

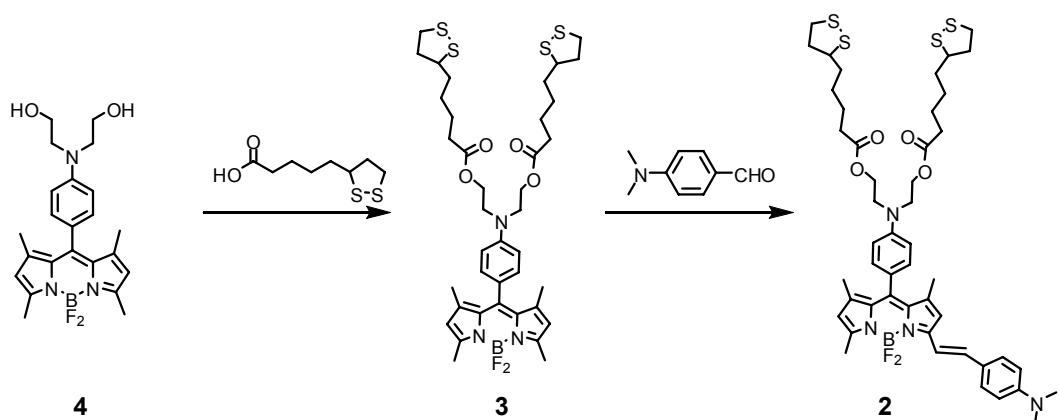
## **BODIPY-functionalized gold nanoparticles as a selective fluoro-chromogenic chemosensor for imaging Cu<sup>2+</sup> in living cells**

**Hye Young Lee,<sup>a</sup> Hyun Jong Son,<sup>a</sup> Jung Mi Lim,<sup>b</sup> Jungmin Oh,<sup>c</sup> Dongmin Kang,<sup>\*b</sup> Won Seok Han<sup>\*a</sup> and Jong Hwa Jung<sup>\*a</sup>**

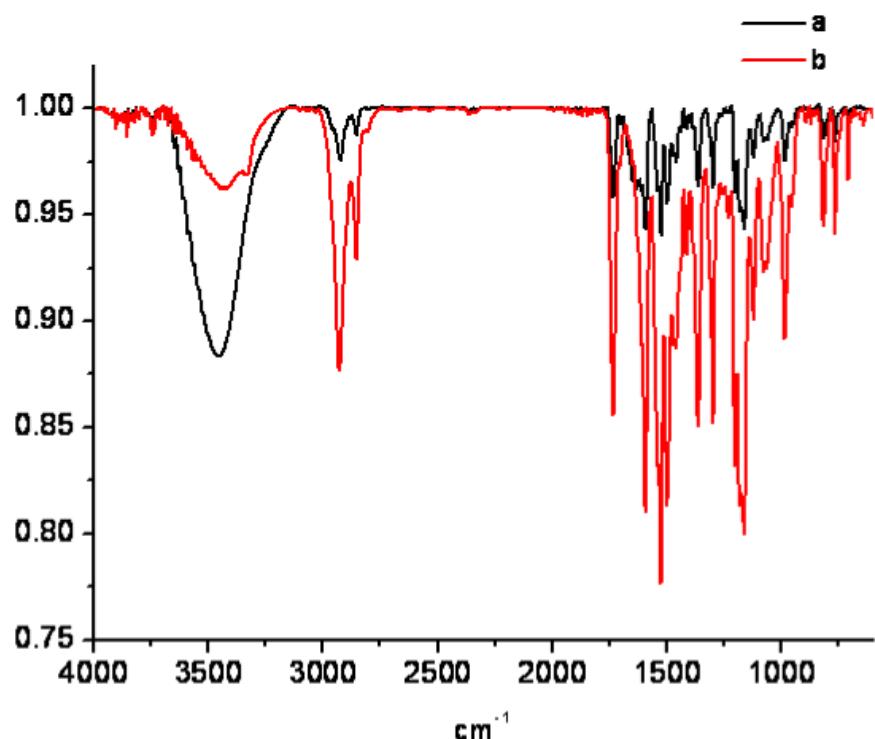
<sup>a</sup>*Department of Chemistry and Research Institute of Natural Science, Gyeongsang National University, Jinju 660-701, Korea. E-mail: [jonghwa@gnu.ac.kr](mailto:jonghwa@gnu.ac.kr)*

<sup>b</sup>*Division of Life and Pharmaceutical Sciences, Ewha Womans University, Seoul 120-750, Korea*

