Synthesis and Molecular Recognition Properties of a Coumarin Derivative

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Abstract. In this paper, a coumarin derivative La was designed and synthesized in two steps with simple synthesis method and high yield. Its recognition performance was studied by UV-Vis spectroscopy. It was found that when iron ion (III) was added, the absorption value of the probe molecule La was significantly enhanced, while other metal ions studied did not cause significant changes. Further research on the relationship between absorbance and iron ion (III) concentration revealed that they have a good linear relationship. This shows that the coumarin derivative La has the ability to detect iron ions (III) qualitatively and quantitatively.

1. Introduction
Coumarins are widely distributed in nature. It is exist in animals, plants and microorganisms. So far, more than a thousand kinds of coumarin derivatives have been found, which can be obtained by natural extraction or artificial synthesis. Coumarin derivatives have been widely used in many fields, such as perfume, medicine and so on. The reason is that most coumarin derivatives have simple structure and good biological activity [1-5].

In 1987, the Nobel Prize for chemistry was awarded to C. J. Pedersen, D. J. cram and J.-M. Lehn, which is a symbol of the new era of chemical research. At this time, the term "chemistry beyond he concept of molecules" was put forward. Its meaning refers to the research on the complex and ordered aggregation with some specific functions, which is bound by intermolecular force. At present, with the deep research of molecular recognition, molecular recognition plays an increasingly important role in synthetic chemistry, life and material science [6-13].

The molecular recognition of coumarin derivatives is also very important [14-19]. According to the characteristics of coumarin derivatives, a coumarin derivative was synthesized and its molecular recognition performance was studied in this paper. This study can be used as the expansion and verification of coumarin derivatives family with potential application prospect.

2. Experimental
2.1. Synthesis of 3-acetyl-4-hydroxycoumarin
3-Acetyl-4-hydroxycoumarin was synthesized according to literature methods (Scheme 1) [20]. 4-hydroxycoumarin 1.62 g (0.01 mol) was added into a two round bottom flask, 2.5 mL (0.01 mol) of phosphorus oxychloride and 9 mL (0.14 mol) of glacial acetic acid were respectively added into the flask for reaction. The mixture was heated at constant temperature (125 °C) and refluxed for 1h. The
above precipitate was added to a round-bottomed flask, poured into anhydrous ethanol (25 mL), heated to dissolve, cooled to crystallize, filtered under reduced pressure, washed with absolute ethanol, and dried in vacuum to obtain the product as white needles. Yield 70.2%. 1H NMR (400 MHz, CDCl3) δ 8.14 (dd, 1H), 8.17 (d, J = 8.0 Hz, 1H), 7.73 (t, 1H), 7.40-7.33 (m, 1H), 7.28 (s, 1H), 2.76 (s, 3H).

**Scheme 1.** Synthetic route of 3-acetyl-4-hydroxycoumarin.

2.2. Synthesis of the Coumarin Derivative La

0.204 g (1 mmol) of 3-acetyl-4-hydroxy-coumarin, 0.109 g (1 mmol) of o-aminophenol and 60 mL of methanol were added to a round-bottomed flask (Scheme 2). The mixture was heated under reflux for about 6 hours. After cooling, the solvent was evaporated under reduced pressure. The obtained residue was recrystallized by methanol. A pale yellow solid product (La) was obtained after vacuum drying. Yield: 89%. m. p. 181.6-182.8 °C 1H NMR (400 MHz, CDCl3) δ 8.07 (dd, 1H), 7.6 (t, 1H), 7.33 (t, 2H), 7.25 (d, 2H), 7.18 (dd, 2H), 7.06 (d, 2H), 2.68 (s, 3H).

**Scheme 2.** Synthetic route of the coumarin derivative La.

3. Results and Discussion

3.1. Spectral Response of La upon the Addition of Iron Ion (III)

In order to study the ion recognition properties of the coumarin derivative La, eight common metal ions were added into the solution of La respectively. Through the change of UV-Vis spectrum, the selective recognition ability of La was demonstrated. It can be seen from the UV-Vis spectrum (Figure 1) that the absorption intensity of La obviously enhanced when ferrie ion was added. And the maximum absorption wavelength has a blue shift. However, the absorption spectrum did not change significantly when other metal ions were added. This shows that the coumarin derivative La has a specific recognition ability for iron ion (III).
3.2. Quantitative Analysis of La for Iron Ion (III)

To further elaborate the quantitative relationship between La and iron ion (III), different equivalent iron ion (III) (0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 2.0, 3.0, 4.0, 5.0, 10.0 eq) were added to La solution (2 × 10^{-5} mol / L) respectively. From the UV-Vis spectrum (Figure 2), it can be found that the absorbance of the mixed solution increases gradually with the increase of iron ion (III) concentration. It can be clearly seen from the relationship between the absorbance and iron ion (III) concentration (Figure 3) that there is a good linear relationship between them. The linear correlation coefficient is R^2 = 99475. Therefore, the coumarin derivative La can also be used for quantitative detection of iron ion (III).

![Figure 1](image1.png)

**Figure 1.** Absorption spectra of La (2 × 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.

![Figure 2](image2.png)

**Figure 2.** Absorption spectra of the coumarin derivative La (2 × 10^{-5} M) on addition of Fe^{3+} (0-10 equiv) in DMF.
3.3. The Sensing Mechanism

The mechanism of the coumarin derivative La for the recognition of iron ions has been explored by the Job’s method. In the 10 mixed solutions, the molar concentration ratio of La and iron ion (III) was from 0.1 to 1, but the total concentrations of La and iron ion (III) remained unchanged ($2 \times 10^{-4}$ mol/L). The absorbance of the mixed solution was measured by UV-Vis spectrum. Then the absorbance and the corresponding molar concentration ratio are compared as Figure 4. It can be seen from the figure that the maximum absorbance occurs at the position with the molar ratio of 0.5. It indicates that the complexation ratio of La and iron ion (III) is 1:1. The proposed sensing mechanism of the coumarin derivative La to iron ion (III) is shown in Scheme 3.
Scheme 3. Proposed sensing mechanism of the coumarin derivative La.

4. Conclusions
The coumarin derivative La was synthesized by two simple steps. It was found that La can selectively recognize iron ions among eight common metal ions by UV-vis spectroscopy. From the study of changes in absorbance and iron ion concentration, it showed that there was a good linear relationship between the absorbance of mixed solutions and the iron ion concentration. This indicates that the coumarin derivative La can not only detect iron ions qualitatively, but also quantitatively.

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6. References
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