

Dimethylaminodiethylenetriamine Derivatives of Fluorescence Chemosensor for Detection of Zn^{2+} In Aqueous Solution

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Abstract. Fluorescent chemosensors for the detection and measurement of metal ions, especially for cations environmental interest such as Fe^{3+} , Co^{2+} , Mn^{2+} , Cu^{2+} , and Zn^{2+} are actively investigated because it shows simplicity, high sensitivity and fast response. New benzenyl derivative bearing pyridine group has been synthesized and studied as fluorescent chemosensor for Zn^{2+} ion. Chemosensor N-{2-[(4-Dimethylamino-benzylidene)-amino]-ethyl}-N'-pyridin-2-ylmethylene-ethane-1,2-diamine was synthesized by condensation of *p*-dimethylaminobenzaldehyde, diethylenetriamine and *o*-pyridinecarbaldehyde and characterized by FT-IR, ¹H-NMR and elemental analysis (CHN). FT-IR showed the appearance of peak azomethine (C=NH) at 1639.46 cm^{-1} , pyridine (C-N) at 1591 cm^{-1} and disappearance of NH_2 peak at 3278.78 cm^{-1} after the condensation reaction in between aldehyde and amine. ¹H-NMR signal at 8.19 ppm, 3.12 ppm and 8.08 ppm was assigned to C=NH, $\text{N}(\text{CH}_3)_2$ and C-N respectively, confirmed the formation of N-{2-[(4-Dimethylamino-benzylidene)-amino]-ethyl}-N'-pyridin-2-ylmethylene-ethane-1,2-diamine. The elemental analysis was found closed to the theoretical value and the percent composition of A is 91.82%. Sensor A exhibits high selectivity and sensitivity towards Zn^{2+} . Other metal ions such Cu^{2+} , Fe^{3+} , Co^{2+} and Ni^{2+} had no such significant effect on the fluorescence. The detection limit of N-{2-[(4-Dimethylamino-benzylidene)-amino]-ethyl}-N'-pyridin-2-ylmethylene-ethane-1,2-diamine for Zn^{2+} was 3.5×10^{-5} M. This sensor exhibits a very good fluorescence sensing ability to Zn^{2+} over a wide range of pH. Therefore it is capable of being a practical system for the monitoring of Zn^{2+} concentrations in real water sample.

1. Introduction

Zinc is the second most abundant transition metal ion in the human body, it plays an indispensable role in various biological activities such as gene expression, neural signal transmission, regulation of metalloenzymes, and DNA binding or recognition [1]. However, excessive amounts of zinc in human cause many severe diseases such as Alzheimer's disease [2], ischemic stroke [3] and epilepsy [4]. Hence it is very important to develop highly selective and sensitive chemosensors for the detection of Zn^{2+} in the environment as well as biological samples.

Owing to its essential roles in biological nutrition systems, the measurement of Zn^{2+} is an active field in analytical chemistry. Compared with numerous traditional analytical techniques, fluorescence molecule sensor display high sensitivity, selectivity, simplicity, and tunability thus have been developed as a powerful tool for detecting the trace amount of analytes. Chemosensors are commonly composed of two parts, a receptor (recognition element) responsible for the molecular recognition of



the analyte and a fluorophore (fluorescence reporter) responsible of signaling the recognition event and both are connected through a spacer or also known as a linker [5]. Up to now, a number of fluorescence chemosensors for Zn^{2+} have been reported, which include the fluorophores such as rhodamine, coumarin, BODIPY, and the receptors such as dipicolylamine, and quinolone [6]. These chemosensors are capable of binding with Zn^{2+} . However, a problem with fluorophore chemosensor is their ability to selectively recognize metal ions especially involving selectivity towards one metal cation in mixing with other metal cations. The selectivity of chemosensor towards metal cation is depending on the energy produced by the compound in complexing with the metal cation.

Here we designed and synthesized *N*-{2-[(4-Dimethylamino-benzylidene)-amino]-ethyl}-*N'*-pyridin-2-ylmethylene-ethane-1,2-diamine as a chemosensor for Zn^{2+} which bears a diethylenetriamine and pyridyl moiety acting as the selective receptor of Zn^{2+} and 4-dimethylaminobenzyl as fluorescence signal. The effects of selectivity, pH and competition ions were reported. Dimethylaminobenzyl moiety was selected in this study due to its suitability and performance as a fluorophore with high energy [7]. As for receptor, diethylenetriamine and 2-pyridinecarbaldehyde, were combined to be able to coordinate with metal ions. The coordination can likely influence the fluorescence of the molecule because of the presence of strong donor N atom.

2. Experimental

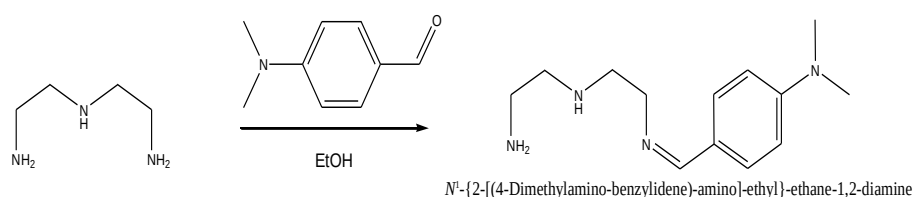
2.1. Materials and physical methods

All reagents and solvents were commercially available of analytical grade and were used without further purification. 4-dimethylaminobenzaldehyde, diethylenetriamine and 2-pyridinecarbaldehyde were obtained from Sigma. ^1H NMR spectra were recorded on a Bruker Varian 600 Hz using chloroform- d and acetone- d_6 solutions with TMS as an internal standard. The fluorescence spectra were recorded with a Luminescence Spectrometer LS 55 equipped with quartz cuvettes of 1 cm path length. The elemental analysis was carried out on Thermo Finnigan Flash EA 110 Elemental Analyzer. Infrared spectra were obtained on Perkin Elmer 100 spectrophotometer in the range 4000–600 cm^{-1} .

