Supplementary Information for:

Improved Ligand-assisted Reprecipitation Method Synthesized Aqueous-phase $CsPbBr_3$ Perovskite Nanocrystals and Their Electrochemiluminescence Behavior

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Chemicals and Reagents

The raw materials for the synthesis of $CsPbBr_3$ NCs used in this paper are cesium trifluoroacetate (Cs-TFA, 98%; Alfa Aesar), lead bromide ($PbBr_2$, 99.999%), cesium bromide (CsBr, 99.99%), N-N-dimethylacetamide (DMA, 99.9%), 4-bromo-butyric acid (BBA, 98%), and oleylamine (OLA, 80-90%). They were purchased from Aladdin Chemical Reagent Co., Ltd.
The materials for electrochemiluminescence (ECL) detection of TFA-BBA-CPB NCs employed in this paper are N-N-Diethyl-ethanamine (TEA), potassium peroxydisulfate ($K_2S_2O_8$), Na_2HPO_4, and NaH_2PO_4. They were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Tetrachloroauric (Ⅲ) acid tetrahydrate ($HAuCl_4{\cdot}4H_2O$), N-acetyl-L-cysteine (NAC), sodium borohydride ($NaBH_4$), L-glutathione reduced (GSH), Histidine (His), and acetyl choline (AChE) were purchased from Aladdin Reagent Company (Shanghai, China). Ascorbic acid (AA), glucose (Glu), and urea were obtained from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Potassium permanganate ($KMnO_4$) was obtained from Lisheng Chemical Reagent Co. Ltd. (Shanghai, China). 0.1 M phosphate buffer solutions (PBS, pH 7.4) containing 0.1 M $K_2S_2O_8$ as coreactant was used as electrolyte in electrochemistry and ECL analysis. Ultrapure water was fabricated in the laboratory by AFX-1002-U. All chemical reagents were of analytical grade and used directly without further purification.

W-LARP method Synthesized aqueous-phase $CsPbBr_3$ NCs

The entire synthesis procedure was carried out via a ligand-assisted reprecipitation method in water without using any inert gas (Fig. S1). 0.8 mmol Cs-TFA and 0.4 mmol $PbBr_2$ were added to a transparent reagent bottle containing 10 mL DMA solutions. The mixed solutions were warmed to 60°C and kept under magnetic stirring for 50 min. Subsequently, 2 mmol OLA and 2 mmol BBA solutions were successively and rapidly injected into the above solutions. In order to make the ligands react entirely, it is crucial to continue heating and stirring for 15 min. Then, 1 mL of the precursor was quickly injected into 12 mL aqueous solutions within 10 seconds under vigorous stirring at 60 °C. The reaction mixture was centrifuged at 5000 rpm for 10 min, and the yellow precipitate solid at the bottom of the centrifugal tube was discarded. The supernatant was kept clear after being centrifuged at 10000 rpm for 15 min again. After centrifugation, the supernatant was retained for subsequent characterization.
In addition, we also synthesized $CsPbBr_3$ NCs employing $PbBr_2$ and CsBr to compare our work in aqueous solutions, and the whole synthesis step was similar to the synthesis of TFA-BBA-$CsPbBr_3$ NCs. 0.4 mmol CsBr and 0.4 mmol $PbBr_2$ were added to a transparent reagent bottle containing 10 mL DMA solutions, hearted to 60°C, and kept under magnetic stirring for 50 min. Subsequently, 2 mmol OLA and 2 mmol BBA solutions were continuously and rapidly injected into the above solutions. In order to make the ligands react entirely, it is vital to continue heating and stirring for 15 min. Then, 1 mL of the precursor was quickly injected into 12 mL aqueous solutions within 10 seconds under vigorous stirring at 60 °C. The reaction mixture was centrifuged at 5000 rpm for 10 min, and the yellow precipitate solid in the bottom of the centrifugal tube was discarded. The supernatant was removed and centrifuged at 10000 rpm for 15 min. After centrifugation, the supernatant was retained for subsequent characterization.[1,2]

