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A phthalazine-based two-in-one chromogenic receptor for detecting Co^{2+} and Cu^{2+} in aqueous environment

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Abstract

A new multifunctional and highly selective chemosensor **1** for Co^{2+} and Cu^{2+} was designed and synthesized. **1** could simultaneously detect both Co^{2+} and Cu^{2+} by changing its color from pale yellow to pink and to orange, respectively, in a near-perfect aqueous solution. The binding modes of **1** to Co^{2+} and Cu^{2+} were determined to be a 2:1 complexation stoichiometry through Job plot, ESI-mass spectrometry analysis and ^1H NMR titration. The detection limits (1.5 and 2.1 μM) of **1** for Co^{2+} and Cu^{2+} were lower than the DEP guideline (1.7 μM for Co^{2+}) and the WHO guideline (31.5 μM for Cu^{2+}) for the drinking water. The chemosensor **1** could be used to quantify Co^{2+} and Cu^{2+} in water samples. Moreover, **1** could be used as a practical, visible colorimetric test kits for both Co^{2+} and Cu^{2+}. The sensing mechanisms of Co^{2+} and Cu^{2+} by **1** were supported by theoretical calculations.

Keywords: cobalt ion, copper ion, colorimetric chemosensor, phthalazine, test kit, theoretical calculation

1. Introduction

Cobalt ion plays an important role in the metabolism of iron and the synthesis of haemoglobin, and is also an important component of vitamin B12 and other biological compounds.[1-3] Apart from its biological role, exposure to high level of cobalt ion causes severe effects on human beings and animals. The toxicological effects of Co^{2+} on human beings include various diseases and disabilities such as asthma, decreased cardiac output, cardiac enlargement, heart disease, lung disease and vasodilation.[4-7] For these reasons, the determination of trace amounts of Co^{2+} in biological and environmental samples is essential.

Copper ion, as the third most abundant essential trace element in the human body, plays an important role in many fundamental physiological processes in organisms.[8,9] Copper ion dependent enzymes act as catalysts to help a number of body functions to provide energy for biochemical reactions, transform melanin for pigmentation of the skin, assist the formation of crosslinks in collagen and elastin, and thereby maintain and repair connective tissues.[10-12] However, with excessive loading, copper ion can cause extremely negative health effects such as gastrointestinal disturbance and liver or kidney damage.[13-15] Therefore, the development of new analytical methods for the selective determination of Cu^{2+} is also desirable.

Many approaches, such as inductively coupled plasma atomic emission spectrometry, atomic absorption spectroscopy, fluorescence techniques and electrochemical methods, have been employed to detect trace amounts of Co^{2+} and Cu^{2+}.[16-19] However, most of these methods require sophisticated equipment, tedious sample preparation procedures, and trained operators. In contrast, colorimetric methods can conveniently and easily monitor target ions with the naked eye.[20-23] Colorimetric methods have therefore attracted considerable attention in the detection of toxic metal ions including Co^{2+} and Cu^{2+}.[24-40] Compared with the many known colorimetric organic molecule sensors for Zn^{2+}, Cu^{2+} and Hg^{2+}, there are a few colorimetric chemosensors for Co^{2+}.[24-34] Among them, only two examples showed the sensing property for cobalt ion in a fully aqueous solution.[24,25] Therefore, there is a great need for the development of new colorimetric chemosensors that can detect Co^{2+} selectively and sensitively in fully aqueous solutions.

Schiff bases with π electrons in C=N group and nitrogen in aromatic ring offer a good possibility for chelation with transition metal ions. The chelation to transition metal ions would enhance ICT (intramolecular charge transfer) transition or make LMCT (ligand to metal charge transfer) transition, which could be utilized for the detection of transition metal ions.[3,9,16,21,41] In this regard, we expected that the presence of phthalazine and quinoline moieties in a Schiff base might be a good receptor toward the specific transition metal ions by a color change.[24,26,34,42-43]

Herein, we report on a new Schiff base chemosensor **1** with both the phthalazine and the quinoline groups. The receptor **1** exhibited an exclusive sensing property towards Co^{2+} and Cu^{2+} via color changes from pale yellow to pink and to orange in near-perfect aqueous solution. Moreover, the colorimetric test kits coated with **1** was used to simultaneously detect both Co^{2+} and Cu^{2+}. Additionally, the theoretical calculations supported the experimental data and the sensing mechanism.

Experimental section

General information. All the solvents and reagents (analytical grade and spectroscopic grade) were obtained from Sigma-Aldrich and used as received. ^{1}H NMR and ^{13}C N MR measurements were performed on a Varian 400 MHz and 100 MHz spectrometer, respectively and chemical shifts were recorded in ppm. Electrospray ionization mass s pectra (ESI-MS) were collected on a Thermo Finnigan (San Jose, CA, USA) LCQ_{TM} Advantage MAX quadruple ion trap instrument. Elemental analysis for carbon, nitroge n, and hydrogen was carried out by using a Flash EA 1112 elemental analyzer (ther mo) in Organic Chemistry Research Center of Sogang University, Korea. UV-vis spect ra were recorded at room temperature using a Perkin Elmer model Lambda 25 UV/Vi s spectrometer.

Synthesis of receptor 1. 1-Hydrazinophthalazine hydrochloride (0.401 g, 2 mmol) was dissolved in 35 mL of methanol, and quinolin-2-carboxaldehyde (0.340 g, 2.1 mmol) was added over 10 min. The solution was stirred for 1 h at 80 ^{o}C. The pale red product was

filtered and washed with methanol and ether. The yield: 0.628 g (88.8 %). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 14.4 (s, 1H), 9.20 (s, 1H), 9.16 (d, 1H), 9.01 (s, 1H), 8.85 (d, 1H), 8.63 (d, 1H), 8.20-8.11 (m, 4H), 8.07 (d, 1H), 7.88 (t, 1H), 7.72 (t, 1H). ^{13}C NMR (DMSO-d_6,100 MHz) δ 155.16 (s, 1C), 153.94 (s, 1C), 151.97 (s, 1C), 148.81 (s, 1C), 147.34 (s, 1C), 140.91 (s, 1C), 138.58 (s, 1C), 136.46 (s, 1C), 133.68 (s, 1C), 130.91 (m, 5C), 128.54 (s, 1C), 123.01 (s, 1C), 122.22 (s, 1C). LRMS (ESI): *m/z* calcd for $C_{18}H_{13}N_5$+H^+ ([M+H^+]), 300.12; found, 300.32. Anal. calcd for $C_{18}H_{13}N_5$ (343.42): C, 72.20; H, 4.38; N, 23.40; Found: C, 72.53; H, 4.31; N, 23.37.

UV-vis titration measurements of 1 with Co^{2+} ion. Receptor **1** (0.9 mg, 0.003 mmol) was dissolved in dimethyl sulfoxide (DMSO, 1 mL) and 10 μL of the receptor **1** (3 mM) was diluted to 2.990 mL bis-tris buffer solution to make the final concentration of 10 μM. $Co(NO_3)_2 \cdot 6H_2O$ (3.0 mg, 0.01mmol) was dissolved in bis-tris buffer (10 mL). 0.75 - 16 μL of the Co^{2+} solution (1 mM) was transferred to receptor **1** solution (10 μM) prepared above. After mixing them for a few seconds, UV-vis spectra were taken at room temperature.

Job plot measurements of 1 with Co^{2+} ion. Receptor **1** (0.9 mg, 0.003mmol) was dissolved in DMSO (1 mL). 20, 18, 16, 14, 12, 10, 8, 6, 4, and 2 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 4.980 mL. $Co(NO_3)_2 \cdot 6H_2O$ (9.0 mg, 0.03 mmol) was dissolved in bis-tris buffer solution (10 mL). 0, 2, 4, 6, 8, 10, 12, 14, 16, and 18 μL of the $Co(NO_3)_2$ solution were added to each diluted receptor **1** solution. Each vial had a total volume of 3 mL. After shaking the vials for a few minutes, UV-vis spectra were taken at room temperature.

^{1}H NMR titrations of 1 with Co^{2+} ion. For ^{1}H NMR titrations of receptor **1** with Co^{2+}, five NMR tubes of receptor **1** (2.5 mg, 0.01 mmol) dissolved in DMSO-d_6 were prepared and then five different concentrations (0, 0.002, 0.005, 0.008 and 0.01 mmol) of $Co(NO_3)_2$ dissolved in DMSO-d_6 were added to each solution of receptor **1**. After shaking them for a minute, ^{1}H NMR spectra were taken at room temperature

Competitive experiments of 1 with Co^{2+} ion. Receptor **1** (0.9 mg, 0.003 mmol) was dissolved in DMSO (1 mL) and 10 μL of the receptor **1** (3 mM) was diluted to 2.990 mL bis-tris buffer solution to make the final concentration of 10 μM. MNO_3 (M = Na, K, 0.01 mmol), $M(NO_3)_2$ (M = Mn, Ni, Cu, Zn, Fe, Cd, Mg, Ca, Pb, 0.01 mmol), or $M(NO_3)_3$ (M = Al, Ga, In, Fe, Cr, 0.01 mmol) were separately dissolved in bis-tris buffer (1 mL). 1.5 μL of each metal solution (10 mM) was taken and added into 3 mL of each receptor **1** solution (10 μM) prepared above to make 0.5 equiv. Then, 1.5 μL of $Co(NO_3)_2$ solution (10 mM) was added into the mixed solution of each metal ion and receptor **1** to make 0.5 equiv. After mixing them for a minute, UV-vis spectra were taken at room temperature.

