

## Supporting Information

### Disassembly Mediated Fluorescence Recovery of Gold Nanodots for Selective Sulfide Sensing

**Zhiqin Yuan<sup>a</sup>, Meihua Peng<sup>a</sup>, Lei Shi<sup>a</sup>, Yi Du<sup>a</sup>, Na Cai<sup>a</sup>, Yan He<sup>\*a</sup>, Huan-Tsung Chang<sup>b</sup> and  
Edward S. Yeung<sup>a</sup>**

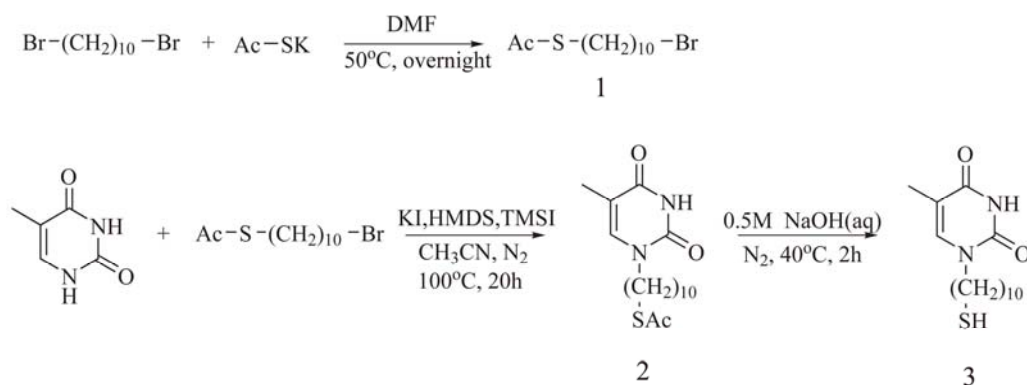
<sup>a</sup>College of Chemistry and Chemical Engineering, College of Biology, State Key Laboratory of Chemo/Biosensing and Chemometrics, Hunan University, Changsha, P. R. China. Fax: 86-731-88823074; Tel: 86-731-88821904;  
E-mail: yanhe2021@gmail.com.

<sup>b</sup>Department of Chemistry, National Taiwan University, 1, Section 4, Roosevelt Road, Taipei 106, Taiwan. Tel and fax: 011-886-2-33661171.

## Experimental

**Chemicals.** 11-mercaptoundecanoic acid (MUA), tetrakis(hydroxymethyl) phosphonium chloride (THPC) and glutathione (GSH) were purchased from Sigma Aldrich (Milwaukee, USA). Sodium hydroxide, anhydrous ethanol, hexane, tetrahydrofuran (THF), acetonitrile (CH<sub>3</sub>CN), acetic ether (EtOAc), dimethylformamide (DMF), sodium hydroxide (NaOH), chloroauric acid (HAuCl<sub>4</sub>), concentrated nitric acid (HNO<sub>3</sub>) and hydrochloric acid (HCl) were obtained from Sinopharm Chemical Reagent Corporation (Shanghai, China). Thymine, ethanethioic acid potassium salt (Ac-SK), hexamethyldisilazane (HDMS), trimethylsilyl chloride (TMSI) and 1,10-dibromodecane were purchased from Alfa Aesar (Tianjin, China). Aqueous solution of F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, Ac<sup>-</sup>, Citrite<sup>3-</sup>, CN<sup>-</sup>, EDTA<sup>2-</sup>, N<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, S<sup>2-</sup>, S<sub>2</sub>O<sub>3</sub><sup>2-</sup>, SCN<sup>-</sup>, SDS<sup>-</sup>, and SO<sub>4</sub><sup>2-</sup> were prepared from sodium fluoride (NaF), sodium chloride (NaCl), potassium iodide (KI), sodium acetate (NaAc), trisodium citrate, Ethylenediaminetetraacetic acid disodium salt (EDTA-2Na), sodium azide (NaN<sub>3</sub>), sodium nitrite, sodium nitrate (NaNO<sub>3</sub>), sodium sulfide (Na<sub>2</sub>S), sodium thiosulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>), potassium thiocyanate (KSCN), Sodium dodecyl sulfate (SDS), and sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>) respectively. Buffer solutions from pH2 to pH11 were prepared according to a standard textbook. TSH was dissolved in THF, and other materials were dissolved in water. All chemicals were used without further purification. Ultrapure water was obtained from Millipore system. All glassware was cleaned by fresh aqua regia.

