

Electronic Supplementary Information

Visual Detection of Ca²⁺ Based on Aggregation-induced Emission of Au(I)–Cys Complexes with Superb Selectivity

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Experimental details

Materials

Hydrogen tetrachloroaurate trihydrate (HAuCl₄·3H₂O), Glutathione (GSH), L-cysteine and Trithylenetetramine (TETA) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All other chemical reagents were of analytical reagent grade and used without further purification. All solutions were prepared with water purified by a Milli-Q system (Millipore, Bedford, MA, USA). Fetal bovine serum (FBS) was obtained from HyClone (Thermo Fisher Scientific, Inc.). The milk was purchased from a convenience store. Drinking water (DW) was collected directly from a home water tap.

Instruments

Absorption spectra were recorded on a UV/Vis spectrometer (Lambda 25, PerkinElmer, USA) with Milli-Q water as the reference solution. Photoexcitation and emission spectra were recorded using a fluorescence spectrometer (F-4600, Hitachi Co. Ltd., Japan) with a Xenon lamp as excitation source, slit widths for the excitation and emission were set at 10 and 10 nm respectively. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry was carried out on a Bruker Daltonics ultrafleXtreme system. The accurate concentrations of real samples were determined by an Inductive Coupled Plasma Atomic Emission Spectrometer (PerkinElmer, Optima 8000). The detection range, selectivity, real sample analysis data were collected on a Multilabel Plate Readers (VICTOR X4, PerkinElmer Inc., USA): optical excitation filter 355/40 nm; emission filter 616/8.5 nm; lamp energy 4000. Digital photographs were taken by a digital camera (Canon PowerShot SX240 HS).

Synthesis of Au(I)–Cys Complex

The Au(I)-GSH complexes were synthesized according to Luo's method. The Au(I)-Cys complexes were synthesized in accordance with the previous literature with slight modification.¹ 1 mL aqueous solutions of HAuCl₄ (1%) and 0.35 mL Cys (100 mM) mixed with 10.65 mL of ultrapure water under gentle stirring at 25 °C for 5 min. NaOH (0.5 M) was

then added to the mixture to bring the pH to 7.0, after that the solution was aged for about 1 h. The solution of Au(I)-Cys was stored at 4 °C before use.

Measurement

A stock solution of CaCl_2 (0.1 M) was prepared, for Ca^{2+} detection, 10 μL different concentrations of Ca^{2+} were firstly mixed with 10 μL TETA- H_2SO_4 (20%, pH=11.5) working buffer, then the mixture was added into the Au(I)-Cys solution (0.8 mM) to a final volume of 100 μL . After mixing and incubating at room temperature for 20 min, the luminescent intensities were collected on a Multilabel Plate Readers. The selectivity of the sensing system toward Ca^{2+} (400 μM) was evaluated by using 10-fold concentrations (4.0 mM) of cations including Li^+ , Na^+ , K^+ , Ag^+ , Mg^{2+} , Ca^{2+} , Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , Ba^{2+} , Hg^{2+} , Pb^{2+} , Al^{3+} , Fe^{3+} , In^{3+} , Bi^{3+} , La^{3+} , Zr^{4+} .

Real sample analysis

The samples were acidified to pH 2.0 with HCl and incubated for 3 h at 80°C to dissociate Ca^{2+} ions from proteins,² then the solutions were filtrated with 4.5 μm membrane filters. The drinking water and FBS samples were diluted 10 times with working buffer and the milk sample was diluted 100 times with working buffer before analysis. The total concentrations of Ca^{2+} determined by the method in the three samples are summarized in Table S1. The spiked recoveries were also studied and summarized in Table S2.



Figure S1. Digital photograph of as-prepared Au(I)-Cys complexes.

