SYNTHESIS AND PHOTOPHYSICAL PROPERTIES OF IRIDIUM(III) COMPLEXES WITH N-HETEROCYCLIC CARBENE LIGANDS FOR LIGHT EMITTING DIODE APPLICATION

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UNIVERSITI PENDIDIKAN SULTAN IDRIS

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NURUL HUSNA AS SAEDAH BINTI BAIN

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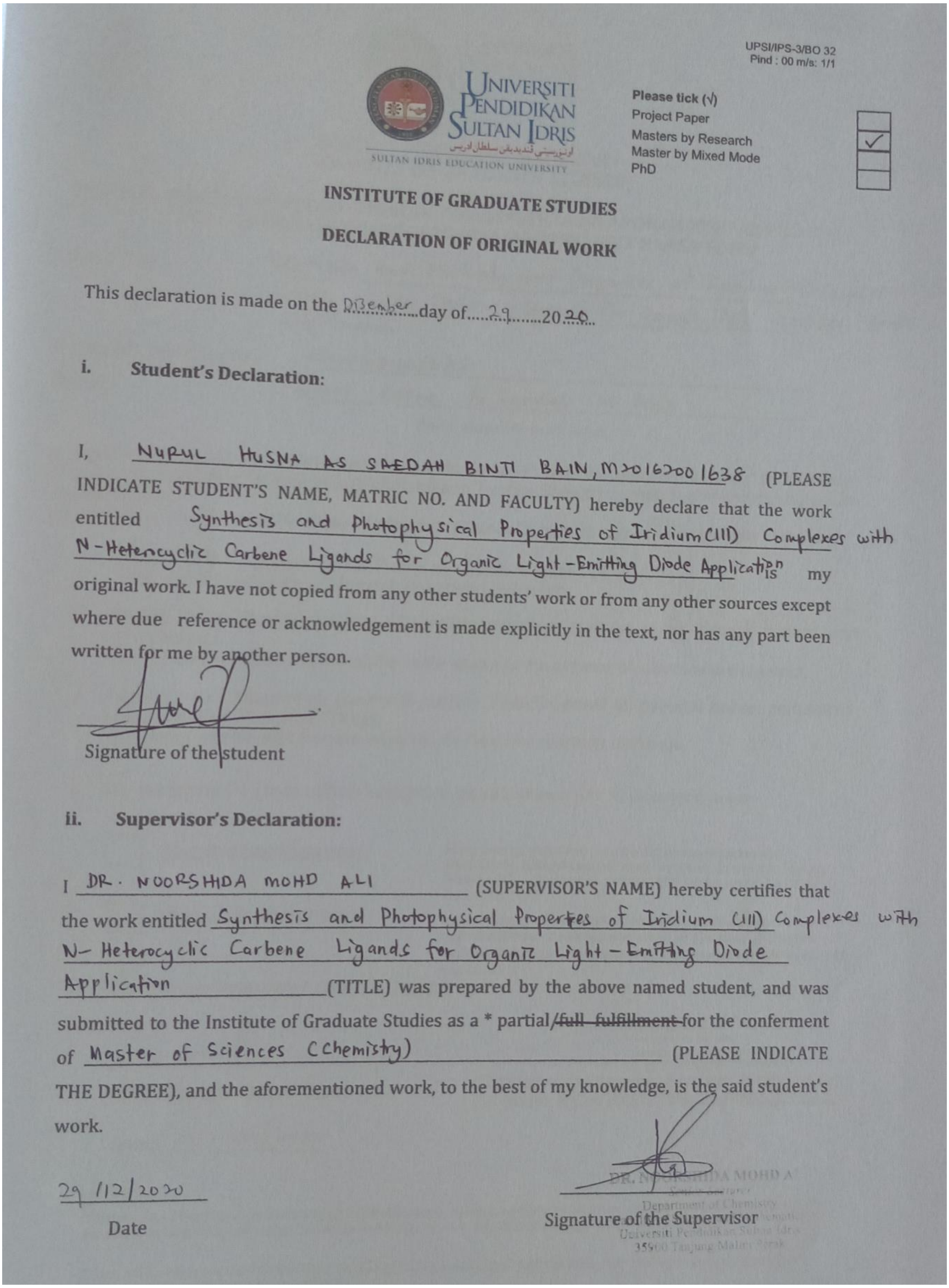

