

Durham E-Theses

The Design and Synthesis of Luminescent Iridium and Platinum Complexes featuring Bi-, Tri- and Tetra-dentate Ligands

DAVID PATRICK O'FARRELL

How to cite:

O'FARRELL, DAVID PATRICK (2020) The Design and Synthesis of Luminescent Iridium and Platinum Complexes featuring Bi-, Tri- and Tetra-dentate Ligands. Doctoral thesis, Durham University.

Use policy

The full-text may be used and/or reproduced, and given to third parties in any format or medium, without prior permission or charge, for personal research or study, educational, or not-for-profit purposes provided that:

- a full bibliographic reference is made to the original source
- a <https://etheses.durham.ac.uk/id/eprint/13741/> is made to the metadata record in Durham E-Theses
- the full-text is not changed in any way

The full-text must not be sold in any format or medium without the formal permission of the copyright holders.

Please consult the [full Durham E-Theses policy](#) for further details.



**The Design and Synthesis of Luminescent
Iridium and Platinum Complexes featuring
Bi-, Tri- and Tetra-dentate Ligands**

David O'Farrell

A thesis submitted for the degree of Doctor of Philosophy

Department of Chemistry

June 2020

Abstract

Luminescent transition metal complexes have a broad range of applications from display technologies and lighting to bio-imaging. A total of 85 iridium(III) and platinum(II) complexes featuring bidentate, tridentate and tetradentate ligands have been synthesized in this work with the aims of: (i) developing efficient emitters for potential incorporation into light-emitting electrochemical cells (LECs) and (ii) contributing novel design structures to the field of coordination photochemistry.

Chapter 2 focuses on Ir(III) complexes of the type $[\text{Ir}(\text{C}^{\wedge}\text{N})_2(\text{N}^{\wedge}\text{N})]\text{PF}_6$ which feature an $\text{N}^{\wedge}\text{C}$ -cyclometalating ligand based on 2-phenylpyridine (ppyH) and an $\text{N}^{\wedge}\text{N}$ ligand based on a bipyridine (bpy), pyrazolo[3,4-*b*]pyridine (pp), or 7-azaindole (az). Colour tuning of emission from $\lambda_{\text{max}} = 450$ nm to 677 nm in solution was achieved by variation of both ligands. Impressive quantum yields of 53-57% were obtained by addition of mesityl and difluorophenyl groups to the periphery of the $\text{C}^{\wedge}\text{N}$ ligand.

Chapter 3 describes the synthesis of cationic Ir(III) complexes bearing tridentate $\text{N}^{\wedge}\text{C}^{\wedge}\text{N}$ ligands in combination with bpy derivatives, phenanthroline, pp- or az-based $\text{N}^{\wedge}\text{N}$ ligands. Metathesis of the chloride ligand to phenylacetylide or cyanide red- and blue shifted the emission, respectively, by approximately 40-100 nm ($1630\text{-}3200\text{ cm}^{-1}$) with a marginal increase in quantum yield ($\phi_{\text{PL}} \leq 6\%$).

In Chapter 4, platinum(II) and iridium(III) complexes bearing *para*-anisidine-linked tetradentate ligands are reported. The emission maxima of cyclometalated complexes of the type $[\text{Pt}(\text{N}^{\wedge}\text{N}^{\wedge}\text{N}^{\wedge}\text{C})]\text{PF}_6$ and $\text{Ir}(\text{N}^{\wedge}\text{N}^{\wedge}\text{N}^{\wedge}\text{C})\text{Cl}_2$ were blue shifted by 23-93 nm ($504\text{-}3020\text{ cm}^{-1}$) compared to their non-cyclometalated $\text{N}^{\wedge}\text{N}^{\wedge}\text{N}^{\wedge}\text{N}$ -based counterparts. Metathesis of the axial chloride(s) in Ir complexes with cyanide and phenylacetylene induced a > 100 nm ($> 2300\text{ cm}^{-1}$) blue shift in emission with a negligible effect on quantum yield ($\phi_{\text{PL}} \leq 6\%$).

Finally, in Chapter 5, di-iridium and di-platinum complexes containing *para*-anisidine-linked bis-bidentate $\text{N}^{\wedge}\text{N}\text{--}\text{N}^{\wedge}\text{N}$ or bis-tridentate $\text{N}^{\wedge}\text{C}^{\wedge}\text{N}\text{--}\text{N}^{\wedge}\text{C}^{\wedge}\text{N}$ bridging ligands were synthesized, where $\text{N}^{\wedge}\text{N} = \text{bpy}$ or pp and $\text{N}^{\wedge}\text{C}^{\wedge}\text{N} = \text{dipyridylbenzene}$ ($\phi_{\text{PL}} \leq 17\%$). Addition of a second metal centre in the bis-tridentate series lowered quantum yield and red shifted emission. The mixed Ir(III)-Pt(II) complex was only emissive at low temperature. Metathesis of the $\text{Pt}(\text{N}^{\wedge}\text{C}^{\wedge}\text{N})\text{Cl}$ -type complex with phenylacetylene raised the quantum yield and marginally blue shifted emission whereas a larger red shift was seen in the analogous cyanide-containing Pt complex.

Declaration

The research described herein was undertaken at the Department of Chemistry at Durham University between October 2015 and July 2019. All of the work is my own, except where specifically stated otherwise. No part has previously been submitted for a degree at this or at any other university.

Statement of Copyright

The copyright of this thesis rests with the author. No quotations should be published without prior consent and information derived from it should be acknowledged.

Acknowledgements

I would first and foremost like to acknowledge PolyPhotonix Ltd, the Centre for Process Innovation and Durham University's Centre for Doctoral Training in Energy for funding my research within the University and at Sedgefield's NETPark, and for allowing me to attend various summer schools, conferences and summits.

Next, I would like to say a huge thank you to Professor Gareth Williams, for his support, guidance and accommodating temperament throughout. A kind, easy-going yet thorough supervisor who I deeply respect and I am extremely grateful for all of his help he gave me towards writing this thesis.

I couldn't have asked for a more fun and friendly group to work in. Thank you to: Eddy for our daily chats (mostly) about football, Mel for being literally the kindest person I've ever meet, Emma for her insistence for tea (and biscuit) breaks and to Raminder for having an answer to every chemistry (or non-chemistry!) question I asked you. Thank you all for helping me get started in the lab and for welcoming me into the group so generously. I don't even know where to begin with acknowledging the newer generation of Rebecca, Chris, Amit and Yana. I hope I haven't passed on too many of my bad habits. You've all been incredible to work with and I've no doubt you will remain excellent friends. I'd also like to thank Jamie, Chris, Ben, Elizabeth, Jack and all of our other MChem students for making my time in the lab so enjoyable.

I want to thank everybody in the department including all service staff, cleaners and the stores, solvents and waste team who all work tirelessly to assist myself and other researchers. A big thanks especially to Ivan and Miriam for keeping our office and lab so clean despite my daily attempts at launching the remains of my lunch across the office towards the bin with variable success.

Outside of Chemistry, I've been lucky enough to have had some amazing housemates - Drew and Olivia, thank you for sharing my enthusiasm for triathlon and for motivating me to train, albeit no way near as frequently as you two! Thanks to everybody within the Durham music scene for the opportunities to play in DUPO and DUOS orchestras, in DULOG shows, in Hatfield's Kinky Jeff, at Jazz Soc events and not forgetting of course, playing in the brilliant Cathedral City! It was a pleasure to perform with you - I had such a 'grate' time and it will always be a highlight of my (lengthy) time in Durham.

Finally, I owe everything to my family, my fiancée Rachael and her family; without your love, support and kindness, I definitely wouldn't have got this thesis written. Rachael, thank you beyond words for just everything and I can't wait to share the next chapter of our lives together. Grandpa and Nanny - I've no doubt how proud you both would be to see me finally become Dr. O'Farrell!

Abbreviations

AgOTf	silver trifluoromethanesulfonate
AIPE	aggregation-induced phosphorescent emission
ASAP	atmospheric solids analysis probe
aq.	aqueous
az	7-azaindole
B3LYP	Becke, 3-parameter, Lee-Yang-Parr hybrid exchange-correlation energy functional
bis-dfp ₂ pyH	2,4-bis[2',4''-bis(fluoranyl)phenyl]pyridine
[BMIM]PF ₆	1-butyl-3-methylimidazolium hexafluorophosphate
bpy	2,2'-bipyridine
ca.	circa (about)
CBP	4,4'-bis(<i>N</i> -carbazolyl)-1,1'-biphenyl
CE _{max}	current efficiency, maximum
CMOS	complementary metal oxide semiconductor
COSY	correlation spectroscopy
CP	conjugated polymer
dba	bis(dibenzylideneacetone)
DCM	dichloromethane
DCTB	<i>trans</i> -2-[3-(4- <i>tert</i> -butylphenyl)-2-methyl-2-propenylidene
dfppyH	2-(2',4'-difluorophenyl)pyridine
DFT	density functional theory
diMe ₂ dpybH	2,2'-(4,6-dimethyl-1,3-phenylene)dipyridine.
DIPA	diisopropylamine
diph ₂ bpy	4,4'-diphenyl-2,2'-bipyridine
di ^t Bu ₂ bpy	4,4'-di- <i>tert</i> -butyl-bipyridine
dmabpy	4,4'-dimethylamino-2,2'-bipyridine
DMAE	2-dimethylaminoethanol
DMAP	4-(dimethylamino)pyridine
dmbpy	4,4'-dimethyl-2,2'-bipyridine
DMF	dimethylformamide
dmobpy	4,4'-dimethoxy-2,2'-bipyridine
DMSO	dimethyl sulfoxide
DPPE	1,2-bis(diphenylphosphino)ethane
dppf	1,1'-bis(diphenylphosphino)ferrocene

DPPP	1,3-bis(diphenylphosphino)propane
dpybH	dipyridylbenzene
EL	electroluminescence
[EMIM]PF ₆	1-ethyl-3-methylimidazolium hexafluorophosphate
EPA	diethyl ether : isopentane : ethanol (2 : 2 : 1)
ES	electrospray (ionisation mass spectrometry)
EQE	external quantum efficiency
equiv.	equivalent
fppyH	2-(4'-fluorophenyl)pyridine
FTO	fluorine-doped tin oxide
GPES	general purpose electrochemical system
HMBC	heteronuclear multiple-bond correlation spectroscopy
HMPA	hexamethylphosphoramide
HOMO	highest occupied molecular orbital
HPLC	high performance liquid chromatography
HSQC	heteronuclear single-quantum correlation spectroscopy
IC	internal conversion
ir	irreversible
ISC	inter-system crossing
iTMC	ionic transition metal complex
ITO	indium tin oxide
k_f	fluorescence rate constant
k_{ISC}	inter-system crossing rate constant
k_{nr}	non-radiative decay rate constant
k_p	phosphorescence rate constant
k_r	radiative decay rate constant
LANL2DZ	Los Alamos National Laboratory 2-double-zeta basis set
LC	ligand-centred
LCMS	liquid chromatography–mass spectrometry
LEC	light-emitting electrochemical cell
LED	light-emitting diode
LLCT	ligand-to-ligand charge transfer
L_{max}	luminance, maximum
LMCT	ligand-to-metal charge transfer
LUMO	lowest unoccupied molecular orbital

MALDI	matrix assisted laser desorption/ionisation
MC	metal-centred
mCP	microchannel plate
mes-dfppyH	2-(2',4'-difluorophenyl)-4-(2'',4'',6''-trimethylphenyl)pyridine
MeTHF	2-methyltetrahydrofuran
MLCT	metal-to-ligand charge transfer
M_s	spin quantum number
NaO ^t Bu	sodium <i>tert</i> -butoxide
NBu ₄ Cl	tetrabutylammonium chloride
NBu ₄ PF ₆	tetrabutylammonium hexafluorophosphate
<i>n</i> BuLi	<i>N</i> -butyl lithium
NHC	<i>N</i> -heterocyclic carbene
NIR	near-infrared
NMR	nuclear magnetic resonance
NOESY	nuclear overhauser effect spectroscopy
OLED	organic light-emitting diode
OXD7	1,3-bis(2-(4- <i>tert</i> -butylphenyl)-1,3,4-oxadiazol-5-yl)benzene
PEDOT:PSS	poly(3,4-ethylenedioxythiophene) polystyrene sulfonate carbene
PE _{max}	power efficiency, maximum
phbpy	6-phenyl-2,2'-bipyridine
phen	1,10-phenanthroline
pic	2-picolylamine
PL	photoluminescence
PLQY	photoluminescence quantum yield
PMMA	poly(methyl methacrylate)
POP	bis(2-diphenylphosphino)phenyl ether
pp	1 <i>H</i> -pyrazolo[3,4- <i>b</i>]pyridine
ppm	parts per million
ppyH	2-phenylpyridine
PVK	poly(9-vinylcarbazole)
qr	quasi-reversible
QTof	quadrupole time-of-flight
RPM	revolutions per minute
RT	room temperature
S ₀	singlet ground state

S_1	first singlet excited state
S_2	second singlet excited state
sat.	saturated
SCE	saturated calomel electrode
sh	shoulder
S_n	n^{th} singlet ground state
SOC	spin-orbit coupling
T_0	triplet ground state
T_1	first triplet excited state
$t_{1/2}$	time for luminance to decay to half of its maximum value
T_2	second triplet excited state
TA	transient absorption
TADF	thermally activated delayed fluorescence
TBAOTf	tetrabutylammonium trifluoromethanesulfonate
TD-DFT	time-dependent density functional theory
tfppyH	2-(2,3,4-trifluorophenyl)pyridine
THF	tetrahydrofuran
TLC	thin-layer chromatography
T_n	n^{th} triplet ground state
t_{on}	time to reach a threshold luminance, typically the maximum luminance
TPBI	2,2'2''-(1,3,5-benzinetriyl)-tris(1-phenyl-1- <i>H</i> -benzimidazole)
tpy	2,2';6',2''-terpyridine
TQD	tandem quadrupole
UV	ultraviolet
λ_{max}	wavelength, maximum
ϕ	photoluminescence quantum yield
τ	lifetime

Table of Contents

Abstract	i
Declaration	ii
Statement of Copyright	ii
Acknowledgements	iii
Abbreviations.....	iv
Chapter 1 – Introduction.....	1
1.1 Luminance in metal complexes	1
1.1.1 What is luminance?	1
1.1.2 The efficiency of luminance in metal complexes.....	2
1.2 Light-emitting electrochemical cells.....	5
1.2.1 Introduction	5
1.2.2 Device architecture.....	5
1.2.3 Operation.....	7
1.2.4 Fabrication methods.....	8
1.2.5 Performance parameters.....	8
1.2.6 LEC development.....	9
1.2.6.1 <i>Device design and fabrication</i>	9
1.2.6.2 <i>Design of new emitters</i>	11
1.3 Aims and objectives of research.....	16
Chapter 2 – Iridium complexes featuring bidentate ligands	17
2.1 Introduction	17
2.2 iTMC design strategies for improved quantum yield	18
2.3 iTMC design strategies for colour tuning	23
2.3.1 Blue-emitting iTMCs	23
2.3.2 Red-emitting iTMCs	29
2.4 Aims and objectives.....	31
2.5 Results and discussion: [Ir(ppy) ₂ (bpy)]PF ₆ -based complexes	33
2.5.1 Synthesis	34
2.5.2 Crystallography	37
2.5.3 Electrochemistry	38
2.5.4 DFT	39
2.5.5 Photophysical properties.....	40
2.5.5.1 <i>Absorption</i>	40
2.5.5.2 <i>Emission</i>	43
2.6 Results and discussion: pyrazolopyridine- and azaindole-based complexes	49
2.6.1 Synthesis.....	50

2.6.2	Crystallography	52
2.6.3	Electrochemistry	53
2.6.4	DFT	55
2.6.5	Photophysical properties	56
2.6.5.1	<i>Absorption</i>	56
2.6.5.2	<i>Emission</i>	58
2.7	Summary	65
Chapter 3 – Iridium complexes featuring tridentate ligands		67
3.1	Introduction	67
3.2	Synthesis of dpybH and dpyb-based complexes.....	69
3.3	Complexes containing N [^] C [^] N ligands.....	70
3.4	Complexes with other tridentate ligands (not displaying N [^] C [^] N-coordination).....	79
3.5	Aims and objectives	80
3.6	Results and discussion: [Ir(N [^] C [^] N)(N [^] N)X] ⁺ complexes bearing a symmetrical N [^] N ligand	82
3.6.1	Synthesis	83
3.6.2	Crystallography	87
3.6.3	Electrochemistry	88
3.6.4	DFT	90
3.6.5	Photophysical properties	91
3.6.5.1	<i>Absorption</i>	91
3.6.5.2	<i>Emission</i>	92
3.7	Results and discussion: Asymmetric [Ir(N [^] C [^] N)(N [^] N)X] ⁺ complexes.....	101
3.7.1	Synthesis	101
3.7.2	Crystallography	105
3.7.3	Electrochemistry	107
3.7.4	DFT	108
3.7.5	Photophysical properties	111
3.7.5.1	<i>Absorption</i>	111
3.7.5.2	<i>Emission</i>	112
3.8	Summary	115
Chapter 4 – Platinum and Iridium complexes featuring tetradentate ligands		117
4.1	Introduction	117
4.2	Platinum complexes containing tetradentate ligands	117
4.2.1	N-linked C [^] N [^] N [^] C-type Pt(II) complexes.....	119
4.2.2	N-linked N [^] C [^] C [^] N-type Pt(II) complexes.....	120

4.2.3	N-linked N [^] N [^] C [^] C-type Pt(II) complexes	123
4.3	Iridium complexes containing tetradentate ligands.....	123
4.4	Aims and objectives.....	126
4.5	Results and discussion: Pt(II) complexes featuring tetradentate ligands.....	127
4.5.1	Synthesis	127
4.5.2	Crystallography	130
4.5.3	Electrochemistry	131
4.5.4	DFT	132
4.5.5	Photophysical properties.....	133
4.5.5.1	<i>Absorption</i>	133
4.5.5.2	<i>Emission</i>	134
4.6	Results and discussion: Ir(III) complexes featuring tetradentate ligands.....	137
4.6.1	Synthesis	137
4.6.2	Crystallography	145
4.6.3	Electrochemistry	145
4.6.4	DFT	146
4.6.5	Photophysical properties.....	147
4.6.5.1	<i>Absorption</i>	147
4.6.5.2	<i>Emission</i>	148
4.7	Summary.....	150
Chapter 5 – Dinuclear complexes of Platinum and Iridium.....		153
5.1	Introduction.....	153
5.2	Di-iridium complexes.....	154
5.2.1	N [^] N-type di-iridium complexes: A to F	154
5.2.2	N [^] C-type bridged di-iridium complexes: G to S	155
5.3	Di-platinum complexes.....	158
5.4	Heteronuclear platinum and iridium complexes.....	159
5.5	Aims and objectives.....	160
5.6	Results and discussion: N [^] N-bridged di-iridium(III) complexes	162
5.6.1	Synthesis	163
5.6.2	Electrochemistry	165
5.6.3	Photophysical properties.....	166
5.6.3.1	<i>Absorption</i>	166
5.6.3.2	<i>Emission</i>	169
5.7	Results and discussion: Ir and Pt complexes bearing p-anisidine-linked tetradentate ligands	177
5.7.1	Synthesis	177
5.7.2	Crystallography	183

5.7.3	Electrochemistry	184
5.7.4	DFT	186
5.7.5	Photophysical properties	187
5.7.5.1	<i>Absorption</i>	187
5.7.5.2	<i>Emission</i>	189
5.8	Summary	192
Chapter 6 – Conclusions and Future Work.....		195
6.1	Conclusions	195
6.2	Future Work	200
Chapter 7 – Experimental		203
7.1	General procedures	203
7.1.1	Materials	203
7.1.2	Instrumentation	203
7.1.3	Photophysical characterisation.....	204
7.1.4	Electrochemical characterisation.....	205
7.1.5	Density functional theory.....	205
7.1.6	Crystallography	205
7.2	Synthesis of ligands and precursors.....	205
7.2.1	Suzuki cross-coupling	205
7.2.2	Stille cross-coupling	206
7.2.3	Lithium-halogen exchange/transmetallation	206
7.2.4	Copper-catalysed amination	206
7.2.5	Buchwald-Hartwig amination	207
7.2.6	Synthesis of Chapter 2 ligands and precursors.....	207
7.2.7	Synthesis of Chapter 3 ligands and precursors.....	221
7.2.8	Synthesis of Chapter 4 ligands and precursors.....	222
7.2.9	Synthesis of Chapter 5 ligands and precursors.....	227
7.3	Synthesis of iridium chloro-bridged dimers.....	231
7.3.1	General procedure	231
7.3.2	Bidentate C [^] N dimers.....	231
7.3.3	Tridentate N [^] C [^] N dimers.....	233
7.4	Synthesis of complexes	235
7.4.1	General procedure for mono- and di-iridium complexes containing bidentate ligands.....	235
7.4.2	General procedure for iridium complexes containing tridentate ligands	236
7.4.3	General metathesis procedure	236
7.4.4	General procedure for platinum complexes.....	236
7.4.5	Synthesis of Chapter 2 complexes	237

7.4.6	Synthesis of Chapter 3 complexes	262
7.4.7	Synthesis of Chapter 4 complexes	276
7.4.8	Synthesis of Chapter 5 complexes	282
Bibliography.....		299
Appendix		315
Crystal structure information		315
LEC performance data		338
Structures of complexes		341

Chapter 1 - Introduction

1.1 Luminance in metal complexes

1.1.1 What is luminance?

Luminescence occurs when an energetically excited state relaxes back to the ground state with the emission of radiation in the form of light. In the case of photoluminescence, the excited state is generated by the absorption of photon(s) and the emission of radiation can be fluorescent or phosphorescent in nature.

Fluorescence describes the relaxation of an excited state with the emission of a photon via a spin-allowed transition. Typically this transition is between the first excited singlet state and the ground state (i.e. $S_1 \rightarrow S_0$) because higher excited singlet states (i.e. S_1 and S_2) are more likely to lose energy through non-radiative processes such as internal conversion (IC) and vibrational relaxation which occur at faster timescales (10^{-12} s) than fluorescence (10^{-9} s).¹ Emission can occur to higher vibrational levels of the ground state, but a thermal equilibrium is quickly reached.²

Phosphorescence, in contrast, describes the emission of light via a spin-forbidden transition e.g. $T_1 \rightarrow S_0$. The spin selection rule formally forbids transitions from triplet excited states in organic molecules, but the inclusion of heavy elements can partially relax this rule via spin-orbit coupling (SOC) to promote intersystem crossing (ISC) and produce phosphorescence which lasts on the order of milliseconds.²

A Jablonski diagram first proposed by Alexander Jablonski in 1935, is used to represent the radiative and non-radiative processes available to a particular species (**Figure 1.1**).² The ground, first and second electronic singlet and triplet states are depicted S_0 & T_0 , S_1 & T_1 , and S_2 & T_2 respectively. Multiple vibronic states may be coupled within each electronic energy state. Vertical lines represent transitions between states to illustrate the instantaneous nature of light absorption.¹

The molecular orbitals in metal complexes are described approximately as being centred on either the metal or the ligand. There are four main types of electronic transition possible to describe the excited state: ligand-centred (LC), ligand-to-metal charge transfer (LMCT), metal-to-ligand charge transfer (MLCT) and metal-centred (MC) (**Figure 1.2**). The relative energies of these transitions are influenced by the identity and oxidation state of the metal and the identity of the ligands. The energies and locations of the highest-occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) can often be calculated by density-functional theory (DFT) to elucidate the nature of the lowest energy excited state. Electrochemical measurements can also prove useful, the reduction potential providing information about the LUMO and the oxidation potential about the HOMO.¹

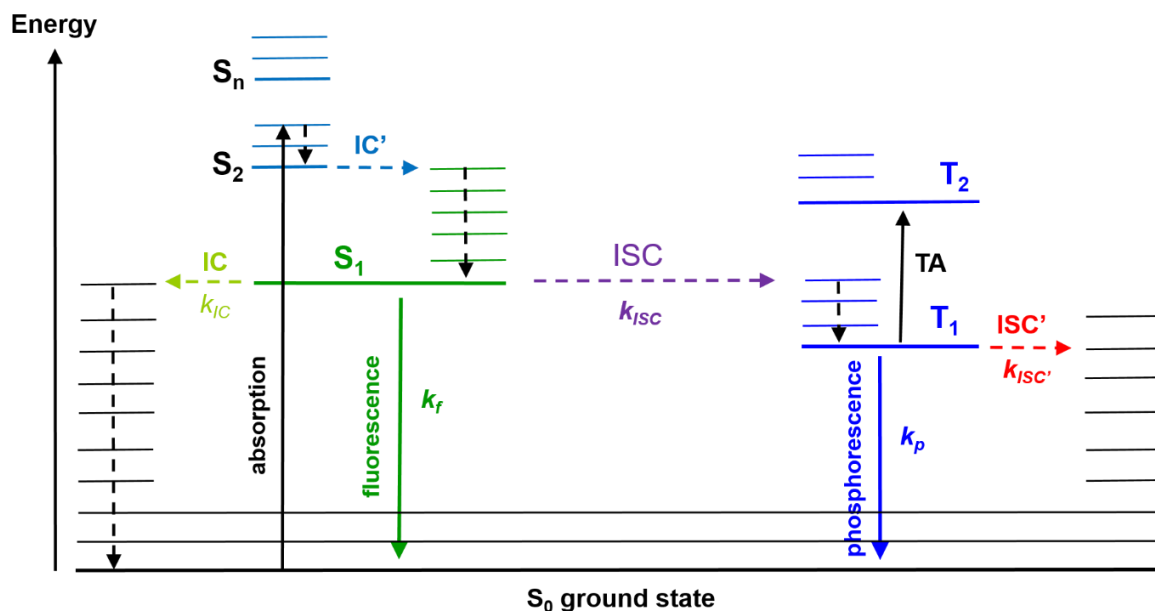


Figure 1.1: A Jablonski diagram showing the electronic and vibrational states for absorption, non-radiative decay and radiative decay via fluorescence or phosphorescence.

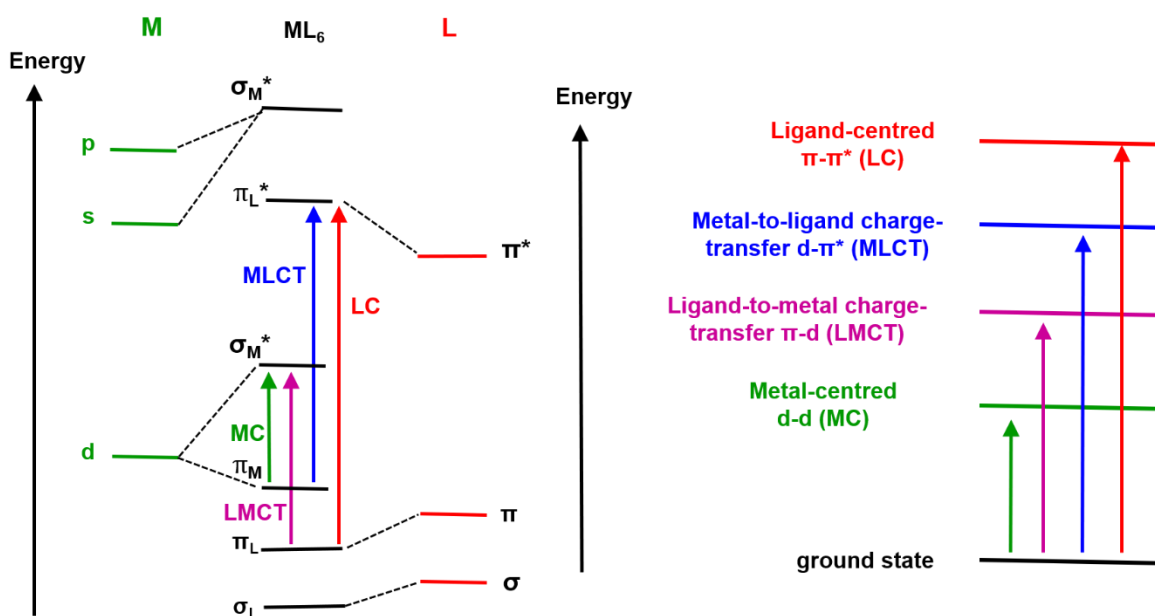


Figure 1.2: Diagrams showing the energy levels of molecular orbitals between which the excitations occur for an arbitrary metal complex (left) and the relative energies of these transitions as an energy level diagram in which the ground state is represented as having $E=0$ (right).

1.1.2 The efficiency of luminance in metal complexes

The efficiency of luminescence is quantified by the quantum yield, ϕ_{lum} , which is simply the ratio of the number of photons emitted to the number of photons absorbed. The quantum yield, also known as the photoluminescence quantum yield (PLQY), can be calculated using equation 1 with the assumption that the emissive state is formed with unitary efficiency. Equations 2 and 3 define the rates of radiative and non-radiative decay, k_r and k_{nr} respectively. The luminance lifetime, τ , is defined as the reciprocal of the experimentally determined rate constant of decay (equation 4).

$$\Phi_{lum} = \frac{k_r}{k_r + k_{nr}} \quad (1)$$

$$k_r = \Phi \tau^{-1} \quad (2)$$

$$k_{nr} = (\tau^{-1} - k_r) \quad (3)$$

$$\tau = \frac{1}{k_r + k_{nr}} \quad (4)$$

Luminescence is favoured by high rates of radiative decay and by low rates of non-radiative decay. Efficient phosphorescence is often hard to achieve due to the spin-forbidden nature of the transition which makes k_r low. The use of heavy metals such as iridium and platinum promote SOC in which the $M_S = 0$ component of the triplet is mixed with the singlet, therefore the spin-selection rule is relaxed and k_r is raised.

Equally important for efficient phosphorescence is suppression of k_{nr} which, apart from by lowering the temperature, can be achieved by raising the energy of MC excited states so they are higher in energy than that of the emitting triplet excited state. MC ^3d-d states are deactivating because they often involve population of antibonding orbitals which results in significant distortion in the excited state (**Figure 1.3**). Iridium(III) complexes with d^6 electron configuration adopt a low-spin octahedral arrangement because this geometry offers the greatest stabilization according to ligand field theory, the two highest-energy orbitals, $d_{x^2-y^2}$ and d_{z^2} remaining unoccupied (**Figure 1.4**).³ These orbitals are made less thermally accessible by large ligand field splitting arising from 3rd row transition metals and strong-field ligands with good σ -donating and/or π -accepting character. C-deprotonated cyclometalated ligands are strong σ -donors which cause large d orbital splitting and raise the deactivating metal d-d states higher in energy, helping to keep k_{nr} low. Cyclometallation involves the deprotonation of the aromatic C–H upon binding and the subsequent formation of a covalent metal–carbon bond; hence cyclometallating ligands are anionic. A common example of such a ligand is 2-phenylpyridine (ppyH). Cyclometallation also introduces more MLCT character into the lowest-lying excited state and this involvement of the metal in electronic transitions is key to promoting the formally-forbidden phosphorescent emission through its beneficial effect on k_r .⁴

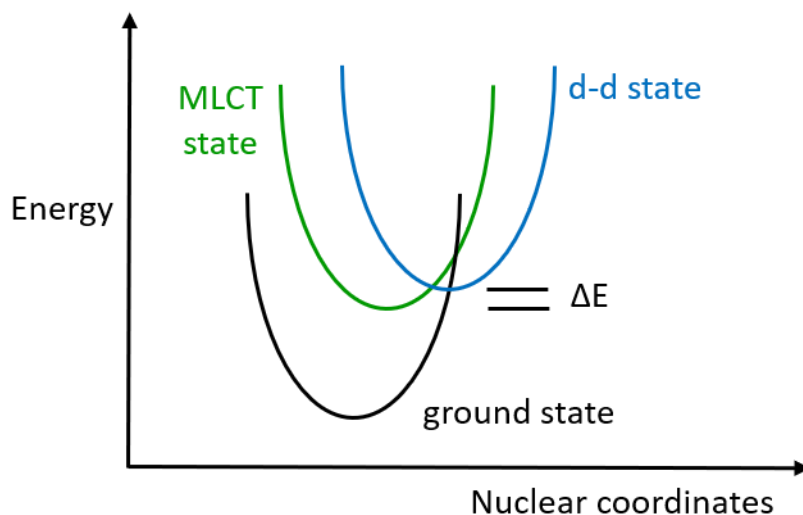


Figure 1.3: A close-lying d-d state can provide a drainpipe for deactivation of a lower-lying state at RT.

Another method of reducing k_{nr} is to decrease the amount of structural distortion in the excited state relative to the ground state. This is because a large difference between ground- and excited-state geometries results in a large overlap of vibrational wavefunctions (**Figure 1.5**)⁵ which favours intramolecular transfer of energy from electronic to vibrational excited states i.e. non-radiative decay.⁶ One way to reduce vibrational deactivation of excited states for efficient luminescence is often therefore to increase the complex's rigidity; this may be achieved through the use of ligands with high denticity. Tridentate⁴ and tetradentate⁷ ligands offer increased structural rigidity to the metal centre in comparison to bidentate ligands.⁸

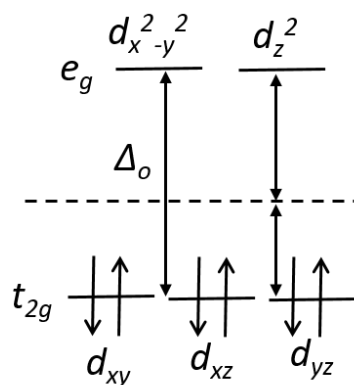


Figure 1.4: Simplified splitting of Ir^{III} d-orbitals due to an octahedral ligand field and the low-spin arrangement of electrons.

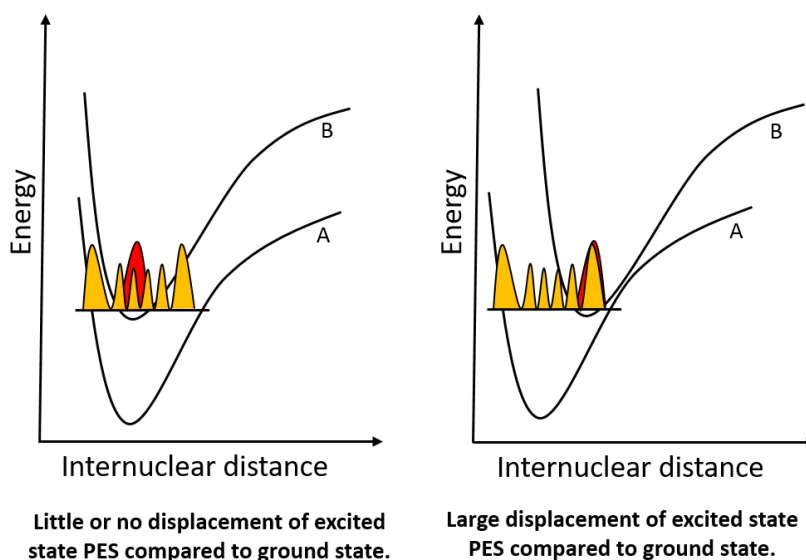


Figure 1.5: Overlap of vibrational wavefunctions of excited and ground states is favoured by a large displacement of potential energy surfaces (PES). A = ground state, B = excited state.

1.2 Light-emitting electrochemical cells

1.2.1 Introduction

Luminescent ionic transition metal complexes (iTMCs) have a wide range of applications from biological and cellular probes to photodynamic therapy and chemical sensing.^{9–14} However, one of the most promising applications of iTMCs is within the field of solid-state lighting, in particular, the light-emitting electrochemical cell (LEC) technology. This technology, alongside organic light-emitting diodes (OLEDs), is one of the leading examples of thin-film solid-state lighting making it a promising candidate for the next generation of high-performance, energy-efficient lighting. In contrast to conventional incandescent bulbs and LCD displays, LECs operate with low voltages without the need for a backlight. LECs also give higher colour purity, faster response time and improved contrast ratio compared to LED displays. With a broad range of potential applications in advertising, consumer electronics and novelty goods, LEC technology will be crucial in tackling the emerging climate crisis by reducing the electricity consumption and carbon emissions associated with artificial lighting which, in 2012, accounted for 20% of global electricity consumption (3 PWh) and 7% of global CO₂ production (2 Gt).¹⁵

1.2.2 Device architecture

The LEC device architecture is extremely simple; it consists of a light-emitting layer sandwiched between two electrodes (**Figure 1.6**). The light-emitting layer is traditionally a fluorescent conjugated polymer (CP) or a phosphorescent iTMC. During electroluminescence (EL), quantum mechanics shows that holes and electrons recombine to form excited states with a statistical triplet : singlet ratio of 3 : 1. Therefore the electroluminescence efficiency of fluorescent emitters is limited to 25% whereas the ability of phosphorescent iTMCs to harvest the symmetric triplet states in

addition to the antisymmetric singlet state means the internal quantum efficiency of iTMC-based LECs can theoretically reach 100%.^{16,17}

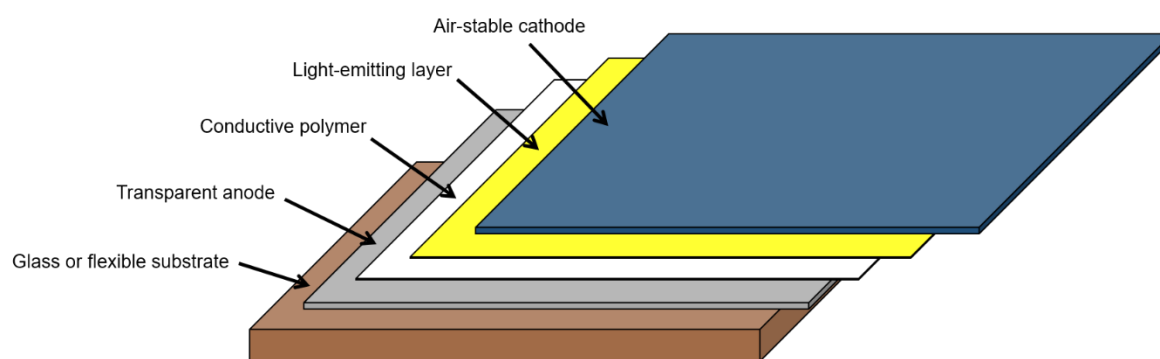


Figure 1.6: Structure of an LEC. Typically the light-emitting layer and conductive PEDOT:PSS polymer is sandwiched between an ITO anode and an aluminium cathode. The PEDOT:PSS layer aids charge injection from the anode whilst creating a uniform surface morphology for the light-emitting CP or iTMC.

The LEC architecture is much simpler than that of the OLED because, unlike OLEDs, the transition metal complex in LECs is ionic so it can act as both the light emitter and the charge carrier therefore no hole- or electron-transporting layers are required. Consequently, LEC manufacture is easier, cheaper and less energy-intensive than OLED manufacture. LECs can be processed from solutions of materials without the need for multi-layer vacuum sublimation. Additionally, the choice of suitable ionic LEC emitters is potentially far greater than the range of neutral OLED emitters.¹⁵

Cyclometalated iridium(III) complexes are by far the most studied class of iTMCs in LECs due to their excellent solid-state photoluminescence properties and their high solubility in benign solvents. Furthermore, Ir(III) complexes display wide colour tunability, covering almost the whole of the visible spectrum, due to the spatial separation of frontier molecular orbitals that makes it possible to modulate the energy levels of the HOMO and LUMO independently. In complexes of the type $[\text{Ir}(\text{C}^{\wedge}\text{N})_2(\text{N}^{\wedge}\text{N})]^+$, the HOMO is usually centred on the electron rich cyclometalating $\text{C}^{\wedge}\text{N}$ ligand whereas the LUMO typically resides on the electron deficient $\text{N}^{\wedge}\text{N}$ ancillary ligand (**Figure 1.7**). Therefore, by changing the electronic properties of both ligands through incorporation of different side groups, the HOMO and LUMO energy levels can be altered independently of one another and thus the HOMO-LUMO gap can be fine-tuned to shift emission towards the red or the blue.

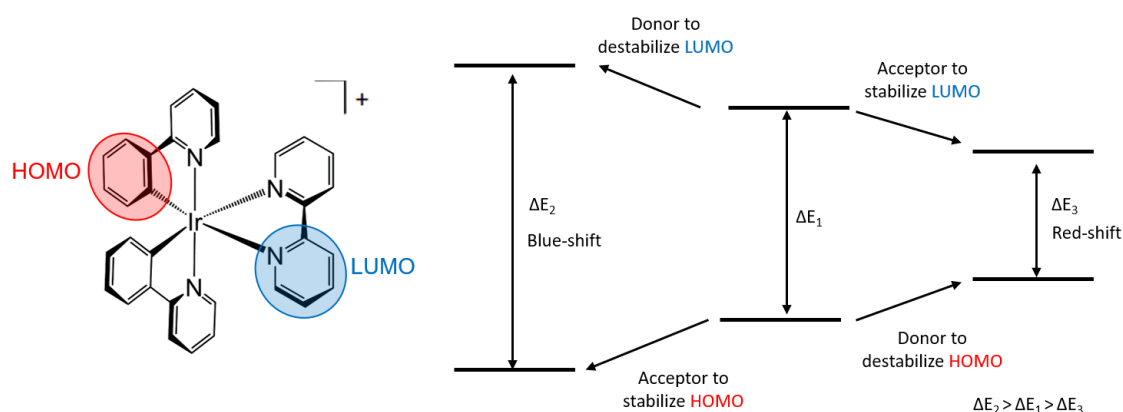


Figure 1.7: Illustration of where the HOMO and LUMO orbitals typically reside on a cationic iridium(III) species (left) and colour tuning strategies based on the independent modulation of the frontier molecular orbital energies (right).

1.2.3 Operation

Two models have been used to describe the operational mechanism of LECs, namely the electrochemical doping model and the electrodynamic model. The electrochemical doping mechanism, first proposed by Pei and co-workers in the mid-1990s, states that the spatially separated ions induce p- and n-type doping near the anode and cathode respectively. Highly conductive p- and n-doped regions form at the electrodes and extend over time until an intrinsic undoped layer is formed between them. The applied potential drops across this p-n junction to allow carrier recombination to occur (**Figure 1.8a**).¹⁸

At the turn of the century, the electrodynamic model was first proposed (**Figure 1.8b**); this model assumes that the accumulation of ions results in the formation of an electric double layer at both the cathode and anode which causes a sharp drop in potential near the electrode interfaces to promote charge injection from the electrodes. Carrier recombination occurs in the bulk of the emissive layer (the field-free region) where anions and cations are not separated.¹⁹

In 2010, it was shown that the electrochemical and electrodynamic models are essentially limits of one master model.²⁰ In short, LECs with poor carrier injection behave in a manner that resembles the electrodynamic model whereas in LECs with higher rates of carrier injection the electrochemical model is most accurate. Therefore, the relative charge injection rates at both electrodes determine the position of the light-emitting junction. The charge injection rate depends on several factors including the applied bias, the energy of the injection barrier, ion mobility and the temporal evolution of both the p- and n-doped regions. Consequently, the position of the light-emitting junction often shifts during operation due to an imbalance in charge injection vs. transport leading to exciton quenching and thus a reduction in device performance.

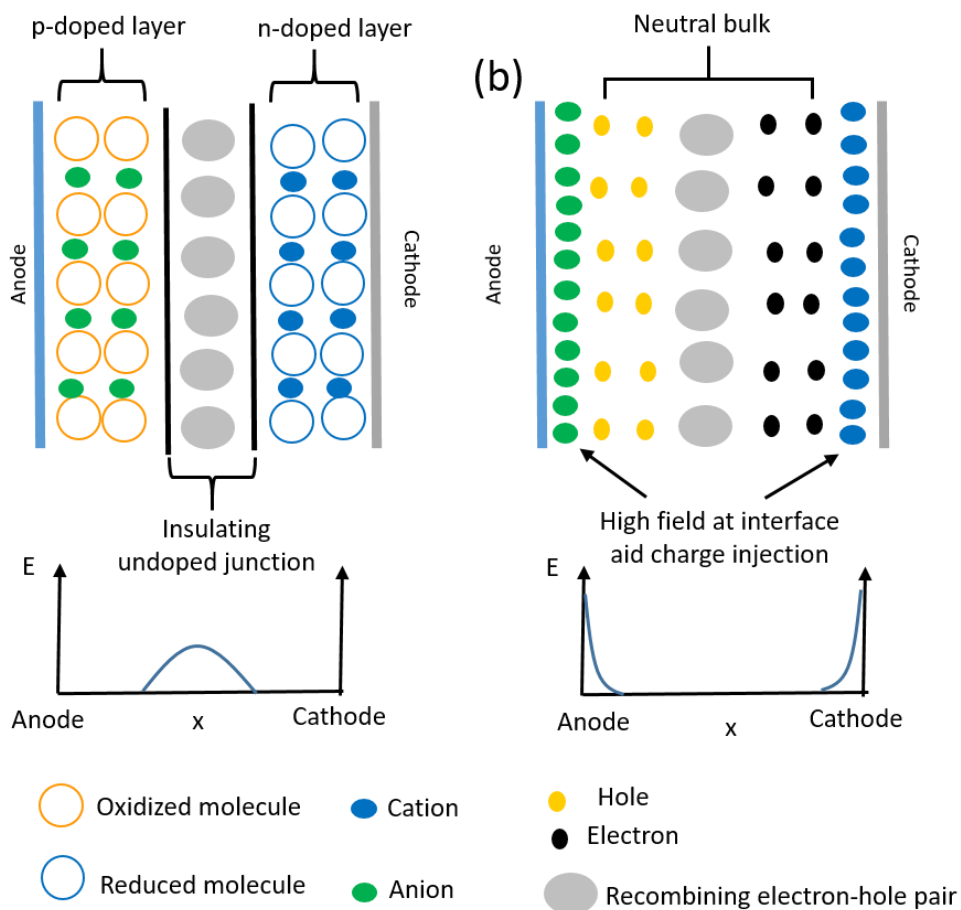


Figure 1.8: Electrochemical (a) and electrodynamic (b) models proposed for the LEC operation. The associated spatial distribution of the electric field is shown underneath.

1.2.4 Fabrication methods

iTMC-based LECs have been fabricated using a range of industry-relevant solution-based deposition techniques including spin coating, spray-deposition, dip coating, slot-die coating and doctor blade coating. For each technique, a uniform wet thin film of material is deposited onto a lightweight and/or flexible substrate. The solvent evaporates to leave behind a thin solid film of uniform thickness, typically around 100 nm. Each technique has unique advantages and disadvantages concerning the amount of material required, scalability, solution wastage, cost and complexity. For large-scale device manufacture, most of the above techniques are compatible with roll-to-roll and inkjet processing.¹⁶

1.2.5 Performance parameters

The performance of LEC devices can be measured by several parameters listed below:

- **Luminance (L):** Flux of light emitted by the device, measured in candela per unit of surface area (typically cd m^{-2}).
- **Lumen (lm):** The total quantity of visible light emitted by a source per unit of time. Lumen does not consider the spread or divergence of the light being emitted by the source in contrast to candela (cd). Lumen is related to the candela via the equation:

$$lm = cd \cdot sr \quad (5)$$

where sr is the steradian or square radian of the light emission (a full sphere has a solid angle of 4π steradians).

- **Turn-on time (t_{on}):** Time needed to reach maximum luminance or a threshold luminance value, typically 100 cd m^{-2} .
- **Lifetime:** Time taken for luminance to decay or to drop below a threshold value. Half-lifetimes ($t_{1/2}$) are frequently reported as the time taken to reach half of the maximum luminance.
- **External quantum efficiency (EQE):** The percentage of injected electrons that are released from the device as photons. For a bottom-emitting organic device, the maximal EQE can be estimated using the equation:

$$EQE = \frac{b\phi}{2n^2} \quad (6)$$

where ϕ is the PLQY of the emissive material, b is the recombination efficiency (equal to one for perfect carrier balance) and n is the refractive index of the glass substrate. The degree of carrier balance can be estimated by comparing the PLQY and EQE values.

- **Current density:** Flux of current through the device, measured in ampere per surface unit (typically A m^{-2}).
- **Current efficiency (CE):** The amount of emitted light per electric flux, measured in candela per ampere (cd A^{-1}).
- **Power efficiency (PE):** The amount of light emitted per electric input, measured in lumens per watt (lm W^{-1}).

1.2.6 LEC development

This next section will summarise recent progress that has been made in the LEC field regarding the design of new devices and the design of new iTMC emitters.

1.2.6.1 Device design and fabrication

In the last decade, many non-conventional LECs have been made in an attempt to expand the versatility and performance of this technology. Metal-free transparent electrodes made out of graphene or carbon nanotubes have been developed to create stretchable LECs for use in wearable electronics, smart skins and minimally invasive biomedical devices. Flexible LECs have also been fabricated using light-emitting gels as the active layer which consist of an iTMC, ionic additive, elastomeric material like polydimethylsiloxane (PDMS) and a gelation agent like metal oxides and/or fumed silica nanoparticles. These non-conventional LECs have dramatically widened the

substrate scope of LECs to include paper and textiles as well as 3D substrates such as kitchen forks and artwork.^{21,22}

Enhancements in LEC performance have been achieved by improving the balance between charge transport and charge recombination. In single layer iTMC-based LECs, ionic additives such as ionic liquids, e.g. [BMIM]PF₆, or lithium salts, e.g. LiPF₆, are typically formulated within the active layer to balance charge transport as the size and hence ion mobility of the Li⁺ cation more closely matches the PF₆⁻ anion in comparison to the Ir³⁺ cation. The use of these ionic additives has led to a dramatic decrease in LEC turn-on time and concurrent increase in lifetime.^{23,24} High performing host-guest LECs, in which the iTMC is doped into a host hole- or electron-transporting material such as a polymer or small molecule, have also been fabricated to reduce the degree of iTMC self-quenching (i.e. triplet-triplet annihilation) in the emissive layer. The carrier transporting properties and energy bandgaps of the host can be tailored to suit the guest iTMC, as can the exact host-guest ratio to make the recombination zone as central as possible. The host-guest approach has even been extended to include neutral transition metal complexes such as the blue-emitting FlrPic (**Figure 1.9**).^{25–27}

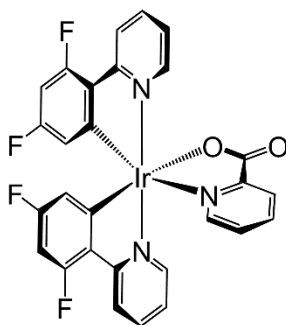


Figure 1.9: Structure of Flrpic. Flrpic = bis(2-(4,6-difluorophenyl)pyridinato-C²,N)(picolinato)iridium(III)

Other strategies to balance charge transport and recombination processes within the device include the use of metal oxide electrodes, e.g. ZnO and MoO₃, to reduce the energetic charge injection barriers, as well as the development of multi-layered LECs such as tandem LECs containing combinations of iTMC, polymer and recently gold nanoparticles.^{28,29} The thickness of the emissive layer is also another important parameter which has been optimized in sandwich-type LECs; as the thickness of the emissive layer increases, the amount of self-quenching decreases but if the distance between the recombination zone and the doped layers becomes too great, the carrier mobility deteriorates and the recombination zone becomes less centralized leading to increased exciton quenching.^{30,31} Finally, pulsed current operation has significantly improved LEC lifetime and efficiency compared to traditional constant current driving; this can be attributed to the fact that during pulsed current driving the doped layers do not extend significantly with time and the device has time to relax between current pulses to mitigate the extent of exciton quenching.^{32–34}

1.2.6.2 Design of new emitters

As mentioned previously, cationic iridium(III) complexes have been by far the most popular choice of iTMC for LECs. A review of LEC-containing cationic Ir(III) complexes is given in Chapter 2 including an overview of iTMC design strategies and principles to optimize their performance in LECs. Despite its popularity, the high cost and scarcity of iridium has led to the development of other transition metal-containing emitters in the context of developing sustainable and high-performing LECs. The motivation for developing this next generation of emitters originates from the limitations of current emitters which are particularly severe in the blue and red regions of the visible spectrum. Blue-emitting LECs lack stability due to the degradation of the iTMC which may occur following an over-charge injection process or a population of dissociative excited states upon charge recombination. Red-emitting LECs suffer from the inherent poor luminescence properties of the emitter that arise due to the energy gap law facilitating non-radiative decay. Furthermore, phase separation within the iTMC formulation can severely impact the quality of the active layer morphology resulting in low performing devices.¹⁶

Copper(I) complexes are arguably one of the most exciting alternatives to iridium(III) emitters due to the lower cost of copper, its high natural abundance, well-known chemistry and the promising photoluminescence properties of an ever-expanding range of Cu(I) complexes spanning almost the entire visible spectrum. Copper(I) complexes have no MC states which are typically degradative non-radiative pathways for iridium; instead they may emit via a TADF mechanism which involves thermal population of the energetically higher singlet excited states from the triplet state via reverse inter-system crossing and hence all the generated excitons in the lowest excited singlet state can be harvested. Much work over the last decade has focused on the optimization of heteroleptic complexes of the type $[\text{Cu}(\text{N}^{\wedge}\text{N})(\text{P}^{\wedge}\text{P})]^+$ (where $\text{N}^{\wedge}\text{N}$ = diamine, phen, derivatives of bpy and $\text{P}^{\wedge}\text{P}$ = derivatives of POP, xantphos, DPPE and DPPP) through rational ligand design. Recently, Sessolo, Ortí, Housecroft and co-workers tuned the steric bulk and Tolman cone angle of several xantphos derivatives and found that the addition of *tert*-butyl groups was beneficial to device performance due to a larger spatial separation of Cu(I) ions.³⁵ The LEC containing complex (i) (**Figure 1.10**) achieved the fastest turn-on time ($t_{\text{on}} = 1$ minute), the highest maximum luminance ($L_{\text{max}} = 370 \text{ cd m}^{-2}$) and the highest current efficiency ($\text{CE}_{\text{max}} = 3.7 \text{ cd A}^{-1}$) of the series driven under an average pulsed current of 100 A m^{-2} (50% duty cycle, 1kHz), exceeding the performance parameters of its non-*tert*-butyl analogue ($t_{\text{on}} = 10$ minutes, $L_{\text{max}} = 145 \text{ cd m}^{-2}$, $\text{CE}_{\text{max}} = 3.0 \text{ cd A}^{-1}$).³⁶ The most stable device contained complex (ii) (**Figure 1.10**) whose half-life ($t_{1/2} = 54$ minutes) was significantly longer than that of the device containing complex (i) ($t_{1/2} = < 5$ minutes). Both devices, however, suffered from shorter lifetimes than their non-*tert*-butyl analogues ($t_{1/2} = 0.8 \text{ h}$ and 15 h), although caution is needed in deriving a direct comparison between these values because the average pulsed

current density differed. The authors found that the increased structural rigidity of the xantphos diphosphine ligand provides enhanced electrochemical stability, reversibility and higher solid-state PLQYs compared to POP, for example, ϕ of (ii) = 59% vs. 43%.³⁷

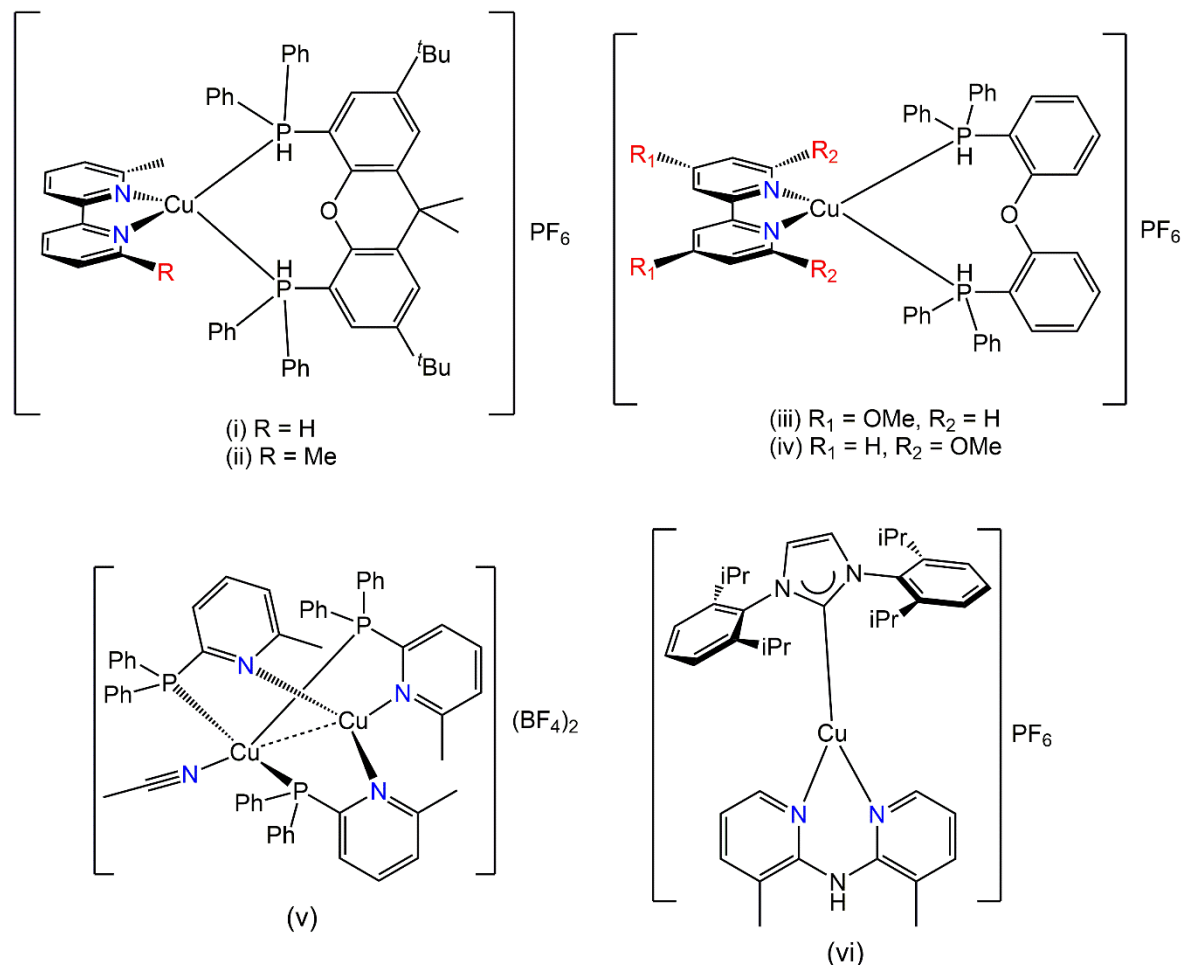


Figure 1.10: Structures of copper(I) complexes (i) to (vi) which have been tested in LECs.

Tuning of the N[^]N ligand has also been done by varying the steric demands of bpy ligands to stabilize the distorted tetrahedral geometry of Cu(I) complexes. Bromo-, chloro-³⁸, CF_3 -³⁹, methyl-⁴⁰, methoxy-⁴¹, alkylthio-, phenylthio- and phenyloxy⁴²-substituted bpys, often symmetrically substituted at the *ortho* position to induce twisting of the bipyridyl units coupled with a tilting of the heterocyclic ring plane, lead to enhanced luminescence as the photoinduced flattening distortion is limited. Upon excitation to an MLCT state, the tetrahedral Cu(I) ion is transiently oxidised to Cu(II), which has a preference for square planar geometry; the accompanying distortion in the excited state opens up non-radiative decay pathways which deactivate the excited state and lower luminescence efficiency.

Costa and co-workers discovered that the addition of N[^]N substituents with more negative σ_p parameters resulted in enhanced photoluminescence (PL) and electroluminescence (EL) properties. They added the methoxy group, the substituent with the most negative σ_p value in their work ($\sigma_p = -0.27$), to the 4' and 6' positions of bpy. The LEC containing complex (iii) (**Figure 1.10**) achieved a

maximum luminance of 54 cd m^{-2} and a maximum current efficiency of 0.35 cd A^{-1} driven under a pulsed current of 5 mA compared to the device containing the unsubstituted bpy analogue with corresponding performance parameters of 14 cd m^{-2} and 0.08 cd A^{-1} .⁴³ Under the same operation conditions, the LEC containing complex (iv) (**Figure 1.10**) achieved a maximum luminance of 25 cd m^{-2} after 7.2 minutes with a half-life of 2.6 h whereas the device containing the unsubstituted bpy analogue took twice as long to reach a maximum luminance of 22 cd m^{-2} with a half-life of 0.5 h.⁴¹ The enhanced performances of (iii) and (iv) were rationalised in terms of the strong electron-donating influence of the methoxy group which strengthens the metal-ligand coordination and prevents significant structural distortion upon excitation. Not only does the methoxy group strengthen the ligand to metal $n \rightarrow d\sigma$ interaction, it also enhances π -back bonding as the more electron-rich metal donates electrons back into the π^* -antibonding orbital of the ligand. The authors of the study also comment that the easy rotation of the methoxy moiety further shields the coordination sphere of the Cu(I) metal ion, inhibiting solvent-assisted ligand exchange processes in coordinative solvents.⁴¹

Phosphine-pyridine ($P^{\wedge}N$) and N-heterocyclic carbene (NHC) ligands are two other types of ligand that have been incorporated into Cu(I) complexes. Nierengarten and others prepared a series of dinuclear Cu(I) complexes from 2-diphenylphosphino-6-methylpyridine and tested the complex with the highest solid-state PLQY of the series, (v) ($\phi = 81\%$, **Figure 1.10**) in a PVK-host LEC. Under a constant bias of 7 V, the LEC containing (v) reached a maximum luminance of 5 cd m^{-2} after ≈ 3 minutes and displayed a half-life of ≈ 5 minutes.⁴⁴ The emitted colour was white due to the combination of emission bands from (v) ($\lambda_{\text{max}} = 492 \text{ nm}$, neat powder) and PVK.

Gaillard and co-workers reported a family of 19 blue-emitting Cu(I) complexes containing both NHC-ligands and dipyridylamine-based ligands. Under a pulsed current of 2.5 mA, the best-performing device containing complex (vi) (**Figure 1.10**) achieved a maximum luminance and current efficiency of 80 cd m^{-2} and 0.24 cd A^{-1} respectively.⁴⁵

Recent spectro-electrochemical and electrochemical impedance spectroscopy studies on NHC copper(I)-based LECs have determined that the device performance is limited during the hole injection process; the addition of a hole transporting layer (i.e. CBP) to decouple hole/electron injection enhanced the performance parameters of the device containing (vi) to $L_{\text{max}} = 160 \text{ cd m}^{-2}$ and $CE_{\text{max}} = 1.2 \text{ cd A}^{-1}$. These studies also revealed that the degradation mechanism of the NHC-Cu(I) emitter goes all the way back to the synthesis of the iTMC; specifically the formation of homoleptic or dinuclear species, which are extremely efficient luminescence quenchers, during the reaction or over time in solution.⁴⁶ The conditions of preparing the active layer are also critical i.e. the type of solvent, ageing time, deposition technique etc. therefore this work clearly shows the need to optimize every aspect of the iTMC synthesis and device fabrication, not just iTMC design.

Osmium(II) is another transition metal whose photophysical properties have been extensively investigated over the past four decades. The appeal of Os(II) lies in the inherent ground and excited state stability of its polypyridyl complexes and its reversible redox chemistry. In 2016, Elliott and co-workers reported one of the first examples of Os(II)-based LECs which contained bis-1,2,3-triazol-4-yl ligands.⁴⁷ They prepared three such heteroleptic Os(II) bitriazolyl complexes which displayed deep-red/near-infrared (NIR) emission in aerated MeCN ($\lambda_{\text{max}} = 713\text{-}732\text{ nm}$) and they incorporated two of them in LECs with the ionic liquid [BMIM]PF₆ driven under a bias of 3 V. It was found the introduction of the triazole ligand led to an overall reduction in the current density and operational lifetime of LECs compared with a device containing the parent complex, [Os(bpy)₃](PF₆)₂ (complex (vii)), **Figure 1.11**), whose performance parameters were: $L_{\text{max}} = 259\text{ }\mu\text{Wcm}^{-2}$, $t_{1/2} > 18$ hours and $\text{EQE}_{\text{max}} = 0.06\%$.

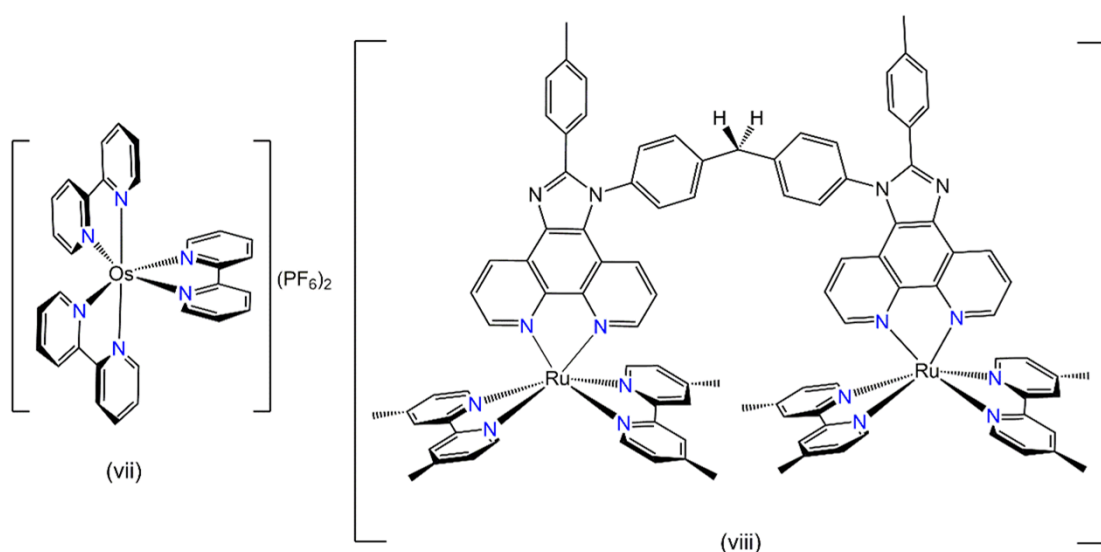


Figure 1.11: Structures of osmium(II) (left) and di-ruthenium(II) (right) complexes, ((vii) and (viii)) respectively, which have been used in LECs.

Near-IR-emitting LECs have also been fabricated using dinuclear ruthenium phenanthroimidazole complexes.⁴⁸ Near-IR emitters have promising applications in bio-imaging, telecommunications and wound healing but the EQE values of electroluminescent devices are usually low due to the intrinsic difficulty of the energy gap law that strongly favours non-radiative decay at longer wavelengths. Bideh and Shahroosv found that the use of a dinuclear complex proved to be an effective strategy. The inclusion of electron-donating methyl groups on the bpy units of complex (viii) (**Figure 1.11**) red shifted the EL spectrum by 55 nm (1260 cm^{-1}) to $\lambda_{\text{max}} = 690\text{ nm}$ and improved surface morphology of the LEC which had L_{max} , $t_{1/2}$ and EQE values of 742 cd m^{-2} , 18 minutes and 0.68% respectively.

LECs containing other luminescent transition metals of rhenium(I),⁴⁹ zinc(II), platinum(II), palladium(II) and tin(IV)⁵⁰ have been fabricated by Massi, Costa and others. The yellow-emitting LEC

($\lambda_{\max} = 535 \text{ nm}$) containing complex (ix) (**Figure 1.12**) suffered from poor stability and efficiency under a constant bias of 6 V ($t_{1/2} = 40 \text{ minutes}$, $\text{CE}_{\max} = 0.06 \text{ cd A}^{-1}$) but the authors point to the fact that this is the first example of a rhenium-LEC in the literature. They used a methylated tetrazole ligand whose photophysical properties can be significantly changed (i.e. blue shift of $\lambda_{\max}$ by about 30 nm, $\Delta E = 1010 \text{ cm}^{-1}$), in a reversible manner, when the tetrazole ring becomes protonated by addition of triflic acid.⁵¹

The metals Zn^{2+} , Pt^{2+} , Pd^{2+} and Sn^{4+} were contained in tetradentate porphyrin rings (**Figure 1.12**) and the effect of changing the metal core on LEC performance was investigated. Costa and co-workers placed bulky 3,5 di-*tert*-butyl-phenyl substituents at the *meso* position in an attempt to enhance the quality of the film morphology and prevent aggregation-induced self-quenching arising from the close proximity between porphyrins. Each metal core provides different radiative mechanisms i.e. TADF for Zn^{2+} , phosphorescence for Pt^{2+} , fluorescence for Zn^{2+} and dual fluorescence/TADF emission for Pd^{2+} . All of the complexes produce deep red-emitting LECs ($\lambda_{\max} = 650\text{-}750 \text{ nm}$) but there is a trade-off between device efficiency and stability, for example, the Pt-LEC exhibits the highest EQE of 0.16% but has a lifetime of only a few hours whereas the lifetimes of the Zn- and Sn-LECs are much longer (hundreds of hours) but their EQEs are only 0.017% and 0.0061% respectively.⁵⁰

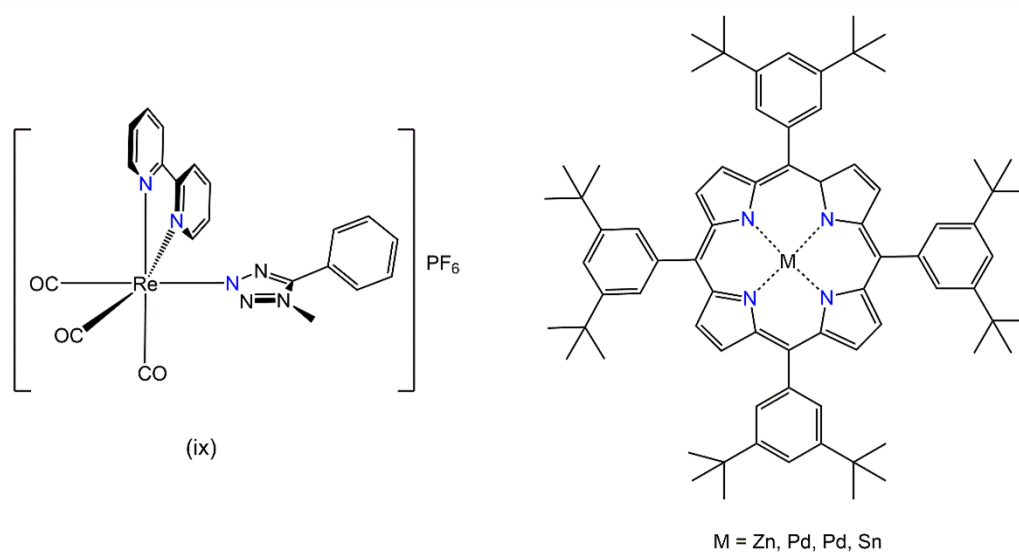


Figure 1.12: Structures of the Re(I) complex (ix), left, and the metallated porphyrins (right) which have been used in LECs.

Finally, there are many examples of small molecule-based LECs in the literature as well as LECs containing quantum dots and perovskite nanoparticles; a good review of these types of emitters in LECs was written by Costa and Fresta in 2017.¹⁶

1.3 Aims and objectives of research

The aims of this research are to continue the exploration of novel iridium and platinum complexes featuring bidentate, tridentate and tetradentate ligands. The choice and combination of ligands is varied to produce complexes whose emissions span the visible spectrum. A combination of bidentate bpy- and pyrazolopyridine-derived ligands (Chapter 2), tridentate N[^]C[^]N ligands (Chapter 3) and tetradentate ligands (Chapter 4) with iridium(III) and platinum(II) are investigated to see if increasing complex rigidity can enhance the PLQY. In addition, a series of dinuclear iridium(III) and platinum(II) complexes containing a *p*-anisidine-based linker have been synthesized to investigate the effect of two metal centres on photophysical properties (Chapter 5). In complexes bearing a monodentate chloride ligand, metathesis of the chloride with phenylacetylene and AgCN has been achieved in an attempt to further enhance photophysical properties whilst, at the same time, red- or blue shifting the emission. All complexes reported in this thesis have been fully characterised and the subsequent chapters 2-5 include discussions on their RT and low temperature photochemistry, electrochemistry, X-ray crystallography in addition to theoretical DFT and TD-DFT simulations. Chapter 6 describes the conclusions drawn from this body of research and includes possible avenues for future work.

Chapter 2 - Iridium complexes featuring bidentate ligands

2.1 Introduction

The development of cationic tris-bidentate iridium(III) complexes continues to be a prosperous and well-documented field of research. The excellent luminescent properties of $[\text{Ir}(\text{C}^{\wedge}\text{N})_2(\text{N}^{\wedge}\text{N})]^+$ -type complexes have led to many applications, including as the emitter in iTMC-based LEC devices.^{52,53} Moreover, synthesis of both the bidentate ligands and Ir complexes is straightforward; the $\text{C}^{\wedge}\text{N}$ and $\text{N}^{\wedge}\text{N}$ ligands, typically based on 2-phenylpyridine (ppyH) and 2,2'-bipyridine (bpy) frameworks respectively, can be synthesized using metal-catalysed cross couplings (e.g. Suzuki, Stille or Negishi couplings) whilst the complex is obtained after a 2-step procedure involving a chloro-bridged Ir dimer. **Figure 2.1** displays the 2-step synthesis of the archetype complex, $[\text{Ir}(\text{ppy})_2(\text{bpy})]\text{PF}_6$, which was first synthesized by Watts *et al.* in 1986.⁵⁴ The dimer $[\text{Ir}(\text{ppy})_2\mu\text{-Cl}]_2$ is cleaved by bpy under mild conditions to give $[\text{Ir}(\text{ppy})_2(\text{bpy})]\text{Cl}$ which can then be subjected to ion-exchange to form $[\text{Ir}(\text{ppy})_2(\text{bpy})]\text{PF}_6$ which is usually more soluble and easier to purify than the corresponding chloride complex.

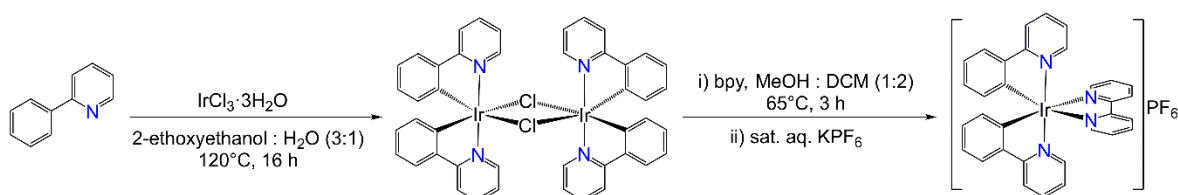


Figure 2.1: Synthetic route to $[\text{Ir}(\text{ppy})_2(\text{bpy})]\text{PF}_6$.

The first example of an LEC containing an ionic iridium(III) complex (complex (i), **Figure 2.2**) was reported by Slinker *et al.* in 2004.⁵⁵ They fabricated a yellow-emitting single-layer device with a brightness of 330 cd m^{-2} and a luminous power efficiency of over 10 lm W^{-1} at 3 V. This seminal work led to the design and fabrication of many iTMC-based LECs in an attempt to optimize device manufacture and performance sufficiently for commercial application of this technology, in particular, improving device stability and performance at either extreme of the visible spectrum. The complexes discussed in this literature review have all been used in LECs. However, as no devices were prepared for this body of work, their LEC performance data are less relevant so have been tabulated in the Appendix (**Table 8.1** and **Table 8.2**) rather than being discussed in detail. Instead we shall examine how a range of iTMC design strategies have led to enhanced PL.

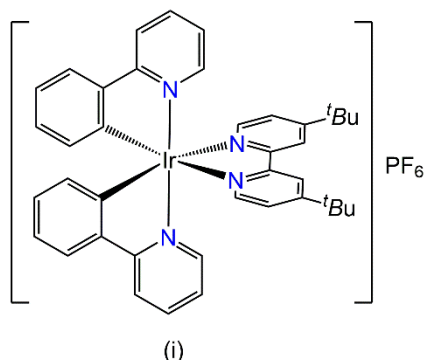


Figure 2.2: Structure of complex (i), $[Ir(ppy)_2(di^tBu_2bpy)]PF_6$; the first cationic Ir(III) complex used in an LEC.

2.2 iTMC design strategies for improved quantum yield

LEC lifetimes are often limited by degradation of the Ir-iTMC during device operation which can be caused by water-assisted ligand-exchange reactions. Hence, the use of bulky hydrophobic ligands to shield the iridium core from nucleophilic attack is an established strategy to enhance LEC stability^{52,53} Furthermore, sterically demanding ligands provide a greater spatial separation between Ir(III) cations in the solid state which reduces the extent of self-quenching.

Peripheral steric bulk can be added to either C[^]N or N[^]N ligands in $[Ir(C^{\wedge}N)_2(N^{\wedge}N)]PF_6$ -type complexes. Several examples of ppyH-based cyclometalating ligands bearing non-chelating methyl, methoxy, phenyl, adamantyl, *tert*-butyl, triphenylsilyl, triphenylamine and mesityl substituents are shown in **Figure 2.3**.^{56–65} The mesityl group (1,3,5-trimethylphenyl) is a relevant example of a sterically-demanding moiety which has been added to the position *trans* to the Ir–N bond of the C[^]N ligand in eight complexes, (ii) to (ix) (**Figure 2.4**).

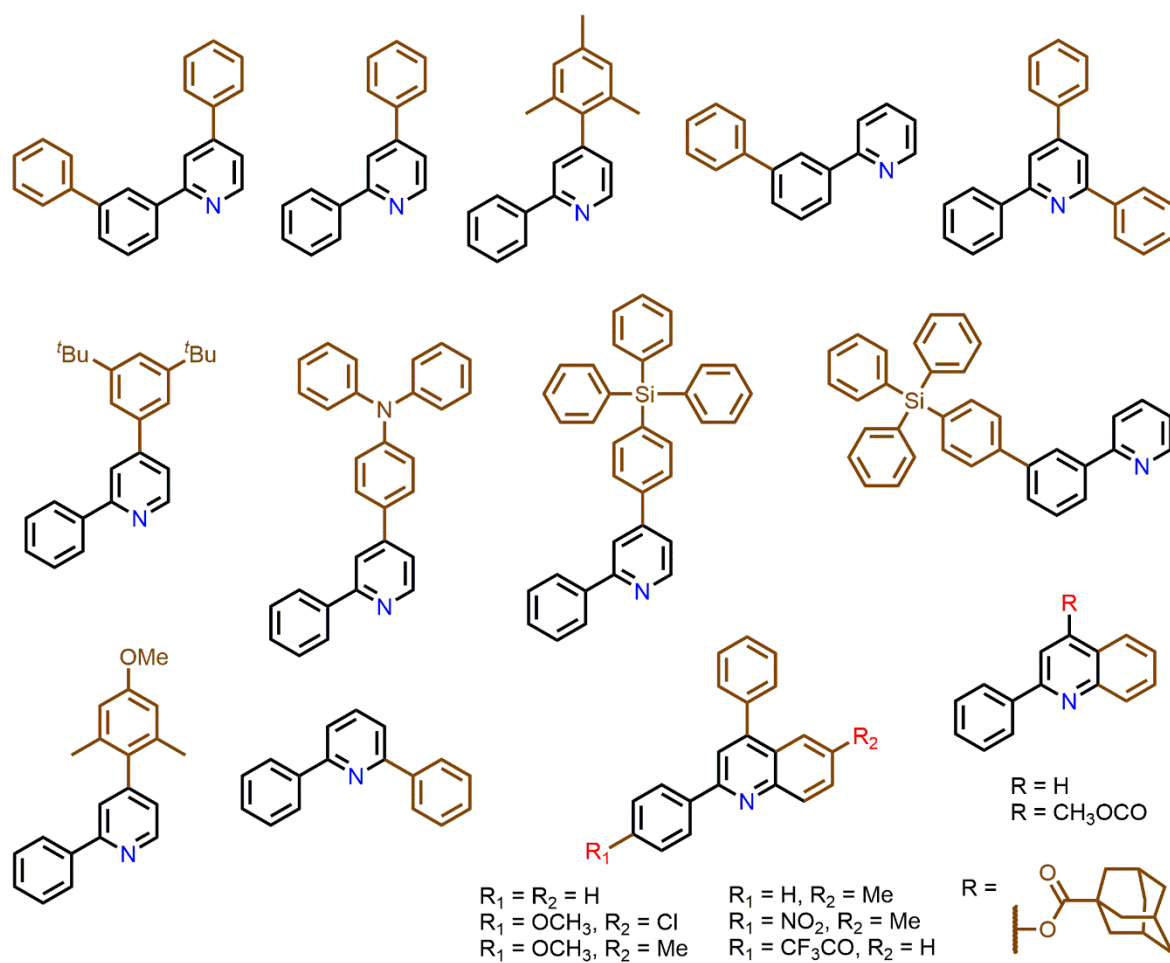


Figure 2.3: Structures of cyclometalating ligands whereby phenyl-based steric bulk (highlighted in brown) has been incorporated onto the ppyH framework. Coordinating nitrogen atom is coloured in blue.

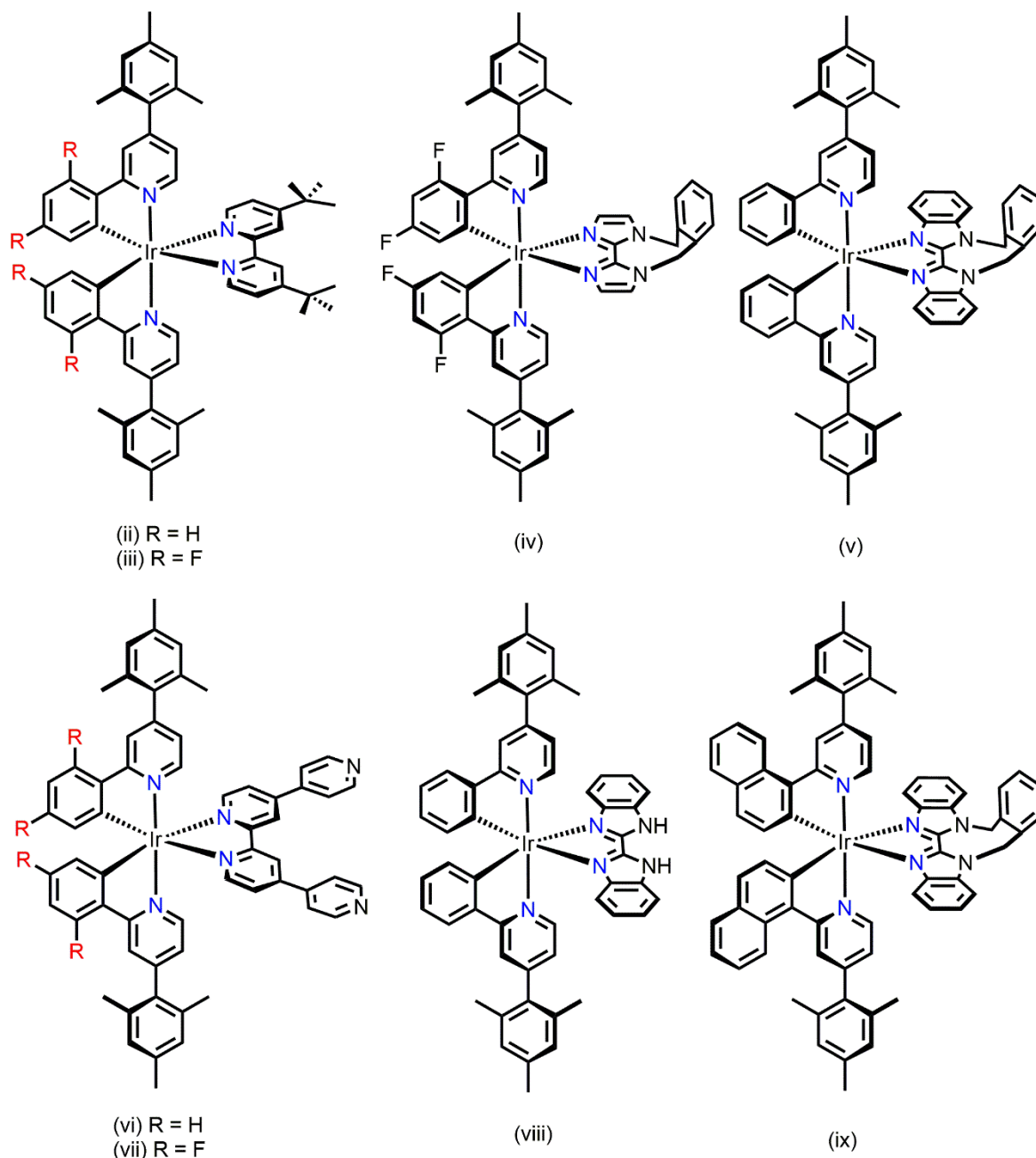


Figure 2.4: Structures of complexes (ii) to (ix) which bear bulky mesityl-containing cyclometalating ligands.

The emissions of (ii) to (ix) span from deep blue ($\lambda_{\text{max}} = 459 \text{ nm}$) to red ($\lambda_{\text{max}} = 638 \text{ nm}$) and the bluest emitting complex, (iv) has the highest quantum yield in the series of 90% (**Table 2.1**). The bracketed values in the rows of complexes (ii), (iii), (vi) and (viii) refer to data for the equivalent complexes without the mesityl groups.^{13,66,67} Addition of mesityl groups to the ppy or dfppy ligands of (iii), (vi) and (viii) increases quantum yield by as much as 45%. The inclusion of the mesityl group has a minimal effect on emission colour, for example, the emission maxima of (vi) and its non-mesityl-containing equivalent differ by only 4 nm ($\lambda_{\text{max}} = 638 \text{ vs. } 642 \text{ nm}$, $\Delta E = 98 \text{ cm}^{-1}$) whilst the emission maxima of (ii) and (iii) are identical to their ppy or dfppy equivalents. Replacing the pyridine unit of ppy with naphthalene, however, red shifts emission by 26 nm (792 cm^{-1}) due to the extension of the π -system which raises the HOMO energy ($\lambda_{\text{max}} = 586, 623 \text{ nm}$ (ix) vs. $\lambda_{\text{max}} = 560, 580 \text{ nm}$ (v)).

Sterically-demanding N[^]N ligands can also be used to shield the iridium centre, as shown by the examples in **Figure 2.5** which feature bpy-based ligands with peripheral hydrophobic groups.^{56,68–73} Complexes (x) and (xi) are examples of complexes bearing a bulky N[^]N ligand, in this case, diph₂bpy (**Figure 2.5**).⁵⁶ They are both orange emitters at RT with emission maxima of 604 nm and 625 nm respectively (**Table 2.1**). The emission of (x) is similar to that of its bpy analogue ($\lambda_{\text{max}} = 598$ nm) but its quantum yield ($\phi = 25\%$) is 9% higher.

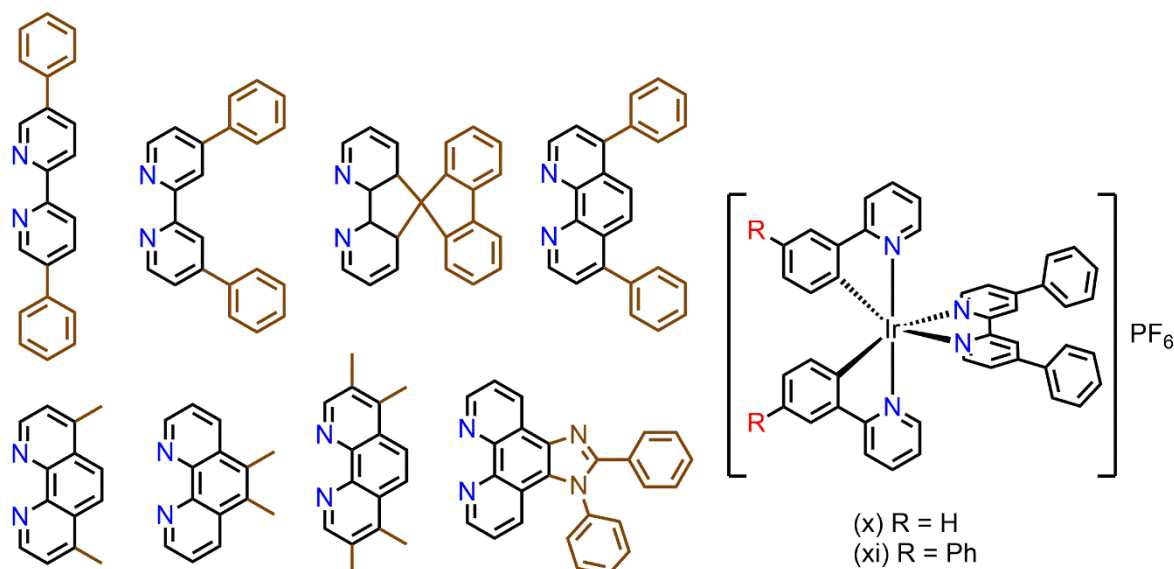


Figure 2.5: Selection of N[^]N ligands based on bpy (left) bearing sterically-demanding peripheral substituents (highlighted in brown). Structures of complexes (x) and (xi) which contain the bulky N[^]N ligand, diph₂bpy. Coordinating nitrogen atoms are coloured in blue.

Another well-known method to increase LEC stability is to incorporate intramolecular π – π interactions within the iTMC; this is most often achieved by adding an aromatic group to the *ortho* position of the N[^]N ligand to facilitate face-to-face π – π stacking between the N[^]N and C[^]N ligands. **Figure 2.6** displays several examples of N[^]N ligands capable of π – π stacking via their peripheral phenyl or naphthyl group(s).^{74–81} X-ray crystallography and DFT calculations of complexes (xii) and (xiii) (**Figure 2.6**) confirm that face-to-face π -stacking occurs between the phenyl rings of phbpy and ppy (highlighted in red and blue respectively). These intramolecular interactions limit the amount of expansion along the N–Ir–N vector in the excited state which reduces the risk of H₂O attack. The quantum yields and emissions of complexes (xii) and (xiii) are similar to that of [Ir(ppy)₂(bpy)]PF₆ as all three complexes are yellow/orange emitters ($\lambda_{\text{max}} = 585$ –600 nm) with quantum yields below 15% (**Table 2.1**).^{79,82,83}

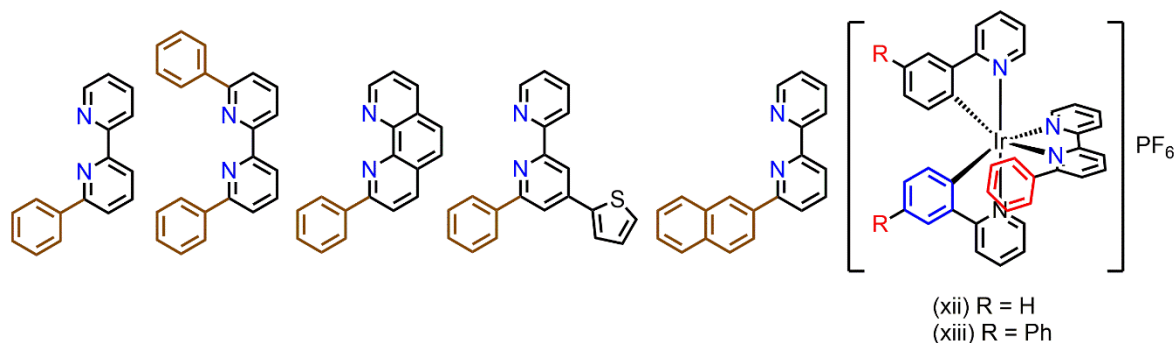


Figure 2.6: Selection of N^N ligands based on bpy (left) featuring a 6-phenyl or 6-naphthyl substituent (highlighted in brown) which can form intramolecular π - π stacking interactions with the C^N ligand as illustrated by the red- and blue-coloured aromatic systems of complexes (xii) and (xiii) (right).

Sometimes the two strategies of using N^N ligands that are both sterically-demanding and capable of π -stacking are combined to further improve iTMC stability (Figure 2.7).^{79,84} Complexes (xiv) and (xv) (Figure 2.7) feature similar bpy-based ligands which:

- form π - π stacking interactions with ppy via their common 6-phenyl substituent.
- bear a peripheral steric shield in the form of a di-O-alkylated phenyl group in the 4'-position.

Complexes (xiv) and (xv) differ according to their O-alkyl chain but their RT photophysical properties in MeCN solution lie within a close range i.e. $\lambda_{\text{max}} = 593\text{-}595$ nm, $\phi = 7\text{-}10\%$ and $\tau = 0.13\text{-}0.15$ μs (Table 2.1).³³

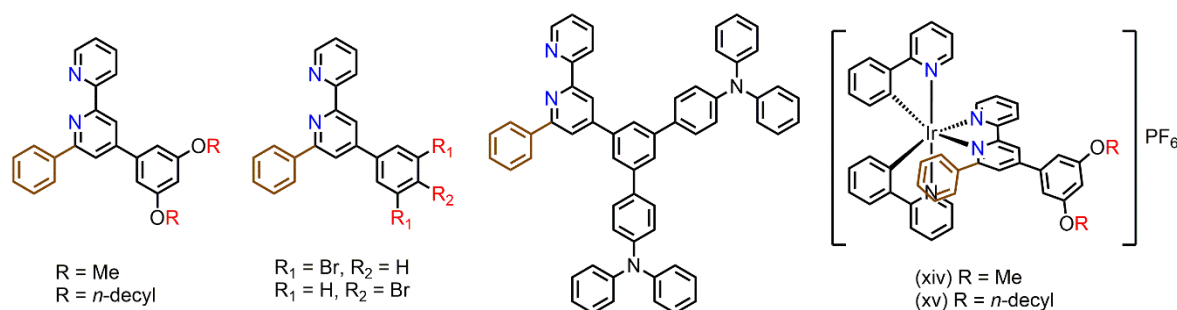


Figure 2.7: Selection of bpy-based ligands containing both a 6-phenyl substituent for π - π stacking (highlighted in brown) and large sterically demanding phenyl-based groups in the 4'-position (left). Structures of complexes (xiv) and (xv), right, which feature a bulky 6-phenyl-substituted bpy ligand.

Finally, iTMC stability can be improved by modifying the synthetic procedure to remove chloride counter-ions which are detrimental to device performance. Schneider *et al.* found that these trace chloride impurities, which originate from the chloro-bridged dimer, were responsible for batch-to-batch variability in LEC performance of devices based on [Ir(ppy)₂(bpy)]PF₆. Therefore, they proposed a chloride-free route which involved the addition of AgPF₆ as well as NH₄PF₆ during ion-exchange to ensure all chloride ions are removed as AgCl.⁸⁵

These iTMC design strategies have resulted in LECs with lifetimes of months, as exemplified by the half-lives of the LECs containing complexes (xii) and (xiii) which are 1290 h and 2800 h respectively (Appendix **Table 8.1**).^{79,80}

Table 2.1: Photophysical properties of (i) to (xv) in degassed MeCN at RT, ^a = degassed DCM. Bracketed values in the rows of complexes (ii), (iii), (vi) and (viii) correspond to the photophysical properties of identical complexes but without the mesityl groups. Bracketed values along the row of complex (x) refer to the equivalent complex bearing an unsubstituted bpy ligand.

Complex	λ_{max} /nm	ϕ /%	τ / μs	$k_r \times 10^5 \text{ s}^{-1}$	$k_{nr} \times 10^5 \text{ s}^{-1}$
(i) ⁵⁵	581	24	0.56	4.3	14
(ii) ⁸⁶	592 (592)	28 (31)	0.64 (0.58)	3.0 (3.6)	13 (14)
(iii) ⁸⁷	515 (515)	80 (72)	1.4 (1.4)	5.8 (5.3)	1.5 (2.1)
(iv) ⁸⁷	459, 487	90	2.2	4.1	0.46
(v) ⁸⁸	560, 580	89	1.8	4.9	0.60
(vi) ^{a,89,(66,67)}	638 (642)	14 (1.1)	0.31 (1.4)	4.5 (0.059)	28 (7.2)
(vii) ^{a,89}	565	34	0.99	3.4	6.7
(viii) ^{88,(a,13)}	500, 527 (534)	78 (33)	1.3 (1.9)	6.2 (1.7)	1.8 (3.5)
(ix) ⁸⁸	586, 623	44	7.7	0.58	0.73
(x) ^{a,56}	604 (598)	25 (16)	0.36 (0.30)	6.9 (5.2)	21 (28)
(xi) ^{a,56}	625	17	0.29	6.0	29
(xii) ⁷⁹	595	3	0.50	0.6	19
(xiii) ^{a,80}	600	13	0.26	5.0	34
(xiv) ⁷⁹	593	7	0.15	4.7	62
(xv) ⁷⁹	595	10	0.13	7.7	69

2.3 iTMC design strategies for colour tuning

2.3.1 Blue-emitting iTMCs

Blue-emitting LECs play a fundamental role in the fabrication of white LECs because, when combined with the large known library of orange-emitters, they can produce white emission.⁹⁰ White LECs have many potential applications such as in indoor lighting, but they remain elusive due to the lack of blue LECs with good colour purity and sufficiently high efficiency.⁹¹ One of the challenges associated with creating blue-emitting LECs is the general red shift in emission in going from PL to EL meaning that even complexes with very deep-blue PL fail to produce sufficiently blue-emitting LECs. This red shift in emission is due to the formation of excimers or the formation of strong intermolecular interactions between ions which accumulate in the emissive layer. Furthermore, polarisation of molecular orbitals or chemical changes to the iTMC can occur under electrical biases which often results in red shifted EL emission.^{92,93} Nevertheless, there are several strategies for targeting blue-emitting iTMCs which are examined below.

The first strategy to achieve blue emission is to add electron-withdrawing substituents, for example fluorine atoms, onto the cyclometalating ligand to lower the energy of the HOMO. **Figure 2.8** displays the structures of complexes **1-3** and **7-9** whose C[^]N ligands contain an increasing number of fluorine atoms from 0 to 4 resulting in a blue shift in emission from ≈ 580 nm to ≈ 520 nm ($\Delta E = 2030\text{ cm}^{-1}$, **Table 2.2**).^{82,94–98} The numbering of complexes used in this example carries through into section **2.5** and represents a complex synthesized in this thesis whereas complexes labelled in roman numerals are only reported in the open literature.

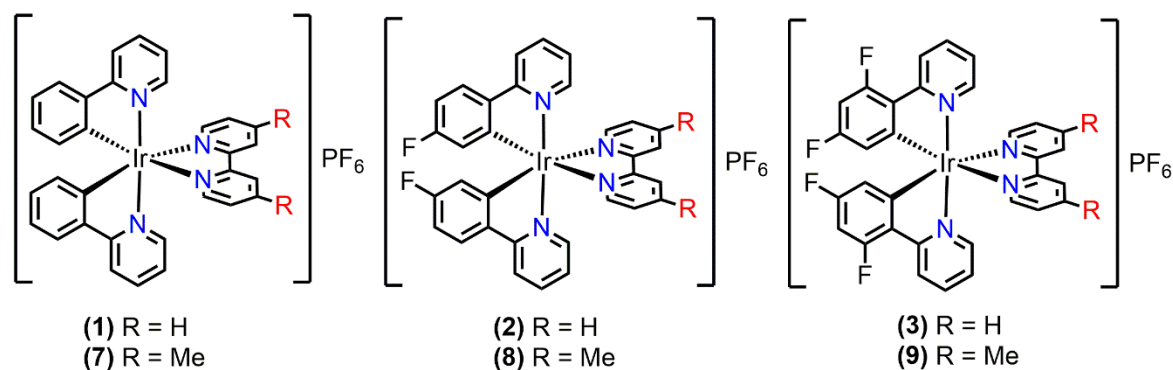


Figure 2.8: Structures of complexes **1** and **7** (left), **2** and **8** (middle) and **3** and **9** (right) which contain ppy, fppy and dfppy cyclometalating ligands respectively.

Figure 2.9 shows examples of ppyH-based ligands bearing other electron-withdrawing groups such as $-\text{CF}_3$ and $-\text{SO}_2\text{Me}$ which have also been shown to produce blue-emitting complexes,^{32,97,99–106} for example, the emission maximum of complex (xvi) (**Figure 2.10**)¹⁰⁰ is over 100 nm (4060 cm^{-1}) bluer than that of its ppy-based analogue (complex (i), **Figure 2.2**, $\lambda_{\text{max}} = 470$ vs. 581 nm, **Table 2.2**).⁵⁵ There is controversy over the use of fluorine atoms in iTMCs as they are believed to be detrimental to device performance by negatively affecting the electrochemical and thermal stability of complexes.^{96,107,108} Hence, many fluorine-free emitters have been developed such as complex (xvii) (**Figure 2.10**)¹⁰⁶ which has blue/green emission ($\lambda_{\text{max}} = 515$ nm, **Table 2.2**) partly as a result of replacing the phenyl ring of the C[^]N ligand with pyrimidine, an electron-poor heterocycle.¹⁰⁶

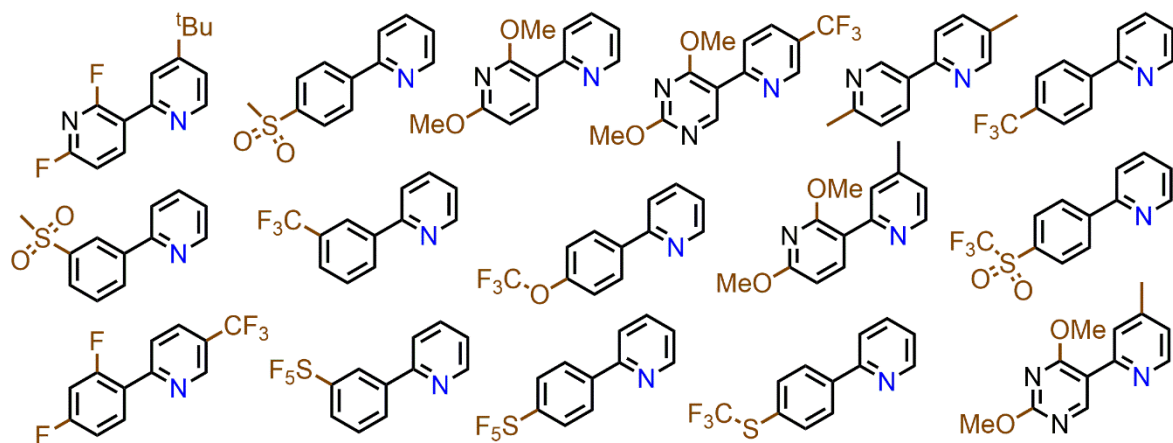


Figure 2.9: Selection of ppyH-based ligands bearing electron-withdrawing substituents (highlighted in brown). Coordinating nitrogen atom is coloured in blue.

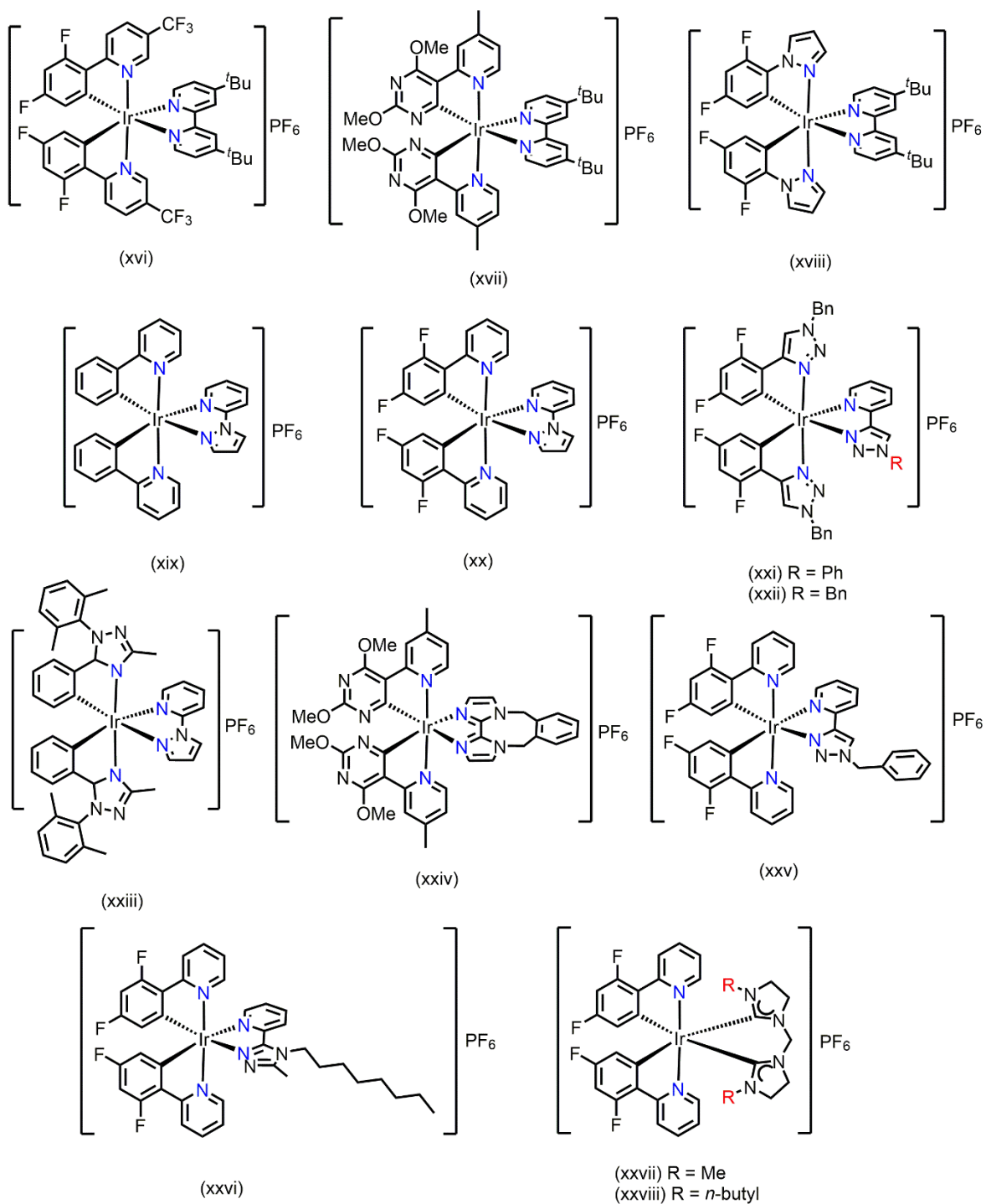


Figure 2.10: Structures of blue-emitting complexes (xvi) to (xxviii).

Table 2.2: Photophysical properties of complexes **1-4**, **6-10**, **12** and (xvi) to (xxviii) in degassed MeCN at RT, ^a = degassed DCM, ^b = thin film, ^{sh} = shoulder.

Complex	λ_{max} /nm	Φ /%	τ / μs	$k_r \times 10^5 \text{ s}^{-1}$	$k_{nr} \times 10^5 \text{ s}^{-1}$
1 ⁸²	585	14	0.43	3.3	20
2 ⁹⁷	557	36	0.22	16	29
3 ^{a,98}	520	26	0.56	4.6	13
4 ^{a,109}	565	9	4.5	1.2	1.0
6 ^{a,109}	507	54	4.6	0.2	2.1
7 ^{94/95}	580/573	23/16	0.31/0.49	7.4/3.3	25/17
8 ^{b,96}	540	57	-	-	-
9 ⁹⁴	522	96	0.66	15	0.6
10 ^{a,110}	491, 520	80	2.2	3.6	0.9
12 ¹¹¹	464, 490	73	3.7	2.0	0.7
(xvi) ¹⁰⁰	470	68	2.3	3.0	1.4
(xvii) ¹⁰⁶	515	81	1.4	6.0	1.4
(xviii) ¹¹²	495	40	1.3	3.0	4.5
(xix) ¹¹³	475, 503 ^{sh}	23	1.6	1.5	4.9
(xx) ¹¹³	452, 480 ^{sh}	20	1.6	1.2	4.9
(xxi) ¹¹⁴	461	0.03	0.008	0.38	1300
(xxii) ¹¹⁴	452	0.05	0.010	5.0	1000
(xxiii) ¹¹⁵	438	< 0.1	0.015	0.67	670
(xxiv) ¹⁰⁶	446, 475, 510	80	9.0	0.89	0.22
(xxv) ^{a,116}	452, 483	22	0.63	3.5	12
(xxvi) ^{a,117}	453, 485	-	-	-	-
(xxvii) ^{a,118}	452, 482	20	2.1	0.96	3.8
(xxviii) ^{a,118}	452, 482	26	2.2	1.2	3.4

A second strategy is to use cyclometalating ligands with nitrogen-rich heterocycles because they are more electron-rich and therefore have higher-lying π^* orbitals.⁹² **Figure 2.11** displays examples of C^N ligands containing pyrazole, tetrazole, 1,2,3-triazole, 1,2,4-triazole and 1,3,4-oxadiazole rings.^{112,114,119–124} The effectiveness of this strategy is proven by the 495 nm RT emission maximum of complex (xviii) in MeCN (**Figure 2.10** and **Table 2.2**)¹¹² compared to 515 nm for its dfppy analogue.⁸⁷

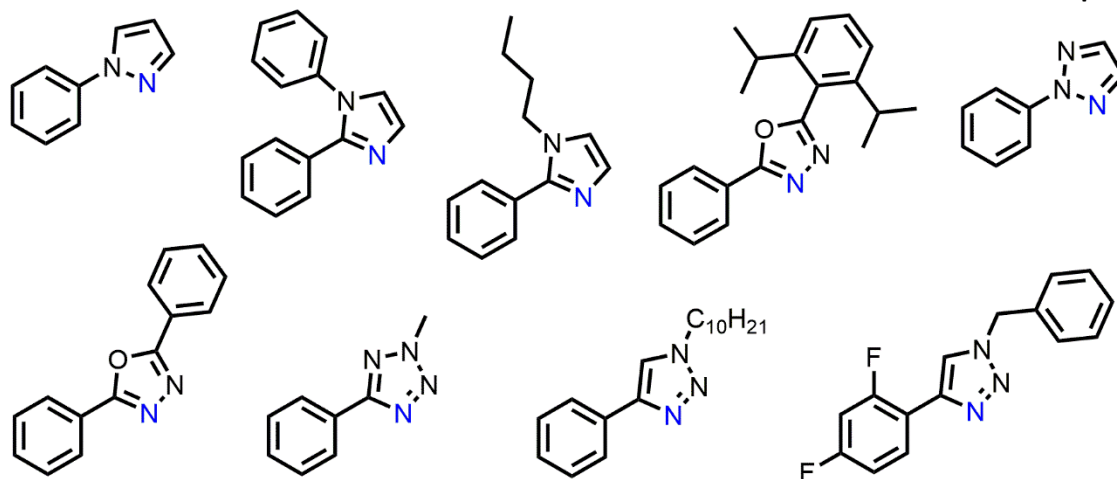


Figure 2.11: Structure of non-ppyH-based cyclometalating ligands which contain a 5-membered N-heterocyclic ring in place of pyridine. Coordinating nitrogen is coloured in blue.

In the third strategy, the N[^]N ligand can be modified to target blue emission by the addition of electron-donating groups. The emissions of complexes **4**, **6**, **7**, **9**, **10**, and **12** (Table 2.2) become increasingly blue as the strength of the electron-donating group increases in the order methyl < methoxy < N,N-dimethylamino (Figure 2.12).^{94,95,109–111} All six complexes are bluer emitters than the bpy-containing complexes **1** and **3** (Figure 2.8), complex **10** demonstrating the most significant blue shift of over 90 nm (3270 cm⁻¹) compared to **1** (λ_{max} = 491, 520 vs. 585 nm). The numbering of complexes used in this example carries through into section 2.5 and again represents complexes synthesized in this thesis as opposed to complexes labelled in roman numerals which have only been reported in the literature.

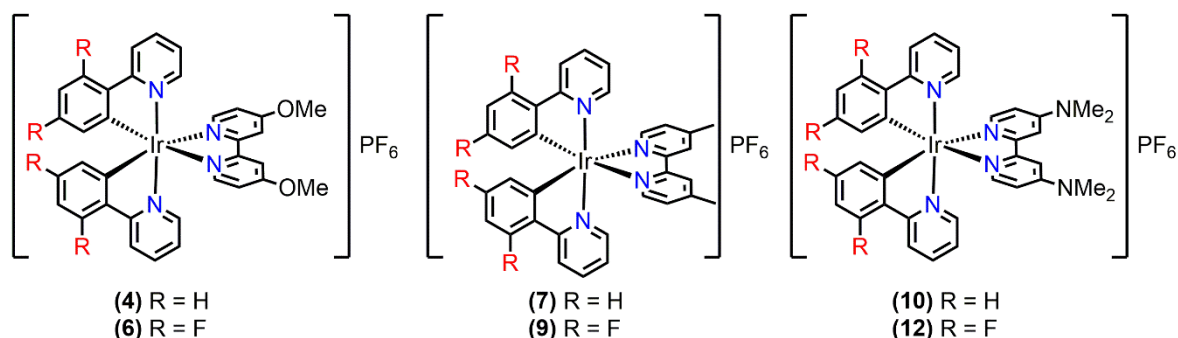


Figure 2.12: Structures of complexes **4** and **6** (left), **7** and **9** (middle) and **10** and **12** (right) which contain electron-donating methoxy, methyl and N,N-dimethylamino substituents on their bpy ligands.

A fourth strategy consists of enriching the electron density of the ancillary ligand with nitrogen-rich heterocycles; multiple examples of electron-rich non-bpy-based N[^]N ligands are shown in Figure 2.13.^{91,106,130–133,113,116,117,125–129} The following three comparisons of bpy- vs. non-bpy-based complexes highlight the effectiveness of this approach:

1. Simply changing one half of bpy to pyrazole in complex (xx) (Figure 2.10), blue shifts emission by almost 70 nm (2890 cm⁻¹) from λ_{max} = 520 nm (complex **3**, Figure 2.8) to λ_{max} = 452, 480 nm (Table 2.2).^{98,113}

2. An even greater blue shift of 110 nm (3960 cm^{-1}) is observed between the emissions of complexes (xix) (**Figure 2.10**) and **1** (**Figure 2.8**), ($\lambda_{\text{max}} = 475, 503$ vs. 585 nm, **Table 2.2**) by modifying bpy in the same way.^{82,113}
3. Replacing $\text{di}^t\text{Bu}_2\text{bpy}$ in complex (xvii) with the 2'-biimidazole ligand in complex (xxiv) (**Figure 2.10**) blue shifts the emission maximum from 515 nm to 446, 475, 510 nm ($\Delta E = 3000\text{ cm}^{-1}$, **Table 2.2**).⁹⁶

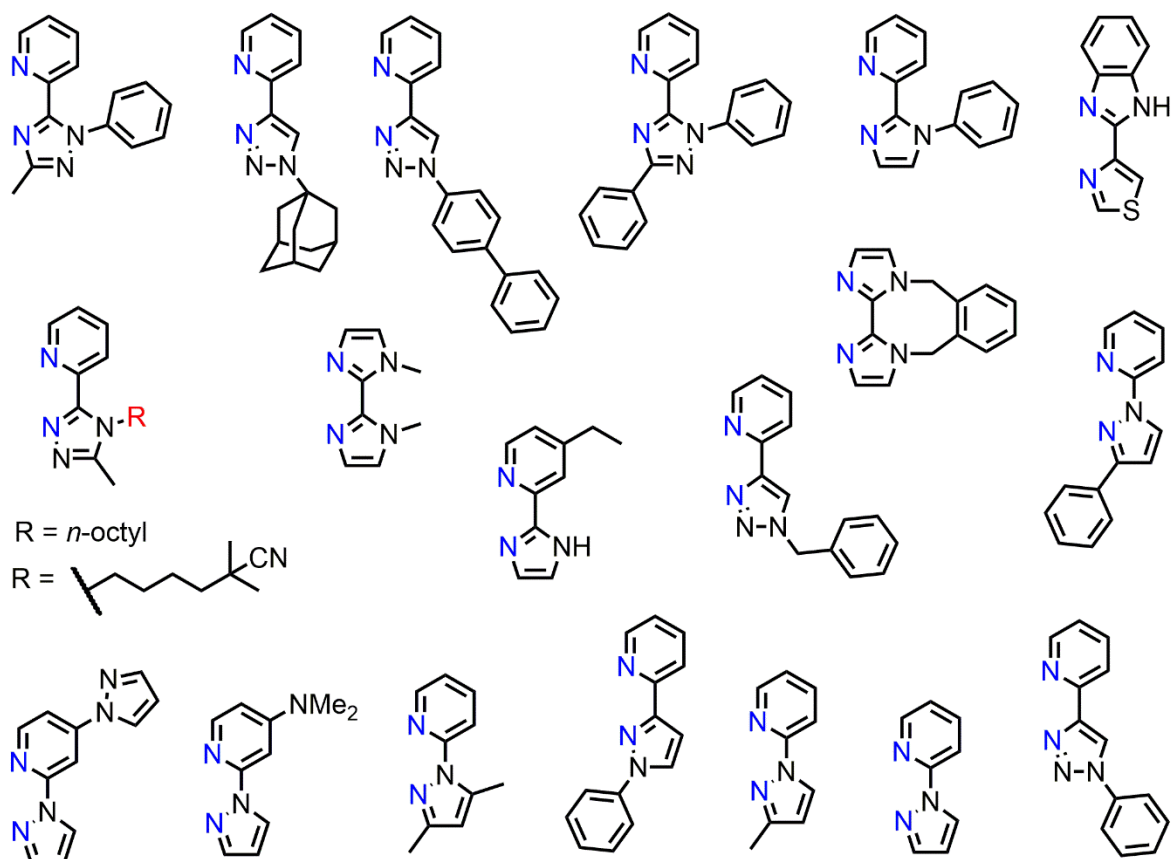


Figure 2.13: Selection of non-bpy-based N^N ligands containing nitrogen-rich heterocycles. Coordinating nitrogen atoms are coloured in blue.

The fifth and final strategy identified uses ancillary ligands with strong ligand fields such as carbenes (**Figure 2.14**).^{118,134} Complexes (xxvii) and (xxviii) (**Figure 2.10**) produced similar blue PL to complex (xxv) ($\lambda_{\text{max}} = 452, 482$ nm, **Table 2.2**).¹¹⁸

A combination of strategies two and four has been employed in complexes (xxi) to (xxiii) (**Figure 2.10**) to generate very deep-blue emission.^{94,114} The best example of this combined approach is complex (xxiii) which features nitrogen-rich C^N and N^N ligands and has an emission maximum of 438 nm in MeCN at RT (**Table 2.2**); this is one of the bluest complexes reported to date.

The bluest-emitting LECs were of those containing complexes (xxv), (xxvi) and (xxviii) (**Figure 2.10**) whose EL maxima were near-identical ($\lambda_{\text{max}} = \approx 456, \approx 487$ nm) and only red shifted by 4-6 nm ($127\text{--}255\text{ cm}^{-1}$) relative to their PL (Appendix, **Table 8.2**).^{116–118}

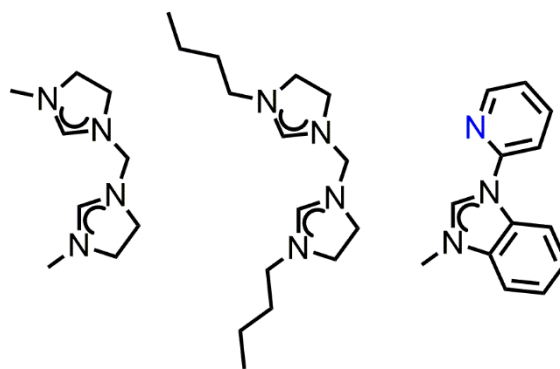


Figure 2.14: Selection of carbene ligands that have been used in blue-emitting iridium complexes.

2.3.2 Red-emitting iTMCs

Red-emitting LECs play an important role in the generation of white light through colour mixing with blue-emitting LECs. They also have potential applications in signalling (e.g. traffic and railway signalling) but there are currently few examples of deep-red emitting LECs with wavelengths greater than 640 nm.¹³⁵ There are three strategies to address this problem, as detailed below.

The first strategy is to add electron-donating groups onto the cyclometalating ligand to raise the energy of the HOMO; **Figure 2.15** displays examples of such ligands containing the ppy framework.^{56,112,136–141} The ppy ligands of (xxix) (**Figure 2.16**)¹³⁶ bear three methoxy groups each which results in deep-red RT emission peaking at 685 nm (**Table 2.3**); this represents a red shift of over 100 nm (2610 cm^{-1}) compared to the ppy equivalent (complex (i), **Figure 2.2**, $\lambda_{\text{max}} = 581\text{ nm}$).⁵⁵

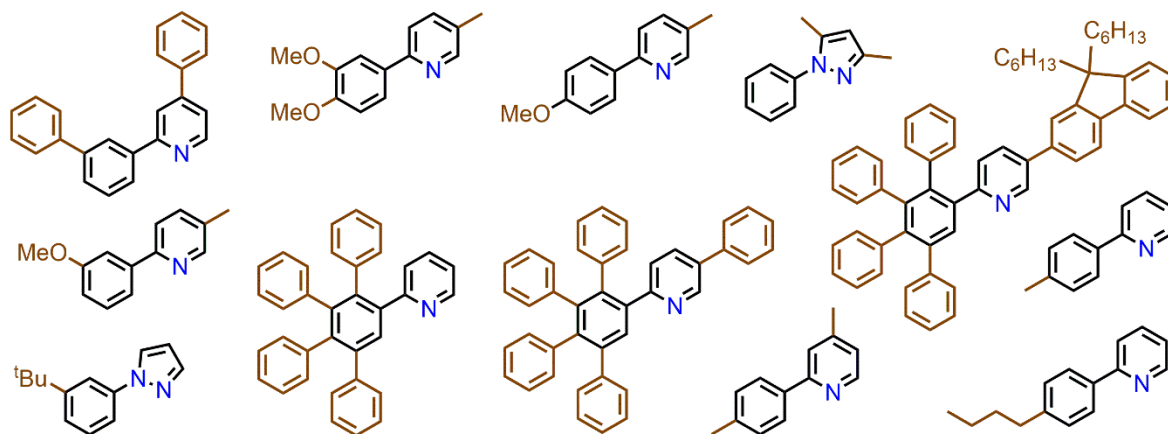


Figure 2.15: Selection of cyclometalating ligands based on a ppy or a 2-phenyl-3-pyrazoline motif bearing electron-donating substituents (highlighted in brown) which have been used to create red-emitting complexes.

The second strategy sees electron-withdrawing substituents added to the ancillary ligand to lower the energy of the LUMO. There are few examples to demonstrate this approach but complex (xxx) (**Figure 2.16**) is one of the few-known cationic Ir(III) complexes with electron-withdrawing substituents on its N[^]N ligand.¹³⁷ Addition of the $-\text{CO}_2\text{Et}$ groups to the bpy ligand of (xxx) red shifts emission maximum by over 100 nm (2660 cm^{-1}) from 581 nm to 687 nm (**Table 2.3**).¹⁴²

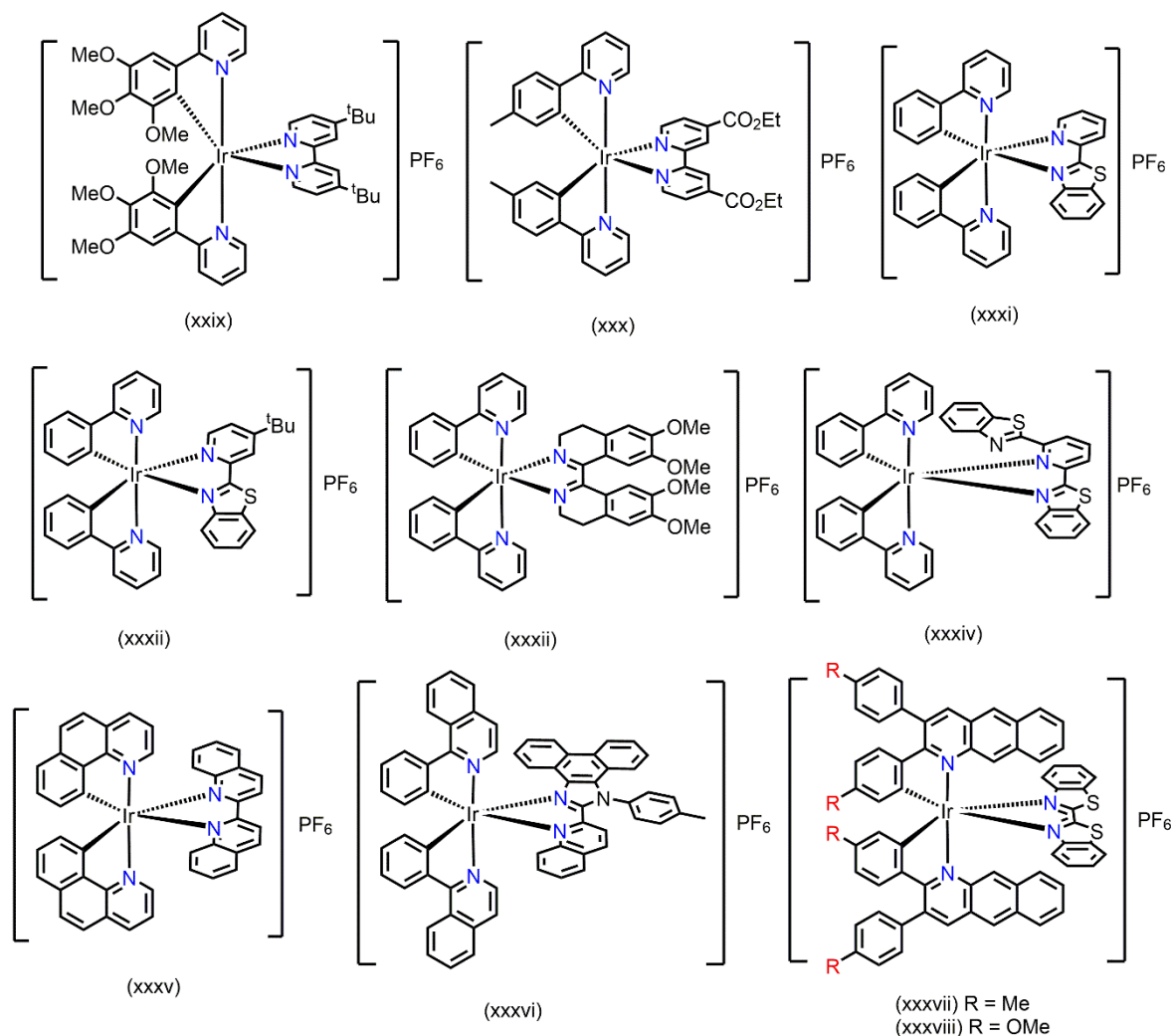


Figure 2.16: Structures of red-emitting complexes (xxix) to (xxxviii).

Table 2.3: Photophysical properties of complexes (xxix) to (xxxviii) in degassed MeCN at RT, ^a = degassed DCM. Bracketed values in the rows of complexes (xxix), (xxxv) and (xxxvi) refer to the ppy-based analogues Bracketed values in the row of complex (xxx) refer to the bpy-based analogue.

Complex	λ_{max} /nm	Φ /%	τ / μs	$k_r \times 10^5 \text{ s}^{-1}$	$k_{nr} \times 10^5 \text{ s}^{-1}$
(xxix) ^{136,(55)}	685 (581)	0.2 (24)	3.2 (0.56)	6.3 (4.3)	3100 (14)
(xxx) ^{137,(142)}	687 (581)	2 (18)	0.069 (0.23)	2.9 (7.8)	140 (36)
(xxxi) ^{a,143}	644	7.7	220	3.5	42
(xxxii) ^{a,143}	636	14	330	4.3	26
(xxxiii) ^{a,144}	620, 710	0.4	-	-	-
(xxxiv) ^{a,143}	652	4.1	170	2.4	57
(xxxv) ^{135,(a,145)}	518, 644, 712 (656)	5.1 (20)	170 (750)	3.0 (2.7)	56 (11)
(xxxvi) ¹⁴⁶	603, 630 (614)	9 (16)	-	-	-
(xxxvii) ¹⁴⁰	778, 849	-	200	-	-
(xxxviii) ¹⁴⁰	770, 837	-	280	-	-

The final strategy increases ligand conjugation in order to reduce the HOMO–LUMO gap by the use of ligands with extended aromatic π -systems.^{91,135,139,140,143–147} **Figure 2.17** shows examples of $N^{\wedge}N$ ligands containing quinoline, isoquinoline, 1,3-benzothiazole, benzoimidazole, benzoxazole, quinazoline and 9,10-phenanthroimidazole motifs. Complexes (xxxi) to (xxxiv) (**Figure 2.16**)^{143,144} contain isoquinoline- and benzothiazole-based ancillary ligands and their emission maxima, which range between 620 and 710 nm (**Table 2.3**), are significantly red shifted relative to that of $[\text{Ir}(\text{ppy})_2(\text{bpy})]\text{PF}_6$, (complex **1**, **Figure 2.8**, $\lambda_{\text{max}} = 585 \text{ nm}$).⁸²

Extension of the π -system of the cyclometalating ligand is also possible as demonstrated by the 7,8-benzoquinoline cyclometalating ligands of complex (xxxv) (**Figure 2.16**).¹³⁵ The combination of conjugated $C^{\wedge}N$ and $N^{\wedge}N$ ligands in (xxxv) leads to redder emission than its ppy analogue ($\lambda_{\text{max}} = 644, 712 \text{ vs. } 656 \text{ nm}$, **Table 2.3**).¹⁴⁵ The azaanthracene-containing complexes (xxxvii) and (xxxviii) (**Figure 2.16**) display emission in the NIR region ($\lambda_{\text{max}} = 778, 849 \text{ nm}$ and $770, 837 \text{ nm}$ respectively).¹⁴⁰ NIR solid-state lighting devices have received considerable attention recently for bioimaging applications because NIR light can penetrate deep into human tissue; a review on this topic has been written by Lu, Su and co-workers.¹⁴⁸

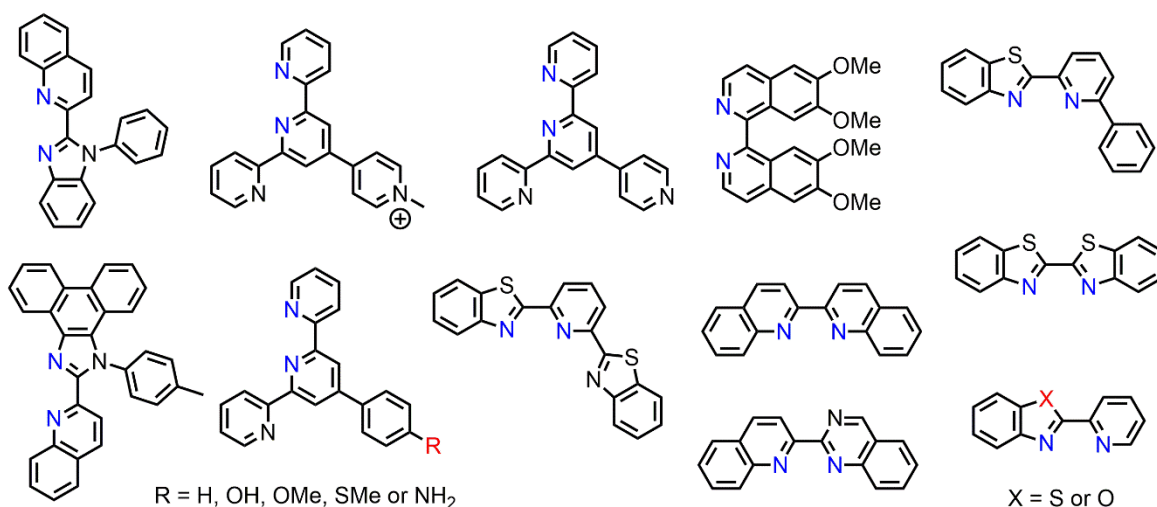


Figure 2.17: Selection of $N^{\wedge}N$ ligands used in red-emitting cationic $\text{Ir}(\text{III})$ complexes, most of which possess increased π -conjugation. Coordinating nitrogen atoms are coloured in blue.

The emission of LECs containing complexes (xxxi), (xxxv) and the ppy analogue of (xxxvi) (**Figure 2.16**) all surpassed 660 nm (Appendix, **Table 8.2**),^{135,144,146} the reddest EL came from the device containing the ppy equivalent of (xxxvi) ($\lambda_{\text{max}} = 692 \text{ nm}$) whilst the emissions of the LECs containing complexes (xxxvii) and (xxxviii) were in the NIR range ($\lambda_{\text{max}} = 882$ and 790 nm respectively.). The EL of (xxxvii) was red shifted by over 100 nm (1520 cm^{-1}) with respect to its PL (**Table 2.3**).

2.4 Aims and objectives

As evident from the above literature review, there are a huge number of iridium(III) complexes containing ppy- and bpy-based ligands, all of which are easily colour-tuned by incorporation of

electron-withdrawing and/or electron-donating substituents. There are several well-known iTMC design principles for the synthesis and application of iTMCs in LECs; one of these principles is to use sterically demanding ligands to shield the metal centre from nucleophilic attack and increase cation separation to reduce luminescence self-quenching effects. In particular, adding steric bulk to the C[^]N ligand at the position *trans* to the Ir–N bond has been shown to retard iTMC degradation during LEC operation; only a limited number of bulky substituents have been reported to date.⁵⁷ Efficient deep-blue EL emission is difficult to achieve due to the significant red shift in EL relative to PL; the use of electron-rich heterocycles as alternatives to bpy (and ppy) is one strategy to shift emission towards the blue by destabilization of the LUMO. A wide range of nitrogen-rich heterocyclic ancillary ligands have been reported already but there is still a lot of unexplored potential within this area.

Hence, this work aims to:

1. Evaluate and review the entire series of [Ir(C[^]N)₂(N[^]N)]PF₆ complexes where C[^]N = ppy, fppy, dfppy and N[^]N = bpy, dmbpy, dmbpy, dmabpy, as this series has not been reported before in its entirety, nor has a comprehensive photophysical study been conducted.
2. Investigate the effects of adding steric bulk to the position *trans* to the Ir–N bond on the cyclometalating ligand, as this bond is particularly susceptible to cleavage by nucleophiles during LEC operation.
3. Investigate the colour-tuning ability of two new classes of N[^]N heterocyclic ancillary ligand containing a 1*H*-pyrazolo[3,4-*b*]pyridine and 7-azaindole framework.

To achieve these aims we have synthesized and studied the properties of four types of complex:

- Complexes where C[^]N = ppy, fppy, dfppy and N[^]N = bpy, dmbpy, dmbpy, dmabpy [**1-12**] (**Figure 2.18**, section 2.5).
- Complexes containing sterically-demanding dfppy-based ligands with difluorophenyl [**13-15**] and mesityl groups [**16-18**] added *trans* to the Ir–N bond (**Figure 2.18**, section 2.5).
- Complexes with an N[^]N ligand containing a pyrazolo[3,4-*b*]pyridine motif [**19-27**] (**Figure 2.32**, section 2.6).
- Complexes with an N[^]N ligand containing a 7-azaindole motif [**28-34**] (**Figure 2.32**, section 2.6).

2.5 Results and discussion: $[\text{Ir}(\text{ppy})_2(\text{bpy})]\text{PF}_6$ -based complexes

Complexes **1-18** (Figure 2.18) will be discussed in this section.

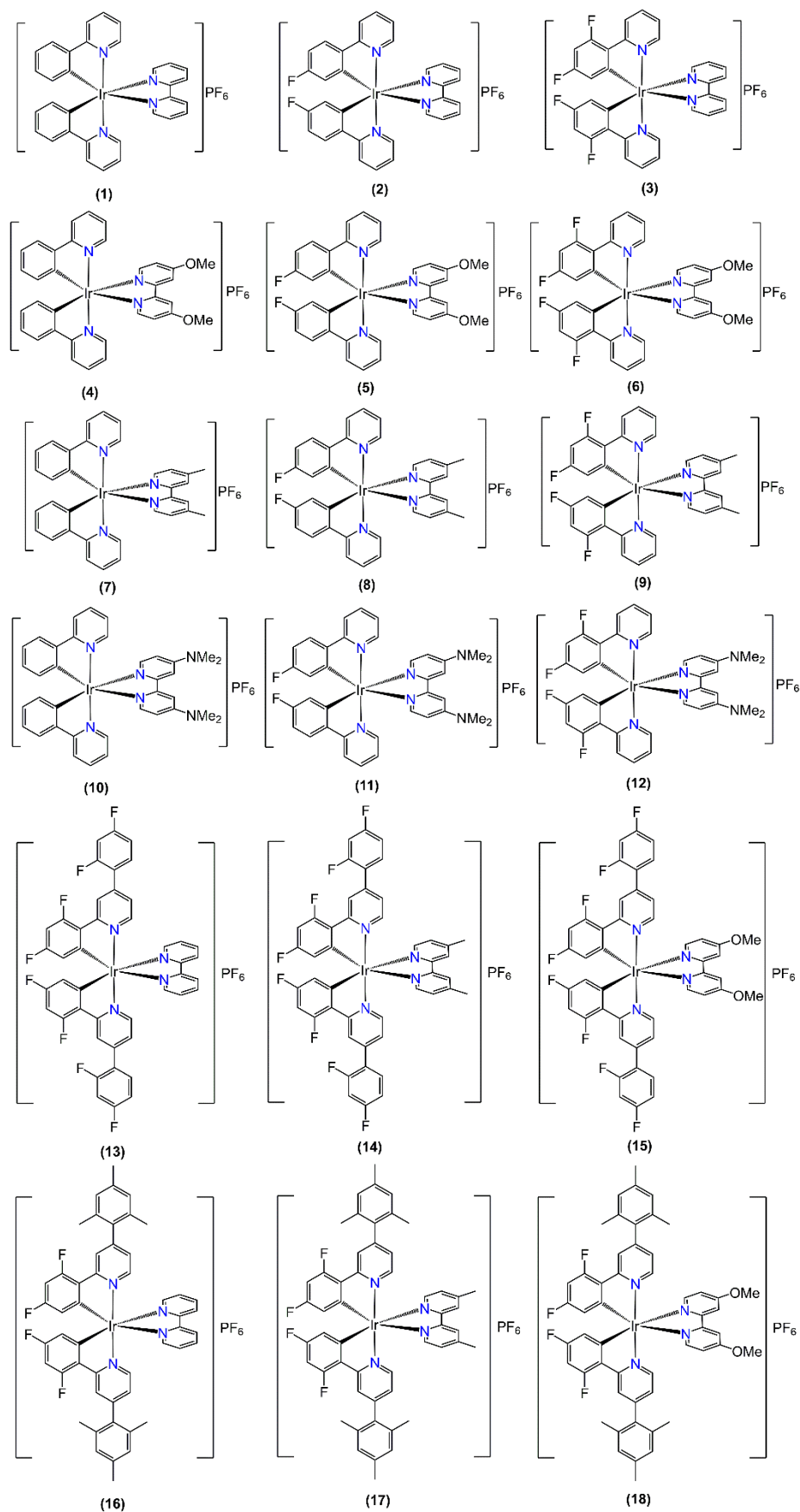


Figure 2.18: Structures of complexes **1-18**.

2.5.1 Synthesis

A total of five C^N ligands and four N^N coordinating bipyridines were used to prepare complexes **1-18**. The five C^N ligands consist of: ppyH (2-phenylpyridine), fppyH (4'-fluorophenylpyridine), dfppyH (2,4'-difluorophenylpyridine), bis-dfp₂pyH (2,4-bis[2',4''-bis(fluoranyl)phenyl]pyridine) and mes-dfppyH (2-(2'4''-difluorophenyl)-4-(2''4''6''-trimethylphenyl)pyridine). The four N^N ligands consist of: bpy (2,2'-bipyridine), dmbpy (4,4'-dimethyl-2,2'-bipyridine), dmbpy (4,4'-dimethoxy-2,2'-bipyridine) and dmabpy (4,4'-bis-(*N,N*-dimethylamino)-2,2'-bipyridine).

The synthesis of the fluorinated cyclometalating ligands was achieved by palladium-catalysed Suzuki cross-coupling. The mes-dfppyH ligand was prepared via two consecutive cross-couplings starting from 2,4-dibromopyridine (**Figure 2.19**). Substitution at the more reactive 2-position was firstly achieved using a 2 : 1 molar ratio of 2,4-dibromopyridine to 2,4-difluorophenylboronic acid. Small amounts of the 4-substituted and 2,4-disubstituted products were obtained but were easily separated from the 2-substituted product using gradient column chromatography. Substitution at the 4-position was then accomplished under similar conditions using an excess (1.5 equiv.) of 1,3,5-trimethylphenylboronic acid. The bis-dfp₂pyH ligand was prepared in a single step by a double substitution of 2,4-dibromopyridine with 2.5 equivalents of 2,4-difluorophenylboronic acid. The fppyH and dfppyH ligands were synthesized under identical conditions from a single Suzuki coupling of 2-bromopyridine with either 4-fluorophenylboronic acid or 2,4-difluorophenylboronic acid.

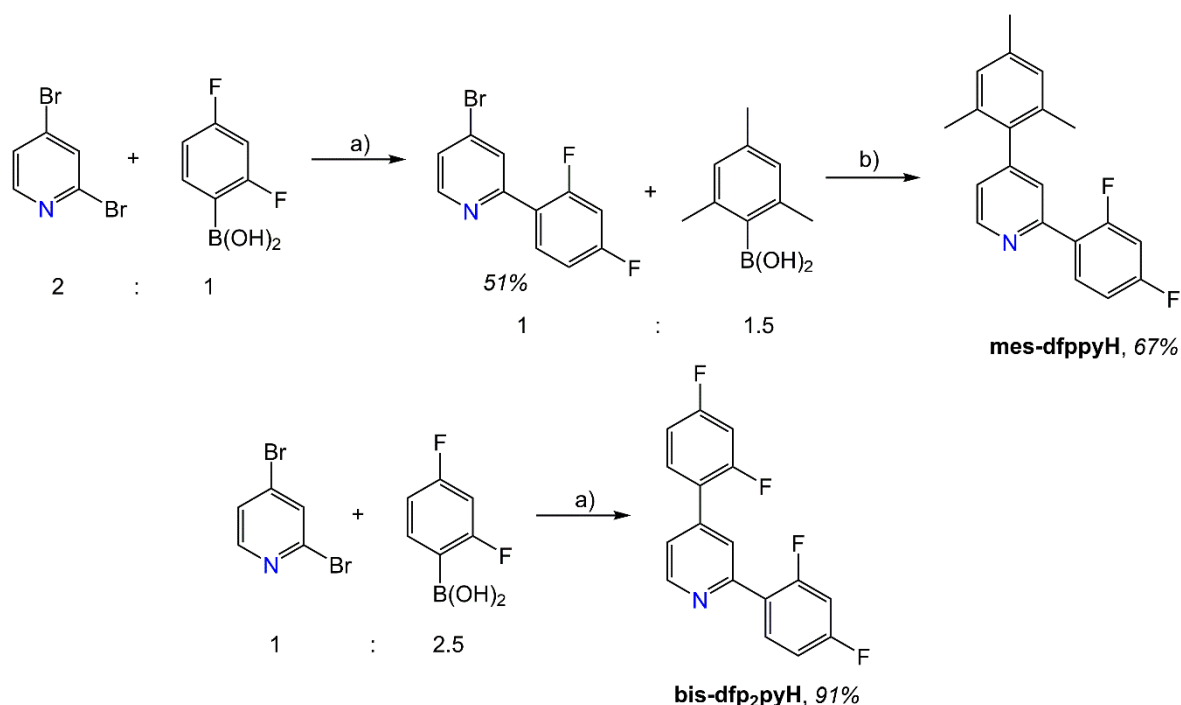


Figure 2.19: Synthesis of mes-dfppyH and bis-dfp₂pyH ligands from 2,4-dibromopyridine using Suzuki cross-couplings: a) Na₂CO₃ (2 equiv.), Pd(OAc)₂ (4.5% mol), PPh₃ (0.1 equiv.) in EtOH : toluene : H₂O (2 : 2 : 1) stirred at 100°C under an inert atmosphere for 24 h; b) K₂CO₃ (2.5 equiv.), Pd(PPh₃)₄ (5% mol), 1,4-dioxane : H₂O (3 : 1) stirred at 100°C under an inert atmosphere for 24 h.

The synthesis of dmabpy, the only N^N ligand not available commercially, was achieved via either of two routes. (**Figure 2.20**). The first route was a direct radical homo-coupling of 4-dimethylaminopyridine (DMAP) using *n*BuLi and HMPA in THF at 0°C; this radical homo-coupling method is a proven route to 4,4'-disubstituted bipyridines.¹⁴⁹ In our ligands, a 7% yield of dmabpy was obtained despite the use of the radical stabilizing solvent, HPMA, which had been shown to significantly increase product yield in the literature.¹⁵⁰ The second route was through a Stille cross-coupling, which required the conversion of DMAP to the 2-iodo- and 2-stannyl analogues in the first step using a lithium-halogen exchange procedure. The subsequent Stille coupling also gave only a modest yield of 20%; the low yields of dmabpy for both routes were probably due to the difficulty in purifying dmabpy.

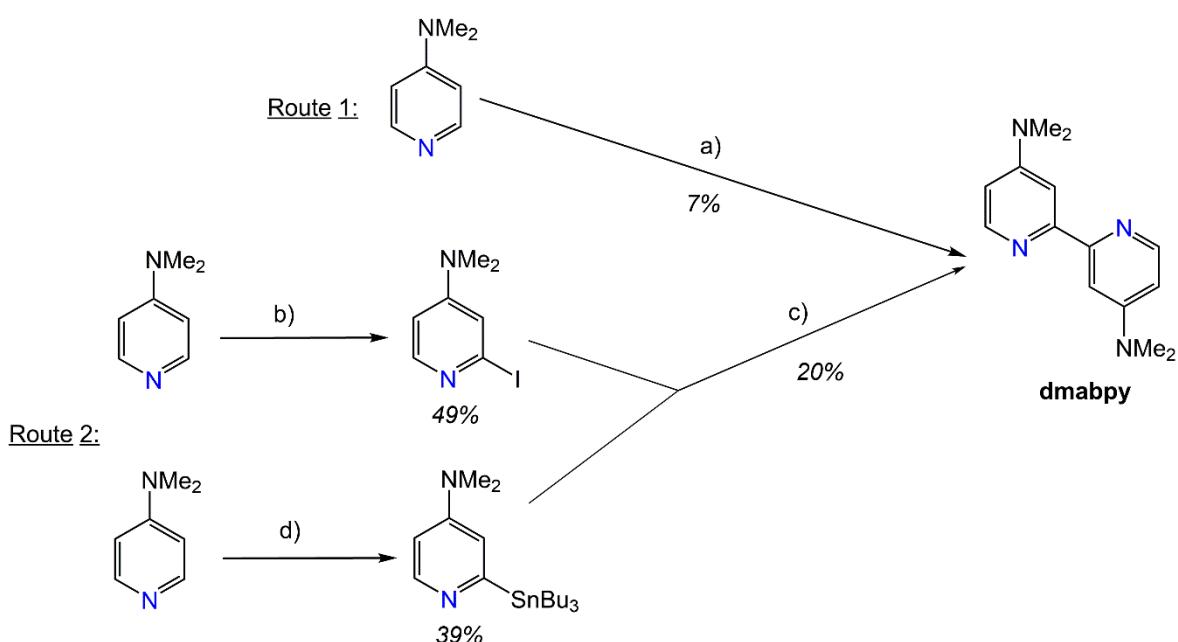


Figure 2.20: Synthesis of dmabpy using one of either two routes: a) *n*BuLi, DMAE, hexane, 0°C, 1 h followed by HMPA in THF, 0°C to RT, 16 h; b) *n*BuLi, DMAE, hexane, 0°C, 1 h followed by I₂ in THF, -78°C to RT, 16 h; c) Pd(PPh₃)₄, PPh₃, CuI, DMF, 125°C, 48 h; d) *n*BuLi, DMAE, hexane, 0°C, 1 h followed by SnBu₃Cl in hexane, -78°C to RT, 16 h.

Complexes **1-18** were prepared according to a general procedure as outlined in **Figure 2.21** for the preparation of **1**.^{151–153} Overnight reflux of ppyH with IrCl₃·3H₂O in a solvent mixture of 2-ethoxyethanol and H₂O yielded the dimeric [Ir(ppy)₂μ-Cl]₂ as a bright yellow precipitate which was isolated by centrifugation and washed with H₂O and EtOH. The dimer was readily cleaved with 2.2 equivalents of bpy upon reflux in a solvent mixture of DCM and MeOH to yield the chloride salt which then underwent ion exchange by addition of a saturated aqueous solution of KPF₆. In this instance, simply washing the crude mixture with MeOH and ether was sufficient to purify **1** but most complexes required column chromatography and recrystallization(s) to isolate the pure products.

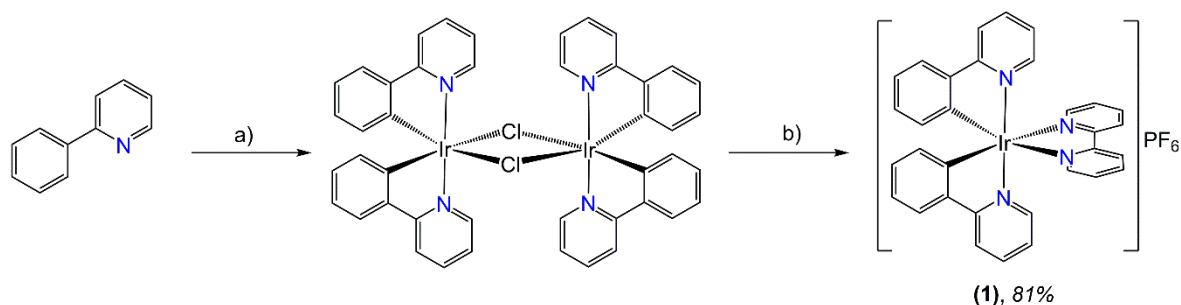


Figure 2.21: Synthesis of complex **1**: a) $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$, 2-ethoxyethanol : H_2O (3 : 1), 120°C , 16 h; b) *bpy* (2.2 equiv), DCM : MeOH (5 : 3), 65°C , 3 h followed by sat. aq. KPF_6 .

As a representative example, **Figure 2.22** displays the ^1H NMR spectrum of complex **17** in d_6 -acetone, assigned with the aid of ^1H - ^1H COSY, ^1H - ^1H NOESY, ^1H - ^{13}C HMBC and ^1H - ^{13}C HSQC analysis. The pattern of proton signals in **17** matches the rest of the *bpy* series **1-18** in that the most downfield peak (at 8.78 ppm) is assigned to protons *ortho* to the *bpy* nitrogen atoms (i.e. H^{14}) whereas the most upfield peak in the aromatic region (at 5.86 ppm) corresponds to the protons adjacent to the cyclometalating carbon (i.e. H^{10}). The protons of each dfppy unit are magnetically equivalent to each other, but the protons attached to the mesityl groups are in separate environments which generates five unique signals (highlighted in yellow). The peaks assigned to protons H^2 and H^4 occur as two singlets at 6.98 and 7.03 ppm whilst the singlets in the aliphatic region at 1.92, 2.13 and 2.31 ppm correspond to the three methyl groups. The singlets associated with the 1- and 5-methyl groups are broad due to the rotation of the mesityl groups occurring on a similar timescale to NMR which allows the exchange of H^1 and H^5 protons. The exchange of protons H^2 and H^4 also explains why their peaks are broader than the other aromatic signals.¹⁵⁴

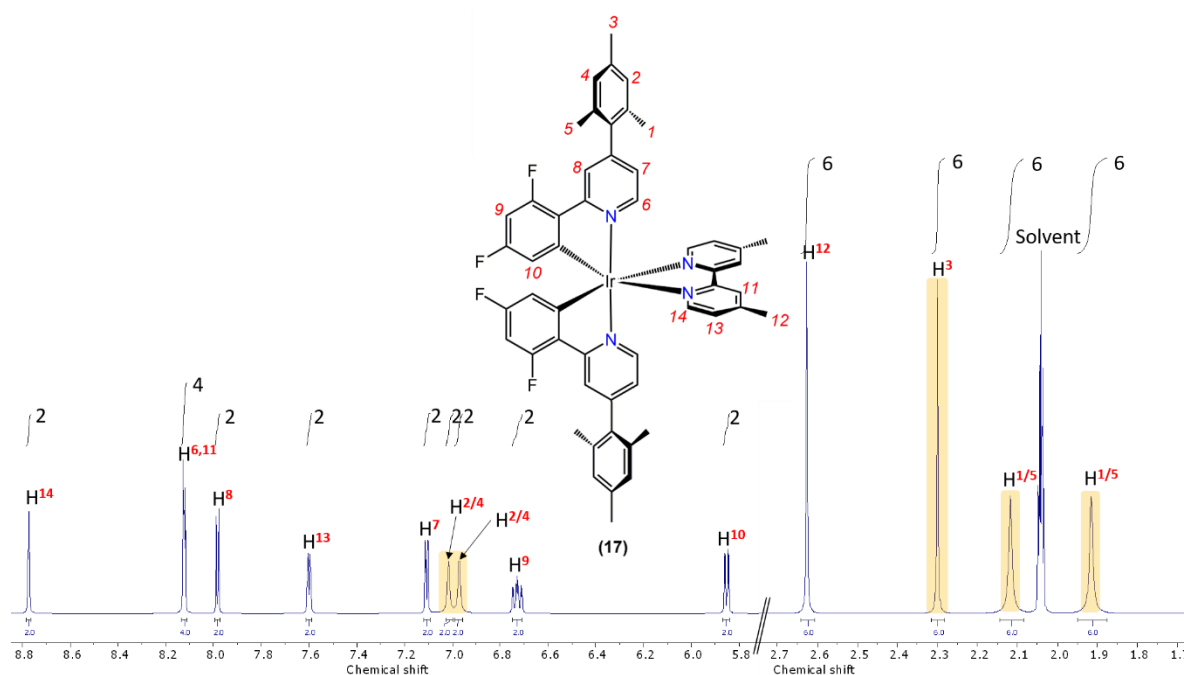


Figure 2.22: ^1H NMR spectrum of **17** in d_6 -acetone, 600 MHz. The proton signals from the mesityl groups are highlighted in yellow.

2.5.2 Crystallography

Crystals of **15** and **16** were obtained by slow evaporation of MeCN solutions (**Figure 2.23**). In both cations, the iridium occupies a distorted pseudo-octahedral geometry. Selected bond lengths and angles of **15** and **16** are tabulated in **Table 2.4** alongside crystallography data for **3** and **6** to allow for a direct comparison against the analogous complexes without the difluorophenyl or mesityl groups respectively.^{10,109} All four complexes share similar M–L bond lengths and angles so we shall consider the values for only one complex, **15**. The Ir–C bonds of **15** are shorter than the Ir–N bonds of the cyclometalating ligand by ≈ 0.03 Å and shorter than the Ir–N bonds of the ancillary by ≈ 0.12 Å. This is presumably due to the strong trans influence of the cyclometalating carbon atoms. The acute M–L bond angles, which range between 77° and 80° , likely reflect the geometric constraints imposed by the binding of C[^]N and N[^]N ligands that form 5-membered chelating rings.

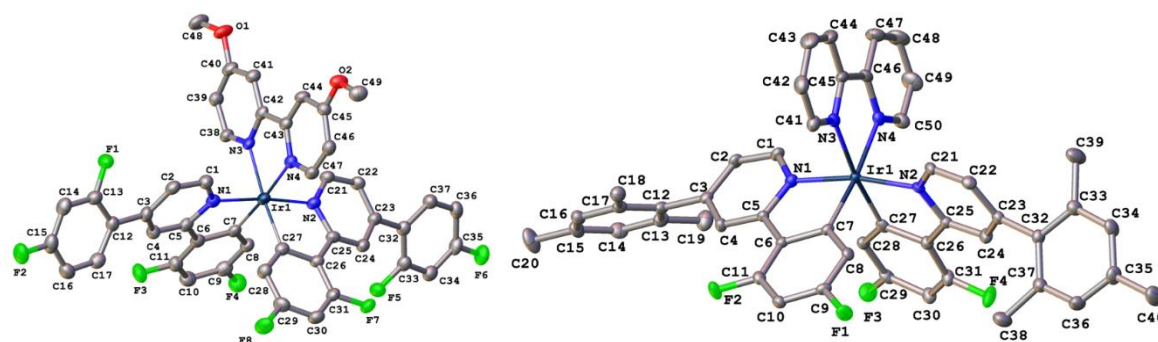


Figure 2.23: Crystal structures of the cations **15** (left) and **16** (right). The PF_6^- counter-ion is omitted for clarity.

Table 2.4: Selected bond lengths and angles from crystal structures **3**, **6**, **15** and **16**.

Complex	15	6 ¹⁰⁹	16	3 ¹⁰
Ir ¹ –N ¹ bond length /Å	2.037(4)	2.064(5)	2.051(3)	2.057(3)
Ir ¹ –N ² bond length /Å	2.039(4)	2.050(5)	2.044(3)	2.049(4)
Ir ¹ –N ³ bond length /Å	2.136(4)	2.140(5)	2.128(3)	2.121(3)
Ir ¹ –N ⁴ bond length /Å	2.129(4)	2.135(5)	2.126(3)	2.141(3)
Ir ¹ –C ⁷ bond length /Å	2.011(5)	2.009(6)	2.008(3)	2.010(4)
Ir ¹ –C ²⁷ bond length /Å	2.017(5)	2.017(6)	2.000(4)	2.015(4)
N ³ –Ir ¹ –N ⁴ bond angle /Å	76.71(2)	76.3(2)	76.96(1)	77.46(1)
N ¹ –Ir ¹ –C ⁷ bond angle /Å	80.42(2)	80.0(7)	80.69(1)	80.38(2)
N ² –Ir ¹ –C ²⁷ bond angle /Å	80.08(2)	80.3(3)	80.59(1)	80.71(2)
C ⁴ –C ³ –C ¹² –C ¹⁷ torsion angle /°	34.4(7)	-	58.9(4)	-
C ⁴ –C ³ –C ¹² –C ¹³ torsion angle /°	31.0(5)	-	60.4(4)	-
C ² –C ³ –C ¹² –C ¹⁷ torsion angle /°	34.6(5)	-	58.7(4)	-
C ² –C ³ –C ¹² –C ¹³ torsion angle /°	31.3(7)	-	60.2(5)	-
C ²² –C ²³ –C ³² –C ³³ torsion angle /°	41.7(5)	-	58.7(5)	-
C ²² –C ²³ –C ³² –C ³⁷ torsion angle /°	38.7(7)	-	58.8(4)	-
C ²⁴ –C ²³ –C ³² –C ³³ torsion angle /°	39.27()	-	54.0(4)	-
C ²⁴ –C ²³ –C ³² –C ³⁷ torsion angle /°	36.2(5)	-	54.2(5)	-

The torsional angles of the peripheral phenyl groups on the C[^]N ligands of **15** and **16** reveal significant differences. The average dihedral angles of the difluorophenyl substituents of **15** are 32.8° (C^{2/4}–C³–C¹²–C^{13/17}) and 39.0° (C^{22/24}–C²³–C³²–C^{33/37}) whilst the corresponding dihedral angles

of the mesityl groups in **16** are 59.6° and 56.4°. The larger dihedral angles of the mesityl groups in **16** is likely to be due to the presence of an additional substituent in the 5-position. Interestingly, the dihedral angles of **16** are smaller than the dihedral angles of a similar cationic mes-dfppy-containing complex reported by Zysman-Colman's group ($\approx 79^\circ$) whose N[^]N ligand is di^tBu₂bpy.⁸⁷

2.5.3 Electrochemistry

Table 2.5 shows the electrochemical parameters of complexes **1-18**, obtained by cyclic voltammetry with NBu₄PF₆ as the supporting electrolyte using the ferrocene/ferrocenium couple as a reference ($E_{1/2} = 0.42$ V vs. SCE). All 18 complexes display a single reversible oxidation in the window +0.93 to +1.80 V and a single reversible reduction in the region of -1.12 to -1.80 V. The oxidation of **1-18** is thought to involve the iridium and cyclometalating ligand; this hypothesis is based on: (i) previous studies on ppy- and bpy-type systems;^{56,82,94–98,109,111} (ii) DFT data (section 2.5.4) and (iii) the fact that the addition of electron-withdrawing fluorine atoms on the C[^]N ligand shifts the oxidation potential to more positive values, for example, $E_{1/2}^{\text{ox}} = 1.80$ V (**3**) vs. 1.27 V (**1**).

Table 2.5: Electrochemical properties of complexes **1-18** recorded in a 0.1 M electrolyte solution of NBu₄PF₆ in MeCN. Values were measured at a scan rate of 200 mV s⁻¹ and are reported relative to SCE, measured using ferrocene as the standard ($E_{1/2}^{\text{ox}} = 0.42$ vs. SCE). $\Delta E_{1/2} = E_{1/2}^{\text{ox}} - E_{1/2}^{\text{red}}$. $\Delta E_{\text{H-L}}$ refers to the HOMO-LUMO gap calculated using DFT.

Complex	$E_{1/2}^{\text{ox}} / \text{V}$	$E_{1/2}^{\text{red}} / \text{V}$	$\Delta E_{1/2} / \text{V}$	$\Delta E_{\text{H-L}}$
1	+1.27	-1.37	2.64	2.63
2	+1.48	-1.32	2.80	2.79
3	+1.80	-1.12	2.92	2.96
4	+1.37	-1.34	2.71	2.83
5	+1.13	-1.71	2.84	3.02
6	+1.71	-1.26	2.97	3.20
7	+0.93	-1.77	2.70	2.70
8	+1.52	-1.32	2.84	2.88
9	+1.62	-1.37	2.99	3.05
10	+1.34	-1.55	2.89	3.00
11	+1.31	-1.70	3.01	3.18
12	+1.47	-1.77	3.24	3.36
13	+1.68	-1.23	2.91	3.00
14	+1.76	-1.21	2.97	3.09
15	+1.18	-1.80	2.98	3.24
16	+1.21	-1.71	2.92	2.82
17	+1.59	-1.38	2.97	2.97
18	+1.56	-1.41	2.97	3.13

The reduction of **1-18** is thought to involve the N[^]N ligand in agreement with the literature and our DFT results. Furthermore, the addition of electron-donating methyl, methoxy and *N,N*-dimethylamino substituents onto the bpy ligand shifts the reduction potential to more negative values, as exemplified by the reduction potentials of **12** ($E_{1/2}^{\text{red}} = -1.77$ V) vs. **3** ($E_{1/2}^{\text{red}} = -1.12$ V).

The electrochemical $\Delta E_{1/2}$ values of **1-12** align closely with their HOMO-LUMO energy gaps, as calculated by DFT, and increase in accordance with the addition of electron-withdrawing fluorine atoms onto the C[^]N ligand and/or electron-donating -Me, -OMe and -NMe₂ groups onto the N[^]N ligand. The $\Delta E_{1/2}$ values of the bulkier complexes **13-18**, however, align less well with HOMO-LUMO gaps; whilst $\Delta E_{1/2}$ values lie within a close 0.07 V range (2.91 to 2.98 V), the calculated ΔE_{H-L} values vary considerably from 2.82 to 3.24 V.

2.5.4 DFT

DFT studies of **1-18** were performed using the B3LYP functional and the LANL2DZ basis set. **Figure 2.24** displays the frontier molecular orbital diagrams and energies for complexes **3**, **13**, and **16-18**. These five complexes were chosen to illustrate the effect of adding difluorophenyl (**13** vs. **3**) and mesityl groups (**16** vs. **3**) to the dfppy ligand and to show the trend across the series of mes-dfppy-containing complexes with bpy (**16**), dmbpy (**17**) and dmobpy (**18**) ancillaries.

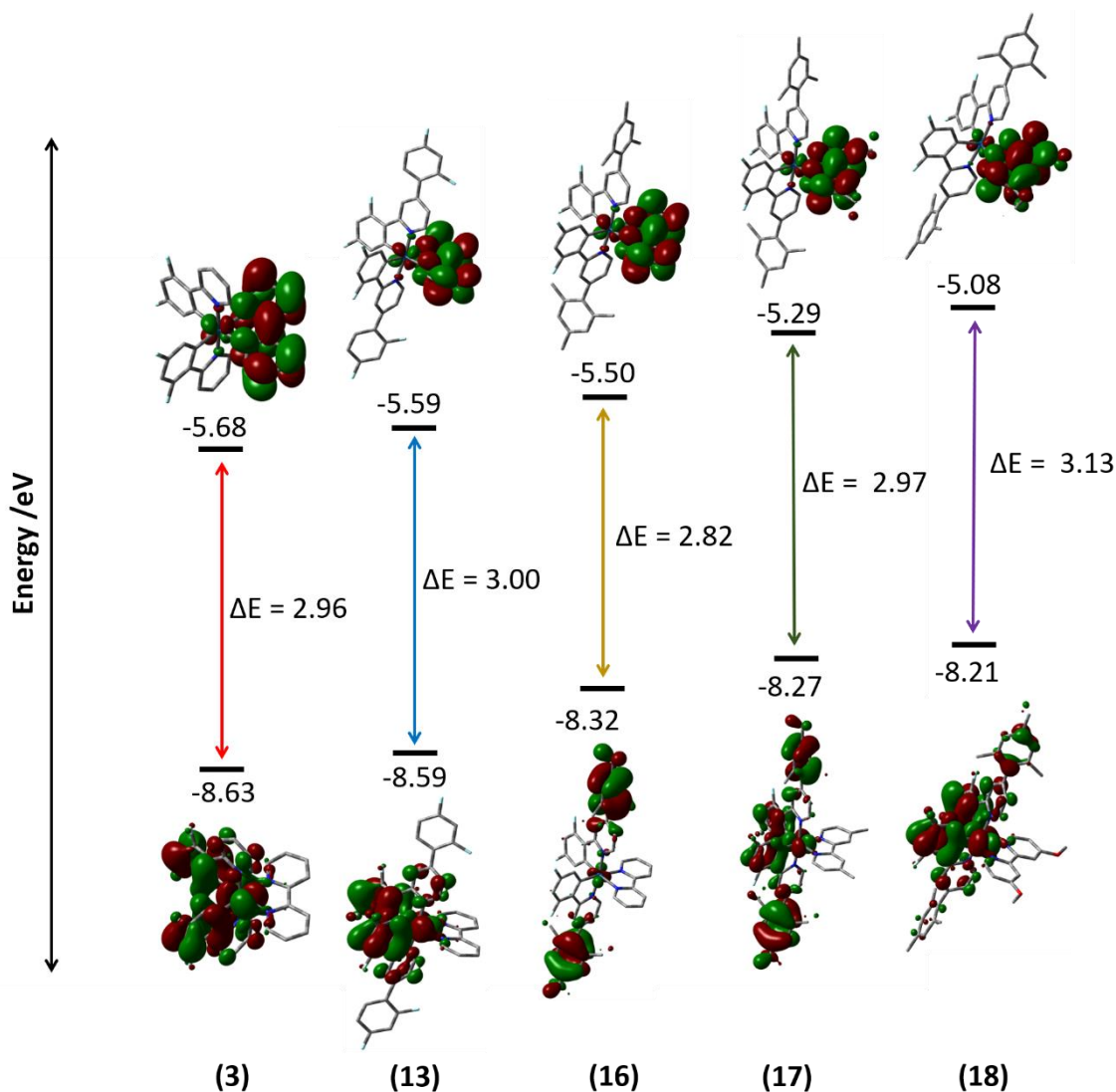


Figure 2.24: HOMO and LUMO diagrams and energies of complexes **3**, **13** and **16-18**, as calculated by DFT.

The HOMO and LUMO locations of **3** and **13** are nearly identical; their HOMOs are calculated to be over the iridium and the cyclometalating ligand and their LUMOs are distributed across the bpy ancillary. Whilst the LUMO in **16** is located on the same part of the complex as **3** and **13** (i.e. on the bpy unit), its HOMO mainly resides on the mesityl groups of the C^N ligand with a small contribution from the metal. This difference in the HOMO locations of **16** vs. **3** and **13** could be due to the fact that the excited state of **16** involves significant contributions from HOMO-1→LUMO and HOMO-2→LUMO transitions, whereas the main contributor to the excited states of **3** and **13** is a HOMO→LUMO transition (70%). The HOMO and LUMO locations and excited states of **3** and **13** are representative of the DFT and TD-DFT results obtained for the other bis-dfp₂py complexes (**14** and **15**) and for the less bulky complexes (**1**, **2** and **4-12**). The HOMO and LUMO locations of **1-15** are in agreement with previously reported [Ir(ppy)₂(bpy)]⁺-type complexes.^{82,94,98,109,110}

The LUMOs of **17** and **18** are similarly located on the ancillary ligand. Their HOMOs also reside on the iridium and the cyclometalating ligand but differ in terms of their distribution across mes-dfppy, for example, the HOMO of **17** involves a larger contribution from the mesityl groups whilst the HOMO of **18** occupies the dfppy unit to a larger extent. The HOMO location of **18** is in agreement with similar cationic mes-dfppy-containing complexes reported in the literature.^{88,89} As observed for complex **16**, the excited states of **17** and **18** involve considerable contributions from lower-lying HOMO orbitals, for example, the largest contribution to the excited state of **17** is a HOMO-2→LUMO transition (55%) but for **18** it is a HOMO-4→LUMO transition (51%). HOMO and LUMO energies rise across the series in parallel with a widening of the HOMO-LUMO gap from 2.82 V (**16**) to 3.13 V (**18**). These trends are consistent with the addition of increasingly electron-donating substituents (i.e. methyl (**17**) and methoxy (**18**)) onto bpy which destabilize the LUMO by greater amounts.

2.5.5 Photophysical properties

The photophysical properties of complexes **1-18** recorded in degassed MeCN at RT and in EPA or butyronitrile at 77 K are tabulated in **Table 2.6**. The selection of complexes in the following graphs illustrates trends which may be common to several complexes in the series.

2.5.5.1 Absorption

Figure 2.25 displays the absorption spectra for complexes **1-3** (upper) and **1, 4, 7** and **10** (lower) illustrating the effect of varying the fluorine content of the cyclometalating ligand and of varying the bpy substituents, respectively. The high energy bands of complexes **1-3**, which are usually considered as originating from ligand-centred (LC) π - π^* transitions,¹⁰⁹ occur within a 19 nm band (247-266 nm) with molar absorptivities in excess of $3.8 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ (**Figure 2.25, upper**). The positions of the less intense red shifted bands, assigned to metal-to-ligand-charge transfer (MLCT) transitions, remain almost constant with a tolerance of 6 nm (297-303 nm).¹⁰⁹ The corresponding

^1LC and $^1\text{MLCT}$ molar extinction coefficients for the dfppy-containing complex, **3**, are consistently higher than those of the ppy (**1**) and fppy (**2**) equivalents (**Table 2.6**).

