DESIGN AND SYNTHESIS OF SCHIFF BASE LIGANDS AND THEIR APPLICATIONS IN METAL ION SENSING

M.Sc. Thesis

By

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DESIGN AND SYNTHESIS OF SCHIFF BASE LIGANDS AND THEIR APPLICATIONS IN METAL ION SENSING

A THESIS

Submitted in partial fulfilment of the requirements for the award of the degree
of
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by
MOHAMMAD JUNAID

DISCIPLINE OF CHEMISTRY

INDIAN INSTITUTE OF TECHNOLOGY

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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **DESIGN AND SYNTHESIS OF SCHIFF BASE LIGANDS AND THEIR APPLICATIONS IN METAL ION SENSING**

in the partial fulfilment of the requirements for the award of the degree of **MASTER OF SCIENCE** and submitted in the **DISCIPLINE OF CHEMISTRY, Indian Institute of Technology Indore**, is an authentic record of my own work carried out during the time period from July 2018 to June 2020 under the supervision of Dr. Shaikh M Mobin, Associate Professor IIT Indore

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

Signature of the student with date
MOHAMMAD JUNAID

This is to certify that the above statement made by the candidate is correct to the best of my/our knowledge.

June 22, 2020

Signature of the Supervisor (with date)
(Dr. Shaikh M. Mobin)

MOHAMMAD JUNAID has successfully given his M.Sc. Oral Examination held on **24th June 2020**

Signature of Supervisor of MSc thesis
Date:22/06/2020

Convener, DPGC
Date: 26-06-2020

Signature of PSPC Member 1
Date:26/06/2020

Signature of PSPC Member 2
Date: 26/06/2020

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Mohammad Junaid

(MSc. II year)

Dedicated to my Mother ……

ABSTRACT

We have designed and synthesized the Schiff base ligands HL_1 {E-1-(((pyren-1-ylmethyl) amino) methyl) naphthalen-2-ol)}, HL_2 ((Z)-5-((3,4-dihydroxybenzylidene) amino) isophthalic acid) and ((Z)-5-((2-hydroxy-3-methoxybenzylidene) amino) isophthalic acid) by simple condensation reaction in between primary amine and aldehyde. These Schiff base linkers have been characterized by the Mass spectrometry, ^1H NMR spectrometry. HL_1 and HL_2 have been further analysed by Ultraviolet-Visible and fluorescence spectrometry. These ligands are highly selective towards the sensing of Al^{3+} among a wide range of metal cations. Sensing capability of these ligands are observed by the UV-Vis. and fluorescence titration methods. Titration of ligands with Al^{3+} ions by the fluorescence spectroscopy showed a distinct fluorescence quenching (turn off) mechanism at specific wavelength. Schiff base ligands (HL_1 and HL_2) was found to be highly selective and sensitive towards the sensing of Al^{3+} even in the presence of other metal cations with LOD value 14 nm for HL_2. Limit of detection for HL_1 is 24 nM and for HL_2 is 14 nm.

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ACRONYMS

TEA	Triethyl-amine
DMSO	Dimethyl-sulfoxide
TMS	Tetramethyl-silane
NMR	Nuclear Magnetic Resonance
RDS	Rate Determining Step
MLCT	Metal to Ligand Charge Transfer
ICT	Intramolecular Charge Transfer
PET	Photoinduced Electron Transfer
FRET	Fluorescence Resonance Energy
CHEF	Chelation Enhancement Fluorescence Effect
CHEQ	Chelation Enhancement Quenching Effect
ESIPT	Excited State Intramolecular Proton Transfer
N	Nitrogen
O	Oxygen

Chapter 1

Introduction

1.1 Schiff base

Schiff base ligands were first prepared and characterised by a German chemist, Hugo Schiff, in 1864. Schiff base are organic compound that have an imine or azomethine functional group. Schiff base are synthesized by a simple condensation reaction of primary amine with aldehyde [1]. Metals are bind to the Schiff base ligand through the azomethine nitrogen and another substituent which is connected to the aldehyde aromatic ring. Metal complex of Schiff base have different geometries which are biologically active complexes, such as in pharmaceutical industry, medicinal chemistry because of large number of biological activities like antimicrobial [3], analgesic, anthelmintic antioxidant, anticancer, antitubercular, anti-HIV [6] properties. Schiff base forms an important class of the most widely used organic compounds and have variety of applications in many fields such as analytical, biological [4-5], and inorganic chemistry. The nitrogen atom of imine group may be participated in the formation of hydrogen bond with the active centre of cell constituents and involve in cell processes [7]. Apart from these applications, Schiff base are also used as catalysts, corrosion inhibitors, pigments [2] and in organic synthesis and Schiff base oligomer which are capable of forming polymer metal complexes with metal salts this allow the ligand to carry out the metal ion from the industrial waste [11]. Schiff base also used to remove the toxic heavy metals contaminants from aqueous waste water stream [12] Biological activities of Schiff base are reported by the introduction of transition metals. Structurally Schiff base is an analogue of an aldehyde in which the carbonyl group (C=O) is substitute by the imine (C=N) group [2]. Schiff base that have the phenyl substituents are more stable [9] and easily synthesized, while those which have the alkyl substituents are relatively unstable. Schiff base of aliphatic aldehydes are relatively unstable and readily polymerizable, while aromatic aldehydes are more stable [8]. Mostly yield of aromatic Schiff base are more than the

aliphatic aldehydic base. Schiff base are fromed from an aldehydes or ketones is a reversible reaction and generally takes place under acidic condition or under reflux condition

1.1 Mechanism of Schiff base

Mechanism of Schiff base consists of two steps. In this ~~case amine is~~ a nucleophile and aldehydic carbonyl carbon is an electrophile. In first step of mechanism, amine attack on carbonyl carbon of the aldehyde to give an intermediate called carbinolamine via an addition reaction. The intermediate released the H_2O with the help of acid or base catalysed mechanism. Water is released from the alcoholic intermediate via the acid catalysed mechanism; generally, this step is the rate determining step (RDS) of Schiff base preparation. If acid concentration is very high then amine is protonated and becomes non-nucleophilic. Reaction shift backward side and formation of carbinolamine cannot happen.