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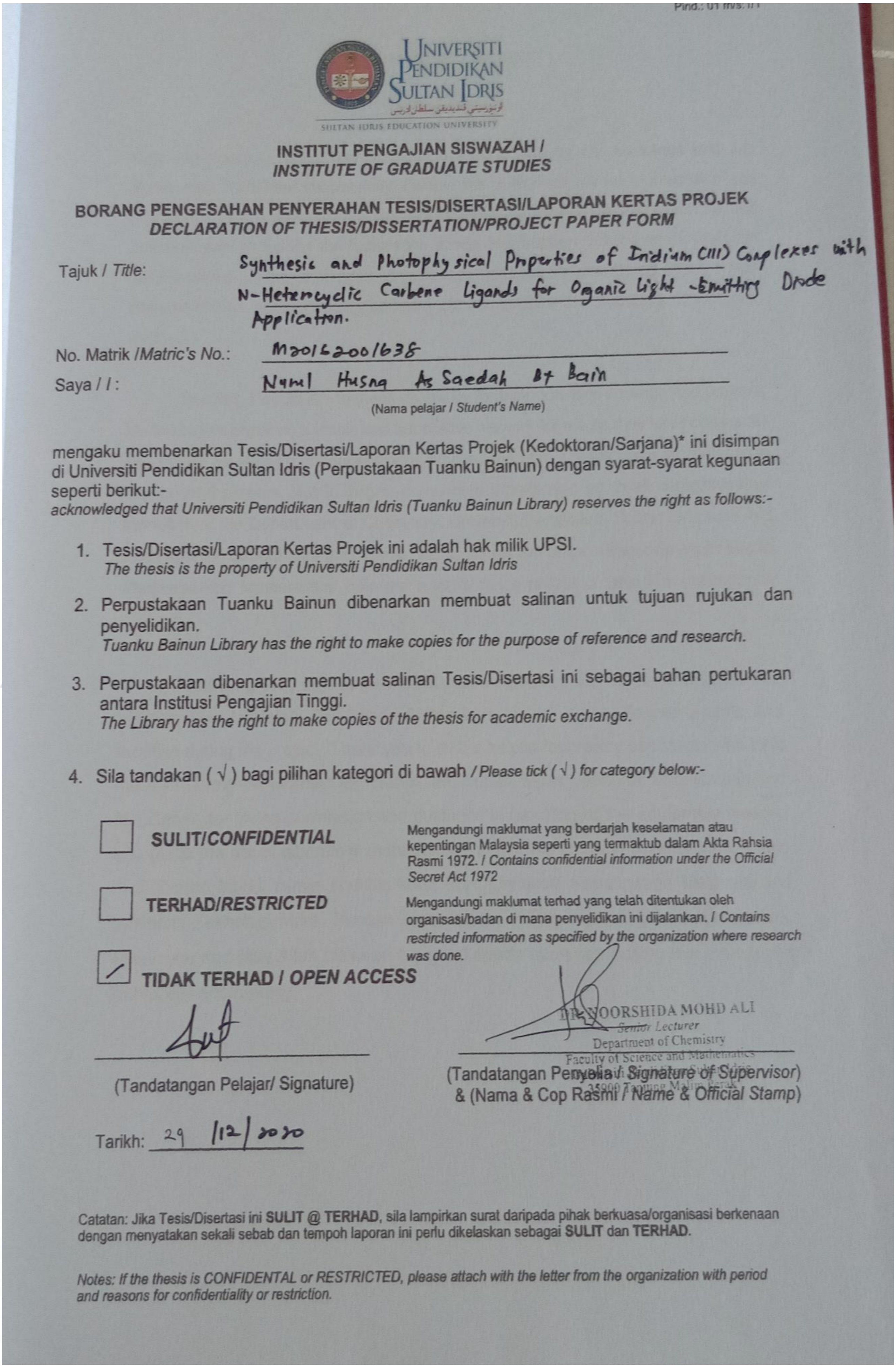

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ABSTRACT

This research aimed to synthesise iridium(III) complexes with N-heterocyclic carbene (NHC) ligands and investigate their photophysical properties. Complexes of chlorobis(2,4-difluorophenylpyridine)(pyridyltriazole)iridium(III) **(C1)**, bis(2,4-difluorophenylpyridine)(4-methylbenzylpyridyltriazole)iridium(III) ion **(C2)**, bis(2,4-difluorophenylpyridine)(hexylpyridyltriazole)iridium(III) ion **(C3)** and bis(2,4-difluorophenylpyridine)(2,6-difluorobenzylpyridyltriazole)iridium(III) ion **(C4)** were synthesised by reaction between dichloro-bridged iridium(III) dimer, $[Ir(2,4\text{-}F_2ppy)_2(\mu\text{-}Cl)]_2$ and corresponding triazolium salts. Iridium(III) complexes were characterised by Carbon, Hydrogen, Nitrogen and Sulphur (CHNS) elemental analyser and spectroscopic techniques: ^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR), Fourier Transform-Infrared (FTIR) and Liquid Chromatography-Mass Spectrometry (LCMS). The molecular structure of **C1** was determined by single crystal X-Ray Diffraction (XRD) technique. The photophysical study was performed using spectroscopic techniques: Ultraviolet-Visible (UV-Vis) and fluorescence. The results of the IR spectra showed strong frequency bands in the at 1595–1400 cm^{-1} were due to ν(C=N) and ν(C=C). The ^{1}H NMR spectra displayed the proton signals of phenylpyridine and pyridinetriazole in the aromatic region between δ 5.00 and 10.00 ppm. The ^{13}C NMR spectra showed aromatic carbon signals in the range δ 80–150 ppm and δ 0–50 ppm for aliphatic carbon that matches with the corresponding number of carbon atoms in **C1**–**C4**. Complexes of **C1**, **C2**, **C3** and **C4** exhibited ESI spectra at m/z 754.22, 823.17, 803.11 and 847.15, respectively. X-Ray crystallographic study confirmed iridium(III) ion in **C1** was coordinated to one pyridine-triazole, one chloro and two difluorophenylpyridine ligands in a distorted octahedral geometry. Steady-state emission spectroscopy demonstrated **C1**, **C2**, **C3** and **C4** emitted blue-green light in dichloromethane solution with an emission maximum at 472 nm, 452 nm, 471 nm and 470 nm, respectively. In conclusion, electronic properties of iridium(III) complexes with NHC ligands have tuned the lowest-unoccupied molecular orbital (LUMO) energy to the blue region. The implication of this study is these iridium(III) complexes can be studied as an alternative material to enhance luminescence efficiency of organic light-emitting diode (OLED).