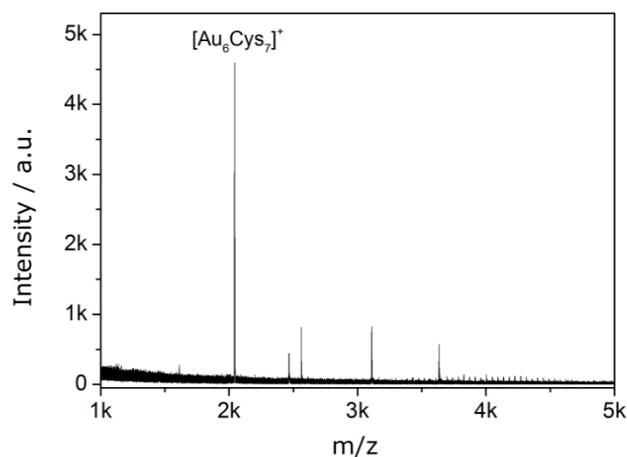


Figure S2. MALDI-TOF mass spectrum of Au(I)-Cys complexes.

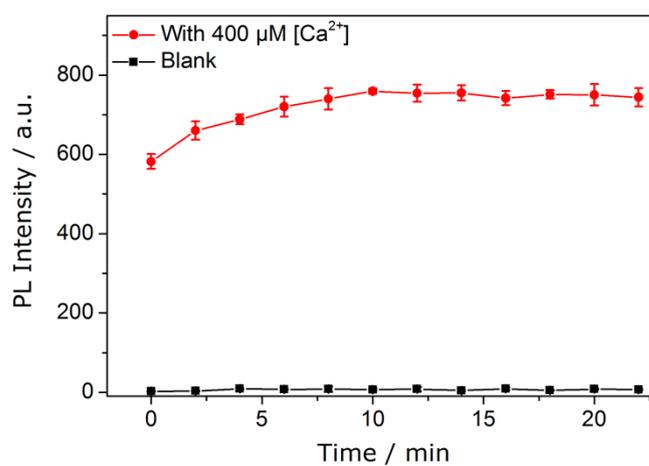


Figure S3. The luminescence intensities of Au(I)-Cys complexes in the absence and presence of Ca^{2+} as a function of time. The luminescence intensity of aggregated complexes rapidly reached to a high value after Ca^{2+} was added and increased gradually to a plateau in 10 min.

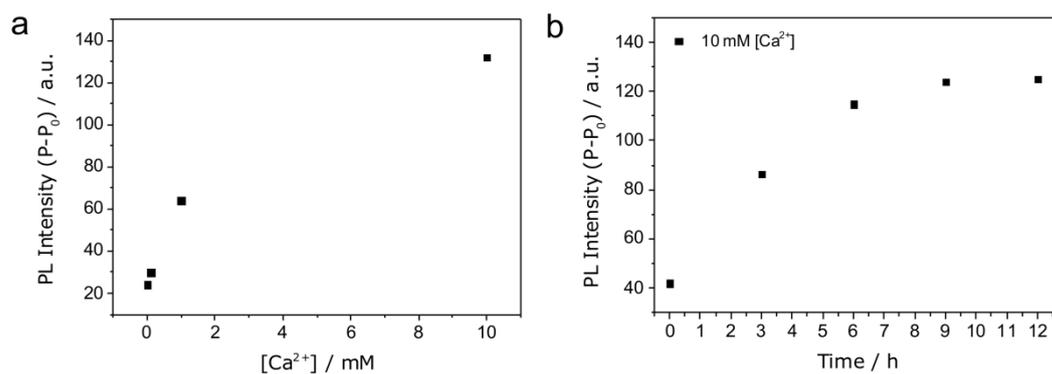


Figure S4. (A) Luminescence intensity of Au-GSH complexes in the presence of different concentrations of Ca²⁺; (B) Luminescence intensity of Au-GSH complexes in the presence of 1 mM Ca²⁺ as a function of time.