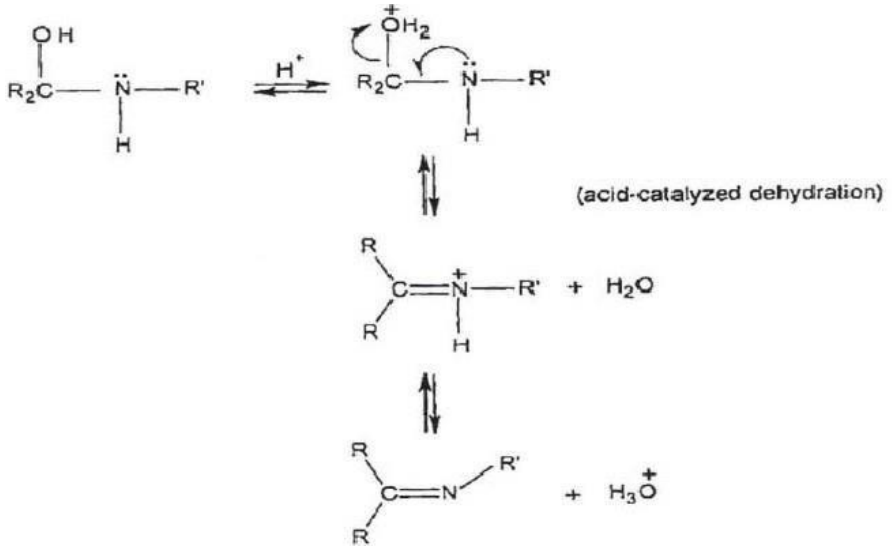


Figure 1: Mechanism of Schiff-base formation via carbinolamine intermediate

The carbinolamine is also dehydrated by the base catalysed mechanism. This mechanism is very similar to the E_2 (elimination) of alkyl halides only difference is that, it is not a concerted mechanism. This reaction is going through two steps via an anionic intermediate. Formation of Schiff base consist of two types of reactions, first is addition and second is elimination reaction [12].

1.3 What is Chemosensor?

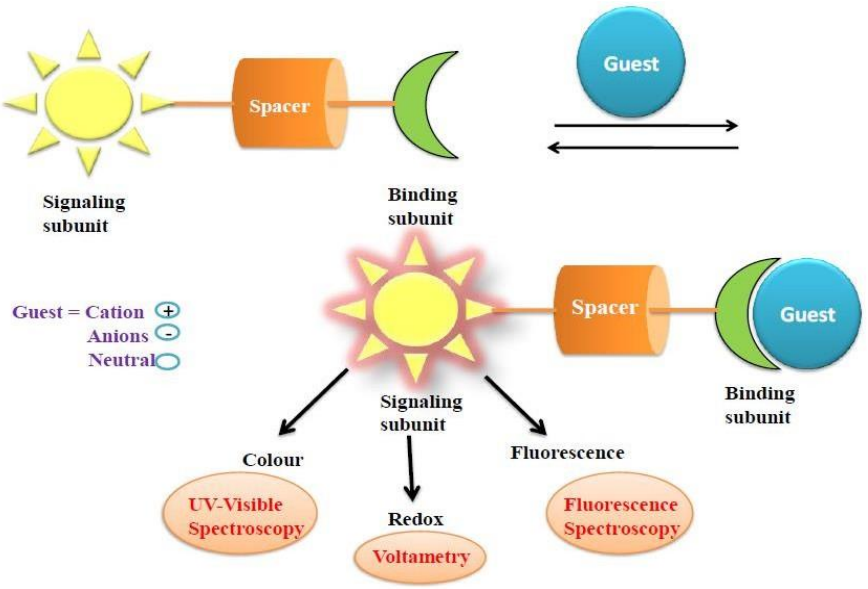
Organic molecule which have a chromophore, binding site, and interaction between binding sites and chromophore are called chemosensors [13]. If the sites of binding show non-reversible reactions, then the chemosensor are called chemodosimeters [14]. F. Goppelsröder in 1867 reported the first chemosensor, and was used for the detection of aluminium ion by forming a ring of morin chelate [39]. This results to the development of a number of fluorescent chemosensors for the sensing of many metal cations. In fact, the early chemosensors were used for the detection of metal cations [15].

1.4 Parts of Chemosensor and its Classification

Chemosensor consist of three parts**:** (a) An active unit (moiety that change the properties of indicator) and (b) A receptor (moiety that shows the selective binding), (c) and a spacer, geometry of the complex is modify by the spacer and it also change the electronic interaction of binding units [16-17].

Chemosensor can be classified according to the behaviour of the emitted signal by the chemosensor. In an optical sensor, a spectroscopic measurement is associated with the recognition process. For example, reflectance or luminescence measurements, absorbance etc [20]. Physicochemical properties of chemosensor vary upon interaction with a guest analyte so that fluorescence spectra are varying as compared with the ligands. Chemosensor framework usually has two integrated components. First is a signalling chromophore and guest receptor is a guest components which have an ability of recognition of guest analyte and these components are linked by a spacer and this moiety is called fluorophore-spacer-receptor scaffold [5] When a guest analyte is interact with the receptor, show the variation in some photophysical properties via

different process such as emission wavelength , fluorescence enhancement, and fluorescence intensity, fluorescent quenching, shift in original fluorescence signal and fluorescent lifetime in terms of calorimetric (colour), fluorescent and electrochemical (redox) chemosensor [28]. (Figure 2) and such variation gives an indication of the analytes binding.



Guest = Cations, Anions, Neutral and Biomolecules

Figure 2: Schematic presentation of interaction of chemosensor with guest analyte

Chemosensors are applied in process control, food analysis, metal sensing, environmental monitoring, medical diagnosis, and many other disciplines [14]. Main approaches used in designing of colorimetric sensors for the detection of guest analytes in solution is the transfer of energy from donor to acceptor components through non-radiative pathway [17].

1.5 Photophysical mechanism

In such cases the photophysical mechanism of signal propagation involves binding of the guest with a receptor that is part of the sensor.

Chromophores which are directly linked to the binding site mainly consist of aromatic organic moiety such as pyrene, nitrobenzene, anthraquinone and azobenzene system etc. [18] Chromophores which are fluorescent give rise to dual responses in both their fluorescence emission and fluorescence absorption [19].

