

# Cation Sensing of Pyridoxal Derived Sensors Towards Fe (II) Ion in Pure Aqueous Solution

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## Abstract

A novel sensor (L) was synthesized using Schiff base reaction of pyridoxal with orthophenylene diamine and was characterized by various spectroscopic techniques such as FTIR, <sup>1</sup>H NMR and Mass spectrometry. The cation recognition ability of the synthesized sensor was investigated by experimental (UV-VIS, IR and <sup>1</sup>H NMR) and theoretical (B3LYP/6-31G\*\*) methods. Among the tested anions, the developed sensor showed a naked-eye detectable color change from colorless to yellow and spectral changes in the presence of Fe(II) due to the formation of hydrogen bonded complexes with these cations followed by the partial deprotonation of sensor. With a micromolar detection limit, the developed sensor proved highly efficient and can be utilized for the colorimetric detection of Fe(II) ions.

**Keywords:** Cation chemosensor; Fe (II); Vitamin B6 cofactor

## Introduction

Designing of chemosensors which are capable of recognizing and sensing cations is one of the most burgeoning areas in research, because of their important role in different biology, industrial and environmental processes [1-24]. Among the various chemosensing systems, colorimetric sensors have great advantages due to its ability to offer a simple, sensitive, selective, accurate and economical method for the detection of a target analyte without the role of sophisticated instrumentation [25-28]. The criteria for good sensors are stability, metal selectivity, metal affinity, signal transduction, kinetically rapid sensitization, ease of delivery to target systems and availability. More importantly, the sensor should work in pure aqueous medium. Among the transition metals, iron in the form of Fe<sup>2+</sup>/Fe<sup>3+</sup>, is the most important bioactive metal as it plays a crucial function in the transport and storage of oxygen and also in electron transfer in diverse metalloenzymes. It is truly ubiquitous in living systems and tracking its homeostasis using a suitable technique is of great significance to clarify its biological effects [29,30]. However, both its deficiency (hypoferremia) and excess (hyperferremia) can induce a variety of diseases. Several serious diseases such as Alzheimer, Parkinson's and Huntington's disease etc. known to occur due to the cellular toxicity caused by iron ions [31-35]. The biological importance as well as the adverse effects of the metal ions Fe<sup>2+</sup>/Fe<sup>3+</sup> encourage us to develop some novel chromogenic sensors using the vitamin B6 cofactor. In this work, the cation sensing of the receptors L was investigated. The molecular structure of the receptor L was shown in Figure 1. The cation sensors developed showed striking color change in pure aqueous medium for the selective detection of cations Fe<sup>2+</sup>. Different analytical parameters of the receptors such as the binding constant for the interaction of cations with the receptors, binding stoichiometry, detection limit, effect of pH, interference of other metal ions etc. were

studied in this chapter. Also, the experimental outcomes were complemented with theoretical results.

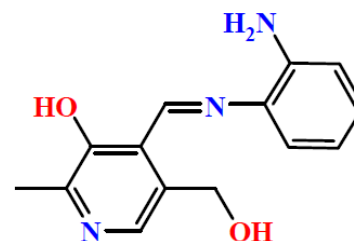


Figure 1: Synthesized receptor L.

## Materials and Methods

The reagents and chemicals were purchased commercially either from SpectroChem Pvt. Ltd or Sigma-Aldrich. Solvents such as DMSO and methanol were used without any further purification. The cations used for the sensing studies were in the form of their sulphates/chloride salts, and were purchased from Rankem Pvt. Ltd., India.

All the experiments were carried out at 298 K, unless otherwise mentioned. <sup>1</sup>H NMR spectra were recorded on a BRUKER AVANCE II 400 MHz NMR in DMSO-d<sub>6</sub> using Tetramethylsilane (TMS) as an internal standard. The IR spectra were recorded on a Perkin-Elmer IR Spectrophotometer using KBr pellet. The mass spectra were recorded on a Waters, Q-TOF micromass (LC-MS). Melting point were recorded with a digital melting point apparatus VMP-DS "VEEGO" and is uncorrected. UV-Vis spectra were recorded on a VARIAN CARY 50 Spectrophotometer in the wavelength range of 200-700 nm with a quartz cuvette (path length=1 cm at 25°C) and width of the slits used is 2.5/5 nm. For all the spectroscopic experiments, stock solutions of the

receptors ( $1.0 \times 10^{-3}$  M and  $1.0 \times 10^{-4}$  M) and the metal ions ( $1.0 \times 10^{-3}$  M and  $1.0 \times 10^{-4}$  M) were prepared in water and stored under a dry atmosphere. These solutions were used for various experiments after appropriate dilutions. For spectroscopic titrations, required concentration of the receptor (2 ml) was taken directly into the cuvette and the spectra were recorded after successive addition of selective metal ions by using micropipette.