UV-vis titration measurements of 1 with Cu^{2+} ion. Receptor **1** (0.9 mg, 0.003 mmol) was dissolved in DMSO (1 mL) and 10 μL of the receptor **1** (3 mM) was diluted to 2.990 mL bis-tris buffer solution to make the final concentration of 10 μM. $Cu(NO_3)_2 \cdot 2.5H_2O$ (2.3 mg, 0.01mmol) was dissolved in bis-tris buffer (10 mL). 0.75 - 16 μL of the Cu^{2+} solution (1 mM) was transferred to receptor **1** solution (10 μM) prepared above. After mixing them for a few seconds, UV-vis spectra were taken at room temperature.

Job plot measurements of 1 with Cu^{2+} ion. Receptor **1** (0.9 mg, 0.003 mmol) was dissolved in DMSO (1 mL). 20, 18, 16, 14, 12, 10, 8, 6, 4, and 2 μL of the receptor **1** solution were taken and transferred to vials. Each vial was diluted with bis-tris buffer solution to make a total volume of 4.980 mL. $Cu(NO_3)_2 \cdot 2.5H_2O$ (6.9 mg, 0.03 mmol) was dissolved in bis-tris buffer solution (10 mL). 0, 2, 4, 6, 8, 10, 12, 14, 16, and 18 μL of the $Cu(NO_3)_2$ solution were added to each diluted receptor **1** solution. Each vial had a total volume of 3 mL. After shaking the vials for a few minutes, UV-vis spectra were taken at room temperature.

Competitive experiments of 1 with Cu^{2+} ion. Receptor **1** (0.9 mg, 0.003 mmol) was dissolved in DMSO (1 mL) and 10 μL of the receptor **1** (3 mM) was diluted to 2.990 mL bis-tris buffer solution to make the final concentration of 10 μM. MNO_3 (M = Na, K, 0.01 mmol), $M(NO_3)_2$ (M = Mn, Ni, Co, Zn, Fe, Cd, Mg, Ca, Pb, 0.01 mmol), or $M(NO_3)_3$ (M = Al, Ga, In, Fe, Cr, 0.01 mmol) were separately dissolved in bis-tris buffer (1 mL). 1.5 μL of each metal solution (10 mM) was taken and added into 3 mL of each receptor **1** solution (10

μM) prepared above to make 0.5 equiv. Then, 1.5 μL of $Cu(NO_3)_2$ solution (10 mM) was added into the mixed solution of each metal ion and receptor **1** to make 0.5 equiv. After mixing them for a minute, UV-vis spectra were taken at room temperature.

Determination of Co^{2+} and Cu^{2+} in water samples. UV-vis spectral measurements of water samples containing Co^{2+} and Cu^{2+} were carried by adding 25 μL of 3 mmol/L stock solution of **1** and 0.60 mL of 50 mmol/L bis-tris buffer stock solution to 2.375 mL sample solutions. After well mixed, the solutions were allowed to stand at 25 °C for 2 min before the test.

Colorimetric test kit. Receptor **1** (3.5 mg, 0.1 mmol) was dissolved in methanol (10 mL). Receptor **1**-test kits were prepared by immersing filter papers into receptor **1** solution (10 mM), and then dried in air. MNO_3 (M = Na, K, 10 nmol), $M(NO_3)_2$ (M = Mn, Fe, Ni, Co, Cu, Zn, Cd, Mg, Ca, Pb, 10 nmol), or $M(NO_3)_3$ (M = Al, Ga, In, Fe, Cr, 10 nmol) were separately dissolved in bis-tris buffer (10 mL). The test kits prepared above were added into different metal solutions, and then dried at room temperature.

Theoretical calculation methods. All DFT/TDDFT calculations based on the hybrid exchange-correlation functional B3LYP[45,46] were carried out using Gaussian 03 program[47]. The 6-31G** basis set[48,49] was used for the main group elements, whereas the Lanl2DZ effective core potential (ECP)[50-52] was employed for Co and Cu. In vibrational frequency calculations, there is no imaginary frequency for the optimized geometries of **1**, **1**-Co^{3+} and **1**-Cu^{2+}, suggesting that these geometries represent local minima. For all calculations, the solvent effect of water was considered by using the Cossi and Barone's CPCM (conductor-like polarizable continuum model)[53-54]. To investigate the electronic properties of singlet excited states, time-dependent DFT (TDDFT) was performed in the ground state geometries of **1**, **1**-Co^{3+} and **1**-Cu^{2+}. The 40 singlet-singlet excitations were calculated and analyzed. The GaussSum 2.1[55] was used to calculate the contributions of molecular orbitals in electronic transitions.

Results and discussion

The receptor **1** was obtained by coupling 1-hydrazinophthalazine with quinolin-2-carboxaldehyde with an 88.8% yield in methanol (Scheme 1) and analyzed by ^{1}H NMR, ESI mass spectrometry and elemental analysis.

Spectroscopic studies of 1 toward Co^{2+} and Cu^{2+}

To examine the colorimetric properties of **1**, the UV-vis absorption was measured with various metal ions (Na^{+}, K^{+}, Mg^{2+}, Ca^{2+}, Al^{3+}, Ga^{3+}, In^{3+}, Cr^{3+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} Cd^{2+}, Hg^{2+}, Ag^{+} and Pb^{2+}) in bis-tris buffer (10 mM, pH 7.0). As shown in Fig. 1a, the significant spectral changes for Co^{2+} and Cu^{2+} were observed at 512 nm and 472 nm, respectively, and Fe^{2+} had a small change in UV-vis absorption. Importantly, only both Co^{2+} and Cu^{2+} showed significant changes of color from pale yellow to pink and to orange, respectively (Fig. 1b). Additionally, we examined the fluorometric changes of **1** toward various cations and anions, but no fluorescent enhancements were observed for both ions. For example, the fluorescent tests for the anions is shown in Fig. S1. These results demonstrated that receptor **1** can serve as a potential candidate of "naked-eye" chemosensor for Cu^{2+} and Co^{2+} by different color changes in aqueous solution.

First of all, the binding properties of **1** with Co^{2+} were studied by UV-vis titration experiments. On treatment with Co^{2+} to solution of **1**, the absorption band at 382 nm significantly decreased, and a new band at 512 nm gradually reached a maximum at 0.5 equiv of Co^{2+} (Fig. 2). Four isosbestic points were observed at 269, 290, 336 and 439 nm, indicating that only one product was generated from **1** upon binding to Co^{2+}. The Job plot analysis[56] showed a 1:2 stoichiometry of Co^{2+} to **1** (Fig. S2). At this stage, it is not clear whether the Co^{3+}-2•**1** complex formed one by one or in a concerted way. To further examine the binding mode between **1** and Co^{2+}, a positive-ion ESI mass experiment was carried out (Fig. 3). Unexpectedly, a Co^{3+} complex with the 1:2 stoichiometry was observed as a major peak, although Co^{2+} was used as the standard metal ion. A peak at m/z 655.067 was assigned to [2•**1**+Co^{3+}-2•H]$^{+}$ (calcd. 655.153). Based on our previous experience,[24] we assume that the Co^{2+}-2•**1** complex formed from the reaction of **1** with Co^{2+} would be oxidized to the Co^{3+}-2•**1** by oxygen molecule. To prove our proposal for the oxidation of Co^{2+} to Co^{3+} in

Co^{2+}-2•**1** complex, we carried out the sensing test under the degassed conditions. When Co^{2+} was mixed with **1** under the degassed condition, pale-orange color appeared (Fig. S3) and subsequent exposure to air rendered the color of the solution change to pink. These results indicated that the Co^{2+}-2•**1** complex (pale-orange) under the degassed condition was oxidized to the Co^{3+}-2•**1** complex (pink) in air. Moreover, the ^1H NMR titration of Co^{2+} with **1** was conducted in air (Fig. S4). We expected that the Co^{2+}-2•**1** complex has a paramagnetic character, while the Co^{3+}-2•**1** complex with N6-type ligand does a diamagnetic character.[57,58] Upon the addition of Co^{2+} up to 0.5 equiv into the **1** solution, the ^1H NMR signals of the cobalt complex showed sharp signals, suggesting that a diamagnetic Co^{3+} complex existed. Further addition of Co^{2+} (1 eq>) rendered the signals disappear because of a paramagnetic character of an excess Co^{2+}. All these results led us to conclude that the high-spin Co^{2+}-2•**1** complex was oxidized to the low-spin Co^{3+}-2•**1** complex by oxygen. Based on the Job plot, ESI mass spectrometry analysis, the experiments under the degassed conditions, and ^1H NMR titration, a hexa-coordinated structure for Co^{3+}-2•**1** complex was proposed (Scheme 2).

