Supporting information for

Metal-Induced Aggregation of Mononucleotides-Stabilized Gold Nanoparticles: An Efficient Approach for Simple and Rapid Colorimetric Detection of Hg(II)

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EXPERIMENTAL SECTION

Reagents and Apparatus. $HAuCl_4 \cdot 4H_2O$ was purchased from Shenyang Research Institute of Nonferrous Metals, China. The four kinds of mononucleotide, i.e., deoxyadenosine triphosphate (dATP), deoxyguanosine triphosphate (dGTP), deoxycytidine triphosphate (dCTP), and dTTP were purchased from Shanghai Sangon Biological Technology & Services Co., Ltd., China. Metal ion solutions were prepared from nitrate salts. All other reagents were of analytical reagent grade and were used without further purification or treatment. UV−vis absorption spectra were recorded on a Hitachi U-4100 UV-vis spectrophotometer (Kyoto, Japan). Transmission electron microscopy (TEM) was performed on a transmission microscope (Tecnai F-20). The pH was measured by a model 868 pH meter (Orion). Ultra pure water with an electric resistance of 18.2 MΩ was supplied through a Milli-Q water purification system. ICP-MS experiments were performed on X series 2 (Thermo fisher). All work solutions were prepared with 0.01 M Tris-HCl buffer solution (pH 7.2, 25 mM $KClO_4$).

Preparation of T-AuNPs and Surface Modification. AuNPs, which are typically about 13 nm in diameter, were synthesized through the method proposed by Natan et al.[1] The procedure is briefly described as following: 100 mL of 1.0 mM $HAuCl_4$ solution was heated as well as stirred vigorously; 10 mL of 38.8 mM sodium citrate solution was then rapidly added into the boiling solution and the color of the solution changed from light yellow to wine-red immediately. The solution was boiled for another 10 min, followed by further stirring for 15 min. And the solution was

gradually cooled to room temperature. Then it was filtered through a 0.32-μM membrane filter and stored in a refrigerator at 4°C before being used. The concentration of AuNPs was measured by UV-vis spectroscopy based on an extinction coefficient of 2.7×10^8 $M^{-1} \cdot cm^{-1}$ at $\lambda = 520$ nm for 13-nm particles.[2]

For the surface modification of AuNPs with mononucleotides, an aliquot of 20 μL (2.0 mM) dTTPs , dATPs, dGTPs or dCTPs was added to 980 μL of AuNPs colloidal solutions. After incubating for 10 min at room temperature, the resulting mixture was subjected to centrifugation at the speed of 12000 g for 10 min. The supernatant fluid was removed, while the oil-liked AuNPs precipitate was dissolved in the Tris-HCl buffer to keep the final volume identical. To testify the modification process of AuNPs, zeta potentials of AuNPs and dTTPs-modified AuNPs were measured in Tris-HCl buffer solution by the Zetasizer Nano. These mononucleotides-modified AuNPs solutions were stored at 4 °C in a freezer for further use.

Transmission Electron Microscopy. The samples for TEM analysis were prepared by pipetting 10 μL of the colloidal solutions onto standard holey carbon-coated copper grids and the grids were dried in air for about 6 hours. Then the grids were loaded into the vacuum chamber of the electron microscope for detection. These samples were not subjected to heavy metal staining or other treatments.

Performance of Hg^{2+} Sensing. A 100-μL aliquot of the first-prepared dTTPs/AuNPs (T-AuNPs) solution was added to a 500 μL volumetric pipe, 50.0 μL Hg^{2+} solution of different concentration was then added, and the mixture was diluted to 500 μL with the Tris-HCl buffer solution. After the mixture was incubated for 10 min at room temperature, its absorption was detected by UV-vis spectrophotometer. For selectivity measurements, the separate solution method was used throughout by using the solutions of corresponding metal ions.

For recording time course of the interaction of Hg^{2+} with T-AuNPs, the absorption titrations of T-AuNPs by Hg^{2+} ions were run by directly adding small aliquots (typically 10 μL) of the metal stock solutions to 500 μL of the Tris-HCl buffer solution containing 3.0 nM AuNPs and 40 μM dTTPs in a quartz sample cuvette (1.0 cm × 1.0 cm). The absorbance of AuNPs was recorded at 680 nm.

Real Sample Analysis. The tap water sample was collected after discharging tap water for 5 min and boiled for another 5 min to remove chlorine. River water sample was obtained from Xiang River passing through Changsha City of China. The sample collected was first filtered through a column (packed with an anionic-exchange resin) to remove oils and other organic impurities. Then the Hg^{2+} concentrations of these samples were detected by the present method and inductively coupled plasma/mass spectroscopy (ICP-MS), respectively.

