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A highly selective fluorescent probe for Al³⁺ based on 4-aminoantipyrine

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HIGHLIGHTS

G R A P H I C A L A B S T R A C T

- ► We designed and synthesized a new Schiff base fluorescent probe.
- The probe showed high sensitivity for Al³⁺ over other metal ions in aqueous solution.
- ► The other metal ions have no effect on the detection of Al³⁺.

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ABSTRACT

A novel and simple Schiff base based on 2-pyridine formaldehyde and 4-aminoantipyrine was synthesized and characterized as a fluorescent probe. In the presence of Al^{3+} , the fluorescent intensity has a dramatic enhancement over other examined metal ions in aqueous solution. The method of Job's plot indicated the formation of 1:1 complex between probe and Al^{3+} , and the possible binding mode of the system was also proposed. Moreover, other examined metal ions had no effect on the detection of Al^{3+} . © 2013 Elsevier B.V. All rights reserved.

Introduction

Aluminum is the third most abundant element after oxygen and silicon in the earth's crust [1]. In addition, compound derivatives from aluminum are widely used in food additives, water treatment and medicine [2]. However, the overload amounts of aluminum to human being will lead to the malfunction of central nervous system because of its ubiquitous distribution in daily life of human [3]. A number of methods have been developed to determine aluminum, such as spectrophotometry, electrochemistry and chromatography [4–8]. Compared to these methods, fluorimetric methods for detection of aluminum are very popular due to its operational simplicity, high selectivity, sensitivity, rapidity, low cost of

equipment. Up till now, a few fluorescent probes have been developed for the detection of aluminum. However, the poor selectivity in aqueous solution hinders the practical applications [9–15]. Therefore, it is of great demand to develop new fluorescent sensor in aqueous solution.

SPECTROCHIMICA ACTA

In recent years, Schiff base as a good ligand for metal ions were widely used in many areas [16–20], especially in chemosensors [21–26]. Herein, we reported on the structural and spectroscopic properties of a new Schiff base derived from 2-pyridine formalde-hyde and 4-aminoantipryine, which was synthesized in only one step as shown in Scheme 1. The probe exhibits remarkably enhanced intensity in its fluorescence emission in presence of AI^{3+} in aqueous solution over other metal ions examined. The method of Job's plot confirmed the formation of 1:1 between AI^{3+} and probe. In addition, other metal ions in aqueous solution have no effect on the selectivity to AI^{3+} .

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Scheme 1. The synthesis of P1.

Experiment

Apparatus

IR spectra were recorded on Nicolet AVATAR360 infrared spectrometer. The MS spectra were performed on Bruker ESQUTRE LC-MC. ¹H NMR spectra were recorded by Bruker AVANCE-400 spectrometer. The fluorescence spectra were recorded on Hitachi F-7000FL spectrophotometer.

Materials

The solution of metal ions was prepared from their chloride salts and nitrate salts of analytical grade. The value of pH was adjusted by HCl (0.10 mol L^{-1} and 1.0 mol L^{-1}) and NaOH (0.10 mol L^{-1} and 1.0 mol L^{-1}) at room temperature. All chemicals were of analytical grade. All measurements of spectra were carried out in aqueous solution with 1% ethanol as cosolvent.

The synthesis of Schiff base

The synthetic route of Schiff base (P1) is shown in Scheme 1. It was prepared by refluxing a mixture of 0.50 mL 2-pyridine formaldehyde and 10 mmol 4-aminoantipyrine in 30.0 mL absolute ethanol for 8 h with HAc (3 d). The solvent was rotary evaporated and then was poured into 2.0 mL absolute ethanol. Pale yellow crystal was afforded after cooling with a yield of 98%. The structure was characterized by various spectroscopic analyses. m.p. 163.1– 164.0 °C. IR (KBr pellet, cm⁻¹): 3441, 3402, 1635, 1561, 1413, 757. Ms: m/z: 315 ([M + Na]⁺). ¹H NMR (400 MHz, CDCl₃): δ



Fig. 1. The fluorescent spectra of P1 in different solvents ([P1] = 1.0 \times 10 $^{-5}$ mol L^{-1} , λ_{ex} = 340 nm).



