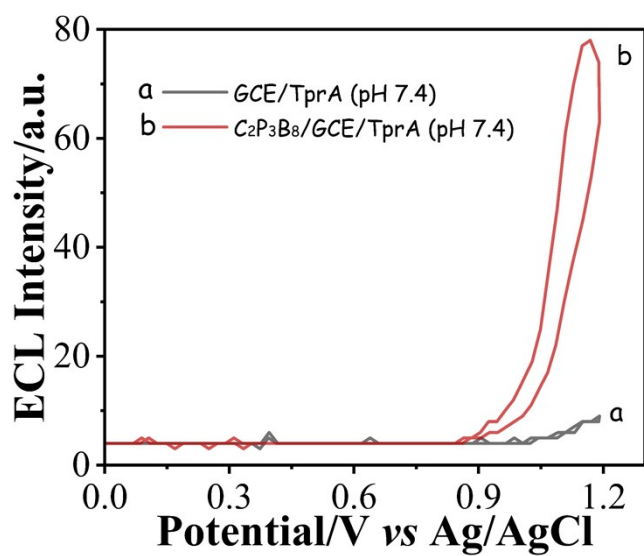


Fig. S7 ECL intensity-potential curves of bare GCE (line a) and C₂P₃B₈ modified GCE (C₂P₃B₈/GCE) in pH 7.4 PBS with 25 mM TPrA (line b). The PMT of anodic ECL analysis was biased at 600 V.

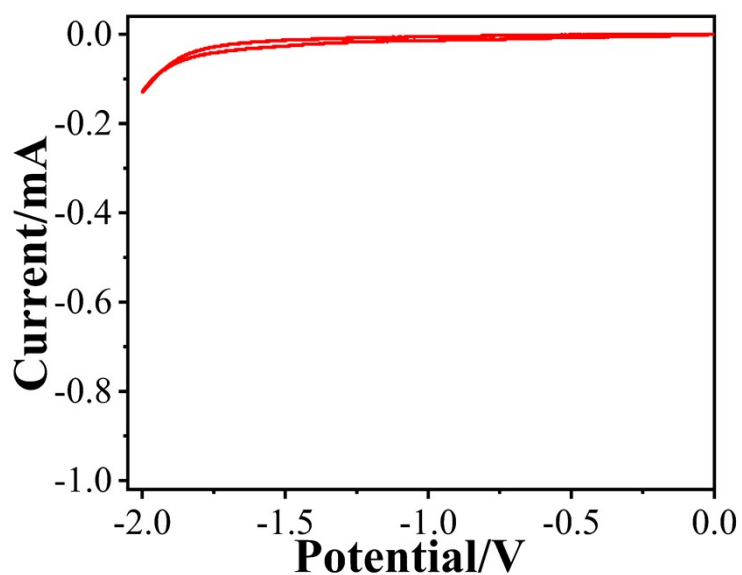


Fig. S8 CV of bare GCE in PBS solution without K₂S₂O₈.

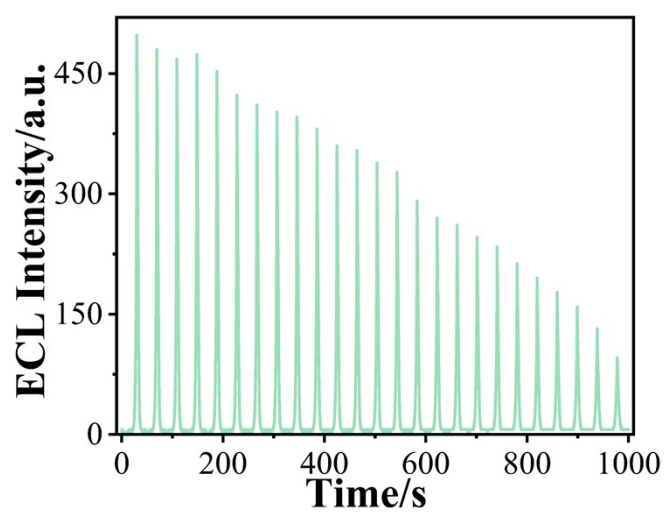


Fig. S9 ECL signals of the AQDs without PEG protection in pH 7.4 PBS containing 0.1 M $K_2S_2O_8$ under a continuous potential step from 0 and -2.0 V.

Table S1. Calculated relative ECL efficiency.

System	$\int_a^b I dv$	$\int_a^b i dv$	Φ
$Ru(bpy)_3^{2+}/K_2S_2O_8$	842.762	1.18×10^{-4}	100%
$C_2P_3B_8$ AQDs/ $K_2S_2O_8$	536.213	9.52×10^{-4}	7.9%

References:

1. M. Hesari, M. S. Workentin and Z. Ding, Highly efficient electrogenerated chemiluminescence of Au_{38} nanoclusters. *ACS Nano* 2014, 8, 8543-8553.