Electronic Supplementary Information

N-1-(2-mercaptoethyl) thymine Modification of Gold Nanoparticles: a Highly Selective and Sensitive Colorimetric Chemosensor for Hg^{2+}

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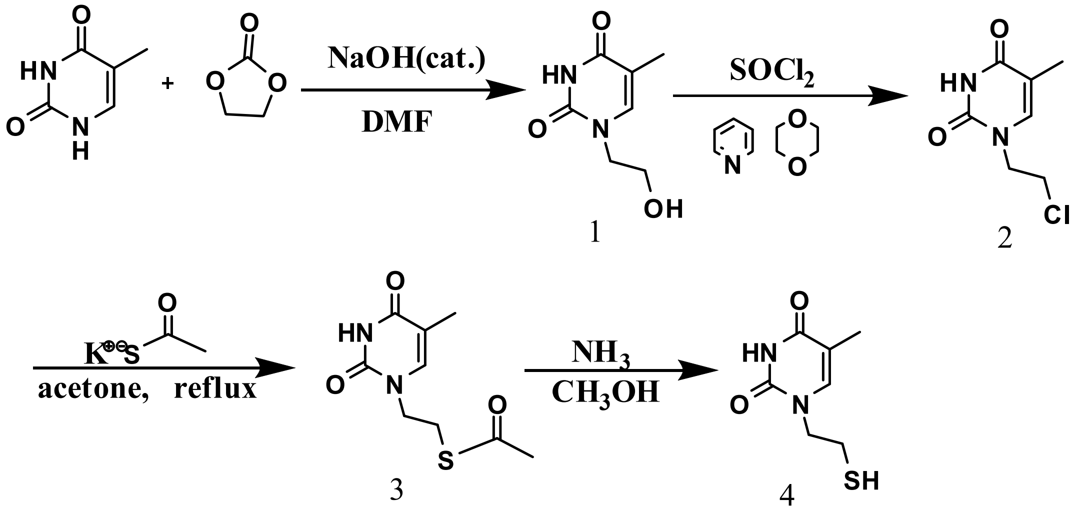
Synthesis of N-1-(2-mercaptoethyl) thymine

N-1-(2-mercaptoethyl) thymine was synthesized as following procedure using thymine as a precursor. The structure of the target product was confirmed by ^{1}HNMR (Fig. S1).



