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RESEARCH ARTICLE

CHARACTERIZATION OF AN Al^{3+}-SELECTIVE FLUORESCENT PROBE BASED ON RHODAMINE B DERIVATIVE BEARING A 1,2,4-TRIAZOLE AS SUBUNIT

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ABSTRACT

Rhodamine B is an excellent fluorescent dye with good photostability, high fluorescence quantum yields, low sensitivity to pH, high molar absorption coefficient, and long absorption and emission wavelengths, especially its fluorescence can be regulated by its unique spiro structure switch, which has been widely used for the detection of many heavy metal ions. Excessive emissions or uptake of $A1^{3+}$ will not only damage the ecological environment, but also endanger human health, but the detection using fluorescent probe method was limited because of its poor coordination property. Based on this, a rhodamine derivative **P** was designed and synthesized as Al^{3+}-selective fluorescent probe with excitation wavelength of 530 nm in ethanol. Among the common metal ions and anions, **P** displayed fluorescence enhancement toward Al^{3+}. The linear range of probe **P** to Al^{3+} was 20 to 100 µM, and the detection limit was 6.6 µM. The method of continuous variation (Job's method) determined **P**–Al^{3+} complex of 1:1 stoichiometry.

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INTRODUCTION

Aluminum (Al) is the most abundant metal on Earth (1). Due to its unique metallic properties, it is widely used in daily life. But excessive intake of Al can cause neurologic disorders, such as Alzheimer's disease, dialysis encephalopathy, and osteomalacia (1,2). Preventing Al^{3+} contamination in and ensuring human health has become a global consensus, because Al^{3+} is not an essential element for the human body and difficult to metabolize, more importantly, it has the potential for accumulation (3). Among the methods used for the detection of Al^{3+}, fluorescent probe method has the advantage of low coat, easy operation, little or no harm to body, which made it is an important tool in the biological study (4-9). Fluorescent probes based on rhodamine B derivatives had long excitation and emission wavelength, high quantum yields and good selectivity and sensitivity, many fluorescent probes for the detection metal ions, anions and small molecules had been designed and reported (10-14). Song *et al* reported a Cu^{2+}-selective fluorescent probe based on rhodamine B, among the common metal ions, only the addition of Cu^{2+} caused the color change of testing solution to right pink (15). Liu *et al* synthesized a rhodamine B based Al^{3+}-selective fluorescent probe (16), which showed dual channel properties to Al^{3+} and Cr^{3+}, naked eye observed color change was produced after the addition of Al^{3+} or Cr^{3+} to the solution of the proposed probe.

Based the above mentioned, a 1,2,4-triazole contained rhodamine B derivative **P** was synthesized and characterized as Al^{3+}-selective fluorescent probe (Figure 1).

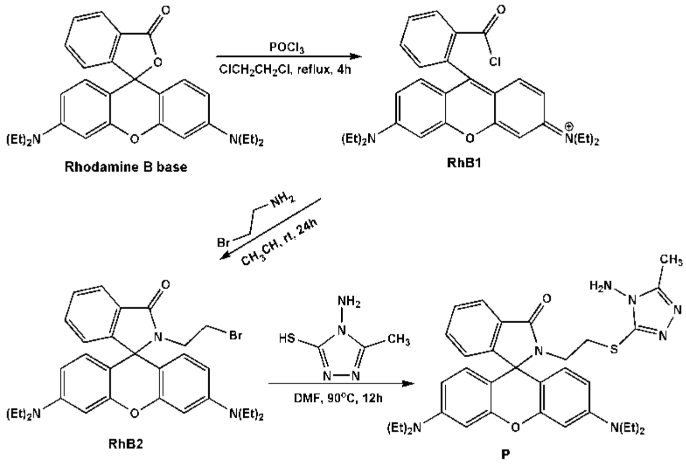

Figure 1. Synthetic route of probe P.

EXPERIMENTAL SECTION

Materials: All reagents are commercially available and used directly. The salts are NaCl, KCl, $AgNO_3$, $CaCl_2$, $MgCl_2$, $ZnCl_2$, $PbCl_2$, $CuCl_2$, $HgCl_2$, $CdCl_2$, $CoCl_2$, $NiCl_2$, $MnCl_2$,

$CrCl_3$, KI, $NaNO_3$, NaCl, $NaClO_4$, KBr, KH_2PO_4, Na_2S, Na_2CO_3, Na_2SO_4.

Synthesis of Probe P: RhB1 and RhB2 were synthesized as reported methods (17,18). 0.1579 g (0.29 mmol) RhB2, 0.0455g (0.35 mmol, 1.2 folds) 3-methyl-4-amino-5-thiol-1,2,4-triazole and 0.1603 g (1.16 mmol, 4 folds) anhydrous K_2CO_3 were mixed in 20 mL DMF. The mixture was stirred at 90 °C for 12 h, and the color of the mixture changed from red to orange. Cooled to room temperature, 100 mL ice-water was added to the mixture, which was extracted with CH_2Cl_2. After removing CH_2Cl_2, purification by silica gel column elution was conducted to obtain pure probe **P** (petroleum ether:ethyl acetate = 2:1, v:v).

