Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 98 (2012) 14–17

Contents lists available at SciVerse ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Fe^{3+}-selective fluorescent probe based on aminoantipyrine in aqueous solution

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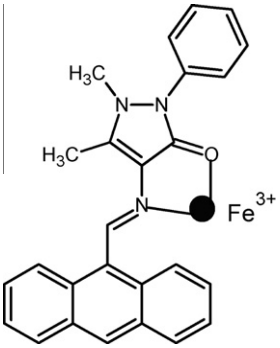
HIGHLIGHTS

- We designed and synthesized a new Schiff base fluorescent probe.
- The probe showed high sensitivity for Fe^{3+} over other metal ions in aqueous solution.
- The other metal ions have no effect on the detection of Fe^{3+}.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 23 April 2012
Received in revised form 25 July 2012
Accepted 12 August 2012
Available online 22 August 2012

Keywords:
Anthraldehyde
Aminoantipyrine
Fluorescence
Fe^{3+}

ABSTRACT

A novel and simple Schiff base composed with 9-anthraldehyde and 4-aminoantipyrine was synthesized and characterized as a fluorescent probe. In the presence of Fe^{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 Fe^{3+}, and the possible binding mode of the system was also proposed. Moreover, other examined metal ions had no effect on the detection of Fe^{3+}.

Introduction

As a convenient and efficient method, numerous fluorescent sensors have been synthesized and developed to detect important metal ions, such as Zn^{2+}, Hg^{2+}, Cu^{2+}, Pb^{2+}, Ag^{+}, Ni^{2+} [1–6]. Iron is one of the most essential elements in the biological systems and plays an important part in many chemical and biological processes [7]. There is an evidence indicated that either its overload or deficiency may induce many diseases, including dysfunction of organs and certain cancers [8,9]. Up to now, a serious of fluorescent sensors for Fe^{3+} has been designed and synthesized [10–15]. But most of them were reported in organic solvent and the synthesis methods are always too complicated, which limit their application. Therefore, it is of great demand of developing simple fluorescent probe for Fe^{3+} in aqueous solution.

For decades, Schiff base are widely designed and prepared for its high yield and one-step procedure via condensation of amines and aldehydes [16]. Recently, a lot of examples were reported, where Schiff base can be used as fluorescent chemosensors [17–21]. Herein we report the synthesis and characterization of a new Schiff base prepared from 9-anthraldehyde and 4-aminoantipyrine. The results show that it can be seen as a highly selective and sensitive probe for Fe^{3+} in aqueous solution.

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http://dx.doi.org/10.1016/j.saa.2012.08.025

Experiment

Materials

All the chemicals were of analytical grade. The solution of metal ions was prepared from their chloride salts and nitrate salts of analytical grade. All measurements of spectra were carried out in aqueous solution with 1% ethanol as cosolvent. The value of pH was adjusted by NaOH (0.1 mol L^{-1} and 1 mol L^{-1}) and HCl (0.1 mol L^{-1} and 1 mol L^{-1}) at room temperature.

Apparatus

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

The synthesis of the Schiff base (P1)

The Schiff base (Scheme 1) was prepared by refluxing a mixture of 9-anthraldehyde (9 mmol) and 4-aminoantipyrine (10 mmol) in absolute ethanol (30 mL) for 8 h with AcOH (3 d). After cooling to room temperature, orange crystal was afforded with a yield of 96%. The proposed molecular structure and its purity were confirmed by various spectroscopic analyses. m.p. 230-231°C. IR (KBr pellet, cm^{-1}): 3407, 3048, 1645, 1590, 755. Ms: m/z: 392.46 ($[M+H]^+$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.041 (1H, S), 8.9445 (2H, d), 8.482 (1H, S), 8.0135 (2H, d), 7.461-7.549 (9H, m), 3.229 (3H, S), 2.579 (3H, S).

Results and analysis

Spectral studies

To examine the sensitivity of P1, fluorescence emission spectra of P1 with 1 equiv various metal ions were investigated in aqueous solution. As shown in Fig. 1, P1 displays weak fluorescence emission at 516 nm without the addition of metal ions. To our surprise, a dramatic enhancement in the fluorescent intensity was observed in the presence of Fe^{3+}. While the addition of other metal ions, such as Ag^+, Pb^{2+}, Na^+, K^+, Hg^{2+}, Cd^{2+}, Ba^{2+}, Zn^{2+}, Mg^{2+}, Cu^{2+}, Ni^{2+}, Ca^{2+}, Al^{3+} and Fe^{2+}, have no distinct influence on fluorescent intensity. This means that P1 exhibits high fluorescent selectivity to Fe^{3+} over other metal ions.

