SYNTHESIS AND PHOTOPHYSICAL PROPERTIES OF BLUE PHOSPHORESCENT IRIDIUM(III) COMPLEXES WITH ALKOXY-FUNCTIONALISED PHENYLPYRIDINE CYCLOMETALATING LIGANDS FOR POTENTIAL OLED APPLICATIONS

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SINTESIS DAN SIFAT FOTOFIZIK KOMPLEKS IRIDIUM(III) BERPENDAR FOSFOR BIRU DENGAN LIGAN SIKLOMETALASI FENILPIRIDINA BERFUNGSI ALKOKSI UNTUK POTENSI APLIKASI OLED

NUR KHALIESA BINTI ZULKARNAEN

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ABSTRACT

This research aims to synthesise and characterise new blue phosphorescent iridium(III) complexes and analyse their photophysical properties. Three iridium(III) complexes were synthesised: bis(2-(2-butoxy-4-fluorophenyl)pyridine)(2,6 difluorobenzyltriazolpyridine)iridium(III) ion (C1), bis(2-(2-ethoxy-4-fluorophenyl)pyridine)(2,6-difluorobenzyltriazolpyridine)iridium(III) ion (C2) and bis(2-(2-butoxy-4-fluorophenyl)pyridine)(imidazolpyridine)iridium(III) ion (C3). Complexes of C1 and C2 were obtained via reaction of dichloro-bridged iridium(III) dimers with N-heterocyclic carbene ligands, while C3 was prepared using the same dimer reacted with 2-(1*H*-imidazol-2-yl)pyridine. All complexes were characterised using spectroscopic techniques: ^{1}H, ^{13}C and distortionless enhancement by polarisation transfer 135 (DEPT-135) nuclear magnetic resonance (NMR), Fourier transform infrared (FTIR) and liquid chromatography-mass spectrometry using electrospray ionisation (LC-ESI/MS). Photophysical properties were analysed using ultraviolet-visible (UV-Vis) absorption and photoluminescence (PL) spectroscopy. ^{1}H NMR spectra showed aromatic proton signals between 4.90 and 9.10 ppm attributed to phenylpyridine, triazole-derived pyridine and imidazolium moieties. ^{13}C NMR spectra showed resonances consistent with the number of carbon atoms in each complex, while DEPT-135 distinguished CH_3, CH_2 and CH groups. FTIR spectra confirmed the presence of phenyl and pyridine functionality groups in the ranges of 1615–1495 cm^{-1} and 1514–1406 cm^{-1}, respectively. ESI-MS spectra displayed molecular ions $[M]^+$ at m/z 953 (C1) and 770 (C3), while $[M+Na]^+$ at 920 (C2). Emission spectra showed C1 and C2 emit dark blue light with a dominant emission peak (λ_{em} = 435 nm) and vibronic shoulders at 459 and 463 nm, respectively. C3 emits greenish-blue light with two emission peaks (λ_{em} = 435 and 464 nm) and vibronic shoulder at 492 nm. Among these, C1 showed the highest photoluminescence quantum yield (PLQY = 0.72) and short emission lifetime (τ = 1.36 ns). In conclusion, new blue phosphorescent iridium(III) complexes were successfully synthesised and characterised, with C1 demonstrating dark blue emission and the highest PLQY. As an implication, this study offers an alternative approach to improve blue phosphorescence efficiency in organic light-emitting diode (OLED) applications.

SINTESIS DAN SIFAT FOTOFIZIK KOMPLEKS IRIDIUM(III) BERPENDAR FOSFOR BIRU DENGAN LIGAN SIKLOMETALASI FENILPIRIDINA BERFUNGSI ALKOKSI UNTUK POTENSI APLIKASI OLED

ABSTRAK

Kajian ini bertujuan untuk mensintesis dan mencirikan kompleks iridium(III) berpendar fosfor biru yang baharu serta menganalisis sifat fotofiziknya. Tiga kompleks iridium(III) disintesis: ion bis(2-(2-butoksi-4-fluorofenil)piridina)(2,6-difluorobenziltriazolpiridina iridium(III) (C1), ion bis(2-(2-etoksi-4-fluorofenil)piridina)(2,6-difluorobenziltriazolpiridina)iridium(III) (C2) dan ion bis(2-(2-butoksi-4-fluorofenil)piridina)(imidazolpiridina)iridium(III) (C3). Kompleks C1 dan C2 diperoleh melalui tindak balas dimer iridium(III) titian-dikloro dengan ligan karbena N-heterosiklik, manakala C3 disediakan menggunakan dimer sama bertindak balas dengan 2- (1*H*-imidazol-2-il)piridina. Semua kompleks dicirikan menggunakan teknik spektroskopi: ^{1}H, ^{13}C dan peningkatan nirherotan melalui pemindahan pengutuban 135 (DEPT-135) resonans magnetik nukleus (NMR), inframerah transformasi Fourier (FTIR) dan kromatografi cecair- spektrometri jisim menggunakan pengionan semburan elektro (LC-ESI/MS). Sifat fotofizik dianalisis menggunakan spektroskopi serapan ultralembayung boleh nampak (UV-Vis) dan foto pendarcahaya (PL). Spektrum ^{1}H NMR menunjukkan isyarat proton aromatik antara 4.90 dan 9.10 ppm merujuk kepada fenilpiridina, piridina terbitan triazola dan moieti imidazolium. Spektrum ^{13}C NMR menunjukkan resonans konsisten dengan bilangan atom karbon dalam setiap kompleks, manakala DEPT-135 membezakan kumpulan CH_3, CH_2 dan CH. Spektrum FTIR mengesahkan kehadiran kumpulan berfungsi fenil dan piridina, masing-masing dalam julat 1615–1495 cm^{-1} dan 1514–1406 cm^{-1}. Spektra ESI-MS menunjukkan ion molekul $[M]^+$ pada m/z 953 (C1) dan 770 (C3), manakala $[M+Na]^+$ pada 920 (C2). Spektrum pancaran menunjukkan C1 dan C2 memancarkan cahaya biru gelap dengan satu puncak pancaran dominan (λ_{em} = 435 nm) dan bahu vibronik, masing-masing pada 459 dan 463 nm. C3 memancarkan cahaya hijau kebiruan dengan dua puncak pancaran (λ_{em} = 435 dan 464 nm) dan bahu vibronik pada 492 nm. Antara semua kompleks, C1 menunjukkan hasil kuantum foto pendarcahaya tertinggi (PLQY = 0.72) dan jangka hayat pancaran pendek (τ = 1.36 ns). Kesimpulannya, kompleks iridium(III) berpendar fosfor biru baharu berjaya disintesis dan dicirikan, dengan C1 mempamerkan pancaran biru gelap dan PLQY tertinggi. Sebagai implikasi, kajian ini menawarkan pendekatan alternatif untuk meningkatkan kecekapan pendar fosfor biru dalam aplikasi diod pemancar cahaya organik (OLED).

