

**SYNTHESIS AND CHARACTERIZATION OF KETOHYDRAZONE
LIGANDS AND ITS COMPLEXES WITH ALUMINIUM(III) AND ZINC(II)
AS POTENTIAL EMITTING MATERIAL IN OLED**

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TABLE OF CONTENTS

CHAPTER	TITLE	PAGE
	TITLE	i
	DECLARATION	ii
	DEDICATION	iii
	ACKNOWLEDGEMENT	iv
	ABSTRACT	v
	ABSTRAK	vi
	TABLE OF CONTENTS	vii
	LIST OF TABLES	x
	LIST OF FIGURES	xi
	LIST OF ABBREVIATIONS	xiv
	LIST OF APPENDICES	xv
1	INTRODUCTION	
1.1	Metal Complexes	2
1.2	Metal Chelate Complexes	2
1.3	The Fluorescence Process	3
1.4	Aluminium	5
1.5	Zinc	5
1.6	Complex with Exocyclic C=N group	6
1.7	Ketohydrazone ligand	7
1.8	OLED	8
1.9	Statement of Problem	9
1.10	Objectives of Research	10
1.11	Scope of Study	10

2	EXPERIMENTAL	
2.1	Reagents and chemicals	11
2.2	Instrumentation	11
2.3	Synthesis of ligands	12
2.3.1	Synthesis of NDB Ligand	12
2.3.2	Synthesis of NDS Ligand.	13
2.3.3	Synthesis of NDF Ligand.	14
2.4	Preparation of Ligand Solution	15
2.5	Preparation of Al(II) Stock Solution	15
2.6	Preparation of Zn(II) Stock Solution	15
2.7	Preparation of Buffer Solution	16
2.8	Determination of Ligand – Complex Stoichiometry	16
2.9	Synthesis of Aluminium Complexes	17
2.10	Synthesis of Zinc Complexes	17
2.11	Determination of Fluorescence Intensity of Ligands	17
2.12	Determination of Fluorescence Intensity of Aluminium Complexes.	18
2.13	Determination of Fluorescence Intensity of Zinc Complexes.	20
3	RESULTS AND DISCUSSION	
3.1	Synthesis of Ligands	19
3.2	Characterization of Ligands	
3.2.1	Physical Properties	21
3.2.2	UV-Vis Spectrum	21
3.2.3	IR Analysis	22
3.2.4	NMR Analysis	23
3.3	Determination of Complex Stoichiometry	
3.3.1	Aluminium(III) Complexes	24
3.3.2	Zinc(II) Complexes	29

3.4	Synthesis and Characterization of Complexes	
3.4.1	Aluminium (III) Complexes	33
3.4.1.1	Physical Properties	33
3.4.1.2	UV-Vis Spectrum	34
3.4.1.3	IR Analysis	35
3.4.2	Zinc (II) Complexes	36
3.4.2.1	Physical Properties	36
3.4.2.2	UV-Vis Spectrum	37
3.4.2.4	IR Analysis	37
3.5	Determination of Fluorescence Properties of Ligands and Complexes.	38
4	CONCLUSIONS AND RECOMMENDATIONS	
4.1	Conclusions	42
4.2	Recommendations	43
	REFERENCES	44
	APPENDICES	47

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JUDUL: SYNTHESIS AND CHARACTERIZATION OF KETOHYDRAZONE

LIGANDS AND ITS COMPLEXES WITH ALUMINIUM(III) AND ZINC(II)

AS POTENTIAL EMITTING MATERIAL IN OLED

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SYNTHESIS AND CHARACTERIZATION OF KETOHYDRAZONE LIGANDS
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POTENTIAL EMITTING MATERIAL IN OLED

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alhamdulillah...

For special person in my life, my mum and dad;

thanks for being my big supporter..

Brothers and sisters;

thanks for encouraging and supporting me and also to someone who

always by my side..Mohd Fadly Atan

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ABSTRACT

Ketohydrazone is a molecule that is able to act as a bidentate ligand through the O of C=O and N of N=C in the molecule. Three ketohydrazone ligands had been fully synthesized through the condensation reaction between 2-hydroxynaphthaldehydes with various hydrazine, salicylic hydrazide, benzyhydrazide and 2-furoic acid hydrazide in a 1:1 stoichiometry. The ligands had been characterized using infrared, ^1H NMR and ultraviolet-visible spectrometer. Complexation reaction between all ligands and metal, with a stoichiometry of 1:2 for Zinc(II) : ligand and 1:3 for Aluminium(III) : ligand were carried out. All six complexes obtained were characterized using FTIR and UV-Vis spectrometer. The fluorescence properties of each ligands and complexes were investigated using luminescence spectrofluorometer at fluorescence emission wavelength at 406 nm and excitation wavelength at 470 nm. Results showed that all the ligands and molecules synthesized have the fluorescence properties and complexation with metal enhanced the intensity of the fluorescence. It was observed that complex of $\text{Al}(\text{NDB})_3$ showed the best potential as an emitting material for OLED as it has the highest fluorescence intensity compared to others.

ABSTRAK

Ketohidrazon merupakan sebatian molekul yang berupaya berfungsi sebagai ligan bidentat melalui O daripada C=O dan N daripada N=C di dalam molekulnya. Tiga ligan ketohidrazon telah berjaya disintesis melalui proses kondensasi antara 2-hidroksinaftaldehida dan beberapa kumpulan hidrazon, salisilik hidrazida,, 2-furoik hidrazida, dan benzhidrazida. mengikut nisbah stoikiometri 1 : 1. Semua ligan yang telah disintesis dicirikan melalui spektroskopi IR, UV-Vis dan ¹H-RMN. Tindak balas pengkompleksan antara ligan yang telah disintesis dengan dua logam yang berasingan, iaitu aluminium dan zinc telah dijalankan dengan nisbah ion logam : ligan 1 : 3 bagi pengkompleksan dengan Aluminium dan 1 : 2 bagi pengkompleksan dengan Zinc. Enam kompleks yang terhasil dicirikan melalui spektroskopi IR dan UV-Vis. Ciri-ciri pendarfluor bagi tindak balas pengkompleksan dan ligan yang terhasil telah dikaji menggunakan spektrometer pendarfluor pada panjang gelombang pemancaran 470 nm. Hasil yang diperolehi menunjukkan bahawa semua ligan dan kompleks yang disintesis menunjukkan sifat pendarfluor dan pengkompleksan dengan logam dapat meningkatkan keamatan pendarfluornya.. Melalui kajian ini, dapat dinyatakan bahawa kompleks Al(NDB)₃ menunjukkan potensi yang baik sebagai bahan pemancar dalam diod pemancar cahaya organik (OLED) memandangkan kompleks ini menunjukkan keamatan pendarfluor yang tertinggi.

LIST OF TABLES

TABLE NO.	TITLE	PAGE
2.1	Mole fraction and volume of metal and ligand solution used	16
3.1	Physical properties of each ligands	21
3.2	Main absorption bands according to types of electronic transition in UV-Vis spectrum of ligands	22
3.3	Functional groups and their frequencies of IR absorption band for each ligands	23
3.4	Chemical shift of protons in ^1H NMR spectrum ligands	24
3.5	Physical properties of Aluminium(III) complexes	34
3.6	Functional groups and their wave numbers for Aluminium(III) complexes	35
3.7	Physical properties of Zinc(II) complexes	37
3.8	Functional groups and their wavenumbers for Aluminium(III) complexes	38
3.9	Fluorescence intensity of ligands and complexes	40

LIST OF FIGURES

FIGURE NO.	TITLE	PAGE
1.1	Jablonski diagram	4
1.2	Structure of ketohydrazone ligand	7
1.3	The basic structure of the OLED	9
2.1	Synthesis of NDB ligand.	12
2.2	Synthesis of NDS ligand.	13
2.3	Synthesis of NDF ligand.	14
3.1	Graph of absorbance versus mole fraction of NDB ligand	25
3.2	Graph of absorbance versus mole fraction of NDS ligand	26
3.3	Graph of absorbance versus mole fraction of NDF ligand	26
3.4	Structure of Al(NDB) ₃ complex	27

3.5	Structure of $\text{Al}(\text{NDF})_3$ complex	28
3.6	Structure of $\text{Al}(\text{NDS})_3$ complex	28
3.7	Graph of absorbance versus mole fraction of NDB ligand.	29
3.8	Graph of absorbance versus mole fraction of NDF ligand	30
3.9	Graph of absorbance versus mole fraction of NDS ligand	30
3.10	Structure of $\text{Zn}(\text{NDB})_2$ complex	31
3.11	Structure of $\text{Zn}(\text{NDF})_2$ complex	32
3.12	Structure of $\text{Zn}(\text{NDS})_2$ complex	32
3.13	Synthesis of $\text{Al}(\text{NDB})_3$ complex	33
3.14	UV-Vis spectrum for NDF ligand and $\text{Al}(\text{NDF})_3$ complex	34
3.15	Synthesis of $\text{Zn}(\text{NDB})_2$ complex	36
3.16	Fluorescence spectrum of $\text{Al}(\text{NDB})_3$ complex and NDB ligand	39
3.17	Fluorescence spectrum of NDS ligand and $\text{Al}(\text{NDS})_3$ complex	39

3.18	Fluorescence spectrum of NDF ligand and $\text{Al}(\text{NDF})_3$ complex	40
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LIST OF ABBREVIATIONS/ TERMS/ SYMBOLS

NDB		2-Hydroxynaphthaldehyde benzoilhydrazide
NDF		2-Hydroxynaphthaldehyde furoilhydrazide
NDS		2-Hydroxynaphthaldehyde salicyloilhydrazide
Al(NDB) ₃		Aluminium tri(2-Hydroxynaphthaldehyde benzoilhydrazide)
Al(NDF) ₃		Aluminium tri(2-Hydroxynaphthaldehyde furoilhydrazide)
Al(NDB) ₃		Aluminium tri(2-Hydroxynaphthaldehyde salicyloilhydrazide)
Zn (NDB) ₂		Zinc di(2-Hydroxynaphthaldehyde benzoilhydrazide)
Zn (NDF) ₂		Zinc di(2-Hydroxynaphthaldehyde furoilhydrazide)
Zn (NDS) ₂		Zinc di(2-Hydroxynaphthaldehyde salicyloilhydrazide)
Al(III)		Aluminium(III)
Zn(II)		Zinc(II)
Λ_{emi}	-	Wavelength of emission
Λ_{emi}	-	Wavelength of excitation
FTIR	-	Fourier Transform Infrared
LS		Luminescence Spectrometer
DMSO		Dimethylsulfoxide
NMR		Nucleus magnetic resonance
UV-Vis	-	Ultraviolet-visible
OLED		Organic Light Emitting Diode

LIST OF APENDICES

APPENDIX.	TITLE	PAGE
A	UV-Vis spectrum of ligands	47
B	IR spectrum of NDB ligand.	48
C	IR spectrum of NDS ligand	49
D	IR spectrum of NDF ligand.	50
E	NMR spectrum of NDB ligand.	51
F	NMR spectrum of NDF ligand	52
G	UV-Vis spectra for $\text{Al}(\text{NDB})_3$ with different mole fraction NDB	53
H	UV-Vis spectra for $\text{Al}(\text{NDF})_3$ with different mole fraction of NDF ligand	54
I	UV-Vis spectra for $\text{Zn}(\text{NDF})_2$ different mole fraction of NDF	55
J	UV-Vis spectra for $\text{Zn}(\text{NDS})_2$ different mole fraction of NDS	56

K	UV-Vis spectra for NDB ligand and Al(NDB) ₃ complex	57
L	UV-Vis spectra for NDS ligand and Al(NDS) ₃ complex	58
M	IR spectrum for Al(NDB) ₃	59
N	IR spectrum of Al(NDF) ₃	60
O	IR Spectrum of Al(NDS) ₃	61
P	IR Spectrum of Zn(NDB) ₂	62
Q	IR Spectrum of Zn(NDF) ₂	63
R	IR Spectrum of Zn(NDS) ₂	64

CHAPTER 1

INTRODUCTION

Since organic light-emitting diodes (LEDs) using 8-hydroxyquinoline aluminum as the emitting layer was reported to emit green light in 1987 [1], organic LEDs have received considerable attention due to their potential application in various displays. The organic devices (OLED) offer the clear advantages such as low cost, high luminous efficiency, and wide selection of emission colors through the molecular design of organic materials. These devices are able to produce all emission colors in accordance with a wide selection of organic emitting materials. Most of the reported electroluminescence of organic compounds in OLEDs are either aromatic molecules or organic polymers [2].

Emitting material for organic LEDs can be classified into three types according to their molecular structure: organic dyes, chelate metal complexes and polymers. There is still a big challenge in developing emitting materials to exhibit highly efficient blue-light, for example oxadiazole, cyclopentadiene derivative and others. The second is to add blue-light emitting dyes into a polymer, such as oligomeric PPV doped in polymer mixture. The third one is to make blue-light emitting bilayer or trilayer films from light-emitting materials with electron transporting and hole-transporting material. The final one is to synthesize chelate metal complexes [3].

1.1 Metal Complexes

A complex has been defined as a species formed by the association of two or much simpler species each capable of independent existence. When one of the simpler species is a metal ion, the resulting entity is known as a metal complex. A characteristic feature of such a complex is that the metal atom occupies a central position in it, as exemplified by cobalt in hexamminecobalt (III) ion, and others [4].

The metal-centered structure may carry a positive, negative or zero charge. Complex ions are, of course, always associated with ions of opposite charge and the term metal complex is customarily applied to the compound itself.

Almost every kind of metal atom can serve as a central atom although some kinds do so more readily than others. Atoms of the transition series, for example, function in this way par excellence but atoms of the alkali metals are rarely found in this role.

Typically, the chemistry of complexes is dominated by interactions between s and p orbitals of the ligands and the d (or f) orbitals of the metal ions. Because of this, the simple octet rule fails in the case of complexes, and to understand the chemistry of these systems, a deeper understanding of chemical bonding rules is necessary.

These organic molecules were useful due to their solubility. They could be applied to a surface as a film via evaporation of their solvent.

1.2 Metal Chelate Complex

Some ligands are attached to the metal atom by more than one donor atom in such a manner as to form a heterocyclic ring. An example of such a ring is the one formed in some complex by the glycinate ion. This type of ring has been given a special name – chelate ring and the molecule or ion from which it is formed is known as chelation. The

first chelating molecules discovered were those with two donor atoms and it was the caliper like mode of attachment of the molecules to the metal atom that is suggested to be called as chelate, which is derived from the Greek word. Any metal complex in which one or more chelate rings are present is defined as a metal chelate [5].

Complexes of chelating ligands are in general more stable thermodynamically than those with an equivalent number of monodentate ligands. This special effect, called chelate effect, is an effect that can be explained as arising from a large positive entropy change when one replaces two or more ligands [6].

1.3 The Fluorescence Process

Fluorescence is the result of a three-stage process that occurs in certain molecules (generally polyaromatic hydrocarbons or heterocycles) called fluorophores or fluorescent dyes [7]. A fluorescent probe is a fluorophore designed to localize within a specific region of a biological specimen or to respond to a specific stimulus. The process responsible for the fluorescence of fluorescent probes and other fluorophores is illustrated by the simple electronic-state diagram (Jablonski diagram) shown in Figure 1.

Stage 1 : Excitation

A photon of energy $h\nu_{EX}$ is supplied by an external source such as a lamp or a laser and absorbed by the fluorophore, creating an excited electronic singlet state (S_1'). This process distinguishes fluorescence from chemiluminescence, in which the excited state is populated by a chemical reaction.

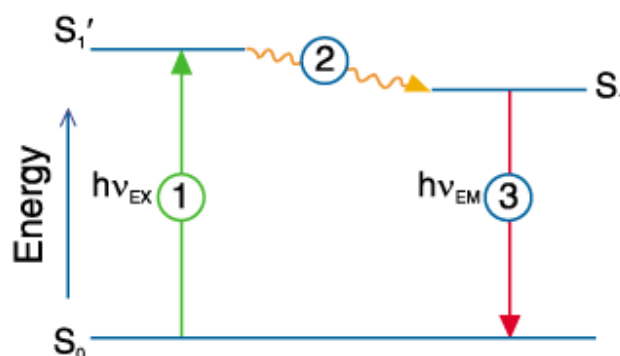


Figure 1.1 Jablonski diagram illustrating the processes involved in the creation of an excited electronic singlet state by optical absorption and subsequent emission of fluorescence. The labeled stages **1**, **2** and **3** are explained in the adjoining text.

Stage 2 : Excited-State Lifetime

The excited state exists for a finite time (typically 1–10 nanoseconds). During this time, the fluorophore undergoes conformational changes and is also subject to a multitude of possible interactions with its molecular environment. These processes have two important consequences. First, the energy of S_1' is partially dissipated, yielding a relaxed singlet excited state (S_1) from which fluorescence emission originates. Second, not all the molecules initially excited by absorption (Stage 1) return to the ground state (S_0) by fluorescence emission. Other processes such as collisional quenching, fluorescence resonance energy transfer and intersystem crossing (see below) may also depopulate S_1 .

Stage 3 : Fluorescence Emission

A photon of energy $h\nu_{EM}$ is emitted, returning the fluorophore to its ground state S_0 . Due to energy dissipation during the excited-state lifetime, the energy of this photon is lower, and therefore of longer wavelength, than the excitation photon $h\nu_{EX}$.

1.4 Aluminium

Aluminium is the most abundant metals on the earth's surface and is widely distributed. Alumina is normally found in combination with silica in such rocks, but it does occur naturally as the minerals bauxite, boehmite, diaspore, gibbsite and others. The thermal conductivity depends upon the impurities present and the amount of cold work to which the metal has been subjected [8].

Aluminum is stable in air and resistant to corrosion by sea water and many fresh waters and chemical agents. This is due to protection of the metal by a thin, tough, transparent oxide film.

The hydrolysis of aqueous aluminium can be partially or completely prevented by complexation with ligands. Aluminium(III) is a hard acid and, such as prefers hard bases such as oxygen or fluorine. It forms strong hydroxide complexes as part of its hydrolysis behavior, but it also complexes strongly with fluoride. Complexes of aluminium with organic oxygen-containing ligands posses high stability constants. Aluminium(III) forms complexes of the greatest stability with ligands containing strongly basic O atoms and N atoms [9].

Although the hydrolysis of aluminium makes determination of formation constants quite problematic, the existence of good linear relationships between the formation constants of complexes of different metals containing the same hard oxygen donor groups allows the estimation of possible values for aluminium complexes and the design of new chelating ligands.

1.5 Zinc

Zinc is a metallic chemical element with symbol Zn and with weight 65.38. It has a melting point of 419.58°C and boiling point of 907°C. Zinc is a lustrous bluish-white metal. It is found in group IIb of the periodic table. It is brittle and crystalline at ordinary temperatures, but when heated to between 110°C and 150°C it becomes ductile and

malleable; it can then be rolled into sheets. It is a fairly reactive metal. Although it is not abundant in nature, it is of great commercial importance [10]. There are five stable isotopes of zinc, which are ^{64}Zn (48.89%), ^{66}Zn (27.81%), ^{67}Zn (4.11%), ^{68}Zn (18.57%) and ^{70}Zn (0.62%). The electronic configuration of Zinc is $\{\text{Ar}\} 3d^{10}4s^2$. The melting points and boiling points of zinc are low compared with most metals. When zinc atoms are excited, normally only one (4s) electron is promoted to a higher energy level. The electronic description of ground states is: $\text{Zn } 3d^{10}4s^1$; $\text{Zn}^+ 3d^9 4s^1$; $\text{Zn}^{2+} 3d^{10}$.

Zinc dissolves readily in alkali giving hydrogen and a solution containing anionic species. Zinc is also dissolved by aqueous solution of ammonia and ammonium salts. For coordination properties, zinc is always form stable complex with coordination number 4. However, it can also form complex with 5 or six ligands that consist of O (oxygen), N (nitrogen), or phosphorus.[10,11].

1.6 Complex with Exocyclic C=N Group

The luminescent compounds containing an exocyclic C=N group include azomethine and azines. The C=N group maybe regarded as intermediate between the ethylene group C=C and the azo group N=N. These compounds exhibit properties typically observed in diarylethylenes and azo compounds. At the same time, the asymmetry of the C=N group is the reason why compounds of this class display some very special properties.

The most widely used method for synthesizing azomethines is based on condensation of aldehydes with primary amines. The rate of azomethine formation depends on the basicity of the amine. The more basic the amine, the faster the reaction. The solvent also strongly affects the reaction rate.

The main structural factor determining the luminescence properties of azomethine is the presence of $-\text{CH}=\text{N}$ groups with lone pair electrons at the nitrogen atom. The

luminescence intensity is determined by the degree of conjugation along the entire molecule and increases with the donor-acceptor interaction of the substituents [12].

1.7 Ketohydrazone Ligand

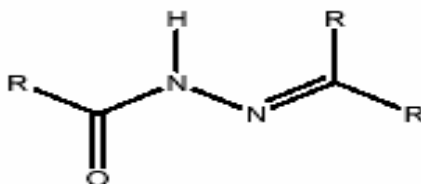


Figure 1.2 : Structure of ketohydrazone ligand

Ketohydrazone with both oxygen and nitrogen donors coordinated to metal ion formed a stable complex. Ketohydrazone have been synthesized by condensation reaction between aldehyde/ketone with hydrazide. The aluminium(III)-ketohydrazone complex in solution shows high luminescence of blue-green colour with emission wavelength at 465 nm.[13].

Ketohydrazone is a chelating ligand that can form complex with an ion metal by two electron-donating atom, atom oxygen and nitrogen. The ligand shows phenomenon tautomerism (keto-enol) formation in certain conditions. The most frequently encountered tautomerism systems are those in which tautomers differ in the position of a hydrogen atom.

Comparing to the other metal-chelate complexes, metal-ketohydrazone complex shows high quantum yield photoluminescence and high light emission efficiency.. This research will be carried out to investigate the potential of metal-ketohydrazone complex used as emitting material in LED [1].