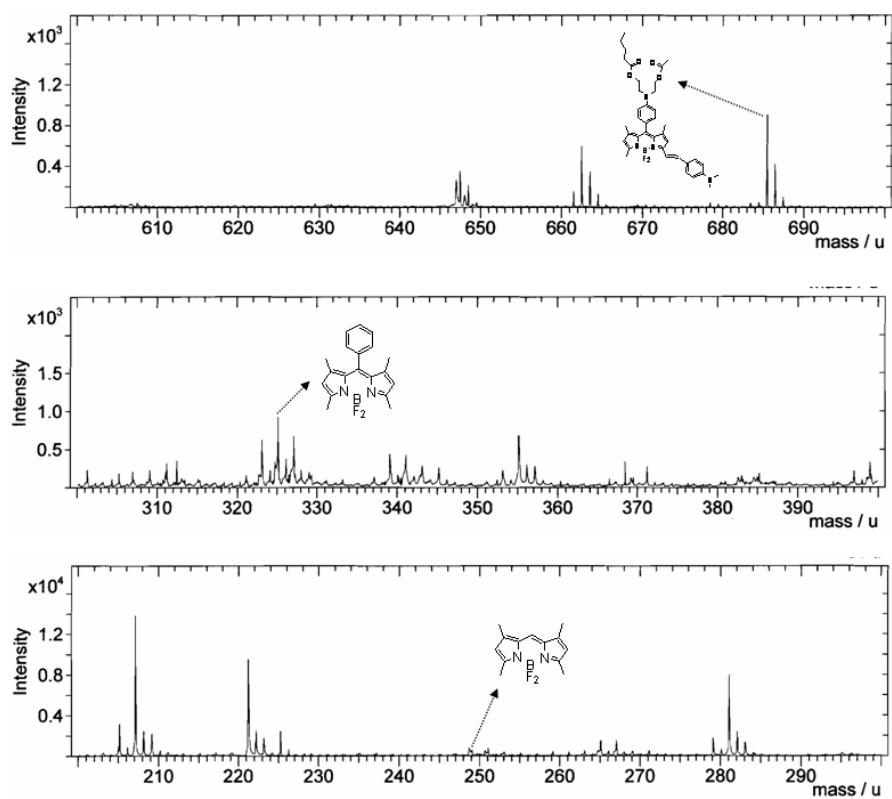
<sup>c</sup>*Chuncheon Center, Korea Basic Science Institute, Chuncheon 200-701, Korea*



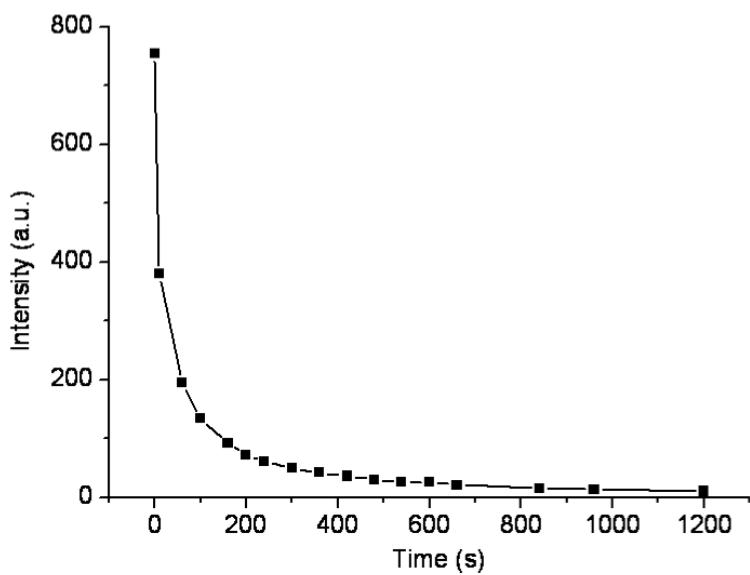
**Scheme S1.** Synthetic route for **2**.



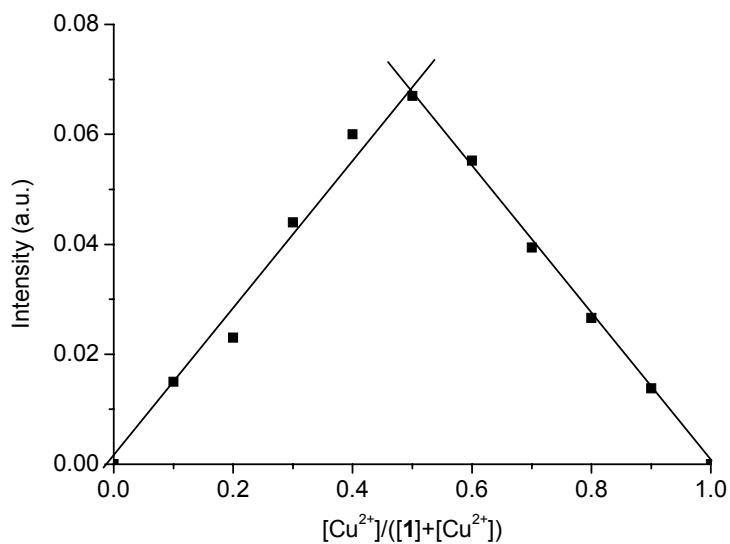
**Fig. S1** Infrared spectra of (a) **1** and (b) **2**.



