Supporting Information

Fluorescent Poly(tannic acid)-based Nanoprobe for Selective and Sensitive Detection of Bismuth Ions

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1. Experiments

1.1 Optimization of synthesis conditions for FPTA NPs

To enhance fluorescence intensity of prepared FPTA NPs, the effect of various experimental conditions was explored. The fluorescence signal was determined by changing the concentration of TA from 0.01 g/mL to 0.05 g/mL, the concentration of NaOH from 0.001 g/mL to 0.005 g/mL, the addition amount of H_2O_2 from 1 mL to 5 mL and the reflux reaction time from 1 h to 5 h, respectively. As shown in Fig.S1, using 0.03 g/mL of TA, 0.003 g/mL of NaOH and 4 mL of H_2O_2 and reflux time for 3 h were finally screened out to be the optimized reaction conditions for synthesizing FPTA NPs.

1.2 Calculation of quantum yield of FPTA NPs

Quinine sulfate (Qs) was used as the standard reference material to measure the fluorescence quantum yield (QY) of the FPTA NPs. Firstly, a certain amount of Qs was dissolved in 0.1 M H_2SO_4 solution, and the absorbance A at 350 nm was recorded, by the way, the absorbance was kept below 0.1. Subsequently, the fluorescence emission peak integral area F of the same solution excited at 350 nm was recorded, thus, the linear fitting line between absorbance A as X axis and integral area F as Y axis is obtained, and the slope [K_{Qs}] is also obtained. The same experimental method is used to measure the FPTA NPs solution and obtain the slope [K_s]. The quantum yield of Qs is reported to be 54 % [1], according to the following formula to calculate the QY of FPTA NPs.

$$\Phi_s = \Phi_{Qs} \times \frac{\eta_s^{\,2} F_s A_{Qs}}{\eta_{Qs}^{\,2} A_s F_{Qs}} = 54\,\% \times \frac{K_s}{K_{Qs}}$$

Where Φ is the QY, subscripts S and Qs refer to FPTA NPs and quinine sulfate, η is the refractive index of the solvent, for these aqueous solutions, $\eta_s/\eta_{Qs}=1$.

1.3 FPTA NPs functionalized filter paper strips for visual detection

The filter paper was first cut into circular paper strips (each with a diameter of 5 mm), immersed in FPTA NPs solution (1.7 mg/mL) for 10 minutes, and then removed from the FPTA NPs solution and dried in air. The FPTA NPs-functionalized paper

strips were stored in a sealed bag for further use. Various concentrations of Bi^{3+} (15 μL) were dropped onto the FPTA NPs-functionalized paper strips and dried in air, respectively. Photographs of the test paper were taken using a smartphone under both natural light and a 365 nm UV lamp.

1.4 Spectroscopic titrations

Based on the photophysical results of FPTA NPs in presence of Bi^{3+}, its ability to bind to FPTA NPs was evaluated by spectroscopic titration with Bi^{3+} addition. The stoichiometric ratio of FPTA NPs with Bi^{3+} was analyzed through a Job's plot. The mixed solutions were prepared with different proportions of Bi^{3+} to FPTA NPs, specifically 1:9, 2:8, 3:7, 4:6, 5:5, 6:4, 7:3, 8:2, and 9:1. For each of these proportions, the adsorption intensities of the mixed solutions were measured at 278 nm. These intensities were then plotted against the concentration, expressed as $(A-A_0)$ versus the ratio of $[Bi^{3+}]$ to the total concentration of $[Bi^{3+}]+[\text{FPTA NPs}]$.