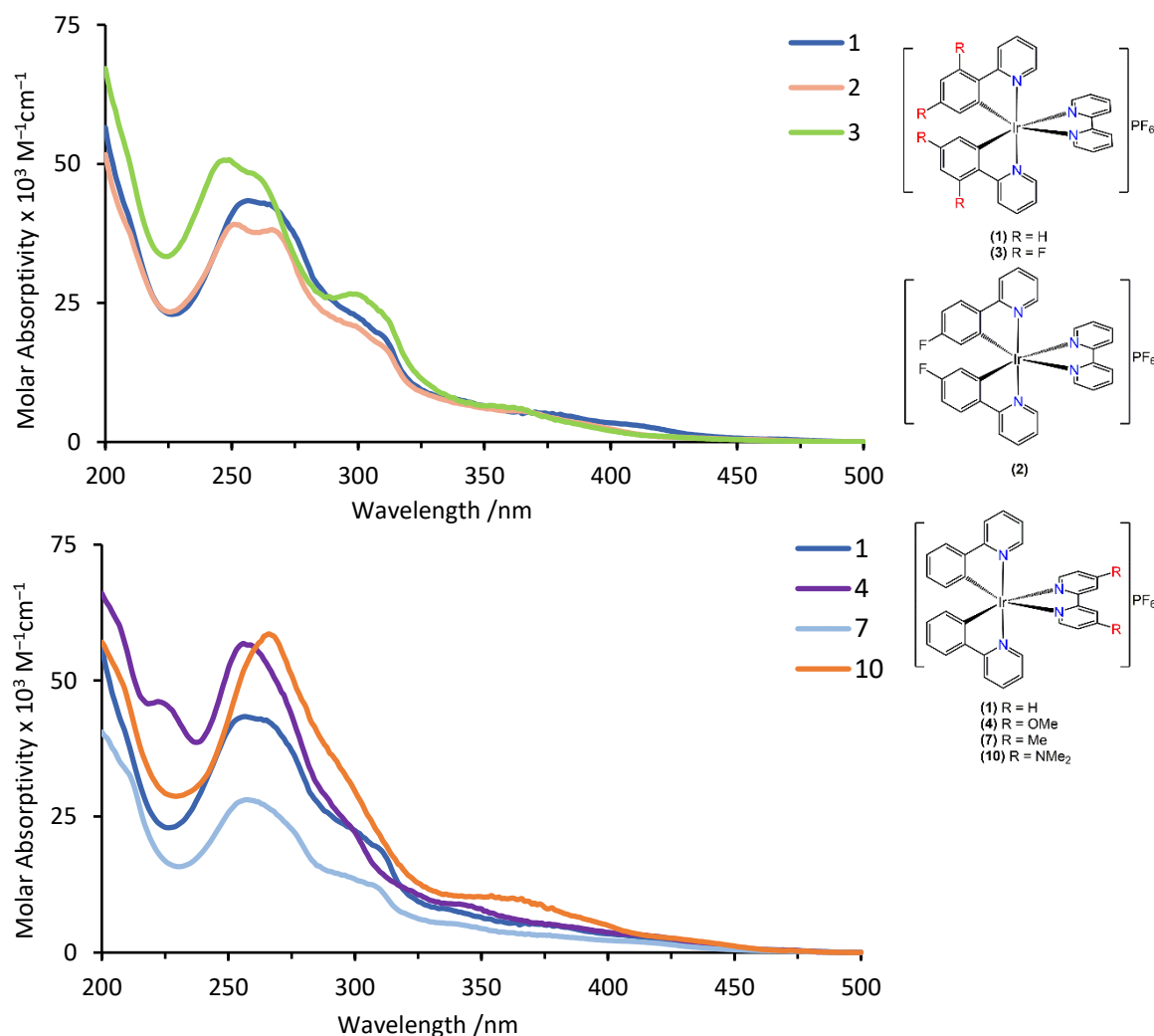


Figure 2.25: Absorbance spectra of complexes **1-3** (upper) and **1, 4, 7, and 10** (lower) in MeCN.

The $\pi\text{-}\pi^*$ and MLCT bands of the dmbpy-, dmbpy- and dmabpy-containing complexes **4**, **7** and **10** occur at similar wavelengths to the unsubstituted bpy complex, **1**, with a range of molar absorptivities from 0.9×10^4 to $7.3 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ (**Figure 2.25, lower**). Increasing the strength of the electron-donating substituents from methyl (**7**) to *N,N*-dimethylamino (**10**) shifts the high energy band from 257 nm to 266 nm ($\Delta E = 1320 \text{ cm}^{-1}$). The profiles of **1**, **4** and **7** feature an MLCT transition between 334 and 341 nm, but in complex **10** this transition is shifted to a longer wavelength (353 nm, $\epsilon = 1.4 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$), matching the results obtained by Nazeeruddin *et al.* on the same complex.¹¹⁰

Figure 2.26 compares the spectra belonging to the bis-dfp₂py- (**14**) and mes-dfppy-containing complexes (**17**) bearing the same N[^]N ligand i.e. dmbpy. The profile of complex **9** ($\text{C}^{\wedge}\text{N} = \text{dfppy}$) is included as a reference. The mesityl groups in **17** confer only a small change in the profile with increased molar absorptivities across the spectrum; a similar trend to that reported in the

literature.^{87,89} The bis-dfp₂py groups in **14** further increase molar absorptivities above those of **17**. All three complexes exhibit one or two intense bands between 249 and 263 nm arising from π - π^* transition(s) at the ancillary dmbpy ligand. This LC assignment agrees with the results obtained for **9** by Zanoni *et al.*⁹⁴ and with the high molar absorptivities which range between 5×10^4 and 7×10^4 M⁻¹cm⁻¹. Bands between 293 and 309 nm can be ascribed to mixed spin-character excited states (i.e. LC and MLCT transitions)⁹⁴ due to strong spin-orbit coupling whereas bands from 364 nm to 451 nm can be assigned to largely spin-allowed MLCT transitions with $\epsilon \leq 9.8 \times 10^3$ M⁻¹cm⁻¹.

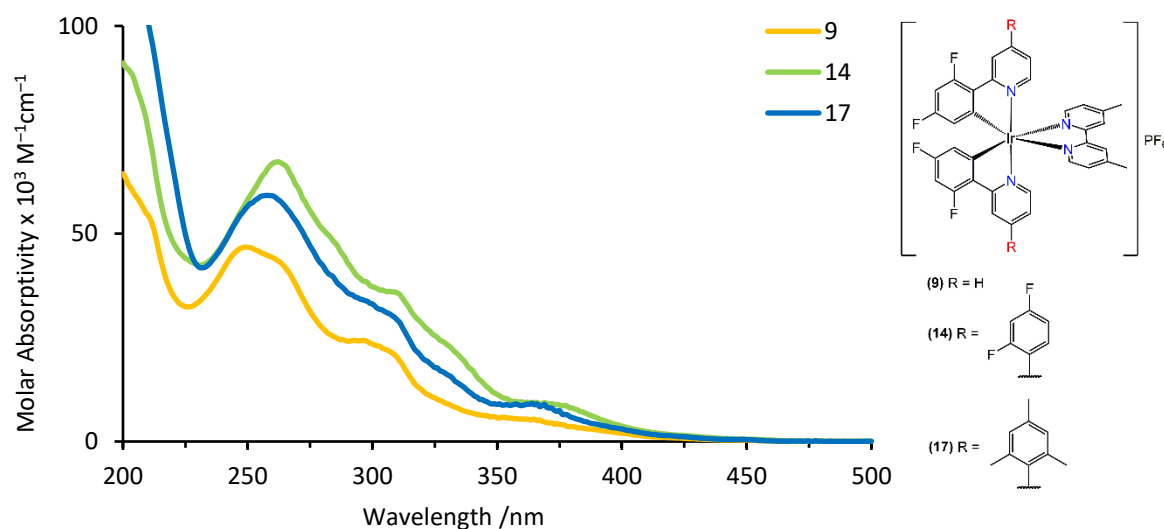


Figure 2.26: Absorbance spectra of complexes **9**, **14** and **17** in MeCN.

The absorption spectra for the bis-dfp₂py series of complexes **13-15** bearing bpy (**13**), dmbpy (**14**) and dmbpy (**15**) ancillary ligands are shown in **Figure 2.27, upper**. Again, there is little difference between the profiles in this series; their intense and moderately intense bands occur in the regions of 258-263 nm and 308-315 nm respectively with corresponding molar absorptivities of $6.2 \times 10^4 \leq \epsilon \leq 8.6 \times 10^4$ M⁻¹cm⁻¹ and $3.8 \times 10^4 \leq \epsilon \leq 5.1 \times 10^4$ M⁻¹cm⁻¹. Whilst complex **15** has the highest energy ¹LC transition ($38,800$ cm⁻¹) of the series, its MLCT transition ($31,700$ cm⁻¹) occurs at a lower energy than those of **13** and **14**.

The absorption spectra of the mes-dfp₂py series, **16-18**, are almost identical (**Figure 2.27, lower**) and generally reproduce that of a similar mes-dfp₂py complex reported in the literature (N⁺N = di^tBu₂bpy).⁸⁷ Changing the identity of the ancillary ligand from bpy (**16**), to dmbpy (**17**) to dmbpy (**18**) has a minimal effect on the position and intensity of the π - π^* and MLCT bands which both occur within narrow 3 nm ranges (257-260 nm and 297-300 nm). Molar absorptivity values for these transitions are $4.6 \times 10^4 - 6.3 \times 10^4$ M⁻¹cm⁻¹ and $2.6 \times 10^4 - 3.6 \times 10^4$ M⁻¹cm⁻¹.

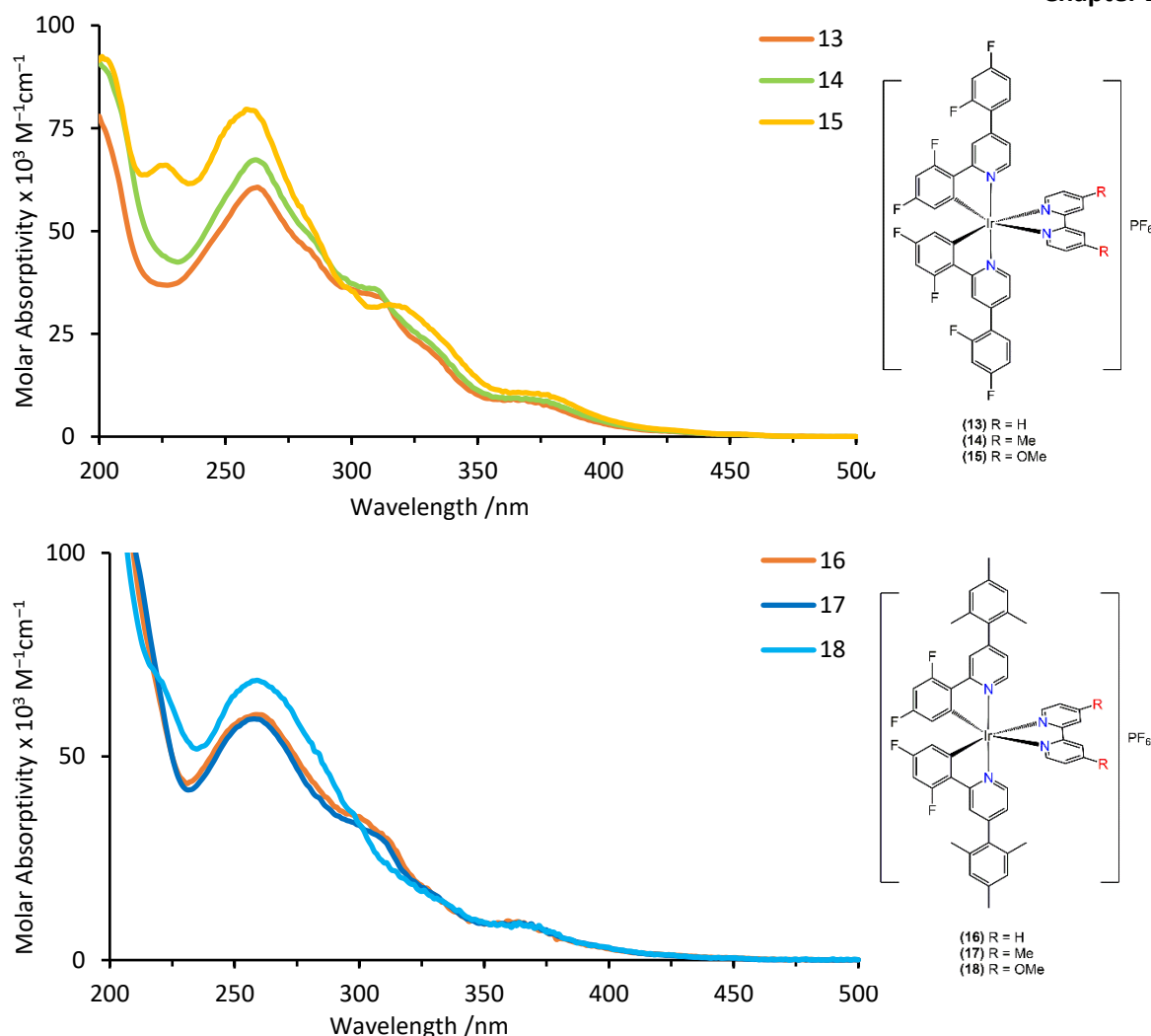


Figure 2.27: Absorbance spectra of complexes **13-15** (upper) and **16-18** (lower) in MeCN.

2.5.5.2 Emission

Figure 2.28 displays the normalised RT emissions of complexes **1**, **4**, **6-10**, **15** and **18** recorded in degassed MeCN. **Figure 2.28, upper**, shows the emissions of **7-9** illustrating the effect of varying the fluorine content of the cyclometalating ligand from ppy (**7**) to fppy (**8**) to dfppy (**9**). The profiles of all three complexes are nearly identical with a single broad emission peak in the orange to green regions of the visible spectrum. Emissions become increasingly blue across the series as a result of the increased C[^]N fluorination and subsequent increasing stabilization of the HOMO which is situated on the iridium and cyclometalating ligand (section 2.5.4). Successive addition of two fluorine atoms blue shifts the emission maximum by approximately 36 nm (1130-1210 cm⁻¹) each, from 592 nm (**7**) to 520 nm (**9**), matching results reported in the literature.⁹⁴

The RT emissions of complexes **1**, **4**, **7** and **10** show the effect of altering the bpy substituents (**Figure 2.28, middle**). Addition of methoxy, methyl and *N,N*-dimethylamino substituents to bpy, in complexes **4**, **7** and **10**, blue shifts emission relative to the reference unsubstituted bpy complex, **1** ($\lambda_{\text{max}} = 610$ nm). Whilst the methoxy and methyl substituents only induce a 15-18 nm (413-498

cm^{-1}) blue shift, the addition of the two strongly electron-donating *N,N*-dimethylamino groups in complex **10** blue shifts emission by 120 nm (4060 cm^{-1}) to $\lambda_{\text{max}} = 489, 515 \text{ nm}$ associated with a significant destabilization of the LUMO situated on the bpy ligand. Its uniquely structured emission profile with increased colour purity arises from a LC state.¹¹¹

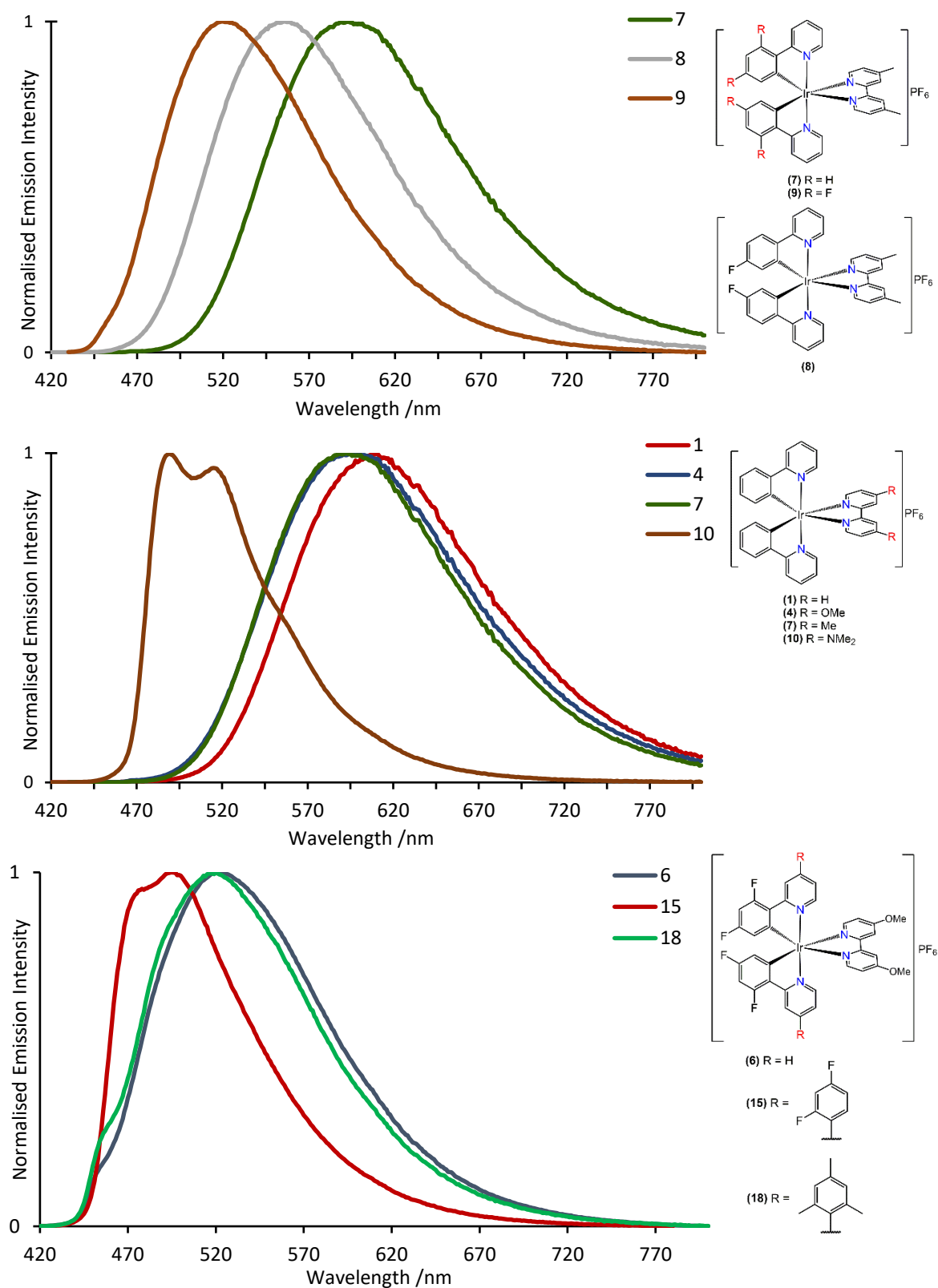


Figure 2.28: Normalised RT emission spectra of **7-9** (upper), **1, 4, 7** and **10** (middle) and **6, 15** and **18** (lower) in degassed MeCN, $\lambda_{\text{exc}} = 410 \text{ nm}$ (**1, 4, 7** and **8**), $\lambda_{\text{exc}} = 405 \text{ nm}$ (**6, 10, 15** and **18**), $\lambda_{\text{exc}} = 415 \text{ nm}$ (**9**).

A comparison between the RT emissions of bis-dfp₂py- and mes-dfppy-containing complexes **15** and **18** is made in **Figure 2.28, lower**. The dfppy-based analogue, complex **6**, is used as a reference. The mesityl groups of **18** have a negligible impact on emission and only blue shift the peak by 3 nm ($\lambda_{\text{max}} = 523$ vs. 520 nm, $\Delta E = 110 \text{ cm}^{-1}$). However, addition of a second difluorophenyl group to the dfppy ligand produces a 45 nm (1800 cm^{-1}) blue shift in emission (λ_{max} of **15** = 478, 497 nm). The addition of fluorine atoms is an established method to target blue emission;^{94,109} we demonstrate an example of a complex (**15**) bearing one of the most fluorinated cyclometalating ligands reported¹⁰⁰ (bis-dfp₂py = 4 fluorine atoms) which has achieved one of the bluest emissions for this [Ir(C[^]N)₂(N[^]N)]PF₆ structure type where C[^]N and N[^]N are ppy- and bpy-based ligands respectively.

Figure 2.29 illustrates the difference between the spectra at RT and 77 K for complexes **1**, **10** and **13-15**. **Figure 2.29, upper**, compares the profiles of complexes **1** and **10** which are blue shifted at low temperature. Upon cooling, complex **1** displays green emission with maxima at 510 nm and 536 nm representing one of the bluest shifts (by 100 nm, $\Delta E = 3210 \text{ cm}^{-1}$) compared to RT in the series **1-18**. The blue emission of complex **10** at RT becomes even bluer at 77 K, with increased vibronic structure ($\lambda_{\text{max}} = 475, 512 \text{ nm}$). The larger rate of non-radiative decay in **1** than in **10** ($k_{\text{nr}} = 27 \times 10^5 \text{ s}^{-1}$ vs. $2 \times 10^5 \text{ s}^{-1}$) is qualitatively consistent with the more pronounced blue shift of **1** at low temperature as it implies a greater degree of structural distortion in the excited state.

The RT and 77 K emissions of the bis-dfp₂py series **13-15** are shown in **Figure 2.29, lower**. Methoxy and methyl functionalisation of bpy in complexes **14** and **15** causes a blue shift in emission at RT compared to the unsubstituted bpy complex, **13**, from a maximum of 531 nm to $\approx 498 \text{ nm}$ ($\approx 1270 \text{ cm}^{-1}$), consistent with a destabilization of the LUMO. There is a shoulder in the RT spectrum of **15** at 478 nm. Emissions of **13-15** are bluer and more vibronically structured at low temperature; all three complexes exhibit nearly identical spectra with sharp emission maxima at $\approx 457 \text{ nm}$ and $\approx 490 \text{ nm}$ in addition to a shoulder at $\approx 532 \text{ nm}$. The same functionalisation of bpy in complexes **1-12** (i.e. the addition of methyl and methoxy groups) result in profiles with different peak values at low temperature, as exemplified by the emission maxima of the bpy-, dmbpy- and dmbpy-containing complexes **1**, **4** and **7** (**Figure 2.30**) which range between 471-510 nm and 507-536 nm. Complex **4**, which has the bluest emission of the three, displays the biggest hypsochromic shift from RT of 124 nm (4420 cm^{-1}) in line with its largest non-radiative rate of decay ($k_{\text{nr}} = 3.2 \times 10^6 \text{ s}^{-1}$).

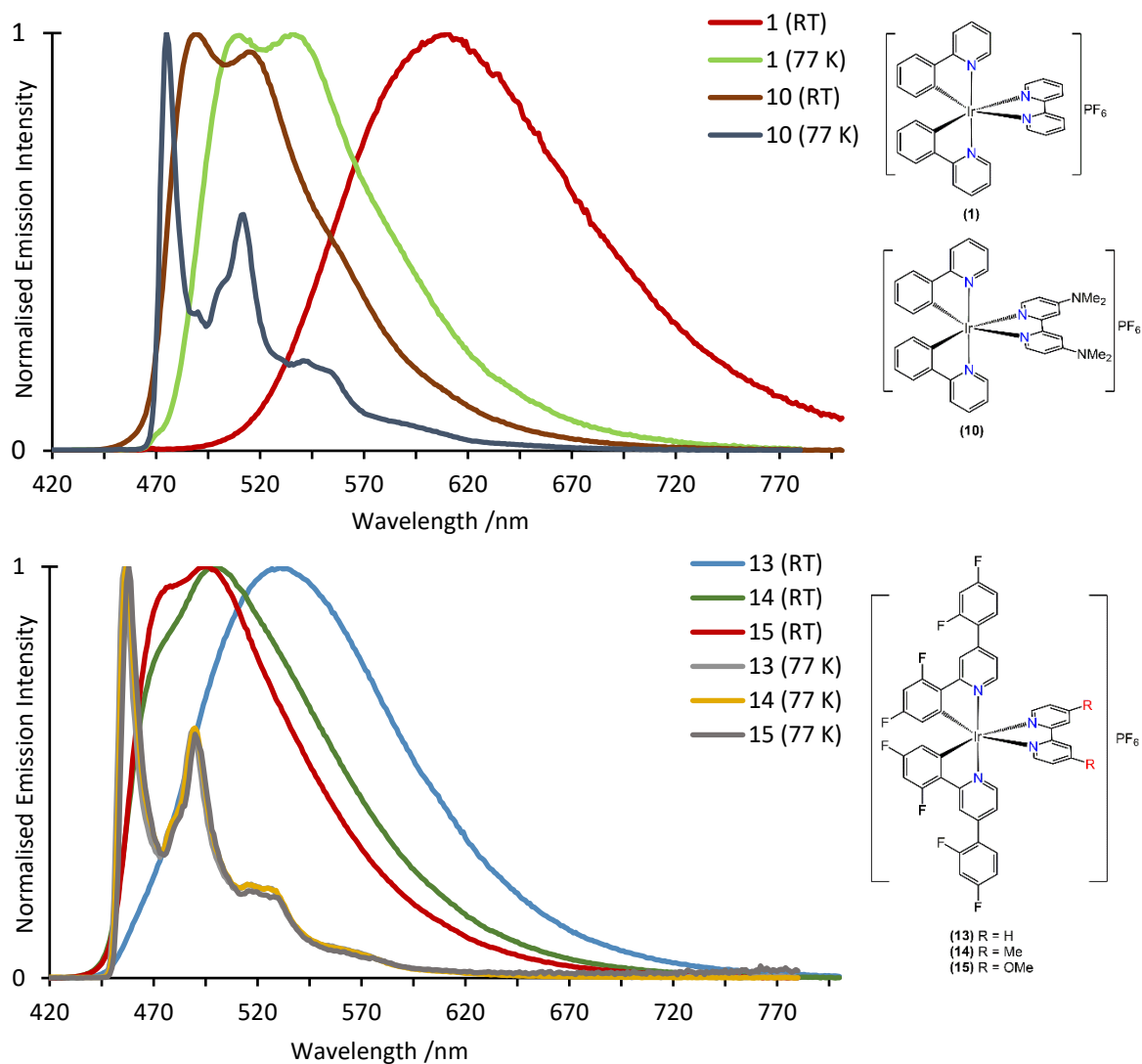


Figure 2.29: Normalised emission spectra of **1** and **10** (upper) and **13-15** (lower) in degassed MeCN at RT ($\lambda_{exc} = 405$ nm (**10** and **13-15**), $\lambda_{exc} = 410$ nm (**1**)) and in EPA at 77 K ($\lambda_{exc} = 400$ nm (**10** and **13-15**), $\lambda_{exc} = 410$ nm (**1**)).

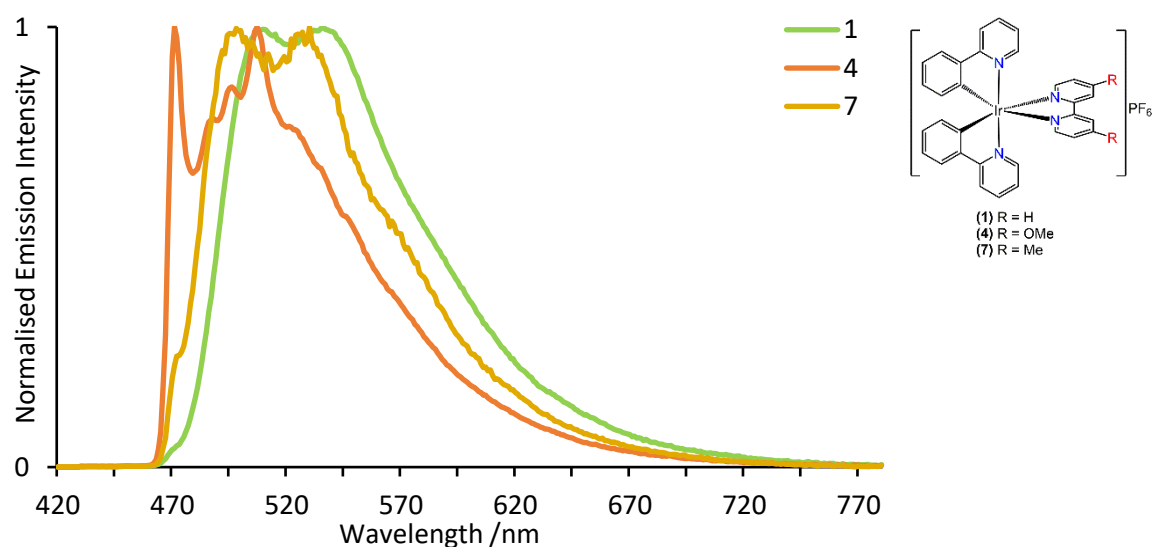


Figure 2.30: 77 K emission spectra of complexes **1**, **4** and **7** in EPA, $\lambda_{exc} = 400$ nm (**7**), $\lambda_{exc} = 410$ nm (**1** and **4**).

Figure 2.31, displays the 77 K spectra of complexes **4-6** to demonstrate the effect of changing the cyclometalating ligand from ppy to fppy and dfppy. All three profiles are similar with narrow twin emission peaks in the blue/green region from 448 nm to 507 nm. The incorporation of fluorine atoms to the C[^]N ligands in **5** (2 fluorine atoms) and **6** (4 fluorine atoms) blue shifts emission compared to **4** (C[^]N = ppy) by 13 nm (603 cm⁻¹) and 23 nm (1090 cm⁻¹) respectively. This trend is also observed at RT but to a greater extent ($\Delta\lambda_{\text{max}} = 72$ nm, $\Delta E = 2310$ cm⁻¹).

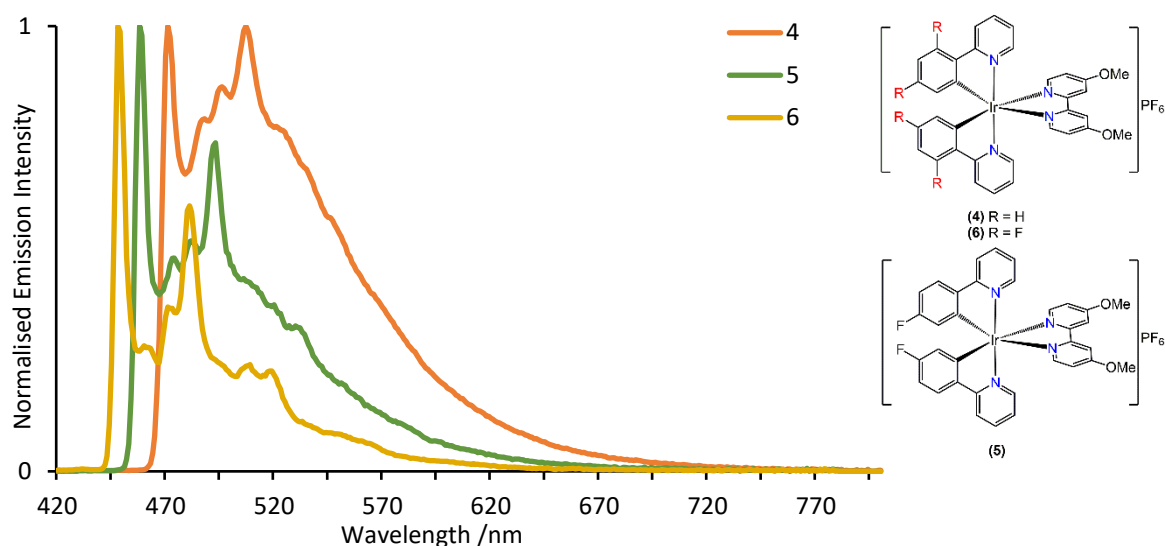


Figure 2.31: 77 K emission spectra of complexes **4-6** in EPA, $\lambda_{\text{exc}} = 400$ nm (**5** and **6**), $\lambda_{\text{exc}} = 410$ nm (**4**).

The quantum yields for complexes **1-12** range from 8% to 53% and are largely in line with literature values (**Table 2.6**).^{82,94–98,109–111} The quantum yields of the bis-dfp₂py- and mes-dfppy-containing complexes **13-18**, which reach 57%, are generally higher than the quantum yields of their dfppy-based counterparts (**3**, **6** and **9**) by as much as 16%. The increase in PLQY for the mes-dfppy-based complexes **16-18** is in agreement with similar complexes reported in the literature,^{87,155} although our values recorded are still not as high as those reported by Monkman and Bryce where values for the neutral complexes Ir(mes-dfppy)₂pic and Ir(dfppy)₂pic were $\phi = 92\%$ and 54% respectively.¹⁵⁶

Radiative decay rates are comparable across the series **1-18** ($k_r = 0.8 \times 10^5$ s⁻¹ to 3.8×10^5 s⁻¹) and are a similar order of magnitude to the rates of non-radiative decay in the majority of complexes. The non-radiative decay rates of the three most red-emitting complexes **1**, **4** and **7** are somewhat higher than the others ($k_{nr} \geq 1.7 \times 10^6$ s⁻¹) which reflect their lower quantum yields ($\phi \leq 14\%$).

RT lifetimes of the *N,N*-dimethylamino-containing complexes **10-12** ($\tau = 2.4$ - 6.1 μ s) are up to several microseconds longer than the rest of the series **1-18** ($\tau = 0.3$ - 1.7 μ s). Upon cooling, the lifetimes of **1-12** are extended up to a maximum lifetime of 6.1 μ s for complex **5**. The lifetimes of **13-18** also increase at low temperature ($\tau = 2.1$ - 3.6 μ s) but are shorter than those of **1-12**.

Table 2.6: Photophysical properties of complexes **1-18** recorded in degassed MeCN at RT ($\lambda_{exc} = 410$ nm. ^a $\lambda_{exc} = 400$ nm. ^b $\lambda_{exc} = 405$ nm. ^c $\lambda_{exc} = 415$ nm) and recorded in EPA at 77 K ($\lambda_{exc} = 400$ nm, ^d $\lambda_{exc} = 410$ nm, ^e = butyronitrile solvent. Aerated PLQYs and lifetimes are shown in brackets.

Complex	1 ^d	2	3	4 ^d	5	6 ^b	7	8	9 ^c
Absorption Maxima /nm ($\epsilon / M^{-1} cm^{-1}$)	256 (43800) 265 (43900) 303 (21800) 334 (9150) 370 (5930) 405 (3740) 465 (716)	251 (38900) 266 (38200) 297 (21100) 361 (5610) 454 (433)	247 (60200) 258 (62300) 298 (38200) 356 (6630) 417 (991) 445 (409)	256 (52800) 297 (18100) 341 (8680) 385 (5270) 413 (3680) 467 (498)	254 (46800) 267 (42300) 298 (23700) 333 (10500) 369 (6130) 456 (358)	248 (61300) 298 (19900) 362 (6020) 445 (296)	257 (21200) 306 (9490) 339 (9680) 405 (3960) 456 (670)	254 (36000) 267 (29300) 305 (16400) 366 (6300) 426 (1100) 456 (416)	249 (40700) 263 (37700) 293 (21100) 365 (4840) 444 (346)
λ_{max} / nm	610	569	539	595	555	523	592	555	520
PLQY /% degassed (aerated)	8.0 (0.2)	28 (2.3)	43 (3.0)	8.1 (1.6)	25 (2.6)	40 (2.4)	14 (1.9)	38 (2.4)	48 (3.0)
Lifetime /ns degassed (aerated)	347 (67)	985 (82)	1450 (99)	290 (57)	840 (86)	1510 (80)	498 (63)	1210 (72)	1500 (96)
$k_r \times 10^5 s^{-1}$	2.3	2.8	3.0	2.8	3.0	2.6	2.9	3.1	3.2
$k_{nr} \times 10^5 s^{-1}$	27	7.3	3.9	32	8.9	4.0	17.2	5.1	3.5
77 K λ_{max} / nm	510, 536	476, 507	450, 482	471, 507	458, 493	448, 481	498, 530	459, 473, 493	449, 481
77 K Lifetime / μs	4.6	5.4	4.3	4.7	6.1	4.6	4.6	5.6	4.4

Complex	10 ^b	11 ^{a,e}	12 ^b	13 ^b	14 ^b	15 ^b	16 ^b	17 ^b	18 ^b
Absorption Maxima /nm ($\epsilon / M^{-1} cm^{-1}$)	266 (73400) 353 (14000) 472 (399)	265 (58700) 455 (9970) 459 (351)	264 (26600) 285 (17700) 371 (4460) 448 (159)	263 (61500) 308 (37500) 367 (8580) 452 (586)	261 (86300) 309 (50700) 372 (8360) 451 (540)	258 (86400) 315 (32100) 371 (10700) 452 (573)	260 (63100) 297 (37600) 361 (9470) 418 (1350) 446 (536)	259 (46400) 298 (36900) 364 (9770) 418 (1530) 447 (512)	257 (58000) 300 (25900) 368 (7750) 447 (412)
λ_{max} / nm	489, 515	470, 499	463, 489	531	498	478, 497	536	519	520
PLQY /% degassed (aerated)	51 (0.9)	53 (0.8)	48 (0.60)	53 (4.0)	57 (3.8)	43 (3.7)	39 (3.3)	55 (3.2)	56 (3.1)
Lifetime /ns degassed (aerated)	2390 (36)	3920 (47)	6120 (72)	1490 (109)	1660 (106)	1350 (111)	1280 (98)	1500 (82)	1470 (80)
$k_r \times 10^5 s^{-1}$	2.1	1.4	0.78	3.6	3.4	3.2	3.1	3.6	3.8
$k_{nr} \times 10^5 s^{-1}$	2.0	1.2	0.85	3.2	2.6	4.3	4.7	3.0	3.0
77 K λ_{max} / nm	475, 512	462, 496	452, 485	456, 489	457, 490	458, 490	450, 483	450, 483	450, 483
77 K Lifetime / μs	3.8	4.2	5.2	2.6	2.3	2.1	3.6	2.7	2.8

2.6 Results and discussion: pyrazolopyridine- and azaindole-based complexes

Complexes **19-34** (Figure 2.32) will be discussed in this section.

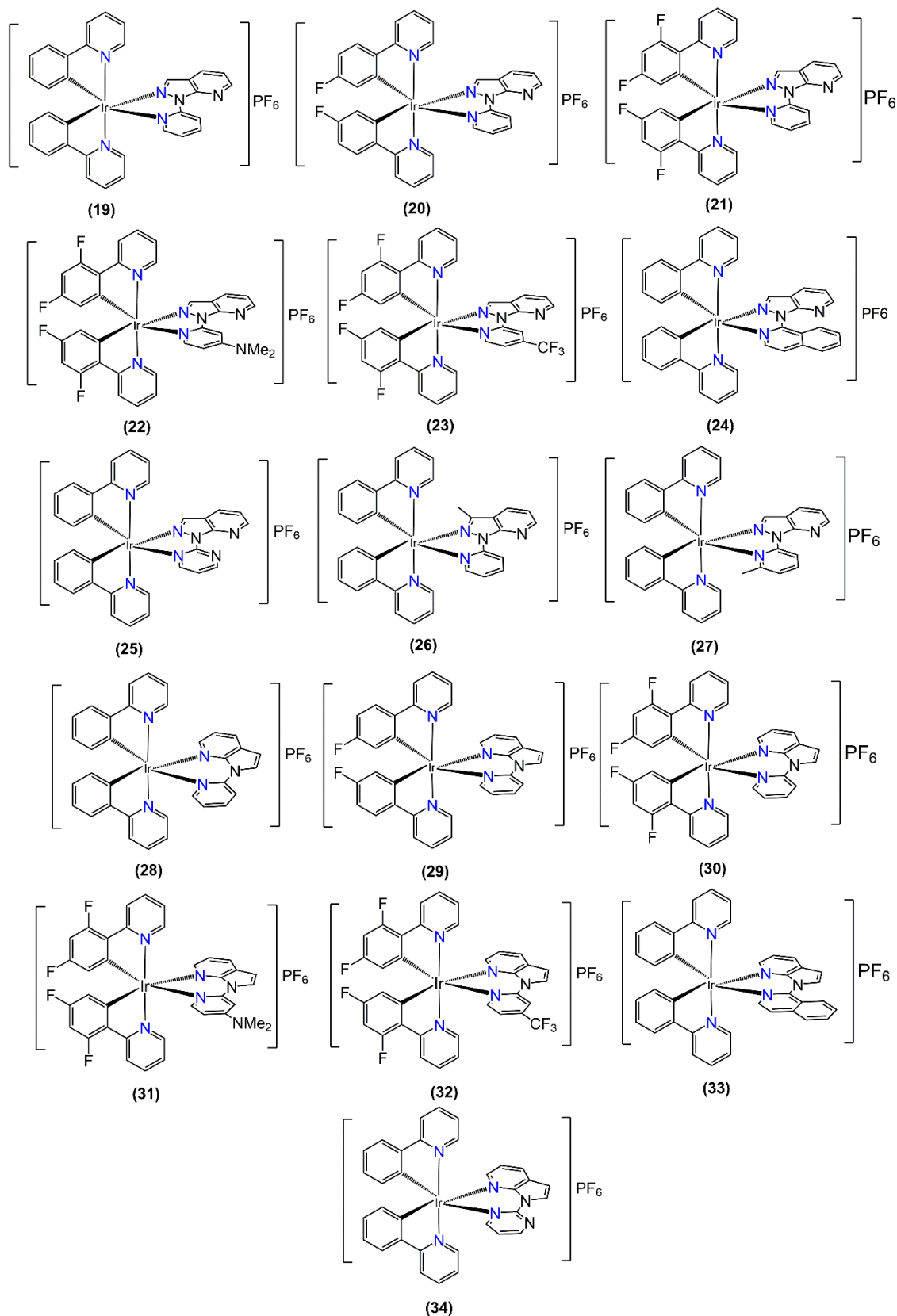


Figure 2.32: Structures of complexes **19-34**.

The 1*H*-pyrazolo[3,4-*b*]pyridine (pp) unit was chosen as the N[^]N framework because this group: (i) was easy to synthesize; (ii) represented a novel structure; (iii) was very similar to bpy in terms of binding mode and chelation size and (iv) had the potential to shift PL emission further towards the blue than the bpy-based complexes due to the more electron-rich *N*-heterocyclic ring system. An analogous series of [Ir(C[^]N)₂(N[^]N)]PF₆ complexes where N[^]N = a derivative of 7-azaindole (az) were synthesized to see if their photophysical properties would be any different from the pp-based complexes given the az unit is identical to the pp unit in terms of structure with the exception of the lack of one of the two nitrogen atoms in the 5-membered ring. 7-Azaindole-based N[^]N ligands are equally original in the field of luminescent iTMCs; there are only a few literature examples of az-containing complexes to date and most have been investigated for their potential anti-cancer properties.^{157,158}

2.6.1 Synthesis

Complexes **19-34** contain one of twelve pp- or az-based ligands (labelled L¹-L¹²) which were prepared by the copper-catalysed *N*-arylation of 7-azaindole (azH) or 1*H*-pyrazolo[3,4-*b*]pyridine (ppH) using the general conditions reported by Buchwald and co-workers for the copper-diamine catalysed *N*-arylation of pyrazoles (**Figure 2.33**).¹⁵⁹ The pp substrate was prepared from the reaction of hydrazine monohydrate and 2-chloro-3-pyridinecarboxaldehyde (or 3-acetyl-2-chloropyridine in the case of L¹¹). Ligands L¹-L¹² were synthesized in yields of up to 95%; the lowest yields obtained were for ligands L⁷ (20%) and L⁸ (14%), presumably because they were the only two in the series prepared from a less reactive aryl chloride (i.e. 1-chloroisoquinoline) instead of an aryl bromide whose carbon-halogen bond is weaker.

Ligands L¹³ and L¹⁴ were prepared solely to investigate the substrate scope of the Buchwald-Hartwig amination (**Figure 2.33**). Whilst the coupling of 8-bromoquinoline with 7-azaindole produced L¹³ in a yield of 45%, the reaction to form the equivalent pp-ligand failed to proceed even when using the more reactive 8-iodoquinoline. The contrast in reactivity of the azH and ppH substrates towards 8-bromoquinoline might be due to the reduced nucleophilicity of the ppH amine, which would also rationalise the lower yields obtained for L¹, L⁵ and L⁹ vs. L², L⁶ and L¹⁰ (yields of the pp-based ligands L³ and L⁷ are only marginally higher than their az equivalents L⁴ and L⁸). The reaction between ppH and 8-bromoquinoline might have proceeded using different conditions and substrates such as a Cu₂O-catalyst¹⁶⁰ or 8-quinoline boronic acid.^{161,162} Ligand L¹⁴ was prepared from 2,4-dibromopyridine; the 2- and 4-substituted side-products were easily separated by column chromatography. The formation of L¹⁴ is proof that the substrate scope of this CuI-catalysed amination includes 4-substituted arylhalides.

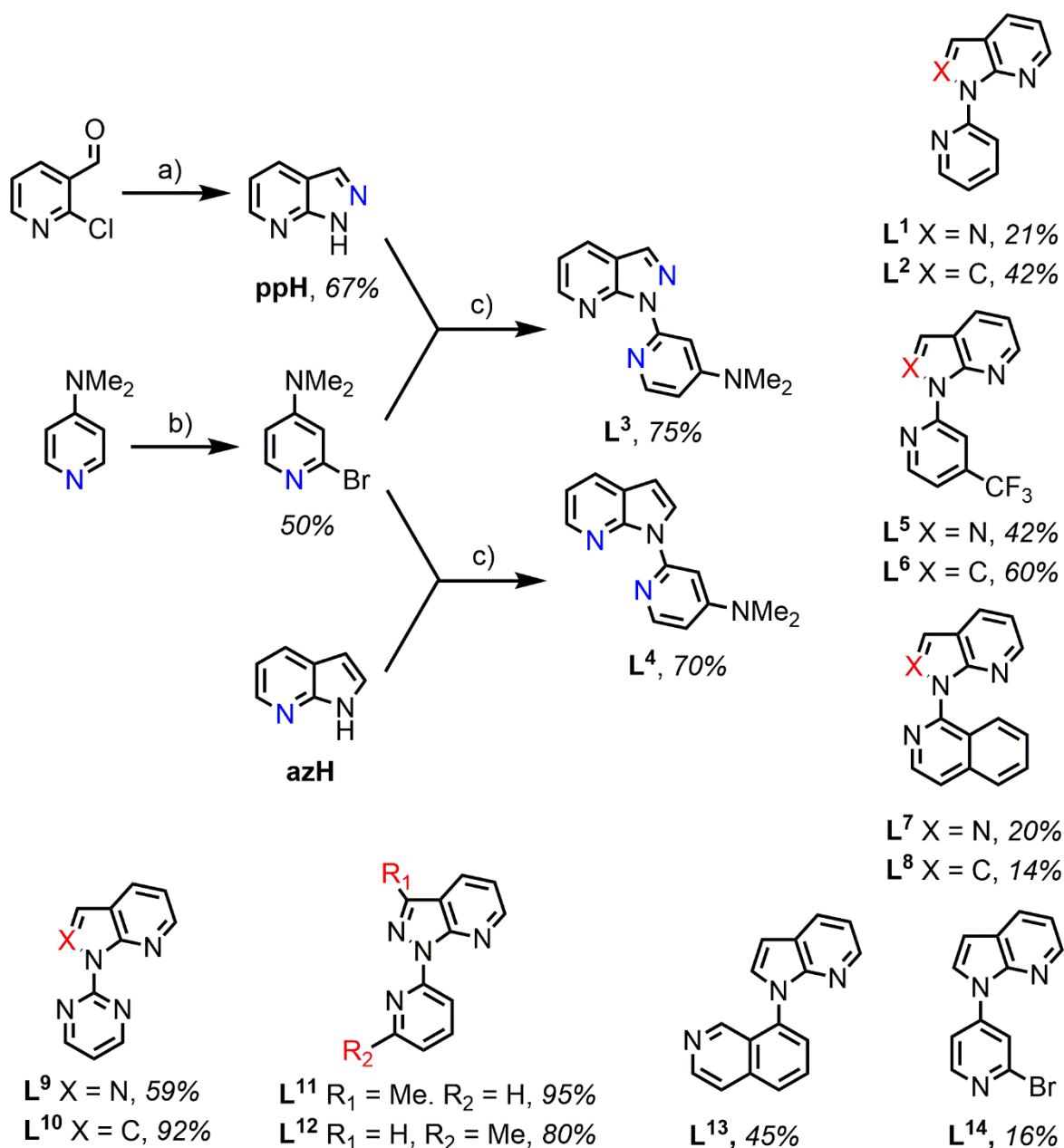


Figure 2.33: Synthesis of pyrazolopyridine- (L^3) and azaindole-based (L^4) ligands involving copper-catalysed Buchwald-Hartwig aminations: a) H_2N-NH_2 , p -TsOH, 130°C , 16 h; b) $n\text{BuLi}$, DMAE, hexane, 0°C , 1 h followed by CBr_4 in hexane, -78°C to RT, 16 h; c) 2-bromopyridine (1.2 equiv.), CuI, K_2CO_3 , 1,2-trans-diaminocyclohexane, 100°C , 16 h. Also shown are the structures and yields obtained for the other ligands in the series, L^1 , L^2 and L^5 - L^{14} .

The pp- and az-ligands were reacted with one of three iridium dimers, $[\text{Ir}(\text{ppy})_2\mu\text{-Cl}]_2$, $[\text{Ir}(\text{fppy})_2\mu\text{-Cl}]_2$ or $[\text{Ir}(\text{dfppy})_2\mu\text{-Cl}]_2$, under the same conditions as reported for the bipyridine systems (**Figure 2.21**), to afford a total of 16 complexes, **19-34** in yields between 8% and 89%. The purification procedure of **19-34** required column chromatography followed by recrystallization(s). All complexes displayed good solubility in polar solvents such as MeCN but when left in solution for several days, there were signs of degradation by ^1H NMR. (**Figure 2.34**).

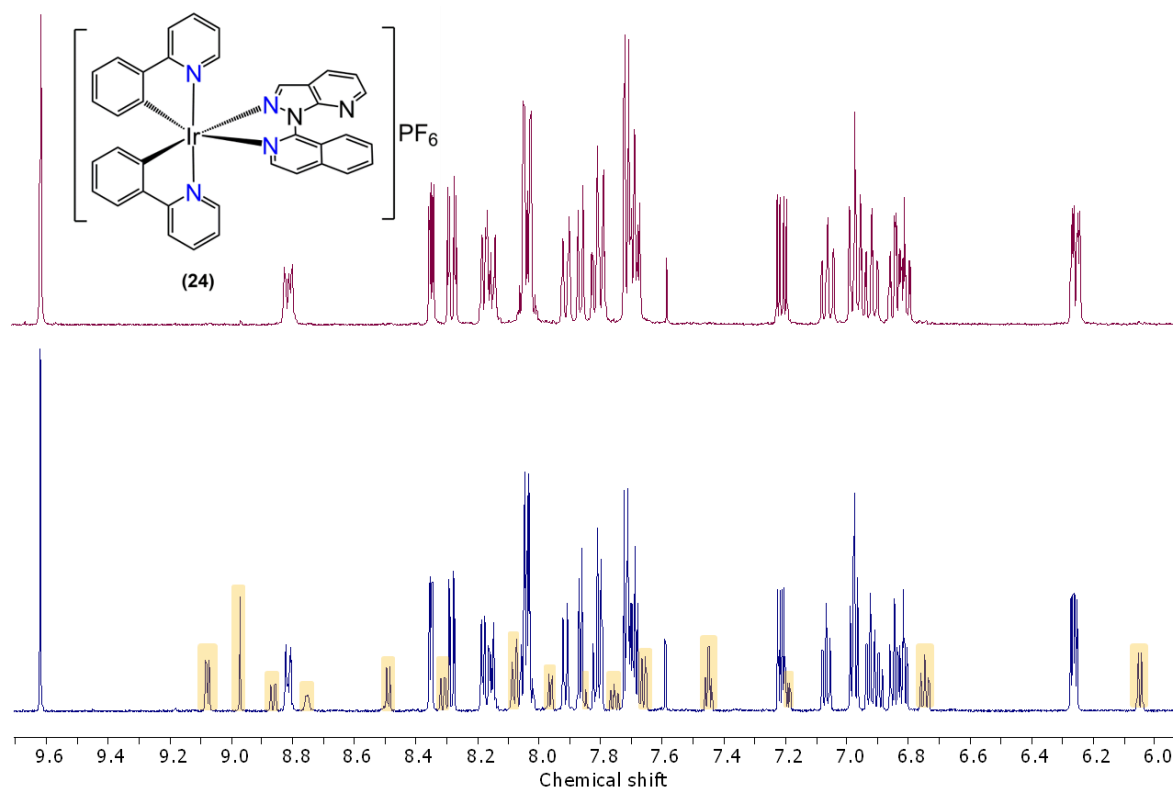


Figure 2.34: ^1H NMR spectra of **24** after column chromatography and two recrystallizations from MeCN and ether (upper). When left in MeCN solution for eight days, **24** becomes impure and multiple impurity peaks (highlighted in yellow) appear (lower).

An important feature of the pp-based ligands is that they have two modes of metal chelation. $\text{N}^{\wedge}\text{N}$ Coordination can happen via the pyrazole or pyridine nitrogen of the pyrazolopyridine moiety thus creating a 5- or 6-membered ring respectively (**Figure 2.35**). In contrast, the az-based ligands can only bind to the iridium centre via the pyridine nitrogen.

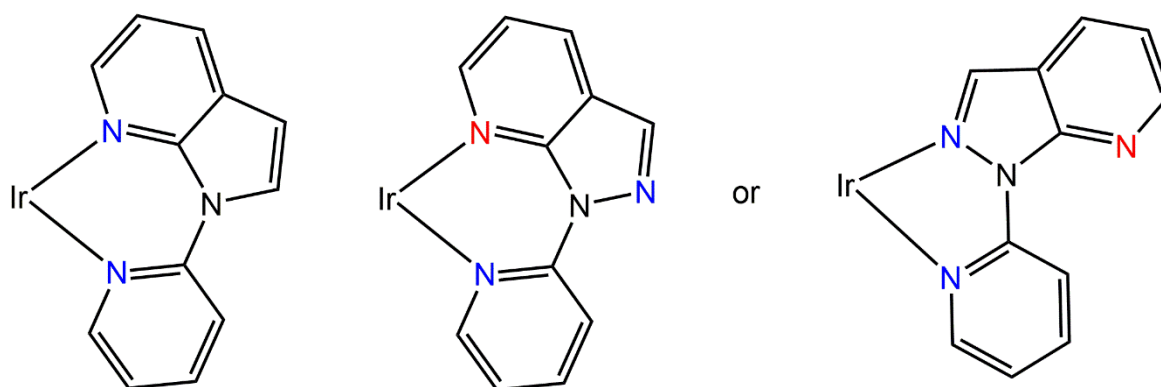


Figure 2.35: Azaindole-based ligands only have one binding mode to iridium (left) whereas pp-based ligands have two binding modes; via the nitrogen of the pyridine ring (coloured in red, middle) or the pyrazole ring (coloured in blue, right).

2.6.2 Crystallography

Crystals of **21**, **26** and **30** were prepared by slow evaporation of an MeCN solution. X-ray crystallography reveals that the pp-based ligand L^1 of complex **21** coordinates to the iridium centre via the pyrazole nitrogen rather than via the fused pyridine nitrogen to create a 5-membered

chelate ring (**Figure 2.36**). Ligand L^{11} of complex **26** also coordinates to iridium in the same manner as L^1 , despite the presence of the methyl group on the pyrazole ring. On the other hand, the az-based ligand L^2 of complex **30** can only bind to the metal centre via the nitrogen of the fused pyridine ring to create a larger 6-membered chelate ring. The N–Ir–N bond angles involving the ancillary ligand (N^3 –Ir– N^5 or N^3 –Ir– N^6) are consequently $\sim 10^\circ$ bigger in **30** than in **21** and **26** (86° vs. 76° , **Table 2.7**). All other bond lengths and angles of **21**, **26** and **30** involving the metal centre are similar. The binding preference of L^1 and other pp-based ligands could be due to the better overlap of the iridium and nitrogen orbitals in the smaller chelate ring meaning its formation is thermodynamically favoured over the larger ring size.

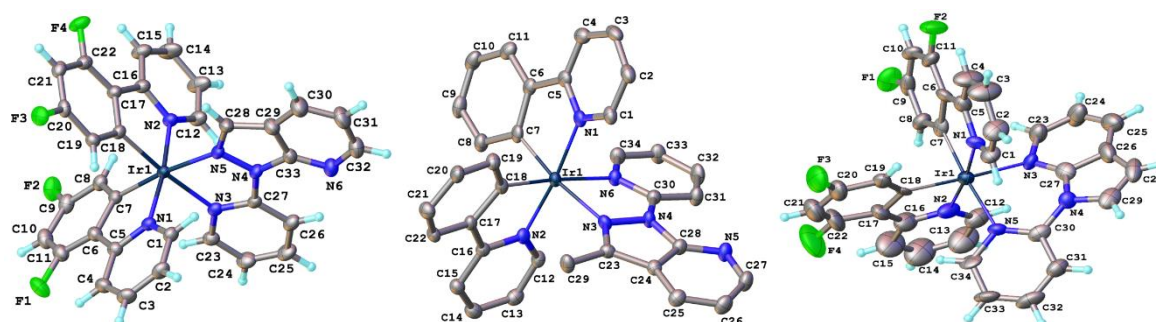


Figure 2.36: Crystal structures of **21** (left), **26** (middle) and **30** (right). The PF_6^- counter-ion is omitted for clarity.

Table 2.7: Selected bond lengths and angles for crystal structures of **21**, **26** and **30**.

Complex	21	26	30
Ir ¹ –N ¹ bond length /Å	2.050(3)	2.047(3)	2.046(1)
Ir ¹ –N ² bond length /Å	2.044(3)	2.044(3)	2.036(1)
Ir ¹ –N ³ bond length /Å	2.147(3)	2.146(3)	2.130(1)
Ir ¹ –N ⁵ bond length /Å	2.108(3)	-	2.151(1)
Ir ¹ –N ⁶ bond length /Å	-	2.158(3)	-
Ir ¹ –C ⁷ bond length /Å	1.994(4)	2.010(3)	2.020(1)
Ir ¹ –C ¹⁸ bond length /Å	2.014(4)	2.014(3)	2.003(1)
C ⁷ –Ir ¹ –N ¹ bond angle /°	80.51(1)	80.40(1)	80.1(5)
C ¹⁸ –Ir ¹ –N ² bond angle /°	80.06(1)	80.69(1)	80.8(5)
C ¹⁸ –Ir ¹ –N ³ bond angle /°	174.20(1)	99.25(1)	176.5(4)
N ¹ –Ir ¹ –N ² bond angle /°	172.95(1)	173.31(1)	172.9(4)
C ⁷ –Ir ¹ –N ⁵ bond angle /°	173.56(1)	-	175.3(5)
C ⁷ –Ir ¹ –N ⁶ bond angle /°	-	96.13(1)	-
N ³ –Ir ¹ –N ⁵ bond angle /°	76.23(1)	-	85.8(4)
N ³ –Ir ¹ –N ⁶ bond angle /°	-	75.78(1)	-

2.6.3 Electrochemistry

The electrochemical properties of the pp-based complexes **19–27** and az-based complexes **28–34**, measured in an electrolyte solution of 0.1 M NBu₄PF₆ in MeCN, are shown **Table 2.8** and **Table 2.9** respectively. Complexes **19–27** have a single reversible oxidation in the window +1.12 to +1.82 V, and an irreversible reduction between -1.43 and -1.66 V (**Table 2.8**). Complexes **26** and **27** also display a second irreversible reduction at -2.01 and -2.17 V respectively. Based on previous electrochemical studies of $[Ir(C^N)_2(N^N)]^+$ -type complexes,¹⁵³ the oxidation is thought to involve

the metal and cyclometalating parts of the complex, due to the strong covalency of the Ir–C bonds. This assignment is supported by DFT results (section 2.6.4) and by the more positive oxidation potentials of dfppy-containing complexes **21-23** (+1.56 to +1.82 V) with respect to ppy-containing complexes **19** and **24-27** (+1.12 to +1.55 V).

Conversely, DFT studies suggest that the reduction of **19-27** involves the gain of an electron from an orbital encompassing the pp ligand. The $\Delta E_{1/2}$ values of **19-27** still correlate well with their theoretical ΔE_{H-L} values, despite the use of a less accurate method to estimate their irreversible reduction potentials i.e. by using cathodic peak potential. There is only a slight discrepancy ($\Delta E \approx 0.1$ V) between the $\Delta E_{1/2}$ and ΔE_{H-L} values of **22** and **25**.

Table 2.8: Electrochemical properties of complexes **19-27** recorded in a 0.1 M electrolyte solution of NBu_4PF_6 in MeCN. Values were measured at a scan rate of 200 mV s^{-1} and are reported relative to SCE, measured using ferrocene as the standard ($E_{1/2}^{ox} = 0.42$ vs. SCE). E_p^{red} is the cathodic peak potential. $\Delta E_{1/2} = E_{1/2}^{ox} - E_p^{red}$. ΔE_{H-L} refers to the HOMO-LUMO gap calculated using DFT.

Complex	$E_{1/2}^{ox}/V$	E_p^{red}/V	$\Delta E_{1/2}/V$	$\Delta E_{H-L}/eV$
19	+1.34	-1.56 ^{ir}	2.90	2.88
20	+1.49	-1.55 ^{ir}	3.04	3.05
21	+1.70	-1.48 ^{ir}	3.18	3.24
22	+1.56	-1.61 ^{ir}	3.17	3.28
23	+1.82	-1.60 ^{ir}	3.02	3.06
24	+1.43	-1.43 ^{ir}	2.86	2.80
25	+1.12	-1.66 ^{ir}	2.78	2.88
26	+1.55	-1.45, -2.01	3.00	3.04
27	+1.29	-1.65, -2.17	2.94	2.98

The az-based complexes, **28-34** behave in a similar manner to the pp-based complexes, **19-27**, in that they also display a single reversible oxidation but across a slightly larger range of +1.36 to +1.72 V (Table 2.9). Complexes **28-34** display an irreversible reduction within the region of -1.42 to -1.93 V. Complexes **32** and **34** also display a second irreversible reduction at -1.79 and -1.90 V respectively. As observed in the pp series, oxidation of dfppy-containing complexes, **30-32** occurs at more positive potentials than ppy-containing complexes **28, 33** and **34** (+1.53 to +1.72 V vs. +1.36 to +1.39 V). This observation, in combination with DFT results, suggests oxidation of **28-34** is associated with a similar part of the complex as in the pp series i.e. the metal and cyclometalating ligand. The fact that the reduction window of **28-34** is cathodically shifted with respect to the reductions of **19-27** suggests the reductions of the az complexes involves the ancillary ligand. Consequently, the $\Delta E_{1/2}$ values of the az series are larger than the pp series by 0.4 V (e.g. 3.30 V (**28**) vs. 2.90 V (**19**)), however, this figure is not exact due to the increased uncertainty in estimating the reduction potentials of **19-34** by using E_p^{red} . Electrochemical $\Delta E_{1/2}$ values and DFT-calculated HOMO-LUMO gaps of **28-34** still correlate well although there is a larger difference between the absolute $\Delta E_{1/2}$ and ΔE_{H-L} values compared to **19-27**. A key difference between the electrochemical properties

of the pp and az complexes **19-34** vs. the bipyridine series **1-18** is the reversibility of the reduction i.e. the reductions of **19-34** are irreversible whereas the reductions of **1-18** are almost always reversible.

Table 2.9: Electrochemical properties of complexes **28-34** recorded in a 0.1 M electrolyte solution of NBu₄PF₆ in MeCN. Values were measured at a scan rate of 200 mV s⁻¹ and are reported relative to SCE, measured using ferrocene as the standard ($E_{1/2}^{ox} = 0.42$ vs. SCE). E_p^{red} is the cathodic peak potential. $\Delta E_{1/2} = E_{1/2}^{ox} - E_p^{red}$. ΔE_{H-L} refers to the HOMO-LUMO gap calculated using DFT.

Complex	$E_{1/2}^{ox}$ /V	E_p^{red} /V	$\Delta E_{1/2}$ /V	ΔE_{H-L} /eV
28	+1.37	-1.93 ^{ir}	3.30	3.44
29	+1.48	-1.91 ^{ir}	3.39	3.59
30	+1.68	-1.83 ^{ir}	3.51	3.77
31	+1.53	-1.91 ^{ir}	3.44	3.84
32	+1.72	-1.42 ^{ir} , -1.79 ^{ir}	3.14	3.26
33	+1.36	-1.63 ^{ir}	2.99	3.07
34	+1.39	-1.55, -1.90 ^{ir}	2.94	3.18

2.6.4 DFT

DFT calculations were performed on complexes **19-34** using the B3LYP functional and the LANL2DZ basis set. **Figure 2.37** displays the frontier molecular orbitals of complexes **21**, **30**, **33** and **34**. These four complexes were chosen to allow a direct comparison between equivalent pp (**21**) and az (**30**) complexes and between complexes containing an isoquinoline- (**33**) and pyrimidine-based (**34**) az ancillary.

The HOMO orbitals of **21** and **30** are located mainly over the iridium centre and the cyclometalating phenyl ring of the dfppy ligand whereas the LUMOs of **21** and **30** reside primarily over the entirety of the pp or az ligand. The major contribution to their excited states is a HOMO→LUMO transition (66-70%). Whilst **21** and **30** share identical HOMO energies (-8.66 eV), the LUMO of **30** is higher in energy than that of **21** by 0.53 eV (-4.89 eV vs. -5.43 eV). The larger HOMO-LUMO gap of **30** is consistent with its larger $\Delta E_{1/2}$ value (section 2.6.3). The results obtained for **21** and **30** are typical for the entire pp and az series with the exceptions of **33** and **34** whose LUMOs are distributed unevenly across their N[^]N ligands. The LUMOs of **33** and **34** are located to a larger extent over the isoquinoline and pyrimidine units of L⁸ and L¹⁰ respectively. Complex **33** has a smaller HOMO-LUMO gap than **34** by 0.11 eV, presumably due to the increased conjugation provided by the isoquinoline moiety. The HOMOs of **21** and **30** are lower in energy than **33** and **34** (-8.66 eV vs. -7.89 eV and -8.11 eV) due to the increased stabilization provided by their fluorinated cyclometalating ligands (i.e. dfppy vs. ppy).

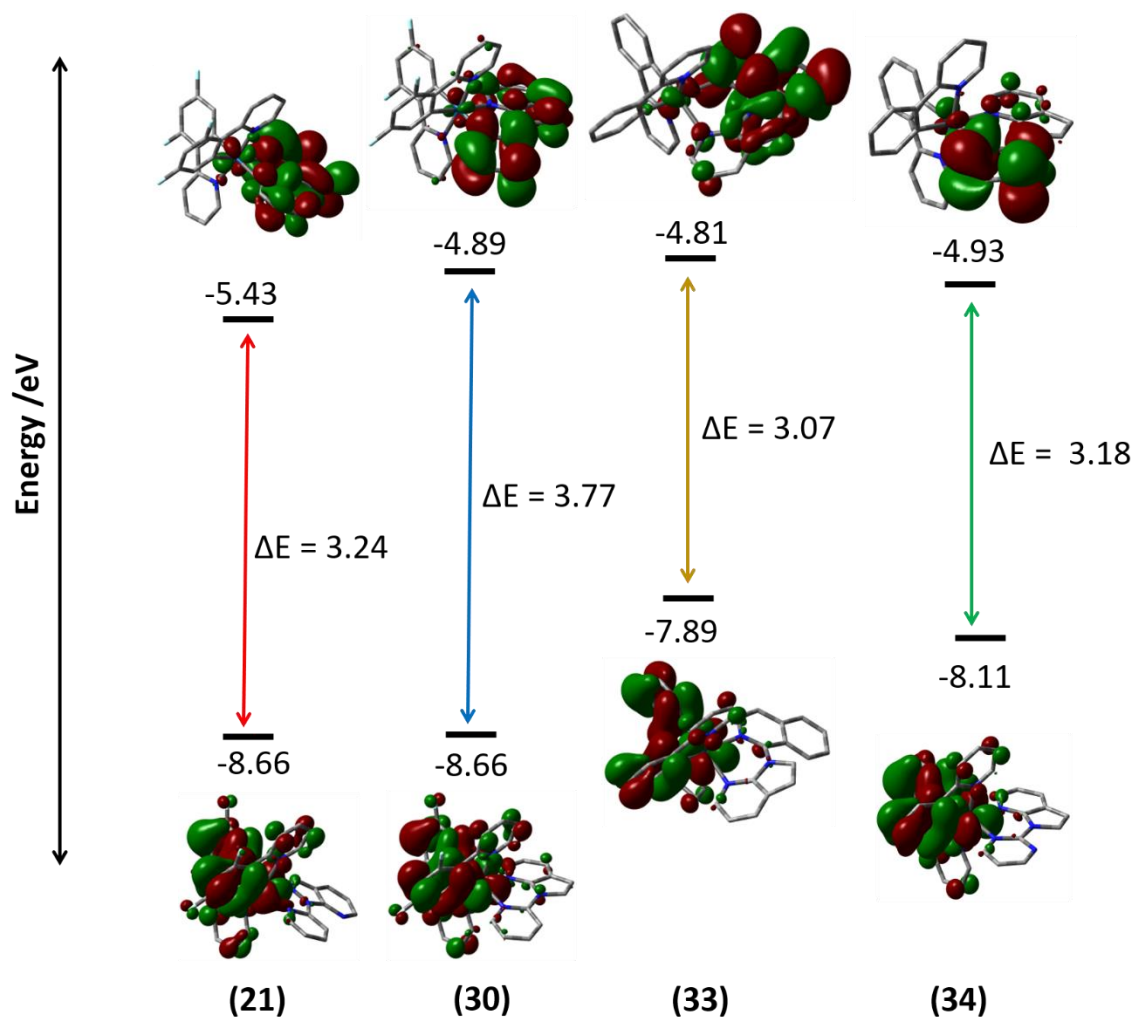


Figure 2.37: HOMO and LUMO diagrams and energies of complexes **21**, **30**, **33** and **34**, calculated by DFT.

2.6.5 Photophysical properties

The photophysical properties of complexes **19–34**, recorded in degassed MeCN at RT and in EPA at 77 K, are tabulated in **Table 2.10**.

2.6.5.1 Absorption

Figure 2.38, upper, displays the absorbance spectra of complexes **19**, **20** and **25–27**. These five pp-based complexes share similar profiles with 2–3 high energy bands below 293 nm, medium intensity bands between 307 and 330 nm and low intensity bands beyond 363 nm. The high intensity bands likely correspond to spin-allowed $\pi-\pi^*$ ^1LC transitions involving the C[^]N or N[^]N ligands whereas the medium and low intensity bands can be ascribed to spin-forbidden transitions involving metal-to-ligand charge transfer (i.e. $^1\text{MLCT}$ and $^3\text{MLCT}$). These assignments are based on previous studies of $[\text{Ir}(\text{C}^{\wedge}\text{N})_2(\text{N}^{\wedge}\text{N})]^+$ -type complexes where C[^]N and N[^]N are ppy- and bpy-based ligands respectively.^{94,95,97,98,109,111} The high, medium and low intensity bands have molar absorptivities of $1.6 \times 10^4 \leq \epsilon \leq 7.1 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$, $1.6 \times 10^4 \leq \epsilon \leq 3.3 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ and $4.8 \times 10^3 \leq \epsilon \leq 6.3 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$. Replacement of ppy (**19**) with fppy (**20**) confers a reduction in molar absorptivities across the

spectrum whereas the addition of methyl groups to the pp ligand (**26** and **27**) generally increases them. The pyrimidine variant (**25**) is closer in profile to that of **19**.

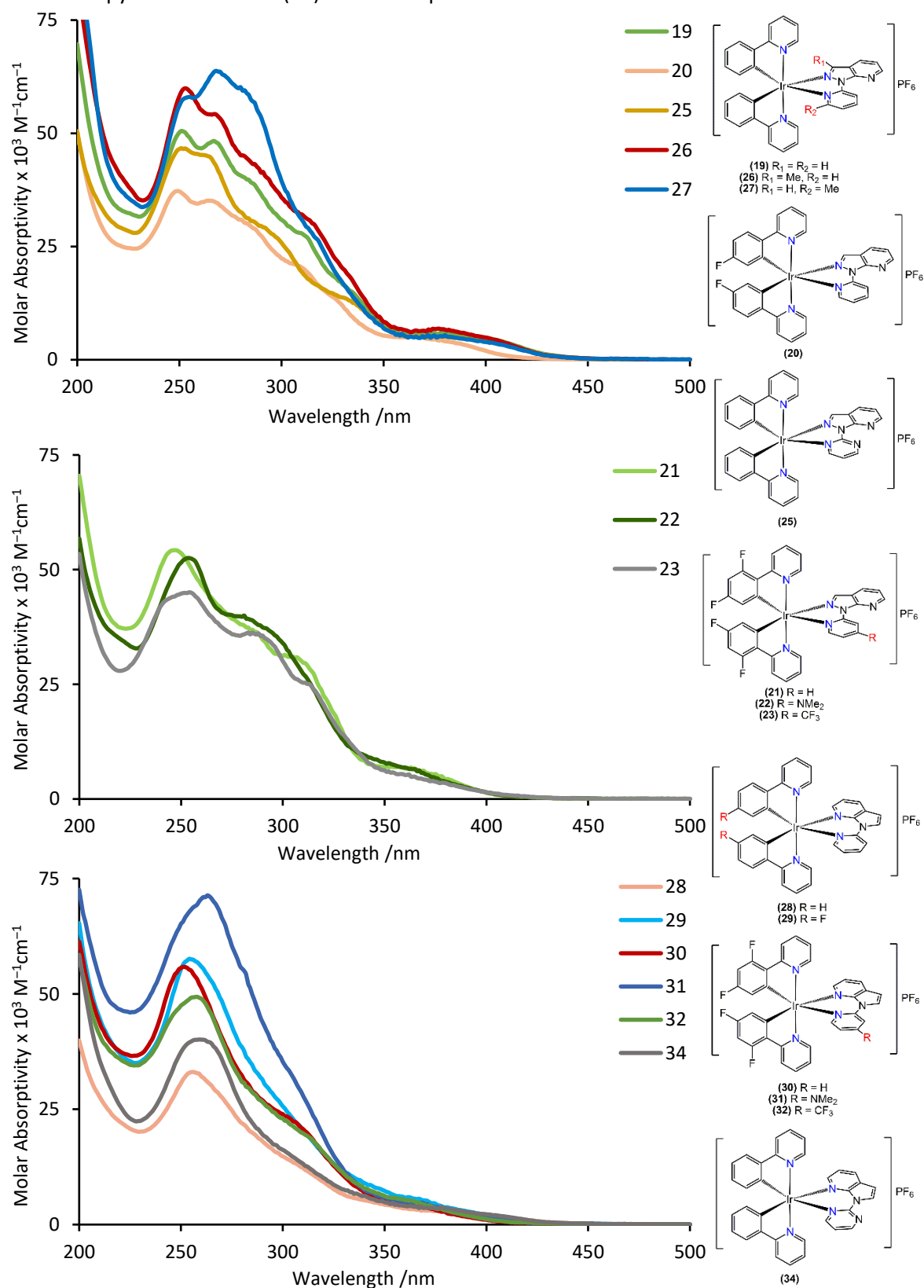


Figure 2.38: Absorbance spectra of complexes **19**, **20** and **25-27** (upper), **21-23** (middle) and **28-32** and **34** (lower) in MeCN.

The molar absorptivities for the high intensity bands of the dfppy-containing complexes **21-23** lie in a similar range to **19, 20** and **25-27** ($3.1 \times 10^4 \leq \epsilon \leq 5.7 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$, **Figure 2.38, middle**). Their $\pi-\pi^*$ peak occurs between 246 and 254 nm with a shoulder at 286-293 nm. The intensity and position of the MLCT bands of **21-23** (303-312 nm) also approximately match those of **19, 20** and **25-27**. The similarity of all three spectra indicate the addition of a $-\text{CF}_3$ or $-\text{NMe}_2$ substituent to the pp ligand in **22** and **23** has a minimal impact on absorption.

The profiles of the az series of complexes **28-32** and **34** are displayed in **Figure 2.38, lower**. These six complexes exhibit a single defined $\pi-\pi^*$ band between 251 and 263 nm with a broader range of molar absorptivities than the pp series ($3.2 \times 10^4 \leq \epsilon \leq 7.2 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$). The MLCT transitions beyond 350 nm are less well-defined than the pp complexes **19-27**. In this series, the profiles of the dfppy-containing complexes **30-32** resemble the profiles of the other az-based complexes **28, 29** and **34**.

The profiles of the two isoquinoline-containing complexes **24** and **33** resemble each other closely but differ significantly from the other complexes (**Figure 2.39**). Their spectra consist of a series of small peaks or shoulders across a wide range from 228 to 469 nm. Both complexes have three bands below 271 nm, attributed to spin-allowed LC $^1\pi-\pi^*$ transitions of both the cyclometalated and ancillary ligands ($\epsilon \geq 3.6 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$).¹⁴⁶ Their moderately intense bands at 348-351 nm and 361-377 nm are assigned to spin-allowed $^1\text{MLCT}$ and ligand-to-ligand charge transfer ($^1\text{LLCT}$) transitions ($5.0 \times 10^3 \leq \epsilon \leq 1.8 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$). Their low intensity bands at 469 nm ($\epsilon \leq 2.6 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$) arise from spin-forbidden ^3LC , $^3\text{MLCT}$ and $^3\text{LLCT}$ transitions.¹⁶³

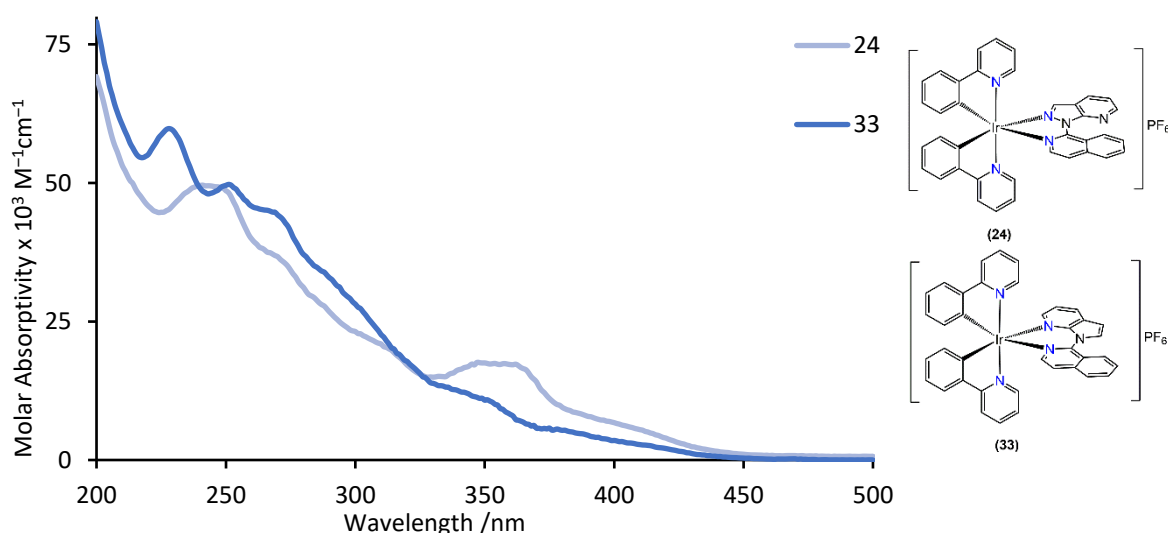


Figure 2.39: Absorbance spectra of complexes **24** and **33** in MeCN.

2.6.5.2 Emission

In the literature, we observed that the use of nitrogen-rich heterocycles can result in bluer emission,^{91,106,130-133,113,116,117,125-129} our novel series of ligands featuring a pp or az motif demonstrates the results that can be achieved through this approach (**Figure 2.40**). Complexes **21**

and **30** containing pp- and az-based N^N ligands respectively are compared to the bluest complex of the bipyridine series (**12**) bearing the dmabpy ancillary. The two novel complexes share nearly identical profiles with 0,0 emission maxima between 450 and 453 nm which represents a blue shift of 10-13 nm ($477\text{-}624\text{ cm}^{-1}$) compared to **12**. As the cyclometalating ligand in all three complexes is dfppy, the colour change observed is ascribed to a rise in the LUMO energy which presumably occupies the N^N ancillary.¹¹¹

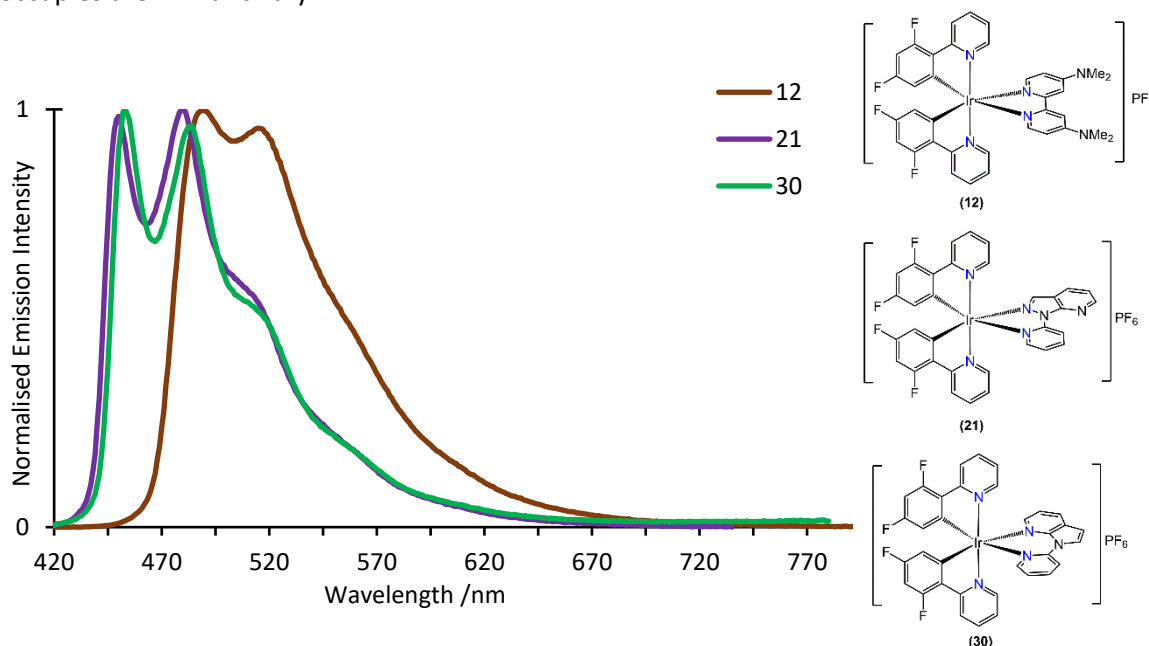


Figure 2.40: Normalised RT emission spectra of complexes **12**, **21** and **30** in degassed MeCN, $\lambda_{exc} = 405\text{ nm}$ (**12**), $\lambda_{exc} = 400\text{ nm}$ (**21** and **30**).

Figure 2.41 illustrates the effect on emission of C^N and N^N ligand modification in pp-based complexes. Increasing the fluorine content of the cyclometalating ligands across the series **19-21** causes a progressive blue shift in emission (**Figure 2.41, upper**) from 473 nm (**19**) to 460 nm (**20**) to 450 nm (**21**), associated with an increasing stabilization of the HOMO.

In **Figure 2.41, middle**, the addition of the electron-donating -NMe₂ substituent to the pp ligand (**22**) has a negligible effect on emission, with 2 nm (98 cm^{-1}) redder emission than the unsubstituted pp-based complex, **21**. This result is contrary to what was observed in the bpy series whereby the incorporation of *N,N*-dimethylamino substituents to bpy confers a large blue shift in emission by 76-121 nm ($3050\text{-}4060\text{ cm}^{-1}$).^{110,111} As already discussed, the pp-based complexes are bluer emitters than their bpy-counterparts due to a greater destabilization of the LUMO; thus, the effect of adding the *N,N*-dimethylamino substituent in **22** has little difference. However, the addition of the electron-withdrawing -CF₃ substituent in the same position (**23**) red shifts emission significantly by 25-55 nm ($1030\text{-}2420\text{ cm}^{-1}$) to a single peak at 505 nm, which can be assigned to a stabilization of the LUMO. The emissions of all three complexes occur from the lowest-lying triplet state (T_1), which comprises contributions from ^3LC , $^1\text{MLCT}$ and $^3\text{MLCT}$ transitions. The broader profile of **23** suggests

a higher charge-transfer character to its triplet state whilst the structured profiles of **21** and **22** indicate a higher ligand-centered contribution.¹⁶⁴

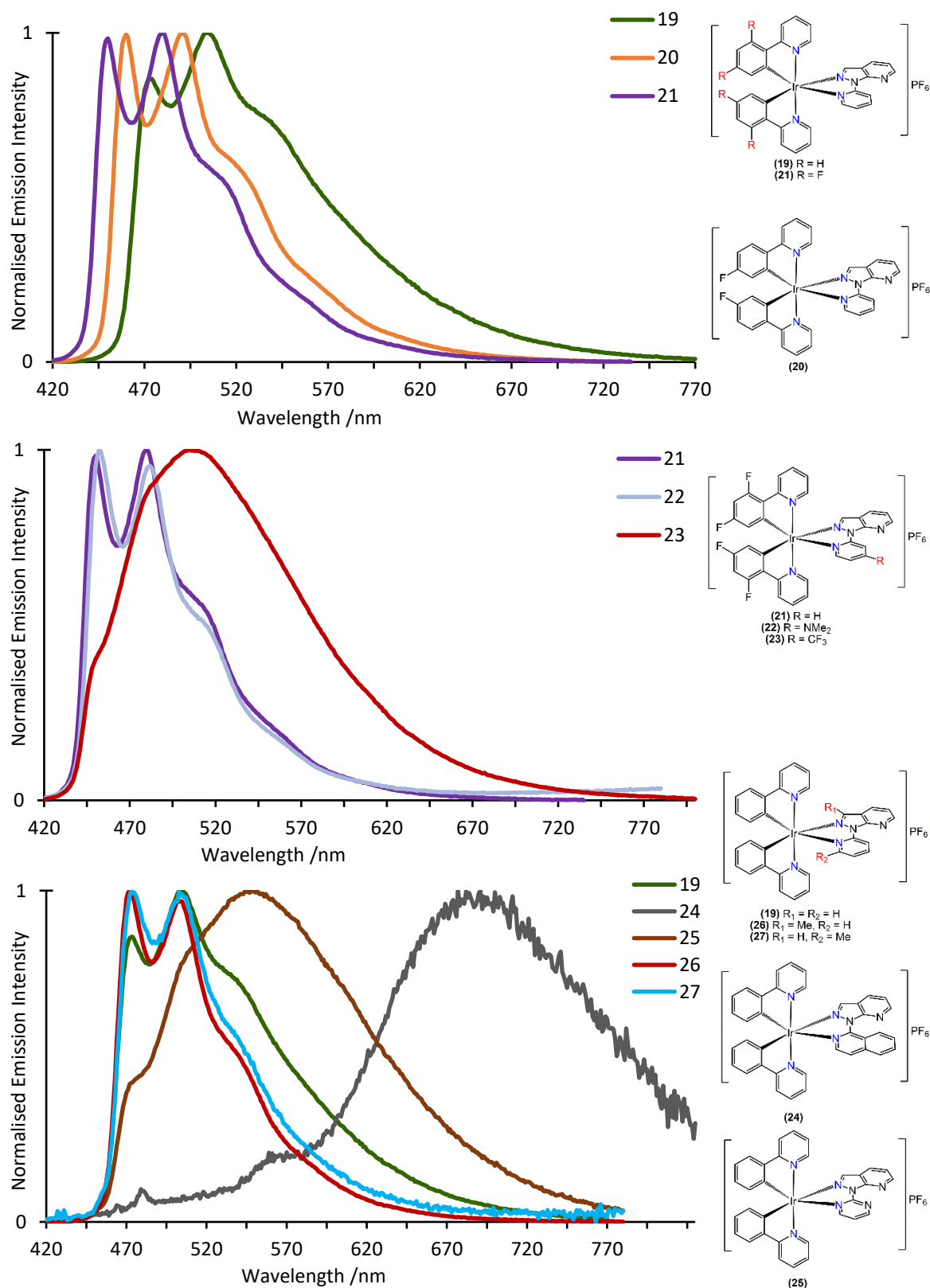


Figure 2.41: Normalised RT emission spectra of complexes **19-21** (upper), **21-23** (middle) and **19** and **24-27** (lower) in degassed MeCN, $\lambda_{exc} = 420$ nm (**24**), $\lambda_{exc} = 400$ nm (**19-23** and **25-27**).

The spectra of the five ppy-containing complexes **19** and **24-27** are shown in **Figure 2.41**, lower. Complexes **19**, **26** and **27** share nearly identical profiles to each other with 0,0 emission maxima at

approximately 473 nm; the addition of a methyl group to the pp ligand in **26** and **27** has a minimal effect on PL other than a decrease in relative intensity of the 0,2 component band. Replacement of the pyridine half of the pp ligand with an isoquinoline unit (**24**) imparts a significant red shift in emission to $\lambda_{\text{max}} = 677$ nm which can be rationalised by the extended conjugation of the isoquinoline-based pp ligand. A similar red shift in emission has been observed by Huang and co-workers through the conversion of both pyridine rings of bpy to isoquinoline in Ir(III) complexes containing the C^N ligand 1-phenylisoquinoline ($\lambda_{\text{max}} = 710$ vs. 588 nm).¹⁶⁵ Substitution with pyrimidine (**25**) does not alter emission maxima significantly but its profile changes such that the most intense peak is now at 549 nm (which was a shoulder in **19**) with a series of two shoulders at 472 nm and 512 nm (which were the twin emission peaks of **19**). Similar emissions between pyridine- and pyrimidine-containing Ir(III) complexes have been reported by Su and co-workers.¹⁴⁰

The emissions of the pp series are similar to their az-counterparts (**Figure 2.41**) at RT with the exceptions of the isoquinoline- and pyrimidine-containing complexes **24** and **25** whose profiles differ substantially from their az equivalents (**33** and **34** respectively). In **Figure 2.42** we highlight the difference between the emissions of **24** and **33** both at RT and at 77 K. Upon cooling, the emission maximum of **24** is blue shifted by 181 nm (5390 cm^{-1}) from 677 to 496 nm. The 77 K peak is accompanied by several vibrational bands at higher energies ($\lambda_{\text{max}} = 522, 604$ and 652 nm). The az analogue, **33**, is an orange emitter at RT with an unstructured profile peaking at 609 nm; it also undergoes a blue shift when cooled in EPA (to $\lambda_{\text{max}} = 506, 544$ and 586 nm), although to a lesser extent than **24**. The rigidochromic effect of cooling on both complexes indicates that their RT emissions originate from either a ^3LC or $^3\text{MLCT}$ state.¹⁶⁶

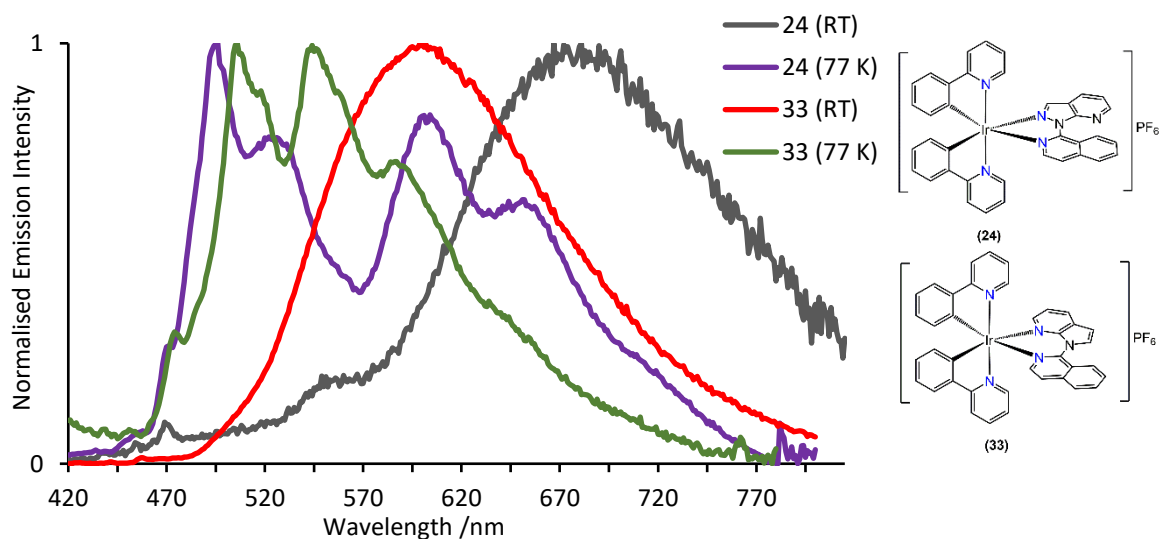


Figure 2.42: Normalised emission spectra of complexes **24** and **33** at RT in degassed MeCN ($\lambda_{\text{exc}} = 410$ nm (**33**) and $\lambda_{\text{exc}} = 420$ nm (**24**)) and at 77 K in EPA ($\lambda_{\text{exc}} = 400$ nm).

The 77 K emission of complex **23** is highly structured with vibrational bands at 452, 482 and 517 nm (**Figure 2.43**); this represents a blue shift of 53 nm (2320 cm^{-1}) compared to RT. Whilst the profile

of **23** is largely unstructured at RT, the spectrum of the CF₃-containing az-analogue (**32**) is considerably more structured with a bluer emission peak (483 vs. 505 nm) and more defined secondary peaks and shoulders at 454 nm and 514 nm respectively (**Figure 2.44**), indicative of a less distorted excited state.¹⁵² Upon cooling, its emission profile remains similar but is shifted to a longer wavelength ($\lambda_{\text{max}} = 506, 544, 587$ nm).

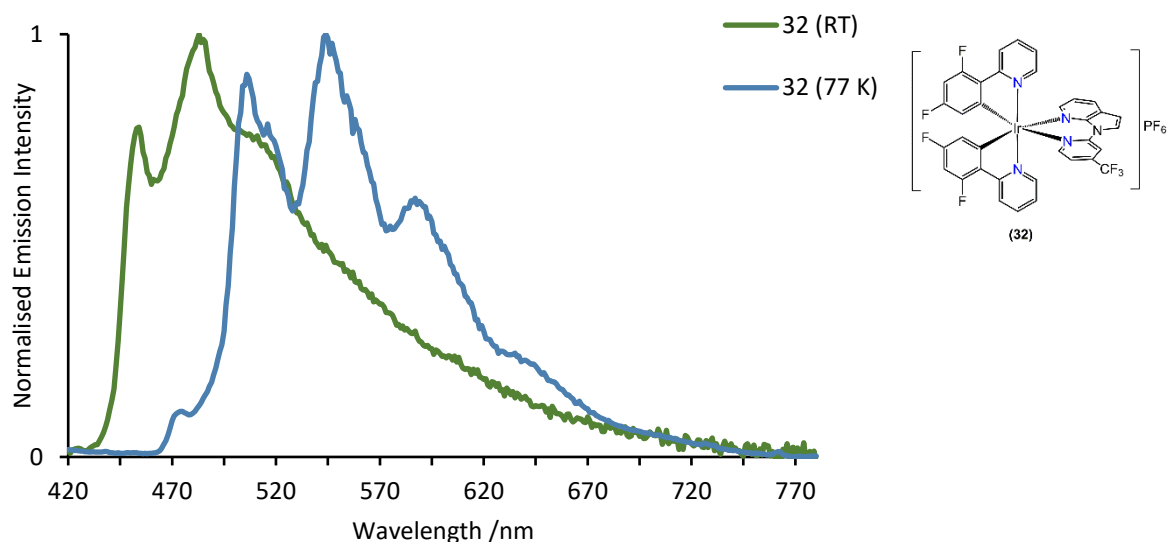


Figure 2.43: Normalised emission spectra of complex **23** at RT in degassed MeCN ($\lambda_{\text{exc}} = 400$ nm) and at 77 K in EPA ($\lambda_{\text{exc}} = 400$ nm).

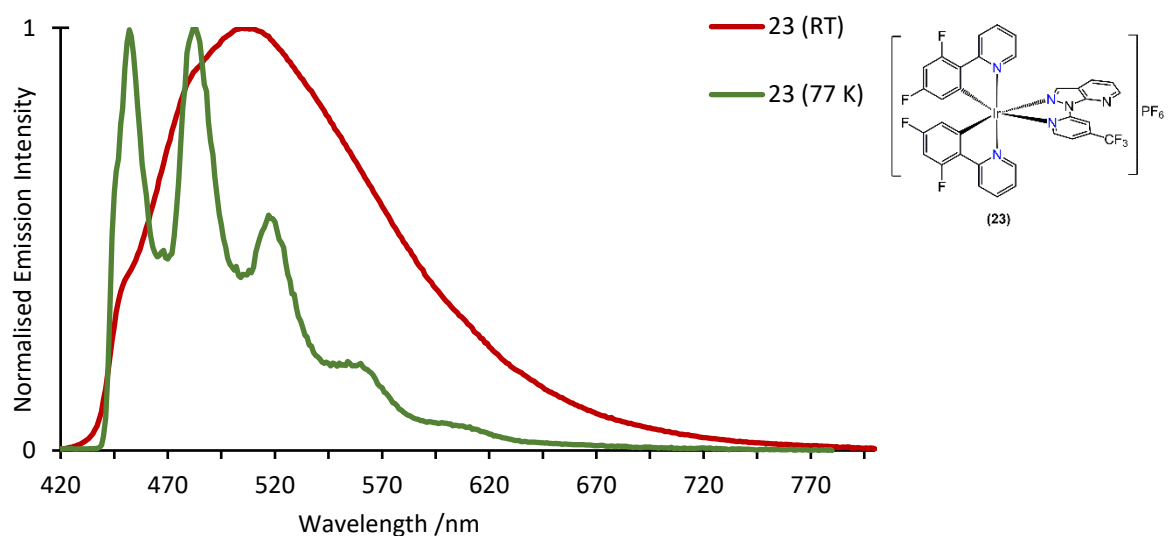


Figure 2.44: Normalised emission spectra of complex **32** at RT in degassed MeCN ($\lambda_{\text{exc}} = 400$ nm) and at 77 K in EPA ($\lambda_{\text{exc}} = 400$ nm).

The emissions of the remaining pp complexes are nearly identical to their az counterparts at 77 K, as exemplified by the emissions of the pp complexes **19** and **21** vs. the analogous az complexes **28** and **30** (**Figure 2.45**). All four profiles are blue shifted and more structured than at RT, following a similar rigidochromic trend as commented on above,¹⁶⁶ with a sharp 0,0 peak between 445 and 469 nm, 0,1 peak between 477 and 504 nm and a series of shoulders which extend into the green and yellow. The pp complexes **19** and **21** are consistently slightly bluer emitters than their az

equivalents, **28** and **30**, by 3-4 nm ($137\text{-}200\text{ cm}^{-1}$), for example, $\lambda_{\text{max}} = 466\text{ nm}$ (**19**) vs. 469 nm (**28**). Fluorination of ppy in both series (**21** and **30**) results in a blue shift of approximately 20 nm ($949\text{-}1010\text{ cm}^{-1}$) compared to **19** and **21**; a trend also noted at RT.

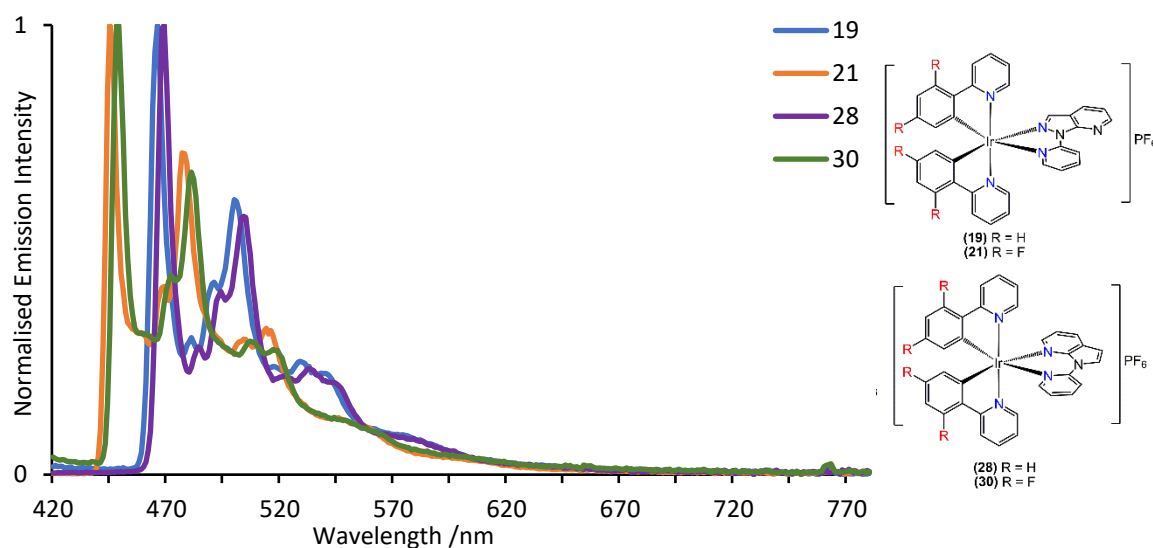


Figure 2.45: Normalised emission spectra of complexes **19**, **21**, **28** and **30** at 77 K in EPA ($\lambda_{\text{exc}} = 400\text{ nm}$).

Complexes containing pp-based ligands generally have higher quantum yields than the corresponding az-containing complexes, for example, **19** achieves the maximum quantum yield in the pp series of 30% representing an increase of 26% compared to its az-counterpart (**Table 2.10**). The maximum quantum yield obtained in the az series is 10% (complex **31**). The difference in PLQY values is thought to be associated with the smaller chelate ring size created by the ancillary pp ligand which confers greater structural rigidity;¹⁶⁷ this explanation is supported by the consistent reduction in rates of non-radiative decay observed in the pp series compared to the az series, for example, $k_{\text{nr}} = 28 \times 10^5\text{ s}^{-1}$ (**28**) vs. $2.7 \times 10^5\text{ s}^{-1}$ (**19**). The only exception to this trend is complex **24** whose unexpectedly high rate of non-radiative decay ($k_{\text{nr}} = 8.7 \times 10^6\text{ s}^{-1}$) is accompanied by a low quantum yield of 1%. Radiative decay rates of **19-34** range between $4 \times 10^3\text{ s}^{-1}$ and $160 \times 10^3\text{ s}^{-1}$ with little difference in values recorded between the pp and az series. Lifetimes of pp complexes are generally longer than az complexes both at RT (by an order of magnitude i.e. microsecond vs. nanosecond) and at 77 K (within the same order of magnitude i.e. microsecond). Cooling to low temperature results in extended lifetimes as long as $12\text{ }\mu\text{s}$ (complex **23**) due to the suppression of non-radiative decay pathways. The following exceptions are noted:

1. RT lifetimes of complexes **24** and **25** (110 and 340 ns respectively) are shorter than the RT lifetimes of their az equivalents, **33** and **34** (3.8 and 0.65 μs respectively).
2. 77 K lifetimes of complexes **20** and **33** (3.7 and 3.0 μs respectively) are shorter than their lifetimes measured at RT.

Table 2.10: Photophysical properties of complexes **19-34** recorded in degassed MeCN at RT ($\lambda_{exc} = 400$ nm, $^a\lambda_{exc} = 410$ nm, $^b\lambda_{exc} = 420$ nm) and in EPA at 77 K ($\lambda_{exc} = 400$ nm). ^{sh} = shoulder.

Aerated PLQYs and lifetimes are shown in brackets.

Complex	19	20	21	22	23	24 ^b	25	26
Absorption Maxima /nm (ϵ /M ⁻¹ cm ⁻¹)	252 (53100)	249 (37700)	246 (45000)	254 (57100)	247 (48800)	241 (54100)	251 (43200)	254 (55700)
	268 (55200)	264 (41300)	286 (30800)	293 (93500)	254 (47800)	248 (53500)	262 (42000)	269 (53900)
	281 (48400)	283 (38100)	304 (26000)	303 (35500)	286 (34700)	270 (39800)	292 (15800)	312 (27900)
	310 (28400)	307 (18700)	356 (6530)	364 (5650)	312 (28700)	308 (22000)	330 (15900)	376 (6310)
	380 (5650)	364 (5300)	416 (317)	417 (411)	443 (114)	348 (18000)	376 (6210)	464 (146)
	463 (145)	454 (80)	444 (92)	446 (118)		361 (17400)	464 (136)	
						469 (2550)		
λ_{max} /nm	473 ^{sh} , 504	460, 490,	450, 480,	452, 482, 514 ^{sh}	505	677	472 ^{sh} , 549	472, 503
PLQY /% degassed (aerated)	30 (0.7)	26 (0.6)	20 (0.9)	20 (1.3)	25 (1.1)	0.55 (0.3)	5.6 (0.9)	21 (0.8)
Lifetime /ns degassed (aerated)	2610 (58)	5140 (104)	5460 (225)	2190 (141)	3110 (147)	114 (83)	343 (49)	2720 (74)
$K_r \times 10^5$ s ⁻¹	1.2	0.5	0.4	0.9	0.8	0.5	1.6	0.8
$K_{nr} \times 10^5$ s ⁻¹	2.7	1.4	1.5	3.6	2.4	87	28	2.9
77 K λ_{max} /nm	466, 500	455, 489	445, 477	447, 479	452, 482, 517	496, 522, 604, 652	466, 501	466, 500
77 K Lifetime / μ s	5.6	3.7	7.1	5.1	11.9	3.6	6.8	6.4

Complex	27	28	29	30	31	32	33 ^a	34
Absorption Maxima /nm (ϵ /M ⁻¹ cm ⁻¹)	251 (54900)	256 (31500)	254 (49100)	251 (57200)	263 (71600)	257 (44900)	228 (49000)	259 (61400)
	270 (70500)	377 (3170)	368 (5390)	306 (22400)	364 (4660)	311 (17800)	251 (40800)	376 (3670)
	287 (62100)	467 (126)	426 (309)	357 (4670)	420 (577)	365 (4780)	269 (36400)	466 (120)
	315 (32700)		457 (108)	419 (327)	450 (293)	419 (360)	351 (10100)	
	378 (4820)			448 (122)		448 (112)	377 (5040)	
	465 (130)						469 (203)	
λ_{max} /nm	473, 503	475, 507, 542 ^{sh}	462, 494, 523 ^{sh}	453, 484, 512 ^{sh}	456, 486, 513 ^{sh}	454, 483, 514 ^{sh}	609	474, 504, 539 ^{sh}
PLQY /% degassed (aerated)	0.9 (0.4)	3.9 (0.7)	5.7 (0.8)	4.8 (1.4)	10.4 (1.3)	0.6 (0.3)	1.3 (0.1)	7.5 (1.0)
Lifetime /ns degassed (aerated)	105 (37)	347 (69)	772 (117)	570 (169)	1110 (127)	72 (46)	3790 (313)	649 (82)
$K_r \times 10^5$ s ⁻¹	0.8	1.1	0.7	0.8	0.9	0.8	0.04	1.2
$K_{nr} \times 10^5$ s ⁻¹	94	28	12	17	8.1	138	2.6	14
77 K λ_{max} /nm	466, 501	469, 504	458, 492	449, 481	450, 483	506, 544, 587	506, 544, 586	468, 503
77 K Lifetime / μ s	6.4	5.5	6.6	5.7	4.9	5.8	3.0	5.7

2.7 Summary

In summary, a total of 34 bidentate complexes of the form $[\text{Ir}(\text{C}^{\wedge}\text{N})_2(\text{N}^{\wedge}\text{N})]\text{PF}_6$ have been synthesized where $\text{C}^{\wedge}\text{N}$ = ppy, fppy, dfppy and derivatives of dfppy and $\text{N}^{\wedge}\text{N}$ = bpy, dmbpy, dmbpy, dmabpy and derivatives of ppH or azH. Their photophysical properties have been evaluated in solution at RT and at 77 K. The bipyridine series **1-12** have quantum yields in deoxygenated solution as high as 53%, in agreement with related literature.^{82,94–98,109–111} PL emission has been successfully blue shifted from $\lambda_{\text{max}} = 610$ nm to 463 nm ($\Delta E = 5200 \text{ cm}^{-1}$) by increasing the fluorine content of the cyclometalating ligand and by adding electron-donating substituents such as methyl, methoxy and *N,N*-dimethylamino to the $\text{N}^{\wedge}\text{N}$ ligand. Increasing the steric bulk of the cyclometalating ligand by adding a mesityl or a second difluorophenyl group to the position *trans* to the Ir–N bond increases the quantum yield by as much as 16% (i.e. ϕ of **14** = 57%), with a negligible effect on emission wavelength. The photophysical properties reported for this series of complexes are in line with similar literature complexes containing the identical mes-dfppy $\text{C}^{\wedge}\text{N}$ ligand.^{86–89}

PL emissions as blue as $\lambda_{\text{max}} = 450$ nm and as red as $\lambda_{\text{max}} = 677$ nm are achieved in complexes bearing a novel class of $\text{N}^{\wedge}\text{N}$ ligand containing a pyrazolopyridine motif (**19-27**); these values align with some of the bluest^{106,113–117} and reddest^{143,144} emitters in the literature. X-ray crystallography shows that this class of ligand selectively binds to iridium via the nitrogen of the pyrazole ring to form a 5-membered chelate ring whereas the equivalent azaindole-based ligands, which differ from their pp counterparts by just a single nitrogen, can only bind via the fused pyridine nitrogen to form a larger 6-membered ring. The photophysical properties of the pp complexes are generally superior to the az series (**28-34**), for example $\phi_{\text{max}} = 30\%$ (**19**) vs. 10% (**31**); this suggests that the increased rigidity and structural integrity offered by the smaller 5-membered ring size enhances luminescence. The pp ligand of **26** still coordinates via the pyrazole nitrogen despite the presence of the *ortho*-bound methyl group.

Chapter 3 - Iridium complexes featuring tridentate ligands

3.1 Introduction

Interest in the synthesis and excited-state properties of iridium complexes containing tridentate ligands began around the turn of the 21st century.¹⁶⁸ From Sauvage and co-workers' comprehensive review of bis-tridentate ruthenium(II) and osmium(II) complexes, published in 1994,¹⁶⁹ emerged several attractive reasons for studying metal complexes with tridentate ligands:

- 1) Complexes with tridentate ligands can have different excited state properties from those of analogues with bidentate ligands; for example, tridentate ligands could have a more extended framework for coordination, which can lead to different frontier molecular orbitals.
- 2) Tridentate ligands may offer increased rigidity which can help prevent distortion of the complex upon formation of the excited state.
- 3) The achiral nature of symmetrical bis-tridentate complexes means that the purification of multi-metallic bis-tridentate complexes is easier than multi-metallic arrays of tris-bidentate archetypal complexes which are intrinsically chiral.
- 4) Tridentate systems can easily be incorporated into linear assemblies by substitution at the central position of a tridentate ligand. This leads to a single product in which the substituents are at 180° to one another, co-axial with the metal and with a fixed distance between them; this is very difficult to achieve in complexes such as *fac*-Ir(ppy)₃ due to the difficulty in controlling the relative disposition of the two substituted ligands out of the three that are present.¹⁷⁰

The increase in structural rigidity of complexes containing tridentate ligands is often at the expense of a strained metal-ligand coordination which can be detrimental to luminescence, as exemplified by the ruthenium complexes [Ru(tpy)₂]²⁺ and [Ru(bpy)₃]²⁺ (**Figure 3.1**). The former is essentially non-emissive due to the weaker ligand field created by the poorer bite angle of the tpy ligand and sub-optimal M–L bond distances whilst the latter is the classic luminescent transition metal complex.¹⁷¹

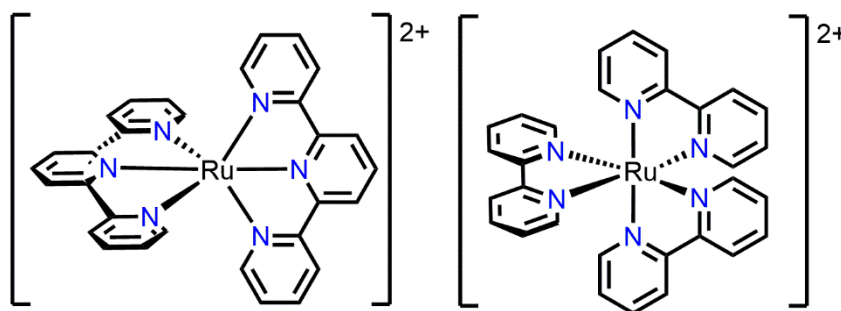


Figure 3.1: Structures of [Ru(tpy)₂]²⁺ (left) and [Ru(bpy)₃]²⁺ (right).

Replacing tpy with the isoelectronic and structurally equivalent ligand, 1,3-di(2-pyridyl)benzene (dpybH), has a significant effect on the redox and excited state properties of $N^{\wedge}C^{\wedge}N$ -containing complexes due to the introduction of cyclometallation which raises the energy of deactivating, non-radiative d-d states so they become less thermally accessible at RT.^{172,173} A prime example of the benefits that cyclometallation may confer is evident in platinum(II) chemistry in the case of Pt(dpyb)Cl vs. [Pt(tpy)Cl]⁺ (**Figure 3.2**). The former is highly luminescent in degassed solution at RT ($\phi = 60\%$, $\tau = 7.2 \mu s$) whereas the latter is essentially non-emissive under the same conditions.^{4,174} Platinum(II) complexes containing several types of tridentate ligand including $C^{\wedge}N^{\wedge}N$, $N^{\wedge}C^{\wedge}N$, $C^{\wedge}N^{\wedge}C$ and $N^{\wedge}N^{\wedge}N$ ligands have been reported and their promising PL properties exploited for applications in OLEDs.¹⁷⁵ In the case of Pt($N^{\wedge}N^{\wedge}N$), the use of N-deprotonable azole units, i.e. triazoles and tetrazoles, constitutes a compelling alternative to the C-cyclometallating ligand¹⁷⁶ and indeed such complexes (**Figure 3.2**) produce some of the highest EQE values for solution-processed platinum-based OLEDs at 5.6%.¹⁷⁷ Some of the most recent literature on tridentate Pt(II) complexes is cited as this topic is beyond the scope of this chapter.^{178–183}

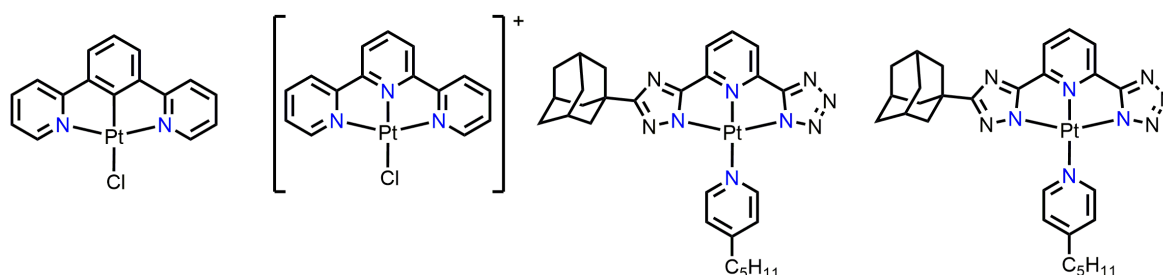


Figure 3.2: From left to right, structures of Pt(dpyb)Cl, [Pt(tpy)Cl]⁺ and two asymmetric Pt(II) derivatives featuring triazole and tetrazole moieties.

Since the work of Sauvage *et al.* in the 1990s, related tridentate compounds of several other metal ions have been prepared, including Rh(III)¹⁸⁴, Pd(II)¹⁸⁵, Au(III)¹⁷⁴, Sn(IV),¹⁸⁶ Ag(I)¹⁸⁷ and Hg(II)¹⁸⁷. Although the $N^{\wedge}C^{\wedge}N$ binding mode is already established in Ru(II), Os(II) and Pt(II) chemistry and its favourable influence on luminescence is recognised, $N^{\wedge}C^{\wedge}N$ coordination in iridium(III) chemistry presents a rather different challenge. Williams *et al.* found that the reaction of dpybH with IrCl₃·*n*H₂O resulted mainly in complexation through binding mode 2 (**Figure 3.3**), in which dpybH acts as a bidentate ligand like ppy.¹⁷⁰ For Ir(III), cyclometallation at the C⁴ position of the phenyl ring is kinetically favoured over reaction at the more hindered C² position. Therefore, in order to block this undesired competitive reaction and direct metalation towards the C² (i.e. binding mode 1), a substituent is required, for example, methyl groups in the 4' and 6' positions.¹⁸⁸ Even just a single substituent in the 5' position, for example, a methoxy group is sufficient to ensure binding mode 1 and yield the chloro-bridged dimer [Ir(diMe₂dpyb)Cl(μ-Cl)]₂. X-ray diffraction of the d₆-DMSO solvate formed upon heating i.e. Ir(diMe₂dpyb)Cl₂(DMSO) confirms this $N^{\wedge}C^{\wedge}N$ mode of binding.

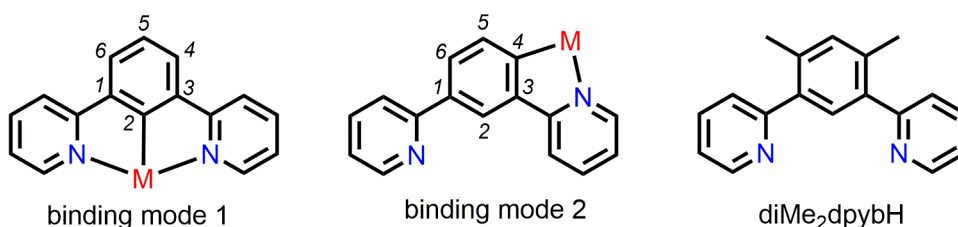


Figure 3.3: $N^{\wedge}C^{\wedge}N$ and $N^{\wedge}C$ binding modes of 2,6-di(2-pyridyl)benzene (left and middle respectively). Structure of diMe₂dpybH (right). diMe₂dpybH = 2,2'-(4,6-dimethyl-1,3-phenylene)dipyridine.

3.2 Synthesis of dpybH and dpyb-based complexes

Sauvage and co-workers prepared dpybH by reaction of 1,3-dicyanobenzene with acetylene under 10 atm pressure at 130°C, catalysed by Co(Cp)(COD) (**Figure 3.4**).¹⁷³ To avoid the need to use explosive acetylene gas, palladium-catalysed cross-couplings are preferably used nowadays to form aryl-aryl bonds (**Figure 3.5**).¹⁷³ A wide range of dpyb-based complexes are prepared via a chloro-bridged $N^{\wedge}C^{\wedge}N$ -iridium dimer such as the dimer illustrated in **Figure 3.6**.^{188–190} The iridium dimer is typically prepared by an overnight reflux of a dpybH derivative with IrCl₃·3H₂O in a solvent mixture of ethoxyethanol and H₂O.¹⁵¹

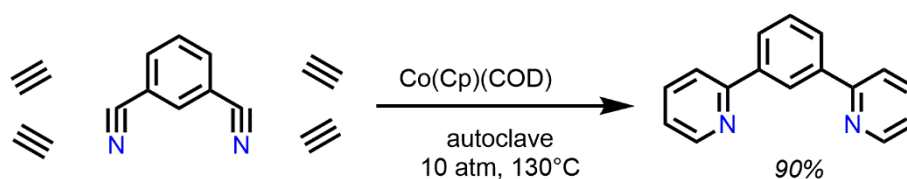


Figure 3.4: Synthesis of 1,3-di(2-pyridyl)benzene from 1,3-dicyanobenzene and acetylene. Cp = cyclopentadiene, COD = 1,5-cyclo-octadiene.

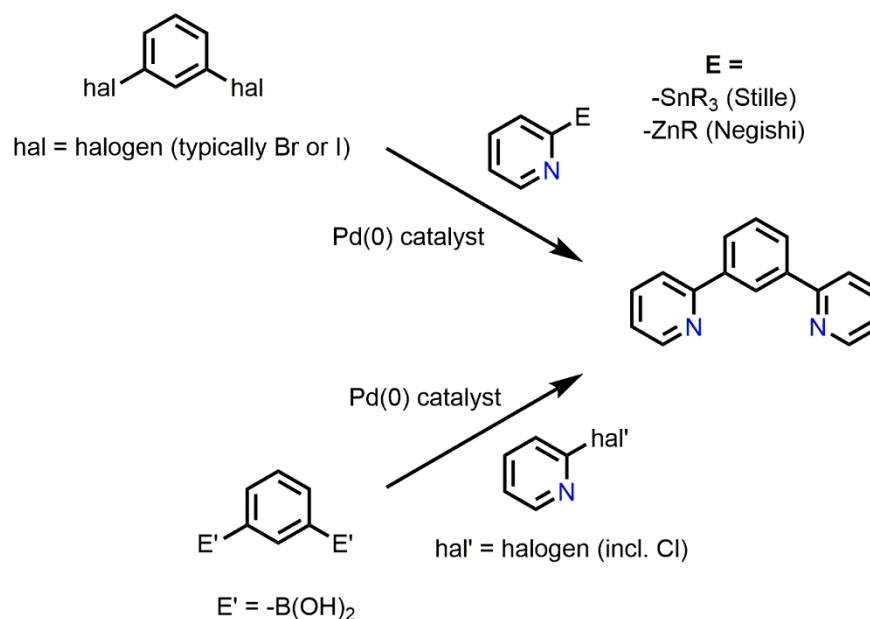


Figure 3.5: Generic cross-coupling reactions for the synthesis of dpybH. Top: 1,3-dihalogenated benzenes react with 2-pyridylstannanes or related zinc reagents. Bottom: 1,3-benzenediboronic acid reacts with halopyridines. In both cases conventional low-cost catalysts such as Pd(PPh₃)₂Cl₂ or Pd(PPh₃)₄ can be used.

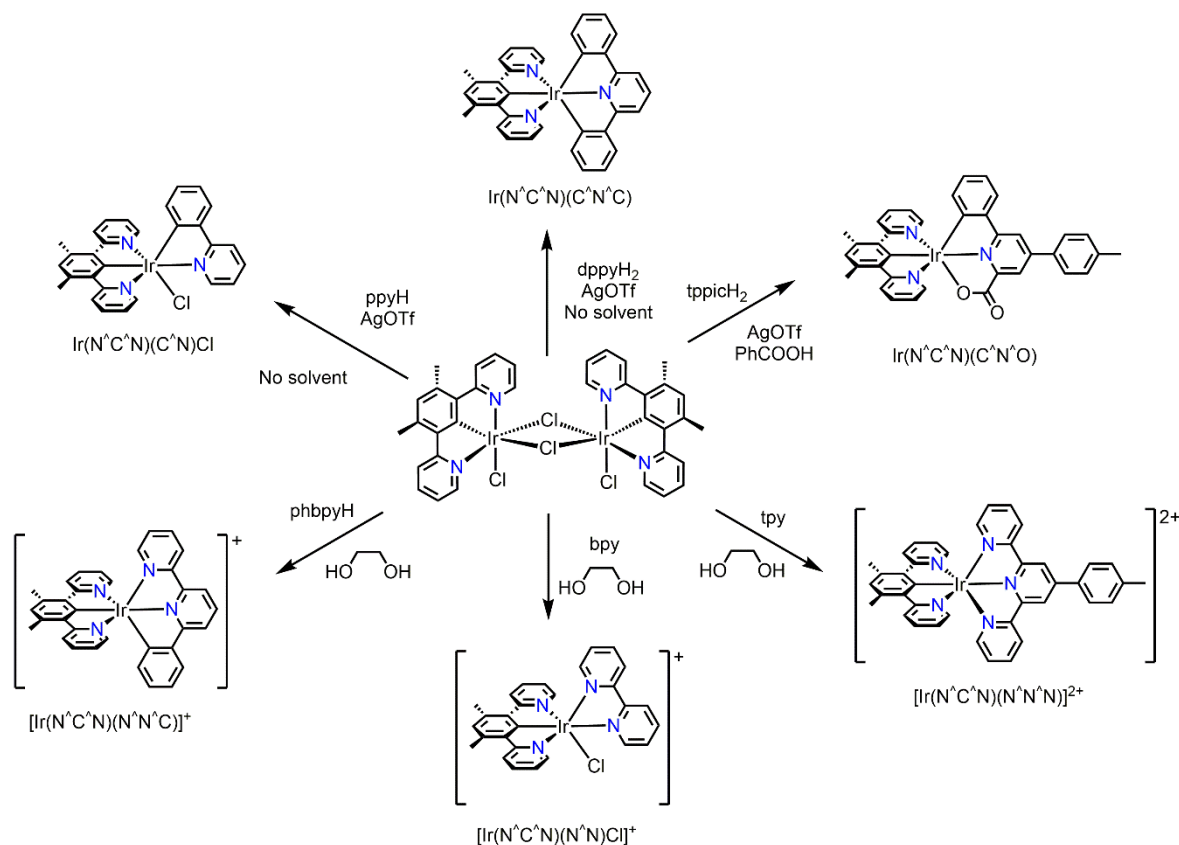


Figure 3.6: Structures of a range of iridium(III) $\text{N}^{\wedge}\text{C}^{\wedge}\text{N}$ -based complexes produced from the chloro-bridged $[\text{Ir}(\text{diMe}_2\text{dpyb})\text{Cl}(\mu\text{-Cl})]_2$ intermediate. dppyH_2 = 2,6'-diphenylpyridine, tppicH_2 = 4-p-tolyl-6-phenylpicolinic acid, phbpyH = 6-phenyl-2,2'-bipyridine.

3.3 Complexes containing $\text{N}^{\wedge}\text{C}^{\wedge}\text{N}$ ligands

Table 3.1 displays the PL properties of the Ir^{III} complexes featuring mononuclear tridentate $\text{N}^{\wedge}\text{C}^{\wedge}\text{N}$ ligands that are shown in **Figure 3.7** (data was not provided by the authors for complexes not listed in the table). Complexes **A-D** and **H-L** are all cationic green emitters featuring a neutral bpy- or imidazole-based $\text{N}^{\wedge}\text{N}$ ligand in addition to a chloride. Complex **L** has the highest quantum yield of this series ($\phi = 21\%$) and the highest rate of radiative decay by an order of magnitude ($k_r = 9.5 \times 10^5 \text{ s}^{-1}$). The substituents attached to the central phenyl ring of the $\text{N}^{\wedge}\text{C}^{\wedge}\text{N}$ ligand have a significant influence on the colour of PL emission, for example, replacement of the electron-donating 3',5'-dimethyl groups of **A** with electron-withdrawing fluorine atoms (**C**) shifts the emission maximum from 502 to 484 nm (741 cm^{-1}). The trifluoromethyl groups of **B**, however, do not significantly alter the emission energy compared to that of **A** despite their electron-withdrawing nature. Replacement of the methyl groups in **H** and **K** with CF_3 groups leads to a 8-17% increase in quantum yield as shown by the PLQYs of **J** and **L** ($\phi = 14\%$ and 21%) which are the two highest values in the series. Emission of the CF_3 -containing complexes **J** and **L** is red shifted by 84 nm (2950 cm^{-1}) and 10 nm (383 cm^{-1}) with respect to **H** and **K**. Photophysical properties are relatively unaffected by the identity of the $\text{N}^{\wedge}\text{N}$ ligand, for example, the photophysical properties of complexes **A**, **H** and **K** which contain bpy, benzimidazole- and methylated benzimidazole-based ancillaries are very similar and their emission maxima lie within a small range between 493 and 506 nm.

Most of the reported complexes are charge-neutral and contain a bidentate ancillary ligand which is C[^]N in nature i.e. a derivative of ppy. Complexes **Z** and **AA**, which differ by the 3,5' substituent attached to the central phenyl ring of their benzothiazole-based N[^]C[^]N ligand, have the highest quantum yields in the Ir(N[^]C[^]N)(N[^]C)Cl series of 89%. The methyl and -CF₃ substituents of **Z** and **AA** do not influence emission energy whatsoever as both complexes possess identical emission maxima of 572 nm; this trend is also observed more generally between methyl and CF₃-containing complexes **A** and **C** of the type [Ir(N[^]C[^]N)(N[^]N)Cl]⁺. The quantum yields of the green-emitting complexes **O** and **U** are also high (78% and 77% respectively). The electron-donating methyl group in **U** results in an 8 nm (256 cm⁻¹) bathochromic shift in emission presumably due to the increased stabilization of the LUMO which likely resides on the C[^]N ligand.

The emission from complexes **AG**, **AJ** and **AM** increases in energy from 503 to 487 nm (653 cm⁻¹) as a result of the increasing electron-withdrawing ability of the substituent attached to the central phenyl dpyb ring in the order: Me < F < CF₃. This blue shift in emission is most likely due to the increasing stabilization of the HOMO which is located on the cyclometalating ligand. Contrary to what might be expected on the basis of the energy gap law, the quantum yields of **AG**, **AJ** and **AM** decrease significantly across the series from 71% to 20%. Substitution of the ppy ligand in **AJ** with dfppy (i.e. complex **AQ**) leads to a 98 nm (3340 cm⁻¹) red shift in emission; this bathochromic shift is rationalised by the increased stabilizing influence of the fluorine substituents on the LUMO which is likely to reside on the C[^]N ligand. The quantum yields of **AQ** and the other dfppy-containing complexes, **AN** and **AS**, range between 20% and 46%; these values are equal or lower than the PLQYs of the analogous ppy-based complexes, **AG**, **AJ** and **AM**, consistent with the energy gap law.

Extending the conjugation of the N[^]C[^]N ligand with isoquinoline, benzothiazole, benzoxazole and methyl-benzimidazole side arms typically lowers emission energy relative to complexes containing pyridine- or pyrazole-based side arms. A typical example of this trend can be seen by contrasting the emission energies of **W** (λ_{max} = 611, 653 nm) and **AG** (λ_{max} = 503, 537 nm) which vary by over 100 nm (3510 cm⁻¹). Complex **W** has the reddest PL emission in the Ir(N[^]C[^]N)(N[^]C)Cl series of complexes. The emission maxima of complexes **AD**, **AE** and **O**, which feature benzothiazole, benzoxazole and methyl-benzimidazole-based N[^]C[^]N ligands respectively, are increasingly blue shifted from 588 nm (**AD**) to 576 nm (**AE**) to 555 nm (**O**). Quantum yields also increase across the series from 50% (**AD**) to 78% (**O**). These photophysical trends might be explained by the higher charge density of the N vs. O vs. S atoms which could stabilize the HOMO by a greater amount whilst also increasing ligand field strength to raise the energy of deactivating MC d-d states.

Metathesis of the chloride ligand in Ir(N[^]C[^]N)(N[^]C)Cl systems almost always leads to an improvement in PLQY. The 20% quantum yield of **AN** can be raised close to unity (ϕ = 97%) by replacement of the chloride with isocyanate (**AP**). Replacement with cyanide (**AO**) results in an

equally impressive rise in quantum yield to 93%. The improvement in quantum yield by over 70% in **AO** and **AP** is due to the stronger ligand fields of the thiocyanate and cyanide ligands compared to chloride which reduces non-radiative decay pathways. This is confirmed by the lower non-radiative decay rate constants of **AO** ($k_{nr} = 23 \times 10^4 \text{ s}^{-1}$) and **AP** ($k_{nr} = 2 \times 10^4 \text{ s}^{-1}$) vs. **AN** ($k_{nr} = 190 \times 10^4 \text{ s}^{-1}$). Complexes **AN**, **AO** and **AP** are blue emitters with emission maxima between 476 and 487 nm; this proves that metathesis has only a small effect on emission energies in this series of complexes.

The photophysical properties of complexes **Y**, **AC**, **AW** and **AX**, which feature a phenylacetylide-based ligand, differ from the properties of their chloride-containing analogues, **W**, **Z** and **AM** in several ways:

- 1) **Y** vs. **W**: Metathesis with 3,5-bis(trifluoromethyl)phenylacetylene leads to an increase in quantum yield from 40% to 51%. The emission of **Y** is 8 nm (217 cm^{-1}) red shifted relative to **W**. Both complexes are red emitters with emission maxima in the range 603-653 nm.
- 2) **AC** vs. **Z**: Metathesis with phenylacetylene results in a huge decrease in quantum yield from 89% to 29%. The emission maximum of 572 nm remains unchanged.
- 3) **AW** vs. **AM**: Metathesis with 4-ethynyl-*N,N*-dimethylaniline leads to a 37% increase in PLQY from 20% to 57%. The emission maximum of **AW** ($\lambda_{\text{max}} = 572 \text{ nm}$) is red shifted by 85 nm (3050 cm^{-1}). RT luminescence lifetime increases by an order of magnitude to 4 μs .
- 4) **AX** vs. **AM**: Metathesis with 4-cyanophenylacetylene also raises quantum yield and red shifts emission. The rise in quantum yield is less than in 3) (ϕ of **AX** = 46%) but the emission energy of **AX** is lowered by greater amount (λ_{max} of **AX** = 590 nm). RT lifetime increases from 0.4 to 3.3 μs .

The one consistent trend observed in all four complexes **Y**, **AC**, **AW** and **AX** is the shift of their emission to equal or lower energies than their chloride counterparts. This bathochromic shift in emission might be a consequence of the acetylide's lower lying π^* -antibonding orbitals which would lower the energy of any MCLT transition contributing to their phosphorescence.

The synthetic procedure for metathesis with an acetylene requires a base (usually KOH,^{179,184} Et₃N^{178,180–182} or DIPA¹⁸³) to deprotonate the acetylene, a CuI catalyst and a solvent such as DMF, MeOH or DCM. Overnight reflux yielded the metathesized product after work-up and purification by column chromatography and/or recrystallization. KCN is used for cyanide metathesis using a standard MeOH reflux¹⁹¹ or a microwave-assisted ethylene glycol solution. Haga and co-workers' microwave irradiation procedure has also been used successfully to metathesize the chloride to bromide and iodide using NaBr and NaI respectively.¹⁹²

The bis-tridentate series consists of 15 complexes, **AY** to **BM**. Three pairs of complexes demonstrate the effects of adding *tert*-butyl groups to the N[^]C[^]N and N[^]N[^]C ligands; these pairs are: **AZ** vs. **AY**, **BB** vs. **BA** and **BD** vs. **BC**. Two clear trends are observed:

- 1) Emissions from the *tert*-butyl-containing complexes, **AZ**, **BB** and **BD** are consistently red shifted by 3-10 nm (124-385 cm⁻¹) with respect to their chloride counterparts.
- 2) The quantum yields of **AZ**, **BB** and **BD** are lower than their chloride counterparts, for example, ϕ of **BC** = 63% vs. ϕ of **BD** = 43%.

DFT studies reveal that the LUMO is located on the flanking pyridine units of the N[^]C[^]N ligand; this frontier molecular orbital extends over the periphery of the N[^]N[^]C component. The HOMO, in contrast, is situated largely on the central phenyl ring of the N[^]C[^]N ligand as observed in complexes of the type [Ir(N[^]C[^]N)(N[^]N)X]⁺ and Ir(N[^]C[^]N)(C[^]N)X. The red shift in emission of **AZ**, **BB** and **BD** is therefore consistent with an increased LUMO stabilization induced by the electron-donating *tert*-butyl substituent. The energy gap law might explain the lower PLQYs of **AZ**, **BB** and **BD** relative to **AY**, **BA** and **BC**.

Replacing the flanking pyridines of the N[^]C[^]N ligand of **BA** and **BB** with isoquinoline (**BC** and **BD**) red shifts emission by roughly 88 nm (2810-2970 cm⁻¹) due to the extension of π -conjugation which reduces the π - π^* and MLCT energy gap. Despite the lower energy of their emissions, the quantum yields of **BC** and **BD** (63% and 43% respectively) are much higher than the PLQYs of **BA** and **BB** (25% and 22% respectively). The quantum yields of **BE**, **BF** and **BG** increase from close to zero (**BE**) to 21% (**BG**) due to the increase in the number of cyclometalating M-L bonds from 1 to 3. The four red-emitting [Ir(N[^]C[^]N)(N[^]N[^]C)]PF₆-type complexes, **BH**, **BI**, **BJ** and **BK**, share similar photophysical properties; their emission maxima range between 625 and 644 nm whilst their quantum yields are between 3-6%. Addition of phenyl, 3,5-dimethylbenzene or bromo groups therefore has a minimal impact on the emission colour and PLQY.

The two Ir(N[^]C[^]N)(C[^]N[^]O)-type complexes, **BL** and **BM** were synthesized via a solvent-free procedure which involved grinding the ligating carboxylic acid, chloro-bridged tridentate iridium dimer, benzoic acid and AgOTf together before heating and stirring under an inert atmosphere. Despite this simple and elegant synthesis, the quantum yields of **BL** and **BM**, ϕ = 2.7% and 5.3% respectively, are lower than related Ir(N[^]C[^]N)(C[^]N[^]C)-type complexes, for example, **BG** (ϕ = 21%). Furthermore, the lifetimes of **BL** and **BM** (τ = 170 and 110 ns) are significantly shorter than the 3.9 μ s lifetime of **BG**. The poorer performances of **BL** and **BM** are largely due to their high non-radiative rate constants in the order of 10⁶ s⁻¹. The authors hypothesize that photochemical cleavage of the Ir-O bond, promoted by the strong *trans* influence of the trans-disposed cyclometalating ligand, could explain their high k_{nr} values. Complex **BM** has 1210 cm⁻¹ redder emission than **BL** (λ_{max} = 603

vs. 562 nm) because an additional stabilization will be possible in the excited state of **BM** by rotation of the *p*-tolyl group into a co-planar confirmation which will maximize conjugation.

There are also examples of multinuclear Ir complexes featuring N[^]C[^]N ligands that have been reported - these will be discussed in Chapter 5.

Table 3.1: Photophysical properties of iridium complexes shown in **Figure 3.7**, measured in degassed MeCN or DCM at RT. Aerated PLQYs and lifetimes are shown in brackets. ^{sh} = shoulder.

Reference	Complex	$\lambda_{\max}^{\text{abs}} / \text{nm} (\epsilon / \text{M}^{-1}\text{cm}^{-1})$	$\lambda_{\max}^{\text{em}} / \text{nm}$	PLQY / %	$\tau / \mu\text{s}$	$k_r \times 10^4 \text{ s}^{-1}$	$k_{nr} \times 10^4 \text{ s}^{-1}$
193	A	247 (34900), 275 (27900), 387 (10100), 439 (1390), 469 (680)	502, 535	11 (0.46)	1.5 (0.038)	8	59
153	B	248 (97600), 289 (77400), 336 (24300), 387 (11400), 426 (3700)	506, 540, 580	6	4.1 (1.3)	1	23
153	C	254 (15100), 270 (15800), 352 (3800), 370 (4200)	484, 518	3	2.3 (1.3)	1	43
193	D	252 (73600), 290 (102000), 404 (12500), 445 (2630), 474 (1260)	509, 543	1.9 (< 0.1)	1.7 (0.049)	1	58
153	H	242 (800), 298 (600), 373 (400), 482 (100)	493, 522	6	0.2 (0.01)	4	108
153	J	238 (4800), 290 (2300), 350 (1300), 411 (600), 441 (300), 502 (100)	577	14	1.5 (1.0)	9	57
153	K	243 (3800), 288 (3600), 320 (1000), 390 (1000), 467 (100)	506, 534	4	1.3 (0.2)	3	74
153	L	242 (4900), 302 (2500), 338 (1200), 390 (900), 423 (600), 491 (100)	516	21	0.2 (0.2)	95	360
191	M	250 (52200), 307 (32000), 346 ^{sh} (16400), 406 (6270), 462 (9250), 488 (8880), 538 ^{sh} (2450), 584 (880)	493	-	-	-	-
191	N	250 (52200), 307 (32000), 346 ^{sh} (16400), 406 (6270), 462 (9250), 488 (8880), 538 ^{sh} (2450), 584 (880)	468	63	1.4	44	26
192	O	244 (50000), 299 (38700), 360 (7700), 404 (14000), 425 (15600), 472 (3100), 523 (840)	555	78 (59)	1.8 (1.6)	44	12
192	P	244 (40000), 300 (29400), 361 (5440), 403 (11400), 424 (12900), 470 ^{sh} (2640), 531 (500)	553	87	1.7	50	8
192	Q	250 ^{sh} (53500), 267 ^{sh} (42400), 299 (38500), 359 (8660), 404 (15100), 423 (15900), 474 ^{sh} (3490),	553	81	1.8	44	10
192	R	242 (54900), 299 (37800), 353 (7900), 392 (15800), 413 (19000), 506 (350)	526	84	2.2	39	7
192	S	236 (68300), 272 (56200), 298 (63700), 360 (6900), 419 (12900), 437 (15900), 482 (3400), 530 (880)	563	75	1.5	51	17
192	T	247 (50500), 298 (37200), 380 (17900), 398 (18200), 496 (360)	513	24	1.0	25	79
192	U	236 (50000), 300 (44600), 361 (6500), 405 (13500), 426 (15200), 473 (3000), 526 (750)	563	77	1.4	55	16
192	V	245 (65400), 296 (50100), 379 (22200), 396 (23100), 490 (270)	512	22	0.8	29	99
184	W	259 (29100), 320 (12400), 347 (7810), 414 (4280), 455 (5590), 477 (6490), 549 (870), 591 (440)	611, 653	40	1.7 (0.49)	-	-
194	X	259 (55490), 306 (26595), 329 (16480), 342 (15380), 395 ^{sh} (8895), 439 ^{sh} (11575), 467 (13450)	583, 621	13	2.9	-	-
184	Y	250 (52200), 307 (32000), 346 (16400), 406 (6270), 462 (9250), 488 (8880), 538 (2450), 584 (880)	603, 644	51	1.7 (0.38)	-	-
195	Z	-	572	89	110	-	-
196	AA	-	572	89	1.9	46	6
196	AB	-	557	15	0.39	38	220

Reference	Complex	$\lambda_{\max}^{\text{abs}}/\text{nm}$ ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$)	$\lambda_{\max}^{\text{em}}/\text{nm}$	PLQY /%	$\tau/\mu\text{s}$	$k_r \times 10^4 \text{ s}^{-1}$	$k_{nr} \times 10^4 \text{ s}^{-1}$
¹⁹⁶	AC	-	572	29	1.9	16	39
¹⁹⁶	AD	-	588	50	1.1	25	25
¹⁹⁶	AE	-	576	66	2.1	31	16
¹⁹⁶	AF	-	569	85	2.2	38	7
¹⁹⁷	AG	264 (35900), 288 (34900), 369 (7360), 397 (10100), 418 (11300), 457 (3330), 494 (1300)	503, 537	71	1.4 (0.1)	51	20
¹⁹⁷	AJ	286 (36300), 363 (8310), 390 (9650), 412 (10800), 451 (3260), 488 (1200)	495, 529	66	1.5 (0.2)	44	23
¹⁹⁷	AM	260 (44800), 280 (40300), 358 (9100), 381 (11300), 402 (14000), 438 (3640), 473 (1540)	487, 516	20	0.4 (0.1)	51	210
¹⁹⁷	AN	278 (42200), 351 (9660), 375 (11700), 393 (13600), 433 (2860), 467 (1520)	476, 508	20	0.4 (0.1)	49	190
¹⁵³	AO	247 (22700), 281 (16900), 371 (4300), 406 (4900), 479 (700)	480, 515	93	0.3 (0.03)	310	23
¹⁵³	AP	241 (33600), 287 (23100), 352 (4800), 386 (5700), 406 (6700), 485 (700)	487, 521	97	1.9 (0.2)	51	2
¹⁹⁷	AQ	259 (45600), 272 (45300), 373 (8940), 429 (11100), 461 (8020), 506 (3080), 541 (2470)	593	46	3.3 (1.1)	14	16
¹⁵³	AS	232 (16300), 274 (14600), 340 (2500), 364 (2700), 382 (4400), 458 (400)	462, 497	26	0.8 (0.2)	33	95
¹⁹⁷	AW	254 (43800), 266 (42900), 364 (7990), 418 (9920), 451 (6880), 492 (3040), 523 (2200)	572	57	4.0 (2.0)	14	11
¹⁵³	AX	234 (39800), 266 (35700), 321 (24000), 370 (8700), 422 (5100), 473 (4800), 556 (2000)	590	46	3.3 (1.1)	14	16
¹⁹⁸	AY	281 (35400), 373 (10000), 395 (10800), 464 (1100)	490, 526, 570 ^{sh}	72	1.81	40	15
¹⁹⁸	AZ	282 (36600), 374 (11400), 392 (12500), 460 (1200)	493, 529, 571 ^{sh}	64	3.37	19	11
¹⁹⁸	BA	284 (32600), 397 (7500), 430 (8000), 456 (6100)	505, 540 ^{sh}	25	1.27	20	59
¹⁹⁸	BB	281 (44300), 374 (8300), 436(8800), 463 (6700)	515, 556 ^{sh}	22	0.81	27	96
¹⁹⁸	BC	304 (20900), 347 (11200), 486 (8300), 580 (800)	594, 641 ^{sh}	63	1.77	36	21
¹⁹⁸	BD	310 (26000), 457 (8500), 490 (10500), 580 (1100)	602, 650 ^{sh}	43	1.73	25	33
^{188,189}	BE	261 (38500), 270 (35300), 298 (26000), 335 ^{sh} (13100), 377 (10100), 435 (700), 465 (500)	560	< 10 ⁻³	-	-	-
¹⁹⁰	BF	240 (24500), 265 (22100), 294 (16600), 367 (5360), 411 (5490), 479 (640)	632	2.3	0.12 (0.049)	19	810
¹⁸⁸	BG	244 (53900), 269 (46900), 458 (5510), 481 (6820), 510 (7340)	585	21	3.9 (0.1)	6	21

Reference	Complex	$\lambda_{\text{max}}^{\text{abs}}/\text{nm}$ ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$)	$\lambda_{\text{max}}^{\text{em}}/\text{nm}$	PLQY/%	$\tau/\mu\text{s}$	$k_r \times 10^4 \text{ s}^{-1}$	$k_{nr} \times 10^4 \text{ s}^{-1}$
190	BH	232 (61700), 242 (61600), 284 (65150), 372 (17870), 411 (12100), 479 (1800)	639	2.8	0.13 (0.053)	22	750
190	BI	232 (65300), 293 (60900), 375 (23200), 412 (13200), 479 (1940),	636	6.3	0.15 (0.057)	42	630
190	BJ	235 (58000), 286 (50700), 376 (16360), 425 (8160), 483 (1600)	625	4.8	0.19 (0.063)	25	500
190	BK	229 (149000), 273 (122000), 293 (136000), 375 (47500), 420 (23400), 481 (4160)	644	2.9	0.10 (0.047)	29	970
188	BL	245 (34500), 290 (16600), 315 (10400), 341 (6500), 363 (5900), 393 (4900), 428 (460), 459 (2800),	562	2.7 (0.43)	0.17 (<0.1)	16	570
188	BM	242 (32800), 273 (35700), 337 (13500), 393 (6900), 429 (6700), 459 (4300), 489 (1700)	603	5.3 (0.92)	0.11 (0.039)	48	860

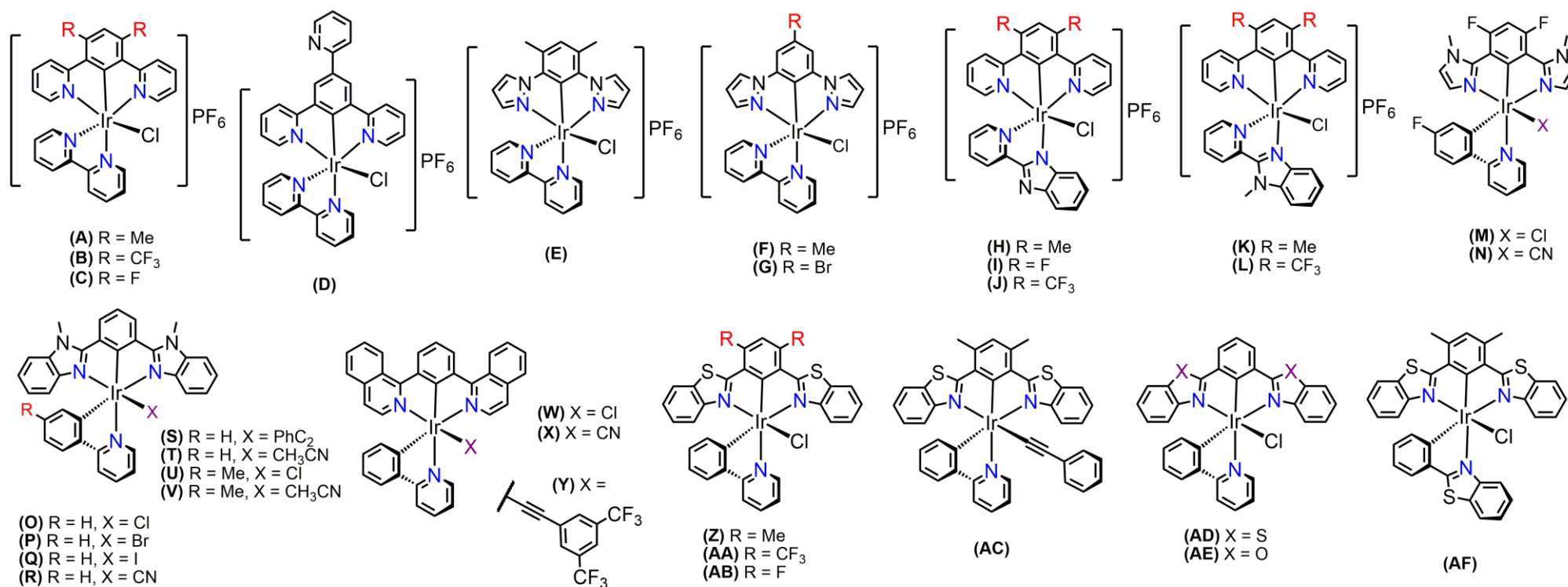


Figure 3.7: Structures of iridium complexes **A-BS** containing $N^{\wedge}C^{\wedge}N$ tridentate ligands.

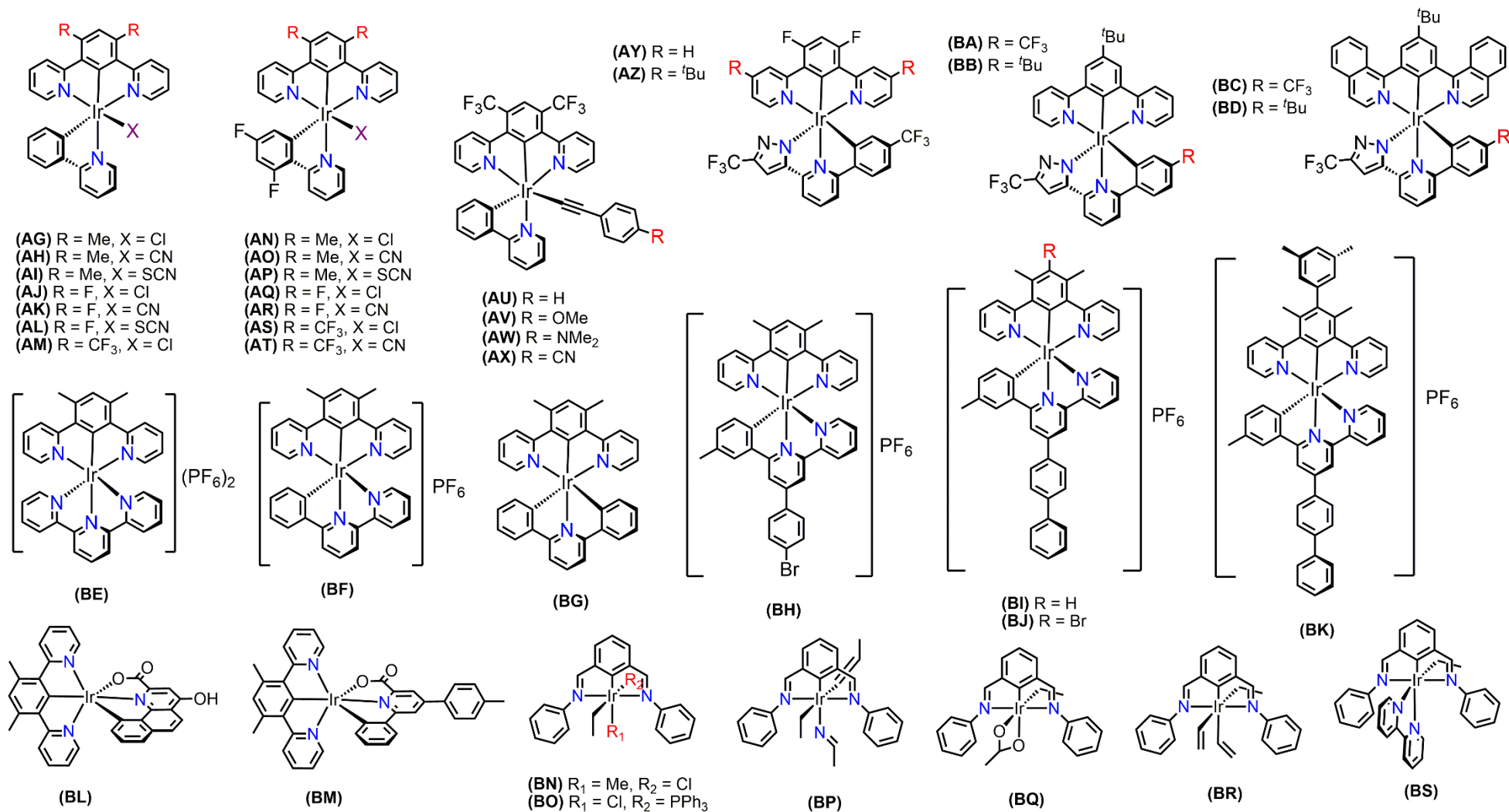


Figure 3.7 continued.

3.4 Complexes with other tridentate ligands (not displaying N⁺C⁺N⁻ coordination)

Figure 3.8 highlights some key literature examples of iridium complexes containing tridentate ligands that do not chelate in an N⁺C⁺N⁻ manner. The emissive properties of the bis-tpy complexes, (i) to (iii), synthesized by Williams *et al.* in 1999, were limited to quantum yields < 3%. Addition of *p*-tolyl groups to the tpy ligand in (ii) and (iii) shifted emission maximum from 458 to 506 nm ($\Delta E = 2070 \text{ cm}^{-1}$); this red shift in emission is due to the extra stabilization in the excited states of (ii) and (iii) provided by the *p*-tolyl unit which can orientate in a roughly co-planar alignment to increase π -conjugation.¹⁹⁹

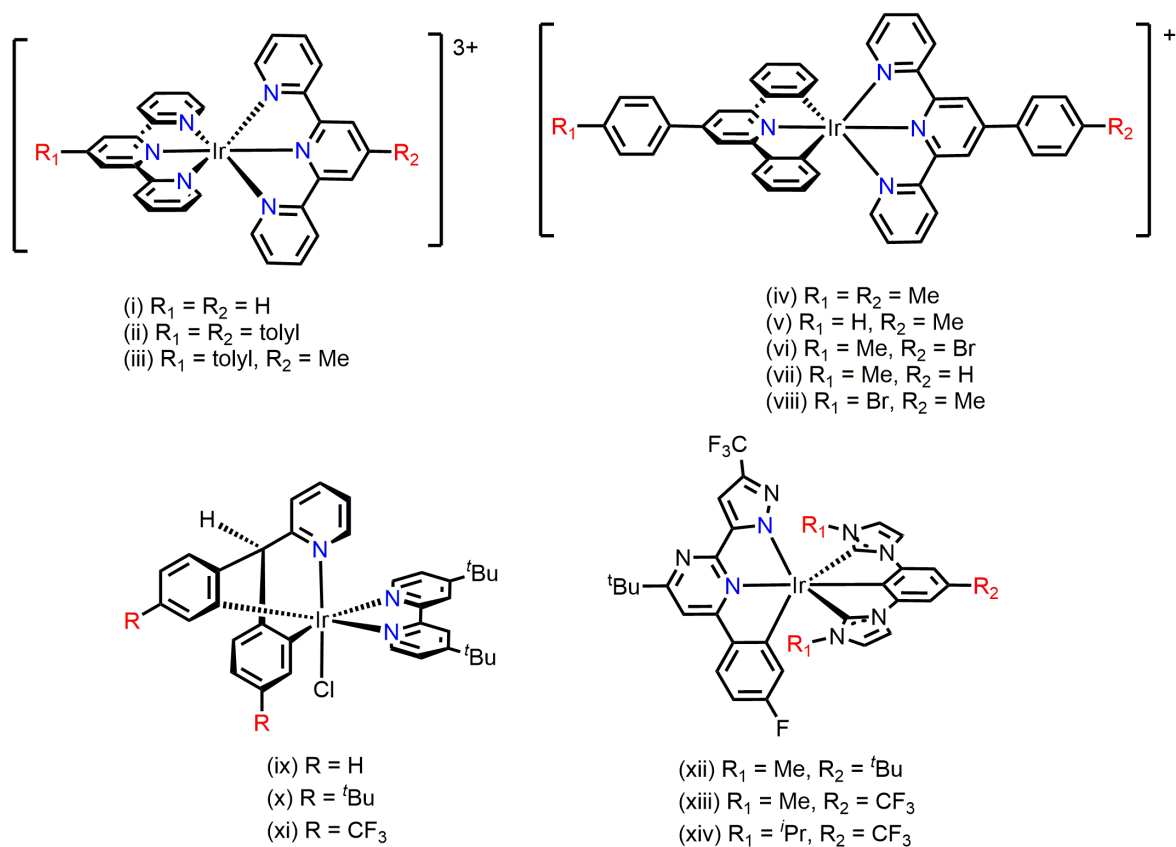


Figure 3.8: Examples of non-N⁺C⁺N⁻-coordinating iridium complexes (i) to (xiv)

The photophysical properties of the bis-anionic C⁺N⁺C⁻ series of complexes, (iv) to (viii), are similar to the $[\text{Ir}(\text{N}^+\text{N}^+\text{N})_2]^{3+}$ -type complexes (i) to (iii), for example, the quantum yields of (iv) to (viii) are equally poor with a maximum PLQY of 3.5%. Complexes (iv) to (viii) are red emitters and the addition of methyl and/or bromo substituents only shifts emission by a maximum of 8 nm ($\lambda_{\text{max}} = 654\text{--}662 \text{ nm}$, $\Delta E = 185 \text{ cm}^{-1}$). The introduction of cyclometallation in (iv) to (viii) keeps their quantum yields in a similar range to (i) to (iii) despite their $\approx 160\text{--}200 \text{ nm}$ ($5040\text{--}7320 \text{ cm}^{-1}$) red shifted emission.^{200,201}

Zysman-Colman and co-workers synthesized a series of tripodal C[∧]C[∧]N complexes (ix) to (xi) with yellow-red PL and PLQYs of 8%, 6% and 26% respectively. DFT calculations reveal the HOMO involves the iridium, chloride and the two phenyl rings of the tridentate ligand whereas the LUMO is almost exclusively located on the di-^tBu₂bpy. The electron-donating *tert*-butyl groups of (x) therefore destabilize the HOMO whilst the electron-withdrawing trifluoromethyl substituents of (xi) stabilize the HOMO - this results in colour-tuning of (x) and (xi) emission from red ($\lambda_{\text{max}} = 630$ nm) to yellow ($\lambda_{\text{max}} = 581$ nm).²⁰²

Some complexes bearing monoanionic C[∧]C[∧]C moieties, for example, N-heterocyclic carbene (NHC)-pincer type ligands, have remarkable PL properties with quantum yields close to unity.^{203–210} The terminal NHC fragments exert a stronger destabilization than the Ir–N dative bond does on the MC d-d excited states and ultimately improve emission efficiency. Complexes (xii) to (xiv) are recent examples of bis-tridentate NHC-complexes which have been used in OLEDs. The solution-state PLQYs of (xii) to (xiv) are 96%, 97% and 100% respectively. The blue-green emitting complexes have PL emission maxima between 473 and 515 nm. Their emissive state is a mixture of ³MLCT, ³LC and ³LLCT excited states.²⁰⁸

3.5 Aims and objectives

Compared to the large body of research already undertaken on neutral iridium complexes of the type Ir(N[∧]C[∧]N)(N[∧]C)X, the study of cationic [Ir(N[∧]C[∧]N)(N[∧]N)X]⁺-type systems is a relatively unexplored field of research. The performances of cationic complexes, however, are typically inferior to neutral complexes, as demonstrated by the substantial difference in maximum quantum yields of both systems: [Ir(N[∧]C[∧]N)(N[∧]N)X]⁺, $\phi_{\text{max}} = 21\%$ ¹⁵³ vs. Ir(N[∧]C[∧]N)(N[∧]C)X, $\phi_{\text{max}} = 89\%$.^{195,196} Complexes containing tridentate N[∧]C[∧]N ligands are amenable to colour-tuning strategies, in a similar fashion to bidentate [Ir(C[∧]N)₂(N[∧]N)]⁺ systems, due to the localisation of the HOMO and LUMO orbitals on the cyclometalating tridentate and ancillary ligands respectively. Metathesis of the chloride ligand in neutral N[∧]C[∧]N complexes with cyanide, thiocyanate or acetylide derivatives can often enhance PL performance.^{153,184,192,197} The procedure for acetylide metathesis requires a base such as KOH, DIPA or Et₃N, an acetylene derivative, CuI and the chloro-bound precursor in a suitably polar solvent such as DMF, DCM or MeOH. To date, the metathesis procedure has only been reported in neutral complexes and not cationic systems i.e. with N[∧]N-type ligands.^{178–184} The library of pyrazolopyridine and azaindole ligands discussed in Chapter 2 are suitable candidates for inclusion in [Ir(N[∧]C[∧]N)(N[∧]N)Cl]⁺ systems to create further classes of novel iridium phosphors.

Hence, this work aims to:

1. Synthesize a library of [Ir(N[∧]C[∧]N)(N[∧]N)Cl]PF₆ complexes where N[∧]C[∧]N = dpyb with 3',5'-dimethyl, 4'-methoxy or 4'-bromo substituent(s) in the central phenyl ring and N[∧]N = bpy, dmbpy, dmobpy and phen.

2. Develop a methodology for chloride metathesis in these symmetrical ionic complexes with cyanide and phenylacetylene derivatives, mirroring that in the existing literature for neutral complexes.
3. Investigate the coordination chemistry and PL properties of a range of asymmetric $[\text{Ir}(\text{N}^{\wedge}\text{C}^{\wedge}\text{N})(\text{N}^{\wedge}\text{N})\text{Cl}]\text{PF}_6$ complexes where $\text{N}^{\wedge}\text{N}$ contains a pyrazolo[3,4-*b*]pyridine or 7-azaindole framework, allowing exploration of the differences between 5- and 6-membered chelation in the $\text{N}^{\wedge}\text{N}$ ligand.

To achieve these aims we have synthesized three types of complex:

- Complexes with a symmetrical $\text{N}^{\wedge}\text{N}$ ligand ($\text{N}^{\wedge}\text{N}$ = bpy, dmbpy, dmobpy or phen [35-46], **Figure 3.9**, section 3.6).
- Complexes with a symmetrical $\text{N}^{\wedge}\text{N}$ ligand ($\text{N}^{\wedge}\text{N}$ = dmbpy or phen) whereby the monodentate chloride has been replaced with phenylacetylide [47, 49] or cyanide [48, 50] (**Figure 3.9**, section 3.6).
- Complexes with an asymmetrical $\text{N}^{\wedge}\text{N}$ ligand ($\text{N}^{\wedge}\text{N}$ = a pyrazolo[3,4-*b*]pyridine- or 7-azaindole-based ligand as used in bidentate systems in Chapter 2 [50-58], **Figure 3.23**, section 3.7).

3.6 Results and discussion: $[\text{Ir}(\text{N}^{\wedge}\text{C}^{\wedge}\text{N})(\text{N}^{\wedge}\text{N})\text{X}]^+$ complexes bearing a symmetrical $\text{N}^{\wedge}\text{N}$ ligand

Complexes **35-50** (Figure 3.9) will be discussed in this section.

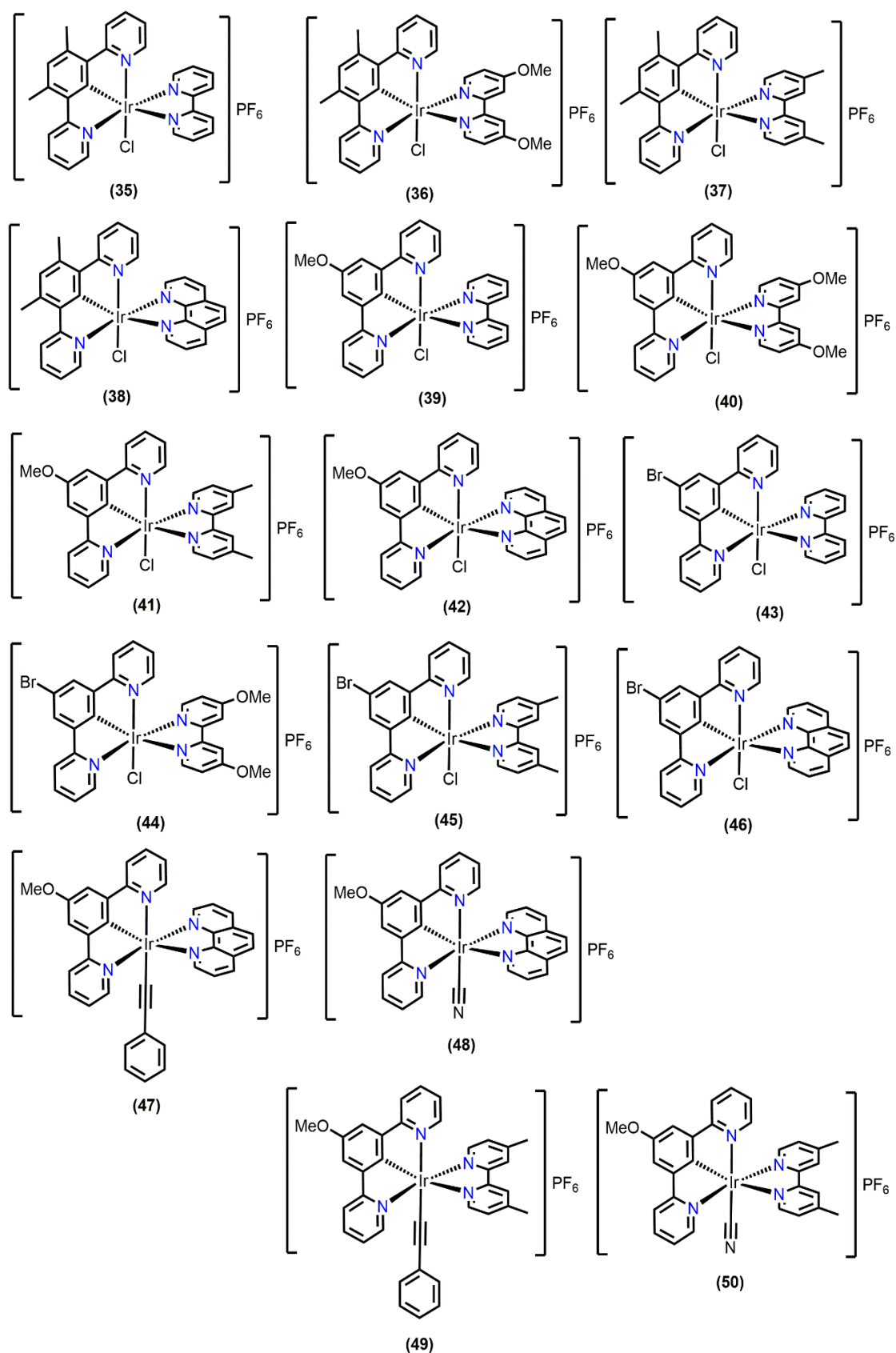


Figure 3.9: Structures of complexes **35-50**.

3.6.1 Synthesis

The 3,5-dimethyl, 4-methoxy and 4-bromo-dpybH derivatives investigated in this chapter were all synthesized via Stille coupling of a 1,3-dibrominated benzene derivative and 2-(tributylstannyl)pyridine according to previous literature procedures.^{188,211,212} A 1 : 2.2 ratio of aryl halide to 2-(tributylstannyl)pyridine was used due the purity of the commercial tin reagent being around 84%. The 3,5-dimethyl and 4-methoxy-dpybH ligands, HL¹⁵ and HL¹⁶, were synthesized in moderate to high yields of 51% and 74% respectively whereas the yield of 4-bromo-dpybH, HL¹⁷, was lower (23%) due to the formation of the mono- and tri-substituted side products which were difficult to separate using column chromatography (**Figure 3.10**). Overnight reaction of ligands HL¹⁵, HL¹⁶ and HL¹⁷ with IrCl₃·3H₂O in 2-ethoxyethanol and H₂O (3 : 1) at 120°C yielded chloro-bridged iridium dimers [Ir(L¹⁵)Cl(μ-Cl)]₂, [Ir(L¹⁶)Cl(μ-Cl)]₂ and [Ir(L¹⁷)Cl(μ-Cl)]₂ as yellow-orange precipitates which were isolated by centrifugation following an identical method to that described for the iridium dimers bearing bidentate ligands discussed in Chapter 2.

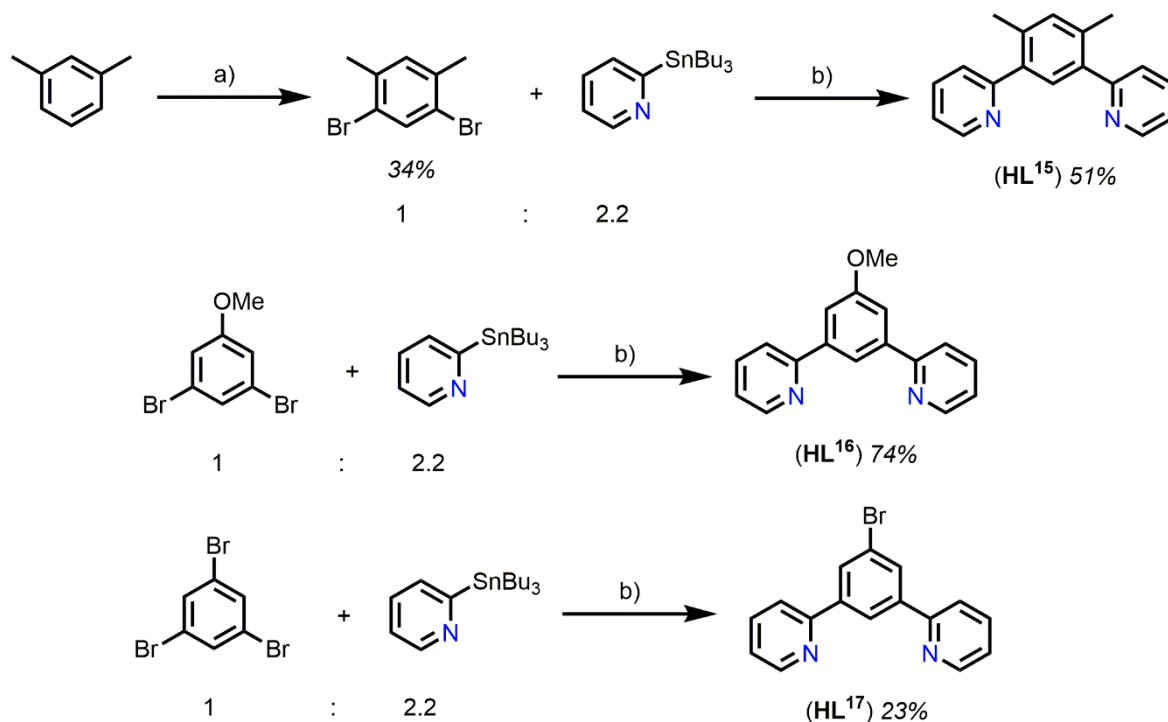


Figure 3.10: Synthesis of HL¹⁵, HL¹⁶ and HL¹⁷: a) Br₂ (2.3 equiv.), I₂ (2% mol), RT, 16 h; b) Pd(PPh₃)₂Cl₂ (3.7% mol), LiCl (7.3 equiv.), toluene, 110°C, 48 h.

