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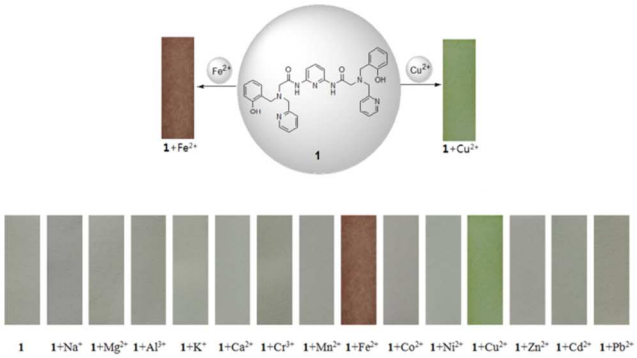
Graphical Abstract

The receptor **1** provides a novel approach for the simultaneous colorimetric recognition of two metal ions Fe^{2+} and Cu^{2+}.



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A single colorimetric sensor for multiple target ions: the simultaneous detection of Fe^{2+} and Cu^{2+} in aqueous media

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This study demonstrates the design, synthesis and sensing properties of a simple and efficient chemosensor **1** (**1** = 2,6-bis((2-(((pyridine-2-yl)methylamino)methyl)phenol)ethylamido)pyridine) to rapidly detect Fe^{2+} and Cu^{2+} in aqueous solution (Bis-tris buffer/DMF (8/2, v/v)), exploiting UV-vis spectral analysis, naked-eye and paper devices. The sensor **1** showed significant absorption spectra at 455 nm for Fe^{2+} and 660 nm for Cu^{2+}, which are responsible for color changes due to the metal-to-ligand charge-transfer. The binding modes of **1** with Fe^{2+} or Cu^{2+} have been investigated by Job plot and ESI-Mass analysis. In addition, the sensor **1** could be recyclable simply through treatment with a proper reagent such as EDTA. Moreover, the sensor has been used in the development of practically viable colorimetric kits.

Introduction

Biologically relevant metal cations play crucial roles in many physiological and pathological processes.[1,2] Therefore, the development of chemosensors for the detection of the metal cations is vibrant area of investigation due to the potential applications of these chemosensors as diagnostic tools in medical, physiological and environmental applications.[3] Among metal cations, iron and copper ions have bio-importance and are the first and third most abundant transition elements, respectively, in human body.

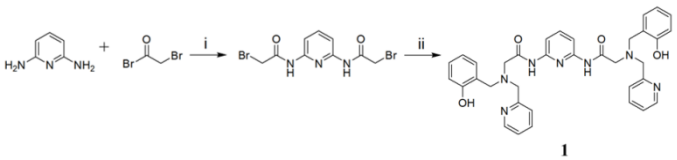
In well-nourished people the total iron content is ~4 g (70% in Hgb, 25% in storage).[4] In proportion to the amounts of iron in human body, iron is the most essential transition element responsible for carrying the oxygen in heme and acts as cofactor in enzymatic reactions of mitochondrial respiratory chain.[5-8] However, iron deficiency leads to anemia, liver and kidney damages, diabetes, and heart diseases.[9-13] Accretion of iron in the central nervous system has been involved in a number of diseases such as Parkinson's, Huntington's and Alzheimer's disease, associated with an increased quantity of iron.[14-19] In addition, two oxidation states (Fe^{2+} and Fe^{3+}) of iron are one of the important redox pairs in biological systems.

