Supporting Information (SI)

A colorimetric "naked-eye" Cu(II) chemosensor and pH indicator in an 100% aqueous solution.

Jin Young Noh, Gyeong Jin Park,* Yu Jeong Na, Hyun Yong Jo, Seul Ah Lee, Cheal Kim*

Department of Fine Chemistry, Seoul National University of Science and Technology, Seoul 139-743, Korea. Fax: +82-2-973-9149; Tel: +82-2-970-6693; E-mail: qkrdn112@naver.com and chealkim@seoultech.ac.kr

1. Materials and Instrumentation.

All solvents and reagents were obtained from TCI or Aldrich. ^{1}H NMR and ^{13}C NMR measurements were performed on a Varian 400 MHz spectrometer and chemical shifts are recorded in ppm. Absorption spectra were recorded at 25°C using a Perkin Elmer model Lambda 2s UV-vis spectrometer. Electrospray ionization mass spectra (ESI-MS) were collected on a Thermo Finnigan (San Jose, CA, USA) LCQ™ Advantage MAX quadruple ion trap instrument. Elemental analysis for carbon, nitrogen, and hydrogen was carried out by using a Flash EA 1112 elemental analyzer (thermo) in Organic Chemistry Research Center of Sogang University, Korea.

2. Synthesis of the receptor 1

A solution of triaminoguanidinium chloride (0.7 g, 5 mmol) in distilled water was added to a solution containing furfural (423 μL, 5 mmol) in ethanol. The mixture was refluxed for 4 h under nitrogen. The solution was then cooled to room temperature and the solvent was evaporated. The beige product was recrystallized from acetonitrile. The yield was 85 % (1.61 g). ^{1}H NMR (methanol-d_4, 400 MHz) δ:12.2 (s, 3H), 8.67 (s, 3H), 7.97 (s, 3H), 7.22 (d, 3H), 6.74 (t, 3H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 148.58, 148.38, 146.3, 140.6, 116.03, 112.75. Calcd for $C_{16}H_{15}ClN_6O_3$ (374.78): C, 51.28; H, 4.03; N, 22.42%. Found: C, 51.39; H, 4.47; N, 22.27%. FAB MS m/z (M^+) : calcd, 339.12; found, 339.13.

3. Preparation of 1-Cu^{2+}, 1-Ni^{2+} and 1-Cd^{2+} complexes

$Cu(NO_3)_2 \cdot 2.5H_2O$ (0.28 g, 1.2 mmol) was added to a stirred solution of receptor **1** (0.37 g, 1 mmol) in methanol (30 mL). The solution was stirred for 1 day at room temperature until the precipitate appeared. The resulting precipitate was filtered and washed 5 times with diethyl ether. **1**-Ni^{2+} and **1**-Cd^{2+} complexes were also synthesized in the same way above. $Ni(NO_3)_2 \cdot 4H_2O$ (0.37 g, 1.2 mmol) and $Cd(NO_3)_2 \cdot 4H_2O$ (0.35 g, 1.2 mmol) were used as metal sources.

4. UV-vis titration measurements

Receptor **1** (1.87 mg, 0.005mmol) was dissolved in distilled water (DW, 0.5 mL) and 9 μL of the receptor **1** (10 mM) were diluted with 2.991 mL bis-tris buffer solution to make the final concentration of 30 μM. $Cu(NO_3)_2$ (11.9 mg, 0.05mmol) was dissolved in DW (5 mL). 1.8-63 μL of the Cu^{2+} solution (10 mM) were transferred to receptor **1** solution (30 μM) prepared above. After mixing them for a few seconds, UV-vis absorption spectra were taken at room temperature.

5. Job plot measurement

Receptor **1** (1.87 mg, 0.005 mmol) was dissolved in DW (0.5 mL). 50, 45, 40, 35, 30, 25, 20, 15, 10, 5 and 0 μL of the receptor **1** solution were taken and transferred to vials. Each vial was diluted with buffer solution to make a total volume of 4.950 mL. $Cu(NO_3)_2$ (1.19 mg, 0.005 mmol) was dissolved in bis-tris buffer (5 mL). 0, 5, 10, 15, 20, 25, 30, 35, 40, 45 and 50 μL of the $Cu(NO_3)_2$ solution were added to each diluted receptor **1** solution. Each vial had a total volume of 5 mL. After shaking the vials for a few minutes, UV-vis absorption spectra were taken at room temperature.