First-principles calculation setting

First-principles calculations based on density functional theory (DFT) were carried out via the Vienna ab-initio simulation package (VASP), and the crystal model of $CsPbBr_3$ NCs was constructed using Materials Studio.[3,4] The projected augmented wave was employed to resolve the ion-electron exchange interaction potential in the system, and the electron exchange-correlation function adopted the generalized gradient approximation. Meanwhile, the exchange-correlation energy applied to the perdew burke emperor, and the ultrasoft pseudopotential calculated the relevant pseudopotential. Subsequently, the plane wave truncation

energy was set to 450.0 eV, and the static self-consistency convergence threshold was selected to 5.0×10^{-7} eV/atom in the calculation process. The electronic structure converged, and the static self-consistent field was terminated when the energy difference between adjacent electron steps was less than or equal to 10^{-5}eV/atom. The atomic positions need to be fully optimized in the crystal structure. Meanwhile, the electronic and crystal structure optimization was completed when all atomic residual stress components were less than 0.01 eV/Å. In this case, the Brillouin zone integration was performed a 3x3x1 Monkhorst-Pack grid with a Gaussian spread set to 0.05 eV. The adsorption energy was calculated by using the following equation.

$$E_{ads} = E_{total} - E_{sub} - E_{mol} \quad \text{* MERGEFORMAT (1)}$$

Where E_{ads} indicates the adsorption energy of the substrate on the adsorbate. E_{total} is the total energy of the substrate and the adsorbate. Meanwhile, E_{sub} is the energy of the substrate, together with E_{mol} is the energy of the adsorbed molecular.[5]

Preparation of TFA-BBA-CPB NCs|GCE

Glassy carbon electrodes (GCE, 3 mm diameter, CH Instruments, Inc.) were wet-polished primarily with 0.3 and 0.05 μm alumina slurry and then cleaned thoroughly with ultrapure water. Subsequently, the GCEs were sequentially sonicated in 1:1 nitric acid, ethanol, and double-distilled water and then dried in air at room temperature. Afterward, 2.5 μL of TFA-BBA-CPB NCs solution was dropped on the surface of the GCE and dried at room temperature. The modified electrode was designated as TFA-BBA-CPB NCs|GCE.[6]

Preparation of MnO_2|TFA-BBA-CPB NCs|GCE

MnO_2 was electrodeposited on the surface of TFA-BBA-CPB NCs|GCE via chronoamperometry method at -0.2 V for 300 s in the mixture solution of 20 mM $KMnO_4$ and 90 mM H_2SO_4 (V/V=1:1). The resulting electrode was recorded as MnO_2|TFA-BBA-CPB NCs|GCE and rinsed thoroughly with distilled water. Subsequently, the electrode was dried with N_2 immediately for characterization and application.

The detection process of GSH

100 μL of 1 μM GSH solution was taken in an Eppendorf tube, and MnO_2|TFA-BBA-CPB NCs|GCE was placed and incubated for 10 min. Subsequently, the electrode was gently rinsed with PBS (pH 7.4) and dried naturally.[7]

The test procedure of ECL

The ECL signals were obtained through ECL transient technology with stepping the potential from 0 V to -2 V in 0.1 M PBS (pH 7.4) containing 0.1 M $K_2S_2O_8$. The pulse periods at -2 V and 0 V were 1 s and 10 s, respectively. The change in ECL intensity (ΔI) was calculated using the following equation.

$$\Delta I = (I_2 - I_1) / I_0 \quad \text{* MERGEFORMAT (2)}$$

where I_0 stands for the ECL intensity of TFA-BBA-CPB NCs|GCE. I_1 represents the ECL intensity of MnO_2|TFA-BBA-CPB NCs|GCE, and I_2 stands for the ECL intensity of MnO_2|TFA-BBA-CPB NCs|GCE treated with the GSH.

Design of interference experiment

Five potential interfering substances in blood were selected to formulate solutions, e.g., AA, Glu, His, Urea, and AchE. Afterward, the reaction system was added with the above substances to detect the change in ECL values, examining the specificity and selectivity of the design for the detection of GSH. Where, $C_{interfering\ substance} = 1.0 \times 10^{-5}$ M, $C_{GSH} = 1.0 \times 10^{-6}$ M.

