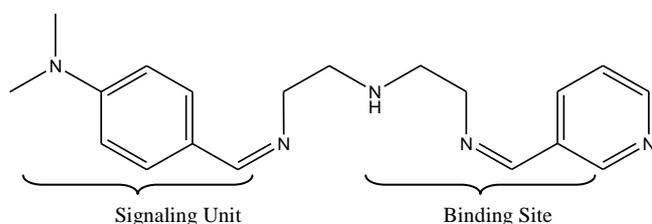


Fluorescent Chemosensor Bearing Amine and Benzenyl Functionality for Fe³⁺ Ions Detection in Aqueous Solution

Sharizal Hasan, Salamiah Zakaria, and Siti Nur Ain Mohd Adnan

Abstract—Recently designing of fluorescent chemosensor for heavy metal ions detection with high specificity and sensitivity have been explored. In this works, two steps synthesis of A was prepared using Schiff base technique. Monocondensed ligand was prepared by reacting diethylenetriamine with 4-dimethylaminobenzaldehyde, followed by attaching 3-pyridinecarbaldehyde on the other side of diethylenetriamine. Sensor A was fully characterized by FT-IR, ¹H-NMR and elemental analysis (CHN). The signal at 1639.46 cm⁻¹ in FT-IR spectrum was assigned to C=N, formed after condensation reaction in between aldehyde and amine. NH₂ peak at 3278.78 cm⁻¹ still appeared proved the monocondensed ligand. ¹H-NMR values at 8.19 ppm and 2.72 ppm were assigned to HC=N and -NH₂ respectively. Dicondensed ligand was formed after addition of 3-pyridinecarboxaldehyde. NH₂ signal in both FT-IR and ¹H-NMR spectrum was absent indicating both amines in triamine undergone condensation to form dicondensed. ¹H-NMR spectrum at 8.19 ppm was assigned to (HC=N) appeared due to the formation of imine proton. The fluorescent spectral measurements revealed that A was selective towards Fe³⁺ ions but not for other metal ions such as Co²⁺, Ni²⁺, Cu²⁺ and Zn²⁺. The detection limit of A was 6.49 × 10⁻⁵ M and expected to be useful as chemical sensor.

Index Terms—Diethylenetriamine, Fe³⁺ ion, Fluorescence Chemosensor, Schiff base.



I. INTRODUCTION

The detection of heavy metal ions are important in many applications, including environmental monitoring, waste management, developmental biology, and clinical toxicology. Transition metal ions represent an environmental concern when present in excess amounts, but at the same time some of them are present as essential elements in living organism. Among various transition metals, iron is the most abundant essential trace element in the human body which plays vital

roles in many biological processes [1]. Lack of iron in primary stages can cause anemia [2], kidney failure and heart diseases [3] Therefore, the demand for fast detection and selective sensor of Fe³⁺ from other ions is important applications in environment and biological systems.

A number of techniques, such as inductively coupled plasma atomic emission spectrometry [4], electrochemical methods and fluorescence techniques, have been developed for Fe³⁺ analysis. However, most of these techniques require expensive equipment, sample pretreatment, and trained operators [5]. Among these methods, much effort has been made in colour changes and emission fluorescent changes because they offers advantages such as sensitivity, selectivity, rapid response time, local observation and lower detection limits [6].

The development of efficient fluorescent chemosensors for various cations has received great attention because of the sensitivity of the techniques related to environmental and biological aspects [7]. A fluorescent chemosensors commonly consists of two parts, a receptor (recognition element) responsible for the molecular recognition of the metal ion linked to a fluorophore (fluorescence reporter) which responsible of signaling the recognition event [8]. The interaction of the analyte with the binding site caused changes in the electronic properties (e.g., enhancement or inhibition of absorption or fluorescence) of the signalling subunit resulting in sensing of the target ion. Therefore, an ideal fluorescent chemosensor must meet two basic requirements: firstly, the receptor must have the strongest affinity with the relevant target (binding-selectivity). Secondly, on the basis of good binding-selectivity, the fluorescence signal should avoid environmental interference (signal-selectivity) [9]. In this respect Schiff base ligands are very attracting to be used as sensing material for chemosensor because they are easy to coordinate with metal ions [10].

