

Supporting Information for
Dye-Surfactant Co-Assembly as the Chromogenic Indicator for Nanomolar Level
Detection of Cu(I) Ions via Color-changing Response

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EXPERIMENTAL SECTION

Materials and methods: All solvents were of analytical grade and used without further purification. Each chemical used for the synthesis and for spectroscopic titration was of the best grade available. ^1H NMR and ^{13}C NMR spectra were recorded with a Bruker Advance DRX 400 spectrometer operating at 400 and 100 MHz for ^1H and ^{13}C NMR spectroscopy. IR spectra were recorded on Perkin Elmer FT-IR spectrometer BX. HRMS analyses were performed with Q-TOF YA263 high resolution (Waters Corporation) instruments.

Sample preparation for Sensing: Sensing of the metal ions in micellar medium was carried out by adding either 10 μL (for UV-vis studies) or 5 μL (for fluorescence studies) DMSO solution of **1** from a stock (1×10^{-3} M) in into the Brij-58 (1 mM), SDS (8 mM) or CTAB (1 mM) micelle solution to make the final volume of 1 mL followed by addition of water solution of the metal ions (2 μM). Fluorescence spectra were recorded by exciting **1** at 435 nm wavelength. Therefore, the final concentration of DMSO in all the studies was less than 1%.

Spectroscopic studies: UV-vis absorption spectra were obtained on a Shimadzu UV-2100 spectrophotometer. Fluorescence spectra were recorded keeping 10/10 slit width on a Cary-Eclipse spectrofluorophotometer. The excitation wavelength was fixed at 430 nm.

Scanning Electron Microscopy: Solution of **1** (concentration 10 μM) in SDS (8 mM) medium with and without Cu^+ ions were drop cast over the double-sided tape attached onto the brass stubs. Then they were allowed to air-dry overnight. The samples were then sputtered with gold vapor and analyzed on a Quanta 200 SEM operated at 15 kV.

Theoretical Study: At first only the compound **1** was energy minimized in water using B3LYP/6-31G* method in Gaussian 03 program. Then with the energetically most stable configuration of the compound, all possible compound- Cu^+ conjugates were made and minimized using a combination of semi-empirical PM3 and Gaussian B3LYP/6-31G* method. The HOMO-LUMO energy gap between different compound-copper conjugates was determined by using ChemCraft software.

Design of Paper Strips: The compound-coated paper strips were prepared by spiking the rectangular shaped (1 x 1.5 cm) filter paper discs with 40 μL of CH_2Cl_2 solution of **1** (0.02 mM) was drop-cast onto the filter paper strips using a micropipette. The concentration of **1** in the solution as well as the time of emersion were systematically optimized to obtain a stable, optimum color for the paper strips. The solution absorbed in filter paper within 30 min. Then the paper discs were left overnight for air-drying. The stability of the paper strips was verified over a couple of days under ambient conditions. Finally, the paper strips were ready for

sensing. The Cu⁺-induced color changes against the concentrations of Cu⁺ were quantified using freely available image processing software, ImageJ.

Stoichiometry determination by Job plot. The Job plot is a method of continuous variation for determining the stoichiometry of interaction between the two species. The total molar concentration of the two binding species (here, **1** and the Cu⁺) was kept constant (1 x 10⁻⁴ M) and the mole fraction was varied. Further, the change in absorbance was plotted against the mole fraction. The maxima or minima thus obtained gave the stoichiometry of interaction. In all cases, we have plotted $\Delta A^*[\text{Cu}^+] \text{ vs } [\mathbf{1}] / \{[\text{Cu}^+] + [\mathbf{1}]\}$. Where, $\Delta A = A - A_0$, A = absorbance of probe molecule after addition of Cu⁺ at 472 nm, and A₀ = absorbance of probe molecule without Cu⁺. $[\mathbf{1}] / \{[\text{Cu}^+] + [\mathbf{1}]\}$ is the mole fraction of the probe molecule in the mixture.