Instrument and Apparatus

The morphology of the samples was investigated by transmission electron microscope (TEM) and high-resolution transmission electron microscope (HRTEM) (F200X G2, FEI Talos, America). The X-ray diffraction (XRD) patterns for phase evolution were obtained through the nickel-filtered Cu Kα radiation in the 2θ range 10-60° at a scan speed of 1.0° 2θ min^{-1} (Ultima IV, Rigaku, Japan). Phase identification was made using standard files. Fourier transform infrared spectroscopy (FTIR) was carried out on an FTIR spectrometer (Nicolet iS-10, Thermo Fisher Scientific, America). The X-ray photoelectron spectroscopy (XPS) was utilized employing an X-ray electron spectrometer (ESCALAB Xi+, Thermo Scientific, America) equipped with an Al Kα source. The Ultraviolet-Visible (UV-Vis) absorption spectra were measured by employing a UV-Vis spectrophotometer (UV-1800PC, Shanghai MEPULDA Instrument Co., China). A fluorescence spectrophotometer (WFY-28, Tianjin Topu Instrument Co., China) was adopted to record the photoluminescence (PL) spectra at room temperature using a 0.5 W 405 nm laser as the excitation source. Fluorescence lifetimes were carried out using a fluorescent lifetime spectrometer (FLS1000, Edinburgh, Britain) based on a time-correlated single photon counting technique under a picosecond pulsed diode laser excitation of 375 nm. Ultraviolet photoelectron spectroscopy (UPS) measurements of TFA-BBA-$CsPbBr_3$ NCs was measured in an ultrahigh-vacuum chamber with a 4D beamline equipped with an electron analyzer and heating element (Thermo ESCALAB 250XI). Results were corrected for charging effects using an Au internal reference. The ECL measurement was measured through an RFAS-1 automatic electrochemiluminescence spectrophotometer (Xi'an Remex Analysis Instrument Co. Ldt. Xi'an, China) with a three-electrode system where a modified GCE was used as the working electrode, a Pt wire as the counter electrode, and Ag/AgCl as the reference electrode. The photomultiplier

tube (PMT) was biased at 850 V in the experiments. Cyclic voltammetry (CV) was recorded with a CHI660C electrochemical analyzer (Shanghai, China). All experiments were carried out at room temperature.

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Table S1. The respective energies of $CF_3CO_2^-$, BBA and $CsPbBr_3$ and the adsorption energy.

Type	Energy Type	Energy magnitude (eV)	Absorption Energy *Eads*(eV)
BBA	E_{mol}	-50.187068	
$CF_3CO_2^-$	E_{mol}	-41.705806	
$CsPbBr_3$	E_{sub}	-602.849280	
$CsPbBr_3$+BBA	E_{total}	-654.328450	-1.292102
$CsPbBr_3$+$CF_3CO_2^-$+BBA	E_{total}	-696.932700	-2.190546

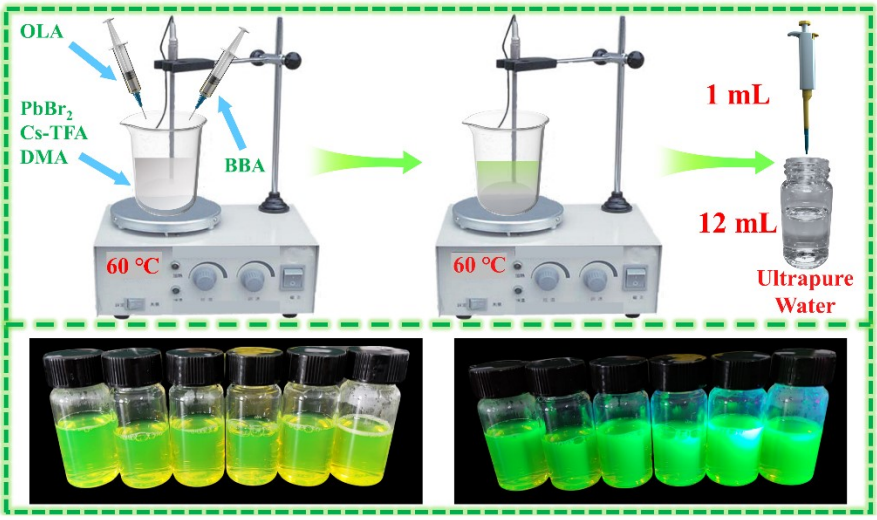


Fig. S1 Synthesis method of TFA-BBA-CPB NCs in aqueous solutions.