Basic spectroscopic procedures: To prepare 2.0 mM stock solutions of **P** in DMF for the experiment. The required metal ions and anions were dissolved in deionized water. The slit widths for excitation and emission were configured to 10 nm, with an excitation wavelength established at 530 nm.

RESULT AND DISCUSSION

Selectivity measurement of P: Selectivity is the key property of fluorescent probes, which decide the further use in real sample detection. The selectivity experiment was firstly studied.

The testing metal ions and anions were Zn^{2+}, Al^{3+}, Hg^{2+}, Cu^{2+}, Cr^{3+}, Cd^{2+}, Fe^{3+}, Mg^{2+}, K^+, Ag^+, Ca^{2+}, Na^+, SO_4^{2-}, CO_3^{2-}, Br^-, I^-, ClO_4^-, NO_3^-, S^{2-}, $H_2PO_4^-$. Only the addition of Al^{3+} (100 μM) to the solution of **P** (50 μM) in ethanol caused spiro ring opening of rhodamine B, the color of the solution changed from colorless to pink with an obvious fluorescence enhancement (Figure 2). So, probe **P** was characterized as Al^{3+}-selective fluorescent probe.

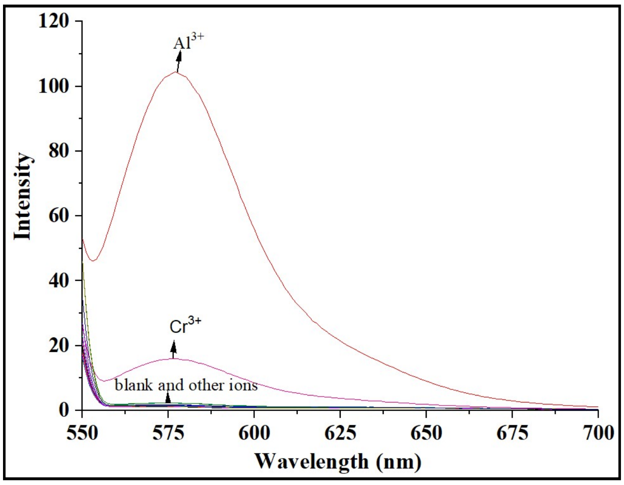

Figure 2. Fluorescence spectra of probe P (50 μM) against various metal ions (100 μM) and anions (100 μM) in ethanol.

Fluorescent titration experiment of P to Al^{3+}: In order to study the sensitivity of **P** to Al^{3+}, fluorescent titration experiment of **P** (50 μM) to Al^{3+} was produced in ethanol (Figure 3). With the increase of Al^{3+} concentration (0-50 μM), the fluorescent intensity enhanced gradually, and linear response in the range of 20-100 μM was obtained with detection limit 6.6 μM of Al^{3+}.

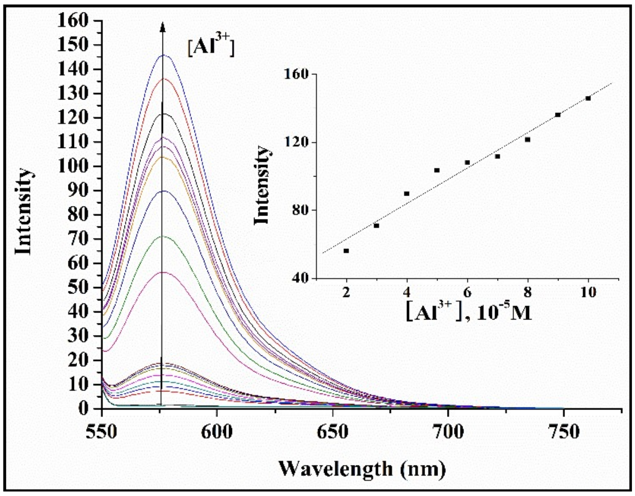

Figure 3. Fluorescence titration of probe P (50 μM) with different concentrations of Al^{3+} (0-50 μM) in ethanol.

Competition experiment of P for Al^{3+}: In order to investigate the interference of other metal ions on the reaction between fluorescent probe **P** and Al^{3+}, we conducted a competition experiment, and the results were shown in Figure 4. In the ethanol solution of the fluorescent probe **P**-Al^{3+}, various metal ions (Zn^{2+}, Al^{3+}, Hg^{2+}, Cu^{2+}, Cr^{3+}, Cd^{2+}, Fe^{3+}, Mg^{2+}, K^+, Ag^+, Ca^{2+}, Na^+) were added, resulting in different degrees of change in fluorescence intensity.

Upon comparing the extent of these changes, we found that the addition of Cu^{2+} and Zn^{2+} significantly affected the reaction between fluorescent probe **P** and Al^{3+}, likely because these two ions acted as quenchers, leading to a decrease in fluorescence intensity. In contrast, other ions had minimal impact, indicating that fluorescent probe **P** exhibited good selectivity for Al^{3+}.