Organic light emitting diode (OLED) considered promising for applications in new types of flat panel displays since first reported by Tang and Van Slyke [14] on the

highly efficient electroluminescence (EL) from organic thin-films. The developments in the field of electroluminescence are roughly divided between the use of inorganic and organic materials.

Similar properties were reported in several metal–chelate complexes having aromatic ligands, which chelate through a phenolic oxygen and doubly bound nitrogen to zinc or aluminum. From earlier studies, the metal–chelate complex is believed to be a promising emitting material. On the other hand, oxadiazole compounds are also known to have excellent electron transport ability and efficient fluorescence properties. Several research groups reported efficient bluish-green emission in the devices using the oxadiazole compounds [15].

From Suning Wang study, he reported that for two derivatives of 7-azaindole for aluminium complexes, although the compounds has a blue emission band at ca. 450 nm, it is very weak and the steric factors may be responsible for the problem [16].

Wong Hon Loong reported that the ketohydrazone ligands have been successfully synthesized by condensation reaction between 2-hydroxy-1-naphthaldehyde and 4-hydroxybenzhiyrazide. The aluminium(III)-ketohydrazone complex in solution form shows high luminescence of blue-green colour with emission wavelength 465nm [13].

Abdul Malik, in his research used complex of ketohydrazone as a spectrofluometric method for determination of aluminium in water. He found out that interaction between aluminium and ligand shows good pendarflour interaction [17].

1.8 OLED

Figure 1.3 shows the basic structure of an OLED. If the emissive layer material of an organic compound, it is known as an Organic Light Emitting Material (OLED).

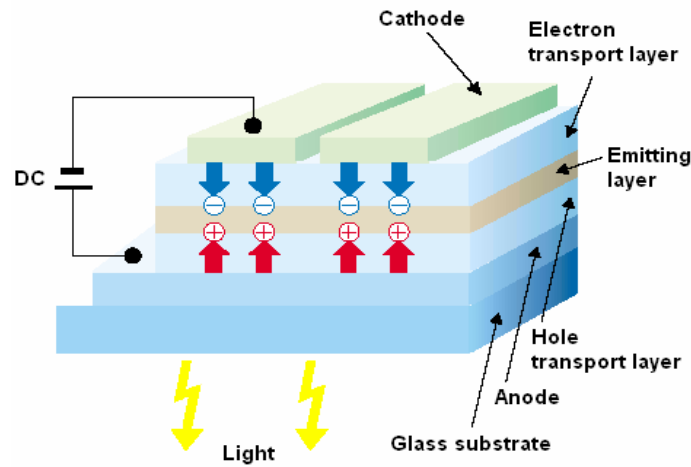


Figure 1.3 : The basic structure of the OLED.

OLED devices are manufactured by forming a series of layers on a glass substrate. These layers consist of an ITO (Indium Tin Oxide) anode on glass, a hole transporting layer (HTL), an electron-transporting layer (ETL) which often also serves as the emissive layer). To be a semiconductor, the organic emissive material must have conjugated pi bonds. The emissive material can be a small organic molecule in a crystalline phase, or a polymer. The organic molecules used in OLED devices have the property of accepting energy (placing them in the excited state) and then emit that energy as light when they return to the original state (the ground state) [18].

In an OLED device, when a voltage is applied, the holes (+) injected at the anode and the electrons (-) injected at the cathode recombine in the light-emitting layer, exciting the organic molecules and emitting light.

1.9 Statement of Problem

There is a big challenge in developing emitting materials which can exhibit highly efficient blue-light emission. The current lifetime of blue light is only 10,000 hours compared to white light is 20,000 hours, and both red and green light lifetimes are up to approximately 40,000 hours. This problem may come from many origins. Three of which

are the sensitivity of the emitting material to humidity, oxygen, and contamination [1]. One effective way to solve the problem is to synthesize new organic materials with better properties.

This research focused on synthesizing ketohydrazone ligand and complexes and investigation of the potential of metal-ketohydrazone complexes as emitting material in OLED.

1.10 Objectives of the Research

The objectives of the research are:

- 1) To synthesize ketohydrazone ligands and complexes.
- 2) To characterize all the ligands and complexes
- 3) To study the luminescent properties of complexes.
- 4) To determine the most potential complexes for emitting material.

1.11 Scope of Study

This research focused on the synthesis of the ketohydrazone ligands and metal complexes, aluminium(III) or zinc(II) complexes. The synthesized products were characterized by FTIR, UV-Vis Spectrometer, and NMR. The intensity of luminescence of ligands and complexes was measured using a Luminescence Spectrofluorometer (LS).

CHAPTER II

EXPERIMENTAL

2.1 Reagents and Chemicals

All the reactions were carried out in an inert atmosphere of dry nitrogen. The solvents used in this research were obtained from Aldrich and Fluka. All products were dried in vacuum while all the glass wares were dried overnight in an oven.

2.2 Instrumentations

Instruments that were used in this research are:

i) Nuclear Magnetic Resonance Spectrometer (NMR)

The NMR proton spectrum of products was recorded using Bruker Avance 300 Spectrometer using DMSO- d_6 as a solvent in the range between 0-15 ppm. 1H chemical shifts are relative to tetramethylsilane.

ii) Ultraviolet-Visible Spectrometer (UV-Vis)

All the UV-Vis spectra were recorded using Spectrophotometer UV-Vis Shimadzu Model 2501 PC. Quartz cell with 10 mm size was used. The spectrum was recorded at wavelength of 200 nm to 600 nm.

iii) Fourier Transform Infrared Spectrometer (FTIR)

Infrared spectrum was recorded using FTIR Shimadzu 8000 Spectrometer in the spectral range of 4000 cm^{-1} to 400 cm^{-1} . Approximately 1 mg of sample was ground with

100 mg of potassium bromide using pestle and mortar. The fine powder was then transferred to the 'dye' and 10 tonne of pressure was applied for 2 minutes. The resulting pellet was put in the sample holder and the FTIR spectrum was recorded.

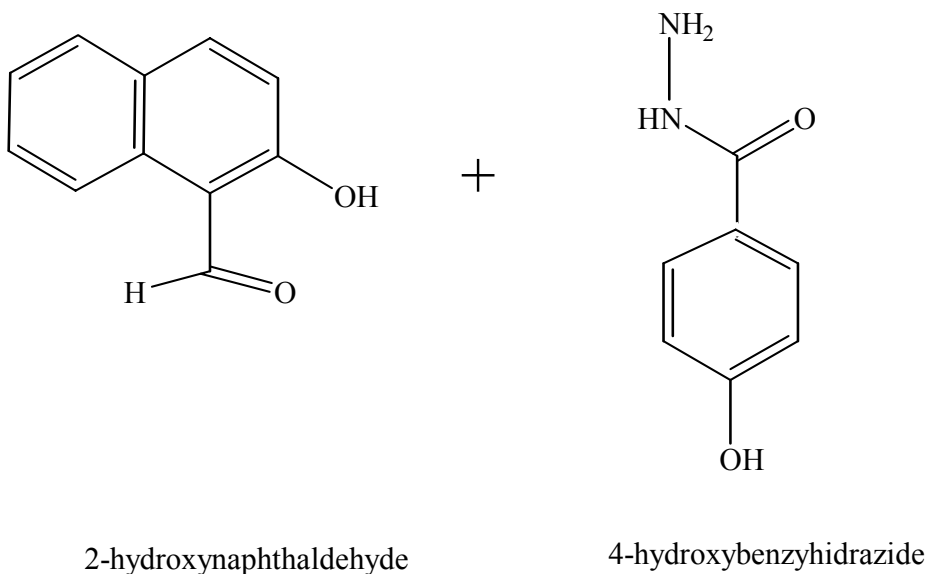
iv) Luminescence Spectrofluorometer (LS)

Perkin Elmer Luminescence Spectrofluorometer model LS55 was used to record fluorescence spectrum. A quartz cell with 10 mm in size was used.

2.3 Synthesis of Ligands

2.3.1 Synthesis of 2-Hydroxynaphthaldehyde Benzoilhydrazide (NDB) ligand.

2-Hydroxynaphthaldehyde (0.8609 g, 5 mmol) was dissolved in absolute methanol (10 mL) in a 3-necked round bottomed flask. 4-Hydroxybenzyhydrazide (0.7601 g, 5 mmol), which was dissolved in an absolute methanol, was added into the flask. The reaction mixture was then heated with stirring at 80°C for 2.5 hours. The light yellow precipitate formed was filtered by suction and dried in a vacuumed dessicator. The product was then recrystallized using methanol.



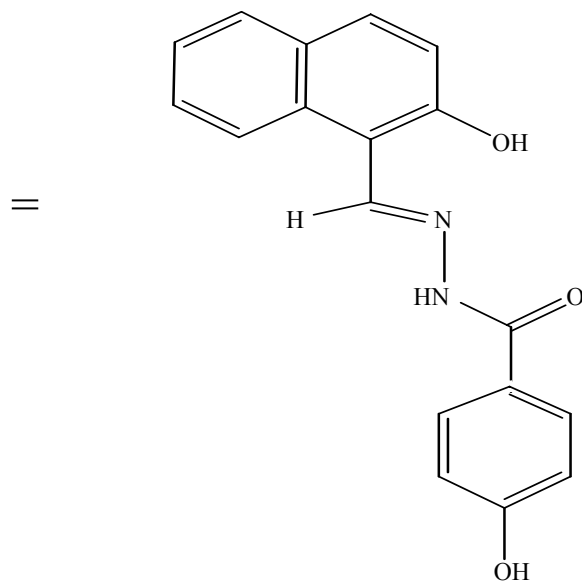
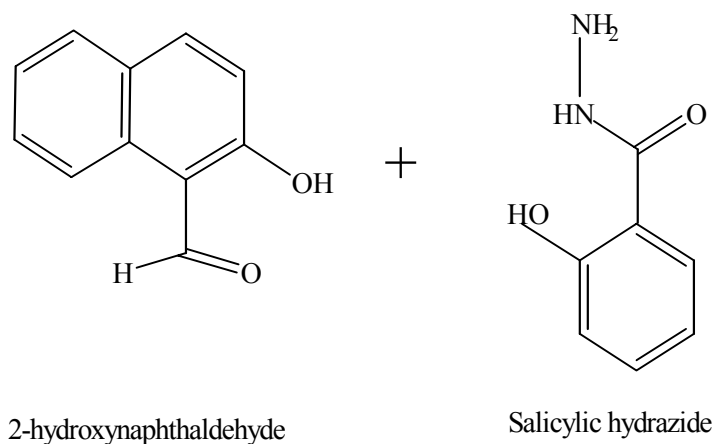


Figure 2.1 : Synthesis of 2-Hydroxynaphthaldehyde benzoilhydrazone (NDB) ligand.

2.3.2 Synthesis of 2-Hydroxynaphthaldehyde Salicyloilhydrazone (NDS) Ligand

2-Hydroxynaphthaldehyde (0.8609 g, 5 mmol) was dissolved in absolute methanol (10 mL) in a 3-necked round bottomed flask. Salicylic hydrazide (0.7601 g, 5 mmol), which was dissolved in an absolute methanol, was added into the flask. The reaction mixture was then heated with stirring at 80°C for 2.5 hours. The light yellow precipitate formed was filtered by suction and dried in a vacuumed dessicator. The product was then recrystallized using methanol.



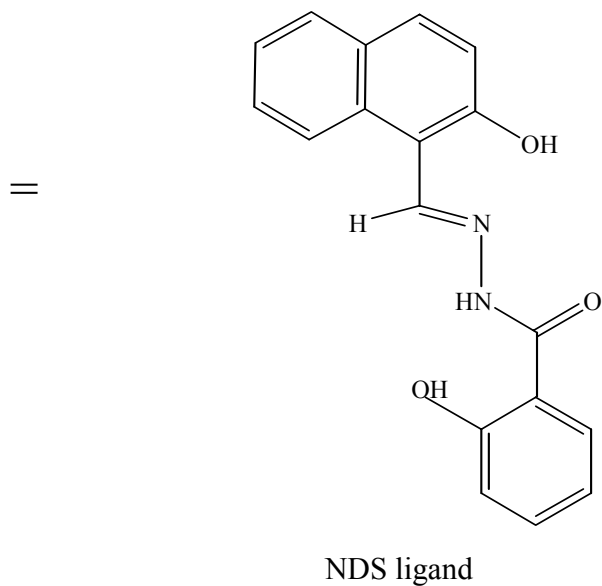
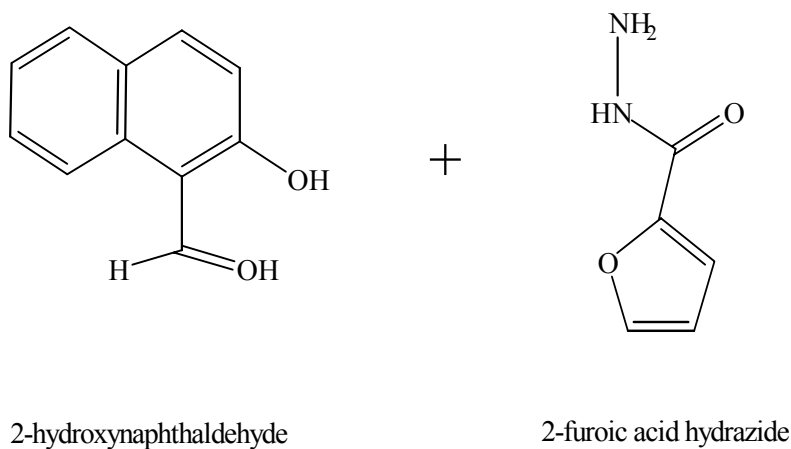


Figure 2.2 : Synthesis of 2-Hydroxynaphthaldehyde salicyloylhydrazone (NDS) ligand

2.3.3 Synthesis of 2-Hydroxynaphthaldehyde Furoilhydrazone (NDF) Ligand.

2-Hydroxynaphthaldehyde (0.8609 g, 5 mmol) was dissolved in absolute methanol (10 mL) in a 3-necked round bottomed flask. 2-Furoic acid hydrazide (0.6306 g, 5 mmol), which was dissolved in an absolute methanol, was added into the flask. The reaction mixture was then heated with stirring at 80⁰C for 2.5 hours. The light yellow precipitate formed was filtered by suction and dried in a vacuumed dessicator. The product was then recrystallized using methanol.



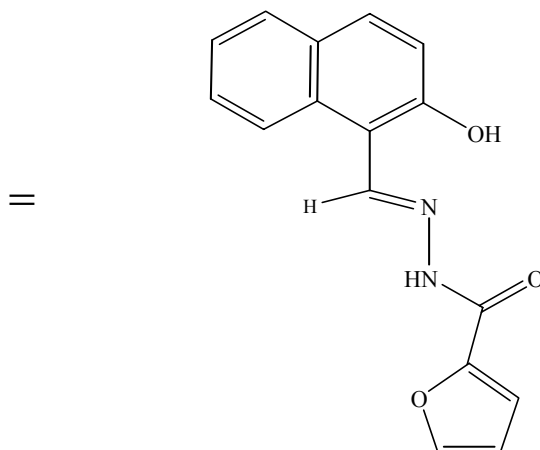


Figure 2.3 : Synthesis of 2-Hydroxynaphthaldehyde furoilhydrazide (NDF) ligand.

All the ligands obtained were characterized using NMR, UV-Vis and IR spectroscopy.

2.4 Preparation of Ligand Solution.

A 1×10^{-3} M ligand solution for each ligand was prepared by dissolving 0.306 g of NDB and NDS ligand and 0.264 g of NDF ligand in 100 mL volumetric flask. Another 1×10^{-4} M ligand solution was prepared by pipetting 10 mL of the 1×10^{-3} M solution in a 100 mL volumetric flask by the addition of methanol up to mark.

2.5 Preparation of Aluminium Nitrate Stock Solution

Solution of Al(III) (1×10^{-2} M) was prepared by dissolving aluminium nitrate nanohydrate (0.3752 g, 1 mmol) in 100 mL volumetric flask and added with deionized water. Another 1×10^{-4} M of solution was prepared by pipetting the solution (1mL) into 100 mL volumetric flask.

2.6 Preparation of Zinc Acetate Dihydrate Stock Solution

Solution of Zn(II) (1×10^{-3} M) was prepared by dissolving zinc acetate dihydrate (0.0220 g, 1 mmol) in 100 mL volumetric flask and added with deionized water. This

solution was next being diluted by pipetting 10mL of this solution in a 100 mL volumetric to make 1×10^{-4} M solution of Zn(II).

2.7 Preparation of Buffer Solution

Buffer solution was prepared by mixing sodium acetate trihydrate (31.473 mL, 1.0 M) and glacial acetic acid (17.485 mL, 1.0 M). Deionized water was then added until the pH become 5.1.

2.8 Determination of Ligand-Complex Stoichiometry

Metal solution (1×10^{-4} M) was pipeted into a 10 mL Erlenmeyer flask which contained a ligand solution (1×10^{-4} M) to give a 2 mL volume of solution with different volume to give a different mole fraction. Buffer solution (3 mL, pH 5.1), which was made up from sodium acetate trihydrate and glacial acetic acid in distilled water, was added to the mixture solution. Deionized water was added until the mark. The flask was swirled to give a homogeneous solution. After 5 minutes, UV-Vis spectrum was recorded.

Table 2.1 : Mole fraction and volume of metal and ligand solution used

Ligand mole Fraction	Volume of ligand, mL	Volume of Metal ,mL
0.500	1.00	1.00
0.665	1.33	0.67
0.750	1.50	0.5
0.800	1.60	0.40
0. 835	1.67	0.33

2.9 Synthesis of Aluminium Complexes

Ligand NDB (0.0918 g, 3 mmol), NDS (0.0918 g, 3 mmol) and NDF (0.0792 g, 3 mmol) each were weighed and dissolved in absolute methanol in a 3-necked round-bottomed flask. The solution was stirred under nitrogen at room temperature. Aluminium nitrate nanohydrate (0.0375 g, 1 mmol) was added to the solution. The mixture was stirred under nitrogen for an hour until a yellow precipitate was formed. The solid was collected by suction filtration and dried in vacuum dessicator.

All the complexes obtained were characterized using UV-Vis and IR spectroscopy

2.10 Synthesis of Zinc Complexes.

NDB ligand (0.0612 g, 2 mmol), NDS (0.0612 g, 2 mmol) and NDF (0.0528 g, 2 mmol) were weighed and dissolved in absolute methanol in a 3-necked round-bottomed flask. The solution was stirred under nitrogen at room temperature. Zinc acetate dihydrate (0.0220 g, 1 mmol) was added to the solution. The mixture was stirred under nitrogen for an hour until a yellow precipitate was formed. The solid was collected by suction filtration and dried in vacuumed dessicator.

All the complexes obtained were characterized using UV-Vis and IR spectroscopy.

2.11 Determination of Fluorescence Intensity of Ligands

Solution of NDB ligand (1 mL, 1×10^{-4} M) was pipeted into a 10 mL Erlenmeyer flask. Buffer solution (3 mL, pH 5.1), which was made up from sodium acetate trihydrate and glacial acetic acid in distilled water, was added to the solution. Deionized water was added until the mark. The flask was swirled to give a homogeneous solution. After 5 minutes, UV-Vis spectrum was recorded.

The fluorescence spectrum of ligand solution ($1 \times 10^{-4} \text{M}$) was recorded at wavelength of excitation 406 nm . This wavelength was choosed because the excitation occurred at this wavelength for both ligand and complex.

Similar procedure was repeated for other ligands.

2.12 Determination of Fluorescence Intensity of Aluminium Complexes

Ligand solution of NDB (3 mL, $1 \times 10^{-4} \text{M}$) was pipeted into 10 mL volumetric flask. Aluminium(III) solution (1 mL, $1 \times 10^{-4} \text{M}$) was added to the solution followed by buffer solution with pH 5.1 (2 mL). The mixture was then added with deionized water until the mark. The fluorescence spectrum was recorded at wavelength of excitation, $\lambda_{\text{exc}} = 406 \text{ nm}$ and wavelength of emission, $\lambda_{\text{emi}} = 0$ using Perkin Elmer Luminescence Spectrometer model LS55.

Similar procedure was repeated for other aluminium complexes

2.15 Determination of Fluorescence Intensity of Zinc Complexes

Ligand solution of NDB (2 mL, $1 \times 10^{-4} \text{M}$) was pipeted into 10 mL volumetric flask. Zinc(II) solution (1 mL, $1 \times 10^{-4} \text{M}$) was added to the solution followed by buffer solution with pH 5.1 (2 mL). The mixture was then added with deionized water until the mark. The fluorescence spectrum was recorded at wavelength of excitation, $\lambda_{\text{exc}} = 406 \text{ nm}$ and wavelength of emission, $\lambda_{\text{emi}} = 0$ using Perkin Elmer Luminescence Spectrometer model LS55.

Similar procedure was repeated for other zinc complexes

CHAPTER III

RESULTS AND DISCUSSION

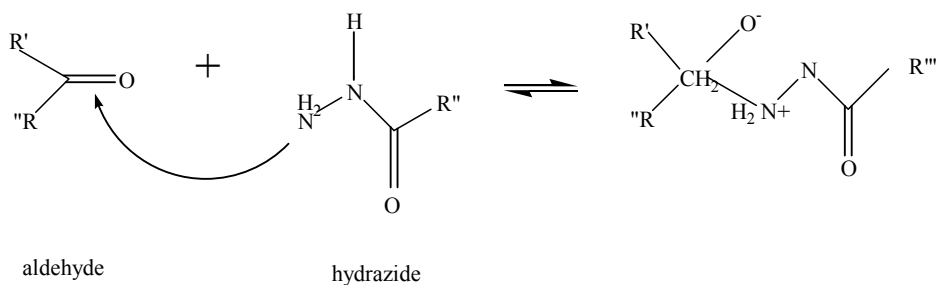
3.1 Synthesis of Ligands.