The three iridium dimers were cleaved by 1-2 equivalents of N[^]N ligand (N[^]N = bpy, dmbpy, dmobpy or phen) aided by the addition of excess chloride scavenger, AgOTf. Literature procedures indicated the requirement of ethylene glycol as a solvent,^{153,193} but we found the reaction proceeded in toluene which simplified work-up due to the lower boiling point of toluene (110°C vs. 197°C). A longer reaction time of 16 h was, however, required using toluene compared to literature conditions which require only 2 h at reflux. Ion exchange was carried out by dropwise addition of a saturated aqueous solution of KPF₆ into an MeCN solution of the chloride salt. Complexes **35-46**

were obtained in yields between 23% and 81% after purification by column chromatography and recrystallization; the synthetic route to **35** is shown in **Figure 3.11**. The tridentate complexes were generally a little less soluble than the bidentate complexes but still readily dissolved in MeCN.

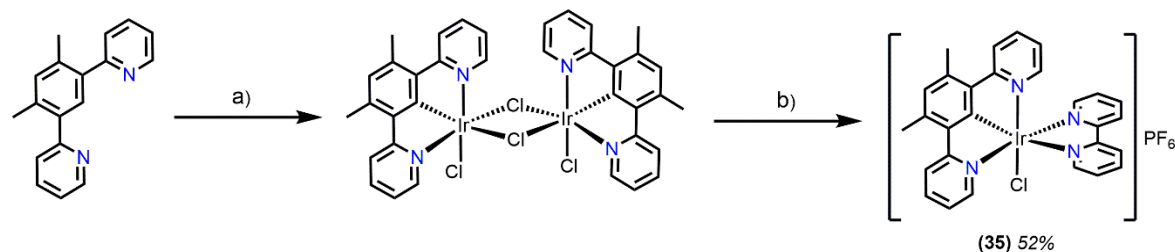


Figure 3.11: Synthesis of **35**: a) $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ (1 equiv.), 2-ethoxyethanol : H_2O (3 : 1), 120°C , 16 h; b) bpy (2 equiv.), AgOTf (4 equiv.), toluene, 110°C , 16 h followed by sat. aq. KPF_6 . A 52% yield was achieved for the second step. Identical conditions were used to prepare **36-46** using different iridium dimers and/or $\text{N}^{\wedge}\text{N}$ ligands.

Complexes **35-50** were obtained as a single non-isomeric product with a non-chiral iridium centre. The protons of the $\text{N}^{\wedge}\text{N}$ ligand, however, are chemically and magnetically inequivalent because one nitrogen is *trans* to the cyclometalating carbon whereas the other nitrogen is *trans* to the chloride. This means that each pair of protons has different ^1H NMR signals. **Figure 3.12** shows the ^1H NMR spectrum of **38** in d^6 -acetone whose protons $\text{H}^1\text{-H}^{12}$ are assigned with the aid of $^1\text{H}\text{-}^1\text{H}$ -COSY and $^1\text{H}\text{-}^1\text{H}$ -NOESY analysis. Proton signals $\text{H}^5\text{-H}^8$ are shifted upfield relative to the signal from their equivalent proton $\text{H}^1\text{-H}^4$ on the opposite half of phen due to the increased shielding $\text{H}^5\text{-H}^8$ experience from the phenyl ring of the $\text{N}^{\wedge}\text{C}^{\wedge}\text{N}$ ligand. This effect, known as a diamagnetic ring current,²¹³ occurs due to the magnetic field of the phenyl ring which lies perpendicular to the aromatic π -system and opposes the direction of the external magnetic field to shield protons that lie underneath the aromatic ring. Such an effect has been observed previously in complexes of ruthenium(II).²¹⁴

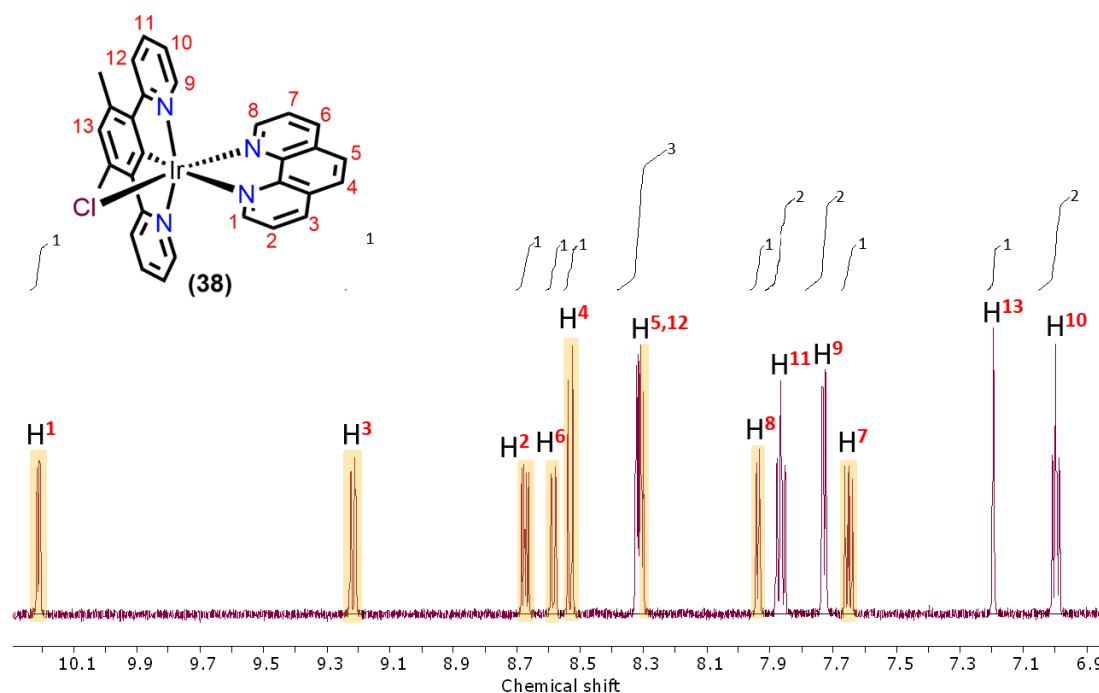


Figure 3.12: The aromatic ^1H NMR region of **38** in d_6 -acetone (600 MHz). The signals corresponding to the magnetically inequivalent phen protons are highlighted in yellow.

Metathesis of cationic iridium complexes with phenylacetylene was achieved after extensive reaction optimization (**Figure 3.13**). It was found to require harsher conditions than those described for metathesis in neutral complexes, probably due to the high activation barrier associated with the transition state which involves partial removal of the chloride from an already positively charged complex. DMF was required as the solvent due to its high boiling point – no reaction was observed in lower boiling point solvents such as MeOH and MeCN. Furthermore, DIPA was required as the base as the reaction with Et_3N failed to proceed. However, KOH proved to be too strong a base, or too nucleophilic, as it resulted in complex degradation after heating for 48 h.

Purification by column chromatography and recrystallization produced **47** and **49** in yields of 15% and 35% respectively. Over half of the starting material was recovered in each case, indicating poor conversion. This also made purification difficult as both the starting material and product had similar R_f values so a very gradual gradient of MeOH in DCM (0-1.6%) was required to separate the complexes. Despite our best efforts to improve the conversion of **41/42** into the acetylide-containing product **47/49** by: (i) using large excesses of acetylene and DIPA; (ii) using one equivalent of CuI and (iii) increasing the reaction time to 5 days, a significant amount of starting material was still recovered from the reaction.

Substituted phenylacetylenes gave poor results. 4-Methyl, 4-methoxy and 4-(*N*-dimethylamino)phenylacetylene showed signs of metathesised product by mass spectrometry whilst 3,5-bis(trifluoromethyl)phenylacetylene gave no conversion.

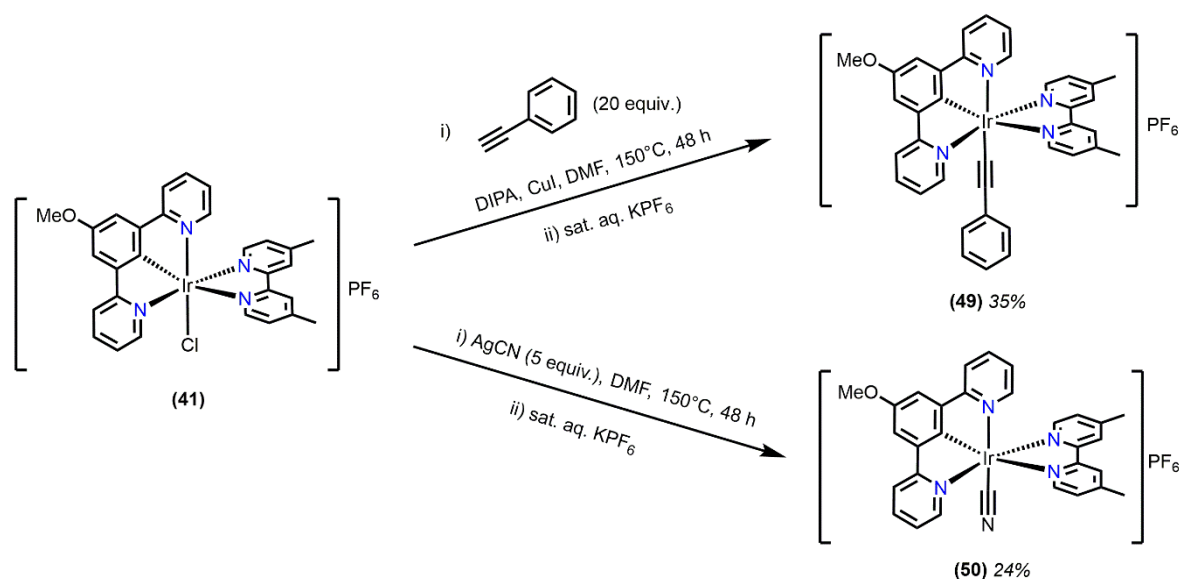


Figure 3.13: Synthesis of metathesized tridentate complexes using phenylacetylene (upper) and AgCN (lower) to yield complexes **49** and **50** respectively.

Metathesis with cyanide was carried out following a similar procedure to that with phenylacetylene (**Figure 3.13**). Contrary to literature precedent, we used AgCN instead of KCN as our cyanide source due to availability but found the reaction still proceeded, although not to completion.^{153,192,194} Reaction colour typically changed from a lighter yellow to a darker yellow/brown after 1-2 days due to the formation of AgCl which was removed by centrifugation during work-up before ion exchange.^{153,191,192,194,197} An approximate 40% conversion of **42** into the cyanide-containing complex **48** was achieved after 2 days' reflux at 150°C, as demonstrated by ¹H NMR spectroscopy (**Figure 3.14**). Complex **48** was obtained in a 24% yield after purification by column chromatography and recrystallization. Extension of the reaction time to 5 days made negligible difference to the conversion of **41** and **42** and to the yields obtained for **48** and **50**.

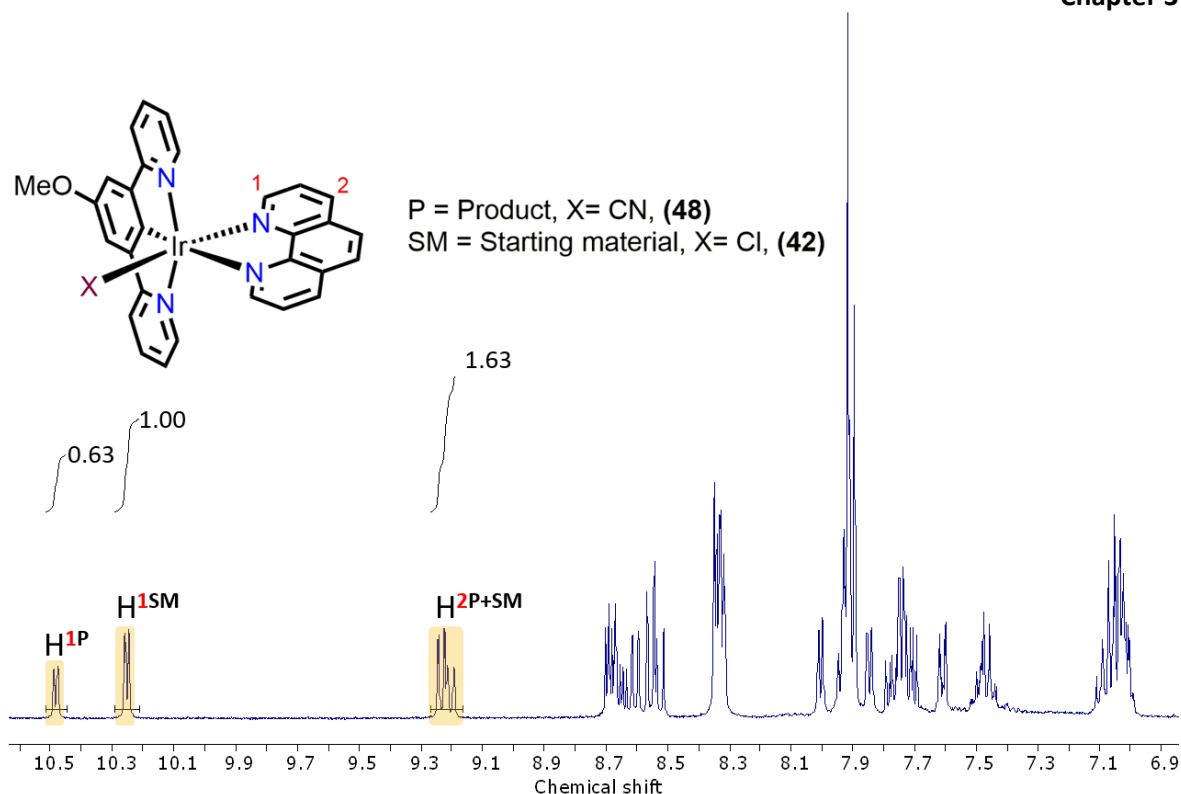


Figure 3.14: Crude ^1H NMR spectrum of the aromatic region of **48** in d_6 -acetone (400 MHz) showing the conversion ratio of metathesized to non-metathesized complex to be approximately 2 : 3.

3.6.2 Crystallography

Crystals of **38** and **41** suitable for X-ray diffraction analysis were prepared by slow evaporation from MeCN (**Figure 3.15**). Selected bond lengths and angles are collated in **Table 3.2**. Bond lengths and angles involving the metal are similar in both cases despite the different functionalizations of the tri- and bi-dentate ligands. Complexes **38** and **41** have a distorted pseudo-octahedral geometry with $\text{N}^{\text{NCN}}\text{--Ir--N}^{\text{NCN}}$ bonds angles of 161.2° and 159.8° respectively. This distortion is due to the geometric constraints associated with binding of the tridentate ligand that forms a 5-membered chelate with iridium. The shortest M–L bond lengths of **38** and **41** at $\approx 1.94 \text{ \AA}$ involve the cyclometalating phenyl of the $\text{N}^{\wedge}\text{C}^{\wedge}\text{N}$ ligand. Conversely, the longest M–L bond lengths of **38** ($2.16 \text{ \AA}$) and **41** ($2.15 \text{ \AA}$) involve the $\text{N}^{\wedge}\text{N}$ ligand. In both cases, the Ir–N bond that is opposite the cyclometalating carbon is the longer of the two bonds between Ir and the bidentate ancillary by $0.12\text{--}0.13 \text{ \AA}$; this result, which is also observed in neutral $\text{Ir}(\text{N}^{\wedge}\text{C}^{\wedge}\text{N})(\text{N}^{\wedge}\text{C})\text{Cl}$ -type systems,¹⁵³ is expected due to the stronger *trans* influence of the cyclometalating carbon vs. pyridine nitrogen.

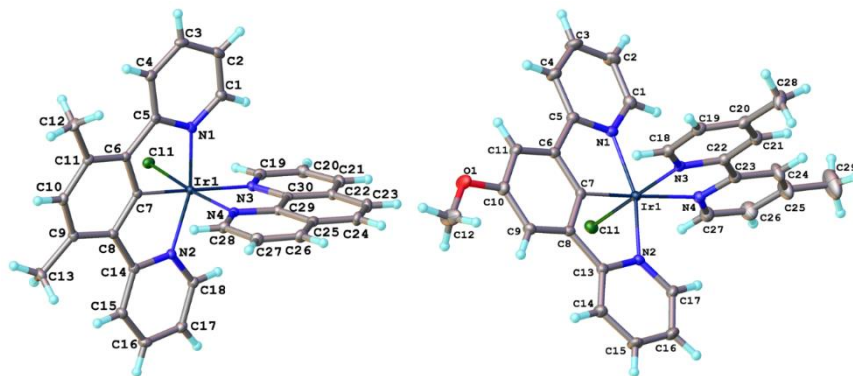


Figure 3.15: Crystal structures of **38** (left) and **41** (right). The PF_6^- counter-ion is omitted for clarity.

Table 3.2: Selected bond distances and bond angles of complexes **38** and **41**.

Complex	38	41
Ir ¹ –N ¹ bond length / Å	2.052(2)	2.061(2)
Ir ¹ –N ² bond length / Å	2.047(2)	2.068(2)
Ir ¹ –C ⁷ bond length / Å	1.943(2)	1.938(2)
Ir ¹ –N ³ bond length / Å	2.162(2)	2.036(2)
Ir ¹ –N ⁴ bond length / Å	2.038(2)	2.151(2)
Ir ¹ –Cl ¹ bond length / Å	2.354(2)	2.342(2)
N ¹ –Ir ¹ –N ² bond angle / °	161.20(7)	159.82(7)
N ³ –Ir ¹ –N ⁴ bond angle / °	79.36(7)	78.55(7)
C ⁷ –Ir ¹ –N ¹ bond angle / °	80.57(8)	80.34(8)
C ⁷ –Ir ¹ –N ² bond angle / °	80.64(8)	79.48(8)
N ³ –Ir ¹ –Cl ¹ bond angle / °	92.51(5)	78.55(7)
N ⁴ –Ir ¹ –Cl ¹ bond angle / °	171.85(5)	94.60(5)

3.6.3 Electrochemistry

Table 3.3 shows the relevant electrochemical parameters obtained for complexes **35–50** using cyclic voltammetry in MeCN using the ferrocene/ferrocenium couple as a reference. Complexes **35–46** display a single reversible oxidation in the window between +1.10 and +1.61 V. Based on previous studies,¹⁵³ the oxidation is likely to be associated with redox processes involving the iridium centre and the $\text{N}^+\text{C}^-\text{N}$ ligand due to the high degree of covalency of the Ir–C bonds. DFT calculations support this prediction (section 3.6.4). As expected, the oxidations of **35–46** typically occur at more positive potentials than neutral complexes due to their cationic nature.^{153,192,196} The +1.10 to +1.61 V oxidation window of **35–46** compares to the oxidation potentials of the equivalent dmbpy- and phen-based complexes, $[\text{Ir}(\text{ppy})_2(\text{dmbpy})]\text{PF}_6$ and $[\text{Ir}(\text{ppy})_2(\text{phen})]\text{PF}_6$ of +1.23 and +1.25 V.²¹⁵

Complexes **47–50** also display a single reversible oxidation between +0.95 and +1.04 V. The oxidation potentials of the metathesized complexes **47** and **49** are less positive than **35–46** which reflects the changing position of the HOMO to include the acetylide ligand as well as the iridium and cyclometalating phenyl ring.

Table 3.3: Electrochemical properties of complexes **35-58** recorded in a 0.1 M electrolyte solution of NBu_4PF_6 in MeCN. Values were measured at a scan rate of 200 mV s^{-1} and are reported relative to SCE, measured using ferrocene as the standard ($E_{1/2}^{\text{ox}} = 0.42 \text{ vs. SCE}$). $E_{\text{p}}^{\text{red}}$ is the cathodic peak potential. $\Delta E_{1/2} = E_{1/2}^{\text{ox}} - E_{\text{p}}^{\text{red}}$. $\Delta E_{\text{H-L}}$ refers to the HOMO-LUMO gap calculated using DFT.

Complex	$E_{1/2}^{\text{ox}} / \text{V}$	$E_{\text{p}}^{\text{red}} / \text{V}$	$\Delta E_{1/2} / \text{V}$	$\Delta E_{\text{H-L}} / \text{eV}$
35	+1.47	-1.26 ^{qr} , -1.95 ^{ir}	2.73	2.88
36	+1.44	-1.15 ^{qr} , -1.67 ^{ir}	2.59	3.09
37	+1.15	-1.75 ^{qr}	2.90	2.96
38	+1.61	-1.20 ^{qr} , -1.72 ^{ir}	2.81	2.93
39	+1.28	-1.36 ^{qr} , -1.83 ^{ir}	2.64	2.56
40	+1.21	-1.68 ^{qr} , -2.26 ^{ir}	2.89	2.79
41	+1.41	-1.40 ^{qr} , -1.92 ^{ir}	2.81	2.65
42	+1.25	-1.39 ^{qr} , -1.83 ^{ir}	2.64	2.61
43	+1.10	-1.84 ^{qr}	2.94	2.88
44	+1.51	-1.26 ^{qr} , -2.27 ^{ir}	2.77	3.12
45	+1.31	-1.23 ^{qr} , -1.76 ^{ir}	2.54	2.97
46	+1.17	-1.67 ^{ir} , -2.19 ^{ir}	2.84	2.94
47	+0.95	-1.78 ^{qr}	2.73	2.69
48	+0.97	-1.70 ^{qr}	2.67	2.11
49	+0.96	-1.84 ^{qr}	2.82	2.72
50	+1.04	-1.74 ^{qr}	2.78	2.15

Complexes **35-46** display a quasi-reversible or irreversible reduction in the window -1.15 to -1.84 V. Ten of the twelve also display a second irreversible reduction in the region -1.67 to -2.27 V in agreement with both cationic and neutral complexes of tridentate $\text{N}^{\wedge}\text{C}^{\wedge}\text{N}$ chelation.^{153,192,196} Based on DFT calculations, the first reduction can be attributed to the addition of an electron from an orbital encompassing the bidentate $\text{N}^{\wedge}\text{N}$ ancillary, as was seen in the tris-bidentate family of complexes discussed in Chapter 2. Complexes **37** and **43** only display a single quasi-reversible reduction at -1.75 and -1.84 V respectively and it is possible that their second reduction potentials occur at more negative potentials than the range permitted by the solvent window. These values are comparable with the equivalent dmbpy- and phen-based reversible reductions of $[\text{Ir}(\text{ppy})_2(\text{dmbpy})]\text{PF}_6$ and $[\text{Ir}(\text{ppy})_2(\text{phen})]\text{PF}_6$ of -1.21^{215,216} and -1.16 V.⁵⁹ Using cathodic peak potential to define the reductions of **35-50** reduces the accuracy with which their E^{red} and $\Delta E_{1/2}$ is estimated but nevertheless, the lack of a clear structure-electrochemical relationship proves that different substituents alter the oxidation and reduction potentials simultaneously.

The metathesized complexes **47-50** display a single quasi-reversible reduction between -1.70 and -1.84 V which is also associated with the $\text{N}^{\wedge}\text{N}$ ligand. Their reduction window lies in between the first and second reduction potentials of the chloride complexes **41** ($E_{\text{p}}^{\text{red}} = -1.40, -1.92 \text{ V}$) and **42** ($E_{\text{p}}^{\text{red}} = -1.39, -1.83 \text{ V}$).

The $\Delta E_{1/2}$ values of **35-50** range from 2.54 V to 2.94 V; complexes **45** and **43** have the smallest and largest $\Delta E_{1/2}$ values, respectively. Electrochemical $\Delta E_{1/2}$ values do not generally align well with

HOMO-LUMO gaps calculated by DFT, for example, **44** and **50** have the largest and smallest $\Delta E_{\text{H-L}}$ values of the series of 3.12 eV and 2.15 eV despite nearly identical electrochemical $\Delta E_{1/2}$ values of ≈ 2.78 V. The emissive states of **35-50** are therefore complicated and clearly involve large contributions from several orbitals including the HOMO and the LUMO.

3.6.4 DFT

DFT calculations on complexes **35-50** were performed using B3LYP and the LANL2DZ basis set. Calculations show that emission from **35-50** is dominated by HOMO $\rightarrow$ LUMO transitions (63-70%). The HOMO is consistently localised over the iridium and the tridentate ligand whereas the LUMO resides on the phen or bpy derivative across the series, as demonstrated by the frontier orbital diagrams of **41**, **49** and **50** (Figure 3.16). The HOMO energies of **41**, **49** and **50** are -7.91 eV, -8.03 eV and -7.24 eV respectively whilst their LUMO energies are -5.26 eV, -5.09 eV and -5.31 eV. Metathesis of the chloride in **41** with phenylacetylide and cyanide does not affect the location of the HOMO and LUMO orbitals (Figure 3.16). The same observation is made in the other metathesized series of **42**, **47** and **48**. Metathesis does, however, impact the relative HOMO and LUMO energies, for example, substitution with phenylacetylide widens the DFT-calculated HOMO-LUMO gap of **41** from 2.65 to 2.72 eV due to the combined effect of HOMO stabilization and LUMO destabilization. On the other hand, cyanide metathesis decreases the HOMO-LUMO gap of **41** to $\Delta E = 2.15$ eV due to simultaneous raising of the HOMO energy and lowering of the LUMO energy. The same trend is seen in complexes **42**, **47** and **48** whose HOMO-LUMO gaps are 2.61 eV, 2.69 eV and 2.11 eV (Table 3.3) HOMO-LUMO gaps of **35-50** as calculated by DFT align closely with their PL emission maxima but not with their electrochemical data.

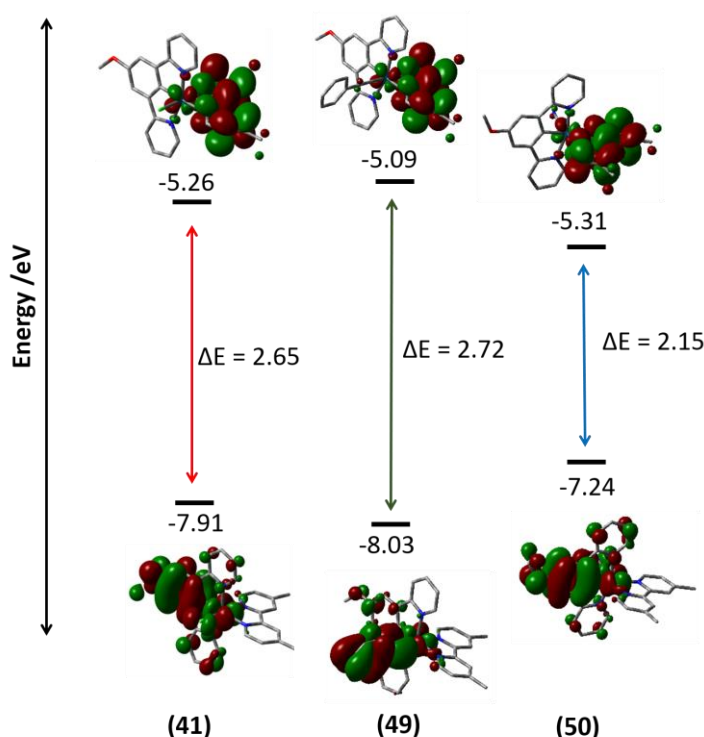


Figure 3.16: HOMO and LUMO orbital diagrams and energies for **41**, **49** and **50**.

3.6.5 Photophysical properties

The photophysical properties of **35-50**, measured in MeCN at RT and in EPA at 77 K, are summarised in **Table 3.4**.

3.6.5.1 Absorption

Absorption spectra of **35-38**, **40-42**, **44** and **47-50** are displayed in **Figure 3.17**. These ten complexes were selected to allow the comparison of absorption spectra of complexes featuring different N[^]N ligands (**35-38**), different substituents attached to the N[^]C[^]N phenyl ring (**36**, **40** and **44**) and either phenylacetylene (**47** and **49**) or cyanide (**48** and **50**) in place on the monodentate chloride ligand.

All twelve complexes display one or several intense high energy ¹LC π - π^* bands at 295 nm or lower. Molar absorptivities for these ¹LC bands are below $1.1 \times 10^5 \text{ M}^{-1}\text{cm}^{-1}$. The medium intensity spin-allowed ¹MLCT and ¹LLCT bands occur between 309 and 349 nm ($7.9 \times 10^2 \leq \epsilon \leq 1.6 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$) followed by the weakly intense spin-forbidden ³MLCT and ³LC transitions which occur at wavelengths of 384 nm or higher ($\epsilon \leq 9.7 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$). Molar extinction coefficients for these ¹MLCT and ³MLCT transitions are at least an order of magnitude lower than the coefficient values for the ¹LC transitions, with the exception of **42** and **50** whose molar absorptivities are roughly the same order of magnitude ($\epsilon \approx 10^3$).

Across the series **35-38**, it is clear that changing the bpy derivative from bpy (**35**) to dmbpy (**36**) to dmbopy (**37**) has made a negligible difference to absorbance as all three complexes display three ¹LC bands which appear as indistinct peaks or shoulders with molar absorptivities in the region of $3 \times 10^4 - 6 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ (**Figure 3.17, upper**). The phen-containing complex (**38**), however, has just two ¹LC bands at 230 and 273 nm.

Complexes **36**, **40** and **44** have contrasting profiles. Complex **40** displays a single large π - π^* band at 272 nm with a molar absorptivity of $\approx 8 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ whereas the profiles of **36** and **44** have multiple less intense bands/shoulders between 242 and 295 nm with smaller molar absorptivities of $< 6 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$. The spectra of **36** and **44** are unique in that they extend beyond 450 nm and include weak ³MLCT/LC ³ π - π^* transitions at 471 and 478 nm respectively ($\epsilon \leq 430 \text{ M}^{-1}\text{cm}^{-1}$).

Between 200 and 320 nm, the profiles of the phenylacetylene- and cyanide-containing complexes, **47** and **48**, are similar to their parent chloride complex, **42**, in that they all contain two distinct ¹LC π - π^* peaks: the first at 229 nm and the second between 271 and 275 nm (**Figure 3.17, lower**). The spectra of **42** and **48**, whose high energy peaks around $5 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ are approximately $3 \times 10^4 - 4 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ less than those of **47**, also display several shoulders at 254, 292 (**42**) and 288 nm (**48**). Beyond 320 nm, the profiles of the three complexes are nearly identical with their lowest energy bands occurring between 416 and 431 nm ($\epsilon \leq 7 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$).

In the analogous series of metathesized complexes, the spectra of **49** and **50** are markedly different. Whilst the profile of the acetylide-based complex, **49**, matches that of its chloride counterpart, **41**, (albeit the single ^1LC peak is $\approx 3 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ less intense and occurs at slightly lower energy), the molar absorptivities of **50** are extremely small. The molar absorptivities of **41** and **49** between 200 and 300 nm ($1.5 \times 10^5 - 1.9 \times 10^5 \text{ M}^{-1}\text{cm}^{-1}$) are much larger than the absorptivities of other complexes in this series.

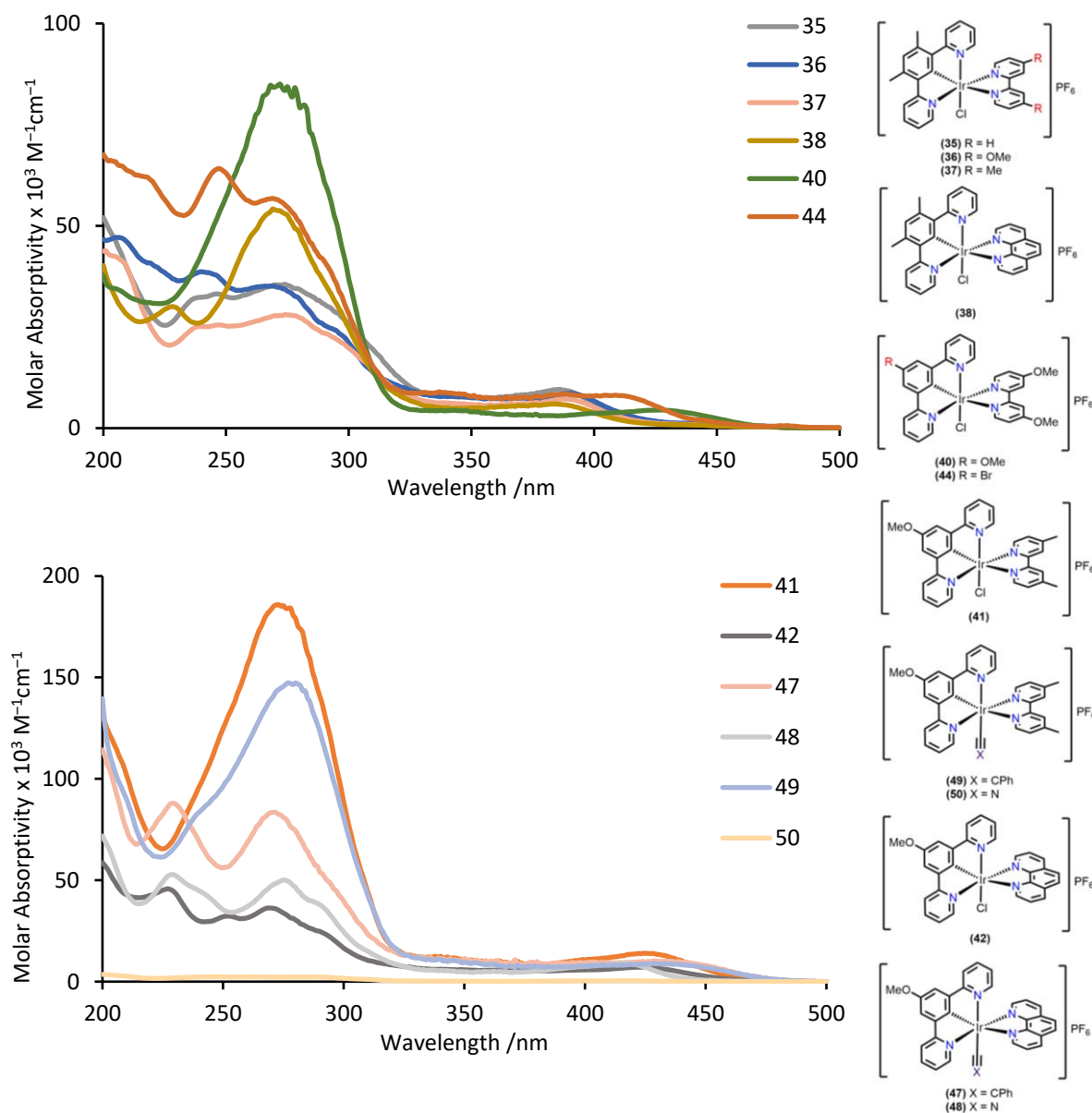


Figure 3.17: Absorption spectra of **35-38**, **40** and **44** (upper) and **41**, **42** and **47-50** (lower) in MeCN.

3.6.5.2 Emission

The normalised PL emission spectra of **35-38**, **41** and **45** at RT are shown in **Figure 3.18**. The comparison of **35-38** demonstrates the change in emission caused by altering the N[^]N ligand whilst comparison of **37**, **41** and **45** shows the effect on emission of changing the N[^]C[^]N phenyl substituent.

The spectra of **35**, **36** and **37** are virtually identical to one another; both show vibrational structure with their main emission peak lying within a narrow 4 nm range ($\lambda_{\text{max}} = 498\text{-}502\text{ nm}$) (**Figure 3.18, upper**). Replacement of the bpy derivative with phen in **38** causes a $\approx 60\text{ nm}$ ($2030\text{-}2190\text{ cm}^{-1}$) red shift in emission to a single peak at 559 nm. This bathochromic shift is due to the increased conjugation that phen provides over bpy which lowers the energy of the LUMO in agreement with DFT calculations.

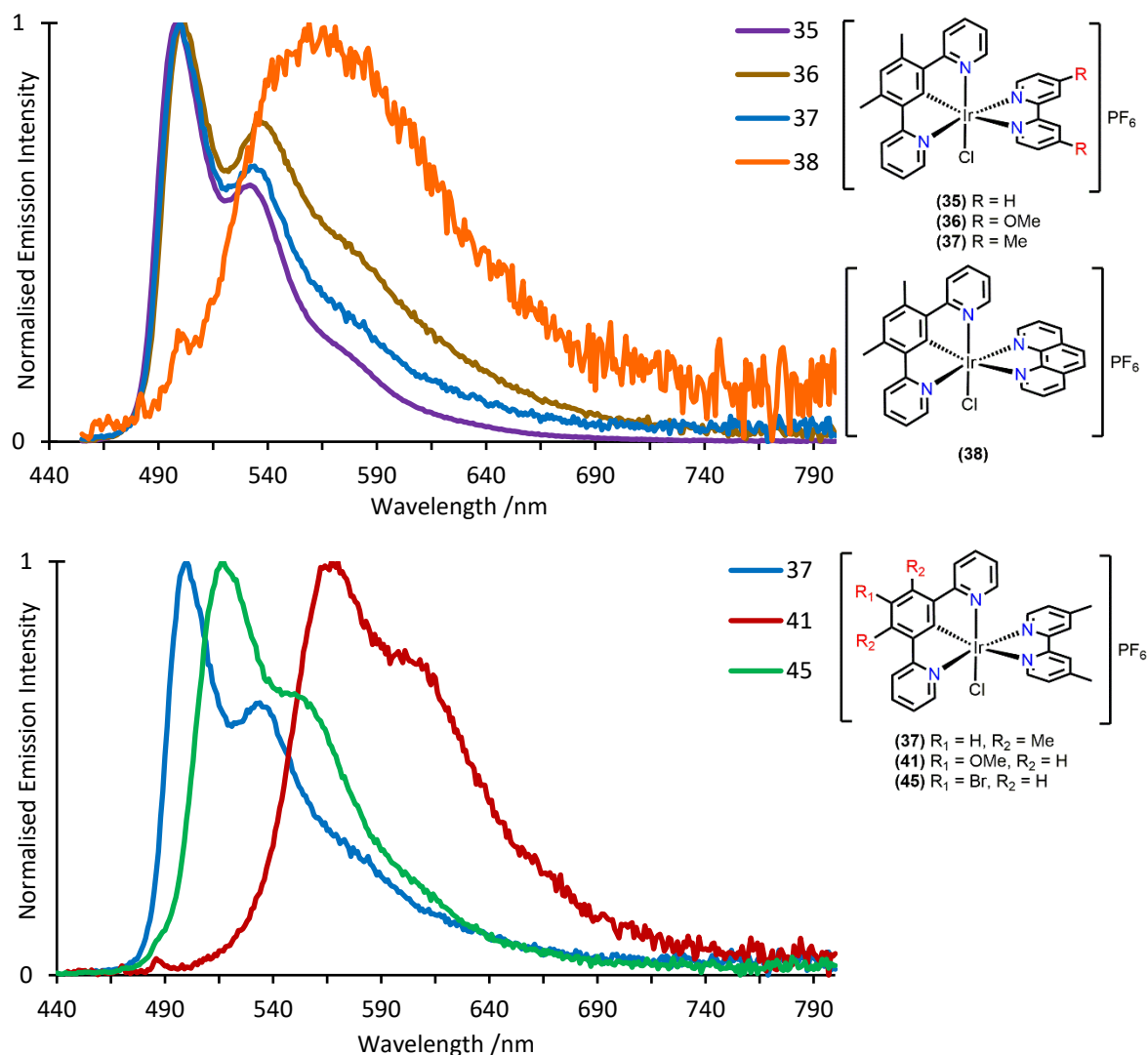


Figure 3.18: Normalised RT emission spectra of **35-38** (upper) and **37, 41** and **45** (lower) in degassed MeCN, $\lambda_{\text{exc}} = 435\text{ nm}$ for **35-38**, $\lambda_{\text{exc}} = 435\text{ nm}$ for **41** and **45**.

Analysis of the PL maxima of **37**, **41** and **45** reveals the effects of changing the substituent attached to the central N^{^C^N} ring (**Figure 3.18, lower**). In this series of complexes, **37** has the bluest emission of $\lambda_{\text{max}} = 500\text{ nm}$ with a shoulder at 534 nm, **45** has blue-green emission of $\lambda_{\text{max}} = 517\text{ nm}$ with a shoulder at 550 nm and **41** has green emission of $\lambda_{\text{max}} = 567\text{ nm}$. The red shift in emission from **37** to **41** can be explained by the replacement of the two electron-donating methyl groups on the central ring of the tridentate ligand with a single more donating methoxy group. The blue shift in

emission from **41** to **45** is expected due to the increased stabilization effect of the electron-withdrawing bromide towards the HOMO.

Figure 3.19 shows the PL emissions of **41**, **42** and **47-50** at RT which illustrate the effects of metathesizing the chloride in **41** and **42** with phenylacetylene (**47** and **49**) and cyanide (**48** and **50**).

Complex **41** is a yellow-orange-emitter with $\lambda(0,0) = 567$ nm (**Figure 3.19, upper**). Metathesis with phenylacetylene red shifts emission by 39 nm (1140 cm^{-1}) to a single and broad emission peak centred at 606 nm, characteristic of a $^3\text{MLCT}$ transition, whereas metathesis with cyanide blue shifts emission by 48 nm (1630 cm^{-1}) relative to **41** to $\lambda_{\text{max}} = 519, 549$ nm. The observed changes to emission colour can be explained by DFT analysis (section **3.6.4**) which illustrates the contrasting effects of the acetylide and cyanide groups on the size of the HOMO-LUMO gap i.e. narrowing and widening respectively.

Metathesis of the chloride in **42** with cyanide induces the same blue shift in emission but by a much greater amount (**Figure 3.19, lower**). Emission of the cyanide-containing complex, **50**, is blue shifted by over 100 nm (3270 cm^{-1}) relative to **42** ($\lambda_{\text{max}} = 519$ nm (**50**) vs. 625 nm (**42**)). Metathesis with phenylacetylene has little impact on the PL emission maxima of **42**, in contrast to **49** vs. **41** whose emission differ by 39 nm (1140 cm^{-1}).

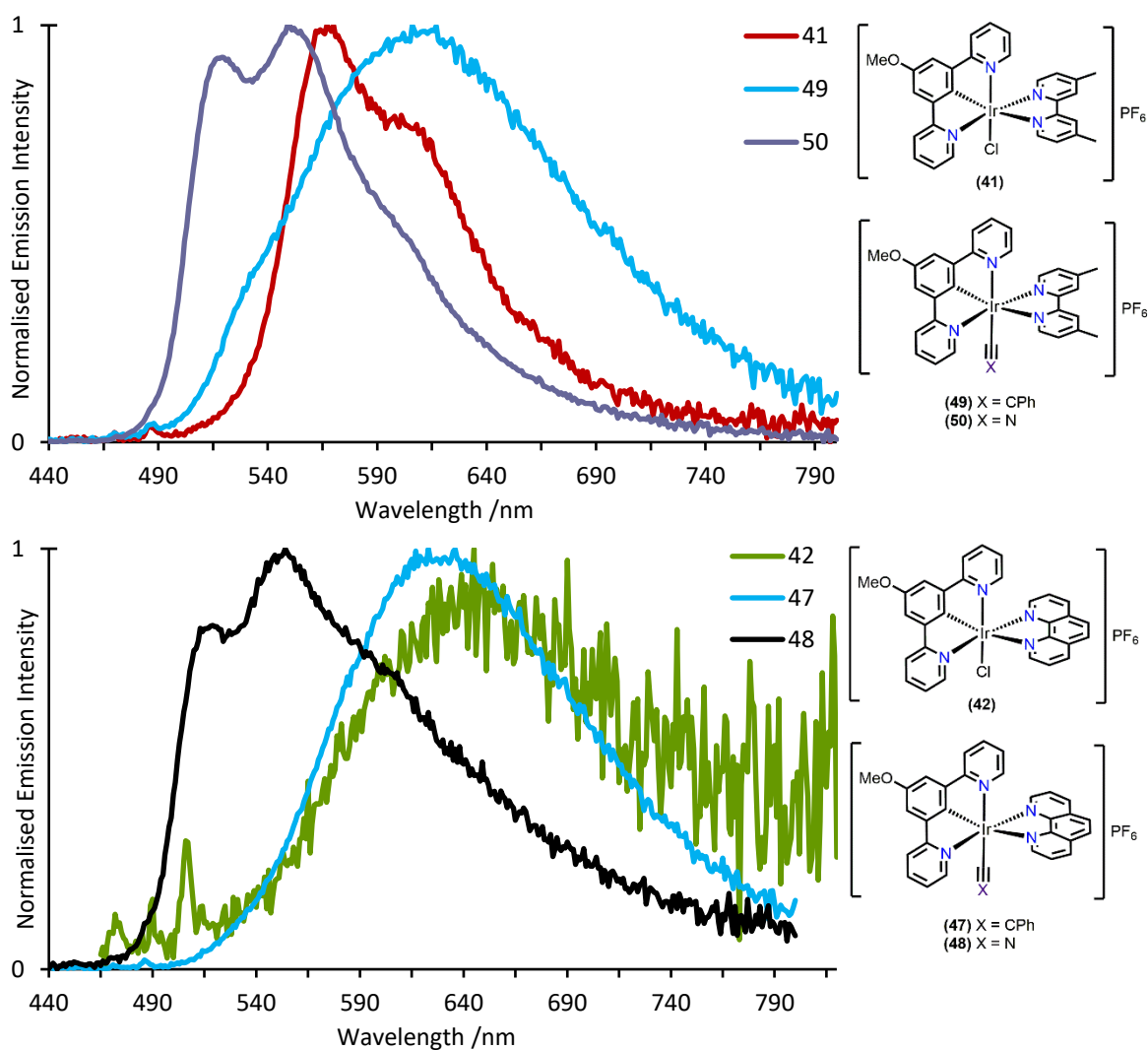


Figure 3.19: Normalised RT emission spectra of **41**, **49** and **50** (upper) and **42**, **47** and **48** (lower) in degassed MeCN, $\lambda_{exc} = 425$ nm.

Upon cooling, the emission profiles of **35-46** blue shift and become more vibronically structured. The largest difference between RT and 77 K emission is seen in the phen series of complexes, **38**, **42** and **46**, for example, the emission of **38** is shifted by 68 nm (2480 cm^{-1}) at 77 K compared to RT (77 K $\lambda_{max} = 491, 527$ nm vs. RT $\lambda_{max} = 559$ nm, **Figure 3.20**). The bpy series **35-38** are the bluest emitters both at 77 K and at RT; the dmobpy-containing complex, **36**, has the bluest emission at low temperature ($\lambda_{max} = 471, 508$ nm, **Figure 3.20**).

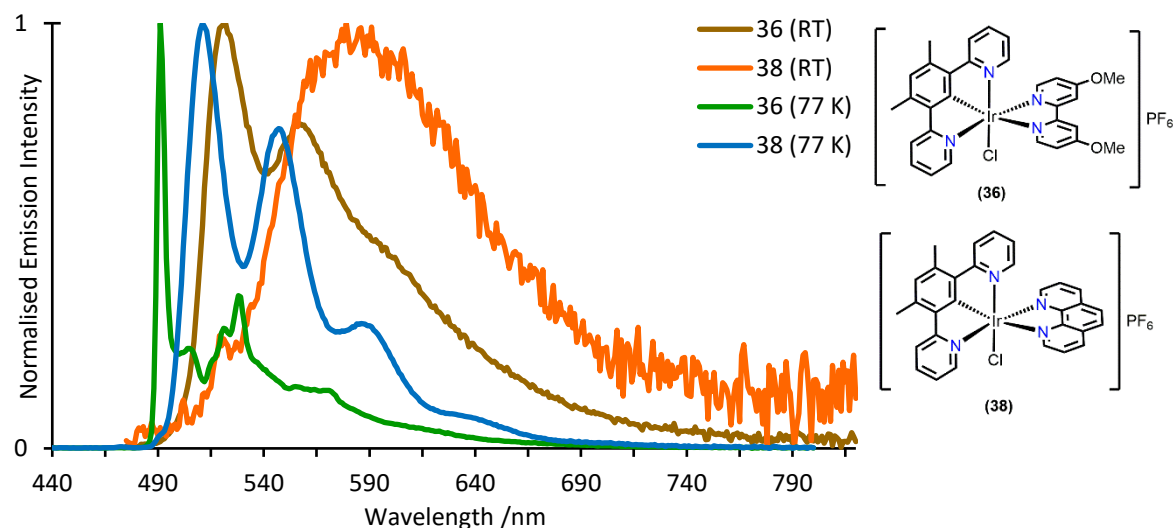


Figure 3.20: Normalised emissions of **36** and **38** at RT in degassed MeCN ($\lambda_{exc} = 435$ nm) and at 77 K in EPA ($\lambda_{exc} = 400$ nm).

Figure 3.21 displays the emission profiles of the metathesized complexes **49** and **50** at RT and at 77 K. The cyanide-containing complexes **48** and **50** have 77 K emission maxima of 501 and 505 nm respectively. Their emission is blue shifted by 10-12 nm ($385\text{--}467\text{ cm}^{-1}$) relative to the emission of their chloride analogues, **41** and **42**, at 77 K - this trend is also observed at RT but by a much greater amount i.e. 48 nm (1630 cm^{-1}) and 106 nm (3270 cm^{-1}) difference in λ_{max} . Emissions of the phenylacetylene-containing complexes **47** and **49** at low temperature are red shifted by 7 nm ($260\text{--}262\text{ cm}^{-1}$) with respect to their chloride analogues which matches their behaviour at RT. There is an 87 nm (2770 cm^{-1}) difference between the emission maxima of **49** and **50** at RT ($\lambda_{max} = 606$ nm (**49**) vs. $\lambda_{max} = 519$ nm (**50**)). Complex **50** still has the bluest emission of the two at 77 K, however, the difference between their emission maxima is reduced to only 17 nm ($\lambda_{max} = 522, 565$ nm (**49**) vs. $\lambda_{max} = 505, 546$ nm (**50**), $\Delta E = 645\text{ cm}^{-1}$).

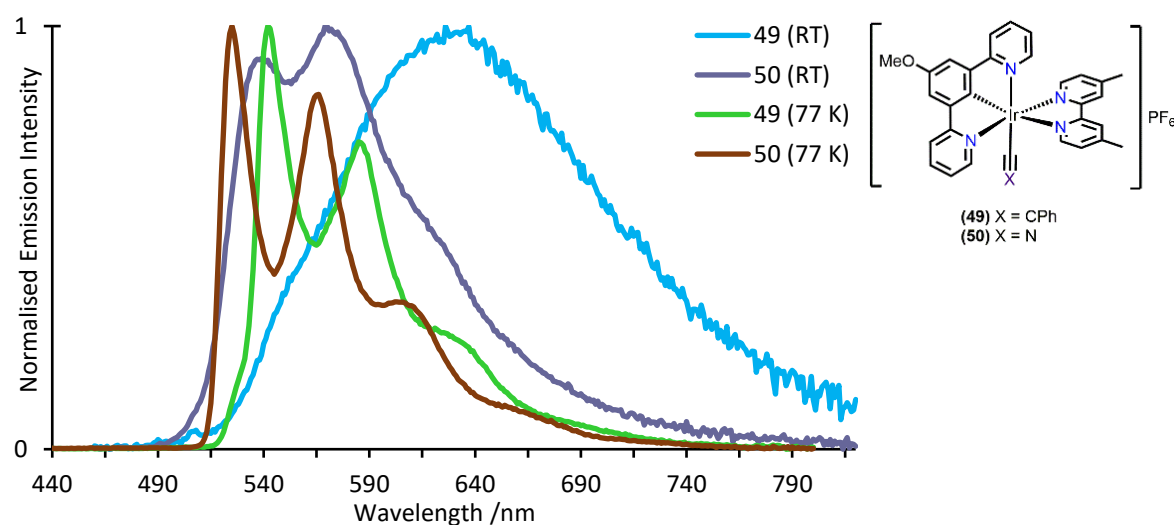


Figure 3.21: Normalised emissions of **49** and **50** at RT in degassed MeCN, $\lambda_{exc} = 425$ nm, and at 77 K in EPA (**49**) or butyronitrile (**50**), $\lambda_{exc} = 400$ nm.

Figure 3.22 displays the 77 K emission profiles of **35-38** (upper), **38, 42** and **46** (middle) and **41, 49** and **50** (lower). These graphs allow the comparison of the effects on low temperature emission of changing the N[^]N ligand (upper), changing the substituent attached to the central phenyl ring (middle) and replacing the chloride ligand with phenylacetylide or cyanide (lower).

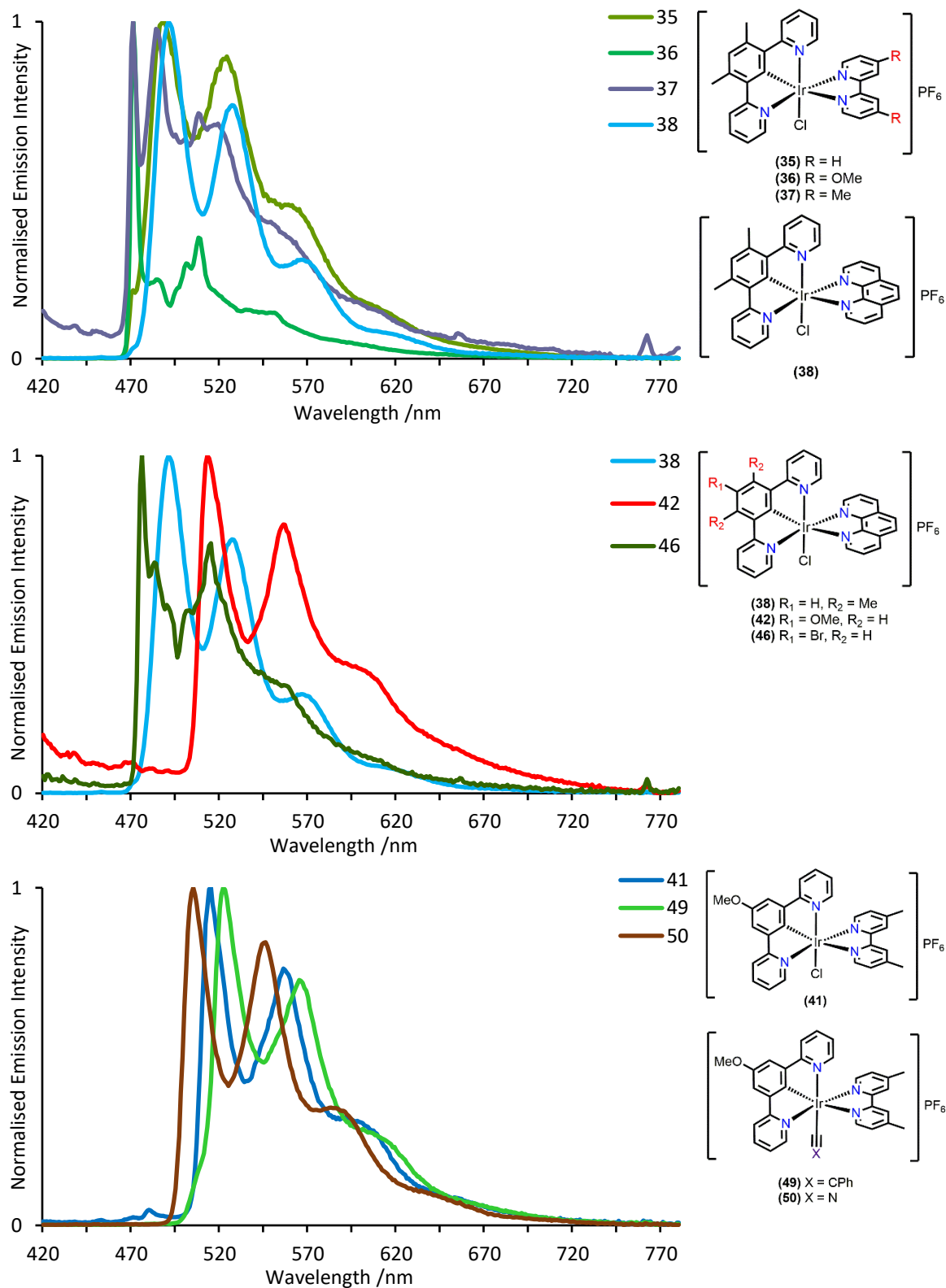


Figure 3.22: Normalised 77 K emission spectra of **35-38** (upper), **38, 42** and **46** (middle) and **41, 49** and **50** (lower) in EPA (or butyronitrile for **50**). $\lambda_{exc} = 400$ nm

The 77 K emission maxima of **35-38** are spread over a 20 nm range (**Figure 3.22, upper**). Complexes **36** and **37** have the bluest emissions with identical emission maxima of 471 nm. Complex **35** has the next bluest emission of $\lambda_{\text{max}} = 488$ nm, closely followed by **38** at $\lambda_{\text{max}} = 491$ nm. This trend is not consistent across the series of other non-metathesized complexes **39-42** and **43-46** because their emission maxima only differ by 3 nm i.e. λ_{max} of **39-42** = 513-516 nm and λ_{max} of **43-46** = 475-478 nm.

The 77 K spectra of **38**, **42** and **46** are similar in that they all feature a sharp and intense high energy peak and a less intense, broader, lower energy peak separated by approximately 36-43 nm (**Figure 3.22, middle**). The emission maxima of **38**, **42** and **46** are as follows: 491, 513 and 476 nm therefore the order of increasing emission energy is: **42** < **38** < **46**, just as was observed at RT. This trend of increasing emission energy across the series is due to the replacement of the strongly electron-donating methoxy group on the central phenyl ring of the N[^]C[^]N ligand (**42**) with less donating methyl substituents (**38**) which presumably stabilizes the HOMO by a greater amount. Furthermore, replacement of the methyl groups with bromide is likely to lower the HOMO energy even further (**46**).

Just as observed at RT, complex **49** has redder emission than **41** at 77 K ($\lambda_{\text{max}} = 522$ vs. 515 nm, **Figure 3.22, lower**). This 7 nm (260 cm⁻¹) red shift is due to the metathesis of the chloride ligand with phenylacetylide which causes a stabilization of the LUMO and a destabilization of the HOMO. Conversely, complex **50** has bluer emission than **41** both at 77 K and at RT resulting from a simultaneous stabilization of the HOMO and destabilization of the LUMO. The blue shift in 77 K emissions of **41**, **49** and **50** compared to RT confirms the MLCT nature of their excited states due to suppression of vibrational microstates at low temperature.

The RT photophysical properties of **35-50** in degassed MeCN and at 77 K in EPA are shown in **Table 3.4**. Complex **35** has the highest quantum yield of 5.6% but the PLQYs of the other non-metathesized complexes **36-46** are much lower with a maximum value of 1.2%. The photophysical properties of **35-38** differ from the properties of **39-46** in two ways:

1. The lifetimes of **35-38** range from 690-997 ns which is an order of magnitude lower than the lifetimes of **39-46** (1.9 - 5.3 μ s).
2. The non-radiative rate constants of **35-38** range from $1 \times 10^6 \text{ s}^{-1}$ to $1.4 \times 10^6 \text{ s}^{-1}$ which is an order of magnitude larger than the k_{nr} values of **39-46** ($1.9 \times 10^5 \text{ s}^{-1}$ to $5.4 \times 10^5 \text{ s}^{-1}$).

One possible explanation for the higher rates of non-radiative decay in **35-38** might be because there is more distortion between the ground and excited states compared to **39-46** due to the smaller size of their central N[^]C[^]N phenyl ring substituents (i.e. methyl vs. methoxy and bromo).

Complex **50** has the highest quantum yield of the metathesized series **47-50** of 2.5%. All of the metathesized complexes have higher quantum yields than their chloride analogues, **41** and **42**, by

as much as 2%. This increase is largely due to the significant increase in the rates of radiative decay of **47-50** by up to two orders of magnitude compared to **41** and **42**, for example, k_r of **50** = $2.4 \times 10^4 \text{ s}^{-1}$ vs. k_r of **41** = $8 \times 10^2 \text{ s}^{-1}$. The higher k_r values of the cyanide-containing complexes **48** and **50** are supported by DFT calculations (section 3.6.4) which show that the iridium contributes more to the HOMOs of **48** and **50** than it does in **41** and **42** therefore raising the degree of metal character in the excited states of **48** and **50**.

Lifetimes are typically extended at low temperature up to a maximum value of 14 μs for **50**, due to the suppression of non-radiative decay processes which dominate at RT resulting in poor PL. The exceptions are **41** and **42** whose 77 K lifetimes (0.8 and 1.1 μs respectively) are shorter than their RT lifetimes (5.3 and 3.1 μs). The large difference in 77 K lifetimes between **41** and **50** (13.5 μs) is surprising as the only difference in structure between the two complexes is the identity of the monodentate cyanide vs. chloride ligand. The 77 K lifetimes of the metathesized complexes **47-50**, which range from 3.6 to 14.3 μs , are consistently longer than those of their chloride counterparts, **41** and **42**.

Table 3.4: Photophysical properties of complexes **35-50** recorded in degassed MeCN at RT, $\lambda_{exc} = 425$ nm. ^a $\lambda_{exc} = 435$ nm. Photophysical properties of **35-50** recorded in EPA at 77 K, $\lambda_{exc} = 400$ nm. ^b = butyronitrile solvent. ^{sh} = shoulder. Aerated PLQYs and lifetimes are shown in brackets.

Complex	35 ^a	36 ^a	37 ^a	38 ^a	39	40	41	42
Absorption Maxima /nm ($\epsilon / M^{-1} cm^{-1}$)	240 (43100)	242 (43200)	241 (31100)	230 (29500)	243 (34400)	272 (57500)	242 (32533)	229 (49900)
	248 (52000)	247 (42600)	248 (31600)	273 (60100)	248 (33800)	345 (7790)	249 (31778)	254 (9420)
	273 (40200)	270 (39700)	276 (34800)	386 (8690)	281 (32500)	427 (8020)	279 (31506)	271 (6300)
	387 (9490)	295 (28200)	390 (9270)	468 (514)	312 (16200)		344 (7469)	292 (3690)
	438 (1270)	392 (9650)	438 (1240)		344 (6810)		426 (8728)	426 (4430)
	468 (635)	471 (430)	470 (475)		425 (8620)			
λ_{max} / nm	498, 532	502, 537	500, 534	559	537, 571	574	567	625
PLQY /% degassed (aerated)	5.6 (0.3)	1.1 (0.2)	0.6 (0.1)	0.2 (0.1)	0.0 (0.0)	0.2 (0.0)	0.4 (0.1)	0.1 (0.1)
Lifetime /ns degassed (aerated)	879 (34)	866 (35)	690 (35)	997 (113)	3630 (62)	5090 (43)	5260 (54)	3060 (52)
$k_r \times 10^4 s^{-1}$	6.41	1.32	0.81	0.17	0.03	0.04	0.08	0.03
$k_{nr} \times 10^4 s^{-1}$	107	114	144	100	28	20	19	33
77 K λ_{max} / nm	488, 524	471, 508	471, 484, 508	491, 527	514, 555	516, 560	515, 556	513, 556
77 K Lifetime / μs	6.0	3.3	2.9	6.9	7.6	10.7	0.8	1.1

Complex	43	44	45	46	47 ^b	48	49	50 ^b
Absorption Maxima /nm ($\epsilon / M^{-1} cm^{-1}$)	244 (33200)	247 (44600)	246 (55500)	226 (102000)	229 (26300)	229 (39400)	277 (83000)	246 (1640)
	277 (29600)	269 (39500)	270 (47700)	252 (80700)	271 (25000)	275 (37300)	430 (5190)	262 (1610)
	291 (24800)	387 (4030)	277 (46900)	270 (85600)	431 (3200)	288 (29100)		289 (1560)
	384 (5330)	409 (5650)	289 (39500)	291 (54800)		416 (7000)		309 (787)
	406 (5910)	478 (338)	408 (9040)	407 (1490)				349 (1020)
	442 (1240)		444 (1840)	442 (2940)				419 (2040)
	475 (328)		476 (468)	475 (684)				
λ_{max} / nm	520, 560 ^{sh}	522, 554 ^{sh}	517, 550 ^{sh}	520	623	519, 554	606	519, 549
PLQY /% degassed (aerated)	0.8 (0.1)	1.0 (0.1)	1.2 (0.3)	0.2 (0.1)	2.1 (0.9)	0.8 (0.3)	1.3 (0.5)	2.5 (0.4)
Lifetime /ns degassed (aerated)	2360 (58)	2920 (52)	2630 (62)	1850 (6)	91 (36)	270 (81)	2680 (37)	1060 (115)
$k_r \times 10^4 s^{-1}$	0.32	0.35	0.46	0.08	23	3.10	0.48	2.39
$k_{nr} \times 10^4 s^{-1}$	42	34	38	54	1080	367	37	92
77 K λ_{max} / nm	475, 514	478, 517	476, 515	476, 515	520, 562	501, 541	522, 565	505, 546
77 K Lifetime / μs	4.8	4.5	4.2	5.3	12.0	3.6	9.1	14.3

3.7 Results and discussion: Asymmetric $[\text{Ir}(\text{N}^{\wedge}\text{C}^{\wedge}\text{N})(\text{N}^{\wedge}\text{N})\text{X}]^+$ complexes

Complexes **51-58** (Figure 3.23) will be discussed in this section.

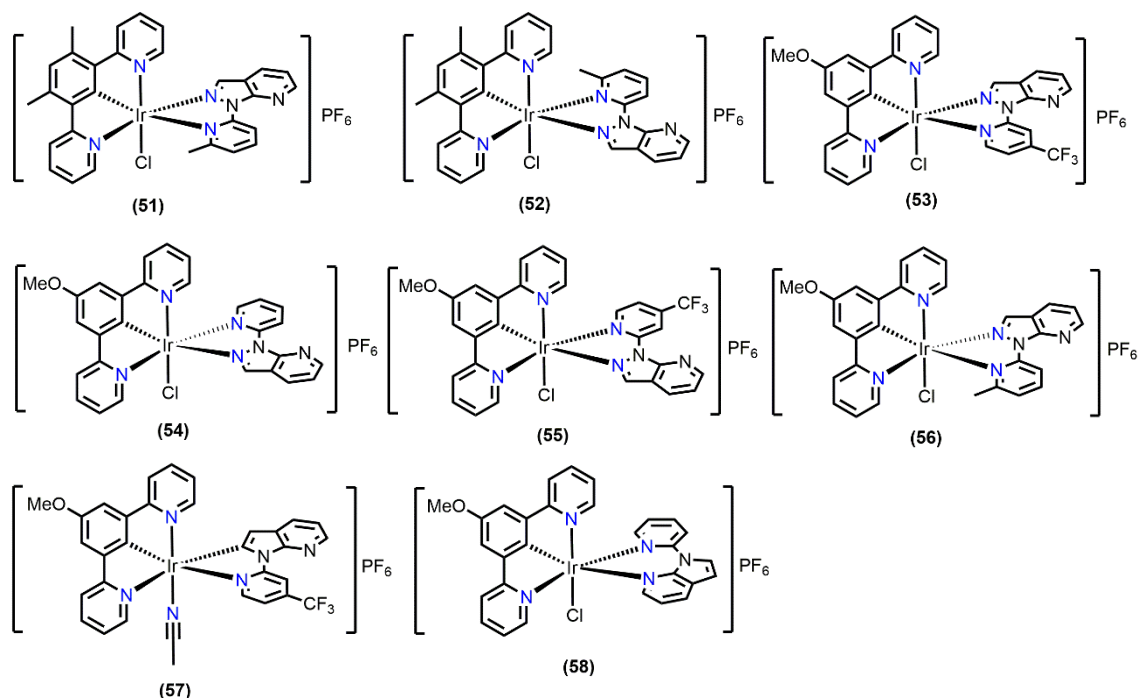


Figure 3.23: Structures of complexes **51-58**.

3.7.1 Synthesis

Exactly the same reaction conditions, work-up procedure and purification methods were used to synthesize the eight asymmetric tridentate complexes **51-58** using either pyrazolopyridine or azaindole ligands. Purification of the asymmetric complexes was significantly more challenging, however, due to the possible formation of two structurally isomeric products in which either the nitrogen of the pyridine ring or that of the fused aromatic ring is *trans* to the cyclometalating carbon (binding modes A and B respectively, Figure 3.24).

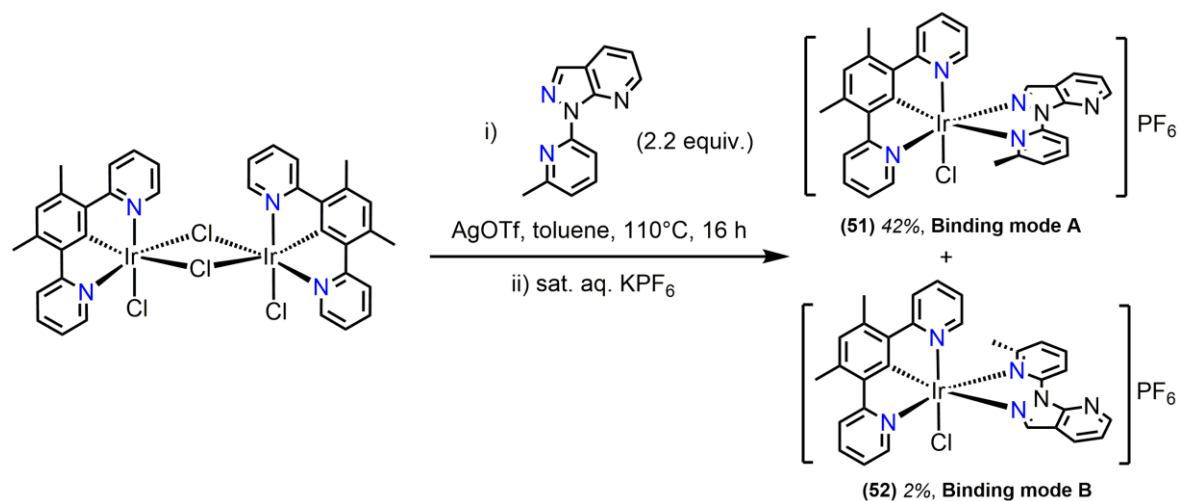


Figure 3.24: Synthesis of complexes featuring an asymmetric N[^]N ligand following the same procedure used to synthesize complexes **36-50**. In this case, however, the formation of two structural isomeric products is possible, as in the case of **51** (upper) and **52** (lower).

The first complexes in this series to be investigated are **51** and **52**. The presence of two sets of peaks in the crude ¹H NMR spectrum of **51** suggest the presence of two (or more) species with similar structures (**Figure 3.25**). The integral peak ratio of approximately 1 : 0.45 was consistent across the entire spectrum. Furthermore, each set of peaks had a total integral area of 25 protons which matches the number of protons in **51**. The crude LCMS trace of **51** shows two peaks with identical *m/z* values of 695 = [M-PF₆] at retention times of 2.05 and 2.16 minutes. This evidence led us to believe that the two species were in fact isomers. We tentatively used the distinctive singlet peaks at 9.48 and 7.56 ppm in the crude ¹H NMR spectrum of **51**, corresponding to H¹, as a diagnostic tool to confirm the binding mode of the pyrazolopyridine ligand L¹³. The diamagnetic ring current effect (section 3.6.1) of the N[^]C[^]N central phenyl ring in **51** shields H¹, which sits directly underneath the cyclometalating ring within the magnetic field generated by the aromatic π-system.^{213,214} Therefore, the H¹ peak at 7.56 ppm is assigned to complex **51** whereas the most downfield H¹ peak at 9.48 ppm corresponds to its isomer, complex **52**.

Column chromatography followed by recrystallization from MeCN, ether and hexane allowed isolation of the pure major product (i.e. **51**) in a 42% yield. X-ray crystallography of **51** confirmed that the coordination mode of L¹³ is that of binding mode A (section 3.7.2). Our hypothesis is correct as the H¹ singlet in pure **51** occurs at 7.56 ppm. Analytical HPLC was required to isolate the pure minor product (i.e. **52**) left from the combined recrystallized supernatants in a yield of 2%. Again, X-ray crystallography and ¹H NMR spectroscopy (**Figure 3.25**) confirmed that the coordination of L¹³ is that of binding mode B with an upfield H¹ singlet occurring at 9.48 ppm.

Complexes **53** and **55** were isolated from the same crude reaction mixture; in this instance, silica gel column chromatography alone successfully purified each isomer, however, a very slow gradient of MeOH (0-2%) in DCM was required due to the very similar R_f values of **53** and **55** (0.33 and 0.34 respectively).

After column chromatography of **51-56** to remove excess N[^]N ligand amongst other impurities, the ratio of major to minor products could be calculated by ^1H NMR spectroscopy. The isomeric ratios of **51-56**, shown in **Table 3.5**, are calculated based on the integral ratio of the singlet H^1 signals. In each of the four reactions, there is a preference for the pyrazolopyridine ligand to bind with the pyridine, pyrimidine or isoquinoline unit trans to the cyclometalating carbon of the N[^]C[^]N ligand, i.e. binding mode A, presumably due to the better π -accepting ability of this unit. One or several recrystallizations were necessary to purify the major product, or the minor isomer in the case of **54**.

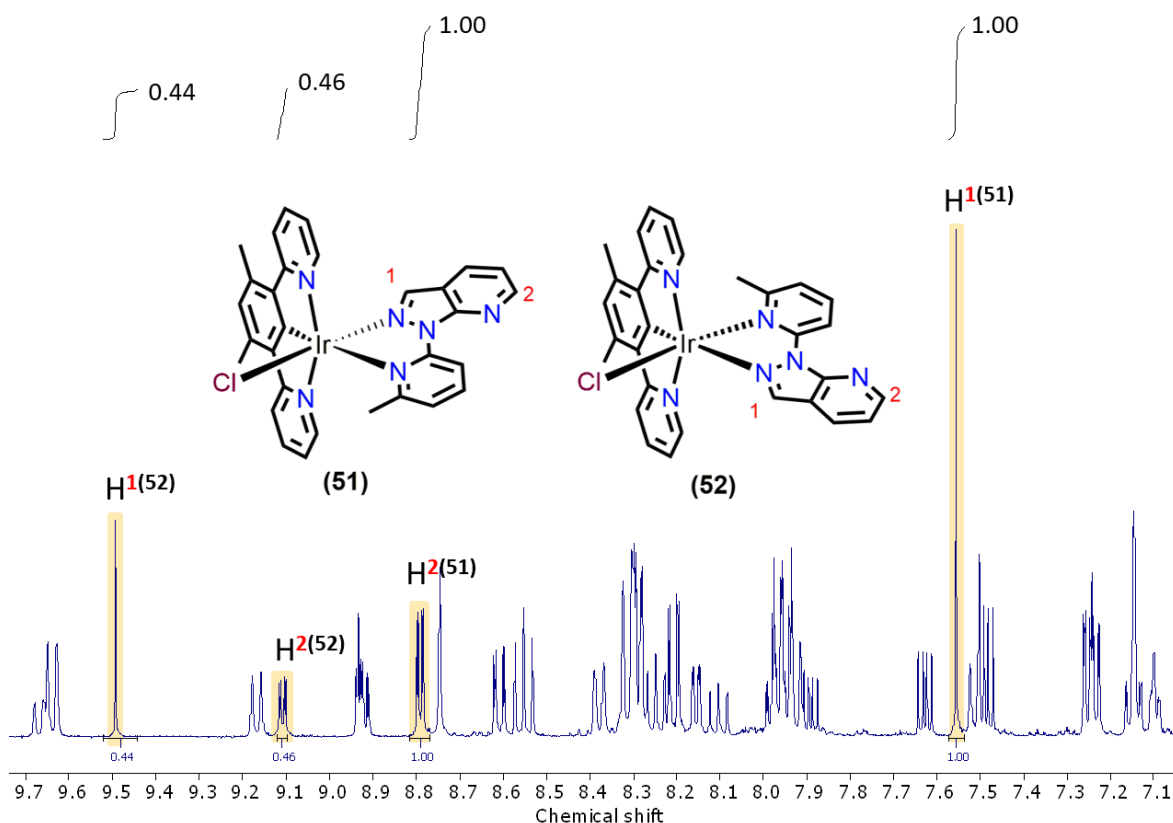


Figure 3.25: ^1H NMR spectrum of **51/52** after column chromatography (alumina, MeCN : H_2O : sat. aq. KNO_3 (97 : 2 : 1)). The characteristic ^1H singlets of **51** and **52** at 7.56 and 9.48 ppm respectively (highlighted in yellow) reveal the intrinsic isomeric ratio of the reaction. The same isomeric ratio of $\approx 1:0.45$ is seen for the H^2 signals of **51** and **52** at 8.78 and 9.10 ppm respectively (also highlighted in yellow).

Table 3.5: Table showing the isomeric ratios of the reactions to form **51/52**, **53/55**, **54** and **56**, as calculated by the integral ratio of H^1 singlet protons in the crude ^1H NMR spectra. The major isomer refers to the geometry whereby the pyridine, pyrimidine or isoquinoline nitrogen is *trans* to the cyclometalating carbon (binding mode A) and the minor isomer refers to the geometry whereby the pyrazolopyridine nitrogen is *trans* to the cyclometalating carbon (binding mode B). *Minor isomer isolated exclusively.

Complex	Major : Minor Isomer Ratio
51 : 52	1 : 0.45
55 : 53	1 : 0.63
54*	1 : 0.43
56	1 : 0.36

The yields of **51-56** are shown in **Table 3.6**. The higher yields of complexes **51**, **53** and **56**, which all adopt binding mode A, reflect the preference of the pyrazolopyridine ligand class to bind with the pyridine, pyrimidine or isoquinoline nitrogen *trans* to the cyclometalating carbon rather than the nitrogen of the pyrazolopyridine.

Table 3.6: Yields obtained for the final step in the synthesis of **51-56**.

Complex	Yield /%	Complex	Yield /%
51	42	52	2
53	16	54	14
55	13	56	22

Complexes **57** and **58** contain azaindole-based $N^{\wedge}N$ ligands. During the recrystallization of **57**, a rather unusual phenomenon occurred. Two types of crystal formed after several days from a solution of MeCN, ether and hexane containing an impure mixture of **57** after column chromatography; one in which L^6 binds in an $N^{\wedge}N$ fashion with the azaindole nitrogen *trans* to the cyclometalating carbon and the other in which L^6 cyclometalates to iridium via the indole ring which is *trans* to a solvent molecule of MeCN (section 3.7.2). A second recrystallization was sufficient to yield the pure $[Ir(N^{\wedge}C^{\wedge}N)(C^{\wedge}N)MeCN]PF_6$ -type complex, **57**, in a yield of 27%. The $[Ir(N^{\wedge}C^{\wedge}N)(N^{\wedge}N)Cl]PF_6$ -type complex could not be isolated from the supernatant of the recrystallization in its pure form.

Figure 3.26 shows the ^1H NMR spectrum of **57**; characteristic peaks are the singlet at 4.84 ppm of integral area = 1 corresponding to H^4 and the singlet at 2.45 ppm of integral area = 3 corresponding to the three H^1 protons of MeCN. The H^4 signal is shifted downfield by several ppm relative to the typical shifts of other aromatic protons in **51-58** because H^4 is shielded by the diamagnetic ring current created by the cyclometalating phenyl ring of the $N^{\wedge}C^{\wedge}N$ ligand.²¹³

Despite the likelihood of isomer formation in the azaindole-class of complexes i.e. **58**, it was not possible to calculate an isomeric ratio due to the lack of the characteristic H^1 singlet.

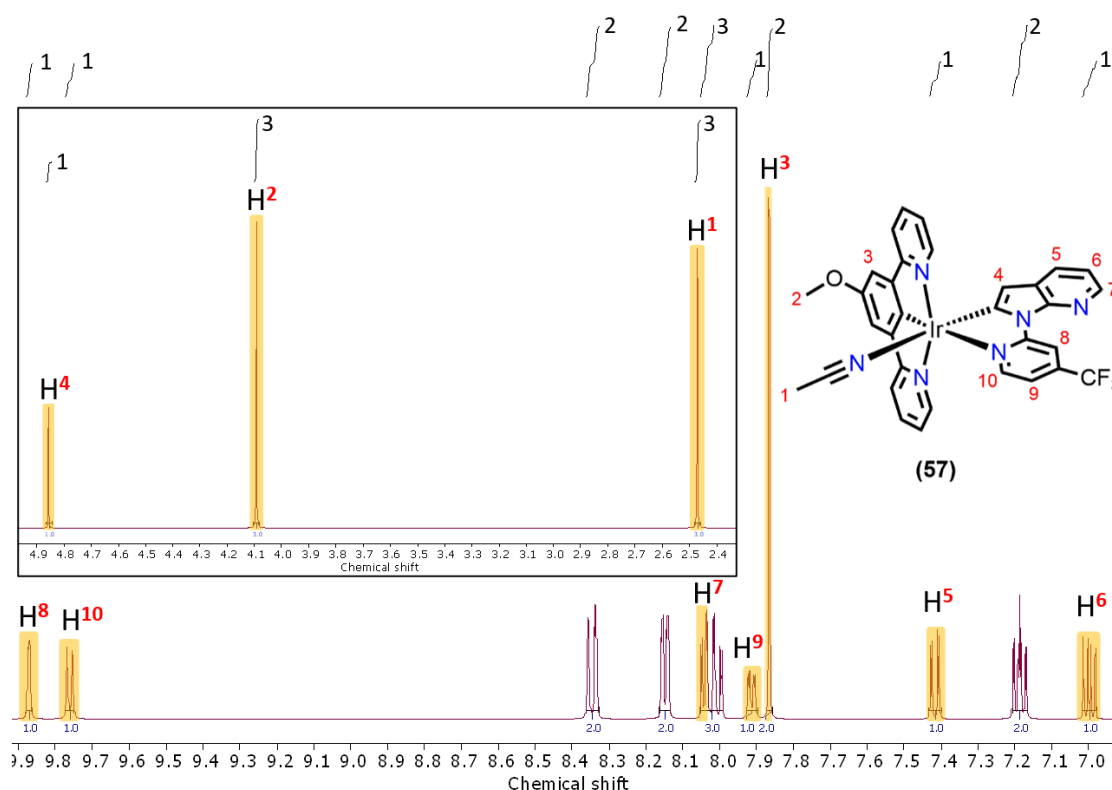


Figure 3.26: ^1H NMR spectrum (aliphatic region shown in boxed insert) of **57** showing the assignment of protons H^{1-10} (highlighted in yellow) which support an $\text{N}^{\wedge}\text{C}$ binding mode of ligand L^6 . Characteristic signals of H^1 and H^4 protons occur at 2.45 and 4.84 ppm respectively.

3.7.2 Crystallography

Crystals of **51** and **52** were prepared by slow evaporation from MeCN (**Figure 3.27**). Selected bond lengths and angles are shown in **Table 3.7**. The bond lengths between iridium and the $\text{N}^{\wedge}\text{C}^{\wedge}\text{N}$ ligand in **51** and **52** are very similar to one another and only differ by a maximum of 0.02 Å. The Ir–Cl bond lengths in both complexes are also nearly identical. The Ir–N bond lengths involving the $\text{N}^{\wedge}\text{N}$ ligand, however, vary significantly between **51** and **52** with **51** having Ir–N bond lengths of 2.00 and 2.27 Å whilst **52** has Ir–N bond lengths of 2.10 and 2.11 Å. In each complex, the bond between Ir and the pyrazolopyridine nitrogen (i.e. N^3) is shorter than the bond involving the pyridine (i.e. N^6). The strong *trans* influence of the cyclometalating phenyl is likely to play a part in dictating the relative ratio of Ir–N bond lengths involving L^{13} . The more imbalanced Ir– N^3 /Ir– N^6 bond length ratio in **51** could suggest that the *trans* influence of the pyrazolo N is stronger than that of the pyridine N.

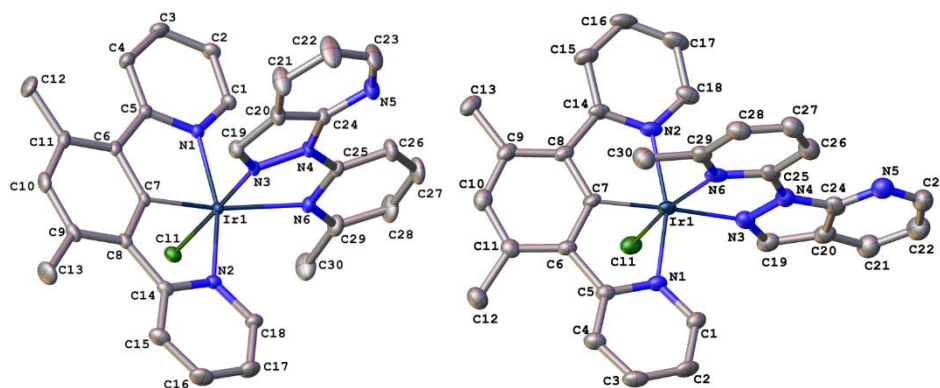


Figure 3.27: Crystal structures of **51** (left) and **52** (right) corresponding to binding modes A and B respectively. The PF_6^- counter-ion is omitted for clarity.

Table 3.7: Selected bond lengths and angles for crystal structures **51** and **52**.

Complex	51	52	Complex	51	52
Ir ¹ –C ⁷ bond length / Å	1.937(2)	1.950(5)	N ¹ –Ir ¹ –N ² bond angle / °	162.01(7)	160.44(2)
Ir ¹ –N ¹ bond length / Å	2.052(2)	2.054(4)	N ¹ –Ir ¹ –C ⁷ bond angle / °	81.22(7)	80.59(2)
Ir ¹ –N ² bond length / Å	2.039(2)	2.057(4)	C ⁷ –Ir ¹ –N ² bond angle / °	80.79(7)	79.96(2)
Ir ¹ –N ³ bond length / Å	1.999(2)	2.102(4)	N ³ –Ir ¹ –N ⁶ bond angle / °	76.14(6)	77.66(2)
Ir ¹ –N ⁶ bond length / Å	2.268(4)	2.106(4)	N ³ –Ir ¹ –C ⁷ bond angle / °	92.29(7)	174.58(2)
Ir ¹ –Cl ¹ bond length / Å	2.353(2)	2.333(1)	N ⁶ –Ir ¹ –Cl ¹ bond angle / °	104.84(5)	166.78(1)

Ir(III) occupies a distorted octahedral geometry in both complexes due to the constraints enforced by the binding of the $\text{N}^{\wedge}\text{C}^{\wedge}\text{N}$ ligand. This geometry, proven by the obtuse $\text{N}^{\text{NCN}}\text{--Ir--N}^{\text{NCN}}$ bond angles in **51** and **52** of $\approx 161^\circ$, is typical of both neutral and cationic complexes of tridentate $\text{N}^{\wedge}\text{C}^{\wedge}\text{N}$ chelation in the literature.^{153,193}

X-ray crystallography also confirms the contrasting coordination modes of L^6 in **86** and **57** (**Figure 3.28**). Selected bond lengths and angles are shown in **Table 3.8**. Not only is the coordination mode of L^6 different between the two complexes (i.e. $\text{N}^{\wedge}\text{N}$ vs. $\text{N}^{\wedge}\text{C}$), its orientation with respect to the $\text{N}^{\wedge}\text{C}^{\wedge}\text{N}$ ligand is also reversed i.e. in **86** the azaindole nitrogen is *trans* to the cyclometallating carbon whereas in **57** it is the CF_3 -pyridine nitrogen that is *trans* to the $\text{N}^{\wedge}\text{C}^{\wedge}\text{N}$ -carbon. The change in orientation in **57** occurs due to the strong *trans* influence of the $\text{N}^{\wedge}\text{C}^{\wedge}\text{N}$ ligand for the π -accepting pyridine. As expected, cyclometalation in **57** results in a much shorter Ir–C bond (1.98 Å) than the corresponding Ir–N bond in **86** (2.15 Å).

X-ray crystallography confirms that the orientation of the azaindole ligand L^2 in **58** matches that of **86** but in this instance, no $\text{N}^{\wedge}\text{C}$ binding occurs in MeCN solution. We speculate that the preference of $\text{N}^{\wedge}\text{C}$ binding in **57** is favoured by the CF_3 -pyridine substituent which could increase the acidity of the indole ring.

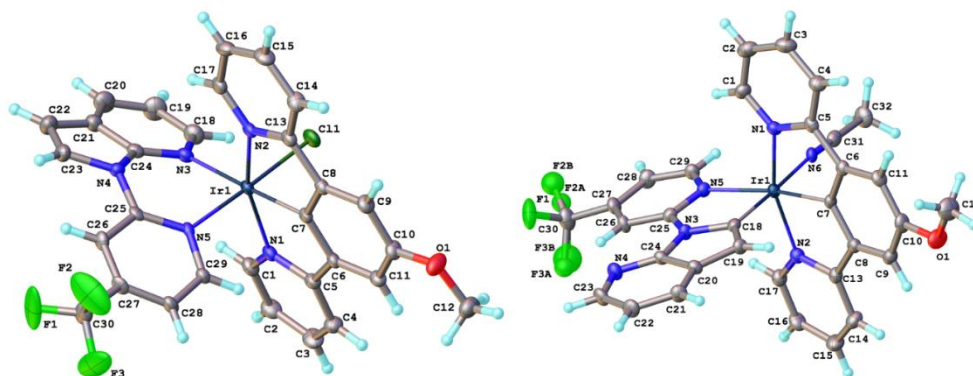


Figure 3.28: Crystal structures of **86** (left) and **57** (right) showing the unique $N^{\wedge}C$ binding mode of ligand L^6 . The PF_6^- counter-ion is omitted for clarity.

Table 3.8: Selected bond lengths and angles for crystal structures **86** and **57**.

Complex	86	57	Complex	86	57
Ir ¹ –C ⁷ bond length / Å	1.948(5)	1.947(4)	N ¹ –Ir ¹ –N ² bond angle / °	159.28(2)	158.97(1)
Ir ¹ –N ¹ bond length / Å	2.066(4)	2.066(3)	N ¹ –Ir ¹ –C ⁷ bond angle / °	79.62(2)	79.29(1)
Ir ¹ –N ² bond length / Å	2.079(4)	2.060(3)	C ⁷ –Ir ¹ –N ² bond angle / °	79.89(2)	79.87(1)
C ²⁷ –C ³⁰ bond length / Å	1.504(7)	1.500(6)	N ³ –Ir ¹ –N ⁵ bond angle / °	87.99(2)	-
Ir ¹ –N ⁵ bond length / Å	2.076(4)	2.166(3)	N ³ –Ir ¹ –C ⁷ bond angle / °	177.52(2)	-
Ir ¹ –N ³ bond length / Å	2.149(4)	-	N ⁵ –Ir ¹ –Cl ¹ bond angle / °	178.29(1)	-
Ir ¹ –Cl ¹ bond length / Å	2.325(4)	-	N ⁵ –Ir ¹ –C ⁷ bond angle / °	-	167.81(1)
Ir ¹ –N ⁶ bond length / Å	-	2.106(3)	C ¹⁸ –Ir ¹ –N ⁶ bond angle / °	-	175.36(1)
Ir ¹ –C ¹⁸ bond length / Å	-	1.979(4)	C ¹⁸ –Ir ¹ –N ⁵ bond angle / °	-	78.44(1)

3.7.3 Electrochemistry

The electrochemical properties of **51–58** are shown in **Table 3.9**. Complexes **51–58** have a single quasi-reversible or irreversible oxidation in the window +0.74 to +1.18 V. Based on DFT calculations (section 3.7.4), the oxidation corresponds to loss of an electron from the HOMO which spans the iridium and cyclometalating phenyl ring of the tridentate ligand. The presence of the electron-donating methoxy group on the $N^{\wedge}C^{\wedge}N$ ligands of **53–58** shifts their oxidation to less positive potentials than **51** and **52** in accordance with a destabilization of the HOMO.

Complexes **51–58** display an irreversible reduction between -1.68 and -2.26 V which is likely to be associated with electron transfer processes involving the LUMO, primarily located on the $N^{\wedge}N$ ligand. Complex **57** has the most negative reduction potential of -2.26 V – this is consistent with cyclometallation of the ancillary which would increase electron density on the pyrazolopyridine ring and raise LUMO energy. The second most negative reduction potential of -1.94 V belongs to that of another azaindole-containing complex, **58**. On the other hand, the most negative reduction potential of any pyrazolopyridine-based complex is that of **53/55** (-1.88 V). These findings, which are further corroborated by DFT data, indicate that the LUMOs of **57** and **58** are higher in energy than **51–56**.

The $\Delta E_{1/2}$ values of **51-58** range from 2.68 to 3.04 V. The $\Delta E_{1/2}$ values of the series align with PL emission maxima with the exception of **57** whose $\Delta E_{1/2}$ value of 3.00 V is surprisingly large given its green PL emission (section 3.7.5). Nevertheless, it is important to acknowledge the reduced accuracy to which oxidations and reductions are estimated in this series of complexes as anodic and cathodic peak potentials are measured.

Table 3.9: Electrochemical properties of complexes **51-58** recorded in a 0.1 M electrolyte solution of NBu_4PF_6 in MeCN. Values were measured at a scan rate of 200 mV s^{-1} and are reported relative to SCE, measured using ferrocene as the standard ($E_{1/2}^{\text{ox}} = 0.42 \text{ vs. SCE}$). E_p^{ox} and E_p^{red} are the anodic and cathodic peak potentials respectively. $\Delta E_{1/2} = E_p^{\text{ox}} - E_p^{\text{red}}$. $\Delta E_{\text{H-L}}$ refers to the HOMO-LUMO gap calculated using DFT.

Complex	$E_p^{\text{ox}} / \text{V}$	$E_p^{\text{red}} / \text{V}$	$\Delta E_{1/2} / \text{V}$	$\Delta E_{\text{H-L}} / \text{eV}$
51	+1.18 ^{qr}	-1.80 ^{ir}	2.98	3.28
52	+1.18 ^{qr}	-1.86 ^{ir}	3.04	3.23
53	+0.94 ^{ir}	-1.88 ^{ir}	2.82	2.67
54	+1.00 ^{ir}	-1.68 ^{qr}	2.68	2.83
55	+0.94 ^{ir}	-1.88 ^{ir}	2.82	2.61
56	+0.98 ^{qr}	-1.71 ^{ir}	2.69	2.86
57	+0.74 ^{ir}	-2.26 ^{ir}	3.00	3.34
58	+0.94 ^{ir}	-1.94 ^{ir}	2.88	3.25

3.7.4 DFT

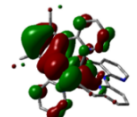
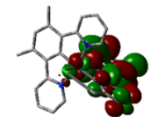
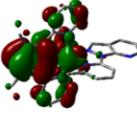
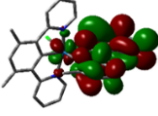
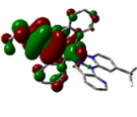
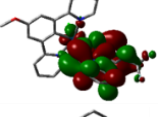
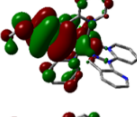
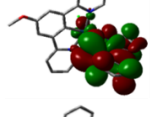
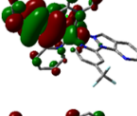
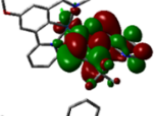
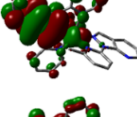
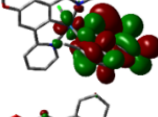
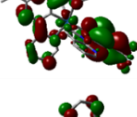
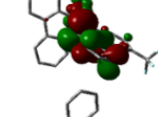
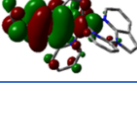
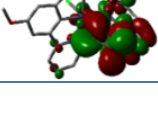
Frontier molecular orbital diagrams of **51-58**, displayed in **Table 3.10**, were obtained by ground state DFT calculations using the B3LYP functional and the LANL2DZ basis set. Throughout the series, the HOMO is located over the iridium and the central phenyl ring of the $\text{N}^{\wedge}\text{C}^{\wedge}\text{N}$ ligand whereas the LUMO encompasses the $\text{N}^{\wedge}\text{N}$ ligand. The exception is **57** whose frontier molecular orbitals both appear to be distributed largely over the $\text{N}^{\wedge}\text{C}$ -coordinated pyrazolopyridine ligand. Additionally, the tridentate ligand makes a small contribution to its HOMO whilst the iridium centre contributes to its LUMO. Consequently, all of the excited state transitions of **51-58** are described as being a mixture of MLCT and LLCT (**Table 3.10**). TD-DFT calculations confirmed the nature of the excited state in **51-58** to be mainly HOMO→LUMO in character (62-70%). The remaining contributions to the excited states of **51-58** occur from +1/-1 and +2/-2 levels of the HOMO and LUMO, with the exception of **57** whose excited state has minor contributions from HOMO-9 (11%) and HOMO-7 (13%) orbitals.

The HOMO-LUMO energy gaps of **51-58** range from 2.60 eV to 3.28 eV. Each pair of isomers possesses similar HOMO and LUMO energies and similar HOMO-LUMO energy gaps with a maximum HOMO-LUMO gap variation of 0.07 eV in the case of **53** and **55**. This result is consistent with electrochemical and photophysical data which reveal similar electrochemical $\Delta E_{1/2}$ values ($\Delta \Delta E_{1/2} = 0.06 \text{ V}$) and PL emission maxima ($\Delta \Delta \lambda_{\text{max}} = 13 \text{ nm}$) between each pair of isomers. The trend in HOMO-LUMO energy gaps between the series, however, does not align with their PL emission, for example, complex **57** has the largest $\Delta E_{\text{H-L}}$ value of 3.34 V despite its green PL emission ($\lambda_{\text{max}} =$

523, 557 nm) which is approximately 40 nm (1580 cm^{-1}) lower in energy than that of the bluest complex, **51** (section 3.7.5).

Complexes **51** and **52** have the most stable HOMO energies of -8.43 eV and -8.34 eV respectively, in agreement with their most anodically-shifted oxidation potentials. Likewise, the most unstable LUMOs are those of **57** and **58** (-4.69 eV and -4.79 eV respectively); this supports their large reduction potentials which are the most negative of the series.

Table 3.10: Calculated S_1 excited state energies and frontier molecular orbital diagrams for complexes **51-58** using DFT and TD-DFT (B3LYP/LANL2DZ).

Complex	HOMO	HOMO Energy /eV	LUMO	LUMO Energy /eV	ΔE_{H-L} /eV	Major Orbital Contribution (%)	Energy		Oscillator Strength	Assignment
							eV	nm		
51		-8.43		-5.15	3.28	HOMO→LUMO (67), HOMO→LUMO+2 (15)	0.98	1260.8	0.0258	Mixed MLCT/LLCT
52		-8.34		-5.11	3.23	HOMO→LUMO (69)	2.59	478.4	0.0019	Mixed MLCT/LLCT
53		-8.25		-5.58	2.67	HOMO→LUMO (70)	2.08	596.8	0.0001	Mixed MLCT/LLCT
54		-8.07		-5.24	2.83	HOMO→LUMO (68), HOMO-1→LUMO (13)	2.70	458.8	0.0304	Mixed MLCT/LLCT
55		-8.23		-5.62	2.61	HOMO→LUMO (67), HOMO→LUMO+1 (11)	2.39	517.9	0.0196	Mixed MLCT/LLCT
56		-7.98		-5.12	2.86	HOMO→LUMO (67), HOMO-1→LUMO (18), HOMO-2→LUMO (12)	2.56	484.5	0.0014	Mixed MLCT/LLCT
57		-8.03		-4.69	3.34	HOMO→LUMO (62), HOMO-9→LUMO (11), HOMO-7→LUMO (13)	1.64	754.3	0.0018	Mixed MLCT/LLCT
58		-8.04		-4.79	3.25	HOM→LUMO (67), HOMO-2→LUMO (13)	2.90	427.5	0.0076	Mixed MLCT/LLCT

3.7.5 Photophysical properties

The photophysical properties of **51-58**, tabulated in **Table 3.11** were recorded at RT in degassed MeCN and at 77 K in EPA.

3.7.5.1 Absorption

Absorption spectra of **51-58** are displayed in **Figure 3.29**. The upper graph shows the profiles of the pyrazolopyridine-containing complexes **51-56**. This includes the two pairs of isomers, **51 & 52** and **53 & 55** which all share similar profiles to one another (**Figure 3.29, upper**). All four complexes have a strong absorption band between 276 nm and 289 nm ($\epsilon \geq 2.4 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$) which can be assigned to the spin-allowed LC $^1\pi-\pi^*$ transitions of both the $\text{N}^{\wedge}\text{C}^{\wedge}\text{N}$ and $\text{N}^{\wedge}\text{N}$ ligands. Within this high energy region, complexes **51** and **52** have identical emission maxima of 276 nm with molar absorptivities of $3 \times 10^4 - 6 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$. The absorption maxima of the other pair of isomers (**53** and **55**), however, are more intense ($\approx 1 \times 10^5 \text{ M}^{-1}\text{cm}^{-1}$) and occur at 282 and 280 nm respectively. Complex **51** is the only one of the series whose profile includes several peaks and shoulders between 245-289 nm in addition to a shoulder at 314 nm which can be assigned to a spin-allowed mixed $^1\text{MLCT}$ and $^1\text{LLCT}$ transition. The profiles of **51/52** and **53/55** differ beyond 380 nm; **51** and **52** have low intensity peaks at 381 and 386 nm ($\approx 1 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$) whilst the peaks of **53** and **55** occur at 417 and 419 nm. These bands correspond to spin-forbidden $^3\text{MLCT}$ and ^3LC transitions.

The profiles of **54** and **56** display broadly similar profiles. Their high-energy LC $^1\pi-\pi^*$ transitions appear as two less-well defined peaks than **53** and **55** occurring between 241-255 nm and 280-289 nm with molar absorptivities of $5 \times 10^4 - 7 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$. Both complexes have a mixed $^1\text{MLCT}$ and $^1\text{LLCT}$ shoulder at ≈ 315 nm and a low intensity $^3\text{MLCT}/^3\text{LC}$ band at 421 and 417 nm respectively ($\epsilon \leq 7.5 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$).

Figure 3.29, lower displays the azaindole-containing complexes **57** and **58**. In **57**, the azaindole ligand cyclometalates via $\text{N}^{\wedge}\text{C}$ coordination whereas the ligand acts as a neutral $\text{N}^{\wedge}\text{N}$ chelator in **58**. The three high-energy ^1LC bands of **57** occur at wavelengths of 234, 272 and 298 nm and are much more intense than the peaks of the other seven complexes with molar absorptivities in excess of $1.5 \times 10^5 \text{ M}^{-1}\text{cm}^{-1}$. On the other hand, **58** displays just the single ^1LC band at 280 nm with a molar absorptivity of roughly $1.1 \times 10^5 \text{ M}^{-1}\text{cm}^{-1}$. Furthermore, both complexes share a low intensity $^3\text{MLCT}/\text{LC } ^3\pi-\pi^*$ band between 419 to 424 nm.

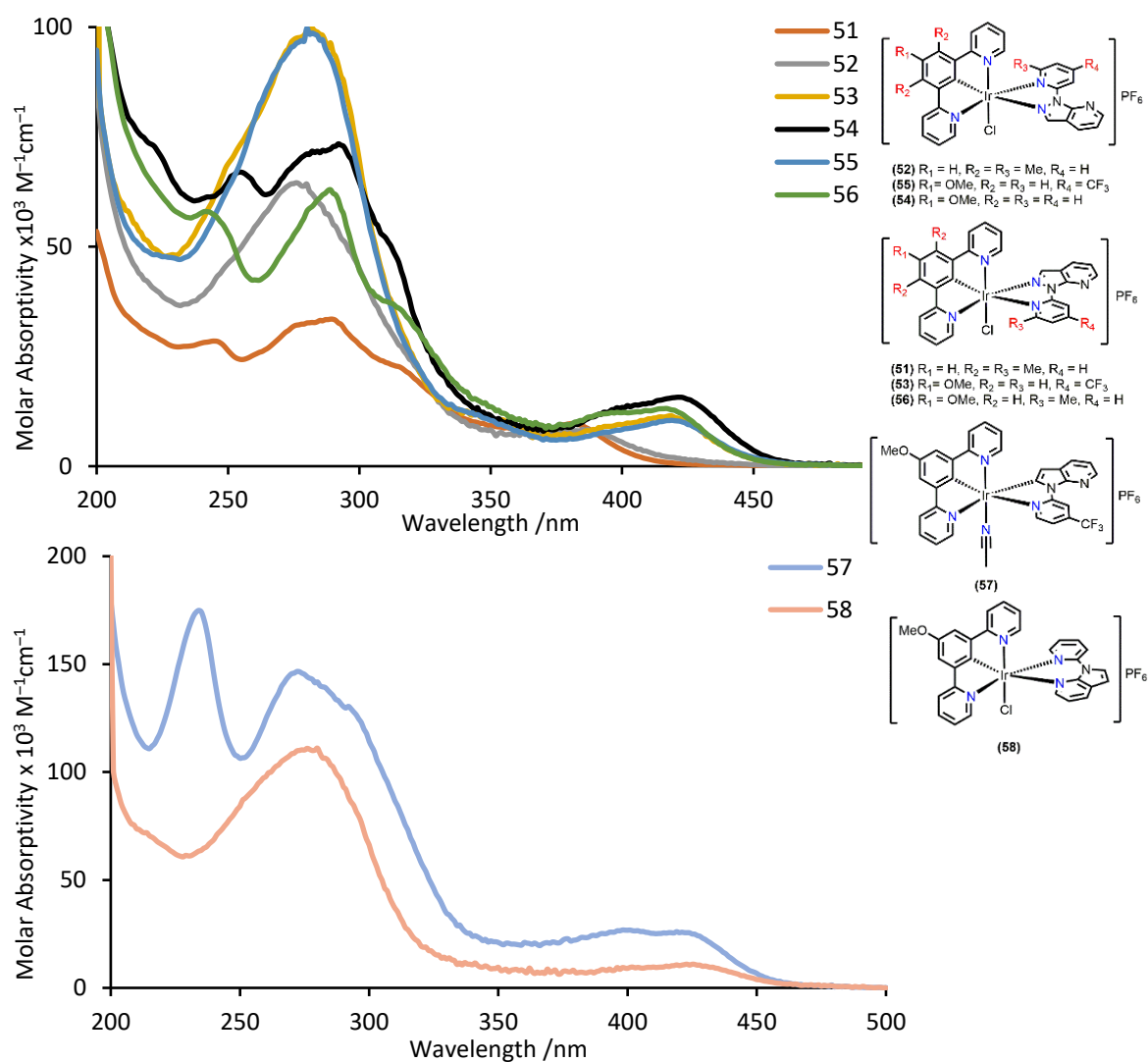


Figure 3.29: Absorbance spectra of complexes **51-56** (upper) and **57** and **58** (lower) in MeCN.

3.7.5.2 Emission

Figure 3.30 displays the RT emission spectra of **52**, **57** and **58** (the emissions of the other five complexes are too weak to be included). There are two distinct peaks in the spectrum of **57** of equal intensity at 523 and 557 nm – this corresponds to green emission. The profiles of **52** and **58** also feature two maxima but the lower energy peak resembles more of a shoulder to the more intense higher energy peak. The higher energy peaks of **52** and **58** occur at 496 and 556 nm respectively which equates to blue-green and green emission.

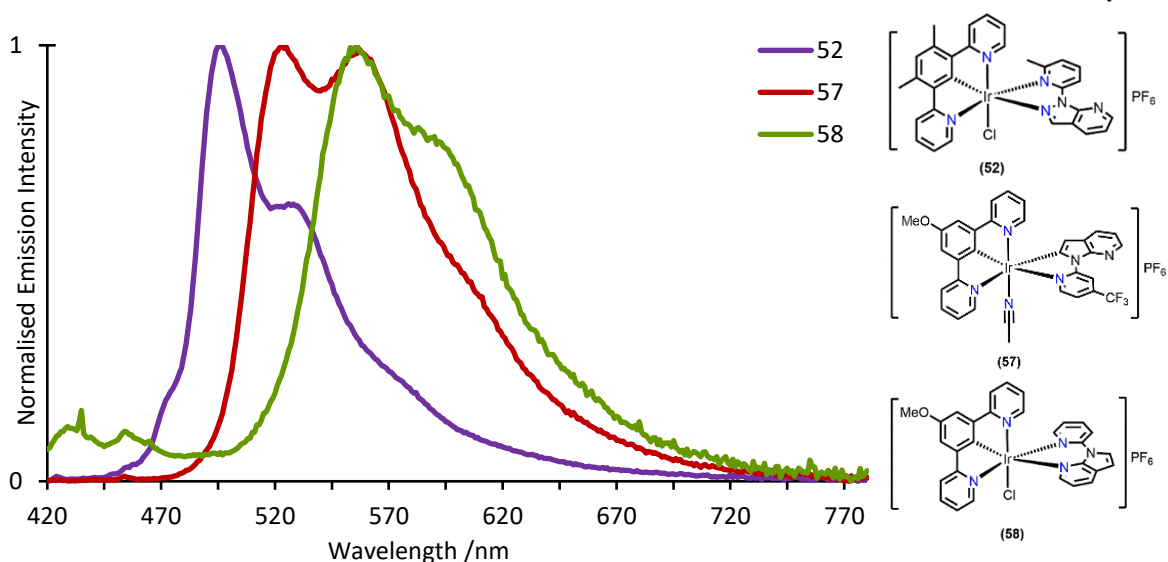


Figure 3.30: Normalised RT emission spectra of **52**, **57** and **58** in degassed MeCN, $\lambda_{exc} = 400$ nm.

Figure 3.31 shows a comparison of the RT and 77 K profiles of **52** and **58**. At low temperature, the emissions of **52** and **58** are raised to higher energies by 13 nm (543 cm^{-1}) and 46 nm (1620 cm^{-1}) respectively; a trend also seen in complex **57** which has been omitted from **Figure 3.31** for clarity. The profiles of **52** and **58** become more vibronically structured at 77 K with the appearance of several peaks due to the increase in rigidity and the suppression of non-radiative decay pathways at low temperature.

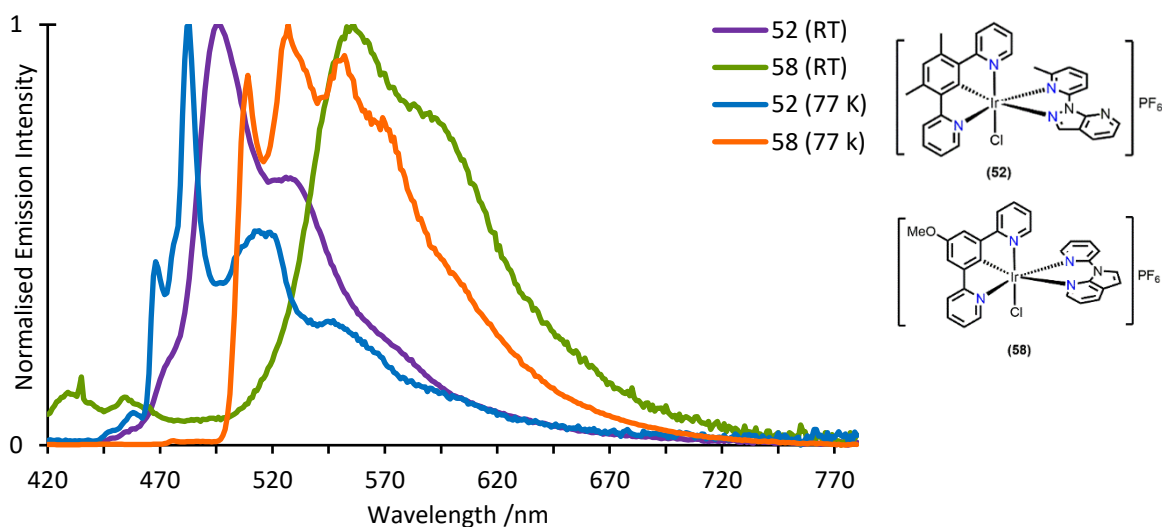


Figure 3.31: Normalised emission spectra of **52** and **58** at RT in degassed MeCN and at 77 K in EPA, $\lambda_{exc} = 400$ nm.

The low temperature emission profiles of **51-57** in EPA are shown in **Figure 3.32**. Whilst complexes **51** and **53-56** were virtually non-emissive at RT, they did emit upon cooling due to the increase in rigidification and the suppression of non-radiative decay pathways which dominated at RT. Despite their structural similarities, the low temperature emission maxima of the isomer pair **51** and **52** differed by 16 nm (709 cm^{-1}) with λ_{max} values of 467 and 483 nm respectively (**Figure 3.32, upper**). Conversely, the 77 K emission maxima of the other isomer pair **53** and **55** only differ by 2 nm (78 cm^{-1}) with λ_{max} values of 506 and 508 nm respectively.

Figure 3.32, lower displays the low temperature emission profiles of **54**, **56** and **57**. The pyrazolopyridine-based complexes, **54** and **56** have closely matching 77 K spectra - both contain a series of three peaks: a high intensity peak between 504 and 511 nm; a subsidiary peak of lower intensity between 547 and 549 nm and a low energy shoulder at 591 and 581 nm respectively. Upon cooling, the emission of complex **57**, which displayed green emission at RT, is blue shifted by 14 nm ($\lambda_{\text{max}} = 509$ vs. 523 nm, $\Delta E = 526 \text{ cm}^{-1}$).

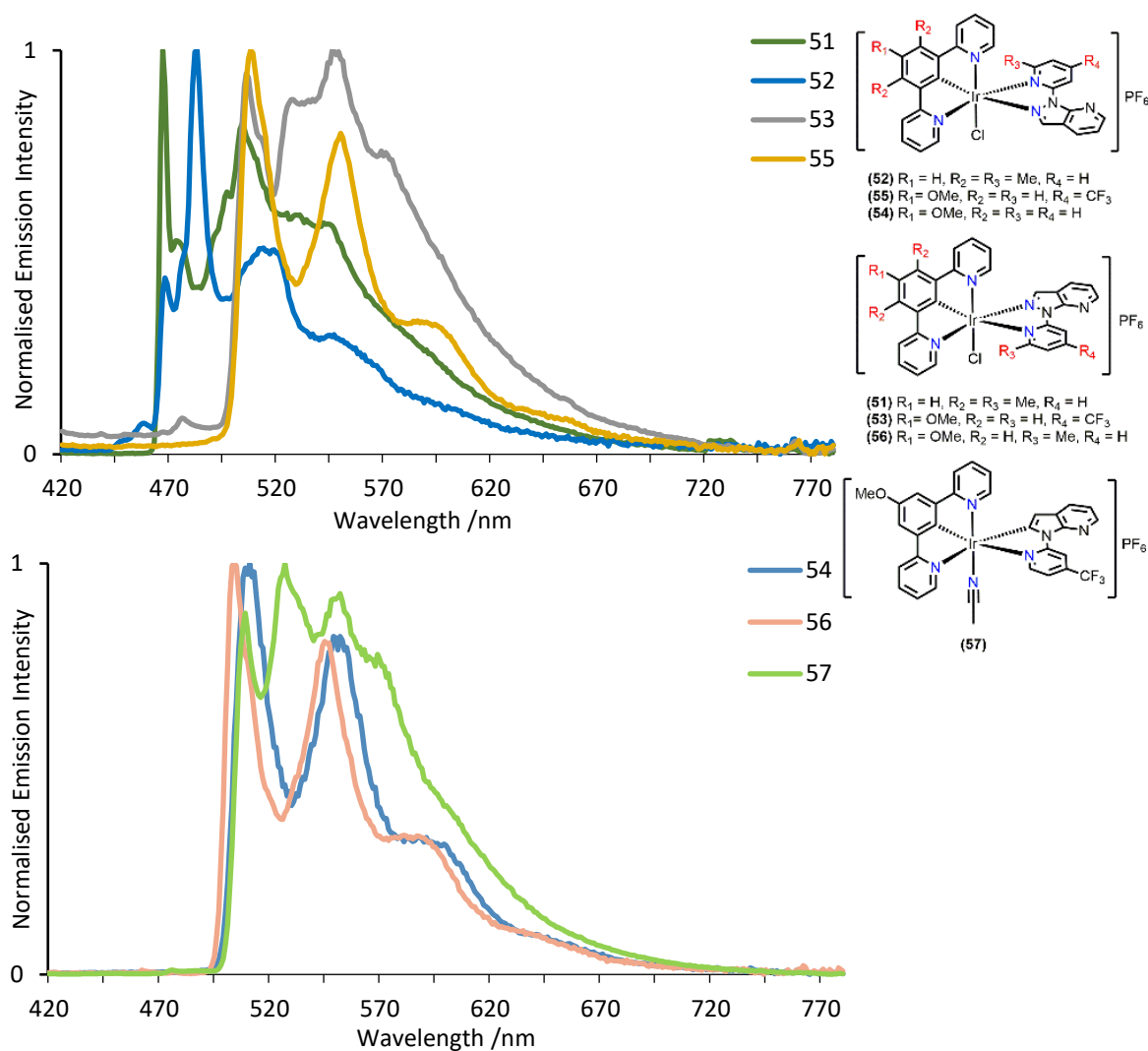


Figure 3.32: Normalised 77 K emission spectra of **51-53** and **55** (upper) and **54**, **56** and **57** (lower) in EPA, $\lambda_{\text{exc}} = 400 \text{ nm}$.

Photophysical properties of **51-58** recorded in degassed MeCN at RT and in EPA or butyronitrile at 77 K are shown in **Table 3.11**. Complex **52** has the highest quantum yield of the series at 5%. This is followed by **57** with a PLQY of 3%. The quantum yields of the remaining six complexes are below 2%. The high quantum yields of **52** and **57** are due to their higher radiative decay rates ($k_r = 3.4 \times 10^5 \text{ s}^{-1}$ and $3.7 \times 10^5 \text{ s}^{-1}$ respectively) which are approximately an order of magnitude larger than the k_r values of the rest of the series. Their non-radiative decay rate constants, however, are in line with the k_{nr} values of the other complexes ($k_{nr} = 3.8 \times 10^6 \text{ s}^{-1}$ to $21 \times 10^6 \text{ s}^{-1}$). The performance of the series **51-58** is inferior to the few $[\text{Ir}(\text{N}^{\wedge}\text{C}^{\wedge}\text{N})(\text{N}^{\wedge}\text{N})\text{Cl}]\text{PF}_6$ -type complexes reported in the literature whose PLQYs typically exceed 20%.¹⁵³

The RT lifetimes of **51-58** range from 0.5 to 2.6 μs , similar to complexes prepared by Whittle and Brulatti.^{153,193} At low temperature, **51-58** have significantly longer lifetimes than at RT (2 to 11 μs) due to the increase in rigidity and the suppression of deactivating non-radiative decay pathways. Complex **54** has the biggest increase between its 77 K and RT lifetime by 9 μs .

Table 3.11: Photophysical properties of complexes **51-58** recorded in degassed MeCN at RT, $\lambda_{\text{exc}} = 400 \text{ nm}$. Photophysical properties at 77 K recorded in EPA, $\lambda_{\text{exc}} = 400 \text{ nm}$, ^a = butyronitrile solvent. Aerated PLQYs and lifetimes are shown in brackets.

Complex	51	52	53	54 ^a
Absorption Maxima /nm ($\epsilon / \text{M}^{-1} \text{cm}^{-1}$)	245 (34300)	276 (24000)	282 (81700)	223 (34200)
	276 (38600)	386 (3550)	417 (9620)	255 (31900)
	289 (40300)	469 (368)		280 (33900)
	314 (27400)			292 (35000)
	381 (11700)			314 (22700)
	436 (477)			421 (7480)
	468 (148)			
$\lambda_{\text{max}} / \text{nm}$	483, 515	496, 526	497, 530	561
PLQY /% degassed (aerated)	0.1 (0.1)	5.1 (0.3)	0.2 (0.1)	0.2 (0.1)
Lifetime /ns degassed (aerated)	1140 (53)	1490 (39)	1710 (19)	1780 (47)
$k_r \times 10^5 \text{ s}^{-1}$	0.13	3.38	0.11	0.09
$k_{nr} \times 10^5 \text{ s}^{-1}$	88	64	58	56
77 K $\lambda_{\text{max}} / \text{nm}$	467, 504	483, 514	506, 546	511, 549
77 K Lifetime / μs	3.4	2.9	3.7	11.0

Complex	55	56	57	58
Absorption Maxima /nm ($\epsilon / \text{M}^{-1} \text{cm}^{-1}$)	280 (76600)	241 (39400)	234 (82100)	280 (43400)
	419 (8020)	289 (42700)	272 (86900)	399 (3460)
		315 (24400)	298 (61300)	424 (4180)
		417 (8920)	398 (12600)	
		478 (129)	419 (12200)	
$\lambda_{\text{max}} / \text{nm}$	499, 533	564	523, 557	556
PLQY /% degassed (aerated)	0.1 (0.1)	0.1 (0.1)	3.4 (0.3)	1.6 (0.2)
Lifetime /ns degassed (aerated)	488 (62)	2640 (50)	939 (77)	1990 (51)
$k_r \times 10^5 \text{ s}^{-1}$	0.24	0.03	3.66	0.78
$k_{nr} \times 10^5 \text{ s}^{-1}$	205	38	103	49
77 K $\lambda_{\text{max}} / \text{nm}$	508, 550	504, 547	509, 527, 552	510, 536, 578
77 K Lifetime / μs	2.2	7.1	10.8	3.7

The labile chloride ligand is likely to be a contributing factor to the low PLQYs of the asymmetric series, as well as the symmetric non-metathesized complexes.²¹⁷ Unfortunately, it was not straightforward to synthesize and purify **51-58** on a large enough scale to attempt the metathesis. Furthermore, racemisation was likely to occur during the reaction which would have made the purification of an already low-yielding reaction difficult.

3.8 Summary

In summary, a total of 20 novel iridium(III) complexes of the type $[\text{Ir}(\text{N}^{\wedge}\text{C}^{\wedge}\text{N})(\text{N}^{\wedge}\text{N})\text{Cl}]\text{PF}_6$ have been prepared and their photophysical properties have been fully characterised. The symmetric series **35-46** feature either bpy, dmbpy, dmobpy or phen as the bidentate $\text{N}^{\wedge}\text{N}$ ligand and have PL emission maxima ranging from 498 to 625 nm. Colour tuning has been achieved by changing the identity of

the N[^]N ligand and by altering the substituent(s) attached to the central N[^]C[^]N phenyl (i.e. Me, OMe or Br) thereby independently changing the HOMO and LUMO energies. The maximum solution-state PLQY achieved for the symmetric series is 6% which is far inferior to the quantum yields of equivalent tris-bidentate complexes such as those reported in Chapter 2. Nevertheless, the low quantum yields of **35-46** are consistent with the performances of [Ir(N[^]C[^]N)(N[^]N)Cl]PF₆-type complexes found in the literature.^{153,193} The benefits to PL of the increased rigidity offered by the tridentate ligand could be more prominent in the solid-state where the number of quenching interactions is reduced.

Although chloride metathesis in neutral tridentate iridium complexes has been reported,^{153,184,191,192,194,196,197} we present the first four examples of metathesized cationic complexes featuring cyanide or phenylacetylide ligands. The procedure involves a 3 day 150°C reflux of the chloride complex in DMF with either AgCN or phenylacetylene. A DIPA base and CuI catalyst are required for acetylene metathesis as stated in the literature. Harsh reactions conditions are necessary to overcome the high activation barrier to the transition state which will involve partial removal of the chloride ligand from an already positively charged complex. Quantum yields of the cyanide- and phenylacetylide-containing complexes **47-50** are up to 2% higher than their chloride analogues **41** and **42**, but the quantum yields of **47-50** are still far inferior to the performances of previously reported uncharged metathesized complexes of the type Ir(N[^]C[^]N)(C[^]N)X, (X ≠ Cl).^{184,191,192,194,196,197} Metathesis of the chloride ligand with cyanide blue shifts emission whilst metathesis with phenylacetylene lowers the emission energy, in agreement with related literature.^{184,191,192,194,196,197} Metathesis induces a larger change in the energy of the HOMO than the energy of the LUMO.

A total of eight tridentate complexes featuring pyrazolopyridine- and azaindole-based ligands have also been synthesized. The reaction generates two structural isomers due to the asymmetric nature of the N[^]N ligand; the isomers differ in whether the pyrazolopyridine/azaindole ring is *trans* to the cyclometalating carbon or *trans* to the chloride. Separation/purification of the isomer(s) has been successful by column chromatography and/or recrystallization. NMR analysis reveals a preference for the pyrazolopyridine ligands to bind with either the pyridine, pyrimidine or isoquinoline ring *trans* to the cyclometalating carbon. Isomers generally have similar electrochemical and photophysical properties, but PL emission maxima can differ by up to 13 nm (543 cm⁻¹) at RT i.e. **51** and **52**. The solution-state photophysical properties of **51-58** are no better than those of **35-50**.

Chapter 4 – Platinum and Iridium complexes featuring tetradentate ligands

4.1 Introduction

This chapter will cover tetradentate complexes of platinum and iridium. The progression from bi- to tri- to tetra-coordinating ligands mirrors that of some endeavour in the field by others, as researchers have sought to develop improved phosphorescent emitters by employing more rigid complexes. The thinking defining the strategy is that the increased structural rigidity provided by higher coordinating ligands, such as tetradentate chelates, could further suppress distortion in the excited state and lead to further reduction in non-radiative decay pathways.

4.2 Platinum complexes containing tetradentate ligands

The tendency of d^8 transition metal ions to form square planar geometries makes them well suited to forming complexes with tetradentate ligands that can coordinate in a planar manner. The large spin-orbit coupling constant of platinum and the square planar geometry of its +2 oxidation state have led to the design of several cyclometalated Pt(II) complexes with tetradentate ligands, some of which show excellent phosphorescence properties.²¹⁸ Indeed the excellent photophysical properties of such Pt(II) species have been exploited recently in OLEDs to create devices with high efficiency and stability, as detailed in reviews by Li and Wang.^{219,220}

The reasons for developing cyclometalated tetradentate platinum complexes stem from the poor photophysical properties and thermal stabilities of some bis-bidentate cyclometalated complexes. For example, *cis*-Pt(ppy)₂ (**Figure 4.1**) is virtually non-emissive at RT and its lack of phosphorescence is attributed partly to the flexibility of the planes of the two bidentate ligands relative to one another.⁸ A simple solution is to link the two bidentate ligands together to form a tetradentate ligand – this should increase both the thermal stability of the molecules and the rigidity of the structure. The two bidentate halves can be linked directly to form a 5-membered central chelate ring,^{221,222} for example, phen or bpy directly link the two O[^]N halves of complexes (i) and (ii) (**Figure 4.1**). These two O[^]N[^]N[^]O salen-like complexes, reported by Che in 2003, were amongst the first examples of Pt(II) complexes containing tetradentate ligands. Complexes (i) and (ii) were yellow-orange emitters in DCM solution and had PLQYs of 12% and 60%.²²³ In a more recent strategy, the bidentate halves of a tetradentate ligand are linked indirectly via a carbon, oxygen or nitrogen-based group to form a larger 6-membered chelate (**Figure 4.2**). Carbon-based linking groups include a simple aliphatic CH₂ chain,^{224,225} a carbonyl group²²⁶ or a quaternary carbon centre.^{227–230} These complexes, as well as other N– and O–linked tetradentate complexes, are discussed in detail in the excellent 2016 review by Che and co-workers.⁵ Here, we shall focus only on recently published or

relevant Pt(II) complexes containing carbon and nitrogen ligating atoms. The reader is referred to other sources for oxygen-coordinating tetradentate Pt(II) complexes.²³¹

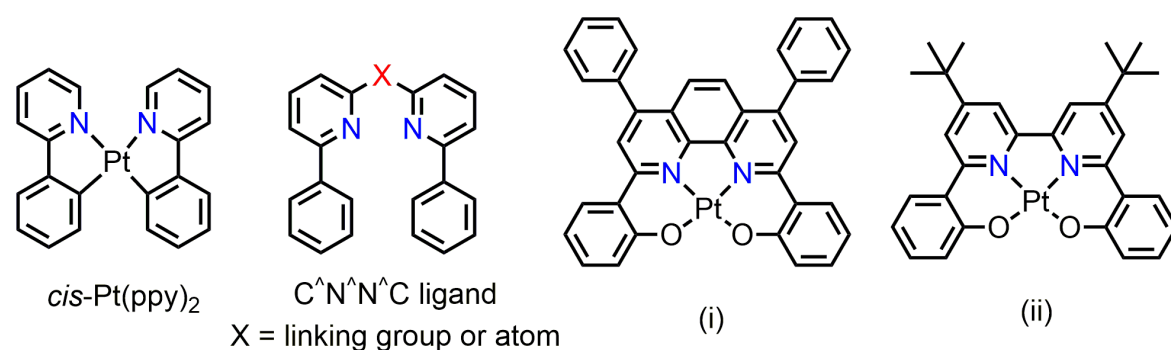


Figure 4.1: Structure of *cis*-Pt(ppy)₂, non-emissive at RT (far-left). Structure of a tetradentate C^NN^NC ligand whose bidentate side arms are linked via a group or atom denoted X (second from left). Structures of two Pt(II) complexes (i) and (ii) containing tetradentate ligands as reported by Che in 2003 (right and far-right).

The photophysical properties of Pt(II) tetradentate complexes of the types N^{232,233,242,243,234–241}C²⁴⁴C²⁴⁴N²⁴⁴ with an oxygen atom linker have been extensively investigated and a selection of recently published high-performing oxygen-linked Pt(II) complexes are shown in **Figure 4.2**. The structures of (iii) to (xi) are very similar as they all contain the same N^{232,233,242,243,234–241}C²⁴⁴C²⁴⁴N²⁴⁴-core consisting of a terminal pyridine group, a carbazole group and an O-linked phenyl group. All of the ligands are synthesized via a Cu^I-catalysed C–O cross-coupling of a phenol derivative and a 2-bromo-9-(pyridin-2-yl)-9*H*-carbazole derivative in DMSO with picolinic acid and K₃PO₄ as a base. The complexes differ only in the identity of the terminal *N*-heterocyclic ring and the choice of substituents. Increasing the degree of methylation from (iii) to (v) has no effect on PL emission as all three complexes are deep blue emitters with solution-state λ_{max} values of 450±1 nm. Increasing the degree of methylation from (iii) to (v) does not significantly alter quantum yield either but a decrease in lifetime is observed from 12.7 to 9.0 μs.²³²

Li *et al.* synthesized (vi) to (viii) to investigate the effect of the pyridine substituent on PL performance. The PL emission maxima of (vi) and (vii) are 442 and 444 nm respectively which represents a 5-7 nm ($251\text{-}353\text{ cm}^{-1}$) blue shift with respect to (v).²³² DFT calculations reveal that the LUMO is almost exclusively located on the pyridine ring so the hypsochromic shift of (vi) and (vii) is a result of the increased LUMO destabilization that the strongly electron-donating -NMe_2 and $\text{-}^t\text{Bu}$ substituents induce relative to the methyl group of (v). On the other hand, (viii) has bathochromic PL emission compared to (v)-(vii) due to the presence of the electron-withdrawing carbazolyl group which stabilizes the LUMO to produce an emission maximum of 496 nm. The PLQYs of (vi), (vii) and (viii) are 80%, 95% and 53% respectively.²³⁸ Zhang and co-workers reported solution-state quantum yields of 100% in a series of Pt(II) complexes containing terminal 1,2,3-triazole fragments. Complexes (ix) to (xi) are blue-green emitters with emission maxima in the range of 484 to 493 nm.

Yellow, orange and red emission was achieved by substituting the triazole unit with different O-, S- and N-heterocyclic rings such as ozazole and isoquinoline.²⁴⁰

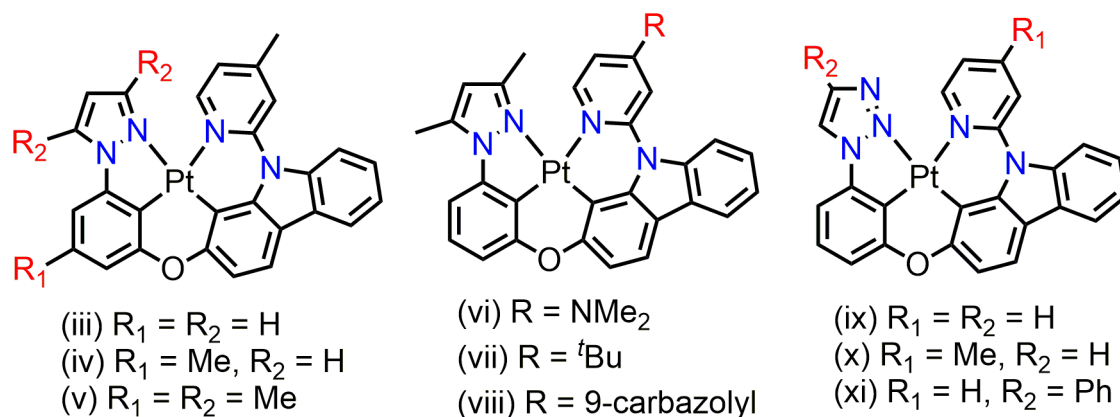


Figure 4.2: Structures of some recently published Pt(II) complexes, (iii)-(xi), containing oxygen-linked $N^C^C^N$ -based tetradentate ligands.

4.2.1 N-linked $C^N^N^C$ -type Pt(II) complexes

Amine-linked tetradentate ligands are typically synthesized via Buchwald-Hartwig aminations. The nitrogen linker could be part of a fused ring system such as a carbazole,^{245–249} or it could be a tertiary amine such as the examples shown in **Figure 4.3**. The corresponding photophysical data for these complexes are shown in **Table 4.1**. The majority of complexes in **Figure 4.3** have the $C^N^N^C$ mode of coordination. The 4-methoxy-substituted complex, **C**, has the highest quantum yield of 78% and the quantum yields of **A**, **B**, **J** and **O** also surpass 70% which is interesting given the structural simplicity of **A–C** in particular. The PL emissions of **A–K** are fairly similar because these complexes differ only in the substituents attached to *p*-anisidine or to the terminal phenyl rings. The highest energy emission peaks of **A–L** occur within a narrow 25 nm range (488–513 nm) but some complexes have one or more lower energy shoulders at wavelengths as long as 662 nm in the case of **D**. Analysis of **H–K** shows that increasing the fluorine content of bidentate side arms blue shifts emission sequentially by 9–10 nm from ppy to fppy to dfppy. However, increasing the fluorine content beyond dfppy actually results in red shifted emission as demonstrated by the PL of **K**, containing the triple-fluorinated ppy units (tfppy), whose λ_{max} of 496 nm is 7 nm (289 cm^{-1}) red shifted compared to the emission maximum of **J**.²⁵⁰ A similar bathochromic shift is observed between the emissions of phosphinate-based iridium complexes with dfppy²⁵¹ and tfppy²⁵² cyclometalating ligands whose RT emission maxima in DCM solution are 485 and 499 nm respectively. Emission is shifted from green ($\lambda_{max} = 512, 548\text{ nm}$) to yellow-orange through the use of naphthalene and thiophene groups respectively, as demonstrated by the emission maxima of the naphthyl-containing complex **M**, $\lambda_{max} = 535, 580\text{ nm}$ and the thiophene-based complex **O**, $\lambda_{max} = 579, 599\text{ nm}$. Extending the conjugation of the thiophene moiety by introduction of benzothiophene units shifts emission further into the red as shown by the 635 nm emission

maximum of **P**. Substitution of thiophene with benzothiophene, however, reduces the quantum yield dramatically from 74% to 4%. Complex **X** contains two bpy-based side arms but the relative positions of the bpy nitrogen atoms prevent the ligand from acting as an N[^]N[^]N[^]N-type chelator. The 2,3-bpy units still bind in an N[^]C fashion and the effect of the cyclometalating pyridine is to blue shift emission by 14 nm (603 cm⁻¹) to $\lambda_{\text{max}} = 475$ nm, reduce quantum yield by 65% to $\phi = 10\%$ and lengthen luminescence lifetime from 1 to 27 μs , compared to the dfppy analogue, **J**. The 27 μs RT lifetime of **X** is one of the longest lifetimes in the series. These findings can be attributed to a reduced ³MLCT character of **X** compared to **J**.²⁵³

4.2.2 N-linked N[^]C[^]C[^]N-type Pt(II) complexes

Figure 4.3 includes seven Pt(II) complexes with the N[^]C[^]C[^]N coordination pattern; these are complexes **Q** and **S-X**. Analysis of **Q**, **S** and **T** demonstrates the effect of changing the substituent attached to the non-Pt-bound phenyl ring. The 3,5-di-*tert*-butyl-substituted (**T**) and 4-OC₆H₁₃-substituted complexes (**Q**) have impressive quantum yields of 58% and 50% respectively; this represents an increase of roughly 40% compared to the PLQY of the unsubstituted complex **S**, ($\phi = 14\%$). Functionalisation of the non-Pt-bound phenyl ring only results in a slight bathochromic shift of up to 14 nm (364 cm⁻¹) as **Q**, **S** and **T** are all red-emitters with λ_{max} between 613 and 627 nm. The comparison of **S** with **U** reveals that the replacement of the terminal pyridines by pyrazole units is sufficient to blue shift emission by over 130 nm (4350 cm⁻¹) from $\lambda_{\text{max}} = 613$ to 484 nm. A concurrent increase in PLQY to 56% is also observed due to the increased efficiency of emission as dictated by the energy-gap law. Double methylation of the pyrazole ring in **W** raises the PLQY even higher to 63% with a negligible alteration to PL emission energy.⁷

Table 4.1: Photophysical properties of Pt(II) complexes **A-Z** containing tetradentate ligands shown in **Figure 4.3**, measured in degassed DCM or MeCN at RT, ^{sh} = shoulder.

Reference	Complex	$\lambda_{\max}^{\text{abs}}/\text{nm}$ ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$)	$\lambda_{\max}^{\text{em}}/\text{nm}$	PLQY /%	$\tau/\mu\text{s}$	$K_r \times 10^4 \text{ s}^{-1}$	$K_{nr} \times 10^4 \text{ s}^{-1}$
7	A	324 (25229), 342 (26272), 384 (4903), 407 (5969)	512, 548	74	7.6	-	-
7	B	268 (29196), 329 (18970), 387 (3891)	488, 523	75	11	-	-
254	C	272 (72400), 289 (57500), 323 (34600), 337 (38900), 363 (24500), 399 (7580)	506, 541, 588 ^{sh}	78	8.3	9.4	12
152	D	230 (15990), 267 (16300), 330 (8250), 343 (2060)	488, 523, 559, 662 ^{sh}	46	11	4.1	4.8
255	E	268 (12000), 335 (11000)	508, 544, 580	1.5	0.55	-	-
255	F	268 (15200), 388 (2800)	500, 534, 570	1.8	0.48	-	-
255	G	261 (18500), 336 (15200)	490, 525, 651	4.4	0.78	-	-
256	H	-	508	30	5.6	-	-
256	I	-	499	39	1.0	-	-
253	J	235 (33000), 266 (44000), 325 (24000)	489	75	1.3	5.7	1.9
256	K	-	496	46	1.7	-	-
257	L	270, 317, 360, 417	513, 546 ^{sh}	27	2.0	-	-
254	M	257 (75900), 309 (38900), 349 (25900), 397 (6370)	535, 580	12	60	0.2	1.5
254	O	252 (45700), 283 (74100), 325 (38900), 359 (34600), 378 (40700), 424 (6700), 468 (3800)	579, 599, 706 ^{sh}	74	15	4.9	1.8
254	P	358, 383, 443	635	4	5.9	0.68	1.6
258	Q	335, 399, $\approx$ 410-560	627, 675	50	5.8	0.85	0.87
152	R	303 (14560), 312 (17964), 369 (20349)	520, 548	33	19	0.02	3.6
7	S	274 (28553), 324 (17411), 338 (17435), 409 (9656), 507 (1350)	613	14	7.6	-	-
259	T	-	621	58	5.5	10	8
7	U	302 (24401), 335 (16243), 351 (28521), 370 (8493), 421 (3367), 442 (2880)	484, 512	56	4.9	-	-
7	V	304 (21396), 334 (10307), 348 (13294), 365 (5021), 408 (1656), 428 (1401)	474	37	3.4	-	-
7	W	307 (28076), 342 (10328), 357 (18193), 376 (4722), 428 (1835), 451 (1560)	488, 516	63	5.7	-	-
253	X	258 (41000), 281 (28000), 341 (20000)	475	10	27	0.037	0.33
260	Y	261 (27300), 392 (10300), 418 (8500), 519 (2300)	660	< 1	0.85	-	-
260	Z	260 (26500), 371 (12900), 456 (2700)	555	17	4.4	-	-

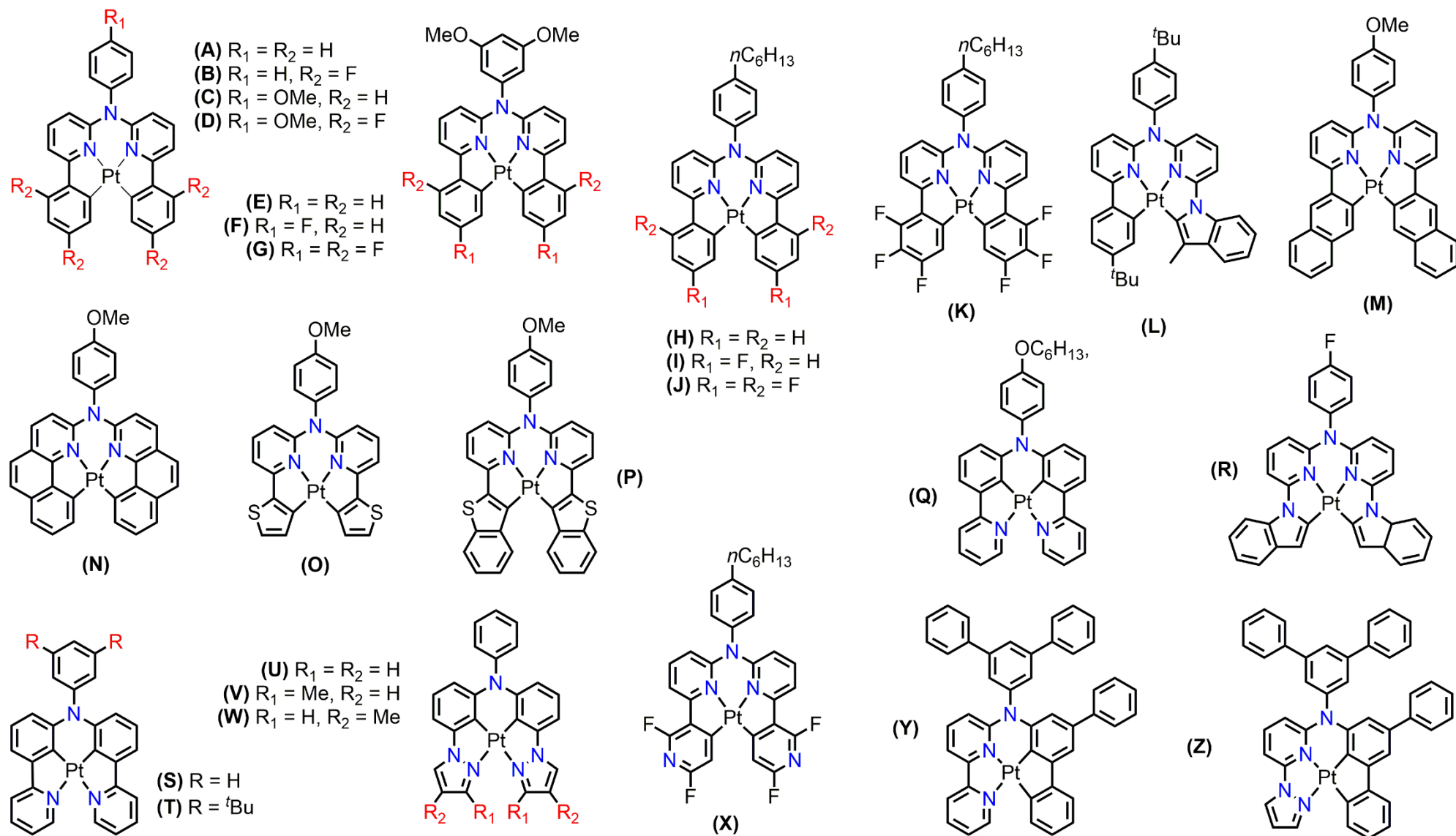


Figure 4.3: Structures of Pt(II) complexes **A-Z** containing tetradentate ligands.

4.2.3 N-linked N[^]N[^]C[^]C-type Pt(II) complexes

Huo's initial attempts at achieving N[^]N[^]C[^]C coordinated Pt(II) using the standard acetic acid reflux conditions failed. Instead of the C[^]C[^]N[^]N tetradentate complex, his team obtained the tridentate Pt(N[^]N[^]C)Cl complex in a 65% yield (**Figure 4.4**). In an attempt to force double cyclometalation, they modified the ligand design to include two *m*-phenylbenzene groups and in this way they were able to produce two Pt(C[^]C[^]N[^]N)-type complexes **Y** and **Z** (**Figure 4.3**) in yields of 38% and 22% respectively after a week-long reflux of the ligand and K₂PtCl₄ in MeCN. The conversion rate was very slow but the reaction was accelerated to some extent by addition of the phase transfer catalyst NBu₄Cl. This mode of coordination offered no advantages over the other types of coordination mentioned above as **Z** had only a moderate PLQY of 17% and **Y** had a much lower quantum yield of less than 1%.²⁶⁰ The quantum efficiencies of **Y** and **Z** appear to be dictated by the energy gap law as **Y** is a deep red emitter in solution at RT ($\lambda_{\text{max}} = 600 \text{ nm}$, $\phi = 0.1\%$) whereas **Z** is a bright yellow emitter ($\lambda_{\text{max}} = 550 \text{ nm}$, $\phi = 17\%$).²⁶⁰

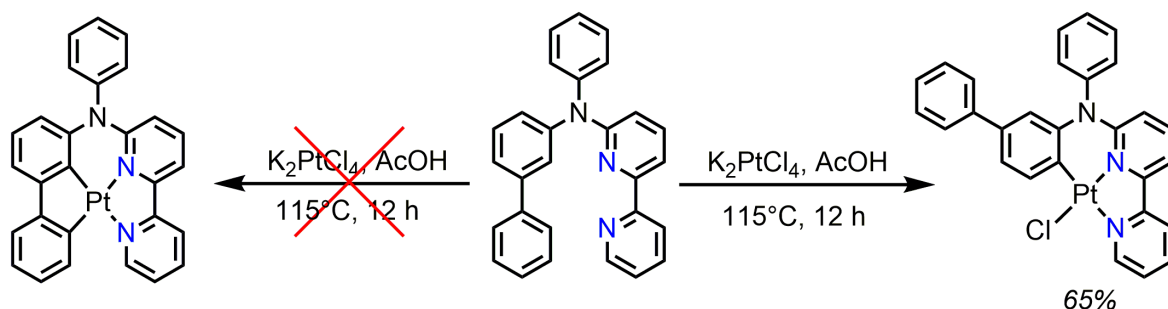


Figure 4.4: Failed attempt at N[^]N[^]C[^]C coordination of platinum(II); the Pt(N[^]N[^]C)Cl complex formed instead in a 65% yield. Introduction of additional phenyl rings led to the desired coordination mode, as in **Y** and **Z** (**Figure 4.3**).

4.3 Iridium complexes containing tetradentate ligands

Iridium(III) complexes containing tetradentate ligands are not uncommon in the field of catalysis. For example, several groups have reported iridium complexes featuring S[−]^{261,262}, Si[−]^{262,263}, P[−]^{264–266} and O[−]²⁶⁶ donating tetradentate ligands and N[^]N[^]N[^]N-type macrocyclic ligands.^{267–270} To date, however, only four journal articles discuss tetradentate Ir(III) complexes in the context of luminescence. Most of the complexes from these four papers are shown in **Figure 4.5** and their photophysical properties are detailed in **Table 4.2**.

In 2017, Chen *et al.* synthesized a family of iridium complexes supported by a tetradentate trianionic O[^]N[^]C[^]O ligand scaffold which include complexes **A–F**. These six complexes are moderately phosphorescent in solution and in PMMA film; **A** has the highest quantum yield of 18% in degassed DCM whereas **E** has the highest quantum yield of 51% in PMMA film. The emissions of **A–C** and **D–F** range between 597–631 nm and 586–626 nm respectively; the slight blue shift in emission of the latter series of complexes is due to the replacement of the methylated imidazoline

axial ligand with an *N*-heterocyclic carbene. Much larger differences in PL were seen with PPh₃ and pyridazine- or pyridine-derived axial ligands.²⁷¹

Complexes **G** and **H** are very weak blue-green emitters with short lifetimes ($\tau \leq 130$ ns) and low PLQYs ($\phi \leq 1.8\%$) therefore the addition of the *tert*-butyl group in **H** has a negligible effect of PL properties. The analogous complexes in which the N[^]N ligand was replaced with two *cis*-arranged chloride ligands were completely non-emissive, presumably due to the ligand field being too weak.²⁷²

The blue-green emitting complexes **I-L**, synthesized by Xia and co-workers in 2018, contain a dianionic C[^]C[^]C[^]C[^] tetradentate ligand and a cyclometalated ppy group. The 73% quantum yield of **J** in MeTHF solution is impressive, but it is overshadowed by the remarkable solution-state PLQYs of **I**, **K** and **L** which approach unity. Complexes **I-L** have short lifetimes of 1.6-3.9 μ s. The rigidity imposed by the butylene chain of the tetradentate ligand increases quantum efficiency and forces a *cis* arrangement of the NHC moieties. Methyl and fluorine substituents on the ppy ligand both act to blue shift emission by 18 nm (717 cm^{-1}) from $\lambda_{\text{max}} = 510$ to 492 nm for the methylated complexes **K** and **L** and by 37 nm (1530 cm^{-1}) from $\lambda_{\text{max}} = 510$ to 473 nm for the dfppy-complex **J**.²⁷³

Finally, the four blue-green-emitting complexes **M-P** feature an N3C chelating tetradentate ligand. Their emission maxima range from 480 to 504 nm according to the substituents attached to the monodentate N-donating ligand. Non-radiative decay rates of **M-P**, which range between $2.4 \times 10^6\text{ s}^{-1}$ and $9 \times 10^6\text{ s}^{-1}$, are an order of magnitude larger than their corresponding rates of radiative decay.²⁷⁴

Table 4.2: RT photophysical properties of Ir(III) complexes **A-P**, measured in degassed MeCN or DCM, containing tetradentate ligands as shown in **Figure 4.5**

Reference	Complex	$\lambda_{\text{max}}^{\text{abs}} / \text{nm} (\epsilon / \text{M}^{-1}\text{cm}^{-1})$	$\lambda_{\text{max}}^{\text{em}} / \text{nm}$	PLQY / %	$\tau / \mu\text{s}$	$K_r \times 10^4 \text{ s}^{-1}$	$K_{nr} \times 10^4 \text{ s}^{-1}$
271	A	283 (16100), 311 (10800), 354 (13400), 393 (6420), 429 (3070), 500 (1420)	597	18	1.6	-	-
271	B	261 (40800), 283 (29700), 366 (20300), 394 (9980), 438 (3330), 500 (1150)	626	11	0.9	-	-
271	C	266 (45100), 286 (30400), 368 (22800), 404 (9740), 436 (4550), 504 (1770)	631	10	1.0	-	-
271	D	283 (24200), 295 (21600), 339 (14700), 390 (6410), 480 (1150)	586	12	0.5	-	-
271	E	260 (43600), 284 (38800), 356 (18100), 392 (10700), 480 (1540)	613	12	0.4	-	-
271	F	266 (42700), 280 (36900), 307 (18800), 362 (23300), 396 (13800), 480 (1470)	626	6	0.4	-	-
272	G	253 (25300), 266 (25200), 321 (11900)	490	1.8	0.12	-	-
272	H	252 (23900), 264 (22800), 318 (10700)	484	1.4	0.13	-	-
273	I	244 (16500), 272 (24500), 344 (4000), 376 (2600), 402 (2100), 444 (1100)	510	≈100	3.9	26	-
273	J	234 (94100), 266 (56800), 324 (12300), 342 (6700), 374 (3800), 400 (2700), 430 (1000)	473	73	1.6	46	17
273	K	234 (137000), 272 (40300), 342 (5200), 376 (2900), 404 (2400), 440 (1000)	492	≈100	3.1	32	-
273	L	234 (43900), 272 (27800), 340 (4800), 376 (2600), 404 (2100), 440 (900)	492	≈100	2.4	42	-
274	M	294 (21200), 326 (14400), 353 (10700)	480	< 1	0.011	78	900
274	N	273 (31100), 298 (32500), 364 (10300)	496	1.5	0.041	37	240
274	O	292 (19500), 320 (11700), 358 (8300)	495	1.2	0.032	38	310
274	P	295 (19500), 319 (11900), 362 (8400)	504	1.2	0.014	86	710

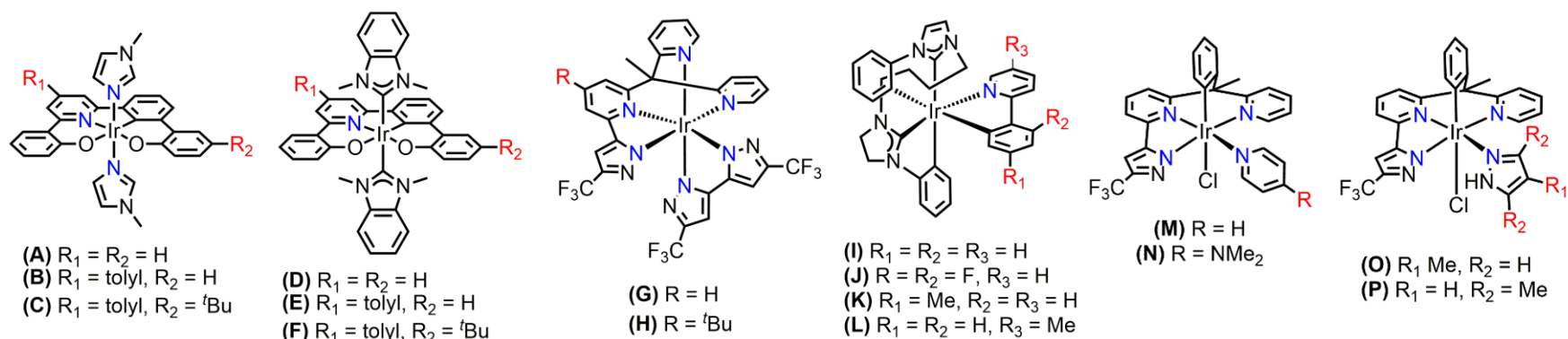


Figure 4.5: Structures of Ir(III) complexes **A-P** bearing tetradentate ligands.

4.4 Aims and objectives

As the short literature review above suggests, luminescent iridium(III) complexes incorporating tetradentate ligands is an extremely new and unexplored area of research; only a handful of such complexes have been reported, and all since the work in this thesis commenced, so there is enormous scope and potential within this field for the design and synthesis of other types of tetradentate scaffold.

The binding of iridium to the tetradentate *p*-anisidine ligands discussed in section 4.2.3 (for example, complex **C** in **Figure 4.3**) has not previously been attempted. The synthetic work detailed in this chapter aims to answer the following questions:

- 1) Does iridium coordinate in an identical tetradentate fashion to platinum with $N^{\wedge}N^{\wedge}N^{\wedge}N$ and $N^{\wedge}N^{\wedge}N^{\wedge}C$ -type ligands but leaving two axial chloride ligands?
- 2) Is it possible to metathesize these axial chlorides with phenylacetylene and AgCN using the methodology described for tridentate iridium complexes in Chapter 3.
- 3) Can we obtain any di-iridium species bridged by the *p*-anisidine-linker in an $\{N^{\wedge}N\}$ - $\{N^{\wedge}N\}$ -type fashion?
- 4) Can we force $N^{\wedge}N^{\wedge}C^{\wedge}C$ coordination with platinum and/or iridium?

To achieve these aims we have synthesized three types of complex:

- Platinum(II) complexes of the types $[Pt(N^{\wedge}N^{\wedge}N^{\wedge}N)](PF_6)_2$, $[Pt(N^{\wedge}N^{\wedge}N^{\wedge}C)]PF_6$, $Pt(C^{\wedge}N^{\wedge}N^{\wedge}C)$ and $Pt(N^{\wedge}N^{\wedge}C)Cl$ [59–62] (**Figure 4.6**, section 4.5).
- Iridium complexes of the types $[Ir(N^{\wedge}N^{\wedge}N^{\wedge}N)Cl_2]PF_6$ and $[Ir(N^{\wedge}N^{\wedge}N^{\wedge}C)Cl_2]$ [63 and 65] (**Figure 4.17**, section 4.6).
- Metathesized iridium complexes of the types $[Ir(N^{\wedge}N^{\wedge}N^{\wedge}N)(CCPh)Cl]PF_6$ and $[Ir(N^{\wedge}N^{\wedge}N^{\wedge}C)CN_2]$ [64 and 66] (**Figure 4.17**, section 4.6).

4.5 Results and discussion: Pt(II) complexes featuring tetradentate ligands

Complexes **59-62** (Figure 4.6) will be discussed in this section.

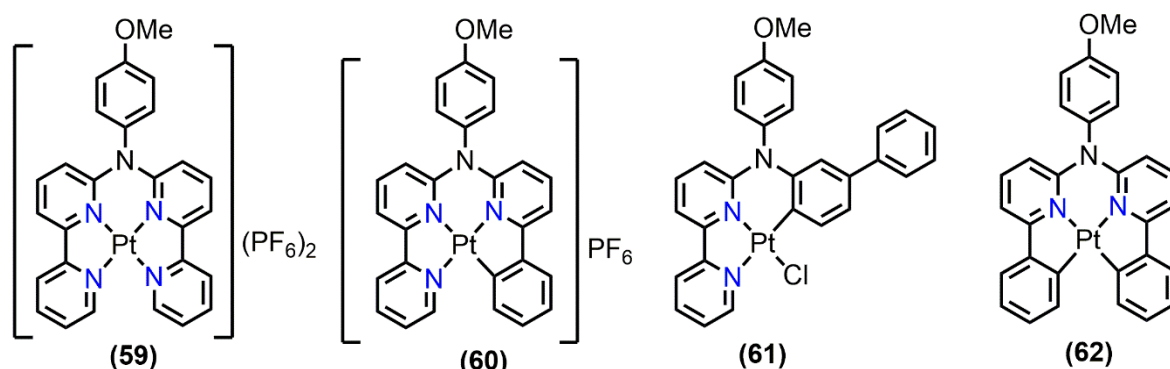


Figure 4.6: Structures of platinum complexes **59-62**.

4.5.1 Synthesis

The four tetradentate ligands were synthesized via a Buchwald-Hartwig amination of *para*-anisidine with an aryl bromide. Three different aryl bromides were required: (i) 6-bromo-bpy ($N^{\wedge}N$); (ii) 6-bromo-ppyH ($N^{\wedge}CH$) and (iii) 3-bromobiphenyl ($CH^{\wedge}CH$). 6-Bromo-ppyH was prepared from bromination of ppyH using carbon tetrabromide whilst 6-bromo-bpy was prepared by a Stille coupling of 2,6-dibromopyridine with 2-(tributylstannyl)pyridine in a 2 : 1 ratio (Figure 4.7).

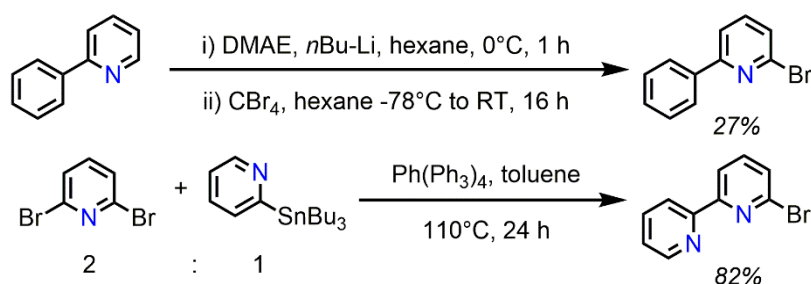


Figure 4.7: Synthesis of $N^{\wedge}N$ and $N^{\wedge}CH$ side arms.

The $N^{\wedge}N^{\wedge}CH$ ligand was synthesized via two separate aminations of *p*-anisidine, firstly with 6-bromo-bpy and secondly with 6-bromo-ppyH. An equimolar ratio of *p*-anisidine to 6-bromo-bpy in the first step ensured that the amination only proceeded once. The secondary amine intermediate was purified by silica gel column chromatography (hexane-EtOAc) and its identity confirmed by mass spectrometry and ^1H NMR spectroscopy (Figure 4.8). The characteristic broad NH peak occurred at 6.55 ppm in $CDCl_3$. Reaction of this intermediate with 6-bromo-ppy under identical conditions to those used in the first step yielded the $N^{\wedge}N^{\wedge}CH$ ligand in an overall yield of 27% (Figure 4.9). The $N^{\wedge}N^{\wedge}CH^{\wedge}CH$ ligand was also synthesized via two separate aminations of *p*-anisidine, firstly with 3-bromobiphenyl and secondly with 6-bromo-bpy, although the order of aminations was probably not important. The $N^{\wedge}N^{\wedge}N$ and $CH^{\wedge}N^{\wedge}N^{\wedge}CH$ ligands were obtained by a double amination of *p*-anisidine with either 2.5 equivalents of 6-bromo-bpy or 3 equivalents of 2,6-dibromopyridine. The large excess of 2,6-dibromopyridine to *p*-anisidine ensured a bromine atom was available for

the subsequent Suzuki coupling with phenylboronic acid to obtain the CH^NN^NCH ligand in an overall yield of 35% (**Figure 4.9**).¹⁵²

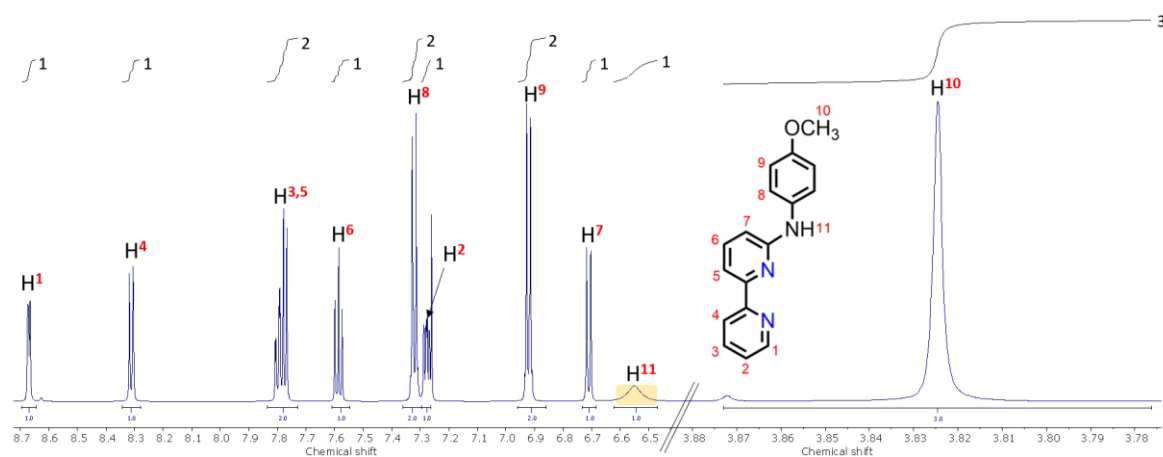


Figure 4.8: ¹H NMR spectrum of N-(4-methoxyphenyl)-[2,2'-bipyridin]-6-amine in CDCl₃, 600 MHz. The characteristic broad NH singlet at 6.55 ppm is highlighted in yellow.

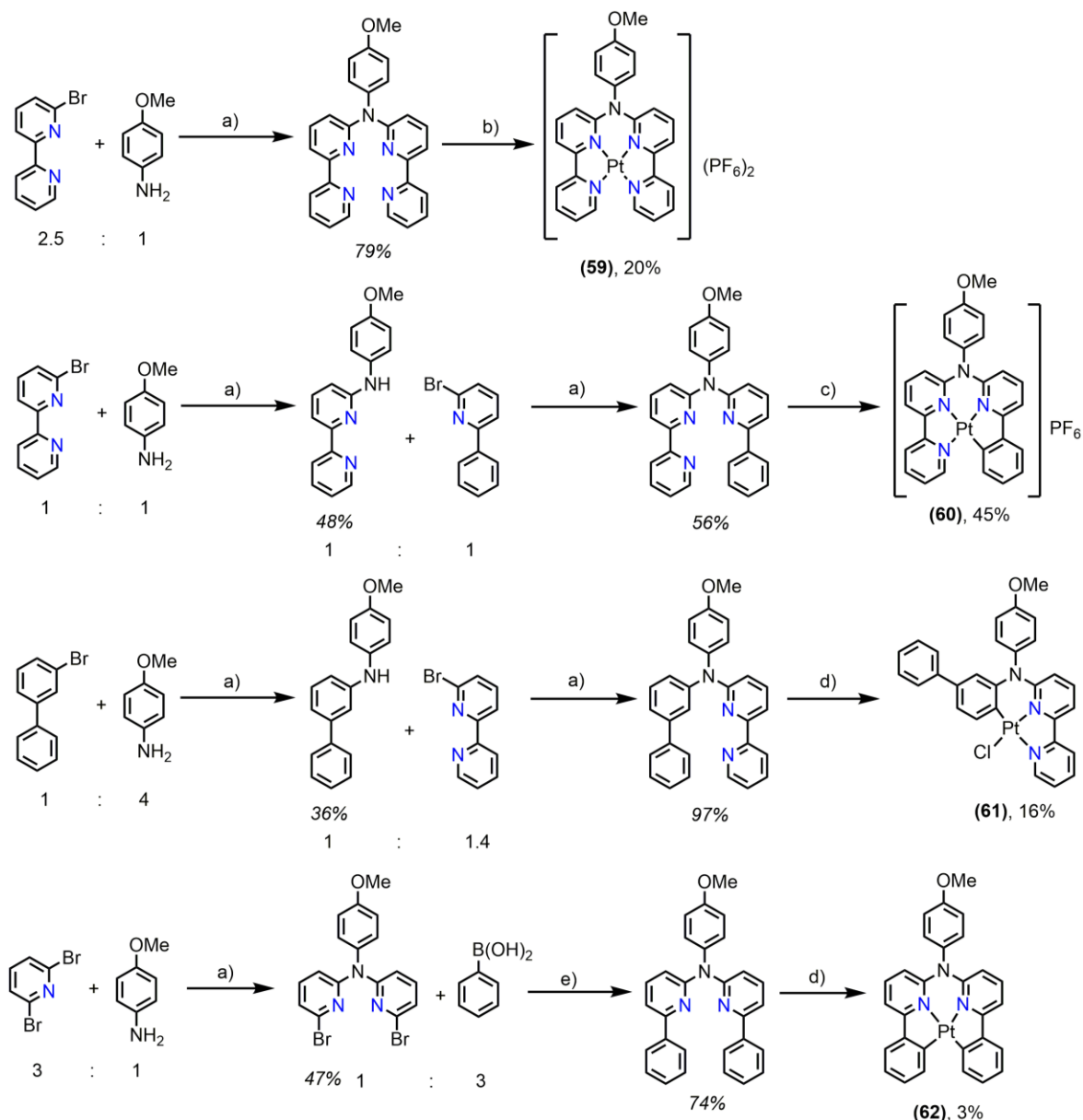


Figure 4.9: Synthesis of **59-62**. a) $Pd(dba)_2$, $dppf$, NaO^tBu , toluene, $110^\circ C$, 24 h; b) K_2PtCl_4 , MeCN : H_2O (3 : 1), $90^\circ C$, 3 days followed by sat. aq. KPF_6 ; c) K_2PtCl_4 , glacial acetic acid, $118^\circ C$, 3 days followed by sat. aq. KPF_6 ; d) K_2PtCl_4 , glacial acetic acid, $118^\circ C$, 3 days and e) $Pd(PPh_3)_4$, K_2CO_3 , 1,4-dioxane : H_2O (3 : 1).

Platinum complexes **59-62** were synthesized by a 3-day reflux of K_2PtCl_4 and ligand (1 : 1.2 ratio) in either glacial acetic acid (for **60-62**) or MeCN and H_2O (for **59**). The cationic complexes **59** and **60** underwent ion exchange by pipetting the crude reaction mixtures into an aqueous saturated solution of KPF_6 . A milder solvent mixture i.e. MeCN and H_2O could be used for the synthesis of **59** because no cyclometallation was required. Yields of **59-62** ranged from 3% to 45% (**Figure 4.9**). Complexes **60-62** were very insoluble and deuterated DMSO was required to record ^1H and ^{13}C NMR spectra. Complex **59**, on the other hand, was highly soluble in $CDCl_3$ and its ^1H NMR spectrum is

shown in **Figure 4.10**. The most downfield peak at 8.30 ppm corresponds to the protons adjacent to the nitrogen on the terminal pyridine rings (H^1).

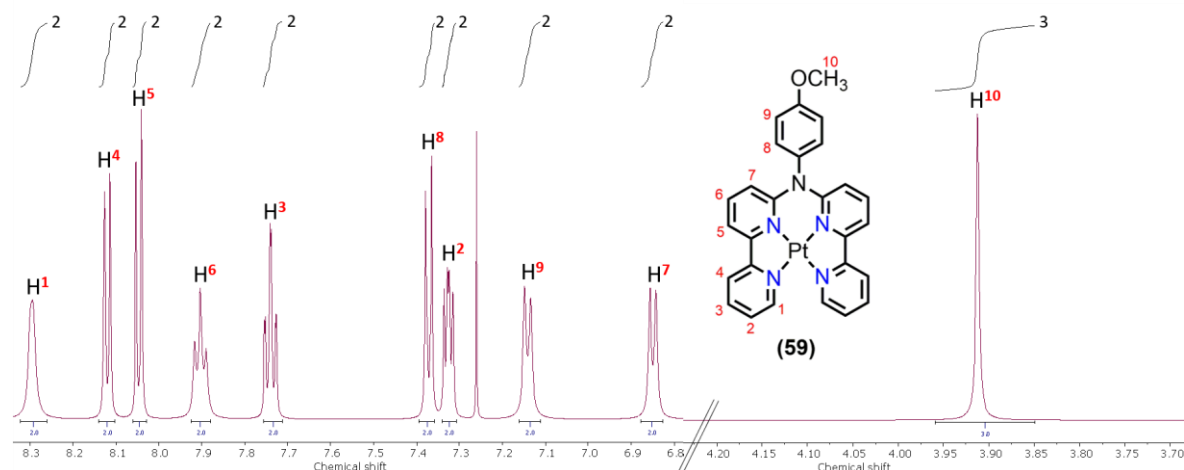


Figure 4.10: ^1H NMR spectrum of **59** in CDCl_3 , 600 MHz.