6. Competitive experiments

Receptor **1** (1.87 mg, 0.005 mmol) was dissolved in DW (0.5 mL) and 9 μL of the receptor **1** (10 mM) were diluted with 2.991 mL bis-tris buffer solution to make the final concentration of 30 μM. $M(NO_3)$ (M = Na, K 0.018 mmol), $M(NO_3)_2$ (M = Mn, Co, Ni, Cu, Zn, Cd, Mg, Ca, Pb, 0.018 mmol), $M(ClO_3)_2$ (M = Fe, 0.018 mmol) or $M(NO_3)_3$ (M = Al, Ga, In, Fe, Cr, 0.018 mmol) were dissolved in bis-tris buffer (10 mL), respectively. 30 μL of each metal solution (18 mM) were taken and added into 3 mL of each receptor **1** solution (30 μM) prepared above to make 6 equiv. Then, 30 μL of $Cu(NO_3)_2$ solution (18 mM) were added into the mixed solution of each metal ion and receptor **1** to make 6 equiv. After mixing them for a minute, fluorescence spectra were taken at room temperature.

7. pH titration

Receptor **1** (1.87 mg, 0.005 mmol) was dissolved in DW (0.5 mL) and 9 μL of the receptor **1** (10 mM) were diluted to nine bis-tris buffer solutions (2.991 mL) with different pH values (2, 3, 4, 5, 5.1, 5.2, 5.3, 5.4, 5.5, 5.6, 5.7, 5.8, 5.9, 6, 7, 8, 9, 10, 11 and 12) to make the final concentration of 30 μM. $Cu(NO_3)_2$ (4.28 mg, 0.018mmol) was dissolved in bis-tris buffer solution (1mL). 30 μL of the copper solution (18 mM) were taken and added into receptor **1** in bis-tris buffer solutions (30 μM) prepared above to make 6 equiv. After mixing them for a few minutes, UV-vis absorption spectra were taken at room temperature.

8. Practical applications with the environmental samples

Receptor **1** (1.87 mg, 0.005 mmol) was dissolved in DW (0.5 mL) and 9 μL of the receptor **1** (10 mM) were diluted to three samples (2.991 mL, distilled water, tap water and soda) to make the final concentration of 30 μM. $Cu(NO_3)_2$ (4.28 mg, 0.018mmol) was dissolved in bis-tris buffer solution (1mL). 30 μL of the copper solution (18 mM) were taken and added into the three samples, distilled water, tap water and soda (30 μM), prepared above. After shaking the vials for a few minutes, the samples were observed by naked-eye.

