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Construction of A Turn On Probe for Al^{3+} Based on Rhodamine B Derivative

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Abstract

As an unnecessary element for human body, aluminum can cause a variety of diseases when ingested in excess, so it is of great significance for Al^{3+} detection. A new rhodamine probe with excellent photochromic properties based on Al^{3+}-induced ring-opening mechanism of the rhodamine spirolactam was proposed. Upon binding with Al^{3+}, the generated 1:1 P1-Al^{3+} complex, confirmed by Job's plot titrations analysis. Could exhibit a remarkable fluorescence enhancement with a limit of detection (LOD) of 0.33 μM, and colorimetric response toward Al^{3+} in presence of other common metal ions and anions. The design thought can enrich the development of probes for Al^{3+}.

Keywords: Al^{3+}; Probe; Turn on.

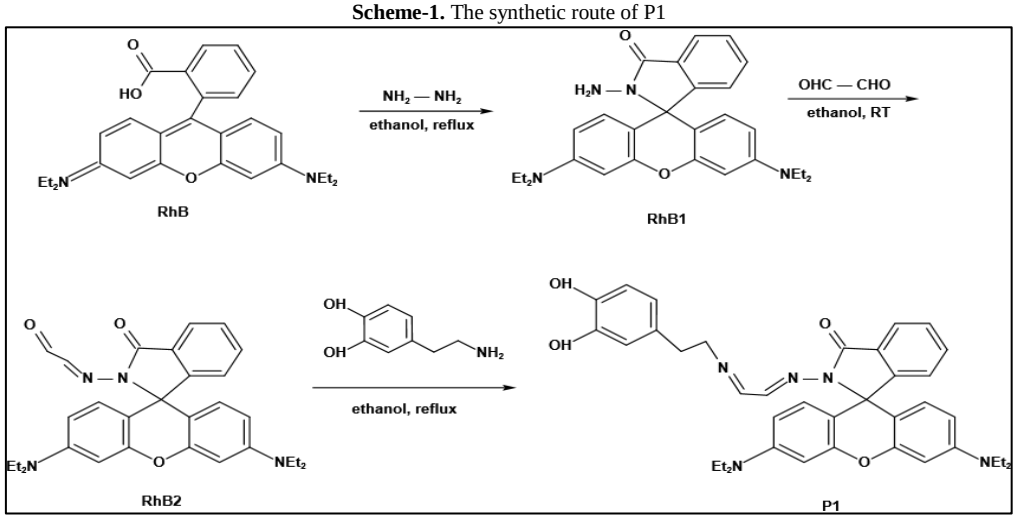
1. Introduction

As the most abundant metallic element in the Earth's crust, aluminum is continuously used in various fields of industry and life. However, metal aluminum accumulation in human body will cause a variety of diseases and physiological dysfunction, such as bone marrow, liver, central nervous system and reproductive system are also damaged to varying degrees [1-4]. Therefore, in order to avoid the threat to human and animal and plant life caused by excessive metal aluminum, the detection technology of metal aluminum ion has been widely concerned by researchers in recent years [5-9]. Fluorescent probe method can be operated simply, quickly and visually, so it has been widely studied with the advantages of high sensitivity, good selectivity and low detection limit [10, 11]. Compared to other metal ions, design of Al^{3+}-probes has always been a bottleneck because of its spectroscopic properties and poor coordination ability.

Among various fluorescent dyes, rhodamine dyes have excellent photochemical properties such as good photostability, high fluorescence quantum yield and large molar extinction coefficient [12, 13]. In particular, rhodamine dye itself is colorless and non-fluorescent, after its combination with specific analytes, the corresponding spiral ring structure will undergo ring opening reaction [14-17], where the process not only can show obvious absorption and fluorescence enhancement, but also can result in the color change. Because of its unique "on-off" features in light of structural changes between spiral and open ring, it has been widely used as a fluorescent fluorophore to construct probes for metal ions. Additionally, it is necessary to consider the geometry of coordination sites for the recognition of metal ion. In light of some reports, introduction of O and N donor atoms to the designed probes can promote the coordination ability of Al^{3+} based on hard and soft acids and bases theory [18-24]. Recently, an article related to Facile preparation of a rhodamine B derivative-based fluorescent probe for visual detection of iron [25], ad a review on developments in rhodamine-based chemosensors havs been reported [26].