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LIST OF ABBREVIATIONS

bFppy	2-(2-butoxy-4-fluorophenyl)pyridine
C1	bis(2-(2-butoxy-4-fluorophenyl)pyridine)(2,6 difluorobenzyltriazolpyridine)iridium(III) ion, $[Ir(bFppy)_2(F_2bpyta)]Br$
C2	bis(2-(2-ethoxy-4-fluorophenyl)pyridine)(2,6-difluorobenzyltriazolpyridine)iridium(III) ion, $[Ir(eFppy)_2(F_2bpyta)]Br$
C3	and bis(2-(2-butoxy-4-fluorophenyl)pyridine)(imidazolpyridine)iridium(III) ion, $[Ir(eFppy)_2(impy)]^+$
CIE	Commission Internationale de l'Eclairage
CT	Charge-transfer
D1	μ-Chloride Bridged Dimer $[Ir(bFppy)_2(\mu\text{-}Cl)_2]$
D2	μ-Chloride Bridged Dimer $[Ir(eFppy)_2(\mu\text{-}Cl)_2]$
DEPT	Distortionless enhancement by polarisation transfer
dFppy	2,4-difluorophenylpyridine
DFT	Density functional theory
eFppy	2-(2-ethoxy-4-fluorophenyl)pyridine
F2bpyta	2-(2,6-difluorobenzyl)-(1,2,4-triazol-1-yl)pyridine bromide
FTIR	Fourier transform infrared
HOMO	Highest occupied molecular orbital
HSQC	Heteronuclear single quantum coherence
ILCT	Intraligand charge transfers

impy	2-(1*H*-Imidazol-2-yl)pyridine
ISC	Intersystem crossing
L1	2-(2-butoxy-4-fluorophenyl)pyridine
L2	2-(2-ethoxy-4-fluorophenyl)pyridine
L3	2-(1H-1,2,4-triazol-1-yl)pyridine
L4	2-(2,6-difluorobenzyl)-(1,2,4-triazol-1-yl)pyridine bromide
LC	Ligand-centred
LC-MS	Liquid chromatography-mass spectrometry
LECs	Light-emitting electrochemical cells
LLCT	Ligand-to-ligand charge transfers
LMCT	Ligand-to-metal charge-transfer
LUMO	lowest unoccupied molecular orbitals
m/z	Mass-to-charged ratio
MC	Metal-centred
MC	Metal-centred
MLCT	Metal-to-ligand charge-transfer
ms	Microsecond
NHC	N-heterocyclic carbenes
NMR	Nuclear magnetic resonance
ns	Nanosecond
OLED	Organic light-emitting diodes
PLQY	Photoluminescent quantum yield
ppy	2-phenylpyridine
SOC	Spin-orbit coupling
TDDFT	Time-dependent DFT

TLC	Thin layer chromatography
UV	Ultraviolet
λ_{abs}	Absorption wavelength
λ_{em}	Emission wavelength

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CHAPTER 1

INTRODUCTION

1.1 Preface

This study focuses on the design, synthesis, and photophysical characterisation of new blue-emitting phosphorescent iridium(III) complexes for potential use in optoelectronic applications, particularly OLEDs. Electronic structure and emission properties were tuned through strategic modification of both cyclometalating and ancillary ligands. These complexes function as model systems for examining how ligand architecture affects photophysical characteristics, including emission wavelength, quantum efficiency, and excited-state dynamics.

This chapter provides a general overview of the basic concepts related to luminescent and luminescent transition metals complexes with primary focus on phosphorescent cyclometalated iridium(III) complexes. The chapter begins with a

description of the basic concepts of luminescent and definitions of different types of luminescent. Then, this chapter continues with a description of the unique characteristics possessed by luminescent transition metal complexes that have been studied extensively. Emphasis is placed on cyclometalated iridium(III) complexes which are known for their excellent photophysical characteristics such as high quantum yield and easily adjustable emissions. Then, this chapter is followed by an overview of N-heterocyclic ligands that are known for their strong σ-donating abilities and their capability as ancillary ligands for phosphorescence iridium(III) complexes. This chapter then explains the importance and potential of phosphorescent iridium(III) complexes in obtaining blue emission where blue emission is very important in organic light-emitting diode (OLED) and is still an ongoing interest in research. Next, this chapter continues with a discussion of the research problem to identify the challenges in producing and obtaining pure blue emitters for OLED. The objectives and significance of the study are then stated to formulate the direction of the study which involve designing, synthesising and investigating the new complex of iridium(III) for OLED applications.

1.2 Luminescent

Luminescence is the process by which a substance (organic, inorganic or even a living organism) naturally emits light beyond the thermal radiation produced by the heat within that substance (Brik & Srivastava, 2023). Luminescence is the emission of light caused by chemical reactions due to electron transition from higher energy of molecular orbitals to lower energy of molecular orbitals. It is closely related to spectroscopy,

which studies the general laws of absorbing and emitted radiation by matter (Chopra et al., 2022). Table 1.1 outlines the essential ideas and definitions of luminescence.

Table 1.1

Fundamental concepts and definitions of luminescence

Terminology of Luminescence	Methods of excitation
Photoluminescence	Emission takes place after the absorption of photons by the system. Excitation is often caused by a low-energy light source that emits photons such as ultraviolet and visible light. PL is classified into two types based on how long the afterglow lasts after stimulation: Phosphorescence and Fluorescence
Thermoluminescence	Refers to temperature-dependent phosphorescence. TL refers to the emission of light upon heating of a material that has absorbed energy from electromagnetic radiation.
Cryoluminescence	Occurs when a luminous material emits light upon cooling.
Electroluminescence	Refers to the phenomenon of light emission that occurs when an electric field is applied to a material.
Cathodoluminescence	The excitant consists of a stream of high-energy electrons, commonly referred to as cathode rays.
Chemiluminescence	Refers to the phenomenon where visible light is emitted because of chemical reactions. Various types of chemiluminescence are: 1. Bioluminescence, which occurs when living organisms produce light during biochemical process. 2. Electrochemiluminescence, which is generated by electrochemical reactions typically occurring in solutions 3. Lyoluminescence, which manifests when a solid that has been heavily irradiated is dissolved in a solvent. 4. Candoluminescence, where substances emit light upon heating, distinct from blackbody radiation, exemplified by the limelight which is the luminescence of CaO after it has been heated and

Terminology of Luminescence	Methods of excitation
	has been historically utilised for stage lighting in theaters.
Mechanoluminescence	Light is produced after a mechanical action or impact on a solid. Mechanoluminescence subtypes can be identified based on mechanical impact type: 1. Piezoluminescence, when mechanical pressure is applied to some solids, it can produce glowing light. 2. Fractoluminescence, when a solid is fractured, crashed or broken and energy is released as a light. 3. Triboluminescence, when the light is produced by scratching or rubbing a luminescent material. 4. Sonoluminescence, when the light is emitted following the implosion of a bubble in a liquid, triggered by an ultrasound wave.
Radioluminescence	Refers to the phenomenon where luminescent light is stimulated by ionizing radiation.
Crystalloluminescence	Refers to the emission of light that occurs during the crystallisation process from a solution.

