Research paper

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A novel Schiff-base fluorescent probe based on 1,8-naphthyridine and naphthalimide for Al^{3+}

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ABSTRACT

A novel Schiff-base, 7-acetamino-4-methyl-1,8-naphthyridine-2-carbaldehyde-(1',8'-naphthalenedicarbonyl) hydrazone **(HL)** was designed, synthesized and evaluated as a fluorescent probe. The fluorescence properties of this probe towards various metal ions were investigated by UV–vis and fluorescence spectra in methanol. Test results indicated that the probe had high selectivity towards Al^{3+} over other commonly coexisting metal ions. Upon addition of Al^{3+}, the fluorescence intensity at 414nm increased significantly due to the inhibition of the PET process. The binding constant (Ka) of Al^{3+} binding to **HL** was calculated to be 5.64×10^4 M^{-1} from a Benesi-Hildebrand plot, and the detection limit (LOD) of **HL** for sensing Al^{3+} was calculated to be 0.13 μM. The binding stoichiometry between **HL** and Al^{3+} was determined as 1∶ 1 by the Job's plot. Furthermore, the probe was chemically reversible for Al^{3+} in

methanol by the addition of Na_2EDTA solution.

KEYWORDS: Fluorescent probe; 1,8-Naphthyridine; Naphthalimide; Aluminum ion; Photo-induced electron transfer; Reversibility.

1. Introduction

Aluminum is the third most abundant metal element in the earth's crust , whose content is second only to oxygen and silicon [1-3]. Aluminum can be widely used in aluminum alloy, aircraft, automobiles, trains, ships and other manufacturing industries [4]. In addition, aluminum has a good ductility, so it is also extensively utilized in food packaging [5-10]. However, improper use of aluminum has some side effects on human health such as metabolic disturbance, cerebral injury, and even to the risk of Alzheimer's disease and Parkinson's disease [11-13]. Hence, the World Health Organization (WHO) stipulated that the daily human intake of aluminum should be controlled within 10 mg and a weekly tolerable dietary intake should be controlled at 7 mg · kg^{-1} of the body weight [14]. The WHO also limited the concentration of aluminum in drinking water to be 7.41 μM [15-17]. Additionally, high aluminum contents in plants may affect the growth of root and seed [18, 19]. As a result, it's essential to develop some analytical methods for detecting and monitoring Al^{3+} to maintain its concentration at a constant level.

In recent years, compared with the other traditional detection methods including AMS, AAS, GFAAS, ICP-AAS, and IC-AES, the fluorescent chemosensors have attracted significant interest due to their high sensitivity, good selectivity, short

response time, good reproducibility, operational simplicity and real-time monitoring [20-23]. However, the relatively poor coordination ability blocks the development of Al^{3+} chemosensors. As a hard acid, aluminum ion prefers to coordinate with hard bases such as N and O atoms [24-26]. Owing to the intriguing structures and bonding properties, 1,8-naphthyridine (napy) and its derivatives are widely used in the coordination chemistry, pharmaceutical and molecular recognition fields [27-29]. Therefore, 1,8-naphthyridine group could be used as a binding unit for developing a Al^{3+} fluorescent probe [30]. 1,8-Naphthalimide (Naph) and its derivatives have high fluorescence quantum yield, moderate fluorescence emission, large Stokes shift, perfect photostability and feasible structural modifications, so they can be widely utilized as fluorophores in the field of fluorescence sensing [31]. Thus, 1,8-Naphthalimide group could be also used as the fluorophore of a fluorescent probe [32].

Taking these factors into account, we designed and synthesized a simple fluorescent probe based on 1,8-naphthyridine and Naphthalimide, which was highly selective and responsive to Al^{3+}. The fluorescence intensity of **HL** exhibits significant enhancement upon the interaction of **HL** with Al^{3+} in methanol due to the inhibition of the PET process. The binding stoichiometry between **HL** and Al^{3+} (1：1) was studied by the Job's plot titration curve. The binding constant was calculated to be 5.64×10^{4} M^{-1} by the Benesi-Hildebrand plot. Additionally, the fluorescence probe showed a quite low detection limit (0.13 μM) of a micromolar concentration level. Significantly, the probe was chemically reversible in the presence of Na_2EDTA, which offered a potentiality for detecting Al^{3+} in environmental and biological system circularly and

reversibly.

