STRUCTURAL MODIFICATION OF LIGHT-EMITTING IRIDIUM-BASED IONIC TRANSITION METAL COMPLEXES AND THEIR USES IN LIGHT-EMITTING ELECTROCHEMICAL CELLS (LECs)

Dissertation

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vorgelegt von
Jude Eko Namanga

Bochum – 2015
I declare that this dissertation is my own original work and was written without any unauthorized help. All references and other sources used in the work have been appropriately acknowledged. Further, I declare that no part of this dissertation has been submitted elsewhere for the purpose of academic examination, either in its original or similar form.

Jude Eko Namanga, October 2015

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1\textsuperscript{st} referee: Prof. Dr. Anja-Verena Mudring

2\textsuperscript{nd} referee: Prof. Dr. Anjana Devi

Chairman: Prof. Dr. Martin Muhler
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Abstract

The aim of this research is to improve the efficiencies and stability of light emitting electrochemical cell (LEC) devices based on ionic iridium transition metal complexes via two different approaches: 1) By designing and synthesizing efficient and stable ionic iridium transition metal complexes for application in LEC devices. 2) By optimizing the LEC device operating conditions (varying parameters such as the average current density and duty cycle of the applied pulsed current).

Chapter 1 presents a general introduction to the work highlighting the evolution in the lighting technology over the years to the invention of organic lighting. It also introduces the LEC technology (one type of organic lighting) together with some of its achievements. The chapter ends with a motivation for this research work.

Chapter 2 focuses on the design and synthesis of cyclometallated ligands to be used in the synthesis of efficient and stable Ir-iTMCs (iridium ionic transition metal complexes). Chapter 3 focuses on the synthesis of efficient and stable red to deep red emitting Ir-iTMCs and their incorporation in LEC devices to investigate their electroluminescence properties. Chapter 4 covers the synthesis of efficient and stable yellow to deep green emitting Ir-iTMCs and with more focus in the green region and fabrication of LEC devices to investigate their electroluminescence properties. Chapter 5 describes the synthesis of Ir-iTMCs with sky blue to blue emissions and their electroluminescence behaviors. Chapter 6 features preliminary studies on the influence of different parameters of the device operating conditions on the overall performance of the LEC devices. Finally Chapter 7 gives a general conclusion to the work and outlook for further research efforts.
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List of acronyms and/or abbreviations

A/m² Amper per meter square
Å Ångström
[BMIM]⁺ 1-butyl-3-methylimidazolium
bpy 2,2'-bipyridine
biq 2,2'-biquinoline
Bphen bathophenanthroline or 4,7-diphenyl-1,10-phenanthroline
bzqu benzo[h]quinoline
C^N ligand cyclometallating ligand
CV cyclic voltammetry
CF₃ trifluoromethane
cd/m² candela per meter square
cd/A candela per Amper
DFT density functional theory
DMSO dimethyl sulfoxide (d₆)
dmbpy 4,4'-dimethyl-2,2'-bipyridine
dmBphen bathocuproine or 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline
E₁/₂ standard half-cell potential
EW electron withdrawing
ED electron donating or electrodynamic model
ECD electrochemical doping model
eV electron Volt
EQE external quantum efficiency
Et₂O diethyl ether
SSL solid-state lighting
LEC light-emitting electrochemical cell
PLECs polymer light emitting electrochemical cells
LED light-emitting diode
OLED organic light-emitting diode
Ir-iTMCs iridium ionic transition metal complexes
iTMC ionic transition metal complex
IL ionic liquid
HOMO highest occupied molecular orbital
LUMO lowest unoccupied molecular orbital
SOC spin orbit coupling
LLCT ligand to ligand charge transfer
LMCT ligand to metal charge transfer
MLCT metal to ligand charge transfer
MC metal centered
³MC triplet metal centered excited state
LC ligand centered
Δ₀ octahedral field splitting
lm  luminance
lm/W  lumens per Watt
t1/2  halflife or lifetime
PF6  hexafluorophosphat
δ  chemical shift [ppm]
ppm  parts per million
N^N  ancillary ligand
4Fppy  2-(4-fluorophenyl)pyridine
3Fppy  2-(3-fluorophenyl)pyridine
3,4Fppy  2-(3,4-difluorophenyl)pyridine
3,5Fppy  2-(3,5-difluorophenyl)pyridine
P5Fpy  5-fluoro-2-phenylpyridine
4Fp5Fpy  2-(4-fluorophenyl)-5-fluoropyridine
3,5Fp5Fpy  2-(3,5-difluorophenyl)-5-fluoropyridine
pbpy  6-phenyl-2,2´-bipyridine
5dmbpy  5,5´-dimethyl-2,2´-bipyridine
dtb-bpy  4,4´-di-tert-butyl-2,2´-bipyridine
phen  1,10-phenanthroline
na-iqu  1-(1-naphthyl)isoquinoline
2na-2qu  2-(2-naphthyl)quinoline
3Fpqu  2-(3-fluorophenyl)quinoline
4Fpqu  2-(4-fluorophenyl)quinoline
3Fp-iqu  1-(3-fluorophenyl)isoquinoline
4Fp-iqu  1-(4-fluorophenyl)isoquinoline
2na5Fpy  5-fluoro-2-(2-naphthyl)pyridine
na5Fpy  5-fluoro-2-(1-naphthyl)pyridine
phn-iqu  1-(9-phenanthryl)isoquinoline
phn5Fpy  5-fluoro-2-(9-phenanthryl)pyridine
py3,5mpz  (3,5-dimethyl)-1H-pyridylpyrazole
3,5ppz  3,5-difluorophenyl-1H-pyrazole
pyimz  pyridylimidazole
PEDOT:PSS  poly(3,4-ethylenedioxythiophene):poly(styrene sulfonic acid)
NMR  nuclear magnetic resonance
MeCN  acetonitrile (d3)
UV-Vis  ultraviolet visible spectroscopy
PL  photoluminescence
PLQY  photoluminescence quantum yield
CFL  compact fluorescent light bulb
OLT  optical line termination
Chapter 1

Introduction
Chapter 1

Introduction

1.1 The world of lighting technology

A quest for a safer, more efficient and stable light source has led to a constant evolution of lighting technology. There has been a continuous progress in the improvement of lighting technologies: from oil lamps, candles, gas lamps age to the 19th century developed and still used incandescent lamp and, in the 20th century through fluorescent lamps to halogen and high pressure discharge lamp [1-5]. These different lamp types were better light source compared, but also had significant draw backs such as the very low efficiencies of the incandescent lamp or the poor colour quality of low pressure discharge lamps [6,7]. The invention of Light Emitting Diodes (LED) was a significant breakthrough in lighting technology. The phenomenon of light emission by a material under an electrical bias (electroluminescence (EL)) was first observed by H.J. Round of Marconi Labs, on a crystal of silicon carbide [8]. In the mid 1920s, Losev also reported the EL of zinc oxide and silicon carbide crystals when subjected to an electrical bias [9]. Since then, tremendous research has lead to the different types of LED for various applications including lighting [10-14].

1.2 Organic electroluminescence

Electroluminescence of an organic molecule was first observed for anthracene and the first organic EL device, based on a polymer, polyvinyl carbazole, was demonstrated in 1957 [15, 16]. The replacement of the inorganic light emitting material in LEDs led to their organic counterpart “Organic Light Emitting Diodes (OLEDs)”. In OLEDs, the light emitting material is typically a polymer [17], a small fluorescent molecule [18] or a phosphorescent transition metal complex embedded in a charge transporting matrix [19-22]. One major advantage of OLEDs over
inorganic LEDs is that they can be used in large area lighting applications by even using low cost processing techniques such as inkjek printing and roll-to-roll coating [23-25]. Intense research in OLED technology led to the improvement of efficiencies, brightness and lifetimes so that OLED flat panel displays for computer monitors and TV screen are commercialized [26]. Yet OLEDs for lighting applications are awaiting a breakthrough for global commercialization. For lighting applications, a typical OLED consist of several layers (hole injection layer (HIL), hole transporting and electron blocking layer (HTL/EBL), electron transporting and hole blocking layer (ETL/HBL) and electron injection layer (EIL), figure 1.1) to facilitate injection and transportation of charges (holes and electrons) to the emitting layer (EML) [27]. The preparation of such complex multilayer stacks is almost exclusively achieved by vacuum evaporation. This is a technically quite demanding and also economically expensive process. Although recently the preparation of OLED devices facilitated by partial or full solution processes have been reported [28-31]. Unfortunately, the performances of devices prepared this way are still significantly lower compared to vacuum evaporated OLEDs [32-34]. Rigorous encapsulation, air sensitive multilayer stack required for charge injection and use of air sensitive low work function metal for the cathode are some of the high demands limiting the OLED technology for lighting application.

These drawbacks can be overcome by Light Emitting Electrochemical Cells (LECs) which feature a less complex device architecture (figure 1.1). The layer structure can be prepared by easy solution based processes such as spin coating, inkjek printing and roll-to-roll printing. No additional layers are required for charge injection, allow the use of non air sensitive metals such as aluminium as cathode and less rigorous encapsulation are some of the advantages making the LEC technology very promising for lighting application.
1.3 Light Emitting Electrochemical Cells (LECs)

LECs consist of a single active layer composed of an ionic material sandwiched between two electrodes: generally an indium tin oxide (ITO) anode and aluminium (Al) cathode (figure 1.1). The first LEC device was reported by Pei et al., in 1995 [35] based on a polymer blend of a conjugated polymer, a conducting polymer and an inorganic salt. LECs based on polymer are generally referred to as PLECs [35-37]. A year later, another type of LEC based on ionic Transition Metal Complexes (iTMC-LECs) was reported by Lee et al., [38]. iTMC-LECs differ from PLECs in that they are intrinsically ionic and do not need an ionic additive to form the ionic emissive layer.

1.4 Device operation mechanism of LECS

Until now, the general operation mechanism of a LEC is still not completely understood and under discussion. Two models have been presented to explain the different processes involved during the operation of a LEC device. One of these models is the Electrodynamic Model (ED).

The ED states that upon subjecting a LEC device to a bias, ions migrate in the applied electric field which leads to the formation of electric double layers at the
electrode interfaces which facilitates charge injection into the emissive layer. This model also states that, the potential within the LEC drops mainly across the electrode/organic interface and light emission occurs from the so-called field free region in the bulk of the emissive layer (figure 1.2: a and c).

On the other hand, the Electrochemical Doping Model (ECD) argues that the organic semiconducting materials behave p-type and n-type like near the anode and cathode, respectively. As a result, highly conducting p-doped and n-doped regions are formed which facilitate charge injection into the emitting layer (figure 1.2: b and d). The critical view of the ECD model is that the potential within the LEC drops mainly across the p-i-n junction where light emission occurs. So far the debate on which model best describes the LEC operation mechanism is still on-going [27,39-43].

**Figure 1.2**: Idealized electronic and ionic charge distribution, potential profiles and electric fields in light-emitting electrochemical cells. Potential profiles, charge distributions and electric fields as predicted by (a), (c), the ED and (b), (d) the ECD models. The thick black line in (a) and (b) represents the potential profile (in eV). Furthermore, the yellow line in (c) and (d) indicates the electric fields [27].
1.5 Transition metals in iTMC-LECs from a spectroscopic view: the importance of iridium

Mostly low spin (ls) d$^6$ metal cations in octahedral surrounding are used in iTMC-LECs. The d-orbitals of the TM (transitions metal) splits upon interaction with an octahedral ligand field into three stabilized $t_{2g}$ ($d_{xy}$, $d_{xz}$, $d_{yz}$) and two destabilized $e_g$ ($d_{z^2}$, $d_{x^2-y^2}$) orbitals as shown in Figure 1.3. Several factors contribute to the energy difference ($\Delta_o$) between these two levels; the oxidation state of the metal center (the higher the oxidation state, the higher the $\Delta_o$ splitting), the size of the d orbitals (for nd orbitals, where n is the principal quantum number, $\Delta_o$ progressively increases with n from n = 3 to n = 5) and finally, the field strength exerted by the ligands, following the spectrochemical series.

![Figure 1.3: Low spin d$^6$ orbital configuration in octahedral field](image)

In early studies, 3d metals (such as Fe and Cu) were investigated for their use in iTMC-LECs, since they are more abundant and cheaper compared to 4d and 5d metals. Taking Fe$^{II}$ (3d$^6$) as an example, the $\Delta_o$ splitting is very small, hence the lowest-lying excited state is metal centered ($^1$MC) in nature and therefore not emissive (figure 1.4) [44]. A step down the periodic table to the divalent 4d metal Ru$^{II}$ (4d$^6$) ion, the $\Delta_o$ splitting is increased and for the same type of ligand the lowest excited state is a metal-to-ligand charge transfer triplet state ($^3$MLCT). Indeed, a good number of Ru based complexes have been investigated for their application in LECs [45-49]. However, the $^3$MLCT states in these complexes are relatively close to the $^3$MC states which can be thermally populated, opening a way to a competitive radiationless deactivated pathway to either the ground state or degradation
products [45] (Figure 1.4). These drawbacks limit the use of Ru based complexes in LECs. Thus, another step down the periodic table is needed to ensure that the $\Delta_o$ splitting is sufficiently large so that the $^3\text{MC}$ state are located at high enough energies so that they do not affect the emission properties (figure 1.4). This scenario is realized in complex compounds of Os$^{\text{II}}$ (5d$^6$). Unfortunately, the emission of Os(II) complexes are typically in the red region of the visible spectrum due to their low lying $^3\text{MLCT}$ states [51,52].

![Figure 1.4: Qualitative excited state description for Fe$^{\text{II}}$, Ru$^{\text{II}}$ and Os$^{\text{II}}$ metal complexes [41].](image)

Considering all the above mentioned factors affecting the octahedral field splitting $\Delta_o$, Ir$^{\text{III}}$ moves into focus as an ion with suitably high $\Delta_o$ splitting. It is an ion belonging to the third row of the d-block (5d) of the periodic table with fittingly high charge [52]. Consequently, the electronic configuration of Ir$^{\text{III}}$ is always in a low-spin arrangement (t$_{2g}^{6}$e$_g^0$). With this large $\Delta_o$ splitting, the low-lying excited state of iridium ionic transition metal complexes (Ir-iTMCs) lies on one of the ligands. Thus, the emission of Ir-iTMCs generally comes from the MLCT, ligand centered (LC) and ligand-ligand charge transfer (LLCT) transitions (Figure 1.5), making the $^3\text{MC}$ states inaccessible [41].
An additional effect observed in Ir-iTMCs which enhances their efficiency as emitting materials in LECs is spin-orbit coupling (SOC). The high SOC of Ir(III) yields almost unitary intersystem crossing efficiency from singlet to triplet excited states. Therefore Ir(III) complexes always exhibit an efficient spin-forbidden phosphorescence emission [53-56]. The first Ir(III) cationic complex (figure 1.6) for application in LECs was reported by J. D. Slinker et al., in 2004 [57]. Since then, several other Ir(III) complexes have been reported with emission covering the entire visible spectrum [27,41,55,58,59].
1.6 Photophysical properties of Ir-iTMCs

The photophysical properties of Ir-iTMCs are strongly influenced by the nature of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). Thus, it is important to determine the energy and atomic orbital composition of these frontier molecular orbitals to fully understand their photophysical properties [27,41,54]. The HOMO in Ir-iTMCs is a mixture of Ir d-orbitals ($t_{2g}$) and the phenyl π-orbitals of the cyclometalated ($C^N$) ligands, whereas the LUMO is usually located on the neutral ancillary ligand ($N^N$) (Figure 1.7a). With the LUMO and HOMO located on different parts of the Ir-iTMCs, it is possible to fine tune the HOMO-LUMO energy gap difference by either stabilizing the HOMO and LUMO by adding electron withdrawing substituents or by destabilizing the HOMO and LUMO by adding electron donating substituents to the $C^N$ and/or $N^N$ ligands (figure 1.7b).

![Figure 1.7](image.png)

**Figure 1.7:** a) Chemical structure of a typical heteroleptic Ir-iTMC [27], b) Illustration of change in the LUMO-HOMO energy gap with electron withdrawing (EW) or electron donating (ED) groups at the ligand.

Most cationic iridium complexes based on commercially available ligands (for example the archetype complex in figure 1.8) emit light in the orange region of the visible spectrum. In order to have emission with shorter wavelengths, the phenyl rings of the $C^N$ ligands are usually decorated with electron withdrawing groups.
such as –F and –CF₃. On the contrary, decorating the phenyl rings of the C^N ligands with electron donating groups such as alkyl groups will lead to emission with longer wavelengths. It is also possible to either blue shift or red shift the emission wavelength by using strong field C^N and N^N ligands or N^N ligands with a low lying LUMO respectively [27,41,55,60].

1.7 Structural stability of Ir-iTMCs

A detailed study of the electronic structure of Ir-iTMCs revealed generally a σ-antibonding interaction between the nitrogen unhybridized orbital of the C^N ligands and the dz² (one of the e_g) orbital of the iridium cation ³MC level. The antibonding interaction (N_{C^N}–Ir–N_{C^N}) is along the vertical axis (figure 1.8) and its strength strongly depends on the ³MC character of the complex. Metal centered transitions involve the transfer of electrons from the Ir-ðπ-orbitals (t₂g orbitals) to its dσ* orbitals (e_g antibonding orbitals ³MC). The population of the ³MC states increases the strength of the σ-antibonding interaction between the iridium atom and nitrogen atoms of the C^N ligands, leading to an elongation of the N_{C^N}–Ir–N_{C^N} bonds paving openings for nucleophilic attacks on the iridium center. An attack on the iridium center would lead to the opening of the metal complex by cleavage of one of the N_{C^N}–Ir bonds resulting to a non emitting iridium complex [41,61].

![Figure 1.8](image-url)

**Figure 1.8:** a) Chemical structure of a typical heteroleptic Ir-iTMC [Ir(ppy)₂(bpy)][PF₆], b) representation of the valence orbital showing the σ-antibonding interaction between the iridium atom and nitrogen atom of C^N ligands [41,61].
One major drawback of LECs in general is the short lifetime of the devices. The lifetime of a LEC device primarily relies on the intrinsic stability of the Ir-iTMC used therein. So far, the only successful structural modification which led to an increase in the device lifetime was the introduction of an intra-molecular π-π stacking between a substituted phenyl ring on the N^N ligand and the phenyl ring of one of the C^N ligands to overcome the σ-antibonding interaction (figure 1.9) [62].

![Chemical structure of Ir-iTMC with intra-molecular π-π stacking](image)

**Figure 1.9**: Chemical structures of the first Ir-iTMC with an intra-molecular pi-pi stacking between a substituted phenyl ring on the N^N ligand and the phenyl ring of one of the C^N ligand [Ir(ppy)$_2$(pbpy)][PF$_6$].

### 1.8 Synthesis of Ir-iTMCs

In general, where the C^N and N^N ligands are commercially available, the synthesis of Ir-iTMCs involves two steps; firstly, the synthesis of an intermediate chloro-bridge bi-metallic complex of the C^N ligand with general formula [Ir(C^N)$_2$Cl]$_2$, followed by the transformation to the heteroleptic iridium complex by opening of the chloro-bridging bi-metallic complex in the presence of the N^N ligand. The syntheses are carried out under inert conditions in suitable solvents [61-64].

### 1.9 LEC operating conditions and figure of merits

LEC are usually operated either under a constant voltage driven mode or a pulse current mode [65].
1.9.1 Constant voltage driving

Upon biasing a LEC device at a constant voltage (usually voltages less than 5 V), the ions within the emissive layer start migrating toward the oppositely charged electrodes. Accumulation of the migrating ions close to the surface of the electrodes results in the formation of electric double layers which will facilitate the injection of charges into the emissive layer. Under this driving condition, the **luminance** (flux of light emitted by the device, measured in candela per surface unit (cd/m^2)) and **current density** (flux of current flowing through the device, measured in ampere per surface area (A/m^2)) are recorded over time. It was observed that in the constant voltage driven mode, the **turn-on time** (t_{on}: the time needed for the device to reach its maximum luminance,) was fairly long. For example, LEC devices with [Ir(ppy)\(_2\)(bpy)][PF\(_6\)] and [Ir(ppy)\(_2\)(phen)][PF\(_6\)]\\([61]\) (where ppy is 2-phenylpyridine, bpy is 2,2'-bipyridine and phen is 1,10-phenanthroline, figure 1.9) showed turn-on times of 70.2 and 160 hours, respectively. The delay in turn-on times was attributed to the slow ionic movement of the large cationic iridium complex. To solve this problem, an Ionic Liquid (IL) was added to the emissive layer which resulted to a drop in the turn-on times to 7.2 and 6.4 hours for [Ir(ppy)\(_2\)(bpy)][PF\(_6\)] and [Ir(ppy)\(_2\)(phen)][PF\(_6\)], respectively [61].

![Diagram](image)

**Figure 1.9:** Chemical structures of [Ir(ppy)\(_2\)(bpy)][PF\(_6\)] and [Ir(ppy)\(_2\)(phen)][PF\(_6\)].
The decrease in the turn-on times on addition of different ionic liquid (IL) to the emissive layer has been reported [61, 63, 64]. Unfortunately, an improvement in the turn-on time of LEC devices was achieved at the expense of the device lifetime ($t_{1/2}$: the time needed for the device to reach half of its maximum luminance). The drop in $t_{1/2}$ were from 668 to 69 hours and 567 to 73 hours for [Ir(ppy)$_2$(bpy)][PF$_6$] and [Ir(ppy)$_2$(phen)][PF$_6$], respectively. The inverse relationship between $t_{on}$ and $t_{1/2}$ has been confirmed by other authors, but still is not fully understood [66, 67].

1.9.2 Pulse current driving

In the pulsed current driven mode, a pulsed current with a constant current density and frequency is applied to the device while the luminance and voltage are recorded over time. Upon biasing the device, an initial high voltage is observed. This high voltage causes a fast migration of the ions toward the electrodes. An electric double layer is formed which then allows the injection of charges into the emissive layer. At this point, the operating voltage drops rapidly to a value required to sustain the applied current density. It has recently been reported that the pulse current driven mode gives an overall better device performances compared to the constant voltage driven mode [65].

Other figures of merit includes: **Efficacy** (or current efficiency): Emitted light per electric flux, measured in candela per ampere (cdA$^{-1}$). **Power efficiency**: Flux of light per electric input, measured in lmW$^{-1}$. **Total emitted energy ($E_{tot}$)**: It is calculated by integrating the radiant flux of the device vs. time from $t = 0$ (application of bias) to $t = t_{1/5}$ (time needed for the luminance to drop to 1/5 of its maximum value). When $E_{tot}$ is divided by the electrode area, it yields the total emitted energy density $U_{tot}$ which allows devices having electrodes of different shapes to be compared. **External quantum efficiency (EQE)**: The ratio of photons emerging from the device per injected electron. EQE is also defined through the equation [41,68]:
\[ EQE = b \phi / 2n^2 \]  

Where \( b \) is the fraction of electrons and holes that recombine to form excitons, \( \phi \) is the exciton-to-photon generation efficiency and \( 1/2n^2 \) is the amount of photons that can escape the device or outcoupling efficiency.

1.10 Motivation

The future of solid state lighting is shifting more and more towards organic lighting with the recent shortage of rare metals which are used in CFLs and LED. In organic solid state lighting, LECs possess several advantages over OLEDs such as simpler device architecture, cheap solution processable techniques like spin coating, slot-die coating and roll-to-roll printing and not being sensitive to the work function of the electrodes allowing the use of air stable electrodes. All together, LECs are promising as a low cost large area future lighting technology. Although LECs possess all the above mentioned advantages over OLEDs, their device performance and stability are by far inferior compared to those of OLEDs. The first aim of this research work is to design and synthesize new stable and efficient Ir-iTMCs emitting in the three main colours of red, green and blue with high color purity and then to fabricate LECs with the new Ir-iTMCs and strive for higher device performance and stability through device optimization processes.
1.11 References

1. A. Burghart, B. Müller, W. Hanseder, 100 years of OSRAM, 2006.
15. R. L. Zhigang, Organic light-emitting materials and devices, 2015, Taylor and Francis group, LLC.
25. J. Hast, M. Tuomikoski, R. Suhonen, K. Väisänen, M. Välimäki, T. Maaninen, P. Apilo, A. Alastalo, A. Maaninen, *Roll-to-Roll Manufacturing of Printed OLEDs*, ISSN 0097-966X/13/4401-0192-$1.00 \copyright$ **2013** SID.
Chapter 2

The Ligands: Designs toward efficient and stable Ir-iTMCs
Chapter 2

The Ligands: Designs toward efficient and stable Ir-iTMCs

2.1 Introduction

The overall performance of a LEC device incorporating a cationic iridium metal complex in the active layer partly depends on the intrinsic properties of the Ir-iTMC. The intrinsic properties such as the photophysical properties and stability of the Ir-iTMCs strongly depend on the types of ligands involved in the molecular structure of the complexes. As already mentioned in chapter 1, so far, Ir-iTMCs have been realized using two types of ligand: a cyclometallating (C^N) ligand and an ancillary (N^N) ligand with each of these ligands contributing to the different frontier molecular orbitals (MOs) of the complex. Early works on Ir-iTMC syntheses for LEC application were focused on the use of ligands designed mainly to tune the emission wavelength of the complexes [1-5]. The C^N ligands of early reported Ir-iTMCs were based on the phenylpyridine parent structure. Over the years, new heterocyclic C^N systems (such as phenylazole and thienylpyridine) have been used in Ir-iTMCs for LEC application [6-12]. Diimine ligands remain the ligand of choice as the ancillary ligands as they are readily available [4,5,13,14]. The achievement of Ir-iTMCs with emission from the blue to red regions of the visible spectrum was a promising step towards obtaining white light emitting LECs which require a balanced mixture of Ir-iTMCs with red, green and blue or orange and sky-blue emissions. Nevertheless, LEC devices with emission covering the visible spectrum demonstrated short lifetimes and/or low efficiency [4,5]. Some reported approaches to overcome these major drawbacks are highlighted below.
2.2 Approaches to improve the efficiency of LEC devices through structural modification of the Ir-iTMCs

One of the identified causes of the low efficiency of LEC devices is the quenching of luminance by exciton-exciton interaction during device operation due to the very small inter-complex distances within the thin film of the emissive layer [15,16]. To solve this problem, commercially available ligands with bulky side groups were used in the syntheses of Ir-iTMCs. In addition, new C^N and N^N ligands with higher steric demand were designed, synthesized and used for new bulky Ir-iTMCs [17,18,19]. One of the widely used commercially available bulky N^N ligand is the 4,4-di-tert-butyl-2,2-bipyridine (dtb-bpy). In particular, the dtb-bpy ligand is seen as a suitable N^N ligand due to the bulky di-tert-butyl groups substituted at the 4th position of each of the pyridine rings (figure 2.1). Several authors including Slinker et al., [19,20] and Bolink et al., [21-23] have demonstrated the improvement in the efficiencies of LECs by increasing the inter-complex distances by using dtb-bpy among others as the N^N ligand. However, Ruben et al. [17] showed that there is a certain limit above which further increase in the inter-complex distances is detrimental to the performance of the LEC device.

![Chemical structure of 4,4-di-tert-butyl-2,2-bipyridine (dtb-bpy)](image)

**Figure 2.1:** Chemical structure of 4,4-di-tert-butyl-2,2-bipyridine (dtb-bpy).
2.3 Improving the lifetime of LEC devices through structural modification of the Ir-iTMCS

On the other hand, the short lifetime of LEC devices is attributed to the presence of strong σ-antibonding interactions of the ligand with the Ir\textsuperscript{III} ion within the Ir-iTMCS (Chapter 1, 1.7). The only reported direct structural modification of the complex to overcome the antibonding interactions was the introduction of π-π stacking between a phenyl ring substituted at the 6\textsuperscript{th} position of one of the pyridine ring of the N^N ligand and the phenyl ring of one of the C^N ligands. The success of this approach made the 6-phenyl-2,2-bipyridine (pbpy) type ligands suitable for the design of new approaches to improve the stability of cationic iridium complexes [17,24,25]. The π-π stacking approach was first reported in a complex with only six membered aromatic rings demonstrating an enhancement in LEC device lifetime by using this complex [26]. Similar enhancement in a LEC device lifetime was observed when a π-π stacking was introduced in a complex with a phenylpyrazole type C^N ligands [27]. Notwithstanding, the inability of the π-π stacking to improve the stability of several different reported Ir-iTMCS over the years have recently led to a question by researcher if the π-π stacking indeed leads to stability improvement [14,28,29].

2.4 Results and discussion

Tremendous research efforts have led to significant improvement in the overall device performance and stability of LECs. However, the achieved performances are still not good enough to be considered for practical applications. For improvement of efficiencies and/or lifetime of LEC devices, four different groups of C^N ligands were designed and synthesized to be used in the syntheses of long-time stable Ir-iTMCS with emission maxima covering the whole visible spectrum.

The first group of ligands contains non-substituted ligands. Some of these ligands contain extended conjugated π-systems (such as naphthyl, quinoline and
phenanthryl) to be used in the synthesis of Ir-iTMCs that emit in the red region of the visible spectrum. This group of ligands possesses no additional special structural designs for stability enhancement or efficiency improvement. 2-Phenylpyridine (ppy), phenyl[-1H]pyrazole (ppz) and benzoquinoline (bzqu) are commercially available while the other three ligands (1-(1-naphthyl)isoquinoline (na-iqu), 1-(9-phenanthryl)isoquinoline (phn-iqu) and 2-(2-naphthyl)quinoline (2na-qu)) were synthesized (figure 2.2).

**Figure 2.2:** Chemical structures of non substituted C^N ligands.
The second group of ligands was specially designed to improve the stability of Ir-iTMCs by reducing the strength of the σ-antibonding interactions between the C^N nitrogen and the iridium center. It has been proven by DFT calculation that there is an increase in the Ir-N_C^N bond length on moving from the ground state geometry to the first excited state geometry of Ir-iTMCs [23]. This elongation in the Ir-N_C^N bonds arises from the enhancement of the already existing Ir-N_C^N antibonding interaction by thermal population of the triplet metal center state (3MC). As a result, the difference in the Ir-N_C^N bond length from the ground state geometry to that of the first excited state is significant which could lead to the breaking of one of the Ir-N_C^N bonds. Increasing the Ir-N_C^N bond length in the ground state will lead to a reduction in the strong σ-antibonding interaction and also lessen the change in the Ir-N_C^N bond length between the ground state and first excited state geometries. The design of C^N ligands of the phenylpyridine family with an electron withdrawing group substituted on the pyridine ring were used to investigated the above mentioned concept. The electron withdrawing group will reduce the electron density on the pyridine ring and subsequently the electron lone pair donating ability of the sp² nitrogen atom of the pyridine ring to the iridium center. The resulting Ir-N_C^N bond length is expected to be slightly longer compared to the Ir-N_C^N bond length of the non substituted C^N ligands. The following ligands were synthesized to be used in the syntheses of red or deep red emitting Ir-iTMCs (figure 2.3).
The next group of ligands was designed following a literature known approach. The approach involves decorating the phenyl ring of the C^N ligand with electron withdrawing groups such as –F and -CF$_3$, preferably at the meta and para positions relative to the coordinating carbon atom [19]. It is reported that it results in shifting the emission wavelength to higher energies (shorter wavelengths). Ir-iTMCs with
phenyl fluorinated C^N ligands have been observed to have high photoluminescence quantum yields (PLQY) [21-23].

For further stability enhancement, the fluorine was selectively substituted at the ortho position (relative to the coordinating carbon) on the phenyl ring of the C^N ligands. With the fluorine at this position, F-N intra-molecular interactions are expected between the two C^N ligands. The F-N intra-molecular interactions would then be expected to improve the stability of the Ir-iTMCs in two different ways. 1) By formation of a cage structure which will prevent opening of the complex and at the same time prevent nucleophilic attack on the Iridium center. 2) An increase in the Ir-N_{C^N} bond length by reducing the electron donating ability of C^N nitrogen atom to the iridium center leading to a decrease in the σ-antibonding interaction as explained above. The following phenyl fluorinated C^N ligands were synthesized (figure 2.4 a and b).

![Chemical structures of three C^N ligands with fluorinated phenyl ring.](image)

**Figure 2.4a:** Chemical structures of three C^N ligands with fluorinated phenyl ring.
The last group of C^N ligands was made by combining two different structural modifications already mentioned with the aim of a further increase or improvement in the desired properties (figure 2.5). 5-Methyl-2-(4-fluorophenyl)pyridine (4Fp5mpy) and 5-methyl-2-(3,5-difluorophenyl)pyridine (3,5Fp5mpy) were designed to be used in the synthesis of Ir-iTMCs with bluish emission as shown in chapter 5.
Figure 2.5: Chemical structures of C^N ligands with substituents on both the phenyl and pyridine rings.

Almost all the N^N ligands used in the synthesis of the Ir-iTMCs are commercially available except for the two shown below (figure 2.6).
2.5 Conclusions

A total of 24 C^N ligands with different structural variations to improve the efficiency and stability of Ir-iTMCs for LEC applications were successfully synthesized and characterized. 18 out of the 24 ligands were completely new. The design concept for ligand structural modifications towards a stability enhancement of the Ir-iTMCs include attaching a fluorine substituent to the pyridine ring of the C^N ligands and having the fluorine substituted ortho to the coordinating carbon atom of the phenyl ring in the C^N ligands. The generally known approach of fluorinating the phenyl ring of the C^N ligand for obtaining Ir-iTMCs with high PLQY was also applied. Two N^N ligands with electron rich pyrazole ring were also synthesized to be used in the synthesis of Ir-iTMCs with bluish green to blue emissions.
## 2.6 Solid state structures

**Table 2.1:** Crystallographic data for 1-(1-naphthyl)isoquinoline (na-iqu).

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</thead>
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<tr>
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<tr>
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<tr>
<td>R indices (all data)</td>
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![Molecular structure](image)

**Figure 2.7:** Molecular structure of 1-(1-naphthyl)isoquinoline. (na-iqu) (ellipsoids plotted at 40% probability level).
Table 2.2: Crystallographic data for 2-(4-fluorophenyl)-5-fluoropyridine (4Fp5Fpy).

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<td>R indices (all data)</td>
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</tr>
</tbody>
</table>

Figure 2.8: Molecular structure of 2-(4-fluorophenyl)-5-fluoropyridine (4Fp5Fpy) (ellipsoids plotted at 40% probability level).
2.7 Experimental and Methods

2.7.1 Synthesis and characterizations

The phenylpyridine type C^N ligands with a carbon-carbon (C-C) bond formation were synthesized by a Suzuki coupling reaction following a modified literature method [30]. The C^N ligands and N^N ligands with a carbon-nitrogen (C-N) bond formation were prepared by an Ullman coupling reaction following a modified literature reported method [31]. The C^N and N^N ligands were prepared using commercially available starting materials without any further purification. The type, purity and supplier of the starting materials used in the synthesis of both the ligands and the Ir-iTMCs (chapter 2 to 5) are summarized in table 2a (appendix).

The ligands were characterized by $^1$H and $^{13}$C NMR and, when crystals of sufficient quality were obtained by single crystal X-ray diffraction (SXRD).

The $^1$H and $^{13}$C NMR of the ligands and complexes were recorded at 400 or 200 MHz and 100 or 50 MHz respectively on a Bruker DRX 400 or DRX 200 instruments at room temperature. The $^{31}$P NMR for complexes with phosphorus containing ligands was recorded at 166 MHz on a Bruker DRX 400 instrument. The $^1$H, $^{13}$C and $^{31}$P chemical shift (δ) are reported in parts per million (ppm) from low to high field and the coupling constant (J) are expressed in hertz (Hz). The following standard abbreviations are used for the multiplicity: s = singlet, d = doublet, t = triplet, sept = septet, dd = doublet of doublet, dt = doublet of triplet, td = triplet of doublet, ddd =doublet of doublet of doublet, dddd =doublet of doublet of doublet of doublet of doublet, m = multiplet (belonging to 1 H), comp = multiplet (belonging to 2 or more protons). Intensity data for ligands and complexes were collected on a Stoe IPDS-I single-crystal X-ray diffractometer with graphite monochromated Mo-Kα radiation (= 0.71073 Å) at 170(2) K. Data reduction was carried out with the program package X-red (X-red. Stoe & Cie: Darmstadt, Germany, 2002 [32]) and numerical absorption
corrections were carried out with the program X-Shape (X-Shape. Stoe & Cie: Darmstadt, Germany, 2002). Crystal structure solution by direct methods using SIR92 (Altomare, A.; Cascarano, G.; Giacovazzo, C. J. Appl. Crystallogr. 1993, 26, 343. [33]) yielded the heavy atom positions. Subsequent difference Fourier analyses and least squares refinement with SHELXL-97 (Sheldrick, W.S. SHELXL-97; Universität Göttingen: Göttingen, Germany, 1997. [34]) allowed for the location of the remaining atom positions. In the final step of the crystal structure refinement hydrogen atoms of idealized –CH, –CH₂ and –CH₃ groups were added and treated with the riding atom mode; their isotropic displacement factor was chosen as 1.2 times the preceding carbon atom for –CH, –CH₂ groups and 1.5 for –CH₃ groups. The crystal structures were visualized using Diamon 3.2 software.

2.7.2 General synthetic method for the ligands with a C-C bond formation: Suzuki coupling

Aryl-boronic acid (1.3 eq.) was added to a mixture of the pyridine halide (1 eq.), potassium phosphate (2 eq.) and palladium acetate (1.4 mol% of 1 eq. of the pyridine halide) in ethylene glycol. The mixture was refluxed at 80 °C for 24 hours. The mixture was then allowed to cool to room temperature, then added to a brine solution and extracted four times with diethyl ether (the extraction step was monitored by TLC chromatography). The ether content was concentrated using a rota-vapour and the crude ligand was obtained as a viscous liquid or solid. The ligands were purified by column chromatography on aluminium oxide 90 (neutral active, 0.063-0.200 mm) built with petroleum ether. A mixture of petroleum ether and ethyl acetate (8:2) was used to elute the ligands. The petroleum ether/ethyl acetate fraction was concentrated using a rota vapour. The product was received as a liquid or solid.

2-(4-fluorophenyl)-5-fluoropyridine (4Fp5Fpy): 5-fluoro-2-bromopyridine (12.7 mmol, 2.236 g), 4-fluorobenzeneboronic acid (14.29 mmol, 2.0 g), Pd(OAc)$_2$ (1.43
mol-%, 30 mg), potassium phosphate (8.0 mmol, 5.2 g), ethylene glycol (50 mL), **colourless solid (yield: 1.85 g, 76.2%).** $^1$H NMR (CDCl$_3$, 200 MHz): $\delta$ 8.56 (d, $J = 2.7$ Hz, 1H), 7.95 (comp, 2H), 7.71 (dd, $J = 8.8$, 4.2 Hz, 1H), 7.49 (m, 1 H), 7.18 (tt, $J = 8.5$, 2.2 Hz, 2H). $^{13}$C NMR (CDCl$_3$, 50 MHz): $\delta$ 138.7, 138.2, 138.0, 137.8, 128.8, 128.6, 124.0, 123.6, 121.0, 116.0, 115.4.

**2-(3,5-difluorophenyl)-5-fluoropyridine (3,5Fp5Fpy):** 5-fluoro-2-bromopyridine (5.68 mmol, 1.0 g), 3,5-fluorobenzeneboronic acid (6.39 mmol, 1.009 g), Pd(OAc)$_2$ (1.43 mol-%, 15 mg), potassium phosphate (4.0 mmol, 2.7 g), ethylene glycol (25 mL) **white solid (yield: 0.84 g, 71.2%).** $^1$H NMR (CDCl$_3$, 200 MHz): $\delta$ 8.56 (d, $J = 3.0$ Hz, 1 H), 7.90 (td, $J = 8.8$, 6.8, 6.5 Hz, 1H), 7.76 (dddd, $J = 8.8$, 4.2, 2.0, 0.7, 0.5 Hz, 1H), 7.47 (td, $J = 8.8$, 3.2 Hz, 1 H), 6.88 (comp, 2H). $^{13}$C NMR (CDCl$_3$, 50 MHz): $\delta$ 161.7, 156.6, 153.6, 138.7, 138.2, 136.0, 135.9, 129.1, 129.0, 126.2, 125.8.

**2-(3,5-difluorophenyl)pyridine (3,5Fppy):** 2-bromopyridine (0.025 mol, 2.41 mL), 3,5-fluorobenzeneboronic acid (0.028 mol, 4.496 g), Pd(OAc)$_2$ (1.43 mol-%, 60 mg), potassium phosphate (12.0 mmol, 10.8 g), ethylene glycol (80 mL) **white solid (yield: 4.2 g, 71.2%).** $^1$H NMR (CDCl$_3$, 200 MHz): $\delta$ 8.64 (d, $J = 4.8$, 1H), 7.74 (td, $J = 9.8$, 7.5, 2.0, 1.7 Hz, 1H), 7.62 (dt, $J = 7.8$, 1.2, 1.0 Hz, 1 H), 7.48 (comp. 2H), 7.24 (ddd, $J = 7.3$, 4.8, 1.2 Hz, 1 H), 6.79 (tt, $J = 8.8$, 2.5 Hz, 1 H). $^{13}$C NMR (CDCl$_3$, 50 MHz): $\delta$ 161.1, 154.1, 150.0, 149.6, 146.6, 137.2, 123.2, 120.6, 110.0, 109.5, 104.3.

**2-(4-fluorophenyl)-5-methylpyridine (4Fp5mpy):** 5-methyl-2-bromopyridine (12.7 mmol, 2.184 g), 4-fluorobenzeneboronic acid (14.29 mmol, 2.0 g), Pd(OAc)$_2$ (1.43 mol-%, 30 mg), potassium phosphate (8.0 mmol, 5.2 g), ethylene glycol (50 mL) **colourless solid (yield: 2.20 g, 92.3%).** $^1$H NMR (CDCl$_3$, 200 MHz): $\delta$ 8.55 (s, 1 H), 7.99 (comp, 2 H), 7.60 (d, $J = 1.2$ Hz, 1 H), 7.59 (d, $J = 2.2$ Hz, 1 H), 7.20 (dd, $J = 8.5$, 2.2 Hz, 1 H), 7.15 (dd, $J = 8.5$, 2.2 Hz, 1 H), 2.40 (s, 3 H). $^{13}$C NMR (CDCl$_3$, 50 MHz): $\delta$ 160.8, 153.7, 149.5, 137.5, 133.6, 131.6, 128.5, 128.4, 119.8, 115.8, 115.4, 18.1.
2-(3,5-difluorophenyl)-5-methylpyridine (3,5Fp5mpy): 5-methyl-2-bromopyridine (5.81 mmol, 1.0 g), 3,5-difluorobenzeneboronic acid (6.53 mmol, 1.032 g), Pd(OAc)$_2$ (1.43 mol-%, 15 mg), potassium phosphate (4.0 mmol, 2.7 g), ethylene glycol (30 mL) **colourless solid (yield: 1.05 g, 88.2%)**. $^1$H NMR (CDCl$_3$, 50 MHz): $\delta$ 8.53 (s, 1 H), 7.61 (d, $J$ = 1.52 Hz, 2 H), 7.53 (dd, $J$ = 8.84, 2.27 Hz, 2 H), 6.83 (tt, $J$ = 8.59, 2.27 Hz, 1 H), 2.40 (s, 3 H). $^{13}$C NMR (CDCl$_3$, 50 MHz): $\delta$ 165.9, 150.4, 150.0, 139.3, 139.0, 137.8, 132.5, 127.4, 120.1, 109.7, 103.8, 17.7.

5-fluoro-2-phenylpyridine (p5Fpy): 5-fluoro-2-bromopyridine (11.3 mmol, 2.0 g), benzeneboronic acid (12.7 mmol, 1.5 g), Pd(OAc)$_2$ (1.43 mol-%, 30 mg), potassium phosphate (8.0 mmol, 5.2 g), ethylene glycol (50 mL) **colourless solid (yield: 1.21 g, 62.1%)**. $^1$H NMR (CDCl$_3$, 200 MHz): $\delta$ 8.6 (d, $J$ = 3.0 Hz, 1 H), 7.99 (dd, $J$ = 8.3, 4.2 Hz, 1 H), 7.98 (d, $J$ = 9.6 Hz, 1 H), 7.77 (ddd, $J$ = 8.8, 4.2, 0.5 Hz, 1 H), 7.50 (comp, 4 H). $^{13}$C NMR (CDCl$_3$, 50 MHz): $\delta$ 138.3, 137.9, 137.4, 128.9, 128.8, 126.8, 126.8, 125.9, 125.5, 121.4, 121.3.

5-fluoro-2-(9-phenanthryl)pyridine (phn5Fpy): 5-fluoro-2-bromopyridine (9.3 mmol, 1.63 g), 9-phenanthracenylboronic acid (10.48 mmol, 2.327 g), Pd(OAc)$_2$ (1.43 mol-%, 30 mg), potassium phosphate (8.0 mmol, 5.2 g), ethylene glycol (50 mL) **brownish white solid (yield: 2.55 g, 90.1%)**. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 8.86 (d, $J$ = 1.26 Hz, 1 H), 8.81 (d, $J$ = 2.78 Hz, 1 H), 8.75 (d, $J$ = 3.03 Hz, 1 H), 8.05 (d, $J$ = 1.26 Hz, 1 H), 8.01 (d, $J$ = 1.52 Hz, 1 H), 7.89 (s, 1 H), 7.69 (comp, 6 H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 137.9, 137.4, 131.2, 130.8, 130.5, 129.0, 128.6, 127.2, 126.9, 126.8, 126.7, 126.6, 126.3, 126.0, 125.9, 123.7, 123.3, 123.0, 122.6.

1-(9-phenanthryl)isoquinoline (phin-isqu): 1-bromoisoquinoline (4.8 mmol, 1.0 g), 9-phenanthracenylboronic acid (5.4 mmol, 1.2 g), Pd(OAc)$_2$ (1.43 mol-%, 15 mg), potassium phosphate (4.0 mmol, 2.7 g), ethylene glycol (50 mL) **brownish white solid (yield: 1.10 g, 84.6%)**. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 8.85 (d, $J$ = 8.5 Hz, 1 H), 8.8 (d, $J$ = 8.0 Hz, 1 H), 8.35 (d, $J$ = 8.0 Hz, 1 H), 8.30 (d, $J$ = 8.5 Hz, 1 H), 8.16 (dd, $J$ =
8.3, 1.2 Hz, 1 H), 7.98 (dd, J = 7.3, 1.2 Hz, 2 H), 7.88 (td, J = 6.8, 1.5 Hz, 1 H), 7.70 (comp, 6 H). $^{13}$C NMR (CDCl$_3$, 100 MHz): δ 159.4, 148.0, 137.3, 136.4, 131.8, 131.4, 130.9, 130.6, 130.3, 129.9, 129.6, 129.2, 128.9, 127.6, 127.2, 127.1, 126.9, 126.8, 126.7, 126.6, 123.3, 123.0, 122.6.

**5-fluoro-2-(1-naphthyl)pyridine (na5Fpy):** 5-fluoro-2-bromopyridine (0.014 mol, 2.5 g), 1-naphthaleneboronic acid (0.0159 mol, 2.174 g), Pd(OAc)$_2$ (1.43 mol-%, 30 mg), potassium phosphate (8.0 mmol, 5.4 g), ethylene glycol (50 mL) colourless liquid (yield: 2.30 g, 73.6%). $^1$H NMR (CDCl$_3$, 200 MHz): δ 8.86 (d, J = 2.78 Hz, 1 H), 8.36 (dd, J = 8.3, 4.2 Hz, 1 H), 7.98 (d, J = 9.6 Hz, 1 H), 7.71 (d, J = 1.77 Hz, 1 H), 7.51 (dd, J = 6.82, 1.26 Hz, 1 H), 7.46 (d, J = 4.29 Hz, 1 H), 7.45 (d, J = 3.79 Hz, 1 H), 7.22 (comp, 4 H). $^{13}$C NMR (CDCl$_3$, 50 MHz): δ 160.5, 142.4, 137.9, 137.4, 137.0, 133.7, 128.6, 127.3, 126.9, 126.7, 126.1, 125.9, 125.2, 120.3.

