



A novel selective colorimetric chemosensor for cobalt ions in a near perfect aqueous solution



Yu Jeong Na, Ye Won Choi, Ga Rim You, Cheal Kim*

Department of Fine Chemistry and Department of Interdisciplinary Bio IT Materials, Seoul National University of Science and Technology, Seoul 139-743, Republic of Korea

ARTICLE INFO

Article history:

Received 15 June 2015

Received in revised form

17 September 2015

Accepted 18 September 2015

Available online 25 September 2015

Keywords:

Cobalt ion

Colorimetric chemosensor

LMCT

Solid sensor

ABSTRACT

A novel chemosensor **1** (**1** = 2-(N-(2-hydroxybenzyl)-N-((pyridin-2-yl)methyl)amino)-N-(2-hydroxyphenyl)acetamide) was synthesized and characterized. The receptor **1** showed a selective colorimetric sensing ability for cobalt ion by changing color from colorless to pale violet in a near perfect aqueous solution, facilitating naked eye detection of Co^{3+} through the oxidation of Co^{2+} to Co^{3+} . This phenomenon could be possibly explained by ligand-to-metal charge-transfer. Moreover, the detection limit ($1.8 \mu\text{M}$) of **1**-Co complex is comparable to the environmental protection agency (EPA) guideline ($1.7 \mu\text{M}$) in drinking water. Practically, **1** also functioned when supported by silica, indicating that receptor **1** had the potential for working as optical solid sensors.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

The design and synthesis of efficient artificial receptors for various cations have received much interest in the last decade due to the essential roles that cations play in biology, the environment and chemistry [1]. Cobalt is an essential trace element found in rocks, minerals, soils and seawater, and plays an important role in various biological systems [2]. It is well known that Co^{2+} plays an essential part in the metabolism of iron and the synthesis of hemoglobin, and is also a main component of vitamin B_{12} and other biological compounds [3]. However, exposure to high levels of cobalt can cause toxicological effects, including heart disease, thyroid enlargement, asthma, decreased cardiac output, lung disease, dermatitis and vasodilation [4–9]. In addition, it is a significant environmental pollutant. On the other hand, cobalt deficiency in the human body may also lead to a pathological condition [10]. Therefore, a highly sensitive and selective analytical method to detect cobalt(II) ions is of great importance to avoid these toxic effects.

Up to now, much effort has been made to detect cobalt(II) ions based on different analytical strategies, among which colorimetric methods have attracted considerable attention. Colorimetric method can conveniently and easily monitor target ions with the naked eye [11–14], while the most of approaches such as

inductively coupled plasma atomic emission spectrometry [15], atomic absorption spectroscopy [16], fluorescence techniques [17–22] and electrochemical methods [23], require sophisticated equipment, tedious sample preparation procedures, and trained operators. Therefore, the colorimetric method is a valuable tool regarding the detection of toxic metal ions including Co^{2+} .

Coumarin has been frequently used in recent years as the chromophores to prepare sensors for metal cations [24,25]. In addition, a pyridyl group is well-known as a binding site [26]. Therefore, we designed to combine the coumarin derivative, 2-chloro-N-(2-((3-nitro-2-oxo-2H-chromen-4-yl)amino)phenyl)acetamide, with 2-(aminomethyl)-pyridine (Scheme 1).

Herein, we present the synthesis of a novel chemosensor **1** composed of the pyridyl moiety and 2-chloro-N-(2-((3-nitro-2-oxo-2H-chromen-4-yl)amino)phenyl)acetamide group. Sensor **1** detected Co^{2+} by color change from colorless to pale violet via the ‘naked-eye’ with high selectivity in a near perfect aqueous solution. Moreover, receptor **1** had the potential for working as optical solid sensors.

