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Transition metal complexes for electronic and sensing applications

by

Maria C. DeRosa, B.Sc.

**A Thesis submitted to the Faculty of Graduate Studies
in partial fulfillment of the requirements for the degree of
Doctor of Philosophy**

Carleton University

Ottawa, Canada

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Transition Metal Complexes for Electronic and Sensing Applications

Submitted by

Maria C. DeRosa, B.Sc.

in partial fulfillment of the requirements
for the degree of Doctor of Philosophy

Chair, Department of Chemistry

Thesis Supervisor

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Abstract

This thesis is comprised of four studies on a series of ruthenium, platinum, and iridium complexes for use in a variety of electronic and sensing applications.

In the first study, the cyanamide absorption $\nu(\text{NCN})$ of the mixed-valence complexes: $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-L})]^{3+}$, *trans, trans*- $[\{\text{Ru}(\text{NH}_3)_4(\text{py})\}_2(\mu\text{-L})]^{3+}$, and *mer, mer*- $[\{\text{Ru}(\text{NH}_3)_3(\text{bpy})\}_2(\mu\text{-L})]^{3+}$, where py = pyridine, bpy = 2,2'-bipyridine, and L = $\text{Me}_2\text{dicyd}^{2-}$ or dicyd^{2-} was examined in a number of solvents to confirm the effect of inner sphere (bridging and spectator ligands) and outer sphere (solvent) perturbations on metal-metal coupling. Transformations of the $\nu(\text{NCN})$ band on the infrared timescale demonstrate that these complexes span the range of Class II to Class III behaviour. The IR spectrum of *trans, trans*- $[\{\text{Ru}(\text{NH}_3)_4(\text{py})\}_2(\mu\text{-Me}_2\text{dicyd})]^{3+}$ in acetonitrile is consistent with Class III behaviour, and as such, its properties ($\Delta G_r' = 1250 \text{ cm}^{-1}$; $H = 3740 \text{ cm}^{-1}$), can be considered benchmarks for delocalization in these systems.

The second study investigates the conductivity of the complex $[\{\text{Pt}(\text{trpy})\}_2(\mu\text{-Me}_2\text{dicyd})][\text{PF}_6]_2[\text{I}_3]_x$, where trpy = 2,2',6',2''-terpyridine, as a function of dopant concentration, x . Room temperature conductivity measurements reveal two maxima at $x = 0.8$ ($8 \mu\text{S cm}^{-1}$) and $x = 1.3$ ($40 \mu\text{S cm}^{-1}$), which can be related to “p-type” and “n-type” conductivity, respectively, through partially oxidized π -stacked Me_2dicyd orbitals. The conductivity of doped samples of $[\{\text{Pt}(\text{trpy})\}_2(\mu\text{-Me}_2\text{dicyd})](\text{CF}_3\text{SO}_3)_2$ and $[\{\text{Pt}(\text{trpy})\}_2(\mu\text{-Cl}_2\text{dicyd})](\text{CF}_3\text{SO}_3)_2$ were also explored to determine the effect of the counter anion and the bridging ligand substituents on conductivity. These complexes were also found to be weak semiconductors with conductivity in the $\mu\text{S cm}^{-1}$ range.

A third study reports unimolecular luminescent oxygen sensors developed by the covalent attachment of cyclometalated Ir (III) complexes onto poly(dimethylsiloxane) (PDMS). $[\text{Ir}(\text{ppy})_2(\text{vpy})\text{Cl}]$, $[\text{Ir}(\text{ppy})_2(\text{vppy})]$, $[\text{Ir}(\text{ppy})_2(\text{fppy})]$, $[\text{Ir}(\text{ppy})_2(\text{vacac})]$, $[\text{Ir}(\text{C6})_2(\text{vacac})]$, where ppy = 2-phenylpyridine, vpy = 4-vinylpyridine, vppy = 2-(4-vinylphenyl)pyridine, fppy = 4-(2-pyridyl)benzaldehyde, vacac = allylacetoacetate, and C6 = Coumarin 6, were synthesized and tethered to PDMS either via a Si-C or an imine linker. Evaluation of the polymer-bound systems reveals significantly improved oxygen sensitivity over dispersions of the free luminophores in PDMS.

A final study presents a novel approach to the synthesis of electrochromic redox polymers. The complex *trans*- $[\text{Ru}(\text{trpy})(\text{vpy})\text{Cl}_2]$ was synthesized and covalently attached by hydrosilation to hydride-terminated PDMS yielding $\text{Ru}(\text{trpy})(\text{PDMS-py})\text{Cl}_2$. This redox polymer displays electrochromism in the spectroelectrochemistry of its Ru (III/II) couple, confirming that hydrosilation is a viable methodology for the preparation of novel electrochromic materials

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List of Abbreviations

ΔG_c	Free energy of comproportionation
ΔG_e	Electrostatic free energy
ΔG_{ex}	Free energy of antiferromagnetic exchange
ΔG_i	Inductive free energy
ΔG_{IP}	Free energy of ion-pairing
$\Delta G_{r'}$	Free energy of resonance exchange
ΔG_s	Entropic free energy
ΔG_{th}	Thermal energy barrier to electron transfer
bpy	2,2'-bipyridine
C6	Coumarin 6

CD ₃ CN	Deuterated acetonitrile
COSY	Correlated spectroscopy
CV	Cyclic voltammetry
DCNQI	<i>N,N'</i> -dicyanoquinonediimine
D _{ct}	Charge transport diffusion coefficient
DEPT135	Distortionless enhancement by polarization transfer
dH ₂ O	Distilled water
dicyd ²⁻	1,4-dicyanamidobenzene
DMF	<i>N,N'</i> -dimethylformamide
DMPSEpy	4-(2-(dimethylphenylsilyl)ethyl)pyridine
DMSO	Dimethylsulfoxide
ECD	Electrochromic display
E_F	Fermi energy level
E_g	Energy gap
E_{IT} (or λ)	Energy of the intervalence transition
f	Oscillator strength
Fc	Ferrocene
FIB	poly(hexafluoroisopropyl- <i>co</i> -heptafluoro- <i>n</i> -butyl methacrylate)
fppy	4-(2-pyridyl)benzaldehyde
FWHM	Full width at half maximum
H	Metal-metal coupling element
H_{ad}	Acceptor-donor coupling element (Hush model)
HMBC	Heteronuclear multiple bond coherence

$H_{MM'}$	Metal-metal coupling element (CNS model)
HMQC	Heteronuclear multiple quantum coherence
HOMO	Highest occupied molecular orbital
IT	Intervalence transition
K_c	Comproportionation constant
K_{SV}	Stern-Volmer quenching constant
LMCT	Ligand-to-metal charge transfer
LUMO	Lowest unoccupied molecular orbital
Me ₂ DCNQI	2,5-dimethyl- <i>N,N'</i> -dicyanoquinonediimine
Me ₂ dicyd ²⁻	2,5-dimethyl-1,4-dicyanamidobenzene
MLCT	Metal-to-ligand charge transfer
MMCT	Metal-to-metal charge transfer
N.H.E.	Normal hydrogen electrode
NIR	Near-infrared
NMR	Nuclear magnetic resonance
OTTLE	Optically transparent thin layer electrode
pcyd ⁻	Phenylcyanamide
PDMS	Poly(dimethylsiloxane)
phen	1,10-phenanthroline
PMMA	Poly(methylmethacrylate)
ppy	2-phenylpyridine
PS	Polystyrene
PSP	Pressure-sensitive paint

py	Pyridine
pz	Pyrazine
Q	Quantum yield
Q_s	Quenching sensitivity
ROESY	Rotational overhauser correlation spectroscopy
SV	Stern-Volmer
TBAB	Tetrabutylammonium bromide
TBAH	Tetrabutylammonium hexafluorophosphate
TCNQ	7,7,8,8-tetracyano- <i>p</i> -quinodimethane
T_g	Glass-transition temperature
TOCSY	Total correlated spectroscopy
trpy	2,2':6',2''-terpyridine
TTF	Tetrathiafulvalene
vacac	Allylacetoacetate
VOA	Variable optical attenuator
vppy	2-(4-vinylphenyl)pyridine
vpy	4-vinylpyridine
λ_{outer}	Outer-sphere reorganizational energy
τ	Luminescence lifetime

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Foreword

Much of the recent focus in inorganic and organometallic chemistry has been centred on the optimization of molecular systems for incorporation into functional materials. Transition metal complexes have been developed for use in numerous fields such as conducting and magnetic materials, catalysis, non-linear optics, and sensor technology. This thesis examines a number of platinum group (Ru, Pt, Ir) coordination and organometallic complexes as potential building blocks for functional materials.

Widespread interest in the development of electronic devices based on molecular systems has concentrated on reversible and robust “molecular switches” for electronic and optical applications. Mixed-valence complexes can be thought of as simple models for these nanodevices. In chapter 1, the perturbation of metal-metal coupling in a series of ruthenium mixed-valence complexes is investigated using IR spectroelectrochemistry. Electrochromic systems, materials in which a reversible change in transmittance is caused by an electrochemically induced process, may one day be employed in optical switches. In chapter 4, a novel redox polymer based on an electrochromic ruthenium complex is prepared and studied.

The search for high temperature superconductors has lead to great developments in the field of “molecular metals”, molecular compounds with metallic-like electrical conductivities. In chapter 2, a new family of weakly conducting materials is prepared based on the supramolecular assembly of planar π -stacked platinum dinuclear complexes.

Luminescent transition metal complexes have been used in a variety of areas such as solar energy conversion, electron transfer studies, and electroluminescent devices. In

chapter 3, luminescent cyclometalated Ir (III) complexes have been synthesized and investigated for use in oxygen sensing and more specifically for pressure sensitive paints.

Increasingly, hybrid polymers with both inorganic and organic components have been shown to be promising candidates for use in functional materials. In chapters 3 and 4, ruthenium and iridium complexes are tethered to poly(dimethylsiloxane) and the effect of attachment on the photophysical and electrochemical properties of the systems are probed.

Chapter 1: IR spectroelectrochemistry of Mixed-Valence Ruthenium Complexes

1.1 Introduction

Since the preparation of the Creutz-Taube ion (Figure 1.1)¹, mixed-valence metal complexes showing significant metal-metal interaction have been the focus of intense study.² In recent years, much of the experimental and theoretical effort in this area has been devoted to the purposeful control of metal-metal interaction, i.e. the electronic delocalization. The intention is for these complexes to be adapted for use in molecular devices, such as molecular wires and switches.³ But before one can embark on the construction of any type of molecular device, it is important to first probe the chemical architecture that expresses the desired electronic properties. For this reason, complexes where metal-metal interactions are, to some extent, “tunable”, are deserving of in depth study. For a given metal ion, this tuning could be effected by changing the nature of the bridging or spectator ligands (inner coordination sphere) or the solvent (outer coordination sphere).

Figure 1.1: The Creutz-Taube ion

The degree of metal-metal coupling experienced in a symmetric mixed-valence complex can be described using potential energy diagrams (Figure 1.2). The left-hand parabola represents the potential energy surface for $M - L - M^+$ and the right hand parabola represents the same for $M^+ - L - M$, where M is the donor metal centre, M^+ is the acceptor metal centre, and L is the bridging ligand. The energy needed to photoexcite the

odd electron to the higher state is shown on Figure 1.2 as E_{IT} (also known as λ) and is the energy of the intervalence transition (IT) or the metal-to-metal charge transfer (MMCT) band. H is the metal-metal coupling element, ΔG_{th} is the thermal energy barrier to electron transfer, and $\Delta G_r'$ is the free-energy of resonance exchange, a measure of metal-metal interaction.

Figure 1.2: Potential energy curves for Class I (light line in both A and B), Class II (A) and Class III (B) symmetric mixed valence complexes.

Robin and Day assembled a generally accepted system of classification for mixed-valence systems, based on the degree of metal-metal coupling.⁴ Class I complexes are completely valence trapped with no interaction between the two metal centres (the light line in both A and B of Figure 1.2). These complexes generally exhibit the properties of the isolated mononuclear complexes. The opposite is true for Class III complexes (Figure 1.2B). In these systems, complete delocalization over the two

interacting metal centres exists, resulting in properties that are different from the isolated moieties. The thermal energy barrier to electron transfer disappears, allowing free movement of the odd electron over both metal centres. Class II behaviour describes the intermediate case, where there is weak coupling between the metal centres (Figure 1.2A). Recently, a new class of mixed-valence complexes, Class II-III, has been proposed to describe a number of compounds with characteristic features of both localized and delocalized behaviour.⁵ This group of complexes shows localized electronic oxidation states, but delocalized solvent effects *i.e.* electron transfer is too rapid to couple with solvent-dipole reorganizations. In these cases, the barrier to electron transfer has no solvent contribution; it is due only to intramolecular structural changes.

1.1.1 Metal-Metal coupling

Metal-metal coupling can occur through two major routes: through direct overlap of the metal orbitals⁶ or through superexchange. Superexchange describes electron exchange between two metal centres through the orbitals of a bridging ligand.³ This process can be thought of as charge transfer through two major pathways, one of which will be preferred because of the energetics of the system. The pathways are: through the ligand's highest occupied π -molecular orbital (π -HOMO) or through its lowest unoccupied π -molecular orbital (π -LUMO). The former process is known as hole-transfer superexchange and is shown for a mixed-valence ruthenium complex in Figure 1.3.

Figure 1.3: Schematic of the hole-transfer superexchange mechanism.

This concerted mechanism involves transfer of an electron from the bridging ligand's π -HOMO to the Ru(III) orbital and a simultaneous transfer of an electron from the Ru(II) orbital to the ligand's π -HOMO. Essentially, a hole moves from the acceptor to donor orbitals, hence the term hole-transfer. The case where the transfer of the electron is mediated by the ligand's π -LUMO orbital is termed electron transfer. In order for superexchange to occur, the bridging ligand must possess an orbital that spans the entire molecule and is an energy and symmetry match with the donor and acceptor orbitals of the metal centres.³ Generally, extended π -systems satisfy these criteria.

Recently, Evans et al reported a quantitative study of hole-transfer superexchange for mixed-valence polyammineruthenium complexes, incorporating the bridging ligand 1,4-dicyanamidobenzene (dicyd²⁻; see Figure 1.4) and its substituted derivatives.⁷ Metal-

metal interaction in these complexes ranged from very weakly to strongly coupled systems.

Figure 1.4: The 1,4-dicyanamidobenzene dianion (dicyd²⁻)

The 1,4-dicyanamidobenzene dianion, and substituted variations of this ligand, are π -donors which allow for the extension of the Ru(III) π -acceptor wavefunction onto the dicyd²⁻ π -HOMO, permitting superexchange through the hole-transfer mechanism.

The inner coordination sphere of the metal centre can greatly affect the degree of metal-metal coupling by the perturbation of the $d\pi$ -orbital energy. For example, Ru $d\pi$ -orbitals are stabilized by the replacement of a strongly σ -donating ligand, such as an ammine, with a weaker σ -donor or a π -acceptor, such as a pyridine or bipyridine. This serves to reduce the gap between the ligand's π -HOMO and the metal $d\pi$ -orbitals, thus increasing metal-metal coupling through the hole-transfer superexchange mechanism.⁷

The outer coordination sphere, i.e. the solvent, of a mixed-valence complex can also have a large effect on the metal-metal coupling observed, especially in complexes with ammine spectator ligands. Donor-acceptor interactions between solvent molecules and the ammine ligands transfer electron density to the ruthenium ion (see Figure 1.5).

Figure 1.5: Donor-acceptor interaction between a donor solvent and ammine proton

This destabilizes the $d\pi$ -orbitals, thereby increasing the gap between them and the ligand π -HOMO orbitals and reducing metal-metal coupling.⁷ The donor number⁸ of a solvent (the ΔH_f in kcal/mol from the reaction of the solvent with SbCl_5) is a useful empirical measure of the donating strength of a solvent and, consequently, its ability to decouple the metal and ligand orbitals. Table 1.1 is a table of solvents used in this study and their donor numbers.

Table 1.1: Donor Number Values for Several Solvents

Solvent	Donor Number
Nitromethane	2.7
Acetonitrile	14.1
Dimethyl Sulfoxide	29.8

1.1.1.1 Experimental Determination of Metal-Metal Coupling

An experimental measure of the degree of electronic coupling in a strongly-coupled mixed-valence complex is provided by the comproportionation constant³, K_c ,

which is defined by the equilibrium in equation 1.1 for a Class I or Class II complex, or in equation 1.2 for a Class III complex.

The free energy of comproportionation (ΔG_c) can be calculated, as shown in equations 1.3 and 1.4, using cyclic voltammetry to determine the difference in potential of the metal-centered redox couples, $\Delta E = E_{M2} - E_{M1}$.

$$\Delta G_c = nF\Delta E = RT \ln Q = RT \ln K_c \quad (1.4)$$

There are five factors^{7,9} that contribute to ΔG_c , as shown in equation 1.5.

$$\Delta G_c = \Delta G_s + \Delta G_e + \Delta G_i + \Delta G_{ex} + \Delta G_r \quad (1.5)$$

where ΔG_s is related to the statistical distribution of the comproportionation equilibrium, ΔG_e describes the electrostatic repulsion of the two like charged metal centres, ΔG_i accounts for the inductive effect of competing coordination of bridging ligand by the metal centres, ΔG_{ex} represents the stabilization of the reactants by antiferromagnetic

exchange, and ΔG_r is the free energy of resonance exchange. Recently, a study by Geiger and coworkers demonstrated that a sixth term, ΔG_{IP} , should be included in equation 1.5 to account for the effect of ion-pairing on the comproportionation constant.¹⁰

The ΔG_r term is the only component of ΔG_c that actually represents metal-metal coupling. The equilibria described by equations 1.1 and 1.2 result in the formation of two mixed-valence complexes, thus the free energy of resonance exchange for a single mixed-valence complex is described by equation 1.6:

$$2\Delta G_r' = \Delta G_r \quad (1.6)$$

Figure 1.2 shows $\Delta G_r'$ with respect to the potential energy curves for a given mixed-valence complex.