**1-(1-naphthyl)isoquinoline (1naisoqu):** 1-chloroisouquinoline (0.02 mol, 3.38 g), 1-naphthaleneboronic acid (0.023 mol, 4.0 g), Pd(OAc)$_2$ (1.43 mol-%, 60 mg), potassium phosphate (16.0 mmol, 10.8 g), ethylene glycol (100 mL) white solid (yield: 4.80 g, 94.1%). $^1$H NMR (CDCl$_3$, 400 MHz): δ 8.56 (d, J = 5.81 Hz, 1 H), 7.85 (dd, J = 5.81, 2.27 Hz, 1 H), 7.78 (dd, J = 9.35, 1.26 Hz, 2 H), 7.71 (d, J = 1.77 Hz, 1 H), 7.57 (dd, J = 5.56, 0.76 Hz, 1 H), 7.51 (dd, J = 6.82, 1.26 Hz, 1 H), 7.46 (d, J = 4.29 Hz, 1 H), 7.45 (d, J = 3.79 Hz, 1 H), 7.22 (comp, 4 H). $^{13}$C NMR (CDCl$_3$, 100 MHz): δ 160.5, 142.4, 137.0, 136.5, 133.7, 130.2, 128.9, 128.4, 128.3, 127.8, 127.7, 127.3, 126.9, 126.4, 126.1, 126.0, 125.9, 125.2, 120.3.

**2-(2-naphthyl)quinoline (2na-qu):** 2-chloroquinoline (0.02 mol, 3.38 g), 2-naphthaleneboronic acid (0.023 mol, 4.0 g), Pd(OAc)$_2$ (1.43 mol-%, 60 mg), potassium phosphate (16.0 mmol, 10.8 g), ethylene glycol (100 mL), colourless solid (yield: 4.95 g, 97.1%). $^1$H NMR (CDCl$_3$, 200 MHz): δ 8.56 (d, J = 1.77 Hz, 1 H), 8.29 (dd, J = 8.59, 1.77 Hz, 1 H), 8.21 (dd, J = 6.06, 2.78 Hz, 1 H), 8.16 (s, 1 H), 7.93 (dd, J = 8.84, 5.81 Hz, 3 H), 7.81 (d, J = 2.27 Hz, 1 H), 7.78 (d, J = 1.77 Hz, 1 H), 7.68 (t,
$J = 1.52\ \text{Hz, 1 H})$ 7.45 (comp, 3 H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 137.2, 136.8, 133.9, 130.0, 129.6, 129.4, 128.9, 128.6, 127.7, 127.5, 127.4, 127.2, 126.6, 126.5, 126.4, 125.1, 119.2.

5-fluoro-2-(2-naphthyl)pyridine (2na5Fpy): 5-fluoro-2-bromopyridine (5.0 mmol, 0.84 g), 2-naphthaleneboronic acid (5.75 mmol, 1.0 g), Pd(OAc)$_2$ (1.43 mol-%, 15 mg), potassium phosphate (4.0 mmol, 2.7 g), ethylene glycol (25 mL) colourless oil (yield: 0.85 g, 76.2%). $^1$H NMR (CDCl$_3$, 200 MHz): $\delta$ 8.56 (d, $J = 2.78\ \text{Hz, 1 H}$), 8.39 (d, $J = 1.26\ \text{Hz, 1 H}$), 8.03 (dd, $J = 8.59, 1.77\ \text{Hz, 1 H}$), 7.87 (dd, $J = 8.84, 5.81\ \text{Hz, 3 H}$), 7.79 (dd, $J = 6.06, 2.53\ \text{Hz, 1 H}$), 7.46 (dd, $J = 6.32, 3.28\ \text{Hz, 2 H}$), 7.19 (s, 1 H).

2-(4-fluorophenyl)pyridine (4Fppy): 2-bromopyridine (0.049 mol, 4.7 mL), 4-fluorobenzeneboronic acid (0.058 mol, 8.25 g), Pd(OAc)$_2$ (1.43 mol-%, 120 mg), potassium phosphate (36.0 mmol, 21.0 g), ethylene glycol (150 mL) white solid (yield: 7.85 g, 92.5%). $^1$H NMR (DMSO, 400 MHz): $\delta$ 8.66 (ddd, $J = 4.80, 1.77, 1.01\ \text{Hz, 1 H}$), 8.14 (dd, $J = 8.84, 5.56\ \text{Hz, 2 H}$), 7.93 (dt, $J = 8.08, 1.01\ \text{Hz, 1 H}$), 7.86 (td, $J = 7.58, 1.77\ \text{Hz, 1 H}$), 7.33 (ddd, $J = 7.33, 4.80, 1.26\ \text{Hz, 1 H}$), 7.32 (d, $J = 2.02\ \text{Hz, 1 H}$), 7.30 (t, $J = 2.27, 2.02\ \text{Hz, 1 H}$), 7.28 (d, $J = 2.27\ \text{Hz, 1 H}$). $^{13}$C NMR (DMSO, 100 MHz): $\delta$ 164.0, 161.6, 154.9, 149.4, 137.1, 135.1, 128.6, 128.5, 122.4, 119.9, 115.6.

2-(3-fluorophenyl)pyridine (3Fppy): 2-bromopyridine (0.049 mol, 4.7 mL), 3-fluorobenzeneboronic acid (0.058 mol, 8.25 g), Pd(OAc)$_2$ (1.43 mol-%, 120 mg), potassium phosphate (36.0 mmol, 21.0 g), ethylene glycol (150 mL) colourless liquid (yield: 7.81 g, 91.9%). $^1$H NMR (CDCl$_3$, 200 MHz): $\delta$ 8.71(dt, $J = 4.80, 1.26\ \text{Hz, 1 H}$), 7.80 (m, $J = 2.27, 1.52, 1.01\ \text{Hz, 1 H}$), 7.75 (m, $J = 2.53, 2.02, 1.26\ \text{Hz, 1 H}$), 7.74 (t, $J = 1.52, 1.77\ \text{Hz, 1 H}$), 7.70 (dd, $J = 2.27, 1.01\ \text{Hz, 1 H}$), 7.43 (tdd, $J = 8.08, 5.81, 0.51\ \text{Hz, 1 H}$), 7.24 (ddd, $J = 8.84, 6.57, 2.53, 2.27\ \text{Hz, 1 H}$), 7.12 (tdd, $J = 8.59, 2.53, 1.01\ \text{Hz, 1 H}$). $^{13}$C NMR (CDCl$_3$, 50 MHz): $\delta$ 165.7, 160.9, 155.9, 149.7, 141.7, 136.9, 130.1, 122.6, 120.5, 116.0, 115.5, 114.0.
**2-(3-fluorophenyl)quinoline (3Fpqu):** 2-chloroquinoline (0.0153 mol, 2.5 g), 3-fluorobenzeneboronic acid (0.0198 mol, 2.78 g), Pd(OAc)$_2$ (1.43 mol-%, 45 mg), potassium phosphate (10.4 mmol, 7.04 g), ethylene glycol (80 mL) **white solid** (yield 2.6 g, 76.2%). $^1$H NMR (DMSO, 400 MHz): $\delta$ 8.46 (d, $J = 8.59$ Hz, 1 H), 8.16 (d, $J = 8.84$ Hz, 1 H), 8.11 (comp, 3 H), 8.00 (dd, $J = 8.08, 1.01$ Hz, 1 H), 7.79 (ddd, $J = 8.34, 7.07, 1.52$ Hz, 1 H), 7.59 (comp, 2 H), 7.59 (tdd, $J = 8.59, 2.53, 0.76$ Hz, 1 H). $^{13}$C NMR (DMSO, 100 MHz): $\delta$ 163.9, 161.5, 154.5, 147.4, 137.3, 130.7, 130.0, 129.1, 127.7, 127.1, 126.7, 123.2, 118.6, 116.4, 113.7.

**2-(4-fluorophenyl)quinoline (3Fpqu):** 2-chloroquinoline (0.0153 mol, 2.5 g), 4-fluorobenzeneboronic acid (0.0198 mol, 2.78 g), Pd(OAc)$_2$ (1.43 mol-%, 45 mg), potassium phosphate (10.4 mmol, 7.04 g), ethylene glycol (80 mL) **white solid** (yield: 2.6 g, 76.2%). $^1$H NMR (DMSO, 400 MHz): $\delta$ 8.43 (d, $J = 8.84$ Hz, 1 H), 8.83, (dd, $J = 9.09, 5.56$ Hz, 2 H), 8.11 (d, $J = 8.59$ Hz, 1 H), 8.07 (d, $J = 8.59$ Hz, 1 H), 7.98 (dd, $J = 8.08, 1.26$ Hz, 1 H), 7.78 (ddd, $J = 8.34, 7.07, 1.52$ Hz, 1 H), 7.59 (ddd, $J = 8.08, 6.82, 1.26$ Hz, 1 H), 7.37 (t, $J = 9.09, 8.84$ Hz, 2 H). $^{13}$C NMR (DMSO, 100 MHz): $\delta$ 164.4, 161.9, 154.9, 147.4, 137.2, 135.1, 129.9, 129.4, 129.0, 127.7, 126.8, 126.4, 116.4, 115.7, 115.5.

**1-(3-fluorophenyl)isoquinoline (3Fp-iqu):** 1-chloroisoquinoline (0.0153 mol, 2.5 g), 3-fluorobenzeneboronic acid (0.0198 mol, 2.78 g), Pd(OAc)$_2$ (1.43 mol-%, 45 mg), potassium phosphate (10.4 mmol, 7.04 g), ethylene glycol (80 mL) **brownish liquid** (yield: 2.16 g, 63.0%). $^1$H NMR (DMSO, 400 MHz): $\delta$ 8.58 (d, $J = 5.56$ Hz, 1 H), 8.03 (d, $J = 8.08$ Hz, 1 H), 7.99 (ddd, $J = 8.59, 1.01$ Hz, 1 H), 7.84 (d, $J = 5.81$ Hz, 1 H), 7.77 (ddd, $J = 8.08, 6.82, 1.01$ Hz, 1 H), 7.62 (ddd, $J = 8.59, 6.82, 1.26$ Hz, 1 H), 7.57 (ddd, $J = 8.08, 5.81$ Hz, 1 H), 7.47 (comp, 2 H), 7.36 (tdd, $J = 8.08, 2.78, 1.01$ Hz, 1 H). $^{13}$C NMR (DMSO, 100 MHz): $\delta$ 163.2, 160.8, 158.2, 141.9, 141.5, 136.3, 130.2, 127.8, 127.1, 126.3, 125.9, 125.6, 120.3, 116.3, 115.4.
**1-(4-fluorophenyl)isoquinoline (4Fp-iqu)**: 1-chloroisoquinoline (0.0153 mol, 2.5 g), 4-fluorobenzeneboronic acid (0.0198 mol, 2.78 g), Pd(OAc)$_2$ (1.43 mol-%, 45 mg), potassium phosphate (10.4 mmol, 7.04 g), ethylene glycol (80 mL) **brown solid (yield: 2.1 g, 61.5%)**. $^1$H NMR (DMSO, 400 MHz): δ 8.59 (d, $J = 5.56$ Hz, 1 H), 8.04 (d, $J = 8.08$ Hz, 1 H), 7.99 (dd, $J = 8.59, 1.01$ Hz, 1 H), 7.84 (d, $J = 5.81$ Hz, 1 H), 7.79 (ddd, $J = 8.34, 6.82, 1.26$ Hz, 1 H), 7.72 (ddd, $J = 8.84, 2.27$ Hz, 2 H), 7.63 (ddd, $J = 8.59, 6.82, 1.26$ Hz, 1 H), 7.38 (tt, $J = 8.84, 2.27$ Hz, 2 H). $^{13}$C NMR (DMSO, 400 MHz): δ 163.5, 161.1, 141.9, 136.3, 135.5, 131.8, 130.2, 127.7, 127.1, 126.5, 125.7, 123.0, 115.2, 115.0.

**2-(3,4-difluorophenyl)pyridine (3,4dFppy)**: 2-bromopyridinne (0.025 mol, 2.41 mL), 3,4-difluorobenzeneboronic acid (0.028 mol, 4.496 g), Pd(OAc)$_2$ (1.43 mol-%, 60 mg), potassium phosphate (10.4 mmol, 7.04 g), ethylene glycol (80 mL) **colourless liquid (yield: 3.5 g, 73.2%)**. $^1$H NMR (DMSO, 400 MHz): δ 8.84 (s, 1 H), 8.08 (dd, $J = 7.83, 2.02$ Hz, 1 H), 7.91 (comp, 3 H), 7.73 (m, 1 H), 7.48 (dd, $J = 5.56, 2.02$ Hz, 1 H), 7.35 (s, 1 H). $^{13}$C NMR (DMSO, 100 MHz): δ 153.6, 150.9, 149.4, 141.4, 137.2, 136.2, 128.1, 122.8, 120.1, 117.6, 115.3.

**2.7.3 General synthetic method for the ligands with a C-N bond formation: Ullman coupling**

L-proline, potassium phosphate, the respective pyrazole, a bromo-aryl, copper iodide and dry dimethyl sulfuoxide were transferred into a Schlenk flask and refluxed at 110 C for 48 hours (the reactions were carried out under argon). The resulting mixture was partitioned between an aqueous and an ethyl acetate (1:1) mixture. The aqueous phase was further extracted with ethyl acetate four times. The combined organic fraction was washed with a brine solution, dried over sodium carbonate and concentrated using a rota-vapour. The crude products were purified by column chromatography on silicon oxide 90 (neutral active, 0.063-0.200 mm) built with petroleum ether. A mixture of petroleum ether and ethyl acetate (8:2) was used to
elute the ligands. The petroleum ether/ethyl acetate fraction was concentrated using a rota vapour. The product was received as a liquid.

1-(3,5-difluorophenyl)pyrazole (3,5dFppz): L-proline (0.004 mol, 0.46 g), potassium phosphate (0.04 mol, 8.5 g), pyrazole (0.02 mol, 1.362 g), 1-bromo-3,5-difluorobenzene (0.022 mol, 2.53 mL, 4.245 g), copper iodide (0.002 mmol, 0.38 g), dry dimethyl sulfoxide (30 mL), colourless liquid (yield: 3.1 g, 86.0%). $^1$H NMR (CDCl$_3$, 400 MHz): δ 8.76 (d, $J = 5.81$ Hz, 1 H), 7.99 (d, $J = 8.34$ Hz, 1 H), 7.86 (d, $J = 5.81$ Hz, 1 H), 7.77 (t, $J = 2.78$ Hz, 1 H), 7.76 (dd, $J = 14.91$, 4.55 Hz, 1 H), 7.52 (t, $J = 8.08$, 7.07 Hz, 1 H), $^{13}$C NMR (CDCl$_3$, 400 MHz) 121.1, 126.9, 127.2, 127.6, 127.8, 130.4, 136.8, 141.9, 158.1.

1-(2-pyridyl)pyrazole (pypz): L-proline (0.004 mol, 0.46 g), potassium phosphate (0.04 mol, 8.5 g), pyrazole (0.02 mol, 1.362 g), 2-bromopyridine (0.022 mol, 2.10 mL, 3.476 g), copper iodide (0.002 mmol, 0.38 g), dry dimethyl sulfoxide (30 mL), brownish liquid (yield: 2.5 g, 86.1%). $^1$H NMR (CDCl$_3$, 400 MHz): δ 8.57 (dd, $J = 2.53$, 0.51 Hz, 1 H), 8.36 (d, $J = 4.29$ Hz, 1 H), 7.97 (dd, $J = 8.08$, 0.76 Hz, 1 H), 7.73 (comp, 2 H), 7.11 (m, $J = 7.33$, 4.80, 2.27 Hz, 1 H), 6.44 (m, $J = 2.27$, 1.77 Hz, 1 H) $^{13}$C NMR (CDCl$_3$, 400 MHz): δ 107.7, 112.3, 126.9, 138.6, 141.9, 147.9, 151.5.

3,5-dimethyl-1-(2-pyridyl)pyrazole (py3,5dmpz): L-proline (0.008 mol, 0.92 g), potassium phosphate (0.08 mol, 17 g), 3,5-dimethylpyrazole (0.04 mol, 3.85 g), 2-bromopyridine (0.044 mol, 4.20 mL, 6.96 g), copper iodide (0.004 mmol, 0.74 g), dry dimethyl sulfoxide (70 mL), colourless liquid (yield: 4.1 g, 94.7%). $^1$H NMR (DMSO, 400 MHz): δ 8.42 (dd, $J = 3.79$, 1.01 Hz, 1 H), 7.92 (m, 1 H), 7.81 (d, $J = 8.34$ Hz, 1 H), 7.36 (m, 1 H), 6.09 (s, 1 H), 2.58 (s, 3 H), 2.20 (s, 3 H). $^{13}$C NMR (DMSO, 100 MHz): δ 153.0, 148.8, 147.4, 140.6, 128.1, 121.0, 115.2, 109.0, 14.2, 13.3.
2.8 References

Chapter 3

Red LEC devices based on red emitting Ir-iTMCs
Chapter 3

Red LEC devices based on red emitting Ir-iTMCs

3.1 Introduction

Red LEC devices could find application in traffic lights, car back lights as well as in decoration lighting. Even more importantly, red is one of the primary colours required for the generation of white light for general lighting applications. Hence there is an extreme need for the development of very efficient and stable red emitting Ir-iTMCs for LEC application toward a low-cost lighting technology for various applications.

Tuning of the emission wavelength of Ir-iTMCs towards the red region of the visible spectrum, hence longer wavelength, can be achieved by either destabilization of the HOMO or/and stabilization of the LUMO by substituting electron donating or electron withdrawing groups to the phenyl ring of the C^N ligands or the N^N ligand respectively [1-3]. Another reported approach to obtain red emitting Ir-iTMCs is by extending the aromatic system (extending the conjugation) of the C^N and N^N ligands [2-4] or a combination of both approaches [2,3,5]. Rodríguez-Redondo et al., [6] reported two deep red emitting Ir-iTMCs with emission maxima at 687 nm for both complexes based on the former approach. The difference between the two Ir-iTMCs is the extended alkyl-chain length of the substituent on the N^N ligand of one of the complexes. The long lifetime of a LEC device based on the described complex (37 h) compared to that of the other complex (0.52 h) was attributed to the extended alkyl-chain length. It was explained that the complex with the long alkyl-chain substituent should leads to larger inter-complex distances within the thin film of the emissive layer resulting in less inter-complex interactions during device operation which eventually led to the longer lifetime of the device. Zhao et al., [4] reported four Ir-iTMCs with 1-phenyl-isoquinoline as the C^N ligand and four different N^N ligands with varying degree of conjugation (2-pyridyl-quinoline, 2,2′-
biquinoline, 1,1′-biisoquinoline, and 2-(2-quinolinyl)quinoxaline). The complexes emit in the red region of the visible spectrum with emission maxima in the range of 637 to 732 nm. However, no LEC device data of the complexes were reported. The red emitting complex [Ir(ppy)₂(biq)][PF₆] where ppy is 2-phenylpyridine and biq is 2,2′-biquinoline firstly reported by Su et al., 2008 [7] as a red dopant in a white LEC device has also been used as a red dopant in different host guest systems for efficiency improvement [8] or for other white emitting LECs [9]. Oxadiazole [10] and imidazole [11] N^N ligands based red emitting cationic iridium complexes have also been reported towards efficiency enhancement. LEC devices fabricated using the above mentioned complexes were driven under a constant voltage mode. As highlighted in chapter one, such driven mode leads to low device lifetime. Constable et al. [12] reported a series of orange-red to red emitting Ir-iTMCs with a 2,2′:6,2′-terpyridine like N^N ligands. The authors selectively choose the N^N ligands so as to introduce the intra-molecular π-π stacking between the phenyl ring of one of the C^N ligands and the pendent pyridine ring of the N^N ligand to enhance the structural stability of the red emitting Ir-iTMCs in LEC during device operation. Indeed the expected π-π intramolecular stacking was observed for all the reported complexes with electroluminescence maxima in the range 598 to 695 nm. The highest luminance observed for one of the LEC devices was 60 cd/m² which is among the highest luminances reported for red LEC devices driven in a pulsed current mode. However, all the reported LEC devices demonstrated lifetimes less than 10 h implying that there was no enhancement in the device stability via the introduction of a π-π stacking within the molecular structure of the complexes. So far, reported red LECs driven with the pulsed current mode show current efficiency of less than 0.7 cd/A and even lower values for power efficiency with none of these red LEC devices demonstrating a lifetime of more than 50 h.

Red LEC devices could find application in traffic lights, car back lights as well as in decoration lighting. Even more importantly, red is one of the primary colours
required for the generation of white light for general lighting applications. Hence there is an extreme need for the development of very efficient and stable red emitting Ir-iTMCS for LEC application toward a low-cost lighting technology for various applications.

**Results and discussion**

### 3.2 New designs for red emitting Ir-iTMCS

Red emitting complexes with varying degree of extended aromatic systems in one series were designed and synthesized for application in LEC devices. In another series, for the first time fluorine substituted ligands were explored for for red-light emitting Ir-iTMCS with improved stability and efficiencies.

#### 3.2.1 Red emitting Ir-iTMCS with extended aromatic systems

Four red emitting Ir-iTMCS with the general formula [Ir(C^N)2(N^N)][PF6] were the C^N ligands are 1-(1-naphthyl)isoquinoline (na-iqu), 2-(2-naphthyl)quinoline (2na-qu), 1-(9-phenanthracenyl)isoquinoline (phnqu) and benzo[h]quinoline (bzqu), while the N^N ligand is 2,2´-biquinoline were designed and synthesized (figure 3.1). 2,2´-Biquinoline is the N^N ligand of choice for the synthesis of Ir-iTMCS with red emission because the extended aromatic ring are arranged is such a way that they protect (shield) the iridium center from nucleophilic attack.
Figure 3.1: Chemical structures of $[\text{Ir}(\text{na-iqu})_2(\text{biq})][\text{PF}_6]$], $[\text{Ir}(2\text{na-2qu})_2(\text{biq})][\text{PF}_6$] $[\text{Ir}(\text{phn-iqu})_2(\text{biq})][\text{PF}_6]$ and $[\text{Ir}(\text{bzqu})_2(\text{biq})][\text{PF}_6$]

The complex with the benzoquinoline (bzqu) as the C$^\text{N}$ ligands was designed to reduce the vibrational modes of the complex during device operation toward device lifetime improvement by increasing the rigidity of the C$^\text{N}$ ligands.
3.2.2 Fluorinated Ir-iTMCs with red emission: towards stability improvement

Another advantage for using 2,2’-biquinoline (biq) as the N^N ligand is the low lying LUMO of the complexes. With such an ancillary ligand the thermal population of the \(^3MC\) state is made less feasible due to the large energy gap between the LUMO and the \(^3MC\) state. If the observed \(\sigma\)-antibonding interaction between the N\(_{C^N}\) and the Ir-center can be reduced in the ground state geometry, there is a possibility of increasing the overall stability of the complex. This could be achieved if the molecular geometry of the ground state and the first excited state will have only a little difference arising from the change in the N\(_{C^N}\)-Ir bond length. Four complexes with completely new C\(^N\) ligands where a fluorine substituent is introduced to the pyridine ring were designed and synthesized for the proof of concept (figure 3.2 a and b).

![Chemical structures of complexes](image)

**Figure 3.2a:** Chemical structures of \([\text{Ir} (p5Fpy)_2 (biq)][PF_6]\) and \([\text{Ir} (na5Fpy)_2 (biq)][PF_6]\).
A fluorine substituent on the pyridine ring is expected to reduce the electron density on the pyridine ring of the C^N ligands and thereby reducing the lone pair donor strength of the sp^2 hybridized nitrogen to the iridium center. This could lead to a slightly increase in the N_C^N-Ir bond length in the ground state geometry. As such, the σ-antibonding interactions is also expected to decrease with the slight increase in the N_C^N-Ir bond length. It is generally known that the shorter the bond length, the stronger the bond and it is getting more difficult to break such a bond. However, in this case with an antibonding interaction along the bond axis, it is believed that the shorter the bond length, the stronger the antibonding interaction hence the likeliness of bond breaking. Nevertheless, there should exist a bond length which is slightly longer than the expected bond length with the possible smallest strength of the σ-antibonding interaction which will lead to a stronger and stable bond. The design of the pyridine fluorinated complexes (figure 3.2) are based on the above described proposition which is expected to result in complexes with enhanced structural stability for application in LECs. The complex [Ir(phen5Fpy)(2)(pbpy)][PF_6]]
(figure 3.3) was synthesized to study the effect of changing the ancillary ligand from biq to pbpy in a complex with the pyridine fluorinated C\(^{\text{N}}\) ligands.

\[
\text{[Ir(phen5Fpy)_2(pbpy)][PF}_6\text{)}]
\]

Figure 3.3: Chemical structure of [Ir(phen5Fpy)_2(pbpy)][PF\(_6\)].

3.2.3 Fluorinated Ir-iTMCs with red emission: towards stability and efficiency improvements

Electron withdrawing substituents are generally used in the design of Ir-iTMCs to blue shift their emission wavelengths toward the green or blue region of the visible spectrum [1-3]. It has also been reported that fluorinated Ir-iTMCs with green emission demonstrated high photoluminescence quantum yields [13]. In order to improve the efficiency of red emitting Ir-iTMCs, a fluorine substituent is added to the phenyl ring of the C\(^{\text{N}}\) ligands while using the 2,2′-biquinoline with a low lying LUMO to keep the emission of the complexes in the red region of the visible spectrum. To further improve the stability of the complexes, the fluorine is selectively substituted ortho to the coordinating carbon of the phenyl ring of the C\(^{\text{N}}\) ligands. Ortho fluorine substituents are involved in F-N intra-molecular interactions with the nitrogen atom of the other C\(^{\text{N}}\) ligand which is expected to form a cage
arrangement of the complex (for example figure 3.22). The cage arrangement will prevent the opening of the complex and result in complexes with an enhanced structural stability. The F-N intramolecular interaction was first identified in green emitting Ir-iTMCs (chapter 4) and the approach was also applied for the red emitting Ir-iTMCs (the formation of F-N intra-molecular interaction is explained in details in the next chapter). The following six complexes were designed and synthesized to investigate the above mentioned concepts (figure 3.4).

Figure 3.4a: Chemical structures of [Ir(4Fppy)$_2$(biq)][PF$_6$], [Ir(3Fppy)$_2$(biq)][PF$_6$], [Ir(4Fp2qu)$_2$(biq)][PF$_6$] and [Ir(3Fp2qu)$_2$(biq)][PF$_6$].
Figure 3.4b: Chemical structures of [Ir(3Fp-iqu)2(biq)][PF6], [Ir(4Fp-iqu)2(biq)][PF6] and [Ir(3Fp-iq)2(biq)][PF6].

The aromaticity of the pyridine ring was extended for some of the complexes as shown in figure 3.4a and 3.4b to further red shift the emission wavelengths of the complexes.

3.3 Photophysical properties

The absorption properties of the complexes were investigated in acetonitrile solution while their photoluminescence properties were studied in their solid state on powder samples or thin films.

3.3.1 Absorption studies

The absorption spectra for [Ir(phn-iqu)2(biq)][PF6], [Ir(2na-2qu)2(biq)][PF6], [Ir(na-iqu)2(biq)][PF6] and [Ir(bzqu)2(biq)][PF6] are shown in figure 3.5. All the complexes except for complex [Ir(phnqu)2(biq)][PF6] show intense absorption below 300 nm which is assigned to the ligand centered (LC) transitions of both the C^N and N^N
ligands. The weak absorption in 300 to 350 nm region is assigned to the metal to ligand charge transfer (\(^1\)MLCT). Absorptions from 350 nm extending into the visible region are assigned to the metal to ligand charge transfer (\(^3\)MLCT), ligand-to-ligand charge transfer (\(^3\)LLCT) and ligand centered (\(^3\)LC) transitions. While for \([\text{Ir(phn-1qu)}_2\text{(biq)}][\text{PF}_6]\) a broad and intense absorption around 300 nm is seen which could be assigned to the LC and \(^1\)MLCT. The absorption bands at 400 and 500 nm are assigned to the \(^3\)MLCT, \(^3\)LLCT and \(^3\)LC transitions [4].

\[\text{Figure 3.5: Absorption spectra of } [\text{Ir(phn-1qu)}_2\text{(biq)}][\text{PF}_6], [\text{Ir(2na-2qu)}_2\text{(biq)}][\text{PF}_6], [\text{Ir(1na-iqu)}_2\text{(biq)}][\text{PF}_6] \text{ and } [\text{Ir(bzqu)}_2\text{(biq)}][\text{PF}_6].\]

In general, all complexes where a ligand bears a fluorinated pyridine ring show absorption bands in the three regions corresponding to the LC transitions of both ligands (absorptions below 300 nm), the \(^1\)MLCT (300 to 350 nm) and the \(^3\)MLCT, \(^3\)LLCT and \(^3\)LC transitions (above 350 nm). The absorption bands are more intense in the 350 to 400 nm region for \([\text{Ir(p5Fpy)}_2\text{(biq)}][\text{PF}_6]\) and \([\text{Ir(2na5Fpy)}_2\text{(biq)}][\text{PF}_6]\)
complexes. While the complexes $[\text{Ir(phn5Fpy)}_2(\text{biq})][\text{PF}_6]$ and $[\text{Ir(phn5Fpy)}_2(\text{pbpy})][\text{PF}_6]$ show a unique and defined weak absorption band centered around 455 nm which can be attributed to a transition involving the phn5Fpy C$^\text{N}$ ligand.

![Absorption spectra](image)

**Figure 3.6:** Absorption spectra of $[\text{Ir(p5Fpy)}_2(\text{biq})][\text{PF}_6]$, $[\text{Ir(2na5Fpy)}_2(\text{biq})][\text{PF}_6]$, $[\text{Ir(phn5Fpy)}_2(\text{pbpy})][\text{PF}_6]$, $[\text{Ir(phn5Fpy)}_2(\text{biq})][\text{PF}_6]$ and $[\text{Ir(2na5Fpy)}_2(\text{biq})][\text{PF}_6]$.

The complexes with a fluorinated phenyl ring show similar and well defined absorption bands in the three different regions corresponding to the LC transitions of both ligands (absorptions below 300 nm), the $^1\text{MLCT}$ (300 to 350 nm) and the $^3\text{MLCT}$, $^3\text{LLCT}$ and $^3\text{LC}$ transitions (above 350 nm extending into the visible region).
Figure 3.7: Absorption spectra of [Ir(3Fppy)$_2$(biq)][PF$_6$], [Ir(4Fppy)$_2$(biq)][PF$_6$], [Ir(3Fpqu)$_2$(biq)][PF$_6$], [Ir(4Fpqu)$_2$(biq)][PF$_6$], [Ir(4Fp-iqu)$_2$(biq)][PF$_6$]) and [Ir(3Fp-iqu)$_2$(biq)][PF$_6$].

3.3.2 Photoluminescence studies

The photoluminescence (PL) studies were performed on powder samples for all the complexes and the results are summarized in Table 3.1. All the complexes emit in the red to deep red region of the visible spectrum when excited at 360 nm. The PL spectra of the complexes with extended aromatic systems are shown in Figure 3.8.
Figure 3.8: Emission spectra of [Ir(phn-1qu)_2(biq)][PF_6], [Ir(2na-2qu)_2(biq)][PF_6], [Ir(1na-iqu)_2(biq)][PF_6] and [Ir(bzqu)_2(biq)][PF_6], excited at 360 nm.

A typical emission spectrum is seen for [Ir(phn-iqu)_2(biq)][PF_6] with two emission maxima at 680 and 800 nm in the deep red region and another emission in the deep blue region with an emission maximum around 400 nm. The emission spectrum for [Ir(bzqu)_2(biq)][PF_6] also shows a broad weak emission around 500 nm together with the expected strong red emission with emission maximum at 644 nm. The emission observed for these two complexes with shorter wavelengths suggest that excited electrons relax radiatively directly to the ground state from higher excited state other than the LUMO. All the pyridine fluorinated complexes show emission spectra featuring one emission maximum in the range 635 to 683 nm (figure 3.9). A red shift in the emission maximum is observed by changing the N-N ligand to more increased π-systems going from [Ir(phn5Fpy)_2(pbpy)][PF_6] to
[Ir(phen5Fpy)2(biq)][PF6] due to the low lying level of the LUMO for the biq complex compared to the pbpy complex. It can be seen that the emission spectra for the pyridine fluorinated complexes are more structured compared to the emission spectra for the complexes with extended aromatic systems. The phenyl ring of the fluorinated pyridine C^N ligands has a greater character in the HOMO due to the influence of the fluorine substituent and the observed emissions are more ligand centered (LC). While emission from the complexes with the extended aromatic systems are more metal to ligand centered due to the larger contribution of the iridium d-orbitals to the HOMO.

**Figure 3.9:** Photoluminescence spectra of [Ir(p5Fpy)2(biq)][PF6], [Ir(2na5Fpy)2(biq)][PF6], [Ir(phen5Fpy)2(pbpy)][PF6], [Ir(phen5Fpy)2(biq)][PF6] and [Ir(2na5Fpy)2(biq)][PF6], excited at 360 nm.
Just like the absorption spectra, the PL spectra for the phenyl fluorinated complexes are very similar with main emission maxima in the range of 638 to 651 nm. All the complexes have a weak emission band centered around 515 nm as shown in figure 3.10. In this case the more intense wavelength emissions around 650 nm arise from the relaxation of the excited electrons from the LUMO (located on the biq ancillary ligand) to the HOMO located on the metal t_{2g} orbital resulting to the observed structureless emission bands. While the weak emission bands at shorter wavelength arise from a LC emission from the LUMO of the biq acillary ligand to the HOMO located on the phenyl ring of the C^N ligands since they are expected to be more stabilized due to the fluorine substituent.

![Photoluminescence spectra of \([\text{Ir}(3\text{Fppy})_2(\text{biq})][\text{PF}_6]],[\text{Ir}(4\text{Fppy})_2(\text{biq})][\text{PF}_6]],[\text{Ir}(3\text{Fpqu})_2(\text{biq})][\text{PF}_6]],[\text{Ir}(4\text{Fpqu})_2(\text{biq})][\text{PF}_6]],[\text{Ir}(4\text{Fp-iqu})_2(\text{biq})][\text{PF}_6]] and [\text{Ir}(3\text{Fp-iqu})_2(\text{biq})][\text{PF}_6]].

Figure 3.10: Photoluminescence spectra of \([\text{Ir}(3\text{Fppy})_2(\text{biq})][\text{PF}_6]],[\text{Ir}(4\text{Fppy})_2(\text{biq})][\text{PF}_6]],[\text{Ir}(3\text{Fpqu})_2(\text{biq})][\text{PF}_6]],[\text{Ir}(4\text{Fpqu})_2(\text{biq})][\text{PF}_6]],[\text{Ir}(4\text{Fp-iqu})_2(\text{biq})][\text{PF}_6]] and [\text{Ir}(3\text{Fp-iqu})_2(\text{biq})][\text{PF}_6]].
The emission maxima of the complexes are further red shifted by extending the aromatic system of the pyridine ring of the CN ligands for some of the complexes.

Thin film; The PL spectra (thin film) of some complexes measured from fabricated LEC devices (where the emissive layer consist of a mixture of the complex and an ionic liquid (IL)) show a single emission band (figure 3.12) and the results are summarized in table 3.1. For the complexes with the extended aromatic system ([Ir(2na-2qu)₂(bqu)][PF₆] and [Ir(bzqu)₂(bqu)][PF₆]) and the [Ir(2na5Fpy)₂(bqu)][PF₆], a red shift in the emission maximum greater than 20 nm was observed on going from powder to thin film. The red shift in the emission wavelength could be attributed to the change in inter-complex interactions due to the present of the IL (1-butyl-3-methylimidazolium hexafluorophosphate, [BMIM][PF₆]) in the thin films. However there was no such shift in the emission maximum of [Ir(p5Fpy)₂(bqu)][PF₆] on going from powder to thin film suggesting the shift in the PL cannot be attributed to the presence of the IL. On the other hand, there was both a red and blue shift in the emission maximum of the phenyl fluorinated complexes as seen in table 3.1. It can be suggested that the shift in the emission maximum comparing the photoluminescence of the samples as powder and thin film is an intrinsic property of each complex which is influenced by the packing arrangement of the complexes in these two different forms.
Table 3.1: Photoluminescence properties of the red emitting Ir-iTMCs.

<table>
<thead>
<tr>
<th></th>
<th>Powder sample</th>
<th>Thin film</th>
<th>PLQY [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ir(phn-qu)_2(biq)][PF_6]</td>
<td>680, 800</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Ir(2na-2qu)_2(biq)][PF_6]</td>
<td>656</td>
<td>679</td>
<td>5.34</td>
</tr>
<tr>
<td>[Ir(na-iqu)_2(biq)][PF_6]</td>
<td>712</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Ir(bzqu)_2(biq)][PF_6]</td>
<td>644, 511</td>
<td>662</td>
<td>25.02</td>
</tr>
<tr>
<td>[Ir(p5Fpy)_2(biq)][PF_6]</td>
<td>656</td>
<td>656</td>
<td>14.44</td>
</tr>
<tr>
<td>[Ir(php5Fpy)_2(pbpy)][PF_6]</td>
<td>668</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Ir(php5Fpy)_2(biq)][PF_6]</td>
<td>683</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Ir(na5Fpy)_2(biq)][PF_6]</td>
<td>650</td>
<td>680</td>
<td>4.31</td>
</tr>
<tr>
<td>[Ir(2na5Fpy)_2(biq)][PF_6]</td>
<td>635</td>
<td></td>
<td>16.81</td>
</tr>
<tr>
<td>[Ir(4Fppy)_2(biq)][PF_6]</td>
<td>638, 511</td>
<td>644</td>
<td>27.46</td>
</tr>
<tr>
<td>[Ir(3Fppy)_2(biq)][PF_6]</td>
<td>638, 515</td>
<td>629</td>
<td>20.42</td>
</tr>
<tr>
<td>[Ir(3Fpqu)_2(biq)][PF_6]</td>
<td>651, 515</td>
<td>652</td>
<td>8.9</td>
</tr>
<tr>
<td>[Ir(4Fpqu)_2(biq)][PF_6]</td>
<td>644, 517</td>
<td>629</td>
<td>16.71</td>
</tr>
<tr>
<td>[Ir(4Fp-iqu)_2(biq)][PF_6]</td>
<td>643, 516</td>
<td>642</td>
<td>10.39</td>
</tr>
<tr>
<td>[Ir(3Fp-iqu)_2(biq)][PF_6]</td>
<td>646, 669, 517</td>
<td>661</td>
<td>5.84</td>
</tr>
</tbody>
</table>

It was found that the PLQY of the fluorinated complexes were higher compared to the non-fluorinated complexes except for the [Ir(bzqu)_2(biq)][PF_6] with a high PLQY of 25.02% which can be attributed to a reduction in the radiationless vibrational relaxation process of excited electrons by the use of a more rigid bzqu C^N ligand. PLQY of 20% and 27% were obtained for [Ir(4Fppy)_2(biq)][PF_6] and [Ir(3Fppy)_2(biq)][PF_6] respectively making these complexes to be among the red
emitting Ir-iTMCs with very high PLQY. In general, a majority of the PLQY of the synthesized complexes are higher compared to most literature known complexes with similar emission maximum.

![Figure 3.11: Thin film photoluminescence spectra of...](image)

**Figure 3.11:** Thin film photoluminescence spectra of [Ir(4Fppy)$_2$(biq)][PF$_6$], [Ir(3Fppy)$_2$(biq)][PF$_6$], [Ir(3Fpqu)$_2$(biq)][PF$_6$], [Ir(4Fpqu)$_2$(biq)][PF$_6$], [Ir(4Fp-iqu)$_2$(biq)][PF$_6$] and [Ir(3Fp-iqu)$_2$(biq)][PF$_6$].

### 3.4 Electrochemical studies

The electrochemical properties were investigated by cyclic voltammetry (CV) using tetraethylammonium hexafluorophosphosphate as the electrolyte. For all compounds a solution of the complex in acetonitrile and/or acetone was used.

For [Ir(2na-2qu)$_2$(biq)][PF$_6$] and [Ir(na-iqu)$_2$(biq)][PF$_6$], the complexes with extended aromatic systems, a single irreversible and for [Ir(bzqu)$_2$(biq)][PF$_6$] a
quasi-reversible oxidation potential and double reversible reduction potentials were observed. The reduction and oxidation half potentials ($E_{1/2\text{red}}$ and $E_{1/2\text{ox}}$ respectively), the estimated LUMO and HOMO energy level calculated from the $E_{1/2\text{red}}$ and $E_{1/2\text{ox}}$ respectively and the HOMO-LUMO energy gap of the complexes are summarized in table 3.2 and their cyclic voltammograms are shown in the appendix (figure 3a).

**Table 3.2:** Electrochemical properties of complexes with extended aromatic systems and fluorinated pyridine C^N ligands measured in acetonitrile.

<table>
<thead>
<tr>
<th></th>
<th>$E_{1/2\text{red}}$ [V]</th>
<th>$E_{1/2\text{ox}}$ [V]</th>
<th>LUMO [eV]</th>
<th>HOMO [eV]</th>
<th>Energy gap [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ir(2na-2qu)(_2)(biq)][PF(_6)]</td>
<td>-1.27, -0.71</td>
<td>1.51</td>
<td>-3.53</td>
<td>-4.09</td>
<td>-6.31</td>
</tr>
<tr>
<td>[Ir(na-iqu)(_2)(biq)][PF(_6)]</td>
<td>-1.53, -0.93</td>
<td>1.24</td>
<td>-3.27</td>
<td>-3.87</td>
<td>-6.04</td>
</tr>
<tr>
<td>[Ir(bzqu)(_2)(biq)][PF(_6)]</td>
<td>-1.59, -0.99</td>
<td>1.25</td>
<td>-3.21</td>
<td>-3.81</td>
<td>-6.05</td>
</tr>
<tr>
<td>[Ir(p5Fpy)(_2)(biq)][PF(_6)]</td>
<td>-1.38, -0.81</td>
<td>1.39</td>
<td>-3.42</td>
<td>-3.99</td>
<td>-6.19</td>
</tr>
<tr>
<td>[Ir(na5Fpy)(_2)(biq)][PF(_6)]</td>
<td>-1.59, -1.04</td>
<td>1.09</td>
<td>-3.21</td>
<td>-3.76</td>
<td></td>
</tr>
<tr>
<td>[Ir(2na5Fpy)(_2)(biq)][PF(_6)]</td>
<td>-1.49, -0.92</td>
<td>1.22</td>
<td>-3.31</td>
<td>-3.88</td>
<td>-6.02</td>
</tr>
</tbody>
</table>

**Figure 3.12:** Cyclic voltammogram of [Ir(p5Fpy)\(_2\)(biq)][PF\(_6\)] measured in an acetonitrile solution.
Three of the fluorinated pyridine C^N ligand-based red emitting Ir-iTMCs show similar reduction potentials like those for the red emitting complexes with extended aromatic systems. The N^N ligand (where the LUMO lies and where the reduction occurs) is the same for all the complexes. All three complexes display irreversible oxidation potentials. The electrochemical properties of the complexes are also summarized in table 3.2 and the cyclic voltammogram of [Ir(p5Fpy)$_2$(biq)][PF$_6$] is shown in figure 3.12. The other two cyclic voltammograms for [Ir(2na5Fpy)$_2$(biq)][PF$_6$] and [Ir(na5Fpy)$_2$(biq)][PF$_6$] are shown in the appendix (figure 3b).

To be able to compare results from both solvents, the electrochemical properties of [Ir(4Fppy)$_2$(biq)][PF$_6$] and [Ir(3Fppy)$_2$(biq)][PF$_6$] were measured in both solvents. No significant shift in the reduction and oxidation potentials of other literature reported complexes were seen upon changing the solvent from acetonitrile to dimethylsulfoxide used in the CV measurements [14]. Similar results were also expected in this case. On the contrary there was a cathodic shift in both the reduction and oxidation potentials of approximately 180 mV upon changing the solvent from acetonitrile to acetone for both [Ir(4Fppy)$_2$(biq)][PF$_6$] (figure 3.13) and [Ir(3Fppy)$_2$(biq)][PF$_6$] (figure 3.14). The obtained results are summarized are in table 3.3. Interestingly, the nature of the potential waves for both complexes remains unaffected upon the change in the solvent. The differences between the $E_{1/2ox}$ and the two $E_{1/2red}$ of both complexes in the different solvents were also the same (table3.3). This implies that the LUMO and HOMO energy levels of both complexes were modified by the solvent in the same way which resulted to an unaffected LUMO-HOMO energy gap.
Table 3.3: Electrochemical properties of $[\text{Ir(4Fppy)}_2(\text{biq})][\text{PF}_6]$ and $[\text{Ir(3Fppy)}_2(\text{biq})][\text{PF}_6]$ measured in acetonitrile and acetone solutions.

<table>
<thead>
<tr>
<th></th>
<th>$E_{1/2\text{red}}$ [V]</th>
<th>$E_{1/2\text{ox}}$ [V]</th>
<th>LUMO [eV]</th>
<th>HOMO [eV]</th>
<th>Energy gap [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Ir(4Fppy)}_2(\text{biq})][\text{PF}_6]$</td>
<td>-1.62, -1.02</td>
<td>1.45</td>
<td>-3.18</td>
<td>-3.78</td>
<td>-6.25</td>
</tr>
<tr>
<td>in acetone</td>
<td>-1.76, -1.17</td>
<td>1.27</td>
<td>-3.04</td>
<td>-3.63</td>
<td>-6.07</td>
</tr>
<tr>
<td>$[\text{Ir(3Fppy)}_2(\text{biq})][\text{PF}_6]$</td>
<td>-1.46, -0.88</td>
<td>1.57</td>
<td>-3.34</td>
<td>-3.92</td>
<td>-6.37</td>
</tr>
<tr>
<td>in acetone</td>
<td>-1.64, -1.05</td>
<td>1.37</td>
<td>-3.16</td>
<td>-3.75</td>
<td>-6.17</td>
</tr>
</tbody>
</table>

* measured in acetonitrile

Because of the change in the potentials at which the reduction and oxidation of the complexes occur during the CV measurements upon changing the solvent from acetonitrile to acetone, it is impossible to compare the shift in the reduction and oxidation potentials of different complexes measured in the two different solvents.

Figure 3.13: Cyclic voltammogram of $[\text{Ir(4Fppy)}_2(\text{biq})][\text{PF}_6]$ measured in acetonitrile and acetone solution.
Figure 3.14: Cyclic voltammogram of [Ir(3Fppy)$_2$(biq)][PF$_6$] measured in acetonitrile and acetone solution.

The cyclic voltammogram of [Ir(3Fp2qu)$_2$(biq)][PF$_6$], [Ir(4Fp2qu)$_2$(biq)][PF$_6$], [Ir(4Fp-iqu)$_2$(biq)][PF$_6$] and [Ir(3Fp-iqu)$_2$(biq)][PF$_6$] are shown in figure 3.15 and their electrochemical properties are summarized in table 3.4. Again, the reduction potentials of the complexes are very similar due to the same N^N ligand in the complexes. The oxidation potentials of the complexes with the fluorine substituted ortho to the coordinating carbon of the C^N ligands are quasi-reversible while the complexes with the meta substituted fluorine all show irreversible oxidation potentials.
Figure 3.15: Cyclic voltammogram of phenyl fluorinated C\(^N\) ligands measured in acetone.

<table>
<thead>
<tr>
<th>Complex</th>
<th>(E_{1/2\text{red}})</th>
<th>(E_{1/2\text{ox}})</th>
<th>LUMO</th>
<th>HOMO</th>
<th>Energy gap [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>[\text{Ir(3Fp2qu)}_2(\text{biq})][\text{PF}_6] ]</td>
<td>-1.58, -0.97</td>
<td>1.46</td>
<td>-3.22</td>
<td>-3.83</td>
<td>-6.26</td>
</tr>
<tr>
<td>[\text{Ir(4Fp2qu)}_2(\text{biq})][\text{PF}_6] ]</td>
<td>-1.59, -1.01</td>
<td>1.44</td>
<td>-3.21</td>
<td>-3.79</td>
<td>-6.24</td>
</tr>
<tr>
<td>[\text{Ir(4Fp-iqu)}_2(\text{biq})][\text{PF}_6] ]</td>
<td>-1.57, -1.00</td>
<td>1.43</td>
<td>-3.22</td>
<td>-3.80</td>
<td>-6.23</td>
</tr>
<tr>
<td>[\text{Ir(3Fp-iqu)}_2(\text{biq})][\text{PF}_6] ]</td>
<td>-1.58, -0.98</td>
<td>1.44</td>
<td>-3.21</td>
<td>-3.84</td>
<td>-6.24</td>
</tr>
</tbody>
</table>

Table 3.4: Electrochemical properties of four complexes with phenyl fluorinated C\(^N\) ligands measured in acetone.
In general the band gaps (energy gap) for the fluorinated complexes with biquinoline as the N^N ligand are in the range expected for red emitting Ir-iTMCs. Extending the aromaticity of the pyridine ring of the C^N ligands do not influence the band gaps of the complexes. Likewise, changing the position of the fluorine substituent from the ortho to the meta position relative to the coordinating carbon of the C^N ligands do not have any significant influence on the band gaps of the complexes. This implies that the fluorine atom possesses the same electron withdrawing strength on the phenyl ring of the C^N ligands. However, the quasi-reversible oxidation potentials of the ortho fluorinated complexes are opposed to the irreversible oxidation of the meta fluorinated complexes suggesting a stonger ligand contribution to the HOMO of the ortho fluorinated complexes.