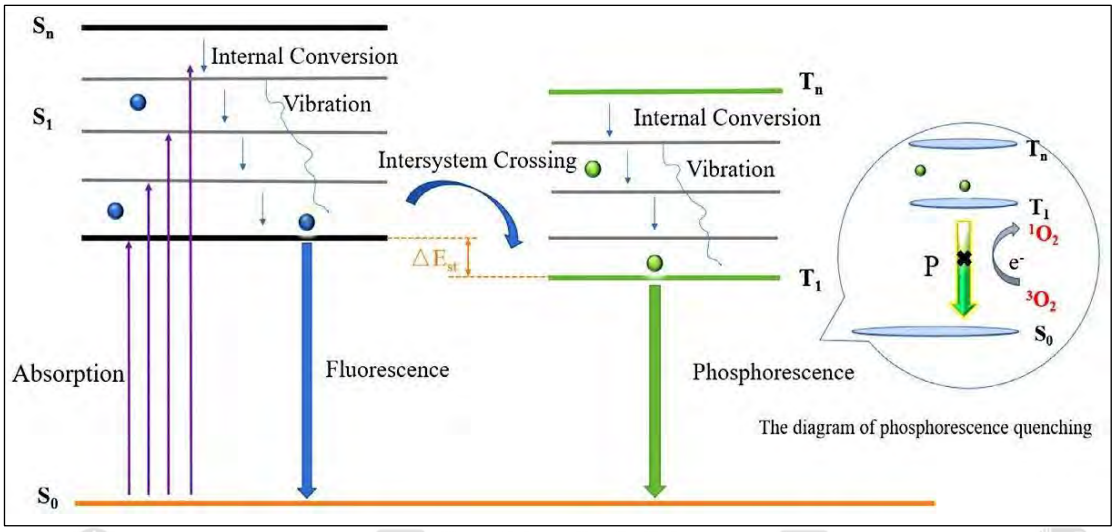
Adapted from Brik & Srivastava, 2023

Fluorescence and phosphorescence represent two primary forms of photoluminescence, which at the molecular level arise from electronic transitions between the singlet excited state (S_1) and the triplet excited state (T_1) to the singlet ground state (Chatterjee et al., 2020). Based on the Jablonski energy level diagram, (Figure 1.1) when a substance is exposed to excitation light, it absorbs photons from the ground state (S_0) to either the higher singlet state (S_n) or the lowest singlet state S_1. This process results in the formation of singlet excitons. Photons release through vibration relaxation to produce fluorescence when the single exciton returns to S_0. As the singlet exciton returns to S_0, the photons are released through vibration relaxation and emit fluorescence. Triplet exciton formation occurs when the singlet exciton reaches to the lowest triplet state T_1 or a higher triplet state T_n through intersystem

crossing (ISC). Photons are then released from T_1 or T_n to S_0, resulting in the emission of phosphorescence (Zhao et al., 2022).

Figure 1.1

Jablonski energy level diagram



Adapted from Zhao et al., 2022

Furthermore, fluorescence is a rapidly decaying emission after the end of excitation in the range less than 10^{-6} s due to the transitions allowed between levels of the same multiplicity in the molecules of electrons along with the hole in the crystal and fluorescence occurs when electrons return to their ground state from an excited singlet state. Phosphorescence, on the other hand, is luminescence that persists after excitation ceases which persisting for more than 10^{-6} s and can last for hours at times and it occurs because the excited molecule can operate at a level from which radiative transitions are forbidden through quantum selection rules (Kumar & Mishra, 2022).

1.3 Luminescent Transition Metal Complexes

Luminescent transition metal complexes have gained popularity in recent decades due to their intriguing photochemical and photophysical properties (Zhang & Wong, 2020). The excellent photophysical and chemical properties of transition metal-based luminescent complexes have made them widely studied and applied in electrochemiluminescence analysis, such as field effect transistors, light-emitting diodes, organic electroluminescent devices, photorefractive, light-emitting electrochemical cells, and biological media to label product (Zhang et al., 2019). Recently, luminescent transition metal complexes have played an increasingly important role in developing high-performance photofunctional materials (Haque et al., 2019; Tang et al., 2021).

There is a long history of study of transition metal complexes due to their intriguing photophysical and photochemical properties, and the basic concepts regarding their excited states have been formulated about 30 years ago (Balzani et al., 2008; Balzani & Campagna, 2007; Koshevoy et al., 2020; Paw et al., 1998; Stufkens, 1990; Vlček, 2000; Yersin, 2004). Some general rules are that the use of metal-*d* orbitals in conjunction with ligand π or π* orbitals allows for extremely long-lived charge-transfer (CT) excited states, ligand-to-metal charge-transfer (LMCT) excited states for good donor ligands, and metal-to-ligand charge-transfer (MLCT) excited states for good π accepting ligands (Koshevoy et al., 2020). Aside from that, the 4*d* and 5*d* elements have inherently high ligand fields, with a typical Inter-System Crossing (ISC) of unity (100%) and the most effective triplet emitting complexes contain Re(I), Ru(II), Os(II), Ir(III), Ir(I), Pt(II), Au(I), or Au(III) (Koshevoy et al., 2020).

Next, transition metal complexes possessing a ligand-based lowest unoccupied molecular orbitals (LUMO) and a metal-centred highest occupied molecular orbital (HOMO) can have metal to ligand-based charge transfer (MLCT) excited states that last for nano- to microseconds, which allow the luminescence and diffusion-controlled photochemical reactions to take place (Sinha & Wenger, 2023). Based on the established photophysical principle from extensive study of many precious metal complexes, it has been found that MLCT excited states have longer lifetimes and higher luminescence quantum yields when the energy gap between the lowest excited state and the electronic ground state is larger (Caspar & Meyer, 1982). Hence, to increase the energy gap between the lowest excited state and the electronic ground state, a choice of low-valence metal centres and very strong π-acceptor ligands makes it possible to achieve efficient MLCT transitions and their associated excited states, which has long been of interest to chemists due to their rich redox properties and robustness (Yam et al., 2020).