2. Experimental section

2.1 . Materials and instruments

The materials used for this study were obtained from commercial suppliers and used without further purification. ^{1}H NMR spectra were measured on the JNM-ECS 400 MHz spectrometer. Chemical shifts are reported in ppm using TMS as an internal standard. ESI-MS were determined on a Bruker esquire 6000 spectrometer. UV–vis absorption spectra were measured with a Shimadzu UV-240 spectrophotometer. Fluorescence spectra were determined on a Hitachi RF-4500 spectrophotometer equipped with quartz cuvettes of 1 cm path length. The melting point was determined on a Beijing XT4-100x microscopic melting point apparatus.

2.2 . Synthesis

2.2.1. Synthesis of 7-amino-2,4-dimethyl-1,8-naphthyridine

7-Amino-2,4-dimethyl-1,8-naphthyridine was synthesized and purified from 2, 6-diaminopyridine according to a modified version of the literature procedure [33a,b].

2.2.2. Synthesis of 7-acetamino-2,4-dimethyl-1,8-naphthyridine

7-Acetamino-2,4-dimethyl-1,8-naphthyridine was synthesized from 7-amino-2,4-dimethyl-1,8-naphthyridine according to a modified version of the literature method [33c,d].

2.2.3. Synthesis of 7-acetamino-4-methyl-1,8-naphthyridine-2-carbaldehyde [34]

7-Acetamino-4-methyl-1,8-naphthyridine-2-carbaldehyde (4g, 0.0186mo) and selenium dioxide (3.2g, 0.0288mol) were added to 1,4-dioxane (200 ml), and the

reaction mixture was refluxed for 6h with stirring . The mixture was filtered while hot, and the crude product was obtained by concentration in vacuum. The final product was purified by column chromatography using 50：1 dichloromethane / ethanol as the eluent (0.58g). Yield: 29%; mp: 224-226 ℃. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) (Figure S1): δ_H 10.20 (m, 1H), 8.67 (d, 1H, J=8.8Hz), 8.46 (d, 1H, J=9.2Hz), 7.87(s, 1H), 2.80 (s, 3H), 2.32 (s, 3H).

2.2.4. Synthesis of N-aminonaphthalimide

Synthesis of N-aminonaphthalimide was synthesized from 1,8-naphthalicanhydride according to a modified version of the literature method [35]. Yield: 57%; mp: 262-264 ℃. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) (Figure S2): δ_H 8.63 (d, 2H, J=7.2Hz), 8.23 (d, 2H, J=8.4Hz), 7.77 (t, 2H, J=7.2Hz, J=8.4Hz), 5.54 (s, 2H, -NH_2).

2.2.5. Synthesis of 7-acetamino-4-methyl-1,8-naphthyridine-2-carbaldehyde-(1',8'-naphthalenedicarbonyl) hydrazone (HL)

The synthetic route of the probe **(HL)** was shown in Scheme 1. The solution of 7-acetamino-4-methyl-1,8-naphthyridine-2-carbaldehyde (0.2292 g, 1.0 mmol) in ethanol (20 ml) was added to another solution containing N-aminonaphthalimide (0.2546 g, 1.2 mmol) in ethanol (20 ml). The mixture was stirred and refluxed for 24 h. After the reaction was completed, an excess amount of solvent was removed under reduced pressure. Then the yellow solid was precipitated after cooling to room temperature and the solid was filtered, washing 5 times with ethanol. Then obtained product was then dried in vacuum. Yield: 54 %; mp: 259-260 ℃. ^{1}H NMR (400 MHz, DMSO-d_6, TMS) (Figure S3): δ_H 11.17 (s, 1H), 8.90 (s, 1H), 8.65 (d, J=9.2Hz, 1H),

8.57 (d, J=7.2Hz, 2H), 8.51-8.54 (m, 1H), 8.47 (d, J=7.2Hz, 2H), 8.20 (s, 1H), 7.93 (t, J=7.6Hz, 2H), 2.81 (s, 3H), 2.20 (s,3H). FT-IR (KBr, cm^{-1}) (Figure S4): 1692 (C=N). ESI-MS (Figure S8) calculated for $[M+H]^+$ 424.4382, found 424.1904.