Based on the UV-vis titration of **1** with Co^{2+}, the association constant (*K*) of **1** with Co^{2+} was calculated by using Li's equations[59] (see the Supporting Information and Fig. S5). The *K* value was determined to be 1.0×10^{10} M^{-2} (± 2.5 %) which was within range of those (10^4~10^{22}) previously reported for cobalt chemosensors.[12-34] The detection limit ($3\sigma/k$)[60] of **1** as a colorimetric sensor for Co^{2+} was found to be 1.5×10^{-6} M (Fig. S6), which is lower than that (1.7×10^{-5} M) recommended by environmental protection agency (EPA).[61] Moreover, the detection limit was compatible to those ($0.64 \sim 1.3 \times 10^{-6}$ M) of previously reported cobalt chemosensors in a near-perfect aqueous solution.[24,25] Thus, the receptor **1** could be a powerful tool for the detection of cobalt ion in water samples.

To further check the practical applicability of receptor **1** as a Co^{2+} selective sensor, the competition experiments were conducted (Figs. 4 and S7). Upon treatment with 0.5 equiv of Co^{2+} in the presence of the same concentration of other metal ions, there were no obvious interferences for the detection of Co^{2+} in the presence of most metal ions, while Ga^{3+}, Cu^{2+}, Mg^{2+}, Ni^{2+}, and Ca^{2+} showed the interferences of 11, 18, 11, 13, and 22 %, respectively. Thus, **1** could be used as a selective colorimetric sensor for Co^{2+} in the presence of most competing metal ions. In addition, we investigated the effect of pH on the

absorption response of receptor **1** to Co^{2+} ion in a series of solutions with pH values ranging from 2 to 12 (Fig. 5). The color of the Co^{2+}-2•**1** complex remained in the pink color between pH 3 and 12. These results indicated that Co^{2+} could be clearly detected by the naked eye or UV-vis absorption measurements using **1** over the wide pH range of 3.0-12.0.

Next, the binding properties of **1** with Cu^{2+} were studied by UV-vis titration experiments. Upon the addition of Cu^{2+} into **1**, the absorption band at 382 nm significantly decreased, and a new band at 472 nm gradually increased up to 0.5 equiv of Cu^{2+} (Fig. 6). A clear isosbestic point was also observed at 431 nm, indicating that only one product was generated from **1** upon binding to Cu^{2+}. The Job plot[56] analysis showed a 1:2 stoichiometry for Cu^{2+} to **1** (Fig. S8). At this stage, it is also not clear whether the Cu^{2+}-2•**1** complex formed one by one or in a concerted way. To further examine the binding mode between **1** and Cu^{2+}, a positive-ion ESI mass experiment was carried out. It showed that the peak at m/z 758.933 was assigned to $[2•\mathbf{1}+Cu^{2+}-2•H+Na^{+}+ 3 \text{ solvents}]^{+}$ (calcd. 759.185) (Fig. 7). Based on the Job plot and ESI mass spectrometry analysis, a hexa-coordinated structure for Cu^{2+}-2•**1** complex was proposed (Scheme 3).

Based on the UV-vis titration of **1** with Cu^{2+}, the association constant (*K*) of **1** with Cu^{2+} was determined by the Li's equations[59] (Fig. S9). The *K* value was determined to be 1.0 x 10^{9} M^{-2} (± 3.0 %) which was within the range of those (10^{3}~10^{12}) reported for Cu^{2+} chemosensors.[16-19] The detection limit ($3\sigma/k$)[60] of **1** as a colorimetric sensor for Cu^{2+} was found to be 2.1 x 10^{-6} M (Fig. S10), which was much lower than that (3.0 x 10^{-5} M) recommended by WHO in drinking water.[62] In addition, the detection limit was compatible to those (0.9 ~ 2.7 x 10^{-6} M) of previously reported copper chemosensors in a near-perfect aqueous solution.[14,63,64]

To further check the practical applicability of receptor **1** as a Cu^{2+} selective sensor, the competition experiments were conducted (Figs. 8 and S11). Upon treatment with 0.5 equiv of Cu^{2+} in the presence of the same concentration of other metal ions, there were some interferences for the detection of Cu^{2+}, which were 11 % for Al^{3+}, 10 % for Zn^{2+}, 17 % for Fe^{2+}, 24 % for Mg^{2+}, 25 % for Cr^{3+}, 34 % for Co^{2+}, 23 % for Ni^{2+}, 28 % for Na^{+}, 36 % for K^{+}, and 31 % for Mn^{2+}, respectively. Nevertheless, the changes of color were still detectable in presence of those interfering metal ions (Figs. 8b). Thus, **1** could be used as a selective

colorimetric sensor for Cu^{2+} in the presence of most competing metal ions. In addition, we investigated the effect of pH on the absorption response of receptor **1** to Cu^{2+} ion in a series of solutions with pH values ranging from 2 to 12 (Fig. 9). The color of the Cu^{2+}-2•**1** complex remained in the orange color between pH 3 and 12. These results indicated that Cu^{2+} could be clearly detected by the naked eye or UV-vis absorption measurements using **1** over the wide pH range of 3.0-12.0.

Determination of Co^{2+} and Cu^{2+} ions in water samples

In order to examine the practical properties of the chemosensor **1** in environmental samples, the chemosensor **1** was applied for the determination of Co^{2+} and Cu^{2+} in water samples, using the calibration curves of **1** toward Co^{2+} and Cu^{2+} (Figs. S12 and S13). Tap water and drinking water samples were chosen. Each sample was analyzed for three replicates. The standard addition method was used and the samples were spiked with different amount of Co^{2+} or Cu^{2+}. As shown in Tables 1 and 2, a suitable recovery and R.S.D. values of the water samples were obtained. These results indicated that the chemosensor **1** is suitable for determination of Co^{2+} or Cu^{2+} concentration in such samples with a good precision and accuracy.

Colorimetric test-kits

To further investigate the practical application of receptor **1**, test kits were prepared by immersing filter papers in a methanol solution of **1** and then drying air. These test kits were utilized to sense Co^{2+} and Cu^{2+} ions among different cations. As shown in Fig. 10, when the test kits coated with **1** were added into different cation solutions (1.0 μM), the obvious color changes were observed only with Co^{2+} and Cu^{2+} in bis-tris buffer solution. Importantly, this is the first example that **1** could detect the lowest concentrations of both cobalt and copper ions by a simple test strip in aqueous solution, to the best of our knowledge. Therefore, the test kits coated with the receptor **1** solution would be convenient to simultaneously detect Co^{2+} and Cu^{2+} by different colors in the presence of other metal ions.

Theoretical calculations

To understand the sensing mechanisms of Co^{2+} and Cu^{2+} with **1**, theoretical

calculations were performed in parallel to the experimental studies. As Job plots and ESI-mass spectrometry analyses showed that **1** reacted with Co^{2+} and Cu^{2+} in the 2:1 stoichiometric ratio, respectively, all theoretical calculations were performed with the 2:1 stoichiometry. Co^{3+}-2•**1** complex was optimized with a diamagnetic character (S=0, DFT/uB3LYP/main group atom: 6-31G** and Co: Lanl2DZ/ECP), because Co^{2+}-2•**1** complex was oxidized to Co^{3+}-2•**1** one which has a diamagnetic property based on the NMR titration. Cu^{2+}-2•**1** complex was optimized with a paramagnetic character (S=1/2, DFT/uB3LYP/main group atom: 6-31G** and Cu: Lanl2DZ/ECP). The significant structural properties of the energy-minimized structures were shown in Fig. S14.

We also investigated the absorption to the singlet excited states of **1**, Co^{3+}-2•**1**, and Cu^{2+}-2•**1** species via TDDFT calculations. In case of **1**, the main molecular orbital (MO) contribution of the first lowest excited state was determined for HOMO → LUMO transition (381.48 nm, Figs. S15 and S16), which indicated intramolecular charge transfer (ICT) band from -NH- and -N=N- of hydrazinophthalazine to -N=C- and quinoline. In case of Co^{3+}-2•**1** complex, the excited states of 15th, 16th and 22th (502.63, 494.51 and 469.61 nm) were found to be relevant to the color change (yellow to pink) showing predominant LMCT and ICT (Figs. S17 and S18). The LMCT mainly indicated the MOs changes from -NH- and -N=N- of hydrazinophthalazine to metal centered orbitals, and the MOs changes of the ICT were similar to that of **1**. In case of Cu^{2+}-2•**1** complex, the excited states of 13th and 14th (492.02 and 483.05 nm) were found to be relevant to the color change (yellow to orange) showing predominant ICT, and slight LMCT and d-d transition (Figs. S19, S20 and S21). The MOs changes of the predominant ICT were also similar to that of **1**. All theoretical results are well consistent with the experimental absorption wavelengths within 5-14 nm deviations (5 nm for Co^{2+} and 14 nm for Cu^{2+}). Thus, the chelation of Co^{2+} with **1** mainly showed the LMCT and ICT, and that of Cu^{2+} with **1** mainly showed ICT transition, which induced the different color change of **1** in the presence of Cu^{2+} and Co^{2+}.

