Electronic Supplementary Information

A ratiometric optical strategy for bromide and iodide ions sensing based on target-induced competitive coordination of metal-organic nanosystem

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Experimental

1. Chemicals

Mercaptosuccinic acid and thiosemicarbazide were supplied by Adamas Reagent, Ltd., China. $HgCl_2$, HNO_3 (wt. 68%), Na_2HPO_4, KH_2PO_4, KIO_3, NaClO, Na_2S, Na_2SO_4, $Zn(NO_3)_2$, Na_2CO_3, NaAc, NaF, NaCl, $NaIO_4$, NaBr, and KI were obtained from Aladdin Reagent Co., Ltd., Shanghai, China. Phosphate buffer (PB, 1/15 M) with different pH values were prepared according to a standard protocol. All chemicals used were of analytical reagent grade. Ultrapure water (18 MΩ cm) was used in all experiments.

2. Instruments

Transmission electron microscopy (TEM) and high resolution TEM (HRTEM) analyses were obtained with a Talo F200X transmission electron microscope (FEI, Czech Republic). An F-4500 spectrofluorometer (Hitachi, Japan) was applied for collecting fluorescence spectra. Photomultiplier tube (PMT) voltage was fixed at 700 V, and the slits were set at 5 nm for both excitation and emission. X-ray photoelectron spectroscopy (XPS) spectra were taken on a Thermo ESCALAB 250XI surface analysis system. A Bruker IFS 113v spectrometer (Bruker, Germany) was utilized for recording Fourier transform infrared (FT-IR) spectrum. Ultraviolet visible (UV-vis) absorption spectra were collected on a UV-vis 2450 spectrophotometer (Shimadzu, Japan). Fluorescence lifetimes were measured with a Fluorolog-3 fluorescence spectrophotometer (Horiba, USA). The dynamic light scattering (DLS) was measured using a NanoBrook Omni particle size and zeta potential analyzer (Brook, China). A pH meter (FE28, Mettler-Toledo, Switzerland) was used for the measurement of solution pH values.

3. Formula expressing about Rayleigh scattering theory

According to the Rayleigh scattering theory, the scattering intensity is closely related to the volume and morphology of particles. The formula is expressed as follows:[1]

$$I = \frac{24\pi^3 \nu^2 N}{\lambda^4}\left(\frac{n_1^2 - n_0^2}{n_1^2 + 2n_0^2}\right)^2 I_0 \qquad (1)$$

where I_0 and I are the intensities of excitation light and scattering light, respectively. ν and N denote the volume of nanoparticles and the number of nanoparticles per unit volume, respectively. λ is wavelength. n_0 and n_1 denote the refractive index of medium and scatterer, respectively. According to the above formula, the scattering intensity is proportional to the square of the particle volume.

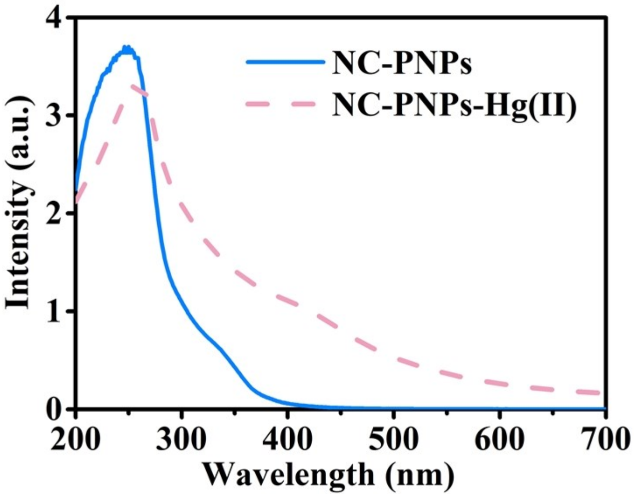

Fig. S1 UV-vis absorption spectra of the NC-PNPs and NC-PNPs-Hg(II) nanosystem. Conditions: [NC-PNPs] = 0.88 mg/mL, [NC-PNPs-Hg(II)] = 40% v/v, PB (pH 5.0).