Herein, we envisioned a new Al^{3+}-selective probe based on rhodamine motif (Scheme 1). The purpose of dopamine introduction was to provide N and O sites for enhanced coordination of Al^{3+}. The results demonstrated that the particular molecular structure gave rise to the satisfactory selectivity toward Al^{3+}.

Scheme-1. The synthetic route of P1



2. Materials and Methods

2.1. Reagents and Instruments Materials and Methods

All reagents and solvents are of analytical grade and used directly. Absorption spectra were measured by a Hitachi U-2910 spectrophotometer. Fluorescence emission spectra were conducted on a Hitachi 4600 spectrofluorometer.

2.2. Synthesis of P

RhB1 and RhB2 were synthesized in a high yield from rhodamine B following a literature procedure [27]. To a stirred solution of Compound RhB2 (0.18 g, 0.3 mmol) in 40 mL ethanol was added dropwise dopamine (0.075 g, 0.5 mmol) in 20 mL ethanol. The mixture was then heated at reflux for 5 h and monitored by TLC. After the reaction was completed, the solution was cooled to room temperature. The precipitate so obtained was filtered and washed with cold ethanol. So obtained product **P1** was used in this work.

2.3. General Spectroscopic Methods

Metal ions and **P1** were dissolved in deionized water and DMSO to obtain 1.0 mM stock solutions, respectively. For all fluorescence measurements, excitation and emission slit widths were both 10 nm, excitation wavelength was set as 520 nm.

3. Results

3.1. Selectivity of P

To validate the selectivity of **P1** in practice, some common alkali or alkaline-earth metals, heavy and transition metal ions, anions were added to the ethanol media of **P1**. The free **P1** displayed a very weak fluorescence, most metal ions and anions did not induce any obvious fluorescent change, only Fe^{3+} and Cu^{2+} caused the ignored fluorescence enhancement at 590 nm, for Al^{3+}, the F/F_0 value was almost 100-fold as seen in Figure 1a. The UV–vis responses of P**1** to the above metal ions and anions were also tested as shown in Figure 1b. Similarly, only Al^{3+} induced a notable enhancement of absorbance at 558 nm.

Fig-1(a). Fluorescent emission changes of **P1** (10 μM) in the presence of different metal ions and anions (10 μM) in ethanol