**Synthesis of TSH.** TSH was synthesized according to a previous literature with slight modification.<sup>1</sup>



#### Compound 1

In a 100 mL round bottom flask, 1,10-Dibromodecane and ethanethioic acid potassium salt were dissolved in 15 mL DMF and stirred overnight at 50 °C. Then the resulting solution was poured into 250 mL water, and extracted with dichloromethane. The organic layer was washed with a saturated aqueous NaCl solution and dried over Na<sub>2</sub>SO<sub>4</sub>. Solvent removal yielded a yellow oil, which was chromatographed (hexane/EtOAc = 10:1) to yield the product as a white solid (1.45 g, yield 61.4%).

#### Compound 2

In a 50 mL three-necked flask, thymine (278 mg, 2.2 mmol), thioacetic acid S-(10-bromodecyl) ester (650 mg, 2.2 mmol), potassium iodide (366 mg, 2.2 mmol), hexamethyldisilazane (249 mg, 1.54 mmol) and Trimethylsilyl chloride (239 mg, 2.2 mmol) were added in 5 mL of dry acetonitrile. The mixture was refluxed at 100 °C for 20 h under nitrogen. After the resulting mixture was cooled to room temperature, the solvent and the volatile reagents were removed under reduced pressure to yield a solid residue. The residue was dissolved in dichloromethane and

the precipitating salt was removed by gravity filtration, then the resulting dichloromethane solution was washed with water and the organic phase dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent was evaporated to dryness to give a crude solid. Purification by flash chromatography over silica gel eluting with hexane/EtOAc (2:1), afforded the title compound as a white solid (556 mg, 74.0%).

### Compound 3

Thioacetic acid S-[10-(5-methyl-2,4-dioxo-3,4-dihydro-2H-pyrimidine-1-yl)-decyl] ester (320 mg, 1.07 mmol) was added to 10 mL of a 0.5 M sodium hydroxide solution and stirred for 2 h at 40 °C. The resulting solution was then acidified using 5 mL of 3 M hydrochloric acid and extracted three times with AcOEt. And the organic phase was filtered, and evaporated. to yield a crude product, then purified by flash chromatography (eluent ethylacetate/hexane 4:6 to 3:1) to yield a pure product 205 mg (74%). The characterization data of TSH are shown later in the supporting information.

**Synthesis of fluorescent AuNDs.** TSH/MUA co-modified AuNDs were synthesized with follow procedures. Typically, 500  $\mu\text{L}$  1 M NaOH solution and 12  $\mu\text{L}$  80% THPC solution were first introduced into 40 mL ultrapure water. The mixture was stirred for 5 minutes, and then 2 mL 24 mM  $\text{HAuCl}_4$  solution was added rapidly. The color of the solution turns from light-yellow to brown in one minute, indicating the formation of small AuNPs. At this point, 12  $\mu\text{L}$  100 mM TSH solution was added to obtain TSH protected AuNPs. After stirring for another 15 minutes at room temperature, the solution was stored at 4 °C for further use.

After aging for one day, 1 mL stock AuNP solution was mixed with 200  $\mu$ L 0.1 M carbonate buffer of pH 9.0 and 75  $\mu$ L 0.1 M MUA ethanol solution in a thermomixer (800 rpm, 25 °C). The solution turns to light yellow from brown within 1 hour, indicating the formation of fluorescent AuNDs. After ligand exchange for 2 hours, the reaction is stopped. The resulting AuND solution was purified by centrifugation at 13000 rpm for 20 minutes to remove large aggregates, and then using a 10 kDa cutoff filter to remove the excess TSH and MUA molecules.