2.3. UV-vis and fluorescence spectra measurements

Stock solutions of 1×10^{-3} M various metal ions and **HL** were prepared in ethanol and DMF, respectively. Additionally, the stock solution of Na_2EDTA was also prepared in ethanol. All absorption and emission spectra were performed in a quartz optical cell of 1 cm optical path length at room temperature. All fluorescence measurements were carried out upon excitation at 360 nm, and the emission was recorded from 370 to 600 nm. Both excitation and emission slit widths were 5 nm.

3. Results and discussion

The experimental emission spectra of **HL** after the addition of Al^{3+} in different solvents are shown in (Figure S5). It can be seen in Figure S5 that the fluorescence intensity of **HL** after the addition of Al^{3+} is the highest in methanol compared with that in other solvents. Thus, we choose methanol as the buffer solution to perform experiments.

3.1. UV-vis studies of HL towards Al^{3+}

The UV-vis absorption spectra of **HL** towards Al^{3+} were shown in Figure 1a. The absorbances at 318 nm, 333 nm, and 356 nm were gradually increased with the addition of Al^{3+} ion, while the absorbance at 385 nm was gradually decreased. Meanwhile, an isobestic point was observed at 380 nm. These changes which were compared to

the original absorbance demonstrated the formation of a stable complex between **HL** and Al^{3+} ion.

In addition, the UV-vis absorption spectra of **HL** towards various metal ions (Ag^{+}, Ca^{2+}, Co^{2+}, Cu^{2+}, Fe^{3+}, In^{3+}, Mg^{2+}, Na^{+}, Pb^{2+}, Ba^{2+}, Cd^{2+}, Cr^{3+}, Fe^{2+}, Ga^{3+}, K^{+}, Mn^{2+}, Ni^{2+}, Zn^{2+} and Al^{3+}) was also investigated as shown in Figure 1b. Upon the addition of Al^{3+} to the **HL** solution, the absorbances at 318 nm, 333 nm and 356 nm were increased, while the other cations did not give rise to the enhancement of these absorbances. These results suggest that **HL** as a fluorescence probe has high selectivity towards Al^{3+} over other commonly coexistent metal ions by UV-vis method.

3.2. Fluorescence studies of HL towards Al^{3+}

HL alone exhibited weak fluorescence emission with excited at 360 nm in methanol (Figure 2a). However, upon addition of Al^{3+}, the fluorescence intensity at 414 nm was enhanced remarkably. Under the identical conditions as used for Al^{3+}, no significant change of the fluorescence spectrum was observed in the presence of other cations except for Ni^{2+}, Fe^{3+} and Cd^{2+}, which resulted in small changes in fluorescence intensity compared with Al^{3+}. These results indicated that **HL** showed an efficient Al^{3+} selective OFF-ON fluorescent behavior.

To obtain more insight into the fluorescent properties of **HL** as a chemosensor for Al^{3+}, fluorescence titration experiments of **HL** towards increasing amounts of Al^{3+} were carried out (Figure 2b). The fluorescence intensity at 414 nm was gradually enhanced with the progressive addition of Al^{3+}. Furthermore, this probe showed a nice linear relationship between the fluorescence intensity (F/F_{min}) and the concentration of

Al^{3+} (Figure 2b, inset). Thus this fluorescent probe **HL** could detect Al^{3+} quantitatively.

3.3. Interference studies from other metal ions.

As we all know, high selectivity of a chemosensor for sensing the analytes in the presence of other species is one of the most important characterizations. To further confirm the selectivity of **HL** towards Al^{3+}, the fluorescence spectrum of **HL** towards Al^{3+} in the presence of other metal ions (*1 equiv.*) was also measured. It could be noted from Figure 3 that all the coexistent metal ions did not influence the emission intensity of **HL**-Al^{3+} obviously. These results demonstrate that **HL** displayed a high selectivity for Al^{3+} even in the presence of other metal ions.

