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A colorimetric sensor for the sequential detection of Cu^{2+} and CN^- in fully aqueous media: practical performance of Cu^{2+}

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Abstract

A new highly selective colorimetric chemosensor **1** (E)-9-(((5-mercapto-1,3,4-thiadiazol-2-yl)imino)methyl)-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinolin-8-ol was designed and synthesized for the sequential detection of Cu^{2+} and CN^-. This sensor **1** exhibited an obvious color change from yellow to orange in the presence of Cu^{2+} in fully aqueous solution. The detection limit (0.9 μM) of **1** for Cu^{2+} is far lower than the WHO limit (31.5 μM) for drinking water. Additionally, the resulting Cu^{2+}-2•**1** complex can be further used to detect toxic cyanide through a color change from orange to yellow, indicating the recovery of **1** from Cu^{2+}-2•**1**. Importantly, chemosensor **1** could be used to detect and quantify Cu^{2+} in water samples, and colorimetric test strip of **1** for the detection of Cu^{2+} could be useful for all practical purposes.

Keywords: copper ion, cyanide, Schiff-base, colorimetric, sequential detection, multifunctional

Introduction

The development of selective and sensitive chemosensors for the detection of metal ions and anions has received considerable attention in recent decades due to their important roles in biological and environmental processes.[1] Among various metal ions, copper serves as an essential cofactor by constituting the active part in a large variety of enzymes, including superoxide dismutase, cytochrome *c* oxidase and tyrosinase.[2] Thus, daily ingestion of copper is indispensable for our good health.[3] On the other hand, unregulated overloading of copper can induce severe neurodegenerative diseases including Alzheimer's, Parkinson's and prion diseases.[4] Furthermore, Cu^{2+} is a significant environmental pollutant due to its widespread use. The World Health Organization (WHO) has set the safe limit of copper in drinking water at 2 ppm (31.5 μM).[5] Thus, development of chemosensors for the detection and monitoring of Cu^{2+}, with high sensitivity, low detection limit and quick response, is in great demand.[6]

Cyanide is one of the primarily concerned anions, because of its rapid and powerful poisonous action.[7] Its toxicity results from its propensity to bind to the iron in cytochrome *c* oxidase, interfering with electron transport and resulting in hypoxia.[8] Even a very small amount of the cyanide can also cause diseases of the vascular, cardiac, visual, endocrine, central nervous and metabolic systems.[9] In spite of its extreme toxicity, cyanides are still used industrially in the synthesis of organic chemicals, polymers, metallurgy as well as in gold mining.[10] Therefore, the development of chemosensors for the recognition and detection of cyanide is also of great significance.

Unlike some analytical techniques, such as atomic absorption spectrometry,[11] fluorescence techniques,[12] and electrochemical methods,[13] colorimetric methods can conveniently and easily monitor target ions in the visible range with high sensitivity, specificity, simplicity, low cost, and rapid tracking of analytes in biological, toxicological, and environmental samples.[14] Therefore, the colorimetric methods have attracted considerable attention in the detection of toxic metal cations and anions, including copper and cyanide.

Based on the above-mentioned needs, we attempted to design and synthesize a new multifunctional chemosensor for the detection of both Cu^{2+} and CN^-. The new type of

chemosensor consisted of a julolidine moiety and a thiadiazole moiety. Interestingly, the new chemosensor **1** showed a sequential detection of Cu^{2+} and CN^- in an aqueous solution.

In the current paper, we report the synthesis, characterization, and sensing properties of **1** as a selective colorimetric chemosensor for the sequential detection of Cu^{2+} and CN^-. The receptor **1** displayed a highly selective and sensitive colorimetric recognition toward Cu^{2+} by a change in color from yellow to orange, and the in situ formed Cu^{2+}-2•**1** complex exhibited highly selective recognition of CN^- through a color change from orange to yellow in fully aqueous solution. Moreover, **1** could be also used to quantify Cu^{2+} in water samples and as a practical, visible colorimetric detection kit for Cu^{2+}.

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 NMR measurements were performed on a Varian 400 MHz and 100 MHz spectrometer and chemical shifts were recorded in ppm. Electrospray ionization mass spectra (ESI-MS) were collected on a Thermo Finnigan (San Jose, CA, USA) LCQ_{TM} Advantage MAX quadrupole ion trap instrument by infusing samples directly into the source using a manual method. Spray voltage was set at 4.2 kV, and the capillary temperature was at 80 ^oC. Absorption spectra were recorded at room temperature using a Perkin Elmer model Lambda 2S UV/Vis spectrometer. Elemental analysis for carbon, nitrogen, and hydrogen was carried out using a Flash EA 1112 elemental analyzer (thermo) at the Organic Chemistry Research Center of Sogang University, Korea.

*Synthesis of receptor **1***

A solution of 5-amino-1,3,4-thiadiazole-2-thiol (0.15 g, 1.1 mmol) in absolute ethanol was added to a solution containing 8-hydroxyjulolidine-9-carboxaldehyde (0.20 g, 0.9 mmol) in absolute ethanol. Two drops of HCl were added into the reaction solution and it was stirred for 12 h at room temperature. An orange precipitate was filtered, washed several times with methylene chloride and hexane, and dried in vacuum to obtain the pure orange

solid. Yield: 0.21 g (71%). ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 14.17 (s, 1H), 12.25 (s, 1H), 8.35 (s, 1H), 7.00 (s, 1H), 3.32 (m, 4H), 2.59 (m, 4H), 1.84 (m, 4H); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C): δ = 185.61, 166.12, 164.52, 159.01, 149.93, 132.09, 115.26, 107.87, 105.64, 50.37, 49.89, 27.18, 21.69, 20.65, 20.23. LRMS (ESI): m/z calcd. For $C_{15}H_{16}N_4OS_2$-H^+: 331.07; found 331.20. Anal. calcd for $C_{15}H_{16}N_4OS_2$: C, 54.19; H, 4.85; N, 16.85%. Found: C, 54.17; H, 4.87; N, 16.90%.

*UV-vis titration measurements of **1** with Cu^{2+} ion*

Receptor **1** (3.3 mg, 0.01 mmol) was dissolved in dimethyl sulfoxide (DMSO, 1 mL) and 3 μL of the receptor **1** (10 mM) were diluted to 2.997 mL of bis-tris buffer (10 mM bis-tris, pH = 7.0) to make the final concentration of 10 μM. $Cu(NO_3)_2{\cdot}2.5H_2O$ (2.4 mg, 0.01 mmol) was dissolved in bis-tris buffer (10 mL). 1.2-15 μL of the $Cu(NO_3)_2$ solution (1 mM) were transferred to the receptor **1** solution (10 μM) prepared above. After mixing them for a few seconds, UV-vis spectra were taken at room temperature.

