

# Highly Sensitive and Selective Turn-on Fluorescent and Chromogenic Probe for Cu<sup>2+</sup> and ClO<sup>-</sup> Based on a *N*-Picolinyl Rhodamine B-Hydrazide Derivative

Yunlong Liu,<sup>a</sup> Yue Sun,<sup>a</sup> Jun Du,<sup>b</sup> Xin Lv,<sup>a</sup> Yun Zhao,<sup>a</sup> Maliang Chen,<sup>a</sup> Pi Wang<sup>a</sup> and Wei Guo<sup>\*a</sup>

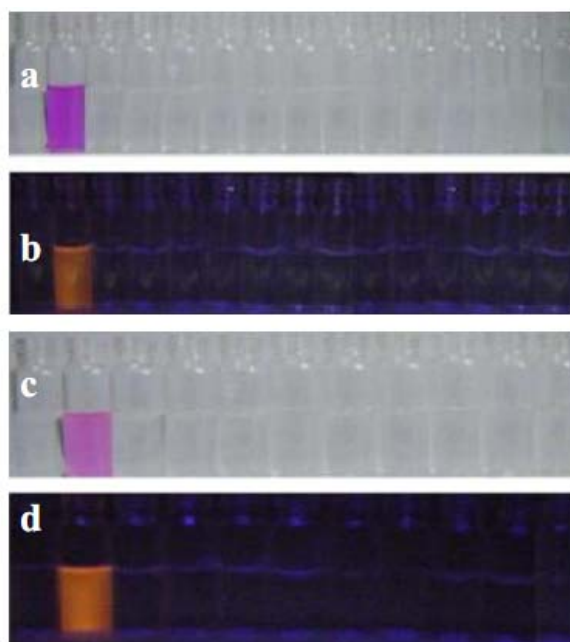
<sup>a</sup> School of Chemistry and Chemical Engineering, Shanxi University, Taiyuan 030006, China. Email: guow@sxu.edu.cn

<sup>b</sup> Key Laboratory of Chemical Biology and Molecular Engineering of Ministry of Education, Shanxi University

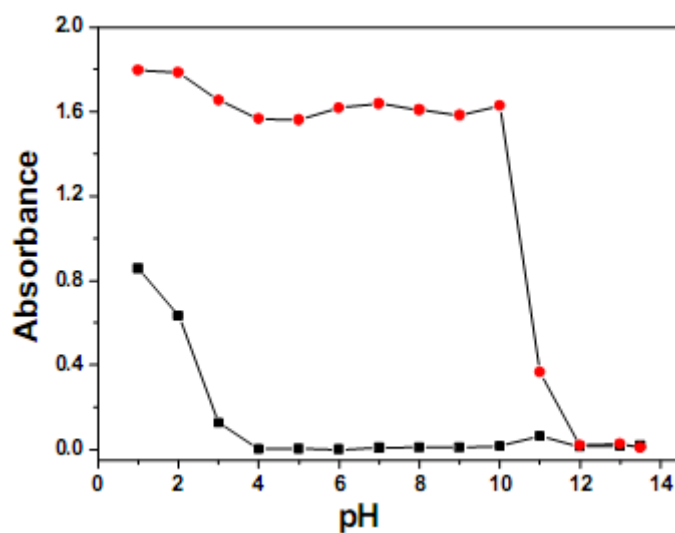
## Electronic Supplementary Information (ESI†)

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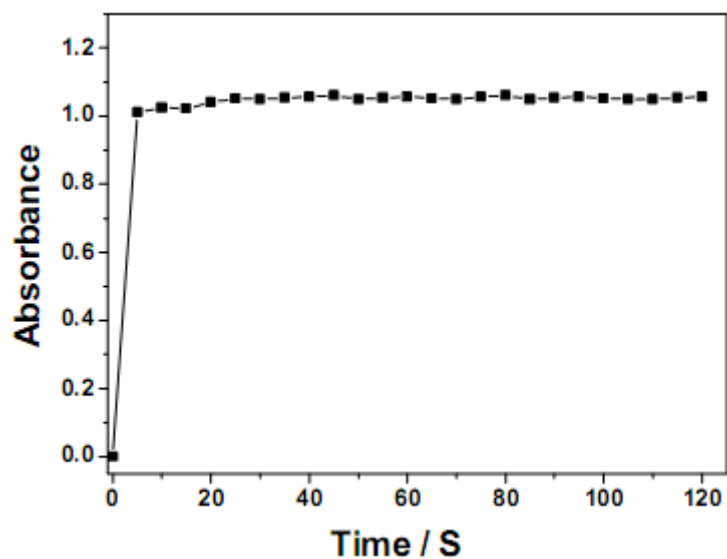
1. The fluorescent and the color changes of **1** to various metal ions and anions (**Fig. S1**).
2. The spectra responses of **1** in the absence and presence of Cu<sup>2+</sup> in different pH values (**Fig. S2**).
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14. <sup>1</sup>H NMR chart of **1** (**Fig. S14**).
15. <sup>13</sup>C NMR chart of **1** (**Fig. S15**).
16. EI-MS chart of **1** (**Fig. S16**).