GSH/MUA co-modified and only MUA capped AuNDs were synthesized according to previous methods.<sup>2-3</sup>

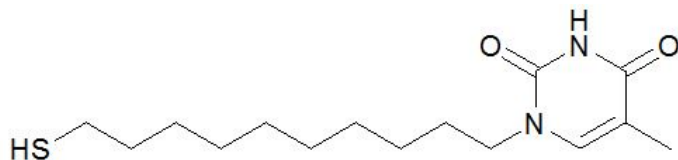
**Characterization.** <sup>1</sup>HNMR data of TSH was collected using a INOVA-400 nuclear magnetic resonance spectrometer (Varian, USA). Mass spectral analysis of TSH was performed using a Trace2000 PolarisQ mass spectrometer (Thermo Finnigan, USA). The fluorescence spectra of AuNDs were obtained using a F-7000 fluorescence spectrophotometer (Hitachi, Japan). The UV absorption spectra of the AuNDs were obtained using a UV-1800 spectrophotometer (Shimadzu, Japan). High resolution transmission electron microscopy (HRTEM) images were collected with a Tecnai F20 high resolution transmission electron microscope (FEI, USA). Dynamic light scattering and zeta potential measurements were performed with a Zetasizer Nano ZS (Malvern, U.K.).

## References

- 1 J. F. Zhou, D. A. Beattie, R. Sedev and J. Ralston, *Langmuir*, 2007, **23**, 9170.
- 2 Z. Yuan, M. Peng, Y. He and E. S. Yeung, *Chem. Commun.*, 2011, **47**, 11981.

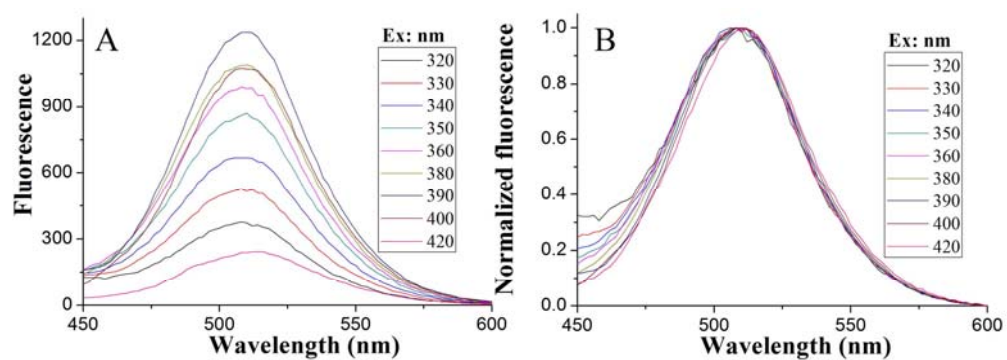
- 3 C.-C. Huang, Z. Yang, K.-H. Lee and H.-T. Chang, *Angew. Chem. Int. Ed.*, 2007, **46**, 6824.

### Characterization of TSH.

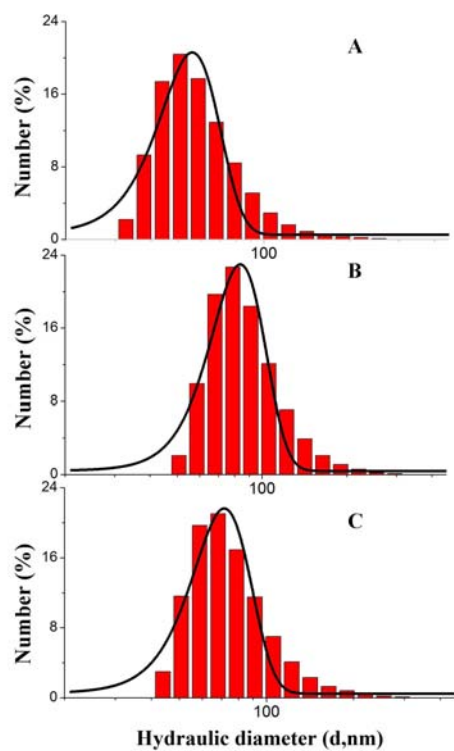


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 1.28~1.37 (m, 14H), 1.58~1.64 (m, 2H), 1.93 (s, 3H), 2.52 (q,  $J$  = 7.20 Hz, 2H), 3.68 (t,  $J$  = 7.20 Hz, 2H), 6.98 (d,  $J$  = 1.20 Hz, 1H), 8.62 (s, 1H).