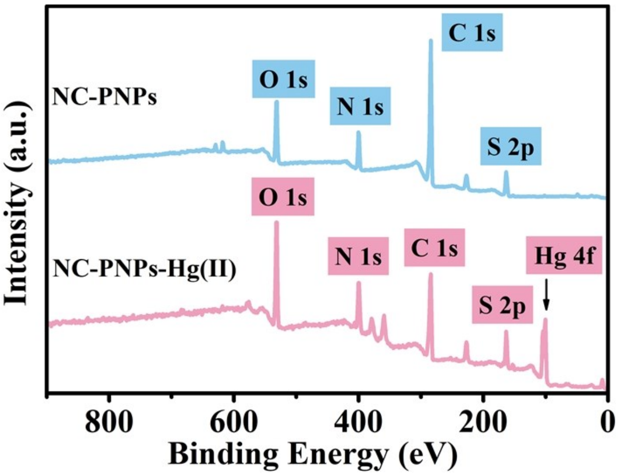

Fig. S2 XPS spectra of the NC-PNPs and NC-PNPs-Hg(II) nanosystem.

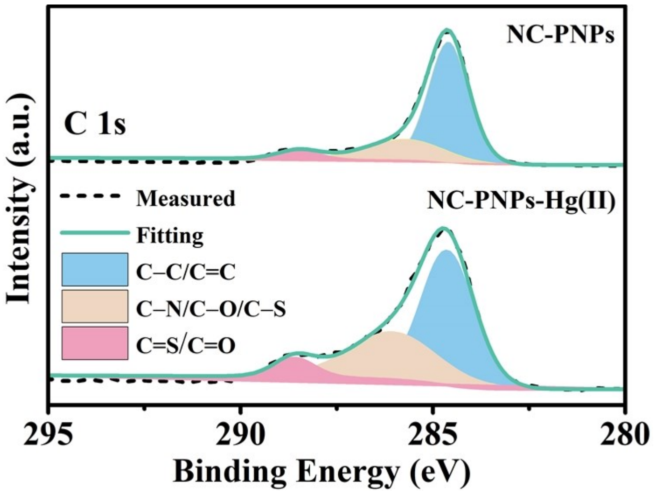

Fig. S3 The high-resolution C1s spectra of the NC-PNPs and NC-PNPs-Hg(II) nanosystem.

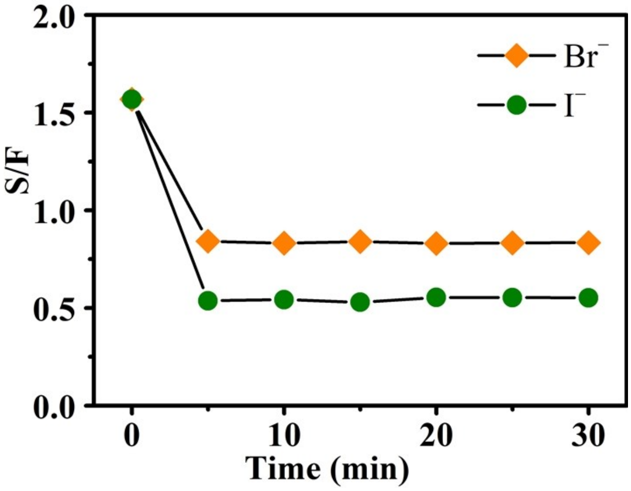

Fig. S4 Effect of reaction time on the ratio of SOS and FL of the NC-PNPs-Hg complex in the presence of Br^-/I^-. [NC-PNPs-Hg(II)] = 40% v/v, PB (pH 5.0), [Br^-] = 200 μM, [I^-] = 200 μM.