*Job plot measurement of **1** with Cu^{2+} ion*

Receptor **1** (3.3 mg, 0.01 mmol) was dissolved in DMSO (1 mL) and 30 μL of the receptor **1** (10 mM) were diluted to 29.97 mL of bis-tris buffer to make the final concentration of 10 μM. $Cu(NO_3)_2{\cdot}2.5H_2O$ (2.4 mg, 0.01 mmol) was dissolved in bis-tris buffer (1 mL) and 30 μL of the copper solution (10 mM) were diluted to 29.97 mL of bis-tris buffer to make the final concentration of 10 μM. 4.5, 4.0, 3.5, 3.0, 2.5, 2.0, 1.5, 1.0, and 0.5 mL of the **1** solution were taken and transferred to vials. 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, and 4.5 mL of the copper solution were added to solutions of **1** prepared above. Each vial had a total volume of 5 mL. After shaking the vials for a few seconds, UV-vis spectra were taken at room temperature.

*Competition of **1** towards various metal ions*

Receptor **1** (3.3 mg, 0.01 mmol) was dissolved in DMSO (1 mL) and 3 μL of this solution (10 mM) were diluted with 2.994 mL of bis-tris buffer to make the final concentration of 10 μM. MNO_3 (M = Na, K; 0.01 mmol), $M(NO_3)_2$ (M = Mn, Co, Ni, Cu, Zn, Cd, Mg, Ca, Pb; 0.01 mmol), $M(ClO_3)_2$ (M = Fe; 0.01 mmol) and $M(NO_3)_3$ (M = Al, Fe, Cr, Ga, In; 0.01 mmol) were separately dissolved in bis-tris buffer (1 mL). 1.5 μL of each metal solution (10 mM) were taken and added into 3mL of each receptor **1** (10 μM) prepared above

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

Determination of Cu^{2+} in water samples

UV-vis spectra measurements of water samples containing Cu^{2+} were carried by adding 9 μL of 10 mM stock solution of **1** and 0.60 mL of 50 mM bis-tris buffer stock solution to 1.791 mL sample solutions. 0.60 mL of DMSO were taken and added into the sample solution. The sample solution had a total volume of 3 mL. After well mixed, the solutions were allowed to stand at 25 ˚C before the test.

Colorimetric test strips towards metal ions

Receptor **1** (1.0 mg, 0.003 mmol) was dissolved in DMSO (1 mL). Receptor **1**-test strips were prepared by immersing filter papers into receptor **1** solution (3 mM), and then dried in oven. MNO_3 (M = Na, K; 0.2 μmol), $M(NO_3)_2$ (M = Mn, Co, Ni, Cu, Zn, Cd, Mg, Ca, Pb; 0.2 μmol), $M(ClO_3)_2$ (M = Fe; 0.2 μmol) or $M(NO_3)_3$ (M = Al, Fe, Cr, Ga, In; 0.2 μmol) were separately dissolved in buffer (40 mL). The test strips prepared above were added into different metal solutions (5 μM), and then dried at room temperature.

*UV-vis titration measurements of Cu^{2+}-2•**1** complex with cyanide*

Receptor **1** solution (30 μM, 1.5 mL) and Cu^{2+} solution (15 μM, 1.5 mL) were prepared and mixed to make copper complex. Tetraethylammonium cyanide (TEACN, 83.1 mg, 0.2 mmol) was dissolved in bis-tris buffer (1 mL). 4.5-58.5 μL of the CN^- solution (200 mM) were poured into the ready-made copper complex solution. UV-vis spectra were recorded in an indicated time after the addition.

*Job plot measurement of Cu^{2+}-2•**1** complex with cyanide*

Receptor **1** (6.6 mg, 0.02 mmol) was dissolved in DMSO (1 mL) and $Cu(NO_3)_2{\cdot}2.5H_2O$ (2.4 mg, 0.01 mmol) was dissolved in bis-tris buffer (1 mL). The two solutions were mixed to make Cu^{2+}-2•**1** complex. 27, 24, 21, 18, 15, 12, 9, 6 and 3 μL of the Cu^{2+}-2•**1** complex solution were taken and transferred to vials. Each vial was diluted with bis-tris buffer to make a total volume of 2.970 mL. TEACN (1.7 mg, 0.01 mmol) was

dissolved in bis-tris buffer (1 mL). 3, 6, 9, 12, 15, 18, 21, 24 and 27 μL of the TEACN solution were added to each diluted Cu^{2+}-2•**1** solution. Each vial had a total volume of 3 mL. After reacting them for a few seconds, UV-vis spectra were taken at room temperature.

*Competition of Cu^{2+}-2•**1** complex towards various anions*

Receptor **1** (3.3 mg, 0.01 mmol) was dissolved in DMSO (1 mL) and $Cu(NO_3)_2 \cdot 2.5H_2O$ (1.2 mg, 0.005 mmol) was dissolved in bis-tris buffer (1 mL). The two solutions were mixed to make **1**-Cu^{2+} complex and 9 μL of this solution (5 mM) were diluted with 2.901 mL of bis-tris buffer to make the final concentration of 30 μM. Tetraethylammonium salts (TEAX) (X = F^-, Cl^-, Br^-, I^-, and CN^-; 0.2 mmol) and tetrabutylammonium salts (TBAX) (X = OAc^-, $H_2PO_4^-$, N_3^-, and SCN^-; 0.2 mmol) were dissolved bis-tris buffer (1 mL), respectively. 45 μL of each anion solution (200 mM) were taken and added into 2.91 mL of each Cu^{2+}-2•**1** complex solution prepared above to make 200 equiv. Then, 45 μL of the cyanide solution (200 mM) were added into the mixed solution of each anion and Cu^{2+}-2•**1** complex to make 200 equiv. After mixing them for a few minutes, UV-vis spectra were taken at room temperature.

CN^- reversibility

Receptor **1** (3.3 mg, 0.01 mmol) was dissolved in DMSO (1 mL) and $Cu(NO_3)_2 \cdot 2.5H_2O$ (1.2 mg, 0.005 mmol) was dissolved in bis-tris buffer (1 mL). The two solutions were mixed to make **1**-Cu^{2+} complex and 9 μL of this solution (5 mM) were diluted with 2.946 mL of bis-tris buffer to make the final concentration of 30 μM. After mixing it for a few seconds, UV-vis spectrum was taken at room temperature. TEACN (0.2 mmol) was dissolved in buffer solution (1 mL) and 45 μL of the cyanide solution (200 mM) were added to the solution of Cu^{2+}-2•**1** complex prepared above. After mixing it for a minute, UV-vis spectrum was taken. For the reversibility study, another 4.5 μL of the Cu^{2+} ion solution (10 mM) was added to the above solution. After mixing it for a minute, UV-vis spectrum was taken at room temperature. The same experimental procedure was repeated one more time.

