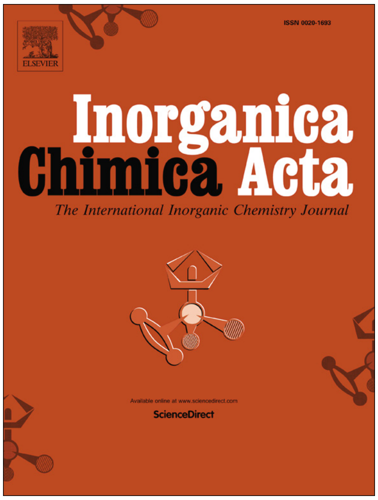


Research paper

A simple fluorescent-colorimetric probe for selective switch-on detection of Al^{3+} in ethanol

Cong Liu, Li-mei Liu, Tian-rong Li, Kui Liu, Zheng-yin Yang

PII: S0020-1693(19)31362-3
DOI: https://doi.org/10.1016/j.ica.2019.119327
Reference: ICA 119327

To appear in: *Inorganica Chimica Acta*

Received Date: 6 September 2019
Revised Date: 29 November 2019
Accepted Date: 29 November 2019

Please cite this article as: C. Liu, L-m. Liu, T-r. Li, K. Liu, Z-y. Yang, A simple fluorescent-colorimetric probe for selective switch-on detection of Al^{3+} in ethanol, *Inorganica Chimica Acta* (2019), doi: https://doi.org/10.1016/j.ica.2019.119327

A simple fluorescent-colorimetric probe for selective switch-on detection of Al^{3+} in ethanol

Cong Liu[1], Li-mei Liu[1],Tian-rong Li[1], Kui Liu*[1,2], Zheng-yin Yang*[1]

[1]*College of Chemistry and Chemical Engineering, State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, P.R. China*

[2]*College of Chemical Engineering and Technology, Tianshui Normal University,TianShui, GanSu 741001, China.*

***Corresponding author. Tel: +86 931 8913515; Fax: +86 931 8912582; e-mail: yangzy@lzu.edu.cn (Z.Y. Yang)，liuk2019@lzu.edu.cn（K.. Liu）*

Abstract

A novel and simple fluorescent probe, 7-methoxychromone-3-carbaldehyde-(3’4’5’-trimethoxybenzoyl) hydrazone (**L**), was designed and synthesized. The probe **L** presented outstanding “turn-on” fluorescence response towards Al^{3+} over most other competitive ions in ethanol. The detection limit of **L** for recognizing Al^{3+} was measured to be 2.14×10^{-7} M. According to these excellent properties, the detecting of Al^{3+} on filter papers was studied successfully. Photoinduced electron transfer (PET) process, coupled with the C=N isomerisation process, is put forward to interpret the obvious fluorescence response.

Key words: Fluorescent probe; Aluminum ion; Colorimetric; Test kits.

1. Introduction

It is well known that aluminum is the third most abundant element in the earth's crust (about 8% by weight) and the essential metal ion in the human body [1-2]. Aluminum plays very important ~~roles~~ roles in most natural processes and in water resource. And aluminum is extensively used in numerous fields, from the industrial fields to daily supplies, which includes aerospace industry, automobiles, computers, various packaging items, electrical equipment, food additives, building materials, clinical drugs , water purification and so on [3-5]. The concentration of Al^{3+} couldn't exceed 7.41μM in drinking water on the basis of World Health Organization (WHO) [6-8]. Currently, a large number of medical studies have shown that the excessive aluminum level in organism is harmful to human health. It can cause diseases such as Alzheimer's disease, Parkinson's disease, Osteoporosis and Osteomalacia, etc. [9-13]. Hence, it is very vital to design and synthesize effective chemical probes for the selective detection of Al^{3+} in organisms and environments.

Typical instrumentation methods for identifying Al^{3+} ions, including atomic absorption spectroscopy and inductively-coupled plasma mass spectrometry, have been reported [14-15]. Since these techniques require relatively complex sample preparation or sample pretreatment schemes and are generally not portable, they can't be used for on-site detections of Al^{3+} ions. Fluorescent sensors own many advantages such as simple operation, low detection limit, fast time response and portability， which have been one of the most favorable methods for detecting metal ions [16-21]. Up to now, many fluorescent probes for the detection of Al^{3+} have been reported in the literature [22-28]. Generally, Al^{3+} is a hard-acid and prefers to coordinate with ligands containing N and O as hard-base donor sites [29-30]. Massive Schiff-base compounds and their metal complexes have been used as Al^{3+} sensors. In recent years, some simple metal ion sensors have shown their superiority due to their good sensing performance and clear signal transmission mechanism. Obtaining new Al^{3+} probes with simple molecular structure is very appealing and significant.

From what have been discussed above, we synthesized a new fluorescent probe **L** which equipped with good selectivity for detecting Al^{3+}. The structure of probe **L** has been confirmed by ^1H NMR and ESI-mass methods and the recognition behaviors of **L** were studied by UV–vis and fluorescence measurements. With the coordination between **L** and Al^{3+}, **L** presented obvious fluorescence enhancement at 480 nm in ethanol media. Moreover, **L** could be used as a practical, visible colorimetric test tool for Al^{3+}.

