

## Supplementary information for

# “ICT-not-quenching” near infrared ratiometric fluorescent detection of picric acid in aqueous media

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**Materials.** Picric acid, trinitrotoluene (TNT), dinitrotoluene (DNT), chlorobenzene, CF<sub>3</sub>COOH and dansyl chloride reagents were purchased from Aladdin (China). Other chemicals and solvents were used as received if not noted. Squaraine dye, **DNSA-SQ**, was synthesized and purified as reported previously.<sup>S1</sup> Cationic squaraine dye, **DPA-SQ**, was synthesis and purified according to the reported literature.<sup>S2</sup>

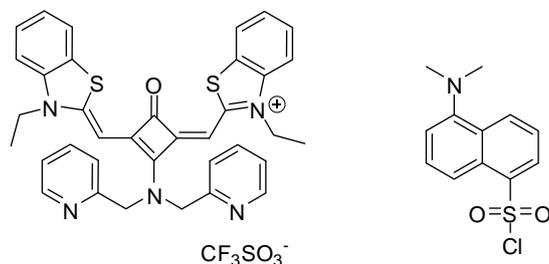
## Measurements

Absorption and emission spectra were collected by using a Shimadzu 1750 UV-visible spectrometer and a RF-5301 fluorescence spectrometer (Japan), respectively.

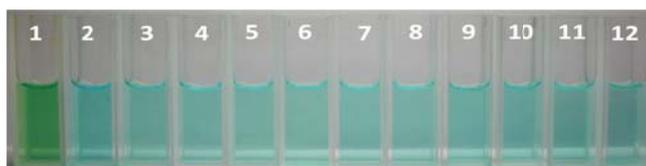
**Sample Preparation and Titration.** Stock solutions of PA and relative chemicals were prepared with concentration of  $1.0 \times 10^{-2}$  M. Stock solution of **DNSA-SQ** ( $5.0 \times 10^{-4}$  M) was prepared in CH<sub>3</sub>CN and further diluted to  $5.0 \times 10^{-6}$  M for titration experiments. UV and fluorescence spectra were monitored within 30 seconds.

S1. Y. Xu, Q. Liu, X. Li, C. Wesdemiotisa and Y. Pang, *Chem. Commun.*, 2012, **48**, 11313-11315.

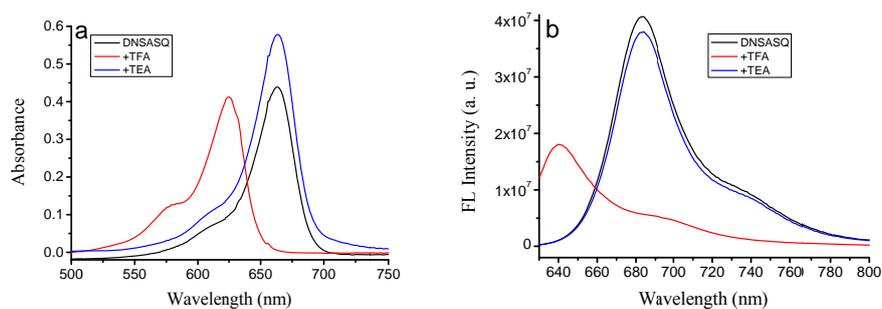
S2. Y. Xu, Z. Li, A. Malkovskiy, S. Sun, and Y. Pang, *J. Phys. Chem. B*, 2010, **114**, 8574-8580.



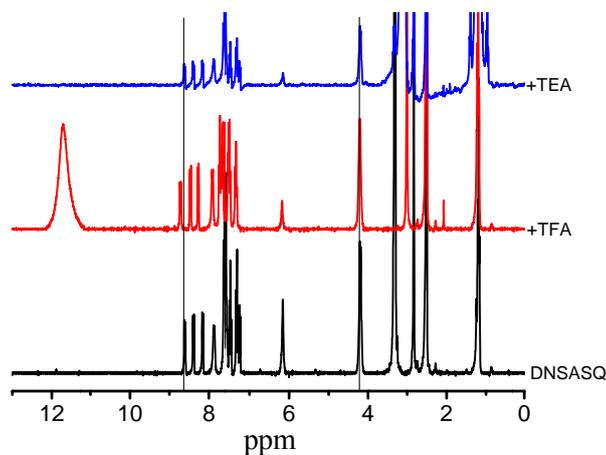
**Scheme S1** Structures of **DPA-SQ** and dansyl chloride.



