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Synthesis and Characterization of an Al^{3+}-Selective Fluorescent Probe

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Abstract

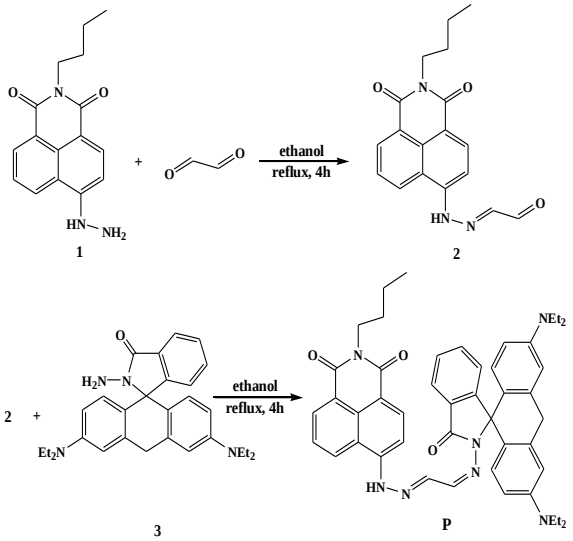
*A new fluorescent probe **P** based on rhodamin B was synthesized and characterized as an Al^{3+}-selective fluorescent probe in ethonal. The linear range of probe **P** to Al^{3+} was 2.0×10^{-6}-1.6×10^{-5} M with a detection limit of 6.7×10^{-7} M.*

Keywords: *Fluorescent probe; Rhodamin B; Al^{3+}.*

I. INTRODUCTION

Among the detection methods of metal ions, fluorescent peobes are easily obtainable, and the results are visual inspection[1-4]. Many different heavy metal ions selective fluorescent probes have been synthesized and reported[3-6]. It has been found that Al^{3+} can be enriched in the human body, and if the content of Al^{3+} in organisms is too high, it will cause a toxic effect of metabolic disorder and damage the human brain cells. The World Health Organization stipulates that aluminum's daily intake should not exceed 0.6 mg/kg[6]. Therefore, the detection of Al^{3+} is of great significance.

In this work, a rhodamine B derivative **P** was synthesized and characterized as an Al^{3+}-selective fluorescent probe (**Scheme 1**). The study showed the proposed probe **P** has good selectivity and sensitivity to Al^{3+} compared to other tested metal ions.



Scheme 1 Synthesis route of probe **P**

II. MATERIALS METHODS

A. Reagents and instruments

All reagents and solvents are commercially available and used directly.

Fluorescence emission spectra were measured on a Hitachi F-4600 spectrofluorometer. UV-Vis spectra were obtained on a Hitachi U-2910 spectrophotometer. Mass (MS) spectra were recorded on a Thermo TSQ Quantum Access Agillent 1100. pH values were conducted on a pH-meter PBS-3C.

B. Synthesis of P

Compounds **1** and **3** were synthesized as a reported method, respectively.[3,5]

Synthesis of compound **2**. Compound **1** (0.2 mmol) and glyoxal (0.3 mmol) were mixed and stirred in ethanol (30 mL) under reflux for 4 h. After the reaction was finished, the yellow precipitate so obtained was filtered and used directly. Yields: 80.3 %. MS: 322.1 $[M\text{-}H^+]^-$.

Synthesis of probe **P**. 1.0 mmol compound **2** and 1.0 mmol **3** were mixed in ethanol (40 mL) and stirred under reflux for 4 h; the mixture was cooled to room temperature. The red precipitate so obtained was filtered and dried in vacuum and used directly. Yields: 85.6 %. MS m/z: 762.80 $[M+H^+]^+$.

C. General spectroscopic methods

1.0 mM stock solutions were obtained by dissolving metal ions and **P** in deionized water and DMSO. Before spectroscopic measurements, the solution was freshly prepared by diluting the high concentration stock solution to the corresponding solution. For all measurements, excitation and emission slit widths were all 2.5 nm; excitation wavelength was 430 nm.

III. RESULTS AND DISCUSSION

A. Selectivity of P

Firstly, the selectivity of the proposed probe **P** (10 μM) was measured, and the testing ions were Na^+, K^+, Ag^+, Ca^{2+}, Mg^{2+}, Ba^{2+}, Co^{2+}, Zn^{2+}, Cu^{2+}, Cd^{2+}, Pb^{2+}, Hg^{2+}, Cr^{3+}, Ni^{2+}, and Al^{3+} (10 μM), respectively (**Figure 1**). The results showed that only the addition of Al^{3+} caused an obvious fluorescent enhancement of the tested solution. The competition experiment was also carried out. The addition of various metal ions (10 μM) to the system of **P** (10 μM) with Al^{3+} (10 μM) did not cause the change of

fluorescent intensity (**Figure 2**). These all proved that **P** has good selectivity to Al^{3+}.