Copper plays an important role as a redox catalyst in biological processes such as electron transfer reactions involving oxidation of various organic substrates.[20-31] The adult human body contains 1.4-2.1 mg of copper per kilogram of body weight under normal conditions.[30] At high concentrations, copper becomes toxic and causes oxidative stress and disorders associated with neurodegenerative diseases including Alzheimer's, Parkins's, Menke's, Wilson's and prion diseases.[31-34] The World Health Organization (WHO) has recommended the maximum limit of copper in drinking water to be at 2 ppm (30 μM).[20] In view of the significance of iron and copper ions, therefore, it is very necessary to efficiently monitor the presence of iron and copper metal ions. As a result, the development of simple and rapid sensors for iron and copper ions has attracted wide research interest. The most attractive approach for iron and copper detection is a colorimetric method, because they can be easily observed and determined by eye, rather than by using large, sophisticated, and expensive analytical instruments.[35-43] Therefore, there is a strong demand for new colorimetric chemosensors that can achieve naked-eye detection in the visible wavelength region without the requirement of equipment.[43-45] In addition, paper-based assays using the colorimetric method are attractive for portable point-of-measurement (POM) monitoring and on-site detection due to advantages which include low cost, portability, ease of use, high speed, and low reagent and sample consumption.[46,47]

Recently, we demonstrated that the chemosensor obtained from the displacement of dipicolylamine by PAP (2-(((pyridin-3-yl)methylamino)methyl)phenol) showed a change of the sensing property from a fluorogenic sensing for Zn^{2+} to a colorimetric sensing for Co^{2+} ions.[48] These results led us to design a new chemosensor that two dipicolylamines attached to

the skeleton of the pyridyl amide[49] are displaced with the two PAP groups (Scheme 1). To this end, we synthesized the new chemosensor **1** and tested its sensing properties to a variety of metal ions. Surprisingly, the **1** showed colorimetrically the simultaneous detection of Fe^{2+} and Cu^{2+}.

Herein, we report on the development of a colorimetric sensor based on PAP platform for rapid determination of Fe^{2+} and Cu^{2+} in aqueous solution (Bis-tris buffer/DMF = 8/2, v/v, pH 7.0). The solution colors of **1** with Fe^{2+} and Cu^{2+} changed from colorless to light orange and to green, respectively. To our best knowledge, it is the second report that the simultaneous detection of Fe^{2+} and Cu^{2+} could be carried out colorimetically by **1** in aqueous solution.[11] In particular, it is very valuable to detect Fe^{2+} and Cu^{2+} with naked-eye, because Fe^{2+} and Cu^{2+} are well known fluorescent quenchers due to their paramagnetic nature which makes it practically difficult to develop fluorescent sensors for their detection.



Scheme 1. Synthesis of **1**. (i) pyridine, 1h. (ii) PAP, TEA, 4h.

Experimental section

General information

All the solvents and reagents (analytical grade and spectroscopic grade) were obtained commercially and used as received. 2,6-Bis(chloroethylamido)pyridine[49] and 2-(((pyridin-3-yl)methylamino)methyl)phenol[50] were prepared according to the procedure reported in the literature. ^1H and ^{13}C NMR spectra were recorded on a Varian 400 MHz spectrometer and chemical shifts are recorded in ppm. Absorption spectra were recorded at room temperature 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) LCQTM Advantage MAX quadrupole ion trap instrument. 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

2,6-Bis(chloroethylamido)pyridine (0.7370 g, 2.1 mmol), 2-(((pyridin-3-yl)methylamino)methyl)phenol (0.8570 g, 4 mmol) and triethylamine (588 μL, 4.2 mmol) were dissolved in acetonitrile (30 mL). After the reaction solution was stirred for 4 h at room temperature, the liquid was removed under reduced pressure to obtain brown oil, which was purified by silica gel column chromatography (1/8, v/v, THF : EA). Yield: 0.78 g (63.5 %). ^1H NMR (DMSO-d_6, 400 MHz): δ 10.32 (s, 2H), 10.02 (s, 2H), 7.77 (m, 5H), 7.41 (d, 2H), 7.26 (t, 2H), 7.21 (d, 2H), 7.12 (t, 2H), 6.82 (d, 2H), 6.76 (t, 2H), 3.91 (s, 4H), 3.81 (s, 4H), 3.43 (s, 4H); HRMS (ESI) m/z calcd for $C_{35}H_{35}N_7O_4$ + H^+: 618.28 $[M+H]^+$; Found: 618.13; Anal. calcd for $C_{35}H_{35}N_7O_4$: C, 68.06; H, 5.71; N, 15.87. Found: C, 67.69; H, 5.85; N, 16.17.