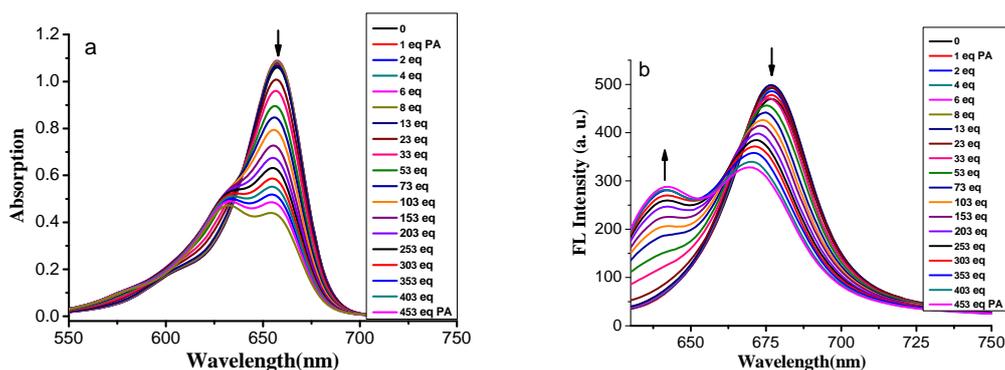
**Fig. S1** Color changes of **DNSA-SQ** (5  $\mu\text{M}$ ) to PA (100  $\mu\text{M}$ ) and common compounds (100  $\mu\text{M}$ ) that could interfere with the colorimetric detection for PA (1: PA; 2: TNT; 3: DNT; 4: NB; 5: Chlorobenzene; 6: Bromobenzene; 7: toluene; 8: Tap water; 9: NaOH; 10:  $\text{Zn}^{2+}$ ; 11: NaCl; 12: None).



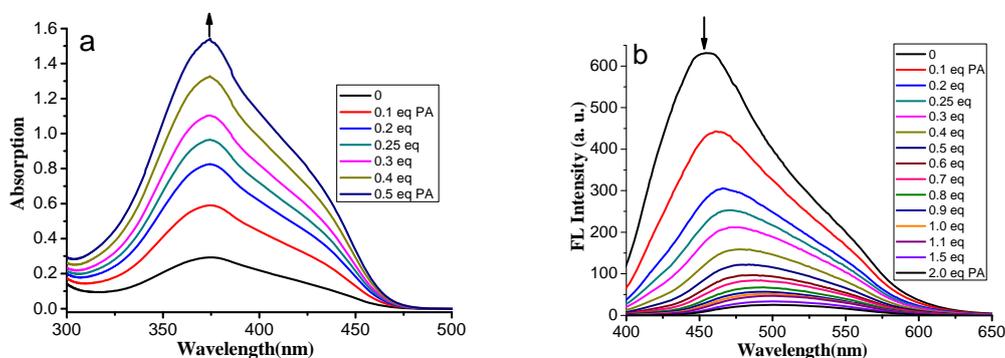
**Fig. S2** Absorption (a) and fluorescence (b) spectra change of **DNSA-SQ** (5  $\mu\text{M}$ ) in  $\text{CH}_3\text{CN}$  upon addition of TFA and triethylamine (TEA).



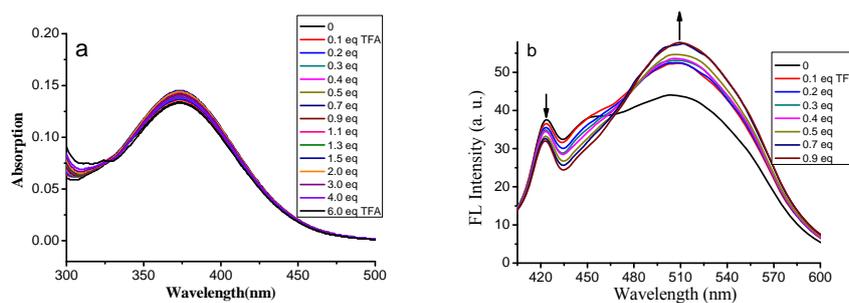
**Fig. S3**  $^1\text{H}$  NMR spectra in  $\text{DMSO}-d_6$  at room temperature (300 MHz). (A) **DNSA-SQ**, (B) a mixture of **DNSA-SQ** and TFA in a 1:3 molar ratio, and (C) a mixture of **DNSA-SQ**, TFA, and triethylamine (TEA) in a 1:3:6 molar ratio.



