A colorimetric organic chemo-sensor for Co2+ in a fully aqueous environment

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ARTICLE TYPE

A colorimetric organic chemo-sensor for Co^{2+} in a fully aqueous environment

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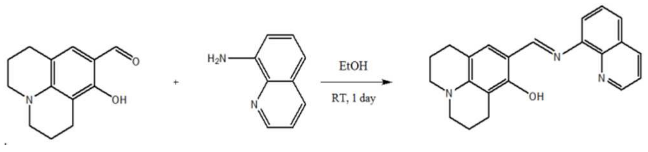
A new highly selective and sensitive colorimetric chemosensor 1 for Co^{2+} was developed. The receptor 1 sensed Co^{2+} by changing its color from yellow to orange in aqueous solution. Moreover, 1 could be used as a practical, visible colorimetric test kits for Co^{2+}.

Cobalt as a transition metal ion plays an important role in the metabolism of iron and the synthesis of hemoglobin, and is also an important component of vitamin B12 and other biological compounds.[1-9] However, excess cobalt from overexposure to environmental water polluted by Co^{2+} 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, dermatitis and vasodilation.[10-14] Therefore, the determination of trace amounts of Co^{2+} in biological and environmental samples is essential. Many approaches, such as inductively coupled plasma atomic emission spectrometry,[15] atomic absorption spectroscopy,[16] fluorescence techniques[17-22] and electrochemical methods[23] have been employed to detect trace amounts of Co^{2+}. 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.[24-27] Colorimetric methods have therefore attracted considerable attention in the detection of toxic metal ions including Co^{2+}.

Notably, compared with the many known colorimetric organic molecule sensors[27-34] for Zn^{2+}, Cu^{2+}, Al^{3+}, and Hg^{2+}, there are only four colorimetric organic sensors for Co^{2+}.[3,6,35,36] In addition, those sensors are too limited for viable applications in a real-world environment. For example, two of the four cannot be used for cobalt ions in aqueous solution[6,36] and the other two require rather high proportions of organic solvents (e.g., HEPES/ CH$_3$CN buffer (3:2, v/v)[3] and DMSO/ H$_2$O (3:1, v/v)[35]) for practical applications. 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.

The julolidine moiety is a well-known chromophore[37] and chemosensors with the julolidine moiety are usually water-soluble.[37,38] In addition, the quinoline group has a good optical property.[39,40] Therefore, the combination of the julolidine and the quinoline groups would be expected to have good optical properties and water solubility as chemosensors for detecting heavy and transition metal ions. Moreover, the combination form of the julolidine and the quinoline groups has three potential binding sites (two nitrogen atoms of quinoline and an oxygen atom of julolidine), which might act as good donors toward Co^{2+}.[6,8] Therefore, we synthesized a new chemosensor **1** ((E)-9-((quinolin-8-ylimino)methyl)-1,2,3,5,6,7-hexahydropyrido[3,2,1-ij]quinolin-8-ol) with both the julolidine and quinolone moieties, and tested its sensing properties toward various metal ions. Importantly, the receptor **1** showed a very effective and practical colorimetric recognition of Co^{2+} in a fully aqueous solution.

Herein, we report **1** based on the combination of julolidine and quinoline for selective detection of cobalt ion in a near-perfect



Scheme 1 Synthesis of receptor **1**.

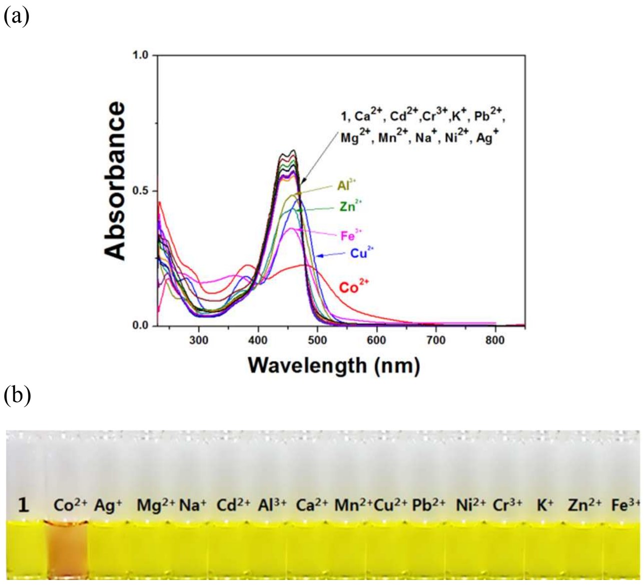


Fig. 1 (a) UV-vis spectra changes of **1** (20 µM, buffer-methanol (999:1, v/v)) upon addition of 0.7 equiv of various metal ions. (b) Colorimetric changes of **1** (20 µM) upon the addition of various metal ions (0.7 equiv).

