Novel pyrazine derivative as "turn on" fluorescent sensor for the highly selective and sensitive detection of Al^{3+}

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Abstract

In this study, a novel pyrazine-derived fluorescent sensor bearing the furan unit (**1**) has been designed, synthesized and characterized. This sensor **1** showed large enhancement in fluorescence emission intensity at 517 nm in the presence of Al^{3+} and it also showed high selectivity and sensitivity for Al^{3+} over other common environmentally and biologically important metal ions, for the detection limit of **1** towards Al^{3+} could reach at 10^{-7} mol/L. Moreover, the enhancement of fluorescence emission intensity was attributed to the chelation-enhanced fluorescence (CHEF) phenomenon upon complexation of **1** with Al^{3+}.

1 Introduction

Compared with other traditional analytical methods, including ion selective electrodes [1], voltammetric methods [2] and colorimetric sensors [3], the development of fluorescent sensors for the sensing and recognition of environmentally and biologically important metal ions have attracted considerable attention of current researchers, due to their simplicity, high sensitivity, good selectivity and rapid response time [4-8]. Among all the common metal ions, Al^{3+} is of great importance in the biological and physical systems [9-10]. Aluminum is well known as the third most abundant element in the earth's crust and has broad applications in modern life, such as packing materials, clinical drugs, food additives and water purification [11-14]. Aluminum itself and its ionic state are widely distributed in the air, water and soil, and can accumulate in human body [15-16]. Al^{3+} is an indispensable metal ion in human body but can cause damage when it is exposed to high concentration levels [17-18]. The excessive Al^{3+} can damage the central nervous system and immune system of human body [19-20], resulting in many human illnesses, such as dementia, encephalopathy, Alzheimer's disease, Parkinson's disease, osteomalacia and breast cancer [21-25]. Moreover, high concentration of Al^{3+} in ecosystem can affect the growth of plant roots and freshwater fishes, causing product reduction [26-27]. Thus, it is of great significance to design and synthesize fluorescent sensors for detecting and monitoring Al^{3+} in environmental and biological samples [28].

There have been only a few reports about the development of fluorescent sensors for the detection and recognition of Al^{3+}, because of the poor coordination ability of Al^{3+} compared to transition metal ions [29]. S. L. Hu et al. reported a simple pyrazoline-based fluorescent sensor that displayed fluorescence quenching behavior with high selectivity for Al^{3+} in aqueous solution [30]. A sensor based on a dibenzo-18-crown-6-derivative which showed colorimetric and fluorometric dual-signaling responses for Al^{3+} based on internal charge transfer (ICT) mechanism was designed and synthesized by Y. P. Li et al [31]. T. H. Ma et al. described a novel dual-channel fluorescent sensor with a single chromophore for Al^{3+} [32]. Y. Lu et al. developed a photoinduced electron transfer (PET)-based fluorescent sensor which possessed dual PET processes by simultaneously introducing both nitrogen and sulfur donors [33], and a rhodamine-azacrown derivative which was selectively responded to Al^{3+} in acetonitrile was discussed by X. X. Fang et al [34]. Therefore, it is of great challenge to develop Al^{3+} selective and sensitive fluorescent sensors [35-39].

Keeping these in mind, we have designed and synthesized a novel pyrazine-derived hydrazone Schiff-base ligand called 2-Acetylpyrazine (2'-furan formyl) hydrazone (**1**) through a three-step reaction (Scheme 1). From the experimental process, it was evident that this compound **1** had good selectivity and high sensitivity for Al^{3+} over a wide range of other environmentally and biologically important metal ions investigated, and the remarkable enhancement in fluorescence emission intensity at 517 nm in the presence of Al^{3+} was observed in ethanol. Furthermore, this compound **1** could respond Al^{3+} in a reversible manner, which developed it for practical application. Therefore, this compound **1** could be used as a fluorescent sensor to detect and recognize Al^{3+} in ethanol.

2 Experimental

2.1 Materials

2-furan formic acid, hydrazine hydrate, acetyl pyrazine, hydrogen peroxide, concentrated sulfuric acid, absolute ethanol and salts of Al^{3+}, Ba^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, K^{+}, Mg^{2+}, Mn^{2+}, Na^{+}, Ni^{2+}, Pb^{2+} and Zn^{2+} were obtained from commercial suppliers and used without further purification. Stock solution of compound **1** (10 mM) was prepared in absolute ethanol. Stock solutions (10 mM) of the salts of Al^{3+}, Ba^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, K^{+}, Mg^{2+}, Mn^{2+}, Na^{+}, Ni^{2+}, Pb^{2+} and Zn^{2+} in absolute ethanol were also prepared. Distilled water was used throughout all experiments.

2.2 Methods

^{1}H NMR spectra were measured on the JNM-ECS 400MHz instruments using TMS as an internal standard in DMSO-d_6. The ESI-MS data were obtained in ethanol from a Bruke Esquire 6000 spectrometer. UV-vis absorption spectra were recorded on a Perkin Elmer Lamda 35 UV-vis spectrophotometer in ethanol medium at 298 K. Fluorescence emission spectra were generated on a Hitachi RF-4500 spectrophotometer equipped with quartz cuvettes of 1 cm path length. Melting points were determined on a Beijing X-4 microscopic melting point apparatus without correction.

