Supporting Information

A New Quinoline-Based Acylhydrazone for Highly Selective Fluorescence Recognition of Cu(II) and Sulfide in Aqueous Solution

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Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-919611. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. Fax: +44 (0)1223 336033 or e-mail: deposit@ccdc.cam.ac.uk.

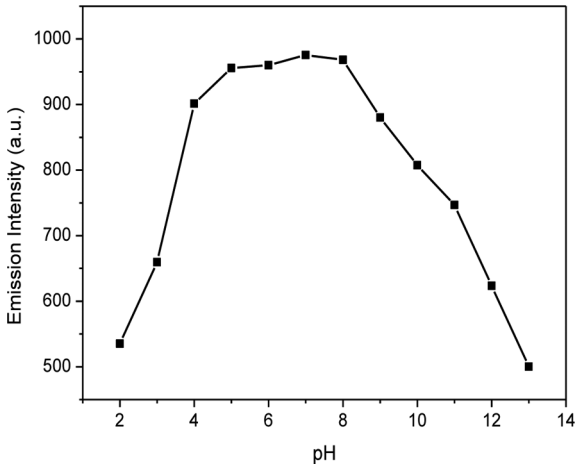

Fig. S1. pH effect on the fluorescence intensity of probe **1** (1 μM) in water (1‰ DMSO) solution.

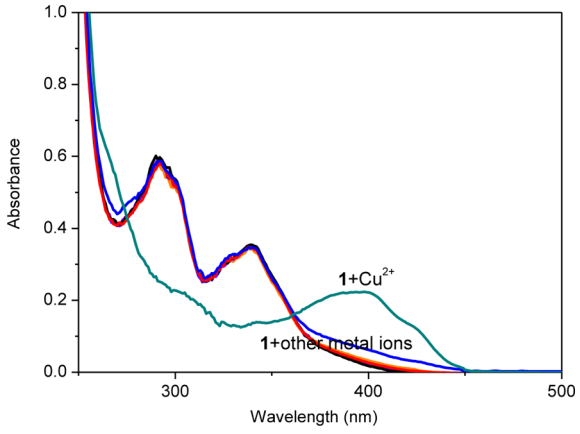

Fig. S2. Absorption spectra of probe **1** (20 ìM) in the presence of 1 equiv. of various metal ion species (Cu^{2+},Ni^{2+}, Hg^{2+}, Ag^{+}, Ba^{2+}, Mg^{2+}, Fe^{2+}, K^{+}, Al^{3+}, Mn^{2+}, Na^{+}, Sr^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, Cr^{3+}, Fe^{3+}, Pb^{2+} in HEPES).

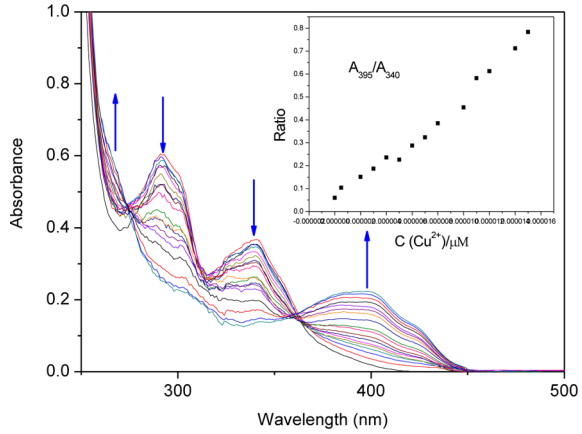

Fig. S3. Absorbance spectra of **1** solution (20 μM) in HEPES buffer (1‰ DMSO, HEPES 20 mM, pH = 7.4) in the presence of Cu^{2+} (0-1 μM). Inset: ratio of absorbance at 395 nm and absorbance at 340 nm as a function of Cu^{2+} concentration.

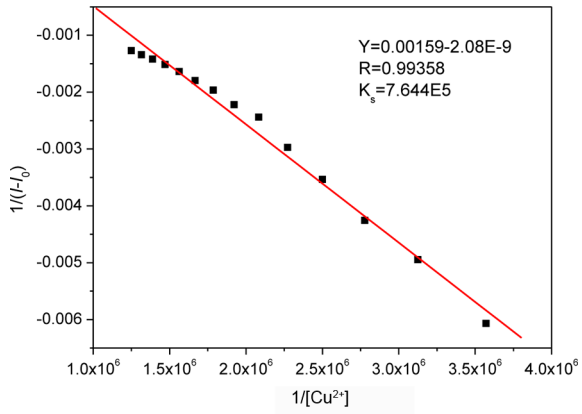

Fig. S4. Benesi–Hildebrand plot using Eq. (1), assuming 1:1 stoichiometry for association between receptor 1 and Cu^{2+}: fluorescent titration results (523 nm).

The binding stoichiometry of receptor **1** with Cu^{2+} was calculated through the Benesi–Hildebrand equation, which was given as follows:

$$\frac{1}{I-I_0} = \frac{1}{I_\infty - I_0}\left[\frac{1}{K_S[Cu^{2+}]}+1\right]$$

I_0 is the fluorescence intensity of free **1**, I_∞ is the fluorescence intensity measured with excess amount of Cu^{2+}, I is the fluorescence intensity with Cu^{2+}, K_s is the association constant, and $[Cu^{2+}]$ is the concentration of Cu^{2+} added (M). As shown in Figure 4, the plot of $1/(I\text{-}I_0)$ against $1/[Cu^{2+}]$ shows a linear relationship (R = 0.99358), indicating that receptor **1** associates with Cu^{2+}+**1** in a 1:1 stoichiometry. The association constant, K_s, between **1** and Cu^{2+}, was determined from the ratio of intercept/slope to be 7.644×10^5 M^{-1}.

