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Salophen Imine Based Colorimetric and Fluorescent Probe for detecting Fe^{3+} and Sn^{2+} ions

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Abstract

A salophen imine based chemosensor has been synthesized, and its sensing behavior toward various metal ions was investigated by UV-Vis and fluorescence spectroscopy. In acetonitrile solution, Fe^{3+}, and Sn^{2+} ions coordinate to the imine through NONO binding site which induces a visual color and absorption spectral changes as well as strong fluorescence. Binding affinity towards Fe^{3+} is found to be of higher magnitude compared to the Sn^{2+}. Receptor 1 on binding with Fe^{3+} and Sn^{2+} shows fluorescence enhancement which is due to the inhibition of PET mechanism.

Keywords: Schiff's base, colorimetric titration, cation, 1:1 complex, UV-Vis and Fluorescence spectroscopy

1. INTRODUCTION

The selective sensing of cations is one of the most important areas of organic chemistry, supramolecular chemistry, drug delivery and environmental chemistry because of its potential clinical applications [1-2] . Iron is one of the most important element among heavy metals for metabolic processes, being indispensable for plants and animals and therefore it is extensively distributed in environmental and biological materials[3]. Both its deficiency and overdose can induce a wide variety of diseases. For instance, in heme the metal centre is an iron ion, Iron-deficiency leads to anemia. Iron overdose can damage heart and brain and other storage sites in the body and lead to heart attack or stroke[4]. Therefore, the development of analytical methods for the sensitive and selective determination of Fe^{3+}, is highly desirable. Because of its operational simplicity, low cost, real time monitoring and high selectivity, fluorescent detection has become the promising strategy used for Fe^{3+} detection[5-6]. Recently, some fluorescent chemosensors for ferric have been reported[7]. Usually N or O donor centers and receptors containing imine (CH=N)[8], hydroxyl (–OH)[9], amide (–CONH)[10], urea ($(NH_2)_2C=O$))[11], thiourea ($(NH_2)_2C=S$)[12], pyrrole (–NH)[13], coumarin derivatives[14] act as binding sites for cations. The colorimetric sensing, a direct visual observation sensing method, is simple in monitoring the process without resorting to any complicated spectroscopy methods. The development of chemosensor capable of undergoing fluorescence enhancement in presence of metal ions has always been attracting because of easier and more efficient mode of detection. We have primarily emphasized on receptor 1, a new sensor which is easy to prepare and display high sensitivity, selectivity, stability over the other receptors and the colorimetric and fluorescent sensing ability of receptor **1** towards cations. In this way, this paper concerns the development of novel colorimetric and fluorescent probe for cation sensing.

3. RESULTS AND DISCUSSION

3.1 Synthesis and characterization of receptor 1

Receptor **1** (Fig. 1) was prepared by a condensation reaction between *o*-phenylene diamine and 5-nitro salicylaldehyde. To 4.6mmol (0.108 g) of *o*-phenylene diamine dissolved in dichloromethane, 9.2 mmol (0.334 g) of 5-nitro salicylaldehyde in ethanol was slowly added and refluxed for three hours at 70-75°C. After completion of the reaction the solvent was removed under reduced pressure to yield the crude yellow coloured precipitate. Yield- 85-90 %. IR (KBr plates (cm^{-1}): C=N- 1619, C=C-1481, OH-3416. m/z: 406.0458.

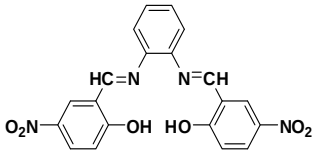
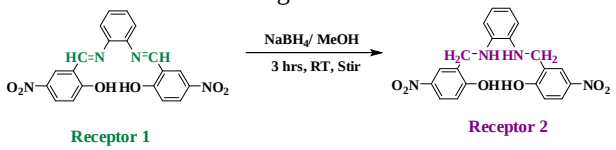


Fig. 1: Structure of receptor 1

The product was insoluble in most of the organic solvents like $CHCl_3$, CH_3CN, CH_2OH, C_2H_5OH etc..and soluble only in dimethyl sulfoxide (DMSO). However it encountered a solubility problem in DMSO-d_6 hence it become difficult to characterize receptor 1 by NMR spectroscopic techniques. Sample partially dissolved in DMSO-d_6 was used for ^1H NMR studies and the data is as

follows, ^{1}H NMR (400 MHz, DMSO-d_6 δ ppm) 7.16 - 8.44 (aromatic protons), 8.13 (s 2H (CH=N)), 10.31 (s 2H, (OH)). In order to confirm the formation of imine unambiguously receptor 1 was derivatised to improve its solubility. Imine functionality was reduced using $NaBH_4$/ MeOH to result in an amine. (Scheme-1). After reduction, the amine obtained was soluble in all organic solvents. High resolution mass spectrum of receptor 2 showed the m/z value of 410.3760, which indicates that the imine functionality is converted to amine. Both receptor 1 and 2 were used for cation sensing studies.