SINTESIS DAN SIFAT FOTOFIZIKAL KOMPLEKS IRIDIUM(III) DENGAN LIGAN N-HETEROSIKLIK KARBENA UNTUK APLIKASI DIOD PEMANCAR CAHAYA ORGANIK

ABSTRAK

Kajian ini bertujuan untuk mensintesis kompleks iridium(III) dengan ligan N-heterosiklik karbena (NHC) dan mengkaji sifat fotofizikalnya. Kompleks klorobis(2,4-diflorofenilpiridina)(piridiltriazola)iridium(III) **(C1)**, ion kompleks bis(2,4-diflorofenilpiridina)(4-metilbenzilpiridiltriazola)iridium(III) **(C2)**, ion kompleks bis(2,4-diflorofenilpiridina)(heksilpiridiltriazola)iridium(III) **(C3)** dan ion kompleks bis(2,4-diflorofenilpiridina)(2,6-diflorobenzilpiridiltriazola)iridium(III) **(C4)** disintesis melalui tindak balas antara dimer iridium(III) titian-dikloro, $[Ir(2,4\text{-}F_2ppy)_2(\mu\text{-}Cl)]_2$ dan garam triazola yang sepadan. Kompleks iridium(III) dicirikan dengan penganalisa unsur Karbon, Hidrogen, Nitrogen dan Sulfur (CHNS) dan teknik spektroskopi: ^1H dan ^{13}C Resonans Magnet Nukleus (NMR), Inframerah Transformasi Fourier (FTIR) dan Spektroskopi Jisim Kromatografi Cecair (LCMS). Struktur molekul **C1** ditentukan melalui teknik kristalografi tunggal Belauan Sinar-X (XRD). Kajian fotofizikal dilakukan menggunakan teknik spektroskopi: Sinaran Ultralembayung Boleh Nampak (UV-Vis) dan pendarfluor. Hasil keputusan spektrum IR menunjukkan jalur frekuensi kuat di kawasan 1595–1400 cm^{-1} adalah disebabkan oleh ν(C=N) dan ν(C=C). Spektrum ^1H NMR menunjukkan isyarat proton fenilpiridina dan piridina-triazola di kawasan aromatik antara δ 5.00 dan 10.00 ppm. Spektrum ^{13}C NMR menunjukkan isyarat karbon aromatik dalam julat δ 80-150 ppm dan karbon alifatik pada δ 0–50 ppm yang sepadan dengan bilangan atom karbon pada **C1**–**C4**. Kompleks **C1**, **C2**, **C3** dan **C4** menunjukkan spektrum ESI masing-masing pada m/z 754.22, 823.17, 803.11 dan 847.15. Kajian kristalografi sinar-X mengesahkan bahawa, ion iridium(III) dalam **C1** dikoordinasikan ke satu ligan piridina-triazola, satu kloro dan dua diflorofenilpiridina dalam geometri oktahedral terherot. Spektroskopi pancaran keadaan-stabil menunjukkan bahawa **C1**, **C2**, **C3** dan **C4** memancarkan cahaya biru-hijau dalam larutan diklorometana dengan pancaran maksimum masing-masing pada 472 nm, 452 nm, 471 nm dan 470 nm. Kesimpulannya, sifat elektronik kompleks iridium(III) dengan ligan NHC telah menalakan orbital molekul tidak terisi tenaga terendah (LUMO) ke kawasan biru. Implikasi daripada kajian ini adalah kompleks iridium(III) ini dapat dikaji sebagai bahan alternatif untuk meningkatkan kecekapan pendarkilau diod pemancar cahaya organik (OLED).

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4.14 Luminescence spectra of complexes **C1**: [Ir(III)(2,4-F_2ppy)$_2$(**L1**)]Cl], **C2**: [Ir(III)(2,4-F_2ppy)$_2$(**L2**)]PF_6, **C3**: [Ir(III)(2,4-F_2ppy)$_2$(**L3**)]PF_6 and **C4**: [Ir(III)(2,4-F_2ppy)$_2$(**L4**)]PF_6 in air-equilibrated dichloromethane at 298 K. 70

4.15 Luminescence photograph of **C1** (greenish-blue), **C2** (blue), **C3** (greenish-blue) and **C4** (greenish-blue) in dichloromethane under UV light. 71

LIST OF ABBREVIATIONS

Å	Equal to one-tenth of a millimicron
acac	Acetylacetonate
ATR	Attenuated total reflectance
bo	Boronyl
Brp	2-bromo-2-propene-1-ol
Btp	[2,6-bis(1,2,3-triazole-4-yl)]pyridine
Bzq	Benzoquinoline
C	Carbon
C^N	Cyclometallating ligand
cm	centimetre
CT	Charge transfer
ECL	Electrochemiluminescence
EQEs	External quantum efficiency
equiv	equivalent
ETL	Electron transporting layer
fac	Facial