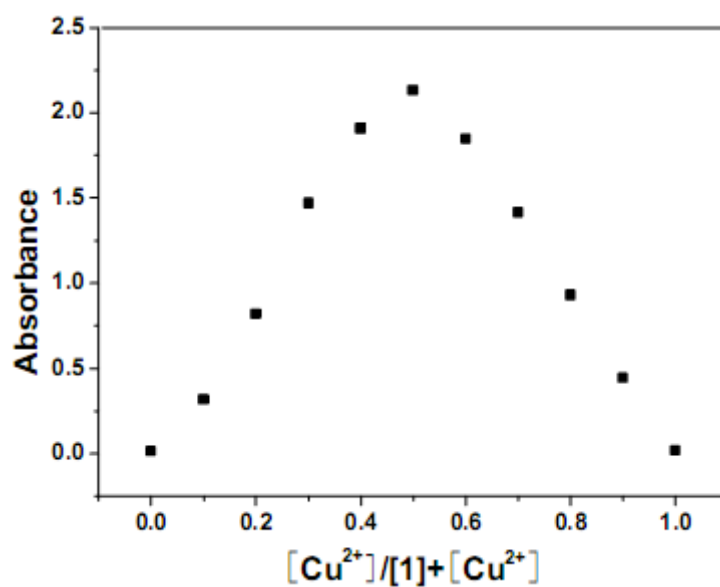
**Figure S1.** Color (a) and fluorescence (b) changes of **1** in 9:1 (v/v) MeCN/water solution (10 mM Tris-HCl, pH 7.0) in the presence of different metal cations (From left to right: **1** only, Cu<sup>2+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Mn<sup>2+</sup>, Fe<sup>2+</sup>, Ca<sup>2+</sup>, Zn<sup>2+</sup>, Co<sup>2+</sup>, Pb<sup>2+</sup>, Hg<sup>2+</sup>, Cd<sup>2+</sup>, Ni<sup>2+</sup> and Ag<sup>+</sup>). Color (c) and fluorescence (d) changes of **1** in 7:3 (v/v) MeOH-Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>/NaOH buffer (30 mM, pH 12.0) in the presence of different anions (From left to right: **1** only, ClO<sup>-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SiO<sub>3</sub><sup>2-</sup>, H<sub>2</sub>O<sub>2</sub>, SO<sub>4</sub><sup>2-</sup>, AcO<sup>-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>; ClO<sub>3</sub><sup>-</sup>; MnO<sub>4</sub><sup>-</sup>).



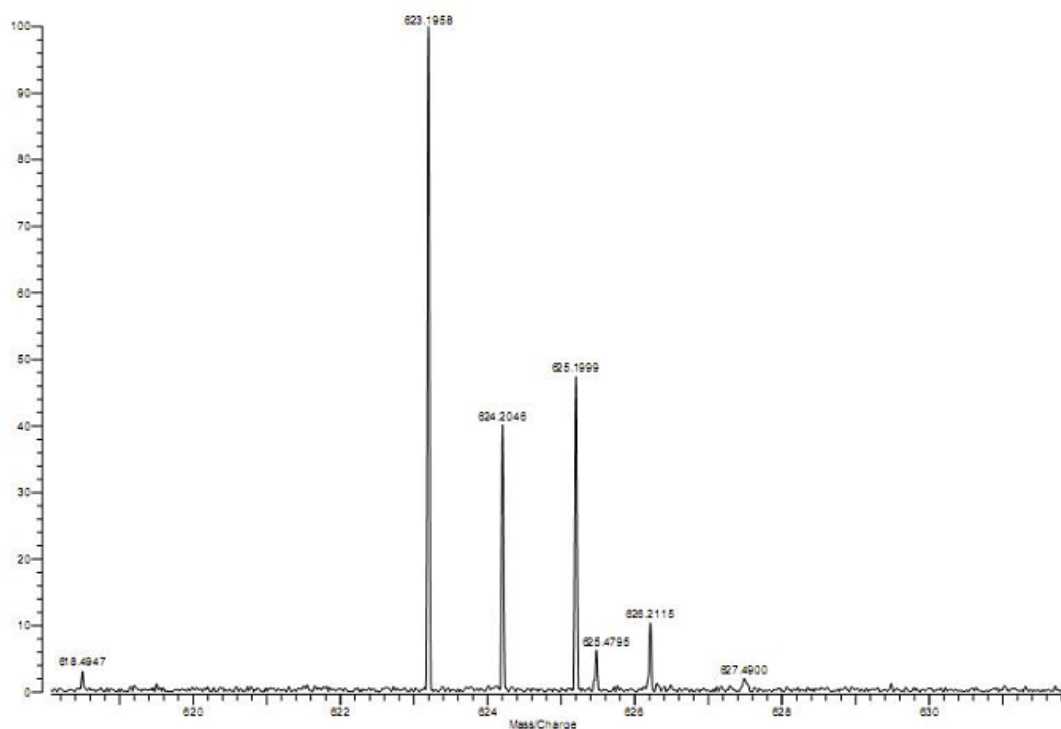
**Figure S2.** Changes in absorption (565 nm) of **1** (20 μM) in 9:1 (v/v) MeCN/water solution measured with and without Cu<sup>2+</sup> (3 equiv.) as a function of pH. **1**+ Cu<sup>2+</sup> (red), **1** (black).



