Electronic Supplementary Material (ESI) for Analyst

Supporting information

Determination of Trace Amount of Cu^{2+} with a Multi-responsive Colorimetric and Reversible Chemosensor

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Characterization Spectra and Data of Compound 1

Yield: 0.49 g (75%). m.p. 162-163 ℃.

^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 8.217 (1 H, s, CH=N), 7.990 (1 H, d, J=8.4 Hz, Rh-H), 7.460 (2 H, t, J=6.6 Hz, Rh-H), 7.090 (1 H, d, J=8 Hz, Rh-H), 6.571 (2 H, s, Rh-H), 6.461 (2 H, d, J=2.4 Hz, Rh-H), 6.275 (2 H, q, J=2.6 Hz, Rh-H), 4.501 (2 H, s, Cp-H), 4.216 (2 H, s, Cp-H), 3.832 (5 H, s, Cp-H), 3.316 (8 H, dd, J=7.2 Hz, J=14.4 Hz, CH_2), 1.136 (12 H, t, J=7.0 Hz, CH_3); ^{13}C NMR (100MHz, $CDCl_3$), δ (ppm): 164.3, 153.0, 151.7, 148.9, 148.5, 132.9, 129.5, 128.1, 123.6, 123.2, 109.8, 108.1, 106.2, 97.8, 79.2, 69.9, 69.1, 67.9, 65.4, 44.3, 12.6; ESI-MS: *m/z* 653.3 for [**1**+H]$^+$, HRMS (ES): *m/z* calcd for $C_{39}H_{40}N_4O_2Fe$: 652.2493 [M^+]; found: 652.2495.