Fluorophores are particularly attractive optical molecules and have recently found applications in self-assembled chemosensors, for signal amplification by allosteric catalysis, in supramolecular analytical chemistry, and as fluorescent and photochromic chemosensors. Among various fluorophore, 4-dimethylaminobenzaldehyde is one of the most useful tools due high Stokes shift [11], [12], which makes it appropriate for constructing chemosensor. Therefore, 4-dimethylaminobenzaldehyde was chosen as a fluorophore, diethylenetriamine and 3-pyridinecarbaldehyde used as an ionophore due to their high fluorescence quantum yield and good coordination ability. Herein, we report a convenient and efficient route for the preparation of A i.e. N-{2-[(4-Dimethylamino-benzylidene)-amino]-ethyl}-N'-pyr

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idin-3-ylmethylene-ethane-1,2-diamine by using schiff base technique and its new application as a cation sensor. Chemosensor A shows excellent selectivity and sensitivity towards Fe^{3+} over other metal ions in aqueous solution.

II. EXPERIMENTAL

A. Materials and Instruments

All commercial grade chemicals and solvents were used without further purification. 4-diaminobenzaldehyde, diethylenetriamine and 3-pyridinecarbaldehyde were obtained from Sigma. The elemental analysis was carried out on Thermo Finnigan Flash EA 110 Elemental Analyzer. Infrared spectra were obtained on Perkin Elmer 100 spectrophotometer on KBr discs in the range $4000\text{--}600\text{ cm}^{-1}$. ^1H NMR spectra were recorded on a Bruker Varian 600 Hz using chloroform- d and acetone- d_6 solutions with TMS as internal standard. The fluorescence spectra were recorded on Luminescence Spectrometer LS 55 equipped with quartz cuvettes of 1 cm path length. The excitation and emission slit widths were 10 nm. All emission spectra was recorded at $24 \pm 1^\circ\text{C}$. Stock solutions for analysis were prepared (0.1 M for compound A ($\text{CH}_3\text{OH}/\text{H}_2\text{O}$, 9:1 (v/v), $\text{Tris-HNO}_3 = 10\text{ mM}$, $\text{pH} = 7.0$) immediately before the experiments. The solutions of metal ions were prepared from perchlorate salts of Cu^{2+} , Zn^{2+} , Co^{2+} , Ni^{2+} and Fe^{3+} . The studies on the binding properties of A were carried out in solution ($\text{CH}_3\text{OH}/\text{H}_2\text{O}$, 9:1 (v/v), $\text{Tris-HNO}_3 = 10\text{ mM}$, $\text{pH} = 7.0$). The different metal ion solutions (10 equiv.) were prepared by dissolving the desired amount of metal salts in H_2O . The fluorescence titration was performed with a series of $5 \times 10^{-5}\text{ M}$ solutions of A containing various equivalents of Fe^{3+} ions. Binding studies were confirmed by job's plot and nonlinear curve fitting methods. The association constant (K_a) were calculated by the linear Benesi-Hildebrand equation from fluorescence (Eq. (1)) study by,

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

where F , F_0 and F_α are the emission intensities, respectively in the absence and infinite concentration of the metal ion (M^{n+}) [13].

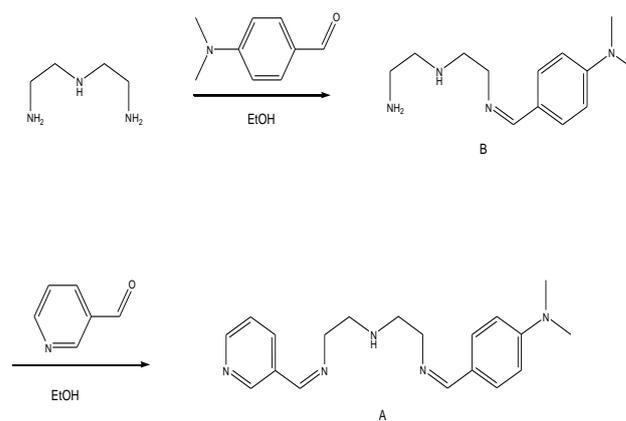
B. Synthesis

A convenient synthetic route for compound A from commercially available compounds is provided and depicted in Scheme 1.

Compound B: Diethylenetriamine (0.01 mol) and 4-dimethylaminobenzaldehyde (0.01 mol) were dissolved in ethanol (50 ml). The reaction mixture was stirred and refluxed for 6 h. After the solvent was evaporated under reduced pressure, the oily product was dried in dessicator overnight to removed 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, $J = 7.8\text{ Hz}$, 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), 7.13 (dd, $J = 8.8, 2.8\text{ Hz}$, 0H), 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.

