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Journal:	*New Journal of Chemistry*
Manuscript ID:	NJ-ART-01-2015-000125
Article Type:	Paper
Date Submitted by the Author:	16-Jan-2015
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A diaminomaleonitrile based selective colorimetric chemosensor for copper(II) and fluoride ions

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Abstract

A new and simple colorimetric receptor **1**, based on 2,3-diaminomaleonitrile moiety and julolidine moiety, has been synthesized and characterized. **1** showed a selective colorimetric sensing ability for copper (II) ion by changing color from yellow to colorless, and could be utilized to monitor Cu^{2+} over a wide pH range of 4-12. The detection limit of **1** (2.1 μM) for Cu^{2+} ion is much lower than that recommended by WHO in drinking water (30 μM). Moreover, the receptor **1** can also detect fluoride by color change from yellow to orange, distinguishing the fluoride ion effectively from anions such as CH_3COO^- and CN^-. It was also found that the **1**-F^- complex was reversibly bound and could be simply reverted back through treatment with a proper reagent such as HCl. The sensing mechanism for F^- was theoretically supported by DFT and TD-DFT calculations.

Keywords: colorimetric, copper (II) ion, fluoride, deprotonation, theoretical calculations

Introduction

Recognition of heavy and transition metal ions by chemosensors has received considerable attention not only because of their important functions, but also for their potential toxicity to the environment and biological systems.[1,2] Copper ions, the third most abundant metal ion (after Fe^{3+} and Zn^{2+}), is involved in a variety of fundamental physiological processes.[3-7] Indeed, copper homeostasis is tightly controlled by several factors, including copper transport proteins and chaperones,[8] otherwise, unregulated Cu(II) can cause many problems. For instance, excess intake of Cu^{2+} can cause neurodegenerative diseases including Alzheimer's, Parkinson's, Menke's, Wilson's, and prion diseases on human health.[9-11] On the other hand, copper deficiency is associated with myelopathy.[12] Copper is also a significant metal pollutant due to its widespread use in life science, medicine, chemistry and biotechnology. The toxicity of copper ion has a bad effect on microorganisms even at submicromolar concentration.[13] Therefore, the design and synthesis of highly sensitive and selective chemosensors for Cu^{2+} is still a great demand.

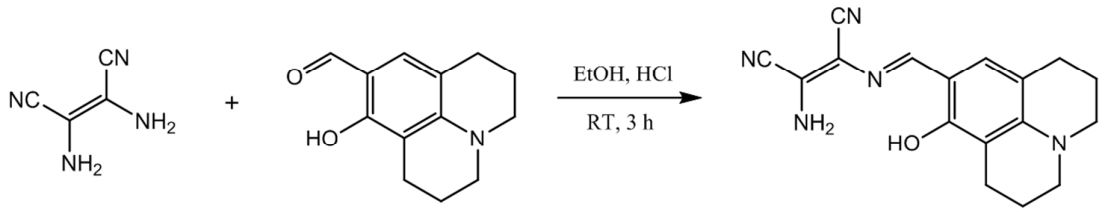
Given the significance of anions in biological and environmental processes, correct identification of anions is another point of interest.[14-16] Among the anions, fluoride, the smallest anion with a high charge density, is of particular interest due to their fundamental role in dental care and osteoporosis treatment.[15,17] For example, F^- is often added to drinking water, toothpaste, and some drugs. However, fluoride is absorbed easily by the body and excreted slowly from the body.[18] Therefore, the presence of excess fluoride ions results in dental and skeletal fluorosis, bone diseases, mottling of teeth, lesions of the thyroid, liver and other organs.[19-26] In addition, they contribute significantly to environmental pollution.[27] Therefore, detecting and monitoring fluoride anion is very important for environment and human health care. To note, many anion sensors are not capable of distinguishing fluoride ion effectively from certain anion mixtures, such as CH_3COO^- and CN^-, because they possess similar basicity to F^- and can easily form hydrogen bonds. Therefore, the achievement of specific optical F^- sensing is still a challenge.

Till now, various methods, including fluorescence techniques, inductively-coupled plasma mass spectroscopy and electrochemical methods have been employed to detect copper ion and fluoride.[28] However, these methods often require expensive, sophisticated and time

consuming procedures. Therefore, the most attractive approach focuses on novel colorimetric chemosensors, which allow naked-eye detection of the color change without resorting to the use of expensive instruments.[29-33] Colorimetric materials have advantages, such as low costs, high response rates, simple method and high selectivity.[34-37] Therefore, development of colorimetric sensors that are capable of recognizing both copper and fluoride ions in aqueous environment would be useful.

