



A COLORIMETRIC SENSOR FOR THE RECOGNITION AND QUANTIFICATION OF Fe^{2+}/Fe^{3+} SPECIES

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Abstract

A simple and easily synthesized colorimetric chemosensor based on oxygen and nitrogen binding and signaling unit, has been synthesized in one-step procedure. Sensor showed immediate responses towards Fe^{2+} and Fe^{3+} species through change in absorption spectrum. Moreover, instant color change from yellow to pink can be easily observed by naked-eye. Thus, this sensor provides an approach in recognizing biologically important element through simple and easily affordable technique.

Keywords: Fe^{2+} , Fe^{3+} , sensor, colorimetry



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Introduction

Iron is the most plentiful transition metal for both plants and animals. It plays many important roles in cellular metabolism, enzyme catalysis, cofactor in many enzymatic reactions, as an oxygen carrier in haemoglobin and act as mediator in electron transport [1-5]. Besides, its importance, its imbalance causes many diseases like diabetes, heart diseases, anemia, liver and kidney diseases. Hence, its proper level in human body is very important. Therefore, its recognition gains importance from past decades. A chromogenic “naked eye” chemosensors have become potentially important over other recognition methods for metal ion recognition due to their sensitivity, selectivity, and ability to detect very low concentrations and no requirement for costly instruments. In literature, various fluorescent and colorimetric “turn-on” chemosensors have been developed for the detection of Fe^{3+} and Fe^{2+} [6-8]. A colorimetric sensor is beneficial because the analyte ion can be detected at low concentration without any other interferences ensuing in the improved sensitivity of the method. Various other determination methods of iron mainly exploit highly sophisticated instruments such as capillary electrophoresis (CE) [9], inductively coupled plasma-atomic emission spectrometry (ICP-AES) [10] and flame atomic absorption spectroscopy (FAAS) [11], which is not always

convenient due to their high operational cost, skillful required to run the instrument, complicated and laborious sample preparation methods and high maintenance charges.

Consequently, development of a cheap chromogenic sensor with simple synthetic approach and high empathy for metal capturing should be intended for sensing purposes. Among various types of sensors, Schiff base derivatives appeared us possibly good sensors due to their high affinity towards transition metals and easy to synthesize.

Experimental

Materials and Instruments

All the reagents namely ethylene diamine (Sigma-Aldrich), copper(II) nitrate trihydrate (HPLC Lab Reagents), nickel(II) nitrate (Merck), iron(III) nitrate anhydrous (Thomas Baker), iron(II) sulphate (Loba Chemie), manganese(II) acetate (Sigma-Aldrich), chromium(III) nitrate (Loba Chemie), cobalt(II) nitrate (Loba Chemie), zinc(II) nitrate hexahydrate (HPLC Lab Reagents), lead(II) nitrate (Fischer Scientific), mercuric(II) chloride (Merck), cadmium(II) nitrate tetrahydrate (CDH), tetraethylammonium fluoride (Acros organics), potassium chloride (Fischer Scientific), potassium bromide (Fischer Scientific), sodium acetate (Qualigens), were purchased and used as such. Different solvents (acetonitrile, methanol) were purchased from Merck (India) and were dried before use.

All the parameters were optimized using stock solution of sensor (1 mM), This stock solution was diluted further to get desired concentration of solution for various spectroscopic measurements. Stock solutions of various cations and anions (1 mM) were prepared by dissolving respective amounts of corresponding salts in methanol.

Infrared spectra were routinely obtained as thin films on a Bruker alpha Eco-ATR spectrometer. The solution ¹H NMR spectrum was recorded at 25°C on BRUKER AVANCE II 400-NMR spectrometer. Chemical shifts in ppm are reported relative to tetramethylsilane (TMS). UV-Vis absorption spectral measurements were carried out at room temperature using EI 2375 double beam spectrophotometer in the range 200-800 nm.

Synthesis of sensor

Sensor was prepared by the procedure reported in literature. Briefly, a solution of 2-hydroxy-4-methoxybenzophenone (2 mmol) in methanol (30 mL) was added to a solution of ethylenediamine (1 mmol) in methanol (20 mL). The contents were refluxed for 6 hours and thereafter, washed with diethyl ether. It resulted in yellow crystalline solid which was filtered. Yield: 86 %; M.Pt: 225-230 °C; FT-IR (cm⁻¹): 1495, 1540 (C=C), 1602 (C=N), 3032 (OH); ¹H NMR (400 MHz, CDCl₃): δ (ppm) 3.84 (s, 6H, OCH₃), 5.23 (s, 4H, NCH₂CH₂N), 6-8 (phenyl protons), 10.47 (2H, -OH).

Photo-physical studies

Colorimetric response of sensor towards metallic species

The colorimetric response of Schiff base solution was studied by the addition of various metal ion solutions. Briefly, in 2 mL of methanolic solution of sensor (0.5 mM), 1 mL of methanolic solution of metal ion (1 mM; Cr³⁺, Mn²⁺, Fe²⁺, Fe³⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Cd²⁺, Pb²⁺ and Hg²⁺ solution) was added, respectively. The colorimetric changes were recorded after the addition of each metal ion.