### Synthesis of Fe<sup>2+</sup> L complex

Receptor L was synthesized according to our reported method [33]. Hot ethanolic solution of receptor L (0.306 g, 0.0011 mol) and to it corresponding FeSO<sub>4</sub> (0.305 g, 0.0011 mol) were added together with constant stirring. The mixture was refluxed for 3 h at 70-80°C. On cooling, reddish brown colored solid metal complex of Fe<sup>2+</sup>. L were precipitated out. The precipitated metal complex was filtered, washed with cold ethanol and dried under vacuum. Yield: 70%; M.P.=280°C; FT-IR (KBr disc,  $\nu_{\max}/\text{cm}^{-1}$ ): 3159, 2842, 2745, 2645, 2361, 2338, 1687, 1622.19, 1541, 1503, 1403, 1372, 1291, 1254, 1212, 1152, 1094, 1027, 957, 901, 833, 765, 735, 667, 645, 607, 563, 523, 456.

### Results and Discussion

Receptor L was synthesized by following the reported method [36-38], and its sensing ability was tested towards various metal ions. The colorimetric sensing ability of receptor L was investigated in aqueous solution upon addition of various metal ions such as Al<sup>3+</sup>, Cd<sup>2+</sup>, Co<sup>2+</sup>, Cr<sup>3+</sup>, Cu<sup>2+</sup>, Fe<sup>3+</sup>, Mn<sup>2+</sup>, Ni<sup>2+</sup>, Ba<sup>2+</sup>, Fe<sup>2+</sup>, Fe<sup>3+</sup>, Hg<sup>2+</sup> and Zn<sup>2+</sup>. The receptor L alone gave absorbance peak at 250 nm and 350 nm. Upon addition of equivalent amount of each cation, receptor L showed almost no change in absorption peak in the presence of Al<sup>3+</sup>, Cd<sup>2+</sup>, Co<sup>2+</sup>, Cr<sup>3+</sup>, Fe<sup>3+</sup>, Mn<sup>2+</sup>, Ni<sup>2+</sup>, Ba<sup>2+</sup>, Hg<sup>2+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup>, while the presence of Fe<sup>2+</sup> ion led to a red shift and gave rise to new broad absorption band between 350 nm to 650 nm (Figure 2). Also, selective sensing of Fe<sup>2+</sup> ion was done in an aqueous system through a color change from colorless to yellow. No detectable color change of L was observed in the presence of other tested metal ions. These results clearly delineated the selective Fe<sup>2+</sup> sensing ability of the receptor L in pure aqueous medium.

The binding ability of receptor L with Fe<sup>2+</sup> was further studied by UV-V is titration experiment. Upon successive addition of Fe<sup>2+</sup> to the solution of receptor L, the new charge transfer absorption band in the visible region was observed (Figure 3). From the UV-Vis absorption titration, the association constant (K) of receptor L with the Fe<sup>2+</sup> was calculated using B-H equation (inset Figure 3) and the K value was found to  $9.81 \times 10^{-4}$  M. Good linearity was observed in the 45  $\mu$ M to 95  $\mu$ M range for Fe<sup>2+</sup> ion with the detection limit down to  $8.1 \times 10^{-6}$  M (Figure 4).

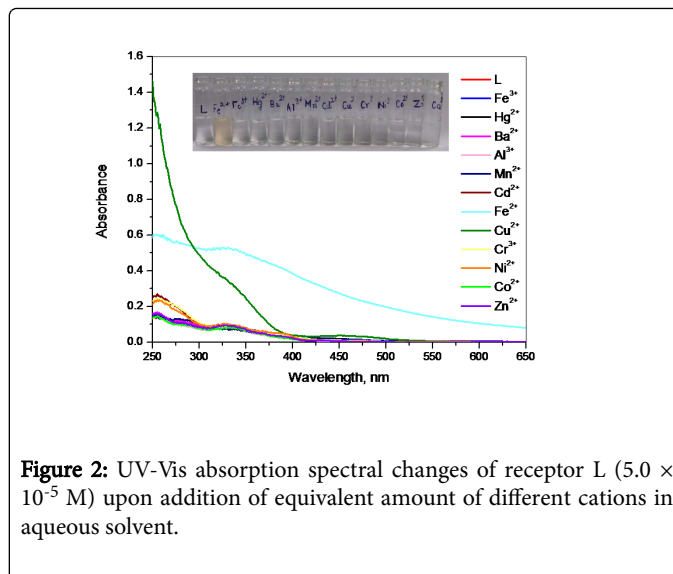


Figure 2: UV-Vis absorption spectral changes of receptor L ( $5.0 \times 10^{-5}$  M) upon addition of equivalent amount of different cations in aqueous solvent.