FIrpic	bis[2-(4,6-difluorophenyl)pyridinato-C_2,N](picolinato) iridium(III)
FTIR	Fourier transform-infrared
G	gram
H	Hydrogen
HOMO	Highest occupied molecular orbital
HTL	Hole transporting layer
L^L	Ancillary ligand
L^L	Bidentate ancillary ligand
LCMS	Liquid Chromatography-Mass Spectrometry
LEEC	Light emitting electrochemical cells
LMCT	Ligand-to-metal charge transfer
LUMO	Lowest unoccupied molecular orbital
m/z	Mass-to-charge ratio
mer	Meridional
mg	milligram
Ml	millilitre
MLCT	Metal-to-ligand charge transfer

mmol	millimole
MO	Metal orbital
mtzpy	2-(5-methyl-2H-1,2,4-triazol-3-yl)pyridine
Mv	Millivolts
NHC	N-heterocyclic carbene
NIR	Near Infra-Red
nm	Nanometer
NMR	Nuclear Magnetic Resonance
OLED	Organic light emitting diode
ORTEP	The Oak Ridge Thermal Ellipsoid Plot
phtzpy	2-(5-phenyl-2H-1,2,4-triazol-3-yl)pyridine)
ppo	1-phenyl-1,2-propanedione-2-oxime
ppz	Phenylpyrazole
SSL	Solid state lighting
tmd	2,2,6,6-tetramethylheptane-3,5-diketonate
Λ_{em}	Emission wavelength
λ_{max}	Maximum absorption wavelength

CHAPTER 1

INTRODUCTION

This chapter contains a general introduction about the luminescence studies and N-heterocyclic carbene (NHC). Besides, the problem statements, the significance of this study, the research's goals and hyphotesis are discussed throughout this chapter.

1.1 Background of Study

Phosphorescent iridium(III) complexes have many attractive properties that make them very useful for various applications such as dopants in light-emitting electrochemical cells (LEECs) and organic light-emitting diode (OLEDs) particularly for flat panel displays and lighting devices. Recently, iridium(III) complexes with cyclometallating phenylpyridine ligands have been studied intensively due to their unique optical properties as they have high emission of quantum efficiencies ($\Phi_p = 0.1 – 0.9$) and long-lived excited states (Klubek, 2014; Monti, Kessler, Delgado, Frey, Bazzanini, Accorsi & Baranoff, 2013; Omae, 2016; Yanling, Shuai, Godefroid, Jinghai, & Zhijian, 2015). Since these interesting properties and other related uses of the iridium(III) complexes strongly depend on the characteristics of their ground and excited states (Henwood et al., 2016a; Sajoto, Djurovich, Tamayo, Yousufuddin, Bau, Thompson & Forrest, 2005), it is important to have a deep investigation regarding the interactions between these states and thus come up with a systematic strategy to alter the photophysical properties by designing novel high emission iridium(III) complexes.

1.2 Luminescence, Fluorescence and Phosphorescence

Luminescence is the emission of light from any substance and occurs from an electronically excited state. The process begins with the absorption of a photon by a molecule and will result in the formation of an excited state by the promotion of an electron to a higher energy unfilled orbital. Then, this excited state will be deactivated and decay to the ground state. The ways the excited state decay to the ground state can be any of these three ways: (i) photochemistry (decomposition of the original molecule), (ii) luminescence (radiative decay by the emission of a photon that is divided into two categories depending on the nature of the excited state which can be a fluorescence or phosphorescence) and lastly (iii) non-radiative decay by the loss of the thermal energy (Atkin & De Paula, 2009).

Theoretically, fluorescence requires an electron in an excited singlet state, which is the exciting orbital is paired by the opposite spin to the second electron in the ground state orbital. Then, return to the ground state is a spin allowed transition and occurs rapidly through photon emission. The emission rates of fluorescence are usually 10^8 s^{-1} or faster. Emission without multiplicity switch is referred to as fluorescence (typically S1-> S2 transition) according to choice rules (Atkin & De Paula, 2009).

Phosphorescence involves the emission of a photon but from excited triplet states whereby the electron has the same spin orientation in the excited orbital as the ground state electron. Transitions to the ground state are spin-forbidden and the emission rates are slow which is 10^3 to 100 s^{-1}, so phosphorescence lifetimes are usually milliseconds to seconds. The term phosphorescence according to selection rules refers to emission in which the spin multiplicity changes (typically T_1 -> T_2 transition) (Atkin & De Paula, 2009).

Figure 1.1 is a Joblonski diagram that shows the excitation and decay processes (Klubek, 2014). Light of specific wavelength interacts with an electron and causes it's excited to a higher energy level. On this diagram, as a result of this absorption, the electron occupies the S_2 orbital which is the higher energy level. However, once an electron is excited, there are many ways that energy may be dissipated. The first is through vibrational relaxation, a non-radiative process and it occurs between vibrational levels. So generally, electrons will not change from one electronic level to another through this process. Each energy level (S_0, S_2, T_1) has a set of vibrational levels (Atkin & De Paula, 2009). Vibrational relaxation causes the electron to occupy the lower vibrational state.

