Electronic Supplementary Information (ESI)

For

Gold(I)-pyrazolato complex as a switch-on luminescent probe for cysteine: in situ formation of fluorescent nanoparticles and rose-like microspheres

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A. Experimental Section.

Materials.

All chemicals, unless otherwise noted, were purchased from Sigma-Aldrich Chemical Co. Solvents (AR and HPLC grades) were purchased from commercial sources and used without further purification.

Instrumentations.

FT-IR spectra were measured using a Nicolet Avatar 360 FT-IR spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker Biospin Avance (400 MHz) NMR spectrometer. Electrospray ionization mass spectra were acquired with a Perkin Elemer, Flexar SQ 300. UV-vis spectra were recorded with an Agilent 8453 spectrophotometer. Elemental analyses of C, H, and N were determined using an Elementar Vario EL cube CHNS analyzer. The steady-state photoluminescence spectra (PL) for all samples were recorded at room temperature on a PTI QM/TM spectrofluorometer (Birmingham, NJ, USA). Corrections of excitation and emission for the detector response were performed ranging from 200 – 900 nm. Transmission electronic microscopy (TEM) and scanning electronic microscopy (SEM) were performed using TECNAI F-30 and JEM-2011 microscopes, respectively.

Synthesis of 3-thienyl-5-phenyl-1H-pyrazole ($C_{13}H_{10}N_2S$).

Under nitrogen atmosphere, 2-thiophenecarbonyl chloride (27 mmol, 2.886 mL), $PdCl_2(PPh_3)_2$ (0.18 mmol，207.9 mg), CuI (0.54 mmol, 102.6 mg), trimethylamine (36 mmol, 5.04 mL) and acetylene benzene (18 mmol, 1.977 mL) were slowly added to anhydrous THF (150 mL) in a 250 mL round-bottom flask. The solution was stirred at room temperature for 2 h, followed by the addition of hydrazine (3.0 mmol, 2.625 mL) and CH_3CN (36 mL). After an additional stirring for 16 h, the resultant solution was washed with water (100 mL × 3), and the product was extracted by using CH_2Cl_2 (100 ml) and dried under vacuum to yield yellow solid. Yield = 66%. ^{1}H NMR (400 MHz, DMSO) δ 7.81 (d, J = 7.5 Hz, 2H), 7.46 (dd, J = 10.7, 4.9 Hz, 4H), 7.36 (t, J = 7.3 Hz, 1H), 7.12 (dd, J = 4.9, 3.7 Hz, 1H), 7.04 (s, 1H). IR(cm^{-1}): 530w , 703m, 840m, 1063w, 1167w, 1403s, 1447s, 1554s, 1607s, 1655s. Elemental analysis (%): calculated: C 68.99, H 4.45, N 12.38, S 14.17; experimental: C: 68.45, H: 4.55, N: 12.48, S: 13.94.

Synthesis of gold(I)-pyrazolato complex (1)

A CH_2Cl_2 solution (30 mL) containing 3-thienyl-5-phenyl-1H-pyrazole (1 mmol) was slowly added to another CH_2Cl_2 solution (30 mL) containing Au(tht)Cl (whereas tht = tetrahydrothiophene). The mixture was stirred in dark for 0.5 h, followed by dried under reduced pressure to yield white crude product. The product was re-dissolved in minimum amount of MeOH. The MeOH solution was filtered, dried and the product was re-crystallized in the mixture of CH_2Cl_2 and n-hexane in a 2 to 1 ratio. Yield = 20%. ^{1}H NMR (400 MHz, DMSO) δ 7.81 (d, J = 7.5 Hz, 2H), 7.46 (dd, J = 10.7, 4.9 Hz, 4H), 7.36 (t, J = 7.3 Hz, 1H), 7.12 (dd, J = 4.9, 3.7 Hz, 1H), 7.04 (s, 1H). Elemental analysis

(%): calculated: C: 34.04, H: 2.20, N: 6.11, S: 6.99; experimental: C: 33.89, H: 2.18, N: 5.99, S: 7.05.