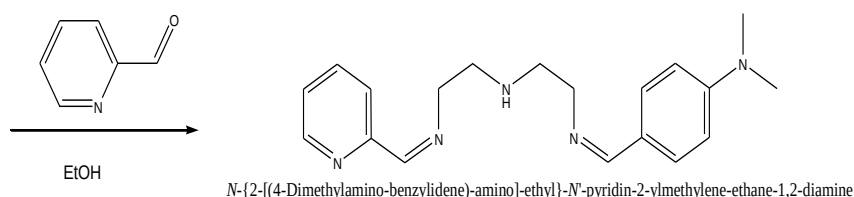
2.2. Synthesis of *N*-{2-[(4-Dimethylamino-benzylidene)-amino]-ethyl}-*N'*-pyridin-2-ylmethylene-ethane-1,2-diamine (A)

To prepare unsymmetrical Schiff base involves two steps; monocondensed and dicondensed.

Step 1



Step 2



Scheme 1. Synthesis of *N*-{2-[(4-Dimethylamino-benzylidene)-amino]-ethyl}-*N'*-pyridin-2-ylmethylene-ethane-1,2-diamine.

Step 1

To the stirred solution of the diethylenetriamine (10 mmol) in ethanol (30 ml), was added dropwisely a solution of the 4-dimethylaminobenzaldehyde (10 mmol) in ethanol (30 ml). After addition was completed, the mixture was stirred and refluxed for 6 h. During this time the mixture turn to yellow solution. Then the solution was evaporated under reduced pressure, the oily product was dried in desiccator overnight to remove excess solvent to afford a yellow solid product. Yield: 2.2 g (84%). IR (cm^{-1}): 1633 (C=N), 3278.78 (NH_2), 1602.60 (Ar, C=C). ^1H NMR (600 MHz, Acetone- d_6) δ 9.74 (s, 1H), 8.96 – 8.81 (m, 2H), 8.44 (d, J = 7.8 Hz, 1H), 8.18 – 8.11 (m, 1H), 7.91 – 7.83 (m, 1H), 7.56 – 7.48 (m, 2H), 7.48 – 7.39 (m, 1H), 7.35 – 7.24 (m, 1H), 6.78 – 6.67 (m, 2H), 3.65 – 3.48 (s, 2H), 3.12 (s, 7H), 2.59 – 2.49 (m, 1H), 1.94 (s, 2H) ppm. Anal. Calc. for $\text{C}_{13}\text{H}_{22}\text{N}_4$: C, 66.63; H, 9.36; N, 23.91. Found: C, 60.65; H, 8.99; N, 22.27.

Step 2

To the stirred solution of the precursor (10 mmol) in ethanol (30 ml), a solution of 10 mmol in 30 ml ethanol of 2-pyridinecarbaldehyde was added and the solution was refluxed for 48 h. Then the solution was evaporated under reduced pressure, the oily product was dried in desiccator overnight to remove excess solvent to afford a yellow solid product. Yield: 3.3 g (76%). IR (cm^{-1}): 1633 (C=N), 3278.78 (NH_2), 1602.60 (Ar, C=C), 1521.13 (Ar, C=C). ^1H NMR (600 MHz, Chloroform- d) δ 8.08 (m, 4H), 3.59 (d, J = 6.2 Hz, 2H), 2.87 (d, J = 12.9, 4.5 Hz, 6H), 2.62 (s, 1H), 1.94 (d, J = 2H).

2.3. General procedure for fluorescence experiments

All fluorescence spectra were recorded on a Luminescence Spectrometer LS 55 after the addition of perchlorate metal salts in ($\text{CH}_3\text{OH}/\text{H}_2\text{O}$, 9:1 (v/v), Tris-HNO_3 = 10 mM, pH = 7.0), while keeping the ligand concentration constant (5×10^{-5} M). Solutions of metal ions were prepared from the perchlorate salts of Fe^{3+} , Co^{2+} , Ni^{2+} , Zn^{2+} and Cu^{2+} . The selectivity of N-{2-[(4-Dimethylamino-benzylidene)-amino]-ethyl}-N'-pyridin-2-ylmethylene-ethane-1,2-diamine (A) to analytes was measured with the concentration of N-{2-[(4-Dimethylamino-benzylidene)-amino]-ethyl}-N'-pyridin-2-ylmethylene-ethane-1,2-diamine (A) 5×10^{-5} M and 1×10^{-3} M analytes. The titration experiments were carried out by taking 5×10^{-5} M of N-{2-[(4-Dimethylamino-benzylidene)-amino]-ethyl}-N'-pyridin-2-ylmethylene-ethane-1,2-diamine (A) with the increasing concentration of Fe^{3+} , Cu^{2+} , Co^{2+} , Ni^{2+} and Zn^{2+} respectively.