Receptor 1 Receptor 2

Scheme 1: synthesis of receptor 2

3.2 Colorimetric Analysis

The colorimetric sensing responses of the receptor 1 towards different metal cations like Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and Sn^{2+} was studied. The colorimetric titration was carried out in DMSO solution. The color change was visualized by direct eye experiments, visual inspection of the receptor 1 shows color change from yellow to pale orange for Fe^{3+}, and yellow to colorless for the addition of 200µL of Sn^{2+} ion (Fig. 2a). The addition of other cations like Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} did not show any color changes. Colorimetric sensing responses of the receptor 2 towards metal cations was also studied. The addition of cations like Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and Sn^{2+} to receptor 2 did not result in any color changes (Fig. 2b) this indicates that the presence of imine functionality is necessary for the sensing action.

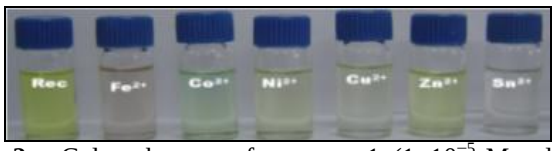


Fig. 2a: Color changes of receptor 1 (1×10^{-5} M soln in DMSO) before and after the addition of 200µL of respective cations (1.5×10^{-3} M soln in DMSO) (From left to right: R, R+ Fe^{3+}, R+ Co^{2+}, R+ Ni^{2+}, R+ Cu^{2+}, R+ Zn^{2+} and R+ Sn^{2+}).

Fig. 2b: Color changes of receptor 2 (1×10^{-5} M soln in CH_3CN) before and after the addition of 200µL of respective cations (1.5×10^{-3} M soln in CH_3CN) (From left to right: R, R+ Fe^{3+}, R+ Co^{2+}, R+ Ni^{2+}, R+ Cu^{2+}, R+ Zn^{2+} and R+ Sn^{2+}).

3.3 UV-Vis Spectroscopic Studies

The recognition between receptor 1 and different metal cations was investigated by UV–vis spectroscopy in DMSO solution. The stock solution of receptor 1 at a concentration of 1.0×10^{-5} mol/L, and the stock solution of metal ions at a concentration of 1.5×10^{-3} mol/L was used for UV-Vis studies. The electronic spectroscopy of the receptor 1 in the absence of any cation solution reveals three types of transitions. The absorption band in the range 280 nm is most possibly due to the excitation of the π electrons of the aromatic system. The absorption band at 370 nm for receptor 1 is almost due to the transition between the π orbital localized on the azomethine group (C=N). The band in the region around 450 nm is due to presence of n− π* transition of azomethine group (C=N). Upon the addition of 200 µL of Fe^{3+} ion (1.5×10^{-3}M in DMSO) to the receptor 1, the peak at 290 nm increases and the peaks at 380 and 420 nm are decreasing and new intense peak was observed at 520 nm. Similar spectral changes are observed for Sn^{2+} ion (Fig. 3b).

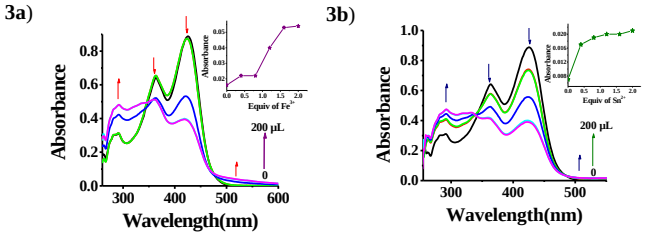


Fig. 3a: UV-vis spectral changes of receptor 1 (1 x 10^{-5} M, soln in DMSO) upon titration with Fe^{3+} (1.5 x 10^{-3} M, soln in DMSO). (Inset: Changes of absorbance upon addition of Fe^{3+} ion at 520 nm). **Fig. 3b:** UV-vis spectral changes of receptor 1 (1 x 10^{-5} M, soln in DMSO) upon titration with Sn^{2+} (1.5 x 10^{-3}M, soln in DMSO). (Inset: Changes of absorbance upon addition of Sn^{2+} ion at 509 nm).

From the UV–vis absorption spectroscopy measurements, the binding constant (K_{app}) of the Fe^{3+} and Sn^{2+} (in DMSO) complexes of the receptor 1 was calculated. The Benesi–Hildebrand (B–H) plot was used for the binding constant calculation. Δε can be derived from the intercept while K_{app} can be calculated from the slope based on the linear least square fitting line. The binding constant of the receptor 1 with the corresponding cations is shown in the Table 1. Receptor 1 shows a higher binding constant value for Fe^{3+} (3.18 x 10^4) than for Sn^{2+} (2.20 x 10^3). Job's plot studies reveal the stoichiometry of the complex formed between receptor 1 and Fe^{3+} and Sn^{2+} ions as 1:1 (Fig. 4a and 4b).