Most luminescent transition metal complexes can utilise both singlet and triplet states simultaneously, unlike classical fluorescent materials that emit light from singlet states, which greatly increases the efficiency of light-emitting electrochemical cells (LECs) and organic light-emitting diodes (OLEDs) (Tao & Wong, 2023). Intersystem crossing (ISC) from singlet to the triplet state due to the very strong spin-orbit coupling (SOC), allow phosphorescence to be exhibited by the transition metal complexes. SOC is a relativistic effect that describes the interaction between orbit momentum and spin momentum of an electron, and its strength scales with Z_{eff}^4/n^3, where Z_{eff} represents the effective nuclear charge and n represents the principal quantum number of valence electrons (Li et al., 2021). Under the Condon approximation of Fermi's Golden Rule,

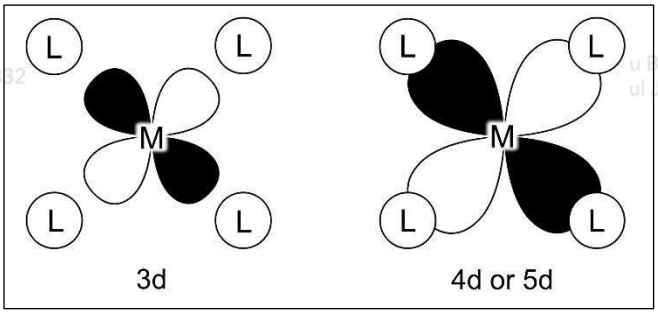
ISC rates are determined by the direct Spin-Orbit Coupling matrix element (SOCME) of the coupling singlet (S_n) and triplet (T_m) excited states ($<S_n|H_{SOC}|T_m>$) as well as the difference in energy between their potential energy minima of the two excited states (ΔEST). ISC efficiency can be controlled through different metal centres with different spin-orbit coupling constants related to their different masses or 'heaviness', which related to how easily spin-forbidden excited states can be accessed and most complexes typically exhibit this state as a triplet resulting from diamagnetic heavy transition metal complex excitation (Yam et al., 2020). As a result, triplet excited states have different emissive lifetimes which is significant for their performance as OLED.

Coordination complexes of 4*d* and 5*d* orbitals have excellent photophysical and photochemical properties. Compared to 4*d* and 5*d* orbitals, 3*d* metals have much weaker ligand field which imposed by a given coordination environment, because their more contracted orbitals have weaker spatial overlaps with the ligand orbitals (Wegeberg & Wenger, 2021) whereas 4*d* and 5*d* orbitals form stronger bonds with ligands and overlap more efficiently with ligand orbitals due to their expanded orbitals (Figure 1.2). In addition, 4*d* and 5*d* metal complexes have greater energy gaps between the individual metal-centred (MC) states and sizeable energy gap between the lowest MC state and the electronic ground state and thus allow 4*d* and 5*d* metal complexes to form long excited state lifetime and produce high luminescence quantum yield. However, there have been significant advances in this area over the past few years with $3d^6$ metal complexes and other types of photoactive first-row transition metal compounds as well and Fe(II) is by far the best investigated case among $3d^6$ compounds (Dierks, Vulkanidovic & Bauer, 2021). The installation of photoactive MLCT excited states to Fe(II) is theoretically possible, but extremely difficult (Liu et al., 2016) as it is

mainly because the lowest excited MLCT states of Fe(II) complexes deactivate very quickly within femtosecond to picosecond time scales (Cebrián & Mauro, 2018; Oppermann et al., 2022; Paulus et al., 2020; Sinha & Wenger, 2023). Therefore, because of their weak ligand fields, first-row transition metals with open shell configurations can be challenging because they produce energy-low metal-centred (MC) excited states, which can be deactivated non-radiatively by quickly deactivating the MLCT excited state and returning them to the electronic ground state (Wegeberg & Wenger, 2022).

Figure 1.2

Diagram showing how metal d-orbitals overlap with ligand orbitals



Adapted from Wegeberg & Wenger, 2021

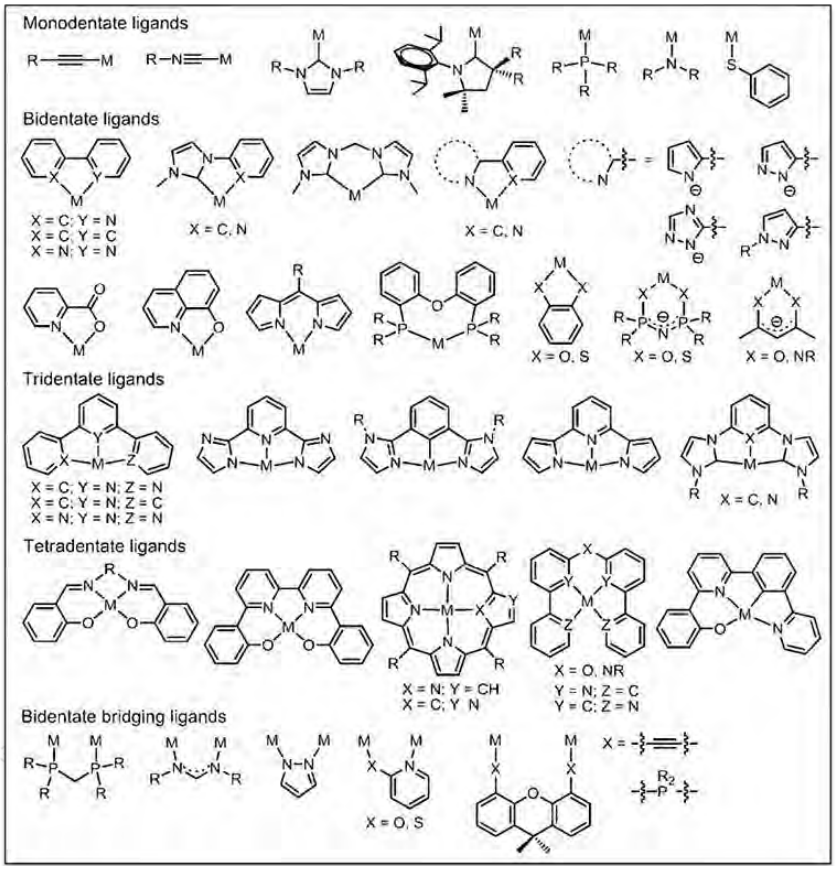
Studies of strongly luminescent complexes of transition metal centres have focused mainly on transition metal centres with d^6 (for example: rhenium(I), ruthenium(II), osmium(II), or iridium(III) or d^8 (for example: platinum(II), palladium(II), and gold(III) (Lee & Lo, 2022). Due to their favourable electronic structures, transition metal complexes of precious $4d^6$ and $5d^6$ ions, such as ruthenium(II) and iridium(III), have been extensively investigated in the photophysics and photochemistry fields as they produce long-lasting and emissive MLCT excited

states with attractive redox properties (Wegeberg & Wenger, 2022). In addition, the presence of heavy metal atoms in transition metal complexes of the second and third rows leads to phosphorescence, which enhances spin-orbit coupling, resulting in efficient ISC from singlet-to-triplet excited-state manifolds upon photoexcitation (To, Wan, Tong & Che, 2020).