Alternatively, the receptor and signalling subunit may be covalently linked by a 'spacer' group [16]. When receptor is covalently linked with the binding site, the binding event in many colorimetric sensors communicated from the receptor to the chromophore via conjugation with aromatic compounds such as oxadiazole, porphyrin and quinoxaline etc.[18] Advantages of chemosensors over conventional methods, such as selective and sensitive detection, sample preparation, low cost, rapid and convenient method. Until now, in the field of aluminium sensing, several fluorescence turn-on and turn off sensors [40] have been described, wherein the photophysical mechanism of sensing is based on photoinduced electron transfer (PET) that takes place from nonbonding electrons to the HOMO of the excited chromophore,[26] chelation-enhanced fluorescence effect (CHEF) happened due to the lowering the energy of nonbonding electrons that involved in coordination by inhibiting the PET mechanism,[27] chelation enhancement quenching effect (CHEQ), fluorescence resonance energy transfer (FRET) [28] it take place from one chromophore to another chromophore, metal to ligand charge transfer (MLCT) [29] metal should be in zero or low oxidation state, excited state intramolecular proton transfer (ESIPT) [25] or C=N isomerization [32]. Among these, (Intramolecular charge transfer) ICT [21] leads to variation in intensity as well as in spectral shifts, whereas PET leads to the variation in the intensity of emission. CHEF and CHEQ also provided fluorescence quenched and enhancement with or without any spectral changes [30]. Chemosensors for selective Al^{3+} ions are limited, its coordination ability is very poor [34], Al^{3+} ions act as a hard acid due to this it prefers the hard coordination sphere of N and O electron donating atoms [31]. Generally, chemosensors used for the sensing of environmentally and

biologically important anions, cations, biomolecule (such as proteins and DNA) [43] as well as small neutral molecules.

1.6 Aluminium and its importance

Aluminium (Al) is the third abundant element after silicon and oxygen in the earth's crust [35]. With the industrial pollution and acidic rain, a trivalent cation of Al^{3+} is dissolve and widely exists in the environment. Approximately 50 - 60% of the world's fertile soils are acidic, and the toxicity of Al is considered an important limiting factor of plant production on acidic soils [37]. Increasing level of Al^{3+} from soil by acidic rain and human activities is poisonous for growing plants [36]. Aluminium is found in its ionic form in water bodies, most plant and animal tissue. Generally aluminium use in food additive, aluminium based pharmaceuticals products, aluminium containers, aluminium packaging materials, electrical equipment and in water treatment etc. [38] According to W.H.O report, daily intake of aluminium by human being is 3−10 mg. Excessive exposure of Al^{3+} ions by the human body results to lots of diseases such as memory loss, decreased liver and kidney function, gastrointestinal problems, microcytic hypochromic anaemia, speech problems etc. The toxicity of aluminium causes the neurodegenerative diseases such as Alzheimer's and Parkinson's and is responsible for intoxication in haemodialysis patients [40]. Atomic emission spectrometry, atomic absorption spectrometry and cyclic-voltammetry [41] are the conventional method used for Al^{3+}detection [42]. Sensing of Al^{3+} is very important for controlling its concentration and its direct impact on human health. Various kinds of sensors have been reported for selective Al^{3+} detection [39]. Disadvantage of these sensors are their complicated synthesis, low water solubility, and lack of sensitivity and selectivity towards the metal ions. For practical applications, an ideal sensor should be water-soluble.

Chapter 2

Experimental section

2.1 Chemicals and materials

Commercially available starting material such as 5-aminoisophthalic acid (Sigma-Aldrich), 3,4-dihydroxybenzaldehyde (Sigma-Aldrich), 2-hydroxy-1-naphthaldehyde (Sigma-Aldrich), ortho-vanillin (Sigma-Aldrich), 1-pyrenemethylamine hydrochloride (Sigma-Aldrich), methanol and ethanol (Spectro-chem), Triethyl amine (Spectro-chem) were used as received. Chemicals were used without any purification. Merck 60 F_{254} plates of 0.25 nm thickness were used for TLC. For titration experiment, we used cations viz., chloride salts of Na^{+}, K^{+}, Ca^{2+}, Mg^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Cr^{3+} and nitrate salt of Al^{3+} ions.

2.2 Instrumentation

^{1}H NMR of synthesized material were done in DMSO-d6, and CDCl3 deuterium solvent using Fourier transform Nuclear Magnetic Resonance spectrometer, Model AVANCE III 400 Ascend Bruker Bio-spin International AG, Switzerland at 400 Mhz. using DMSO-d6, CDCl3 as solvent and TMS as internal standard on the delta (δ) scale. The mass spectra were recorded on Brucker-Daltonics micro TOF - QII mass spectrometer, UV-Visible spectra were recorded on a Schimadzu UV spectrometer in the wavelength range 200-800 nm and PTI (Photon Technology International) fluorescence spectrophotometer used for fluorescence spectroscopy.

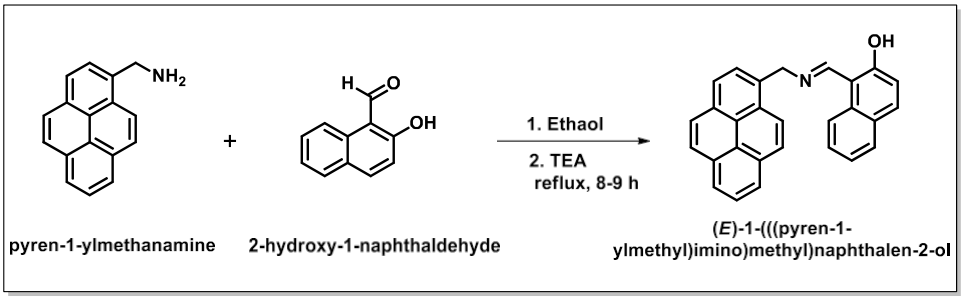
2.3 General method of sample preparation for UV-vis and fluorescence spectroscopy

A stock solution of ligand was prepared in methanol (CH_3OH) of 0.1 mM concentration and the same stock solution was used for UV-visible and fluorescence spectroscopy. The solutions of the metal cations were prepared using their chloride and nitrate salts, in order of 0.1 mM

concentration, in deionised water. Solutions of ligands (0.1 mM) were prepared in methanol. The spectra of these solutions were recorded by UV-visible and fluorescence spectroscopy.

