

## Electronic Supplementary Information

### Highly Sensitive and Selective Colorimetric and Off-On Fluorescent Probe for Cu<sup>2+</sup> Based on Rhodamine Derivative

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#### Apparatus and reagents

Melting points were measured with a WRS-1B digital melting point apparatus (Shanghai, China). Nuclear magnetic resonance (NMR) spectra were measured with a Bruker WM-300 spectrometer, and chemical shifts were given in ppm from tetramethylsilane. Mass spectra (MS) were recorded on a Thermo TSQ Quantum Mass Spectrometer. Fluorescence emission spectra were conducted on a Perkin Elmer LS55 luminescence spectrometer. Absorption spectra were determined on a Beckman DU-800 spectrophotometer. The pH measurements were carried out on a PHS-3C meter. Elemental analysis was performed with a Vario III elemental analyzer.

Doubly distilled water was used throughout the experiments. All the materials for synthesis were purchased from commercial suppliers and used without further purification.

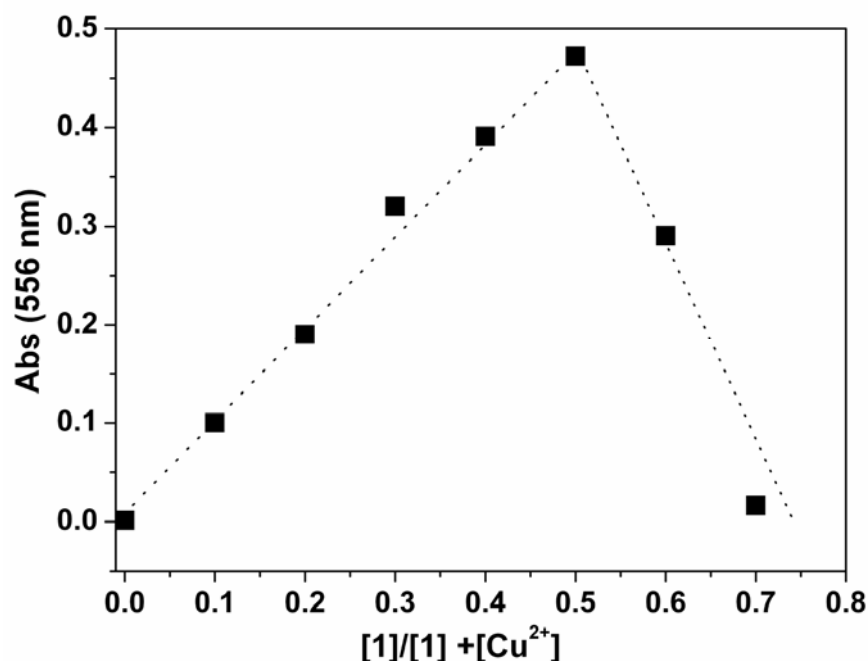
### **General procedure for spectroscopic measurements**

A  $1.0 \times 10^{-4}$  M stock solution of **1** was prepared in DMSO. To 10 mL glass tubes, a proper amount of  $\text{Cu}^{2+}$  stock solution (1 mM) and 0.1 mL **1** ( $1.0 \times 10^{-4}$  M) were added subsequently and then diluted with methanol/HEPES buffer (0.02 M, pH 6.0) (8:2, v/v). The resulting solution was mixed thoroughly. For all measurements, excitation and emission slit widths were 10 nm and 3 nm, respectively, excitation wavelength was 510 nm and the emission intensities were recorded at 580 nm.