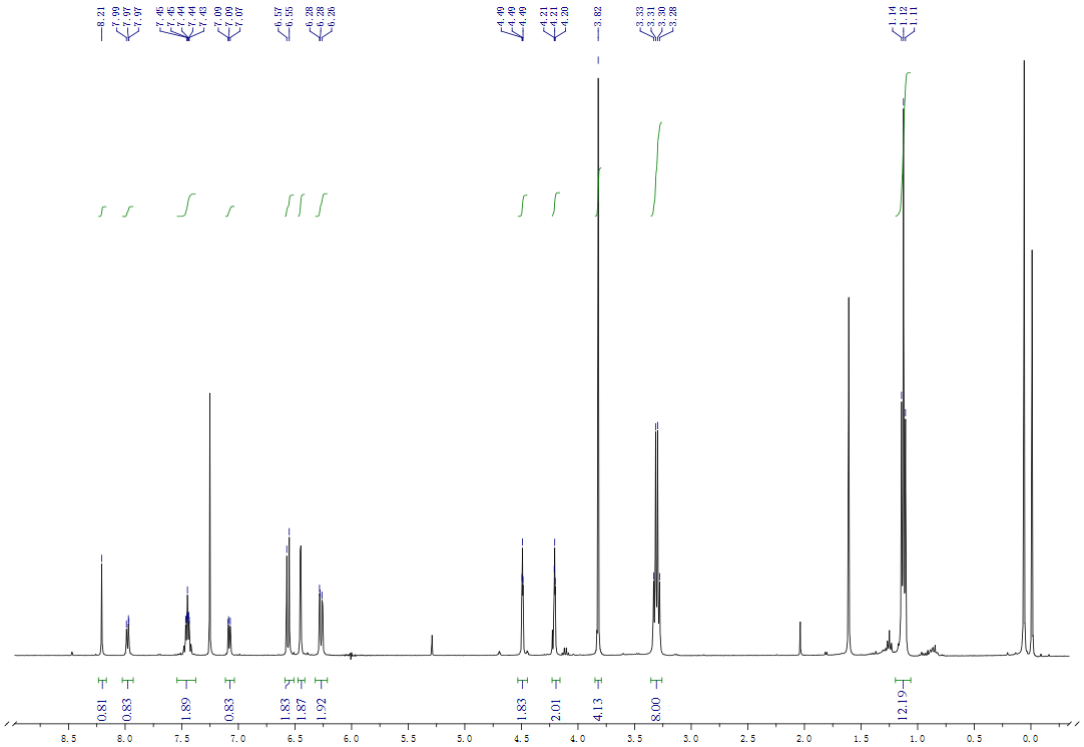

Fig. S1. ^{1}H NMR of compound **1**

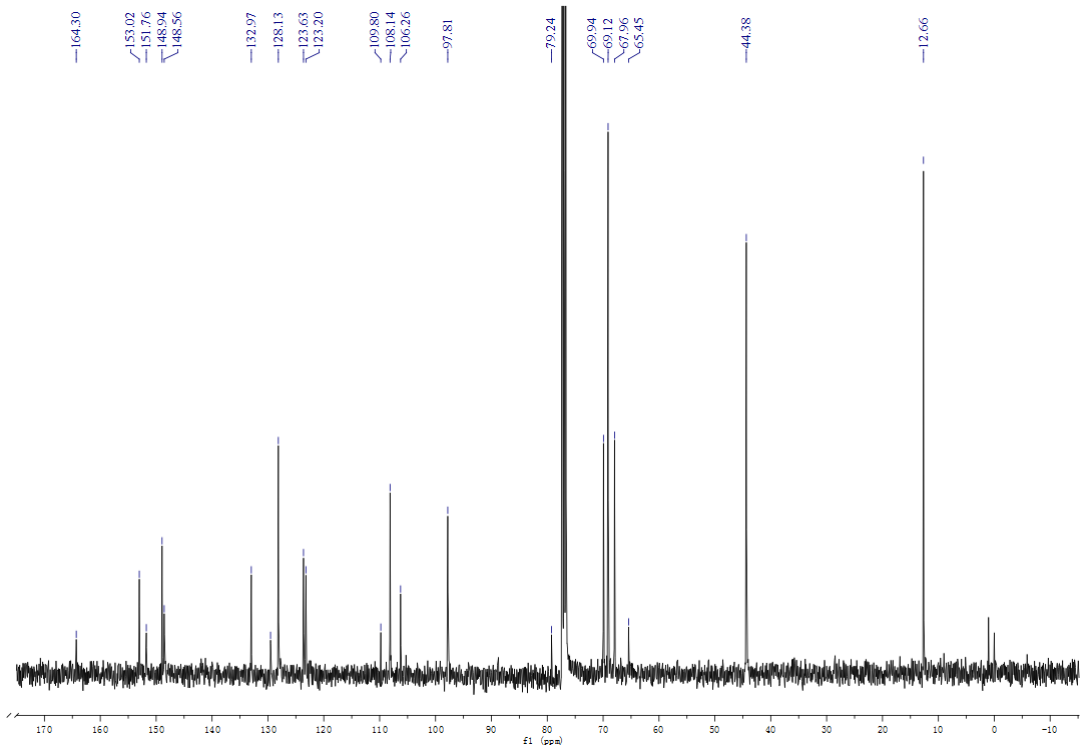

Fig. S2. ^{13}C NMR of compound **1**

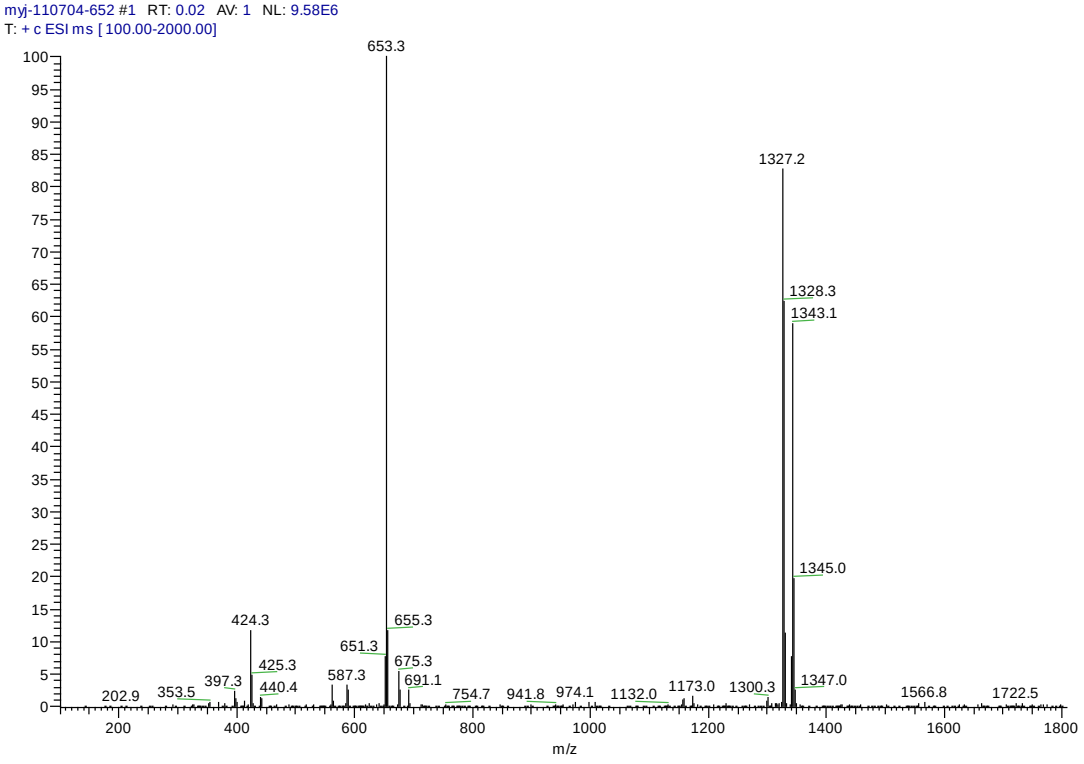

Fig. S3. ESI-MS of compound **1**