aqueous solution (bis-tris/MeOH buffer (999:1, v/v)). **1** sensed Co^{2+} selectively by a change of color from yellow to orange with a fast response time.

The receptor **1** was obtained by the condensation reaction of 8-hydroxyjulolidine-9-carboxaldehyde and quinolin-8-amine with an 88.8% yield in ethanol (Scheme 1). **1** was characterized by ^1H-NMR, ^{13}C-NMR, ESI-mass spectrometry and elemental analysis. Importantly, **1** showed a good stability to hydrolysis as shown in Fig. S1†, while some Schiff bases are prone to undergo a fast hydrolysis of C=N in water.[41]

The colorimetric sensing abilities of **1** were primarily investigated in bis-tris buffer (10 mM, pH 7.0) containing 0.1 % methanol upon addition of various metal ions (Ag^+, Al^{3+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Fe^{3+}, K^+, Mg^{2+}, Mn^{2+}, Na^+, Ni^{2+}, Pb^{2+}, and Zn^{2+}) as their nitrate salts. Upon the addition of 0.7 equiv of each cation, the **1** showed almost no change in absorption peak in the presence of Ag^+, Ca^{2+}, Cd^{2+}, Cr^{3+}, K^+, Mg^{2+}, Mn^{2+}, Na^+, Ni^{2+} and Pb^{2+}, while the presence of Al^{3+}, Zn^{2+}, Fe^{3+}, and Cu^{2+} led to a redshift of the absorption maxima to different extents (Fig. 1a). Most importantly, only Co^{2+} showed a distinct spectral change (Fig. 1a) and a color change from yellow to orange (Fig. 1b), indicating that receptor **1** can serve as a potential candidate of "naked-eye" chemosensor for Co^{2+} in aqueous solution. To the best of our knowledge, the receptor **1** is the only colorimetric organic chemosensor for Co^{2+} in a near-perfect aqueous solution. The binding properties of **1** with Co^{2+} were further studied by UV-vis titration experiments. On treatment with Co^{2+} ion of a solution of **1**, the absorption bands at 441 and 459 nm significantly decreased, and two new bands at 390 and 500 nm gradually reached maxima at 0.5 equiv of Co^{2+} (Fig. 2).

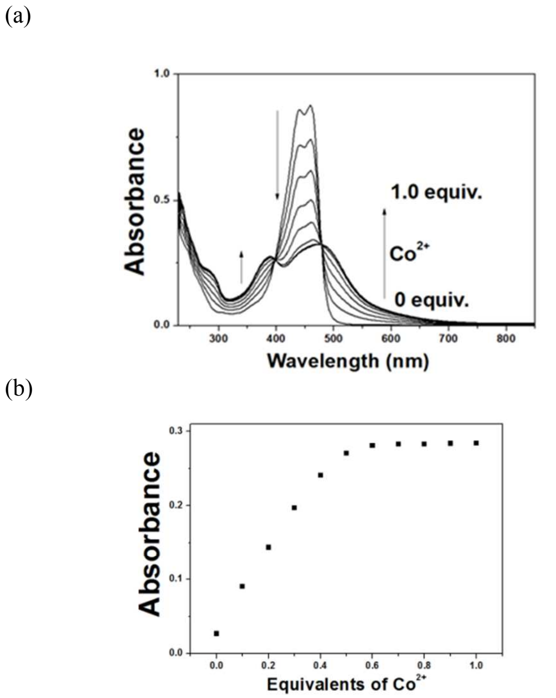
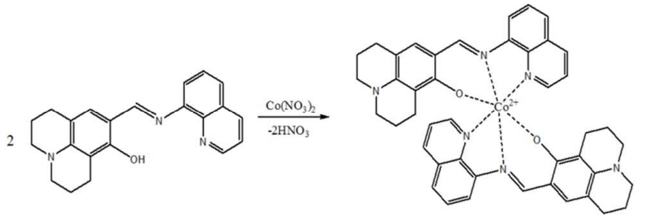


Fig. 2 (a) UV-vis spectra changes of **1** (20 µM) in the presence of different concentrations of Co^{2+} ion in buffer-methanol (999:1, v/v). (b) Absorption at 500 nm versus the number of equiv of Co^{2+} added.