In order to evaluate the free energy of resonance exchange, all other components of the free energy of comproportionation must be factored out. Evans et al⁷ were able to factor out the free energy of resonance exchange, $\Delta G_r'$, from the free energy of comproportionation, ΔG_c , for the majority of the mixed-valence complexes of interest in this study and this has created an opportunity to determine the magnitude of $\Delta G_r'$ required to achieve a delocalized mixed-valence state in these systems. For these symmetric systems, ΔG_s was estimated to be approximately 290 cm^{-1} .¹¹ ΔG_e was calculated using equation 1.7 under the assumption that the medium is a dielectric and there is a unit difference in ionic charge between the two centres.¹²

$$\Delta G_e = \frac{1}{4\pi\epsilon\epsilon_0 R_{12}} \quad (1.7)$$

R_{12} represents the donor-acceptor distance, ϵ is the solvent's static dielectric, and ϵ_0 is the permittivity of free space. By using crystal structure data from $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-dicyd})][\text{OTs}]_4$ and *mer*, *mer*- $[\{\text{Ru}(\text{NH}_3)_3(\text{bipyridine})\}_2(\mu\text{-dicyd})][\text{ClO}_4]_4$, R_{12} was estimated to be 13.1 Å for the complexes of this study.¹³ ΔG_{ex} is one half the separation of the singlet ground state and the triplet excited states, and was estimated using room-temperature magnetic moments and the Van Vleck equation for magnetic susceptibility.¹⁴ It describes the stabilization of a reactant complex (it therefore has an opposite sign compared to the other factors), and can contribute significantly to ΔG_c in hole-transfer systems. ΔG_i is considered to be constant for the complexes of this study, since the competition between metal ions for coordination to the bridging ligand should not change significantly with the changes in spectator ligands.⁷ Its value was determined based on the assumption that ΔG_s and ΔG_e will contribute considerably to ΔG_c only for the weakly coupled case. For the most weakly-coupled case in these systems, $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-Cl}_4\text{dicyd})]^{3+}$ in water, where $\text{Cl}_4\text{dicyd}^{2-}$ is 2,3,5,6-tetrachloro-1,4-dicyanamidobenzene, ΔG_c equals 520 cm^{-1} .⁷ When the contributions of ΔG_e (110 cm^{-1}) and ΔG_s (290 cm^{-1}) were removed, the remaining 120 cm^{-1} was considered to be due to ΔG_i , since ΔG_{ex} and ΔG_r are expected to account for very little in the weakly coupled examples. The non-exchange contributions to the free energy of comproportionation ($\Delta G_i + \Delta G_e + \Delta G_s$) will be referred to as ΔG_{ne} .⁷ The remaining contributor to the free energy of comproportionation is ΔG_r , the free energy of resonance exchange, and was determined using equation 1.8.

$$\Delta G_r = \Delta G_c + \Delta G_{ex} - \Delta G_{ne} \quad (1.8)$$

A list of $\Delta G_r'$ values for the complexes of this study are found in Table 1.2.

Table 1.2: Free energy of resonance exchange values for the polyammineruthenium complexes of this study⁷

Complex (solvent)	$\Delta G_r'$ (cm ⁻¹)
$[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-Me}_2\text{dicyd})]^{3+}$ (Nitromethane)	Not available
$[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-Me}_2\text{dicyd})]^{3+}$ (Acetonitrile)	1210
$[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-Me}_2\text{dicyd})]^{3+}$ (DMSO)	605
$[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-dicyd})]^{3+}$ (DMSO)	470
$[\{\text{Ru}(\text{NH}_3)_4(\text{pyridine})\}_2(\mu\text{-Me}_2\text{dicyd})]^{3+}$ (Acetonitrile)	1460
$[\{\text{Ru}(\text{NH}_3)_4(\text{bipyridine})\}_2(\mu\text{-Me}_2\text{dicyd})]^{3+}$ (all solvents)	Not available
$[\{\text{Ru}(\text{NH}_3)_4(\text{bipyridine})\}_2(\mu\text{-dicyd})]^{3+}$ (all solvents)	Not available

1.1.1.2 Theoretical Modeling of Metal-Metal Coupling

There are two main models with which the experimentally determined $\Delta G_r'$ value can be compared. The Hush model evaluates metal-metal coupling by assessing the oscillator strength, f , of the IT band. The Mulliken-Hush equation (equation 1.9) is derived by equating experimental and theoretical equations for f .¹⁵

$$H_{ad} = \frac{2.06 \times 10^{-2}}{r} \left(\epsilon_{\max} \cdot \Delta \nu_{1/2} \cdot E_{IT} \right)^{1/2} \quad (1.9)$$

where H_{ad} is the acceptor-donor coupling element (H on Figure 1.2), $\epsilon_{\max}$ is the molar absorptivity of the IT, $\Delta \nu_{1/2}$ is the bandwidth of the IT at half height, E_{IT} is the energy at

the IT band maximum, and r is the transition dipole moment length, which is held fixed and is taken from metal-metal distance in crystallographic data.

The Hush model has been demonstrated to be applicable only to weakly coupled mixed-valence complexes. In these Class II complexes, the free energy of resonance exchange can be related to the metal-metal coupling element by:¹⁶

$$\Delta G_r' = H^2 / E_{IT} \quad (1.10)$$

In the mixed-valence dicyd²⁻ bridged complexes of this study, the Hush model appears to be appropriate for systems with weak coupling, but as coupling increases the correlation between theory and experiment appears more scattered (see Figure 1.6).⁷ To some degree, this may be attributed to the value of r in equation 1.9, as this value should get smaller as the extent of donor-acceptor mixing increases. A more appropriate model for strongly-coupled mixed-valence complexes was developed by Creutz, Newton, and Sutin (CNS model).¹⁷

Figure 1.6: Comparison of experimentally calculated $\Delta G_r'$ and theoretically calculated H_{ad}^2/E_{IT} (Hush model) for pentaammine (filled squares), tetraammine (filled circles), and triammine (filled triangles) complexes from reference 7.

The CNS model focuses on the superexchange mechanisms, rather than the oscillator strength of the IT band, for modeling metal-metal coupling in mixed-valence complexes. Using the two pathways through which superexchange can take place, electron transfer and hole transfer, the metal-metal coupling element is described by equation 1.11:

$$H_{MM'} = \frac{H_{ML}H_{M'L}}{2\Delta E_{ML}^{eff}} + \frac{H_{LM}H_{LM'}}{\Delta E_{ML}^{eff}} \quad (1.11)$$

where $H_{MM'}$ is the metal-metal coupling element, H_{ML} and $H_{M'L}$ are the metal-ligand coupling elements of the electron transfer pathway, H_{LM} and $H_{LM'}$ are the ligand-metal

coupling element for the hole-transfer pathway and the denominators are the reduced energy gaps between the metal and ligand orbitals.¹⁷ Since the systems of this study undergo hole-transfer superexchange preferentially, the first term of this equation can be ignored. A second assumption used is that $H_{LM} = H_{LM'}$.⁷ This simplifies equation 1.11 to:

$$H_{MM'} = \frac{H_{LM}^2}{\Delta E_{LM}^{eff}} \quad (1.12)$$

Equation 1.12 can be used to calculate $H_{MM'}$ with the spectroscopic parameters of the ligand-metal charge transfer (LMCT) band. The reduced energy gap⁷ is calculated using equation 1.13:

$$\Delta E_{LM}^{eff} = \left[0.5 \left(\frac{1}{E_{LMCT}} + \frac{1}{E_{LMCT} - E_{IT}} \right) \right]^{-1} \quad (1.13)$$

The CNS approach appears to be the more suitable model for determining the metal-metal coupling in the mixed-valence complexes in this study based on the improved correlation between $\Delta G_r'$ and H_{MM}^2/E_{IT} as seen in Figure 1.7.⁷

Figure 1.7: Comparison of experimentally calculated $\Delta G_r'$ and theoretically calculated H_{MM}^2/E_{IT} (CNS model) for pentaammine (filled squares), tetraammine (filled circles), and triammine (filled triangles) complexes from reference 7.

However, even the CNS model seems to break down when dealing with the most strongly coupled complexes, as seen by the curvature in data point distribution. This implies that the more strongly coupled complexes in this study may be bordering on Class III behaviour, where the relationship described between the metal-metal coupling element and the free energy of resonance exchange in equation 1.10 no longer applies. Instead, equation 1.14 can be used:¹⁶

$$\Delta G_r' = H - \Delta G_{th} \quad (1.14)$$

where ΔG_{th} is the thermal energy barrier for the Class I case (see Figure 1.2 B).

1.1.2 Lifetimes of States and Infrared Spectroscopy

According to quantum mechanics, the lifetime of a state and its energy are related in such a way that the shorter the lifetime of a state, the wider the range of energies this state can occupy. Suppose an atom can occupy two different interchangeable sites (at frequencies ν_1 and ν_2). If the lifetime of the atom in each state is much greater than $2\pi\Delta\nu$, the two absorptions will be distinguishable. As the lifetimes shorten, the absorptions broaden and merge. Eventually, if the lifetimes are very short, a single absorption at the average of the two frequencies is obtained.¹⁹ By using this information and applying it to infrared spectral transformations of different mixed-valence complexes in varying media, one can make conclusions regarding the rate of electron transfer, *i.e.* the extent of delocalization, between the two metal centres.

The theoretical maximum rate constant for a barrierless intramolecular electron transfer is dictated by the nuclear frequency factor ($\nu_n = 10^{12} - 10^{13} \text{ s}^{-1}$), thus an experimental technique with a timescale on the order of 10^{-13} s or shorter would be necessary in order to provide a true indication of Class III behaviour. As the typical timescales for ^1H NMR ($1-10^{-5} \text{ s}$), Mössbauer (10^{-7} s) and for EPR ($10^{-5}-10^{-9} \text{ s}$) spectroscopies are relatively long, the detection of averaged signals using these techniques may not necessarily be indicative of complete electronic delocalization. Infrared spectroscopy, on the other hand, has been recognized as a powerful means to examine electron transfer in mixed-valence systems, as its timescale ($10^{-11}-10^{-13} \text{ s}$), presents an almost instantaneous view of a fluxional molecule.²⁰ If there is little coupling between the two metal centres, the transfer rate will be slow, and separate peaks for a given infrared absorption should be observed. As coupling between the two metals

increases, and the transfer rate approaches that of the infrared timescale, the peaks will broaden. Rapid intramolecular exchange (10^{12}s^{-1}) can result in spectral coalescence with some band broadening.²⁰ⁱ If the two metal centres are strongly coupled (intramolecular exchange 10^{13}s^{-1}), then complete coalescence occurs and only an average peak will be seen. Hence, infrared spectroscopy can be a powerful technique in determining the extent of electronic delocalization with respect to its time scale.

There are several studies in the literature that have employed infrared spectroscopy to confirm the extent of metal-metal interaction. Typically, these complexes have substituents which are easily seen on an IR spectrum, *e.g.* carbonyls and cyanides. Pierce and Geiger^{20p} examined the carbonyl stretching frequency of a series of biphenyl-bridged mixed-valence chromium carbonyl complexes using infrared and low-temperature flow electrochemical experiments, to determine the effect of biphenyl twist on electron delocalization. The splitting of $\nu(\text{CO})$ bands upon oxidation to the mixed-valence state, or the appearance of new pairs of $\nu(\text{CO})$ bands, led to the conclusion that the complexes were localized with respect to the infrared time scale.

Van Order et. al.^{20w} studied a series of dinuclear chromium carbonyl complexes linked by a biphenyl group and/or a diphosphino- (or arsino-) methane group. The appearance of a new carbonyl stretch in the mixed-valence IR spectrum of the biphenyl bridged molecule indicated the localized nature of the complex. The carbonyl stretches in the spectra of the doubly bridged mixed-valence complexes, however, showed no signs of splitting or broadening, which is indicative of a delocalized case. Similar manganese carbonyl complexes, bridged by the fulvalenyl cation and diphosphinomethane, show evidence of valence trapping on the IR timescale.^{20t}

The infrared spectroscopy of carbonyl- and cyanide-containing models of the Creutz-Taube ion has also been investigated. Sheiring and coworkers have examined the stretching bands of axial and equatorial cyanide ligands in the Creutz-Taube analogue, $[(\text{NC})_5\text{M}(\mu\text{-pz})\text{M}(\text{CN})_5]^{5-}$, where pz = pyrazine and M = Fe, Ru, and Os. Splitting of the cyanide stretches confirmed that the complex was a Class II system.^{20e} A $\text{Mo}(\text{CO})_3(\text{PPr}_3)_2$ based analogue showed delocalized behaviour on the infrared time scale.^{20s}

Chin et. al.^{20o} have used the boron-hydrogen band ($2600\text{-}2400\text{ cm}^{-1}$) to examine electron transfer in iron and cobalt metallocarborane complexes. The mixed-valence dinuclear iron complex showed both Fe(II) and Fe(III) $\nu(\text{BH})$ bands, and therefore was classified as a localized complex. The infrared spectrum of the analogous cobalt complex, on the other hand, showed no common features with that of the fully oxidized or fully reduced spectra. Instead, a new boron-hydrogen stretch was observed at the average of the Co(III) and Co(II) frequencies, indicative of delocalized behaviour.

The two components of the $\nu(\text{Fe}_3\text{O})$ vibration in a trinuclear iron (III, III, II) molecule were examined in a variable temperature infrared absorption study.^{20q} While displaying evidence of localized behaviour, band broadening at increasing temperature ($T = 80 - 410\text{ K}$) suggested borderline behaviour.

Meyer and coworkers have demonstrated that conflicting results can be obtained when using infrared absorptions as markers for electronic delocalization.^{20x,y} In the complex $[(\text{bpy})_2(\text{Cl})\text{Os}(\text{pz})\text{Os}(\text{Cl})(\text{bpy})_2]^{3+}$, the presence of the symmetric $\nu(\text{pz})$ stretch at 1599 cm^{-1} is evidence for localized oxidation states. In contrast, the $\nu(\text{bpy})$ ring

stretching modes from 1400 - 1500 cm^{-1} are averaged in the mixed valence state. This demonstrates that care must be taken when choosing a reliable marker in the infrared spectrum. Typically, bridging ligand stretches are preferred.

1.1.3 Research Strategy

Since the cyanamide moiety has such an intense infrared absorption in a region where very little else absorbs (2200-2000 cm^{-1}), infrared techniques should be very useful in determining the degree of delocalization in the mixed-valence ruthenium dicyd²⁻ complexes. When both the metal centres of the complex are of an equivalent oxidation state, only one $\nu(\text{NCN})$ band should be present. When the mixed-valence complex is formed, any changes to this band should indicate the extent of metal-metal coupling. If there is only weak coupling between the two metals, the $\nu(\text{NCN})$ band should split into two peaks. As the complex approaches Class III behaviour, the band may be broadened in the mixed-valence complex. The $\nu(\text{NCN})$ band for a completely delocalized, Class III complex should show no signs of splitting or broadening and should be at the average frequency of the $\nu(\text{NCN})$ bands of a similar Class II complex.

It would be of some theoretical and practical significance to know the magnitude of resonance exchange required to achieve a delocalized state in a mixed-valence complex. In this study, the infrared spectra of a series of mixed valence complexes of the form $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-L})]^{3+}$, *trans*, *trans*- $[\{\text{Ru}(\text{NH}_3)_4(\text{py})\}_2(\mu\text{-L})]^{3+}$, and *mer*, *mer*- $[\{\text{Ru}(\text{NH}_3)_3(\text{bpy})\}_2(\mu\text{-L})]^{3+}$, where py = pyridine, bpy = 2,2'-bipyridine and L = $\text{Me}_2\text{dicyd}^{2-}$, dicyd²⁻ in dimethyl sulfoxide (DMSO), acetonitrile, and nitromethane are

examined in an attempt to confirm the effects of inner- and outer-sphere perturbation on metal-metal coupling and to determine the Class II (localized) - Class III (delocalized) boundary on the infrared time-scale.

1.2 Methods and Materials

Ammonium hexafluorophosphate (Aldrich), tetrabutyl ammonium bromide (Aldrich), cerium ammonium nitrate (Aldrich), sodium perchlorate (Aldrich), and CM-Sephadex C25 cation exchange resin (bead size: 40-125 microns, Sigma) were used as received. Sodium chloride (99+%, reagent grade, Anachemia) was used as received and made up to various concentrations. 2,3-dichlorophenylcyanamide had been prepared previously by published methods.²¹ Organic solvents were Anachemia *Accusolv* grade unless otherwise noted, were dried with an appropriate reagent, distilled in glass at reduced pressure, and stored under argon. Acetonitrile was distilled in the presence of phosphorous pentoxide, dimethyl sulfoxide and nitromethane (HPLC grade, 96+%, Sigma) were dried overnight with, and distilled in the presence of aluminum oxide (neutral, chromatography grade, Woelm) activated by heating to 300 °C for three hours in a muffle furnace. *mer*-[Ru(NH₃)₃(bipyridine)(H₂O)][BPh₄]₂ was prepared by literature methods.^{13b, 22} [$\{Ru(NH_3)_5\}_2(\mu-L)\][PF_6]_4$ ^{13a, 23}, *trans*, *trans*-[$\{Ru(NH_3)_4(py)\}_2(\mu-L)\][PF_6]_4$,³ where py = pyridine, *mer*, *mer*-[$\{Ru(NH_3)_3(bpy)\}_2(\mu-L)\][ClO_4]_4$ ^{13b}, where L = Me₂dicyd²⁻, dicyd²⁻ and bpy = 2,2'-bipyridine, and [Ru(NH₃)₅(2,3,5,6-tetrachlorophenylcyanamide)][PF₆]₂²⁵ were synthesized according to reported methods.

All spectroelectrochemistry was performed at ambient temperatures using an OTTLE cell (optically transparent thin layer electrode), similar in design to that of Hartl.^{7,26} The cell consisted of two CaF_2 plates separated by two polyethylene spacers (total width 0.4 mm). The spacer was fitted with two 0.1 mm diameter platinum wires and a Ag/AgCl reference electrode. Two sections of gold foil (500 line/inch, 60% transmittance, Buckbee Mears) were placed in contact with the platinum wires, and acted as the working and counter electrodes. Wires were secured to tin-coated copper wires, to which alligator clips were attached for electrochemistry. Samples were introduced to the cell using 2 mL luer-lock syringes using the cell's inlet and outlet ports. 0.1 M TBAH was used as the supporting electrolyte. The cell was masked with electrical tape to ensure that the incident radiation beam passed only through the working electrode. Potentials were controlled using a BAS CV-27 voltammograph. Electrochemistry was monitored by UV-Vis-NIR spectra obtained from a Varian Cary 5 UV-Vis-NIR spectrophotometer. IR spectra were performed on a Bohem Michelson 120 FTIR spectrometer and were analysed using Bohem Grams/386 v3.04 Level II software.

