

## A Selective and Ratiometric Cu<sup>2+</sup> Fluorescent Probe Based on Naphthalimide Excimer-Monomer Switching

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### General methods

Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. Flash chromatography was carried out on silica gel 60 (230-400 mesh ASTM; Merck). Thin layer chromatography (TLC) was carried out using Merck 60 F<sub>254</sub> plates with a thickness of 0.25 mm. Preparative TLC was performed using Merck 60 F<sub>254</sub> plates with the thickness of 1 mm.

Melting points were measured using a Büchi 530 melting point apparatus. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded using Bruker 250 MHz or Varian 500 MHz. Chemical shifts were given in ppm and coupling constants (*J*) in Hz. UV absorption spectra were obtained on UVIKON 933 Double Beam UV/VIS Spectrometer. Fluorescence emission spectra were obtained using RF-5301/PC Spectrofluorophotometer (Shimadzu).

### Synthesis

#### 2,2'-(piperazine-1,4-diyl)bis(N-(2-butyl-1,3-dioxo-2,3-dihydro-1H-benzo[de]isoquinolin-6-yl)acetamide) (1)

4-(2-chloroacetyl)amino-*N*-n-butyl-1,8-naphthalimide (100 mg, 0.29 mmol), piperazine (12 mg, 0.145 mmol), *N,N*-diisopropylethylamine (DIPEA) (0.5 mL) and potassium iodide (30 mg) were added to acetonitrile (30 mL). After stirred and refluxed for 10 h under nitrogen atmosphere, the mixture was cooled to room temperature and the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (CH<sub>2</sub>Cl<sub>2</sub>:MeOH = 100:1) to afford **1**. Yield: 78 mg (77%). Mp: 171-173 °C. <sup>1</sup>H-NMR (DMSO, 400 MHz) δ 0.97 (t, *J* = 7.2 Hz, 6H), 1.41 (m, *J* = 7.2 Hz, 4H), 1.67 (m, *J* = 7.2 Hz, 4H), 2.86 (s, 8H), 3.48 (s, 4H), 4.09 (t, *J* = 7.2 Hz, 4H), 7.98 (t, *J* = 6.2 Hz, 2H), 8.43 (d, *J* = 6.2 Hz, 2H), 8.52-8.60 (m, 6H), 10.58 (s, 2H). <sup>13</sup>C-NMR (DMSO, 100 MHz) δ 13.82, 19.89, 22.18, 29.38, 28.40, 29.76, 31.37, 122.51, 124.56, 126.89, 128.40, 129.19, 129.74, 131.13, 131.56, 131.57, 132.65, 162.99, 163.52, 169.22. HRMS (ESI) calcd for C<sub>40</sub>H<sub>43</sub>N<sub>6</sub>O<sub>6</sub> [MH<sup>+</sup>] 703.3244, found 703.3249.

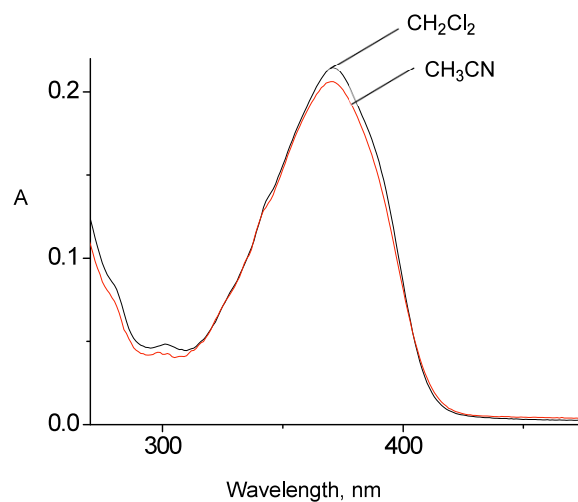


Figure S1. UV-Vis absorption spectra of **1** in  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_3\text{CN}$ .