Fig. 2. UV–Vis absorbance of P1 and P1–Al³⁺ ([P1] = [M] = 1.0×10^{-5} mol L⁻¹).

9.795 (1H, S), 8.693 (2H, d), 7.989 (1H, d), 7.490 (2H, t), 7.46 (1H, t), 7.408 (2H, d), 7.335 (1H, t), 3.194 (3H, S), 2.529 (3H, S).

Results and discussion

The effect of solvents on fluorescent spectra

The fluorescent spectra of P1 for $\lambda_{ex} = 340$ nm have been recorded in various solvents and were displayed in Fig. 1. P1 exhibits different fluorescent emission and intensity in different solvents. The fluorescent emission was fixed at 430 nm in DMF, while it was fixed at 445 nm in aqueous solution. Taking into account of the economic cost and practical application, the experiments were carried out in aqueous media.

The selectivity of probe towards metal ions

The representative absorbance spectra of P1 ($5 \times 10^{-5} \text{ mol L}^{-1}$) in aqueous media before and after addition of Al³⁺ were shown in Fig. 2. The absorption spectra of P1 exhibited only a very weak band over 350 nm region. When Al³⁺ was added, a remarkable enhancement in absorbance at 345 nm was observed. These observations preliminary indicated that P1 had a response to Al³⁺ ion in aqueous solution.



Fig. 3. The fluorescent emission of P1 with 1 equiv various metal ions ([P1] = [M] = 1.0×10^{-5} mol L⁻¹, λ_{ex} = 340 nm).



Fig. 4. The fluorescence emission of different concentrations of Al^{3+} ([P1] = $2.0 \times 10^{-5} \text{ mol } L^{-1}$, $\lambda_{ex} = 340 \text{ nm}$). Inset: fluorescence intensity at 445 nm as a function of Al^{3+} concentration.

As shown in Fig. 3, the fluorescence spectra of P1 with various metal ions in aqueous solution were conducted to examine the selectivity. The solution of P1 emits fluorescence very weakly. The addition of 1 equiv of Al³⁺ induced a dramatic enhancement in fluorescent intensity, which was attributed to the formation of a P1–Al³⁺ complex. While no significant changes was found with the addition of other metal ions, such as Na⁺, K⁺, Pb²⁺, Ag⁺, Hg²⁺, Cd²⁺, Ba²⁺, Mg²⁺, Ni²⁺, Zn²⁺, Ca²⁺, Cu²⁺ and Fe³⁺. To further investigate the interaction of Al³⁺, a fluorescence titration experiment was carried out. It can be seen from Fig. 4 that a linear increase of fluorescence intensity of P1 was observed by increasing the amount of Al³⁺. The linear equation was determined to be *I* = 18.7692C + 107.1538 (*n* = 11, *R* = 0.9962). While the concentration of Al³⁺ ranges from 4.0×10^{-6} mol L⁻¹ to 1.6×10^{-5} mol L⁻¹ and the detection limit is 3.2×10^{-7} mol L⁻¹.

The influence of pH, response time and ionic strength on fluorescent spectra

Furthermore, the effect of pH on the fluorescent spectra of P1 in the absence and presence of Al³⁺ were investigated. The NaOH–HCl was used by alkali or acid and Tris-HCl buffer used by neutral. The



Fig. 5. The influence of pH on the fluorescent intensity of P1 in the absence and presence of Al^{3+} ([P1] = [Al^{3+}] = 1.0×10^{-5} mol L^{-1} , λ_{ex} = 340 nm).



Fig. 6. The influence of response time on the fluorescent intensity of P1 in the absence and presence of A^{13+} ([P1] = $[Al^{3+}] = 1.0 \times 10^{-5}$ mol L^{-1} , $\lambda_{ex} = 340$ nm).

results showed that P1 exhibited very weak fluorescent emission between pH 7.0 and 11.9, but the fluorescent intensity increased when the pH value was smaller than 7.0. In the presence of AI^{3+} , fluorescent intensity increased remarkably in the range of pH 2.3–8.5 as shown in Fig. 5. These results indicated that the AI^{3+} recognition process is free from pH interference under near neutral conditions. All the spectral experiments carried out in Tris-HCl (10 mM, pH = 7.2) aqueous buffer solution.