3.4. Reversible test of HL towards Al^{3+} by Na_2EDTA

It's significant for a fluorescence probe to detect the analytes reversibly. To confirm the reversibility of **HL** towards Al^{3+}, we added *1 equiv of* Na_2EDTA to the solution of **HL** and Al^{3+}. It can be seen from Figure 4 that the fluorescence intensity at 414 nm decreased upon addition Na_2EDTA to the mixture, while the fluorescence of the system was recovered with addition of Al^{3+} again. These results illustrated that **HL** was a reversible fluorescent probe for detecting Al^{3+} in methanol.

3.5. Binding constant, stoichiometry and detection limit

The association constant of **HL** with Al^{3+} and the detection limit (LOD) of **HL** for sensing Al^{3+} were obtained from the fluorescence titration experiments. The association constant (Ka) of **HL** with Al^{3+} was determined by the Benesi-Hildebrand Eq. (1) [36]: $\frac{1}{F-F_{min}}=\frac{1}{K(F_{max}-F_{min})[Al^{3+}]}+\frac{1}{F_{max}-F_{min}}$ (1) where F is the fluorescence intensity at

414 nm at any given Al^{3+} concentration, F_{min} is the fluorescence intensity at 414 nm in the absence of Al^{3+}, and F_{max} is the maximum fluorescence intensity at 414 nm in the presence of Al^{3+}. The binding constant was calculated by plotting 1/ ($F-F_{min}$) against 1/ [Al^{3+}] (Figure S6). The data was linearly fitted well according to Eq. (1) and the association constant (Ka) value was $5.64\times10^4\ M^{-1}$. The detection limit for sensing Al^{3+} was calculated to be 0.13 μM by the Stern-Volmer plot [37] (Figure S7): DL＝3σ/K where σ is the standard deviation of the blank solution and K is the slope of the calibration curve. Additionally, the binding stoichiometry was determined by the Job's plot (Figure 5). As shown in Figure 5, the fluorescence emission intensity at 414 nm reached maximum when the molar fraction of **HL** in **HL**- Al^{3+} was 0.5, which gave a solid evidence for the formation of a 1∶ 1 complex between **HL** and Al^{3+}. To better understand the binding mode of **HL** towards Al^{3+}, the ESI mass spectra of **HL** in the presence of Al^{3+} was carried out (Figure S8). The m/z peak for **HL** in the presence of Al^{3+} at 573.2957 corresponding to [**HL**＋Al^{3+}＋$2NO_3^-$]$^+$. The result further confirm the 1∶1 binding stoichiometry between **HL** and Al^{3+}.

3.6. Proposed sensing mechanism of HL towards Al^{3+}

The proposed reaction mechanism of **HL** with Al^{3+} was illustrated in Scheme 2 based on the optical properties, Job's plot and the ^1H NMR titration experiments of **HL** towards Al^{3+}. The nitrogen atom (1,8-naphthyridine ring) could transfer an electron to the excited fluorophore (naphthalimide ring) to quench its fluorescence emission. Upon the addition of Al^{3+} to the **HL** solution, this nitrogen atom participates in the coordination process between **HL** and Al^{3+}. Thus the PET process was restrained and

the fluorescence emission intensity at 414 nm enhanced [38-42]. This sensing mechanism was further confirmed by the ^{1}H NMR titration experiments of **HL** towards Al^{3+} (Figure S9). Upon addition of Al^{3+}, the proton signals of H_a and H_b were shifted downfield by 0.032 ppm and 0.051 ppm respectively. Similarly, the proton signal of methyl hydrogen of the acetamide group was shifted downfield by 0.053 ppm. Additionally, the signals of protons of the aromatic rings were also shifted downfield. These changes demonstrated that the nitrogen atom of the 1,8-naphthyridine ring and the CN group as well as the oxygen atom of the carbonyl group might participate in the coordination of **HL** with Al^{3+}.

4. Conclusion

In conclusion, we have designed and synthesized a simple fluorescence probe based on 1,8-naphthyridine moiety and naphthalimide unit, which showed an high selectivity for Al^{3+} over other metal ions through the inhibition of the photo-induced electron transfer (PET) process. The binding ratio of **HL**-Al^{3+} complex was determined to be 1：1 according to the Job's plot and ^{1}H NMR titration experiments. In addition, this probe may have potential applications to detect micromolar concentrations of Al^{3+} in both biological assays and the environmental systems reversibly due to its low detection limit.

