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Pyrrole Based Schiff Base as a Highly Sensitive Fluorescent Sensor for Fe^{3+} and Sn^{2+} Ions

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A B S T R A C T

Condensation product of *o*-aminophenol and pyrrole-2-carboxylaldehyde behaves as a fluorescent sensor for Fe^{3+} and Sn^{2+} ions in aqueous medium over the other metal ions like Na^{+}, K^{+}, Mg^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Mn^{2+} and Cr^{3+}. In aqueous solution, Fe^{3+} and Sn^{2+} ions coordinate to the receptor through a NON binding site which induces a strong fluorescence enhancement. Receptor can be applied as fluorescence enhanced probes for transition metal ions due to the inhibition of photo induced electron transfer (PET) mechanism.

1. Introduction

In recent years there has been a significant interest in the design and development of fluorescent sensors for detecting transition metal ions[1]. Various transition metal ions are crucial for the life of living organisms. Iron plays an essential role in a variety of vital cell functions such as oxygen metabolism and electron transfer processes in DNA and RNA synthesis. Irregular levels of iron could be related to some serious diseases, such as Huntington's, Parkinson's and Alzheimer's diseases[2-3]. Therefore, the development of selective as well as sensitive fluorescent sensors for ferric ions presents a challenge. However, only a few examples of fluorescent chemosensors for Fe^{3+} have been described[4-6]. Tin alloys are used in electric circuits, pewter, and dental amalgams. The organic tin bonds are the most dangerous forms of tin for humans. Tin bonds can cause depression, liver damage, malfunctioning of immune systems, chromosomal damage, shortage of red blood cells and brain damage[7-9]. On the other hand, as a simple, efficient and economic method, fluorescent signaling has been widely used in biological and environmental science[10-15].

This created an interest to study the sensing ability of the simple imine bases that act as cation sensors. Condensation product of *o*-aminophenol and pyrrole-2-carboxylaldehyde (receptor) behaves as a fluorescent sensor for Fe^{3+} and Sn^{2+} ions in aqueous medium over the other metal ions like Na^{+}, K^{+}, Mg^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Mn^{2+} and Cr^{3+}. In aqueous solution, Fe^{3+}, and Sn^{2+} ions coordinate to the receptor through a NON binding site which induces a strong fluorescence enhancement. The emission peak of the receptor at λ_{max}= 450 nm, on excitation with 360 nm wavelength, showed an enhancement when interacted with Fe^{3+} and Sn^{2+}. There are no intensity changes observed upon the addition of other metal ions into the receptor. Receptor can be applied as fluorescence enhanced probes for transition metal ions due to the inhibition of photo induced electron transfer (PET) mechanism.

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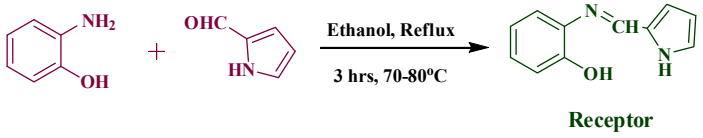
2. Experimental

2.1 Materials and Spectroscopic Methods

O-Aminophenol, pyrrole-2-carboxylaldehyde, iron (III) chloride, zinc (II) chloride, cadmium (II) acetate, tin (II) chloride, mercury (II) nitrate, manganese (II) acetate, chromium (III) chloride, sodium acetate, potassium chloride, magnesium (II) sulphate and analytical grade solvents such as acetonitrile (CH_3CN) and ethanol (EtOH) were purchased from Sigma Aldrich and used as such. Fluorescence emission spectra were recorded in a Shimadzu RF-5301 PC spectrofluorophotometer at a scan rate of 500 nm/ slit width with Ex: 10 nm Em: 10 nm. Excitation wavelength set was 360 nm. 5×10^{-5} M solutions of the receptor in CH_3CN and 1.5×10^{-3} M solutions of the cations in H_2O were prepared. 0.2 eq. (20 µL) - 2 eq. (200µL) of guest solution was added to 3 ml of receptor taken in the cuvette.

2.2 Synthesis and Characterization of Receptor

Receptor was prepared by a simple condensation reaction between *o*-aminophenol with pyrrole-2-carboxylaldehyde in good yield. Ethanalic solution of *o*-aminophenol was slowly added to an ethanolic solution of pyrrole-2-corboxylaldehyde. The reaction mixture was refluxed for three hours at 70-80ºC (**Scheme 1**).