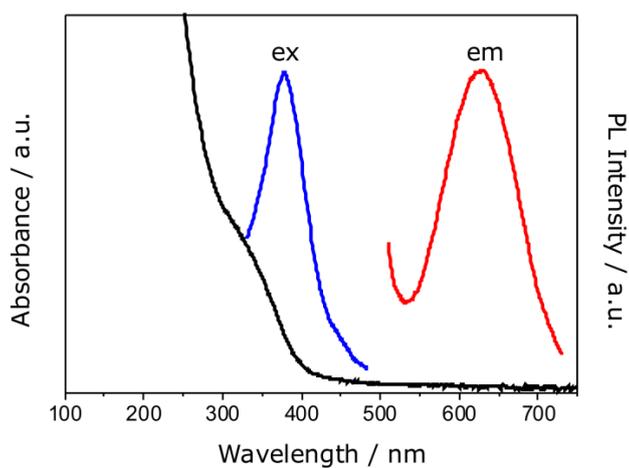


Figure S5. UV-vis absorption spectrum (black line), photoexcitation (blue line, $\lambda_{\text{em}} = 615$ nm), photoemission (red line, $\lambda_{\text{ex}} = 375$ nm) spectra of Au(I)-Cys complexes aggregated by Ca²⁺.

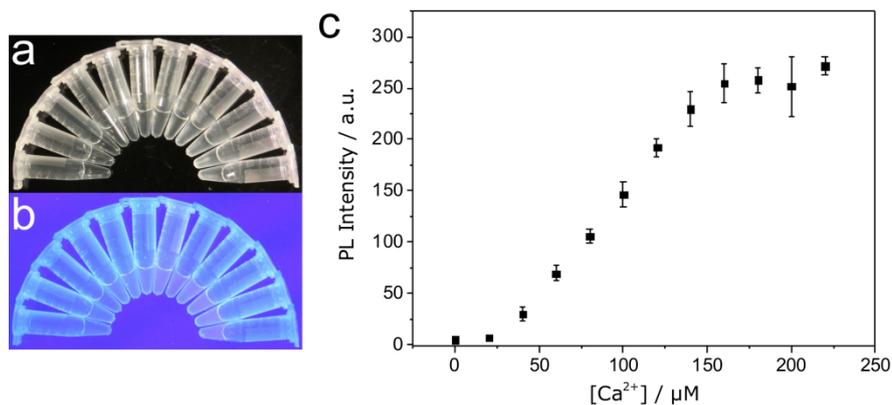


Figure S6. Digital photos of increasing concentrations of Ca^{2+} (0, 20, 40, 60, 80, 100, 120, 140, 160, 180, 200, 220 μM) with 0.2 mM Au(I)-Cys complexes under (a) visible light and (b) UV light; (c) Luminescence intensities of Au(I)-Cys complexes as a function of the concentrations of Ca^{2+} .

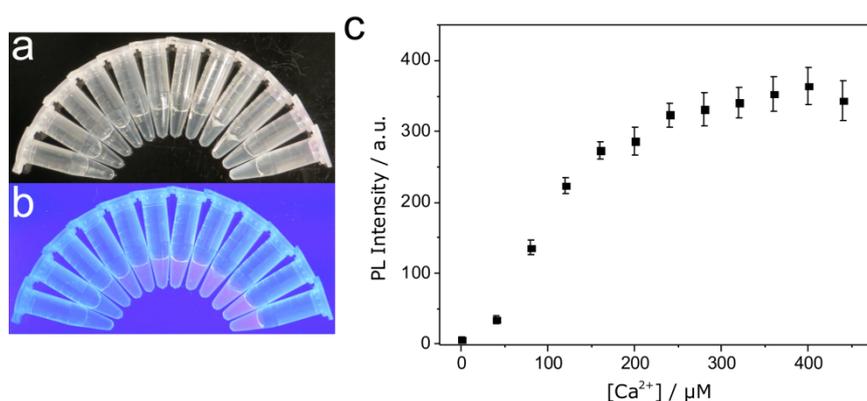


Figure S7. Digital photos of increasing concentrations of Ca^{2+} (0, 40, 80, 120, 160, 200, 240, 280, 320, 360, 400, 440 μM) with 0.4 mM Au(I)-Cys complexes under (a) visible light and (b) UV light; (c) Luminescence intensity changes at 615 nm of Au(I)-Cys complexes as a function of the concentrations of Ca^{2+} .