Binding constant calculation. For interaction of **1** with Cu⁺, we followed the Benesi-Hildebrand equation for 1:1 stoichiometry. The changes in absorbance were recorded at λ_{max} (nm). The absorbance values obtained in the calibration curve plot were plotted as a function of the ratio of the molar concentration of the 1: Cu⁺ ($[\text{D}]_0: [\text{G}]_0$) according to the Benesi-Hildebrand equation.

$$[\text{D}]_0/\text{Abs.} = (1/[\text{G}]_0) (1/K\varepsilon) + 1/\varepsilon \quad (4)$$

where, $[\text{G}]_0$ = concentration of metal ions; Abs. = absorbance of the charge transfer band; $[\text{D}]_0$ = initial concentration of **1**; K = the binding constant and ε = molar absorptivity of complex.

A plot of $x = 1 / [\text{G}]_0$ against $y = [\text{D}]_0/\text{Abs.}$ yielded intercept as $1/\varepsilon$ and the slope as $1/K\varepsilon$ from where the binding constant and the molar absorptivity were obtained. The concentration of the acceptor was kept greater than the donor and fixed so that a wide concentration range could be examined.

Fluorescence Decay Experiment. Fluorescence lifetime values were measured by using a time-correlated single photon counting fluorimeter (Horiba Jobin Yvon). The system was excited with nano LED of Horiba - Jobin Yvon with a pulse duration of 1.2 ns. Average fluorescence lifetimes (τ_{av}) for the exponential iterative fitting were calculated from the decay times (τ_i) and the relative amplitudes (a_i) using the following relation

$$\tau_{\text{av}} = (a_1\tau_1^2 + a_2\tau_2^2 + a_3\tau_3^2) / (a_1\tau_1 + a_2\tau_2 + a_3\tau_3)$$

Where a_1 , a_2 and a_3 are the relative amplitudes and τ_1 , τ_2 , and τ_3 are the lifetime values, respectively. For data fitting, a DAS6 analysis software version 6.2 was used.

Detection limit determination. The method used for the calculation of the detection limit is known as the blank variability method. In this method, the calibration curve was prepared by recording absorption spectra of **1** in SDS micelle with different amounts of Cu⁺ ions

From the equation obtained from the calibration plot, the added Cu⁺ concentrations were calculated. Then another calibration curve was drawn between the C_{real} (added metal ions, μM) vs. C_{calc.} (Calculated amount of metal ions, μM). This afforded a value of the slope (b).

The fluorescence of **1** in pH 7 buffered medium without Cu⁺ ion was taken as blank reading. A total of 10 replicates of the blank were measured. The standard deviation from the blank readings was calculated by fitting the absorbance reading into the equation obtained from the first calibration curve (titration spectra). Using this standard deviation value, we calculated the decision limit by the following equation.

$$L_C = t_c \times s \times (1 + 1/N)^{1/2} \dots \dots \dots (1)$$

where, N = the number of blank replicates taken; the value of t_c for 10 blank readings is 1.833, and s = the standard deviation value.