Receptor

Scheme 1. Synthesis of Receptor

On cooling, pale brown precipitate of the product settled. The precipitate was filtered and recrystallized from ethanol and dried in vacuum oven. Yield: 85 %; m.p. 129° C; IR (KBr, cm^{-1}) ν: (CH=N) 1628, (N-H) 3214, (OH) 3354 (**Fig. 1**). ^1H NMR (300 MHz, $CDCl_3$ δ ppm): = 9.5 (s, 1H, -OH), 8.35 (s, 1H, -CH═N-), 6.25-6.31(s, 1H, -NH), 6.65-6.66 (d, 2H), 6.79-6.84 (t, 1H), 6.89-6.92 (d, 2H), 7.03-7.17 (t, 2H) (**Fig. 2**).

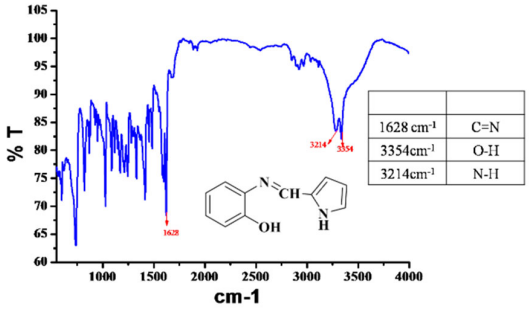


Fig. 1. FTIR Spectrum

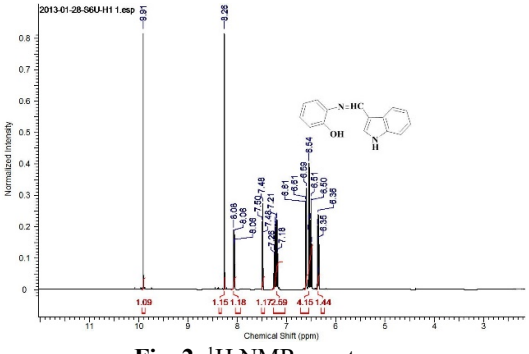


Fig. 2. ^1H NMR spectrum

3. Results and Discussion

3.1 Fluorescence Spectroscopic Studies

The fluorescence spectrum of the receptor was recorded in CH_3CN (receptor) and H_2O at room temperature conditions. The excitation wavelength radiation was selected at 360 nm. Free receptor exhibited a normal emission band at 410 ((phenol–imine form) and a tautomer emission (Keto amine) band at 450 nm. **Fig. 1** shows the fluorescence titration spectrum of receptor with different alkali and alkaline earth metal ions (Na^+, K^+ and Mg^{2+}), and transitions metal ions (Fe^{3+}, Cd^{2+}, Zn^{2+}, Sn^{2+}, Mn^{2+}, Hg^{2+}, Cr^{3+}). The results showed that the alkali and alkaline earth metal ions and Cd^{2+}, Zn^{2+}, Mn^{2+}, Hg^{2+}, Cr^{3+} did not cause significant changes in fluorescence emission spectra of receptor except for Sn^{2+} and Fe^{3+} ions (**Fig. 3**).

Fluorescence emission intensity at 450 nm was gradually increasing upon the incremental (0-200µL) addition of Fe^{3+} (**Fig. 4**) and Sn^{2+} (**Fig. 5**) into the receptor. The Fe^{3+} and Sn^{2+} ions are likely to bind to the receptor via the three NON-atoms of the receptor moiety. Fe^{3+} and Sn^{2+} have paramagnetic character and both exhibit a marked fluorescence enhancement. The fluorescence enhancement is mainly suggesting the inhibition of thermodynamically favorable photo induced electron transfer (PET) mechanism. The PET process occurs due to the transfer of electron density, originating at the lone pairs of

electrons on N atoms of the receptor moiety, to the LUMO of the fluorophore. Electron transfer is then inhibited and the fluorophore is not quenched. This type of mechanism is called inhibition of photoinduced electron transfer mechanism. The fluorescence enhanced response is due to the coordination of the transition metal ions to the receptor.