4.5.2 Crystallography

Crystals of **60** were prepared by slow recrystallization of the product from a DMF and ether solution. Crystals of **61** were prepared by slow evaporation of a MeCN solution. The structures of **60** and **61** are shown in **Figure 4.11**. The platinum cation undergoes tetradentate $\text{C}^{\wedge}\text{N}^{\wedge}\text{N}^{\wedge}\text{N}$ chelation in **60**; all of the bond lengths between the ligand and the platinum centre lie in a close range between 1.99 and 2.04 Å. The shortest of the platinum bonds is not the Pt–C bond as one might expect due to the effect of cyclometallation, but the Pt– N^4 bond; this could be because N^4 is part of a larger 6-membered chelate ring. The N^3 –Pt– N^4 and C^{21} –Pt– N^2 angles are 173° and 175° respectively therefore the complex is non-planar; the asymmetric nature of the ligand could explain this slight distortion of planarity. The $\text{N}^{\wedge}\text{N}^{\wedge}\text{C}^{\wedge}\text{C}$ ligand of complex **61** fails to bind platinum in a tetradentate coordination; instead the ligand acts as a tridentate $\text{N}^{\wedge}\text{N}^{\wedge}\text{C}$ chelator with a monodentate chloride occupying the fourth coordination site. Even when the reaction conditions were changed for those described by Huo and co-workers for platinum $\text{N}^{\wedge}\text{N}^{\wedge}\text{C}^{\wedge}\text{C}$ coordination, i.e. MeCN solvent and a reaction time of a week,²⁶⁰ tridentate binding still occurred. This is because the anisole group lacks an extra phenyl ring that points “down” so tridentate $\text{N}^{\wedge}\text{N}^{\wedge}\text{C}$ coordination will always be favoured. On the other hand, the 3,5-diphenylbenzene group of **Z** (**Figure 4.3**) means that there is always a phenyl *ortho* to the first Pt–C bond to promote tetradentate binding. In **61**, the shortest platinum bond is the Pt–C bond at 1.98 Å and the longest platinum bond is the Pt–Cl bond at 2.32 Å. Complex **61** is also slightly off being non-planar as the N^2 –Pt– Cl^1 and C^{12} –Pt– N^3 bond angles are 171° and 174° respectively.

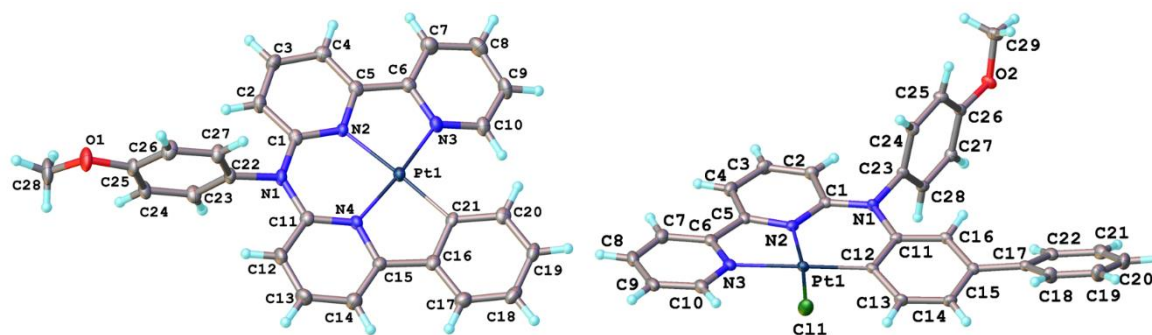


Figure 4.11: Crystal structures of **60** (left) and **61** (right). The PF_6^- counter-ion of **60** is omitted for clarity.

Table 4.3: Selected bond lengths and angles for crystal structures **60** and **61**.

Complex	60	Complex	61
Pt ¹ –N ³ bond length / Å	2.027(3)	Pt ¹ –N ³ bond length / Å	2.082(3)
Pt ¹ –N ² bond length / Å	2.040(3)	Pt ¹ –N ² bond length / Å	1.992(6)
Pt ¹ –N ⁴ bond length / Å	1.992(3)	Pt ¹ –C ¹² bond length / Å	1.981(5)
Pt ¹ –C ²¹ bond length / Å	2.005(3)	Pt ¹ –Cl ¹ bond length / Å	2.318(3)
N ³ –Pt ¹ –N ² bond angle / °	80.90(1)	N ³ –Pt ¹ –N ² bond angle / °	81.53(6)
N ² –Pt ¹ –N ⁴ bond angle / °	93.38(1)	N ² –Pt ¹ –C ¹² bond angle / °	93.50(7)
C ²¹ –Pt ¹ –N ⁴ bond angle / °	82.32(1)	Cl ¹ –Pt ¹ –C ¹² bond angle / °	94.03(5)
C ¹ –N ¹ –C ¹¹ bond angle / °	131.6(3)	C ¹ –N ¹ –C ¹¹ bond angle / °	128.75(2)
N ³ –Pt ¹ –N ⁴ bond angle / °	172.89(1)	N ² –Pt ¹ –Cl ¹ bond angle / °	170.85(4)
C ²¹ –Pt ¹ –N ² bond angle / °	175.14(1)	C ¹² –Pt ¹ –N ³ bond angle / °	173.86(7)

4.5.3 Electrochemistry

The electrochemical properties of **59–62** are displayed in **Table 4.4**. All four complexes display a single irreversible oxidation between +1.17 and +1.39 V and a single irreversible or quasi-reversible reduction potential in the window -1.47 to -1.94 V. Electrochemical $\Delta E_{1/2}$ values vary across the series from 2.64 V (**59**) to 3.27 V (**61**). One of the oxidation potentials will be associated with ionisation from an orbital spanning the Pt^{II} centre and the cyclometalating phenyl ring as shown by the DFT-calculated HOMO locations of **60–62**, which cover the cyclometalating phenyl rings, the platinum centre and the chloride ligand in the case of **61** (section 4.5.4). The reduction potentials of **59–62** are associated with electron transfer processes that occur within the LUMO which cover either the bpy or ppy side arms. The trend of $\Delta E_{1/2}$ values increasing across the series **59**, **60** and **62** is a result of the increase in cyclometallation, for example, the smallest $\Delta E_{1/2}$ value is that of **59** ($\Delta E_{1/2}$ = 2.64 V) with four N-donors whereas the largest $\Delta E_{1/2}$ value ($\Delta E_{1/2}$ = 3.02 V) belongs to **62** which has two cyclometalating donors. Complex **61** has the largest $\Delta E_{1/2}$ value in the series of $\Delta E_{1/2}$ = 3.27 V. The trend in $\Delta E_{1/2}$ values of **59**, **60** and **62** closely matches the trend in HOMO-LUMO gaps as calculated by DFT, although the accuracy of $\Delta E_{1/2}$ values is somewhat reduced in all four complexes because their irreversible redox processes were defined using anodic and cathodic peak potentials.

Table 4.4: Electrochemical properties of complexes **59-62** recorded in a 0.1 M electrolyte solution of NBu_4PF_6 in DCM. Values were measured at a scan rate of 200 mV s^{-1} and are reported relative to SCE, measured using ferrocene as the standard ($E_{1/2}^{\text{ox}} = 0.42 \text{ vs. SCE}$). E_p^{ox} and E_p^{red} are the anodic and cathodic peak potentials respectively. $\Delta E_{1/2} = E_p^{\text{ox}} - E_p^{\text{red}}$. $\Delta E_{\text{H-L}}$ refers to the HOMO-LUMO gap calculated using DFT.

Complex	$E_p^{\text{ox}} / \text{V}$	$E_p^{\text{red}} / \text{V}$	$\Delta E_{1/2} / \text{V}$	$\Delta E_{\text{H-L}} / \text{eV}$
59	+1.17 ^{ir}	-1.47 ^{ir}	2.64	2.57
60	+1.36 ^{ir}	-1.59 ^{qr}	2.95	3.03
61	+1.33 ^{ir}	-1.94 ^{qr}	3.27	2.54
62	+1.39 ^{ir}	-1.63 ^{ir}	3.02	3.46

4.5.4 DFT

Figure 4.12 depicts the frontier molecular orbital diagrams and energies of **59-62**, calculated using B3LYP and the LANL2DZ basis set. The HOMOs of **60-62** are located mainly over their one (**60**) or two (**61** and **62**) phenyl rings but in complex **59** the HOMO exclusively resides on its anisole ring due to the lack of phenyl units. In contrast, the LUMOs of **59-62** are located on their pyridine rings to a large extent, although the spatial separation of the frontier molecular orbitals of **62** is less distinct. LUMO energies increase across the series from -8.51 eV (**59**) to -1.70 eV (**62**); HOMO energies follow the same general trend from -11.09 eV to -5.12 eV (**Table 4.5**). The increase in orbital energies across the series can be explained by the fact that the calculations were performed in a vacuum; this means the HOMO and LUMO energies of the charged complexes **59** and **60** are artificially low and cannot be compared directly with the orbital energies of the uncharged complexes **61** and **62**. The major orbital contribution to all four complexes is a HOMO→LUMO transition at 69-71%. As the degree of nitrogen donation increases, the HOMO-LUMO energy gap narrows from 3.46 eV (**62**), to 3.03 eV (**60**) to 2.57 eV (**59**), in line with $\Delta E_{1/2}$ values. Complex **61** has the smallest HOMO-LUMO gap in the series of 2.54 eV.

Table 4.5: HOMO and LUMO energies of **59-62** including their HOMO-LUMO energy gap and major orbital contribution as calculated by DFT.

Complex	HOMO Energy /eV	LUMO Energy /eV	$\Delta E_{\text{H-L}} / \text{eV}$	Major Orbital Contribution
59	-11.09	-8.51	2.57	HOMO→LUMO (71%)
60	-8.47	-5.44	3.03	HOMO→LUMO (69%)
61	-5.12	-2.58	2.54	HOMO→LUMO (70%)
62	-5.16	-1.70	3.46	HOMO→LUMO (70%)

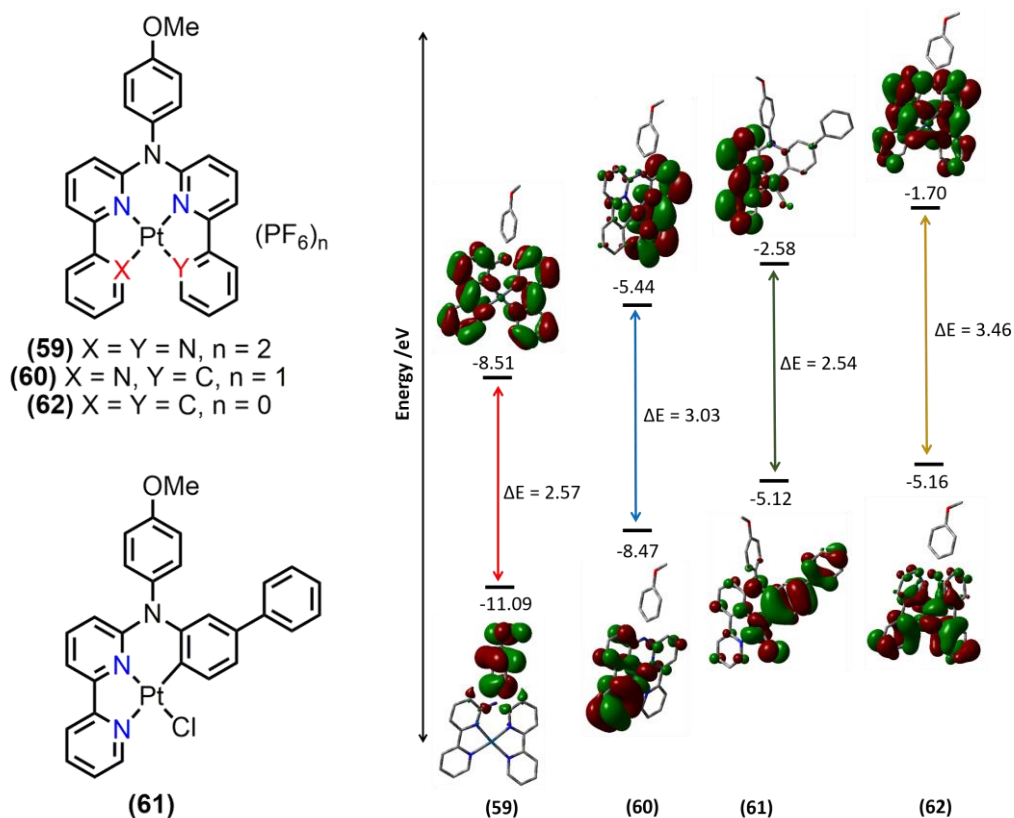


Figure 4.12: HOMO and LUMO orbitals and energies of complexes **59-62** as calculated by DFT.

4.5.5 Photophysical properties

4.5.5.1 Absorption

The absorption spectra of **59-62** recorded in DCM are shown in **Figure 4.13**. The complexes present differing profiles but share some common features:

- 1) An intense high energy peak between 256 and 288 nm (with the exception of **60** whose intense peak is instead a shoulder).
- 2) A series of less intense peaks and shoulders occurring at longer wavelengths between 325 and 411 nm.

The absorbance of **61** has an extended lower energy $^3\text{MLCT}$ tail which continues beyond 450 nm with a broad, weak peak centred at 479 nm ($\epsilon = 2.9 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$). The ϵ values of the high energy bands of **59** and **61**, which represent $\pi\text{-}\pi^*$ transitions of the ligands, are between 1.9×10^4 and $2.8 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$. The $^1\text{LC } \pi\text{-}\pi^*$ transitions of **60** and **62** at 274 and 263 nm are much weaker with $\epsilon \leq 8.0 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$. The medium intensity bands between 325 and 388 nm ($2.8 \times 10^3 \leq \epsilon \leq 8.9 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$) represent $^1\text{MLCT}$ and $^1\text{LLCT}$ transitions.

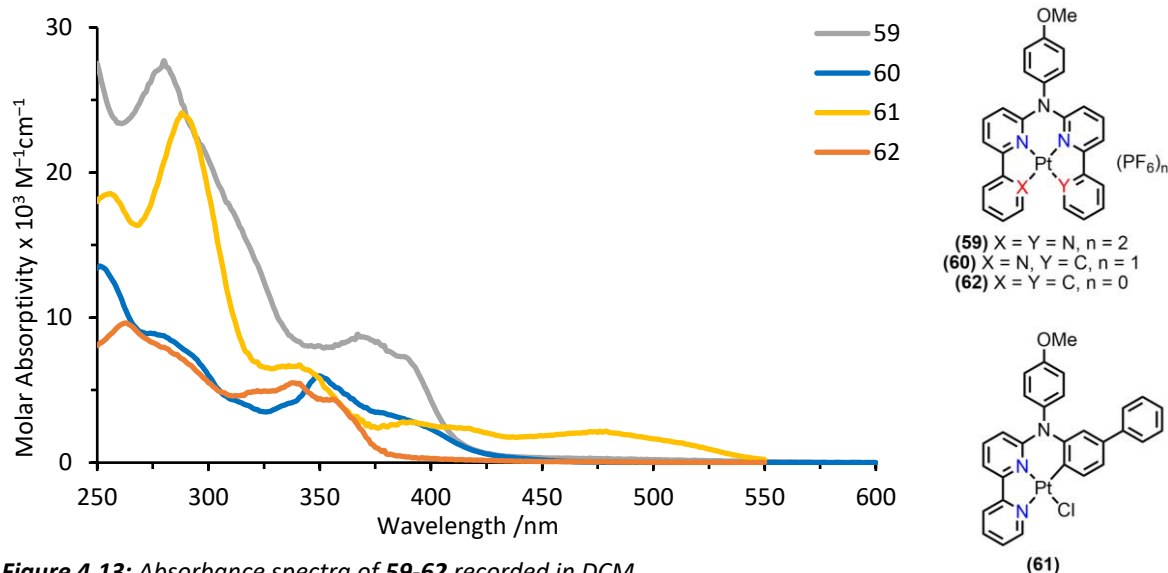


Figure 4.13: Absorbance spectra of **59-62** recorded in DCM.

4.5.5.2 Emission

Figure 4.14 shows the RT emission of complexes **60-62** in degassed DCM. The profiles of **61** and **62** are broad and unstructured whereas the profile of **60** is a lot more structured and has two distinct peaks of roughly equal intensities at higher energies than the broad peaks of **61** and **62**. Complex **59** is too weakly emitting at RT for its emission profile to be shown. The broad profiles of **61** and **62** suggest a large degree of $^3\text{MLCT}$ character to their excited states whilst the more structured higher energy profile of **60** indicates substantial LC character to its excited state. The reddest emission is that of the $\text{N}^{\wedge}\text{N}^{\wedge}\text{C}$ -type Pt complex **61** with an emission maximum of 646 nm; this supports its expansive absorbance profile, shown in **Figure 4.13**, which extends beyond 500 nm with low intensity $^3\text{MLCT}$ bands at 411 and 479 nm. The low emission energy of **61** is presumably due to the combination of bpy acceptor vs. pyridine acceptor and the effect of cyclometallation which result in a low energy LUMO and a high energy HOMO.

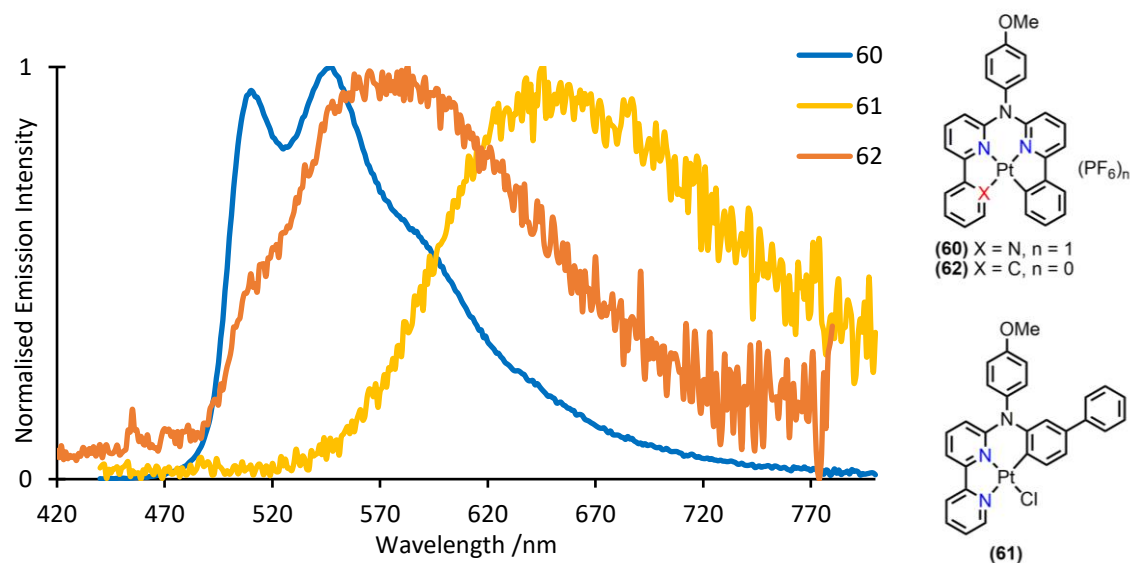


Figure 4.14: Normalised RT emission spectra of **60-62** recorded in degassed DCM, $\lambda_{\text{exc}} = 425 \text{ nm}$

The emissions of the remaining complexes then get sequentially bluer in the order **62** ($\lambda_{\text{max}} = 583$ nm) and **60** ($\lambda_{\text{max}} = 510, 547$ nm). The contrasting PL emissions of **59-62** can be partly explained by DFT calculations which indicate a widening HOMO-LUMO gap in the order **61** < **59** < **60** to reflect the shift in PL emission across the series from red to orange to blue-green. The yellow emission of **62** is not rationalised by DFT as calculations predict **62** to be the bluest emitter in the series. It is indeed interesting that there is over a 70 nm (2460 cm^{-1}) difference between the emissions of **60** and **62** given that there is only a single atom difference between the two complexes i.e. $\text{N}^{\wedge}\text{N}^{\wedge}\text{N}^{\wedge}\text{C}$ in the former and $\text{C}^{\wedge}\text{N}^{\wedge}\text{N}^{\wedge}\text{C}$ in the latter.

Figure 4.15 shows the 77 K emission profiles of **59-62**. The profiles at 77 K are a lot more structured than at RT and reflect the increased structural rigidity at low temperature due to the lack of accessible vibrational microstates. Complexes **59-62** generally have two fairly sharp peaks separated by roughly 40-50 nm and one or more smaller peak(s) or shoulder(s) at lower energies. The profiles of **59**, **60** and **62** are all similar in terms of shape and position of peaks but the relative intensities of the peaks differ. Complex **61** also has a similar shaped profile to the other complexes but it is red shifted by roughly 60 nm ($1910\text{-}2180 \text{ cm}^{-1}$).

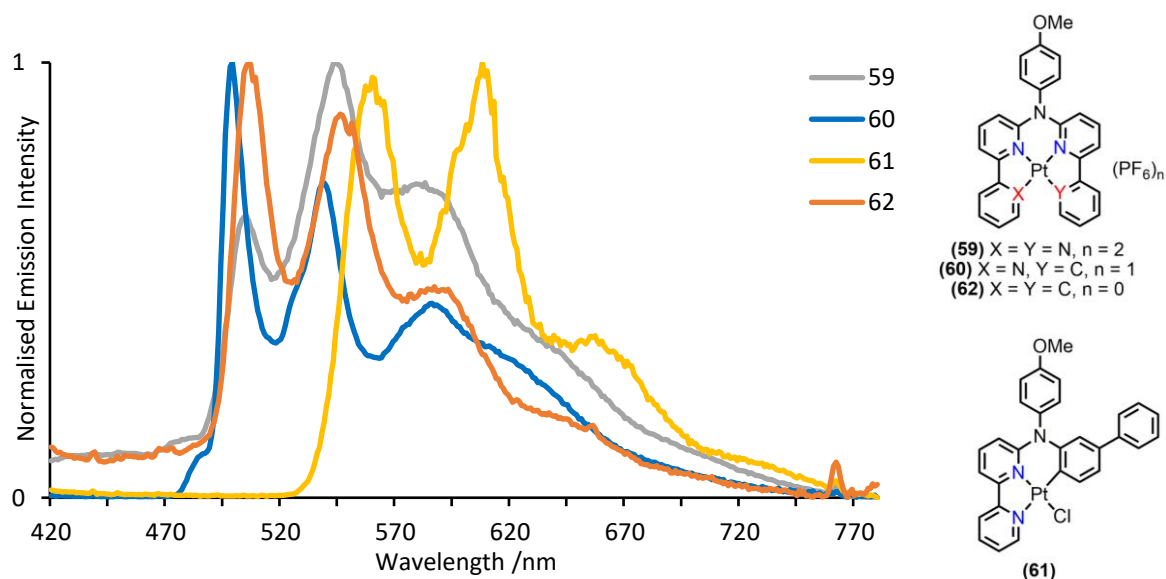


Figure 4.15: Normalised emission profiles of **59-62** at 77 K in butyronitrile ($\lambda_{\text{exc}} = 400$ nm).

The 77 K emission maxima of **59-62** are significantly blue shifted with respect to their RT maxima as typified by the 77 K and RT emissions of **60** which are 499 and 510 nm respectively (**Figure 4.16**); this hypsochromic shift suggests a large amount of MLCT character in its excited state. Complex **60** has the bluest emission at RT and at 77 K whereas **61** has the reddest emission at both temperatures. The emission of **59** at low temperature is 50 nm (2180 cm^{-1}) redder than $[\text{Pt}(\text{bpy})_2]^{2+}$ whose emission peak lies at 455 nm.

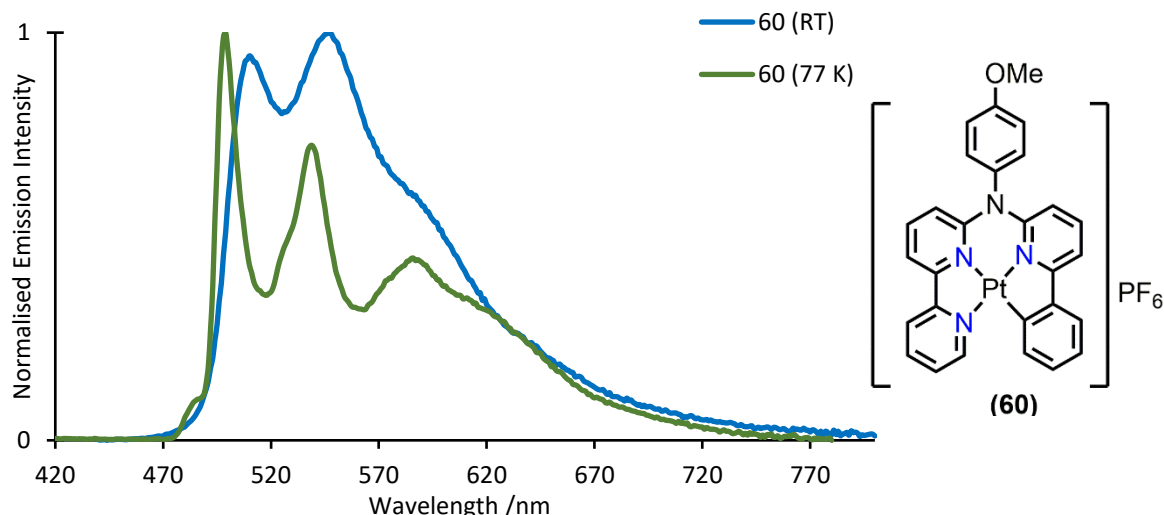


Figure 4.16: Normalised emission profiles of **60** at RT in degassed DCM ($\lambda_{exc} = 425$ nm) and at 77 K in butyronitrile ($\lambda_{exc} = 400$ nm).

The remaining photophysical data for **59-62** is tabulated below (**Table 4.6**). Complex **59** has a quantum yield of 0.3% and a RT lifetime at RT of 590 ns in degassed DCM. The lack of cyclometallation in **59** means there is no spin-orbit coupling mixed into the excited state; the lack of metal character is reflected by its low radiative rate constant of $4.8 \times 10^3 \text{ s}^{-1}$ which is the lowest k_r in the series. At low temperature, the luminescence lifetime of **59** lengthens to 3.8 μs which is still 20 μs shorter than the 77 K lifetime of $[\text{Pt}(\text{bpy})_2]^{2+}$.²⁷⁵ This trend of longer lifetimes at 77 K vs. RT is true for the entire Pt series and is due to the inaccessibility of MC d-d states and the rigid environment that inhibits non-radiative decay through transfer into vibrations.

Table 4.6: Photophysical properties of **59-62** recorded in degassed DCM at RT ($\lambda_{exc} = 425$ nm) and at 77 K in butyronitrile ($\lambda_{exc} = 400$ nm). Aerated PLQYs and lifetimes are shown in brackets.

Complex	59	60	61	62 ²⁵⁴
Absorption Maxima /nm	280 (27700)	274 (2920)	256 (18500)	263 (7980)
($\epsilon / \text{M}^{-1} \text{cm}^{-1}$)	367 (8850)	350 (5980)	288 (24100)	325 (5320)
	388 (7310)	376 (3490)	341 (6740)	338 (6060)
			388 (2810)	
			411 (3350)	
			479 (2930)	
$\lambda_{max} / \text{nm}$	603	510, 547	646	583
PLQY /% degassed(aerated)	0.3 (0.3)	5.9 (2.6)	0.4 (0.4)	78 (40)
Lifetime /ns degassed (aerated)	590 (195)	2630 (1160)	93 (75)	8300 (3030)
$k_r \times 10^5 \text{ s}^{-1}$	0.048	0.22	0.42	0.94
$k_{nr} \times 10^5 \text{ s}^{-1}$	17	3.6	107	1.2
77 K $\lambda_{max} / \text{nm}$	505, 544	499, 539, 586	560, 608	506, 546
77 K Lifetime /μs	3.8	10.3	7.9	12

The RT 2.6 μs lifetime of **60** is consistent with emission from a $^3\pi-\pi^*$ state with MLCT admixture. DFT calculations further support this mixed state which show a contribution to the HOMO of **60** from both platinum and the cyclometalating phenyl ring of the ligand. These results are consistent with the photophysical properties of similar neutral $\text{Pt}(\text{C}^{\wedge}\text{N}^{\wedge}\text{N}^{\wedge}\text{C})$ -type complexes prepared by Huo.⁷

The 6% quantum yield of **60**, however, is far inferior to the PLQYs of Huo's complexes⁷ and other *p*-anisidine-linked Pt complexes in the literature^{152,254,255} whose quantum yields surpass 70%. The poor quantum efficiency of **60** can be explained largely by its high rate of non-radiative decay ($k_{nr} = 3.6 \times 10^5 \text{ s}^{-1}$) compared to the k_{nr} values of literature complexes which are typically an order of magnitude smaller. As **60** is cationic and features only a single cyclometalating donor, its MC d-d states might be lower in energy and thus more populated at RT than literature Pt(C[^]N[^]N[^]C)-type complexes; this would render it more susceptible to deactivation pathways.

Complex **61** has one of the lowest quantum yields ($\phi = 0.4\%$) and shortest RT lifetimes ($\tau = 93 \text{ ns}$) in the series. The poor quantum yield of **61** can be explained by its large non-radiative decay rate constant of $1.1 \times 10^7 \text{ s}^{-1}$ which is roughly two orders of magnitude larger than similar Pt complexes previously reported.²⁶⁰ Literature data is provided for complex **62** from the thesis of Mickaële Bonneau.²⁵⁴ It has the highest quantum yield of the series of 78%, the longest RT lifetime of 8.3 μs , the highest radiative rate constant of $9.4 \times 10^4 \text{ s}^{-1}$ and the lowest k_{nr} value of $1.2 \times 10^5 \text{ s}^{-1}$. The double cyclometallation provided by the C[^]N[^]N[^]C ligand of **62** could account for its superior photophysical properties over the rest of the series.

4.6 Results and discussion: Ir(III) complexes featuring tetradentate ligands

Complexes **63-66** and **88-90** (Figure 4.17) will be discussed in this section.

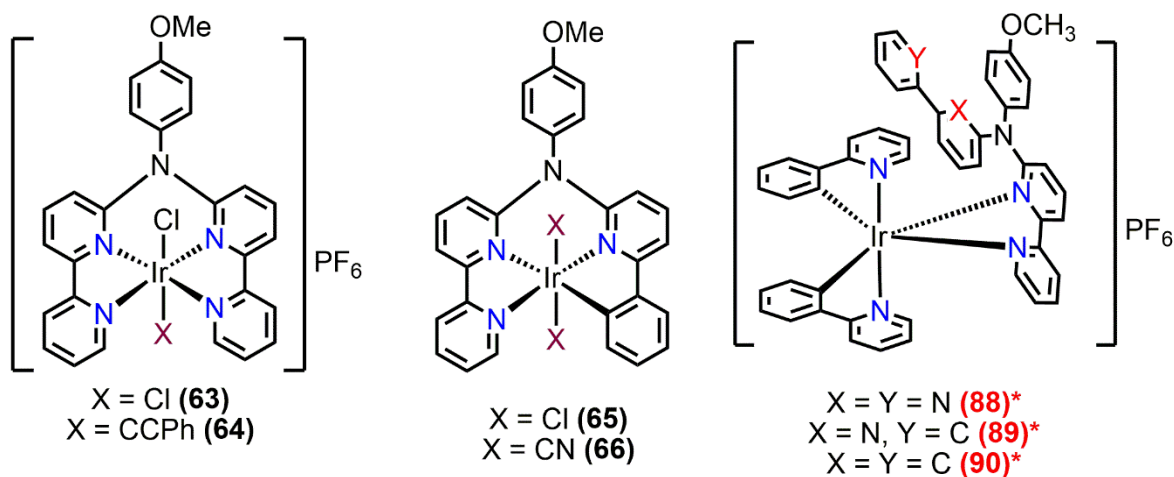


Figure 4.17: Structures of iridium complexes **63-66** and **88-90**.

*Not purified

4.6.1 Synthesis

The first investigation was to see if the N[^]N[^]N[^]N ligand could act as a bridging ligand for the creation of a di-iridium complex via bis-N[^]N coordination. After all, this ligand had two bpy side arms and we know that bpy is a suitable N[^]N chelator in mononuclear complexes. The N[^]N[^]N[^]N ligand and $[\text{Ir}(\text{ppy})_2\mu\text{-Cl}]_2$ were reacted together in an equimolar ratio in a mixture of MeOH and DCM (Figure 4.18), according to the general procedure for the synthesis of bidentate $[\text{Ir}(\text{C}^{\wedge}\text{N})_2(\text{N}^{\wedge}\text{N})]\text{PF}_6$

complexes. Purification of the crude dark yellow solid by column chromatography on alumina (DCM : MeOH 0-2%) yielded a lighter yellow solid, **88**, which glowed a light orange colour under UV irradiation ($\lambda_{\text{exc}} = 365 \text{ nm}$).

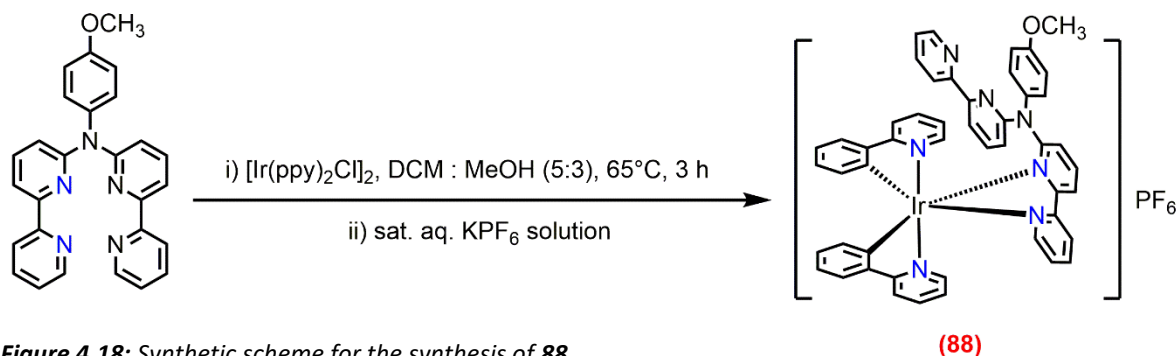


Figure 4.18: Synthetic scheme for the synthesis of **88**.

The ^1H NMR spectrum of this yellow solid, shown in **Figure 4.19**, reveals the presence of two species with suspected methoxy peaks at 3.74 and 3.82 ppm. There are two unresolved peaks in the LCMS trace at retention times of 3.14 and 3.26 minutes each with m/z values equal to 932 which corresponds to $[\text{M-PF}_6]^+$ where M equals the mononuclear product. Therefore, we speculate that the two species are structural isomers which differ according to the orientation of the ancillary ligand. This indicates that the $\text{N}^{\wedge}\text{N}^{\wedge}\text{N}^{\wedge}\text{N}$ ligand is just too sterically hindered to accommodate two iridium ions because the bpy units are “inward facing”. When the bpy units are “outward facing”, however, two iridium ions can coordinate on either side and this has led to the synthesis of several di-iridium complexes which are discussed in Chapter 5. The reactions to generate complexes **89** and **90** were also attempted using identical conditions to those described in **Figure 4.18** but with the $\text{N}^{\wedge}\text{N}^{\wedge}\text{N}^{\wedge}\text{CH}$ and $\text{N}^{\wedge}\text{N}^{\wedge}\text{CH}^{\wedge}\text{CH}$ ligands respectively - ^1H NMR spectroscopy and mass spectrometry suggest the formation of the mono-iridium $[\text{Ir}(\text{ppy})_2(\text{N}^{\wedge}\text{N})]^+$ -type products.

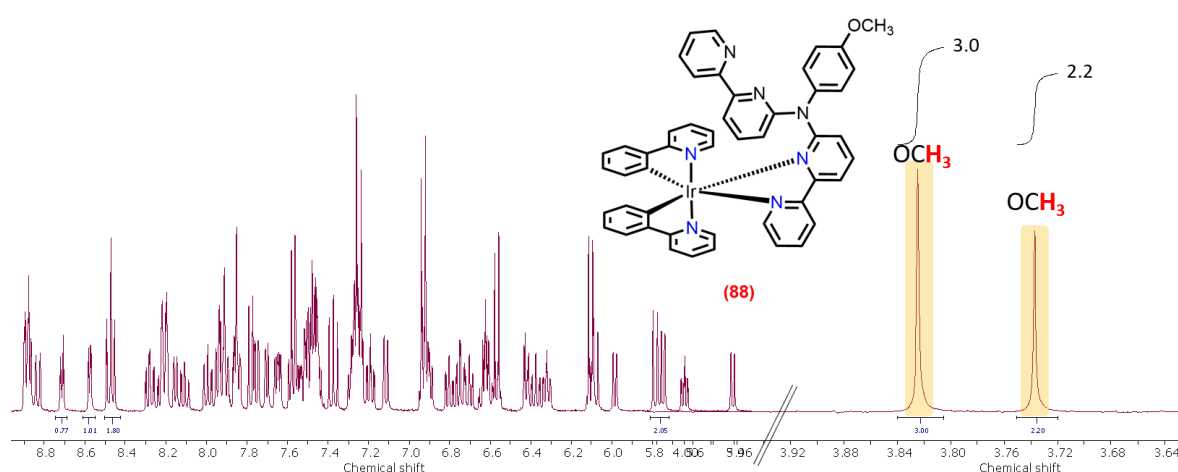


Figure 4.19: ^1H NMR spectrum of an impure mixture of **88** after column chromatography in d_6 -acetone, 400 MHz. The aliphatic peaks at 3.74 and 3.82 ppm (highlighted in yellow) could correspond to the methoxy peaks of the structural isomers with differing orientations of the $\text{N}^{\wedge}\text{N}$ ligand.

The second investigation was to see if the $N^{\wedge}N^{\wedge}N^{\wedge}$ ligand could act as a tetradentate chelator of iridium. Overnight reaction of $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ and ligand in 2-ethoxyethanol and H_2O (3 : 1) at 120°C , following the general procedure for the synthesis of iridium dimers, yielded an orange precipitate upon addition of an aqueous saturated solution of KPF_6 (**Figure 4.20**). Purification by silica gel column chromatography (DCM : MeOH 0-2%) followed by recrystallization from acetone and hexane yielded the $[\text{Ir}(N^{\wedge}N^{\wedge}N^{\wedge})\text{Cl}_2]\text{PF}_6$ complex, **63**, as a yellow solid in a 28% yield. Mass spectrometry and NMR spectroscopy confirmed the identity of **63**; an m/z peak of $694 = [\text{M}-\text{PF}_6]^+$ was seen in the LCMS trace whilst ten proton signals are evident in the ^1H NMR spectrum (**Figure 4.21**), performed in d_3 -MeCN, matching its ten unique proton environments. Each bpy unit is equivalent therefore the Ir(III) ion presumably sits in a pseudo-octahedral geometry with two axial chloride ligands. The most downfield peak at 9.36 ppm is assigned to the protons *ortho* to the terminal bpy nitrogens (i.e. H^1) whilst the *p*-anisidine methoxy singlet occurs at 3.94 ppm.

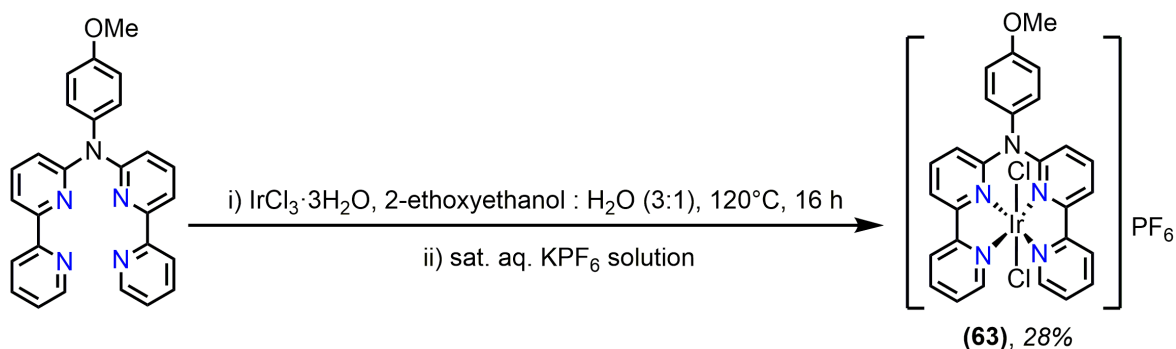


Figure 4.20: Synthetic scheme for the synthesis of complex **63**.

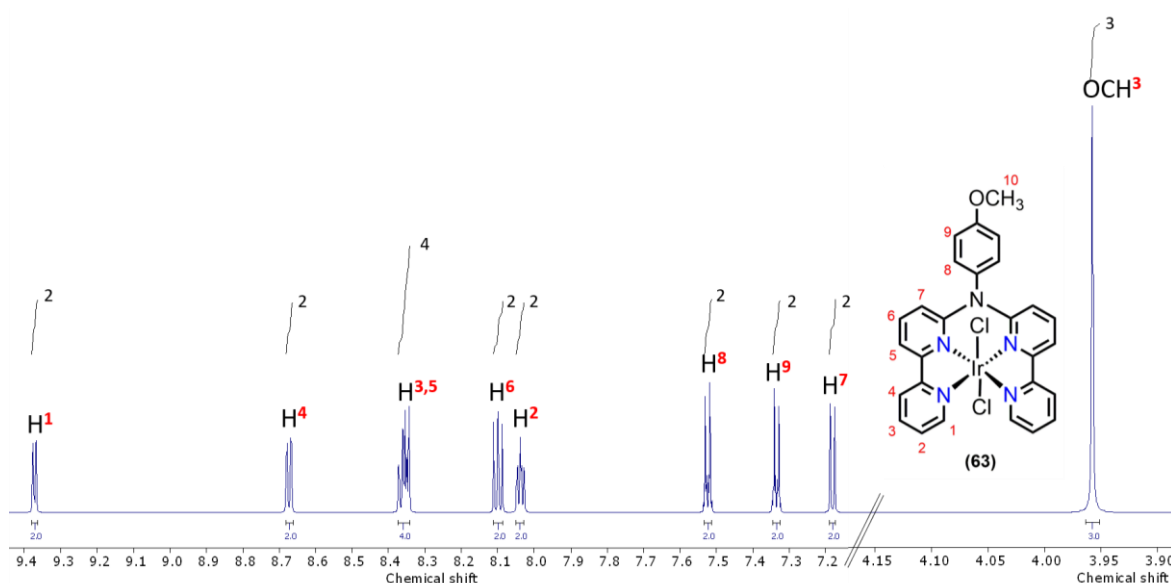


Figure 4.21: ^1H NMR spectrum of complex **63** in d_3 -MeCN, 700 MHz. Assignments were made with the aid of ^1H - ^1H COSY and ^1H - ^1H NOESY analysis.

Metathesis of **63** with phenylacetylene produced **64** in a yield of 19% after purification by column chromatography on alumina (**Figure 4.22**). Complex **64** had an R_f value of 0.19 in 1% MeOH, 99% DCM and eluted just after the complex containing phenyl acetylide and iodide axial ligands whose R_f value in the same solvent ratio was 0.24. The identity of this iodo species is suggested by the molecular cation peak of $m/z = 760$ with a retention time of 2.68 minutes (**Figure 4.23**). The iodide would have come from the CuI catalyst. The ^1H NMR spectrum of a co-eluted fraction is shown in **Figure 4.24**; the most downfield signal from the iodide complex is at 9.81 ppm whereas the most downfield signal of **64** is at 9.69 ppm. Only a few milligrams of the iodide complex could be isolated in approximately 90% purity.

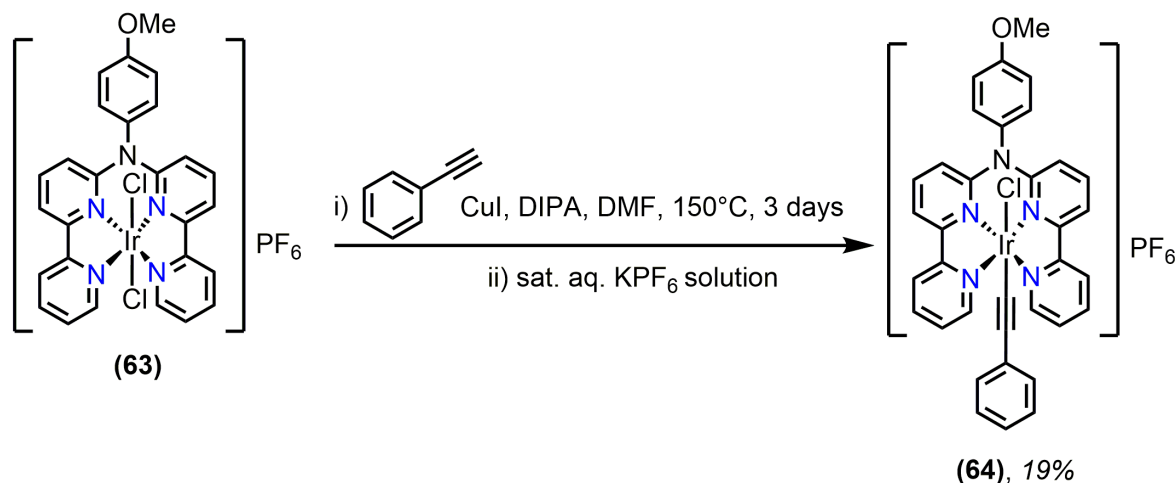


Figure 4.22: Synthetic scheme for the synthesis of complex **64**.

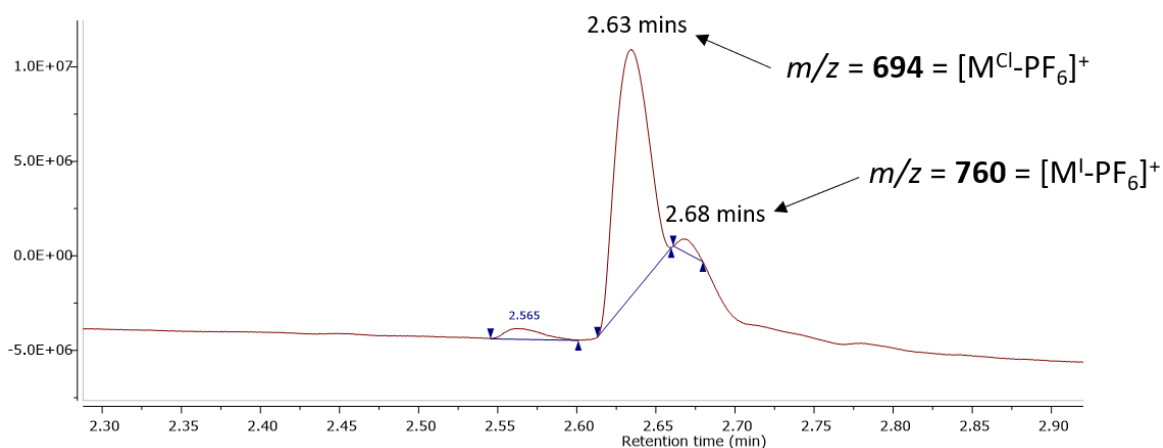


Figure 4.23: LCMS trace of a co-eluted fraction from the column to purify **64**. The chloride-bound product i.e. **64**, M^{Cl} , has a retention time of 2.63 mins and a molecular cation peak of $m/z = 694$ whilst the suspected iodo-analogue, M^{I} , has a slightly longer retention time of 2.68 minutes and an m/z value of 760.

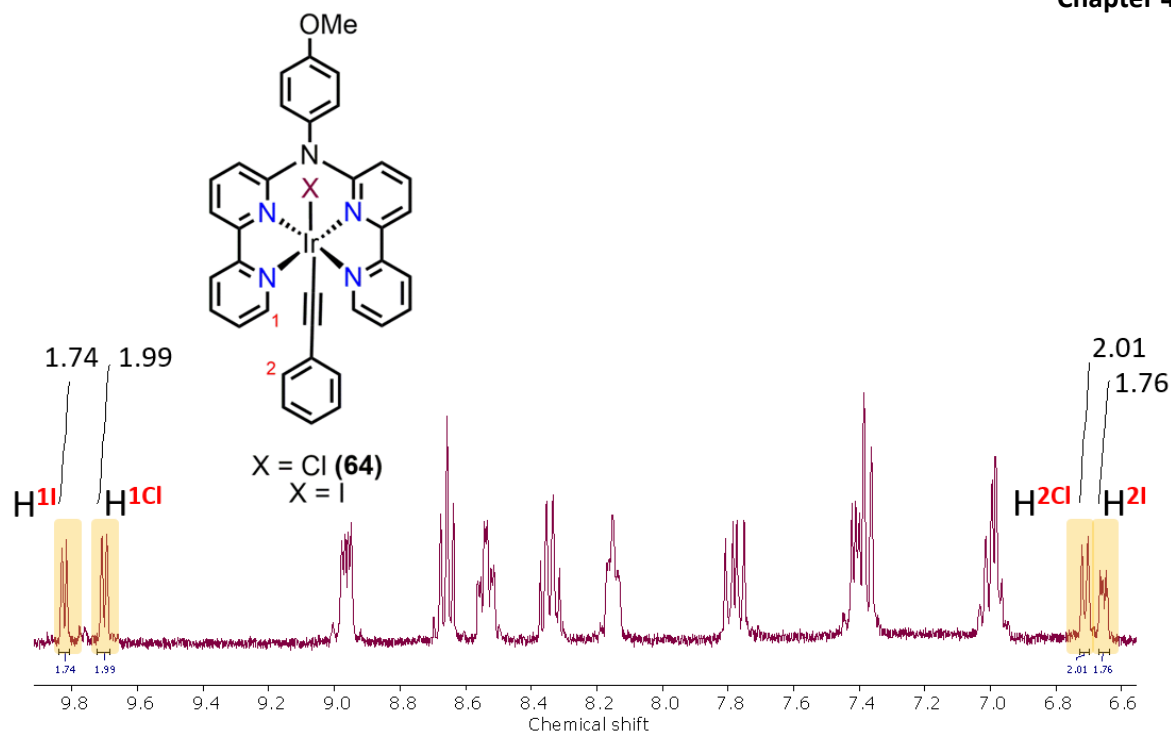


Figure 4.24: Aromatic region from the ^1H NMR spectrum of a co-eluted fraction from the column to purify **64** in d_6 -acetone, 400 MHz, to yield **64** and the suspected iodo analogue. Characteristic signals are highlighted in yellow.

Metathesis of **63** with AgCN resulted in the di-cyano complex, $[\text{Ir}(\text{N}^{\wedge}\text{N}^{\wedge}\text{N}^{\wedge}\text{N})\text{CN}_2]\text{PF}_6$, as suggested by the molecular cation peak of $m/z = 676$ in the LCMS trace at a retention time of 1.24 minutes. The crude mixture was purified by silica gel column chromatography and the suspected di-cyano complex eluted at 9% MeOH in DCM; its ^1H NMR spectrum is shown in **Figure 4.25**. The product was poorly soluble in MeCN and could not be purified sufficiently for full characterisation.

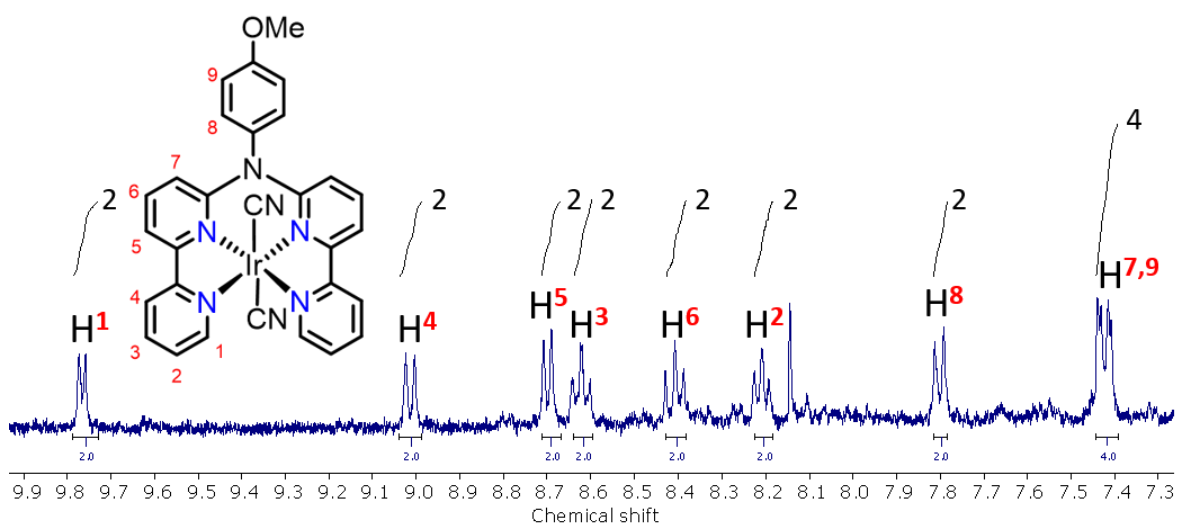


Figure 4.25: Aromatic region from the ^1H NMR spectrum of the di-cyano complex formed from the reaction of **63** with AgCN after purification by column chromatography in d_6 -acetone, 400 MHz.

Tetradentate chelation of iridium by the $N^{\wedge}N^{\wedge}N^{\wedge}CH$ ligand was also successful resulting in the neutral $Ir(N^{\wedge}N^{\wedge}N^{\wedge}C)Cl_2$ complex under identical conditions as those used for the synthesis of **63**. Isolation of the dark red precipitate by centrifugation and purification by silica gel column chromatography (DCM : MeOH 0–2%) and recrystallization from DCM and hexane yielded **65** as an orange solid in a yield of 21% (**Figure 4.26**).

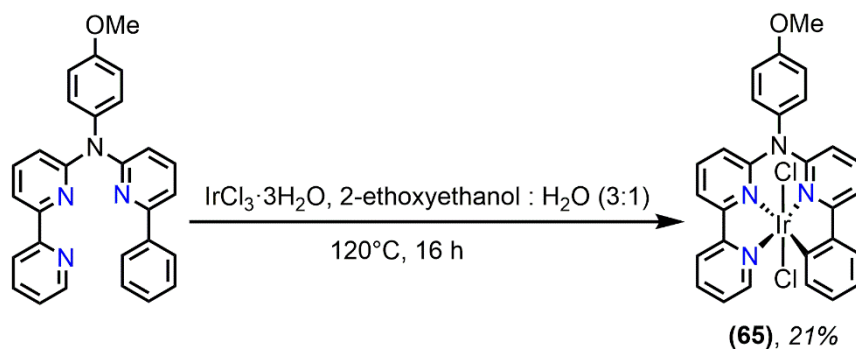


Figure 4.26: Synthetic scheme for the synthesis of complex **65**.

The identity of **65** was confirmed by mass spectrometry and NMR spectroscopy; the LCMS trace revealed an $[M+H]^+$ peak of $m/z = 693$ at a retention time of 1.78 minutes whilst the ^1H NMR spectrum in $CDCl_3$ (**Figure 4.27**) featured 17 signals with an integral area of 21 protons which matches the number of proton environments and the total number of protons respectively in **65**. We speculate that the Ir(III) ion occupies a distorted pseudo-octahedral geometry with two axial chlorides. The most downfield peak at 9.83 ppm is assigned to the proton *ortho* to the bpy nitrogen whereas the two most upfield signals in the aromatic region at 6.60 and 6.92 ppm correspond to the protons attached to the central pyridine units at the positions *ortho* to the *p*-anisidine linker. A similar trend in proton shifts was observed in the ^1H NMR spectrum of **63** (**Figure 4.21**). The singlet associated with the methoxy group of **65**, which appears at 3.95 ppm, almost exactly matches that of **63** ($\delta = 3.94$ ppm) even with the use of a different deuterated solvent.

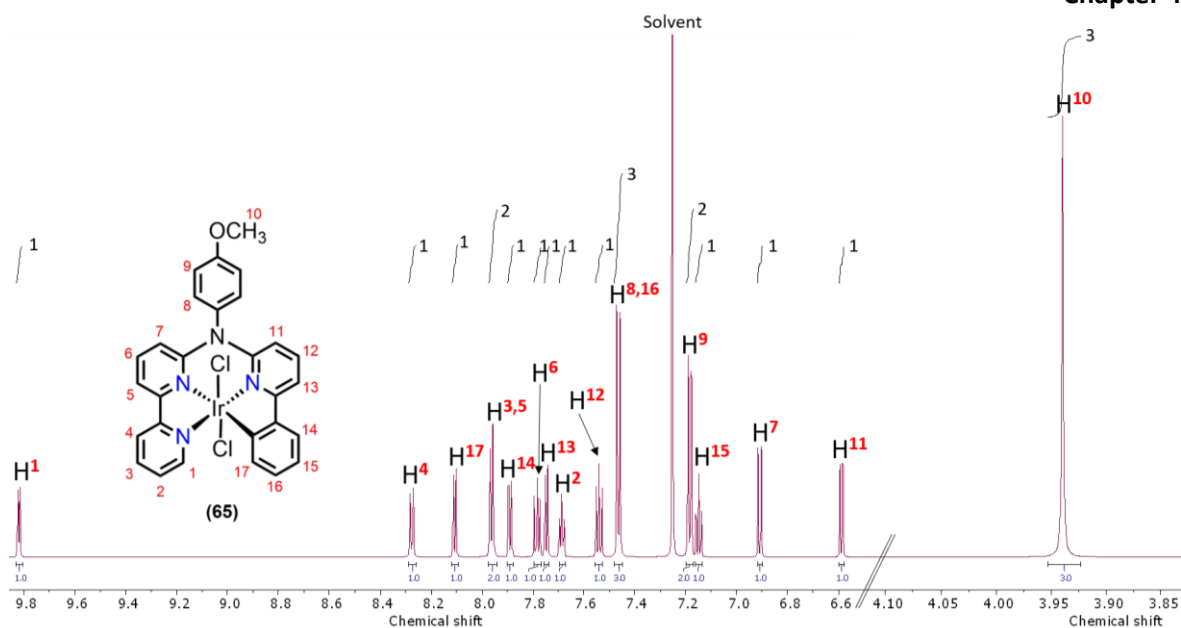


Figure 4.27: ^1H NMR spectrum of complex **65** in CDCl_3 , 700 MHz.

Reaction of **65** with ten equivalents of AgCN yielded the di-cyano complex **66** in a 22% yield as a very insoluble light green solid (**Figure 4.28**). The reaction went to completion after 3 days' reflux in dry DMF and the di-cyano complex formed exclusively. Metathesis of **65** with phenylacetylene, on the other hand, gave a poor conversion after 3 days' reflux. Conversion was measured by the integral area ratio of the two most downfield signals in the ^1H NMR spectrum (**Figure 4.29**), likely to correspond to the terminal bpy *ortho* proton, as a small upfield shift of 0.12 ppm is observed in the metathesized product(s) relative to the starting chloride complex **65**. It was not possible to isolate the mono- or di-acetylide complexes in their pure forms even after column chromatography (DCM : MeOH 0–2%). Molecular cation peaks of both the mono- and di-acetylide complexes were seen by mass spectrometry with m/z values of 764 (retention time = 2.32 minutes) and 824 (retention time = 2.69 minutes) respectively (**Figure 4.30**). A large molecular cation peak of m/z = 690 at a retention time of 2.38 minutes corresponding to the starting complex **65**, was also evident.

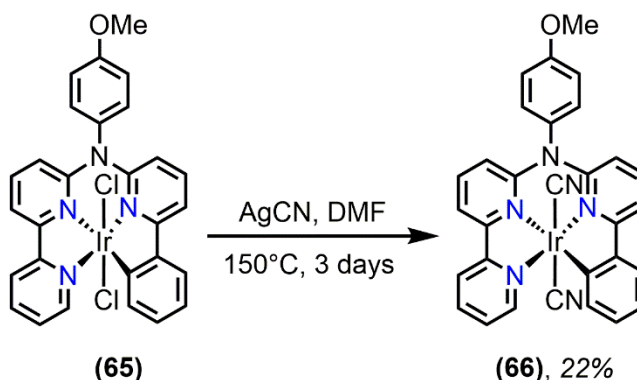


Figure 4.28: Synthetic scheme for the synthesis of complex **66**.

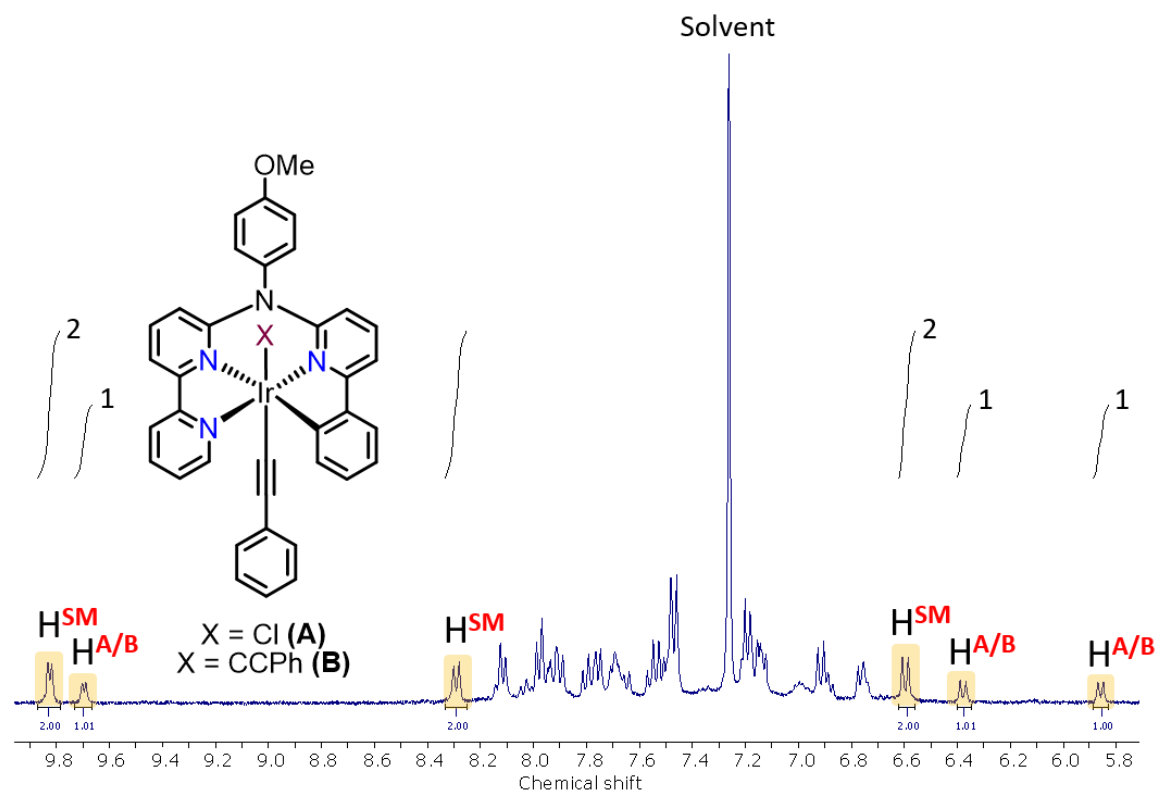


Figure 4.29: ¹H NMR spectrum of the crude reaction mixture of the metathesis of **65** with phenylacetylene after alumina column chromatography in CDCl₃, 400 MHz. A = mono-acetylide product; B = di-acetylide product and SM = starting material i.e. **65**.

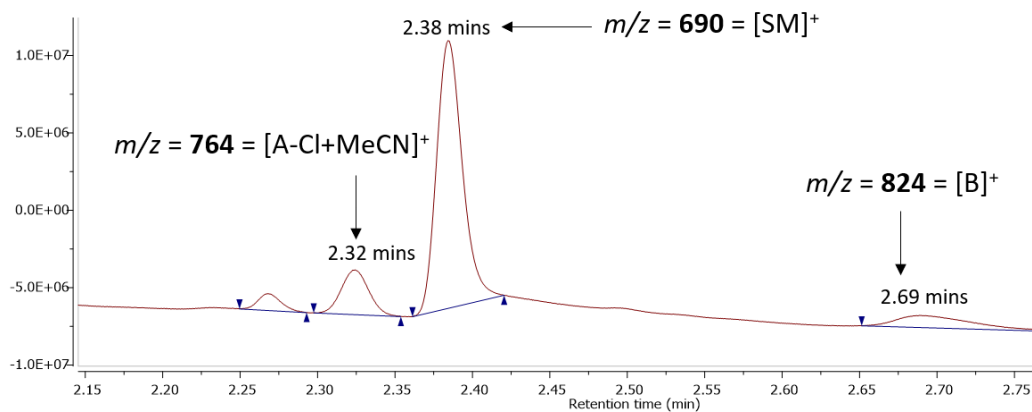


Figure 4.30: LCMS trace of the crude reaction mixture from the metathesis of **63** with phenylacetylene. A = mono-acetylide product; B = di-acetylide product and SM = starting material i.e. **65**.

Chelation of iridium by N[^]N[^]CH[^]CH and CH[^]N[^]N[^]CH ligands was unsuccessful; their respective reactions with IrCl₃·3H₂O in 2-ethoxyethanol and H₂O (3 : 1) remained as black solutions after an overnight reflux.

4.6.2 Crystallography

Crystal structures of complexes **88** and **89** were obtained by slow evaporation of a solution in MeCN (**Figure 4.31**). The binding mode of both complexes is of the type $[\text{Ir}(\text{C}^{\wedge}\text{N})_2(\text{N}^{\wedge}\text{N})]\text{PF}_6$. The presence of two isomers in the ^1H NMR spectrum of **88** could arise according to the orientation of the *p*-anisidine ligand. There is also evidence of two possible structural isomers of complex **89** by NMR spectroscopy and mass spectrometry; two suspected methoxy peaks are seen in the ^1H NMR aliphatic region at 3.59 and 3.68 ppm whilst the LCMS trace shows unresolved peaks at retention times of 3.01 and 3.05 minutes with equal m/z values of 931 corresponding to $[\text{M}-\text{PF}_6]^+$. The isomers could differ according to which bpy unit of the $\text{N}^{\wedge}\text{N}^{\wedge}\text{CH}^{\wedge}\text{CH}$ ligand coordinates to the iridium centre. Unfortunately, no crystal structures of any of the tetradentate Ir complexes **63-66** could be obtained.

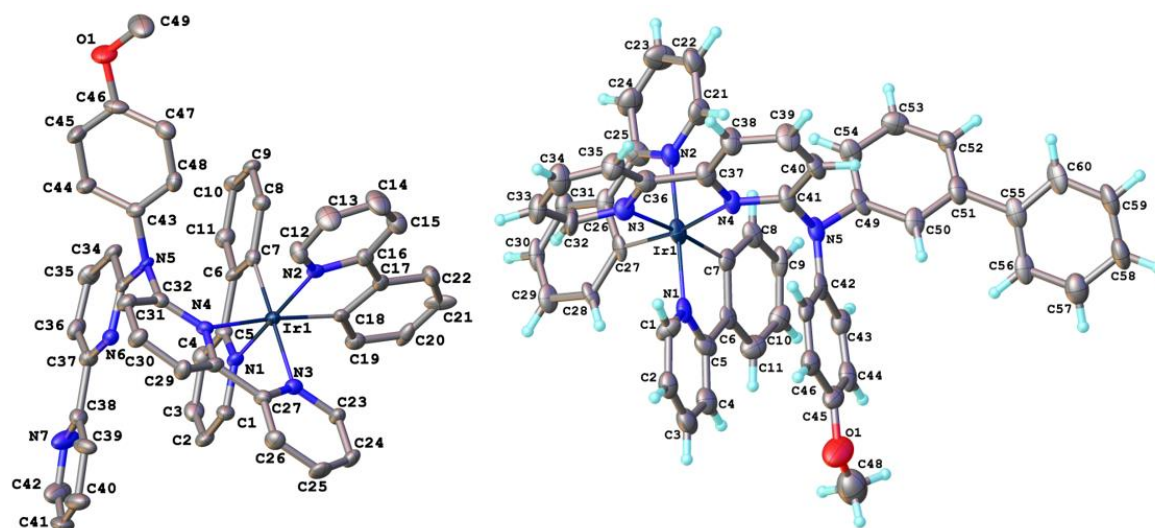


Figure 4.31: Crystal structures of **88** (left) and **89** (right). The PF_6^- counter-ion is omitted for clarity.

4.6.3 Electrochemistry

The electrochemical properties of **63-66** are shown in **Table 4.7**. All four complexes display a single quasi-reversible or irreversible oxidation potential in the window +0.73 to +1.15 V. Complexes **65** and **66** have a single quasi-reversible/irreversible reduction potential of -2.08 and -1.79 V respectively whereas complexes **63** and **64** display two irreversible reduction potentials. The first reduction potentials of **63** and **64** occur in the window -1.53 to -1.55 V and the second of their reduction potentials are both at -1.98 V. The $\Delta E_{1/2}$ values of the ionic complexes **63** and **64** ($\Delta E_{1/2} \approx 2.47$ V) are smaller than the $\Delta E_{1/2}$ values of the neutral complexes **65** and **66** ($\Delta E_{1/2} = 2.81$ and 2.94 V respectively). The single oxidation potential of the complexes is likely to be associated with the iridium(III) centre and the cyclometalating ligand as supported by DFT results (section 4.6.4) which show the HOMO orbitals of all four complexes are located partly over the metal centre and phenyl ppy ring. The reduction potentials of **63** and **64** are less negative than the reduction potentials of **65** and **66** – this could be explained by the cationic nature of the former set of complexes which

would make them better electron acceptors than the latter neutral duo. This hypothesis considers the irreversibility of all four complexes' redox processes and the reduced accuracy by which these processes are estimated through measurement of anodic (E_p^{ox}) and cathodic (E_p^{red}) peak potentials.

Table 4.7: Electrochemical properties of complexes **63-66** recorded in a 0.1 M electrolyte solution of NBu_4PF_6 in MeCN for **63** and **64** and DCM for **65** and **66**. Values were measured at a scan rate of 200 mV s^{-1} and are reported relative to SCE, measured using ferrocene as the standard ($E_{1/2}^{ox} = 0.42\text{ vs. SCE}$). E_p^{ox} and E_p^{red} are the anodic and cathodic peak potentials respectively. $\Delta E_{1/2} = E_p^{ox} - E_p^{red}$.

Complex	E_p^{ox}/V	E_p^{red}/V	$\Delta E_{1/2}/V$	$\Delta E_{H-L}/eV$
63	+0.95 ^{ir}	-1.53 ^{ir} , -1.98 ^{ir}	2.48	3.16
64	+0.91 ^{ir}	-1.55 ^{ir} , -1.98 ^{ir}	2.46	2.20
65	+0.73 ^{ir}	-2.08 ^{ir}	2.81	2.46
66	+1.15 ^{qr}	-1.79 ^{qr}	2.94	2.82

4.6.4 DFT

Figure 4.32 shows the energies and diagrams of the frontier molecular orbitals of **63-66**. The HOMOs of the cationic complexes **63** and **64** are located exclusively over the axial chloride ligands and the iridium centre whereas the LUMOs are located equally over the two bpy units. The LUMOs of **65** and **66** reside over the single bpy unit whereas the HOMOs have an extra contribution from the phenyl ppy ring in addition to the metal and the axial chlorides. The frontier molecular orbitals of **63** and **64** are lower in energy than those of the neutral complexes **65** and **66** by roughly 2-4 eV – this is because the calculations were performed in a vacuum so the orbital energies of the charged complexes **63** and **64** are artificially low and cannot be compared directly with the HOMO and LUMO energies of the uncharged complexes **65** and **66**. The HOMO and LUMO orbitals of **63** are both destabilized by the metathesis of an axial chloride ligand with phenylacetylene. The LUMO is destabilized by a much lesser extent than the HOMO so the 3.16 eV HOMO-LUMO gap of **63** shrinks to 2.20 eV in **64**. On the other hand, metathesis of the chloride ligands in **65** with cyanide stabilizes both frontier molecular orbitals but the HOMO is stabilized to a greater extent than the LUMO so the 2.46 eV HOMO-LUMO gap of **65** widens to 2.82 eV in **66**. The major orbital contribution to the excited state of all four complexes is a HOMO→LUMO transition (69-70%).

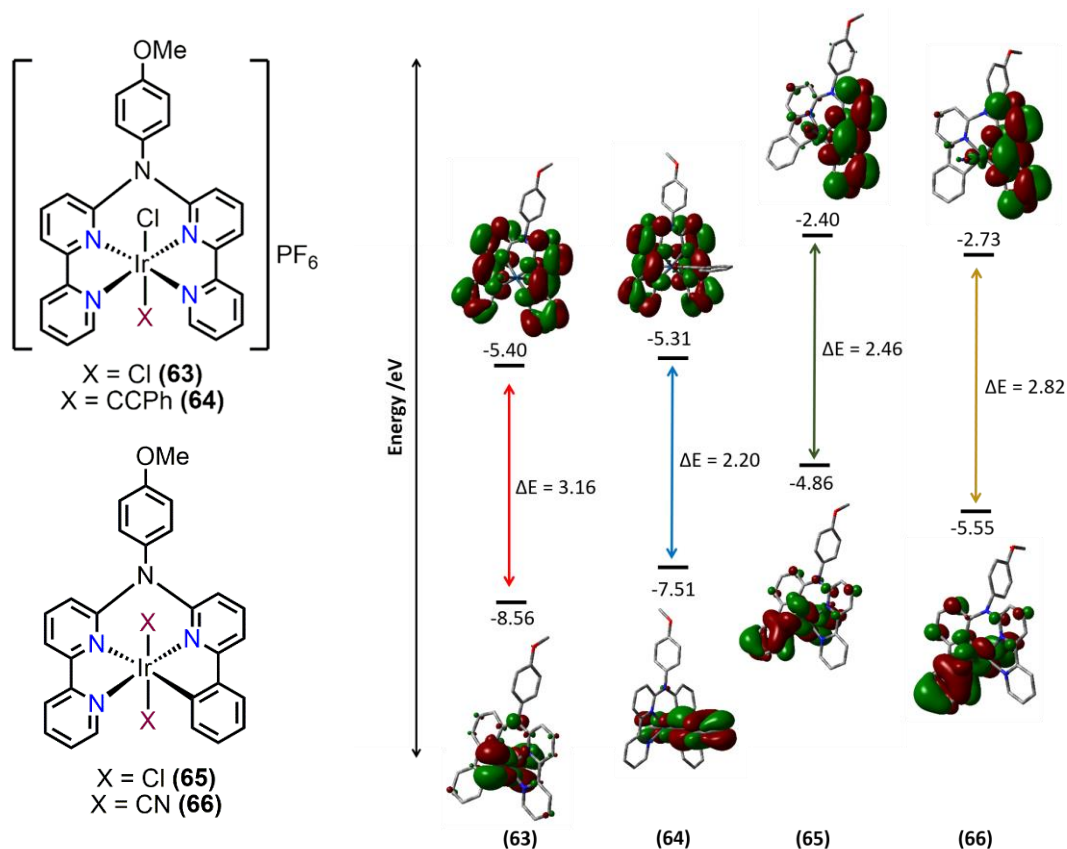


Figure 4.32: HOMO and LUMO orbitals and energies of **63–66** as calculated by DFT.

4.6.5 Photophysical properties

4.6.5.1 Absorption

The absorption spectra of **63–66** are shown in **Figure 4.33**. All four complexes show intense bands between 256 and 298 nm associated with ¹LC π – π^* transitions. Complexes **63–65** have a distinct peak within this region whereas **66** has a series of small peaks/shoulders at 256, 279 and 298 nm. The absorption coefficients for the LC transitions of **63** and **64** range between 1.4×10^4 and $3.2 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ whereas the coefficient for **65** and **66** are an order of magnitude lower with $\epsilon \leq 5.5 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$. The weaker bands between 341 and 368 nm ($1.4 \times 10^3 \leq \epsilon \leq 1.1 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$) of all four complexes are more characteristic of d– π^* MLCT transitions as observed in bidentate [Ir(bpy)₂Cl₂]⁺-type systems.^{276,277} The MLCT bands of the metathesized complexes **64** and **66** are slightly blue shifted by 4–6 nm (340 – 495 cm^{-1}) with respect to their di-chloride analogues. The lowest energy MLCT transitions of **63–65** occur at 447, 457 and 420 nm respectively ($\epsilon \leq 7.5 \times 10^2 \text{ M}^{-1}\text{cm}^{-1}$).

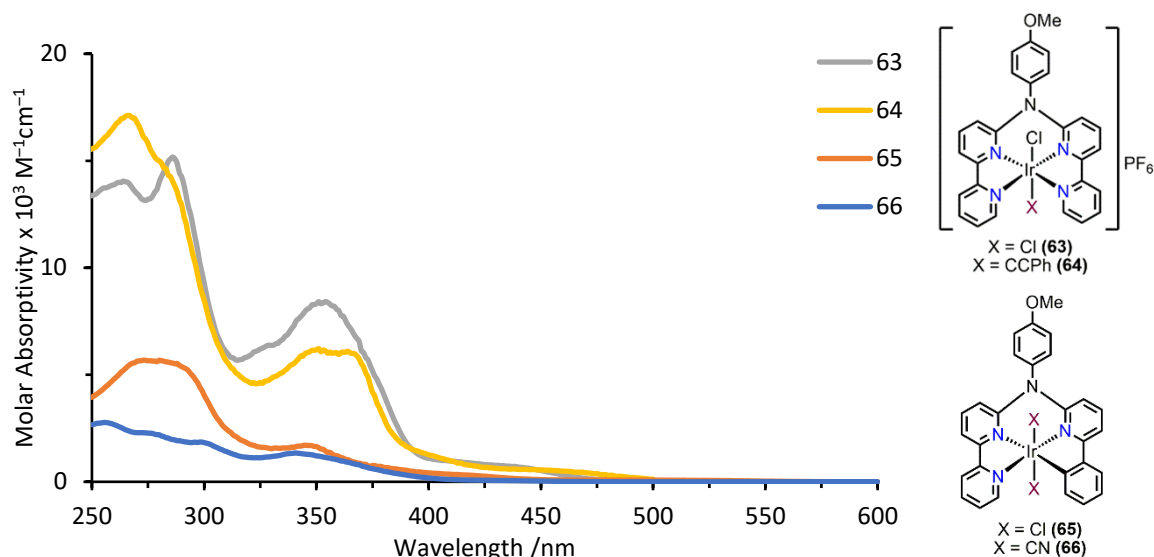


Figure 4.33: Absorbance spectra of **63-66** recorded in MeCN (**63** and **64**) and DCM (**65** and **66**).

4.6.5.2 Emission

The RT PL emission profiles for complexes **63**, **64** and **66** are shown in **Figure 4.34**. All three profiles are broad and unstructured. The excited states of **63** and **64** are likely to be of mixed LC/MLCT character in accordance with related literature examining $[\text{Ir}(\text{bpy})_2\text{Cl}_2]^+$ which suggests the energy gap between $\pi-\pi^*$ and $d-\pi^*$ states is small.^{276,277} Emission of **65** is too weak for inclusion in the figure. The emission maxima of **64** and **66** are relatively close together at 589 and 576 nm respectively whereas the emission of **63** is redder ($\lambda_{\text{max}} = 687 \text{ nm}$). DFT calculations fail to rationalise the observed photophysical properties. The emission maximum of **64** is blue shifted by 98 nm (2420 cm^{-1}) compared to the maximum of **63**; this is likely to be a result of the increased ligand field splitting induced by the strong σ -donating acetylide ligand which acts to raise the energy of the MLCT excited state.

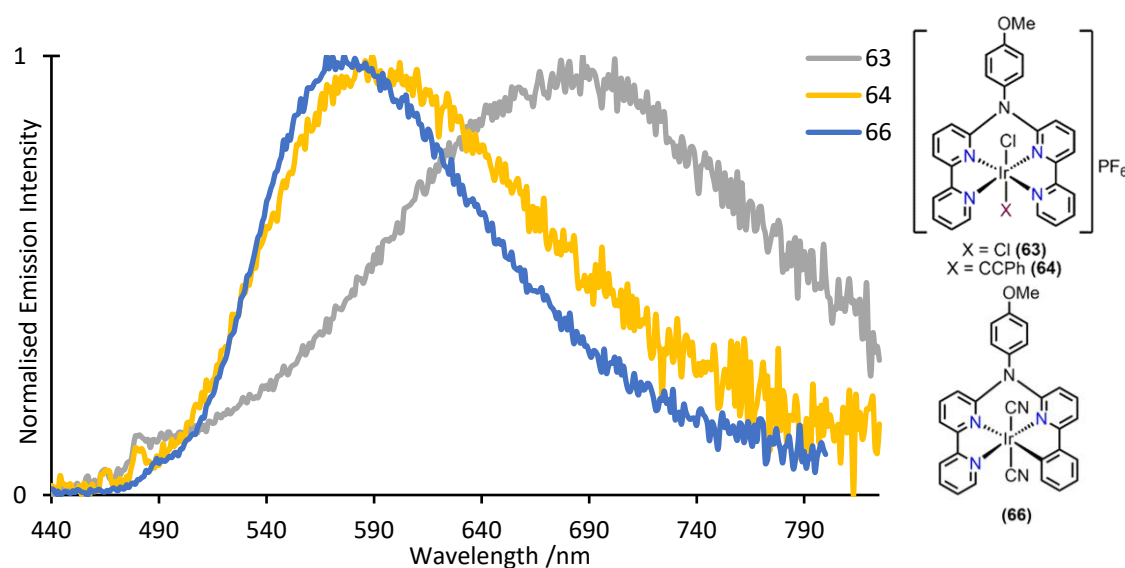


Figure 4.34: Normalised RT emission spectra of **63**, **64** and **66** recorded in degassed MeCN (**63** and **64**, $\lambda_{\text{exc}} = 420 \text{ nm}$) and degassed DCM (**66**, $\lambda_{\text{exc}} = 425 \text{ nm}$).

The low temperature PL emission spectra of **63-66** are shown in **Figure 4.35**. The profile of **63** is largely unstructured with a broad peak at 643 nm and a shoulder at 563 nm. The profiles of **64-66** are more structured, for example, **65** has two fairly broad peaks at 557 and 600 nm whereas the two peaks in the spectrum of **64** at 487 and 524 nm are much sharper. The highest energy 77 K emission maximum of **66** are blue shifted by 89 nm (3170 cm^{-1}) with respect to its RT emission maximum (**Figure 4.36**). The 77 K lifetimes of the four complexes range from 3.1 to 5.9 μs and are greatly increased compared to their lifetimes at RT. The largest change in lifetime from RT to 77 K is observed in **65** whose 77 K lifetime of 3.1 μs is exactly an order of magnitude larger than its 0.31 μs RT lifetime. On the other hand, the lifetime of **63** only increases by a factor of 2.4 at 77 K compared to RT ($\tau = 3.4$ vs. 1.4 μs).

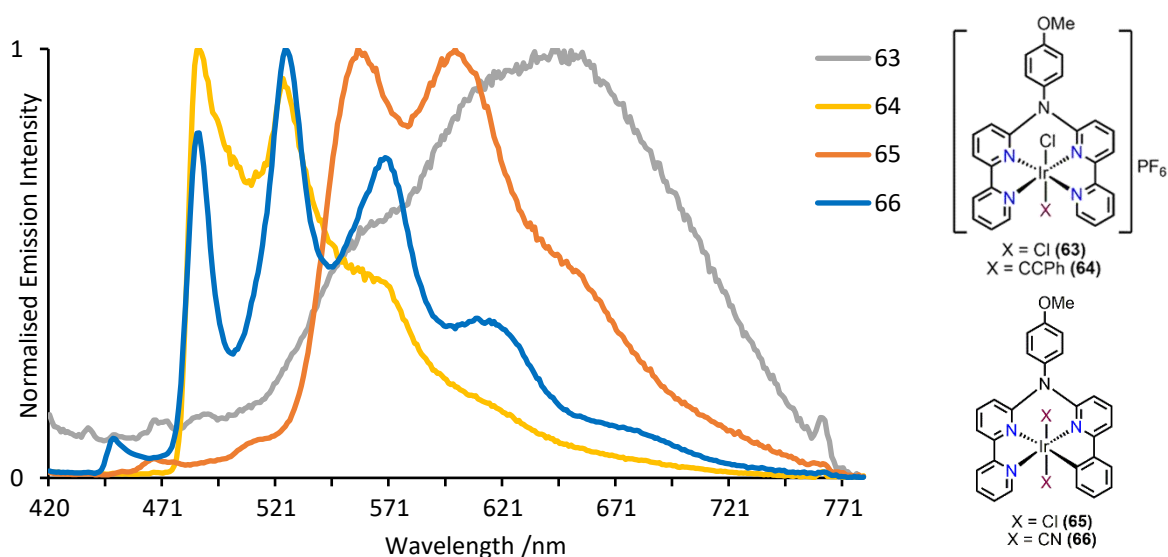


Figure 4.35: Normalised 77 K emission spectra of **63-66** in butyronitrile (**63** and **64**) and EPA (**65** and **66**), $\lambda_{\text{exc}} = 400\text{ nm}$

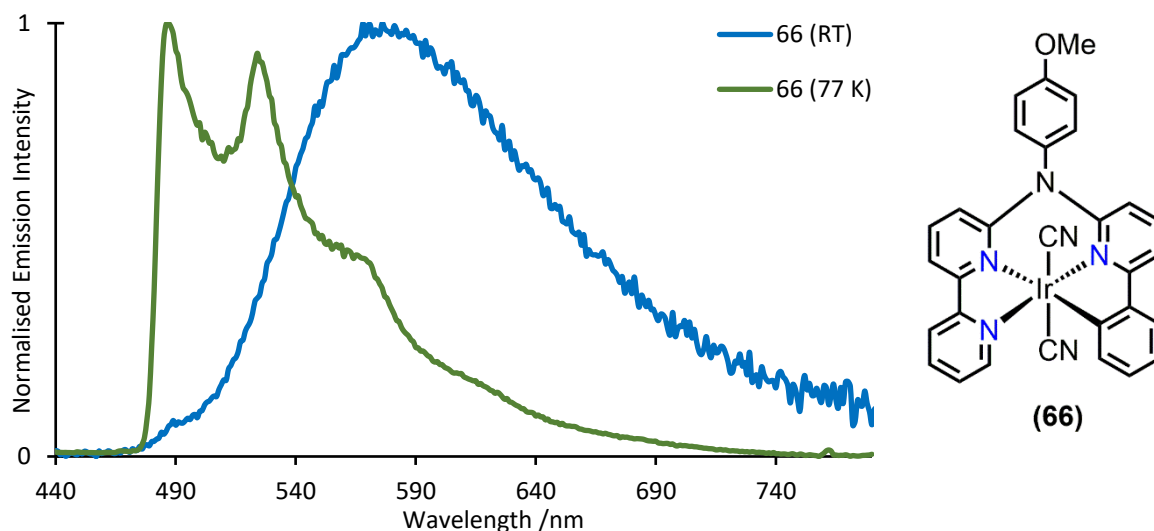


Figure 4.36: Normalised emission spectra of **66** at RT in degassed DCM ($\lambda_{\text{exc}} = 425\text{ nm}$) and at 77 K in EPA ($\lambda_{\text{exc}} = 400\text{ nm}$).

Table 4.8 shows the photophysical properties of the four iridium complexes in MeCN (**63** and **64**) and DCM (**65** and **66**). The quantum yields are again disappointingly low; **66** has the highest PLQY of the series at 2%, followed by **63** ($\phi = 1\%$). The PLQYs of **64** and **65** are below 1%. Metathesis of the chloride ligands of **65** with cyanide raise the quantum yield by 1.4% whereas metathesis of the chloride ligand of **63** with phenylacetylide reduces the quantum yield from 1.0% to 0.4%. The low quantum yields of **63** and **65** might be rationalised by their di-axial chloride ligands which fail to provide sufficient ligand field strength for PL performance, similar to the complexes bearing tridentate ligands discussed in Chapter 3. It is disappointing that the quantum yield of **66** is not higher, given that the complex contains three C^- donors and that the rigidity associated with the tetradentate $N^{\wedge}N^{\wedge}N^{\wedge}C$ ligand might be expected to help reduce vibrational non-radiative decay.

Table 4.8: Photophysical properties of **63-66** recorded in degassed MeCN at RT ($\lambda_{exc} = 420$ nm) and in butyronitrile at 77 K ($\lambda_{exc} = 400$ nm) for complexes **63** and **64**, ^a photophysical properties of **65** and **66** were recorded in degassed DCM at RT ($\lambda_{exc} = 425$ nm) and in EPA at 77 K ($\lambda_{exc} = 400$ nm). Aerated PLQYs and lifetimes are shown in brackets.

Complex	63	64	65 ^a	66 ^a
Absorption Maxima /nm ($\epsilon / M^{-1} cm^{-1}$)	264 (14000)	266 (31500)	267 (5480)	256 (2770)
	286 (15200)	287 (25400)	292 (5270)	279 (2200)
	351 (8420)	345 (10900)	345 (1740)	298 (1860)
	447 (616)	368 (10700)	420 (301)	341 (1350)
		457 (751)		
λ_{max} / nm	687	589	664	576
PLQY /% degassed (aerated)	1.0 (0.9)	0.4 (0.0)	0.1 (0.1)	1.5 (1.5)
Lifetime /ns degassed (aerated)	1390 (950)	880 (20)	310 (35)	480 (48)
$k_r \times 10^5 s^{-1}$	0.065	0.044	0.049	0.31
$k_{nr} \times 10^5 s^{-1}$	7.2	11	33	20
77 K λ_{max} / nm	643	487, 524	557, 600	487, 525, 569
77 K Lifetime / μs	3.4	5.9	3.1	3.6

The lifetimes of the $N^{\wedge}N^{\wedge}N^{\wedge}N$ complexes **63** and **64** are 1390 and 880 ns respectively whereas the lifetimes for the $N^{\wedge}N^{\wedge}N^{\wedge}C$ complexes are much shorter with values of 310 (**65**) and 480 ns (**66**). The $N^{\wedge}N^{\wedge}N^{\wedge}C$ series of complexes have higher rates of radiative and non-radiative decay than $N^{\wedge}N^{\wedge}N^{\wedge}N$ complexes, for example, the k_r and k_{nr} values of **66** are $3.1 \times 10^4 s^{-1}$ and $2 \times 10^6 s^{-1}$ compared to $4.4 \times 10^3 s^{-1}$ and $1.1 \times 10^6 s^{-1}$ respectively for **64**. Cyclometallation could play a role in dictating the relative rate constants for radiative and non-radiative decay.

4.7 Summary

In conclusion, a series of four tetradentate ligands have been prepared containing a dual combination of bpy, ppy or biphenyl units joined together by a *para*-anisidine linker. The four tetradentate ligands of types: (i) $N^{\wedge}N^{\wedge}N^{\wedge}N$, (ii) $N^{\wedge}N^{\wedge}N^{\wedge}CH$, (iii) $N^{\wedge}N^{\wedge}CH^{\wedge}CH$, and (iv) $CH^{\wedge}N^{\wedge}N^{\wedge}CH$ were prepared via Buchwald-Hartwig aminations. Inspiration for our series of *p*-anisidine-linked ligands came from the work by Huo *et al.* who reported a series of platinum complexes containing aniline-linked tetradentate ligands in 2010.⁷

Three of the four ligands coordinated platinum in a tetradentate fashion to create two novel platinum complexes of the types $[\text{Pt}(\text{N}^{\wedge}\text{N}^{\wedge}\text{N}^{\wedge}\text{N})](\text{PF}_6)_2$, **59**, and $[\text{Pt}(\text{N}^{\wedge}\text{N}^{\wedge}\text{N}^{\wedge}\text{C})]\text{PF}_6$, **60**, in addition to the $\text{Pt}(\text{C}^{\wedge}\text{N}^{\wedge}\text{N}^{\wedge}\text{C})$ complex, **62**, which has previously been reported by our group.^{152,254} Reaction of the $\text{N}^{\wedge}\text{N}^{\wedge}\text{CH}^{\wedge}\text{CH}$ ligand with K_2PtCl_4 in acetic acid yielded the $\text{Pt}(\text{N}^{\wedge}\text{N}^{\wedge}\text{C})\text{Cl}$ complex, **61**, instead of the desired $\text{Pt}(\text{N}^{\wedge}\text{N}^{\wedge}\text{C}^{\wedge}\text{C})$ complex. Emission maxima of **59-62** at RT ranged from 510 to 646 nm and quantum yields of up to 6% were achieved. The luminescence of **59**, **60** and **62** was far inferior to the luminescence properties of other Pt(II) complexes containing tetradentate ligands reported in the literature and it is difficult to explain why the quantum yields are so low compared to the literature compounds given their similarity in structure.

Two novel iridium complexes containing tetradentate $\text{N}^{\wedge}\text{N}^{\wedge}\text{N}^{\wedge}\text{N}$ and $\text{N}^{\wedge}\text{N}^{\wedge}\text{N}^{\wedge}\text{CH}$ ligands (**63** and **65**) were synthesized using identical conditions for the synthesis of chloro-bridged iridium dimers i.e. reflux of $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ and tetradentate ligand in 2-ethoxyethanol and H_2O overnight. The yellow and orange complexes, **63** and **65**, contained a single iridium ion in a pseudo-octahedral environment with two axial chloride ligands. Both were weak red emitters in solution with emission maxima of 664 and 687 nm and quantum yields of 1%. We report the first two examples of chloride metathesis in iridium complexes containing tetradentate ligands in the synthesis of **64** and **66** whose structure types are $[\text{Ir}(\text{N}^{\wedge}\text{N}^{\wedge}\text{N}^{\wedge}\text{N})(\text{CCPh})\text{Cl}]\text{PF}_6$ and $\text{Ir}(\text{N}^{\wedge}\text{N}^{\wedge}\text{N}^{\wedge}\text{C})\text{CN}_2$ respectively. Chloride metathesis was carried out using the procedure developed for the metathesis of complexes **47-50** containing tridentate $\text{N}^{\wedge}\text{C}^{\wedge}\text{N}$ ligands, as discussed in Chapter 3. The metathesized complexes **64** and **66** were both yellow emitters ($\lambda_{\text{max}} = 576\text{-}589$ nm) but still suffered from low quantum yields with a maximum PLQY of 1.5%. DFT calculations predict the excited states of **63-66** to have a major contribution from a HOMO→LUMO transition with the HOMO occupying the axial ligands and iridium centre whilst the LUMO covers the bpy unit(s). The HOMO is also distributed over the phenyl rings of **65** and **66**.

Chapter 5 - Dinuclear complexes of Platinum and Iridium

5.1 Introduction

In contrast to the widely explored area of mononuclear iridium systems, the study of di- and multi-nuclear iridium(III) complexes is a comparatively untouched field. Di-iridium complexes were initially viewed as inferior emitters to mononuclear complexes because the PLQYs of the few-known di-iridium species, containing bridging ligands such as chloride, were typically lower than those of mononuclear complexes obtained from them. Furthermore, the preparation of di-iridium complexes is likely to be synthetically more challenging due to the high probability of obtaining a mixture of diastereoisomers. Recent judicious molecular design, however, has shown that di-iridium complexes do not necessarily have inferior photophysical properties to mononuclear complexes. A variety of recently reported di-iridium complexes featuring conjugated bridging ligands are indeed very efficient emitters with solution-state PLQYs approaching 100%. The incorporation of a bridging ligand and second iridium centre generates several key advantages over mononuclear complexes, such as: (i) the opportunity to modulate the flexibility and length of the bridging ligand to control aggregation-induced phosphorescent emission (AIPE); (ii) the introduction of intramolecular π - π interactions; (iii) an increased spin-orbit coupling (which may lead to an increase in k_r); (iv) the opportunity to extend the conjugation of the bridging ligand to target efficient red-emitters and (v) the possibility of dual emission originating from the lowest energy excited states of mixed character.²⁷⁸

On the other hand, interest in the luminescence properties of di-platinum complexes has gained momentum in the past ten years. The square planar Pt(II) geometry allows for aggregate- and excimeric-based emission in the ground and excited states respectively via inter- and/or intramolecular π - π interactions; these interactions drastically influence the resulting emissive properties of the complex because the emission from aggregates and excimers is typically red-shifted compared to that of the isolated monomer. The occurrence of intramolecular interactions in di-platinum(II) complexes depends on the separation and relative disposition of the units, or in other words, the length and flexibility of the linker. Williams *et al.* published a detailed review of luminescent multinuclear platinum complexes in 2018 which feature one or more platinum complexes per molecule or which contain Pt(II) and one (or more) other metal centres such as Ir(III) or Ru(II).²⁷⁹ In the same year, Bryce and co-workers also published an excellent review of di-iridium(III) complexes and their application in LECs and OLEDs; this includes bis(μ -Cl), bis(μ -N⁺C⁺O)-type and N⁺O-type bridged di-iridium(III) complexes.²⁷⁸

In keeping with the synthetic work discussed in this Chapter, this review will mainly focus on N⁺N- and N⁺C-type bridged di-iridium complexes and will also give a few brief examples of relevant di-

platinum and heteronuclear Ir(III)-Pt(II) complexes. We provide some other recent reviews of binuclear platinum²⁸⁰ and iridium complexes.²⁸¹

Before starting the review, it is important to draw attention to the ruthenium complexes (i) to (iv) displayed in **Figure 5.1** because they feature the identical bridging N[^]C[^]N tridentate ligand as used in our series of novel mono-, di- and hetero-nuclear platinum(II) and iridium(III) complexes. The *p*-anisidine-based bridging ligand has only ever been reported in the context of ruthenium chemistry by Zhong *et al.* five years ago. The four di-ruthenium complexes shown in **Figure 5.1** were synthesized and characterised by single-crystal X-ray analysis, DFT, TD-DFT and electrochemistry. The electronic form of the singly oxidised state was a fully charge-delocalised system that was biased towards the ruthenium components in complex (iv) and biased towards the amine bridge in complexes (i) and (ii). The vinyl-functionalized di-ruthenium complex (iii) was electro-polymerised into a film which displayed multistate NIR electrochromism for potential applications as molecular logic gates.²⁸² The luminescence properties of complexes (i) to (iv) were not investigated, but mononuclear [Ru(N[^]C[^]N)(N[^]N[^]N)]⁺ complexes are known to be only weak emitters.

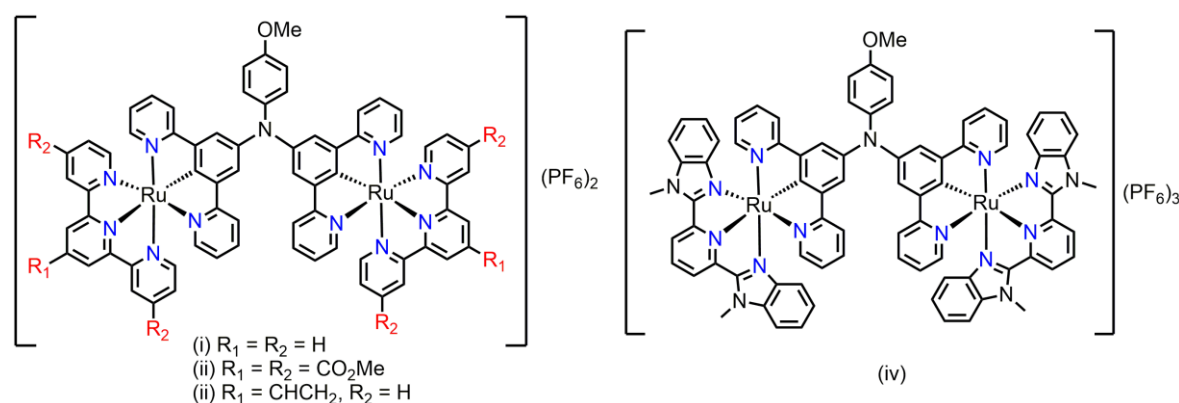


Figure 5.1: Ruthenium complexes (i) to (iv) featuring the identical *p*-anisidine-bridged bis-tridentate ligand, as used for our series of novel mono- and di-nuclear (III) and Pt(II) systems discussed later in this chapter.

5.2 Di-iridium complexes

The following section refers to di-iridium complexes, **A-S**, shown in **Figure 5.2** and whose PL data are listed in **Table 5.1**.

5.2.1 N[^]N-type di-iridium complexes: **A** to **F**

Luisa De Cola and co-workers reported two dinuclear iridium complexes connected by a conjugated bridging ligand containing three (**A**) or four (**B**) phenyl units. Complexes **A** and **B** display a broad, structureless red PL emission in MeCN at RT with λ_{max} values of 608 and 606 nm. These bands are attributed to the ³MLCT transition involving the coordinated bipyridine linker. The length of the phenyl chain has very little effect on the photophysical properties of the two complexes, for example, the quantum yields of **A** and **B** are 9% and 18% respectively whilst their luminescence lifetimes are 390 and 410 ns.²⁸³ Complexes **D** and **S** are the first examples of dinuclear ionic iridium

complexes that display AIPE. In neat film, the PLQYs of **D** and **S** are 37% and 26% respectively, but they show almost no emission in solution; this suggests that the complexes might be AIPE active. Complex **S** is one of the most red-emitting ionic Ir(III) complexes reported with its 692 nm RT emission maximum red shifted by 48 nm (1080 cm^{-1}) compared to **D** - this may be due to the more extended conjugation in the ancillary ligand of **S**.²⁸⁴ The dumbbell shaped dinuclear complexes **E** and **F** featuring an oligophenylene-ethynylene spacer emit at 588 and 521 nm respectively in MeCN. DFT calculations conclude that the lowest triplet excited state corresponds to a $^3\pi-\pi^*$ state located on the conjugated spacer. The HOMO of complex **E** resides on the phenylene-ethynylene linker and the LUMO is located on the bpy unit. The calculated HOMO-LUMO gap in both **E** and **F** is 3.2 eV which is consistent with their $\Delta E_{1/2}$ values of 2.66 and 2.64 V respectively. The similar oxidation potentials of **E** and **F** (+0.99 and +1.06 V respectively) prove that the oxidation involves the π -conjugated spacer rather than the end capping iTMCs.²⁸⁵

5.2.2 N[^]C-type bridged di-iridium complexes: **G** to **S**

The diastereotopic pair of complexes, **J** and **K**, were easily separated by column chromatography with isolated yields of around 25% for each isomer. Their photophysical properties are practically identical with quantum yields of 65% and emission maxima of 622 and 625 nm respectively.²⁸⁶ The strong *trans* effect of the cyclometalating carbon of the N[^]C[^]N ligand dictates the orientation of the ppy ligand such that the ppy pyridine is *trans* to the cyclometalating carbon. The radiative rate constants of **J** and **K** are over four times bigger than the rate constant of the mononuclear analogue ($k_r = 9 \times 10^5\text{ s}^{-1}$ vs. $2 \times 10^5\text{ s}^{-1}$); this highlights the benefit of adding the second metal ion in terms of increased spin-orbit coupling. The quantum yields of **J** and **K** ($\phi = 65\%$) are also slightly higher than the PLQY of the mononuclear complex ($\phi = 59\%$) despite the latter's blue shifted emission ($\lambda_{\text{max}} = 595\text{ nm}$).²⁸⁶ Finally, Kozhevnikov, Williams and co-workers synthesized complexes **G-I** and **L-P** which all feature a 4,6-diarylpyrimidine as bis-N[^]C coordinating bridging ligands. Similar to **J** and **K**, the strong *trans* influence of the metallated rings dictates the relative disposition of the ligands. The dithienylpyrimidine-containing complex, **L**, has the reddest emission peaking at 572 nm whilst the highest energy emission ($\lambda_{\text{max}} = 517\text{ nm}$) is that of the cyanide-containing complex, **N**. Interestingly, the emission of complex **M** is red-shifted by 35 nm (1230 cm^{-1}) with respect to its chloride analogue, **N**. The variation in emission energies of **G-I** and **L-P** arises from a larger stabilization/destabilization of the HOMO than the LUMO. All eight complexes are very efficient emitters with PLQYs ranging from 88% (i.e. **G** and **N**) to 100% (i.e. **I**, **O** and **P**). Furthermore, the phosphorescence lifetimes ($\tau \approx 500\text{ ns}$) are unusually short for complexes of such brightness. These impressive properties can be rationalised by the high rates of radiative decay ($2.4 \times 10^5 - 2.8 \times 10^6\text{ s}^{-1}$), possibly due to greater spin-orbit coupling facilitated by the second Ir centre, and to the low k_{nr} values ($1.5 \times 10^4 - 2.1 \times 10^5\text{ s}^{-1}$) that could be linked to the rigidity of the binuclear scaffold.²⁸⁷

Table 5.1: Photophysical properties of di-iridium shown in **Figure 5.2**, measured in degassed MeCN, DCM, toluene or thin film at RT, ^{sh} = shoulder. Aerated values are shown in brackets.

Reference	Complex	$\lambda_{\text{max}}^{\text{abs}}/\text{nm}$ ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$)	$\lambda_{\text{max}}^{\text{em}}/\text{nm}$	PLQY/%	τ/ns	$k_r \times 10^5 \text{ s}^{-1}$	$k_{nr} \times 10^5 \text{ s}^{-1}$
283	A	250 (90000), 270 (83000), 295 (69000), 330 (65000), 355 (60000), 450 (4000),	608	9 (2)	390 (72)	-	-
283	B	225 (75000), 265 (70000), 295 (59000), 340 (61000), 355 (60000), 450 (4000)	606	18 (2)	410 (75)	-	-
288	C	250 (93534), 337 (40055), 360 (32847), 390 (14454), 457 (9198), 606 (2492)	-	-	-	-	-
284	D	252, 369	644	37	48	78	130
285	E	217, 270, 372	588	0.9	400	0.23	28
285	F	245, 305, 363	521	<1	1200	0.06	85
287	G	281 (70400), 309 (49600), 376 (31500), 404 (29800), 442 (22600), 494 (9510), 526 (7120)	568, 599 ^{sh}	88	570 (230)	15	2.1
287	H	279 (79300), 303 (55800), 358 (32700), 372 (38600), 397 (33200), 430 (24300), 477 (8970), 514 (6560)	570	91	590 (220)	15	1.5
287	I	277 (53600), 335 (27600), 360 (34300), 409 (29700), 433 (25200), 473 (13700), 498 (7070)	528, 557 ^{sh}	100	360 (160)	28	-
286	J	250 (68800), 287 (54000), 339 (31900), 398 (16300), 448 (9930), 498 (18900), 537 (10800),	622	65	760 (520)	8.6	4.6
286	K	250 (69700), 286 (52900), 340 (32800), 399 (16500), 447 (10700), 497 (19700), 537 (10900),	625	65	730 (460)	8.9	4.8
287	L	281 (62300), 305 (36200), 337 (31800), 358 (42200), 407 (30300), 446 (25300), 489 (36800), 514 (16100), 554 (2100)	572, 611 ^{sh}	94	4000 (380)	2.4	0.15
287	M	279 (63400), 312 (41500), 360 (32300), 408 (28600), 441 (24400), 484 (11400), 520 (8080)	552, 582 ^{sh}	94	440 (210)	21	1.4
287	N	279 (56300), 315 (38800), 353 (33000), 409 (33500), 460 (12300), 491 (5390)	517, 547 ^{sh}	88	590 (240)	15	2.0
287	O	270 (54700), 310 (39500), 326 (31100), 363 (30400), 398 (25600), 438 (18500), 484 (10300), 514 (7300)	554, 576 ^{sh}	100	550 (160)	18	-
287	P	260 (56500), 281 (51500), 327 (34900), 354 (36500), 385 (22500), 430 (17500), 474 (13400), 500 (7800)	526, 557 ^{sh}	100	590 (230)	17	-
289	Q	-	-	-	-	-	-
289	R	-	-	-	-	-	-
284	S	254, 376	692	26	39	68	190

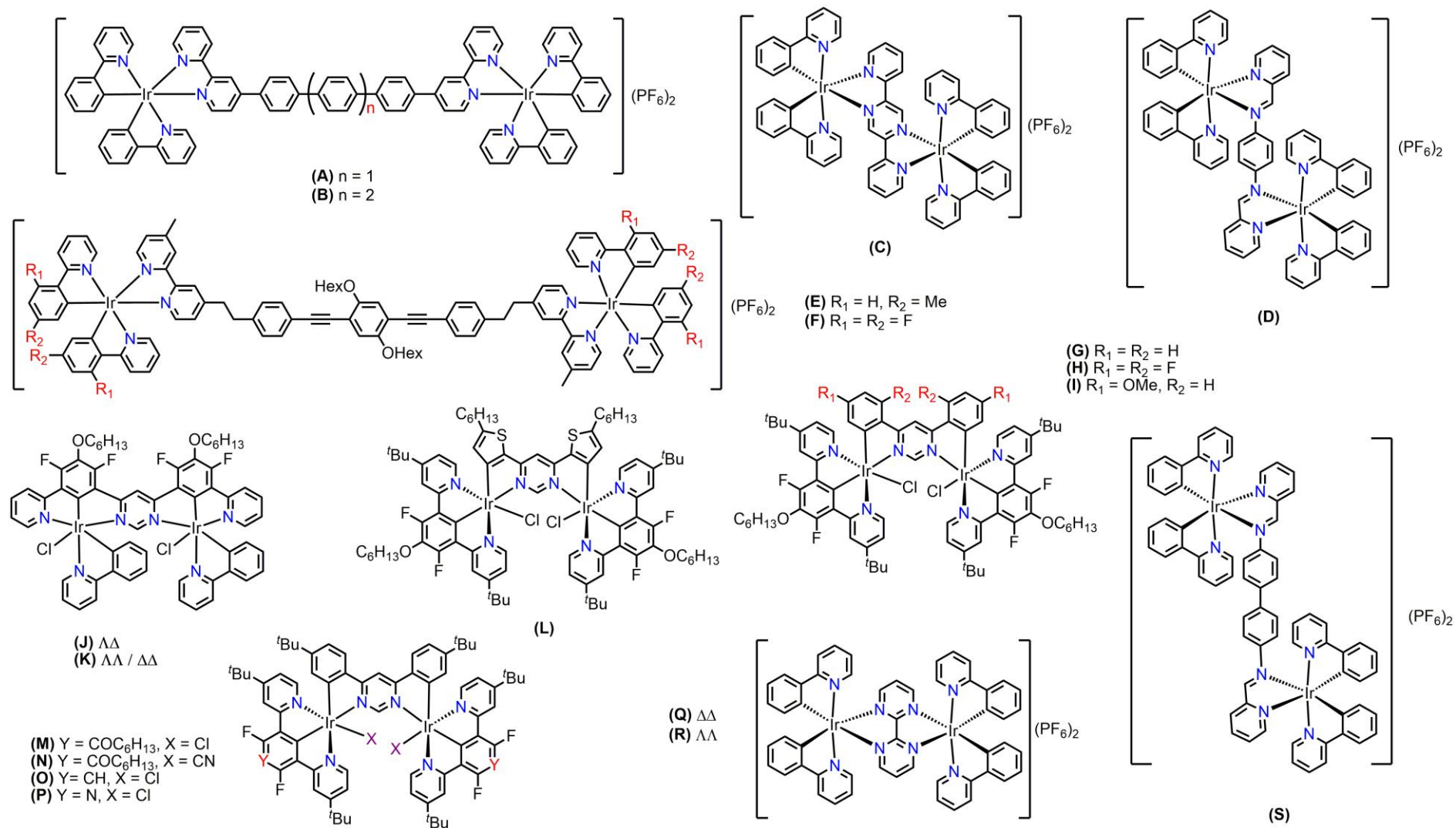


Figure 5.2: Structures of di-iridium complexes A-S.

5.3 Di-platinum complexes

A few examples of di-platinum complexes featuring N⁺C⁺N components are shown in **Figure 5.3**. The platinum N⁺C⁺N units of complex (v) were held together via a rigid xanthene linker which facilitated deep red intramolecular excimer emission in DCM solution that peaked at 690 nm. The di-platinum complex was obtained after an 11-day reflux in MeCN and H₂O with an excess of K₂PtCl₄; shortening the reaction time to 3 days and using only 1.1 equivalents of K₂PtCl₄ to xanthene-linked ditopic pro-ligand yielded the mono-platinum complex. The mono-platinum complex displayed green emission ($\lambda_{\text{max}} = 510, 542 \text{ nm}$) due to the lack of intramolecular Pt–Pt interactions. Complex (v) had a luminescence lifetime of 1.7 μs and a quantum yield of 20% which is fairly impressive given that much of the emission is in the NIR region where efficiencies invariably fall off.²⁹⁰ Guerchais and co-workers synthesized complexes (vi) and (vii), which contain two platinum chromophoric units connected through a polyether chain via either the phenylacetylene ligand (vi) or the central benzene ring of the tridentate ligand (vii).²⁹¹ The presence of the flexible bridge favours intramolecular π – π interactions via a folded state. The RT spectral profile of (vii) in degassed DCM at a concentration of 10^{-5} M appears as a very broad band featuring several peaks likely to be the sum of two electronic transitions i.e. the monomer-like emission for which the maximum is located at 547 nm and the red shifted excimer emission which peaks at 670 nm. The excimer interactions of the acetylide-linked complex (vi) are much stronger than the interactions of complex (vii) as shown by TD-DFT calculations and by its NIR emission which peaks at 692 nm representing a 22 nm (475 cm^{-1}) red shift compared to the excimer emission of (vii). Complexes (vi) and (vii) display a positive solvatochromism i.e. a bathochromic shift of emission in more polar solvents such as MeCN. The quantum yields of (vi) and (vii) are both approximately 8% but again these values are highly solvent dependent, for example, the PLQY of (vi) in THF is 22% and that of (vii) in MeCN is 8%. The form of the di-platinum complexes, i.e. extended or folded, can be controlled by the choice of solvent or by reversible cation binding to the polyether oxygen atoms. The monomeric analogue of (vii) containing the 4-oxyethylene unit ending in a free -OH group, displays nearly identical emission to (vii) ($\lambda_{\text{max}} = 547, 580 \text{ nm}$) but possesses a much higher quantum yield of 24%.

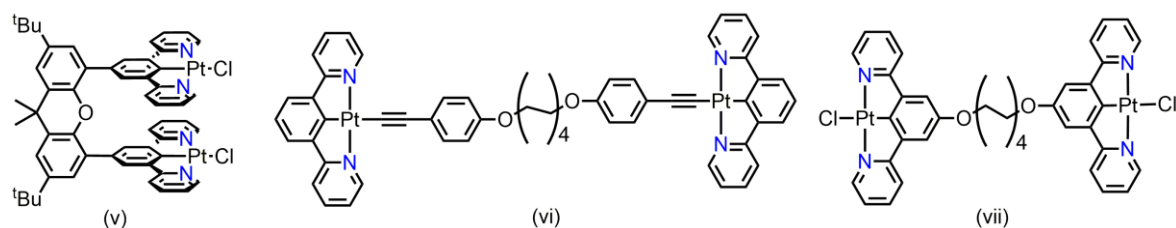


Figure 5.3: Structures of some dinuclear Pt(II) complexes (v) to (vii) with rigid (left) and flexible (centre and right) bridging ligands.

Metathesis of the monodentate chloride ligand in $\text{Pt}(\text{N}^{\wedge}\text{C}^{\wedge}\text{N})\text{Cl}$ -type complexes with an acetylide or cyanide generally leads to an increase in PLQY but the effect on emission energy varies depending on the electronic properties of both the platinum complex and the acetylene- or cyano-derivative. Metathesis usually has a bigger influence on the energy of the HOMO than the LUMO due to the strong σ -donating ability of the acetylide or cyanide ligand which contributes substantially to the HOMO.

5.4 Heteronuclear platinum and iridium complexes

Hosseini and co-workers studied the photophysical properties of several heteronuclear iridium and platinum complexes shown in **Figure 5.4**. Complexes (viii) and (ix) were synthesized from the reactions of the $\text{Pt}(\text{dpyb})\text{DMSO}$ and $\text{Ir}(\text{ppy})_2(\text{dpm-py})$ mononuclear complexes, where dpm-py = a variant of 5-(4-pyridyl)-dipyrromethane, in DCM at RT for 3 or 14 days. The iridium centres of complexes (viii) and (ix) have emission maxima of 741 and 705 nm; the emissions of the platinum centres are blue shifted with peaks of 534 and 532 nm respectively. The iridium and platinum complexes act as acceptors and donors respectively which are bridged by a pyridyl unit. The methyl groups of (ix) keep the electron-rich dipyrinate and the adjacent electron-deficient pyridyl bridge perpendicular to one another thereby limiting the rotational degrees of freedom and the charge-transfer character of its excited state; this results in an impressive quantum yield of 74%.²⁹²

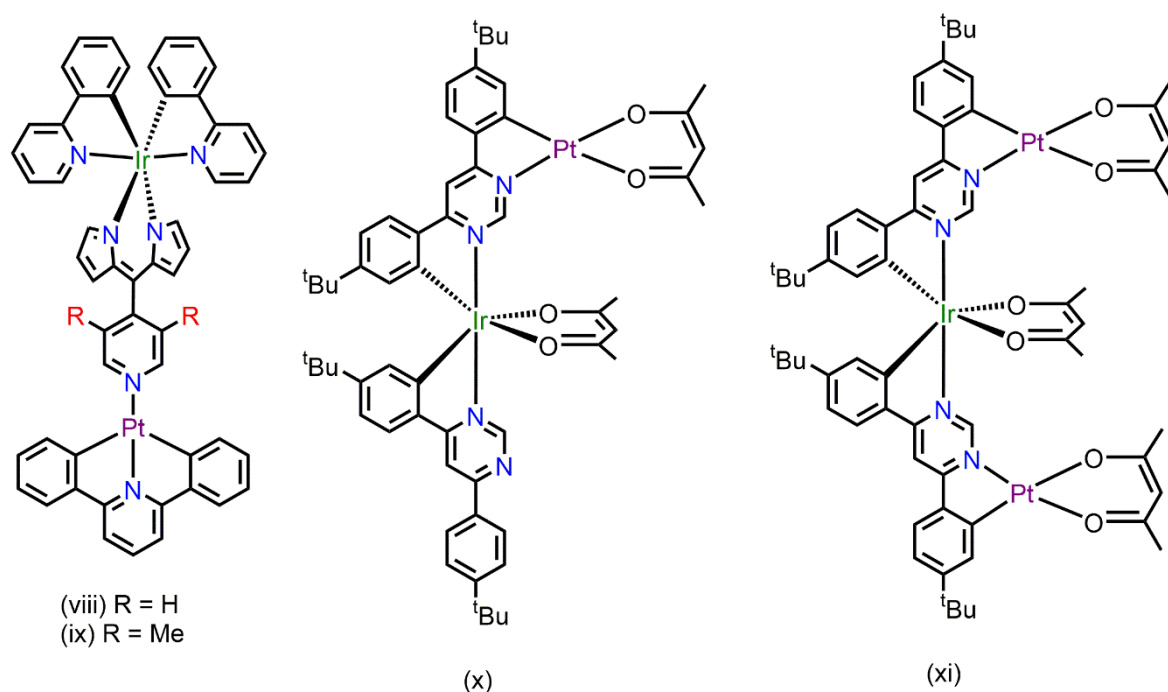


Figure 5.4: Structures of heteronuclear Pt(II) and Ir(III) complexes (viii) to (xi).

Complex (x) has a quantum yield of 85% in degassed toluene, which is exceptional considering its deep red emission maximum of 615 nm.²⁹³ Adding a second platinum centre i.e. complex (xi) further red shifts emission to 626 nm in degassed DCM. This trend can be rationalised by electrochemical

data and DFT calculations which suggest that the red shift is primarily due to a stabilization of the LUMO which is located on the pyrimidine ring. Adding the second platinum centre presumably increases the rigidity of the ligand scaffold but at the expense of a lowered radiative rate constant ($k_r = 1.3 \times 10^6 \text{ s}^{-1}$ vs. $7.1 \times 10^5 \text{ s}^{-1}$) and quantum yield ($\phi = 85\%$ vs. 41%).²⁹⁴

5.5 Aims and objectives

The above literature review demonstrates the impressive luminescence properties of di-metallic platinum and iridium complexes. The addition of the second metal ion sometimes leads to an increase in SOC and consequent rise in the radiative decay rate constant, even though the mechanism by which SOC becomes more efficient remains unclear. Furthermore, the second metal ion could lead to an increase in rigidity which can help to reduce rates of non-radiative decay. This observation is true for both di-iridium and di-platinum complexes. There are relatively few examples of charge neutral and cationic di-iridium complexes reported in the literature; the mononuclear complexes are typically linked via their N[^]N- or N[^]C-type ligands. The Ir^{III} cations could coordinate to a mutually common heterocycle (e.g. 2-phenylpyrimidine) or the metal ions could be linked via a long oligomer chain. There are some examples of di-iridium complexes featuring linked tridentate ligands in the literature,^{190,295,296} but this area of research still presents scope for further development.

Di-platinum complexes facilitate both inter- and intra-molecular π - π interactions; the extent of which can be controlled by the nature of the ligand and by the length and/or flexibility of the tether. The ratio of monomer vs. excimer emission in solution varies depending on the concentration of the complex in solution; excimer emission is favoured in more concentrated solutions and vice versa. Finally, there are only a few examples of mixed heteronuclear platinum-iridium complexes in the literature; these complexes typically display orange-red PL and their quantum yields are as high as 85%.

Hence, this work aims to:

1. Synthesize a library of di-iridium(III) complexes of the type $[\{\text{Ir}(\text{ppy})_2\}(\text{N}^{\wedge}\text{N})_2]^{2+}$, where N[^]N is a *p*-anisidine-based bridging ligand with either bidentate bpy or pyrazolopyridine coordinating arms, and compare the PL properties of this library with mono-iridium analogues.
2. Synthesize a *p*-anisidine-linked N[^]C[^]N bridging ligand and investigate its coordination to one or more platinum(II) and/or iridium(III) centres to create a series of mono-, di- and hetero-nuclear complexes.
3. Investigate the metathesis of the monodentate chloride ligand in the mono- and di-nuclear iridium and platinum complexes with cyanide and phenylacetylene.

To achieve these aims we have synthesized three types of complex:

- Mono-iridium complexes of the type $[\text{Ir}(\text{ppy})_2(\text{N}^{\wedge}\text{N})]\text{PF}_6$ where $\text{N}^{\wedge}\text{N}$ = 4-bromo bpy [67] or a 4-bromo pp-based ligand [73] (Figure 5.5, section 5.6).
- Di-iridium complexes featuring a bpy-based [68-72] or pyrazolopyridine-based [74-78] $\text{N}^{\wedge}\text{N}$ bridging ligand (Figure 5.5, section 5.6).
- Mono-platinum complexes of the type $\text{Pt}(\text{N}^{\wedge}\text{C}^{\wedge}\text{N}-\text{N}^{\wedge}\text{CH}^{\wedge}\text{N})\text{X}$ where $\text{N}^{\wedge}\text{C}^{\wedge}\text{N}-\text{N}^{\wedge}\text{CH}^{\wedge}\text{N}$ = a *p*-anisidine-linked bis-tridentate ligand bound to Pt(II) at one of the sites only and $\text{X} = \text{Cl}$, CN or CCPh [79-81] (Figure 5.15, section 5.7).
- Mono-, di-, and hetero-nuclear platinum(II) and iridium(III) complexes featuring the same *p*-anisidine-linked tridentate $\text{N}^{\wedge}\text{C}^{\wedge}\text{N}$ bridging ligand as described above [82-85] (Figure 5.15, section 5.7).

5.6 Results and discussion: N^N-bridged di-iridium(III) complexes

Complexes **67-78** (Figure 5.5) will be discussed in this section.

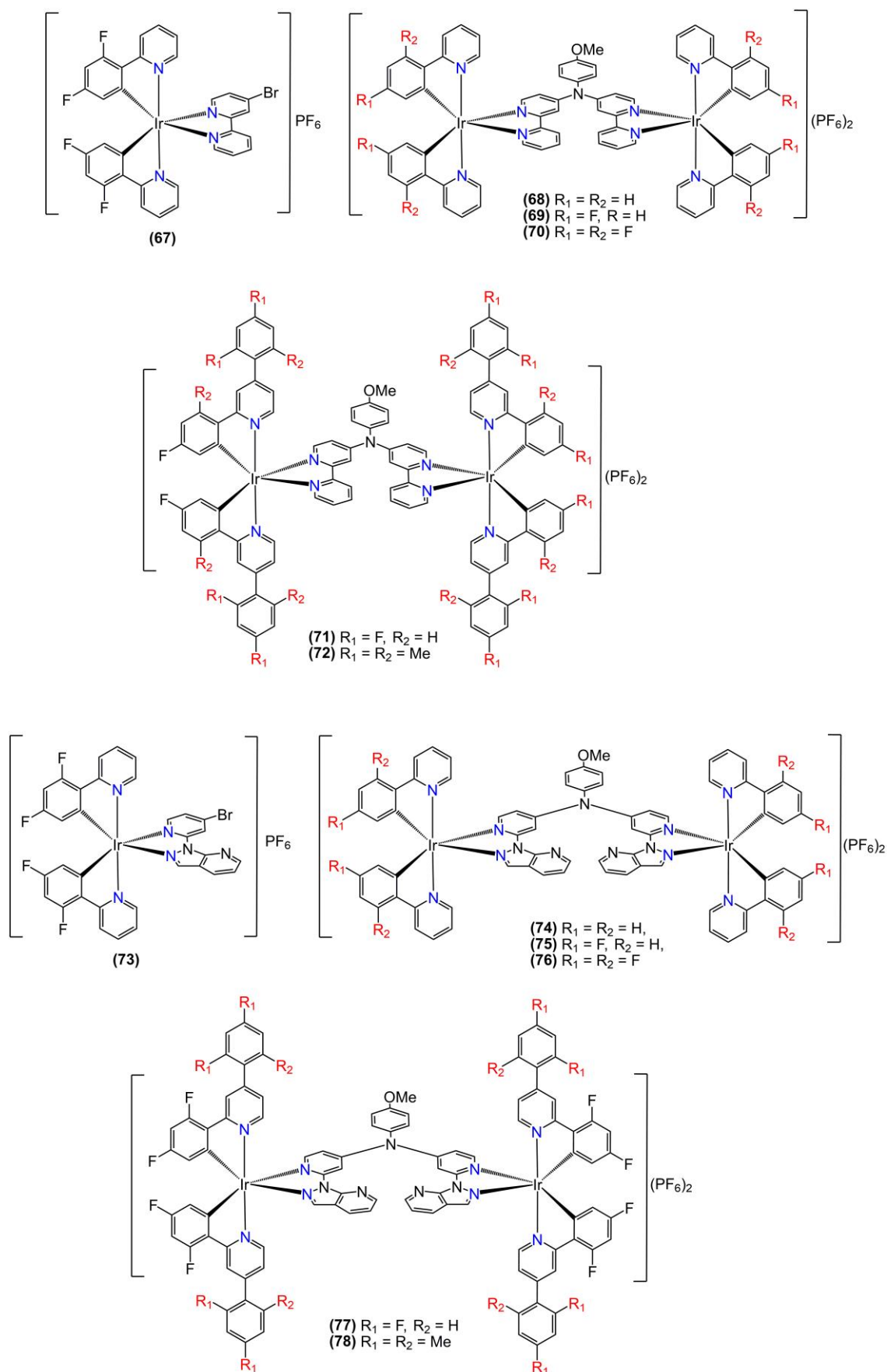


Figure 5.5: Structures of complexes **67-78**.

5.6.1 Synthesis

Following the failure of the “inward facing” bpy-based $N^{\wedge}N^{\wedge}N^{\wedge}N$ ligand from Chapter 4 to coordinate to two iridium centres, the analogous *p*-anisidine-based ligand featuring “outward facing” bpy units was synthesized via a 2-step procedure. A Stille coupling between 2,4-dibromopyridine and 2-(tributylstannyl)pyridine, followed by a subsequent double amination of *p*-anisidine with 4-bromo-bpy (L^{18}), yielded the desired ligand, L^{19} , in a 63% yield after purification by column chromatography on alumina (**Figure 5.6**). Interestingly, the mono-aminated product formed as a side product, eluting in a 15% yield after the doubly-aminated product. A 2.2 ratio of 2,4-dibromopyridine to tin reagent ensured that stannylation only occurred once at the more reactive 2-position of the pyridine ring. The pyrazolopyridine-based bridging ligand (L^{21}) was synthesized in a three step procedure as follows: (i) formation of 1*H*-pyrazolo[3,4*b*]pyridine (ppH) from 2-chloro-3-pyridinecarboxaldehyde and hydrazine monohydrate; (ii) amination of ppH with 2,4-dibromopyridine to yield the 4-bromo-pp product (L^{20}) and (iii) double amination of *p*-anisidine with 4-bromo-pp. Despite a 2.2 ratio of 4-bromo-pp to *p*-anisidine, some of the singly-aminated product was isolated as a white solid in a 4% yield after alumina column chromatography whereas the doubly-aminated product was eluted first in an 18% yield as a pale yellow solid.

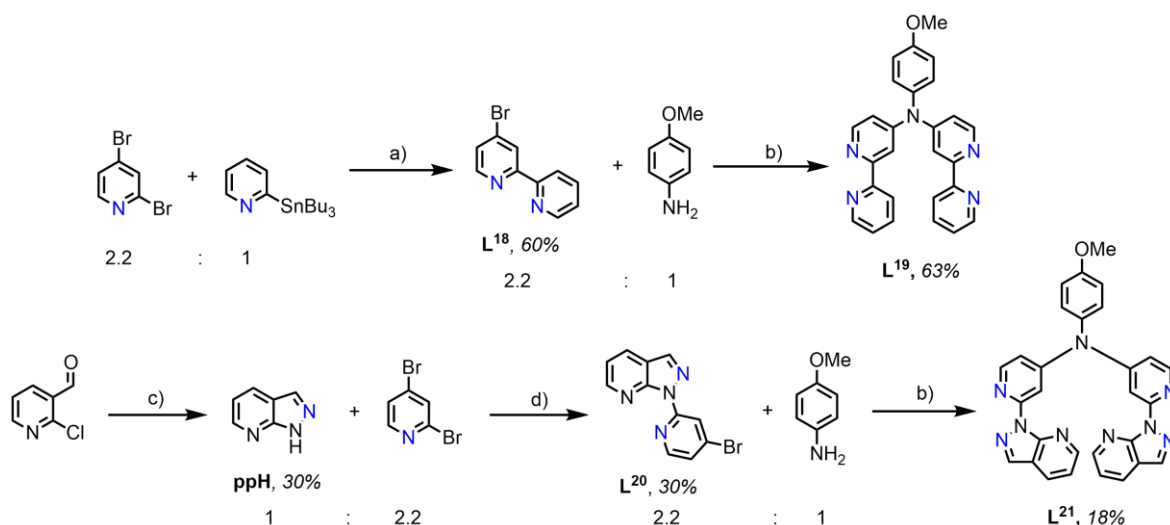


Figure 5.6: Synthesis of “outward-facing” $N^{\wedge}N^{\wedge}N^{\wedge}N$ bridging ligands: a) $Pd(PPh_3)_4$, toluene, 110°C, 24 h; b) $NaOtBu$, $Pd_2(dba)_3$, *dppf*, toluene, 110°C, 36 h; c) H_2N-NH_2 , *p*-TsOH, 130°C, 16 h; d) K_2CO_3 , *CuI*, 1,2-transdiaminocyclohexane, 1,4-dioxane, 100°C, 24 h.

The dinuclear complexes were synthesized according to the general procedure for the synthesis of the mononuclear bidentate complexes; specifically, a 3-hour reflux of the $N^{\wedge}N$ -bridging ligand with a chloro-bridged iridium dimer such as $[Ir(ppy)_2\mu-Cl]_2$ in DCM and MeOH followed by ion exchange of the chloride counter-ion with PF_6^- by addition of a saturated aqueous solution of KPF_6 . Complex **68** was isolated in a 72% yield after column chromatography (**Figure 5.7**). The other nine di-metallic complexes were purified under the same conditions, with one or more recrystallizations, to yield

orange-yellow solids in yields of 2% to 77%. The apparent doublet OCH₃ peak at 3.86 ppm in the ¹H NMR spectrum of **68** (Figure 5.8) indicates the presence of two diastereoisomers which are the $\Lambda\Lambda/\Delta\Delta$ and $\Lambda\Delta/\Delta\Lambda$ forms associated with the chirality at the iridium centres.

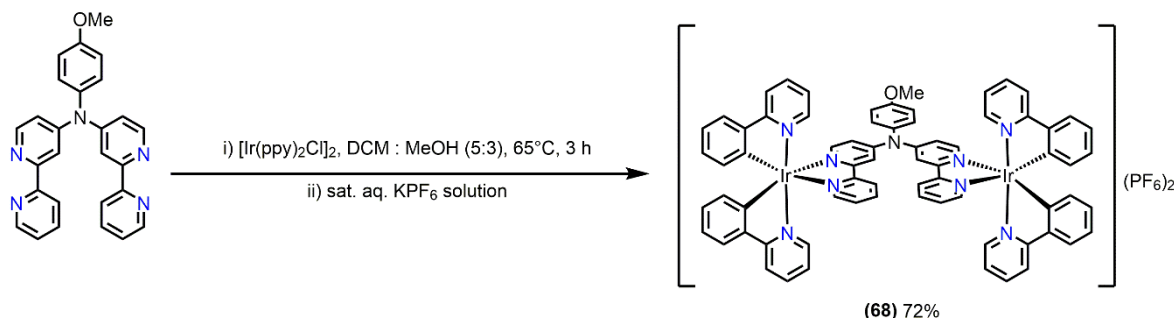


Figure 5.7: Synthetic scheme for the synthesis of complex **68**.

A similar diastereotopic pattern of ¹H NMR peaks can be seen in the ¹H NMR spectrum of complex **74** (Figure 5.9) as indicated again by the apparent doublet methoxy signal occurring at 3.91 ppm. In this instance, some resolution of diastereotopic peaks can be seen, for example, in the doublet of H⁸ and the doublet of doublets of H¹³ at 6.37 and 9.46 ppm respectively. Protons were assigned with the aid of ¹H-¹H-COSY and ¹H-¹H-NOESY analysis. The most upfield shifts occurring around 6-7 ppm are associated with protons attached to the phenyl ppy ring in a similar manner to the ¹H NMR spectrum of **68** (Figure 5.8) and the spectra of the ppy-based mononuclear complexes discussed in Chapter 2. The signals from the N[^]N ligand in **74** extend beyond 9.4 ppm and lie much further downfield than the most downfield signal from the N[^]N ligand of **68** occurring at 8.46 ppm.

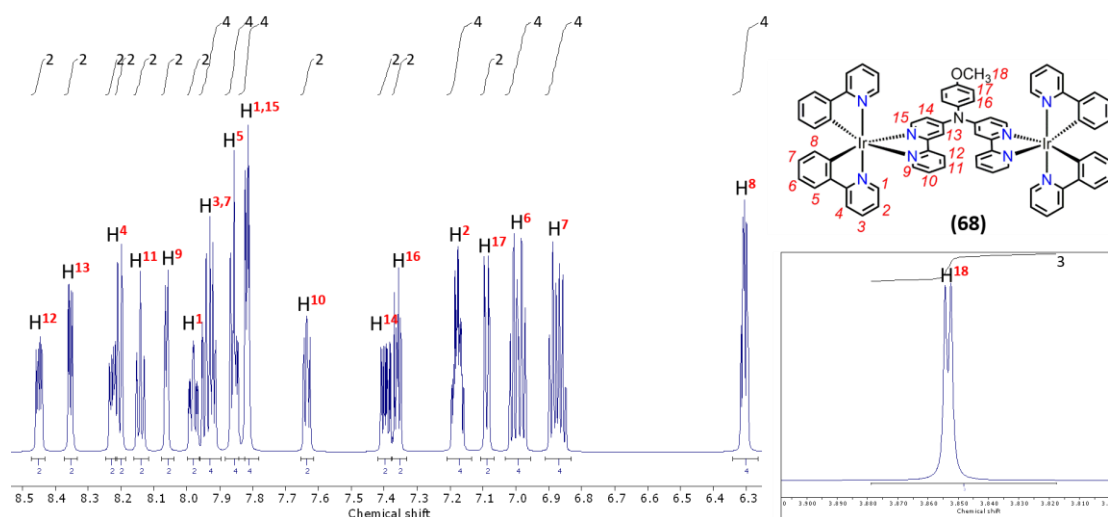


Figure 5.8: ¹H NMR spectrum of **68** in d₆-acetone, 700 MHz, inset: aliphatic region from 3.8-3.9 ppm.

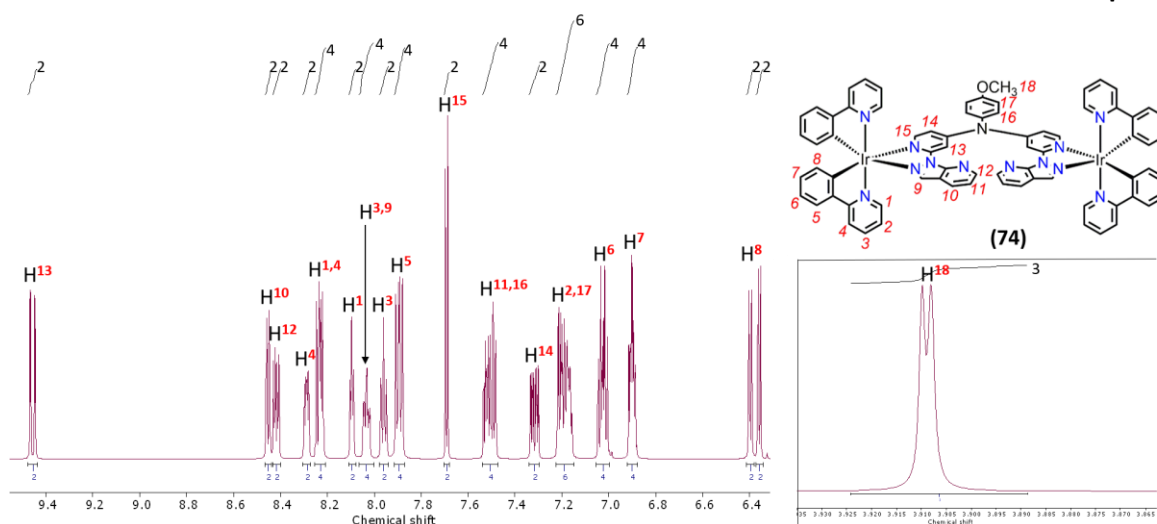


Figure 5.9: ^1H NMR spectrum of **74** in d_6 -acetone, 700 MHz; inset: aliphatic region from 3.8–3.9 ppm.

5.6.2 Electrochemistry

Table 5.2 highlights the electrochemical properties of the mononuclear complexes **67** and **73** and the dinuclear systems **68–72** and **74–78**. All twelve complexes display a single quasi-reversible or irreversible oxidation potential in the window +0.84 to +1.54 V. The oxidation potentials of **68–70** occur at +0.84, +1.33 and +1.54 V respectively – the shift to more positive potentials coincides with an increasing fluorine content of the cyclometalating ligand which suggests the oxidation process is associated with electron transfer occurring on the $\text{C}^{\wedge}\text{N}$ ligand. This same anodic shift of oxidation potentials with increasing fluorine content of the $\text{C}^{\wedge}\text{N}$ ligand is also observed in the pyrazolopyridine (pp)-based series of di-iridium complexes **74–76** whose oxidations take place inside a narrower range ($E_{\text{p}}^{\text{ox}} = +0.93$ to +1.28 V) to **68–70**. The bis-dfp₂py and mes-dfppy-containing complexes, **71** and **72**, featuring the bridging bpy ligand have irreversible oxidation potentials of +1.21 and +1.03 V respectively; these are 0.33–0.51 V less positive than the oxidation potential of the equivalent dfppy complex **70** ($E_{\text{ox}} = +1.54$ V). In the pp-based series, the bis-dfp₂py and mes-dfppy-containing complexes, **77** and **78** have oxidation potentials of +1.20 and +1.21 V respectively – these values are also less positive than the oxidation potential of the dfppy-based analogue, **76** ($E_{\text{ox}} = +1.28$ V) although by a lesser amount.

The bpy-containing complexes **67–72** feature two reduction potentials in the regions of –1.20 to –1.70 V and –1.54 to –1.90 V. The less negative potentials are all irreversible and likely stem from redox processes associated with the LUMO occurring on the bpy-bridging ligand. This intuitive hypothesis based on the likely site of lowest-energy π^* orbitals is supported by DFT studies on the mononuclear equivalents **1–3** and **67**, where $\text{C}^{\wedge}\text{N} = \text{ppy}$, fppy and dfppy and $\text{N}^{\wedge}\text{N} = \text{bpy}$ or 4-bromo-bpy, which indicate that the LUMO lies exclusively on the ancillary ligand. The first reduction potentials of **68–70** are –1.70, –1.48 and –1.41 V respectively – this trend towards less negative $E_{\text{p}}^{\text{red}}$ values across the series is probably a consequence of the increased fluorination within the $\text{C}^{\wedge}\text{N}$

ligand whose stabilizing influence is also felt by the LUMO to a small degree. The second reduction potentials of **68-70** also follow a similar trend to less negative values from -1.90 to -1.65 V. Complex **72** has the least negative reduction potentials in this series of -1.20 and -1.54 V; this could reflect the increasing electron-donating ability of its mesityl groups. The second reduction potentials of **67-72** are either reversible or quasi-reversible. DFT and TD-DFT calculations could not be performed on the dinuclear set of complexes **68-72** and **74-78** due to their large size.

Table 5.2: Electrochemical properties of complexes **67-78** recorded in a 0.1 M electrolyte solution of NBu_4PF_6 in MeCN. Values were measured at a scan rate of 200 mV s^{-1} and are reported relative to SCE, measured using ferrocene as the standard ($E_{1/2}^{\text{ox}} = 0.42 \text{ vs. SCE}$). E_p^{ox} and E_p^{red} are the anodic and cathodic peak potentials respectively. $\Delta E_{1/2} = E_p^{\text{ox}} - E_p^{\text{red}}$.

Complex	$E_p^{\text{ox}} / \text{V}$	$E_p^{\text{red}} / \text{V}$	$\Delta E_{1/2} / \text{V}$
67	+1.32 ^{qr}	-1.48 ^{ir} , -1.61	2.80
68	+0.84 ^{qr}	-1.70 ^{ir} , -1.90	2.54
69	+1.33 ^{ir}	-1.48 ^{ir} , -1.67	2.81
70	+1.54 ^{qr}	-1.41 ^{ir} , -1.65	2.95
71	+1.21 ^{ir}	-1.67 ^{ir} , -1.86	2.88
72	+1.03 ^{ir}	-1.20 ^{ir} , -1.54	2.23
73	+1.41 ^{qr}	-1.60 ^{ir} , -1.80 ^{qr}	3.01
74	+0.93 ^{ir}	-2.08 ^{ir}	3.01
75	+1.19 ^{ir}	-1.93 ^{ir}	3.12
76	+1.28 ^{qr}	-1.90 ^{ir}	3.18
77	+1.20 ^{ir}	-1.87 ^{ir}	3.07
78	+1.21 ^{ir}	-1.85 ^{ir}	3.06

The irreversible reductions of the pp-series of dinuclear complexes **74-78** occur within a more negative region than the reductions of the bpy series **68-72**. The reduction potentials of **74-78** are in a window of -1.85 to -2.08 V and the values become increasingly less negative across the series from -2.08 V (**74**) to -1.85 V (**78**). The more negative reduction potentials of **74-78** are likely to be a consequence of the increased electron density associated with the pyrazolopyridine system vs. the bpy unit. Complexes **74-78** only display a single reduction potential within the solvent accessible window. Irreversible or quasi-reversible redox processes of **67-78** were estimated using anodic and cathodic peak potentials so the accuracy of their tabulated oxidation and reduction potentials is suboptimal, however, general electrochemical trends within the series can still be determined.

5.6.3 Photophysical properties

The photophysical data for complexes **67-78**, measured in degassed MeCN at RT and in EPA at 77 K, are tabulated in **Table 5.3**.

5.6.3.1 Absorption

Figure 5.10, upper shows the absorption spectra of the bpy-based iridium(III) systems **67-72**. The mononuclear complex **67** is included in this section as a reference to the dinuclear complexes **68-72**. The profiles of the bpy-based systems are similar in that they all feature a single broad intense

peak in the high energy region between 246-285 nm. The high extinction coefficients of these bands ($2.3 \times 10^4 \leq \epsilon \leq 1.9 \times 10^5 \text{ M}^{-1}\text{cm}^{-1}$) are suggestive of spin-allowed $\pi-\pi^*$ ^1LC transitions of the bridging *p*-anisidine ligand. Furthermore, they all feature a much weaker and broader low energy band between 362-371 nm ($\epsilon \leq 4.5 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$) which can be attributed to $^3\text{MLCT}$ transitions. The medium intensity band around 300 nm, associated with mixed MLCT and LLCT transitions in **67** is much more prominent than in the di-iridium complexes.

The absorption spectra of the pp-based complexes **73-78** have similar profiles to the bpy-based systems (**Figure 5.10, middle**). The mono-iridium complex **73** is included as a reference for the pp-based di-iridium complexes. Their intense ^1LC transitions occur between 242-283 nm ($9.8 \times 10^4 \leq \epsilon \leq 1.6 \times 10^5 \text{ M}^{-1}\text{cm}^{-1}$) and their weak bands of $^3\text{MLCT}$ and ^3MC character occur beyond 353 nm ($\epsilon \leq 5.3 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$). Medium intense bands between 308-325 nm are visible in the spectra of **73** and **75-77**. The highest energy bands of the mononuclear complexes **67** and **73**, which occur at 246 and 242 nm respectively, are blue shifted by 5-25 nm ($810\text{-}3870 \text{ cm}^{-1}$) compared to the highest energy bands of the di-iridium systems.

Absorption profiles are relatively unaffected by variation of the bridging ligand as shown by the near identical profiles of complexes **70** and **76** (**Figure 5.11**), which both possess dfppy as their $\text{C}^{\wedge}\text{N}$ ligand, except for a slight blue shift in the lowest energy band of **76** (354 vs. 362 nm, $\Delta E = 785 \text{ cm}^{-1}$).

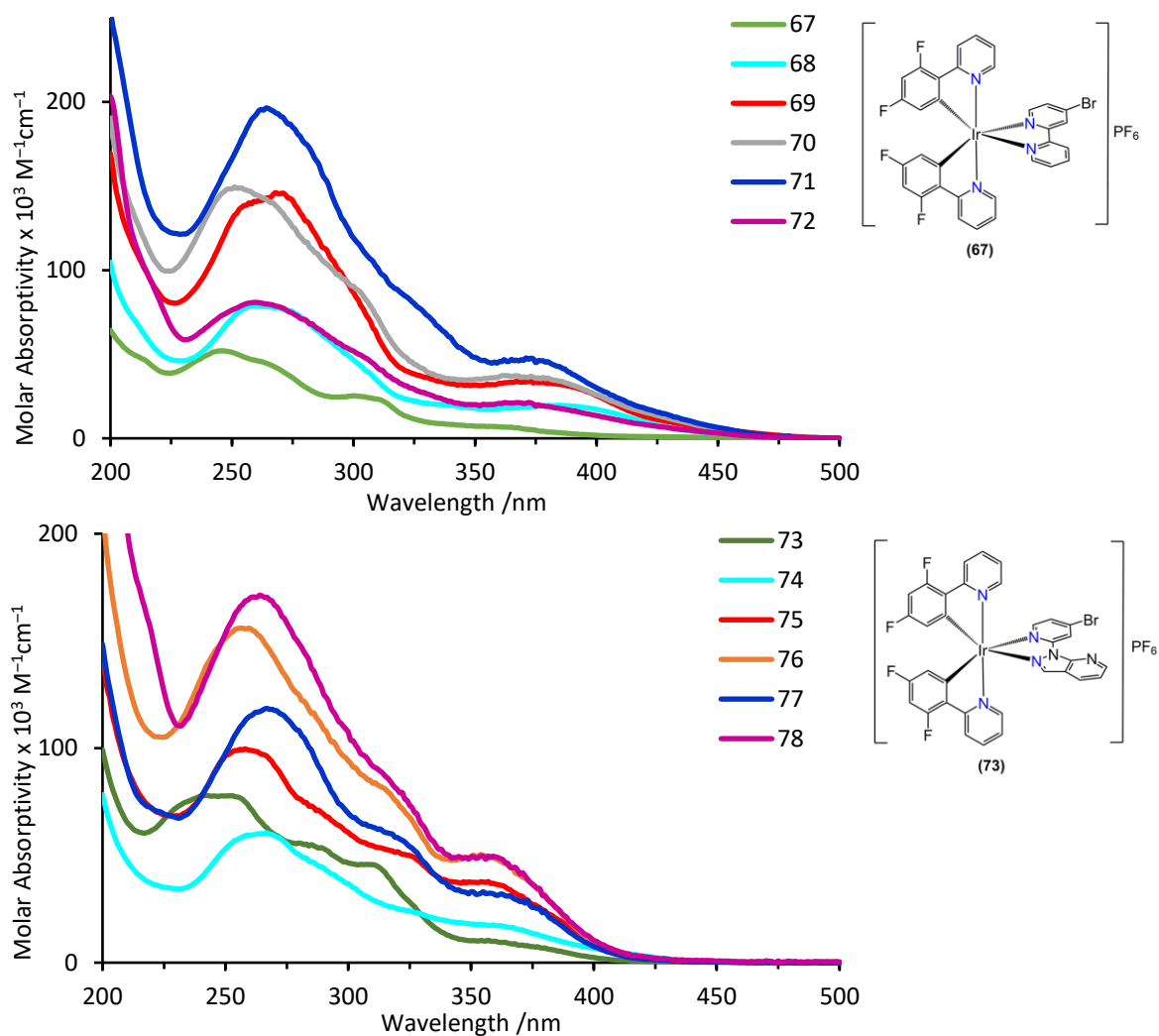
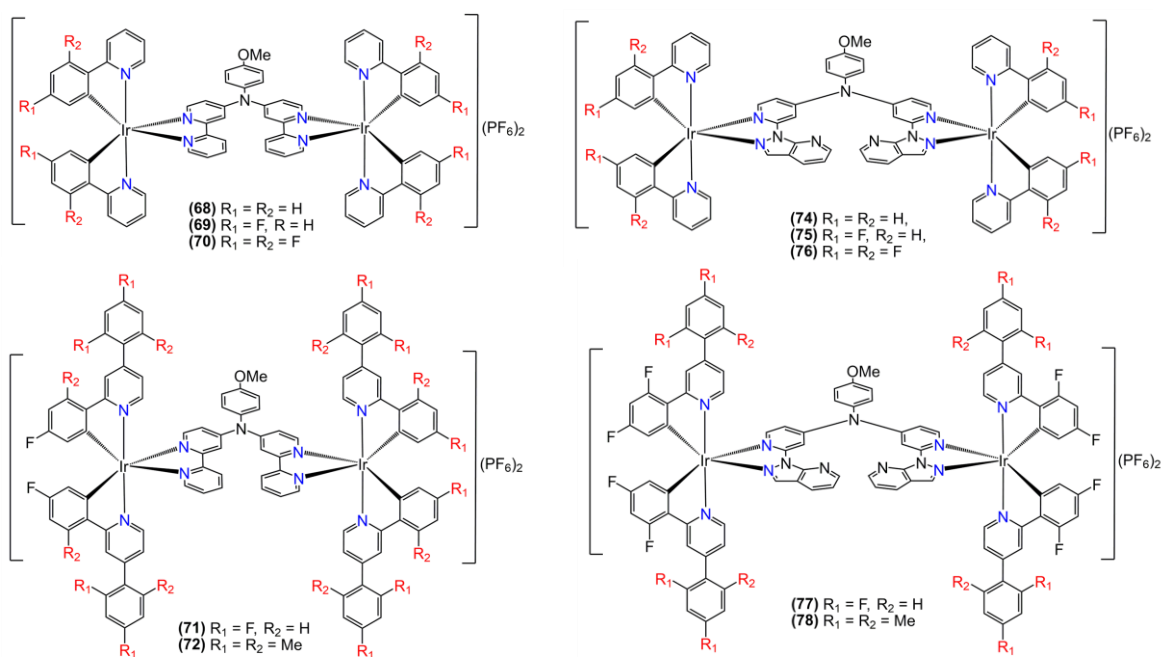


Figure 5.10: Absorption spectra of **67-72** (upper) and **73-78** (middle) in MeCN. Structures of **68-72** and **74-78** are shown in the lower figure.



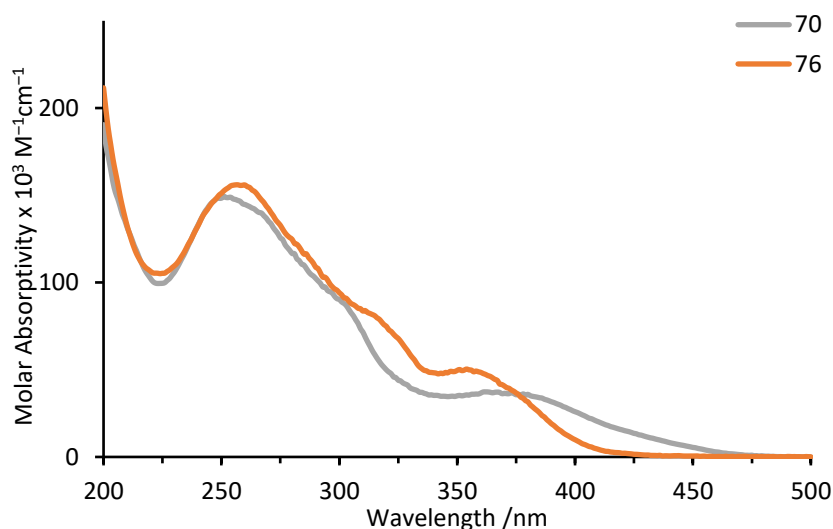


Figure 5.11: Absorption spectra of complexes **70** and **76** in MeCN. Structures of **70** and **76** are shown in **Figure 5.10, lower**.

5.6.3.2 Emission

Figure 5.12 shows the RT emission of **67-78** in degassed MeCN. The bpy-based complexes display unstructured emission profiles, characteristic of a ³MLCT-type excited state, with a single broad emission peak between 558-617 nm which roughly corresponds to yellow emission (**Figure 5.12, upper**). The emission maxima of **68-71** increase sequentially in energy across the series from 617 to 560 nm in line with an increase in fluorination of their C[^]N ligands from ppy (**68**) to fppy (**69**) to dfppy (**70**) and finally to bis-dfp₂py (**71**). This trend is presumably a consequence of the increasing HOMO stabilization induced by the fluorine atoms. The emission peaks of **71** and **72** are identical ($\lambda_{\text{max}} = 560\text{-}561\text{ nm}$) despite the replacement of the second difluorophenyl group by a mesityl group in the latter. The dfppy-containing complexes **67** and **70** have emissions centered at 558 and 571 nm respectively. Whilst the 13 nm (408 cm⁻¹) red shift in emission of the di-iridium species **70** cannot exclusively be rationalised by the addition of the second iridium ion, it could contribute to this bathochromic shift, in addition to the change in N[^]N ligand.

The emissions of the pp-series of complexes **73-78** are significantly blue shifted compared to the equivalent bpy-based systems; **Figure 5.12, middle**, which displays the spectra of **70** and **76**, illustrates a prime example of this trend. The emission maxima of **70** and **76** differ by over 100 nm ($\lambda_{\text{max}} = 571\text{ (70) vs } 453\text{ nm (76)}$, $\Delta E = 4560\text{ cm}^{-1}$) due to the higher electron density of the fused pyrazolopyridine group of the pp ligand compared to the pyridine ring of the bpy ancillary, which destabilizes the LUMO by a greater amount. Furthermore, the profiles of **73-78** (**Figure 5.12, lower**) are more structured than the bpy series due to their bluer emissions and resulting higher degrees of ¹LC character in their excited states. The emission maxima of these blue-green emitting complexes range between 450-552 nm. The same blue shift in emission (from $\lambda_{\text{max}} = 516$ to 453 nm) is seen across the series **74-77** due to the increase in fluorination of the cyclometalating ligand.

The following differences were noted in the behaviour of the pp-based complexes compared to the bpy-based systems:

- 1) Despite the 13 nm (408 cm^{-1}) red shift in emission of **70** vs. **67**, the equivalent pp-based complexes **76** and **73** do not display this shift as their emission colours are similar ($\lambda_{\text{max}} = 453\text{ vs. }450\text{ nm}$, $\Delta E = 147\text{ cm}^{-1}$).
- 2) The emissions of **76** and **77** are equally blue despite the additional difluorophenyl groups in the latter complex; emissions of the equivalent bpy-based complexes **71** and **70** differed by 11 nm (344 cm^{-1}).
- 3) Addition of the mesityl groups in **78** red shifted emission by 15 nm (708 cm^{-1}) from $\lambda_{\text{max}} = 468\text{ to }453\text{ nm}$, in contrast to the negligible difference in the emissions of **72** vs. **70**.

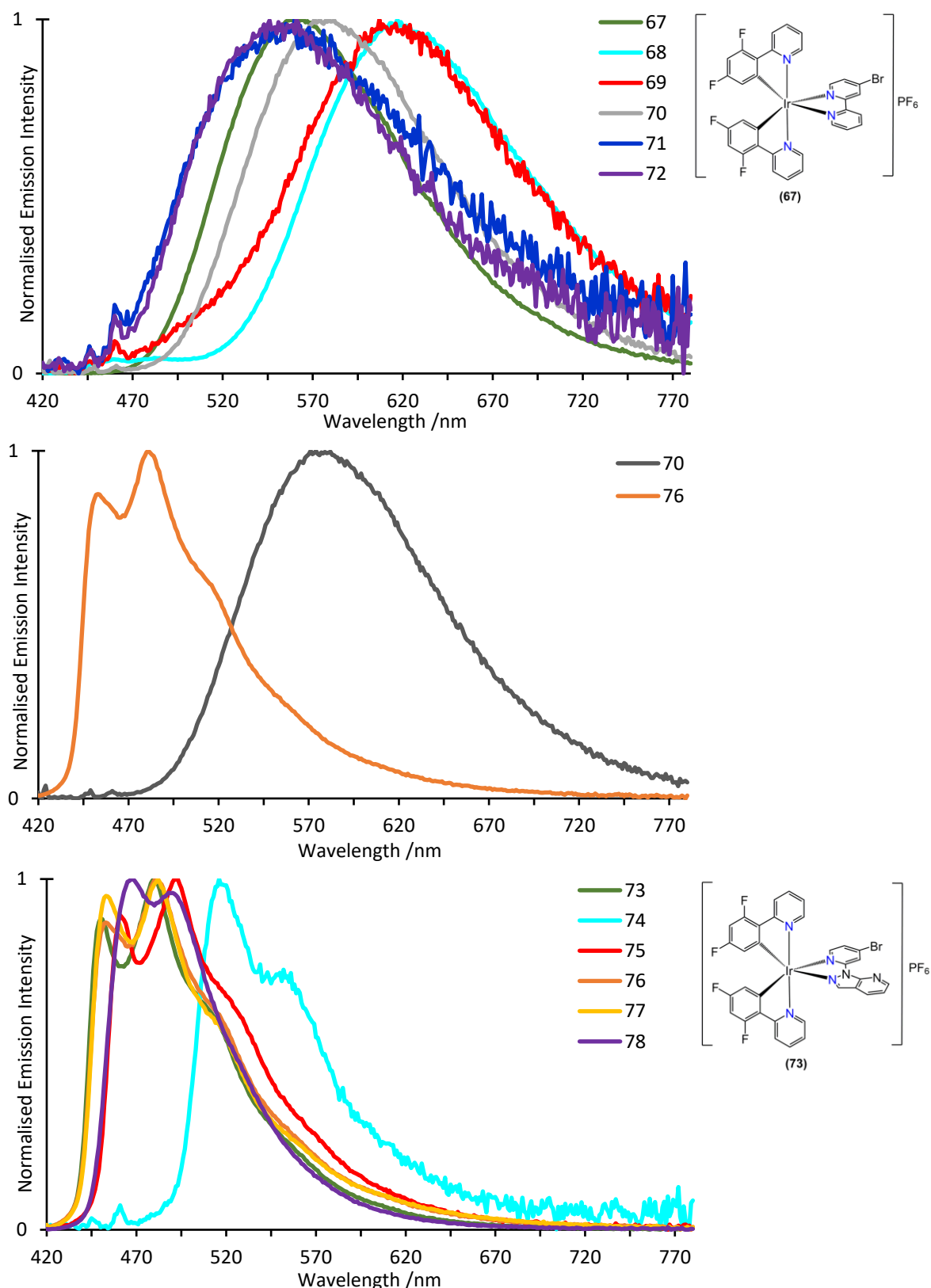


Figure 5.12: Normalised RT emission spectra of **67-72** (upper), **70** and **76** (middle) and **73-78** (lower) in degassed MeCN, $\lambda_{exc} = 425$ nm. Structures of **68-72** and **74-78** are shown in **Figure 5.10, lower**.

Figure 5.13 and **Figure 5.14** display the 77 K emission spectra of **67-78** recorded in EPA. At low temperature, the profiles of the bpy series of complexes **67-72** (**Figure 5.13, upper**) are consistently higher in energy, more structured and less broad than at RT. The hypsochromic shifts of 77 K

emission maxima range between 59 and 91 nm ($1710\text{-}3490\text{ cm}^{-1}$), as demonstrated by the spectra of **70** at RT and at 77 K ($\Delta\lambda_{\text{max}} = 86\text{ nm}$, $\Delta E = 3110\text{ cm}^{-1}$, **Figure 5.13, middle**). Emission trends that are mirrored at 77 K include:

- 1) An increasing blue shift across the series **68-70** from $\lambda_{\text{max}} = 558$ to 485 nm associated with a change in C^N ligand from ppy to dfppy.
- 2) A red shift in emission of **70** with respect to the mono-iridium reference **67** ($\lambda_{\text{max}} = 485$ vs 467 nm).

A key difference between RT and 77 K emissions is the overlapping profiles of the dfppy-based complexes **70-72** at low temperature. All three species have 0,0 emission maxima at 77 K within a narrow 3 nm (128 cm^{-1}) range between 483-486 nm. Lifetimes at 77K, which range between 2.7 and 6.0 μs , are roughly ten times longer than at RT ($\tau = 77\text{-}1080\text{ ns}$) due to the usual reduction of non-radiative decay pathways at low temperature.

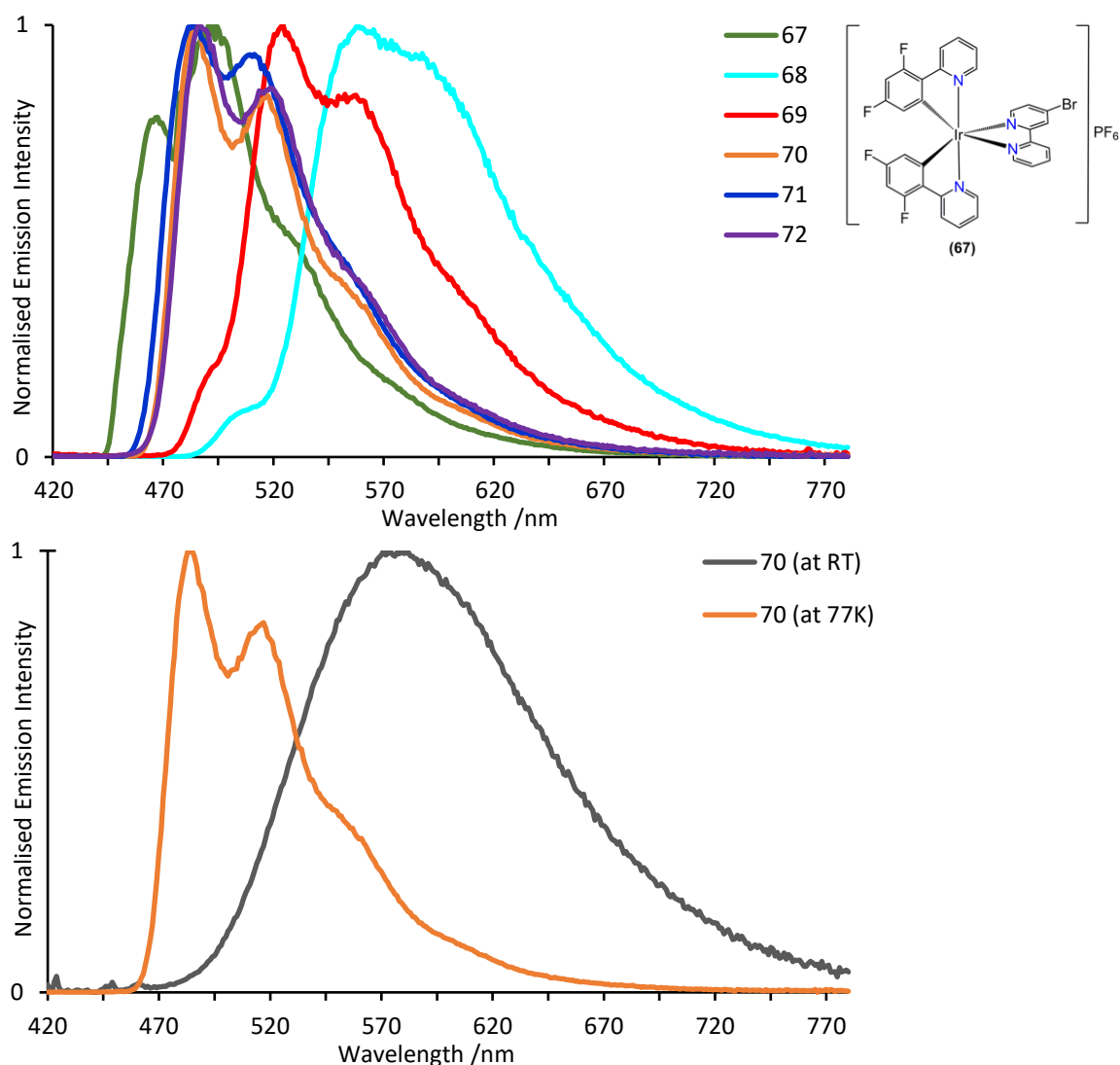
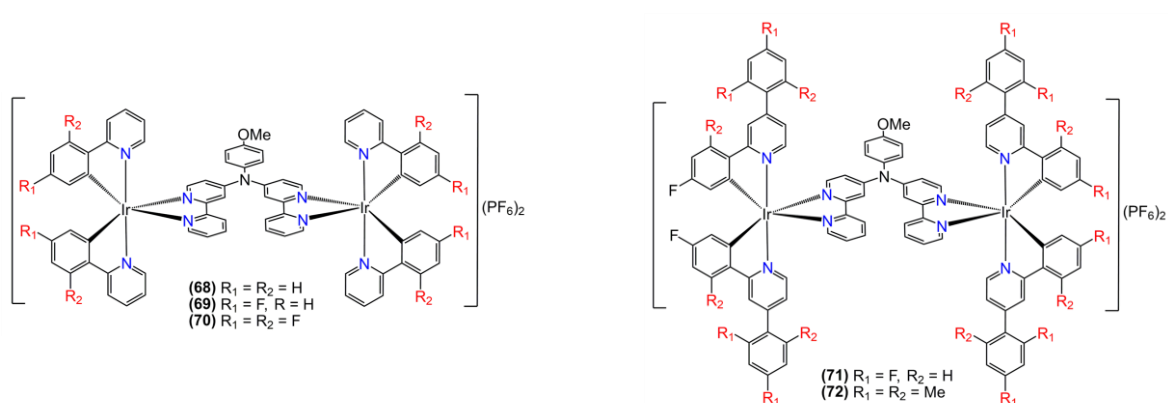


Figure 5.13: Normalised 77 K emission spectra of **67–72** in EPA, $\lambda_{exc} = 400$ nm (upper) and normalised emission spectra of **70** at 77 K and at RT in degassed MeCN, $\lambda_{exc} = 425$ nm (middle). Structures of **68–72** are shown in the lower figure.



In contrast, the emission maxima of **73–78** at 77 K (**Figure 5.14, upper**) do not shift significantly from their RT values as exemplified by complex **77** (**Figure 5.14, middle**). The exception, however, is **78** which does display a 19 nm (904 cm^{-1}) blue shift when cooled ($\lambda_{max} = 449$ vs. 468 nm); this result might suggest that the excited state of **78** involves the largest $^3\text{MLCT}$ contribution, which becomes reduced upon cooling.