2. Experimental

2.1. Materials and apparatus

All commercially obtained chemical reagents were analytical grade and were used without further purification. The metal-ions' solutions used in the whole experiment were prepared from corresponding nitrate and chloride salts. ($NaNO_3$, KNO_3, $LiClO_4$, $Zn(NO_3)_2$▪ $6H_2O$, $Cu(NO_3)_2$▪ $3H_2O$, $Mg(NO_3)_2$▪ $6H_2O$, $Ni(NO_3)_2$▪

$6H_2O$, $Co(NO_3)_2$▪ $6H_2O$, $Cd(NO_3)_2$▪ $4H_2O$, $Ca(NO_3)_2$, $MnCl_2$▪$4H_2O$, $BaCl_2$, $HgCl_2$, $Al(NO_3)_3$▪ $9H_2O$, $Fe(NO_3)_3$▪ $9H_2O$, $CrCl_3$). Deionized water was used throughout the entire experiments. ^1H NMR spectra were acquired on the Bruker 400 MHz instruments. The ^1H NMR spectrum of ligand was obtained in DMSO-d_6 and ^1H NMR titrations were carried out dissolving **L** and metal salts in DMSO-d_6 respectively at room temperature. Electrospray ionization mass spectra (ESI-MS) were conducted by a Bruker esquire 6000 spectrometer and we used DMF as solvent. Fluorescence measurements were recorded on a Hitachi RF-4500 spectrophotometer. UV-visible measurements were determined on a Shimadzu UV-240 spectrophotometer. The melting point of **L** was acquired by a Beijing XT4-100x microscopic melting point apparatus.

2.2. Synthesis

2.2.1. Synthesis of 7-methoxychromone-3-carbaldehyde

Based on the literature procedures, we synthesized 7-methoxychromone-3-carbaldehyde [31].

2.2.2. Synthesis and characterization of **L**

The synthetic route of 7-methoxychromone-3-carbaldehyde-(3’4’5’-trimethoxybenzoyl) hydrazone was shown in **Scheme 1**. 3’4’5’-trimethoxybenzoyl-hydrazine (0.1131 g, 0.5 mM) in 15 mL ethanol was added to 7-methoxychromone-3-carbaldehyde (0.1020 g, 0.5 mM) in

15 mL ethanol. Then the above mixed solvent was refluxed and stirred for 6 h. A yellow precipitate appeared and then the mixture was filtered and washed several times with ethanol. Finally, the yellow solid was obtained. Yield: 62%, mp: 153-155 ℃. ^{1}H NMR (400MHz, DMSO-d_6, TMS) (**Fig. S1**): δ(ppm): 12.090 (s, 1H, -NH-), 8.971 (d, 1H, J=0.8Hz , $H^{6'}$), 8.340 (d,1H, J=0.8Hz, $H^{2'}$), 7.760 (d, 1H, J=8.8Hz, H^5), 7.459 (s, 2H, -CH=, H^2), 6.607~6.582 (m, 2H, H^6, H^8), 3.187 (s, 12H, -OCH_3); MS(ESI) (**Fig. S2**): m/z=413.3352 $[M+H]^+$.

2.3. General information

Solutions of the probe **L** (5×10^{-3} M) and metal ions (5×10^{-3} M) were prepared in DMF and CH_3CH_2OH-H_2O respectively. We carried out all spectroscopic studies in ethanol (**Fig. S3**) and the fluorescence spectra were recorded upon excitation at 370 nm. Both the excitation slit width and emission slit width were 5 nm throughout fluorescence measurements. The detection limit of **L** sensing Al^{3+} was determined according to the fluorescence titration analysis and the following equation (detection limit = $3\sigma/k$) [32]. Meanwhile, the association constant of **L**-Al^{3+} complex was calculated by Benesi–Hildebrand equation (E_q.(1)) [33].

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

3. Results and discussion

3.1. Absorption studies

UV–Vis titration experiment was carried out in ethanol at room temperature. The work solution was prepared by diluted probe **L** (20 μL) to ethanol (2 mL) to make a final concentration of 50.0 μM. Then Al^{3+} (0-1.5 *equiv.*) was added to the solution of **L** (50.0 μM) prepared above and mixed them for a few seconds. The absorption spectrum of **L** with the addition of different concentrations of Al^{3+} was demonstrated in **Fig.1**. Upon the addition of Al^{3+}, an obvious absorption band centering at 370 nm appeared and a clear isosbestic point at 300 nm indicated the formation of complex between free probe **L** and Al^{3+} [34-35].

3.2. Emission studies

The selectivity of **L** was studied by fluorescence analysis and the fluorescence properties of **L** were performed with various metal cations (Li^{+}, Na^{+}, K^{+}, Mg^{2+}, Ba^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Ca^{2+}, Hg^{2+}, Fe^{3+}, $Cr^{3+}$and Al^{3+}) in ethanol. As shown in **Fig. 2**, **L** alone exhibited comparatively weak fluorescence intensity. When **L** (50.0 μM) was treated with different metal cations (1.0 *equiv.*), only Al^{3+} induced significant fluorescence enhancement at 480 nm accompanied by a change of the fluorescence color from colorless to strong yellow and the quantum yield increased to 12.36%. The turn-on fluorescence induced by Al^{3+} could be explained by photoinduced electron transfer (PET) phenomenon and C=N isomerisation process in Schiff base structrues [36-37]. The above experimental results indicated that **L** has a good selectivity for identifying Al^{3+}.