Results and discussion

*Synthesis and characterization of receptor **1***

Receptor **1** was synthesized by the condensation reaction of 5-amino-1,3,4-thiadiazole-2-thiol and 8-hydroxyjulolidine-9-carboxaldehyde in ethanol (Scheme 1) and characterized by ^{1}H NMR, ^{13}C NMR, ESI-mass spectrometry and elemental analysis.

*Spectral and colorimetric response of **1** toward Cu^{2+}*

The sensing abilities of **1** were primarily investigated in bis-tris buffer (10 mM, pH 7.0) upon addition of various metal ions such as 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+}, and Pb^{2+}. Upon the addition of 0.5 equiv of each cation, Cu^{2+} and Cd^{2+} induced distinct spectral changes, while other metal ions showed either no or slight change in the absorption spectra relative to the free receptor **1** (Fig. 1(a)). We presumed that Cd^{2+} with an oxophilic character bound to **1**, and that Cu^{2+} strongly did to **1** by Irving-Williams series of stability. Importantly, the color of the solution of **1** changed from yellow to orange in the presence of only Cu^{2+} ion (Fig. 1(b)), indicating that receptor **1** can serve as a potential chemosensor for "naked-eye" detection of Cu^{2+} in aqueous solution.[15,16]

The binding properties of **1** with Cu^{2+} were further studied by UV-vis titration experiments (Fig. 2). The peak at 450 nm in the UV-vis spectrum decreased gradually upon the addition Cu^{2+}, while a new band at 525 nm gradually reached a maximum at 0.5 equiv of Cu^{2+}. Meanwhile, two clear isosbestic points were observed at 385 nm and 492 nm, indicating that only one product was generated from **1** upon binding to Cu^{2+}. The band with molar extinction coefficient in the thousands (1.0×10^{5} M^{-1} cm^{-1} at 525 nm) was too large to be Cu-based d-d transitions, and thus was considered as ligand-based transitions.[17] Therefore, the color change could be explained by ligand-to-metal charge-transfer (LMCT) mechanism.

The Job plot analysis[18] revealed a 1:2 stoichiometric ratio between the Cu^{2+} ion and **1** (Fig. 3). The positive-ion mass spectrum of **1** with 0.5 equiv of Cu^{2+} showed the formation of the 2•**1**-2•H^{+}+Cu^{3+} complex (*m/z* 725.07, calcd. *m/z* 725.07) (Fig. 4). Additionally, we carried out FT-IR measurements to understand the binding mode of Cu^{2+}-2•**1** complex (Fig. S1). FT-IR spectrum of Cu^{2+}-2•**1** complex showed that the characteristic stretching frequency (3077

cm^{-1}) of the OH group at equilibrium state of keto and enol forms disappeared. Based on the Job plot, UV-vis titration, ESI-mass spectrometry analysis and FT-IR measurements, we proposed the structure of a 2:1 complex of **1** and Cu^{2+} as shown in Scheme 2.

From the UV-vis titration data, the association constant for Cu^{2+}-2·**1** complexation was determined to be 1.0×10^{10} M^{-2} using Li's equations (Fig. S2).[19] This value was within the range of those (10^3-10^{12}) reported for Cu^{2+} sensing chemosensors.[20] The detection limit[21] of receptor **1** for Cu^{2+} ions on the basis of 3σ/K was found to be 0.9 μM (Fig. S3), which is much lower than the WHO limit for Cu^{2+} (31.5 μM) in drinking water.[4] Therefore, receptor **1** can serve as a good indicator for monitoring Cu^{2+} ion in drinking water.

The preferential selectivity of **1** as a colorimetric sensor for Cu^{2+} was studied in presence of different cations such as Na^+, K^+, Mg^{2+}, Ca^{2+}, Al^{3+}, Ga^{3+}, In^{3+}, Cr^{3+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+}. Upon addition of 0.5 equiv of each metal ion into the mixed solution of **1** and Cu^{2+}, there was no interference in the detection of Cu^{2+} from all metal ions tested (Fig. 5). This result strongly indicated that receptor **1** could be an excellent chemosensor for the practical detection of Cu^{2+} in water samples.

Furthermore, a calibration curve was also constructed for quantitative determination of Cu^{2+} by **1** (Fig. S4). Receptor **1** exhibited a good linear relationship between the absorbance of **1** and Cu^{2+} concentration (1.00-10.00 μM) with a correlation coefficient of R^2 = 0.999 (n = 3), which means that **1** could be suitable for the quantitative detection of Cu^{2+}. In order to examine the applicability of the chemosensor **1** in environmental samples, the chemosensor was applied for the determination of Cu^{2+} in pure water samples. First, two tap water samples were prepared. As shown in Table 1, satisfactory recovery and R.S.D. values of the water samples were exhibited. Second, we prepared two drinking water samples. The results are also summarized in Table 1, which exhibited satisfactory recovery and R.S.D. values for the drinking water samples.

For practical application of receptor **1**, test strips were prepared by immersing filter papers in a DMSO solution of **1** and then dried in oven. These test strips were used to sense Cu^{2+} among different cations. As shown in Fig. 6, when the test strips coated with **1** were added to different cation solutions (5 μM), the clear color change was observed only for Cu^{2+}

in bis-tris buffer solution. Therefore, the test strips coated with the receptor **1** solution would be convenient for detecting Cu^{2+} below the guideline of WHO. Importantly, this is the first example that **1** could detect the lowest concentration of copper by a simple test strip in aqueous solution, to the best of our knowledge. These results support that receptor **1** could have a practical application for detecting Cu^{2+} in environmental samples.

*Spectral and colorimetric response of Cu^{2+}-2•**1** complex toward CN^-*

Since we and others have already shown that cyanide ions co-ordinate well to Cu^{2+} ions to form a very stable complex $Cu(CN)_x$,[22] the selectivity of Cu^{2+}-2•**1** complex toward CN^- was investigated using the copper-cyanide affinity. The absorbance spectral study of Cu^{2+}-2•**1** complex with various anions was carried out in bis-tris buffer (10 mM, pH 7.0; Fig. 7). The addition of CN^- to Cu^{2+}-2•**1** complex showed a significant change in the UV-vis spectrum (Fig. 7 (a)) and a color change from orange to yellow (Fig. 7(b)), while no change was observed with other anionic species such as OAc^-, F^-, Cl^-, Br^-, I^-, $H_2PO_4^-$, N_3^-, and SCN^- under identical conditions.