Compound A: Compound B (0.012 mol) and 3-pyridinecarbaldehyde (0.012 mol) were dissolved in ethanol (50 ml). The reaction mixture was stirred and refluxed for 48 h. After the solvent was evaporated under reduced pressure, the oily product was dried in dessicator overnight to removed excess solvent. 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, $J = 6.2\text{ Hz}$, 2H), 2.87 (d, $J = 12.9, 4.5\text{ Hz}$, 6H), 2.62 (s, 1H), 1.94 (d, $J = 2\text{ Hz}$).



Scheme 1. Chemical structure and synthetic route of compound A.

III. RESULTS AND DISCUSSIONS

A. Synthetic Design of Chemosensor A

The two step synthesis of the benzenyl based chemosensor A is shown in Scheme 1. Briefly, Schiff base reaction between 4-dimethylaminobenzaldehyde and diethylenetriamine in ethanol affords the product B which is then purified by the recrystallization in methanol and characterized by analytical and spectroscopic techniques.

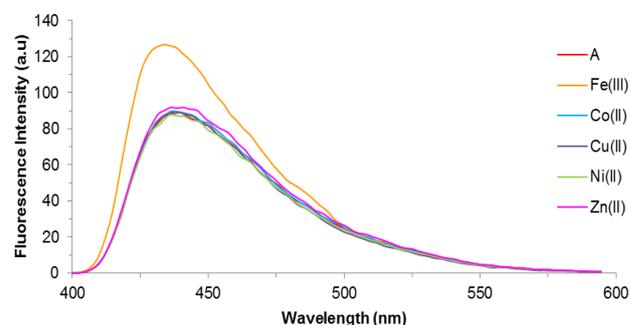


Fig. 1. Fluorescence spectral changes of A ($5 \times 10^{-5}\text{ M}$) ($\text{CH}_3\text{OH}/\text{H}_2\text{O}$, 9:1 (v/v), $\text{Tris-HNO}_3 = 10\text{ mM}$, $\text{pH} = 7.0$) in the presence of various metal ions (0-10 equiv. of each, $\lambda_{\text{ex}} = 385.6\text{ nm}$).

B. Evaluation of Selectivity

A significant feature of a sensor is its high selectivity towards specific analyte over others. Hence, the selectivity of the sensor for metal cations was initially examined in solution

(CH₃OH/H₂O, 9:1 (v/v), Tris-HNO₃ = 10 mM, pH = 7.0). The fluorescence emission spectra of the A with metal ions were studied. As shown in Fig. 1, the emission maximum and the fluorescence intensity slightly changed after treatment with Fe³⁺, while other metal ions (such as Cu²⁺, Zn²⁺, Co²⁺ and Ni²⁺) caused no significant change. Sensor A showed a weak fluorescence. As a result, A exhibits a selective detection of Fe³⁺ when compared to other metal ions by a fluorescence turn-on response. The competitive experiments were carried out in the presence of 1 equiv. of Fe³⁺ mixed with 1 equiv. of miscellaneous metal ions, including Cu²⁺, Zn²⁺, Co²⁺ and Ni²⁺, respectively. Compared the probe with Fe³⁺, there were no distinct variations in the emission intensity of the probe with the mixture of Fe³⁺ and other interfering metal ions. The emission intensity of the solution at 126.67 nm (emission maxima) is shown in Fig. 2.

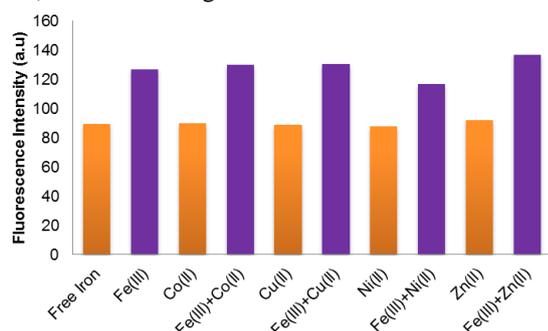


Fig. 2. Fluorescence emission spectra changes of competitive selectivity of A (5×10^{-5} M) (CH₃OH/H₂O, 9:1 (v/v), Tris-HNO₃ = 10 mM, pH = 7.0) toward Fe³⁺ (1 equiv.) in the presence of other metal ions (1 equiv.).

