KETOHYDRAZONE COMPLEXES 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 hydrazides: salisylic hydrazide, benzyhydrazide and 2-furoic acid hydrazide in a 1:1 stoichiometry. The ligands had been characterized using infrared, ^{1}HNMR and ultraviolet-visible spectrometer. Complexation reaction between all ligands and metals, 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 excited at 406 nm. It was found that the compounds emitted blue light at λ_{max} = 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 $Al(NDB)_3$ 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 hidrazida, salisilik hidrazida,, 2-furoik hidrazida, dan benzihidrazida.mengikut nisbah stoikiometri 1 : 1. Semua ligan yang telah disintesis dicirikan melalui spektroskopi IR, UV-Vis dan ^{1}H-RMN. Tindak balas pengkompleksan antara ligan yang telah disintesis dengan dua logam yang berasingan, iaitu aluminium dan zink telah dijalankan dengan nisbah ion ligam : ligan 1 : 3 bagi pengkompleksan dengan aluminium dan 1 : 2 bagi pengkompleksan dengan zink. 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 405nm. Didapati sebatian-sebatian tersebut memancarkan cahaya biru pada λ_{max} = 470 nm. Hasil yang diperolehi menunjukkan bahawa semua ligan dan kompleks yang disintesis menunjukkan sifat pendarfluor dan pengkompleksan dengan logam dapat meningkatkan keamatan pendarfluornya.. Kompleks $Al(NDB)_3$ menunjukkan potensi yang terbaik sebagai bahan pemancar dalam diod pemancar cahaya organik (OLED) memandangkan kompleks ini menunjukkan keamatan pendarfluor yang tertinggi.

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 fluorescence properties for two derivatives of 7-azaindole complexes with aluminium. 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, the research was focused on synthesizing the new complexes as blue light emitting material and their potential as the emitting material in OLED.

Experimental

Synthesis of Ligands

2-Hydroxynaphthaldehyde was dissolved in absolute methanol in a 3-necked round bottomed flask. Solution of 4-Hydroxybenzhydrazide in absolute methanol was added into the flask. The reaction mixture was then heated with stirring under nitrogen at 80^0C, for 2.5 hours. The light yellow precipitate formed was filtered by suction and dried in a vacummed dessicator. The product, 2-hydroxynaphthaldehyde benzoilhydrazide 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-Metal 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 were mixed together followed by addition of buffer solution at 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. By using the following formula;

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

n = no. of mole ligand bonded with metal

X_{max}= mole of ligand at maximum absorption

the value of n was calculated.

It was found that the metal : ligand stoichiometry are 1:2 for zinc complexes and 1:3 for aluminium complexes.

Synthesis of Complexes

tris(2-hydroxynaphthaldehyde 4-hydroxybenzhydrazide Aluminium(III) ($Al(NDB)_3$) Complex.

A quantity of NDB ligand (0.0918 g, 3 mmol), was weighed and dissolved in absolute ethanol in a 3-necked round-buttomed flask. The solution was stirred under nitrogen at room temperature. Aluminium nitrate nonahydrate (0.0375 g, 1 mmol) was added to the solution. The mixture was stirred under nitrogen until a yellow precipitate was formed. The solid was collected by suction filtration and dried in vacuum dessicator. By taking note that aluminium : ligand stoichiometry is 1:3, the same procedure were repeated for synthesis of tris(2-hydroxynaphthaldehyde salicyloihydrazide Aluminium(III) ($Al(NDS)_3$) and tris(2-hydroxynaphthaldehyde furoilhydrazide Aluminium(III) ($Al(NDF)_3$).

Tris(2-hydroxynaphthaldehyde benzoilhydrazide Aluminium(III) ($Al(NDB)_3$) Complex.

A quantity of NDB ligand (0.0612 g, 2 mmol), was weighed and dissolved in absolute methanol in a 3-necked round-buttomed 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 until a yellow precipitate was formed. The solid was collected by suction filtration and dried in vacuumed dessicator. By taking note that zinc : ligand stoichiometry is 1:2, the same procedure were repeated for synthesis of di(2-hydroxynaphthaldehyde salicyloihydrazide Zinc(II) ($Zn(NDS)_2$) and di(2-hydroxynaphthaldehyde furoilhydrazide Zinc(II) ($Zn(NDF)_2$).

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

Determination of Fluorescence Intensity of Ligands

Ligand solution (1 mL, $1x10^{-4}$ 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.