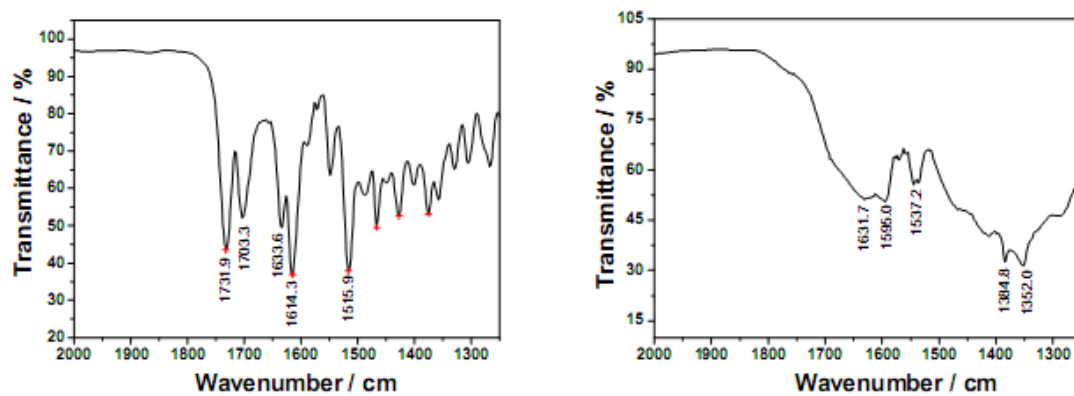
**Figure S3.** Time course of the absorption response of **1** (20  $\mu\text{M}$ ) in 9:1 (v/v) MeCN/water solution (10 mM Tris-HCl, pH 7.0) upon addition of 3 equiv. of  $\text{Cu}(\text{NO}_3)_2$ .



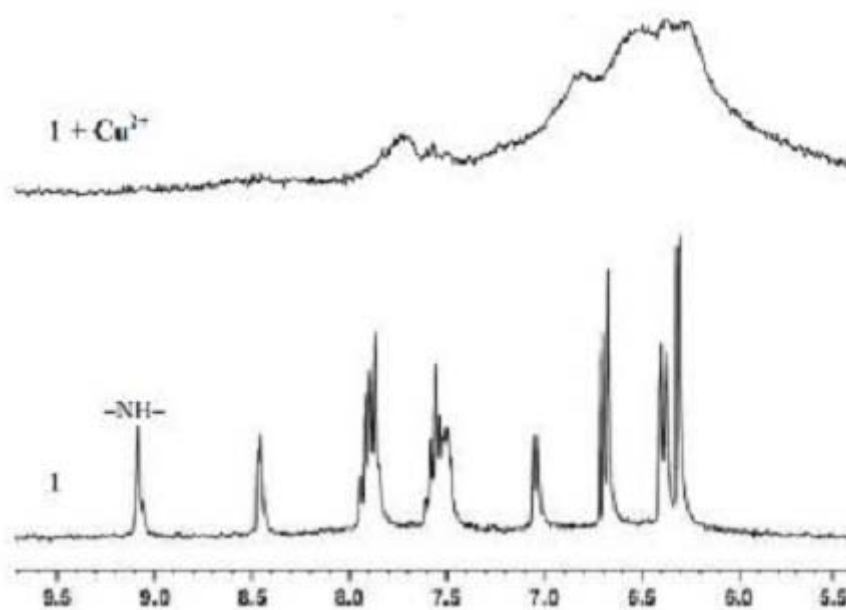
**Figure S4.** Job's plots between **1** and  $\text{Cu}^{2+}$  in 9:1 (v/v) MeCN/water solution (10 mM Tris-HCl, pH 7.0). Total concentration of **1** +  $\text{Cu}^{2+}$  was kept constant at 100  $\mu\text{M}$ .