Three ligands synthesized were ketohydrazone ligands that contains carbonyl group. These ligands were synthesized by a condensation reaction between aldehyde and hydrazides, in a 1:1 mole ratio. The reaction were carried out in reflux temperature in absolute methanol as solvent. In this research, the aldehyde used is the same, 2-hydroxynaphthaldehyde for each reaction, and only the hydrazides varies, which are 4-hydroxybenzyhydrazide, salicylic hydrazide and 2-furoic acid hydrazide.

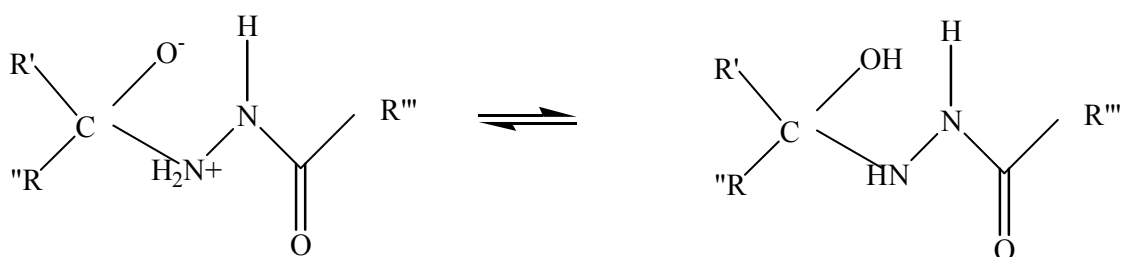
In general, the condensation reaction between substituted hydrazines with aldehydes or ketones is rapid and complete. The mechanism of these reaction involved nucleophilic attack at the carbonyl carbon atom as the first step, followed by elimination of water.

Scheme 3.1 shows how the ketohydrazone ligand was formed from the reaction between aldehyde and hydrazide. It shows the formation process of NDB ligand, NDS ligand and NDF ligand. The reaction start by the attack of nitrogen nucleophilic from hydrazide to carbonyl carbon atom of aldehyde group [19]. It was followed by protonation of molecule by nitrogen group. The reaction stop by the elimination of water after the formation of ketohydrazone.

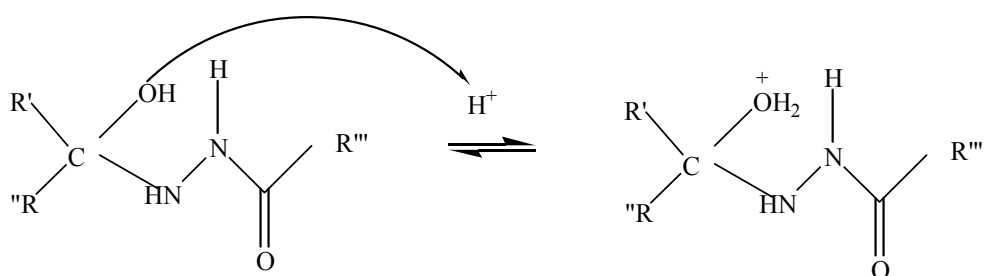
Step 1 : Attack of nitrogen nucleophilic to carbonyl carbon atom.



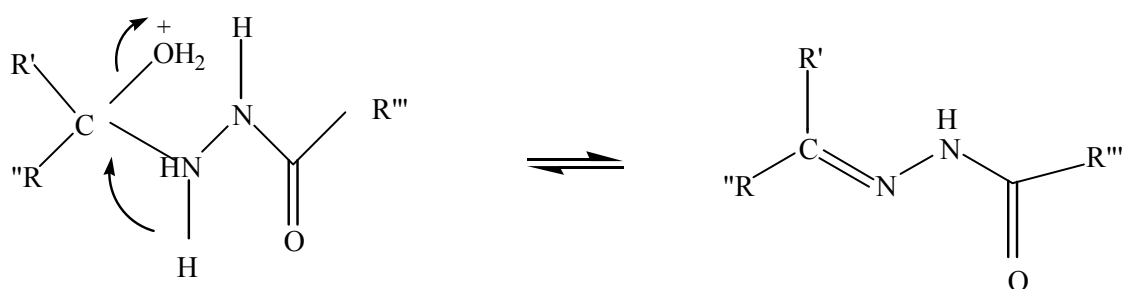
Step 2 : Protonation by nitrogen group.



Step 3 : Protonation of hydroxyl group



Step 4 : Elimination of water.



Scheme 3.1 : Mechanism of condensation reaction between aldehyde or ketone with substituted hydrazine in the formation of ketohydrazone ligand.

3.2. Characterization of ligands.

3.2.1 Physical Properties

Table 3.1 shows the physical properties of all ligands synthesized. From the reaction, the percentage of yield for NDB ligand is 64%, NDF ligand is 69% and NDS ligand is 74%. Each of the ligands is yellow in colour and has melting points more than 200°C.

Table 3.1 : Physical properties of each ligands

Ligand	Phase	Colour	Melting point (°C)
NDS	Solid	Light yellow	249 - 251
NDF	Solid	Dark yellow	215 - 218
NDB	Solid	Light yellow	264 - 267

3.2.2 UV-Vis Spectrum

UV-Vis spectrum for each ligands were recorded with concentration of 1×10^{-4} M. Main absorption bands are given in Table 3.2. The spectrum for each ligand was shown in Appendix A.

From the UV-Vis spectrum, it was observed there were five main absorption band for the transition of π electron of C=O, C=N and aromatic ring. From the spectrum, the absorption band for $\pi \rightarrow \pi^*$ transition for C=O occurred at 314 nm for NDS ligand , 311 nm for ligand NDB and 313 nm for NDF ligand . Meanwhile, for absorption band of $\pi \rightarrow \pi^*$ transition for C=N occurred at 326 nm for NDF ligand, 327 nm for ligand NDS and 325 nm for ligand NDB.

Table 3.2 : Main absorption bands according to types of electronic transition in UV-Vis spectra of ligands

Ligands	Electronic Transition (nm)				
	$\pi \rightarrow \pi^*$			$n \rightarrow \pi^*$	
	C=O	C=N	Aromatic ring	C=O	C=N
NDB	311	325	361 and 375	425	425
NDS	314	327	363 and 385	426	426
NDF	313	326	364and 377	433	433

Substitution on the carbonyl group by an auxochrome with lone pair of electrons, -NHR, gave a pronounced hypsochromic effect on the $n \rightarrow \pi^*$ transition [20]. The auxochrome attached to the carbonyl group on NDF ligand caused a bathochromic shift on the $\pi \rightarrow \pi^*$ [21], which was 313 nm. Primary and secondary bands of polynuclear aromatic system in the ligand, shifted to longer wavelengths, as the result of conjugation extension and OH group that with n elements. These n elements interacted with the π system of the aromatic rings.

In overall, absorption caused by transition $n \rightarrow \pi^*$ for C=O and C=N occurred at lower energy level compared to the transition of $\pi \rightarrow \pi^*$. It is due to the energy barrier between molecule π and π^* is larger than between n and π^* . Thus, higher energy is needed for the transition from orbital π to π^* .

3.2.3 IR Analysis

The infrared spectra of all ligands were recorded as KBr disk and is shown in Appendix B, C and D. The main absorption bands are given in Table 3.3. IR spectra for each ligands show 5 main absorption band. Absorption at $3500 - 3200 \text{ cm}^{-1}$ is due to the hydroxyl group (OH). Some of this band are quite broad due to the intermolecular hydrogen bonding.

Table 3.3 : Functional groups and their frequencies of IR absorption band for each ligands

Ligand	Frequency(cm^{-1})					
	OH	NH	C=O	C=N	C-O	C=C Aromatic
NDS	3500-3200	3059.9	1644.2	1603.7	-	1457.1 and 1388.7
NDB	3210	3167.9	1635.5	1590.2	-	1538.1 and 1497.1
NDF	3437.9	3138.9	1642.3	1602.7	1196.7	1465.8 and 1392.5

The observed band at $3500\text{-}3200\text{ cm}^{-1}$ is assigned as the intermolecular bonded O-H. The sharp and intense band at 3167.9 cm^{-1} for NDB ligand, 3059.9 cm^{-1} for NDS ligand and 3138.9 cm^{-1} for NDF ligand is consistent with the presence of a N-H group while the band of medium intensity $1605 - 1590\text{ cm}^{-1}$ is characteristic of the amine C=N, from through the condensation between aldehyde and hydrazide. The absorption band for N-H had shifted to a lower frequency that maybe due to the formation of the enol form of the ligands. The strong band at 1642.3 cm^{-1} for NDF ligand, 1635.5 cm^{-1} for NDB and 1644.2 cm^{-1} for NDS are assigned to the C=O group of the hydrazide.

The presence of the C=N and C=O absorption bands in the spectrum confirmed the completeness of the condensation reaction in solid.

3.2.4 NMR Analysis

Spectrum ^1H NMR (Appendix E, F) for each ligand was taken using the $\text{DMSO-}d_6$ as the solvent. The data of the spectrum was shown in the Table 3.4

Table 3.4 : Chemical shift of protons in ligand

Ligand	Chemical Shift				
	OH	NH	N=CH	Aromatic	C=CH
NDB	12.90 s, 12.00 s	10.25 s	9.49 s	6.9-8.2 m	-
NDF	12.63 s	12.25 s	9.50 s	7.3-8.2 m	7.2 d
NDS	12.72 s, 11.99 s	11.69 s	9.51 s	6.9 m-8.3 m	-

The NMR spectrum of the ligand shows a broad singlet centred at 12.72 ppm which is assigned to the resonance of the proton of the OH group attached to the naphthaldehyde ring. The singlet at 11.99 is due to the O=C-NH proton signal while the singlet at 9.50 ppm for NDF ligand, 9.51 ppm for NDS ligand and 9.49 ppm for NDB ligand are assigned to as the imine N=C-H proton resonance. All the spectra show the aromatic proton between 6.9-8.3 ppm.

The duplet at 7.2 ppm for ligand NDF is due to the proton in furan ring of the ligand.. The singlet at 12.90 ppm for NDB ligand, 12.63 for NDF ligand and 12.72 ppm for NDS ligand are assigned to as resonance of OH proton . The presence of amide O=C-NH proton resonance in the ^1H NMR spectrum indicated that the ligand exists as the keto form .

Based on the IR, UV-Vis and ^1H -NMR spectra obtained, we expected that all ligands were successfully synthesized.

3.3 Determination of Complex Stoichiometry

3.3.1 Aluminium Complexes

By using Job method, the stoichiometry between metal and ligand was determined. Based on the intensity of UV-Vis absorption at wavelength of 425 nm

(Appendix G, H) which is the wavelength where the absorption of the complex occurred, a graph of absorbance versus ligand mole fraction was plotted which indicated that the maximum absorbance occurred at that mole fraction [22]. Thus, the number of mole ligand bonding to metal, n :

$$n = \frac{X_{\max}}{(1-X_{\max})} \quad (\text{Eq 3.1})$$

X = mole fraction.

n = no. of mole ligand bonded with metal

X_{\max} = maximum absorption

Therefore, the stoichiometry of complex was equal to 1 : n

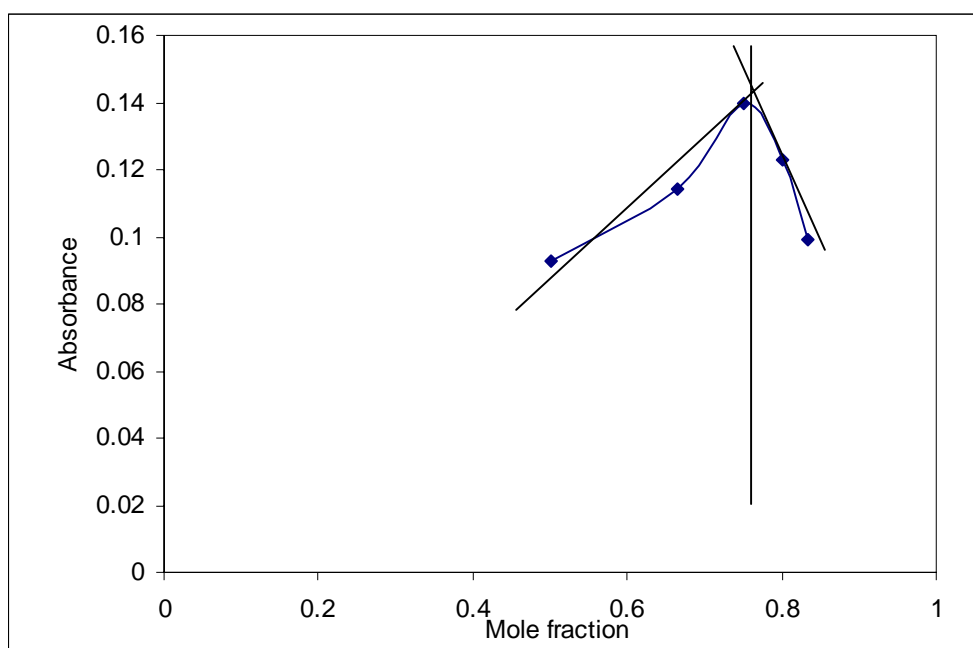


Figure 3.1 : Graph of absorbance versus mole fraction of NDB ligand.

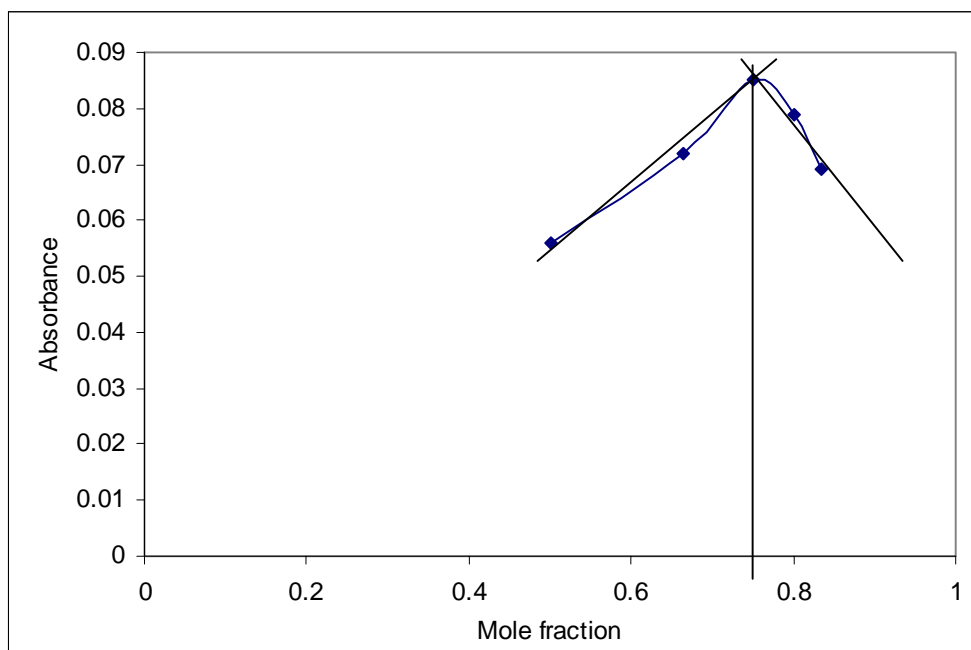


Figure 3.2 : Graph of absorbance versus mole fraction of NDS ligand.

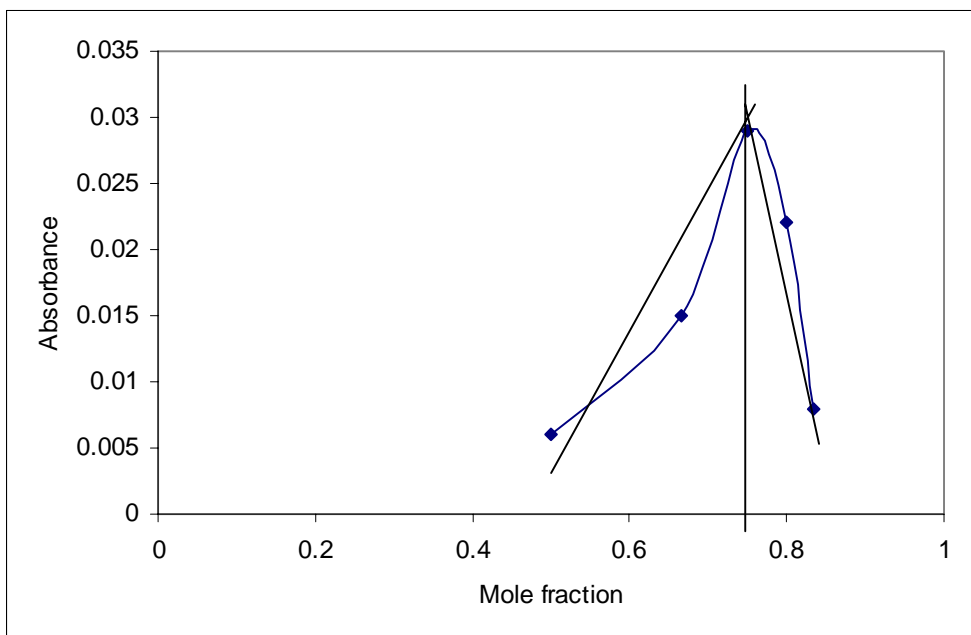


Figure 3.3 : Graph of absorbance versus mole fraction of NDF ligand.

From Figure 3.1 – 3.3 above, it was observed that value of X_{\max} is equal to 0.75, which will give the value of n ;

$$n = X_{\max} / (1 - X_{\max}) \quad (\text{Eq. 3.1})$$

X = mole fraction.

n = no. of mole ligand bonded with metal

X_{\max} = maximum absorption

$$n = 0.75 / (1 - 0.75)$$

$$n = 3.$$

Therefore, the stoichiometry of Al (III) complex was 1:3, where 3 moles of ligand bond to 1 mole of Al (III) ion.

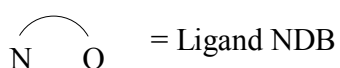
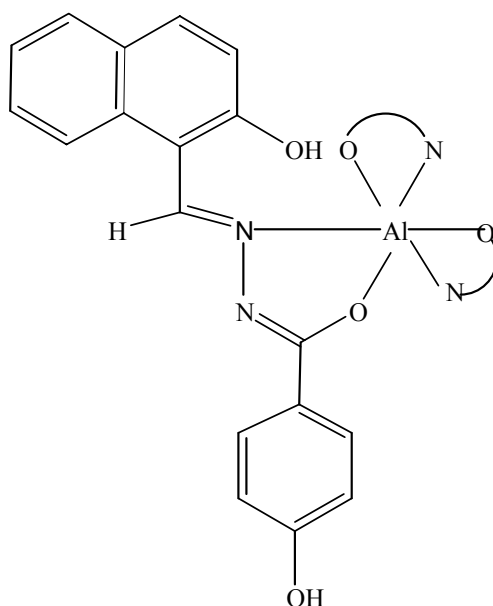


Figure 3.4 : Structure for Aluminium tri(2-Hydroxynaphthaldehyde benzoilhydrazide) $[\text{Al}(\text{NDB})_3]$ complex

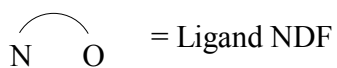
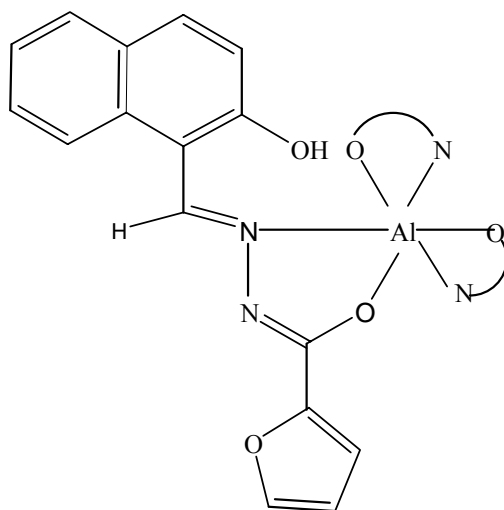


Figure 3.5 : Structure for Aluminium tri(2-Hydroxynaphthaldehyde furoilhydrazone) $[Al(NDF)_3]$ complex.