2.3 Synthesize of compound 1 (2-Acetylpyrazine (2’-furan formyl) hydrazone)

Ethyl 2-furan formate (**2**) and 2-furan formylhydrazine (**3**) were prepared by the reported method [40]. A solution of acetyl pyrazine (0.750 g, 5.952 mmol) in absolute ethanol (10 mL) was added to a solution containing 2-furan formylhydrazine (0.726 g, 5.952 mmol) in absolute ethanol (30 mL). The mixture was stirred and refluxed for 19 h, and the obtained light green solution was then cooled to room temperature. Then the light green product was filtered, washing five times with absolute ethanol (10 mL). The obtained crude product was recrystallized from absolute ethanol to afford the desired product **1** as a light green powder (0.68 g, 49.67 %) (Scheme 1). m.p. 196-197 □, ^{1}H NMR (400 MHz, DMSO-d$_6$) (Fig. S1) 10.93 (s, 1H, -NH-), 9.22 (s, 1H, H$_4$), 8.70-8.64 (m, 2H, H$_{5,6}$), 7.99 (d, 1H, J = 1.6 Hz, H$_1$), 7.44 (d, 1H, J = 3.2 Hz, H$_3$), 6.74 (dd, 1H, J = 3.2 Hz, 1.6 Hz, H$_2$), 2.44 (s, 3H, -CH$_3$). MS (ESI) (Fig. S2) m/z 231.0743 $[M + H^+]^+$, 253.0558 $[M + Na^+]^+$, 483.1249 $[2M + H^+]^+$.

2.4 Analysis

Test solutions were prepared by placing 10 μL of the probe stock solution into cuvettes, adding an appropriate aliquot of each metal ion stock, and diluting the solution to 2 mL with ethanol. For all fluorescence measurements, excitation wavelength was at 382 nm, and the excitation and emission slit width were both 3.0 nm.

The binding constant values were determined from the emission intensity data following the modified Benesi–Hildebrand equations (1) [41]:

$$\frac{1}{F - F_{\min}} = \frac{1}{K(F_{\max} - F_{\min})[Al^{3+}]} + \frac{1}{F_{\max} - F_{\min}} \qquad (1)$$

where F$_{\min}$, F, and F$_{\max}$ are the emission intensities of the organic moiety considered in the absence of aluminum ion, at an intermediate aluminum concentration, and at a concentration of complete interaction, respectively, and where *K* is the binding constant concentration.

3 Results and discussion

3.1 UV-vis titration of compound 1 with Al^{3+}

We first investigated the UV-vis spectra of compound **1** towards the increasing concentration of Al^{3+} in ethanol. As shown in Fig. 1, the intense absorption band centered at 306 nm with a shoulder at 382 nm was observed in the UV-vis spectra of compound **1** in ethanol, which was attributed to the absorption band of pyrazine. However, the addition of Al^{3+} to the ethanol solution of **1** caused decrease in absorption intensity at 306 nm and a new band centered at 382 nm with increasing intensity was observed, resulting in two isosbestic points at 237 nm and 336 nm, which indicated that a stable complex was formed between **1** and Al^{3+} during the titration (Fig. 1). From the results above, we could conclude that the pyrazine unit in compound **1** participated in the coordination with Al^{3+}.

3.2 Fluorescence responses of compound 1 towards various metal ions

In order to explore the selectivity of compound **1** for Al^{3+} over a variety of environmentally and biologically important metal ions, the fluorescence responses of **1** towards various metal ions (Al^{3+}, Ba^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, K^+, Mg^{2+}, Mn^{2+}, Na^+, Ni^{2+}, Pb^{2+}, Zn^{2+}) were discussed in ethanol. As can be seen from Fig. 2, compound **1** in the absence of any metal ion displayed nearly no fluorescence emission in the range of 410-680 nm. However, when Al^{3+} was added to the solution of **1**, the fluorescence emission intensity at 517 nm enhanced significantly, and there were almost no change in the fluorescence emission spectrum upon addition of other metal ions investigated under identical conditions (Fig. 2). These results indicated that this compound **1** had high selectivity for Al^{3+} over other environmentally and biologically important metal ions in ethanol.

3.3 Selectivity of compound 1 for Al^{3+} in the presence of other metal ions

To obtain insight into the selectivity of compound **1** towards Al^{3+}, competition experiments were carried out in ethanol by measuring the fluorescence responses at 517 nm of compound **1** to Al^{3+} in the presence of other environmentally and biologically important metal ions. As illustrated in Fig. 3, when Cu^{2+} and Fe^{2+} were added to the mixture of compound **1** and Al^{3+}, the fluorescence emission intensity at 517 nm was remarkably quenched. Nevertheless, Co^{2+}, Fe^{3+}, Ni^{2+} and Zn^{2+} made the fluorescence intensity at 517 nm quenched slightly but it was relatively detectable. However, other metal ions investigated had nearly no influence on the sensing ability of compound **1** for Al^{3+} (Fig. 3). These results proved that the selectivity was high for compound **1** towards Al^{3+} in the presence of most environmentally and biologically important metal ions.

3.4 Fluorescence titration of compound 1 with Al^{3+}

The change in fluorescence emission spectrum of compound **1** upon addition of various concentration of Al^{3+} in ethanol was shown in Fig. 4. Upon excitation at 382 nm, there were almost no fluorescence emission in the range of 410-680 nm in the solution of free **1**. It was probably due to the photoinduced electron-transfer (PET) phenomenon from the Schiff-base nitrogen atom to pyrazine with no chelation-enhanced fluorescence (CHEF) effect that quenched the fluorescence emission of **1**. Nevertheless, upon addition of increasing concentration of Al^{3+}, the fluorescence emission intensity at 517 nm enhanced gradually without any change in emission wavelength (Fig. 4). We hypothesized that the complexation of compound **1** and Al^{3+} made highly efficient CHEF effect occurred from the Schiff-base nitrogen atom to pyrazine [42-44] (Scheme 2). As a result, the fluorescence emission intensity at 517 nm enhanced by about 164-fold in the presence of 1 *equiv.* of Al^{3+} (Fig. S3). Additional, the binding constant (K) of compound **1** with Al^{3+} was measured as 2.36×10^{7} M^{-1} from fluorescence titration fitting curve using the Benesi–Hildebrand equation (1) (Fig. S4), and it was within the range 10^{3}–10^{9} M^{-1} of those reported Al^{3+} selective sensors [45-48]. The detection limit of compound **1** for Al^{3+} was also estimated to be 10^{-7} M level which was conducted by using fluorescence titration spectrum (Fig. S5). From these results above, it was concluded that compound **1** could be used as a fluorescent sensor with high selectivity and sensitivity for Al^{3+} over other environmentally and biologically important metal ions, for the detection limit was sufficiently low for this sensor **1** to monitor and control Al^{3+} in environmental and biological systems.