2.4 Synthesis of E-1-(((pyren-1-ylmethyl) amino) methyl) naphthalen-2-ol

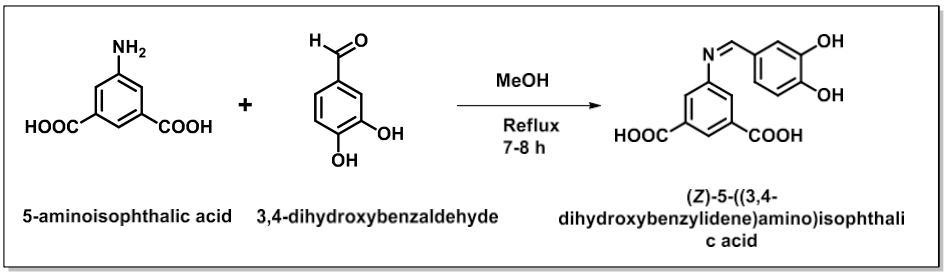
We have taken 200 mg (0.746 mmol) of 1-pyrenemethylamine hydrochloride then add triethyl amine (0.5mL, 0.72 g/mL) in 10 mL of ethanol. After complete dissolution we added 130 mg (0.750 mmol) of 2-hydroxy-1-naphthaldehyde in 1:1 ratio in a single necked round bottom flask (RBF). The content of the reaction mixture was heated and reflux for 8-9 hours by using dean stark apparatus. The disappearance of amine was observed by the TLC. When reaction is completed, solvent was evaporated by using rotary evaporator under vacuum and washed with ethanol several times. Light green compound was formed which was dried under high vacuum. (LCMS (m/z): 408.14 [M+Na], mass=250 mg, Yield = 75%); ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C, Si $(Me)_4$): δ = 15.12 (s, 1H, -OH), 9.00 (s, 1H, HC=N), 8.32 (d, *J* = 9.2 Hz, 1H), 8.22 (m, 4H), 8.14 – 7.96 (m, 4H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.70 (d, *J* = 9.2 Hz, 1H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.22 (t, *J* = 7.4 Hz, 1H), 6.98 (d, *J* = 9.2 Hz, 1H), 5.56 (s, 2H, -CH_2). ppm **(Figure 3)**



Scheme 1: The synthetic scheme for the preparation of **HL_1.**

2.5 Synthesis of (Z)-5-((3,4-dihydroxybenzylidene) amino) isophthalic acid

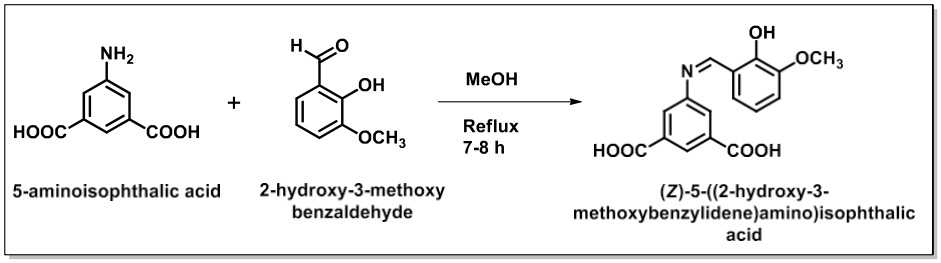
We have taken 200 mg (1.1 mmol) of 5-aminoisophthalic acid and 155 mg (1.1 mmol) of 3,4-dihydroxy benzaldehyde in 1:1 ratio in a single necked round bottom flask (RBF). 5-aminoisophthalic acid was dissolved in 10 mL of methanol, after complete dissolution we added 1.1 millimole of 3,4-dihydroxy-benzaldehyde. The content of the reaction mixture was heated and reflux for 7-8 hours by using dean stark apparatus. The disappearance of amine was observed by the TLC. When reaction is completed, solvent was evaporated by using rotary evaporator under vacuum and washed with methanol several times. Orange compound was formed which was dried under high vacuum. (LCMS (m/z): 302.07 [M+H], mass= 240 mg, Yield = 68 %); ^{1}H NMR (DMSO-d_6, 400 MHz, 25 °C, Si $(Me)_4$): δ = 9.69 (s, 2H, Ar.-H), 9.38 (s, 1H, Ar.-H), **8.50** (s, 1H, HC=N), 8.30 (s, 1H, Ar.-H), 7.89 (s, 2H, Ar.-H), 7.36 (s, 1H, Ar.-H), 7.24 (d, *J* = 9.4 Hz, 1H, Ar.-H), 6.91 – 6.84 (m, 1H, Ar.-H), 5.59 (s, 1H, -OH). ppm **(Figure 4)**



Scheme 2: The synthetic scheme for the preparation of **HL_2.**

2.6 Synthesis of (Z)-5-((2-hydroxy-3-methoxybenzylidene) amino) isophthalic acid

We have taken 200 mg (1.1 mmol) of 5-aminoisophthalic acid and 170 mg (1.1 mmol) of 2-hydroxy-3-methoxybenzaldehyde in 1:1 ratio in a single necked round bottom flask (RBF). 5-aminoisophthalic acid dissolved in 10 mL of methanol, after complete dissolution we added 1.1 millimole of 2-hydroxy-3-methoxybenzaldehyde. The content of the reaction mixture was heated and reflux for 7-8 hours by using dean stark apparatus. The disappearance of amine was observed by the TLC. When reaction is completed, solvent was evaporated by using rotary evaporator under vacuum and washed with methanol several times. Bright orange compound was formed which was dried under high vacuum. (LCMS (m/z): 338.06 [M+Na], mass = 250 mg, Yield = 67.5%); ^{1}H NMR (DMSO-d6, 400 MHz, 25 °C, Si $(Me)_4$): δ = 3.37 (s, 2H, -COOH), 12.71 (s, 1H, -OH), **9.10** (s, 1H, -HC=N), 8.39 (s, 1H, Ar.-H of carboxylic acid), 8.12 (s, 2H, Ar.-H of carboxylic acid), 7.40 – 7.29 (m, 1H, Ar.-H), 7.17 (d, *J* = 7.9 Hz, 1H, Ar.-H), 6.93 (t, *J* = 8.0 Hz, 1H, Ar.-H), 3.84 (s, 3H, $-OCH_3$) ppm **(Figure 5)**



Scheme 3. The synthetic scheme for the preparation of $\mathbf{HL_3}$

Chapter 3

Result and Discussion

3.1 Characterization of E-1-(((pyren-1-ylmethyl) amino) methyl) naphthalen-2-ol

3.1.1 ^{1}H NMR spectroscopy

The general ^{1}H NMR spectrum of the ligand in $CDCl_3$ solvent shows the following signals: 15.12 ppm peak corresponds to the phenolic (O-H) group because of intramolecular proton transfer, 9.00 ppm peak corresponds to the HC=N, 5.56 ppm peak corresponds to the hydrogen of methylene ($-CH_2$) and rest of peak corresponds to the aromatic hydrogen **(Figure 3).**