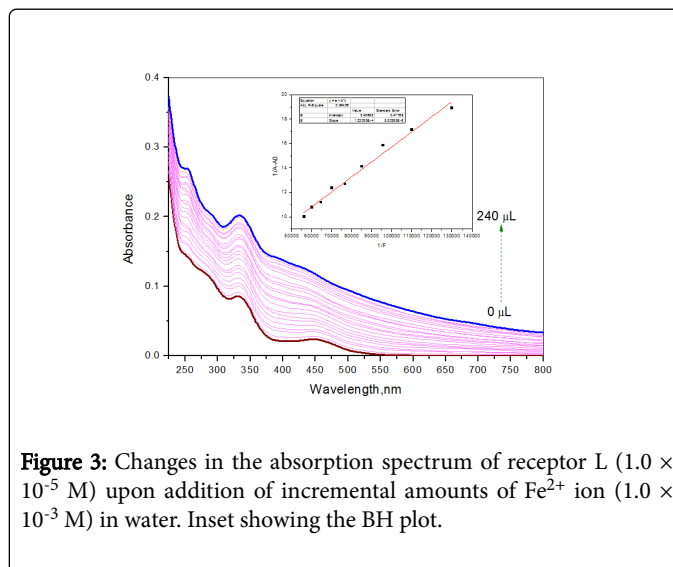


Figure 3: Changes in the absorption spectrum of receptor L ( $1.0 \times 10^{-5}$  M) upon addition of incremental amounts of Fe<sup>2+</sup> ion ( $1.0 \times 10^{-3}$  M) in water. Inset showing the BH plot.