3. Results and discussions

3.1. Synthesis

The synthesis of the unsymmetrically substituted benzenyl proceed in two steps, i.e., monocondensation of 4-dimethylaminobenzaldehyde with a diethylenetriamine to give N1-{2-[(4-Dimethylamino-benzylidene)-amino]-ethyl}-ethane-1,2-diamine, which are then allowed to react with 2-pyridinecarbaldehyde. The monocondensed product of amine also known as half unit where the primary amine group forms an imine or enamine bond and the other is unchanged, have a potential to react with other carbonyl moieties to form unsymmetrical ligands capable of binding transition metal ions. Condensation of the 'half unit' shows two bands in IR reign ($3298.01\text{-}2809.63 \text{ cm}^{-1}$) [8]. These two bands are assigned to the primary amine stretchings. An intense band around 1638.80 cm^{-1} in the spectrum of the half unit and N-{2-[(4-Dimethylamino-benzylidene)-amino]-ethyl}-N'-pyridin-2-ylmethylene-ethane-1,2-diamine are assigned to the azomethine (C=N) vibrations [9]. ^1H NMR spectrum of the half unit azomethine (C=N) and NH_2 protons show a singlet at 8.19 and 2.17 ppm which closely resembles that of similarly reported compound [10]. The half unit, the ligand shows the aromatic proton as multiplet in the range 6.9-7.8 ppm. The absence of NH_2 proton in the monocondensed ligand shows that the unsymmetrical dicondensed ligand is formed. IR spectrum of N-{2-[(4-Dimethylamino-benzylidene)-amino]-ethyl}-N'-pyridin-2-ylmethylene-ethane-1,2-diamine displayed two bands at 1640 and 1588 cm^{-1} due to (C=N) of azomethine and pyridyl moieties, respectively. The pyridine proton has the signal at 9.23 ppm which confirmed the formation dicondensed ligand.

3.2. Selectivity

The fluorescence selectivity of N-{2-[(4-Dimethylamino-benzylidene)-amino]-ethyl}-N'-pyridin-2-ylmethylene-ethane-1,2-diamine (A) toward various metal ions (Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , and Zn^{2+}) were first studied in Tris- HNO_3 buffer solution (pH 7.0). N-{2-[(4-Dimethylamino-benzylidene)-amino]-ethyl}-N'-pyridin-2-ylmethylene-ethane-1,2-diamine (A) has strong fluorescence emission ($\lambda_{\text{max}} = 450$ nm). The fluorescence enhancement observed for Zn^{2+} as shown in Figure 1.

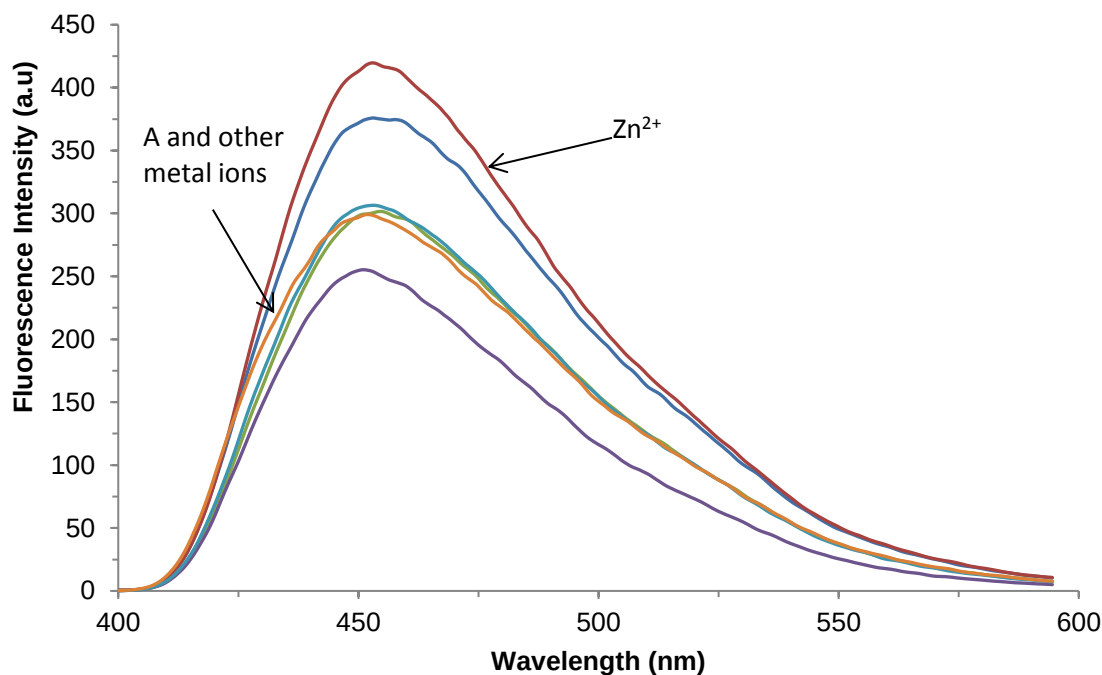


Figure 1. Fluorescence spectra of N-{2-[(4-Dimethylamino-benzylidene)-amino]-ethyl}-N'-pyridin-2-ylmethylene-ethane-1,2-diamine (A) upon addition of Zn^{2+} and other metal ions.

