Selective Recognition of Fe$^{3+}$ by a Simple Schiff Base Chemosensor

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Abstract. A simple and easily synthesized Schiff base chemosensor 1 was prepared by the one-step condensation reaction of 3-acetyl-4-hydroxycoumarin and 1-naphthylamine. The metal ion recognition ability of the chemosensor was measured by UV-Vis spectrophotometer. It demonstrated that its absorbance at 327 nm enhanced upon addition of Fe$^{3+}$ significantly. The absorption intensities at 327 nm fitted good linear relation ($R^2=0.9928$) to Fe$^{3+}$ concentration in DMF. 1 is able to recognize Fe$^{3+}$ selectively over other ions. The synthesized chemosensor 1 would be useful to detect Fe$^{3+}$ qualitatively and quantitatively.

1. Introduction

Various ions play a very important role in human production and life. Iron is an indispensible trace element in human body. It is an important component of hemoglobin, myoglobin and many enzymes. If the body is lack of iron, it can affect the synthesis of hemoglobin and myoglobin, and reduce the activity of some enzymes, such as cytochrome c, ribonucleotide reductase and succinate dehydrogenase. These enzymes are closely related to biological oxidation, tissue respiration, decomposition and synthesis of neurotransmitters. Therefore, the lack of iron can cause many physiological changes, which leads to low immunity, reduced intelligence and anti infection ability of the body. These cause neurological disorders, reduced work efficiency and other diseases [1, 2]. However, excessive iron can also cause adverse consequences, such as affecting the absorption of zinc and resulting in zinc deficiency. After excessive absorption of iron, it reaches the important organs such as the heart, liver, and lungs through the blood circulation, and deposits in these organs, causing a serious diseases, such as hemochromatosis. Therefore, the detection of iron ion is very important.

In the past, people could only detect and identify various ions through tedious experiments or expensive instruments. However, with the development of chemical research, various colorimetric / fluorescent reagents have been synthesized, and colorimetric / fluorescent molecular probes have also become a hot research direction in the field of chemistry [3-6].

Coumarins are a kind of plant metabolites widely existing in nature. By adding groups to coumarin derivatives, various colorimetric/fluorescent substances with excellent optical properties can be obtained. This kind of material has stable optical properties and is a very important colorimetric/fluorescent reagent.

In order to develop iron ion probe, we designed a coumarin-based Schiff base derivative. The probe molecule 1 was obtained in high yield by one-step synthesis. It was found by UV-Vis spectrum that 1 can selectively recognize Fe$^{3+}$ without interference of other metal ions.
2. Experimental
Chemosensor 1 was synthesized (Scheme 1) by one step starting from 3-acetyl-4-hydroxycoumarine and 1-naphthylamine. 3-acetyl-4-hydroxycoumarin (0.204 g, 1 mmol) and 1-naphthylamine (0.143 g, 1 mmol) were added into 60 mL of methanol. The mixture was stirred and refluxed for 8 h. Subsequently, the mixture was concentrated and purified by chromatography using petroleum (60-90 °C)/acetic ether (7:3, v/v) as the eluent to produce compound 1. Yield: 85%. m. p. 183.9-184.3 °C. 

\[ \begin{align*} \text{1H NMR (400 MHz, CDCl3)} & \delta 16.16 (s, 1H), 8.17 (d, J = 8.0 Hz, 1H), 7.95-8.01 (m, 1H), 7.90-7.93 (m, 1H), 7.57-7.65 (m, 4H), 7.41 (d, J = 8.0 Hz, 1H), 7.29-7.34 (m, 3H), 2.66 (s, 3H). \end{align*} \]

Scheme 1. Synthetic route of 1.

3. Results and Discussion

3.1. Spectral Response of 1 Upon the Addition of Fe$^{3+}$
In order to study the selective recognition ability of chemosensor 1 to various metal ions, different metal ions ($2 \times 10^{-4}$ mol/L) were added to the solution of chemosensor 1 ($2 \times 10^{-5}$ mol/L). The UV-Vis spectrum of the mixed solution in Figure 1 shows that the absorption value of the chemosensor 1 solution at 327 nm is only 0.28. After adding Hg$^{2+}$, Al$^{3+}$, Mn$^{2+}$, Mg$^{2+}$, Ni$^{2+}$, Zn$^{2+}$, there was no significant change. However, the absorption value of the solution significantly increased to 0.83 (2.96 times) after adding Fe$^{3+}$. It can be seen that compared with other metal ions, the chemosensor 1 has a high selectivity for Fe$^{3+}$.