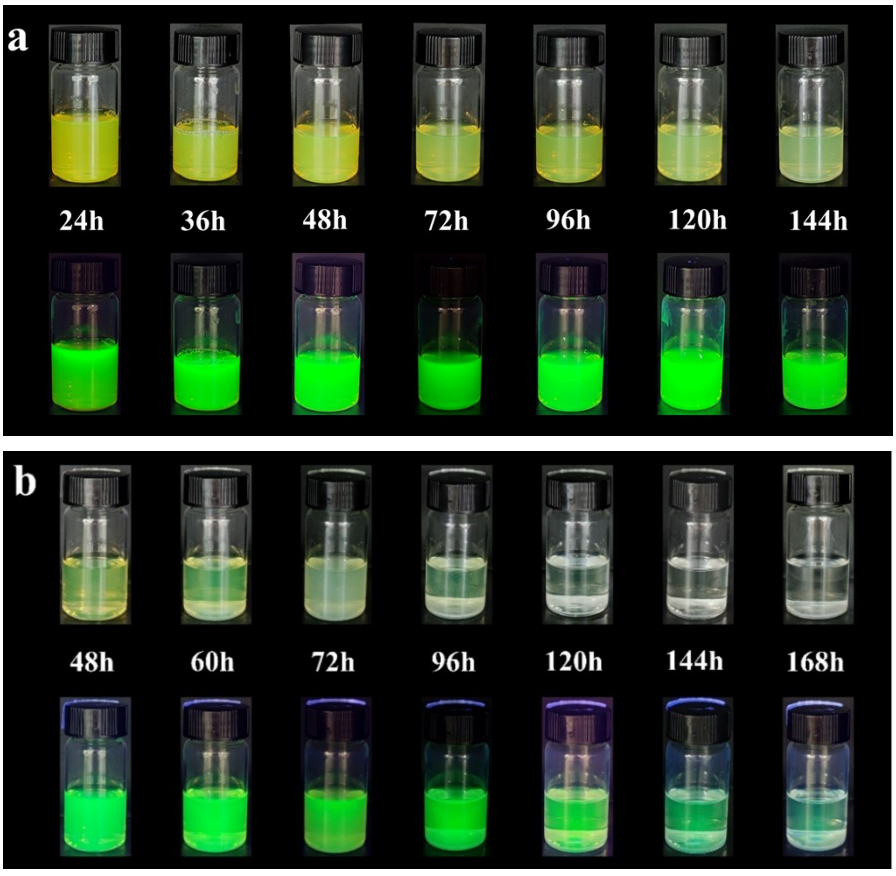


Fig. S2 Sample photographs of (a) TFA-BBA-CPB NCs and (b) BBA-CPB NCs under natural light and UV light irradiation at 365 nm excitation wavelength with time.

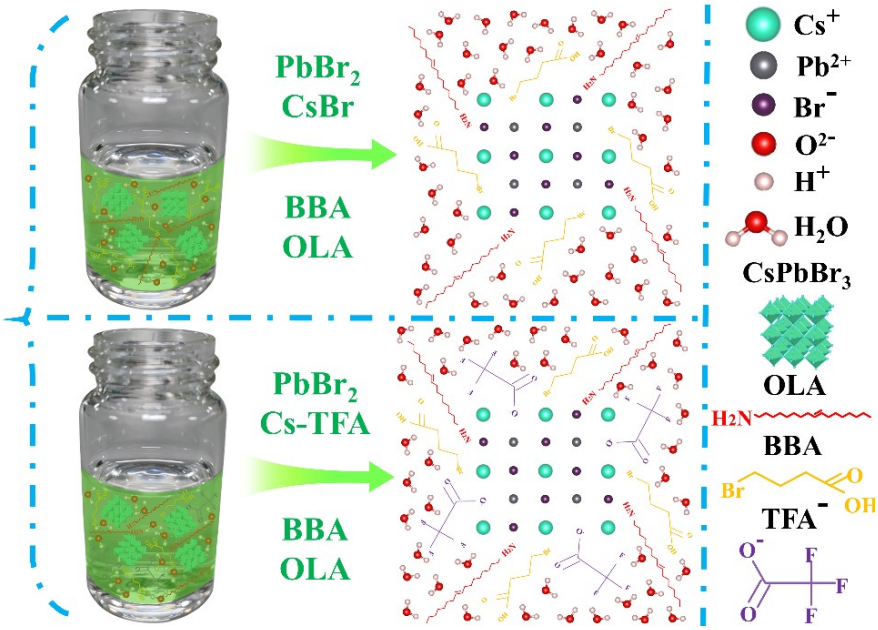


Fig. S3 Mechanistic investigations of TFA-BBA-CPB NCs and BBA-CPB NCs in aqueous solutions.