Meanwhile, two clear isosbestic points were observed at 398 and 479 nm, indicating that only one product was generated from **1** upon binding to Co^{2+}. The Job plot analysis[42] showed a 2:1 stoichiometry for the Co^{2+}-2•**1** complex (Fig. S2†). To examine the binding mode between **1** and Co^{2+} further, a positive-ion ESI mass experiment was carried out (Fig. S3†). Unexpectedly, a Co^{3+} complex with 2:1 stoichiometry was observed as a major peak, although Co^{2+} was used as the standard metal ion. A peak at m/z 743.25 was assigned to $[2•\mathbf{1}+Co^{3+}-2•H]^+$ (calcd. 743.20). This phenomenon could be explained by one of two possibilities: the first is that a Co^{2+}-2•**1** complex is oxidized to the Co^{3+}-2•**1** complex under ESI-mass experimental conditions, and the other is that after its formation from the reaction of Co^{2+} with **1**, the Co^{2+}-2•**1** complex is oxidized to the Co^{3+}-2•**1** complex. To determine the correct reason, we first observed the change of UV-vis spectrum of the Co^{2+}-2•**1** complex after Co^{2+} was mixed with **1**. No change of the UV-vis spectrum was observed up to 1 day, suggesting that the oxidation state of Co^{2+} of the Co^{2+}-2•**1** complex formed from the reaction of Co^{2+} with **1** was retained.



Scheme 2 Proposed structure of a 2:1 complex of **1** and Co^{2+}.

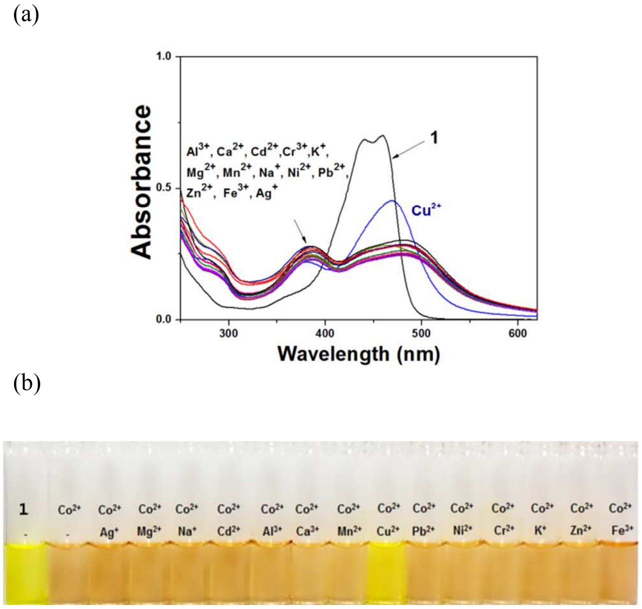


Fig. 3 (a) Competitive selectivity of **1** (20 μM) towards Co^{2+} (0.7 equiv) in the presence of other metal ions (0.7 equiv). (b) Colorimetric changes of **1** (20 μM) in the presence of Co^{2+} (0.7 equiv) and other metal ions (0.7 equiv).