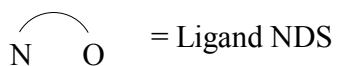
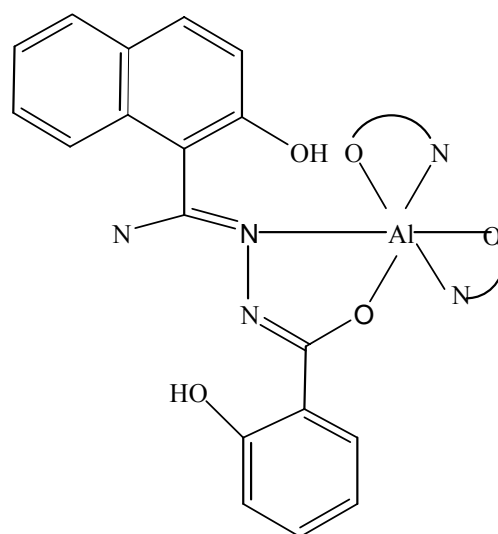


Figure 3.6 : Structure for Aluminium tri(2-Hydroxynaphthaldehyde salicyloilhydrazone) $[Al(NDS)_3]$ complex

3.3.2 Zn(II) Complexes

By using Job method, the stoichiometry between metal and ligand was determined. Based on the intensity of UV-Vis absorption at wavelength of 425 nm (Appendix I, J), which is the wavelength where the absorption of the complex occurred, a graph of absorbance versus ligand mole fraction was plotted which indicated that the maximum absorbance occurred at that mole fraction [22]. Thus, the number of mole ligand bonding to metal, n:

$$n = \frac{X_{\max}}{(1-X_{\max})} \quad (\text{Eq. 3.1})$$

X = mole fraction.

n = no. of mole ligand bonded with metal

X_{\max} = mole fraction of ligand at maximum absorption

Therefore, the stoichiometry of complex was equal to n

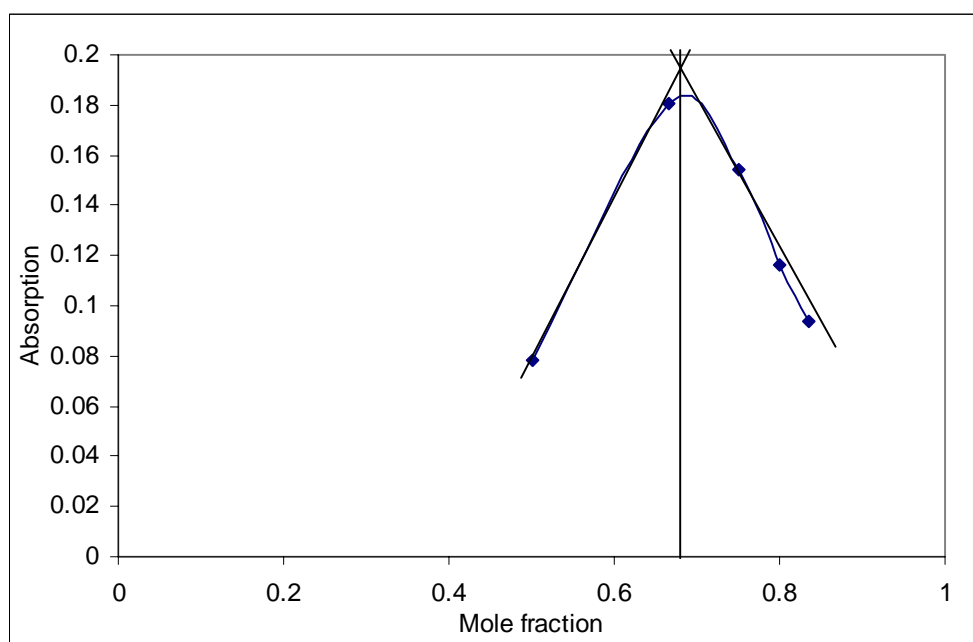


Figure 3.7 : Graph of absorbance versus mole fraction of NDB ligand

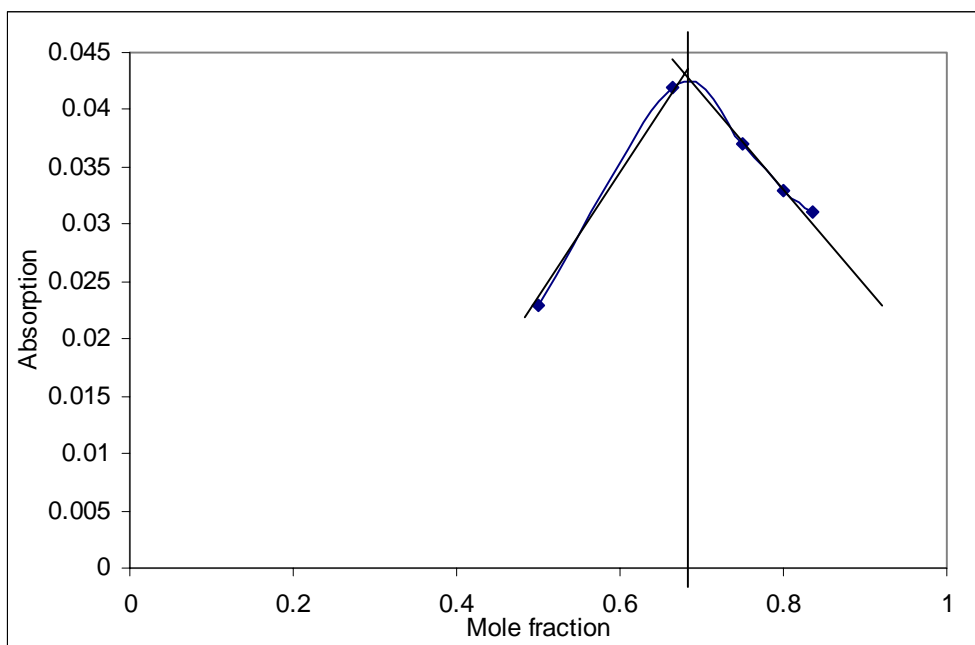


Figure 3.8 : Graph of absorbance versus mole fraction of NDF ligand

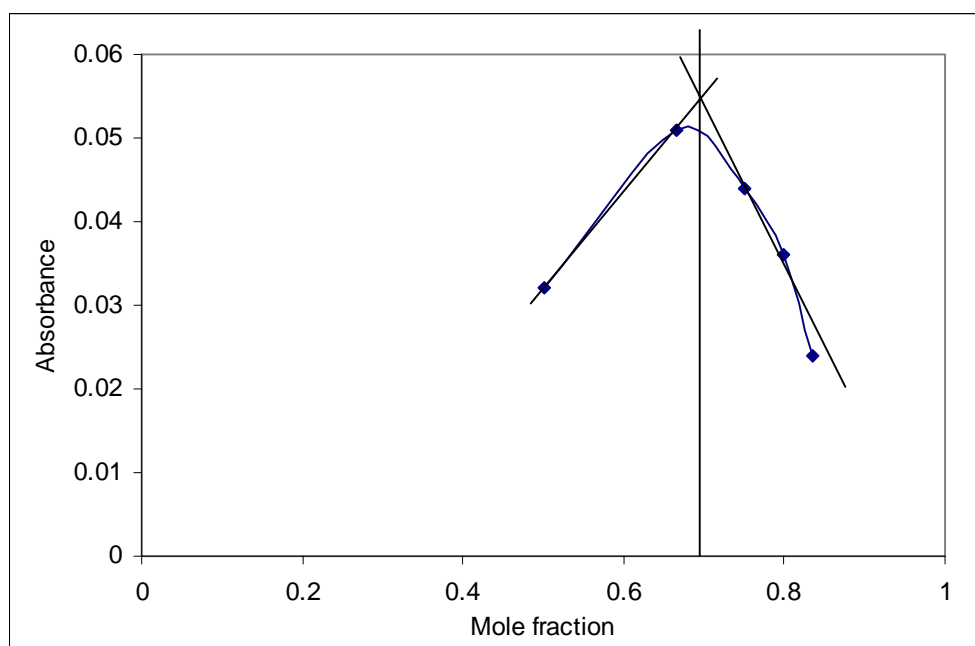


Figure 3.9 : Graph of absorbance versus mole fraction of NDS ligand.

From Figure 3.7-3.9 , it was observed that value of X_{\max} is equal to 0.665, which will give the value of n ;

n	$=$	$X_{\max} / (1 - X_{\max})$	Eq. 3.1
X	$=$	mole fraction of ligand	
n	$=$	no. of mole ligand bonded with metal	
X_{\max}	$=$	mole fraction of ligand at maximum absorption	
n	$=$	$0.665 / (1 - 0.665)$	
n	\sim	2	

Therefore, the stoichiometry of zinc complexes was 1:2, where 2 moles of ligand bond to 1 mole of Zn (II) ion.

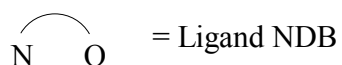
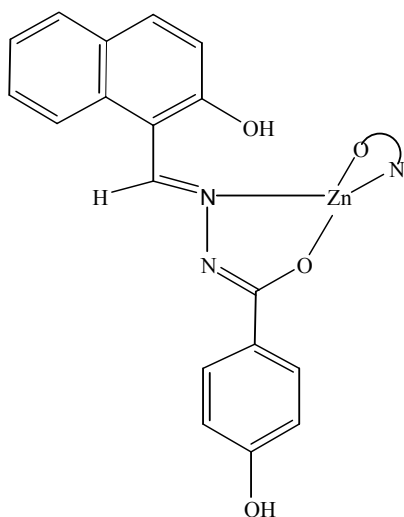


Figure 3.10 : Structure for Zinc di(2-Hydroxynaphthaldehyde benzoilhydrazide) $[Zn(NDB)_2]$ complex

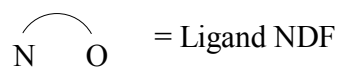
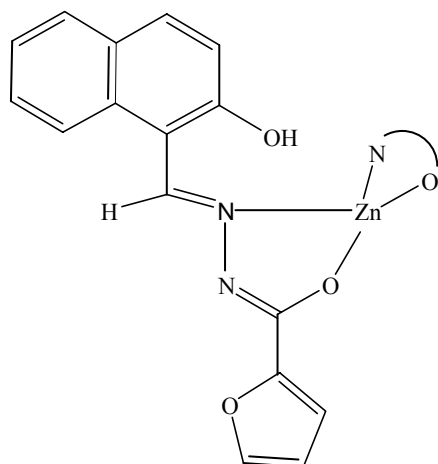


Figure 3.11 : Structure for Zinc di(2-Hydroxynaphthaldehyde furoilhydrazone) $[Zn(NDF)_2]$ complex

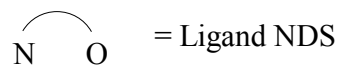
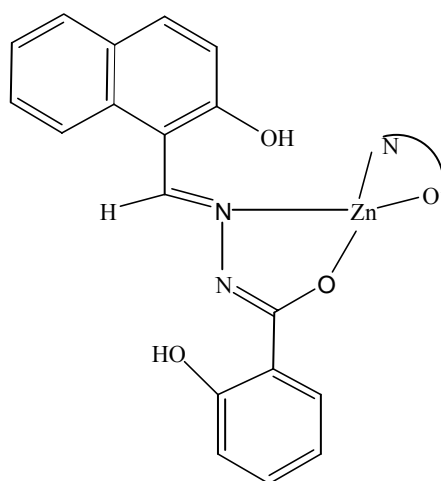


Figure 3.12 : Structure for Zinc di(2-Hydroxynaphthaldehyde salicyloilhydrazone) $[Zn(NDS)_2]$ complex.

3.4 Synthesis and Characterization of Complexes

3.4.1. Al(III) Complexes

In this reaction, enol anion from the ligands had reacted with ion Al(III) to form a neutral complex. Ligands had reacted with Al(III) to form coordination complex, in a stoichiometry of 1:3 which is 1 mole fraction of metal reacted with 3 mole fraction of ligand.. The complexes were characterized using FTIR and UV-Vis spectroscopy. Figure 3.13 shows the reaction between ligand NDB and aluminium nitrate nanohydrate.

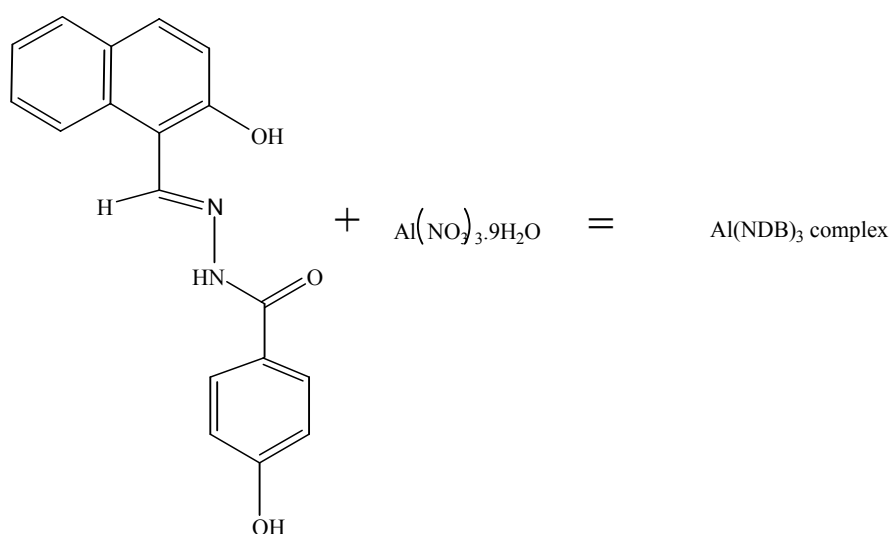


Figure 3.13 : Synthesis of Aluminium tri(2-Hydroxynaphthaldehyde benzoilhydrazone) [Al(NDB)₃] complex.

3.4.1.1 Physical Properties

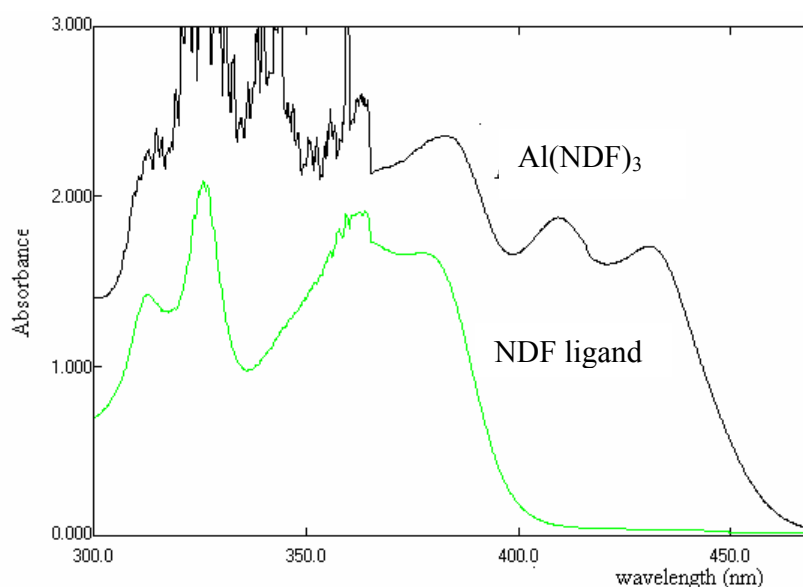
All complexes show no different in colour with its ligand. The percentage of yield for Al(NDF)₃ is 42.1%, 39.0% for Al(NDS)₃ and 40.2% for Al(NDB)₃. All the complexes obtained were characterized using IR and UV-Vis spectrometer. Table 3.5 shows the physical properties for all the complexes.

Table 3.5 Physical properties of Al(III) complexes

Complex	Colour	Phase	Melting points
Al(NDF) ₃	Dark yellow	Solid	> 300 °C
Al(NDS) ₃	Light Yellow	Solid	> 300 °C
Al(NDB) ₃	Light Yellow	Solid	> 300 °C

3.4.1.2 UV-Vis Spectrum

Figure 3.14 shows the UV-Vis spectrum for free NDF ligand, and complex of aluminium. The other complexes (Appendix K, L) also show the same pattern as this spectrum. From this figure we can observed some different between these two spectrum. UV-Vis spectrum for complex shows that wavelengths of electronic transitions of $\pi \rightarrow \pi^*$ for C=O or C=N had disappeared due to coordination of ligand to the metal through the π electron..

**Figure 3.14 :** UV-Vis spectrum for NDF ligand and Al(NDF)₃.

Batochromic shift for aromatic complex occurred at 410 nm and new absorption band formed at 435 nm that could be assigned as the charge transfer transition between metal and ligand.

From the data obtained, it was proved that the Al(III) complexes had been successfully synthesized for ligand NDF, NDS, and NDB.

3.4.1.3 IR Analysis

IR spectrum was recorded as KBr disk. The result (Appendix M, N, O) is shown in the Table 3.6. From the spectrum we can see the NH band absorption had disappeared, suggesting that coordination between O from enol group to the metal had occurred. The disappearance of C=O absorption around 1630-1645 cm^{-1} shows that double bond of the group was broken and bonded to the metal.

Table 3.6 : Functional groups and their wave numbers for Al(III) complexes.

Complex	Frequency(cm^{-1})			
	OH	C=O	C=N	CO
Al(NDB) ₃	3394	-	1605.6	1384.8
Al(NDF) ₃	3436.9	-	1604.7	1385.8
Al(NDS) ₃	3450.4	-	1604.7	1386.7

By comparing the FTIR spectrum between ligand and complex, we can observed that there is an appearance of OH group, in the region of 3300-3450 cm^{-1} . This indicates that this group did not involved in the coordination with metal. The stretching frequency of C=N had shifted to a higher wavelength due to the bonding of free electrons N toward metal, which causes an inductive effect of C=N [23]. It causes the double bond characteristic of C=N reduced, thus higher the frequency of C=N for the complex.

From the spectra we can see that the NH band absorption had disappeared, suggesting that coordination between O from enol group to the metal had occurred. The disappearance of C=O absorption around 1630-1645 cm^{-1} appearance of new peak in the range of 1380 – 1395 cm^{-1} for C-O absorption shows that double bond of the group was broken and bonded to the metal.

3.4.2 Zn(II) Complexes

In this reaction, enol anion from the ligands had reacted with ion Zn(II) to form a neutral complex. Ligands had reacted with Zn(II) to form coordination complex, in a stoichiometry of 1:2 which is 1 mole fraction of metal reacted with 2 mole fraction of ligand.. The complexes were characterized using FTIR and UV-Vis spectroscopy. Figure 3.15 shows the reaction between NDB ligand and Zinc acetate dihydrate.

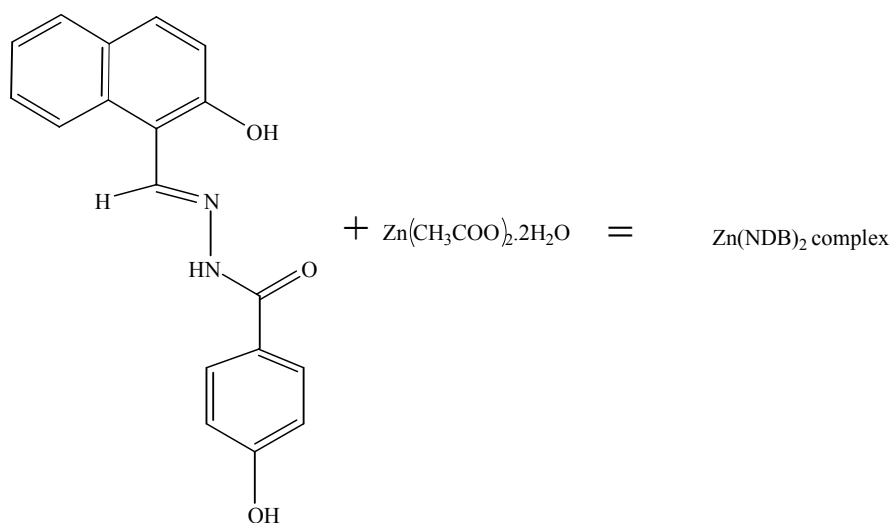


Figure 3.15 : Synthesis of Zinc di(2-Hydroxynaphthaldehyde benzoilhydrazone) [Zn(NDB)₂]. complex.

3.4.2.1 Physical Properties

All complexes show no different in colour with its ligand. The percentage of yield for Zn(NDF)₂ is 49.3%, 39.8% for Zn(NDS)₂ and 52.8% for Zn(NDB)₂. All the

complexes obtained were characterized using IR and UV-Vis spectrometer. Table 3.7 shows the physical properties for all the complexes.

Table 3.7 :Physical properties of Zn (II) complexes.

Complex	Colour	Phase	Melting points
Zn(NDF) ₂	Dark yellow	Solid	More than 300 ⁰ C
Zn(NDS) ₂	Light Yellow	Solid	More than 300 ⁰ C
Zn(NDB) ₂	Light Yellow	Solid	More than 300 ⁰ C

3.4.2.2 UV-Vis Spectrum

A UV-Vis spectra of all Zinc complexes were recorded. The pattern for all complexes shows the same as in Aluminium complexes. UV-Vis spectrum for complex shows that wavelengths of electronic transitions of $\pi \rightarrow \pi^*$ for C=O and C=N had shifted to a higher wavelength due to coordination of ligand to the metal through the π electron.

Bathochromic shift for aromatic complex occurred at 410 nm and new absorption band formed at 431 nm that could be assigned as the charge transfer transition between metal and ligand.

3.4.2.3 IR Analysis

IR spectrum was recorded as KBr disk. The result (Appendix P, Q, R) is shown in the Table 3.8. By comparing the FTIR spectrum between ligand and complex, we can observe that there is an appearance of OH group, in the region of 3300-3450cm⁻¹. This indicates that this group did not involve in the coordination with metal. The stretching

frequency of C=N had shifted to a higher wavelength due to the bonding of free electrons N toward metal, which causes an inductive effect of C=N [23]. It causes the double bond characteristic of C=N reduced, thus higher the frequency of C=N for the complex.

Table 3.8 : Functional groups and their wavenumbers for Zn(II) complexes.

Complex	Frequency(cm^{-1})			
	OH	C=O	C=N	CO
Zn(NDB) ₂	3200-3500	-	1604.7	1390.6
Zn(NDF) ₂	3425.3	-	1617.2	1382.9
Zn(NDS) ₂	3200-3500	-	1604.7	1388.5

From the spectrum we can see the NH band absorption had disappeared, suggesting that coordination between O from enol group to the metal had occurred. The disappearance of C=O absorption around $1630\text{-}1645\text{ cm}^{-1}$ and appearance of new peak in the range of $1380\text{--}1395\text{ cm}^{-1}$ for C-O absorption band shows that double bond of the group was broken and bonded to the metal.

3.5 Determination of Fluorescence Properties of Ligand and Complexes

From the spectrum of ligand, the emission peak around 470 nm corresponding to the emission peak of λ 406 nm indicate that all the ligands synthesized are fluorescence molecule. The excitation and emission spectrum of the compounds showed that there are 5 absorption bands at λ 336nm, 396 nm, 406nm 473 nm and 535 nm. The excitation peak at λ 396 nm was chosen because this is the main excitation peak for both ligand and complex.

From all the fluorescence spectrum of Zn (II) complex and Al (III) complex, we might observed that the intensity of emission peak at λ 470 nm corresponding to excitation wavelength of 396 nm for complex is higher compared to the ligand. The intensity of excitation of complex is greatly higher for each complexes.

Figure 3.14-3.15 shows the fluorescence spectra for ligand and complexes.