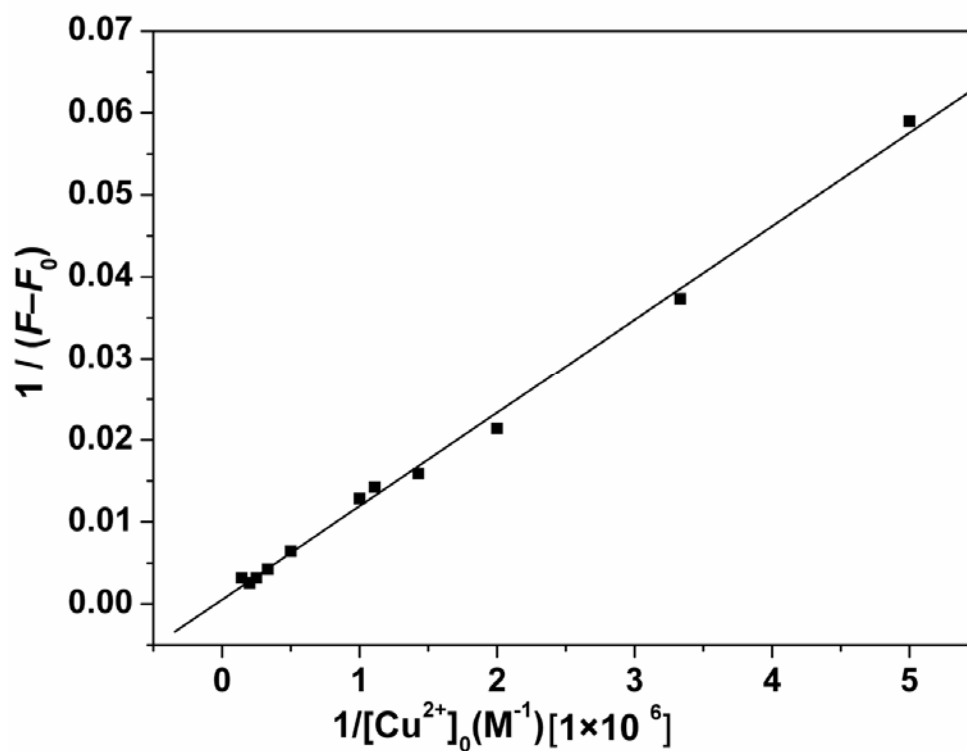
### **Synthesis of probe 1**

Rhodamine B hydrazide was synthesized in a high yield from rhodamine B following a literature procedure.<sup>[1]</sup> It was then reacted with glyoxal following a reported method to give Compound **2**.<sup>[2]</sup> To a stirred solution of Compound **2** (0.511 g, 1 mmol) in 40 mL ethanol was added dropwise  $\text{N}_2\text{S}_2$ <sup>[3]</sup> (0.24 g, 1.2 mmol) in 20 mL ethanol. The mixture was then heated at reflux for 5 h and monitored by TLC. After the reaction was completed, the solution was cooled to room temperature. The precipitate so obtained was filtered and washed with cold ethanol. The crude product was purified by recrystallization from ethanol to afford **1**. Yields: 0.50 g (80%). Mp: 209.2-210.5 °C; <sup>1</sup>H-NMR ( $\delta$ : ppm,