The increase in fluorescence intensity can be attributed due to the formation of the complex. The incorporation of Zn^{2+} effectively increases the conformational rigidity of the ligand and enhanced fluorescence intensity complex [11]. When same equivalent metal ions were added to N-{2-[(4-Dimethylamino-benzylidene)-amino]-ethyl}-N'-pyridin-2-ylmethylene-ethane-1,2-diamine (A), it was found that Fe^{3+} , Co^{2+} , Ni^{2+} and Cu^{2+} caused fluorescence quenched respectively. The results show significant separation in between Zn^{2+} and other metal. This method was used to determine the selectivity for metal ions reported in a previous study [12]. Therefore N-{2-[(4-Dimethylamino-benzylidene)-amino]-ethyl}-N'-pyridin-2-ylmethylene-ethane-1,2-diamine (A) has a better selectivity towards Zn^{2+} over other metal ions tested under the same conditions. The selectivity of N-{2-[(4-Dimethylamino-benzylidene)-amino]-ethyl}-N'-pyridin-2-ylmethylene-ethane-1,2-diamine (A) for Zn^{2+} over other metal was further investigated by competition experiments. High fluorescence intensity of Zn^{2+} and N-{2-[(4-Dimethylamino-benzylidene)-amino]-ethyl}-N'-pyridin-2-ylmethylene-ethane-1,2-diamine (A) affected by the presence of other metal ions. As shown in Figure 2 the individual fluorescence intensity of other metal ions were quenched. When comparing with the individually intensity of competition metals show the presence of Zn^{2+} ion in the mixture is higher than the intensity of metal itself with N-{2-[(4-Dimethylamino-benzylidene)-amino]-ethyl}-N'-pyridin-2-ylmethylene-ethane-1,2-diamine (A). The fluorescence intensity of N-{2-[(4-Dimethylamino-benzylidene)-amino]-ethyl}-N'-pyridin-2-ylmethylene-ethane-1,2-diamine (A) with Zn^{2+} decreasing in the presence of competition metal ion [13]. This shows that other metal ions are also capable of binding with N-{2-[(4-Dimethylamino-benzylidene)-amino]-ethyl}-N'-pyridin-2-ylmethylene-ethane-1,2-diamine (A). These results suggest that although the presence Fe^{3+} , Co^{2+} , Ni^{2+} and Cu^{2+} can quench the fluorescence, the total intensity is still good enough for detection of Zn^{2+} .

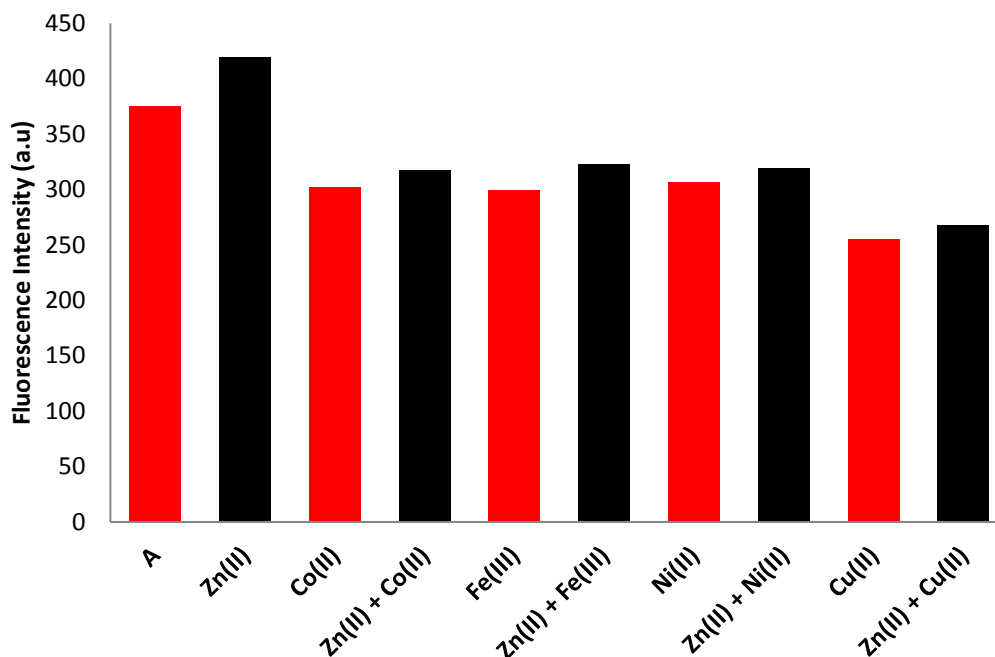


Figure 2. The selectivity of N-{2-[(4-Dimethylamino-benzylidene)-amino]-ethyl}-N'-pyridin-2-ylmethylene-ethane-1,2-diamine (A) for Zn^{2+} in the presence of other metal ions (Co^{2+} , Fe^{3+} , Ni^{2+} and Cu^{2+}) in $\text{CH}_3\text{OH}/\text{H}_2\text{O}$, 9:1 (v/v), $\text{Tris-HNO}_3 = 10 \text{ mM}$, $\text{pH} = 7.0$. The black bars represent the fluorescence intensity of A upon the addition of different metal ions. The red bars represent fluorescence intensity of N-{2-[(4-Dimethylamino-benzylidene)-amino]-ethyl}-N'-pyridin-2-ylmethylene-ethane-1,2-diamine (A) upon the addition of different metal ions in the presence of Zn^{2+} .