Background IR spectra were taken, first, on solvents and electrolyte only, and then, on the native sample, in the range of interest for this study (2200-1950 cm^{-1} for the IR spectra in all solvents). A negative potential was then applied, and the current was allowed to return to the background level prior to acquisition of the IR spectrum. The electrochemistry was also monitored on the Cary 5 spectrophotometer and the mixed-valence spectra were compared to those obtained by Evans.⁷ A positive potential was applied in order to regenerate the Ru(III)-Ru(III) species. All spectral transformations shown were found to be reversible (>97%).

1.2.1 Preparation of *mer*-[Ru(NH₃)₃(bpy)(2,3-Cl₂pcyd)][ClO₄]₂

2,3-Dichlorophenylcyanamide (0.2 g, 1.3 mmol) was dissolved in acetone (100mL) and degassed on a double-manifold vacuum line equipped with argon as the inert gas. Solid *mer*-[Ru(NH₃)₃(bpy)(H₂O)][B(Ph)₄]₂ (1 g, 1.0 mmol) was quickly added and the solution was degassed one final time. After 16 hours of stirring, tetrabutylammonium bromide, TBAB (3.0 g) was added to the solution to precipitate the complex *mer*-[Ru(NH₃)₃(bpy)(2,3-Cl₂pcyd)][Br] (0.43g, 66% yield). The product was dissolved in distilled water (50mL) and was oxidized with a solution of cerium (IV) ammonium nitrate (0.39g, 0.66 mmol) in distilled water (15 mL). The solution was stirred for ten minutes and *mer*-[Ru(NH₃)₃(bpy)(2,3-Cl₂pcyd)][PF₆]₂ (0.40g, 77% yield) was precipitated from the solution by the addition of ammonium hexafluorophosphate (1.2 g). The product was converted to a bromide salt by the addition of TBAB (2 g) to an acetonitrile (20 mL) solution of the complex. *mer*-[Ru(NH₃)₃(bpy)(2,3-Cl₂pcyd)][Br]₂ (0.2 g, 60% yield) was dissolved in a minimum of 1 M NaCl (~ 20 mL), was loaded onto a CM Sephadex C25 cation exchange column, and was eluted with 1M NaCl. The blue/green product band was preceded by a purple band containing the Ru(II) complex. The desired complex was precipitated by the addition of solid sodium perchlorate (1g/10 mL of eluent). *mer*-[Ru(NH₃)₃(bpy)(2,3-Cl₂pcyd)][ClO₄]₂ (0.15g, 22% yield from starting materials) was collected by vacuum filtration and was washed sparingly with cold water. (**Caution!** *Perchlorate salts are potentially explosive, particularly when dry. Exercise caution when handling these salts.*) The complex was recrystallized by ether diffusion into a concentrated acetonitrile solution. Elem. Anal. Calcd for

$C_{17}H_{20}Cl_4N_7O_8Ru$: C, 29.45; H, 2.91; N, 14.14. Found: C, 29.72; H, 3.29; N, 14.35. IR (KBr); $\nu(NCN) = 2117\text{ cm}^{-1}$; UV-vis $\epsilon_{250} = 1.19 \times 10^4\text{ M}^{-1}\text{cm}^{-1}$, $\epsilon_{287} = 2.13 \times 10^4\text{ M}^{-1}\text{cm}^{-1}$, $\epsilon_{385} = 4.92 \times 10^3\text{ M}^{-1}\text{cm}^{-1}$, $\epsilon_{800} = 3.83 \times 10^3\text{ M}^{-1}\text{cm}^{-1}$.

1.3 Results

1.3.1. Mononuclear Complex Characterization:

The novel complex *mer*-[Ru(NH₃)₃(bpy)(2,3-Cl₂pcyd)][ClO₄]₂ was synthesized to provide a model for the effect of oxidation state on the $\nu(NCN)$ band in the absence of metal-metal coupling. The successful synthesis of the complex was confirmed by elemental analysis and it was characterized by IR and UV-vis absorption spectroscopies, cyclic voltammetry and UV-vis spectroelectrochemistry.

Figure 1.8: IR spectrum of *mer*-[Ru(NH₃)₃(bpy)(2,3-Cl₂pcyd)][ClO₄]₂ (KBr pellet). The $\nu(\text{NCN})$ band is shown at 2117 cm⁻¹.

The infrared spectrum (Figure 1.8) of the mononuclear complex shows an intense $\nu(\text{NCN})$ band at 2117 cm⁻¹, within the expected range for a deprotonated phenylcyanamide complex.²⁷ The electronic spectrum (Figure 1.9) is assigned by analogy to Ru(NH₃)₅(2,3-Cl₂pcyd)²⁺²⁵ and is characterized by intense bipyridine π - π^* transitions in the UV, and formally forbidden and allowed cyanamide to Ru(III) LMCT transitions at 385 and 800 nm, respectively. Both bands are red-shifted relative to the bands in the ruthenium pentaammine spectrum, indicative of the stabilizing effect of the bipyridine ligand on the metal $d\pi$ orbitals.

Figure 1.9: Electronic absorption spectrum of *mer*-[Ru(NH₃)₃(bpy)(2,3-Cl₂pcyd)]⁴⁺ in acetonitrile.

The electrochemistry of the complex was explored using cyclic voltammetry (Figure 1.10). The complex displays a quasi-reversible Ru(III/II) couple at 0.55 V vs. N.H.E., consistent with more stabilized metal-based LUMO in relation to the analogous pentaammine system.²⁵ Spectroelectrochemistry experiments (see Figure 1.11) showed a bleaching of the LMCT transition, and the growth of a new MLCT transition at 530 nm ($\epsilon = 4.50 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$) upon reduction to Ru(II). All spectral changes were fully reversible.

Figure 1.10: Cyclic voltammogram of *mer*-[Ru(NH₃)₃(bpy)(2,3-Cl₂pcyd)]⁴⁺ in acetonitrile (0.1 M TBAH) using platinum counter and working electrodes, silver wire pseudo-reference (ferrocene internal reference) at 100mV/s scan rate. The Ru(III/II) couple lies at 0.55 vs. N.H.E.

Figure 1.11: Oxidation of *mer*-[Ru(NH₃)₃(bpy)(2,3-Cl₂pcyd)][ClO₄]₂ in acetonitrile (0.1 M TBAH).

The IR-spectroelectrochemistry of the complex was explored and is described in section 1.3.2.

1.3.2 IR-spectroelectrochemistry of the mononuclear complexes.

The infrared spectral changes observed for *mer*-[Ru(NH₃)₃(bpy)(2,3-Cl₂pcyd)][ClO₄]₂ and [Ru(NH₃)₅(2,3,5,6-Cl₄pcyd)][PF₆]₂ upon reduction to Ru(II) are shown in Figures 1.12 and 1.13, respectively.

Figure 1.12: IR spectra showing the reduction of the Ru^{III} complex *mer*-[Ru(NH₃)₃(bpy)(2,3-Cl₂pcyd)][ClO₄]₂ in nitromethane, to the Ru^{II} complex.

Figure 1.13: IR spectra showing the reduction of the Ru^{III} $[\text{Ru}(\text{NH}_3)_5(2,3,5,6\text{-Cl}_4\text{pcyd})][\text{PF}_6]_2$, in nitromethane, to the Ru^{II} complex.

The infrared spectra of both mononuclear complexes show a bleaching of the lower energy $\nu(\text{NCN})$ vibration and the development of a new absorbance at higher energy as a result of reduction. The new stretch is assigned to the $\nu(\text{NCN})$ band for the cyanamide bonded to $\text{Ru}(\text{II})$. The shift of the $\nu(\text{NCN})$ to higher energies upon metal reduction is opposite to that seen for stretching vibrations in carbonyl and cyanide complexes.²⁰ The polarizability of the cyanamide group can be invoked to explain this result (see discussion). The intensity of this new stretch in the Ru^{II} pentaammine complex is noticeably weaker than in the Ru^{II} triammine bipyridine complex. Oxidation of the $\text{Ru}(\text{II})$ complexes leads to a full regeneration of the $\text{Ru}(\text{III})$ spectrum.

1.3.3 IR-spectroelectrochemistry of the dinuclear complexes.

The spectroelectrochemistry of all complexes were performed at ambient temperature. The generation of the mixed-valence complexes were judged to be complete upon the loss of the first isosbestic point and the appearance of a second isosbestic point. Spectroelectrochemistry of all complexes were also monitored by UV-Vis-NIR spectroscopy (see reference 7 for details). Reduction to the mixed-valence complexes results in the appearance of an intervalence transition (IT) in the near-IR and further reduction to the [II-II] state causes the loss of the IT band. While all spectral changes were found to be reversible, with greater than 95% recovery of the [III,III] complex's spectrum from that of the [II,II] complex, some complexes were more robust in the mixed-valence state than others. The pentaammine complexes were particularly unstable as mixed-valence complexes; spectra had to be taken quickly in order for reversibility to be conserved. The tetraammine complexes were more stable, but would decompose if left for more than five to ten minutes in the mixed valence state. The triammine complexes were the most inert in the mixed valence state, and showed no signs of decomposition if left standing for ten minutes or more. The solvent also had an effect on the stability of the mixed valence complex. For example, the $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-Me}_2\text{dicyd})]^{3+}$ complex was particularly unstable in DMSO, making it necessary to be extremely efficient in order to maintain reversibility. The same complex in nitromethane, however, was considerably more stable. The variation in stability for these complexes can be rationalized by the donating ability of the spectator ligands and solvent around the ruthenium centres. The more donating the coordination sphere, the less stable the Ru(II)

centre, leading to lability of the anion bridging ligand. Since amines are good σ -donor ligands, this effect will be most noticeable in the pentaammine complexes, and least in the triammines. Furthermore, since DMSO is the most donating solvent used in this study, it is reasonable that the mixed valence complexes are least stable in this medium due to the solvent-amine donor-acceptor interaction (Figure 1.5).

1.3.3.1 Pentaammine ruthenium dimers

Figures 1.14-1.20 show the results of the infrared spectroelectrochemistry experiments performed on $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-Me}_2\text{dicyd})][\text{PF}_6]_4$ in three solvents of varying donor strength. In DMSO, two $\nu(\text{NCN})$ bands are produced by the reduction of the $\text{Ru}^{\text{III}}\text{-Ru}^{\text{III}}$ complex to the mixed-valence species (Figure 1.14): an intense absorbance at lower energy (2040 cm^{-1}) and a weak band at higher energy (2160 cm^{-1}). Upon further reduction to the $\text{Ru}^{\text{II}}\text{-Ru}^{\text{II}}$ complex (Figure 1.15), the lower energy band disappears and the higher energy band intensifies. Similar spectral changes are observed during the reduction of the analogous dicyd^{2-} complex, $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-dicyd})][\text{PF}_6]_4$, in DMSO (Figure 1.16 and 1.17) except that the higher energy $\nu(\text{NCN})$ band in the mixed-valence spectrum is more sharply defined.

Figure 1.14: IR spectra showing the reduction of the Ru^{III}-Ru^{III} complex, $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-Me}_2\text{dicyd})][\text{PF}_6]_4$ in DMSO, to the mixed-valence Ru^{III}-Ru^{II} complex

Figure 1.15: IR spectra showing the reduction of the mixed valence complex $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-Me}_2\text{dicyd})]^{3+}$ in DMSO to the fully reduced Ru^{II}-Ru^{II} complex.

Figure 1.16: IR spectra showing the reduction of the Ru^{III}-Ru^{III} complex, $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-dicyd})][\text{PF}_6]_4$ in DMSO, to the mixed-valence Ru^{III}-Ru^{II} complex.

Figure 1.17: IR spectra showing the reduction of the mixed valence complex, $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-dicyd})]^{3+}$ in DMSO, to the fully reduced Ru^{II}-Ru^{II} complex.

In acetonitrile, reduction to the mixed-valence complex (Figure 1.18) causes a broadening of the $\nu(\text{NCN})$ absorbance and a shift to lower energy (2060 cm^{-1}). Further reduction to the [II-II] complex results in a loss of reversibility. This is likely due to the lability of the anion ligand when coordinated to Ru^{II} , particularly in a coordinating solvent such as acetonitrile.²⁸

Figure 1.18: IR spectra showing the reduction of the $\text{Ru}^{\text{III}}\text{-Ru}^{\text{III}}$ complex, $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-Me}_2\text{dicyd})][\text{PF}_6]_4$ in acetonitrile, to the mixed-valence $\text{Ru}^{\text{III}}\text{-Ru}^{\text{II}}$ complex

The infrared spectrum of the mixed-valence complex in nitromethane (Figure 1.19) shows a decrease in the oscillator strength of the $\nu(\text{NCN})$ vibration centred at 2090 cm^{-1} and some increase in the peak width relative to the spectrum of the fully oxidized complex. The spectrum of the fully reduced species (Figure 1.20) shows the appearance of a new band at higher energies (2150 cm^{-1}) and the loss of the low energy absorption.

Figure 1.19: IR spectra showing the reduction of the Ru^{III}-Ru^{III} complex, $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-Me}_2\text{dicyd})][\text{PF}_6]_4$ in nitromethane, to the mixed-valence Ru^{III}-Ru^{II} complex.

Figure 1.20: IR spectra showing the reduction of the mixed valence complex $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-Me}_2\text{dicyd})]^{3+}$ in nitromethane to the fully reduced Ru^{II}-Ru^{II} complex.

Figure 1.21: IR spectra showing the reduction of the $\text{Ru}^{\text{III}}\text{-Ru}^{\text{III}}$ complex, $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-Me}_2\text{dicyd})][\text{PF}_6]_4$ in CD_3CN , to the mixed-valence $\text{Ru}^{\text{III}}\text{-Ru}^{\text{II}}$ complex.

In order to determine if any other features in the IR spectrum could be used to follow changes in metal-metal coupling, a series of full scale IR spectra in CD_3CN (from 6000 cm^{-1} to 1000 cm^{-1}) were taken during the reduction of $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-Me}_2\text{dicyd})][\text{PF}_6]_4$ to the mixed-valence state (see Figure 1.21). While no other major changes in the IR spectrum (other than those in the range of the cyanamide stretch) were found useful, the growth of the IT band for the complex (seen at 6000 cm^{-1} , the instrument limit) could be observed. There is no indication of additional intervalence transitions or interconfigurational $d\pi\text{-}d\pi$ bands at lower energy that can be used as evidence for localized oxidation states.⁵

1.3.3.2 Tetraammine ruthenium dimers.

Figure 1.22 and Figure 1.23 show the spectral transformations upon reduction of *trans, trans*- $[\{\text{Ru}(\text{NH}_3)_4(\text{py})\}_2(\mu\text{-Me}_2\text{dicyd})][\text{PF}_6]_4$ in acetonitrile to the mixed-valence and fully reduced species, respectively.

Figure 1.22: IR spectra showing the reduction of the Ru^{III}-Ru^{III} complex, *trans, trans*-[$\{\text{Ru}(\text{NH}_3)_4(\text{py})\}_2(\mu\text{-Me}_2\text{dicyd})\][PF₆]₄ in acetonitrile, to the mixed-valence Ru^{III}-Ru^{II} complex.$

Figure 1.23: IR spectra showing the reduction of the mixed valence complex *trans, trans*-[$\{\text{Ru}(\text{NH}_3)_4(\text{py})\}_2(\mu\text{-Me}_2\text{dicyd})\]^{3+}$ in acetonitrile, to the fully reduced Ru^{II}-Ru^{II} complex

Similarly to the pentaammine case in nitromethane, the reduction of the complex to its mixed-valence state results in a decrease in oscillator strength, but in this case with no apparent band broadening (Figure 1.22). The spectrum of the fully reduced species (Figure 1.23) shows the further loss of the low energy $\nu(\text{NCN})$ vibration and the appearance of a new absorption at higher wavenumbers (2135 cm^{-1}).

1.3.3.3 Triammine ruthenium dimers

Results of the infrared spectroelectrochemistry experiment performed on *mer*, *mer*- $[\{\text{Ru}(\text{NH}_3)_3(\text{bpy})\}_2(\mu\text{-Me}_2\text{dicyd})][\text{ClO}_4]_4$ and *mer*, *mer*- $[\{\text{Ru}(\text{NH}_3)_3(\text{bpy})\}_2(\mu\text{-dicyd})][\text{ClO}_4]_4$ in DMSO, acetonitrile, and nitromethane are shown in Figures 1.24-1.35. For the most part, these complexes all show similar behavior despite changes in the outer coordination sphere (solvent) and in the substituents on the dicyd²⁻ bridge.

Figure 1.24: IR spectra showing the reduction of the Ru^{III}-Ru^{III} complex, *mer, mer*-[$\{\text{Ru}(\text{NH}_3)_3(\text{bpy})\}_2(\mu\text{-Me}_2\text{dicyd})\][\text{ClO}_4]_4$ in DMSO, to the mixed-valence Ru^{III}-Ru^{II} complex.

Figure 1.25: IR spectra showing the reduction of the mixed valence complex *mer, mer*-[$\{\text{Ru}(\text{NH}_3)_3(\text{bpy})\}_2(\mu\text{-Me}_2\text{dicyd})]^{3+}$ in DMSO, to the fully reduced Ru^{II}-Ru^{II} complex.

Figure 1.26: IR spectra showing the reduction of the Ru^{III}-Ru^{III} complex, *mer, mer*-[Ru(NH₃)₃(bpy)]₂(μ-Me₂dicyd)[ClO₄]₄ in acetonitrile, to the mixed-valence Ru^{III}-Ru^{II} complex.