2,3-Diaminomaleonitrile represents a class of organic π-conjugated compound with electronic donor (D) and acceptor (A) parts connected by single and double bonds, exhibiting interesting electronic properties due to an intramolecular charge transfer (ICT).[38] The julolidine moiety is a well-known chromophore and chemosensors with the julolidine moiety are usually water-soluble.[39,40] Therefore, we designed and synthesized a new chemosensor **1** based on the combination of the maleonitrile moiety and the julolidine moiety, and tested its sensing properties towards various cations and anions. As expected, the receptor **1** showed a very effective and practical colorimetric recognition of Cu^{2+} and F^- in aqueous solution.

Herein, we report a new multi-functional chemosensor **1** for Cu^{2+} and F^-, which was synthesized in one step by condensation reaction of 2,3-diaminomaleonitrile and 8-hydroxyjulolidine-9-carboxaldehyde (Scheme 1). Receptor **1** can detect Cu^{2+} by color change from yellow to colorless via the 'naked-eye' with high selectivity in aqueous environment. Receptor **1** also showed colorimetric response toward F^- in aqueous solution, while there was no change in presence of other anions. In particular, it was able to distinguish F^- from other anions that can form strong hydrogen bonds, e.g. CH_3COO^-.



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

2. Experimental

2.1. Materials and instrumentation

All solvents and reagents (analytical grade and spectroscopic grade) were obtained from Sigma-Aldrich and used as received. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian 400 spectrometer. Chemical shifts (δ) are reported in ppm, relative to tetramethylsilane $Si(CH_3)_4$. Absorption spectra were recorded at room temperature using a Perkin Elmer model Lambda 2S UV/Vis spectrometer. Electrospray ionization mass spectra (ESI-mass) were collected on a Thermo Finnigan (San Jose, CA, USA) LCQTM Advantage MAX quadrupole ion trap instrument.

2.2. Synthesis of 1

2,3-Diaminomaleonitrile (0.11 g, 1 mmol) and 8-hydroxyjulolidine-9-carboxaldehyde (0.23 g, 1 mmol) were dissolved in 5 mL of ethanol, followed by addition of three drops of hydrochloric acid into the reaction mixture. On stirring the solution for 3 h at room temperature yielded a brown solid, which was collected by filtration, washed with diethyl ether and air-dried. Yield: 80%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.95 (s, 1H), 8.24 (s, 1H), 6.77 (s, 1H), 4.48 (s, 2H), 3.30 (m, 4H), 2.68 (t, J = 8 Hz, 4H), 1.95 (m, 4H). ^{13}C NMR (400 MHz, DMSO-d_6) δ 158.28, 155.89, 147.13, 130.42, 121.78, 115.30, 114.25, 113.52, 107.53, 105.17, 104.34, 49.43, 48.19, 26.49, 21.22, 20.33, 19.89 ppm. ESI-MS m/z $[M\text{-}H^{+}]^{-}$: calcd, 306.14; found, 306.20. Anal. calcd for $C_{17}H_{17}N_5O$ (307.14): C, 66.43; H, 5.58; N, 22.79%. Found: C, 66.87; H, 5.42; N, 22.51%.

2.3. UV-vis titration of 1 with Cu^{2+}

Receptor **1** (3.1 mg, 0.01 mmol) was dissolved in MeCN (1 mL) and 3 μL of this solution (10 mM) were diluted with 2.997 mL MeCN/Bis-tris buffer (6:4, v/v) to make the final concentration of 10 μM. $Cu(NO_3)_2$ (2.4 mg, 0.01 mmol) was dissolved in MeCN/Bis-tris buffer (6:4, v/v, 1mL). Then, 3-51 μL of the copper nitrate (10 mM) solution were added to each receptor solution (10 μM, 3mL) prepared above. After mixing them for a few seconds, UV-vis spectra were taken at room temperature.

2.4. Job plot measurement

Receptor **1** (3.1 mg, 0.01 mmol) and $Cu(NO_3)_2$ (2.4 mg, 0.01 mmol) were dissolved in MeCN (1 mL), respectively. Next, 0.15 mL of the receptor **1** solution were diluted to 29.85 mL with MeCN/bis-tris buffer (6:4, v/v) to make the concentration of 50 μM. The $Cu(NO_3)_2$ solution was diluted in the same way. Then, 5, 4.5, 4, 3.5, 3, 2.5, 2, 1.5, 1, 0.5 and 0 mL of the receptor **1** solution were taken and transferred to vials. Solutions of the Cu^{2+} ion (0, 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5 and 5 mL) were added to each receptor solution separately. Each vial had a total volume of 5 mL. After shaking the vials for a few minutes, UV-vis spectra were taken at room temperature.