3.3. Effects of pH

Any chemosensor to be considered for application in bio-imaging applications need to have high intensity of the spectroscopic signal at physiological pH. Since many chemosensors were sensitive to pH we studied the sensitivity of fluorescence emission in presence and absence of Zn^{2+} examined in a pH range from 3.0 to 12.0. The results of both N-{2-[(4-Dimethylamino-benzylidene)-amino]-ethyl}-N'-pyridin-2-ylmethylene-ethane-1,2-diamine (A) and N-{2-[(4-Dimethylamino-benzylidene)-amino]-ethyl}-N'-pyridin-2-ylmethylene-ethane-1,2-diamine (A)/ Zn^{2+} shows high fluorescence intensities at pH range between 5.0-7.0 (Figure 3). These results indicate that Zn^{2+} could be clearly detected by the fluorescence spectra measurement at environmentally and physiologically relevant pH range (6.0–7.6) [16]. Chemosensor containing nitrogen donors are highly sensitive to environmental pH as the protonation degree of nitrogen are dependent on the pH. Any small change in pH environment of N-{2-[(4-Dimethylamino-benzylidene)-amino]-ethyl}-N'-pyridin-2-ylmethylene-ethane-1,2-diamine (A) near the physiological pH area were well tolerated. While in the basic conditions ($\text{pH} > 7.0$), the fluorescence intensity of N-{2-[(4-Dimethylamino-benzylidene)-amino]-ethyl}-N'-pyridin-2-ylmethylene-ethane-1,2-diamine (A)/ Zn^{2+} was also gradually decreased may be due to the formation of Zn(II) hydroxide complex in this alkaline mixed solutions [14]. Hydrogen bonding form water cluster caused deprotonating, hindered the excitation of the energy which is responsible for the quenching of fluorescence intensity [15]. There is no specific explanation at pH range 3.0–5.0. Thus further study needed to investigate the effect of protonation towards the intensity of fluorophore. To ensure strong emission, the following experiments were carried out in solutions at pH 7.0.

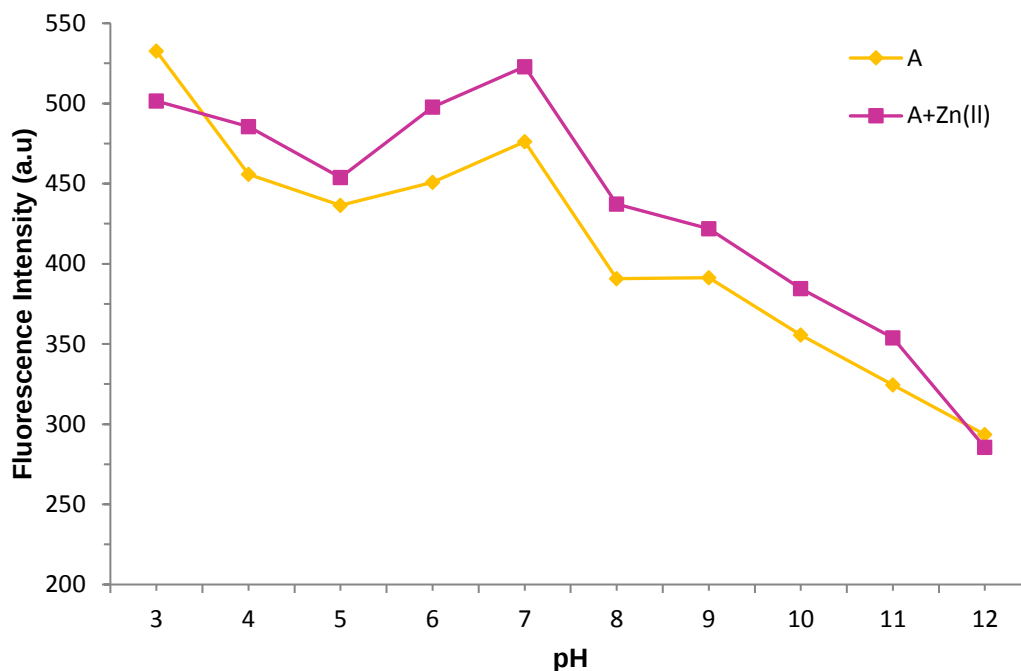


Figure 3. Influences of pH on the fluorescence spectra of N-{2-[(4-Dimethylamino-benzylidene)-amino]-ethyl}-N'-pyridin-2-ylmethylene-ethane-1,2-diamine (A) with Zn^{2+} .

3.4. Stoichiometry of complexation

For determination of stoichiometry between N-{2-[(4-Dimethylamino-benzylidene)-amino]-ethyl}-N'-pyridin-2-ylmethylene-ethane-1,2-diamine (A) and Zn^{2+} , Job's plot analyses were used.