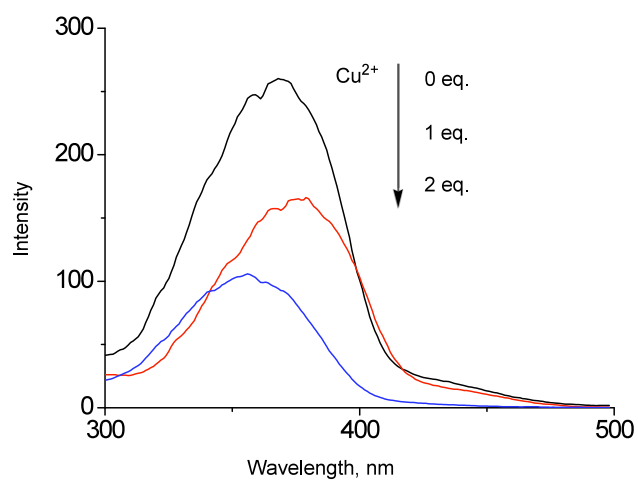


Figure S2. Fluorescence excitation spectra of **1** and **1**/ $\text{Cu}^{2+}$  complex in  $\text{CH}_3\text{CN}$ .

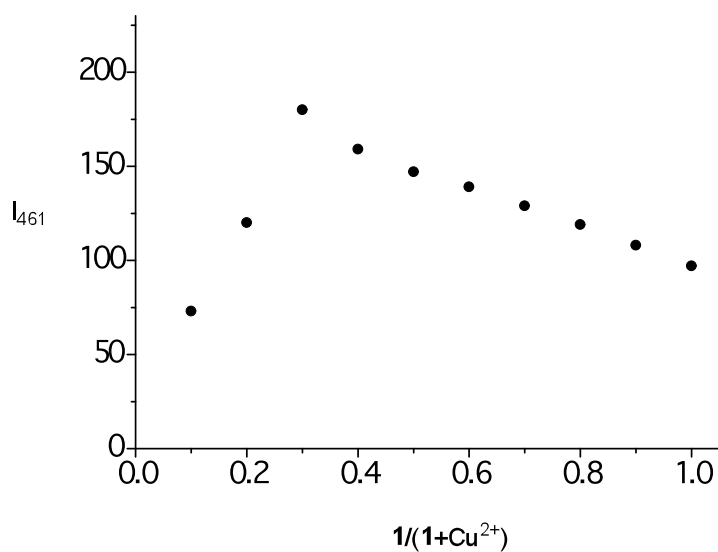


Figure S3. Job's plot of **1** in aqueous solutions ( $CH_3CN$ :HEPES = 50:50; HEPES, 0.5 M, pH 7.4) showing the 2:1 stoichiometry of the complex between  $Cu^{2+}$  ion and **1**. The total concentration of sensor and  $Cu^{2+}$  is 10  $\mu M$ . Fluorescence is recorded at 461 nm.

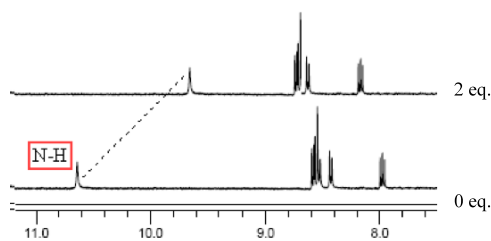


Figure S4.  $^1H$ -NMR spectra of **1** in the presence of a different amount of  $Zn^{2+}$  in  $CD_3CN$ .