2.5. UV-vis titration of 1 with F^-

Receptor **1** (3.1 mg, 0.01 mmol) was dissolved in DMSO (1 mL) and 3 μL of the **1** (10 mM) were diluted with 2.997 mL DMSO/Bis-tris buffer (97:3, v/v) to make the final concentration 10 μM. Tetraethylammonium fluoride (9-180 μL, 100 mM) was added to each receptor solution (10 μM, 3 mL) prepared above. After mixing them for a few seconds, UV-vis spectra were taken at room temperature.

2.6. ^{1}H NMR titration of 1 with F^-

Three NMR tubes of **1** (3.1 mg, 0.01 mmol) dissolved in DMSO-d_6 (0.7 mL) were prepared, and three different equiv (0, 0.5, and 1 equiv) of tetraethylammonium fluoride dissolved in DMSO-d_6 (0.5 mL) were added to **1** solution separately. After shaking them for a minute, ^{1}H NMR were run.

2.7. Calculation method

All theoretical calculations were performed by using the Gaussian 03 suite. The singlet ground states (S_0) of **1** and **1**-F^- species were optimized by DFT methods with Becke's three parameterized Lee-Yang-Parr (B3LYP) exchange functional with 6-311G** basis set.[41] The optimized geometries are shown in Fig. S1. In vibrational frequency calculations, there was no imaginary frequency for **1** and **1**-F^- species, suggesting that the optimized **1** and **1**-F^- species represented local minima.

3. Results and discussions

The colorimetric chemosensor **1** for copper ion and fluoride was synthesized by condensing 2,3-diaminomaleonitrile with 8-hydroxyjulolidine-9-carboxaldehyde (Scheme 1), and characterized by ^{1}H NMR, ^{13}C NMR, ESI-mass spectrometry, and elemental analysis.

3.1. Colorimetric sensing of 1 for Cu^{2+}

The colorimetric selective sensing abilities of receptor **1** with various metal ions in a mixture of MeCN/bis-tris buffer (6:4, v/v) were monitored by UV-vis absorption spectra (Fig. 1a). Only the addition of Cu^{2+} induced a distinct spectral change, while other 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+}, Zn^{2+}, Ag^{+}, Cd^{2+}, Hg^{2+}, and Pb^{2+} did induce little or small spectral changes. Consistent with the change of UV-vis spectrum, the solution color of **1** in the presence of Cu^{2+} ion changed from yellow to colorless (Fig. 1b). This result indicated that receptor **1** can serve as a potential candidate for a "naked-eye" chemosensor for Cu^{2+} in aqueous solution.

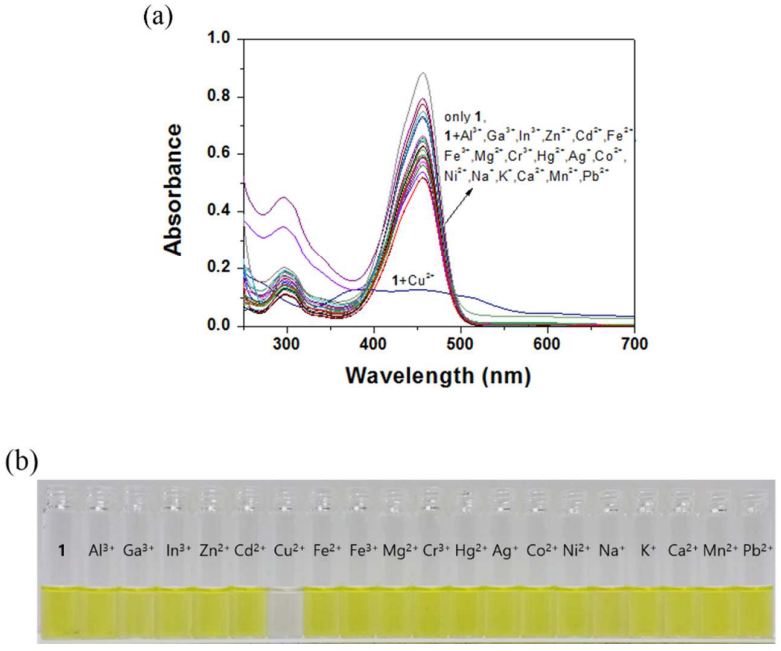


Figure 1. (a) Absorption spectra change of **1** (10 μM) in the presence of 3 equiv of various

metal ions in a mixture of MeCN/bis-tris buffer (6:4, v/v). (b) Color change of receptor **1** (10 μM) in the presence of 3 equiv of various metal ions in a mixture of MeCN/bis-tris buffer (6:4, v/v).