The detection limit (L_D) was calculated as double the decision limit obtained,

$$L_D = 2 L_C \dots \dots \dots (2)$$

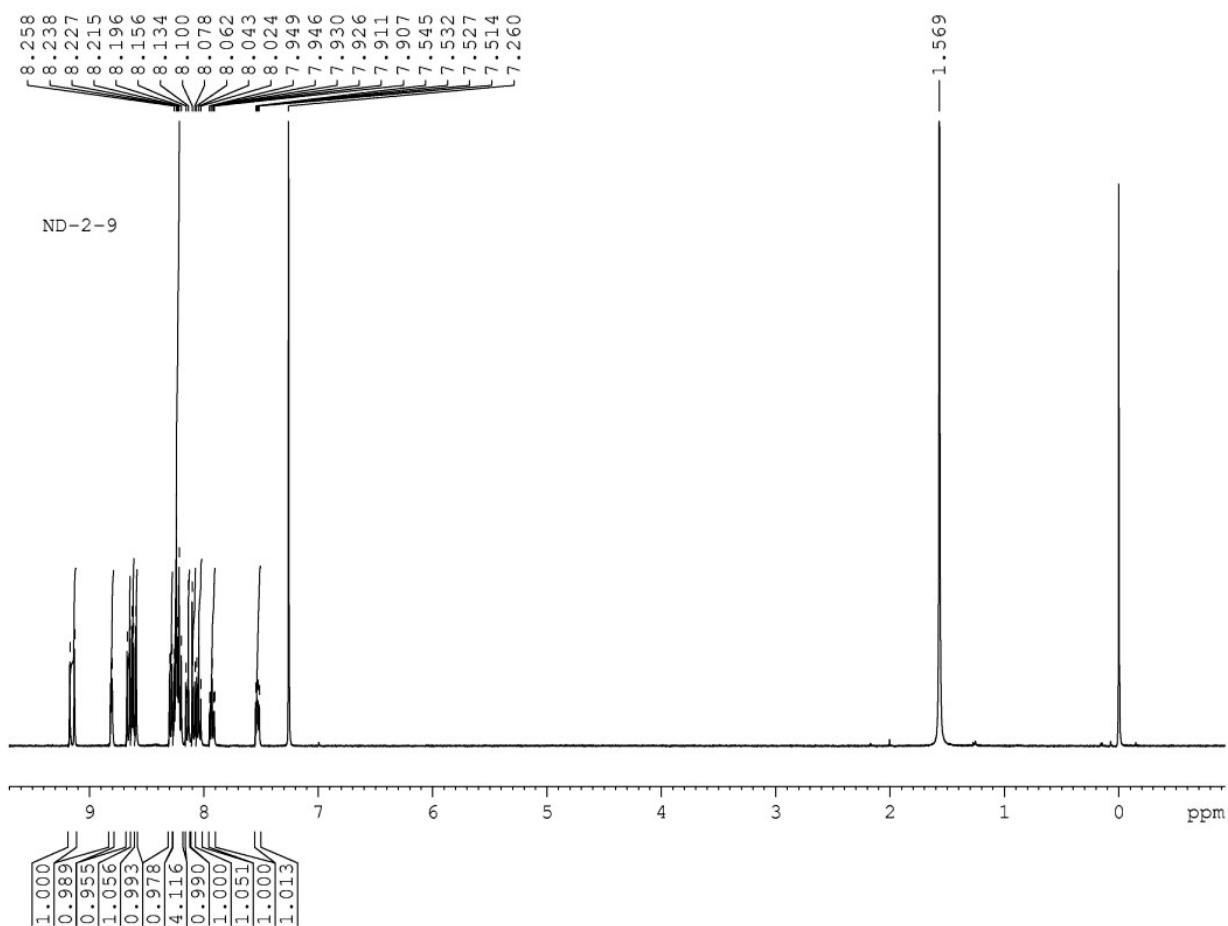
In concentration terms, the detection limit appeared as,