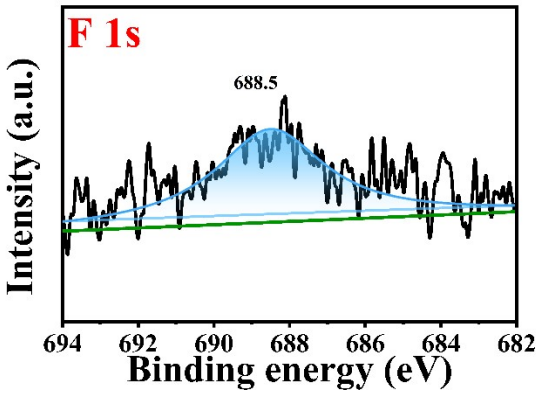
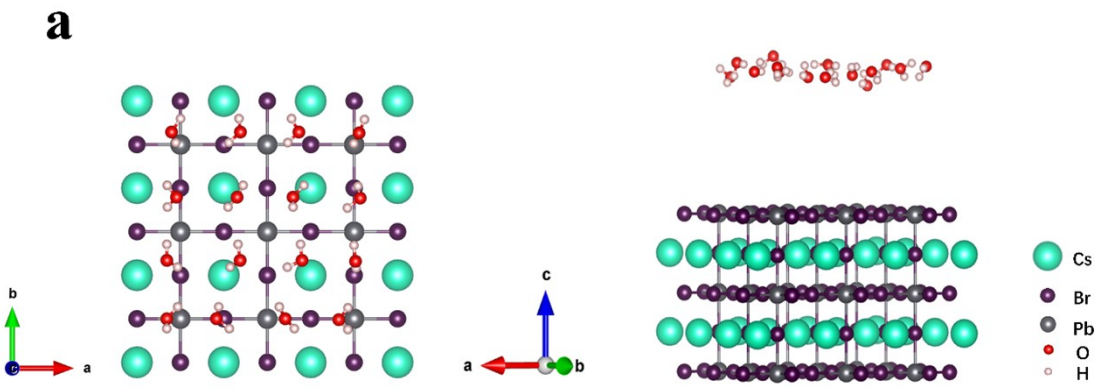


Fig. S4 XPS energy spectrum of F 1s in TFA-BBA-CPB NCs.



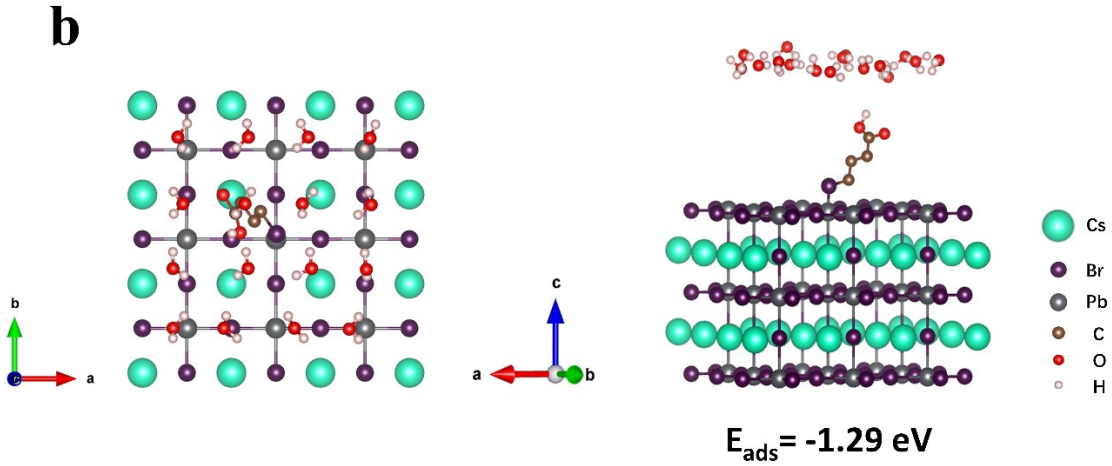


Fig. S5 Crystal structure model of CPB NCs (a)before and (b)after the introduction of BBA.