UV-vis titrations

dissolved in DMF (2 mL) and 20 μL of the receptor **1** (3 mM) were diluted with 2.980 mL Bis-tris buffer/DMF (8/2) to make the final concentration of 20 μM. $Fe(ClO_4)_2$ (20.79 mg, 0.08 mmol) was dissolved in Bis-tris buffer/DMF (8/2, 4 mL) and 0.6-6 μL of the Fe^{2+} solution (20 mM) were transferred to receptor **1** solution (20 μM) prepared above. After mixing them for a few second, UV-vis spectra were taken at room temperature.

For Cu^{2+} ion; Receptor **1** (3.7 mg, 0.006 mmol) was dissolved in DMF (2 mL) and 20 μL of the receptor **1** (3 mM) were diluted with 2.980 mL Bis-tris buffer/DMF (8/2) to make the final concentration of 20 μM. $Cu(NO_3)_2$ (18.9 mg, 0.08 mmol) was dissolved in Bis-tris buffer/DMF (8/2, 4 mL) and 0.6-6 μL of the Cu^{2+} solution (20 mM) were transferred to receptor **1** solution (20 μM) prepared above. After mixing them for a few second, UV-vis spectra were taken at room temperature.

Job plot measurements

For Fe^{2+} ion; Receptor **1** (1.48 mg, 0.0024 mmol) was dissolved in DMF (40 mL). 5, 4.5, 4, 3.5, 3, 2.5, 2, 1.5, 1 and 0.5 mL of the receptor **1** solution were taken and transferred to vials. $Fe(ClO_4)_2$ (0.98 mg, 0.0024 mmol) was dissolved in Bis-tris buffer/DMF (8/2, 4 mL). 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5 and 5 mL of the Fe^{2+} ion were taken and transferred to each receptor **1** solution prepared above. 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.

For Cu^{2+} ion; Receptor **1** (1.48 mg, 0.0024 mmol) was dissolved in DMF (40 mL). 5, 4.5, 4, 3.5, 3, 2.5, 2, 1.5, 1, and 0.5 mL of the receptor **1** solution were taken and transferred to vials. $Cu(NO_3)_2$ (0.98 mg, 0.0024 mmol) was dissolved in Bis-tris buffer/DMF (8/2, 4 mL). 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5 and 5 mL of the Cu^{2+} ion were taken and transferred to each receptor **1** solution prepared above. 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.

Competition with other metal ions

For Fe^{2+} ion; Receptor **1** (3.7 mg, 0.006 mmol) was dissolved in DMF (1 mL) and 20 μL of the receptor **1** (3 mM) were diluted with 2.980 mL Bis-tris buffer/DMF (8/2) to make the final concentration of 20 μM. MNO_3 (M = Na, K, 0.08 mmol) or $M(NO_3)_2$ (M = Mg, Ca, Mn, Co, Ni, Cu, Zn, Cd, Pb, 0.08 mmol) or $M(NO_3)_3$ (M = Al, Cr, Fe 0.08 mmol) or $M(ClO_4)_2$ (M = Fe, 0.08 mmol) were dissolved in Bis-tris buffer/DMF (8/2, 4 mL), respectively. 6 μL of each metal solution (20 mM) were taken and added into 3 mL of each receptor **1** solution (20 μM) prepared above to make 2 equiv. Then, 6 μL of the Fe^{2+} solution (20 mM) were added into the mixed solution of each metal ion and receptor **1** to make 2

equiv. After mixing them for a few second, UV-vis spectra were taken at room temperature.

For Cu^{2+} ion; Receptor **1** (3.7 mg, 0.006 mmol) was dissolved in DMF (1 mL) and 20 μL of the receptor **1** (3 mM) were diluted with 2.980 mL Bis-tris buffer/DMF (8/2) to make the final concentration of 20 μM. MNO_3 (M = Na, K, 0.08 mmol) or $M(NO_3)_2$ (M = Mg, Ca, Mn, Co, Ni, Cu, Zn, Cd, Pb, 0.08 mmol) or $M(NO_3)_3$ (M = Al, Cr, Fe 0.08 mmol) or $M(ClO_4)_2$ (M = Fe, 0.08 mmol) were dissolved in Bis-tris buffer/DMF (8/2, 4 mL), respectively. 6 μL of each metal solution (20 mM) were taken and added into 3 mL of each receptor **1** solution (20 μM) prepared above to make 2 equiv. Then, 6 μL of the Cu^{2+} solution (20 mM) were added into the mixed solution of each metal ion and receptor **1** to make 2 equiv. After mixing them for a few second, UV-vis spectra were taken at room temperature.