The effect of reaction time in Tris-HCl (10 mM, pH = 7.2) aqueous buffer solution was depicted in Fig. 6. No obvious fluorescence variation of P1 was observed even over a period of 2 h at 445 nm, the interaction of P1 with Al^{3+} was completed in less than 5 min, and the fluorescence intensity was stable at least 2 h. Thus the reaction time of 10 min may be used for this system.

The effect of ionic strength on the fluorescent spectra of P1–Al³⁺ in Tris-HCl (10 mM, pH = 7.2) aqueous buffer solution was depicted in Fig. 7. Various concentrations of KCl were used as the ionic strength regulator. With the ionic strength increasing, no obvious fluorescent intensity variation of P1–Al³⁺ was observed at 445 nm. These observations indicated that the ionic strength had no effect on fluorescent response of P1–Al³⁺.



Fig. 7. The influence of ionic strength on the fluorescent intensity of P1–Al³⁺ ([P1] = [Al³⁺] = 1.0×10^{-5} mol L⁻¹, $\lambda_{ex} = 340$ nm).



Fig. 8. The Job's plot for P1 and Al³⁺.



Scheme 2. The biding mode of P1 and Al³⁺.

The mechanism of the complex coordination

To determine the stoichiometry between P1 and Al³⁺, the method of Job's plot has been carried out with the total concentration of



Fig. 10. Metal ion selectivity of P1 $(1.0 \times 10^{-5} \text{ mol } \text{L}^{-1})$ in aqueous solution. The red bars represent the fluorescent intensity of P1 and Al³⁺ $(1:1, 1.0 \times 10^{-5} \text{ mol } \text{L}^{-1})$. The black bars represent the fluorescence changes that occur upon the addition of competing ions to the solution containing P1 and Al³⁺ $(1:1, 1.0 \times 10^{-5} \text{ mol } \text{L}^{-1})$. 0: only P1; 1: blank; 2: Ag⁺; 3: Pb²⁺; 4: Na⁺; 5: K⁺; 6: Hg²⁺; 7: Cd²⁺; 8: Ba²⁺; 9: Zn²⁺; 10: Mg²⁺; 11: Cu²⁺; 12: Ni²⁺; 13: Ca²⁺; 14: Fe³⁺; 15: Cr³⁺, 16: Ga³⁺, 17: SCN⁻, 18: SO²₄, 19: CrO²₄, 20: Br⁻, 21: Cr2O²₇, 22: PO³⁻₄, 23: ClO³₅, 24: F⁻, 25: Cl⁻, 26: I⁻, 27: S₂O²₈, 28: NO³₅, 29: HSO⁻₄, 30: CO²₃, 31: HCO³₃, 32: H₂PO⁻₄, 33: AcO⁻, 34: all the metal ions and anions. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

 1.0×10^{-4} mol L⁻¹ [27]. It can be seen clearly from Fig. 8 that the maximum was at a molar fraction of 0.5, which indicated the formation of 1:1 between P1 and Al³⁺. According to literature [28–31], the binding mode of P1 and Al³⁺ was also proposed as shown in Scheme 2. It was inferred that Al³⁺ coordinated with oxygen atom of C=O, the nitrogen atom of C=N and pyridine, where two five-number rings formed.

Furthermore, IR spectra of P1 and P1–Al³⁺ were taken in KBr disks, respectively, and the results were shown in Fig. 9. The peak at 1719 cm⁻¹, which corresponds to the characteristic carbonyl absorption of P1, was shifted to 1642 cm⁻¹ upon chelating with Al³⁺. These results indicate that carbonyl group is involved in Al³⁺ coordination [32,33].

In order to further confirm the P1 coordinating with Al³⁺, the EDTA-adding experiments were conducted to examine the reversibility of the probe P1. The results displayed that, the fluorescence



Fig. 9. IR spectra of P1 (a) and P1-Al³⁺ complex (b) in KBr disks.

Table 1	
Determination of Al^{3+} in samples ($n = 5$).	