3.5 Electroluminescence studies

LEC devices were fabricated incorporating some of the complexes (from all the three different groups of complexes) to investigate their electroluminescence properties. The LEC devices in this research work were all fabricated as briefly described in the experimental section of this chapter. A more detail fabrication process is described in the experimental section of chapter 6. All the LEC devices have the configuration ITO/PEDOT:PSS/Ir-iTMC:IL(3:1)/Al and their performances were measured using a Botest OLED lifetime test system OLT. All the fabricated LEC devices were driven under a pulsed current mode with an average current density of 100 A/m^2 at a frequency of 1000 Hz and a block wave with a duty cycle of 50% except otherwise stated.

The electroluminescence of [Ir(phn-i-qu)_2(biq)][PF_6], [Ir(2na-2-qu)_2(biq)][PF_6] and [Ir(1na-i-qu)_2(biq)][PF_6] could be seen with the human eyes to be in the deep red region. However, the luminance of these LEC devices was too low and could not be detected by the sensor of the Botest-system. The luminance and operating voltage behaviors over time for complex [Ir(bzqu)_2(biq)][PF_6] is shown in figure 3.16.
Figure 3.16: Luminance and operating voltage vs time during a LEC device operation based on [Ir(bzqu)₂(biq)][PF$_6$].

A maximum luminance of 33.65 cd/m$^2$ was achieved giving a current efficiency and power efficiency of 0.33 cd/A and 0.2 lm/W, respectively. The luminance is lower than expected for this complex with a high PLQY of 25.02%. This suggests that the processes responsible for the PL are different compared to the EL. The luminance of the device also depends on effective formation of excitons and what fraction of the excitons relaxes radiatively. Nevertheless, the high PLQY of the complex implies that the device performance could be improved. Interestingly, the LEC device demonstrated an enhanced device stability reaching a lifetime of 280 h. The use of a more rigid C$^N$ ligand could be the reason for the improvement in the device lifetime. The small HOMO-LUMO energy gap of red emitting Ir-iTMCs also paves way for the relaxation of an excited state via a vibrational radiationless process. Increasing molecular vibration of the Ir-iTMC during device operation could lead to degradation of the complex via bond breaking. The use of a more rigid C$^N$ ligand should reduce the overall molecular vibration of the complex leading to an enhanced
stability of the complex during device operation. Based on this considerations, the long lifetime of the LEC device fabricated using [Ir(bzqu)_2(biq)][PF_6] is attributed to the use of a more rigid bzqu C^N ligand.

Another red LEC device based on [Ir(p5Fpy)_2(biq)][PF_6] reached a lifetime of 263 h with an initial maximum luminance of 68.4 cd/m^2 (figure 3.17) resulting in current and power efficiencies of 0.68 cd/A and 0.45 lm/W, respectively. The improvement in the device lifetime is attributed to the reduction in the strength of the σ-antibonding interaction between the N_C^N and the Ir atom by using a fluorinated pyridine ring as part of the C^N ligands. A second red LEC device incorporating [Ir(na5Fpy)_2(biq)][PF_6] displayed a rather low luminance of 2.5 cd/m^2. Remarkable about this device is its stability showing no drop in luminance during 300 hours of continuous operation (figure 3c, appendix). It has been proven that indeed introducing an electron withdrawing substituent such as fluorine to the pyridine ring of the C^N ligands of red emitting cationic iridium complexes is a good approach for enhancing the structural stability of the complexes leading to long lived red LEC devices.
Figure 3.17: Luminance and operating voltage vs time during a LEC device operation of [Ir(p5Fpy)₂(biq)][PF₆].

The operating voltage of the LEC device based on [Ir(p5Fpy)₂(biq)][PF₆] was observed to gradually increase over time compared to that of [Ir(bzqu)₂(biq)][PF₆] which appear to be virtually constant over time during device operation. The [Ir(bzqu)₂(biq)][PF₆] complex can be considered to be a better charge transporter than the [Ir(p5Fpy)₂(biq)][PF₆] complex.

A dramatic improvement in the efficiency without compromising the stability of red LEC devices was obtained using [Ir(4Fppy)₂(biq)][PF₆] and [Ir(3Fppy)₂(biq)][PF₆]. Device performances with current and power efficiencies of 1.31 cd/A and 0.93 lm/W, respectively, at an initial maximum luminance of 131 cd/m² reaching a lifetime of 288 h was reached for the red LEC device based on [Ir(3Fppy)₂(biq)][PF₆] (figure 3.18). Even better efficiencies of 3.25 cd/A and 2.3 lm/W for the current and power efficiencies respectively with an initial maximum luminance of 336 cd/m².
and a lifetime of 168 hours was achieved for another red LEC device based on [Ir(4Fppy)$_2$(biq)][PF$_6$] (figure 3.19). As expected, fluorinating the phenyl ring of the C$^\wedge$N ligands led to a dramatic improvement in the device performance of red emitting Ir-iTMCs.

Figure 3.18: Luminance and operating voltage vs time during a LEC device operation of [Ir(3Fppy)$_2$(biq)][PF$_6$].

The operating voltages of both devices based on [Ir(3Fppy)$_2$(biq)][PF$_6$] and [Ir(4Fppy)$_2$(biq)][PF$_6$] appear to be constant throughout the device operation. This implies good charge transporting property of these red emitting Ir-iTMCs.
3.6 Conclusions

Fifteen new Ir-iTMCs with emission in the red to deep red region of the visible spectrum were successfully synthesized. UV-Vis absorption and PL studies on all the complexes were performed and their electrochemical properties were studied by cyclic voltammetry. The complexes were structurally characterized by $^1$H and $^{13}$C NMR spectroscopy and SXRD on the obtained single crystals. The complexes displayed high PLQY, reaching a maximum value of 27 % for the $[\text{Ir}(4\text{Fppy})_2(biq)]\text{[PF}_6]$ complex. In general the performances of the red LEC devices incorporating the newly synthesized complexes were far above reported performances for other complexes with similar emission maxima when operated under similar conditions [6-12].
Using a more rigid C^N ligand (bzqu) in the synthesis of a red Ir-iTMC ([Ir(bzqu)2(biq)][PF6]), resulted in an improvement of its LEC device stability reaching 280 h. Also, adding a fluorine substituent to the pyridine ring of the C^N ligand led to an enhancement in the stability of the LEC devices. For example, a LEC device based on complex [Ir(p5Fpy)2(biq)][PF6] demonstrated a lifetime of 263 h with an initial maximum luminance of 68.4 cd/m². Another deep red LEC device based on [Ir(3Fppy)2(biq)][PF6] was operated for 300 h without any drop in luminance (however, the maximum luminance of this device was 2.5 cd/m²).

Notably high efficiencies for red LEC devices were achieved by using red emitting Ir-iTMCs with fluorine substituent on the phenyl ring of the C^N ligands in device fabrication. Performances of 1.32 cd/A and 0.97 lm/W for the current and power efficiencies respectively at an initial maximum luminance of 132 cd/m² were demonstrated by a red LEC device based on [Ir(3Fppy)2(biq)][PF6]. A remarkable feature of the device is its lifetime reaching a value of 288 h. The enhanced device stability is understood to be as a result of the improvement in the structural stability of the complex via the F-N intramolecular interactions between the two C^N ligands. Very high device performance of 3.25 cd/A and 2.27 lm/W for the current and power efficiencies without any device optimization was achieved from a LEC device based on [Ir(4Fppy)2(biq)][PF6]. The LEC device demonstrated an initial maximum luminance of 325 cd/m² and reaching a lifetime of 186 h. The performances reported for red LEC devices in this work show significant improvements compared to literature data and mark a great step toward using LEC devices in practical applications.
3.7 Solid state structures

Table 3.5: Crystallographic data for [Ir(bzqu)$_2$(biq)][PF$_6$].

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<td>Space group</td>
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Figure 3.20: Detail of the single crystal structure of [Ir(bzqu)$_2$(biq)][PF$_6$] (ellipsoids plotted at 40% probability level). The counter anion PF$_6$, ethyl acetate and hydrogen atoms are omitted for clarity.
Figure 3.21: Details of the single crystal structure of [Ir(3Fpqu)₂(biq)][PF₆] (ellipsoids plotted at 40% probability level) showing the F-N intramolecular interactions between the two C^N ligands (b) and π-π intramolecular interactions between the biq N^N ligand and the quinoline ring of the C^N ligands (a). The counter anion PF₆, ethyl acetate and hydrogen atoms are omitted for clarity.
Table 3.6: Crystallographic data for [Ir(3Fpqu)\(_2\)(biq)][PF\(_6\)] and [Ir(4Fp-iqu)\(_2\)(biq)][PF\(_6\)].

<table>
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<td>C(<em>{48})H(</em>{30})F(_8)N(<em>4)P(</em>{Ir})</td>
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<td>-15 ≤ h ≤ 15, -16 ≤ k ≤ 16, -18 ≤ l ≤ 18</td>
</tr>
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3.8 Experimental

3.8.1 Synthesis and characterization

In general, the light emitting complexes were synthesized in a two step process. The first step is the synthesis of the dichloro-bridged diiridium complex and the second step is the synthesis of the light emitting complex via opening of the dichloro-bridged intermediate complex in the presence of the ancillary ligand. All commercially available materials were used as received without any further purification.

The dichloro-bridged intermediate diiridium complexes were synthesized according to the modified literature procedure reported by M. Nonoyama, [15] and E. Holder et al., [16]. While the light emitting Ir-iTMCs were also synthesized according to the modified literature procedure reported by J.D. Slinker et al., [17]. The intermediate...
complexes were not characterized while the light emitting Ir-iTMCs were characterized as described below.

### 3.8.2 Characterization techniques used for the Ir-iTMCs

The light emitting Ir-iTMCs were characterized by $^1$H and $^{13}$C NMR spectroscopy and by SXRD on the obtained single crystal of some of the complexes as described in the experimental section of Chapter 2. The Ir-iTMCs were further characterized by UV-Vis absorption spectroscopy in an acetonitrile solution with concentration of $10^{-5}$ M using a CARY 300 scan photospectrometer. The absorption spectra were recorded from 200 to 800 nm. The photoluminescence spectra of the complexes in their powder form were measured using the Fluorolog 3 system with an excitation wavelength of 360 nm. Using the same Fluorolog 3 instrument, the PLQYs were measured using the absolute integration sphere method with barium sulfate as the reflection standard. Cyclic voltammetric measurements were performed on a µAUTOLAB type III potentiostat/galvanostat instrument with a scan rate of 100 mV/s in dry acetonitrile or acetone solvent with the three electrode configuration: a glassy carbon electrode as the working electrode, an aqueous saturated calomel electrode as the operating reference electrode and a platinum wire as the counter electrode. A 0.1 M solution of tetraethylammonium hexafluorophosphate in acetonitrile or acetone was used as the supporting electrolyte and ferrocene was selected as the internal standard. The measurements were carried out in an argon glove box with water and oxygen levels less than 0.5 ppm. All the spectra and voltammograms were plotted using Origin lab 7 software.

### 3.8.3 Summarized description of LEC device fabrication and characterization

Glass substrate with patterned ITO was cleaned and treated with UV/ozone prior to use. A PEDOT:PSS layer of approximately 45 nm is then spin coated on the ITO substrate and baked at 150 °C for 15 minutes. The emissive layer (app. 90 nm) is then spin coated from a mixed acetonitrile solution (23 mg/mL) containing the Ir-
iTMC and an IL (1-butyl-3-methylimidazolium hexafluorophosphate, [BMIM][PF$_6$]) a 3: ratio 1. The device is dried under vacuum for at least 2 h followed by thermal evaporation of the aluminium cathode. Finally the device is encapsulated with a glass cover using an UV-setting glue in an argon glove box with water and oxygen levels less than 0.1 ppm. The LEC device performance was investigated using a Botest OLED lifetime test system OLT and the LEC device was driven under a pulsed current mode. The thin film PL spectra were measured using an AvaSpec-2048 TEC-FT2 fiber-optic spectrometer with an excitation wavelength of 380 nm.

3.8.4 General synthetic procedure for the dichloro-bridged intermediate diiridium complexes

IrCl$_3$ x H$_2$O (1 eq.) was transferred into a two neck Schlenk flask in an Ar-glovebox, degassed water and degassed 2-methoxyethanol were added to the Schlenk flask via canula while stirring the reaction mixture. The required C$^N$ ligand (2.15 eq.) was then added to the reaction mixture and refluxed at 120 °C for 18 hours. The mixture was allowed to cool to room temperature (by the help of an ice bath). The precipitate formed was filtered using a P3 frit, further washed with distilled water and degassed diethyl ether three times each. The obtained precipitate was dried under vacuum and stored in an argon glovebox. All synthetic and work-up processes were done under inert atmosphere.

[Ir(p5Fpy)$_2$Cl]$_2$:: IrCl$_3$ xH$_2$O (0.75 g, 2.51 mmol), 5-fluoro-2-phenylpyridine (0.91 g, 5.25 mmol), water (5 mL), 2-methoxyethanol (20 mL), yellow powder (yield: 1.43 g, 92.2%).

[Ir(na5Fpy)$_2$Cl]$_2$: IrCl$_3$ xH$_2$O (0.44 g, 1.47 mmol), 5-fluoro-2-(1-naphthalene)pyridine (0.972 g, 3.08 mmol), water (5 mL), 2-methoxyethanol (20 mL), brown powder (yield: 0.45 g, 45.4%).
[Ir(2na-2qu)_2Cl_2]: IrCl_3 xH_2O (0.84 g, 2.81 mmol), 2-(2-naphthyl)quinoline (1.50 g, 6.04 mmol), water (5 mL), 2-methoxyethanol (20 mL), brown powder (yield: 1.45 g, 70.1%).

[Ir(phen5Fpy)_2Cl_2]: IrCl_3 xH_2O (0.57 g, 1.92 mmol), 5-fluoro-2-(9-phenanthryl)pyridine (1.1 g, 4.02 mmol), water (5 mL), 2-methoxyethanol (20 mL), brown powder (yield: 1.25 g, 84.3%).

[Ir(phen-iq)_2Cl_2]: IrCl_3 xH_2O (0.14 g, 0.48 mmol), 1-(9-napththalene)isoquinoline (0.305 g, 1.01 mmol), water (3 mL), 2-methoxyethanol (15 mL), brown powder (yield: 0.31 g, 77.2%).

[Ir(4Fppy)_2Cl_2]: IrCl_3 xH_2O (10.0 g, 33.5 mmol), 2-(4-fluorophenyl)pyridine (12.1 g, 72.02 mmol), water (50 mL), 2-methoxyethanol (200 mL), yellow powder (yield: 16.8 g, 87.6%).

[Ir(3Fppy)_2Cl_2]: IrCl_3 xH_2O (9.07 g, 30.01 mmol), 2-(3-fluorophenyl)pyridine (11.0 g, 64.52 mmol), water (50 mL), 2-methoxyethanol (200 mL), yellow powder (yield: 11.9 g, 69.3%).

[Ir(naph-iq)_2Cl_2]: IrCl_3 xH_2O (0.4 g, 1.33 mmol), 1-(1-naphthyl)isoquinoline (1.49 g, 2.88 mmol), water (5 mL), 2-methoxyethanol (20 mL), brown powder (yield: 0.76 g, 77.6%).

[Ir(bzqu)_2Cl_2]: IrCl_3 xH_2O (6.18 g, 20.7 mmol), benzo[h]quinoline (7.76 g, 43.3 mmol), water (50 mL), 2-methoxyethanol (200 mL), brownish yellow powder (yield: 11.4 g, 94.2%).

[Ir(2na5Fpy)_2Cl_2]: IrCl_3 xH_2O (0.44 g, 1.47 mmol), 5-fluoro-2-(1-naphthalene)pyridine (0.972 g, 3.08 mmol), water (5 mL), 2-methoxyethanol (20 mL), brown powder (yield: 0.72 g, 72.6%).
[Ir(3Fpqu)₂Cl₂]: IrCl₃ xH₂O (1.27 g, 4.28 mmol), 2-(3-fluoropyridine)quinoline (2.0 g, 8.96 mmol), water (10 mL), 2-methoxyethanol (40 mL), brown powder (yield: 2.4 g, 83.4%).

[Ir(4Fpqu)₂Cl₂]: IrCl₃ xH₂O (1.27 g, 4.28 mmol), 2-(4-fluoropyridine)quinoline (2.0 g, 8.96 mmol), water (10 mL), 2-methoxyethanol (40 mL), brown powder (yield: 1.88 g, 65.6%).

[Ir(4Fp-iqu)₂Cl₂]: IrCl₃ xH₂O (1.02 g, 3.42 mmol), 1-(4-fluoropyridine)isoquinoline (1.6 g, 7.16 mmol), water (10 mL), 2-methoxyethanol (40 mL), brown powder (yield: 1.82 g, 79.2%).

[Ir(3Fp-iqu)₂Cl₂]: IrCl₃ xH₂O (1.02 g, 3.42 mmol), 1-(4-fluoropyridine)isoquinoline (1.6 g, 7.16 mmol), water (10 mL), 2-methoxyethanol (40 mL), brown powder (yield: 1.56 g, 68.1%).

### 3.8.5 General synthetic procedure for the light emitting Ir-iTMCs

The required amount of the ancillary ligand (N^N ligand, 2.15 eq.) and chloro-bridged iridium dimer (1 eq.) were transferred into a two neck Schlenk flask in an Ar-glovebox. Degassed ethylene glycol was added (via a cannula) and the reaction mixture was stirred at 150 °C for 20 hours (under refluxing and pressure regulating conditions) which resulted to a clear coloured solution. The solution was allowed to cool to room temperature and transferred into another schlenk flask containing degassed distilled water. While stirring, triethyl amine (NEt₃) was added to adjust pH=8 and the solution was washed with diethyl ether. An excess aqueous solution of ammonium hexafluorophosphate (NH₄PF₆) was added to the aqueous phase resulting in the precipitation of the desired heteroleptic iridium complex. The product was then filtered and washed with degassed water (3x) and degassed diethylether (3x) and then dried under vacuum. The synthesized complexes were purified using column chromatographic technique. A silica gel 60 (0.063-0.200 mm)
column built with dichloromethane was used and the complex was eluted using a dichloromethane/ethyl acetate mixture (9:1). The solvent mixture was reduced by removing of all the dichloromethane resulting in immediate or slow precipitation of the desired product. The obtained product was dried under vacuum and stored in an argon glove box. The synthetic, work-up and purification processes were done under inert atmosphere.

**[Ir(p5Fpy)$_2$(biq)][PF$_6$]:** [Ir(p5Fpy)Cl]$_2$ (0.5 g, 0.43 mmol), 2,2’-biquinoline (0.205 g, 0.884 mmol), ethylene glycol (25 mL), red powder (yield: 0.55 g, 68.1%). $^1$H NMR (MeCN, 400 MHz): $\delta$ 8.81 (d, $J = 8.59$ Hz, 2 H), 8.72 (d, $J = 8.59$ Hz, 2 H), 8.08 (dd, $J = 3.79$, 1.52 Hz, 2 H), 8.03 (d, $J = 3.54$ Hz, 2 H), 7.98 (d, $J = 3.54$ Hz, 2 H), 7.85 (t, $J = 2.78$ Hz, 2 H), 7.73 (dd, $J = 7.83$, 2.78 Hz, 2 H), 7.69 (dd, $J = 6.57$, 1.77 Hz, 2 H), 7.62 (ddd, 8.08, 7.07, 1.26 Hz, 2 H), 7.23 (ddd, $J = 8.84$, 6.82, 1.52 Hz, 2 H), 7.06 (td, $J = 7.58$, 1.52 Hz, 2 H), 6.95 (td, $J = 7.58$, 1.52 Hz, 2 H), 6.34 (dd, $J = 6.57$, 1.01 Hz, 2 H). $^{13}$C NMR (MeCN, 100 MHz): $\delta$ 163.8, 159.7, 147.6, 146.7, 141.9, 141.0, 128.9, 138.2, 130.8, 129.8, 129.6, 128.6, 128.4, 127.5, 126.1, 125.7, 124.6, 122.4, 121.7, 120.6, 120.4.

**[Ir(2na-2qu)$_2$(biq)][PF$_6$]:** [Ir(2na-2qu)Cl]$_2$ (0.4 g, 0.271 mmol), 2,2’-biquinoline (0.149 g, 0.582 mmol), ethylene glycol (25 mL), dark red powder (yield: 0.39 g, 65.3%). $^1$H NMR (MeCN, 400 MHz): $\delta$ 8.48 (d, $J = 8.84$ Hz, 2 H), 8.41 (s, 2 H), 8.21 (d, $J = 8.84$ Hz, 2 H), 7.95 (d, $J = 8.84$ Hz, 2 H), 7.93 (dd, $J = 8.08$, 1.26 Hz, 2 H), 7.92 (d, $J = 1.52$ Hz, 2 H), 7.82 (d, $J = 8.34$ Hz, 4 H), 7.66 (dd, $J = 8.84$, 0.76 Hz, 2 H), 7.44 (ddd, $J = 8.34$, 7.07, 1.01 Hz, 2 H), 7.41 (ddd, $J = 8.08$, 6.82, 1.01 Hz, 2 H), 7.27 (m, 2 H), 7.18 (dd, $J = 5.81$, 2.78 Hz, 2 H), 6.84 (s, 2 H), 6.78 (ddd, $J = 8.84$, 6.82, 1.52 Hz, 2 H). $^{13}$C NMR (MeCN, 100 MHz): $\delta$ 170.3, 169.1, 158.7, 147.0, 146.7, 145.2, 140.2, 140.1, 139.7, 136.6, 134.7, 130.6, 130.4, 129.9, 129.6, 129.2, 128.8, 128.6, 128.3, 128.0, 127.4, 127.2, 126.8, 125.4, 125.3, 123.9, 120.6, 118.6.

**[Ir(naqu)$_2$(biq)][PF$_6$]:** [Ir(naqu)Cl]$_2$ (0.4 g, 0.271 mmol), 2,2’-biquinoline (0.149 g, 0.582 mmol), ethylene glycol (25 mL), brown solid (yield: 0.36 g, 60.3%). $^1$H
NMR (MeCN, 400 MHz): δ 8.65 (d, J = 5.56 Hz, 2 H), 8.41 (d, J = 8.84 Hz, 2 H), 8.06 (d, J = 8.84 Hz, 2 H), 8.02 (dt, J = 8.34, 1.26 Hz, 4 H), 7.97 (dd, J = 8.08, 1.26 Hz, 2 H), 7.86 (dd, J = 5.81, 0.76 Hz, 2 H), 7.73 (dd, J = 8.34, 1.52 Hz, 4 H), 7.65 (dd, J = 8.34, 6.32 Hz, 2 H), 7.55 (dd, J = 7.07, 1.26 Hz, 2 H), 7.52 (dd, J = 6.32, 1.77 Hz, 2 H), 7.49 (comp, 4 H), 7.44 (dd, J = 6.57, 1.26 Hz, 2 H), 7.32 (dd, J = 6.32, 1.26 Hz, 2 H), 7.29 (comp, 4 H).

$^{13}$C NMR (MeCN, 100 MHz): δ 159.7, 159.5, 156.1, 155.6, 141.9, 136.6, 133.3, 131.8, 130.0, 129.5, 129.2, 128.6, 128.2, 127.9, 127.7, 127.5, 127.1, 126.0, 125.7, 125.3, 124.9, 124.1, 123.3, 121.0, 119.9, 118.6.

$\text{[Ir(na5Fpy)$_2$(biq)][PF}_6]$:

$\text{[Ir(na5Fpy)Cl]}_2$ (0.4 g, 0.385 mmol), 2,2´-biquinoline (0.212 g, 0.827 mmol), ethylene glycol (25 mL), **dark red powder (yield: 0.31 g, 38.7%).**

$^1$H NMR (MeCN, 400 MHz): δ 8.80 (d, J = 8.84 Hz, 2 H), 8.72 (d, J = 8.84 Hz, 2 H), 8.55 (dd, J = 9.60, 5.31 Hz, 2 H), 8.39 (d, J = 8.59 Hz, 2 H), 7.99 (dd, J = 8.34, 1.52 Hz, 2 H), 7.96 (t, J = 2.78 Hz, 2 H), 7.76 (comp, 6 H), 7.55 (dd, J = 8.59, 7.07, 1.52 Hz, 2 H), 7.44 (dd, J = 8.08, 7.07, 1.01 Hz, 2 H), 7.39 (dd, J = 8.08, 6.82, 1.01 Hz, 2 H), 7.36 (d, J = 8.34 Hz, 2 H), 6.89 (ddd, J = 8.84, 6.82, 1.52 Hz, 2 H), 6.57 (d, J = 8.34 Hz, 2 H). $^{13}$C NMR (MeCN, 100 MHz): δ 164.3, 159.7, 155.5, 151.8, 147.5, 141.2, 139.5, 139.2, 135.4, 131.2, 130.7, 130.6, 129.6, 129.2, 128.6, 128.4, 127.3, 127.1, 125.7, 125.3, 124.9, 124.1, 123.3, 121.0, 119.9, 118.6.

$\text{[Ir(2na5Fpy)$_2$(biq)][PF}_6$):

$\text{[Ir(2na5Fpy)Cl]}_2$ (0.4 g, 0.385 mmol), 2,2´-biquinoline (0.212 g, 0.827 mmol), ethylene glycol (25 mL), **red powder (yield: 0.55 g, 68.8%).**

$^1$H NMR (MeCN, 400 MHz): δ 8.77 (d, J = 8.84 Hz, 2 H), 8.70 (d, J = 8.59 Hz, 2 H), 8.28 (d, J = 5.56 Hz, 2 H), 8.25 (d, J = 5.81 Hz, 2 H), 8.15 (d, J = 9.09 Hz, 2 H), 8.00 (d, J = 7.83 Hz, 2 H), 7.94 (t, J = 2.78 Hz, 2 H), 7.81 (ddd, J = 9.09, 6.57, 1.52 Hz, 2 H), 7.77 (d, J = 8.84 Hz, 2 H), 7.47 (t, J = 7.58 Hz, 2 H), 7.36 (d, J = 7.83 Hz, 2 H), 7.28 (comp, 4 H), 6.90 (ddd, J = 8.84, 6.82, 1.52 Hz, 2 H), 6.69 (s, 2 H). $^{13}$C NMR (MeCN, 100 MHz): δ 163.2, 163.1, 159.8, 159.7, 157.2, 147.8, 142.0, 141.1, 140.7, 139.1, 138.8, 134.6, 130.7, 129.8, 129.6, 128.6, 128.4, 128.3, 127.9, 127.5, 126.8, 126.2, 126.0, 125.4, 124.5, 123.9, 121.8, 121.5, 121.4.
[Ir(3Fppy)₂(biq)][PF₆]: [Ir(3Fppy)Cl]₂ (0.727 g, 0.635 mmol), 2,2’-biquinoline (0.349 g, 1.366 mmol), ethylene glycol (40 mL), red powder (yield: 0.75 g, 62.8%).

¹H NMR (DMSO, 400 MHz): δ 9.00 (d,  J = 8.08 Hz, 2 H), 8.99 (m, 2 H), 8.15 (dd,  J = 8.34, 1.26 Hz, 2 H), 8.10 (d,  J = 8.08 Hz, 2 H), 7.89 (dd,  J = 7.58, 0.76 Hz, 2 H), 7.85 (dd,  J = 4.29, 1.52 Hz, 2 H), 7.82 (d,  J = 7.83 Hz, 2 H), 7.73 (d,  J = 7.58 Hz, 2 H), 7.63 (m, 2 H), 7.27 (td,  J = 7.33, 1.26 Hz, 2 H), 7.04 (comp, 4 H), 6.62 (t,  J = 8.34 Hz, 2 H).

¹³C NMR (DMSO, 100 MHz): δ 168.8, 167.0, 166.4, 160.2, 150.6, 147.1, 144.7, 141.8, 138.4, 131.2, 129.5, 129.0, 126.5, 126.0, 124.4, 123.3, 122.3, 120.9, 119.7, 116.5.

[Ir(4Fppy)₂(biq)][PF₆]: [Ir(4Fppy)Cl]₂ (0.727 g, 0.635 mmol), 2,2’-biquinoline (0.349 g, 1.366 mmol), ethylene glycol (40 mL), red powder (yield: 0.97 g, 81.1%).

¹H NMR (DMSO, 400 MHz): δ 9.04 (d,  J = 8.84 Hz, 2 H), 8.97 (d,  J = 8.84 Hz, 2 H), 8.20 (d,  J = 8.08 Hz, 2 H), 8.15 (d,  J = 8.08 Hz, 2 H), 7.95 (dd,  J = 8.84, 5.81 Hz, 2 H), 7.94 (d,  J = 9.60 Hz, 2 H), 7.90 (d,  J = 5.56 Hz, 2 H), 7.81 (d,  J = 8.84 Hz, 2 H), 7.64 (t,  J = 7.58 Hz, 2 H), 7.30 (ddd,  J = 9.09, 7.07, 1.26 Hz, 2 H), 7.12 (t,  J = 6.06 Hz, 2 H), 6.86 (td,  J = 8.84, 2.53 Hz, 2 H), 5.78 (dd,  J = 7.07, 2.53 Hz, 2 H).

¹³C NMR (DMSO, 100 MHz): δ 163.8, 162.2, 159.3, 158.3, 150.1, 149.0, 145.8, 140.1, 138.2, 137.7, 129.7, 128.1, 127.6, 126.0, 125.4, 122.3, 120.7, 118.7, 114.9, 108.3.

[Ir(bzqu)₂(biq)][PF₆]: [Ir(bzqu)Cl]₂ (1.0 g, 0.856 mmol), 2,2’-biquinoline (0.481 g, 1.8 mmol), ethylene glycol (50 mL), red powder (yield: 1.14 g, 70.1%).

¹H NMR (DMSO, 400 MHz): δ 9.10 (d,  J = 8.84 Hz, 2 H), 8.92 (d,  J = 8.84 Hz, 2 H), 8.54 (dd,  J = 8.08, 1.01 Hz, 2 H), 8.26 (dd,  J = 5.30, 1.01 Hz, 2 H), 8.04 (dd,  J = 8.08, 1.26 Hz, 2 H), 7.91 (d,  J = 8.84 Hz, 2 H), 7.87 (d,  J = 9.09 Hz, 2 H), 7.83 (d,  J = 8.84 Hz, 2 H), 7.54 (dd,  J = 8.08, 5.31 Hz, 2 H), 7.48 (d,  J = 8.08 Hz, 4 H), 7.07 (t,  J = 7.58 Hz, 2 H), 6.92 (ddd,  J = 9.09, 6.82, 1.26 Hz, 2 H), 5.99 (d,  J = 7.33 Hz, 2 H).

¹³C NMR (DMSO, 100 MHz): δ 159.9, 156.2, 155.2, 149.9, 147.6, 145.2, 141.3, 139.3, 137.5, 137.1, 133.7, 130.7, 130.0, 129.3, 129.2, 128.7, 128.1, 127.9, 127.8, 127.3. 127.1, 126.7, 126.7, 124.1, 122.6, 122.1, 120.2, 118.7.
\[\text{[Ir(3Fpqu)\textsubscript{2}(biq)]PF\textsubscript{6}}\]: [Ir(3Fpqu)Cl\textsubscript{2} (0.727 g, 0.54 mmol), 2,2’-biquinoline (0.29 g, 1.162 mmol), ethylene glycol (40 mL), \textbf{red powder (yield: 0.75 g, 66.9\%)}]. \textsuperscript{1}H NMR (DMSO, 400 MHz): \(\delta\) 8.81 (d, \(J = 8.59\) Hz, 1 H), 8.74 (d, \(J = 8.59\) Hz, 2 H), 8.57 (d, \(J = 8.84\) Hz, 1 H), 8.45 (d, \(J = 8.59\) Hz, 1 H), 8.30 (dd, \(J = 8.84, 2.27\) Hz, 1 H), 8.26 (d, \(J = 8.84\) Hz, 1 H), 8.19 (d, \(J = 8.34\) Hz, 1 H), 8.14 (d, \(J = 8.84\) Hz, 1 H), 8.08 (comp, 4 H), 7.97 (d, \(J = 9.09\) Hz, 1 H), 7.91 (dd, \(J = 8.08, 1.01\) Hz, 1 H), 7.84 (comp, 2 H), 7.68 (td, \(J = 8.08, 1.77\) Hz, 1 H), 7.60 (comp, 4 H), 7.53 (d, \(J = 8.84\) Hz, 1 H), 7.39 (d, \(J = 8.08\) Hz, 1 H), 7.35 (d, \(J = 8.08\) Hz, 1 H), 7.21 (tt, \(J = 8.59, 1.77\) Hz, 1 H), 7.10 (ddd, \(J = 15.92, 8.34, 5.05\) Hz, 1 H), 6.85 (m, 1 H), 6.73 (ddd, \(J = 9.09, 6.82, 1.52\) Hz, 1 H), 6.60 (dd, \(J = 10.36, 7.83\) Hz, 1 H). \textsuperscript{13}C NMR (DMSO, 100 MHz): \(\delta\) 168.1, 167.4, 167.1, 157.7, 153.2, 147.7, 146.8, 145.4, 145.1, 141.4, 139.2, 138.9, 138.0, 135.1, 129.0, 128.0, 127.3, 126.9, 126.0, 125.9, 125.2, 124.6, 124.0, 123.7, 122.7, 121.9, 121.3, 119.2, 116.7, 115.9, 115.6, 115.3.

\[\text{[Ir(4Fpqu)\textsubscript{2}(biq)]PF\textsubscript{6}}\]: [Ir(4Fpqu)Cl\textsubscript{2} (0.727 g, 0.54 mmol), 2,2’-biquinoline (0.29 g, 1.162 mmol), ethylene glycol (40 mL), \textbf{red powder (yield: 0.55 g, 49.1\%)}]. \textsuperscript{1}H NMR (DMSO, 400 MHz): \(\delta\) 8.76 (d, \(J = 8.59\) Hz, 2 H), 8.54 (d, \(J = 8.84\) Hz, 2 H), 8.35 (d, \(J = 8.84\) Hz, 2 H), 8.22 (d, \(J = 8.84\) Hz, 2 H), 8.10 (dd, \(J = 8.59, 1.01\) Hz, 2 H), 8.06 (dd, \(J = 8.84, 5.81\) Hz, 2 H), 7.99 (dd, \(J = 8.08, 1.26\) Hz, 2 H), 7.60 (td, \(J = 8.08, 1.01\) Hz, 2 H), 7.45 (s, 2 H), 7.42 (d, \(J = 1.26\) Hz, 2 H), 7.41 (dd, \(J = 14.91, 3.79\) Hz, 2 H), 7.22 (ddd, \(J = 8.84, 6.82, 1.26\) Hz, 2 H), 6.91 (td, \(J = 8.84, 2.53\) Hz, 2 H), 6.88 (ddd, \(J = 8.84, 6.82, 1.52\) Hz, 2 H), 5.96 (dd, \(J = 9.85, 2.53\) Hz, 2 H). \textsuperscript{13}C NMR (DMSO, 100 MHz): \(\delta\) 170.2, 168.6, 163.9, 161.4, 169.4, 155.2, 151.5, 146.5, 146.3, 141.9, 141.1, 140.8, 131.0, 130.1, 129.4, 129.2, 128.9, 127.3, 126.9, 125.9, 123.8, 121.2, 117.6, 110.3.

\[\text{[Ir(4Fp-iqu)\textsubscript{2}(biq)]PF\textsubscript{6}}\]: [Ir(4Fp-iqu)Cl\textsubscript{2} (0.727 g, 0.54 mmol), 2,2’-biquinoline (0.29 g, 1.162 mmol), ethylene glycol (40 mL), \textbf{red powder (yield: 0.85 g, 75.8\%)}]. \textsuperscript{1}H NMR (DMSO, 400 MHz): \(\delta\) 8.93 (d, \(J = 8.84\) Hz, 2 H), 8.89 (d, \(J = 8.84\) Hz, 2 H), 8.77 (d, \(J = 9.09\) Hz, 2 H), 8.38 (dd, \(J = 9.09, 5.81\) Hz, 2 H), 8.10 (dd, \(J = 8.34, 1.26, 1.01\) Hz, 2 H), 8.06 (dd, \(J = 7.83, 1.52\) Hz, 2 H), 7.86 (comp, 4 H), 7.80 (d, \(J = 6.57\) Hz, 2 H), 7.68
(d, J = 8.84 Hz, 2 H), 7.61 (td, J = 7.83, 0.76 Hz, 2 H), 7.55 (d, J = 6.57 Hz, 2 H), 7.29 (ddd, J = 8.84, 7.07, 1.52 Hz, 2 H), 6.96 (td, J = 8.84, 2.78 Hz, 2 H), 6.06 (dd, J = 9.60, 2.78 Hz, 2 H). $^{13}$C NMR (DMSO, 100 MHz): δ 166.2, 163.3, 160.7, 159.7, 155.0, 146.7, 142.0, 141.5, 141.0, 136.3, 133.5, 132.2, 131.1, 129.5, 128.9, 127.9, 127.6, 126.9, 125.7, 124.9, 121.9, 118.7, 116.8, 109.7.

$[^{3}]$Ir(3Fp-iqu)$_2$(biq)[PF$_6$]: [Ir(3Fp-iqu)Cl]$_2$ (0.5 g, 0.372 mmol), 2,2′-biquinoline (0.20 g, 0.799 mmol), ethylene glycol (40 mL), red powder (yield: 0.54 g, 69.9%). $^1$H NMR (DMSO, 400 MHz): δ 8.97 (s, 2 H), 8.87 (s, 4 H), 8.70 (d, J = 8.34 Hz, 1H), 8.13 (d, J = 7.83 Hz, 2 H), 8.08 (dd, J = 8.34, 1.52, 1.26 Hz, 2 H), 7.99 (dd, J = 7.58, 1.26 Hz, 2 H), 7.88 (d, J = 8.59 Hz, 2 H), 7.83 (d, J = 6.32 Hz, 2 H), 7.79 (dd, J = 8.08, 1.26 Hz, 2 H), 7.62 (dd, J = 8.08, 5.31 Hz, 2 H), 7.44 (d, J = 6.82 Hz, 2 H), 7.28 (qd, J = 8.34, 1.52, 1.26 Hz, 2 H), 7.18 (dd, J = 8.08, 2.27 Hz, 1 H), 6.67 (t, J = 8.84, 8.59 Hz, 2 H), 5.75 (s, 2 H). $^{13}$C NMR (DMSO, 100 MHz): δ 166.6, 165.6, 164.3, 158.0, 157.7, 146.4, 146.3, 145.1, 144.6, 140.6, 140.2, 140.0, 139.5, 139.2, 135.0, 133.8, 130.1, 129.6, 129.2, 129.0, 128.6, 127.3, 126.9, 126.7, 125.2, 124.5, 124.1, 123.7, 122.6, 122.4, 119.8, 118.9, 114.7.

$[^{3}]$Ir(phn-iqu)$_2$(biq)[PF$_6$]: [Ir(phn-iqu)Cl]$_2$ (0.256 g, 0.148 mmol), 2,2′-biquinoline (0.081 g, 0.319 mmol), ethylene glycol (25 mL), dark red solid (yield: 0.11 g, 30.9%). The yield of the reaction was too low, hence the obtained complex was used for other measurements and for device fabrication.

$[^{3}]$Ir(phn5Fpy)$_2$(pbpy)[PF$_6$]: [Ir(phn5Fpy)Cl]$_2$ (0.4 g, 0.258 mmol), 6-phenyl-2,2′-bipyridine (0.13 g, 0.556 mmol), ethylene glycol (25 mL), brown powder (yield: 0.39 g, 67.8%). Complex was not completely soluble in NMR solvent (MeCN) and the NMR spectra could not be resolved.

$[^{3}]$Ir(phn5Fpy)$_2$(biq)[PF$_6$]: [Ir(phn5Fpy)Cl]$_2$ (0.648 g, 0.258 mmol), 2,2′-biquinoline (0.13 g, 0.556 mmol), ethylene glycol (30 mL), brown powder (yield: 0.38 g,
64.7\%

Complex was not completely soluble in NMR solvent (MeCN) and the NMR spectra could not be resolved.
3.9 References

Chapter 4

Yellow to deep green LECs: more focus in the green region
Chapter 4

Yellow to deep green LECs: more focus in the green region

4.1 Introduction

The solid state electroluminescent (EL) and photoluminescence maxima of most unsubstituted Ir-iTMCs are in the yellow to orange region of the visible spectrum [1-9]. For example, the EL of the archetype Ir-iTMC [Ir(ppy)$_2$(bpy)][PF$_6$] employed in LECs occurs at 590 nm which is similar to the PL maxima of 595 and 602 obtained in 2-methyltetrahydrofuran and acetonitrile solutions respectively [8,9]. A well known approach to blue shift the emission maximum is to decorate the phenyl ring of the C$^N$ ligands with electron withdrawing groups or to attach electron donating groups to the ancillary N$^N$ ligand [10-12]. The overall outcome is the systematic stabilization and/or destabilization of the HOMO and LUMO by the electron withdrawing C$^N$ and electron donating N$^N$ ligands, respectively. Among the many known electron withdrawing groups, -F and –CF$_3$ have been widely used to blue shift the emission maximum of Ir-iTMCs [12-18]. On the other hand, alkyl groups such as –methyl and di-tert-butyl (dtb) together with the amines have been positioned on the N$^N$ ligands to obtained blue shifted emissions of Ir-iTMCs [10,19-21]. In particular, the di-tert-butyl group has been the electron donating group of choice for many researchers [12,13,20,21] as a substituent on the N$^N$ ligand as its bulky nature also prevents a close packing of the Ir-iTMCs which will lead to less exciton-exciton quenching during a LEC device operation. On replacing the parent diimine bpy ligand of the archetype complex with an electron rich dtb-bpy diimine ligand, a blue shift in the emission maximum together with an increase in the device luminance was reported [2]. Both, the shift in the PL of the Ir-iTMC and the performance improvement of the LEC device is attributed to the use of the bulky and electron donating dtb substituent on the diimine ligand. On the other hand, a good number of green emitting Ir-iTMCs have been reported where the blue shift in the emission maximum is achieved by adding fluorine substituents to the four and/or
six positions of the phenyl ring of the C^N ligands with different types of diimine N^N ligands (including the phenanthroline type ligands) [14-17,21,22]. The LEC device performances of such fluorinated complexes are quite enhanced compared to the non-fluorinated complexes. Under a pulsed current driven mode with an average current density of 100 A/m^2 at a frequency of 1000 Hz and a block wave with a duty cycle of 50%. The team of H.J. Bolink has reported a series of green LEC devices with maximum luminance greater than 1000 cd/m^2 based on fluorinated Ir-iTMCs with the dtb-bpy N^N ligand [20,21,23]. It is understood that the fluorine substituent increases the PLQY of the complexes which leads to LEC devices with enhanced performances. Nevertheless, the stability of the LEC devices based on these fluorinated complexes were much lower compared to the non-fluorinated complexes. The most stable green LEC device driven under the above mentioned pulsed current mode demonstrated a lifetime of 59.8 h [23]. It is understood that the improvement in the device performance by adding fluorine substituents comes with a systematic drop in the device lifetime implying fluorine substituents are detrimental to the stability of the device under operation [22]. A correlation between the numbers of fluorine substituent on an Ir-iTMC to the lifetime of the LEC device was reported by D. Tordera et al., [23]. The authors established an inverse relationship between the number of fluorine substituents on the Ir-iTMC and the device lifetime. The authors together with other authors strongly recommended that fluorine substituents should be avoided in the design of Ir-iTMCs with blue shifted emissions for application as emitting materials in LEC devices. E. Constable et al., [24] recently reported five green emitting Ir-iTMCs with sulfanyl or sulfone functionalized ppy C^N ligands. The solid state PLQY of the reported complexes were lower compared to a similar complex with a fluorine substituent at the same position reported by the same group, but no LEC device data of the green emitting sulfanyl and sulfone functionalized complexes were reported. Green to green-blue emitting Ir-iTMCs where a methoxy- and methyl- substituted 2,3´-bipyridine are used as the C^N ligands and dtb-bpy as the N^N ligand have also been recently
reported by Evariste et al., [25]. The LEC devices based on the newly reported complexes demonstrated luminance slightly lower but comparable to the fluorinated Ir-iTMCs. It would be expected that the lifetime of these green non-fluorinated Ir-iTMCs are much longer since they are fluorine free. Actually, the device stability was dramatically reduced, with the most stable LEC device living for 2.6 h compared to the 59.8 h for the LEC devices based on fluorinated Ir-iTMCs. So far, it is not clear what class of electron withdrawing groups can be used to blue shift the emission of Ir-iTMCs to the green region without causing a drop in the device lifetime.

**Results and Discussions**

4.2 Fluorinated Ir-iTMCs with yellow to deep green emissions

Although fluorine substituents have been reported to be detrimental to the stability of LECs devices in general, a series of fluorinated Ir-iTMCs were synthesized for application in LEC devices and studied. Apart from the already mentioned N\textsubscript{C=N} -Ir $\sigma$-antibonding interaction, it can be suggested that the short lifetime of green LEC devices is also due to inter-complex interactions (such as hydrogen bonding) which are present because of the use of certain substituent groups. Fluorine can be considered as one of these substituents as well as other functional groups containing nitrogen and oxygen atoms which are well known to undergo hydrogen bonding. During the off-state of the device, there is a systematic arrangement of ions within the emissive layer where possible intermolecular interactions such as hydrogen bonding could exist. Upon biasing the device, ions are forced to move towards the electrode with opposite charge. The instantaneous and fast migration of the ions, when the device is biased in systems where intermolecular interactions exist, could lead to a weakening or even a breaking of certain bonds. The overall effect will be the reduction in the structural stability of the complexes and consequently a drop in the device lifetime. This could explain why the non fluorinated complexes with the
methoxy substituents where also less stable. One approach to improve structural stability and hence the device lifetime can be to have the electron withdrawing substituent (in this case the fluorine) substituted at positions were it is partially or fully restricted from interacting with another nearby molecule.

On the other hand, having a methyl substituent on the pyridine ring of the C^N ligands for the non fluorinating complexes will increase the electron density on the pyridine ring. This will lead to an increase in the N_C^N-Ir σ-antibonding interaction and a drop in the lifetime of the device. Though the dtb substituent has some advantages toward efficient improvement as highlighted above, it should be noted that the dtb is a strong electron donating group. As a result, complexes with the dtb substituent on their N^N ligand will have a destabilized LUMO, reducing the energy difference between the LUMO and the iridium excited \(^3\)MC state which is involved in the N_C^N-Ir σ-antibonding interaction. The overall effect is the reduction in the device lifetime via population of the \(^3\)MC state. This could also contribute to the reported short lifetime of both the non fluorinated and fluorinated complexes with the dtb-bpy N^N ligand.

Fluorinated complexes with different types of C^N and/or N^N ligands were therefore designed and synthesized to fully understand the effects of the substituents on the performance and stability of LEC devices.

4.2.1 Ir-iTMCs based on 2-(4-fluorophenyl)pyridine (4Fppy) C^N ligands

A library of complexes with 4Fppy as the C^N ligands and different N^N ligands were synthesized to investigate their structural-performance relationship when applied in a LEC device. One group of the complexes is based on the bpy type N^N ligands (figure 4.1).
Figure 4.1: Chemical structures of \(\text{[Ir}(4\text{Fppy})_2(\text{bpy})]\)[PF\(_6\)], \(\text{[Ir}(4\text{Fppy})_2(5\text{dmbpy})]\)[PF\(_6\)], \(\text{[Ir}(4\text{Fppy})_2(\text{dmbpy})]\)[PF\(_6\)] and \(\text{[Ir}(4\text{Fppy})_2(\text{dtb-bpy})]\)[PF\(_6\)].

bpy N^N type ligands were also changed to more electron transporting and rigid phenanthroline type N^N ligands in the second group of complexes (figure 4.2).
Figure 4.2: Chemical structures of \([\text{Ir}(4\text{Fppy})_2(\text{phen})][\text{PF}_6]\), \([\text{Ir}(4\text{Fppy})_2(\text{Bphen})][\text{PF}_6]\) and \([\text{Ir}(4\text{Fppy})_2(\text{dmBphen})][\text{PF}_6]\).