$$x_D = 2 \times C = 2 L_C / b \dots \dots \dots (3)$$

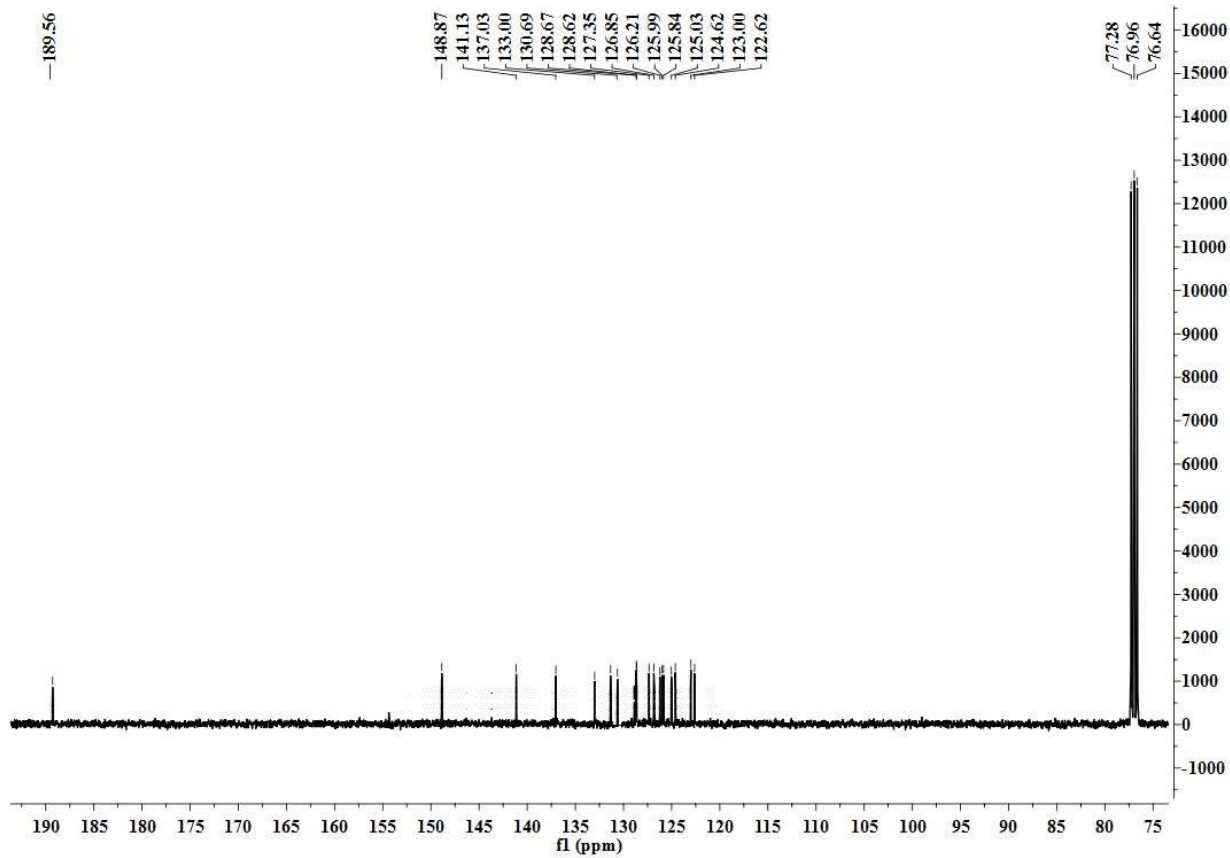
where, b = slope of the second calibration curve (C_{real} vs. C_{calc.}).

Synthesis and characterization of compound 1

0.7 g (5 mmol) freshly distilled 2-acetylpyridine and 1.15 g (5 mmol) pyrene carboxaldehyde were taken in 6 mL of ethanol. Then 0.36 g of NaOH in 3 mL of water was mixed in it. The reaction mixture was stirred for 24 h at room temperature. The product was precipitated from reaction mixture and washed with ethanol. Yellow solid; (Yield: 120 mg, 92 %), IR (neat, cm^{-1}): 3408.9, 2925.5, 2069.9, 1575.9, 1320.4, 1026.4, 844.9, 669.7; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.53 (t, $J = 2.8$ Hz, 1H), 7.93 (t, $J = 4$ Hz, 1H), 8.04 (t, $J = 3.8$ Hz, 1H), 8.09 (d, $J = 4.4$ Hz, 1H), 8.20 – 8.24 (m, 4H), 8.29 (d, $J = 4$ Hz, 1H), 8.59 (s, 1H), 8.62 (d, $J = 2.8$ Hz, 1H), 8.66 (d, $J = 4$ Hz, 1H), 8.81 (d, $J = 2$ Hz, 1H), 9.15 (d, $J = 4$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 189.2, 154.4, 148.9, 141.2, 137.0, 133.1, 130.7, 128.7, 127.4, 126.8, 125.5, 124.6, 123.0, 122.6; HRMS m/z calcd for $\text{C}_{24}\text{H}_{15}\text{NO}$ ($\text{M}+\text{Na}$) $^+$ 356.1051, found 356.1053.



^1H -NMR of compound 1 in CDCl_3 medium.



