Supporting Information

For

PET-based aqueous-stable two-phase perovskite nanoprobe for quantization of capsaicin in food sample

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Experimental section

Materials

Cesium bromide (CsBr, Aladdin, 99.0%), lead bromide ($PbBr_2$, Aladdin, 99.99%), oleic acid (OA, Aladdin, 85%), oleyl amine (OAm, Aladdin, 80 - 90.0%), polyethylene glycol-600 (PEG-600, Solarbio, 100%), 2-methylimidazole (2-Met, Macklin, 98%), ethyl acetate (EA, Sinopharm, AR), Capsaicin (Cap, Macklin, 97%), glucose (Glu, Sinopharm, AR), fructose (Fru, Sinopharm, AR), phenylalanine (Phe, Sinopharm, AR), histidine (His, Sinopharm, AR), tryptophan (Try, Sinopharm, AR), dopamine (Dop, Aladdin, AR), citric acid (CA, Sinopharm, AR), ascorbic acid (AA, Sinopharm, AR), lysine (Lys, Aladdin, AR), urea (Urea, Aladdin, AR) and N,N-dimethylacetamide (DMA, Sinopharm, AR) were used directly without further purifications. Other reagents were analytical grade reagents that have not been processed. 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 Jasco FP-6500 fluorescent spectrofluorometer (Jasco, Japan), and the 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 was performed on a Bruker (Karlsruhe, Germany) D8 Advance X-ray diffractometer monitored at scanning steps of 0.02^o in the 2θ ranging from 10^o to 50^o with graphite monochromatized Cu-Kα radiation (λ = 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).

Synthesis of aqueous-based two-phase $CsPb_2Br_5$/$CsPbBr_3$ PQDs

In a typical synthesis of two-phase $CsPb_2Br_5$/$CsPbBr_3$ PQDs (tpPQDs), 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 raw materials were heated to 60 ℃ 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 ℃ and successively injected to the above solution swiftly. For the sake of making the ligands

react fully, the reaction system was kept on stirring for 60 min at 60 ℃. Then, 1 mL of the above mixed precursor solution was quickly injected into 10.0 mL of EA (stock solution) and stirred for around 2 min. Next, the above mixed solution was kept at 60 ℃ for 60 min to ensure sufficient crystallization of perovskite. 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 were immediately added into 20 mL deionized water, followed by ultrasonication processing for dissolving the NCs in water solution. Finally, the chartreuse and totally aqueous tpPQDs solution (~1.85 mg mL^{-1}) was obtained and kept at 4 °C refrigerator for further use.

Optimizing the experimental conditions

In order to achieve highly sensitive detection of Cap, we optimized the pH value of the detection system. Firstly, 100 μL tpPQDs solution and 25 μL Cap (1 mM) standard solution were incubated with 50 μL HEPES buffer (50 mM) at different pH values for 10 min. Then, the final volume of the mixture was adjusted to 500 μL with ultrapure water. Finally, the FL spectra of these mixtures were measured. Test conditions: λ_{ex}= 365 nm, and the excitation and emission slit widths were set 5 and 5 nm, respectively.

Fluorescence detection procedure for Cap

For the detection of Cap, 100 μL tpPQDs solution, 50 μL HEPES buffer (pH=5.0) and standard Cap solution and ultrapure water were added to a final volume of 500 μL. The final concentration of Cap ranged from 0 to 300 μM. The obtained solution was excited by 365 nm laser with excitation and emission slit widths of 5 and 5 nm, respectively.

Real sample analysis

Red pepper powders were purchased at a local supermarket. It was dissolved in ethanol and then ultrasounded for 10 min followed by filtrating through a 0.22 μm filter membrane and collecting the filtrate. The filtrate was diluted 100-fold with HEPES buffer (pH 5.0) for subsequent analysis. The standard addition method was used to determine the concentration of Cap in the actual samples. That is, 100 μL tpPQDs solution, 50 μL of HEPES buffer (pH = 5.0), 250 μL of diluted real samples and different amounts of Cap standard solution were in turn added to a centrifuge tube. The volume of the above mixture was set with ultrapure water to 500 μL. After being mixed with a vortex mixer, the mixture was balanced for 10 min before FL spectrum measurements were performed.