In order to study the binding properties of Cu^{2+}-2•**1** complex with CN^-, a UV-vis titration was carried out (Fig. 8). On gradual addition of CN^- to a solution of Cu^{2+}-2•**1** complex, the absorption band at 454 nm increased with distinct isosbestic points at 417 nm and 492 nm, indicating the formation of only one UV-active species. Moreover, the final UV-vis spectrum of Cu^{2+}-2•**1** with CN^- was nearly identical to that of **1**, indicating that **1** was reproduced (Fig. S5). The Job plot analysis[18] revealed a 1:1 stoichiometric ratio between the Cu^{2+}-2•**1** complex and CN^- (Fig. S6). Moreover, the negative ion mass spectrum (Fig. S7) demonstrated that Cu^{2+}-2•**1** complex released the **1**($-H^+$) (*m/z* 331.20*,* calcd. *m/z* 331.07) by demetallation mechanism due to the formation of the stable complex $Cu(CN)_x$. Based on the UV-vis titration, Job plot and ESI-mass spectrometry analysis, we propose the demetallation mechanism of Cu^{2+}-2•**1** complex by CN^- as shown in Scheme 3. The detection limit[21] of Cu^{2+}-2•**1** ensemble for the analysis of CN^- was found to be 210 μM on the basis of 3σ/K (Fig. S8).

The preferential selectivity of Cu^{2+}-2•**1** toward CN^- was studied in the presence of

various competing anions. For competition tests, Cu^{2+}-2•**1** complex was treated with 200 equiv of CN^- in the presence of the same concentration of other anions. The presence of other background anions showed no change in absorbance (Fig. 9 (a)) and color (Fig. 9 (b)), except for $H_2PO_4^-$, which inhibited slightly.

To examine the reversibility of receptor **1** toward Cu^{2+} in bis-tris buffer solution, CN^- was added to the mixed solution of receptor **1** and Cu^{2+} (Fig. 10). The solution color changed from orange to yellow (the original color of **1**). Upon addition of Cu^{2+} into the mixture solution again, the absorbance at 450 nm disappeared accompanied by a color change from yellow to orange. These results indicated that receptor **1** could be recycled simply through treatment with CN^-. Such reversibility and regeneration are important for the fabrication of chemosensors to sense CN^- in aqueous environmental solution.

Conclusion

We have developed a new colorimetric sensor **1**, based on the combination of julolidine and thiadiazole, for the sequential detection of Cu^{2+} and CN^-. The receptor **1** displayed a highly selective and sensitive colorimetric recognition toward Cu^{2+} by color change from yellow to orange, and enabled the analysis of Cu^{2+} ions with a sensitivity limit of 0.9 μM, which was below the WHO acceptable limit (31.5 μM) in drinking water. Moreover, **1** could be also used to detect and quantify Cu^{2+} in water samples and as a practical, visible colorimetric test strip for quantifying Cu^{2+} as low as 5 μM in aqueous environment. Furthermore, the Cu^{2+}-2•**1** complex can be used as a colorimetric sensor for cyanide through a change in color from orange to yellow in aqueous solution. Therefore, these results may contribute to the development of a novel type of chemosensors for the sequential recognition of Cu^{2+} and CN^- by a colorimetric method in aqueous solution.

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Supplementary data

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

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15 The sensing abilities of **1** were investigated without bis-tris buffer under the same

condition. Any effects of the bis-tris buffer were not observed.

16 One of the referees suggested that UV-vis selectivity of **1** would be better carried out for Pd^{2+} and Pt^{2+}. Therefore, we performed the UV-vis selectivity of **1** for Pd^{2+} and Pt^{2+}, and found that Pd^{2+} showed the color and UV-vis changes like the Cu^{2+}, while Pt^{2+} did no change (Fig. S9). Nevertheless, the resulting **1**-Pd^{2+} complex did not recognize CN^-. Therefore, we did not further studied the spectral and photophysical properties with Pd^{2+}, because Pd^{2+} and Pt^{2+} do not appear much in our environment.

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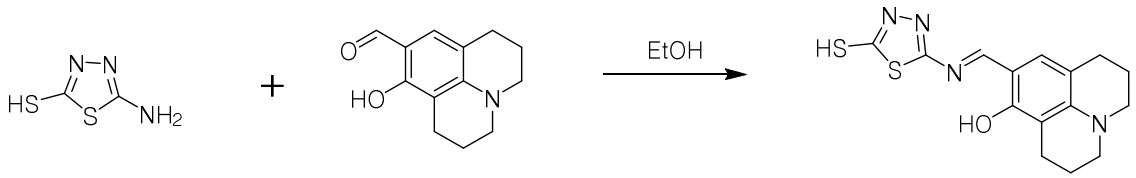
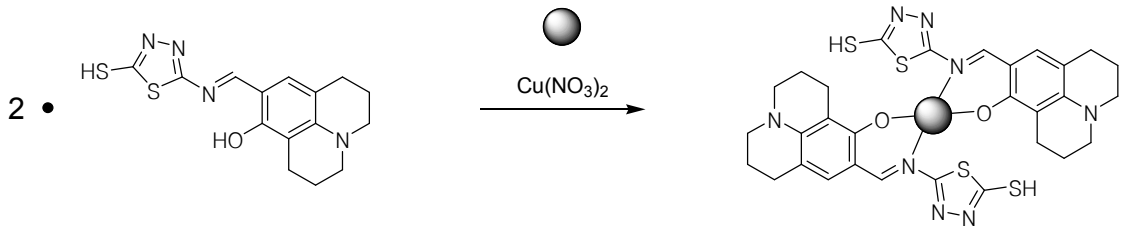
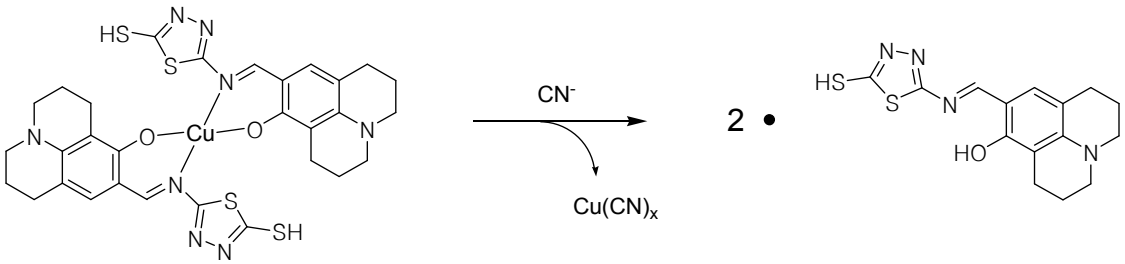


Scheme 1. Synthetic procedure of receptor **1**.



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



Scheme 3. Proposed sensing mechanism of Cu^{2+}-2•**1** complex for cyanide.

Table 1 Determination of Cu^{2+} 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	-	-
	6.00	5.87	97.8	1.42
Drinking water	0.00	0.00	-	-
	7.00	7.13	101.9	0.95

[**1**] = 30 μmol/L in 10 mM bis-tris buffer-DMSO solution (8:2, pH 7.0).

Figure captions

Fig. 1 (a) Absorption spectral changes of **1** (10 μM) in the presence of 0.5 equiv of different metal ions in bis-tris buffer (10 mM bis-tris, pH = 7.0). (b) The color changes of **1** (30 μM) upon addition of various metal ions (0.5 equiv) in bis-tris buffer (10 mM bis-tris, pH = 7.0).

