Supporting Information

Functionalized Fluorescent Gold Nanodots: Synthesis and Application for Pb^{2+} Sensing

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Experimental

Chemicals. 11-mercaptoundecanoic acid (MUA) and tetrakis (hydroxymethyl) phosphonium chloride (THPC) were purchased from Sigma Aldrich (Milwaukee, USA). Sodium hydroxide, ethylenediaminetetraacetic acid, disodium salt (EDTA-2Na), anhydrous ethanol, sodium borohydride, chloroauric acid ($HAuCl_4$), quinine sulfate, concentrated nitric acid (HNO_3) and hydrochloric acid (HCl) were obtained from Sinophrarm Chemical Reagent Corporation (Shanghai, China). All chemicals were used without further purification. Ultrapure water was obtained from Millipore system. All glassware was cleaned by fresh aqua regia. Aqueous solution of K^+, Na^+, Ca^{2+}, Mg^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}, ,Ag^+, Cd^{2+}, Mn^{2+}, Hg^{2+}, Pb^{2+} and Fe^{3+} were prepared from KCl, NaCl, $CaCl_2$, $MgCl_2{\cdot}6H_2O$, $CuCl_2{\cdot}2H_2O$, $Zn(Ac)_2{\cdot}2H_2O$, $NiCl_2{\cdot}6H_2O$, $Co(Ac)_2{\cdot}4H_2O$, $AgNO_3$, $CdCl_2{\cdot}2H_2O$, $Mn(Ac)_2{\cdot}9H_2O$, $Hg(NO_3)_2$, $Pb(Ac)_2{\cdot}3H_2O$ and $FeCl_3$, respectively. Buffer solutions from pH 2 to pH 11 were prepared according to standard procedures in the textbook.

Synthesis of fluorescent AuNDs. Typically, 500 μL 1 M NaOH solution and 12 μL 80% THPC solution were first introduced into 40 mL ultrapure water. The mixture was stirred for 5 minutes, and then 2 mL 23.3 mM $HAuCl_4$ 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, 200 μL 117.5 mM GSH solution was added to obtain GSH protected AuNPs. After stirring for another 15 minutes at room

temperature, the solution was transferred to 4 □ for further use.

After aging for one day, 1 mL stock AuNP solution was mixed with 200 μL 0.1 M carbonate buffer of pH 9.0 and 75 μL 0.1 M MUA ethanol solution in a thermomixer. 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 GSH and MUA molecules.

Characterization. The fluorescence spectra of AuNDs were obtained using a F-7000 fluorescence spectrophotometer (Hitachi, Japan). The UV absorption spectra of the gold clusters were obtained using a UV-2450 spectrophtometer (Shimadzu, Japan). High resolution transmission electron microscopy (HRTEM) was performed on a Tecnai F20 high resolution transmission electron microscope (FEI, USA).

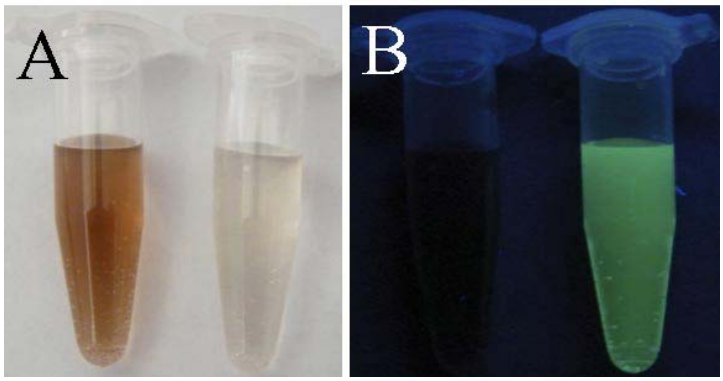

Figure S1. Photographs of the GSH capped AuNDs before (left) and after (right) MUA ligand exchange under room light (A) and under 365 nm UV light illumination (B).

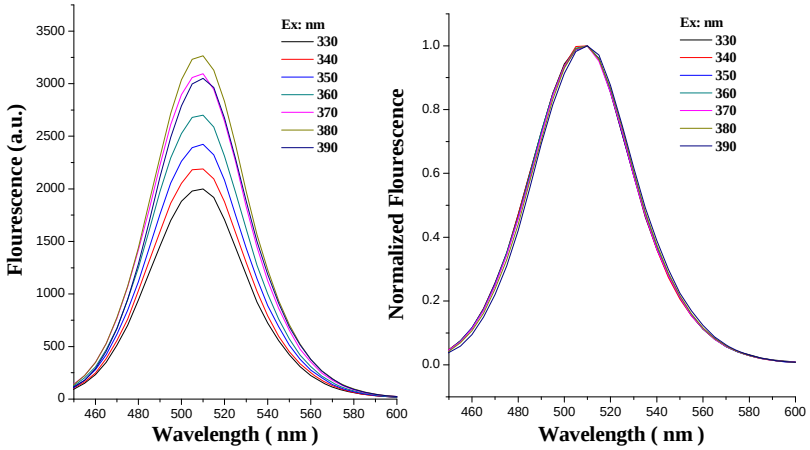

Figure S2. Original (A) and normalized fluorescence (B) spectra of the AuNDs at different excitation wavelength.