Competitive experiments were carried out to further ascertain the efficient selectivity of **L (Fig.3)** in ethanol. Compared with **L**-Al^{3+} solution, the fluorescence intensity hardly change when most metal ions of Li^+, Na^+, K^+, Mg^{2+}, Ba^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Ca^{2+}, Hg^{2+}, Fe^{3+} and Cr^{3+} (1 *equiv.*) were added to **L**-Al^{3+} solution respectively. With the addition of Cr^{3+}, the fluorescence emission intensity at 480 nm was diminished. However, it still exhibited sufficient turn-on emission intensity for the detection of Al^{3+}. All of these observations indicated **L** could be a promising selective fluorescent probe towards Al^{3+} over most competing mental ions.

Fluorescence titration experiment was done for the purpose of getting more insight into the sensing properties of **L** (**Fig.4.**). The fluorescence intensity at 480 nm was monotonically increased with gradual addition of Al^{3+}. Moreover, the probe **L** showed a commendable linear relationship between the fluorescence emission intensity and the concentration of Al^{3+} within a certain range (**Fig. S4**). The detection limit of **L** towards Al^{3+} was calculated to be 2.14×10^{-7} M according to $3\sigma/k$ by means of the mentioned fluorescence titration. Based on the analysis of the titration profiles by Benesi–Hildebrand equation, the association constant for **L**-Al^{3+} complex was estimated to be 6.07×10^3 M^{-1} (**Fig. S5**).

3.3. Binding studies

The method of Job's plot analysis was applied to confirm and corroborate the stoichiometry between the probe **L** and Al^{3+}. Among all experimental processes, the total concentration of **L** and Al^{3+} was maintained to a constant of 50.0 μM with a continuously variable molar fraction ([**L**]/([**L**] + [Al^{3+}]). As shown in **Fig. 5**, the fluorescence emission intensity at 480 nm reached a maximum with a molar fraction of 0.5. The Job's plot analysis illustrated 1:1 stoichiometric complexation between **L** and Al^{3+}. Besides, it was found that the appearance of a peak at m/z 491.865 could be assigned to [**L** + Al^{3+} + H_2O + $2OH^-$]$^+$ in the ESI-MS spectrum, providing further evidence for the formation of 1:1 complex between **L** and Al^{3+} (**Fig. S6**).

3.4. Application of probe **L**

In order to achieve more convenient operating process, the selectivity of **L** for colorimetric detection of Al^{3+} was investigated under nature light and a 365 nm UV lamp respectively. Interestingly, only **L**-Al^{3+} solution showed the change of color from colorless to yellow (**Fig.6 Left**). Inspired by the obvious color change of **L**-Al^{3+} solution, we also performed experiments for a colorimetric detection of Al^{3+} on filter papers with different metal ions. Some round filter papers was prepared by dip-coating solution of **L** (0.5 mmol), followed by drying them in the air for about 6 h. Prepared filter papers were dropped by solutions of various metal ions (0.5 mmol) respectively and then dried in air. It was found that the probe-immersed filter papers after interaction with Al^{3+} exhibited a naked-eye sensitive color change from a dark blue to a fluorescent yellow under UV light (**Fig.6 Right**). Consequently, this easily available test paper could be used to roughly estimate whether the system contains Al^{3+}.

3.5. The proposed mechanism

In an endeavor to better understand the binding mode between probe **L** and Al^{3+}, ^{1}H NMR titration experiments were studied. **Fig. 7(a)** and **Fig. 7(b)** displayed the ^{1}H

NMR spectra of the free **L** and L with the addition of 1.0 *equiv.* Al^{3+}, respectively. Compared with **Fig. 7(a)** and **Fig. 7(b)**, it was obviously found that the peak of –NH– was shifted to downfield from 12.090 ppm to 12.169 ppm. Meanwhile, the proton peak of –CH= and H^2 exhibited an up-field shift from 7.459 ppm to 7.441 ppm. Peak for the proton of $H^{2'}$ shifted downfield from 8.971 ppm to 9.013 ppm. These significant spectral changes demonstrated the N atom of the –N=CH– group and two O atoms of carbonyl groups participated in the coordination processes. The coordination between **L** and Al^{3+} changed the electron distribution in the chemosensor. According to some literature, aluminum ion always formed five or six membered rings when it was involved in the formation of complexes [38-47]. Based on the analyses of the experimental results above, the binding mode of **L** with Al^{3+} was proposed (**Scheme 2**).

3.6. Comparisons with some of the previously reported Al^{3+} fluorescent probes

We compared this designed Al^{3+} fluorescent probe with some of the previously reported probes, including solvent, interfering, and detection limit, etc. As shown in **Table.1**, each of the listed probes has some good properties, but it is subject to Cu^{2+} and some other interfering metals. And during the detection of Al^{3+}, the solvents used in these experiments are also environmental unfriendly. The probe proposed in this paper detects Al^{3+} in an environmental friendly ethanol solvent, and Cu^{2+} has no effect on the detection of Al^{3+}. Additionally, **L** has a lower detection limit compared with some reported probes. In summary, **L** is a favorable fluorescent probe with good selectivity and sensitivity to Al^{3+} ions.