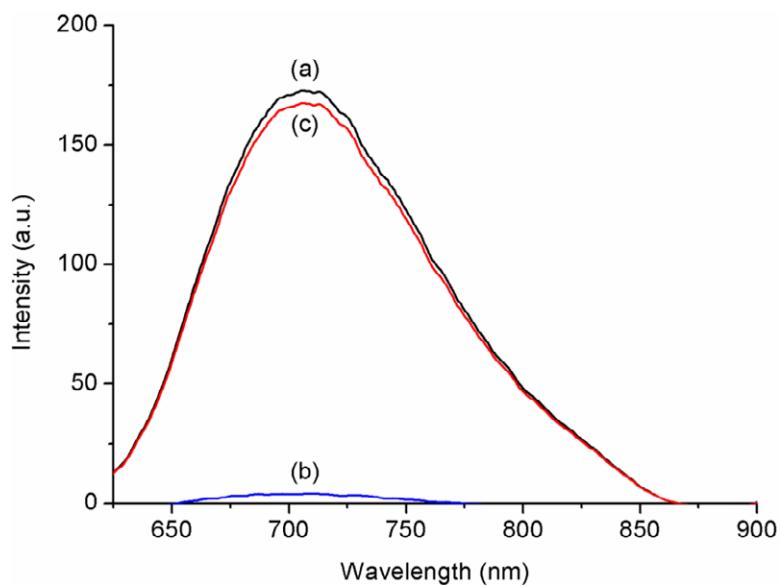
**Fig. S2** TOF-SIMS spectra of **1**.



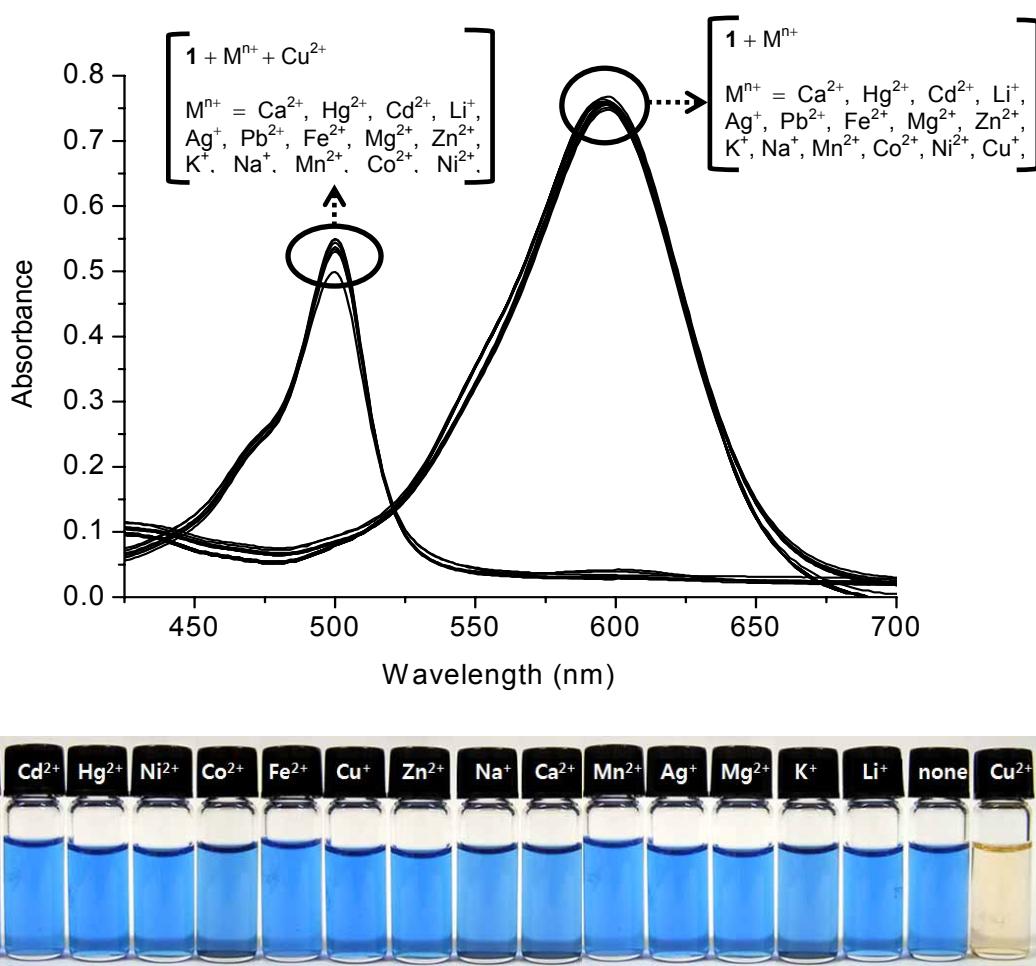
**Fig. S3** Time course of the fluorescence intensity of **1** (10  $\mu$ M) in 20 mM HEPES (10% CH<sub>3</sub>CN, pH 7.4) at 25 °C at the addition of Cu<sup>2+</sup> (40 equiv).