These transition metal complexes can undergo a variety of electronic transitions due to their various metal *d* electron configurations, oxidation states, coordination numbers, and geometries (Yam et al., 2020) which depend mainly on the identity of the metal centre and the chemical structure of the ligands (Schwehr et al., 2022). However, the electronic properties of the coordinated ligands play an important role as the emissive triplet excited states of the complexes depends strongly on the electronic properties of the coordinated ligands. Figure 1.3 illustrates the structures of ligands commonly used in the design of luminescent metal complexes (To et al., 2020). Systematic alteration of the electronic properties of ligands can alter the spectroscopic and emission properties of metal complexes which is essential for the development of luminescent materials with tuneable luminescence colour since ligands often participate in the excited states of complexes (Yam & Law, 2020). Non-emissive metal-centred (MC) excited states can be destabilised by strong σ-donor or π-acceptor ligands and thus enabling applications such as photoredox catalysis, chemo sensing, OLED and solar energy conversion by facilitating the population of the ^{3}CT/^{3}IL excited states (Lee & Lo, 2022). Hence, luminescence properties of metal complexes can be controlled through modification of ligands and the choice of metal centre.

Figure 1.3

Examples of ligands that are often used to design Luminescent Metal Complexes. Abbreviations: M, Metal; R, alkyl or aryl substituent



Adapted from To et al., 2020

1.4 Cyclometalated Iridium(III) Complexes

Cyclometalated iridium(III) complexes has an advantage over most other transition metals due to its photophysical properties such as large ligand-filed splitting that prevents the thermal formation of non-radiative metal centred (^{3}MC) *d–d* states, allowing colour tuning over a wide range (Na et al., 2018). Besides, there are six coordination positions available at the iridium(III) ion which permits for a wide range of ligands to be coordinated and allows for fine tuning of the complex's physical properties, making luminescent iridium(III) complexes an area of considerable interest

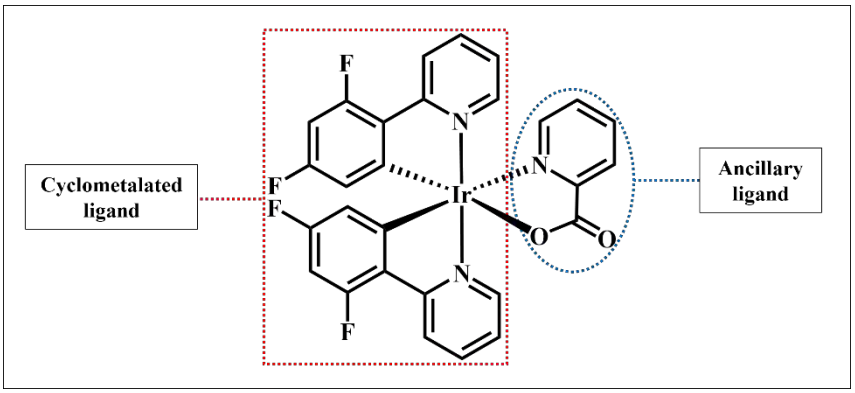
(Kritchenkov et al., 2020). Due to their strong spin-orbit coupling which allow for efficient intersystem crossing of singlets to triplets and long lifetimes, cyclometalated iridium(III) complexes have the ability to produce highly efficient emission which makes them suitable for energy transfer and photoredox catalysis and are frequently employed in several applications such as organic light-emitting diodes (OLEDs) as well as photocatalysts for solar energy conversion and synthetic organic chemistry (Schreier et al., 2022).

Additionally, cyclometalated iridium(III) complexes have other unique photophysical properties such as emission wavelengths spanning the entire visible spectrum and extending into the near infrared (Zhang et al., 2020; Zhang & Qiao, 2021). Furthermore, they also display very quick triplet radiative decay due to their notable spin-orbit coupling which results in extremely high quantum yields for photoluminescence (Cañada et al., 2020). Besides, iridium(III) complexes are highly advantageous to eliminate background autofluorescence interferences due to having phosphorescence lifetimes in the microsecond range, hundreds or thousands of times longer than fluorescence lifetimes. In addition, iridium(III) complexes have much shorter lifetimes compared to lanthanides, photoluminescent materials and other d^6 or d^8 transition metal complexes, which allow rapid signal acquisition and reducing the time the cells are exposed to the excitation light source (Zhou et al., 2022). Their excited-state and redox features are also tuneable through ligand and coordination environment modifications which makes them suitable for a wide range of applications (Schreier et al., 2022). Hence, cyclometalated iridium(III) complexes have been widely studied and utilised in photophysical and photochemical studies due to their remarkably favourable properties.

Majority of synthesised iridium(III) complexes can be classified into two types which are homoleptic or heteroleptic complexes that utilise three bidentate ligands (Tao & Wong, 2023). Homoleptic iridium(III) complexes are consist of three identical ligands, while heteroleptic iridium(III) complexes are distinguished by the presence of different ligands. Heteroleptic iridium(III) complexes are composed of two equivalent C^N ligands which are known as cyclometalated ligand as well as an extra ancillary ligand (Burlov et al., 2023). The photophysical, electrochemical and electroluminescent properties of iridium(III) complexes can easily be adjusted though the modification of cyclometalated and/or ancillary ligands by the addition of functionalised substituents (Li et al., 2022). Figure 1.4 depicts the structure of a well-known cyclometalated heteroleptic iridium(III) complexes, bis (2-(4,6-difluorophenyl)pyridinato-C^2,N)(picolinato)iridium(III), or FIrpic (Adachi et al., 2001).

Figure 1.4

Structure of heteroleptic cyclometalated iridium(III) complex



Adapted from Adachi et al., 2001

1.5 Cyclometalating Ligand

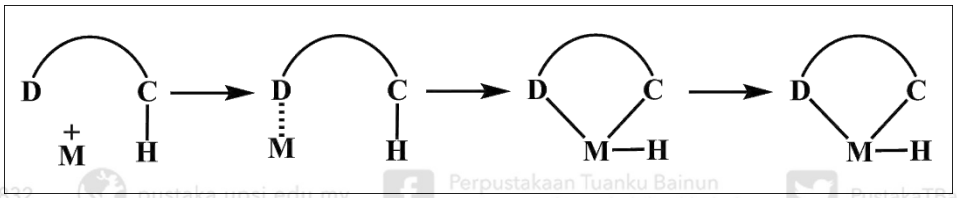
Three identical bidentate monoanionic ligands that surrounded one iridium(III) core ion is the foundation structure of homoleptic cyclometalated iridium(III) complexes (Kapturkiewicz, 2016). Whereas heteroleptic cyclometalated iridium(III) complexes are commonly incorporated with two bidentate cyclometalating ligands (HC^N) which are often similar and an ancillary ligand (L or X^Y) within the coordination sphere of the iridium centre, represented by the general formula $[Ir(C^N)_2(X^Y)]^n$, in which n =+1, 0, -1 (Monti et al., 2021). The majority of the cyclometalating ligands consists of one neutral coordinating component and one anionic component. The Ir–C bond formed between the iridium(III) ion and the carbon atom of C^N ligands is generally strong enough and equivalent to covalent bonds, which result in a structure that is both multiply bonded and compact, with significant electronic interactions occurring between the *d*-orbital of the iridium(III) ion and the π-orbital of the ligands (Kapturkiewicz, 2016). The distinguishable room temperature phosphorescence that is characteristic of cyclometalated iridium(III) chelates are caused by the presence of a heavy metal ion along with a significant spin-orbit coupling effect (Kapturkiewicz, 2016).