MS (ESI):  $m/z$  (%) = 299 ( $[\text{M} + \text{H}]^+$ , 67), 641 ( $[\text{2M} + 2\text{Na} - \text{H}]^+$ , 56), 641 ( $[\text{2M} + 2\text{Na} - \text{H}]^+$ , 100).

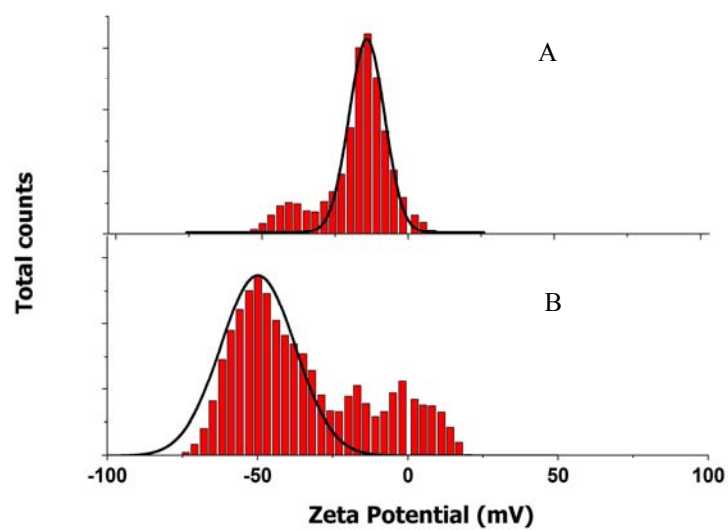


**Figure S1.** Fluorescence (A) and normalized fluorescence (B) spectra of the freshly prepared AuNDs under different excitation wavelengths.

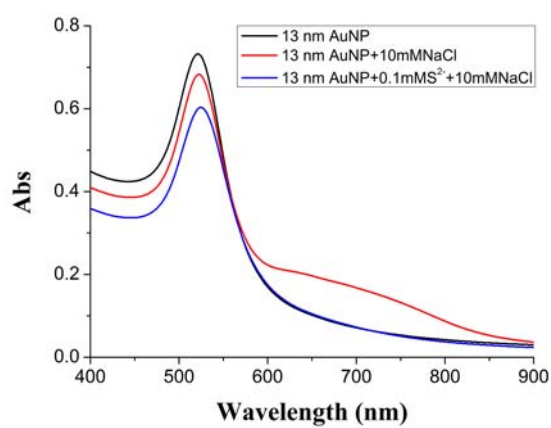


**Figure S2.** Hydrodynamic size distribution of freshly prepared AuNDs (A), aged AuNDs before (B) and after (C) addition of sulfide in water as measured by dynamic light scattering (DLS).