In addition, the influence of different concentrations of Fe^{3+} was also evaluated when the concentration of Fe^{3+} changed from 1.0×10^{-6} mol L^{-1} to 2.25×10^{-5} mol L^{-1}. It can be seen from Fig. 2 that the fluorescent intensity at 516 nm increased with the increase of concentration of Fe^{3+}. When the change of fluorescent intensity was plotted against the concentration of Fe^{3+}, a good linearity relationship was observed in the range of 1.0×10^{-6}–2.0×10^{-5} mol L^{-1} with a correlation coefficient of 0.9954. The regression equation is $I_{516} = 342.16 + 41.35c$ (10^{-5} mol L^{-1}) and was shown in Fig. 3. Based on the definition of detection limit, the limit of detection for Fe^{3+} is up to 2.11×10^{-7} mol L^{-1}.

The influence of pH and response time

The influence of pH on the fluorescent intensity of P1 in the absence and presence of Fe^{3+} has been determined in the pH range of 2.4-12.4. As shown in Fig. 4, the results show that P1 has very weak fluorescence emission between pH 4.3 and 12.4. While the value of pH was smaller than 4.3, it shows that fluorescent intensity increased sharply. In the presence of Fe^{3+}, the enhancement of the fluorescent intensity kept platform over a pH range (4.3-7.2). So the all spectral experiments were carried out at pH 5.3.

The response time of the reaction system in (pH = 5.3) aqueous solution were investigated (Fig. 5). No obvious fluorescence variation of P1 was observed even over a period of 2 h at 516 nm, the interaction of P1 with Fe^{3+} was completed in less than 10 minutes. Thus a reaction time of 10 minutes may be used for this system.

Stoichiometry and reaction mechanism

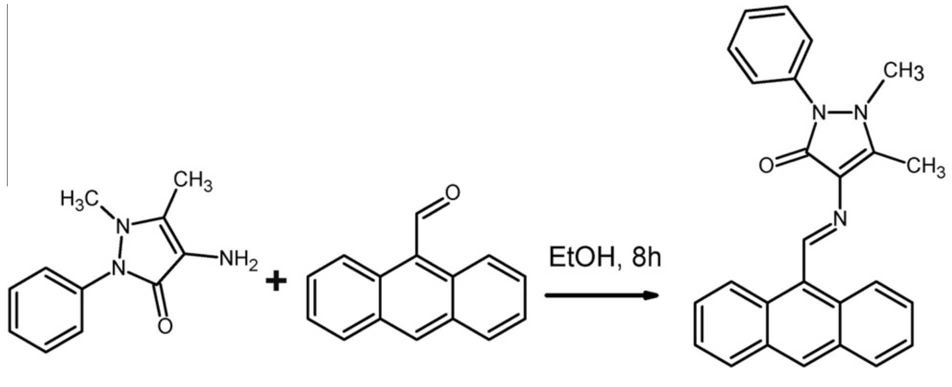
To further understand the binding behavior and determine the stoichiometry of the complex, the Job's plot [22] for the system was performed in aqueous solution by keeping the total concentration of P1 and Fe^{3+} at 1×10^{-4} $molL^{-1}$ and changing the molar ration of Fe^{3+} ($[Fe^{3+}]/[Fe^{3+} + P1]$) from 0 to 1. As shown in Fig. 6, the result shows that a maximum at a molar fraction of 0.5, indicating the formation of 1:1 complex of P1 and Fe^{3+}.

In order to further confirm the P1 coordinating with Fe^{3+}, the EDTA-adding experiments were conducted to examine the reversibility of the probe P1. The results displayed that, the fluorescence intensities of solution containing P1 and Fe^{3+} decrease with increasing EDTA concentration. When Fe^{3+} was added to the system again, the fluorescence could be reproduced again. These findings indicated that P1 reversibly coordinated with Fe^{3+}.