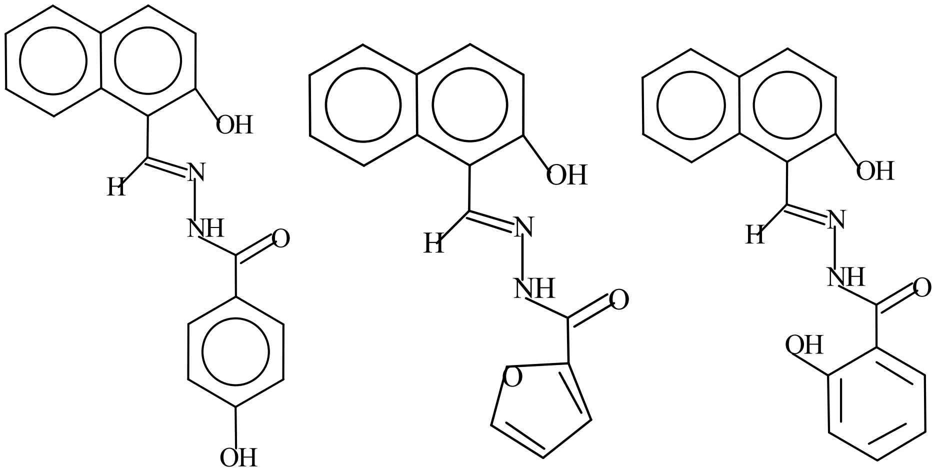
After 5 minutes, fluorescence spectrum was recorded using Perkin Elmer Luminescence Spectrometer model LS55. The ligands were excited at 406 nm.

Determination of Fluorescence Intensity of Complexes

Ligand solution (3 mL, 1x10^{-4} M) was pipeted into 10 mL volumetric flask. Metal solution (1 mL, 1x10^{-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 complexes were ecited at 406 nm.

Results and Discussion

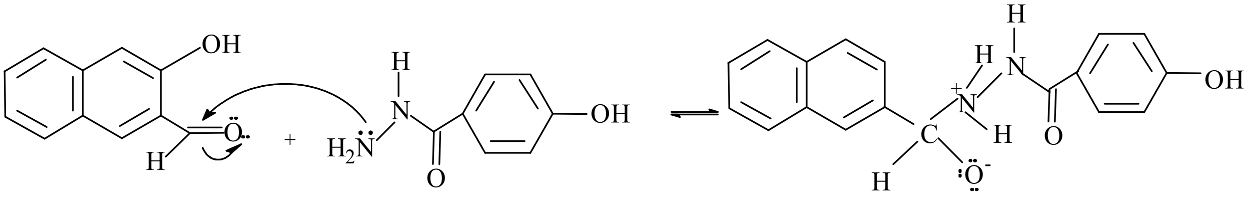
The percentage yield for NDB ligand is 64%, NDF ligand is 69% and NDS ligand is 74%. Each of the ligands is yellow in colour and has melting points higher than 200^{0}C. Figure 1 shows the structure for ligands. Based on the IR, UV-Vis and ^{1}H-NMR data obtained, as discussed below we expected that all ligands were successfully synthesized.



NDB NDF

NDS

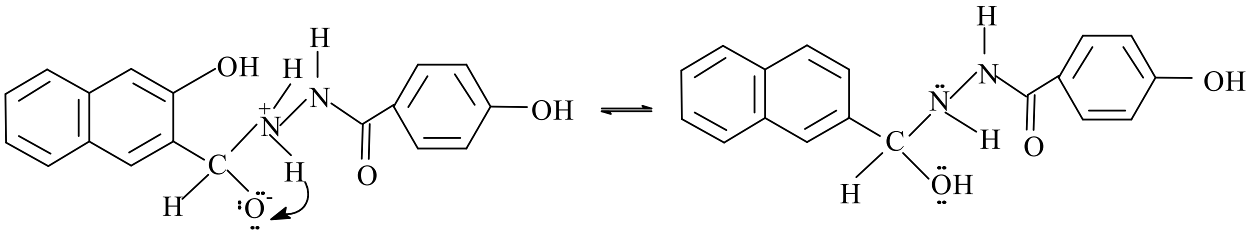
Figure 1 : Molecular structures of ligands.



