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*Original Article*

# Fluorescent Probe for $Al^{3+}$ Based on Naphthalene Derivative

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***Abstract*** *- A new probe for $Al^{3+}$ based on the $Al^{3+}$ induced reversible coordination with the proposed probe P1 was described. It displayed a highly selective and sensitive "turn-on" fluorescent response toward $Al^{3+}$.*

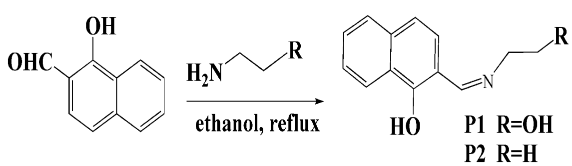
***Keywords*** *- $Al^{3+}$, Fluorescent probe, Turn on.*

## I. INTRODUCTION

Aluminum has been widely used in many industrial and domestic fields, posing a severe threat to biospheres and human health.[1-3] In this regard, detection of $Al^{3+}$ in living biosystems is of great importance for monitoring aluminum contamination and understanding its biological functions.[4-6] Fluorescent probes have been proven to be useful for sensing biologically important species in vitro and/or in vivo because of their non-destructive character, instantaneous response, simplicity, and high sensitivity. [7-10]

Schiff bases can coordinate with various metal ions and form stable complexes, known to be good ligands for metal ions.[11-15] Based on our previous research,[16-20] it is necessary to consider the geometry of coordination sites for a certain metal ion. The introduction of O and N donor atoms to the structure of compounds proved the coordination ability of the proposed probes to $Al^{3+}$. Meanwhile, the naphthaldehyde derivative as the fluorophore was chosen due to its excellent photophysical properties and easy molecular structure modification.[21,22]

A new and simple $Al^{3+}$-selective fluorescent probe P1 based on naphthalene derivative was synthesized and characterized (Scheme 1).




**Scheme 1 The synthetic routes of compounds**

## II. EXPERIMENTAL SECTION

### *A. Reagents and Instruments*

All reagents and solvents are of analytical grade and used without further purification. The metal ions salts employed were common commercial available ones.

Fluorescence emission spectra were conducted on a Hitachi4600 spectrofluorometer. Nuclear magnetic resonance (NMR) spectra were measured with a Brucker AV 400 instrument, and chemical shifts were given in ppm from tetramethylsilane (TMS).

### *B. Synthesis of P1-2*

2-Hydroxy-1-naphthaldehyde (0.0100 g, 0.058 mmol) and 2-Aminoethanol (0.1 mL) were mixed in ethanol (40 mL). The reaction mixture was stirred at 80 ºC for 4 h and then cooled to room temperature, and the solution was removed under reduced pressure. Then the mixture was poured into petroleum ether, and the residue obtained was filtered and washed with ethanol and then dried in a vacuum to afford P1 as a brown solid. Yields: 83.4%. $^{1}H$ NMR ($d_6$-DMSO): 8.98 (s, 1H), 7.97 (d, 1H), 7.84 (d, 1H), 7.54 (d, 1H), 7.35 (t, 1H), 7.11 (t, 1H), 6.65 (d, 1H), 3.62 (t, 2H), 3.40 (t, 2H), 3.33, (b, 1H), 2.54 (b, 1H).$^{13}C$ NMR: 178.79, 159.79, 137.69, 136.01, 129.35, 128.35, 126.79, 125.51, 122.47, 118.74, 105.94, 60.82, 56.55, 53.47, 19.03.

### *C. General Spectroscopic Methods*

All fluorescence spectra were recorded at room temperature (25 ºC). Test solutions were prepared by placing 50 μL of the probe stock solution (1 mM) and an appropriate aliquot of individual ions stock solution into a test tube and then diluting the solution with ethanol to 5 mL. For P1-2 fluorescent measurements, excitation and emission slit widths were 10/10 nm, and the excitation wavelength was 370 nm.

## III. RESULTS AND DISCUSSION

### *A. Fluorescence spectra of P1-2*

To validate the selectivity of P1 in practice, $Ag^{+}$, $Ca^{2+}$, $Mg^{2+}$, $Zn^{2+}$, $Pb^{2+}$, $Cu^{2+}$, $Hg^{2+}$, $Cd^{2+}$, $Cr^{3+}$, $Fe^{3+}$, $Al^{3+}$ were added to the solution of P1 (Fig.1a). The various metal ions did not induce any obvious fluorescent enhancement, and only $Al^{3+}$ caused the fluorescence change at 470 nm. For $Al^{3+}$, the $F/F_0$ value was almost 100-fold, while the values for other metal ions were less than 10-fold. The above experimental results suggested that P1 was an $Al^{3+}$-selective "off-on" probe, favored over those showing fluorescence quenching under metal ions binding in terms of sensitivity and selectivity concerns.[23-25] Compound P2 was very similar to P1 in structure except for the lack of a phenolic group. Fig.1b showed the fluorescence spectra of compound P2 under the same condition in the presence of above mentioned different metal ions. The emission of P2 peaked at 470 nm and had no response upon the addition of $Al^{3+}$ as found as compound P1.