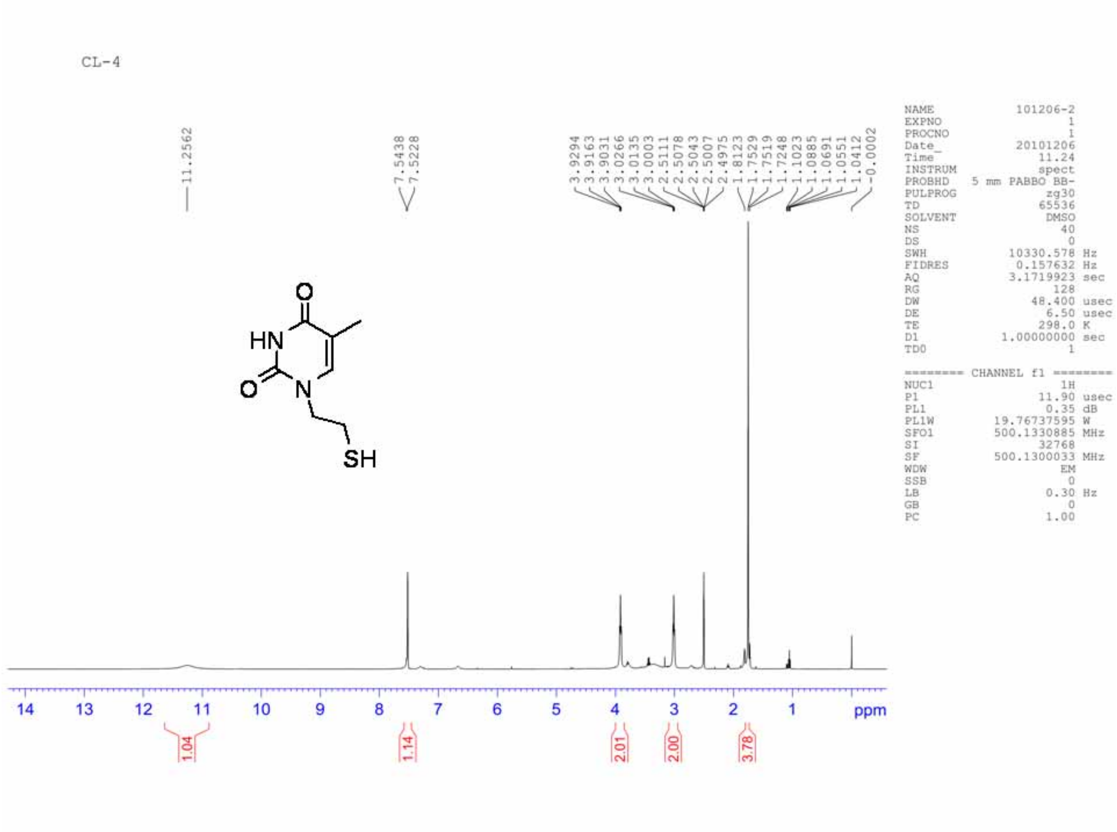
Synthetic Route of Ligand

Compound 1: Thymine (4.66 g, 37 mmol) was suspended in DMF (50 mL) and (4.9 g, 111 mmol) ethylene carbonate was added. After addition of a catalytic amount of NaOH (35 mg), the mixture was heated to 150 °C and kept refluxing for 6 h (TLC). DMF was removed in vacuo and the residue was yellow ropy liquid**.** The residue was washed with CH_3OH and after vacuum filtering, the filtrate was dried in vacuo. Then, the residue was crystallized from CH_2Cl_2 to give 3.99g (63%) of **1** as a white solid. (R_f=0.3, CH_2Cl_2/CH_3OH=15/1) 1H-NMR (δ: ppm, DMSO): 11.12 (s, 1H, NH), 7.43 (s, 1H, CH), 4.87 (s, 1H, OH), 3.66-3.68 (t, 2H, CH_2), 3.54-3.56 (t, 2H, CH_2), 1.72-1.80 (t, 3H, CH_3).

Compound 2: Compound **1** (2.009g, 11.8 mmol) was suspended in 1, 4-dioxane (45 mL) and heated to be dissolved. Then, at 80 °C add excess thionyl chloride drop by drop in 0.5h. (8mL thionyl chloride in 10mL 1, 4-dioxane). The mixture was refluxed for about 5h (TLC). After removal of the solvent in vacuo, the residue was resuspended in $CHCl_3$. After vacuum filtering and rotary evaporation, the residue was crystallized from CH_3OH to give 1.73g (78%) of 2 as a brownish solid. (R_f=0.4, CH_3OH/CH_2Cl_2=1/14) ^{1}H-NMR (δ: ppm, DMSO): 11.31 (s, 1H, NH), 7.546-7.549 (d, 1H, CH), 3.95-3.98 (t, 2H, CH_2), 3.83-3.85 (t, 2H, CH_2), 1.75-1.76(d, 3H, CH_3).

Compound 3: Compound **2** (1.15 g, 6.07 mmol) was suspended in acetone (35 mL). After addition of solid potassium thioacetate (874 mg, 7.6 mmol), the mixture was heated to reflux for 12 h. The suspension was concentrated in vacuo, the residue was washed several times with acetone to give 1.3 g (94%) of **3** as a white solid. ^{1}H-NMR (δ: ppm, DMSO): 11.23 (s, 1H, NH), 7.46-7.48 (d, 1H, CH), 3.78-3.80 (t, 2H, CH_2), 3.11-3.13 (t, 2H, CH_2), 2.32 (s, 3H, CH_3), 1.74 (d, 3H, CH_3).