3.5 The reversibility and regeneration of the binding of Al^{3+} by 1

Then the reversibility and regeneration of compound **1** were tested by adding $EDTANa_2$ into a mixture of **1** and Al^{3+} in ethanol. As can be seen from Fig. 5, upon addition of $EDTANa_2$, the fluorescence emission intensity at 517 nm decreased significantly. It was evident that $EDTANa_2$ was a good chelating agent with Al^{3+}, and the bound Al^{3+} of compound **1** could be removed upon complexation of $EDTANa_2$ with Al^{3+}, so the compound **1** was free from **1**-Al^{3+} solution. However, when the excessive Al^{3+} was added to the solution above, the recovered fluorescence emission was observed again, and the fluorescence emission spectrum was almost identical to that of **1**-Al^{3+} solution (Fig. 5). These results clearly demonstrated that the reversibility and regeneration of compound **1** for Al^{3+} were perfect, which could develop **1** for practical application.

3.6 Binding stoichiometry between compound 1 and Al^{3+}

To determine the stoichiometry of compound **1** with Al^{3+} in the complex, a Job's plot was conducted by using fluorescence emission intensity at 517 nm as a function of molar fraction of Al^{3+}. As depicted in Fig. 6, the maximum fluorescence value was achieved when the molar fraction of Al^{3+} reached 0.5, which suggested that a 1□1 complex was formed between compound **1** and Al^{3+} in ethanol (Fig. 6). Moreover, two peaks at 292.9729 ($[\mathbf{1} + Al^{3+} + 2H_2O]^{3+}$) and 372.8739 ($[\mathbf{1} + Al^{3+} + CH_3CH_2OH + 4H_2O - 2H^+]^+$) from the electrospray ionization mass spectra (ESI-MS) of complex **1**-Al^{3+} gave another reliable proof of the 1:1 binding stoichiometry of **1** with Al^{3+} (Fig. S6).

Finally, we explored ^1H NMR titration experiments to further demonstrate the proposed binding mode of compound **1** towards Al^{3+} (Fig. S7, Fig. S8). The addition of 1.0 *equiv.* of Al^{3+} into compound **1** in DMSO-d_6 made the proton signal of the imino group (at δ 10.931 ppm) decrease and broaden, shifting up-field slightly to δ

10.902 ppm. Simultaneously, the signal of the third proton H_3 of the furan group (at δ 9.219 ppm) was slightly up-field to δ 9.213 ppm, and the proton signals of the pyrazine group were slightly down-field shifted, while almost no change were observed in the signals of other protons in compound **1** (Fig. S7). Furthermore, when the amount of Al^{3+} reached 2.0 *equiv.*, there were almost no further change in the signals of all the protons in compound **1** (Fig. S8), which proved the 1:1 binding stoichiometry of **1** with Al^{3+}. From the results above, it could be concluded that the oxygen atom of the carbonyl group, the nitrogen atom of the Schiff-base and one nitrogen atom of the pyrazine group in compound **1** simultaneously participated in the coordination with Al^{3+} (Scheme 2), which was in accordance with the UV-vis analysis.

4 Conclusion

In conclusion, a novel pyrazine-derived fluorescent sensor **1** bearing the furan unit has been designed and synthesized through a three-step reaction. It was evident that this sensor **1** showed remarkable enhancement in fluorescence emission intensity at 517 nm in the presence of Al^{3+} with high selectivity and sensitivity over other environmentally and biologically important metal ions, and it could respond Al^{3+} in a reversible manner which developed **1** for practical application. The binding constant of this sensor **1** with Al^{3+} and the detection limit of **1** for Al^{3+} were calculated from fluorescence titration spectrum. The 1:1 stoichiometry between **1** and Al^{3+} was also conducted from Job's plot and electrospray ionization mass spectrometry (ESI-MS). In addition, the binding mode of **1** towards Al^{3+} was obtained by ^1H NMR titration experiments. Therefore, this sensor **1** could be utilized as a fluorescent chemosensor for Al^{3+} and might accelerate the development of other novel pyrazine-based sensors.

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References

1 J. D. R. Thomas, G. J. Moody, T. H. Ryan, B. Fleet, M. Whitfield, K. Garbett and A. Craggs, *Proc. Anal. Div. Chem. Soc.*, 1975, 12, 48-64.

2 L. K. Mudashiru, A. C. Aplin and B. R. Horrocks, *Anal. Methods.*, 2011, 3, 927-936.

3 X. Q. Wang, Y. Si, X. Mao, Y. Li, J. Y. Yu, H. P. Wang and B. Ding, *Analyst.*, 2013, 138, 5129-5136.

4 M. L. Zhao, L. G. Ma, M. Zhang, W. G. Cao, L. T. Yang and L. J. Ma, *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.*, 2013, 116, 460-465.

5 L. Y. Yang, Q. Song, K. Damit-Og and H. S. Cao, *Sensor. Actuat. B-Chem.*, 2013, 176, 181-185.

6 Z. P. Dong, Y. P. Guo, X. Tian and J. T. Ma, *J. Lumin.*, 2013, 134, 635-639.

7 D. Y. Liu, J. Qi, X. Y. Liu, Z. G. Cui, H. X. Chang, J. T. Chen, H. R. He and G. M. Yang, *Anal. Methods.*, 2014, 6, 3578-3581.

8 S. B. Maity and P. K. Bharadwaj, *J. Lumin.*, 2014, 155, 21-26.

9 R. J. P. Williams, *Coord. Chem. Rev.*, 1996, 149, 1-9.

10 J. I. Mujika, E. Rezabal, J. M. Mercero, F. Ruiperez, D. Costa, J. M. Ugalde and X. Lopez, *Comput. Struct. Biotechnol. J.*, 2014, 9, 1-13.