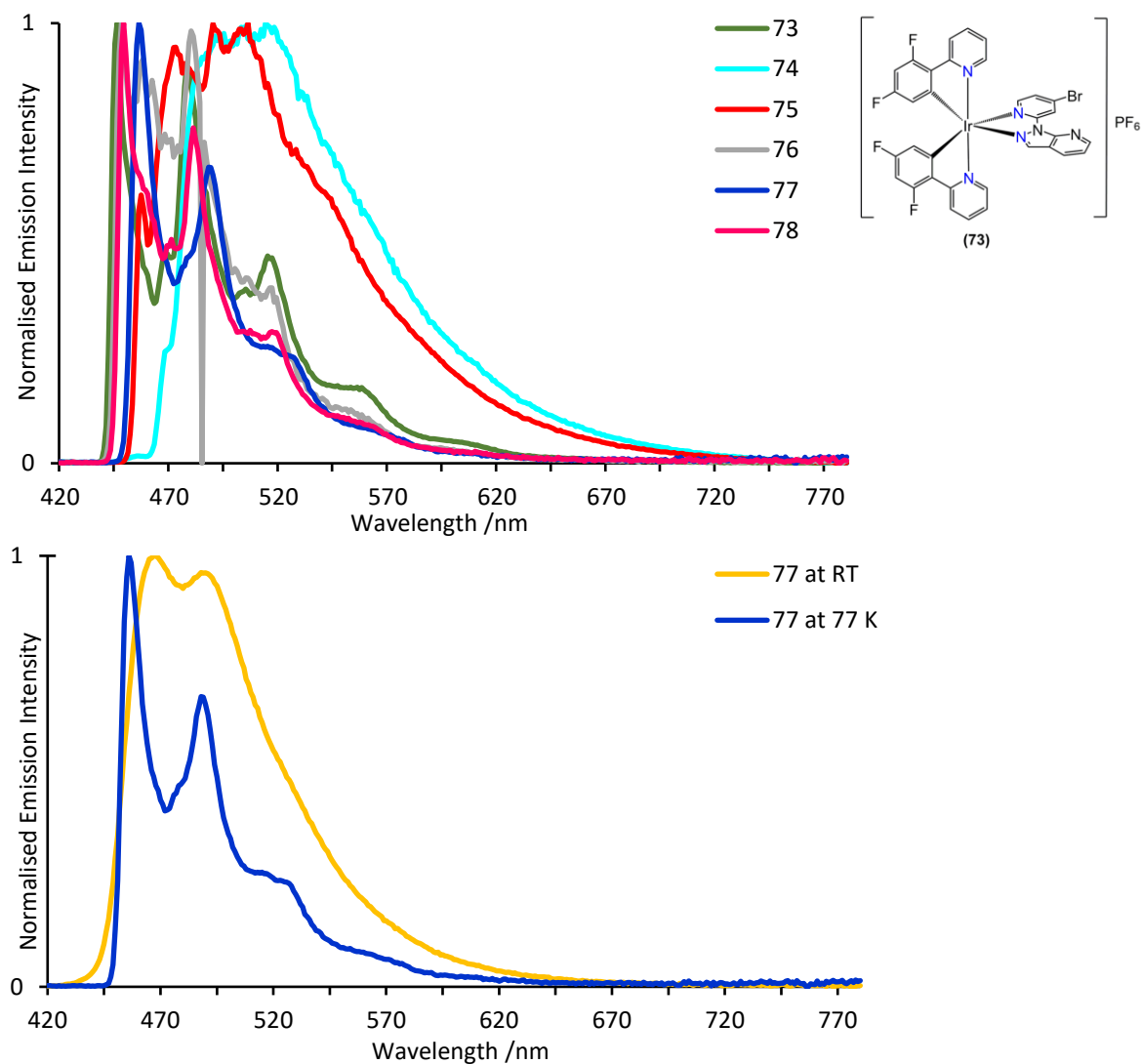
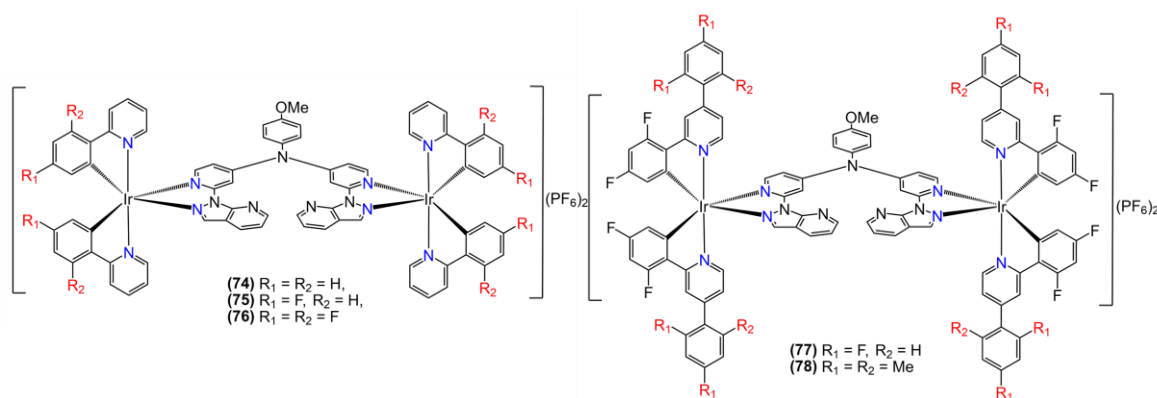


Figure 5.14: Normalised 77 K emission spectra of **73-78** in EPA, $\lambda_{exc} = 400$ nm (upper) and normalised emission spectra of **77** at 77 K and at RT in degassed MeCN, $\lambda_{exc} = 425$ nm (middle). Structures of **74-78** are shown in the lower figure.



The maximum quantum yield of the di-iridium bpy series **68-72** is 5%, substantially inferior to that of the reference compound, **67** whose PLQY is 32%. The low quantum yields of **68-72** appear to be primarily due to high rates of non-radiative decay, as typified by the non-radiative rate constants of **68** and **67** ($k_{nr} = 5.3 \times 10^5$ s $^{-1}$ vs. 6.7×10^4 s $^{-1}$). Notably, radiative rate constants do not increase

with the addition of the second iridium ion as the k_r values of both **67** and **68** are $\approx 3 \times 10^4 \text{ s}^{-1}$. The emissions of the di-iridium complexes are red shifted with respect to **67** so their quantum efficiencies could be expected to be lowered in accordance with the energy gap law,²⁹⁷ though perhaps not by such a large amount.

Quantum yields of di-iridium pp-based series are also inferior to the quantum yield of the reference compound **73**, with the exception of **77** whose PLQY is higher than the reference ($\phi = 17\%$ vs. 8%). The PLQYs of the remaining di-iridium series are $\leq 4\%$. The high performance of **77** is related to its higher rate of radiative decay than **73** ($1.6 \times 10^4 \text{ s}^{-1}$ vs. $3.4 \times 10^3 \text{ s}^{-1}$). In fact, the majority of di-iridium pp-based complexes have higher radiative decay rates compared to mononuclear equivalents. The entire series, however, suffer from high non-radiative decay rates, which can partly explain their lower quantum efficiencies with respect to **68**; for example, the k_{nr} values of **77** and **73** are $8.0 \times 10^4 \text{ s}^{-1}$ and $4.0 \times 10^4 \text{ s}^{-1}$ respectively.

Table 5.3: Photophysical properties of complexes **67-78** recorded in degassed MeCN at RT ($\lambda_{\text{exc}} = 405 \text{ nm}$) and in EPA at 77 K ($\lambda_{\text{exc}} = 400 \text{ nm}$). Aerated PLQYs and lifetimes are shown in brackets.

Complex	67	68	69	70	71	72
Absorption Maxima /nm ($\epsilon / \text{M}^{-1} \text{cm}^{-1}$)	246 (60600)	259 (93600)	253 (180000)	251 (169000)	264 (160000)	260 (75800)
	261 (53500)	274 (90100)	268 (193000)	270 (152000)	281 (142000)	305 (44800)
	301 (25300)	285 (23300)	367 (44900)	302 (99300)	371 (25400)	362 (20000)
	311 (23000)			362 (42100)		
	365 (6420)					
$\lambda_{\text{max}} / \text{nm}$	558	617	607	571	560	561
PLQY /% degassed (aerated)	32.3 (4.3)	4.8 (1.8)	2.5 (1.5)	0.8 (0.4)	0.3 (0.2)	0.3 (0.2)
Lifetime /ns degassed (aerated)	1020 (132)	181 (70)	77 (51)	475 (28)	1080 (26)	719 (31)
$k_r \times 10^4 \text{ s}^{-1}$	3.17	2.65	3.24	0.16	0.030	0.047
$k_{nr} \times 10^4 \text{ s}^{-1}$	6.65	52.7	127	20.9	9.25	13.9
77 K $\lambda_{\text{max}} / \text{nm}$	467, 492	558	524, 552	485, 517	483, 511	486, 518
77 K Lifetime / μs	4.9	2.7	3.5	6.0	5.3	5.8

Complex	73	74	75	76	77	78
Absorption Maxima /nm ($\epsilon / \text{M}^{-1} \text{cm}^{-1}$)	242 (79100)	267 (8550)	258 (137000)	257 (156983)	267 (61900)	264 (147000)
	254 (78500)	362 (2450)	325 (70000)	319 (97630)	322 (29800)	359 (42700)
	283 (55900)	463 (310)	355 (52700)	354 (50700)	360 (16500)	445 (509)
	308 (49000)		454 (378)	444 (484)	452 (256)	
	356 (10200)					
	444 (171)					
$\lambda_{\text{max}} / \text{nm}$	450, 480	516, 552	461, 493	453, 481	453, 482	468, 488
PLQY /% degassed (aerated)	8.0 (0.8)	0.5 (0.1)	2.7 (0.6)	4.1 (0.6)	17.1 (3.1)	4.0 (0.9)
Lifetime /ns degassed (aerated)	2320 (211)	796 (59)	403 (83)	794 (116)	1040 (174)	633 (124)
$k_r \times 10^4 \text{ s}^{-1}$	0.34	0.046	0.68	0.51	1.64	0.63
$k_{nr} \times 10^4 \text{ s}^{-1}$	3.96	12.5	24.1	12.1	7.95	15.2
77 K $\lambda_{\text{max}} / \text{nm}$	446, 478	514	457, 473, 490, 506	448, 458, 480	456, 488	449, 481
77 K Lifetime / μs	8.0	2.2	2.9	10.0	3.1	5.2

5.7 Results and discussion: Ir and Pt complexes bearing *p*-anisidine-linked tetradentate ligands

Complexes **79-85** (Figure 5.15) will be discussed in this section.

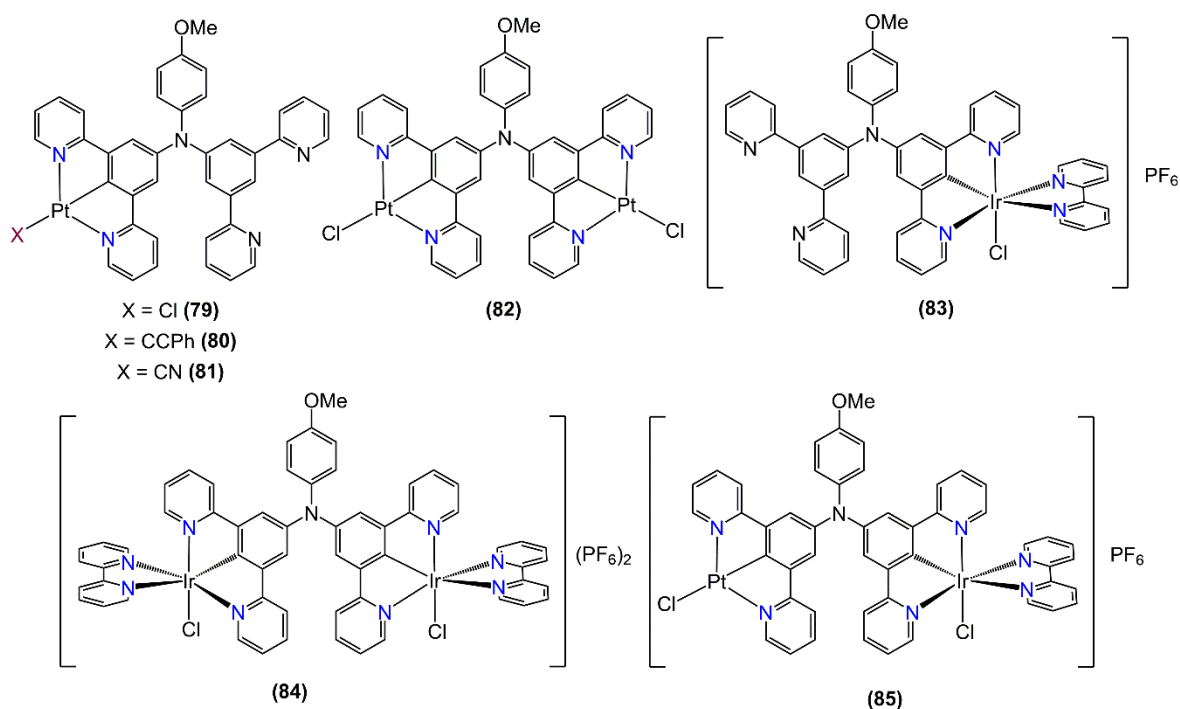


Figure 5.15: Structures of complexes **79-85**.

5.7.1 Synthesis

Following the theme of *para*-anisidine-based ligands containing bidentate N[^]N, C[^]N or C[^]C units to offer tetradentate ligation to Pt(II) and Ir(III) units in Chapter 4, and to provide access to di-iridium complexes in section 5.6, it was a natural progression to incorporate a tridentate unit. The 4-bromo-N[^]C[^]N unit (HL¹⁷), already utilised in the chemistry of Chapter 3, was prepared via a double stannylation of 1,3,5-tribromobenzene using 2.2 equivalents of 2-(tributylstannyl)pyridine (Figure 5.16). A double Buchwald-Hartwig amination of *p*-anisidine with HL¹⁷ yielded the final N[^]C[^]N bridging ligand (H₂L²²) as a yellow solid in an overall yield of 16% after silica gel column chromatography. This ligand features in all seven mono-, di- and hetero-nuclear platinum and iridium complexes **79-85** discussed in this section.

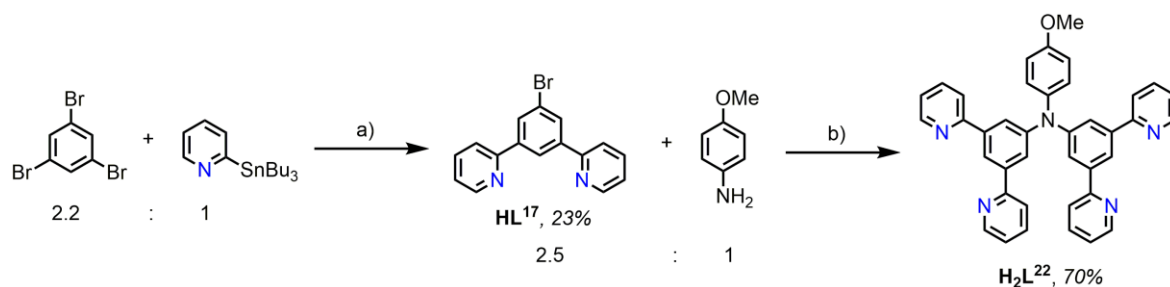


Figure 5.16: Synthesis of the N[^]C[^]N bridging ligand, H₂L²²: a) LiCl, Pd(PPh₃)₂Cl₂, toluene, 110°C, 48 h; b) NaO^{*t*}Bu, Pd₂(dba)₃, toluene, 110°C, 36 h.

The mono and di-platinum complexes, **79** and **82** respectively, were prepared by reaction of H_2L^{22} with K_2PtCl_4 . Complex **79** was isolated as a yellow-orange solid in a yield of 7% by using 1.05 equivalents of ligand to K_2PtCl_4 and by using a mild solvent combination of MeCN and H_2O instead of the standard platination solvent of glacial acetic acid^{152,153,298} (**Figure 5.17, upper**). A small amount of **82** formed during the reaction but its low solubility meant an accurate estimate of the relative amounts of **79** vs. **82** could not be calculated from analysis of the crude ^1H NMR spectrum. Fortunately, both complexes were separable by silica gel column chromatography with a gradient of 0-2% MeOH in DCM. Complex **82** eluted first (R_f = 0.56, 2% MeOH, 98% DCM) as a red solid followed by **79** (R_f = 0.44, as above). The di-platinum complex was favoured by increasing the K_2PtCl_4 : ligand ratio to 1 : 2.5 and by using glacial acetic acid. After the column, complexes were further purified by recrystallizations from either DCM and hexane (**79**) or DMF and ether (**82**).

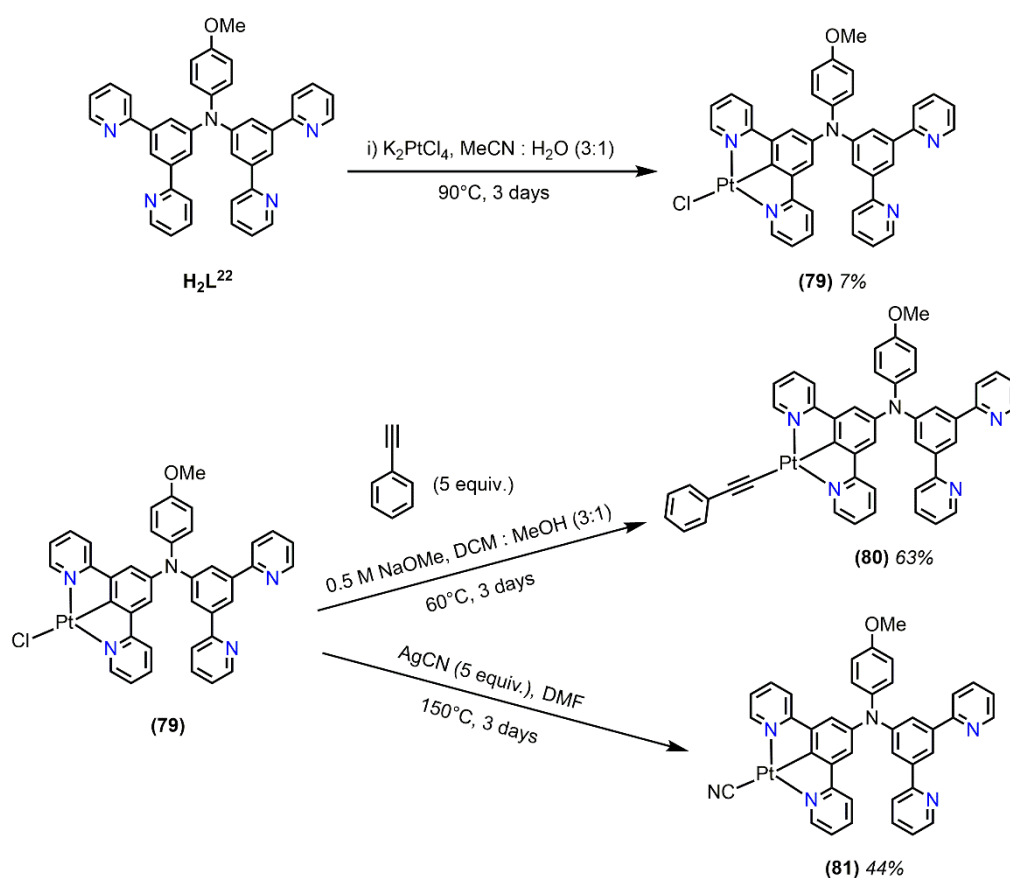


Figure 5.17: Synthetic scheme for the synthesis of complex, **79** (upper) and metathesis of **79** with phenylacetylene and AgCN to yield **80** and **81** respectively (middle and lower).

Complex **79** was subsequently subjected to chloride metathesis with phenylacetylene and AgCN to produce **80** and **81** respectively (**Figure 5.17, lower**). Although the literature $Pt(N^{\wedge}C^{\wedge}N)CN$ examples were prepared from the $Pt(N^{\wedge}C^{\wedge}N)Cl$ analogues by overnight RT stirring in MeCN with KCN,^{299,300} we decided to apply our general cyanide metathesis conditions that had been optimized for cationic iridium systems discussed in Chapter 3. We were pleased that the reaction proceeded at the first attempt. Column chromatography on alumina (DCM : MeOH 0-0.5%) yielded the cyanide-

containing complex, **81**, as an orange solid in a yield of 44%. Complex **79** subsequently underwent chloride metathesis with phenyl acetylene to produce the acetylide-based complex, **80**, in a 63% yield.

The synthesis of **80** was accomplished according to literature procedures for the preparation of similar acetylene-based platinum complexes.^{298,301} Deprotonation of phenylacetylene was achieved after 30 minutes stirring in a 0.5 M solution of NaOMe in MeOH at RT. Complex **79** was subsequently added as a solution in MeOH and DCM (3 : 1) and the reaction mixture was stirred under reflux for 72 h. Pure **80** was obtained as a yellow solid in a yield of 63% after washing with H₂O, MeOH and hexane. There was no noticeable difference in the solubilities of **79-81** as all three complexes were readily soluble in solvents such as DCM.

The ¹H NMR spectra of the mono-platinum complexes **79-81** in CDCl₃ are shown in **Figure 5.18**. Prominent platinum satellites can be seen in the H¹ doublet of doublets of **79** at 9.28 ppm which is the most de-shielded signal in the spectrum. Protons H⁶ and H⁷ are the most shielded of the aromatic protons with shifts of 6.82 and 7.13 ppm respectively. The single peak in the aliphatic region corresponds to the methoxy protons at 3.76 ppm. In the spectrum of complex **80**, the phenylacetylene protons appear as a collection of two multiplets at 7.58 (H¹⁵) and 7.27 ppm (H^{16,17}). The peak corresponding to the terminal N[^]C[^]N protons (H¹) appears at 9.49 ppm and is therefore less shielded than the equivalent protons in **79**, due to the different electronic properties of the acetylide vs. chloride ligand. On the other hand, the signal for the equivalent H¹ protons in **81** occurs furthest upfield at 9.14 ppm. There is little change in shift values of all other proton environments, H² to H¹⁴, between all three complexes **79-81**.

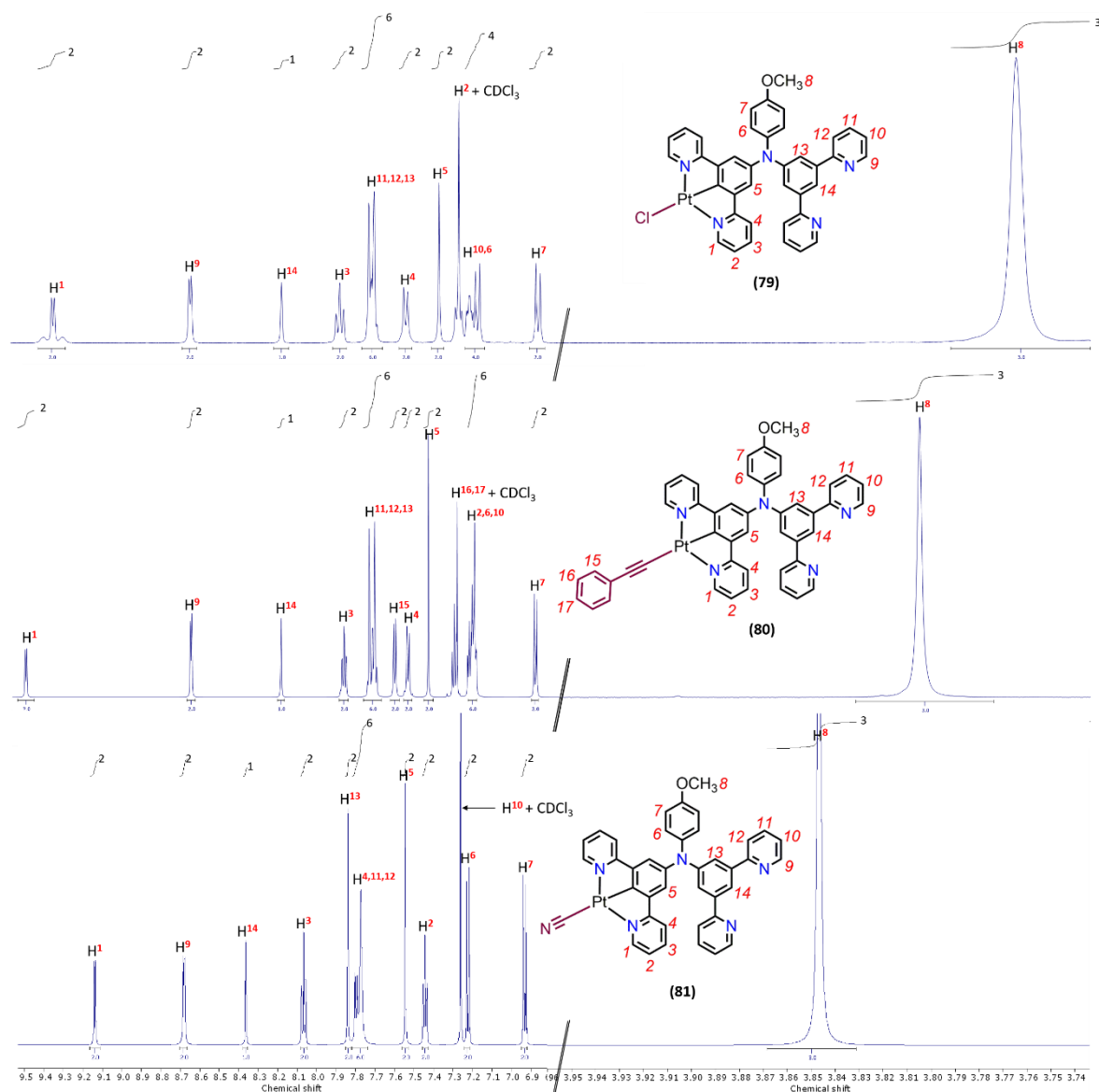
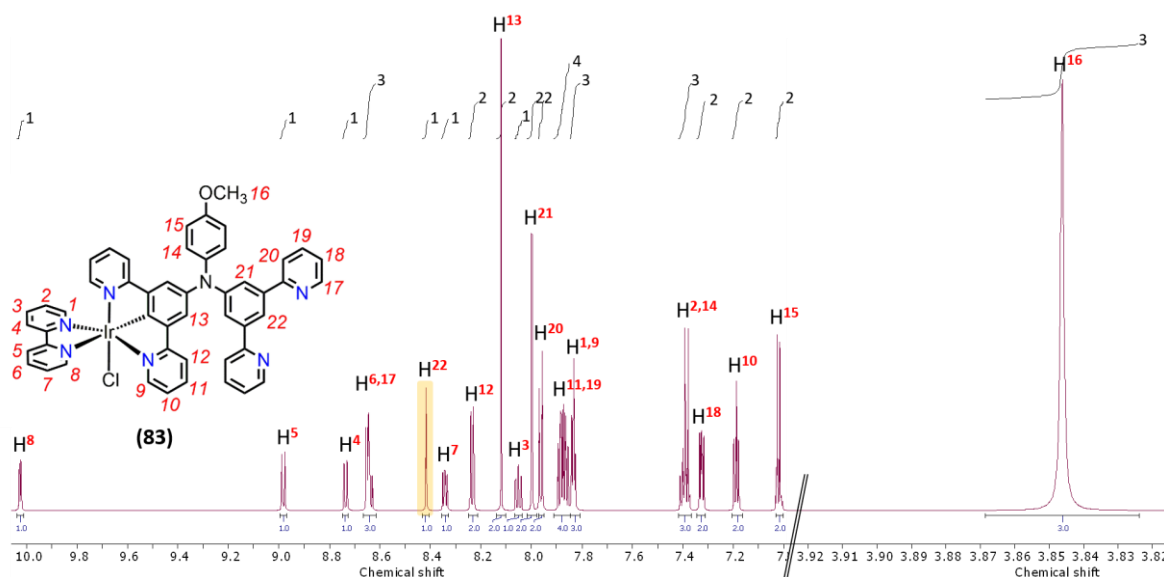


Figure 5.18: ^1H NMR spectra of **79** (upper), **80** (middle) and **81** (lower) in CDCl_3 , 700 MHz.

The mono-iridium complex, **83**, was synthesized via a 2-step procedure using identical conditions to those described for the synthesis of iridium complexes featuring tridentate ligands discussed in Chapter 3 (**Figure 5.19**). Reaction of $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ with 1.5 equivalents of H_2L^{22} in 2-ethoxyethanol and H_2O (3 : 1) gave the chloro-bridged $[\text{Ir}(\text{HL}^{22})\text{Cl}(\mu\text{-Cl})]_2$ dimer as a red solid which was used without further purification or characterisation. An excess of ligand ensured coordination of iridium into only one of the two $\text{N}^{\wedge}\text{C}^{\wedge}\text{N}$ sites on the *p*-anisidine-based ligand. $[\text{Ir}(\text{HL}^{22})\text{Cl}(\mu\text{-Cl})]_2$ was subsequently split open with 2.2 equivalents of bpy in toluene overnight according to the general procedure for the synthesis of iridium complexes bearing tridentate ligands. Dimer cleavage was facilitated by the addition of 4.4 equivalents of the chloride scavenger AgOTf . Precipitation into an aqueous saturated solution of KPF_6 , followed by purification by silica gel column chromatography with a gradient of 0–2% MeOH in DCM yielded **83** as an orange solid.

Evidence for the formation of the mono-iridium complex, **83**, was confirmed by observation of the $[\text{M-PF}_6]^+$ peak corresponding to $m/z = 964$ in the LCMS trace. Furthermore, the ^1H NMR spectrum (**Figure 5.20**) integrates to 22 protons and the triplet at 8.42 ppm (highlighted in yellow) corresponding to H^{22} clearly shows the lack of cyclometallation of a second iridium centre. The protons attached to the bpy ring are magnetically inequivalent and there is a large difference between the chemical shifts associated with the protons of each pyridine ring, for example, H^8 and H^1 shifts are 10.02 and 7.83 ppm respectively. As observed for other tridentate iridium complexes, this magnetic inequivalence is due to the diamagnetic ring current of the $\text{N}^-\text{C}^+\text{N}$ moiety which shields the protons that lie underneath the phenyl ring – in this instance H^1 - H^4 are shielded so their signals appear upfield relative to the signals of H^5 - H^8 . The difference in signals between the bpy rings decreases from H^1/H^8 to H^4/H^5 such that the multiplets of H^4 and H^5 lie within a close range ($\delta = 8.74$ - 8.99 ppm).



The di-iridium analogue, **84**, was prepared by exactly the same methods as **83** with the exception of the first step to synthesize the chloro-bridged iridium dimer. In this instance a 4 : 1 ratio of $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ to HL¹⁷ was used to favour the formation of a supposed polymeric dimer, $[\text{Ir}(\text{L}^{22})\text{Cl}(\mu\text{-Cl})_2]_2$, with iridium coordinated at both N^C^N sites on the ligand thus creating a polymeric or oligomeric

chain with repeating iridium centres separated by alternating chloride and *p*-anisidine bridges. This dimer, also a red solid, was split open using 2.2 equivalents of bpy which resulted in exclusive formation of the di-iridium complex, **84**, as a red solid in a yield of 15% after column chromatography.

Two routes were available to the mixed Pt and Ir complex, **85**, as highlighted in **Figure 5.21**. Platinum could be added to the second N^{^C^N} coordination site of the mono-iridium complex, **83** via reaction with K₂PtCl₄. Alternatively, iridium could be incorporated into the second N^{^C^N} site of the mono-platinum complex, **79**, via reaction with IrCl₃·3H₂O to form a tentatively formulated mixed Pt-Ir chloro-bridged dimer that could undergo subsequent opening with bpy. Both routes successfully led to **85** in overall yields of 16% and 11% respectively after column chromatography on alumina.

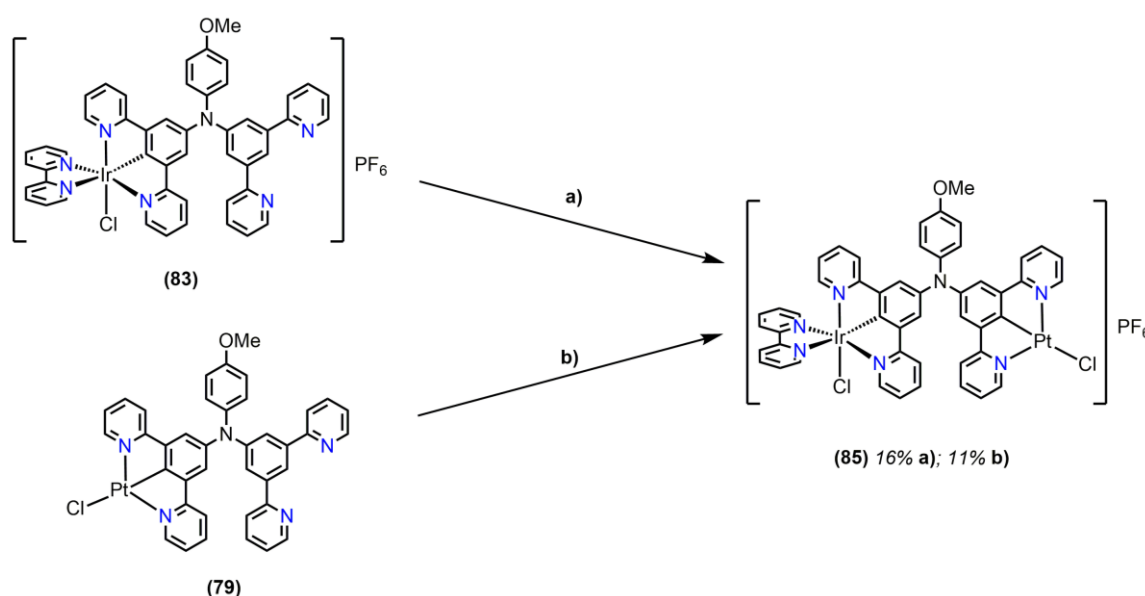


Figure 5.21: Synthetic scheme for the synthesis of the heteronuclear Ir-Pt complex **85** via two routes: a) K₂PtCl₄ (1.2 equiv.), glacial acetic acid, 118°C, 3 days; b) IrCl₃·3H₂O, 2-ethoxyethanol : H₂O (3 : 1), 120°C, 16 h, followed by bpy (2.2 equiv.), AgOTf, toluene, 110°C, 16 h, followed by sat. aq. KPF₆ solution.

Figure 5.22 displays the ¹H NMR spectra of **84** and **85** in *d*₃-MeCN. Due to the symmetrical nature of **84**, there are now only 16 proton environments. The aromatic signals range from 7.04 to 9.90 ppm and the bpy protons H¹-H⁴ are shielded with respect to H⁵-H⁸ due to the diamagnetic ring current of the N^{^C^N} ligand, as seen in the mononuclear analogue, **83**. The most shielded and deshielded bpy protons are H¹ and H⁸ respectively (δ = 9.90 and 7.68 ppm, both highlighted in yellow). Incorporation of platinum to give **85** breaks the symmetry and creates five new proton environments. There is negligible difference between the proton shifts of H¹-H¹⁶ in both spectra. The incompletely resolved ³J ¹⁹⁵Pt-¹H platinum satellites in the ¹H NMR spectrum of **85** lead to the widened baseline around the doublet of H¹⁷ at 9.16 ppm (highlighted in yellow).

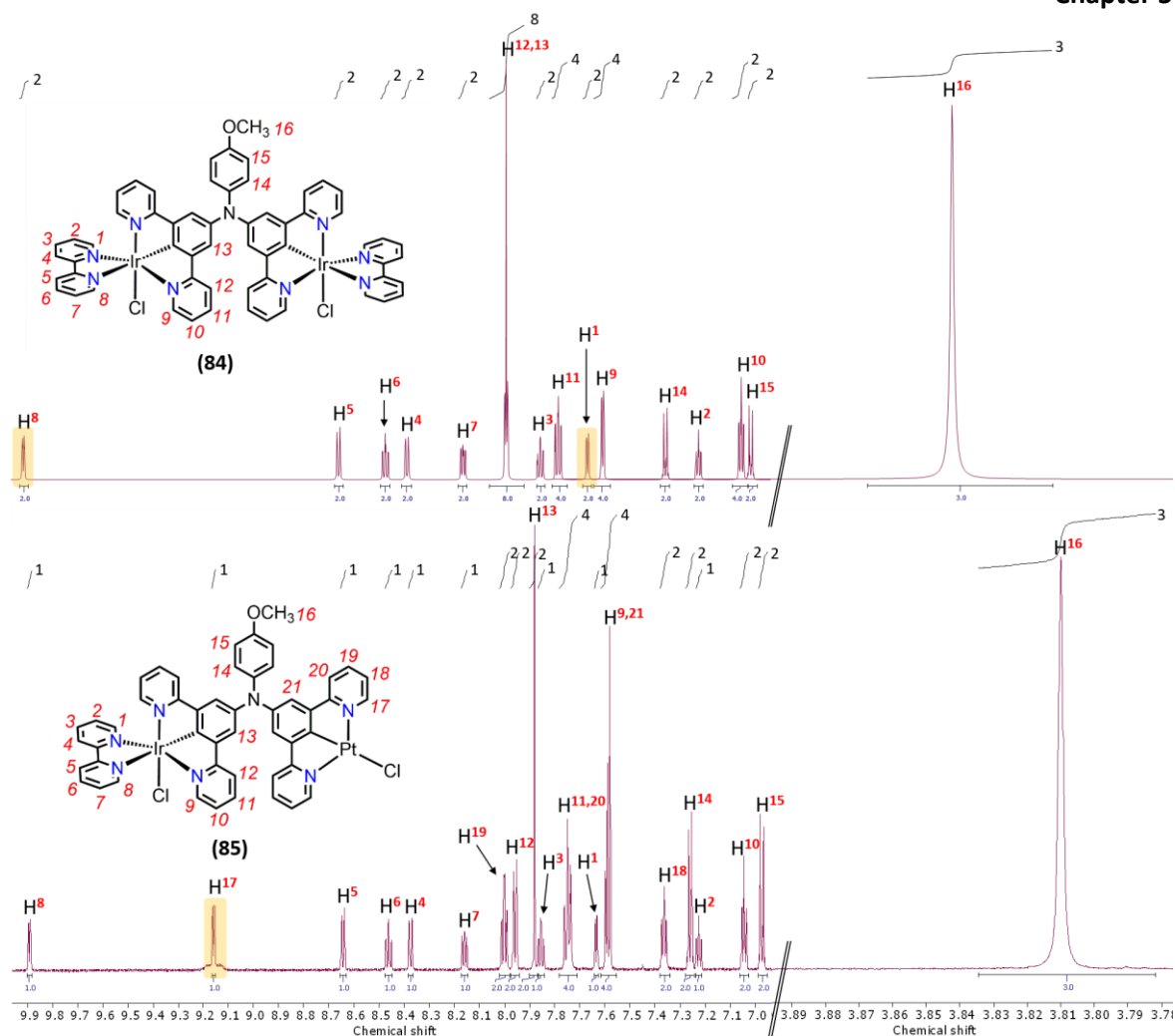


Figure 5.22: ^1H NMR spectra of **84** (upper) and **85** (lower) in d_3 -MeCN, 700 MHz.

5.7.2 Crystallography

Crystals of the di-iridium complex **84** suitable for X-ray diffraction were obtained by slow evaporation from MeCN. The structure of the cation is displayed in **Figure 5.23** alongside its crystal packing arrangement. The two iridium centres occupy a pseudo-octahedral geometry and there is negligible difference between the bond lengths and angles surrounding each iridium site (**Table 5.4**). The cations form off-centered stacks and the closest Ir...Ir distance is 10.68 Å. The Ir–C bond lengths at 1.94 Å are shorter than any of the Ir–N bond lengths which range between 2.03–2.15 Å. The longest and shortest Ir–N bonds involve the bpy ligand; specifically, the bonds of Ir¹–N⁴ and Ir²–N⁹ are the longest due to the stronger *trans* influence exerted by the cyclometalating carbons of L²² compared to the anionic chloride ligands. Conversely, the Ir–N bond lengths involving the tridentate ligand lie within a narrow range between 2.05–2.07 Å.

The *para*-anisidine tertiary amine linker is non-planar and the dihedral angles between the planes of the N¹C¹N¹ units are 41° and 57° whilst the C¹–N¹–C²⁷ bond angle is 119°. The C¹–N¹ and C²⁷–N¹ bond lengths are similar at 1.45 and 1.41 Å respectively.

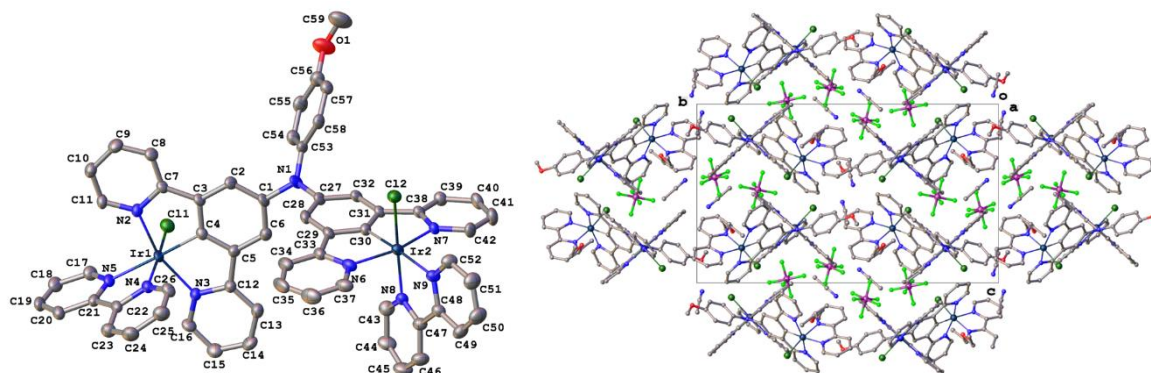


Figure 5.23: Crystal structure of **84** (left) and its crystal packing (right). The PF_6^- counter-ions are omitted for clarity.

Table 5.4: Selected bond lengths and angles for crystal structure **84**.

Complex 84: Selected Bond Lengths (Å) and Angles (°)					
$\text{N}^1\text{--C}^1$	1.449(7)	$\text{Ir}^2\text{--N}^6$	2.052(5)	$\text{C}^{30}\text{--Ir}^2\text{--N}^7$	79.9(2)
$\text{N}^1\text{--C}^{27}$	1.413(7)	$\text{Ir}^1\text{--N}^4$	2.146(4)	$\text{C}^{30}\text{--Ir}^2\text{--N}^6$	80.0(2)
$\text{N}^1\text{--C}^{53}$	1.397(8)	$\text{Ir}^2\text{--N}^9$	2.148(5)	$\text{N}^5\text{--Ir}^1\text{--Cl}^1$	173.21(1)
$\text{Ir}^1\text{--Cl}^1$	2.354(8)	$\text{Ir}^1\text{--N}^5$	2.040(5)	$\text{N}^8\text{--Ir}^2\text{--Cl}^2$	172.27(1)
$\text{Ir}^2\text{--Cl}^2$	2.352(5)	$\text{Ir}^2\text{--N}^8$	2.031(5)	$\text{C}^4\text{--Ir}^1\text{--Cl}^1$	87.95(2)
$\text{Ir}^1\text{--C}^4$	1.935(5)	$\text{C}^1\text{--N}^1\text{--C}^{27}$	118.7(5)	$\text{C}^{30}\text{--Ir}^2\text{--Cl}^2$	90.07(2)
$\text{Ir}^2\text{--C}^{30}$	1.937(5)	$\text{N}^5\text{--Ir}^1\text{--N}^4$	78.93(2)	$\text{C}^1\text{--N}^1\text{--C}^{27}\text{--C}^{28}$	40.6(9)
$\text{Ir}^1\text{--N}^2$	2.066(5)	$\text{N}^8\text{--Ir}^2\text{--N}^9$	78.53(2)	$\text{C}^{27}\text{--N}^1\text{--C}^1\text{--C}^6$	56.9(9)
$\text{Ir}^2\text{--N}^7$	2.061(5)	$\text{C}^4\text{--Ir}^1\text{--N}^2$	80.2(2)	$\text{C}^1\text{--N}^1\text{--C}^{53}\text{--C}^{54}$	39.0(9)
$\text{Ir}^1\text{--N}^3$	2.051(5)	$\text{C}^4\text{--Ir}^1\text{--N}^3$	80.2(2)	$\text{C}^{27}\text{--N}^1\text{--C}^{53}\text{--C}^{58}$	33.0(1)

5.7.3 Electrochemistry

The electrochemical properties of complexes **79–85** are displayed in **Table 5.5** using an electrolyte solution of NBu_4PF_6 in DCM or MeCN. Platinum complexes **79–82** display a single irreversible or quasi-reversible oxidation in the window +0.89 to +1.16 V in addition to a single irreversible reduction potential in the window -1.10 to -1.50 V. Across the series of mono-platinum complexes **79–81**, there is a general shift of the cyclic voltammograms to the right; i.e. the oxidation potentials become more positive and the reduction potentials become less negative. The redox processes of all seven complexes are defined using anodic and cathodic peak potentials – this reduces the accuracy with which their oxidation and reduction potentials are estimated. Nevertheless, there is a general trend of $\Delta E_{1/2}$ values to reduce across the series **79–81** (from $\Delta E_{1/2} = 2.34$ to 2.26 V). Adding a second Pt centre shifts the redox processes to less positive/more negative values as shown by the E_p^{ox} and E_p^{red} values of **82** which are +0.89 and -1.50 V respectively. DFT studies of **79–82** (section 5.7.4) reveal that the HOMO encompasses the metal centre(s) in addition to the central phenyl and *p*-anisidine core, but the covalency in the Pt–C bond means that the oxidations of **79–82** are likely to involve both the metal and the ligand. The reduction potential could be associated primarily with the pyridyl rings of the $\text{N}^{\wedge}\text{C}^{\wedge}\text{N}$ ligand which, according to DFT calculations, is where the LUMO resides. Complex **82** only has a single oxidation and reduction potential despite the two Pt centres; the redox processes observed by cyclic voltammetry may therefore be occurring at both Pt sites

simultaneously. Alternatively, the oxidation of the second platinum might be outside the electrochemical window of the solvent. Electrochemical $\Delta E_{1/2}$ values are not altered significantly by addition of a second platinum centre as the $\Delta E_{1/2}$ values of **79** and **82** are within a close range ($\Delta E_{1/2} = 2.34\text{--}2.39\text{ V}$).

The mono- and di-iridium complexes, **83** and **84**, display a single irreversible oxidation potential at +0.95 and +0.82 V respectively and quasi-reversible reduction potential(s) at -1.69 V (**83**), -1.76 (**84**) and -2.07 V (**84**). The redox potentials of **84** are less positive/more negative than those of **83** which is counterintuitive as the reduction of the di-cationic species (**84**) might be expected to be easier than that of the mono-cationic complex (**83**). Consequently, the $\Delta E_{1/2}$ value of **83** is 0.06 V smaller than that of **84** ($\Delta E_{1/2} = 2.58\text{ vs. }2.64\text{ V}$). The oxidation potentials of **83** and **84** are associated with electron transfer occurring on the HOMO orbital as DFT calculations of **83** show the HOMO is located over the iridium centre as well as the central N⁺C⁺N phenyl and *p*-anisidine core, akin to complexes **79–82**. The reduction potentials of **83** and **84** are likely to be associated with electron transfer on the bpy ancillary i.e. the LUMO. This prediction is supported by the different number of observed reduction potentials in **83** and **84**; the latter complex has two bpy ancillaries and therefore each reduction potential at -1.76 and -2.07 V may reflect successive reductions of each bpy unit.

Table 5.5: Electrochemical properties of complexes **79–85** recorded in a 0.1 M electrolyte solution of NBu₄PF₆ in DCM for **79–82** and in MeCN for **83–85**. Values were measured at a scan rate of 200 mV s⁻¹ and are reported relative to SCE, measured using ferrocene as the standard ($E_{1/2}^{\text{ox}} = 0.42\text{ vs. SCE}$). E_p^{ox} and E_p^{red} are the anodic and cathodic peak potentials respectively. $\Delta E_{1/2} = E_p^{\text{ox}} - E_p^{\text{red}}$. $\Delta E_{\text{H-L}}$ refers to the HOMO-LUMO gap calculated using DFT.

Complex	E_p^{ox}/V	$E_p^{\text{red}}/\text{V}$	$\Delta E_{1/2}/\text{V}$	$\Delta E_{\text{H-L}}/\text{eV}$
79	+1.03 ^{qr}	-1.31 ^{ir}	2.34	2.80
80	+1.10 ^{ir}	-1.21 ^{ir}	2.31	2.78
81	+1.16 ^{ir}	-1.10 ^{ir}	2.26	2.79
82	+0.89 ^{ir}	-1.50 ^{ir}	2.39	2.62
83	+0.95 ^{ir}	-1.69 ^{qr}	2.64	1.47
84	+0.82 ^{ir}	-1.76 ^{qr} , -2.07 ^{qr}	2.58	-
85	+0.72 ^{ir} , +1.01 ^{ir}	-1.68 ^{qr} , -2.13 ^{ir}	1.97	1.37

Finally, the heteronuclear complex, **85**, displays two irreversible oxidations (at +0.72 and +1.01 V) and two irreversible/quasi-reversible reductions (at -1.68 and -2.13 V). The two redox processes of **85** are likely to involve separate contributions from each half of the bridging ligand/metal coordination sphere. DFT studies show the HOMO is located on the Ir–N⁺C⁺N part of **85** therefore we tentatively assign the first and second oxidations to be occurring on the metal and the cyclometalating ligand. The LUMO of **85** does not cover the bpy ligand so the reduction potentials of **85** at -1.68 V and -2.13 V might be associated with redox processes occurring on this *p*-anisidine

unit. Complex **85** also has the smallest $\Delta E_{1/2}$ value in the series **79-85** at 1.97 V. This finding is supported by DFT calculations which suggest **85** has the smallest HOMO-LUMO gap of 1.37 eV.

5.7.4 DFT

Figure 5.24 displays the frontier molecular orbitals of **79-83** and **85** calculated by using the LAN2DZ basis set and the B3LYP hybrid functional; DFT and TD-DFT data is tabulated in **Table 5.6**. The HOMO of the mono-platinum complexes **79-81** is distributed over most of the complex including the platinum, *para*-anisidine and monodentate ligand but excluding the pyridines of the N⁺C⁺N moiety. On the other hand, the LUMO lies exclusively over the entire N⁺C⁺N ring that is coordinated to platinum. The LUMO covers both halves of the di-platinum complex **82** equally. The main contributor to the excited states of **79-82** is a HOMO→LUMO transition (70%) or a HOMO→LUMO+1 transition (61%) in the case of **81**.

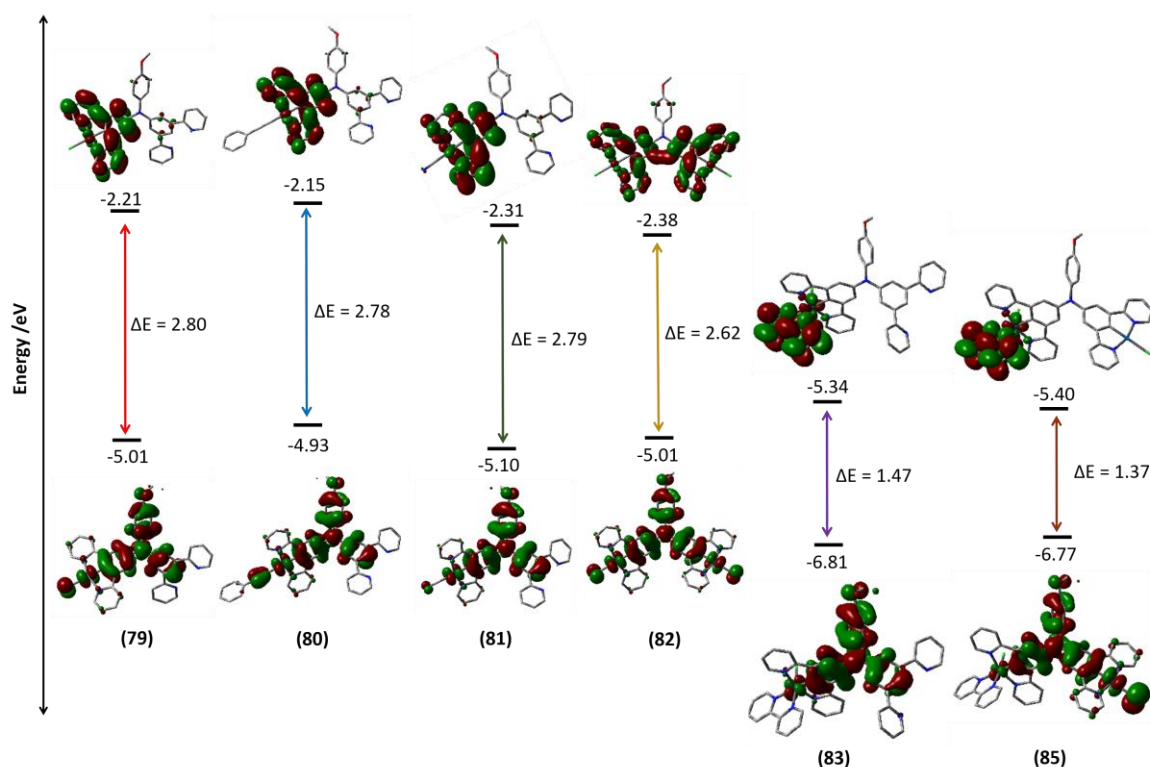


Figure 5.24: Frontier molecular orbital diagrams and energies of **79-83** and **85** which include HOMOs of all six complexes (**79-83** and **85**), the LUMOs of **79, 80, 82, 83** and **85** and the LUMO+1 orbital of **81**.

HOMO→LUMO transitions also contribute the most to the excited states of complexes **83** and **85**. Their HOMOs are located on the iridium centre, the two phenyl rings and the *para*-anisidine unit; the HOMO of **85** extends further over the platinum and chloride groups. The LUMOs of both complexes reside exclusively on the bpy and chloride ligands. These results are consistent with the DFT studies on the mono-iridium complexes discussed in Chapter 3 whose frontier molecular orbitals are located in the same regions as **83** and **85**. The locations and energies of the HOMOs and LUMOs are relatively unaffected by the inclusion of platinum in the vacant N⁺C⁺N coordination site of **83**. The orbital energies of the cationic and di-cationic complexes **83** and **85** appear artificially

lower than the orbital energies of the neutral complexes **79-82** because the DFT calculations were performed in a vacuum; hence the HOMO and LUMO energies of **83** and **85** vs. **79-82** cannot be directly compared. Unfortunately, the structure of **84** was too complicated for computational analysis.

Table 5.6: DFT and TD-DFT results for complexes **79-83** and **85**.

Complex	Energy /eV			Major Orbital Contribution	Oscillator Strength	Excitation Energy	
	HOMO	LUMO	ΔE_{H-L}			/eV	/nm
79	-5.01	-2.21	2.80	HOMO→LUMO (70%)	0.0450	2.27	546.5
80	-4.93	-2.15	2.78	HOMO→LUMO (70%)	0.0432	2.26	548.6
81	-5.10	-2.31	2.79	HOMO→LUMO+1 (61%)	0.0346	2.28	544.6
82	-5.01	-2.38	2.62	HOMO→LUMO (70%)	0.0414	2.12	585.1
83	-6.81	-5.34	1.47	HOMO→LUMO (70%)	0.0003	1.09	1142.6
85	-6.77	-5.40	1.37	HOMO→LUMO (69%)	0.0003	1.03	1207.5

5.7.5 Photophysical properties

The photophysical properties of complexes **79-85** at RT and at 77 K are summarised in **Table 5.7**.

5.7.5.1 Absorption

The absorption spectra of **79-82** measured in DCM are shown in **Figure 5.25, upper**. The profiles of **79-81** are similar in shape. High intensity bands between 255 and 322 nm are associated with $^1\pi-\pi^*$ transitions of the *p*-anisidine scaffold. The spin-allowed nature of this transition gives rise to large extinction coefficients especially for the mono-platinum species ($\epsilon \geq 1.3 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$). Absorbances at longer wavelengths beyond 360 nm are attributed to transitions involving the metal and the *p*-anisidine ligand i.e. MLCT transitions.

The spectra of **79-82** are markedly different from the absorption spectra of the platinum complexes **59-62** discussed in Chapter 4 that feature tetradentate ligands. Specifically, there is a distinct lack of prominent features between 350 and 400 nm in the spectra of **79-82** unlike **59-62** which all include a pronounced peak with extinction coefficients in the order of $10^3 \text{ M}^{-1}\text{cm}^{-1}$. These transitions were attributed to $^1\text{MLCT}$ and $^1\text{LLCT}$ transitions. The $^1\text{MLCT}$ and $^1\text{LLCT}$ transitions of **79-82** appear at lower energies in the form of broad and weakly intense bands in the region of 460-470 nm.

The absorption profiles of **83-85** measured in MeCN are also similar to one another (**Figure 5.25, middle**). The profiles feature two high intensity bands in the high energy region $\lambda < 300 \text{ nm}$ with extinction coefficients in the range $3.3 \times 10^4 \leq \epsilon \leq 9.4 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$. The first transition occurs between 239-249 nm and the second more intense peak ranges from 282 to 293 nm. Both peaks are associated with ^1LC transitions and are marginally higher in energy than the equivalent transitions in **79-82**. The lower energy ^1LC peaks of **84** and **85** are red shifted with respect to **83** by roughly 10 nm ($1100\text{-}1330 \text{ cm}^{-1}$) but this is the only noticeable difference between the three

spectra. The profiles of **83-85** tail off beyond 300 nm but **84** and **85** have a small shoulder of medium intensity at ≈ 316 nm ($5.2 \times 10^4 \leq \epsilon \leq 5.6 \times 10^4$ M⁻¹cm⁻¹) which is associated with charge transfer transitions between the iridium and/or platinum centres and *p*-anisidine. Complexes **83-85** have a further two very weakly intense transitions in the low energy region between 372-383 nm and 449-455 nm. These bands reflect ¹MLCT transitions involving the platinum and/or iridium centres with typical ϵ values of $\leq 7.4 \times 10^3$ M⁻¹cm⁻¹.

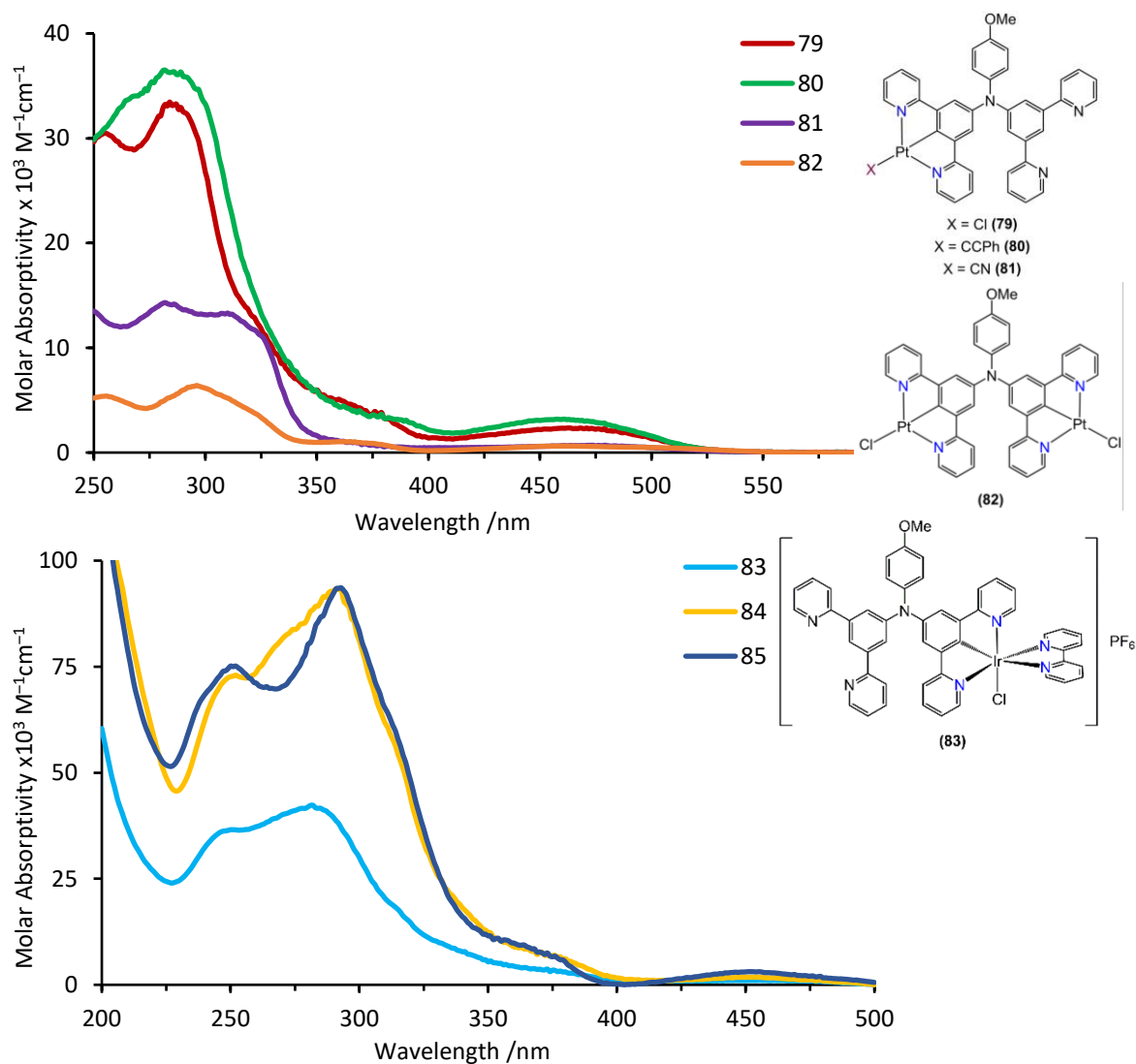
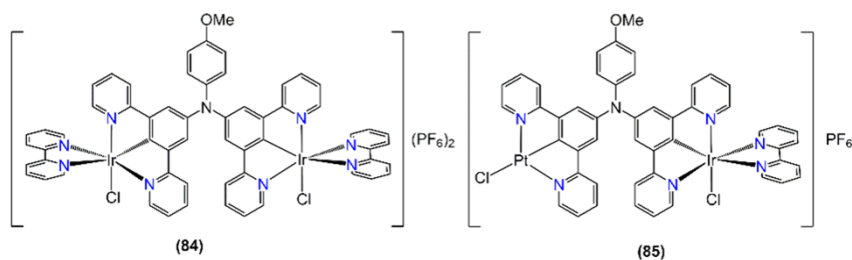


Figure 5.25: Absorbance spectra of **79-82** in DCM (upper) and **83-85** in MeCN (middle). Structures of **84** and **85** are shown in the lower figure.



5.7.5.2 Emission

The red-emitting platinum complexes **79**, **80** and **82** have broad and unstructured RT emission profiles, measured in degassed DCM (**Figure 5.26**). Complexes **79** and **80** display single broad emission peaks at 644 and 635 nm respectively whereas **82** has a maximum at 619 nm and a lower energy shoulder at 666 nm. The 9 nm (220 cm^{-1}) blue shift of **80** vs. **79** is likely to reflect the stronger stabilizing influence of the phenylacetylide ligand towards the HOMO with respect to the chloride.

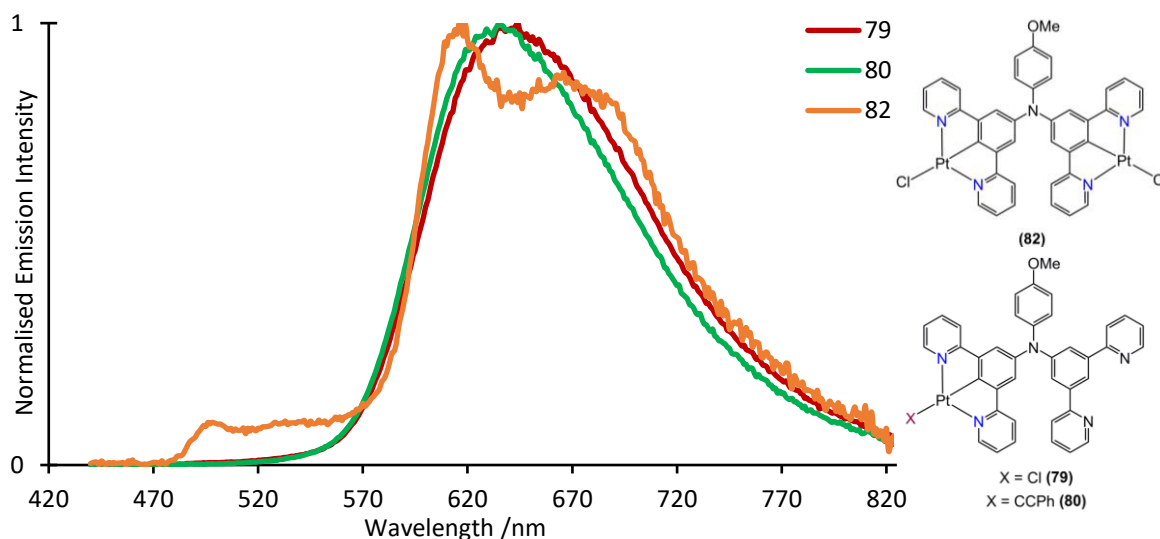


Figure 5.26: Normalised RT emission spectra of **79**, **80** and **82** in degassed DCM, $\lambda_{\text{exc}} = 425\text{ nm}$.

The slightly more structured profile of **82** suggests 0,0 is not the highest contributor to the emission due to considerable excited state distortion. No concentration dependence to the lifetimes or emission profiles of **79-82** were detected which indicate a lack of excimer formation, consistent with their lack of structural planarity. The remaining complexes in this section (**81** and **83-85**) were virtually non-emissive at RT even in degassed solution.

The low temperature emissions of **79-85** are displayed in **Figure 5.27**. The 77 K emissions of **79** and **80** peak at 575 and 563 nm respectively and are blue shifted by roughly 70 nm ($1860\text{-}2010\text{ cm}^{-1}$) with respect to their RT emissions (**Figure 5.27, upper**). Their 77 K profiles feature two peaks or shoulders and this higher degree of structural rigidity reflects the decreased rate of non-radiative decay at low temperature. The 77 K emission profile of **82** is also blue shifted compared to RT but by a much smaller amount than the blue shift observed for **79** and **80**. The 77 K emission profile of **82** features a major peak at 654 nm, a minor peak at 600 nm and a shoulder at approximately 700 nm in contrast to its RT profile which is narrower and less structured with the major peak occurring at 619 nm. The smaller blue shift of **82** compared to **79** and **80** might be due to the increased structural rigidity provided by the second platinum centre which would suppress a larger number of vibrational microstates when cooled. The spectrum of **81** remains unstructured even at low temperature with a single broad emission peak at 545 nm making it the bluest of the platinum

series. The 77 K lifetimes of **79-80** are several microseconds longer than their RT lifetimes, for example, the 77 K and RT lifetimes of **80** are 5.5 and 1.0 μs respectively.

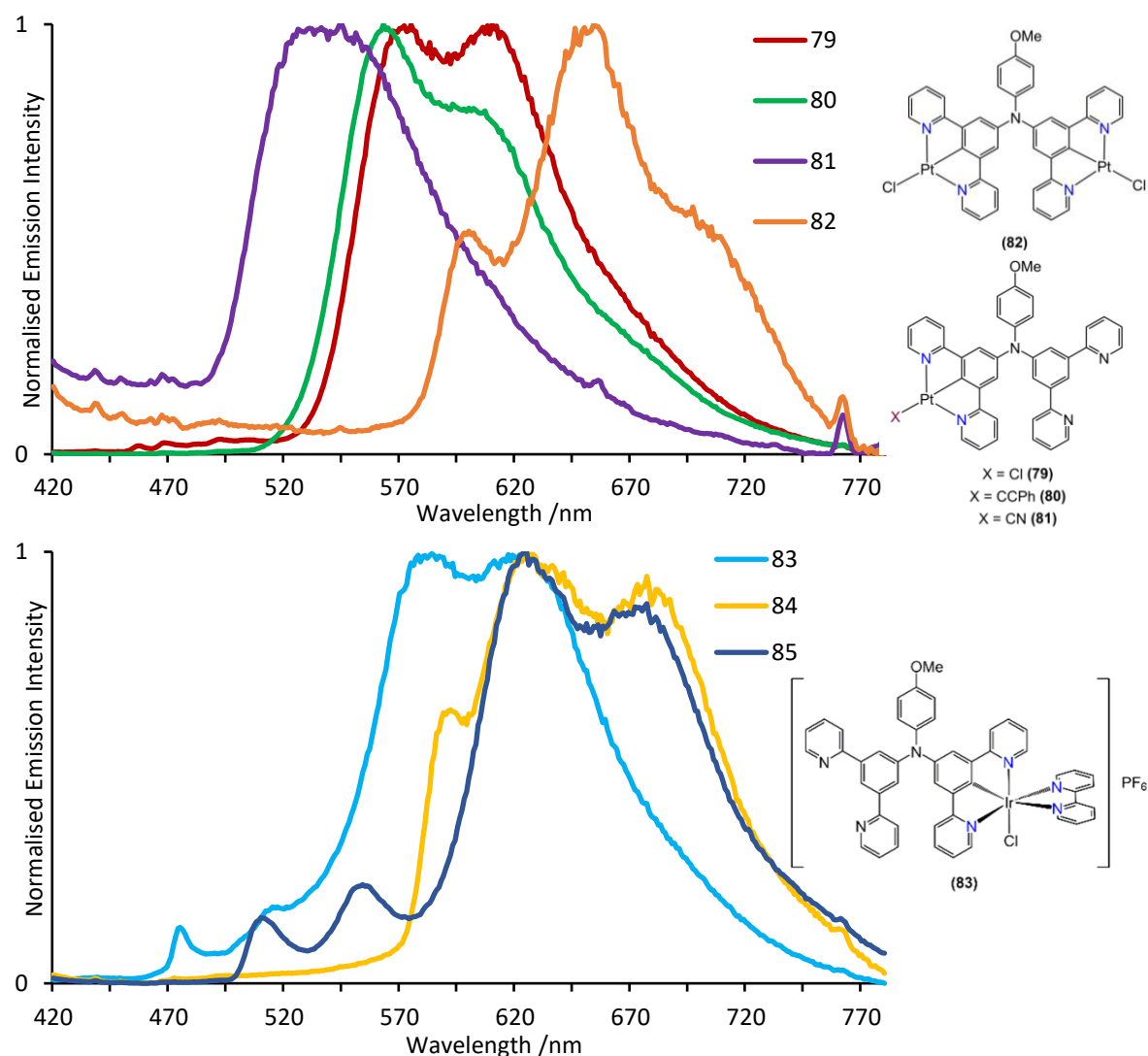
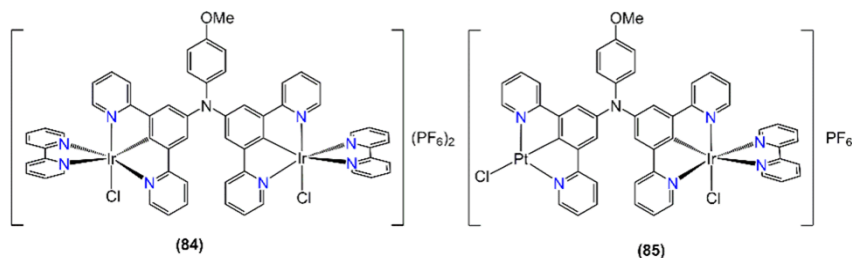


Figure 5.27: Normalised 77 K emission spectra of **79-82** (upper) measured in EPA (**79** and **80**) and butyronitrile (**81**) and of **83-85** (middle) measured in butyronitrile, $\lambda_{\text{exc}} = 400$ nm. Structures of **84** and **85** are shown in the lower figure.



Complexes **84** and **85** have near-identical emission profiles at 77 K with 0,0 and 0,1 maxima at 624-625 and 677 nm (**Figure 5.27, middle**). The former also features a small peak at 592 nm. Complex **83**, on the other hand, has bluer emission than **84** and **85** at low temperature with maxima at 584 and 624 nm. Unfortunately, **83-85** were hardly emissive at RT. The same hypothesis that was made to rationalise the bluer emissions of **79** and **80** vs. **82** could be applied to **83-85** in that the second

metal ions in **84** and **85** provide a greater degree of structural rigidity vs. the mono-metallic complex, **83**. The microsecond lifetimes of **83-85** at 77 K are consistently an order of magnitude longer than their RT lifetimes, for example, the 77 K and RT lifetimes of **85** are 8.1 and 0.43 μs respectively. The difference between the 77 K and RT lifetimes of **83-85** is far greater than in **79-82**, which suggests a greater suppression of non-radiative decay pathways in the iridium-containing complexes at low temperature.

Complexes **79** and **80** have the highest quantum yields in the series **79-85** with PLQYs of 14% (**Table 5.7**). The remaining complexes in the series are virtually non-emissive at RT in degassed DCM or MeCN ($\phi \leq 2\%$). The low PLQYs of **81** and **83-85**, although disappointing, are consistent with the performances of many other red-emitting mono- or multi-metallic complexes found in the literature.^{291,301,302} Metathesis of the chloride ligand in **79** with phenylacetylene (**80**) has a negligible effect on quantum yield. On the other hand, coordinating a second platinum centre in the vacant N[^]C[^]N site (**82**) drastically reduces quantum yield from 14% to 2%, mainly due to a decrease in radiative decay ($k_r = 2.1 \times 10^4 \text{ s}^{-1}$ vs. $2.6 \times 10^3 \text{ s}^{-1}$) despite the predicted larger SOC in the di-platinum complex which would favour phosphorescence. The lack of RT emission in the other complexes is attributable to a combination of low rates of radiative decay and high rates of non-radiative decay, as typified by the decay rates of the non-emissive complex **84** ($k_r = 9.5 \times 10^2 \text{ s}^{-1}$ and $k_{nr} = 1.4 \times 10^6 \text{ s}^{-1}$). The radiative decay rates of emitting complexes are two orders of magnitude larger than in **84** whilst their non-radiative rates of decay are smaller by the same factor, for example, the k_r and k_{nr} values of **80** are $1.4 \times 10^4 \text{ s}^{-1}$ and $8.4 \times 10^4 \text{ s}^{-1}$ respectively.

Table 5.7: Photophysical properties of complexes **79-85** recorded in degassed DCM (**79-82**) or MeCN (**83-85**) at RT, $\lambda_{exc} = 425$ nm, and in butyronitrile at 77 K, $\lambda_{exc} = 400$ nm. ^a = EPA solvent for 77 K measurements. Aerated PLQYs and lifetimes are shown in brackets.

Complex	79 ^a	80 ^a	81	82
Absorption Maxima /nm ($\epsilon / M^{-1} cm^{-1}$)	282 (14300)	282 (36500)	255 (30500)	256 (53800)
	310 (13300)	379 (3660)	284 (33500)	296 (64100)
	322 (11700)	461 (3190)	318 (13900)	361 (10400)
	472 (864)		376 (5350)	378 (7890)
			464 (3360)	462 (6270)
				500 (4820)
λ_{max} / nm	644	635	804	619, 666
PLQY /% degassed (aerated)	14.1 (0.4)	14.4 (0.5)	0.2 (0.1)	2.0 (0.3)
Lifetime /ns degassed (aerated)	6580 (263)	1020 (235)	1540 (873)	7620 (526)
$k_r \times 10^5 s^{-1}$	0.21	0.14	0.011	0.026
$k_{nr} \times 10^5 s^{-1}$	1.31	0.84	6.48	1.29
77 K λ_{max} / nm	575, 610	563	545	600, 654
77 K Lifetime / μs	9.9	5.5	0.8	5.0

Complex	83	84	85
Absorption Maxima /nm ($\epsilon / M^{-1} cm^{-1}$)	245 (33400)	249 (72400)	239 (65200)
	282 (37400)	291 (93400)	252 (75200)
	377 (3140)	316 (51700)	293 (93600)
	455 (1040)	383 (5370)	315 (56100)
		449 (2010)	372 (7370)
			452 (2940)
λ_{max} / nm	583	692	792
PLQY /% degassed (aerated)	0.1 (0.1)	0.1 (0.1)	0.1 (0.1)
Lifetime /ns degassed (aerated)	883 (146)	692 (53)	427 (108)
$k_r \times 10^5 s^{-1}$	0.015	0.0095	0.026
$k_{nr} \times 10^5 s^{-1}$	11	14	23
77 K λ_{max} / nm	584, 624	592, 625, 677	624, 677
77 K Lifetime / μs	5.8	3.2	8.1

5.8 Summary

In summary, ten novel di-cationic di-iridium complexes of the type $[Ir(C^N)_2(N^N-N^N)](PF_6)_2$, where C^N = ppy, fppy, dfppy, bis-dfp₂py and mes-dfppy and N^N-N^N = a ditopic bpy or pp-based ligand bridged via a *p*-anisidine linker, have been synthesized under the same methodology as used in the mono-iridium complexes. “Outward-facing” N^N units successfully coordinated two iridium ions in a pseudo-octahedral environment, whereas “inward-facing” N^N units produced only mono-iridium complexes due to steric hindrance (Chapter 4). The pure di-iridium complexes were isolated in a racemic mixture of $\Lambda\Lambda/\Delta\Delta$ and $\Lambda\Delta/\Delta\Lambda$ forms. The dinuclear species with pyrazolopyridine side arms are bluer emitters than the analogous di-iridium complexes with bpy coordinating arms (λ_{max} = 453-516 nm vs. 560-617 nm). This trend, presumably due to the destabilizing influence of the electron-rich fused *N*-heterocyclic ring towards the LUMO, was also observed in mono-iridium complexes of the same type (Chapter 2). The pp-based complexes are amongst the bluest di-iridium species reported to date;^{303,304} their blue-green emission arises from a combination of fluorinated

C[^]N ligand, electron-rich N[^]N ligand and non-conjugated *p*-anisidine linker. The bluest and highest performing di-iridium PL emitter was **77** which contains a bis-dfp₂py cyclometalating ligand and a pp-bridged ancillary (ϕ = 17%). The quantum efficiency of **77** is comparable with the performance of similar mono-iridium complexes of the same type and emission colour.^{23,56,94,95,98,109–111,305,306} The low PLQYs of the remaining nine complexes ($\phi \leq 5\%$) are far inferior to those of other yellow-red-emitting di-iridium complexes found in the literature.^{283,284,286}

Furthermore, a series of iridium and platinum complexes have been synthesized containing a *p*-anisidine-linked bis-tridentate ligand featuring two N[^]C[^]N binding sites. This series of seven include the mono- and di-nuclear complexes of Pt and Ir of the types [Ir(N[^]C[^]N)(N[^]N)Cl]_n(PF₆)_n and [Pt(N[^]C[^]N)Cl]_n (where N[^]C[^]N = dpyb, N[^]N = bpy and *n* = 1 or 2), as well as a mixed heteronuclear Pt-Ir complex. Their syntheses use identical methodologies to that reported for mononuclear Ir and Pt complexes discussed in Chapters 3 and 4 respectively. Although some di-ruthenium complexes containing the identical *p*-anisidine-(N[^]C[^]N)₂ linker have been reported previously,^{282,307} this work represents the first examples of iridium and platinum complexes featuring this bridging ligand. Both homonuclear Pt complexes are deep-red emitters: addition of a second platinum centre is detrimental to quantum yield (ϕ = 14% (**79**) vs. 2% (**82**)) but emission colour remains relatively unaffected. Addition of a second iridium centre red shifts emission from orange to deep red (a trend commonly observed in the literature)²⁸⁶ but both iridium complexes and the mixed Ir-Pt complex are very poorly emitting in degassed MeCN at RT. The poor PL of the mixed Ir-Pt and mono-Ir complexes is consistent with some of the literature^{153,193,292} but the low quantum yield of the di-iridium complex (ϕ = 0.1%) is disappointing compared to some of the best performing (charge-neutral) di-iridium complexes found in the literature whose PLQYs approach unity.²⁸⁷

Chapter 6 - Conclusions and Future Work

6.1 Conclusions

A total of 85 complexes of the 3rd row transition metal ions iridium(III) and platinum(II) have been synthesized. The preparation of novel ligands offering bidentate, tridentate and tetradentate coordination modes to the metal centres has presented complexes with interesting photophysical properties. Moreover, the incorporation of a second metal centre has generated homo- and hetero-dinuclear complexes with unique and innovative structures which represent a significant contribution to the field of transition metal coordination photochemistry.

In Chapter 2, a large library of cationic iridium(III) complexes of the type $[\text{Ir}(\text{C}^{\wedge}\text{N})_2(\text{N}^{\wedge}\text{N})]\text{PF}_6$ were synthesized, where $\text{C}^{\wedge}\text{N}$ = ppy, fppy or dfppy and $\text{N}^{\wedge}\text{N}$ = bpy, dmbpy, dmbpy or dmabpy, with the aims of exploring colour-tuning strategies and increasing quantum yields by altering the substituents attached to both cyclometalating and ancillary ligands. We successfully tuned PL emission from red ($\lambda_{\text{max}} = 610$ nm) to blue ($\lambda_{\text{max}} = 463$ nm) by incorporation of electron-withdrawing fluorine atoms onto the $\text{C}^{\wedge}\text{N}$ ligand and electron-donating groups (e.g. *N,N*-dimethylamino) onto the $\text{N}^{\wedge}\text{N}$ ligand. Furthermore, increasing the steric bulk of the cyclometalating ligand by addition of mesityl groups to the position *trans* to the Ir–N bond (**Figure 6.1**), increases quantum yield by up to 16% to achieve a maximum PLQY value of 57%, as has previously been demonstrated by Bryce and Zysman-Colman in related systems.^{87,156} Addition of a second difluorophenyl group to the $\text{C}^{\wedge}\text{N}$ ligand at the same position also increases quantum yield by as much as 10% and, unlike the mesityl group, blue shifts emission by as much as 45 nm (1800 cm^{-1}), associated with a stabilization of the HOMO.³⁰⁸

We were able to expand emission range ($\lambda_{\text{max}} = 450\text{--}677$ nm) by using more electron-rich $\text{N}^{\wedge}\text{N}$ ligands containing a 1*H*-pyrazolo[3,4-*b*]pyridine (pp) motif and by extending conjugation in these systems using an isoquinoline unit.¹⁵⁹ The pp-based complexes consistently gave higher quantum yields and bluer emissions than the analogous azaindole-containing complexes (e.g. $\phi_{\text{max}} = 30\%$ vs. 10%) possibly due to the smaller chelation size offered by pp ligands which might increase rigidity (**Figure 6.1**).

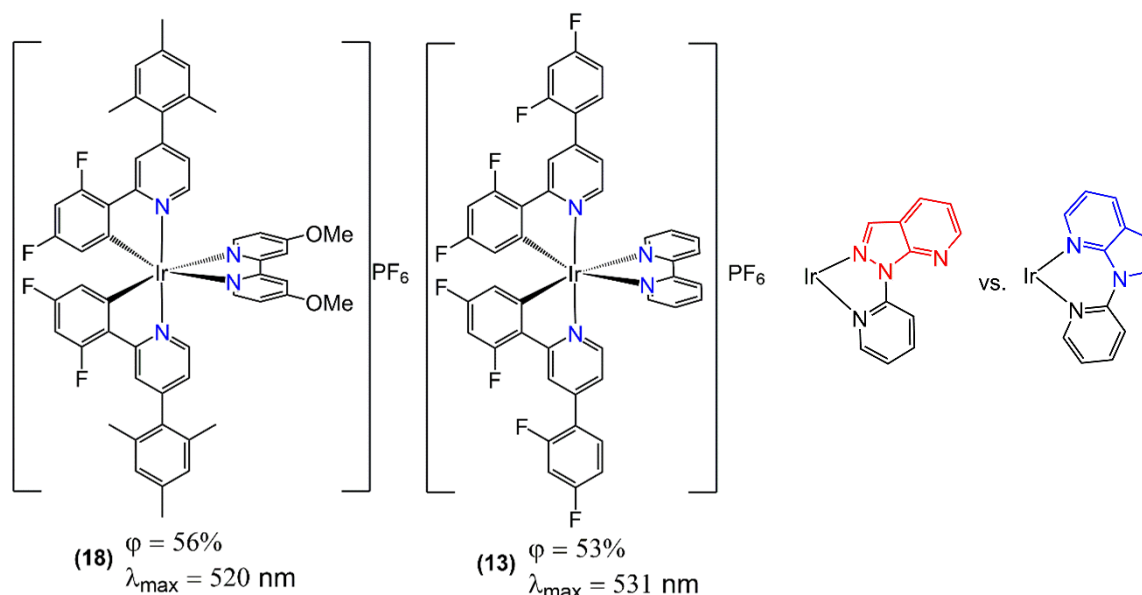


Figure 6.1: Structures and key photophysical properties of complexes **18** and **13** which bear bulky mesityl- and difluorophenyl-containing cyclometalating ligands (left). The ligands containing *pp* and *az* motifs (highlighted in red and blue respectively) have different binding modes; the *pp*-series form a smaller 5-membered chelate ring with iridium whereas the *az*indole series can only coordinate via a larger 6-membered ring (right).

In Chapter 3, we attempted to improve the performance of cationic iridium(III) complexes using a tridentate $\text{N}^{\wedge}\text{C}^{\wedge}\text{N}$ cyclometalating ligand. However, all twenty complexes, which were of the type $[\text{Ir}(\text{N}^{\wedge}\text{C}^{\wedge}\text{N})(\text{N}^{\wedge}\text{N})\text{Cl}]^+$ where $\text{N}^{\wedge}\text{C}^{\wedge}\text{N}$ = a derivative of dipyridyl benzene and $\text{N}^{\wedge}\text{N}$ = bpy, dmbpy, dmbpy or phen, suffered from low solution-state quantum yields ($\phi = \leq 6\%$). Metathesis of the monodentate chloride with acetylide and cyanide, (**Figure 6.2**), in what we believe to be the first examples of such a reaction involving cationic $[\text{Ir}(\text{N}^{\wedge}\text{C}^{\wedge}\text{N})(\text{N}^{\wedge}\text{N})\text{Cl}]^+$ -type complexes, only had a minimal impact on quantum efficiency ($\Delta\phi = 2\%$) and their performances remain inferior to many $\text{Ir}(\text{N}^{\wedge}\text{C}^{\wedge}\text{N})(\text{C}^{\wedge}\text{N})\text{Cl}$ -type complexes found in the literature.^{184,191,192,194,196,197} We found that PL emissions from cyanide-containing complexes are blue shifted with respect to their parent chloride complexes by roughly 50-100 nm ($1630\text{-}3270 \text{ cm}^{-1}$) whereas acetylide-containing complexes emit at equal or lower energies ($\Delta E = 51\text{-}1140 \text{ cm}^{-1}$) than chloride analogues in accordance with the literature concerning neutral Ir(III) complexes.^{178–184,191}

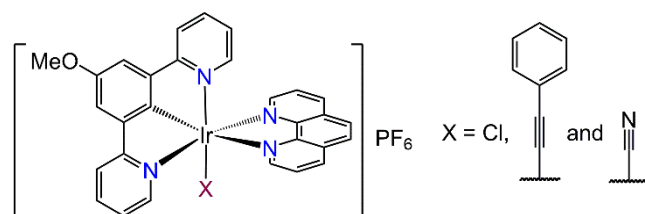


Figure 6.2: Example of an iridium(III) complex bearing an $\text{N}^{\wedge}\text{C}^{\wedge}\text{N}$ -tridentate ligand. Metathesis of the chloride ligand with phenylacetylide and cyanide was successful in two complexes.

The combination of *pp*- and *az*-based ligands with the tridentate ligands generates structural isomers that differ according to which N-donor of the bidentate ligand is *trans* to the metalated

carbon atom of the $N^{\wedge}C^{\wedge}N$ ligand; pp-based ligands have a slight preference for the pyridine ring to coordinate in this position, over the pyrazole ring. The isomers generally have similar photophysical properties to each other, but their quantum yields are no higher than the bpy- or phen-containing systems.

In Chapter 4, iridium(III) and platinum(II) complexes featuring *para*-anisidine-linked tetradentate ligands were synthesized with the objective of investigating their coordination to platinum(II) and iridium(III). Two novel platinum complexes of the types $[Pt(N^{\wedge}N^{\wedge}N^{\wedge}N)](PF_6)_2$ and $[Pt(N^{\wedge}N^{\wedge}N^{\wedge}C)]PF_6$ were prepared (**Figure 6.3**). Cyclometalation was found to boost the quantum yield from 0.3% to 5.9% and blue shift emission from orange to green ($\lambda_{max} = 603$ vs. 510, 547 nm), however, our quantum yields are still lower than the PLQY values of many neutral $Pt(C^{\wedge}N^{\wedge}N^{\wedge}C)$ -type complexes found in the literature.^{7,152,254}

Metathesis of the axial chlorides with phenylacetylene and AgCN in the equivalent iridium complexes of the types $[Ir(N^{\wedge}N^{\wedge}N^{\wedge}N)Cl_2]PF_6$ and $[Ir(N^{\wedge}N^{\wedge}N^{\wedge}C)Cl_2]$, blue shifted emission by 13-23 nm (383 - 504 cm^{-1}) without altering quantum yield significantly (**Figure 6.3**). Although the performances of all four orange-red-emitting complexes were very poor ($\phi \leq 2\%$) in comparison to previously reported iridium complexes containing C- and N-donating tetradentate ligands,^{273,274} they represent the first iridium complexes of these structure types and the first examples of chloride metathesis in these systems.

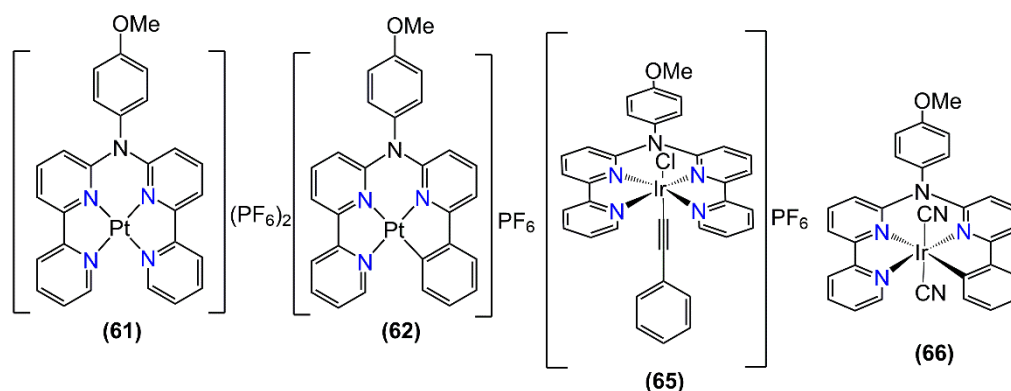


Figure 6.3: Structures of platinum complexes **61** and **62** bearing $N^{\wedge}N^{\wedge}N^{\wedge}N$ and $N^{\wedge}N^{\wedge}N^{\wedge}C$ -type tetradentate ligands (left). The same two ligands successfully coordinated to iridium in a tetradentate fashion with axial chlorides that underwent metathesis with phenylacetylene and AgCN to yield **65** and **66** respectively (right).

The failure of the “inward-facing” bpy units of the $N^{\wedge}N^{\wedge}N^{\wedge}N$ ligand described in Chapter 4 to coordinate two iridium(III) ions led to the synthesis of two *para*-anisidine-linked bridging ligands with “outward-facing” $N^{\wedge}N$ units, discussed in Chapter 5. A library of ten di-iridium complexes of the type $[{Ir}(C^{\wedge}N)_2]_2(\mu-N^{\wedge}N)](PF_6)_2$ were prepared, where $C^{\wedge}N$ = ppy, fppy, dfppy, bis-dfp₂py and mes-dfppy and $\mu-N^{\wedge}N$ = a bis-bidentate ligand comprised of two bpy or pp units (**Figure 6.4**).

Comparison of this library against related mono-iridium complexes in Chapter 2 highlighted some key similarities and differences:

- 1) The di-iridium complexes were less emissive in solution ($\phi_{\text{max}} = 17\%$ vs. $\phi_{\text{max}} = 53\%$).
- 2) The emission maxima of di-iridium bpy-based complexes were red shifted by 7 to 38 nm ($186\text{--}1100\text{ cm}^{-1}$) whereas those of the pp series remained roughly unchanged.
- 3) Di-iridium pp complexes were bluer emitters than the di-iridium bpy series. Addition of a second difluorophenyl group to the cyclometalating dfppy ligands also increased quantum yield by as much as 13% and blue shifted emission by 11 nm (344 cm^{-1}). On the other hand, mesityl pendants had a minimal effect on the photophysical properties of the di-iridium library.

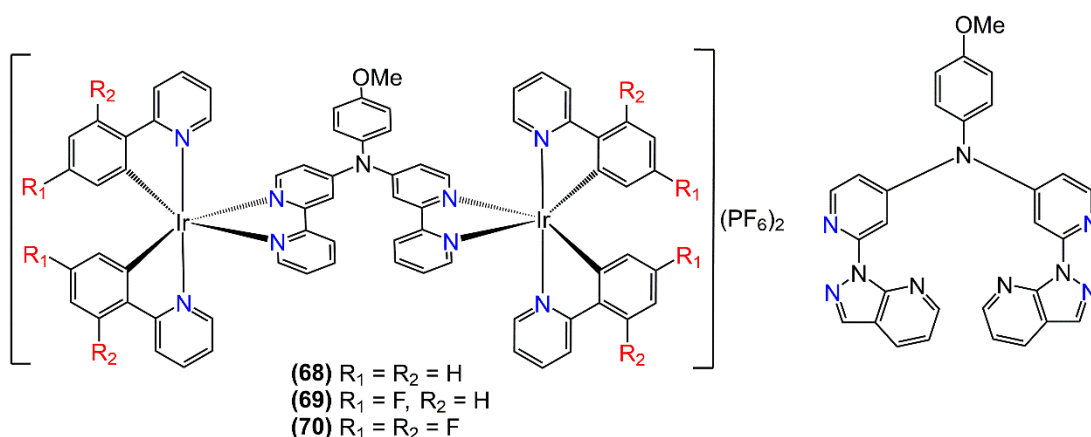


Figure 6.4: Structures of **68-70** (left) - three of the five di-iridium complexes featuring the *para*-anisidine-linked bpy ligand. The analogous five complexes were synthesized using the *para*-anisidine-linked pp ligand (right).

Finally, we aimed to investigate the binding of iridium(III) and platinum(II) ions to a *para*-anisidine-linked tridentate $\text{N}^{\wedge}\text{C}^{\wedge}\text{N}$ bridging ligand possessing two metal binding sites. We successfully synthesized the mono- and di-metallic complexes of Pt(II) and Ir(III), in addition to the heteronuclear Ir-Pt complex (**Figure 6.5**). Addition of a second Pt centre is detrimental to quantum yield ($\phi = 14\%$ vs. 2%) but emission energy is relatively unaffected as both the mono- and di-Pt complexes are red emitters in solution at RT. In contrast, the addition of a second Ir centre red shifts emission by approximately 8 nm (230 cm^{-1}) but only at 77 K as both mono-Ir and di-Ir complexes, in addition to the mixed Ir-Pt complex, are virtually non-emissive at RT. In comparison to the performance of other di-Pt, di-Ir and mixed Ir-Pt complexes found in the literature, we conclude that our *para*-anisidine-linked tridentate $\text{N}^{\wedge}\text{C}^{\wedge}\text{N}$ bridging ligand is a poorer scaffold.^{286,290,292}

Two platinum complexes of the types $\text{Pt}(\text{N}^{\wedge}\text{C}^{\wedge}\text{N})\text{CN}$ and $\text{Pt}(\text{N}^{\wedge}\text{C}^{\wedge}\text{N})\text{C}\equiv\text{CPh}$ were prepared to investigate colour-tuning compared to $\text{Pt}(\text{N}^{\wedge}\text{C}^{\wedge}\text{N})\text{Cl}$, where $\text{N}^{\wedge}\text{C}^{\wedge}\text{N}$ = our *para*-anisidine-linked tridentate bridging ligand, (**Figure 6.5**). The acetylide and cyanide-containing complexes exhibited bluer emissions than the chloride complex by 9-40 nm ($220\text{--}1030\text{ cm}^{-1}$) without any increase in quantum yield ($\phi \leq 14\%$). Again, from comparison with similar previously reported acetylide- and

cyanide-containing Pt complexes, we conclude that our *para*-anisidine-linked N[^]C[^]N ligand is a poorer scaffold for platinum coordination.^{298–302}

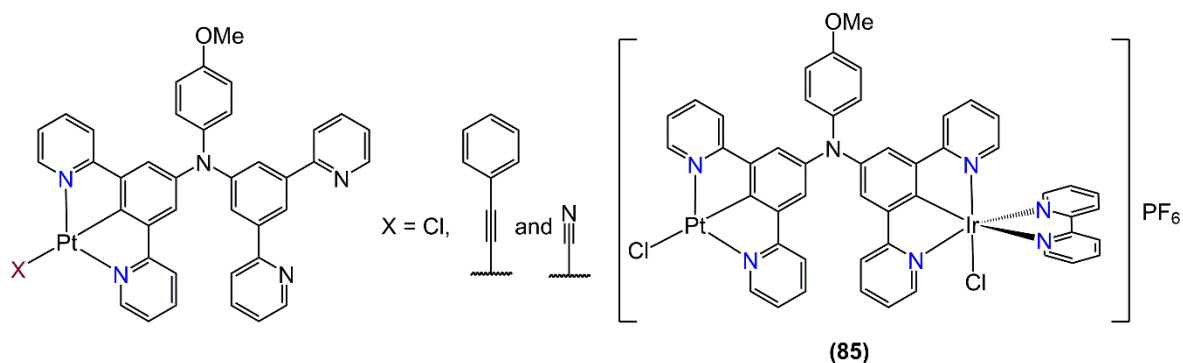


Figure 6.5: Structures of the chloride-, acetylide- and cyanide-containing Pt complexes (left) and the heteronuclear Pt-Ir complex, **85** (right).

There are several lessons to be learnt from undertaking this research into the development of luminescent complexes of iridium(III) and/or platinum(II) for LECs which feature ligands with various chelation modes. The first lesson, in essence, is that simplicity is key. Whilst the use of tridentate ligands represents a relatively new and unexplored approach in the field of Ir-ITMC-based LEC emitters, such complexes generally perform worse than the archetypal tris-bidentate emitters used in the very first examples of ITMC-based LECs in the mid-2000s. Increasing the coordination number from two to four, including chloride metathesis, is unprecedented in this research area but again, the PL properties of our four Ir(III) complexes bearing tetradentate N[^]N[^]N[^]N and N[^]N[^]N[^]C-based ligands were far inferior to those complexes possessing much simpler design structures. This moral applies to di-iridium complexes too as adding a second metal centre failed to increase quantum yields above those of mononuclear equivalents.

Secondly, LEC performance is as much influenced by the device architecture, fabrication procedures and operation modes than it is by the structure of the ITMC itself and the design of the ligand scaffold. Meeting all of the LEC design principles through a rational and systematic approach to ligand design does not guarantee efficient EL – in fact many complexes with excellent PL can perform poorly within a device due to the many different modes of operation and emissive layer formulations that are documented in the literature. Moreover, a variety of performance parameters are measured and reported which makes it extremely challenging to draw direct comparisons between previously reported complexes; the literature reviews in this thesis highlight the need for consistency and uniformity regarding the reporting of LEC performance data.

The final lesson to be learnt is that it is extremely difficult to break away from the paradigm of using [Ir(C[^]N)₂(N[^]N)]PF₆-based complexes as LEC emitters where C[^]N and N[^]N contain ppy- and bpy-based frameworks respectively. The reasons for this are multi-fold: (i) they are very easy to synthesize in

high yields (i.e. few number of synthetic steps with simple purification); (ii) ppy- and bpy-based precursors are widely available at a low cost; (iii) they are highly soluble in MeCN and other polar solvents for device coating and (iv) they have excellent PL (and EL) properties. All other structure types of iridium, e.g. complexes discussed in Chapters 3-5, cannot provide the same attractive benefits. As such, the two complexes shown in **Figure 6.1** (complexes **13** and **18**) are probably the most promising candidates for use in small-scale LEC devices because they can be produced on a large scale in overall yields of 2-21% in 3-4 synthetic steps, they can be purified easily using column chromatography and recrystallization, and they have excellent quantum yields in excess of 50%.

6.2 Future Work

There are many opportunities to build on and expand the work reported in this thesis. Five of the most obvious areas of future development include:

- 1) The testing of iridium complexes within the active layer of LECs; in particular, complexes of the type $[\text{Ir}(\text{C}^{\wedge}\text{N})_2(\text{N}^{\wedge}\text{N})]\text{PF}_6$ would be most suitable for incorporation into devices due to their high synthetic yields, ease of purification and respectable photophysical properties.
- 2) The addition of different peripheral groups, other than mesityl and difluorophenyl, to the $\text{C}^{\wedge}\text{N}$ ligand in the position *trans* to the Ir–N bond to assess whether photophysical properties of the resulting complexes are further enhanced (**Figure 6.6**).
- 3) The investigation of pH dependence in the pp-series of complexes to find out if protonation of the fused pyridine nitrogen affects PL. Additionally, metal-binding titrations are possible on complex **25** due to the free $\text{N}^{\wedge}\text{N}$ site of its pyrimidine-containing pp ligand which would be suitable for metal, e.g. Zn^{2+} , coordination (**Figure 6.6**).
- 4) The preparation of more chloride metathesis examples in tridentate and tetradentate systems of Ir and Pt. Metathesis of dinuclear systems could also be explored with different ligands, for example, isothiocyanates, functionalised arylacetylides and arylthiols etc.
- 5) The investigation of different aniline-based linkers in tetradentate or bridging tridentate ligands, for example, if 4-bromoaniline were used as the amine linker instead of *para*-anisidine (**Figure 6.6**), extension of the bridge at the 4-position would be possible via metal catalysed cross coupling of the bromo group.

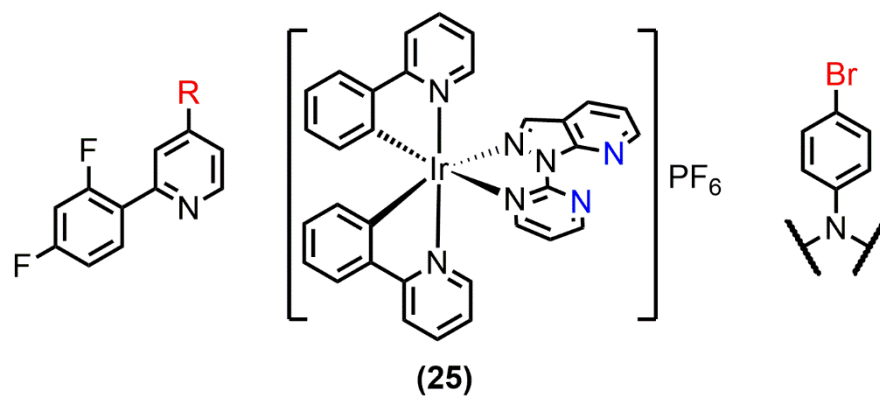


Figure 6.6: Future work could involve the incorporation of different bulky groups to the C^N ligand in tris-bidentate Ir(III) systems e.g. R = ^tBu, quinoline, isoquinoline etc. (left). The PL of complex **25** (middle) could be affected by the coordination of a first-row transition metal in the free N^N site (highlighted in blue) or by protonation of one or both N atoms. The use of 4-bromoaniline as the amine bridge in bis-tridentate and tetradentate ligands would allow extension of the linker via metal-catalysed cross-coupling (right).

Chapter 7 - Experimental

7.1 General procedures

7.1.1 Materials

Reagents were obtained from commercial sources and used without further purification unless specified. Tetrabutylammonium hexafluorophosphate for electrochemical measurements was recrystallized from hot ethanol several times. Solvents used were laboratory grade, except for photophysical studies where HPLC grade acetonitrile was used. Dry solvents were either purchased from Sigma Aldrich, Acros Organics, Fisher Scientific or dried in house using a Pure Solv 400 solvent purification system. Glassware for moisture sensitive reactions was dried in an oven overnight prior to use. Water was using the Purite_{STILL}plus system with $\leq 18 \Omega \text{ m}^{-2}$ conductivity.

7.1.2 Instrumentation

NMR spectra were recorded on a Bruker Avance-400 (400 MHz ^1H and 100 MHz ^{13}C) spectrometer. Two-dimensional NMR (COSY, HSQC, HMBC and NOESY) were recorded on a Varian VNMRS-600 (600 MHz) or VNMRS-700 (700 MHz) spectrometer. Chemical shifts (δ) are reported in ppm referenced to residual protio-solvent resonances and coupling constants (J) are reported in hertz (Hz).

Electrospray ionisation (ES^+) mass spectra were recorded using a Waters Acquity TQD Tandem Quadrupole mass spectrometer with acetonitrile or methanol as the carrier solvent. High resolution mass spectra were obtained using a QToF mass spectrometer. ASAP experiments were performed on a Waters Xevo QToF mass spectrometer. MALDI experiments were performed on Autoflex II ToF mass spectrometer (Bruker Daltonik GmbH) with a *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) matrix.

Thin layer chromatography (TLC) was performed on neutral alumina (Merck Art 5550) or silica (Merck Art 5554) and visualised by UV irradiation at 254 and 365 nm wavelengths. Column chromatography was carried out either manually using neutral alumina or silica or automatically using RediSep R_f silica cartridges on a Teledyne Combi-flash instrument. Complex **52** was purified by HPLC using an Interchim PuriFlash 450 system equipped with an Ace C18-AR (4.6 x 20 mm, 5 μm) column with gradient elution of 50% H_2O with 0.1% formic acid : 50% MeCN to 100% MeCN over 10 minutes.

Melting points were measured on a Gallenkamp melting point apparatus.

7.1.3 Photophysical characterisation

UV-Vis absorption spectra were recorded using a Biotech Instruments UVIKON XS spectrometer operating with LabPower software. Samples were contained in optically matched quartz cuvettes with a path length of 1 cm. All spectra were run against a reference of pure solvent. ϵ values were determined by a dilution technique of three individually prepared stock solutions and graphical application of the Beer-Lambert law:

$$A = \epsilon cl \quad (7)$$

where A is absorbance (at $\lambda_{\max}$), ϵ is the molar extinction coefficient, l is path length, and c is the concentration of the sample.

Solution-state luminescence spectra were acquired on a Jobin Yvon Spex Fluoromax-2 spectrometer. Quartz fluorescent cuvettes of path length 1 cm, modified for attachment to a vacuum line, were used and the absorbance of each solution at the excitation wavelength was below 0.1 to avoid inner filter effects. Samples that were to be measured in the absence of air were degassed within the cuvette by three freeze-pump-thaw cycles. Emission was detected at right angles to the excitation source with appropriate filters used where required to remove second order peaks. All emission spectra were corrected after acquisition for dark count and for the spectral response of the detector. Luminescence quantum yields were determined relative to $[\text{Ru}(\text{bpy})_3\text{Cl}]_3$ in aqueous solution ($\phi_{st} = 0.028$).²⁶² Emission spectra of the complex and reference were measured under identical conditions and the quantum yield (ϕ) was determined by equation:

$$\phi = \phi_{st} \times \left(\frac{I}{I_{st}} \right) \times \left(\frac{A_{st}}{A} \right) \times \frac{n^2}{n_{st}^2} \quad (8)$$

where I represents the overall integrated intensity, A the absorbance at the excitation wavelength, n the refractive index of the solvent and the subscript st denotes the respective values for the standard.

Excited-state lifetime measurements were measured using an Edinburgh Instruments OB920 spectrometer. Luminescence lifetimes of the complexes were measured by time-correlated single-photon counting method, using an EPL405 pulsed-diode laser as the excitation source (404 nm, pulse-length of 60 ps). The laser repetition rate was selected so that the pulse period was < 5 times longer than the complex lifetime. Emission was detected at right angles to the excitation source, after passage through a monochromator, using a Peltier-cooled R928. Lifetimes were obtained by least-squares fitting to a mono-exponential decay and goodness-of-fit was assessed from the residuals. Low temperature (77 K) experiments were performed using a glass vacuum cold finger apparatus built in house. A small amount of sample was dissolved in either a 2 : 2 : 1 solvent mix of diethyl ether : isopentane : ethanol (EPA) or butyronitrile and placed into a glass tube. The cold finger was filled with liquid nitrogen and the tube containing the sample was inserted.

7.1.4 Electrochemical characterisation

Cyclic voltammetry was carried out in a background electrolyte solution of tetrabutylammonium hexafluorophosphate (0.1 M) in either MeCN or DCM, controlled with an Autolab PGSTAT30 potentiostat connected to a PC running GPES software. A three-electrolyte assembly was employed using platinum wire counter and reference electrodes and a glassy carbon working electrode. The electrodes were placed in a cell which was filled with 4 ml of the desired solution and purged with nitrogen.

7.1.5 Density functional theory

DFT geometry optimisations, frequency, stability and TD-DFT excitation calculations were performed using the GaussView 4.1 software package. Geometry optimizations, DFT and TD-DFT calculations of the complexes were performed using the B3LYP hybrid functional and the LANL2DZ basis set.^{309–311}

7.1.6 Crystallography

Single-crystal X-ray data was collected on a Bruker D8Venture diffractometer (I μ S microfocus sources, focusing mirrors, CMOS Photon100 detector) using λ MoK α (λ = 0.71073 Å) radiation, equipped with Cryostream (Oxford Cryosystems) open-flow nitrogen cryostates. The temperature at the crystals was maintained at 120.0 K. All structures were solved by direct methods and refined by full-matrix least squares on F² for all data using SHELXTL190³¹² and OLEX2191³¹³ software by Dr. D. S. Yufit (University of Durham).

7.2 Synthesis of ligands and precursors

7.2.1 Suzuki cross-coupling

General procedure: An aryl halide, an aryl boronic acid, Na₂CO₃ and PPh₃ were dissolved in a mixture of EtOH, toluene and H₂O (2 : 2 : 1). The reaction mixture was degassed by three freeze-pump-thaw cycles and put under a nitrogen atmosphere. The catalyst, Pd(OAc)₂, was then added to the solution and the mixture was heated at 100°C for 24 h. After cooling to RT, the solvents were evaporated and the residue re-dissolved in a mixture of DCM and H₂O (2 : 1). The organic layer was extracted with DCM (typically 2 x 10 ml) and washed with brine (3 x 10 ml). The organic layer was dried over MgSO₄, filtered and the solvent removed under reduced pressure. The crude product was purified by column chromatography on silica gel.

Modified Suzuki cross-coupling procedure: Same as general procedure with the following exceptions: (i) K₂CO₃ base instead of Na₂CO₃; (ii) Pd(PPh₃)₄ catalyst instead of Pd(OAc)₂ and PPh₃; (iii) 1,4-dioxane : H₂O (3 : 1) solvent mixture instead of EtOH, toluene and H₂O; (iv) during work-up the organic layer was subsequently washed with a saturated aqueous solution of NaHCO₃ (3 x 10 ml) in addition to brine.

7.2.2 Stille cross-coupling

General procedure: An aryl halide (1 equiv.), a stannane derivative and LiCl (7.3 equiv.) were added to dry toluene. The reaction mixture was degassed by three freeze-pump thaw cycles and put under a nitrogen atmosphere. The catalyst, $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, was then added to the solution and the mixture was heated at 110°C for 48 h. After cooling to RT, saturated aqueous KF (*ca.* 10 ml) was added and the mixture was left to stir for a further 30 minutes. The suspension was filtered and the insoluble grey residue washed with portions of toluene. The filtrate was removed under reduced pressure and the residual orange-brown oil re-dissolved in DCM (typically 100 ml). After washing with saturated aqueous NaHCO_3 (3 x 15 ml), the organic layer was dried over MgSO_4 , filtered and the solvent removed under reduced pressure. The crude product was purified by column chromatography on silica gel.

Modified Stille cross-coupling procedure: Same as general procedure with the following exception: $\text{Pd}(\text{PPh}_3)_4$ catalyst instead of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ and LiCl.

7.2.3 Lithium-halogen exchange/transmetallation

General procedure: *N*-Butyl lithium solution (2.5 M in hexanes) was added dropwise to a solution of 2-dimethylaminoethanol (DMAE) in THF or hexane at 0°C and stirred for 1 h. A pyridine derivative was added and the solution stirred for 1.5 h at 0°C . After cooling to -78°C , a solution of either iodine in THF, carbon tetrabromide in hexane or tributyl tin chloride in hexane was added dropwise over the course of 30 minutes and the reaction left to warm to RT overnight. The reaction was quenched with H_2O (typically 20 ml) and the solvents removed under reduced pressure. The residue was re-dissolved in saturated aqueous $\text{Na}_2\text{S}_2\text{O}_3$ solution (typically 20 ml) and the product extracted with EtOAc (5 x 20 ml). The combined organic layers were washed with brine (10 ml), dried over MgSO_4 , filtered and the solvent removed under reduced pressure. The crude product was purified by column chromatography on silica gel.

Modified lithium-halogen exchange/transmetallation procedure: Same as general procedure with the following exception: during work-up the product was extracted with ether (3 x 15 ml) and DCM (3 x 15 ml) as opposed to EtOAc.

7.2.4 Copper-catalysed amination

General procedure: A suspension of aryl halide (0.8-3 equiv.), secondary amine (1 equiv.), copper(I) iodide (10% mol), K_2CO_3 (2.1 equiv.) in 1,4-dioxane was thoroughly degassed by three freeze-pump-thaw cycles and put under a nitrogen atmosphere. *Trans*-1,2-diaminocyclohexane (0.2 equiv.) was added and the reaction was heated under reflux at 100°C for 24-36 h under a nitrogen atmosphere. Upon cooling to RT, the mixture was filtered through Celite and the solvent removed under reduced pressure. The crude product was purified by column chromatography on silica gel or alumina.

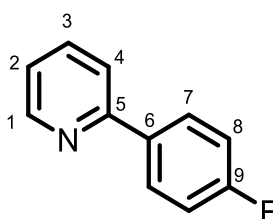
7.2.5 Buchwald-Hartwig amination

General procedure: A suspension of *p*-anisidine (1 equiv.), aryl bromide (0.25-3 equiv.), sodium *tert*-butoxide (1-2.5 equiv.), dppf (4% mol) in dry toluene was thoroughly degassed by three freeze-pump-thaw cycles and put under a nitrogen atmosphere. After addition of Pd(dba)₂ (2% mol), the reaction was heated under reflux at 110°C for 24-36 h under a nitrogen atmosphere. Upon cooling to RT, H₂O (typically 10 ml) was added and the organic layer extracted with EtOAc (3 x 10 ml), washed with H₂O (1 x 10 ml), dried over MgSO₄, filtered and the solvent removed under reduced pressure. The crude product was purified by column chromatography on silica gel or alumina. In some cases, recrystallization was also necessary to isolate the pure compound.

Modified Buchwald-Hartwig amination: Same as the general procedure with the following exceptions: (i) 10% mol of dppf was added; (ii) Pd₂(dba)₃ (10% mol) catalyst instead of Pd(dba)₂ and (iii) reaction time was increased to 48 h.

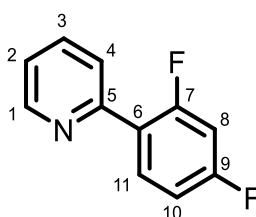
7.2.6 Synthesis of Chapter 2 ligands and precursors

2-(4'-Fluorophenyl)-pyridine (*fppyH*)



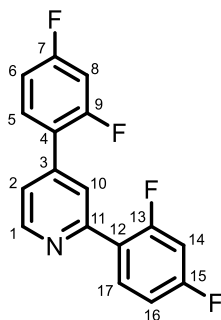
This compound was made following the general Suzuki cross-coupling procedure using 2-bromopyridine (0.55 ml, 5.8 mmol), 4-fluorobenzene boronic acid (1.21 g, 8.7 mmol, 1.5 equiv.), K₂CO₃ (0.18 g, 1.3 mmol, 0.2 equiv.), PPh₃ (0.13 g, 0.50 mmol, 9% mol), Pd(OAc)₂ (35 mg, 0.16 mmol, 2.8% mol), EtOH (40 ml), toluene (40 ml) and H₂O (20 ml). Column chromatography (hexane : ether 0-10%) yielded the title compound as a white solid (0.64 g, 65%). ¹H NMR (CDCl₃, 600 MHz): δ 8.68 (d, 1H, *J* = 5, H¹), 7.98 (dd, 2H, *J* = 9, 6, H⁸), 7.75 (m, 1H, H³), 7.68 (d, 1H, *J* = 8, H⁴), 7.23 (m, 1H, H²), 7.16 (t, 2H, *J* = 9, H⁷); ¹³C NMR (CDCl₃, 151 MHz): δ 163.7 (d, *J* = 248, C⁹), 156.6 (s, C⁵), 149.8 (s, C¹), 137.0 (s, C³), 135.7 (d, *J* = 3, C⁶), 128.9 (d, *J* = 8, C⁸), 122.2 (s, C²), 120.4 (s, C⁴), 115.8 (d, *J* = 22, C⁷); ¹⁹F NMR (CDCl₃, 376 MHz): δ -113.2 (s); ES⁺: 174.0709 [M+H]⁺ (mass for C₁₁H₉NF = 174.0719). The remaining experimental data obtained agreed with that reported in the literature.³¹⁴

2-(2',4'-Difluorophenyl)pyridine (*dfppyH*)



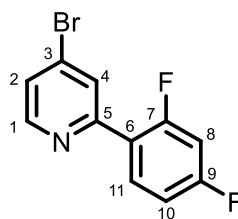
This compound was made following the general Suzuki cross-coupling procedure using 2-bromopyridine (0.51 ml, 5.28 mmol), 2,4-difluorobenzene boronic acid (1.00 g, 6.33 mmol, 1.2 equiv.), Na₂CO₃ (1.12 g, 10.6 mmol, 0.5 equiv.), PPh₃ (0.14 g, 0.53 mmol, 10% mol), Pd(OAc)₂ (40 mg, 0.178 mmol, 3% mol), EtOH (15 ml), toluene (15 ml) and H₂O (7.5 ml). Column chromatography (hexane : DCM 50-90%) yielded the title compound as a yellow liquid (0.70 g, 70%). ¹H NMR (CDCl₃, 600 MHz): δ 8.67 (m, 1H, H¹), 7.98 (td, 1H, *J* = 9, 7, H¹⁰), 7.68 (m, 2H, H^{3,4}), 7.18 (ddd, 1H, *J* = 7, 5, 2, H²), 6.96 (m, 1H, H¹¹), 6.87 (ddd, 1H, *J* = 13, 9, 3, H⁸); ¹³C NMR (CDCl₃, 151 MHz): δ 163.2 (dd, *J* = 251, 12, C⁷), 160.6 (dd, *J* = 253, 12, C⁹), 152.5 (d, *J* = 3, C¹), 149.8 (s, C²), 136.4 (s, C⁵), 132.2 (dd, *J* = 10, 5, C¹⁰), 124.2 (d, *J* = 9, C⁴), 123.8 (dd, *J* = 12, 4, C⁶), 122.4 (s, C³), 111.8 (dd, *J* = 21, 4, C¹¹), 104.3 (dd, *J* = 27, 25, C⁸); ¹⁹F NMR (CDCl₃, 376 MHz): δ -109.3 (d, *J* = 9), -112.9 (dd, *J* = 9, 2); ES⁺: 192.0623 [M+H]⁺ (mass for C₁₁H₈NF₂ = 192.0625). The remaining experimental data obtained agreed with that reported in the literature.³¹⁵

2,4-Bis[2',4''-bis(fluoranyl)phenyl]pyridine (bis-dfp₂pyH)



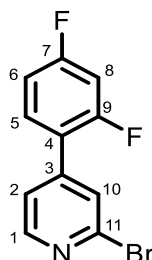
This compound was made following the general Suzuki cross-coupling procedure using 2,4-dibromopyridine (0.26 g, 1.1 mmol), 2,4-difluorobenzene boronic acid (0.42 g, 2.7 mmol, 2.5 equiv.), Na₂CO₃ (0.23 g, 2.2 mmol, 2 equiv.), PPh₃ (28 mg, 0.11 mmol, 10% mol), Pd(OAc)₂ (14 mg, 62 μmol, 6% mol), EtOH (5 ml), toluene (5 ml) and H₂O (2.5 ml). Column chromatography (hexane : ether 0-40%) yielded the title compound as a white solid (0.29 g, 91%); m.p. 117°C; ¹H NMR (CDCl₃, 600 MHz): δ 8.76 (dd, 1H, *J* = 5, 1, H¹), 8.04 (td, 1H, *J* = 9, 7, H¹⁷), 7.88 (m, 1H, H¹⁰), 7.50 (td, 1H, *J* = 9, 6, H⁵), 7.41 (dt, 1H, *J* = 5, 1, H²), 7.02 (m, 2H, H^{6,16}), 6.95 (dddd, 2H, *J* = 23, 11, 9, 3, H^{8,14}); ¹³C NMR (CDCl₃, 151 MHz): δ 164.3 (d, *J* = 12, C⁷), 162.6 (d, *J* = 12, C¹⁵), 161.3 (dd, *J* = 78, 12, C¹³), 159.6 (dd, *J* = 78, 12, C⁹), 153.1 (d, *J* = 3, C¹²), 150.1 (s, C¹), 143.4 (d, *J* = 2, C⁴), 132.4 (dd, *J* = 10, 4, C¹⁷), 131.4 (ddd, *J* = 10, 5, 2, C⁵), 124.1 (dd, *J* = 9, 4, C¹⁰), 123.8 (dd, *J* = 12, 4, C¹¹), 122.8 (dd, *J* = 13, 4, C³), 122.4 (d, *J* = 4, C²), 112.2 (m, C^{6,16}), 104.7 (m, C^{8,14}); ¹⁹F NMR (CDCl₃, 376 MHz): δ -108.4 (d, *J* = 9), -108.9 (d, *J* = 9), -112.5 (d, *J* = 9), -112.8 (d, *J* = 9); ES⁺: 304.0749 [M+H]⁺ (mass for C₁₇H₁₀NF₄ = 304.0754); R_f: 0.31 (70% hexane, 30% ether).

2-(2',4'-Difluorophenyl)-4-bromopyridine



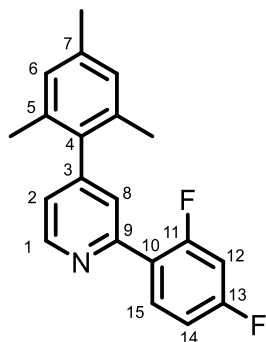
This compound was made following the general Suzuki cross-coupling procedure using 2,4-dibromopyridine (0.20 g, 0.84 mmol), 2,4-difluorobenzene boronic acid (0.13 g, 0.84 mmol, 1.0 equiv.), Na_2CO_3 (0.18 g, 1.70 mmol, 2.0 equiv.), PPh_3 (22 mg, 80 μmol , 10% mol), $\text{Pd}(\text{OAc})_2$ (50 mg, 22 μmol , 3% mol), EtOH (4 ml), toluene (4 ml) and H_2O (2 ml). Column chromatography (hexane : ether 0-6%) yielded the title compound a white solid (39 mg, 17%). ^1H NMR (CDCl_3 , 700 MHz): δ 8.52 (d, 1H, $J = 5$, H^1), 8.01 (td, 1H, $J = 9$, 7, H^{11}), 7.95 (m, 1H, H^4), 7.43 (dd, 1H, $J = 5$, 2, H^2), 7.01 (m, 1H, H^{10}), 6.93 (ddd, 1H, $J = 11$, 9, 3, H^8); ^{13}C NMR (CDCl_3 , 176 MHz): δ 163.7 (dd, $J = 253$, 12, C^9), 160.8 (dd, $J = 253$, 12, C^7), 153.9 (d, $J = 3$, C^6), 150.4 (s, C^1), 133.4 (s, C^3), 132.4 (dd, $J = 10$, 4, C^{11}), 127.5 (d, $J = 11$, C^4), 125.8 (s, C^2), 122.7 (dd, $J = 11$, 4, C^5), 112.2 (dd, $J = 21$, 4, C^{10}), 104.7 (dd, $J = 27$, 25, C^8); ^{19}F NMR (CDCl_3 , 376 MHz): δ -108.0 (dd, $J = 9$, 1), -112.3 (d, $J = 9$); ES^+ : 269.9748 $[\text{M}+\text{H}]^+$ (mass for $\text{C}_{11}\text{H}_7\text{NF}_2\text{Br} = 269.9730$). The remaining experimental data obtained agreed with that reported in the literature.³¹⁶

4-(2',4'-Difluorophenyl)-2-bromopyridine



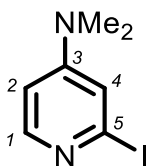
This compound was made following the general Suzuki cross-coupling procedure using 2,4-dibromopyridine (1.04 g, 4.40 mmol), 2,4-difluorobenzene boronic acid (1.52 g, 9.68 mmol, 2.2 equiv.), Na_2CO_3 (1.03 g, 9.68 mmol, 2.2 equiv.), PPh_3 (12 mg, 44 μmol , 10% mol), $\text{Pd}(\text{OAc})_2$ (30 mg, 0.132 mmol, 3% mol), EtOH (12 ml), toluene (12 ml) and H_2O (6 ml). Column chromatography (hexane : ether 0-15%) yielded the title compound as a white solid (0.27 g, 23%); m.p. 73°C; ^1H NMR (CDCl_3 , 700 MHz): δ 8.39 (d, 1H, $J = 5$, H^1), 7.60 (t, 1H, $J = 2$, H^{10}), 7.42 (td, 1H, $J = 8$, 6, H^5), 7.38 (dt, 1H, $J = 5$, 2, H^2), 6.99 (tdd, 1H, $J = 8$, 3, 1, H^6), 6.93 (ddd, 1H, $J = 11$, 8, 3, H^8); ^{13}C NMR (CDCl_3 , 176 MHz): δ 163.7 (dd, $J = 253$, 12, C^7), 160.1 (dd, $J = 253$, 12, C^9), 150.3 (s, C^1), 145.4 (d, $J = 3$, C^4), 142.7 (s, C^{11}), 131.2 (dd, $J = 10$, 3, C^5), 127.6 (d, $J = 3$, C^{10}), 122.6 (d, $J = 4$, C^2), 121.2 (dd, $J = 13$, 4, C^3), 112.4 (dd, $J = 22$, 3, C^6), 105.1 (m, C^8); ES^+ : 269.9751 $[\text{M}+\text{H}]^+$ (mass for $\text{C}_{11}\text{H}_7\text{NF}_2\text{Br} = 269.9730$); R_f : 0.26 (85% hexane : 15% ether).

2-(2',4'-Difluorophenyl)-4-(2'',4'',6''-trimethylphenyl)pyridine (mes-dfppyH)

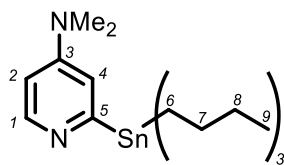


This compound was made following the modified Suzuki cross-coupling procedure using 2-(2,4-difluorophenyl)-4-bromopyridine (0.100 g, 0.37 mmol), mesityleneboronic acid (92 mg, 0.56 mmol, 1.5 equiv.), K_2CO_3 (0.13 g, 0.93 mmol, 2.5 equiv.), $Pd(PPh_3)_4$ (22 mg, 19 μ mol, 5% mol), 1,4-dioxane (3.9 ml) and H_2O (1.3 ml). Column chromatography (hexane : EtOAc 0-6%) yielded the title compound a pale yellow oil (77 mg, 67%). ^1H NMR ($CDCl_3$, 600 MHz): δ 8.77 (d, 1H, $J = 5$, H^1), 8.09 (m, 1H, H^{15}), 7.60 (m, 1H, H^8), 7.09 (dd, 1H, $J = 5, 1$, H^2), 7.03 (m, 1H, H^{14}), 6.98 (s, 2H, H^6), 6.91 (ddd, 1H, $J = 11, 9, 3$, H^{12}), 2.36 (s, 3H, $^7-CH_3$), 2.06 (s, 6H, $^5-CH_3$); ^{13}C NMR ($CDCl_3$, 151 MHz): δ 163.2 (dd, $J = 252, 12$, C^{13}), 160.6 (dd, $J = 252, 12$, C^{11}), 152.7 (d, $J = 3$, C^{10}), 150.0 (s, C^4), 149.9 (s, C^1), 137.6 (s, C^7), 136.2 (s, C^3), 135.2 (s, C^5), 132.2 (dd, $J = 10, 4$, C^{15}), 128.4 (s, C^6), 125.3 (d, $J = 11$, C^8), 123.8 (dd, $J = 11, 4$, C^9), 123.5 (s, C^2), 111.9 (dd, $J = 21, 4$, C^{14}), 104.4 (dd, $J = 27, 25$, C^{12}), 21.0 (s, $^7-CH_3$), 20.6 (s, $^5-CH_3$); ^{19}F NMR ($CDCl_3$, 376 MHz): δ -109.2 (d, $J = 9$), -112.7 (d, $J = 9$); ES^+ : 310.1411 $[M+H]^+$ (mass for $C_{20}H_{18}NF_2 = 310.1407$). The remaining experimental data obtained agreed with that reported in the literature.¹⁵⁶

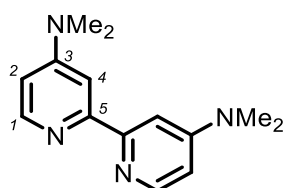
2-Iodo-4-N,N-dimethylaminopyridine



This compound was made following the general lithium-halogen exchange procedure using *n*-butyl lithium (6.55 ml, 16 mmol, 4 equiv.), DMAE (0.83 ml, 8 mmol, 2 equiv.), THF (10 ml), and 4-dimethylaminopyridine (0.50 g, 4.1 mmol) which was added quickly as a solid. Iodine (2.6 g, 10 mmol, 2.5 equiv.) in THF (17 ml) was added at $-78^\circ C$. Column chromatography (hexane : EtOAc 0-50%) yielded the title compound as a yellow oil (0.50 g, 49%); ^1H NMR ($CDCl_3$, 600 MHz): δ 7.75 (m, 1H, H^1), 6.74 (m, 1H, H^4), 6.32 (m, 1H, H^2), 2.84 (m, 6H, $N(CH_3)_2$); ^{13}C NMR ($CDCl_3$, 151 MHz): δ 154.7 (s, C^3), 149.4 (s, C^1), 119.1 (s, C^5), 116.2 (s, C^4), 106.4 (s, C^2), 39.1 (s, $N(CH_3)_2$); ES^+ : 248.9898 $[M+H]^+$ (mass for $C_7H_{10}N_2I = 248.9889$). The remaining experimental data obtained agreed with that reported in the literature.³¹⁷

2-(Tributylstannyl)-4-*N,N*-dimethylaminopyridine

This compound was made following the modified transmetallation procedure using *n*-butyl lithium (6.55 ml, 16 mmol, 4 equiv.), DMAE (0.83 ml, 8.2 mmol, 2 equiv.), hexane (10 ml) and 4-dimethylaminopyridine (0.50 g, 4.1 mmol) which was added quickly as a solid. Tributyltin chloride (2.8 ml, 10 mmol, 2.5 equiv.) in hexane (10 ml) was added at -78°C. Column chromatography (EtOAc : Et₃N 0-2%) yielded the title compound as a dark brown oil (0.66 g, 39%); ¹H NMR (CDCl₃, 700 MHz): δ 8.31 (d, 1H, *J* = 6, H¹), 6.63 (m, 1H, H⁴), 6.34 (dd, 1H, *J* = 6, 3, H²), 2.93 (s, 6H, N(CH₃)₂), 1.54 (m, 6H, H⁷), 1.31 (m, 6H, H⁸), 1.08 (m, 6H, H⁶), 0.86 (m, 9H, H⁹); ¹³C NMR (CDCl₃, 176 MHz): δ 172.1 (s, C⁵), 152.1 (s, C³), 150.1 (s, C¹), 115.5 (s, C⁴), 105.5 (s, C²), 38.9 (s, N(CH₃)₂), 29.2 (s, C⁷), 27.4 (s, C⁸), 13.7 (s, C⁹), 9.7 (s, C⁶); ES⁺: 405.2025 [M+H]⁺ (mass for C₁₉H₃₇N₂Sn = 405.2005). The remaining experimental data obtained agreed with that reported in the literature.³¹⁷

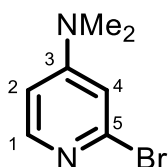
4,4'-Bis-(*N,N*-dimethylamino)-2,2'-bipyridine (*dmabpy*)

Two separate solutions of 2-iodo-4-*N,N*-dimethylaminopyridine (0.19 g, 0.78 mmol, 1.2 equiv.) in dry DMF (2 ml) and 2-(tributylstannyl)-4-*N,N*-dimethylaminopyridine (0.26 g, 0.64 mmol) in dry DMF (2 ml) were thoroughly degassed by three freeze-pump-thaw cycles and put under a nitrogen atmosphere. After addition of Pd(PPh₃)₄ (74 mg, 64 μmol, 10% mol) and PPh₃ (0.22 g, 0.83 mmol, 1.3 equiv.) to the former solution and addition of CuI (24 mg, 0.13 mmol, 0.2 equiv.) to the latter solution, both solutions were stirred at RT for 20 minutes. The 2-(tributylstannyl)-4-*N,N*-dimethylaminopyridine solution was transferred to the 2-iodo-4-*N,N*-dimethylaminopyridine solution via syringe and the reaction mixture was heated under reflux at 125°C for 48 h under a nitrogen atmosphere. Upon cooling to RT, the solvent was removed under reduced pressure and the residue re-dissolved in an aqueous NaOH solution (10 ml, 30% wt) and DCM (15 ml). The organic layer was separated and extracted with DCM (6 x 10 ml), dried over MgSO₄, filtered and the solvent removed under reduced pressure. Purification by column chromatography (silica, DCM : EtOH : Et₃N, 94 : 4 : 2) followed by recrystallization from H₂O : MeOH (1.5 : 1) yielded the title compound as a pale yellow solid (31 mg, 20%); ¹H NMR (CDCl₃, 600 MHz): δ 8.30 (d, 2H, *J* = 6, H¹), 7.69 (d, 2H,

$J = 3$, H^4), 6.51 (dd, 2H, $J = 6, 3$, H^2), 3.09 (s, 12H, $N(CH_3)_2$); ^{13}C NMR ($CDCl_3$, 151 MHz): δ 156.9 (s, C^5), 155.4 (s, C^3), 149.1 (s, C^1), 106.6 (s, C^2), 104.3 (s, C^4), 39.5 ($N(CH_3)_2$); ES^+ : 243.1603 $[M+H]^+$ (mass for $C_{14}H_{19}N_4 = 243.1610$). The remaining experimental data obtained agreed with that reported in the literature.³¹⁸

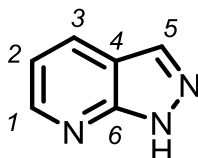
Alternative Synthesis: *N*-butyl lithium (2.7 ml, 2.5 M, 6.8 mmol, 4 equiv.) was added dropwise to a solution of DMAE (0.34 ml, 3.4 mmol, 2 equiv.) in hexane (10 ml) at 0°C and the solution stirred for 45 minutes. 4-Dimethylaminopyridine (0.21 g, 1.7 mmol) was added quickly as a solid and the resulting red solution was stirred for 1 h at 0°C before addition of THF (10 ml). After a further 1.5 h stirring at 0°C, HMPA (8 ml, 46 mmol, 27 equiv.) dried over molecular sieves was added and the purple solution was left to rise to RT overnight. The reaction was quenched with H_2O (10 ml) and the aqueous layer was extracted and washed with portions of ether (3 x 10 ml). A precipitate, which formed in the aqueous layer overnight, was filtered and washed with several small portions of ice-cold H_2O to yield the title compound as an off-white solid (14 mg, 7% yield).

2-Bromo-4-dimethylaminopyridine



This compound was made following the modified lithium-halogen exchange procedure using *n*-butyl lithium (6.4 ml, 16 mmol, 4 equiv.), DMAE (0.8 ml, 8.0 mmol, 2 equiv.), hexane (10 ml) and 4-dimethylaminopyridine (0.49 g, 4.0 mmol) which was added quickly as a solid. Carbon tetrabromide (3.31 g, 10 mmol, 2.5 equiv.) in hexane (10 ml) was added at -78°C. Column chromatography (hexane : ether 20-85%) yielded the title compound as a white solid (0.40 g, 50%); ^1H NMR ($CDCl_3$, 600 MHz): δ 7.94 (d, 1H, $J = 6$, H^1), 6.64 (d, 1H, $J = 2$, H^4), 6.43 (dd, 1H, $J = 6, 2$, H^2), 2.99 (s, 6H, $N(CH_3)_2$); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 155.8 (s, C^5), 149.3 (s, C^1), 143.2 (s, C^3), 109.2 (s, C^4), 106.2 (s, C^2), 39.2 (s, $N(CH_3)_2$); ES^+ : 201.0036 $[M+H]^+$ (mass for $C_7H_{10}N_2Br = 201.0027$). The remaining experimental data obtained agreed with that reported in the literature.³¹⁹

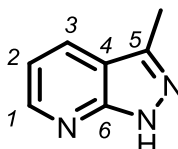
1*H*-Pyrazolo[3,4-*b*]pyridine (*ppH*)



Hydrazine monohydrate (4 ml, 82 mmol, 29 equiv.) was added dropwise to 2-chloro-3-pyridinecarboxylaldehyde (0.40 g, 2.8 mmol) and *p*-TsOH (1.42 g, 8.3 mmol, 2.9 equiv.) in an ice bath. The suspension was heated to 130°C overnight. Upon cooling to RT, H_2O (8 ml) was added and the organic layer was extracted with EtOAc (3 x 7 ml), washed with brine (2 x 5 ml), dried over $MgSO_4$,

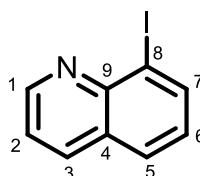
filtered and the solvent removed under reduced pressure. Recrystallization from DCM and hexane yielded the title compound as a light brown solid (0.23 g, 67%); ^1H NMR (CDCl_3 , 700 MHz): δ 14.03 (s, 1H, NH), 8.59 (dd, 1H, $J = 5, 2$, H^1), 8.08 (s, 1H, H^5), 8.05 (dd, 1H, $J = 8, 2$, H^3), 7.07 (dd, 1H, $J = 8, 5$, H^2); ^{13}C NMR (CDCl_3 , 176 MHz) δ 151.7 (s, C^4), 148.5 (s, C^1), 133.5 (s, C^5), 130.4 (s, C^3), 116.8 (s, C^2), 115.3 (s, C^6); ES^+ : 120.0552 $[\text{M}+\text{H}]^+$ (mass for $\text{C}_6\text{H}_6\text{N}_3 = 120.0562$). The remaining experimental data obtained agreed with that reported in the literature.³²⁰

3-Methyl-1H-pyrazolo[3,4-b]pyridine



Hydrazine monohydrate (13 ml, 267 mmol, 28 equiv.) was added dropwise to 3-acetyl-2-chloropyridine (1.50 g, 9.6 mmol) and *p*-TsOH (4.8 g, 28 mmol, 2.9 equiv.) in an ice bath. The suspension was heated to 130°C overnight. Upon cooling to RT, H_2O (30 ml) was added and the organic layer was extracted with EtOAc (4 x 20 ml), washed with brine (2 x 10 ml), dried over MgSO_4 , filtered and the solvent removed under reduced pressure to yield the title compound as a pale yellow solid (1.04 g, 81%); ^1H NMR (CDCl_3 , 600 MHz): δ 12.39 (s, 1H, NH), 8.60 (dd, 1H, $J = 5, 1$, H^1), 8.06 (dd, 1H, $J = 8, 1$, H^3), 7.14 (dd, 1H, $J = 8, 5$, H^2), 2.62 (s, 3H, CH_3); ^{13}C NMR (CDCl_3 , 151 MHz): δ 152.7 (s, C^6), 148.7 (s, C^1), 142.5 (s, C^5), 129.9 (s, C^3), 116.2 (s, C^2), 115.1 (s, C^4), 12.6 (s, CH_3); ES^+ : 134.0711 $[\text{M}+\text{H}]^+$ (mass for $\text{C}_7\text{H}_8\text{N}_3 = 134.0718$). The remaining experimental data obtained agreed with that reported in the literature.

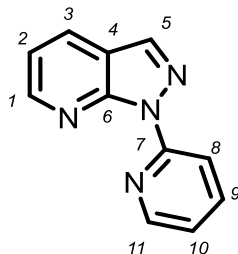
8-Iodoquinoline



A suspension of 8-bromoquinoline (0.30 g, 1.4 mmol), NaI (0.87 g, 5.8 mmol, 4 equiv.), CuI (28 mg, 0.14 mmol, 10% mol) in dry toluene (2 ml) was thoroughly degassed by three freeze-pump-thaw cycles and put under a nitrogen atmosphere. After the addition of *N,N*-dimethylethylenediamine (31 μL , 0.29 mmol, 0.2 equiv.), the suspension was heated under reflux at 110°C for 21 h under a nitrogen atmosphere. Upon cooling to RT, the solvent was evaporated and the residue re-dissolved in DCM (20 ml). The organic phase was washed with 1 M saturated NaOH solution (3 x 10 ml), H_2O (3 x 10 ml), dried over MgSO_4 , filtered and dried under reduced pressure. Purification by column chromatography (silica, hexane-EtOAc 0-10%) yielded the title compound as an orange oil (0.26 g, 71%); ^1H NMR (CDCl_3 , 600 MHz): δ 9.01 (dd, 1H, $J = 4, 2$, H^1), 8.34 (dd, 1H, $J = 7, 1$, H^7), 8.09 (dd, 1H,

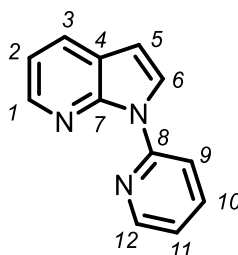
$J = 8, 2, \text{H}^3$), 7.80 (dd, 1H, $J = 8, 1, \text{H}^5$), 7.44 (dd, 1H, $J = 8, 4, \text{H}^2$), 7.26 (m, 1H, H^6); ^{13}C NMR (CDCl_3 , 151 MHz) δ 151.6 (s, C^1), 147.2 (s, C^9), 140.2 (s, C^7), 136.9 (s, C^3), 129.0 (s, C^4), 128.9 (s, C^5), 127.8 (s, C^6), 122.1 (s, C^2), 103.5 (s, C^8); ES^+ : 255.9637 $[\text{M}+\text{H}]^+$ (mass for $\text{C}_9\text{H}_7\text{NI} = 255.9623$). The remaining experimental data obtained agreed with that reported in the literature.³²¹

Ligand L^1



This compound was made following the general copper-catalysed amination procedure using 2-bromopyridine (80 μl , 0.82 mmol, 0.8 equiv.), 1H-pyrazolo[3,4-*b*]pyridine (0.12 g, 0.97 mmol), CuI (19 mg, 97 μmol), K_2CO_3 (0.28 g, 2.1 mmol), *trans*-1,2-diaminocyclohexane (20 μL , 0.17 mmol) and 1,4-dioxane (2 ml). Column chromatography (alumina, hexane : EtOAc 0-60%) yielded the title compound an orange oil (34 mg, 21%). ^1H NMR (CDCl_3 , 600 MHz): δ 8.69 (dd, 1H, $J = 5, 2, \text{H}^1$), 8.67 (m, 1H, H^{11}), 8.37 (d, 1H, $J = 8, \text{H}^8$), 8.24 (s, 1H, H^5), 8.12 (dd, 1H, $J = 8, 2, \text{H}^3$), 7.88 (m, 1H, H^9), 7.23 (m, 2H, $\text{H}^{2,10}$); ^{13}C NMR (CDCl_3 , 151 MHz) δ 151.7 (s, C^7), 150.5 (s, C^4), 149.7 (s, C^1), 149.1 (s, C^{11}), 138.4 (s, C^9), 135.4 (s, C^5), 130.4 (s, C^3), 121.5 (s, C^{10}), 118.2 (s, C^2), 117.8 (s, C^6), 116.0 (s, C^8); ES^+ : 197.0836 $[\text{M}+\text{H}]^+$ (mass for $\text{C}_{11}\text{H}_9\text{N}_4 = 197.0827$). The remaining experimental data obtained agreed with that reported in the literature.¹⁶⁰

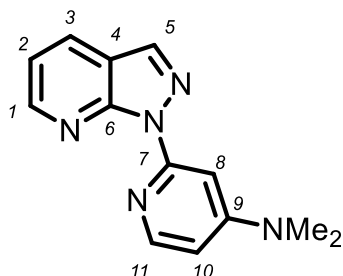
Ligand L^2



This compound was made following the general copper-catalysed amination procedure using 7-azaindole (0.50 g, 4.2 mmol), 2-iodopyridine (0.45 ml, 4.2 mmol, 1 equiv.), K_2CO_3 (1.22 g, 8.8 mmol), CuI (80 mg, 0.42 mmol), *trans*-1,2-diaminocyclohexane (101 μl , 0.84 mmol) and 1,4-dioxane (20 ml). Column chromatography (silica, hexane : EtOAc 0-6%) yielded the title compound as a colourless oil (0.34 g, 42%), ^1H NMR (CDCl_3 , 700 MHz): δ 8.92 (dt, 1H, $J = 8, 1, \text{H}^{12}$), 8.46 (ddd, 1H, $J = 5, 2, 1, \text{H}^9$), 8.39 (dd, 1H, $J = 5, 2, \text{H}^3$), 8.38 (d, 1H, $J = 4, \text{H}^6$), 7.91 (dd, 1H, $J = 8, 2, \text{H}^1$), 7.81 (ddd, 1H, $J = 8, 7, 2, \text{H}^{11}$), 7.12 (dd, 1H, $J = 8, 5, \text{H}^2$), 7.10 (ddd, 1H, $J = 7, 5, 1, \text{H}^{10}$), 6.62 (d, 1H, $J = 4, \text{H}^5$); ^{13}C NMR (CDCl_3 , 176 MHz): δ 150.8 (s, C^8), 148.2 (s, C^9), 147.5 (s, C^4), 143.1 (s, C^3), 138.2 (s, C^{11}), 129.0 (s, C^1), 126.4 (s, C^6), 123.3 (s, C^7), 120.3 (s, C^{10}), 117.1 (s, C^2), 115.7 (s, C^{12}), 102.6 (s, C^5); ES^+ : 196.0846

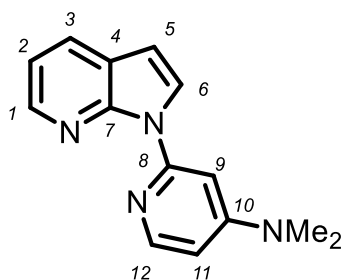
$[M+H]^+$ (mass for $C_{12}H_{10}N_3 = 196.0875$). The remaining experimental data obtained agreed with that reported in the literature.¹⁶⁰

Ligand **L**³



This compound was made following the general copper-catalysed amination procedure using 1*H*-pyrazolo[3,4-*b*]pyridine (0.14 g, 1.13 mmol), 2-bromo-4-dimethylaminopyridine (0.27 g, 1.36 mmol, 1.2 equiv.), CuI (22 mg, 0.11 mmol), K_2CO_3 (0.33 g, 2.38 mmol), *trans*-1,2-diaminocyclohexane (27 μ l, 0.23 mmol) and 1,4-dioxane (8 ml). Column chromatography (alumina, DCM : MeOH 0-1.5%) yielded the title compound as a light brown oil (0.20 g, 75%); ^1H NMR ($CDCl_3$, 700 MHz): δ 8.68 (dd, 1H, $J = 5, 2$, H^1), 8.29 (d, 1H, $J = 6$, H^{11}), 8.19 (s, 1H, H^5), 8.10 (dd, 1H, $J = 8, 2$, H^3), 7.50 (d, 1H, $J = 2$, H^8), 7.20 (dd, 1H, $J = 8, 5$, H^2), 6.48 (dd, 1H, $J = 6, 2$, H^{10}), 3.08 (s, 6H, $N(CH_3)_2$); ^{13}C NMR ($CDCl_3$, 176 MHz) δ 156.3 (s, C^9), 152.8 (s, C^7), 150.5 (s, C^6), 149.7 (s, C^1), 148.9 (s, C^{11}), 134.5 (s, C^5), 130.2 (s, C^3), 117.8 (s, C^2), 117.6 (s, C^4), 105.4 (s, C^{10}), 98.4 (s, C^8), 39.5 (s, $N(CH_3)_2$); ES^+ : 240.1241 $[M+H]^+$ (mass for $C_{13}H_{14}N_5 = 240.1249$); R_f : 0.66 (96% DCM, 4% MeOH).

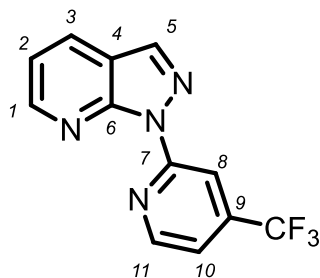
Ligand **L**⁴



This compound was made following the general copper-catalysed amination procedure using 7-azaindole (32 mg, 0.27 mmol), 2-bromo-4-dimethylaminopyridine (59 mg, 0.30 mmol, 1.1 equiv.), CuI (4 mg, 21 μ mol), K_2CO_3 (78 mg, 0.56 mmol), *trans*-1,2-diaminocyclohexane (6.4 μ L, 54 μ mol) and 1,4-dioxane (1.2 ml). Column chromatography (silica, hexane : EtOAc 0-40%) yielded the title compound as a white solid (45 mg, 70%); m.p. 113°C; ^1H NMR ($CDCl_3$, 700 MHz): δ 8.38 (m, 1H, H^1), 8.32 (d, 1H, $J = 4$, H^6), 8.16 (d, 1H, $J = 2$, H^9), 8.12 (d, 1H, $J = 5$, H^{12}), 7.92 (m, 1H, H^3), 7.12 (m, 1H, H^2), 6.59 (d, 1H, $J = 4$, H^5), 6.41 (dt, 1H, $J = 5, 2$, H^{11}), 3.09 (m, 6H, $N(CH_3)_2$); ^{13}C NMR ($CDCl_3$, 176 MHz) δ 156.3 (s, C^{10}), 151.7 (s, C^8), 148.2 (s, C^{12}), 147.6 (s, C^4), 143.0 (s, C^1), 128.9 (s, C^3), 127.2 (s,

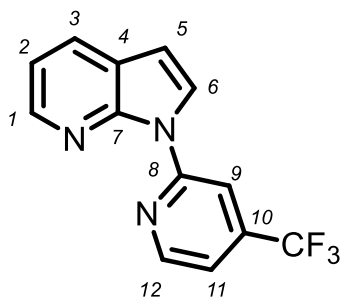
C⁶), 123.3 (s, C⁷), 116.8 (s, C²), 104.5 (s, C¹¹), 101.8 (s, C⁵), 98.5 (s, C⁹); 39.5 (m, N(CH₃)₂); ES⁺: 239.1304 [M+H]⁺ (mass for C₁₄H₁₅N₄ = 239.1297); R_f: 0.29 (60% hexane, 40% EtOAc).

Ligand L⁵



This compound was made following the general copper-catalysed amination procedure using 1*H*-pyrazolo[3,4-*b*]pyridine (44 mg, 0.37 mmol), 2-bromo-4-(trifluoromethyl)pyridine (0.10 g, 0.44 mmol, 1.2 equiv.), CuI (6 mg, 19 μmol), K₂CO₃ (0.11 g, 0.78 mmol), *trans*-1,2-diaminocyclohexane (8.9 μL, 74 μmol) and 1,4-dioxane (2 ml). Column chromatography (silica, DCM : MeOH 0-1.5%) yielded the title compound as a pale yellow solid (41 mg, 42%); m.p. 82°C; ¹H NMR (CDCl₃, 700 MHz): δ 8.83 (d, 1H, *J* = 5, H¹¹), 8.79 (s, 1H, H⁸), 8.73 (m, 1H, H¹), 8.28 (s, 1H, H⁵), 8.15 (dd, 1H, *J* = 8, 2, H³), 7.44 (d, 1H, *J* = 5, H¹⁰), 7.28 (dd, 1H, *J* = 8, 5, H²); ¹³C NMR (CDCl₃, 176 MHz) δ 152.5 (s, C⁷), 150.8 (s, C⁴), 150.1 (s, C¹), 150.1 (s, C¹¹), 140.8 (q, *J* = 34, C⁹), 136.3 (s, C⁵), 130.6 (s, C³), 122.8 (q, *J* = 273, ⁹-CF₃), 118.8 (s, C²), 118.2 (s, C⁶), 116.7 (q, *J* = 3, C¹⁰), 111.7 (q, *J* = 4, C⁸); ¹⁹F NMR (CDCl₃, 376 MHz): δ -64.7 (s); ES⁺: 265.0713 [M+H]⁺ (mass for C₁₂H₈N₄F₃ = 265.0701); R_f: 0.59 (96% DCM, 4% MeOH).

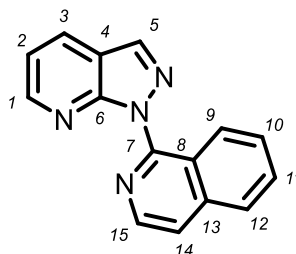
Ligand L⁶



This compound was made following the general copper-catalysed amination procedure using 7-azaindole (44 mg, 0.37 mmol), 2-bromo-4-(trifluoromethyl)pyridine (0.10 g, 0.44 mmol, 1.2 equiv.), CuI (6 mg, 19 μmol), K₂CO₃ (0.11 g, 0.78 mmol), *trans*-1,2-diaminocyclohexane (8.9 μL, 74 μmol) and 1,4-dioxane (2 ml). Column chromatography (silica, hexane : ether 0-40%) yielded the title compound as a pale orange solid (59 mg, 60%); m.p. 92°C; ¹H NMR (CDCl₃, 600 MHz): δ 9.45 (m, 1H, H⁹), 8.61 (d, 1H, *J* = 5, H¹²), 8.43 (m, 2H, H^{1,6}), 7.95 (dd, 1H, *J* = 8, 2, H³), 7.35 (d, 1H, *J* = 5, H¹¹), 7.19 (dd, 1H, *J* = 8, 5, H²), 6.66 (d, 1H, *J* = 4, H⁵); ¹³C NMR (CDCl₃, 151 MHz) δ 151.7 (s, C⁸), 149.2 (s, C¹²), 147.9 (s, C⁴), 143.6 (s, C¹), 140.6 (q, *J* = 34, C¹⁰), 129.3 (s, C³), 126.1 (s, C⁶), 123.6 (s, C⁷), 123.2 (m, ¹⁰-

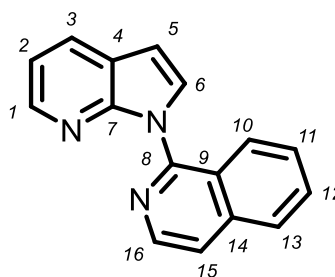
CF_3), 117.8 (s, C^2), 115.7 (q, $J = 3$, C^{11}), 111.6 (q, $J = 4$, C^9), 103.7 (s, C^5); ^{19}F NMR (CDCl_3 , 376 MHz): δ -64.6 (s); ES^+ : 264.0760 $[\text{M}+\text{H}]^+$ (mass for $\text{C}_{13}\text{H}_9\text{N}_3\text{F}_3 = 264.0749$); R_f : 0.69 (80% hexane, 20% ether).

Ligand L^7



This compound was made following the general copper-catalysed amination procedure using 1*H*-pyrazolo[3,4-*b*]pyridine (0.23 g, 1.9 mmol), 1-chloroisoquinoline (0.53 g, 2.3 mmol, 1.2 equiv.), CuI (36 mg, 0.19 mmol), K_2CO_3 (0.79 g, 5.7 mmol), *trans*-1,2-diaminocyclohexane (45 μL , 0.38 mmol) and 1,4-dioxane (8 ml). Column chromatography (silica, hexane : EtOAc 0-40%) yielded the title compound as an off-white solid (91 mg, 20%); m.p. 125°C; ^1H NMR (CDCl_3 , 700 MHz): δ 9.31 (d, 1H, $J = 8$, H^9), 9.00 (s, 1H, H^5), 8.82 (dd, 1H, $J = 4$, 1, H^1), 8.46 (d, 1H, $J = 6$, H^{15}), 8.20 (dd, 1H, $J = 8$, 1, H^3), 7.94 (d, 1H, $J = 8$, H^{12}), 7.79 (m, 2H, $\text{H}^{11,14}$), 7.71 (t, 1H, $J = 8$, H^{10}), 7.15 (dd, 1H, $J = 8$, 4, H^2); ^{13}C NMR (CDCl_3 , 176 MHz): δ 159.3 (s, C^4), 153.4 (s, C^1), 149.5 (s, C^7), 140.4 (s, C^{15}), 139.2 (s, C^8), 131.2 (s, C^{11}), 130.8 (s, C^3), 128.9 (s, C^{10}), 127.7 (s, C^9), 126.9 (s, C^{12}), 124.5 (s, C^5), 122.6 (s, C^{14}), 122.3 (s, C^{13}), 119.0 (s, C^2), 114.1 (s, C^6); ES^+ : 247.0976 $[\text{M}+\text{H}]^+$ (mass for $\text{C}_{15}\text{H}_{11}\text{N}_4 = 247.0984$); R_f : 0.24 (50% hexane, 50% EtOAc).

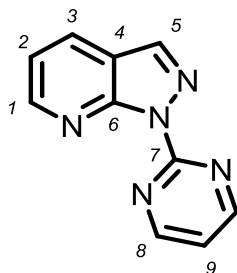
Ligand L^8



This compound was made following the general copper-catalysed amination procedure using 7-azaindole (66 mg, 0.56 mmol), 1-chloroisoquinoline (0.10 g, 0.61 mmol, 1.1 equiv.), CuI (8 mg, 42 μmol), K_2CO_3 (0.16 g, 1.17 mmol), *trans*-1,2-diaminocyclohexane (13 μL , 0.11 mmol) and 1,4-dioxane (2 ml). Column chromatography (alumina, hexane : EtOAc 0-15%) yielded the title compound as an orange solid (19 mg, 14%); m.p. 83°C; ^1H NMR (CDCl_3 , 600 MHz): δ 8.54 (d, 1H, $J = 6$, H^{16}), 8.30 (dd, 1H, $J = 5$, 1, H^1), 8.04 (dd, 1H, $J = 8$, 1, H^3), 7.94 (d, 1H, $J = 8$, H^{10}), 7.78 (m, 2H, $\text{H}^{13,15}$), 7.75 (m, 1H, H^{11}), 7.67 (d, 1H, $J = 4$, H^5), 7.55 (m, 1H, H^{12}), 7.16 (dd, 1H, $J = 8$, 5, H^2), 6.76 (d, 1H, $J = 4$, H^6); ^{13}C NMR (CDCl_3 , 151 MHz) δ 150.3 (s, C^8), 149.0 (s, C^4), 143.9 (s, C^1), 141.8 (s, C^{16}), 138.6 (s,

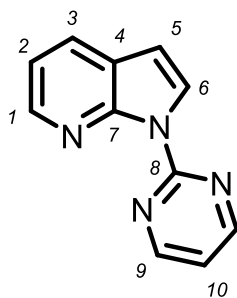
C¹⁴), 131.0 (s, C¹¹), 129.5 (s, C⁵), 129.4 (s, C³), 127.9 (s, C¹²), 127.0 (s, C¹⁰), 126.4 (s, C¹³), 125.0 (s, C⁹), 121.5 (s, C¹⁵), 121.4 (s, C⁷), 117.2 (s, C²), 102.5 (s, C⁶); ES⁺: 246.1038 [M+H]⁺ (mass for C₁₆H₁₂N₃ = 246.1031); R_f: 0.50 (60% hexane, 40% EtOAc).

Ligand L⁹

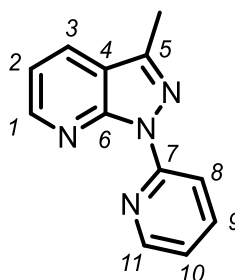


This compound was made following the general copper-catalysed amination procedure using 1H-pyrazolo[3,4-*b*]pyridine (0.23 g, 1.89 mmol), 2-bromopyrimidine (0.36 g, 2.27 mmol, 1.2 equiv.), CuI (36 mg, 0.19 mmol), K₂CO₃ (0.79 g, 5.71 mmol), *trans*-1,2-diaminocyclohexane (45 μL, 0.38 mmol) and 1,4-dioxane (8 ml). Column chromatography (silica, DCM : Et₃N 1%) yielded the title compound as a brown oil (0.18 g, 59%); ¹H NMR (CDCl₃, 700 MHz): δ 8.94 (d, 2H, *J* = 5, H⁸), 8.80 (dd, 1H, *J* = 5, 2, H¹), 8.31 (s, 1H, H⁵), 8.15 (dd, 1H, *J* = 8, 2, H³), 7.29 (dd, 1H, *J* = 8, 5, H²), 7.26 (m, 1H, H⁹); ¹³C NMR (CDCl₃, 176 MHz): δ 159.0 (s, C⁸), 157.0 (s, C⁷), 151.0 (s, C⁴), 150.4 (s, C¹), 136.9 (s, C⁵), 130.5 (s, C³), 118.8 (s, C²), 118.4 (s, C⁹), 118.3 (s, C⁶); ES⁺: 198.0768 [M+H]⁺ (mass for C₁₀H₈N₅ = 198.0780); R_f: 0.16 (99% DCM, 1% Et₃N).

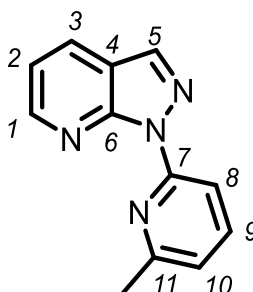
Ligand L¹⁰



This compound was made following the general copper-catalysed amination procedure using 7-azaindole (0.10 g, 0.85 mmol), 2-bromopyrimidine (0.16 g, 1.02 mmol, 1.2 equiv.), CuI (16 mg, 85 μmol), K₂CO₃ (0.25 g, 1.78 mmol), *trans*-1,2-diaminocyclohexane (20 μL, 0.17 mmol) and 1,4-dioxane (3.2 ml). Column chromatography (alumina, DCM : Et₃N 1%) yielded the title compound as a pale yellow oil (0.15 g, 92%); ¹H NMR (CDCl₃, 600 MHz): δ 8.85 (d, 2H, *J* = 5, H⁹), 8.57 (m, 1H, H¹), 8.29 (d, 1H, *J* = 4, H⁶), 7.94 (dd, 1H, *J* = 8, 2, H³), 7.19 (dd, 1H, *J* = 8, 5, H²), 7.16 (t, 1H, *J* = 5, H¹⁰), 6.65 (d, 1H, *J* = 4, H⁵); ¹³C NMR (CDCl₃, 151 MHz): δ 158.8 (s, C⁹), 157.0 (s, C⁸), 147.9 (s, C⁴), 144.8 (s, C¹), 129.3 (s, C³), 127.4 (s, C⁶), 123.9 (s, C⁷), 118.0 (s, C²), 117.4 (s, C¹⁰), 104.3 (s, C⁵); ES⁺: 197.0821 [M+H]⁺ (mass for C₁₁H₉N₄ = 197.0827); R_f: 0.51 (99% DCM, 1% Et₃N).

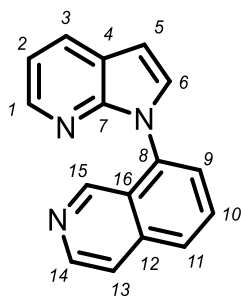
Ligand **L¹¹**

This compound was made following the general copper-catalysed amination procedure using 3-methyl-1*H*-pyrazolo[3,4-*b*]pyridine (0.20 g, 1.5 mmol), 2-bromopyridine (0.18 ml, 1.8 mmol, 1.2 equiv.), K₂CO₃ (0.44 g, 3.2 mmol), CuI (29 mg, 0.15 mmol), *trans*-1,2-diaminocyclohexane (36 μ l, 0.30 mmol) and 1,4-dioxane (8 ml). Purification by column chromatography (silica, DCM : MeOH : Et₃N 98 : 1 : 1) yielded the title compound as a light brown oil (0.30 g, 95%), ¹H NMR (CDCl₃, 700 MHz): δ 8.57 (m, 2H, H^{1,11}), 8.38 (d, 1H, *J* = 8, H⁸), 7.95 (dd, 1H, *J* = 8, 2, H³), 7.77 (ddd, 1H, *J* = 8, 7, 2, H⁹), 7.11 (m, 2H, H^{2,10}), 2.58 (s, 3H, CH₃); ¹³C NMR (CDCl₃, 176 MHz): δ 151.3 (s, C⁷), 150.9 (s, C⁶), 149.3 (s, C¹), 148.8 (s, C¹¹), 144.2 (s, C⁵), 138.1 (s, C⁹), 129.5 (s, C³), 120.7 (s, C¹⁰), 117.6 (s, C⁴), 117.4 (s, C²), 115.2 (s, C⁸), 12.5 (s, CH₃); ES⁺: 211.0990 [M+H]⁺ (mass for C₁₂H₁₁N₄ = 211.0984); R_f: 0.38 (1% Et₃N, 1% MeOH, 98% DCM).

Ligand **L¹²**

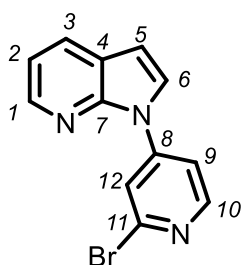
This compound was made following the general copper-catalysed amination procedure using 1*H*-pyrazolo[3,4-*b*]pyridine (0.10 g, 0.84 mmol), 2,6-dibromopyridine (0.15 ml, 1.3 mmol, 1.5 equiv.), K₂CO₃ (0.24 g, 1.8 mmol), CuI (16 mg, 84 μ mol), *trans*-1,2-diaminocyclohexane (20 μ l, 0.17 mmol, 0.2 equiv.) and 1,4-dioxane (8 ml). Purification by column chromatography (silica, hexane : EtOAc 0-70%) yielded the title compound as a white solid (0.14 g, 80%); m.p. 104°C; ¹H NMR (CDCl₃, 700 MHz): δ 8.65 (dd, 1H, *J* = 5, 2, H¹), 8.27 (s, H⁵), 8.26 (d, 1H, *J* = 8, H⁸), 8.13 (dd, 1H, *J* = 8, 2, H³), 7.79 (t, 1H, *J* = 8, H⁹), 7.23 (dd, 1H, *J* = 8, 5, H²), 7.13 (d, 1H, *J* = 8, H¹⁰), 2.68 (s, 3H, CH₃); ¹³C NMR (CDCl₃, 176 MHz): δ 158.6 (s, C¹¹), 150.6 (s, C⁷), 150.5 (s, C⁶), 149.4 (s, C¹), 138.6 (s, C⁹), 135.3 (s, C⁵), 130.5 (s, C³), 121.4 (s, C¹⁰), 118.1 (s, C²), 117.7 (s, C⁴), 113.4 (s, C⁸), 24.8 (s, CH₃); ES⁺: 211.0980 [M+H]⁺ (mass for C₁₂H₁₁N₄ = 211.0984); R_f: 0.43 (100% EtOAc).

Ligand **L**¹³



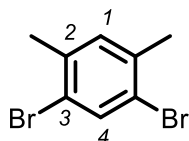
This compound was made following the general copper-catalysed amination procedure using 7-azaindole (44 mg, 0.37 mmol), 8-bromoquinoline (93 mg, 0.45 mmol, 1.2 equiv.), CuI (7 mg, 19 μ mol), K₂CO₃ (0.11 g, 0.78 mmol), *trans*-1,2-diaminocyclohexane (8.9 μ L, 74 μ mol) and 1,4-dioxane (2 ml). Column chromatography (alumina, hexane : EtOAc 0-16%) yielded the title compound as a white solid (41 mg, 45%); m.p. 133°C; ¹H NMR (CDCl₃, 700 MHz): δ 8.91 (dd, 1H, *J* = 4, 2, H¹⁵), 8.31 (dd, 1H, *J* = 5, 2, H¹¹), 8.25 (dd, 1H, *J* = 8, 2, H¹⁴), 8.11 (dd, 1H, *J* = 8, 1, H¹), 8.02 (dd, 1H, *J* = 8, 2, H⁹), 7.90 (dd, 1H, *J* = 7, 1, H³), 7.78 (d, 1H, *J* = 4, H⁶), 7.72 (dd, 1H, *J* = 8, 7, H²), 7.45 (dd, 1H, *J* = 8, 4, H¹³), 7.13 (dd, 1H, *J* = 8, 5, H¹⁰), 6.73 (d, 1H, *J* = 4, H⁵); ¹³C NMR (CDCl₃, 176 MHz): δ 150.8 (s, C¹⁵), 148.8 (s, C⁸), 143.9 (s, C⁴), 143.4 (s, C¹¹), 136.4 (s, C¹⁴), 135.1 (s, C⁷), 131.7 (s, C⁶), 129.7 (s, C¹²), 129.1 (s, C⁹), 128.1 (s, C¹), 127.6 (s, C³), 126.5 (s, C²), 121.8 (s, C¹³), 121.3 (s, C¹⁶), 116.7 (s, C¹⁰), 100.7 (s, C⁵); ES⁺: 246.1021 [M+H]⁺ (mass for C₁₆H₁₂N₃ = 246.1031); R_f: 0.24 (90% hexane, 10% EtOAc).

Ligand **L**¹⁴

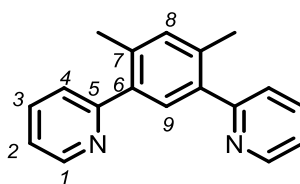


This compound was made following the general copper-catalysed amination procedure using 7-azaindole (0.50 g, 4.2 mmol), 2,4-dibromopyridine (2.98 g, 13 mmol, 3 equiv.), K₂CO₃ (1.23 g, 8.9 mmol), CuI (80 mg, 0.42 mmol), *trans*-1,2-diaminocyclohexane (101 μ L, 0.84 mmol) and 1,4-dioxane (8 ml). Column chromatography (silica, hexane : EtOAc 0-15%) yielded the title compound as a white solid (0.19 g, 16%); m.p. 141°C; ¹H NMR (CDCl₃, 600 MHz): δ 8.41 (m, 2H, H^{1,10}), 8.27 (m, 1H, H¹²), 8.01 (dd, 1H, *J* = 6, 2, H⁹), 7.95 (dd, 1H, *J* = 8, 2, H³), 7.59 (d, 1H, *J* = 4, H⁶), 7.19 (dd, 1H, *J* = 8, 5, H²), 6.70 (d, 1H, *J* = 4, H⁵); ¹³C NMR (CDCl₃, 151 MHz): δ 150.9 (s, C¹⁰), 148.0 (s, C⁴), 147.1 (s, C⁸), 144.2 (s, C¹), 143.1 (s, C¹¹), 129.7 (s, C³), 125.3 (s, C⁶), 122.8 (s, C⁷), 119.6 (s, C¹²), 118.2 (s, C²), 115.0 (s, C⁹), 105.0 (s, C⁵); ES⁺: 273.9983 [M+H]⁺ (mass for C₁₂H₉N₃Br = 273.9980); R_f: 0.20 (84% hexane : 16% EtOAc).