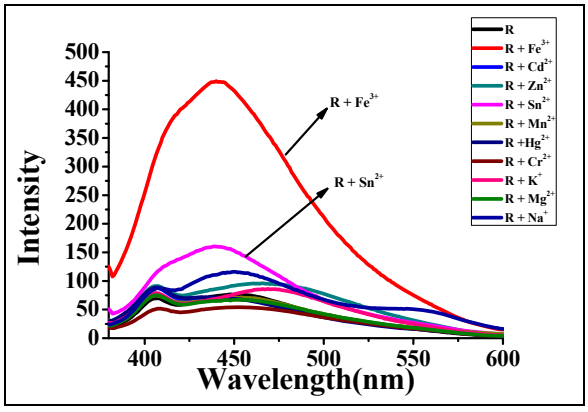


Fig. 3. Fluorescence spectra of free receptor in the presence of different metal ions (excitation wavelength at - 360 nm).

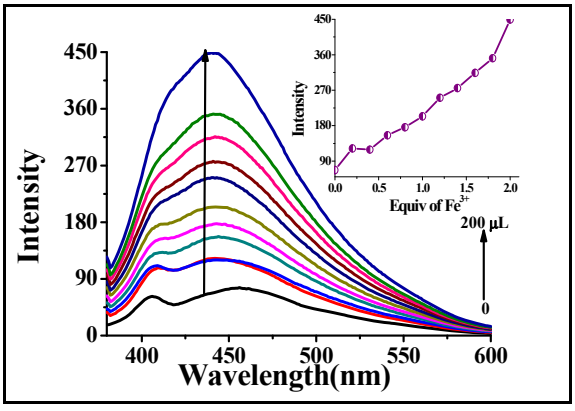


Fig. 4. Fluorescence titration spectrum of receptor upon the gradual addition of (0-200µL) Fe^{3+} ions in H_2O (Inset: Changes of fluorescence emission upon addition of Fe^{3+} ion at 450 nm) (Excited at 360 nm).

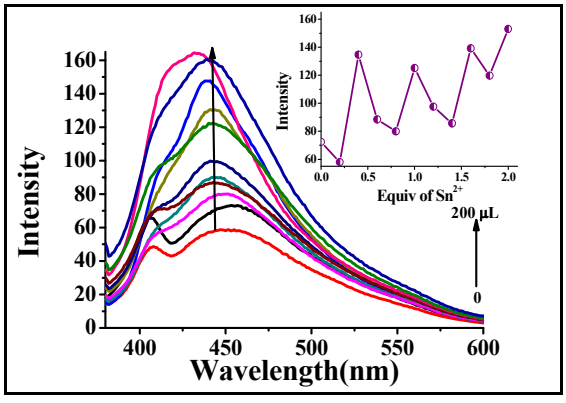


Fig. 5. Fluorescence titration spectrum of receptor upon the gradual addition of (0-200µL) Sn^{2+} ions in H_2O (Inset: Changes of fluorescence emission upon addition of Fe^{3+} ion at 450 nm) (Excited at 360 nm).

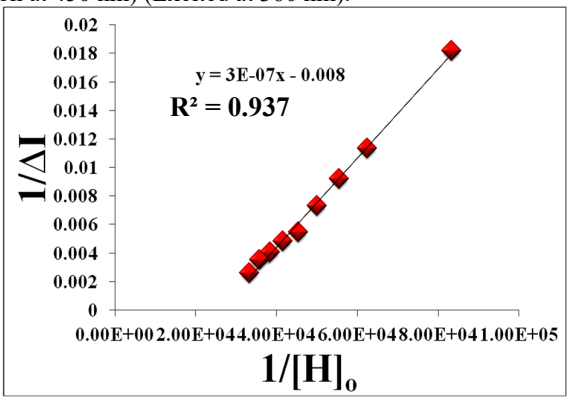


Fig. 6. BH plot (R+ Fe^{3+} in H_2O)