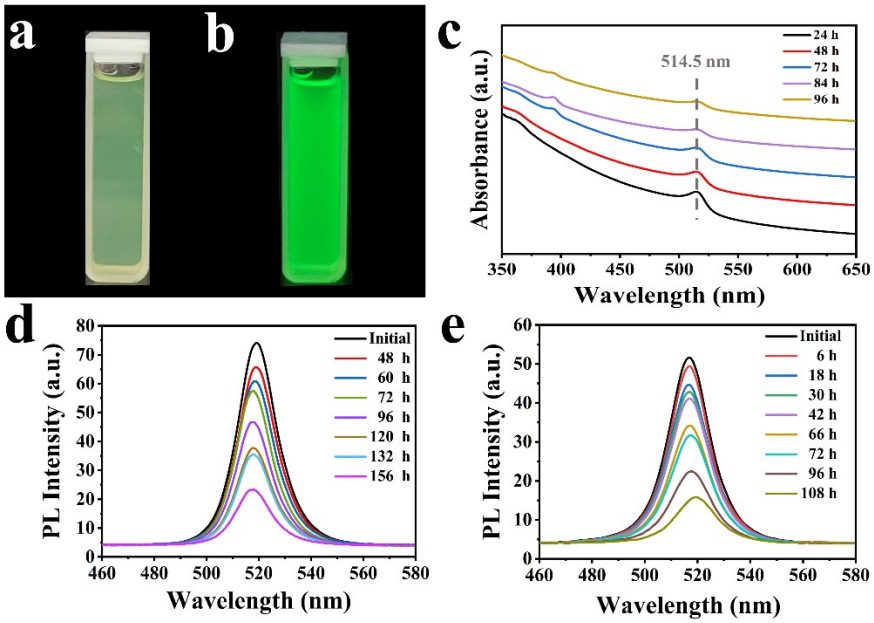


Fig. S6 Sample photographs of TFA-BBA-CPB NCs in quartz cuvette (a) under natural light and (b) UV irradiation at 365 nm excitation wavelength. (c) UV-vis absorption spectra and (d) the fluorescence emission spectra of TFA-BBA-CPB NCs. (e) The fluorescence emission spectra of BBA-CPB NCs in aqueous solutions.

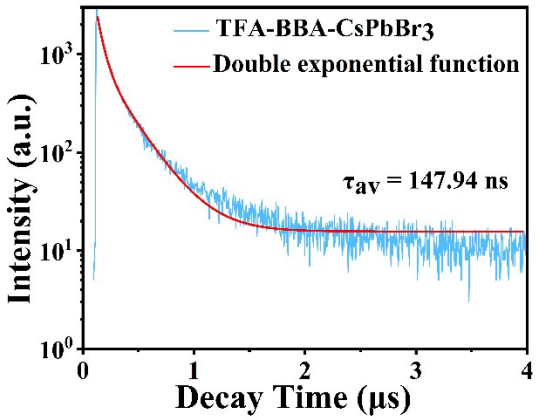


Fig. S7 TRPL decay spectrum at 518 nm under the excitation of 375 nm for TFA-BBA-CPB NCs.