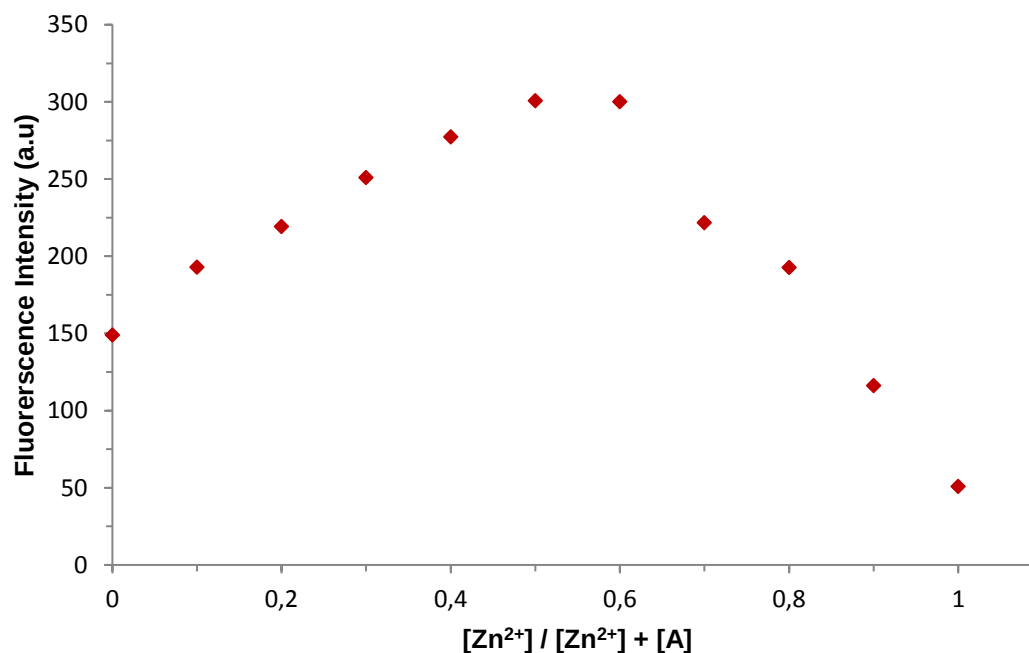


Figure 4. Job's plot of N-{2-[(4-Dimethylamino-benzylidene)-amino]-ethyl}-N'-pyridin-2-ylmethylene-ethane-1,2-diamine (A) with Zn^{2+} in $\text{CH}_3\text{OH}/\text{H}_2\text{O}$, 9:1 (v/v), $\text{Tris-HNO}_3 = 10 \text{ mM}$, $\text{pH} = 7.0$.

The method is that keeping total concentration of N-{2-[(4-Dimethylamino-benzylidene)-amino]-ethyl}-N'-pyridin-2-ylmethylene-ethane-1,2-diamine (A) and Zn^{2+} at 10.0 mM and changing the molar ratio of Zn^{2+} from 0.1 to 0.9. From Figure 4 when molar fraction of Zn^{2+} was 0.5, the fluorescence maxima at 300 nm got to maximum, indicating that forming a 1:1 complex between N-{2-[(4-Dimethylamino-benzylidene)-amino]-ethyl}-N'-pyridin-2-ylmethylene-ethane-1,2-diamine (A) and Zn^{2+} . The stoichiometric ratio and the apparent binding constant of the ligand with Zn^{2+} were also determined using Benesi–Hildebrand relation as follows [2]:

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

where, F_0 and F are the fluorescence intensities in the absence and presence of Zn^{2+} respectively. F_α is the fluorescence intensity in the presence of excess amount of Zn^{2+} . Therefore, for 1:1 complex formation, the double reciprocal plot of $1/(F-F_0)$ against $1/[\text{Zn}^{2+}]$ should give a straight line; from the slope and intercept of which, the equilibrium constant (K) can be calculated. Inset of Figure 5 shows the representative linear fitting using Eq. (1) and confirm 1:1 stoichiometry between N-{2-[(4-Dimethylamino-benzylidene)-amino]-ethyl}-N'-pyridin-2-ylmethylene-ethane-1,2-diamine (A) and Zn^{2+} .

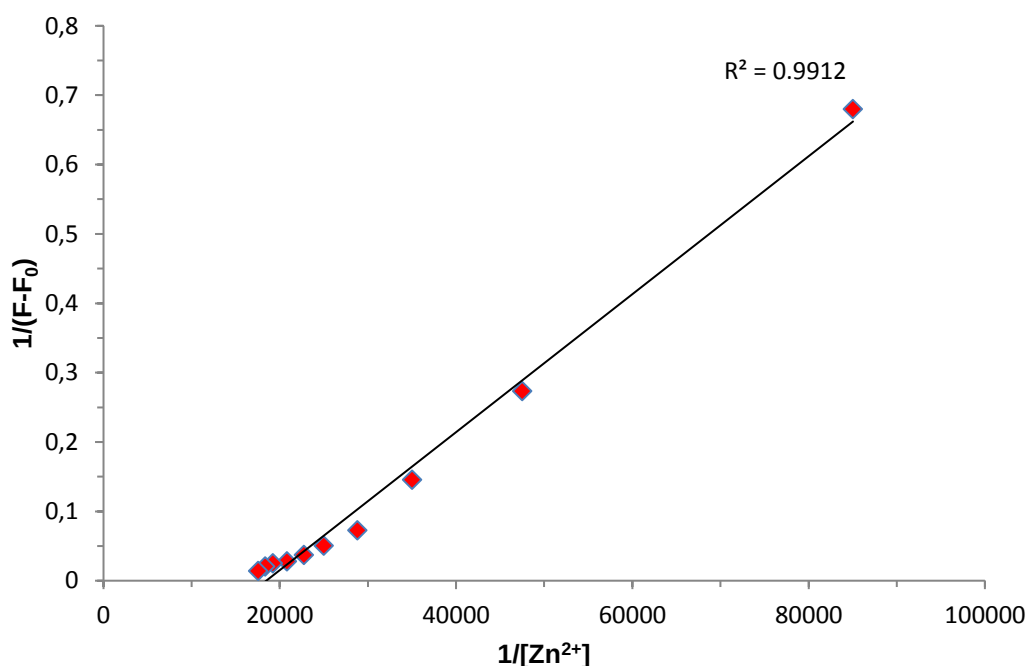
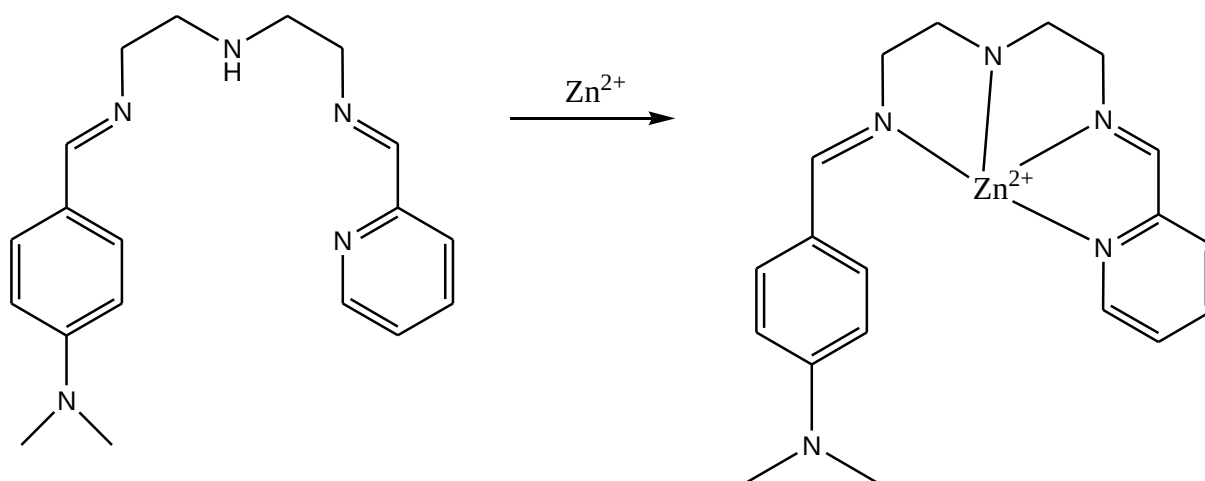