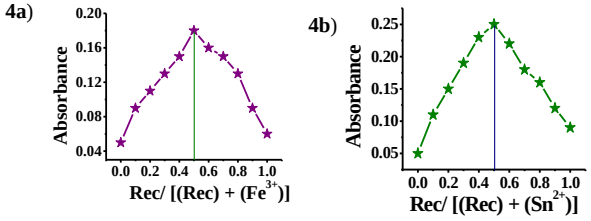


Fig. 4a: Jobs plot between receptor 1 and Fe^{3+} . **Fig. 4b.** Jobs plot between receptor 1 and Sn^{2+}.

Table 1: Binding constant values and stichiometry for receptor 1 with Fe^{3+} and Sn^{2+} ions

Receptor + ions	Binding constant (K_{app})	Stoichiometry
Receptor 1+ Fe^{3+}	3.18 x 104	1:1
Receptor 1+ Sn^{2+}	2.20 x 103	1:1

3.4 Fluorescence Spectroscopic Studies

Fluorescence titration experiments were carried out with receptor 1 in DMSO (1 x 10^{-5} M) solution and the maximum excitation wavelength was selected at 360 nm. The receptor 1 in the absence of any cations showed emission maxima at 525 nm. Fluorescence spectra (Figures 5a & 5b) show the changes in the intensities of the fluorescence emission maxima of receptor 1 in the absence and presence of cations. Upon introduction of Fe^{3+} ions, the emission spectrum of receptor 1 exhibited variations, which is consistent with the PET (Photo induced Electron Transfer**)** signaling mechanism. When increasing concentrations of Fe^{3+} ions were added to receptor 1 an increase in the intensity of the emission maximum at 400 nm and decrease in the intensity at 500 nm (Fig.5a), was observed suggesting that the PET process is inhibited. This is an very important feature in the fluorescence amplified probes for paramagnetic metal ions based on the PET signaling mechanism. The fluorescence enhanced response is due to the coordination of the transition metal ions to receptor 1. The similar fluorescence enhancement behavior was also observed for Sn^{2+} ions (Fig. 5b). Successive addition of tin solution (1.5 x 10^{-3} M in DMSO) to receptor 1 resulted in an increase in the intensity of the emission maximum at 425 nm and 525 nm (Fig.5b) which shows that the electron donating nitrogen of the receptor 1 in the exited state participates in [N–Sn^{2+}] complexation. For receptor 1, phenolic oxygen can provide a nice binding pocket for Sn^{2+}. Since Fe^{3+} and Sn^{2+} have paramagnetic character both exhibits a marked fluorescence enhancement.

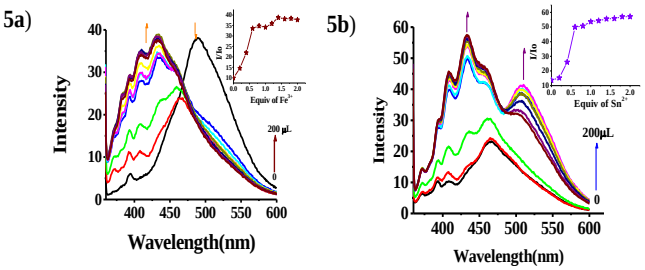
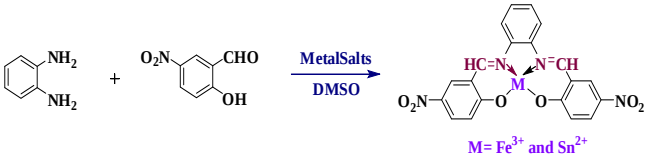


Fig. 5a. Fluorescence titration spectrum of receptor 1 upon the gradual addition of (0-200µL) $FeCl_3$ in DMSO. (Inset: Changes of fluorescence emission upon addition of Fe^{3+} ion at 425 nm.) **Fig. 5b.** Fluorescence titration spectrum of receptor 1 upon the gradual addition of (0-200µL) $SnCl_2$ in DMSO. (Inset: Changes of fluorescence emission upon addition of Sn^{2+} ion at 450 nm.)



Scheme 1. Proposed binding mechanism between the receptor **1** and cations.

2.0 CONCLUSION

To conclude, receptor 1 is highly sensitive towards Fe^{3+} and Sn^{2+} ions by colorimetric and fluorescent response. The receptor changed from yellow to pale orange for Fe^{3+}, and yellow to colorless for the addition of 200µL of Sn^{2+} ion. Receptor 1 shows a higher binding constant value for Fe^{3+} (3.18 x 10^4) than for Sn^{2+} (2.20 x 10^3). Jobs plot studies reveal the stoichiometry of the complex formed between receptor 1 with Fe^{3+} and Sn^{2+} ions to be 1:1 complexes. The receptor 1 show fluorescent enhancement upon the addition of paramagnetic Fe^{3+} and Sn^{2+} cations. Receptor 1 can be applied as fluorescence enhanced probes for transition metal ions due to the inhibition of PET mechanism.

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