Based on the basic results, a possible coordination of P1 and Fe^{3+} was proposed and shown in Scheme 2. It was assumed that a five-membered ring formed by the metal ion, nitrogen atom and oxygen atom according to literature [23–27].

The interference from other metal ions

Ion selectivity study has been performed in aqueous solution. Due to the existence of other metal ions and anions of Ag^+, Pb^{2+},



Scheme 1. The synthesis of P1.

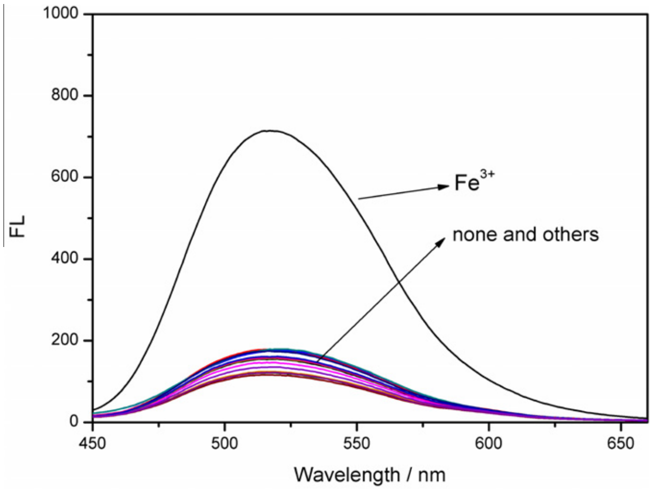


Fig. 1. The fluorescent emission of P1 with 1 equiv various metal ions ([P1] = [M] = 1 × 10^{-5} $molL^{-1}$, λ_{ex} = 375 nm).

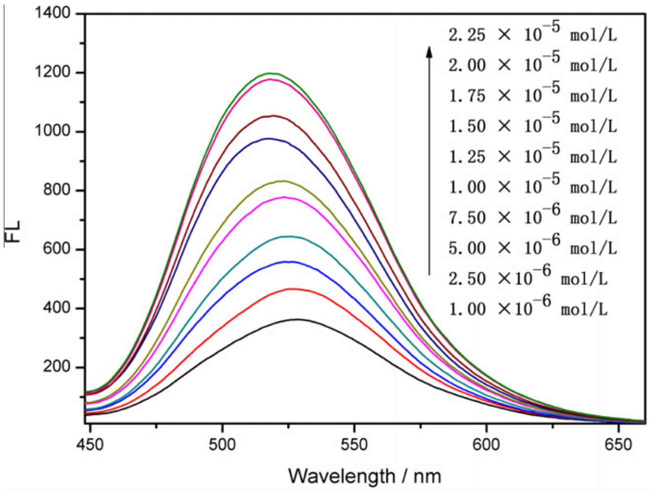


Fig. 2. The fluorescence emission of different concentrations of Fe^{3+} ([P1] = 2.0 × 10^{-5} $molL^{-1}$, λ_{ex} = 375 nm).

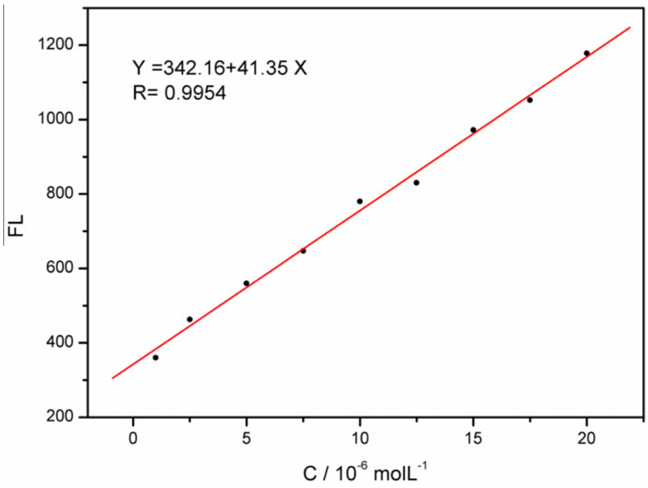


Fig. 3. The linear relationship of the fluorescent intensity at 516 nm (λ_{ex} = 375 nm).