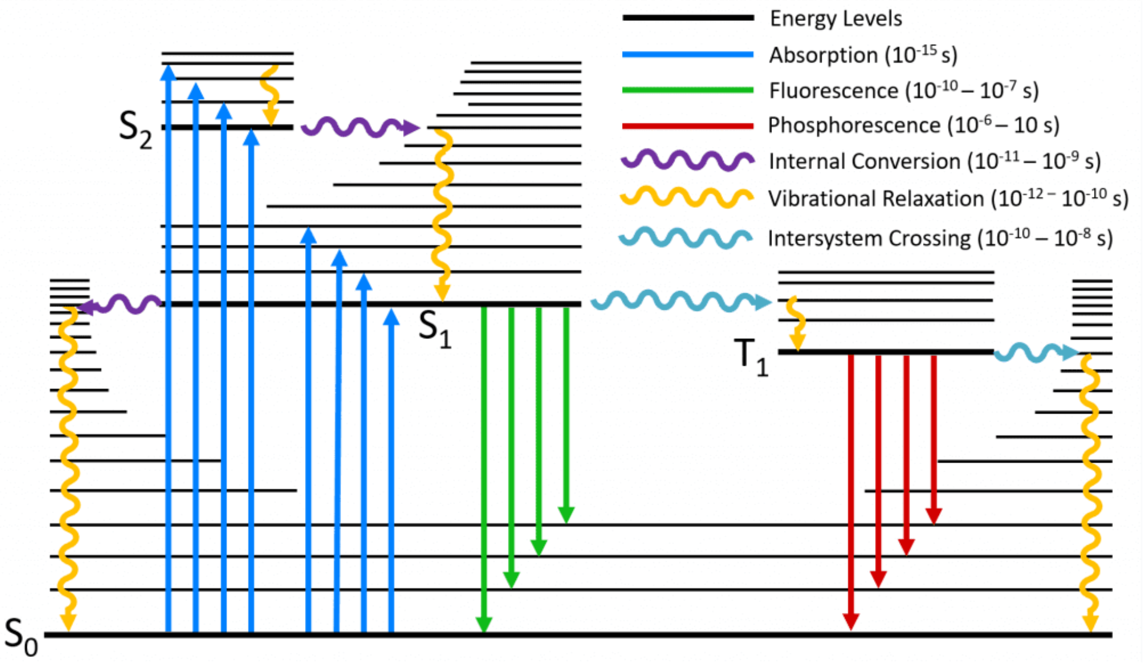


Figure 1.1. Joblonski Diagram Shows the Excitation and Decay Processes (Klubek, 2014).

However, if the vibrational energy levels strongly overlap with the electronic energy levels, the excited electron can move from a vibrational level in one electronic state to a higher vibrational level in a lower electronic state. This process is called internal conversion as in this diagram showing the electron to switch from S_2 to S_1. No energy is emitted. As the electron now occupies an excited vibrational level (S_1), it can relax further to the ground vibrational level. From there, it is finally possible for the electron to return to the ground electron state, S_0. The process of emission is called fluorescence. Usually, due to a lack of overlap between vibrational and electronic excited states, and a large energy difference between the ground state and first excited state, the internal conversion is very slow for an electron to return to the ground state (Chan, Tong, To, Yang, Du, Phillips, & Che, 2017; Sajoto, 2008).

The other way of relaxation to the ground singlet state, S_0 is by phosphorescence which is caused by an intercrossing system or sometimes called spin-orbit coupling. The difference is that the electron makes a transition from a singlet to a triplet state (Jean, 2005; Lamansky, Djurovich, Murphy, Abdel-Razzaq, Lee, Adachi,Thompson, 2001).

1.3 Luminescence Complexes of Transition Metal Ions

The studies of luminescence complex of transition metal ions have become much interest nowadays due to their rich photophysical and photoluminescence properties. Previous researches have reported about various transition metals ions with d^8 electronic configurations such as Pt(II) (Che et al., 2010; Kalinowski, Fattori, Cocchi, & Williams, 2011; Sun et al., 2011; Uesugi, Tsukuda, Takao, & Tsubomura, 2013) and Au(II) (Pell, Wilsin, Skelton, 2016; Poethig & Strassner, 2011); with d^6 electronic configuration such as Ir(III) (Adachi, Baldo & Forrest, 2001b; Baranoff et al., 2011; Lamansky et al., 2001; Monti et al., 2013; Orselli et al., 2007), Ru(III) (Gao & Bard, 2000; Yang & Gordon, 2005; Welby et al., 2013; Shang, Jiang, Wei, Zhang, & Luo, 2019) and Os(III) (Lu, Tao, Chi, & Tung, 2005; Tung, Wu & Liu, 2004) that have been utilized to form phosphorescent OLED dopants. Previously, they had shown that several families of these complexes are very interesting from the electrochemical, photochemical and photophysical views.

Besides, compared to conventional organic fluorophores which are only singlet emitters, complexes of transition metal ions can harvest both singlet and triplet excitons generated from electron-hole recombination by their strong spin-orbit coupling effects (Ali et al., 2017; Baranoff et al., 2011; Henwood et al., 2016a). In addition, the presence of transition metal ions addition with one or more organic ligands in the complexes is the strong factor that promising the display of mixed singlet-triplet states that lead to high photophysical properties. This is because they can promote an efficient intersystem crossing and thus make their lifetime longer (Barbante et al., 2013; Monti et al., 2013).

In general, singlet-singlet absorptions are an electronic transition from metal orbitals to empty ligand orbitals or centered on the ligand, which is from π orbitals to empty π^* orbitals without the changing of spin, which is allowed by large extinction coefficients. On the contrary, singlet-triplet absorptions are transitions with the spin change, therefore associated with small extinction coefficients (Jean, 2005; Maroń & Małecki, 2014).

This classification of the various electronic transition can be described by the schematic energy level diagram shown in Figure 1.2 which is the case for the octahedral metal complex. In the diagram, each molecular orbital is labelled as metal (M) or ligand (L) according to its localisation. Specifically, there are three fundamental types of electronic transitions: -

(i) transitions between metal orbital's (MO's) predominantly localised on the central metal,

(ii) transitions between MO's predominantly localised on the ligands, usually called central ligand (LC) and

(iii) transitions between MO's of different localisation, which cause the displacement of the electronic charge from the ligands to the metal or vice versa. These transitions are called Charge transfer (CT) transitions and more specifically, can be distinguished into ligand-to-metal charge-transfer (LMCT) and metal-to-ligand charge-transfer (MLCT) transitions (Balzani, Juris, Venturi, Campagna, & Serroni, 1996; Congrave, 2018). Of these, the MLCT transition has the lowest energy absorption which has the longest wavelength (Adachi et al., n.d.; Huo, Deaton, Rajeswaran, & Lenhart, 2006).