![Figure 1. Absorption spectra of 1 ($2 \times 10^{-5}$ M) without and with 10 equiv. of different cations (Fe$^{3+}$, Hg$^{2+}$, Al$^{3+}$, Mn$^{2+}$, Mg$^{2+}$, Cu$^{2+}$, Ni$^{2+}$, Zn$^{2+}$) in DMF.](image-url)
3.2. The Selectivity of \(1\) towards \(\text{Fe}^{3+}\)

The selectivity of chemosensor \(1\) towards \(\text{Fe}^{3+}\) was also studied by cation-competitive experiments (Figure 2). The diagram displayed that the absorbance intensities of \(1\) after adding 10 equiv. \(\text{Fe}^{3+}\) were almost unaffected by other cations. In other words, \(1\) could maintain its sensing response to \(\text{Fe}^{3+}\) in the presence of other relevant cations. These results indicated that \(1\) could serve as a chemosensor for \(\text{Fe}^{3+}\) with high selectivity and strong anti-interference ability.

![Figure 2](image)

**Figure 2.** Cation selectivity of \(1\) towards \(\text{Fe}^{3+}\). Black bars: absorbance intensities of \(1\) (2\( \times \)10\(^{-5}\) M) and different cations (2\( \times \)10\(^{-4}\) M) in DMF. Red bars: absorbance intensities of \(1\) (2\( \times \)10\(^{-5}\) M) after addition of \(\text{Fe}^{3+}\) (2\( \times \)10\(^{-4}\) M) without and with the presence of different cations (2\( \times \)10\(^{-4}\) M).

3.3. Quantitative Analysis of \(1\) for \(\text{Fe}^{3+}\)

In order to study the quantitative relationship between \(1\) and \(\text{Fe}^{3+}\), we performed the experiment of absorbance changing with iron ion concentration. It can be found from the UV-Vis spectrum of Figure 3 that the absorption value of \(1\) is low without adding \(\text{Fe}^{3+}\), but the absorption value increases after adding \(\text{Fe}^{3+}\). With the increase of \(\text{Fe}^{3+}\) concentration, the absorption value of the mixed solution also increases. It can be seen that there is a certain relationship between the UV-Vis absorption value of the mixed solution and the concentration of \(\text{Fe}^{3+}\) added.

![Figure 3](image)

**Figure 3.** Absorption spectra of chemosensor \(1\) (2 \( \times \) 10\(^{-5}\) M) on addition of \(\text{Fe}^{3+}\) (0-10 equiv) in DMF.
To further explore this relationship, we have made a graph of the relationship between
the absorption value and Fe\textsuperscript{3+} concentration. Figure 4 is a dot plot with Fe\textsuperscript{3+} concentration as the abscissa
and the absorption value of the mixture as the ordinate. From the graph, it can be found that with
the concentration from low to high, the absorption value of the mixture is also increasing, and it keeps a
nearly straight rising state. The linear analysis of the image shows that the linear correlation
coefficient is $R^2 = 0.9928$, indicating that there is a good linear relationship between the absorption
value and the concentration of iron ions. Therefore, chemosensor 1 can be used to qualitatively detect
iron ions.

![Figure 4](image)

**Figure 4.** The corresponding linear ability of the absorbance versus the Fe\textsuperscript{3+} concentrations in
DMF.

3.4. The Sensing Mechanism

To elucidate the mechanism of interaction between the chemosensor 1 and Fe\textsuperscript{3+}, the
stoichiometry of chemosensor 1 and Fe\textsuperscript{3+} in the complex need to be determined. Job’s method was
employed with the absorbance intensity changes at 327 nm as a function of molar fraction of 1. It
exhibited a maximum absorbance at a mole fraction of 0.5 (Figure 5), indicating that the complex
stoichiometry of Fe\textsuperscript{3+} is 1:1 for 1. According to the stoichiometry, the proposed sensing mechanism
is shown in Scheme 1.

![Figure 5](image)

**Figure 5.** Job’s plot for determining the stoichiometry for chemosensor 1 and Fe\textsuperscript{3+} in DMF.

Total concentration of 1 + Fe\textsuperscript{3+} = 2×10\textsuperscript{-4} M.
4. Conclusions
In this paper, a coumarin-based Schiff base probe molecule 1 was synthesized by a one-step synthesis method. The UV-Vis spectroscopy studies revealed that chemosensor 1 is highly selective for Fe$^{3+}$ compared to other metal ions studied with increasing intensity at 327 nm by nearly three times. The results show that 1 can qualitatively detect Fe$^{3+}$ without interference from other metal ions. Through further research on the relationship between absorbance and the concentration of Fe$^{3+}$, it is found that the absorbance enhances with the increase of Fe$^{3+}$ concentration and there is a good linear relationship between them. It shows that chemosensor 1 can detect Fe$^{3+}$ quantitatively.

5. Acknowledgments
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