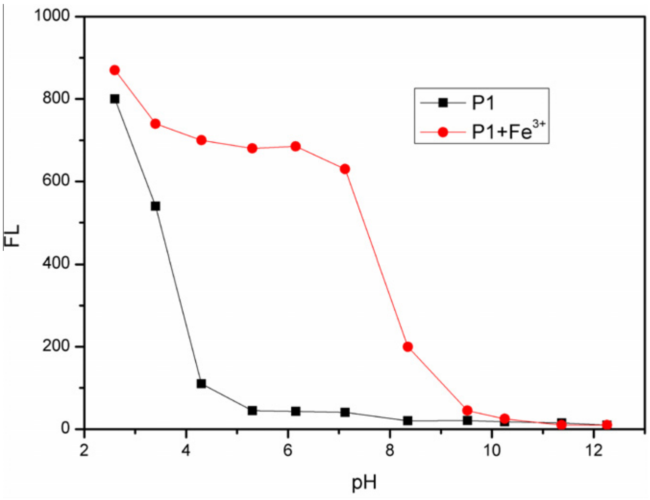


Fig. 4. The influence of pH on the fluorescent intensity of P1 in the absence and presence of Fe^{3+} ([P1] = [Fe^{3+}] = 1 × 10^{-5} $molL^{-1}$, λ_{ex} = 375 nm).

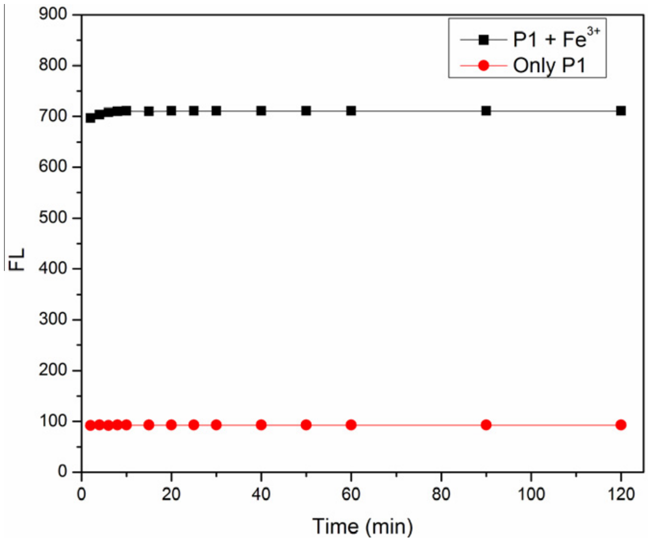


Fig. 5. The influence of response time on the fluorescent intensity of P1 in the absence and presence of Fe^{3+} ([P1] = [Fe^{3+}] = 1 × 10^{-5} $molL^{-1}$, λ_{ex} = 375 nm).

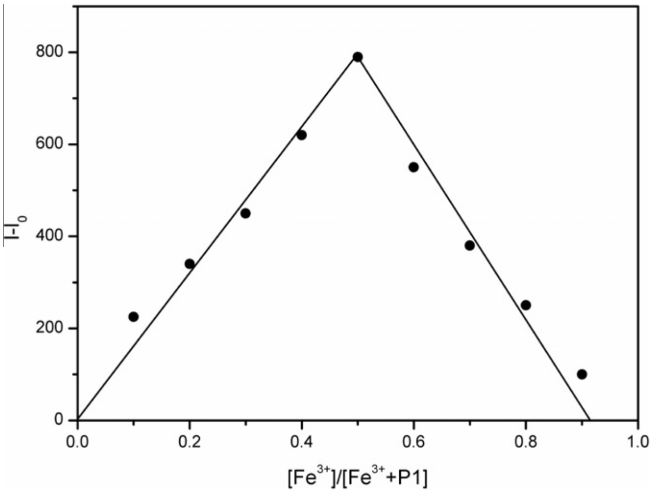
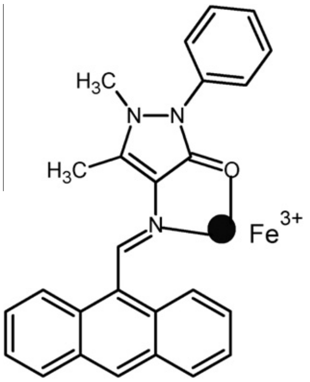


Fig. 6. The job's plot for P1 and Fe^{3+}.



Scheme 2. The biding mode of P1 and Fe^{3+}.