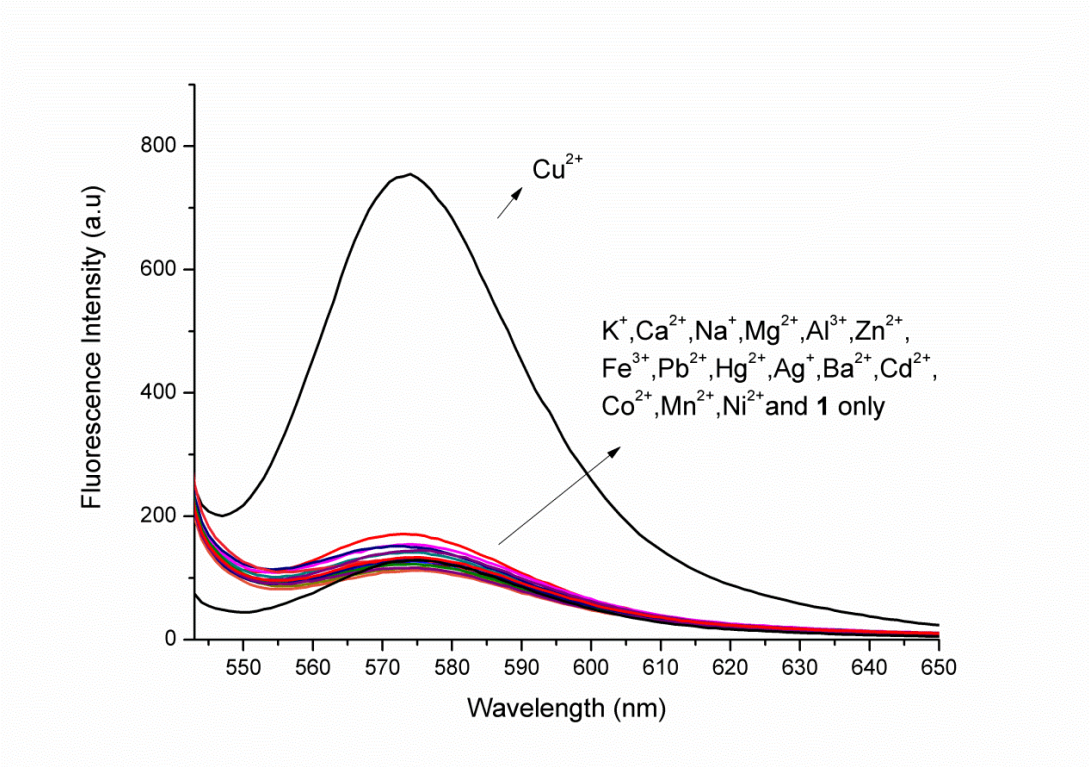

Fig. S4 Fluorescence spectra of compound **1** (20 μM) in CH_3CN/HEPES (1:3, v/v, pH 7.1) in the presence of different metal ions (1 equiv.) under the excitation wavelength of 530 nm.