Fig. 2 Absorption spectral changes of **1** (10 μM) upon addition of Cu^{2+} (up to 0.5 equiv) in bis-tris buffer at room temperature. Inset: Absorption at 525 nm versus the number of equiv of Cu^{2+} added.

Fig. 3 Job plot for the binding of receptor **1** and Cu^{2+}, where the intensity at 525 nm was plotted against the mole fraction of Cu^{2+}. The total concentrations of Cu^{2+} with receptor **1** were 10 μM.

Fig. 4 Positive-ion electrospray ionization mass spectrum of **1** (100 μM) upon addition of Cu^{2+} (50 μM).

Fig. 5 (a) Competitive selectivity of **1** (10 μM) toward Cu^{2+} (0.5 equiv) in the presence of other metal ions (0.5 equiv). (b) Color changes of **1** (30 μM) in the presence of Cu^{2+} (0.5 equiv) and other metal ions (0.5 equiv).

Fig. 6 Photographs of the filter papers coated with **1** (3 mM) for detecting Cu^{2+} ion (5 μM) in the presence of various metal ions.

Fig. 7 (a) Absorption spectral changes of the Cu^{2+}-2•**1** complex (15 μM) in the presence of 200 equiv of different anions in bis-tris buffer solution. (b) The color changes of the Cu^{2+}-2•**1** complex (15 μM) upon addition of various anions (200 equiv) in bis-tris buffer solution.

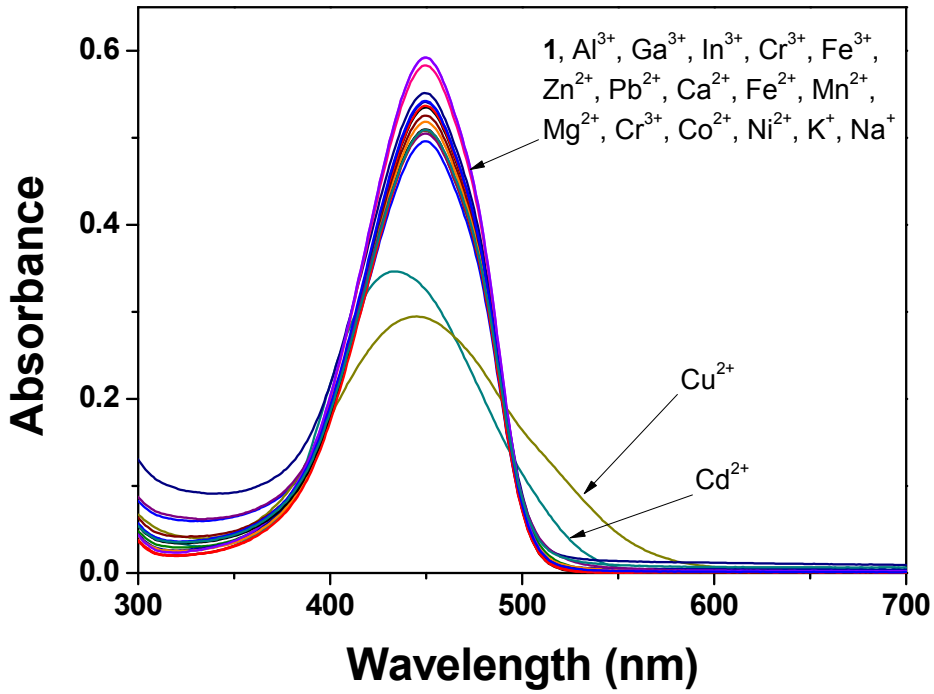
Fig. 8 Absorption spectral changes of Cu^{2+}-2•**1** (15 μM) upon addition of CN^- (up to 260 equiv) in bis-tris buffer at room temperature. Inset: Absorption at 454 nm versus the number of equiv of Cu^{2+} added.

Fig. 9 (a) Competitive selectivity of Cu^{2+}-2•**1** (15 μM) toward CN^- (200 equiv) in the presence of other anions (200 equiv). (b) Color changes of Cu^{2+}-2•**1** (15 μM) in the presence of CN^- (200 equiv) and other anions (200 equiv).

Fig. 10 (a) Reversible UV-vis spectral changes of Cu^{2+}-2•**1** (15 μM) after the sequential addition of Cu^{2+} and CN^- in bis-tris buffer solution. (b) The color changes of **1** (30 μM) after

the sequential addition of Cu^{2+} and CN^- in bis-tris buffer solution.

(a)



(b)

