



A SCHIFF BASE FLUORESCENT CHEMOSENSOR FOR DETECTION OF Zn^{2+}

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Abstract: A highly sensitive Schiff base fluorescent probe-(E)-2-((quinolin-8-ylmethylene) amino) quinolin-8-ol (H_5L) was synthesized which can be used as chemosensor for detection of Zn^{2+} . The complexation of H_5L with Zn^{2+} in ethanol solution resulted in red shift with an enhancement of fluorescent emission intensity. Fluorescent studies with other transition metals didn't showed impressive results. The molecule H_5L could easily distinguish Zn^{2+} from Cd^{2+} showing chemosensor property. Using Benesi – Hildebrand relation the stoichiometric ratio for complexation was found out to be 1:1. The molecule exhibited excellent fluorescent chemosensor activity for Zn^{2+} over a wide range of pH.

Index Terms - Fluorescence, chemosensor, Schiff Base

1. INTRODUCTION

In recent years several developments has been done in design and synthesis of chemosensors that can be used for detection of transition metal ions. These sensors play an important role in study difference processes where metal ions contribute significantly like chemical, biological and environmental processes.[1-4]. Metal ions like Ca^{2+} , Fe^{2+} , Cu^{2+} , Mg^{2+} , Mn , Co^{2+} , Zn^{2+} , Fe^{3+} have biological significance.[5-7]. Excessive or insufficient intake of these ions may lead to various health problems like liver & kidney damage, diabetes, Alzheimer's and Parkinson's disease arthritis etc [8, 9]. This results in drastic need of regulation of concentration of this ion in the environment as well as in human body. Regulation of concentration of these ions requires detection of these ions both in environment as well in biological system. There are various literatures available for spectroscopic methods of detection of such ions like absorption spectroscopy, inductively coupled plasma optical emission spectroscopy, electrochemical methods, flame absorption spectroscopy etc. [10-12]. However these techniques have several disadvantages like high machine cost, low sensitivity, complex processes etc. Out of all the available techniques for detection of ions fluorescence based technique are very cost effective and they detect such ions with high sensitivity. These fluorescent techniques can be designed using a Schiff base. They can easily bind with metal ions resulting in fluorescent activity.

Zn^{2+} is an important trace element of human body. It is the second most abundant transition element after iron [13]. Zn^{2+} plays an important role in biological activity like muscle contraction, protein synthesis, cellular metabolism, immune system etc. deficiency of Zn^{2+} may lead to immune deficiency, diarrhoea, retardation in growth etc. however excess of Zn^{2+} may lead to serious disorders like Parkinson's disease, Alzheimer's disease and epilepsy[14, 15]. So it is important to regulate concentration of Zn^{2+} in our body. Also there is a great need of developing a cost effective, high sensitive sensor that can detect Zn^{2+} from other transition elements having similar chemical properties like Cd^{2+}

Zn^{2+} ions can be detected using Schiff Base as the nitrogen atom of the azomethine $C=N$ group in Schiff base has a strong affinity for transition metal ions. Due to this property Schiff base can be used as chemosensor. Schiff bases metal complexes can also show antitumor and antioxidative activities[16, 17]. In addition they can serve as an excellent tool for optical sensing of metal ions with very high sensitivity. Schiff bases are capable of forming stable complex with metal ions that can show excellent coordination, high stability, excellent fluorescent properties and biological activity[18]. However synthesis of these compounds is a challenging task because they are affected by various factors like pH, metal ligand ratio, solvent used, temperature, coordination geometry etc [19]. Thus design and synthesis of fluorescent chemosensor using Schiff Base is of great research interest. Till date many metal ions sensors with high sensitivity has been