4. Conclusion

In conclusion, we have successfully synthesized and characterized a chromone-based Schiff base derivative as a fluorescent-colorimetric probe for recognizing Al^{3+} in ethanol solution. **L** produced an obvious fluorescence enhancement at 480 nm in the presence of Al^{3+} and owned excellent selectivity and sensitivity towards Al^{3+} over other common metal ions. The detection limit of **L** for detecting Al^{3+} was 0.214 μM, which is much lower than that suggested by the WHO (7.41 μM). Moreover, the fluorescent probe **L** has been successfully applied to identify Al^{3+} as test kits on solid state.

References

[1] S. Yumoto, H. Nagai, H. Matsuzaki, T. Kobayashi, W. Tada, Y. Ohki, S. Kakimi, K. Kobayashi, Nucl. Instr. and Meth. in Phys. Res. B. 172 (2000) 925-929.

[2] P.D. Darbre, D. Pugazhendhi, F. Mannello, J. Inorg. Biochem. 105 (2011) 1484–1488.

[3] M.G. Soni, S.M. White, W.G. Flamm, G.A. Burdock, Regul. Toxicol. Pharm. 33 (2001) 66-79.

[4] V.K. Gupta, A.K. Singh, N. Mergu, Electrochim. Acta. 117 (2014) 405–412.

[5] Y.G. Zhao, Z.H. Lin, H.P. Liao, C.Y. Duan, Q.J. Meng, Inorg. Chem. Commun. 9 (2006) 966–968.

[6] Z. Krejpcio, R.W. Wojciak, J. Pol, Environ. Stud. 11 (2002) 251-254.

[7] J. Barcelo, C. Poschenrieder, Environ. Exp. Bot. 48 (2002) 75-92.

[8] T. Han, X. Feng, B. Tong, J. Shi, L. Chen, J. Zhi, Y. Dong, Chem. Commun. 48

(2012) 416-418.

[9] D.P. Perland, A.R. Brody, Science. 208 (1980) 297-299.

[10] C.S. Cronan, W.J. Walker, P.R. Bloom, Nature. 324 (1986) 140-143.

[11] D.P. Perl, D.C. Gajdusek, R.M. Garruto, R.T. Yanagihara, C.J. Gibbs, Science. 217 (1982) 1053-1055.

[12] S. Polizzi, E. Pira, M. Ferrara, M. Bugiani, A. Papaleo, R. Albera, S. Palmi, Neurotoxicology. 23 (2002) 761-764.

[13] J.R. Walton, NeuroToxicology. 27 (2006) 385-394.

[14] A. Tong, Y. Akama, S. Tanaka, Analyst. 115 (1990) 947-949.

[15] G. P. C. Rao, K. Seshaiah, Y. K. Rao and M. C. Wang, J. Agric. Food. Chem. 54 (2006) 2868-2872.

[16] Y. Li, J. Wu, X. Jin, J. Wang, S. Han, W. Wu, J. Xu, W. Liu, X. Yao, Y. Tang , Dalton. Trans. 43 (2014) 1881-1887.

[17] J. Wu, W. Liu, J. Ge, H. Zhang, P. Wang, Chem. Soc. Rev. 40 (2011) 3483-3495.

[18] J. Du, M. Hu, J. Fan, X. Peng, Chem. Soc. Rev. 41 (2012) 4511-4535.

[19] Z. Zheng, Z. Yu, M. Yang, F. Jin, Q. Zhang, H. Zhou, J. Wu, Y. Tian, Organoment. Chem. 78 (2013) 3222-3234.

[20] D. T. Quang and J. S. Kim, Chem. Rev. 110 (2010) 6280-6301.

[21] H. N. Kim, W. X. Ren, J. S. Kim and J. Yoon, Chem. Soc. Rev. 41 (2012) 3210-3244.

[22] A. Sahana, A. Banerjee, S. Lohar, B. Sarkar, S. K. Mukhopadhyay, D. Das, Inorg. Chem. 52 (2013) 3627-3633.

[23] S. Das, A. Sahana, A. Banerjee, S. Lohar, D.A. Safin, M.G. Babashkina, M. Bolte, Y. Garcia, I. Hauli, S.K. Mukhopadhyayd, D. Das, Dalton. Trans. 42 (2013) 4757-4763.

[24] K.K. Upadhyay, A. Kumar, Org. Biomol. Chem. 8 (2010) 4892-4897.

[25] M. Shellaiah, Y.H. Wu, H.C. Lin, Analyst. 138 (2013) 2931-2942.

[26] D. Maity, T. Govindaraju, Inorg. Chem. 49 (2010) 7229-7231.

[27] Y.W. Liu, C. H. Chen, A.T. Wu, Analyst. 137 (2012) 5201-5203.

[28] X. Sun, Y.W. Wang, Y. Peng, Org. Lett. 14 (2012) 3420-3423.

[29] Y. Xu, J. Meng, L. Meng, Y. Dong, Y. Cheng, C. Zhu, Chem. Eur. J. 16 (2010) 12898-12903.

[30] R. Joseph, J.P. Chinta, C.P. Rao, J. Org. Chem. 75 (2010) 3387-3395.

[31] T. Hogberg, M. Vora, S.D. Drake, L.A. Mitscher, D.T. Chu, Acta Chem. Scand. B 38 (1984) 359–366.

[32] S. Samanta, S. Goswam, A. Ramesh, G. Das, Sensor. Actuat. B-Chem. 194 (2014) 120–126.

[33] H.A. Benesi, J.H. Hildebrand, J. Am. Chem. Soc. 71 (1949) 2703–2707.