Conclusion

Phthalazine-based chemosensor **1** was developed for detection of Co^{2+} and Cu^{2+} ions

in a near-perfect aqueous solution. **1** showed highly selective response to Co^{2+} and Cu^{2+} which showed the color changes from pale-yellow to pink and to orange, respectively. The chemosensor **1** could be used to detect and quantify Co^{2+} and Cu^{2+} ions with detection limits of 1.5 μM (Co^{2+}) and 2.1 μM (Cu^{2+}) in water samples. Moreover, **1** could be successfully applied to test kits for detecting both Co^{2+} and Cu^{2+}, and this is the first example that **1** could detect the lowest concentrations of them by a simple test strip in aqueous solution, to the best of our knowledge. Furthermore, the sensing mechanisms of Co^{2+} and Cu^{2+} were explained by theoretical calculations. Therefore, these results indicate that receptor **1** can serve as a novel multifunctional "naked-eye" chemosensor for Cu^{2+} and Co^{2+} by different color changes in a near-perfect aqueous solution.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://????.

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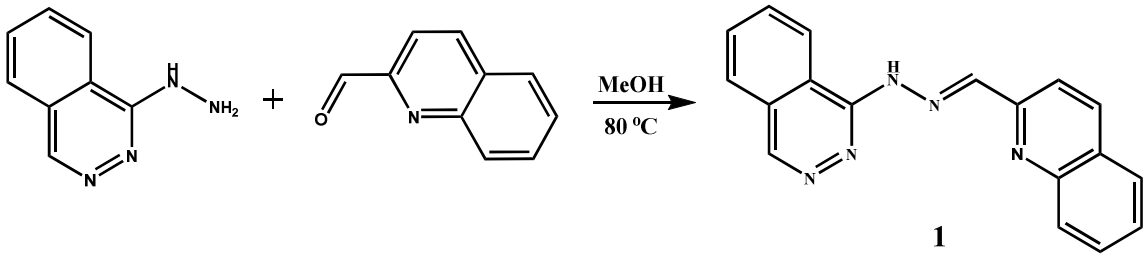
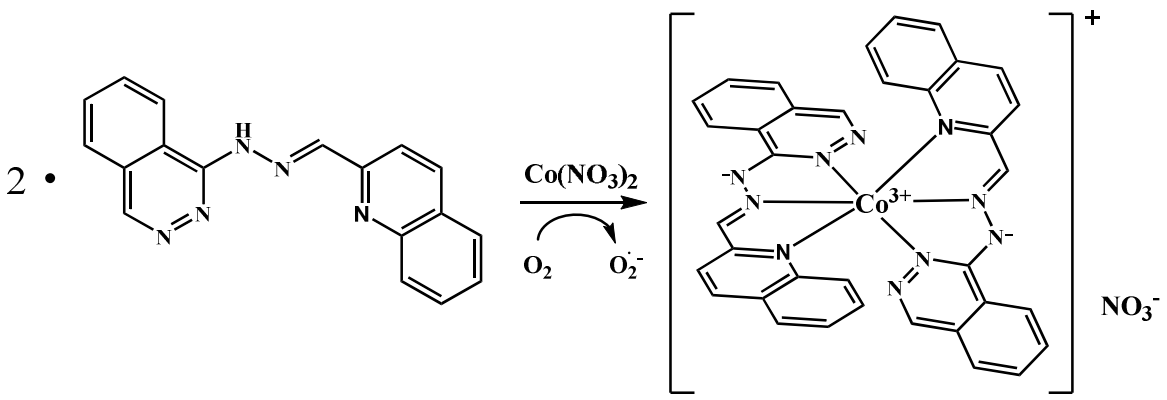
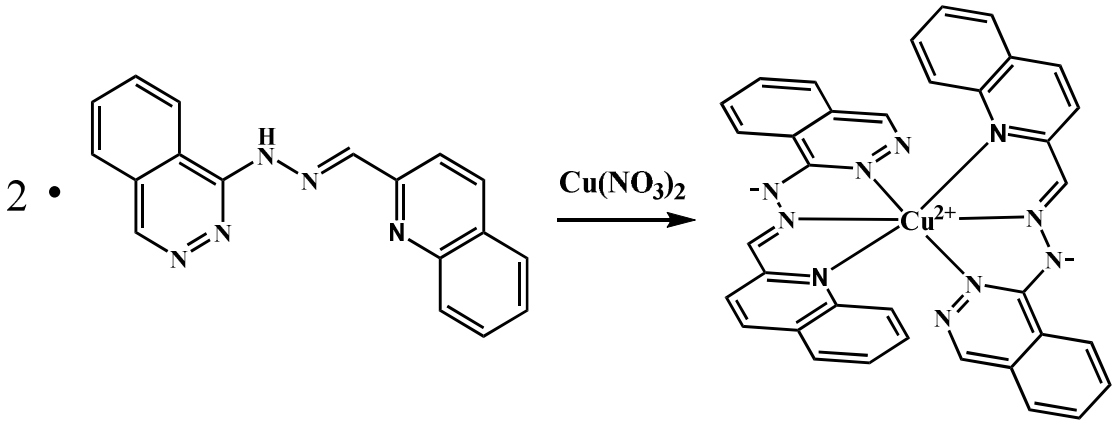


Scheme 1. Synthesis of **1**.



Scheme 2. Proposed sensing mechanism of **1** for Co^{2+} ion and proposed structure of Co^{3+}-2•**1** complex.



Scheme 3. Proposed structure of Cu^{2+}-2•**1** complex.

Table 1. Determination of Co(II) in water samples.

Sample	Co(II) added (μmol/L)	Co(II) found (μmol/L)	Recovery (%)	R.S.D. (n = 3) (%)
Tap water	0.00	0.00		
	5.00 [a]	4.97	99.4	3.80
Drinking water	0.00	0.00		
	4.00 [b]	4.09	102.3	3.56

Conditions: [**1**] = 25 μmol/L in 10 mM bis-tris buffer-DMSO solution (999:1, pH 7.0). a. 5.00 μmol/L of Co^{2+} ion was artificially added into tap water. b. 4.00 μmol/L of Co^{2+} ion was artificially added into tap water.

Table 2. Determination of Cu(II) in water samples.

Sample	Cu(II) added (μmol/L)	Cu(II) found (μmol/L)	Recovery (%)	R.S.D. (n = 3) (%)
Tap water	0.00	0.00		
	4.00 [a]	3.91	97.8	4.61
Drinking water	0.00	0.00		
	3.00 [b]	3.03	101.0	3.88

Conditions: [**1**] = 25 μmol/L in 10 mM bis-tris buffer-DMSO solution (999:1, pH 7.0). a. 4.00 μmol/L of Co^{2+} ion was artificially added into tap water. b. 3.00 μmol/L of Co^{2+} ion was artificially added into tap water.

Figure Captions

Fig. 1 (a) Absorption spectral change of receptor **1** (10 μM) in presence of 0.5 equiv of various metal ions in bis-tris buffer (10 mM, pH 7). (b) The color changes of receptor **1** (10 μM) in presence of 0.5 equiv of various metal ions in bis-tris buffer.

Fig. 2 Absorption spectral changes of **1** (10 μM) in the presence of different concentrations of Co^{2+} (from 0 to 0.6 equiv) at room temperature. Inset: Plot of the absorbance at 512 nm as a function of Co^{2+} concentration.

Fig. 3 Positive-ion electrospray ionization mass spectrum of **1** (20 μM) upon addition of $Co(NO_3)_2$ (0.5 equiv).

Fig. 4 (a) Absorption spectral changes of **1** (10 μM) upon addition of Co^{2+} (0.5 equiv) in the absence and presence of 0.5 equiv of various metal ions in bis-tris buffer (10 mM, pH 7). (b) The color changes of **1** (10 μM) upon addition of Co^{2+} (0.5 equiv) in the absence and presence of 0.5 equiv of various metal ions in bis-tris buffer.

Fig. 5 (a) UV-vis absorption (512 nm) of Co^{2+}-2•**1** complex at different pH (2-12). (b) The color changes of **1** and Co^{2+}-2•**1** complex at different pH (2-12), respectively.

Fig. 6 Absorption spectral changes of **1** (10 μM) in the presence of different concentrations of Cu^{2+} (from 0 to 0.5 equiv) at room temperature. Inset: Plot of the absorbance at 472 nm as a function of Cu^{2+} concentration.