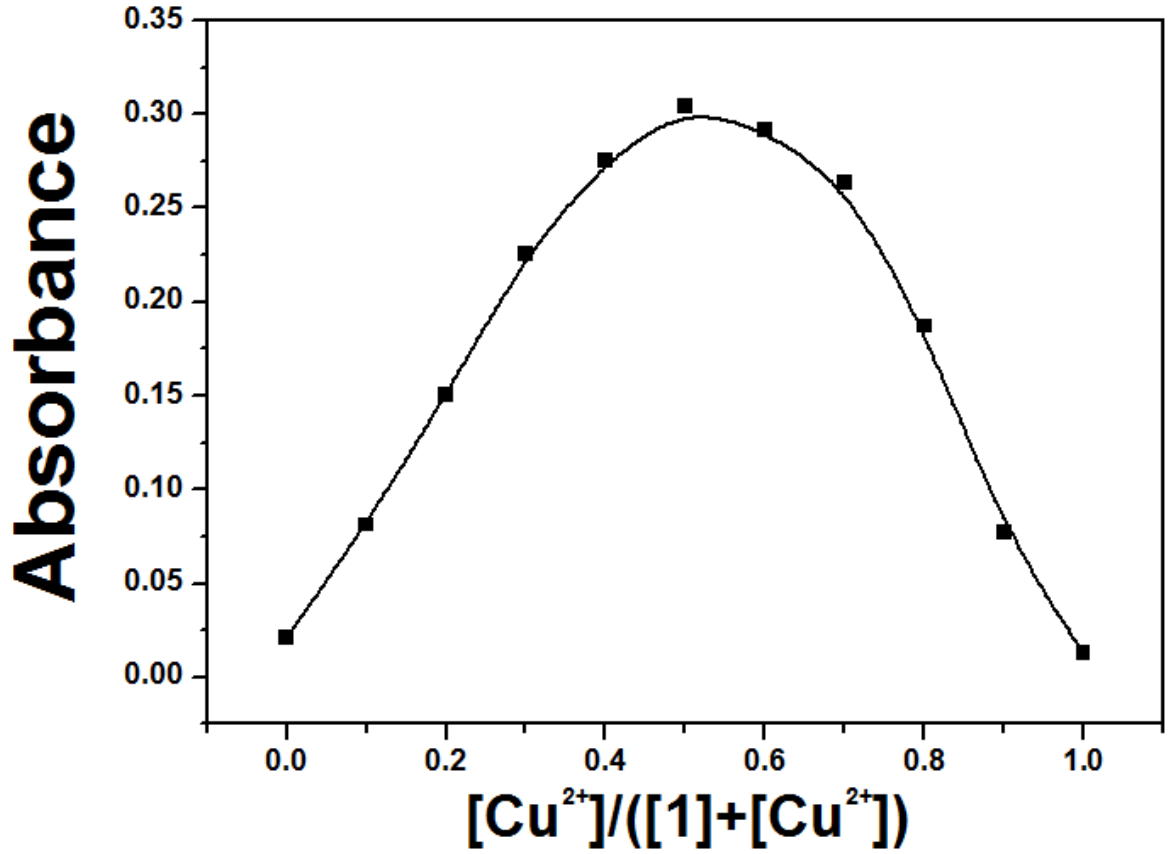

Fig. S1. Job plot for the binding of **1** with Cu^{2+}. Absorbance at 420 nm was plotted as a function of the molar ratio $[Cu^{2+}]/([\mathbf{1}] + [Cu^{2+}])$. The total concentration of copper ions with receptor **1** was 3.0×10^{-5} M

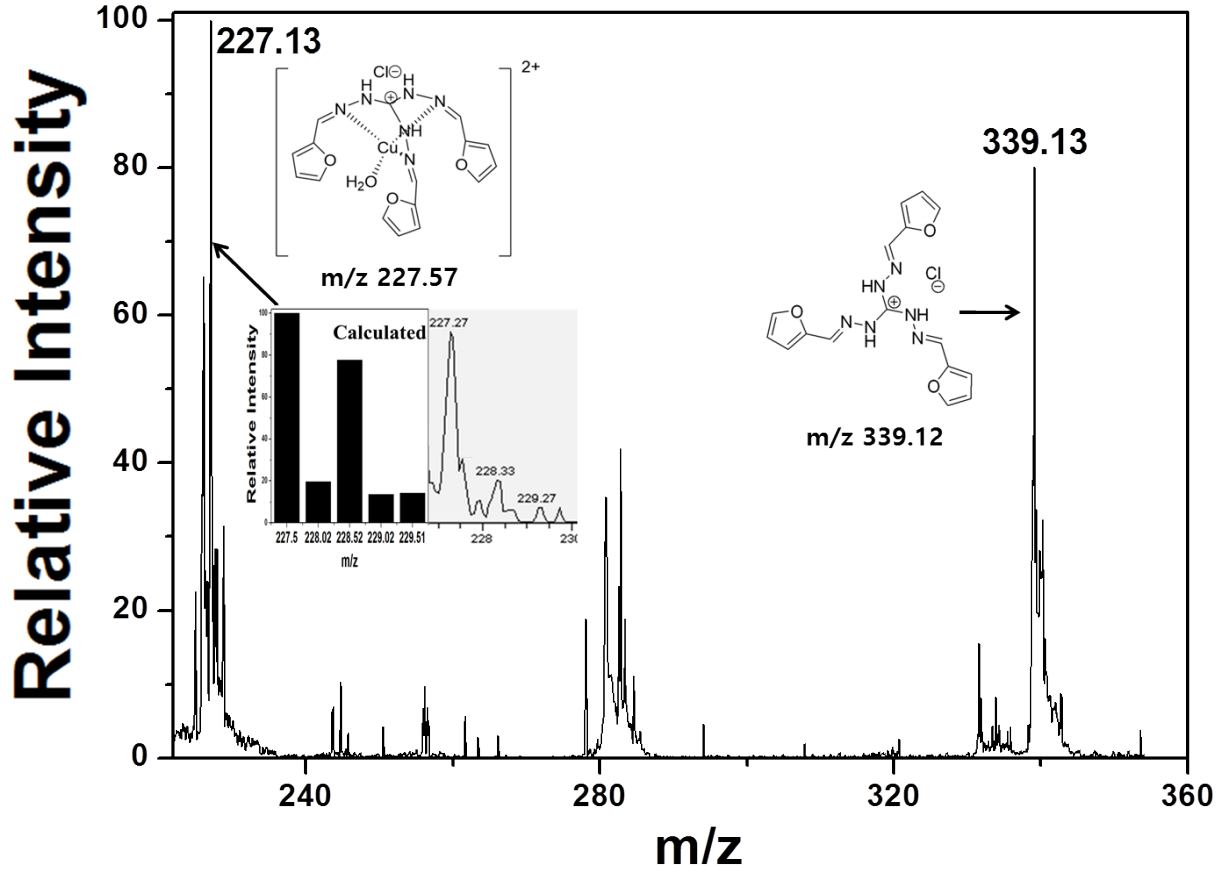

Fig. S2. Positive-ion electrospray ionization mass spectrum of **1** upon addition of $Cu(NO_3)_2$ (1.0 equiv) in CH_3OH.