[34] T. Hogberg, M. Vora, S.D. Drake, L.A. Mitscher, D.T.W. Chu, Acta. Chem. Scand. B 38 (1984)359-366.

[35] M. Mameli, M.C. Aragoni, V. Lippolis, Inorg. Chem. 48 (2009) 9236-9249.

[36] H.S. Jung, K.C. Ko, J.H. Lee, S.H. Kim, S. Bhuniya, J.Y. Lee, Y. Kim, S.J. Kim, J.S. Kim, Inorg. Chem. 49 (2010) 8552–8557.

[37] L.M. Tian, J Xue, Z.Y. Yang, Tetrahedron. Lett. 59 (2018) 4110–4115.

[38] Z.C. Liao, Z.Y. Yang, Y. Li, B.D. Wang, Q.X. Zhou, Dyes. Pigments. 97 (2013) 124-128.

[39] T.Q. Liu, X.J. Wan, Y.W. Yao, Sensor. Actuat. B-Chem. 254 (2017) 1094-1100.

[40] J.L. Zhu, Y.H. Zhang, L. Wang, T.M. Sun, M. Wang, Y.P. Wang, D.Y. Ma, Q.Q. Yang, Y.F. Tang, Tetrahedron. Lett. 57 (2016) 3535-3539.

[41] J.C. Qin, J. Yan, B.D. Wang, Z.Y. Yang, Tetrahedron. Lett. 57 (2016) 1935-1939.

[42] W. Wang, Z. Mao, M. Wang, L. Liu, D. W-J. Kwong, C. Leung, M. D.L. Ma, Chem. Commun. 52 (2016) 3611-3614.

[43] J.F. Tian, X.X. Yan, H. Yang, F.L. Tian, RSC Adv. 129 (2015) 107012-107019.

[44] Y. Li, C.Y. Liao, S.S. Huang, H. Xu, B.Z. Zheng, J. Du, D. Xiao, RSC Adv. 30 (2016) 25420-25426..

[45] X.X. Zhang, R.J. Wang, G. Liu, C.B. Fan, Tetrahedron. 72 (2016) 8449-8455.

[46] E.F. Feng, R.M. Lu, C.B. Fan, C.H. Zheng, S.Z. Pu, Tetrahedron. Lett. 58 (2017) 1390-1394.

[47] A.K. Saini, K. Natarajan, S.M. Mobin, Chem. Commun, 53 (2017) 9870.

[48] W. Cao, X.J. Zheng, J.P. Sun, W.T. Wong, D.C. Fang, J.X. Zhang, L.P. Jin, Inorg. Chem. 53 (2014) 3012-3021.

[49] K.B. Kim, D.M. You, J.H. Jeon, Y.H. Yeon, J.H. Kim, Tetrahedron. Lett. 55 (2014) 1347-1352.

[50] F.U. Rahman, A. Ali, S.K. Khalil, R. Guo, P. Zhang, H. Wang, Z.T. Li, D.W. Zhang, Talanta. 164 (2017) 307–313.

[51] M. Kumar, A. Kumar, M.S.H. Faizi, S. Kumar, M.K. Singh, S.K. Sahu, S. Kishor, R.P. John, Sensor. Actuat. B-Chem. 260 (2018) 888-899.

[52] Z. Liao, Y. Liu, S.F. Han, D. Wang, J.Q. Zheng, X.J. Zheng, L.P. Jin, Sensor. Actuat. B-Chem. 244 (2017) 914–921.

[53] J. Kumar, M.J Sarma, P. Phukan, D.K. Das, 44 (2015) 4576-4581.

Acknowledgments

This work is supported by the National Natural Science Foundation of China (21761019).

List of Figure captions

Fig.1. UV–vis spectrum of **L** (50.0 μM) with increasing concentration of Al^{3+} (0-1.5 *equiv.*) in ethanol solution.

Fig.2. Fluorescence spectrum of **L** (50.0 μM) before and after addition of various metal ions (1.0 *equiv.*) of Li^+, Na^+, K^+, Mg^{2+}, Ba^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Ca^{2+}, Hg^{2+}, Fe^{3+}, Cr^{3+} and Al^{3+} in ethanol solution.

Fig.3. Fluorescence response of **L**-Al^{3+} and **L**-Al^{3+} solution with the addition of other various metal ions in ethanol. Black bar: **L** (50.0 μM) in the presence of 1.0 *equiv*. of various metal ions. Red bar: **L** (50.0μM) with 1.0 *equiv*. of Al^{3+} in the presence of 1.0 *equiv*. of other various metal ions.

Fig.4. Fluorescence emission titration spectrum of **L** (50.0 μM) upon addition of Al^{3+} (0-1.0 *equiv.*) in ethanol.

Fig.5. Job's plot for determining the stoichiometry between probe **L** and Al^{3+} in ethanol solution. The total concentration of **L** and Al^{3+} is 5.0×10^{-5} mol/L.

Fig.6. Application of **L** (Left: **L** recognized Al^{3+} by naked-eye under a 365 nm UV lamp and sunlight respectively. Right: Fluorescence color changes of **L** (0.5 mM) loaded filter paper in the presence of various metal ions(0.5 mM) under illumination using a 365 nm UV lamp.)

Fig.7. ^1H NMR spectra of **L** (a) and **L** with Al^{3+} (b) (1.0 *equiv.*) in DMSO-d_6.

Scheme 1. The synthetic route of ligand (**L**).