2. Figures

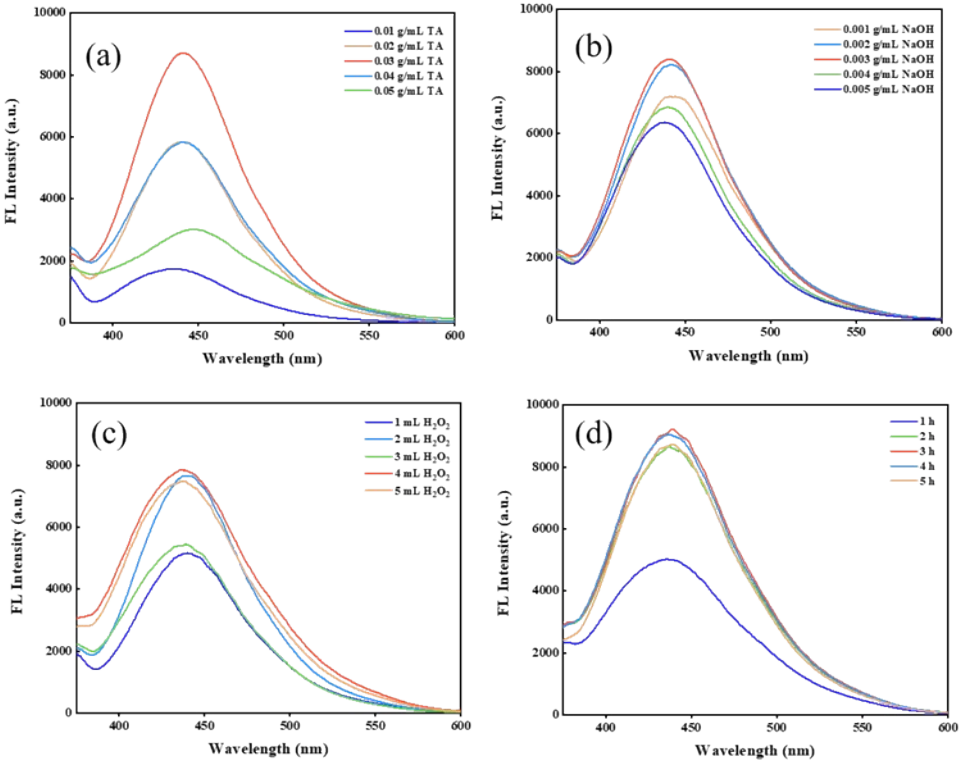

Fig.S1 Fluorescence intensity of FPTA NPs under different synthesized conditions: (a) TA dosage; (b) NaOH content; (c) H_2O_2 content and (d) reflux reaction time.

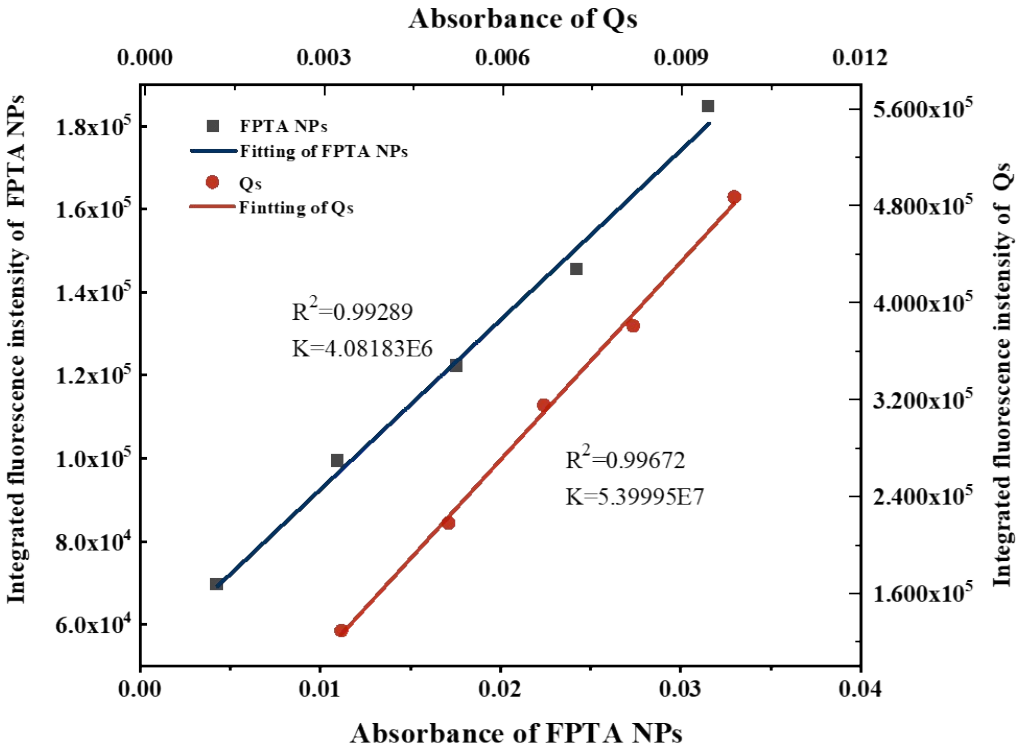

Fig.S2 Relationship between integrated fluorescence intensity and absorbance of FPTA NPs and Qs and related data.