Figure 1.27: IR spectra showing the reduction of the mixed valence complex *mer, mer*-[Ru(NH₃)₃(bpy)]₂(μ-Me₂dicyd)]³⁺ in acetonitrile to the fully reduced Ru^{II}-Ru^{II} complex

Figure 1.28: IR spectra showing the reduction of the Ru^{III}-Ru^{III} complex, *mer, mer*-[$\{\text{Ru}(\text{NH}_3)_3(\text{bpy})\}_2(\mu\text{-Me}_2\text{dicyd})\][\text{ClO}_4]_4$ in nitromethane, to the mixed-valence Ru^{III}-Ru^{II} complex.

Figure 1.29: IR spectra showing the reduction of the mixed valence complex *mer, mer*-[$\{\text{Ru}(\text{NH}_3)_3(\text{bpy})\}_2(\mu\text{-Me}_2\text{dicyd})]^{3+}$ in nitromethane to the fully reduced Ru^{II}-Ru^{II} complex.

Figure 1.30: IR spectra showing the reduction of the Ru^{III}-Ru^{III} complex, *mer*, *mer*-[$\{\text{Ru}(\text{NH}_3)_3(\text{bpy})\}_2(\mu\text{-dicyd})\][\text{ClO}_4]_4$ in DMSO, to the mixed-valence Ru^{III}-Ru^{II} complex.

Figure 1.31: IR spectra showing the reduction of the mixed valence complex *mer*, *mer*-[$\{\text{Ru}(\text{NH}_3)_3(\text{bpy})\}_2(\mu\text{-dicyd})\]^{3+}$ in DMSO to the fully reduced Ru^{II}-Ru^{II} complex.

Figure 1.32: IR spectra showing the reduction of the Ru^{III}-Ru^{III} complex, *mer, mer*-[$\{\text{Ru}(\text{NH}_3)_3(\text{bpy})\}_2(\mu\text{-dicyd})][\text{ClO}_4]_4$ in acetonitrile, to the mixed-valence Ru^{III}-Ru^{II} complex.

Figure 1.33: IR spectra showing the reduction of the mixed valence complex *mer, mer*-[$\{\text{Ru}(\text{NH}_3)_3(\text{bpy})\}_2(\mu\text{-dicyd})]^{3+}$ in acetonitrile, to the fully reduced Ru^{II}-Ru^{II} complex.

Figure 1.34: IR spectra showing the reduction of the Ru^{III}-Ru^{III} complex, *mer, mer*-[Ru(NH₃)₃(bpy)]₂(μ-dicyd)[ClO₄]₄ in nitromethane, to the mixed-valence Ru^{III}-Ru^{II} complex.

Figure 1.35 : IR spectra showing the reduction of the mixed valence complex *mer, mer*-[Ru(NH₃)₃(bpy)]₂(μ-dicyd)³⁺ in nitromethane, to the fully reduced Ru^{II}-Ru^{II} complex.

Generally speaking, in all three solvents, reduction of the triammine bipyridine complexes to the mixed valence state results in a decrease in intensity of the $\nu(\text{NCN})$ vibration with no significant broadening of the peak, similar to that of *trans*, *trans*- $[\{\text{Ru}(\text{NH}_3)_4(\text{py})\}_2(\mu\text{-Me}_2\text{dicyd})][\text{PF}_6]_4$ in acetonitrile. Further reduction to the $\text{Ru}^{\text{II}}\text{-Ru}^{\text{II}}$ species leads to the appearance of a new band at higher energies.

The fully oxidized spectra of *mer*, *mer*- $[\{\text{Ru}(\text{NH}_3)_3(\text{bpy})\}_2(\mu\text{-Me}_2\text{dicyd})]^{4+}$ in acetonitrile (Figure 1.26) and nitromethane (Figure 1.28) have an additional weak band at higher energy that is not observed in either the pentaammine or the tetraammine dinuclear [III-III] complexes or for *mer*, *mer*- $[\{\text{Ru}(\text{NH}_3)_3(\text{bpy})\}_2(\mu\text{-dicyd})]^{4+}$. This band does not appear to be an artifact, and reduces in intensity with reduction of the [III-III] complex. The two $\nu(\text{NCN})$ bands may arise from either syn and anti conformations of the bridging ligand, or symmetric and anti-symmetric combinations of $\nu(\text{NCN})$.

As can be noted in Figures 1.30-1.35, the reduction of *mer*, *mer*- $[\{\text{Ru}(\text{NH}_3)_3(\text{bpy})\}_2(\mu\text{-dicyd})][\text{ClO}_4]_4$ appears to be similar to the $\text{Me}_2\text{dicyd}^{2-}$ bridged complex, with its behavior in DMSO (Figure 1.30) being the only exception. In this solvent, a noticeable broadening and bathochromic shift as well as reduced oscillator strength relative to the [III-III] $\nu(\text{NCN})$ band are the results of the reduction to the mixed-valence state.

1.4 Discussion

Interpretation of the IR spectroelectrochemical results requires an understanding of the effect of resonance on the cyanamide group. The protonated form of the phenylcyanamide ligand shows an infrared stretch with mostly nitrile character, typically

around 2250 cm^{-1} .²⁷ Deprotonation of the cyanamide ligand leads to the formation of a resonance-stabilized three-atom π -system (scheme 1), in which there are two pairs of non-bonding electrons that can be delocalized over a three-atom system, generating two resonance forms.

Scheme 1.1: Resonances forms of the phenylcyanamide ligand

Deprotonation of the cyanamide group and coordination of a metal ion will shift the $\nu(\text{NCN})$ to lower energies (2120 cm^{-1})²⁷, but the magnitude of this effect depends on the contribution of each resonance form to the electronic structure of the cyanamide group, as influenced by the nature of the metal ion. As resonance form **A** resembles an organic carbodiimide, its $\nu(\text{NCN})$ band should be within the range of $2100\text{--}2150\text{ cm}^{-1}$.²⁷ Resonance form **B** should have a $\nu(\text{NCN})$ absorbance that approaches the value for a neutral phenylcyanamide (2250 cm^{-1}). Dicyd²⁻ derivatives show the same effect, however, the $\nu(\text{NCN})$ is typically shifted to lower frequencies by approximately 20 cm^{-1} when compared to similar phenylcyanamide ligands.²⁷

1.4.1 Mononuclear complexes

Upon reduction to Ru^{II} , the $\nu(\text{NCN})$ vibrations of both triamine bipyridine (Figure 1.12) and pentaamine (Figure 1.13) monomers undergo shifts to higher energy. While linkage isomerism has been observed in some mononuclear phenylcyanamide

complexes²⁹ and has been used to explain shifts in the IR absorption, all ruthenium polyamine phenylcyanamide or dicyanamidobenzene crystal structures have shown end-on coordination only.^{13, 27} Thus, the hypsochromic shift must be rationalized by greater contribution of resonance form **B** to the cyanamide group when the nitrile moiety is coordinated to Ru(II), as nitrile ligands are π -acceptors and are expected to be favoured by the π -donor Ru(II).

The $\nu(\text{NCN})$ vibration in the pentaammine complex shows a noticeable decrease in oscillator strength in its Ru^{II} state. This decrease is due to a smaller vibrational dipole moment as a consequence of electronic factors involving the metal ion, its coordination sphere, and the cyanamide ligand. This effect has been previously reported in other Ru^{II} pentaammine mononuclear complexes, where the $\nu(\text{NCN})$ of the protonated phenylcyanamide ligands practically disappears.³⁰ The variation in the $\nu(\text{NCN})$ band strength may have similar origins to that seen for the $\nu(\text{C}\equiv\text{C})$ band of symmetric and asymmetric acetylenes, but further study is needed.

1.4.2 Dinuclear complexes

The mixed-valence spectra of $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-Me}_2\text{dicyd})]^{3+}$ and $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-dicyd})]^{3+}$ in DMSO (Figures 1.14 and 1.16) are consistent with a Class II description. By analogy with what occurs with the mononuclear complexes, reduction shifts the $\nu(\text{NCN})$ to higher frequencies. Consequently, the band at 2160 cm^{-1} can be assigned to the cyanamide group bound to Ru(II). The band at 2040 cm^{-1} must therefore be associated with the cyanamide group bound to Ru(III). The shift to lower energies relative to that of

the [III-III] complex can be rationalized by the dominating contribution of resonance form A to the cyanamide group bound to Ru (III) (see Scheme 1.2).

Scheme 1.2: Resonance form of the dicyd²⁻ in a Class II complex

The carbodiimide resonance form may be the principal contributor due to the high polarizability of the dianion ligand together with the asymmetry of the metal charges. These factors may allow electron density to be preferentially polarized toward the Ru(III) centre.

Previous studies on $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-Me}_2\text{dicyd})]^{3+}$ have demonstrated that the magnitude of metal-metal coupling increases as the donor number of the solvent is decreased. Thus, the infrared spectra of the mixed-valence complex $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-Me}_2\text{dicyd})]^{3+}$, in DMSO, acetonitrile and nitromethane (Figures 1.14-1.20) represent the transformation of the $\nu(\text{NCN})$ with increasing metal-metal coupling. In DMSO (Figure 1.14), a strong donor solvent, the splitting of the single cyanamide stretch for the III-III species into two for the II-III species indicates that electron-transfer between the two ruthenium centres is slow in comparison to the infrared time-scale and classifies the complex as a valence-trapped Class II system. The mixed-valence spectrum in acetonitrile (Figure 1.18), shows a single red-shifted, broadened $\nu(\text{NCN})$ relative to that of the [III-III] complex. This is consistent with an intermediate case where the electron transfer rate is approaching that of the infrared time scale. The temperature dependence

of the IR spectrum was examined in the range of -10 to 50 °C but no significant effects were observed. Figure 1.19, obtained in nitromethane, displays a mixed-valence $\nu(\text{NCN})$ band with reduced broadening in comparison to 1.18, and no shift in energy compared to the [III-III] spectrum. The small degree of broadening may indicate that this mixed-valence complex is not quite delocalized. However, the peak position appears at the average of the two bands seen in the valence-trapped DMSO spectrum of the same complex, suggesting that this is indeed a Class III case.

The replacement of σ -donating ammine ligands with poor σ -donating pyridine moieties has been demonstrated to stabilize the ruthenium $d\pi$ orbitals, reducing the $d\pi$ - π -HOMO gap and increasing metal-metal coupling in the dicyd²⁻ systems. Thus, the behaviour of the mixed-valence complexes *trans*, *trans*-[$\{\text{Ru}(\text{NH}_3)_4(\text{py})\}_2(\mu\text{-Me}_2\text{dicyd})\]^{3+}$ in acetonitrile, as well as *mer*, *mer*-[$\{\text{Ru}(\text{NH}_3)_3(\text{bpy})\}_2(\mu\text{-dicyd})\]^{3+}$ and *mer*, *mer*-[$\{\text{Ru}(\text{NH}_3)_3(\text{bpy})\}_2(\mu\text{-Me}_2\text{dicyd})\]^{3+}$ in DMSO, acetonitrile, and nitromethane (Figure 1.22-1.35), should be reflective of a more delocalized state. In general, the mixed-valence complexes in all solvents displayed behaviour similar to that seen for [$\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-Me}_2\text{dicyd})\]^{3+}$ in nitromethane, except without any evidence of band broadening. Therefore, these systems can be classified as Class III, with the exception of *mer*, *mer*-[$\{\text{Ru}(\text{NH}_3)_3(\text{bpy})\}_2(\mu\text{-dicyd})\]^{3+}$ in DMSO (Figure 1.30), where the broadened appearance of this cyanamide stretch is suggestive of valence trapping. This is further indication of weaker superexchange metal-metal coupling mediated by the dicyd²⁻ bridging ligand compared to the Me₂dicyd²⁻ bridging ligand, as has been described previously.⁷ Methyl groups are good donor ligands, and could destabilize the bridging π -HOMO to further reduce the energy gap with the Ru $d\pi$ orbitals.

The main objective of this study was to determine a free energy benchmark for delocalization in these mixed valence systems. The experimental $\Delta G_r'$ values for these complexes given in Evans et al,⁷ have been suggested to be overestimates (see Figure 1.7), thus the values used in this study have been reduced by 200 cm⁻¹. For $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-Me}_2\text{dicyd})]^{3+}$ in DMSO and acetonitrile, $\Delta G_r'$ values are 400 and 1010 cm⁻¹, respectively. At 1010 cm⁻¹, valence trapping is indicated by the broadening of the cyanamide stretch due to multiple $\nu(\text{NCN})$ bands. Unfortunately, the $\Delta G_r'$ value in nitromethane could not be factored from the free energy of comproportionation because a value for the free energy of antiferromagnetic exchange was unattainable.³¹ A complex with a higher $\Delta G_r'$ value than 1010 cm⁻¹ needed to be evaluated in order to find the threshold above which delocalized behaviour is observed. The IR spectrum of *trans*, *trans*- $[\{\text{Ru}(\text{NH}_3)_4(\text{py})\}_2(\mu\text{-Me}_2\text{dicyd})]^{3+}$ (Figure 1.22) is very similar to that seen for *mer*, *mer*- $[\{\text{Ru}(\text{NH}_3)_3(\text{bpy})\}_2(\mu\text{-Me}_2\text{dicyd})]^{3+}$, consistent with strong metal-metal coupling and a delocalized mixed-valence state. The free energy of resonance exchange for this tetraammine complex is 1250 cm⁻¹, hence it is reasonable to propose that the onset of delocalization with respect to the infrared time scale occurs between $\Delta G_r' = 1010 \text{ cm}^{-1}$ and $\Delta G_r' = 1250 \text{ cm}^{-1}$. Accordingly, the $\Delta G_r'$ value of 1250 cm⁻¹ can be considered a benchmark for delocalization in our systems. These systems span the complete range of Class II to Class III complexes and interpretation of their spectroscopic and physical properties must reflect this transformation.⁷

The general criterion for delocalization in symmetric mixed-valence complexes can be seen in the dependence of the thermal barrier to electron transfer ΔG_{th} on the donor-acceptor resonance exchange integral H , as shown in equation 1.15,¹⁸ where E_{IT} (or

λ) is the energy of photoinduced electron transfer that can be estimated from the energy of the intervalence transition in a weakly coupled symmetric Class II complex.³

$$\Delta G_{th} = \frac{E_{IT}}{4} \left(1 - \frac{2H}{E_{IT}} \right)^2 \quad (1.15)$$

Thus, when $2H = E_{IT}$, there is no thermal barrier to electron transfer and the result is a fully delocalized system. For the Class III system, *trans, trans*- [$\{\text{Ru}(\text{NH}_3)_4(\text{py})\}_2(\mu\text{-Me}_2\text{dicyd})$]³⁺ in acetonitrile, the calculated value for $2H = 7480 \text{ cm}^{-1}$ (see reference 7). The E_{IT} value for the tetraammineruthenium mixed-valence complexes can be estimated to equal 7670 cm^{-1} from the intervalence band energy of the weakly coupled Class II complex, *trans, trans*- [$\{\text{Ru}(\text{NH}_3)_4(\text{py})\}_2(\mu\text{-Cl}_4\text{dicyd})$]³⁺ in DMSO.⁷ The difference between $2H$ and E_{IT} , while not large, may be significant. When the difference in energy between intervalence and ligand-to-metal charge transfer states is small, symmetric and antisymmetric mixing of these states may significantly perturb the energies and oscillator strengths of the charge transfer transitions.³²

It is also possible to estimate the magnitude of resonance exchange needed to achieve a delocalized state in these mixed-valence systems. The free energy of resonance exchange in a Class III system can be equated to the resonance exchange integral according to equation 1.14. A commonly used approximation for ΔG_{th} is described in equation 1.16:

$$4\Delta G_{th} = E_{IT} \quad (1.16)$$

For *trans, trans*- [$\{\text{Ru}(\text{NH}_3)_4(\text{py})\}_2(\mu\text{-Me}_2\text{dicyd})$] $^{3+}$ in acetonitrile, $\Delta G_r' = 1250 \text{ cm}^{-1}$, and $\frac{E_{IT}}{4}$ can be estimated to be 1920 cm^{-1} , once again from the intervalence band energy of the Class II complex *trans, trans*- [$\{\text{Ru}(\text{NH}_3)_4(\text{py})\}_2(\mu\text{-Cl}_4\text{dicyd})$] $^{3+}$ in DMSO. As a result, equation 1.14 yields $H = 3170 \text{ cm}^{-1}$.³³ This is very close to the value of $H = 3360 \text{ cm}^{-1}$ calculated by the CNS model,^{17, 7} but lower than that derived from the complex's intervalence band energy, $H = 3740 \text{ cm}^{-1}$.⁷ A more accurate estimation of ΔG_{rh} can be obtained considering the complex in acetonitrile will have a larger outer-sphere reorganizational energy (λ_{outer}) than in DMSO, and the difference can be calculated using the equation:

$$\lambda_{\text{outer}} = \frac{\Delta e^2}{2a} \left(\frac{1}{\epsilon_{\text{op}}} - \frac{1}{\epsilon_s} \right) \quad (1.17)$$

where e is $1.602 \times 10^{19} \text{ C}$, $2a$ is taken as the metal-metal distance ($13.1 \text{ \AA}$), ϵ_{op} is equal to the square of the refractive index of the solvent and ϵ_s is the static dielectric of the solvent. The difference in λ_{outer} is 800 cm^{-1} , thus a more appropriate value for $\frac{\lambda}{4}$ or $\left(\frac{E_{IT}}{4}\right)$ is 2120 cm^{-1} . The new H value (3370 cm^{-1}) is in even closer agreement with the CNS value.

The comparison of this benchmark with the results of similar studies could test the general applicability of this work. In studies of mixed-valent ruthenium cluster complexes by Ito, Kubiak and co-workers, strong electronic coupling was evident by the presence of a single, albeit broadened, $\nu(\text{CO})$ band in the infrared spectrum of $\text{Ru}_3(\mu_3\text{-$

O)(μ -CH₃CO₂)₆(CO)(L)(μ_2 -pz), where pz = pyrazine and L = 4-dimethylaminopyridine.^{19i, 19l} Calculation of the metal-metal coupling element using the Hush model (equation 1.9) for this borderline Class III complex yielded $H = 2180 \text{ cm}^{-1}$, considerably lower than the degree of metal-metal coupling needed for delocalization in the dicyd²⁻ family of complexes. It is possible that the discrepancy in H values can be attributed to the use of the Hush model, which has previously been demonstrated to be inappropriate for strongly coupled systems (see section 1.1.1.2). Any comparison of benchmarks between different families of mixed-valent systems must be made carefully, however, as E_{IT} or λ will likely be different in each family, thus the condition for delocalization will also be dissimilar.