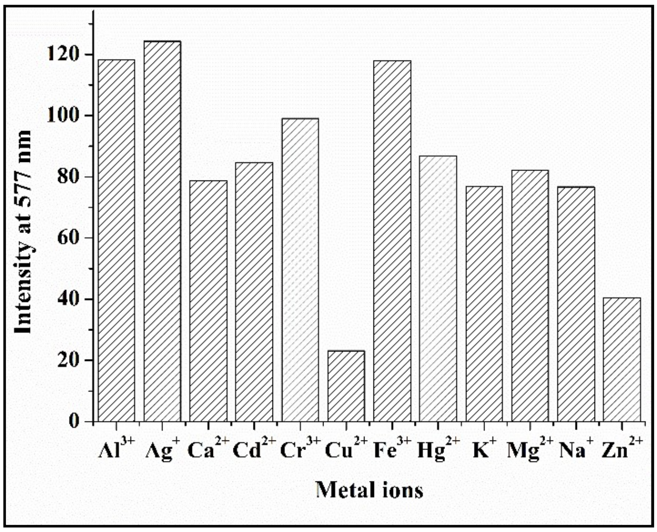

Figure 4. Competition experiment of probe P (50 μM) against Al^{3+} (100 μM) in the presence of metal ions (100 μM) in ethanol.

Proposed binding mode of P with Al^{3+}: Job's plot experiment was produced to speculate the binding mode of **P** with Al^{3+}. It can be seen from Figure 5 that when the concentration of **P** and Al^{3+} both were 25 μM, the fluorescence of the reaction is the strongest, so the optimal binding ratio of fluorescent probe **P** to Al^{3+} can be determined to be 1:1.

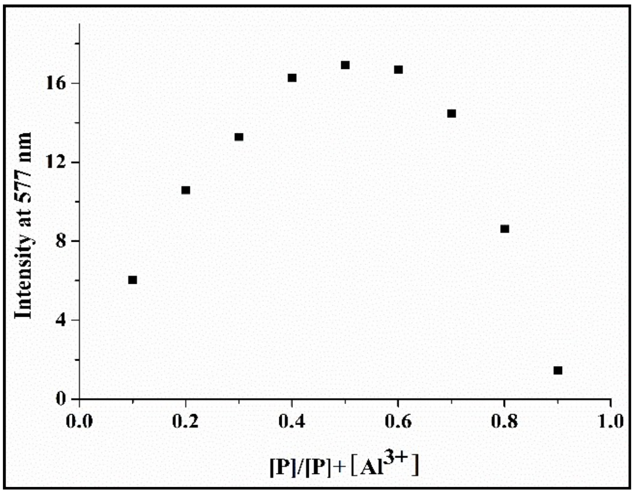

Figure 5. The Job-plot indicating the 1:1 stoichiometry for P-Al^{3+} complex. Total concentration of P and Al^{3+} was kept as 50 µM.

Reversibility of the P-Al^{3+} system: A reversibility experiment of **P**-Al^{3+} system was studied using EDTA as a complexing agent (Figure 6). It can be seen from Figure 6 that **P** (50 µM) showed no fluorescent signal in ethanol (Figure 6a), the addition of Al^{3+} (100 µM) making an enhancement of fluorescence at 577 nm (Figure 6b), and the induce of EDTA (200 µM) to **P**-Al^{3+} system in ethanol, the fluorescence response at 577 nm disappeared (Figure 6c), and then addition of excessive Al^{3+} (200 µM and 400 µM) resulted in the reappearance of a significant fluorescence response, as shown in Figure 6d and Figure 6e. This experiment showed that the sensing process of **P** with Al^{3+} was reversible.

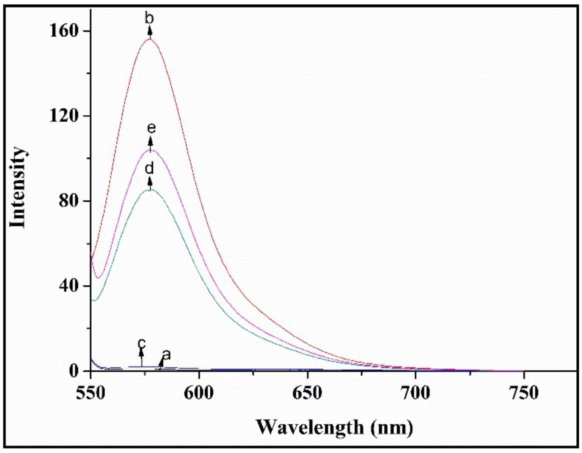

Figure 6. Reversibility of the P-Al^{3+} system in ethanol phase. (a) P (50 µM); (b) P (50 µM) + Al^{3+} (100 µM); (c) P (50 µM) + Al^{3+} (100 µM) + EDTA (200 µM); (d) P (50 µM) + Al^{3+} (100 µM) + EDTA (200 µM) + Al^{3+} (200 µM); (e) P (50 µM) + Al^{3+} (100 µM) + EDTA (200 µM) + Al^{3+} (400 µM).

CONCLUSION

A rhodamine B based Al^{3+}-selective fluorescent probe **P** was characterized. In ethanol, **P** showed "off-on" response to Al^{3+} based on the Al^{3+}- induced reversible ring-opening mechanism of the rhodamine spirolactam.

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