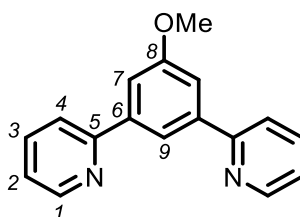
7.2.7 Synthesis of Chapter 3 ligands and precursors

4,6-Dibromo-meta-xylene

A solution of meta-xylene (5.0 ml, 41 mmol) and iodine (0.20 g, 0.81 mmol, 0.02 equiv.) under nitrogen was wrapped in foil and put in an ice bath. Bromine (4.8 ml, 93 mmol, 2.3 equiv.) was added dropwise over the course of 30 minutes and the solution was left to stir at RT overnight under a nitrogen atmosphere. The reaction was quenched with 1 M saturated aqueous KOH (100 ml) and the organic layer was washed with H₂O (4 x 50 ml). Recrystallization twice from EtOH at 75°C yielded the title compound as a white solid (3.63 g, 34%); ¹H NMR (CDCl₃, 700 MHz): δ 7.68 (s, 1H, H⁴), 7.10 (s, 1H, H¹), 2.31 (s, 6H, CH₃); ¹³C (CDCl₃, 176 MHz): δ 137.0 (C³), 135.1 (s, C⁴), 132.7 (s, C¹), 122.2 (C²), 22.4 (CH₃); ES⁺: 261.9010 [M+H]⁺ (mass for C₈H₈Br₂ = 261.8993). The remaining experimental data obtained agreed with that reported in the literature.³²²

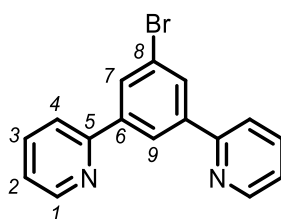
Ligand HL¹⁵

This compound was made following the general Stille cross-coupling procedure using 4,6-dibromo-meta-xylene (2.50 g, 9.5 mmol), 2-(tributylstannyl)-pyridine (7.70 ml, 24 mmol, 2.5 equiv.), LiCl (2.93 g, 69 mmol, 7.3 equiv.), Pd(PPh₃)₂Cl₂ (0.25 g, 0.35 mmol, 3.7% mol) and toluene (20 ml). Column chromatography (hexane-ether 0-100%) yielded the title compound as an off-white solid (1.41 g, 51%); ¹H NMR (CDCl₃, 700 MHz): δ 8.68 (ddd, 2H, J = 5, 2, 1, H¹), 7.72 (td, 2H, J = 8, 2, H³), 7.47 (s, 1H, H⁹), 7.44 (dt, 2H, J = 8, 1, H⁴), 7.22 (m, 3H, H^{2,8}), 2.40 (s, 6H, CH₃); ¹³C NMR (CDCl₃, 176 MHz): δ 159.9 (s, C⁵), 149.3 (s, C¹), 138.2 (s, C⁶), 136.2 (s, C³), 135.9 (s, C⁷), 133.4 (s, C⁸), 131.2 (s, C⁹), 124.3 (s, C⁴), 121.7 (s, C²), 20.1 (s, CH₃); ES⁺: 261.1367 [M+H]⁺ (mass for C₁₈H₁₇N₂ = 261.1392). The remaining experimental data obtained agreed with that reported in the literature.¹⁸⁸

Ligand HL¹⁶

This compound was made following the general Stille cross-coupling procedure using 1,3-dibromo-5-methoxy-benzene (2.50 g, 9.4 mmol), 2-(tributylstannyl)-pyridine (7.61 ml, 24 mmol, 2.5 equiv.), LiCl (2.91 g, 69 mmol, 7.3 equiv.), Pd(PPh₃)₂Cl₂ (0.25 g, 0.35 mmol, 3.7% mol) and toluene (20 ml). Column chromatography (hexane-EtOAc 0-50%) yielded the title compound as a pale yellow solid (1.82 g, 74%); ¹H NMR (CDCl₃, 700 MHz): δ 8.71 (ddd, 2H, *J* = 5, 2, 1, H¹), 8.19 (t, 1H, *J* = 2, H⁹), 7.83 (dt, 2H, *J* = 8, 1, H⁴), 7.77 (td, 2H, *J* = 8, 2, H³), 7.65 (d, 2H, *J* = 2, H⁷), 7.26 (m, 2H, H²), 3.98 (s, 3H, OCH₃); ¹³C NMR (CDCl₃, 176 MHz): δ 160.7 (s, C⁸), 157.2 (s, C⁵), 149.7 (s, C¹), 141.4 (s, C⁶), 136.9 (s, C³), 122.5 (s, C²), 121.0 (s, C⁴), 118.3 (s, C⁹), 113.3 (s, C⁷), 55.8 (s, OCH₃); ES⁺: 263.1190 [M+H]⁺ (mass for C₁₇H₁₅N₂O = 263.1184). The remaining experimental data obtained agreed with that reported in the literature.²¹¹

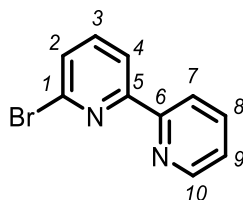
Ligand HL¹⁷



This compound was made following the general Stille cross-coupling procedure using 1,3,5-tribromobenzene (5.0 g, 16 mmol), 2-(tributylstannyl)-pyridine (11.5 ml, 36 mmol, 2.2 equiv.), LiCl (4.92 g, 116 mmol, 7.3 equiv.), Pd(PPh₃)₂Cl₂ (0.41 g, 0.59 mmol, 3.7% mol) and toluene (20 ml). Column chromatography (hexane-EtOAc 0-30%) yielded the title compound as a white solid (1.16 g, 23%); ¹H NMR (CDCl₃, 600 MHz): δ 8.72 (ddt, 2H, *J* = 5, 2, 1, H¹), 8.56 (t, 1H, *J* = 2, H⁹), 8.23 (m, 2H, H⁷), 7.82 (m, 2H, H⁴), 7.79 (ddd, 2H, *J* = 8, 7, 1, H³), 7.28 (m, 2H, H²); ¹³C NMR (CDCl₃, 151 MHz): δ 155.8 (s, C⁵), 149.9 (s, C¹), 141.8 (s, C⁶), 137.0 (s, C³), 130.4 (s, C⁷), 124.1 (s, C⁹), 123.7 (s, C⁸), 122.9 (s, C²), 120.9 (s, C⁴); ES⁺: 311.0171 [M+H]⁺ (mass for C₁₆H₁₂N₂Br = 311.0184). The remaining experimental data obtained agreed with that reported in the literature.²¹²

7.2.8 Synthesis of Chapter 4 ligands and precursors

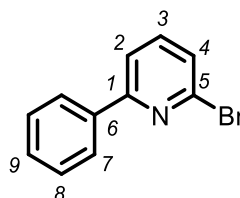
6-Bromo-2,2'-bipyridine



This compound was made following the modified Stille cross-coupling procedure using 2,6-dibromopyridine (2.50 g, 11 mmol), 2-(tributylstannyl)-pyridine (2.15 ml, 5.6 mmol, 0.56 equiv.), Pd(PPh₃)₄ (0.44 g, 0.38 mmol, 3.6% mol) and toluene (20 ml). Reaction time was shortened to 24 h. Column chromatography (hexane : EtOAc 0-12%) yielded the title compound as a white solid (1.13 g, 82%); ¹H NMR (CDCl₃, 700 MHz): δ 8.67 (m, 1H, H¹⁰), 8.41 (dt, 1H, *J* = 8, 1, H⁷), 8.38 (dd, 1H, *J* = 8,

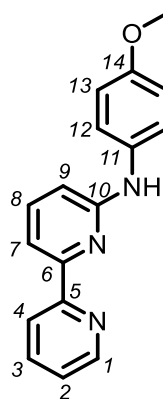
1, H²), 7.82 (m, 1H, H⁸), 7.67 (t, 1H, $J = 8$, H³), 7.49 (dd, 1H, $J = 8, 1$, H⁴), 7.33 (ddd, 1H, $J = 8, 5, 1$, H⁹); ¹³C (CDCl₃, 176 MHz): δ 157.4 (s, C⁵), 154.6 (s, C⁶), 149.3 (s, C¹⁰), 141.7 (s, C¹), 139.4 (s, C³), 137.2 (s, C⁸), 128.2 (s, C⁴), 124.4 (s, C⁹), 121.7 (s, C⁷), 119.9 (s, C²); ES⁺: 234.9880 [M+H]⁺ (mass for C₁₀H₈N₂Br = 234.9871). The remaining experimental data obtained agreed with that reported in the literature.³²³

2-Bromo-6-phenylpyridine



This compound was made following the general lithium-halogen exchange procedure using *n*-butyl lithium (5.6 ml, 14 mmol, 3 equiv.), DMAE (0.70 ml, 7.0 mmol, 2 equiv.), hexane (9 ml) and 2-phenylpyridine (0.50 ml, 3.5 mmol) which was added dropwise as a solution in hexane (4.5 ml). Carbon tetrabromide (4.18 g, 13 mmol, 3.6 equiv.) in hexane (4.5 ml) was added at -78°C. Column chromatography (hexane : EtOAc 0-4%) yielded the title compound as a grey solid (0.22 g, 27%); ¹H NMR (CDCl₃, 700 MHz): δ 7.99 (m, 2H, H⁷), 7.66 (dd, 1H, $J = 8, 1$, H⁴), 7.57 (t, 1H, $J = 8$, H³), 7.47 (m, 2H, H⁸), 7.43 (m, 1H, H⁹), 7.40 (m, 1H, H²); ¹³C NMR (CDCl₃, 176 MHz): δ 158.6 (s, C¹), 142.2 (s, C⁶), 139.1 (s, C³), 137.7 (s, C⁵), 129.7 (s, C⁹), 128.9 (s, C⁷), 127.1 (s, C⁸), 126.4 (s, C²), 119.1 (s, C⁴); ES⁺: 233.9923 [M+H]⁺ (mass for C₁₁H₉NBr = 223.9918). The remaining experimental data obtained agreed with that reported in the literature.³²⁴

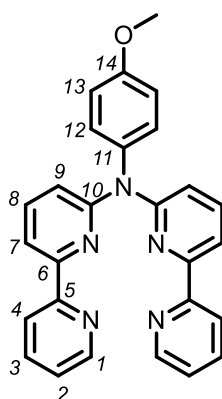
N-(4-Methoxyphenyl)-[2,2'-bipyridin]-6-amine



This compound was made following the general Buchwald-Hartwig amination procedure using *p*-anisidine (0.10 g, 0.81 mmol), 6-bromo-2,2'-bipyridine (0.19 g, 0.81 mmol, 1 equiv.), sodium *tert*-butoxide (78 mg, 0.81 mmol, 1 equiv.), dppf (18 mg, 32 μ mol), Pd(dba)₂ (10 mg, 16 μ mol) and toluene (8 ml). Column chromatography (silica, hexane : EtOAc 0-30%) yielded the title compound as a yellow oil (0.11 g, 48%); ¹H NMR (CDCl₃, 600 MHz): δ 8.67 (m, 1H, H¹), 8.31 (d, 1H, $J = 8$, H⁴),

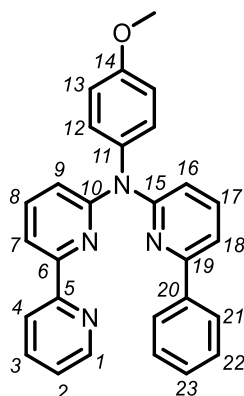
7.79 (m, 2H, H^{3,7}), 7.59 (t, 1H, *J* = 8, H⁸), 7.32 (m, 2H, H¹²), 7.28 (ddd, 1H, *J* = 8, 5, 1, H²), 6.92 (m, 2H, H¹³), 6.71 (d, 1H, *J* = 8, H⁹), 6.55 (s, 1H, NH), 3.82 (s, 3H, OCH₃); ¹³C NMR (CDCl₃, 151 MHz): δ 156.7 (s, C¹⁰), 156.4 (m, C⁵), 156.3 (s, C¹⁴), 154.7 (m, C⁶), 149.3 (d, *J* = 6, C¹), 138.8 (m, C⁸), 136.9 (s, C³), 133.5 (s, C¹¹), 123.9 (s, C¹²), 123.6 (m, C²), 121.1 (s, C⁴), 114.7 (s, C¹³), 112.0 (s, C⁷), 108.0 (m, C⁹), 55.7 (s, OCH₃); ES⁺: 278.1298 [M+H]⁺ (mass for C₁₇H₁₆N₃O = 278.1293). The remaining experimental data obtained agreed with that reported in the literature.³²⁵

N[^]*N*[^]*N*[^]*N*



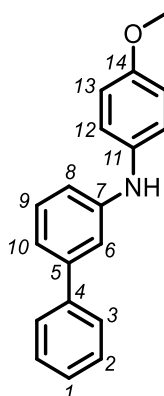
This compound was made following the general Buchwald-Hartwig amination procedure using *p*-anisidine (0.10 g, 0.81 mmol), 6-bromo-2,2'-bipyridine (0.48 g, 2.03 mmol, 2.5 equiv.), sodium *tert*-butoxide (0.20 g, 2.03 mmol, 2.5 equiv.), dppf (18 mg, 32 μmol), Pd(dba)₂ (10 mg, 16 μmol) and toluene (8 ml). Column chromatography (alumina, hexane : EtOAc 0-20%) yielded the title compound as pale yellow solid (0.28 g, 79%); m.p. 125°C; ¹H NMR (CDCl₃, 700 MHz): δ 8.63 (ddd, 2H, *J* = 5, 2, 1, H¹), 8.06 (m, 2H, H⁷), 8.04 (dt, 2H, *J* = 8, 1, H⁴), 7.69 (m, 2H, H⁸), 7.65 (td, 2H, *J* = 8, 2, H³), 7.28 (m, 2H, H¹²), 7.23 (ddd, 2H, *J* = 7, 5, 1, H²), 7.12 (dd, 2H, *J* = 8, 1, H⁹), 6.99 (m, 2H, H¹³), 3.87 (s, 3H, OCH₃); ¹³C NMR (CDCl₃, 176 MHz): δ 157.9 (s, C¹⁴), 157.4 (s, C¹⁰), 156.3 (s, C⁵), 154.2 (m, C⁶), 148.9 (s, C¹), 138.2 (s, C⁸), 137.7 (s, C¹¹), 137.0 (s, C³), 129.9 (s, C¹²), 123.6 (s, C²), 121.3 (s, C⁴), 116.4 (s, C⁹), 114.9 (s, C¹³), 114.7 (s, C⁷), 55.7 (s, OCH₃); ES⁺: 432.1817 [M+H]⁺ (mass for C₂₇H₂₂N₅O = 432.1824); R_f: 0.41 (80% hexane, 20% EtOAc).

N[^]*N*[^]*N*[^]*CH*

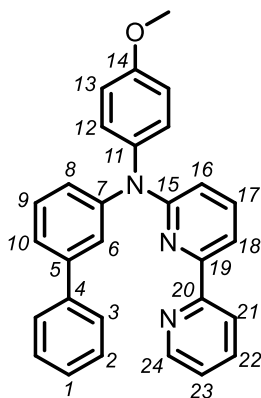


This compound was made following the general Buchwald-Hartwig amination procedure using *N*-(4-methoxyphenyl)-6-phenyl-2-pyridinamine (80 mg, 0.43 mmol), 2-bromo-6-phenylpyridine (0.10 g, 0.43 mmol, 1 equiv.), sodium *tert*-butoxide (42 mg, 0.43 mmol, 1.5 equiv.), dppf (7 mg, 12 μ mol), Pd(dba)₂ (4 mg, 6 μ mol) and toluene (6.5 ml). Column chromatography (silica, hexane : EtOAc 0-25%) yielded the title compound as a beige solid (69 mg, 56%); m.p. 168°C; ¹H NMR (CDCl₃, 700 MHz): δ 8.62 (m, 1H, H¹), 8.05 (t, 2H, *J* = 7, H^{4,7}), 7.88 (m, 2H, H²¹), 7.70 (t, 1H, *J* = 7, H⁸), 7.65 (td, 1H, *J* = 7, 2, H³), 7.61 (m, 1H, H¹⁷), 7.39 (m, 1H, H¹⁸), 7.36 (m, 2H, H²²), 7.33 (m, 1H, H²³), 7.28 (m, 2H, H¹²), 7.23 (m, 1H, H²), 7.17 (m, 1H, H⁹), 6.98 (m, 3H, H^{13,16}), 3.87 (s, 3H, OCH₃); ¹³C NMR (CDCl₃, 176 MHz): δ 157.9 (s, C¹⁴), 157.8 (s, C¹⁵), 157.4 (s, C¹⁰), 156.3 (m, C⁵), 155.3 (s, C¹⁹), 154.0 (m, C⁶), 148.9 (m, C¹), 139.3 (s, C²⁰), 138.2 (s, C⁸), 138.0 (s, C¹⁷), 137.7 (s, C¹¹), 137.1 (s, C³), 129.9 (s, C¹²), 128.9 (s, C²³), 128.7 (s, C²²), 126.8 (s, C²¹), 123.6 (s, C²), 121.4 (s, C⁴), 116.5 (s, C⁹), 114.9 (s, C¹³), 114.7 (s, C⁷), 114.6 (s, C¹⁶), 113.8 (s, C¹⁸), 55.7 (s, OCH₃); ES⁺: 431.1868 [M+H]⁺ (mass for C₂₈H₂₃N₄O = 431.1872); R_f: 0.63 (60% hexane, 40% EtOAc).

(p-Tolyl)-3-biphenylamine

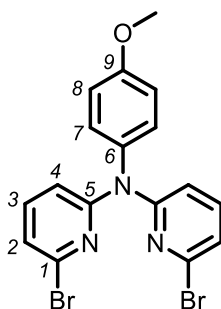


This compound was made following the general Buchwald-Hartwig amination procedure using *p*-anisidine (1.48 g, 12 mmol), 3-bromobiphenyl (0.50 ml, 3 mmol, 0.25 equiv.), sodium *tert*-butoxide (0.72 g, 7.5 mmol, 2.5 equiv.), dppf (66 mg, 120 μ mol), Pd(dba)₂ (55 mg, 60 μ mol) and toluene (15 ml). Column chromatography (silica, hexane : EtOAc 0-10% followed by hexane : ether 0-4%) and recrystallization twice from hexane and DCM yielded the title compound as a white solid (0.30 g, 36%); m.p. 100°C; ¹H NMR (CDCl₃, 700 MHz): δ 7.56 (m, 2H, H³), 7.41 (m, 2H, H²), 7.34 (m, 1H, H¹), 7.29 (t, 1H, *J* = 8, H¹⁰), 7.13 (d, 3H, *J* = 10, H^{6,12}), 7.07 (d, 1H, *J* = 8, H⁸), 6.89 (m, 3H, H^{9,13}), 5.78 (s, 1H, NH), 3.81 (s, 3H, OCH₃); ¹³C NMR (CDCl₃, 176 MHz): 155.4 (s, C¹⁴), 145.5 (s, C⁴), 142.5 (s, C⁵), 141.3 (s, C⁷), 135.5 (s, C¹¹), 129.7 (s, C¹⁰), 128.6 (s, C²), 127.2 (s, C¹), 127.1 (s, C³), 122.5 (s, C¹²), 118.7 (s, C⁸), 114.7 (s, C¹³), 114.6 (s, C⁹), 114.4 (s, C⁶), 55.6 (s, OCH₃); ES⁺: 276.1392 [M+H]⁺ (mass for C₁₉H₁₈NO = 276.1388); R_f: 0.22 (90% hexane : 10% ether).



This compound was made following the general Buchwald-Hartwig amination procedure using *p*-tolyl-3-biphenylamine (0.20 g, 0.73 mmol), 6-bromo-2,2'-bipyridine (0.24 g, 1.02 mmol, 1.4 equiv.), sodium *tert*-butoxide (0.11 g, 1.09 mmol, 1.5 equiv.), dppf (16 mg, 29 μ mol), Pd(dba)₂ (9 mg, 15 μ mol) and toluene (5 ml). Column chromatography (silica, hexane : EtOAc 0-10%) yielded the title compound as a light brown solid (0.30 g, 97%); m.p. 131°C; ¹H NMR (CDCl₃, 600 MHz): δ 8.61 (m, 1H, H²⁴), 8.06 (dd, 1H, *J* = 7, 1, H²¹), 7.91 (d, 1H, *J* = 8, H¹⁸), 7.61 (td, 1H, *J* = 7, 1, H²²), 7.54 (m, 4H, H^{3,10,17}), 7.36 (m, 4H, H^{2,6,8}), 7.30 (m, 1H, H¹), 7.25 (m, 3H, H^{9,12}), 7.20 (ddd, 1H, *J* = 7, 5, 1, H²³), 6.92 (m, 2H, H¹³), 6.70 (d, 1H, *J* = 8, H¹⁶), 3.83 (s, 3H, OCH₃); ¹³C NMR (CDCl₃, 151 MHz): δ 158.3 (s, C¹⁵), 157.3 (s, C¹⁴), 156.4 (s, C²⁰), 154.0 (s, C¹⁹), 148.9 (s, C²⁴), 146.5 (s, C⁷), 142.1 (s, C⁵), 141.0 (s, C⁴), 138.7 (s, C¹¹), 138.4 (s, C¹⁷), 136.9 (s, C²²), 129.4 (s, C²), 128.9 (s, C¹²), 128.8 (s, C⁸), 127.4 (s, C¹), 127.2 (s, C³), 124.6 (s, C⁹), 124.6 (s, C¹⁰), 123.5 (s, C²³), 122.8 (s, C⁶), 121.2 (s, C²¹), 114.9 (s, C¹³), 112.8 (s, C¹⁸), 112.7 (s, C¹⁶), 55.6 (s, OCH₃); ES⁺: 430.1904 [M+H]⁺ (mass for C₂₉H₂₄N₃O = 430.1919); R_f: 0.20 (90% hexane : 10% EtOAc).

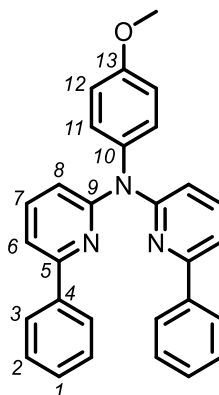
4-Methoxy-*N,N*-di(2-bromopyrid-6-yl)-benzylamine



This compound was made following the general Buchwald-Hartwig amination procedure using *p*-anisidine (1.0 g, 8.1 mmol), 2,6-dibromopyridine (5.8 g, 24 mmol, 3 equiv.), sodium *tert*-butoxide (3.9 g, 41 mmol, 2.5 equiv.), dppf (0.18 g, 0.33 mmol), Pd(dba)₂ (94 mg, 0.16 mmol) and toluene (15 ml). Column chromatography (silica, hexane : EtOAc 0-10%) yielded the title compound as a pale yellow solid (1.64 g, 47%); m.p. 138°C; ¹H NMR (CDCl₃, 600 MHz): δ 7.36 (t, 2H, *J* = 8, H³), 7.13 (m, 2H, H⁷), 7.06 (d, 2H, *J* = 8, H²), 6.93 (m, 4H, H^{4,8}), 3.83 (s, 3H, OCH₃); ¹³C NMR (CDCl₃, 151 MHz): 158.5 (s, C⁹), 157.2 (s, C¹), 139.5 (s, C⁵), 139.4 (s, C³), 136.1 (s, C⁶), 129.7 (s, C⁷), 121.7 (s, C²), 115.3 (s, C⁸),

114.4 (s, C⁴), 55.6 (s, OCH₃); ES⁺: 433.9507 [M+H]⁺ (mass for C₁₇H₁₄N₃OBr₂ = 433.9504); R_f: 0.41 (90% hexane : 10% EtOAc).

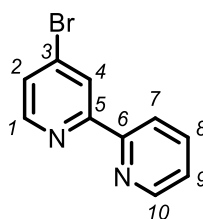
CH[^]N[^]N[^]CH



This compound was made following the modified Suzuki cross-coupling procedure using 4-methoxy-*N,N*-di(2-bromopyrid-6-yl)-benzylamine (0.50 g, 1.16 mmol), phenylboronic acid (0.42 g, 3.5 mmol, 3 equiv.), K₂CO₃ (0.40 g, 2.9 mmol, 2.5 equiv.), Pd(PPh₃)₄ (66 mg, 57 μmol, 10% mol), 1,4-dioxane (7.5 ml) and H₂O (2.5 ml). Column chromatography (silica, hexane : EtOAc 0-100%) followed by recrystallization from DCM and hexane yielded the title compound as a white solid (0.37 g, 74%); m.p. 187°C; ¹H NMR (CDCl₃, 700 MHz): δ 7.85 (m, 4H, H³), 7.59 (t, 2H, *J* = 8, H⁷), 7.33 (m, 8H, H^{1,2,6}), 7.25 (m, 2H, H¹¹), 7.01 (d, 2H, *J* = 8, H⁸), 6.95 (m, 2H, H¹²), 3.84 (s, 3H, OCH₃); ¹³C NMR (CDCl₃, 176 MHz): δ 157.8 (s, C¹³), 157.7 (s, C⁹), 155.2 (s, C⁵), 139.3 (s, C⁴), 137.9 (s, C⁷), 137.8 (s, C¹⁰), 129.8 (s, C¹¹), 128.8 (s, C¹), 128.6 (s, C²), 126.7 (s, C³), 114.8 (s, C¹²), 114.6 (s, C⁸), 113.7 (s, C⁶), 55.6 (s, OCH₃); ES⁺: 430.1938 [M+H]⁺ (mass for C₂₉H₂₄N₃O = 430.1919); R_f: 0.37 (92% hexane : 8% EtOAc).

7.2.9 Synthesis of Chapter 5 ligands and precursors

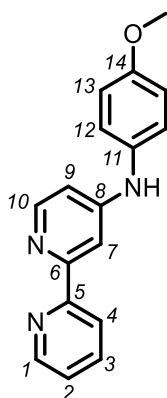
Ligand **L**¹⁸



This compound was made following the modified Stille cross-coupling procedure using 2,4-dibromopyridine (1.46 g, 6.2 mmol, 2.2 equiv.), 2-(tributylstannyl)-pyridine (1.20 ml, 2.9 mmol, 1 equiv.), Pd(PPh₃)₄ (0.12 g, 0.10 mmol, 3.6% mol) and toluene (10 ml). Reaction time was shortened to 24 h. Purification by column chromatography (hexane-EtOAc 0-10%) yielded the title compound as a white solid (0.45 g, 60%); ¹H NMR (CDCl₃, 700 MHz): δ 8.66 (ddd, 1H, *J* = 5, 2, 1, H¹⁰), 8.61 (m, 1H, H⁴), 8.45 (m, 1H, H¹), 8.37 (dt, 1H, *J* = 8, 1, H⁷), 7.79 (m, 1H, H⁸), 7.44 (dd, 1H, *J* = 5, 2, H²), 7.30 (ddd, 1H, *J* = 8, 5, 1, H⁹); ¹³C NMR (CDCl₃, 176 MHz): δ 157.5 (s, C⁵), 154.9 (s, C⁶), 149.9 (s, C¹), 149.3

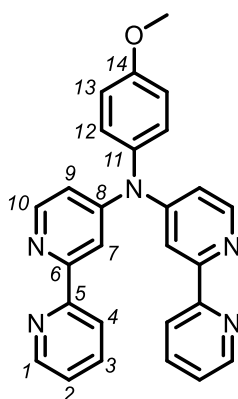
(s, C¹⁰), 137.1 (s, C⁸), 134.0 (s, C³), 126.9 (s, C²), 124.6 (s, C⁴), 124.3 (s, C⁹), 121.4 (s, C⁷); ES⁺: 234.9863 [M+H]⁺ (mass for C₁₀H₈N₂Br = 234.9871). The remaining experimental data obtained agreed with that reported in the literature.³²⁶

(p-Tolyl)-2,2'-bipyridyl-4-ylamine



This compound was made following the general Buchwald-Hartwig amination procedure using *p*-anisidine (0.10 g, 0.81 mmol), 4-bromo-2,2'-bipyridine (0.44 g, 1.87 mmol, 2.3 equiv.), sodium *tert*-butoxide (0.20 g, 2.03 mmol, 2.5 equiv.), dppf (18 mg, 32 μmol), Pd(dba)₂ (10 mg, 16 μmol) and toluene (7 ml). Column chromatography (alumina, hexane : EtOAc 0-50% plus 1% Et₃N) followed by recrystallization from DCM and hexane yielded the title compound as a pink oil (33 mg, 15%); ¹H NMR (CDCl₃, 700 MHz): δ 8.62 (m, 1H, H¹), 8.34 (d, 1H, *J* = 8, H⁴), 8.30 (d, 1H, *J* = 6, H¹⁰), 7.80 (d, 1H, *J* = 2, H⁷), 7.77 (td, 1H, *J* = 8, 2, H³), 7.26 (m, 1H, H²), 7.15 (d, 2H, *J* = 9, H¹²), 6.91 (m, 2H, H¹³), 6.68 (dd, 1H, *J* = 6, 2, H⁹), 6.17 (s, 1H, NH), 3.81 (s, 3H, OCH₃); ¹³C NMR (CDCl₃, 176 MHz): δ 157.1 (s, C¹⁴), 157.0 (s, C⁶), 156.6 (s, C⁵), 153.0 (s, C⁸), 150.0 (s, C¹⁰), 149.1 (s, C¹), 136.9 (s, C³), 132.5 (s, C¹¹), 125.2 (s, C¹²), 123.6 (s, C²), 121.3 (s, C⁴), 114.9 (s, C¹³), 108.4 (s, C⁹), 106.5 (s, C⁷), 55.7 (s, OCH₃); ES⁺: 278.1307 [M+H]⁺ (mass for C₁₇H₁₆N₃O = 278.1293); R_f: 0.22 (70% hexane : 29% EtOAc : 1% Et₃N).

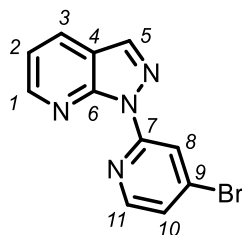
Ligand L¹⁹



This compound was made following the modified Buchwald-Hartwig amination procedure using *p*-anisidine (88 mg, 0.72 mmol), 4-bromo-2,2'-bipyridine (0.37 g, 1.57 mmol, 2.2 equiv.), sodium *tert*-butoxide (0.17 g, 1.79 mmol, 2.5 equiv.), dppf (40 mg, 72 μmol), Pd₂(dba)₃ (65 mg, 71 μmol) and toluene (8 ml). Column chromatography (alumina, hexane : EtOAc 0-30% plus 1% Et₃N) yielded the

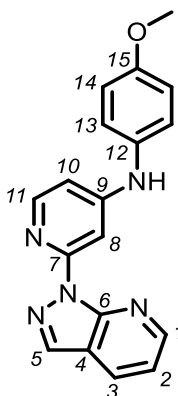
title compound as a beige solid (0.19 g, 63%); m.p. 167°C; ^1H NMR (CDCl_3 , 600 MHz): δ 8.56 (d, 2H, $J = 4$, H^1), 8.48 (d, 2H, $J = 6$, H^{10}), 8.34 (d, 2H, $J = 8$, H^4), 8.09 (m, 2H, H^7), 7.78 (m, 2H, H^3), 7.26 (m, 2H, H^2), 7.19 (d, 2H, $J = 9$, H^{12}), 6.97 (m, 4H, $\text{H}^{9,13}$), 3.85 (s, 3H, OCH_3); ^{13}C NMR (CDCl_3 , 151 MHz): 158.5 (s, C^{14}), 157.7 (s, C^6), 156.0 (s, C^5), 153.9 (s, C^8), 150.3 (s, C^{10}), 149.3 (s, C^1), 137.0 (m, $\text{C}^{3,11}$), 129.4 (s, C^{12}), 123.9 (s, C^2), 121.4 (s, C^4), 116.4 (s, C^9), 115.8 (s, C^{13}), 113.6 (s, C^7), 55.7 (s, OCH_3); ES^+ : 432.1813 $[\text{M}+\text{H}]^+$ (mass for $\text{C}_{27}\text{H}_{22}\text{N}_5\text{O} = 432.1824$); R_f : 0.36 (70% hexane : 29% EtOAc : 1% Et_3N).

Ligand L^{20}



This compound was made following the general copper-catalysed amination procedure using 1H-pyrazolo[3,4-*b*]pyridine (0.05 g, 0.42 mmol), 2,4-dibromopyridine (0.22 g, 0.92 mmol, 2.2 equiv.), K_2CO_3 (0.12 g, 0.88 mmol), CuI (8 mg, 42 μmol), *trans*-1,2-diaminocyclohexane (10 μl , 84 μmol) and 1,4-dioxane (2 ml). Column chromatography (silica, hexane : EtOAc 0-50%) yielded the title compound as a brown solid (34 mg, 30%); m.p. 79°C; ^1H NMR (CDCl_3 , 700 MHz): 8.70 (m, 2H, $\text{H}^{1,8}$), 8.47 (d, 1H, $J = 5$, H^{11}), 8.25 (s, 1H, H^5), 8.13 (dd, 1H, $J = 8$, 2, H^3), 7.38 (dd, 1H, $J = 5$, 2, H^{10}), 7.26 (dd, 1H, $J = 8$, 5, H^2); ^{13}C NMR (CDCl_3 , 176 MHz): δ 152.3 (s, C^7), 150.6 (s, C^6), 149.9 (s, C^1), 149.5 (s, C^{11}), 136.0 (s, C^5), 134.3 (s, C^9), 130.5 (s, C^3), 124.6 (s, C^{10}), 118.7 (s, C^8), 118.6 (s, C^2), 118.0 (s, C^4); ES^+ : 274.9939 $[\text{M}+\text{H}]^+$ (mass for $\text{C}_{11}\text{H}_8\text{N}_4\text{Br} = 274.9932$); R_f : 0.53 (60% hexane, 40% EtOAc).

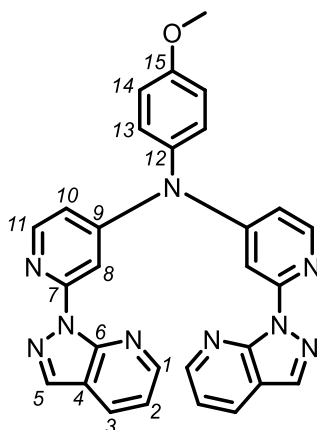
(*p*-Tolyl)-1-(2-pyridinyl)-1H-pyrazolo[3,4-*b*]pyridyl]-4-ylamine



This compound was made following the modified Buchwald-Hartwig amination procedure using *p*-anisidine (88 mg, 0.72 mmol), ligand L^{20} (0.43 g, 1.57 mmol, 2.2 equiv.), sodium *tert*-butoxide (0.17 g, 1.79 mmol, 2.5 equiv.), dppf (40 mg, 72 μmol), $\text{Pd}_2(\text{dba})_3$ (65 mg, 71 μmol) and toluene (8 ml). Column chromatography (alumina, hexane : DCM 0-100% plus 1% Et_3N) followed by recrystallization twice from hexane and DCM yielded the title compound as a white solid (9 mg,

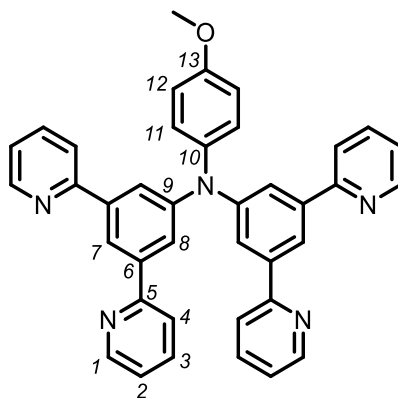
4%); m.p. 139°C; ^1H NMR (CDCl_3 , 600 MHz): δ 8.67 (dd, 1H, $J = 5, 2$, H^1), 8.29 (d, 1H, $J = 6$, H^{11}), 8.21 (s, 1H, H^5), 8.12 (dd, 1H, $J = 8, 2$, H^3), 7.74 (d, 1H, $J = 2$, H^8), 7.22 (m, 3H, $\text{H}^{2,13}$), 6.93 (m, 2H, H^{14}), 6.66 (dd, 1H, $J = 6, 2$, H^{10}), 6.31 (s, 1H, NH), 3.83 (s, 3H, OCH_3); ^{13}C NMR (CDCl_3 , 151 MHz): δ 157.3 (s, C^{15}), 154.0 (s, C^9), 152.7 (s, C^7), 150.5 (s, C^6), 149.7 (s, C^1), 149.3 (s, C^{11}), 134.9 (s, C^5), 132.2 (s, C^{12}), 130.4 (s, C^3), 125.3 (s, C^{13}), 118.1 (s, C^2), 117.8 (s, C^4), 115.0 (s, C^{14}), 107.1 (s, C^{10}), 100.3 (s, C^8), 55.7 (s, OCH_3); ES^+ : 318.1364 $[\text{M}+\text{H}]^+$ (mass for $\text{C}_{18}\text{H}_{16}\text{N}_5\text{O} = 318.1355$); R_f : 0.85 (97% DCM : 2% MeOH : 1% Et_3N).

Ligand L^{21}



Isolation of the supernatant from the second recrystallization of (*p*-tolyl)-1-(2-pyridinyl)-1*H*-pyrazolo[3,4-*b*]pyridyl-4-ylamine yielded the title compound as a pale yellow solid (65 mg, 18%); m.p. 124°C; ^1H NMR (CDCl_3 , 600 MHz): δ 8.47 (dt, 2H, $J = 4, 2$, H^1), 8.45 (dd, 2H, $J = 6, 2$, H^{11}), 8.14 (d, 2H, $J = 2$, H^5), 8.11 (d, 2H, $J = 2$, H^8), 8.05 (dt, 2H, $J = 7, 2$, H^3), 7.22 (dd, 2H, $J = 9, 2$, H^{13}), 7.13 (ddd, 2H, $J = 7, 4, 2$, H^2), 6.96 (dd, 2H, $J = 9, 2$, H^{14}), 6.93 (dt, 2H, $J = 6, 2$, H^{10}), 3.81 (s, 3H, OCH_3); ^{13}C NMR (CDCl_3 , 151 MHz): δ 158.8 (s, C^{15}), 154.3 (s, C^9), 152.9 (s, C^7), 150.4 (s, C^6), 149.8 (s, C^{11}), 149.7 (s, C^1), 136.4 (s, C^{12}), 135.1 (s, C^5), 130.2 (s, C^3), 129.5 (s, C^{13}), 118.1 (s, C^2), 117.6 (s, C^4), 115.7 (s, C^{14}), 114.1 (s, C^{10}), 108.0 (s, C^8), 55.6 (OCH_3); ES^+ : 512.1935 $[\text{M}+\text{H}]^+$ (mass for $\text{C}_{29}\text{H}_{22}\text{N}_9\text{O} = 512.1947$); R_f : 0.91 (alumina, 97% DCM : 2% MeOH : 1% Et_3N).

Ligand H_2L^{22}



This compound was made following the modified Buchwald-Hartwig amination procedure using *p*-anisidine (0.10 g, 0.81 mmol), 2,2'-(5-bromo-1,3-phenylene)bis-pyridine (0.63 g, 2.03 mmol 2.5 equiv.), sodium *tert*-butoxide (0.20 g, 2.03 mmol, 2.5 equiv.), Pd₂(dba)₃ (74 mg, 81 μmol), dppf (45 mg, 81 μmol) and toluene (10 ml). Column chromatography (silica, DCM : EtOAc 0-50%) yielded the title compound as a yellow solid (0.33 g, 70%); m.p. 226°C; ¹H NMR (CDCl₃, 600 MHz): δ 8.61 (ddd, 4H, *J* = 5, 2, 1, H¹), 8.26 (t, 2H, *J* = 2, H⁷), 7.82 (d, 4H, *J* = 2, H⁸), 7.66 (m, 8H, H^{3,4}), 7.22 (m, 2H, H¹¹), 7.16 (ddd, 4H, *J* = 7, 5, 1, H²), 6.85 (m, 2H, H¹²), 3.77 (s, 3H, OCH₃); ¹³C NMR (CDCl₃, 151 MHz): δ 157.2 (s, C⁵), 156.2 (s, C¹³), 149.6 (s, C¹), 149.3 (s, C⁹), 141.3 (s, C⁶), 140.7 (s, C¹⁰), 136.7 (s, C³), 127.0 (s, C¹¹), 122.6 (s, C⁸), 122.3 (s, C²), 120.9 (s, C⁴), 120.0 (s, C⁷), 115.0 (s, C¹²), 55.5 (s, OCH₃); ES⁺: 584.2446 [M+H]⁺ (mass for C₃₉H₃₀N₅O = 584.2450); R_f: 0.36 (44% DCM : 56% EtOAc). The remaining experimental data obtained agreed with that reported in the literature.²⁸²

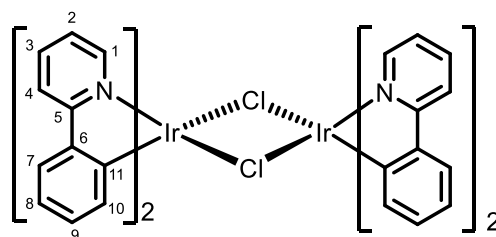
7.3 Synthesis of iridium chloro-bridged dimers

7.3.1 General procedure

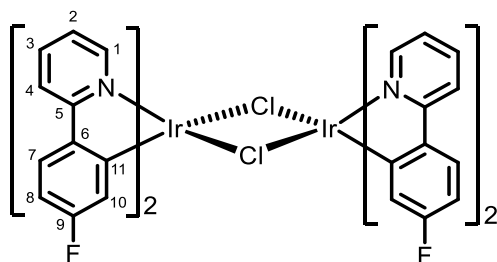
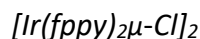
A solution of IrCl₃·3H₂O and either C[^]N or N[^]C[^]N ligand in a solvent mixture of 2-ethoxyethanol and H₂O (3 : 1) was heated under reflux at 120°C for 24 h. Upon cooling to RT, the product as a yellow/orange/red precipitate was isolated by centrifugation (2000 RPM for 5 minutes) and washed successively with H₂O and EtOH. The crude product was used in subsequent steps without further purification or characterization.

7.3.2 Bidentate C[^]N dimers

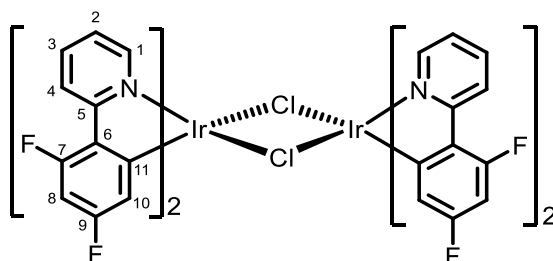
[Ir(ppy)₂μ-Cl]₂



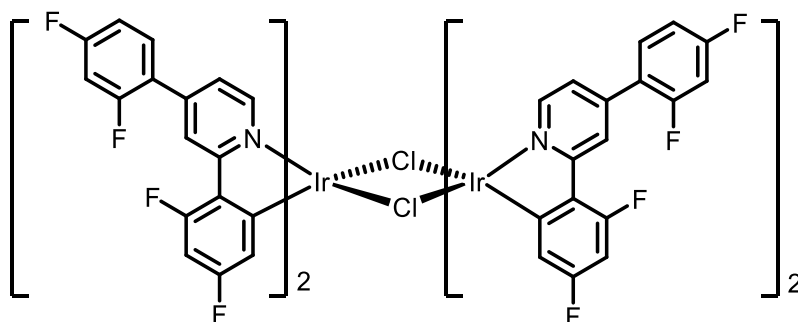
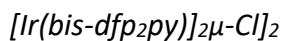
This compound was made following the general procedure using IrCl₃·3H₂O (0.12 g, 0.41 mmol), 2-phenylpyridine (0.20 ml, 1.4 mmol, 3.4 equiv.), 2-ethoxyethanol (15 ml) and H₂O (5 ml) to yield the title compound as a bright yellow solid (0.17 g, 83% yield); m.p 124°C; ¹H NMR (CDCl₃, 600 MHz): δ 9.24 (m, 4H, H⁴), 7.87 (d, 4H, *J* = 8, H¹), 7.73 (td, 4H, *J* = 8, 2, 4H, H²), 7.48 (m, 4H, H⁷), 6.77 (ddd, 4H, *J* = 8, 6, 2, H³), 6.74 (m, 4H, H⁸), 6.56 (m, 4H, H⁹), 5.93 (m, 4H, H¹⁰); ¹³C NMR (CDCl₃, 151 MHz): δ 168.7 (s, C⁵), 151.8 (s, C¹), 145.5 (s, C⁶), 143.8 (s, C¹¹), 136.3 (s, C³), 130.7 (s, C¹⁰), 129.2 (s, C⁹), 123.8 (s, C⁷), 122.2 (s, C²), 121.5 (s, C⁸), 118.5 (s, C⁴); ES⁺: 499.0911 [M/2-Cl]⁺ (mass for IrC₂₂H₁₆N₂ = 499.0920). The remaining experimental data obtained agreed with that reported in the literature.¹⁵¹



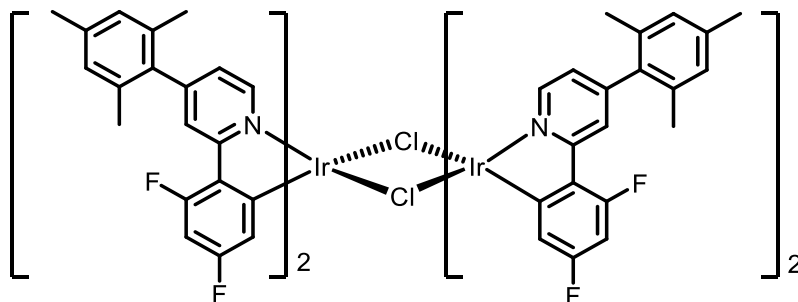
This compound was made following the general procedure using $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ (0.54 g, 1.8 mmol), 4-fluoro-2-phenylpyridine (0.69 g, 4.0 mmol, 2.2 equiv.), 2-ethoxyethanol (30 ml) and H_2O (10 ml) to yield the title compound as a bright yellow solid (0.74 g, 72% yield). m.p 66°C ; ^1H NMR (CDCl_3 , 700 MHz): δ 9.13 (m, 4H, H^1), 7.83 (d, 4H, $J = 8$, H^4), 7.77 (m, 4H, H^3), 7.50 (dd, 4H, $J = 9, 6$, H^7), 6.80 (ddd, 4H, $J = 8, 6, 2$, H^2), 6.52 (td, 4H, $J = 9, 3$, H^8), 5.53 (dd, 4H, $J = 10, 3$, H^{10}); ^{13}C NMR (CDCl_3 , 176 MHz): δ 167.6 (s, C^5), 163.5 (s, C^{11}), 162.1 (s, C^6), 151.5 (s, C^1), 140.1 (d, $J = 2$, C^9), 136.9 (s, C^3), 125.5 (d, $J = 10$, C^7), 122.3 (s, C^2), 118.7 (s, C^4), 116.8 (d, $J = 18$, C^{10}), 109.0 (d, $J = 24$, C^8); ^{19}F NMR (CDCl_3 , 400 MHz): δ -110.4 (s); ES^+ : 535.0721 $[\text{M}/2\text{-Cl}]^+$ (mass for $\text{IrC}_{22}\text{H}_{14}\text{F}_2\text{N}_2 = 535.0731$). The remaining experimental data obtained agreed with that reported in the literature.¹⁵¹



This compound was made following the general procedure using $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ (0.44 g, 1.5 mmol), 2,4-difluoro-2-phenylpyridine (0.62 g, 3.2 mmol, 2.2 equiv.), 2-ethoxyethanol (30 ml) and H_2O (10 ml) to yield the title compound as a bright yellow solid (0.61 g, 69% yield). m.p 60°C ; ^1H NMR (CDCl_3 , 700 MHz): δ 9.12 (m, 4H, H^1), 8.31 (d, 4H, $J = 8$, H^4), 7.83 (td, 4H, $J = 8, 1$, H^3), 6.83 (ddd, 4H, $J = 8, 6, 1$, H^2), 6.34 (m, 4H, H^8), 5.29 (dd, 4H, $J = 9, 2$, H^{10}); ^{13}C NMR (CDCl_3 , 176 MHz): 165.4 (d, $J = 7$, C^5), 163.2 (m, C^{11}), 161.8 (d, $J = 13$, C^9), 161.2 (s, C^7), 151.5 (s, C^1), 137.7 (s, C^3), 128.0 (m, C^6), 122.9 (d, $J = 20$, C^4), 122.7 (s, C^2), 112.9 (m, C^{10}), 98.3 (m, C^8); ^{19}F NMR (CDCl_3 , 400 MHz): δ -107.7 (d, $J = 10$), -110.3 (d, $J = 10$); ES^+ : 571.0547 $[\text{M}/2\text{-Cl}]^+$ (mass for $\text{IrC}_{22}\text{H}_{12}\text{F}_4\text{N}_2 = 571.0543$). The remaining experimental data obtained agreed with that reported in the literature.¹⁵¹

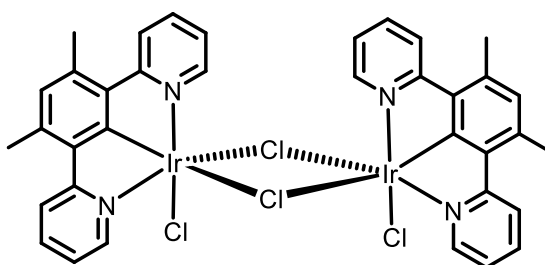
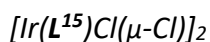


This compound was made following the general procedure using $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ (80 mg, 0.23 mmol), 2,4-difluoro-2-phenylpyridine (0.15 g, 0.51 mmol, 2.2 equiv.), 2-ethoxyethanol (4.5 ml) and H_2O (1.5 ml) to yield the title compound as a bright yellow solid (0.18 g).

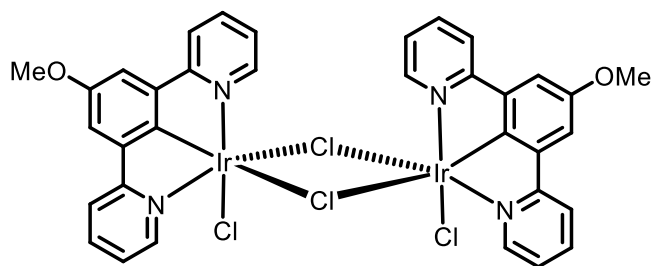
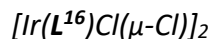


This compound was made following the general procedure using $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ (42 mg, 0.12 mmol), 2-(2,4-difluorophenyl)-4-(2,4,6-trimethylphenyl)pyridine (77 mg, 0.25 mmol, 2.1 equiv.), 2-ethoxyethanol (3 ml) and H_2O (1 ml) to yield the title compound as a bright yellow solid (77 mg).

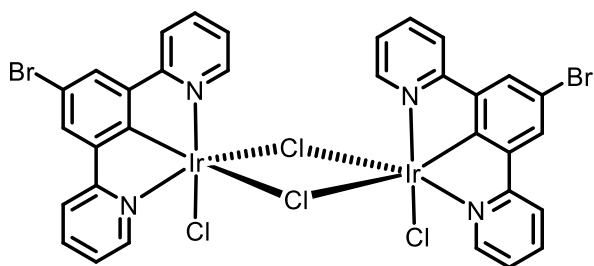
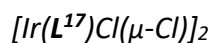
7.3.3 Tridentate N⁺C⁺N dimers



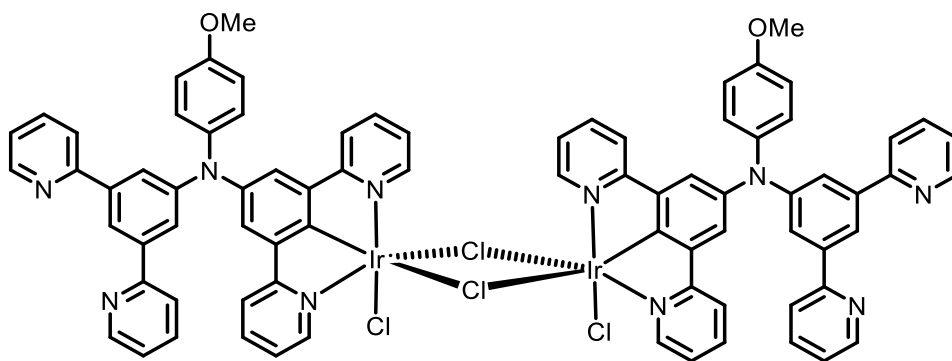
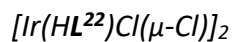
This compound was made following the general procedure using $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ (0.42 g, 1.2 mmol), ligand HL^{15} (0.69 g, 2.7 mmol, 2.2 equiv.), 2-ethoxyethanol (30 ml) and H_2O (10 ml) to yield the title compound as an orange solid (0.534 g).



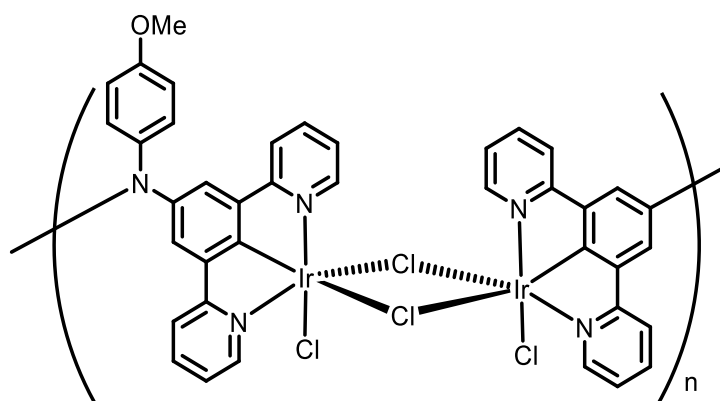
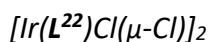
This compound was made following the general procedure using $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ (0.43 g, 1.2 mmol), ligand HL^{16} (0.71 g, 2.7 mmol, 2.2 equiv.), 2-ethoxyethanol (30 ml) and H_2O (10 ml) to yield the title compound as a bright orange solid (0.533 g).



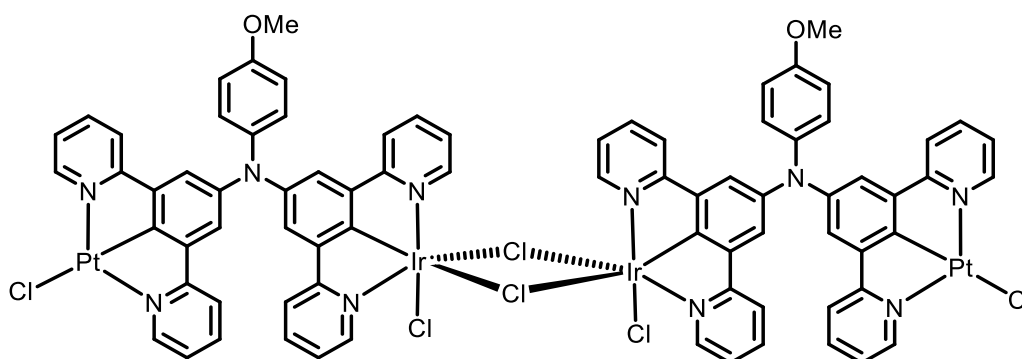
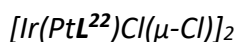
This compound was made following the general procedure using $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ (0.47 g, 1.34 mmol), ligand HL^{17} (0.50 g, 1.61 mmol, 1.2 equiv.), 2-ethoxyethanol (30 ml) and H_2O (10 ml) to yield the title compound as a yellow solid (0.63 g).



This compound was made following the general procedure using $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ (0.15 g, 0.41 mmol), ligand H_2L^{22} (0.36 g, 0.62 mmol, 1.5 equiv.), 2-ethoxyethanol (18 ml) and H_2O (6 ml) to yield the title compound as a red solid (0.237 g).



This compound was made following the general procedure using $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ (0.24 g, 0.69 mmol), ligand H_2L^{22} (0.10 g, 0.17 mmol, 0.25 equiv.), 2-ethoxyethanol (18 ml) and H_2O (6 ml) to yield the title compound as a red solid (0.22 g).



This compound was made following the general procedure using $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ (46 mg, 0.13 mmol), complex **79** (0.16 g, 0.19 mmol, 1.5 equiv.), 2-ethoxyethanol (9 ml) and H_2O (3 ml) to yield the title compound as a red solid (0.139 g).

7.4 Synthesis of complexes

7.4.1 General procedure for mono- and di-iridium complexes containing bidentate ligands

A suspension of iridium dimer (1 equiv.) and N^N ligand (1-2.5 equiv.) in a solvent mixture of MeOH and DCM (3:5) were heated under reflux for 3-6 h at 65°C. Upon cooling to RT, the solvents were removed under reduced pressure and the residue re-dissolved in the minimum amount of MeCN. The solution was added dropwise to a saturated aqueous solution of KPF_6 and a precipitate formed. A small spatula of AgPF_6 was added (ca. 50 mg) and the suspension was stirred for 15 minutes at RT. The precipitate was collected by filtration and washed successively with H_2O , EtOH and ether. The crude product was purified by washing, by column chromatography on silica or alumina gel and/or by recrystallization.

7.4.2 General procedure for iridium complexes containing tridentate ligands

A suspension of iridium dimer (1 equiv.), N^N ligand (1-2.2 equiv.) and AgOTf (4.4 equiv.) in toluene were heated under reflux for 16 h at 110°C. After cooling to RT, the solvent was removed under reduced pressure and the residue re-dissolved in MeCN. Silver chloride was removed by centrifugation (2000 RPM for 5 minutes) and a saturated aqueous solution of KPF₆ was added to the supernatant to yield a precipitate. After stirring for 15 minutes, the precipitate was isolated by filtration and washed with H₂O (3 x 10 ml), EtOH (1 x 10 ml) and ether (1 x 10 ml). The crude product was purified by column chromatography on silica gel or alumina and/or by recrystallization.

7.4.3 General metathesis procedure

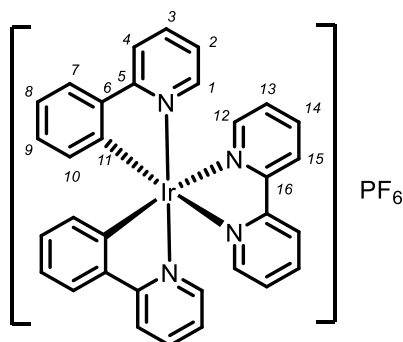
Iridium complex (1 equiv.) and either (i) CuI (18% mol), phenylacetylene (20 equiv.) and diisopropylamine (20 equiv.); or (ii) AgCN (5 equiv.) were added to DMF (4 ml). The reaction mixture was thoroughly degassed by three freeze-pump-thaw cycles and put under a nitrogen atmosphere. The reaction was heated under reflux at 150°C for 48 h under a nitrogen atmosphere. After cooling to RT, the solvent was removed under reduced pressure and the residue was re-dissolved in the minimum amount of MeCN. The solution was added dropwise to a saturated aqueous solution of KPF₆ to yield a precipitate. After stirring for 15 minutes, the precipitate was isolated by filtration and washed with H₂O (3 x 10 ml). The crude product was purified by column chromatography on silica gel or alumina and/or by recrystallization.

7.4.4 General procedure for platinum complexes

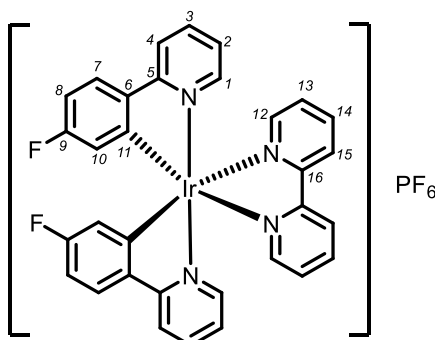
A solution of K₂PtCl₄ and ligand in glacial acetic acid was thoroughly degassed by three freeze-pump-thaw cycles and put under a nitrogen atmosphere. The reaction was heated under reflux at 118°C for 3 days under a nitrogen atmosphere. Upon cooling to RT, the solvent was removed by centrifugation (2000 RPM for 5 minutes) and the residue was washed with H₂O (3 x 10 ml), MeOH (1 x 10 ml) and ether (1 x 10 ml). The crude product was extracted with several portions of DCM and purified by column chromatography on silica gel or alumina and/or by recrystallization.

Modified procedure for platinum complexes: Same as the general procedure with the following exceptions: (i) a solvent mixture of MeCN and H₂O (3 : 1) was used instead of acetic acid and (ii) the reaction was heated at 90°C instead of 118°C.

7.4.5 Synthesis of Chapter 2 complexes

[Ir(ppy)₂(bpy)]PF₆ (1)

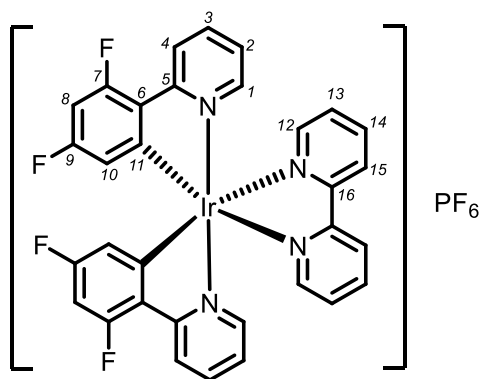
This compound was made following the general procedure for complexes containing bidentate ligands using $[\text{Ir}(\text{ppy})_2\mu\text{-Cl}]_2$ (0.327 g, 0.326 mmol), 2,2'-bipyridine (0.112 g, 0.717 mmol, 2.2 equiv.), MeOH (7.8 ml) and DCM (13 ml). Successive washing with MeOH (2 x 5 ml) and ether (3 x 5 ml) yielded the title compound as a yellow solid (0.651 g, 81%); ^1H NMR (d_6 -acetone, 600 MHz): δ 8.85 (d, 2H, $J = 8$, H^{12}), 8.30 (td, 2H, $J = 8$, 1, H^{13}), 8.24 (d, 2H, $J = 8$, H^1), 8.11 (m, 2H, H^{15}), 7.96 (m, 2H, H^2), 7.90 (m, 2H, H^7), 7.83 (d, 2H, $J = 6$, H^4), 7.71 (ddd, 2H, $J = 8$, 5, 1, H^{14}), 7.16 (ddd, 2H, $J = 8$, 6, 1, H^3), 7.04 (td, 2H, $J = 7$, 1, H^8), 6.92 (td, 2H, $J = 7$, 1, H^9), 6.35 (dd, 2H, $J = 7$, 1, H^{10}); ^{13}C NMR (d_6 -acetone, 151 MHz): δ 168.8 (s, C^5), 157.1 (s, C^{16}), 161.7 (s, C^{15}), 151.4 (s, C^6), 150.25 (s, C^4), 145.1 (s, C^{11}), 140.6 (s, C^{13}), 139.7 (s, C^2), 132.6 (s, C^{10}), 131.4 (s, C^9), 129.6 (s, C^{14}), 126.0 (s, C^7), 125.9 (s, C^{12}), 124.6 (s, C^3), 123.5 (s, C^8), 121.0 (s, C^1); ^{19}F NMR (d_6 -acetone, 400 MHz): δ -72.6 (d, $J = 707$); ES^+ : 655.1609 $[\text{M-PF}_6]^+$ (mass for $\text{IrC}_{32}\text{H}_{24}\text{N}_4 = 655.1607$). The remaining experimental data obtained agreed with that reported in the literature.³²⁷

[Ir(fppy)₂(bpy)]PF₆ (2)

This compound was made following the general procedure for complexes containing bidentate ligands using $[\text{Ir}(\text{fppy})_2\mu\text{-Cl}]_2$ (63 mg, 66 μmol), 2,2'-bipyridine (23 mg, 0.15 mmol, 2.2 equiv.), MeOH (3 ml) and DCM (5 ml). Successive washing with MeOH (2 x 3 ml) and ether (2 x 3 ml) yielded the title compound as a yellow solid (0.10 g, 92%); ^1H NMR (d_6 -acetone, 600 MHz): δ 8.84 (m 2H, H^{12}), 8.30 (m, 2H, H^{13}), 8.22 (d, 2H, $J = 8$, H^1), 8.15 (m, 2H, H^{15}), 7.99 (m, 4H, $\text{H}^{2,7}$), 7.83 (m, 2H, H^4), 7.72 (dt, 2H, $J = 8$, 4, H^{14}), 7.18 (m, 2H, H^3), 6.82 (td, 2H, $J = 9$, 3, H^8), 5.96 (dd, 2H, $J = 9$, 3, H^{10}); ^{13}C NMR

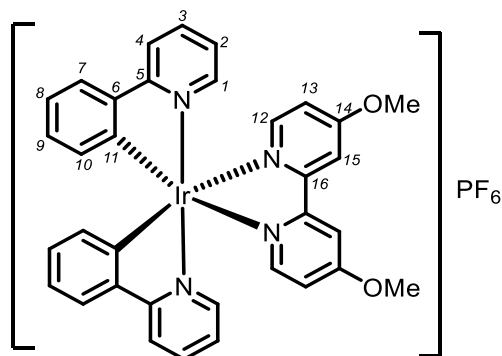
(*d*₆-acetone, 151 MHz): δ 167.3 (s, C⁵), 164.5 (d, *J* = 253, C⁹), 156.8 (s, C¹⁶), 154.3 (d, *J* = 6, C⁶), 151.6 (s, C¹⁵), 150.1 (s, C⁴), 141.4 (s, C¹¹), 140.8 (s, C¹³), 139.9 (s, C²), 129.6 (s, C¹⁴), 128.1 (d, *J* = 9, C⁷), 125.8 (s, C¹²), 124.5 (s, C³), 121.0 (s, C¹), 118.3 (d, *J* = 18, C¹⁰), 110.5 (d, *J* = 23, C⁸); ¹⁹F NMR (*d*₆-acetone, 376 MHz): δ -72.6 (d, *J* = 708), -110.8 (s); ES⁺: 691.1422 [M-PF₆]⁺ (mass for IrC₃₂H₂₂N₄F₂ = 691.1419). The remaining experimental data obtained agreed with that reported in the literature.⁹⁷

[Ir(dfppy)₂(bpy)]PF₆ (3**)**



This compound was made following the general procedure for complexes containing bidentate ligands using [Ir(dfppy)₂μ-Cl]₂ (66 mg, 55 μmol), 2,2'-bipyridine (20 mg, 0.13 mmol, 2.2 equiv.), MeOH (3 ml) and DCM (5 ml). Successive washings with MeOH (2 x 3 ml) and ether (2 x 3 ml) yielded the title compound as a yellow solid (77 mg, 83%); ¹H NMR (*d*₆-acetone, 600 MHz): δ 8.86 (dt, 2H, *J* = 8, H¹²), 8.38 (d, 2H, *J* = 9, H¹), 8.34 (td, 2H, *J* = 8, 1, H¹³), 8.21 (d, 2H, *J* = 5, H¹⁵), 8.05 (m, 2H, H²), 7.92 (m, 2H, H¹⁴), 7.74 (m, 2H, H⁴), 7.24 (m, 2H, H³), 6.75 (ddd, 2H, *J* = 12, 9, 2, H⁸), 5.79 (dd, 2H, *J* = 9, 2, H¹⁰); ¹³C NMR (*d*₆-acetone, 151 MHz): δ 164.8 (d, *J* = 7, C⁵), 163.7 (d, *J* = 13, C⁶), 161.6 (d, *J* = 13, C⁷), 156.8 (s, C¹⁶), 155.6 (d, *J* = 7, C¹¹), 152.0 (s, C¹⁵), 150.8 (s, C⁴), 141.2 (s, C¹³), 140.8 (s, C²), 130.0 (s, C¹⁴), 128.9 (m, C⁹), 126.1 (s, C¹²), 125.2 (s, C³), 124.6 (s, C¹), 114.7 (dd, *J* = 18, 3, C¹⁰), 99.8 (t, *J* = 27, C⁸); ¹⁹F NMR (*d*₆-acetone, 376 MHz): δ -72.7 (d, *J* = 707), -107.9 (d, *J* = 11), -110.1 (d, *J* = 11); ES⁺: 727.1220 [M-PF₆]⁺ (mass for IrC₃₂H₂₀N₄F₄ = 727.1230). The remaining experimental data obtained agreed with that reported in the literature.³²⁸

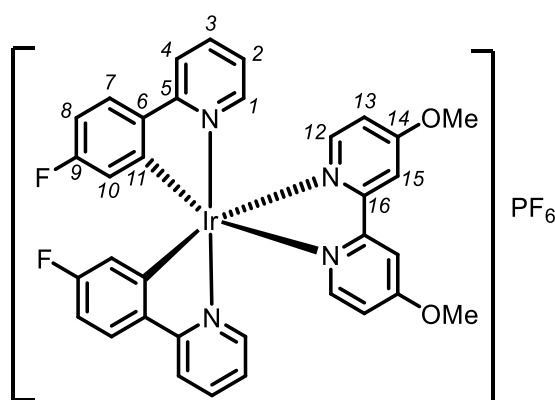
[Ir(ppy)₂(dmobpy)]PF₆ (4**)**



This compound was made following the general procedure for complexes containing bidentate ligands using [Ir(ppy)₂μ-Cl]₂ (61 mg, 61 μmol), 4,4'-dimethoxy-2,2'-bipyridine (31 mg, 0.14 mmol,

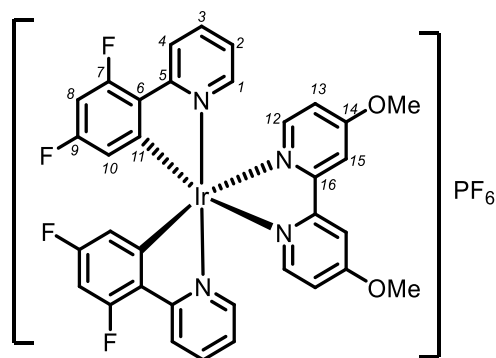
2.2 equiv.), MeOH (3 ml) and DCM (5 ml). Column chromatography (silica, DCM : MeOH 0-5%) yielded the title compound as a yellow solid (84 mg, 80%); ^1H NMR (d_6 -acetone, 700 MHz): δ 8.30 (s, 2H, H^{12}), 7.89 (d, 2H, $J = 8$, H^1), 7.75 (t, 2H, $J = 8$, H^2), 7.65 (dd, 4H, $J = 11, 8$, $\text{H}^{7,15}$), 7.58 (d, 2H, $J = 6$, H^4), 7.02 (m, 4H, $\text{H}^{3,8}$), 6.89 (t, 2H, $J = 8$, H^9), 6.84 (m, 2H, H^{13}), 6.29 (d, 2H, $J = 8$, H^{10}), 4.14 (s, 6H, OCH_3); ^{13}C NMR (d_6 -acetone, 176 MHz): δ 168.3 (s, C^{14}), 168.1 (s, C^5), 158.1 (s, C^{16}), 151.1 (s, C^6), 150.5 (s, C^{15}), 148.7 (s, C^4), 143.7 (s, C^{11}), 137.9 (s, C^2), 132.0 (s, C^{10}), 130.8 (s, C^9), 124.8 (s, C^7), 123.3 (s, C^3), 122.4 (s, C^8), 119.5 (s, C^1), 115.9 (s, C^{13}), 110.4 (s, C^{12}), 57.4 (s, OCH_3); ^{19}F NMR (d_6 -acetone, 376 MHz): δ -72.9 (d, $J = 713$); ES^+ : 715.1807 $[\text{M-PF}_6]^+$ (mass for $\text{IrC}_{34}\text{H}_{28}\text{N}_4\text{O}_2 = 715.1818$). The remaining experimental data obtained agreed with that reported in the literature.¹⁰⁹

[Ir(fppy)₂(dmobpy)]PF₆ (5)



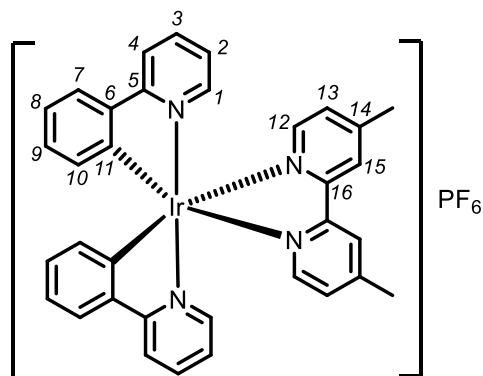
This compound was made following the general procedure for complexes containing bidentate ligands using $[\text{Ir}(\text{fppy})_2\mu\text{-Cl}]_2$ (21 mg, 18 μmol), 4,4'-dimethoxy-2,2'-bipyridine (90 mg, 40 μmol , 2.2 equiv.), MeOH (1.8 ml) and DCM (3 ml). Column chromatography (silica, DM : MeOH 0-2%) yielded the title compound as a light green solid (28 mg, 85%); m.p. 313°C; ^1H NMR (d_6 -acetone, 600 MHz): δ 8.36 (d, 2H, $J = 3$, H^{15}), 8.22 (d, 2H, $J = 8$, H^1), 7.98 (m, 4H, $\text{H}^{2,7}$), 7.89 (d, 2H, $J = 6$, H^{12}), 7.87 (ddd, 2H, $J = 6, 2, 1$, H^4), 7.26 (dd, 2H, $J = 6, 3$, H^{13}), 7.21 (ddd, 2H, $J = 8, 6, 2$, H^3), 6.80 (m, 2H, H^8), 5.94 (dd, 2H, $J = 10, 3$, H^{10}), 4.08 (s, 6H, OCH_3); ^{13}C NMR (d_6 -acetone, 151 MHz): δ 169.2 (s, C^{14}), 167.7 (s, C^5), 164.7 (d, $J = 253$, C^9), 158.4 (s, C^{16}), 155.1 (d, $J = 6$, C^6), 152.6 (s, C^{12}), 150.2 (s, C^4), 141.6 (d, $J = 2$, C^{11}), 139.9 (s, C^2), 128.2 (d, $J = 9$, C^7), 124.6 (s, C^3), 121.0 (s, C^1), 118.4 (d, $J = 18$, C^{10}), 115.2 (s, C^{13}), 112.6 (s, C^{15}), 110.4 (d, $J = 23$, C^8), 57.5 (s, OCH_3); ^{19}F NMR (d_6 -acetone, 376 MHz): δ -72.3 (m), -111.0 (s); ES^+ : 751.1635 $[\text{M-PF}_6]^+$ (mass for $\text{C}_{34}\text{H}_{26}\text{N}_4\text{IrO}_2\text{F}_2 = 751.1635$); R_f : 0.49 (98% DCM, 2% MeOH).

[Ir(dfppy)₂(dmobpy)]PF₆ (6)



This compound was made following the general procedure for complexes containing bidentate ligands using [Ir(dfppy)₂μ-Cl]₂ (67 mg, 55 μmol), 4,4'-dimethoxy-2,2'-bipyridine (24 mg, 0.1 mmol, 2.4 equiv.), MeOH (3.6 ml) and DCM (6 ml). Recrystallization from DCM and hexane yielded the title compound as a yellow solid (56 mg, 56%); ¹H NMR (*d*₆-acetone, 600 MHz): δ 8.37 (d, 2H, *J* = 8, H¹), 8.35 (d, 2H, *J* = 3, H¹⁵), 8.05 (m, 2H, H²), 7.96 (m, 2H, H⁴), 7.92 (d, 2H, *J* = 6, H¹²), 7.27 (ddd, 2H, *J* = 8, 6, 1, H³), 7.23 (dd, 2H, *J* = 6, 3, H¹³), 6.71 (ddd, 2H, *J* = 12, 9, 2, H⁸), 5.79 (dd, 2H, *J* = 9, 2, H¹⁰), 4.08 (s, 6H, OCH₃); ¹³C NMR (*d*₆-acetone, 151 MHz): δ 169.1 (s, C¹⁴), 165.1 (d, *J* = 12, C⁶), 164.7 (d, *J* = 7, C⁵), 163.2 (dd, *J* = 70, 13, C⁹), 161.3 (d, *J* = 13, C⁷), 158.0 (s, C¹⁶), 152.3 (s, C¹²), 150.3 (s, C⁴), 140.3 (s, C²), 128.7 (m, C¹¹), 124.8 (s, C³), 124.2 (d, *J* = 20, C¹), 115.1 (s, C¹³), 114.4 (dd, *J* = 18, 3, C¹⁰), 112.4 (s, C¹⁵), 99.1 (t, *J* = 27, C⁸), 57.2 (s, OCH₃); ¹⁹F NMR (*d*₆-acetone, 376 MHz): δ -72.6 (d, *J* = 708), -108.1 (d, *J* = 11), -110.3 (d, *J* = 11); ES⁺: 755.1554 [M-PF₆]⁺ (mass for IrC₃₄H₂₄N₄F₄ = 755.1543). The remaining experimental data obtained agreed with that reported in the literature.¹⁰⁹

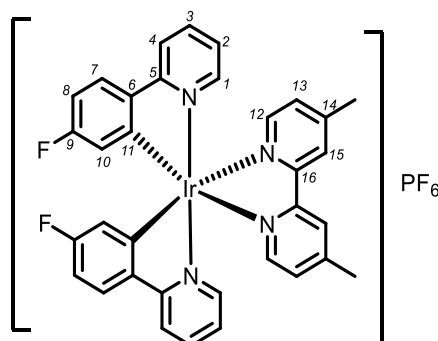
[Ir(ppy)₂(dmbpy)]PF₆ (7)



This compound was made following the general procedure for complexes containing bidentate ligands using [Ir(ppy)₂μ-Cl]₂ (73 mg, 68 μmol), 4,4'-dimethyl-2,2'-bipyridine (28 mg, 0.15 mmol, 2.2 equiv.), MeOH (3 ml) and DCM (5 ml). Column chromatography (silica, DM : MeOH 0-2%) and recrystallization twice from MeCN and ether yielded the title compound as a yellow solid (46 mg, 41%); m.p. 316°C; ¹H NMR (*d*₆-acetone, 600 MHz): δ 8.70 (m, 2H, H¹⁵), 8.22 (m, 2H, H¹), 7.95 (ddd, 2H, *J* = 8, 7, 2, H²), 7.90 (d, 2H, *J* = 6, H¹²), 7.88 (dd, 2H, *J* = 8, 1, H⁷), 7.82 (ddd, 2H, *J* = 6, 2, 1, H⁴), 7.51 (ddd, 2H, *J* = 6, 2, 1, H¹³), 7.16 (ddd, 2H, *J* = 7, 6, 1, H³), 7.02 (m, 2H, H⁸), 6.90 (td, 2H, *J* = 8, 1,

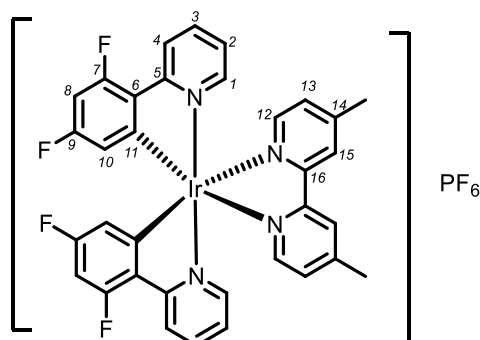
H⁹), 6.35 (m, 2H, H¹⁰), 2.59 (s, 6H, CH₃); ¹³C NMR (*d*₆-acetone, 151 MHz): δ 168.9 (s, C⁵), 156.7 (s, C¹⁶), 153.0 (s, C¹⁴), 151.8 (s, C⁶), 150.9 (s, C¹²), 150.1 (s, C⁴), 145.1 (s, C¹¹), 139.6 (s, C²), 132.7 (s, C¹⁰), 131.3 (s, C⁹), 130.1 (s, C¹³), 126.4 (s, C¹⁵), 125.9 (s, C⁷), 124.6 (s, C³), 123.4 (s, C⁸), 120.9 (s, C¹), 21.5 (s, CH₃); ¹⁹F NMR (*d*₆-acetone, 376 MHz): δ -72.6 (d, *J* = 708); ES⁺: 683.1940 [M-PF₆]⁺ (mass for C₃₄H₂₈N₄Ir = 683.1920); R_f: 0.49 (98% DCM, 2% MeOH). The remaining experimental data obtained agreed with that reported in the literature.⁹⁴

[Ir(*fppy*)₂(*dmbpy*)]PF₆ (8**)**



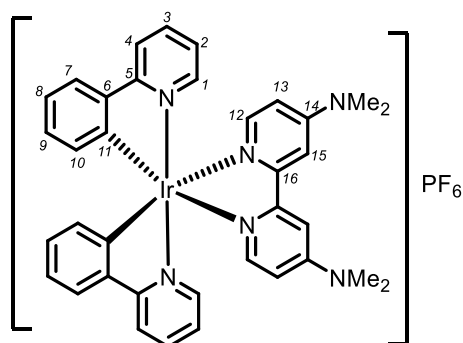
This compound was made following the general procedure for complexes containing bidentate ligands using [Ir(*fppy*)₂μ-Cl]₂ (0.36 g, 0.32 mmol), 4,4'-dimethyl-2,2'-bipyridine (0.13 g, 0.70 mmol, 2.2 equiv.), MeOH (7.5 ml) and DCM (12.5 ml). Recrystallization twice from MeCN and ether yielded the title compound as a light green solid (0.22 g, 41%); m.p. 361°C; ¹H NMR (*d*₆-acetone, 700 MHz): δ 8.71 (s, 2H, H¹²), 8.23 (d, 2H, *J* = 8, H¹), 7.98 (m, 4H, H^{2,7}), 7.96 (d, 2H, *J* = 6, H¹⁵), 7.82 (m, 2H, H⁴), 7.54 (m, 2H, H¹³), 7.19 (ddd, 2H, *J* = 8, 6, 1, H³), 6.81 (td, 2H, *J* = 9, 3, H⁸), 5.94 (dd, 2H, *J* = 9, 3 H¹⁰), 2.60 (s, 6H, CH₃); ¹³C NMR (*d*₆-acetone, 176 MHz): δ 167.6 (s, C⁵), 164.7 (d, *J* = 253, C⁹), 156.6 (s, C¹⁶), 154.9 (d, *J* = 6, C⁶), 153.3 (s, C¹⁴), 151.0 (s, C¹⁵), 150.1 (s, C⁴), 141.6 (d, *J* = 2, C¹¹), 140.0 (s, C²), 130.3 (s, C¹³), 128.2 (d, *J* = 9, C⁷), 126.6 (s, C¹²), 124.6 (s, C³), 121.1 (s, C¹), 118.4 (d, *J* = 18, C¹⁰), 110.5 (d, *J* = 23, C⁸), 21.5 (s, CH₃); ¹⁹F NMR (*d*₆-acetone, 376 MHz): δ -72.6 (d, *J* = 708), -110.9 (s); ES⁺: 719.1730 [M-PF₆]⁺ (mass for IrC₃₄H₂₆N₄F₂ = 719.1732); R_f: 0.37 (silica, 92% DCM, 8% MeOH). The remaining experimental data obtained agreed with that reported in the literature.⁹⁶

[Ir(*dfppy*)₂(*dmbpy*)]PF₆ (9**)**

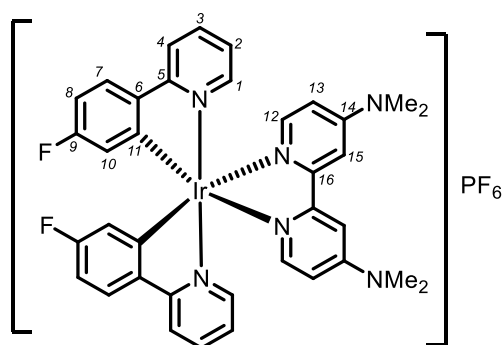


This compound was made following the general procedure for complexes containing bidentate ligands using $[\text{Ir}(\text{dfppy})_2\mu\text{-Cl}]_2$ (73 mg, 60 μmol), 4,4'-dimethyl-2,2'-bipyridine (29 mg, 0.13 mmol, 2.2 equiv.), MeOH (3 ml) and DCM (5 ml). Recrystallization from acetone and hexane yielded the title compound as a yellow solid (0.10 g, 93%); ^1H NMR (d_6 -acetone, 700 MHz): δ 8.56 (m, 2H, H^2), 8.30 (d, 2H, $J = 9$, H^1), 7.80 (td, 2H, H^{12}), 7.72 (d, 2H, $J = 6$, H^4), 7.52 (m, 2H, H^{15}), 7.24 (m, 2H, H^{13}), 7.09 (m, 2H, H^3), 6.56 (m, 2H, H^8), 5.68 (dd, 2H, $J = 8$, 2, H^{10}), 2.62 (s, 6H, CH_3); ^{13}C NMR (d_6 -acetone, 176 MHz): δ 164.6 (d, $J = 12$, C^{11}), 164.4 (d, $J = 8$, C^5), 163.2 (d, $J = 13$, C^6), 162.4 (d, $J = 1$, C^7), 155.4 (s, C^{16}), 153.4 (s, C^{14}), 149.2 (s, C^{15}), 148.8 (s, C^4), 139.1 (s, C^2), 129.2 (s, C^{13}), 127.6 (m, C^9), 126.8 (s, C^{12}), 123.8 (s, C^3), 123.7 (s, C^1), 114.1 (m, C^{10}), 99.2 (t, $J = 27$, C^8), 21.6 (s, CH_3); ^{19}F NMR (d_6 -acetone, 376 MHz): δ -72.9 (d, $J = 713$), -105.6 (d, $J = 11$); -108.6 (d, $J = 11$); ES^+ : 787.1462 $[\text{M-PF}_6]^+$ (mass for $\text{IrC}_{34}\text{H}_{24}\text{N}_4\text{O}_2\text{F}_4 = 787.1441$). The remaining experimental data obtained agreed with that reported in the literature.⁹⁴

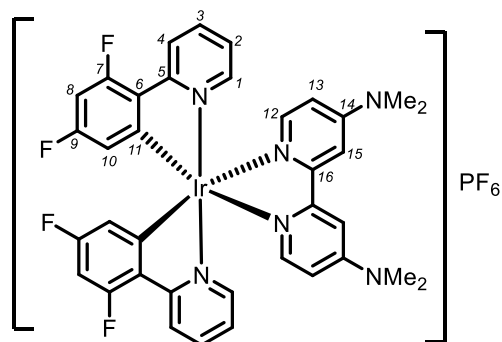
$[\text{Ir}(\text{ppy})_2(\text{dmabpy})]\text{PF}_6$ (10**)**



This compound was made following the general procedure for complexes containing bidentate ligands using $[\text{Ir}(\text{ppy})_2\mu\text{-Cl}]_2$ (95 mg, 89 μmol), 4,4-bis(*N,N*-dimethylamino)-2,2'-bipyridine (49 mg, 0.20 mmol, 2.3 equiv.), MeOH (3 ml) and DCM (5 ml). Column chromatography (silica, DCM : MeOH 0-2%) and recrystallization once from MeCN and ether and twice from acetone and hexane yielded the title compound as a yellow solid (4 mg, 5%); ^1H NMR (d_6 -acetone, 700 MHz): δ 8.20 (m, 2H, H^1), 7.93 (ddd, 2H, $J = 8$, 7, 1, H^2), 7.89 (dd, 2H, $J = 6$, 1, H^4), 7.85 (m, 2H, H^7), 7.78 (d, 2H, $J = 3$, H^{12}), 7.45 (d, 2H, $J = 7$, H^{15}), 7.20 (ddd, 2H, $J = 7$, 6, 1, H^3), 6.98 (m, 2H, H^8), 6.85 (td, 2H, $J = 7$, 1, H^9), 6.74 (dd, 2H, $J = 7$, 3, H^{13}), 6.35 (m, 2H, H^{10}), 3.20 (s, $\text{N}(\text{CH}_3)_2$); ^{13}C NMR (d_6 -acetone, 176 MHz): δ 169.4 (s, C^5), 157.2 (s, C^{16}), 156.2 (s, C^{14}), 153.9 (s, C^{11}), 149.9 (s, C^4), 149.7 (s, C^{15}), 145.3 (s, C^6), 139.0 (s, C^2), 132.8 (s, C^{10}), 131.1 (s, C^9), 125.8 (s, C^7), 124.1 (s, C^3), 122.7 (s, C^8), 120.6 (s, C^1), 110.5 (s, C^{13}), 106.8 (s, C^{12}), 39.8 (s, $\text{N}(\text{CH}_3)_2$); ^{19}F NMR (d_6 -acetone, 376 MHz): δ -72.7 (m); ES^+ : 741.2468 $[\text{M-PF}_6]^+$ (mass for $\text{IrC}_{36}\text{H}_{34}\text{N}_6 = 741.2451$). The remaining experimental data obtained agreed with that reported in the literature.³²⁹

[Ir(fppy)₂(dmabpy)]PF₆ (11)

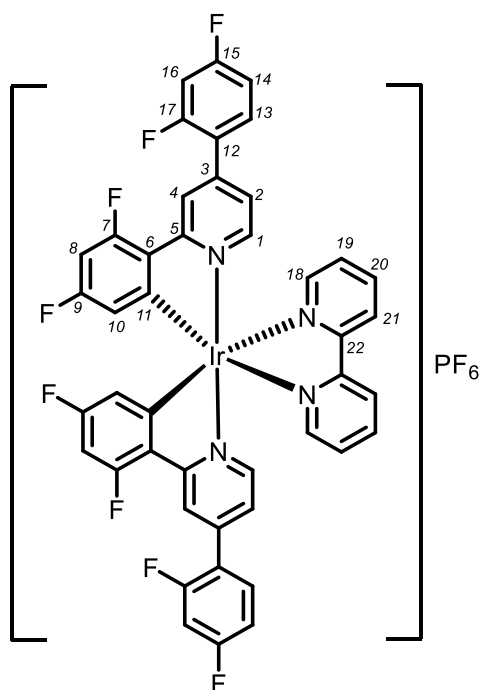
This compound was made following the general procedure for complexes containing bidentate ligands using $[\text{Ir}(\text{fppy})_2\mu\text{-Cl}]_2$ (51 mg, 45 μmol), 4,4-bis(*N,N*-dimethylamino)-2,2'-bipyridine (29 mg, 91 μmol , 2.2 equiv.), MeOH (3 ml) and DCM (5 ml). Successive washing with MeOH (3 x 1 ml) and ether (3 x 1 ml) followed by recrystallization from MeCN and ether yielded the title compound as a dark yellow solid (54 mg, 55%); m.p. > 400°C; ^1H NMR (d_6 -acetone, 600 MHz): δ 8.20 (d, 2H, J = 8, H^1), 7.96 (m, 4H, $\text{H}^{2,7}$), 7.88 (m, 2H, H^4), 7.77 (d, 2H, J = 3, H^{15}), 7.47 (d, 2H, J = 7, H^{12}), 7.24 (ddd, 2H, J = 8, 6, 1, H^3), 6.76 (m, 4H, $\text{H}^{8,13}$), 5.95 (ddd, 2H, J = 10, 3, H^{10}), 3.20 (s, 12H, $\text{N}(\text{CH}_3)_2$); ^{13}C NMR (d_6 -acetone, 151 MHz): δ 168.0 (s, C^5), 164.7 (d, J = 252, C^9), 157.0 (s, C^6), 156.9 (s, C^{16}), 156.1 (s, C^{14}), 149.8 (s, C^4), 149.6 (s, C^{12}), 141.7 (d, J = 2, C^{11}), 139.4 (s, C^2), 127.9 (d, J = 9, C^7), 124.2 (s, C^3), 120.7 (s, C^1), 118.4 (d, J = 17, C^{10}), 110.5 (s, C^{13}), 109.8 (d, J = 23, C^8), 106.8 (s, C^{15}), 39.8 (s, $\text{N}(\text{CH}_3)_2$); ^{19}F NMR (d_6 -acetone, 376 MHz): δ -72.6 (d, J = 708), -111.5 (s); ES^+ : 777.2243 $[\text{M-PF}_6]^+$ (mass for $\text{IrC}_{36}\text{H}_{32}\text{N}_6\text{F}_2$ = 777.2263); R_f : 0.50 (silica, 90% DCM, 10% MeOH).

[Ir(dfppy)₂(dmabpy)]PF₆ (12)

This compound was made following the general procedure for complexes containing bidentate ligands using $[\text{Ir}(\text{dfppy})_2\mu\text{-Cl}]_2$ (32 mg, 26 μmol), 4,4-bis(*N,N*-dimethylamino)-2,2'-bipyridine (14 mg, 58 μmol , 2.2 equiv.), MeOH (3 ml) and DCM (5 ml). Successive washing with MeOH (2 x 3 ml) and ether (2 x 3 ml) yielded the title compound as a yellow solid (47 mg, 93%); ^1H NMR (d_6 -acetone, 600 MHz): δ 8.36 (dt, 2H, J = 9, H^1), 8.04 (ddd, 2H, J = 9, 8, 1, H^2), 7.96 (ddd, 2H, J = 6, 2, 1, H^4), 7.77 (d, 2H, J = 3, H^{15}), 7.47 (d, 2H, J = 7, H^{12}), 7.30 (ddd, 2H, J = 8, 6, 1, H^3), 6.76 (dd, 2H, J = 7, 3, H^{13}), 6.67 (ddd, 2H, J = 13, 9, 2, H^8), 5.79 (dd, 2H, J = 9, 2, H^{10}), 3.20 (s, 12H, $\text{N}(\text{CH}_3)_2$); ^{13}C NMR (d_6 -acetone,

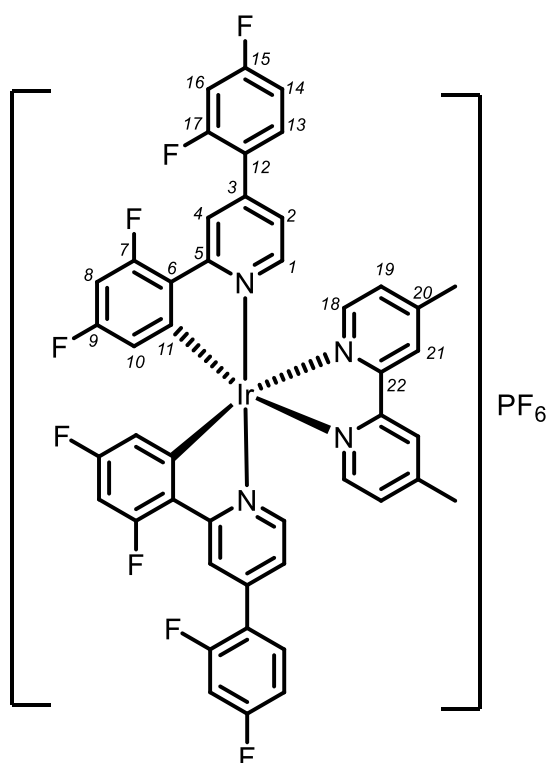
151 MHz): δ 165.2 (d, $J = 7$, C⁵), 163.7 (d, $J = 13$, C⁶), 161.4 (m, C⁷), 158.3 (d, $J = 7$, C¹¹), 156.7 (s, C¹⁶), 156.1 (s, C¹⁴), 150.2 (s, C⁴), 149.5 (s, C¹²), 140.0 (s, C²), 128.9 (d, $J = 3$, C⁸), 124.6 (s, C³), 124.2 (d, $J = 20$, C¹), 114.5 (dd, $J = 17$, 3, C¹⁰), 110.5 (s, C¹³), 106.8 (s, C¹⁵), 98.8 (t, $J = 27$, C⁹), 39.7 (s, N(CH₃)₂); ¹⁹F NMR (*d*₆-acetone, 376 MHz): δ -72.7 (d, $J = 707$), -108.6 (d, $J = 10$), -110.6 (d, $J = 10$); ES⁺: 813.2076 [M-PF₆]⁺ (mass for IrC₃₆H₃₀N₆F₄ = 813.2074). The remaining experimental data obtained agreed with that reported in the literature.³²⁹

[Ir(*bis*-dfp₂py)₂(bpy)]PF₆ (13**)**



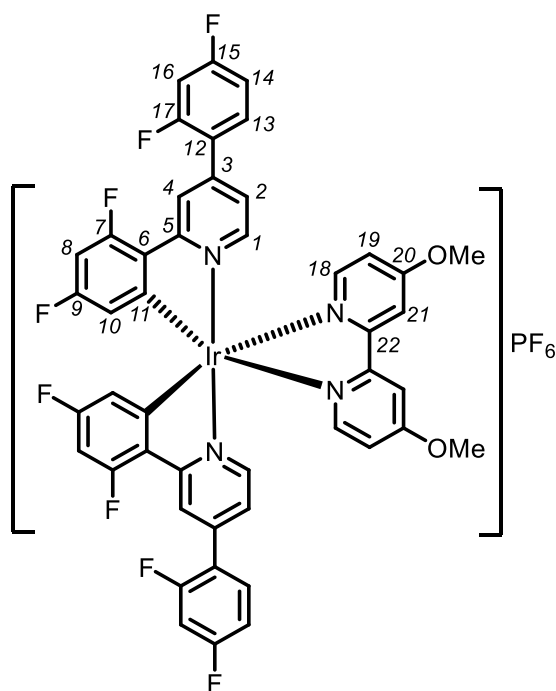
This compound was made following the general procedure for complexes containing bidentate ligands using [Ir(*bis*-dfp₂py)₂μ-Cl]₂ (39 mg, 23 μmol), 2,2'-bipyridine (8 mg, 51 μmol, 2.2 equiv.), MeOH (3 ml) and DCM (5 ml). Column chromatography (silica, DCM : MeOH 0-2%) and recrystallization from MeCN and ether yielded the title compound as a yellow solid (24 mg, 47%); m.p. 377°C; ¹H NMR (*d*₆-acetone, 600 MHz): δ 8.92 (d, 2H, $J = 8$, H¹⁸), 8.57 (s, 2H, H⁴), 8.38 (td, 2H, $J = 8$, 2, H¹⁹), 8.29 (m, 2H, H²¹), 8.01 (m, 2H, H¹), 7.84 (td, 2H, $J = 9$, 6, H¹³), 7.79 (ddd, 2H, $J = 8$, 6, 1, H²⁰), 7.46 (dt, 2H, $J = 6$, 2, H²), 7.26 (m, 4H, H^{14,16}), 6.81 (ddd, 2H, $J = 13$, 9, 2, H⁸), 5.96 (dd, 2H, $J = 9$, 2, H¹⁰); ¹³C NMR (*d*₆-acetone, 151 MHz): δ 165.1 (d, $J = 7$, C³), 164.5 (dd, $J = 331$, 13, C⁹), 164.1 (m, C¹⁵), 162.8 (dd, $J = 331$, 13, C⁷), 162.4 (dd, $J = 555$, 13, C¹⁷), 156.9 (s, C²²), 155.7 (s, C⁶), 152.2 (s, C²¹), 150.8 (s, C¹), 146.7 (s, C⁵), 141.4 (s, C¹⁹), 133.2 (dd, $J = 11$, 3, C¹³), 130.1 (s, C²⁰), 128.8 (m, C¹¹), 126.3 (s, C¹⁸), 124.6 (d, $J = 3$, C²), 124.0 (dd, $J = 21$, 4, C⁴), 122.2 (dd, $J = 11$, 3, C¹²), 115.0 (dd, $J = 18$, 3, C¹⁰), 113.7 (m, C¹⁴), 105.9 (t, $J = 27$, C¹⁶), 100.0 (t, $J = 27$, C⁸); ¹⁹F NMR (*d*₆-acetone, 376 MHz): δ -72.6 (m), -107.8 (m), -111.4 (m); ES⁺: 951.1482 [M-PF₆]⁺ (mass for IrC₄₄H₂₄N₄F₈ = 951.1479); R_f: 0.47 (96% DCM, 4% MeOH).

*[Ir(bis-dfp₂py)₂(dmbpy)]PF₆ (**14**)*

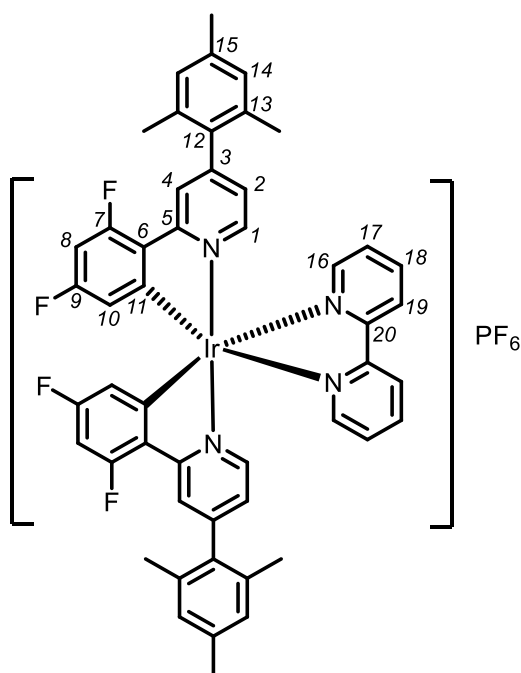


This compound was made following the general procedure for complexes containing bidentate ligands using $[Ir(bis-dfp_2py)_2\mu-Cl]_2$ (44 mg, 27 μ mol), 4,4'-dimethyl-2,2'-bipyridine (11 mg, 60 μ mol, 2.2 equiv.), MeOH (3 ml) and DCM (5 ml). Column chromatography (silica, DCM : MeOH 0-2%) and recrystallization from DCM and hexane yielded the title compound as a yellow solid (47 mg, 78%); m.p > 400°C; ^1H NMR (d_6 -acetone, 600 MHz): δ 8.77 (m, 2H, H¹⁸), 8.56 (m, 2H, H¹), 8.08 (d, 2H, J = 6, H²¹), 8.00 (m, 2H, H⁴), 7.84 (td, 2H, J = 9, 6, H¹³), 7.59 (m, 2H, H¹⁹), 7.46 (dt, 2H, J = 6, 2, H²), 7.26 (m, 4H, H^{14,16}), 6.79 (ddd, 2H, J = 13, 9, 2, H⁸), 5.95 (dd, 2H, J = 9, 2, H¹⁰), 2.62 (s, 6H, CH₃); ^{13}C NMR (d_6 -acetone, 151 MHz): δ 165.2 (d, J = 7, C⁵), 165.0 (dd, J = 251, 12, C¹⁵), 164.8 (m, C⁹), 162.6 (dd, J = 260, 13, C⁷), 161.4 (dd, J = 252, 12, C¹⁷), 156.6 (s, C²²), 156.1 (d, J = 7, C¹¹), 153.8 (s, C²⁰), 151.3 (s, C²¹), 150.6 (s, C⁴), 146.6 (s, C³), 133.2 (m, C¹³), 130.6 (s, C¹⁹), 128.8 (dd, J = 4, 3, C⁶), 126.8 (s, C¹⁸), 124.6 (d, J = 3, C²), 123.9 (dd, J = 21, 3, C¹), 122.2 (dd, J = 12, 4, C¹²), 115.0 (m, C¹⁰), 113.7 (dd, J = 22, 4, C¹⁴), 105.9 (t, J = 27, C¹⁶), 99.8 (t, J = 27, C⁸), 21.6 (s, CH₃); ^{19}F NMR (d_6 -acetone, 376 MHz): δ -72.5 (d, J = 708), -107.8 (m), -111.5 (dd, J = 1221, 9); ES⁺: 979.1807 [M-PF₆]⁺ (mass for IrC₄₆H₂₈N₄F₈ = 979.1792); R_f: 0.41 (96% DCM, 4% MeOH).

[Ir(bis-dfp₂py)₂(dmobpy)]PF₆ (15)

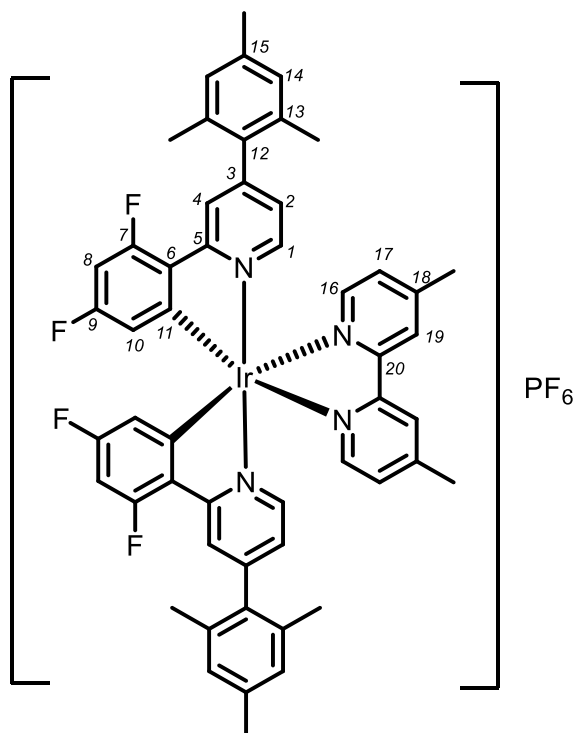


This compound was made following the general procedure for complexes containing bidentate ligands using $[\text{Ir}(\text{bis-dfp}_2\text{py})_2\mu\text{-Cl}]_2$ (60 mg, 36 μmol), 4,4'-dimethoxy-2,2'-bipyridine (18 mg, 79 μmol , 2.2 equiv.), MeOH (3 ml) and DCM (5 ml). Column chromatography (silica, DM : MeOH 0-2%) and recrystallization from MeCN and ether yielded the title compound as yellow solid (25 mg, 30%); m.p. 344°C; ^1H NMR (d_6 -acetone, 700 MHz): δ 8.56 (s, 2H, H^4), 8.41 (d, 2H, $J = 3$, H^{21}), 8.05 (d, 2H, $J = 6$, H^1), 8.00 (d, 2H, $J = 7$, H^{18}), 7.85 (td, 2H, $J = 9, 6$, H^{13}), 7.47 (dt, 2H, $J = 6, 2$, H^2), 7.26 (m, 6H, $\text{H}^{14,16,19}$), 6.77 (m, 2H, H^8), 5.94 (dd, 2H, $J = 9, 2$, H^{10}), 4.10 (s, 6H, OCH_3); ^{13}C NMR (d_6 -acetone, 176 MHz): δ 169.6 (s, C^{20}), 165.3 (s, C^5), 165.1 (dd, $J = 251, 12$, C^{15}), 164.8 (dd, $J = 256, 13$, C^9), 162.7 (dd, $J = 260, 13$, C^7), 161.4 (dd, $J = 251, 12$, C^{17}), 158.5 (s, C^{22}), 156.4 (d, $J = 6$, C^6), 153.0 (s, C^{18}), 150.6 (s, C^1), 146.6 (s, C^3), 133.3 (dd, $J = 10, 4$, C^{13}), 128.9 (m, C^{11}), 124.6 (d, $J = 4$, C^2), 123.9 (d, $J = 17$, C^4), 122.3 (dd, $J = 13, 4$, C^{12}), 115.5 (s, C^{19}), 115.1 (dd, $J = 17, 3$, C^{10}), 113.8 (dd, $J = 22, 4$, C^{14}), 112.9 (s, C^{21}), 106.0 (t, $J = 26$, C^{16}), 99.7 (t, $J = 27$, C^8), 57.6 (s, OCH_3); ^{19}F NMR (d_6 -acetone, 376 MHz): δ -72.6 (d, $J = 708$), -107.5 (d, $J = 11$), -108.3 (d, $J = 9$), -109.9 (d, $J = 11$), -113.2 (d, $J = 9$); ES^+ : 1011.1698 $[\text{M-PF}_6]^+$ (mass for $\text{C}_{46}\text{H}_{28}\text{N}_4\text{IrO}_2\text{F}_8 = 1011.1691$); R_f : 0.34 (98% DCM, 2% MeOH).

[Ir(mes-dfppy)₂(bpy)]PF₆ (16)

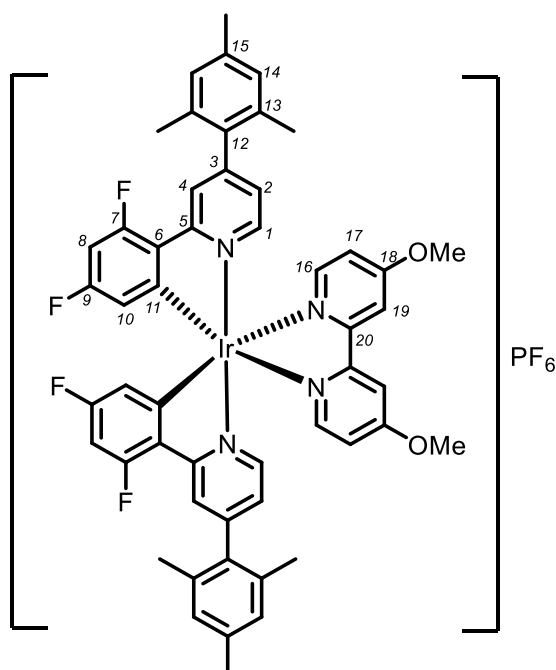
This compound was made following the general procedure for complexes containing bidentate ligands using $[\text{Ir}(\text{mes-dfppy})_2\mu\text{-Cl}]_2$ (50 mg, 30 μmol), 2,2'-bipyridine (11 mg, 65 μmol , 2.2 equiv.), MeOH (3 ml) and DCM (5 ml). Column chromatography (silica, DM : MeOH 0-2%) and recrystallization from MeCN and ether yielded the title compound as yellow solid (33 mg, 50%); m.p. 367°C; ^1H NMR (d_6 -acetone, 700 MHz): δ 8.92 (d, 2H, $J = 8$, H^{16}), 8.39 (td, 2H, $J = 8$, 1, H^{17}), 8.34 (m, 2H, H^{19}), 8.14 (s, 2H, H^4), 8.02 (m, 2H, H^1), 7.80 (ddd, 2H, $J = 8$, 6, 1, H^{18}), 7.11 (dd, 2H, $J = 6$, 2, H^2), 7.02 (s, 2H, H^{14}), 6.98 (s, 2H, H^{14}), 6.75 (ddd, 2H, $J = 12$, 9, 2, H^8), 5.89 (dd, 2H, $J = 9$, 2, H^{10}), 2.31 (s, 6H, $^{15}\text{-CH}_3$), 2.13 (s, 6H, $^{13}\text{-CH}_3$), 1.91 (s, 6H, $^{13}\text{-CH}_3$); ^{13}C NMR (d_6 -acetone, 176 MHz): δ 165.2 (d, $J = 7$, C^5), 164.8 (dd, $J = 256$, 13, C^9), 162.5 (dd, $J = 260$, 13, C^7), 157.1 (s, C^{20}), 155.8 (d, $J = 7$, C^6), 154.2 (s, C^3), 152.3 (s, C^{19}), 150.9 (s, C^1), 141.3 (s, C^{17}), 139.3 (s, C^{15}), 136.0 (s, C^{12}), 135.7 (m, C^{13}), 130.0 (s, C^{18}), 129.6 (d, $J = 16$, C^{14}), 129.1 (dd, $J = 4$, 3, C^{11}), 126.4 (s, C^2), 126.3 (s, C^{16}), 125.7 (d, $J = 20$, C^4), 114.8 (dd, $J = 18$, 3, C^{10}), 99.9 (t, $J = 27$, C^8), 21.2 (s, $^{15}\text{-CH}_3$), 20.7 (m $^{13}\text{-CH}_3$); ^{19}F NMR (d_6 -acetone, 376 MHz): δ -72.6 (d, $J = 708$), -107.7 (d, $J = 11$), -109.9 (d, $J = 11$); ES^+ : 963.2833 $[\text{M-PF}_6]^+$ (mass for $\text{C}_{50}\text{H}_{40}\text{N}_4\text{IrF}_4 = 963.2795$); R_f : 0.43 (98% DCM, 2% MeOH).

[Ir(mes-dfppy)₂(dmbpy)]PF₆ (17)



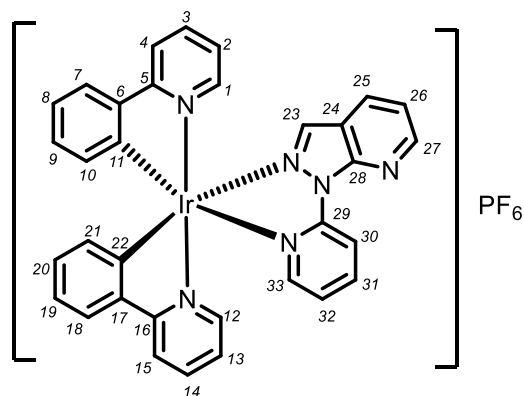
This compound was made following the general procedure for complexes containing bidentate ligands using $[\text{Ir}(\text{mes-dfppy})_2\mu\text{-Cl}]_2$ (39 mg, 23 μmol), 4,4'-dimethyl-2,2'-bipyridine (10 mg, 51 μmol , 2.2 equiv.), MeOH (3 ml) and DCM (5 ml). Recrystallization from MeCN and ether yielded the title compound as a light green solid (24 mg, 45%); m.p 385°C; ^1H NMR (d_6 -acetone, 600 MHz): δ 8.78 (s, 2H, H^{16}), 8.13 (m, 4H, $\text{H}^{1,19}$), 7.99 (m, 2H, H^4), 7.61 (m, 2H, H^{17}), 7.12 (dd, 2H, $J = 6, 2$, H^2), 7.03 (s, 2H, H^{14}), 6.98 (s, 2H, H^{14}), 6.74 (m, 2H, H^8), 5.86 (dd, 2H, $J = 9, 2$, H^{10}), 2.64 (s, 6H, $^{18}\text{-CH}_3$), 2.31 (s, 6H, $^{15}\text{-CH}_3$), 2.13 (s, 6H, $^{13}\text{-CH}_3$), 1.92 (s, 6H, $^{13}\text{-CH}_3$); ^{13}C NMR (d_6 -acetone, 151 MHz): δ 165.2 (d, $J = 7$, C^5), 164.7 (dd, $J = 254, 13$, C^9), 162.4 (dd, $J = 260, 13$, C^7), 156.6 (s, C^{20}), 156.1 (d, $J = 7$, C^{11}), 154.0 (s, C^3), 153.7 (s, C^{18}), 151.4 (s, C^{19}), 150.7 (s, C^4), 139.2 (s, C^{15}), 136.0 (s, C^{13}), 135.6 (d, $J = 24$, C^{12}), 130.5 (s, C^{17}), 129.5 (d, $J = 14$, C^{14}), 129.1 (s, C^6), 126.8 (s, C^{16}), 126.3 (s, C^2), 125.6 (d, $J = 19$, C^1), 114.7 (m, C^{10}), 99.6 (t, $J = 27$, C^8), 21.5 (s, $^{18}\text{-CH}_3$), 21.2 (s, $^{15}\text{-CH}_3$), 20.6 (m, $^{13}\text{-CH}_3$); ^{19}F NMR (d_6 -acetone, 376 MHz): δ -72.6 (d, $J = 708$), -107.8 (d, $J = 11$), -110.0 (d, $J = 11$); ES^+ : 991.3115 $[\text{M-PF}_6]^+$ (mass for $\text{IrC}_{52}\text{H}_{44}\text{N}_4\text{F}_4 = 991.3108$); R_f : 0.43 (silica, 92% DCM, 8% MeOH).

$[Ir(mes\text{-}dfppy)_2(dmobpy)]PF_6$ (**18**)



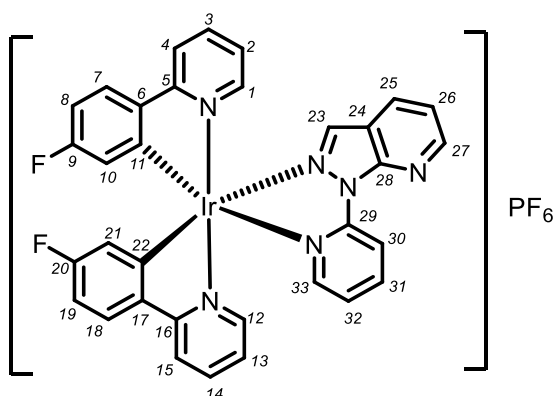
This compound was made following the general procedure for complexes containing bidentate ligands using $[Ir(mes\text{-}dfppy)_2\mu\text{-Cl}]_2$ (37 mg, 22 μmol), 4,4'-dimethoxy-2,2'-bipyridine (11 mg, 48 μmol , 2.2 equiv.), MeOH (3 ml) and DCM (5 ml). Recrystallization from MeCN and ether yielded the title compound as a light green solid (24 mg, 47%); m.p. 353°C; ^1H NMR (d_3 -MeCN, 700 MHz): δ 8.05 (m, 4H, $H^{4,19}$), 7.86 (d, 2H, $J = 6$, H^{16}), 7.71 (d, 2H, $J = 6$, H^1), 7.08 (dd, 2H, $J = 6$, 3, H^{17}), 6.99 (m, 4H, H^{14}), 6.96 (dd, 2H, $J = 6$, 2, H^2), 6.65 (td, 2H, $J = 9$, 4, H^8), 5.79 (dd, 2H, $J = 9$, 4, H^{10}), 4.03 (s, 6H, OCH_3), 2.30 (s, 6H, $^{15}\text{-CH}_3$), 2.09 (s, 6H, $^{13}\text{-CH}_3$), 1.94 (s, 6H, $^{13}\text{-CH}_3$); ^{13}C NMR (d_3 -MeCN, 176 MHz): δ 169.2 (s, C^{18}), 165.1 (d, $J = 7$, C^5), 164.6 (m, C^9), 162.2 (dd, $J = 260$, 13, C^7), 158.2 (s, C^{20}), 156.1 (d, $J = 7$, C^{11}), 153.6 (s, C^3), 152.9 (s, C^{16}), 150.2 (s, C^1), 139.3 (s, C^{15}), 136.0 (s, C^{12}), 135.8 (m, C^{13}), 129.4 (m, C^{14}), 129.1 (m, C^6), 125.9 (s, C^2), 125.6 (d, $J = 19$, C^4), 115.1 (s, C^{17}), 114.5 (m, C^{10}), 112.5 (s, C^{19}), 99.4 (t, $J = 27$, C^8), 57.8 (s, OCH_3), 21.1 (s, $^{15}\text{-CH}_3$), 20.6 (m, $^{13}\text{-CH}_3$); ^{19}F NMR (d_3 -MeCN, 700 MHz): δ -72.9 (d, $J = 707$), -108.4 (d, $J = 11$); -110.0 (d, $J = 11$); ES^+ : 1023.3030 $[M\text{-}PF_6]^+$ (mass for $IrC_{52}H_{44}N_4O_2F_4 = 1023.3006$); R_f : 0.38 (silica, 95% DCM, 5% MeOH).

[Ir(ppy)₂(L¹)]PF₆ (19)



This compound was made following the general procedure for complexes containing bidentate ligands using $[\text{Ir}(\text{ppy})_2\mu\text{-Cl}]_2$ (73 mg, 68 μmol), ligand **L¹** (28 mg, 0.14 mmol, 2.1 equiv.), MeOH (3 ml) and DCM (5 ml). Column chromatography (alumina, DCM : MeOH 0-2%) followed by recrystallization from MeCN and ether yielded the title compound as a yellow solid (61 mg, 53%); m.p. 287°C; ¹H NMR (*d*₆-acetone, 700 MHz): δ 9.62 (d, 1H, *J* = 9, H³³), 8.95 (dd, 1H, *J* = 5, 1, H²⁷), 8.52 (dd, 1H, *J* = 8, 1, H²⁵), 8.40 (m, 1H, H³²), 8.25 (dd, 2H, *J* = 8, 3, H^{1,12}), 8.20 (m, 1H, H^{4or15}), 8.08 (s, 1H, H²³), 8.04 (m, 1H, H^{4or15}), 7.96 (m, 3H, H^{2,13,30}), 7.91 (m, 2H, H^{7,18}), 7.65 (dd, 1H, *J* = 8, 5, H²⁶), 7.53 (m, 1H, H³¹), 7.16 (ddd, 1H, *J* = 7, 6, 1, H^{3or14}), 7.13 (ddd, 1H, *J* = 7, 6, 1, H^{3or14}), 7.05 (m, 2H, H^{8,19}), 6.93 (dtd, 2H, *J* = 13, 8, 1, H^{9,20}), 6.42 (d, 1H, *J* = 8, H^{10or21}), 6.38 (d, 1H, *J* = 8, H^{10or21}); ¹³C NMR (*d*₆-acetone, 176 MHz): δ 168.6 (s, C^{5or16}), 168.3 (s, C^{5or16}), 153.2 (s, C²⁷), 152.6 (s, C²⁸), 151.2 (s, C²⁹), 150.6 (s, C^{4or15}), 150.5 (s, C^{4or15}), 150.3 (s, C^{6or17}), 149.7 (s, C³⁰), 147.2 (s, C^{6or17}), 145.4 (s, C^{11or22}), 145.1 (s, C^{11or22}), 142.5 (s, C³²), 140.6 (s, C²³), 139.8 (s, C^{2or13}), 139.8 (s, C^{2or13}), 133.8 (s, C²⁵), 132.8 (s, C^{10or21}), 132.5 (s, C^{10or21}), 131.3 (s, C^{9or20}), 130.9 (s, C^{9or20}), 125.9 (s, C^{7or18}), 125.6 (s, C^{7or18}), 125.1 (s, C³¹), 124.5 (s, C^{3or14}), 124.5 (s, C^{3or14}), 123.7 (s, C^{8or19}), 123.6 (s, C^{8or19}), 121.8 (s, C²⁶), 120.8 (s, C^{1or12}), 120.8 (s, C^{1or12}), 119.7 (s, C²⁴), 115.5 (s, C³³); ¹⁹F NMR (*d*₆-acetone, 376 MHz): δ -72.6 (d, *J* = 708); ES⁺: 695.1694 [M-PF₆]⁺ (mass for IrC₃₃H₂₄N₆ = 695.1668); R_f: 0.49 (96% DCM, 4% MeOH).

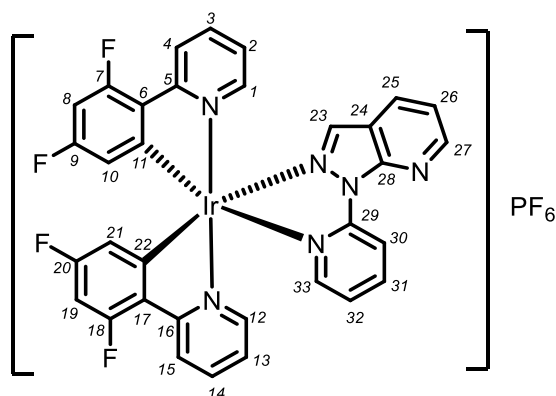
[Ir(fppy)₂(L¹)]PF₆ (20)



This compound was made following the general procedure for complexes containing bidentate ligands using $[\text{Ir}(\text{fppy})_2\mu\text{-Cl}]_2$ (72 mg, 63 μmol), ligand **L¹** (27 mg, 0.14 mmol, 2.2 equiv.), MeOH (3

ml) and DCM (5 ml). Recrystallization from MeCN and hexane yielded the title compound as a yellow solid (98 mg, 89%); m.p. 334°C; ^1H NMR (d_6 -acetone, 600 MHz): δ 9.63 (d, 1H, $J = 9$, H^{33}), 8.96 (dd, 1H, $J = 5$, 2, H^{27}), 8.52 (dd, 1H, $J = 8$, 2, H^{25}), 8.43 (ddd, 1H, $J = 9$, 8, 1, H^{32}), 8.25 (dd, 2H, $J = 8$, 3, $\text{H}^{1,12}$), 8.22 (s, 1H, H^{23}), 8.19 (m, 1H, $\text{H}^{4\text{or}15}$), 8.01 (m, 6H, $\text{H}^{2,13,7,18,30,4\text{or}15}$), 7.66 (dd, 1H, $J = 8$, 5, H^{26}), 7.57 (ddd, 1H, $J = 9$, 8, 1, H^{31}), 7.19 (ddd, 1H, $J = 7$, 6, 1, $\text{H}^{3\text{or}14}$), 7.16 (ddd, 1H, $J = 7$, 6, 1, $\text{H}^{3\text{or}14}$), 6.85 (tdd, 2H, $J = 9$, 5, 3, $\text{H}^{8,19}$), 6.02 (dd, 1H, $J = 10$, 3, $\text{H}^{10\text{or}21}$), 5.98 (dd, 1H, $J = 10$, 3, $\text{H}^{10\text{or}21}$); ^{13}C NMR (d_6 -acetone, 151 MHz): δ 167.4 (s, $\text{C}^{5\text{or}16}$), 167.1 (s, $\text{C}^{5\text{or}16}$), 165.4 (s, $\text{C}^{6\text{or}17}$), 165.1 (s, $\text{C}^{6\text{or}17}$), 163.7 (s, $\text{C}^{9\text{or}20}$), 163.5 (s, $\text{C}^{9\text{or}20}$), 153.4 (s, C^{27}), 153.2 (d, $J = 6$, C^{29}), 152.6 (s, C^{28}), 150.7 (s, $\text{C}^{4\text{or}15}$), 150.6 (s, $\text{C}^{4\text{or}15}$), 149.9 (s, C^{30}), 142.8 (s, C^{32}), 141.8 (d, $J = 2$, $\text{C}^{11\text{or}22}$), 141.6 (d, $J = 2$, $\text{C}^{11\text{or}22}$), 141.1 (d, $J = 2$, C^{23}), 140.2 (d, $J = 9$, $\text{C}^{2,13}$), 133.9 (s, C^{25}), 128.2 (d, $J = 9$, $\text{C}^{7\text{or}18}$), 127.8 (d, $J = 10$, $\text{C}^{7\text{or}18}$), 125.3 (s, C^{31}), 124.6 (d, $J = 4$, $\text{C}^{3,14}$), 121.9 (m, C^{26}), 121.0 (d, $J = 7$, $\text{C}^{1,12}$), 119.7 (s, C^{24}), 118.7 (d, $J = 19$, $\text{C}^{10\text{or}21}$), 118.3 (d, $J = 18$, $\text{C}^{10\text{or}21}$), 115.6 (s, C^{33}), 110.9 (d, $J = 13$, $\text{C}^{8\text{or}19}$), 110.7 (d, $J = 13$, $\text{C}^{8\text{or}19}$); ^{19}F NMR (d_6 -acetone, 376 MHz): δ -72.7 (d, $J = 707$), -110.9 (d, $J = 176$); ES^+ : 731.1494 $[\text{M-PF}_6]^+$ (mass for $\text{IrC}_{33}\text{H}_{22}\text{N}_6\text{F}_2 = 731.1480$); R_f : 0.09 (silica, 95% DCM, 5% MeOH).

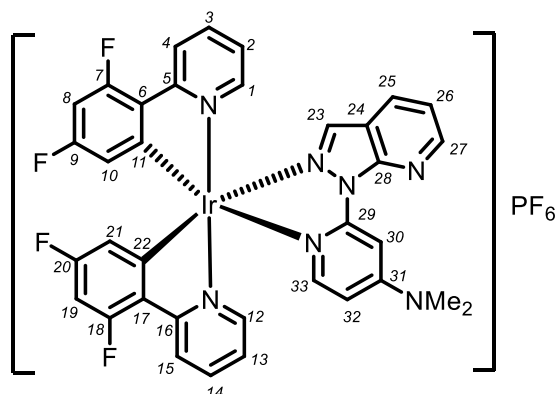
$[\text{Ir}(\text{dfppy})_2(\text{L}^1)]\text{PF}_6$ (**21**)



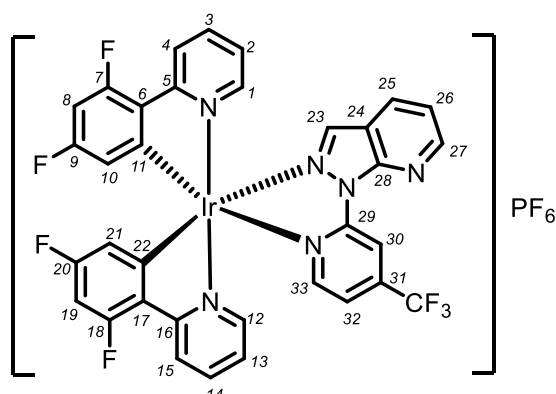
This compound was made following the general procedure for complexes containing bidentate ligands using $[\text{Ir}(\text{dfppy})_2\mu\text{-Cl}]_2$ (77 mg, 63 μmol), ligand L^1 (28 mg, 0.143 mmol, 2.3 equiv.), MeOH (3 ml) and DCM (5 ml). Recrystallization from MeCN and hexane twice yielded the title compound as a yellow solid (80 mg, 69%); m.p. 328°C; ^1H NMR (d_6 -acetone, 600 MHz): δ 9.63 (dt, 1H, $J = 9$, 1, H^{33}), 8.97 (dd, 1H, $J = 5$, 2, H^{27}), 8.52 (dd, 1H, $J = 8$, 2, H^{25}), 8.47 (ddd, 1H, $J = 9$, 8, 2, H^{32}), 8.41 (m, 2H, $\text{H}^{1,12}$), 8.36 (s, 1H, H^{23}), 8.28 (ddd, 1H, $J = 6$, 2, 1, $\text{H}^{4\text{or}15}$), 8.13 (ddd, 1H, $J = 6$, 2, 1, $\text{H}^{4\text{or}15}$), 8.08 (m, 3H, $\text{H}^{2,13,30}$), 7.68 (dd, 1H, $J = 8$, 5, H^{26}), 7.59 (ddd, 1H, $J = 8$, 6, 1, H^{31}), 7.25 (ddd, 1H, $J = 7$, 6, 1, $\text{H}^{3\text{or}14}$), 7.21 (ddd, 1H, $J = 7$, 6, 1, $\text{H}^{3\text{or}14}$), 6.79 (m, 2H, $\text{H}^{8,19}$), 5.87 (dd, 1H, $J = 9$, 2, $\text{H}^{10\text{or}21}$), 5.83 (dd, 1H, $J = 9$, 2, $\text{H}^{10\text{or}21}$); ^{13}C NMR (d_6 -acetone, 151 MHz): δ 165.5 (s, $\text{C}^{9\text{or}20}$), 165.2 (s, $\text{C}^{9\text{or}20}$), 164.8 (d, $J = 7$, $\text{C}^{5\text{or}16}$), 164.6 (d, $J = 7$, $\text{C}^{5\text{or}16}$), 163.7 (d, $J = 12$, C^{29}), 163.4 (m, $\text{C}^{7\text{or}18}$), 163.2 (s, $\text{C}^{7\text{or}18}$), 161.6 (s, $\text{C}^{6\text{or}17}$), 161.4 (s, $\text{C}^{6\text{or}17}$), 153.7 (s, C^{27}), 152.8 (s, C^{28}), 151.3 (m, $\text{C}^{4,15}$), 150.2 (s, C^{30}), 143.2 (s, C^{32}), 141.6 (s, C^{23}), 141.0 (d, $J = 10$, $\text{C}^{2,13}$), 134.1 (s, C^{25}), 129.3 (m, $\text{C}^{11\text{or}22}$), 129.1 (m, $\text{C}^{11\text{or}22}$), 125.6 (s, C^{31}), 125.2 (s, $\text{C}^{3,14}$),

124.7 (d, $J = 20$, C^{1,12}), 122.2 (s, C²⁶), 119.8 (s, C²⁴), 115.8 (s, C³³), 115.2 (dd, $J = 19$, 2, C^{10or21}), 114.8 (dd, $J = 18$, 3, C^{10or21}), 100.0 (td, $J = 27$, 12, C^{8,19}); ¹⁹F NMR (*d*₆-acetone, 376 MHz): δ -72.6 (d, $J = 708$), -110.0 (d, $J = 11$), -110.4 (d, $J = 11$); ES⁺: 767.1284 [M-PF₆]⁺ (mass for IrC₃₃H₂₀N₆F₄ = 767.1292); R_f: 0.38 (silica, 95% DCM, 5% MeOH).

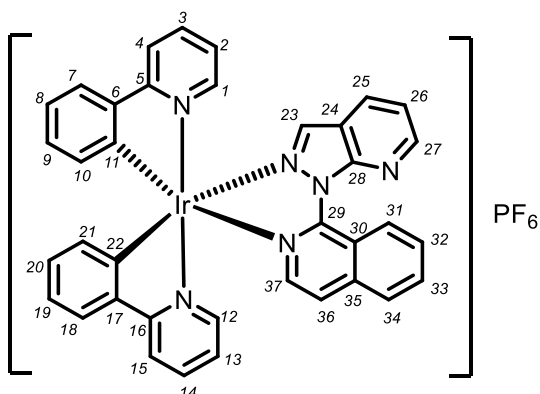
[Ir(dfppy)₂(L³)]PF₆ (22)



This compound was made following the general procedure for complexes containing bidentate ligands using [Ir(dfppy)₂μ-Cl]₂ (29 mg, 24 μmol), ligand L³ (12 mg, 50 μmol, 2.1 equiv.), MeOH (1.8 ml) and DCM (3 ml). Recrystallization three times from acetone and hexane yielded the title compound as a yellow solid (6 mg, 15%); m.p. 278°C; ¹H NMR (*d*₆-acetone, 700 MHz) δ 8.97 (dd, 1H, $J = 5$, 2, H²⁷), 8.86 (d, 1H, $J = 3$, H³⁰), 8.50 (dd, 1H, $J = 8$, 2, H²⁵), 8.40 (m, 2H, H^{1,12}), 8.26 (s, 1H, H²³), 8.24 (dd, 1H, $J = 6$, 1, H^{4or15}), 8.18 (dd, 1H, $J = 6$, 1, H^{4or15}), 8.07 (m, 2H, H^{2,13}), 7.64 (dd, 1H, $J = 8$, 5, H²⁶), 7.43 (d, 1H, $J = 7$, H³³), 7.30 (ddd, 1H, $J = 7$, 6, 1, H^{3or14}), 7.23 (ddd, 1H, $J = 7$, 6, 1, H^{3or14}), 6.76 (m, 3H, H^{8,19,32}), 5.89 (dd, 1H, $J = 9$, 2, H^{10or21}), 5.80 (dd, 1H, $J = 9$, 2, H^{10or21}), 3.28 (s, 6H, N(CH₃)₂); ¹³C NMR (*d*₆-acetone, 176 MHz): δ 165.2 (m, C^{5or16}), 164.7 (s, C^{5or16}), 163.8 (m, C^{9or20}), 163.6 (m, C^{9or20}), 163.0 (s, C^{7or18}), 161.6 (s, C^{7or18}), 157.7 (s, C³¹), 153.6 (s, C²⁷), 152.2 (s, C²⁴), 151.1 (s, C^{4or15}), 151.0 (s, C^{4or15}), 151.0 (s, C²⁹), 148.0 (s, C³³), 140.8 (m, C^{2or13}), 140.8 (d, $J = 3$, C^{2or13}), 140.2 (s, C²³), 133.9 (s, C²⁵), 129.6 (m, C^{11or22}), 129.2 (d, $J = 1$, C^{6,17}), 129.0 (m, C^{11or22}), 125.1 (s, C^{3or14}), 125.1 (s, C^{3or14}), 124.6 (m, C^{1,12}), 121.9 (s, C²⁶), 119.8 (s, C²⁸), 115.3 (m, C^{10or21}), 114.7 (m, C^{10or21}), 108.3 (s, C³²), 99.7 (m, C^{8,19}), 96.2 (s, C³⁰), 40.0 (s, N(CH₃)₂); ¹⁹F NMR (*d*₆-acetone, 376 MHz): δ -72.7 (m), -108.3 (dd, $J = 168$, 11), -110.4 (dd, $J = 120$, 11); ES⁺: 810.1723 [M-PF₆]⁺ (mass for IrC₃₅H₂₅N₇F₄ = 810.1714); R_f: 0.26 (silica, 95% DCM, 5% MeOH).

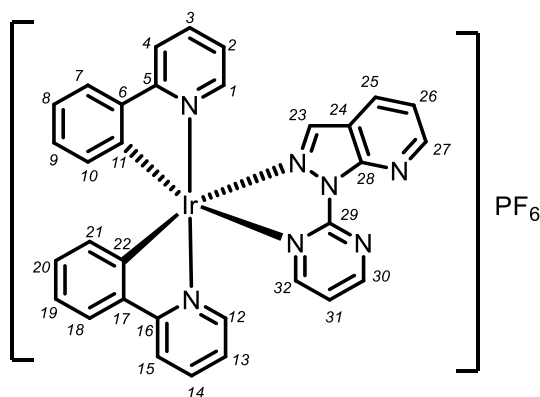
$[Ir(dfppy)_2(L^5)]PF_6$ (**23**)

This compound was made following the general procedure for complexes containing bidentate ligands using $[Ir(dfppy)_2\mu\text{-Cl}]_2$ (54 mg, 45 μmol), ligand L^5 (26 mg, 99 μmol , 2.2 equiv.), MeOH (3 ml) and DCM (5 ml). Recrystallization from acetone and hexane yielded the title compound as a yellow solid (44 mg, 51%); m.p. 345°C; ^1H NMR (d_6 -acetone, 600 MHz) δ 9.89 (m, 1H, H^{30}), 9.03 (dd, 1H, $J = 5$, 2 H^{27}), 8.56 (dd, 1H, $J = 8$, 2, H^{25}), 8.45 (s, 1H, H^{23}), 8.41 (m, 2H, $H^{1,12}$), 8.38 (d, 1H, $J = 6$, H^{33}), 8.29 (m, 1H, $H^{3\text{or}14}$), 8.22 (m, 1H, $H^{3\text{or}14}$), 8.09 (m, 2H, $H^{2,13}$), 7.87 (dd, 1H, $J = 6$, 1, H^{32}), 7.73 (dd, 1H, $J = 8$, 5, H^{26}), 7.22 (ddd, 2H, $J = 7$, 6, 1, $H^{4,15}$), 6.81 (m, 2H, $H^{8,19}$), 5.84 (dt, 1H, $J = 9$, 2, $H^{10,21}$); ^{13}C NMR (d_6 -acetone, 151 MHz): δ 165.2 (dd, $J = 48$, 13, $C^{9\text{or}20}$), 164.5 (d, $J = 7$, $C^{5\text{or}16}$), 164.4 (d, $J = 7$, $C^{5\text{or}16}$), 163.5 (dd, $J = 48$, 13, $C^{9\text{or}20}$), 163.1 (dd, $J = 40$, 13, $C^{7\text{or}18}$), 161.3 (dd, $J = 39$, 13, $C^{7\text{or}18}$), 154.0 (s, C^{27}), 153.0 (s, C^{24}), 152.2 (s, C^{33}), 151.9 (dd, $J = 457$, 7, C^{31}), 151.7 (s, $C^{3\text{or}14}$), 151.4 (s, $C^{3\text{or}14}$), 142.7 (s, C^{23}), 142.5 (q, $J = 35$, C^{29}), 141.2 (s, $C^{2\text{or}13}$), 141.1 (s, $C^{2\text{or}13}$), 134.5 (s, C^{25}), 129.2 (dd, $J = 5$, 3, $C^{11\text{or}22}$), 129.2 (dd, $J = 5$, 3, $C^{11\text{or}22}$), 125.3 (s, $C^{4\text{or}15}$), 125.2 (s, $C^{4\text{or}15}$), 124.7 (s, $C^{1\text{or}12}$), 124.7 (s, $C^{1\text{or}12}$), 124.6 (s, $C^{6\text{or}17}$), 124.6 (s, $C^{6\text{or}17}$), 123.2 (q, $J = 274$, CF_3), 122.5 (s, C^{26}), 121.1 (q, $J = 3$, C^{32}), 120.0 (s, C^{28}), 115.0 (m, $C^{10,21}$), 112.1 (q, $J = 4$, C^{30}), 100.2 (td, $J = 27$, 21, $C^{8,19}$); ^{19}F NMR (d_6 -acetone, 376 MHz): δ -65.7 (s), -72.7 (d, $J = 708$), -107.8 (dd, $J = 196$, 11), -110.0 (dd, $J = 203$, 11); ES^+ : 835.1165 $[\text{M-PF}_6]^+$ (mass for $\text{C}_{34}\text{H}_{19}\text{N}_6\text{F}_7\text{Ir} = 835.1165$); R_f : 0.41 (silica, 90% DCM, 10% MeOH).

 $[Ir(ppy)_2(L^7)]PF_6$ (**24**)

This compound was made following the general procedure for complexes containing bidentate ligands using $[\text{Ir}(\text{ppy})_2\mu\text{-Cl}]_2$ (73 mg, 68 μmol), ligand L^7 (28 mg, 0.14 mmol, 2.1 equiv.), MeOH (3 ml) and DCM (5 ml). Column chromatography (alumina, DCM : MeOH 0-2%) followed by recrystallization from MeCN and ether yielded the title compound as a yellow solid (61 mg, 53%); m.p. 302°C; ^1H NMR (d_6 -acetone, 700 MHz): δ 10.05 (s, 1H, H^{23}), 9.05 (d, 1H, $J = 8$, H^{31}), 8.44 (dd, 1H, $J = 4, 2$, H^{27}), 8.43 (m, 1H, $\text{H}^{10\text{or}12}$), 8.39 (dd, 1H, $J = 9, 2$, H^{25}), 8.29 (m, 1H, H^{34}), 8.21 (d, 1H, $J = 8$, $\text{H}^{4\text{or}15}$), 8.11 (m, 3H, $\text{H}^{32,33,37}$), 8.06 (m, 1H, $\text{H}^{4\text{or}15}$), 8.03 (m, 1H, $\text{H}^{10\text{or}12}$), 7.91 (m, 2H, $\text{H}^{3\text{or}14,7\text{or}18}$), 7.86 (d, 1H, $J = 6$, H^{36}), 7.78 (m, 2H, $\text{H}^{3\text{or}14,7\text{or}18}$), 7.28 (dd, 1H, $J = 9, 4$, H^{26}), 7.06 (m, 2H, $\text{H}^{2\text{or}13,8\text{or}19}$), 6.92 (m, 3H, $\text{H}^{9\text{or}20,2\text{or}13,8\text{or}19}$), 6.83 (td, 1H, $J = 8, 1$, $\text{H}^{9\text{or}20}$), 6.35 (m, 1H, $\text{H}^{10\text{or}21}$), 6.33 (m, 1H, $\text{H}^{10\text{or}21}$); ^{13}C NMR (d_6 -acetone, 176 MHz): δ 169.5 (s, $\text{C}^{5\text{or}16}$), 168.4 (s, $\text{C}^{5\text{or}16}$), 159.7 (s, C^{24}), 158.4 (s, C^{27}), 151.5 (s, $\text{C}^{10\text{or}12}$), 150.7 (s, $\text{C}^{10\text{or}12}$), 150.5 (s, C^{30}), 149.9 (s, $\text{C}^{6\text{or}17}$), 148.2 (s, $\text{C}^{6\text{or}17}$), 145.4 (s, $\text{C}^{11\text{or}22}$), 145.3 (s, $\text{C}^{11\text{or}22}$), 141.0 (s, C^{36}), 139.9 (s, C^{25}), 139.6 (s, $\text{C}^{3\text{or}14}$), 139.2 (s, $\text{C}^{3\text{or}14}$), 135.2 (s, C^{23}), 134.3 (s, C^{34}), 132.9 (s, C^{29}), 132.9 (s, $\text{C}^{10\text{or}21}$), 132.5 (s, $\text{C}^{10\text{or}21}$), 132.4 (s, C^{32}), 131.4 (s, $\text{C}^{9\text{or}20}$), 130.3 (s, $\text{C}^{9\text{or}20}$), 129.5 (s, C^{33}), 126.2 (s, C^{37}), 126.0 (s, $\text{C}^{7\text{or}18}$), 125.7 (s, C^{31}), 125.2 (s, $\text{C}^{7\text{or}18}$), 124.4 (s, $\text{C}^{2\text{or}13}$), 123.6 (s, $\text{C}^{8\text{or}19}$), 123.6 (s, $\text{C}^{2\text{or}13}$), 122.6 (s, $\text{C}^{8\text{or}19}$), 121.7 (s, C^{26}), 121.4 (s, C^{35}), 120.7 (s, $\text{C}^{4\text{or}15}$), 120.2 (s, $\text{C}^{4\text{or}15}$), 116.5 (s, C^{28}); ^{19}F NMR (d_6 -acetone, 376 MHz): δ -72.6 (d, $J = 708$); ES^+ : 745.1826 $[\text{M-PF}_6]^+$ (mass for $\text{IrC}_{37}\text{H}_{26}\text{N}_6 = 745.1825$); R_f : 0.39 (92% DCM, 8% MeOH).

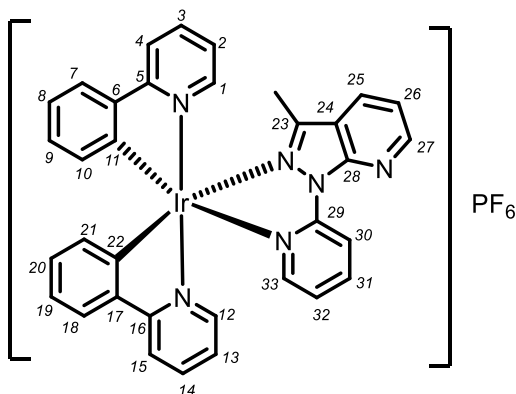
$[\text{Ir}(\text{ppy})_2(\text{L}^9)]\text{PF}_6$ (25**)**



This compound was made following the general procedure for complexes containing bidentate ligands using $[\text{Ir}(\text{ppy})_2\mu\text{-Cl}]_2$ (0.20 g, 0.187 mmol), ligand L^9 (92 mg, 0.47 mmol, 3 equiv.), MeOH (6 ml) and DCM (10 ml). Recrystallization twice from MeCN and ether yielded the title compound as a yellow solid (61 mg, 19%); m.p. 287°C; ^1H NMR (d_6 -acetone, 700 MHz) δ 9.18 (dd, 1H, $J = 5, 2$, H^{32}), 8.94 (dd, 1H, $J = 5, 2$, H^{25}), 8.48 (dd, 1H, $J = 8, 2$, H^{27}), 8.28 (m, 5H, $\text{H}^{1,4,12,15,30}$), 8.13 (s, 1H, H^{23}), 8.00 (ddd, 2H, $J = 11, 8, 7$, $\text{H}^{3,14}$), 7.91 (ddd, 2H, $J = 8, 3, 1$, $\text{H}^{7,18}$), 7.64 (m, 2H, $\text{H}^{26,31}$), 7.17 (m, 2H, $\text{H}^{2,13}$), 7.06 (m, 2H, $\text{H}^{8,19}$), 6.93 (dtd, 2H, $J = 10, 8, 1$, $\text{H}^{9,20}$), 6.38 (m, 2H, $\text{H}^{10,21}$); ^{13}C NMR (d_6 -acetone, 176 MHz): δ 168.5 (s, $\text{C}^{5\text{or}16}$), 168.3 (s, $\text{C}^{5\text{or}16}$), 161.8 (s, C^{32}), 159.2 (s, C^{30}), 157.5 (s, C^{29}), 154.0 (s, C^{25}), 153.3 (s, C^{24}), 151.3 (s, $\text{C}^{10\text{or}12}$), 150.9 (s, $\text{C}^{10\text{or}12}$), 149.1 (s, $\text{C}^{11\text{or}22}$), 146.8 (s, $\text{C}^{11\text{or}22}$), 145.4 (s, $\text{C}^{6\text{or}17}$), 145.3 (s, $\text{C}^{6\text{or}17}$), 142.4 (s, C^{23}), 140.1 (s, $\text{C}^{3\text{or}14}$), 140.0 (s, $\text{C}^{3\text{or}14}$), 133.4 (s, C^{27}), 132.9 (s, $\text{C}^{10\text{or}21}$), 132.7 (s, $\text{C}^{10\text{or}21}$), 131.4 (s, $\text{C}^{9\text{or}20}$), 131.0 (s, $\text{C}^{9\text{or}20}$), 126.0 (s, $\text{C}^{7\text{or}18}$), 125.7 (s, $\text{C}^{7\text{or}18}$), 124.8 (s, $\text{C}^{2\text{or}13}$), 124.6 (s,

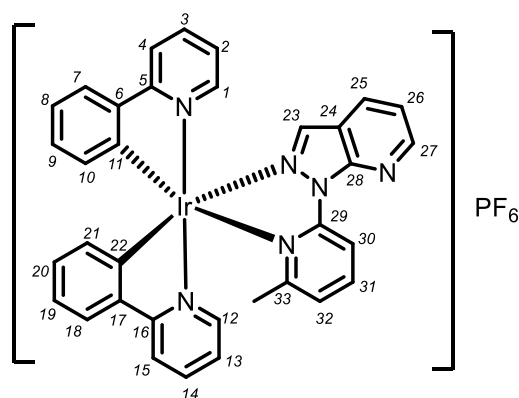
C^{2or13}), 124.0 (s, C^{8or19}), 123.8 (s, C^{8or19}), 122.4 (s, C^{26}), 121.8 (s, C^{31}), 121.0 (s, C^{4or15}), 121.0 (s, C^{4or15}), 119.8 (s, C^{28}); ^{19}F NMR (d_6 -acetone, 376 MHz): δ -72.6 (d, J = 708); ES^+ : 696.1630 $[M-PF_6]^+$ (mass for $C_{32}H_{23}N_7Ir$ = 696.1621); R_f : 0.36 (silica, 96% DCM, 4% MeOH).

$[Ir(ppy)_2(L^{11})]PF_6$ (26**)**



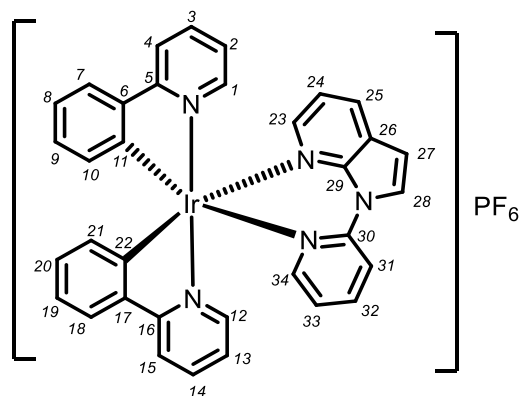
This compound was made following the general procedure for complexes containing bidentate ligands using $[Ir(ppy)_2\mu-Cl]_2$ (50 mg, 47 μ mol), ligand **L¹¹** (22 mg, 0.10 mmol, 2.1 equiv.), MeOH (3 ml) and DCM (5 ml). Column chromatography (silica, DCM : MeOH 0-2%) and recrystallization from (i) MeCN and ether and (ii) from acetone and hexane yielded the title compound as a yellow solid (15 mg, 19%); m.p. 334°C; ^1H NMR ($CDCl_3$, 700 MHz): δ 9.63 (d, 1H, J = 9, H^{33}), 8.94 (dd, 1H, J = 5, 2, H^{27}), 8.49 (dd, 1H, J = 8, 2, H^{25}), 8.36 (m, 2H, $H^{1or12,32}$), 8.26 (d, 2H, J = 8, $H^{4,15}$), 7.99 (m, 3H, $H^{1or12,3,14}$), 7.91 (m, 2H, $H^{7,18}$), 7.84 (m, 1H, H^{30}), 7.64 (dd, 1H, J = 8, 5, H^{26}), 7.45 (ddd, 1H, J = 7, 6, 1, H^{31}), 7.16 (m, 2H, $H^{2,13}$), 7.06 (m, 1H, H^{8or19}), 7.02 (m, 1H, H^{8or19}), 6.93 (td, 1H, J = 8, 1, H^{9or20}), 6.90 (td, 1H, J = 8, 1, H^{9or20}), 6.40 (m, 1H, H^{10or21}), 6.27 (m, 1H, H^{10or21}), 2.21 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 176 MHz): δ 169.0 (s, C^{5or16}), 168.3 (s, C^{5or16}), 153.5 (s, C^{27}), 153.3 (s, C^{23}), 152.8 (s, C^{28}), 151.6 (s, C^{29}), 151.2 (s, C^{1or12}), 150.6 (s, C^{1or12}), 149.7 (s, C^{6or17}), 149.4 (s, C^{30}), 148.7 (s, C^{6or17}), 145.4 (s, C^{11or22}), 145.1 (s, C^{11or22}), 142.4 (s, C^{32}), 139.9 (s, C^{3or14}), 139.9 (s, C^{3or14}), 133.2 (s, C^{10or21}), 133.2 (s, C^{25}), 132.0 (s, C^{10or21}), 131.6 (s, C^{9or20}), 131.1 (s, C^{9or20}), 126.1 (s, C^{7or18}), 126.0 (s, C^{7or18}), 124.8 (s, C^{2or13}), 124.6 (s, C^{2or13}), 124.5 (s, C^{31}), 124.0 (s, C^{8or19}), 123.5 (s, C^{8or19}), 121.4 (s, C^{26}), 121.1 (s, C^{4or15}), 121.0 (s, C^{4or15}), 119.8 (s, C^{24}), 115.3 (s, C^{33}), 12.4 (s, CH_3); ^{19}F NMR ($CDCl_3$, 376 MHz): δ -72.6 (d, J = 708); ES^+ : 709.1834 $[M]^+$ (mass for $C_{34}H_{26}N_6Ir$ = 709.1825); R_f : 0.25 (98% DCM, 2% MeOH).

[Ir(ppy)₂(L¹²)]PF₆ (27)



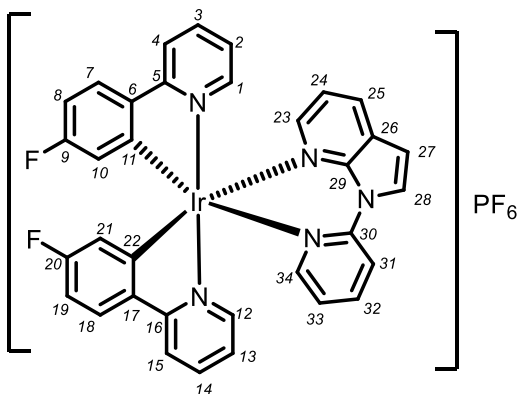
This compound was made following the general procedure for complexes containing bidentate ligands using $[\text{Ir}(\text{ppy})_2\mu\text{-Cl}]_2$ (50 mg, 47 μmol), ligand **L¹²** (22 mg, 0.10 mmol, 2.1 equiv.), MeOH (3 ml) and DCM (5 ml). Column chromatography (silica, DCM : MeOH 0-2%) followed by recrystallization from MeCN and ether yielded the title compound as a yellow solid (50 mg, 63%); m.p. 268°C; ¹H NMR (CDCl₃, 700 MHz): δ 9.67 (d, 1H, J = 8, H³²), 8.94 (dd, 1H, J = 5, 2, H²⁷), 8.50 (dd, 1H, J = 8, 2, H²⁵), 8.30 (m, 2H, H^{10or12,31}), 8.27 (t, 2H, J = 8, H^{4,15}), 8.09 (m, 1H, H^{10or12}), 8.00 (m, 2H, H^{3,14}), 7.88 (m, 2H, H^{7,18}), 7.84 (s, 1H, H²³), 7.63 (dd, 1H, J = 8, 5, H²⁶), 7.44 (d, 1H, J = 8, H³⁰), 7.22 (ddd, 1H, J = 7, 6, 1, H^{20or13}), 7.11 (ddd, 1H, J = 7, 6, 1, H^{20or13}), 7.05 (td, 1H, J = 8, 1, H^{8or19}), 6.96 (td, 1H, J = 8, 1, H^{8or19}), 6.90 (td, 1H, J = 8, 1, H^{9or20}), 6.85 (td, 1H, J = 8, 1, H^{9or20}), 6.34 (m, 1H, H^{10or21}), 6.21 (m, 1H, H^{10or21}), 2.18 (s, 3H, CH₃); ¹³C NMR (CDCl₃, 176 MHz): δ 169.0 (s, C^{5or16}), 168.1 (s, C^{5or16}), 163.0 (s, C³³), 153.2 (m, C^{6,17}), 153.0 (s, C²⁷), 152.9 (s, C²⁸), 151.8 (s, C^{10or12}), 151.8 (s, C²⁹), 150.7 (s, C^{10or12}), 144.9 (s, C^{11or22}), 144.8 (s, C^{11or22}), 142.7 (s, C³¹), 139.9 (s, C^{30or14}), 139.9 (s, C^{30or14}), 139.8 (s, C²³), 133.8 (s, C²⁵), 132.8 (s, C^{10or21}), 131.8 (s, C^{10or21}), 131.3 (s, C^{9or20}), 131.2 (s, C^{9or20}), 126.1 (s, C^{7or18}), 125.8 (s, C^{7or18}), 125.0 (s, C³⁰), 125.0 (s, C^{20or13}), 124.4 (s, C^{20or13}), 124.0 (s, C^{8or19}), 123.1 (s, C^{8or19}), 121.9 (s, C²⁶), 121.2 (s, C^{4or15}), 120.9 (s, C^{4or15}), 119.9 (s, C²⁴), 113.0 (s, C³²), 28.5 (s, CH₃); ¹⁹F NMR (CDCl₃, 376 MHz): δ -72.6 (m); ES⁺: 709.1831 [M]⁺ (mass for C₃₄H₂₆N₆Ir = 709.1825); R_f: 0.37 (98% DCM, 2% MeOH).

[Ir(ppy)₂(L²)]PF₆ (28)



This compound was made following the general procedure for complexes containing bidentate ligands using $[\text{Ir}(\text{ppy})_2\mu\text{-Cl}]_2$ (50 mg, 47 μmol), ligand L^2 (20 mg, 0.10 mmol, 2.2 equiv.), MeOH (3 ml) and DCM (5 ml). Recrystallization from MeCN yielded the title compound as a yellow solid (17 mg, 22%); m.p. > 400°C; ^1H NMR (d_6 -acetone, 600 MHz): δ 8.51 (m, 1H, $\text{H}^{1\text{or}12}$), 8.44 (d, 1H, $J = 4$, H^{28}), 8.34 (m, 2H, $\text{H}^{1\text{or}12,4\text{or}15}$), 8.26 (dd, 1H, $J = 8, 1$, H^{23}), 8.20 (ddd, 1H, $J = 9, 7, 2$, H^{32}), 8.13 (d, 1H, $J = 9$, H^{31}), 8.09 (d, 1H, $J = 8$, $\text{H}^{4\text{or}15}$), 8.06 (m, 2H, $\text{H}^{3\text{or}14,34}$), 7.93 (m, 1H, $\text{H}^{7\text{or}18}$), 7.90 (m, 1H, $\text{H}^{3\text{or}14}$), 7.84 (dd, 1H, $J = 6, 1$, H^{25}), 7.74 (dd, 1H, $J = 8, 1$, $\text{H}^{7\text{or}18}$), 7.23 (ddd, 1H, $J = 8, 6, 1$, $\text{H}^{2\text{or}13}$), 7.18 (m, 4H, $\text{H}^{2\text{or}13,24,27,33}$), 7.02 (td, 1H, $J = 8, 1$, $\text{H}^{8\text{or}19}$), 6.97 (td, 1H, $J = 8, 1$, $\text{H}^{8\text{or}19}$), 6.87 (dtd, 2H, $J = 15, 8, 1$, $\text{H}^{9,20}$), 6.28 (m, 1H, $\text{H}^{10\text{or}21}$), 6.22 (m, 1H, $\text{H}^{10\text{or}21}$); ^{13}C NMR (d_6 -acetone, 151 MHz): δ : 168.6 (s, $\text{C}^{5\text{or}16}$), 168.2 (s, $\text{C}^{5\text{or}16}$), 152.8 (s, C^{34}), 151.1 (s, $\text{C}^{1\text{or}12}$), 150.9 (s, $\text{C}^{1\text{or}12}$), 150.9 (s, $\text{C}^{6\text{or}17}$), 149.6 (s, $\text{C}^{6\text{or}17}$), 147.6 (s, C^{26}), 147.6 (s, C^{25}), 146.0 (s, C^{30}), 145.3 (s, $\text{C}^{11\text{or}22}$), 145.1 (s, $\text{C}^{11\text{or}22}$), 142.3 (s, C^{32}), 139.9 (s, $\text{C}^{3\text{or}14}$), 139.7 (s, $\text{C}^{3\text{or}14}$), 133.2 (s, C^{23}), 132.9 (s, $\text{C}^{10\text{or}21}$), 132.5 (s, $\text{C}^{10\text{or}21}$), 131.3 (s, $\text{C}^{9\text{or}20}$), 131.3 (s, $\text{C}^{9\text{or}20}$), 129.8 (s, C^{28}), 126.4 (s, C^{29}), 126.3 (s, $\text{C}^{7\text{or}18}$), 125.8 (s, $\text{C}^{7\text{or}18}$), 124.5 (s, $\text{C}^{2\text{or}13}$), 124.3 (s, $\text{C}^{2\text{or}13}$), 123.7 (s, C^{33}), 123.7 (s, $\text{C}^{8\text{or}19}$), 123.6 (s, $\text{C}^{8\text{or}19}$), 121.4 (s, $\text{C}^{4\text{or}15}$), 121.1 (s, C^{24}), 120.7 (s, $\text{C}^{4\text{or}15}$), 119.1 (s, C^{31}), 108.6 (s, C^{27}); ^{19}F NMR (d_6 -acetone, 376 MHz): δ -72.7 (d, $J = 707$); ES^+ : 694.1682 $[\text{M-PF}_6]^+$ (mass for $\text{IrC}_{34}\text{H}_{25}\text{N}_5 = 694.1716$); R_f : 0.50 (silica, 90% DCM, 10% MeOH).

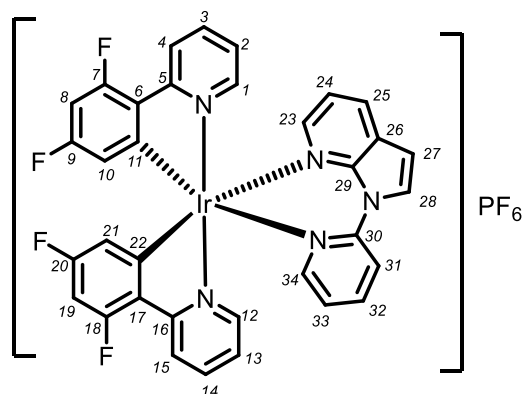
$[\text{Ir}(\text{fppy})_2(\text{L}^2)]\text{PF}_6$ (**29**)



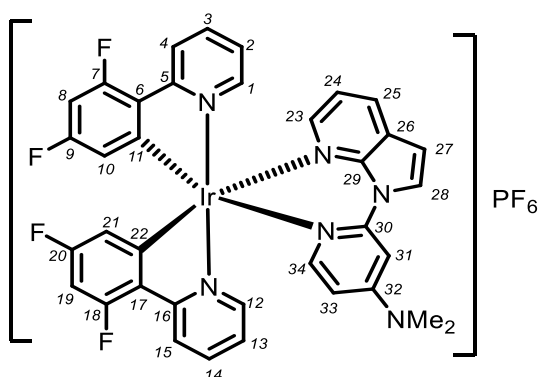
This compound was made following the general procedure for complexes containing bidentate ligands using $[\text{Ir}(\text{fppy})_2\mu\text{-Cl}]_2$ (53 mg, 47 μmol), ligand L^2 (20 mg, 0.10 mmol, 2.2 equiv.), MeOH (2.4 ml) and DCM (4 ml). Column chromatography (silica, DCM : MeOH 0-2%) and recrystallization from MeCN and ether yielded the title compound as a yellow solid (55 mg, 68%); m.p. 317°C; ^1H NMR (d_6 -acetone, 600 MHz): δ 8.52 (m, 1H, $\text{H}^{1\text{or}12}$), 8.45 (d, 1H, $J = 4$, H^{28}), 8.35 (m, 2H, $\text{H}^{4\text{or}15,1\text{or}12}$), 8.29 (dd, 1H, $J = 8, 1$, H^{23}), 8.23 (ddd, 1H, $J = 9, 7, 2$, H^{32}), 8.16 (d, 1H, $J = 9$, H^{31}), 8.10 (m, 2H, $\text{H}^{4\text{or}15,3\text{or}14}$), 8.05 (m, 2H, $\text{H}^{7\text{or}18,34}$), 7.93 (td, 1H, $J = 8, 1$, $\text{H}^{3\text{or}14}$), 7.90 (dd, 1H, $J = 6, 1$, H^{25}), 7.85 (dd, 1H, $J = 9, 6$, $\text{H}^{7\text{or}18}$), 7.25 (m, 3H, $\text{H}^{2\text{or}13,24,33}$), 7.20 (ddd, 1H, $J = 7, 6, 1$, $\text{H}^{2\text{or}13}$), 7.17 (d, 1H, $J = 4$, H^{27}), 6.82 (td, 1H, $J = 9, 3$, $\text{H}^{8\text{or}19}$), 6.77 (td, 1H, $J = 9, 3$, $\text{H}^{8\text{or}19}$), 5.88 (dd, 1H, $J = 10, 3$, $\text{H}^{10\text{or}21}$), 5.83 (dd, 1H, $J = 10, 3$, $\text{H}^{10\text{or}21}$); ^{13}C NMR (d_6 -acetone, 151 MHz): δ 167.4 (s, $\text{C}^{5\text{or}16}$), 167.1 (s, $\text{C}^{5\text{or}16}$), 165.3 (d, $J = 11$, $\text{C}^{9\text{or}20}$),

163.6 (d, $J = 11$, C^{9or20}), 154.1 (d, $J = 6$, C^{6or17}), 152.9 (s, C^{34}), 151.2 (s, C^{1or12}), 151.1 (s, C^{1or12}), 150.8 (d, $J = 6$, C^{6or17}), 149.6 (s, C^{29}), 147.7 (s, C^{25}), 146.0 (s, C^{30}), 142.6 (s, C^{32}), 141.8 (d, $J = 2$, C^{11or22}), 141.6 (d, $J = 2$, C^{11or22}), 140.4 (s, C^{3or14}), 140.2 (s, C^{3or14}), 133.6 (s, C^{23}), 129.9 (s, C^{28}), 128.7 (d, $J = 9$, C^{7or18}), 128.1 (d, $J = 9$, C^{7or18}), 126.5 (s, C^{26}), 124.6 (s, C^{2or13}), 124.4 (s, C^{2or13}), 124.0 (s, C^{33}), 121.6 (s, C^{4or15}), 121.3 (s, C^{24}), 121.0 (s, C^{4or15}), 119.3 (s, C^{31}), 118.8 (d, $J = 18$, C^{10or21}), 118.4 (d, $J = 18$, C^{10or21}), 110.8 (dd, $J = 23, 1$, $C^{8,19}$), 108.8 (s, C^{27}); ^{19}F NMR (d_6 -acetone, 376 MHz): δ -72.6 (d, $J = 707$), -110.4 (d, $J = 82$); ES^+ : 730.1510 $[\text{M-PF}_6]^+$ (mass for $\text{IrC}_{34}\text{H}_{23}\text{N}_5\text{F}_2 = 730.1528$); R_f : 0.24 (95% DCM, 5% MeOH).

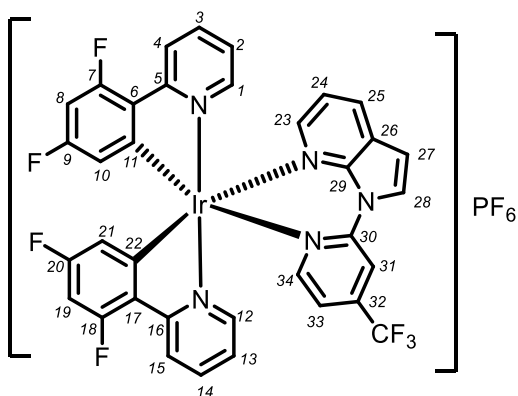
$[\text{Ir}(\text{dfppy})_2(\text{L}^2)]\text{PF}_6$ (30**)**



This compound was made following the general procedure for complexes containing bidentate ligands using $[\text{Ir}(\text{dfppy})_2\mu\text{-Cl}]_2$ (57 mg, 47 μmol), ligand L^2 (20 mg, 0.10 mmol, 2.1 equiv.), MeOH (2.4 ml) and DCM (4 ml). Column chromatography (silica, DCM : MeOH 0-2%) and recrystallization from MeCN and ether yielded the title compound as a yellow solid (28 mg, 33%); m.p. 301°C; ^1H NMR (d_6 -acetone, 600 MHz): δ 8.64 (m, 1H, H^{1or12}), 8.51 (d, 1H, $J = 9$, H^{4or15}), 8.48 (m, 1H, H^{1or12}), 8.46 (d, 1H, $J = 4$, H^{28}), 8.31 (dd, 1H, $J = 8, 1$, H^{23}), 8.25 (ddd, 2H, $J = 9, 7, 2$, $H^{4or15,32}$), 8.17 (m, 2H, $H^{3or14,31}$), 8.07 (m, 1H, H^{34}), 8.00 (m, 1H, H^{3or14}), 7.92 (dd, 1H, $J = 6, 1$, H^{25}), 7.30 (m, 4H, $H^{2,13,24,33}$), 7.18 (d, 1H, $J = 4$, H^{27}), 6.72 (m, 2H, $H^{8,19}$), 5.76 (dd, 1H, $J = 9, 2$, H^{10or21}), 5.71 (dd, 1H, $J = 9, 2$, H^{10or21}); ^{13}C NMR (d_6 -acetone, 151 MHz): δ 164.7 (d, $J = 7$, C^{5or16}), 164.4 (d, $J = 7$, C^{5or16}), 164.1 (m, $C^{9,20}$), 163.0 (m, C^{7or18}), 161.2 (dd, $J = 260, 13$, C^{7or18}), 155.1 (m, C^{6or17}), 153.0 (s, C^{34}), 151.9 (d, $J = 7$, C^{6or17}), 151.7 (s, C^{1or12}), 151.7 (s, C^{1or12}), 149.5 (s, C^{29}), 147.7 (s, C^{25}), 145.9 (s, C^{30}), 142.9 (s, C^{32}), 141.1 (s, C^{3or14}), 141.0 (s, C^{3or14}), 133.9 (s, C^{23}), 129.9 (s, C^{28}), 129.2 (m, C^{11or22}), 129.0 (m, C^{11or22}), 126.7 (s, C^{26}), 125.2 (d, $J = 20$, C^{4or15}), 125.1 (s, C^{2or13}), 124.9 (s, C^{2or13}), 124.4 (d, $J = 20$, C^{4or15}), 124.3 (s, C^{33}), 121.6 (s, C^{24}), 119.4 (s, C^{31}), 115.1 (dd, $J = 18, 3$, C^{10or21}), 114.8 (dd, $J = 18, 3$, C^{10or21}), 109.0 (s, C^{27}), 100.0 (td, $J = 27, 11$, $C^{8,19}$); ^{19}F NMR (d_6 -acetone, 376 MHz): δ -72.6 (d, $J = 708$), -107.4 (dd, $J = 111, 11$), -109.6 (dd, $J = 283, 11$); ES^+ : 766.1303 $[\text{M-PF}_6]^+$ (mass for $\text{IrC}_{34}\text{H}_{21}\text{N}_5\text{F}_4 = 766.1339$); R_f : 0.23 (95% DCM, 5% MeOH).