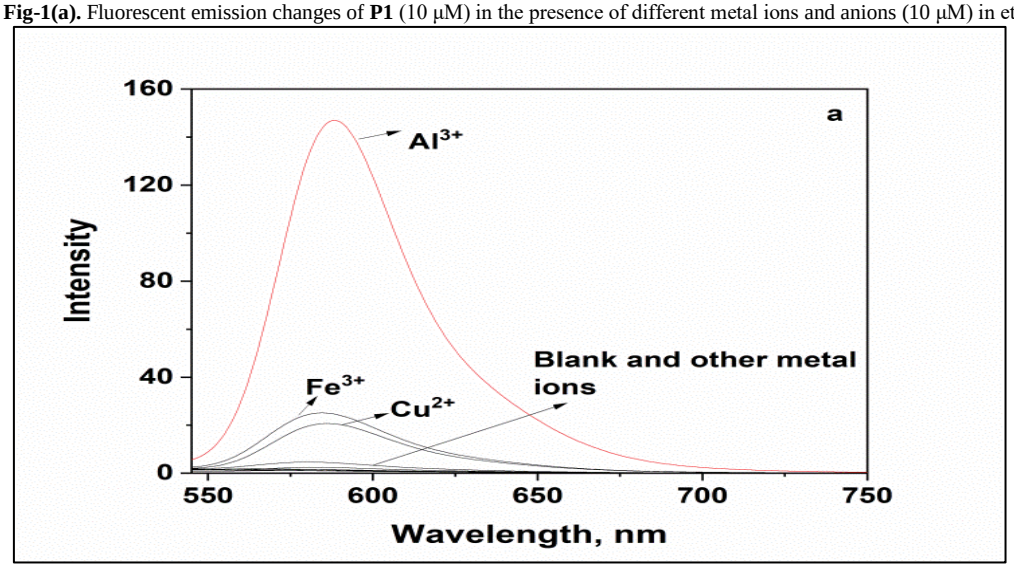
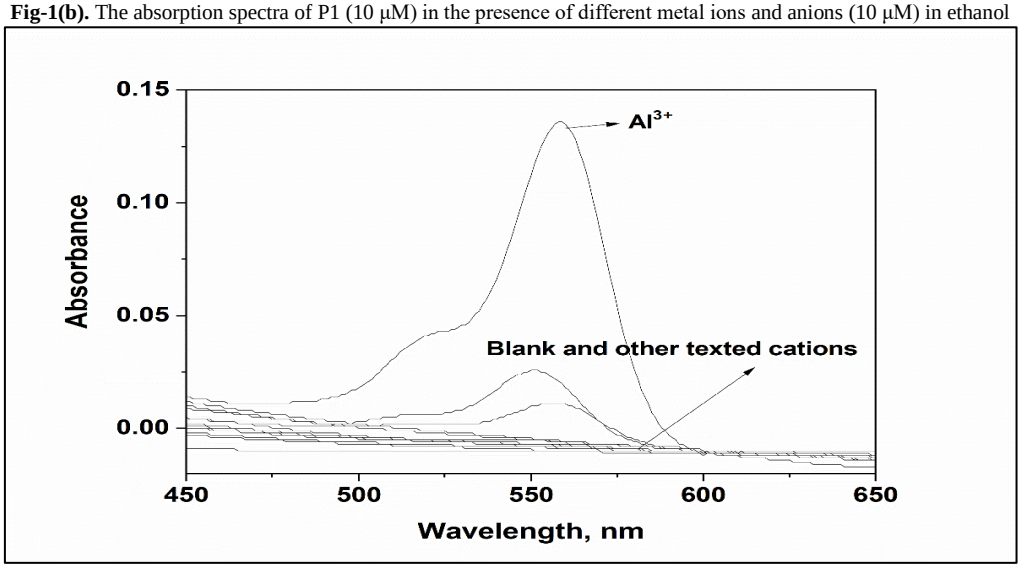


Fig-1(b). The absorption spectra of P1 (10 μM) in the presence of different metal ions and anions (10 μM) in ethanol



3.2. Competitive Capacity of P

In the competition experiments, the fluorescence properties of **P1** toward above-mentioned metal ions were measured. The results showed that fluorescence intensity at 590 nm based on the addition of the Al^{3+} was not obviously influenced by the addition of excess metal ions as depicted in Figure 2a. Also, it was investigated that the fluorescence response of **P1** toward Al^{3+} in the presence of anions such as Br^-、NO_3^-、SO_4^{2-}、ClO_4^-、$H_2PO_4^-$、I^-、HPO_4^{2-}. Similarly, the intervention of these anions caused no obvious interference toward the fluorescent signal of the compound **P1**-Al^{3+}.

Fig-2(a). Fluorescence response of P1 (10 μM) to 10 μM of Al^{3+} or to the mixture of 10 μM of other metal ions with 10 μM of Al^{3+} in ethanol