XPS analysis

The peaks other than the common Br3d, Pb4f, C1s, N1s, O1s and Cs3d peaks were detected. The remaining weak peaks at 20.2 ($Pb5d^3$), 159.1 (PbS), 181.5 ($Cs4p^1$), 228.7 (S2s), 255.3 (Br3s), 413.1 ($Pb4d^5$), 436.1 ($Pb4d^3$), 558.1 (Zn Auger), 644.7 ($Pb4p^3$), 738.9 eV ($Cs3d^3$), 761.8 ($Pb4p^1$), 918.0 (Cs Auger), and 979.9 (O Auger) correspond to elements present in the tpPQDs. The peaks corresponding to ITO mostly are not existing in tpPQDs due to complete covereage of the substrate by tpPQDs, which are most of the peaks still come from the obtained tpPQDs owing to the obtained tpPQDs with highly pure after washing, denoted as 1*-13*.[1-3]

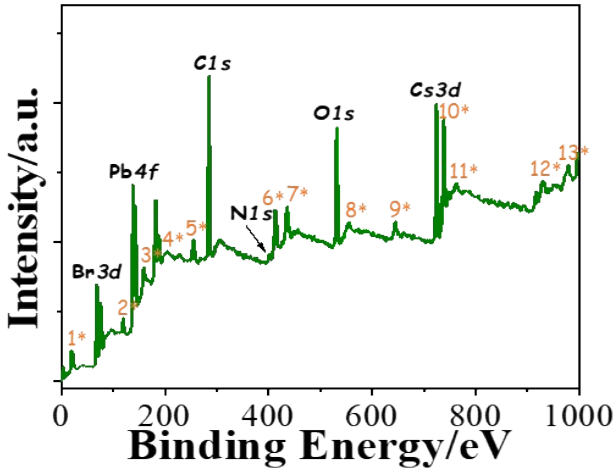

Fig. S1 The wide range XPS survey of tpPQDs.

Evaluation of the FL performance of tpPQDs with time goes

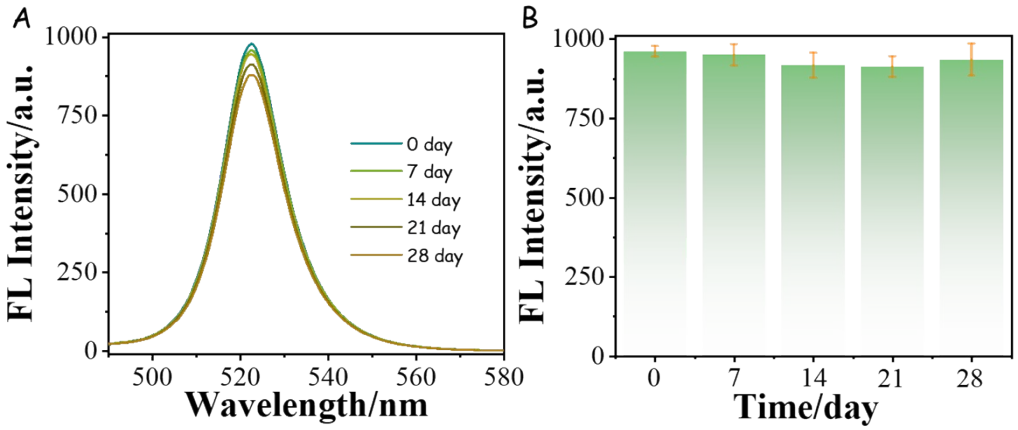

Fig. S2 (A) The FL emission spectra of tpPQDs as time goes; (B) The trend of FL intensity over time corresponding to *Fig. S2A*.

Evaluation of the FL performance of tpPQDs with pH change

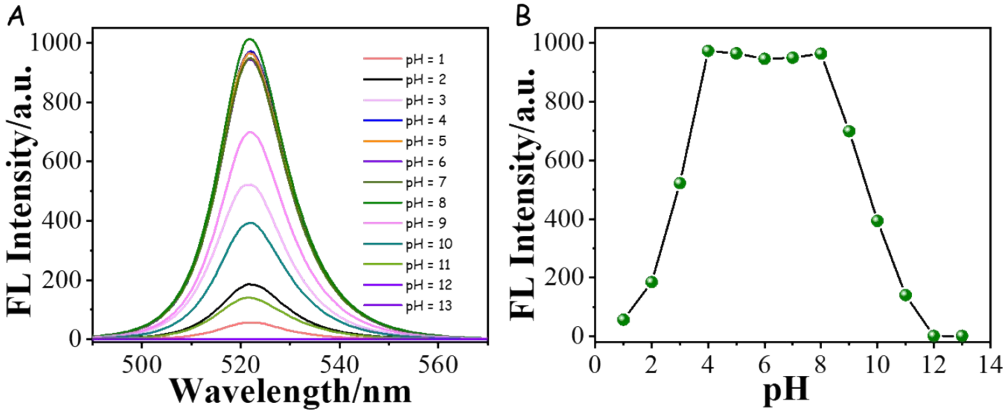

Fig. S3 (A) FL intensities at 521 nm of the tpPQDs at various pH values; and (B) relative FL intensity variation tendency at 521 nm (λ_{ex} = 365 nm).