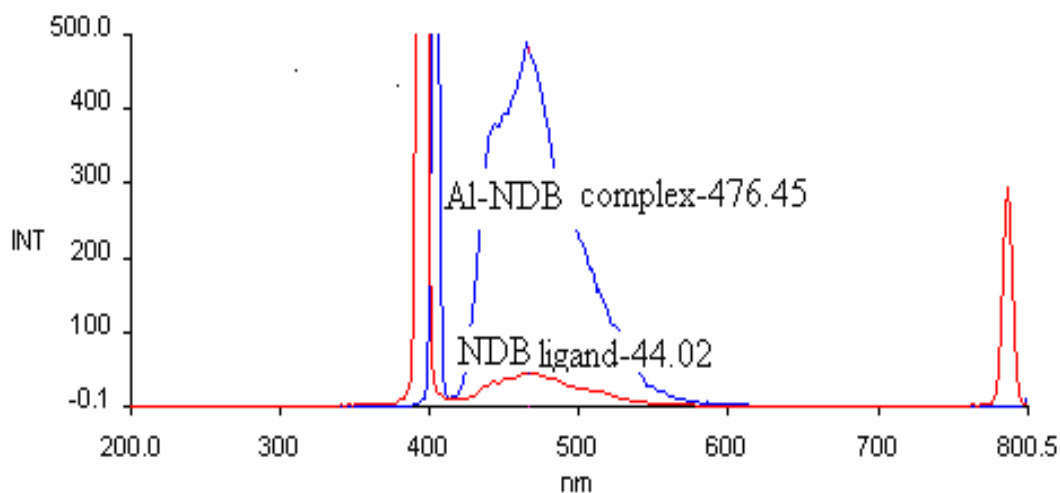


Figure 3.16 Fluorescence spectrum of ligand NDB and $\text{Al}(\text{NDB})_3$ complex

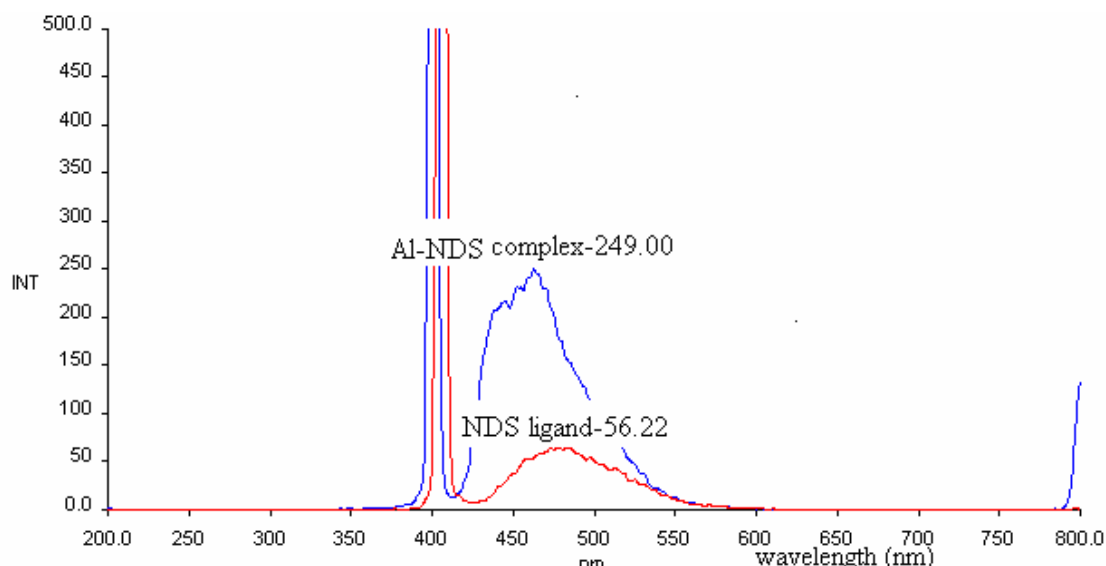


Figure 3.17 : Fluorescence spectrum of ligand NDS and $\text{Al}(\text{NDS})_3$ complex.

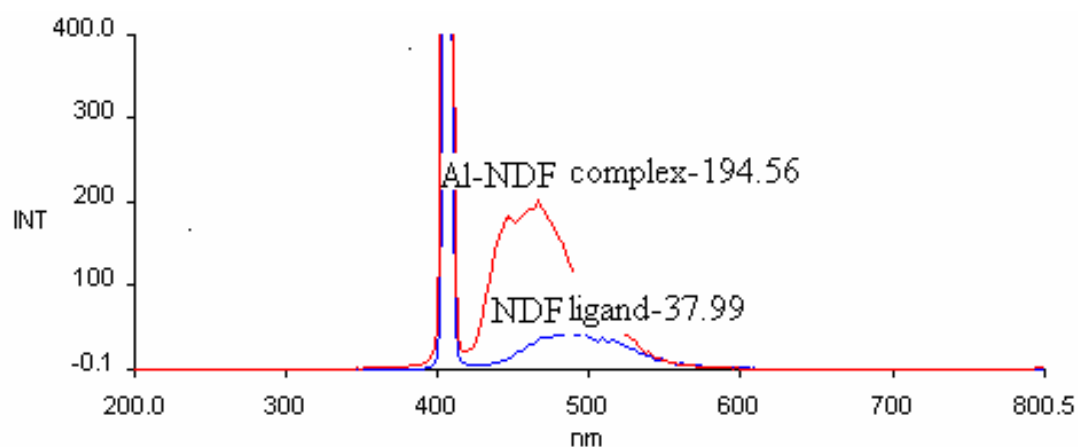


Figure 3.18 : Fluorescence spectrum of ligand NDF and $\text{Al}(\text{NDF})_3$ complex

All of the compound in this study are fluorescent as all of them contain aromatic rings and π bond conjugation system, where it is said to have high rigidity of molecules [24]. Table 3.9 shows the fluorescence intensity for ligands and complexes.

Table 3.9 : Fluorescence intensity of ligands and complexes

Compound	Fluorescence intensity
NDF Ligand	37.99
NDS Ligand	56.22
NDB Ligand	44.02
$\text{Al}(\text{NDF})_3$	194.56
$\text{Al}(\text{NDB})_3$	476.45
$\text{Al}(\text{NDS})_3$	249.00
$\text{Zn}(\text{NDF})_2$	94.04
$\text{Zn}(\text{NDS})_2$	102.10
$\text{Zn}(\text{NDB})_2$	196.20

Normally, a rigid molecule has the ability to emit high fluorescence radiation. It is because rigidity of molecules able to decrease the rate of collisional quenching, thus give more time to form emission of molecules through fluorescence. For chelate ligand, it will

experience fluorescence intensity when it is in complex form by coordinating to metal, as a result of the increasing of rigidity of molecules which will increase the population exciting to the higher state thus enhance the intensity of fluorescence.

The metal does not exhibit fluorescent characteristic. Ketohydrazone, under the influence of metal, forms a rigid chelate ring. When illuminated under an ultraviolet light, the ligand absorbs a light energy and occurs $\pi \rightarrow \pi^*$ transition, then the ligand causes photoluminescent during radiative decay [25]. the role of the central atom is to provide the stability to the ligand.

Theoretically, luminescence of molecule using the chelate as the emitter decreases as the metal ion size increases. This may be attributed to the decrease in fluorescence yield as the metal ion size increases [26].

However, aluminium complexes exhibit greater luminescence properties which may be contributed by more ligand coordinating to the metal, compared to zinc complexes. The strong blue luminescence observed may be due to the coordination of bridging ligands to the metal centre, which increases the rigidity of the ligand and reduces the loss of energy via un-radiation pathway, thus, enhancing the $\pi \rightarrow \pi^*$ irradiation probability. Different complexes exhibit different luminescence characteristic illustrating that different substitutes exert different effects on luminescence [27].

CHAPTER IV

CONCLUSIONS AND RECOMMENDATIONS

4.1 Conclusion

Three ketohydrazone ligands had been successfully synthesized and characterized. All of them were synthesized from the reaction between 2-hydroxynaphthaldehydes with various hydrazine; salicylic hydrazide, benzyhydrazide and 2-furoic acid hydrazide in 1:1 stoichiometry. The light yellow solid was obtained in percentage of yield in the range of 64-74 % with melting points between 240-270 °C.

Complexation between metal ; aluminium and zinc, and ligands shows two different stoichiometry. From the Job method carried out, the stoichiometry of Zn (II) : ligand was found out to be 1 : 2 and which shows that 3 mole fraction of ligand bound to 2 mole of zinc. However, for complexation with Al (III), the result shows that the stoichiometry of metal bind with ligand is 1: 3. Hence, the complexation reactions between all ligands with these two metal in accordance to the stoichiometry were carried out. All of the complex obtained were light yellow solid, except for complexes of ligand F, which is dark yellow solid. All the complexes and ligands obtained were characterized using FTIR, NMR and UV-Vis spectroscopy.

From the study on fluorescence spectrum for each ligand and complex, it was revealed that all these products have the fluorescence properties as all of them contain aromatic rings and π bond conjugation system. Complexation with metal will increase the fluorescence of compounds as it causes the increase in rigidity of molecule especially with chelating ligand . Al(III) complexes shows better fluorescence intensity than Zn (II) complexes as it has a higher coordination number and thus increases the rigidity of molecules.

As a conclusion, Al(III) complexes show a better potential to be the emitting material for OLED devices as it shows a good fluorescence properties compared to Zn(II) complexes. However, among all the complexes, Al(NDB)₃ had the best potential for this purpose as it shows the highest intensity of fluorescence.

4.2 Recommendations

For further works, the parameters in the formation of the complexes should be varied, to give a better percentage of yield and higher fluorescence, for example stability of the complexes, repeatability, effect of foreign ions and others. Furthermore the complexes obtained can be fabricated as the OLED material to see the real potential of these complexes as the emitting material. Variety of metal can be used in order to see the effect of metal on fluorescence properties of complexes.

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Synthesis and Characterization of Ketohydrazone Ligands and Its Complexes with Aluminium(III) and Zinc(II) as Potential Emitting Material in OLED.

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Abstract– Ketohydrazone is a molecule that is able to act as a bidentate ligand through the O of C=O and N of N=C in the molecule. Three ketohydrazone ligands had been fully synthesized through the condensation reaction between 2-hydroxynaphthaldehydes with various hydrazine, salicylic hydrazide, benzyhydrazide and 2-furoic acid hydrazide in a 1:1 stoichiometry. The ligands had been characterized using infrared, ¹HNMR and ultraviolet-visible spectrometer. Complexation reaction between all ligands and metal, with a stoichiometry of 1:2 for Zn (II) : ligand and 1:3 for Al(III) : ligand were carried out. All six complexes obtained were characterized using FTIR and UV-Vis spectrometer. The fluorescence properties of each ligands and complexes were investigated using luminescence spectrofluorometer at fluorescence emission wavelength at 406 nm and excitation wavelength at 470 nm. Results showed that all the ligands and molecules synthesized have the fluorescence properties and complexation with metal enhanced the intensity of the fluorescence. It was observed that complex of Al(Bhn)₃ showed the best potential as an emitting material for OLED as it has the highest fluorescence intensity compared to others.

Keywords *ketohydrazone, fluorescence, OLED,.*

Abstrak– Ketohidrazon merupakan sebatian molekul yang berupaya berfungsi sebagai ligan bidentat melalui O daripada C=O dan N daripada N=C di dalam molekulnya. Tiga ligan ketohidrazon telah berjaya disintesis melalui proses kondensasi antara 2-hidroksinaftaldehida dan beberapa kumpulan hidrazon, salisilik hidrazida,, 2-furoik hidrazida, dan benzihidrazida. mengikut nisbah stoikiometri 1 : 1. Semua ligan yang telah disintesis dicirikan melalui spektroskopi IR, UV-Vis dan ¹H-RMN. Tindak balas pengkompleksan antara ligan yang telah disintesis dengan dua logam yang berasingan, iaitu Aluminium dan Zinc telah dijalankan dengan nisbah ion ligan : ligan 1 : 3 bagi pengkompleksan dengan aluminium dan 1 : 2 bagi pengkompleksan dengan Zinc. Enam kompleks yang terhasil dicirikan melalui spektroskopi IR dan UV-Vis. Ciri-ciri pendarfluor bagi tindak balas pengkompleksan dan ligan yang terhasil telah dikaji menggunakan spektrometer pendarfluor pada panjang gelombang pemancaran 470 nm dengan panjang gelombang pengujaan 470 nm. Hasil yang diperolehi menunjukkan bahawa semua ligan dan kompleks yang disintesis menunjukkan sifat pendarfluor dan pengkompleksan dengan logam dapat meningkatkan keamatan pendarfluornya.. Melalui kajian ini, dapat dinyatakan bahawa kompleks Al(Bhn)₃ menunjukkan potensi yang baik sebagai bahan pemancar dalam diod pemancar cahaya organik (OLED) memandangkan kompleks ini menunjukkan keamatan pendarfluor yang tertinggi.

Kata kunci: *Ketohidrazon, pendarfluor, OLED*

Introduction

Since organic light-emitting diodes (LEDs) using 8-hydroxyquinoline aluminum as the emitting layer was reported to emit green light in 1987 [1], organic LEDs have received considerable attention due to their potential application in various displays. Emitting material for organic LEDs can be classified into three types according to their molecular structure: organic dyes, chelate metal complexes and polymers. Complexes of chelating ligands are in general more stable thermodynamically than those with an equivalent number of monodentate ligands. These organic molecules were useful due to their solubility. They could be applied to a surface as a film via evaporation of their solvent.

Ketohydrazone, a chelating ligand with both oxygen and nitrogen donors coordinated to metal ion formed a stable complex. From earlier studies, the metal–chelate complex is believed to be a promising emitting material. Oxadiazole compounds are also known to have excellent electron transport ability and efficient fluorescence properties. Several research groups reported efficient bluish-green emission in the devices using the oxadiazole compounds [2]. From Suning Wang study, he reported that for two derivatives of 7-azaindole for aluminium complexes, although the compounds has a blue emission band at ca. 450

nm, it is very weak and the steric factors may be responsible for the problem[3].

There is a big challenge in developing emitting materials which can exhibit highly efficient blue-light emission. Thus, this research will focus on the synthesizing the new blue light emitting material and study of the potential of the complexes as the emitting material in OLED.

Experimental

Synthesis of Ligands

2-Hydroxynaphthaldehyde was dissolved in absolute methanol in a 3-necked round bottomed flask. 4-Hydroxybenzhydrazide which was dissolved in an absolute methanol, was added into the flask. The reaction mixture was then heated with stirring at 80⁰C for 2.5 hours. The light yellow precipitate formed was filtered by suction and dried in a vacuumed dessicator. The product was then recrystallized using methanol. The same procedure was repeated for preparation of other ligands by replacing benzhydrazide with salicylichydrazide for 2-Hydroxynaphthaldehyde salicyloilhydrazide (NDS) ligand and 2-furoic acid hydrazide for 2-Hydroxynaphthaldehyde furoilhydrazide (NDF) ligand. All the ligands obtained were characterized using NMR, UV-Vis and IR spectroscopy.

Determination of Ligand-Complex Stoichiometry

By using Job method [4], absorption of different mole fraction of ligand and metal was plotted. Metal solution and ligand solution with different mole fraction was mixed together followed by addition of buffer solution pH 5.1, which was made up from sodium acetate trihydrate and glacial acetic acid followed by addition of deionized water. After 5 minutes, UV-Vis spectrum was recorded.

$$n = X_{\max} / (1 - X_{\max})$$

n = no. of mole ligand bonded with metal

X_{\max} = mole of ligand at maximum absorption

So number of ligand bonded with metal is equal to n.

Based on Job method which shows the molar ratio of metal : ligand stoichiometry, the ratio is 1:2 for Zinc and 1:3 for Aluminium

Synthesis of Complexes

Aluminium Complexes.

NDB ligand (0.0918 g, 3 mmol), NDS (0.0918 g, 3 mmol) and NDF (0.0792 g, 3 mmol) were weighed and dissolved in absolute ethanol in a 3-necked round-bottomed flask. The solution was stirred under nitrogen at room temperature. Aluminium nitrate nanohydrate (0.0375 g, 1 mmol) was added to the solution. The mixture was stirred under nitrogen for an hour until a yellow precipitate was formed. The solid was collected by suction filtration and dried in vacuum dessicator.

Zinc Complexes.

Ligand Bhn (0.0612 g, 2 mmol), Shn (0.0612 g, 2 mmol) and Fhn (0.0528 g, 2 mmol) were weighed and dissolved in absolute methanol in a 3-necked round-bottomed flask. The solution was stirred under nitrogen at room temperature. Zinc acetate dihydrate (0.0220 g, 1 mmol) was added to the solution. The mixture was stirred under nitrogen for an hour until a yellow precipitate was formed. The solid was collected by suction filtration and dried in vacuumed dessicator.

All the complexes obtained were characterized using UV-Vis and IR spectroscopy.

Determination of Fluorescence Intensity of Ligands

Ligand solution (1 mL, 1×10^{-4} M) was pipeted into a 10 mL Erlenmeyer flask. Buffer solution (3 mL, pH 5.1), which was made up from sodium acetate trihydrate and glacial acetic acid in distilled water, was added to the solution. Deionized water was added until the mark. The flask was swirled to give a homogeneous solution. After 5 minutes, UV-Vis spectrum was recorded.

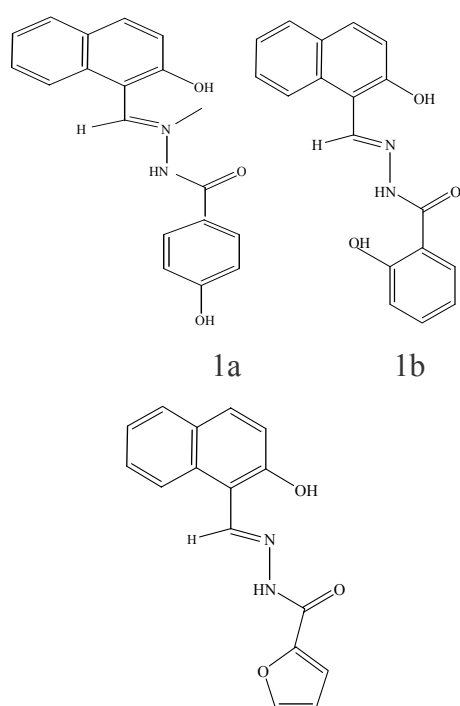
Determination of Fluorescence Intensity of Complexes

Ligand solution (3 mL, 1×10^{-4} M) was pipeted into 10 mL volumetric flask. Metal solution (1 mL, 1×10^{-4} M) was added to the solution followed by buffer solution with pH 5.1 (2

mL). The mixture was then added with deionized water until the mark. The fluorescence spectrum was recorded at wavelength of excitation, $\lambda_{\text{exc}} = 406 \text{ nm}$ and wavelength of emission, $\lambda_{\text{emi}} = 0$ using Perkin Elmer Luminescence Spectrometer model LS55.

Results and Discussion

Three ligands synthesized were ketohydrazone ligands that contains carbonyl group which were 2-Hydroxynaphthaldehyde salicyloylhydrazone (NDS), 2-Hydroxynaphthaldehyde furoilhydrazone (NDF) and 2-Hydroxynaphthaldehyde benzoylhydrazone (NDB). From the reaction, the percentage of yield for NDB ligand is 64%, NDF ligand is 69% and NDS ligand is 74%. Each of the ligands is yellow in colour and has melting points more than 200°C .



1c

Figure 1 : Structures of 1a) NDB, 1b) NDS, 1c) NDF

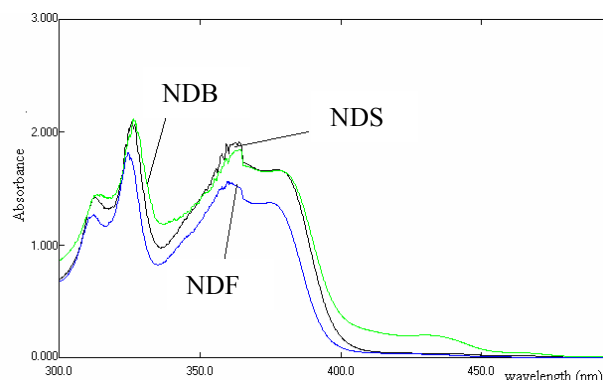


Figure 2 : UV-Vis spectrum for ligands.

Figure 2 shows the UV_Vis spectrum for ligands. There were five main absorption band for the transition of π electron of $\text{C}=\text{O}$, $\text{C}=\text{N}$ and aromatic ring. Substitution on the carbonyl group by an auxochrome with lone pair of electrons, $-\text{NHR}$, gave a pronounced hypsochromic effect on the $n \rightarrow \pi^*$ transition. The auxochrome attached to the carbonyl group on ligands caused a bathochromic shift on the $\pi \rightarrow \pi^*$ [5] transition. Primary and secondary bands of polynuclear aromatic system in the ligand, shifted to longer wavelengths, as the result of conjugation extension and OH group that with n elements. These n elements interacted with the π system of the aromatic rings.

For IR spectrum of ligands, the observed band at $3500\text{--}3200 \text{ cm}^{-1}$ are assigned as the intermolecular bonded O-H. The sharp and intense band at 3167.9 cm^{-1} for NDB ligand, 3059.9 cm^{-1} for NDS ligand and 3138.9 cm^{-1} for NDF ligand is consistent with the presence of a N-H group while the band of

medium intensity $1605 - 1590\text{ cm}^{-1}$ is characteristic of the amine $\text{C}=\text{N}$, from through the condensation between aldehyde and hydrazide. The absorption band for $\text{N}-\text{H}$ had shifted to a lower frequency that maybe due to the formation of the enol form of the ligands. The strong band at 1642.3 cm^{-1} for NDF ligand, 1635.5 cm^{-1} for NDB and 1644.2 cm^{-1} for NDS are assigned to the $\text{C}=\text{O}$ group of the hydrazide.

The presence of the $\text{C}=\text{N}$ and $\text{C}=\text{O}$ absorption bands in the spectrum confirmed the completeness of the condensation reaction in solid.

The singlet at 11.99 in NMR spectrum is due to the $\text{O}=\text{C}-\text{NH}$ proton signal while the singlet at 9.50 ppm for NDF ligand, 9.51 for NDS ligand and 9.49 for NDB ligand are assigned to as the imine $\text{N}=\text{C}-\text{H}$ proton resonance. All the spectra show the aromatic proton between 6.9-8.3 ppm.