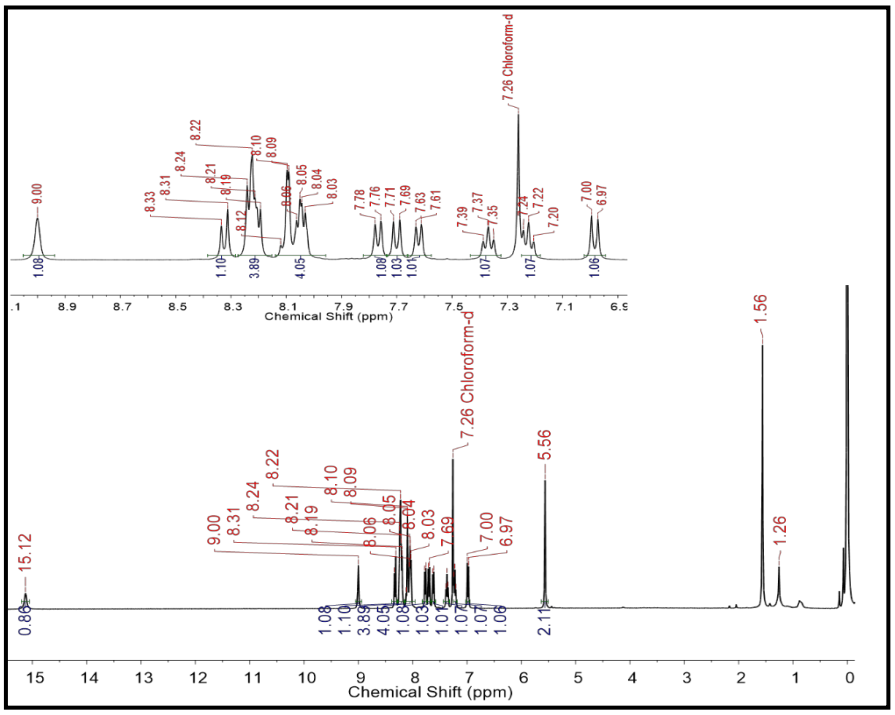


Figure 3: ^{1}H NMR spectrum of **HL_1.**

3.2 Characterization of (Z)-5-((3,4-dihydroxybenzylidene) amino) isophthalic acid

3.2.1 ^{1}H NMR spectroscopy

The general ^{1}H NMR spectrum of the Schiff base HL_2 in DMSO-d_6 solvent shows the following signals: 9.69 ppm peak corresponds to two aromatic hydrogen of carboxylic acid, 8.50 ppm peak corresponds to imine hydrogen (HC=N), 5.59 ppm peak corresponds to the hydrogen of -OH and rest of peak corresponds to the aromatic hydrogen of 3,4-dihydroxybenzaldehyde. **(Figure 4)**

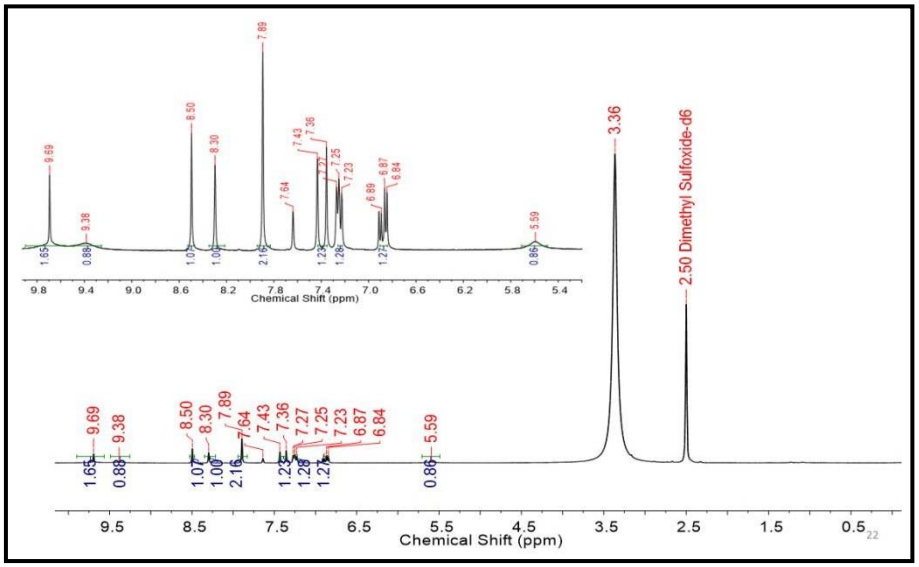


Figure 4: ^{1}H NMR spectrum of **HL_2**.

3.3 Characterization of (Z)-5-((2-hydroxy-3-methoxybenzylidene) amino) isophthalic acid

3.3.1 ^{1}H NMR spectroscopy

The general ^{1}H NMR spectrum of HL_3 in DMSO-d_6 shows the following signals: 13.37 ppm peak corresponds to two hydrogen of carboxylic acid, 12.71 ppm peak corresponds to the hydrogen of (O-H) group because of intramolecular proton transfer, 9.10 ppm peak corresponds to the hydrogen of HC=N, 8.39 ppm peak corresponds to the Ar.-H of carboxylic acid, 8.12 ppm peak corresponds to two Ar.-H of carboxylic acid, 7.40 – 7.29 ppm multiplet peak corresponds to the Ar.-H of 2-hydroxy-3-methoxybenzaldehyde, 7.17 ppm doublet peak corresponds to the Ar.-H of 2-hydroxy-3-methoxybenzaldehyde, 6.93 ppm triplet peak corresponds to Ar.-H of 2-hydroxy-3-methoxybenzaldehyde, 3.84 ppm peak corresponds to the three hydrogen of methoxy. **(Figure 5).**

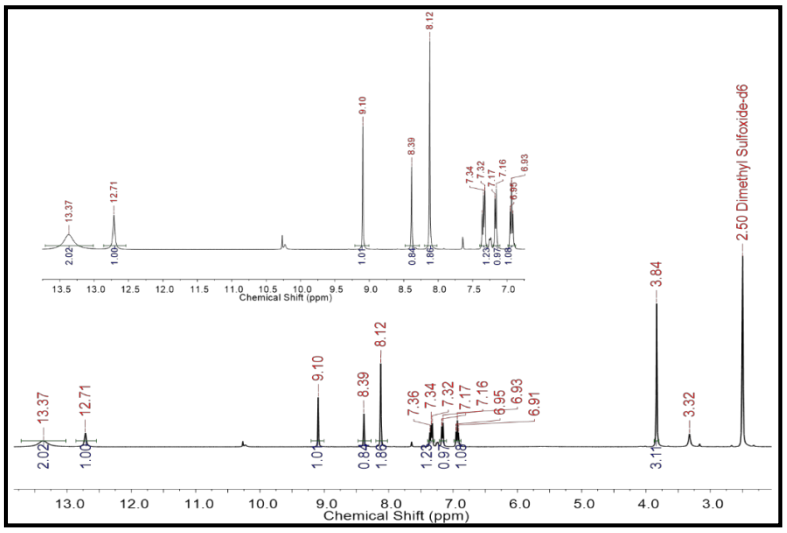


Figure 5: ^{1}H NMR spectrum of **HL_3**.