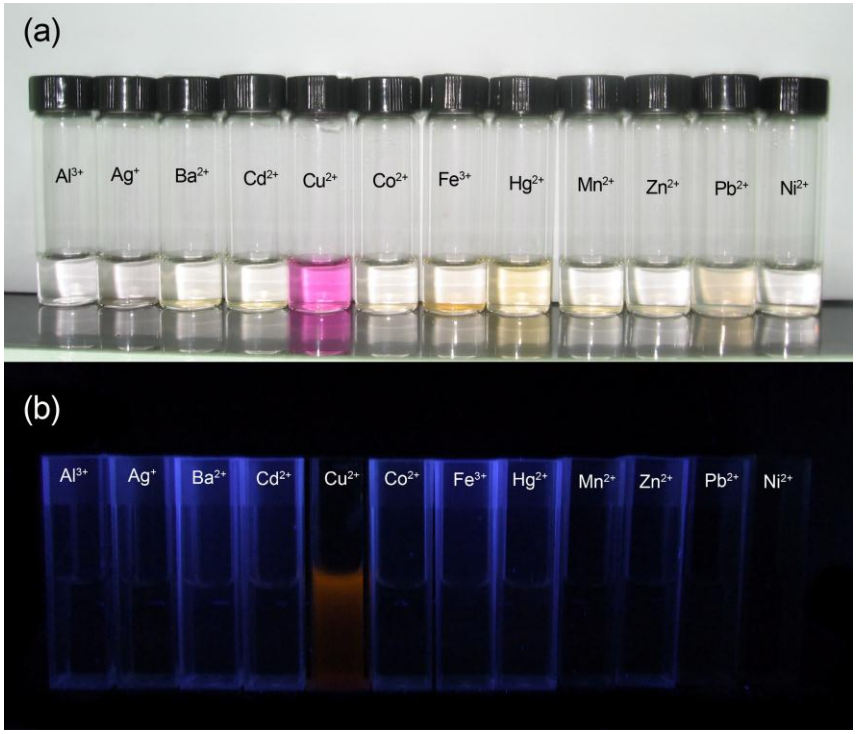

Fig. S5 (a) Visible color change of compound **1** with addition of various metal ions in CH_3CN/HEPES (1/3, v/v) solution; (b) Fluorescence changes of compound **1** with addition of various metal ions in CH_3CN/HEPES (1/3, v/v) solution under 365 nm lamp excitation. The concentration of compound **1** is 20 μM.

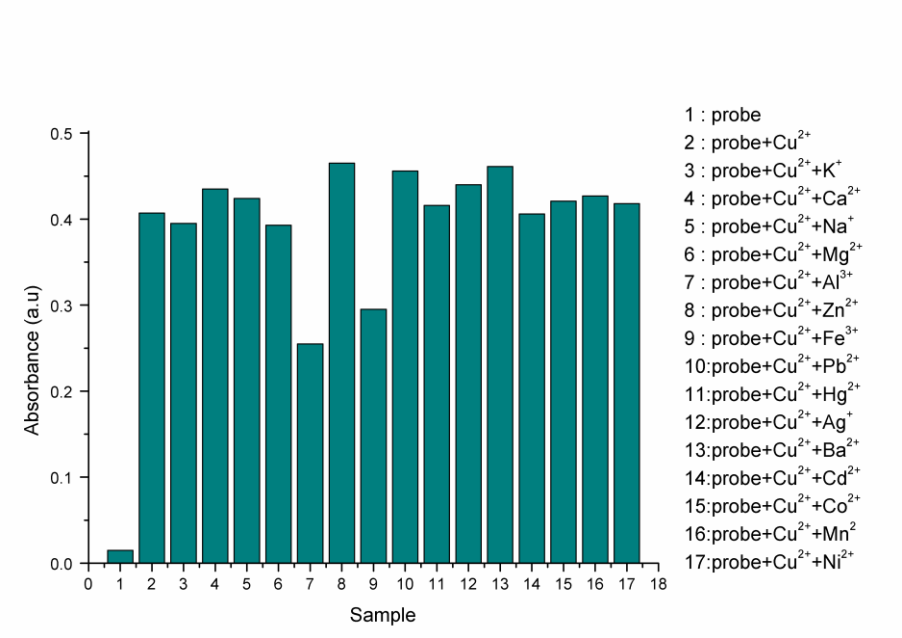

Fig. S6 The absorbance responses of **1** (50 μM, CH_3CN/HEPES, 1:1, v/v, pH 7.1) to Cu^{2+} (2 equiv.) in the presence of other metal ions (4 equiv.)