11 D. Bohrer, P. C. D. Nascimento, R. Binotto and E. Becker, *J. Trace Elem. Med. Biol.*, 2003, 17, 107-115.

12 K. Sakhaee, C. L. Wabner, J. E. Zerwekh, J. B. Copley, L. Pak, J. R. Poindexter and C. Y. C. Pak, *J. Bone. Miner. Metab.*, 1993, 20, 87-97.

13 R. A. Yokel, C. L. Hicks and R. L. Florence, *Food. Chem. Toxicol.*, 2008, 46, 2261-2266.

14 Z. L. Yang, B. Gao, Y. Wang, Y. Q. Zhao and Q. Y. Yue, *J. Environ. Sci.*, 2012, 24, 1908-1916.

15 K. Woodburn, R. Walton, C. Mccrohan and K. White, *Aquat. Toxicol.*, 2011, 105, 535-542.

16 P. J. Oberholster, J. G. Myburgh, P. J. Ashton, J. J. Coetzee and A. M. Botha, *Ecotoxicol. Environ. Saf.*, 2012, 75, 134-141.

17 L. F. Zhang, C. H. Jin, X. B. Lu, J. H. Yang, S. W. Wu, Q. F. Liu, R. Chen, C. Y. Bai, D. Zhang, L. L. Zheng, Y. Q. Du and Y. Cai, *Toxicol.*, 2014, 323, 95-108.

18 R. Ding and Y. J. Yang, *Brain. Res.*, 2010, 1324, 96-102.

19 N. A. Muma and S. M. Singer, *Neurotoxicol. Teratol.*, 1996, 18, 679-690.

20 Y. Z. Zhu, Y. F. Li, L. G. Miao, Y. P. Wang, Y. H. Liu, X. J. Yan, X. Z. Cui and H. T. Li, *Chemosphere.*, 2014, 104, 1-6.

21 W. F. Forbes, J. F. Gentleman and C. J. Maxwell, *Exp. Gerontol.*, 1995, 30, 23-32.

22 A. I. Arieff, *Am. J. Kidney. Dis.*, 1985, 6, 317-321.

23 A. B. Graves, E. White, T. D. Koepsell, B. V. Reifler, G. V. Belle and E. B. Larson, *J. Clin. Epidemiol.*, 1990, 43, 35-44.

24 P. F. Good, C. W. Olanow and D. P. Perl, *Brain. Res.*, 1992, 593, 343-346.

25 P. D. Darbre, F. Mannello and C. Exley, *J. Inorg. Biochem.*, 2013, 128, 257-261.

26 S. Choudhury and P. Sharma, *Plant. Physiol. Biochemistry.*, 2014, 85, 63-70.

27 M. M. P. Camargo, M. N. Fernandes and C. B. R. Martinez, *Aquat. Toxicol.*, 2009, 94, 40-46.

28 Z. C. Liu, Y. X. Li, Y. J. Ding, Z. Y. Yang, B. D. Wang, Y. Li, T. R. Li, W. Luo, W. P. Zhu, J. P. Xie and C. J. Wang, *Sensor. Actuat. B-Chem.*, 2014, 197, 200-205.

29 T. Kiss, *J. Inorg. Biochem.*, 2013, 128, 156-163.

30 S. L. Hu, J. J. Song, G. Y. Wu, C. X. Cheng and Q. Gao, *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.*, 2015, 136, 1188-1194.

31 Y. P. Li, X. M. Liu, Y. H. Zhang and Z. Chang, *Inorg. Chem. Commun.*, 2013, 33, 6-9.

32 T. H. Ma, M. Dong, Y. M. Dong, Y. W. Wang and Y. Peng, *Chem. Eur. J.*, 2010, 16, 10313-10318.

33 Y. Lu, S. S. Huang, Y. Y. Liu, S. He, L. C. Zhao and X. S. Zeng, *Org. Lett.*, 2011, 13, 5274-5277.

34 X. X. Fang, S. F. Zhang, G. Y. Zhao, W. W. Zhang, J. W. Xu, A. M. Ren, C. Q. Wu and W. Yang, *Dyes. Pigments.*, 2014, 101, 58-66.

35 V. K. Gupta, A. K. Singh and L. K. Kumawat, *Sensor. Actuat. B-Chem.*, 2014, 195, 98-108.

36 O. Alici and S. Erdemir, *Sensor. Actuat. B-Chem.*, 2015, 208, 159-163.

37 X. K. Li, J. Wang, L. L. Sun and Z. X. Wang, *Chem. Commun.*, 2010, 46, 988-990.

38 M. Zhang, Y. Q. Liu and B. C. Ye, *Chem. Eur. J.*, 2012, 18, 2507-2513.

39 S. Chen, Y. M. Fang, Q. Xiao, J. Li, S. B. Li, H. J. Chen, J. J. Sun and H. H. Yang, *Analyst.*, 2012, 137, 2021-2023.

40 S. T. Wang, G. Ge, S. F. Guo, Y. Ma, F. C. Qiu, X. Y. Jian and R. F. Chen, *Chinese Journal of Pharmaceuticals.*, 1991, 22, 396-397.

41 V. K. Indirapriyadharshini, P. Karunanithi and P. Ramamurthy, *Langmuir.*, 2001, 17, 4056-4060.

42 J. B. Wang and X. H. Qian, *Org. Lett.*, 2006, 8, 3721-3724.

43 X. Zhang, Y. B. Wu, S. M. Ji, H. M. Guo, P. Song, K. L. Han, W. T. Wu, W. H. Wu, T. D. James and J. Z. Zhao, *J. Org. Chem.*, 2010, 75, 2578-2588.