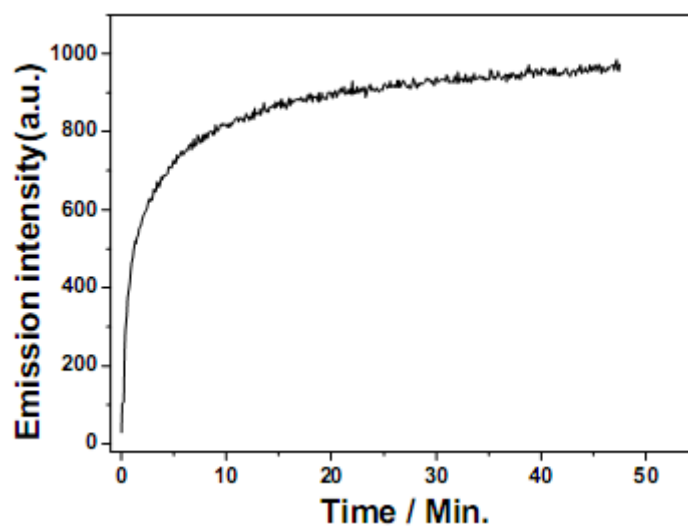
**Figure S5.** The ESI-MS for **1**-Cu<sup>2+</sup>.



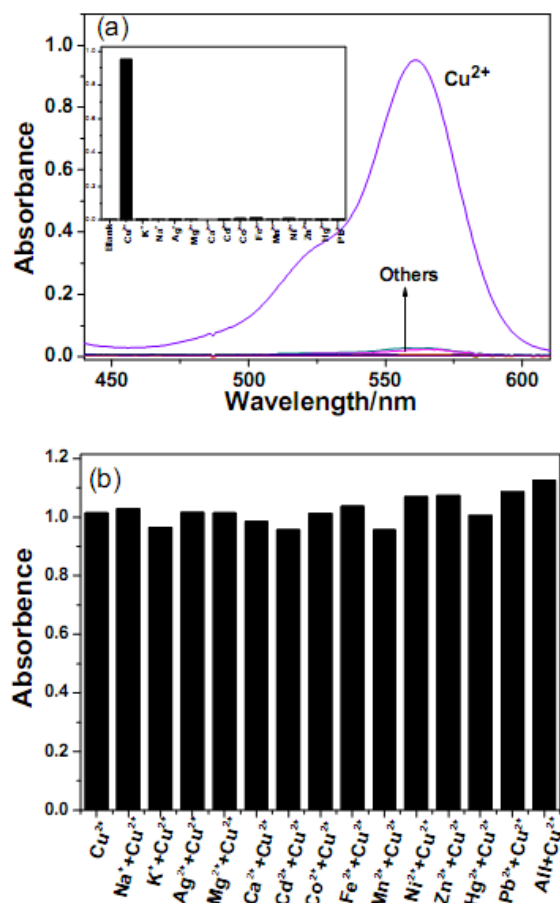
**Figure S6.** IR spectra of **1** (a) and **1**-Cu<sup>2+</sup> (b) were taken in KBr disks.



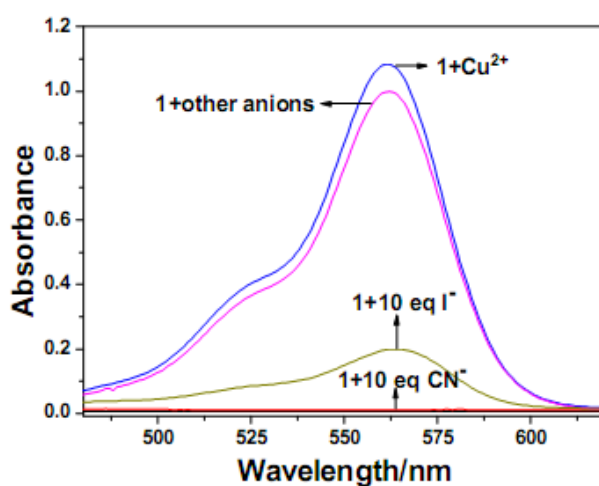
**Figure S7.** <sup>1</sup>H NMR spectral changes of **1** upon addition of 1 equiv of Cu(NO<sub>3</sub>)<sub>2</sub> (CD<sub>3</sub>CN at 25 °C).



**Figure S8.** Time course of the fluorescence response of **1** (20 μM) in 9:1 (v/v) MeCN/water solution (10 mM Tris-HCl, pH 7.0) upon addition of 10 equiv. of Cu(NO<sub>3</sub>)<sub>2</sub>.