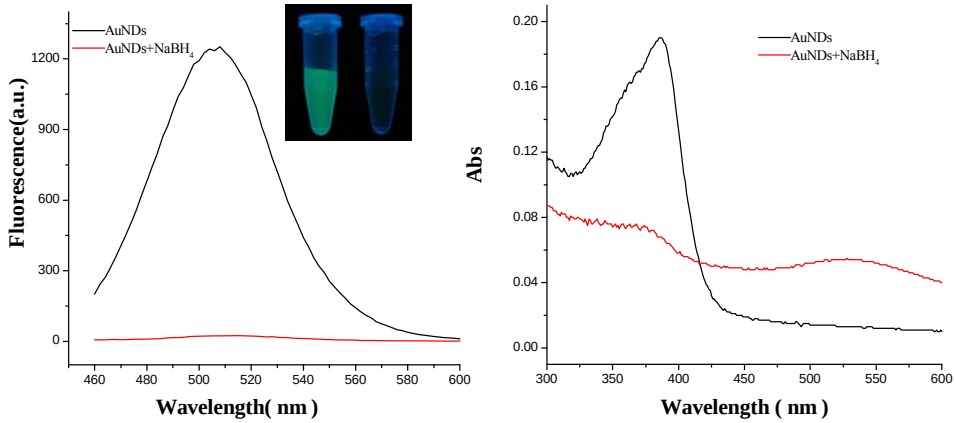

Figure S3. Fluorescence spectra (left) and UV-Vis absorption spectra (right) of the AuNDs before (black line) and after (red line) addition of $NaBH_4$. The image insert shows photographs of AuNDs before and after addition of $NaBH_4$ upon UV light illumination (365 nm).

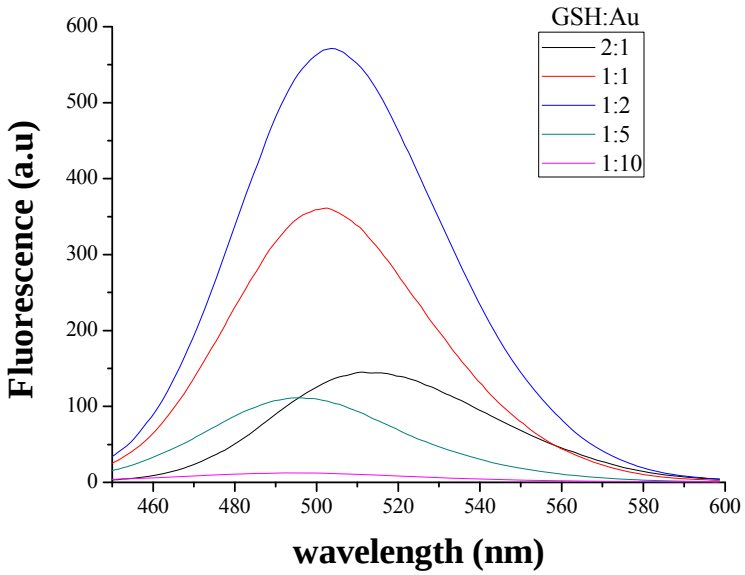

Figure S4. Fluorescence spectra of AuNDs prepared using different GSH-Au molar ratio.

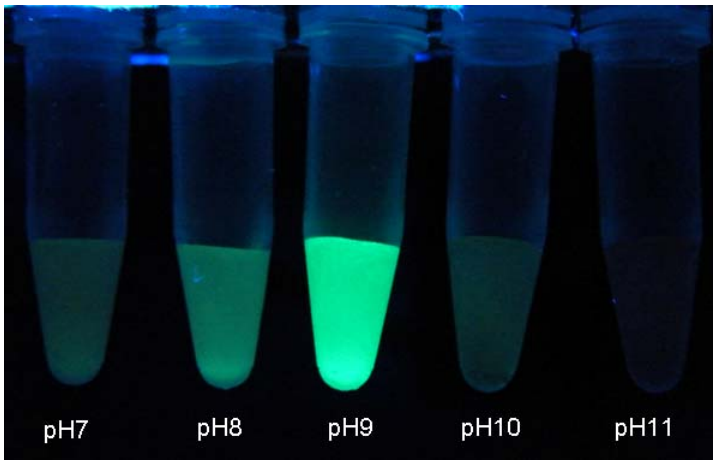

Figure S5. Photographs of AuNDs obtained in ligand exchange reaction solutions of different pH.