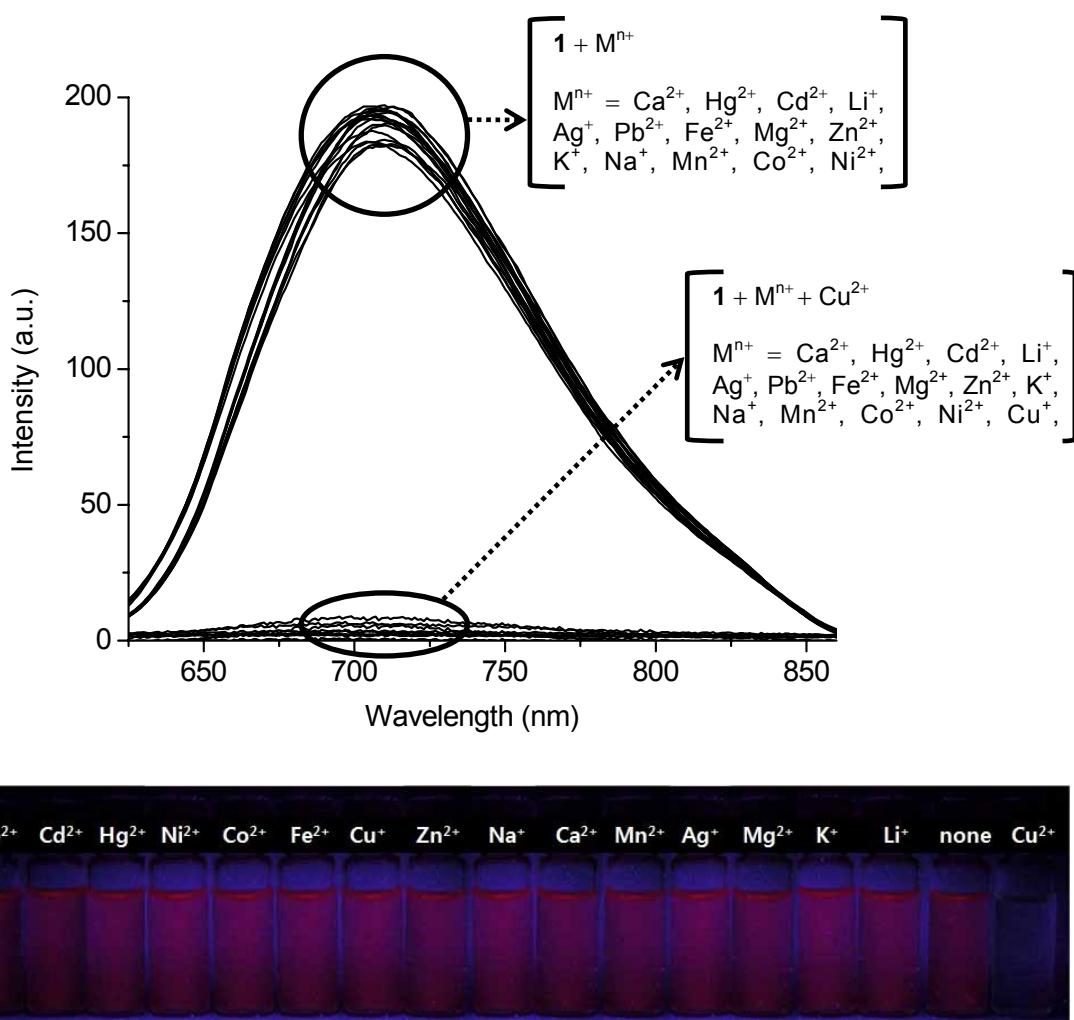
**Fig. S4** Job's plot of 1:1 complexes of **1** and  $Cu^{2+}$ . The pH value was adjusted by using 20 mM HEPES (10%  $CH_3CN$ ), pH 7.4.