Finally, electron rich N^N ligands were used to further shift the emission wavelength into the deep green region of the visible spectrum (figure 4.3).

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4.2.2 Ir-iTMCS based on 2-(3-fluorophenyl)pyridine (3Fppy) C^N ligands

Almost all the reported fluorinated Ir-iTMCS have the fluorine atoms substituted at the fourth and/or sixth positions on the phenyl ring of the C^N ligands (or meta to the coordinating carbon of the phenyl ring of the C^N ligands). After a closer observation of the crystal structures of these meta fluorinated complexes, it was thought that moving the fluorine substituted to the third position or ortho to the coordinating carbon of the phenyl ring of the C^N ligands, the fluorine will be pointing into the complex and thereby preventing the fluorine from interacting with any nearby molecule and hoping to enhance the LEC device stability (lifetime). The following complexes with similar N^N ligands (like those for the 4Fppy based complexes above) were synthesized to study the effect of the change in the position of the fluorine substituent on the performance and stability of LEC devices (figures 4.4, 4.5 and 4.6).
Figure 4.4: Chemical structures of $[\text{Ir}(3\text{Fppy})_2(\text{bpy})][\text{PF}_6]$, $[\text{Ir}(3\text{Fppy})_2(5\text{dmbpy})][\text{PF}_6]$, $[\text{Ir}(3\text{Fppy})_2(\text{dmbpy})][\text{PF}_6]$ and $[\text{Ir}(3\text{Fppy})_2(\text{dtb-bpy})][\text{PF}_6]$. 
Figure 4.5: Chemical structures of [Ir(3Fppy)₂(dMeO-bpy)][PF₆], [Ir(3Fppy)₂(dmBphen)][PF₆], [Ir(3Fppy)₂(phen)][PF₆] and [Ir(3Fppy)₂(Bphen)][PF₆].
4.2.3 Ir-iTMCs with two fluorine substituents on the phenyl ring of the C^N ligands

To further understand the dependence of LEC device lifetime on the number of fluorine atoms in the structure of the Ir-iTMC the following complexes with more than one fluorine substituents were designed and synthesized (figures 4.7 and 4.8).
Figure 4.7: Chemical structures of 3,4-difluorinated phenyl C^N ligands based Ir-iTMcs, [Ir(3,4Fppy)₂(phen)][PF₆], [Ir(3,4Fppy)₂(pypz)][PF₆] and [Ir(3,4Fppy)₂(Bphen)][PF₆].
**Figure 4.8:** Chemical structures of 3,5-difluorinated phenyl C^N ligands based Ir-iTMCs, [Ir(3,5Fppy)_2(phen)][PF_6], [Ir(3,5Fppy)_2(Bphen)][PF_6], [Ir(3,5Fppy)_2(dtb-bpy)][PF_6] and [Ir(3,5Fppy)_2(pyimz)][PF_6].
4.2.4 Ir-iTMCs with fluorinated pyridine ring of the C^N ligands

The idea of stability enhancement as demonstrated with the red complexes was also applied to complexes with yellow to green emissions. However, it is expected that this approach will not be as effective in complexes with yellow to green emission because the LUMO of these complexes are higher in energy than those for the red emitting complexes. Hence the LUMO-^3^MC state energy gap is even smaller making the ^3^MC state more thermally accessible during device operation. A slight elongation of the N_C^N-Ir bond length with a fluorine substituent on the pyridine ring of the C^N ligand may cause the bond to be easily broken when the σ-antibonding interaction strength is increased via thermal population of the ^3^MC state. To verify this idea, the following complexes were synthesized (figure 4.9 and 4.10).

![Chemical structures of complexes](image)

Figure 4.9: Chemical structures of [Ir(p5Fpy)_2(dtb-bpy)][PF_6] and [Ir(3,5Fp5Fpy)_2(dtb-bpy)][PF_6].
Figure 4.10: Chemical structures of [Ir(na5Fpy)$_2$(Bphen)][PF$_6$].

4.2.5 **Introducing the π-π stacking in Ir-iTMCs with fluorine substituented C^N ligands**

Fluorinated complexes with pbpy as the N^N ligand were also synthesized to understand if further improving their LEC device lifetimes through the intramolecular π-π stacking between the pendant phenyl substituent of the N^N ligand and the phenyl ring of one of the C^N ligands (figure 4.11 and 4.12) is possible.

Figure 4.11: Chemical structures of [Ir(p5Fpy)$_2$(pbpy)][PF$_6$] and [Ir(4Fppy)$_2$(pbpy)][PF$_6$].
The last set of complexes contains some non-fluorinated benzoquinoline type C^N ligands for stability enhancement through more rigid ligands (figure 4.13).
Figure 4.13: Chemical structures of [Ir(bzqu)₂(Bphen)][PF₆], [Ir(bzqu)₂(dmBphen)][PF₆], [Ir(bzqu)₂(phen)][PF₆], [Ir(bzqu)₂(dtb-bpy)][PF₆] and [Ir(bzqu)₂(pyz)][PF₆].
The synthesis and photophysical properties of the complexes \([\text{Ir(bzqu)}_2(\text{dtb-bpy})][\text{PF}_6]\) \([\text{Ir(4Fppy)}_2(\text{bpy})][\text{PF}_6]\) and \([\text{Ir(4Fppy)}_2(\text{Bphen})][\text{PF}_6]\) have been previously reported \([14,24,26]\). The complex \([\text{Ir(4Fppy)}_2(\text{bpy})][\text{PF}_6]\) was used as an intermediate in the synthesis of fluorine free sulfanyl and sulfone functionalized Ir-iTMCs by E. Constable et al., \([24]\). No device data has been reported for the LECs based on \([\text{Ir(4Fppy)}_2(\text{bpy})][\text{PF}_6]\) and \([\text{Ir(4Fppy)}_2(\text{Bphen})][\text{PF}_6]\). However, the LEC device based on \([\text{Ir(bzqu)}_2(\text{dtb-bpy})][\text{PF}_6]\) demonstrated very poor performance. The authors suggested that the low device performance was due to the fact that the emission process is only fluorescence and not phosphorescence. These three complexes were also synthesized during this research work and it was found that the PLQY of the complexes were higher compared to the reported values. The enhanced PLQY can be attributed to the synthesis of the complexes using a better synthetic procedure. The synthesis, photophysical and electroluminescence properties of \([\text{Ir(4Fppy)}_2(\text{dtb-bpy})][\text{PF}_6]\) have also been previously reported \([23]\), the complex was re-synthesized during this work for comparison.

4.4 Photophysical properties

4.4.1 Absorption studies

In general, the Ir-iTMCs show absorption bands in the UV to visible regions of the electromagnetic (EM) spectrum which are assigned as follows: The intense absorptions below 300 nm are assigned to the ligand centered (LC) transitions of both the C^N and N^N ligands. The absorption in the 300 to 350 nm region is assigned to the metal to ligand charge transfer (1MLCT). Absorptions from 350 nm extending into the visible region are assigned to metal to ligand charge transfer (3MLCT), ligand-to-ligand charge transfer (3LLCT) and ligand centered (3LC) transitions. The absorption spectra of complexes bearing 4Fppy as the C^N ligand with bpy- and phen-like N^N ligands are shown in figure 4.14. The absorption
The absorption spectra of similar complexes with 3Fppy as the C^N ligands show similar absorption pattern to the 4Fppy based complexes and are assigned to the same transitions. However, the absorption spectra for complexes with the bipyridine like ancillary ligands show a more defined absorption band between 350 to 400 nm (figure 4.15).

Figure 4.14: Absorption spectra [Ir(4Fppy)\textsubscript{2}(bpy)][PF\textsubscript{6}], [Ir(4Fppy)\textsubscript{2}(bphen)][PF\textsubscript{6}], [Ir(4Fppy)\textsubscript{2}(dmbpy)][PF\textsubscript{6}], [Ir(4Fppy)\textsubscript{2}(phen)][PF\textsubscript{6}], [Ir(4Fppy)\textsubscript{2}(phen)][PF\textsubscript{6}], and [Ir(4Fppy)\textsubscript{2}(5dmbpy)][PF\textsubscript{6}].
The absorption spectra of two of the 3Fppy based complexes with the phenanthroline-like ancillary ligands show one intense absorption band in the UV region centered around 300 nm which can be assigned to both the LC and $^1$MLCT transitions (figure 4.16).
The absorption spectra of the other complexes are shown in the appendix (figure 4a to 4g). The absorption spectra are similar to those of the other complexes as shown in figures 4.15 and 4.16 and the absorptions bands are assigned to the same transitions.

4.4.2 Photoluminescence studies

The PL spectra of the complexes were measure in their solid state (on powder sample for all the complexes and on thin film for some of the complexes). The PL properties of the complexes with excitation wavelengths of 360 nm for powder sample and 380 nm for thin film are summarized in table 4.1a and 4.1b.
Table 4.1a: Photoluminescence properties of the Ir-iTMCs.

<table>
<thead>
<tr>
<th></th>
<th>Powder sample</th>
<th>Thin film</th>
<th>PLQY</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ir(4Fppy)$_2$(bpy)]PF$_6$</td>
<td>561</td>
<td>547</td>
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<td>560</td>
<td>78.34</td>
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<tr>
<td>[Ir(4Fppy)$_2$(dmbpy)]PF$_6$</td>
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<td>540</td>
<td></td>
</tr>
<tr>
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<td>544</td>
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<td>[Ir(4Fppy)$_2$(dmBphen)]PF$_6$</td>
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<td>546</td>
<td>74.86</td>
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<tr>
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<td>529</td>
<td>50.66</td>
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<tr>
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<td>[Ir(p5Fpy)$_2$(pbpy)]PF$_6$</td>
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Table 4.1b: Photoluminescence properties of the Ir-iTMCs.

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<tr>
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<th>PL&lt;sub&gt;max&lt;/sub&gt; [nm]</th>
<th>Powder sample</th>
<th>Thin film</th>
<th>PLQY</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ir(p5Fpy)&lt;sub&gt;2&lt;/sub&gt;(dtb-bpy)][PF&lt;sub&gt;6&lt;/sub&gt;]</td>
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<td></td>
<td></td>
<td>65.86</td>
</tr>
<tr>
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<td>521</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Ir(3,5Fp5Fpy)&lt;sub&gt;2&lt;/sub&gt;(dtb-bpy)][PF&lt;sub&gt;6&lt;/sub&gt;]</td>
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<td></td>
<td>535</td>
<td>79.04</td>
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<tr>
<td>[Ir(4Fppy)&lt;sub&gt;2&lt;/sub&gt;(pyimz)][PF&lt;sub&gt;6&lt;/sub&gt;]</td>
<td>531</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Ir(4Fppy)&lt;sub&gt;2&lt;/sub&gt;(py3,5mpz)][PF&lt;sub&gt;6&lt;/sub&gt;]</td>
<td>562</td>
<td></td>
<td>547</td>
<td>50.76</td>
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<tr>
<td>[Ir(3Fppy)&lt;sub&gt;2&lt;/sub&gt;(pyimz)][PF&lt;sub&gt;6&lt;/sub&gt;]</td>
<td>523</td>
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<td></td>
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<tr>
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<td>520</td>
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<tr>
<td>[Ir(3,5Fppy)&lt;sub&gt;2&lt;/sub&gt;(pyimz)][PF&lt;sub&gt;6&lt;/sub&gt;]</td>
<td>506, 566</td>
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<td></td>
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<tr>
<td>[Ir(bzqu)&lt;sub&gt;2&lt;/sub&gt;(py3,5mpz)][PF&lt;sub&gt;6&lt;/sub&gt;]</td>
<td>529</td>
<td></td>
<td></td>
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<tr>
<td>[Ir(bzqu)&lt;sub&gt;2&lt;/sub&gt;(phen)][PF&lt;sub&gt;6&lt;/sub&gt;]</td>
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<td>533</td>
<td></td>
<td></td>
<td>28.41</td>
</tr>
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</table>

Some of the complexes exhibited high PLQY (all PLQY were measured on powder sample), e.g. of 78.34 for [Ir(4Fppy)<sub>2</sub>(Bphen)][PF<sub>6</sub>]. In general, the 4Fppy C^N ligand based complexes display higher PLQYs compared to the 3Fppy complexes except for [Ir(4Fppy)<sub>2</sub>(5dmbpy)][PF<sub>6</sub>] and [Ir(3Fppy)<sub>2</sub>(5dmbpy)][PF<sub>6</sub>] with PLQY of 50.66 and 64.35, respectively. The PLQY of the complexes with phenanthroline as the N^N ligand and those with benzoquinoline as the C^N ligands were observed to be much lower compared to the PLQY of the other complexes.
The PL spectra of the 4Fppy C^N ligands based complexes are shown in figure 4.17. The PL maxima of the complexes strongly depend on the ancillary ligands as all the complexes have the same C^N ligands. Adding electron donating substituents to the N^N ligand blue shift the emission of some of the complexes as expected. The complexes based on the 4Fppy C^N ligands with the bpy- and phen-like N^N ligands all emit in the green to deep green regions of the visible spectrum.

![PL Spectra](image)

**Figure 4.17:** Powder PL spectra of [Ir(4Fppy)_2(bpy)][PF_6], [Ir(4Fppy)_2(Bphen)][PF_6], [Ir(4Fppy)_2(dmbpy)][PF_6], [Ir(4Fppy)_2(phen)][PF_6], [Ir(4Fppy)_2(phen)][PF_6] and [Ir(4Fppy)_2(5dmbpy)][PF_6], excited at 360 nm.

Interestingly, the blue shift in the emission wavelength of some the complexes upon attaching electron donation substituents on the N^N ligand was not observed when the PL spectra were measured from a thin film of the complexes in a device configuration (figure 4.18).
Figure 4.18: Thin film PL spectra of \([\text{Ir}(4\text{Fppy})_2(\text{bpy})][\text{PF}_6], [\text{Ir}(4\text{Fppy})_2(\text{Bphen})][\text{PF}_6], [\text{Ir}(4\text{Fppy})_2(\text{dmbpy})][\text{PF}_6], [\text{Ir}(4\text{Fppy})_2(\text{phen})][\text{PF}_6], [\text{Ir}(4\text{Fppy})_2(\text{phen})][\text{PF}_6]\) and \([\text{Ir}(4\text{Fppy})_2(5\text{dmbpy})][\text{PF}_6]\), excited at 380 nm.

Changing the position of the fluorine substituent on the C\(^N\) ligand from 4Fppy to 3Fppy resulted in a shift in the emission wavelength of complexes as seen on table 4.1a and 4.1b. However, the shift in the emission of the complexes varies from complex to complex with no generalized trend. The powder PL spectra of the 3Fppy based complexes with the bpy and phen-like N\(^N\) ligands are shown in figure 4.19 and figure 4.20, respectively.
Figure 4.18: Powder PL spectra of [Ir(3Fppy)_2(bpy)][PF_6], [Ir3Fppy)_2(dmbpy)][PF_6], [Ir(4Fppy)_2(5dmbpy)][PF_6], [Ir(4Fppy)_2(dtb-pby)][PF_6] and [Ir(4Fppy)_2(dMeO)][PF_6], excited at 360 nm.

Figure 4.20: Powder PL spectra of [Ir(3Fppy)_2(phen)][PF_6], [Ir3Fppy)_2(Bphen)][PF_6] and [Ir(3Fppy)_2(dmBphen)][PF_6], excited at 360 nm.
Analog to the 4Fppy based complexes, the thin film PL spectra (figure 4.21) of the complexes based on the 3Fppy C^N ligands are more structured and show no major difference in the emission maxima compared to the thin film PL spectra of the 4Fppy based complexes. A significant blue shift in the emission spectrum was observed on going from [Ir(4Fppy)₂(Bphen)][PF₆] to [Ir(3Fppy)₂(Bphen)][PF₆] of 32 nm and 63 nm on the thin film and powder PL spectra, respectively. The shift in the emission can be attributed to the molecular arrangement (morphology) of the complexes: [Ir(4Fppy)₂(Bphen)][PF₆] was obtained as a bright greenish powder while [Ir(3Fppy)₂(Bphen)][PF₆] formed a glassy orange solid.

**Figure 4.21:** Thin film PL spectra of [Ir(3Fppy)₂(bpy)][PF₆], [Ir(3Fppy)₂(dmbpy)][PF₆], [Ir(3Fppy)₂(5dmbpy)][PF₆], [Ir(3Fppy)₂(dtb-pby)][PF₆], [Ir(3Fppy)₂(phen)][PF₆], [Ir(3Fppy)₂(Bphen)][PF₆], and [Ir(3Fppy)₂(dmBphen)][PF₆], excited at 380 nm.
Interestingly, increasing the number of fluorine substituents on the phenyl ring of the C^N ligands did not further cause any significant shift in the PL of the complexes toward shorter wavelengths. This implies that there is a certain limit at which the HOMO of the Ir-iTMCs can be stabilized by attaching electron withdrawing substituent such as fluorine to the phenyl ring of the C^N ligands. The PL spectra of some difluorinated complexes with different N^N ligands are shown in figure 4.22 and 4.23 for 3,5-difluorophenyl and 3,4-difluorophenyl substituted C^N ligands, respectively.

![Figure 4.22: Powder PL spectra of [Ir(3,5Fppy)_2(dtbbpy)][PF_6], [Ir3,5Fppy)_2(Bphen)][PF_6], and [Ir(3,5Fppy)_2(phen)][PF_6], excited at 360 nm.](image)
Introducing the π-π intramolecular stacking in Ir-iTMCs with fluorinated C^N ligands by using pbpy as the N^N ligand leads only to a small variation in the PL of the complexes. However, a red shift in the PL maxima compared to similar complexes where no π-π intramolecular interactions are possible was observed. The powder PL spectra of the complexes with π-π stacking are shown in figure 4.24. While the thin film PL spectra of the some of the complexes are shown in the appendix (figure 4h).
Figure 4.2: Powder PL spectra of [Ir(3,5Fp5Fpy)2(pbpy)][PF$_6$], [Ir(4Fppy)2(pbpy)][PF$_6$], [Ir(4Fp5Fpy)2(pbpy)][PF$_6$], [Ir(3Fppy)2(ppby)][PF$_6$] and [Ir(p5Fpy)2(pbpy)][PF$_6$], excited at 360 nm.

The powder PL spectra of Ir-iTMCS with the 4Fppy, 3Fppy, 3,4Fppy, 3,5Fppy and bzqu based C^N ligands with the pyridylazoles type N^N ligands were also measured and the spectra are shown in the appendix (figure 4i). Also the powder PL spectra of the bzqu and p5Fpy based C^N ligands with different diimine ancillary ligands are shown in the appendix (figures 4j and 4k) but not discussed in details in this work.
4.5 Electrochemical studies

The electrochemical properties of the complexes were investigated by cyclic voltammetry and the results are summarized in table 4.2. The measurements were carried out in acetonitrile or acetone solutions. A cathodic shift in the reduction and oxidation potential upon changing the solvent used during the CV measurements from acetonitrile to acetone was observed in the previous chapter for two red emitting Ir-iTMCs. For that reason reduction or oxidation potentials of Ir-iTMCs in different solvents cannot be compared directly. Nonetheless, certain distinct observations would be highlighted and the cyclic voltammogram are shown in the appendix.

**Table 4.2a: Electrochemical properties of the complexes**

<table>
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<th>Complex</th>
<th>$E_{1/2\text{red}}$ [V]</th>
<th>$E_{1/2\text{ox}}$ [V]</th>
<th>LUMO [eV]</th>
<th>HOMO [eV]</th>
<th>Energy gap [eV]</th>
</tr>
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<tbody>
<tr>
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<td>1.40</td>
<td>-3.34</td>
<td>-6.20</td>
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<tr>
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<td>1.52</td>
<td>-3.58</td>
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<tr>
<td>[Ir(4Fppy)$_2$(dmbpy)][PF$_6$]</td>
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<td>1.38</td>
<td>-3.42</td>
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<tr>
<td>[Ir(4Fppy)$_2$(phen)][PF$_6$]</td>
<td>-1.42</td>
<td>1.37</td>
<td>-3.38</td>
<td>-6.17</td>
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<tr>
<td>[Ir(4Fppy)$_2$(dmBphen)][PF$_6$]</td>
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<td>1.37</td>
<td>-3.31</td>
<td>-6.17</td>
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<td>[Ir(4Fppy)$_2$(5dmbpy)][PF$_6$]</td>
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<td>1.41</td>
<td>-3.30</td>
<td>-6.21</td>
<td>2.91</td>
</tr>
<tr>
<td>[Ir(3Fppy)$_2$(bpy)][PF$_6$]</td>
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<td>1.33</td>
<td>-3.41</td>
<td>-6.13</td>
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</tr>
<tr>
<td>[Ir(3Fppy)$_2$(dmbpy)][PF$_6$]</td>
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<td>1.35</td>
<td>-3.24</td>
<td>-6.15</td>
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<tr>
<td>[Ir(3Fppy)$_2$(5dmbpy)][PF$_6$]</td>
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<td>-3.25</td>
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<td>[Ir(3Fppy)$_2$(dtb-bpy)][PF$_6$]</td>
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<td>[Ir(3Fppy)$_2$(dMeObpy)][PF$_6$]</td>
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<td>1.37</td>
<td>-3.37</td>
<td>-6.17</td>
<td>2.80</td>
</tr>
<tr>
<td>[Ir(3Fppy)$_2$(phen)][PF$_6$]</td>
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<td>1.50</td>
<td>-3.53</td>
<td>-6.30</td>
<td>2.77</td>
</tr>
<tr>
<td>[Ir(3Fppy)$_2$(Bphen)][PF$_6$]</td>
<td>-1.65</td>
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<td>-3.15</td>
<td>-5.82</td>
<td>2.67</td>
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<tr>
<td>[Ir(3Fppy)$_2$(dmBphen)][PF$_6$]</td>
<td>-1.51</td>
<td>1.33</td>
<td>-3.29</td>
<td>-6.13</td>
<td>2.84</td>
</tr>
</tbody>
</table>
**Table 4.2b: Electrochemical properties of the complexes**

<table>
<thead>
<tr>
<th>Complex</th>
<th>$E_{1/2\text{red}}$ [V]</th>
<th>$E_{1/2\text{ox}}$ [V]</th>
<th>LUMO [eV]</th>
<th>HOMO [eV]</th>
<th>Energy gap [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ir(3,4Fppy)$_2$(phen)][PF$_6$]</td>
<td>-1.29</td>
<td>1.50</td>
<td>-3.51</td>
<td>-6.30</td>
<td>2.79</td>
</tr>
<tr>
<td>[Ir(3,4Fppy)$_2$(Bphen)][PF$_6$]</td>
<td>-1.38</td>
<td>1.44</td>
<td>-3.42</td>
<td>-6.24</td>
<td>2.82</td>
</tr>
<tr>
<td>[Ir(3,5Fppy)$_2$(dtb-bpy)][PF$_6$]</td>
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<td>1.34</td>
<td>-3.48</td>
<td>-6.14</td>
<td>2.66</td>
</tr>
<tr>
<td>[Ir(3,5Fppy)$_2$(Bphen)][PF$_6$]</td>
<td>-1.28</td>
<td>1.43</td>
<td>-3.52</td>
<td>-6.23</td>
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</tr>
<tr>
<td>[Ir(3,5Fppy)$_2$(phen)][PF$_6$]</td>
<td>-1.33</td>
<td>1.40</td>
<td>-3.47</td>
<td>-6.20</td>
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</tr>
<tr>
<td>[Ir(3,5Fppy)$_2$(pbpy)][PF$_6$]</td>
<td>-1.35</td>
<td>1.40</td>
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<td>-6.20</td>
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</tr>
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<td>1.02</td>
<td>-3.10</td>
<td>-5.80</td>
<td>2.70</td>
</tr>
<tr>
<td>[Ir(4Fp5Fpy)$_2$(pbpy)][PF$_6$]</td>
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<td>1.38</td>
<td>-3.41</td>
<td>-6.18</td>
<td>2.77</td>
</tr>
<tr>
<td>[Ir(3Fppy)$_2$(pbpy)][PF$_6$]</td>
<td>-1.37</td>
<td>1.35</td>
<td>-3.43</td>
<td>-6.15</td>
<td>2.72</td>
</tr>
<tr>
<td>[Ir(p5Fpy)$_2$(pbpy)][PF$_6$]</td>
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<td>1.26</td>
<td>-3.42</td>
<td>-6.06</td>
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<tr>
<td>[Ir(p5Fpy)$_2$(dtb-bpy)][PF$_6$]</td>
<td>-1.51</td>
<td>1.40</td>
<td>-3.29</td>
<td>-6.20</td>
<td>2.91</td>
</tr>
<tr>
<td>[Ir(na5Fpy)$_2$(Bphen)][PF$_6$]</td>
<td>-1.41</td>
<td>1.09</td>
<td>-3.39</td>
<td>-5.89</td>
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<tr>
<td>[Ir(3,5Fp5Fpy)$_2$(dtb-bpy)][PF$_6$]</td>
<td>-1.75</td>
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<td>-3.05</td>
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</tr>
<tr>
<td>[Ir(4Fppy)$_2$(pyimz)][PF$_6$]</td>
<td>-1.15</td>
<td>1.33</td>
<td>-3.65</td>
<td>-6.13</td>
<td>2.48</td>
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<tr>
<td>[Ir(4Fppy)$_2$(py3,5mpz)][PF$_6$]</td>
<td>-1.85</td>
<td>1.38</td>
<td>-2.95</td>
<td>-6.18</td>
<td>3.23</td>
</tr>
<tr>
<td>[Ir(3Fppy)$_2$(pyimz)][PF$_6$]</td>
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<td>1.20</td>
<td>-3.36</td>
<td>-6.00</td>
<td>2.64</td>
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<tr>
<td>[Ir(3Fppy)$_2$(py3,5mpz)][PF$_6$]</td>
<td>-</td>
<td>1.40</td>
<td>-</td>
<td>-6.20</td>
<td></td>
</tr>
<tr>
<td>[Ir(3,5Fppy)$_2$(pyimz)][PF$_6$]</td>
<td>-1.23</td>
<td>1.32</td>
<td>-3.57</td>
<td>-6.12</td>
<td>2.55</td>
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<tr>
<td>[Ir(3,4Fppy)$_2$(py3,5mpz)][PF$_6$]</td>
<td>-</td>
<td>1.50</td>
<td>-</td>
<td>-6.30</td>
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</tr>
<tr>
<td>[Ir(bzqu)$_2$(py3,5mpz)][PF$_6$]</td>
<td>-1.8</td>
<td>1.10</td>
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<td>-5.90</td>
<td>2.90</td>
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<tr>
<td>[Ir(bzqu)$_2$(phen)][PF$_6$]</td>
<td>-1.4</td>
<td>1.09</td>
<td>-3.40</td>
<td>-5.89</td>
<td>2.49</td>
</tr>
<tr>
<td>[Ir(bzqu)$_2$(Bphen)][PF$_6$]</td>
<td>-1.38</td>
<td>1.18</td>
<td>-3.42</td>
<td>-5.98</td>
<td>2.56</td>
</tr>
<tr>
<td>[Ir(bzqu)$_2$(dmBphen)][PF$_6$]</td>
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<td>1.20</td>
<td>-3.31</td>
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<td>2.69</td>
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<tr>
<td>[Ir(bzqu)$_2$(dtb-bpy)][PF$_6$]</td>
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<td>1.01</td>
<td>-3.17</td>
<td>-5.81</td>
<td>2.64</td>
</tr>
</tbody>
</table>
Though a cathodic shift in the potentials was observed with a change in the solvent for the two red complexes in chapter three, the band gap of complexes remain unchanged. Hence it is logical to compare the band gaps of the complexes based on the substituent effect. In general, the band gaps of the complexes are in agreement with the PL maxima and follow a similar trend based on the different substituents.

It was found that complexes with the phenanthroline ancillary ligand show a unique reduction potential pattern irrespective of the C^N ligand as seen in figures 4.25 and 4.26. The cyclic voltammograms of [Ir(4Fppy)2(phen)][PF6] and [Ir(3Fppy)2(phen)][PF6] show a very similar but different reduction potentials patterns compared to similar complexes with different N^N ligands. During the cathodic scan, the reduced species of the complexes are only oxidized much later in the reversed scan. Two suggestion are given for the observed results 1) either there is an electrochemical reaction that takes place during the CV measurements or 2) there is a change in the molecular geometry of the complex from the non-reduced species to the reduced specie and finally to the non-reduced species (after the oxidation of the initially reduced species during the cathodic scan). It would be reasonable to say that the low PLQY of these complexes may be due to certain intrinsic properties belonging to the phenanthroline N^N ligand.
**Figure 4.25:** Cyclic voltammogram of $[\text{Ir}(4\text{Fppy})_2(\text{Bphen})][\text{PF}_6]$, $[\text{Ir}(4\text{Fppy})_2(\text{dmBphen})][\text{PF}_6]$ and $[\text{Ir}(4\text{Fppy})_2(\text{phen})][\text{PF}_6]$.

**Figure 4.26:** Cyclic voltammogram of $[\text{Ir}(3\text{Fppy})_2(\text{Bphen})][\text{PF}_6]$, $[\text{Ir}(3\text{Fppy})_2(\text{dMeO-bpy})][\text{PF}_6]$ and $[\text{Ir}(3\text{Fppy})_2(\text{phen})][\text{PF}_6]$. 
4.6 Electroluminescence studies

The electroluminescence properties of some of the complexes where investigated by fabricating LEC devices incorporating the complexes in the emissive layer. The devices were driven under a pulsed current mode at an average current density of 100 A/m² at a frequency of 1000 Hz and a block wave with a duty cycle of 50%. For a better comprehensive understanding of the relationship between the molecular structure of the complexes and their LEC device performance, the complexes are grouped in sets with particular patterns of structural modifications of the complexes.

4.6.1 The influence of electron donating groups on the N^N ligand on the EL performance of complexes with single fluorinated C^N ligands

The LEC device data for \([\text{Ir}(4\text{Fppy})_2(\text{bpy})][\text{PF}_6]\), \([\text{Ir}(4\text{Fppy})_2(\text{dmbpy})][\text{PF}_6]\) and \([\text{Ir}(4\text{Fppy})_2(\text{dtb-bpy})][\text{PF}_6]\) complexes are summarized in table 4.3, where the C^N ligands remaining unchanged while the electron donating ability of the substituents from unsubstituted bipyridine (bpy) to 4,4'-dimethylbipyridine (dmbpy) to 4,4'-di-tert-butylbipyridine (dtb-bpy) of the N^N ligand increases.

<table>
<thead>
<tr>
<th>Complex</th>
<th>(\text{Lum}_{\text{max}}) [cd/m²]</th>
<th>(t_{1/2}) [h]</th>
<th>Current efficiency [cd/A]</th>
<th>Power Efficiency [lm/W]</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Ir}(4\text{Fppy})_2(\text{bpy})][\text{PF}_6])</td>
<td>1605</td>
<td>668</td>
<td>16</td>
<td>8.7</td>
</tr>
<tr>
<td>([\text{Ir}(4\text{Fppy})_2(\text{dmbpy})][\text{PF}_6])</td>
<td>1594</td>
<td>221</td>
<td>15.9</td>
<td>8.5</td>
</tr>
<tr>
<td>([\text{Ir}(4\text{Fppy})_2(\text{dtb-bpy})][\text{PF}_6])</td>
<td>1193</td>
<td>54.9</td>
<td>11.9</td>
<td>5.4</td>
</tr>
</tbody>
</table>

The luminance, current and power efficiencies of the LEC devices based on \([\text{Ir}(4\text{Fppy})_2(\text{bpy})][\text{PF}_6]\) and \([\text{Ir}(4\text{Fppy})_2(\text{dmbpy})][\text{PF}_6]\) are very similar implying the methyl group on the N^N ligand of \([\text{Ir}(4\text{Fppy})_2(\text{dmbpy})][\text{PF}_6]\) showing no significant
affect to the LEC device performance, while introducing the tert-butyl group to the bipyridine causes a dramatic drop. Also, LEC device lifetime ($t_{1/2}$) decreases by adding alkyl substituents on the N^N ligand of the complexes. A drop in the $t_{1/2}$ from 668 h to 221 h and even to 54.9 h is seen on going from $[\text{Ir}(4\text{Fppy})_2(\text{bpy})][\text{PF}_6]$ with no substituents on the N^N ligand to $[\text{Ir}(4\text{Fppy})_2(\text{dmbpy})][\text{PF}_6]$ with methyl substituents and to $[\text{Ir}(4\text{Fppy})_2(\text{dtb-bpy})][\text{PF}_6]$ with tert-butyl substituents, respectively (figure 4.27).

![Figure 4.27: Maximum luminance and lifetime dependence of LEC devices on the alkyl substituents on the N^N ligand of $[\text{Ir}(4\text{Fppy})_2(\text{bpy})][\text{PF}_6]$, $[\text{Ir}(4\text{Fppy})_2(\text{dmbpy})][\text{PF}_6]$ and $[\text{Ir}(4\text{Fppy})_2(\text{dtb-bpy})][\text{PF}_6]$.](image)

Introducing the methyl substituent on the fifth position of the N^N ligand $[\text{Ir}(4\text{Fppy})_2(5\text{dmbpy})][\text{PF}_6]$ led to a drop in the luminance and efficiencies (1314 cd/m², 13.1 cd/A and 6.6 lm/W) of the device compared to the device based on unsubstituted complex $[\text{Ir}(4\text{Fppy})_2(\text{bpy})][\text{PF}_6]$. The LEC device based on $[\text{Ir}(4\text{Fppy})_2(5\text{dmbpy})][\text{PF}_6]$ show a remarkable drop in the device lifetime of only 45.7 h (figure 4y, appendix) which is the lowest for all the complexes with the alkyl substituents on the N^N ligand.
Similar LEC device performances were observed for the [Ir(3Fppy)$_2$(bpy)][PF$_6$], [Ir(3Fppy)$_2$(dmbpy)][PF$_6$] and [Ir(3Fppy)$_2$(dtb-bpy)][PF$_6$] complexes. The LEC device data of the 3Fppy C$^N$N ligands based complexes are summarized in table 4.4.

**Table 4.4**: LEC device data for [Ir(3Fppy)$_2$(bpy)][PF$_6$], [Ir(3Fppy)$_2$(dmbpy)][PF$_6$] and [Ir(3Fppy)$_2$(dtb-bpy)][PF$_6$].

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\text{Lum}_{\text{max}}$</th>
<th>$t_{1/2}$</th>
<th>Current efficiency</th>
<th>Power efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ir(3Fppy)$_2$(bpy)][PF$_6$]</td>
<td>1492</td>
<td>953</td>
<td>14.9</td>
<td>8.7</td>
</tr>
<tr>
<td>[Ir(3Fppy)$_2$(dmbpy)][PF$_6$]</td>
<td>1431</td>
<td>334</td>
<td>14.3</td>
<td>7.7</td>
</tr>
<tr>
<td>[Ir(3Fppy)$_2$(dtb-bpy)][PF$_6$]</td>
<td>744</td>
<td>286</td>
<td>7.5</td>
<td>2.0</td>
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</table>

Alike complexes based on 2-(4-fluorophenyl)pyridine, the luminance and current efficiency of LEC devices based on complexes using 2-(3-fluorophenyl)pyridine, particularly [Ir(3Fppy)$_2$(bpy)][PF$_6$] and [Ir(3Fppy)$_2$(dmbpy)][PF$_6$], are very similar. Also a drop in the overall LEC device performance was observed for [Ir(3Fppy)$_2$(dtb-bpy)][PF$_6$] using the di-tert-butyl-bipyridine. The drop in the power efficiency of the devices using the complexe with dtbbpy as N$^N$N ligand is accompanied by an increase in the operation voltage of the LEC devices which can be attributed to a change in the charge transporting properties of the Ir-iTMCs. Similar to 4Fppy based complexes, a remarkable drop in the device stability from 953 to 286 h on going from [Ir(3Fppy)$_2$(bpy)][PF$_6$] to [Ir(3Fppy)$_2$(dtb-bpy)][PF$_6$] was observed. The luminance spectra, current and power efficiencies and operating voltage of the LEC device based on [Ir(3Fppy)$_2$(bpy)][PF$_6$] are shown in figures 4.28 and 4.29.
Figure 4.28: Luminance spectra and operating voltage over time for the LEC device based on \([\text{Ir}(3\text{Fppy})_2(bpy)]\text{[PF}_6\text{]}\).

Figure 4.29: Current and power efficiencies over time for the LEC device based on \([\text{Ir}(3\text{Fppy})_2(bpy)]\text{[PF}_6\text{]}\).
In tables 4.3 and 4.4 the presented LEC device performances using complexes with single fluorinated C^N ligands exhibit that the fluorine substituent is not primarily responsible for the short lifetime of the LEC devices as previously reported [23]. It has been clearly demonstrated that the N^N ligand also plays a very important role in the overall performance of the LEC devices. Rather the lifetime of the devices decreases with the introduction of the alkyl (methyl groups) substituent on the N^N ligand and even more with the increase of the size to the alkyl (di-tert-butyl) substituent. The general approach of using ancillary ligands (N^N) incorporating alkyl substituents is to increase the luminance of the device by increasing the inter-complex distances within the thin film of the emissive layer thereby reducing the exciton-exciton interaction (quenching). Again, it can be seen that the hypothesis is biased as LEC devices based on complexes with no substituents on the N^N ligand ([Ir(4Fppy)_2(bpy)][PF_6] and [Ir(3Fppy)_2(bpy)][PF_6]) also demonstrated even higher luminance compared to the devices based on the complexes with the dmbpy and dtb-bpy N^N ligands under the above mentioned driven conditions.

In a second approach the N^N ligands of the 4Fppy and 3Fppy C^N ligands based complexes were changed from the bipyridine-type to the phenanthroline-type to evaluate their performances in LEC devices. The device data for the complexes [Ir(4Fppy)_2(phen)][PF_6], [Ir(4Fppy)_2(Bphen)][PF_6], [Ir(4Fppy)_2(dmBphen)][PF_6], [Ir(3Fppy)_2(phen)][PF_6], [Ir(3Fppy)_2(Bphen)][PF_6] and [Ir(3Fppy)_2(dmBphen)][PF_6] are summarized in table 4.5.
Table 4.5: Summary of LEC device data for 4Fppy and 3Fppy C^N ligands based complexes with the phen type N^N ligands.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Luminance max [	ext{cd/m}^2]</th>
<th>t(_{1/2}) [h]</th>
<th>Current efficiency [cd/A]</th>
<th>Power efficiency [lm/W]</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ir(4Fppy)_2(phen)][PF_6]</td>
<td>1385</td>
<td>91.2</td>
<td>13.9</td>
<td>7.2</td>
</tr>
<tr>
<td>[Ir(4Fppy)_2(Bphen)][PF_6]</td>
<td>1658</td>
<td>474</td>
<td>16.5</td>
<td>9.3</td>
</tr>
<tr>
<td>[Ir(4Fppy)_2(dmBphen)][PF_6]</td>
<td>1555</td>
<td>10.8</td>
<td>15.5</td>
<td>8.2</td>
</tr>
<tr>
<td>[Ir(3Fppy)_2(phen)][PF_6]</td>
<td>1835</td>
<td>132</td>
<td>18.3</td>
<td>9.2</td>
</tr>
<tr>
<td>[Ir(3Fppy)_2(Bphen)][PF_6]</td>
<td>1394</td>
<td>448</td>
<td>13.9</td>
<td>7.7</td>
</tr>
<tr>
<td>[Ir(3Fppy)_2(dmBphen)][PF_6]</td>
<td>1410</td>
<td>15</td>
<td>14.1</td>
<td>7.3</td>
</tr>
</tbody>
</table>

All the LEC devices demonstrated high luminance greater than 1380 cd/m\(^2\) with the highest luminance obtained for the LEC device based on [Ir(3Fppy)_2(phen)][PF_6]. The high luminance of the [Ir(3Fppy)_2(phen)][PF_6] based LEC device is particularly interesting and contrary to expectations as the complex displayed a very low PLQY of 19.08% (table 4.1a). This complex also shows a difference in its electrochemical redox potential as highlighted in section 4.5. The same observations were found for the LEC device based on [Ir(4Fppy)_2(phen)][PF_6] suggesting the observed variations are related to the phenanthroline (phen) ancillary ligand. The luminance of 1658 cd/m\(^2\) for [Ir(4Fppy)_2(Bphen)][PF_6] based LEC was the highest obtained for the 4Fppy based complexes, although lower than the luminance of 1835 cd/m\(^2\) for [Ir(3Fppy)_2(phen)][PF_6] based LEC, but both are having similar power efficiencies. This is due to different operating voltages of the LEC device based on [Ir(4Fppy)_2(Bphen)][PF_6] and [Ir(3Fppy)_2(phen)][PF_6] and can be attributed to the better electron transporting property of Bphen compared to phen. The lifetimes of the LEC devices based on the complexes with the 4Fppy and 3Fppy C^N ligands appears to follow the same trend. The increasing order in the lifetime of the LEC devices with respect to the N^N ligands is Bphen > phen > dmBphen is shown in
figure 4.31 and 4.31. It can be argued that the methyl groups on the dmBphen N^N ligand somehow causes a steric hindrance around the iridium center causing the complexes to be unstable during device operation and finally resulting in the short lifetime of the LEC devices incorporating the dmBphen N^N ligand based complexes.

**Figure 4.30:** Maximum luminance and lifetime dependence of LEC devices on the alkyl substituents on the N^N ligand of [Ir(4Fppy)_2(phen)][PF_6], [Ir(4Fppy)_2(Bphen)][PF_6] and [Ir(4Fppy)_2(dmBphen)][PF_6].
Figure 4.31: Maximum luminance and lifetime dependence of LEC devices on the alkyl substituents on the N^N ligand of \([\text{Ir}(3\text{Fppy})_2(\text{phen})][\text{PF}_6]\), \([\text{Ir}(3\text{Fppy})_2(\text{Bphen})][\text{PF}_6]\) and \([\text{Ir}(3\text{Fppy})_2(\text{dmBphen})][\text{PF}_6]\).

Non-aromatic substituents on the N^N ligands of the complexes like methyl or tert-butyl groups, as per \([\text{Ir}(4\text{Fppy})_2(\text{dmbpy})][\text{PF}_6]\) and \([\text{Ir}(3\text{Fppy})_2(\text{dtb-bpy})][\text{PF}_6]\), will in contrast to aromatic substituents like phenyl groups, as per \([\text{Ir}(4\text{Fppy})_2(\text{Bphen})][\text{PF}_6]\) and \([\text{Ir}(3\text{Fppy})_2(\text{Bphen})][\text{PF}_6]\), lead to an increase in the inter-complex distances but without providing a medium for effective charge transport between the complexes. The poor charge transport of the complexes with the alkyl substituent could be one reason for the decrease in LEC device lifetimes.

Even though LEC devices incorporating the complexes based on the 4Fppy C^N ligands show encouraging lifetimes, the device lifetime of LECs based on the 3Fppy C^N ligands complexes demonstrate further improvement. It was found that with
the fluorine substituent at the ortho position of the phenyl ring of the C^N ligand relative to coordinating carbon atom, fluorine-nitrogen (F-N) intra-molecular interactions between the two C^N ligands of the complexes occur as can be seen from the single crystal structure of some of the complexes (see figures 4.33 and 4.38). The F-N intra-molecular interaction is believed to form a cage structure that prevent opening of the complexes during device operation and hence leading to LEC devices with longer lifetimes. Table 4.6 summarizes some of the LEC device lifetimes of 4Fppy- and 3Fppy-type C^N ligands based complexes with the same N^N ligands. Up to now, no such F-N intramolecular interactions are reported for Ir-iTMCs.

Table 4.6: Comparison of LEC device lifetimes of some selected complexes demonstrating lifetime improvement via the F-N intramolecular interactions.

<table>
<thead>
<tr>
<th>Complex</th>
<th>t_{1/2} [h]</th>
<th>(3Fppy-t_{1/2}) / (4Fppy-t_{1/2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ir(3Fppy)₂(phen)][PF₆]</td>
<td>132</td>
<td>1.44</td>
</tr>
<tr>
<td>[Ir(4Fppy)₂(phen)][PF₆]</td>
<td>91.2</td>
<td>1.44</td>
</tr>
<tr>
<td>[Ir(3Fppy)₂(dmBphen)][PF₆]</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>[Ir(4Fppy)₂(dmBphen)][PF₆]</td>
<td>10.8</td>
<td>1.38</td>
</tr>
<tr>
<td>[Ir(3Fppy)₂(bpy)][PF₆]</td>
<td>953</td>
<td></td>
</tr>
<tr>
<td>[Ir(4Fppy)₂(bpy)][PF₆]</td>
<td>668</td>
<td>1.42</td>
</tr>
<tr>
<td>[Ir(3Fppy)₂(Bphen)][PF₆]</td>
<td>448</td>
<td></td>
</tr>
<tr>
<td>[Ir(4Fppy)₂(Bphen)][PF₆]</td>
<td>474</td>
<td>0.93</td>
</tr>
</tbody>
</table>

It can be seen that the device lifetimes of complexes with that feature F-N intramolecular interactions are approximately 1.4 times longer than those for the complexes with no such intramolecular interactions. This implies that indeed the F-N intramolecular interaction enhances the structural stability against e.g. nucleophilic attack from water molecules remaining in the spin coated layer after device processing is completed. However, the lifetime of LEC devices based on
[Ir(3Fppy)_2(Bphen)][PF_6] and [Ir(4Fppy)_2(Bphen)][PF_6] were found to be almost the same.

Other conditions which are based on the operation mechanism of the LEC devices contribute to the general device performance including the device lifetime, too. This will be discussed more detailed in chapter six (section 6.3).

4.6.2 **Introducing the π-π intramolecular stacking to Ir-iTMCs with fluorinated C^N ligands**

[Ir(4Fppy)_2(pbpy)][PF_6] was synthesized to investigate if the π-π intramolecular stacking between the pendant phenyl ring of the N^N ligand and the fluorinated phenyl ring of one of the C^N ligand will lead to an enhancement in the lifetime of the LEC device compared to a complex where only bipyridine is used as ancillary ligand. The LEC device data of [Ir(4Fppy)_2(pbpy)][PF_6] together with device data for [Ir(4Fppy)_2(bpy)][PF_6] are summarized in table 4.7.

**Table 4.7:** LEC device data for [Ir(4Fppy)_2(pbpy)][PF_6] and [Ir(4Fppy)_2(bpy)][PF_6] complexes.

<table>
<thead>
<tr>
<th></th>
<th>Lum(_{\text{max}}) [cd/m(^2)]</th>
<th>(t_{1/2}) [h]</th>
<th>Current efficiency [cd/A]</th>
<th>Power efficiency [lm/W]</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ir(4Fppy)_2(pbpy)][PF_6]</td>
<td>1443</td>
<td>214</td>
<td>14.4</td>
<td>7.4</td>
</tr>
<tr>
<td>[Ir(4Fppy)_2(bpy)][PF_6]</td>
<td>1605</td>
<td>668</td>
<td>16</td>
<td>8.7</td>
</tr>
</tbody>
</table>

The luminance and efficiencies of the LEC device based on [Ir(4Fppy)_2(pbpy)][PF_6] are slightly lower but comparable to those of the LEC device based on [Ir(4Fppy)_2(bpy)][PF_6]. Nevertheless, the lifetime of the [Ir(4Fppy)_2(pbpy)][PF_6] based LEC device is three times less than that for the [Ir(4Fppy)_2(bpy)][PF_6] based LEC device as seen in table 4.7 and figure 4.32.
Figure 4.32: Maximum luminance and lifetime of LEC devices for \([\text{Ir}(4\text{Fppy})_2(\text{pbpy})][\text{PF}_6]\) and \([\text{Ir}(4\text{Fppy})_2(\text{bpy})][\text{PF}_6]\) complexes.