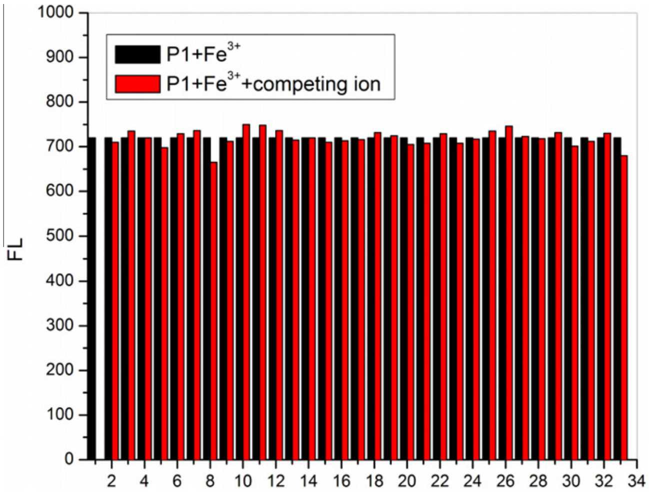


Fig. 7. Metal ion selectivity of P1 (1×10^{-5} $molL^{-1}$) in aqueous solution. The red bars represent the fluorescent intensity of P1 and Fe^{3+} (1:1, 1×10^{-5} $molL^{-1}$). The black bars represent the fluorescence changes that occur upon the addition of competing ions to the solution contaning P1 and Fe^{3+} (1:1, 1×10^{-5} $molL^{-1}$). 1: blank; 2: Ag^+; 3: Pb^{2+}; 4: Na^+; 5: K^+; 6: Hg^{2+}; 7: Cd^{2+}; 8: Ba^{2+}; 9: Zn^{2+}; 10: Mg^{2+}; 11: Cu^{2+}; 12: Ni^{2+}; 13: Ca^{2+}; 14: Al^{3+}; 15: Fe^{2+}; 16: SCN^-; 17: SO_4^{2-}; 18: CrO_4^{2-}; 19: Br^-; 20: $Cr_2O_7^{2-}$; 21: PO_4^{2-}; 22: ClO_3^-; 23: F^-; 24: Cl^-; 25: I^-; 26: $S_2O_8^{2-}$; 27: NO_3^-; 28: HSO_4^-; 29: CO_3^{2-}; 30: HCO_3^-; 31: HPO_4^-; 32: AcO^-; 33: all the metal ions and anions(For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).

Na^+, K^+, Hg^{2+}, Cd^{2+}, Ba^{2+}, Zn^{2+}, Mg^{2+}, Cu^{2+}, Ni^{2+}, Ca^{2+}, Al^{3+}, Fe^{2+}, SCN^-, SO_4^{2-}, CrO_4^{2-}, Br^-, $Cr_2O_7^{2-}$, PO_4^{2-}, ClO_3^-, F^-, Cl^-, I^-, $S_2O_8^{2-}$, NO_3^-, HSO_4^-, CO_3^{2-}, HCO_3^-, HPO_4^-, AcO^- in biological systems, the interference of these ions should be investigated in consideration. As illustrated in Fig. 6, the tolerance of P1 for Fe^{3+} over other metal ions and anions was performed by the competition experiments. The data show that no obvious interference could be observed to the sensing of Fe^{3+} by P1, which means that P1 can be used as a sensitive probe for Fe^{3+} under biological system.(see Fig. 7)

Conclusion

In summary, a highly sensitive chemosensor for Fe^{3+} based on anthraldehyde and antipyrine has been synthesized and structurally characterized. Noteworthily, the new sensor displayed an excellent selectivity towards Fe^{3+}, no significant optical interferences arise from the other examined metal ions such as Ag^+, Pb^{2+}, Na^+, K^+, Hg^{2+}, Cd^{2+}, Ba^{2+}, Zn^{2+}, Mg^{2+}, Cu^{2+}, Ni^{2+}, Ca^{2+}, Al^{3+} and Fe^{2+}. These attributes augur well for the applications of the probe in monitoring Fe^{3+} concentrations in real samples down to micromolar range.

Acknowledgements

The authors thank the Foundation and Cutting-Edge Technology Research Project of Henan Science and Technology Department (122300410260), the International Science Cooperation Project of Henan Province (124300510012) and the Key Scientific and Technological Project of Henan Province (112102310360).

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