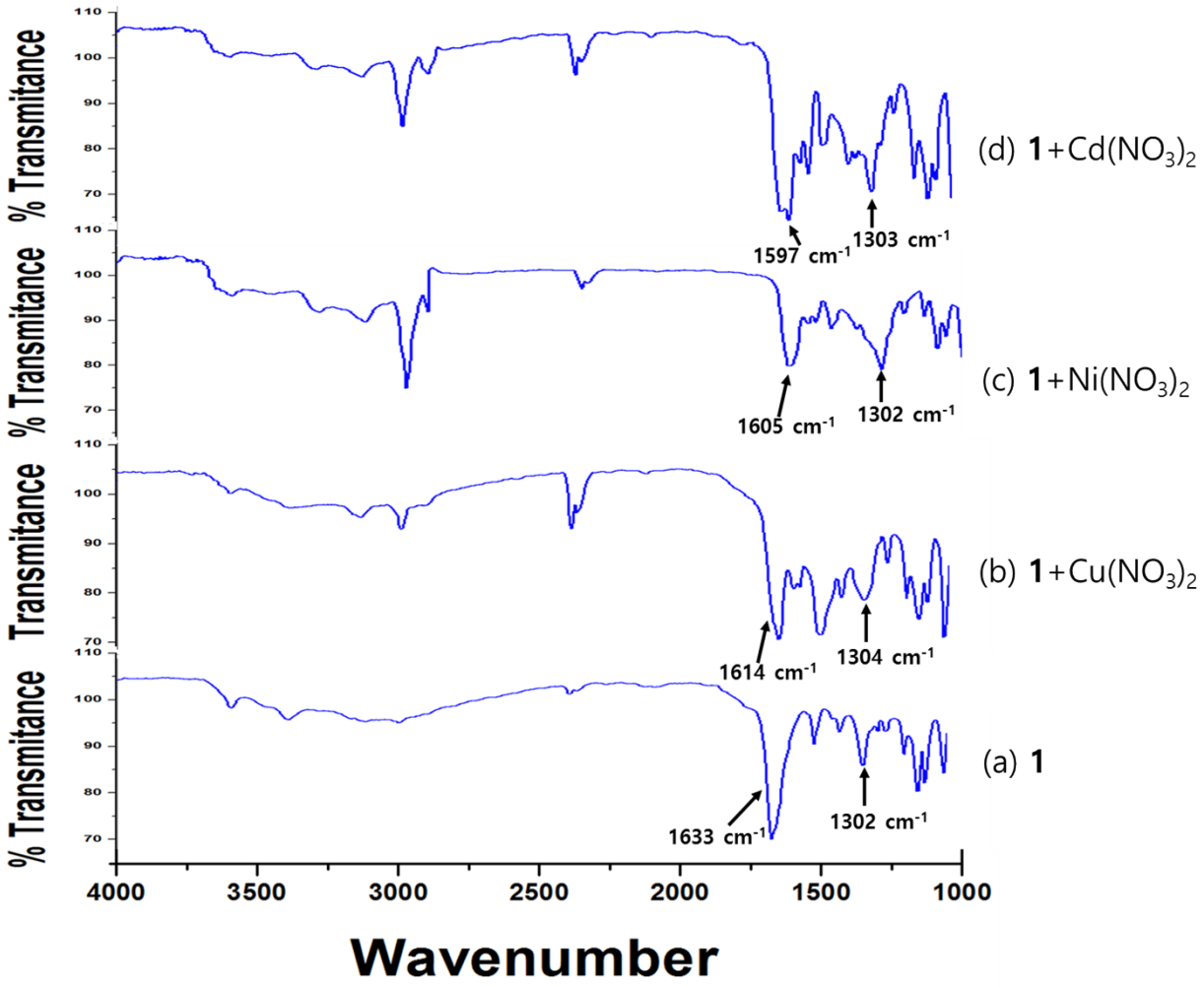

Fig. S3. IR spectra of **1**, **1**-Cu^{2+}, **1**-Ni^{2+} and **1**-Cd^{2+} complexes.