Results and discussion

Synthesis and characterization of receptor 1

The receptor **1** was prepared through a straightforward synthetic route. 2,6-Bis(chloroethylamido)pyridine was treated with 2-(((pyridin-3-yl)methylamino)methyl)phenol in acetonitrile (Scheme 1). The synthesized receptor **1** was characterized by ^1H and ^{13}C NMR, ESI-mass spectrometry analysis, and elemental analysis.

Colorimetric signaling of Fe^{2+} and Cu^{2+} ions

The cation binding properties of **1** were observed by employing aqueous solution (Bis-tris buffer/DMF = 8/2, v/v, pH 7.0) of different cations (Na^+, Mg^{2+}, Al^{3+}, K^+, Ca^{2+}, Cr^{3+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+}). The receptor **1** did not exhibit any absorption band in visible region, as shown in Fig. 1(a). The addition of Fe^{2+} and Cu^{2+} into **1** showed the spectral changes, which were accompanied with visual color change from colorless to light orange and green, respectively (Fig. 1(b)). The presence of other metal ions (Na^+, Mg^{2+}, Al^{3+}, K^+, Ca^{2+}, Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+}) showed no change in the absorption spectrum relative to the free receptor except for Fe^{3+}. The addition of Fe^{3+} into **1** also showed the change of color, but it was proved that the pale yellow color was due to the color of Fe^{3+} itself (Fig. S1). In particular, these results are very valuable, because Fe^{2+} and Cu^{2+} are well known fluorescent quenchers due to their paramagnetic nature which makes it practically difficult to develop fluorescent sensors for their detection.

To further elicit the recognition behaviors of **1** towards Fe^{2+} and Cu^{2+}, UV-vis titrations of **1** with Fe^{2+} and Cu^{2+} were measured, respectively. With an increasing amount of Fe^{2+}, the absorbance at 455 nm gradually increased (Fig. 2). The molar extinction coefficient of this band is $\varepsilon = 3.2 \times 10^3\ M^{-1}\ cm^{-1}$ which is too large to be Fe-based d-d transitions and thus must be metal-based transitions. These results indicate that a colorimetric method could be used for Fe^{2+} assay. To determine

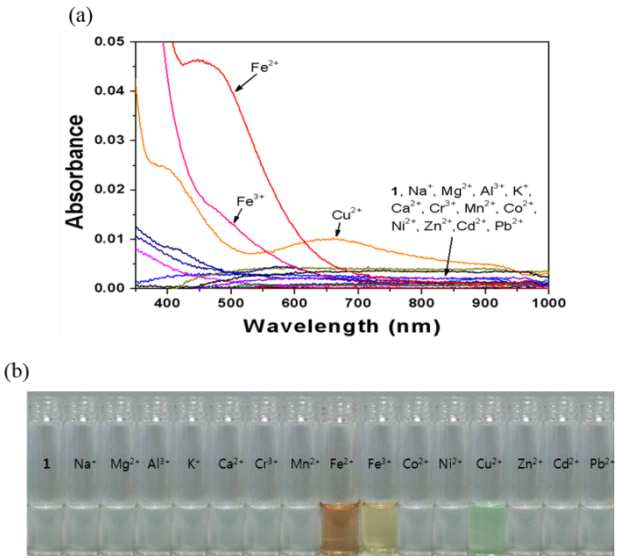


Fig. 1 (a) UV-vis spectra of **1** (20 μM) in the presence of various metal ions (60 μM) in Bis-tris buffer/DMF (8/2, v/v, pH 7.0). (b) Color changes of **1** in the presence of various metal ions.