Study on the mechanism of Cap analysis tpPQDs-based probe

Firstly, the inner filter effect and the FL resonance energy transfer mechanisms can be ruled out since there is no significant overlap between the FL emission/excitation spectra of tpPQDs and the absorption spectrum of Cap (*Fig. 2*).[4,5] Therefore, we speculated that the Cap-triggered FL suppression of tpPQDs may be ascribed to photo-induced electron transfer (PET) mechanism. To validate this hypothesis, UV-vis and UPS spectra analysis were conducted to calculate the highest occupied molecular orbital-lowest unoccupied molecular orbital (*HOMO-LUMO*) energy-level of the tpPQDs and tpPQDs/Cap noncovalent combination. The calculation of *HOMO-LUMO* energy-level was obtained according to the following formulas:[6]

$$E_{HOMO} = -[21.22 - (E_{cutoff} - E_{onset})]\ eV \quad (1)$$

$$E_{LUMO} = [E_{HOMO} + E_g]\ eV \quad (2)$$

wherein, the E_{onset} and E_{cutoff} respectively represent the position of the onset and cutoff binding energies in the UPS spectrum. the E_g represents the absorption edge in the UV-vis spectrum. From UPS spectra, E_{onset} and E_{cutoff} of the tpPQDs were determined as 3.94 and 16.88 eV, respectively (Fig. S4A), and E_{onset} and E_{cutoff} of the tpPQDs/Cap combination were measured as 4.43 and 16.71 eV, respectively (Fig. S4B). Fig. S4C displays that the E_g values of the tpPQDs and tpPQDs/Cap respectively is 2.17 and 2.12 eV. Thus, by above formulas. (1) and (2), the E_{HOMO} and E_{LUMO} of the tpPQDs respectively was determined as -8.28 and -6.11 eV, and the E_{HOMO} and E_{LUMO} of the tpPQDs/Cap respectively was determined as -8.94 and -6.82 eV.

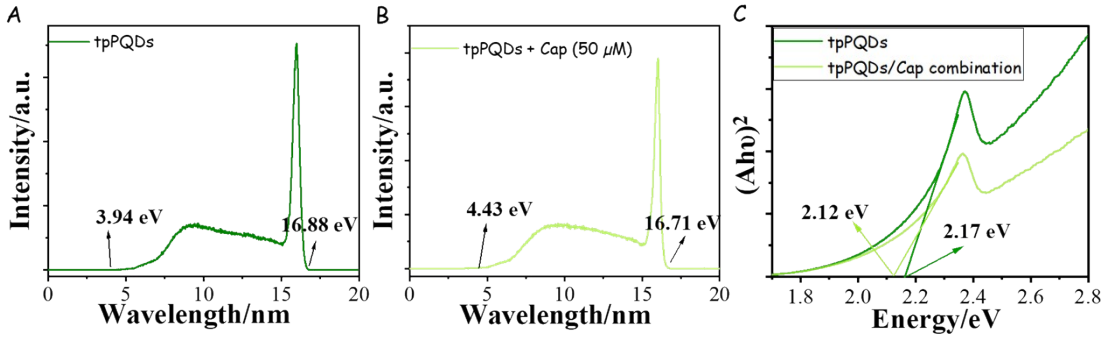

Fig. S4 UPS spectra of the tpPQDs (A) and the tpPQDs/Cap combination (B); C) Optical energy gaps of tpPQDs and tpPQDs/Cap combination.

Optimization of experimental conditions

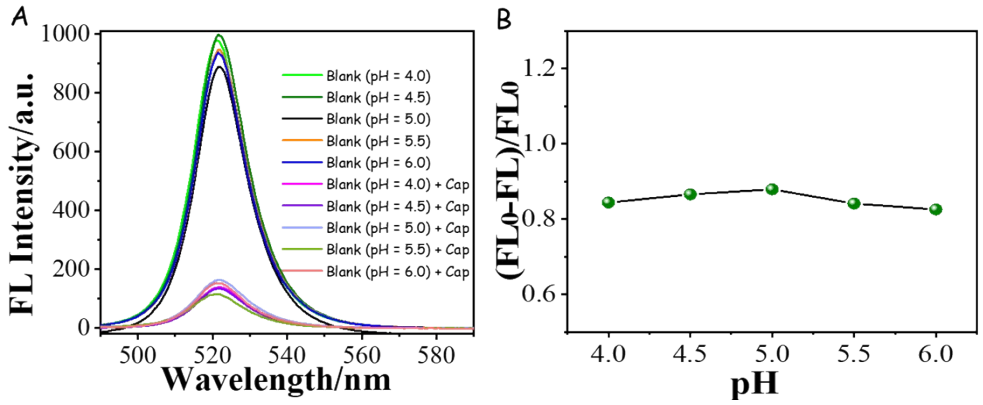

Fig. S5 (A) FL spectra of the tpPQDs or tpPQDs/Cap combination at different HEPES values; (B) Relative FL intensity variation tendency at 521 nm (λ_{ex} = 365 nm). The concentration of Cap was 50 μM.