The binding property of **1** with Cu^{2+} was further studied by UV-vis titration experiment (Fig. 2). Upon the addition of Cu^{2+} to a solution of **1**, the absorbance peak at 450 nm gradually decreased and a new absorbance at 375 nm appeared concomitantly, resulting in a color change from yellow to colorless. This phenomenon might be due to blue shift generated from the decrease in the push-pull effect of the ICT transition.[42] The push-pull electronic effect was weakened due to binding of Cu^{2+} ion to the -OH and $-NH_2$ groups in the receptor **1** with the electron-donating groups (-OH and $-NH_2$) and the electron-withdrawing one (-C≡N group). The isosbestic point at 396 nm was clearly observed, indicating the formation of a single species between the receptor **1** and the cupric ion. The Job plot indicated a 1:1 binding interaction between the receptor **1** and Cu^{2+} (Fig. 3), which was further confirmed by ESI-mass spectrometry analysis (Fig. 4). The negative ion mass spectrum of ESI-mass indicated that a peak at m/z = 506.90 was assignable to **1**-$2H^+$+Cu^{2+}+NO_3^-+CH_3CN+$2H_2O$ [calcd, m/z: 507.09]. For further information on the coordination mode of **1**-Cu^{2+} complex, we carried out ^1H NMR titration of **1** with Cu^{2+}, but it was not successful due to a paramagnetic nature of Cu^{2+} ion. Based on the Job plot and ESI-mass spectrometry analysis, we propose the structure of **1**-Cu^{2+} complex as shown in Scheme 2.

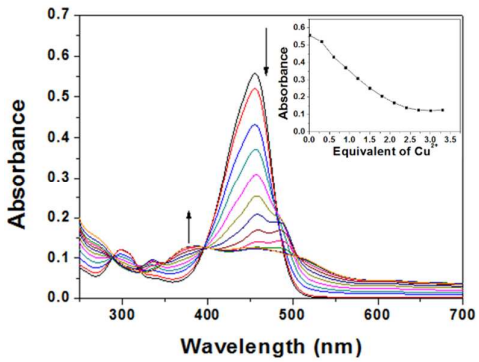


Figure 2. Absorption spectra of receptor **1** (10 μM) upon the addition of Cu^{2+}. Inset: Absorbance at 450 nm versus the number of equiv of Cu^{2+} added.

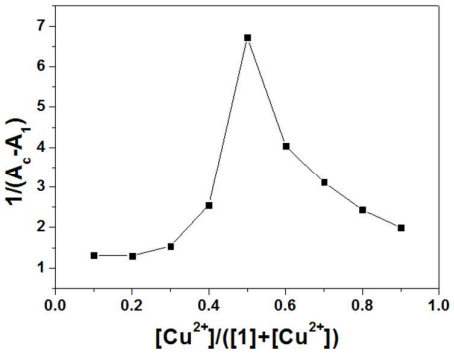


Figure 3. Job plot of receptor **1** and Cu^{2+}. Absorbance at 460 nm was plotted as a function of the molar ratio $[Cu^{2+}]/([\mathbf{1}] + [Cu^{2+}])$. The total concentration of copper ions with receptor **1** was 1.0 x 10^{-5} M.