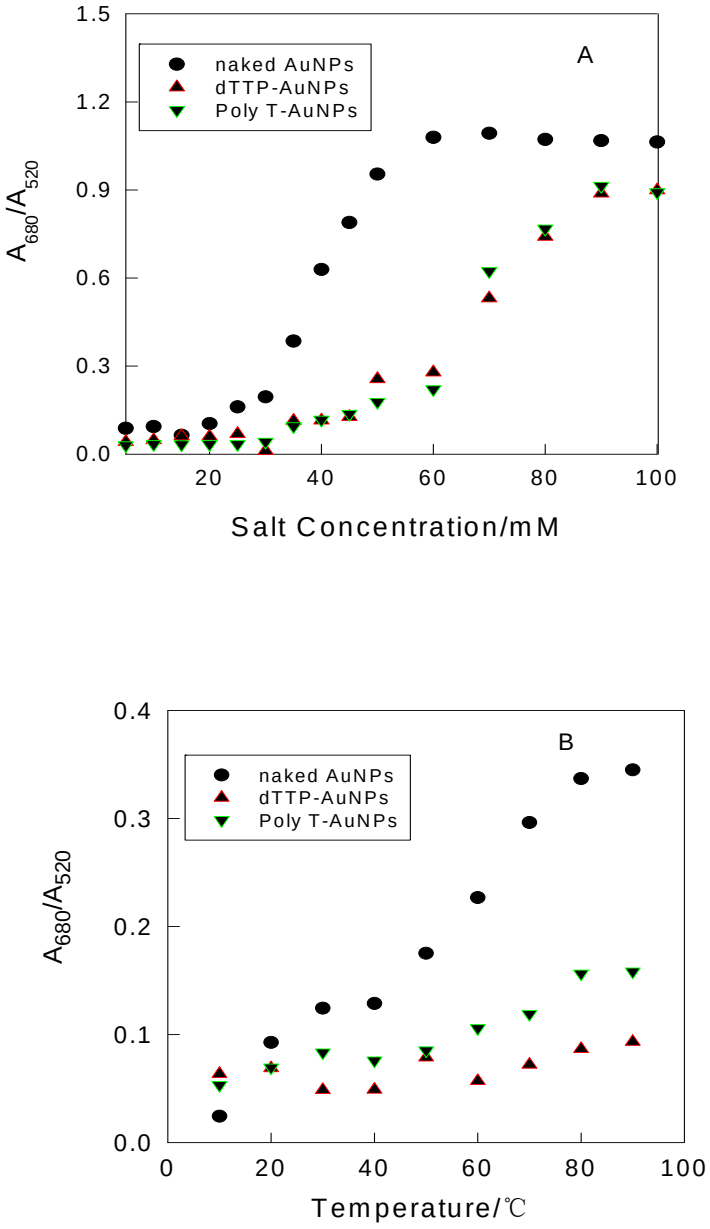

Figure S1. (A) Effects of different concentrations of $KClO_4$ on the stability of T-AuNPs and other AuNPs-based probes. The experiment was carried out under room temperature. (B) Effects of different temperatures on the stability of T-AuNPs and other AuNPs-based probes. The salt concentration of $KClO_4$ is 25 mM.

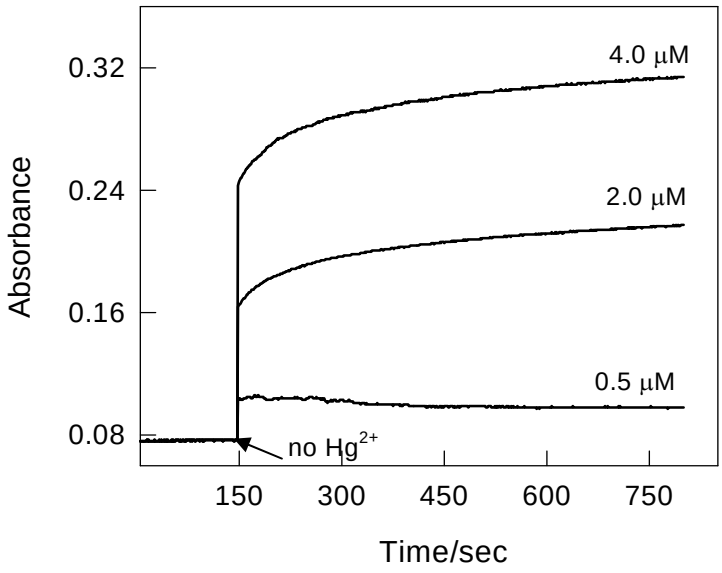

Figure S2. Kinetics of the interaction of T-AuNPs with different concentrations of Hg^{2+} (0.5, 2.0, and 4.0 μM). For each measurement, the cell was filled with 500 μl the Tris-HCl buffer solution containing T-AuNPs, then 10.0 μl Hg^{2+} solution of different concentrations was introduced into the cell. The transition between each regime is marked an arrow. Absorbance was recorded at 680 nm at room temperature.