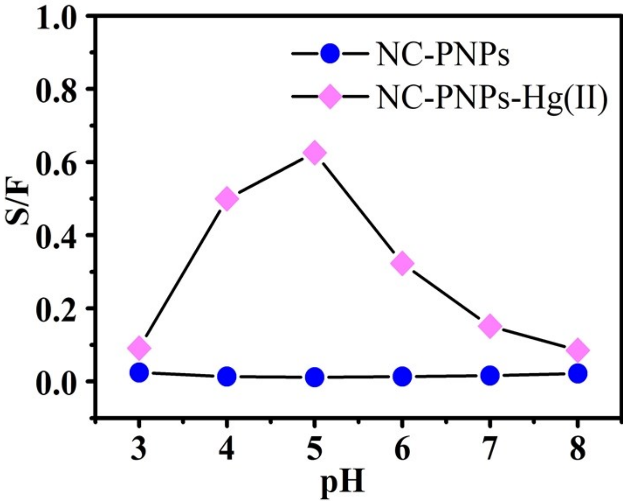

Fig. S5 SOS and FL ratios of the NC-PNPs and NC-PNPs-Hg nanocomplex as a function of pH values. [NC-PNPs] = 0.88 mg/mL; [NC-PNPs-Hg] = 40% v/v.

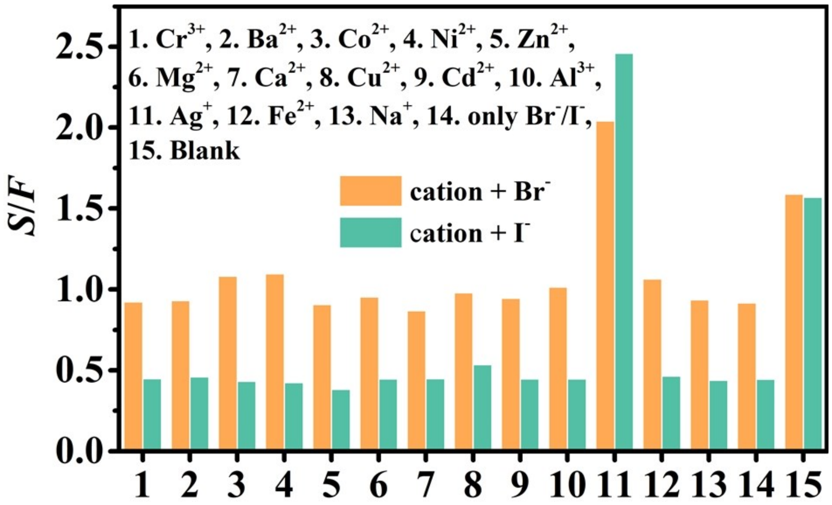

Fig. S6 Selectivity of NC-PNPs-Hg(II) nanosystem for Br^-/I^- (200 μM) in the co-existence of different cations (200 μM).

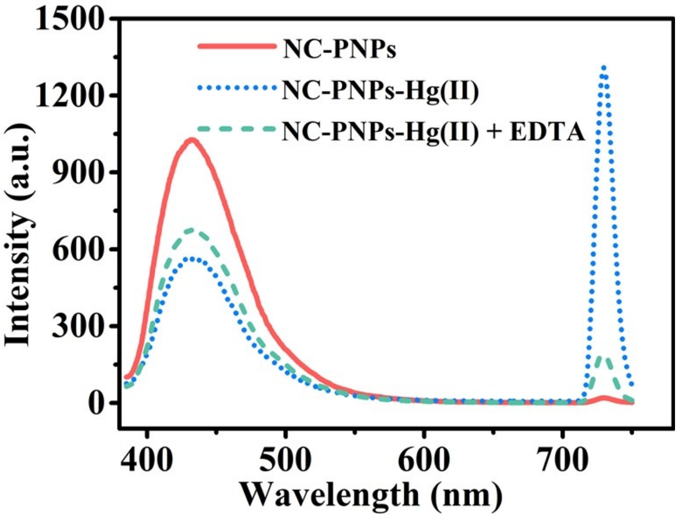

Fig. S7 FL-SOS spectra of NC-PNPs-Hg(II) in the presence of EDTA (1 mM).