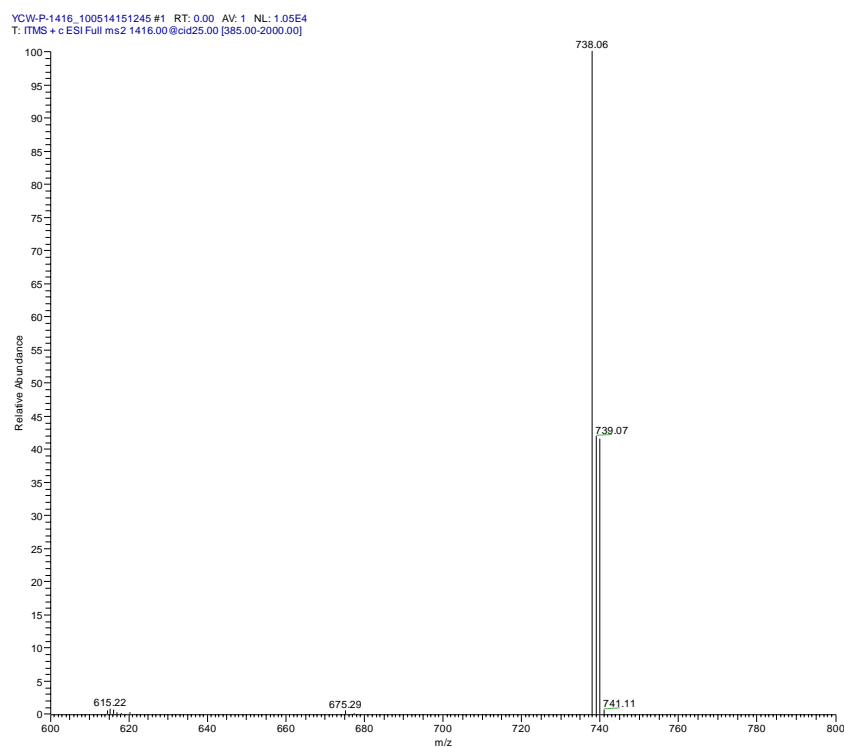
$d_6$ -DMSO): 13.34 (s, 1H, NH), 8.22-8.24 (d, 1H, Ar-H), 7.90- 7.91 (d, 1H, Ar-H), 7.66-7.67 (d, 1H, Ar-H), 7.59-7.61 (t, 1H, Ar-H), 7.53-7.56 (t, 1H, Ar-H), 7.37 (s, 1H, Ar-H), 7.38 (s, 1H, Ar-H), 7.29-7.32 (t, 2H, Ar-H), 7.25-7.28 (t, 1H, Ar-H), 7.02-7.04 (d, 1H, Ar-H), 6.40-6.41 (d, 3H, Ar-H), 6.39 (s, 1H, Ar-H), 6.34-6.35 (d, 1H, N=C-H), 6.32-6.33 (d, 1H, N=C-H), 4.42 (s, 2H, ph-CH<sub>2</sub>), 3.28-3.32 (m, 8H, CH<sub>2</sub>), 1.04-1.07 (t, 12H, CH<sub>3</sub>); <sup>13</sup>C-NMR ( $\delta$ : ppm,  $d_6$ -DMSO): 197.53, 164.91, 152.66, 152.40, 149.07, 146.17, 143.78, 136.88, 135.06, 129.68, 129.37, 128.93, 127.98, 127.76, 127.66, 124.25, 123.81, 108.68, 104.87, 97.85, 65.87, 55.38, 44.12, 38.12, 12.85. ESI-MS  $m/z$ : (**1** + H)<sup>+</sup> calc. for C<sub>38</sub>H<sub>40</sub>N<sub>6</sub>S<sub>2</sub>O<sub>2</sub>: 676.89, Found : 677.27; Anal.Caclcd for C<sub>38</sub>H<sub>40</sub>N<sub>6</sub>S<sub>2</sub>O<sub>2</sub>: C, 67.43; H, 5.96; N, 12.42; Found: C,67.53; H, 6.09; N,12.34.



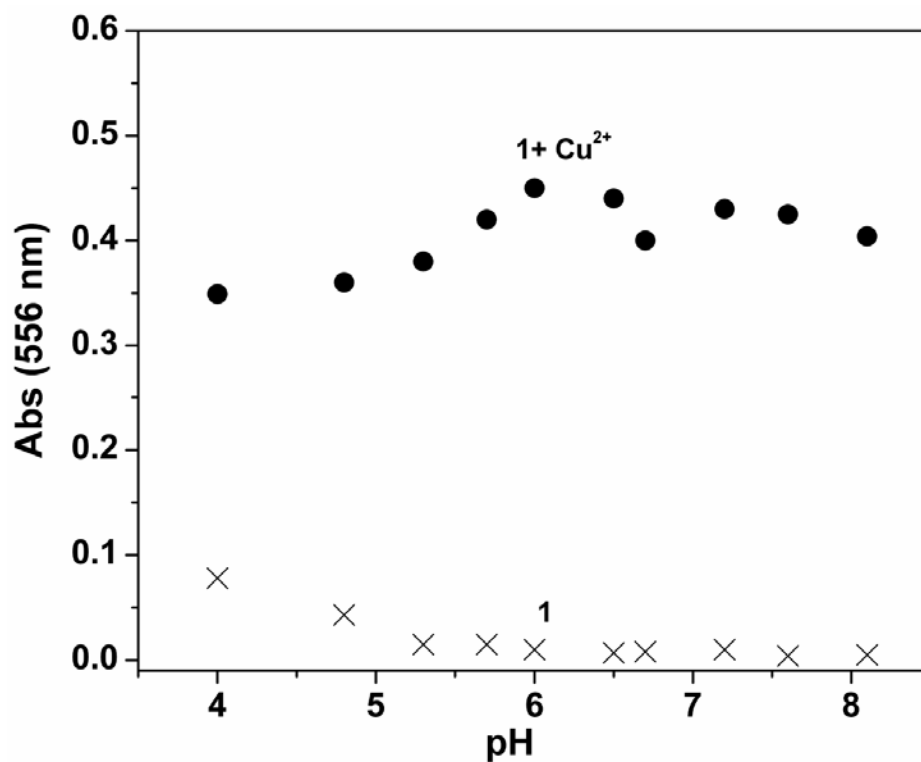
**Fig. S1.** Job's plot of **1** with Cu<sup>2+</sup>. The total concentration of **1** and Cu<sup>2+</sup> was kept at a fixed 50  $\mu$ M.