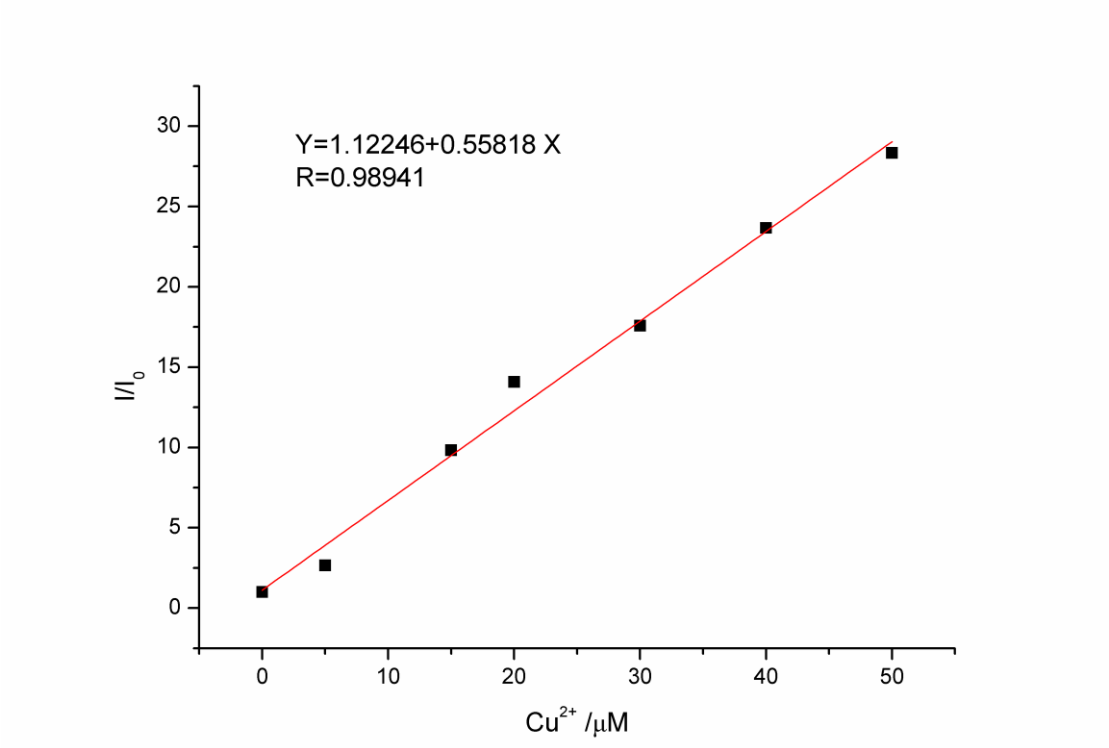

Fig. S7 Value of I/I_0 was proportional to the amount of Cu^{2+} between 5-50 μM with a good linear correlation.