Sample	Al^{3+} measured (10 ⁻⁶ mol L ⁻¹)	Al^{3+} added (10 ⁻⁶ mol L ⁻¹)	Al ³⁺ found $(10^{-6} \text{ mol } \text{L}^{-1})$	Recovery (%)	R.S.D. (%)
River water	5.2	0.5 5	5.68 10.26	99.7 100.6	2.1 3.0
Tap water	8.6	0.5 5	9.25 13.81	99.5 101.5	1.8 2.3

intensities of solution containing P1 and Al³⁺ decrease with increasing EDTA concentration. When Al³⁺ was added to the system again, the fluorescence could be reproduced again. These findings indicated that P1 reversibly coordinated with Al³⁺.

The interference from other metal ions

Under the optical conditions, the influence of other metal ions and anions were tested by premixing P1 with other ions, such as Na⁺, K⁺, Pb²⁺, Ag⁺, Hg²⁺, Cd²⁺, Ba²⁺, Mg²⁺, Ni²⁺, Zn²⁺, Ca²⁺, Cu²⁺, Fe³⁺, Cr³⁺, Ga³⁺, SCN⁻, SO²⁻₄, CrO²⁻₄, Br⁻, Cr₂O²⁻₇, PO³⁻₄, ClO³₃, F⁻, Cl⁻, I⁻, S₂O²⁻₈, NO³₃, HSO⁴₄, CO³⁻₂, HCO³₃, H₂PO⁴₄ and AcO⁻. The experimental results were shown in Fig. 10. Basically, these ions did not induce interference the fluorescent intensity of the sensitivity towards Al³⁺. As a result, P1 can be seen as a highly selectivity and sensitivity for Al³⁺ in aqueous solution.

Preliminary analytical application

In order to examine the applicability of the proposed method in practical sample analysis, the sensor P1 was applied in the determination of AI^{3+} in river water and tap water samples. The river water samples were obtained from the campus of Henan University and simply filtered. All these samples were adjusted pH by Tris-HCl (10 mM, pH = 7.2) aqueous buffer solution and spiked with standard AI^{3+} solutions, then analyzed with proposed sensor P1 and recorded with a F-7000FL spectrofluorimeter. The results were summarized in Table 1, which showed satisfactory recovery and R.S.D. values for all of the samples. Thus, the present probe seems useful for the determination of AI^{3+} in real samples.

Conclusion

In summary, a highly sensitive chemosensor for Al^{3+} based on 2-pyridineformaldehyde and 4-aminoantipyrine has been synthesized and structurally characterized. The new sensor displayed an excellent selectivity towards Al^{3+} , no significant optical interferences arise from the other examined metal ions and anions such as Na⁺, K⁺, Pb²⁺, Ag⁺, Hg²⁺, Cd²⁺, Ba²⁺, Mg²⁺, Ni²⁺, Zn²⁺, Ca²⁺, Cu²⁺, Fe³⁺, Cr³⁺, Ga³⁺, SCN⁻, SO²⁻, CrO²⁻, Br⁻, CrO²⁻, PO³⁻, ClO³, F⁻, Cl⁻, I⁻, S₂O²⁻, NO³, HSO⁴, CO²⁻, HCO³, H₂PO⁴ and AcO⁻. This probe successfully applied to determination of Al³⁺ in water samples analysis.