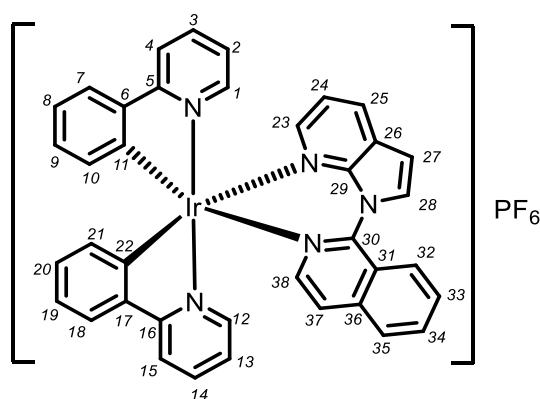
$[Ir(dfppy)_2(L^4)]PF_6$ (**31**)

This compound was made following the general procedure for complexes containing bidentate ligands using $[Ir(dfppy)_2\mu\text{-Cl}]_2$ (60 mg, 50 μmol), ligand L^4 (26 mg, 0.11 mmol, 2.2 equiv.), MeOH (3 ml) and DCM (5 ml). Column chromatography (silica, DCM : MeOH 0-2%) yielded the title compound as a yellow solid (67 mg, 71%); m.p. 317°C; ^1H NMR (d_6 -acetone, 600 MHz): δ 8.59 (m, 1H, $H^{4\text{or}15}$), 8.49 (m, 2H, $H^{1\text{or}12,28}$), 8.39 (m, 1H, $H^{4\text{or}15}$), 8.26 (dd, 1H, $J = 8, 1$, H^{23}), 8.22 (d, 1H, $J = 8$, $H^{1\text{or}12}$), 8.15 (m, 1H, $H^{2\text{or}13}$), 7.97 (m, 1H, $H^{2\text{or}13}$), 7.87 (dd, 1H, $J = 6, 1$, H^{25}), 7.46 (d, 1H, $J = 7$, H^{34}), 7.33 (ddd, 1H, $J = 7, 6, 1$, $H^{3\text{or}14}$), 7.29 (ddd, 1H, $J = 7, 6, 1$, $H^{3\text{or}14}$), 7.24 (dd, 1H, $J = 8, 6$, H^{24}), 7.08 (d, 1H, $J = 4$, H^{27}), 7.05 (d, 1H, $J = 3$, H^{31}), 6.71 (m, 1H, $H^{8\text{or}19}$), 6.67 (m, 1H, $H^{8\text{or}19}$), 6.51 (dd, 1H, $J = 7, 3$, H^{33}), 5.74 (dd, 1H, $J = 9, 2$, $H^{10\text{or}21}$), 5.72 (dd, 1H, $J = 9, 2$, $H^{10\text{or}21}$), 3.16 (s, 6H, $N(\text{CH}_3)_2$); ^{13}C NMR (d_6 -acetone, 151 MHz): δ 165.1 (dd, $J = 13, 4$, $C^{9\text{or}20}$), 164.7 (d, $J = 7$, $C^{5\text{or}16}$), 164.6 (d, $J = 7$, $C^{5\text{or}16}$), 163.4 (dd, $J = 13, 4$, $C^{9\text{or}20}$), 163.1 (dd, $J = 64, 13$, $C^{7\text{or}18}$), 161.4 (dd, $J = 64, 13$, $C^{7\text{or}18}$), 157.5 (m, C^{32}), 155.9 (d, $J = 7$, $C^{6\text{or}17}$), 153.7 (d, $J = 7$, $C^{6\text{or}17}$), 151.4 (s, $C^{4\text{or}15}$), 151.4 (s, $C^{4\text{or}15}$), 151.0 (s, C^{34}), 148.8 (s, C^{30}), 147.5 (s, C^{25}), 145.9 (s, C^{29}), 140.7 (s, $C^{2\text{or}13}$), 140.6 (s, $C^{2\text{or}13}$), 133.5 (s, C^{23}), 130.2 (s, C^{28}), 129.1 (m, $C^{11,22}$), 126.5 (s, C^{26}), 124.9 (s, $C^{3\text{or}14}$), 124.8 (s, $C^{1\text{or}12}$), 124.7 (s, $C^{3\text{or}14}$), 124.3 (s, $C^{1\text{or}12}$), 120.9 (s, C^{24}), 114.8 (m, $C^{10,21}$), 108.0 (s, C^{33}), 107.8 (s, C^{27}), 99.5 (m, $C^{8,19}$), 98.8 (s, C^{31}), 39.8 (s, $N(\text{CH}_3)_2$); ^{19}F NMR (d_6 -acetone, 376 MHz): δ -72.2 (m), -107.7 (dd, $J = 113, 11$), -109.9 (dd, $J = 188, 11$); ES^+ : 809.1744 $[\text{M-PF}_6]^+$ (mass for $\text{IrC}_{36}\text{H}_{26}\text{N}_6\text{F}_4 = 809.1761$); R_f : 0.32 (95% DCM, 5% MeOH).

 $[Ir(dfppy)_2(L^6)]PF_6$ (**32**)

This compound was made following the general procedure for complexes containing bidentate ligands using $[\text{Ir}(\text{dfppy})_2\mu\text{-Cl}]_2$ (27 mg, 23 μmol), ligand **L**⁶ (13 mg, 49 μmol , 2.2 equiv.), MeOH (2.4 ml) and DCM (4 ml). Recrystallization from (i) MeCN twice and (ii) acetone and hexane twice yielded the title compound as a yellow solid (19 mg, 43%); m.p. 335°C; ¹H NMR (*d*₆-acetone, 600 MHz): δ 8.74 (m, 1H, H^{10r12}), 8.67 (d, 1H, *J* = 4, H²⁸), 8.52 (d, 1H, *J* = 8, H^{4or15}), 8.48 (m, 1H, H^{10r12}), 8.45 (s, 1H, H³¹), 8.34 (m, 2H, H^{23,34}), 8.25 (d, 1H, *J* = 8, H^{4or15}), 8.19 (m, 1H, H^{3or14}), 8.02 (m, 1H, H^{3or14}), 7.95 (dd, 1H, *J* = 6, 1, H²⁵), 7.57 (dd, 1H, *J* = 6, 1, H³³), 7.34 (m, 2H, H^{2or13,24}), 7.24 (m, 2H, H^{2or13,27}), 6.75 (m, 2H, H^{8,19}), 5.77 (dd, 1H, *J* = 9, 2, H^{10or21}), 5.69 (dd, 1H, *J* = 9, 2, H^{10or21}); ¹³C NMR (*d*₆-acetone, 151 MHz): δ 164.6 (m, C^{5or16}), 164.3 (m, C^{9,20}), 164.2 (d, *J* = 7, C^{5or16}), 162.9 (m, C^{7or18}), 161.8 (m, C^{7or18}), 155.0 (s, C³⁴), 154.4 (d, *J* = 7, C^{6or17}), 151.9 (s, C^{1or12}), 151.8 (s, C^{1or12}), 151.0 (d, *J* = 7, C^{6or17}), 150.7 (s, C²⁹), 147.8 (s, C²⁵), 146.0 (s, C³⁰), 142.5 (d, *J* = 35, C³²), 141.3 (s, C^{3or14}), 141.1 (s, C^{3or14}), 134.2 (s, C²³), 130.2 (s, C²⁸), 129.3 (m, C^{11or22}), 129.0 (dd, *J* = 5, 3, C^{11or22}), 126.9 (s, C²⁶), 125.3 (d, *J* = 20, C^{4or15}), 125.2 (s, C^{2or13}), 125.0 (s, C^{2or13}), 124.5 (d, *J* = 20, C^{4or15}), 123.2 (d, *J* = 274, C₃F₃), 122.1 (s, C²⁴), 119.5 (q, *J* = 3, C³³), 116.2 (m, C³¹), 115.2 (dd, *J* = 18, 3, C^{10or21}), 114.8 (dd, *J* = 18, 3, C^{10or21}), 109.7 (s, C²⁷), 100.2 (td, *J* = 27, 2, C^{8,19}); ¹⁹F NMR (*d*₆-acetone, 376 MHz): δ -65.8 (s), -72.6 (d, *J* = 708), -107.2 (dd, *J* = 118, 11), -109.4 (dd, *J* = 322, 11); ES⁺: 834.1201 [M-PF₆]⁺ (mass for IrC₃₅H₂₀N₅F₇ = 834.1213); R_f: 0.24 (silica, 95% DCM, 5% MeOH).

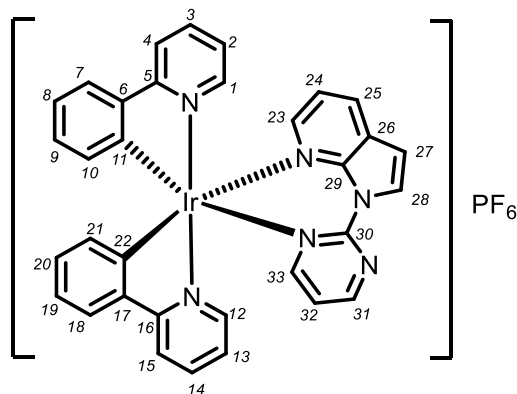
[Ir(ppy)₂(L⁸)]PF₆ (33)



This compound was made following the general procedure for complexes containing bidentate ligands using $[\text{Ir}(\text{ppy})_2\mu\text{-Cl}]_2$ (25 mg, 23 μmol), ligand **L**⁸ (12 mg, 49 μmol , 2.1 equiv.), MeOH (1.8 ml) and DCM (3 ml). Recrystallization from MeCN and ether yielded the title compound as an orange solid (31 mg, 74%); m.p. 336°C; ¹H NMR (*d*₆-acetone, 600 MHz): δ 8.69 (m, 1H, H^{10r12}), 8.66 (m, 1H, H^{10r12}), 8.35 (m, 1H, H^{4or15}), 8.27 (m, 2H, H^{23,32}), 8.23 (d, 1H, *J* = 4, H²⁸), 8.00 (m, 5H, H^{3or14,4or15,7or18,35,38}), 7.83 (m, 4H, H^{3or14,25,34,37}), 7.66 (m, 1H, H^{7or18}), 7.64 (d, 1H, *J* = 7, H²⁴), 7.16 (m, 3H, H^{2or13,27,33}), 7.04 (m, 2H, H^{2or13,8or19}), 6.95 (td, 1H, *J* = 8, 1, H^{8or19}), 6.88 (dtd, 2H, *J* = 13, 8, 1, H^{9,20}), 6.35 (m, 1H, H^{10or21}), 6.22 (m, 1H, H^{10or21}); ¹³C NMR (*d*₆-acetone, 151 MHz): δ 168.3 (s, C^{5or16}), 167.8 (s, C^{5or16}), 151.6 (s, C^{1or12}), 151.4 (s, C^{1or12}), 149.3 (s, C^{6or17}), 149.2 (s, C³¹), 148.9 (s, C³⁰), 148.1 (s, C²⁵), 146.3 (s, C^{6or17}), 145.5 (s, C^{11or22}), 145.2 (s, C^{11or22}), 142.7 (s, C³⁷), 140.1 (s, C²⁹), 139.8 (s, C^{3or14}), 139.6 (s, C^{3or14}), 134.5 (s, C²⁸), 133.6 (s, C³⁵), 133.1 (s, C^{10or21}), 133.0 (s, C³²), 132.5 (s, C^{10or21}), 131.4 (s, C^{9or20}),

131.2 (s, C^{9or20}), 130.1 (s, C³⁴), 128.3 (s, C³⁸), 127.9 (s, C²³), 126.4 (s, C^{7or18}), 125.7 (s, C^{7or18}), 124.9 (s, C³⁶), 124.6 (s, C^{2or13}), 124.2 (s, C^{2or13}), 123.9 (s, C²⁶), 123.8 (s, C^{8or19}), 123.7 (s, C^{8or19}), 122.7 (s, C²⁴), 121.3 (s, C^{4or15}), 120.9 (s, C³³), 120.3 (s, C^{4or15}), 105.9 (s, C²⁷); ¹⁹F NMR (*d*₆-acetone, 376 MHz): δ -72.4 (m); ES⁺: 744.1875 [M-PF₆]⁺ (mass for IrC₃₈H₂₇N₅ = 744.1872); R_f: 0.57 (silica, 90% DCM, 10% MeOH).

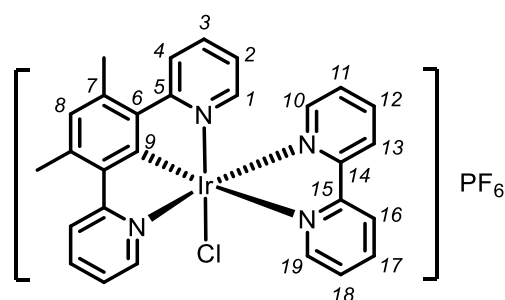
[Ir(ppy)₂(L¹⁰)]PF₆ (34**)**



This compound was made following the general procedure for complexes containing bidentate ligands using [Ir(ppy)₂μ-Cl]₂ (0.20 g, 0.19 mmol), ligand L¹⁰ (92 mg, 0.47 mmol, 2.5 equiv.), MeOH (6 ml) and DCM (10 ml). Column chromatography (silica, DCM : Et₃N 1%) and recrystallization from MeCN and ether yielded the title compound as a yellow solid (25 mg, 8%); m.p. 304°C; ¹H NMR (*d*₆-acetone, 600 MHz): δ 9.01 (dd, 1H, *J* = 5, 2, H³³), 8.78 (d, 1H, *J* = 4, H²⁸), 8.61 (m, 1H, H^{1or12}), 8.40 (dd, 1H, *J* = 6, 2, H³¹), 8.31 (dd, 1H, *J* = 8, 1, H²³), 8.29 (m, 1H, H^{4or15}), 8.22 (m, 1H, H^{4or15}), 8.15 (m, 1H, H^{1or12}), 8.03 (ddd, 1H, *J* = 8, 7, 2, H^{3or14}), 7.98 (ddd, 1H, *J* = 8, 7, 2, H^{3or14}), 7.89 (m, 1H, H^{7or18}), 7.84 (dd, 1H, *J* = 8, 1, H^{7or18}), 7.77 (dd, 1H, *J* = 6, 1, H²⁵), 7.31 (dd, 1H, *J* = 6, 5, H³²), 7.26 (dd, 1H, *J* = 8, 6, H²⁴), 7.21 (dtd, 2H, *J* = 7, 6, 2, H^{2,13}), 7.13 (d, 1H, *J* = 4, H²⁷), 7.02 (m, 2H, H^{8,19}), 6.89 (tdd, 2H, *J* = 8, 4, 1, H^{9,20}), 6.27 (m, 1H, H^{10or21}), 6.20 (m, 1H, H^{10or21}); ¹³C NMR (*d*₆-acetone, 151 MHz): δ 168.6 (s, C^{5or16}), 168.3 (s, C^{5or16}), 162.1 (s, C³¹), 161.4 (s, C³³), 153.4 (s, C³⁰), 151.1 (s, C^{1or12}), 150.9 (s, C^{1or12}), 150.2 (s, C^{6or17}), 147.6 (s, C^{6or17}), 147.2 (s, C²⁵), 145.4 (s, C^{11or22}), 145.2 (s, C²⁹), 145.1 (s, C^{11or22}), 140.1 (s, C^{3or14}), 140.0 (s, C^{3or14}), 133.4 (s, C²³), 132.9 (s, C^{10or21}), 132.4 (s, C^{10or21}), 131.6 (s, C^{9or20}), 131.5 (s, C^{9or20}), 130.2 (s, C²⁸), 128.2 (s, C²⁶), 126.3 (s, C^{7or18}), 126.0 (s, C^{7or18}), 124.7 (s, C^{2or13}), 124.6 (s, C^{2or13}), 124.0 (s, C^{8or19}), 123.9 (s, C^{8or19}), 121.7 (s, C²⁴), 121.4 (s, C^{4or15}), 121.1 (s, C^{4or15}), 120.4 (s, C³²), 108.7 (s, C²⁷); ¹⁹F NMR (*d*₆-acetone, 376 MHz): δ -72.7 (d, *J* = 707); ES⁺: 695.1678 [M-PF₆]⁺ (mass for IrC₃₃H₂₄N₆ = 695.1668); R_f: 0.35 (90% DCM, 10% MeOH).

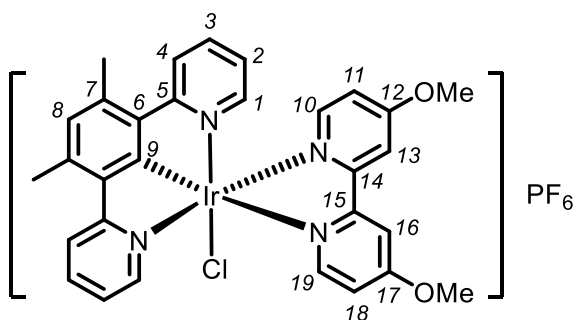
7.4.6 Synthesis of Chapter 3 complexes

$[Ir(L^{15})(bpy)Cl]PF_6$ (**35**)



This compound was made following the general procedure for complexes containing tridentate ligands using $[Ir(L^{15})Cl(\mu-Cl)]_2$ (50 mg, 48 μ mol), 2,2'-bipyridine (17 mg, 0.11 mmol, 2.2 equiv.), AgOTf (54 mg, 0.21 mmol) and toluene (4 ml). Column chromatography (silica, DCM : MeOH 0-2%) followed by recrystallization twice from MeCN and ether yielded the title compound as a yellow solid (39 mg, 52%); m.p. 389°C; ^1H NMR (d_6 -acetone, 600 MHz): δ 9.98 (m, 1H, H^{10or19}), 8.97 (d, 1H, $J = 8$, H^{13or16}), 8.70 (m, 1H, H^{13or16}), 8.64 (td, 1H, $J = 8$, 2, H^{12or17}), 8.33 (td, 3H, $J = 8$, 2, $H^{4,11or18}$), 8.00 (td, 1H, $J = 8$, 2, H^{12or17}), 7.93 (dd, $J = 2H$, 8, 1, H^3), 7.82 (dd, 2H, $J = 6$, 1, H^1), 7.65 (m, 1H, H^{10or19}), 7.32 (ddd, 1H, $J = 8$, 6, 2, H^{11or18}), 7.16 (m, 3H, $H^{2,8}$), 2.92 (s, 6H, CH_3); ^{13}C NMR (d_6 -acetone, 151 MHz): δ 170.2 (s, C^5), 159.2 (s, C^{14or15}), 156.6 (s, C^{14or15}), 154.5 (s, C^{10or19}), 153.0 (s, C^1), 150.1 (s, C^{10or19}), 142.1 (s, C^9), 141.4 (s, C^{12or17}), 140.4 (s, C^3), 140.2 (s, C^{12or17}), 139.6 (s, C^6), 138.6 (s, C^7), 132.7 (s, C^8), 130.1 (s, C^{11or18}), 129.1 (s, C^{11or18}), 125.8 (s, C^{13or16}), 125.7 (s, C^{13or16}), 124.9 (s, C^4), 124.1 (s, C^2), 22.7 (s, CH_3); ^{19}F NMR (d_6 -acetone, 376 MHz): δ -72.7 (d, $J = 707$); ES $^+$: 641.1234 $[M-PF_6]^+$ (mass for $C_{28}H_{23}N_4IrCl = 641.1217$); R_f : 0.23 (98% DCM, 2% MeOH).

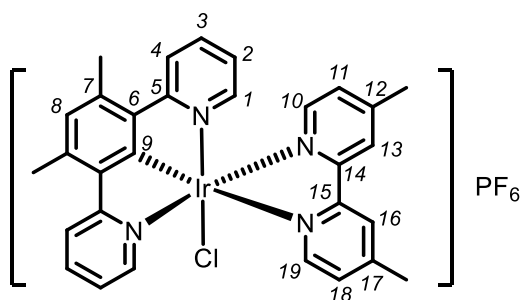
$[Ir(L^{15})(dmobpy)Cl]PF_6$ (**36**)



This compound was made following the general procedure for complexes containing tridentate ligands using $[Ir(L^{15})Cl(\mu-Cl)]_2$ (50 mg, 48 μ mol), 4,4'-dimethoxy-2,2'-bipyridine (23 mg, 0.11 mmol, 2.2 equiv.), AgOTf (54 mg, 0.21 mmol) and toluene (4 ml). Column chromatography (silica, MeCN : H₂O : sat. aq. KNO₃ 98 : 1 : 1) followed by recrystallization from MeCN and ether yielded the title compound as a yellow solid (30 mg, 37%); m.p. > 400°C; ^1H NMR (d_6 -acetone, 600 MHz): δ 9.72 (d, 1H, $J = 7$, H^{10or19}), 8.48 (d, 1H, $J = 3$, H^{13or16}), 8.32 (d, 2H, $J = 8$, H^4), 8.22 (d, 1H, $J = 3$, H^{13or16}), 7.93 (ddd, 2H, $J = 8$, 7, 2, H^3), 7.87 (m, 3H, $H^{1,11or18}$), 7.29 (d, 1H, $J = 7$, H^{10or19}), 7.19 (ddd, 2H, $J = 7$, 6, 2, H^2), 7.13 (s, 1H, H^8), 6.87 (dd, 1H, $J = 7$, 3, H^{11or18}), 4.28 (s, 3H, OCH_3), 3.95 (s, 3H, OCH_3), 2.91 (s, 6H, CH_3).

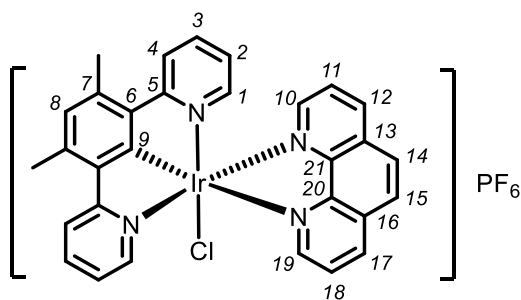
CH_3); ^{13}C NMR (d_6 -acetone, 151 MHz): δ 170.4 (s, C^5), 169.8 (s, $\text{C}^{12\text{or}17}$), 168.7 (s, $\text{C}^{12\text{or}17}$), 159.9 (s, $\text{C}^{14\text{or}15}$), 157.9 (s, $\text{C}^{14\text{or}15}$), 154.7 (s, $\text{C}^{10\text{or}19}$), 152.9 (s, C^1), 151.0 (s, $\text{C}^{10\text{or}19}$), 142.4 (s, C^9), 140.2 (s, C^3), 139.5 (s, C^6), 138.7 (s, C^7), 132.4 (s, C^8), 124.7 (s, C^4), 124.0 (s, C^2), 115.3 (s, $\text{C}^{11\text{or}18}$), 114.5 (s, $\text{C}^{11\text{or}18}$), 112.6 (s, $\text{C}^{13\text{or}16}$), 112.3 (s, $\text{C}^{13\text{or}16}$), 57.7 (s, OCH_3), 57.5 (s, OCH_3), 22.6 (s, CH_3); ^{19}F NMR (d_6 -acetone, 376 MHz): δ -72.7 (d, $J = 707$); ES^+ : 701.1451 $[\text{M-PF}_6]^+$ (mass for $\text{C}_{30}\text{H}_{27}\text{N}_4\text{IrO}_2\text{Cl} = 701.1429$); R_f : 0.27 (MeCN : H_2O : sat. aq. KNO_3 98 : 1 : 1).

$[\text{Ir}(\text{L}^{15})(\text{dmbpy})\text{Cl}]\text{PF}_6$ (37**)**



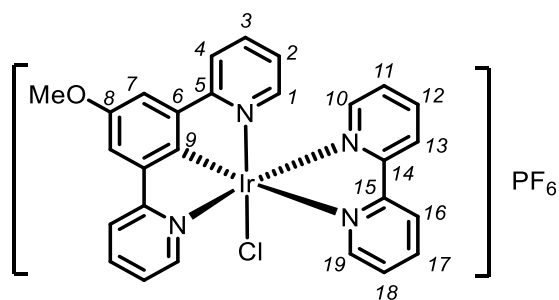
This compound was made following the general procedure for complexes containing tridentate ligands using $[\text{Ir}(\text{L}^{15})\text{Cl}(\mu\text{-Cl})_2]$ (50 mg, 48 μmol), 4,4'-dimethyl-2,2'-bipyridine (20 mg, 0.11 mmol, 2.2 equiv.), AgOTf (54 mg, 0.21 mmol) and toluene (4 ml). Column chromatography (silica, DCM : MeOH 0-2%) followed by recrystallization from MeCN yielded the title compound as a yellow solid (39 mg, 50%); m.p. > 400°C; ^1H NMR (d_6 -acetone, 700 MHz): δ 9.77 (m, 1H, $\text{H}^{10\text{or}19}$), 8.82 (m, 1H, $\text{H}^{13\text{or}16}$), 8.56 (m, 1H, $\text{H}^{13\text{or}16}$), 8.32 (m, 2H, H^4), 8.15 (m, 1H, $\text{H}^{11\text{or}18}$), 7.93 (m, 2H, H^3), 7.81 (m, 2H, H^1), 7.40 (d, 1H, $J = 6$, $\text{H}^{10\text{or}19}$), 7.16 (ddd, 2H, $J = 7, 6, 1$, H^2), 7.14 (s, 1H, H^8), 7.13 (m, 1H, $\text{H}^{11\text{or}18}$), 2.91 (s, 6H, $^7\text{-CH}_3$), 2.84 (s, 3H, $^{12\text{or}17}\text{-CH}_3$), 2.46 (s, 3H, $^{12\text{or}17}\text{-CH}_3$); ^{13}C NMR (d_6 -acetone, 176 MHz): δ 170.3 (s, C^5), 153.6 (s, $\text{C}^{12\text{or}17}$), 158.6 (s, $\text{C}^{14\text{or}15}$), 156.2 (s, $\text{C}^{14\text{or}15}$), 153.4 (s, $\text{C}^{10\text{or}19}$), 152.9 (m, $\text{C}^{1,12\text{or}17}$), 149.4 (s, $\text{C}^{10\text{or}19}$), 142.1 (s, C^9), 140.3 (s, C^3), 139.6 (s, C^7), 138.6 (s, C^6), 132.6 (s, C^8), 130.6 (s, $\text{C}^{11\text{or}18}$), 129.7 (s, $\text{C}^{11\text{or}18}$), 126.4 (s, $\text{C}^{13\text{or}16}$), 126.3 (s, $\text{C}^{13\text{or}16}$), 124.9 (s, C^4), 124.1 (s, C^2), 22.7 (s, $^7\text{-CH}_3$), 21.9 (s, $^{12\text{or}17}\text{-CH}_3$), 21.1 (s, $^{12\text{or}17}\text{-CH}_3$); ^{19}F NMR (d_6 -acetone, 376 MHz): δ -72.6 (d, $J = 707$); ES^+ : 669.1535 $[\text{M-PF}_6]^+$ (mass for $\text{C}_{30}\text{H}_{27}\text{N}_4\text{IrCl} = 669.1530$); R_f : 0.23 (98% DCM, 2% MeOH).

$[\text{Ir}(\text{L}^{15})(\text{phen})\text{Cl}]\text{PF}_6$ (38**)**

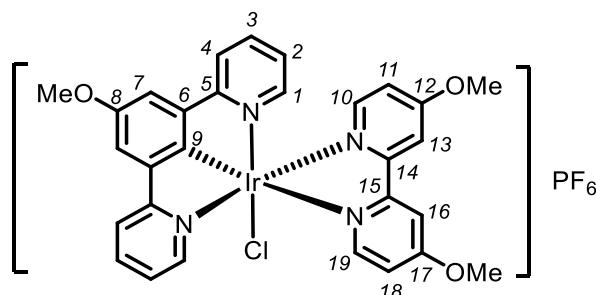


This compound was made following the general procedure for complexes containing tridentate ligands using $[\text{Ir}(\text{L}^{15})\text{Cl}(\mu\text{-Cl})]_2$ (50 mg, 48 μmol), 1,10-phenanthroline (19 mg, 0.11 mmol, 2.2 equiv.), AgOTf (54 mg, 0.21 mmol) and toluene (4 ml). Column chromatography (silica, DCM : MeOH 0-2% and silica, MeCN : H_2O : sat. aq. KNO_3 98 : 1 : 1) followed by recrystallization from MeCN yielded the title compound as a yellow solid (29 mg, 37%); m.p. > 400°C; ^1H NMR (d_6 -acetone, 600 MHz): δ 10.22 (dd, 1H, $J = 5, 1$, $\text{H}^{10\text{or}19}$), 9.23 (dd, 1H, $J = 8, 1$, $\text{H}^{12\text{or}17}$), 8.68 (dd, 1H, $J = 8, 5$, $\text{H}^{11\text{or}18}$), 8.59 (dd, 1H, $J = 8, 1$, $\text{H}^{12\text{or}17}$), 8.54 (d, 1H, $J = 9$, $\text{H}^{14\text{or}15}$), 8.32 (dd, 3H, $J = 9, 4$, $\text{H}^{4,14\text{or}15}$), 7.95 (dd, 1H, $J = 6, 1$, $\text{H}^{10\text{or}19}$), 7.87 (ddd, 2H, $J = 8, 7, 1$, H^3), 7.74 (dd, 2H, $J = 6, 1$, H^1), 7.66 (dd, 1H, $J = 8, 6$, $\text{H}^{11\text{or}18}$), 7.20 (s, 1H, H^8), 7.01 (ddd, 2H, $J = 7, 6, 1$, H^2), 2.95 (s, 6H, CH_3); ^{13}C NMR (d_6 -acetone, 151 MHz): δ 170.1 (s, C^5), 155.1 (s, $\text{C}^{10\text{or}19}$), 153.3 (s, C^1), 151.1 (s, $\text{C}^{10\text{or}19}$), 142.4 (s, C^9), 140.3 (s, $\text{C}^{12\text{or}17}$), 140.3 (s, C^3), 140.3 (s, $\text{C}^{20\text{or}21}$), 139.6 (s, C^6), 139.5 (s, $\text{C}^{12\text{or}17}$), 139.5 (s, $\text{C}^{20\text{or}21}$), 138.7 (s, C^7), 132.8 (s, C^8), 132.8 (s, $\text{C}^{13\text{or}16}$), 132.5 (s, $\text{C}^{13\text{or}16}$), 129.7 (s, $\text{C}^{14\text{or}15}$), 129.1 (s, $\text{C}^{14\text{or}15}$), 128.5 (s, $\text{C}^{11\text{or}18}$), 127.3 (s, $\text{C}^{11\text{or}18}$), 124.8 (s, C^4), 124.0 (s, C^2), 22.7 (s, CH_3); ^{19}F NMR (d_6 -acetone, 376 MHz): δ -72.7 (m); ES $^+$: 655.1232 $[\text{M-PF}_6]^+$ (mass for $\text{C}_{30}\text{H}_{23}\text{N}_4\text{IrCl}$ = 655.1217); R $_f$: 0.14 (98% DCM, 2% MeOH).

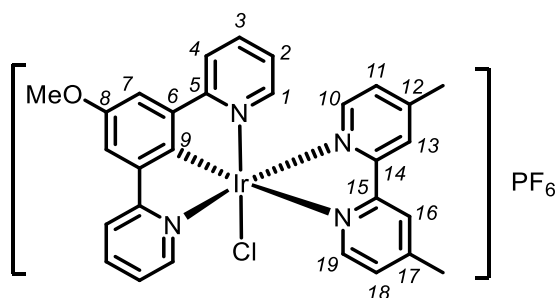
$[\text{Ir}(\text{L}^{16})(\text{bpy})\text{Cl}]\text{PF}_6$ (39**)**



This compound was made following the general procedure for complexes containing tridentate ligands using $[\text{Ir}(\text{L}^{16})\text{Cl}(\mu\text{-Cl})]_2$ (50 mg, 48 μmol), 2,2'-bipyridine (17 mg, 0.11 mmol, 2.2 equiv.), AgOTf (54 mg, 0.21 mmol) and toluene (4 ml). Column chromatography (silica, DCM : MeOH 0-2%) followed by recrystallization from MeCN and ether yielded the title compound as a yellow solid (30 mg, 40%); m.p. 389°C; ^1H NMR (d_6 -acetone, 700 MHz): δ 10.00 (m, 1H, $\text{H}^{10\text{or}19}$), 8.98 (d, 1H, $J = 8$, $\text{H}^{13\text{or}16}$), 8.71 (m, 1H, $\text{H}^{13\text{or}16}$), 8.63 (m, 1H, $\text{H}^{12\text{or}17}$), 8.33 (m, 3H, $\text{H}^{4,11\text{or}18}$), 8.00 (dd, 1H, $J = 8, 2$, $\text{H}^{12\text{or}17}$), 7.96 (ddd, 2H, $J = 8, 7, 2$, H^3), 7.87 (s, 2H, H^7), 7.81 (ddd, 2H, $J = 6, 2, 1$, H^1), 7.70 (ddd, 1H, $J = 6, 2, 1$, $\text{H}^{10\text{or}19}$), 7.37 (m, 1H, $\text{H}^{11\text{or}18}$), 7.19 (ddd, 2H, $J = 7, 6, 2$, H^2), 4.07 (s, 3H, OCH_3); ^{13}C NMR (d_6 -acetone, 176 MHz): δ 169.7 (s, C^5), 161.4 (s, C^6), 159.6 (s, $\text{C}^{14\text{or}15}$), 159.4 (s, C^8), 156.9 (s, $\text{C}^{14\text{or}15}$), 154.4 (s, $\text{C}^{10\text{or}19}$), 153.5 (s, C^1), 150.4 (s, $\text{C}^{10\text{or}19}$), 142.7 (s, C^9), 141.3 (s, $\text{C}^{12\text{or}17}$), 140.7 (s, C^3), 140.3 (s, $\text{C}^{12\text{or}17}$), 130.0 (s, $\text{C}^{11\text{or}18}$), 129.1 (s, $\text{C}^{11\text{or}18}$), 125.8 (s, $\text{C}^{13\text{or}16}$), 125.7 (s, $\text{C}^{13\text{or}16}$), 125.1 (s, C^2), 122.2 (s, C^4), 113.6 (s, C^7), 56.8 (s, OCH_3); ^{19}F NMR (d_6 -acetone, 376 MHz): δ -72.7 (d, $J = 707$); ES $^+$: 643.1005 $[\text{M-PF}_6]^+$ (mass for $\text{C}_{27}\text{H}_{21}\text{N}_4\text{IrClO}$ = 643.1010); R $_f$: 0.23 (98% DCM, 2% MeOH).

$[Ir(L^{16})(dmobpy)Cl]PF_6$ (40)

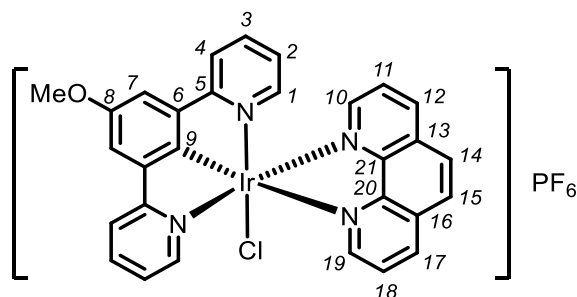
This compound was made following the general procedure for complexes containing tridentate ligands using $[Ir(L^{16})Cl(\mu-Cl)]_2$ (50 mg, 48 μ mol), 4,4'-dimethoxy-2,2'-bipyridine (23 mg, 0.11 mmol, 2.2 equiv.), AgOTf (54 mg, 0.21 mmol) and toluene (4 ml). Column chromatography (silica, DCM : MeOH 0-2%) followed by recrystallization from MeCN and ether yielded the title compound as an orange solid (23 mg, 28%); m.p. 356°C; ^1H NMR (d_6 -acetone, 600 MHz): δ 9.75 (d, 1H, $J = 6$, H^{10or19}), 8.48 (d, 1H, $J = 3$, H^{13or16}), 8.31 (dd, 2H, $J = 8, 1$, H^4), 8.23 (d, 1H, $J = 3$, H^{13or16}), 7.95 (m, 2H, H^3), 7.86 (m, 3H, $H^{1,11or18}$), 7.84 (s, 2H, H^7), 7.33 (d, 1H, $J = 7$, H^{10or19}), 7.21 (ddd, 2H, $J = 7, 6, 1$, H^2), 6.90 (dd, 1H, $J = 7, 3$, H^{11or18}), 4.28 (s, 3H, $^{12or17}-OCH_3$), 4.06 (s, 3H, $^8-OCH_3$), 3.96 (s, 3H, $^{12or17}-OCH_3$); ^{13}C NMR (d_6 -acetone, 151 MHz): δ 168.7 (s, C^5), 168.6 (s, C^{12or17}), 167.6 (s, C^{12or17}), 161.1 (s, C^6), 159.1 (s, C^{14or15}), 158.0 (s, C^8), 157.1 (s, C^{14or15}), 153.4 (s, C^{10or19}), 152.3 (s, C^1), 150.2 (s, C^{10or19}), 141.6 (s, C^9), 139.4 (s, C^3), 123.8 (s, C^2), 120.9 (s, C^4), 114.1 (s, C^{11or18}), 113.5 (s, C^{11or18}), 112.4 (s, C^7), 111.5 (s, C^{13or16}), 111.1 (s, C^{13or16}), 56.6 (s, $^{12or17}-OCH_3$), 56.4 (s, $^{12or17}-OCH_3$), 55.7 (s, $^8-OCH_3$); ^{19}F NMR (d_6 -acetone, 376 MHz): δ -72.6 (d, $J = 707$); ES $^+$: 703.1224 $[M-PF_6]^+$ (mass for $C_{29}H_{25}N_4IrO_3Cl = 703.1221$); R $_f$: 0.22 (98% DCM, 2% MeOH).

 $[Ir(L^{16})(dmobpy)Cl]PF_6$ (41)

This compound was made following the general procedure for complexes containing tridentate ligands using $[Ir(L^{16})Cl(\mu-Cl)]_2$ (50 mg, 48 μ mol), 4,4'-dimethyl-2,2'-bipyridine (20 mg, 0.11 mmol, 2.2 equiv.), AgOTf (54 mg, 0.21 mmol) and toluene (4 ml). Column chromatography (silica, DCM : MeOH 0-2%) followed by recrystallization twice from MeCN and ether yielded the title compound as a yellow solid (18 mg, 23%); m.p. > 400°C; ^1H NMR (d_6 -acetone, 700 MHz): δ 9.79 (d, 1H, $J = 6$, H^{10or19}), 8.82 (m, 1H, H^{13or16}), 8.57 (m, 1H, H^{13or16}), 8.32 (m, 2H, H^4), 8.14 (m, 1H, H^{11or18}), 7.95 (m, 2H, H^3), 7.85 (s, 2H, H^7), 7.80 (ddd, 2H, $J = 6, 2, 1$, H^1), 7.45 (d, 1H, $J = 6$, H^{10or19}), 7.19 (ddd, 2H, $J = 7, 6$,

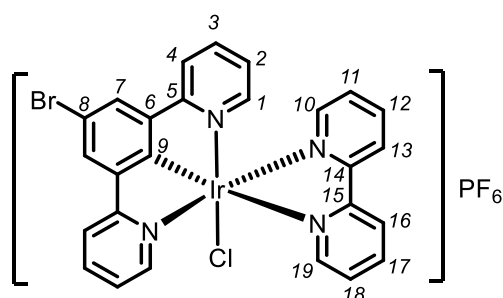
2, H²), 7.17 (m, 1H, H^{11or18}), 4.06 (s, 3H, OCH₃), 2.84 (s, 3H, CH₃), 2.47 (s, 3H, CH₃); ¹³C NMR (*d*₆-acetone, 176 MHz): δ 169.7 (s, C⁵), 161.8 (s, C⁶), 159.2 (s, C⁸), 158.9 (s, C^{14or15}), 156.4 (s, C^{14or15}), 153.5 (s, C^{12or17}), 153.3 (s, C¹), 153.3 (s, C^{10or19}), 152.9 (s, C^{12or17}), 149.6 (s, C^{10or19}), 142.7 (s, C⁹), 140.6 (s, C³), 130.4 (s, C^{11or18}), 129.6 (s, C^{11or18}), 126.3 (s, C^{13or16}), 126.2 (s, C^{13or16}), 125.0 (s, C²), 122.1 (s, C⁴), 113.5 (s, C⁷), 56.8 (s, OCH₃), 21.8 (s, CH₃), 21.1 (s, CH₃); ¹⁹F NMR (*d*₆-acetone, 376 MHz): δ -72.6 (d, *J* = 707); ES⁺: 671.1331 [M-PF₆]⁺ (mass for C₂₉H₂₅N₄IrClO = 671.1323); R_f: 0.23 (98% DCM, 2% MeOH).

[Ir(L¹⁶)(phen)Cl]PF₆ (42**)**



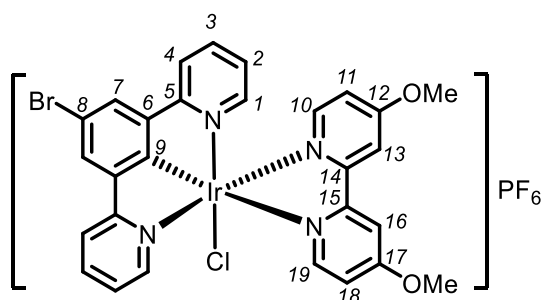
This compound was made following the general procedure for complexes containing tridentate ligands using [Ir(L¹⁶Cl(μ-Cl))₂] (50 mg, 48 μmol), 1,10-phenanthroline (19 mg, 0.11 mmol, 2.2 equiv.), AgOTf (54 mg, 0.21 mmol) and toluene (4 ml). Column chromatography (silica, DCM : MeOH 0-2% and silica, MeCN : H₂O : sat. aq. KNO₃ 98 : 1 : 1) followed by recrystallization from MeCN yielded the title compound as an orange solid 19 mg, 24%); m.p. 396°C; ¹H NMR (*d*₆-acetone, 700 MHz): δ 10.24 (dd, 1H, *J* = 5, 1, H^{10or19}), 9.22 (m, 1H, H^{12or17}), 8.67 (dd, 1H, *J* = 8, 5, H^{11or18}), 8.59 (d, 1H, *J* = 8, H^{12or17}), 8.54 (d, 1H, *J* = 9, H^{14or15}), 8.32 (m, 3H, H^{4,14or15}), 7.99 (m, 1H, H^{10or19}), 7.90 (m, 4H, H^{3,7}), 7.72 (m, 2H, H¹), 7.70 (dd, 1H, *J* = 8, 6, H^{11or18}), 7.04 (td, 2H, *J* = 7, 6, 1, H²), 4.10 (s, 3H, OCH₃); ¹³C NMR (*d*₆-acetone, 176 MHz): δ 169.6 (s, C⁵), 160.5 (s, C⁶), 159.4 (s, C⁸), 155.0 (s, C^{10or19}), 153.7 (s, C¹), 151.4 (s, C^{10or19}), 149.9 (s, C^{13or16}), 147.8 (s, C^{13or16}), 142.8 (s, C⁹), 140.6 (s, C³), 140.3 (s, C^{12or17}), 139.6 (s, C^{12or17}), 132.8 (s, C^{20or21}), 132.4 (s, C^{20or21}), 129.7 (s, C^{14or15}), 129.1 (s, C^{14or15}), 128.4 (s, C^{11or18}), 127.2 (s, C^{11or18}), 124.9 (s, C²), 122.0 (s, C⁴), 113.5 (s, C⁷), 56.8 (s, OCH₃); ¹⁹F NMR (*d*₆-acetone, 376 MHz): δ -72.6 (d, *J* = 707); ES⁺: 667.1013 [M-PF₆]⁺ (mass for C₂₉H₂₁N₄IrClO = 667.1010); R_f: 0.22 (98% DCM, 2% MeOH).

[Ir(L¹⁷)(bpy)Cl]PF₆ (43**)**



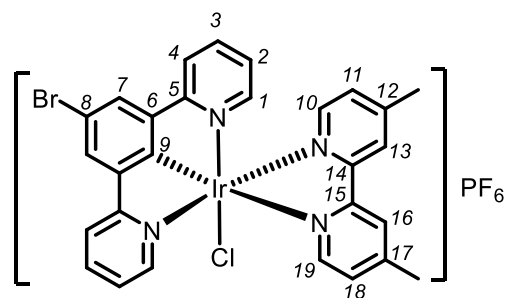
This compound was made following the general procedure for complexes containing tridentate ligands using $[\text{Ir}(\text{L}^{17})\text{Cl}(\mu\text{-Cl})_2]$ (0.10 g, 87 μmol), 2,2'-bipyridine (30 mg, 0.19 mmol, 2.2 equiv.), AgOTf (0.10 g, 0.38 mmol) and toluene (7 ml). Column chromatography (silica, DCM : MeOH 0-2%) followed by recrystallization from acetone and hexane yielded the title compound as a yellow solid (89 mg, 61%); m.p. 388°C; ^1H NMR (d_6 -acetone, 700 MHz): δ 9.98 (dd, 1H, $J = 5, 1$, $\text{H}^{10\text{or}19}$), 8.97 (dt, 1H, $J = 8, 1$, $\text{H}^{13\text{or}16}$), 8.71 (dd, 1H, $J = 8, 1$, $\text{H}^{13\text{or}16}$), 8.64 (td, 1H, $J = 8, 1$, $\text{H}^{12\text{or}17}$), 8.40 (dd, 2H, $J = 8, 1$, H^4), 8.33 (ddd, 1H, $J = 8, 5, 1$, $\text{H}^{11\text{or}18}$), 8.31 (s, 2H, H^7), 8.00 (m, 4H, $\text{H}^{3,12\text{or}17}$), 7.86 (dd, 2H, $J = 6, 1$, H^1), 7.72 (dd, 1H, $J = 6, 1$, $\text{H}^{10\text{or}19}$), 7.35 (ddd, 1H, $J = 7, 6, 1$, $\text{H}^{11\text{or}18}$), 7.25 (ddd, 2H, $J = 7, 6, 1$, H^2); ^{13}C NMR (d_6 -acetone, 176 MHz): δ 169.9 (s, C^9), 168.2 (s, C^5), 159.2 (s, $\text{C}^{14\text{or}15}$), 156.7 (s, $\text{C}^{14\text{or}15}$), 154.5 (s, $\text{C}^{10\text{or}19}$), 153.6 (s, C^1), 150.3 (s, $\text{C}^{12\text{or}17}$), 144.6 (s, C^6), 141.5 (s, $\text{C}^{10\text{or}19}$), 141.0 (s, C^3), 140.5 (s, $\text{C}^{12\text{or}17}$), 130.0 (s, $\text{C}^{11\text{or}18}$), 129.3 (s, C^7), 129.3 (s, $\text{C}^{11\text{or}18}$), 125.8 (s, $\text{C}^{13\text{or}16}$), 125.8 (s, $\text{C}^{13\text{or}16}$), 125.7 (s, C^2), 122.6 (s, C^4), 117.5 (s, C^8); ^{19}F NMR (d_6 -acetone, 376 MHz): δ -72.4 (m); ES^+ : 691.0034 $[\text{M-PF}_6]^+$ (mass for $\text{C}_{26}\text{H}_{18}\text{N}_4\text{IrClBr}$ = 691.0009); R_f : 0.23 (98% DCM, 2% MeOH).

$[\text{Ir}(\text{L}^{17})(\text{dmobpy})\text{Cl}]\text{PF}_6$ (44**)**



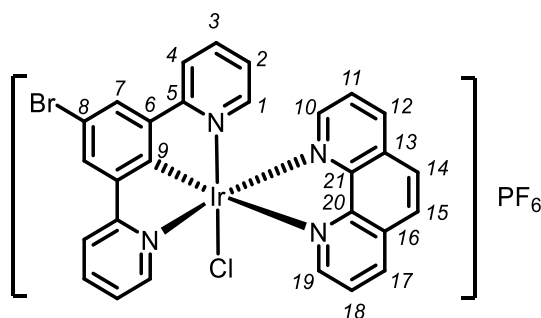
This compound was made following the general procedure for complexes containing tridentate ligands using $[\text{Ir}(\text{L}^{17})\text{Cl}(\mu\text{-Cl})_2]$ (0.10 g, 87 μmol), 4,4'-dimethoxy-2,2'-bipyridine (42 mg, 0.19 mmol, 2.2 equiv.), AgOTf (0.10 g, 0.38 mmol) and toluene (7 ml). Column chromatography (silica, DCM : MeOH 0-2%) followed by recrystallization twice from acetone and hexane yielded the title compound as a yellow solid (0.13 g, 81%); m.p. > 400°C; ^1H NMR (d_6 -acetone, 700 MHz): δ 9.73 (d, 1H, $J = 6$, $\text{H}^{10\text{or}19}$), 8.49 (d, 1H, $J = 3$, $\text{H}^{13\text{or}16}$), 8.39 (ddd, 2H, $J = 8, 2, 1$, H^4), 8.29 (s, 2H, H^7), 8.24 (d, 1H, $J = 3$, $\text{H}^{13\text{or}16}$), 7.99 (ddd, 2H, $J = 8, 7, 2$, H^3), 7.91 (ddd, 2H, $J = 6, 2, 1$, H^1), 7.86 (dd, 1H, $J = 6, 3$, $\text{H}^{11\text{or}18}$), 7.36 (d, 1H, $J = 7$, $\text{H}^{10\text{or}19}$), 7.28 (ddd, 2H, $J = 7, 6, 2$, H^2), 6.88 (dd, 1H, $J = 7, 3$, $\text{H}^{11\text{or}18}$), 4.28 (s, 3H, OCH_3), 3.96 (s, 3H, OCH_3); ^{13}C NMR (d_6 -acetone, 176 MHz): δ 170.8 (s, C^9), 169.8 (s, $\text{C}^{12\text{or}17}$), 168.9 (s, $\text{C}^{12\text{or}17}$), 168.4 (s, C^5), 160.0 (s, $\text{C}^{14\text{or}15}$), 158.0 (s, $\text{C}^{14\text{or}15}$), 154.6 (s, $\text{C}^{10\text{or}19}$), 153.4 (s, C^1), 151.2 (s, $\text{C}^{10\text{or}19}$), 144.7 (s, C^6), 140.8 (s, C^3), 129.2 (s, C^7), 125.6 (s, C^2), 122.4 (s, C^4), 117.1 (s, C^8), 115.3 (s, $\text{C}^{11\text{or}18}$), 114.7 (s, $\text{C}^{11\text{or}18}$), 112.6 (s, $\text{C}^{13\text{or}16}$), 112.3 (s, $\text{C}^{13\text{or}16}$), 57.7 (s, OCH_3), 57.5 (s, OCH_3); ^{19}F NMR (d_6 -acetone, 376 MHz): δ -72.6 (dd, $J = 707, 2$); ES^+ : 751.0251 $[\text{M-PF}_6]^+$ (mass for $\text{C}_{28}\text{H}_{22}\text{N}_4\text{O}_2\text{IrClBr}$ = 751.0221); R_f : 0.30 (98% DCM, 2% MeOH).

[Ir(L¹⁷)(dmobpy)Cl]PF₆ (45)



This compound was made following the general procedure for complexes containing tridentate ligands using $[\text{Ir}(\text{L}^{17})\text{Cl}(\mu\text{-Cl})]_2$ (0.10 g, 87 μmol), 4,4'-dimethyl-2,2'-bipyridine (36 mg, 0.19 mmol, 2.2 equiv.), AgOTf (0.10 g, 0.38 mmol) and toluene (7 ml). Column chromatography (silica, DCM : MeOH 0-2%) followed by recrystallization twice from MeCN, hexane and ether yielded the title compound as a yellow solid (41 mg, 27%); m.p. 377°C; ^1H NMR (d_6 -acetone, 700 MHz): δ 9.78 (d, 1H, $J = 6$, $\text{H}^{10\text{or}19}$), 8.83 (m, 1H, $\text{H}^{13\text{or}16}$), 8.58 (d, 1H, $J = 2$, $\text{H}^{13\text{or}16}$), 8.40 (ddd, 2H, $J = 8, 2, 1$, H^4), 8.30 (s, 2H, H^7), 8.14 (ddd, 1H, $J = 6, 2, 1$, $\text{H}^{11\text{or}18}$), 8.00 (m, 2H, H^3), 7.85 (ddd, 2H, $J = 6, 2, 1$, H^1), 7.49 (d, 1H, $J = 6$, $\text{H}^{10\text{or}19}$), 7.26 (ddd, 2H, $J = 8, 6, 2$, H^2), 7.16 (ddd, 1H, $J = 6, 2, 1$, $\text{H}^{11\text{or}18}$); 2.85 (s, 3H, CH_3), 2.48 (s, 3H, CH_3); ^{13}C NMR (d_6 -acetone, 176 MHz): δ 170.4 (s, C^9), 168.3 (s, C^5), 158.6 (s, $\text{C}^{14\text{or}15}$), 156.3 (s, $\text{C}^{14\text{or}15}$), 153.8 (s, $\text{C}^{12\text{or}17}$), 153.4 (s, C^1), 153.4 (s, $\text{C}^{10\text{or}19}$), 153.3 (s, $\text{C}^{12\text{or}17}$), 149.6 (s, $\text{C}^{10\text{or}19}$), 144.6 (s, C^6), 140.9 (s, C^3), 130.5 (s, $\text{C}^{11\text{or}18}$), 129.8 (s, $\text{C}^{11\text{or}18}$), 129.3 (s, C^7), 126.5 (s, $\text{C}^{13\text{or}16}$), 126.3 (s, $\text{C}^{13\text{or}16}$), 125.6 (s, C^2), 122.5 (s, C^4), 117.3 (s, C^8), 21.8 (s, CH_3), 21.1 (s, CH_3); ^{19}F NMR (d_6 -acetone, 376 MHz): δ -72.6 (dd, $J = 708, 2$) ES⁺: 719.0336 $[\text{M-PF}_6]^+$ (mass for $\text{C}_{28}\text{H}_{22}\text{N}_4\text{IrClBr} = 719.0322$); R_f: 0.27 (98% DCM, 2% MeOH).

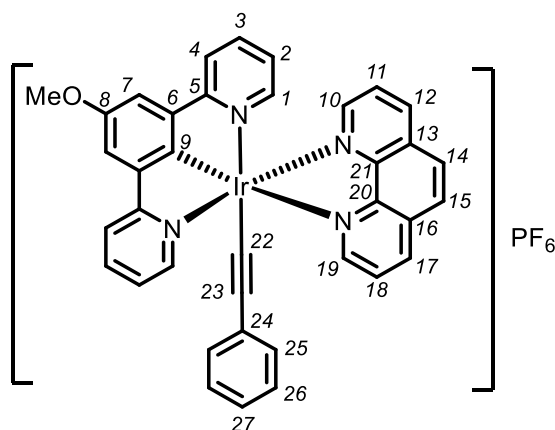
[Ir(L¹⁷)(phen)Cl]PF₆ (46)



This compound was made following the general procedure for complexes containing tridentate ligands using $[\text{Ir}(\text{L}^{17})\text{Cl}(\mu\text{-Cl})]_2$ (0.100 g, 87 μmol), 1,10-phenanthroline (35 mg, 0.19 mmol, 2.2 equiv.), AOTf (99 mg, 0.38 mmol) and toluene (7 ml). Column chromatography (silica, DCM : MeOH 0-2%) followed by recrystallization from MeCN, hexane and ether yielded the title compound as a yellow solid (29 mg, 39%); m.p. 354°C; ^1H NMR (d_6 -acetone, 700 MHz): δ 10.23 (dd, 1H, $J = 5, 1$, $\text{H}^{10\text{or}19}$), 9.24 (dd, 1H, $J = 8, 1$, $\text{H}^{12\text{or}17}$), 8.68 (dd, 1H, $J = 9, 5$, $\text{H}^{11\text{or}18}$), 8.61 (m, 1H, $\text{H}^{12\text{or}17}$), 8.55 (d, 1H, $J = 9$, $\text{H}^{14\text{or}15}$), 8.40 (ddd, 2H, $J = 8, 2, 1$, H^4), 8.35 (s, 2H, H^7), 8.32 (d, 1H, $J = 9$, $\text{H}^{14\text{or}15}$), 8.04 (dd, 1H, $J = 5, 1$, $\text{H}^{10\text{or}19}$), 7.95 (ddd, 2H, $J = 8, 7, 2$, H^3), 7.77 (ddd, 2H, $J = 6, 2, 1$, H^1), 7.69 (dd, 1H, $J = 8, 6$,

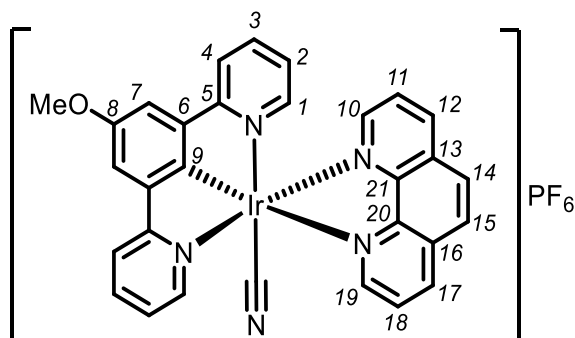
H^{11or18}), 7.10 (ddd, 2H, $J = 7, 6, 1, H^2$); ^{13}C NMR (d_6 -acetone, 176 MHz): δ 169.1 (s, C^9), 168.1 (s, C^5), 155.1 (s, C^{10or19}), 153.8 (s, C^1), 151.3 (s, C^{10or19}), 149.6 (s, C^{20or21}), 147.6 (s, C^{20or21}), 144.7 (s, C^6), 140.8 (s, C^3), 140.4 (s, C^{12or17}), 139.8 (s, C^{12or17}), 132.8 (s, C^{13or16}), 132.4 (s, C^{13or16}), 129.7 (s, C^{14or15}), 129.3 (s, C^7), 129.1 (s, C^{14or15}), 128.4 (s, C^{11or18}), 127.3 (s, C^{11or18}), 125.5 (s, C^2), 122.5 (s, C^4), 117.5 (s, C^8); ^{19}F NMR (d_6 -acetone, 376 MHz): δ -72.6 (dd, $J = 708, 1$); ES^+ : 715.0017 $[M-PF_6]^+$ (mass for $C_{28}H_{18}N_4IrClBr$ = 715.0009); R_f : 0.18 (98% DCM, 2% MeOH).

$[Ir(L^{16})(phen)CCPh]PF_6$ (47**)**



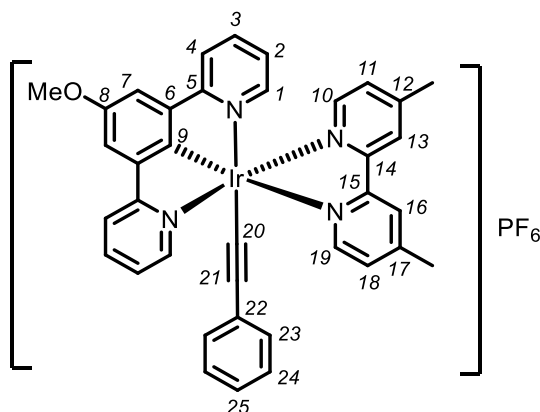
This compound was made following the general metathesis procedure using complex **42** (24 mg, 29 μ mol), CuI (1 mg, 5.2 mmol), phenylacetylene (64 μ L, 0.59 mmol) and diisopropylamine (82 μ L, 0.59 mmol) in DMF. Column chromatography (silica, DCM : MeOH : 0-1.2%) yielded the title compound as a yellow solid (4 mg, 15%); m.p. 329°C; ^1H NMR (d_6 -acetone, 700 MHz): δ 10.47 (dd, 1H, $J = 5, 1, H^{10or19}$), 9.19 (dd, 1H, $J = 8, 1, H^{12or17}$), 8.67 (dd, 1H, $J = 8, 1, H^{12or17}$), 8.64 (dd, 1H, $J = 8, 5, H^{11or18}$), 8.51 (d, 1H, $J = 9, H^{14or15}$), 8.31 (m, 3H, $H^{4,14or15}$), 7.92 (m, 3H, $H^{3,10or19}$), 7.89 (s, 2H, H^7), 7.83 (ddd, 2H, $J = 6, 2, 1, H^1$), 7.77 (dd, 1H, $J = 8, 5, H^{11or18}$), 7.07 (m, 2H, H^{26}), 7.02 (ddd, 2H, $J = 7, 6, 2, H^2$), 7.00 (m, 3H, $H^{25,27}$), 4.09 (s, 3H, OCH_3); ^{13}C NMR (d_6 -acetone, 176 MHz): δ 169.5 (s, C^5), 161.2 (s, C^6), 158.9 (s, C^8), 153.5 (s, C^1), 153.1 (s, C^{10or19}), 152.6 (s, C^{10or19}), 148.8 (s, C^{20or21}), 148.1 (s, C^{20or21}), 142.5 (s, C^9), 140.1 (s, C^3), 139.9 (s, C^{12or17}), 139.6 (s, C^{12or17}), 132.8 (s, C^{13or16}), 132.7 (s, C^{25}), 132.3 (s, C^{13or16}), 129.5 (s, C^{14or15}), 129.4 (s, C^{22}), 129.2 (s, C^{14or15}), 128.7 (s, C^{26}), 128.6 (s, C^{11or18}), 127.2 (s, C^{11or18}), 126.0 (s, C^{27}), 124.8 (s, C^2), 122.0 (s, C^4), 113.4 (s, C^7), 99.8 (s, C^{24}), 78.7 (s, C^{23}), 56.7 (s, OCH_3); ^{19}F NMR (d_6 -acetone, 376 MHz): δ -72.6 (d, $J = 707$); ES^+ : 733.1732 $[M-PF_6]^+$ (mass for $C_{37}H_{26}N_4IrO$ = 733.1713); R_f : 0.28 (DCM : MeOH 98 : 2).

[Ir(L¹⁶)(phen)CCN]PF₆ (48)



This compound was made following the general metathesis procedure using complex **42** (25 mg, 31 μ mol), AgCN (21 mg, 0.15 mmol) and DMF. Column chromatography (silica, DCM : MeOH : 0-4%) followed by recrystallization from acetone and hexane yielded the title compound as a yellow solid (6 mg, 24%); m.p. 374°C; ¹H NMR (*d*₆-acetone, 700 MHz): δ 10.20 (dd, 1H, *J* = 5, 1, H^{10or19}), 9.25 (dd, 1H, *J* = 8, 1, H^{12or17}), 8.72 (dd, 1H, *J* = 8, 1, H^{12or17}), 8.65 (dd, 1H, *J* = 8, 5, H^{11or18}), 8.54 (d, 1H, *J* = 9, H^{14or15}), 8.36 (m, 3H, H^{4,14or15}), 7.98 (ddd, 2H, *J* = 8, 7, 2, H³), 7.92 (s, 2H, H⁷), 7.90 (dd, 1H, *J* = 5, 1, H^{10or19}), 7.83 (ddd, 2H, *J* = 6, 2, 1, H¹), 7.79 (dd, 1H, *J* = 8, 5, H^{11or18}), 7.07 (ddd, 2H, *J* = 7, 6, 2, H²), 4.09 (s, 3H, OCH₃); ¹³C NMR (*d*₆-acetone, 176 MHz): δ 169.3 (s, C⁵), 159.6 (s, C⁸), 157.5 (s, C⁶), 154.0 (s, C^{10or19}), 153.9 (s, C¹), 152.4 (s, C^{10or19}), 148.9 (s, C^{13or16}), 147.6 (s, C^{13or16}), 142.6 (s, C⁹), 140.9 (s, C³), 140.4 (s, C^{12or17}), 140.3 (s, C^{12or17}), 133.1 (s, C^{20or21}), 132.5 (s, C^{20or21}), 129.7 (s, C^{14or15}), 129.3 (s, C^{14or15}), 129.1 (s, C^{11or18}), 127.3 (s, C^{11or18}), 125.3 (s, C²), 122.4 (s, C⁴), 113.9 (s, C⁷), 56.8 (s, OCH₃); ¹⁹F NMR (*d*₆-acetone, 376 MHz): δ -72.7 (d, *J* = 707); ES⁺: 658.1379 [M-PF₆]⁺ (mass for C₃₀H₂₁N₅IrO = 658.1352); R_f: 0.20 (DCM : MeOH 98 : 2).

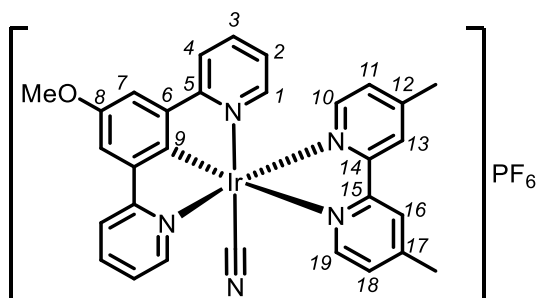
[Ir(L¹⁶)(dmobpy)CCPh]PF₆ (49)



This compound was made following the general metathesis procedure using complex **41** (24 mg, 29 μ mol), CuI (1 mg, 5.2 mmol), phenylacetylene (64 μ L, 0.59 mmol) and diisopropylamine (82 μ L, 0.59 mmol) in DMF. Column chromatography (silica, DCM : MeOH 0-1.6%) and recrystallization from acetone and hexane yielded the title compound as an orange solid (9 mg, 35%); m.p. 320°C; ¹H NMR (*d*₆-acetone, 700 MHz): 10.01 (d, 1H, *J* = 5, H^{10or19}), 8.82 (m, 1H, H^{13or16}), 8.59 (m, 1H, H^{13or16}), 8.30 (m, 2H, H⁴), 8.09 (m, 1H, H^{11or18}), 7.97 (td, 2H, *J* = 8, 2, H³), 7.91 (m, 2H, H¹), 7.83 (s, 2H, H⁷), 7.34 (d,

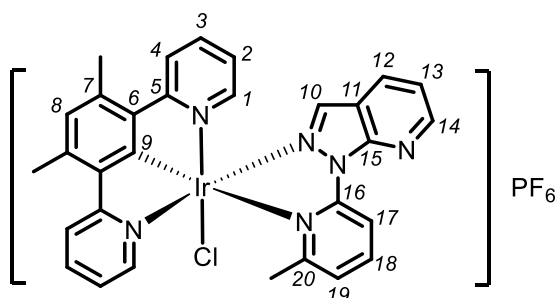
^1H , $J = 6$, $\text{H}^{10\text{or}19}$), 7.22 (m, 1H, $\text{H}^{11\text{or}18}$), 7.17 (ddd, 2H, $J = 8, 6, 2$, H^2), 7.04 (m, 2H, H^{24}), 6.96 (m, 1H, H^{25}), 6.91 (dt, 2H, $J = 8, 2$, H^{23}), 4.05 (s, 3H, OCH_3), 2.82 (s, 3H, CH_3), 2.46 (s, 3H, CH_3); ^{13}C NMR (d_6 -acetone, 176 MHz): δ 169.5 (s, C^5), 162.2 (s, C^6), 158.7 (s, C^8), 157.6 (s, $\text{C}^{14\text{or}15}$), 156.7 (s, $\text{C}^{14\text{or}15}$), 153.1 (s, C^1), 153.0 (s, $\text{C}^{12\text{or}17}$), 152.9 (s, $\text{C}^{12\text{or}17}$), 151.7 (s, $\text{C}^{10\text{or}19}$), 150.9 (s, $\text{C}^{10\text{or}19}$), 142.3 (s, C^9), 140.1 (s, C^3), 132.6 (s, C^{23}), 130.5 (s, $\text{C}^{11\text{or}18}$), 129.5 (s, $\text{C}^{11\text{or}18}$), 129.4 (s, C^{20}), 128.6 (s, C^{24}), 126.3 (s, $\text{C}^{13\text{or}16}$), 126.0 (s, $\text{C}^{13\text{or}16}$), 125.9 (s, C^{25}), 124.9 (s, C^2), 122.0 (s, C^4), 113.4 (s, C^7), 99.6 (s, C^{22}), 79.6 (s, C^{21}), 56.7 (s, OCH_3), 21.8 (s, CH_3), 21.3 (s, CH_3); ^{19}F NMR (d_6 -acetone, 376 MHz): δ -72.6 (d, $J = 708$); ES^+ : 737.2034 $[\text{M-PF}_6]^+$ (mass for $\text{C}_{37}\text{H}_{30}\text{N}_4\text{IrO} = 737.2026$); R_f : 0.25 (DCM : MeOH 98 : 2).

$[\text{Ir}(\text{L}^{16})(\text{dmbpy})\text{CCN}]\text{PF}_6$ (50**)**



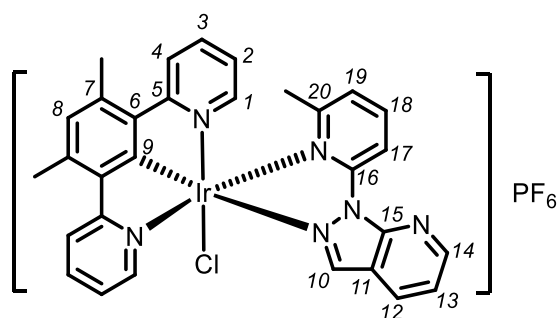
This compound was made following the general metathesis procedure using complex **41** (38 mg, 46 μmol), AgCN (31 mg, 0.23 mmol) and DMF. Column chromatography (alumina, DCM : MeOH : 0-1.5%) followed by recrystallization from MeCN, ether and hexane yielded the title compound as a yellow solid (9 mg, 24%); m.p. 372°C; ^1H NMR (d_3 -MeCN, 600 MHz): δ 9.70 (d, 1H, $J = 6$, $\text{H}^{10\text{or}19}$), 8.60 (m, 1H, $\text{H}^{13\text{or}16}$), 8.35 (m, 1H, $\text{H}^{13\text{or}16}$), 8.25 (dd, 2H, $J = 8, 1$, H^1), 8.03 (m, 3H, $\text{H}^{2,11\text{or}18}$), 7.82 (s, 2H, H^7), 7.79 (dd, 2H, $J = 6, 1$, H^4), 7.21 (m, 3H, $\text{H}^{3,10\text{or}19}$), 7.13 (dd, 1H, $J = 6, 2$, $\text{H}^{11\text{or}18}$), 4.14 (s, 3H, OCH_3), 2.86 (s, 3H, CH_3), 2.50 (s, 3H, CH_3); ^{13}C NMR (d_3 -MeCN, 151 MHz): δ 168.9 (s, C^5), 159.2 (s, C^8), 157.6 (s, C^6), 157.4 (s, $\text{C}^{14\text{or}15}$), 155.9 (s, $\text{C}^{14\text{or}15}$), 153.7 (s, $\text{C}^{12\text{or}17}$), 153.7 (s, $\text{C}^{12\text{or}17}$), 153.3 (s, C^4), 152.3 (s, $\text{C}^{10\text{or}19}$), 150.2 (s, $\text{C}^{10\text{or}19}$), 142.2 (s, C^9), 140.9 (s, C^2), 130.9 (s, $\text{C}^{11\text{or}18}$), 129.3 (s, $\text{C}^{11\text{or}18}$), 126.5 (s, $\text{C}^{13\text{or}16}$), 126.0 (s, $\text{C}^{13\text{or}16}$), 125.3 (s, C^3), 122.3 (s, C^1), 113.8 (s, C^7), 57.0 (s, OCH_3), 21.7 (s, CH_3), 21.2 (s, CH_3); ^{19}F NMR (d_3 -MeCN, 376 MHz): δ -72.6 (m); ES^+ : 662.1677 $[\text{M-PF}_6]^+$ (mass for $\text{C}_{30}\text{H}_{25}\text{N}_5\text{IrO} = 662.1665$); R_f : 0.15 (DCM : MeOH 99 : 1).

$[\text{Ir}(\text{L}^{15})(\text{L}^{12})\text{Cl}]\text{PF}_6$ (51**)**

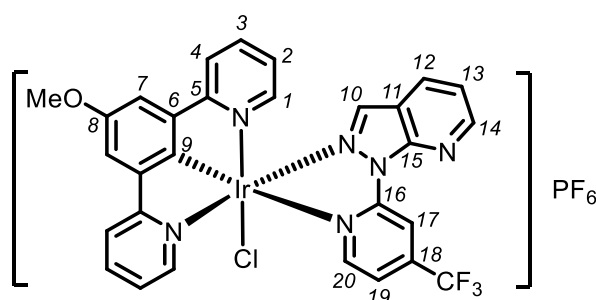


This compound was made following the general procedure for complexes containing tridentate ligands using $[\text{Ir}(\text{L}^{15})\text{Cl}(\mu\text{-Cl})]_2$ (50 mg, 48 μmol), ligand L^{12} (22 mg, 0.11 mmol, 2.2 equiv.), AgOTf (54 mg, 0.21 mmol) and toluene (4 ml). Column chromatography (alumina, DCM : MeOH 0-1.25%) followed by recrystallization from MeCN, ether and hexane and ether yielded the title compound as a yellow solid (49 mg, 42%); m.p. 322°C; ^1H NMR (d_6 -acetone, 700 MHz): δ 9.63 (m, 1H, H^{19}), 8.78 (dd, 1H, $J = 5, 2$, H^{14}), 8.54 (t, 1H, $J = 8$, H^{18}), 8.33 (d, 2H, $J = 8$, H^4), 8.27 (m, 2H, H^1), 8.21 (dd, 1H, $J = 8, 2$, H^{12}), 7.96 (ddd, 2H, $J = 8, 7, 2$, H^3), 7.91 (m, 1H, H^{17}), 7.56 (s, 1H, H^{10}), 7.48 (dd, 1H, $J = 8, 5$, H^{13}), 7.23 (ddd, 2H, $J = 7, 6, 1$, H^2), 7.18 (s, 1H, H^8), 3.49 (s, 3H, $^{20}\text{-CH}_3$), 2.91 (s, 6H, $^7\text{-CH}_3$); ^{13}C NMR (d_6 -acetone, 176 MHz): δ 169.2 (s, C^5), 167.4 (s, C^9), 164.8 (s, C^{20}), 154.4 (s, C^1), 153.1 (s, C^{14}), 152.1 (s, C^{11}), 151.3 (s, C^{16}), 143.1 (s, C^{18}), 141.9 (s, C^{10}), 140.6 (s, C^3), 139.5 (s, C^7), 138.6 (s, C^6), 133.1 (s, C^8), 133.1 (s, C^{12}), 126.4 (s, C^{17}), 125.1 (s, C^4), 124.5 (s, C^2), 121.8 (s, C^{13}), 119.0 (s, C^{15}), 112.4 (s, C^{19}), 28.0 (s, $^{20}\text{-CH}_3$), 22.6 (s, $^7\text{-CH}_3$); ^{19}F NMR (d_6 -acetone, 376 MHz): δ -72.6 (d, $J = 707$); ES^+ : 695.1464 $[\text{M-PF}_6]^+$ (mass for $\text{C}_{30}\text{H}_{25}\text{N}_6\text{IrCl} = 695.1435$); R_f : 0.39 (DCM : MeOH 98 : 2).

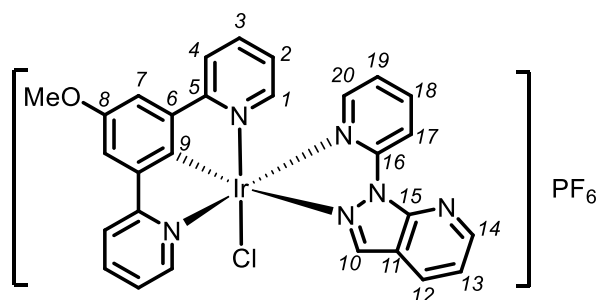
$[\text{Ir}(\text{L}^{15})(\text{L}^{12})\text{Cl}]\text{PF}_6$ (52**)**



This compound was made following the general procedure for complexes containing tridentate ligands using $[\text{Ir}(\text{L}^{15})\text{Cl}(\mu\text{-Cl})]_2$ (50 mg, 48 μmol), ligand L^{12} (22 mg, 0.11 mmol, 2.2 equiv.), AgOTf (54 mg, 0.21 mmol) and toluene (4 ml). Column chromatography (alumina, DCM : MeOH 0-1.25%) followed by HPLC (MeCN : H_2O 1 : 1) yielded the title compound as a yellow solid (2 mg, 2%) m.p. 335°C; ^1H NMR (d_6 -acetone, 600 MHz): δ 9.66 (m, 1H, H^{17}), 9.48 (s, 1H, H^{10}), 9.10 (m, 1H, H^{14}), 8.92 (m, 1H, H^{12}), 8.38 (m, 2H, H^4), 8.14 (m, 2H, H^1), 8.10 (m, 1H, H^{18}), 7.97 (m, 2H, H^3), 7.88 (m, 1H, H^{13}), 7.13 (m, 2H, H^2), 7.10 (m, 2H, $\text{H}^{8,19}$), 2.90 (s, 6H, $^7\text{-CH}_3$), 1.86 (s, 3H, $^{20}\text{-CH}_3$); ^{13}C NMR (d_6 -acetone, 151 MHz): δ 170.5 (s, C^5), 165.0 (s, C^{20}), 158.2 (s, C^{17}), 153.8 (s, C^{16}), 153.3 (s, C^{11}), 152.9 (s, C^1), 152.7 (s, C^{14}), 142.3 (s, C^{18}), 140.0 (s, C^3), 139.3 (s, C^7), 139.0 (s, C^{10}), 134.1 (s, C^{12}), 132.5 (s, C^6), 132.0 (s, C^8), 125.0 (s, C^9), 124.5 (s, C^4), 124.4 (s, C^{19}), 123.5 (s, C^2), 122.0 (s, C^{13}), 121.3 (s, C^{15}), 27.4 (s, $^{20}\text{-CH}_3$), 22.3 (s, $^7\text{-CH}_3$); ^{19}F NMR (d_6 -acetone, 376 MHz): δ -72.6 (d, $J = 707$); ES^+ : 695.1440 $[\text{M-PF}_6]^+$ (mass for $\text{C}_{30}\text{H}_{25}\text{N}_6\text{IrCl} = 695.1435$); R_f : 0.39 (DCM : MeOH 98 : 2).

$[Ir(L^{16})(L^5)Cl]PF_6$ (53)

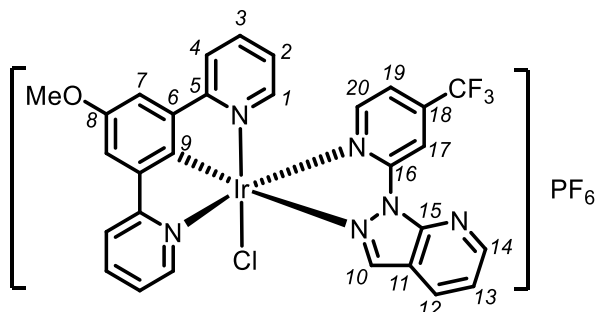
This compound was made following the general procedure for complexes containing tridentate ligands using $[Ir(L^{16})Cl(\mu-Cl)]_2$ (50 mg, 48 μ mol), ligand L^5 (31 mg, 0.12 mmol, 2.5 equiv.), AgOTf (54 mg, 0.21 mmol) and toluene (4 ml). Column chromatography (silica, DCM : MeOH : 0-2%) yielded the title compound as a yellow solid (14 mg, 16%); m.p. 343°C; ^1H NMR (d_6 -acetone, 700 MHz): δ 10.02 (d, 1H, J = 6, H^{20}), 9.91 (m, 1H, H^{17}), 8.88 (dd, 1H, J = 5, 2, H^{14}), 8.49 (dd, 1H, J = 6, 2, H^{19}), 8.35 (m, 2H, H^4), 8.29 (dd, 1H, J = 8, 2, H^{12}), 8.06 (m, 2H, H^1), 7.97 (m, 2H, H^3), 7.89 (s, 2H, H^7), 7.78 (s, 1H, H^{10}), 7.58 (dd, 1H, J = 8, 5, H^{13}), 7.18 (ddd, 2H, J = 7, 6, 1, H^2), 4.09 (s, 3H, OCH_3); ^{13}C NMR (d_6 -acetone, 176 MHz): δ 169.1 (s, C^5), 159.7 (s, C^8), 155.6 (s, C^6), 154.3 (s, C^1), 153.7 (s, C^{14}), 152.6 (s, C^{11}), 152.3 (s, C^{16}), 150.2 (s, C^{20}), 144.0 (s, C^{10}), 142.9 (s, C^9), 141.0 (s, C^3), 133.7 (s, C^{12}), 130.8 (m, C^{18}), 125.0 (s, C^2), 123.7 (d, J = 273, C^{13}), 122.2 (s, C^{13}), 122.1 (s, C^4), 121.3 (d, J = 4, C^{19}), 119.1 (s, C^{15}), 113.4 (s, C^7), 111.6 (m, C^{17}), 56.8 (s, OCH_3); ^{19}F NMR (d_6 -acetone, 376 MHz): δ -65.3 (s), -72.7 (d, J = 707); ES^+ : 751.0950 $[M-PF_6]^+$ (mass for $C_{29}H_{20}N_6IrOF_3Cl$ = 751.0945); R_f : 0.34 (DCM : MeOH 98 : 2).

 $[Ir(L^{16})(L^1)Cl]PF_6$ (54)

This compound was made following the general procedure for complexes containing tridentate ligands using $[Ir(L^{16})Cl(\mu-Cl)]_2$ (50 mg, 48 μ mol), ligand L^1 (23 mg, 0.12 mmol, 2.5 equiv.), AgOTf (54 mg, 0.21 mmol) and toluene (4 ml). Column chromatography (silica, hexane : EtOAc : 0-100% then DCM : MeOH 0-2%) followed by recrystallization twice from MeCN, ether and hexane yielded the title compound as a yellow solid (11 mg, 14%); m.p. 371°C; ^1H NMR (d_6 -acetone, 700 MHz): δ 9.48 (s, 1H, H^{10}), 9.47 (m, 1H, H^{20}), 9.07 (dd, 1H, J = 5, 2, H^{14}), 8.93 (m, 1H, H^{12}), 8.35 (m, 2H, H^4), 8.20 (dd, 2H, J = 6, 1, H^1), 8.13 (m, 1H, H^{19}), 7.98 (m, 2H, H^3), 7.88 (m, 3H, $H^{7,13}$), 7.48 (m, 1H, H^{17}), 7.20 (m, 1H, H^{18}), 7.18 (ddd, 2H, J = 7, 6, 1, H^2), 4.08 (s, 3H, OCH_3); ^{13}C NMR (d_6 -acetone, 176 MHz): δ 169.2 (s, C^5), 160.2 (s, C^6), 159.5 (s, C^8), 153.9 (s, C^1), 153.5 (s, C^{14}), 152.3 (s, C^{17}), 151.4 (s, $C^{11,16}$), 142.7 (s,

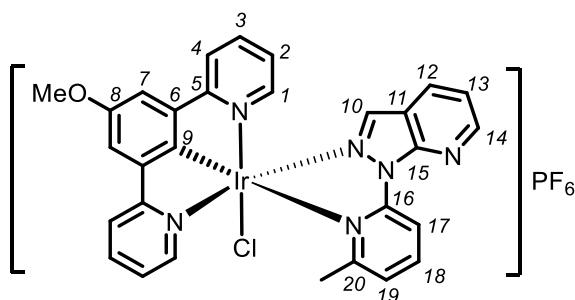
C⁹), 142.3 (s, C¹⁹), 140.9 (s, C³), 140.2 (s, C¹⁰), 134.7 (s, C¹²), 125.0 (s, C²), 124.5 (s, C¹⁸), 122.3 (s, C¹³), 122.1 (s, C⁴), 119.4 (s, C¹⁵), 115.2 (s, C²⁰), 113.5 (s, C⁷), 56.8 (s, OCH₃); ¹⁹F NMR (*d*₆-acetone, 376 MHz): δ -72.7 (dd, *J* = 707, 1); ES⁺: 683.1096 [M-PF₆]⁺ (mass for C₂₈H₂₁N₆IrClO = 683.1071); R_f: 0.36 (DCM : MeOH 98 : 2).

[Ir(L¹⁶)(L⁵)Cl]PF₆ (55**)**



This compound was made following the general procedure for complexes containing tridentate ligands using [Ir(L¹⁶)Cl(μ-Cl)]₂ (50 mg, 48 μmol), ligand L⁵ (31 mg, 0.12 mmol, 2.5 equiv.), AgOTf (54 mg, 0.21 mmol) and toluene (4 ml). Column chromatography (silica, DCM : MeOH : 0-2%) yielded the title compound as a yellow solid (11 mg, 13%) m.p. 350°C; ¹H NMR (*d*₆-acetone, 700 MHz): δ 9.72 (m, 1H, H¹⁷), 9.53 (s, 1H, H¹⁰), 9.12 (dd, 1H, *J* = 5, 2, H¹⁴), 8.97 (dd, 1H, *J* = 8, 2, H¹²), 8.35 (m, 2H, H⁴), 8.20 (m, 2H, H¹), 7.98 (td, 2H, *J* = 8, 2, H³), 7.93 (dd, 1H, *J* = 8, 5, H¹³), 7.88 (s, 2H, H⁷), 7.81 (d, 1H, *J* = 6, H²⁰), 7.48 (dd, 1H, *J* = 6, 2, H¹⁹), 7.18 (ddd, 2H, *J* = 8, 6, 2, H²), 4.08 (s, 3H, OCH₃); ¹³C NMR (*d*₆-acetone, 176 MHz): δ 169.1 (s, C⁵), 159.6 (s, C⁸), 158.9 (s, C⁶), 154.5 (s, C¹⁶), 154.4 (s, C²⁰), 154.0 (s, C¹), 153.8 (s, C¹⁴), 153.7 (s, C¹¹), 142.7 (s, C⁹), 141.4 (s, C¹⁰), 141.0 (s, C³), 135.1 (s, C¹²), 130.6 (m, C¹⁸), 125.1 (s, C²), 122.9 (m, C_{CF₃}), 122.7 (s, C¹³), 122.1 (s, C⁴), 120.4 (s, C¹⁵), 119.9 (d, *J* = 3, C¹⁹), 113.6 (s, C⁷), 111.3 (d, *J* = 4, C¹⁷), 56.8 (s, OCH₃); ¹⁹F NMR (*d*₆-acetone, 376 MHz): δ -65.9 (s), -72.7 (d, *J* = 707); ES⁺: 751.0958 [M-PF₆]⁺ (mass for C₂₉H₂₀N₆IrOF₃Cl = 751.0945); R_f: 0.34 (DCM : MeOH 98 : 2).

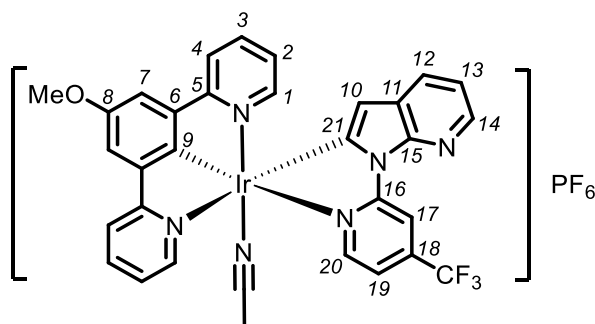
[Ir(L¹⁶)(L¹²)Cl]PF₆ (56**)**



This compound was made following the general procedure for complexes containing tridentate ligands using [Ir(L¹⁶)Cl(μ-Cl)]₂ (54 mg, 51 μmol), ligand L¹² (26 mg, 0.12 mmol, 2.4 equiv.), AgOTf (58 mg, 0.23 mmol) and toluene (4 ml). Column chromatography (alumina, DCM : MeOH : 0-1.5%) followed by recrystallization twice from MeCN, ether and hexane yielded the title compound as a yellow solid (19 mg, 22%); m.p. 365°C; ¹H NMR (*d*₆-acetone, 700 MHz): δ 9.63 (m, 1H, H¹⁷), 8.78 (dd,

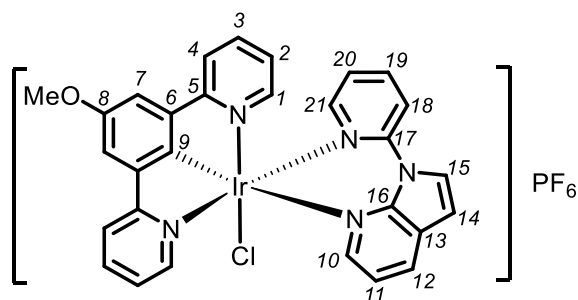
1H, $J = 5, 2$, H¹⁴), 8.54 (t, 1H, $J = 8$, H¹⁸), 8.33 (dd, 2H, $J = 8, 1$, H⁴), 8.24 (m, 3H, H^{1,12}), 7.98 (dd, 2H, $J = 8, 1$, H³), 7.90 (m, 1H, H¹⁹), 7.84 (s, 2H, H⁷), 7.60 (s, 1H, H¹⁰), 7.49 (dd, 1H, $J = 8, 5$, H¹³), 7.25 (ddd, 2H, $J = 7, 6, 1$, H²), 4.08 (s, 3H, OCH₃), 3.50 (s, 3H, CH₃); ¹³C NMR (*d*₆-acetone, 176 MHz): δ 168.5 (s, C⁵), 165.0 (s, C²⁰), 159.6 (s, C⁸), 154.8 (s, C¹), 154.0 (s, C¹⁴), 153.0 (s, C¹¹), 152.2 (s, C⁶), 151.4 (s, C¹⁶), 142.9 (s, C¹⁸), 142.5 (s, C⁹), 141.8 (s, C¹⁰), 140.9 (s, C³), 133.1 (s, C¹²), 126.2 (s, C¹⁹), 125.4 (s, C²), 122.3 (s, C⁴), 121.7 (s, C¹³), 119.0 (s, C¹⁵), 113.4 (s, C⁷), 112.3 (s, C¹⁷), 56.8 (s, OCH₃), 28.1 (s, CH₃); ¹⁹F NMR (*d*₆-acetone, 376 MHz): δ -72.6 (d, $J = 707$); ES⁺: 697.1257 [M-PF₆]⁺ (mass for C₂₉H₂₃N₆IrClO = 697.1228); R_f: 0.21 (DCM : MeOH 96 : 4).

[Ir(L¹⁶)(L⁶)MeCN]PF₆ (57)



This compound was made following the general procedure for complexes containing tridentate ligands using [Ir(L¹⁶)Cl(μ-Cl)]₂ (51 mg, 49 μmol), ligand L⁶ (32 mg, 0.12 mmol, 2.5 equiv.), AgOTf (55 mg, 0.21 mmol) and toluene (4 ml). Column chromatography (alumina, DCM : MeOH : 0-1%) followed by recrystallization from MeCN, ether and hexane yielded the title compound as a yellow solid (24 mg, 27%); m.p. 268°C; ¹H NMR (*d*₆-acetone, 700 MHz): δ 9.86 (m, 1H, H¹⁷), 9.74 (d, 1H, $J = 6$, H²⁰), 8.33 (m, 2H, H¹), 8.13 (m, 2H, H⁴), 8.02 (dd, 1H, $J = 5, 2$, H¹⁴), 8.00 (m, 2H, H²), 7.90 (dd, 1H, $J = 6, 2$, H¹⁹), 7.85 (s, 2H, H⁷), 7.40 (dd, 1H, $J = 8, 2$, H¹²), 7.17 (ddd, 2H, $J = 7, 6, 1$, H³), 6.98 (dd, 1H, $J = 8, 5$, H¹³), 4.84 (s, 1H, H¹⁰), 4.08 (s, 3H, OCH₃), 2.45 (s, 3H, CH₃CN); ¹³C NMR (*d*₆-acetone, 176 MHz): δ 169.5 (s, C⁵), 159.1 (s, C⁶), 158.9 (s, C⁸), 156.4 (s, C¹⁶), 154.0 (s, C⁴), 151.2 (s, C^{18,20}), 151.2 (s, C¹¹), 142.8 (s, C⁹), 140.5 (s, C¹⁴), 140.4 (s, C²), 135.3 (s, C²¹), 127.4 (s, C¹⁵), 126.2 (s, C¹²), 125.0 (s, C³), 124.0 (d, $J = 273$, CF₃), 122.1 (s, C¹), 121.6 (s, CH₃CN), 118.6 (s, C¹³), 116.8 (m, C¹⁹), 112.9 (s, C⁷), 111.0 (m, C¹⁷), 108.1 (m, C¹⁰), 56.7 (s, OCH₃), 3.4 (s, CH₃CN); ¹⁹F NMR (*d*₆-acetone, 376 MHz): δ -65.4 (s), -72.6 (m); ES⁺: 755.1509 [M-PF₆]⁺ (mass for C₃₂H₂₃N₆IrF₃O = 755.1491); R_f: 0.29 (DCM : MeOH 99 : 1).

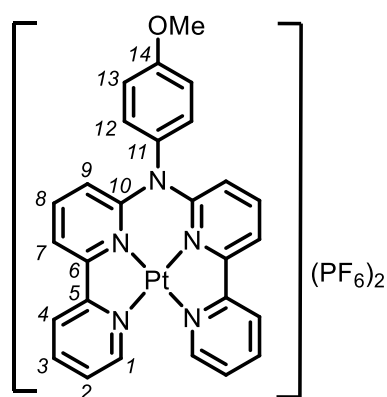
$[Ir(L^{16})(L^2)Cl]PF_6$ (58**)**



This compound was made following the general procedure for complexes containing tridentate ligands using $[Ir(L^{16})Cl(\mu-Cl)]_2$ (50 mg, 48 μ mol), ligand L^2 (24 mg, 0.12 mmol, 2.5 equiv.), AgOTf (54 mg, 0.21 mmol) and toluene (4 ml). Column chromatography (silica, DCM : MeOH : 0-2%) followed by recrystallization from (i) MeCN, ether and hexane and (ii) acetone and hexane yielded the title compound as an orange solid (39 mg, 95%); m.p. 354°C; ^1H NMR (d_6 -acetone, 700 MHz): δ 9.56 (dd, 1H, $J = 5, 1$, H^{10}), 8.67 (dd, 1H, $J = 8, 1$, H^{12}), 8.38 (d, 1H, $J = 4$, H^{15}), 8.36 (ddd, 2H, $J = 8, 2, 1$, H^4), 8.01 (ddd, 2H, $J = 8, 7, 2$, H^3), 7.94 (m, 1H, H^{19}), 7.90 (ddd, 2H, $J = 6, 2, 1$, H^1), 7.88 (dd, 1H, $J = 8, 5$, H^{11}), 7.82 (m, 3H, $H^{7,18}$), 7.79 (m, 1H, H^{21}), 7.40 (d, 1H, $J = 4$, H^{14}), 7.27 (ddd, 2H, $J = 7, 6, 2$, H^2), 6.96 (ddt, 1H, $J = 8, 6, 1$, H^{20}), 4.05 (s, 3H, OCH_3); ^{13}C NMR (d_6 -acetone, 176 MHz): δ 169.6 (s, C^5), 160.7 (s, C^6), 159.4 (s, C^8), 154.1 (s, C^{21}), 153.5 (s, C^1), 151.0 (s, C^{17}), 147.4 (s, C^{10}), 147.0 (s, C^{13}), 143.2 (s, C^9), 142.1 (s, C^{19}), 140.9 (s, C^3), 134.1 (s, C^{12}), 129.6 (s, C^{15}), 126.2 (s, C^{16}), 124.9 (s, C^2), 123.6 (s, C^{20}), 122.6 (s, C^4), 122.2 (s, C^{11}), 119.4 (s, C^{18}), 113.6 (s, C^7), 109.8 (s, C^{14}), 56.7 (s, OCH_3); ^{19}F NMR (d_6 -acetone, 376 MHz): δ -72.6 (d, $J = 707$); ES $^+$: 682.1132 $[M-PF_6]^+$ (mass for $C_{29}H_{22}N_5IrClO = 682.1119$); R $_f$: 0.37 (DCM : MeOH 98 : 2).

7.4.7 Synthesis of Chapter 4 complexes

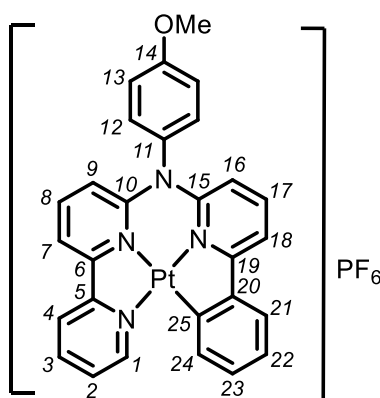
$[Pt(N^{\wedge}N^{\wedge}N^{\wedge}N)](PF_6)_2$ (59**)**



This complex was made following the modified procedure for the synthesis of platinum complexes using K_2PtCl_4 (0.10 g, 0.24 mmol), $N^{\wedge}N^{\wedge}N^{\wedge}N$ (0.13 g, 0.29 mmol, 1.2. equiv.), MeCN (6 ml) and H_2O (2 ml). Upon cooling to RT, the red solution was added dropwise to a saturated aqueous solution of KPF_6 and the resulting precipitate was washed with H_2O (3 x 10 ml), extracted into DCM (3 x 10 ml) and the solvent removed under reduced pressure to yield the title compound as a red solid (45 mg,

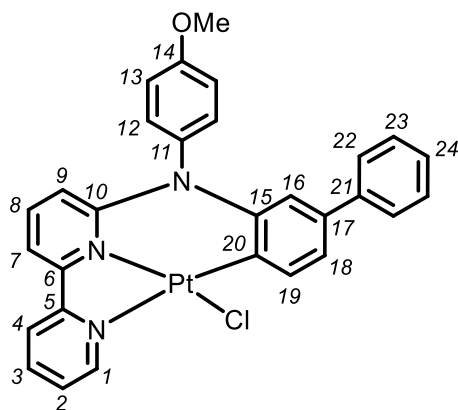
20%); m.p. 248°C; ^1H NMR (CDCl_3 , 600 MHz): δ 8.30 (m, 2H, H^1), 8.12 (dt, 2H, $J = 8, 2$, H^4), 8.05 (dd, 2H, $J = 8, 1$, H^7), 7.90 (t, 2H, $J = 8$, H^8), 7.74 (td, 2H, $J = 8, 2$, H^3), 7.37 (m, 2H, H^{12}), 7.33 (ddd, 2H, $J = 8, 5, 2$, H^2), 7.14 (d, 2H, $J = 8$, H^{13}), 6.85 (m, 2H, H^9), 3.91 (s, 3H, OCH_3); ^{13}C NMR (CDCl_3 , 176 MHz): δ 160.2 (s, C^{14}), 155.0 (s, C^{10}), 152.1 (s, C^5), 150.7 (s, C^6), 149.3 (s, C^1), 141.8 (s, C^8), 137.7 (s, C^3), 132.4 (s, C^{11}), 130.3 (s, C^{12}), 124.9 (s, C^2), 122.3 (s, C^4), 116.6 (s, C^{13}), 116.3 (s, C^7), 115.9 (s, C^9), 55.9 (s, OCH_3); ^{19}F NMR (CDCl_3 , 376 MHz): δ -73.5 (d, $J = 713$); ES^+ : 625.1371 $[\text{M}-2\text{PF}_6]^+$ (mass for $\text{C}_{27}\text{H}_{21}\text{N}_5\text{PtO}$ = 625.1373).

$[\text{Pt}(\text{N}^{\wedge}\text{N}^{\wedge}\text{N}^{\wedge}\text{C})]\text{PF}_6$ (**60**)



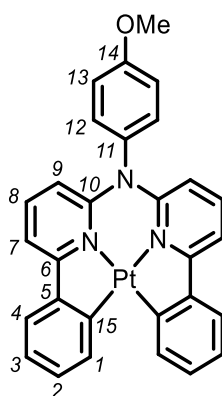
This complex was made following the general procedure for the synthesis of platinum complexes using K_2PtCl_4 (0.10 g, 0.24 mmol), $\text{N}^{\wedge}\text{N}^{\wedge}\text{N}^{\wedge}\text{CH}$ (0.12 g, 0.29 mmol, 1.2. equiv.) and glacial acetic acid (5 ml). Upon cooling to RT, the solvent was removed under reduced pressure and the residue re-dissolved in the minimum amount of MeCN. This solution was added dropwise to a saturated aqueous solution of KPF_6 and the resulting precipitate was washed with H_2O (3 x 10 ml). Purification by column chromatography (silica, DCM : MeOH 0-2%) followed by recrystallization from DMF and ether yielded the title compound as an orange solid (84 mg, 45%); m.p. 366°C; ^1H NMR (d_6 -DMSO, 600 MHz): δ 9.44 (d, 1H, $J = 7$, H^1), 8.79 (d, 1H, $J = 8$, H^4), 8.48 (m, 2H, $\text{H}^{3,7}$), 8.29 (t, 1H, $J = 9$, H^8), 8.06 (t, 1H, $J = 9$, H^{17}), 7.96 (m, 3H, $\text{H}^{2,18,21}$), 7.67 (d, 1H, $J = 8$, H^{24}), 7.53 (dd, 2H, $J = 8, 2$, H^{12}), 7.40 (t, 1H, $J = 8$, H^{23}), 7.35 (dd, 2H, $J = 9, 2$, H^{13}), 7.28 (t, 1H, $J = 8$, H^{22}), 6.93 (d, 1H, $J = 9$, H^9), 6.62 (d, 1H, $J = 9$, H^{16}), 3.94 (s, 3H, OCH_3); ^{13}C NMR (d_6 -DMSO, 151 MHz): δ 164.1 (s, C^{19}), 160.1 (s, C^{14}), 156.9 (s, C^5), 151.1 (s, C^1), 150.9 (s, C^6), 148.5 (s, C^{15}), 147.2 (s, C^{10}), 145.7 (s, C^{20}), 144.5 (m, C^{25}), 140.5 (s, C^3), 139.6 (s, C^{17}), 139.4 (s, C^8), 133.9 (s, C^{11}), 132.0 (s, C^{24}), 131.0 (s, C^{12}), 129.6 (s, C^{23}), 128.1 (s, C^2), 125.1 (s, C^{22}), 124.7 (s, C^4), 124.5 (s, C^{21}), 119.3 (s, C^9), 118.1 (s, C^7), 117.1 (s, C^{13}), 115.3 (s, C^{16}), 113.5 (s, C^{18}), 55.7 (s, OCH_3); ^{19}F NMR (d_6 -DMSO, 376 MHz): δ -70.1 (d, $J = 711$); ES^+ : 623.1361 $[\text{M}-\text{PF}_6]^+$ (mass for $\text{C}_{28}\text{H}_{21}\text{N}_4\text{PtO} = 623.1342$); R_f : 0.26 (DCM : MeOH 98 : 2).

Pt(N[^]N[^]C[^]C) (61)



This complex was made following the general procedure for the synthesis of platinum complexes using K_2PtCl_4 (0.10 g, 0.24 mmol), $N^{\wedge}N^{\wedge}CH^{\wedge}CH$ (0.12 g, 0.29 mmol, 1.2. equiv.) and glacial acetic acid (5 ml). Recrystallization from DMF and ether yielded the title compound as an orange solid (24 mg, 16%); m.p. 304°C; ^1H NMR (d_6 -DMSO, 600 MHz): δ 9.74 (m, 1H, H^1), 8.71 (d, 1H, $J = 8$, H^{16}), 8.69 (d, 1H, $J = 8$, H^4), 8.35 (td, 1H, $J = 8$, 1, H^3), 8.18 (m, 1H, H^7), 8.05 (dd, 1H, $J = 9$, 7, H^8), 7.92 (ddd, $J = 8$, 6, 1, H^2), 7.45 (m, 2H, H^{12}), 7.36 (m, 2H, H^{22}), 7.30 (m, 4H, $H^{13,23}$), 7.26 (m, 1H, H^{24}), 7.07 (dd, 1H, $J = 8$, 2, 1H, H^{18}), 6.83 (dd, 1H, $J = 9$, 1, H^9), 6.63 (d, 1H, $J = 2$, H^{19}), 3.89 (s, 3H, OCH_3); ^{13}C NMR (d_6 -DMSO, 151 MHz): δ 159.2 (s, C^{14}), 155.4 (s, C^5), 153.7 (s, C^6), 147.7 (s, C^{10}), 147.3 (s, C^1), 140.9 (s, C^{21}), 140.2 (s, C^{16}), 139.3 (m, C^{20}), 139.1 (s, C^3), 135.7 (s, C^8), 135.5 (s, C^{11}), 135.4 (s, C^{17}), 131.5 (s, C^{12}), 128.9 (s, C^{23}), 126.7 (s, C^{24}), 126.3 (s, C^2), 125.9 (s, C^{22}), 123.0 (s, C^4), 119.2 (s, C^9), 118.9 (s, C^{18}), 116.5 (s, C^{13}), 116.1 (s, C^7), 115.5 (s, C^{15}), 115.3 (s, C^{19}), 55.6 (s, OCH_3); ASAP: 658.1136 $[M+H]^+$ (mass for $C_{29}H_{23}ClN_3PtO = 658.1156$).

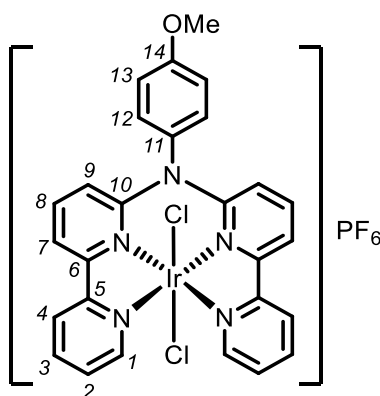
Pt(C[^]N[^]N[^]C) (62)



This complex was made following the general procedure for the synthesis of platinum complexes using K_2PtCl_4 (0.10 g, 0.24 mmol), $CH^{\wedge}N^{\wedge}N^{\wedge}CH$ (0.12, 0.29 mmol, 1.2 equiv.) and glacial acetic acid (5 ml). Recrystallization from DMF and ether yielded the title compound as a yellow solid (4 mg, 3%); m.p. 378°C; ^1H NMR (d_6 -DMSO, 700 MHz): δ 8.17 (d, 2H, $J = 8$, H^7), 8.12 (dd, 2H, $J = 8$, 1, H^4), 8.06 (dd, 2H, $J = 8$, 1, H^1), 8.04 (dd, 2H, $J = 9$, 8, H^8), 7.54 (m, 2H, H^{12}), 7.51 (m, 2H, H^2), 7.33 (td, 2H, $J = 8$, 1, H^3), 7.31 (m, 2H, H^{13}), 6.83 (dd, 2H, $J = 9$, 1, H^9), 3.91 (s, 3H, OCH_3); ^{13}C NMR (d_6 -DMSO, 176 MHz):

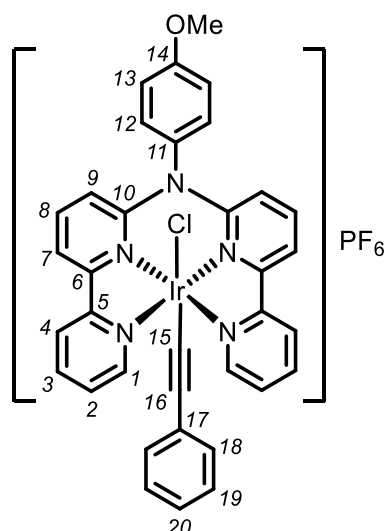
δ 160.3 (s, C⁶), 159.8 (s, C¹⁴), 149.9 (s, C¹⁰), 143.3 (s, C⁵), 141.0 (s, C⁸), 135.3 (s, C¹¹), 133.6 (m, C¹⁵), 132.0 (s, C¹), 131.4 (s, C¹²), 130.5 (s, C²), 125.8 (s, C⁴), 125.4 (s, C³), 116.9 (s, C¹³), 115.4 (s, C⁹), 114.7 (s, C⁷), 55.7 (s, OCH₃); ASAP: 622.1406 [M+H]⁺ (mass for C₂₉H₂₂N₃PtO = 622.1390).

[Ir(N[^]N[^]N[^]N)Cl₂]PF₆ (63**)**



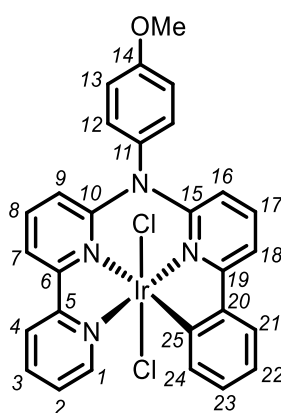
This complex was made following the general procedure for the synthesis of iridium chloro-bridged dimers (section 7.3.1) using IrCl₃·3H₂O (15 mg, 43 μmol), N[^]N[^]N[^]N (20 mg, 0.47 mmol, 1.1 equiv.), 2-ethoxyethanol (1.5 ml) and H₂O (0.5 ml). Upon cooling to RT, a saturated aqueous solution of KPF₆ (4 ml) was added and the resulting precipitate was isolated by centrifugation and washed with H₂O (3 x 5 ml) and ether (1 x 5 ml). Purification by column chromatography (silica, DCM : MeOH 0-2%) followed by recrystallization from acetone and hexane yielded the title compound as a yellow solid (10 mg, 28%); m.p. 258°C; ¹H NMR (*d*₃-MeCN, 700 MHz): δ 9.36 (dt, 2H, *J* = 6, 1, H¹), 8.66 (m, 2H, H⁴), 8.34 (m, 4H, H^{3,7}), 8.08 (dd, 2H, *J* = 9, 8, H⁸), 8.02 (ddd, 2H, *J* = 7, 6, 1, H²), 7.51 (m, 2H, H¹²), 7.32 (m, 2H, H¹³), 7.17 (dd, 2H, *J* = 9, 1, H⁹), 3.94 (s, 3H, OCH₃); ¹³C NMR (*d*₃-MeCN, 176 MHz): δ 162.1, (s, C¹⁴), 158.8 (s, C⁵), 156.2 (s, C⁶), 152.3 (s, C¹), 151.1 (s, C¹⁰), 141.8 (s, C³), 140.4 (s, C⁷), 135.0 (s, C¹¹), 132.1 (s, C¹³), 128.5 (s, C²), 125.7 (s, C⁴), 121.2 (s, C⁹), 120.2 (s, C⁸), 118.1 (s, C¹²), 56.7 (s, OCH₃); ¹⁹F NMR (*d*₃-MeCN, 376 MHz): δ -73.3 (m); ES⁺: 692.0746 [M-PF₆]⁺ (mass for C₂₇H₂₁N₅IrOCl₂ = 692.0729); R_f: 0.18 (DCM : MeOH 98 : 2).

$[Ir(N^{\wedge}N^{\wedge}N^{\wedge}N^{\wedge})(CCPh)Cl]PF_6$ (**64**)



This compound was made following the general metathesis procedure using complex **63** (23 mg, 27 μ mol), CuI (1 mg, 2.7 μ mol, 20% mol), phenylacetylene (60 μ l, 0.55 mmol), diisopropylamine (77 μ l, 0.55 mmol) and DMF. Column chromatography (alumina, DCM : MeOH : 0-2%) yielded the title compound as a yellow solid (5 mg, 19%); m.p. 216°C; ^1H NMR (d_3 -MeCN, 700 MHz): δ 9.38 (dt, 2H, J = 6, 1, H^1), 8.63 (m, 2H, H^4), 8.36 (td, 2H, J = 8, 1, H^3), 8.30 (m, 2H, H^7), 8.11 (dd, 2H, J = 9, 8, H^8), 7.99 (ddd, 2H, J = 7, 6, 1, H^2), 7.55 (m, 2H, H^{12}), 7.29 (d, J = 9, 2H, H^{13}), 7.19 (dd, 2H, J = 9, 1, H^9), 7.01 (m, 2H, H^{19}), 6.98 (m, 1H, H^{20}), 6.69 (m, 2H, H^{18}), 3.93 (s, 3H, OCH_3); ^{13}C NMR (d_3 -MeCN, 176 MHz): δ 162.0 (s, C^{14}), 158.6 (s, C^5), 156.1 (s, C^6), 152.2 (s, C^1), 151.0 (s, C^{10}), 141.5 (s, C^3), 140.1 (s, C^8), 135.2 (s, C^{11}), 132.6 (s, C^{18}), 132.2 (s, C^{12}), 128.7 (s, C^{19}), 128.5 (s, C^2), 127.3 (s, C^{15}), 126.9 (s, C^{20}), 125.6 (s, C^4), 121.2 (s, C^9), 120.0 (s, C^7), 118.0 (s, C^{13}), 95.2 (s, C^{17}), 79.1 (s, C^{16}), 56.7 (s, OCH_3); ^{19}F NMR (d_3 -MeCN, 376 MHz): δ -72.9 (d, J = 707); ES^+ : 758.1459 $[M-PF_6]^+$ (mass for $C_{35}H_{26}N_5ClIrO$ = 758.1432); R_f : 0.19 (DCM : MeOH 99 : 1).

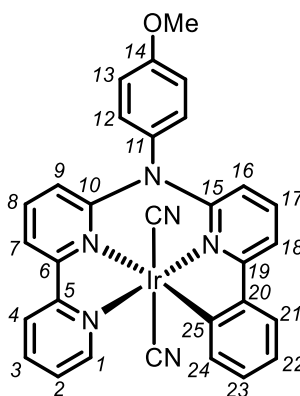
$Ir(N^{\wedge}N^{\wedge}N^{\wedge}C)Cl_2$ (**65**)



This complex was made following the general procedure for the synthesis of iridium chloro-bridged dimers (section 7.3.1) using $IrCl_3 \cdot 3H_2O$ (15 mg, 43 μ mol), $N^{\wedge}N^{\wedge}N^{\wedge}CH$ (20 mg, 0.47 mmol, 1.1 equiv.), 2-ethoxyethanol (1.5 ml) and H_2O (0.5 ml). Upon cooling to RT, H_2O (4 ml) was added and the resulting precipitate was isolated by centrifugation and washed with H_2O (3 x 5 ml) and ether (1 x

5 ml). Purification by column chromatography (silica, DCM : MeOH 0-2%) followed by recrystallization from DCM and hexane yielded the title compound as an orange solid (6 mg, 21%); m.p. 207°C; ^1H NMR (CDCl_3 , 700 MHz): δ 9.83 (d, 1H, $J = 6$, H^1), 8.29 (d, 1H, $J = 8$, H^4), 8.12 (d, 1H, $J = 7$, H^{24}), 7.97 (m, 2H, $\text{H}^{3,7}$), 7.90 (m, 1H, H^{21}), 7.79 (dd, 1H, $J = 9$, 8, H^8), 7.76 (d, 1H, $J = 8$, H^{18}), 7.70 (t, 1H, $J = 6$, H^2), 7.55 (dd, 1H, $J = 9$, 8, H^{17}), 7.47 (m, 3H, $\text{H}^{12,23}$), 7.19 (d, 2H, $J = 9$, H^{13}), 7.16 (td, 1H, $J = 7$, 1, H^{22}), 6.92 (d, 1H, $J = 9$, H^9), 6.60 (dd, 1H, $J = 9$, 1, H^{16}), 3.95 (s, 3H, OCH_3); ^{13}C NMR (CDCl_3 , 176 MHz): δ 167.7 (s, C^{19}), 160.1 (s, C^{14}), 153.9 (s, C^6), 153.8 (s, C^1), 150.4 (s, C^{15}), 149.0 (s, C^{10}), 148.1 (s, C^{20}), 145.4 (s, C^{25}), 137.6 (s, C^3), 136.8 (s, C^{17}), 136.4 (s, C^8), 135.6 (s, C^{11}), 133.7 (s, C^{24}), 131.8 (s, C^{12}), 129.6 (s, C^{23}), 125.9 (s, C^2), 125.1 (s, C^5), 125.0 (s, C^{21}), 123.2 (s, C^{22}), 123.1 (s, C^4), 118.5 (s, C^9), 116.9 (s, C^7), 116.8 (s, C^{13}), 114.4 (s, C^{16}), 112.9 (s, C^{18}), 55.9 (s, OCH_3); ES^+ : 690.0727 $[\text{M-PF}_6]^+$ (mass for $\text{C}_{28}\text{H}_{21}\text{N}_4\text{IrOCl}_2 = 690.0698$); R_f : 0.51 (DCM : MeOH 98 : 2).

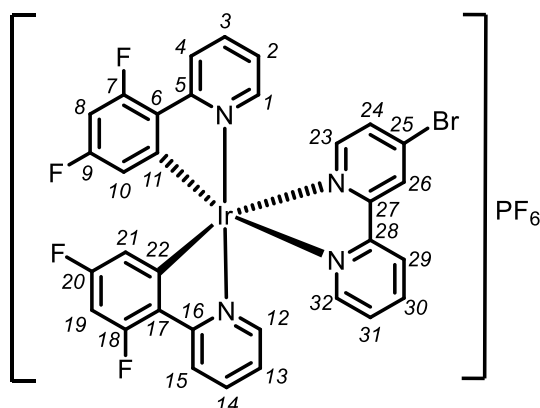
Ir(N^N^N^C)CN₂ (66)



This compound was made following the general metathesis procedure using complex **65** (24 mg, 35 μmol), AgCN (46 mg, 0.35 mmol, 10 equiv.) and DMF. Addition of a saturated aqueous solution of KPF_6 was not required. Column chromatography (alumina, DCM : MeOH : 0-1.25%) followed by recrystallization from DMF and ether yielded the title compound as a light yellow solid (5 mg, 22%); m.p. 370°C; ^1H NMR (d_6 -DMSO, 700 MHz): δ 9.71 (dd, 1H, $J = 6$, 1, H^1), 8.90 (m, 1H, H^4), 8.61 (d, 1H, $J = 8$, H^7), 8.40 (td, 1H, $J = 8$, 1, H^3), 8.22 (dd, 1H, $J = 9$, 8, H^8), 8.13 (m, 1H, H^{24}), 8.07 (m, 2H, $\text{H}^{18,21}$), 8.00 (ddd, 1H, $J = 8$, 6, 1, H^2), 7.93 (dd, 1H, $J = 9$, 8, H^{17}), 7.63 (m, 2H, H^{12}), 7.42 (td, 1H, $J = 8$, 1, H^{23}), 7.32 (m, 2H, H^{13}), 7.24 (m, 1H, H^{22}), 7.15 (d, 1H, $J = 9$, H^9), 6.81 (dd, 1H, $J = 9$, 1, H^{16}), 3.90 (s, 3H, OCH_3); ^{13}C NMR (d_6 -DMSO, 176 MHz): δ 166.6 (m, C^{19}), 159.8 (m, C^{14}), 152.1 (m, C^1), 151.1 (m, C^{15}), 150.1 (m, C^6), 145.6 (m, C^{10}), 144.8 (m, C^{20}), 144.6 (m, C^{25}), 138.7 (m, C^3), 138.2 (m, C^8), 137.6 (m, C^{17}), 135.6 (m, C^{11}), 132.6 (m, C^{24}), 130.8 (m, C^{12}), 130.3 (m, C^5), 128.4 (m, C^{23}), 126.8 (m, C^2), 124.3 (m, C^{21}), 123.9 (m, C^4), 121.9 (m, C^{22}), 118.3 (m, C^9), 117.7 (m, C^7), 116.0 (m, C^{13}), 114.4 (m, C^{16}), 112.7 (m, C^{18}), 54.9 (m, OCH_3); ES^+ : 673.1478 $[\text{M}+\text{H}]^+$ (mass for $\text{C}_{30}\text{H}_{22}\text{IrN}_6\text{O} = 673.1461$); R_f : 0.28 (DCM : MeOH 99 : 1).

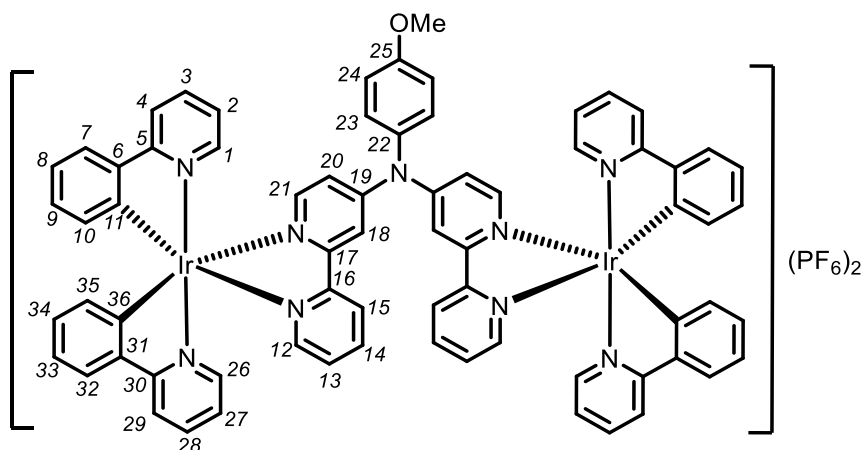
7.4.8 Synthesis of Chapter 5 complexes

$[Ir(dfppy)_2(L^{18})]PF_6$ (**67**)



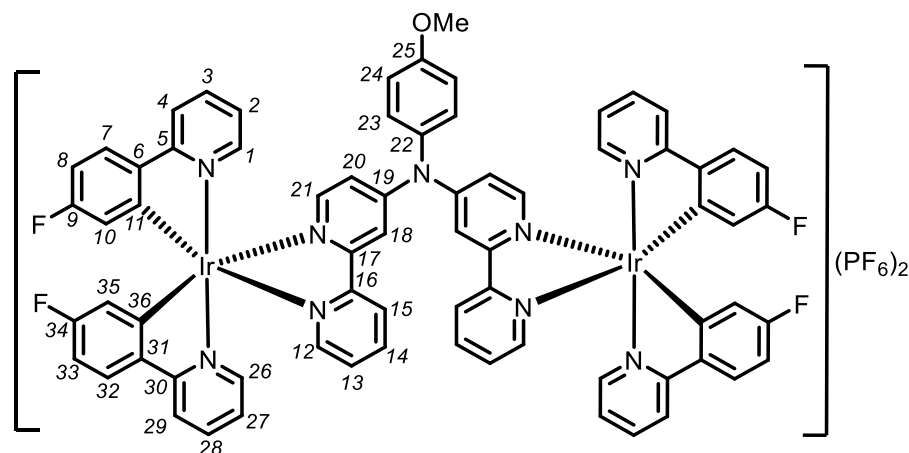
This compound was made following the general procedure for complexes containing bidentate ligands using $[Ir(dfppy)_2\mu-Cl]_2$ (0.13 g, 0.10 mmol), ligand L^{18} (54 mg, 0.23 mmol, 2.2 equiv.), MeOH (6 ml) and DCM (10 ml). Column chromatography (silica, DCM : MeOH 0-2%) followed by recrystallization from acetone and hexane yielded the title compound as a yellow solid (71 mg, 36%); m.p. 335°C; ^1H NMR (d_6 -acetone, 700 MHz): δ 9.11 (d, J = 2, 1H, H^{26}), 8.99 (d, J = 8, 1H, H^{29}), 8.38 (m, 3H, $H^{4,15,30}$), 8.24 (dd, J = 5, 1, 1H, H^{32}), 8.06 (m, 4H, $H^{10r12,3,14,23}$), 7.94 (dd, J = 6, 2, 1H, H^{24}), 7.92 (ddd, J = 6, 2, 1, 1H, H^{10r12}), 7.79 (ddd, J = 8, 5, 1, 1H, H^{31}), 7.25 (tdd, J = 8, 6, 1, 2H, $H^{2,13}$), 6.76 (ddt, J = 13, 9, 2, 2H, $H^{8,19}$), 5.79 (ddd, J = 9, 4, 2, 2H, $H^{10,21}$); ^{13}C NMR (d_6 -acetone, 176 MHz): δ 165.3 (dd, J = 13, 1, C^{9or20}), 164.8 (m, $C^{5,16}$), 163.9 (m, C^{9or20}), 163.2 (d, J = 13, C^{7or18}), 161.7 (m, C^{7or18}), 158.2 (s, C^{27}), 155.8 (s, C^{28}), 155.1 (s, C^{6or17}), 155.1 (s, C^{6or17}), 152.5 (s, C^{23}), 152.3 (s, C^{32}), 151.1 (s, C^{10r12}), 150.9 (s, C^{10r12}), 141.3 (s, C^{30}), 140.9 (s, C^{3or14}), 140.9 (s, C^{3or14}), 137.5 (s, C^{25}), 133.1 (s, C^{24}), 130.6 (s, C^{31}), 129.6 (s, C^{26}), 129.0 (m, $C^{11,22}$), 126.8 (s, C^{29}), 125.3 (s, C^{2or13}), 125.2 (s, C^{2or13}), 124.8 (d, J = 7, C^{4or15}), 124.7 (d, J = 7, C^{4or15}), 114.8 (ddd, J = 18, 13, 2, $C^{10,21}$), 99.9 (td, J = 27, 7, $C^{8,19}$); ^{19}F NMR (d_6 -acetone, 376 MHz): δ -72.6 (m), -107.8 (dd, J = 11, 5), -110.0 (J = 17, 11); ES $^+$: 805.0331 $[M-PF_6]^+$ (mass for $C_{32}H_{19}N_4F_4IrBr$ = 805.0335); R_f : 0.17 (98% DCM, 2% MeOH).

$[{Ir(ppy)_2}_2(L^{19})](PF_6)_2$ (**68**)



This compound was made following the general procedure for complexes containing bidentate ligands using $[\text{Ir}(\text{ppy})_2\mu\text{-Cl}]_2$ (44 mg, 73 μmol), ligand **L**¹⁹ (19 mg, 77 μmol , 1.1 equiv.), MeOH (3 ml) and DCM (5 ml). Column chromatography (silica, DCM : MeOH 0-2%) yielded the title compound as a yellow solid (51 mg, 72%); m.p. 338°C; ¹H NMR (*d*₆-acetone, 700 MHz): δ 8.46 (m, 2H, H¹⁵), 8.36 (dd, *J* = 7, 3, 2H, H¹⁸), 8.23 (ddt, *J* = 8, 4, 1, 2H, H^{4or29}), 8.21 (dt, *J* = 8, 1, 2H, H^{4or29}), 8.15 (m, 2H, H¹⁴), 8.07 (dtd, *J* = 5, 2, 1, 2H, H¹²), 7.99 (dddd, *J* = 8, 7, 3, 1, 2H, H^{1or26}), 7.94 (m, 4H, H^{3,28}), 7.86 (m, 4H, H^{7,32}), 7.82 (m, 4H, H^{1or26,21}), 7.64 (ddt, *J* = 8, 5, 2, 2H, H¹³), 7.40 (ddd, *J* = 12, 7, 3, 2H, H²⁰), 7.37 (m, 2H, H²³), 7.19 (ttdd, *J* = 7, 6, 4, 1, 4H, H^{2,27}), 7.10 (m, 2H, H²⁴), 7.00 (m, 4H, H^{8,33}), 6.88 (m, 4H, H^{9,34}), 6.31 (m, 4H, H^{10,35}), 3.86 (d, *J* = 1, 3H, OCH₃); ¹³C NMR (*d*₆-acetone, 176 MHz): δ 168.7 (s, C^{5,30}), 160.8 (s, C²⁵), 158.1 (s, C¹⁶), 156.7 (s, C¹⁷), 154.9 (s, C¹⁹), 151.9 (s, C²¹), 151.5 (s, C¹²), 151.5 (m, C^{11,36}), 150.2 (s, C^{3,28}), 150.2 (s, C^{1or26}), 145.0 (s, C^{6or31}), 144.9 (s, C^{6or31}), 140.2 (s, C¹⁴), 139.5 (m, C^{1or26}), 135.3 (s, C²²), 132.5 (m, C^{10,35}), 131.2 (m, C^{9,34}), 130.7 (m, C²³), 129.5 (s, C¹³), 125.7 (m, C^{7,32}), 125.7 (s, C¹⁵), 124.5 (m, C^{2,27}), 123.3 (m, C^{8,33}), 120.8 (s, C^{4or29}), 120.7 (s, C^{4or29}), 120.6 (s, C²⁰), 117.6 (s, C¹⁸), 117.1 (m, C²⁴), 56.0 (s, OCH₃); ¹⁹F NMR (*d*₆-acetone, 376 MHz): δ -72.4 (d, *J* = 708); ES⁺: 716.6754 = [(M-2PF₆)/2]⁺ (mass for [(C₇₁H₅₃N₉Ir₂O)/2] = 716.6816); R_f: 0.32 (DCM : MeOH 98 : 2).

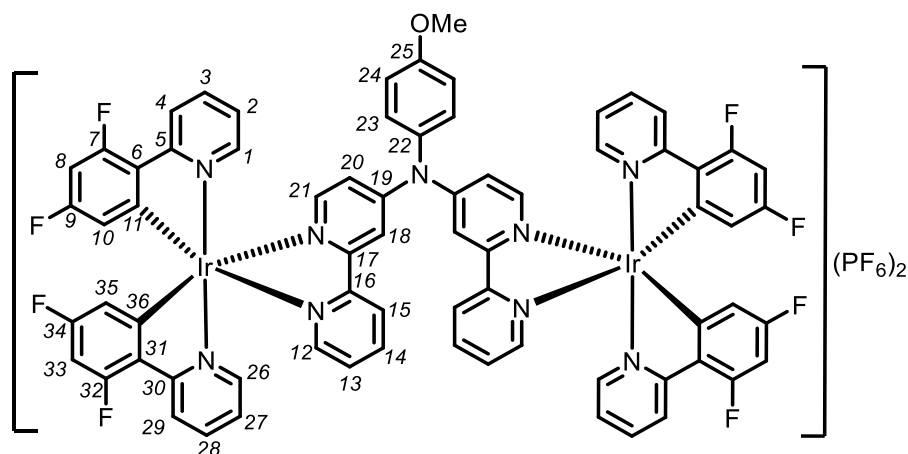
$[\{\text{Ir}(\text{fppy})_2\}_2(\text{L}^{19})](\text{PF}_6)_2$ (69**)**



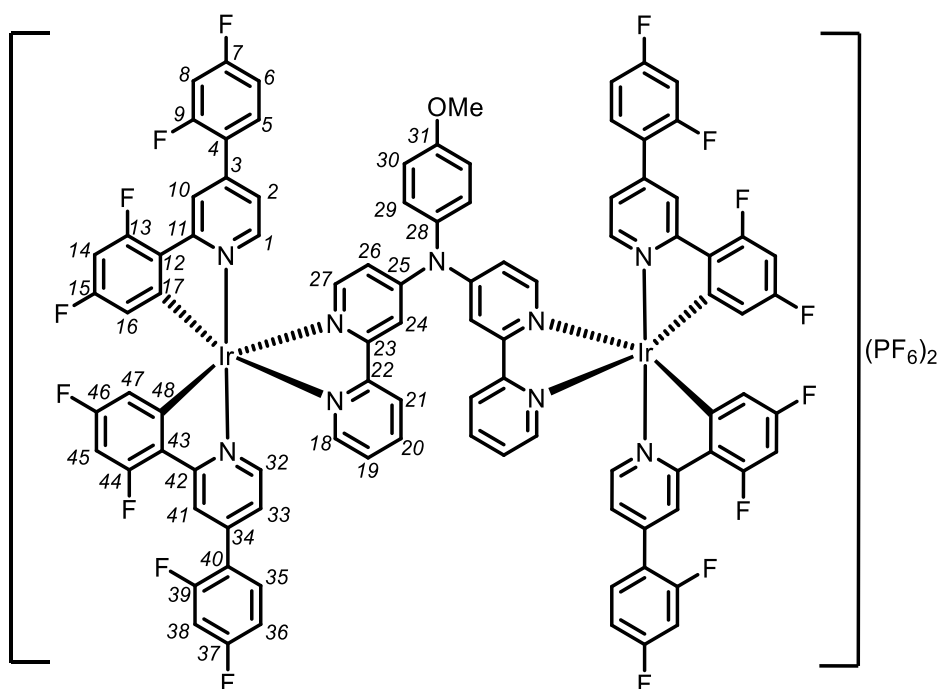
This compound was made following the general procedure for complexes containing bidentate ligands using $[\text{Ir}(\text{fppy})_2\mu\text{-Cl}]_2$ (68 mg, 61 μmol), ligand **L**¹⁹ (27 mg, 64 μmol , 1.05 equiv.), MeOH (3 ml) and DCM (5 ml). Column chromatography (silica, DCM : MeOH 0-2%) yielded the title compound as a yellow solid (82 mg, 77%); m.p. 379°C; ¹H NMR (*d*₆-acetone, 700 MHz): δ 8.47 (ddt, *J* = 8, 6, 1, 2H, H¹⁵), 8.38 (dd, *J* = 9, 3, 2H, H¹⁸), 8.24 (ddt, *J* = 8, 6, 1, 2H, H^{4or29}), 8.21 (m, 2H, H^{4or29}), 8.18 (ddd, *J* = 8, 2, 1, 2H, H¹⁴), 8.13 (ddd, *J* = 6, 2, 1, 2H, H¹²), 8.02 (dddd, *J* = 8, 7, 4, 1, 2H, H^{3or28}), 7.98 (m, 6H, H^{3or28,7,32}), 7.93 (ddd, *J* = 8, 6, 1, 2H, H^{1or26}), 7.87 (dd, *J* = 6, 1, 2H, H²¹), 7.82 (ddd, *J* = 6, 5, 1, 2H, H^{1or26}), 7.67 (m, 2H, H¹³), 7.42 (ddd, *J* = 17, 6, 3, 1H, H²⁰), 7.40 (dd, *J* = 6, 3, 1H, H²⁰), 7.37 (m, 2H, H²³), 7.22 (m, 4H, H^{2,27}), 7.10 (m, 2H, H²⁴), 6.80 (dtd, *J* = 17, 9, 3, 4H, H^{8,33}), 5.91 (m, 4H, H^{10,35}), 3.86 (d, *J* = 2, 3H, OCH₃); ¹³C NMR (*d*₆-acetone, 176 MHz): δ 167.6 (s, C^{5,30}), 164.4 (m, C^{9,34}), 161.0 (m, C²⁵), 158.1

(s, C¹⁷), 156.8 (s, C¹⁶), 155.2 (d, *J* = 2, C¹⁹), 152.2 (s, C²¹), 151.8 (s, C¹²), 150.4 (m, C^{1,26}), 141.6 (d, *J* = 2, C^{6,31}), 141.5 (d, *J* = 2, C^{11,36}), 140.7 (d, *J* = 3, C¹⁴), 140.0 (m, C^{3,28}), 135.3 (s, C²²), 130.8 (s, C²³), 129.8 (s, C¹³), 128.2 (dd, *J* = 10, 7, C^{7,32}), 126.0 (s, C¹⁵), 124.7 (s, C^{2,27}), 121.1 (d, *J* = 12, C^{4,29}), 120.9 (d, *J* = 6, C²⁰), 118.4 (d, *J* = 18, C^{10,35}), 117.8 (s, C¹⁸), 117.2 (d, *J* = 3, C²⁴), 110.6 (dd, *J* = 23, 4, C^{8,33}), 56.2 (s, OCH₃); ¹⁹F NMR (*d*₆-acetone, 376 MHz): δ -72.4 (d, *J* = 708), -110.8 (d, *J* = 1), -110.9 (d, *J* = 6); ES⁺: 752.6578 = [(M-2PF₆)/2]⁺ (mass for [(C₇₁H₄₉F₄N₉Ir₂O)/2] = 752.6628); R_f: 0.27 (DCM : MeOH 98 : 2).

[{Ir(dfppy)₂(L¹⁹)}(PF₆)₂ (70**)**

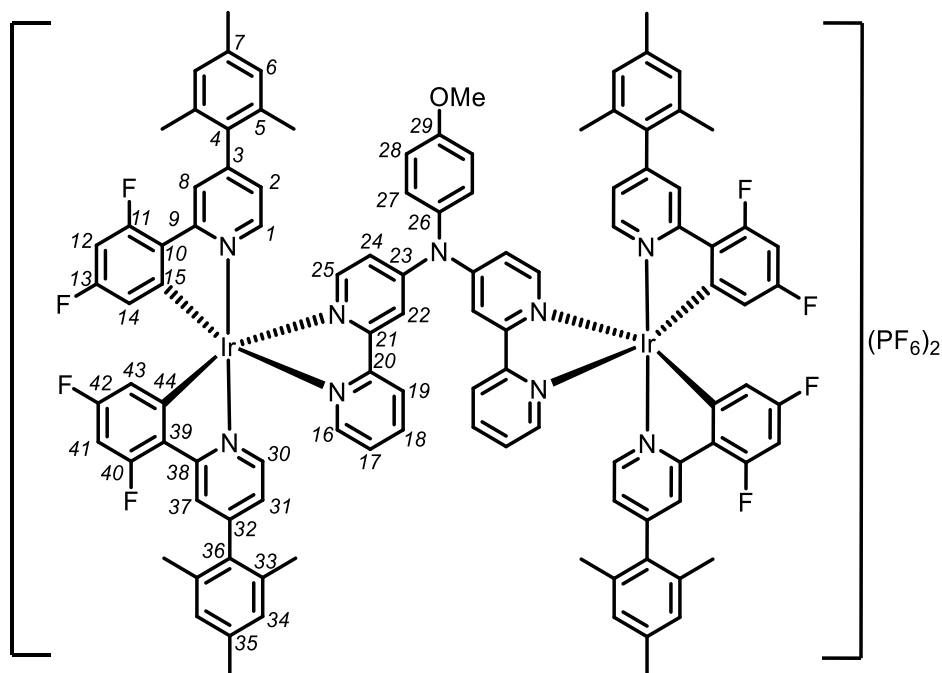


This compound was made following the general procedure for complexes containing bidentate ligands using [Ir(dfppy)₂μ-Cl]₂ (89 mg, 73 μmol), ligand L¹⁹ (33 mg, 76 μmol, 1.05 equiv.), MeOH (3 ml) and DCM (5 ml). Column chromatography (silica, DCM : MeOH 0-2%) yielded the title compound as a yellow solid (96 mg, 70%); m.p. 378°C; ¹H NMR (*d*₆-acetone, 700 MHz): δ 8.48 (ddt, *J* = 10, 8, 1, 2H, H¹⁵), 8.39 (m, 6H, H^{4,29,18}), 8.19 (m, 4H, H^{12,14}), 8.05 (m, 4H, H^{3,28}), 7.91 (m, 6H, H^{1,26,21}), 7.68 (dddd, *J* = 8, 6, 2, 1, 2H, H¹³), 7.40 (dd, *J* = 6, 3, 1H, H²⁰), 7.37 (m, 3H, H^{20,23}), 7.29 (m, 4H, H^{2,27}), 7.10 (m, 2H, H²⁴), 6.72 (dddd, *J* = 15, 12, 9, 2, 4H, H^{8,33}), 5.77 (m, 4H, H^{10,35}), 3.86 (d, *J* = 1, 3H, OCH₃); ¹³C NMR (*d*₆-acetone, 176 MHz): δ 164.8 (d, *J* = 7, C^{5,30}), 164.5 (m, C^{9,34}), 162.5 (m, C^{7,32}), 161.0 (d, *J* = 2, C²⁵), 157.9 (s, C¹⁶), 156.6 (d, *J* = 2, C¹⁷), 155.8 (dd, *J* = 41, 5, C^{6,31}), 155.4 (d, *J* = 4, C¹⁹), 152.2 (s, C²¹), 151.9 (s, C¹²), 150.9 (dd, *J* = 17, 5, C^{1,26}), 140.9 (d, *J* = 4, C¹⁴), 140.7 (m, C^{3,28}), 135.2 (d, *J* = 6, C²²), 130.9 (s, C²³), 129.9 (d, *J* = 2, C¹³), 128.9 (m, C^{11,36}), 126.1 (d, *J* = 3, C¹⁵), 125.2 (d, *J* = 9, C^{2,27}), 124.6 (dd, *J* = 20, 13, C^{4,29}), 121.1 (d, *J* = 11, C²⁰), 117.9 (s, C¹⁸), 117.2 (d, *J* = 5, C²⁴), 114.7 (d, *J* = 18, C^{10,35}), 99.6 (m, C^{8,33}), 56.1 (s, OCH₃); ¹⁹F NMR (*d*₆-acetone, 376 MHz): δ -72.4 (d, *J* = 708), -107.9 (m); -110.1 (m); ES⁺: 788.6401 = [(M-2PF₆)/2]⁺ (mass for [(C₇₁H₄₅F₈N₉Ir₂O)/2] = 788.6439); R_f: 0.29 (DCM : MeOH 98 : 2).

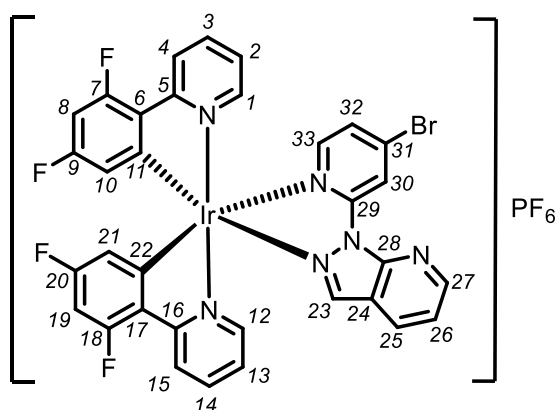
$$[\{\text{Ir}(\text{bis-dfp}_2\text{py})_2\}_2(\text{L}^{19})](\text{PF}_6)_2 \text{ (71)}$$


This compound was made following the general procedure for complexes containing bidentate ligands using $[\text{Ir}(\text{bis-dfp}_2\text{py})_2\mu\text{-Cl}]_2$ (86 mg, 52 μmol), ligand L^{19} (29 mg, 67 μmol , 1.3 equiv.), MeOH (3 ml) and DCM (5 ml). Column chromatography (silica, DCM : MeOH 0-2%) followed by recrystallization twice from DCM and hexane yielded the title compound as a yellow solid (7 mg, 2%); m.p. 352°C; ^1H NMR (d_6 -acetone, 700 MHz): δ 8.56 (d, J = 11, 4H, $\text{H}^{10,41}$), 8.53 (d, J = 8, 2H, H^{21}), 8.44 (d, J = 3, 2H, H^{24}), 8.24 (m, 2H, H^{18}), 8.20 (td, J = 8, 1, 2H, H^{20}), 8.10 (d, J = 6, 2H, $\text{H}^{10\text{or}32}$), 7.99 (m, 4H, $\text{H}^{10\text{or}32,27}$), 7.85 (dtd, J = 26, 9, 6, 4H, $\text{H}^{5,35}$), 7.72 (ddd, J = 8, 6, 1, 2H, H^{19}), 7.49 (tt, J = 6, 2, 4H, $\text{H}^{2,33}$), 7.43 (dd, J = 6, 3, 2H, H^{26}), 7.40 (m, 2H, H^{29}), 7.28 (m, 8H, $\text{H}^{6,8,36,38}$), 7.11 (m, 2H, H^{30}), 6.77 (dddd, J = 17, 12, 9, 2, 4H, $\text{H}^{14,45}$), 5.91 (ddd, J = 11, 9, 2, 4H, $\text{H}^{16,47}$), 3.87 (m, 3H, OCH_3); ^{13}C NMR (d_6 -acetone, 176 MHz): δ 165.8 (m, $\text{C}^{7,37}$), 165.1 (m, $\text{C}^{11,42}$), 164.6 (m, $\text{C}^{13,44}$), 162.9 (m, $\text{C}^{15,46}$), 161.0 (m, C^{31}), 160.1 (m, $\text{C}^{9,39}$), 157.0 (m, $\text{C}^{12,43}$), 156.7 (m, C^{22}), 155.5 (m, C^{23}), 152.4 (m, C^{27}), 152.2 (m, C^{18}), 150.8 (m, $\text{C}^{1,32}$), 150.7 (m, C^{25}), 146.6 (m, $\text{C}^{3,34}$), 141.0 (m, C^{20}), 135.3 (m, C^{28}), 133.3 (m, $\text{C}^{5,35}$), 130.9 (m, C^{29}), 130.2 (m, C^{19}), 128.9 (m, $\text{C}^{17,48}$), 126.2 (m, C^{21}), 124.7 (m, $\text{C}^{2,33}$), 123.9 (m, $\text{C}^{10,41}$), 122.2 (m, $\text{C}^{4,40}$), 121.1 (m, C^{26}), 118.1 (m, C^{24}), 117.3 (m, C^{30}), 114.9 (m, $\text{C}^{16,47}$), 113.8 (m, $\text{C}^{8,38}$), 106.0 (m, $\text{C}^{6,36}$), 99.9 (m, $\text{C}^{14,45}$), 56.2 (s, OCH_3); ^{19}F NMR (d_6 -acetone, 376 MHz): δ -72.3 (d, J = 709), -107.3 (dd, J = 16, 11), -108.2 (dd, J = 33, 9), -109.8 (dd, J = 31, 11), -113.1 (dd, J = 9, 2); ES^+ : 1012.6637 $[(\text{M}-2\text{PF}_6)/2]^+$ (mass for $[(\text{C}_{95}\text{H}_{53}\text{F}_{12}\text{N}_9\text{Ir}_2\text{O})/2 = 1012.6688]$; R_f : 0.34 (DCM : MeOH 98 : 2).

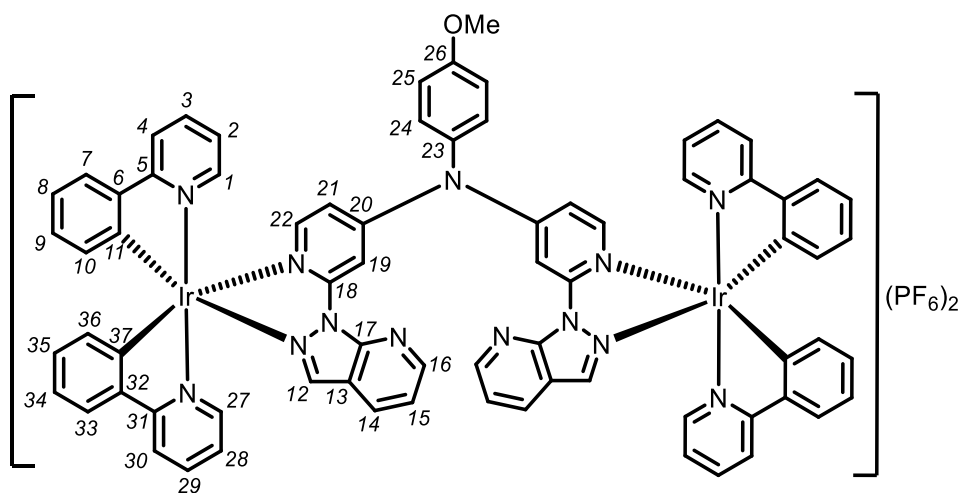
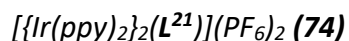
$[\{\text{Ir}(\text{mes-dfppy})_2\}_2(\text{L}^{19})](\text{PF}_6)_2$ (**72**)



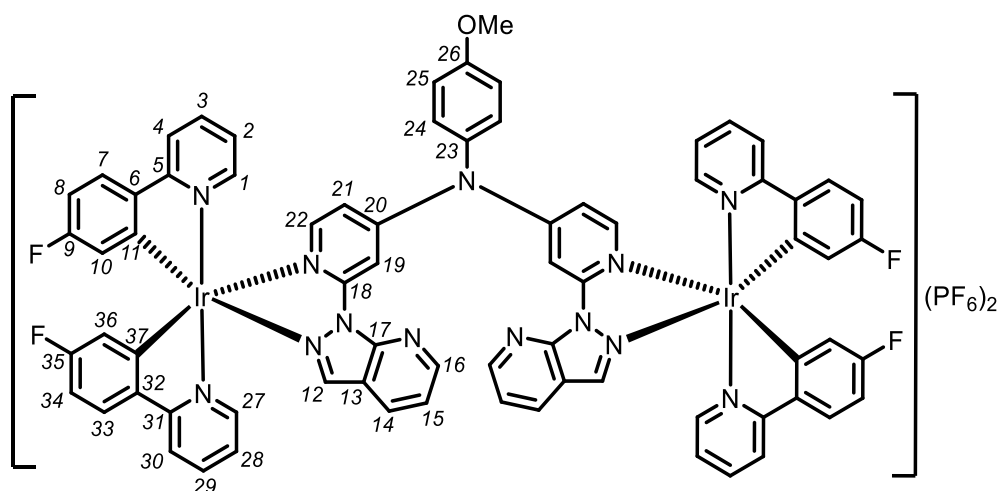
This compound was made following the general procedure for complexes containing bidentate ligands using $[\text{Ir}(\text{mes-dfppy})_2\mu\text{-Cl}]_2$ (43 mg, 29 μmol), ligand L^{19} (12 mg, 31 μmol , 1.3 equiv.), MeOH (3 ml) and DCM (5 ml). Column chromatography (silica, DCM : MeOH 0-2%) followed by recrystallization three times from acetone and hexane yielded the title compound as a yellow solid (6 mg, 11%); m.p. 336°C; ^1H NMR (d_6 -acetone, 700 MHz): δ 8.58 (d, J = 8, 2H, H^{19}), 8.49 (m, 2H, H^{22}), 8.29 (m, 2H, H^{16}), 8.20 (m, 4H, $\text{H}^{10,30,18}$), 8.13 (s, 4H, $\text{H}^{8,37}$), 8.02 (m, 2H, H^{25}), 7.99 (d, J = 6, 2H, $\text{H}^{10,30}$), 7.73 (ddd, J = 8, 6, 1, 2H, H^{17}), 7.43 (dd, J = 7, 2, 2H, H^{24}), 7.39 (d, J = 9, 2H, H^{27}), 7.16 (dd, J = 6, 2, 2H, $\text{H}^{20,31}$), 7.13 (m, 4H, $\text{H}^{20,31,28}$), 7.02 (m, 8H, $\text{H}^{6,34}$), 6.74 (dt, J = 21, 10, 4H, $\text{H}^{12,41}$), 5.85 (ddd, J = 15, 10, 2, 4H, $\text{H}^{14,43}$), 3.88 (s, 3H, OCH_3), 2.32 (s, 12H, $^{50,33}\text{-CH}_3$); 2.13 (s, 12H, $^{50,33}\text{-CH}_3$), 1.97 (s, 6H, $^{70,35}\text{-CH}_3$), 1.91 (s, 6H, $^{70,35}\text{-CH}_3$); ^{13}C NMR (d_6 -acetone, 176 MHz): δ 165.2 (m, $\text{C}^{11,40}$), 165.1 (m, $\text{C}^{9,38}$), 162.4 (m, $\text{C}^{13,42}$), 161.1 (m, C^{29}), 158.3 (m, C^{21}), 156.7 (m, C^{20}), 155.8 (m, $\text{C}^{10,39}$), 155.5 (m, C^{23}), 154.1 (m, $\text{C}^{3,32}$), 152.4 (m, C^{25}), 152.2 (m, C^{16}), 151.2 (m, $\text{C}^{10,30}$), 150.8 (m, $\text{C}^{10,30}$), 141.0 (m, C^{18}), 139.2 (m, $\text{C}^{7,35}$), 136.0 (m, $\text{C}^{4,33}$), 135.6 (m, $\text{C}^{5,33}$), 135.4 (m, C^{26}), 130.7 (m, C^{27}), 130.0 (m, C^{17}), 129.6 (m, $\text{C}^{6,34}$), 129.2 (m, $\text{C}^{15,44}$), 126.4 (m, C^{19}), 126.4 (m, $\text{C}^{2,31}$), 125.6 (m, $\text{C}^{8,37}$), 121.1 (m, C^{24}), 118.3 (m, C^{22}), 117.3 (m, C^{28}), 114.7 (m, $\text{C}^{14,43}$), 99.8 (m, $\text{C}^{12,41}$), 56.3 (m, OCH_3), 21.2 (m, $^{7,35}\text{-CH}_3$), 20.7 (m, $^{5,33}\text{-CH}_3$), 20.6 (m, $^{5,33}\text{-CH}_3$); ^{19}F NMR (d_6 -acetone, 376 MHz): δ -72.4 (d, J = 708), -107.8 (m); -109.9 (m); ES^+ : 1024.7916 $[(\text{M}-2\text{PF}_6)/2]^+$ (mass for $[(\text{C}_{107}\text{H}_{85}\text{F}_8\text{N}_9\text{Ir}_2\text{O})/2 = 1024.8004]$; R_f : 0.37 (DCM : MeOH 98 : 2).

$[Ir(dfppy)_2(L^{20})]PF_6$ (**73**)

This compound was made following the general procedure for complexes containing bidentate ligands using $[Ir(dfppy)_2\mu\text{-Cl}]_2$ (0.10 g, 82 μmol), ligand L^{20} (50 mg, 0.18 mmol, 2.2 equiv.), MeOH (3 ml) and DCM (5 ml). Column chromatography (silica, DCM : MeOH 0-2%) followed by recrystallization from acetone and hexane yielded the title compound as a yellow solid (0.13 g, 77%); m.p. 306°C; ^1H NMR (d_6 -acetone, 700 MHz): δ 9.81 (dd, $J = 2, 1$, 1H, H^{33}), 9.00 (dd, $J = 5, 2$, 1H, H^{27}), 8.54 (dd, $J = 8, 2$, 1H, H^{25}), 8.40 (m, 3H, $H^{4,15,23}$), 8.28 (ddd, $J = 6, 2, 1$, 1H, H^{10r12}), 8.24 (ddd, $J = 6, 2, 1$, 1H, H^{10r12}), 8.09 (m, 2H, $H^{3,14}$), 7.97 (dd, $J = 6, 1$, 1H, H^{30}), 7.78 (dd, $J = 6, 2$, 1H, H^{32}), 7.71 (dd, $J = 8, 5$, 1H, H^{26}), 7.25 (ddd, $J = 7, 6, 2$, 1H, H^{20r13}), 7.23 (ddd, $J = 7, 6, 2$, 1H, H^{20r13}), 6.79 (ddt, $J = 12, 9, 3$, 2H, $H^{8,19}$), 5.85 (dd, $J = 9, 3$, 1H, H^{10or21}), 5.82 (dd, $J = 9, 3$, 1H, H^{10or21}); ^{13}C NMR (d_6 -acetone, 176 MHz): δ 165.0 (dd, $J = 46, 13$, C^{9or20}), 164.5 (d, $J = 7$, C^{5or16}), 164.3 (d, $J = 7$, C^{5or16}), 163.5 (dd, $J = 49, 13$, C^{9or20}), 162.9 (dd, $J = 46, 13$, C^{7or18}), 161.4 (dd, $J = 46, 13$, C^{7or18}), 153.8 (s, C^{27}), 153.6 (s, C^{6or17}), 152.6 (s, C^{28}), 151.5 (s, C^{10r12}), 151.4 (s, C^{29}), 151.2 (s, C^{10r12}), 150.7 (d, $J = 7$, C^{6or17}), 150.6 (s, C^{30}), 142.3 (s, C^{23}), 141.0 (s, C^{3or14}), 140.9 (s, C^{3or14}), 138.1 (s, C^{31}), 134.3 (s, C^{25}), 129.2 (dd, $J = 5, 3$, C^{11or22}), 129.1 (dd, $J = 5, 3$, C^{11or22}), 128.6 (s, C^{32}), 125.2 (s, C^{20r13}), 125.1 (s, C^{20r13}), 124.6 (d, $J = 4$, C^{4or15}), 124.5 (d, $J = 4$, C^{4or15}), 122.3 (s, C^{26}), 119.8 (s, C^{24}), 118.6 (s, C^{33}), 115.0 (dd, $J = 18, 3$, C^{10or21}), 114.8 (dd, $J = 18, 3$, C^{10or21}), 100.0 (td, $J = 27, 19$, $C^{8,19}$); ^{19}F NMR (d_6 -acetone, 376 MHz): δ -72.6 (d, $J = 708$), -107.9 (dd, $J = 190, 11$), -110.1 (dd, $J = 196, 11$); ES^+ : 845.0417 $[\text{M-PF}_6]^+$ (mass for $\text{C}_{33}\text{H}_{19}\text{N}_6\text{F}_4\text{IrBr} = 845.0397$); R_f : 0.26 (98% DCM, 2% MeOH).

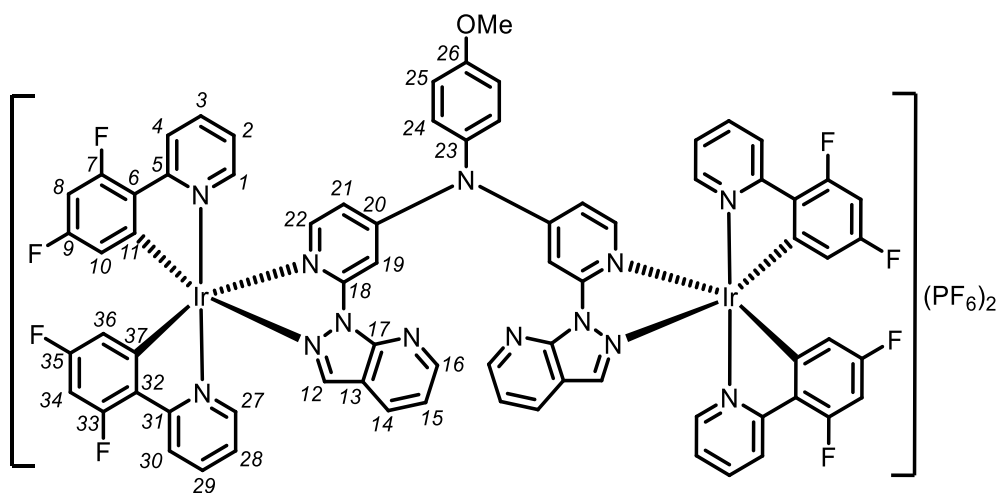


This compound was made following the general procedure for complexes containing bidentate ligands using $[\text{Ir}(\text{ppy})_2\mu\text{-Cl}]_2$ (44 mg, 41 μmol), ligand L^{21} (23 mg, 45 μmol , 1.1 equiv.), MeOH (3 ml) and DCM (5 ml). Column chromatography (silica, DCM : MeOH 0-2%) followed by recrystallizations twice from acetone and hexane and twice from MeOH and H_2O yielded the title compound as a yellow solid (53 mg, 72%); m.p. 398°C; ^1H NMR (d_6 -acetone, 700 MHz): δ 9.46 (dd, $J = 14, 3$, 2H, H^{19}), 8.46 (dd, $J = 8, 2$, 2H, H^{14}), 8.43 (ddd, $J = 11, 5, 2$, 2H, H^{16}), 8.30 (dd, $J = 8, 5$, 2H, $\text{H}^{4\text{or}30}$), 8.24 (m, 4H, $\text{H}^{1\text{or}27,4\text{or}30}$), 8.10 (m, 2H, $\text{H}^{1\text{or}27}$), 8.06 (d, $J = 2$, 2H, H^{12}), 8.04 (tdd, $J = 8, 3, 2$, 2H, $\text{H}^{3\text{or}29}$), 7.97 (m, 2H, $\text{H}^{3\text{or}29}$), 7.90 (m, 4H, $\text{H}^{7,33}$), 7.70 (d, $J = 7$, 2H, H^{22}), 7.52 (m, 4H, $\text{H}^{15,24}$), 7.33 (ddd, $J = 16, 7, 3$, 2H, H^{21}), 7.19 (m, 6H, $\text{H}^{2,28,25}$), 7.03 (m, 4H, $\text{H}^{8,34}$), 6.91 (dddd, $J = 8, 6, 4, 1$, 4H, $\text{H}^{9,35}$), 6.41 (dt, $J = 8, 1$, 2H, $\text{H}^{10\text{or}36}$), 6.37 (d, $J = 8$, 2H, $\text{H}^{10\text{or}36}$), 3.92 (d, $J = 1$, 3H, OCH_3); ^{13}C NMR (d_6 -acetone, 176 MHz): δ 168.9 (s, $\text{C}^{5\text{or}31}$), 168.5 (s, $\text{C}^{5\text{or}31}$), 161.4 (s, C^{26}), 155.8 (s, C^{20}), 152.7 (d, $J = 3$, C^{16}), 152.4 (s, C^{13}), 152.1 (s, C^{18}), 150.7 (d, $J = 2$, $\text{C}^{1\text{or}27}$), 150.5 (s, $\text{C}^{1\text{or}27}$), 150.2 (s, $\text{C}^{11\text{or}37}$), 149.9 (d, $J = 6$, C^{22}), 147.6 (s, $\text{C}^{11\text{or}37}$), 145.5 (s, $\text{C}^{6\text{or}32}$), 145.2 (s, $\text{C}^{6\text{or}32}$), 140.6 (d, $J = 1$, C^{12}), 139.9 (s, $\text{C}^{3\text{or}29}$), 139.9 (d, $J = 2$, $\text{C}^{3\text{or}29}$), 135.2 (s, C^{23}), 134.0 (s, C^{14}), 132.9 (m, $\text{C}^{10\text{or}36}$), 132.6 (s, $\text{C}^{10\text{or}36}$), 131.1 (d, $J = 1$, $\text{C}^{9,35}$), 131.0 (s, C^{24}), 125.9 (d, $J = 2$, $\text{C}^{7\text{or}33}$), 125.7 (s, $\text{C}^{7\text{or}33}$), 124.7 (d, $J = 2$, $\text{C}^{2,28}$), 123.7 (s, $\text{C}^{8\text{or}34}$), 123.6 (s, $\text{C}^{8\text{or}34}$), 121.9 (m, C^{15}), 121.0 (m, $\text{C}^{4\text{or}30}$), 120.9 (m, $\text{C}^{4\text{or}30}$), 119.8 (s, C^{17}), 117.3 (s, C^{25}), 116.7 (s, C^{21}), 106.5 (s, C^{19}), 56.3 (s, OCH_3); ^{19}F NMR (d_6 -acetone, 376 MHz): δ -72.5 (d, $J = 708$); ES^+ : 756.6829 $[(\text{M}-2\text{PF}_6)/2]^+$ (mass for $[(\text{C}_{73}\text{H}_{53}\text{N}_9\text{Ir}_2\text{O})/2 = 756.6877]$; R_f : 0.23 (DCM : MeOH 99 : 1).

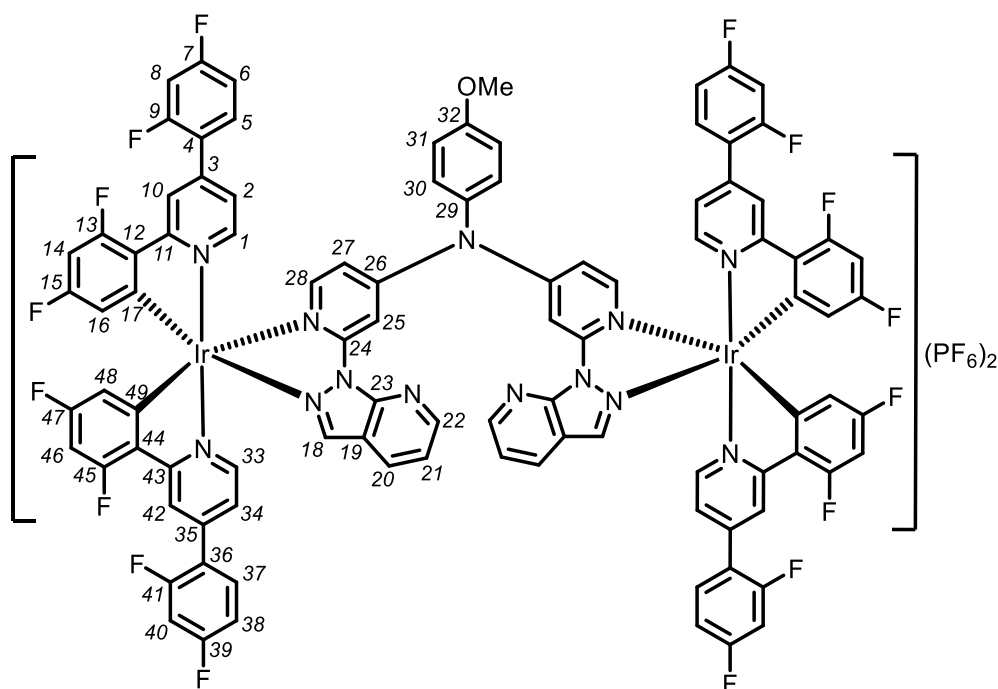
$$[\{\text{Ir}(\text{fppy})_2\}_2(\text{L}^{21})](\text{PF}_6)_2 \text{ (75)}$$


This compound was made following the general procedure for complexes containing bidentate ligands using $[\text{Ir}(\text{fppy})_2\mu\text{-Cl}]_2$ (73 mg, 64 μmol), ligand L^{21} (36 mg, 70 μmol , 1.1 equiv.), MeOH (3 ml) and DCM (5 ml). Column chromatography (silica, DCM : MeOH 0-2%) followed by recrystallization from acetone and hexane, then DCM and hexane, and finally MeOH and H_2O yielded the title compound as a yellow solid (36 mg, 30%); m.p. 338°C; ^1H NMR (d_6 -acetone, 700 MHz): δ 9.48 (dd, J = 15, 2, 2H, H^{19}), 8.46 (m, 2H, H^{14}), 8.42 (ddd, J = 7, 5, 1, 2H, H^{16}), 8.30 (dd, J = 8, 5, 2H, $\text{H}^{4\text{or}30}$), 8.24 (m, 4H, $\text{H}^{1\text{or}27,4\text{or}30}$), 8.21 (dd, J = 2, 1, 2H, H^{12}), 8.08 (m, 4H, $\text{H}^{1\text{or}27,3\text{or}29}$), 8.01 (m, 6H, $\text{H}^{3\text{or}29,7,33}$), 7.76 (d, J = 7, 2H, H^{22}), 7.52 (m, 4H, $\text{H}^{15,24}$), 7.34 (ddd, J = 17, 7, 2, 2H, H^{21}), 7.23 (m, 6H, $\text{H}^{2,28,25}$), 6.84 (m, 4H, $\text{H}^{8,34}$), 6.01 (m, 2H, $\text{H}^{10\text{or}36}$), 5.97 (dd, J = 10, 3, 2H, $\text{H}^{10\text{or}36}$), 3.92 (t, J = 1, 3H, OCH_3); ^{13}C NMR (d_6 -acetone, 176 MHz): δ 167.7 (d, J = 2, $\text{C}^{5\text{or}31}$), 167.3 (s, $\text{C}^{5\text{or}31}$), 164.7 (d, J = 253, $\text{C}^{9\text{or}35}$), 164.5 (d, J = 252, $\text{C}^{9\text{or}35}$), 161.4 (s, C^{26}), 156.0 (s, C^{20}), 153.2 (d, J = 6, $\text{C}^{6,32}$), 152.9 (d, J = 2, C^{16}), 152.3 (s, C^{13}), 152.0 (s, C^{18}), 150.7 (s, $\text{C}^{1\text{or}27}$), 150.5 (d, J = 11, $\text{C}^{1\text{or}27}$), 150.0 (d, J = 6, C^{22}), 142.0 (d, J = 2, $\text{C}^{11\text{or}37}$), 141.7 (s, $\text{C}^{11\text{or}37}$), 141.1 (d, J = 2, C^{12}), 140.4 (s, $\text{C}^{3\text{or}29}$), 140.3 (s, $\text{C}^{3\text{or}29}$), 135.2 (d, J = 4, C^{23}), 134.0 (s, C^{14}), 131.1 (d, J = 2, C^{24}), 128.3 (d, J = 9, $\text{C}^{7\text{or}33}$), 128.0 (d, J = 9, $\text{C}^{7\text{or}33}$), 124.8 (s, $\text{C}^{2\text{or}28}$), 124.7 (s, $\text{C}^{2\text{or}28}$), 122.0 (s, C^{15}), 121.1 (m, $\text{C}^{4\text{or}30}$), 121.0 (d, J = 1, $\text{C}^{4\text{or}30}$), 119.8 (s, C^{17}), 118.8 (d, J = 18, $\text{C}^{10\text{or}36}$), 118.4 (d, J = 18, $\text{C}^{10\text{or}36}$), 117.3 (s, C^{25}), 116.9 (s, C^{21}), 110.9 (dd, J = 23, 17, $\text{C}^{8,34}$), 106.5 (d, J = 3, C^{19}), 56.4 (s, OCH_3); ^{19}F NMR (d_6 -acetone, 376 MHz): δ -72.5 (d, J = 708), -110.7 (d, J = 7), -111.1 (d, J = 3); ES $^+$: 792.6647 $[(\text{M}-2\text{PF}_6)/2]^+$ (mass for $[(\text{C}_{73}\text{H}_{49}\text{F}_4\text{N}_9\text{Ir}_2\text{O})/2] = 792.6689$); R $_f$: 0.31 (DCM : MeOH 99 : 1).

$[\{\text{Ir}(\text{dfppy})_2\}_2(\text{L}^{21})](\text{PF}_6)_2$ (**76**)

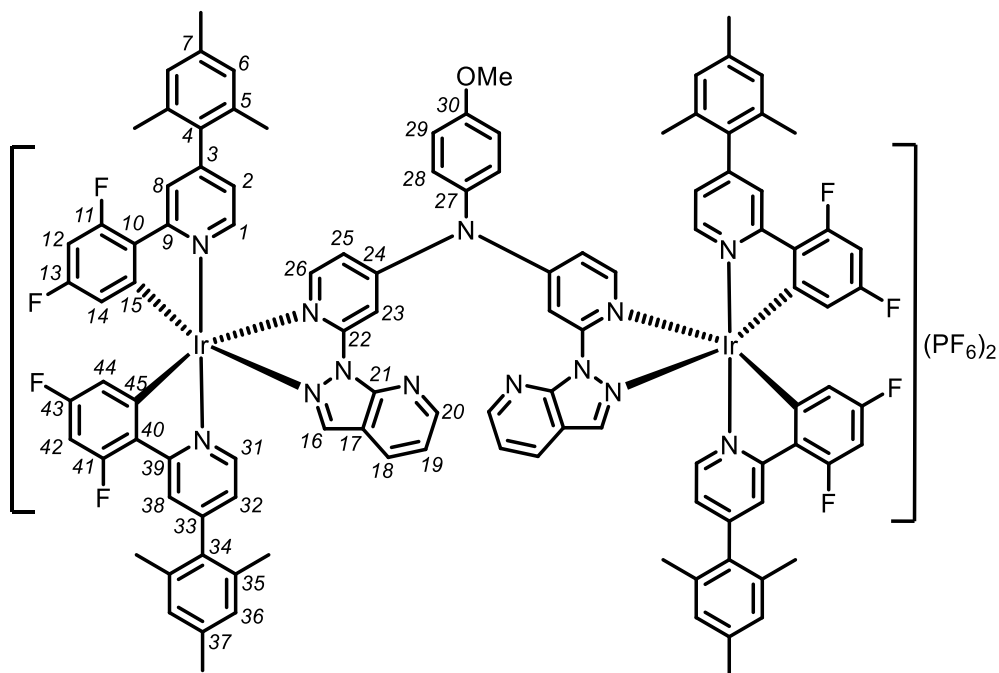


This compound was made following the general procedure for complexes containing bidentate ligands using $[\text{Ir}(\text{dfppy})_2\mu\text{-Cl}]_2$ (72 mg, 60 μmol), ligand **L**²¹ (32 mg, 63 μmol , 1.05 equiv.), MeOH (3 ml) and DCM (5 ml). Column chromatography (silica, DCM : MeOH 0-2%) followed by recrystallization twice from (i) acetone and hexane and (ii) DCM and hexane yielded the title compound as a yellow solid (59 mg, 51%); m.p. 320°C; ¹H NMR (*d*₆-acetone, 700 MHz): δ 9.48 (dd, *J* = 14, 3, 2H, H¹⁹), 8.44 (m, 6H, H^{4or30,14,16}), 8.40 (d, *J* = 8, 2H, H^{4or30}), 8.33 (d, *J* = 1, 2H, H¹²), 8.31 (dt, *J* = 6, 2, 2H, H^{1or27}), 8.18 (m, 2H, H^{1or27}), 8.15 (tt, *J* = 8, 2, 2H, H^{3or29}), 8.07 (td, *J* = 8, 2, 2H, H^{3or29}), 7.81 (d, *J* = 7, 2H, H²²), 7.52 (m, 4H, H^{15,24}), 7.35 (dd, *J* = 7, 3, 1H, H²¹), 7.32 (dd, *J* = 7, 3, 1H, H²¹), 7.29 (dt, *J* = 8, 6, 1, 4H, H^{2,28}), 7.23 (m, 2H, H²⁵), 6.77 (dtd, *J* = 11, 9, 8, 2, 4H, H^{8,34}), 5.86 (dd, *J* = 8, 2, 2H, H^{10or36}), 5.82 (dd, *J* = 8, 2, 2H, H^{10or36}), 3.93 (d, *J* = 2, 3H, OCH₃); ¹³C NMR (*d*₆-acetone, 176 MHz): δ 165.0 (m, C^{5or31}), 164.6 (m, C^{5or31}), 164.5 (m, C^{9or35}), 164.3 (m, C^{9or35}), 162.2 (m, C^{7,33}), 161.5 (s, C²⁶), 156.1 (s, C²⁰), 153.2 (s, C¹⁶), 152.4 (d, *J* = 1, C¹³), 152.0 (s, C¹⁸), 151.7 (m, C^{6,32}), 151.3 (s, C^{1,27}), 150.1 (d, *J* = 4, C²²), 141.5 (d, *J* = 2, C¹²), 141.1 (d, *J* = 15, C^{3,29}), 135.1 (d, *J* = 4, C²³), 134.1 (m, C¹⁴), 131.2 (d, *J* = 3, C²⁴), 129.5 (dd, *J* = 4, 3, C^{11or37}), 129.1 (m, C^{11or37}), 125.4 (s, C^{2or28}), 125.2 (s, C^{2or28}), 124.8 (d, *J* = 9, C^{4or30}), 124.6 (d, *J* = 9, C^{4or30}), 122.1 (m, C¹⁵), 119.8 (s, C¹⁷), 117.4 (s, C²⁵), 117.0 (d, *J* = 3, C²¹), 115.2 (dd, *J* = 18, 2, C^{10or36}), 114.8 (m, C^{10or36}), 106.6 (d, *J* = 4, C¹⁹), 99.9 (m, C^{8,34}), 56.4 (s, OCH₃); ¹⁹F NMR (*d*₆-acetone, 376 MHz): δ -72.5 (d, *J* = 708), -107.7 (dd, *J* = 11, 7), -108.2 (dd, *J* = 11, 2), -110.0 (t, *J* = 10), -110.4 (d, *J* = 11); ES⁺: 828.6447 [(M-2PF₆)/2]⁺ (mass for [(C₇₃H₄₅F₈N₉Ir₂O)/2 = 828.6501]; R_f: 0.19 (DCM : MeOH 98 : 2).