3.4 Characterization of E-1-(((pyren-1-ylmethyl) amino) methyl) naphthalen-2-ol

3.4.1 Mass Spectrometry

The electron impact mass spectra data supports the formation of E-1-(((pyren-1-ylmethyl) amino) methyl) naphthalen-2-ol with molecular ion peak at m/z 408.14 which is corresponds to$[M+Na]^+$, base peak appears at m/z 386.1 and weak isotopic peak appears at m/z 409.1 $[M+1]^+$. This could be attributed to $C_{28}H_{19}NO$. (**Figure 6).**

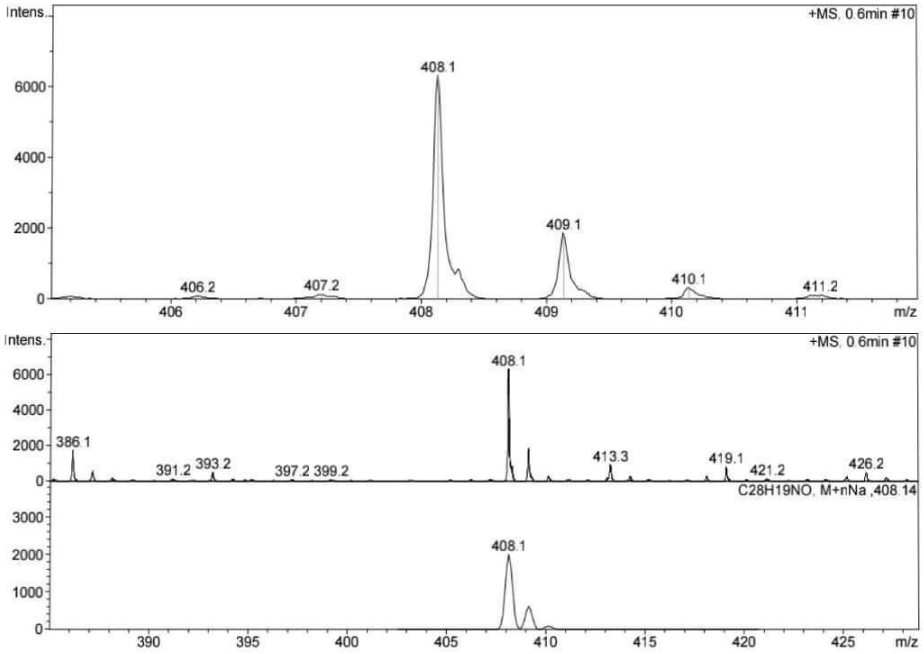


Figure 6: Mass spectra of HL_1 **$C_{28}H_{19}NO$.**

3.5 Characterization of (Z)-5-((3,4-dihydroxybenzylidene) amino) isophthalic acid

3.5.1 Mass Spectrometry

The electron impact mass spectra data supports the formation of (Z)-5-((3,4-dihydroxybenzylidene) amino) isophthalic acid with molecular ion peak at m/z 302.07 $[M+H]^+$, base peak appears at m/z 295.1 and weak isotopic peak appears at m/z 303.1 $[M+1]^+$. This could be attributed to $C_{15}H_{11}NO_6$. **(Figure 7).**

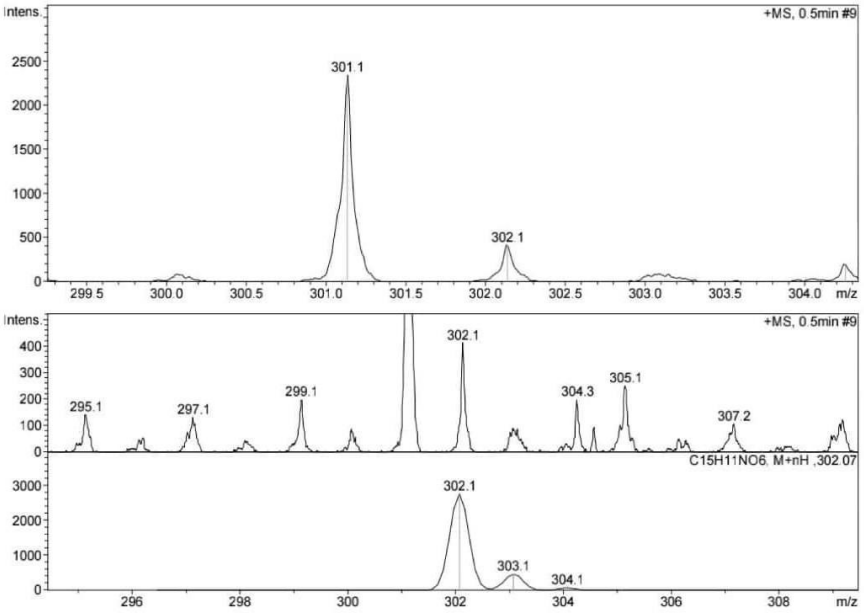


Figure 7: Mass spectra of HL_2 $C_{15}H_{11}NO_6$.

3.6 Characterization of (Z)-5-((2-hydroxy-3-methoxybenzylidene) amino) isophthalic acid

3.6.1 Mass Spectrometry

The electron impact mass spectra data supports the formation of (Z)-5-((2-hydroxy-3-methoxybenzylidene) amino) isophthalic acid with molecular ion peak at m/z 338,06 $[M+Na]^+$, base peak appears at m/z 323.0 and weak isotopic peak appears at m/z 339.1 $[M+1]^+$. This could be attributed to $C_{16}H_{13}NO_6$. (**Figure 8)**