Compound 4: Compound **3** (1.254 g, 5.5 mmol) was suspended in 50 mL degassed methanol, kept under nitrogen. Gaseous ammonia was bubbled through the solution for 20min and the internal temperature rose to 40 °C. The resulting solution was stirred for 60 min and a colorless precipitate was observed. The suspension was filtered and the filtrate was concentrated and the solid thus obtained was dried at 60 °C in vacuo. Yield of **4**: 890 mg (87%). ^{1}H-NMR (δ: ppm, DMSO): 11.26 (s, 1H, NH), 7.53-7.54 (d, 1H, CH), 3.90-3.93 (t, 2H, CH_2), 3.00-3.03 (t, 2H, CH_2), 1.72-1.81 (t, 4H, CH_3, SH).



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FIDRES        0.157632 Hz
AQ           3.1719923 sec
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DW              48.400 usec
DE                6.50 usec
TE               298.0 K
D1          1.00000000 sec
TD0                  1

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PL1               0.35 dB
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Fig. S1. ^{1}HNMR spectrum of as-synthesized compound 4

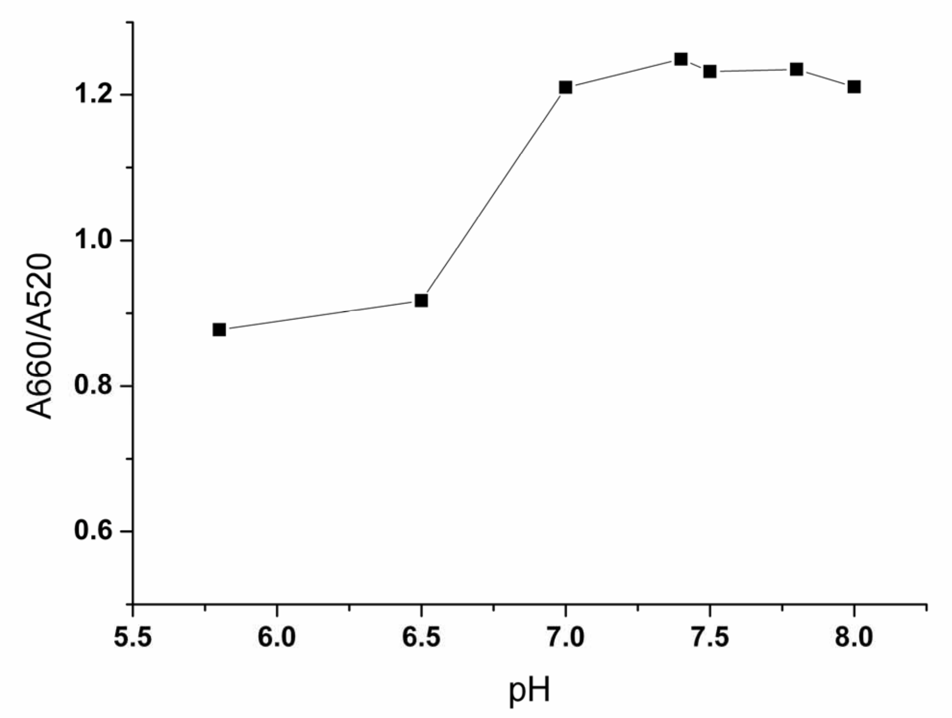

Fig. S2 Effect of the pH value of phosphate buffer solution on the aggregation of functionalized AuNPs in the presence of Hg^{2+}.