Additionally, the fundamental investigations into the core synthetic pathway was led by the rapid evolution of cyclometalated complexes. Cyclometalation takes place when a metal directly interacts with an aromatic carbon–hydrogen (C–H) bond, especially when that bond is adjacent to an electron-donating group like nitrogen as the donor group plays a crucial role in facilitating the metalation process (Chi & Chou, 2010). Figure 1.5 presents the schematic representation of the cyclometalation reaction pathway. In the reaction pathway, the symbol D signify the ancillary donor that may

establish an initial dative bond with the transition metal, which assists in positioning the nearby C–H bond in close proximity to the metal, thereby easing the reaction with the C–H bond. Following this, the intra-molecular cleavage of the C–H bond occurs, resulting in the formation of a metal-carbon bond, which creates a metal-containing cyclic framework and generates a metal–hydride (M–H) fragment. The hydride is then removed (hydride abstraction), which stabilises the system and produces the final metallacyclic complex (Chi & Chou, 2010).

Figure 1.5

Schematic representation of the cyclometalation reaction pathway



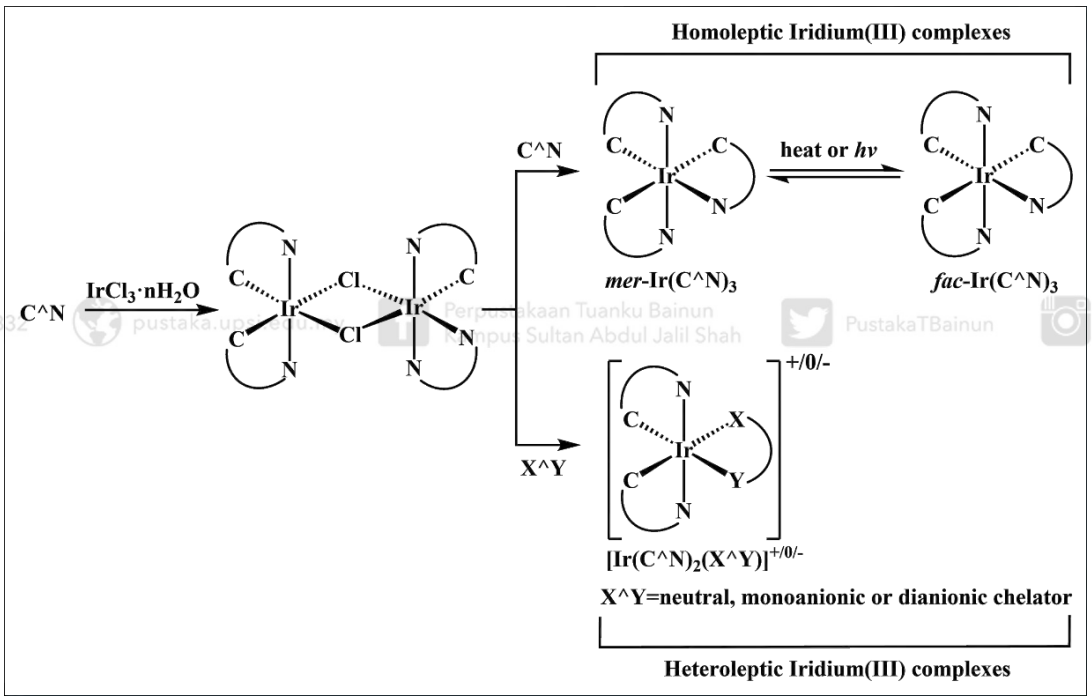
Adapted from Chi & Chou, 2010

Generally, the properties of cyclometalated complexes can be modified through various methods. The overall properties of the complexes are possible to be precisely adjusted by altering the stereoelectronic parameters of the cyclometalated ligands as the correlation between ligands and the properties of complex in cyclometalated compounds can be significantly strong (Zucca & Pilo, 2021). The photophysical properties of metal complexes such as brightness and wavelength emissions are influenced by the molecular structure of the cyclometalated ligands (Abbas et al., 2020; Grzelak et al., 2019). The substitution of electron-donating or electron-withdrawing groups, which may be attached to the phenyl group and function as carbanion donors, or the ligands that serve as heteroatom donors are among the factors influencing photoluminescent emission in metal cyclometalated complexes (Adeloye, 2019). The

schematic illustration of the molecular structures and synthetic routes of homoleptic and heteroleptic cyclometalated iridium(III) complexes are depicted in Figure 1.6. Besides, the selection of appropriate third ligands such as neutral N^N ligands, ionic C^C ligands or monoanionic C^N ligands can control the charge of iridium(III) complexes (No, 2025).

Figure 1.6

The molecular structure and synthetic pathways of the homoleptic $Ir(C^N)_3$ and heteroleptic $Ir(C^N)_2(X^Y)$ complexes



Adapted from Babón et al., 2023 and No, 2025

1.6 N-Heterocyclic Carbenes (NHCs) Ligand

N-heterocyclic carbenes (NHCs) are cyclic compounds that consist of a divalent carbon atom which bonded to at least one nitrogen atom. The alteration on the size of carbene ring, the presence of substituent moieties on nitrogen atoms and additional atoms within

the heterocycle can produce various types of NHCs with different electrical properties (Bharti et al., 2022). NHCs have become essential ligands within decades due to their ability for stabilising unusual oxidation states and coordination modes of both transition metals and main group elements. Moreover, NHCs possess unique features such as highly versatile ligands, have strong electron-donating properties and relatively weak electron-accepting properties that are capable of forming robust metal–ligand bonds (Bonfiglio & Mauro, 2020).