Figure 5. Variation of fluorescence intensity of N-{2-[(4-Dimethylamino-benzylidene)-amino]-ethyl}-N'-pyridin-2-ylmethylene-ethane-1,2-diamine (A) against concentration of Zn^{2+} to determine the association constant.

The association constant of N-{2-[(4-Dimethylamino-benzylidene)-amino]-ethyl}-N'-pyridin-2-ylmethylene-ethane-1,2-diamine (A) with Zn^{2+} in ethanol solution was calculated to be $1.837 \times 10^4 \text{ M}^{-1}$. The high value of association constant K indicates that strong complex formation takes place between Zn^{2+} ion and N-{2-[(4-Dimethylamino-benzylidene)-amino]-ethyl}-N'-pyridin-2-ylmethylene-ethane-1,2-diamine (A). This is due to the presence of pyridyl group, which offers extra binding site. Moreover, this further corroborated 1:1 complex formation based on Job's plot analyses. The proposed mechanism of Zn^{2+} -N-{2-[(4-Dimethylamino-benzylidene)-amino]-ethyl}-N'-pyridin-2-ylmethylene-ethane-1,2-diamine (A) shown in Scheme 2.



Scheme 2. The proposed mechanism for sensing of Zn^{2+} by N-{2-[(4-Dimethylamino-benzylidene)-amino]-ethyl}-N'-pyridin-2-ylmethylene-ethane-1,2-diamine (A).

3.5. Response of the chemosensor N-{2-[(4-Dimethylamino-benzylidene)-amino]-ethyl}-N'-pyridin-2-ylmethylene-ethane-1,2-diamine (A) toward different concentrations of Zn^{2+}

For many practical purposes, it is very important to detect the analytes at low concentrations. Even though N-{2-[(4-Dimethylamino-benzylidene)-amino]-ethyl}-N'-pyridin-2-ylmethylene-ethane-1,2-diamine (A) shows high fluorescence intensity with Zn^{2+} ion which was sensitive enough for practical uses.