^{13}C -NMR of compound **1** in CDCl_3 medium

Additional Spectral Data

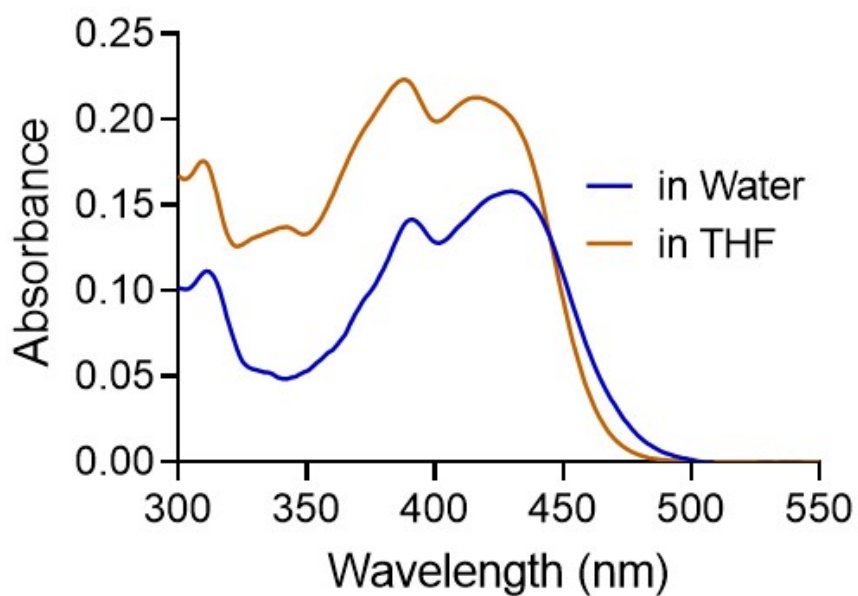


Figure S1. UV-visible spectra of **1** (10 μ M) in THF and water medium.

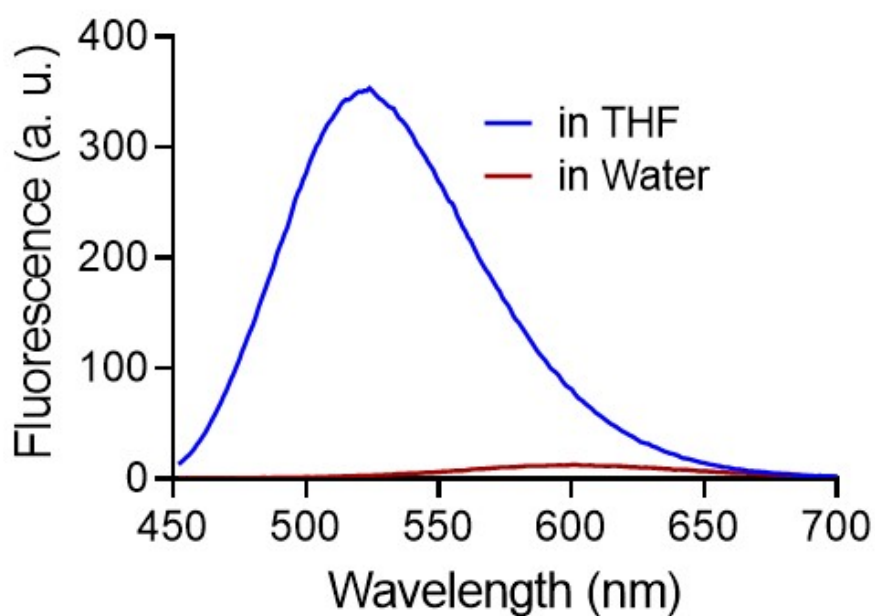


Figure S2. Fluorescence spectra of **1** (10 μ M, λ_{ex} = 430 nm) in THF and water medium.