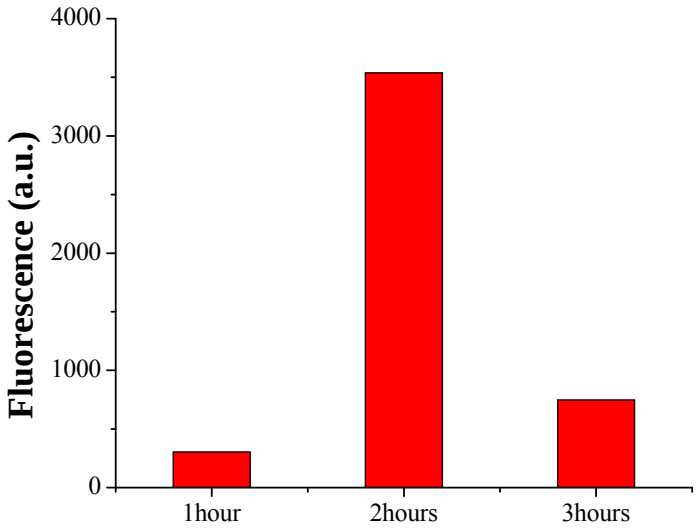

Figure S6. The fluorescence intensity of the AuNDs obtained with different ligand exchange time.

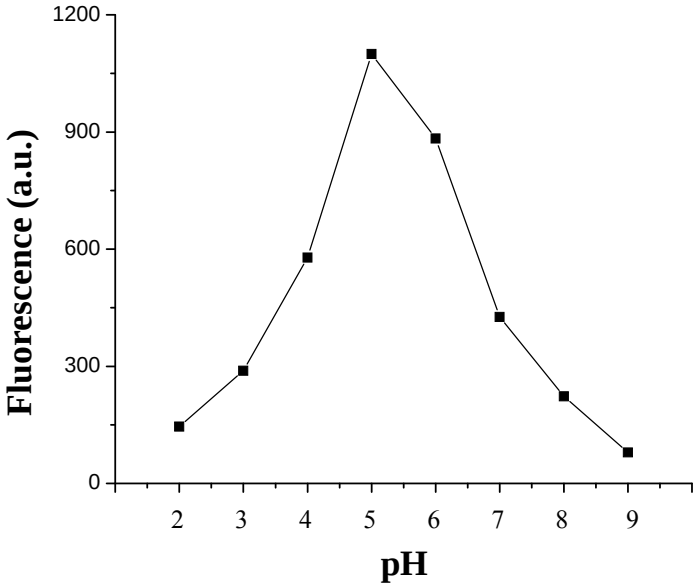

Figure S7. Plot of the AuND fluorescence intensity in buffer solutions of different pH.

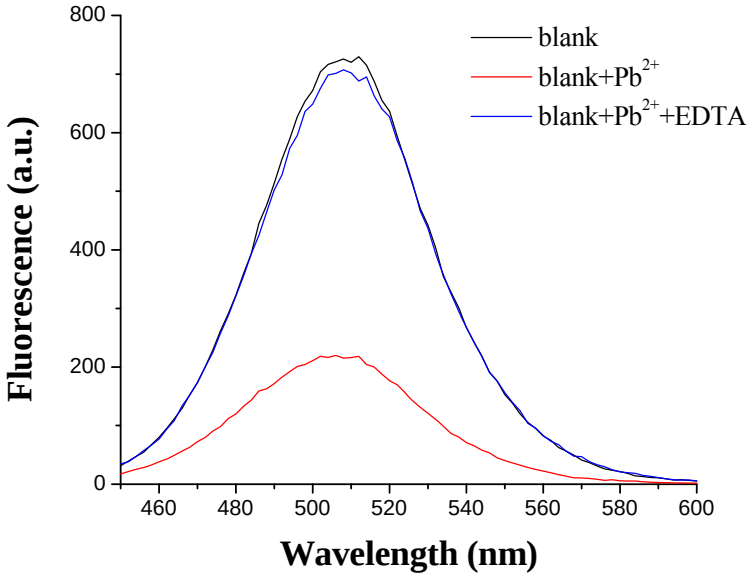

Figure S8. Fluorescence spectra of the as-prepared AuNDs (black line), after adding 1 μM Pb^{2+} (red line), and followed by adding 10 μM EDTA (blue line).