UV-Vis absorption titration of Fe²⁺ and Fe³⁺ ions, respectively with sensor

To 2 mL of methanolic solution of sensor (0.1 mM), 0.01 mL of iron species (Fe³⁺ and Fe²⁺, respectively) solution (0.1 mM) was added. The solution was shaken thoroughly and transferred to a quartz optical cell to record absorption spectrum. A complete titration was done by increasing the concentration of metal solution (0.01 mL) every time and spectral data was recorded from 200 nm to 800 nm till the constant peak appeared.

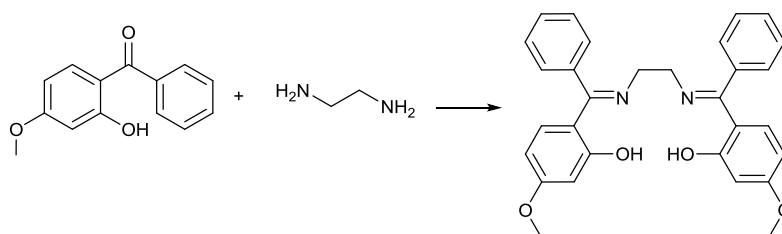
Job's measurement

The binding behavior of **1** towards metallic species (Fe²⁺, Fe³⁺) to form metal-sensor conjugates was studied by Job's method. In this exercise, varying volumes of 0.05 mM methanolic solution of **1** (i.e. 4.0, 3.5, 3.0, 2.5, 2.0, 1.5, 1.0, 0.5, 0 mL) were taken in separate 5 mL glass vials and metallic species (0.05 mM) were added to make the total volume of each vial 4 mL. The spectra were recorded for each solution and graph of absorption versus mole fraction of respective metallic species was plotted.

Result and discussion

Synthesis of Schiff base sensor

Schiff base sensor was synthesized by the condensation reaction of 2-hydroxy-4-methoxybenzophenone with ethylenediamine in methanol at room temperature (Scheme 1), and characterized by IR, NMR.



Scheme 1 Synthetic route for Schiff base sensor

Various characterization studies IR, ¹H NMR spectroscopy revealed the formation of Schiff base sensor.

Photophysical studies

Colorimetric response

Initially, the qualitative evaluation of sensor to recognize various metal ions such as Cr^{3+} , Mn^{2+} , Fe^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , Pb^{2+} and Hg^{2+} was pursued. It showed swift and highly selective colorimetric changes from yellow to pink in the presence of iron species, however, its color remained impassive in the presence of other metallic species. Consistent with changes of color, the addition of Fe^{3+} and Fe^{2+} caused significant bathochromic shift in UV-Vis absorption spectrum of sensor.

UV-Vis spectroscopic studies

To get a quantitative evaluation of the specific interaction between sensor and iron species (Fe^{2+} and Fe^{3+}), UV-Vis titration experiment with incremental addition of metal ion was conducted. The sensor showed significant enhancement in the absorption band present in the region 425-700 nm both for Fe^{3+} and Fe^{2+} ions. Two isosbestic points were generated at 417 nm and 362 nm in case of Fe^{3+} (Fig. 1), and 414 nm and 355 nm in case of Fe^{2+} (Fig. 2) indicating the presence of two species in the solution. In addition to rise in the absorption band centered at 504 nm, subsequent additions of metal ions promoted a gradual decrease of the original absorption band of sensor centered at 380 nm. These significant changes in the UV-Vis spectrum indicated the complex formation of sensor with $\text{Fe}^{3+}/\text{Fe}^{2+}$ ions.

The Job's plot analysis for the binding behaviour of metal conjugate of sensor with iron species suggested a 1:2 stoichiometry for both Fe^{3+} and for Fe^{2+} . It was obtained by plotting maximum absorption at respective wavelengths against mole fraction of metal ion.

The limit of detection for the Fe^{2+} and Fe^{3+} are found to be $8 \mu\text{M}$ and $6.8 \mu\text{M}$ by 3μ

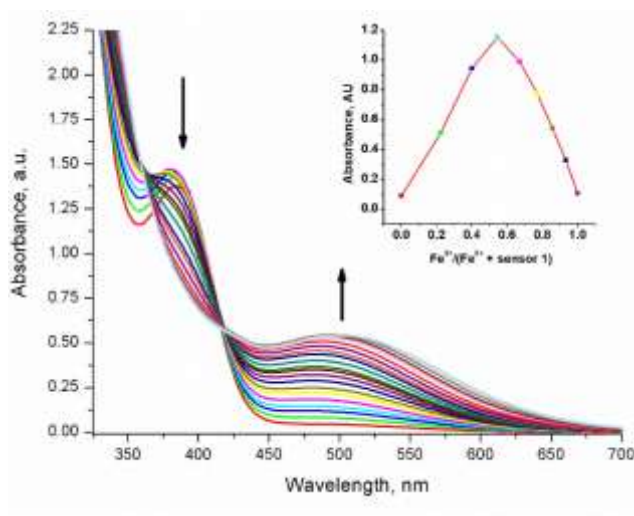


Fig. 1 Changes in absorption spectra obtained upon gradual addition of 0.01 mL Fe^{3+} (0.1 mM) in Sensor 1 (0.1 mM).