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List of Figure captions

Figure 1a. The UV-vis absorption titration spectra of **HL** (10μM) with Al^{3+} (0-1 equiv.) in methanol.

Figure 1b. Absorption spectra of **HL** before and after addition of 1 equiv. of various metal ions in methanol.

Figure 2a. Fluorescence spectra of **HL** (10μM) before and after addition of 1 equiv. of various metal ions of Ag^{+}, Ca^{2+}, Co^{2+}, Cu^{2+}, Fe^{3+}, In^{3+}, Mg^{2+}, Na^{+}, Pb^{2+}, Ba^{2+}, Cd^{2+}, Cr^{3+}, Fe^{2+}, Ga^{3+}, K^{+}, Mn^{2+}, Ni^{2+}, Zn^{2+} and Al^{3+} in methanol.

Figure 2b. Fluorescence emission titration spectra of **HL** (10μM) upon addition of Al^{3+}(0-1 equiv.) in methanol. Inset: Linear fluorescence intensity (F/F_{min}) of **HL** upon addition of Al^{3+}.

Figure 3. Fluorescence response of **HL** and **HL**+Al^{3+} upon the addition of various metal ions in methanol. The black bars represent the fluorescence intensities of **HL** in the presence of various metal ions. The red bars represent the changes in the fluorescence intensities that occur upon the subsequent addition of 1 equiv. of Al^{3+} to the **HL**-metal cation solutions.

Figure 4. The reversibility of **HL** towards Al^{3+} in methanol.

Figure 5. Job plot of **HL** with Al^{3+} at 414 nm in methanol. The total concentration of **HL** and Al^{3+} is 1.0×10^{-5} mol/L.

Scheme 1. The synthetic route of 7-acetamino-4-methyl-1,8-naphthyridine -2-carbal-dehyde-(1’,8’-naphthalenedicarbonyl) hydrazone **(HL)**.

Scheme 2. The proposed sensing mechanism of **HL** towards Al^{3+}.

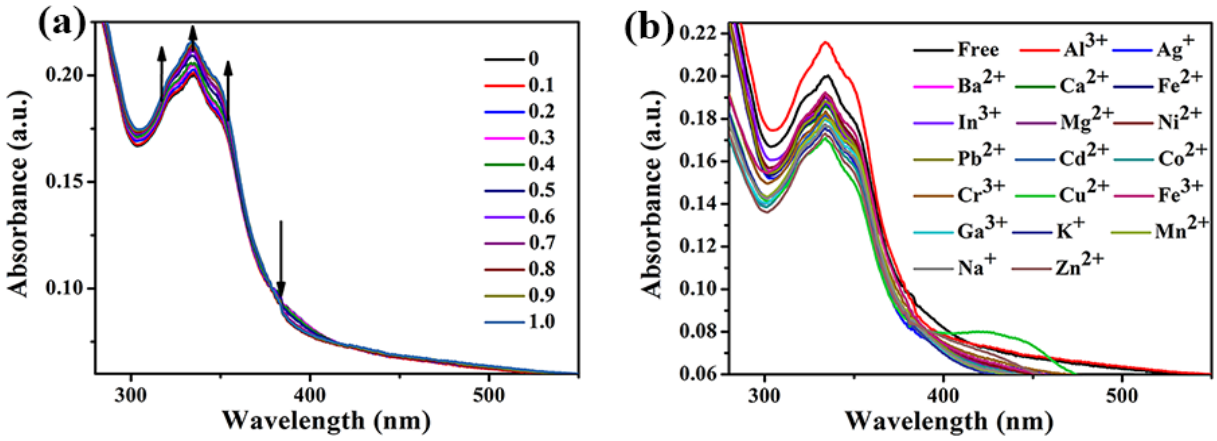


Figure 1a. The UV-vis absorption titration spectra of **HL** (10μM) with Al^{3+} (0-1 equiv.) in methanol. **Figure 1b.** Absorption spectra of **HL** before and after addition of 1 equiv. of various metal ions in methanol.