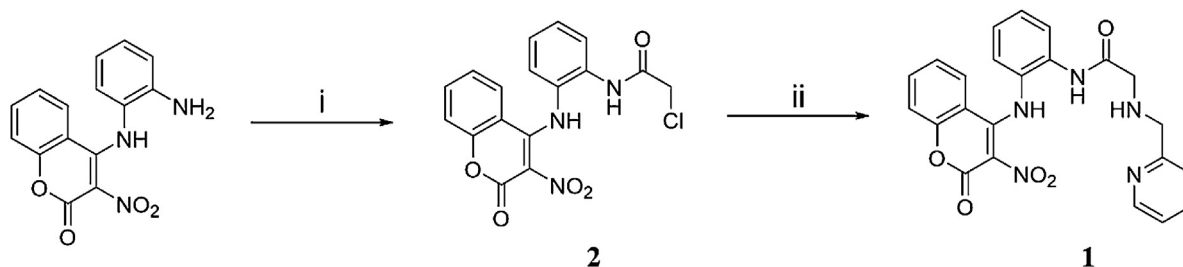
2. Experimental

2.1. Materials and instrumentation

All the solvents and reagents (analytical grade and spectroscopic grade) were obtained from Sigma–Aldrich and used as received. ^1H NMR and ^{13}C NMR spectra were recorded on a Varian 400 MHz and

* Corresponding author.

E-mail address: chealkim@seoultech.ac.kr (C. Kim).



Scheme 1. Synthesis of **1**. (i) chloroacetyl chloride, 3 h. (ii) 2-(aminomethyl)-pyridine, KI, 5 h.

100 MHz spectrometer. Chemical shifts (δ) were reported in ppm, relative to tetramethylsilane $\text{Si}(\text{CH}_3)_4$. 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. ESI-mass spectra of **1** and **1**- Co^{2+} complex were obtained by direct introduction of the solution of samples (100 μM) in CH_3CN into the source at 25 $\mu\text{L}/\text{min}$ using a syringe pump. The spray voltage of the spectrometer was set at 5 kV, and the capillary temperature at 150 $^\circ\text{C}$. 4-((2-Aminophenyl)amino)-3-nitro-2H-chromen-2-one was synthesized according to the literature method [25].

2.2. Synthesis of 2-chloro-N-(2-((3-nitro-2-oxo-2H-chromen-4-yl)amino)phenyl)acetamide (**2**)

4-((2-Aminophenyl)amino)-3-nitro-2H-chromen-2-one (0.80 g, 3 mmol) and chloroacetyl chloride (244 μL , 6 mmol) were dissolved in 5 mL of methylene chloride. Then, the solution was stirred for 3 h at room temperature. The yellow powder was produced, which was collected by filtration, washed with methylene chloride and air-dried. Yield: 80%. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 9.97 (s, 1H), 9.90 (s, 1H), 8.38 (d, $J=8$ Hz, 1H), 7.90 (d, $J=8$ Hz, 1H), 7.80 (t, $J=8$ Hz, 1H), 7.51 (m, 1H), 7.33 (t, $J=8$ Hz, 1H), 7.80 (t, $J=8$ Hz, 1H), 7.24 (d, $J=8$ Hz, 1H), 7.10 (t, $J=8$ Hz, 1H), 4.38 (s, 2H).

2.3. Synthesis of **1**

2-Chloro-N-(2-((3-nitro-2-oxo-2H-chromen-4-yl)amino)phenyl)acetamide **2** (0.74 g, 2 mmol), and 2-(aminomethyl)-pyridine (205 μL , 2 mmol) and potassium iodide (0.58 g, 3.5 mmol) were dissolved in 5 mL of methylene chloride. Then, the solution was stirred for 5 h at room temperature. The yellow powder was produced, which was collected by filtration, washed with methylene chloride and air-dried. Yield: 50%. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 10.11 (s, 1H), 9.88 (s, 1H), 8.28 (d, $J=4$ Hz, 1H), 8.23 (d, $J=8$ Hz, 1H), 7.83 (d, $J=8$ Hz, 1H), 7.72 (t, $J=8$ Hz, 1H), 7.44 (m, 2H), 7.3 (m, 3H), 7.21 (d, $J=8$ Hz, 1H), 7.08 (m, 2H), 3.93 (s, 1H), 3.56 (s, 3H). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ 170.57, 158.30, 155.74, 151.88, 149.37, 147.23, 137.03, 134.83, 133.66, 128.71, 128.59, 126.05, 125.24, 124.89, 123.37, 123.30, 122.89, 117.96, 117.35, 115.07, 59.88, 58.36 ppm. Anal. calcd for $\text{C}_{23}\text{H}_{19}\text{N}_5\text{O}_5$ (445.14): C, 62.02; H, 4.30; N, 15.72%. Found: C, 62.34; H, 4.42; N, 15.51%; IR (cm^{-1} , KBr pellet): 3436 (b, $\nu\text{O}-\text{H}$, typical for intramolecular hydrogen bonded O-H), 3000–2800 ($\nu\text{C}-\text{H}$), 1632 (νCvN), 1610, 1582, 1498, 1459, 1430, 1337, 756.

