Supplementary Material (ESI) for Chemical Communications

Visual and Colorimetric Detection of Hg^{2+} by Cloud Point Extraction with Functionalized Gold Nanoparticles as a Probe

Supplementary Information

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Experimental Section

Chemicals.

Mercaptopropionic acid (MPA) and Triton X-114 (TX-114) was obtained from Acros Organics (Geel, Belgium), homocystine (HCys) was obtained from Sigma Aldrich (Saint Louis, MO, USA), 2, 6-pyridinedicarboxylic acid (PDCA) was purchased from Alfa Aesar (Ward Hill, MA, USA), hydrogen tetrachloroaurate was obtained from Sinopharm Chemical Reagent Co., Ltd (Beijing, China), and sodium tetraborate was bought from Tianjin Jinke Fine Chemical Institute (Tianjin, China). Other chemicals were all purchased from Beijing Chemical Plant (Beijing, China). All these chemicals were of analytical grade or better, and were employed without further purification.

The Hg^{2+} standard solutions were prepared daily by serial dilution of a stock standard solution of 100 μg/mL Hg^{2+} (GBW(E)080124, National Research Center for Certified Reference Materials, China). Ultra pure water (18.3 MΩ) was used throughout. All glass wares were rinsed with aqua regia, and further cleaned by distilled water and ultra pure water successively.

Synthesis, modification and purification of AuNPs

AuNPs (~4 nm) were prepared by $NaBH_4$ reduction of $HAuCl_4$ according to literature[1]. Briefly, into 18 mL water contained in a 50 mL conical flask were sequentially added 0.5-mL $HAuCl_4$ (10 mM) and 0.5-mL sodium citrate (10 mM) with stirring. After strrring for 5 min, 0.5 mL of freshly prepared $NaBH_4$ (0.1 M) was injected, and the solution color turned into orange immediately. Then the conical flask was removed from stirrer and settled for 2 h. TEM analysis showed the obtained AuNPs have an average size of 4 nm. The particle concentration of Au NPs, calculated by Beer's law using an extinction coefficient at 520 nm[2], was about 15 nM. For modifying the surface of the AuNPs with MPA and HCys (bound to the AuNP surface through the Au-S bond), 20-μL MPA (10 mM) and 20-μL HCys (2 mM) were in sequent added into the above prepared AuNP solution with stirring. After stirred continuously for 2 h, 1.2 mL of freshly prepared $NaBH_4$ (0.1 M) was added, and the solution was stored in refrigerator (4ºC) overnight. For purification, CPE was conducted to remove the relatively large particles of the AuNPs, which can be extracted into the TX-114 rich phase in the absence of Hg^{2+} and thus reduced the detection sensitivity for Hg^{2+}. In brief, into the modified AuNPs solutions were added 0.3% (w/v) TX-114 and 0.05% (w/v) NaCl. The blended solution was incubated in 35 ºC water bath for 30 min, and then centrifuged at 5000 rpm for 10 min. This procedure was repeated 2-3 times until the surfactant-rich phase was nearly clear and colourless. The obtained aqueous-rich phase was ready for use in detection of Hg^{2+}.

CPE procedure

CPE procedures were conducted as follows. Into a glass centrifugal tube with Hg^{2+} standard solution were in sequent added 100-μL buffer solution (0.2 M sodium phosphate dibasic-citric acid, pH 7.5), 200-μL PDCA (60 mM), 200-μL MPA-HCys-AuNPs (~15 nM), 200-μL TX-114 (6%, w/v), and 600-μL NaCl (1%, w/v). The mixture was diluted to 10 mL with water. After mixing and incubating at 60°C in water bath for 30 min, the tube was centrifuged at 2000 rpm (~640 g) at room temperature for 10 min to facilitate the phase separation. The up aqueous-rich phase was removed, and the obtained TX-114 rich phase (~50 μL) was transferred into a well of the 384-well plate for recording the absorbance at 520 nm with a multimode microplate spectrophotometer (Varioscan Flash, Thermo, USA). Note Tris-HCl buffer solution rather than sodium phosphate dibasic-citric acid was used in studying the interference of Ca^{2+}.