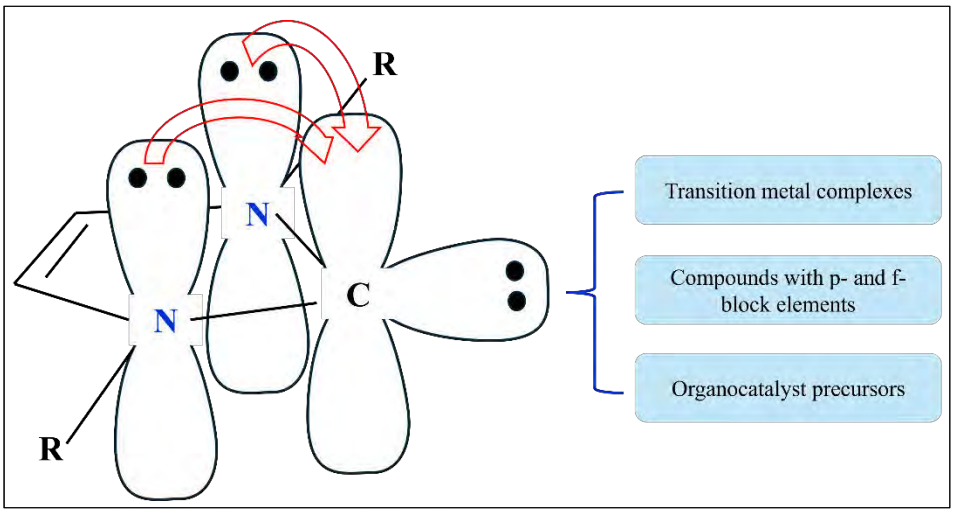
Furthermore, NHCs have been extensively used as ligands on blue-emitting iridium(III) complexes due to their high field strengths (He et al., 2021). The lowest unoccupied molecular orbital (LUMO) for homoleptic iridium(III) complexes with cyclometalating NHCs is strongly destabilised by strongly σ-donating and weakly π-accepting NHCs, which increases the energy of the emitting triplet state and makes these complexes capable to be use as phosphorescent blue emitters (Mackenzie et al., 2023). The first iridium(III) complex with NHCs ligand, phenyl-3-heptylimidazolin-2-ylidene ligand was reported by Lappert and coworkers in 1982 (Hitchcock et al., 1982).

Numerous NHCs have astounding stability can be attributed to both steric and electronic influences (Scattolin & Nolan, 2020a). The high stability of the carbene in terms of reactivity was due to the presence of large, bulky groups near the carbene carbon which aids in protecting the molecule from self-reaction, that could lead to dimerization. More significantly, the electronic stabilisation of the carbene is due to the presence of nitrogen atoms adjacent to the carbene carbon which play a vital role by donating electron density due to their π-donor nature, which assists in filling the vacant

p-orbital on the carbene carbon (Scattolin & Nolan, 2020a) as shown in Figure 1.7.

Figure 1.7

The electronic stabilisation of classical N-heterocyclic carbenes (NHCs) is achieved through π-donation from neighbouring nitrogen atoms

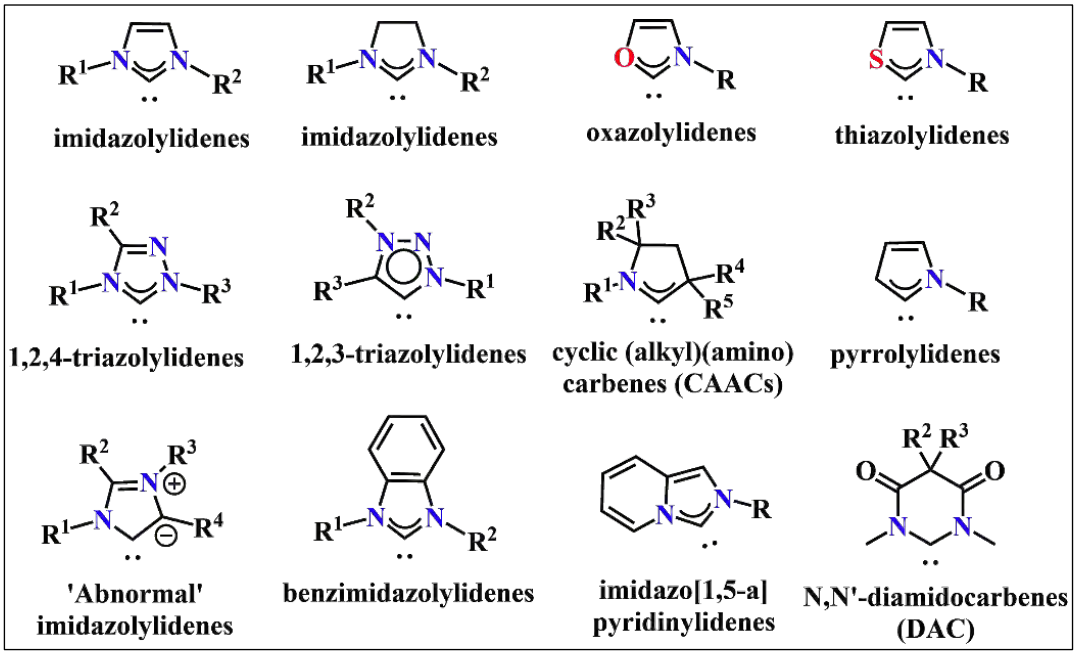


Adapted from Scattolin & Nolan, 2020

Additionally, extra stability can be achieved by NHCs that are based on heteroaromatic or fused heteroaromatic due to their partial aromaticity (Scattolin & Nolan, 2020). Besides, nitrogen heterocycles are fundamental in defining the properties of NHCs (Bharti et al., 2022). A majority of NHCs are five-membered heterocycles, and the majority are derived from the imidazole and imidazolydiene molecules (Cazin, 2011) as shown in Figure 1.8 and among these, the most commonly employed are imidazolylidenes, imidazolidinylidenes, pyrrolylidenes, oxazolylidenes, thiazolylidenes and triazolylidenes (Scattolin & Nolan, 2020). Some structural features of imidazolylidene are similar in all variants of NHC, which contribute to the stabilisation of carbenes and changes in the structure and substituents of imidazolylidene develops diverse behaviour in NHCs (Bharti et al., 2022).

Figure 1.8

Examples of some important classes of NHC



Adapted from Scattolin & Nolan, 2020

1.7 Organic Light Emitting Diode (OLED) Application

Organic light-emitting diodes (OLEDs) function as coloured light sources and employed in the displays of smartphones and television screens, in addition to being used in lighting panels (Hong et al., 2021). Currently, OLEDs are predominantly dominating the portable display sector and are significantly challenging the large-area display market with commendable efficiency and operational reliability. In particular, major smartphone and smartwatch manufacturers such as Samsung, Apple, LG, Sony, Nokia, Huawei, Xiaomi, Oppo, OnePlus and Vivo are promoting their flagship products featuring high-quality OLED screens (Siddiqui et al., 2023). The attractiveness of OLEDs lies in their ability to provide high efficiency while remaining lightweight,

exceptional colour quality, a broad viewing angle of 180º, a very fast response rate and authentic black colour in display applications (Cai & Su, 2018).

OLED devices are capable of emitting light from either entirely organic molecules or organometallic molecules (Kirlikovali & Spokoyny, 2017). The process of light emission in OLED involves the recombination of electrons and holes, leading to the production of 25% singlet excitons and 75% triplet excitons. Fluorescent emitters which are generally highly conjugated organic molecules are unable to access the triplet excitons and consequently lose the remaining energy as heat. In contrast, OLEDs that feature phosphorescent emitters can achieve efficiencies four times higher compared to OLEDs with fluorescent emitters (Kirlikovali & Spokoyny, 2017).