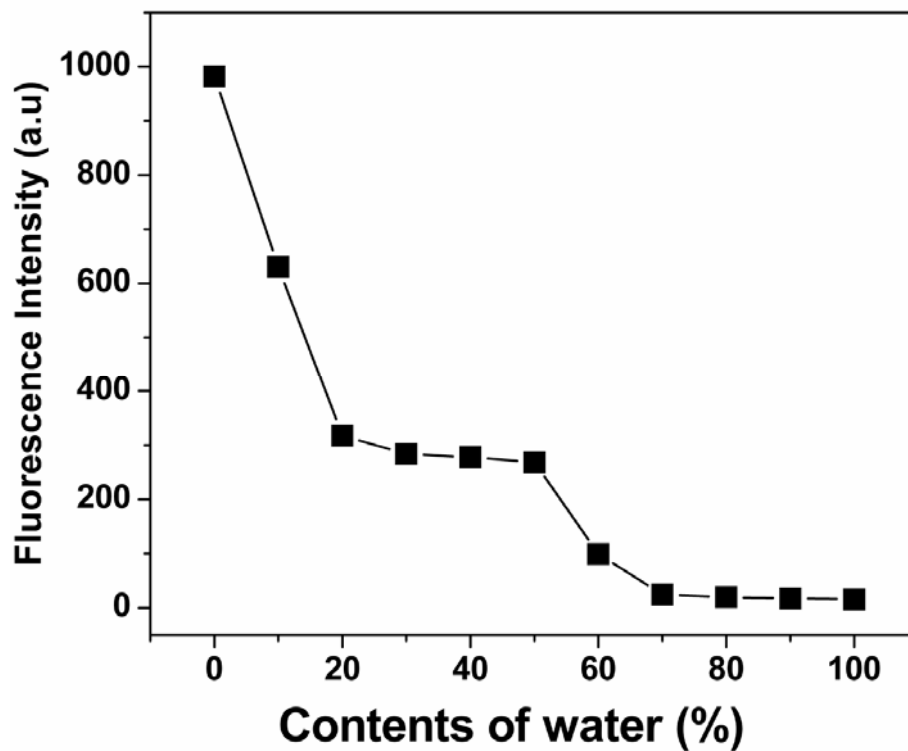
**Fig. S2.** Benesi-Hildebrand plot of **1**, assuming 1:1 stoichiometry for association between **1** and  $Cu^{2+}$ .



**Fig. S3.** Partial ESI-MS (ES+) mass spectrum of **1** in the presence of 1.0 equiv. of  $Cu^{2+}$  in ethanol.



**Fig. S4.** Absorbance of free **1** (10 μM) (×) and after addition of 50 μM Cu<sup>2+</sup> (•) in HEPES buffers as a function of different pH values.



**Fig. S5.** Effect of water content on the fluorescence intensity of **1** (1.0 μM) upon addition of Cu<sup>2+</sup> (50 μM).