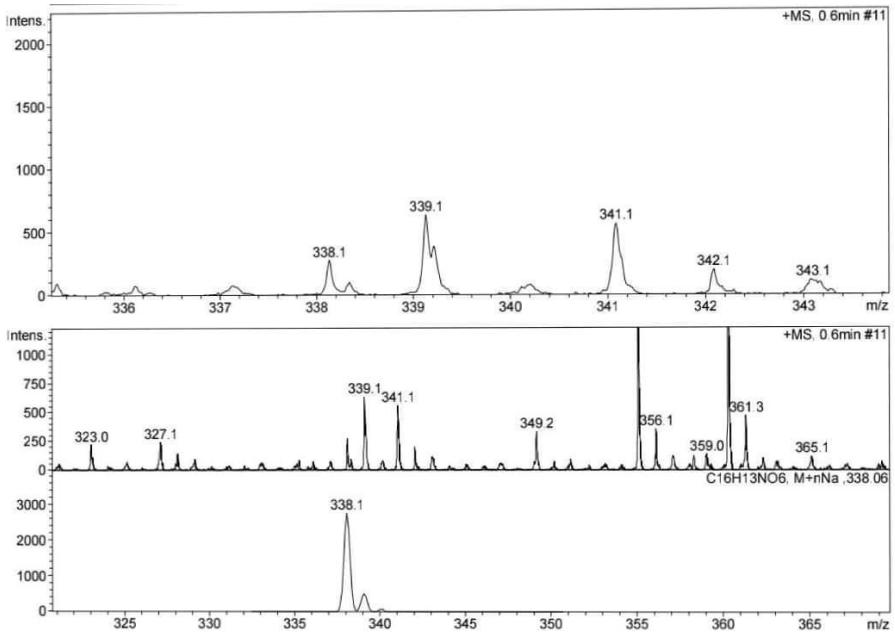


Figure 8: Mass spectra of **HL_3 $C_{16}H_{13}NO_6$.**

3.7 Photophysical Properties

3.7.1 Sensing of HL_1 by UV Vis. absorption spectroscopy

Absorption spectrum of the HL_1 was recorded after dissolving in CH_3OH-H_2O, displayed one prominent absorption band at wavelengths 325 nm due to π–π* electronic transitions. Upon successive adding of cumulative concentrations of Al^{3+} (0–2 equivalents), only Al^{3+} ions disturbed the absorption signal of HL_1 and other metal ions did not affect the absorption spectra. In the presence of Al^{3+} ions, the colour of the solution of HL_1 changes from light green to colourless. Al (III) complexes underwent the bathochromic shift of 17 nm, indicating the nitrogen and oxygen coordinated with the metal ion.

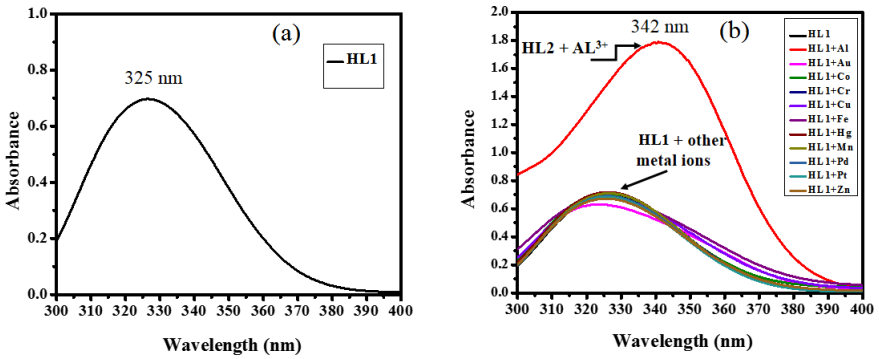


Figure 9: (a) UV-visible absorption spectra of **HL_1 (0.1 mM). (b)** Competitive absorption spectra of **HL_1** in the presence of different metal ions. (**HL_1**, c = 0.1 mM) in MeOH, concentration of different metal ions including Al^{3+} (0.1 mM).

3.7.2 Sensing of HL_1 by Fluorescence spectroscopy

We have determined the fluorogenic signalling behaviour of HL_1 solution towards the sensing of Al^{3+} ions. (Fig. 10b) shows the fluorescence spectrum of the HL_1 in the presence of 2 equivalents of Al^{3+}. The free ligand showed a broad band at 425 nm. U~~pon successi~~ve addition of Al^{3+} ion (0–2 equiv.), the peak at 425 nm decreased, whereas a new peak at 480 nm is developed. Upon the addition of almost two equivalents of Al^{3+}, the fluorescent intensity at 425 nm decreased by almost 15 times that of the ligand. The limit of detection is found to be 24 nM. But, on addition of various metal cations in methanolic solution of ligand HL_1 show no any change in fluorescence spectra (Fig. 10a). This is clearly shows that the other metal cations such as Na^{+}, Ca^{2+}, Mg^{2+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Hg^{2+}, Cr^{3+} does not interfere with sensing of HL_1 for Al^{3+} ions. According to the acid base theory, Al^{3+} ions is a strong lewis acid it accept the elecrons from non bonding electron of oxygen and nitrogen in vacant orbital. That's responsible for the fluorescence quenching, because of fluorecence quenching (decreased in the fluorescence intensity) fluorescent molecule converted in to the weak fluorescent molecule. Most probable reason of fluorescence quenching is happened may be due to the excited state reaction, complex formation, collission and paramagnetic metal cations.

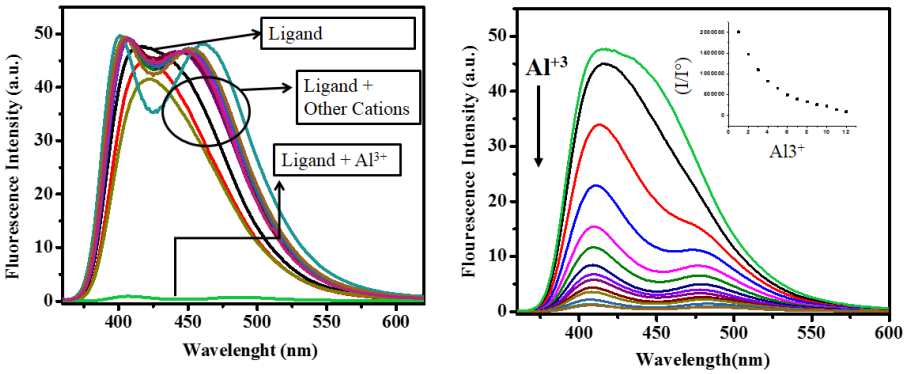


Figure 10: (a) Effect of fluorescence intensity of HL_1 at 425 nm with addition of Al^{3+} along with other metal ions. Conditions: HL_1(c = 0.1 mM), concentration of different metal ions including Al^{3+} (0.1 mM). **(b)** Fluorescence emission spectra obtained by the titration of HL_1 with Al^{3+}.