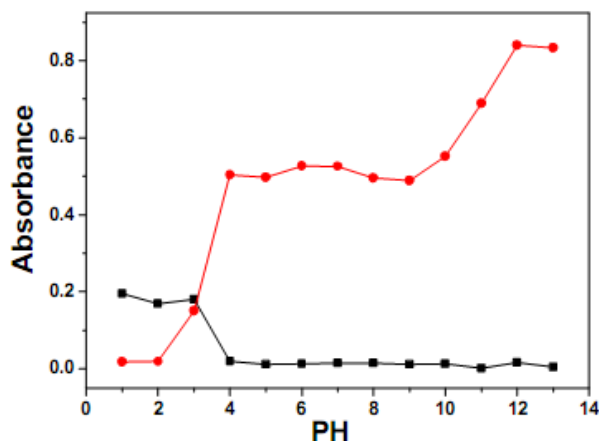


**Figure S9.** (a) The UV-vis spectra of **1** (20 μM) upon addition of 3 equiv of Cu<sup>2+</sup> and various other metal ions (3 equiv) in 9:1 (v/v) MeCN/water solution (10 mM Tris-HCl, pH 7.0). (b) Optical density of **1** (20 μM) to 3 equiv of Cu<sup>2+</sup> in 9:1 (v/v) MeCN/water solution (10 mM Tris-HCl, pH 7.0) containing 3 equiv of various metal ions.

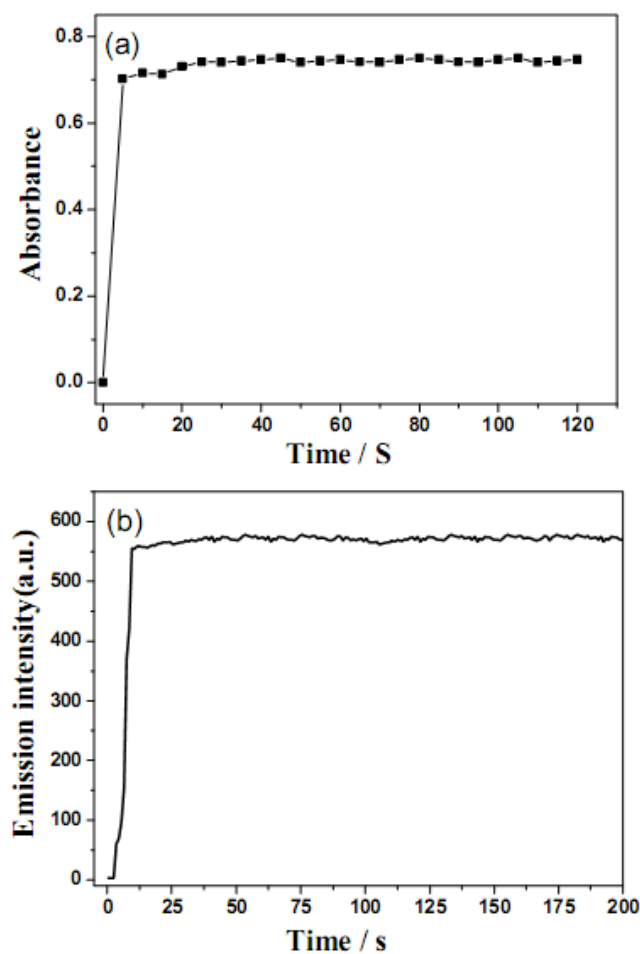


**Figure S10.** The UV-vis spectra of **1** (20 μM) in 9:1 (v/v) MeCN/water solution (10 mM Tris-HCl, pH 7.0) in the presence of Cu<sup>2+</sup> and various anions [Cu<sup>2+</sup>: 3 equiv; I<sup>-</sup> and CN<sup>-</sup>: 10 equiv; other anions (F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SiO<sub>3</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup>, AcO<sup>-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, ClO<sub>3</sub><sup>-</sup>,

$\text{MnO}_4^-$ : 5 equiv].