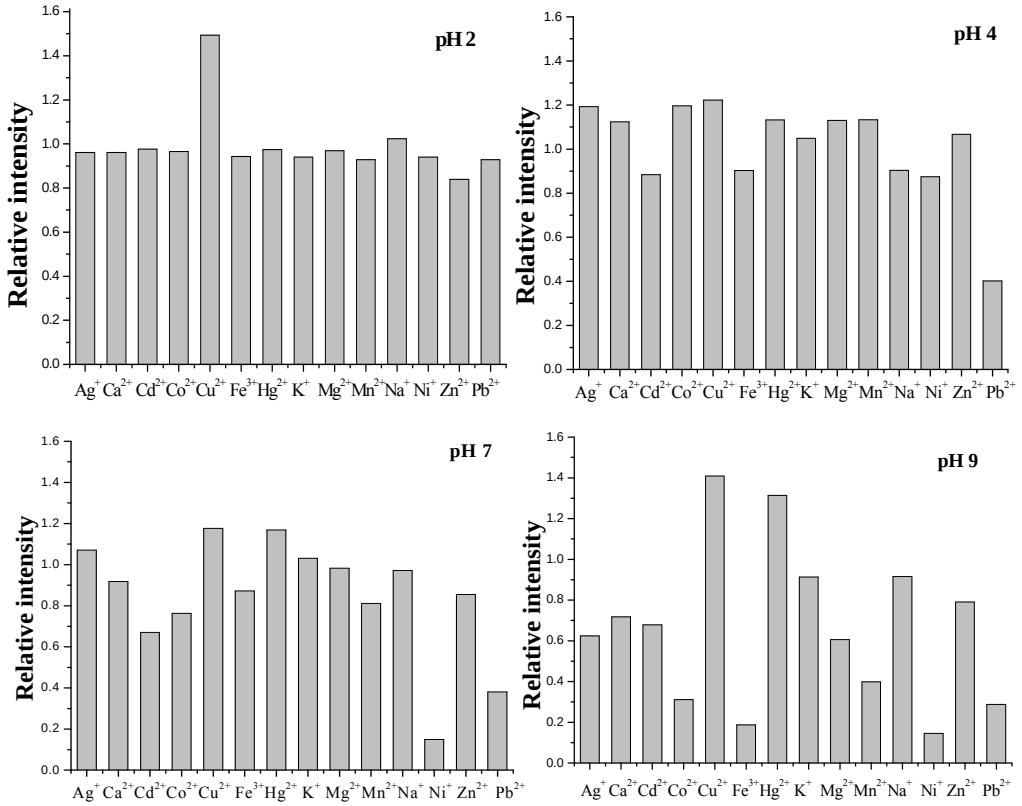

Figure S9. Selectivity of the AuND probes in the presence of 1 μM of various metal ions under different solution pH.

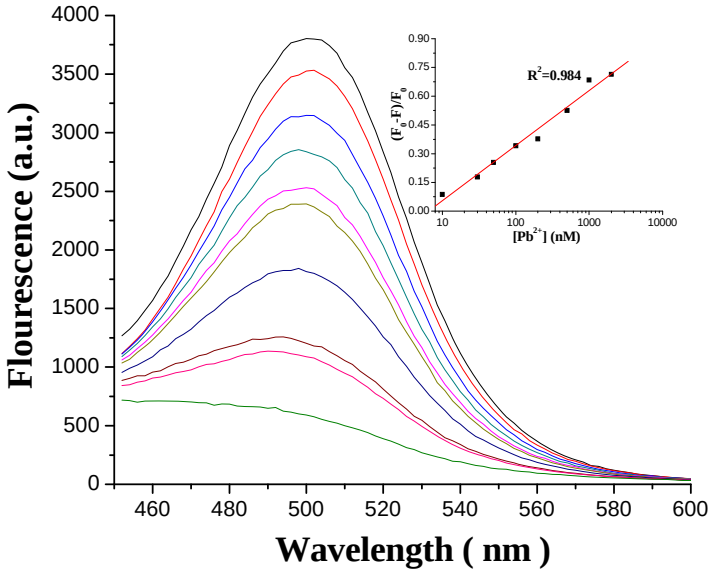

Figure S10. Fluorescence emission spectra of AuNDs in the water sample from a local lake in the presence of 0, 10, 30, 50, 100, 200, 500, 1000, 2000 and 5000 nM Pb^{2+}. Inset: Plot of the relative fluorescence reduction versus the Pb^{2+} concentration.