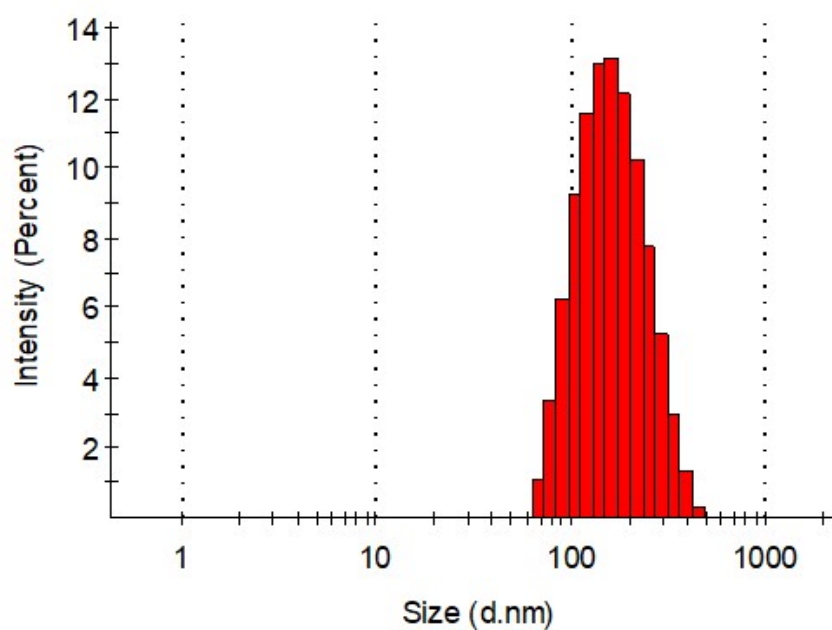


Figure S3. Determination of hydrodynamic diameter of **1** (10 μM) in water medium using dynamic light scattering experiment.

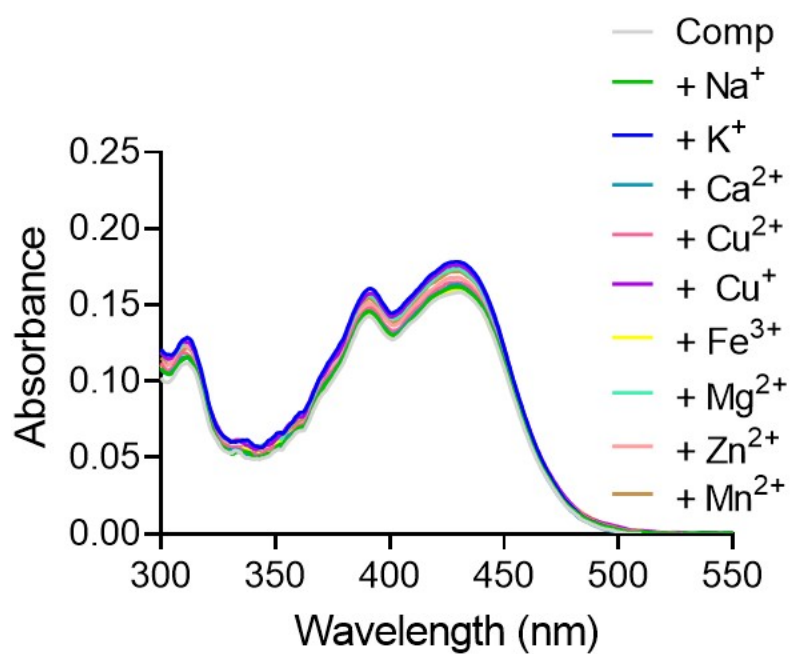


Figure S4. UV-visible spectra of **1** (10 μM) with different metal ions (2 μM) in water medium.

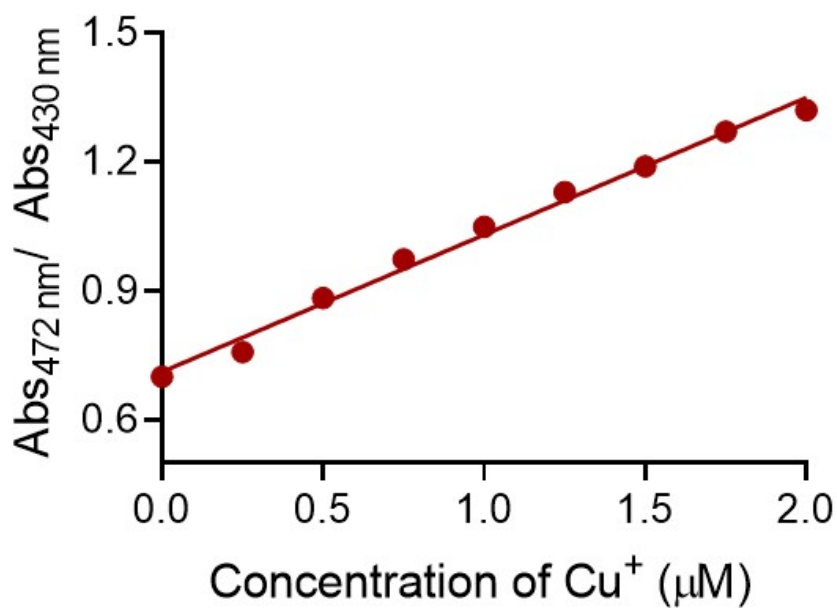


Figure S5. Ratiometric changes in absorbance (at 472 nm/ 430 nm) of **1** (10 μM) upon addition of Cu⁺ (0 – 2 μM) in SDS (8 mM) micelle.