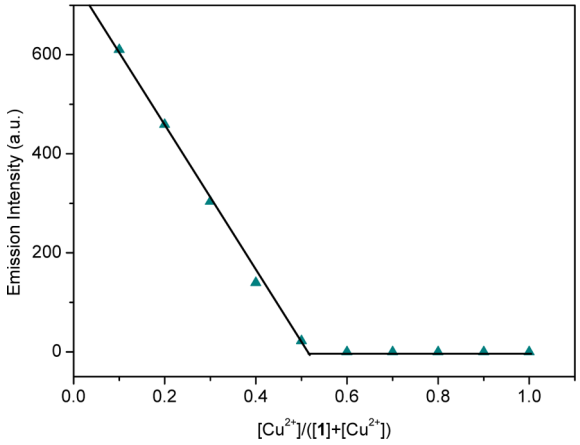

Fig. S5. Job's plot analysis of the binding stoichiometry of **1** and Cu^{2+}. The total concentration of $[Cu^{2+}]$+[**1**] was kept as 1.0×10^{-5} M in the test solution, the fluorescence intensity was monitored at 523 nm.

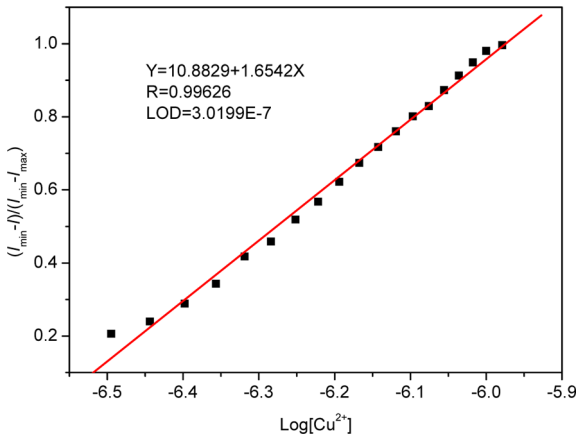

Fig. S6. Normalized response of fluorescence intensity of **1** to log[Cu^{2+}] in HEPES buffer (1‰ DMSO, HEPES 20 mM, pH = 7.4). ([**1**] = 1 μM, λ_{em} = 523 nm).

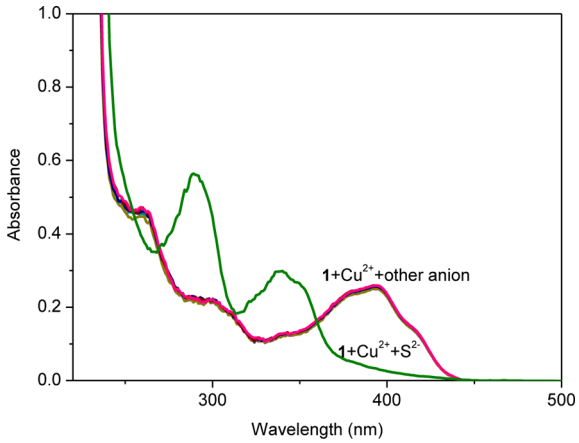

Fig. S7. Absorption spectra of (**1**+Cu^{2+}+S^{2-}) (20 μM) in the presence of 100 μM of various anion species.

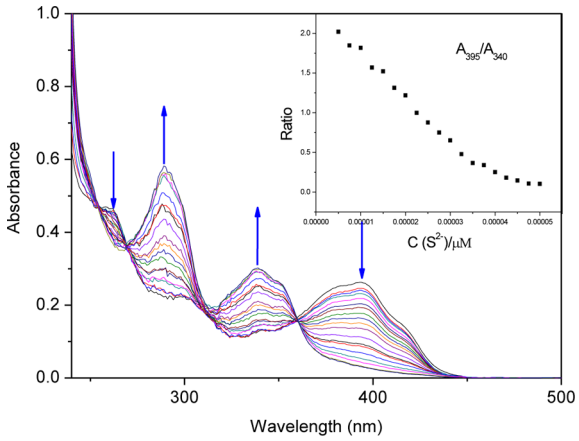

Fig. S8. Absorbance spectra of **1**+Cu^{2+} (20 μM) in HEPES buffered (20 mM, pH = 7.4) solution in the presence of S^{2-} (0-100 μM). Inset: ratio of absorbance at 395 nm and absorbance at 340 nm as a function of S^{2-} concentration.

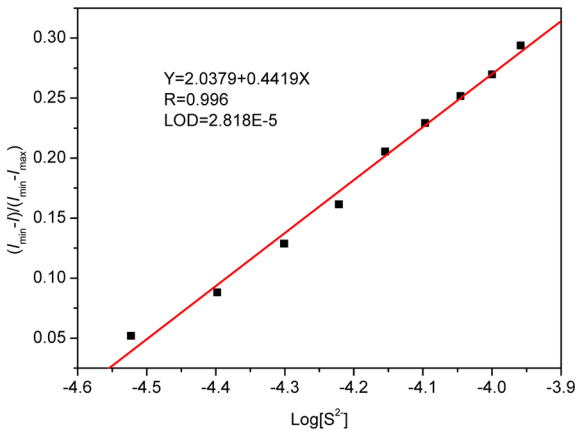

Fig. S9. Normalized response of fluorescence intensity of **1**-Cu^{2+} to log[S^{2-}] in HEPES buffer (HEPES 20 mM, pH = 7.4). ([**1**-Cu^{2+}] = 1 μM, λ_{em} = 523 nm).