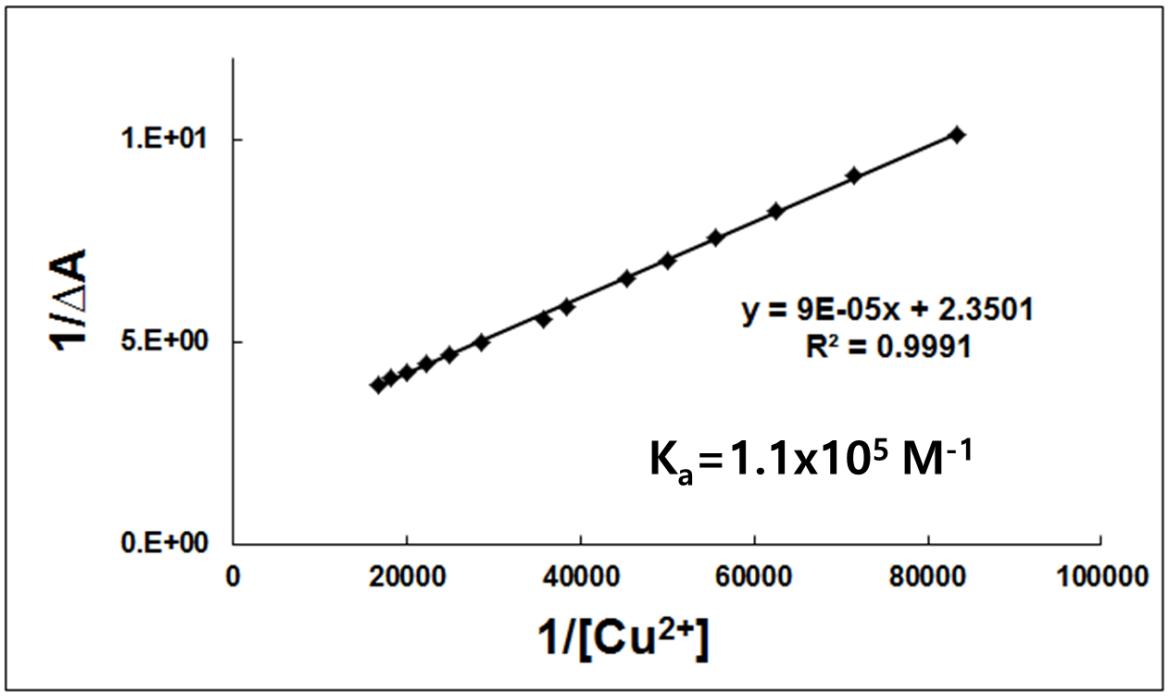

Fig. S4. Benesi-Hildebrand plot (absorbance at 311 nm) of **1** (10 μM), assuming 1:1 stoichiometry for association between **1** and Cu^{2+}.

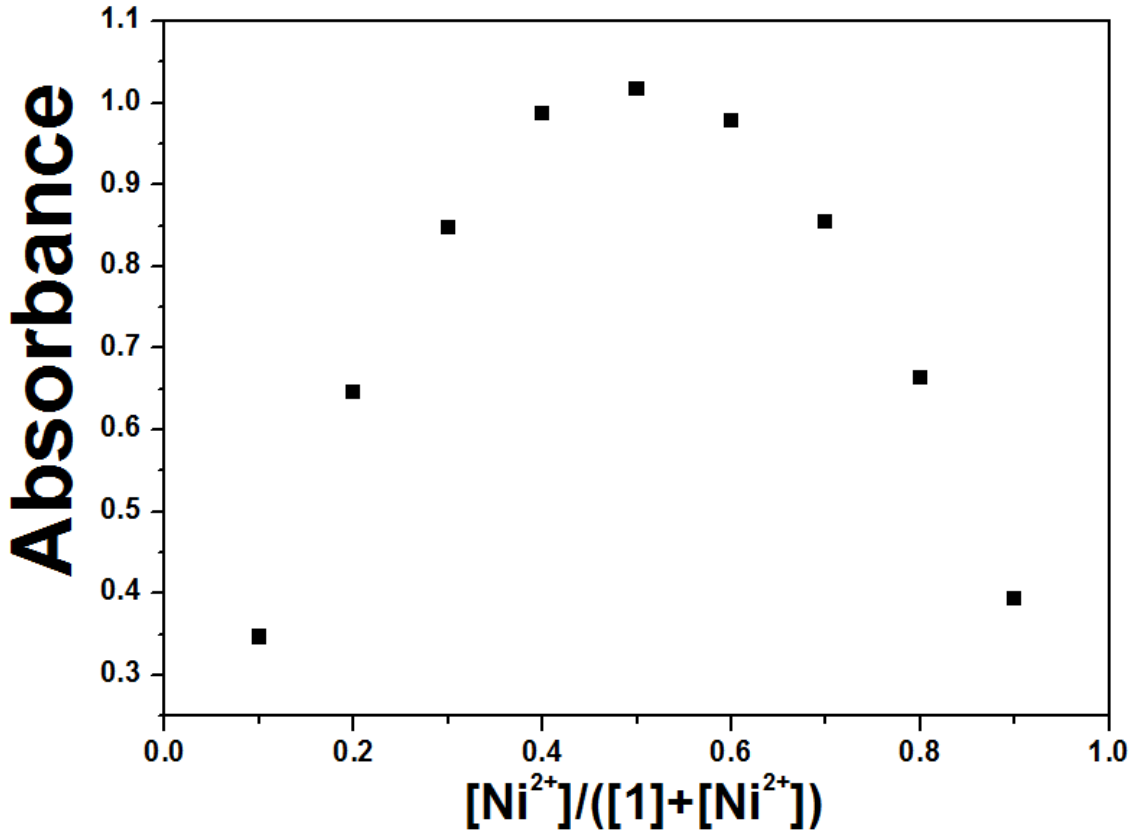

Fig. S5. Job plot for the binding of **1** with Ni^{2+}. Absorbance at 485 nm was plotted as a function of the molar ratio $[Ni^{2+}]/([\mathbf{1}] + [Ni^{2+}])$. The total concentration of nickel ions with receptor **1** was 3.0×10^{-4} M