Scheme 2. The proposed binding mechanism of **L** for Al^{3+}.

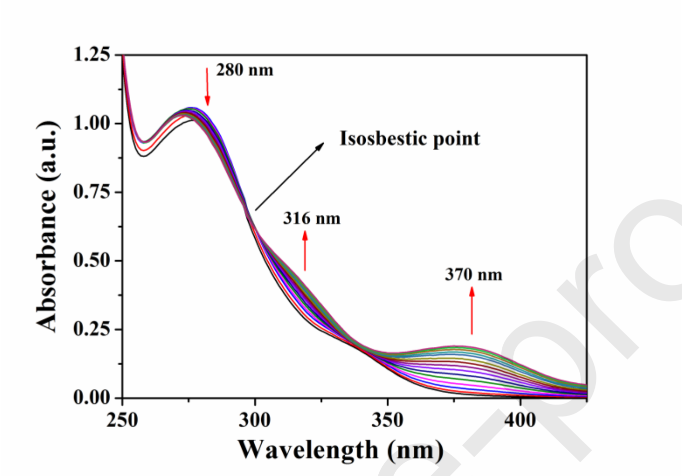


Fig.1. UV–vis spectrum of **L** (50.0 μM) with increasing concentration of Al^{3+} (0-1.5 *equiv.*) in ethanol solution.

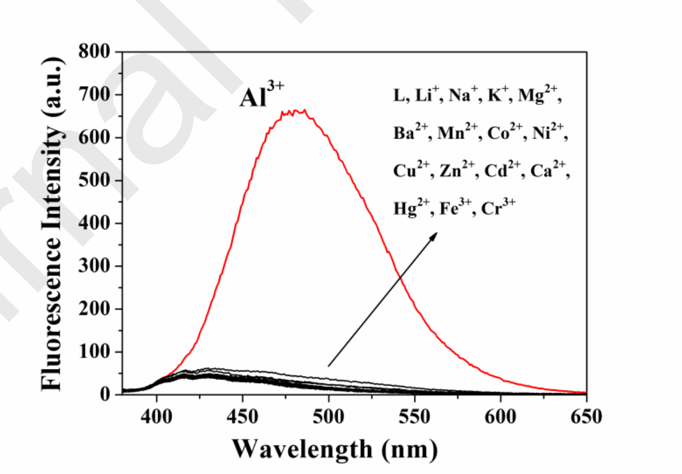


Fig.2. Fluorescence spectrum of **L** (50.0 μM) before and after addition of various metal ions (1.0 *equiv.*) of Li^+, Na^+, K^+, Mg^{2+}, Ba^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Ca^{2+}, Hg^{2+}, Fe^{3+}, Cr^{3+} and Al^{3+} in ethanol solution.

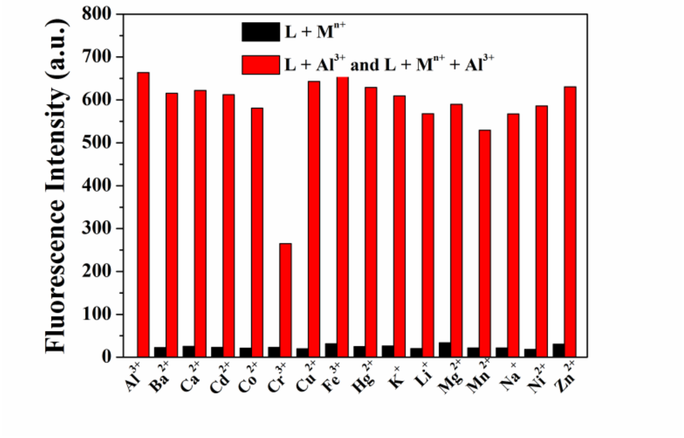


Fig.3. Fluorescence response of **L**-Al^{3+} and **L**-Al^{3+} solution with the addition of other various metal ions in ethanol. Black bar: **L** (50.0 μM) in the presence of 1.0 *equiv*. of various metal ions. Red bar: **L** (50.0μM) with 1.0 *equiv*. of Al^{3+} in the presence of 1.0 *equiv*. of other various metal ions.

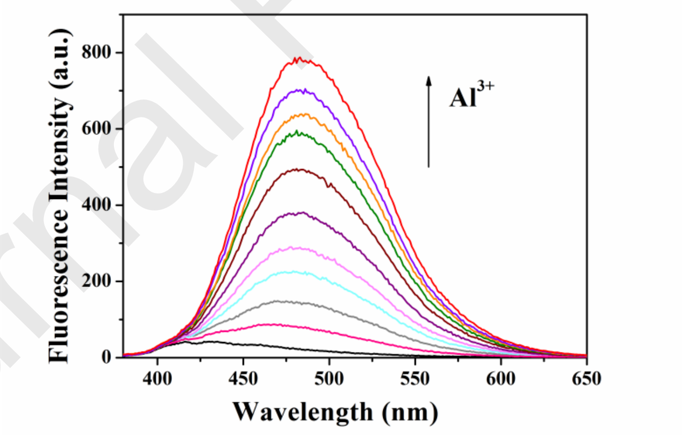


Fig.4. Fluorescence emission titration spectrum of **L** (50.0 μM) upon addition of Al^{3+} (0-1.0 *equiv*.) in ethanol.