A dramatic drop in the lifetime for the LEC device incorporating \([\text{Ir}(3\text{Fppy})_2(\text{pbpy})][\text{PF}_6]\) of 2.8 h was observed, too. The complex \([\text{Ir}(3\text{Fppy})_2(\text{pbpy})][\text{PF}_6]\) was found to have both, the F-N and \(\pi-\pi\) intramolecular interactions as can be seen from its single crystal structure (figure 4.37). However, it can be understood that the double intramolecular interactions led to a strained complex which is very unstable under the operating condition of a LEC device. A similar result was observed for a LEC device based on \([\text{Ir}(3,5\text{Fp5Fpy})_2(\text{pbpy})][\text{PF}_6]\) (also having both the F-N and \(\pi-\pi\) intramolecular interactions, figure 4.38) with a device lifetime of 4.3 h.

4.6.3 Do fluorinated pyridine rings of the C\(^N\) ligands also lead to LEC device lifetime improvement for greenish emitting Ir-iTMCs?

Introducing a fluorine at the 5\(^{th}\) position (meta to the pyridines nitrogen) of the pyridine ring for the complex \([\text{Ir}(4\text{Fp5Fpy})_2(\text{pbpy})][\text{PF}_6]\) results in a decrease in the lifetime of the device from 214 hours for a LEC based on \([\text{Ir}(4\text{Fppy})_2(\text{pbpy})][\text{PF}_6]\) to
only 25 h. The fast drop in the device lifetime based on [Ir(4Fp5Fpy)₂(pbpy)][PF₆] indicates that the additional fluorine substituent to the pyridine ring of the C^N ligand somehow causes a reduction in the structural stability of the complex resulting in degradation of the complex during device operation. Also, a LEC device lifetime of only 4.8 h was obtained for [Ir(3,5Fp5Fpy)₂(dtb-bpy)][PF₆]. To summarize those results leads to the conclusion that applying both concepts for stabilization, the N-F-interaction and the π-π-stacking approach, will result in strong destabilization due to structural straining and possible vulnerability to nucleophilic attack by e.g. water or oxygen molecules.

It should be noted that each of the complexes having the fluorine substituents on the pyridine ring of the C^N ligand also feature at least one other intramolecular interaction. For example the F-N intramolecular interaction is present for the [Ir(3,5Fp5Fpy)₂(dtb-bpy)][PF₆] and the π-π intramolecular interactions for [Ir(4Fp5Fpy)₂(pbpy)][PF₆]. As a result, in a future work the approach of using C^N ligands with fluorinated pyridine rings to improve the lifetime of LEC devices as demonstrated with the red emitting Ir-iTMCs should be investigated without using other stabilizing effects like the π-π stacking.

4.7 Conclusions

The approach of using fluorine as an electron withdrawing substituent on the phenyl ring of the C^N ligands to blue shift the emission of Ir-iTMCs is also beneficial toward improving the efficiencies of LEC devices as fluorine containing Ir-iTMCs were found to have high PLQYs. However, the high efficiencies for the fluorinated Ir-iTMCs were achieved at the expense of the device stability (a decrease in the device lifetime). As such it was concluded that the fluorine substituents are detrimental to the overall device stability and that fluorine free green emitting complexes be designed for LEC applications [23].
Owing to the fact that fluorinated starting materials for the synthesis of green emitting Ir-iTMCs are cheap and commercially available together with the benefit of obtaining very efficient green LEC devices, a library of fluorinated complexes with different structural modifications and a few non fluorinated complexes were designed and synthesized in this work for LEC application. The aim being to fully investigate if, indeed, the fluorine substituent is primarily responsible for the short LEC device lifetimes based on fluorinated Ir-iTMCs.

A total of 34 fluorinated complexes (32 completely new Ir-iTMCs) together with 5 non fluorinated complexes (4 completely new Ir-iTMCs) were successfully synthesized and characterized by \(^1\)H and \(^{13}\)C NMR and UV-Vis spectroscopy. Single crystal X-ray diffraction was used to confirm the chemical structures of some of the complexes. All the complexes were obtained with good purity levels as analyzed by the integration of the \(^1\)H NMR peaks.

The PL and electrochemical properties of the complexes were studies using spectrofluorimetry and cyclic voltammetry respectively. Both the PL maxima and the band gap energies of the complexes were found to depend strongly on the nature of the C^N and/or N^N ligands and also on the type of substituents on these ligands. The general trend in the shift in the PL due to ligand type and substituent effect were found to be as expected with a blue shifted PL maxima upon decorating the phenyl ring of the C^N ligands with fluorine atoms.

One strategy used to study the dependence of LEC device lifetime on fluorine substituent is to keep the fluorinated C^N ligand the same and vary the N^N ligands. One example is the use of 4Fppy C^N ligand with bpy (having no alkyl substituents), dmbpy (with methyl substituent) and dtb-bpy (with the di-tert-butyl substituent) N^N type ligands. It was found that the lifetime of the LEC devices decrease with the introduction of a methyl group from \([\text{Ir}(4\text{Fppy})_2(\text{bpy})]^{2-}[\text{PF}_6]^- (t_{1/2} = 668 \text{ h})\) to \([\text{Ir}(4\text{Fppy})_2(\text{dmbpy})]^{2-}[\text{PF}_6]^- (t_{1/2} = 221 \text{ h})\), with even a further drop in the device
lifetime by increasing the size of the alkyl substituent to dtb for [Ir(4Fppy)$_2$(dtb-bpy)][PF$_6$] ($t_{1/2} = 54.9$ h). Upon changing the location of the fluorine substituent on the phenyl ring of the C^N ligands from the \textit{meta} to the \textit{ortho} (from 4Fppy to 3Fppy C^N ligand) positions with respect to the coordinating carbon atom, a similar trend in the drop of the LEC device lifetime was observed on going from [Ir(3Fppy)$_2$(bpy)][PF$_6$] ($t_{1/2} = 953$ h) to [Ir(3Fppy)$_2$(dmbpy)][PF$_6$] ($t_{1/2} = 334$ h) to [Ir(3Fppy)$_2$(dtb-bpy)][PF$_6$] ($t_{1/2} = 286$ h). This observation clearly shows that the lifetime of the green LEC devices was affected more by the alkyl substituents on the N^N ligand and not primarily by the fluorine substituent on the C^N ligands.

A similar variation in the LEC device lifetimes was found by changing the N^N ligand from the bipyridine- (bpy-) type to the phenanthroline- (phen-) type for both the 4Fppy and 3Fppy based Ir-iTMCs. It was also noticed that the variation in the device lifetimes among the 4Fppy and 3Fppy based complexes with phenanthroline (phen), bathophenanthroline (Bphen) and 2,9-dimethyl bathophenanthroline (dmBphen) as the N^N ligands were similar even though the position of the fluorine substituent differs between the two groups of complexes. It is evident that the overall stability of LEC devices based on the fluorinated Ir-iTMCs does not only depend on the substituent on the C^N ligands but also on the type of the N^N ligand and also the substituents on the N^N ligands.

Interestingly, two F-N intramolecular interactions were observed between the ortho substituted fluorine atom on one of the C^N ligands and the nitrogen atom of the pyridine ring of the other C^N ligand for the 3Fppy based Ir-iTMCs (for example figure 4.32). A further increased in the lifetime of approximately 43\% was obtained for LEC devices based on the 3Fppy complexes compared to the 4Fppy based complexes. The increase in the lifetime is attributed to the F-N intramolecular interactions. It should be noted that this is the first time that F-N intramolecular interactions are reported.
Another approach to improve the lifetime of green LEC devices based on fluorinated Ir-iTMCs is by introducing the $\pi$-$\pi$ intramolecular stacking between a pendent phenyl ring on the $N^N$ ligand and the fluorinated phenyl ring of the one of the $C^N$ ligands. The approach was unsuccessful as the lifetime was rather decreased upon introduction of the $\pi$-$\pi$ stacking from 668 h for [Ir(4Fppy)$_2$(bpy)][PF$_6$] to 214 h for [Ir(4Fppy)$_2$(p bpy)][PF$_6$] LEC based devices.

So far, the 2-(3,4-difluorophenyl)pyridine and 2-(3,5-difluorophenyl)pyridine $C^N$ ligands based Ir-iTMCs were not used in the fabrication of LEC devices. It would be interesting to see how these complexes perform when applied in LEC devices and to study the dependence of the LEC device lifetime on the number and position of the fluorine substituents on the phenyl ring of the $C^N$ ligands. Another interesting trend not covered in this work will be to evaluate how the green emitting bzqu (benzoquinoline) $C^N$ ligand based Ir-iTMCs perform when applied in a LEC device and to compared the device lifetimes of these non-fluorinated Ir-iTMCs with those of fluorinated Ir-iTMCs. The above mentioned further work is on going.

In general, the lifetime of green LEC devices reported in this work are significantly higher reaching 668 and 953 hours for [Ir(3Fppy)$_2$(bpy)][PF$_6$] and [Ir(4Fppy)$_2$(bpy)][PF$_6$], respectively, compared to literature data [12,21,23]. Also high luminance (more than 1300 cd/m$^2$) and efficiencies greater than 13 cd/A and 7 lm/W for current and power efficiencies respectively were achieved for most of the LEC devices.
4.8 Solid state structures

Table 4.8: Crystallographic data for [Ir(3Fppy)2(dmbpy)][PF6].

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
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<tbody>
<tr>
<td>Empirical formula</td>
<td>C24H28N4F8Ir</td>
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<td>Formula weight [g/mol]</td>
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<td>Triclinic</td>
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<tr>
<td>Space group</td>
<td>P-1</td>
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<tr>
<td>Unit cell dimensions</td>
<td>a, b, c[Å] = 8.5658(10), 12.6844(15), 16.1249(21)</td>
</tr>
<tr>
<td></td>
<td>α, β, γ[°] = 95.819(15), 101.803(15), 92.107(14)</td>
</tr>
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<td>Cell volume [Å3]</td>
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</tr>
<tr>
<td>Density [g/cm³]</td>
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</tr>
<tr>
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<td>2</td>
</tr>
<tr>
<td>Abb. Coef. [/mm]</td>
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</tr>
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<td>F(000)</td>
<td>843.8</td>
</tr>
<tr>
<td>Temp [°C]</td>
<td>293(2)</td>
</tr>
<tr>
<td>θ range [°]</td>
<td>2.4 – 28.1</td>
</tr>
<tr>
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</tr>
<tr>
<td>Reflns collected</td>
<td>16319</td>
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<td>7593</td>
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<tr>
<td>GOOF</td>
<td>0.963</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R_all = 0.57, wR2_all = 0.091</td>
</tr>
</tbody>
</table>

Figure 4.33: Detail of the single crystal structure of [Ir(3Fppy)2(dmbpy)][PF6] (ball and stick plotted) showing the F-N intramolecular interactions between the two C=N ligands. The counter anion PF6, ethyl acetate and hydrogen atoms are omitted for clarity.
### Table 4.9: Crystallographic data for \([\text{Ir(4Fppy)}_2(\text{bpy})][\text{PF}_6]\).

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
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<tbody>
<tr>
<td>Empirical formula</td>
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</tr>
<tr>
<td>Formula weight [g/mol]</td>
<td>837.7</td>
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<td>Crystal system</td>
<td>Triclinic</td>
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<td>Space group</td>
<td>P-1</td>
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<tr>
<td>Unit cell dimensions</td>
<td>(a, b, c [\text{Å}] = 14.0310(17), 15.8591(19), 17.4881(20))</td>
</tr>
<tr>
<td></td>
<td>(\alpha, \beta, \gamma [^\circ] = 66.114(13), 81.065(14), 67.946(14))</td>
</tr>
<tr>
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</tr>
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<td>(\theta) range [°]</td>
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</tr>
<tr>
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<tr>
<td>Uniq. Reflns</td>
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<td>GOOF</td>
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<td>(R_{\text{obs}} = 0.026, \text{ wR}^2_{\text{obs}} = 0.054)</td>
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<td>R indices (all data)</td>
<td>(R_{\text{all}} = 0.059, \text{ wR}^2_{\text{all}} = 0.060)</td>
</tr>
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</table>

**Figure 4.34:** Detail of the single crystal structure of \([\text{Ir(4Fppy)}_2(\text{bpy})][\text{PF}_6]\) (ball and stick plotted). The counter anion \(\text{PF}_6\), dichloromethane and hydrogen atoms are omitted for clarity.
**Table 4.10:** Crystallographic data for [Ir(4Fppy)₂(Bphen)][PF₆].

<table>
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<th>Value</th>
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</thead>
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<td>Space group</td>
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<td>a, b, c [Å] = 12.0505(14), 24.5940(22), 15.0761(19)</td>
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<tr>
<td></td>
<td>α, β, γ [°] = 90.000(0), 98.889(15), 90.000(0)</td>
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**Figure 4.35:** Detail of the single crystal structure of [Ir(4Fppy)₂(Bphen)][PF₆] (ball and stick plotted). The counter anion PF₆, anisole and hydrogen atoms are omitted for clarity.
Table 4.11: Crystallographic data for \([\text{Ir(4Fppy)}_2(\text{phen})][\text{PF}_6]\).

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<td>R indices</td>
<td>(R_{\text{obs}} = 0.026,) (wR_{2\text{obs}} = 0.054)</td>
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<tr>
<td>R indices (all data)</td>
<td>(R_{\text{all}} = 0.043,) (wR_{2\text{all}} = 0.056)</td>
</tr>
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</table>

Figure 4.36: Details of the single crystal structure of \([\text{Ir(4Fppy)}_2(\text{phen})][\text{PF}_6]\) (ellipsoids plotted at 40% probability level). The counter anion \(\text{PF}_6\) and hydrogen atoms are omitted for clarity.
Table 4.12: Crystallographic data for [Ir(p5Fpy)$_2$(pbpy)][PF$_6$].

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
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<tbody>
<tr>
<td>Empirical formula</td>
<td>$C_{38}H_{26}F_8N_4$Ir</td>
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<tr>
<td>Formula weight [g/mol]</td>
<td>913.8</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>$P 1 2 1/c 1$</td>
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<tr>
<td>Unit cell dimensions</td>
<td>$a, b, c [\text{Å}] = 13.1801(9), 12.6400(11), 20.8794(15)$</td>
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<td>Density [g/cm$^3$]</td>
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<td>Abb. Coef. [/mm]</td>
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<td>F(000)</td>
<td>1783.6</td>
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<tr>
<td>Temp [$^\circ$C]</td>
<td>293(2)</td>
</tr>
<tr>
<td>$\theta$ range [$^\circ$]</td>
<td>2.4 - 25.0</td>
</tr>
<tr>
<td>Index range</td>
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</tr>
<tr>
<td>Reflns collected</td>
<td>24024</td>
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<tr>
<td>Uniq. Reflns</td>
<td>6078</td>
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<tr>
<td>No Param</td>
<td>469</td>
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<tr>
<td>GOOF</td>
<td>0.856</td>
</tr>
<tr>
<td>R indices</td>
<td>$R_{\text{obs}} = 0.021, wR2_{\text{obs}} = 0.038$</td>
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<tr>
<td>R indices (all data)</td>
<td>$R_{\text{all}} = 0.036, wR2_{\text{all}} = 0.040$</td>
</tr>
</tbody>
</table>

**Figure 4.37**: Detail of the single crystal structure of [Ir(p5Fpy)$_2$(pbpy)][PF$_6$] (ellipsoids plotted at 40% probability level) show the $\pi$-$\pi$ intramolecular interaction. The counter anion PF$_6$ and hydrogen atoms are omitted for clarity.
**Table 4.13:** Crystallographic data for [Ir(3Fppy)$_2$(pbpy)][PF$_6$].

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<th>Property</th>
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<tbody>
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<td>Empirical formula</td>
<td>C$<em>{38}$H$</em>{26}$F$_8$N$_4$Ir</td>
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<tr>
<td>Formula weight [g/mol]</td>
<td>913.8</td>
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<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
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<tr>
<td>Space group</td>
<td>$P 1 2_1/c$</td>
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<td>Unit cell dimensions</td>
<td>$a, b, c[\text{Å}] = 15.3051(19), 14.8887(12), 15.4736(17)$</td>
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<td>F(000)</td>
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<td>Temp [$^\circ$C]</td>
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<td>$\theta$ range [$^\circ$]</td>
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<td>GOOF</td>
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<td>R indices</td>
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<td>R indices (all data)</td>
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*Figure 4.38:* Detail of the single crystal structure of [Ir(3Fppy)$_2$(pbpy)][PF$_6$] (ellipsoids plotted at 30% probability level) features the π-π and F-N intramolecular interactions. The counter anion PF$_6$ and hydrogen atoms are omitted for clarity.
Table 4.14: Crystallographic data for [Ir(3,5Fp5Fpy)$_2$(pbpy)][PF$_6$].

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<th>Property</th>
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<td>Space group</td>
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<td>Abb. Coef. [/mm]</td>
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<td>F(000)</td>
<td>1783.6</td>
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<td>Temp [°C]</td>
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<td>θ range [°]</td>
<td>2.4 - 25.0</td>
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<tr>
<td>Index range</td>
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<td>Reflns collected</td>
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<td>GOOF</td>
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<td>R indices (all data)</td>
<td>$R_{\text{all}} = 0.036$, $wR^2_{\text{all}} = 0.040$</td>
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</tbody>
</table>

Figure 4.39: Detail of the single crystal structure of [Ir(3,5Fp5Fpy)$_2$(pbpy)][PF$_6$] (ball and stick plotted) features the π-π and F-N intramolecular interactions. The counter anion PF$_6$ and hydrogen atoms are omitted for clarity.
Table 4.15: Crystallographic data for [Ir(bzqu)$_2$(py3,5mpz)][PF$_6$].

<table>
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<tr>
<th>Property</th>
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<tbody>
<tr>
<td>Empirical formula</td>
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<td>Space group</td>
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<td>GOOF</td>
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<td>R indices (all data)</td>
<td>$R_{\text{all}} = 0.097$, $wR^2_{\text{all}} = 0.141$</td>
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</table>

Figure 4.39: Detail of the single crystal structure of [Ir(bzqu)$_2$(py3,5mpz)][PF$_6$] (ball and stick plotted). The counter anion PF$_6$, ethyl acetate and hydrogen atoms are omitted for clarity.
4.9 Experimental

4.9.1 Synthesis and characterizations

The synthetic procedures for obtaining the diiridium intermediate complexes and the heteroleptic Ir-iTMCs are the same as described in the experimental section of chapter 3 together with the characterization techniques for the Ir-iTMCs and the device fabrication method.

4.9.2 Synthesis of diiridium intermediate complexes not described in chapter three

\[[\text{Ir}(3,5\text{Fppy})_2\text{Cl}]_2\]: \text{IrCl}_3 \times \text{H}_2\text{O} (2.87 \text{ g}, 9.61 \text{ mmol}), 2-(3,5-difluorophenyl)pyridine (3.84 \text{ g}, 20.66 \text{ mmol}), \text{ water} (25 \text{ mL}), 2\text{-methoxyethanol} (80 \text{ mL}), \text{yellow powder (yield: 4.1 g, 70.2\%)}.

\[[\text{Ir}(3,4\text{Fppy})_2\text{Cl}]_2\]: \text{IrCl}_3 \times \text{H}_2\text{O} (0.9 \text{ g}, 3.18 \text{ mmol}), 2-(3,4-difluorophenyl)pyridine (1.28 \text{ g}, 6.67 \text{ mmol}), \text{ water} (10 \text{ mL}), 2\text{-methoxyethanol} (40 \text{ mL}), \text{yellow powder (yield: 1.1 g, 58.3\%)}.

\[[\text{Ir}(4\text{Fp5Fpy})_2\text{Cl}]_2\]: \text{IrCl}_3 \times \text{H}_2\text{O} (0.74 \text{ g}, 0.25 \text{ mmol}), 5\text{-fluoro2-(4-fluorophenyl)pyridine} (1.0 \text{ g}, 5.23 \text{ mmol}), \text{ water} (5 \text{ mL}), 2\text{-methoxyethanol} (20 \text{ mL}), \text{yellow powder (yield: 0.92 g, 60.5\%)}.

\[[\text{Ir}(3,5\text{Fp5Fpy})_2\text{Cl}]_2\]: \text{IrCl}_3 \times \text{H}_2\text{O} (0.347 \text{ g}, 1.143 \text{ mmol}), 5\text{-fluoro2-(3,5-difluorophenyl)pyridine} (0.5 \text{ g}, 2.39 \text{ mmol}), \text{ water} (5 \text{ mL}), 2\text{-methoxyethanol} (20 \text{ mL}), \text{yellow powder (yield: 0.52 g, 77.3\%)}.

\[[\text{Ir}(\text{ppz})_2\text{Cl}]_2\]: \text{IrCl}_3 \times \text{H}_2\text{O} (2.972 \text{ g}, 9.955 \text{ mmol}), 1\text{-phenyl-1H-pyrazole} (3.0 \text{ g}, 20.81 \text{ mmol}), \text{ water} (10 \text{ mL}), 2\text{-methoxyethanol} (50 \text{ mL}), \text{cream white powder (yield: 4.11 g, 80.3\%)}.
4.9.3 Synthesis of Ir-iTMCs

\[\text{[Ir(4Fppy)\textsubscript{2}(bpy)]\textsubscript{2}[PF\textsubscript{6}]}\]: \[\text{[Ir(4Fppy)\textsubscript{2}Cl]}\textsubscript{2} (0.727 g, 0.635 mmol), 2,2´-bipyridine (0.214 g, 1.366 mmol), ethylene glycol (30 mL), yellow powder (yield: 0.77 g, 72.4%).\]

\(\text{H NMR (DMSO, 400 MHz): } \delta 8.75 (d, J = 8.08 \text{ Hz}, 2 \text{ H}), 8.23 (d, J = 8.08 \text{ Hz}, 2 \text{ H}), 7.88 (\text{comp}, \text{ 4 H}), 7.46 (dd, J = 5.31, 1.77 \text{ Hz}, 2 \text{ H}), 7.56 (d, J = 5.05 \text{ Hz}, 2 \text{ H}), 7.10 (\text{comp}, \text{ 4 H}), 6.64 (t, J = 8.34 \text{ Hz}, 2 \text{ H}), 6.07 (dd, J = 8.34, 6.06 \text{ Hz}, 2 \text{ H}). \)

\(\text{C NMR (DMSO, 100 MHz): } \delta 170.2, 169.3, 166.9, 166.6, 165.8, 153.1, 153.0, 149.7, 149.3, 149.1, 148.8, 148.0, 147.9, 145.4, 140.5, 140.4, 140.3, 139.0, 138.8, 138.5, 131.8, 129.7, 129.3, 124.3, 123.5, 121.1, 120.9, 120.1, 119.9, 117.1, 116.7, 116.5. \)

\[\text{[Ir(4Fppy)\textsubscript{2}(Bphen)]\textsubscript{2}[PF\textsubscript{6}]}\]: \[\text{[Ir(4Fppy)\textsubscript{2}Cl]}\textsubscript{2} (0.727 g, 0.635 mmol), bathophenanthroline (0.454 g, 1.366 mmol), ethylene glycol (30 mL), yellowish green powder (yield: 0.98 g, 75.7%).\]

\(\text{H NMR (DMSO, 400 MHz): } \delta 8.37 (d, J = 5.31 \text{ Hz}, 2 \text{ H}), 8.32 (d, J = 8.34 \text{ Hz}, 2 \text{ H}), 8.24 (s, 2 \text{ H}), 8.11 (dd, J = 8.59, 5.81 \text{ Hz}, 2 \text{ H}), 8.07 (d, J = 5.56 \text{ Hz}, 2 \text{ H}), 7.98 (td, J = 8.08, 1.01 \text{ Hz}, 2 \text{ H}), 7.67 (\text{comp}, 12 \text{ H}), 7.13 (td, J = 7.07, 1.01 \text{ Hz}, 2 \text{ H}), 6.94 (td, J = 8.84, 2.53 \text{ Hz}, 2 \text{ H}), 5.93 (dd, J = 9.60, 2.27 \text{ Hz}, 2 \text{ H}). \)

\(\text{C NMR (DMSO, 100 MHz): } \delta 170.2, 165.7, 164.2, 161.7, 153.3, 150.5, 150.1, 149.3, 146.7, 140.6, 139.1, 135.3, 129.8, 129.7, 129.0, 128.8, 127.5, 126.2, 124.0, 120.2, 117.0, 109.8, 109.5. \)

\[\text{[Ir(4Fppy)\textsubscript{2}(dmbpy)]\textsubscript{2}[PF\textsubscript{6}]}\]: \[\text{[Ir(4Fppy)\textsubscript{2}Cl]}\textsubscript{2} (0.727 g, 0.635 mmol), 4,4´-dimethyl-2,2´-bipyridine (0.251 g, 1.366 mmol), ethylene glycol (30 mL), pale green powder (yield: 0.68 g, 61.8%).\]

\(\text{H NMR (DMSO, 400 MHz): } \delta 8.76 (s, 2 \text{ H}), 8.27 (d, J = 8.08 \text{ Hz}, 2 \text{ H}), 8.03 (dd, J = 8.59, 5.56 \text{ Hz}, 2 \text{ H}), 7.97 (td, J = 8.08, 1.52 \text{ Hz}, 2 \text{ H}), 7.73 (d, J = 5.56 \text{ Hz}, 2 \text{ H}), 7.62 (dd, J = 5.81, 0.76 \text{ Hz}, 2 \text{ H}), 7.53 (dd, J = 5.56, 0.76 \text{ Hz}, 2 \text{ H}), 7.19 (ddd, J = 7.33, 6.06, 1.52 \text{ Hz}, 2 \text{ H}), 6.87 (td, J = 8.84, 2.53 \text{ Hz}, 2 \text{ H}), 5.78 (dd, J = 9.60, 2.53 \text{ Hz}, 2 \text{ H}), 2.55 (s, 6 \text{ H}). \)

\(\text{C NMR (DMSO, 100 MHz): } \delta 165.6, 161.6, 154.9, 153.8, 151.7, 149.2, 148.7, 140.3, 139.0, 129.3, 127.4, 125.6, 123.9, 120.2, 116.8, 109.3, 20.9. \)
[Ir(4Fppy)₂(phen)][PF₆]: [Ir(4Fppy)₂Cl]₂ (0.727 g, 0.635 mmol), 1,10-phenanthroline (0.246 g, 1.366 mmol), ethylene glycol (30 mL), green powder (yield: 0.55 g, 50.2%).¹H NMR (DMSO, 400 MHz): δ 8.92 (dd, J = 8.08, 1.52 Hz, 2 H), 8.41 (s, 2 H), 8.28 (comp, 4 H), 8.08 (comp, 4 H), 7.91 (td, J = 8.08, 1.52 Hz, 2 H), 7.47 (dd, J = 5.81, 0.76 Hz, 2 H), 7.03 (td, J = 7.07, 1.26 Hz, 2 H), 6.93 (td, J = 8.84, 2.53 Hz, 2 H), 5.90 (dd, J = 9.35, 2.53 Hz, 2 H).¹³C NMR (DMSO, 100 MHz): δ 170.2, 165.6, 164.2, 161.6, 152.8, 150.9, 149.1, 145.9, 140.6, 139.0, 131.2, 126.3, 127.2, 123.8, 120.1, 116.9, 109.5.

[Ir(4Fppy)₂(dmBphen)][PF₆]: [Ir(4Fppy)₂Cl]₂ (0.727 g, 0.635 mmol), bathocuproine (0.492 g, 1.366 mmol), ethylene glycol (30 mL), green powder (yield: 0.97 g, 73.3%).¹H NMR (DMSO, 400 MHz): δ 8.31 (d, J = 8.34 Hz, 2 H), 8.06 (s, 2 H), 8.02 (dd, J = 8.59, 5.81 Hz, 2 H), 7.98 (dd, J = 8.34, 1.52 Hz, 2 H), 7.88 (s, 2 H), 7.77 (dd, J = 5.81, 0.76 Hz, 2 H), 7.64 (comp, 10 H), 7.14 (td, J = 7.33, 1.26 Hz, 2 H), 6.82 (td, J = 8.84, 2.53 Hz, 2 H), 5.70 (dd, J = 9.60, 2.53 Hz, 2 H), 2.18 (s, 6 H).¹³C NMR (DMSO, 100 MHz): δ 165.7, 164.0, 163.4, 160.9, 152.6, 150.1, 148.1, 139.9, 139.1, 135.4, 129.7, 129.5, 128.9, 128.2, 127.4, 127.2, 124.7, 123.5, 120.2, 116.6, 116.4, 109.3, 109.1, 27.1.

[Ir(4Fppy)₂(5dmbpy)][PF₆]: [Ir(4Fppy)₂Cl]₂ (0.727 g, 0.635 mmol), 5,5’-dimethyl-2,2’-bipyridine (0.251 g, 1.366 mmol), ethylene glycol (30 mL), green powder (yield: 0.95g, 86.4%).¹H NMR (DMSO, 400 MHz): δ 8.74 (d, J = 8.34 Hz, 2 H), 8.27 (d, J = 8.08 Hz, 2 H), 8.11 (dd, J = 8.34, 1.26 Hz, 2 H), 8.04 (dd, J = 8.59, 5.56 Hz, 2 H), 7.97 (td, J = 8.34, 1.26 Hz, 2 H), 7.63 (comp, 4 H), 7.19 (td, J = 7.07, 1.01 Hz, 2 H), 6.88 (td, 8.84, 2.53 Hz, 2 H), 5.78 (dd, J = 9.60, 2.78 Hz, 2 H), 2.25 (s, 6 H).¹³C NMR (DMSO, 100 MHz): δ 165.6, 164.1, 161.6, 153.5, 152.9, 149.5, 148.9, 140.3, 139.0, 138.7, 127.3, 124.1, 123.9, 120.2, 116.8, 109.6, 18.1.

[Ir(4Fppy)₂(dtb-bpy)][PF₆]: [Ir(4Fppy)₂Cl]₂ (0.727 g, 0.635 mmol), 4,4’-di-tert-butyl-2,2’-bipyridine (0.366 g, 1.366 mmol), ethylene glycol (30 mL), pale green
powder (yield: 0.96 g, 79.6%). \(^{1}\)H NMR (MeCN, 400 MHz): δ 8.53 (d, \(J = 1.77\) Hz, 2 H), 8.05 (dd, \(J = 8.08, 0.76\) Hz, 2 H), 7.90 (d, \(J = 6.32\) Hz, 2 H), 7.88 (comp, 4 H), 7.59 (dq, \(J = 5.81, 0.76\) Hz, 2 H), 7.55 (dd, \(J = 6.06, 2.02\) Hz, 2 H), 7.09 (ddd, \(J = 7.58, 5.81, 1.52\) Hz, 2 H), 6.84 (td, \(J = 8.84, 2.53\) Hz, 2 H), 5.92 (dd, \(J = 9.60, 2.53\) Hz, 2 H), 1.45 (s, 18 H). \(^{13}\)C NMR (MeCN, 100 MHz): δ 166.1, 164.7, 164.1, 162.2, 155.3, 153.7, 149.9, 148.7, 140.2, 138.5, 126.7, 125.2, 123.2, 121.7, 119.7, 109.3, 35.24, 29.18.

\([\text{Ir(3Fppy)}_2(\text{bpy})][\text{PF}_6]\): [Ir(3Fppy)$_2$Cl]$_2$ (0.727 g, 0.635 mmol), 2,2′-bipyridine (0.214 g, 1.366 mmol), ethylene glycol (30 mL), yellow powder (yield: 0.62 g, 58.3%). \(^{1}\)H NMR (DMSO, 400 MHz): δ 8.95 (d, \(J = 8.08\) Hz, 2 H), 8.37 (dd, \(J = 7.83, 6.32\) Hz, 2 H), 8.30 (m, 2 H), 8.00 (m, 2 H), 7.94 (dd, \(J = 8.84, 1.26\) Hz, 2 H), 7.92 (dd, \(J = 8.08, 2.02\) Hz, 2 H), 7.76 (ddd, \(J = 11.12, 5.81, 1.01\) Hz, 2 H), 7.60 (d, \(J = 6.06\) Hz, 2 H), 7.16 (comp, 4 H), 6.68 (t, \(J = 9.09, 8.34\) Hz, 2 H). \(^{13}\)C NMR (DMSO, 100 MHz): δ 169.8, 167.5, 166.3, 155.8, 150.2, 149.8, 148.6, 140.7, 139.0, 129.6, 125.8, 124.0, 121.7, 120.6, 117.0.

\([\text{Ir(3Fppy)}_2(\text{dmbpy})][\text{PF}_6]\): [Ir(3Fppy)$_2$Cl]$_2$ (0.727 g, 0.635 mmol), 4,4′-dimethyl-2,2′-bipyridine (0.251 g, 1.366 mmol), ethylene glycol (30 mL), yellowish green solid (yield: 0.95 g, 86.4%). \(^{1}\)H NMR (DMSO, 400 MHz): δ 8.76 (d, \(J = 1.77\) Hz, 2 H), 8.23 (d, \(J = 7.83\) Hz, 2 H), 7.86 (comp, 4 H), 7.56 (comp, 4 H), 2.55 (s, 6 H). \(^{13}\)C NMR (DMSO, 100 MHz): δ 168.3, 167.5, 165.1, 164.7, 164.5, 163.9, 156.6, 153.2, 153.0, 150.1, 150.0, 149.8, 147.5, 147.3, 146.9, 146.2, 146.0, 145.3, 143.6, 140.1, 136.9, 136.5, 129.9, 127.6, 127.5, 123.9, 123.7, 122.5, 122.3, 121.5, 119.2, 118.1, 114.7, 114.5, 109.7, 18.9.

\([\text{Ir(3Fppy)}_2(\text{5dmbpy})][\text{PF}_6]\): [Ir(3Fppy)$_2$Cl]$_2$ (0.727 g, 0.635 mmol), 5,5′-dimethyl-2,2′-bipyridine (0.251 g, 1.366 mmol), ethylene glycol (30 mL), green powder (yield: 0.86 g, 78.2%). \(^{1}\)H NMR (DMSO, 400 MHz): δ 8.90 (d, \(J = 8.08\) Hz, 2 H), 8.30 (td, \(J = 8.08, 1.52\) Hz, 2 H), 8.28 (d, \(J = 8.34\) Hz, 2 H), 8.05 (dd, \(J = 8.51, 1.52\) Hz, 2 H),
7.98 (dd, J = 8.08, 1.26 Hz, 2 H), 7.94 (dd, J = 5.31, 0.76 Hz, 2 H), 7.72 (dd, J = 7.58, 5.56, 1.01 Hz, 2 H), 7.64 (dd, J = 5.81, 0.76 Hz, 2 H), 7.20 (ddd, J = 7.33, 6.06, 1.26 Hz, 2 H), 6.88 (td, J = 9.09, 2.53 Hz, 2 H), 5.81 (dd, J = 9.60, 2.78 Hz, 2 H), 2.25 (s, 6 H).

$^{13}$C NMR (DMSO, 100 MHz): δ 165.6, 161.6, 155.2, 153.4, 150.0, 148.9, 140.3, 139.9, 139.1, 128.8, 127.5, 125.0, 123.9, 120.2, 116.9, 109.4, 20.5

$[\text{Ir(3Fppy)}_2(\text{dtb-bpy})][\text{PF}_6]$: $[\text{Ir(3Fppy)}_2\text{Cl}]_2$ (0.727 g, 0.635 mmol), 4,4'-'di-tert-buty-2,2'-bipyridine (0.366 g, 1.366 mmol), ethylene glycol (30 mL), yellowish green powder (yield: 6.5 g, 53.9%). $^1$H NMR (DMSO, 400 MHz): δ 8.76 (d, J = 6.32 Hz, 2 H), 8.23 (d, J = 7.83 Hz, 2 H), 7.86 (comp, 4 H), 7.75 (d, J = 5.81 Hz, 2 H), 7.56 (comp, 4 H), 7.11 (d, J = 7.58 Hz, 2 H), 7.08 (dd, J = 6.06, 1.26 Hz, 2 H), 6.62 (t, J = 8.84, 8.34 Hz, 2 H), 1.45 (s, 18 H). $^{13}$C NMR (DMSO, 100 MHz): δ 168.3, 167.5, 165.1, 164.7, 164.5, 163.9, 156.6, 153.2, 153.0, 150.1, 150.0, 149.8, 147.5, 147.3, 146.9, 146.2, 146.0, 145.3, 143.6, 140.1, 136.9, 136.5, 129.9, 127.6, 127.5, 123.9, 123.7, 122.5, 122.3, 121.5, 119.2, 118.1, 114.7, 114.5, 109.7, 35.24, 29.18

$[\text{Ir(3Fppy)}_2(\text{dMeObpy})][\text{PF}_6]$: $[\text{Ir(3Fppy)}_2\text{Cl}]_2$ (0.727 g, 0.635 mmol), 4,4'-dimethoxy-2,2'-bipyridine (0.295 g, 1.366 mmol), ethylene glycol (30 mL), green powder (yield: 0.65, 0.57%). $^1$H NMR (DMSO, 400 MHz): δ 8.49 (d, J = 2.53 Hz, 2 H), 8.23 (d, J = 8.08 Hz, 2 H), 7.90 (dd, J = 8.59, 1.01 Hz, 2 H), 7.85 (dd, J = 7.83, 2.27 Hz, 2 H), 7.68 (d, J = 6.57 Hz, 2 H), 7.63 (d, J = 5.56 Hz, 2 H), 7.33 (dd, J = 6.32, 2.78 Hz, 2 H), 7.11 (comp, 4 H), 6.61 (t, J = 8.84, 8.34 Hz, 2 H), 4.02 (s, 6 H). $^{13}$C NMR (DMSO, 100 MHz): δ 167.4, 165.7, 164.7, 154.7, 148.4, 147.2, 146.2, 136.3, 127.8, 122.1, 121.3, 119.0, 118.0, 114.6, 112.6, 110.0, 54.8

$[\text{Ir(3Fppy)}_2(\text{phen})][\text{PF}_6]$: $[\text{Ir(3Fppy)}_2\text{Cl}]_2$ (0.727 g, 0.635 mmol), 1,10-phenanthroline (0.246 g, 1.366 mmol), ethylene glycol (30 mL), green powder (yield: 0.72 g, 65.7%). $^1$H NMR (MeCN, 400 MHz): δ 8.74 (dd, J = 8.34, 1.26 Hz, 2 H), 8.39 (dd, J = 5.05, 1.26 Hz, 2 H), 8.28 (dd, J = 3.28, 1.52 Hz, 2 H), 8.05 (d, J = 8.34 Hz, 2 H), 7.89 (dd, J = 8.34, 5.05 Hz, 2 H), 7.80 (d, J = 7.83 Hz, 2 H), 7.75 (ddd, J = 8.08, 7.58,
1.52 Hz, 2 H), 7.36 (dd, \( J = 5.31, 0.76 \) Hz, 2 H), 7.18 (ddd, \( J = 15.66, 7.83, 5.31 \) Hz, 2 H), 6.78 (ddd, \( J = 8.84, 5.81, 1.26 \) Hz, 2 H), 6.70 (td, \( J = 8.34, 1.01 \) Hz, 2 H). 13C NMR (MeCN, 100 MHz): \( \delta 167.5, 166.9, 151.5, 150.9, 149.6, 148.1, 146.4, 138.7, 138.0, 131.5, 128.1, 126.8, 124.4, 120.7, 119.7, 119.6. 

[Ir(3Fppy)2(Bphen)][PF6]: [Ir(3Fppy)2Cl]2 (0.727 g, 0.635 mmol), bathophenanthroline (0.454 g, 1.366 mmol), ethylene glycol (30 mL), yellowish orange glass-like solid (yield: 0.65 g, 50.4%). 1H NMR (MeCN, 400 MHz): \( \delta 8.43 (d, J = 5.31, 2 \) H), 8.20 (s, 2 H), 8.19 (d, \( J = 1.26 \) Hz, 2 H), 8.09 (dd, \( J = 8.34, 0.76 \) Hz, 2 H), 7.81 (comp, 6 H), 7.65 (comp, 10 H), 7.54 (ddd, \( J = 6.06, 1.26, 0.76 \) Hz, 2 H), 7.18 (ddd, \( J = 16.42, 7.83, 5.31 \) Hz, 2 H), 6.88 (ddd, \( J = 7.33, 6.06, 1.52 \) Hz, 2 H), 6.71 (td, \( J = 8.34, 1.26 \) Hz, 2 H). 13C NMR (MeCN, 100 MHz): \( \delta 169.9, 167.5, 167.0, 151.0, 150.7, 150.4, 150.0, 149.6, 147.0, 138.5, 138.1, 135.3, 129.4, 128.6, 127.0, 126.0, 124.5, 122.8, 120.7, 119.7, 116.6, 116.3. 

[Ir(3Fppy)2(dmBphen)][PF6]: [Ir(3Fppy)2Cl]2 (0.727 g, 0.635 mmol), bathocuproine (0.492 g, 1.366 mmol), ethylene glycol (30 mL), yellow powder (yield: 0.97 g, 73.3%). 1H NMR (DMSO, 400 MHz): \( \delta 8.23 (d, J = 8.08 \) Hz, 2 H), 8.07 (dd, \( J = 8.84, 5.05 \) Hz, 2 H), 7.91 (comp, 4 H), 7.86 (d, \( J = 5.31 \) Hz, 2 H), 7.83 (d, \( J = 7.58 \) Hz, 2 H), 7.65 (comp, 10 H), 7.04 (comp, 4 H), 6.52 (t, \( J = 8.34 \) Hz), 2.23 (d, \( J = 9.09 \) Hz). 13C NMR (DMSO, 100 MHz): \( \delta 169.3, 168.2, 163.1, 149.3, 149.1, 147.3, 146.6, 137.5, 134.4, 128.8, 128.0, 127.5, 126.5, 123.9, 123.1, 122.3, 120.0, 118.9, 115.5, 115.2, 25.3. 

[Ir(3,4Fppy)2(phen)][PF6]: [Ir(3,4Fppy)2Cl]2 (0.4 g, 0.328 mmol), 1,10-phenanthroline (0.127 g, 0.706 mmol), ethylene glycol (30 mL), pale green powder (yield: 0.31 g, 52.6%). 1H NMR (DMSO, 400 MHz): \( \delta 8.96 (ddd, J = 8.34, 2.53, 1.26 \) Hz, 2 H), 8.43 (dd, \( J = 4.29, 1.26 \) Hz, 2 H), 8.36 (dd, \( J = 5.05, 1.26 \) Hz, 2 H), 8.24 (d, \( J = 8.08 \) Hz, 2 H), 8.08 (dd, \( J = 8.34, 5.05 \) Hz, 2 H), 7.98 (dd, \( J = 8.59, 4.29 \) Hz, 2 H), 7.85 (m, 2 H), 7.37 (dd, \( J = 5.31, 0.76 \) Hz, 2 H), 7.19 (dd, \( J = 10.36, 8.34 \) Hz, 2 H), 6.90 (t, \( J =
7.33 Hz, 2 H). $^{13}$C NMR (DMSO, 100 MHz): δ 170.2, 165.6, 165.4, 165.1, 156.2, 154.0, 151.5, 151.0, 150.7, 150.0, 149.6, 149.1, 145.8, 143.2, 139.5, 139.2, 138.8, 131.8, 131.3, 128.4, 127.5, 124.4, 123.4, 122.3, 120.9, 120.1, 118.2, 114.4, 112.1.

$[\text{Ir}(3,4\text{Fppy})_2(\text{Bphen})][\text{PF}_6]$: $[\text{Ir}(3,4\text{Fppy})_2\text{Cl}]_2$ (0.4 g, 0.328 mmol), bathophenanthroline (0.234 g, 0.706 mmol), ethylene glycol (30 mL), yellowish green powder (yield: 0.47 g, 68.2%). $^1$H NMR (DMSO, 400 MHz): δ 8.44 (d, $J = 5.30$ Hz, 1 H), 8.35 (d, $J = 5.31$ Hz, 1 H), 8.28 (d, $J = 7.83$ Hz, 2 H), 8.25 (d, $J = 4.29$ Hz, 2 H), 8.06 (d, $J = 5.31$ Hz, 2 H), 8.01 (m, 2 H), 7.91 (td, $J = 8.34$, 1.52 Hz, 2 H), 7.70 (td, $J = 7.33$, 1.52 Hz, 5 H), 7.66 (d, $J = 7.83$ Hz, 5 H), 7.55 (d, $J = 5.81$ Hz, 2 H), 7.18 (m, 2 H), 7.01 (ddd, $J = 7.58$, 0.60, 1.26 Hz, 2 H). $^{13}$C NMR (DMSO, 100 MHz): δ 164.0, 163.7, 149.4, 148.8, 148.6, 148.1, 144.8, 141.5, 137.1, 133.4, 130.5, 130.2, 128.1, 127.3, 125.9, 124.5, 122.8, 121.8, 120.5, 118.4, 110.4.

$[\text{Ir}(3,5\text{Fppy})_2(\text{dtb-bpy})][\text{PF}_6]$: Ir(3,5Fppy)$_2$Cl$_2$ (0.5 g, 0.411 mmol), 4,4’-di-tert-butyl-2,2’-bipyridine (0.237 g, 0.884 mmol), ethylene glycol (30 mL), green powder (yield: 0.35 g, 43.1%). $^1$H NMR (DMSO, 400 MHz): δ 8.89 (d, $J = 1.77$ Hz, 2 H), 8.31 (d, $J = 8.08$ Hz, 2 H), 7.93 (td, $J = 8.08$, 1.52 Hz, 2 H), 7.87 (d, $J = 6.06$ Hz, 2 H), 7.85 (d, $J = 2.27$ Hz, 2 H), 7.74 (ddd, $J = 6.06$, 0.20 Hz, 2 H), 7.55 (d, $J = 5.81$, 0.76 Hz, 2 H), 7.14 (ddd, $J = 7.33$, 4.80, 1.26 Hz, 2 H), 6.70 (td, $J = 9.35$, 2.27 Hz, 2 H), 1.41 (s, 18 H). $^{13}$C NMR (DMSO, 100 MHz): δ 161.4, 163.7, 149.4, 148.8, 148.6, 148.1, 144.8, 141.5, 137.1, 133.4, 130.5, 130.2, 128.1, 127.3, 125.9, 124.5, 122.8, 121.8, 120.5, 118.4, 110.4.

$[\text{Ir}(3,5\text{Fppy})_2(\text{Bphen})][\text{PF}_6]$: Ir(3,5Fppy)$_2$Cl$_2$ (0.5 g, 0.411 mmol), bathophenanthroline (0.293 g, 0.884 mmol), ethylene glycol (30 mL), orange powder (yield: 0.56 g, 64.8%). $^1$H NMR (DMSO, 400 MHz): δ 8.43 (d, $J = 5.31$ Hz, 2 H), 8.35 (d, $J = 8.08$ Hz, 2 H), 8.25 (s, 2 H), 8.07 (d, $J = 5.30$ Hz, 2 H), 7.94 (dd, $J = 9.85$, 2.27 Hz, 2 H), 7.91 (d, $J = 8.08$, 1.52 Hz, 2 H), 7.69 (comp, 12 H), 7.57 (d, $J = 5.05$ Hz, 2 H), 7.02 (ddd, $J = 7.58$, 5.81, 1.26 Hz, 2 H), 6.78 (td, $J = 9.60$, 2.27 Hz, 2 H). $^{13}$C NMR
(DMSO, 100 MHz): δ 169.0, 166.5, 165.9, 161.0, 158.7, 150.4, 150.0, 148.3, 146.7, 138.8, 135.2, 129.9, 129.0, 127.7, 126.3, 124.2, 123.2, 122.8, 120.7, 108.5, 105.1.

[Ir(3,5Fppy)₂(phen)][PF₆]: Ir(3,5Fppy)₂Cl₂ (0.5 g, 0.411 mmol), 1,10-phenanthroline (0.159 g, 0.884 mmol), ethylene glycol (30 mL), yellowish green powder (yield: 0.45 g, 60.1%). ¹H NMR (DMSO, 400 MHz): δ 8.95 (dd, J = 8.08, 1.26 Hz, 2 H), 8.42 (s, 2 H), 8.35 (dd, J = 5.31, 1.26 Hz, 2 H), 8.30 (d, J = 8.08 Hz, 2 H), 8.08 (dd, J = 8.08, 5.30 Hz, 2 H), 7.91 (dd, J = 9.85, 2.27 Hz, 2 H), 7.86 (td, J = 8.84, 1.26 Hz, 2 H), 7.39 (d, J = 5.31 Hz, 2 H), 6.92 (ddd, J = 7.33, 6.06, 1.26 Hz, 2 H), 6.75 (td, J = 9.60, 2.02 Hz, 2 H). ¹³C NMR (DMSO, 100 MHz): δ 166.6, 164.3, 163.4, 148.6, 147.5, 145.9, 143.7, 137.2, 136.4, 129.1, 126.2, 125.2, 121.8, 120.4, 118.3, 106.1, 103.0.