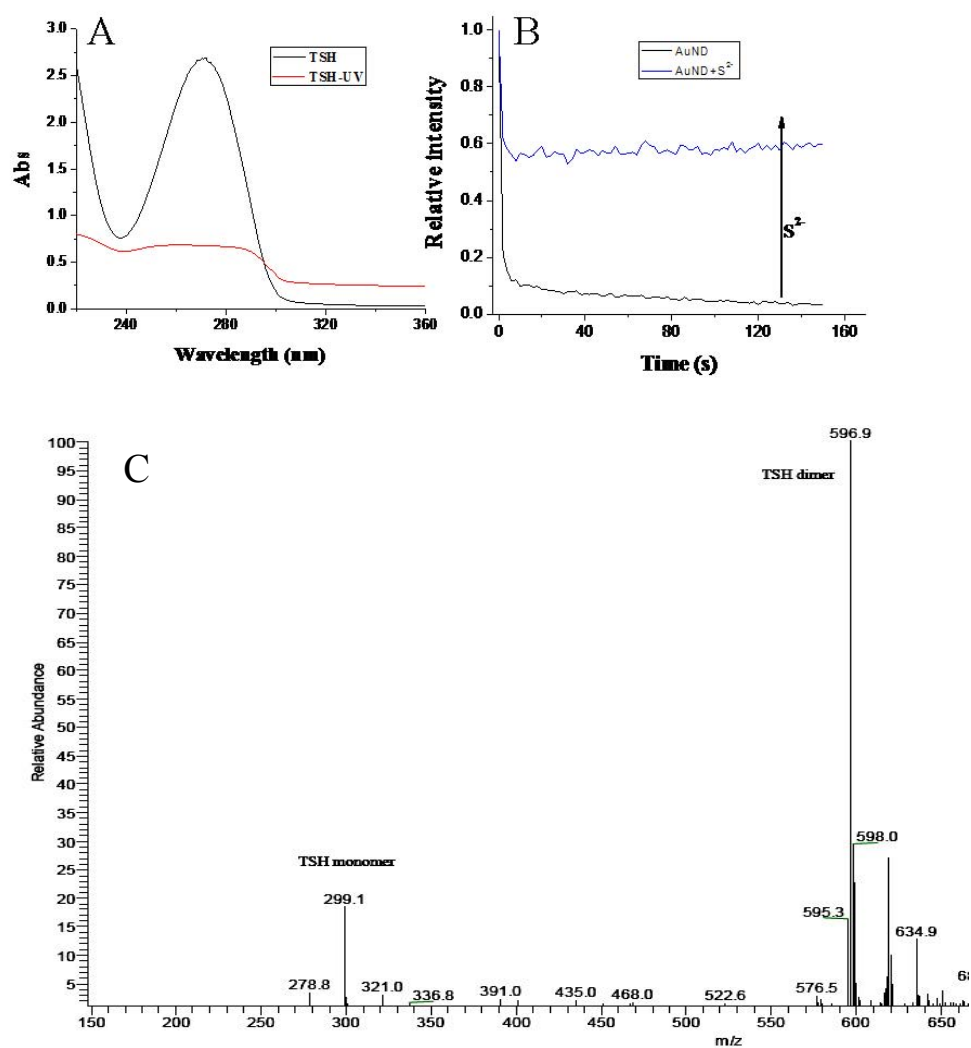




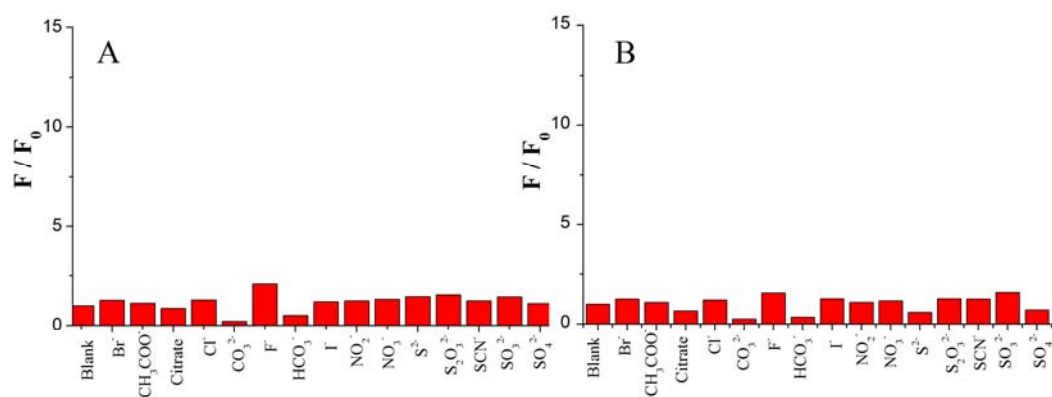
**Figure S3.** Zeta potentials of aged AuNDs before (A) and after (B) adding sulfide.