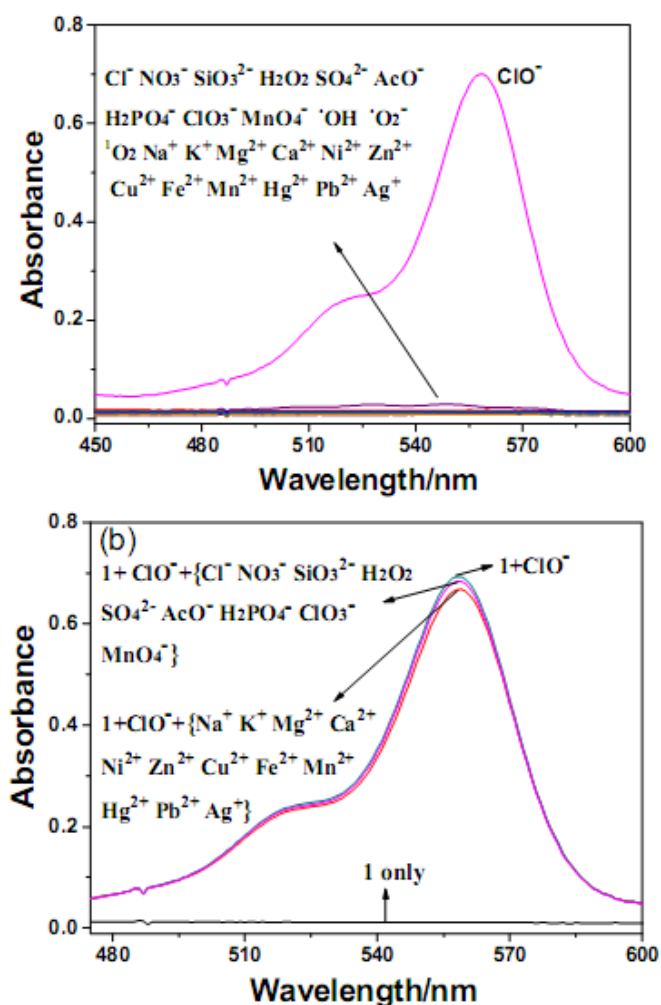


**Figure S11.** Effect of pH on the reaction of **1** (20  $\mu\text{M}$ ) with  $\text{ClO}^-$  (15 equiv) in 7:3 (v/v) MeOH/water solution; **1**+  $\text{ClO}^-$  (red), **1** (black). Absorption intensity was measured at 558 nm.



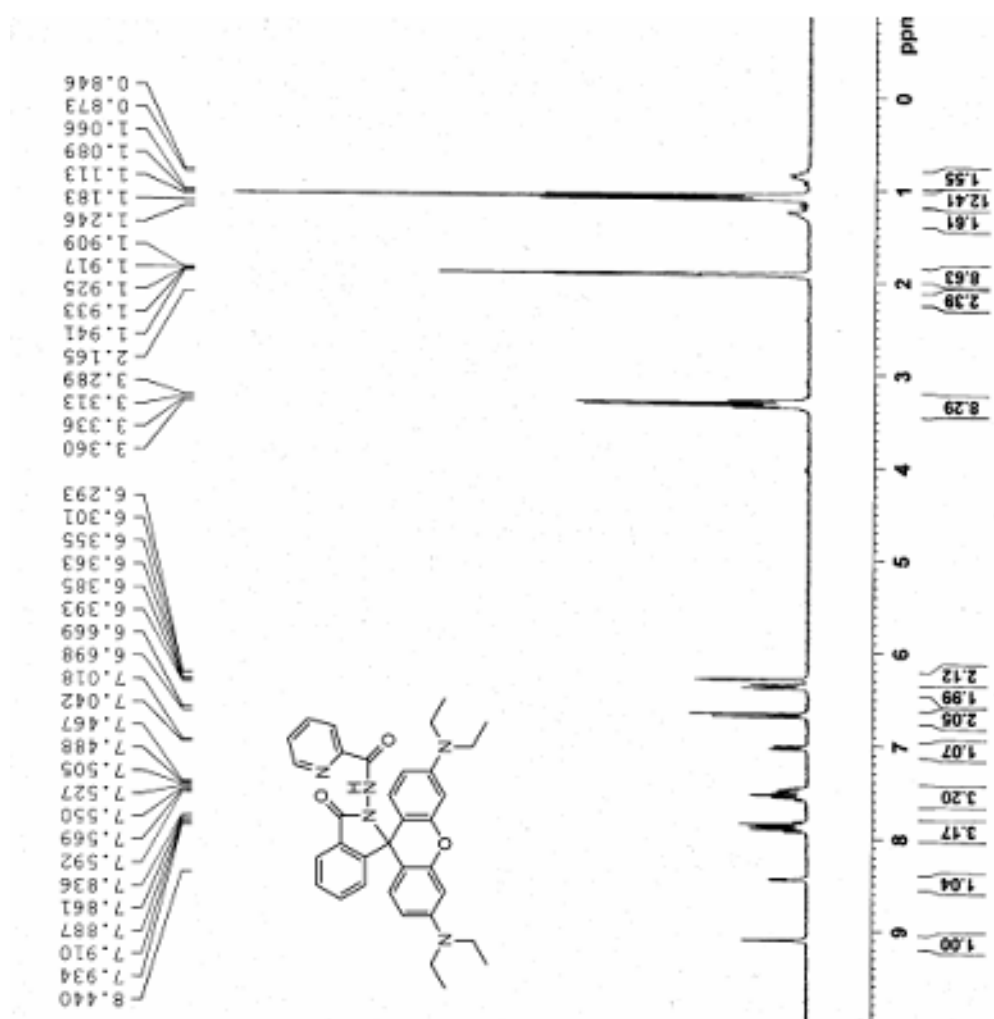
**Figure S12.** Time course of the absorption (a) and fluorescence response (b) of **1** [20  $\mu\text{M}$  in (a) and 10  $\mu\text{M}$  in (b)] in 7:3 (v/v) MeOH- $\text{Na}_2\text{B}_4\text{O}_7/\text{NaOH}$  buffer (30 mM, pH