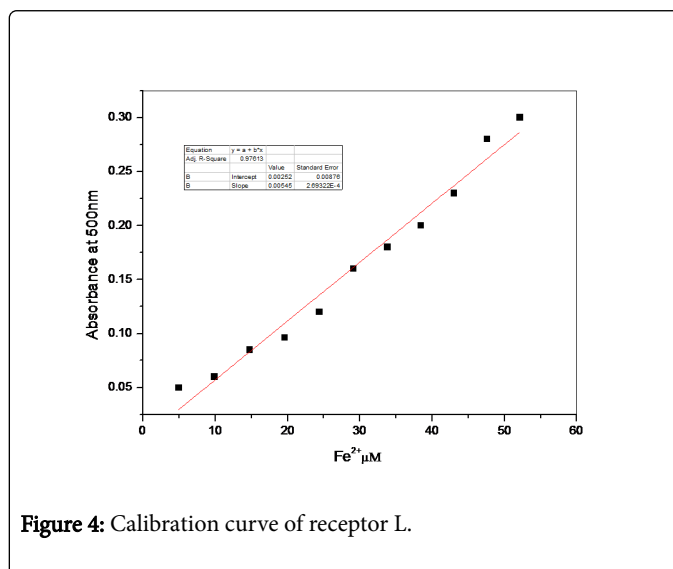
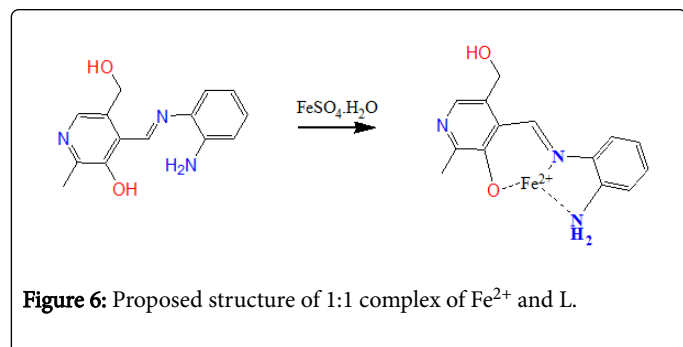
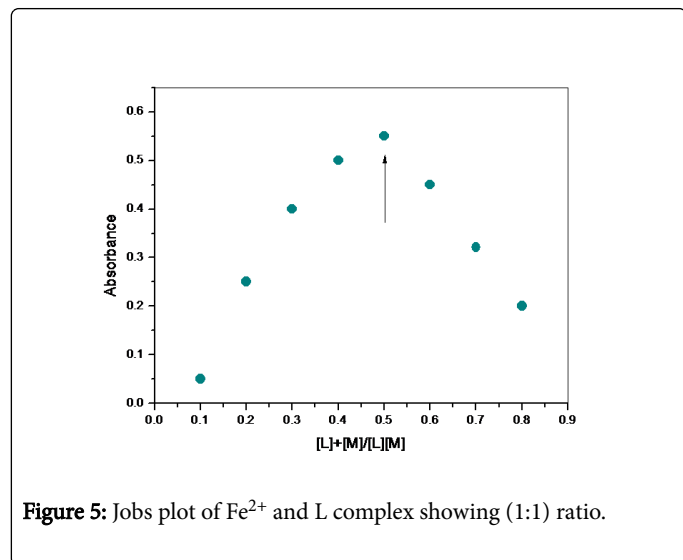
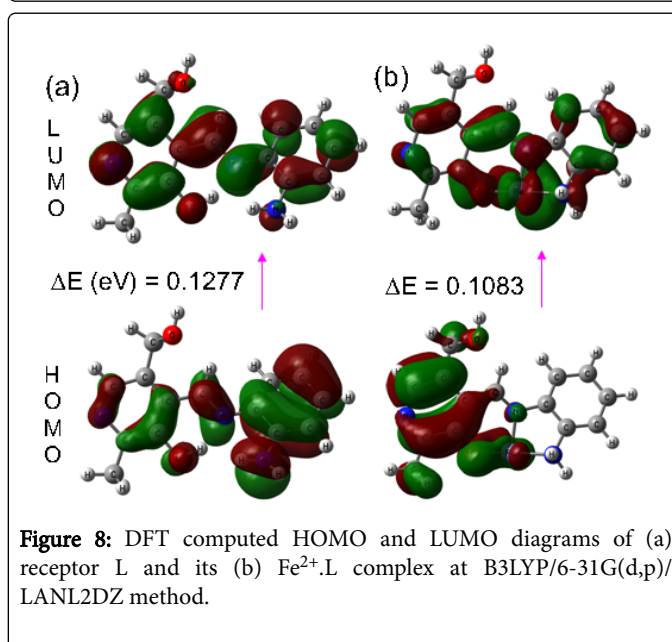
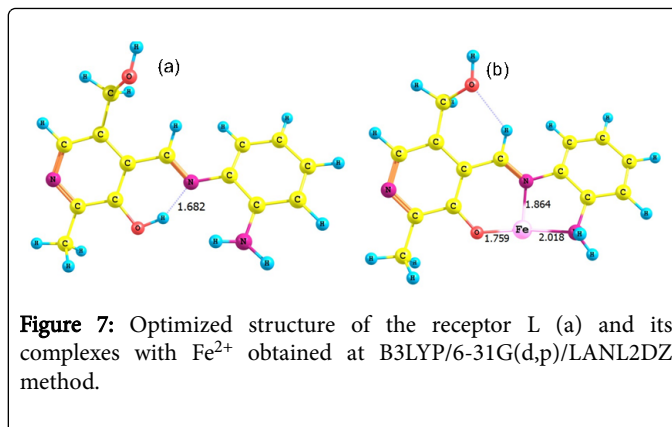


Figure 4: Calibration curve of receptor L.

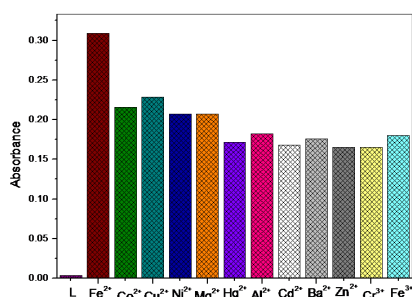
The Job plot analysis showed a 1:1 stoichiometry for the  $\text{Fe}^{2+}$  and L complex (Figure 5). Accordingly, the proposed structure of 1:1 complex formation of receptor L with  $\text{Fe}^{2+}$  was shown in Figure 6.