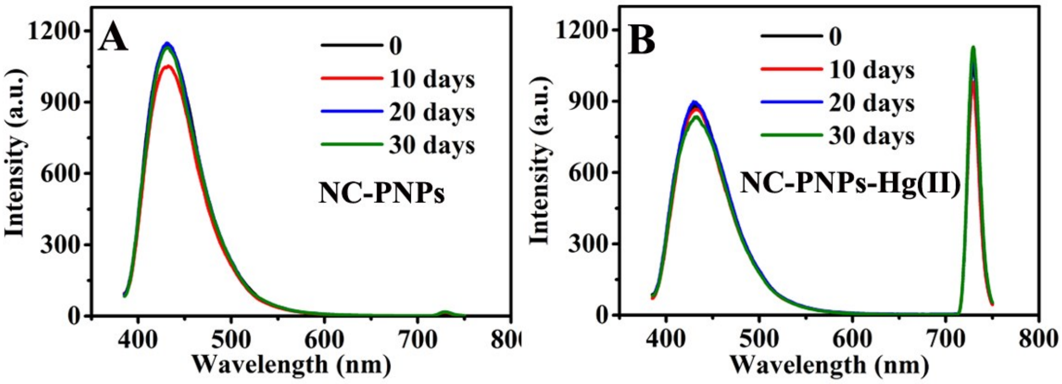

Fig. S8 FL and SOS spectra of NC-PNPs and NC-PNPs-Hg(II) solutions as a function of standing time at room temperature.

Table S1 The fitted parameter and average lifetime (τ_{ave}) values of NC-PNPs and NC-PNPs-Hg(II) (λ_{ex} = 365 nm; λ_{em} = 430 nm).

	τ_1 (ns)	α_1 (%)	τ_2 (ns)	α_2 (%)	χ^2	τ_{ave} (ns)
NC-PNPs	27.33	88.36	3.00	11.64	1.007	24.50
NC-PNPs + Hg(II) (50 μM)	27.19	87.71	3.99	12.29	1.156	24.34
NC-PNPs + Hg(II) (200 μM)	24.87	88.66	3.91	11.34	1.079	22.49

The average lifetime of NC-PNPs before and after addition of Hg(II), τ_{ave}, is measured using the following equation:[2]

$$\tau_{ave} = (\alpha_1 \tau_1 + \alpha_2 \tau_2)/(\alpha_1 + \alpha_2) \qquad (2)$$

where α_1 and α_2 are the fractional contributions of time-resolved decay lifetime of τ_1 and τ_2, respectively. The χ^2 values in Table S1 represent the goodness of the exponential fits to the raw data.

Table S2 Comparison of different ratiometric methods for Br$^-$/I$^-$ detection.

Ratiometric sensors	Target	Linear range (μM)	Detection limit (μM)	Ratiometric signals	Reference
Gold nanoparticles	Total Br	Not given	8.8	Absorbance	[3]
Benzothiazole-based organic cation-Hg(II) complex	Br$^-$	0–12	0.022	FL	[4]
Benzothioxanthene derivative	Br$^-$	300–60000	750	FL	[5]
Cationic thiophene diblock copolymers	Br$^-$	Not given	Not given	FL	[6]
NC-PNPs-Hg(II) nanocomplex	Br$^-$	15–360	5.46	FL-SOS	This work
N-doped C-dots	I$^-$	0.09–50	0.06	FL	[7]
Ag-DQAg	I$^-$	Not given	3.54	FL	[8]
Benzothioxanthene derivative	I$^-$	200–6000	620	FL	[5]
Cationic thiophene diblock copolymers	I$^-$	Not given	Not given	FL	[6]
NC-PNPs-Hg(II) nanocomplex	I$^-$	5–300	0.9	FL-SOS	This work

Table S3 Detection of I^- and Br^- in real water and food samples, respectively (n = 3).

Samples	Analyte	Spiked (mM)	Found (mM)	Recovery (%)	RSD (%)
Kelp	I^-	0	ND [a]		
		0.100	0.115	110.48	6.41
		0.192	0.188	97.74	1.57
Tea	I^-	0	ND [a]		
		0.160	0.157	98.09	3.68
		0.300	0.302	100.66	8.03
Potable water	Br^-	0	ND [a]		
		0.096	0.119	123.95	3.54
		0.192	0.249	129.99	3.44
Beibei reservoir water	Br^-	0	ND [a]		
		0.100	0.115	114.59	9.39
		0.200	0.194	97.20	1.02

[a] ND: not detected.

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