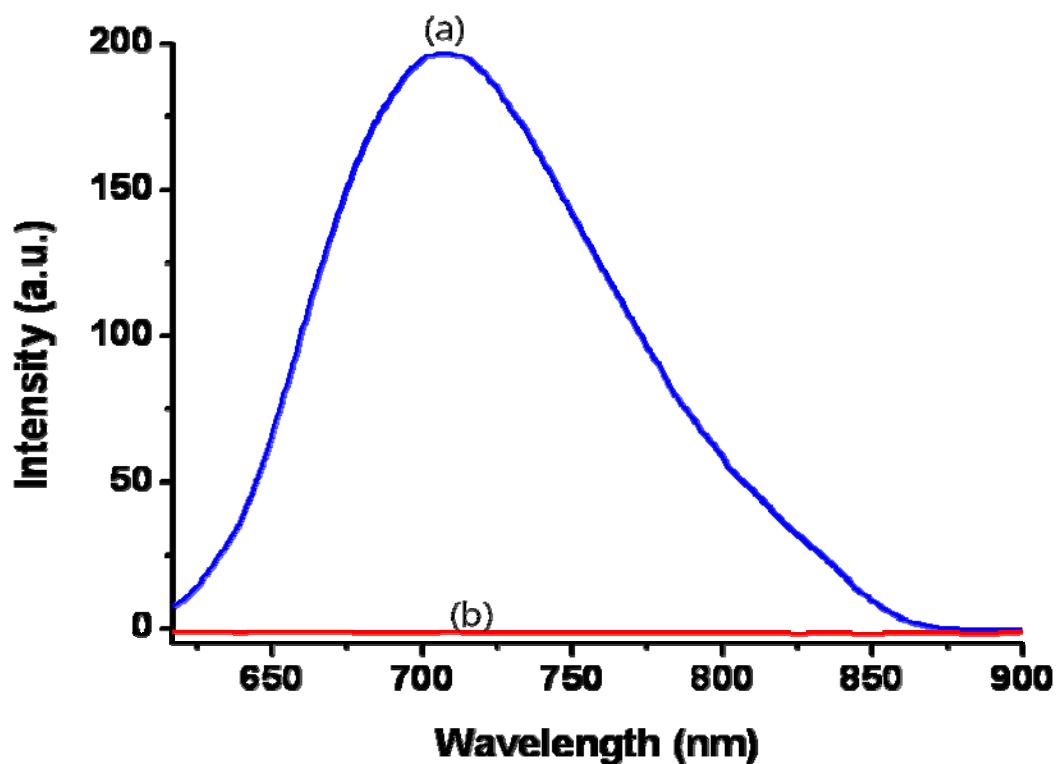
**Fig. S5** Fluorescence spectra of **1** ( $10 \mu M$ ) (a) without and (b) with  $Cu^{2+}$  ions and (c) after treatment with EDTA.



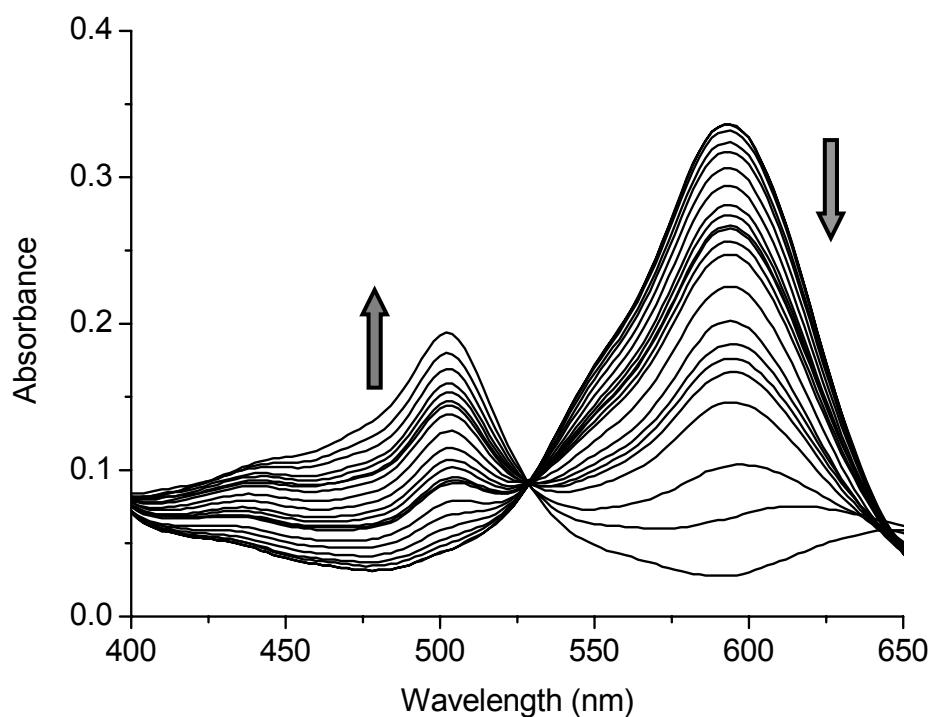
**Fig. S6** Absorption spectra of **1** (10  $\mu$ M) upon addition of Ca<sup>2+</sup>, Hg<sup>2+</sup>, Cd<sup>2+</sup>, Li<sup>+</sup>, Ag<sup>+</sup>, Pb<sup>2+</sup>, Fe<sup>2+</sup>, Mg<sup>2+</sup>, Zn<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup>, Mn<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup> and Cu<sup>+</sup> (4 equiv) in aqueous solution. Absorption spectra of **1** (10  $\mu$ M) upon addition of Ca<sup>2+</sup>, Hg<sup>2+</sup>, Cd<sup>2+</sup>, Li<sup>+</sup>, Ag<sup>+</sup>, Pb<sup>2+</sup>, Fe<sup>2+</sup>, Mg<sup>2+</sup>, Zn<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup>, Mn<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup> and Cu<sup>+</sup> (4 equiv), and subsequent addition of Cu<sup>2+</sup> (8 equiv) in aqueous solution. For all measurements, the pH value was adjusted by using 20 mM HEPES (10% CH<sub>3</sub>CN), pH 7.4. The inset is visual color changes upon addition of metal ions.