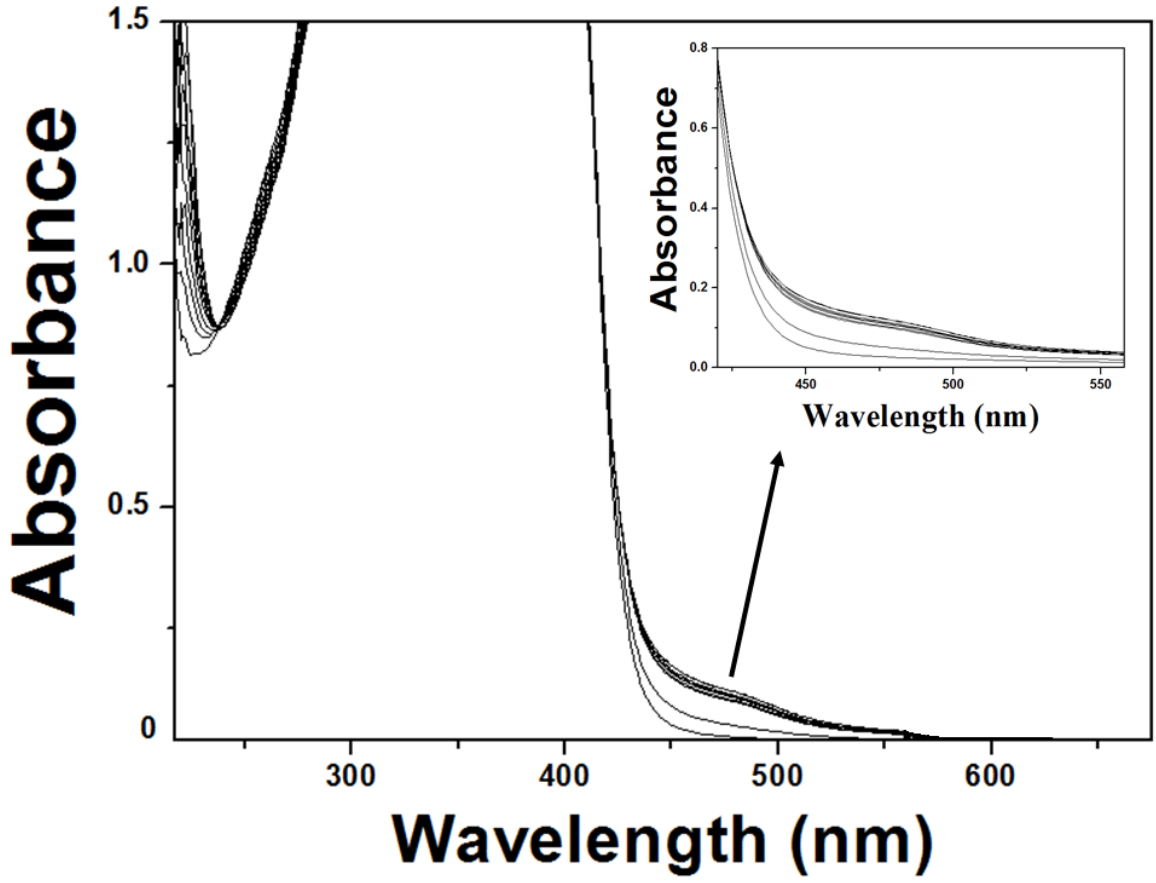

Fig. S6. UV-Vis spectra changes of **1** (120 μM) in the presence of different concentrations of Ni^{2+} ions in buffer-DW (999:1, v/v) solution. Inset: the enlarged spectra from 420 to 560 nm.