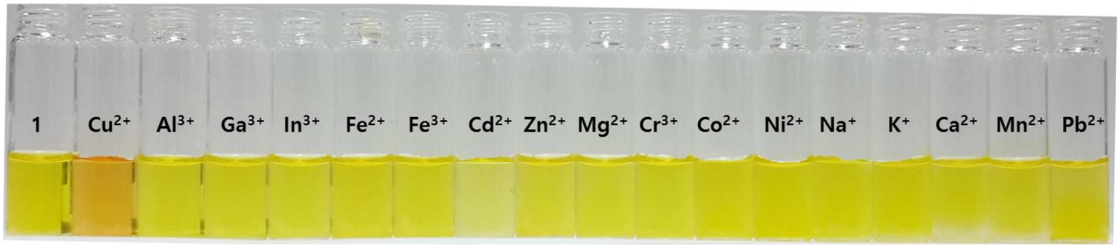


Fig. 1

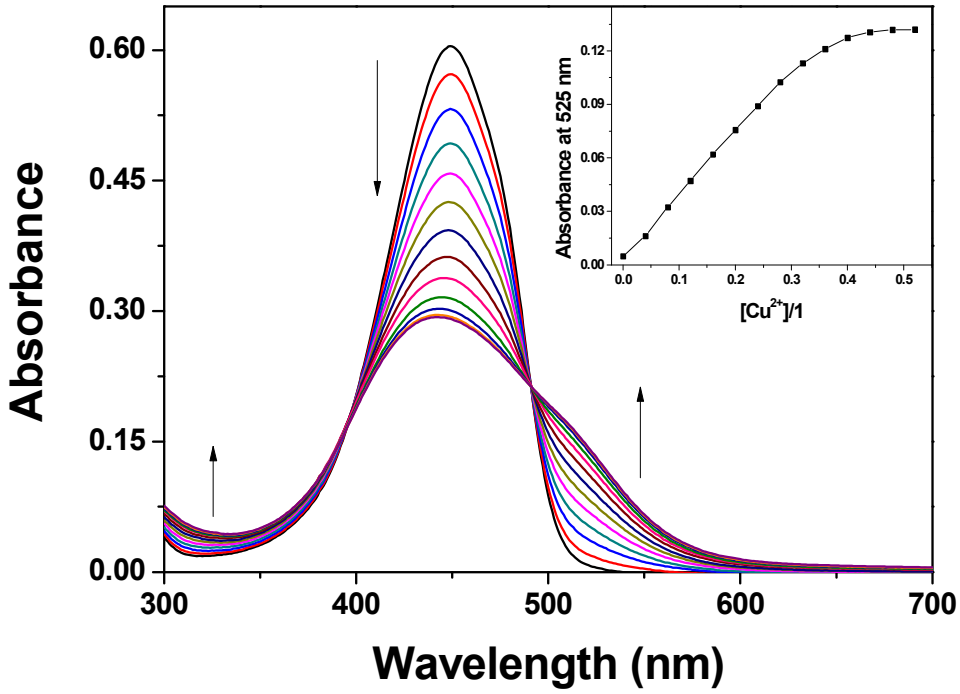


Fig. 2

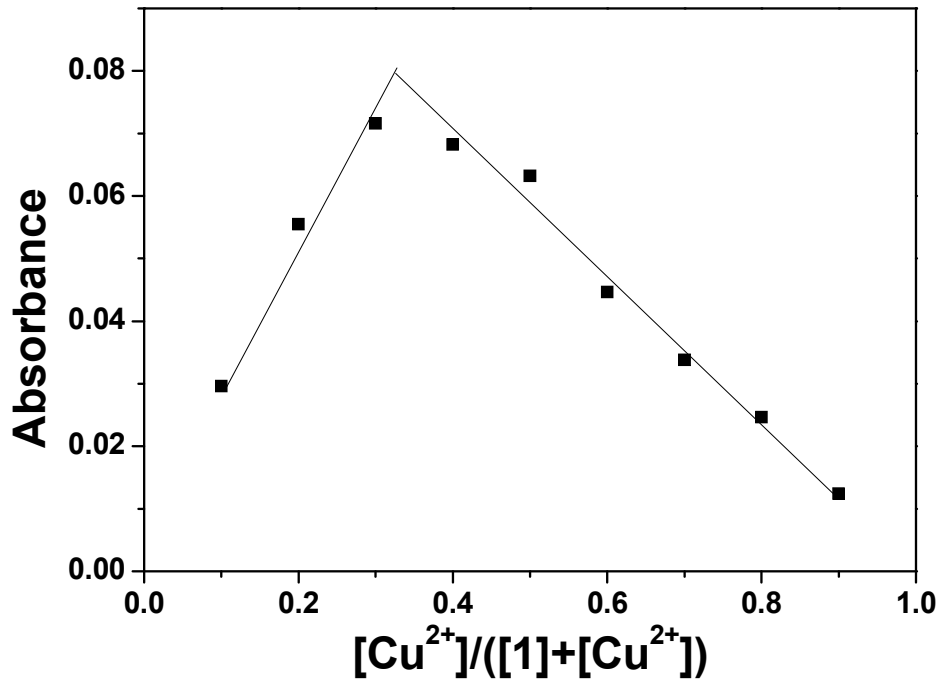


Fig. 3

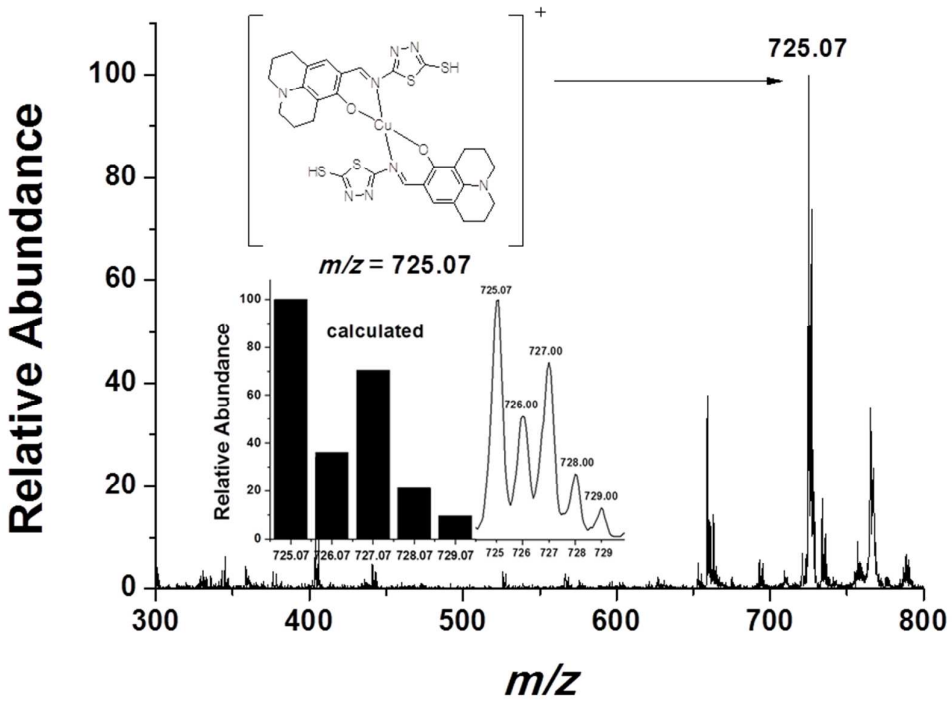
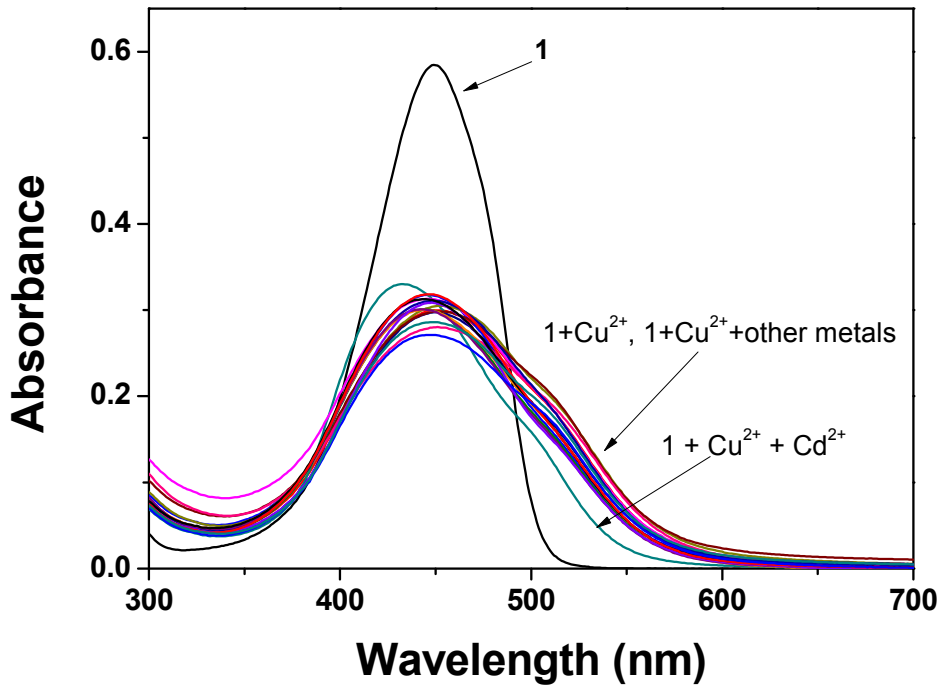