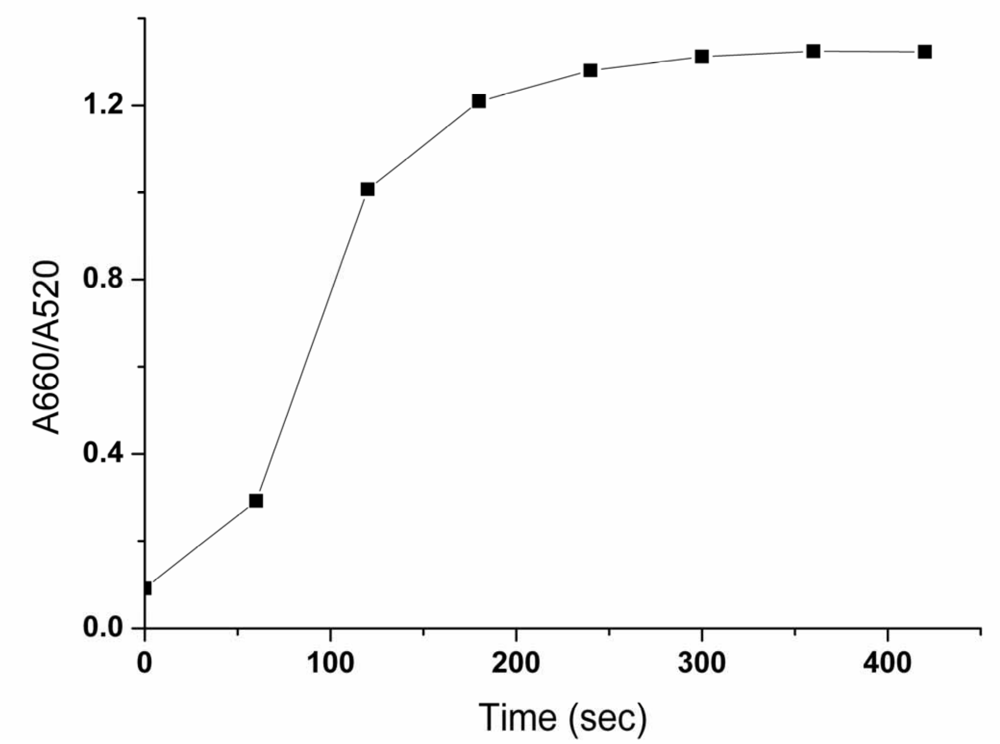

Fig. S3 Plot of A660/A520 against time in the presence of 1μM Hg^{2+}. The aggregation kinetic of 1.0mL of the mixture solution containing 150 μL of as-prepared stock solution of thymine-modified AuNPs and 850 μL of phosphate buffer solution (50mM, pH 7.4) after the addition of 1μM Hg^{2+}.

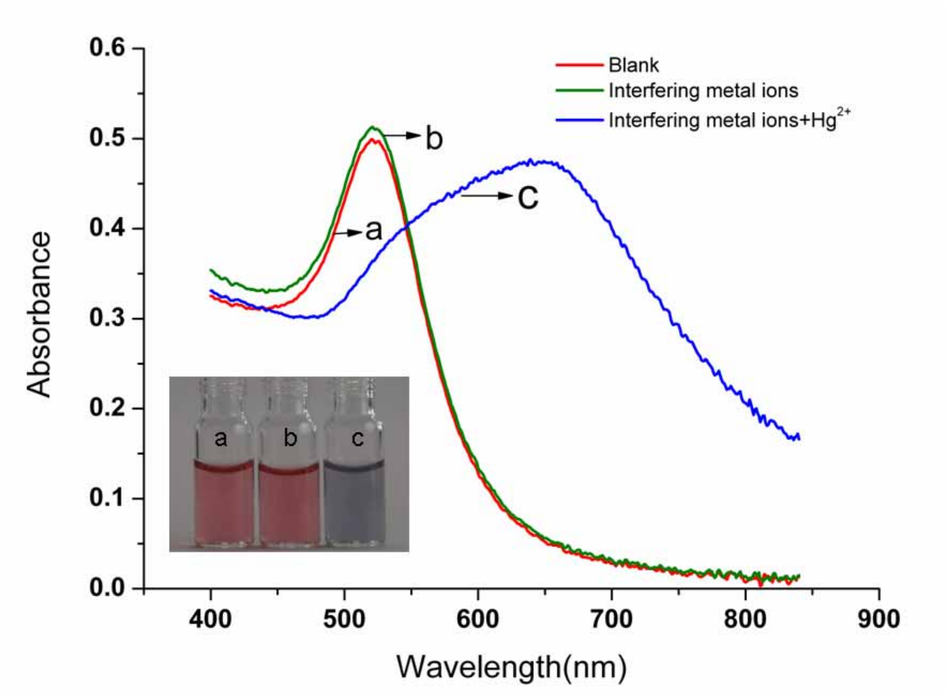

Fig. S4 Extinction spectra of solutions (a) T-S–AuNPs, (b) in the presence of mixture of different interfering metal ions (Cd^{2+}, Mg^{2+}, Co^{2+}, Zn^{2+}, Pb^{2+}, Mn^{2+}, Ni^{2+}, Cr^{3+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, Na^{+}, each concentration was 10μM), (c) in the presence of 1μM Hg^{2+} with the mixture of interfering metal ions (adding 1μM Hg^{2+} to solution b). Inset image is corresponding colorimetric response.