2-hydroxynaphthaldehyde 4-hydroxybenzhydrazide

dipolar intermediate

Attack of nitrogen nucleophilic to carbonyl atom



dipolar intermediate

Protonation by nitrogen group

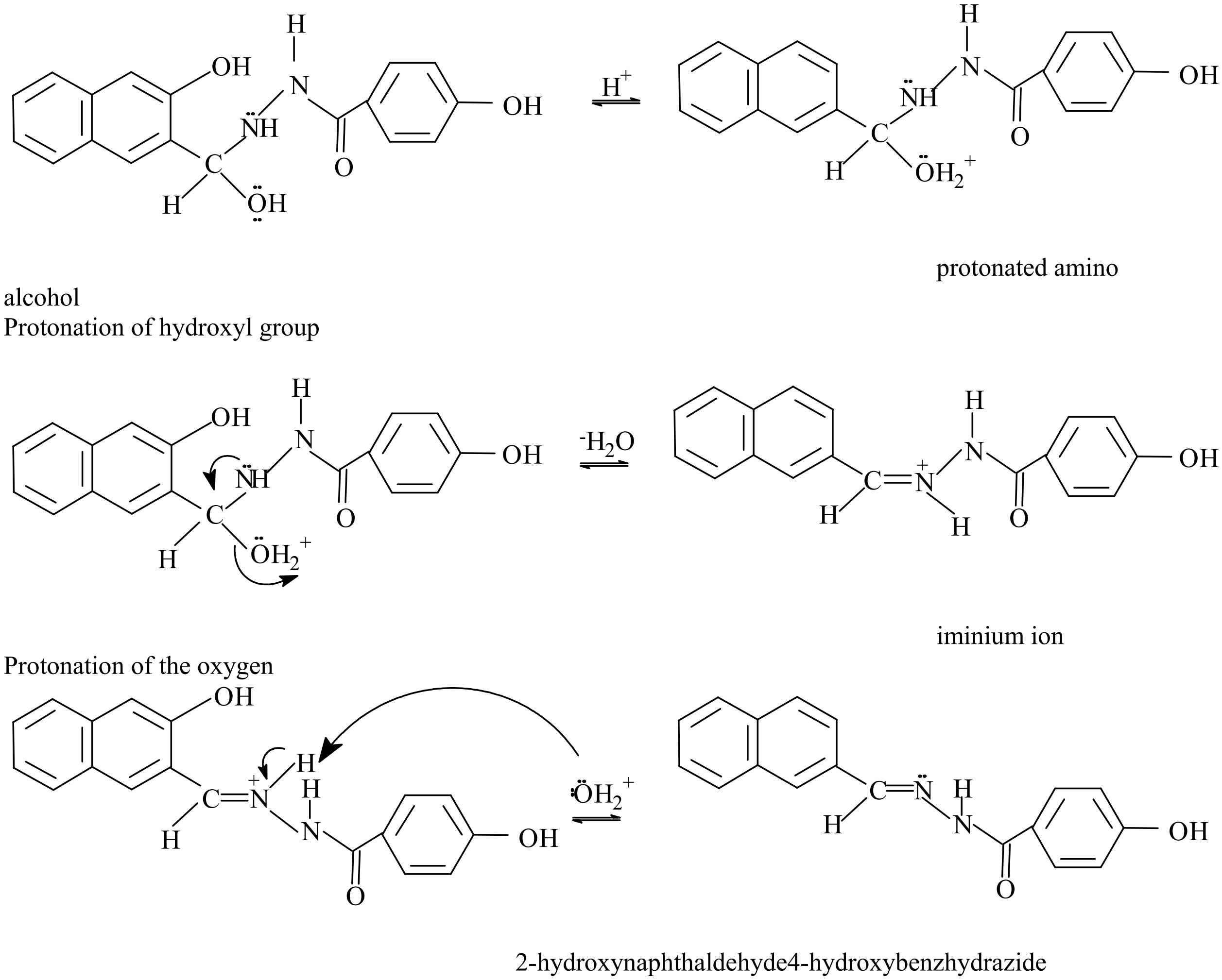


Table 1 : Main absorption bands according to types of electronic transition in UV-Vis spectra of ligands.

Ligands	**Electronic Transition (nm)**				
	π → π*			**n → π***	
	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	364 and 377	433	433

Table 1 shows the UV-Vis data for ligands. Substitution on the carbonyl group by an auxochrome with lone pair of electrons, -NHR, gave a pronounced hypsochromic effect on the n → π* transition. The auxochrome attached to the carbonyl group on ligands caused a bathochromic shift on the π → π* transition [5]. Overall, absorption caused by transition of n → π* for C=O and C=N occurred at lower energy level compared to the transition of π → π*. 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*.

Table 2 : IR data for ligands

Ligands	**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

Table 2 shows the data for IR spectra of ligands. From IR data , the observed band at 3500-3200 cm^{-1} are assigned as the 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 cm^{-1} is characteristic of the amine C=N, formed 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.