[Ir(3,5Fp5Fpy)₂(pbpy)][PF₆]: [Ir(3,5Fp5Fpy)₂Cl₂ (0.627 g, 0.571 mmol), 6-phenyl-2,2'-bipyridine (0.285 g, 1.228 mmol), ethylene glycol (30 mL), green soild (yield: 0.51 g, 47.1%). ¹H NMR (MeCN, 400 MHz): δ 8.63 (dd, J = 8.08, 1.26 Hz, 1 H), 8.27 (t, J = 7.83 Hz, 1 H), 8.22 (td, J = 9.60, 1.52 Hz, 1 H), 7.99 (dd, J = 9.09, 5.31 Hz, 1 H), 7.89 (comp, 4 H), 7.78 (comp, 2 H), 7.56 (t, J = 2.78 Hz, 1 H), 7.51 (ddd, J = 7.83, 5.56, 1.01 Hz, 1 H), 7.48 (dd, J = 7.83, 1.26 Hz, 1 H), 7.42 (dd, J = 9.60, 2.53 Hz, 1 H), 7.09 (td, J = 7.58, 1.01 Hz, 1 H), 7.03 (dd, J = 9.60 2.27 Hz, 1 H), 6.95 (t, J = 7.33 Hz, 2 H), 6.45 (td, J = 9.60, 2.53 Hz, 1 H), 5.98 (td, J = 9.85, 9.60, 2.27 Hz, 1 H). ¹³C NMR (MeCN, 100 MHz): δ 170.3, 165.1, 158.7, 156.7, 156.8, 156.6, 156.2, 150.0, 139.8, 139.7, 139.2, 138.9, 138.2, 137.7, 137.4, 130.4, 128.7, 128.2, 127.6, 127.0, 126.1, 125.9, 125.7, 124.3, 121.2, 120.9, 107.8, 106.7.

[Ir(4Fppy)₂(pbpy)][PF₆]: [Ir(4Fppy)₂Cl₂ (0.727 g, 0.635 mmol), 6-phenyl-2,2'-bipyridine (0.317 g, 1.366 mmol), ethylene glycol (30 mL), yellow powder (yield: 0.86 g, 74.7%). ¹H NMR (MeCN, 400 MHz): δ 8.60 (dd, J = 8.08, 1.26 Hz, 1 H), 8.58 (dt, J = 8.34, 1.01 Hz, 1 H), 8.24 (t, J = 7.83 Hz, 1 H), 8.17 (td, J = 8.34, 1.77 Hz, 1 H), 7.93 (comp, 4 H), 7.87 (comp, 2 H), 7.77 (dq, J = 5.81, 0.76 Hz, 1 H), 7.71 (dd, J = 5.81, 1.77 Hz, 1 H), 7.68 (d, J = 5.56 Hz, 1 H), 7.49 (dd, J = 7.83, 1.26 Hz, 1 H), 7.46 (dd, J =
7.83, 5.56, 1.26 Hz, 1 H), 7.38 (dd, \( J = 8.59 \), 5.81 Hz, 1 H), 7.18 (ddd, \( J = 8.84 \), 6.06, 1.77 Hz, 1 H), 7.08 (dd, \( J = 9.09 \), 5.81 Hz, 1 H), 7.03 (tt, \( J = 7.58 \), 1.26 Hz, 1 H), 6.85 (d, \( J = 5.81 \) Hz, 2 H), 6.73 (td, \( J = 9.09 \), 8.59, 2.53 Hz, 2 H), 6.35 (td, \( J = 9.85 \), 8.59, 2.53 Hz, 1 H), 5.55 (dd, \( J = 9.85 \), 2.53 Hz, 1 H), 5.08 (dd, \( J = 9.85 \), 2.53 Hz, 1 H).

\[ \text{[Ir(4Fp5Fpy)\textsubscript{2}(pbpy)][PF\textsubscript{6}]} : \text{[Ir(4Fp5Fpy)\textsubscript{2}Cl\textsubscript{2}} (0.5 g, 0.41 mmol), 6-phenyl-2,2'-bipyridine (0.205 g, 0.884 mmol), ethylene glycol (30 mL), yellow powder (yield: 0.53 g, 67.8%). \]

\[ \text{\textsuperscript{1}H NMR (MeCN, 400 MHz): } \delta 8.61 (dd, \( J = 8.34 \), 1.26 Hz, 1 H), 8.95 (d, \( J = 8.34 \) Hz, 1 H), 8.27 (t, \( J = 8.08 \), 7.83 Hz, 1 H), 8.18 (td, \( J = 8.08 \), 1.52 Hz, 1 H), 7.95 (t, \( J = 8.84 \) Hz, 1 H), 7.94 (dd, \( J = 9.09 \), 2.02 Hz, 1 H), 7.88 (dq, \( J = 5.56 \), 1.52, 0.76 Hz, 1 H), 7.83 (ddd, \( J = 9.09 \), 7.83, 2.78 Hz, 1 H), 7.74 (ddd, \( J = 9.09 \), 7.58, 2.78 Hz, 1 H), 7.64 (comp, 2 H), 7.50 (ddd, \( J = 9.09 \), 7.83, 1.26 Hz, 2 H), 7.48 (comp, 2 H), 7.31 (dd, \( J = 8.59 \), 5.56 Hz, 1 H), 7.04 (td, \( J = 7.58 \), 1.26 Hz, 1 H), 6.85 (comp, 2 H), 6.74 (td, \( J = 8.84 \), 2.53 Hz, 2 H), 6.36 (td, \( J = 8.59 \), 2.53 Hz, 1 H), 5.62 (dd, \( J = 9.60 \), 2.78 Hz, 1 H), 5.20 (dd, \( J = 9.85 \), 2.53 Hz, 1 H).

\[ \text{\textsuperscript{13}C NMR (MeCN, 100 MHz): } \delta 165.2, 164.1, 162.3, 159.2, 158.5, 156.6, 156.5, 156.0, 152.6, 150.1, 148.1, 139.5, 138.5, 138.3, 137.9, 137.8, 137.6, 137.2, 129.8, 128.7, 127.7, 127.4, 127.3, 126.6, 126.5, 126.4, 126.0, 125.9, 124.9, 123.5, 122.2, 119.8, 119.6, 115.9, 115.7, 109.4, 109.2, 107.8, 107.6. \]

\[ \text{[Ir(3Fppy)\textsubscript{2}(pbpy)][PF\textsubscript{6}]} : \text{[Ir(3Fppy)\textsubscript{2}Cl\textsubscript{2}} (0.727 g, 0.635 mmol), 6-phenyl-2,2'-bipyridine (0.317 g, 1.366 mmol), ethylene glycol (30 mL), yellowish green solid (yield: 0.65 g, 56.5%). \]

\[ \text{\textsuperscript{1}H NMR (MeCN, 400 MHz): } \delta 8.70 (ddd, \( J = 4.80 \), 1.77, 1.01 Hz, 1 H), 8.64 (td, \( J = 7.83 \), 1.01 Hz, 1 H), 8.57 (dd, \( J = 8.34 \), 1.52 Hz, 1 H), 8.56 (dd, \( J = 8.08 \), 1.26 Hz, 2 H), 8.39 (dd, \( J = 7.83 \), 1.26 Hz, 1 H), 8.24 (t, \( J = 2.02 \), 1.52 Hz, 1 H), 8.22 (d, \( J = 1.26 \) Hz, 1 H), 7.96 (d, \( J = 7.83 \), 2 H), 7.93 (dd, \( J = 7.33 \), 1.77 Hz, 1 H), 7.91 (dd, \( J = 7.83 \), 1.26 Hz, 1 H), 7.86 (comp, 2 H), 7.85 (m, 1 H), 7.55 (dd, \( J = 8.08 \), 1.26 Hz, 1 H), 7.38 (dd, \( J = 8.59 \), 5.81 Hz, 1 H), 7.18 (ddd, \( J = 8.84 \), 6.06, 1.77 Hz, 1 H), 7.08 (dd, \( J = 9.09 \), 5.81 Hz, 1 H), 7.03 (tt, \( J = 7.58 \), 1.26 Hz, 1 H), 6.85 (d, \( J = 5.81 \) Hz, 2 H), 6.73 (td, \( J = 9.09 \), 8.59, 2.53 Hz, 2 H), 6.35 (td, \( J = 9.85 \), 8.59, 2.53 Hz, 1 H), 5.55 (dd, \( J = 9.85 \), 2.53 Hz, 1 H), 5.08 (dd, \( J = 9.85 \), 2.53 Hz, 1 H). \]
1.52 Hz, 1 H), 7.42 (dd, \(J = 7.85, 1.01\) Hz, 1 H), 7.41 (ddd, \(J = 7.58, 6.06, 1.52\) Hz, 1 H), 7.01 (dd, \(J = 5.31, 2.53\) Hz, 1 H), 6.95 (m, 1 H), 6.83 (t, \(J = 7.58\) Hz, 2 H), 6.59 (ddd, \(J = 10.36, 5.31, 2.53\) Hz, 1 H), 6.47 (ddd, \(J = 9.85, 8.08, 1.01\) Hz, 1 H), 5.99 (tdd, \(J = 8.08, 2.78, 1.01\) Hz, 1 H).

\(^{13}\)C NMR (MeCN, 100 MHz): \(\delta 168.3, 166.4, 164.7, 158.6, 156.2, 155.6, 155.4, 155.1, 150.3, 149.4, 148.7, 148.3, 147.1, 139.1, 138.6, 137.8, 137.5, 136.5, 129.7, 128.6, 128.2, 127.6, 127.2, 126.6, 126.3, 125.1, 124.2, 123.5, 122.7, 121.8, 120.3, 119.2, 119.0, 118.7.

\([\text{Ir}(p5Fpy)_2(pbpy)]\text{[PF}_6\text{]}\): \([\text{Ir}(p5Fpy)_2\text{Cl}]_2\) (0.5 g, 0.436 mmol), 6-phenyl-2,2´-bipyridine (0.214 g, 0.938 mmol), ethylene glycol (30 mL), orange solid (yield: 0.42 g, 52.7%). \(^1\)H NMR (DMSO, 400 MHz): \(\delta 8.87 (\text{dd, } J = 8.34, 1.26\) Hz, 1 H), 8.83 (d, \(J = 8.34\) Hz, 1 H), 8.37 (t, \(J = 8.08\) Hz, 1 H), 8.24 (td, \(J = 7.58, 1.52\) Hz, 1 H), 8.19 (dd, \(J = 9.35, 5.56\) Hz, 1 H), 8.15 (dd, \(J = 9.35, 5.56\) Hz, 1 H), 8.04 (comp, 2 H), 7.95 (ddd, \(J = 9.09, 7.83, 2.53\) Hz, 1 H), 7.87 (t, \(J = 3.03, 2.78\) Hz, 1 H), 7.73 (dd, \(J = 5.56, 1.01\) Hz, 1 H), 7.68 (dd, \(J = 7.83, 1.26\) Hz, 1 H), 7.60 (dd, \(J = 5.56, 1.01\) Hz, 1 H), 7.59 (dd, \(J = 7.58, 1.01\) Hz, 1 H), 7.43 (t, \(J = 3.03, 2.78\) Hz, 1 H), 7.31 (dd, \(J = 7.83, 0.76\) Hz, 1 H), 6.93 (t, \(J = 7.58, 7.33\) Hz, 1 H), 6.90 (td, \(J = 7.58, 1.01\) Hz, 1 H), 6.81 (td, \(J = 7.58, 7.33, 1.26\) Hz, 1 H), 6.73 (t, \(J = 7.83, 7.58\) Hz, 2 H), 6.62 (d, \(J = 0.51\) Hz, 1 H), 6.53 (td, \(J = 7.58, 1.01, 0.51\) Hz, 1 H), 6.35 (td, \(J = 7.33, 1.01\) Hz, 1 H), 5.87 (dd, \(J = 7.58 1.01\) Hz, 1 H), 5.52 (dd, \(J = 7.33, 0.76\) Hz, 1 H). \(^{13}\)C NMR (DMSO, 100 MHz): \(\delta 1.63.2, 162.6, 161.5, 156.9, 156.2, 154.7, 154.4, 153.7, 153.2, 147.6, 147.2, 143.6, 139.8, 137.8, 137.6, 136.7, 135.8, 135.6, 135.3, 135.1, 128.5, 128.2, 127.6, 126.7, 126.3, 125.8, 125.3, 125.1, 124.5, 124.3, 123.4, 122.8, 122.5, 121.8, 120.5, 119.1, 118.2, 117.0.

\([\text{Ir}(p5Fpy)_2(dtb-bpy)]\text{[PF}_6\text{]}\): \([\text{Ir}(p5Fpy)_2\text{Cl}]_2\) (0.5 g, 0.436 mmol), 4,4´-di-tert-butyl-2,2´-bipyridine (0.248 g, 0.938 mmol), ethylene glycol (30 mL), yellowish orange powder (yield: 51 g, 61.6%). \(^1\)H NMR (MeCN, 400 MHz): \(\delta 8.53 (\text{d, } J = 1.52\) Hz, 2 H), 8.12 (dd, \(J = 9.09, 5.56\) Hz, 2 H), 7.84 (d, \(J = 5.81\) Hz, 2 H), 7.78 (d, \(J = 7.58\) Hz, 2 H), 7.75 (ddd, \(J = 9.09, 7.83, 2.78\) Hz, 2 H), 7.54 (dd, \(J = 5.81, 1.77\) Hz, 2 H), 7.52 (t, \(J =
2.78 Hz, 2 H), 7.08 (td, $J = 7.58, 1.26$ Hz, 2 H), 6.96 (td, $J = 7.58, 1.01$ Hz, 2 H), 6.36 (dd, $J = 7.58, 0.76$ Hz, 2 H) 1.44 (s, 18 H).

$^{13}$C NMR (MeCN, 100 MHz): $\delta$ 164.4, 164.0, 159.2, 156.7, 155.5, 149.8, 149.2, 142.8, 137.2, 136.9, 131.3, 130.0, 126.0, 125.1, 124.6, 122.3, 121.8, 120.6, 35.2, 29.1.

$[\text{Ir} (\text{na5Fpy})_2 (\text{Bphen})][\text{PF}_6]$: $[\text{Ir} (\text{na5Fpy})_2 \text{Cl}_2$ (0.5 g, 0.481 mmol), bathophenanthroline (0.343 g, 1.03 mmol), ethylene glycol (30 mL), orange powder (yield: 0.66 g, 61.5%). $^1$H NMR (DMSO, 400 MHz): $\delta$ 8.80 (dd, $J = 9.35, 5.31$ Hz, 2 H), 8.66 (d, $J = 8.84$ Hz, 2 H), 8.24 (s, 2 H), 8.17 (d, $J = 5.31$ Hz, 2 H), 8.07 (ddd, $J = 9.35, 7.58, 2.78$ Hz, 2 H), 7.97 (d, $J = 5.31$ Hz, 2 H), 7.86 (d, $J = 7.33$ Hz, 2 H), 7.80 (t, $J = 2.78, 2.53$ Hz, 2 H), 7.65 (comp, 12 H), 7.48 (d, $J = 8.59$ Hz, 2 H), 7.45 (t, $J = 7.58$ Hz, 2 H), 6.42 (d, $J = 8.34$ Hz, 2 H). $^{13}$C NMR (DMSO, 100 MHz): $\delta$ 165.0, 158.4, 156.0, 155.0, 151.0, 150.7, 147.4, 139.2, 138.9, 136.7, 135.9, 131.7, 131.2, 130.7, 130.3, 130.1, 130.0, 129.5, 128.1, 127.9, 127.1, 127.0, 126.6, 125.3, 124.1, 121.8.

$[\text{Ir}(3,5Fp5Fpy)_2 (\text{dtb-bpy})][\text{PF}_6]$: $[\text{Ir}(3,5Fp5Fpy)_2 \text{Cl}_2$ (0.538 g, 0.457 mmol), 4,4’-di-tert-butyl-2,2’-bipyridine (0.264 g, 0.984 mmol), ethylene glycol (30 mL), green powder (yield: 0.62 g, 67.3%). $^1$H NMR (MeCN, 400 MHz): $\delta$ 8.53 (d, $J = 1.77$ Hz, 2 H), 8.07 (dd, $J = 9.09, 5.31$ Hz, 2 H), 7.91 (d, $J = 5.81$ Hz, 2 H), 7.75 (ddd, $J = 9.09, 7.58, 2.53$ Hz, 2 H), 7.56 (comp, 4 H), 7.46 (t, $J = 2.53$ Hz, 2 H), 6.60 (td, $J = 9.60, 2.53$ Hz, 2 H), 1.44 (s, 18 H). $^{13}$C NMR (MeCN, 100 MHz): $\delta$ 164.5, 163.0, 155.2, 149.7, 138.1, 137.8, 125.9, 125.7, 125.4, 122.1, 121.3, 107.8, 107.5, 104.4, 104.3, 104.0, 35.1, 28.9.

$[\text{Ir}(4Fppy)_2 (\text{pyimz})][\text{PF}_6]$: $[\text{Ir}(4Fppy)_2 \text{Cl}_2$ (0.727 g, 0.635 mmol), 2-(1H-imidazol-2-yl)pyridine (0.198 g, 1.366 mmol), ethylene glycol (30 mL), pale green powder (yield: 0.40 g, 38.1%). The number of protons and carbons from the $^1$H and $^{13}$C NMR spectra show the presence of two different Ir-iTMCs. The expected complex and another complex from the deprotonation of the hydrogen atom directly bonded to the nitrogen of the imidazole ring of the ancillary ligand. The same results were obtained for $[\text{Ir}(3Fppy)_2(\text{pyimz})][\text{PF}_6]$ complex.
[Ir(4Fppy)$_2$(py3,5mpz)][PF$_6$]: [Ir(4Fppy)$_2$Cl]$_2$ (0.727 g, 0.635 mmol), 2-(3,5-dimethyl-1H-pyrazol-1-yl)pyridine (0.238 g, 1.366 mmol), ethylene glycol (30 mL), pale green powder (yield: 0.66 g, 58.7%). $^1$H NMR (DMSO, 400 MHz): δ 8.28 (dd, $J$ = 7.83, 1.26 Hz, 2 H), 8.24 (dd, $J$ = 7.83, 1.52 Hz, 2 H), 8.02 (comp, 4 H), 7.91 (d, $J$ = 5.31 Hz, 1 H), 7.71 (dd, $J$ = 15.66, 5.05 Hz, 2 H), 7.48 (td, $J$ = 6.32, 1.77 Hz, 1 H), 7.31 (td, $J$ = 7.33, 1.26 Hz, 1 H), 7.23 (td, $J$ = 7.33, 1.26 Hz, 1 H), 7.31 (t, $J$ = 8.59, 2.53 Hz, 1 H), 6.52 (s, 1 H), 5.74 (dd, $J$ = 9.85, 2.53 Hz, 1 H), 5.68 (dd, $J$ = 9.35, 2.53 Hz, 1 H), 2.89 (s, 3 H), 1.66 (s, 3 H). $^{13}$C NMR (DMSO, 100 MHz): δ 163.4, 162.9, 161.7, 159.2, 152.4, 149.9, 149.1, 147.5, 146.7, 146.3, 143.4, 139.3, 138.1, 136.9, 125.2, 124.9, 122.0, 121.4, 118.0, 114.5, 114.1, 112.2, 110.8, 107.5, 106.7, 12.4, 10.5.

[Ir(3Fppy)$_2$(pyimz)][PF$_6$]: [Ir(3Fppy)$_2$Cl]$_2$ (0.727 g, 0.635 mmol), 2-(1H-imidazol-2-yl)pyridine (0.198 g, 1.366 mmol), ethylene glycol (30 mL), pale green powder (yield: 0.40 g, 38.1%). The number of protons and carbons from the $^1$H and $^{13}$C NMR spectra show the presence of two different Ir-iTMCs. The expected complex and another complex from the deprotonation of the hydrogen atom directly bonded to the nitrogen of the imidazole ring of the ancillary ligand. The same results were obtained for [Ir(4Fppy)$_2$(pyimz)][PF$_6$] complex

[Ir(3Fppy)$_2$(py3,5mpz)][PF$_6$]: [Ir(3Fppy)$_2$Cl]$_2$ (0.727 g, 0.635 mmol), 2-(3,5-dimethyl-1H-pyrazol-1-yl)pyridine (0.238 g, 1.366 mmol), ethylene glycol (30 mL), yellowish green solid (yield: 0.55 g, 48.9%). $^1$H NMR (DMSO, 400 MHz): δ 8.34 (d, $J$ = 8.08 Hz, 1 H), 8.24 (comp, 4 H), 8.02 (t, $J$ = 7.33 Hz, 1 H), 7.94 (td, $J$ = 7.83, 2.53 Hz, 2 H), 7.85 (d, $J$ = 7.07 Hz, 2 H), 7.71 (d, $J$ = 6.32 Hz, 1 H), 7.64 (d, $J$ = 6.32 Hz, 1 H), 7.50 (td, $J$ = 6.06, 1.77 Hz, 1 H), 7.25 (m, 2 H), 7.13 (t, $J$ = 7.58 Hz, 1 H), 7.02 (td, $J$ = 7.58, 2.53 Hz, 1 H), 6.60 (t, $J$ = 8.59 Hz, 1 H), 6.54 (m, 1 H), 2.90 (s, 3 H), 1.67 (d, $J$ = 13.14 Hz, 1 H). $^{13}$C NMR (DMSO, 100 MHz): δ 169.5, 169.1, 167.0, 166.4, 165.6, 154.6, 149.7, 149.2, 148.2, 145.9, 141.9,138.9, 138.5, 128.0, 126.7, 124.6, 124.0, 123.4, 121.2, 120.1, 116.9, 116.0, 114.7, 113.4, 14.7, 12.4.
[Ir(3,5Fppy)2(pyimz)][PF6]: [Ir(3,5Fppy)2Cl]2 (0.5 g, 0.411 mmol), 2-(1H-imidazol-2-yl)pyridine (0.128 g, 0.884 mmol), ethylene glycol (30 mL), **yellowish green solid (yield: 0.21 g, 29.6%).** The number of protons and carbons from the 1H and 13C NMR spectra show the presence of two different Ir-iTMCs. The expected complex and another complex from the deprotonation of the hydrogen atom directly bonded to the nitrogen of the imidazole ring of the ancillary ligand. The same results were obtained for [Ir(4Fppy)2(pyimz)][PF6] complex

[Ir(3,4Fppy)2(py3,5mpz)][PF6]: [Ir(3,4Fppy)2Cl]2 (0.4 g, 0.328 mmol), 2-(3,5-dimethyl-1H-pyrazol-1-yl)pyridine (0.123 g, 0.706 mmol), ethylene glycol (30 mL), **pale green solid (yield: 0.39 g, 66.7%).** 1H NMR (DMSO, 400 MHz): δ 8.26 (comp, 4 H), 8.05 (t, J = 8.08 Hz, 1 H), 7.94 (comp, 4 H), 7.84 (dt, J = 5.81, 0.76 Hz, 1 H), 7.76 (dd, J = 6.32, 0.76 Hz, 1 H), 7.64 (dt, J = 5.81, 0.51 Hz, 1 H), 7.50 (ddd, J = 8.34, 7.07, 1.26 Hz, 1 H), 7.16 (comp, 4 H), 6.55 (d, J = 14.40 Hz, 2 H), 2.90 (s, 3 H), 1.68 (dd, J = 17.18, 10.61, 10.36 Hz, 3 H). 13C NMR (DMSO, 100 MHz): δ 164.0, 163.5, 152.8, 147.6, 147.4, 146.6, 144.1, 141.1, 140.1, 136.8, 122.8, 121.6, 121.4, 118.2, 118.0, 112.7, 111.4, 110.2, 109.8, 12.6, 10.7.

[Ir(bzqu)2(py3,5mpz)][PF6]: [Ir(bzqu)2Cl]2 (1.0 g, 0.856 mmol), 2-(3,5-dimethyl-1H-pyrazol-1-yl)pyridine (0.319 g, 1.84 mmol), ethylene glycol (40 mL), **greenish brown solid (yield: 0.65 g, 43.8%).** 1H NMR (DMSO, 400 MHz): δ 8.61 (d, J = 8.08 Hz, 2 H), 8.36 (dd, J = 5.31, 1.01 Hz, 1 H), 8.35 (d, J = 8.59 Hz, 1 H), 8.21 (dd, J = 7.07, 1.52 Hz, 1 H), 8.16 (dd, J = 5.31, 1.01 Hz, 1 H), 7.96 (t, J = 9.09 Hz, 2 H), 7.89 (dd, J = 14.40, 8.84 Hz, 2 H), 7.72 (dd, J = 8.08, 5.31 Hz, 1 H), 7.66 (dd, J = 8.08, 5.31 Hz, 2 H), 7.52 (d, J = 8.08 Hz, 1 H), 7.45 (d, J = 7.83 Hz, 1 H), 7.34 (ddd, J = 8.34, 7.07, 1.01 Hz, 1 H), 7.13 (t, J = 7.83, 7.33 Hz, 1 H), 7.05 (t, J = 7.83, 7.33 Hz, 1 H), 6.46 (s, 1 H), 6.12 (dd, J = 7.33, 2.27 Hz, 2 H), 2.91 (s, 3 H), 1.40 (s, 1 H). 13C NMR (DMSO, 100 MHz): δ 168.8, 155.0, 154.5, 153.3, 148.7, 147.5, 147.4, 147.2, 144.5, 144.1, 143.5, 139.9, 138.7, 136.1, 132.3, 128.1, 127.9, 127.6, 127.2, 125.2, 122.7, 122.5, 121.4, 121.1, 118.9, 118.2, 112.9, 111.5, 13.3, 12.5.
[Ir(bzqu)$_2$(phen)][PF$_6$]: [Ir(bzqu)$_2$Cl]$_2$ (1.0 g, 0.856 mmol), 1,10-phenanthroline (0.331 g, 1.84 mmol), ethylene glycol (40 mL), orange powder (yield: 0.78 g, 53.3%). $^1$H NMR (DMSO, 400 MHz): δ 8.85 (dd, $J = 8.34, 8.08, 1.26$ Hz, 2 H), 8.51 (dd, $J = 8.34, 8.08, 1.01$ Hz, 2 H), 8.39 (s, 2 H), 8.20 (dd, $J = 5.05, 1.52$ Hz, 2 H), 7.97 (d, $J = 8.84$ Hz, 2 H), 7.96 (dd, $J = 5.56, 1.26$ Hz, 2 H), 7.93 (dd, $J = 8.08, 5.05$ Hz, 2 H), 7.87 (d, $J = 8.84$ Hz, 2 H), 7.55 (d, $J = 7.58$ Hz, 2 H), 7.45 (dd, $J = 8.08, 5.56$ Hz, 2 H), 7.20 (t, $J = 7.58$ Hz, 2 H), 6.35 (d, $J = 6.82$ Hz, 2 H). $^{13}$C NMR (DMSO, 100 MHz): δ 154.2, 148.9, 146.6, 144.4, 144.3, 138.22, 136.6, 135.3, 131.5, 128.9, 127.4, 127.2, 126.4, 126.1, 124.8, 124.5, 122.0, 120.5, 118.1.

[Ir(bzqu)$_2$(Bphen)][PF$_6$]: [Ir(bzqu)$_2$Cl]$_2$ (1.0 g, 0.856 mmol), bathophenanthroline (0.661 g, 1.84 mmol), ethylene glycol (40 mL), golden yellow powder (yield: 0.96 g, 54.6%). $^1$H NMR (DMSO, 400 MHz): δ 8.58 (d, $J = 8.34$ Hz, 2 H), 8.29 (d, $J = 5.30$ Hz, 2 H), 8.24 (s, 2 H), 8.13 (dd, $J = 5.56$ Hz, 2 H), 8.00 (d, $J = 8.84$ Hz, 2 H), 7.93 (s, 2 H), 7.91 (d, $J = 4.80$ Hz, 2 H), 7.64 (comp, 10 H), 7.58 (d, $J = 7.83$ Hz, 2 H), 7.56 (dd, $J = 7.83, 5.31$ Hz, 2 H), 7.22 (t, $J = 7.83$ Hz, 2 H), 6.37 (d, $J = 7.07$ Hz, 2 H). $^{13}$C NMR (DMSO, 100 MHz): δ 168.0, 154.2, 148.5, 147.6, 146.7, 145.0, 144.8, 138.1, 135.1, 133.1, 131.5, 127.6, 127.4, 127.2, 126.7, 126.5, 126.2, 125.1, 124.5, 123.9, 121.9, 120.5, 118.1.

[Ir(bzqu)$_2$(dmBphen)][PF$_6$]: [Ir(bzqu)$_2$Cl]$_2$ (1.0 g, 0.856 mmol), bathocuproine (0.663 g, 1.84 mmol), ethylene glycol (40 mL), yellow powder (yield: 1.01 g, 55.9%). $^1$H NMR (DMSO, 400 MHz): δ 8.60 (dd, $J = 8.08, 1.01$ Hz, 2 H), 8.22 (dd, $J = 5.56, 1.26$ Hz, 2 H), 8.08 (s, 2 H), 7.94 (d, $J = 8.84$ Hz, 2 H), 7.90 (d, $J = 8.84$ Hz, 2 H), 7.75 (s, 2 H), 7.63 (comp, 10 H), 7.57 (dd, $J = 8.08, 5.56$ Hz, 2 H), 7.43 (d, $J = 8.08$ Hz, 2 H), 6.96 (t, $J = 7.58$ Hz, 2 H), 5.91 (d, $J = 7.33$ Hz, 2 H), 1.95 (s, 6 H). $^{13}$C NMR (DMSO, 100 MHz): δ 170.2, 164.2, 156.5, 149.9, 149.8, 148.5, 146.0, 139.7, 137.5, 135.5, 133.8, 129.7, 129.5, 129.4, 128.9, 128.0, 127.3, 126.7, 124.6, 124.1, 122.5, 119.7, 27.5.
[Ir(bzqu)$_2$(dtb-bpy)][PF$_6$]: [Ir(bzqu)$_2$Cl]$_2$ (1.0 g, 0.856 mmol), 4,4′-di-tert-butyl-2,2′-bipyridine (0.494 g, 1.84 mmol), ethylene glycol (40 mL), yellowish green powder (yield: 0.78 g, 47.3%). $^1$H NMR (DMSO, 400 MHz): δ 8.90 (d, $J = 1.77$ Hz, 2 H), 8.08 (dd, $J = 5.56$, 1.01 Hz, 2 H), 7.98 (d, $J = 8.84$ Hz, 2 H), 7.76 (d, $J = 5.81$ Hz, 2 H), 7.63 (dd, $J = 8.08$, 5.31 Hz, 2 H), 7.60 (dd, $J = 7.33$, 1.77 Hz, 2 H), 7.54 (d, $J = 7.83$ Hz, 2 H), 7.17 (t, $J = 7.83$, 7.33 Hz, 2 H), 6.23 (d, $J = 7.70$ Hz, 2 H), 5.75 (s, 2 H), 1.39 (s, 18 H). $^{13}$C NMR (DMSO, 100 MHz): δ 163.5, 156.4, 155.5, 150.0, 148.5, 147.8, 140.1, 137.5, 133.7, 129.6, 129.4, 128.3, 126.7, 125.4, 124.1, 122.8, 122.2, 120.1, 35.6, 29.9.

[Ir(ppz)$_2$(pbpy)][PF$_6$]: [Ir(ppz)$_2$Cl]$_2$ (1.0 g, 0.973 mmol), 6-phenyl-2,2′-bipyridine (0.485 g, 2.09 mmol), ethylene glycol (50 mL), green powder (yield: 1.53 g, 92.1%). $^1$H NMR (MeCN, 400 MHz): δ 8.52 (dd, $J = 6.57$, 1.26 Hz, 1 H), 8.50 (dt, $J = 8.34$, 1.01 Hz, 1 H), 8.33 (dd, $J = 3.03$, 0.51 Hz, 1 H), 8.25 (t, $J = 8.08$, 7.83 Hz, 1 H), 8.22 (dd, $J = 2.27$, 1.26 Hz, 1 H), 8.21 (dq, $J = 5.31$, 0.76 Hz, 1 H), 8.16 (ddd, $J = 8.34$, 7.58, 1.52 Hz, 1 H), 7.59 (dd, $J = 7.83$, 1.26 Hz, 1 H), 7.49 (ddd, $J = 7.58$, 5.56, 1.26 Hz, 1 H), 7.36 (dd, $J = 2.27$, 0.79 Hz, 1 H), 7.27 (dd, $J = 7.83$, 1.26 Hz, 1 H), 6.99 (tt, $J = 7.58$, 1.26 Hz, 1 H), 6.95 (dd, $J = 16.42$, 0.76 Hz, 1 H), 6.94 (s, 1 H), 6.82 (t, $J = 7.58$ Hz, 2 H), 6.79 (dd, $J = 7.33$, 1.26 Hz, 1 H), 6.76 (dd, $J = 2.78$, 2.27 Hz, 1 H), 6.57 (ddd, $J = 9.09$, 7.58, 1.52 Hz, 2 H), 6.56 (comp, 2 H), 6.32 (td, $J = 7.58$, 1.26 Hz, 1 H), 5.98 (dd, $J = 7.58$, 1.26 Hz, 1 H), 5.46 (dd, $J = 7.58$, 1.01 Hz, 1 H). $^{13}$C NMR (MeCN, 100 MHz): δ 165.2, 157.6, 157.4, 150.0, 142.3, 142.2, 139.2, 139.1, 138.5, 138.3, 132.4, 132.1, 131.7, 129.0, 128.7, 128.6, 127.5, 127.4, 126.9, 126.8, 126.2, 124.9, 124.5, 122.9, 122.3, 121.0, 111.4, 111.2, 108.0, 107.7.
4.10 References

15. C. D. Sunesh, Y. Choe, Materials Chemistry and Physics, 2015, 156, 206-213.
Chapter 5

Toward blue LECs
Chapter 5

Toward blue LECs

5.1 Introduction

Stable and efficient sky-blue to deep blue LECs remain the biggest challenge in the LEC technology especially toward application in solid state lighting [1]. Blue light is one of the primary colours together with red and green needed for the production of white light. Over the past years, several Ir-iTMCs have been reported with sky-blue to deep blue emissions in solution [2-6]. In some cases, a green shift in the emission wavelength is observed when the previously dissolved blue emitting complexes are used in LECs [7,8]. Deep blue emitting Ir-iTMCs are in particular not easy to obtain due to the large band gap required for such emitters. The LUMO of blue Ir-iTMCs are located closer in energy to the $^3$MC state because of their large band gaps, making the $^3$MC state thermally accessible especially during a LEC device operation. The population of the $^3$MC state is detrimental to the overall performance of LEC devices in at least two ways: 1) the $^3$MC state is known to relax to the ground state via a radiationless pathway thereby causing a drop in the device efficiencies. 2) The strong $\sigma$-antibonding interactions between the nitrogen atoms of the C$^N$ ligands and the iridium atom become even stronger with the population of the $^3$MC state. This will lead to an opening of the complex via breaking of one of the N$_C^N$-Ir bonds causing an overall dramatic drop in device stability [1,9].

Several designs of the C$^N$ and N$^N$ ligands have been pursued over the past years for the syntheses of Ir-iTMCs with blue emission [2,3]. Among the many different structural modification strategies, two general approaches are common to many researchers for obtaining Ir-iTMCs with blue emission. One of which is to decorate the phenyl ring of the C$^N$ ligands with electron withdrawing groups such as –F and –CF3 [7,10] and the other approach is to reduce the size of the nitrogen contain ring from a six to a five membered ring while increase the number of nitrogen atoms in
the ring [11,12] or a combination of both approaches [13,14]. A good number of complexes have been reported with sky-blue to deep blue emission again mostly in solution based on the above mentioned structural modification strategies. Unfortunately, LEC devices fabricated with such complexes demonstrated very poor device performances [2,3]. Bolink et al. recently reported a host guest approach for obtaining a blue LEC device wherein a neutral blue emitting complex FIrpic was doped into an ionic matrix (the host material) [15]. However, the performance of the blue host-guest LEC device was not different from those earlier reported.

Stable and efficient blue LECs remain a major weakness in the LEC technology. Hence there is a need for the development of stable and efficient blue emitting Ir-iTMCs for LEC application.

Results and discussion

5.2 Ir-iTMCs with expected sky blue to deep blue emissions

Three different groups of Ir-iTMCs were synthesized to investigate their performance when used in a LEC device. It has been demonstrated in chapters three and four that a fluorine substituted ortho to the coordinating carbon of the phenyl ring of the C^N ligand partakes in an intra-molecular F-N interaction with the nitrogen of the other C^N ligand. This F-N intra-molecular interaction was also shown to improve the lifetime of LEC devices. To implement this approach with a blue shift the emission wavelength, 3,5 difluorinated phenylpyrazole C^N ligand was used for the synthesis of one group of complexes. The fluorine substituents at the 3-positions are expected to form the F-N intra-molecular interactions to enhance the stability of the Ir-iTMCs. In the following three complexes with 6-phenyl-2,2´-bipyridine (bppy), 4,4´-di-tert-butyl-2,2´-bipyridine (dtb-ppy) and 4,4´-dimethoxy-2,2´-bipyridine as the ancillary ligands were synthesized (figure 5.1).
Figure 5.1: Chemical structures of [Ir(3,5Fppz)₂(pbpy)][PF₆] [Ir(3,5Fppz)₂(dtb-bpy)][PF₆] and [Ir(3,5Fppz)₂(dMeO-bpy)][PF₆].

The next set of complexes are structural modifications from a literature know complex, [Ir(ppy)₂(dppb)][PF₆], (figure 5.2) with bis(diphenylphosphino)benzene (dppb) as the ancillary ligand [16]. In order to improve the photoluminescence quantum yield (PLQY) and also the stability of the complexes by increasing the energy gap between the LUMO and \(^3\)MC state, both the phenyl and pyridine ring of the C^N ligands were substituted with fluorine e.g. in [Ir(4Fp5Fpy)₂(dppb)][PF₆]. Both the HOMO and the LUMO will be stabilized by the electron withdrawing fluorine substituent which is expected to result in an increase of the LUMO-\(^3\)MC
energy gap while maintaining the HOMO-LUMO band gap. The 3,5-difluorinated phenyl ring approach of the C^N ligand was also used to further improve the stability of the Ir-iTMC through the F-N interaction using [Ir(3,5Fp5Fpy)2(dpb)][PF6]. The last synthesized complex with the dpbb ancillary ligand has a methyl substituent on the pyridine ring of the C^N ligands to give a complex with a larger band gap [Ir(4Fp5mpy)2(dpb)][PF6]. The molecular structures of the four bis(diphenylphosphino)benzene based complexes are shown below.

Figure 5.2: Chemical structures of [Ir(ppy)2(dpbb)][PF6] [Ir(4Fp5Fpy)2(dpbb)][PF6], [Ir(3,5Fp5Fpy)2(dpbb)][PF6] and [Ir(4Fp5mpy)2(dpbb)][PF6].
The ancillary ligand bis(diphenylphosphino)propane was used to synthesize the next set of complexes to make the ancillary ligand more flexible. The following four complexes with 2-phenylpyridine (ppy), 2-(4-methylphenyl)pyridine (4mppy), 2-(4-fluorophenyl)pyridine (4Fppy) and phenyl(1-H)pyrazole (ppz) as the C^N ligands were synthesized (figure 5.3).

![Chemical structures of complexes](image)

**Figure 5.3:** Chemical structures of [Ir(ppy)_2(dppp)][PF_6], [Ir(4mppy)_2(dppp)][PF_6], [Ir(4Fppy)_2(dppp)][PF_6] and [Ir(ppz)_2(dppp)][PF_6].
5.3 Photophysical properties

5.3.1 UV-Vis absorption studies.

The absorption spectra of the complexes were measured in acetonitrile solution (1 x 10^{-5} M). The absorption spectra of [Ir(3,5Fppz)_2(pbpy)][PF_6], [Ir(3,5Fppz)_2(dtb-bpy)][PF_6] and [Ir(3,5Fppz)_2(dMeO-bpy)][PF_6] are shown in figure 5.4. The strong absorption bands below 300 nm are assigned to spin-allowed π-π* intra-ligand transitions of both C^N and N^N ligands. The second strong absorption bands between 300-350 nm correspond to spin-allowed metal to ligand charge transfer (1MLCT) transitions while the weak absorption bands from 350 nm extending to the visible region are assigned to spin-orbit-enhanced metal to ligand charge transfer (3MLCT), ligand-to-ligand charge transfer (3LLCT) and ligand centered (3LC) transitions [17,18].

![Absorption spectra](image)

**Figure 5.4**: Absorption spectra of [Ir(3,5Fppz)_2(pbpy)][PF_6], [Ir(3,5Fppz)_2(dtb-bpy)][PF_6] and [Ir(3,5Fppz)_2(dMeO-bpy)][PF_6].

The absorption pattern of the bis(diphenylphosphino)benzene based complexes (figure 5.5) are quite different from those above with all the complexes absorbing
below 400 nm. Only \([\text{Ir}(3,5\text{Fp}5\text{Fpy})_2(\text{dppb})][\text{PF}_6]\) is showing an absorption band below 300 nm which is assigned to the spin allowed \(\pi-\pi^*\) intra-ligand transitions of the \(\text{C}^\text{N}\). The band centered around 300 nm for \([\text{Ir}(\text{ppy})_2(\text{dppb})][\text{PF}_6]\) could be assigned to a mixture of spin-allowed \(\pi-\pi^*\) intra-ligand transition of the \(\text{C}^\text{N}\) and the metal to ligand charge transfer (\(^1\text{MLCT}\)) transitions. While the bands between 300 and 350 nm for \([\text{Ir}(3,5\text{Fp}5\text{Fpy})_2(\text{dppb})][\text{PF}_6]\), \([\text{Ir}(4\text{Fp}5\text{Fpy})_2(\text{dppb})][\text{PF}_6]\) and \([\text{Ir}(3,5\text{Fp}5\text{mpy})_2(\text{dppb})][\text{PF}_6]\) correspond to the spin allowed metal to ligand charge transfer (\(^1\text{MLCT}\)) transitions. All the complexes show absorption in the 350 to 400 nm region which is assigned to the metal to ligand charge transfer (\(^3\text{MLCT}\)), ligand-to-ligand charge transfer (\(^3\text{LLCT}\)) and ligand centered (\(^3\text{LC}\)) transitions [17,18].

Figure 5.5: Absorption spectra of \([\text{Ir}(\text{ppy})_2(\text{dppb})][\text{PF}_6]\), \([\text{Ir}(3,5\text{Fp}5\text{Fpy})_2(\text{dppb})][\text{PF}_6]\), \([\text{Ir}(4\text{Fp}5\text{Fpy})_2(\text{dppb})][\text{PF}_6]\) and \([\text{Ir}(3,5\text{Fp}5\text{mpy})_2(\text{dppb})][\text{PF}_6]\).

The absorption spectra of \([\text{Ir}(\text{4mppy})_2(\text{dppp})][\text{PF}_6]\), \([\text{Ir}(\text{ppy})_2(\text{dppp})][\text{PF}_6]\), \([\text{Ir}(4\text{Fppy})_2(\text{dppp})][\text{PF}_6]\) and \([\text{Ir}(\text{ppz})_2(\text{dppp})][\text{PF}_6]\) (figure 5.6) based on bis(diphenylphosphino)propane as the ancillary ligand show strong spin allowed \(\pi-\pi^*\) intra-ligand transitions of \(\text{C}^\text{N}\) absorption below 300 nm. All the complexes show
absorption in the 300 to 400 nm region which are assigned to the same transitions as those for the bis(diphenylphosphino)benzene complexes except for [Ir(ppz)₂(dppe)]PF₆ which interestingly does not show any of the charge forbidden transitions above 350 nm.

![Absorption spectra](image)

**Figure 5.6:** Absorption spectra of [Ir(4mppy)₂(dppp)]PF₆, [Ir(ppy)₂(dppp)]PF₆, [Ir(4Fppy)₂(dppp)]PF₆ and [Ir(ppz)₂(dppp)]PF₆.

### 5.3.2 Photoluminescence studies

The emission maxima of the complexes in the powder form under photoexcitation are summarized in table 5.1. [Ir(3,5Fppz)₂(pbpy)]PF₆ shows a red shift in the emission spectrum compared to [Ir(3,5Fppz)₂(dtb-bpy)]PF₆ and [Ir(3,5Fppz)₂(dMeO-bpy)]PF₆ despite their similar absorption spectra. The observed red shift for [Ir(3,5Fppz)₂(pbpy)]PF₆ is due to a low lying energy level of the LUMO based on the pbpy N^N ligand when compared to the other two complexes with electron donating dtb- and MeO- groups substituted on their ancillary (N^N) ligands. In addition, pbpy is known for forming an intramolecular π-
Stacking which will result in a denser molecular packing as opposed to the other complexes with bulky dtb and MeO side groups. Two emission maxima are seen from the $\text{[Ir(3,5Fppz)₂(dtb-bpy)]\[PF₆]}$ spectrum.

Figure 5.7: Photoluminescence spectra of $\text{[Ir(3,5Fppz)₂(pbpy)]\[PF₆]}$, $\text{[Ir(3,5Fppz)₂(dtb-bpy)]\[PF₆]}$ and $\text{[Ir(3,5Fppz)₂(dMeO-bpy)]\[PF₆]}$.

The emission spectra of the complexes based on the bis(diphenylphosphino)benzene ancillary ligand show three different types of structured bands which are related to the modification of the frontier MO by the different substituents. The complex $\text{[Ir(ppy)₂(dpbpb)]\[PF₆]}$ with no substituted C^N ligand is showing two peaks on the emission spectrum: an emission maximum at 487 nm, a side band at 513 nm and a shoulder in the emission spectrum at 560 nm. The maximum emission is understood to be the C^N ligand centered emission since the soft ancillary ligand which has contribution to the frontier MO will cause a large octahedral splitting of the Ir-d orbitals. When fluorine was substituted on the 4 and 5 positions of the phenyl and pyridine rings of the C^N ligands to improve the stability of the complex ($\text{[Ir(4Fp5Fpy)₂(dpbpb)]\[PF₆]}$) as explained in section 5.21 above, a similar emission spectrum was obtained. The differences are the 6 nm shift.
of emission maximum and the more intense emission arising from the side band at 513 nm for the fluorinated complex. While complex [Ir(3,5Fp5Fpy)₂(dppb)][PF₆] with two fluorinated phenyl C^N ligands has an emission spectrum similar to the other two complexes but with a new side band at 466 nm in the deep blue region. Interestingly, when the substituent on the 5 position of the pyridine-ring of [Ir(4Fp5Fpy)₂(dppb)][PF₆] was changed from a fluorine to a methyl group [Ir(4Fp5mpy)₂(dppb)][PF₆], the emission maximum of the complex was shifted to the green region at 528 nm. This is contrary to expectation: the LUMO is lying on the pyridine ring of the C^N ligand, while adding electron donating substituents to this part of the ligand should cause a destabilization of the LUMO resulting to a blue shift in the emission. Hence it is believed that a different ³MC alters the emission as suggested in the next subsection.

**Figure 5.8:** Photoluminescence spectra of [Ir(ppy)₂(dppb)][PF₆], [Ir(3,5Fp5Fpy)₂(dppb)][PF₆], [Ir(4Fp5Fpy)₂(dppb)][PF₆] and [Ir(3,5Fp5mpy)₂(dppb)][PF₆], excited at 360 nm.
Table 5.1: Photoluminescence data for all complexes excited at 360 nm.