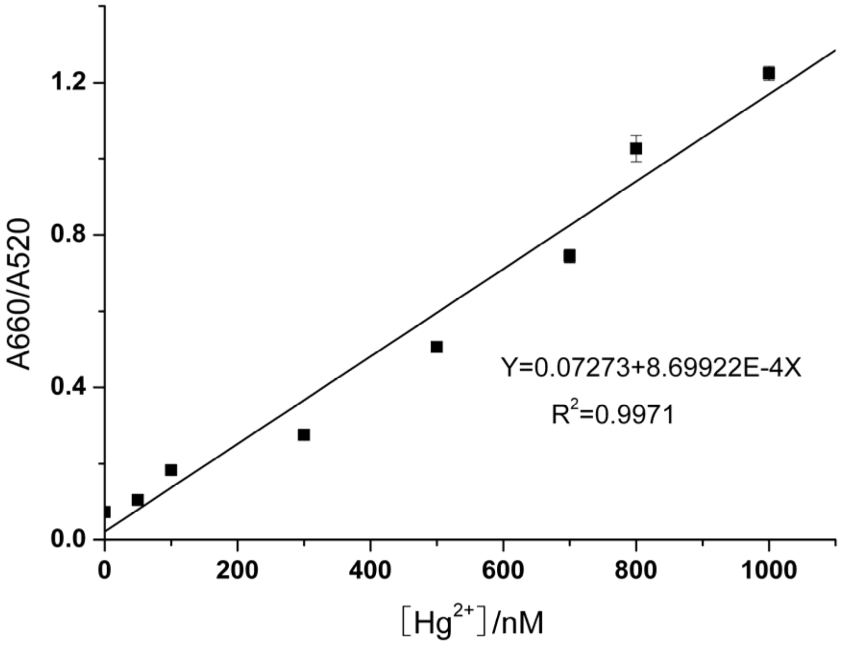

Fig. S5. A plot of A660/A520 versus the concentration of Hg^{2+}. (Hg^{2+} detection in tap water) The incubation time was 5 min. The error bars represent standard deviations based on three independent measurements.

Table 1

Comparison of DNA aptamer-based sensing methods for the detection of Hg^{2+} with our proposed method.

Method	Recognition probe	Assisted probe	General applicability	LOD[#]	Ref.
Colorimetric	N-1-(2-mercaptoethyl) thymine	Gold nanoparticles	Generic	2.8 nM	Our work
	ssDNA	Gold nanoparticles	not report	100 nM	J. S. Lee *et al.* (2007 Angew. Chem. Int. Ed)
	Poly-T_n ssDNA	Gold nanoparticles, salt	not report	250 nM	C. W. Liu *et al.* (2008 Chem Comm)
	DNA G-Quadruplex	Hemin，H_2O_2-ABTS	generic	50 nM	T. Li *et al.* (2009 Anal. Chem)
Colorimetric and Fluorometric	Thymine-rich ssDNA	Gold nanoparticles, FAM	generic	40 nM	H. Wang *et al.* (2008 Anal Chem)
Fluorometric	Faka DNA	Fluorescein, dabcyl	generic	40 nM	A. Ono and H. Togashi (2004 Angew. Chem. Int. Ed)
Scanometric	ssDNA	Gold nanoparticles, silver amplication	generic	10 nM	J. S. Lee and C. A. Mirkin (2008 Anal. Chem)
Electrochemic	ssDNA	Fc tags	generic	0.5 nM	S. J. Liu *et al.* (2009Anal. Chem.)

[#] LOD: Limit of detection

Reference

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