44 T. Y. Cheng, Y. F. Xu, S. Y. Zhang, W. P. Zhu, X. H. Qian and L. P. Duan, *J. Am. Chem. Soc.*, 2008, 130, 16160-16161.

45 Y. G. Zhang, Z. H. Shi, L. Z. Yang, X. L. Tang, Y. Q. An, Z. H. Ju and W. S. Liu, *Inorg. Chem. Commun.*, 2014, 39, 86-89.

46 D. Zhou, C. Y. Sun, C. Chen, X. N. Cui and W. J. Li, *J. Mol. Struct.*, 2015, 1079, 315-320.

47 K. Velmurugan, S. Mathankumar, S. Santoshkumar, S. Amudha and R.

Nandhakumar, *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.*, 2015, 139, 119-123.

48 X. P. Ye, S. B. Sun, Y. D. Li, L. H. Zhi, W. N. Wu and Y. Wang, *J. Lumin.*, 2014, 155, 180-184.

Figure Captions

Fig. 1 Change in UV-vis absorption of compound **1** (100 μM) measured in ethanol upon addition of various concentration of Al^{3+} (0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.2, 2.4, 2.6, 2.8, 3.0, 3.4, 3.8, 4.2, 4.6, 5.0 *equiv.*, respectively).

Fig. 2 Fluorescence spectra of **1** (50 μM) upon addition of Al^{3+} (1 *equiv.*) and other metal ions (5 *equiv.*) in ethanol with an excitation at 382 nm.

Fig. 3 The fluorescence intensity at 517 nm of **1** (50 μM) with Al^{3+} (1 *equiv.*) in the presence of various metal ions (5 *equiv.*) under the same conditions in ethanol. ((1) Al^{3+}; (2) $Al^{3+} + Ba^{2+}$; (3) $Al^{3+} + Ca^{2+}$; (4) $Al^{3+} + Cd^{2+}$; (5) $Al^{3+} + Co^{2+}$; (6) $Al^{3+} + Cr^{3+}$; (7) $Al^{3+} + Cu^{2+}$; (8) $Al^{3+} + Fe^{2+}$; (9) $Al^{3+} + Fe^{3+}$; (10) $Al^{3+} + K^{+}$; (11) $Al^{3+} + Mg^{2+}$; (12) $Al^{3+} + Mn^{2+}$; (13) $Al^{3+} + Na^{+}$; (14) $Al^{3+} + Ni^{2+}$; (15) $Al^{3+} + Pb^{2+}$; (16) $Al^{3+} + Zn^{2+}$) (λ_{ex} = 382 nm).

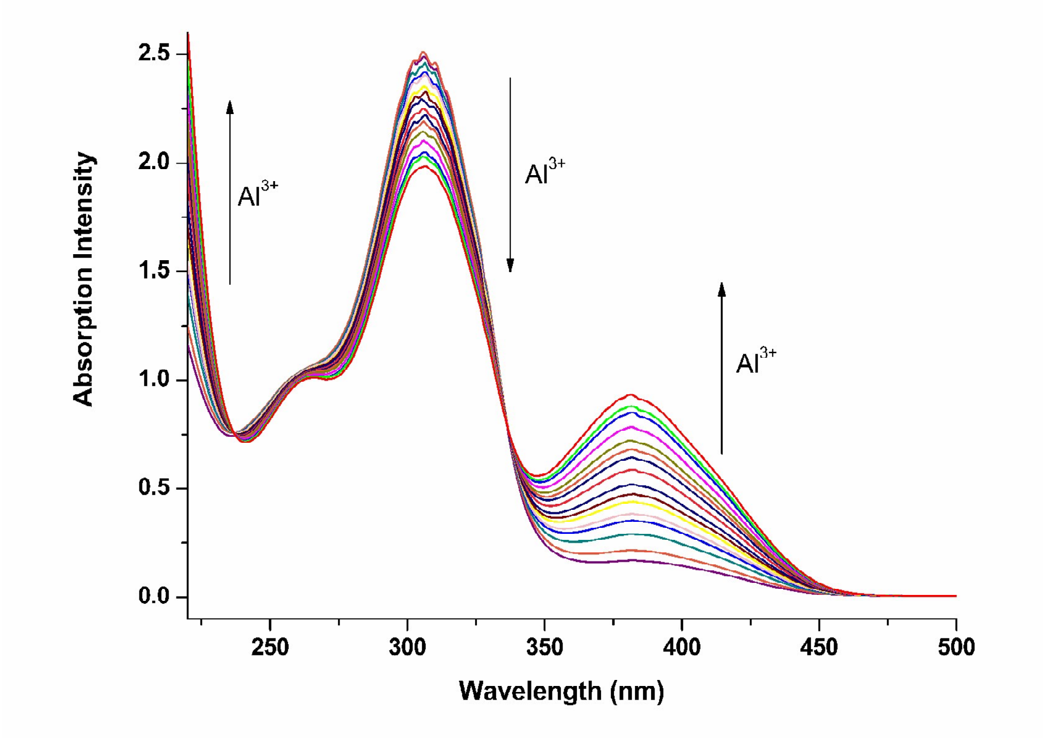
Fig. 4 Fluorescence spectra of **1** (50 μM) upon the titration of Al^{3+} (0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0 *equiv.*, respectively) in ethanol with an excitation at 382 nm.

Fig. 5 Fluorescence response of ethanol solution of **1** (50 μM) and Al^{3+} (1 *equiv.*) upon addition of $EDTANa_2$ (1 *equiv.*) with an excitation at 382 nm.

Fig. 6 Job's plot for determining the stoichiometry between **1** and Al^{3+} in ethanol ($X_{Al}=[Al^{3+}]/([Al^{3+}] + [\mathbf{1}])$, the total concentration of **1** and $Al^{3+}$was 100 μM).

Scheme 1 The synthetic route of compound **1**.

Scheme 2 Proposed mechanism for detection of Al^{3+} by **1**.