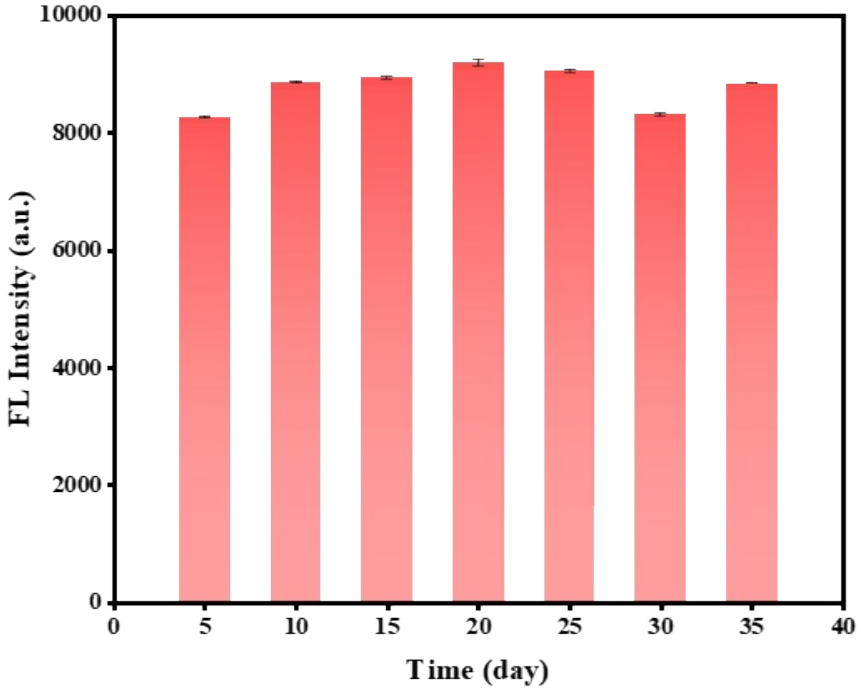

Fig.S3 Fluorescence intensity of FPTA NPs after 35 days at 4°C.

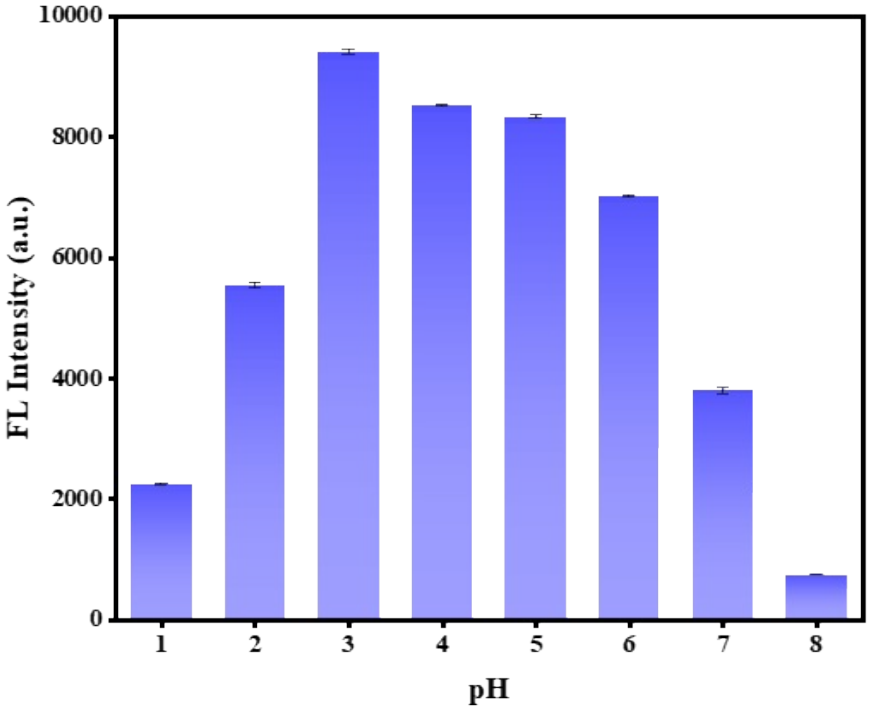

Fig.S4 Fluorescence intensity of FPTA NPs at different pH environments.