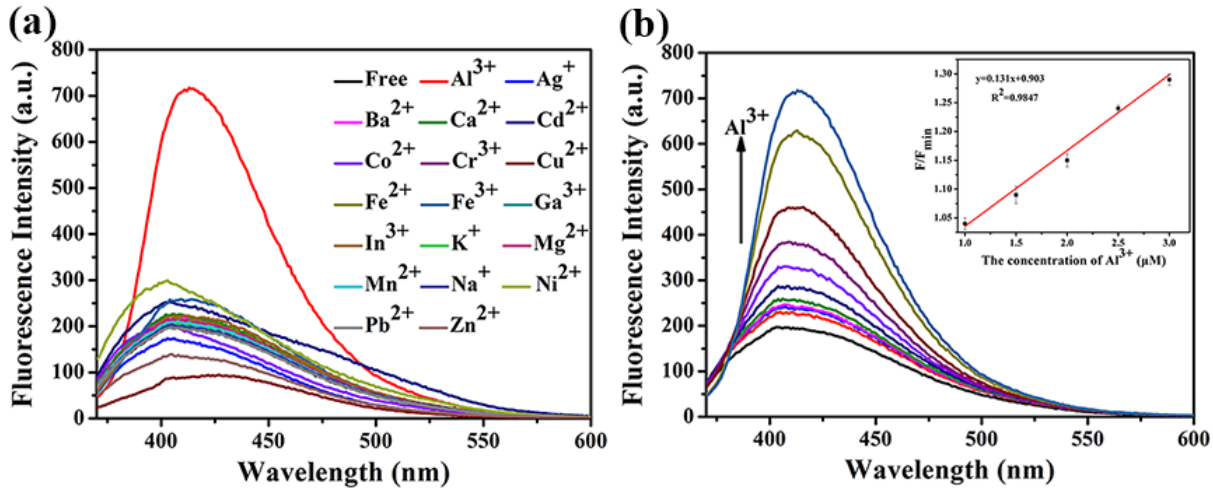


Figure 2a. Fluorescence spectra of **HL** (10μM) before and after addition of 1 equiv. of various metal ions of Ag^{+}, Ca^{2+}, Co^{2+}, Cu^{2+}, Fe^{3+}, In^{3+}, Mg^{2+}, Na^{+}, Pb^{2+}, Ba^{2+}, Cd^{2+}, Cr^{3+}, Fe^{2+}, Ga^{3+}, K^{+}, Mn^{2+}, Ni^{2+}, Zn^{2+} and Al^{3+} in methanol. **Figure 2b.** Fluorescence emission titration spectra of **HL** (10μM) upon addition of Al^{3+}(0-1 equiv.) in methanol. Inset: Linear fluorescence intensity (F/F_{min}) of **HL** upon addition of Al^{3+}.

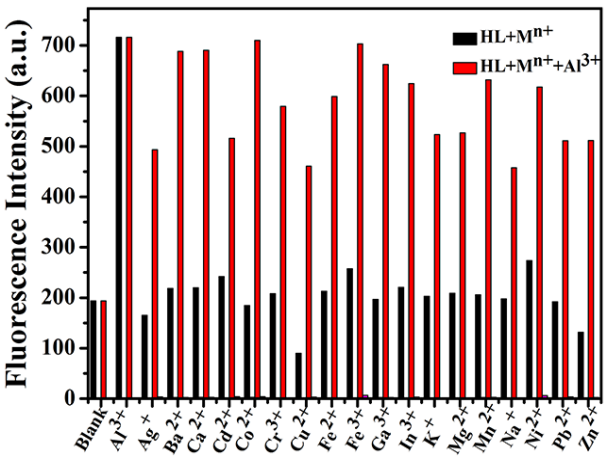


Figure 3. Fluorescence response of **HL** and **HL**+Al^{3+} upon the addition of various metal ions in methanol. The black bars represent the fluorescence intensities of **HL** in the presence of various metal ions. The red bars represent the changes in the fluorescence intensities that occur upon the subsequent addition of 1 equiv. of Al^{3+} to the **HL**-metal cation solutions.