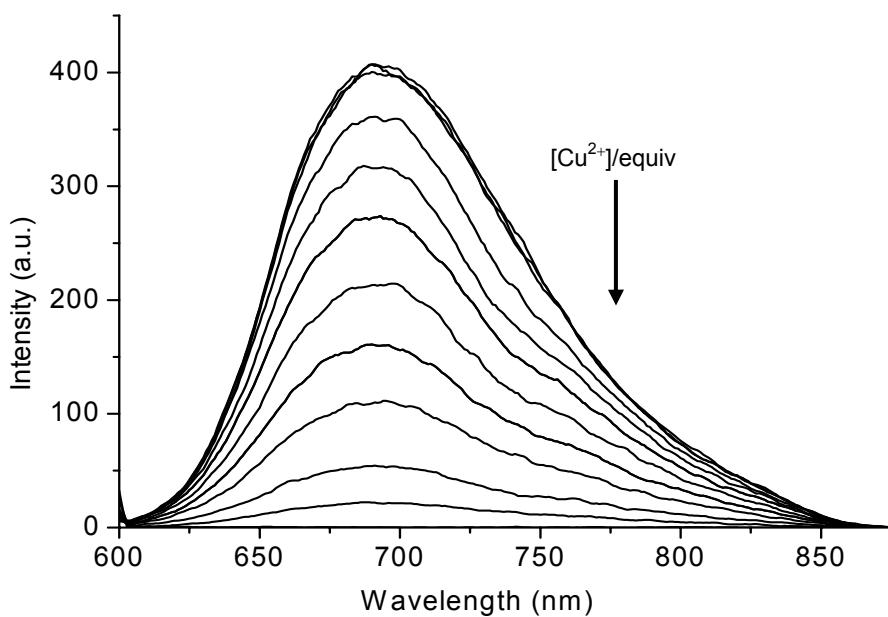
**Fig. S7** Fluorescence responses of **1** (10  $\mu$ M) upon addition of  $\text{Ca}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Li}^+$ ,  $\text{Ag}^+$ ,  $\text{Pb}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cu}^+$  (8 equiv) in aqueous solution. Fluorescence responses of **1** (10  $\mu$ M) upon addition of  $\text{Ca}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Li}^+$ ,  $\text{Ag}^+$ ,  $\text{Pb}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cu}^+$  (8 equiv), and subsequent addition of  $\text{Cu}^{2+}$  (8 equiv) in aqueous solution. For all measurements, the pH value was adjusted by using 20 mM HEPES (10%  $\text{CH}_3\text{CN}$ ), pH 7.4. Excitation was provided at 598 nm, and the emission was monitored at 704 nm. The inset is visual fluorescence changes upon addition of metal ions.



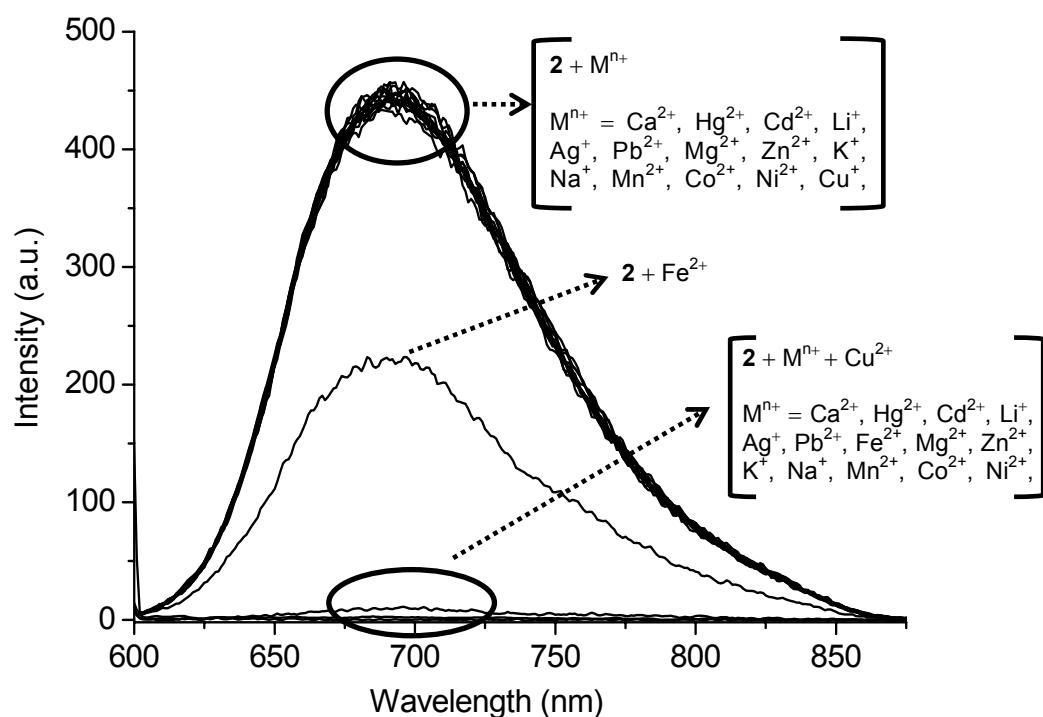
**Fig. S8** Fluorescence responses of 10  $\mu$ M **1** (a) without and (b) with  $\text{Cu}^{2+}$  ion ((100  $\mu$ M) in the presence of cysteine (100  $\mu$ M) and glutathione (100  $\mu$ M) in 20 mM HEPES (10%  $\text{CH}_3\text{CN}$ ) at pH 7.4 ( $\lambda_{\text{ex}} = 598$  nm).