Table 3 : NMR data for ligands

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	-

Table 3 shows the NMR data for ligands dissolved in d_6-DMSO. The presence of amide O=C-NH proton resonance in the ^{1}H NMR spectrum indicated that the ligand exists as the keto form .

Figure 2 shows the molecular structure of Al(NDB)$_3$ and Zn(NDF)$_2$. the characterization of complexes were discussed below.

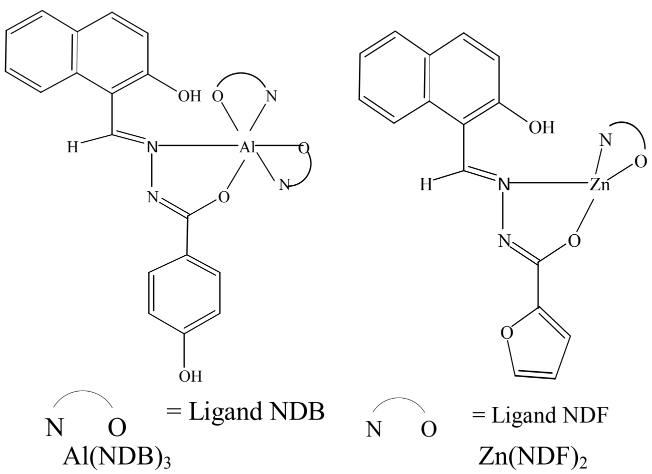


Figure 2 : Structure for complexes

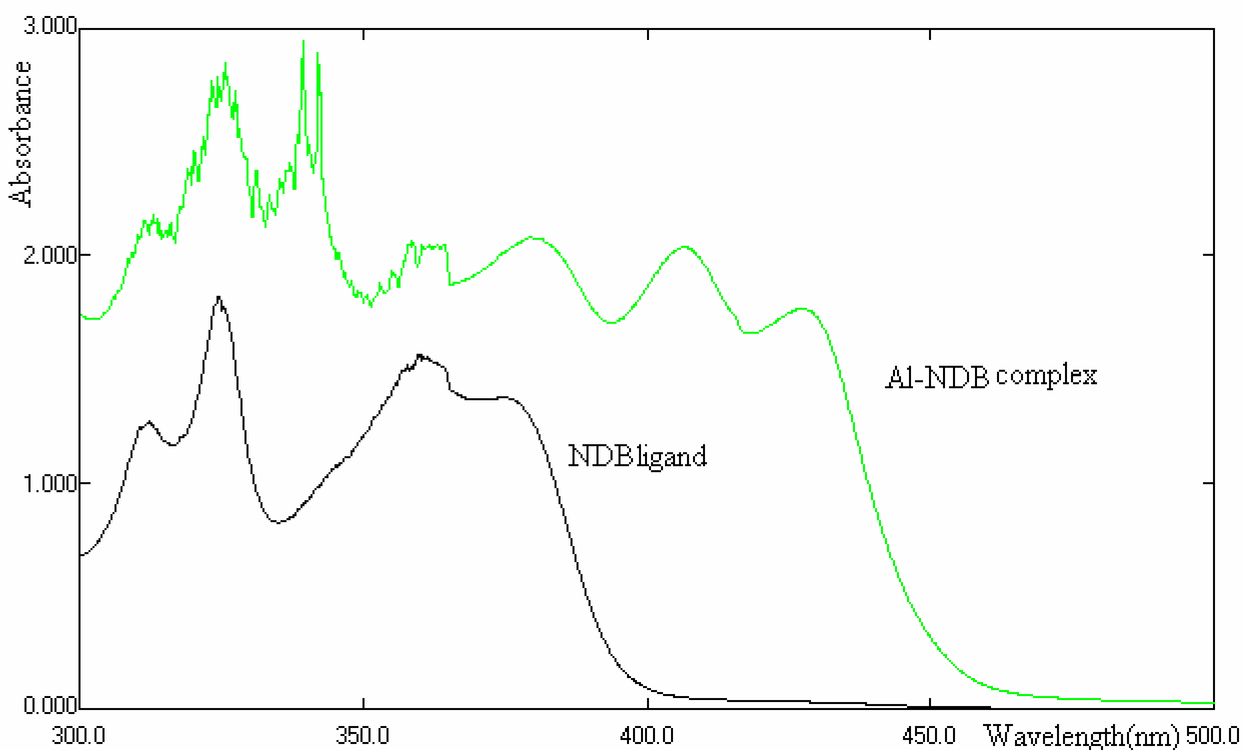


Figure 3 : UV-Vis spectra for NDB ligand and Al(NDB)$_3$ complex

Figure 3 shows the UV-Vis spectrum for NDB ligand and Al(NDB)$_3$ complex as representative spectrum for the complexes. UV-Vis spectrum for complex shows that absorption due to electronic transition in C=O and C=N had shifted to longer wavelength. 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 [6].