the stoichiometry of the **1**-Fe^{2+} complex, Job method for the absorbance was applied (Fig. 3).[51] It showed that the absorbance exhibited a maximum at a molar fraction of 0.7, indicating a 2:1 stoichiometry of Fe^{2+} to **1** in the complex. This was further confirmed by the ESI-mass analysis (Fig. S2). The $[\mathbf{1} + 2Fe + H_2O]^{2+}$ complex was calculated to be m/z 372.57 and measured to be m/z 372.80. Based on the Job plot and ESI-mass spectrometry analysis, we propose the structure of a 2:1 complex of Fe^{2+} and **1** as shown in Scheme 2. We presume that each iron in the proposed structure would have penta-coordinate environment with a solvent or ClO_4-, because iron(II) ion usually forms penta- or hexa-coordinate complexes. From the 2:1 binding mode, the association constant (log K) was calculated to be 9.22 on the basis of Li's equation (Fig. S3).

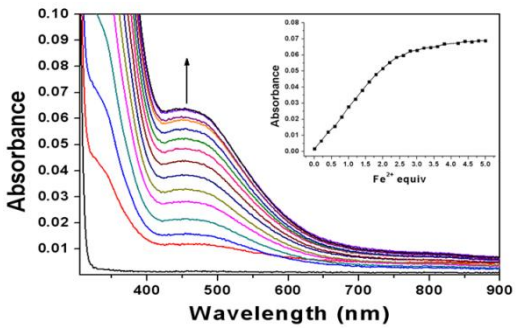
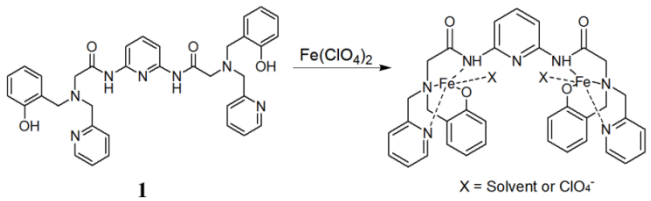


Fig. 2 UV-vis spectral titration of **1** (20 μM) with Fe^{2+} (0-60 μM) in Bis-tris buffer/DMF (8/2, v/v). Inset: Absorbance of **1** at 455 nm as a function of equiv of Fe^{2+}.



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Scheme 2. Proposed structure of a 1:2 complex of **1** with Fe^{2+}.

This value is within the range of those (5.17-17) reported for Fe^{2+}-binding chemosensors.[4,52-54] The absorption titration profile of **1** with Fe^{2+} demonstrated that the detection limit of Fe^{2+} is 2.94 μM on the basis of 3σ/K (Fig. S4).[55] According to the drinking water standards and health advisories proposed by U.S. Environmental Protection Agency (EPA), the safety amount of iron is limited to 0.3 mg/L (5.36 μM).[56] Hence, the receptor **1** could monitor trace of Fe^{2+} in industrial, environmental and biological analysis.

UV-vis titration of **1** with Cu^{2+} showed two absorption bands at 400 nm (ε = 1.3 x 103 $M^{-1}cm^{-1}$) and 660 nm (ε = 0.5 x 103 $M^{-1}cm^{-1}$), which might be due to a metal-to-ligand charge-transfer (MLCT) process (Fig. 4). The MLCT is responsible for the change of color from colorless to green, which is perceptible to the naked-eye. The stoichiometry of complexation of **1** and Cu^{2+} was studied using Job plot, which showed 2:1 ratio of Cu^{2+} and **1** (Fig. S5). The stoichiometry of Cu^{2+} with **1** was also supported by ESI-mass spectrometry analysis (Fig. 5). The $[\mathbf{1} + 2Cu]^{2+}$ complex was calculated to be m/z 740.11 and measured to be m/z 740.00. Based on the Job plot and ESI-mass spectrometry analysis, we propose the structure of a 2:1 complex of Cu^{2+} and **1** as shown in Scheme 3. We presume that each copper in the proposed structure would have tetra- or penta-coordinate environment without/with a NO_3-, because copper(II) ion prefers to form tetra- or penta-coordinate complexes. From the 2:1 binding mode, the association constant (log K) of **1**-Cu^{2+} complex was calculated