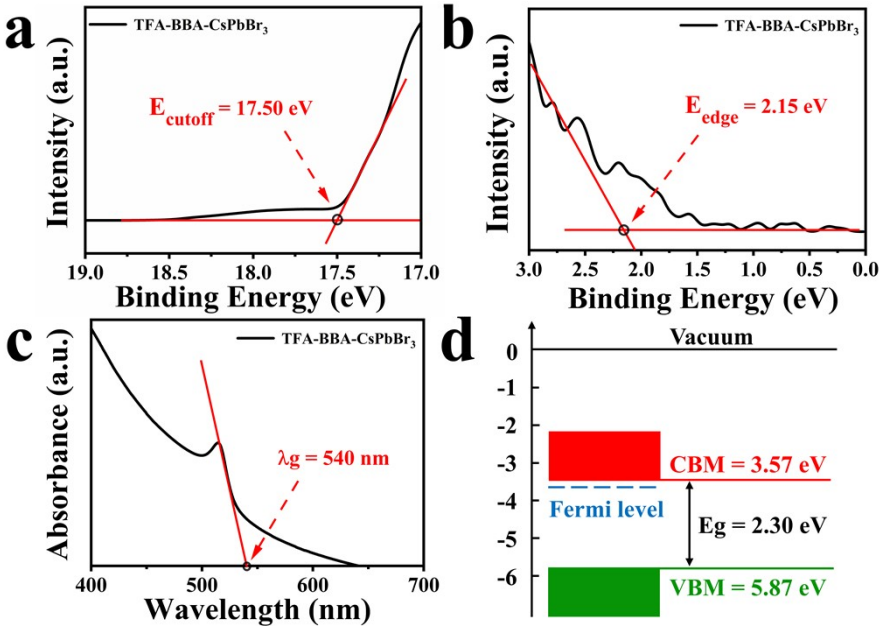


Fig. S8 UPS spectra of TFA-BBA-CPB NCs in the photoemission (a) cutoff and (b) Fermi edge. (c) UV-vis absorption spectrum of TFA-BBA-CPB NCs. (d) Schematic representation of the band structure for TFA-BBA-CPB NCs at the interface.

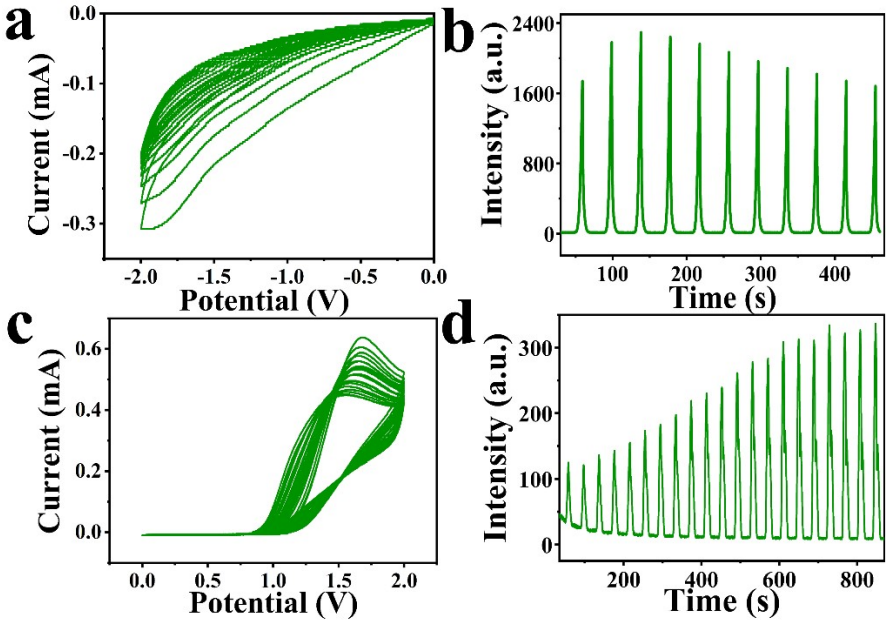


Fig. S9 CVs of TFA-BBA-CPB NCs|GCE in air-free 0.1 M pH 7.4 PBS (a) containing 0.1 M $K_2S_2O_8$ and (c) 0.2 M TEA at a scan rate of 0.1 V/s. ECL-time curve of TFA-BBA-CPB NCs with a potential window between 0.0 V and (b) -2.0 V or (d) +2.0 V.

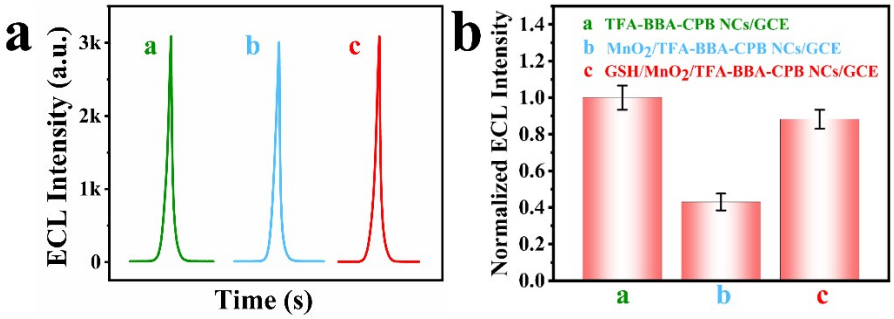


Fig. S10 (a) ECL-time curves of TFA-BBA-CPB NCs (a) before, (b) during (the 14th circle), and (c) after ECL measurements. (b) The changes of ECL intensity of (a) TFA-BBA-CPB NCs|GCE, (b) MnO_2|TFA-BBA-CPB NCs|GCE, and (c) MnO_2|TFA-BBA-CPB NCs|GCE treated with 1 μM GSH in 0.1 M $K_2S_2O_8$.

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