reported. A variety of chemosensor for Zn^{2+} has been developed showing different applications [20-25]. However many of these sensors suffers from interference of other transition metal ions having similar properties like Cd^{2+} . Cd^{2+} show similar chemical properties and respond with similar spectral changes including change in fluorescent intensity and shift in the wavelength. In this research work a Schiff base fluorescent probe (H_5L) (E)-2-((quinolin-8-ylmethylene) amino)quinolin-8-ol has been designed and synthesized in one step reaction of 2-aminoquinolin-8-ol and quinoline-8-carbaldehyde in ethanol solution (**Scheme I**). This molecule showed prominent fluorescent enhancement in presence of Zn^{2+} while no significant spectral changes was observed in presence of other metal ions including Cd^{2+} . The molecule was characterized using FT-IR, 1H and ^{13}C NMR. Photophysical properties like absorption and emission were studied in presence of different solvents and presence of different metal ions using steady state absorption and fluorescence spectroscopy.

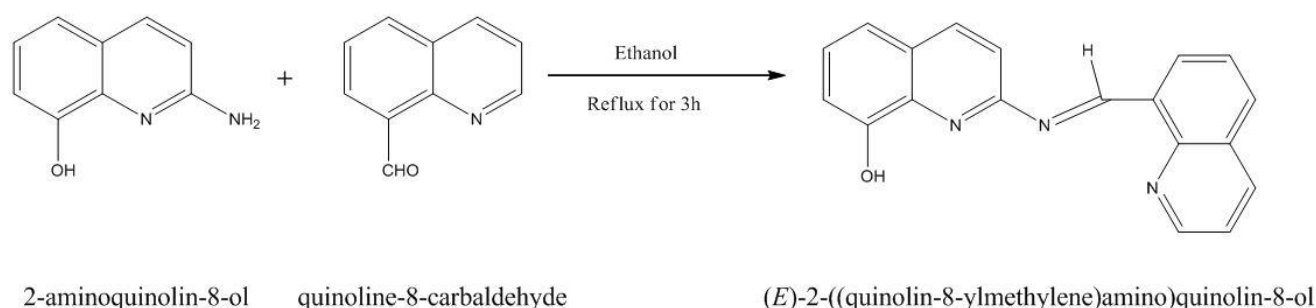
2. Materials and Methods.

2.1 Materials and reagents.

2-aminoquinolin-8-ol and quinoline-8-carbaldehyde were obtained from Sigma- Aldrich Chemicals. Spectroscopic grade solvents were obtained from Sigma- Aldrich Chemicals and Sisco Research Laboratory (SRL) Pvt. Ltd. Ultrapure chemical reagents were obtained from Lancaster and S.D fine Chemicals. The solution of the metal ions was prepared from their perchlorate salts. Experimental solutions of varying pH were prepared. Analytical grade water was obtained from Elix 10 water purification system. All experiments were carried out at room temperature 300 K unless mentioned otherwise.

2.2 Synthesis and characterization of (E)-2-((quinolin-8-ylmethylene) amino) quinolin-8-ol (H_5L)

0.150 g of 2-aminoquinolin-8-ol and 0.125 g of quinoline-8-carbaldehyde were separately dissolved in pure ethanol. The resultant solution was mixed together to get yellow color. 2-3 drops of acetic acid was added to the solution and was stirred under reflux for 3 hours. The precipitate was filtered, washed with pure ethanol 3 times. The compound was recrystallized with ethanol/chloroform (1/3 v/v) to obtained pure yellow crystals of H_5L with yield of 85%. (**Scheme –I**) IR (ν_{max} , cm^{-1} , KBr): 3377(ν_{OH}), 3192($\nu_{as}(C-H)$), 3047($\nu_s(C-H)$), 1596($\nu_{C=N}$), 1572($\nu_{C=C}$), 1240($\nu(C-O)$), 1128($\nu(C-N)$), 787($\nu(C-H)$); 1H NMR (400 MHz, $CDCl_3$, TMS, δ , ppm): 6.93 (d, H-2), 7.28 (t, H-3), 7.32 (d, H-4), 8.25 (d, H-6), 7.93 (d, H-7), 7.50 (s, H-9), 7.6 (d, H-11) 7.4 (t, H-12) 7.7 (d, H-13) 8.0 (d, H-15) 7.3 (t, H-16), 8.8 (d, H-17); ^{13}C NMR (400 MHz, $CDCl_3$, TMS, δ , ppm): 112.0, 120.3, 120.8, 121.8, 122.7, 126.1, 126.2, 127.6, 129.3, 131.3, 135.4, 135.7, 138.9, 141.6, 149.7, 150.0, 152.7, 153.0, 163.7; Anal. Calc. for $C_{19}H_{13}N_3O$ (299.3): C, 76.25 %; H, 4.36 %; N, 14.04 %. Found: C, 76.40 %; H, 4.32 % ; N, 14.10 %.