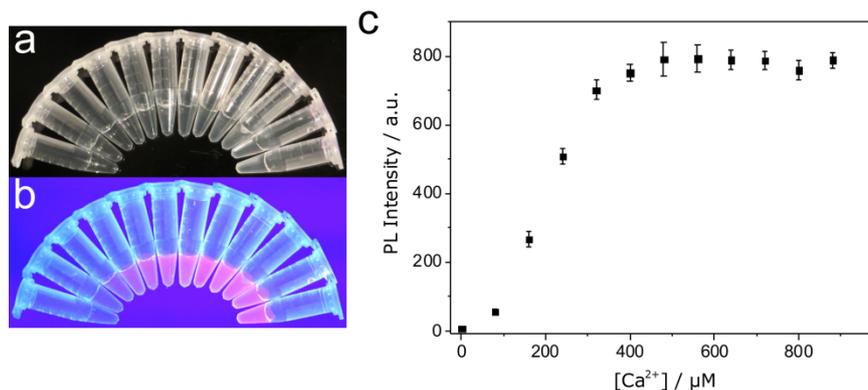


Figure S8. Digital photos of increasing concentrations of Ca²⁺(0, 80, 160, 240, 320, 400, 480, 560, 640, 720, 800, 880 μM) with 0.8 mM Au(I)-Cys complexes under (a) visible light and (b) UV light; (c) Luminescence intensity changes at 615 nm of Au(I)-Cys complexes as a function of the concentrations of Ca²⁺.

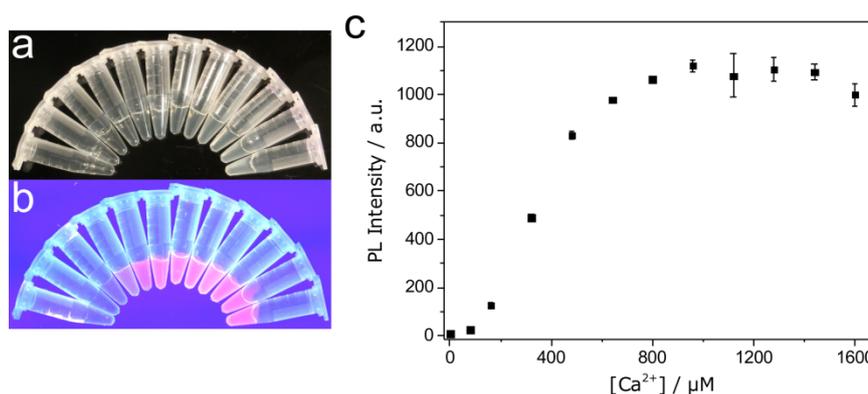


Figure S9. Digital photos of increasing concentrations of Ca²⁺(0, 80, 160, 320, 480, 640, 800, 960, 1120, 1280, 1440, 1600 μM) with 1.6 mM Au(I)-Cys complexes under (a) visible light and (b) UV light; (c) Luminescence intensity changes at 615 nm of Au(I)-Cys complexes as a function of the concentrations of Ca²⁺.

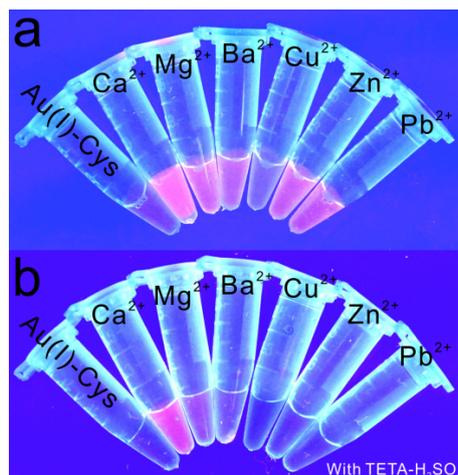


Figure S10. The digital photos of Au-Cys complexes under UV light in the presence of Ca^{2+} , Mg^{2+} , Ba^{2+} , Cu^{2+} , Zn^{2+} , Pb^{2+} without (a) and with TETA- H_2SO_4 (b).