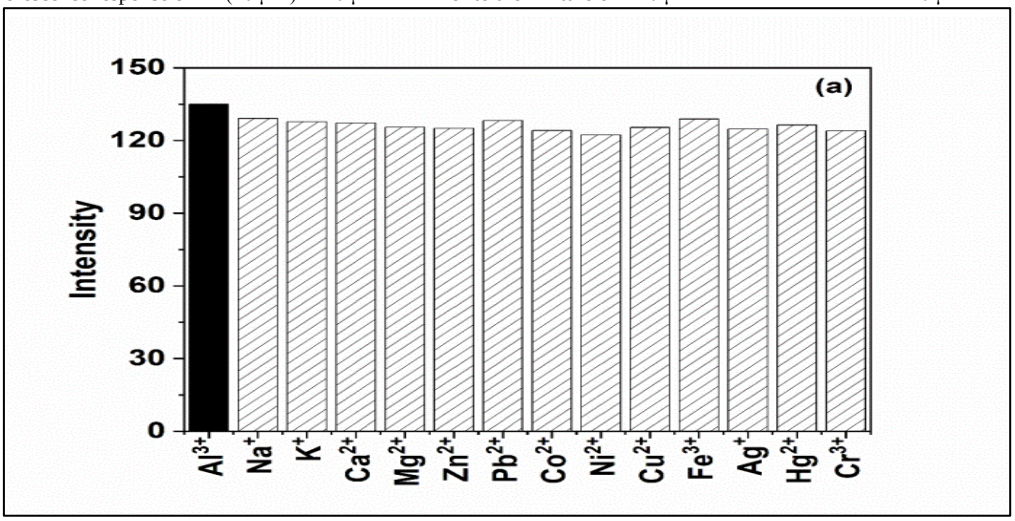
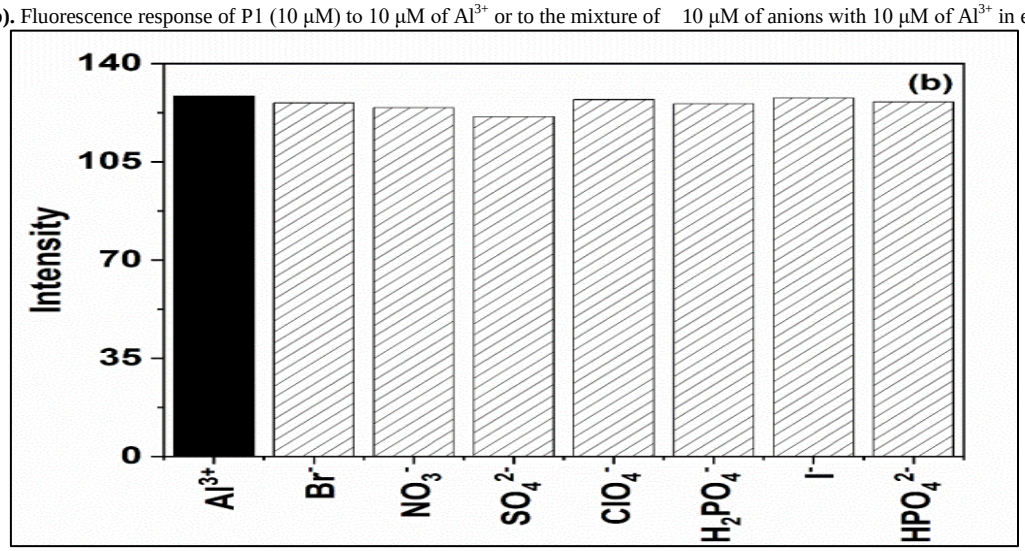


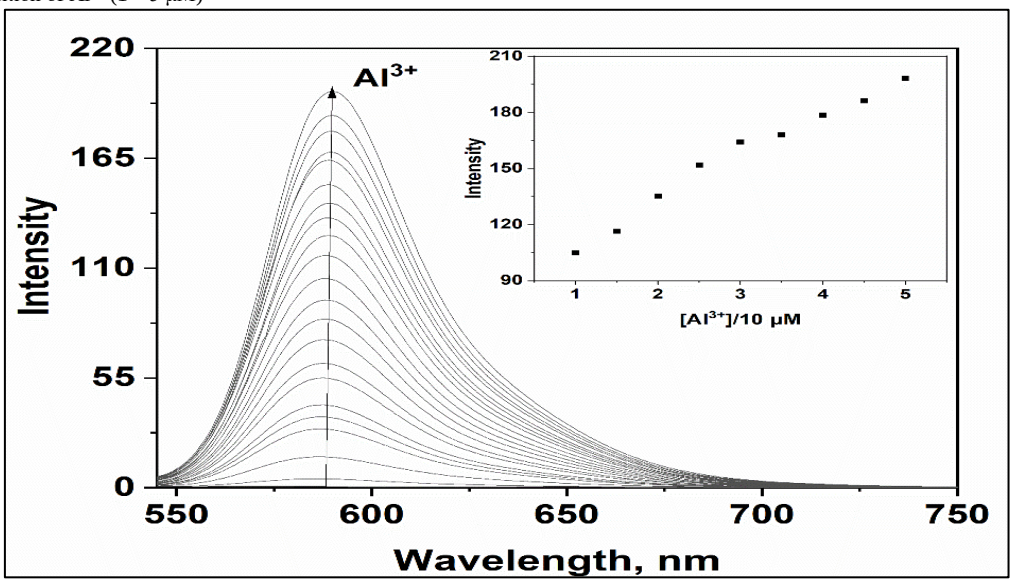
Fig-2(b). Fluorescence response of P1 (10 μM) to 10 μM of Al^{3+} or to the mixture of 10 μM of anions with 10 μM of Al^{3+} in ethanol