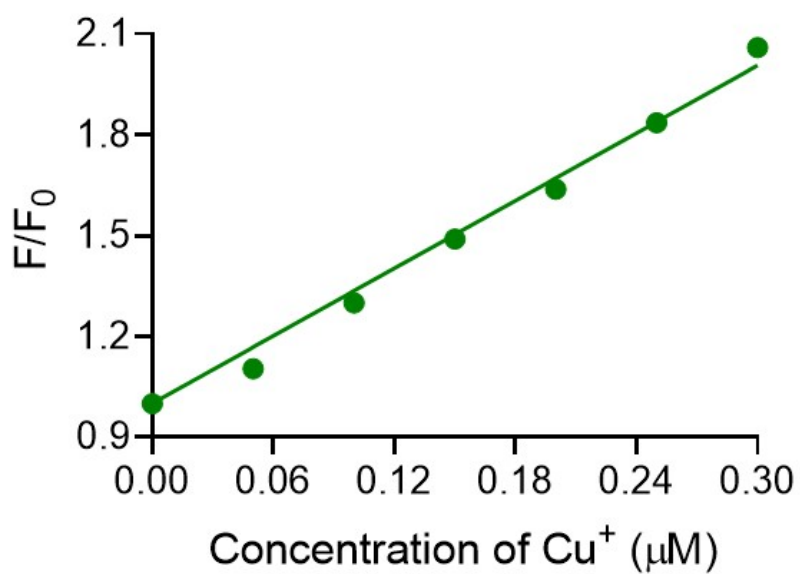


Figure S6. Stern-Volmer plot of **1** (10 μM) upon addition of Cu⁺ (0 – 0.3 μM) in SDS (8 mM) micelle.

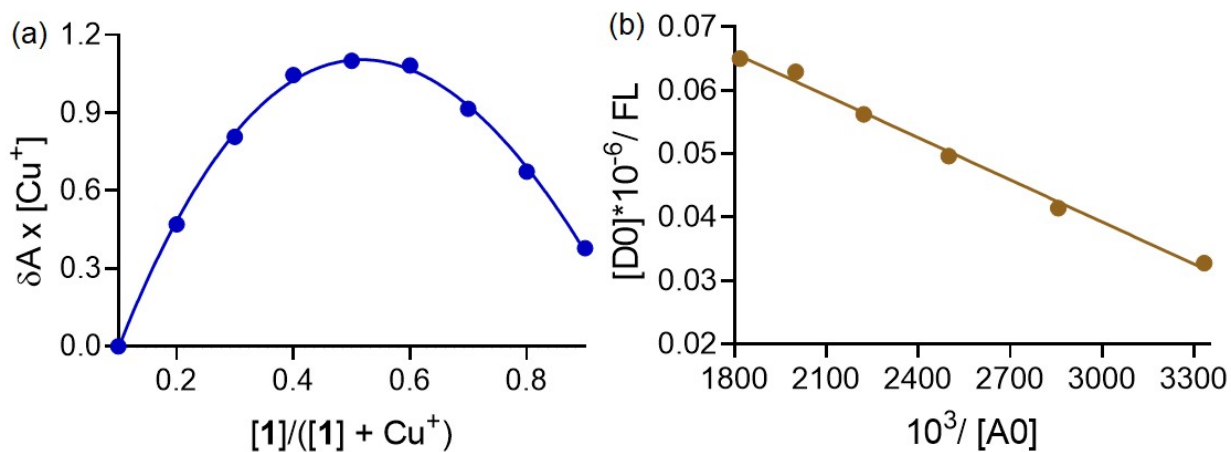


Figure S7. (a) Job's plot of **1** with Cu^+ in SDS (8 mM) micelle. (b) Determination of binding constant of **1** with Cu^+ in SDS (8 mM) micelle.