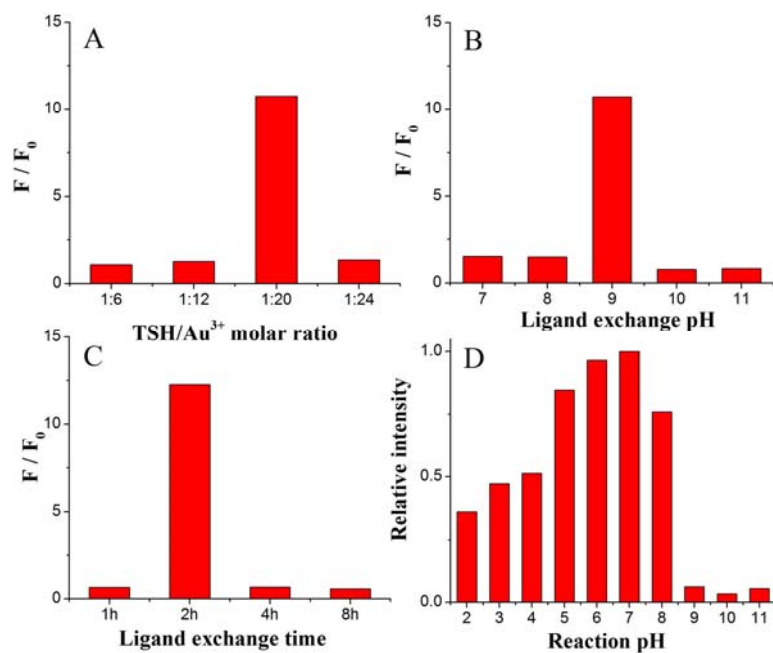
**Figure S4.** Absorption spectra of citrate stabilized AuNPs (black), in the presence of 10 mM NaCl without (red) and with (blue) addition of sulfide.



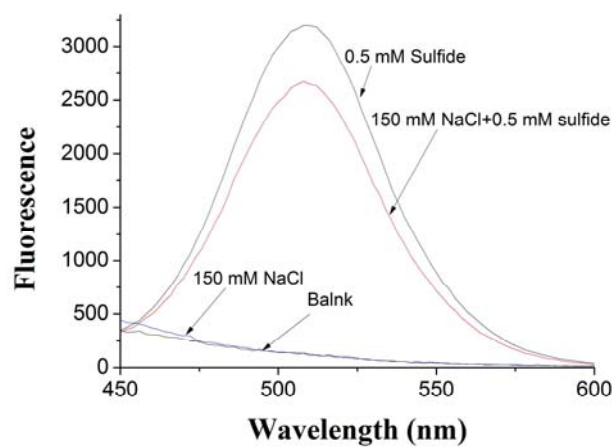
**Figure S5.** UV-vis absorption spectra of TSH (in ethanol/H<sub>2</sub>O) before (black) and after (red) UV illumination (A). Normalized time-dependent fluorescence intensity change of aged AuNDs in the absence (black) and presence (blue) of sulfide (B). Mass spectrum of TSH solution after UV illumination (C).



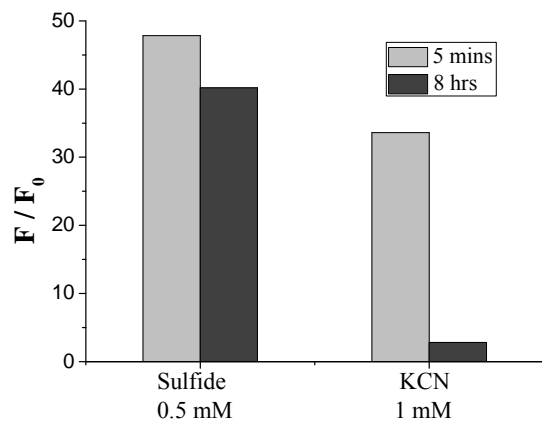
**Figure S6.** Fluorescence enhancement ratio ( $F/F_0$ ) of GSH/MUA (A) and MUA only (B) stabilized AuNDs after adding various anions.