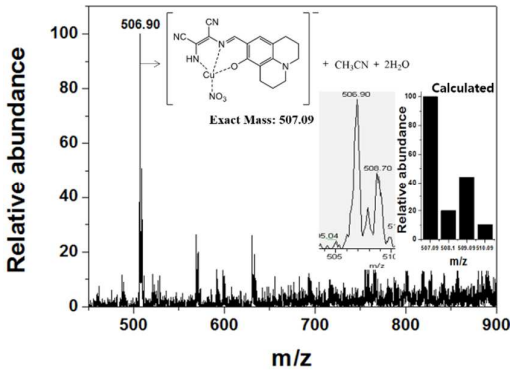
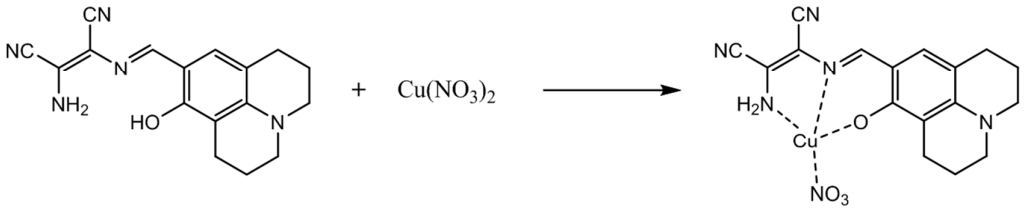


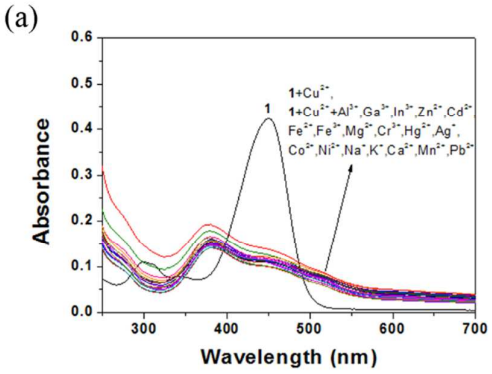
Figure 4. Negative-ion electrospray ionization mass spectrum of **1** (0.1 mM) upon addition of Cu^{2+} (1 equiv).



Scheme 2. Proposed binding mode of **1** with copper ion.

Based on UV-vis titration, the association constant (K) of **1** with the Cu^{2+} ion was calculated using the Benesi-Hildebrand equation (Fig. S2).[43] The K value turned out to be 2.3 x 10^4 M^{-1}, which is within the previously reported values (10^4-10^5) for Cu^{2+}-binding chemosensors.[44] The detection limit (3∂/k) of receptor **1** for the analysis of Cu^{2+} ions was calculated to be 2.1 μM (Fig. S3).[45] The detection limit of **1** for Cu^{2+} was much lower than that recommended by WHO in drinking water (30 μM).[46] Therefore, **1** could be a good indicator for the detection of copper ions in drinking water.

To further check the practical applicability of **1** as a copper ion chemosensor, competitive experiments were conducted by the addition of copper ions (3 equiv) to the solution of **1** containing interfering cations viz. 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+}, Ag^+, Cd^{2+}, Hg^{2+}, and Pb^{2+} (3 equiv). The presence of interfering cations did not result in any significant change in the UV-vis as achieved by the addition of only Cu^{2+} to the solution of **1** (Fig. 5). Thus, receptor **1** could be used as a selective colorimetric sensor for Cu^{2+} even in the presence of the most competing metal ions.



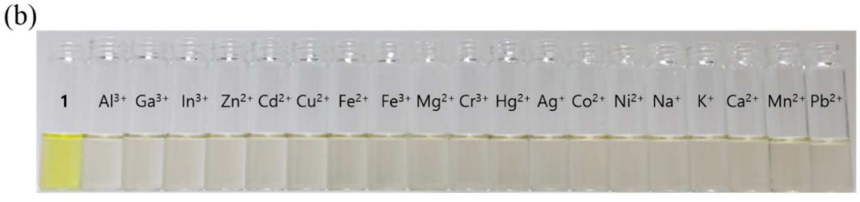


Figure 5. (a) Competitive selectivity of **1** (10 μM) towards Cu^{2+} (3 equiv) in the presence of other metal ions (3 equiv). (b) Colorimetric competitive experiment of **1** (10 μM) in the presence of Cu^{2+} (3 equiv) and other metal ions (3 equiv).

Furthermore, we investigated the effect of pH on the absorption response of receptor **1** to Cu^{2+} ion in a series of buffers with pH values ranging from 2 to 12 (Fig. 6). The color of the **1**-Cu^{2+} complex remained in the colorless region between pH 4 and 12, while its color changed to the original yellow at pH 2 and 3. These results indicate that Cu^{2+} could be clearly detected by the naked eye or UV-vis absorption measurements using **1** over the wide pH range of 4.0-12.0.