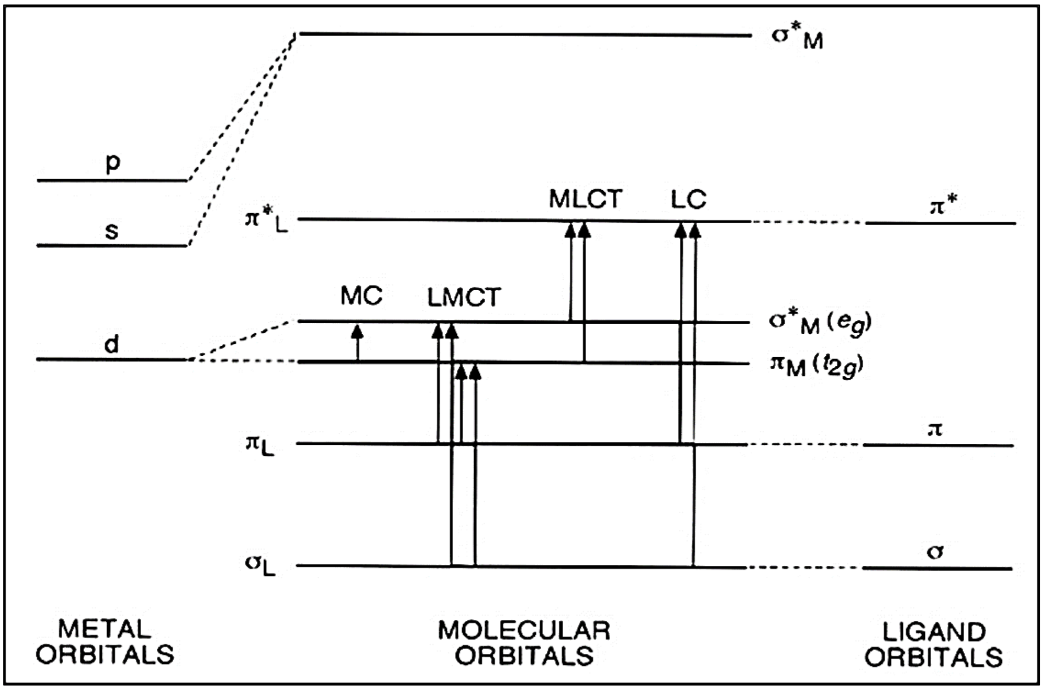


Figure 1.2. The schematic energy-level diagram for an octahedral transition metal complex and various kinds of their electronic transitions (Klubek, 2014).

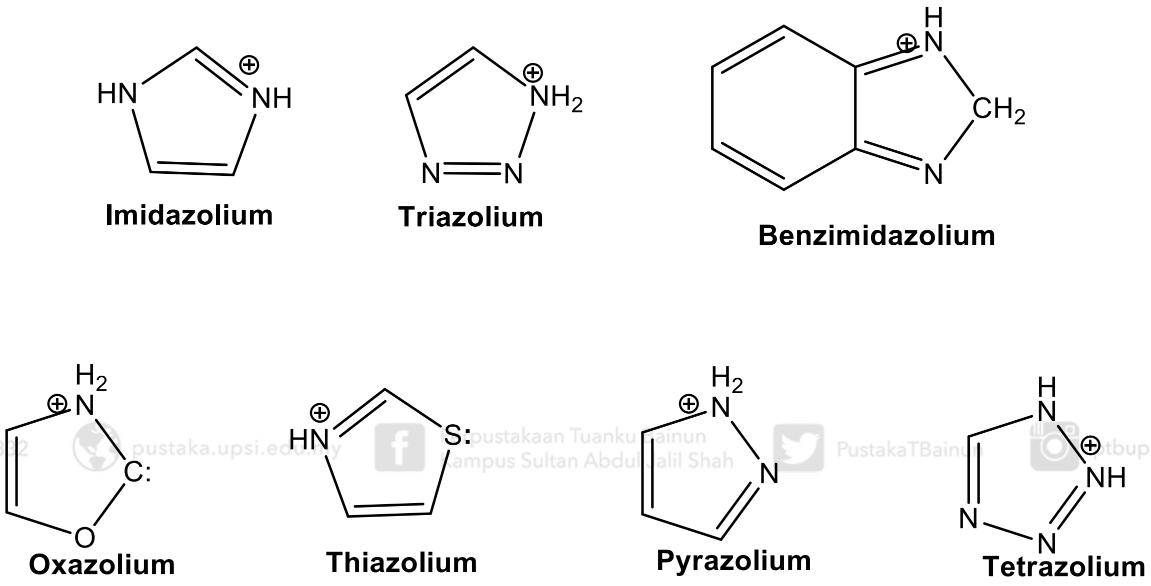
1.4 N-Heterocyclic Carbene Ligand

NHCs are defined as neutral complexes having a divalent carbon atom with a six-electron valence shell. Their incomplete electron octet and coordinative unsaturation, however, render free carbenes inherently unstable and they have been traditionally considered as highly reactive transient intermediates in organic transformations (Hopkinson, Richter, Schedler & Glorius, 2014).