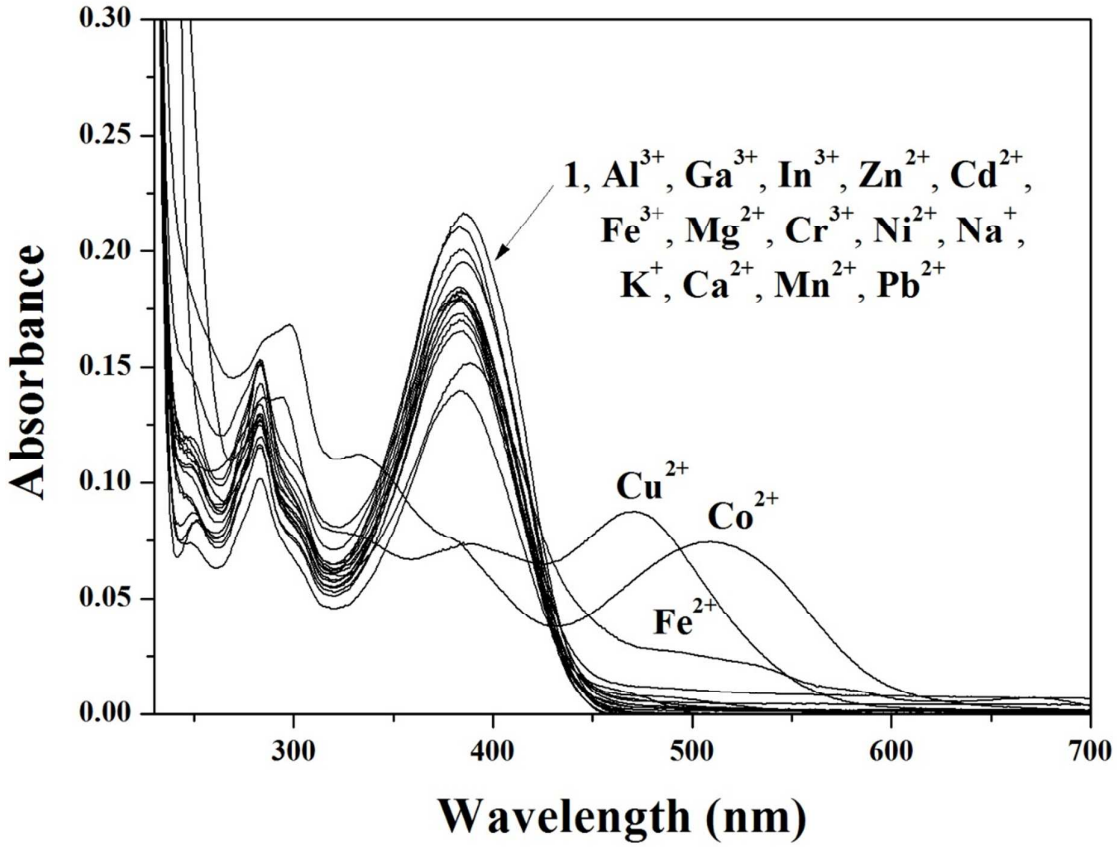
Fig. 7 Positive-ion electrospray ionization mass spectrum of **1** (20 μM) upon addition of $Cu(NO_3)_2$ (0.5 equiv).

Fig. 8 (a) Absorption spectral changes of **1** (10 μM) upon addition of Cu^{2+} (0.5 equiv) in the absence and presence of 0.5 equiv of various metal ions in bis-tris buffer (10 mM, pH 7). (b) The color changes of **1** (10 μM) upon addition of Cu^{2+} (0.5 equiv) in the absence and presence of 0.5 equiv of various metal ions in bis-tris buffer.

Fig. 9 (a) UV-vis absorption (472 nm) of Cu^{2+}-2•**1** complex at different pH (2-12). (b) The color changes of **1** and Cu^{2+}-2•**1** complex at different pH (2-12), respectively.

Fig. 10 Photographs of the filter paper coated with **1** (10 mM) in the presence of various metal ions (1.0 μM).

(a)


0.30
0.25
0.20
0.15
0.10
0.05
0.00
Absorbance
300
400
500
600
700
Wavelength (nm)
1, Al3+, Ga3+, In3+, Zn2+, Cd2+,
Fe3+, Mg2+, Cr3+, Ni2+, Na+,
K+, Ca2+, Mn2+, Pb2+
Cu2+
Co2+
Fe2+

(b)

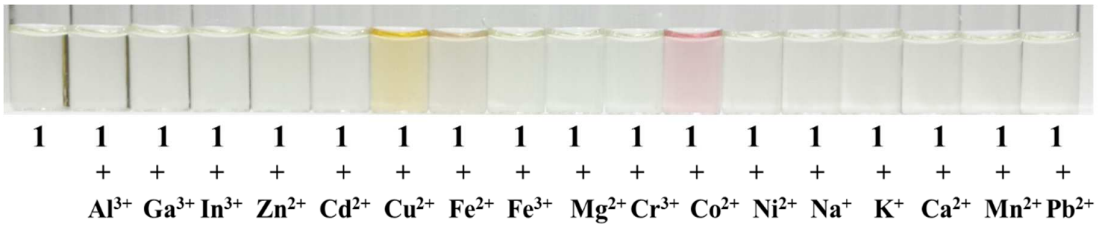

1
1 + Al3+
1 + Ga3+
1 + In3+
1 + Zn2+
1 + Cd2+
1 + Cu2+
1 + Fe2+
1 + Fe3+
1 + Mg2+
1 + Cr3+
1 + Co2+
1 + Ni2+
1 + Na+
1 + K+
1 + Ca2+
1 + Mn2+
1 + Pb2+

Fig. 1

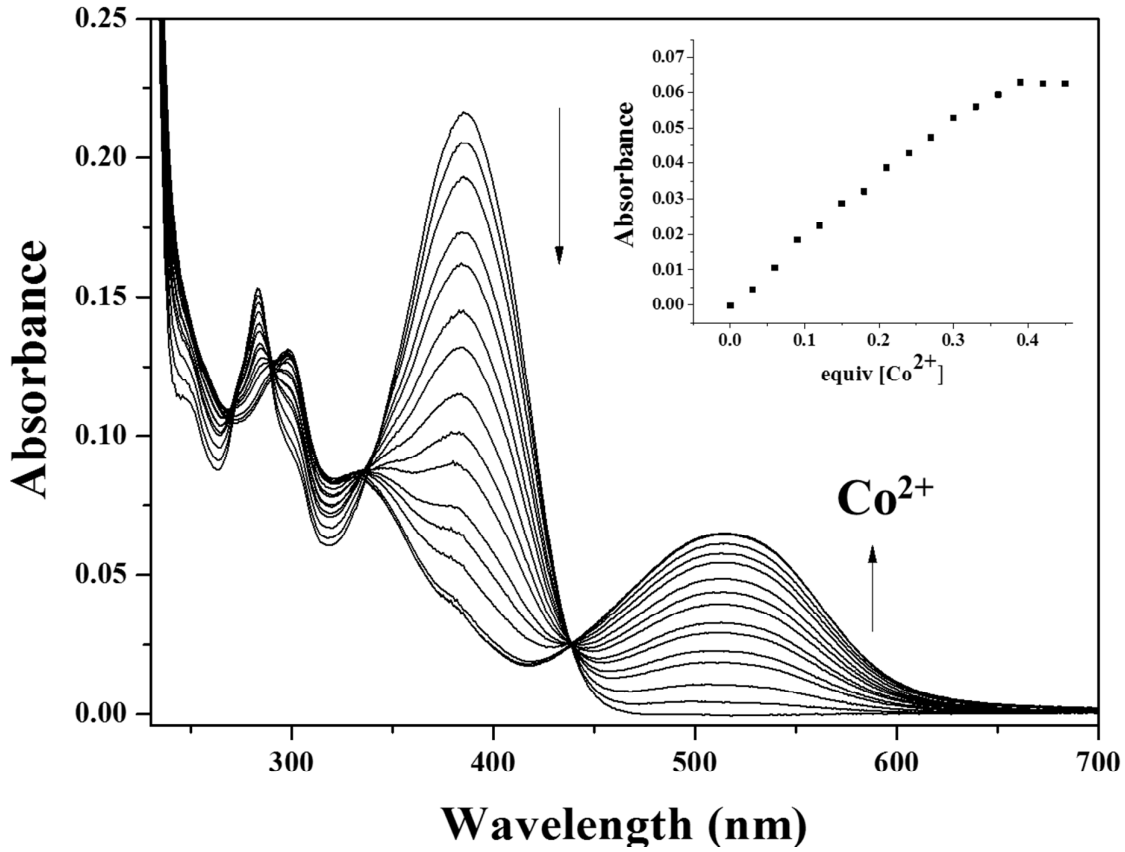

Absorbance
Wavelength (nm)
0.25
0.20
0.15
0.10
0.05
0.00
300
400
500
600
700
Co2+
Absorbance
equiv [Co2+]
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0.00
0.0
0.1
0.2
0.3
0.4