Characterization of AuNPs

The AuNPs extracted into the TX-114 rich phase was characterized by TEM (H-7500, Hitachi, Japan) at 80 kV. TEM samples were prepared by loading 5-μL aliquots of the TX-114 rich phase (at 30 times dilution with 1:1 water and methanol) onto carbon-coated grid sample holders. The Zetasizer Nano instrument (ZEN3600, Malvern) was employed to determine size and Zeta potential.

References

[1] G. K. Darbha, A. K. Singh, U. S. Rai, E. Yu, H. T. Yu and P. C. Ray, J. Am. Chem. Soc., 2008, 130, 8038–8043.

[2] G. K. Darbha, A. Ray, and P. C. Ray, ACS Nano, 2007, 1, 208-214.

Results and Discussion

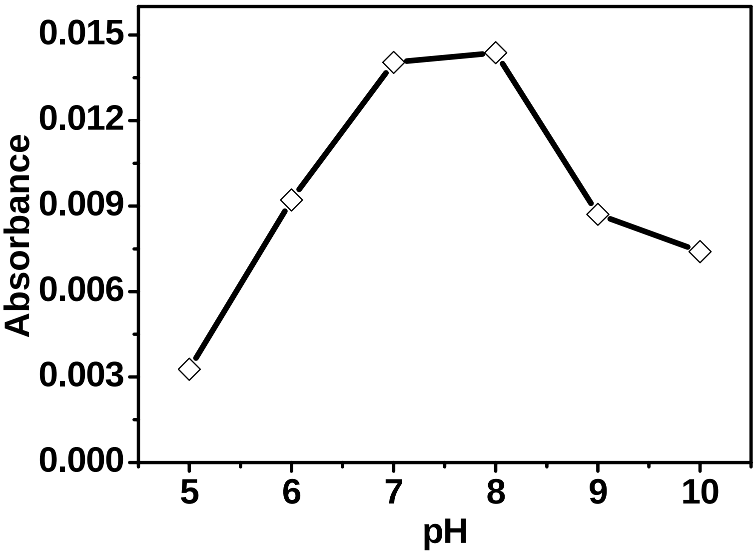

Figure S1. Effects of pH on the absorbance of the TX-114-rich phase.

Conditions: PDCA, 1 μM; MPA-HCys-AuNPs, 0.3 nM; TX-114, 0.18% (w/v); NaCl, 0.02% (w/v); incubation temperature, 40 °C; incubation time, 30 min; centrifugation parameters, 8 min at 2000 rpm.

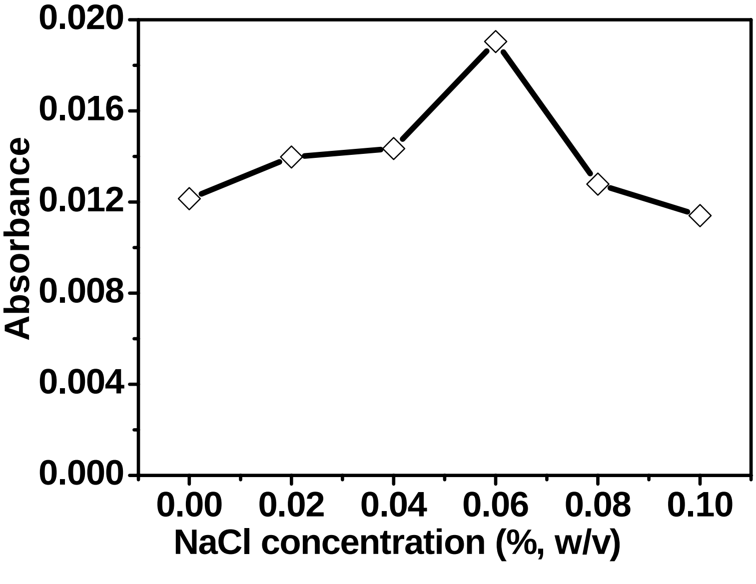

Figure S2. Effects of salinity on the absorbance of the TX-114-rich phase.

Conditions: pH=7.5; PDCA, 1 μM; MPA-HCys-AuNPs, 0.3 nM; TX-114, 0.18% (w/v); incubation temperature, 40 °C; incubation time, 30 min; centrifugation parameters, 8 min at 2000 rpm.