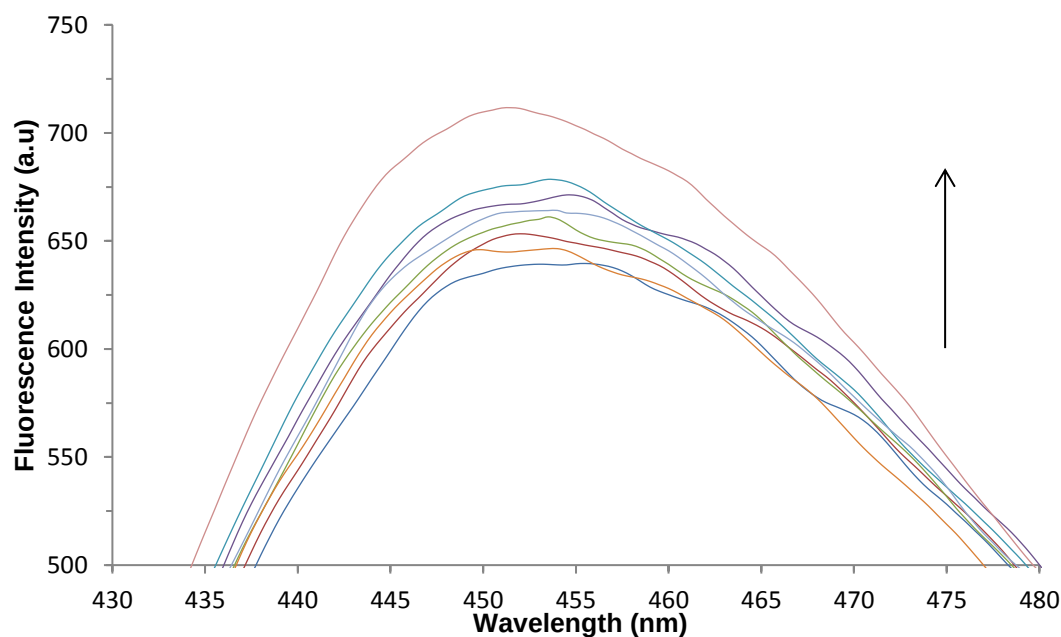


Figure 6. Fluorescence changes of N-{2-[(4-Dimethylamino-benzylidene)-amino]-ethyl}-N'-pyridin-2-ylmethylene-ethane-1,2-diamine (A) (5×10^{-5} M) in the presence of different concentrations of the Zn^{2+} ion.

The sensitivity of chemosensor was examined via the titration between chemosensor and different concentration of Zn^{2+} and achieved a highly selective linear response ($R^2 = 0.99$) to the targeted analyte (Figure 6). From the titration data, the limit of detection (LOD) of N-{2-[(4-Dimethylamino-

benzylidene)-amino]-ethyl}-N'-pyridin-2-ylmethylene-ethane-1,2-diamine (A) was calculated by using the equations: $\text{LOD} = (3 \times \text{standard deviation}) / \text{slope}$. Using the calibration curve (Figure 7), the LOD was found to be $3.5 \times 10^{-5} \text{ M}$.

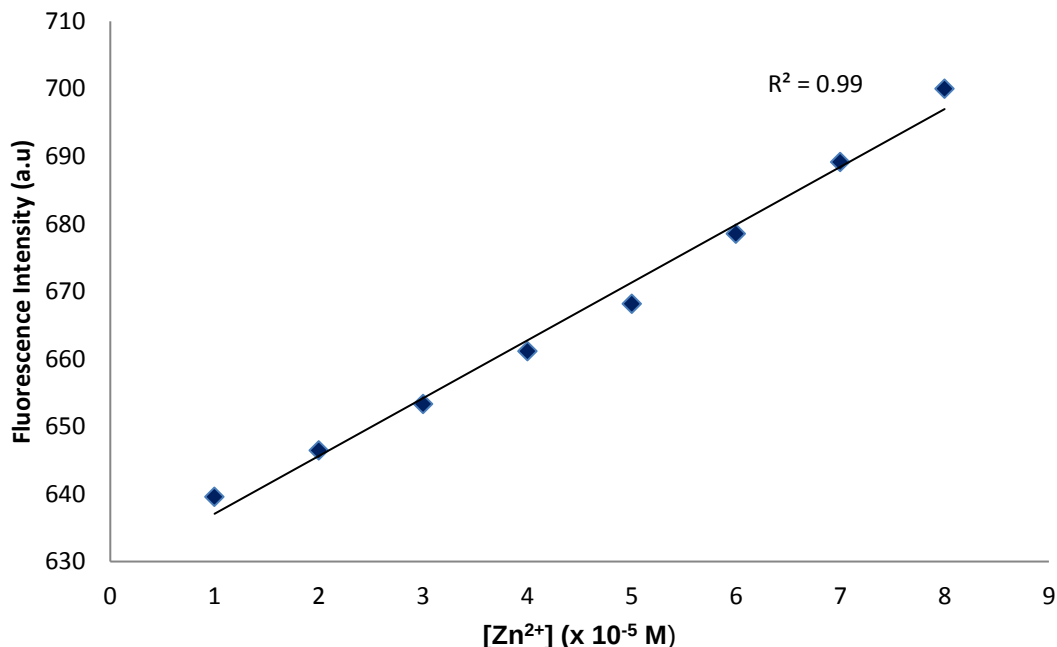


Figure 7. Calibration curve was obtained from the plot of fluorescence intensity with the addition of Zn^{2+} concentration.

4. Conclusion

A Schiff-base fluorescent N-{2-[(4-Dimethylamino-benzylidene)-amino]-ethyl}-N'-pyridin-2-ylmethylene-ethane-1,2-diamine (A) was synthesized and evaluated as a chemoselective Zn^{2+} sensor. The addition of Zn^{2+} to the solution of N-{2-[(4-Dimethylamino-benzylidene)-amino]-ethyl}-N'-pyridin-2-ylmethylene-ethane-1,2-diamine (A) resulted in a pronounced enhancement in the fluorescence intensity while other metal showed decreasing in the fluorescence intensity. The stoichiometric ratio and association constant were evaluated using Benesi–Hildebrand relation giving 1:1 stoichiometry. This further corroborated 1:1 complex formation based on Job's plot analyses. Further, N-{2-[(4-Dimethylamino-benzylidene)-amino]-ethyl}-N'-pyridin-2-ylmethylene-ethane-1,2-diamine (A) exhibits good fluorescence sensing ability to Zn^{2+} at pH=7.0, giving almost constant emission intensity in the physiological conditions. The detection limit is $3.5 \times 10^{-5} \text{ M}$ which indicated that N-{2-[(4-Dimethylamino-benzylidene)-amino]-ethyl}-N'-pyridin-2-ylmethylene-ethane-1,2-diamine (A) may be useful for preliminary detection of Zn^{2+} ions in chemical and environmental applications.

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