Fig. 2

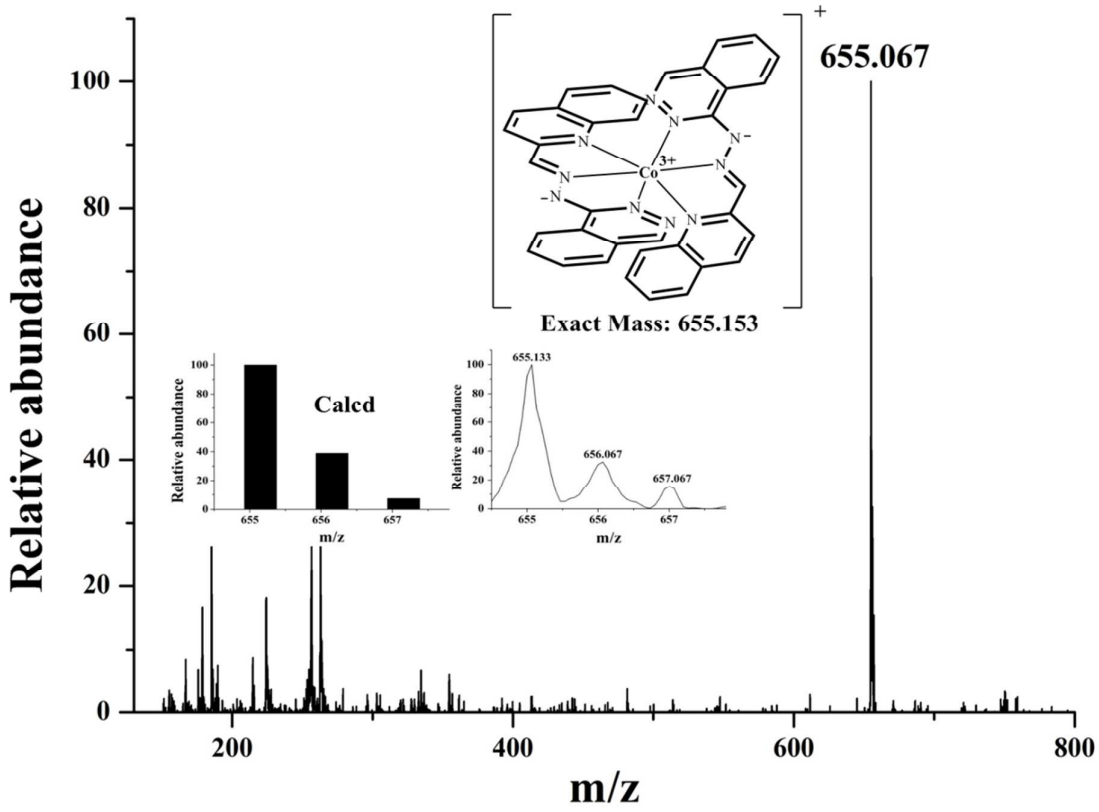
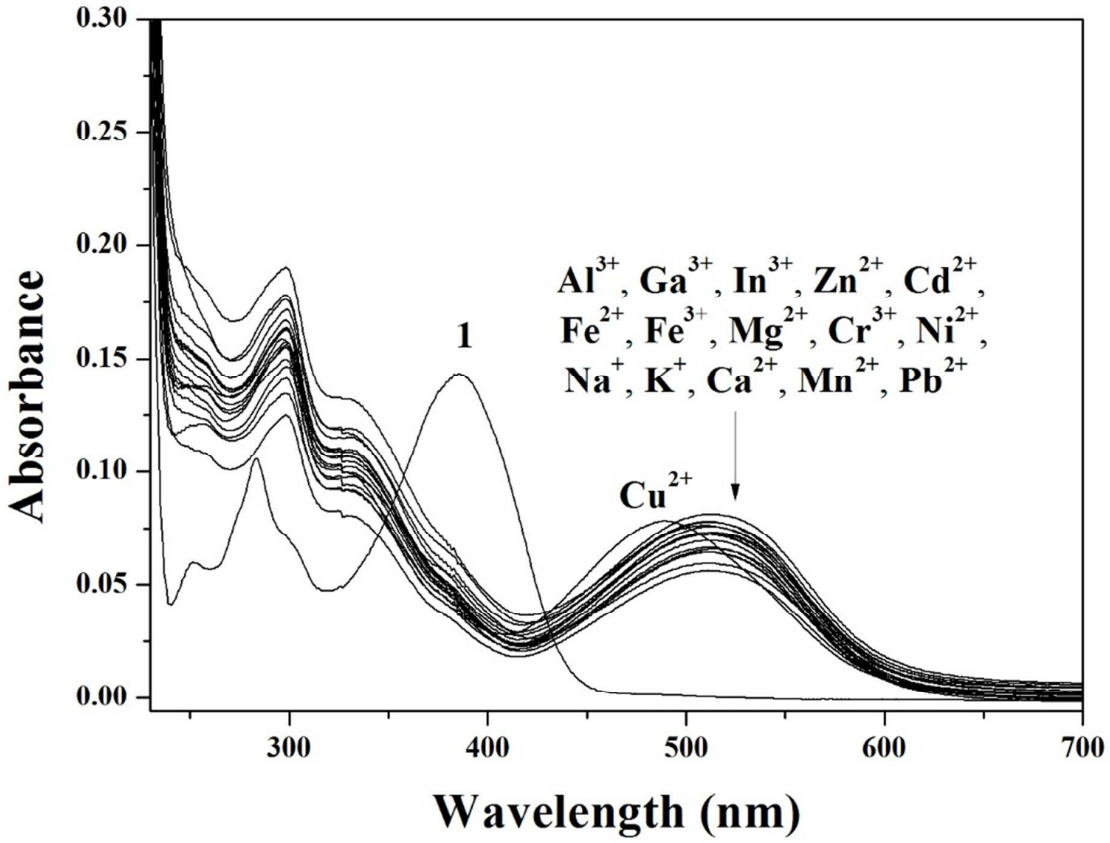

655.067
Exact Mass: 655.153
Calcd
655.133
656.067
657.067
Relative abundance
m/z

Fig. 3

(a)


Absorbance
Wavelength (nm)
0.00
0.05
0.10
0.15
0.20
0.25
0.30
300
400
500
600
700
1
Al3+, Ga3+, In3+, Zn2+, Cd2+,
Fe2+, Fe3+, Mg2+, Cr3+, Ni2+,
Na+, K+, Ca2+, Mn2+, Pb2+
Cu2+

(b)

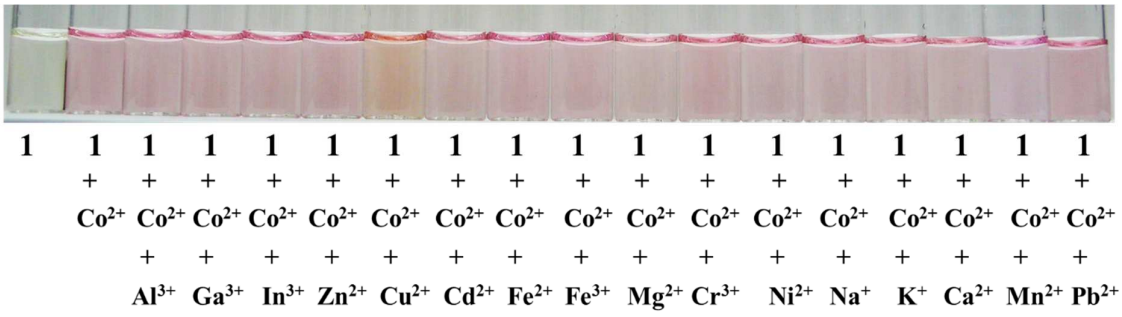
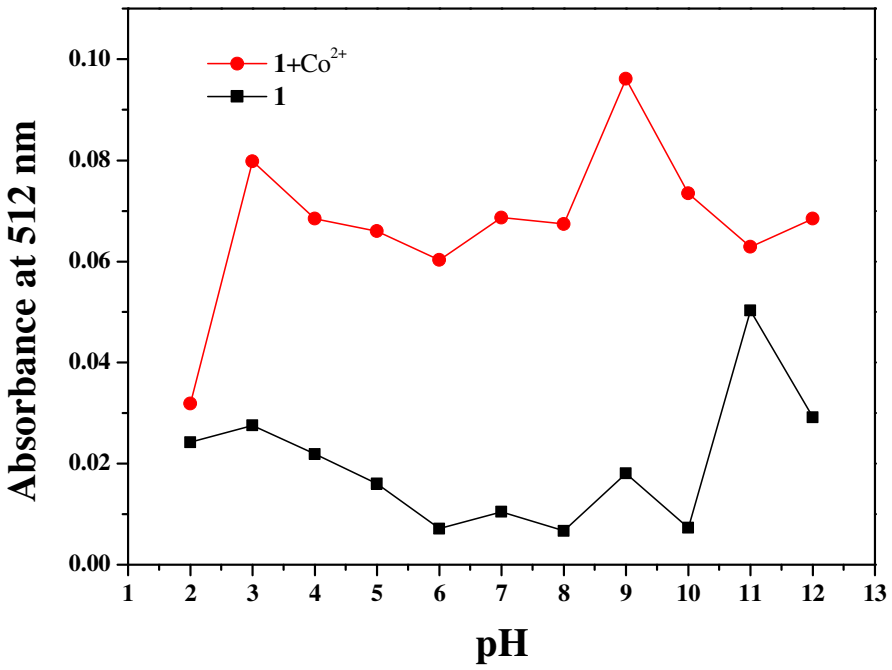