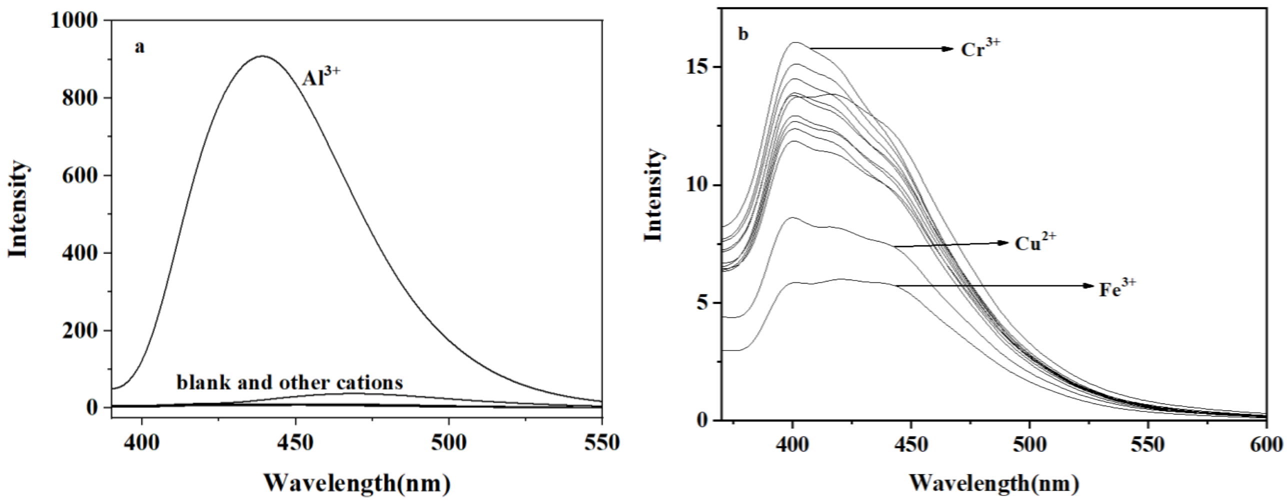



**Fig. 1 Effect of different metal ions (100 μM) ($Ag^{+}$, $Ca^{2+}$, $Mg^{2+}$, $Zn^{2+}$, $Pb^{2+}$, $Cu^{2+}$, $Hg^{2+}$, $Cd^{2+}$, $Cr^{3+}$, $Fe^{3+}$, $Al^{3+}$) on probe P1 (10 μM) in ethanol**

Finally, the fluorescence spectra of P1 in the presence of different concentrations of $Al^{3+}$ in ethanol were recorded (Fig. 2). A significant fluorescence intensity with an emission maximum at 470 nm increased in an $Al^{3+}$ concentration-dependent way. Furthermore, the $F$ was well proportional to the amount of $Al^{3+}$ (2-100 μM) with a good linear correlation ($R$=0.9900). The detection limit was 0.66 μM (based on S/N=3, inset of Fig. 2). The result showed that the probe P1 could detect both qualitatively and quantitatively $Al^{3+}$.

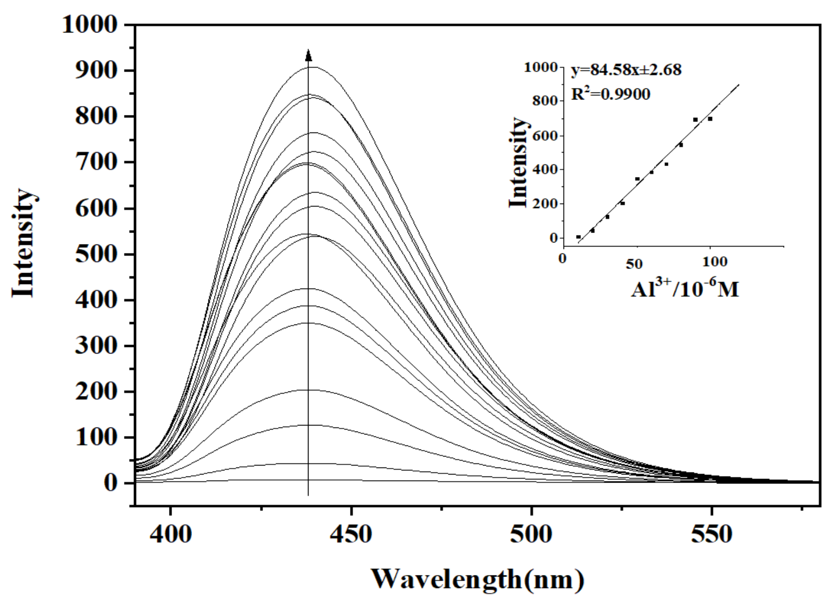



**Fig. 2 Effects of different concentrations of $Al^{3+}$ (0-100 μM) on the fluorescence spectra of probe P1 (10 μM) in ethanol. Inset: Linear fluorescence intensity (*F*) of P1 (10 μM) upon addition of $Al^{3+}$ (2−100 μM)**