The duplet at 7.2 ppm for ligand NDF is due to the proton in furan ring the ligand. The singlet at 12.90 ppm for ligand NDB, 12.63 for ligand NDF and 12.72 ppm for ligand NDS is assigned to as resonance of OH proton. The presence of amide $\text{O}=\text{C}-\text{NH}$ proton resonance in the ^1H NMR spectrum indicated that the ligand exists as the keto form.

Based on the IR, UV-Vis and ^1H -NMR spectra obtained, we expected that all ligands were successfully synthesized.

UV-Vis spectrum for complex shows that wavelengths of electronic transitions of $\pi \rightarrow \pi^*$ for $\text{C}=\text{O}$ and $\text{C}=\text{N}$ had disappeared due to

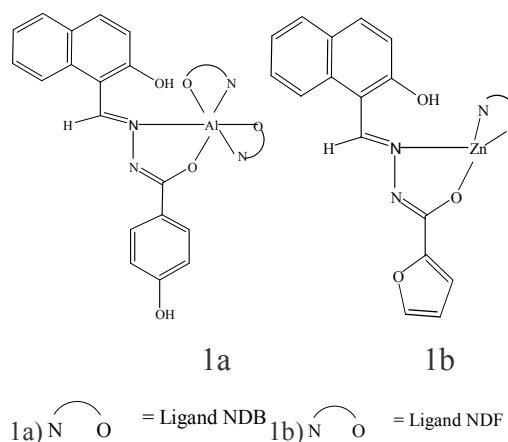


Figure 3 : Structure for 1a) Aluminium tri(2-Hydroxynaphthaldehyde benzoylhydrazide) $[\text{Al}(\text{NDB})_3]$ complex 1b) Zinc di(2-Hydroxynaphthaldehyde furoilhydrazide) $[\text{Zn}(\text{NDF})_2]$ complex

coordination of ligand to the metal through the π electron.

Bathochromic shift for aromatic complex occurred at 410 nm and new absorption band formed at 435 nm that could be assigned as the charge transfer transition between metal and ligand.

By comparing the FTIR spectrum between ligand and complex, we can observed that there is still an appearance of OH group, in the region of $3300-3450\text{ cm}^{-1}$. This indicates that this group did not involved in the coordination with metal. The stretching frequency of $\text{C}=\text{N}$ had shifted to a higher wavelength due to the bonding of free electrons N toward metal, which causes an inductive effect of $\text{C}=\text{N}$ [6]. It causes the double bond characteristic of $\text{C}=\text{N}$ reduced, thus higher the frequency of $\text{C}=\text{N}$ for the complex.

Conclusions

Three ketohydrazone ligands had been successfully synthesized and characterized.

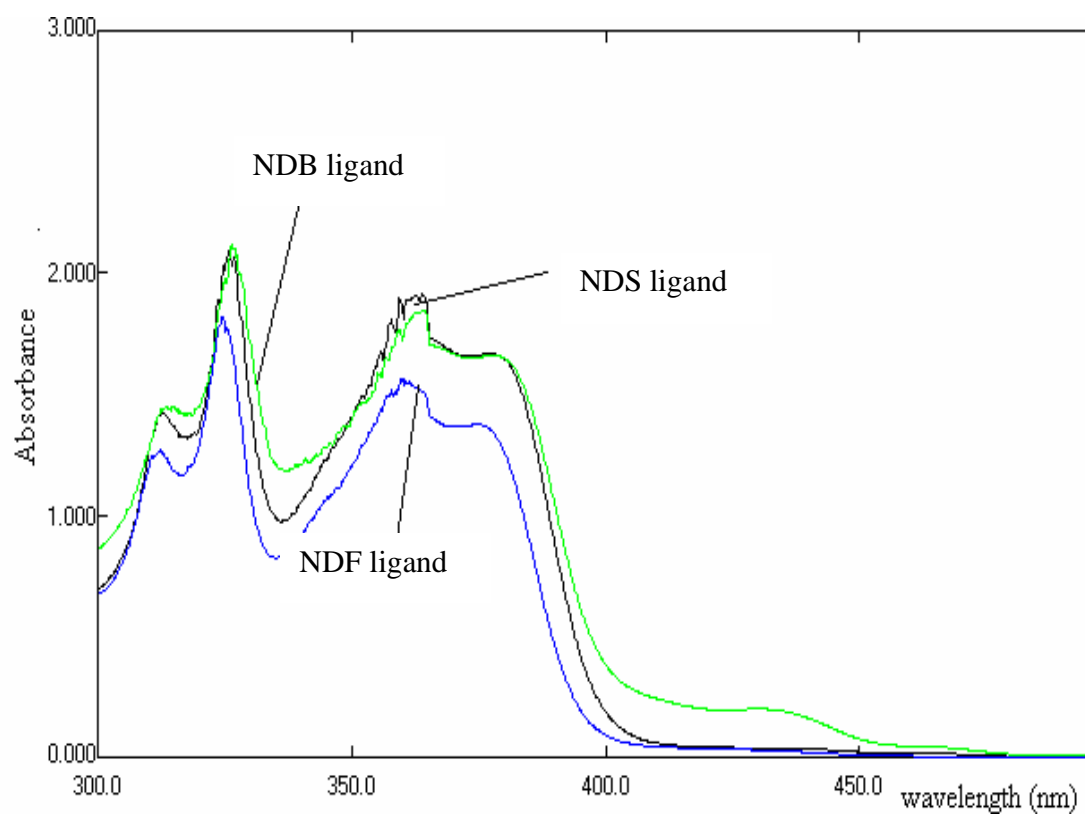
Complexation with metal will increase the fluorescence of compounds as it causes the increase in rigidity of molecule especially with chelating ligand. Al(III) complexes shows better fluorescence intensity than Zn (II) complexes as it has a higher coordination number and thus increases the rigidity of molecules.

As a conclusion, Al(III) complexes show a better potential to be the emitting material for OLED devices as it shows a better fluorescence properties compared to Zn(II) complexes. However, among all the complexes, Al(NDB)₃ had the best potential for this purpose as it shows the highest intensity of fluorescence.

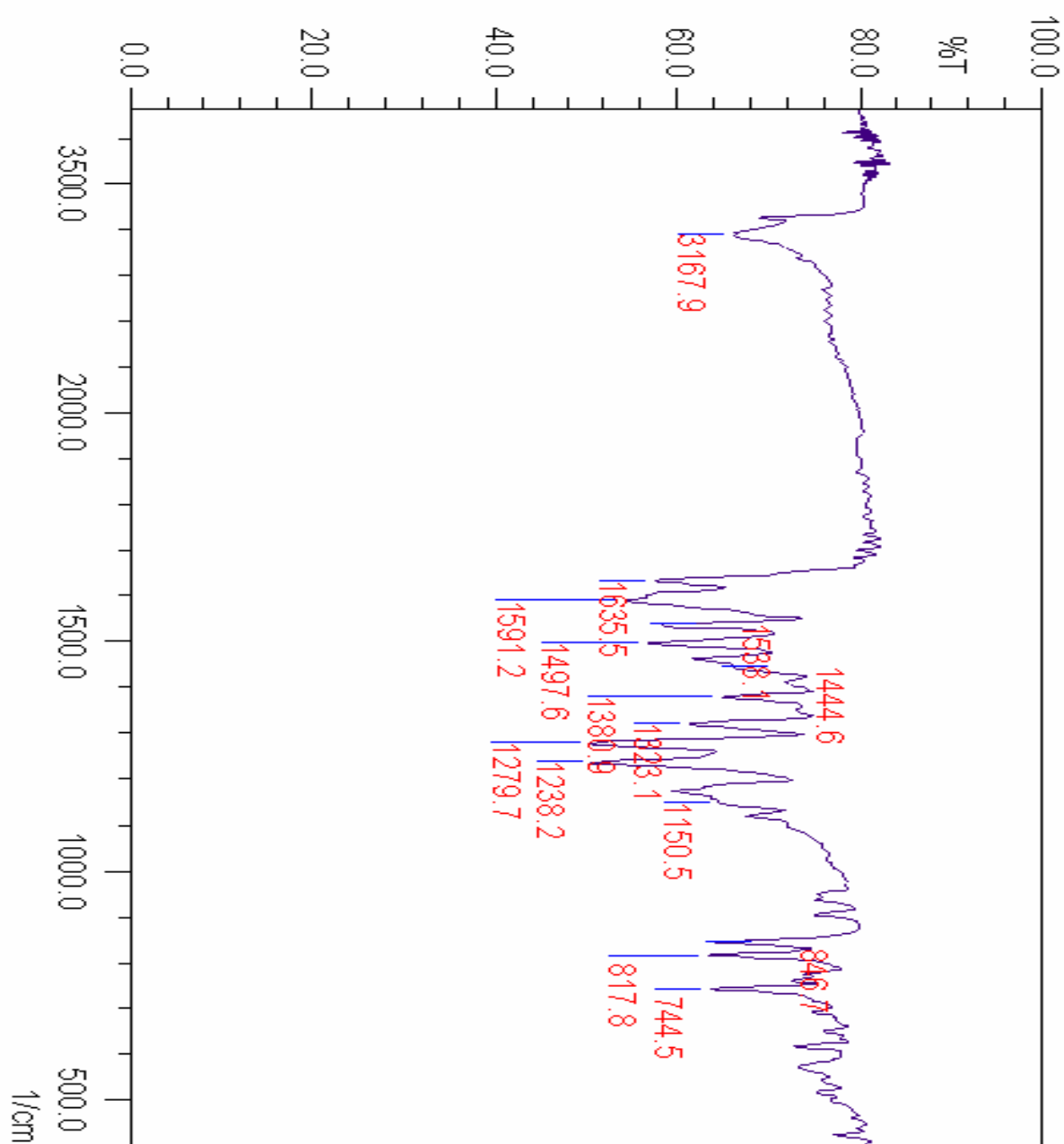
References

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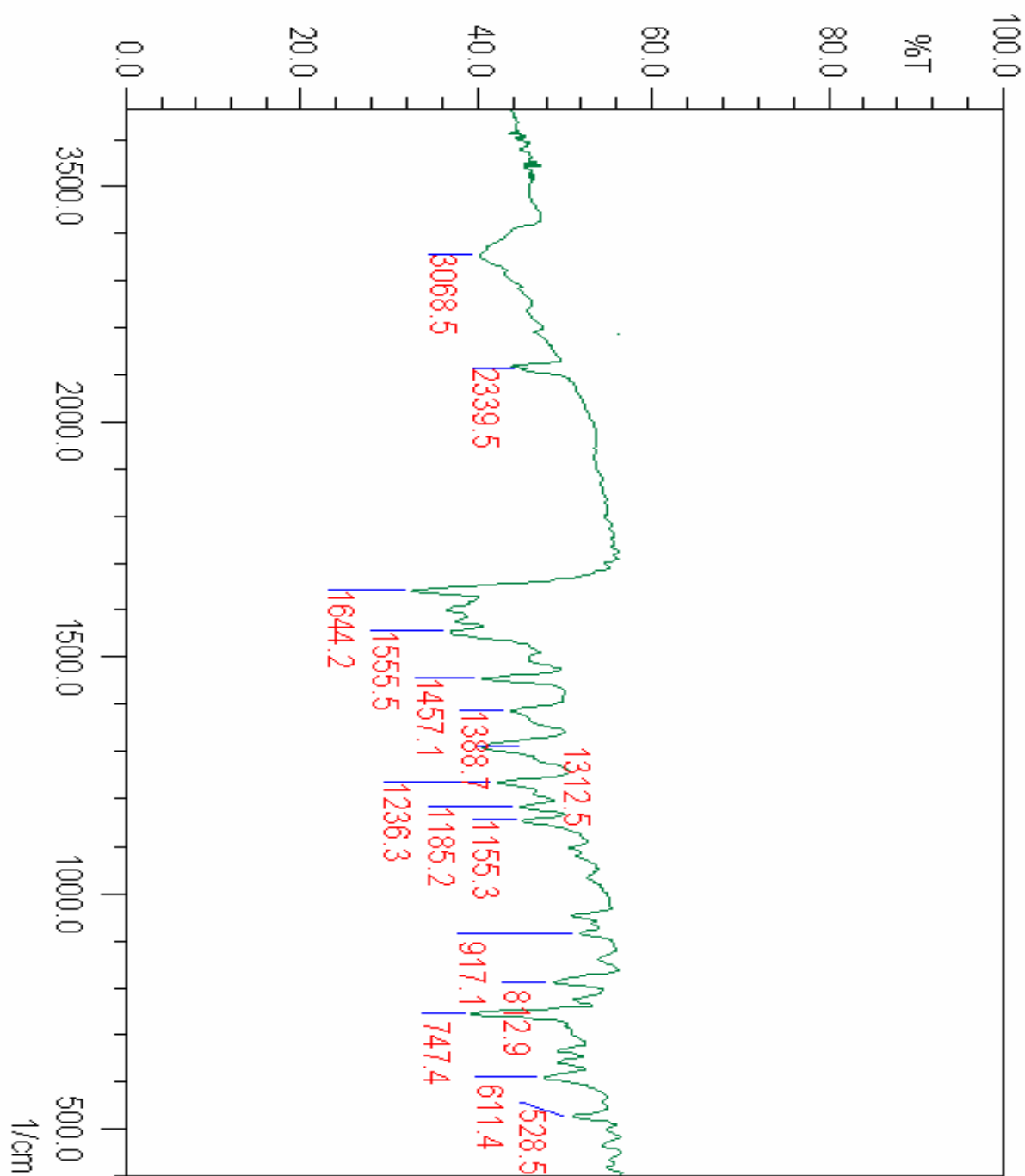
APPENDIX A
UV-Vis Spectra of Ligands



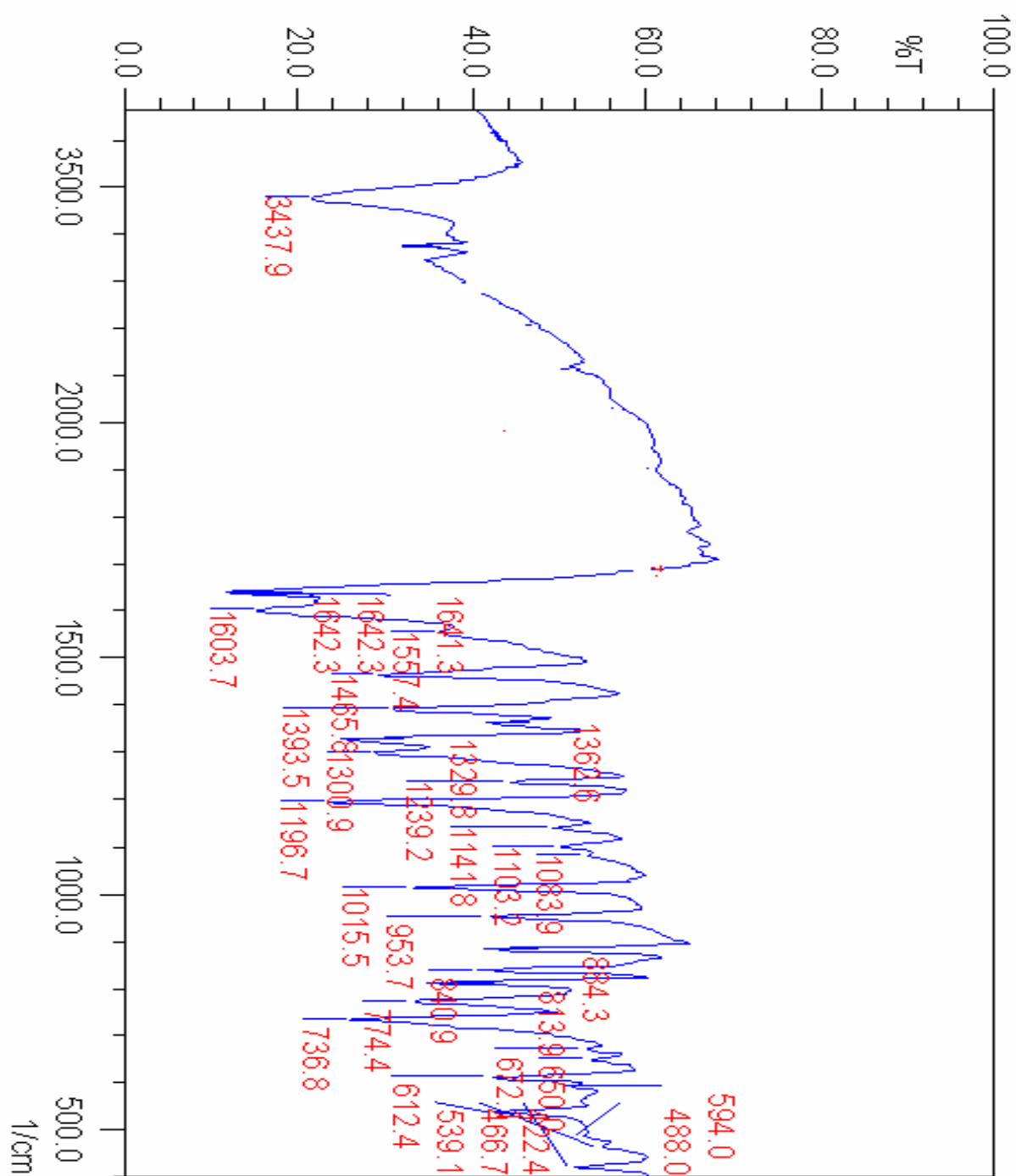
APPENDIX B
IR spectrum of NDB ligand



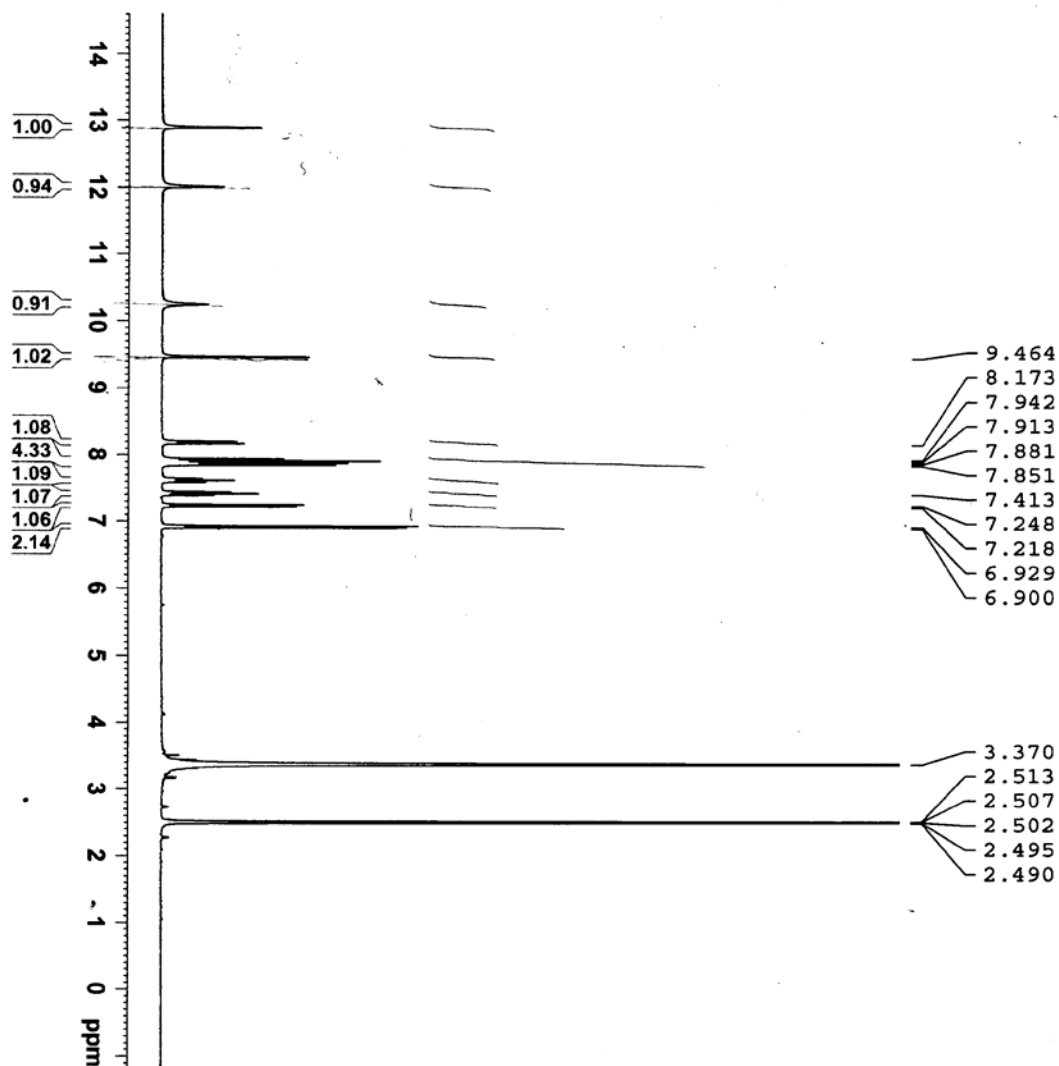
APPENDIX C
IR spectrum of NDS ligand



APPENDIX D
IR spectrum of NDF ligand



APPENDIX E NMR spectrum of NDB ligand



Current Data Parameters
NAME b-keto
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20041209
Time_ 11:22

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PULPROG zg30
TD 65536
SOLVENT DMSO
NS 16
DS 2