3.3. Sensitivity of P

The fluorescence spectra of **P1** in the presence of different concentrations of Al^{3+} ethanol were recorded (Figure 3). When the addition of Al^{3+} to **P1** was gradually increased, a significant fluorescence intensity with an emission maximum at 590 nm enhanceed gradually. Furthermore, the fluorescence intensity at 590 nm was well proportional to the amount of Al^{3+} (1−5 μM) with a good linear correlation (R^2 = 0.9993), and the detection limit was also obtained as 0.33 μM (inset, Figure 3).

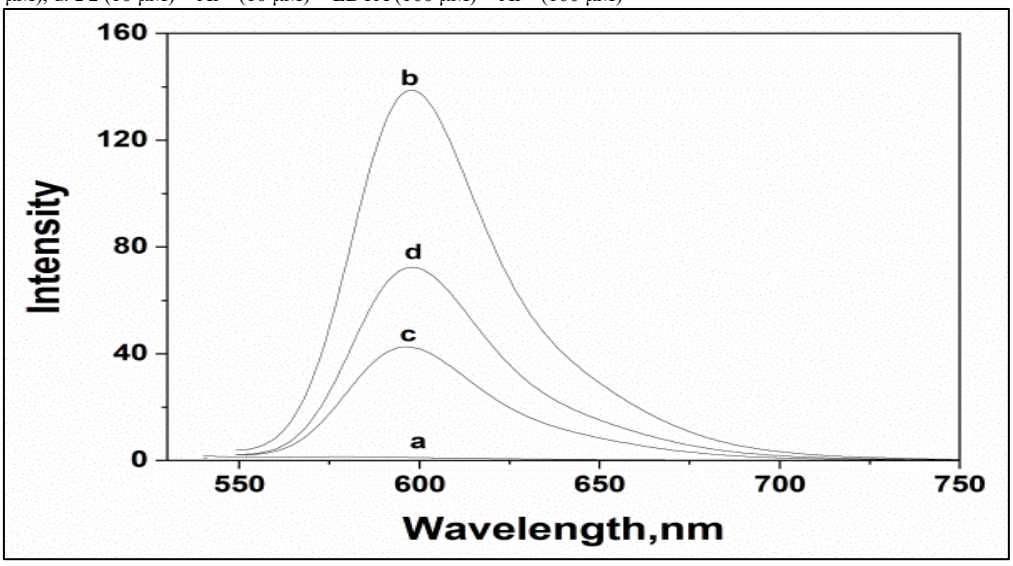
Fig-3. Emission spectra of **P1** (10 μM) in the presence of various concentrations of Al^{3+} ethanol. Inset:Linear fluorescence intensity (*F*) of **P1** (10 μM) upon addition of Al^{3+} (1−5 μM)



3.4. Reversibility of P

The circular detection of the probe is of great significance for the actual detection. Therefore, EDTA was used as complexing agent in the experiment to investigate the reversibility of **P1** in Figure 4. When only 10 μM **P1** was contained in the test solution, there was almost no fluorescence as shown in Figure.4a. When an appropriate amount of Al^{3+} was added, the fluorescence peak at 590 nm appeared (Figure 4b). Then 10 times of excess EDTA was added again, the fluorescence intensity at 590 nm was obviously weakened in Figure 4c, followed by 10 times of Al^{3+} was added. The fluorescence intensity at 590 nm was recovered to a certain extent followed by 10 times of Al^{3+} ,Figure. 4d.