Numerous application across various field have widely utilised luminescent transition metal complexes including as phosphorescent emitters for OLEDs (Benjamin et al., 2016). The ability of cyclometalated iridium(III) complexes to harvest both singlet and triplet excitons which can result in internal quantum efficiencies that can approach 100% have attracted considerable attention in OLEDs (Benjamin et al., 2016). Besides, cyclomelated iridium(III) complexes also possess various interesting feature such as synthetic versatility, colour tunability, good stability in chemical and photochemical, relatively short excited-state lifetimes on the microsecond time scale and highly efficient emission due to a combination of triplet metal-to-ligand charge transfer (MLCT) states and π–π* transitions of the ligands (Benjamin et al., 2016).

1.8 Problem Statement

OLED technology are still struggling with its material systems and the architecture of OLED devices (Hong et al., 2021). There is a pressing need for further innovations to improve the efficiency, lifespan and light output of OLED devices. Red, green and blue (RGB) emitters are the three primary colours required in order to yield full-colour luminescence (Lan et al., 2022; Luo et al., 2023) and these primary colours are the most preferred ones to develop RGB devices (Santos & Marques, 2022). One of the primary challenges is the limited lifespan of blue OLEDs when compared to their red and green counterparts (Hong et al., 2021). Numerous high-potential red and green emitters have been successfully developed and are widely utilised in commercial OLED products. However, high-quality blue emitters continue to pose a significant challenge and the advancement of blue-light emitting materials that demonstrate high efficiency and prolonged lifetimes remains an ongoing area of interest. The development of stable deep-blue emitter is necessary to increase colour spectrum and decrease power consumption of phosphorescent organic light-emitting diodes (Yun et al., 2022).

The lack of blue phosphorescent compounds that exhibit high photoluminescence quantum yields and photostability continues to pose a significant challenge despite the abundance of reports concerning the photophysical properties of cyclometalated transition metal complexes, (Kinzhalov et al., 2022). Iridium(III) complexes are considered the most favourable emitters in OLED compared to other transition metal complexes due to their remarkable properties such as relatively high phosphorescence quantum yield, short triplet lifetimes, excellent colour tunability from blue to deep red, and excellent thermal and electrochemical stability (Ding et al., 2020).

However, even with wide investigation on the photophysical properties of cyclometalated iridium(III) complexes, the development of blue-phosphorescent compounds with high photoluminescence quantum yield (PLQY) are still challenging (Lan et al., 2022). Hence, the development of highly effective blue phosphorescent iridium complexes will be easier if all the previously mentioned issues could be solved.

To generate blue luminescence, it is necessary for the energy of a triplet state in an organometallic emitter to be sufficiently high, which may simultaneously result in the thermal population of higher-lying triplet metal-centred (MC) ligand-field excited states (Kinzhalov et al., 2022). These states are non-emissive, leading to a decrease in the photoluminescence quantum yield Φ and placing electrons into metal-ligand σ^*-antibonding orbitals, which causes the gradual degradation of the compound due to ligand loss. One of the proposed solutions is the use of a secondary set of σ-donor ligands, which would further destabilise the unoccupied *d*-orbitals and their corresponding metal centred excited states, thus improving the efficiency and stability of blue phosphorescence (Kinzhalov et al., 2022).

In general, one of the effective molecular design strategy for deep blue phosphors revolves around the introduction of electron-withdrawing or electron-donating groups at selective positions on the cyclometalated (C^N) ligands (Feng et al., 2016). Typical blue iridium complexes with 2-phenylpyridine (ppy) or bipyridine (pypy) ligands are widely used by researchers because of their inherent benefits, which include high PLQYs, easy synthesis, and easy control over colour emission from sky blue to deep blue (Kang et al., 2021; Zaen et al., 2019). The employment of

phenylpyridine as a cyclometalating ligand framework, with suitable modifications represents a strategic approach to the development of efficient blue phosphors (Lan et al., 2022). Besides, the introduction of methoxy groups at the meta position relative to the iridium centre was proven to exhibit an inductive electron-withdrawing effect (Tao & Wong, 2023).

1.9 Research Objectives

This study was conducted for the following purposes:

1. To synthesise ligands, cyclometalated dimers and iridium(III) complexes.
2. To characterise the synthesised compounds to confirm their structures and compositions.
3. To analyse the photophysical properties of the synthesised cyclometalated iridium(III) complexes.

1.10 Research Hypothesis

There are several common strategies to achieve blue or deep blue emission. First, it is hypothesised that the incorporation of a secondary set of strong σ-donor N-heterocyclic carbene (NHC) ligands into the coordination sphere of the iridium centre will enhance the bonding interactions and emit blue phosphorescence. The NHC ligand which is known for its significant σ-donating strength, was selected as an ancillary ligand to

raise the *d–d** transition state and improve the emission quantum yield (Li et al., 2022).

Besides, it is hypothesised that the incorporation of NHC ligands into the coordination sphere of the iridium centre will raise the lowest unoccupied molecular orbital (LUMO) energy levels, leading to a broader band gap and potentially higher quantum yields of pure deep blue photoluminescence in OLED devices. This effect arises from the strong σ-donating nature of carbene ligands, which can destabilise the unoccupied *d*-orbitals and thus improving the stability and efficiency of blue phosphorescence (Kinzhalov et al., 2022). This could result in higher quantum yields for pure deep blue photoluminescence and better performance than expected in OLED devices.

In addition, it is also hypothesised that modifying cyclometalated (C^N) ligands offers a strategic approach for enhancing the performance of blue phosphors (Lan et al., 2022). The incorporation of electron-donating or electron-withdrawing substituents on the phenyl ring is known to significantly widen the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) (Tao & Wong, 2023).

Hence, the incorporation of electron-donating alkoxy group on the phenyl ring of the cyclometalated ligand and the utilisation of strong σ-donor N-heterocyclic carbene (NHC) ligands within the molecular structure of the complexes are expected to increase the HOMO-LUMO gap and promoting blue emission from the synthesised complexes.

1.11 Research Significant

There is a great deal of importance attached to the design and development of new iridium(III) complexes, as they will provide a fundamental study of how alternative methods can be used to enhance luminescence efficiency in solid-state lighting (SSL), in particular semiconductor light-emitting diodes (LEDs), OLEDs, and polymer light-emitting diodes (PLEDs). 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.

Hence, it is imperative to have detailed and novel research into this topic to contribute to a couple of high lighting efficiency with low fabrication cost products due to this large potential of the iridium(III) complex in SSL technology. For instance, due to their unique disruptive features such as energy-saving, wide viewing angles, fast response times, high contrast, and high colour purity, OLEDs are poised to become the dominant technology in flat panel displays and solid-state lighting in the coming vears (Swayamprabha et al., 2021)