Scheme-I: Reaction scheme for synthesis of (E)-2-((quinolin-8-ylmethylene) amino) quinolin-8-ol (H_5L)

2.3 Physical measurements

IR spectra were measured on PerkinElmer L 120-000A spectrometer with KBr pellets ranging from 4000-400 cm^{-1} . 1H and ^{13}C NMR spectra were recorded on Bruker DPX- 400 MHz spectrometer. Chemical shift was reported as ppm taking $CDCl_3$, tetramethylsilane as standard. Elemental analysis was carried out using PE2400 elemental analyser.

Fluorescence spectra were obtained in PerkinElmer LS 45 spectrofluorometer. Steady state absorption spectra were recorded on Shimadzu UV- 1601PC absorption spectrophotometer. Absorption and fluorescence spectra were measured using Quartz cuvettes of 10 mm optical path length which was obtained

from PerkinElmer, USA (part no. B0831009) and Hellma, Germany (type 111-QS) respectively. For fluorescence emission and excitation spectra measurements, 5 nm band pass was used in excitation and emission side. Fluorescent quantum yield (Φ_f) were calculated by comparing the total fluorescent intensity under the whole fluorescence spectral range with that of standard ($\Phi_f = 0.546$, quinine sulfate in 1 M H₂SO₄) using the following equation[26]

$$\Phi_f^i = \Phi_f^s \cdot \frac{F^i}{F^s} \cdot \frac{1-10^{-A^s}}{1-10^{-A^i}} \cdot \left(\frac{n^i}{n^s}\right)^2$$

Where F is the total fluorescence intensity under whole fluorescence spectral curve, A^i and A^s is the optical density of the sample and standard respectively and n^i is the refractive index of the solvent at 300 K

3. Results and Discussion.

3.1 Steady state spectral properties

The absorption spectra of H₅L were recorded in different homogeneous solvents. Absorption spectra showed two different peak positions at 280 nm and 335 nm. The large value of molar extinction coefficient ($\epsilon \sim 1.5 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$) indicates that absorption is due to $\pi\pi^*$ transition of benzene ring. The peak at 280 nm is observed due to double bond present in azomethine C=N group. The fluorescence emission spectra of H₅L show a single peak at 400-525 nm upon excitement at 335 nm (**Table-I**). Fluorescence spectra show different properties in pure homogeneous solvents due to difference in the polarity of solvents (**Figure -1**). So this fluorescent probe can be further used as polarity sensor probe. The value of fluorescence quantum yield (Φ_f) is low and can be explained by nonradiative decay transition to the lo- lying $\pi\pi^*$ state of nitrogen[27]

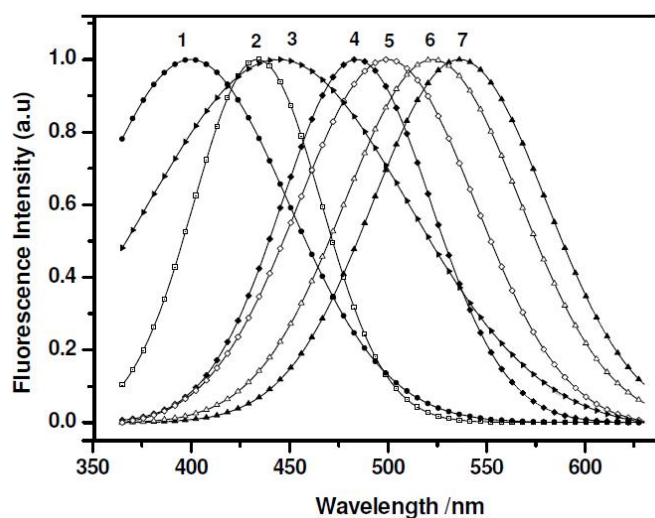


Figure:1 Fluorescence emission spectra of H₅L in presence of different homogeneous solvents.