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References

- S.M.Z. Al-Kindy, Z. Al-Mafrigi, M.S. Shongwe, Luminescence 26 (2011) 462– 470.
- [2] E. Oliveira, H.M. Santos, J.L. Capelo, C. Lodeiro, Inorg. Chim. Acta 381 (2012) 203-211.
- [3] K. Kaur, V.K. Bhardwaj, N. Kaur, N. Singh, Inorg. Chem. Commun. 18 (2012) 79– 82.
- [4] C. Park, K.W. Cha, Talanta 51 (2000) 769-774.
- [5] I.V. Toth, A.O.S.S. Rangel, J.L.M. Santos, J.L.F.C. Lima, J. Agr. Food Chem. 52 (2004) 2450–2454.
- [6] B. Bocca, A. Alimoti, F. Petrucci, N. Violante, G. Sancesario, G. Forte, O. Senofonte, Spectrochim Acta B 59 (2004) 559–566.
- [7] J.W. Di, S.P. Bi, T.Y. Yang, M. Zhang, Sens. Actuat. B: Chem. 99 (2004) 468-473.
- [8] A. Yari, L. Darvishi, M. Shamsipur, Anal. Chim. Acta 555 (2006) 329-335.
- [9] X.J. Xie, Y. Qin, Sens. Actuat. B: Chem. 156 (2011) 213-217.
- [10] J.Q. Ren, H. Tian, Sensors 7 (2007) 3166-3178.
- [11] J. Kawakami, T. Mizuguchi, S. Ito, Anal. Sci. 22 (2006) 1383-1384.
- [12] D. Maity, T. Govindaraju, Chem. Commun. 46 (2010) 4499-4501.
- [13] M. Arduini, F. Felluga, F. Mancin, P. Rossi, P. Tecilla, U. Tonellato, N. Valetinuzzi, Chem. Commun. 13 (2003) 1606–1607.
- [14] Y.W. Wang, M.X. Yu, Y.H. Yu, Z.P. Bai, Z. Shen, F.Y. Li, X.Z. You, Tetrahedron Lett. 50 (2009) 6169–6172.
- [15] A. Banerjee, A. Sahana, S. Das, S. Lohar, S. Guha, B. Sarkar, S.K. Mukhopadhyay, A.K. Mukherjee, D. Das, Analyst 137 (2012) 2166–2175.
- [16] V.C. DaSilveira, J.S. Luz, C.C. Oliveira, İ. Graziani, M.R. Ciriolo, A.M.D.C. Ferreira, J. Inorg. Biochem. 102 (2008) 1090–1103.
- [17] Y. Li, Z.Y. Yang, Inorg. Chim. Acta 362 (2009) 4823-4831.
- [18] P.G. Cozzi, Chem. Soc. Rev. 33 (2004) 410-421.
- [19] H. Miyasaka, N. Matsumoto, H. Okawa, N. Re, E. Gallo, C. Floriani, J. Am. Chem. Soc. 118 (1996) 981–994.
- [20] N. Raman, S. Ali Syed Fathima, J. Raja Dhaveethu, J. Serb. Chem. Soc. 73 (2008) 1063-1071.
- [21] M.H. Yan, T.R. Li, Z.Y. Yang, Inorg. Chem. Commun. 14 (2011) 463-465.
- [22] X.S. Gao, J.T. Wang, Inorg. Chim. Acta 386 (2012) 1-7.
- [23] C.W. Yu, J. Zhang, M.Y. Ding, L.X. Chen, Anal. Methods 4 (2012) 342-344.
- [24] Q.Y. Zhou, W.Z. Liu, L. Chang, F. Chen, Spectrochim. Acta Part A Mol. Biomol. Spectrosc. 92 (2012) 78-83.
- 0n [25] S. Dalapati, S. Jana, M.A. Alam, N. Guchhait, Sens. Actuat. B: Chem. 160 (2011) 1106–1111.
 - [26] J. Zhang, C.W. Yu, G. Lu, Q.Y. Fu, N. Li, Y.X. Ji, New J. Chem. 36 (2012) 819–822.
 - [27] W.C. Vosburgh, R.G. Cooper, J. Am. Chem. Soc. 63 (1941) 437–442.
 - [28] M.J.C. Marenco, C. Fowley, B.W. Hyland, G.R.C. Hamilton, D.G. Riano, J.F. Callan, Tetrahedron Lett. 53 (2012) 670–673.
 - [29] X.H. Jiang, B.D. Wang, Z.Y. Yang, Y.C. Liu, T.R. Li, Z.C. Liu, Inorg. Chem. Commun. 14 (2011) 1224–1227.
 - [30] K.K. Upadhyay, A. Kumar, Org. Biomol. Chem. 8 (2010) 4892-4897.
 - [31] D. Maity, T. Govindarju, Chem. Commun. 46 (2010) 4499-4501.
 - [32] N. Wanichacheva, K.I. Setthakarn, N. Prapawattanapol, O. Hanmeng, V.S. Lee, K. Grudpan, J. Lumin. 132 (2012) 35–40.
 - [33] M.L. Zhao, X.F. Yang, S.F. He, L.P. Wang, Sens. Actuat. B: Chem. 135 (2009) 625– 631.