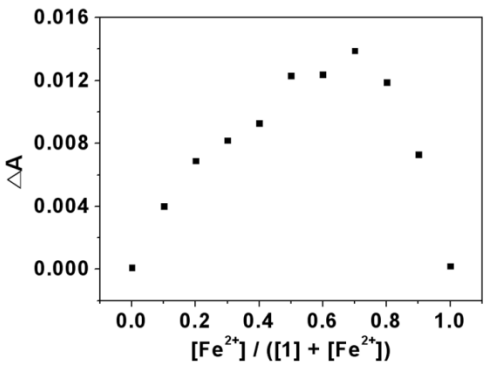


Fig. 3 Job plot of Fe^{2+} complex formation. The total concentration of **1** with Fe^{2+} was 40 μM.

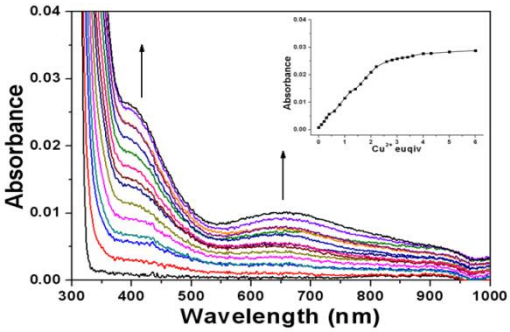


Fig. 4 UV-vis spectral titration of **1** (20 μM) with Cu^{2+} (0-60 μM) in Bis-tris buffer/DMF (8/2, v/v). Inset: Absorbance of **1** at 400 nm as a function of equiv of Cu^{2+}.

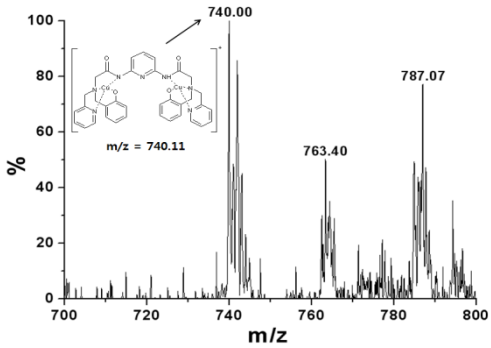
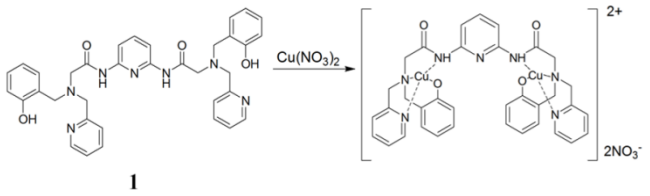


Fig. 5 Positive-ion electrospray ionization mass spectrum of **1** (1.0 x 10^{-4} M) upon addition of 2 equiv of Cu^{2+}.

to be 9.22 from Li's equation (Fig. S6). The detection limit of receptor **1** for the analysis of Cu^{2+} was calculated to be 2.29 μM (Fig. S7), which is far below the WHO guideline (30 μM), making it capable of being a practical system for the monitoring of Cu^{2+} concentrations in aqueous samples.

The competitive binding studies

We studied the preferential selectivity of **1** as a colorimetric chemosensor for the detection of Fe^{2+} and Cu^{2+} in the presence of various competing metal ions. The receptor **1** was treated with 3 equiv of Fe^{2+} in the presence of various metal ions such as Na^+, Mg^{2+}, Al^{3+}, K^+, Ca^{2+}, Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+}. As shown in Figure. 6(a), the presence of other background metal ions showed no or a little change of absorbance at 455 nm. Therefore, the receptor **1** showed an exclusive selectivity toward the detection of Fe^{2+} in the presence of various other metal ions. The change of absorption intensity of **1** was also measured in the presence of Cu^{2+} mixed with various metal ions. Compared to the absorption intensity obtained with Cu^{2+} alone (Fig. 6(b)), the absorbance showed no or a little change in the presence of Na^+, Mg^{2+}, Al^{3+}, K^+, Ca^{2+}, Cr^{3+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+}.