Solvents	λ_{abs}^a (nm)	λ_{fl}^b (nm)	$\Delta\nu_{\text{ss}}^c$ (cm^{-1})	Φ_F^d (10^{-3})
Ethanol	266	500	10303	3.8
	330			
Methanol	252	520	10530	2.4
	336			
Acetonitrile	253	495	10140	4.2
	330			
1,4-Dioxane	255	401	4974	2.7
	335			
N,Ndimethylformamide	270	504	10645	2.6
	328			
Toluene	268	439	7249	3.2
	333			
Dimethylsulfoxide	260	484	9010	2.2
	337			
Chloroform	253	472	8932	5.4
	332			
Ethyl acetate	265	425	6590	4.4
	332			
Tetrahydrofuran	257	430	6220	4.6
	338			

Table-1: steady state spectral property of H₅L in different homogeneous solvents.

3.2 Metal ion titration.

The binding and sensitivity activity of the metal ion of H₅L was carried out at room temperature in ethanol solution. Change of fluorescent spectra of H₅L (~ 4 μ M) in presence of different metal ions is illustrated in (**figure-2**). The fluorescent maxima peak of H₅L (4 μ M) appeared at 500 nm upon excitation at 335 nm. On addition of Zn²⁺ (30 μ M) at room temperature, a red shift at 520 nm was observed in fluorescent maxima with increase in fluorescence emission intensity (**figure -2**). However no change in the fluorescence peak position was observed for other alkali or alkaline earth metal ions like Na⁺, K⁺, Ca²⁺, Mg²⁺, Sr²⁺ or transition metals like Cd²⁺, Ni²⁺, Co²⁺, Cu²⁺, Mn²⁺, Ba²⁺ and Fe³⁺. The H₅L showed either no change in the fluorescence peak position and a negligible amount of change in fluorescence intensity in presence of Mg²⁺ and Cd²⁺ (**Figure -2**). This indicates the selective estimation of Zn²⁺. On increase in concentration of Zn²⁺ (~60 μ M), a significant enhancement of fluorescence intensity was observed at 500 nm with ~ 20 nm red shift. This effect was not observed for other metal ions like Na⁺, K⁺, Ca²⁺, Mg²⁺, Sr²⁺, Cd²⁺, Ni²⁺, Co²⁺, Cu²⁺, Mn²⁺, Ba²⁺ and Fe³⁺ even if concentration was very high (~100 μ M). The increase in fluorescence intensity can be explained due to the formation of H₅L -- Zn²⁺ complex which inhibits C=N isomerisation. Fluorescence intensity profile change of H₅L in presence of other metal ions can be shown in the (**figure -3**) which indicated high selectivity of Zn²⁺.

Further the fluorescence intensity of H₅L (~4 μ M) didn't show much variation on addition of excess amount of different metal ions. Tolerance of fluorescence intensity due to Zn²⁺ (30 μ M) in the presence of 50 times an excess of different metal ions was successfully verified with no significant change in fluorescence intensity (**figure -3**). Fluorescence intensity was quenched in the presence of Co²⁺ and Ni²⁺ due to unoccupied molecular d- orbital. [28]. This proves that all detection of Zn²⁺ didn't face any interference with other metal ions. This indicates that H₅L -- Zn²⁺ complex was hardly affected by the coexistence of these ions. Thus H₅L can be used as selective fluorescence chemosensor for determination of Zn²⁺ in presence of other metal ions.