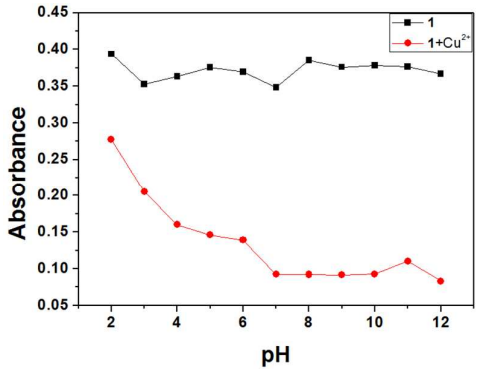


Figure 6. Absorbance of **1** and **1**-Cu^{2+} complex (450 nm) at different pH values (2-12) in a mixture of MeCN/bis-tris buffer (6:4, v/v).

Additionally, we constructed a calibration curve for the determination of Cu^{2+} by **1** (Fig. S4). Receptor **1** exhibited a good linear relationship between the absorbance of **1** and Cu^{2+} concentration (0.10-10.00 μM) with a correlation coefficient of $R^2 = 0.993$ (n = 3), which means that **1** could be suitable for quantitative detection of Cu^{2+} as well.

In order to examine the applicability of the chemosensor **1** in environmental samples, the chemosensor was applied to the determination of Cu^{2+} in water samples. First, two tap water samples were prepared. As shown in Table 1, one can see that satisfactory recovery and

R.S.D. value of the water samples were exhibited. Second, we prepared two drinking water samples. The results were also summarized in Table 1, which exhibited satisfactory recovery and R.S.D. value for the water samples.

Table 1. 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	-	-
	8.00	8.11	101.4	1.4
Drinking water	0.00	0.00	-	-
	6.00	5.92	98.6	0.4

Conditions: [**1**] = 10 μmol/L in 10 mM MeCN/bis-tris buffer solution (6:4, pH 7.0).

3.2. Colorimetric sensing of 1 for F^-

We also examined the selectivity of a variety of anions toward **1**, because the receptors with both the imine and phenol groups showed sometimes the sensing properties towards anions.[47-49] The absorption response of **1** toward tetraethylammonium (TEA) or tetrabutylammonium (TBA) salts or sodium salts of F^-, Cl^-, Br^-, I^-, CN^-, OAc^-, $H_2PO_4^-$, BzO^-, N_3^-, SCN^-, SO_4^{2-} and S^{2-} was carried out in a mixture of DMSO/bis-tris buffer (97:3, v/v) (Fig. 7). Upon the addition 600 equiv of each anion, only F^- induced a noticeable spectral change, while other anions showed either no or a slight change in the absorption spectra relative to the free receptor **1** (Fig. 7a). Consistent with the change in the UV-vis spectrum, the solution color of **1** changed from yellow to orange only with fluoride with a fast response time (Fig. 7b), indicating that receptor **1** can serve as a "naked-eye" indicator for F^-.

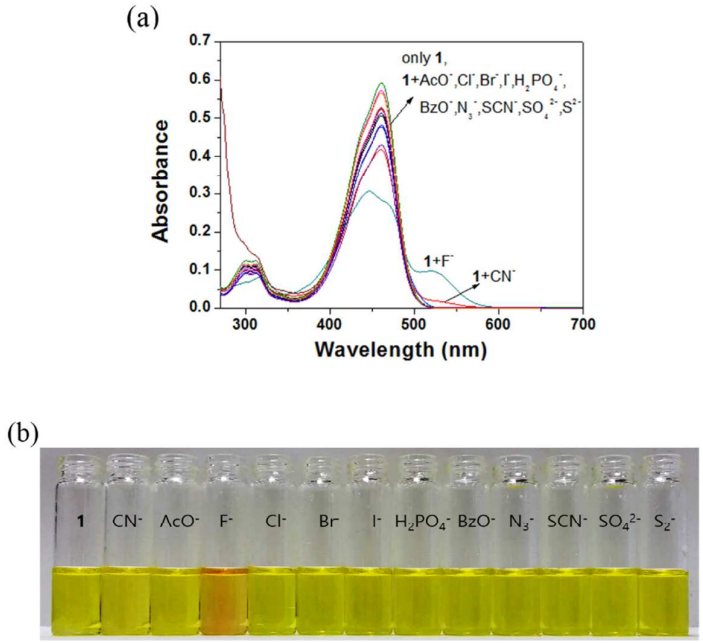


Figure 7. (a) Absorption spectral change of **1** (10 μM) in the presence of 600 equiv of various anions in a mixture DMSO/bis-tris buffer (97:3, v/v). (b) Color change of receptor **1** (10 μM) in the presence of 600 equiv of anions in a mixture DMSO/bis-tris buffer (97:3, v/v).