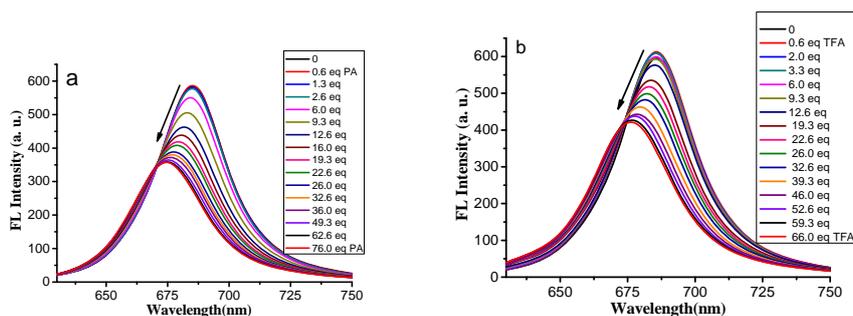
**Fig. S4** UV-Vis (a) and fluorescence (b) spectra of probe **DNSA-SQ** (5 μM) upon addition of PA in aqueous CH<sub>3</sub>CN (1:9, v/v). The arrows indicate the changes in the absorption and fluorescence intensities with the increased PA concentration ( $\lambda_{\text{ex}} = 620$  nm).



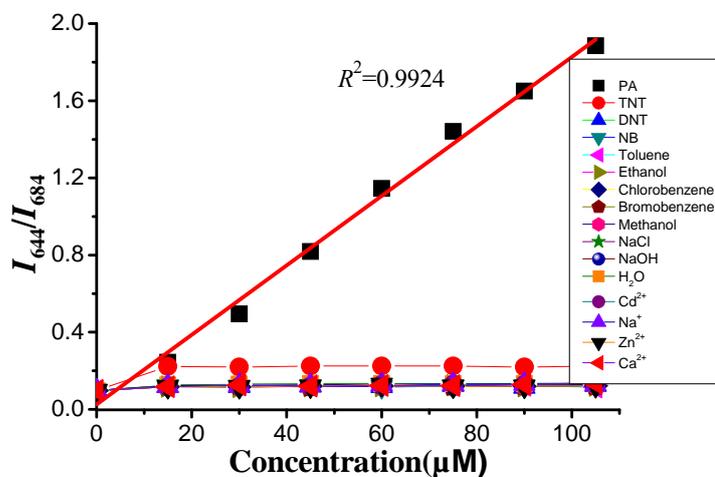
**Fig. S5** UV-Vis (a) and fluorescence (b) spectra of probe **Dansyl chloride** (5 μM) upon addition of increasing concentration of PA in CH<sub>3</sub>CN. The arrows indicate the changes in the absorption and fluorescence intensities with the increased PA concentration ( $\lambda_{\text{ex}} = 380$  nm).



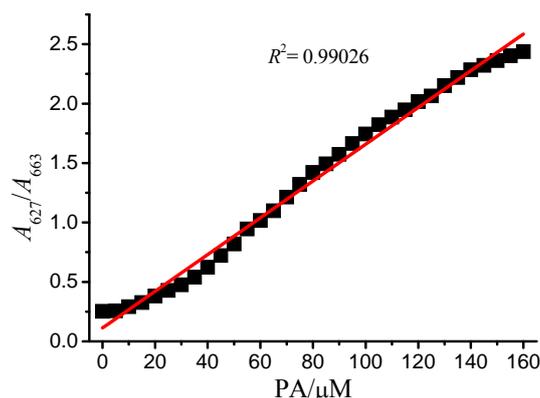
**Fig. S6** UV-Vis (a) and fluorescence (b) spectra change of **Dansyl chloride** (5 μM) upon addition of increasing concentration of TFA in CH<sub>3</sub>CN. ( $\lambda_{\text{ex}} = 380$  nm).



**Fig. S7** Fluorescence spectra change of **DPA-SQ** (5 μM) upon addition of increasing concentration of PA (a) and TFA (b) in CH<sub>3</sub>CN. ( $\lambda_{\text{ex}} = 600 \text{ nm}$ ).

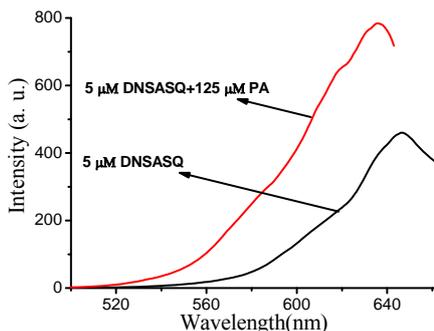


**Fig. S8** Plots of relative fluorescent intensity changes ( $I_{644}/I_{684}$ ) of **DNSA-SQ** (5 μM) to PA and common compounds that could interfere with the fluorescence emission at different concentrations.



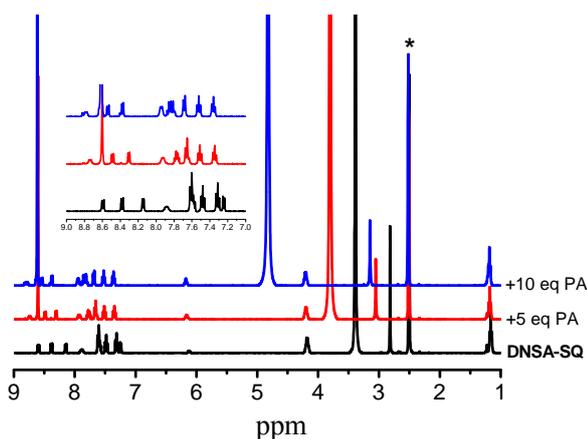
**Fig. S9** The relative absorption intensity change ( $A_{627}/A_{663}$ ) of probe **DNSA-SQ** (5 μM) to the different concentration of PA (5-160 μM).