<table>
<thead>
<tr>
<th>Complex</th>
<th>PL$_{\text{max}}$ [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ir(3,5Fppz)$_2$(pbpy)][PF$_6$]</td>
<td>566</td>
</tr>
<tr>
<td>[Ir(3,5Fppz)$_2$(dtb-bpy)][PF$_6$]</td>
<td>499, 525</td>
</tr>
<tr>
<td>[Ir(3,5Fppz)$_2$(dMeO-bpy)][PF$_6$]</td>
<td>519</td>
</tr>
<tr>
<td>[Ir(ppy)$_2$(dppb)][PF$_6$]</td>
<td>487, 513</td>
</tr>
<tr>
<td>[Ir(3,5Fp5Fpy)$_2$(dppb)][PF$_6$]</td>
<td>466, 498, 527</td>
</tr>
<tr>
<td>[Ir(4Fp5Fpy)$_2$(dppb)][PF$_6$]</td>
<td>493, 513</td>
</tr>
<tr>
<td>[Ir(4Fp5mpy)$_2$(dppb)][PF$_6$]</td>
<td>460, 491, 528</td>
</tr>
<tr>
<td>[Ir(4mppy)$_2$(dppp)][PF$_6$]</td>
<td>468, 498, 526</td>
</tr>
<tr>
<td>[Ir(ppy)$_2$(dppp)][PF$_6$]</td>
<td>460, 493, 517</td>
</tr>
<tr>
<td>[Ir(4Fppy)$_2$(dppp)][PF$_6$]</td>
<td>455, 487, 518</td>
</tr>
<tr>
<td>[Ir(ppz)$_2$(dppp)][PF$_6$]</td>
<td>428, 531</td>
</tr>
</tbody>
</table>

Figure 5.9: Photoluminescence spectra of [Ir(4mppy)$_2$(dppp)][PF$_6$], [Ir(ppy)$_2$(dppp)][PF$_6$], [Ir(4Fppy)$_2$(dppp)][PF$_6$] and [Ir(ppz)$_2$(dppp)][PF$_6$], excited at 360 nm.

The features of the emission spectra of three of the bis(diphenylphosphino)propane complexes are similar showing side bands below 475 nm and emission maxima
around 493 nm (figure 5.9). The small blue shift in the emission maximum from [Ir(4mppy)$_2$(dppp)][PF$_6$] to [Ir(ppy)$_2$(dppp)][PF$_6$] and finally to [Ir(4Fppy)$_2$(dppp)][PF$_6$] is expected with the different ligand substitutions made. Upon adding a methyl group to the phenyl C^N ligand (from ppy to 4mppy) the HOMO is destabilized resulting in a green shift of the emission maximum. On the other hand, adding a fluorine atom instead of a methyl group (from ppy to 4Fppy) is expected to stabilize the HOMO leading to the observed blue shift in the emission maximum. The fourth bis(diphenylphosphino)propane complex with a ppz C^N ligand shows a broad emission spectrum with a maximum at 531 nm. The green shifted emission and the broad nature of the emission spectrum observed for this complex is not fully understood taken into consideration that ppz is a more strong-field ligand compared to ppy.

5.3.3 Understanding the colour shift in the emission spectra of the bis(diphenylphosphino)benzene complexes

In general, the LUMO of blue emitting Ir-iTMCs are closer in energy to the triplet metal centered excited state ($^3$MC) compared to Ir-iTMCs showing green emissions. The relationship between the obtained emission spectra and the energy levels of the HOMO, LUMO and $^3$MC states of the bis(diphenylphosphino)benzene complexes is presented in figure 5.10 below.

![Figure 5.10](image)

Figure 5.10: Suggested changes in the energy level of the HOMO, LUMO and $^3$MC state due to substituent effect on the bis(diphenylphosphino)benzene complexes.
The band gap of \([\text{Ir}(ppy)_2(dpb)]\)[PF_6] and \([\text{Ir}(4Fp5Fpy)_2(dpdb)]\)[PF_6] are expected to be similar since fluorination of the phenyl and pyridine ring should result in a stabilization of both the HOMO and the LUMO. This assumption is supported by an almost same emission maximum of both complexes with a difference of only 6 nm. An increase in the band gap is expected by introducing one more electron-withdrawing fluorine in \([\text{Ir}(3,5Fp5Fpy)_2(dpdb)]\)[PF_6] which is approved by a blue shifted emission of 21 nm compared to the non-substituted complex. A similar or further increase in the band gap for \([\text{Ir}(4Fp5mpy)_2(dpdb)]\)[PF_6] is expected since the HOMO and LUMO are stabilized and destabilized by the fluorine and methyl substituents, respectively. Even if the complex shows emission with side bands in the blue region, the emission maximum is at 528 nm. This could be explained as a too much destabilization of the LUMO resulting in a \(3\text{MC}\) state lying slightly below the LUMO as shown in figure 5.10. It has been reported that fluorinated Ir-iTMCs show high photoluminescence quantum yield (PLQY). Hence, if the above proposed influence of the structural modification of bis(diphenylphosphino)benzene containing complexes is close to being correct, the PLQY of the complexes would be expected to be in the order \([\text{Ir}(3,5Fp5Fpy)_2(dpdb)]\)[PF_6] > \([\text{Ir}(4Fp5Fpy)_2(dpdb)]\)[PF_6] > \([\text{Ir}(ppy)_2(dpdb)]\)[PF_6] > \([\text{Ir}(4Fp5mpy)_2(dpdb)]\)[PF_6]. The order for the two last complexes are expected in this way, because, even if \([\text{Ir}(4Fp5mpy)_2(dpdb)]\)[PF_6] is a fluorinated complex, the PLQY is expected to be the lowest since the \(3\text{MC}\) state of this complex is lying slightly below the LUMO.

5.3.4 PLQY and phosphorescence lifetime studies of the bis(diphenylphosphino)benzene complexes

The PLQY and phosphorescence lifetime of the bis(diphenylphosphino)benzene complexes were measured on powder samples. The results are summarized in table 5.2. Interestingly, the PLQY are in the order as predicted above with a dramatic drop in the PLQY from 86% to 10% for \([\text{Ir}(4Fp5Fpy)_2(dpdb)]\)[PF_6] and \([\text{Ir}(4Fp5mpy)_2(dpdb)]\)[PF_6] respectively. On the other hand the phosphorescence
lifetimes of the complexes are unbelievably long in the range of 50 to 140 µs (figure 5.11). The very long phosphorescence lifetime of the complexes could be an indication that they are not suitable for LEC application as it will lead to population of the excited state during device operation.

**Table 5.2:** PLQY and phosphorescence lifetime ($\tau$ [µs]) of the bis(diphenylphosphino)benzene complexes with excitation at 360 nm.

<table>
<thead>
<tr>
<th>Complex</th>
<th>PLQY ($\Phi_p$) [%]</th>
<th>$\tau$ [µs]</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ir(ppy)$_2$(dppb)]$\text{[PF}_6\text{]}$</td>
<td>28</td>
<td>56</td>
</tr>
<tr>
<td>[Ir(3,5Fp5Fpy)$_2$(dppb)]$\text{[PF}_6\text{]}$</td>
<td>90</td>
<td>137</td>
</tr>
<tr>
<td>[Ir(4Fp5Fpy)$_2$(dppb)]$\text{[PF}_6\text{]}$</td>
<td>86</td>
<td>120</td>
</tr>
<tr>
<td>[Ir(4Fp5mpy)$_2$(dppb)]$\text{[PF}_6\text{]}$</td>
<td>10</td>
<td>51</td>
</tr>
</tbody>
</table>

**Figure 5.11:** Excited state decay (phosphorescence lifetime) of [Ir(ppy)$_2$(dppb)]$\text{[PF}_6\text{]}$, [Ir(3,5Fp5Fpy)$_2$(dppb)]$\text{[PF}_6\text{]}$, [Ir(4Fp5Fpy)$_2$(dppb)]$\text{[PF}_6\text{]}$ and [Ir(4Fp5mpy)$_2$(dppb)]$\text{[PF}_6\text{]}$. 
5.4 Electrochemical properties

The transport of electrons and holes in Ir-iTMC based LEC devices can be treated as a consecutive reduction and oxidation of the Ir-iTMC used in the emissive layer. Hence the electrochemical properties of the Ir-iTMCs play an important role on the performances of LEC devices. The electrochemical properties of the complexes were studied in an acetonitrile solution using tetraethylammonium hexafluorophosphate as the electrolyte by cyclic voltammetry (CV). The results of the CV measurements are summarized in table 5.3.

5.4.1 Phenylpyrazole (ppz) based Ir-iTMCs

The cyclic voltammograms of [Ir(3,5Fppz)2(pbpy)][PF₆], [Ir(3,5Fppz)2(dtb-bpy)][PF₆] and [Ir(3,5Fppz)2(dMeO-bpy)][PF₆] show both quasi-reversible oxidation and reduction potentials figure 5.12. Despite the fact that the C^N ligands of the complexes are the same, the oxidation half potentials (E_{1/2ox}) of the complexes vary significantly. The E_{1/2ox} of [Ir(3,5Fppz)2(pbpy)][PF₆] is 1.47V, a cathodic shift of the E_{1/2ox} by 270 and 60 mV to 1.20 and 1.41 V are observed on moving to [Ir(3,5Fppz)2(dtb-bpy)][PF₆] and [Ir(3,5Fppz)2(dMeO-bpy)][PF₆], respectively. A similar, but opposite, trend is seen for the reduction half potentials (E_{1/2red}) with the E_{1/2red} of -1.52, -1.84 and -1.71 V for [Ir(3,5Fppz)2(pbpy)][PF₆], [Ir(3,5Fppz)2(dtb-bpy)][PF₆] and [Ir(3,5Fppz)2(dMeO-bpy)][PF₆], respectively. In general, the E_{1/2ox} for complexes are expected to be very similar since they all have the same C^N ligands, while the E_{1/2red} should be different because the N^N ligands are different with the order bppy < dtb-ppy < dMeO-ppy. The obtained results imply that the N^N ligands also have an influence on the HOMO level of the complexes. These results are contradicting to the general understanding that the HOMO and LUMO of Ir-iTMCs can be tuned independently because they are lying mainly on the C^N and N^N ligands, respectively. Interestingly, the reduction-oxidation (redox) potential difference (ΔE_{redox}) of the complexes are 2.99, 3.04 and 3.12 V for
[Ir(3,5Fppz)₂(pbpy)][PF₆], [Ir(3,5Fppz)₂(dtb-bpy)][PF₆] and [Ir(3,5Fppz)₂(dMeO-bpy)][PF₆] which happens to follow the order bppy < dtb-ppy < dMeO-ppy. It can be concluded that the change in the $\Delta E_{\text{redox}}$ correspond to the structural modifications made to the Ir-iTMCs.

**Figure 5.12**: Cyclic voltammogram for the phenylpyrazole based complexes.

**Figure 5.13**: Cyclic voltammogram for the bis(diphenylphosphino)benzene based complexes.
**Table 5.3:** Summary of the electrochemical data.

<table>
<thead>
<tr>
<th></th>
<th>$E_{1/2\text{red}}$ [V]</th>
<th>$E_{1/2\text{ox}}$ [V]</th>
<th>LUMO [eV]</th>
<th>HOMO [eV]</th>
<th>Energy gap [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ir(3,5Fppz)$_2$(pbpy)][PF$_6$]</td>
<td>-1.52</td>
<td>1.47</td>
<td>-3.28</td>
<td>-6.27</td>
<td>2.99</td>
</tr>
<tr>
<td>[Ir(3,5Fppz)$_2$(dtb-bpy)][PF$_6$]</td>
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<td>1.2</td>
<td>-2.96</td>
<td>-6.00</td>
<td>3.04</td>
</tr>
<tr>
<td>[Ir(3,5Fppz)$_2$(dMeO-bpy)][PF$_6$]</td>
<td>-1.71</td>
<td>1.41</td>
<td>-3.09</td>
<td>-6.21</td>
<td>3.12</td>
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<tr>
<td>[Ir(ppy)$_2$(dppb)][PF$_6$]</td>
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<td>1.4</td>
<td>-2.7</td>
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<tr>
<td>[Ir(4Fp5Fpy)$_2$(dppb)][PF$_6$]</td>
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<td>1.65</td>
<td>-2.9</td>
<td>-6.45</td>
<td>3.53</td>
</tr>
<tr>
<td>[Ir(4Fp5mpy)$_2$(dppb)][PF$_6$]</td>
<td>-2.17</td>
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</tr>
<tr>
<td>[Ir(4mppy)$_2$(dppp)][PF$_6$]</td>
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<td>-2.69</td>
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<td>3.48</td>
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<tr>
<td>[Ir(ppy)$_2$(dppp)][PF$_6$]</td>
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<td>1.28</td>
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<tr>
<td>[Ir(ppz)$_2$(dppp)][PF$_6$]</td>
<td>-2.03</td>
<td>1.73</td>
<td>-2.77</td>
<td>-6.53</td>
<td>3.76</td>
</tr>
</tbody>
</table>

5.4.2 **Bis(diphenylphosphino)benzene (dppb) based complexes**

Bis(diphenylphosphino)benzene complexes have the same ancillary ligand that do not contribute to the frontier MO, and C^N ligands with different substituents to influence the emission of the complexes. The complexes show an irreversibale reduction and oxidation potentials except for the quasi-reversible reduction potential for [Ir(ppy)$_2$(dppb)][PF$_6$] (figure 5.13). The $E_{1/2\text{red}}$ and $E_{1/2\text{ox}}$ are -2.10, -1.88, -2.17 and 1.40, 1.65, 1.56 V for [Ir(ppy)$_2$(dppb)][PF$_6$], [Ir(4Fp5Fpy)$_2$(dppb)][PF$_6$] and [Ir(4Fp5mpy)$_2$(dppb)][PF$_6$], respectively. As expected, both the HOMO and LUMO of [Ir(4Fp5Fpy)$_2$(dppb)][PF$_6$] are almost equally stabilized by 250 and 220 mV upon adding a fluorine substituent to the phenyl and pyridine rings of the C^N ligands, respectively, compared to [Ir(ppy)$_2$(dppb)][PF$_6$]. While the HOMO is stabilized by 160 mV and the LUMO destabilized by 60 mV on moving from [Ir(ppy)$_2$(dppb)][PF$_6$] to
[Ir(4Fp5mpy)$_2$(dppb)][PF$_6$]. The stabilization of the HOMO and destabilization of the LUMO is due to the fluorine and methyl substituents on the phenyl and pyridine ring of the C$^\wedge$N ligands of [Ir(4Fp5mpy)$_2$(dppb)][PF$_6$], respectively.

Figure 5.14: Cyclic voltammogram for the bis(diphenylphosphino)propane based complexes.

5.4.3 Bis(diphenylphosphino)propane (dppp) based complexes

Irreversible reduction and oxidation potentials were observed for the bis(diphenylphosphino)propane complexes and the cyclic voltammogram of [Ir(4mppy)$_2$(dppp)][PF$_6$] to [Ir(ppy)$_2$(dppp)][PF$_6$] as shown in figure 5.14. The increase in $\Delta E_{\text{redox}}$ together with the stabilization of the frontier MO in order from the ppy complex ([Ir(ppy)$_2$(dppp)][PF$_6$]) to the electron rich ppz complex ([Ir(ppz)$_2$(dppe)][PF$_6$]) has to be pointed out, as can be seen on table 5.3. The peaks observed around 0.4 V on the backward anodic scan suggest that under the conditions of the electrochemical experiments, the species form upon oxidation of [Ir(4mppy)$_2$(dppp)][PF$_6$] and [Ir(ppy)$_2$(dppp)][PF$_6$] are more stable [19].
5.5 Electroluminescence studies

LEC devices were fabricated using all the complexes to investigate their electroluminescence properties. In general, all the LEC devices demonstrated poor performances. The complexes with bis(diphenylphosphino)propane containing complexes emitted no light when used in LEC devices. Also the very poor performances of the some bis(diphenylphosphino)benzene complexes in LEC devices are contrary to the high PLQY of the complexes. However, the extremely long phosphorescence lifetime of these complexes could be the reason for their poor LEC device performances. Such long a phosphorescence lifetime will lead to overpopulation of the LUMO making the thermal population of the anti-bonding triplet metal centered ($^3MC$) state more likely to occur during device operation. Electrons in the $^3MC$ state are known to relax to the ground state via vibrational, radiationless processes causing a significant drop in the luminance of the device. Also, the $^3MC$ state is involved in $\sigma$-antibonding interactions with the $N_{C^\beta N}$ and its population during device operation will increase the strength of the $\sigma$-antibonding interaction which will eventually lead to the breaking of one of the Ir-NC$^\beta$N bonds causing an instant quenching of the electroluminescence property of the Ir-iTMC. Changing from bis(diphenylphosphino)benzene to bis(diphenylphosphino)propane ligand in Ir-iTMCs completely quenches the electroluminescence.

LEC devices based on $[\text{Ir}(3,5\text{Fppz})_2(\text{pbpy})][\text{PF}_6]$, $[\text{Ir}(3,5\text{Fppz})_2(\text{dtb-bpy})][\text{PF}_6]$ and $[\text{Ir}(3,5\text{Fppz})_2(\text{dMeO-bpy})][\text{PF}_6]$ show bluish green to whitish electroluminescence as shown in figure 5.15 with their device performances summarized in table 5.4.
Figure 5.15 LEC devices of [Ir(3,5Fppz)₂(pbpy)][PF₆], [Ir(3,5Fppz)₂(dtb-bpy)][PF₆] and [Ir(3,5Fppz)₂(dMeO-bpy)][PF₆] under operation showing bluish green to whitish electroluminescence.

Table 5.4: Summary of LEC device data for [Ir(3,5Fppz)₂(pbpy)][PF₆], [Ir(3,5Fppz)₂(dtb-bpy)][PF₆] and [Ir(3,5Fppz)₂(dMeO-bpy)][PF₆].

<table>
<thead>
<tr>
<th></th>
<th>Lum_{max} (cd/m²)</th>
<th>t₁/₂ (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ir(3,5Fppz)₂(pbpy)][PF₆]</td>
<td>150</td>
<td>&lt; 10</td>
</tr>
<tr>
<td>[Ir(3,5Fppz)₂(dtb-bpy)][PF₆]</td>
<td>431</td>
<td>&lt; 5</td>
</tr>
<tr>
<td>[Ir(3,5Fppz)₂(dMeO-bpy)][PF₆]</td>
<td>294</td>
<td>&lt; 5</td>
</tr>
</tbody>
</table>

5.6 Conclusion

Greenish blue to blue emitting Ir-iTMCs with general formula [Ir(C^N)₂(L^L)][PF₆] were synthesized. Despite the structural modifications made including the introduction of the F-N intra-molecular interactions to improve the stability of the Ir-iTMCs and the high PLQY observed for some complexes, all the complexes demonstrated poor LEC device performances which, again, are confirming the worse performance of phosphorescent blue emitting Ir-iTMCs used in LEC devices. The primary cause for this and other poor reported blue LEC device performances is expected to be the thermal population of the 3MC state during device operation since its location is close to the LUMO of the large band gap blue emitting Ir-iTMCs. The excited state (phosphorescence) lifetime measurements were done on a PTI (photon Technology International) spectrofluorometer.
5.7 Experimental

5.7.1 Synthesis and characterizations

The synthetic procedures for obtaining the diiridium intermediate complexes and the heteroleptic Ir-iTMCs are the same as described in the experimental section of chapter three together with the characterization techniques for the Ir-iTMCs and the device fabrication method.

5.7.2 Synthesis of diiridium intermediate complexes not described earlier

\[
\text{[Ir(3,5Fppz)Cl}_2\text{]}_2: \text{IrCl}_3 \times \text{H}_2\text{O (2.07 g, 6.95 mmol), 2-(3,5-difluorophenyl)pyrazole (2.6 g, 14.5 mmol), water (25 mL), 2-methoxyethanol (80 mL), cream white powder (yield 3.91 g, 96.1%).}
\]

\[
\text{[Ir(ppy)Cl}_2\text{]}_2: \text{IrCl}_3 \times \text{H}_2\text{O (8.0 g, 26.7 mmol), 2-phenylpyridine (8.0 mL, 55.8 mmol), water (40 mL), 2-methoxyethanol (200 mL), yellow powder (yield 11.6 g, 80.7%).}
\]

\[
\text{[Ir(4Fp5mpy)Cl}_2\text{]}_2: \text{IrCl}_3 \times \text{H}_2\text{O (2.94 g, 10.0 mmol), 2-(4-fluorophenyl)-5-methylpyridine (3.92 g, 20.95 mmol), water (25 mL), 2-methoxyethanol (80 mL), yellow powder (yield 4.9 g, 81.6%).}
\]

\[
\text{[Ir(4mppy)Cl}_2\text{]}_2: \text{IrCl}_3 \times \text{H}_2\text{O (5.0 g, 6.8 mmol), 2-(3,5-difluorophenyl)pyridine (6.1 mL, 14.21 mmol), water (25 mL), 2-methoxyethanol (80 mL), yellow powder (yield 3.25 g, 85.5%).}
\]

5.7.3 Synthesis of Ir-iTMCs

\[
\text{[Ir(3,5Fppz)(pbpy)][PF}_6\text{]}: \text{[Ir(3,5Fppz)Cl}_2\text{]}_2 (0.8 g, 0.683 mmol), 6-phenyl-2,2´-bipyridine (0.341 g, 1.4 mmol), ethyl glycol (40 mL) orange solid (yield: 0.69 g, 54.4%).}^{1}\text{H NMR (MeCN, 400 MHz), } \delta 8.49 \text{(dd, } J = 8.08, 1.01 \text{ Hz, 2 H), 8.32 (dd, } J = 7.58, 1.01 \text{ Hz, 1 H), 8.21 (dd, } J = 7.58, 3.03 \text{ Hz, 1 H), 8.18 (dd, } J = 8.59, 2.27 \text{ Hz, 2 H), 8.15 (m, 1 H), 8.05 (d, } J = 4.55 \text{ Hz, 1 H), 7.88 (m, 1 H), 7.46 (comp, 4 H), 7.05 (comp, 3 H), 6.86 (comp, 3 H), 6.62 (dd, } J = 8.59, 1.77 \text{ Hz, 1 H), 6.55 (m, 1 H), 6.49 (dd, } J = 3.03,
\]
2.53 Hz, 1 H), 6.33 (m, 1 H), 6.13 (dt, J = 8.34, 1.52 Hz, 1 H), 5.84 (m, 1 H), 13C NMR (MeCN, 100 MHz) δ 107.9, 108.2, 110.9, 11.4, 114.2, 115.0, 115.3, 115.7, 115.1, 118.9, 120.1, 120.5, 123.2, 123.3, 123.8, 125.0, 126.5, 126.8, 127.6, 127.7, 127.9, 128.1, 128.5, 128.6, 128.8, 129.3, 136.9, 137.8, 138.7, 139.4, 139.7, 140.4, 145.9, 148.8, 150.6, 155.5, 157.2, 165.2, 170.3.

**[Ir(3,5Fppz)₂(dtb-bpy)][PF₆]**: [Ir(3,5-Fppz)₂Cl₂]₂ (0.8 g, 0.683 mmol), 4,4′-ditertbutyl-2,2′-bipyridine (0.394 g, 1.4 mmol), ethyl glycol (40 mL) pale green solid (yield: 0.71 g, 53.9%). ¹H NMR (MeCN, 400 MHz), δ 8.52 (d, J = 2.02 Hz, 2 H), 8.33 (dd, J = 5.56, 3.03 Hz, 2 H), 8.09 (dd, J = 6.06, 2.78 Hz, 2 H), 7.57 (ddd, J = 5.81, 2.02, 0.76 Hz, 2 H), 6.89 (t, J = 2.02 Hz, 2 H), 6.83 (ddd, J = 8.08, 1.77, 0.76 Hz, 2 H), 6.53 (comp, 4 H), 1.46 (s, 18 H). ¹³C NMR (MeCN, 100 MHz) δ 29.15, 35.32, 96.5, 96.7, 108.0, 111.5, 115.6, 121.8, 125.1, 128.1, 128.2, 139.5, 150.5, 150.7, 155.9, 164.7, 165.3, 167.2, 170.3.

**[Ir(3,5Fppz)₂(dMeO-bpy)][PF₆]**: [Ir(3,5-Fppz)₂Cl₂]₂ (1.0 g, 0.853 mmol), 4,4′-dimethoxy-2,2′-bipyridine (0.797 g, 1.786 mmol), ethyl glycol (60 mL), pale green solid (yield: 0.55 g, 35.5%). ¹H NMR (MeCN, 400 MHz), δ 8.33 (ddd, J = 7.83, 3.03, 0.51 Hz, 2 H), 8.02 (d, J = 2.78 Hz, 2 H), 7.96 (dd, J = 6.57, 2.78 Hz, 2 H), 7.30 (dd, J = 9.09, 2.27 Hz, 2 H), 7.06 (dd, J = 6.32, 2.78 Hz, 2 H), 6.97 (dd, J = 1.77, 0.51 Hz, 2 H), 6.52 (comp, 4 H), 4.05 (s, 6 H). ¹³C NMR (MeCN, 100 MHz) δ 56.5, 96.4, 96.7, 100.2, 100.4, 100.7, 108.0, 111.2, 111.5, 112.3, 112.7, 113.5, 115.5, 115.8, 128.0, 139.5, 145.4, 146.7, 146.9, 151.9, 152.0, 157.5, 168.0, 168.1, 168.7.

**[Ir(ppy)₂(dppb)][PF₆]**: [Ir(ppy)₂Cl₂]₂ (0.4 g, 0.373 mmol), 1,2-bis(diphenylphosphino)benzene (0.358 g, 0.802 mmol), ethyl glycol (25 mL), pale green solid (yield: 0.54 g, 58.1%). ¹H NMR (MeCN, 400 MHz), δ 8.14 (comp, 2 H), 7.99 (comp, 2 H), 7.72 (t, J = 8.84 Hz, 4 H), 7.65 (d, J = 8.08 Hz, 2 H), 7.57 (comp, 6 H), 7.49 (td, J = 7.58, 1.77 Hz, 4 H), 7.42 (dd, J = 6.06, 0.76 Hz, 2 H), 7.09 (td, J = 7.58, 1.26 Hz, 2 H), 7.03 (t, J = 7.07 Hz, 2 H), 6.96 (td, J = 7.58, 1.26 Hz, 2 H), 6.80 (td, J = 7.58,
1.77 Hz, 4 H), 6.35 (comp, 6 H), 6.23 (dd, \( J = 7.58, 3.54 \) Hz, 2 H). \(^{13}\)C NMR (MeCN, 100 MHz) \( \delta \) 120.1, 122.8, 122.9, 124.7, 127.5, 127.6, 128.1, 128.3, 128.5, 128.8, 129.0, 129.7, 130.1, 130.2, 131.3, 132.8, 134.0, 136.7, 137.7, 139.4, 143.2, 152.6, 157.0, 167.1. \(^{31}\)P NMR (CDCN, 161.98 MHz) \( \delta \) -20 (s, 1 P), -144 (sept, \( J = 705.47 \) Hz, 1 P).

\([\text{Ir}(3,5Fp5Fpy)\text{2}(dppb)][PF_6]\): \([\text{Ir}(3,5Fp5Fpy)\text{2}Cl_2]\)\(_2\) (0.228 g, 0.228 mmol), 1,2-bis(diphenylphosphino)benzene (0.219 g, 0.491 mmol), ethyl glycol (25 mL), pale green solid (yield: 0.316 g, 51.2%). \(^1\)H NMR (MeCN, 400 MHz), \( \delta \) 8.24 (comp, 2 H), 8.09 (comp, 2 H), 7.81 (comp, 4 H), 7.69 (td, \( J = 7.58, 1.77 \) Hz, 2 H), 7.56 (comp, 6 H), 7.43 (ddd, \( J = 15.92, 9.09, 2.53 \) Hz, 2 H), 7.30 (dd, \( J = 9.35, 2.27 \) Hz, 2 H), 7.25 (dd, \( J = 4.29, 2.53 \) Hz, 2 H), 7.19 (td, \( J = 7.58, 1.52 \) Hz, 2 H), 6.90 (td, \( J = 8.34, 2.78 \) Hz, 4 H), 6.66 (tt, \( J = 9.60, 2.02 \) Hz, 2 H), 6.64 (d, \( J = 7.33 \) Hz, 2 H), 6.43 (dd, \( J = 7.33, 1.01 \) Hz, 2 H). \(^{13}\)C NMR (MeCN, 100 MHz) \( \delta \) 121.4, 121.5, 125.5, 125.7, 126.1, 126.2, 128.0, 128.1, 129.4, 129.5, 129.9, 130.3, 130.4, 131.0, 131.2, 132.1, 133.7, 133.8, 133.9, 137.3, 137.7, 138.5, 141.9, 163.7, 166.5. \(^{31}\)P NMR (MeCN, 161.98 MHz) \( \delta \) -20 (s, 1 P), -144 (sept, \( J = 705.47 \) Hz, 1 P).

\([\text{Ir}(4Fp5Fpy)\text{2}(dppb)][PF_6]\): \([\text{Ir}(4Fp5Fpy)\text{2}Cl_2]\)\(_2\) (0.231 g, 0.189 mmol), 1,2-bis(diphenylphosphino)benzene (0.182 g, 0.408 mmol), ethyl glycol (25 mL), pale green solid (yield: 0.322 g, 64.6%). \(^1\)H NMR (MeCN, 400 MHz), \( \delta \) 8.18 (comp, 2 H), 8.05 (comp, 2 H), 7.69 (td, \( J = 8.34, 1.77 \) Hz, 4 H) 7.62 (comp, 6 H), 7.55 (td, \( J = 7.83, 2.02 \) Hz, 4 H), 7.46 (ddd, 13.64, 6.82, 2.78 Hz, 2 H), 7.17 (t, \( J = 7.58 \) Hz, 2 H), 7.11 (dd, \( J = 4.04, 2.78 \) Hz, 2 H), 6.91 (dd, \( J = 8.34, 2.53 \) Hz, 2 H), 6.85 (ddd, \( J = 15.16, 6.32, 2.53 \) Hz, 4 H), 6.47 (td, \( J = 8.34, 1.01 \) Hz, 4 H), 5.93 (ddd, \( J = 9.09, 4.29, 2.53 \) Hz, 2 H). \(^{13}\)C NMR (MeCN, 100 MHz) \( \delta \) 110.4, 110.6, 121.3, 121.4, 125.9, 126.1, 127.0, 127.2, 127.5, 127.9, 128.0, 129.2, 129.3, 129.6, 130.1, 130.2, 131.7, 133.4, 133.6, 133.9, 137.0, 137.2, 138.4, 139.3, 140.2, 140.5, 155.9, 158.4. \(^{31}\)P NMR (MeCN, 161.98 MHz) \( \delta \) -20 (s, 1 P), -144 (sept, \( J = 705.47 \) Hz, 1 P).
[Ir(4Fp5mpy)$_2$(dppb)][PF$_6$]:  [Ir(4Fp5mpy)$_2$Cl$_2$]$_2$ (1.0 g, 0.93 mmol), 1,2-bis(diphenylphosphino)benzene (0.797 g, 1.786 mmol), ethyl glycol (60 mL) pale green solid (yield: 1.64 g, 76.2%). $^1$H NMR (MeCN, 400 MHz), δ 8.15 (comp, 2 H), 8.02 (comp, 2 H), 7.68 (t, $J = 8.34$ Hz, 4 H), 7.60 (comp, 4 H), 7.54 (td, $J = 7.83$, 2.27 Hz, 4 H), 7.45 (d, $J = 8.34$ Hz, 2 H), 7.38 (d, $J = 8.59$ Hz, 2 H), 7.14 (s, 2 H), 7.10 (dd, $J = 7.33$, 1.26 Hz, 2 H), 6.85 (td, $J = 8.08$, 1.77 Hz, 4 H), 6.79 (td, $J = 9.09$, 2.27 Hz, 2 H), 6.47 (d, $J = 7.33$ Hz, 2 H), 6.44 (dd, $J = 8.59$, 1.01 Hz, 2 H), 5.82 (ddd, $J = 9.35$, 4.04, 2.53 Hz, 2 H), 1.58 (s, 6 H).$^{13}$C NMR (MeCN, 100 MHz) δ 16.6, 109.9, 110.1, 119.7, 126.3, 127.5, 127.6, 127.9, 128.1, 129.0, 129.1, 129.3, 130.1, 130.2, 131.4, 133.0, 133.5, 133.7, 133.8, 136.9, 137.1, 138.6, 139.2, 139.6, 140.0, 152.3, 161.6, 163.2, 164.1, 170.3, $^{31}$P NMR (MeCN, 161.98 MHz) δ -20 (s, 1 P), -144 (sept, $J = 705.47$ Hz, 1 P).

[Ir(4mppy)$_2$(dppp)][PF$_6$]:  [Ir(4mppy)$_2$Cl$_2$]$_2$ (1.0 g, 0.889 mmol), 1,3-bis(diphenylphosphino)propane (0.788 g, 1.91 mmol), ethylene glycol (60 mL) cream white solid (yield: 1.32 g, 68.3%). $^1$H NMR (MeCN, 400 MHz), δ 8.30 (d, $J = 5.81$ Hz, 2 H), 7.78 (comp, 4 H), 7.56 (t, $J = 7.58$ Hz, 2 H), 7.49 (d, $J = 7.33$ Hz, 2 H), 7.43 (comp, 4 H), 7.32 (d, $J = 8.08$ Hz, 2 H), 7.01 (t, $J = 7.58$ Hz, 2 H), 6.79 (d, $J = 7.83$ Hz, 2 H), 6.73 (t, $J = 7.58$ Hz, 4 H), 6.62 (td, $J = 7.33$, 1.52 Hz, 2 H), 6.34 (t, $J = 8.34$ Hz, 2 H), 6.19 (s, 2 H), 3.16 (m, 2H), 3.02 (m, 2 H), 2.80 (m, 2H), 2.10 (s, 6 H). $^{13}$C NMR (MeCN, 100 MHz) δ 161.98 , 20.5, 23.1, 23.2, 23.3, 119.8, 122.3, 123.6, 123.6, 124.8, 127.1, 127.2, 127.3, 128.2, 128.4, 129.5, 130.3, 130.7, 132.4, 133.1, 133.2, 137.5, 139.1, 141.2, 154.9, 156.3, 167.1, $^{31}$P NMR (MeCN, 161.98 MHz) δ -35 (s, 1 P), -144 (sept, $J = 705.47$ Hz, 1 P).

[Ir(ppy)$_2$(dppp)][PF$_6$]:  [Ir(ppy)$_2$Cl$_2$]$_2$ (1.0 g, 0.932 mmol), 1,3-bis(diphenylphosphino)propane (0.826 g, 2.0 mmol), ethylene glycol (60 mL) pale green solid (yield: 1.54 g, 78.1%). $^1$H NMR (MeCN, 400 MHz), δ 8.35 (d, $J = 5.81$ Hz, 2 H), 7.78 (t, $J = 7.83$ Hz, 4 H), 7.60 (td, $J = 8.34$, 1.01 Hz, 2 H), 7.50 (t, $J = 7.33$ Hz, 4 H), 7.41 (comp, 6 H), 7.01 (t, $J = 7.33$ Hz, 2 H), 6.94 (td, $J = 7.33$, 1.01 Hz, 2 H), 6.89 (t,
$J = \text{7.07 Hz, 2 H}$, 6.72 (td, $J = \text{7.58, 3.03 Hz, 2 H}$), 6.32 (t, $J = \text{8.34 Hz, 4 H}$), 3.15 (m, 2 H), 3.02 (m, 2 H), 2.80 (m, 2 H). 13C NMR (MeCN, 100 MHz) δ 20.5, 22.9, 23.2, 120.1, 122.6, 122.8, 124.8, 127.2, 127.3, 128.2, 128.5, 129.0, 129.3, 129.4, 129.7, 130.1, 130.5, 130.7, 130.9, 131.7, 133.1, 133.2, 137.7, 143.7, 155.2, 155.3, 155.4, 156.2, 167.0, 170.3. 31P NMR (MeCN, 161.98 MHz) δ -35 (s, 1 P), -144 (sept, $J = \text{705.47 Hz, 1 P}$).

$[\text{Ir(4Fppy)}_2(\text{dppp})][\text{PF}_6]$: $[\text{Ir(4Fppy)}_2\text{Cl}_2]^2$ (1.0 g, 0.874 mmol), 1,3-bis(diphenylphosphino)propane (0.775 g, 1.879 mmol), ethylene glycol (60 mL), pale green solid (yield: 1.48 g, 77.3%). 1H NMR (MeCN, 400 MHz), δ 8.32 (d, $J = \text{5.81 Hz, 2 H}$), 7.73 (comp, 4 H), 7.63 (td, $J = \text{7.33, 0.51 Hz, 2 H}$), 7.51 (comp, 4 H), 7.44 (td, $J = \text{7.58, 1.26 Hz, 4 H}$), 7.03 (t, $J = \text{7.58 Hz, 2 H}$), 6.73 (comp, 6 H), 6.37 (t, $J = \text{8.34 Hz, 4 H}$), 6.04 (ddd, $J = \text{9.60, 3.54, 2.53 Hz, 2 H}$), 3.17 (m, 2 H), 3.03 (m, 2 H), 2.82 (m, 2 H). 13C NMR (MeCN, 100 MHz) δ 20.3, 22.4, 22.7, 109.8, 110.0, 120.4, 123.0, 127.0, 127.3, 127.4, 127.5, 128.5, 128.6, 128.7, 129.3, 129.4, 129.5, 130.3, 130.9, 133.0, 133.1, 138.2, 140.1, 155.21, 165.8, 170.3. 31P NMR (MeCN, 161.98 MHz) δ -35 (s, 1 P), -144 (sept, $J = \text{705.47 Hz, 1 P}$).

$[\text{Ir(ppz)}_2(\text{dppp})][\text{PF}_6]$: $[\text{Ir(ppz)}_2\text{Cl}_2]^2$ (1.0 g, 0.972 mmol), 1,3-bis(diphenylphosphino)propane (0.86 g, 2.09 mmol), ethylene glycol (60 mL), white solid (yield: 1.83 g, 87.8%). 1H NMR (MeCN, 400 MHz), δ 7.80 (td, $J = \text{8.34, 1.26 Hz, 4 H}$), 7.75 (dd, $J = \text{3.03, 0.76 Hz, 2 H}$), 7.55 (td, $J = \text{7.58, 1.01 Hz, 2 H}$), 7.48 (td, $J = \text{7.58, 1.52 Hz, 4 H}$), 7.18 (d, $J = \text{2.27 Hz, 2 H}$), 7.10 (td, $J = \text{7.33, 1.26 Hz, 2 H}$), 7.04 (d, $J = \text{8.08 Hz, 2 H}$), 6.94 (td, $J = \text{7.33, 1.26 Hz, 2 H}$), 6.84 (comp, 6 H), 6.40 (comp, 6 H), 6.27 (td, $J = \text{2.53, 0.51 Hz, 2 H}$), 3.10 (m, 2 H), 2.96 (m, 2 H), 2.80 (m, 2 H). 13C NMR (MeCN, 100 MHz) δ 19.8, 22.1, 22.4, 111.8, 123.1, 125.4, 127.0, 127.2, 127.2, 127.3, 128.2, 128.3, 128.4, 128.9, 128.9, 129.9, 130.1, 130.3, 130.6, 130.8, 132.4, 132.7, 132.8, 133.3, 137.9, 138.0, 138.6, 138.9, 140.5, 141.6, 170.1. 31P NMR (MeCN, 161.98 MHz) δ -35 (s, 1 P), -144 (sept, $J = \text{705.47 Hz, 1 P}$).
5.6 References

Chapter 6

A deeper look into LEC devices
Chapter 6
A deeper look into LEC devices

6.1 Introduction

LECs possess several advantages over the OLEDs from their simple device architecture and the use of air stable electrodes making the LEC technology a promising low-cost and large area solution processable solid state lighting [1-4]. Nevertheless, the performance and stability of LEC devices as already mentioned in chapter one are inferior compared to those of OLEDs [5]. It is important to keep in mind that the Ir-iTMCs-based LEC technology is approximately 10 years younger compared to the OLED technology and still in an early stage of development. In general the overall performance and stability of LEC devices can be improved in at least three different ways: 1) through structurally modification of the Ir-iTMCs toward efficient and more stable complexes [6-9]. 2) Optimization of the device architecture (e.g. varying the thickness of the different layers or using the host-guest approach) [10-13]. 3) By operating the LEC devices under optimum conditions [14-16].

The introductory sections of chapters 2 to 5 cover the progress made in the synthesis of new Ir-iTMCs with emission covering the whole visible spectrum for LEC application. The same chapters also cover the significant progress made in achieving more efficient and stable LEC devices during this research work by using efficient and stable Ir-iTMCs with modified structures. On the other hand, there are only a few reports on the improvement of LEC device performance and stability via the optimization of LEC device architecture and their driven conditions. This chapter focuses on investigating the dependence of the overall performance of LEC devices based on the different conditions of the pulsed current driven mode and how the observed dependency varies from complex to complex. In order to appreciate the progress achieved in this chapter, the recent advances reported in this area are first highlighted.
The dependence of LEC device efficiencies on the thickness of the emissive layer was reported by Jhang et al., [9]. The authors demonstrated that the recombination zone within the emissive layer depends on the thickness of the emitting layer which is directly related to the overall efficiency of the LEC device. The best device performance was obtained were the recombination zone is located at the center of the emitting layer. The recombination zone in another reported LEC device was centralized within the emissive layer by using an ionic host material to balance the electron and hole mobility within the emissive layer [17]. In general, LEC devices based on Ir-iTMCs show better hole than electron transporting properties [18]. The efficiencies of a red LEC was improved by a host guest approach as reported by Hu et al., [19]. However, the lifetime of the device was not reported. The uniqueness of the LEC technology lies in the fact that the ionic nature of the emissive layer facilitates charge injection while performing both charge transportation and light emission. As a result the performances of LEC devices do not only depend on the light emitting properties of the Ir-iTMCs used in the emissive layer but also on the charge transporting properties of the Ir-iTMCs.

The third approach to enhance the efficiencies of LEC devices is to optimize the conditions under which the devices are being driven. Most of the early reported LEC device performances were based on a constant voltage driven mode. It was found that the pulse current driven mode has several advantages over the constant voltage driven mode such as higher device stability, lower current, faster turn-on and higher efficiency [20]. The highlighted literature will focus only on LEC device driven under the pulsed current mode. For better comparison, LEC devices are commonly driven under a pulse current mode with an average current density of 100 A/m² at a frequency of 1000 Hz and a block wave duty cycle of 50% for investigating the device performance of new Ir-iTMCs. The efficiencies and stability of a LEC device depend on each of the driven parameters (current density, frequency and duty cycle). Tordera et al., [14] reported a highly stable orange LEC device with an initial
maximum luminance of $670 \text{ cd/m}^2$ with an extrapolated lifetime of $4000 \text{ h}$ using an optimum pulse current driven mode with a current density of $185 \text{ A/m}^2$ at a frequency of $1000 \text{ Hz}$ and a block wave with a duty cycle of $30\%$. The most efficient pulsed current driven LEC device with green emission was reported by Tordera et al., 2013 [15], reaching a current and power efficiencies of $28.2 \text{ cd/A}$ and $17.1 \text{ lm/W}$, respectively. These device efficiencies are the best reported so far under the pulsed current driven mode. However, the lifetime of this efficient green emitting device was $98 \text{ h}$, which is not good enough to be considered for practical applications. Table 6.1 summarises the two above mentioned state-of-the-art device performances together with two other outstanding LEC device performances reported in the CELLO project report (Cost-Efficient lighting devices based on Liquid processes and ionic Organometallic Complexes from 01.01.2010 to 31.12.2012 financed by the European Union)[16]. The chemical structures of the complexes with device data in table 6.1 are shown in figure 6.1.

Table 6.1: Reported state-of-the-art LEC device data operated under different conditions.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Current density [A/m²] (duty cycle)</th>
<th>Lum_{max} [cd/m²]</th>
<th>t_{1/2} [h]</th>
<th>Current efficiency [cd/A]</th>
<th>Power efficiency [lm/W]</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ir(ppy)₂(pbpy)][PF₆]</td>
<td>200 (30%)</td>
<td>1150</td>
<td>6500</td>
<td>5.6</td>
<td>2.2</td>
</tr>
<tr>
<td>[Ir(ppy)₂(dtbbpy)][PF₆]</td>
<td>20</td>
<td>360</td>
<td>1600</td>
<td>18</td>
<td>10.3</td>
</tr>
<tr>
<td>[Ir(ppy)₂(Meppbpy)][PF₆]</td>
<td>187 (30%)</td>
<td>670</td>
<td>&gt;4000</td>
<td>3.6</td>
<td></td>
</tr>
<tr>
<td>[Ir(4Fppy)₂(dtbbpy)][PF₆]</td>
<td>25 (75%)</td>
<td>757</td>
<td>98</td>
<td>28.2</td>
<td>17.1</td>
</tr>
</tbody>
</table>

Within these two publications, it was demonstrated that the overall performance of a LEC device depends on the average current density, frequency and duty cycle of the applied pulsed current.
Figure 6.1: Chemical structures of [Ir(ppy)$_2$(Meppbpy)][PF$_6$], [Ir(4Fppy)$_2$(dtb-bpy)][PF$_6$], [Ir(ppy)$_2$(dtb-bpy)][PF$_6$] and [Ir(ppy)$_2$(pbpy)][PF$_6$].
Results and discussion

6.2 Dependence of LEC device efficiency and stability on the current density and duty cycle of the applied pulsed current

The current density of a LEC device under operation can be varied by keeping the applied pulsed current constant while changing the duty cycle or vice versa. The state of the art device efficiencies and stability of LEC devices achieved by using different driven conditions (the applied current and duty cycle of the pulse current was varied but the pulse frequency was kept constant at 1000 Hz) during this research work are presented below.

6.2.1 Exceptional red LEC device performances

The LEC device performances of [Ir(3Fppy)₂(bqu)][PF₆] and [Ir(4Fppy)₂(bqu)][PF₆] driven under a pulsed current mode with an average current density of 100 A/m² and a block wave with 50% duty cycle (table 6.2) were better than the performances of other reported red LEC device efficiencies with similar emission wavelengths and driven under similar conditions. High values of current and power efficiencies of 3.36 and 1.36 cd/A and 2.97 and 1.23 lm/W for [Ir(4Fppy)₂(bqu)][PF₆] and [Ir(3Fppy)₂(bqu)][PF₆], respectively were achieved without compromising the device lifetime as shown in figure 6.3 and table 6.2 by changing the duty cycle from 50% to 75% and maintaining the average current density at 100 A/m² and the same pulsed frequency of 1000 Hz (figure 6.2).
Figure 6.2: Luminance over time for \([\text{Ir}(3\text{Fppy})_2\text{(bqu)}][\text{PF}_6]\) (a) and \([\text{Ir}(4\text{Fppy})_2\text{(bqu)}][\text{PF}_6]\) (b) operated with an average current density of 100 A/m² at a frequency of 1000 Hz and a block wave with a duty cycle of 75%.
Figure 6.3: LEC device efficiencies and operating voltage over time for [Ir(3Fppy)$_2$(bqu)][PF$_6$] (a) and [Ir(4Fppy)$_2$(bqu)][PF$_6$] (b) operated with an average current density of 100 A/m$^2$ at a frequency of 1000 Hz and a block wave with a duty cycle of 75%
Table 6.2: Summary of LEC device data for \([\text{Ir}(3\text{Fppy})_2(\text{bqu})][\text{PF}_6]\) and \([\text{Ir}(4\text{Fppy})_2(\text{bqu})][\text{PF}_6]\) operated with an average current density of 100 A/m$^2$ at a frequency of 1000 Hz and a block wave with a duty cycle of 50 and 75%.

<table>
<thead>
<tr>
<th>Current density [A/m$^2$] (duty cycle)</th>
<th>Lum$\text{max}$ [cd/m$^2$]</th>
<th>$t_{1/2}$ [h]</th>
<th>Current efficiency [cd/A]</th>
<th>Power efficiency [lm/W]</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Ir}(4\text{Fppy})_2(\text{bqu})][\text{PF}_6])</td>
<td>100 A/m$^2$ (50%)</td>
<td>326</td>
<td>167</td>
<td>3.26</td>
</tr>
<tr>
<td></td>
<td>100 A/m$^2$ (75%)</td>
<td>336</td>
<td>144</td>
<td>3.36</td>
</tr>
<tr>
<td>([\text{Ir}(3\text{Fppy})_2(\text{bqu})][\text{PF}_6])</td>
<td>100 A/m$^2$ (50%)</td>
<td>130</td>
<td>288</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td>100 A/m$^2$ (75%)</td>
<td>138</td>
<td>269</td>
<td>1.38</td>
</tr>
</tbody>
</table>

The change in the duty led to an enhanced power efficient due to the low operating voltage of the device with the 75% duty cycle compared to the 50%. Conclusively, the red LEC efficiencies for \([\text{Ir}(3\text{Fppy})_2(\text{bqu})][\text{PF}_6]\) and \([\text{Ir}(4\text{Fppy})_2(\text{bqu})][\text{PF}_6]\) with thin film emission maxima at 629 and 644 nm respectively operated under the above mentioned conditions demonstrated overall device performances which are significantly higher compared to reported data.