Study of selectivity of the tpPQDs-based sensing system

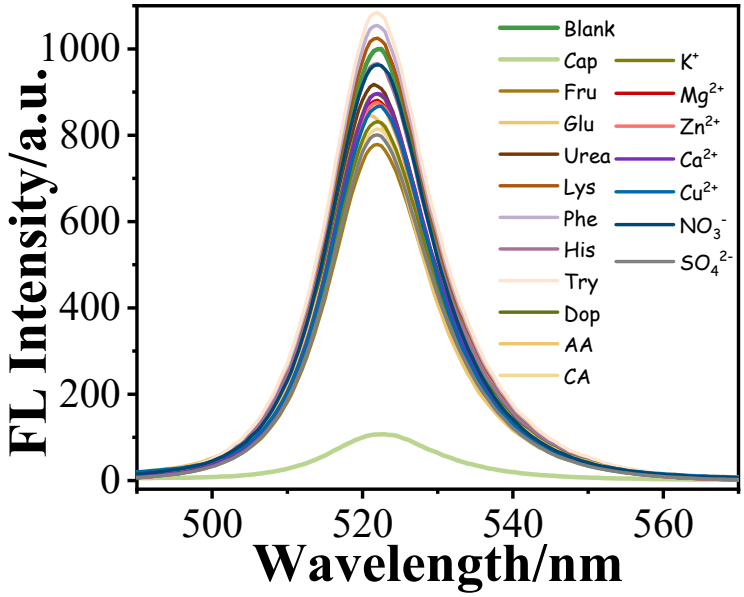

Fig. S6 FL spectra of tpPQDs after react with different interfering substances. The concentration of Cap was 300 μM, and that of other interfering substances was 300 μM, respectively. Test conditions: λ_{ex} = 365 nm, the slit widths of excitation and emission was 5 and 5 nm, respectively.

Table S1 Comparison of the results from the developed tpPQDs-based sensing platform and other strategies for Cap detection.

Methods	Meterials	Linear range	LODs	Reaction time	Real samples	Refs.
Electrochemical	N-doped GrNPs	1-100 μM	0.37 μM	200 s	Chili samples	[7]
SERS	Ag NPs sol.	10-2500 μg L^{-1}	2.9 μg L^{-1}	Within 10 min	Waste oils	[8]
Colorimetric	GO@AuNPs	0.5-120 ng mL^{-1}	0.14 ng mL^{-1}	60 min	Oil samples	[9]
TRFICA	mAbs	11.9-62.5 ng mL^{-1}	1.5 ng mL^{-1}	> 1 min	Serum	[10]
SERS	Fe_3O_4@Ag	10-1.0 × 10^{-3} μM	1.0 × 10^{-2} μM	within 7 min	Vegetable oils	[11]
Electrochemical	Carbon dots	0.05- 500 μM	5.4 nM	Within 5 min	Seasoning	[12]
Colorimetric	MBTH	0.2-4.0 mM	0.17 mM	20-30 s	Extraction	[13]
Fluorescence	tpPQDs	0.5 nM-300 μM	0.21 nM	< 10 s	Red pepper	This work

Table S2 Results of the determination of Cap in red pepper powder samples (n=3).

Sample	Initial value (μM)	Added value (μM)	Found value (μM)[a]	SHUs[b]	Recovery (%)	RSD (%)
Red pepper powder	49.09	0.1	49.27	226	100.2	3.1
	45.82	10	55.21	254	98.9	4.0
	47.64	50	99.74	458	102.2	2.9

[a] The data were obtained from the average of three parallel samples. To ensure the accuracy of the results, it is necessary to adjust the initial concentration value of the Cap within the linear range of 0.5 nM - 300 μM.

[b] Scoville Heat Units (SHUs) were obtained according to the following steps: Firstly, the data of the Cap concentration in μM has been converted to ppm units, then to SHUs assuming that 1 ppm is approximately equal to 15 SHUs.[14,15] Note that the initial SHUs of the actual sample should be 200 times the data in the table, as this data was obtained by diluting the original solution 200 times.

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