Crystal of **1** was mounted with glue at the end of a glass fiber. Data collection was performed on an Oxford Diffraction Gemini E (Enhance Mo X-Ray source, Mo Kα, λ= 0.71073 Å or Cu Kα, λ= 1.54178 Å) equipped with a graphite monochromator and ATLAS CCD detector (CrysAlis CCD, Oxford Diffraction Ltd) at room temperature (293 K). Structures were solved by direct methods (SHELXTL-97) and refined on F^2 using full-matrix least-squares (SHELXTL-97). All non-hydrogen atoms were refined with anisotropic thermal parameters, and all hydrogen atoms were included in calculated positions and refined with isotropic thermal parameters riding on those of the parent atoms. The treatment of **1** for the guest molecules of ethanol involved the use of the SQUEEZE program of PLATON. Crystal data and structure refinement parameters are summarized in *Table S1*. Selected bond lengths and angles are given in *Table S2*.

B. Figures.

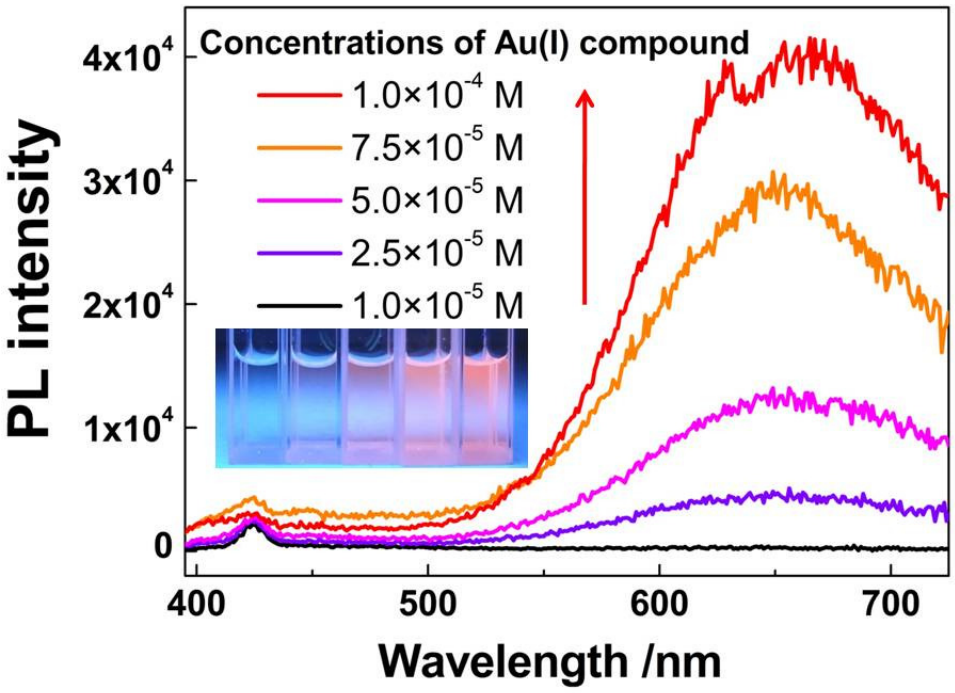

Fig. S1. Emission spectra (λ_{ex} = 365 nm) of **1** (0 to 100 μM) with a fixed concentration of cysteine at 2 mM level.