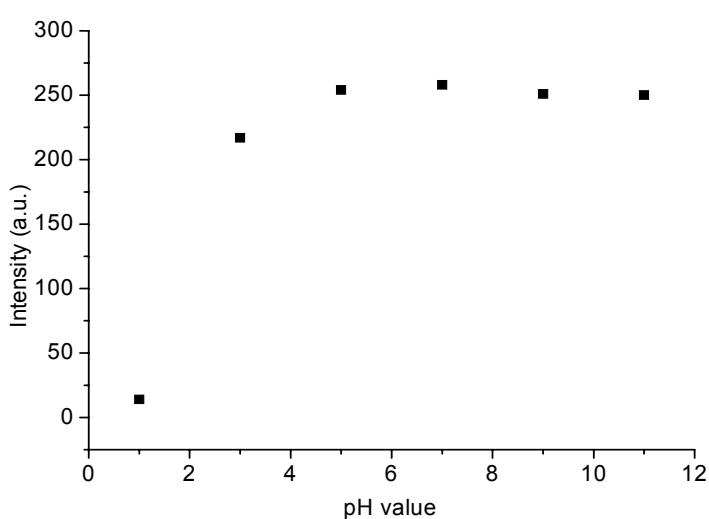
**Fig. S9** Absorption spectra of **2** ( $10 \mu\text{M}$ ) upon addition of increasing  $\text{Cu}^{2+}$  concentrations (0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2, 1.4, 1.6, 1.8, 2.0, 2.5, 3.0, 3.5 and 4.0 equiv) in acetonitrile.



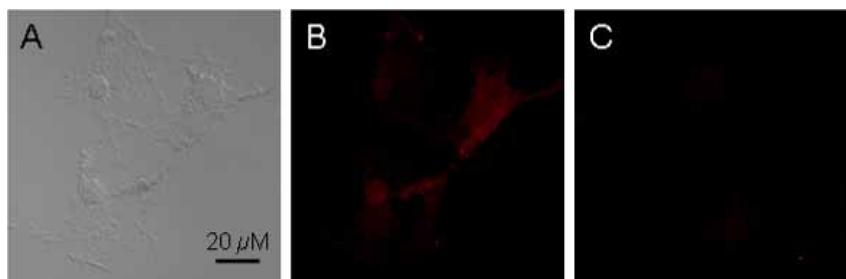
**Fig. S10** Fluorescence responses of **2** ( $10 \mu\text{M}$ ) upon addition of increasing  $\text{Cu}^{2+}$  concentrations (0, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0, 1.5, 2.0, 2.5, 3.0, 4.0 equiv) in acetonitrile. Excitation was provided at 596 nm, and the emission was monitored at 691 nm.