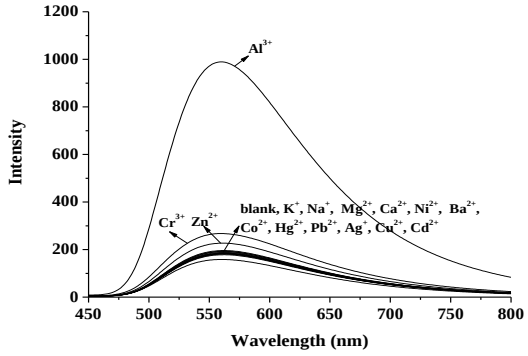


Fig 1: Selectivity of **P** (10 μM) to different metal ions (10 μM) in ethanol.

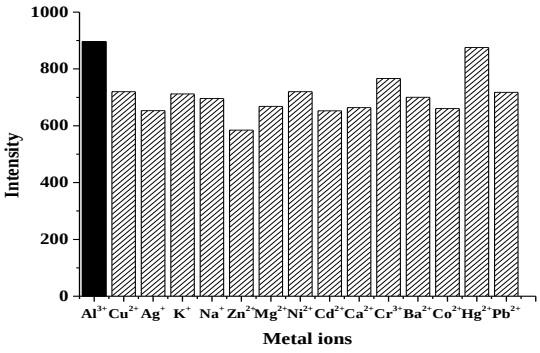


Fig 2: Fluorescence response of **P** (10 μM) to Al^{3+} (10 μM) and the mixture of different metal ions (10 μM) with Al^{3+} (10 μM) in ethanol.

B. Sensitivity behavior of P for Al^{3+}

The sensitivity of **P** was examined by titrating different concentrations of Al^{3+} using fluorescence spectra in **Figure 3**. With the increase in the concentration of Al^{3+}, the fluorescent intensity was enhanced at 560 nm gradually. It showed a linear response in the range of 2.0×10^{-6}-1.6×10^{-5} M Al^{3+} with a detection limit of 8.5×10^{-7} M.

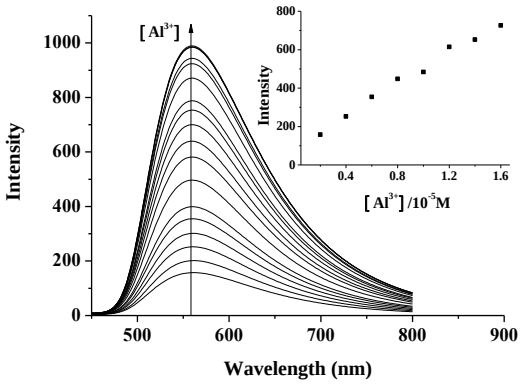


Fig 3: Fluorescence response of **P** (10 μM) to various concentrations of Al^{3+} in ethanol solution. Inset: The fluorescence at 560 nm of **P** (10 μM) as a function of Al^{3+} concentrations (0-16 μM).

C. The proposed reaction mechanism

The binding mode was studied by Job plot analysis and showed a 1:1 stoichiometry for the **P**-Al^{3+} complexation (**Figure 4**). According to the results above mentioned, the coordination mode of **P**-Al^{3+} was proposed, as shown in **Scheme 2**.

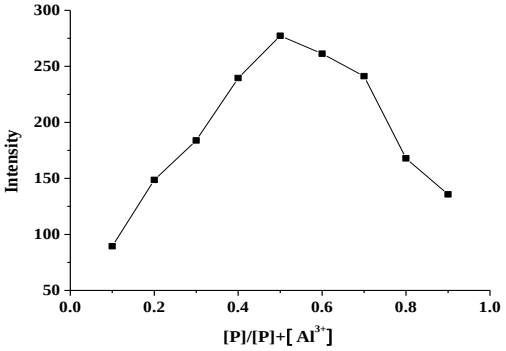
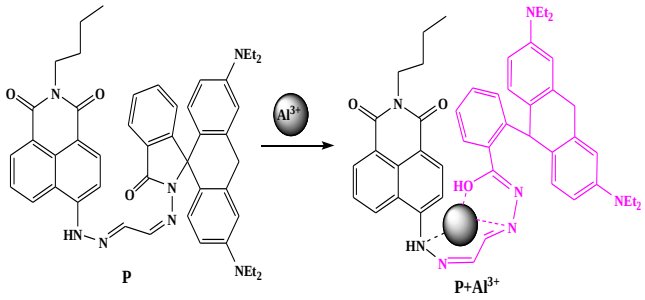


Fig 4: Job's plot of **P** with Al^{3+}. The total concentration of **P** and Al^{3+} was kept at a fixed 10 μM.



Scheme 2 Proposed binding mode of **P** with Al^{3+}.

IV. CONCLUSIONS

In summary, an Al^{3+}-selective fluorescent probe **P** based on rhodamin B was synthesized and characterized. The conception may expand a promising approach to develop selective detection method for Al^{3+} and lead to the development of probes for other metal ions.

ACKNOWLEDGMENT

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