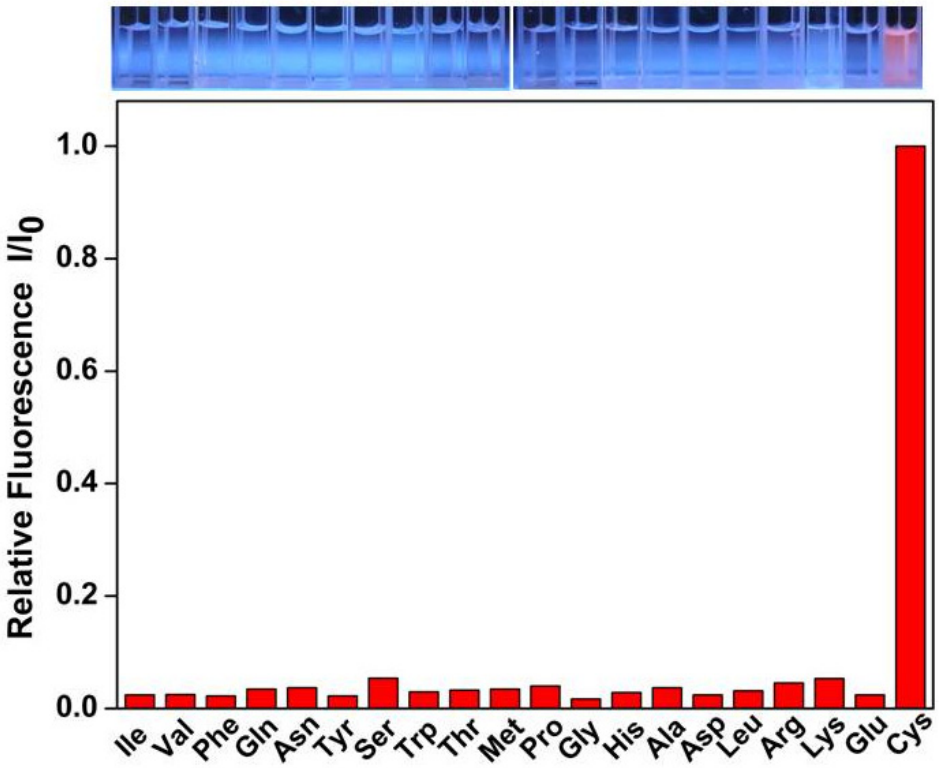

Fig. S2a. (Upper) Photographs taken under UV lamp of aqueous solutions (1% DMSO, v/v) of **1** at 75 μM in the presence of different amino acid at 2 mM level. (Lower) The relative emission intensities at 675 nm compared to "**1** and Cys" were shown.

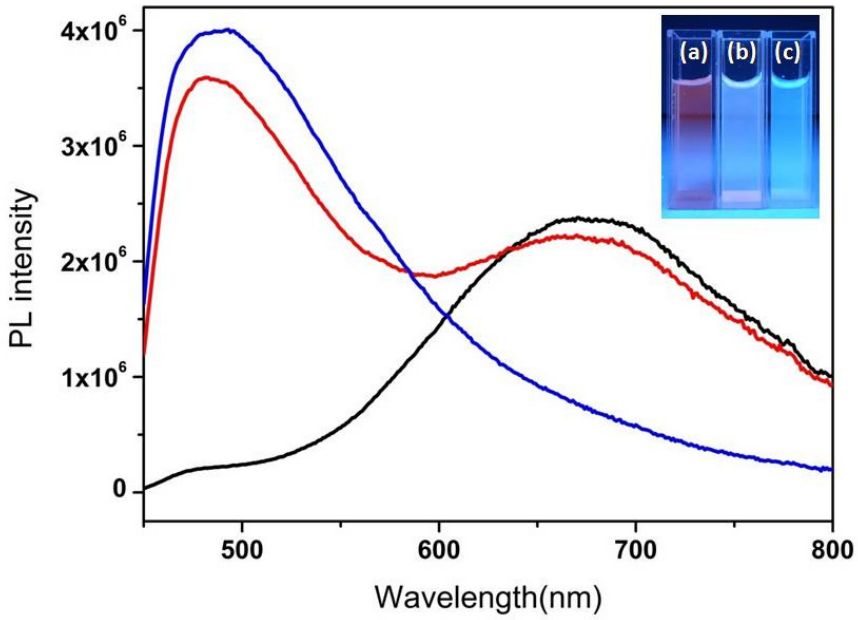

Fig. S2b. Emission spectra of **1** (λ_{ex} = 365 nm) at 75 μM (a) in the presence of cysteine only (2 mM, black line), (b) in the presence of all essential amino acids (2 mM each, red line), and (c) in the presence of all essential amino acids except cysteine (2 mM each, blue line).