The molecular structure of L and its  $\text{L}\cdot\text{Fe}^{2+}$  complex was theoretically optimized in the gas phase by applying the DFT method (B3LYP/6-31G\*\*/LANL2DZ) coded in the computational program Gaussian 09W (Figure 7), and the changes in the electronic properties were compared with the experimental results. The basis set LANL2DZ was considered only for Fe atom whereas 6-31G\*\* for remaining atoms (C, H, N and O). On complexation of 3 with  $\text{Fe}^{2+}$  resulted in the lowering in the interaction energy by -199.80 kcal/mol, which indicates the formation of a stable complex. The Frontier Molecular Orbitals (FMOs) plots (Figure 8) of L and its  $\text{L}\cdot\text{Fe}^{2+}$  complexes was next analyzed which indicate the intramolecular charge transfer occurred between the receptor and  $\text{Fe}^{2+}$ . In addition, it was observed that the band gap between the Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) of L was significantly lowered on complexation with  $\text{Cu}^{2+}$ . These theoretical results corroborate well with the red-shift in the absorption band of L on complexation with  $\text{Fe}^{2+}$  due to ICT process.

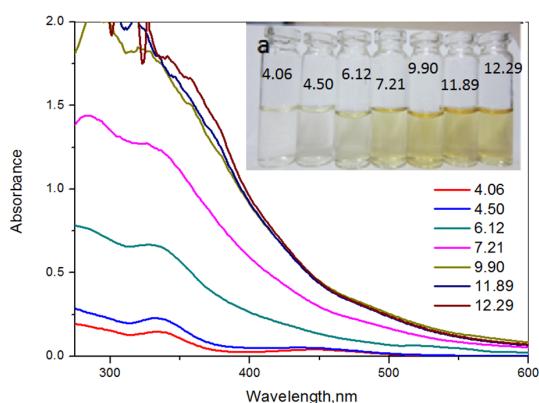


The preferential selectivity of receptor L as colorimetric chemosensor for the detection of  $\text{Fe}^{2+}$  ion in the presence of various competing metal ions was carried out. For competition studies, receptor L was treated with 0.5 equivalent of  $\text{Fe}^{2+}$  in the presence of 0.5 equivalent of other metal ions (Figure 9). No significant interference was observed in the detection of  $\text{Fe}^{2+}$  ion in presence of  $\text{Al}^{3+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Hg}^{2+}$  and  $\text{Zn}^{2+}$  ion. Thus, receptor L could be used as a selective colorimetric sensor for  $\text{Fe}^{2+}$  ion in the presence of most competing metal ions including  $\text{Fe}^{3+}$ .



**Figure 9:** Bar graph of sensor L ( $5 \times 10^{-5}$  M) at 500 nm under competitive environments.

Further, the effect of pH on the absorption response of  $\text{Fe}^{2+}$ .L complex was carried out with different pH values ranging from 4 to 12 (Figure 10). The color of the  $\text{Fe}^{2+}$ .L complexes remained in the yellow region between pH 6 and 12. These results indicate that the detection  $\text{Fe}^{2+}$  ion using receptor L over a wider pH range and importantly in the physiological pH.



**Figure 10:** Effect of pH on the UV-Vis absorption spectra of L ( $5 \times 10^{-5}$  M) containing equimolar amount of  $\text{Fe}^{2+}$ . Inset showing the color change.

In addition, to investigate the practical application of receptor L, a test paper kit was prepared by immersing filter paper in an aqueous solution of receptor L ( $5.0 \times 10^{-5}$  M) and then dried in the air. The dried test paper kit was treated with the  $\text{Fe}^{2+}$  ion solution at  $1.0 \times 10^{-3}$  M. As shown in the Figure 11, the detectable color change of test kit coated with the receptor L solution would be convenient for detecting  $\text{Fe}^{2+}$  metal ions.



**Figure 11:** Test paper kit of receptor L in presence of  $\text{Fe}^{2+}$  ion.

## Conclusion

Receptor L showed micromolar recognition of  $\text{Fe}^{2+}$  ion in a fully aqueous solution. Selective sensing of  $\text{Fe}^{2+}$  ion was done in aqueous system through a colour change from colourless to yellow brown. The Job plot analysis showed a 1:1 stoichiometry for the  $\text{Fe}^{2+}$ .L complex. The K value was found to be  $9.81 \times 10^4$  M. The linearity was observed in the range of  $45 \mu\text{M}$  to  $95 \mu\text{M}$  for  $\text{Fe}^{2+}$  ion with the detection limit down to  $8.1 \times 10^{-6}$  M.

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