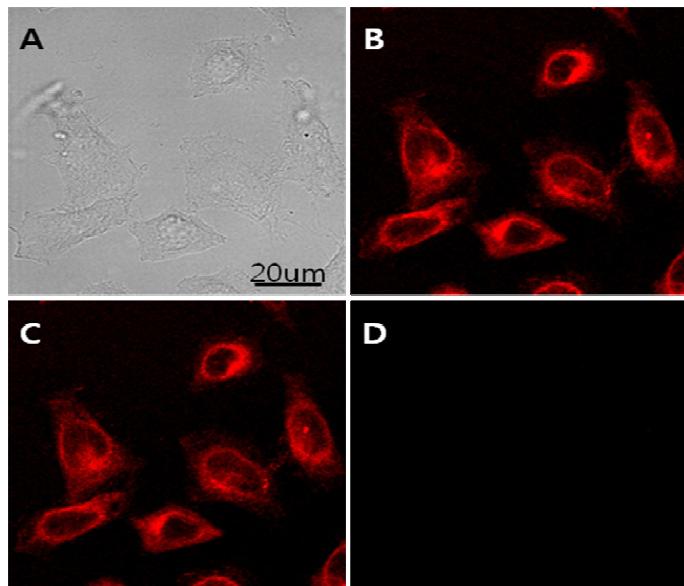
**Fig. S11** Fluorescence responses of **2** ( $10 \mu\text{M}$ ) upon addition of  $\text{Ca}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Li}^+$ ,  $\text{Ag}^+$ ,  $\text{Pb}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cu}^+$  (10 equiv) in acetonitrile. Fluorescence responses of **2** ( $10 \mu\text{M}$ ) upon addition of  $\text{Ca}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Li}^+$ ,  $\text{Ag}^+$ ,  $\text{Pb}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cu}^+$  (10 equiv), and subsequent addition of  $\text{Cu}^{2+}$  (10 equiv) in acetonitrile. Excitation was provided at 596 nm, and the emission was monitored at 691 nm.



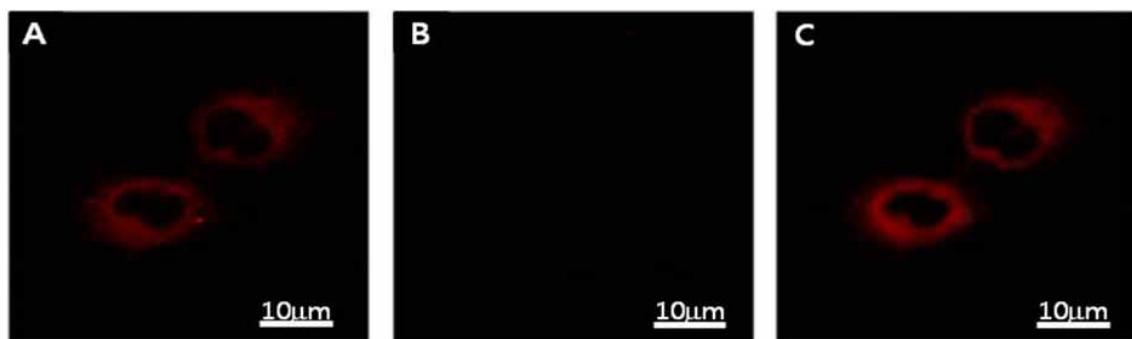
**Fig. S12** Plot of pH values against fluorescence intensity of **1**.



**Fig. S13** Confocal fluorescence images of live Cos-7 cells. The excited light is 633 nm, and the emission is centered at 650 nm. (A) Bright-field transmission image of Cos-7 cells. (B) Fluorescence image of Cos-7 cells incubated with 5  $\mu$ M **1** (0.5% CH<sub>3</sub>CN) at 37 °C. (C) Fluorescence image of Cos-7 cells further incubated with 5  $\mu$ M Cu(ClO<sub>4</sub>)<sub>2</sub> for 1 h at 37 °C.



**Fig. S14** Confocal fluorescence images of live Hela cells. The excited light is 633 nm, and the emission is centered at 650 nm. (A) Bright-field transmission image of Hela cells. (B) Fluorescence image of Hela cells incubated with 5  $\mu$ M **1** (0.5% CH<sub>3</sub>CN). (C) Fluorescence image of **1**-loaded Hela cells further incubated with 5  $\mu$ M Zn(ClO<sub>4</sub>)<sub>2</sub>, Ca(ClO<sub>4</sub>)<sub>2</sub>, and Cd(ClO<sub>4</sub>)<sub>2</sub> for 1 h at 37 °C. (D) Fluorescence image of Hela cells further incubated with 5  $\mu$ M Cu(ClO<sub>4</sub>)<sub>2</sub> for 1 h in the presence of 5  $\mu$ M Zn(ClO<sub>4</sub>)<sub>2</sub>, Ca(ClO<sub>4</sub>)<sub>2</sub>, and Cd(ClO<sub>4</sub>)<sub>2</sub> for 1 h at 37 °C.



**Fig. S15** Confocal fluorescence images of living HeLa cells. The excited light is 633 nm, and the emission is centered at 650 nm. (A) Fluorescence image of HeLa cells incubated with 5  $\mu$ M **1** (0.5% CH<sub>3</sub>CN) at 37 °C. (B) Fluorescence image of **1**-loaded HeLa cells incubated with 5  $\mu$ M Cu<sup>2+</sup> ion at 37 °C. (C) Fluorescence image of **1**+Cu<sup>2+</sup> loaded HeLa cells further incubated with 5  $\mu$ M EDTA at 37 °C.