### *B. Reversibility of P1*

The EDTA-adding experiments were conducted to examine the reversibility of this reaction (Fig. 3). The addition of EDTA to the solution containing P1 and $Al^{3+}$ led to the immediate disappearance of fluorescence (Fig. 3c), whereas the readdition of excess $Al^{3+}$ could recover the fluorescence signal (Fig. 3e). It was proved that probe P1 had certain reversibility, which laid a foundation for recycling in the later stage.

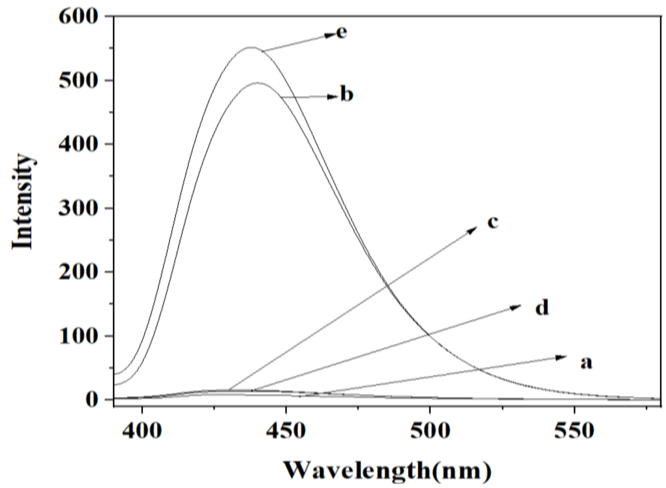



**Fig. 3 In ethanol, the reversibility of P1-$Al^{3+}$ system: a) P1 (10 μM); b) P1 (10 μM)+$Al^{3+}$ (10 μM); c) P1 (10 μM)+$Al^{3+}$ (10 μM) + EDTA (10 μM); d. P1 (10 μM) + $Al^{3+}$ (10 μM) + EDTA (100 mM); e) P1 (10 μM) +$Al^{3+}$ (10 μM) + EDTA (10 μM) + $Al^{3+}$ (100 μM)**

### *C. Proposed mechanism P1with $Al^{3+}$*

The continuous variations (Job's plot) method was obtained from the P1-$Al^{3+}$ system in ethanol (Fig. 4). When the ratio of [$Al^{3+}$]/[P1] was 0.5, the signal reached the maximum, which suggested the formation of 1:1 stoichiometry between P1 and $Al^{3+}$. Accordingly, the structure of the P1–$Al^{3+}$ complex was proposed, in which $Al^{3+}$ coordinated with phenolic hydroxyl and Schiff base.

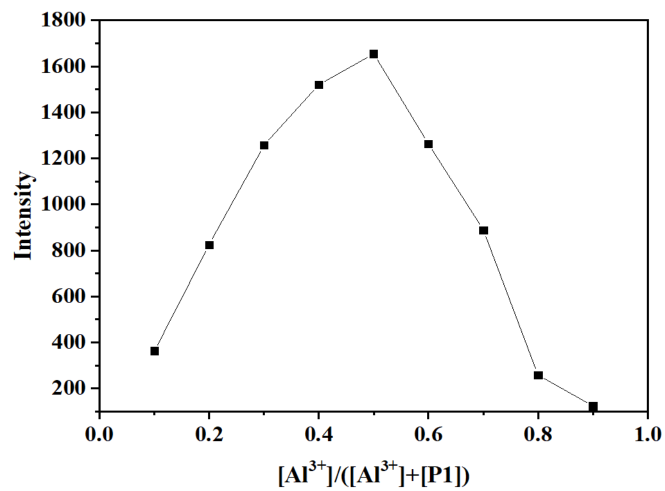



**Fig. 4 Job's plot for P1-$Al^{3+}$ complex. The total concentration of P1 and $Al^{3+}$ was maintained at 50 μM**

## IV. CONCLUSION

In summary, a new naphthalene derivative was developed as the selective and sensitive probe, which could specifically recognize $Al^{3+}$ fluorescent response. Furthermore, it also showed a "turn-on" type of fluorescence response.

## V. ACKNOWLEDGMENT

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