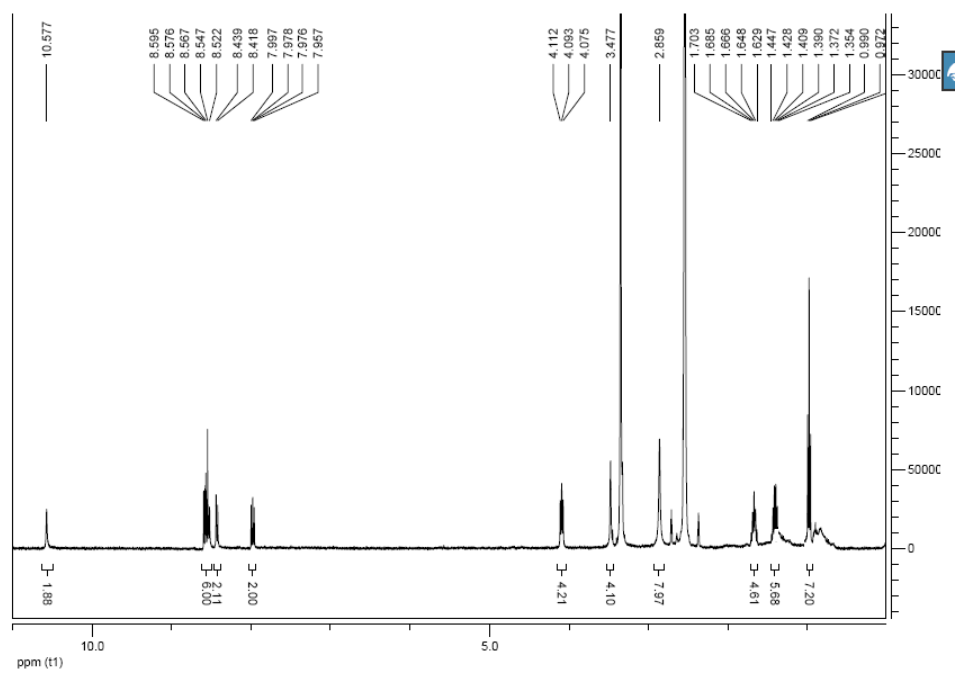


Figure S5.  $^1\text{H-NMR}$  spectra of compound **1** in DMSO.

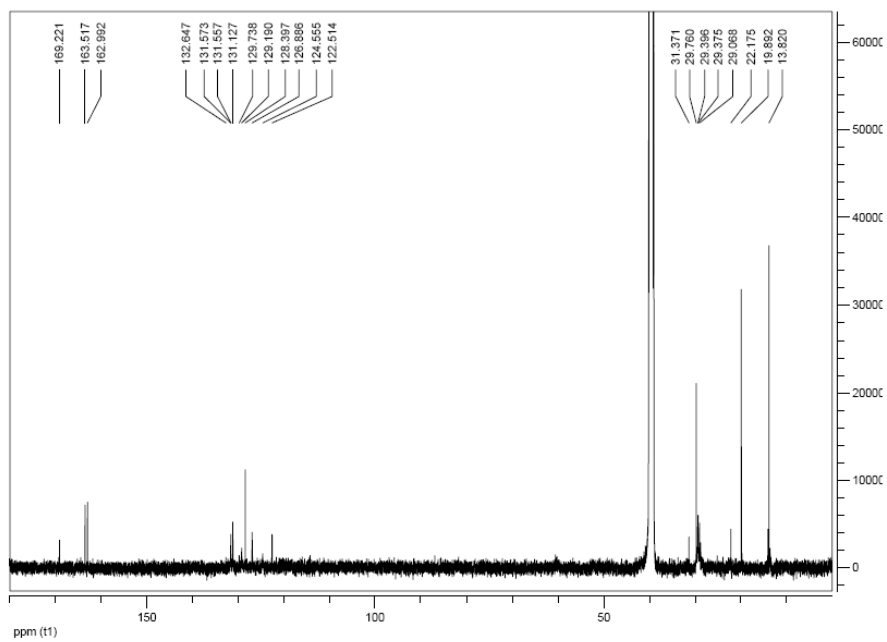


Figure S6.  $^{13}\text{C-NMR}$  spectra of compound **1** in DMSO.