Table 4 shows IR data for complexes. By comparing the FTIR spectrum between ligands and complexes, we can observed the presence of OH group bonded to the aromatic ring, in the region of 3300-3450 cm^{-1}. This indicates that this group did not involved in the coordination with metal. However, the stretching frequency of C=N had shifted to a higher frequency due to the bonding of N atom to the metal.

Table 4: IR data for complexes

Complex	Frequency(cm^{-1})			
	OH	**C=O**	**C=N**	**NO$_3^-$**
NDB Complex	3394 (3200-3500)	Not observed	1605.6 (1604.7)	1384.8 1390.6
NDF Complex	3436.9 (3425.3)	Not observed	1619.1 (1617.2)	1385.8 1382.9
NDS Complex	3450.4 (3200-3500)	Not observed	1604.7 (1604.7)	1386.7 (1388.5)

*Bracket indicates value for zinc complexes

It was also observed that the absorption of NH in amide group had disappeared, suggesting the fornation of enol group and the formation of C=N-O$^-$ before the bonding of oxygen atom with the metal occurred. This also explain why the C=O band is not observed.

Figure 4 shows the spectra of ligand and complex being excited at the same wavelength. Similar spectrum also observed for other complexes.

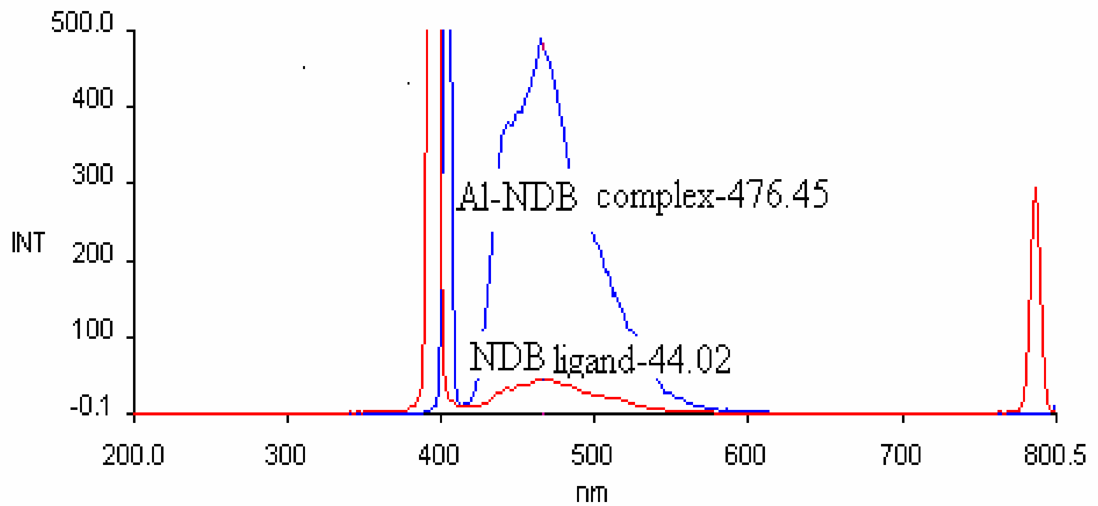


Figure 4 ; Fluorescence spectra of NDB ligand and Al(NDB)$_3$ complex

Table 5 shows the intensity of fluorescence excited at λ_{max} 406nm and emit blue light at λ_{max} 470 nm. It shows that Al(NDB)$_3$ complex has the highest intensity compared to the others and all the aluminium complexes shows higher fluorescence intensity compared to zinc complexes which maybe attributed by more number of ligands bonded to aluminium.

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. For chelate ligand, the intensity of fluorescence increases when it forms complex. Ketohydrazone, under the influence of metal, forms a rigid chelate ring. The central metal ion does not exhibit flourescent characteristic [8].

Table 5 : Fluorescence intensity of ligands and complexes

Compound	Fluorescence intensity (a.u)
NDF	37.99
NDS	56.22
NDB	44.02
$Al(NDF)_3$	194.56
$Al(NDB)_3$	476.45
$Al(NDS)_3$	249.00
$Zn(NDF)_2$	94.04
$Zn(NDS)_2$	102.10
$Zn(NDB)_2$	196.20

Conclusions

Three ketohydrazone ligands had been successfully synthesized and characterized. Complexation with metal increased the fluorescence intensity of the 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. All compounds emitted light in blue region.

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.

Acknowledgement

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