3.7.3 Sensing of HL_2 by UV Vis. absorption spectra

Absorption spectrum of the HL_2 was recorded after dissolving in CH_3OH-H_2O, displays two prominent absorption bands at wavelengths 328 nm and 344 nm due to π–π* and n –π* electronic transitions, respectively. Upon successive adding of cumulative concentrations of Al^{3+} (0–2 equivalents), only Al^{3+} ions disturbed the absorption signal of HL_2 and other metal ions did not affect the absorption spectra. In the presence of Al^{3+} ion, the colour of the solution of HL_2 changes from light orange to colourless. Al (III) complexes underwent the bathochromic shift of 1 nm, indicating the nitrogen and oxygen coordinated with the metal ion.

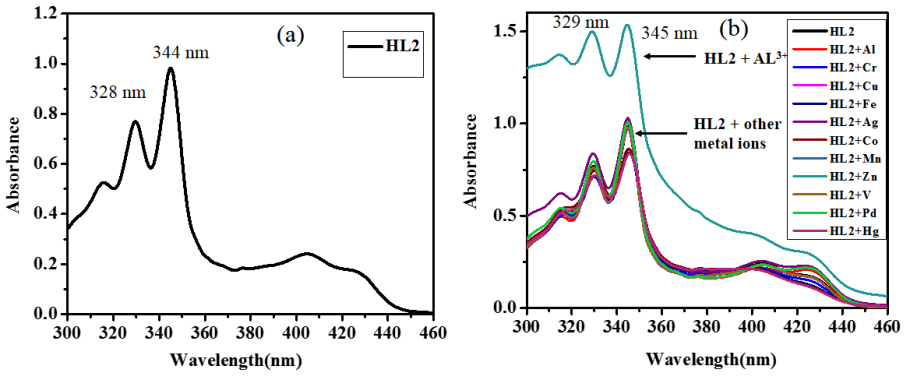


Figure 11: (a) UV-visible absorption spectra of **HL_2** (0.1 mM). **(b)** Competitive absorption spectra of **HL_2** in the presence of different metal ions. (**HL_2**, c = 0.1 mM) in MeOH, concentration of different metal ions including Al^{3+} (0.1 mM).

3.7.4 Sensing of HL_2 by Fluorescence spectroscopy

We have determined the fluorogenic signalling behaviour of HL_2 solution towards the sensing of Al^{3+} ions. (Fig. 12a) shows the fluorescence spectrum of the HL_2 in the presence of 2 equivalents of Al^{3+}. The free ligand showed a broad band at 455 nm. Upon successive addition of Al^{3+} ion (0–2 equiv.), the peak at 455 nm decreased, whereas a new peak at 395 nm is developed. Upon the addition of almost two equivalents of Al^{3+}, the fluorescent intensity at 455 nm decreased by almost 25 times that of the ligand. The limit of detection is found to be 14 nM. But, on addition of various metal cations in methanolic solution of ligand HL_2 show no any change in fluorescence spectra (Fig. 12b). This is clearly shows that the other metal cations such as Na^{+}, Ca^{2+}, Mg^{2+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Hg^{2+}, Cr^{3+} does not interfere with sensing of HL_1 for Al^{3+} ions. According to the acid base theory, Al^{3+} ions is a strong lewis acid it accept the

elecrons from non bonding electron of oxygen and nitrogen in vacant orbital. That's responsible for the fluorescence quenching, because of fluorecence quenching (decreased in the fluorescence intensity) fluorescent molecule converted in to the weak fluorescent molecule. Most probable reason of fluorescence quenching is happened may be due to the excited state reaction, complex formation, collission and paramagnetic metal cations.

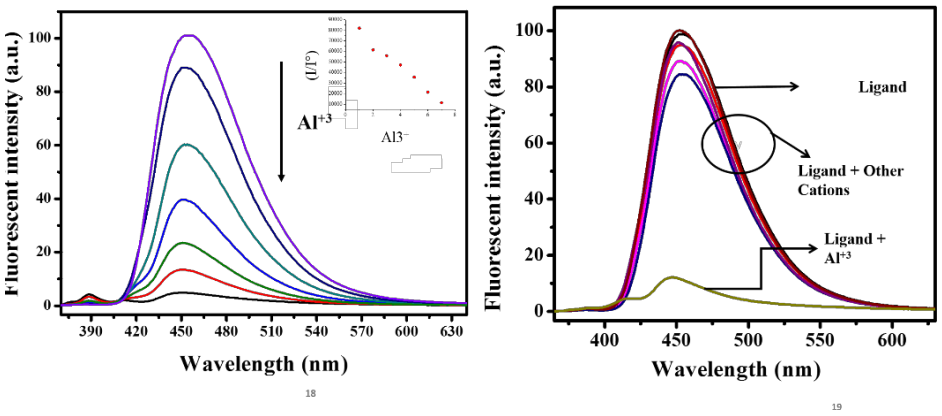


Figure 12: (a) Fluorescence emission spectra obtained by the titration of HL_2 with Al^{3+} **(b)** Effect of fluorescence intensity of HL_2 at 455 nm with addition of Al^{3+} along with other metal ions. Conditions: HL_2(c = 0.1 mM), concentration of different metal ions including Al^{3+} (0.1 mM).

Chapter 4

Conclusion and Future Aspects

We have synthesized the Schiff base ligands (HL_1 and HL_2) and characterized by the mass spectrometry, ^1H NMR, UV-Vis. and fluorescence spectroscopy. Elucidation of ^1H NMR spectra confirms the structure of ligands. HL_1 and HL_2 show the maximum absorption spectra at 325 and 344 nm. Fluorescence intensity of HL_1 and HL_2 is 4.7×10^6 (a.u.) and 3×10^6 (a.u.). From UV-Visible spectra we observed that only addition of Al^{3+} ions (20 µL, 0.5 mM) in ligands (HL_1 and HL_2) solution shows the bathochromic shift from 325 nm to 342 nm and 344 nm to 345 nm. On subsequent addition of Al^{3+} ions (5 µL,0.1 mM) in methanolic solution of ligands (2 mL, 0.1 mM) shows the quenching of the ligands via a fluorescence turnoff mechanism. Quenching is happened may be due to the excited state reaction, collision, complex formation and paramagnetic quenching. Fluorescence spectroscopic titration curve reveals that both the ligands are selective and sensitive towards the detection of Al^{3+}ions even in the presence of wide range of other metal cations.

Crystallization of ligand and its metal complex with aluminium metal ion to know their binding patterns and shape of metal complex. Sketch the Job plot, from this plot we elucidate the stoichiometry ratio of a binding event of metal and ligands. Further, this can be used for intracellular Al^{3+} ions and bioimaging. Synthesis of Schiff base chemosensors with more sensitive and selective with other metal ions and explosives.

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