NHC has played an important role in organic chemistry ever since the first firm evidence of their existence. In the early 1960s, the first application of NHC as ligands for metal complexes reported and surprisingly, the field of NHCs as ligands in transition metal chemistry remained dormant for 23 years (Herrmann, 2015).

1.4.1 Properties of N-Heterocyclic Carbene

In short, NHCs are heterocyclic species containing a carbene carbon and at least one nitrogen atom within the ring structure. Thus, these criteria make NHCs fall with various substitution patterns, ring sizes and degrees of heteroatom stabilisation. Figure 1.3 shows some of the most commonly applied types of NHCs (Schuster, Yang, Raubenheimer, & Albrecht, 2009).



Imidazolium **Triazolium** **Benzimidazolium**

Oxazolium **Thiazolium** **Pyrazolium** **Tetrazolium**

Figure 1.3. Different Types of Carbene Compound (Schuster et al., 2009)

A representation of the general structures of NHC shown in Figure 1.4 (Hopkinson et al., 2014) and the detailing effect of these general features on the stability and reactivity of the NHC described in Table 1.1. The overall electronic and steric effects of these structures explained the remarkable stability of the carbene centre C^2. As demonstrated in Figure 1.4 by the two adamantyl groups bound to the nitrogen atoms, NHC generally features bulky substituents adjacent to the carbene carbon which help to kinetically stabilise the species by sterically disfavouring dimerization to the corresponding olefin and the electronic stabilisation provided by the nitrogen atoms. In contrast to classical carbenes, NHC such as imidazolium salt exhibit a singlet ground-state electronic configuration with the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) best described as a formally sp^2-hybridized lone pair and an unoccupied p-orbital at the C^2 carbon.

Another attractive feature of NHC is that it has structurally diverse analogues that can be prepared and studied. For most classes of NHC, simple variation of the starting materials in a modular synthetic sequence allows for facile modification of the steric and electronic properties of the resulting carbene. The nitrogen-substituents or other groups situated adjacent to C^2 have the largest influence on the steric environment at the carbene centre with different classes of heterocycles having inherently different steric requirements (Poater, 2016).

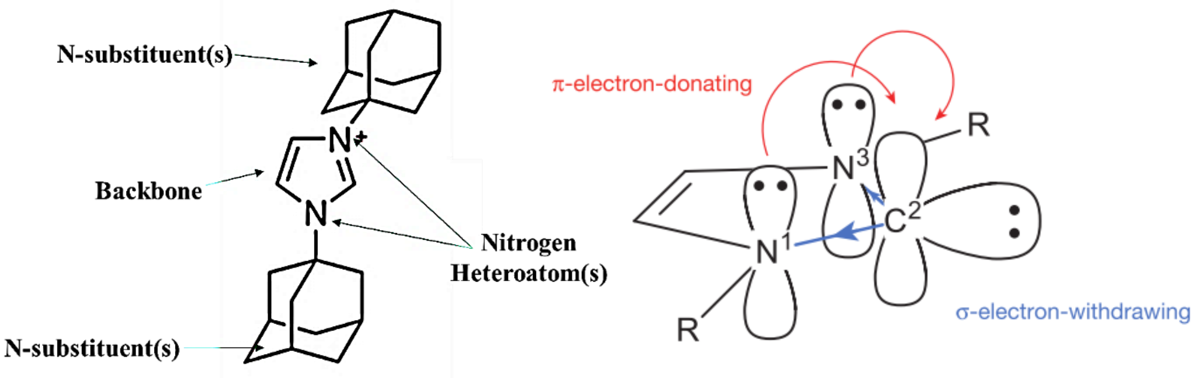


Figure 1.4. General Structural of Imidazole Class Of NHC

Table 1.1.

General Structural Features and The Detailing Effect On The Stability And Reactivity Of The NHC (Sajoto, 2008).

Structural Feature	**Effect on the stability & reactivity of NHC**
Nitrogen Heteroatom	• Sigma-electron-withdrawing • π-electron donating • Inductive and mesomeric stabilisation • Number of heteroatoms affect the carbene electronics
N-substituent	• Kinetic stabilisation from steric bulk • Electronic influence • Potential for asymmetric induction
Backbone	• Electronic stabilisation from aromaticity • Addition of substituent here will affect the carbene electronics

The NHC electronics are primarily governed by the class of heterocycle, with the substitution pattern of the ring backbone. The quantification of these properties facilitates easy comparison both between different NHC and between NHC and other related complexes such as phosphines and allows for a more enlightened selection of the appropriate carbene for any given application (Nelson & Nolan, 2013). Providing this versatile synthetic framework and fine control of electronic properties, NHC has emerged as a useful option for the development of novel luminescent materials that have a wide range of fundamental investigations, photoluminescence applications and light-emitting devices. Similarly, NHC ligands have recently been exploited to manipulate the electrochemical and spectroscopic properties of metal complexes for electrogenerated chemiluminescence (also known as electrochemiluminescence or ECL) (Mercs & Albrecht, 2010; Visbal & Concepcion Gimeno, 2014).

1.5 Problem Statement

Phosphorescent iridium(III) complexes have been extensively studied and are in focus for decades due to their potential application as phosphors in organic light-emitting diodes (OLEDs). The bombardment of using white OLEDs starting from 1999 when it is used extensively as displays in small handheld applications and prototype televisions (Costa, Orti, Bolink, Monti, Accorsi, & Armaroli, 2012).