To explore the interaction between **1** and F^-, UV-vis absorption spectral variation of **1** was investigated during titration with different concentrations of F^- (Fig. 8). Receptor **1** displayed strong absorption bands at 300 nm and 460 nm. With incremental addition of F^-, both the bands decreased, while a new absorbance at 520 nm increased gradually. The absorbance reached a maximum at 600 equiv of fluoride with four isosbestic points observed at 288 nm, 317 nm, 405 and 487 nm. In the process, we presume that the electron density in **1** increased because of the deprotonation of phenol of **1** by F^-. The resulting negative charge on the phenolate oxygen might be responsible for an enhancement of the push-pull effect of the ICT transition[38], which was distinctly visible to the naked eye with a change in color from yellow to orange. The Job plot for the binding between **1** and F^- exhibited a 1:1 stoichiometry (Fig. S5). The positive ion mass spectrum of ESI-mass showed that a peak at m/z = 566.11 was assignable to $[\mathbf{1}\text{-}H^+ + 2TEA]^+$ [calcd, m/z: 566.45], which is corresponding to the receptor $\mathbf{1}^-$

deprotonated by fluoride (Fig. S6). From the UV-vis titration data, the association constant (K) for **1** and fluoride was determined as 1.2 x 10^2 using the Benesi-Hildebrand equation (Fig. S7).[43] The detection limit (3∂/k) of receptor **1** for the analysis of F^- ions was calculated to be 840 μM (Fig. S8).[45]

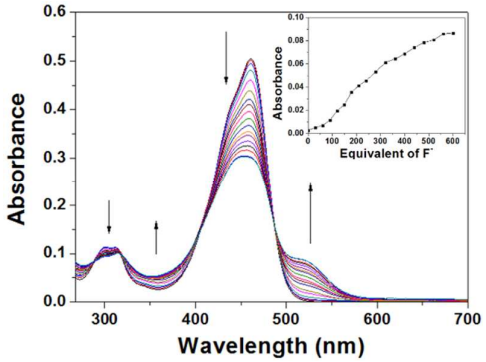
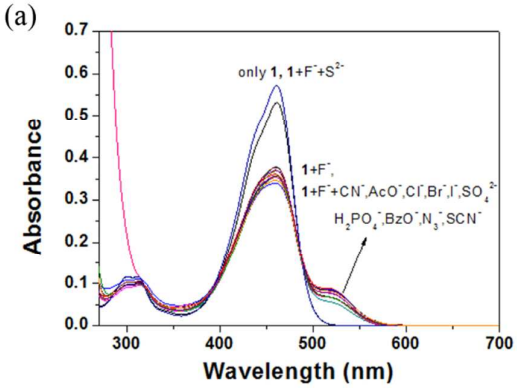


Figure 8. Absorption spectra of receptor **1** (10 μM) upon the addition of F^-. Inset: Absorbance at 520 nm versus the number of equiv of F^- added.

To explore the ability of **1** as a colorimetric sensor for F^- in the presence of other competing anions, competition experiments were performed in the presence of F^- mixed with various anions (Fig. 9). The coexistent anions had no influence on the color change of **1** except for S^{2-}. These results indicate that receptor **1** shows a good selectivity for fluoride anion in the presence of other anions.



(b)

Figure 9. (a) Competitive selectivity of **1** (10 μM) towards F^- (600 equiv) in the presence of other anions (600 equiv). (b) Colorimetric competitive experiment of **1** (10 μM) in the presence of F^- (600 equiv) and other anions (600 equiv).

To understand reversibility between **1** and F^-, HCl-addition experiments were conducted (Fig. S9). After adding 600 equiv of F^- to **1** solution, the color changed from yellow to orange and a new absorbance at 520 nm appeared. Upon addition of HCl (600 equiv) into **1**-F^- solution, the color and the absorbance were recovered. The color change and absorbance were almost reversible with the sequentially alternative addition of F^- and HCl.

The sensing mechanism of **1** toward fluoride was further investigated by ^{1}H NMR titration experiments at room temperature (Fig. 10). In absence of fluoride, the phenolic OH proton (H_4) and the amine NH_2 protons (H_1) appeared as a singlet at 11.16 ppm and 7.30 ppm, respectively, whereas the imine proton (CH=N) at 8.15 ppm as a sharp singlet. Upon the addition of F^- (0.5 equiv), the singlets of H_1 and H_4 were downshifted from 12.90 ppm to 13.34 ppm and from 7.30 ppm to 7.35 ppm due to hydrogen bonding with fluoride, respectively. After the further addition of F^- (1 equiv), the H_1 and H_4 disappeared immediately. Consequently, an up-field shift from 8.15 to 8.14 ppm in the imine proton (H_2) was also observed.