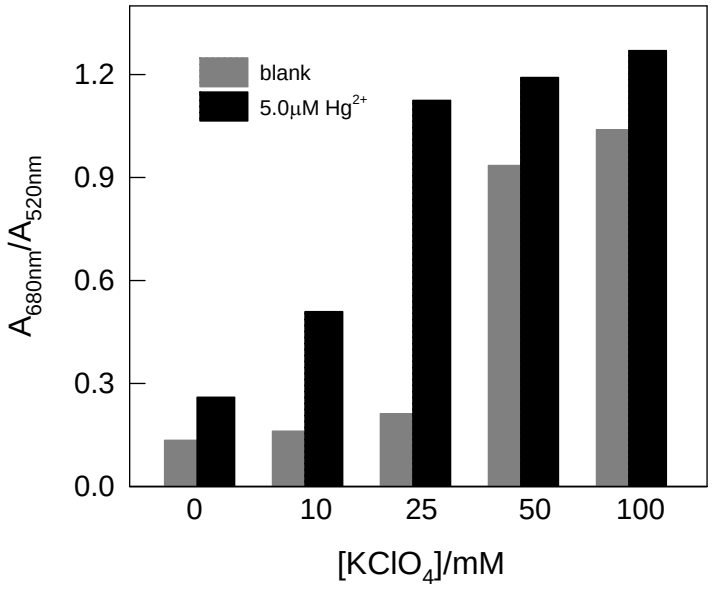

Figure S3. Effects of different concentrations of $KClO_4$ on the aggregation of T-AuNPs in the Tris-HCl buffer solution in the absence and the presence of Hg^{2+}.

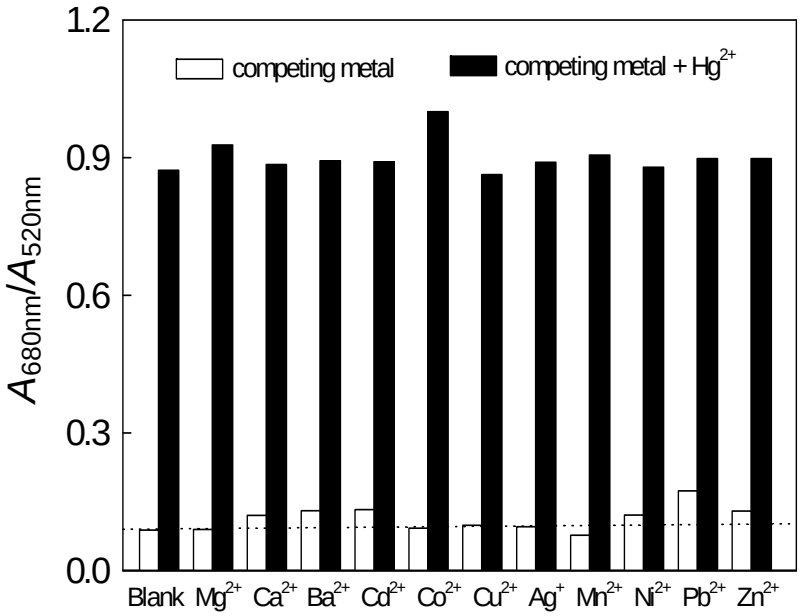

Figure S4. Absorbance change profiles of T-AuNPs at 520 nm and 680 nm (A_{680}nm/A_{520}nm) in the presence of the selected metal ions (10 μM) and the metal ion + 4.0 μM Hg^{2+}.

Table S1. Determination of Hg^{2+} in Water Samples Using the Proposed Method and ICP-MS

Sample	Hg^{2+}(μM)		
	added	proposed method (mean[a] ± S.D.[b])	ICP-MS (mean[a] ± S.D.[b])
tap water	0.5	0.54 ± 0.04	0.55 ± 0.05
tap water	2.0	2.20 ± 0.13	2.35 ± 0.25
river water	0	0.72 ± 0.05	0.74 ± 0.07
river water	0.5	1.25 ± 0.08	1.32 ± 0.10

[a]Mean value for three determinations.
[b]S.D. = standard deviation

References

1. K. C. Grabar, R. G. Freeman, M. B. Hommer and M. J. Natan, *Anal. Chem.*, 1995, **67**, 735–743.
2. L. M. Demers, C. A. Mirkin, R. A. Mucic, R. L. Reynolds, R. Letsinger, R. Elghanian and G. Viswanadham, *Anal. Chem.*, 2000, **72**, 5535-5541.