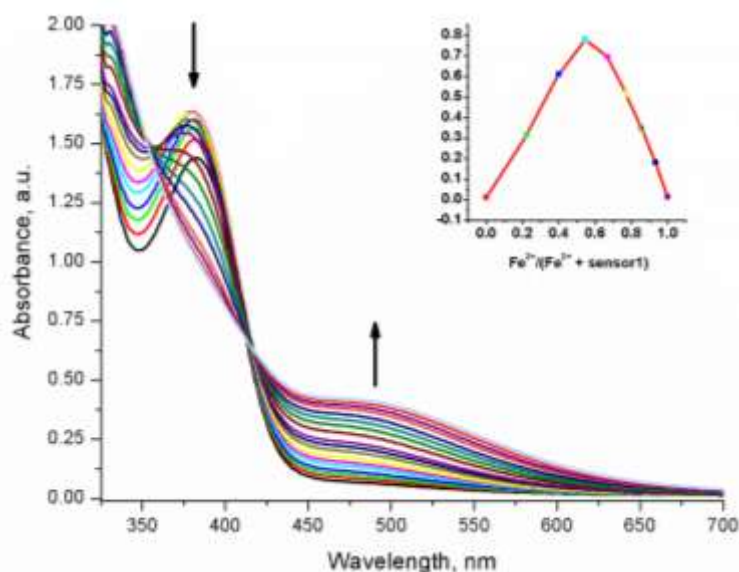


Fig. 2 Changes in absorption spectra obtained upon gradual addition of 0.01 mL Fe^{2+} (0.1 mM) in Sensor **1** (0.1 mM).

Interference study on chromogenic response of sensor

The complex formation of sensor with Fe^{2+} and Fe^{3+} in the presence of aforementioned anions and cations was examined. No coexisting cations or anions interfered with the detection of Fe^{2+} and Fe^{3+} using sensor. Hence, sensor is highly selective for the recognition of both the iron species.

Conclusions

Hence, a simple and effective Schiff base sensor has been synthesized for the recognition of Fe^{2+} and Fe^{3+} species which showed highly intense color in their presence. Therefore, it can be easily observed by naked eye.

References:

- B. D' Autreaux, N.P. Tucker, R. Dixon, S. Spiro, A non-haem iron centre in the transcription factor NorR senses nitric oxide, Nature 437 (2005) 769-772.*
- R.R. Crichton, D.T. Dexter, R.J. Ward, Metal based neurodegenerative diseases - from molecular mechanisms to therapeutic strategies, Coord. Chem. Rev. 252 (2008) 1189-1199.*
- J.J. R. Frausto da silva, R.J.P. Williams, The Biological Chemistry of the Elements. The Inorganic Chemistry of Life, Oxford University Press, New York, NY, 1991.*
- L. Huang, F. Hou, J. Cheong, P. Xi, F. Chen, D. Bai, Z. Zhang, Selective off-on fluorescent chemosensor for detection of Fe^{3+} ions in aqueous media, Org. Biomol. Chem. 10 (2012) 9634-9638.*
- D.M. Strickland, The Resistivity of Iron and Its Application to the Chemical Industry, Ind. Eng. Chem. 15 (1923) 566-569.*
- R. Hudson, G. Hamasaka, T. Osako, Y.M.A. Yamada, C.-J. Li, Y. Uozumi, A. Moores. Highly efficient iron(0) nanoparticle-catalyzed hydrogenation in water in flow, Green Chem. 15 (2013), 2141-2148.*

- A.R. Timerbaev, E. Dabek-Zlotorzynska, A.G.T. Marc van den Hoop, *Inorganic environmental analysis by capillary electrophoresis*, *Analyst* 124 (1999) 811-826.
- P. Vanloot, B. Coulomb, C. Brach-Papa, M. Sergent, J.L. Boudenne, *Multivariate optimization of solid phase extraction applied to iron determination in finished waters*, *Chemosphere* 69 (2007) 1351-1360.
- T. Shampur, I. Sheikhshoae, M.H. Mashhadizadeh, *Flame atomic absorption spectroscopy (FAAS) determination of iron (iii) after pre-concentration onto modified analcime zeolite with 5-((4-nitrophenylazo)-N-(2',4'-dimethoxyphenyl)) salicyldimine by column method*, *J. Anal. At. Spectrom.* 20 (2005) 476-438.