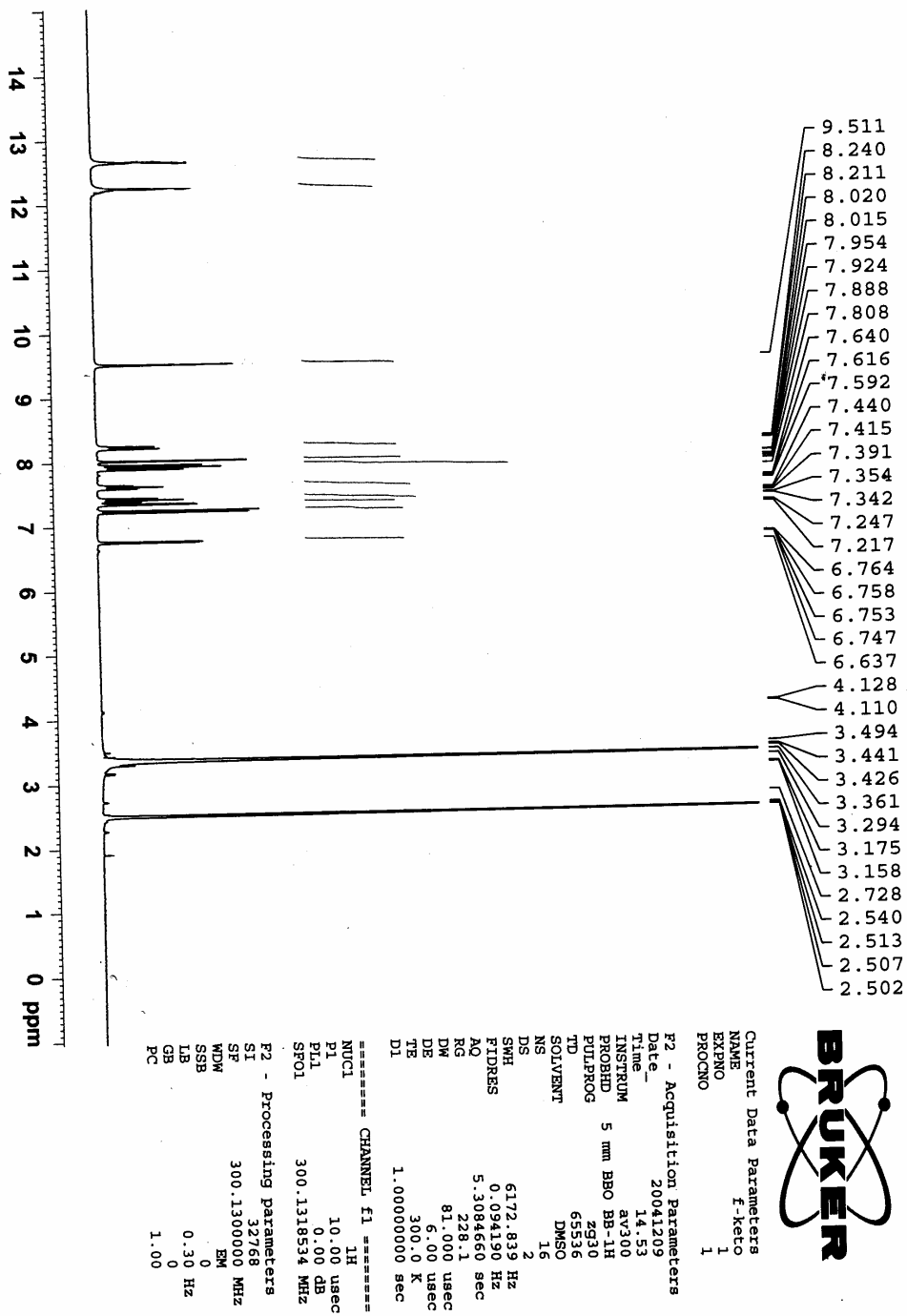
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FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 228.1
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 10.00 usec
PL1 0.00 dB
SFO1 300.1318534 MHz

F2 - Processing parameters
SI 32768
SF 300.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

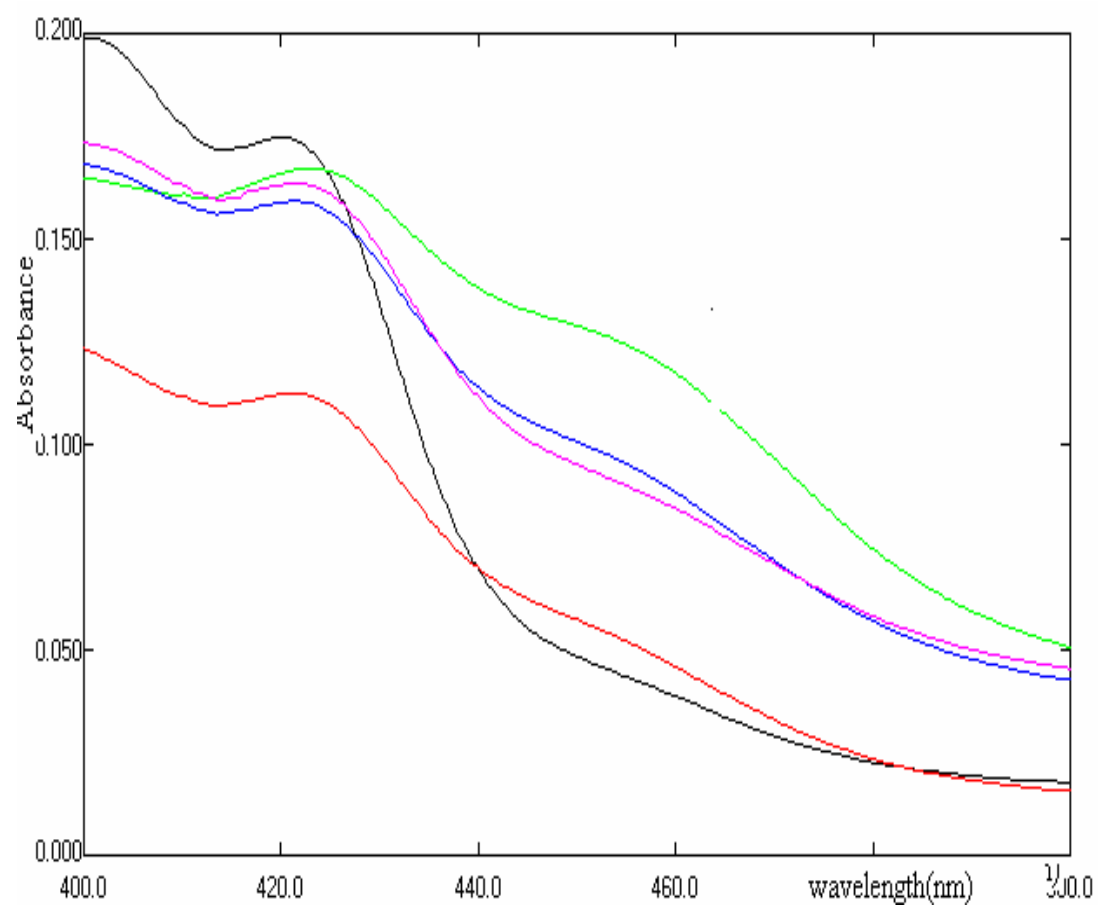
APPENDIX F

NMR spectrum of NDF ligand



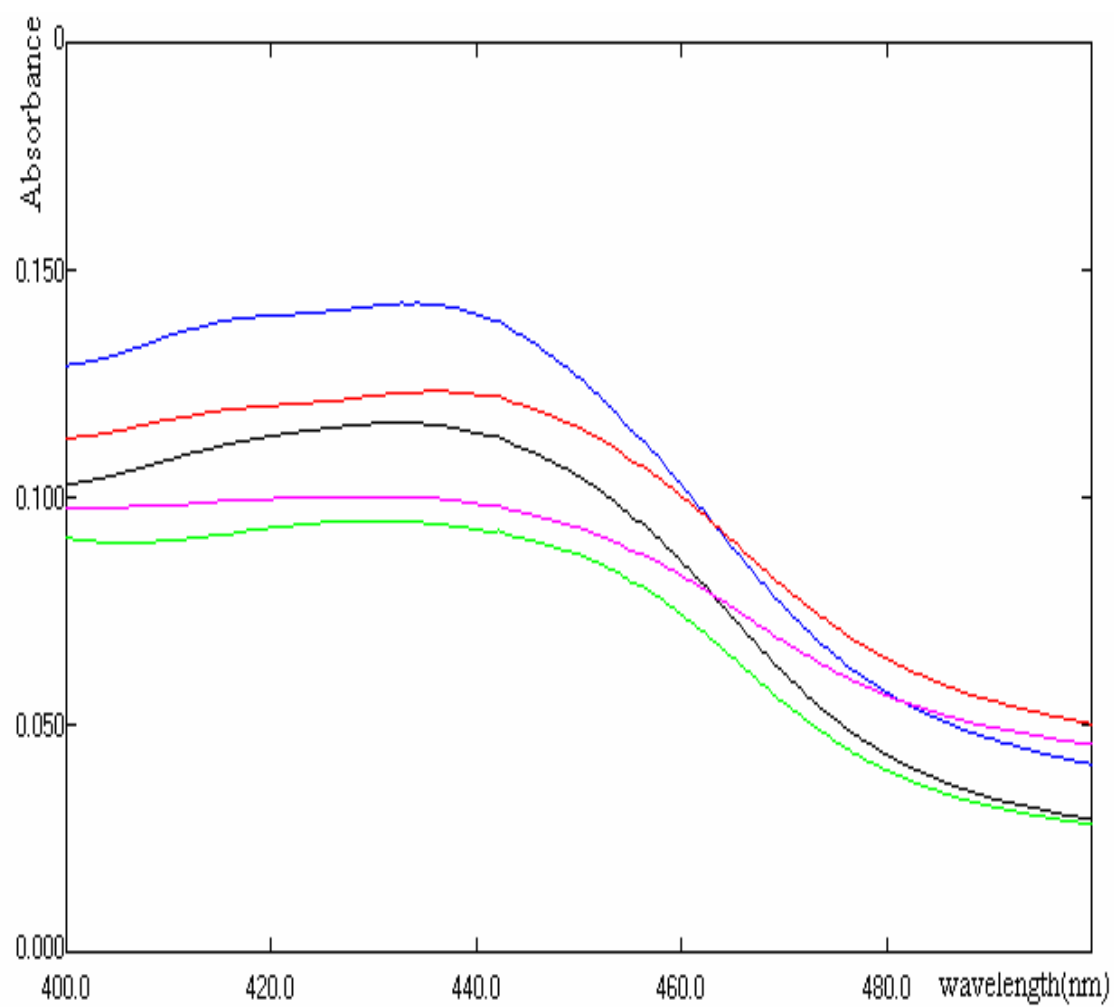
APPENDIX G

UV-Vis spectra for $\text{Al}(\text{NDB})_3$ with different mole fraction NDB



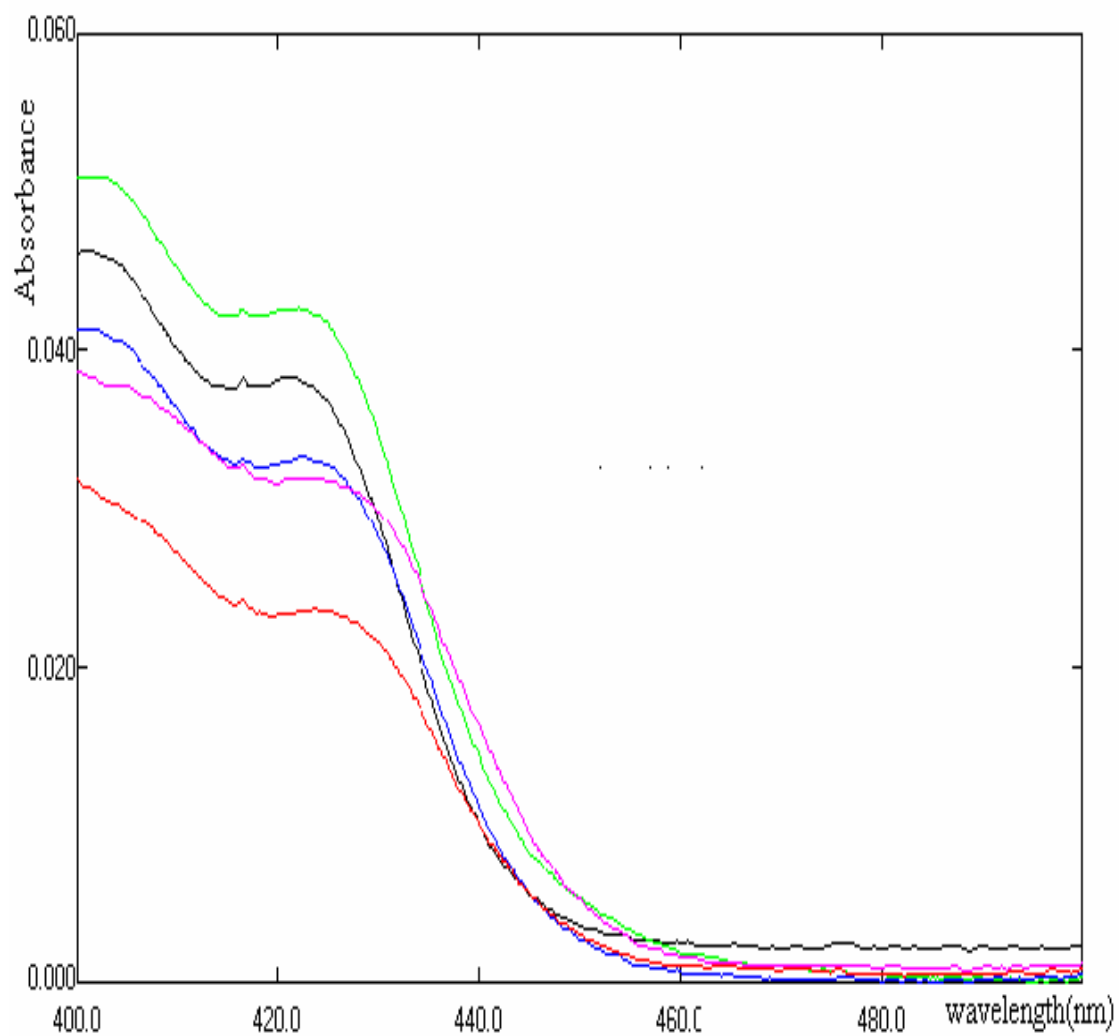
APPENDIX H

UV-Vis spectra for $\text{Al}(\text{NDF})_3$ with different mole fraction of NDF ligand