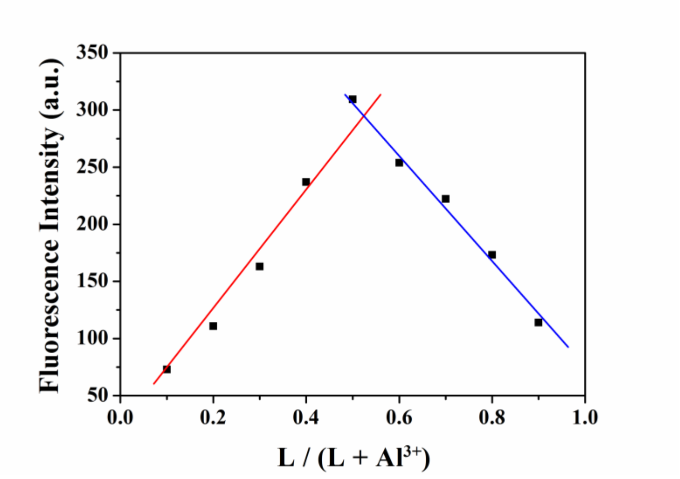


Fig.5. Job's plot for determining the stoichiometry between probe **L** and Al^{3+} in ethanol solution. The total concentration of **L** and Al^{3+} is 5.0×10^{-5} mol/L.

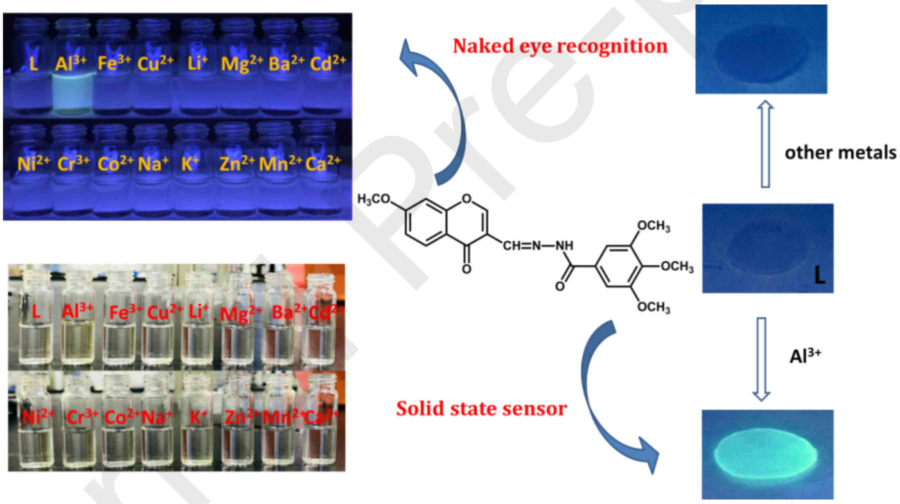


Fig.6. Application of **L** (Left: **L** recognized Al^{3+} by naked-eye under a 365 nm UV lamp and sunlight respectively. Right: Fluorescence color changes of **L** (0.5 mM) loaded filter paper in the presence of various metal ions(0.5 mM) under illumination using a 365 nm UV lamp.)

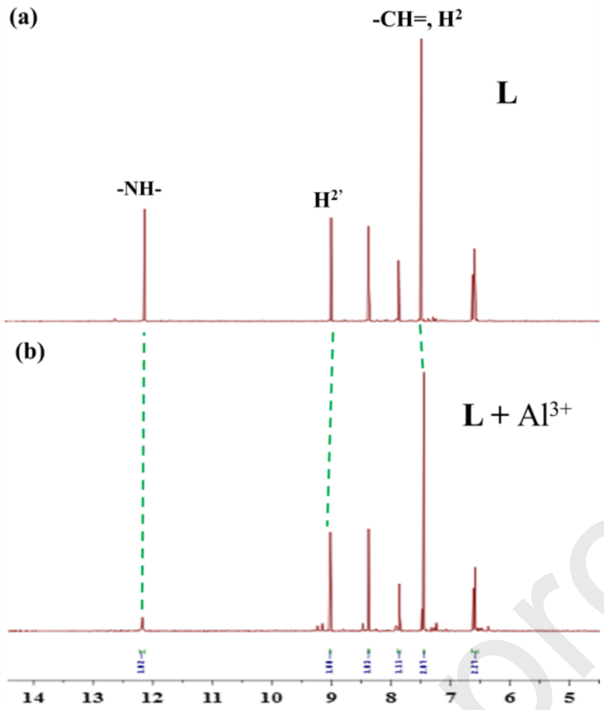
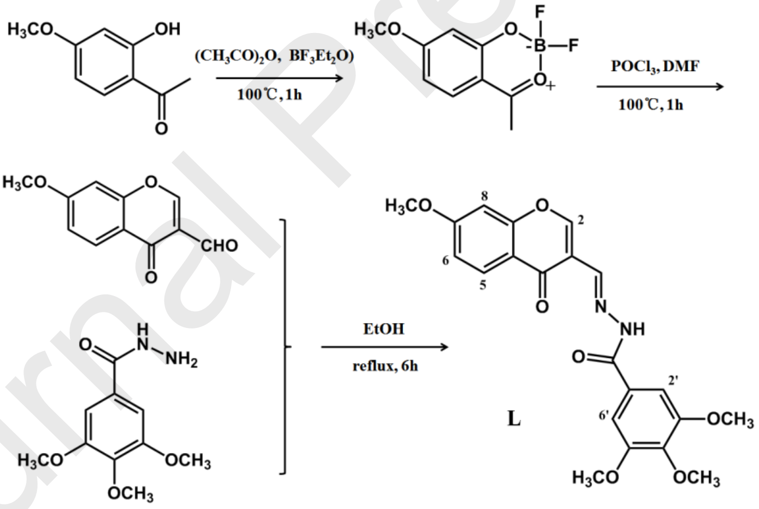
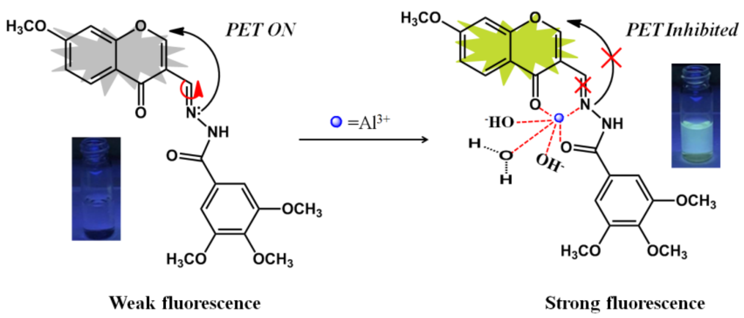