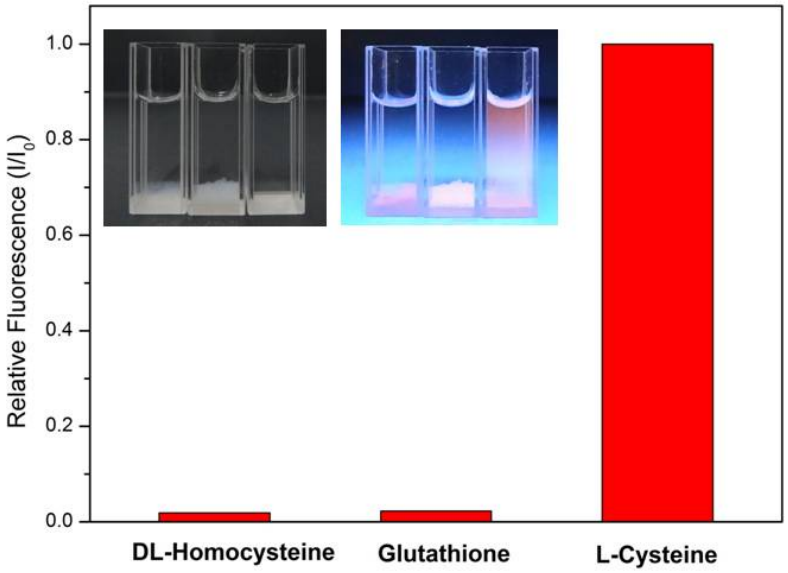

Fig. S3 (Upper) Photographs taken under UV lamp of aqueous solutions (1% DMSO, v/v) of **1** at 75 μM in the presence of homocysteine, glutathione and cysteine at 2 mM level. (Lower) The relative emission intensities at 675 nm compared to "**1** and Cys" were shown.

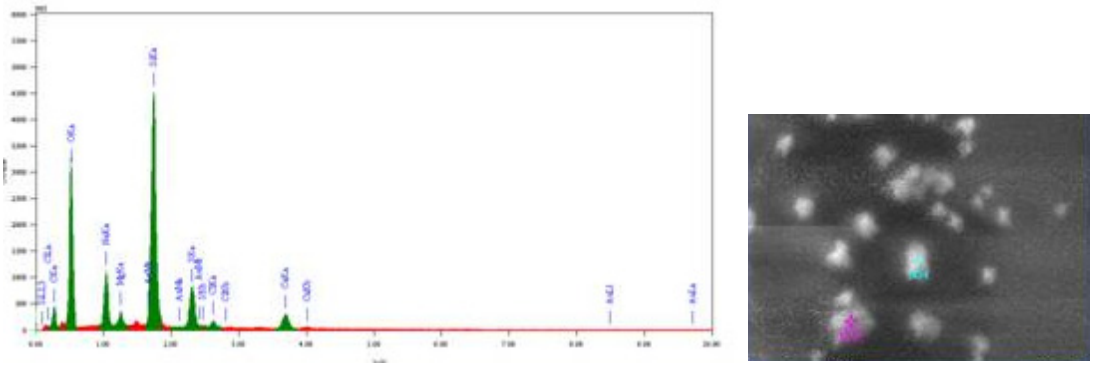

Fig. S4. EDS analysis of the X-ray energy spectra revealed that gold was present at positions of the fluorescent nanoclusters.