2.4. UV-vis titration of **1** with Co^{2+}

Receptor **1** (4.5 mg, 0.01 mmol) was dissolved in DMSO (1 mL) and 12 μL of the **1** (10 mM) were diluted with 2.988 mL bis-tris buffer (10 mM, pH 7.0) to make the final concentration of 40 μM .

$\text{Co}(\text{NO}_3)_2$ (2.9 mg, 0.01 mmol) was dissolved in bis-tris buffer (10 mM, pH 7.0). 0–16.8 μL of the cobalt solution (10 mM) were added to each receptor solution (40 μM , 3 mL) prepared above. After mixing them for a few minutes, UV-vis spectra were taken at room temperature.

2.5. Job plot measurement

Receptor **1** (4.5 mg, 0.01 mmol) and $\text{Co}(\text{NO}_3)_2$ (2.9 mg, 0.01 mmol) were separately dissolved in DMSO and bis-tris buffer (1 mL). 0.15 mL of the receptor **1** solution were diluted to 29.85 mL of bis-tris buffer (10 mM, pH 7.0) to make the concentration of 100 μM . The $\text{Co}(\text{NO}_3)_2$ solution was diluted in the same way. 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. 0, 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5 and 5 mL of the Co^{2+} solution 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.

2.6. Competition with other metal ions

Receptor **1** (4.5 mg, 0.01 mmol) was dissolved in DMSO (1 mL) and 12 μL of this solution (10 mM) were diluted with 2.988 mL of bis-tris buffer (10 mM, pH 7.0) to make the final concentration of 40 μM . MNO_3 ($\text{M}=\text{Na}, \text{K}$, 0.02 mmol) or $\text{M}(\text{NO}_3)_2$ ($\text{M}=\text{Mn}, \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}, \text{Cd}, \text{Mg}, \text{Ca}, \text{Pb}$, 0.02 mmol) or $\text{M}(\text{NO}_3)_3$ ($\text{M}=\text{Fe}, \text{Cr}, \text{Al}, \text{Ga}, \text{In}$, 0.02 mmol) or $\text{M}(\text{ClO}_3)_2$ ($\text{M}=\text{Fe}$, 0.02 mmol) were separately dissolved in bis-tris buffer (10 mM, pH 7.0, 1 mL). 6 μL of each metal solution (20 mM) were taken and added to 3 mL of the solution of receptor **1** (40 μM) to give 1 equiv of metal ions. Then, 6 μL of the Co^{2+} solution (20 mM) was added to the mixed solution of each metal ion and **1** to make 1 equiv. After mixing them for a few minutes, UV-vis spectra were obtained at room temperature.

2.7. pH effect test

A series of buffers with pH values ranging from 2 to 12 was prepared by mixing sodium hydroxide solution and hydrochloric acid in bis-tris buffer. After the solution with a desired pH was achieved, receptor **1** (4.5 mg, 0.01 mmol) was dissolved in DMSO (1 mL), and then 12 μL solution of the receptor **1** (10 mM) were diluted to 2.988 mL with bis-tris buffer (10 mM, pH 7.0) to make the final concentration of 40 μM . $\text{Co}(\text{NO}_3)_2$ (0.02 mmol) was dissolved in bis-tris buffer (10 mM, pH 7.0, 1 mL). 6 μL of the Co^{2+} solution (20 mM) was transferred to each receptor **1** solution (40 μM) prepared above. After mixing them for a few minutes, UV-vis spectra were taken at room temperature.

2.8. Silica support

Receptor **1** (4.5 mg, 0.01 mmol) was dissolved in THF (10 mL). Receptor **1**-silica was prepared by immersing silica

Download English Version:

<https://daneshyari.com/en/article/7145082>

Download Persian Version:

<https://daneshyari.com/article/7145082>

[Daneshyari.com](https://daneshyari.com)