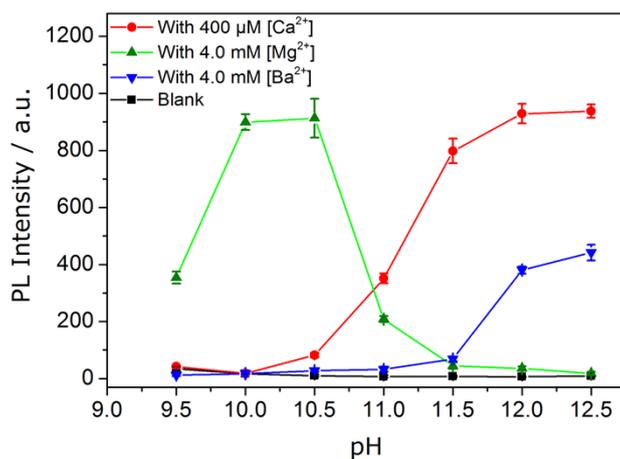


Figure S11. The luminescence intensities of Au(I)-Cys complexes in the absence and presence of Ca^{2+} / Mg^{2+} / Ba^{2+} at different pH and in the presence of TETA. The poor response of Ca^{2+} at low pH was due to the formation of slightly soluble calcium sulfate.

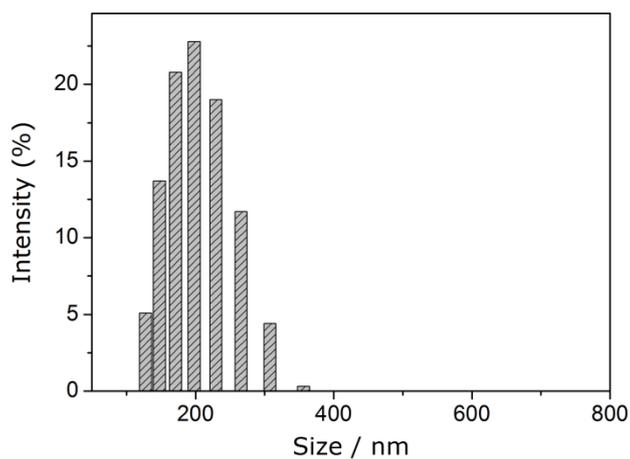


Figure S12. Size distribution of aggregated Au(I)-Cys complexes in the presence of 400 μM Ca^{2+} .

Table S1. Concentrations of Ca^{2+} determined in various samples.

	ICP-AES (mM)	Au(I)-Cys (mM)
DW	0.33 ± 0.02	0.34 ± 0.07
Milk	22.15 ± 0.05	26.31 ± 0.18
FBS	3.39 ± 0.09	3.84 ± 0.26

Table S2. Recovery percentages calculated in different samples.

Sample	Ca^{2+} (μM)			Recovery (%)
	Before spiking	spiked	Total found	
DW	33.0	100	141.5	108.5
milk	22.1	100	109.4	87.3
FBS	33.9	100	126.8	92.9

References

1. Z. T. Luo, X. Yuan, Y. Yu, Q. B. Zhang, D. T. Leong, J. Y. Lee and J. P. Xie, *J. Am. Chem. Soc.*, 2012, **134**, 16662-16670.
2. M. S. Eom, W. Jang, Y. S. Lee, G. Choi, Y. U. Kwon and M. S. Han, *Chem. Commun.*, 2012, **48**, 5566-5568.