1.5 Conclusions

The infrared spectroelectrochemical studies of a series dicyd²⁻ bridged pentaammine, tetraamminepyridine, and triamminebipyridine ruthenium mixed-valence complexes in DMSO, acetonitrile, and nitromethane have been presented. The transformation of the $\nu(\text{NCN})$ band in the infrared spectra of these mixed-valence complexes has demonstrated that this family spans the complete range of Class II to Class III behaviour and has confirmed the effect of inner sphere (bridging and spectator ligands) and outer sphere (solvent) changes on metal-metal communication. This study has also provided an opportunity to investigate the Class II-Class III boundary in these systems. As the infrared spectrum of *trans, trans*- [$\{\text{Ru}(\text{NH}_3)_4(\text{py})\}_2(\mu\text{-Me}_2\text{dicyd})$]³⁺ in acetonitrile is consistent with a Class III description, this complex's properties ($\Delta G_r' = 1250 \text{ cm}^{-1}$; $H = 3740 \text{ cm}^{-1}$) can be regarded as benchmarks for delocalization in the dicyd²⁻ complexes.

1.6 References

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Chapter 2: Semiconductor Properties in Iodine Doped Platinum(II) Dinuclear Complexes

2.1 Introduction

2.1.1 Theory of Conductors, Semiconductors, and Insulators

Materials can be classified as either conductors, semiconductors, or insulators based on their capacity to conduct electricity.¹ Conductivity (σ) in $S\text{ cm}^{-1}$ (or $\Omega^{-1}\text{ cm}^{-1}$) can be calculated using the equation $\sigma = ne\mu$, where n is the number of carriers, e is the charge of the carrier, and μ is the mobility of the carrier. In general, conductivity values can span from 10^6 S cm^{-1} (for metals) to $10^{-20}\text{ S cm}^{-1}$ (for organic insulators) with the room temperature conductivity of a semiconductor falling in the middle of this range. Variable temperature conductivity measurements are required in order to correctly assign a material to one of the three classes. In a true conductor or metal, conductivity decreases with increasing temperature, due to mobility problems at higher temperatures. In semiconductors, conductivity increases at elevated temperatures as the extra thermal energy results in the activation of more carriers.

The electronic behaviour of materials can be explained with band theory. Band theory is essentially an extension of molecular orbital theory for an infinite array of atoms or molecules. Rather than having discrete energy levels as is seen for a free atom, the available energy states in a material form bands as a result of the overlap of energy levels (see Figure 2.1). As the number of energy states increases, the difference in energy between the states decreases such that a continuum of orbitals or a band is formed.

Figure 2.1: Scheme demonstrating the development of bands from the overlap of molecular orbitals for a linear array of one to an infinite number of atoms.

The size of the energy gap between the bonding (valence) and anti-bonding (conduction) bands affects the conductivity of the material (see Figure 2.2). In insulators, there is a large band gap, while in semiconductors, the band gap is small enough that thermal excitation can allow electrons to jump the gap.

Figure 2.2: Band structure for the three classes of materials.

The highest energy level occupied by an electron in a material at 0 K is termed the Fermi energy level (E_F). All levels of lower energy are filled with electrons and all those above this level are empty. A smearing of the Fermi level occurs at higher temperatures, where a fraction of the electrons, determined by the equation:

$$F(E) = \frac{1}{e^{(E-E_F)/kT} + 1} \quad (2.1)$$

will exist at higher energy levels. Only electrons in half-occupied orbitals can participate in the conduction process, thus the position of the Fermi level dictates the electrical properties of the material.

An alternate way to visualize the bands in a material uses a density of states diagram, a plot of the number of states vs. the energy of the state. Figure 2.3 shows the density of states diagram for the different classes of materials.

Figure 2.3: Density of states diagram for the three classes of materials. E_F = Fermi Level; E_g = Energy gap.

Semiconductors can be divided into two subclasses: intrinsic and extrinsic. In an intrinsic semiconductor, thermal energy allows a small number of the electrons to participate in the conduction process. When an electron is promoted to the conduction band, it leaves behind a vacancy, or *hole*, which may be filled by another electron. These holes and electrons are known as intrinsic charge carriers. An extrinsic semiconductor is one whose conducting properties are achieved through the addition of impurities or dopants to the original material. The addition of acceptors capable of generating holes creates *p-type* semiconductors, while donor dopants that add electrons to a material create *n-type* semiconductors. In doped materials, the Fermi level is shifted (see Figure 2.4). In order to classify an *n* or *p* type semiconductor, Hall and thermopower measurements are necessary.

Figure 2.4: Effect of doping on Fermi level in extrinsic semiconductors. Unfilled circles = holes; filled circles = electrons.

2.1.2 Conductivity in “Molecular Metals”

In recent years, new materials with metallic-like conductivities have garnered significant attention. The possibility that organic solids might exhibit high electrical conductivities was suggested in the early 1900s.² This potential was finally realized with the organic charge transfer salt, TTF-TCNQ, where TTF is tetrathiafulvalene, and TCNQ is 7,7,8,8-tetracyano-*p*-quinodimethane: the first molecular crystal with genuine metallic behaviour.³ The conducting properties of organic charge transfer salts arise from the orientation of conjugated planar molecules on top of one another to form “pancake” stack structures within the crystal lattice. The π interactions between molecules making up the stack create a continuum of molecular orbitals (a band structure) and, under the right conditions, can result in conductivity in the direction of the stack.⁴ Work in this area has

lead to a number of variations of the π donor and π acceptor molecules that make up the charge transfer salts, such as TSF (tetraselenafulvalene), TMTSF (tetramethyltetraselenafulvalene), BEDT-TTF (bis(ethylenedithio) tetrathiafulvalene) and DMTCNQ (2,4-dimethyl-TCNQ).⁵ TMTSF salts (also known as Bechgaard salts) and BEDT-TTF salts have been found to be superconducting at low temperature.⁶

Inorganic one-dimensional (1-D) compounds have also shown interesting electrical behaviour. Krogmann salts, partially oxidized tetracyanoplatinate ions, are a well known example.⁷ In these materials, stacking of the planar portions of the molecules allows for overlap of the d_z^2 orbitals, and partial oxidation of the metal centres can lead to metallic conductivity (10^3 S cm^{-1}) at room temperature along the metal-chain axis.

The discovery of the first superconducting charge transfer salt containing a transition metal, TTF[Ni(dmit)₂], where dmit is 1,3-dithiol-2-thione-4,5-dithiolate, has renewed interest in transition metal complexes as building blocks for conducting materials.⁸ Conducting materials based on the metal complexes ML_2 , where L = 1,2-ethanedithiolate, maleonitriledithiolate, bis(trifluoromethyl)ethylenedithiolate, 5,6-dihydro-1,4-dithiin-2,3-dithiolate, 1,2,5-thiadiazole-3,4-dithiol, dithiooxalate, oxalate, diethylthiotetrafulvalenyl dithiolato, and diethylthiotetrafulvalenyl diselenalato have all been described.⁹ [Ni(tmdt)₂], where tmdt is trimethylenetetrathiafulvalenedithiolate, was the first single-component molecular metal discovered and its unique properties are attributed to its small HOMO-LUMO gap.¹⁰

Metal-macrocyclic complexes are another class of inorganic compounds with interesting electrical characteristics. In these complexes, the conductivity is primarily a

result of the oxidation of the ligand π -system. This area has mainly focussed on metal phthalocyanines and porphyrins complexes as these naturally form π -stacking architectures in their crystal lattices. These materials all show weak conductivity but doping by either chemical or electrochemical means leads to a significant improvement in conductivity ($\sigma_{RT} = 10^{-5}$ to $10^{-1} \text{ S cm}^{-1}$).¹¹ Macrocyclic metal complexes axially bridged by bidentate organic ligands have also been prepared and show similar conductivities when doped. Tetrazine bridged phthalocyanine polymers show good conductivities (10^{-2} - $10^{-1} \text{ S cm}^{-1}$) without doping, due to the low lying LUMO of the bridge.¹¹

Supramolecular methods are also suitable for the preparation of new materials as was shown with the successful synthesis of TCNQ stacks in nickel and copper tetraazamacrocyclic systems.¹² Crystal structures of these systems show the TCNQ moiety is not directly coordinated to the metal, but instead linked by hydrogen bonds to the macrocyclic ligand. These materials are good semiconductors with powder conductivities of approx. 10^{-3} to $10^{-2} \text{ S cm}^{-1}$.

One of the most promising groups of conducting materials are the metal compounds of the π -acceptor *N,N'*-dicyanoquinonediimine (DCNQI).

DCNQI

For example, $[\text{Cu}(\text{Me}_2\text{DCNQI})_2]_n$, exhibits metallic conductivity down to 3.5 K with $\sigma = 500,000 \text{ S cm}^{-1}$.¹³ The crystal structure of this material showed that the planar DCNQI molecules form one-dimensional π stacks, interconnected by tetrahedral copper cations.

2.1.3 Research Strategy

By coordinating a donor or acceptor conjugated planar molecule to a metal ion in a square planar coordination sphere, it may be possible to create a new family of conducting materials. On the condition that the new complex is planar, the formation of π stacks in the crystal lattice and appropriate doping could create the right situation for conductivity. To demonstrate that this can be a viable strategy, this chapter describes the examination of dinuclear Pt(II) complexes based on the 1,4-dicyanamidobenzene dianion (dicyd^{2-}). The dicyd^{2-} ligand is the fully reduced analog of the DCNQI molecule, whose importance in the area of molecular metals has already been emphasized. Coordination of this planar ligand to a planar d^8 Pt moiety, $[\text{Pt}(\text{trpy})]^{2+}$, where $\text{trpy} = 2,2':6',2''$ -terpyridine, should present the right conditions for π stacking and perhaps for interesting electrical properties.

2.2 Methods and Materials

All reagents were used as received unless otherwise stated. Platinum (II) chloride was purchased from Pressure Chemical company, 2,2':6',2''-terpyridine (trpy) and ammonium hexafluorophosphate were purchased from Aldrich. $[\text{Pt}(\text{trpy})\text{Cl}]\text{Cl} \cdot 2\text{H}_2\text{O}$ ¹⁴, $[\text{Pt}(\text{trpy})(\text{CF}_3\text{SO}_3)][(\text{CF}_3\text{SO}_3)]$ ¹⁵, $\text{Ti}_2(\text{Me}_2\text{dicyd})$, $\text{Me}_2\text{dicydH}_2$, and $\text{Cl}_2\text{dicydH}_2$ ¹⁶ were

synthesized according to literature procedures. DMF (Spectrophotometric grade, Caledon) was used as received.

Absorption spectra were acquired in DMF using 1.000 cm quartz cells (Wilmad) or 0.200 (Hellma) cm path length, or as a KBr pellet on a Cary 5 UV-Vis-NIR spectrophotometer at ambient temperatures. NMR spectra were acquired on a Bruker AMX-400 at ambient temperatures using #512 sample tubes (Wilmad) in d_6 -DMSO from Canadian Isotopes Limited, and were referenced to solvent resonances. Elemental analyses were performed by Canadian Microanalytical Service, Ltd. of Delta, B.C., Canada. Magnetic susceptibility measurements were performed at Memorial University of Newfoundland.

2.2.1 Metal complex synthesis

All complexes were synthesized based on the procedure developed by Zhang and Al-Mutlaq.¹⁵

[Pt(trpy)Cl][PF₆]₂

A solution of [Pt(trpy)Cl]Cl · 2H₂O (0.85 g, 1.7 mmol) in 100 mL of dH₂O and was heated to 50°C. A solution of ammonium hexafluorophosphate (0.45 g, 2.8 mmol) in 50 mL dH₂O was slowly added with vigorous stirring, forming a bright yellow precipitate. The mixture was stirred for 30 minutes and the precipitate was filtered, washed with dH₂O and acetone and air-dried overnight. The solid was recrystallized by ether diffusion into a concentrated DMF solution, yielding yellow needles that were

collected by filtration, washed with ether, and dried *in vacuo* (0.6 g, 1.05 mmol, 62% yield).

Dinuclear dicyd²⁻ complexes

[{Pt(trpy)}₂(μ-Me₂dicyd)](PF₆)₂, 1

A round bottom flask containing 0.2 g of Tl₂(Me₂dicyd) (0.34 mmol, F.W. 592.89 g · mol⁻¹) was degassed three times on a double-manifold vacuum line and left under argon. A solution of 0.4 g of [Pt(trpy)Cl](PF₆) (0.7 mmol; F.W. 608.81 g · mol⁻¹) in 150 mL of DMF was also degassed three times and was transferred to the flask containing Tl₂(Me₂dicyd) via cannula. The solution was stirred under argon at room temperature for seven days, over which time the colour changed from orange, to forest green, to deep blue. The solution was filtered to remove the white TlCl precipitate, and the dark blue precipitate was crashed out of the filtrate by the addition of 200 mL of diethyl ether. The precipitate was filtered and recrystallized via ether diffusion into a concentrated DMF solution. The microcrystalline blue powder was dried overnight *in vacuo*. [{Pt(trpy)}₂(μ-Me₂dicyd)](PF₆) (0.39 g, 0.29 mmol, 84% yield, F.W. 1330.83 g · mol⁻¹). Anal. Calcd for [{Pt(trpy)}₂(μ-Me₂dicyd)](PF₆)₂ (C₄₀H₃₀N₁₀F₁₂P₂Pt₂): C, 36.10; H, 2.27; N, 10.52. Found: C, 36.04; H, 2.35; N, 10.71. IR (KBr disc): ν(NCN) = 2114 cm⁻¹. ¹H NMR (400 MHz) 7.94–8.63 (terpyridine H, m, 22H), 6.73 (phenyl H, s, 2H), 2.11 (methyl H, s, 6H). ¹³C NMR (100 MHz) 157.8, 154.5, 150.9, 142.9, 141.9, 137.3, 130.8, 129.4, 127.4, 126.0, 124.4, 123.3, and 17.9 ppm.

$[\{\text{Pt}(\text{trpy})\}_2(\mu\text{-Me}_2\text{dicyd})](\text{CF}_3\text{SO}_3)_2$, 2

2 was synthesized in a similar manner to **1**, except $[\text{Pt}(\text{trpy})_2(\text{CF}_3\text{SO}_3)](\text{CF}_3\text{SO}_3)$, and $\text{Me}_2\text{dicydH}_2$ were used as starting materials and triethylamine (NEt_3) was used as a base to deprotonate the ligand. $[\{\text{Pt}(\text{trpy})\}_2(\mu\text{-Me}_2\text{dicyd})](\text{CF}_3\text{SO}_3)_2$ (0.31 g, 0.23 mmol, 68% yield, F.W. $1339.04 \text{ g}\cdot\text{mol}^{-1}$). Anal. Calcd for the hydrate $[\{\text{Pt}(\text{trpy})\}_2(\mu\text{-Me}_2\text{dicyd})](\text{CF}_3\text{SO}_3)_2\cdot\text{H}_2\text{O}$ ($\text{C}_{42}\text{H}_{32}\text{N}_{10}\text{F}_6\text{O}_7\text{S}_2\text{Pt}_2$): C, 37.17; H, 2.38; N, 10.32. Found: C, 36.97; H, 2.35; N, 9.99. IR (KBr disc): $\nu(\text{NCN}) = 2128 \text{ cm}^{-1}$. ^1H NMR (400 MHz) 8.05-8.78 (terpyridine H, m, 22H), 6.84 (phenyl H, s, 2H), 2.17 (methyl H, s, 6H).

$[\{\text{Pt}(\text{trpy})\}_2(\mu\text{-Cl}_2\text{dicyd})](\text{CF}_3\text{SO}_3)_2$, 3

3 was synthesized in a similar manner to **2**, except using $\text{Cl}_2\text{dicydH}_2$ as a starting material. $[\{\text{Pt}(\text{trpy})\}_2(\mu\text{-Cl}_2\text{dicyd})](\text{CF}_3\text{SO}_3)_2$ (0.16 g, mmol, 42% yield, F.W. $1379.9 \text{ g}\cdot\text{mol}^{-1}$). Anal. Calc'd for $[\{\text{Pt}(\text{trpy})\}_2(\mu\text{-Me}_2\text{dicyd})](\text{CF}_3\text{SO}_3)_2$ ($\text{C}_{40}\text{H}_{24}\text{Cl}_2\text{N}_{10}\text{F}_6\text{O}_6\text{S}_2\text{Pt}_2$): C, 34.82; H, 1.75; N, 10.15. Found: C, 34.79; H, 2.03; N, 9.86. IR (KBr disc): $\nu(\text{NCN}) = 2158 \text{ cm}^{-1}$. ^1H NMR (400 MHz) 8.04-8.78 (terpyridine H, m, 22H), 7.07 (phenyl H, s, 2H), 2.11 (methyl H, s, 6H).

2.2.3 Chemical doping of samples

Samples of **1**, **2**, and **3** were placed in an iodine developing chamber for a specified length of time before conductivity measurements were taken. The extent of

doping in **1** was quantified using iodine elemental analysis assuming the dopant species was I_3^- .

2.2.4 Conductivity Measurements

Room temperature powder conductivity measurements were taken using an in-house built two-probe conductivity apparatus, based on the design of Bryce (see figure 2.5).¹⁷ Milligram quantities of the chemically-doped samples were compressed between two steel-pins (A) inside a thick-walled glass capillary tubing sample holder (not shown). A built-in micrometer (B) accurately measured the length of the compressed pellet. The cross-sectional area of the samples were calculated to be 0.0177 cm^2 , based on the diameter of the sample holder. A voltage was applied to the system and the current and/or resistance across the sample was measured.

Figure 2.5: Two-probe conductivity apparatus.