1
1 + Co2+
1 + Co2+ + Al3+
1 + Co2+ + Ga3+
1 + Co2+ + In3+
1 + Co2+ + Zn2+
1 + Co2+ + Cu2+
1 + Co2+ + Cd2+
1 + Co2+ + Fe2+
1 + Co2+ + Fe3+
1 + Co2+ + Mg2+
1 + Co2+ + Cr3+
1 + Co2+ + Ni2+
1 + Co2+ + Na+
1 + Co2+ + K+
1 + Co2+ + Ca2+
1 + Co2+ + Mn2+
1 + Co2+ + Pb2+

Fig. 4

(a)



(b)

pH 2	pH 3	pH 4	pH 5	pH 6	pH 7	pH 8	pH 9	pH 10	pH 11	pH 12
1 + Co^{2+}	1 + Co^{2+}	1 + Co^{2+}	1 + Co^{2+}	1 + Co^{2+}	1 + Co^{2+}	1 + Co^{2+}	1 + Co^{2+}	1 + Co^{2+}	1 + Co^{2+}	1 + Co^{2+}

Fig. 5

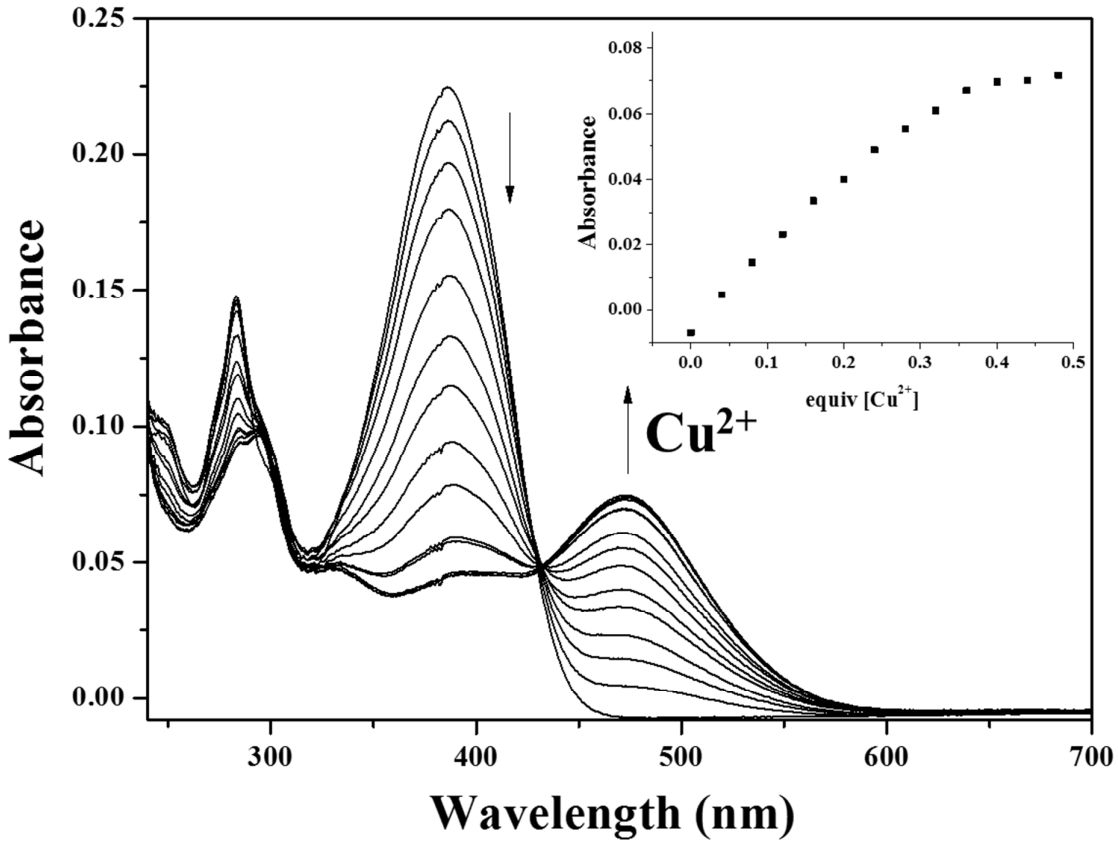

Absorbance
Wavelength (nm)
0.25
0.20
0.15
0.10
0.05
0.00
300
400
500
600
700
Cu2+
Absorbance
equiv [Cu2+]
0.08
0.06
0.04
0.02
0.00
0.0
0.1
0.2
0.3
0.4
0.5

Fig. 6

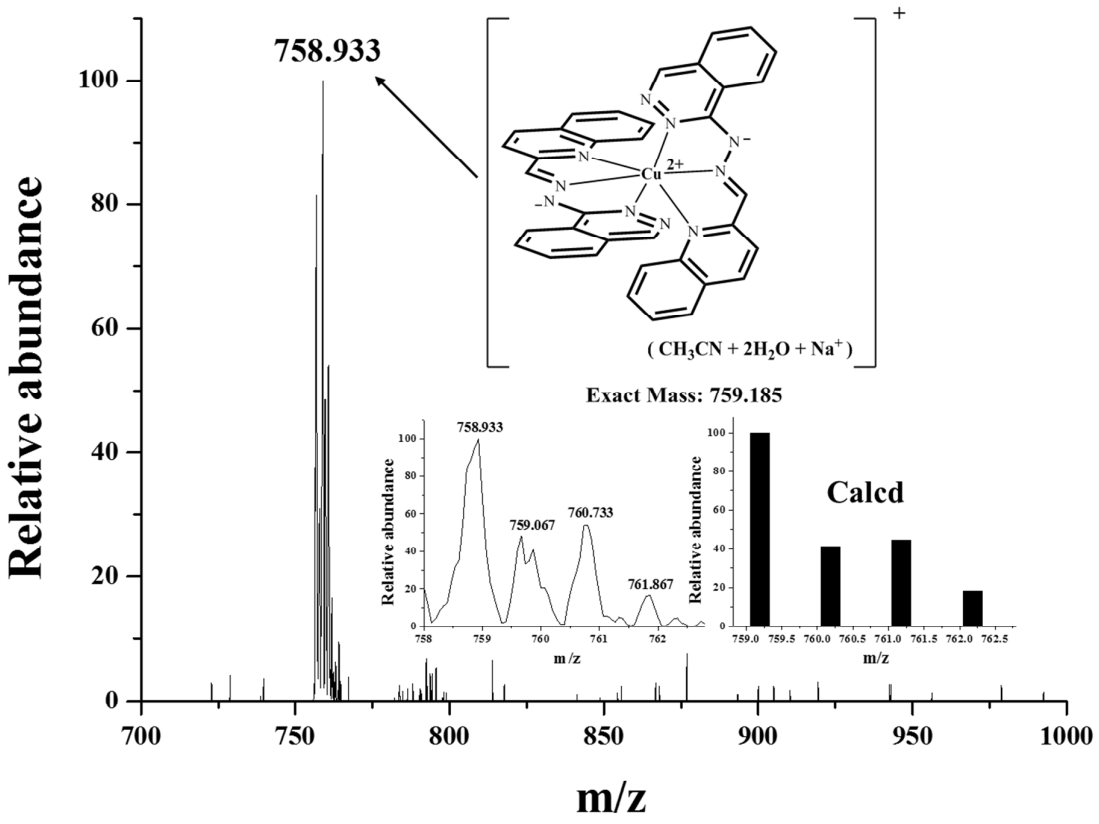
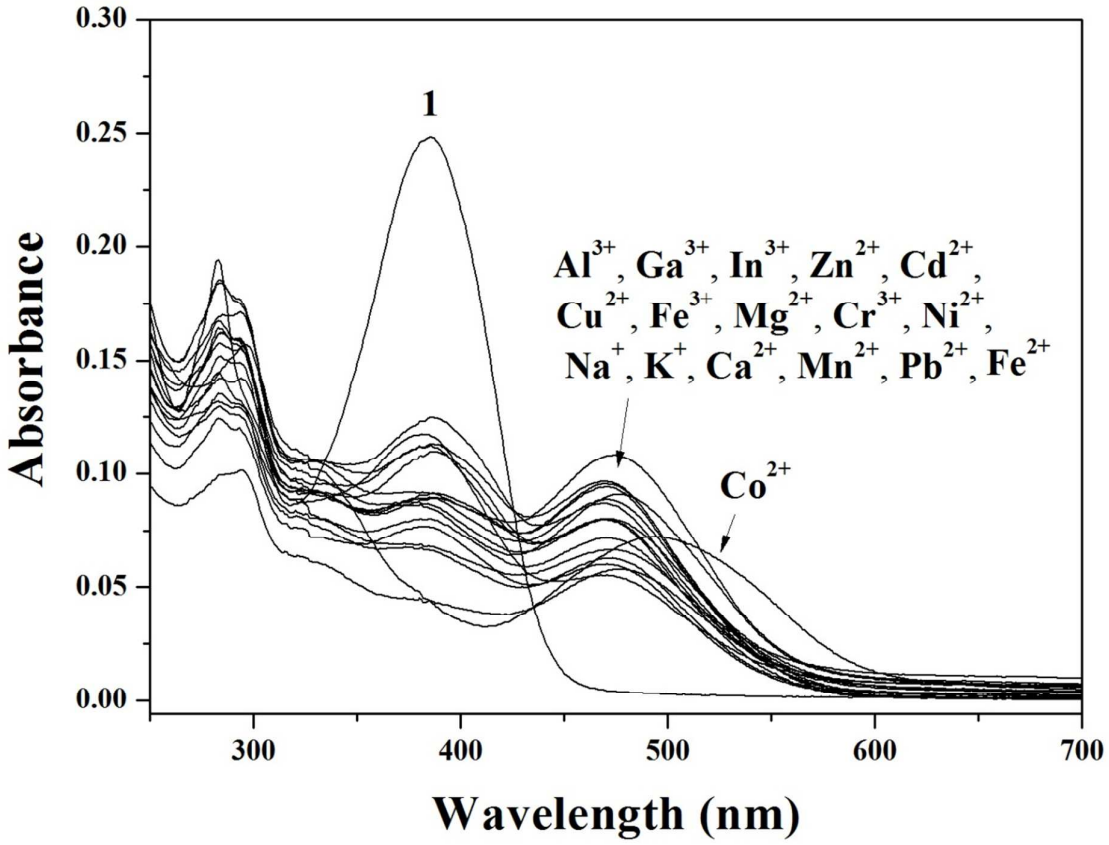