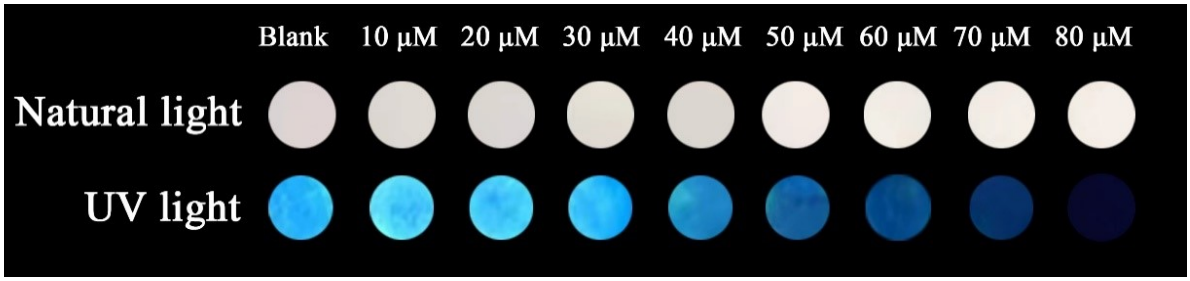

Fig.S5 Photographs of FPTA NPs functionalized paper test strips with different concentrations of Bi^{3+} under natural light and 365 nm UV light, respectively.

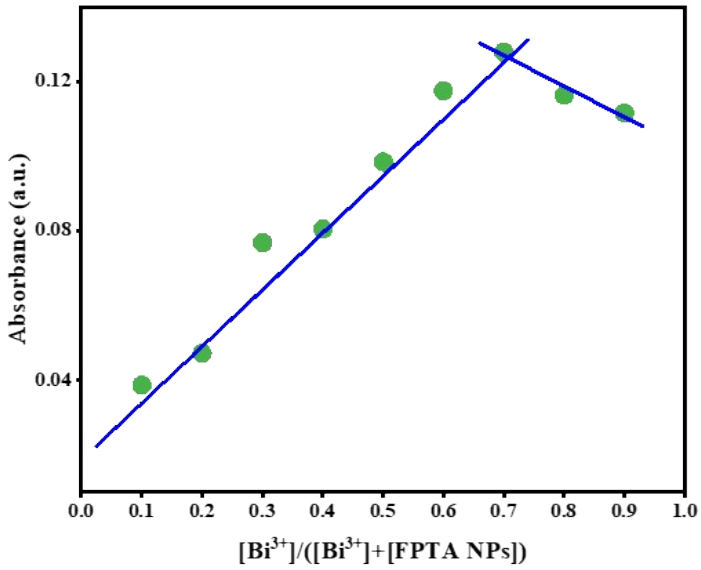

Fig.S6 Job's plot for the determination of the stoichiometry of Bi^{3+} and FPTA NPs.

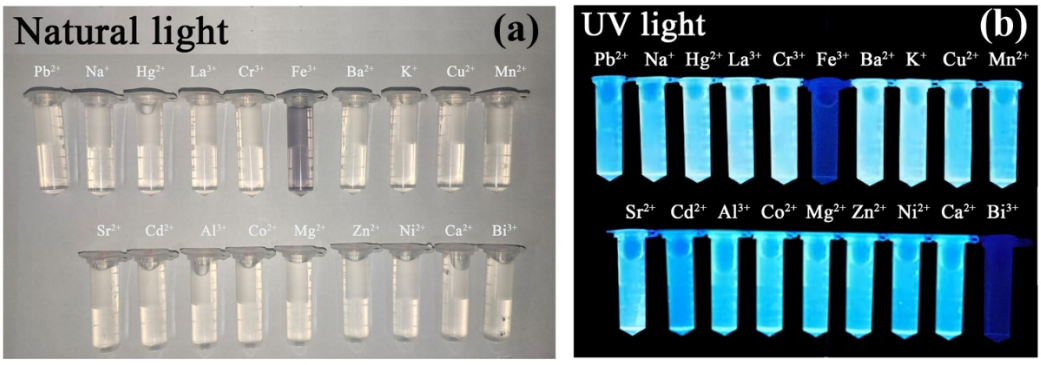

Fig.S7 Photographs of FPTA NPs solution mixed with different kinds of metal ions under natural light and 365 nm UV light, respectively.