2.3 Results and Discussion

2.3.1 Synthesis and Characterization

1, 2, and 3 were prepared according to the method of Zhang and Al-Mutlaq (see scheme 2.1).¹⁵

Scheme 2.1: Synthesis of 1, 2, and 3

The complexes are soluble in only strongly donating solvents such as DMF and DMSO, and all attempts to grow X-ray quality crystals have been unsuccessful. Nevertheless, the elemental analyses are entirely consistent with the proposed stoichiometries. ^1H NMR spectra (see Figures 2.6-2.8) of all three materials show appropriate chemical shifts and integration for symmetric dinuclear complexes and ^{13}C NMR of **1** (see experimental) showed the expected 13 line pattern.

Figure 2.6: ^1H NMR spectrum of **1** in d_6 -DMSO

Figure 2.7: ^1H NMR spectrum of 2 in d_6 -DMSO

Figure 2.8: ^1H NMR spectrum of 3 in d_6 -DMSO

The UV-vis spectrum of **1** in DMF (see figure 2.9) shows bands at 283 nm ($\epsilon = 44000 \text{ M}^{-1}\text{cm}^{-1}$), 334 nm ($\epsilon = 28\,000 \text{ M}^{-1}\text{cm}^{-1}$) and 386 nm (shoulder, $\epsilon = 10\,500 \text{ M}^{-1}\text{cm}^{-1}$) which have been assigned to terpyridine $\pi \rightarrow \pi^*$ and Pt(II) $\rightarrow$ terpyridine metal-to-ligand charge transfer transitions, respectively.^{15a, 18} Also, a broad band at 588 nm ($\epsilon = 2800 \text{ M}^{-1}\text{cm}^{-1}$) is assigned to a $\pi \rightarrow \sigma^*$ ligand-to-metal charge transfer transition arising from the Pt(II)-cyanamide chromophore by analogy to that observed in mononuclear palladium(II) and platinum(II) terpyridine complexes of phenylcyanamide ligands.¹⁵

Figure 2.9: Electronic absorption spectrum of **1** in DMF

2.3.2 Chemical Doping and Conductivity Measurements

Chemical doping of **1** was achieved by exposing a powder sample to iodine in a developing chamber. The oxidation of the bridging ligand was confirmed by the appearance of absorbances associated with the radical anion $\text{Me}_2\text{dicyd}^-$ in the doped complex's DMF solution spectra (see Figure 2.10).¹⁹

Figure 2.10: Qualitative absorption spectra in DMF of **1** at different doping intervals showing the presence of $\text{Me}_2\text{dicyd}^-$ radical.

At different time intervals, samples of doped **1** were taken for conductivity measurements and the combined results of two separate experiments are plotted in Figure 2.11.

Figure 2.11: Plot of conductivity vs. doping time for 1. The results of two different experiments are plotted.

Elemental analysis for iodine were also performed at twelve different doping intervals. By analogy with crystallographic and spectroscopic studies performed on iodine-doped metal phthalocyanine complexes, it is assumed that doping results mainly in the formation of I_3^- .¹¹ These results are plotted in Figures 2.12 and 2.13 and the value of x represents the number of oxidizing equivalents (i.e. $1 \cdot [I_3]_x$). Two conductivity maxima can be observed at $x = 0.82$ ($\sigma = 8\ \mu S\ cm^{-1}$) and $x = 1.3$ ($\sigma = 39\ \mu S\ cm^{-1}$)

Figure 2.12: Conductivity vs. I_3^- equivalences for $1[I_3]x$ ($x = 0-1$). Results of two different experiments are plotted.

Figure 2.13: Conductivity vs. I_3^- equivalences for $1[I_3]x$ ($x = 1-1.6$). Results of two different experiments are plotted.

A powder sample of $[\text{AsPh}_4]_2[\text{Me}_2\text{dicyd}]$ was also doped in the same manner as the platinum complexes. While the samples showed formation of the radical anion (see Figure 2.14), no evidence of conductivity was observed (the lower limit of conductivity for this setup is $10^{-9} \text{ S cm}^{-1}$). In the crystal structure of $[\text{AsPh}_4]_2[\text{Me}_2\text{dicyd}]$, the $\text{Me}_2\text{dicyd}^{2-}$ anions are not π -stacked and are separated by the tetraphenylarsonium anions,²¹ confirming the need for uninterrupted π stacking in conducting materials.

Figure 2.14: Solid state electronic spectrum (KBr pellet) of $[\text{AsPh}_4]_2[\text{Me}_2\text{dicyd}]$ after 2 hours of doping.

Figures 2.11 - 2.13 show very little scatter in data points, thus the observation of double conductivity maxima can be considered to be a real result. Furthermore, the maximum in Figure 2.13, corresponds to a charge of -0.7 for Me_2dicyd , which corresponds well to the charge found for DCNQI in the molecular metal

$[\text{Cu}(\text{Me}_2\text{DCNQL})_2]_n$, where XPS and low temperature X-ray diffraction indicate an average oxidation state of 1.3 for Cu and hence -0.65 for DCNQL.^{4b, 4c} Additional confirmation of these results was obtained through the doping of 2 and 3, both of which showed similar double maxima in their conductivity vs. doping time plots (see Figures 2.15 and 2.16). Maximum conductivity was 3 and $8 \mu\text{S cm}^{-1}$ for 2 and 1 and $2.8 \mu\text{S cm}^{-1}$ for 3. As conductivity in 2 and 3 is noticeably lower than in 1, it is evident that counter ion has a considerable effect on conductivity, likely due to interferences with stacking.

Figure 2.15: Plot of conductivity vs. doping time for 2. The results of two different experiments are plotted.

Figure 2.16: Plot of conductivity vs. doping time for **3**. The results of two different experiments are plotted.

A crystal structure of **1** would unambiguously prove the existence of π stacking in this material. Unfortunately, all attempts at growing X-ray quality crystals have yielded only powders. It is, however, reasonable to suggest that the dinuclear complex is planar, based on the crystal structure of similar mononuclear complexes and of the bridging ligand.^{15, 16} Therefore, it is highly probable that the architecture responsible for conductivity in this family of materials is π stacking of the Me_2dicyd moieties. With this assumption in mind, Figure 2.17 illustrates the interpretation of the conductivity mechanism for the data obtained. The $\text{Me}_2\text{dicyd}^{2-}$ ligand can be oxidized by two full equivalents to yield Me_2DCNQL . Clearly electron movement between filled orbitals is not possible and if the orbitals making up a π stack each possess one electron, there will be a significant coulombic barrier to electron movement. These situations are observed

as the conductivity minima at $x = 0$ and $x = 1$. Conductivity does not drop off completely at $x = 1$ due to the heterogeneity of the doping process. Partial oxidation (less than or more than one equivalent) can facilitate electron movement as seen for the conductivity maxima at $x = 0.82$ or $x = 1.3$ shown in Figures 2.12 and 2.13 respectively. These cases are loosely termed “n-type” and “p-type” conductivity. However, Hall-effect and thermopower measurements would be needed to truly confirm the nature of the charge carrier, but these measurements would likely be ambiguous because of the low conductivity of $1 \cdot [I_3]x$.

Figure 2.17: Schematic to explain the mechanism of conduction in π -stacked orbitals depending on orbital occupancy.

Figure 2.17 implies that the unpaired spins in this material are ferromagnetically ordered. The preparation of molecular magnetic conductors, multi-functional materials with coupled one-dimensional electronic and magnetic properties, is a relatively new challenge for the materials chemist.²¹ To see if $1\cdot[\text{I}_3]_{1.3}$ displayed any interesting magnetic behaviour, variable temperature magnetic susceptibility measurements were performed by Dr. Laurie Thompson at Memorial University. The results give no indication of ferromagnetic ordering at reduced temperatures, and show only the presence of a weak antiferromagnetic interaction (Figure 2.18 and 2.19).

Figure 2.18: Plot of molar magnetic susceptibility vs. temperature for $1\cdot[\text{I}_3]_{1.3}$. No evidence of ferromagnetic ordering can be observed.

Figure 2.19: Plot of the product of molar magnetic susceptibility and temperature vs. temperature for $1\cdot[\text{I}_3]_{1.3}$. The decrease in χT with decreasing temperature is indicative of a weak antiferromagnetic interaction.

2.4 Conclusions and Future Work

With the proper doping, a series of platinum dinuclear complexes $[\{\text{Pt}(\text{trpy})\}_2(\mu\text{-L})]^{2+}$, where $\text{L} = \text{Me}_2\text{dicyd}^{2-}$ and $\text{Cl}_2\text{dicyd}^{2-}$, were found to be weak semiconductors with two conductivity maxima corresponding to “n-type” and “p-type” mechanisms. In particular, the complex $[\{\text{Pt}(\text{trpy})\}_2(\mu\text{-Me}_2\text{dicyd})](\text{PF}_6)_2(\text{I}_3)_x$ displayed conductivity maxima at $x = 0.82$ ($\sigma = 8 \mu\text{S cm}^{-1}$) and $x = 1.3$ ($\sigma = 39 \mu\text{S cm}^{-1}$), corresponding to partial oxidation (less than or more than one equivalent, respectively) of the bridging ligand. These results, in combination with the presence of $\text{Me}_2\text{dicyd}^\cdot$ radical anion absorbances in the visible spectrum of the doped species, strongly suggest that conductivity originates via electron (or hole) movement through partially oxidized π -stacked Me_2dicyd orbitals. The results of this new family of materials suggest that supramolecular assembly of π -stacked architectures can lead to novel conducting materials.

As the complete elimination of the counter ion may lead to more tightly packed π stacks and thus higher conductivity, neutral Pt(II) complexes based on cyclometalated terpy²² or phenyl-bipyridine²² could lead to more conducting materials. Unfortunately, attempts to make phenyl-bipyridine analogs of **1** have so far yielded insoluble powders with ambiguous elemental analyses. Obviously, as powder conductivity is about $100 \times$ smaller than that seen in single crystals¹⁷, growing X-ray quality crystals of more tractable complexes would improve conductivity and also help confirm the conductivity mechanism in this new family of materials.

2.5 References

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Chapter 3:

Luminescent Ir(III) complexes as polymer-bound oxygen sensors

3.1 Introduction

3.1.1 General Introduction to the Photophysics and Photochemistry of Metal Complexes

The study of inorganic photochemistry is valuable in a number of theoretical and practical arenas, from the photophysical study of ground and excited states, to applications in information storage, artificial photosynthesis, photodynamic therapy, and sensor technology. Many of the theories that form the underpinning of inorganic photochemistry have been developed from an understanding of the photochemistry and photophysics of organic molecules.¹ This chapter will begin with a description of these basic photophysical concepts.

The energy states of an atom or molecule and the transitions that connect these states are typically illustrated in a Jablonski diagram (see Figure 3.1). In this diagram, electronic states are grouped by multiplicity where singlet and triplet levels are designated S_n and T_n , respectively, where n = the electronic energy level (ground state = 0, first excited state = 1, etc.) and each electronic state has a number of vibrational energy levels. Transitions between electronic levels are vertical to represent the instantaneous nature of light absorption, as described by the Franck-Condon principle. Upon light absorption, a number of radiative and non-radiative processes can occur. The luminophore molecule is generally excited to a higher vibrational level of an electronic singlet excited state (in this diagram S_1). The molecule can then relax to the lowest vibrational level in a process termed internal conversion. From this excited state, the

emission of light, or fluorescence, can occur to return the molecule to its ground state. Alternatively, intersystem crossing from the singlet excited state to the first triplet state can occur and emission from the triplet state is known as phosphorescence. Non-radiative decay from an excited state to a ground state is also possible.

Figure 3.1: Jablonski diagram

The luminescence lifetime and quantum yield are important photophysical parameters of any luminophore. Both factors are concerned with the emissive and radiationless decay rates, Γ and k , respectively. The luminescence quantum yield, Q , is the ratio of the number of photons emitted to the number of photons absorbed and is given by the equation:

$$Q = \frac{\Gamma}{\Gamma + k} \quad (3.1)$$

The luminescence lifetime, τ , is an average value of the time a molecule spends in the excited state and is defined in the equation:

$$\tau = \frac{1}{\Gamma + k} \quad (3.2)$$

Fluorescence lifetimes are generally on the order of nanoseconds, while phosphorescence lifetimes can be considerably longer. As this triplet-to-singlet transition is forbidden, phosphorescence τ values can range from microseconds to even milliseconds. Triplet lifetimes can be shortened by a process known as the “heavy atom effect”, which is the enhancement of formally spin-forbidden radiative and non-radiative transition rates. Spin orbit coupling in the heavy atom causes mixing of the states of different multiplicity and as a result of this effect, the lifetimes of metal-containing luminophores tend to fall between those of fluorescent and phosphorescent organic molecules.

Radiationless decay rates are chiefly determined by the vibrational overlap (or Franck-Condon factor) between ground and excited states. As the energy difference between the excited and ground states is increased, the vibrational overlap between the states is diminished. This is the origin of the energy gap law: The rate constants of non-radiative transitions decrease exponentially with the energy difference of the ground and excited state.

The Stokes shift is a measure of the separation between absorption and emission energies. Emission energy tends to be red-shifted relative to the absorption energy as a result of several processes. Common causes are: energy losses due to decay by internal conversion to the lowest vibrational level of the excited state, the reorientation of solvent molecules around the dipole of the excited molecule (known as solvent relaxation), and excited state reactions.

3.1.2 Energy Transfer

This process describes the transfer of excited state energy from a donor to an acceptor. Aside from the ‘trivial’ or radiative mechanism where the emission of a photon from one molecule is absorbed by a second molecule, there are two main mechanisms for energy transfer: the Dexter mechanism² (electron exchange) and the Förster mechanism³ (dipole-dipole interactions). In Dexter energy transfer, the HOMO and LUMO of the quencher must fall between those of the energy donor. Simultaneous electron exchange occurs between the donor and acceptor as shown in Figure 3.2. This double electron transfer requires orbital overlap, thus the molecules must be in close contact.

Figure 3.2: Schematic description of Dexter energy transfer, where M is the molecule and Q is the quencher.

Förster energy transfer is due to the dipole-dipole interactions between the donor and the acceptor. In this mechanism, the rate of energy transfer is dependent upon the extent of overlap of the donor's emission spectrum and acceptor's absorption spectrum,

the distance between the molecules, and the orientation of their transition dipoles.

Equation 3.3 describes the rate of Förster energy transfer:

$$k_{ET} = \frac{1}{\tau_d} \left(\frac{R_0}{r} \right)^6 \quad (3.3)$$

where r is the distance between the donor and the acceptor, τ_d is the lifetime of the donor in the absence of acceptor and R_0 is the Förster distance, where transfer efficiency is 50%.

3.1.2.1 Luminescence quenching

Luminescence quenching refers to any process that decreases the luminescence intensity of a given luminophore.⁴ This definition can encompass a number of processes, including excited state reactions, collisional quenching, or complex formation. Two important quenching mechanisms will be described here: Collisional quenching (or dynamic quenching) and static quenching (complex formation). Both these types of quenching require the luminophore and the quencher to be within a ‘volume of action’. Dynamic quenching describes the process whereby a quencher molecule diffuses to within the volume of action of an excited luminophore during the lifetime of its excited state. A bimolecular collision results in energy transfer to the quencher and causes the luminophore to return to its ground state without the emission of a photon. In a static quenching event, a complex is formed between the luminophore and the quencher in the ground state, and this new complex is non-luminescent. Figure 3.3 illustrates these two quenching mechanisms.

Figure 3.3: Illustration of dynamic (A) and static (B) quenching.

The theory of collisional quenching is best described by the Stern-Volmer (SV) relationship. The relationship between the luminophore's emission intensity, I , or excited state lifetime, τ , and quencher concentration is given by equation (3.4):

$$\frac{I_0}{I} = \frac{\tau_0}{\tau} = 1 + k_q \tau_0 [Q] = 1 + K_{SV} [Q] \quad (3.4)$$

in which I_0 and τ_0 are, respectively, the luminophore's intensity and lifetime in the absence of quencher, k_q is the bimolecular quenching constant, and K_{SV} is the Stern-Volmer constant. A linear plot of I/I_0 (or τ/τ_0) vs. $[Q]$ is indicative of a single luminophore environment, and deviations from linear behaviour occur when the luminophore finds itself in a number of environments with differing accessibility to the quencher.

In static quenching, the dependence of luminescence intensity on quencher concentration can be found by considering the equilibrium constant for complex formation:

$$K_s = \frac{[L \cdot Q]}{[L][Q]} \quad (3.5)$$

where $[L - Q]$ is the complex concentration and $[L]$ and $[Q]$ are the concentrations of uncomplexed luminophore and quencher, respectively. Since the complex $L - Q$ is not luminescent, the fraction of luminescence intensity that remains (I/I_0) is related to the fraction of uncomplexed luminophores (L/L_0). Substituting the total concentration of luminophore:

$$[L_0] = [L] + [L - Q] \quad (3.6)$$

into equation (3.5) gives

$$K_s = \frac{[L_0] - [L]}{[L][Q]} = \frac{[L_0]}{[L][Q]} - \frac{1}{[Q]} \quad (3.7)$$

By replacing luminophore concentrations with intensity and rearranging equation (3.5) the result is:

$$\frac{I_0}{I} = 1 + K_s[Q] \quad (3.8)$$

which is identical to the relationship between intensity and quencher concentration for collisional quenching. To best differentiate between these two types of quenching, lifetime measurements can be used. In the case of static quenching, complex formation prevents a fraction of the luminophores from emitting, but the emission lifetime of the uncomplexed fraction remains constant. In dynamic quenching, both the intensity of the luminescence and the lifetime is affected by the quencher.

The study of luminescence quenching can provide insight into a number of fundamental processes, such as diffusion and membrane permeability, and can have practical applications in sensor technology (*e.g.* oxygen sensing).