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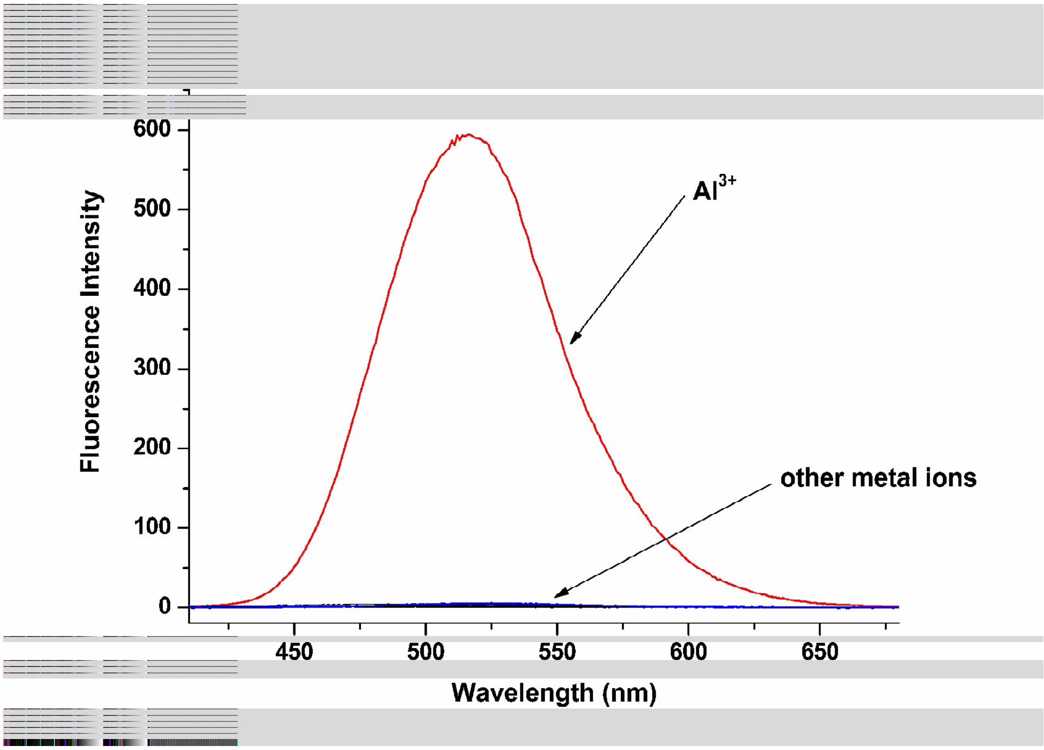

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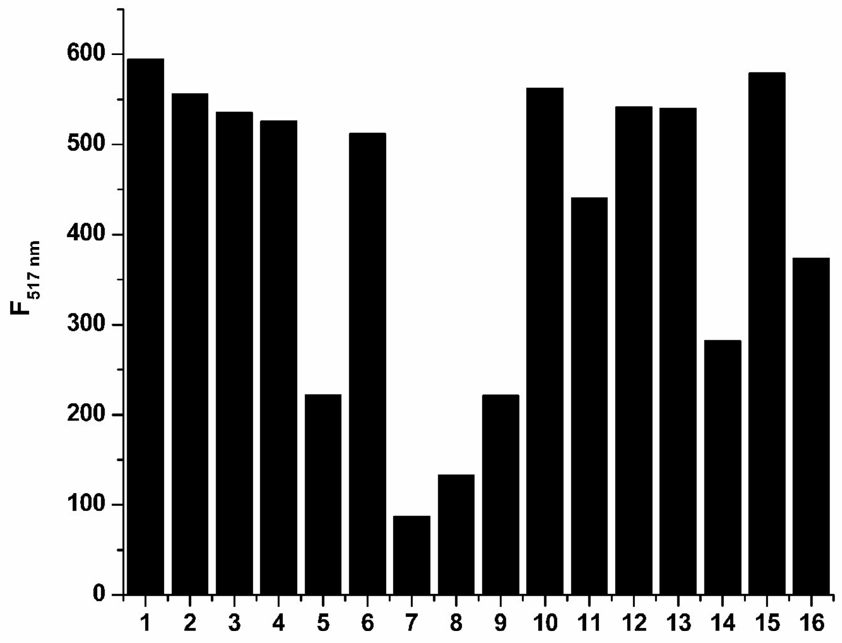


Fig. 3 The fluorescence intensity at 517 nm of **1** (50 μM) with Al^{3+} (1 *equiv.*) in the presence of various metal ions (5 *equiv.*) under the same conditions in ethanol. ((1) Al^{3+}; (2) Al^{3+} + Ba^{2+}; (3) Al^{3+} + Ca^{2+}; (4) Al^{3+} + Cd^{2+}; (5) Al^{3+} + Co^{2+}; (6) Al^{3+} + Cr^{3+}; (7) Al^{3+} +Cu^{2+}; (8) Al^{3+} + Fe^{2+}; (9) Al^{3+} + Fe^{3+}; (10) Al^{3+} + K^{+}; (11) Al^{3+} + Mg^{2+}; (12) Al^{3+} + Mn^{2+}; (13) Al^{3+} + Na^{+}; (14) Al^{3+} + Ni^{2+}; (15) Al^{3+} + Pb^{2+}; (16) Al^{3+} + Zn^{2+}) (λ_{ex} = 382 nm).