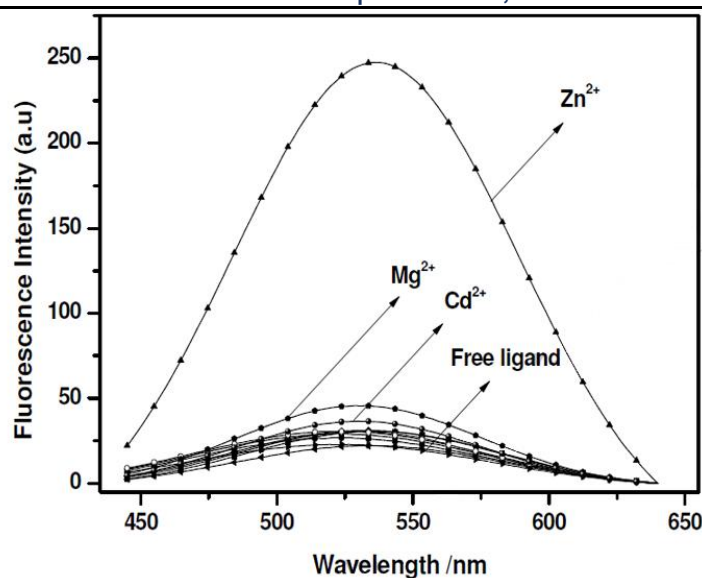


Figure:2 Fluorescence emission spectra of H_5L in the absence (free ligand) and in presence of $30\mu M$ concentration of different metal ions in ethanol.

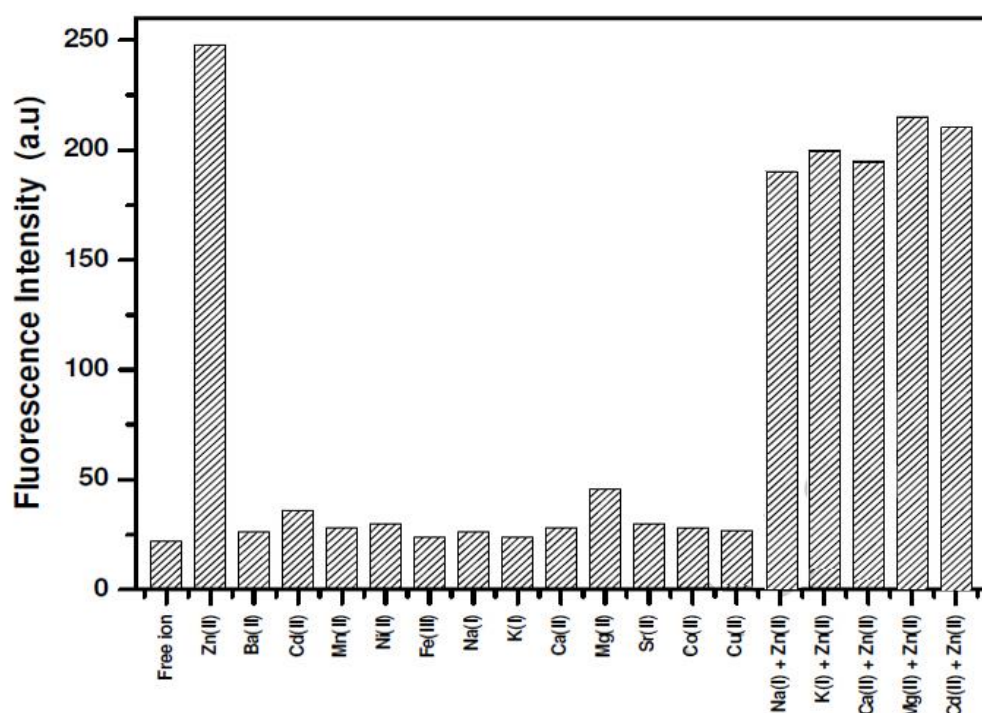


Figure 3: Change of fluorescence intensity profile of H_5L in absence and presence of $30\mu M$ concentration of different metal ions in ethanol.