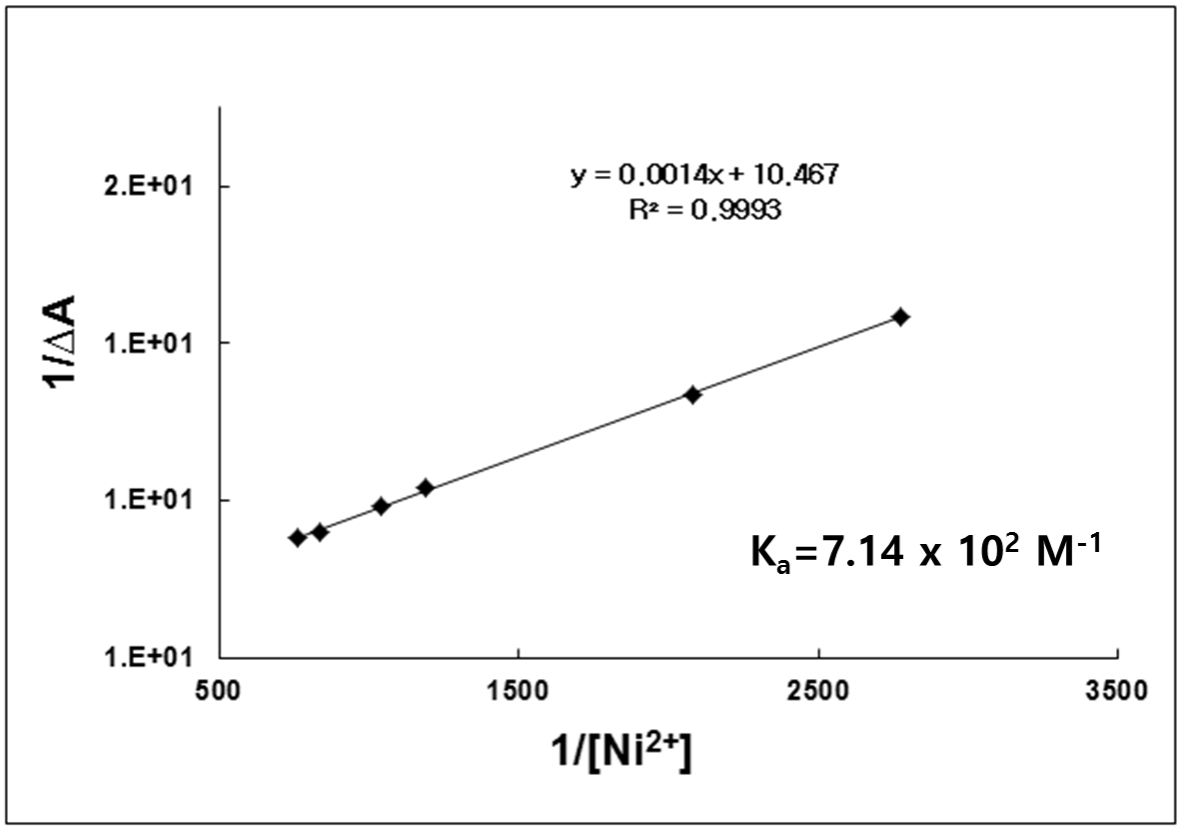

Fig. S7. Benesi-Hildebrand plot (absorbance at 485 nm) of **1** (120 μM), assuming 1:1 stoichiometry for association between **1** and Ni^{2+}.