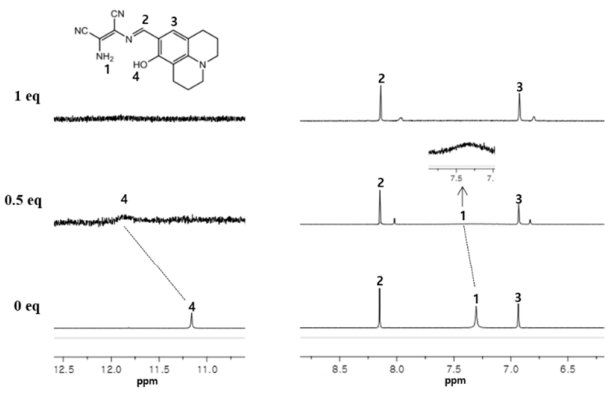
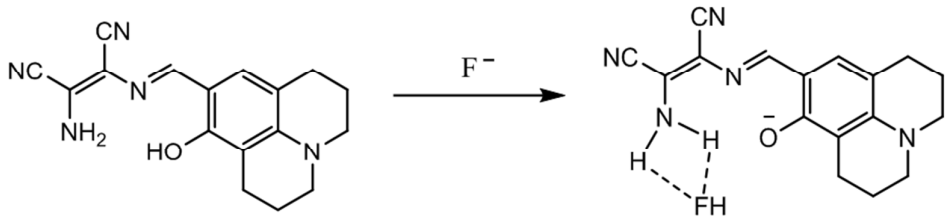


Figure 10. ^{1}H NMR titration of receptor **1** with F^-.

To further support the sensing mechanism of **1** for F^-, DFT/B3LYP calculations for **1** and **1**-F^- were carried out. As shown in Fig. S10, the HOMO-LUMO energy gap in **1**-F^- (2.878 eV) decreased compared to that of **1** (3.046 eV). These results suggested that the deprotonation of phenol of **1** by F^- might make the enhancement of ICT transition. Based on the Job plot, ESI-mass spectrometry analysis, the ^{1}H NMR titration and DFT calculations, we proposed the sensing mechanism of **1** to fluoride as shown in Scheme 3.



Scheme 3. Proposed binding mode of **1** with fluoride.

4. Conclusions

We have developed a new chemosensor **1** based on Schiff base with julolidine and diaminomaleonitrile moieties. **1** could be used as a multifunctional chemosensor for highly selective detection of both Cu^{2+} and F^- ions depending on different solvent systems. It

distinguished Cu^{2+} ion from other metal ions by color change (yellow to colorless) in aqueous media without the need of any expensive equipment. The detection limit of **1** (2.1 μM) for Cu^{2+} ions was much lower than that recommended by WHO in drinking water (30 μM). Moreover, **1** recognized F^- selectively with colorimetric change from yellow to orange. In particular, **1** can distinguish F^- in the presence of other anions such as CH_3COO^- and CN^-. **1**-F^- species could be reversible simply through treatment with a proper reagent such as HCl. DFT and TD-DFT studies supported the experimental data and the proposed sensing mechanism. These results demonstrated that receptor **1** will offer an important guidance to the development of single receptors for recognizing both cations and anions in aqueous solution.

Acknowledgements

Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2012001725 and 2012008875) are gratefully acknowledged.

Supplementary data

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

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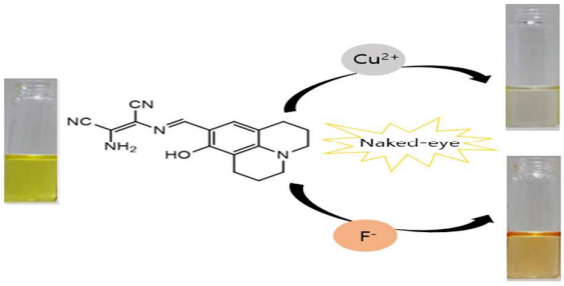
Graphical abstract for TOC



A chemosensor showed colorimetric sensing for copper (II) and fluoride by changing color from yellow to colorless and to orange.