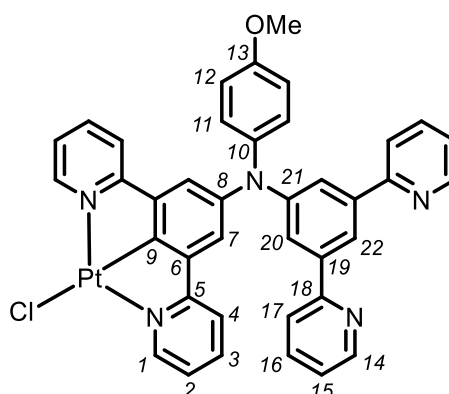
$$[\{\text{Ir}(\text{bis-dfp}_2\text{py})_2\}_2(\text{L}^{21})](\text{PF}_6)_2 \text{ (77)}$$


This compound was made following the general procedure for complexes containing bidentate ligands using $[\text{Ir}(\text{bis-dfp}_2\text{py})_2\mu\text{-Cl}]_2$ (77 mg, 46 μmol), ligand L^{21} (25 mg, 49 μmol , 1.05 equiv.), MeOH (3 ml) and DCM (5 ml). Column chromatography (silica, DCM : MeOH 0-1.5%) yielded the title compound as a yellow solid (15 mg, 14%); m.p. 359°C; ^1H NMR (d_6 -acetone, 700 MHz): δ 9.53 (dd, $J = 19$, 3, 2H, H^{25}), 8.59 (d, $J = 35$, 4H, $\text{H}^{10,42}$), 8.43 (m, 8H, $\text{H}^{10\text{r}33,18,20,22}$), 8.25 (dd, $J = 11$, 6, 2H, $\text{H}^{10\text{r}33}$), 7.88 (m, 4H, $\text{H}^{5\text{or}37,28}$), 7.81 (tdd, $J = 9$, 6, 2, 2H, $\text{H}^{5\text{or}37}$), 7.55 (m, 2H, H^{30}), 7.48 (tt, $J = 8$, 4, 6H, $\text{H}^{2,34,21}$), 7.41 (dd, $J = 7$, 3, 1H, H^{27}), 7.38 (dd, $J = 7$, 3, 1H, H^{27}), 7.26 (m, 10H, $\text{H}^{6,8,38,40,31}$), 6.82 (m, 4H, $\text{H}^{14,46}$), 5.99 (m, 4H, $\text{H}^{16,48}$), 3.93 (d, $J = 2$, 3H, OCH_3); ^{13}C NMR (d_6 -acetone, 176 MHz): δ 167.5 (m, $\text{C}^{7,39}$), 165.2 (d, $J = 1$, $\text{C}^{11\text{or}43}$), 164.9 (d, $J = 2$, $\text{C}^{11\text{or}43}$), 164.4 (m, $\text{C}^{9,41}$), 163.5 (m, $\text{C}^{15,47}$), 162.6 (m, $\text{C}^{13,45}$), 161.6 (s, C^{32}), 156.2 (s, C^{26}), 153.2 (s, $\text{C}^{3,35}$), 153.2 (s, C^{22}), 152.4 (d, $J = 2$, C^{19}), 152.1 (d, $J = 2$, C^{24}), 151.3 (s, $\text{C}^{10\text{r}33}$), 151.0 (s, $\text{C}^{10\text{r}33}$), 150.3 (d, $J = 6$, C^{28}), 147.0 (s, $\text{C}^{4,36}$), 141.7 (s, $\text{C}^{12,44}$), 141.7 (s, C^{18}), 135.1 (s, C^{29}), 134.2 (s, C^{20}), 133.3 (m, $\text{C}^{5,37}$), 131.3 (m, C^{30}), 129.4 (m, $\text{C}^{17\text{or}49}$), 129.0 (m, $\text{C}^{17\text{or}49}$), 124.7 (m, $\text{C}^{2,34}$), 124.0 (m, $\text{C}^{10,42}$), 122.1 (s, C^{21}), 119.9 (s, C^{23}), 117.4 (s, C^{31}), 117.1 (s, C^{27}), 115.5 (s, $\text{C}^{16\text{or}48}$), 115.4 (s, $\text{C}^{16\text{or}48}$), 113.8 (m, $\text{C}^{6,38\text{or}8,40}$), 106.7 (d, $J = 8$, C^{25}), 106.0 (d, $J = 9$, $\text{C}^{6,38\text{or}8,40}$), 100.1 (m, $\text{C}^{14,46}$), 56.4 (s, OCH_3); ^{19}F NMR (d_6 -acetone, 376 MHz): δ -72.5 (d, $J = 708$), -107.1 (dd, $J = 11$, 3), -107.7 (d, $J = 11$), -108.2 (dd, $J = 9$, 4), -108.2 (d, $J = 9$), -109.7 (dd, $J = 11$, 6), -110.0 (d, $J = 11$), -113.0 (d, $J = 9$), -113.1 (dd, $J = 9$, 4); ES $^+$: 1052.6677 $[(\text{M}-2\text{PF}_6)/2]^+$ (mass for $[(\text{C}_{109}\text{H}_{85}\text{F}_8\text{N}_{13}\text{Ir}_2\text{O})/2 = 1052.6750]$; R $_f$: 0.31 (DCM : MeOH 98 : 2).

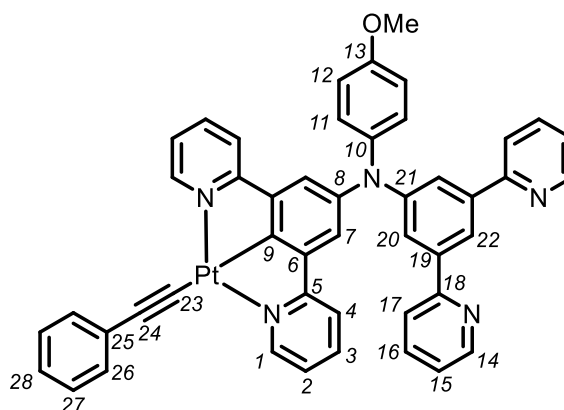
$[\{\text{Ir}(\text{mes-dfppy})_2\}_2(\text{L}^{21})](\text{PF}_6)_2$ (**78**)



This compound was made following the general procedure for complexes containing bidentate ligands using $[\text{Ir}(\text{mes-dfppy})_2\mu\text{-Cl}]_2$ (49 mg, 29 μmol), ligand L^{21} (16 mg, 32 μmol , 1.1 equiv.), MeOH (3 ml) and DCM (5 ml). Column chromatography (alumina, DCM : MeOH 0-2%) followed by recrystallization twice from acetone and hexane yielded the title compound as a yellow solid (34 mg, 49%); m.p. 345°C; ^1H NMR (d_6 -acetone, 600 MHz): δ 9.55 (dd, $J = 8, 3$, 2H, H^{23}), 8.46 (m, 6H, $\text{H}^{16,18,20}$), 8.39 (td, $J = 6, 1$, 2H, $\text{H}^{10,31}$), 8.30 (ddd, $J = 8, 6, 1$, 2H, $\text{H}^{10,31}$), 8.17 (dt, $J = 15, 2$, 4H, $\text{H}^{8,38}$), 7.94 (d, $J = 7$, 2H, H^{26}), 7.55 (m, 2H, H^{28}), 7.52 (dd, $J = 8, 5$, 2H, H^{19}), 7.40 (ddd, $J = 9, 7, 3$, 2H, H^{25}), 7.26 (m, 2H, H^{29}), 7.17 (dd, $J = 6, 2$, 2H, $\text{H}^{20,32}$), 7.14 (dt, $J = 6, 2$, 2H, $\text{H}^{20,32}$), 7.03 (d, $J = 8$, 4H, $\text{H}^{6,36}$), 6.97 (d, $J = 15$, 4H, $\text{H}^{6,36}$), 6.76 (dtd, $J = 11, 9, 2$, 4H, $\text{H}^{12,42}$), 5.94 (dd, $J = 9, 2$, 2H, $\text{H}^{14,44}$), 5.88 (dt, $J = 9, 2$, 2H, $\text{H}^{14,44}$), 3.94 (s, 3H, OCH_3), 2.31 (d, $J = 6$, 12H, $^{5\text{or}35}\text{-CH}_3$), 2.14 (d, $J = 6$, 12H, $^{5\text{or}35}\text{-CH}_3$), 1.97 (s, 6H, $^{7\text{or}37}\text{-CH}_3$), 1.88 (s, 6H, $^{7\text{or}37}\text{-CH}_3$); ^{13}C NMR (d_6 -acetone, 151 MHz): δ 165.3 (m, $\text{C}^{9\text{or}39}$), 164.9 (m, $\text{C}^{9\text{or}39}$), 164.7 (m, $\text{C}^{13\text{or}43}$), 164.4 (m, $\text{C}^{13\text{or}43}$), 162.2 (m, $\text{C}^{11,41}$), 161.6 (s, C^{30}), 156.2 (s, C^{24}), 154.4 (d, $J = 5$, $\text{C}^{3\text{or}33}$), 154.3 (m, $\text{C}^{3\text{or}33}$), 153.1 (d, $J = 8$, C^{20}), 152.4 (s, C^{17}), 152.1 (s, C^{22}), 151.8 (d, $J = 5$, $\text{C}^{10,40}$), 151.3 (dd, $J = 16, 7$, $\text{C}^{1,31}$), 150.3 (s, C^{26}), 141.7 (s, C^{16}), 139.2 (d, $J = 6$, $\text{C}^{7,37}$), 136.0 (s, $\text{C}^{4,34}$), 135.8 (d, $J = 9$, $\text{C}^{5\text{or}35}$), 135.5 (d, $J = 7$, $\text{C}^{5\text{or}35}$), 135.1 (s, C^{27}), 134.2 (s, C^{18}), 131.2 (s, C^{28}), 129.6 (m, $\text{C}^{6,36}$), 129.6 (s, $\text{C}^{15\text{or}45}$), 129.2 (s, $\text{C}^{15\text{or}45}$), 126.4 (d, $J = 11$, $\text{C}^{2,32}$), 125.7 (dd, $J = 20, 14$, $\text{C}^{8,38}$), 122.1 (d, $J = 3$, C^{19}), 119.9 (s, C^{21}), 117.8, 117.4 (s, C^{29}), 117.0 (s, C^{25}), 115.2 (dd, $J = 17, 3$, $\text{C}^{14\text{or}44}$), 114.7 (d, $J = 17$, $\text{C}^{14\text{or}44}$), 106.8 (d, $J = 3$, C^{23}), 100.1 (td, $J = 28, 27, 13$, $\text{C}^{12,42}$), 56.4 (s, OCH_3), 21.2 (s, 12H, $^{7,37}\text{-CH}_3$), 20.7 (m, 24H, $^{5,35}\text{-CH}_3$); ^{19}F NMR (d_6 -acetone, 376 MHz): δ -72.5 (d, $J = 708$), -107.6 (t, $J = 11$), -108.1 (d, $J = 10$), -109.8 (dd, $J = 14, 11$), -110.2 (dd, $J = 10, 5$); ES^+ : 1064.8033 $[(\text{M}-2\text{PF}_6)/2]^+$ (mass for $[(\text{C}_{97}\text{H}_{53}\text{F}_{16}\text{N}_{13}\text{Ir}_2\text{O})/2 = 1064.8066]$; R_f : 0.49 (DCM : MeOH 99 : 1).

Pt(HL²²)Cl (79)

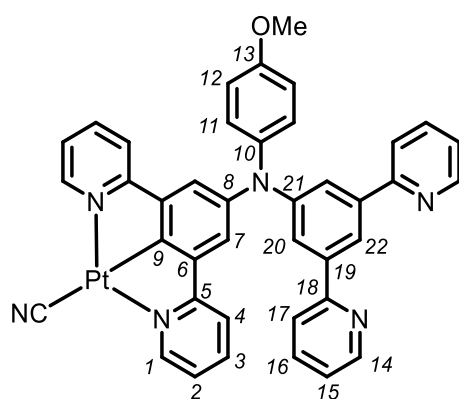
This complex was made following the modified procedure for the synthesis of platinum complexes using K_2PtCl_4 (0.10 g, 0.24 mmol), ligand H_2L^{22} (0.15 g, 0.25 mmol, 1.05 equiv.), MeCN (7.5 ml) and H_2O (2.5 ml). Column chromatography (silica, DCM : MeOH 0-2%) followed by recrystallization from DCM and hexane yielded the title compound as an orange solid (13 mg, 7%); m.p. 328°C; ^1H NMR (CDCl_3 , 700 MHz): δ 9.28 (m, 2H, H^1), 8.59 (dt, $J = 5, 2$, 2H, H^{14}), 8.14 (t, $J = 1$, 1H, H^{22}), 7.82 (td, $J = 8, 1$, 2H, H^3), 7.69 (d, $J = 1$, 2H, H^{20}), 7.66 (m, 4H, $\text{H}^{16,17}$), 7.48 (d, $J = 8$, 2H, H^4), 7.32 (s, 2H, H^7), 7.21 (ddd, $J = 8, 6, 1$, 2H, H^2), 7.16 (m, 2H, H^{15}), 7.13 (m, 2H, H^{11}), 6.82 (m, 2H, H^{12}), 3.76 (s, 3H, OCH_3); ^{13}C NMR (CDCl_3 , 176 MHz): δ 167.0 (s, C^5), 157.2 (s, C^{18}), 156.5 (m, C^9), 155.9 (s, C^{13}), 152.4 (s, C^1), 149.7 (s, C^{19}), 149.6 (s, C^{14}), 144.5 (s, C^8), 142.1 (s, C^6), 141.3 (s, C^{21}), 141.0 (s, C^{10}), 139.2 (s, C^3), 136.9 (s, C^{17}), 126.1 (s, C^{11}), 123.5 (s, C^2), 122.5 (s, C^{15}), 122.5 (s, C^7), 121.1 (s, C^{20}), 121.0 (s, C^{16}), 119.8 (s, C^4), 119.2 (s, C^{22}), 115.1 (s, C^{12}), 55.6 (s, OCH_3); ASAP: 817.2177 $[\text{M}-\text{Cl}+\text{MeCN}+\text{H}]^+$ (mass for $\text{C}_{41}\text{H}_{31}\text{N}_6\text{OPt} = 817.2186$); R_f : 0.44 (DCM : MeOH 98 : 2).

Pt(HL²²)(CCPh) (80)

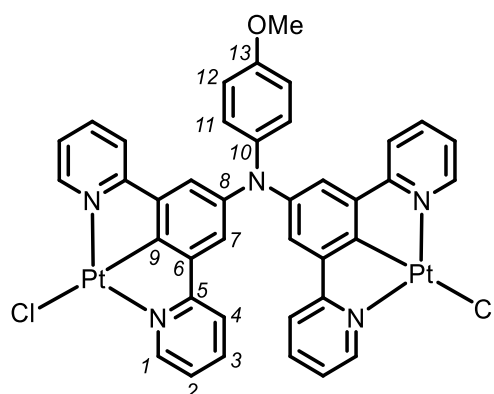
In Schlenk tube A: phenylacetylene (85 μl , 0.78 mmol, 5 equiv.) was added to a 0.5 M solution of sodium methoxide (43 mg, 0.78 mmol) in dry MeOH (2.6 ml). In Schlenk tube B: complex **79** (0.126 g, 0.155 mmol) was added to dry MeOH (60 ml) and dry DCM (20 ml). After stirring both Schlenk tubes for 30 minutes at RT, the contents of Schlenk tube B was transferred to Schlenk tube A via syringe and the reaction was heated at 60°C under nitrogen for 3 days. Upon cooling to RT, the

solvents were removed under reduced pressure. Washing with H₂O, MeOH and hexane yielded the title compound as a yellow solid (85 mg, 63%); m.p. 297°C; ¹H NMR (CDCl₃, 700 MHz): δ 9.49 (m, 2H, H¹), 8.63 (m, 2H, H¹⁴), 8.17 (t, *J* = 2, 1H, H²²), 7.84 (td, *J* = 8, 2, 2H, H³), 7.70 (m, 6H, H^{16,17,20}), 7.58 (m, 2H, H²⁶), 7.52 (m, 2H, H⁴), 7.41 (s, 2H, H⁷), 7.27 (m, 3H, H^{27,28}), 7.18 (m, 6H, H^{2,11,15}), 6.86 (m, 2H, H¹²), 3.81 (s, 3H, OCH₃); ¹³C NMR (CDCl₃, 176 MHz): δ 169.4 (s, C⁵), 157.3 (s, C¹⁸), 155.8 (s, C¹³), 155.7 (s, C¹), 149.9 (s, C¹⁹), 149.7 (s, C¹⁴), 144.6 (s, C⁸), 144.4 (s, C⁶), 141.3 (s, C²¹), 141.2 (s, C¹⁰), 138.7 (s, C³), 136.8 (s, C¹⁷), 136.1 (m, C⁹), 131.8 (s, C²⁶), 128.1 (s, C^{27,28}), 126.1 (s, C¹¹), 125.4 (s, C²³), 123.7 (s, C²), 122.5 (s, C⁷), 122.4 (s, C¹⁵), 121.0 (s, C¹⁶), 120.9 (s, C²⁰), 119.8 (s, C⁴), 119.0 (s, C²²), 115.0 (s, C¹²), 112.1 (m, C²⁵), 79.8 (s, C²⁴), 55.6 (s, OCH₃); ASAP: 878.2433 [M+H]⁺ (mass for C₄₇H₃₄N₅O₄ = 878.2390).

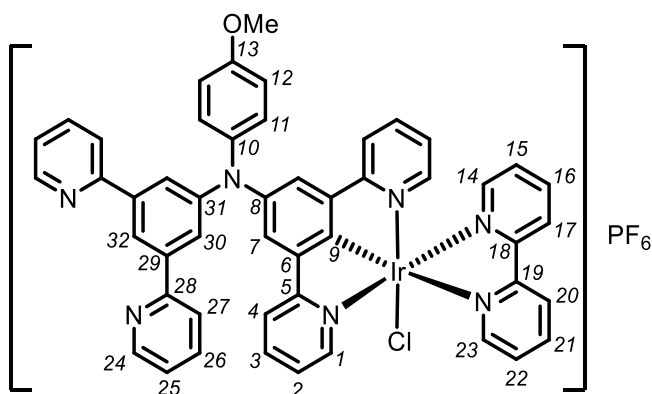
Pt(HL²²)CN (81)



This compound was made following the general procedure for the metathesis of complexes containing tridentate ligands using complex **79** (32 mg, 39 μmol), AgCN (26 mg, 0.20 mmol) and DMF. Column chromatography (alumina, DCM : MeOH : 0-0.5%) yielded the title compound as an orange solid (14 mg, 44%); m.p. 383°C; ¹H NMR (CDCl₃, 700 MHz): δ 9.14 (dd, *J* = 6, 1, 1H, H¹), 8.68 (d, *J* = 5, 2H, H¹⁴), 8.36 (t, *J* = 2, 1H, H²²), 8.07 (td, *J* = 8, 1, 2H, H³), 7.84 (d, *J* = 2, 2H, H²⁰), 7.80 (d, *J* = 8, 2H, H⁴), 7.77 (m, 4H, H^{16,17}), 7.54 (s, 2H, H⁷), 7.44 (ddd, *J* = 8, 6, 1, 2H, H²), 7.27 (m, 2H, H¹⁵), 7.22 (m, 2H, H¹¹), 6.93 (m, 2H, H¹²), 3.85 (s, 3H, OCH₃); ¹³C NMR (CDCl₃, 176 MHz): δ 167.6 (s, C⁵), 157.1 (s, C¹³), 156.5 (s, C¹⁸), 154.3 (s, C¹), 152.3 (m, C⁹), 149.5 (s, C¹⁴), 149.4 (s, C⁸), 148.6 (s, C¹⁹), 142.0 (s, C⁶), 14.6 (s, C²¹), 140.0 (s, C¹⁰), 137.3 (s, C¹⁷), 127.5 (s, C¹¹), 126.1 (s, C²), 124.0 (s, C³), 123.6 (s, C²⁰), 123.2 (s, C⁴), 122.9 (s, C¹⁵), 121.7 (m, C^{7,22}), 121.2 (s, C¹⁶), 115.6 (s, C¹²), 55.7 (s, OCH₃); ASAP: 803.2014 [M+H]⁺ (mass for C₄₀H₂₉N₆PtO = 803.2030); R_f: 0.37 (DCM : MeOH 99 : 1).

$\{PtCl\}_2(L^{22})$ (**82**)

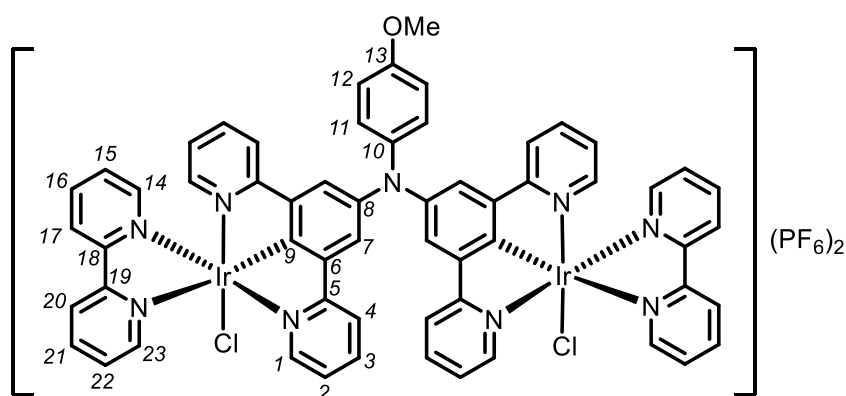
This complex was made following the general procedure for the synthesis of platinum complexes using K_2PtCl_4 (0.30 g, 0.72 mmol, 2.5 equiv.), ligand H_2L^{22} (0.17 g, 0.29 mmol) and glacial acetic acid (12 ml). Recrystallization from DMF and ether yielded the title compound as a red solid (37 mg, 12%); m.p. 363°C; ^1H NMR (d_6 -DMSO, 700 MHz): δ 9.11 (m, 4H, H^1), 8.10 (td, $J = 8, 2$, 4H, H^3), 8.03 (d, $J = 8$, 4H, H^4), 7.58 (s, 4H, H^7), 7.53 (m, 4H, H^2), 7.05 (d, $J = 9$, 2H, H^{11}), 6.91 (d, $J = 9$, 2H, H^{12}), 3.74 (s, 3H, OCH_3); ^{13}C NMR (d_6 -DMSO, 176 MHz): δ 166.2 (s, C^5), 155.2 (m, C^9), 154.5 (s, C^{13}), 151.3 (s, C^1), 144.6 (s, C^6), 141.6 (s, C^8), 140.4 (s, C^3), 135.9 (s, C^{10}), 124.3 (s, C^2), 123.7 (s, C^{11}), 121.7 (s, C^7), 120.8 (s, C^4), 114.9 (s, C^{12}), 55.2 (s, OCH_3); MALDI: 1041.0 $[M]^+$ (mass for $C_{39}H_{27}N_5OPt_2Cl_2 = 1041.0888$); $R_f = 0.56$ (silica, DCM : MeOH 98 : 2).

 $[Ir(HL^{22})(bpy)Cl]PF_6$ (**83**)

This complex was made following the general procedure for complexes containing tridentate ligands using $[Ir(HL^{22})Cl(\mu-Cl)]_2$ (0.24 g, 0.14 mmol), 2,2'-bipyridine (48 mg, 0.31 mmol, 2.2 equiv.), AgOTf (0.16 g, 0.62 mmol) and toluene (24 ml). Column chromatography (alumina, 100% EtOAc followed by DCM : MeOH 0-1.25%) yielded the title compound as an orange solid (0.16 g, 51%); m.p. 321°C; ^1H NMR (d_6 -acetone, 700 MHz): δ 10.02 (ddd, $J = 5, 2, 1$, 1H, H^{14or23}), 8.99 (m, 1H, H^{17or20}), 8.74 (dd, $J = 8, 1$, 1H, H^{17or20}), 8.65 (m, 3H, $H^{16or21,24}$), 8.42 (t, $J = 2$, 1H, H^{32}), 8.34 (ddd, $J = 8, 5, 1$, 1H, H^{15or22}), 8.23 (dd, $J = 8, 1$, 2H, H^4), 8.12 (s, 2H, H^7), 8.05 (m, 1H, H^{16or21}), 8.00 (d, $J = 2$, 2H, H^{30}), 7.96 (dt, $J = 8, 1$, 2H, H^{27}), 7.87 (m, 4H, $H^{3,26}$), 7.83 (ddd, $J = 5, 2, 1$, 3H, $H^{1,14or23}$), 7.39 (m, 3H, $H^{11,15or22}$),

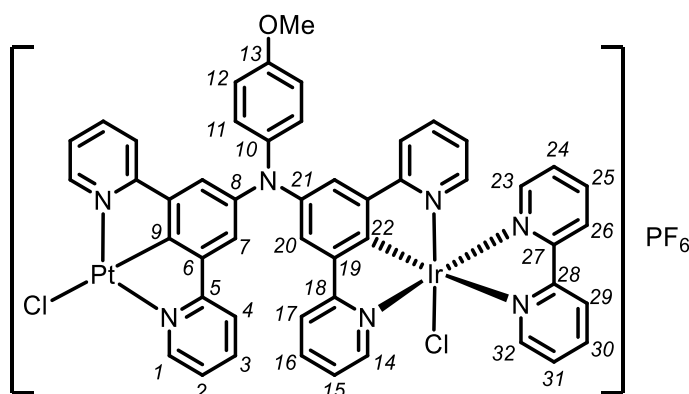
7.33 (ddd, $J = 8, 5, 1$, 2H, H^{25}), 7.19 (ddd, $J = 7, 6, 1$, 2H, H^2), 7.02 (m, 2H, H^{12}), 3.85 (s, 3H, OCH_3); ^{13}C NMR (d_6 -acetone, 176 MHz): δ 169.1 (s, C^5), 166.5 (s, C^8), 159.4 (s, C^{18or19}), 157.5 (s, C^{28}), 157.3 (s, C^{13}), 156.6 (s, C^{18or19}), 154.0 (s, C^{14or23}), 153.3 (s, C^1), 151.1 (s, C^{31}), 150.5 (s, C^{24}), 150.1 (s, C^{14or23}), 146.1 (s, C^9), 143.4 (s, C^6), 141.9 (s, C^{10}), 141.7 (s, C^{29}), 141.2 (s, C^{16or21}), 140.6 (s, C^3), 140.3 (s, C^{16or21}), 137.9 (s, C^{26}), 129.8 (s, C^{15or22}), 129.0 (s, C^{15or22}), 127.6 (s, C^{11}), 125.7 (s, C^{17or20}), 125.6 (s, C^{17or20}), 125.2 (s, C^7), 125.0 (s, C^2), 123.5 (s, C^{25}), 122.2 (s, C^4), 121.2 (s, C^{27}), 120.9 (s, C^{30}), 118.9 (s, C^{32}), 115.9 (s, C^{12}), 55.8 (s, OCH_3); ^{19}F NMR (d_6 -acetone, 376 MHz): δ -72.6 (dd, $J = 707, 2$); ES^+ : 964.2289 $[M-PF_6]^+$ (mass for $C_{49}H_{36}N_7IrOCl = 964.2276$); R_f : 0.51 (DCM : MeOH 99 : 1).

$[Ir(bpy)Cl]_2(L^{22}][PF_6)_2$ (84**)**



This complex was made following the general procedure for complexes containing tridentate ligands using $[Ir(L^{22})Cl-\mu Cl]_2$ (0.10 g, 0.12 mmol), 2,2'-bipyridine (43 mg, 0.27 mmol, 2.2 equiv.), AgOTf (0.14 g, 0.54 mmol) and toluene (10 ml). Column chromatography (silica, DCM : MeOH 0-3%) followed by recrystallization from MeCN, ether and hexane yielded the title compound as a red solid (15 mg, 15%); m.p. 307°C; ^1H NMR (d_3 -MeCN, 700 MHz): δ 9.90 (dd, $J = 5, 1$, 2H, H^{14or23}), 8.66 (dt, $J = 8, 1$, 2H, H^{17or20}), 8.48 (td, $J = 8, 1$, 2H, H^{16or21}), 8.39 (dt, $J = 8, 1$, 2H, H^{17or20}), 8.17 (ddd, $J = 8, 5, 1$, 2H, H^{15or22}), 8.00 (m, 8H, $H^{4,7}$), 7.87 (m, 2H, H^{16or21}), 7.80 (ddd, $J = 8, 7, 1$, 4H, H^3), 7.68 (ddd, $J = 6, 1, 0.9$, 2H, H^{14or23}), 7.62 (dd, $J = 6, 1$, 4H, H^1), 7.37 (m, 2H, H^{11}), 7.24 (ddd, $J = 7, 6, 1$, 2H, H^{15or22}), 7.08 (ddd, $J = 7, 6, 1$, 4H, H^2), 7.04 (m, 2H, H^{12}), 3.84 (s, 3H, OCH_3); ^{13}C NMR (d_3 -MeCN, 176 MHz): δ 168.9 (s, C^5), 164.8 (s, C^8), 159.0 (s, C^{18or19}), 156.6 (s, C^{13}), 156.4 (s, C^{18or19}), 154.4 (s, C^{14or23}), 153.3 (s, C^1), 150.1 (s, C^{14or23}), 146.9 (s, C^6), 143.1 (s, C^9), 143.1 (s, C^{10}), 141.0 (s, C^{16or21}), 140.6 (s, C^3), 140.1 (s, C^{16or21}), 129.8 (s, C^{15or22}), 128.9 (s, C^{15or22}), 125.9 (s, C^{11}), 125.5 (s, C^{17or20}), 125.5 (s, C^{17or20}), 125.0 (s, C^2), 123.9 (s, C^7), 122.1 (s, C^4), 115.9 (s, C^{12}), 56.2 (s, OCH_3); ^{19}F NMR (d_3 -MeCN, 376 MHz): δ -72.9 (d, $J = 707$); ES^+ : 674.6052 $[M-2PF_6/2]^+$ (mass for $[(C_{59}H_{43}N_9Ir_2OCl_2)/2 = 674.6113]$); R_f : 0.13 (DCM : MeOH 98 : 2).

$[\{\text{Ir}(\text{bpy})\text{Cl}\}\{\text{L}^{22}\}\{\text{PtCl}\}]\text{PF}_6$ (**85**)



This complex was made following the general procedure for complexes containing tridentate ligands using $\text{Ir}(\text{PtL}^{22})\text{Cl}\mu\text{-Cl}]_2$ (0.14 g, 65 μmol), 2,2'-bipyridine (22 mg, 0.14 mmol, 2.2 equiv.), AgOTf (73 mg, 0.28 mmol) and toluene (14 ml). Column chromatography (alumina, DCM : MeOH 0-3%) followed by recrystallization from acetone and hexane yielded the title compound as a red solid (6 mg, 11%); m.p. 333°C; ^1H NMR (d_3 -MeCN, 700 MHz): δ 9.89 (m, 1H, $\text{H}^{23\text{or}32}$), 9.16 (m, 2H, H^1), 8.64 (d, $J = 8$, 1H, $\text{H}^{26\text{or}29}$), 8.46 (td, $J = 8$, 1, 1H, $\text{H}^{25\text{or}30}$), 8.37 (m, 1H, $\text{H}^{26\text{or}29}$), 8.16 (ddd, $J = 8$, 6, 1, 1H, $\text{H}^{24\text{or}31}$), 8.00 (td, $J = 8$, 2, 2H, H^3), 7.96 (m, 2H, H^{17}), 7.88 (s, 2H, H^{20}), 7.85 (td, $J = 8$, 1, 1H, $\text{H}^{25\text{or}30}$), 7.75 (m, 4H, $\text{H}^{4,16}$), 7.63 (dt, $J = 6$, 1, 1H, $\text{H}^{23\text{or}32}$), 7.59 (m, 4H, $\text{H}^{7,14}$), 7.36 (ddd, $J = 7$, 6, 1, 2H, H^2), 7.26 (m, 2H, H^{11}), 7.22 (ddd, $J = 7$, 6, 1, 1H, $\text{H}^{24\text{or}31}$), 7.04 (ddd, $J = 7$, 6, 1, 2H, H^{15}), 6.97 (m, 2H, H^{12}), 3.81 (s, 3H, OCH_3); ^{13}C NMR (d_3 -MeCN, 176 MHz): δ 168.9 (s, C^{18}), 167.8 (s, C^5), 164.2 (s, C^{21}), 159.0 (s, $\text{C}^{27\text{or}28}$), 156.8 (m, C^9), 156.5 (s, C^{13}), 156.4 (s, $\text{C}^{27\text{or}28}$), 154.4 (s, $\text{C}^{23\text{or}32}$), 153.3 (s, C^{14}), 152.5 (s, C^1), 150.1 (s, $\text{C}^{23\text{or}32}$), 146.9 (s, C^{22}), 146.1 (s, C^8), 143.0 (s, C^6), 142.9 (s, C^{19}), 142.7 (s, C^{10}), 141.0 (s, $\text{C}^{25\text{or}30}$), 140.8 (s, C^3), 140.6 (s, C^{16}), 140.1 (s, $\text{C}^{25\text{or}30}$), 129.8 (s, $\text{C}^{24\text{or}31}$), 128.9 (s, $\text{C}^{24\text{or}31}$), 125.9 (s, C^{11}), 125.5 (s, $\text{C}^{26\text{or}29}$), 125.4 (s, $\text{C}^{26\text{or}29}$), 124.9 (s, C^{15}), 124.9 (s, C^2), 123.1 (s, C^{20}), 122.9 (s, C^7), 122.1 (s, C^{17}), 121.1 (s, C^4), 115.9 (s, C^{12}), 56.1 (s, OCH_3); ^{19}F NMR (d_3 -MeCN, 376 MHz): δ -72.9 (d, $J = 706$); ES^+ : 600.6030 $[(\text{M}-\text{PF}_6)-\text{Cl}+\text{MeCN}]/2]^+$ (mass for $(\text{C}_{51}\text{H}_{38}\text{N}_8\text{IrOPtCl})/2 = 600.6067$); R_f : 0.56 (DCM : MeOH 99 : 1).

Alternative Synthesis 1: Following the general procedure for the synthesis of platinum complexes using complex **83** (79 mg, 71 μmol), K_2PtCl_4 (35 mg, 85 μmol , 1.2 equiv.) and glacial acetic acid (10 ml). Column chromatography (silica, DCM : MeOH 0-2.5%) followed by recrystallization from acetone and hexane yielded the title compound (14 mg, 16%).

Alternative Synthesis 2: Following the modified procedure for the synthesis of platinum complexes using complex **83** (79 mg, 71 μmol), K_2PtCl_4 (35 mg, 85 μmol , 1.2 equiv.), MeCN (9 ml) and H_2O (3 ml). Column chromatography (silica, DCM : MeOH 0-2.5%) followed by recrystallization from acetone and hexane yielded the title compound (10 mg, 11%).

Bibliography

- 1 H. H. Jaffe and A. L. Miller, *J. Chem. Educ.*, 1966, **43**, 469.
- 2 A. Jablonski, *Nature*, 1933, **131**, 839–840.
- 3 A. Hofmann, L. Dahlenburg and R. van Eldik, *Inorg. Chem.*, 2003, **42**, 6528–6538.
- 4 J. A. G. Williams, A. Beeby, E. S. Davies, J. A. Weinstein and C. Wilson, *Inorg. Chem.*, 2003, **42**, 8609–8611.
- 5 K. Li, G. S. Ming Tong, Q. Wan, G. Cheng, W. Y. Tong, W. H. Ang, W. L. Kwong and C. M. Che, *Chem. Sci.*, 2016, **7**, 1653–1673.
- 6 K. Huang and A. Rhys, *Proc. R. Soc. A*, 1950, **204**, 406–423.
- 7 D. A. K. Vezzu, J. C. Deaton, J. S. Jones, L. Bartolotti, C. F. Harris, A. P. Marchetti, M. Kondakova, R. D. Pike and S. Huo, *Inorg. Chem.*, 2010, **49**, 5107–5119.
- 8 M. Maestri, D. Sandrini, V. Balzani, L. Chassot, P. Jolliet and A. von Zelewsky, *Chem. Phys. Lett.*, 1985, **122**, 375–379.
- 9 K. K. W. Lo, A. W. T. Choi and W. H. T. Law, *Dalton Trans.*, 2012, **41**, 6021–6047.
- 10 X. Li, X. Tong, Y. Yin, H. Yan, C. Lu, W. Huang and Q. Zhao, *Chem. Sci.*, 2017, **8**, 5930–5940.
- 11 S. Monro, K. L. Colón, H. Yin, J. Roque, P. Konda, S. Gujar, R. P. Thummel, L. Lilge, C. G. Cameron and S. A. McFarland, *Chem. Rev.*, 2019, **119**, 797–828.
- 12 R. E. Doherty, I. V Sazanovich, L. K. McKenzie, A. S. Stasheuski, R. Coyle, E. Baggaley, S. Bottomley, J. A. Weinstein and H. E. Bryant, *Sci. Rep.*, 2016, **6**, 22668.
- 13 L. K. McKenzie, I. V Sazanovich, E. Baggaley, M. Bonneau, V. Guerschais, J. A. G. Williams, J. A. Weinstein and H. E. Bryant, *Chem. Eur. J.*, 2017, **23**, 234–238.
- 14 S. Banerjee, M. S. Capper, G. J. Clarkson, H. Huang and P. J. Sadler, *Polyhedron*, 2019, **172**, 157–166.
- 15 R. D. Costa, E. Ortí, H. J. Bolink, F. Monti, G. Accorsi and N. Armaroli, *Angew. Chem. Int. Ed.*, 2012, **51**, 8178–8211.
- 16 E. Fresta and R. D. Costa, *J. Mater. Chem. C*, 2017, **5**, 5643–5675.
- 17 S. B. Meier, D. Tordera, A. Pertegás, C. Roldán-Carmona, E. Ortí and H. J. Bolink, *Mater. Today*, 2014, **17**, 217–223.
- 18 Q. Pei, Y. Yang, G. Yu, C. Zhang and A. J. Heeger, *J. Am. Chem. Soc.*, 1996, **118**, 3922–3929.
- 19 J. D. Slinker, J. A. DeFranco, M. J. Jaquith, W. R. Silveira, Y.-W. Zhong, J. M. Moran-Mirabal, H. G. Craighead, H. D. Abruña, J. A. Marohn and G. G. Malliaras, *Nat. Mater.*, 2007, **6**, 894–899.
- 20 S. van Reenen, P. Matyba, A. Dzwilewski, R. A. J. Janssen, L. Edman and M. Kemerink, *J. Am. Chem. Soc.*, 2010, **132**, 13776–13781.
- 21 A. Asadpoordarvish, A. Sandström, C. Larsen, R. Bollström, M. Toivakka, R. Österbacka and L. Edman, *Adv. Funct. Mater.*, 2015, **25**, 3238–3245.
- 22 Z. Yu, X. Niu, Z. Liu and Q. Pei, *Adv. Mater.*, 2011, **23**, 3989–3994.
- 23 Y. Shen, D. D. Kuddes, C. A. Naquin, T. W. Hesterberg, C. Kusmierz, B. J. Holliday and J. D. Slinker, *Appl. Phys. Lett.*, 2013, **102**, 203305.
- 24 R. Sun, C. T. Liao and H. C. Su, *Org. Electron.*, 2014, **15**, 2885–2892.

- 25 S. Tang, P. Murto, J. Wang, C. Larsen, M. R. Andersson, E. Wang and L. Edman, *Adv. Opt. Mater.*, 2019, **7**, 1900451.
- 26 A. Pertegás, N. M. Shavaleev, D. Tordera, E. Ortí, M. K. Nazeeruddin and H. J. Bolink, *J. Mater. Chem. C*, 2014, **2**, 1605–1611.
- 27 S. Tang, H. A. Buchholz and L. Edman, *J. Mater. Chem. C*, 2015, **3**, 8114–8120.
- 28 H. C. Shih, B. R. Chiou and H. C. Su, *J. Mater. Chem. C*, 2016, **4**, 5610–5616.
- 29 C. Roldán-Carmona, T. Akatsuka, M. Sessolo, S. E. Watkins and H. J. Bolink, *ACS Appl. Mater. Interfaces*, 2014, **6**, 19520–19524.
- 30 Y. P. Jhang, H. F. Chen, H. B. Wu, Y. S. Yeh, H. C. Su and K. T. Wong, *Org. Electron.*, 2013, **14**, 2424–2430.
- 31 X. Li, J. Gao and G. Liu, *Org. Electron.*, 2013, **14**, 1441–1446.
- 32 N. M. Shavaleev, R. Scopelliti, M. Grätzel, M. K. Nazeeruddin, A. Pertegás, C. Roldán-Carmona, D. Tordera and H. J. Bolink, *J. Mater. Chem. C*, 2013, **1**, 2241–2248.
- 33 D. Tordera, J. Frey, D. Vonlanthen, E. Constable, A. Pertegás, E. Ortí, H. J. Bolink, E. Baranoff and M. K. Nazeeruddin, *Adv. Energy Mater.*, 2013, **3**, 1338–1343.
- 34 D. Tordera, S. Meier, M. Lenes, R. D. Costa, E. Ortí, W. Sarfert and H. J. Bolink, *Adv. Mater.*, 2012, **24**, 897–900.
- 35 F. Brunner, A. Babaei, A. Pertegás, J. M. Junquera-Hernández, A. Prescimone, E. C. Constable, H. J. Bolink, M. Sessolo, E. Ortí and C. E. Housecroft, *Dalton Trans.*, 2019, **48**, 446–460.
- 36 S. Keller, A. Pertegás, G. Longo, L. Martínez, J. Cerdá, J. M. Junquera-Hernández, A. Prescimone, E. C. Constable, C. E. Housecroft, E. Ortí and H. J. Bolink, *J. Mater. Chem. C*, 2016, **4**, 3857–3871.
- 37 S. Keller, E. C. Constable, C. E. Housecroft, M. Neuburger, A. Prescimone, G. Longo, A. Pertegás, M. Sessolo and H. J. Bolink, *Dalton Trans.*, 2014, **43**, 16593–16596.
- 38 S. Keller, A. Prescimone, H. Bolink, M. Sessolo, G. Longo, L. Martínez-Sarti, J. M. Junquera-Hernández, E. C. Constable, E. Ortí and C. E. Housecroft, *Dalton Trans.*, 2018, **47**, 14263–14276.
- 39 S. Keller, F. Brunner, J. M. Junquera-Hernández, A. Pertegás, M. G. La-Placa, A. Prescimone, E. C. Constable, H. J. Bolink, E. Ortí and C. E. Housecroft, *Chempluschem*, 2018, **83**, 217–229.
- 40 C. L. Linfoot, M. J. Leidl, P. Richardson, A. F. Rausch, O. Chepelin, F. J. White, H. Yersin and N. Robertson, *Inorg. Chem.*, 2014, **53**, 10854–10861.
- 41 E. Fresta, G. Volpi, M. Milanesio, C. Garino, C. Barolo and R. D. Costa, *Inorg. Chem.*, 2018, **57**, 10469–10479.
- 42 M. Alkan-Zambada, S. Keller, L. Martínez-Sarti, A. Prescimone, J. M. Junquera-Hernández, E. C. Constable, H. J. Bolink, M. Sessolo, E. Ortí and C. E. Housecroft, *J. Mater. Chem. C*, 2018, **6**, 8460–8471.
- 43 M. D. Weber, M. Viciano-Chumillas, D. Armentano, J. Cano and R. D. Costa, *Dalton Trans.*, 2017, **46**, 6312–6323.
- 44 J. J. Cid, J. Mohanraj, M. Mohankumar, M. Holler, F. Monti, G. Accorsi, L. Karmazin-Brelot, I. Nierengarten, J. M. Malicka, M. Cocchi, B. Delavaux-Nicot, N. Armaroli and J. F. Nierengarten, *Polyhedron*, 2014, **82**, 158–172.

- 45 M. Elie, F. Sguerra, F. Di Meo, M. D. Weber, R. Marion, A. Grimault, J. F. Lohier, A. Stallivieri, A. Brosseau, R. B. Pansu, J. L. Renaud, M. Linares, M. Hamel, R. D. Costa and S. Gaillard, *ACS Appl. Mater. Interfaces*, 2016, **8**, 14678–14691.
- 46 M. D. Weber, E. Fresta, M. Elie, M. E. Miehlisch, J. L. Renaud, K. Meyer, S. Gaillard and R. D. Costa, *Adv. Funct. Mater.*, 2018, **28**, 1707423.
- 47 D. A. W. Ross, P. A. Scattergood, A. Babaei, A. Pertegás, H. J. Bolink and P. I. P. Elliott, *Dalton Trans.*, 2016, **45**, 7748–7757.
- 48 B. Nemati Bideh and H. Shahroosvand, *Sci. Rep.*, 2017, **7**, 15739.
- 49 M. V Werrett, G. S. Huff, S. Muzzioli, V. Fiorini, S. Zacchini, B. W. Skelton, A. Maggiore, J. M. Malicka, M. Cocchi, K. C. Gordon, S. Stagni and M. Massi, *Dalton Trans.*, 2015, **44**, 8379–8393.
- 50 K. T. Weber, K. Karikis, M. D. Weber, P. B. Coto, A. Charisiadis, D. Charitaki, G. Charalambidis, P. Angaridis, A. G. Coutsolelos and R. D. Costa, *Dalton Trans.*, 2016, **45**, 13284–13288.
- 51 M. V Werrett, D. Chartrand, J. D. Gale, G. S. Hanan, J. G. MacLellan, M. Massi, S. Muzzioli, P. Raiteri, B. W. Skelton, M. Silberstein and S. Stagni, *Inorg. Chem.*, 2011, **50**, 1229–1241.
- 52 C. E. Housecroft and E. C. Constable, *Coord. Chem. Rev.*, 2017, **350**, 155–177.
- 53 D. Ma, T. Tsuboi, Y. Qiu and L. Duan, *Adv. Mater.*, 2017, **29**, 1603253.
- 54 Y. Ohsawa, S. Sprouse, K. A. King, M. K. DeArmond, K. W. Hanck and R. J. Watts, *J. Phys. Chem.*, 1987, **91**, 1047–1054.
- 55 J. D. Slinker, A. A. Gorodetsky, M. S. Lowry, J. Wang, S. Parker, R. Rohl, S. Bernhard and G. G. Malliaras, *J. Am. Chem. Soc.*, 2004, **126**, 2763–2767.
- 56 K. J. Suhr, L. D. Bastatas, Y. Shen, L. A. Mitchell, G. A. Frazier, D. W. Taylor, J. D. Slinker and B. J. Holliday, *Dalton Trans.*, 2016, **45**, 17807–17823.
- 57 K. J. Suhr, L. D. Bastatas, Y. Shen, L. A. Mitchell, B. J. Holliday and J. D. Slinker, *ACS Appl. Mater. Interfaces*, 2016, **8**, 8888–8892.
- 58 D. Rota Martir, P. Rajamalli, D. B. Cordes, A. M. Z. Slawin and E. Zysman-Colman, *Macromol. Rapid Commun.*, 2018, **39**, 1800501.
- 59 P. Li, G. G. Shan, H. T. Cao, D. X. Zhu, Z. M. Su, R. Jitchati and M. R. Bryce, *Eur. J. Inorg. Chem.*, 2014, **2014**, 2376–2382.
- 60 C. Hierlinger, D. B. Cordes, A. M. Z. Slawin, A. Colombo, C. Dragonetti, S. Righetto, D. Roberto, D. Jacquemin, E. Zysman-Colman and V. Guerchais, *Dalton Trans.*, 2018, **47**, 8292–8300.
- 61 D. R. Whang, K. Sakai and S. Y. Park, *Angew. Chem. Int. Ed.*, 2013, **52**, 11612–11615.
- 62 B. Tong, P. Ma, Q. Mei and Z. Hua, *Inorg. Chim. Acta*, 2014, **421**, 405–409.
- 63 V. Thamilarasan, P. Karunakaran, N. Kavitha, C. Selvaraju and N. Sengottuvelan, *Polyhedron*, 2016, **118**, 12–24.
- 64 B. Tong, J. Qiang, Q. Mei, H. Wang, Q. Zhang and Z. Han, *Z. Naturforsch. B*, 2012, **67**, 213–218.
- 65 T. Li, M. Cui, G. Ran and Q. Song, *Dyes Pigm.*, 2015, **112**, 1–7.
- 66 H. Ahmad, A. Wragg, W. Cullen, C. Wombwell, A. J. H. M. Meijer and J. A. Thomas, *Chem. Eur. J.*, 2014, **20**, 3089–3096.

- 67 B. F. DiSalle and S. Bernhard, *J. Am. Chem. Soc.*, 2011, **133**, 11819–11821.
- 68 H. C. Su, F. C. Fang, T. Y. Hwu, H. H. Hsieh, H. F. Chen, G. H. Lee, S. M. Peng, K. T. Wong and C. C. Wu, *Adv. Funct. Mater.*, 2007, **17**, 1019–1027.
- 69 L. Sun, A. Galan, S. Ladouceur, J. D. Slinker and E. Zysman-Colman, *J. Mater. Chem.*, 2011, **21**, 18083–18088.
- 70 H. J. Bolink, L. Cappelli, E. Coronado, M. Grätzel, E. Ortí, R. D. Costa, P. M. Viruela and M. K. Nazeeruddin, *J. Am. Chem. Soc.*, 2006, **128**, 14786–14787.
- 71 D. Tordera, A. Pertegás, N. M. Shavaleev, R. Scopelliti, E. Ortí, H. J. Bolink, E. Baranoff, M. Grätzel and M. K. Nazeeruddin, *J. Mater. Chem.*, 2012, **22**, 19264–19268.
- 72 E. Sauvageot, P. Lafite, E. Duverger, R. Marion, M. Hamel, S. Gaillard, J. L. Renaud and R. Daniellou, *J. Organomet. Chem.*, 2016, **808**, 122–127.
- 73 C. Dragonetti, L. Falcicola, P. Mussini, S. Righetto, D. Roberto, R. Ugo, A. Valore, F. De Angelis, S. Fantacci, A. Sgamellotti, M. Ramon and M. Muccini, *Inorg. Chem.*, 2007, **46**, 8533–8547.
- 74 R. D. Costa, E. Ortí, H. J. Bolink, S. Graber, C. E. Housecroft and E. C. Constable, *Chem. Commun.*, 2011, **47**, 3207–3209.
- 75 H. J. Bolink, E. Coronado, R. D. Costa, E. Ortí, M. Sessolo, S. Graber, K. Doyle, M. Neuburger, C. E. Housecroft and E. C. Constable, *Adv. Mater.*, 2008, **20**, 3910–3913.
- 76 S. Graber, K. Doyle, M. Neuburger, C. E. Housecroft, E. C. Constable, R. D. Costa, E. Ortí, D. Repetto and H. J. Bolink, *J. Am. Chem. Soc.*, 2008, **130**, 14944–14945.
- 77 R. D. Costa, E. Ortí, H. J. Bolink, S. Graber, C. E. Housecroft, M. Neuburger, S. Schaffner and E. C. Constable, *Chem. Commun.*, 2009, 2029–2031.
- 78 G. E. Schneider, A. Pertegás, E. C. Constable, C. E. Housecroft, N. Hostettler, C. D. Morris, J. A. Zampese, H. J. Bolink, J. M. Junquera-Hernández, E. Ortí and M. Sessolo, *J. Mater. Chem. C*, 2014, **2**, 7047–7055.
- 79 R. D. Costa, E. Ortí, H. J. Bolink, S. Graber, C. E. Housecroft and E. C. Constable, *Adv. Funct. Mater.*, 2010, **20**, 1511–1520.
- 80 A. M. Bunzli, E. C. Constable, C. E. Housecroft, A. Prescimone, J. A. Zampese, G. Longo, L. Gil-Escrig, A. Pertegas, E. Orti and H. J. Bolink, *Chem. Sci.*, 2015, **6**, 2843–2852.
- 81 R. D. Costa, E. Ortí, H. J. Bolink, S. Graber, C. E. Housecroft and E. C. Constable, *J. Am. Chem. Soc.*, 2010, **132**, 5978–5980.
- 82 R. D. Costa, E. Ortí, D. Tordera, A. Pertegás, H. J. Bolink, S. Graber, C. E. Housecroft, L. Sachno, M. Neuburger and E. C. Constable, *Adv. Energy Mater.*, 2011, **1**, 282–290.
- 83 A. M. Bünzli, E. C. Constable, C. E. Housecroft, A. Prescimone, J. A. Zampese, G. Longo, L. Gil-Escrig, A. Pertegás, E. Ortí and H. J. Bolink, *Chem. Sci.*, 2015, **6**, 2843–2852.
- 84 A. M. Bünzli, H. J. Bolink, E. C. Constable, C. E. Housecroft, M. Neuburger, E. Ortí, A. Pertegás and J. A. Zampese, *Eur. J. Inorg. Chem.*, 2012, **2012**, 3780–3788.
- 85 G. E. Schneider, H. J. Bolink, E. C. Constable, C. D. Ertl, C. E. Housecroft, A. Pertegas, J. A. Zampese, A. Kanitz, F. Kessler and S. B. Meier, *Dalton Trans.*, 2014, **43**, 1961–1964.
- 86 C. Hierlinger, E. Trzop, L. Toupet, J. Ávila, M. G. La-Placa, H. J. Bolink, V. Guerchais and E. Zysman-Colman, *J. Mater. Chem. C*, 2018, **6**, 6385–6397.
- 87 A. F. Henwood, A. K. Bansal, D. B. Cordes, A. M. Z. Slawin, I. D. W. Samuel and E. Zysman-Colman, *J. Mater. Chem. C*, 2016, **4**, 3726–3737.

- 88 A. F. Henwood, D. Antón-García, M. Morin, D. Rota Martir, D. B. Cordes, C. Casey, A. M. Z. Slawin, T. Lebl, M. Bühl and E. Zysman-Colman, *Dalton Trans.*, 2019, **48**, 9639–9653.
- 89 D. Rota Martir, G. J. Hedley, D. B. Cordes, A. M. Z. Slawin, D. Escudero, D. Jacquemin, T. Kosikova, D. Philp, D. M. Dawson, S. E. Ashbrook, I. D. W. Samuel and E. Zysman-Colman, *Dalton Trans.*, 2016, **45**, 17195–17205.
- 90 H. C. Su, Y. R. Chen and K. T. Wong, *Adv. Funct. Mater.*, 2019, 1906898.
- 91 L. He, J. Qiao, L. Duan, G. Dong, D. Zhang, L. Wang and Y. Qiu, *Adv. Funct. Mater.*, 2009, **19**, 2950–2960.
- 92 C. Zhang, R. Liu, D. Zhang and L. Duan, *Adv. Funct. Mater.*, 2020, 1907156.
- 93 R. Bai, X. Meng, X. Wang and L. He, *Adv. Funct. Mater.*, 2020, 1907169.
- 94 K. P. S. Zanoni, B. K. Kariyazaki, A. Ito, M. K. Brennaman, T. J. Meyer and N. Y. Murakami Iha, *Inorg. Chem.*, 2014, **53**, 4089–4099.
- 95 M. Lepeltier, T. Kwok-Ming Lee, K. Kam-Wing Lo, L. Toupet, H. Le Bozec and V. Guerschais, *Eur. J. Inorg. Chem.*, 2005, **2005**, 110–117.
- 96 J. E. Namanga, N. Gerlitzki and A. V. Mudring, *Adv. Funct. Mater.*, 2017, **27**, 1605588.
- 97 E. C. Constable, C. D. Ertl, C. E. Housecroft and J. A. Zampese, *Dalton Trans.*, 2014, **43**, 5343–5356.
- 98 X. Li, Y. Yin, P. Gao, W. Li, H. Yan, C. Lu and Q. Zhao, *Dalton Trans.*, 2017, **46**, 13802–13810.
- 99 D. Tordera, M. Delgado, E. Ortí, H. J. Bolink, J. Frey, M. K. Nazeeruddin and E. Baranoff, *Chem. Mater.*, 2012, **24**, 1896–1903.
- 100 M. S. Lowry, J. I. Goldsmith, J. D. Slinker, R. Rohl, R. A. Pascal, G. G. Malliaras and S. Bernhard, *Chem. Mater.*, 2005, **17**, 5712–5719.
- 101 A. K. Pal, D. B. Cordes, A. M. Z. Slawin, C. Momblona, E. Ortí, I. D. W. Samuel, H. J. Bolink and E. Zysman-Colman, *Inorg. Chem.*, 2016, **55**, 10361–10376.
- 102 D. Tordera, A. M. Bünzli, A. Pertegás, J. M. Junquera-Hernández, E. C. Constable, J. A. Zampese, C. E. Housecroft, E. Ortí and H. J. Bolink, *Chem. Eur. J.*, 2013, **19**, 8597–8609.
- 103 C. D. Ertl, L. Gil-Escrig, J. Cerdá, A. Pertegás, H. J. Bolink, J. M. Junquera-Hernández, A. Prescimone, M. Neuburger, E. C. Constable, E. Ortí and C. E. Housecroft, *Dalton Trans.*, 2016, **45**, 11668–11681.
- 104 N. M. Shavaleev, G. Xie, S. Varghese, D. B. Cordes, A. M. Z. Slawin, C. Momblona, E. Ortí, H. J. Bolink, I. D. W. Samuel and E. Zysman-Colman, *Inorg. Chem.*, 2015, **54**, 5907–5914.
- 105 S. Evariste, M. Sandroni, T. W. Rees, C. Roldán-Carmona, L. Gil-Escrig, H. J. Bolink, E. Baranoff and E. Zysman-Colman, *J. Mater. Chem. C*, 2014, **2**, 5793–5804.
- 106 A. F. Henwood, A. K. Pal, D. B. Cordes, A. M. Z. Slawin, T. W. Rees, C. Momblona, A. Babaei, A. Pertegás, E. Ortí, H. J. Bolink, E. Baranoff and E. Zysman-Colman, *J. Mater. Chem. C*, 2017, **5**, 9638–9650.
- 107 Y. Zheng, A. S. Batsanov, R. M. Eddins, A. Beeby and M. R. Bryce, *Inorg. Chem.*, 2012, **51**, 290–297.
- 108 V. Sivasubramaniam, F. Brodkorb, S. Hanning, H. P. Loeb, V. van Elsbergen, H. Boerner, U. Scherf and M. Kreyenschmidt, *J. Fluor. Chem.*, 2009, **130**, 640–649.
- 109 Ł. Skórka, M. Filapek, L. Zur, J. G. Małeck, W. Pisarski, M. Olejnik, W. Danikiewicz and S. Krompiec, *J. Phys. Chem. C*, 2016, **120**, 7284–7294.

- 110 M. K. Nazeeruddin, R. T. Wegh, Z. Zhou, C. Klein, Q. Wang, F. De Angelis, S. Fantacci and M. Grätzel, *Inorg. Chem.*, 2006, **45**, 9245–9250.
- 111 S. Ladouceur, K. N. Swanick, S. Gallagher-Duval, Z. Ding and E. Zysman-Colman, *Eur. J. Inorg. Chem.*, 2013, **2013**, 5329–5343.
- 112 A. B. Tamayo, S. Garon, T. Sajoto, P. I. Djurovich, I. M. Tsyba, R. Bau and M. E. Thompson, *Inorg. Chem.*, 2005, **44**, 8723–8732.
- 113 L. He, L. Duan, J. Qiao, R. Wang, P. Wei, L. Wang and Y. Qiu, *Adv. Funct. Mater.*, 2008, **18**, 2123–2131.
- 114 J. M. Fernández-Hernández, S. Ladouceur, Y. Shen, A. Iordache, X. Wang, L. Donato, S. Gallagher-Duval, M. de Anda Villa, J. D. Slinker, L. De Cola and E. Zysman-Colman, *J. Mater. Chem. C*, 2013, **1**, 7440–7452.
- 115 X. Wang, S. Wang, F. Pan, L. He and L. Duan, *Inorg. Chem.*, 2019, **58**, 12132–12145.
- 116 M. Mydlak, C. Bizzarri, D. Hartmann, W. Sarfert, G. Schmid and L. De Cola, *Adv. Funct. Mater.*, 2010, **20**, 1812–1820.
- 117 B. Chen, Y. Li, W. Yang, W. Luo and H. Wu, *Org. Electron.*, 2011, **12**, 766–773.
- 118 C. H. Yang, J. Beltran, V. Lemaure, J. Cornil, D. Hartmann, W. Sarfert, R. Fröhlich, C. Bizzarri and L. De Cola, *Inorg. Chem.*, 2010, **49**, 9891–9901.
- 119 L. He, Z. Wang, C. Yang, L. Duan, R. Tang, X. Song and C. Pan, *Dyes Pigm.*, 2016, **131**, 76–83.
- 120 B. Beyer, C. Ulbricht, D. Escudero, C. Friebe, A. Winter, L. González and U. S. Schubert, *Organometallics*, 2009, **28**, 5478–5488.
- 121 N. M. Shavaleev, R. Scopelliti, M. Grätzel and M. K. Nazeeruddin, *Inorg. Chim. Acta*, 2012, **388**, 84–87.
- 122 F. Monti, A. Baschieri, I. Gualandi, J. J. Serrano-Pérez, J. M. Junquera-Hernández, D. Tonelli, A. Mazzanti, S. Muzzioli, S. Stagni, C. Roldan-Carmona, A. Pertegás, H. J. Bolink, E. Ortí, L. Sambri and N. Armaroli, *Inorg. Chem.*, 2014, **53**, 7709–7721.
- 123 Z. Wang, L. He, L. Duan, J. Yan, R. Tang, C. Pan and X. Song, *Dalton Trans.*, 2015, **44**, 15914–15923.
- 124 Y. Lan, G. Li, Z. Wang, Y. He, Y. Liu and L. He, *Dyes Pigm.*, 2017, **144**, 158–167.
- 125 C. D. Sunesh, K. Shanmugasundaram, M. S. Subeesh, R. K. Chitumalla, J. Jang and Y. Choe, *ACS Appl. Mater. Interfaces*, 2015, **7**, 7741–7751.
- 126 M. Martínez-Alonso, J. Cerdá, C. Momblona, A. Pertegás, J. M. Junquera-Hernández, A. Heras, A. M. Rodríguez, G. Espino, H. Bolink and E. Ortí, *Inorg. Chem.*, 2017, **56**, 10298–10310.
- 127 C. D. Sunesh, G. Mathai and Y. Choe, *Org. Electron.*, 2014, **15**, 667–674.
- 128 L. He, L. Duan, J. Qiao, D. Zhang, L. Wang and Y. Qiu, *Chem. Commun.*, 2011, **47**, 6467–6469.
- 129 X. Meng, R. Bai, X. Wang, F. Pan and L. He, *Dyes Pigm.*, 2019, **165**, 458–466.
- 130 M. Chen, S. Wang, X. Song and L. He, *J. Phys. Chem. C*, 2018, **122**, 28256–28264.
- 131 C. D. Sunesh, M. S. Subeesh, K. Shanmugasundaram, R. K. Chitumalla, J. Jang and Y. Choe, *Dyes Pigm.*, 2016, **128**, 190–200.
- 132 G. G. Shan, H. B. Li, D. X. Zhu, Z. M. Su and Y. Liao, *J. Mater. Chem.*, 2012, **22**, 12736–12744.

- 133 Q. Zeng, F. Li, T. Guo, G. Shan and Z. Su, *Sci. Rep.*, 2016, **6**, 27613.
- 134 F. Kessler, R. D. Costa, D. Di Censo, R. Scopelliti, E. Ortí, H. J. Bolink, S. Meier, W. Sarfert, M. Grätzel, M. K. Nazeeruddin and E. Baranoff, *Dalton Trans.*, 2012, **41**, 180–191.
- 135 J. E. Namanga, N. Gerlitzki, B. Mallick and A. V. Mudring, *J. Mater. Chem. C*, 2017, **5**, 3049–3055.
- 136 K. Hasan, A. K. Bansal, I. D. W. Samuel, C. Roldán-Carmona, H. J. Bolink and E. Zysman-Colman, *Sci. Rep.*, 2015, **5**, 12325.
- 137 J. L. Rodríguez-Redondo, R. D. Costa, E. Ortí, A. Sastre-Santos, H. J. Bolink and F. Fernández-Lázaro, *Dalton Trans.*, 2009, 9787–9793.
- 138 C. Huang, C. G. Zhen, S. P. Su, Z. K. Chen, X. Liu, D. C. Zou, Y. R. Shi and K. P. Loh, *J. Organomet. Chem.*, 2009, **694**, 1317–1324.
- 139 E. C. Constable, C. E. Housecroft, G. E. Schneider, J. A. Zampese, H. J. Bolink, A. Pertegás and C. Roldan-Carmona, *Dalton Trans.*, 2014, **43**, 4653–4667.
- 140 G. Y. Chen, B. R. Chang, T. A. Shih, C. H. Lin, C. L. Lo, Y. Z. Chen, Y. X. Liu, Y. R. Li, J. T. Guo, C. W. Lu, Z. P. Yang and H. C. Su, *Chem. Eur. J.*, 2019, **25**, 5489–5497.
- 141 H. Chen, T. Xiao, L. Li, D. Anand, Y. He and L. Zhou, *Adv. Synth. Catal.*, 2017, **359**, 3642–3647.
- 142 D. Hanss, J. C. Freys, G. Bernardinelli and O. S. Wenger, *Eur. J. Inorg. Chem.*, 2009, **2009**, 4850–4859.
- 143 C. D. Ertl, C. Momblona, A. Pertegás, J. M. Junquera-Hernández, M. G. La-Placa, A. Prescimone, E. Ortí, C. E. Housecroft, E. C. Constable and H. J. Bolink, *J. Am. Chem. Soc.*, 2017, **139**, 3237–3248.
- 144 V. Criscuolo, C. T. Prontera, M. Pavone, O. Crescenzi, M. G. Maglione, P. Tassini, S. Lettieri, P. Maddalena, C. Borriello, C. Minarini and P. Manini, *ACS Omega*, 2019, **4**, 2009–2018.
- 145 H. C. Su, H. F. Chen, F. C. Fang, C.-C. Liu, C. C. Wu, K. T. Wong, Y. H. Liu and S. M. Peng, *J. Am. Chem. Soc.*, 2008, **130**, 3413–3419.
- 146 J. Yeonah, C. D. Sunesh, R. K. Chitumalla, J. Jang and Y. Choe, *Org. Electron.*, 2018, **54**, 167–176.
- 147 T. Hu, L. Duan, J. Qiao, L. He, D. Zhang, L. Wang and Y. Qiu, *Synth. Met.*, 2013, **163**, 33–37.
- 148 B. Pashaei, S. Karimi, H. Shahroosvand and M. Pilkington, *Adv. Funct. Mater.*, 2020, 1908103.
- 149 J. Chaudhuri, S. Kume, J. Jagur-Grodzinski, M. Szwarc, P. Gros, Y. Fort and P. Caubère, *J. Am. Chem. Soc.*, 1997, **90**, 3071–3080.
- 150 J. Chaudhuri, S. Kume, J. Jagur-Grodzinski and M. Szwarc, *J. Am. Chem. Soc.*, 1968, **90**, 6421–6425.
- 151 K. J. Arm, Ph.D Thesis, University of Durham, 2005.
- 152 M. T. Walden, Ph.D Thesis, University of Durham, 2019.
- 153 P. Brulatti, Ph.D Thesis, University of Durham, 2010.
- 154 J. A. Pople, W. G. Schneider and H. J. Bernstein, *Can. J. Chem.*, 1957, **35**, 1060–1072.
- 155 C. Hierlinger, D. B. Cordes, A. M. Z. Slawin, D. Jacquemin, V. Guerchais and E. Zysman-Colman, *Dalton Trans.*, 2018, **47**, 10569–10577.

- 156 V. N. Kozhevnikov, Y. Zheng, M. Clough, H. A. Al-Attar, G. C. Griffiths, K. Abdullah, S. Raisys, V. Jankus, M. R. Bryce and A. P. Monkman, *Chem. Mater.*, 2013, **25**, 2352–2358.
- 157 Q. Wu, J. A. Lavigne, Y. Tao, M. D'lorio and S. Wang, *Inorg. Chem.*, 2000, **39**, 5248–5254.
- 158 P. Štarha, Z. Trávníček, H. Crlíková, J. Vančo, J. Kašpárková and Z. Dvořák, *Organometallics*, 2018, **37**, 2749–2759.
- 159 J. C. Antilla, J. M. Baskin, T. E. Barder and S. L. Buchwald, *J. Org. Chem.*, 2004, **69**, 5578–5587.
- 160 Y. C. Teo, F. F. Yong and S. Sim, *Tetrahedron*, 2013, **69**, 7279–7284.
- 161 K. S. Rao and T. S. Wu, *Tetrahedron*, 2012, **68**, 7735–7754.
- 162 D. M. T. Chan, K. L. Monaco, R. Li, D. Bonne, C. G. Clark and P. Y. S. Lam, *Tetrahedron Lett.*, 2003, **44**, 3863–3865.
- 163 S. Lamansky, P. Djurovich, D. Murphy, F. Abdel-Razzaq, H. E. Lee, C. Adachi, P. E. Burrows, S. R. Forrest and M. E. Thompson, *J. Am. Chem. Soc.*, 2001, **123**, 4304–4312.
- 164 C. D. Ertl, J. Cerda, J. M. Junquera-Hernandez, A. Pertegas, H. J. Bolink, E. C. Constable, M. Neuburger, E. Orti and C. E. Housecroft, *RSC Adv.*, 2015, **5**, 42815–42827.
- 165 Q. Zhao, S. Liu, M. Shi, C. Wang, M. Yu, L. Li, F. Li, T. Yi and C. Huang, *Inorg. Chem.*, 2006, **45**, 6152–6160.
- 166 A. J. Lees, *Comments Inorg. Chem.*, 1995, **17**, 319–346.
- 167 C. Hierlinger, A. K. Pal, F. Stella, T. Lebl, D. B. Cordes, A. M. Z. Slawin, D. Jacquemin, V. Guerchais and E. Zysman-Colman, *Inorg. Chem.*, 2018, **57**, 2023–2034.
- 168 N. P. Ayala, C. M. Flynn, L. Sacksteder, J. N. Demas and B. A. DeGraff, *J. Am. Chem. Soc.*, 1990, **112**, 3837–3844.
- 169 J. P. Sauvage, J. P. Collin, J. C. Chambron, S. Guillerez, C. Coudret, V. Balzani, F. Barigelletti, L. De Cola and L. Flamigni, *Chem. Rev.*, 1994, **94**, 993–1019.
- 170 J. A. G. Williams, A. J. Wilkinson and V. L. Whittle, *Dalton Trans.*, 2008, 2081–2099.
- 171 A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser and A. von Zelewsky, *Coord. Chem. Rev.*, 1988, **84**, 85–277.
- 172 M. Beley, J. P. Collin and J. P. Sauvage, *Inorg. Chem.*, 1993, **32**, 4539–4543.
- 173 M. Beley, J. P. Collin, R. Louis, B. Metz and J. P. Sauvage, *J. Am. Chem. Soc.*, 1991, **113**, 8521–8522.
- 174 J. A. G. Williams, *Chem. Soc. Rev.*, 2009, **38**, 1783–1801.
- 175 C. Cebrián and M. Mauro, *Beilstein J. Org. Chem.*, 2018, **14**, 1459–1481.
- 176 C. W. Lu, Y. Wang and Y. Chi, *Chem. Eur. J.*, 2016, **22**, 17892–17908.
- 177 C. Cebrián, M. Mauro, D. Kourkoulos, P. Mercandelli, D. Hertel, K. Meerholz, C. A. Strassert and L. De Cola, *Adv. Mater.*, 2013, **25**, 437–442.
- 178 E. Göransson, J. Boixel, C. Monnereau, E. Blart, Y. Pellegrin, H. C. Becker, L. Hammarström and F. Odobel, *Inorg. Chem.*, 2010, **49**, 9823–9832.
- 179 F. Guo, W. Sun, Y. Liu and K. Schanze, *Inorg. Chem.*, 2005, **44**, 4055–4065.
- 180 P. Jarosz, K. Lotito, J. Schneider, D. Kumaresan, R. Schmehl and R. Eisenberg, *Inorg. Chem.*, 2009, **48**, 2420–2428.

- 181 L. M. Hight, M. C. McGuire, Y. Zhang, M. A. Bork, P. E. Fanwick, A. Wasserman and D. R. McMillin, *Inorg. Chem.*, 2013, **52**, 8476–8482.
- 182 C. Y. S. Chung, S. P. Y. Li, K. K. W. Lo and V. W. W. Yam, *Inorg. Chem.*, 2016, **55**, 4650–4663.
- 183 G. S. M. Tong, Y. C. Law, S. C. F. Kui, N. Zhu, K. H. Leung, D. L. Phillips and C. M. Che, *Chem. Eur. J.*, 2010, **16**, 6540–6554.
- 184 L. F. Gildea, A. S. Batsanov and J. A. G. Williams, *Dalton Trans.*, 2013, **42**, 10388–10393.
- 185 S. Gosiewska, M. H. in't Veld, J. J. M. de Pater, P. C. A. Bruijninx, M. Lutz, A. L. Spek, G. van Koten and R. J. M. Klein Gebbink, *Tetrahedron Asymmetry*, 2006, **17**, 674–686.
- 186 A. Růžicka, Z. Padělková, P. Švec, V. Pejchal, L. Česlová and J. Holeček, *J. Organomet. Chem.*, 2013, **732**, 47–57.
- 187 R. A. Haque, H. Z. Zulikha, M. Z. Ghdayeb, S. Budagumpi and A. W. Salman, *Heteroat. Chem.*, 2012, **23**, 486–497.
- 188 A. J. Wilkinson, H. Puschmann, J. A. K. Howard, C. E. Foster and J. A. G. Williams, *Inorg. Chem.*, 2006, **45**, 8685–8699.
- 189 A. J. Wilkinson, A. E. Goeta, C. E. Foster and J. A. G. Williams, *Inorg. Chem.*, 2004, **43**, 6513–6515.
- 190 V. L. Whittle and J. A. G. Williams, *Inorg. Chem.*, 2008, **47**, 6596–6607.
- 191 M. Ashizawa, L. Yang, K. Kobayashi, H. Sato, A. Yamagishi, F. Okuda, T. Harada, R. Kuroda and M. Haga, *Dalton Trans.*, 2009, 1700–1702.
- 192 S. Obara, M. Itabashi, F. Okuda, S. Tamaki, Y. Tanabe, Y. Ishii, K. Nozaki and M. Haga, *Inorg. Chem.*, 2006, **45**, 8907–8921.
- 193 V. L. Whittle, Ph.D Thesis, University of Durham, 2008.
- 194 K. C. Chan, W. K. Chu, S. M. Yiu and C. C. Ko, *Dalton Trans.*, 2015, **44**, 15135–15144.
- 195 J. Kuwabara, T. Namekawa, M. Haga and T. Kanbara, *Dalton Trans.*, 2012, **41**, 44–46.
- 196 J. Kuwabara, T. Namekawa, E. Sakabe, M. Haga and T. Kanbara, *J. Organomet. Chem.*, 2017, **845**, 189–195.
- 197 P. Brulatti, R. J. Gildea, J. A. K. Howard, V. Fattori, M. Cocchi and J. A. G. Williams, *Inorg. Chem.*, 2012, **51**, 3813–3826.
- 198 B. Tong, H. Y. Ku, I. J. Chen, Y. Chi, H. C. Kao, C. C. Yeh, C. H. Chang, S. H. Liu, G. H. Lee and P. T. Chou, *J. Mater. Chem. C*, 2015, **3**, 3460–3471.
- 199 J. P. Collin, I. M. Dixon, J. P. Sauvage, J. A. G. Williams, F. Barigelletti and L. Flamigni, *J. Am. Chem. Soc.*, 1999, **121**, 5009–5016.
- 200 M. Polson, M. Ravaglia, S. Fracasso, M. Garavelli and F. Scandola, *Inorg. Chem.*, 2005, **44**, 1282–1289.
- 201 M. Polson, S. Fracasso, V. Bertolasi, M. Ravaglia and F. Scandola, *Inorg. Chem.*, 2004, **43**, 1950–1956.
- 202 C. Hierlinger, T. Roisnel, D. B. Cordes, A. M. Z. Slawin, D. Jacquemin, V. Guerschais and E. Zysman-Colman, *Inorg. Chem.*, 2017, **56**, 5182–5188.
- 203 C. Y. Kuei, W. L. Tsai, B. Tong, M. Jiao, W. K. Lee, Y. Chi, C. C. Wu, S. H. Liu, G. H. Lee and P. T. Chou, *Adv. Mater.*, 2016, **28**, 2795–2800.
- 204 H. H. Kuo, Z. Zhu, C. S. Lee, Y. K. Chen, S. H. Liu, P. T. Chou, A. K. Y. Jen and Y. Chi, *Adv. Sci.*,

2018, **5**, 1800846.

- 205 H. H. Kuo, Y. T. Chen, L. R. Devereux, C. C. Wu, M. A. Fox, C. Y. Kuei, Y. Chi and G. H. Lee, *Adv. Mater.*, 2017, **29**, 1702464.
- 206 L. Y. Hsu, Q. Liang, Z. Wang, H. H. Kuo, W. S. Tai, S. J. Su, X. Zhou, Y. Yuan and Y. Chi, *Chem. Eur. J.*, 2019, **25**, 15375–15386.
- 207 V. Adamovich, P.-L. T. Boudreault, M. A. Esteruelas, D. Gómez-Bautista, A. M. López, E. Oñate and J.-Y. Tsai, *Organometallics*, 2019, **38**, 2738–2747.
- 208 Y. K. Chen, H. H. Kuo, D. Luo, Y. N. Lai, W. C. Li, C. H. Chang, D. Escudero, A. K. Y. Jen, L. Y. Hsu and Y. Chi, *Chem. Mater.*, 2019, **31**, 6453–6464.
- 209 J. Lin, N. Y. Chau, J. L. Liao, W. Y. Wong, C. Y. Lu, Z. T. Sie, C. H. Chang, M. A. Fox, P. J. Low, G. H. Lee and Y. Chi, *Organometallics*, 2016, **35**, 1813–1824.
- 210 C. Y. Kuei, S. H. Liu, P. T. Chou, G. H. Lee and Y. Chi, *Dalton Trans.*, 2016, **45**, 15364–15373.
- 211 Z. Wang, E. Turner, V. Mahoney, S. Madakuni, T. Groy and J. Li, *Inorg. Chem.*, 2010, **49**, 11276–11286.
- 212 C. J. Yao, R. H. Zheng, Q. Shi, Y. W. Zhong and J. Yao, *Chem. Commun.*, 2012, **48**, 5680–5682.
- 213 A. J. S. Bexon and J. A. G. Williams, *C. R. Chim.*, 2005, **8**, 1326–1335.
- 214 F. Barigelletti, B. Ventura, J. P. Collin, R. Kayhanian, P. Gaviña and J. P. Sauvage, *Eur. J. Inorg. Chem.*, 2000, **2000**, 113–119.
- 215 J. R. Ochola and M. O. Wolf, *Org. Biomol. Chem.*, 2016, **14**, 9088–9092.
- 216 S. C. Yang, G. Chang, G. J. Yang, Y. J. Wang and B. Fang, *Catal. Sci. Technol.*, 2015, **5**, 228–233.
- 217 C. E. Housecroft in *Encyclopedia of Inorganic and Bioinorganic Chemistry*, Wiley, New Jersey, USA, 1st edn, 2006, "Iridium: Inorganic & Coordination Chemistry".
- 218 S. Huo, *Chem. Rec.*, 2018, **18**, 1583–1595.
- 219 T. Fleetham, G. Li and J. Li, *Adv. Mater.*, 2017, **29**, 1601861.
- 220 X. Wang and S. Wang, *Chem. Rec.*, 2019, **19**, 1693–1709.
- 221 S. Zhang, K. Luo, H. Geng, H. Ni, H. Wang and Q. Li, *Dalton Trans.*, 2017, **46**, 899–906.
- 222 L. Zhao, B. Yang, L. Zeng, K. Luo, H. Wang, H. Ni, C. Yang and Q. Li, *Dyes Pigm.*, 2019, **164**, 398–406.
- 223 Y. Y. Lin, S. C. Chan, M. C. W. Chan, Y. J. Hou, N. Zhu, C. M. Che, Y. Liu and Y. Wang, *Chem. Eur. J.*, 2003, **9**, 1263–1272.
- 224 K. Li, G. Cheng, C. Ma, X. Guan, W. M. Kwok, Y. Chen, W. Lu and C. M. Che, *Chem. Sci.*, 2013, **4**, 2630–2644.
- 225 K. Li, X. Guan, C. W. Ma, W. Lu, Y. Chen and C. M. Che, *Chem. Commun.*, 2011, **47**, 9075–9077.
- 226 X. Wang, T. Peng, C. Nguyen, Z. H. Lu, N. Wang, W. Wu, Q. Li and S. Wang, *Adv. Funct. Mater.*, 2017, **27**, 1604318.
- 227 K. Y. Liao, C. W. Hsu, Y. Chi, M. K. Hsu, S. W. Wu, C. H. Chang, S. H. Liu, G. H. Lee, P. T. Chou, Y. Hu and N. Robertson, *Inorg. Chem.*, 2015, **54**, 4029–4038.
- 228 K. Feng, C. Zuniga, Y. D. Zhang, D. Kim, S. Barlow, S. R. Marder, J. L. Brédas and M. Weck,

Macromolecules, 2009, **42**, 6855–6864.

- 229 C. Lee, R. Zaen, K. M. Park, K. H. Lee, J. Y. Lee and Y. Kang, *Organometallics*, 2018, **37**, 4639–4647.
- 230 Z. Wu, T. Xie, Y. Luo, W. Zhuo, J. Gu, X. Yan, X. Sun, K. Zuo, X. Liu, Y. Gan, L. Liang, G. He, W. Liu, X. Gou, D. Tang, H. Shi and J. Hu, *Appl. Organomet. Chem.*, 2019, **33**, e4879.
- 231 S. Wang, C. Bruneau, J. L. Renaud, S. Gaillard and C. Fischmeister, *Dalton Trans.*, 2019, **48**, 11599–11622.
- 232 H. Ma, K. Shen, Y. Wu, F. Xia, F. Yu, Z. Sun, C. Qian, Q. Peng, H. H. Zhang, C. You, G. Xie, X. C. Hang and W. Huang, *Mater. Chem. Front.*, 2019, **3**, 2448–2454.
- 233 X. Yan, Y. Luo, X. Sun, W. Zhuo, J. Gu, K. Zuo, X. Gou, D. Tang, H. Shi, W. Liu and J. Hu, *Appl. Organomet. Chem.*, 2019, **33**, 5125.
- 234 J. Li, F. Liang, Y. Zhao, X. Y. Liu, J. Fan and L. S. Liao, *J. Mater. Chem. C*, 2017, **5**, 6202–6209.
- 235 W. Cai, H. Zhang, X. Yan, A. Zhao, R. He, M. Li, Q. Meng and W. Shen, *Phys. Chem. Chem. Phys.*, 2019, **21**, 8073–8080.
- 236 G. Li, Q. Chen, J. Zheng, Q. Wang, F. Zhan, W. Lou, Y. F. Yang and Y. She, *Inorg. Chem.*, 2019, **58**, 14349–14360.
- 237 T. Fleetham, J. H. Golden, M. Idris, H. M. Hau, D. S. Muthiah Ravinson, P. I. Djurovich and M. E. Thompson, *Inorg. Chem.*, 2019, **58**, 12348–12357.
- 238 G. Li, A. Wolfe, J. Brooks, Z. Q. Zhu and J. Li, *Inorg. Chem.*, 2017, **56**, 8244–8256.
- 239 T. B. Fleetham, L. Huang, K. Klimes, J. Brooks and J. Li, *Chem. Mater.*, 2016, **28**, 3276–3282.
- 240 G. Li, X. Zhao, T. Fleetham, Q. Chen, F. Zhan, J. Zheng, Y. F. Yang, W. Lou, Y. Yang, K. Fang, Z. Shao, Q. Zhang and Y. She, *Chem. Mater.*, 2020, **32**, 537–548.
- 241 D. Zhao, X. Tang, X. Y. Liu, J. Fan and L. S. Liao, *Org. Electron.*, 2017, **50**, 473–479.
- 242 C. You, F. Xia, Y. Zhao, Y. Zhang, Y. Sheng, Y. Wu, X. C. Hang, F. Chen, H. Ma, K. Shen, Z. Sun, T. Ueba, S. Kera, C. Zhang, H. Zhang, Z. K. Chen and W. Huang, *J. Phys. Chem. Lett.*, 2018, **9**, 2285–2292.
- 243 W. Zhang, J. Ma, G. J. Liu, X. Y. Liu, J. Fan and L. S. Liao, *J. Mater. Chem. C*, 2017, **5**, 9496–9503.
- 244 X. C. Hang, T. Fleetham, E. Turner, J. Brooks and J. Li, *Angew. Chem.*, 2013, **125**, 6885–6888.
- 245 G. E. Norby, C.D. Park, B. O’Brien, G. Li, L. Huang and J. Li, *Org. Electron.*, 2016, **37**, 163–168.
- 246 Z. Q. Zhu, K. Klimes, S. Holloway and J. Li, *Adv. Mater.*, 2017, **29**, 1605002.
- 247 Z. Q. Zhu, C. D. Park, K. Klimes and J. Li, *Adv. Opt. Mater.*, 2019, **7**, 1801518.
- 248 G. Li, T. Fleetham, E. Turner, X. C. Hang and J. Li, *Adv. Opt. Mater.*, 2015, **3**, 390–397.
- 249 T. Fleetham, G. Li and J. Li, *ACS Appl. Mater. Interfaces*, 2015, **7**, 16240–16246.
- 250 M. Crespo, *Organometallics*, 2012, **31**, 1216–1234.
- 251 Y. C. Zhu, L. Zhou, H. Y. Li, Q. L. Xu, M. Y. Teng, Y. X. Zheng, J. L. Zuo, H. J. Zhang and X. Z. You, *Adv. Mater.*, 2011, **23**, 4041–4046.
- 252 C. C. Wang, Y. M. Jing, T. Y. Li, Q. L. Xu, S. Zhang, W. N. Li, Y. X. Zheng, J. L. Zuo, X. Z. You and X. Q. Wang, *Eur. J. Inorg. Chem.*, 2013, **2013**, 5683–5693.

- 253 S. Wilde, D. Ma, T. Koch, A. Bakker, D. Gonzalez-Abradelo, L. Stegemann, C. G. Daniliuc, H. Fuchs, H. Gao, N. L. Doltsinis, L. Duan and C. A. Strassert, *ACS Appl. Mater. Interfaces*, 2018, **10**, 22460–22473.
- 254 M. Bonneau, Ph.D Thesis, University of Durham, 2015.
- 255 S. Wilde, D. González-Abradelo, C. G. Daniliuc, M. Böckmann, N. L. Doltsinis and C. A. Strassert, *Isr. J. Chem.*, 2018, **58**, 932–943.
- 256 S. Wilde, L. Stegemann, C. G. Daniliuc, T. Koch, N. L. Doltsinis and C. A. Strassert, *Z. Naturforsch. B*, 2018, **73**, 849–863.
- 257 X. Q. Zhang, Y. M. Xie, Y. Zheng, F. Liang, B. Wang, J. Fan and L. S. Liao, *Org. Electron.*, 2016, **32**, 120–125.
- 258 I. Allison, H. Lim, A. Shukla, V. Ahmad, M. Hasan, K. Deshmukh, R. Wawrzinek, S. K. M. McGregor, J. K. Clegg, V. V Divya, C. Govind, C. H. Suresh, V. Karunakaran, N. U. K. N., A. Ajayaghosh, E. B. Namdas and S. C. Lo, *ACS Appl. Electron. Mater.*, 2019, **1**, 1304–1313.
- 259 H. Fukagawa, T. Shimizu, H. Hanashima, Y. Osada, M. Suzuki and H. Fujikake, *Adv. Mater.*, 2012, **24**, 5099–5103.
- 260 S. Huo, C. F. Harris, D. A. K. Vezzu, J. P. Gagnier, M. E. Smith, R. D. Pike and Y. Li, *Polyhedron*, 2013, **52**, 1030–1040.
- 261 P. A. Dub, B. L. Scott and J. C. Gordon, *Organometallics*, 2015, **34**, 4464–4479.
- 262 N. Takeda, D. Watanabe, T. Nakamura and M. Unno, *Organometallics*, 2010, **29**, 2839–2841.
- 263 M. V. Corona-González, J. Zamora-Moreno, C. A. Cuevas-Chávez, E. Rufino-Felipe, E. Mothes-Martin, Y. Coppel, M. A. Muñoz-Hernández, L. Vendier, M. Flores-Alamo, M. Grellier, S. Sabo-Etienne and V. Montiel-Palma, *Dalton Trans.*, 2017, **46**, 8827–8838.
- 264 M. Carmona, R. Rodríguez, I. Méndez, V. Passarelli, F. J. Lahoz, P. García-Orduña and D. Carmona, *Dalton Trans.*, 2017, **46**, 7332–7350.
- 265 Y. Gloaguen, L. M. Jongens, J. N. H. Reek, M. Lutz, B. de Bruin and J. I. van der Vlugt, *Organometallics*, 2013, **32**, 4284–4291.
- 266 M. R. Kita and A. J. M. Miller, *J. Am. Chem. Soc.*, 2014, **136**, 14519–14529.
- 267 S. Rani, S. Kumar and S. Chandra, *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.*, 2014, **118**, 244–250.
- 268 S. Chandra and S. Verma, *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.*, 2008, **71**, 458–464.
- 269 S. Rani, S. Kumar and S. Chandra, *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.*, 2011, **78**, 1507–1514.
- 270 M. Li, K. Takada, J. I. Goldsmith and S. Bernhard, *Inorg. Chem.*, 2016, **55**, 518–526.
- 271 D. Chen, K. Li, X. Guan, G. Cheng, C. Yang and C. M. Che, *Organometallics*, 2017, **36**, 1331–1344.
- 272 Y. S. Li, J. L. Liao, K. T. Lin, W. Y. Hung, S. H. Liu, G. H. Lee, P. T. Chou and Y. Chi, *Inorg. Chem.*, 2017, **56**, 10054–10060.
- 273 M. A. Esteruelas, A. M. López, E. Oñate, A. San-Torcuato, J. Y. Tsai and C. Xia, *Inorg. Chem.*, 2018, **57**, 3720–3730.
- 274 Y. Yuan, P. Gnanasekaran, Y. W. Chen, G. H. Lee, S. F. Ni, C. S. Lee and Y. Chi, *Inorg. Chem.*,

2020, **59**, 523–532.

- 275 M. Maestri, D. Sandrini, V. Balzani, A. von Zelewsky, C. Deuschel-Cornioley and P. Jolliet, *Helv. Chim. Acta*, 1988, **71**, 1053–1059.
- 276 S. Soman, H. M. Younis, W. R. Browne, J. G. Vos and M. T. Pryce, *Eur. J. Inorg. Chem.*, 2017, **2017**, 5598–5603.
- 277 S. C. Rasmussen, M. M. Richter, E. Yi, H. Place and K. J. Brewer, *Inorg. Chem.*, 1990, **29**, 3926–3932.
- 278 G. Li, D. G. Congrave, D. Zhu, Z. Su and M. R. Bryce, *Polyhedron*, 2018, **140**, 146–157.
- 279 E. V. Puttock, M. T. Walden and J. A. G. Williams, *Coord. Chem. Rev.*, 2018, **367**, 127–162.
- 280 M. Chaaban, C. Zhou, H. Lin, B. Chyi and B. Ma, *J. Mater. Chem. C*, 2019, **7**, 5910–5924.
- 281 Q. C. Zhang, H. Xiao, X. Zhang, L. J. Xu and Z. N. Chen, *Coord. Chem. Rev.*, 2019, **378**, 121–133.
- 282 B. B. Cui, J. H. Tang, J. Yao and Y. W. Zhong, *Angew. Chem. Int. Ed.*, 2015, **54**, 9192–9197.
- 283 E. A. Plummer, J. W. Hofstraat and L. De Cola, *Dalton Trans.*, 2003, 2080–2084.
- 284 G. Li, Y. Wu, G. Shan, W. Che, D. Zhu, B. Song, L. Yan, Z. Su and M. R. Bryce, *Chem. Commun.*, 2014, **50**, 6977–6980.
- 285 R. D. Costa, G. Fernández, L. Sánchez, N. Martín, E. Ortí and H. J. Bolink, *Chem. Eur. J.*, 2010, **16**, 9855–9863.
- 286 P. H. Lanoë, C. M. Tong, R. W. Harrington, M. R. Probert, W. Clegg, J. A. G. Williams and V. N. Kozhevnikov, *Chem. Commun.*, 2014, **50**, 6831–6834.
- 287 R. E. Daniels, S. Culham, M. Hunter, M. C. Durrant, M. R. Probert, W. Clegg, J. A. G. Williams and V. N. Kozhevnikov, *Dalton Trans.*, 2016, **45**, 6949–6962.
- 288 L. Donato, C. E. McCusker, F. N. Castellano and E. Zysman-Colman, *Inorg. Chem.*, 2013, **52**, 8495–8504.
- 289 S. Y. Yao, Y. L. Ou and B. H. Ye, *Inorg. Chem.*, 2016, **55**, 6018–6026.
- 290 S. Develay and J. A. G. Williams, *Dalton Trans.*, 2008, 4562–4564.
- 291 E. Garoni, J. Boixel, V. Dorcet, T. Roisnel, D. Roberto, D. Jacquemin and V. Guerschais, *Dalton Trans.*, 2018, **47**, 224–232.
- 292 C. Bronner, M. Veiga, A. Guenet, L. De Cola, M. W. Hosseini, C. A. Strassert and S. A. Baudron, *Chem. Eur. J.*, 2012, **18**, 4041–4050.
- 293 M. Z. Shafikov, S. Tang, C. Larsen, M. Bodensteiner, V. N. Kozhevnikov and L. Edman, *J. Mater. Chem. C*, 2019, **7**, 10672–10682.
- 294 V. N. Kozhevnikov, M. C. Durrant and J. A. G. Williams, *Inorg. Chem.*, 2011, **50**, 6304–6313.
- 295 V. L. Whittle and J. A. G. Williams, *Dalton Trans.*, 2009, 3929–3940.
- 296 A. Auffrant, A. Barbieri, F. Barigelletti, J.-P. Collin, L. Flamigni, C. Sabatini and J. P. Sauvage, *Inorg. Chem.*, 2006, **45**, 10990–10997.
- 297 M. Bixon, J. Jortner, J. Cortes, H. Heitele and M. E. Michel-Beyerle, *J. Phys. Chem.*, 1994, **98**, 7289–7299.
- 298 E. Rossi, A. Colombo, C. Dragonetti, D. Roberto, R. Ugo, A. Valore, L. Falciola, P. Brulatti, M. Cocchi and J. A. G. Williams, *J. Mater. Chem.*, 2012, **22**, 10650–10655.

- 299 T. Kayano, S. Takayasu, K. Sato and K. Shinozaki, *Chem. Eur. J.*, 2014, **20**, 16583–16589.
- 300 S. Tanaka, K. Sato, K. Ichida, T. Abe, T. Tsubomura, T. Suzuki and K. Shinozaki, *Chem. Asian J.*, 2016, **11**, 265–273.
- 301 C. Baik, W. S. Han, Y. Kang, S. O. Kang and J. Ko, *J. Organomet. Chem.*, 2006, **691**, 5900–5910.
- 302 A. Haque, L. Xu, R. A. Al-Balushi, M. K. Al-Suti, R. Ilmi, Z. Guo, M. S. Khan, W. Y. Wong and P. R. Raithby, *Chem. Soc. Rev.*, 2019, **48**, 5547–5563.
- 303 D. G. Congrave, Y. T. Hsu, A. S. Batsanov, A. Beeby and M. R. Bryce, *Dalton Trans.*, 2018, **47**, 2086–2098.
- 304 J. L. Liao, P. Rajakannu, P. Gnanasekaran, S. R. Tsai, C. H. Lin, S. H. Liu, C. H. Chang, G. H. Lee, P. T. Chou, Z. N. Chen and Y. Chi, *Adv. Opt. Mater.*, 2018, **6**, 1800083.
- 305 B. Park, Y. H. Huh, H. G. Jeon, C. H. Park, T. K. Kang, B. H. Kim and J. Park, *J. Appl. Phys.*, 2010, **108**, 94506.
- 306 K. P. S. Zanoni, M. S. Sanematsu and N. Y. Murakami Iha, *Inorg. Chem. Commun.*, 2014, **43**, 162–164.
- 307 J. H. Tang, J. Y. Shao, Y. Q. He, S. H. Wu, J. Yao and Y. W. Zhong, *Chem. Eur. J.*, 2016, **22**, 10341–10345.
- 308 K. J. Suhr, L. D. Bastatas, Y. Shen, L. A. Mitchell, B. J. Holliday and J. D. Slinker, *ACS Appl. Mater. Interfaces*, 2016, **8**, 8888–8892.
- 309 A. D. Becke, *J. Chem. Phys.*, 1986, **84**, 4524–4529.
- 310 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648–5652.
- 311 C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785–789.
- 312 G. M. Sheldrick, *Acta Crystallogr. A*, 2008, **64**, 112–122.
- 313 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339–341.
- 314 D. L. Ashford, C. R. K. Glasson, M. R. Norris, J. J. Concepcion, S. Keinan, M. K. Brennaman, J. L. Templeton and T. J. Meyer, *Inorg. Chem.*, 2014, **53**, 5637–5646.
- 315 Y. You and S. Y. Park, *J. Am. Chem. Soc.*, 2005, **127**, 12438–12439.
- 316 C. Fan, L. Zhu, B. Jiang, C. Zhong, D. Ma, J. Qin and C. Yang, *Org. Electron.*, 2013, **14**, 3163–3171.
- 317 P. Piyanut, R. Adrian, P. Sascha, M. Su, L. Roland and S. Wolfgang, *Chem. Eur. J.*, 2016, **22**, 5319–5326.
- 318 D. Zhang, J. P. Telo, C. Liao, S. E. Hightower and E. L. Clennan, *J. Phys. Chem. A*, 2007, **111**, 13567–13574.
- 319 D. Cuperly, P. Gros and Y. Fort, *J. Org. Chem.*, 2002, **67**, 238–241.
- 320 US Pat., 15397 20070702, 2008.
- 321 S. Xu, H. H. Chen, J. J. Dai and H. J. Xu, *Org. Lett.*, 2014, **16**, 2306–2309.
- 322 L. F. Tietze, B. Waldecker, D. Ganapathy, C. Eichhorst, T. Lenzer, K. Oum, S. O. Reichmann and D. Stalke, *Angew. Chem. Int. Ed.*, 2015, **54**, 10317–10321.
- 323 T. N. Y. Hoang, M. Humbert-Droz, T. Dutronc, L. Guénée, C. Besnard and C. Piguet, *Inorg. Chem.*, 2013, **52**, 5570–5580.

- 324 M. Hebenbrock, L. Stegemann, J. Kisters, N. L. Doltsinis, J. Muller and C. A. Strassert, *Dalton Trans.*, 2017, **46**, 3160–3169.
- 325 J. Carroll, H. G. Woolard, R. Mroz, C. A. Nason and S. Huo, *Organometallics*, 2016, **35**, 1313–1322.
- 326 T. Daniel, K. Valentin and R. Hans-Ulrich, *Eur. J. Org. Chem.*, 2014, **2014**, 6295–6302.
- 327 J. Il Kim, I. S. Shin, H. Kim and J. K. Lee, *J. Am. Chem. Soc.*, 2005, **127**, 1614–1615.
- 328 J. J. Giner-Casares, M. Perez-Morales, H. J. Bolink, N. Lardies, E. Munoz, G. de Miguel, M. T. Martin-Romero and L. Camacho, *J. Mater. Chem.*, 2008, **18**, 1681–1688.
- 329 F. De Angelis, S. Fantacci, N. Evans, C. Klein, S. M. Zakeeruddin, J. E. Moser, K. Kalyanasundaram, H. J. Bolink, M. Grätzel and M. K. Nazeeruddin, *Inorg. Chem.*, 2007, **46**, 5989–6001.
- 330 R. D. Costa, A. Pertegás, E. Ortí and H. J. Bolink, *Chem. Mater.*, 2010, **22**, 1288–1290.

Appendix

Crystal structure information

Crystal data and structure refinement for ligand H₂L22

Identification code	19srv165
Empirical formula	C ₃₉ H ₂₉ N ₅ O
Formula weight	583.67
Temperature/K	120.0
Crystal system	triclinic
Space group	P-1
a/Å	8.1679(6)
b/Å	11.1871(8)
c/Å	17.0326(12)
α/°	87.667(3)
β/°	83.534(3)
γ/°	73.758(3)
Volume/Å ³	1484.67(19)
Z	2
ρ _{calc} /cm ³	1.306
μ/mm ⁻¹	0.080
F(000)	612.0
Crystal size/mm ³	0.32 × 0.19 × 0.18
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.472 to 58
Index ranges	-11 ≤ h ≤ 11, -15 ≤ k ≤ 15, -23 ≤ l ≤ 23
Reflections collected	30834
Independent reflections	7882 [R _{int} = 0.0458, R _{sigma} = 0.0532]
Data/restraints/parameters	7882/0/407
Goodness-of-fit on F ²	1.085
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0507, wR ₂ = 0.1234
Final R indexes [all data]	R ₁ = 0.0880, wR ₂ = 0.1375
Largest diff. peak/hole / e Å ⁻³	0.29/-0.25

Crystal data and structure refinement for complex 8

Identification code	16srv325
Empirical formula	C ₃₄ H ₂₆ F ₈ IrN ₄ P
Formula weight	865.76
Temperature/K	120.0
Crystal system	monoclinic
Space group	C2/c
a/Å	17.0974(7)
b/Å	16.6951(7)
c/Å	12.3719(5)
α /°	90
β /°	118.7219(13)
γ /°	90
Volume/Å ³	3097.0(2)
Z	4
$\rho_{\text{calc}}/\text{g}/\text{cm}^3$	1.857
μ/mm^{-1}	4.444
F(000)	1688.0
Crystal size/mm ³	0.22 × 0.14 × 0.13
Radiation	MoK α (λ = 0.71073)
2 θ range for data collection/°	4.198 to 59.998
Index ranges	-24 ≤ h ≤ 24, -23 ≤ k ≤ 23, -17 ≤ l ≤ 17
Reflections collected	25186
Independent reflections	4517 [R_{int} = 0.0293, R_{sigma} = 0.0209]
Data/restraints/parameters	4517/0/219
Goodness-of-fit on F^2	1.062
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0158, wR_2 = 0.0340
Final R indexes [all data]	R_1 = 0.0194, wR_2 = 0.0351
Largest diff. peak/hole / e Å ⁻³	0.69/-0.61

Crystal data and structure refinement for complex 15

Identification code	18srv081
Empirical formula	C ₄₆ H ₂₈ F ₁₄ IrN ₄ O ₂ x PF ₆ x 0.5 CH ₃ CN
Formula weight	1178.42
Temperature/K	120.0
Crystal system	triclinic
Space group	P-1
a/Å	11.8207(2)
b/Å	12.3846(3)
c/Å	16.3601(3)
α/°	96.0429(19)
β/°	105.1782(16)
γ/°	95.8225(18)
Volume/Å ³	2277.77(9)
Z	2
ρ _{calc} /cm ³	1.718
μ/mm ⁻¹	3.068
F(000)	1154.0
Crystal size/mm ³	0.27 × 0.16 × 0.06
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.506 to 59
Index ranges	-16 ≤ h ≤ 16, -17 ≤ k ≤ 17, -22 ≤ l ≤ 22
Reflections collected	35955
Independent reflections	12668 [R _{int} = 0.0597, R _{sigma} = 0.0774]
Data/restraints/parameters	12668/4/634
Goodness-of-fit on F ²	1.011
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0480, wR ₂ = 0.1069
Final R indexes [all data]	R ₁ = 0.0705, wR ₂ = 0.1175
Largest diff. peak/hole / e Å ⁻³	1.67/-1.72

Crystal data and structure refinement for complex 16

Identification code	18srv087
Empirical formula	$C_{50}H_{40}F_4IrN_4 \times PF_6 \times CH_3CN$
Formula weight	1151.08
Temperature/K	120.0
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	13.5517(2)
b/Å	20.7433(3)
c/Å	16.4354(3)
$\alpha/^\circ$	90
$\beta/^\circ$	90.3302(15)
$\gamma/^\circ$	90
Volume/Å ³	4620.04(13)
Z	4
ρ_{calc}/cm^3	1.655
μ/mm^{-1}	3.008
F(000)	2288.0
Crystal size/mm ³	0.34 × 0.13 × 0.12
Radiation	MoK α (λ = 0.71073)
2 θ range for data collection/ $^\circ$	4.372 to 59.998
Index ranges	-18 ≤ h ≤ 19, -29 ≤ k ≤ 29, -23 ≤ l ≤ 23
Reflections collected	72994
Independent reflections	13449 [R_{int} = 0.0829, R_{sigma} = 0.0634]
Data/restraints/parameters	13449/0/629
Goodness-of-fit on F ²	1.047
Final R indexes [$ I \geq 2\sigma(I)$]	R_1 = 0.0380, wR_2 = 0.0745
Final R indexes [all data]	R_1 = 0.0602, wR_2 = 0.0831
Largest diff. peak/hole / e Å ⁻³	1.68/-0.85

Crystal data and structure refinement for complex 21

Identification code	17srv157
Empirical formula	$C_{33}H_{20}F_4IrN_6 \times PF_6 \times CH_3CN$
Formula weight	954.77
Temperature/K	120.0
Crystal system	monoclinic
Space group	C2/c
a/Å	26.6364(14)
b/Å	14.5886(8)
c/Å	19.0419(10)
$\alpha/^\circ$	90
$\beta/^\circ$	111.8974(17)
$\gamma/^\circ$	90
Volume/Å ³	6865.6(6)
Z	8
$\rho_{\text{calc}}/\text{cm}^3$	1.847
μ/mm^{-1}	4.029
F(000)	3712.0
Crystal size/mm ³	0.17 × 0.12 × 0.08
Radiation	MoK α (λ = 0.71073)
2 θ range for data collection/ $^\circ$	4.32 to 57
Index ranges	-35 ≤ h ≤ 35, -19 ≤ k ≤ 19, -25 ≤ l ≤ 25
Reflections collected	63870
Independent reflections	8703 [R_{int} = 0.0375, R_{sigma} = 0.0242]
Data/restraints/parameters	8703/15/519
Goodness-of-fit on F^2	1.049
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0301, wR_2 = 0.0795
Final R indexes [all data]	R_1 = 0.0396, wR_2 = 0.0844

Crystal data and structure refinement for complex 26

Identification code	17srv237
Empirical formula	C ₃₄ H ₂₆ IrN ₆ x PF ₆
Formula weight	855.78
Temperature/K	120.0
Crystal system	monoclinic
Space group	P2 ₁ /n
a/Å	12.82558(17)
b/Å	13.30161(18)
c/Å	18.3138(2)
α/°	90
β/°	95.1178(11)
γ/°	90
Volume/Å ³	3111.89(7)
Z	4
ρ _{calc} /cm ³	1.827
μ/mm ⁻¹	4.415
F(000)	1672.0
Crystal size/mm ³	0.29 × 0.25 × 0.12
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.42 to 59.994
Index ranges	-18 ≤ h ≤ 18, -18 ≤ k ≤ 18, -25 ≤ l ≤ 25
Reflections collected	44781
Independent reflections	9062 [R _{int} = 0.0569, R _{sigma} = 0.0445]
Data/restraints/parameters	9062/0/433
Goodness-of-fit on F ²	1.023
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0312, wR ₂ = 0.0670
Final R indexes [all data]	R ₁ = 0.0441, wR ₂ = 0.0724
Largest dif. peak/hole / e Å ⁻³	1.66/-0.82

Crystal data and structure refinement for 27

Identification code	17srv235
Empirical formula	C ₃₆ H ₂₉ F ₆ IrN ₇ P
Formula weight	896.83
Temperature/K	120.0
Crystal system	monoclinic
Space group	P2 ₁ /n
a/Å	13.9102(5)
b/Å	14.2235(5)
c/Å	17.3961(6)
α /°	90
β /°	105.396(1)
γ /°	90
Volume/Å ³	3318.3(2)
Z	4
ρ_{calc} /cm ³	1.795
μ /mm ⁻¹	4.145
F(000)	1760.0
Crystal size/mm ³	0.23 × 0.2 × 0.08
Radiation	MoK α (λ = 0.71073)
2 θ range for data collection/°	4.174 to 59.998
Index ranges	-19 ≤ h ≤ 19, -20 ≤ k ≤ 20, -24 ≤ l ≤ 24
Reflections collected	70502
Independent reflections	9657 [R_{int} = 0.0336, R_{sigma} = 0.0228]
Data/restraints/parameters	9657/29/458
Goodness-of-fit on F ²	1.044
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0393, wR_2 = 0.0821
Final R indexes [all data]	R_1 = 0.0500, wR_2 = 0.0873
Largest diff. peak/hole / e Å ⁻³	5.59/-2.37

Crystal data and structure refinement for complex 30

Identification code	17srv147
Empirical formula	$C_{34}H_{21}F_4IrN_5 \times PF_6 \times 0.5 C_4H_{10}O$
Formula weight	949.79
Temperature/K	200.0
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.4666(9)
b/Å	32.257(3)
c/Å	11.9948(12)
$\alpha/^\circ$	90
$\beta/^\circ$	94.038(3)
$\gamma/^\circ$	90
Volume/Å ³	3653.7(6)
Z	4
$\rho_{\text{calc}}/\text{cm}^3$	1.727
μ/mm^{-1}	3.785
F(000)	1852.0
Crystal size/mm ³	0.34 × 0.04 × 0.02
Radiation	MoK α (λ = 0.71073)
2 θ range for data collection/ $^\circ$	4.998 to 51.998
Index ranges	$-11 \leq h \leq 11$, $-39 \leq k \leq 39$, $-14 \leq l \leq 14$
Reflections collected	38261
Independent reflections	7178 [R_{int} = 0.1283, R_{sigma} = 0.1306]
Data/restraints/parameters	7178/155/482
Goodness-of-fit on F^2	1.178
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0880, wR_2 = 0.1551
Final R indexes [all data]	R_1 = 0.1513, wR_2 = 0.1712
Largest diff. peak/hole / e Å ⁻³	1.21/-3.58

Crystal data and structure refinement for complex 38

Identification code	17srv268
Empirical formula	C ₃₀ H ₂₃ ClIrN ₄ x PF ₆
Formula weight	812.14
Temperature/K	120.0
Crystal system	triclinic
Space group	P-1
a/Å	8.6840(3)
b/Å	10.3584(4)
c/Å	16.3438(6)
α/°	91.7336(13)
β/°	102.4454(13)
γ/°	110.0297(12)
Volume/Å ³	1340.08(9)
Z	2
ρ _{calc} /cm ³	2.013
μ/mm ⁻¹	5.214
F(000)	788.0
Crystal size/mm ³	0.19 × 0.15 × 0.05
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.678 to 57.996
Index ranges	-11 ≤ h ≤ 11, -14 ≤ k ≤ 13, -22 ≤ l ≤ 22
Reflections collected	27789
Independent reflections	7105 [R _{int} = 0.0295, R _{sigma} = 0.0263]
Data/restraints/parameters	7105/0/390
Goodness-of-fit on F ²	1.132
Final R indexes [I >= 2σ (I)]	R ₁ = 0.0176, wR ₂ = 0.0394
Final R indexes [all data]	R ₁ = 0.0203, wR ₂ = 0.0399
Largest diff. peak/hole / e Å ⁻³	0.93/-0.91

Crystal data and structure refinement for complex 39

Identification code	17srv256
Empirical formula	$C_{27}H_{21}ClIrN_4O \times PF_6$
Formula weight	790.10
Temperature/K	120.0
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	8.63465(15)
b/Å	17.7894(3)
c/Å	17.4936(3)
$\alpha/^\circ$	90
$\beta/^\circ$	96.5594(15)
$\gamma/^\circ$	90
Volume/Å ³	2669.52(8)
Z	4
$\rho_{\text{calc}}/\text{cm}^3$	1.966
μ/mm^{-1}	5.234
F(000)	1528.0
Crystal size/mm ³	0.29 × 0.05 × 0.04
Radiation	MoK α (λ = 0.71073)
2 θ range for data collection/ $^\circ$	5.144 to 57.988
Index ranges	$-11 \leq h \leq 11$, $-24 \leq k \leq 24$, $-23 \leq l \leq 23$
Reflections collected	46653
Independent reflections	7078 [$R_{\text{int}} = 0.0779$, $R_{\text{sigma}} = 0.0516$]
Data/restraints/parameters	7078/0/371
Goodness-of-fit on F^2	1.011
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0310$, $wR_2 = 0.0608$
Final R indexes [all data]	$R_1 = 0.0478$, $wR_2 = 0.0666$
Largest diff. peak/hole / e Å ⁻³	1.90/-0.77

Crystal data and structure refinement for complex 41

Identification code	17srv272
Empirical formula	C ₂₉ H ₂₅ ClIrN ₄ O x PF ₆
Formula weight	818.15
Temperature/K	120.0
Crystal system	monoclinic
Space group	P2 ₁ /n
a/Å	8.7936(4)
b/Å	17.9171(7)
c/Å	18.7687(7)
α/°	90
β/°	101.0443(14)
γ/°	90
Volume/Å ³	2902.3(2)
Z	4
ρ _{calc} /cm ³	1.872
μ/mm ⁻¹	4.818
F(000)	1592.0
Crystal size/mm ³	0.19 × 0.03 × 0.02
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.422 to 58.996
Index ranges	-12 ≤ h ≤ 12, -24 ≤ k ≤ 24, -25 ≤ l ≤ 25
Reflections collected	62365
Independent reflections	8087 [R _{int} = 0.0428, R _{sigma} = 0.0275]
Data/restraints/parameters	8087/0/391
Goodness-of-fit on F ²	1.025
Final R indexes [I > 2σ (I)]	R ₁ = 0.0202, wR ₂ = 0.0417
Final R indexes [all data]	R ₁ = 0.0308, wR ₂ = 0.0438
Largest diff. peak/hole / e Å ⁻³	0.84/-0.53

Crystal data and structure refinement for complex 42

Identification code	17srv257
Empirical formula	$C_{29}H_{21}ClIrN_4O \times PF_6 \times 0.5 CH_3CN$
Formula weight	834.64
Temperature/K	120.0
Crystal system	monoclinic
Space group	C2/c
a/Å	34.968(9)
b/Å	8.699(2)
c/Å	19.946(5)
$\alpha/^\circ$	90
$\beta/^\circ$	109.411(7)
$\gamma/^\circ$	90
Volume/Å ³	5722(2)
Z	8
ρ_{calc}/cm^3	1.938
μ/mm^{-1}	4.890
F(000)	3240.0
Crystal size/mm ³	0.11 × 0.05 × 0.01
Radiation	MoK α (λ = 0.71073)
2 θ range for data collection/ $^\circ$	4.842 to 60
Index ranges	-47 ≤ h ≤ 49, -12 ≤ k ≤ 12, -28 ≤ l ≤ 28
Reflections collected	61838
Independent reflections	8352 [R_{int} = 0.0527, R_{sigma} = 0.0367]
Data/restraints/parameters	8352/0/405
Goodness-of-fit on F^2	1.019
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0313, wR_2 = 0.0637
Final R indexes [all data]	R_1 = 0.0510, wR_2 = 0.0695
Largest diff. peak/hole / e Å ⁻³	1.72/-1.31

Crystal data and structure refinement for complex 51

Identification code	17srv337
Empirical formula	$C_{30}H_{25}ClIrN_6 \times PF_6 \times CH_3CN$
Formula weight	883.23
Temperature/K	120.0
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	17.374(3)
b/Å	12.4294(18)
c/Å	14.369(2)
$\alpha/^\circ$	90
$\beta/^\circ$	94.180(4)
$\gamma/^\circ$	90
Volume/Å ³	3094.8(8)
Z	4
ρ_{calc}/cm^3	1.896
μ/mm^{-1}	4.526
F(000)	1728.0
Crystal size/mm ³	0.29 × 0.09 × 0.02
Radiation	MoK α (λ = 0.71073)
2 θ range for data collection/ $^\circ$	4.338 to 60
Index ranges	-24 ≤ h ≤ 24, -17 ≤ k ≤ 17, -20 ≤ l ≤ 20
Reflections collected	59986
Independent reflections	9027 [R_{int} = 0.0798, R_{sigma} = 0.0623]
Data/restraints/parameters	9027/0/437
Goodness-of-fit on F^2	1.150
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0427, wR_2 = 0.0816
Final R indexes [all data]	R_1 = 0.0706, wR_2 = 0.0909
Largest diff. peak/hole / e Å ⁻³	3.40/-2.65

Crystal data and structure refinement for complex 52

Identification code	17srv338
Empirical formula	$\text{C}_{30}\text{H}_{25}\text{ClIrN}_6 \times \text{PF}_6 \times 2 \text{CH}_3\text{CN}$
Formula weight	924.29
Temperature/K	120.0
Crystal system	triclinic
Space group	P-1
a/Å	8.8056(4)
b/Å	11.8575(5)
c/Å	17.3248(7)
$\alpha/^\circ$	81.6294(14)
$\beta/^\circ$	88.5320(15)
$\gamma/^\circ$	71.8709(14)
Volume/Å ³	1700.44(13)
Z	2
$\rho_{\text{calc}}/\text{cm}^3$	1.805
μ/mm^{-1}	4.124
F(000)	908.0
Crystal size/mm ³	0.43 × 0.25 × 0.22
Radiation	MoK α (λ = 0.71073)
2 θ range for data collection/ $^\circ$	4.638 to 59.992
Index ranges	-12 ≤ h ≤ 12, -16 ≤ k ≤ 16, -24 ≤ l ≤ 24
Reflections collected	37645
Independent reflections	9912 [R_{int} = 0.0485, R_{sigma} = 0.0366]
Data/restraints/parameters	9912/66/489
Goodness-of-fit on F^2	1.089
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0195, wR_2 = 0.0453
Final R indexes [all data]	R_1 = 0.0215, wR_2 = 0.0458
Largest diff. peak/hole / e Å ⁻³	0.96/-0.84

Crystal data and structure refinement for complex 56

Identification code	18srv203
Empirical formula	C ₂₉ H ₂₃ ClIrN ₆ O x PF ₆ x CH ₃ CN
Formula weight	885.21
Temperature/K	120.0
Crystal system	triclinic
Space group	P-1
a/Å	8.7255(5)
b/Å	11.7683(7)
c/Å	16.2016(10)
α/°	87.382(3)
β/°	78.394(3)
γ/°	71.743(2)
Volume/Å ³	1547.33(16)
Z	2
ρ _{calc} /cm ³	1.900
μ/mm ⁻¹	4.529
F(000)	864.0
Crystal size/mm ³	0.28 × 0.05 × 0.03
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.42 to 58.996
Index ranges	-12 ≤ h ≤ 12, -16 ≤ k ≤ 16, -22 ≤ l ≤ 22
Reflections collected	33188
Independent reflections	8612 [R _{int} = 0.0446, R _{sigma} = 0.0473]
Data/restraints/parameters	8612/66/429
Goodness-of-fit on F ²	1.066
Final R indexes [I >= 2σ (I)]	R ₁ = 0.0289, wR ₂ = 0.0659
Final R indexes [all data]	R ₁ = 0.0391, wR ₂ = 0.0681
Largest diff. peak/hole / e Å ⁻³	1.25/-1.46

Crystal data and structure refinement for complex 57

Identification code	18srv209
Empirical formula	$\text{C}_{38}\text{H}_{23}\text{F}_3\text{IrN}_6\text{O} \times \text{PF}_6 \times 3 \text{CH}_3\text{CN}$
Formula weight	1024.89
Temperature/K	120.0
Crystal system	triclinic
Space group	P-1
a/Å	8.7529(6)
b/Å	13.2066(9)
c/Å	16.7123(12)
$\alpha/^\circ$	87.291(2)
$\beta/^\circ$	86.472(3)
$\gamma/^\circ$	89.359(2)
Volume/Å ³	1926.0(2)
Z	2
$\rho_{\text{calc}}/\text{cm}^3$	1.767
μ/mm^{-1}	3.597
F(000)	1008.0
Crystal size/mm ³	0.29 × 0.11 × 0.03
Radiation	MoK α (λ = 0.71073)
2 θ range for data collection/ $^\circ$	4.662 to 59
Index ranges	-12 ≤ h ≤ 12, -18 ≤ k ≤ 17, -23 ≤ l ≤ 23
Reflections collected	40348
Independent reflections	10718 [R_{int} = 0.0666, R_{sigma} = 0.0703]
Data/restraints/parameters	10718/55/524
Goodness-of-fit on F^2	1.051
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0393, wR_2 = 0.0901
Final R indexes [all data]	R_1 = 0.0535, wR_2 = 0.0941
Largest diff. peak/hole / e Å ⁻³	2.01/-1.61

Crystal data and structure refinement for complex 60

Identification code	19srv153
Empirical formula	C ₆₃ H ₅₉ F ₁₂ N ₉ O ₄ P ₂ Pt ₂
Formula weight	1686.31
Temperature/K	120.0
Crystal system	triclinic
Space group	P-1
a/Å	13.7961(7)
b/Å	15.2882(7)
c/Å	16.4234(8)
α /°	70.0008(16)
β /°	66.7150(17)
γ /°	81.8056(18)
Volume/Å ³	2989.9(3)
Z	2
ρ_{calc} /cm ³	1.873
μ /mm ⁻¹	4.823
F(000)	1652.0
Crystal size/mm ³	0.22 × 0.08 × 0.03
Radiation	MoK α (λ = 0.71073)
2 θ range for data collection/°	4.604 to 58.996
Index ranges	-19 ≤ h ≤ 19, -21 ≤ k ≤ 21, -22 ≤ l ≤ 22
Reflections collected	64384
Independent reflections	16631 [R_{int} = 0.0376, R_{sigma} = 0.0389]
Data/restraints/parameters	16631/163/827
Goodness-of-fit on F ²	1.023
Final R indexes [$ I \geq 2\sigma(I)$]	R_1 = 0.0283, wR_2 = 0.0621
Final R indexes [all data]	R_1 = 0.0463, wR_2 = 0.0673
Largest diff. peak/hole / e Å ⁻³	2.02/-1.35

Crystal data and structure refinement for complex 61

Identification code	19srv164
Empirical formula	C ₂₉ H ₂₂ ClN ₃ OPt
Formula weight	659.03
Temperature/K	120.0
Crystal system	triclinic
Space group	P-1
a/Å	10.3001(5)
b/Å	10.8846(5)
c/Å	11.2133(5)
α /°	75.8790(16)
β /°	74.6176(17)
γ /°	75.5040(17)
Volume/Å ³	1152.10(9)
Z	2
$\rho_{\text{calc}}/\text{cm}^3$	1.900
μ/mm^{-1}	6.235
F(000)	640.0
Crystal size/mm ³	0.14 × 0.11 × 0.09
Radiation	MoK α (λ = 0.71073)
2 θ range for data collection/°	4.948 to 59.996
Index ranges	-14 ≤ h ≤ 14, -15 ≤ k ≤ 15, -15 ≤ l ≤ 15
Reflections collected	25556
Independent reflections	6715 [R_{int} = 0.0313, R_{sigma} = 0.0280]
Data/restraints/parameters	6715/0/404
Goodness-of-fit on F^2	1.022
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0164, wR_2 = 0.0350
Final R indexes [all data]	R_1 = 0.0205, wR_2 = 0.0357
Largest diff. peak/hole / e Å ⁻³	0.62/-0.66

Crystal data and structure refinement for complex 84

Identification code	19srv174
Empirical formula	C ₆₅ H ₅₄ Cl ₂ F ₁₂ Ir ₂ N ₁₁ O _{1.5} P ₂
Formula weight	1758.43
Temperature/K	120.0
Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	16.1382(11)
b/Å	26.3899(17)
c/Å	16.8288(11)
α/°	90
β/°	111.932(2)
γ/°	90
Volume/Å ³	6648.5(8)
Z	4
ρ _{calc} /cm ³	1.757
μ/mm ⁻¹	4.214
F(000)	3436.0
Crystal size/mm ³	0.31 × 0.07 × 0.01
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.114 to 54.998
Index ranges	-20 ≤ h ≤ 20, -34 ≤ k ≤ 34, -21 ≤ l ≤ 21
Reflections collected	124386
Independent reflections	15238 [R _{int} = 0.0677, R _{sigma} = 0.0468]
Data/restraints/parameters	15238/43/886
Goodness-of-fit on F ²	1.028
Final R indexes [I > 2σ (I)]	R ₁ = 0.0416, wR ₂ = 0.0983
Final R indexes [all data]	R ₁ = 0.0690, wR ₂ = 0.1096
Largest diff. peak/hole / e Å ⁻³	3.53/-2.03

Crystal data and structure refinement for complex 86

Identification code	18srv205
Empirical formula	$\text{C}_{30}\text{H}_{21}\text{ClF}_3\text{IrN}_5\text{O} \times \text{PF}_6 \times 0.5 \text{C}_4\text{H}_{10}\text{O} \times 1.5\text{CH}_3\text{CN}$
Formula weight	995.78
Temperature/K	120.0
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	27.1183(14)
b/Å	11.7090(6)
c/Å	23.2928(12)
$\alpha/^\circ$	90
$\beta/^\circ$	98.5173(19)
$\gamma/^\circ$	90
Volume/Å ³	7314.5(7)
Z	8
$\rho_{\text{calc}}/\text{cm}^3$	1.808
μ/mm^{-1}	3.855
F(000)	3904.0
Crystal size/mm ³	0.32 × 0.21 × 0.11
Radiation	MoK α ($\lambda = 0.71073$)
2 θ range for data collection/ $^\circ$	3.902 to 58
Index ranges	$-36 \leq h \leq 36, -15 \leq k \leq 15, -31 \leq l \leq 31$
Reflections collected	146743
Independent reflections	19419 [$R_{\text{int}} = 0.0532, R_{\text{sigma}} = 0.0360$]
Data/restraints/parameters	19419/47/987
Goodness-of-fit on F^2	1.160
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0457, wR_2 = 0.0867$
Final R indexes [all data]	$R_1 = 0.0648, wR_2 = 0.0932$
Largest diff. peak/hole / e Å ⁻³	2.04/-3.45

Crystal data and structure refinement for complex 87

Identification code	18srv214
Empirical formula	$C_{28}H_{21}ClIrN_6O \times PF_6 \times 1.5 CH_3CN$
Formula weight	891.71
Temperature/K	120.0
Crystal system	triclinic
Space group	P-1
a/Å	7.9387(18)
b/Å	12.850(3)
c/Å	17.640(4)
$\alpha/^\circ$	82.342(5)
$\beta/^\circ$	89.863(5)
$\gamma/^\circ$	86.099(5)
Volume/Å ³	1779.3(7)
Z	2
ρ_{calc}/cm^3	1.664
μ/mm^{-1}	3.940
F(000)	870.0
Crystal size/mm ³	0.27 × 0.02 × 0.01
Radiation	MoK α (λ = 0.71073)
2 θ range for data collection/ $^\circ$	4.206 to 53.998
Index ranges	-10 ≤ h ≤ 10, -16 ≤ k ≤ 16, -22 ≤ l ≤ 22
Reflections collected	26401
Independent reflections	7767 [R_{int} = 0.1118, R_{sigma} = 0.1384]
Data/restraints/parameters	7767/2/434
Goodness-of-fit on F^2	1.018
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0621, wR_2 = 0.1290
Final R indexes [all data]	R_1 = 0.1003, wR_2 = 0.1417
Largest diff. peak/hole / e Å ⁻³	2.57/-1.81

Crystal data and structure refinement for complex 88

Identification code	18srv215
Empirical formula	$C_{49}H_{37}IrN_7O \times PF_6 \times 2 C_3H_6O$
Formula weight	1193.18
Temperature/K	120.0
Crystal system	monoclinic
Space group	C2/c
a/Å	27.481(2)
b/Å	13.2172(11)
c/Å	32.721(3)
$\alpha/^\circ$	90
$\beta/^\circ$	112.121(2)
$\gamma/^\circ$	90
Volume/Å ³	11010.2(17)
Z	8
$\rho_{\text{calc}}/\text{cm}^3$	1.440
μ/mm^{-1}	2.523
F(000)	4784.0
Crystal size/mm ³	0.18 × 0.09 × 0.02
Radiation	MoK α (λ = 0.71073)
2 θ range for data collection/ $^\circ$	4.004 to 54
Index ranges	-35 ≤ h ≤ 35, -16 ≤ k ≤ 16, -41 ≤ l ≤ 41
Reflections collected	61008
Independent reflections	12022 [R_{int} = 0.0908, R_{sigma} = 0.0882]
Data/restraints/parameters	12022/12/657
Goodness-of-fit on F^2	1.093
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0627, wR_2 = 0.1428
Final R indexes [all data]	R_1 = 0.0957, wR_2 = 0.1558
Largest diff. peak/hole / e Å ⁻³	2.66/-3.38

Crystal data and structure refinement for complex 90

Identification code	18srv432
Empirical formula	C ₅₇ H ₅₁ F ₆ IrN ₅ O ₃ P
Formula weight	1191.19
Temperature/K	120.0
Crystal system	monoclinic
Space group	P2 ₁ /n
a/Å	16.580(3)
b/Å	13.560(2)
c/Å	25.841(4)
α/°	90
β/°	95.967(4)
γ/°	90
Volume/Å ³	5778.4(15)
Z	4
ρ _{calc} /cm ³	1.369
μ/mm ⁻¹	2.402
F(000)	2392.0
Crystal size/mm ³	0.24 × 0.18 × 0.06
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.296 to 51.998
Index ranges	-20 ≤ h ≤ 20, -16 ≤ k ≤ 16, -31 ≤ l ≤ 31
Reflections collected	87380
Independent reflections	11331 [R _{int} = 0.1616, R _{sigma} = 0.1187]
Data/restraints/parameters	11331/67/641
Goodness-of-fit on F ²	1.071
Final R indexes [I > 2σ (I)]	R ₁ = 0.0873, wR ₂ = 0.2020
Final R indexes [all data]	R ₁ = 0.1733, wR ₂ = 0.2578
Largest diff. peak/hole / e Å ⁻³	3.72/-1.32

LEC performance data

Table 8.1: LEC performance data of devices containing complexes (i) to (iv) and (x) to (xv) which were discussed in section 2.2. ^a = time to reach maximum luminance, ^b = time to reach one half of maximum luminance, EQE = external quantum efficiency, PE = power efficiency, CE = current efficiency. The bracketed values in the rows of complexes (ii) and (iii) refer to the equivalent ppy-based complexes. The bracketed values in the row of complex (x) refer to the equivalent bpy-containing complex.

Complex	Device Architecture	Operation Mode	$L_{\max}$ /cd m ⁻²	t_{on} /h ^a	$t_{1/2}$ /h ^b	Max EQE /%	λ_{EL} /nm	Max PE /lm W ⁻¹	Max. CE /cd A ⁻¹
(i) ⁵⁵	ITO/PEDOT:PSS/i/Au	Constant voltage (3 V)	330	> 8	-	5	560	> 10	-
(ii) ⁸⁶	ITO/PEDOT:PSS/ii):[BMIM]PF ₆ (4:1)/Al	100 A m ⁻² pulsed current	557 (432)	0.015 (0.67)	0.3 (62)	2.0 (1.8)	578 (582)	2.1 (2.3)	5.6 (4.3)
(iii) ⁸⁷	ITO/PEDOT:PSS/PVK/mCP + iii) + OXD7/TPBI/Ca/Al	Constant voltage (6.2 V)	2940 (1790)	-	-	3.95 (5.42)	-	4.81 (6.23)	-
(iv) ⁸⁷	ITO/PEDOT:PSS/PVK/mCP + iv) + OXD7/TPBI/Ca/Al	Constant voltage (4.8 V)	1090	-	-	3.42	-	4.42	-
(x) ⁵⁶	ITO/PEDOT:PSS/x) + 0.3% LiPF ₆ /LiF/Al	500 A m ⁻² pulsed current	382 (2750)	0.28 (3.18)	232 (33)	0.53 (2.21)	613 (599)	0.55 (3.96)	0.76 (5.50)
(xi) ⁵⁶	ITO/PEDOT:PSS/xi) + 0.3% LiPF ₆ /LiF/Al	500 A m ⁻² pulsed current	673	0.87	92	1.15	631	1.16	1.34
(xii) ⁷⁹	ITO/PEDOT:PSS/xii):[BMIM]PF ₆ (4:1)/Al	Constant voltage (3 V)	109	237	1,290	1.3	-	3.3	3.1
(xiii) ⁸⁰	ITO/PEDOT:PSS/xiii):[BMIM]PF ₆ (4:1)/Al	300 A m ⁻² pulsed current	1020	0.14	2,800	-	-	-	3.5
(xiv) ⁷⁹	ITO/PEDOT:PSS/xiv):[BMIM]PF ₆ (4:1)/Al	Constant voltage (3 V)	183	77	950	3.4	-	8.6	8.2
(xv) ⁷⁹	ITO/PEDOT:PSS/xv):[BMIM]PF ₆ (4:1)/Al	Constant voltage (3 V)	284	33	660	6.1	-	15.3	14.7

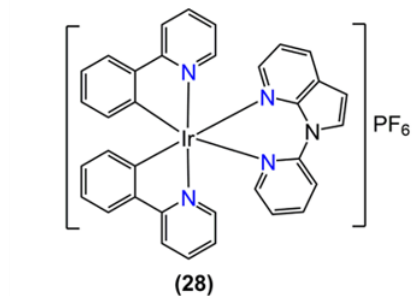
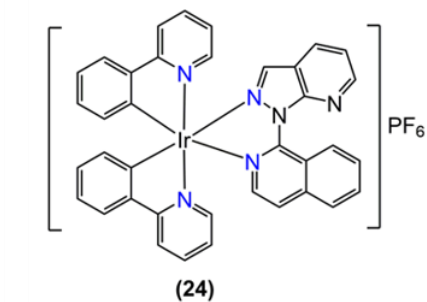
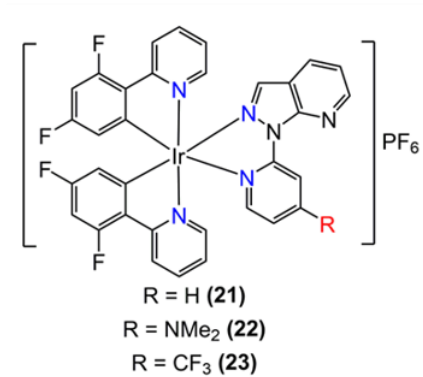
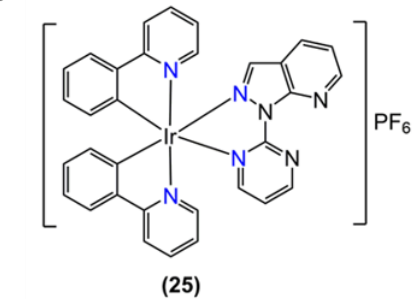
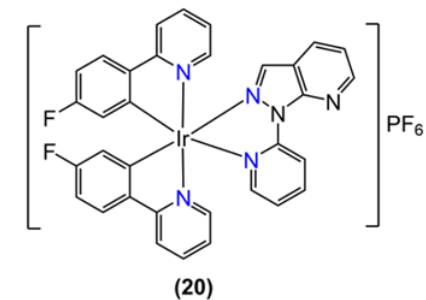
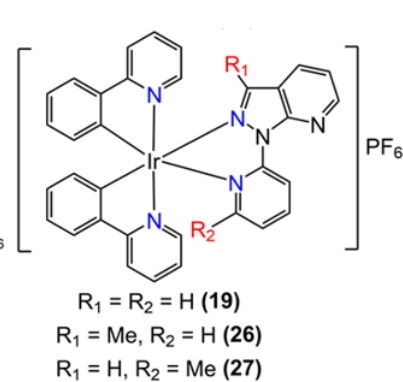
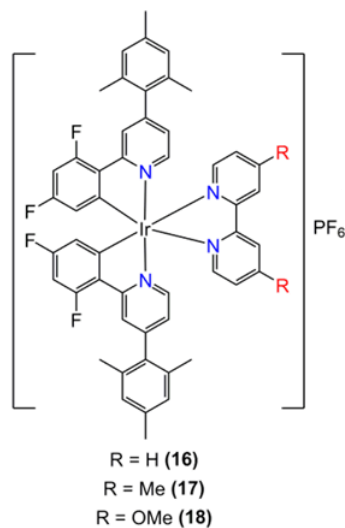
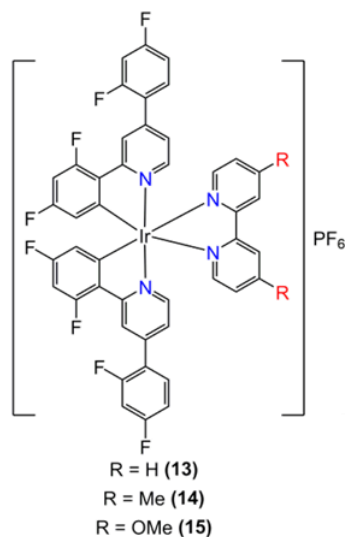
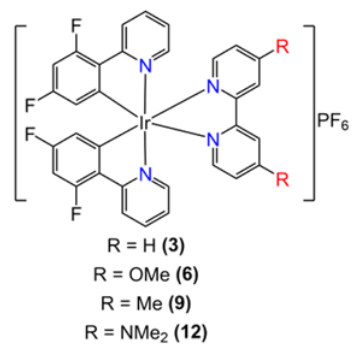
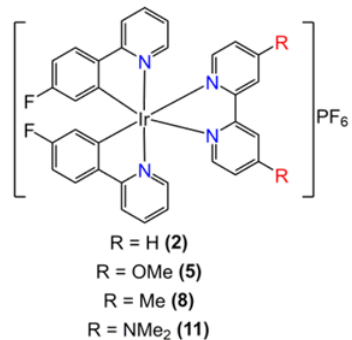
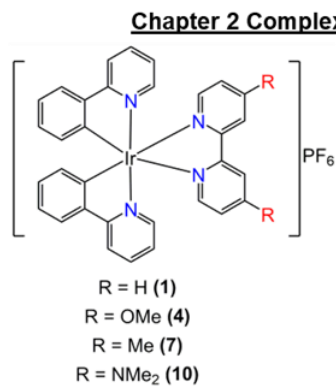
Table 8.2: LEC performance data of devices containing complexes **1-3**, **7**, **8**, **10** and (xvi) to (xxxviii) discussed in section 2.3. ^a = time to reach maximum luminance, ^b = time to reach one half of maximum luminance, ^c = time to reach 1 cd m⁻², EQE = external quantum efficiency, PE = power efficiency, CE = current efficiency, ^{sh} = shoulder. The bracketed values in the row of complex (xxxvi) refer to the equivalent ppy-based complex.

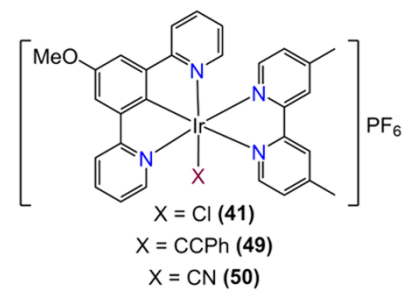
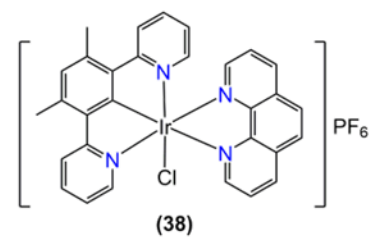
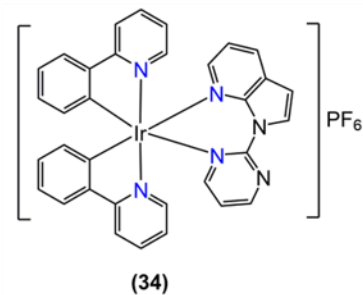
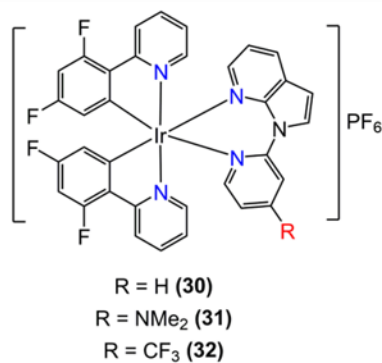
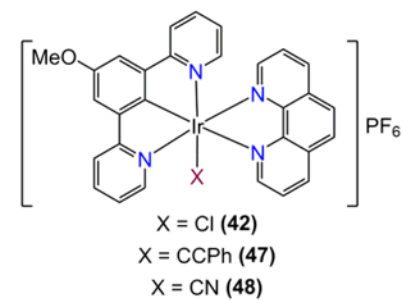
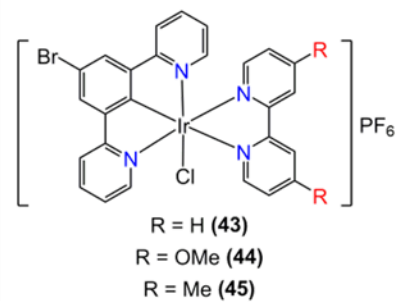
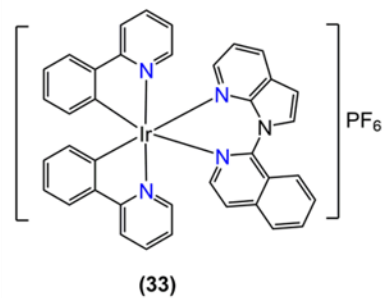
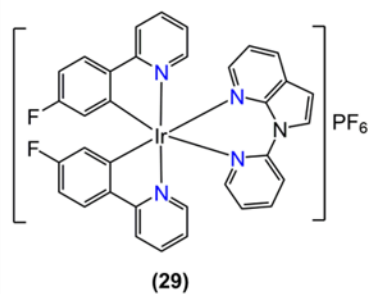
Complex	Device Architecture	Operation Mode	L _{max} /cd m ⁻²	t _{on} /h ^a	t _{1/2} /h ^b	Max EQE /%	λ _{EL} /nm	Max PE /lm W ⁻¹	Max. CE /cd A ⁻¹
1 ⁵⁶	ITO/PEDOT:PSS/ 1 + 0.3% LiPF ₆ /Al	500 A m ⁻² pulsed current	2,750	3.2	33	2.21	599	3.96	5.5
1 ²³	ITO/PEDOT:PSS/ 1 + 0.33% LiPF ₆ /LiF/Al	Constant current (1.5 mA)	3,030	0.0028	137	1.97	-	3.8	6.0
1 ⁸²	ITO/PEDOT:PSS/ 1 :[BMIM]PF ₆ (4:1)/Al	Constant voltage (3 V)	334	7.2	70	3.0	590	8.7	8.3
1 ³³⁰	ITO/PEDOT:PSS/ 1 :[EMIM]PF ₆ (4:1)/Al	Constant voltage (3 V)	497	0.4	81	-	576	4.6	-
2 ⁹⁶	ITO/PEDOT:PSS/ 2 :BMIMPF ₆ (3:1)/Al	100 A m ⁻² pulsed current	1,610	-	668	-	-	8.7	16
3 ³⁰⁵	ITO/PEDOT:PSS/ 3 /CsF/Al	Voltage sweep	11,600	-	-	-	517	2.3	11.8
7 ³⁰⁶	FTO/PEDOT:PSS/ 7 /Al	Voltage sweep	> 100	-	-	-	560	-	14.9
8 ⁹⁶	ITO/PEDOT:PSS/ 8 :BMIMPF ₆ (3:1)/Al	100 A m ⁻² pulsed current	1,590	-	221	-	-	8.5	15.9
10 ¹¹⁰	ITO/ 10 /Ag	Voltage sweep	200	-	-	0.2	-	-	0.43
(xvi) ¹⁰⁰	ITO/PEDOT:PSS/(xvi)/CsF/Al	Constant voltage (3.5 V)	40	-	3.6	0.75	500	-	-
(xvii) ¹⁰⁶	ITO/PEDOT:PSS/(xvii):[BMIM]PF ₆ (4:1)/Al	100 A m ⁻² pulsed current	1060	-	0.33	3.8	492, 521	4.6	10.5
(xviii) ¹¹²	ITO/PEDOT:PSS/(xviii)/Al	Constant voltage (3 V)	1700	0.5 ^c	-	4.6	492	-	-
(xix) ¹¹³	ITO/PEDOT:PSS/(xix):[BMIM]PF ₆ (1:0.35)/Al	Constant voltage (5 V)	52	7.2	-	0.36	486, 508 ^{sh}	-	0.96
(xx) ¹¹³	ITO/PEDOT:PSS/(xx):[BMIM]PF ₆ (1:0.35)/Al	Constant voltage (5 V)	94	0.4	-	1.6	486, 512 ^{sh}	-	4.3
(xxi) ¹¹⁴	ITO/PEDOT:PSS/(xxi)/LiF/Al	Constant voltage (9 V)	7	1.5	6	0.45	569	-	1.3

Complex	Device Architecture	Operation Mode	$L_{\max} / \text{cd m}^{-2}$	$t_{\text{on}} / \text{h}^{\text{a}}$	$t_{1/2} / \text{h}^{\text{b}}$	Max EQE /%	$\lambda_{\text{EL}} / \text{nm}$	Max PE /lm W ⁻¹	Max. CE /cd A ⁻¹
(xii) ¹¹⁴	ITO/PEDOT:PSS/xxii/LiF/Al	Constant voltage (9 V)	3	2	6	0.39	508	-	0.4
(xiii) ¹¹⁵	ITO/PEDOT:PSS/xxiii):[BMIM]PF ₆ (1:0.8)/Al	Constant voltage (4 V)	10.1	0.035	0.035	0.4	469	-	0.72
(xxiv) ¹⁰⁶	ITO/PEDOT:PSS/xxiv):[BMIM]PF ₆ (4:1)/Al	100 A m ⁻² pulsed current	29	-	0.003	0.1	486, 553	< 0.1	0.3
(xxv) ¹¹⁶	ITO/PEDOT:PSS/xxv):TBAOTf (1:1)/Al	Constant voltage (5 V)	31	0.033	0.0567	-	456, 488	-	-
(xxvi) ¹¹⁷	ITO/PEDOT:PSS/xxvi):[BMIM]PF ₆ (1:0.14)/Al	Constant voltage (4.5 V)	4.5	2.33 ^c	-	0.27	457, 486	-	0.26
(xxvii) ¹¹⁸	ITO/PEDOT:PSS/xxvii):TBAOTf (1:1)/Al	Constant voltage (5 V)	22	0.075	0.133	-	488	-	0.73
(xxviii) ¹¹⁸	ITO/PEDOT:PSS/xxviii):TBAOTf (1:1)/Al	Constant voltage (5 V)	24	0.088	0.163	-	456, 488	-	0.37
(xxix) ¹³⁶	ITO/PEDOT:PSS/xxix):[BMIM]PF ₆ (4:1)/Al	Constant voltage (4 V)	18	1.1	2	0.05	≈650	0.013	0.05
(xxx) ¹³⁷	ITO/PEDOT:PSS/xxx):[BMIM]PF ₆ (2:1)/Al	Constant voltage (3 V)	≈35	0.17	0.52	-	630	0.71	0.68
(xxxi) ¹⁴⁴	ITO/PEDOT:PSS/xxxi)/Ag	Constant voltage (7 V)	63	0.67	-	-	662	0.0052	0.023
(xxxii) ¹⁴³	ITO/PEDOT:PSS/xxxii):[BMIM]PF ₆ (4:1)/Al	100 m A ⁻² pulsed current	77	4.6	> 1000	0.7	636	0.47	0.75
(xxxiii) ¹⁴³	ITO/PEDOT:PSS/xxxiii):[BMIM]PF ₆ (4:1)/Al	100 m A ⁻² pulsed current	200	4.3	> 6000	2.0	642	1.22	2.02
(xxxiv) ¹⁴³	ITO/PEDOT:PSS/xxxiv):[BMIM]PF ₆ (4:1)/Al	100 m A ⁻² pulsed current	9	-	> 150	0.14	655	0.06	0.09
(xxxv) ¹³⁵	ITO/PEDOT:PSS/xxxv):[BMIM]PF ₆ (3:1)/Al	100 m A ⁻² pulsed current	34	0.4	280	-	662	0.2	0.33
(xxxvi) ¹⁴⁶	ITO/PEDOT:PSS/xxxvi)/Al	Voltage sweep	525 (808)	-	-	-	618 (692)	-	0.2 (0.73)
(xxxvii) ¹⁴⁰	ITO/PEDOT:PSS/xxxvii)/Ag	Constant voltage (4 V)	-	-	-	-	882	-	-
(xxxviii) ¹⁴⁰	ITO/PEDOT:PSS/xxxviii)/Ag	Constant voltage (4 V)	-	-	-	-	790	-	-

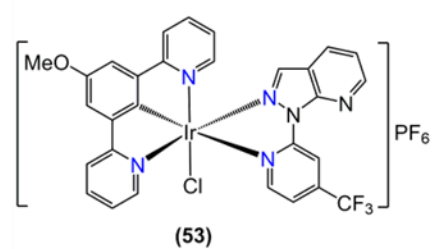
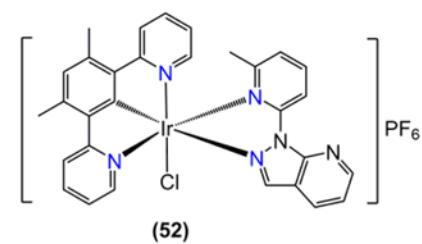
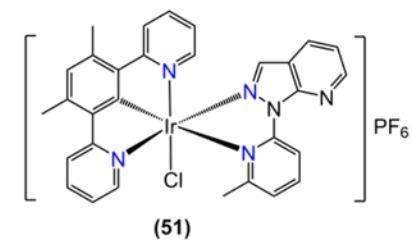
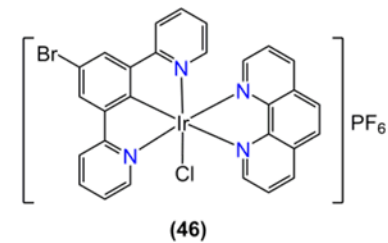
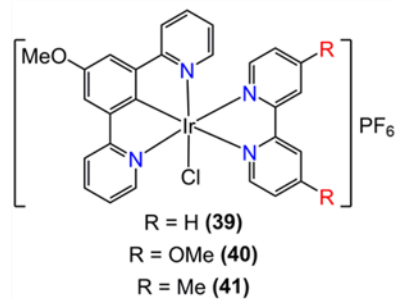
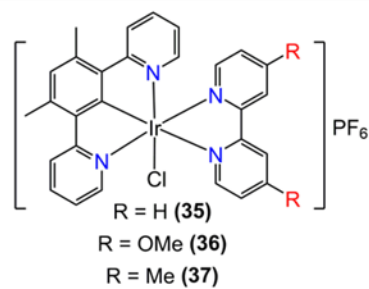
Structures of complexes

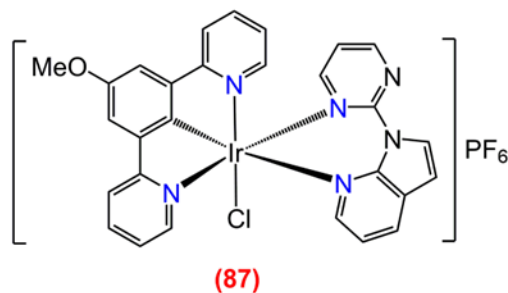
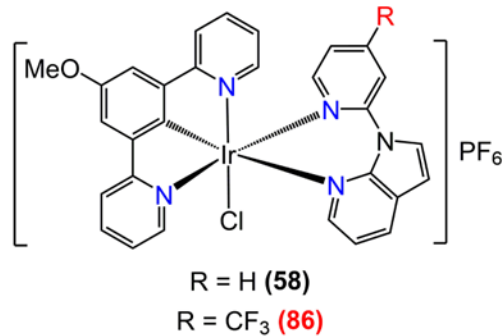
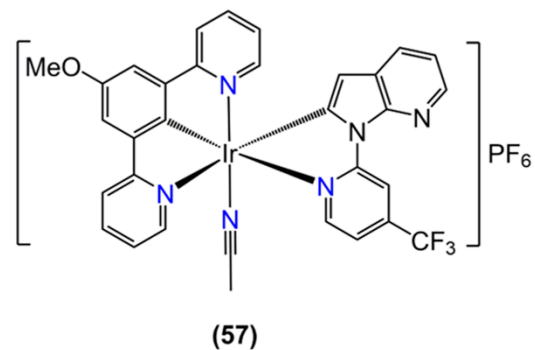
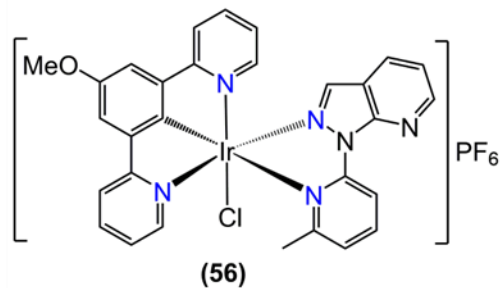
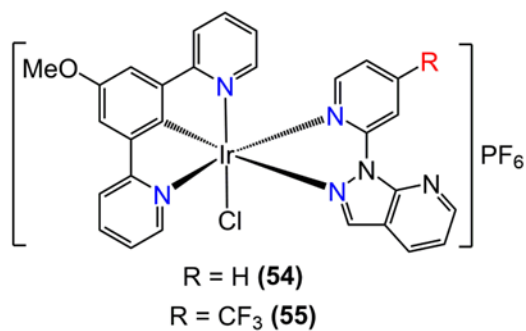
Chapter 2 Complexes:





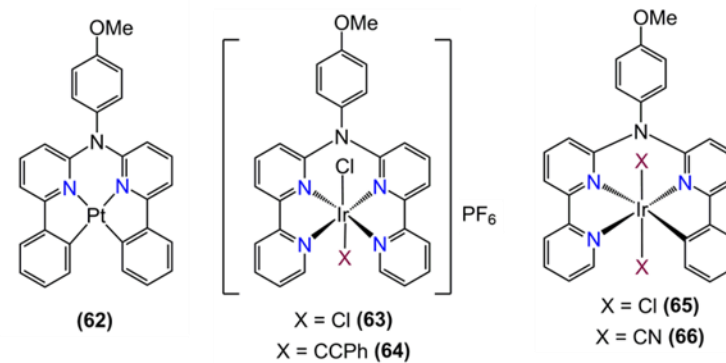
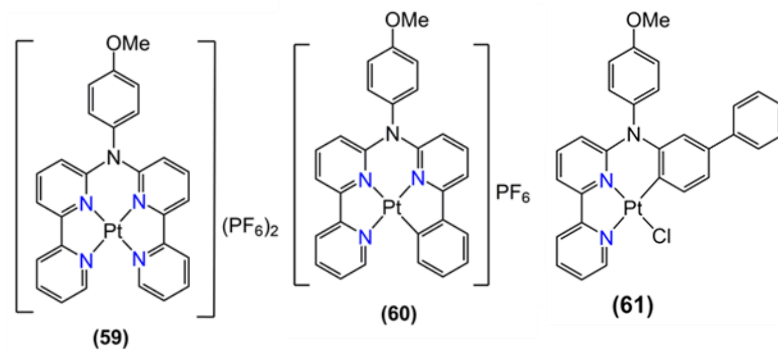
Chapter 3 Complexes:



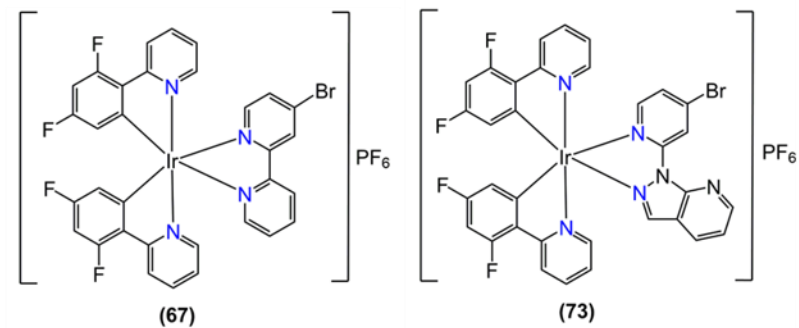


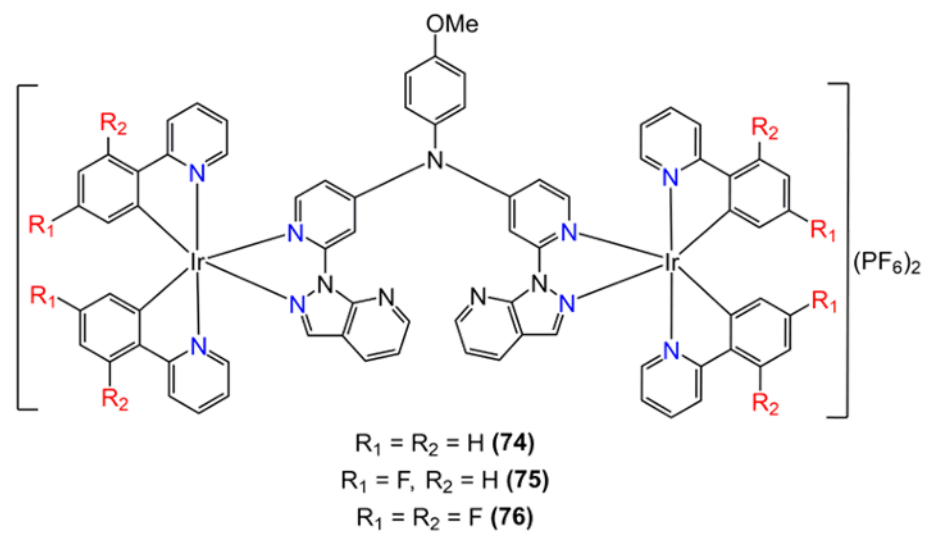
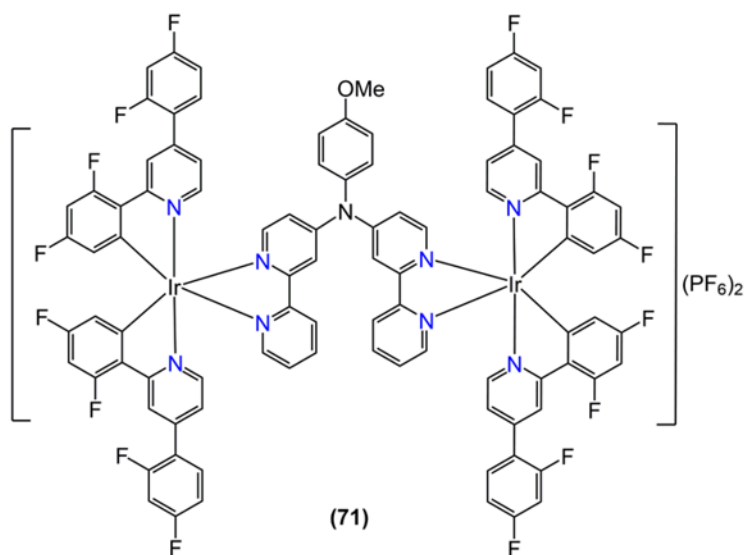
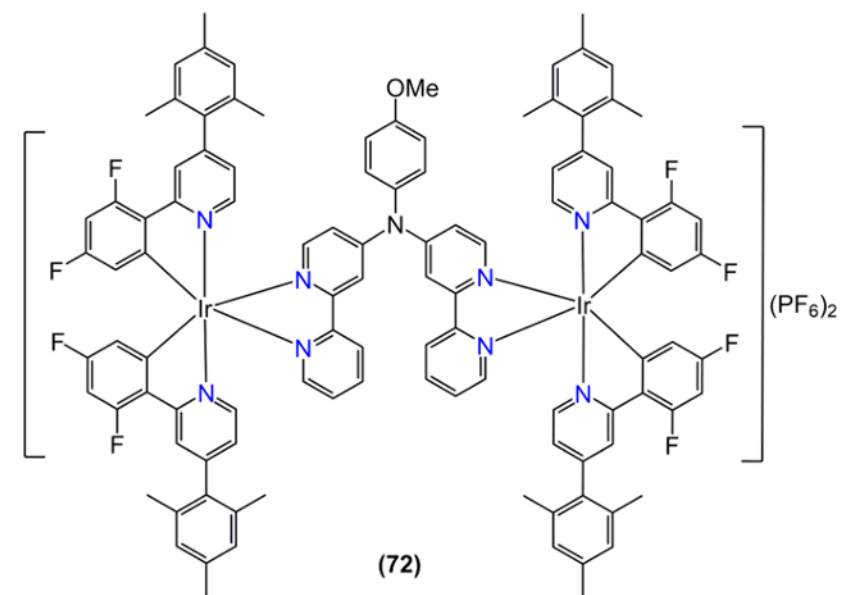
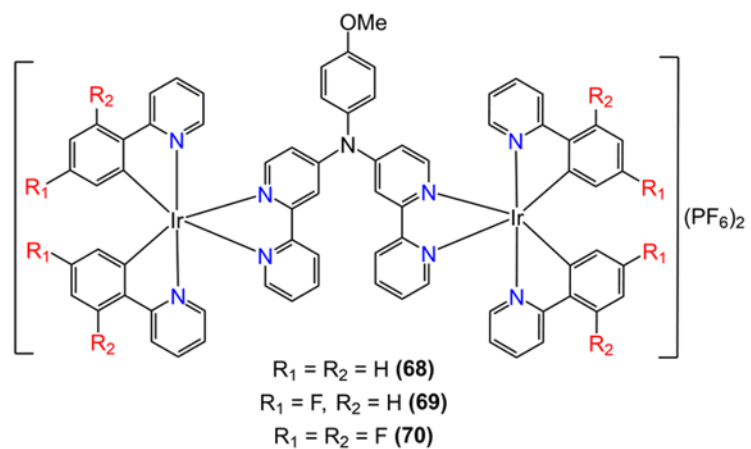
**N.B: Not final compounds -
unstable/unable to purify**

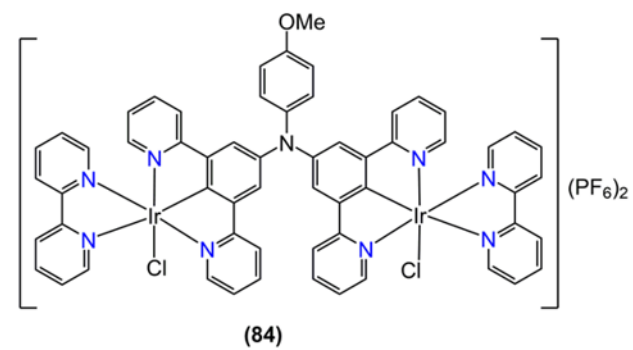
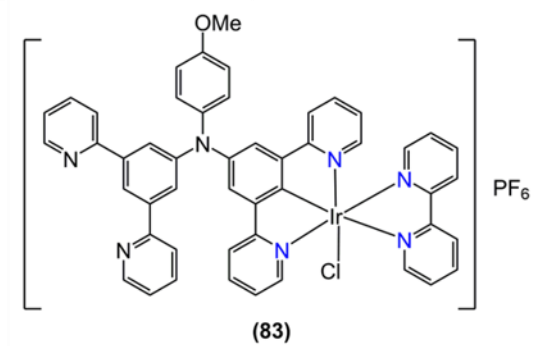
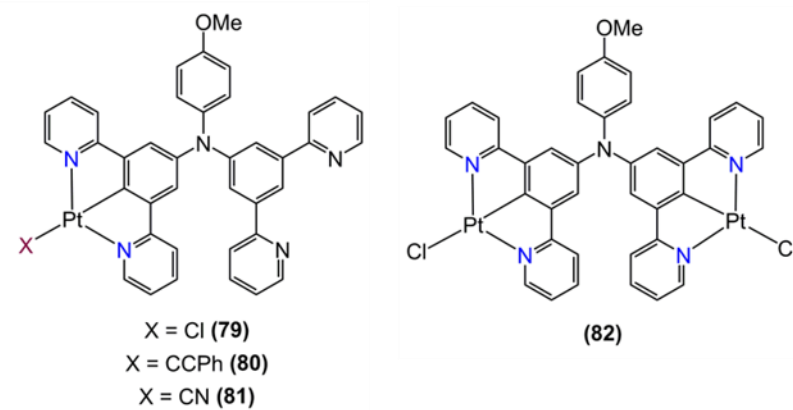
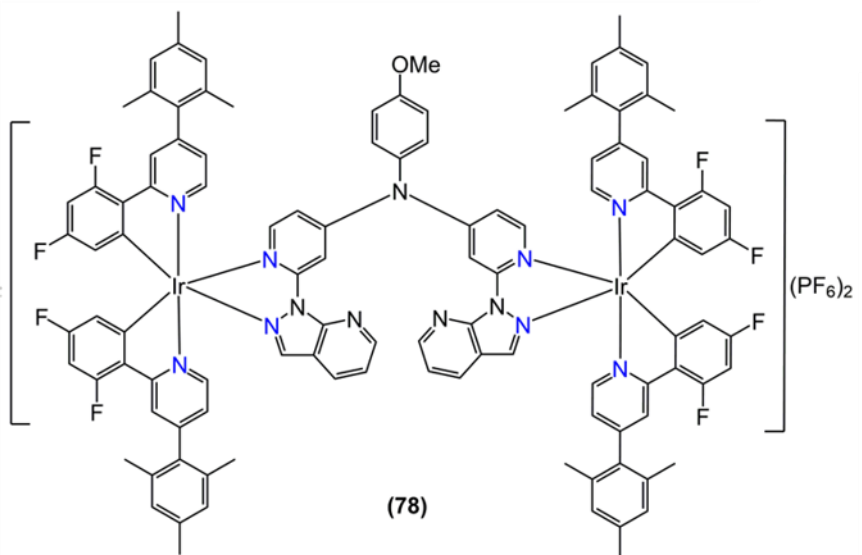
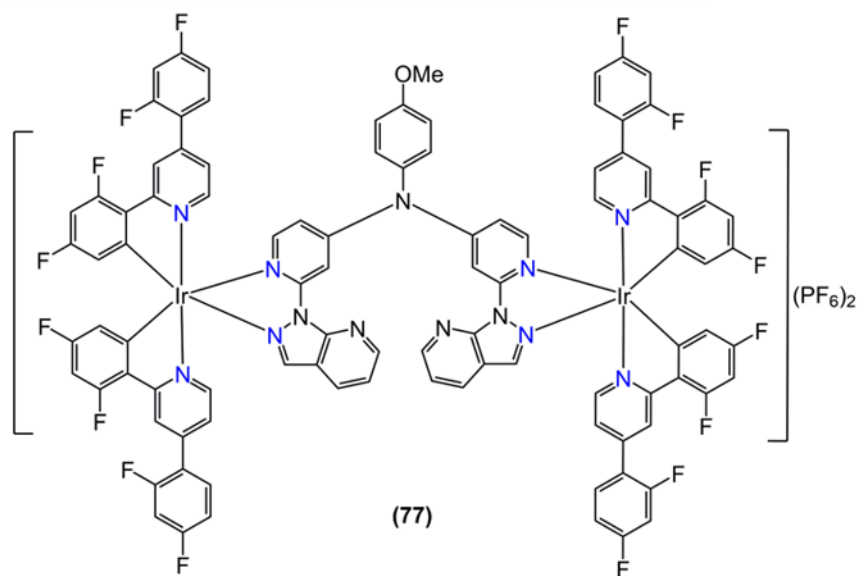
Chapter 4 Complexes:

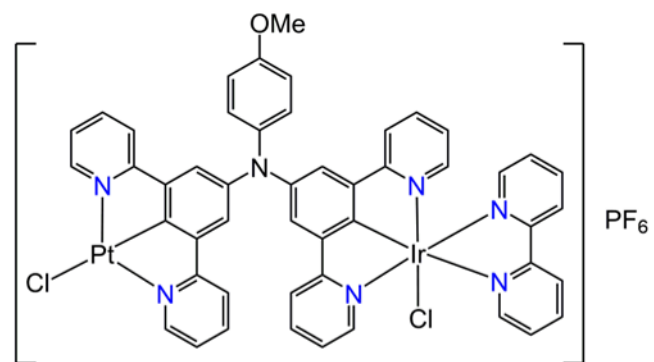


Chapter 5 Complexes:

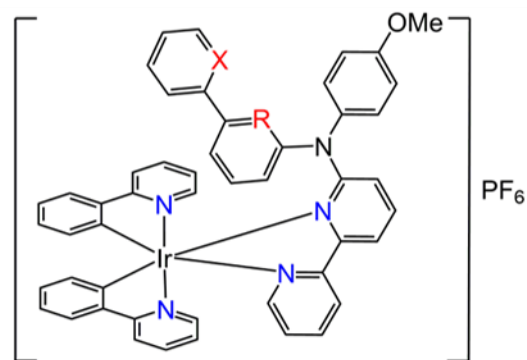








(85)



$\text{R} = \text{X} = \text{N}$ (88)

$\text{R} = \text{N}, \text{X} = \text{C}$ (89)

$\text{R} = \text{X} = \text{C}$ (90)

**N.B: Not final compounds
- unstable/unable to purify**