3.1.3 Oxygen Sensing

The ability to measure oxygen concentrations accurately and reproducibly is of obvious importance in areas ranging from gas purity analysis in medicine to emission analysis in the automotive industry. Early sensors based on electrochemical detection, such as the Clark⁵ or Mancy⁶ cell, are disadvantageous for a number of applications as they consume oxygen as part of their functioning. As the electrolyte in an electrochemical sensor is consumed by the oxygen being measured, these sensors tend to have a limited lifetime. As a result, researchers have recently shifted their attention to non-destructive sensors for oxygen analysis. Paramagnetic oxygen sensors have been developed based on the principle that oxygen causes a concentration dependent distortion of a magnetic field within the sensor.⁷ No oxygen is consumed during the measurement leading to an extended sensor lifetime. Unfortunately, these sensors are limited only to gas analysis. A third family of oxygen sensors exploits the fact that oxygen is an ubiquitous dynamic quencher of the excited states of many luminophores, forming highly reactive singlet oxygen.⁸ The production of reactive singlet oxygen can be a detriment, as singlet oxygen is known to lead to polymer photodegradation, DNA damage, etc.. However, this behaviour can be of benefit to the field of oxygen sensing, where quenching-based luminescent oxygen sensors find a variety of uses ranging from *in vivo*⁹ or other biological measurements,¹⁰ to monitoring ground water oxygen levels,¹¹ from combustion analysis,¹² to luminescence barometry.¹³

Two basic mechanisms have been described for the reaction of $^3\text{O}_2$ with an excited photosensitizer: 1) simple energy transfer from the sensitizer to oxygen and 2)

excited state electron transfer yielding a sensitizer⁺-O₂⁻ ion pair that decays to give singlet oxygen.¹⁴ Simple energy transfer is generally considered to be dominant in luminescent transition metal complexes of ruthenium, osmium, and iridium, although varying degrees of charge transfer character is possible depending on the reaction conditions used and the oxidation potential of the photosensitizer.¹⁵

As these sensors work on the principle of luminescence quenching by oxygen, the Stern-Volmer relationship (introduced earlier as equation 3.4) can be used to relate luminescence intensity and oxygen pressure:

$$\frac{I_0}{I} = \frac{\tau_0}{\tau} = 1 + k_q \tau_0 [Q] = 1 + K_{SV} P_{O_2} \quad (3.9)$$

I_0 and τ_0 are measured at zero oxygen pressure. Unfortunately, measurements at zero oxygen concentration are not always convenient. This is particularly true in luminescence barometry (*e.g.* wind tunnel) experiments. However, if Henry's law is obeyed:

$$[O_2] = S \cdot X \cdot P \quad (3.10)$$

where S = the Henry's Law coefficient of the matrix, X = the mol fraction of oxygen in air, and P = the air pressure, then changes in air pressure over the surface of a substrate will alter the concentration of dissolved oxygen within the substrate in a predictable manner. Therefore, it is more practical to replace oxygen pressure by air pressure and to use $P = 1$ atm as a point of reference. In this case, the relationship between luminescence intensity and air pressure becomes:

$$\frac{I_{ref}}{I} = \frac{\tau_{ref}}{\tau} = A + Q_S \frac{P}{P_{ref}} \quad (3.11).$$

The slope of the modified Stern-Volmer plot (Q_S) is a measure of the quenching

sensitivity of the system due to changes in air pressure.¹⁶ This quenching factor is generally constrained to values between 0 and 1 and can be determined from a linear regression of either a linear part of the Stern-Volmer-type plot or a best fit straight line drawn through the data points.

3.1.4 Pressure Sensitive Paints (PSPs)

“Pressure sensitive paints” are of particular interest to aerospace and automotive industries for flow-visualization¹⁷ in aerodynamic testing. Traditionally, surface pressure measurements require the use of pressure taps or transducers, which are both time consuming and expensive to employ and are impractical for measurements on thin or moving parts (i.e. turbine propeller blades). A far more cost and time efficient method employs a pressure sensitive paint (PSP) in which a luminophore is dispersed or dissolved in an oxygen-permeable polymer matrix. The luminescence detected from a model painted with a PSP will ideally be proportional to the air pressure above the model’s surface and this is illustrated schematically in Figure 3.4.

Figure 3.4. Schematic of a pressure sensitive paint coating a model surface. Filled circles are ground state luminophores while asterisks are excited state luminophores.

Non-ideal SV calibrations, those not exhibiting a linear dependence but rather one with downward curvature, are commonplace in oxygen sensor films¹⁸ and have been ascribed to inhomogeneities in the luminophore microenvironment leading to differences in luminophore accessibility to oxygen. At low pressures, sensitivity is dominated by the luminophores in the most accessible domains. At higher pressures, the easily accessible luminophore molecules are largely quenched and the sensor response is increasingly determined by the quenching in the less accessible sites. One of the main mathematical models created to describe this complex quenching behaviour is the ‘two-site model’ (see equation 3.12):¹⁹

$$I/I_0 = \frac{1}{f_{0_1}/(1 + K_{SV_1} pO_2) + f_{0_2}/(1 + K_{SV_2} pO_2)} \quad (3.12)$$

where f_{0_1} and f_{0_2} are the fraction of total unquenched intensity from site 1 and 2 respectively, and K_{SV_1} and K_{SV_2} are the Stern-Volmer quenching constants for the two sites. While this model works well for quantitatively fitting intensity quenching data, it is generally accepted that a range of different solvation microenvironments is likely to be present in any given sample.

Under ideal conditions, any changes in luminescence intensity of a PSP film would be due exclusively to changes in oxygen concentration. Unfortunately, temperature changes can also affect the luminescence intensity of a PSP.²⁰ Higher temperatures can result in an increase in the non-radiative decay rate of a luminophore. The oxygen permeability of the binder is also temperature dependent due to an increase in polymer total free volume with increasing temperature. It can be exceedingly difficult to deconvolute pressure and temperature sensitivity from a sensor response, leading to purely qualitative results. Thus, generating a PSP system with low to no temperature sensitivity remains a goal in this field.²¹ Alternatively, determination of the temperature distribution across the surface of interest could be facilitated by the incorporation of a temperature sensitive, pressure insensitive luminophore into the PSP.²²

The ideal sensitivity of an oxygen sensor depends to some extent on the use for which the sensor was designed.²³ A high Q_S value is generally preferred as a large difference in intensity is easier to detect. However, if the Q_S value is too high, then the absolute luminescence intensity may be too low to measure. In wind tunnel

measurements, $Q_S = 0.4-0.7$ is considered ideal.^{13a} Sensors with higher Q_S values might be useful in vacuum packaging, for example,²³ while lower Q_S values could be beneficial for detecting oxygen concentration changes in high pressure applications.

3.1.4.1 General considerations for PSPs: Choice of Luminophore

An ideal luminophore for oxygen sensing should fulfill several key requirements: efficient emission (high quantum yield) for improved sensitivity, long excited state lifetime (from hundreds of nanoseconds to microseconds) in order to be quenched efficiently by oxygen, as well as excellent photostability and resistance to singlet oxygen. Ancillary properties can also improve the applicability of a luminophore to oxygen sensing. For example, the Stokes shift of the luminescent dye is important. If the overlap between the absorption and emission band envelopes is significant, the luminophore in the PSP will absorb emission radiation. A large Stokes shift will minimize this internal filtering effect. Also, longer excitation energies, *i.e.* in the visible, are preferred in order to avoid cost and safety issues of the exciting light source.

Commonly used luminophores for PSP applications include organic dyes,²⁴ polycyclic aromatic hydrocarbons,²⁵ metalloporphyrins,²⁶ or polypyridyl transition metal complexes.^{18, 25 a, 27} In general, organic fluorophores have excited state lifetimes that are too short for oxygen quenching. However, organic dyes such as Rose Bengal, Methylene Blue, and Fluorescein Yellow are well known singlet oxygen photosensitizers,^{24a, 28} and thus have been examined for use in oxygen sensing and PSPs. Aromatic hydrocarbons

with long excited-state lifetimes such as pyrene ($\tau = 400$ ns) have also been investigated for sensor applications, but tend to be photochemically unstable.²⁵

Through the modification of ligands or metal centre, luminescent transition metal complexes offer a degree of synthetic control that allows for the systematic alteration of spectroscopic properties. In particular, the incorporation of transition metals with higher atomic number into the luminophore can lead to large spin-orbit coupling, causing mixing of singlet and triplet states such that formally forbidden transitions become allowed, leading to high luminescence quantum yields and excited state lifetimes permitting quenching by O₂. As a result, a number of transition metal luminophores have been investigated for use in PSP technology. A major consideration when designing luminescent transition metal complexes for sensing is that emission is expected to originate from the lowest excited state. Thus, the energy and nature of this state are key to the luminophore's properties.²⁹ The lowest excited state should be a charge-transfer state or a ligand $\pi\text{-}\pi^*$, as metal centred d-d states are typically not luminescent. Furthermore, the d-d states should be well-removed from the emitting level to prevent thermal population of these levels, which can lead to rapid excited-state decay and large temperature sensitivity. The luminophore's emitting state must also be of appropriate energy (≥ 95 kJ mol⁻¹) to allow for efficient energy transfer to ground state oxygen, and to avoid the increased efficiency of radiationless processes due to the energy gap law.

With the proper care in choosing the appropriate system, transition metal complexes are ideal for use in sensor technology. Ruthenium tris-diimine complexes have been intensely investigated for use in oxygen sensing as they fulfill a number of requirements listed above. Extended conjugation of the diimine ligand, *i.e.* from

bipyridine to phenanthroline to diphenylphenanthroline, has lead to improved photophysical characteristics. Unfortunately, many ruthenium complexes, particularly $\text{Ru}(\text{bpy})_3^{2+}$, are deactivated by a thermally accessible d-d state, leading to temperature sensitivity issues.²⁹ Some attention has been paid to Ir(III) complexes,³⁰ which tend to have longer excited state lifetimes and higher quantum yields. Platinum and palladium porphyrins, with excited state lifetimes on the order of tens to hundreds of microseconds, are efficiently quenched by oxygen, and have been examined for sensor use.^{26, 27f} Luminescent compounds based on gold,³¹ copper,³² and lanthanides³³ have also been studied for oxygen sensing applications.

3.1.4.2 General considerations for oxygen sensors: Choice of Binder

The gas-permeable matrix within which the luminophore is dispersed is a key component in any sensor and the choice of this binder depends greatly on the application to which the sensor is intended. Ideally, the binder should exhibit high permeability to oxygen, superior film forming properties, and resistance to singlet oxygen. Oxygen permeability and solubility not only affect the overall sensitivity of the sensor, but also the response time (time required after which measurement is constant) of the system. Depending on the intended use of the sensor, the response time can be a critical feature. For example, the short air bursts in blow-down wind tunnels require PSP response times of ≤ 1 second. Mechanical and chemical robustness are also key characteristics of an effective binder. During wind tunnel testing of a PSP, for example, the binder layer must be resistant to dust and other particles that may impinge on the surface during the

measurement. As singlet oxygen is a by-product of the sensor functioning, it is important that the binder must also be resistant to this reactive species, in order to yield reproducible results. Typically, a polymer binder fulfills many of these requirements, but sol-gels and zeolites can also be successfully employed.^{11 b, 34}

High glass transition temperature (T_g) organic polymers such as polystyrene (PS; $T_g=90\text{ }^\circ\text{C}$) or poly(methylmethacrylate) (PMMA; $T_g=110\text{ }^\circ\text{C}$) can be used as binders for their superior film forming properties, but the drawback is that these binders have low-permeability to oxygen ($P_{\text{PS}} = 1.9 \times 10^{-13} \text{ (cm}^3 \text{ cm)/(cm}^2 \text{ s Pa)}$ and $P_{\text{PMMA}} = 0.116 \times 10^{-13} \text{ (cm}^3 \text{ cm)/(cm}^2 \text{ s Pa)}$, both at 273 K, $1.013 \times 10^5 \text{ Pa}$).³⁵ As a result, the sensors have very long response times. Plasticizers can be added to improve a polymer's gas permeability, but may leach from the binder.^{26 d} Fluorination often results in polymers with enhanced gas permeability and higher photostability as demonstrated by polymers such as poly(hexafluoroisopropyl-*co*-heptafluoro-*n*-butyl methacrylate) (FIB) and poly(2,2,2-trifluoroethyl-*co*-isobutyl methacrylate)^{21a, 36} which are effective matrix materials.

Silicones (polysiloxanes, *e.g.* polydimethylsiloxane, PDMS) have very high oxygen permeabilities ($\sim 300 \times 10^{-13} \text{ (cm}^3 \text{ cm)/(cm}^2 \text{ s Pa)}$ at 273 K, $1.013 \times 10^5 \text{ Pa}$) relative to most organic polymers.³⁵ While silicones are obvious matrix materials, many have extremely low T_g s (*e.g.* PDMS, $-127\text{ }^\circ\text{C}$) and thus form films with rather poor mechanical properties unless cured (*i.e.* crosslinked). Unfortunately, cross-linking can result in non-uniformity within the film, leading to varying luminophore environments.^{19c} It has also been noted that luminophores such as $[\text{Ru}(\text{dpp})_3]\text{Cl}_2$, where dpp is diphenylphenanthroline, have a strong tendency to form aggregates or microcrystallites within these extremely hydrophobic matrices.^{18a, 19a} An alternative approach for

improving mechanical stability is to blend the silicone with high T_g polymers such as PS or PMMA or to add rigidifying agents such as alumina or silica. However, luminophores have been shown to adsorb to the surfaces of rigidifying additives,³⁷ and the multitude of microenvironments created in the blends can lead to unexpected behaviour. Covalent attachment of the luminophore to silicones should alleviate aggregation and lead to improved PSP properties.

3.1.4.3 Advantages of polymer-bound luminophores

The sensors studied to date have predominantly been ones in which the luminophore is dispersed within the host matrix as a solid solution. This can lead to the following behaviours that can result in undesirable properties:

1. Aggregation or microcrystallite formation
2. Leaching
3. Solvation by blend polymers

Luminophore aggregation can lead to problems of self-quenching causing loss of emission intensity. Further emission losses can occur by luminophore leaching or sublimation from the PSP layer.^{18a, 38} If additives or polymer blends are desired to improve PSP properties, the luminophore may partition between the various components, leading to complex or unexpected behaviour.^{16, 37} These problems could be eliminated or at least moderated by covalently attaching the luminophore to the polymer matrix.³⁹ A

recent study by Manners and Winnik et al⁴⁰ has demonstrated the efficacy of this approach. These authors covalently attached ruthenium phenanthroline complexes to polythionylphosphazenes and found improved Stern-Volmer behaviour and significantly increased sensitivity compared to analogous materials where the luminophores are dispersed in a polythionylphosphazene matrix.

Silicones would be ideal matrices for an investigation of the benefits of covalent luminophore binding. They possess high oxygen permeabilities but require blending with, for example, a high T_g polymer to ensure film robustness. Thus, by creating unimolecular sensors based on silicones, it may be possible to determine whether covalent attachment alleviates problems of aggregation, leaching, and solvation by blend polymers.

3.1.5 Hydrosilation

The direct addition of a silane (Si-H) across a π -bond is known as the hydrosilation reaction. This reaction takes advantage of the relatively weak Si-H bond (80-90 kcal/mole)⁴¹ and is an effective method for the formation of carbon-silicon bonds when catalyzed by peroxides, UV light, or more commonly, transition metal catalysts.⁴²

There are two main types of platinum species that are routinely used as catalysts for hydrosilation:⁴¹ zero-valent platinum (e.g. Karstedt's catalyst: $\text{Pt}_2(\text{H}_2\text{C}=\text{C}(\text{SiMe}_2\text{OSiMe}_2\text{C}=\text{C}_2)_n)$) and higher-valent platinum (e.g. Speier's catalyst: chloroplatinic acid, H_2PtCl_6 , in isopropanol). These catalysts can be poisoned by the presence of ligands that have a strong affinity for platinum (e.g. phosphines, pyridines, DMSO, etc.).

It is also possible for these catalysts to reduce carbonyl groups, and react with NH or OH groups. Catalyst poisoning must therefore be considered when choosing an appropriate reaction solvent. Typically, chlorinated hydrocarbons are employed in hydrosilation reactions.

Transition-metal catalyzed hydrosilation is a good candidate reaction for attachment of luminophores to silicones, since a number of relatively inexpensive hydride-containing and hydride-terminated silicone fluids are commercially available.⁴³ For this synthetic strategy the luminophore must be functionalized with a pendent vinyl group to provide a sterically accessible site for the reaction.⁴² Scheme 3.1 illustrates this reaction between a vinyl substituted dye and hydride-terminated PDMS.

Scheme 3.1: General hydrosilation reaction scheme for the attachment of a luminescent dye (D) bearing a pendent vinyl group to hydride-containing polydimethylsiloxane (PDMS).

Unfortunately, dehydrocoupling is a possible side-reaction that may occur, which could yield an insoluble, cross-linked product.⁴¹ Scheme 3.2 shows the cross-linking reaction.

Scheme 3.2: General dehydrocoupling reaction scheme for the cross-linking of two hydride-containing polydimethylsiloxane (PDMS) molecules.

This problem can be minimized by using a higher dye concentration in an attempt to maximize dye-loading, and by the use of a hydride-terminated polymer, with which the dehydrocoupling reaction would lead to longer chains rather than cross-linking.

3.1.6 Imine linker

There is a multitude of reactions that can be utilized to covalently attach a dye to a polymer. The formation of an imine ($\text{C}=\text{N}$) from an aldehyde or ketone and a primary or secondary amine is a convenient method for dye-attachment.⁴⁴ This reaction is acid-catalyzed and can commonly be carried out by refluxing the carbonyl and amine with a drying or azeotroping agent, if necessary, separating the water as formed. Tertiary

aliphatic and aromatic aldehydes react to form imines nearly quantitatively, even at room temperature and without the removal of the water formed during the reaction.

Scheme 3.3: Formation of an imine from a carbonyl and an amine.