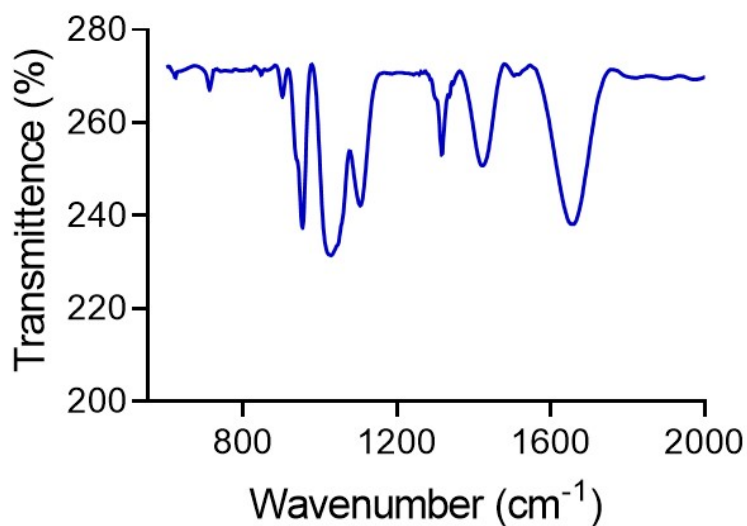


Figure S8. FT-IR spectrum of **1** upon addition of Cu^+ ions.

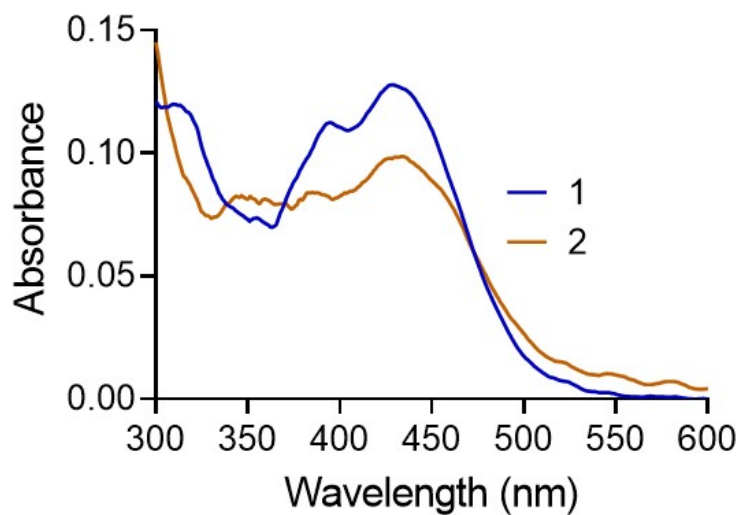


Figure S9. UV-visible spectra of compounds **1** and **2** (10 μM) in SDS (8 mM) micelle.

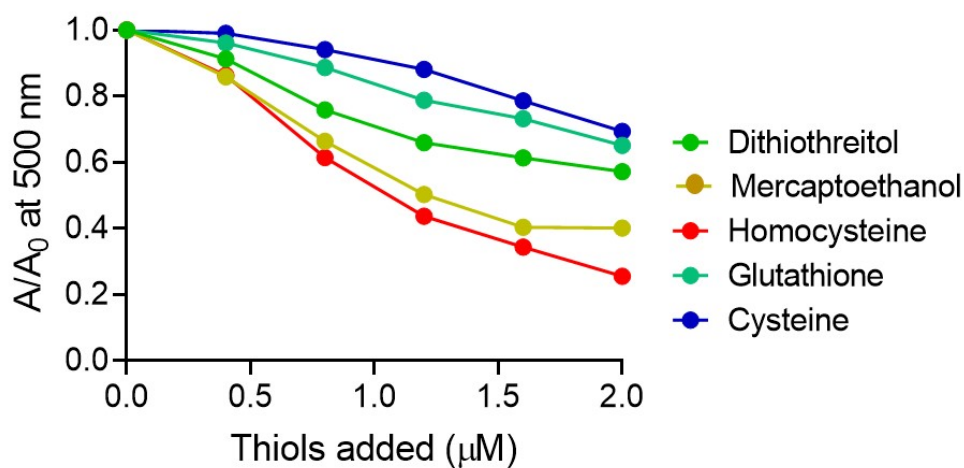


Figure S10. Change in absorbance of **1** + Cu^+ ($[\mathbf{1}] = 10 \mu\text{M}$, $[\text{Cu}^+] = 2 \mu\text{M}$) with thiols in SDS (8 mM) micelle.