C. Stoichiometry and Binding Mode Studies

In order to determine the binding ability and limit of detection of Fe³⁺ with A, the fluorescence titrations of A were performed by gradually increasing the concentration of Fe³⁺. Fluorescence intensity was increased with increasing the concentration Fe³⁺ (0–10 equiv.). According to the fluorescence titration curve (Fig. 3), the peak maxima at 126.67 nm for A versus Fe³⁺ concentration were plotted and a good linear fluorescence response and regression coefficient ($R^2 = 0.9973$) was observed ranging from 0 to 360 μ M (Fig. 4). The Job plot for the binding between A and Fe³⁺ exhibited a 1:1 stoichiometry for the A–Fe³⁺ complex formation (Fig. 5). Complex emission intensity was gradually increased with increasing the concentration of A as it reached a maximum mole fraction is 0.5. Afterwards, the intensity decreased with further addition of A, which eventually established a 1:1 (A:Fe³⁺) binding stoichiometry. In addition, the binding stoichiometry between A and Fe³⁺ was also confirmed by the Benesi–Hildebrand nonlinear curve fitting method (Fig. 6). The association constant was found to be K_a 1.52×10^4 M for the A–Fe³⁺ complex on the basis of Benesi–Hildebrand analysis. This value is within the range (10^3 – 10^5) [14] of those previously reported for Fe³⁺ binding sensors. This K_a value was also supported the Job's plot. The detection limit of A, is 6.49×10^{-5} M. According to the state regulations, the concentration of the iron ions in the sewage discharge is not more than 179 μ M [15]. These results suggest that A could be used as Fe³⁺ sensor in in environmental samples. Precision is an important analytical parameter for sensor application. Based on job plot study, we proposed the structure of A–Fe³⁺

complex as shown in scheme 2.

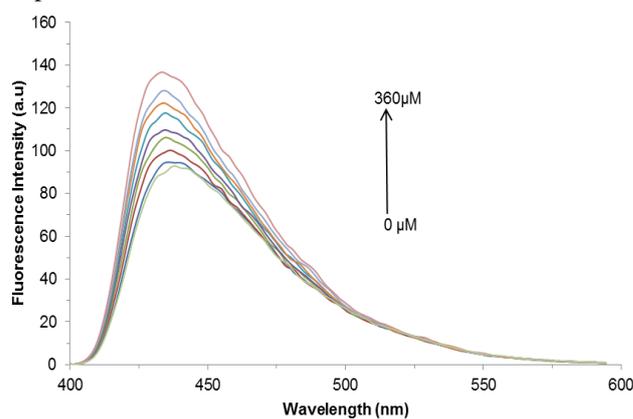


Fig. 3. Fluorescence emission spectra changes of competitive selectivity of A (5×10^{-5} M) (CH₃OH/H₂O, 9:1 (v/v), Tris-HNO₃ = 10 mM, pH = 7.0) toward Fe³⁺ (0–360 μ M) with an excitation wavelength at 385.6 nm.

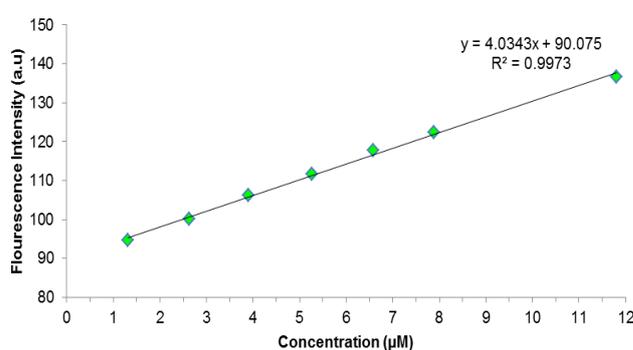


Fig. 4. Fluorescence emission spectra changes of competitive selectivity of A (5×10^{-5} M) (CH₃OH/H₂O, 9:1 (v/v), Tris-HNO₃ = 10 mM, pH = 7.0) toward Fe³⁺ (0–360 μ M) with an excitation wavelength at 385.6 nm.

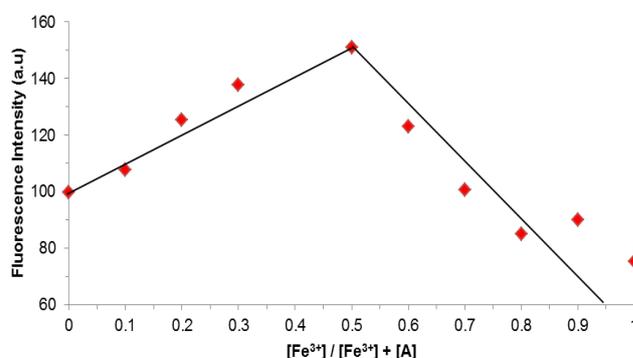


Fig. 5. Job plot of a 1:1 complex of A and Fe³⁺, where the intensity at 150 nm was plotted against the mole fraction of Fe³⁺. The total concentration of Fe³⁺ with receptor A was 10×10^{-5} M.