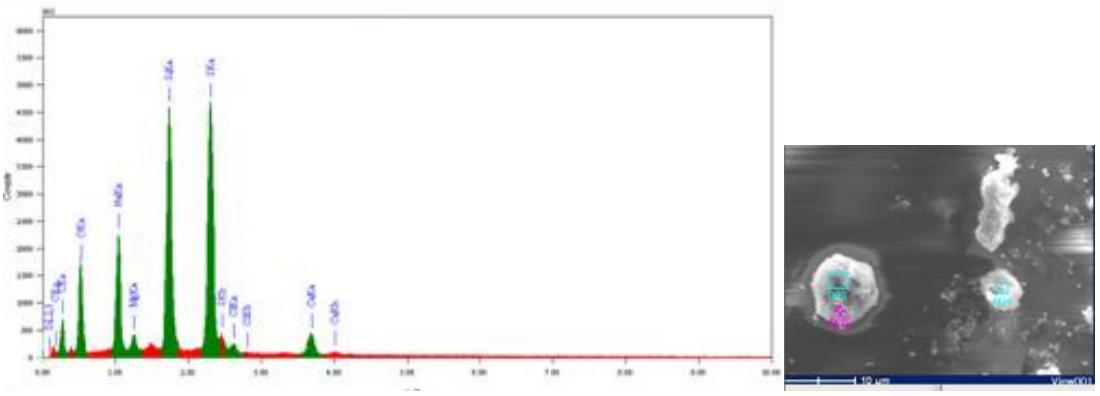

Fig. S5. EDS analysis of the X-ray energy spectra revealed that gold was absent at positions of the microspheres.

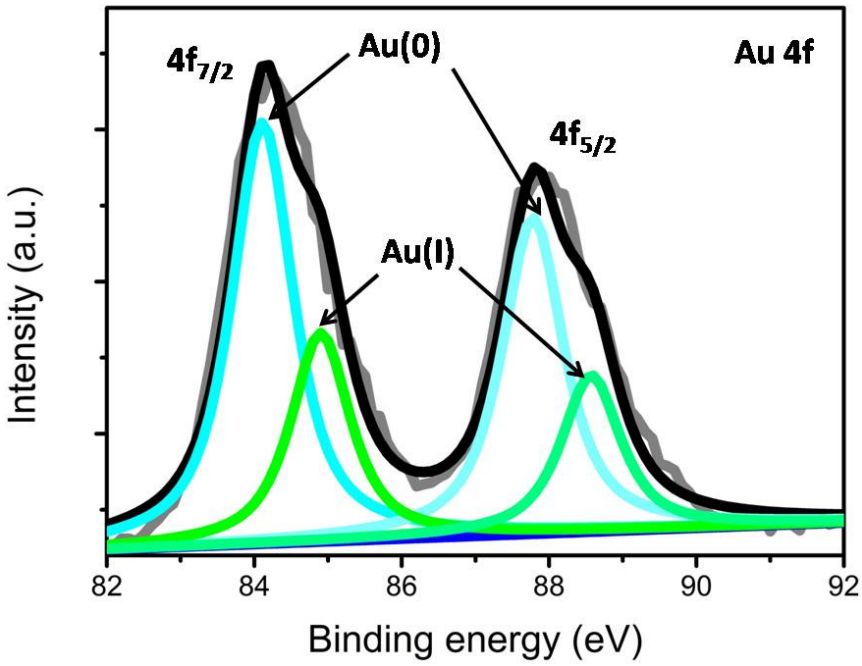

Fig. S6. Spectrum of X-ray photoelectron spectroscopy (XPS) of the "**1** and Cys" solution.