Fig. 4

(a)



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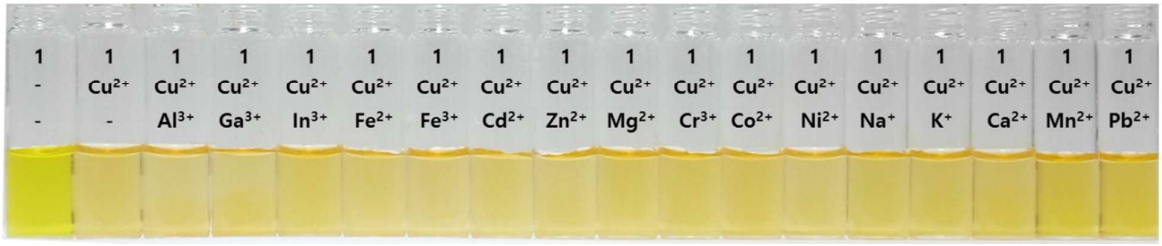


Fig. 5

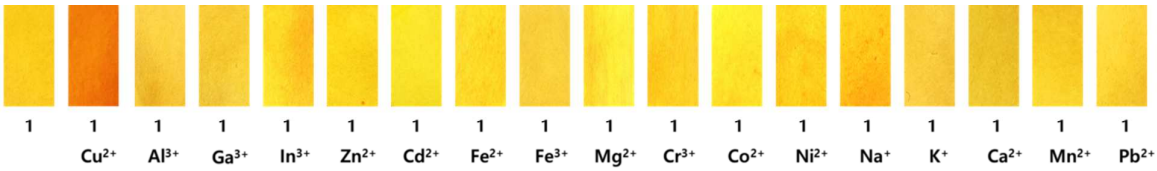
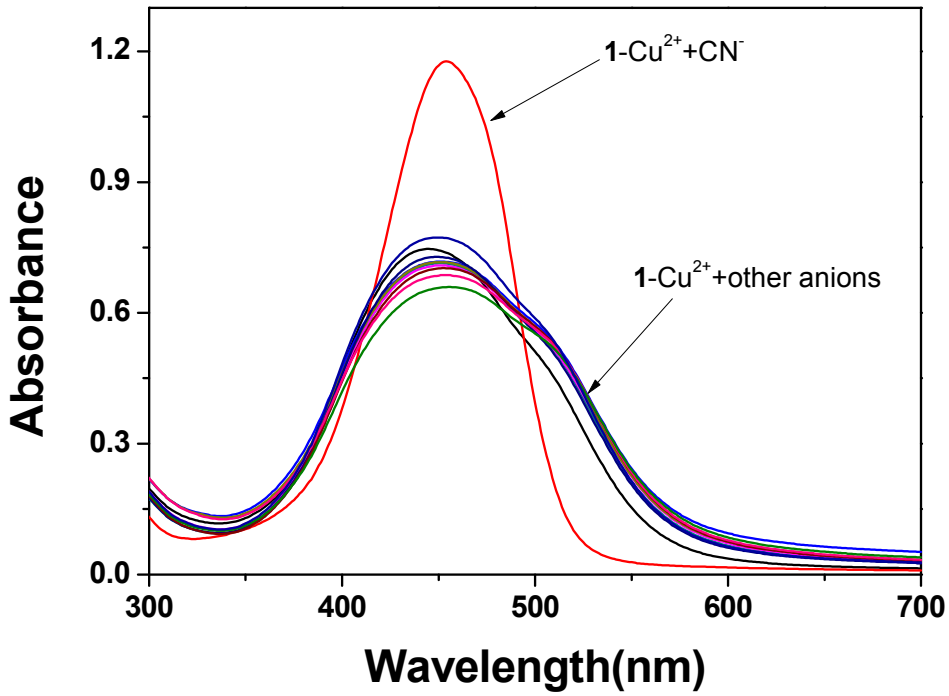


Fig. 6

(a)



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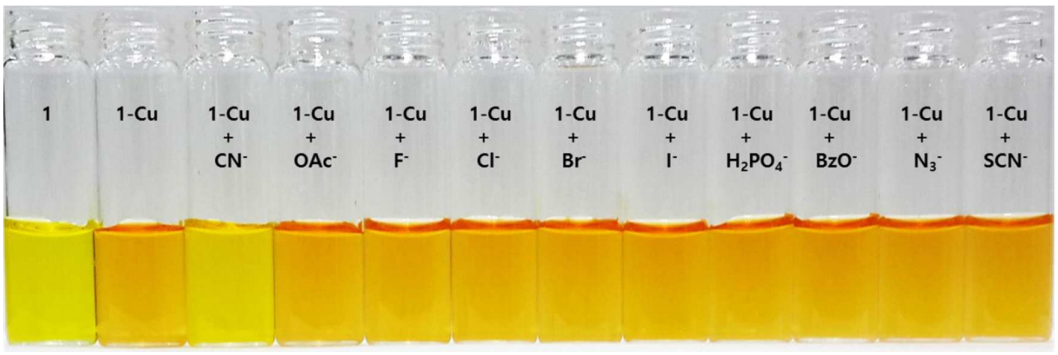