Fig.7. ^{1}H NMR spectra of **L** (a) and **L** with Al^{3+} (b) (1.0 *equiv.*) in DMSO-d$_6$.



Scheme 1. The synthetic route of ligand (**L**).



Scheme 2. The proposed binding mechanism of **L** for Al^{3+}.

Table 1. Comparisons of various properties with previously reported probes used for detecting Al^{3+}

Solvent	Interferingmetal ions	*LOD* (M)	References
DMSO	Cu^{2+} , Fe^{3+} , Pb^{2+}	5.25×10^{-6}	[48]
DMF/HEPES (9:1)	Cu^{2+}, Fe^{3+}	1.00×10^{-6}	[49]
DMF/H_2O (1:1)	Cu^{2+}	1.5×10^{-7}	[50]
DMSO	Cr^{3+}, Na^{+}, K^{+}	4.32×10^{-6}	[51]
DMSO/H_2O (9:1)	Not mentioned	3.66×10^{-6}	[52]
CH_3CN/H_2O (1:1)	Cu^{2+}	5.0×10^{-5}	[53]
Ethanol	/	$\mathbf{2.14\times10^{-7}}$	**This study**

We have no conflicts of interest to declare.

Author statement

Manuscript title:

I have made substantial contributions to the conception or design of the work; or the acquisition, analysis, or interpretation of data for the work; AND
I have drafted the work or revised it critically for important intellectual content; AND
I have approved the final version to be published; AND
I agree to be accountable for all aspects of the work in ensuring that questions related to the accuracy or integrity of any part of the work are appropriately investigated and resolved.

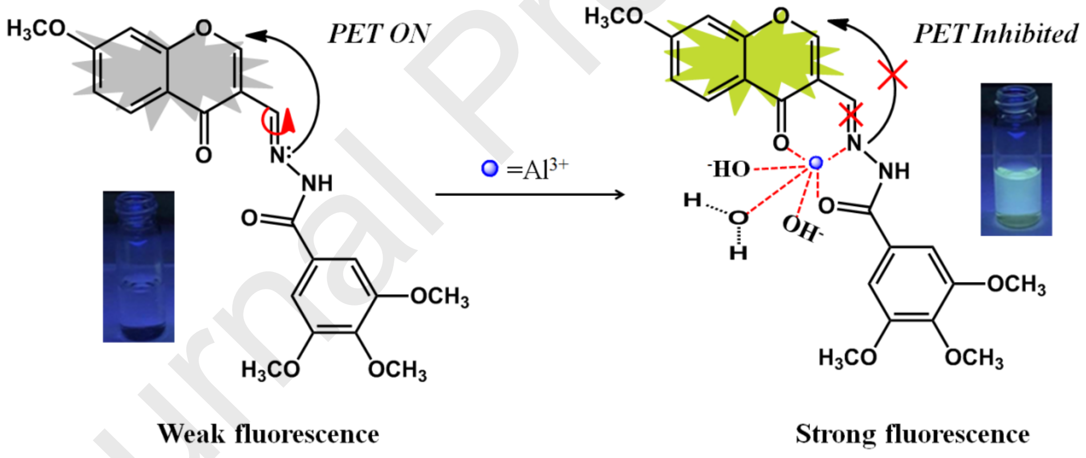
All persons who have made substantial contributions to the work reported in the manuscript, including those who provided editing and writing assistance but who are not authors, are named in the Acknowledgments section of the manuscript and have given their written permission to be named. If the manuscript does not include Acknowledgments, it is because the authors have not received substantial contributions from nonauthors.

Attachment: Yes No (circle)

Cong Liu
Author signature

Cong Liu
Printed name

2019.11.29
Date signed/appended



- We synthesized a simple turn-on fluorescent probe (**L**) for the detection of Al^{3+}.
- The probe showed good selectivity and high sensitivity for Al^{3+} in ethanol, and the detection limit was as low as 2.14×10^{-7}M.
- In this paper, Cu^{2+} didn't interfere with the detection of Al^{3+}.
- The probe has been successfully applied to recognize Al^{3+} on filter papers.