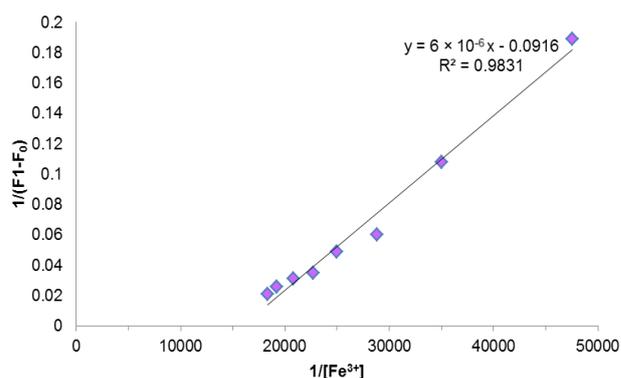


Fig. 6. Benesi–Hildebrand plot of A (5×10^{-5} M) based on 1:1 binding stoichiometry (λ_{ex} = 385.6 nm).

D. Effect of pH

To study the practical applicability of this chemosensor the effects of pH on the fluorescence response of chemosensor A to Fe^{3+} were investigated (Fig. 7). The experiments were carried out at a pH range from 3.0–11.0, with the concentration of fixed at 5×10^{-5} M and Fe^{3+} at 1×10^{-5} M. Sensitivity of A and A- Fe^{3+} at different pH values were studied to explore its photophysical properties in $\text{CH}_3\text{OH}-\text{H}_2\text{O}$ solution (9:1 v/v). The results showed that the sensor A exhibits a weak fluorescence over a wide range of pH except a small enhancement 7.0 pH ranges. In acidic medium (pH <6.0), fluorescence intensity of chemosensor quenched due to the protonation of the amine groups prevents the formation of A- Fe^{3+} complexes. In basic medium (pH >8.0), the partial precipitation of $\text{Fe}(\text{ClO}_4)_3$ perchlorate may decrease in the emission intensity. Therefore, sensor A exhibits good fluorescence response towards Fe^{3+} at pH 7.0, which is favorable for its application in real samples as most of the samples exist at neutral conditions.

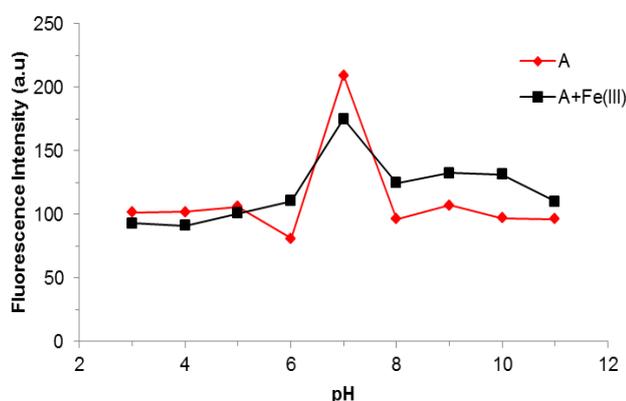
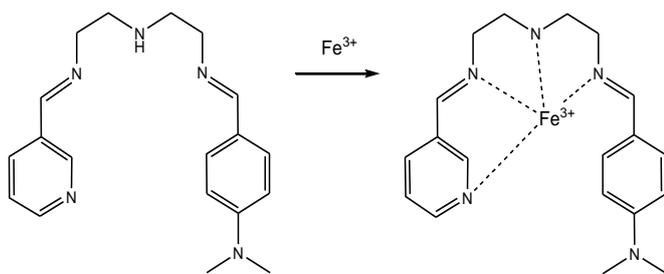


Fig. 7. The variation in fluorescence intensity with the pH of the sensor A (5×10^{-5} M) and corresponding 1.0 equiv. Fe^{3+} .



Scheme 2. Proposed binding mechanism of the chemosensor A with Fe^{3+} .

IV. CONCLUSION

In conclusion, a simple and sensitive benzenyl derived fluorescent chemosensor A was developed for the detection of Fe^{3+} ions in $\text{CH}_3\text{OH}-\text{H}_2\text{O}$ solution with lower detection limit of 6.49×10^{-5} M. The sensor A specifically recognizes Fe^{3+} over other heavy metal ions. The sensor could be applied for monitoring Fe^{3+} in environment at pH7. In future, the sensor A could be used as a potential probe for the detection Fe^{3+} ions in biological and environmental monitoring works.

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