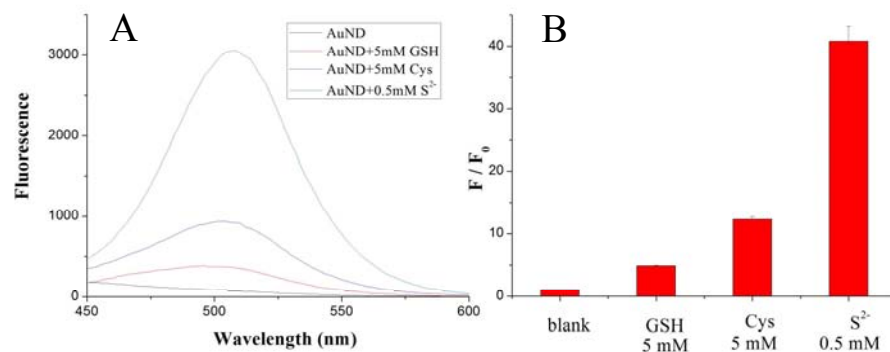
**Figure S7.** The fluorescence enhancement ratio of AuNDs after adding sulfide at different TSH/Au molar ratios (A), reaction pH (B) and reaction time (C). (D) shows the relative fluorescence intensity of AuNDs after adding sulfide under various buffer solutions.



**Figure S8.** Fluorescence spectra of AuNDs after addition of sulfide and high concentration of NaCl.

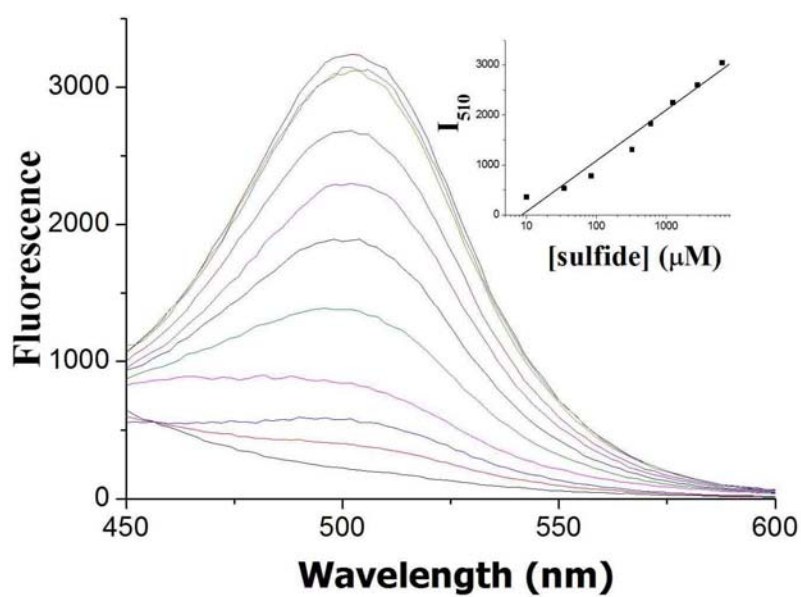


**Figure S9.** Enhancement ratio of AuND fluorescence after addition of 0.5 mM sulfide and 1 mM KCN.



**Figure S10.** Comparison of fluorescence spectra (A) and fluorescence enhancement ratio (B) of AuNDs after adding biothiols and sulfide.





**Figure S11.** Fluorescence spectra of AuNDs in water samples from a local lake in the presence of 0, 9.9, 34.5, 83.3, 320.6, 595.1, 1234.9, 4982.9, 6289.4 and 7692.6  $\mu\text{M}$  sulfide. Inset: Plot of the fluorescence intensity at 510 nm versus the sulfide concentration.