Scheme 3. Proposed structure of a 1:2 complex of **1** with Cu^{2+}.

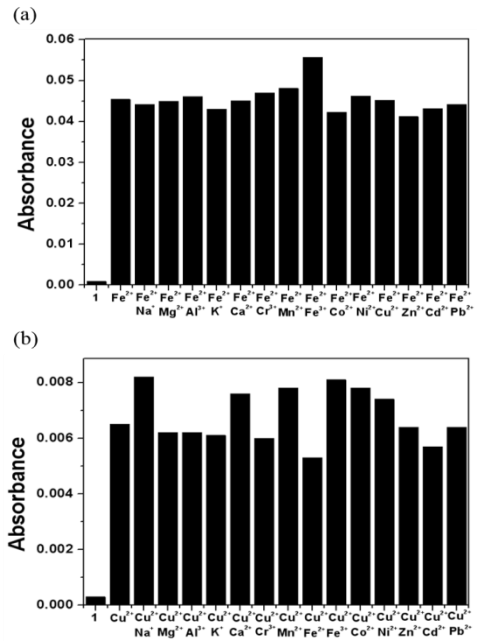


Fig. 6 Effect of competitive metal ions (60 μM) on the interaction between receptor **1** (20 μM) and (a) Fe^{2+} (60 μM), and (b) Cu^{2+} (60 μM), respectively, in Bis-tris buffer/DMF (8/2, v/v).

On the other hand, it is important to figure out how the color of **1** solution changes in the presence of both Fe^{2+} and Cu^{2+}, because both of them showed the same binding constants toward **1**. Therefore, we examined the color of **1** solution in the presence of blended Fe^{2+} and Cu^{2+}, and observed that the receptor **1** showed the color change from colorless to yellow which is a mixed color of orange (for Fe^{2+}) and green (for Cu^{2+}) (Fig. S8). These results indicate that one could also detect the presence of both Fe^{2+} and Cu^{2+} by the color change of **1** under the special conditions.

The effects of pH and EDTA

We investigated the effect of pH on the absorption response of receptor **1** to Fe^{2+} and Cu^{2+}, respectively, in a series of buffers with pH values ranging from 2 to 11 (Fig. 7). The pH studies revealed that the receptor **1** itself did not undergo any significant absorbance enhancement within the pH range from 2-11, which suggested that it was stable over the pH range. The absorption of the **1**-Fe^{2+} complex was very weak at low pH,

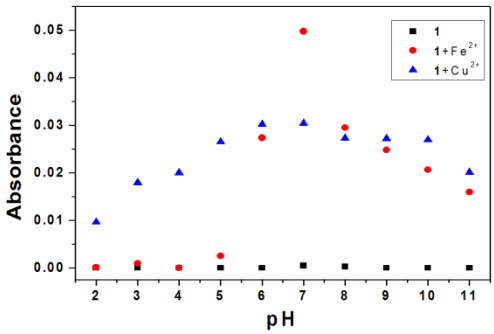


Fig. 7 Effect of pH on the absorbance of **1** at 455 nm (circle for Fe^{2+}) and 400 nm (triangle for Cu^{2+}), respectively, in Bis-tris buffer/DMF (8/2, v/v).

whereas, at high pH, the complex showed a significant response between pH 6 and 11, which includes the biologically relevant range of pH 6.0-7.6. The absorbance of the **1**-Cu^{2+} complex also displayed pH dependence over pH 2-11.