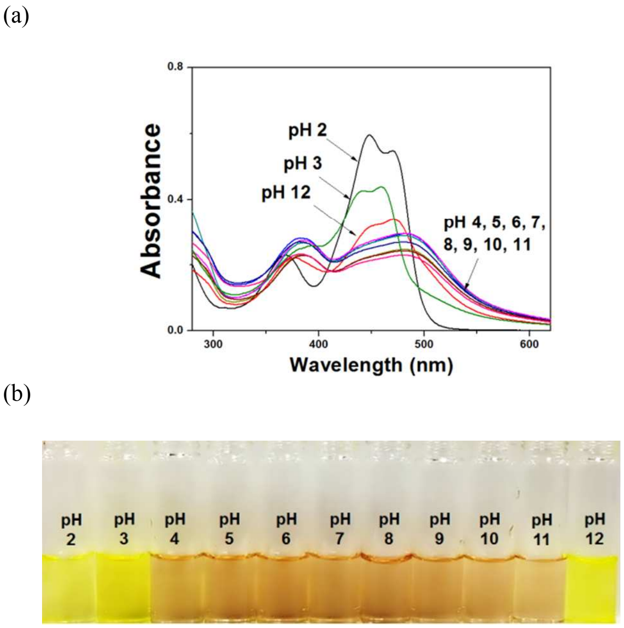


Fig. 4 (a) UV-vis spectra of Co^{2+}-2•**1** complex at different pH (2-12) in buffer solution. (b) The color changes of Co^{2+}-2•**1** complex at different pH (2-12).

To confirm our proof of the oxidation of the cobalt ion of the Co^{2+}-2•**1** complex, we used electron paramagnetic resonance (EPR) spectroscopy. Two EPR samples of the Co^{2+}-2•**1** complex were prepared. One was prepared as soon as Co^{2+} was mixed with **1** and the other 1 h after they were mixed. The two samples showed the same EPR signals (Fig. S4†). The electron paramagnetic resonance (EPR) spectrum of Co^{2+}-2•**1** complex exhibits signals at g=5.47, 4.27, and 2.01, which are characteristic of high-spin (S=3/2) Co^{2+}. Furthermore, we carried out the sensing test under the degassed condition. If there is still a color change for the complexation of Co(II) ion with **1** under the degassed condition, it would say that the sensor **1** detect Co(II), not Co(III), because Co(II)-**1** complex is oxidized to Co(III)-**1** complex only by O_2 molecule without any oxidants. Finally, we observed the color change even under the degassed condition. These results strongly demonstrate that the Co^{2+}-2•**1** complex might be oxidized to Co^{3+}-2•**1** complex under the ESI-mass experimental conditions. Based on the Job plot, UV-vis spectral change, ESI-mass spectrometry analysis, and EPR, we propose the structure of the 2:1 complex of **1** and Co^{2+} as shown in Scheme 2.

Based on UV-vis titration, the association constant (*K*) of **1** with Co^{2+} ion was calculated by using Li's equations[43] (Fig. S5†). The *K* value found was 3.0×10^9 M^{-2} which was much larger than those (10^4~10^7) previously reported for Co^{2+}-binding chemosensors.[2,3,5,9,10] The detection limit[44] of receptor **1** as a colorimetric sensor for the analysis of Co^{2+} ions was found to be 1.28×10^{-6} M (Fig. S6†). In the New Jersey Ground Water Quality Standards rules, the Department of Environmental Protection (DEP) has developed an interim specific groundwater quality criterion[1] for Co^{2+} of $1.7x10^{-6}$ M. Hence, the receptor **1** has a lower detection limit than required by the DEP guidelines and could be a powerful tool for the detection of cobalt in groundwater.

We studied the preferential selectivity of **1** as a colorimetric chemosensor for the detection of Co^{2+} in the presence of various competing metal ions. For competition studies, receptor **1** was treated with 0.7 equiv Co^{2+} in the presence of 0.7 equiv of other metal ions, as indicated in Fig. 3. There was no interference in the detection of Co^{2+} from Ag^+, Al^{3+}, Ca^{2+}, Cd^{2+}, Cr^{3+}, Fe^{3+}, K^+,