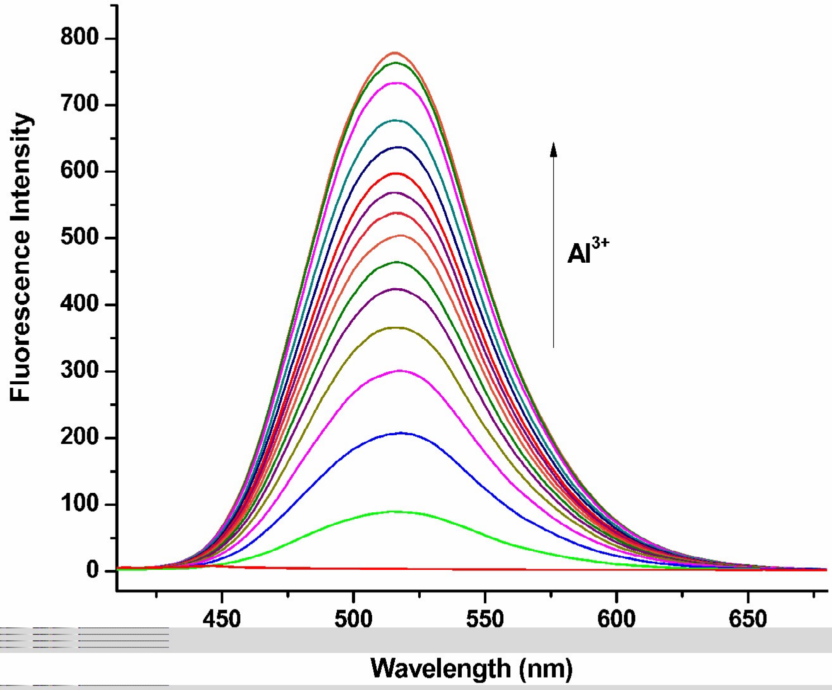


Fig. 4 Fluorescence spectra of **1** (50 μM) upon the titration of Al^{3+} (0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0 *equiv.*, respectively) in ethanol with an excitation at 382 nm.

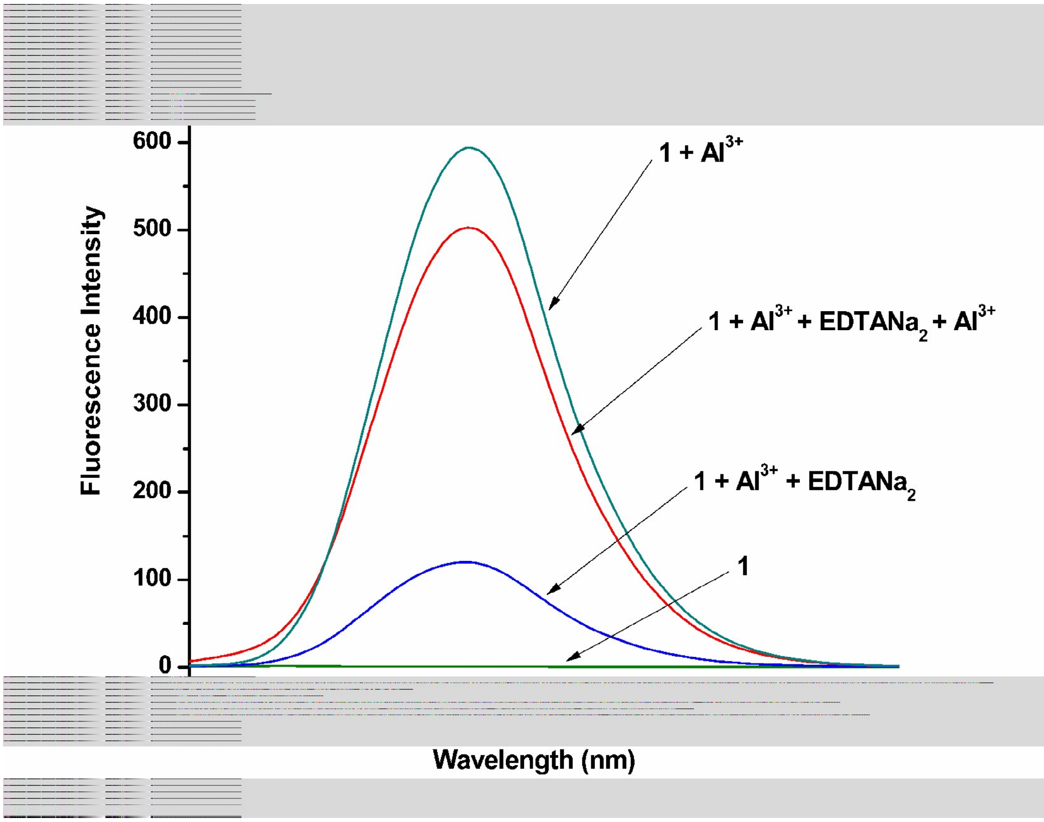


Fig. 5 Fluorescence response of ethanol solution of **1** (50 μM) and Al^{3+} (1 *equiv.*) upon addition of $EDTANa_2$ (1 *equiv.*) with an excitation at 382 nm.