3.3 Influence of Zn^{2+} concentration.

The influence of Zn^{2+} concentration on fluorescence properties of H_5L was carried out in ethanol solution. Excitation and fluorescence emission peak were taken at 335 nm and 500 nm respectively. The fluorescence peak of H_5L was very weak due to isomerisation of $C=N$ double bond. The nitrogen atom in the H_5L has a strong affinity for Zn^{2+} . Therefore with gradual increase in concentration of Zn^{2+} ($\sim 60\mu M$) to H_5L results in increase in fluorescence intensity with a red shift of emission peak from 500 to 520 nm. This is due to prohibition of isomerisation by metal ion binding. **(Figure-4)**. The increase in fluorescence is due to addition of Zn^{2+} resulting in strong complexation with H_5L . However this effect was not observed in presence of other metal ions even at very high concentration ($\sim 100\mu M$). The quantum yield was calculated for H_5L both in presence of Zn^{2+} as well as in Free State. The quantum yield for H_5L was increased from 3.8×10^{-3} for H_5L to 5.6×10^{-1} for $H_5L - Zn^{2+}$ complex.

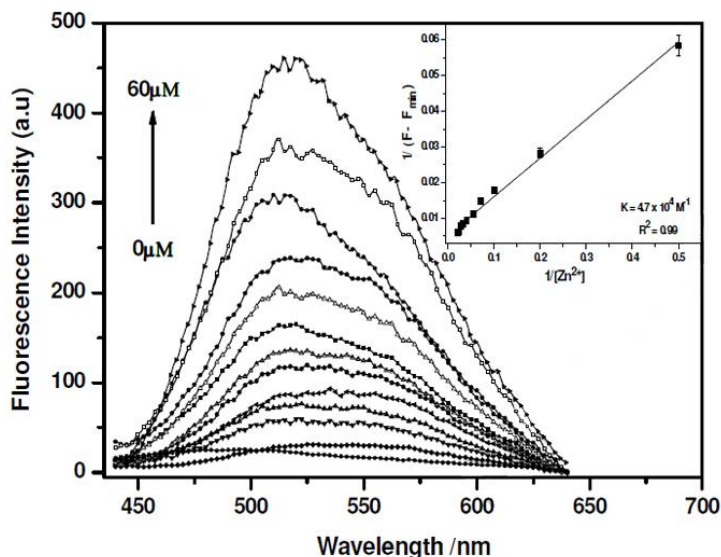


Figure:4 variation of fluorescence intensity of H₅L against different concentration of Zn²⁺
Inset represents the double reciprocal plot for 1:1 complex formation.

3.4 Stoichiometry of complexation.

The Stoichiometry of the H₅ L---Zn²⁺ complex was determined using Job's plot analysis. Total concentration of H₅ L and Zn²⁺ is kept at 10 mM and molar ratio of Zn²⁺ is varied from 0.1 to 0.9 (**Figure-5**). Fluorescence maxima was attained at 520 nm when the molar concentration of Zn²⁺ was 0.5. This indicates 1:1 complex formation between H₅ L and Zn²⁺.

The stoichiometric ratio and apparent binding constant of H₅ L with Zn²⁺ was determined using Benesi – Hildebrand relation which is mentioned below. [29]

$$\frac{1}{F - F_0} = \frac{1}{F_\alpha - F_0} + \frac{1}{K(F_\alpha - F_0)} \times \frac{1}{[Zn^{2+}]}$$

Where F_0 and F represents fluorescence intensity in the absence and presence of Zn²⁺ respectively. F_α represents the fluorescence intensity in presence of excess amount of Zn²⁺. For 1:1 complex formation of H₅ L and Zn²⁺, the double reciprocal plot of $1/F - F_0$ vs. $1/[Zn^{2+}]$ should give a straight line. The equilibrium constant (K) can be calculated using the slope and intercept of the plot. Inset of (**figure 4**) represents the linear fitting using Benesi – Hildebrand relation which confirms the 1:1 stoichiometry of H₅ L---Zn²⁺ complex with association constant of $4.7 \times 10^4 \text{ M}^{-1}$. This further confirms the 1:1 complex formation of H₅ L and Zn²⁺ based on Job's plot analysis. (**Figure -5**)