758.933
Relative abundance
m/z
(CH3CN + 2H2O + Na+)
Exact Mass: 759.185
758.933
759.067
760.733
761.867
Calcd

Fig. 7

(a)


0.30
0.25
0.20
0.15
0.10
0.05
0.00
Absorbance
300
400
500
600
700
Wavelength (nm)
1
Al3+, Ga3+, In3+, Zn2+, Cd2+,
Cu2+, Fe3+, Mg2+, Cr3+, Ni2+,
Na+, K+, Ca2+, Mn2+, Pb2+, Fe2+
Co2+

(b)

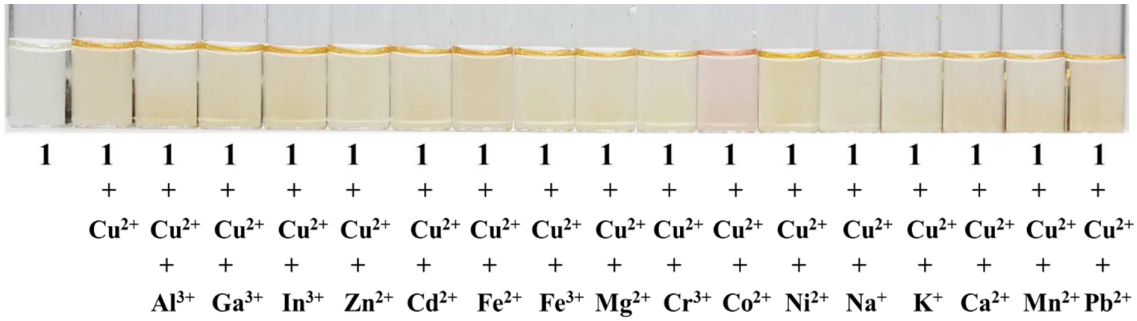
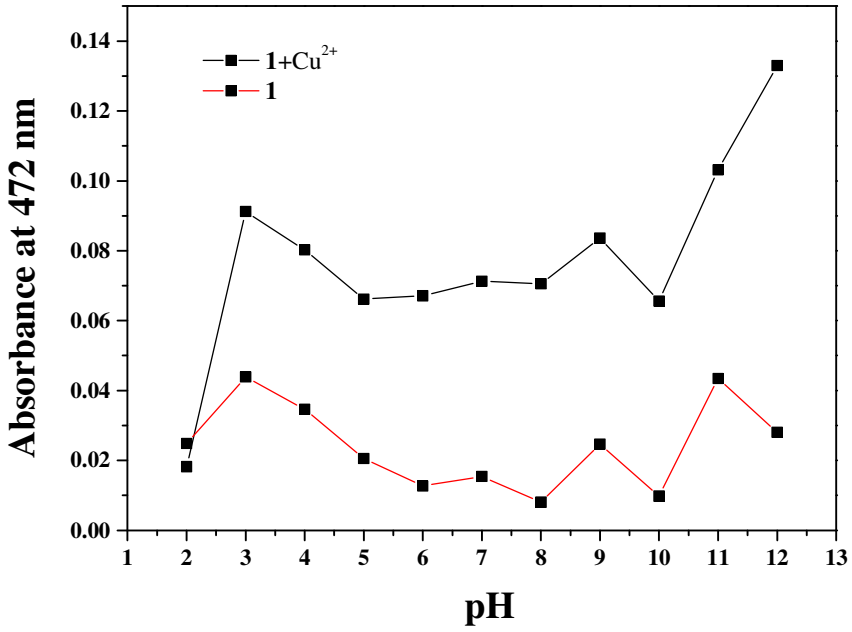

1
1 + Cu2+
1 + Cu2+ + Al3+
1 + Cu2+ + Ga3+
1 + Cu2+ + In3+
1 + Cu2+ + Zn2+
1 + Cu2+ + Cd2+
1 + Cu2+ + Fe2+
1 + Cu2+ + Fe3+
1 + Cu2+ + Mg2+
1 + Cu2+ + Cr3+
1 + Cu2+ + Co2+
1 + Cu2+ + Ni2+
1 + Cu2+ + Na+
1 + Cu2+ + K+
1 + Cu2+ + Ca2+
1 + Cu2+ + Mn2+
1 + Cu2+ + Pb2+

Fig. 8

(a)


Absorbance at 472 nm
pH
1+Cu2+
1
0.00
0.02
0.04
0.06
0.08
0.10
0.12
0.14
1
2
3
4
5
6
7
8
9
10
11
12
13

(b)

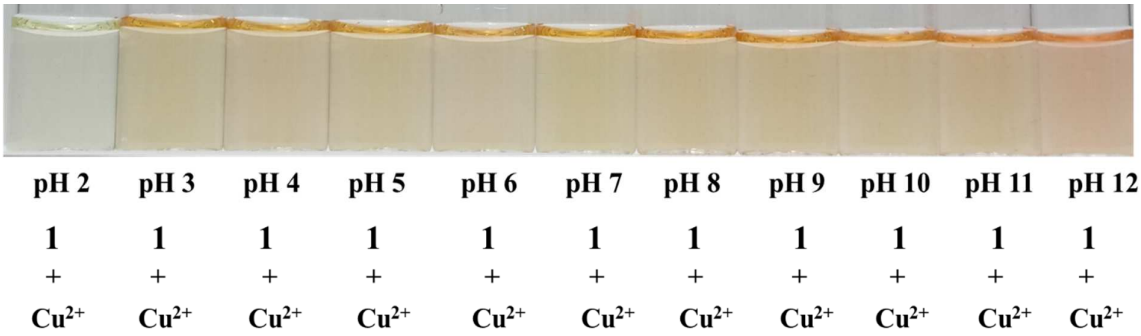

pH 2
pH 3
pH 4
pH 5
pH 6
pH 7
pH 8
pH 9
pH 10
pH 11
pH 12
1 + Cu2+

Fig. 9

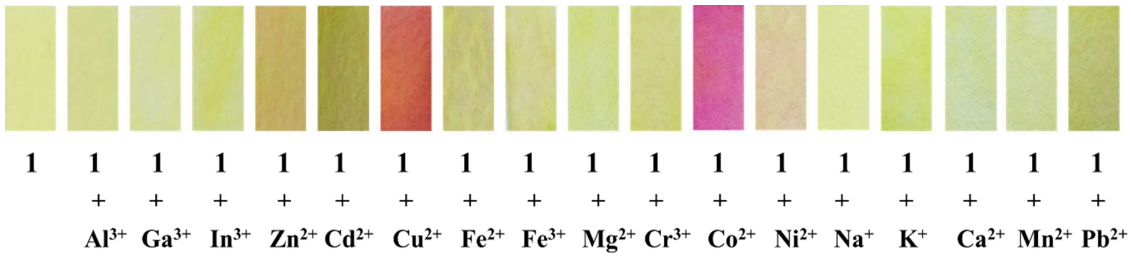
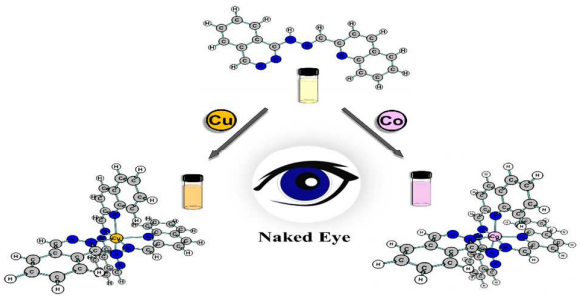

1
1 + Al3+
1 + Ga3+
1 + In3+
1 + Zn2+
1 + Cd2+
1 + Cu2+
1 + Fe2+
1 + Fe3+
1 + Mg2+
1 + Cr3+
1 + Co2+
1 + Ni2+
1 + Na+
1 + K+
1 + Ca2+
1 + Mn2+
1 + Pb2+

Fig. 10

Graphical abstract



A new phthalazine-based sensor **1** was developed as colorimetric sensor and test kits to quantify Co^{2+} and Cu^{2+}.