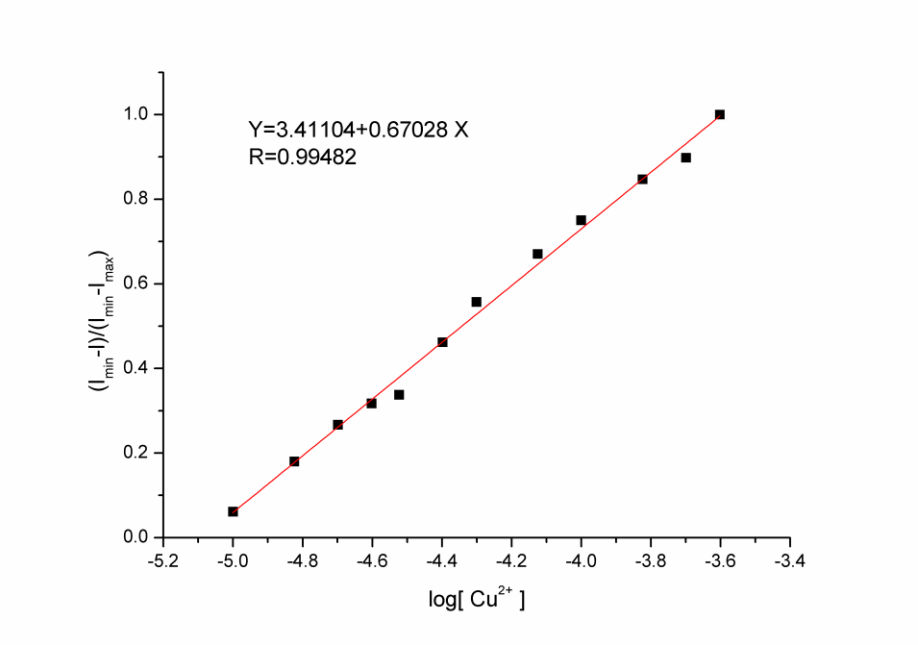

Fig. S8 Absorbance of **1** at different concentrations of Cu^{2+} added, normalized between the minimum absorbance and the maximum absorbance intensity. The detection limit was determined to be 8.147×10^{-6} M. [a, b, c]

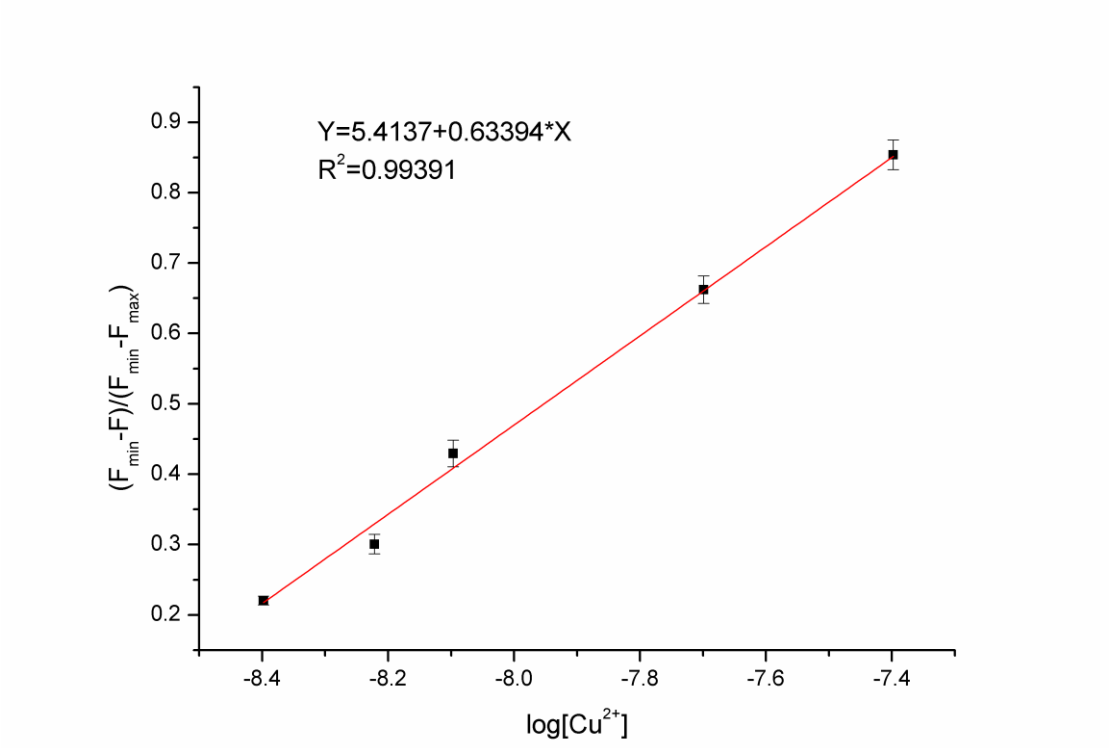

Fig. S9 Emission of **1** at different concentrations of Cu^{2+} added, normalized between the minimum emission and the maximum emission intensity with error bars that display three standard deviations. The detection limit was determined to be 2.0 nM. [a, b, c, d]