12.0) upon addition of 10 equiv of  $\text{ClO}^-$ .

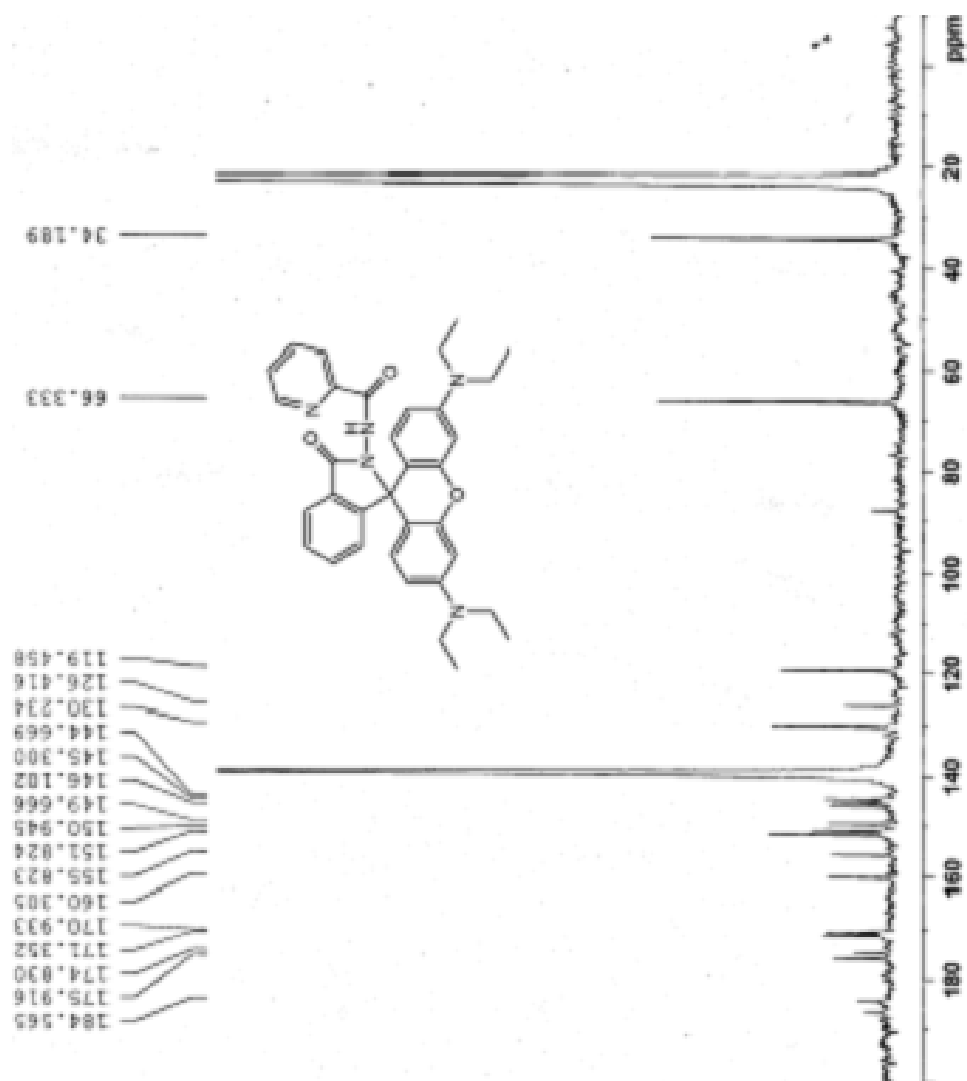


**Figure S13.** (a) The UV-vis spectra of **1** (20  $\mu\text{M}$ ) in 7:3 (v/v) MeOH- $\text{Na}_2\text{B}_4\text{O}_7/\text{NaOH}$  buffer (30 mM, pH 12.0) upon addition of 20 equiv of  $\text{ClO}^-$  and various species. (b) The UV-vis spectra of **1** (20  $\mu\text{M}$ ) to 20 equiv of  $\text{ClO}^-$  in 7:3 (v/v) MeOH- $\text{Na}_2\text{B}_4\text{O}_7/\text{NaOH}$  buffer (30 mM, pH 12.0) containing various species. Species:  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SiO}_3^{2-}$ ,  $\text{H}_2\text{O}_2$ ,  $\text{SO}_4^{2-}$ ,  $\text{AcO}^-$ ,  $\text{H}_2\text{PO}_4^-$  (1 mM);  $\text{ClO}_3^-$  (0.1 mM);  $\text{MnO}_4^-$  (20  $\mu\text{M}$ );  $\cdot\text{OH}$  (100  $\mu\text{M}$   $\text{Fe}^{2+}$  + 1 mM  $\text{H}_2\text{O}_2$ );  $\cdot\text{O}_2^-$  (1 mM  $\text{KO}_2$ );  $^1\text{O}_2$  (1 mM  $\text{Na}_2\text{MoO}_4$  + 2 mM  $\text{H}_2\text{O}_2$ );  $\text{Na}^+$ ,  $\text{K}^+$  (1 mM);  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$  (0.1 mM);  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Ag}^+$  (20  $\mu\text{M}$ ).

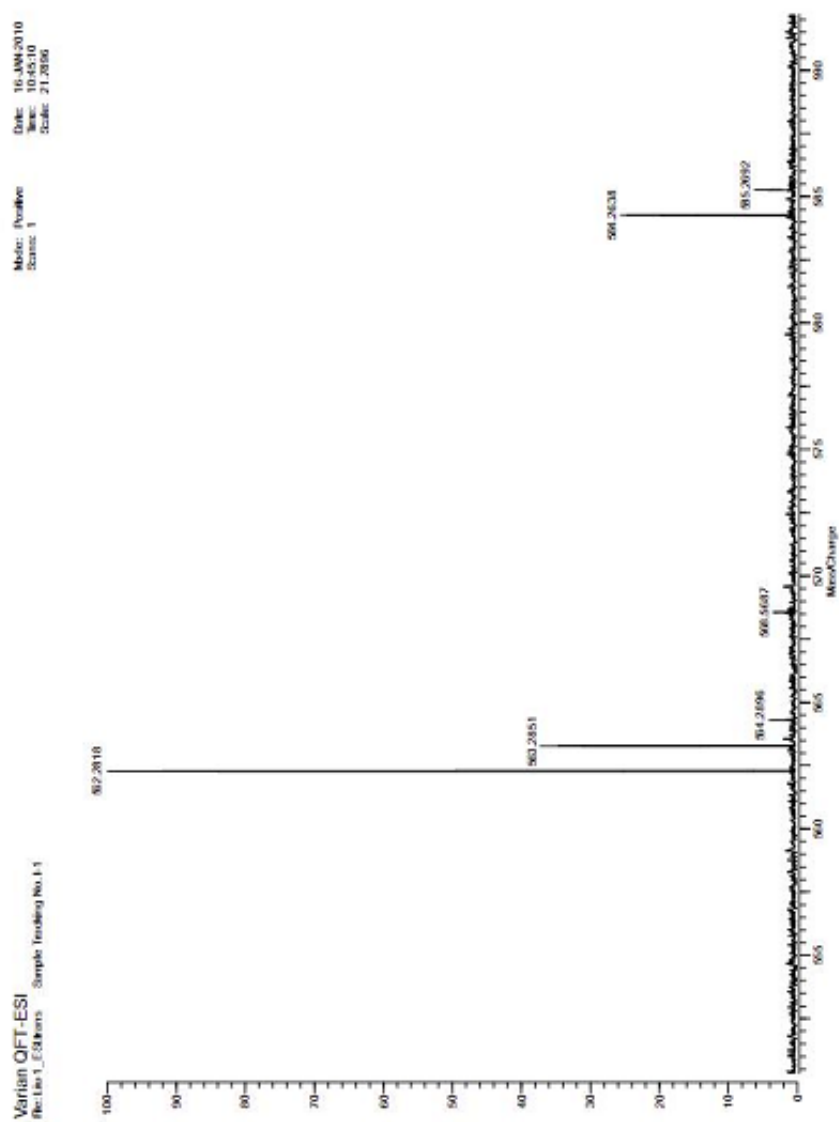




**Figure S14.** The <sup>1</sup>H NMR spectra of **1**.



*Figure S15.* The  $^{13}\text{C}$  NMR spectra of **1**.



*Figure S16.* The ESI-MS for **1**.