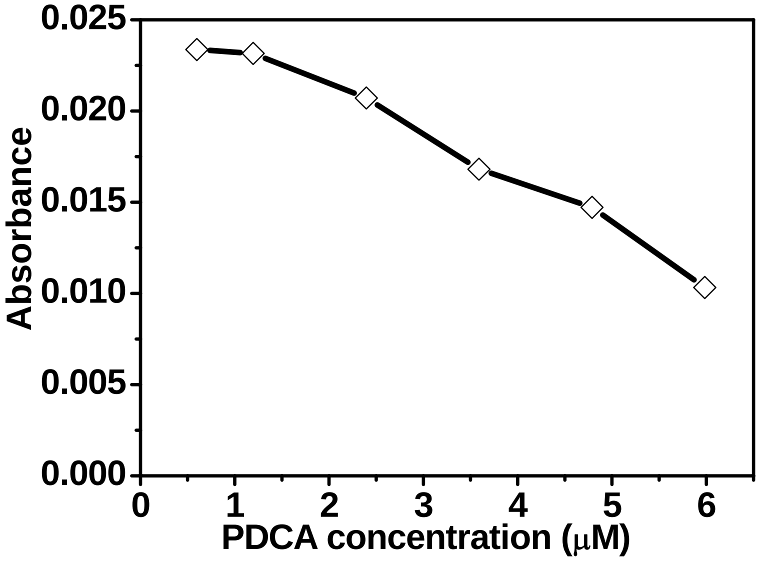

Figure S3. Effects of PDCA concentration on the absorbance of the TX-114-rich phase.

Conditions: pH=7.5; MPA-HCys-AuNPs, 0.3 nM; TX-114, 0.18% (w/v); NaCl, 0.06% (w/v); incubation temperature, 40 °C; incubation time, 30 min; centrifugation parameters, 8 min at 2000 rpm.

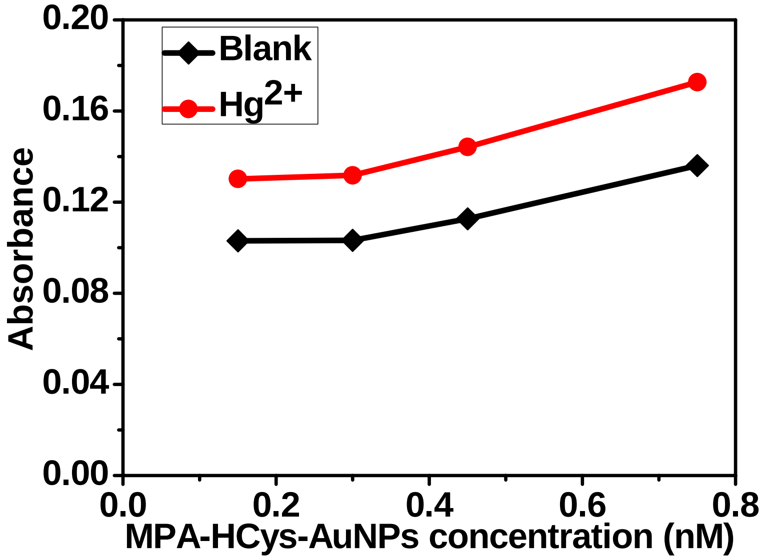

Figure S4. Effects of MPA-HCys-AuNPs concentration on the absorbance of the TX-114-rich phase.

Conditions: pH=7.5; PDCA, 1 µM; TX-114, 0.18% (w/v); NaCl, 0.06% (w/v); incubation temperature, 40 °C; incubation time, 30 min; centrifugation parameters, 8 min at 2000 rpm.

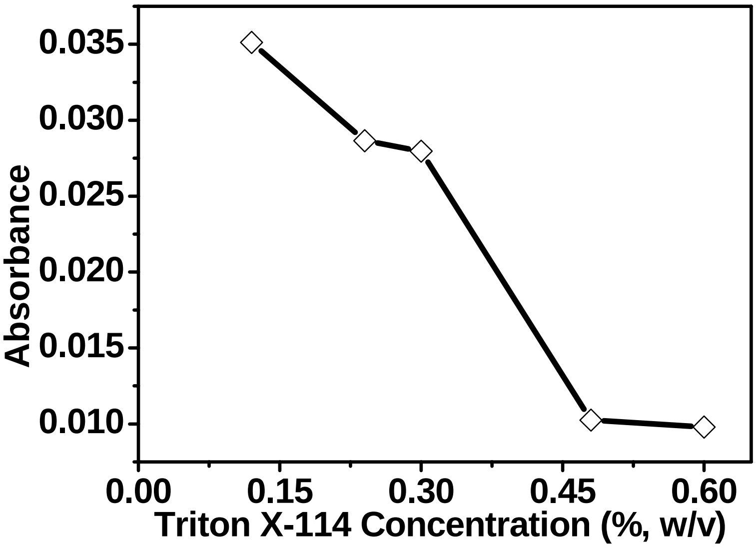

Figure S5. Effects of TX-114 concentration on the absorbance of the TX-114-rich phase.