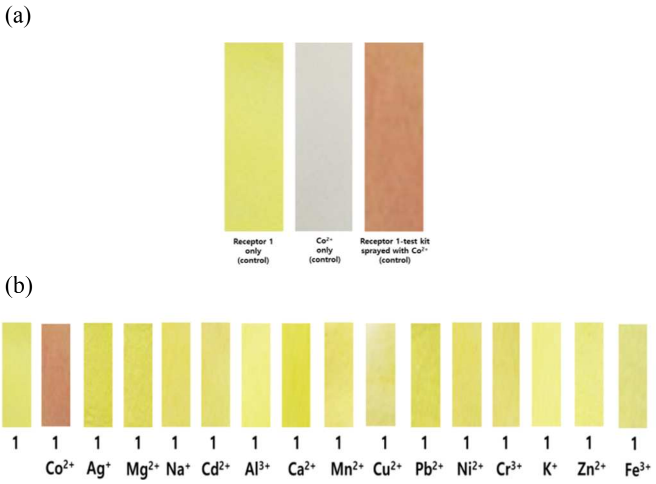


Fig. 5 Photographs of the filter paper coated with **1** used for the detection of Co^{2+}. (a) Left to right: test kit coated with only receptor **1** (control, 20 µM), test kit coated with only Co^{2+} (control, 20 µM), and receptor-**1** test kit immersed into Co^{2+} solution. (b) Receptor-**1** test kits (20 µM) immersed into various metal ions (1.7 µM).

Mg^{2+}, Mn^{2+}, Na^{+}, Ni^{2+}, Pb^{2+}, and Zn^{2+}. However, Cu^{2+} did interfere. Thus, **1** could be used as a selective colorimetric sensor for Co^{2+} in the presence of most competing metal ions.

We investigated the effect of pH on the absorption response of receptor **1** to Co^{2+} ion in a series of buffers with pH values ranging from 2 to 12 (Fig. 4). The color of the Co^{2+}-2•**1** complex remained in the orange region between pH 4 and 11, while its color changed to the original yellow at pH 2, 3, and 12. These results indicate that Co^{2+} could be clearly detected by the naked eye or UV-vis absorption measurements using **1** over the wide pH range of 4.0-11.0. The color change of the Co^{2+}-2•**1** complex from orange to yellow at very low pH (2 and 3) and high pH (>11) might be because of the demetallation of the complex, thus regenerating the receptor **1** with its yellow color.

In addition, to investigate the practical application of receptor **1**, test kits were prepared by immersing filter papers in a methanol solution of **1** (20 µM) and then drying in air. These test kits were utilized to sense Co^{2+} among different cations. As shown in Fig. 5, when the test kits coated with **1** were added to different cation solutions (1.7 µM), the obvious color change was observed only with Co^{2+} in bis-tris buffer solution. Therefore, the test kits coated with the receptor **1** solution would be convenient for detecting Co^{2+} in the presence of other metal ions.

In conclusion, we have reported a simple imine-based colorimetric chemosensor that displays high selectivity and sensitivity for detection of cobalt ions in a fully aqueous solution. Receptor **1** showed selectivity toward Co^{2+} in a 2:1 stoichiometric manner, which induces an obvious color change from yellow to orange. Moreover, receptor **1** could be used as a practically viable probe for monitoring Co^{2+} levels in environmental systems, because the detection limit of **1** for Co^{2+} is below the groundwater quality criterion. Furthermore, we have also developed receptor **1**-based colorimetric test kits for Co^{2+} detection in real-world environments.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [Experimental procedure, Job plots, ESI-mass spectra, X-band EPR spectrum, Li's equation plot, detection limit, UV-spectra of Co^{2+}-2•**1** complex under different pH conditions and photograph of Co^{2+}-2•**1** complex at different pH values (3.1-3.9)]. See DOI: 10.1039/b000000x/

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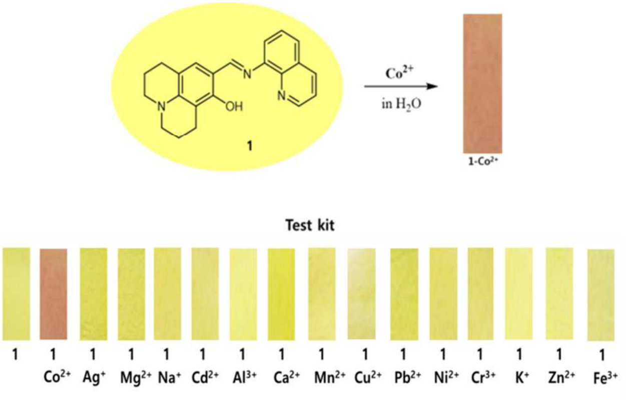
Graphical Abstract for TOC



A novel practical “naked eye” probe for Co^{2+} in a fully aqueous solution has been developed