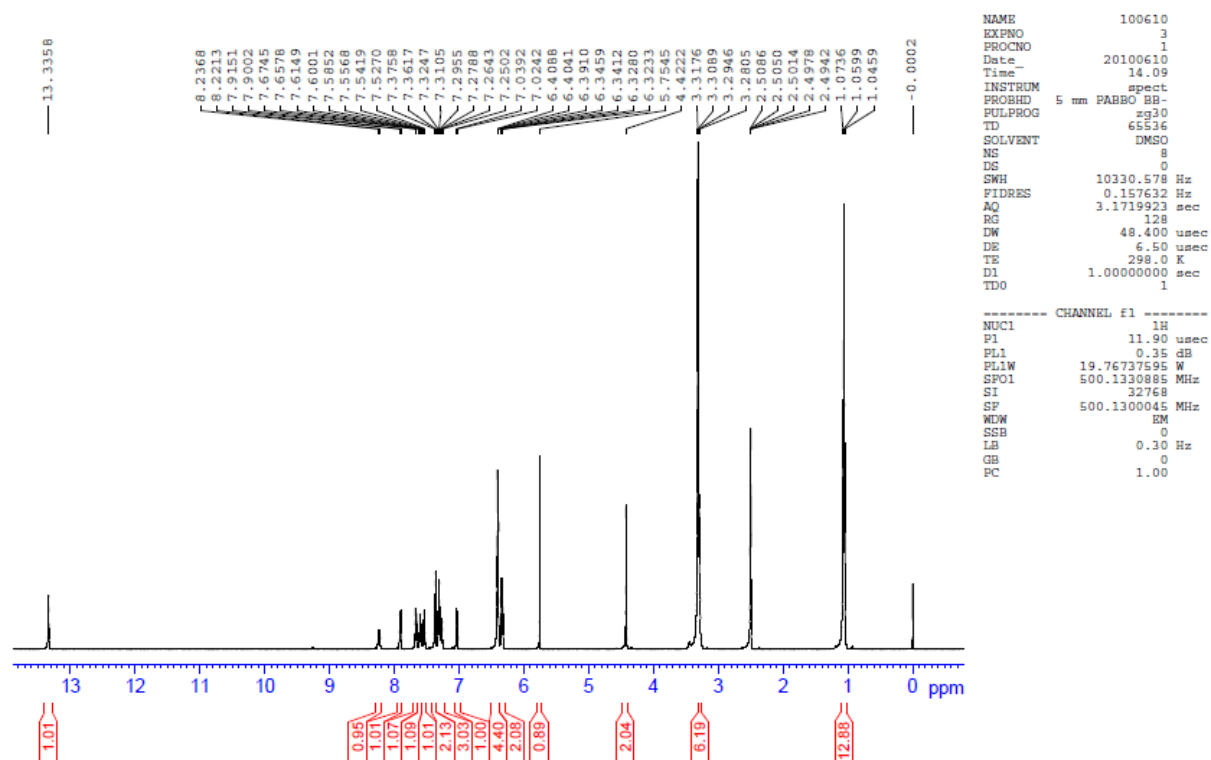


Fig. S6.  $^1\text{H}$  NMR spectrum of **1**.