Fig. 7

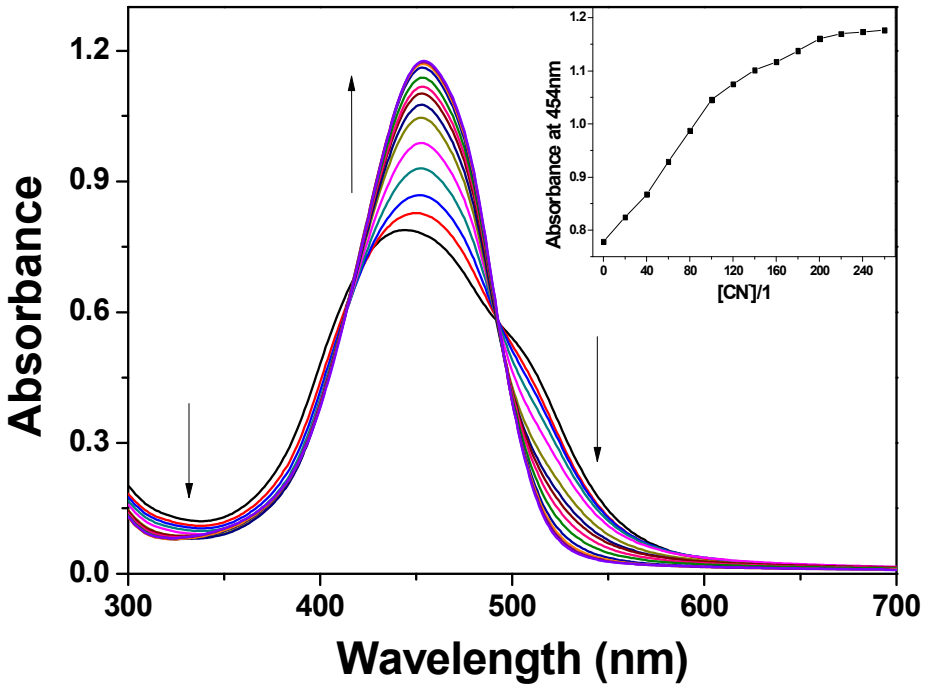
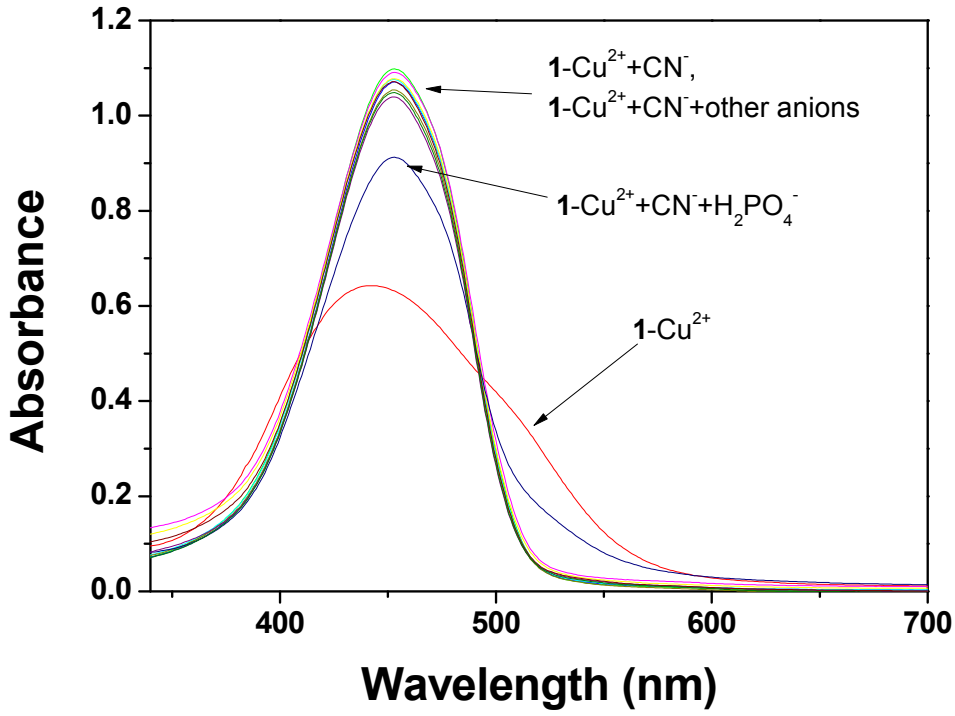


Fig. 8

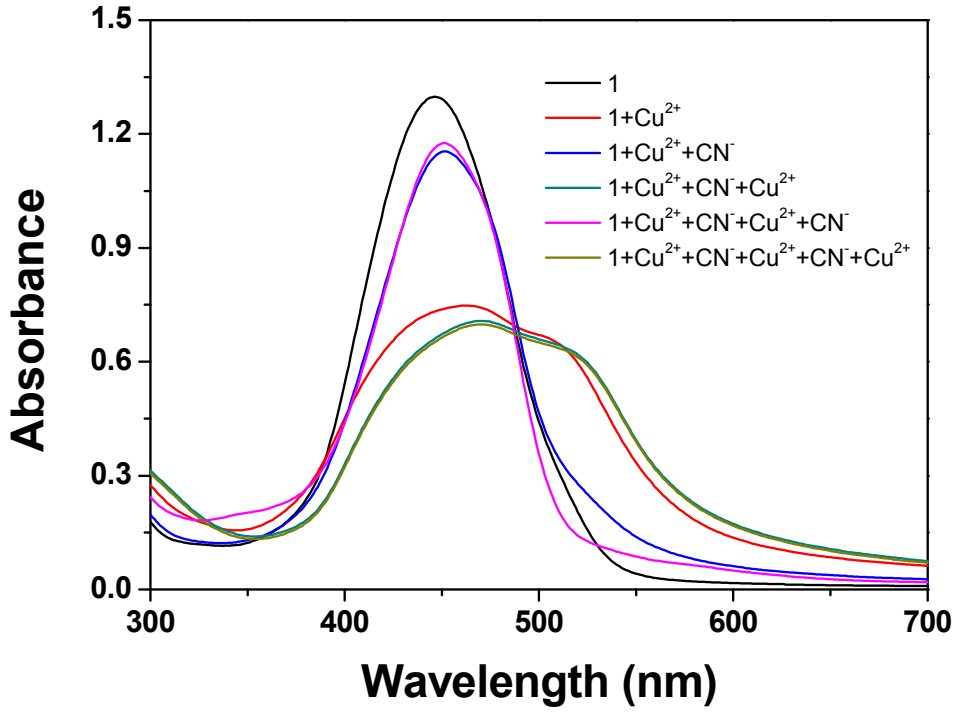
(a)



(b)

Fig. 9

(a)



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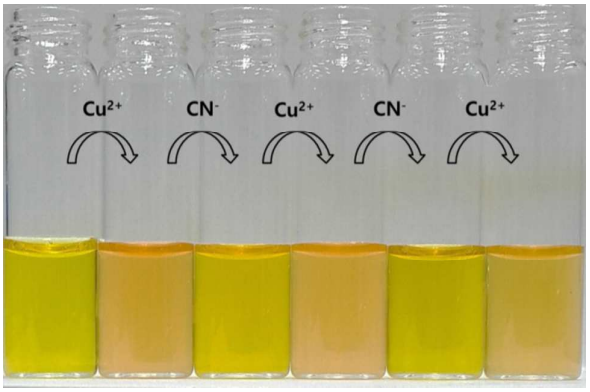
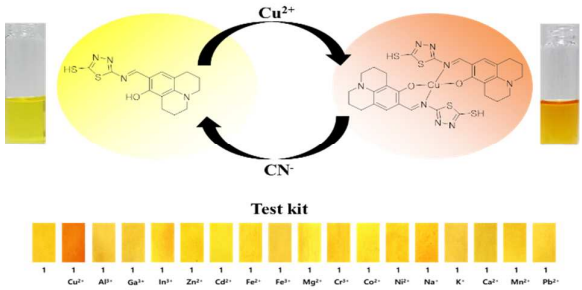


Fig. 10

Graphical abstract



A colorimetric chemosensor was synthesized for sequential detection of Cu^{2+} and CN^-, and used to detect and quantify Cu^{2+}.