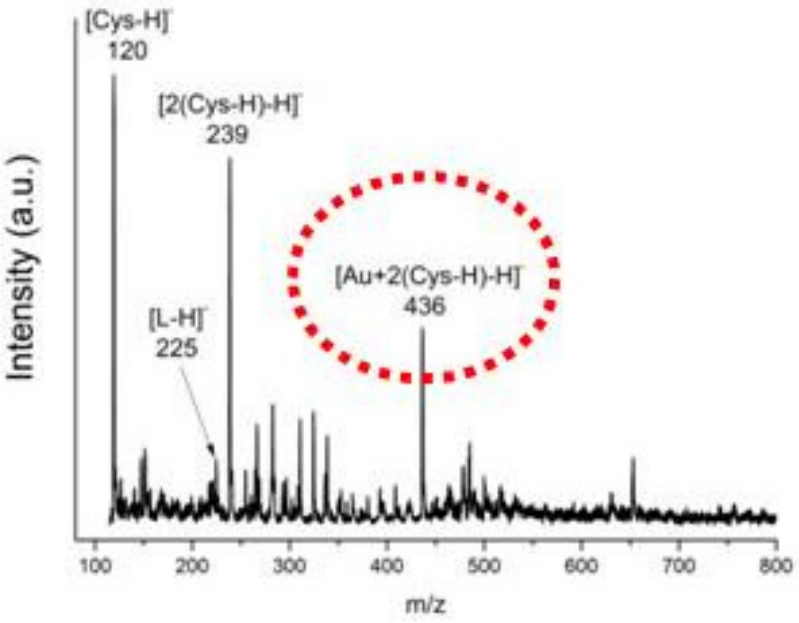

Fig. S7. ESI-MS spectrum of the "**1** and Cys" solution.

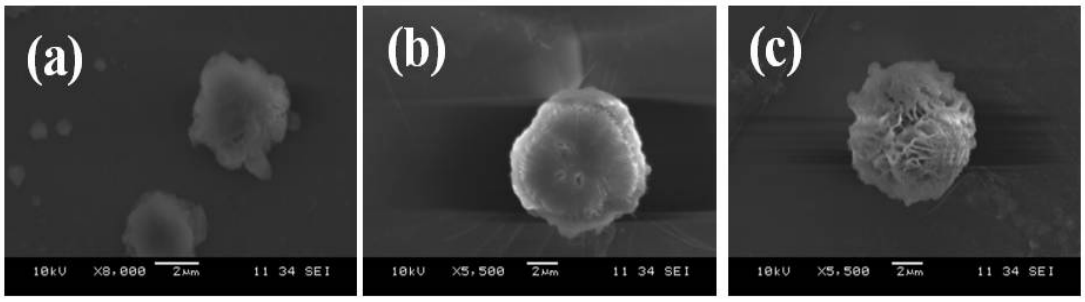

Fig. S8. SEM images of (a) cysteine (2 mM) only and (b) cysteine (2 mM) with 3-thienyl-5-phenyl-1H-pyrazole (75 μM) and (c) cysteine (2 mM) with **1** (75 μM).

C. Tables.

Table S1. Summary of the crystal data and structure refinement parameters for **1**.

	1
Empirical formula	$C_{26}H_{20}Au_2C_{l2}N_4S_2$
Formula weight	917.41
Temperature/K	293(2)
Crystal system	monoclinic
Space group	*C2/c*
a/Å	28.5599(9)
b/Å	4.02280(10)
c/Å	22.5333(7)
α/°	90
β/°	95.540(3)
γ/°	90
Volume/Å^3	2576.78(13)
Z	4
ρ_{calc} mg/mm^3	2.365
Goodness-of-fit on F^2	1.042
Final *R* indexes [$I \geq 2\sigma(I)$][a]	$R_1 = 0.0471$, $wR_2 = 0.1131$
Final *R* indexes [all data][a]	$R_1 = 0.0505$, $wR_2 = 0.1172$

Table S2. The selected bond lengths (Å) and angles (°) for **1**.

1	
Au(1)-N(1)	2.025(6)
Au(1)-Au(1)#1	3.3010(6)
Au(1)-Cl(1)	2.2561(19)
N(1)-Au(1)-Cl(1)	176.68(17)