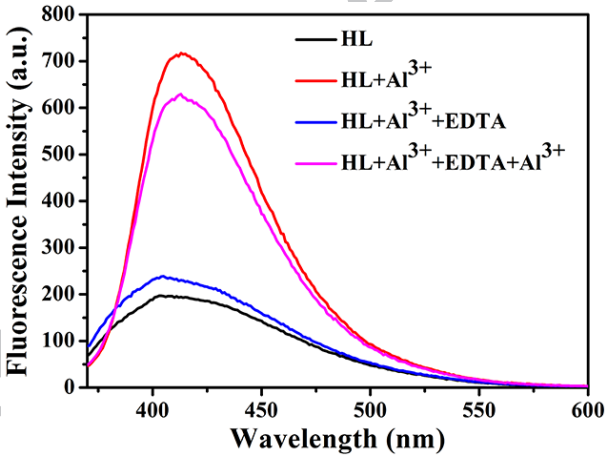


Figure 4. The reversibility of **HL** towards Al^{3+} in methanol.

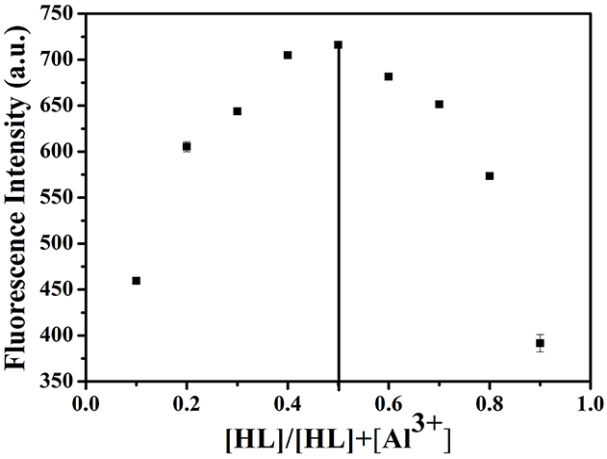
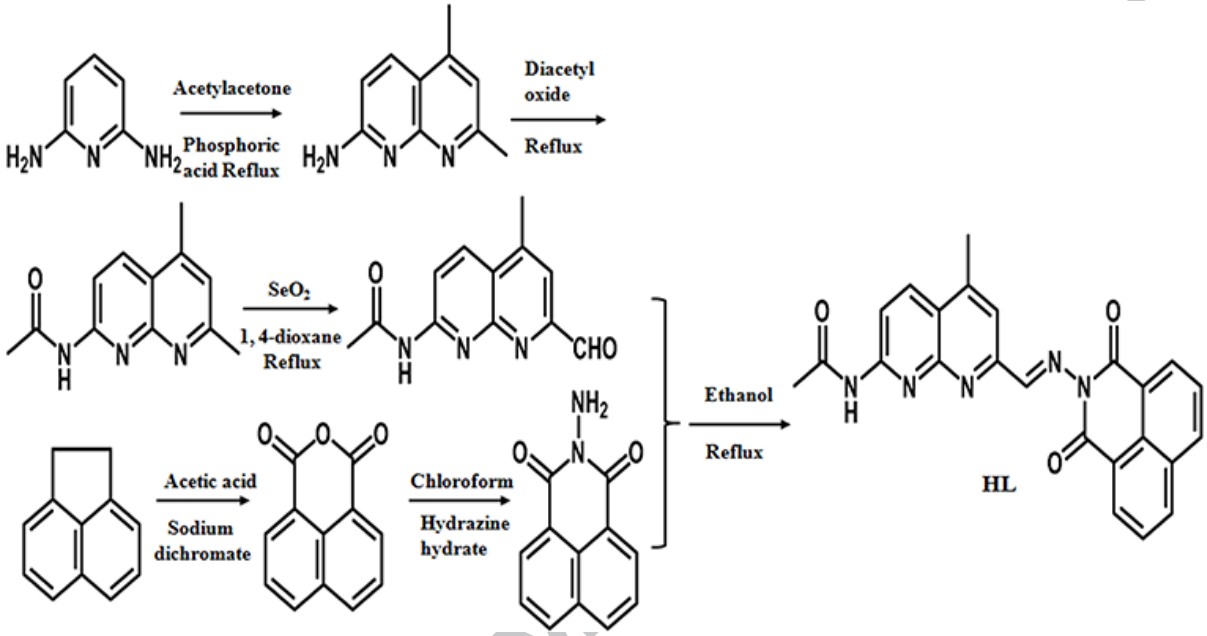
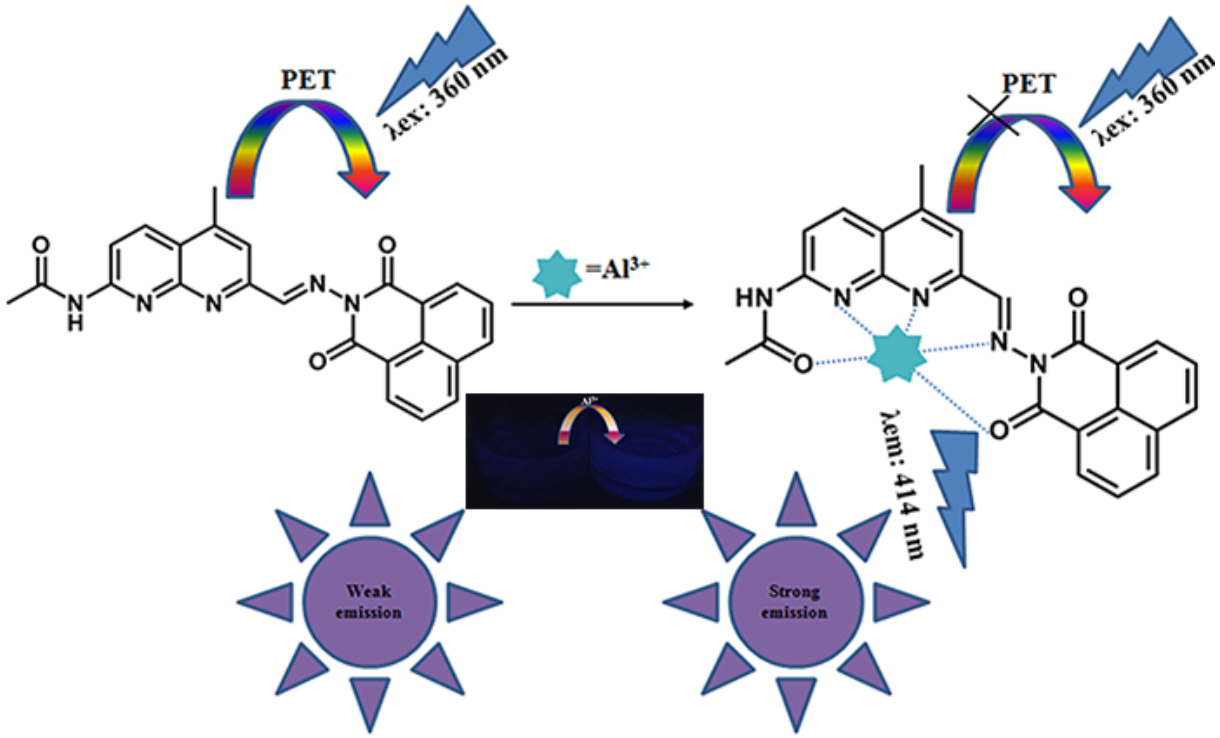


Figure 5. Job plot of **HL** with Al^{3+} at 414 nm in methanol. The total concentration of **HL** and Al^{3+} is 1.0×10^{-5} mol/L.



Scheme 1. The synthetic route of 7-acetamino-4-methyl-1,8-naphthyridine -2-carbal-dehyde-(1',8'-naphthalenedicarbonyl) hydrazone **(HL)**.



Scheme 2. The proposed sensing mechanism of **HL** towards Al^{3+}.

Highlights

- A novel fluorescent probe based on 1,8-naphthyridine and naphthalimide was designed and synthesized.
- The probe exhibited high selectivity towards Al^{3+} over commonly coexistent metal ions.
- The probe was chemically reversible in the presence of Na_2EDTA.
- The proposed binding mechanism between HL and Al^{3+} was investigated in detail.