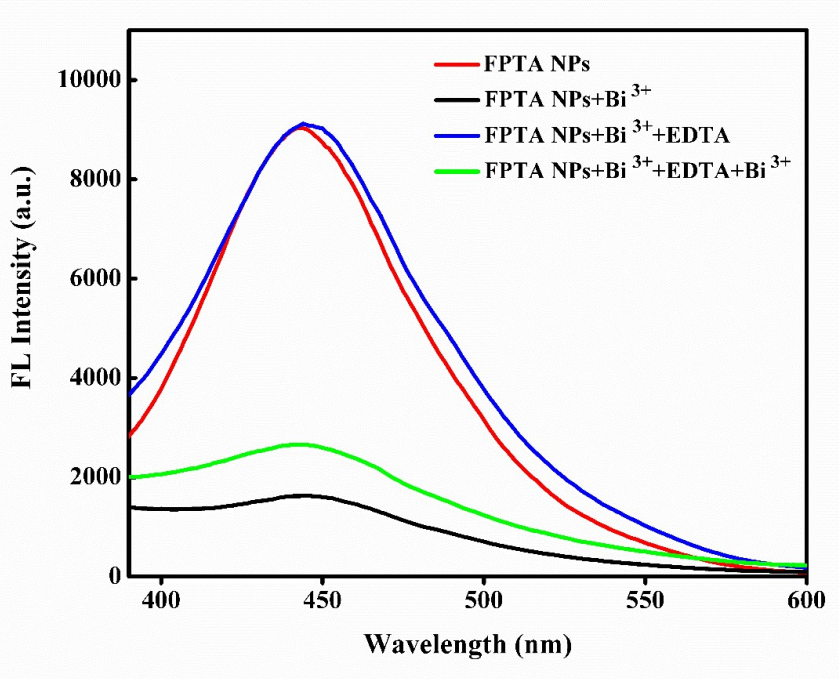

Fig.S8 Dynamic response of FPTA NPs/Bi^{3+} complex with EDTA.

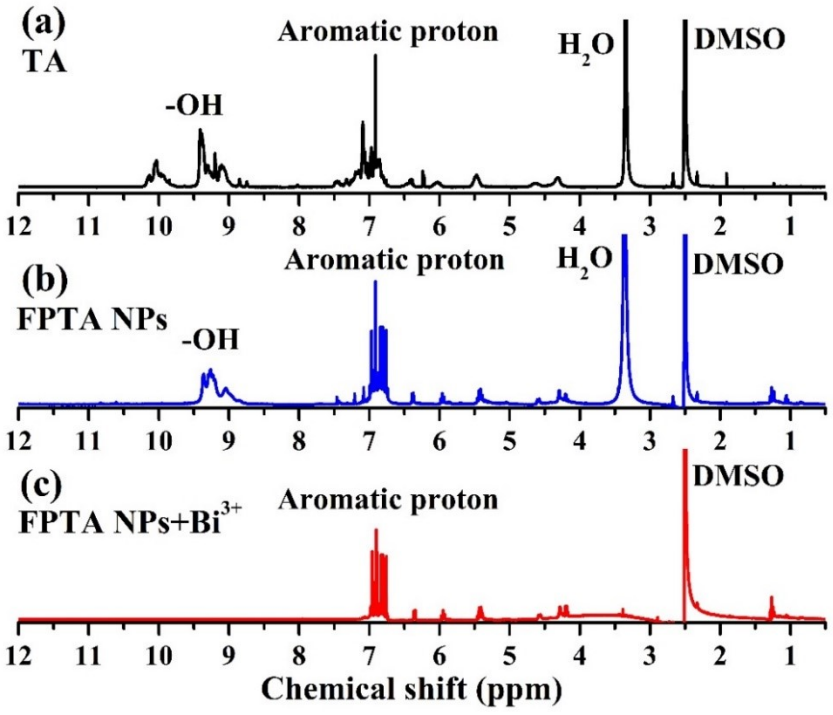

Fig.S9 ^{1}H NMR spectra (DMSO-d6, 400 MHz) of (a) TA, (b) FPTA NPs and (c) FPTA NPs+Bi^{3+} complex, respectively.

3. Table

Table S1. Comparison of Bi^{3+} fluorescent nanoprobe.

Fluorescent Nanoprobe	**Samples**	**Detection range**	**LOD**	**Refs**
5,10,15,20-Tetrakis(4-hydroxyphenyl) porphyrin	water samples	0-10.5 μM	0.027 μM	2
R-β-D-1 containing a 1,2,3-triazole moiety	water samples	2-10 μM	0.065 μM	3
N-hydroxy1,8-naphthalimide (NHN)	water samples	——	2.780 μM	4
CAU-1-$(OH)_2$	water samples	0-100 μM	2.160 μM	5
GSH-CuNPs	——	0-1×10^5 μM	1×10^4 μM	6
FPTA NPs	water samples	0.2-80 μM	0.013 μM	This work

4. References

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