Between three primary colours of phosphorescent such as blue, green and red, phosphorescent red and green emitters are well established with excellent device lifetimes, while the design and development of highly efficient, long-lived blue emitters is still an ongoing challenge (Henwood et al., 2016a). Concerning the performance of iridium-based emitters in OLEDs, a similar problem also exists which corresponding to the performance of deep blue emitter remains elusive (Henwood et al., 2016a). Thus, achieving triplet host energies that are compatible with the emitter and suitable functional device materials has become increasingly difficult to achieve.

In addition, the material used to produce blue light OLED degrades rapidly than the other two colours, which eventually throws off the colour balance and reduces the overall brightness of the display or lighting device (Klubek, 2014). While iridium(III) complexes show deep blue emission, they will show poorer efficiencies compared to their red and green-emitting counterparts previously (Baranoff et al., 2011; Henwood et al., 2016a). Thus, the design and development of blue light-emitting iridium(III) complexes is highly desirable and become an area of significant interest nowadays.

Since the lowest excited state is ligand-centred dominant, employing different cyclometallating ligands enables the excited-state energy of iridium(III) complexes to be varied over a wide spectral range. Up to now, the most strategist to tune the photophysical properties of the phenylpyridine-based iridium(III) complexes have been the substitution of donor or acceptor moieties on the pyridine or the phenyl groups. In principle, the emission colour of iridium(III) complexes is particularly sensitive to the substituents on the ligand attached to the central metal (Henwood & Zysman-Colman, 2016b; Monti et al., 2013). Therefore, appropriate substituents on the phenylpyridine ligands can cause shifting of the light emission from the red to the almost blue region of the visible spectrum.

In this research, iridium(III) complexes with cyclometallated phenylpyridine ligands and NHC ancillary ligand are chosen to be the subject of study due to the high emission quantum efficiencies and long-lived excited state compare to other transition metal (Baranoff et al., 2011; Sajoto et al., 2005). Besides, iridium(III) complexes have been stated previously can forming consistent strong spin-orbit coupling or an intersystem crossing and also having diverse natures of the emissive states that contributing to exhibit intense phosphorescence at room temperature (Tung, Wu & Liu, 2004). For instance, whilst common rubidium(II) and osmium(II) polypyridines emit in the red or near-infrared (NIR) region, the emission of iridium(III) complexes can shift from the red to the blue region of the spectrum, depending on the nature of the ligands resulting high photophysical properties.

1.6 Research Significant

In significant, the design and development of new iridium(III) complexes are very important as it will contribute to the fundamental study of the alternative methods to improve luminescence efficiency of solid-state lighting (SSL) especially for semiconductor light-emitting diodes (LEDs), OLEDs and polymer light-emitting diodes (PLED). In a nutshell, this study will provide a great platform for the local production of high-quality iridium(III) complexes that will be led to the enhancement of solid states technology in Malaysia

Thus, due to this big potential of iridium(III) complex in the SSL technology, there is a vital need to have specific novel research about it that can contribute to a couple of high lighting efficiencies with low fabrication cost. For example, in the field of photonics, the study of OLED emitters is one of the leading technologies for meeting sort of tremendous electricity consumption problem and challenges consequences from the poor efficiencies of commonly used lighting technologies such as an incandescent light bulb or compact fluorescent lighting in electrical devices (Humphreys, 2008).

1.7 Research Objectives

For the above problem statements and the significance of the study, three objectives of this research described below:-

a) To synthesis iridium(III) complexes which coordinate with N-heterocyclic carbene (NHC) based ligands.

b) To characterise the properties of the iridium(III) complexes with NHC based ligands.

c) To investigate the luminescence behaviours of the iridium(III) complexes with NHC based ligands.

1.8 Hypothesis

Emission energies of luminescent cyclometallated iridium(III) complexes are principally determined by the triplet energy of the cyclometallating aromatic ligand (C^N) and hence utilising different types of cyclometallating ligands will allow the excited-state energy of iridium(III) complexes to be varied over a wide spectral range. In addition, the control of the frontier orbital energy level (HOMO-LUMO, Highest Occupied Molecular Orbital-Lowest Unoccupied Molecular Orbital) is the sole method to achieve better blue phosphorescent iridium(III) complexes by appropriate ligand selection. In particular, to blue-shift the emission wavelength in iridium(III) complexes, the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the ligand should be increased by stabilising the HOMO and/or destabilising the LUMO energy levels. Therefore, the substitution of the C^N ligands with EWGs such as fluorine atom will render the HOMO to be more stabilised than the LUMO, and replacing the heterocyclic fragment of the C^N ligands with an N-heterocyclic carbene-based group, is expected to destabilise the LUMO energy and, consequently will increase the emission energy of iridium(III) complexes that coordinate to these ligands as well as pure blue emission at room temperature will be observed. In this study, the modification of NHC based ligand with a different substituent; 4-methylbenzyl, hexyl and 2,6-difluorobenzyl is expecting to alter the HOMO-LUMO energy gap. The stronger the electron-withdrawing ability of the substituent, the higher the HOMO-LUMO energy gap resulting higher blue shifting (Cortés-Arriagada, Sanhueza, González, Dreyse, & Toro-Labbé, 2015). Thus, the series of blue shifting of cyclometallated Ir(III) complexes predicted to be 2,6-difluorobenzyl **>** 4-methylbenzyl **>** hexyl