Conditions: pH=7.5; PDCA, 1 μM; MPA-HCys-AuNPs, 0.3 nM; NaCl, 0.06% (w/v); incubation temperature, 40 °C; incubation time, 30 min; centrifugation parameters, 8 min at 2000 rpm.

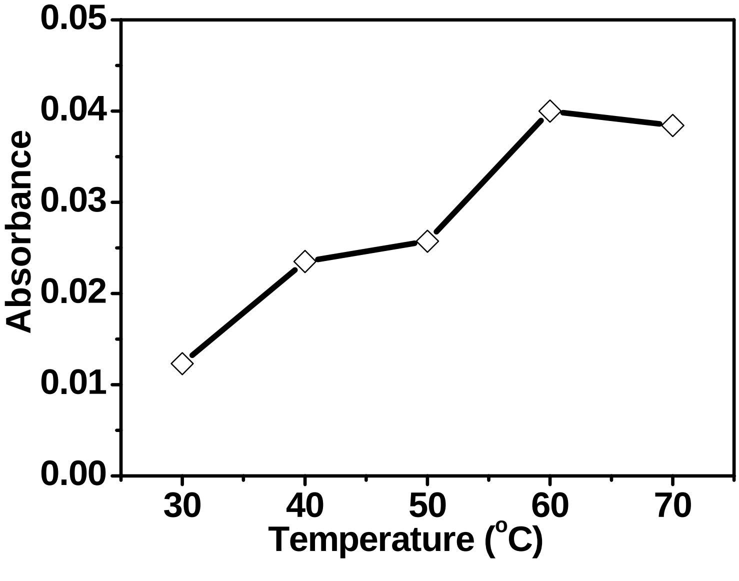

Figure S6. Effects of extraction temperature on the absorbance of the TX-114-rich phase.

Conditions: pH=7.5; PDCA, 1 μM; MPA-HCys-AuNPs, 0.3 nM; NaCl, 0.06% (w/v); TX-114, 0.18% (w/v); incubation time, 30 min; centrifugation parameters, 8 min at 2000 rpm.

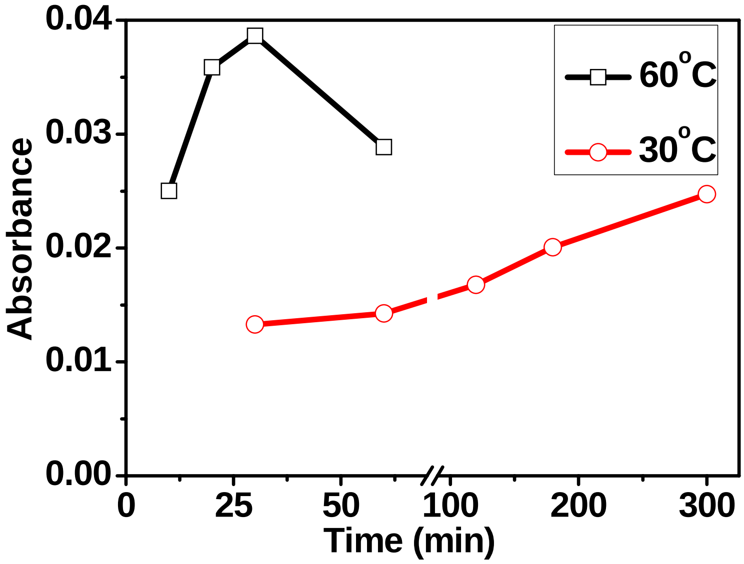

Figure S7. Effects of extraction time on the absorbance of the TX-114-rich phase.

Conditions: pH=7.5; PDCA, 1 μM; MPA-HCys-AuNPs, 0.3 nM; NaCl, 0.06% (w/v); TX-114, 0.18% (w/v); centrifugation parameters, 8 min at 2000 rpm.