A linear relationship between the ratio of the absorption intensity ( $A_{627}/A_{663}$ ) and PA concentration of PA in the range of 5-160 μM was observed, indicating that DNSA-SQ can be used for colorimetric detection of PA.



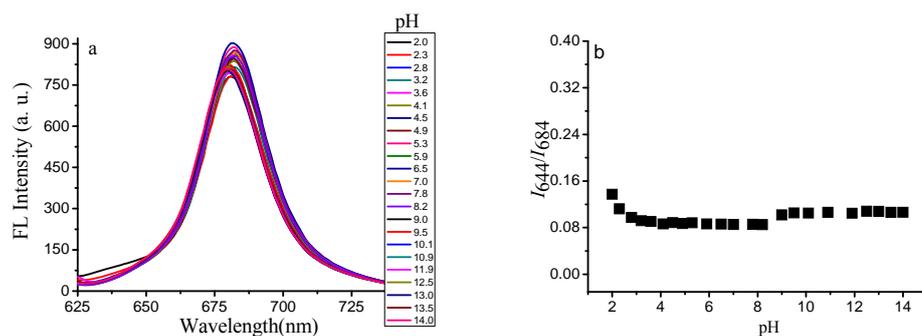
**Fig. S10** Fluorescence excitation spectra of probe **DNSA-SQ** alone (5 μM) and **DNSA-SQ** (5 μM) with 25 equivalent of PA in CH<sub>3</sub>CN, where the emission maxima are 684 and 644 nm respectively.

The excitation spectra of **DNSA-SQ** alone and **DNSA-SQ** with PA illustrate that fluorescent peaks at 684 and 644 nm come from different species (**DNSA-SQ** and protonated **DNSA-SQ**), which can be further supported by the isoemission point at 663 nm.

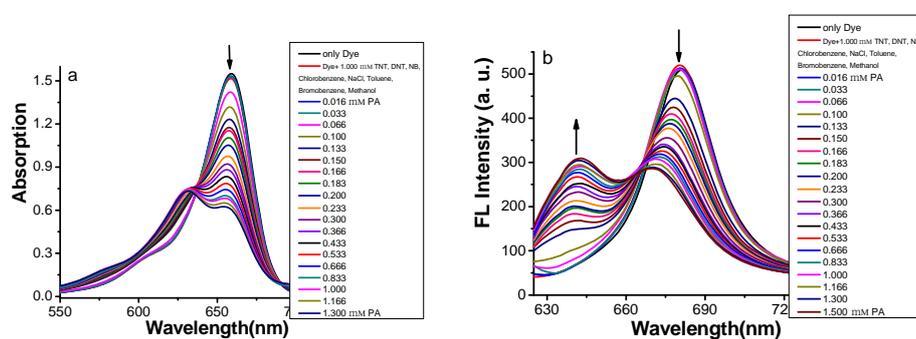


**Fig. S11** <sup>1</sup>H NMR titration of **DNSA-SQ** upon addition of PA in DMSO-*d*<sub>6</sub>, where the starred “\*” signal at 2.5 ppm is attributed to DMSO residue. The inset shows the partial spectra for clarity.

<sup>1</sup>H NMR titration in DMSO-*d*<sub>6</sub> showed that the peak of methyl on dimethylamine phenyl group is shifted downfield from 2.83 to 3.17 (Δδ = 0.34 Hz) with the addition of 10 equivalent PA, indicating the interaction between **DNSA-SQ** and PA is based on the protonation of dimethylamine phenyl group by PA.



**Fig. S12** pH fluorescent titration spectra of **DNSA-SQ** in aqueous  $\text{CH}_3\text{CN}$  solution (a) and relative fluorescent intensity ( $I_{644}/I_{684}$ ) response to pH (b).



**Fig. S13** UV-Vis (a) and fluorescence (b) spectra of probe **DNSA-SQ** ( $5 \mu\text{M}$ ) upon addition of PA in aqueous  $\text{CH}_3\text{CN}$  (1:9, v/v) in the present of other potential interfering compounds including TNT, DNT, NB, chlorobenzene, NaCl, toluene, bromobenzene and methonal (the concentration of various chemicals are 1.0 mM). The arrows indicate the changes in the absorption and fluorescence intensities with the increased PA concentration ( $\lambda_{\text{ex}} = 620 \text{ nm}$ ).