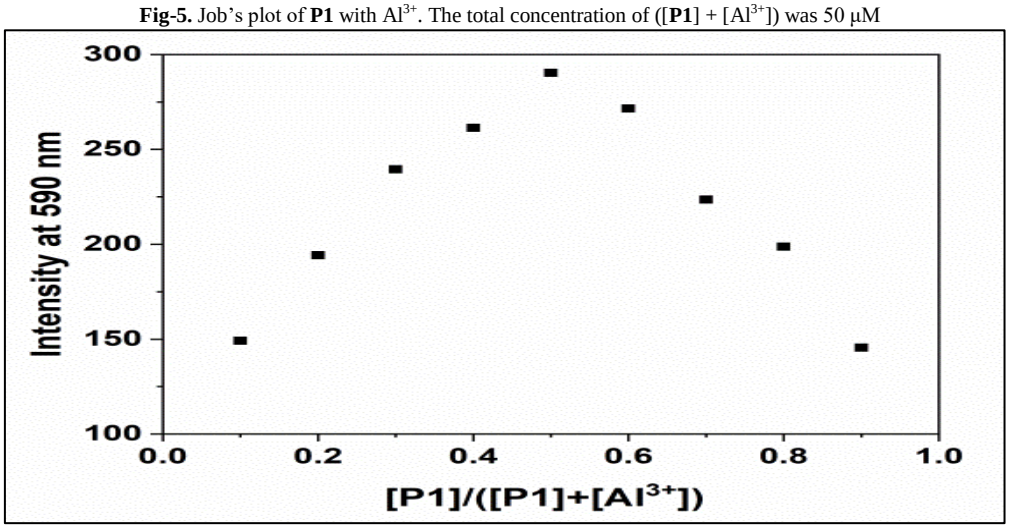
Fig-4. Reversible titration response of **P1** to Al^{3+} in ethanol solution. a. **P1** (10 μM), b. **P1** (10 μM) + Al^{3+} (10 μM), c. **P1** (10 μM) + Al^{3+} (10 μM) + EDTA (100 μM), d. **P1** (10 μM) + Al^{3+} (10 μM) + EDTA (100 μM) + Al^{3+} (100 μM)



3.5. E. Job's Plot

Binding analysis using Job's plot was measured to determine the stoichiometry of **P1**-Al^{3+} complex. As seen from Figure 5, a maximum fluorescence intensity at 590 nm was observed when the molecular fraction of **P1** was close to 0.5.

Fig-5. Job's plot of **P1** with Al^{3+}. The total concentration of ([**P1**] + [Al^{3+}]) was 50 μM



4. Discussion

4. 1. Selectivity of P Discussion

These results based on UV-vis and fluorescence spectra demonstrated the binding between **P1** and Al^{3+}, only the Al^{3+} caused a notable change, which can be ascribed to the spirolactam bond cleavage of rhodamine group, which was like most reported rhodamine-based probes [28]. In terms of sensitivity and selectivity concerns, It is well-known that selective "turn-on" probes was favored over those showing "turn-off" probes [29]. Our designed probe displayed some advantages, which was also a quality in the design of fluorescent probes.

4.2. Competitive Capacity of P

The interference experiment from other metal ions and anions was suggested to note that all the tested species had no obvious influence on the **P1** function, which set the stage for further application in other areas.

4.3. Sensitivity of P

The detection limit of **P1** toward Al^{3+} to be 0.33 μM based on $3\delta_{blank}$/k (where δ_{blank} is the standard deviation of the blank solution and k is the slope of the calibration plot), which is enough to satisfy the U.S. EPA and FDA guidelines of 7.41 μM Al^{3+} for bottled drinking water [30]. The results indicated that **P1** could sensitively detect environmentally relevant levels of Al^{3+}.

4.4. Possible Mechanism

The Job's plot indicated the 1:1 complex formation between **P1** and Al^{3+}. By testing the reversibility of the **P1** with EDTA as a reagent, the results showed that the **P1** had the possibility of recycling. Similar to many rhodamine derivatives-based fluorescent probes, the fluorescence enhancement of **P1** toward Al^{3+} was the result of structural conversion between the spiro and open ring, which was based on the spiro ring-opening mechanism rather than an ion-catalyzed hydrolysis reaction [31].

5. Conclusion

In this paper, a novel fluorescent probe P based on rhodamine B motif was designed and synthesized. The probe **P1** can detect Al^{3+} in dual channel with UV-vis and fluorescence spectroscopy, which showed that this probe had good selectivity, sensitivity, and was also not interfered by other common metals and anions. In the future work, we believed that this kind probe can be used for many practical applications by further modification.

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