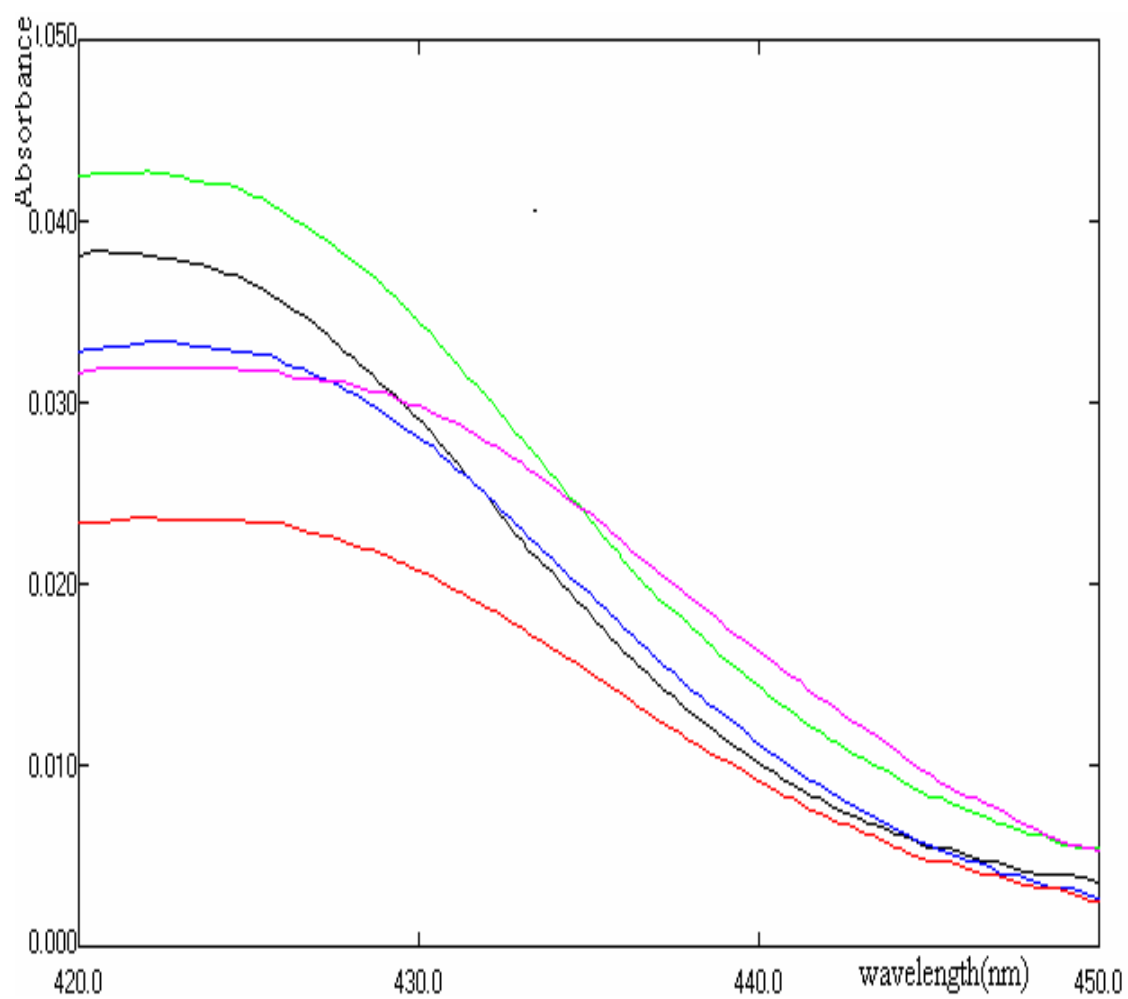
APPENDIX I

UV-Vis spectra for $\text{Zn}(\text{NDF})_2$ with different mole fraction of NDF



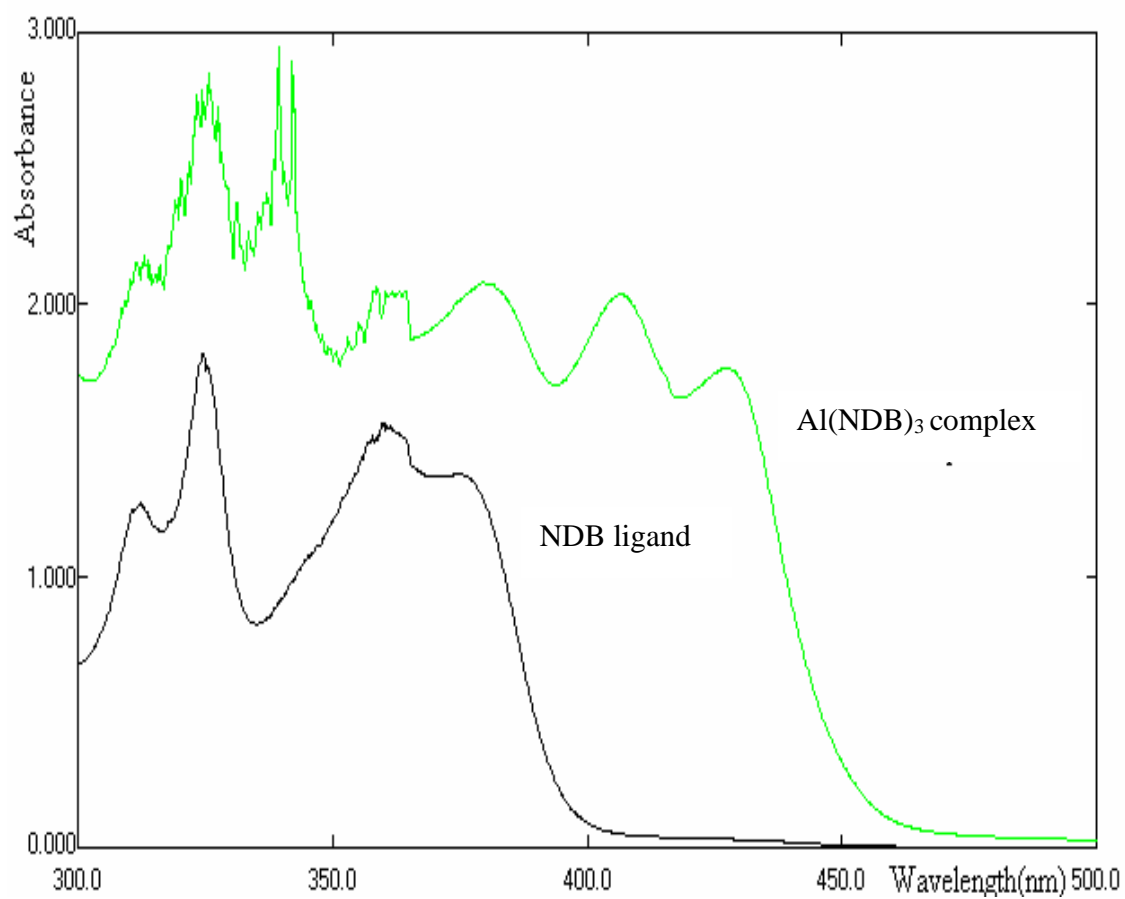
APPENDIX J

UV-Vis spectra for $\text{Zn}(\text{NDS})_2$ with different mole fraction of NDS



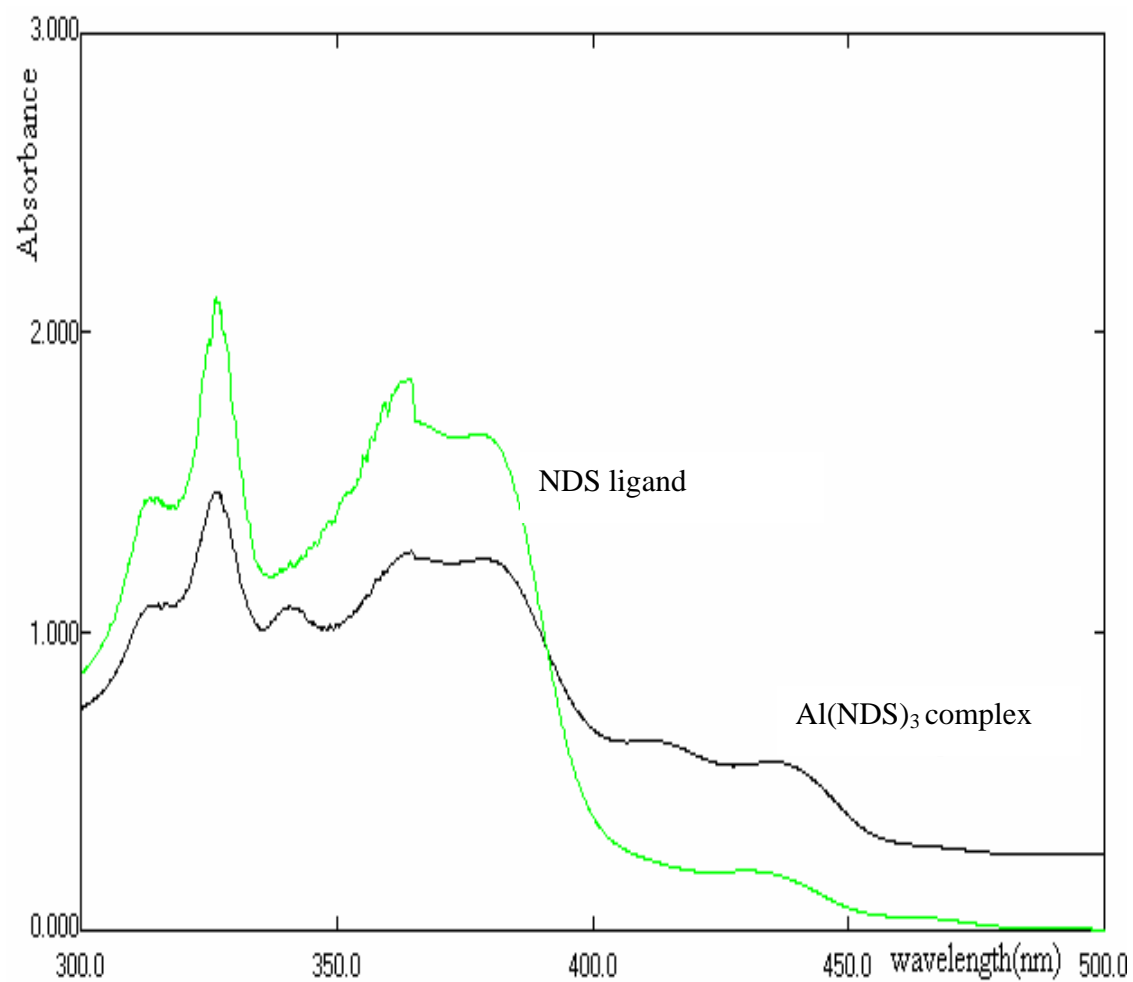
APPENDIX K

UV-Vis spectra for NDB ligand and $\text{Al}(\text{NDB})_3$ complex

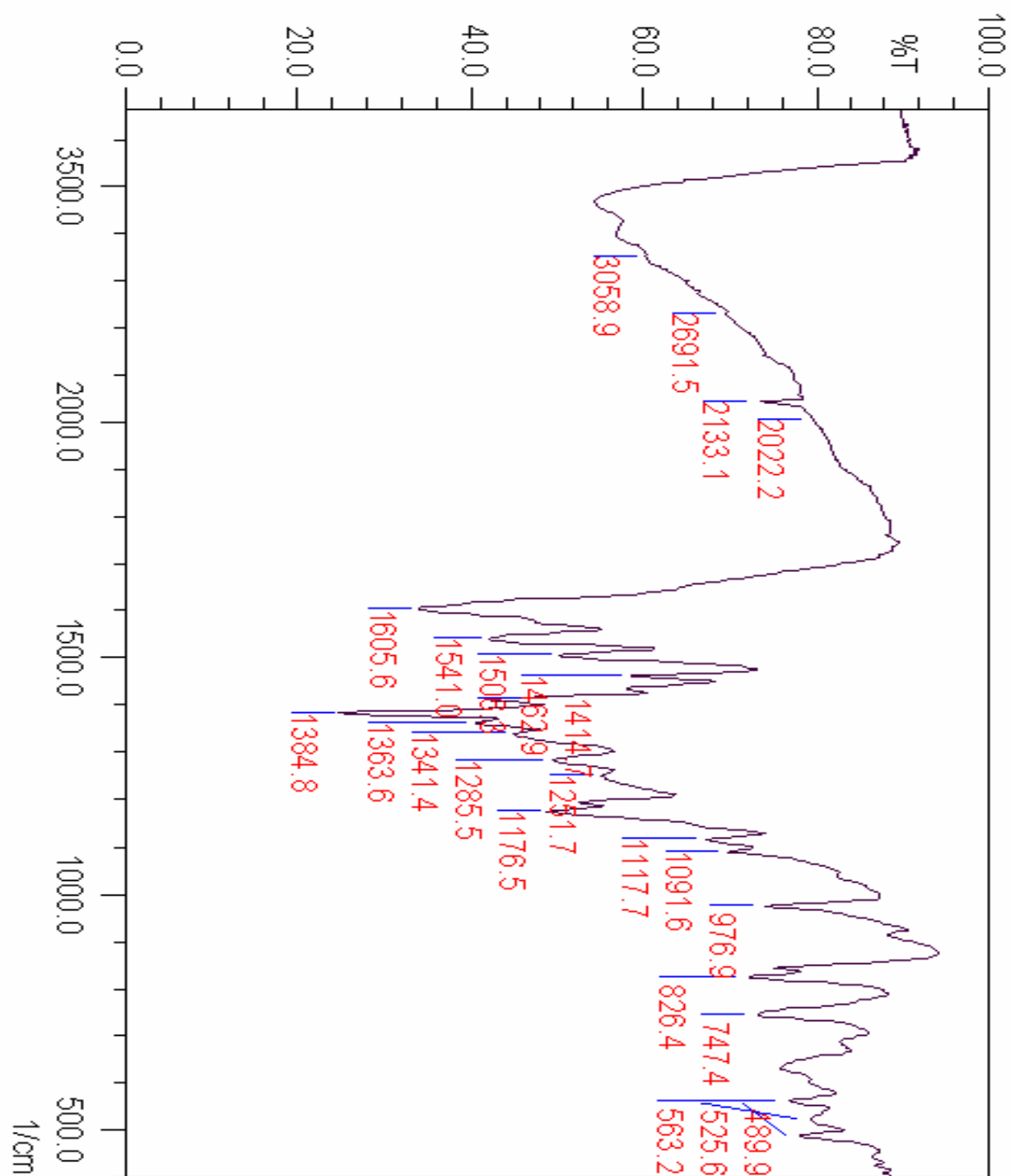


APPENDIX L

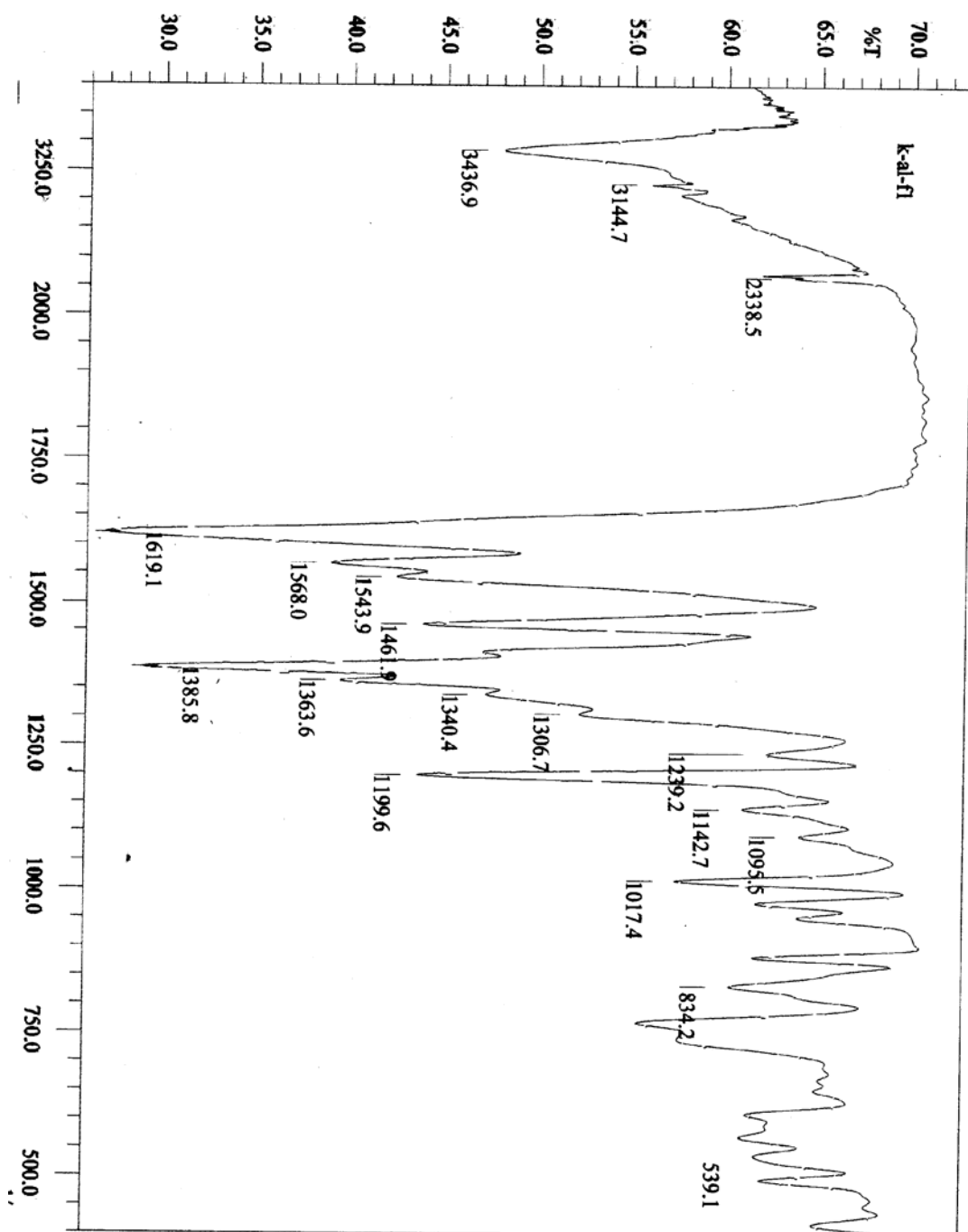
UV-Vis spectra for NDS ligand and $\text{Al}(\text{NDS})_3$ complex



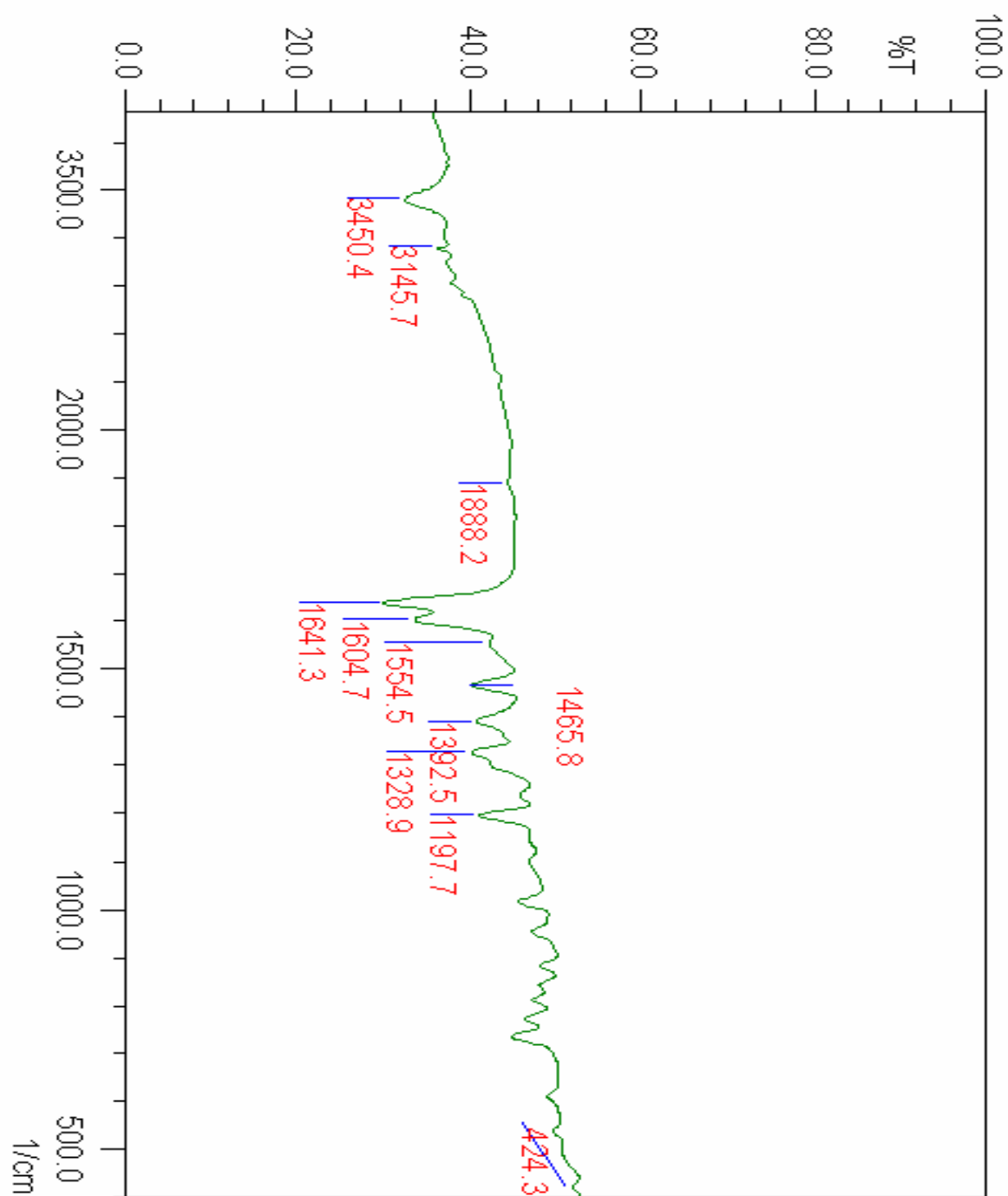
APPENDIX M
IR spectrum for Al(NDB)₃



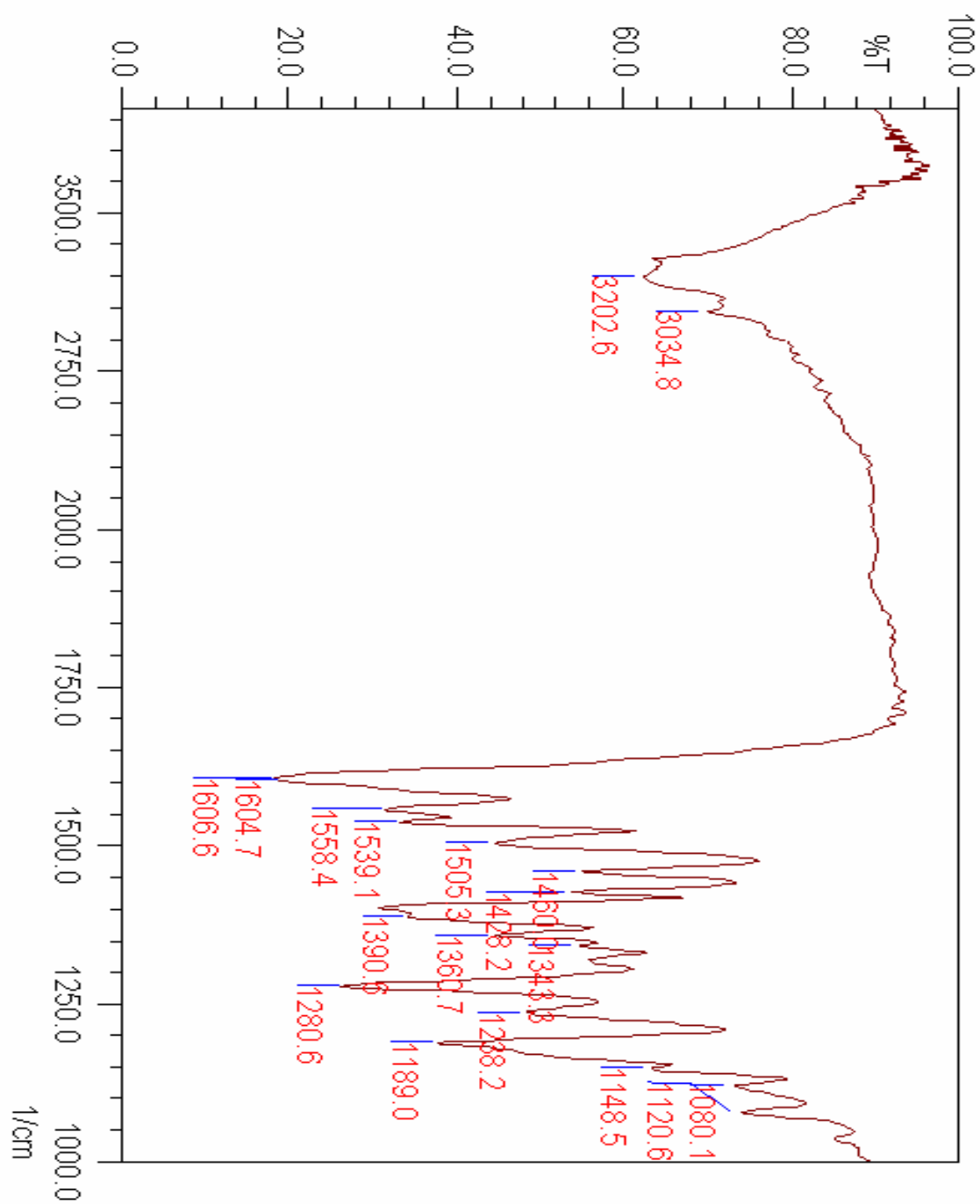
APPENDIX N
IR spectrum of $\text{Al}(\text{NDF})_3$



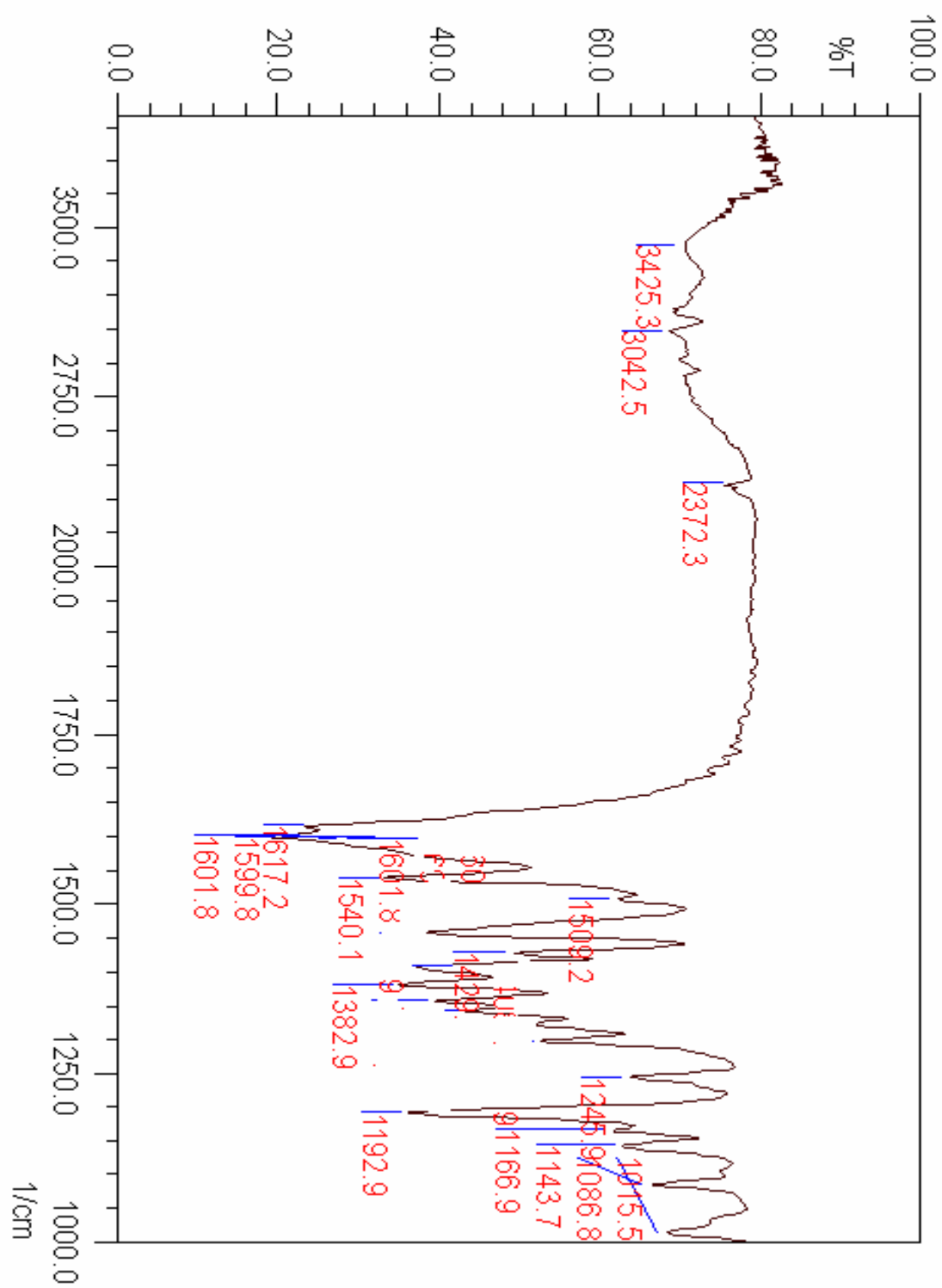
APPENDIX O
IR Spectrum of $\text{Al}(\text{NDS})_3$



APPENDIX P
IR Spectrum of Zn(NDB)₂



APPENDIX Q IR Spectrum of Zn(NDF)₂



APPENDIX R **IR Spectrum of Zn(NDS)₂**