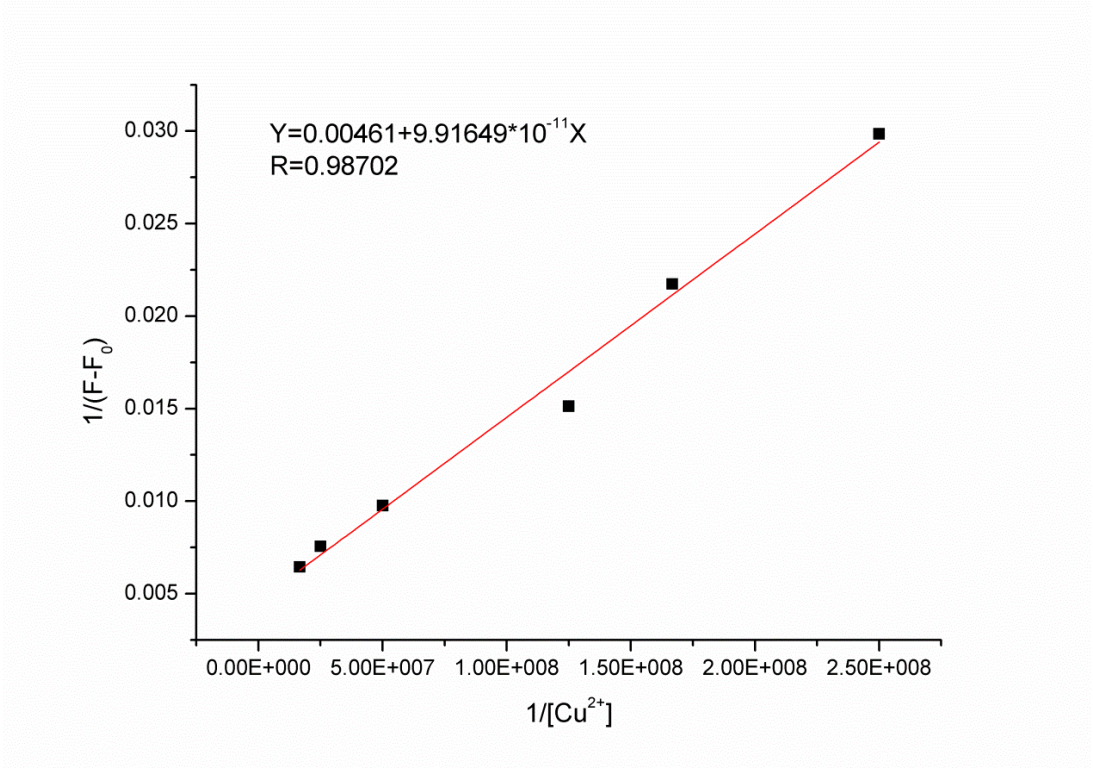

Fig. S10 Benesi-Hildebrand plot, the association constant of **1** with Cu^{2+}, $K=A/B=4.65\times10^{7}\ M^{-1}$.