To validate the reversibility of complexation of **1** with Fe^{2+} and Cu^{2+}, respectively, EDTA-addition experiments were performed. When EDTA was added to the solution of the **1**-Fe^{2+} complex, the absorption intensity at 445 nm decreased (Fig. 8(a)). This is attributed to the stronger complexation of Fe^{2+} with EDTA than with **1**. Further addition of excess Fe^{2+} recovered the spectrum and color of the solution (Fig. 8). This process could be repeated several times. The **1**-Cu^{2+} complex also showed the same reversibility with EDTA (Fig. S9(a) and (b)). The absorbance of the **1**-Cu^{2+} complex at 400 nm decreased by addition of EDTA. Upon addition of Cu^{2+} to the system again, the spectrum of **1**-Cu^{2+} complex was recovered to the original one accompanied by a color change from colorless to green. The absorbance at 740 nm is due to the coordination of Cu^{2+}-EDTA, as shown in Figure S9(c).

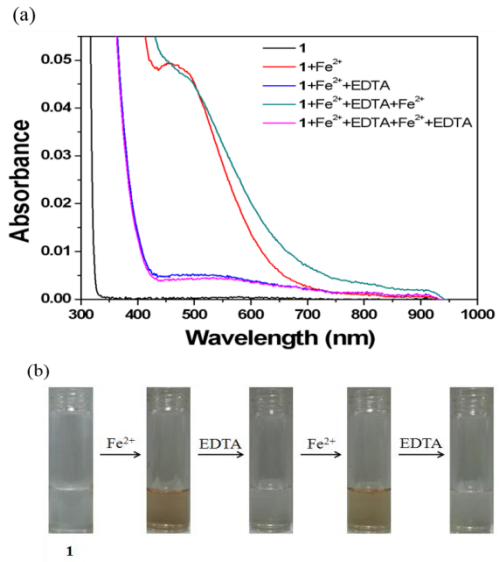


Fig. 8 (a) Reversible changes in absorbance of **1** after the sequential addition of Fe^{2+} and EDTA in Bis-tris buffer/DMF (8/2, v/v). (b) Reversible color changes of **1** after the sequential addition of Fe^{2+} and EDTA in Bis-tris buffer/DMF (8/2, v/v).

These results indicate that receptor **1** could be recyclable simply through treatment with a proper reagent such as EDTA.

Detection of Fe^{2+} and Cu^{2+} on the paper devices

Most of sensors for detection of Fe^{2+} and Cu^{2+} operate only in the solution phase, and thus restrict their practical applications.[7] Therefore, we have developed a colorimetric test kit, which was prepared by immersing filter papers into aqueous medium (Bis-tris buffer/DMF = 8/2) of **1**. The aqueous solutions of different metal ions were sprayed onto these strips. The receptor showed marked orange and green color only in the presence of Fe^{2+} and Cu^{2+}, respectively, as shown in Figure 9. Fe^{3+} exhibited its own color yellow, as already shown in Figure S1. These results indicate that receptor **1** could be a convenient sensor for Fe^{2+} and Cu^{2+} in environmental analyses.

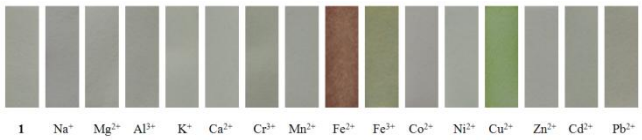


Fig. 9 Colorimetric test kits. Photographs of various cations sprayed on the filter paper coated with **1**.

Conclusion

We have developed a novel colorimetric chemosensor **1** for Fe^{2+} and Cu^{2+} based on PAP platform in aqueous solution. The sensor **1** showed unique color changes upon the binding with Fe^{2+} or Cu^{2+} in aqueous solution (Bis-tris buffer/DMF = 8/2). In addition, the sensor showed good sensitivities with μM-level detection limits, and displayed high selectivity to Fe^{2+} or Cu^{2+} in the presence of other common interference cations. Importantly, the Fe^{2+} and Cu^{2+}-induced chromogenic processes could be reversible by addition of EDTA. Moreover, the easy-to-prepare test kit provided a convenient and reliable detection of Fe^{2+} and Cu^{2+} ions in practical applications. Therefore, the results reported here provide a novel approach for the simultaneous colorimetric recognition of the two most abundant transition metal ions (Fe^{2+} and Cu^{2+}) among the various metal ions.

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Supplementary Information

Supplementary material associated with this article can be found, in the online version.

Notes and references

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‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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