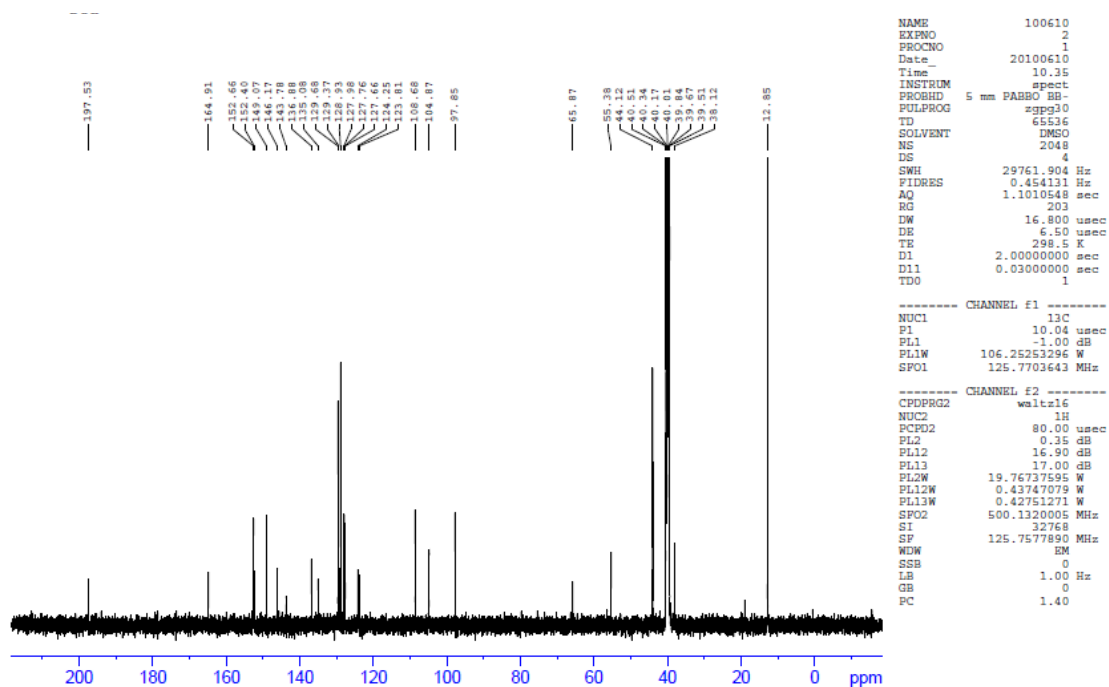
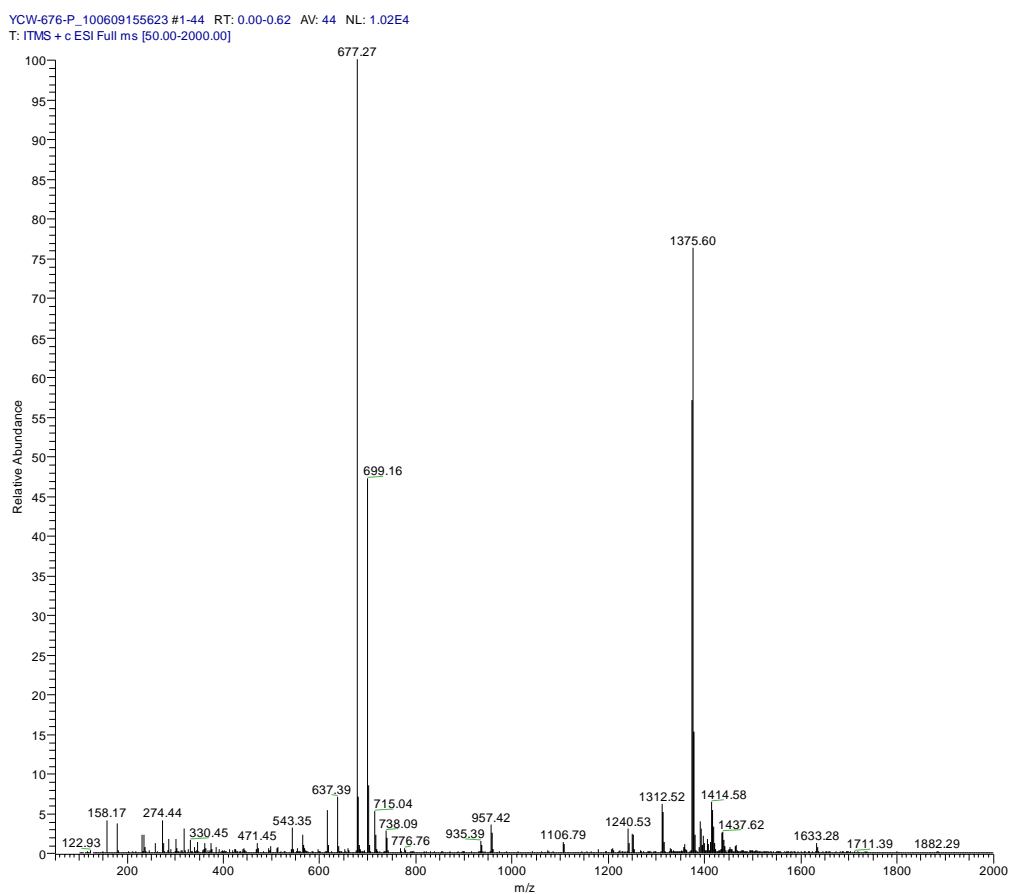


Fig. S7.  $^{13}\text{C}$  NMR spectrum of **1**.



**Fig. S8.** ESI-MS mass spectrum of **1**.

## Reference

- [1] X. F. Yang, X. Q. Guo and Y. B. Zhao, *Talanta*, 2002, **57**, 883.
- [2] J. J. Du , J. L. Fan , X. J. Peng , P. P. Sun , J. Y. Wang , H. L. Li and S. G. Sun, *Org. Lett.*, 2010, **12** , 476.
- [3] Q. S. Zheng, J. S. Zhao, J. C. Wang and L, Yan, *Chem. Reagents*, 2007, **29**, 684.