3.2 Binding Constant and Binding Mechanism

From the UV-vis absorption spectroscopy measurements, the binding constant (K_{app}) of the Fe^{3+} (**Fig. 6**) and Sn^{2+} complexes of the receptor were calculated. Benesi-Hildebrand (B–H) plot was used for the binding constant calculation. Plot can be made with $1/\Delta A$ as a function of $1/[H]_0$. $\Delta\varepsilon$ can be derived from the intercept while K_{app} can be calculated from the slope based on the nonlinear least square fitting curve. Job's plot studies reveal that the stoichiometry of the complex formed between receptor with Fe^{3+} (**Fig. 7**) and Sn^{2+} as 1:1. The binding constant and stoichiometry of the receptor with the corresponding cations is shown in the table 1 and the proposed binding mechanism between the receptor and cations in the **scheme 2**. Receptor shows a higher binding constant value for Fe^{3+} in H_2O (2.66×10^4) than Sn^{2+} in H_2O (1.15×10^4). The receptor was compared with some reported chemosensors for Fe^{3+} and pyrrole functional group (**Table 2**). While each chemosensor showed some advantages such as high sensitivity, no interference and naked eye detection. Our receptor exhibited quite appealing analytical features such as easy synthesis, fluorescence detection selective cation sensing and good detection limit. The present WHO recommended limit for iron in water is 0.3 mg/l (ppm). Our receptor detects Fe^{3+} in lower than WHO permits.

Table 2. Comparison of some chemosensors for Fe^{3+} & pyrrole group

Functional group	Sensing ions	Binding Constant	Stoichiometry	Detection limit	Reference
Pyrrole	Fe^{3+}, Cu^{2+}, Hg^{2+} and Cr^{3+}	$1.2\times10^4 - 8.9\times10^5$	2:1	0.12 – 0.68 µM	[16]
Pyrrole	Cu^{2+}	1.29×10^4	1:1	0.296 µM	[17]
Pyridine	Fe^{2+}, Fe^{3+} & Cu^{2+}	0.216×10^4-1.17×10^4	2:1 &1:1	14-22 µM	[18]
Pyrrole	Cu^{2+}, Zn^{2+} & Hg^{2+}				[19]
Pyrrole	Fe^{3+} & Sn^{2+}	2.66×10^4 & 1.15×10^4	1:1	0.23 µM & 0.11 µM	This work

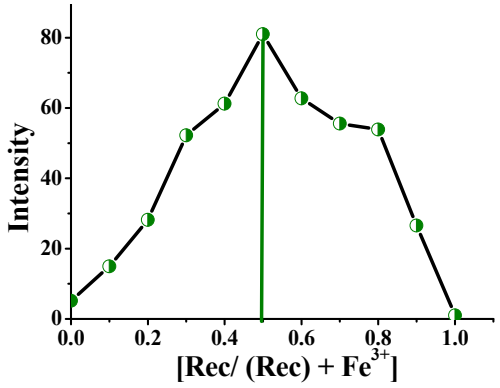
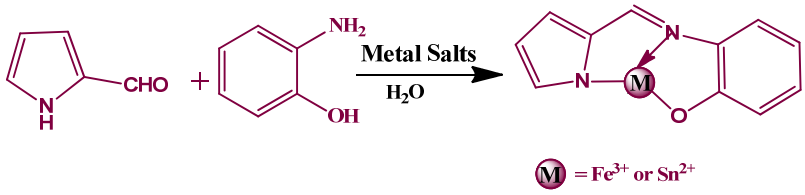


Fig 7. Job's plot (R+ Fe^{3+} in H_2O)



Scheme 2. Proposed binding mechanism between the receptor and cations

Table 1. Binding constant (K_{app}) value of the complex formed for receptor 1 with Fe^{3+} and Sn^{2+} ions

S. No	Receptor + ions	Binding constant (K_{app})	Stoichiometry	Quantum yield (Φ)
1	Rec + Fe^{3+}	2.66×10^4	1:1	0.23
2	Rec + Sn^{2+}	1.15×10^4	1:1	0.11

4. Conclusions

In summary, we have presented a *o*-aminophenol and pyrrole-2-carboxylaldehyde based sensor that showed preferential binding for Fe^{3+} and Sn^{2+} over other Na^+, K^+, Mg^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Mn^{2+} and Cr^{3+} ions. The high selectivity for Fe^{3+} and Sn^{2+} ions is marked by a significant fluorescent enhancement. The enhancement in fluorescence of the receptor on binding Fe^{3+} and Sn^{2+} ions is due to the inhibition of photo induced electron transfer (PET) process.

Conflicts of Interest

There are no conflicts to declare.

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