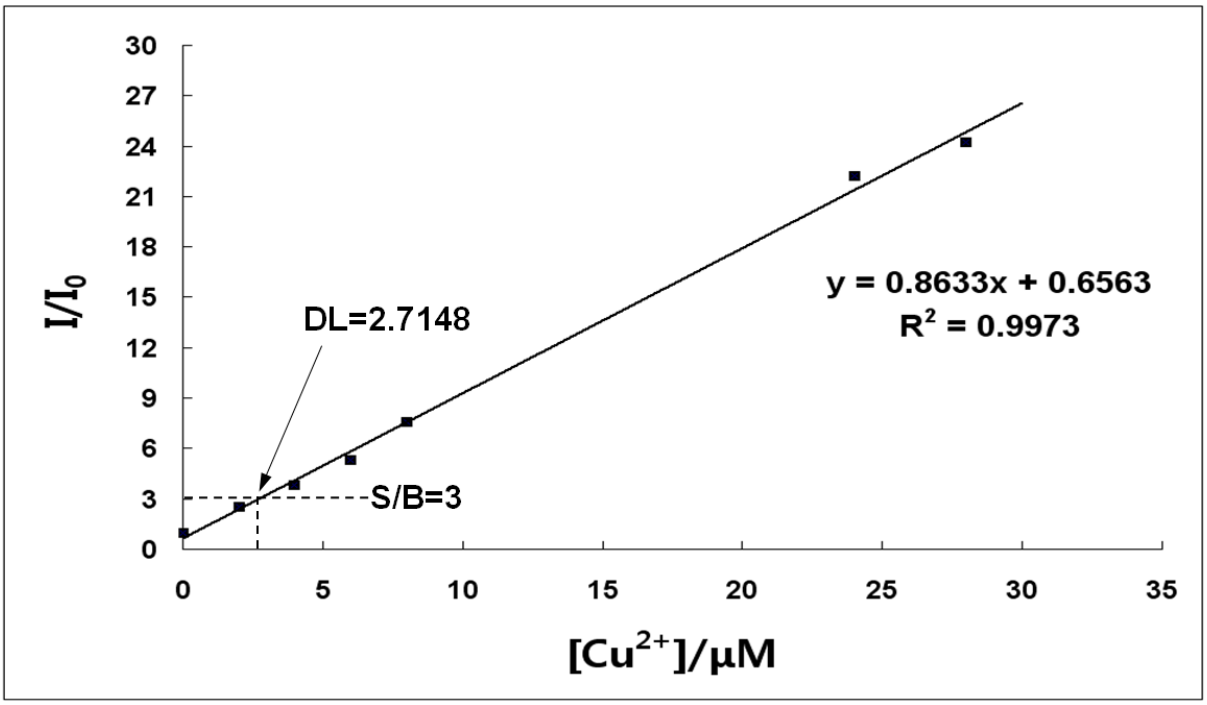

Fig. S8. Determination of the detection limit based on change in the ratio (absorbance at 420 nm) of **1** (30 μM) with Cu^{2+}.

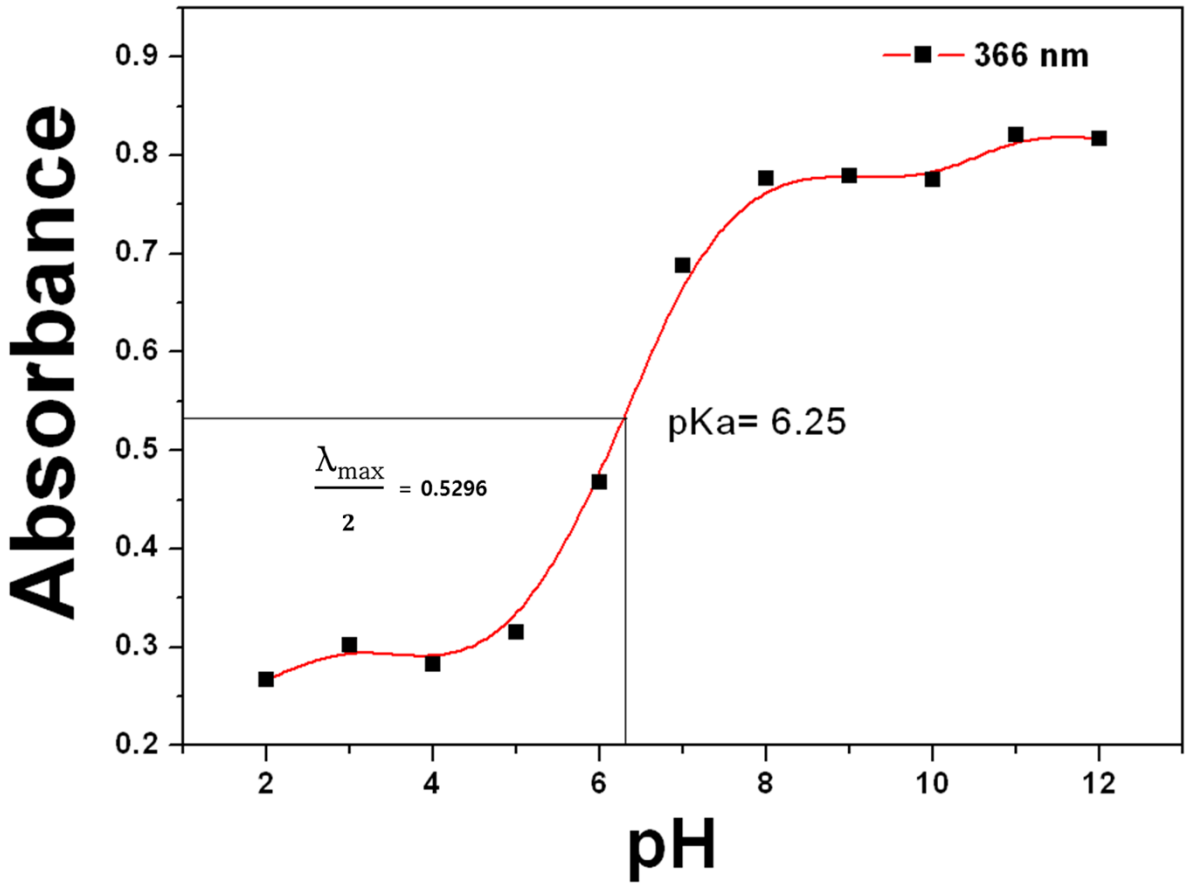

Fig. S9. Determination of the pK_a value of receptor **1.** The absorbance taken at 366 nm was plotted against the pH of the solution.