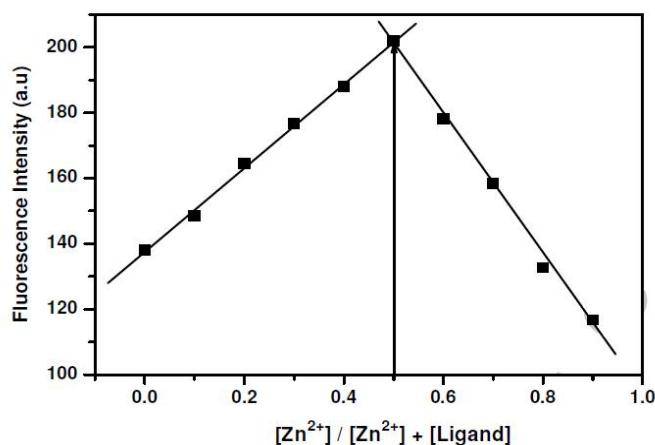


Figure:5 Job's plot of H₅L with Zn²⁺ in ethanol solution.

3.5. Effect of pH

Sensitivity to pH in presence and absence of Zn²⁺ was carried out. No change was observed in fluorescence intensity in free ligand over a wide range of pH. (**Figure-6**). However in the presence of Zn²⁺,

H₅L showed the dependency on pH. H₅L showed weak fluorescence response to Zn²⁺ in acidic environment resulting in weak coordination ability of Zn²⁺. However on increasing the pH to 6.5-10.5 the molecule showed good sensing ability to Zn²⁺. This result indicates that H₅L can be employed as good fluorescence probe for detection of Zn²⁺ over a wide range of pH and also in presence of other metal ions. Black dots in the graph represent presence of Zn²⁺ while white dots represent absence of Zn²⁺.

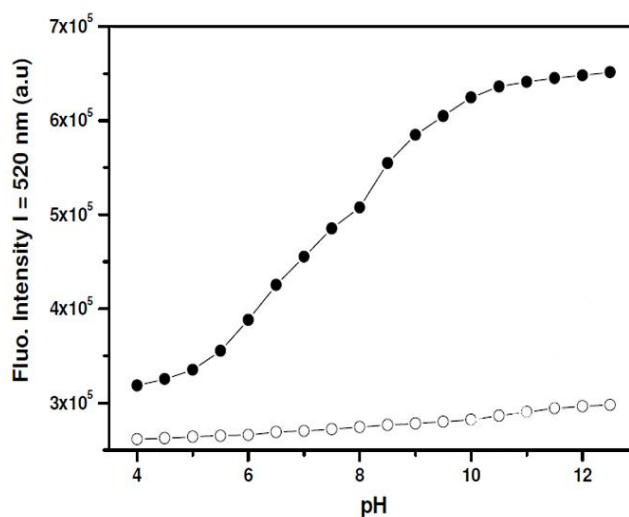


Figure:6 effect of pH on the fluorescence intensity of H₅L in presence and absence of Zn²⁺

4 Conclusions

In this work we have designed and synthesized a Schiff base fluorescence chemosensor H₅L for detection of Zn²⁺. Addition of Zn²⁺ to the ethanol solution of H₅L resulted in a red shift with the enhancement in the fluorescence intensity which was not observed for other metal ions. Also H₅L was able to distinguish between Zn²⁺ from Cd²⁺. The stoichiometry ratio and association constant was evaluated using Benesi – Hildebrand relation which came out to be 1:1. This supported the 1:1 complex formation based on Job's plot analysis. Further this fluorescent probe can be employed as potential candidate to study in various biological environments.

Acknowledgments

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