6.2.2 Toward efficient and stable green, greenish yellow and yellow LEC devices

Different LEC devices with emission in the green, greenish yellow and yellow regions of the visible spectrum were driven under different pulse current conditions. The LEC device performance incorporating \([\text{Ir}(3\text{Fppy})_2(\text{phen})][\text{PF}_6]\) with photoluminescence maximum wavelengths of 532 nm driven under an average current density of 25 A/m$^2$ and block wave with a duty cycle of 50% are shown in figures 6.4 and 6.5. The LEC device data for \([\text{Ir}(3\text{Fppy})_2(\text{phen})][\text{PF}_6]\) and \([\text{Ir}(3\text{Fppy})_2(\text{Bphen})][\text{PF}_6]\) complexes driven under similar but different conditions are summarised in table 6.3.
Figure 6.4: Luminance over time for \([\text{Ir(3Fppy)}_2(\text{phen})][\text{PF}_6]\) operated with an average current density of 25 A/m$^2$ at a frequency of 1000 Hz and a block wave with a duty cycle of 50%.

Figure 6.5: LEC device efficiencies and operating voltage of \([\text{Ir(3Fppy)}_2(\text{phen})][\text{PF}_6]\) over time operated with an average current density of 25 A/m$^2$ at a frequency of 1000 Hz and a block wave with a duty cycle of 50%.
Table 6.3: Summary of LEC device data for [Ir(3Fppy)2(Bphen)][PF6] and [Ir(3Fppy)2(phen)][PF6] operated under different pulsed current mode driven conditions.

<table>
<thead>
<tr>
<th>Current density [A/m²] (duty cycle)</th>
<th>Lummax [cd/m²]</th>
<th>t_on [h]</th>
<th>t₁/₂ [h]</th>
<th>Current efficiency [cd/A]</th>
<th>Power efficiency [lm/W]</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ir(3Fppy)2(phen)][PF6]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100 (50%)</td>
<td>1835</td>
<td>6.7ᵃ</td>
<td>132</td>
<td>18.39</td>
<td>9.24</td>
</tr>
<tr>
<td>50 (50%)</td>
<td>1131</td>
<td>8.2ᵃ</td>
<td>222</td>
<td>22.48</td>
<td>11.56</td>
</tr>
<tr>
<td>25 (50%)</td>
<td>510</td>
<td>0.73</td>
<td>488</td>
<td>20.6</td>
<td>10.8</td>
</tr>
<tr>
<td>18.5 (75%)</td>
<td>360</td>
<td>0.72</td>
<td>327</td>
<td>20.23</td>
<td>13.54</td>
</tr>
<tr>
<td>[Ir(3Fppy)2(Bphen)][PF6]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100 (50%)</td>
<td>1394</td>
<td>5.5ᵃ</td>
<td>448</td>
<td>13.99</td>
<td>7.75</td>
</tr>
<tr>
<td>50 (50%)</td>
<td>900</td>
<td>0.79</td>
<td>500</td>
<td>18.02</td>
<td>10.17</td>
</tr>
<tr>
<td>25 (50%)</td>
<td>522</td>
<td>2.5</td>
<td>950</td>
<td>18.02</td>
<td>10.18</td>
</tr>
<tr>
<td>18.5 (75%)</td>
<td>329</td>
<td>8</td>
<td>1037</td>
<td>18.11</td>
<td>14.7</td>
</tr>
</tbody>
</table>

ᵃ: minutes

The maximum luminance for both devices was reached with a current density of 100 A/m². An increase in both the t_on and t₁/₂ of the device with a decrease in current density at the 50% duty cycle was observed. There is only a little variation in the current efficiencies with the changes in current densities and duty cycles. On the other hand, the maximum power efficiencies for both devices were obtained with the 75% duty cycle. One remarkable difference is the overall device stability of [Ir(3Fppy)2(Bphen)][PF6] compared to [Ir(3Fppy)2(phen)][PF6] especially using a 75% duty cycle with a current density of 18.5 A/m². This can be attributed to the better electron transporting properties of the Bphen N^N ligand for [Ir(3Fppy)2(Bphen)][PF6] complex.

A LEC device incorporating [Ir(4Fppy)2(pbpy)][PF6] with a π-π stacking between the phenyl substituent of the N^N ligand and one of the fluorinated phenyl ring of the C^N ligand was driven at different current densities at a frequency of 1000 Hz and a block wave with a 75% duty cycle and the results are summarised in table 6.4 below.
Table 6.4: Summary of LEC device data for [Ir(4Fppy)$_2$(pbpy)][PF$_6$] operated under different current densities and a block wave with a 75% duty cycle.

<table>
<thead>
<tr>
<th>Current density [A/m$^2$]</th>
<th>$\text{Lum}_{\text{max}}$ [cd/m$^2$]</th>
<th>$t_{\text{on}}$ [h]</th>
<th>$t_{1/2}$ [h]</th>
<th>Current efficiency [cd/A]</th>
<th>Power efficiency [lm/W]</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>1842</td>
<td>1.2 min</td>
<td>133</td>
<td>12.27</td>
<td>7.2</td>
</tr>
<tr>
<td>75</td>
<td>966</td>
<td>8.97</td>
<td>269</td>
<td>12.90</td>
<td>8.6</td>
</tr>
<tr>
<td>18.5</td>
<td>352</td>
<td>0.5</td>
<td>617</td>
<td>19.36</td>
<td>14.4</td>
</tr>
</tbody>
</table>

As expected, an increase in device lifetime with a decrease in current density occurs. The $t_{\text{on}}$ for the LEC device driven with a current density of 75 A/m$^2$ was the longest among the three different tested current densities. However, it should be noted that there are two maxima on the luminance spectrum (figure 6.6). The first luminance maximum is reached within a few minutes after the device was biased, followed by a drop in luminance and then a rise to the second luminance maximum.

![Graph of luminance over time](image)

Figure 6.6: Luminance over time of [Ir(4Fppy)$_2$(pbpy)][PF$_6$] operated with an average current density of 75 A/m$^2$ at a frequency of 1000 Hz and a block wave with a duty cycle of 75%.

A similar phenomenon was reported by Wu et al [21] and Hu et al [22]. They proposed an underlying mechanism to explain the unusual observed double
luminance maximum. It is understood that the first drop in luminance is as a result of the movement of the recombination zone towards the cathode and correlated exciton quenching. Then, the luminance rises again when the ohmic contact of electron injection is achieved near the cathode leading to the movement of the recombination zone towards the center of the emissive layer.

### 6.2.3 Unprecedented LEC device performances with green emission

For the first time LEC device efficiencies of 25 lm/W and 30 cd/A with an initial maximum luminance of 756 cd/m² was achieved by driving a LEC device using [Ir(4Fppy)₂(Bphen)][PF₆] under a pulsed current with a low current density of 25 A/m² at a frequency of 1000 Hz and a block wave with a duty cycle of 75% (figure 6.7). More importantly, this unprecedented green LEC device has a lifetime of 720 hours, making it the most efficient and a highly stable green LEC device reported so far. With the same LEC device, the highest reported luminance of 2251 cd/m² (figure 6.8) under a pulsed current driven mode was obtained by increasing the current density to 100 A/m². The outstanding device performance of [Ir(4Fppy)₂(Bphen)][PF₆] can be attributed to the optimized intrinsic properties of the complex by using a fluorinated C^N ligand (for yielding a high PLQY) and a good electron transporting bathophenanthroline (Bphen) N^N ligand. A summary of LEC device performances incorporating [Ir(4Fppy)₂(Bphen)][PF₆] driven under a pulsed current mode with different conditions are shown in table 6.5.
Figure 6.7: Luminance spectra and operating voltage (a) and current and power efficiencies (b) of [Ir(4Fppy)$_2$(Bphen)][PF$_6$] over time operated with an average current density of 25 A/m$^2$ and a block wave with a duty cycle of 75%.
Table 6.5: Summary of LEC device data for \([\text{Ir}(4\text{Fppy})_2(\text{Bphen})][\text{PF}_6]\) operated under pulsed current mode with different conditions.

<table>
<thead>
<tr>
<th>Current density ( [\text{A/m}^2] ) ( \text{(duty cycle)} )</th>
<th>Luminance ( [\text{cd/m}^2] )</th>
<th>( t_{1/2} ) ( [\text{h}] )</th>
<th>Current efficiency ( [\text{cd/A}] )</th>
<th>Power efficiency ( [\text{lm/W}] )</th>
<th>Operating voltage ( [\text{V}] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 A/m(^2) ( \text{(50%)} )</td>
<td>1658</td>
<td>474</td>
<td>16.5</td>
<td>9.3</td>
<td>5.6</td>
</tr>
<tr>
<td>100 A/m(^2) ( \text{(75%)} )</td>
<td>2251</td>
<td>227</td>
<td>22.5</td>
<td>14.7</td>
<td>4.7</td>
</tr>
<tr>
<td>50 A/m(^2) ( \text{(75%)} )</td>
<td>1558</td>
<td>274</td>
<td>31.1</td>
<td>20.8</td>
<td>4.5</td>
</tr>
<tr>
<td>25 A/m(^2) ( \text{(80%)} )</td>
<td>771</td>
<td>626</td>
<td>31.1</td>
<td>25.1</td>
<td>3.9</td>
</tr>
<tr>
<td>25 A/m(^2) ( \text{(75%)} )</td>
<td>754</td>
<td>720</td>
<td>30.7</td>
<td>25.8</td>
<td>3.7</td>
</tr>
<tr>
<td>25 A/m(^2) ( \text{(70%)} )</td>
<td>735</td>
<td>658</td>
<td>29.7</td>
<td>21.9</td>
<td>4.1</td>
</tr>
<tr>
<td>25 A/m(^2) ( \text{(50%)} )</td>
<td>757</td>
<td>732</td>
<td>30.7</td>
<td>17.5</td>
<td>5.2</td>
</tr>
<tr>
<td>20 A/m(^2) ( \text{(80%)} )</td>
<td>566</td>
<td>740</td>
<td>27.8</td>
<td>22.8</td>
<td>3.7</td>
</tr>
</tbody>
</table>

In general it was observed that the operating voltage for LEC devices driven under a pulsed current with a 75\% duty cycle are lower than those driven with a 50\% duty cycle even with the same current density. Efficiency of 25 lm/W and/or 30 cd/A were achieved under different driven conditions as shown in table 6.5.

Another stable green LEC device based on \([\text{Ir}(4\text{Fppy})_2(\text{bpy})][\text{PF}_6]\) with a lifetime of 991 h was achieved under the same driven conditions. The LEC device based on \([\text{Ir}(4\text{Fppy})_2(\text{bpy})][\text{PF}_6]\) demonstrated high power efficiency and current efficiency of 17.6 lm/W and 22.1 cd/A, respectively (figure 6.8b) at an initial luminance maximum of 547 cd/m\(^2\) (figure 6.8a). The luminance, power and current efficiencies of this LEC remain virtually constant over the first 120 h of device operation. The device data of \([\text{Ir}(4\text{Fppy})_2(\text{bpy})][\text{PF}_6]\) operated under two different pulsed current mode conditions are summarised in table 6.6.
Figure 6.8: Luminance spectra and operating voltage (a) and current and power efficiencies (b) of [Ir(4Fppy)$_2$(bpy)][PF$_6$] over time operated with an average current density of 25 A/m$^2$ at a frequency of 1000 Hz and a block wave with a duty cycle of 75%.
Table 6.5: Summary of LEC device data for $[\text{Ir}(4\text{Fppy})_2(\text{bpy})][\text{PF}_6]$ operated under pulsed current mode with different conditions.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>100 A/m$^2$ (50%)</td>
<td>1605</td>
<td>663</td>
<td>16.0</td>
<td>8.6</td>
<td>5.6</td>
</tr>
<tr>
<td>25 A/m$^2$ (75%)</td>
<td>547</td>
<td>991</td>
<td>22.1</td>
<td>17.6</td>
<td>3.9</td>
</tr>
</tbody>
</table>

Exceptional long lived yellowish green LEC based on $[\text{Ir}(3\text{Fppy})_2(\text{bpy})][\text{PF}_6]$ reaching a lifetime of 2782 h was achieved when the device was operated with an average current density of A/m$^2$ and a block wave with a 75% duty cycle (table 6.6). This is the first time such remarkable long lived LEC is demonstrated based on a fluorinated Ir-iTMC (figure 6a, appendix).

Table 6.6: Summary of LEC device data for $[\text{Ir}(3\text{Fppy})_2(\text{bpy})][\text{PF}_6]$ operated under pulsed current mode with different conditions.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>100 A/m$^2$ (50%)</td>
<td>1492</td>
<td>953</td>
<td>14.9</td>
<td>8.7</td>
<td>5.4</td>
</tr>
<tr>
<td>25 A/m$^2$ (75%)</td>
<td>393</td>
<td>2782</td>
<td>15.8</td>
<td>12.2</td>
<td>3.9</td>
</tr>
</tbody>
</table>

6.3 Evidence of the recombination zone movement within the emissive layer of LEC devices.

The simple device structure of LECs is based on the unique fact that the materials (Ir-iTMCs) which are used in the emissive layer perform the function of the charge transportion as well as of the emitting sites. As a result the overall performance of an Ir-iTMC LEC device will depend on two main factors: 1) the ability of the Ir-iTMC to transport both kinds of charges, the holes and electrons to the recombination
zone and 2) the ability of the Ir-iTMC to emit light via the recombination of holes and electron in the recombination zone. Up to now, it is not possible to state which of the above mentioned properties of an Ir-iTMC affects more the performance of the LEC device.

On the other side, the colour of the light emitted from a LEC device has two variables: the Luminance which can be interpreted as the brightness of the device and the chromaticity which is the property that distinguishes red, green and blue from each other. The physical property of light that gives it its colour is the spectrum (the plot of distribution of the power in the light over the wavelength of the visible spectrum). The shape of the plot determines the chromaticity of the light and the overall vertical scale determines the luminance [23]. One of the commonly used established standard systems to determine the colour of light is the CIE XYZ colour space defined by the International Commission on Illumination (CIE) (figure 6.9) [24]. For simplicity the x and y coordinate values which are recorded over time during device operation will be used to identify the colour of the light emitted. For a stable light source, the values of the x and y coordinates are constant throughout the emitting time. For a LEC devices in particular, a change in the colour coordinates of the emitted light can be caused by one of the following factors among others:

1) A change in the frontier molecular orbital of the Ir-iTMC as a result of a structural rearrangement under an electric field.

2) A movement of the recombination zone within the emissive layer due to unbalanced electrons and holes charge transporting properties of the emitting Ir-iTMC.
Figure 6.9: The CIE colour space chart [22].

When the drop in luminance of a LEC device is a result of structural instability of the Ir-iTMC during device operation, there is a possibility of observing a change in the colour coordinates of the emitted light over time. Such change in the colour coordinate is continuous since the decomposed complex acts as a quencher and is expected to increases over time. A change in colour coordinate was observed for \([\text{Ir}(4Fp5Fpy)_{2}(pbpy)]\text{[PF}_6]\) used in a LEC device which could be due to the structural instability of the complexes during device operation (figure 6.10a).
Figure 6.10a: Continuous change in the colour coordinates of \([\text{Ir}(4\text{Fp5Fpy})_2(\text{pbpy})][\text{PF}_6]\) due to structural instability of the complex during device operation.

Figure 6.10b: Rapid drop in luminance accompanied with a gradual increase in the operating voltage during change in the colour coordinates of \([\text{Ir}(4\text{Fp5Fpy})_2(\text{pbpy})][\text{PF}_6]\) due to structural instability of the complex during device operation.

It was also observed that the change in the colour coordinate and the drop in luminance were accompanied by an increase in the operating voltage figure 6.10b.
Interesting scenarios of changes in the colour coordinates alongside a start in the drop of device luminance at the same time was observed with LEC devices based on [Ir(4Fppy)$_2$(Bphen)][PF$_6$] which is attributed to the movement of the recombination zone within the emissive layer during device operation (figure 11). The LEC device was driven under a pulsed current with an average current density of 100 A/m$^2$ at a frequency of 1000 Hz and a block wave with a 50% duty cycle.

![Graph showing changes in luminance, operating voltage, and colour coordinates over time.]

**Figure 6.11:** Change in the colour coordinates of [Ir(4Fppy)$_2$(Bphen)][PF$_6$] with an immediate start of drop in the luminance of the LEC device and an increase in the operating voltage of the LEC device over time.

In this case, it is believed that the change in the colour coordinates is a result of the movement of the recombination zone towards the cathode since Ir-iTMCs are generally known to be better hole than electron transporters. During the LEC device
operation, the initial luminance and colour coordinates were virtually constant over the first 180 h. As the resistance of the emissive layer increases over time (evident by a gradual increase in the operating voltage) the number of electrons reaching the recombination zone is less compared to the number of holes. As a result, there is a movement of the recombination zone toward the cathode. The time at which the luminance starts to drop is the same as the time when the change in colour coordinate starts as can be seen in figure 6.11. The drop in Luminance could be explained as a result of the polaron induced exciton quenching [25] since the recombination zone is moving into the n-doped region. The colour coordinates becomes stable again after the recombination zone is close to the cathode surface. However, the luminance continues to drop due to the increase in the polaron induced exciton quenching as the recombination zone and the n-dope region are located in the same region within the emissive layer. The movement of the recombination zone occurs even faster with an increase in the block wave duty cycle to 75% as shown in figure 6.12 where the decrease in device lifetime with an increase in the duty cycle for the [Ir(4Fppy)$_2$(Bphen)][PF$_6$] based LEC device can be seen.

![Graph showing luminance and colour coordinate over time](image)

**Figure 6.12:** A faster change in the colour coordinates of [Ir(4Fppy)$_2$(Bphen)][PF$_6$] with an immediate start of drop in the luminance of the LEC device with an increase duty cycle from 50 to 75%.
In the case of a LEC device based on \([\text{Ir}(4\text{Fppy})_2(\text{bpy})][\text{PF}_6]\) the instantaneous drop in luminance occurs at the time when the change in the colour coordinates became stable (figure 6.13). The polaron induced exciton quenching is believed to be less high during the movement of the recombination zone and increases significantly when the recombination zone is closest to the surface of the cathode.

![Figure 6.13](image)

**Figure 6.13:** Change in the colour coordinates of \([\text{Ir}(4\text{Fppy})_2(\text{bpy})][\text{PF}_6]\) with a drop in the luminance of the LEC device and the operating voltage of the LEC device over time.

For \([\text{Ir}(3\text{Fppy})_2(\text{Bphen})][\text{PF}_6]\) the scenario occurs only a few hours after the device was turned on (figure 6.14). But the lifetime of the device is comparable to that of other devices where the drop in luminance started much later. The long lifetime of the device is attributed to the F-N intra-molecular interaction between the two C^N ligands of the Ir-iTMC which prevented structural opening of the complex as
discussed in chapter 4 (section 4.6.1). It is evident that the charge transporting properties of Ir-iTMCs play a greater part in the overall performance of LEC devices.

**Figure 6.14:** Change in the colour coordinates of [Ir(3Fppy)$_2$(Bphen)][PF$_6$] with a drop in the luminance of the LEC device.

### 6.4 Dependence of LEC device lifetime on the charge transporting property of the Ir-iTMC

A LEC device with a host-guest composition of the emissive layer (EML) was fabricated using two different Ir-iTMCs as both the host and the guest to study the dependence of the device lifetime on the charge transporting properties of the host material. Two devices were fabricated with the following composition of the emissive layer: IL:Solid (host & guest) = 3:1 with a host to guest ratio of 9:1. The host materials are Ir-iTMCs ([Ir(3,5Fp5Fpy)$_2$(dtb-bpy)][PF$_6$] (A) and [Ir(ppz)$_2$(pbpy)][PF$_6$] (B)) with green emission while the guest is a red emitting Ir-iTMC ([Ir(p5Fpy)$_2$(bqu)][PF$_6$]). The PL spectra of the host-guest thin films show only one maximum at 639 nm and 640 nm for the A and B host-guest systems, respectively (figure 6.15), implying the emission originate from the guest complex only.
Figure 6.15: PL spectra of **Guest** ([Ir(p5Fpy)$_2$(biq)][PF$_6$]), **Host A** ([Ir(3,5Fp5Fpy)$_2$(dtb-bpy)][PF$_6$]), **Host-Guest A**, **Host B** ([Ir(ppz)$_2$(pbpy)][PF$_6$]) and **Host-Guest B**.

Table 6.7: Summary of the lifetimes and luminance maxima of the host-guest devices: A and B, the host only devices and the guest only device.

<table>
<thead>
<tr>
<th>Device</th>
<th>Luminance [cd/m$^2$]</th>
<th>$t_{1/2}$ [h]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Guest only ([Ir(p5Fpy)$_2$(bqu)][PF$_6$])</td>
<td>68.4</td>
<td>263</td>
</tr>
<tr>
<td>Host A ([Ir(3,5Fp5Fpy)$_2$(dtb-bpy)][PF$_6$])</td>
<td>1458</td>
<td>4.9</td>
</tr>
<tr>
<td>Host-guest A</td>
<td>41</td>
<td>4.3</td>
</tr>
<tr>
<td>Host B ([Ir(ppz)$_2$(pbpy)][PF$_6$])</td>
<td>482</td>
<td>47</td>
</tr>
<tr>
<td>Host-guest B</td>
<td>12</td>
<td>68</td>
</tr>
</tbody>
</table>

The lifetimes and luminance maxima of the host-guest devices A and B, the host only devices and the guest only device are summarized in table 6.7. The luminance of
both host-guest devices are much lower compared to the host only devices meaning the host complexes do not contribute to the emitted light as also seen from the PL spectra. However, the luminance of the host-guest devices are also lower compared to the guest only device implying a less effective host-guest charge transfer processes. Interestingly, the lifetimes of the host-guest devices are similar to the lifetime of the respective host only devices. The drop in the luminance of the host and host-guest devices are very similar (figure 6.16), implying the causes of the drop in luminance of the devices over time is common to both devices.

Figure 6.16: Luminance spectra of a host only device using [Ir(3,5Fp5Fpy)2(dtbbpy)][PF6] and the host-guest device using combination A.

The only common process in both devices is the charge transport since the host is responsible for the charge transport in the host only device and the host-guest device. These preliminary results again suggest that the charge transporting properties of the Ir-iTMCs used in the fabrication of LECs play an important role in the overall stability of the LEC devices. Despite the fact that Ir-iTMCs in LEC devices can perform the charge transporting as well as the emitting function, the
introduction of a suitable host matrix for the Ir-iTMCs can lead to a significant improvement in the overall performance of LEC devices.

6.5 Are ionic liquids (ILs) required for LEC devices driven under the pulsed current mode?

ILs were initially introduced into the emissive layer of LEC devices to enable a better charge injection into the emissive layer. As a result, the turn-on time when these devices were driven under the constant voltage mode, were reduced. The time required for the migration of ions and formation of the electric double layer closer to the electrode surface which facilitates the injection of charges into the emissive layer varies depending on the device driven mode. It was found that LEC devices do not need IL for fast turn on when driven under the pulsed current mode. However, the ionic liquid plays the role of a disperser within the emissive layer, reducing inter-complex interactions, too. The lifetime of a LEC device based on [Ir(4Fppy)_2(pbpy)][PF_6] drops drastically with a rapid increase in the operating voltage when no IL is included in the emissive layer (figure 6.17a and 6.17b)

![Figure 6.17a: Luminance spectra over time for LEC devices based on [Ir(4Fppy)_2(pbpy)][PF_6] with and without IL.](image-url)
Figure 6.17: Operating voltage over time for LEC devices based on \([\text{Ir}(4\text{Fppy})_2(\text{pbpy})][\text{PF}_6]\) with and without IL.

Table 6.8: summarise of LEC device data of some Ir-iTMCs with and without IL

<table>
<thead>
<tr>
<th></th>
<th>(\text{Lum}_{\text{max}}) [cd/m(^2)]</th>
<th>(t_{1/2}) [h]</th>
<th>Power efficiency [lm/W]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>IL</td>
<td>No IL</td>
<td>IL</td>
</tr>
<tr>
<td>([\text{Ir}(3\text{Fppy})_2(\text{Bphen})][\text{PF}_6])</td>
<td>1394</td>
<td>1259</td>
<td>448</td>
</tr>
<tr>
<td>([\text{Ir}(3\text{Fppy})_2(\text{phen})][\text{PF}_6])</td>
<td>1835</td>
<td>1557</td>
<td>132</td>
</tr>
<tr>
<td>([\text{Ir}(4\text{Fppy})_2(\text{pbpy})][\text{PF}_6])</td>
<td>1443</td>
<td>1426</td>
<td>214</td>
</tr>
</tbody>
</table>

The power efficiencies of all devices without IL are lower compared to the devices with IL due to the high operating voltage (table 6.8). This indicates that IL somehow enhances the charge transport properties of the emissive layer. Interestingly, the turn on time for the both devices with IL and those without IL are comparable. For two devices, a significant drop in the device life from 448 and 214 h to 110 and 3.7 h, respectively, was observed. In contrast, for one of the devices, a slight increase in the
lifetime of the device from 132 to 143 h was found. The reason for the slight increase in device lifetime for a \([\text{Ir}(3\text{Fppy})_2(\text{phen})][\text{PF}_6]\) based device when no IL was included in the emissive layer is not understood up to now.

### 6.6 Conclusion

The dependence of the overall LEC performance on the pulsed driven conditions (average current density and duty cycle) has been studied. It was observed that both the average current density and the duty cycle have significant influence on the overall LEC device performances. In general, the luminance decreases with a decrease in the average current density. On the other hand, the lifetime of the devices was found to be improved with a decrease in the average current density. Interestingly, the efficiencies of the LEC devices did not follow any particular trend. Rather a combination of certain driven parameters (average current density and duty cycle) resulted in higher efficiencies. The device performances achieved by varying the operating conditions are summarized in table 6.9.

**Table 6.9:** Outstanding LEC device performances.

<table>
<thead>
<tr>
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<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ir(4Fppy)₂(biq)][PF₆]</td>
<td>629</td>
<td>100 (75%)</td>
<td>236</td>
<td>147</td>
<td>3.36</td>
</tr>
<tr>
<td>[Ir(3Fppy)₂(biq)][PF₆]</td>
<td>644</td>
<td>100 (75%)</td>
<td>136</td>
<td>488</td>
<td>1.36</td>
</tr>
<tr>
<td>[Ir(3Fppy)₂(bpy)][PF₆]</td>
<td>561</td>
<td>25 (75%)</td>
<td>393</td>
<td>327</td>
<td>15.8</td>
</tr>
<tr>
<td>[Ir(4Fppy)₂(bpy)][PF₆]</td>
<td>547</td>
<td>25 (75%)</td>
<td>547</td>
<td>2782</td>
<td>22.1</td>
</tr>
<tr>
<td>[Ir(4Fppy)₂(Bphen)][PF₆]</td>
<td>560</td>
<td>25 (75%)</td>
<td>771</td>
<td>720</td>
<td>30.7</td>
</tr>
</tbody>
</table>

The unprecedented LEC performances summarized in table 6.9 are notably higher compared to those reported in literature.
6.7 Experimental

Figure 6.18: Schematic description of a LEC device fabrication.
6.8 References

22. http://cdn.arstechnica.net/cie_color_bag.png, 04.08.2015, 10.40
Chapter 7

Conclusions and outlook
Chapter 7

Conclusions and outlook

7.1 Conclusions and outlook

Light emitting electrochemical cells (LECs) in their simplest architecture possess several advantages (e.g., they are solution processable, use of air sensitive electrodes, low-cost large area lighting) making the LEC technology a promising next generation cheap solid state lighting. In recent years, LEC devices emitting in the orange region of the visible spectrum have been reported with operational lifetime ($t_{1/2}$) greater than 2500 h [1-4] (and even reaching higher values of 6500 h [4]). However, the efficiencies of these highly stable LEC devices are rather low (in general, less than 6 cd/A and 4 lm/W) with emission in the orange region of visible spectrum. On the other hand, high efficiencies of 28.2 cd/A and 17.1 lm/W have been reported for a green LEC device [5], but demonstrating only a lifetime of 98 h. The lack of LEC devices wherein both high efficiencies and long lifetime (together with emissions in the primary colours of red, green and blue) have been achieved stand as a drawback preventing the use of the LEC technology in practical applications. With this concluding chapter an overview of the achievements made toward obtaining efficient and stable LEC devices with emissions in the red, yellow and green regions of the visible spectrum is given. Some challenges (especially with blue emitting LECs) are highlighted together with some general recommendations for further research work.

A series of new ligands including specific designs were successfully synthesized to be used in the synthesis of new Ir-iTMCs with emissions covering the entire visible spectrum. The specific designs of some ligands used in the synthesis of Ir-iTMCs were made in anticipation of improvement in the efficiency and/or stability of LEC devices. The ligands and the Ir-iTMCs were both characterized by $^1$H and $^{13}$C NMR spectroscopy and were found to have high purity levels by integration of the $^1$H NMR
peaks. Single crystal x-ray diffraction was performed on all obtained single crystals for both the ligands and the Ir-iTMCs. The Ir-iTMCs were further characterized by UV-Vis spectroscopy and their photoluminescence and electrochemical properties were studied using a spectrofluorimetry and cyclic voltammetry, respectively. Overall, the band gap energies calculated from the difference between the reduction and oxidation half potentials were in good agreement with the PL maxima of the complexes and varies with the changes in both the C^N and N^N ligands. The electroluminescence properties of some of the complexes were studied by incorporating the Ir-iTMCs in the fabrication of LEC devices. All fabricated LEC devices were driven under the same pulsed current mode with an average current density of 100 A/m² at a frequency of 1000 Hz and a block wave with a duty cycle of 50% for better comparison, except otherwise stated.

Notable improvements in the lifetimes of red LEC devices greater than 250 h have been achieved in two ways: 1) by using a more rigid benzoquinoline C^N ligand and 2) by using a fluorinated pyridine ring as part of the C^N ligands in the synthesis of the red emitting Ir-iTMCs incorporated into stable red LECs. An unusual approach of introducing a fluorine substituent into the chemical structures (on the phenyl ring of the C^N ligands) of red emitting Ir-iTMCs have led to a dramatic improvement in both the efficiencies (reaching current and power efficiencies of 3.26 cd/A and 2.3 lm/W respectively for [Ir(4Fppy)_2(biq)][PF_6] with a lifetime of 165 h) and lifetime (reaching 288 h for [Ir(3Fppy)_2(biq)][PF_6] with efficiencies of 1.31 cd/A and 0.9 lm/W) of their LEC devices without any optimization in the device architecture or device operating conditions. The emission of the phenyl fluorinated red emitting Ir-iTMCs was retained in the red region of the visible spectrum by the use of the suitable biquinoine N^N ligand with low lying LUMO. This new approach of using more rigid C^N ligands and of incorporating fluorine substituent into the molecular structures of red emitting Ir-iTMCs commences new options in the design of new red efficient and stable Ir-iTMCs for LEC application.
Contrary to literature propositions [6,7], the fluorine substituent was identified not to be the primary cause of the short lifetimes of green LEC devices based on fluorinated Ir-iTMCs. However, the type of nature of the N^N ligands together with the subsituents on the N^N ligands were found to play critical roles in the overall stability of green LEC devices. One interesting example of the influence of the substituent positioned at the N^N ligand on the lifetime of LEC devices based on fluorinated Ir-iTMCs demonstrated in this work is the inverse relationship between the size of the alkyl substituents and the lifetimes of their LEC devices (chapter 4, section 4.6.1). The LEC device based on a simple fluorinated Ir-iTMC ([Ir(4Fppy)_2(bpy)][PF_6]) using a simple not substituted bipyridine as a N^N ligand demonstrated a long lifetime of 668 h together with high luminance and very good efficiencies (1605 cd/m^2, 16 cd/A and 8.7 lm/W).

An up-to-now not observed F-N intramolecular interaction was identified between the two C^N ligands in Ir-iTMCs when the fluorine atom was substituted at the ortho position (relative to the coordinating carbon) on the phenyl ring of the C^N ligands. The ortho substituted fluorine on one C^N ligand interacts with the nitrogen in the pyridine of the other C^N ligand resulting in the formation of a cage-like arrangement of ligands surrounding the central Iridium-atom of the Ir-iTMCs. The lifetimes of LEC devices based on Ir-iTMCs with a F-N intramolecular interaction were found to be approximately 1.4 and 1.7 times longer compared to LECs based on similar fluorinated Ir-iTMCs without the F-N intramolecular interaction. This interesting result was found for green as well as red emitting Ir-iTMCs. New designs of the C^N ligands with fluorine at the ortho positions (which is needed for the formation of the F-N intramolecular interaction) can be used for the synthesis of new efficient and stable Ir-iTMCs for LEC applications. The approach can also be applied in the synthesis of neutral iridium complexes for OLED application.

Nevertheless, obtaining efficient and stable blue LECs based on Ir-iTMCs remain a major challenge. The different structural modification that led to the improvements
in the efficiencies and lifetimes of red and green LECs did not lead to any improvements for complexes for blue LECs. The main problem with blue Ir-iTMCs is the small energetic distance between the LUMO and the $^3$MC state making the $^3$MC state to be easily populated during LEC device operation. Electrons in the $^3$MC state are known to undergo radiationless relaxation via vibrational processes to the ground state. Also the $^3$MC state is involved in the $N_{C=N}$-Ir $\sigma$-antibonding interaction which becomes even stronger with the population of the $^3$MC state. As a result, the easy population of the $^3$MC state in the blue emitting Ir-iTMCs during LEC device operation is believed to be the main reason of the very low efficiencies and extremely short lifetime of blue LECs. The identification, design and synthesis of blue phosphorescent emitters suitable for LEC application require more research efforts.

So far, most of the reported works on LECs are focused on the synthesis of new Ir-iTMCs (introduction section of chapters 2 to 5) with very few reports on the optimization of the device architecture or the device operating conditions (introduction section of chapter 6). Preliminary studies done during the course of this research work on the optimization of the driven conditions (varying the average current density and duty cycle of the applied pulse current) of the LEC devices based on some selected Ir-iTMCs (table 7.1) led to unprecedented LEC device efficiencies reaching up to 31 cdA and 25 lmW and exceptional device lifetimes of more than 700 hours.
Table 7.1: Some obtained LEC device performances

<table>
<thead>
<tr>
<th>Compound</th>
<th>PL [nm]</th>
<th>Current density [A/m^2] (duty cycle)</th>
<th>Lum_{max} [cd/m^2]</th>
<th>t_{1/2} [h]</th>
<th>Current efficiency [cd/A]</th>
<th>Power efficiency [lm/W]</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ir(4Fppy)_2(biq)][PF_6]</td>
<td>629</td>
<td>100 (75%)</td>
<td>236</td>
<td>147</td>
<td>3.36</td>
<td>2.97</td>
</tr>
<tr>
<td>[Ir(3Fppy)_2(biq)][PF_6]</td>
<td>644</td>
<td>100 (75%)</td>
<td>136</td>
<td>488</td>
<td>1.36</td>
<td>1.23</td>
</tr>
<tr>
<td>[Ir(3Fppy)_2(bpy)][PF_6]</td>
<td>561</td>
<td>25 (75%)</td>
<td>393</td>
<td>327</td>
<td>15.8</td>
<td>12.2</td>
</tr>
<tr>
<td>[Ir(4Fppy)_2(bpy)][PF_6]</td>
<td>547</td>
<td>25 (75%)</td>
<td>547</td>
<td>2782</td>
<td>22.1</td>
<td>17.6</td>
</tr>
<tr>
<td>[Ir(4Fppy)_2(Bphen)][PF_6]</td>
<td>560</td>
<td>25 (75%)</td>
<td>771</td>
<td>720</td>
<td>30.7</td>
<td>25.8</td>
</tr>
</tbody>
</table>

The above outstanding device performances and stabilities illustrates that even better efficiencies and lifetimes for LEC devices can be obtained upon optimizing the device driven conditions. Further work in this area is strongly recommended.

The overall performance and stability of LECs have been enhanced during the course of this research work by: 1) the use of efficient and stable Ir-iTMCs (achieved via meticulous ligand designs, chapter 2) in the emissive layer (chapters 3 and 4). And 2) Optimization of the device driven conditions (varying the average current density and duty cycle). The achievements made in this work mark a step ahead toward the long term goal of using the LEC technology for cheap and low-cost large area lighting for several applications.
7.2 References


Appendix

Absorption spectra

Figure 4a: Absorptin spectra of [Ir(3,5Fppy)₂(phen)][PF₆] and [Ir(3,5Fppy)₂(Bphen)][PF₆].

Figure 4b: Absorption spectra of [Ir(bzqu)₂(phen)][PF₆], [Ir(bzqu)₂(Bphen)][PF₆], [Ir(bzqu)₂(dmBphen)][PF₆] and [Ir(bzqu)₂(dtb-pby)][PF₆].
Figure 4c: Absorption spectra of $\text{[Ir(3,5Fppy)$_2$(phen)][PF}_6\text{]}$, $\text{[Ir(5,3Fppy)$_2$(Bphen)][PF}_6\text{]}$ and $\text{[Ir(3,5Fppy)$_2$(dtb/bpz)][PF}_6\text{]}$.

Figure 4d: Absorption spectra of $\text{[Ir(p5Fpy)$_2$(dtb-bpy)][PF}_6\text{]}$, $\text{[Ir(na5Fpy)$_2$(Bphen)][PF}_6\text{]}$ and $\text{[Ir(3,5Fp5Fpy)$_2$(dtb-bpy)][PF}_6\text{]}$. 
Figure 4e: Absorption spectra of $[\text{Ir(3,5Fp5Fpy)2(pbpy)}][\text{PF}_6]$, $[\text{Ir(4Fppy)2(pbpy)}][\text{PF}_6]$, $[\text{Ir(4Fppy)2(pbpy)}][\text{PF}_6]$, $[\text{Ir(3Fppy)2(pbpy)}][\text{PF}_6]$ and $[\text{Ir(5Fppy)2(pbpy)}][\text{PF}_6]$.

Figure 4f: Absorption spectra of $[\text{Ir(4Fppy)2(pyimz)}][\text{PF}_6]$, $[\text{Ir(4Fppy)2(py3,5mpz)}][\text{PF}_6]$, $[\text{Ir(3Fppy)2(pyimz)}][\text{PF}_6]$ and $[\text{Ir(3Fppy)2(py3,5mpz)}][\text{PF}_6]$. 
**Figure 4g:** Absorption spectra of $[\text{Ir}(3,5\text{Fppy})_2(\text{pyimz})][\text{PF}_6]$, $[\text{Ir}(3,4\text{Fppy})_2(\text{py}3,5\text{mpz})][\text{PF}_6]$ and $[\text{Ir}(\text{bzqu})_2(\text{py}3,5\text{mpy})][\text{PF}_6]$. 
Photoluminescence spectra

**Figure 4h:** Thin film PL spectra of $[\text{Ir(4Fppy)$_2$(pbpy)}][\text{PF}_6]$, $[\text{Ir(4Fp5Fpy)$_2$(pbpy)}][\text{PF}_6]$ and $[\text{Ir(3,5Fp5Fpy)$_2$(pbpy)}][\text{PF}_6]$.

**Figure 4i:** Powder PL spectra of $[\text{Ir(4Fppy)$_2$(pyimz)}][\text{PF}_6]$, $[\text{Ir(4Fppy)$_2$(py3,5mpz)}][\text{PF}_6]$, $[\text{Ir(3Fpy)$_2$(pyimz)}][\text{PF}_6]$ and $[\text{Ir(3Fppy)$_2$(py3,5mpz)}][\text{PF}_6]$. 
Figure 4j: Powder PL spectra of [Ir(bzqu)_2(phen)][PF_6], [Ir(bzqu)_2(Bphen)][PF_6], [Ir(bzqu)_2(dmBphen)][PF_6] and [Ir(bzqu)_2(dtbpby)][PF_6].

Figure 4k: Powder PL spectra of [Ir(p5Fpy)_2(dtb-bpy)][PF_6], [Ir(na5Fpy)_2(Bphen)][PF_6] and [Ir(3,5Fp5Fpy)_2(dtb-bpy)][PF_6].
Figure 41: Powder PL spectra of [Ir(3,5Fppy)_2(pyimz)][PF_6], [Ir(3,4Fpy)_2(py3,5mpz)][PF_6] and [Ir(bzqu)_2(py3,5mpz)][PF_6].

Cyclic voltammograms

Figure 3a: Cyclic voltammograms of some complexes with extended aromatic systems measured in acetonitrile.
Figure 3b: Cyclic voltammograms of two complexes with pyridine fluorinated C\(^{\text{N}}\) ligands measured in acetonitrile.

Figure 4m: Cyclic voltammograms of three of the 3Fppy C\(^{\text{N}}\) ligand based complexes measured in acetone.
Figure 4n: Cyclic voltammograms of [Ir(4Fppy)$_2$(pbpy)][PF$_6$] and [Ir(4Fp5Fpy)$_2$(pbpy)][PF$_6$] measured in acetone.
Figure 4o: Cyclic voltammograms of three of the pbpy N^N ligand based complexes measured in acetone.

Figure 4p: Cyclic voltammograms of the pyridine fluorinated C^N ligand based complexes measured in acetone.

Figure 4q: Cyclic voltammograms of three of the 4Fppy C^N ligand based complexes measured in acetone.
Figure 4r: Cyclic voltammograms of the 3,5Fppy C\(^{\text{N}}\) ligand based complexes measured in acetone.

Figure 4s: Cyclic voltammograms of two of the 3,4Fppy C\(^{\text{N}}\) ligand based complexes measured in acetone.
Figure 4t: Cyclic voltammograms of the bzqu C^N ligand based complexes measured in acetone.

Figure 4u: Cyclic voltammograms of two of the 3Fppy C^N ligand based complexes measured in acetone.
Electroluminescence spectra

All the LEC devices in chapter four were operated under a pulsed current driven mode with an average current density of 100 A/m² at a frequency of 1000 Hz and a block wave with a duty cycle of 50%.

Figure 4v: Luminance and operating voltage over time of LEC devices based on [Ir(4Fppy)₂(bpy)][PF₆] and [Ir(4Fppy)₂(dmbpy)][PF₆].

Figure 4w: Luminance and operating voltage over time of LEC devices based on [Ir(3Fppy)₂(Bphen)][PF₆] and [Ir(3Fppy)₂(Phen)][PF₆].
Figure 4x: Luminance and operating voltage over time of LEC devices based on [Ir(4Fppy)$_2$(Bphen)][PF$_6$], [Ir(4Fppy)$_2$(phen)][PF$_6$] and [Ir(4Fppy)$_2$(dmBphen)][PF$_6$].

Figure 4y: Luminance over time of LEC devices based on [Ir(4Fppy)$_2$(5dmbpy)][PF$_6$] and [Ir(4Fppy)$_2$(dtb-bpy)][PF$_6$].
Figure 6a: Luminance over time of LEC devices based on $[\text{Ir}(3\text{Fppy})_2\text{bpy}][\text{PF}_6]$ driven under an average current density of 25 A/m$^2$ and a duty cycle of 75%.

Figure 3c: Luminance over time of LEC devices based on $[\text{Ir}(\text{na5Fpy})_2\text{biq}][\text{PF}_6]$. 
Table 2a: List of Materials, percent purity and supplier.

<table>
<thead>
<tr>
<th>Material</th>
<th>% purity</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. 2-Bromopyridine</td>
<td>99</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>2. 2-Bromo-5-fluoropyridine</td>
<td>97</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>3. 4-Fluorobenzeneboronic acid</td>
<td>97</td>
<td>Alfa Aesar</td>
</tr>
<tr>
<td>4. Palladium acetate</td>
<td>99</td>
<td>Merck KGaA</td>
</tr>
<tr>
<td>5. Potassium phosphate</td>
<td>97</td>
<td>Alfa Aesar</td>
</tr>
<tr>
<td>6. Ethylene glycol</td>
<td>&gt;99</td>
<td>Merck KGaA</td>
</tr>
<tr>
<td>7. 3.5-Difluorobenzeneboronic acid</td>
<td>97</td>
<td>Alfa Aesar</td>
</tr>
<tr>
<td>8. 2-Bromo-5-methylpyridine</td>
<td>98</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>9. Benzenenboronic acid</td>
<td>98</td>
<td>Alfa Aesar</td>
</tr>
<tr>
<td>10. 9-Phenanthracenyboronic acid</td>
<td>-</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>11. 1-Bromoisoquinoline</td>
<td>98</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>12. 1-Naphthaleneboronic acid</td>
<td>97</td>
<td>Alfa Aesar</td>
</tr>
<tr>
<td>13. 1-Chloroisoquinoline</td>
<td>95</td>
<td>Alfa Aesar</td>
</tr>
<tr>
<td>14. 2-Chloroquinoline</td>
<td>98</td>
<td>Alfa Aesar</td>
</tr>
<tr>
<td>15. 2-Naphthaleneboronic acid</td>
<td>97</td>
<td>Alfa Aesar</td>
</tr>
<tr>
<td>16. 3-Fluorobenzeneboronic acid</td>
<td>97</td>
<td>Alfa Aesar</td>
</tr>
<tr>
<td>17. 3,4-Difluorobenzeneboronic acid</td>
<td>98</td>
<td>Alfa Aesar</td>
</tr>
<tr>
<td>18. L-proline</td>
<td>99</td>
<td>Merck KGaA</td>
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<tr>
<td>19. Pyrazole</td>
<td>98</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>20. 1-Bromo-3,5-difluorobenzene</td>
<td>98</td>
<td>Alfa Aesar</td>
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<tr>
<td>21. Dimethyl sulfoxide</td>
<td>&gt;99.9</td>
<td>Merck KGaA</td>
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<tr>
<td>22. Copper iodide</td>
<td>&gt;98</td>
<td>Merck KGaA</td>
</tr>
<tr>
<td>23. 3,5-Dimethyl-1H-pyrazole</td>
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<td>Alfa Aesar</td>
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<tr>
<td>24. Chloroform-D1</td>
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<td>25. TLC Aluminium oxide 60F</td>
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<td>Merck KGaA</td>
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<tr>
<td>26. Aluminium oxide 90 (neutral active, 0.063-0.200 mm)</td>
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<td>Merck KGaA</td>
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<tr>
<td>27. Silica gel 60 (neutral active, 0.063-0.200 mm)</td>
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<td>Merck KGaA</td>
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<tr>
<td>28. Petroleum ether</td>
<td></td>
<td>Merck KGaA</td>
</tr>
<tr>
<td>29. Ethyl acetate</td>
<td>&gt;99.5</td>
<td>Merck KGaA</td>
</tr>
<tr>
<td>30. Diethyl ether</td>
<td>&gt;99</td>
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<tr>
<td>31. Sodium carbonate</td>
<td>Water free</td>
<td>Merck KGaA</td>
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<tr>
<td>32. 2,2'-Biquinoline</td>
<td>98.0</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>33. 2,2'-Bipyrindine</td>
<td>&gt;98.0</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>34. 5,5',6,6'-Dimethyl-2,2'-bipyridine</td>
<td>98</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>35. 4,4',6,6'-Dimethyl-2,2'-bipyridine</td>
<td>99</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>36. 4,4',6,6'-Dimethoxy-2,2'-bipyridine</td>
<td>98</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>37. 4,4',6,6'-Di tert-butyl-2,2'-bipyridine</td>
<td>98</td>
<td>Sigma Aldrich</td>
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<tr>
<td>38. 1,10-Phenanthroline</td>
<td>99</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>39. 4,7-Diphenyl-1,10-phenanthroline</td>
<td>97</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>40. 2,9-Dimethyl-4,7-diphenyl-1,10-phenanthroline</td>
<td>96</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>41. Bis(diphenylphosphino)benzene</td>
<td>97</td>
<td>Sigma Aldrich</td>
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<tr>
<td>42. 1,3-Bis(diphenylphosphino)propane</td>
<td>97</td>
<td>Sigma Aldrich</td>
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<td>43. Benzo[h]quinoline</td>
<td>97</td>
<td>Sigma Aldrich</td>
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<tr>
<td>44. 2-phenylpyridine</td>
<td>98</td>
<td>Sigma Aldrich</td>
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<tr>
<td>45. Phenyl[1H]pyrazole</td>
<td>97</td>
<td>Sigma Aldrich</td>
</tr>
</tbody>
</table>