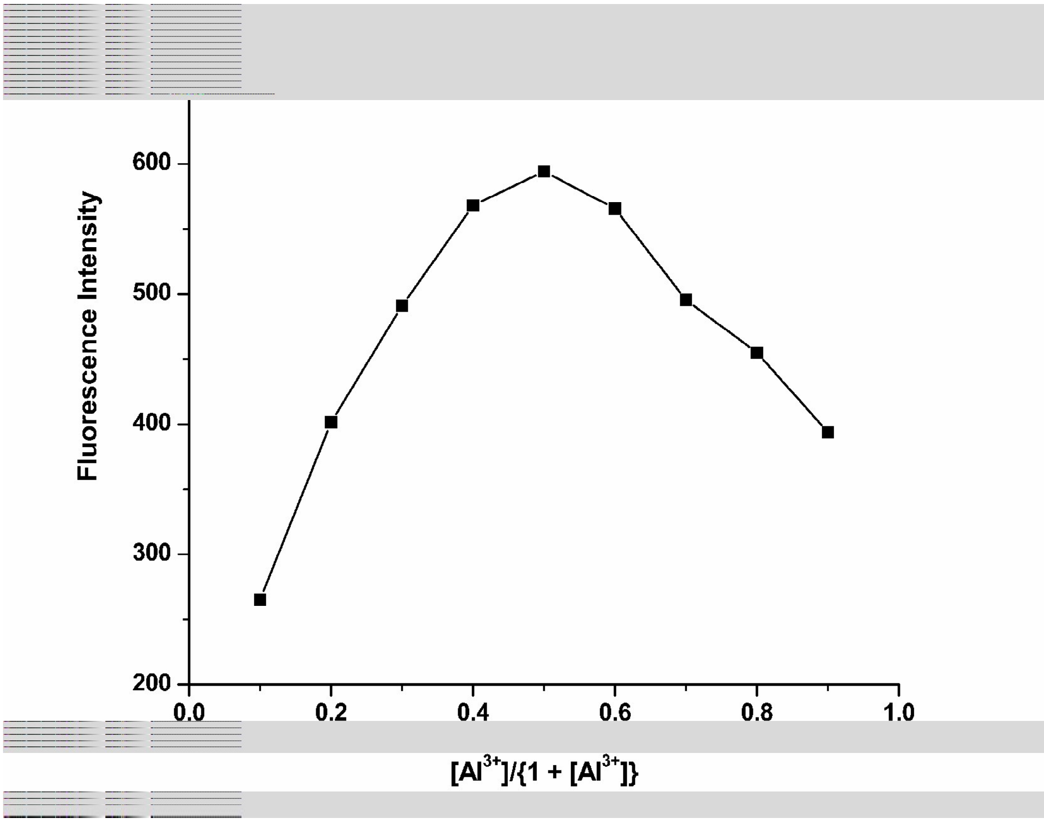
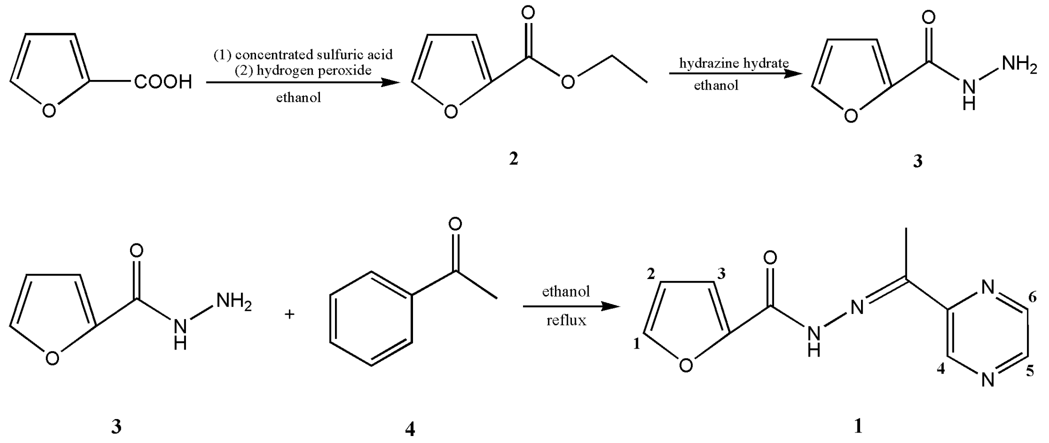
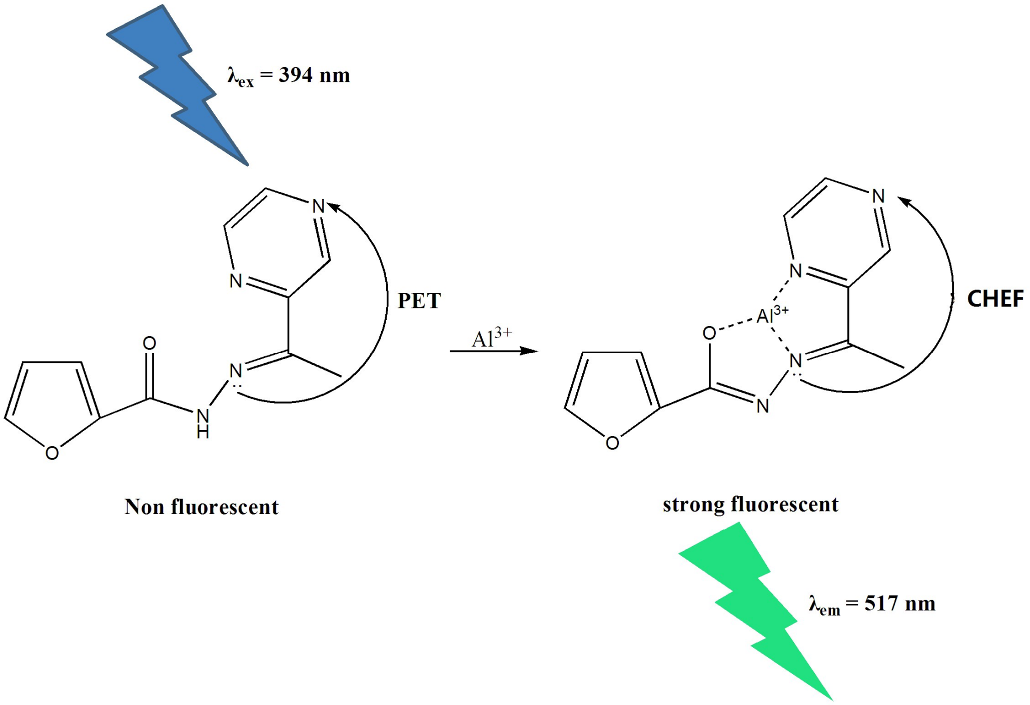


Fig. 6 Job's plot for determining the stoichiometry between **1** and Al^{3+} in ethanol (X_{Al}=[Al^{3+}]/([Al^{3+}] + [**1**]), the total concentration of **1** and Al^{3+}was 100 μM).



Scheme 1 The synthetic route of compound **1**.



Scheme 2 Proposed mechanism for detection of Al^{3+} by **1**.