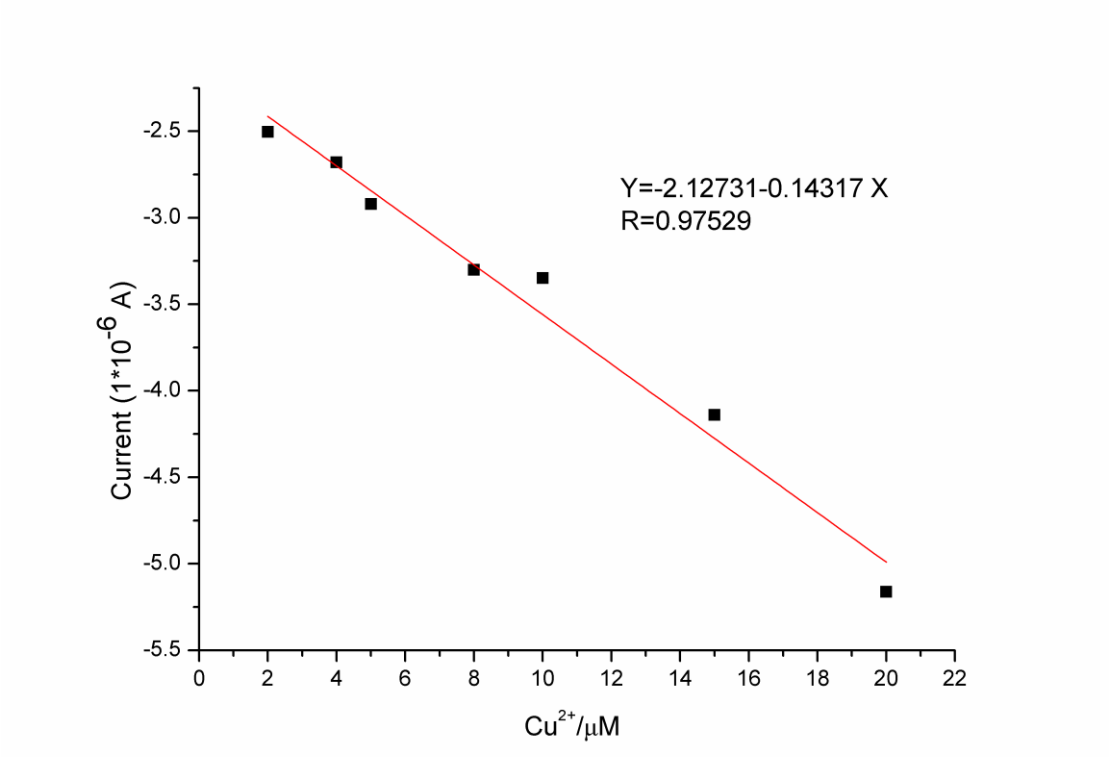

Fig. S11 Variation curve of the oxidation peak currents of free **1** (100 μM) in aqueous solution (CH_3CN/H_2O, 7:3) upon the addition of Cu^{2+}. $(n\text{-}Bu)_4NClO_4$ (0.1 M) was used as supporting electrolyte. The scan rate was 100 mV/s.

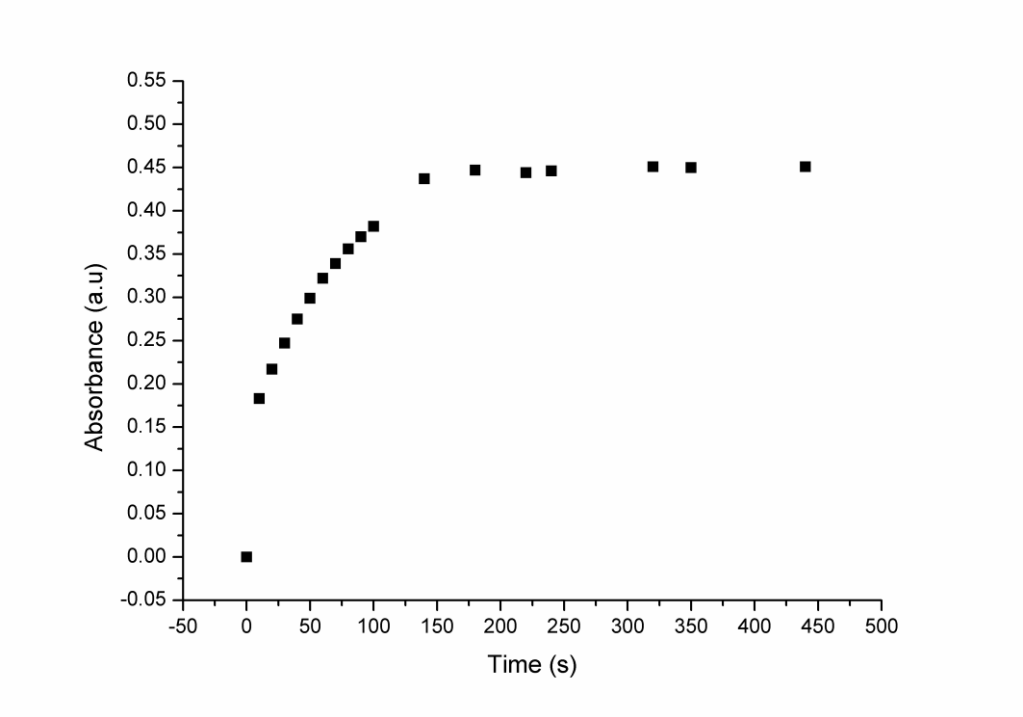

Fig. S12 Time course of compound **1** (50 μM) responding to Cu^{2+} (2 equiv.) in CH_3CN/HEPES (1:1, v/v, pH 7.1) solution.

References:

(a) Lin, W., Yuan, L., Cao, Z., Feng, Y., Long, L., Chem. Eur. J. 2009, 15, 5096.

(b) Shortreed, M., Kopelman, R., Kuhn, M., Hoyland, B., Anal. Chem. 1996, 68, 1414.

(c) Kim, M. H., Jang, H. H., Yi, S., Chang, S. K., Han, M. S., Chem. Commun. 2009, 4838.

(d) Hakonen, A., Anal. Chem. 2009, 81, 4555.