This technique was recently explored using iridium(III)bis(pyridylbenzaldehyde) complexes as cross-linkers in biological molecules. The aldehyde functionalities were reacted with alanine and reduced to form a secondary amine linker.⁴⁵

3.1.7 Cyclometalated Iridium(III) complexes

Focus on the synthesis and study of iridium (III) polyimines has grown over the past thirty years, as their photophysical and electrochemical properties are germane to a number of applications.⁴⁶ For example, modified Ir(III)bis-terpyridine complexes have recently been used as chloride ion sensors,⁴⁷ and as part of porphyrinic triads for modeling photosynthetic processes.⁴⁸ Cyclometalated iridium complexes in particular are gaining increased interest due to their favourable redox behaviour and luminescence characteristics. Ir(III) complexes with monoanionic cyclometalating ligands, such as 2-phenylpyridinato (ppy) are isoelectronic with ruthenium (II) and osmium (II) cationic tris-diimine complexes, and in comparison to Ru(II) and Os(II) analogues, they tend to

have longer excited-state lifetimes and higher quantum yields in solution. For example, the complex $[\text{Ir}(\text{ppy})_3]$ has a lifetime of 2 μs and a quantum yield of 0.4,⁴⁹ which is significantly higher than similar ruthenium complexes such as $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ ($\text{bpy} = 2,2'$ -bipyridine, $\tau_0 = 0.6 \mu\text{s}$, $\phi = 0.042$) or $[\text{Ru}(\text{phen})_3]\text{Cl}_2$ ($\text{phen} = 1,10$ -phenanthroline, $\tau_0 = 0.74 \mu\text{s}$, $\phi = 0.08$).⁵⁰ These improved properties are attributed to greater spin-orbit coupling, due to the heavy Ir(III) metal centre, resulting in more efficient intersystem crossing between singlet and triplet excited states. Also, the strong ligand field strength of the anionic phenyl ligand increases the already large d-orbital splitting of the iridium centre, leading to a larger energy gap between the ligand LUMO and the higher lying e_g orbitals. As a result, non-radiative deactivation is diminished.

A number of possible applications have been envisaged for this family of complexes. The photophysical and electrochemical properties of a number of mononuclear and dinuclear cyclometalated iridium complexes have been investigated for application in photochemical energy conversion⁵¹ or as powerful photoreductants.^{49b} Iridium (III) complexes with aldehyde, isothiocyanato, iodoacetamido, and amino modified phenanthroline, terpyridine, or phenylpyridine ligands have been used as luminescent labels for biological substrates.⁵² Similarly, iridium (III) complexes with bifunctional chelating ligands such as 4'-(4-carboxyphenyl)-2-phenyl-6,6'-bipyridine may also be useful in biological labeling.⁵³ The use of cyclometalated iridium (III) complexes as dopants in molecular or polymeric light-emitting diodes has been explored by a number of research groups.⁵⁴

$\text{Ir(III)tris(bipyridine)}$ and $\text{tris(phenanthroline)}$ complexes are known singlet oxygen photosensitizers.^{14, 55} A recent study of cyclometalated iridium (III) complexes by

Gao et. al has shown these systems are also efficient singlet oxygen photosensitizers in solution, with diffusion controlled rates.⁵⁶ Although many iridium complexes have also been found to be quenchers of singlet oxygen,⁵⁷ which could lead to photostability problems, these complexes were not efficient quenchers. The neutral complex [Ir(ppy)₃] has previously been successfully employed as a luminescent oxygen sensor.^{30c,d} It might be anticipated that the nonionic character of similar iridium complexes would increase their compatibility with non-polar silicone matrices over cationic metal species, and would help avoid any deleterious electrostatic interactions with a hydrosilation catalyst. Thus, cyclometalated complexes of iridium have been selected as the luminophores for this study.

3.1.8 Research Strategy

This study involves the synthesis and characterization of novel Ir (III) luminophores containing ligands with pendent vinyl or carbonyl groups. These complexes can then be bound to PDMS by either the hydrosilation or the imine reaction. The photophysical properties of the systems before and after attachment will be investigated. Oxygen sensitivity of both the luminophores dispersed in PDMS and the attached systems will then be evaluated. In addition, the effect of blend polymers in both cases will be examined.

3.2 Methods and Materials

Solvents were purified as follows: acetone (ACS Reagent grade) was distilled before use; diethyl ether (Anhydrous) and hexanes (Spectrograde) were dried over sodium and distilled and stored under nitrogen; dichloromethane (Laboratory grade) was either used as received or dried over calcium hydride and distilled and stored under nitrogen before use. 2-Ethoxyethanol (Spectrophotometric grade) was used as received. Toluene (Spectrophotometric grade) and acetonitrile (Reagent grade) for spectroscopy were dried over sodium metal and calcium hydride, respectively, and were distilled under nitrogen before use.

Iridium (III) chloride hydrate was purchased from Strem, 2-phenylpyridine, 4-vinylpyridine, allylacetoacetate, and dimethylphenylsilane were purchased from Aldrich, Karstedt's catalyst (platinum divinyltetramethyldisiloxane complex in xylene, 2.1-2.4% Pt), hydride terminated polydimethylsiloxane (Mn 55,000 – 70,000), and aminopropyl terminated polydimethylsiloxane (Mn 25,000 - 35,000) were purchased from Gelest. $[\text{Ir}(\text{ppy})_2\text{Cl}]_2$ (**1**) was prepared according to Watts⁵⁸ and $[\text{Ir}(\text{C}_6\text{H}_5)_2\text{Cl}]_2$ (**2**) was prepared as outlined in Thompson.^{54 b}

Absorption spectra were acquired in dry CH_2Cl_2 or dry acetonitrile on a Cary 5 UV-vis-NIR spectrophotometer at ambient temperatures using quartz cells of either 1.000 (Wilma) or 0.200 (Hellma) cm path length. Emission spectra were acquired in degassed toluene or acetonitrile on a Shimadzu RF-1501 spectrofluorimeter at ambient temperatures using 1.000 cm path length quartz fluorimeter cells (Wilma). To obtain time-resolved fluorescence decays, the samples were excited with the third harmonic of a Surelite Nd:YAG laser generating pulses at 355 nm of 6 ns duration and $\leq 25\text{mJ}$ energy.

The signals from the monochromator/photo-multiplier system were initially captured by a Tektronix 2440 digitizer and transferred to a Power Macintosh computer with software developed in the LabVIEW environment from National Instruments. A total of four shots were averaged to obtain the decay traces. All experiments were done in static 0.7×0.7 cm² fused silica cuvettes, following purging with N₂ gas for 15 minutes. For the quantum yield determinations, the N₂ purged samples were optically matched to an Ir(ppy)₃ standard using a Varian Cary 1E spectrophotometer. The steady-state emission was obtained using a Photon Technology International version 1.23 luminescence spectrometer. Fused silica cuvettes (Luzchem Research, Morin Heights, Quebec, Canada) with a 1.0 cm optical path were employed in these experiments. Toluene was used as the solvent for all lifetime and quantum yield measurements except for the lifetime of **8** which was acquired in acetonitrile.

Cyclic voltammetry was performed with a BAS CV-27 voltammograph and a BAS X-Y recorder. A double-jacketed cell was fitted with a Teflon lid incorporating the three-electrodes and an argon bubbler and was attached to a Haake D8-G circulating bath to maintain the temperature at 25 °C. Platinum disc working and counter electrodes (BAS, 1.6 mm diameter), a silver wire pseudo-reference with a ferrocene as an internal reference, and 0.1 M TBAH (twice recrystallized in 1:1 EtOH/water) as the supporting electrolyte were all used.

NMR spectra were acquired on a Bruker AMX-400 by Keith Bourque at Carleton University or on a Bruker Avance 700 MHz, processed using XWIN NMR 3.0, by Derek Hodgson at Health Canada. 400 MHz experiments were performed at 300 K, while 700 MHz experiments were performed at 284 K. All experiments used CD₂Cl₂ or d₆-acetone

from Canadian Isotopes Limited, and were referenced to solvent resonances. $[\text{Cr}(\text{acac})_3]$ relaxation agent was used to enhance the signal in the ^{29}Si NMR.

Elemental analyses were performed by Canadian Microanalytical Service, Ltd. of Delta, B.C., Canada. Electron Impact Mass Spectrometry (EI-MS) was performed at the University of Ottawa Mass Spectrometry centre.

X-ray structural determinations were performed by either Dr. Glenn Yap at the University of Ottawa (for complex **3**) or Dr. Gary Enright at the National Research Council (for complexes **7** and **14**). The following experimental descriptions were written by the appropriate crystallographer. For **3**: Data were collected on a Bruker AXS SMART 1k CCD diffractometer using 0.3° ω -scans at 0, 90, and 180° in ϕ . Initial unit-cell parameters were determined from 60 data frames collected at different sections of the Ewald sphere. Semi-empirical absorption corrections based on equivalent reflections were applied.⁵⁹ Systematic absences in the diffraction data and unit-cell parameters were uniquely consistent with the reported space group. The structure was solved by direct methods, completed with difference Fourier syntheses and refined with full-matrix least-squares procedures based on F^2 . A molecule of diethyl ether solvent was found cocrystallized in the asymmetric unit. All nonhydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were treated as idealized contributions. All scattering factors are contained in the SHELXTL 6.12 program library.⁶⁰ For **7** and **14**: The single crystal diffraction data were collected at 173 K on a Bruker SMART CCD diffractometer with Mo K radiation ($0.71073 \text{ \AA}$). The program SMART was used for collecting frames of data, indexing reflections, and determination of lattice parameters; SAINT was used for integration of the intensity of reflections and

scaling. SADABS was used for absorption correction, and SHELXTL was used for space group and structure determination, and least-squares refinements on F^2 .⁵⁹ Hydrogen atoms were placed in calculated positions and constrained to ride with the atoms with which they were bonded. In **14**, acetone solvent of crystallization was included. It was found on three sites, only one of which was fully occupied. The second site had occupancy 0.91 and the third site was 0.49.

3.2.1 Synthesis of Unbound Iridium Complexes

[Ir(ppy)₂(vpy)Cl], **3**

4-Vinylpyridine (0.05 mL, 0.46 mmol, F.W. 105.14 g·mol⁻¹) was added to [Ir(ppy)₂Cl]₂ (0.25 g, 0.23 mmol, F.W. 1072.11 g·mol⁻¹) in dichloromethane (20 mL), and the resultant solution was refluxed under nitrogen for 3 days. After cooling to room temperature, toluene (20 mL) was added, the volume was reduced to 20 mL, and the solution was cooled for several hours in a freezer. The yellow microcrystalline product was collected by vacuum filtration, rinsed with 5 mL aliquots of toluene and hexanes, and dried *in vacuo*. X-ray quality crystals were grown by Peter Mosher by hexanes diffusion into a concentrated dichloromethane solution. [Ir(ppy)₂(vpy)Cl] **3** (0.21 g, 0.33 mmol, 70% yield, F.W. 641.19 g·mol⁻¹).

Elemental analysis as the monohydrate C₂₉H₂₃ClIrN₃·H₂O: %Calc'd C 52.68, H 4.12, N 6.35; %Found C 53.01, H 3.74, N 5.93.

¹H NMR (CD₂Cl₂, 700 MHz): 9.80 (N6, 1H, d, 5.67 Hz), 8.15 (N6', 1H, d, 5.69 Hz), 7.97 (N3, 1H, d, 8.04 Hz), 7.82 (N4', N3', 2H, m), 7.76 (N4, 1H, ddd, 7.56, 7.96,

1.49 Hz), 7.63 (P3', 1H, d, 7.11 Hz), 7.59 (P3, 1H, d, 7.69 Hz), 7.28 (N5, 1H, d, 7.54 Hz), 7.26 (V2/6 or V3/5, 2H, m), 7.20 (V2/6 or V3/5, 2H, m), 7.12 (N5', 1H, ddd, 7.26, 7.29, 1.36 Hz), 6.93 (P4, 1H, ddd, 7.73, 7.16, 0.987 Hz), 6.87 (P4', 1H, ddd, 7.95, 6.96, 0.99 Hz), 6.82 (P5, 1H, ddd, 7.51, 7.32, 1.18 Hz), 6.76 (P5', 1H, ddd, 7.49, 7.30, 1.17 Hz), 6.65 (VA, 1H, dd, 17.58, 10.89 Hz), 6.36 (P6, 1H, d, 7.10 Hz), 6.18 (P6', 1H, d, 7.56 Hz), 6.02 (VC, 1H, d, 17.58 Hz), 5.58 (VB, 1H, d, 10.88 Hz) ppm. UV-vis ϵ_{261} 4.00×10^4 , ϵ_{396} 4.44×10^3 L·mol⁻¹cm⁻¹, CV 0.59 V vs. ferrocene (MeCN, 0.1M TBAH)

[Ir(ppy)₂(fppy)], 4

4-(2-Pyridyl)benzaldehyde (fppyH) (1.0 g, 5.5 mmol, F.W. 183.21 g·mol⁻¹), [Ir(ppy)₂Cl]₂ (0.40 g, 0.37 mmol, F.W. 1072.11 g·mol⁻¹, and silver triflate (0.19 g, 0.75 mmol, 256.92 g·mol⁻¹) were all dissolved in 2-ethoxyethanol (25 mL) and heated under nitrogen on an oil bath to 95°C overnight. The deep red solution was cooled and suction filtered through a fritted glass filter to collect a red product mixed with AgCl. Extraction of the mixed solids with CH₂Cl₂ resulted in a deep red solution which was solvent stripped to dryness yielding a dark red powder. Column chromatography on silica gel with CH₂Cl₂ eluted a yellow band of unknown composition. Continued elution with acetone yielded a red band which, upon solvent stripping and drying overnight *in vacuo* yielded [Ir(ppy)₂(fppy)] 4 (0.26 g, 0.38 mmol, 51% yield, F.W. 682.80 g·mol⁻¹).

¹H NMR (CD₂Cl₂, 400 MHz): 9.58 (H_{aldehyde}, s, 1H), 7.93 (d, 1H, 8.1 Hz), 7.84 (d, 2H, 8.2 Hz), 7.71 (d, 1H, 8.1 Hz), 7.6 (m, 6H), 7.47 (m, 2 H), 7.29 (dd, 1H, 8.1 and 1.8 Hz), 7.17 (d, 1H, 1.7 Hz), 6.94 (m, 1H), 6.8 (m, 7H), 6.59 (dd, 1H, 7.6 and 1 Hz). FTIR

$\nu(\text{C}=\text{O})$ 1682 cm^{-1} , UV-Vis $\epsilon_{290} = 3.60 \times 10^4$; $\epsilon_{379} = 7.40 \times 10^3$, CV 0.41 vs. ferrocene (MeCN, 0.1M TBAH)

2-(4-vinylphenyl)pyridine, vppyH

n-Butyllithium (18 mL, 1.5 M solution) was added dropwise through a septum into a flame-dried 3-necked round bottom flask containing a cloudy white suspension of methyl triphenylphosphonium bromide (9.75 g, 27 mmol, F.W. 357.24 $\text{g}\cdot\text{mol}^{-1}$) in diethyl ether (20 mL). The yellow mixture was stirred for 30 minutes. A solution of 4-(2-pyridyl)benzaldehyde (5g, 27 mmol, F.W. 183.21 $\text{g}\cdot\text{mol}^{-1}$) in diethyl ether (20mL) was then added slowly over ten minutes, and the solution was refluxed for 30 minutes under a nitrogen atmosphere. The solution was cooled, gravity filtered, and washed with diethyl ether (150 mL). The filtrate was extracted with distilled water (3×100 mL) and the ether layer was collected and dried over MgSO_4 . Solvent stripping to dryness resulting in a pale yellow oil (1.0 g, 5.5 mmol, 20% yield, F.W. 181.24 $\text{g}\cdot\text{mol}^{-1}$).

^1H NMR (CD_2Cl_2 , 400 MHz): 8.66 (1H, m), 8.00 (2H, d, 8.3 Hz), 7.77 (2H, m), 7.53 (2H, d, 8.5 Hz), 7.23 (1H, m), 6.78 (1H, dd, 17.6 Hz, 10.9 Hz), 5.85 (1H, dd, 17.6 Hz, 0.8 Hz), 5.30 (1H, dd, * Hz, 0.9 Hz) * couldn't be obtained due to overlap with signal due to solvent., FTIR $\nu(\text{C}=\text{C})_{\text{vinyl}}$ 1627 cm^{-1} , MS (EI) $\text{M}^+ = 181$

Alternate preparation of vppyH

Potassium-*tert*-butoxide (21.8 mL, 1.0 M solution in THF) was added dropwise through a septum into a flame-dried Schlenk flask containing a cloudy white suspension of methyl triphenylphosphonium bromide (3.9 g, 10.91 mmol, F.W. 357.24 $\text{g}\cdot\text{mol}^{-1}$) in

diethyl ether (100 mL). The yellow mixture was cooled in an ice/water bath and stirred for 30 minutes. A solution of 4-(2-pyridyl)benzaldehyde (1 g, 5.46 mmol, F.W. 183.21 g·mol⁻¹) in diethyl ether (15 mL) was then added slowly over ten minutes via cannula. The resultant solution was shielded from light, allowed to gradually warm to room temperature, and stirred overnight. Distilled water (50 mL) was added to the solution, and the ether layer was separated and washed three times with aliquots of distilled water (3 × 50 mL). The yellow ether layer was then dried over MgSO₄. Solvent stripping to dryness resulted in a pale yellow oil which was purified by column chromatography on silica gel, eluting with 15% ether in hexanes (0.47 g, 2.6 mmol, 47% yield, F.W. 180.23 g·mol⁻¹). Spectral characteristics were identical to those listed above.

***fac*-[Ir(ppy)₂(vppy)], 5**

2-(4-Vinylphenyl)pyridine (1.0g, 5.5 mmol, F.W. 180.23 g·mol⁻¹), [Ir(ppy)₂Cl]₂ (0.8g, 0.75 mmol, F.W. 1072.11 g·mol⁻¹), and silver triflate (0.38 g, 1.5 mmol, F. W. 256.06 g·mol⁻¹) were all dissolved in 2-ethoxyethanol (15 mL) and heated using an oil bath under nitrogen to 95°C overnight. The deep yellow solution was cooled and gravity filtered to remove the grey AgCl precipitate. The filtrate was solvent-stripped to dryness and was purified by column chromatography (silica gel) using 2:1 hexanes/ diethyl ether as the eluent to remove unreacted vppy. The mobile phase was switched to 1:1 hexanes/ether to elute the bright yellow product band, which was solvent-stripped to dryness to yield [Ir(ppy)₂(vppy)] 5 (0.09 g, 0.13 mmol, 18% yield, F.W. 680.83 g·mol⁻¹).

Elemental analysis as the monohydrate C₃₅H₂₆N₃Ir·H₂O: %Calc'd C 60.15, H 4.04, N 6.01; %Found C 60.56, 4.12, 5.64).

^1H NMR (CD_2Cl_2 , 700 MHz): 7.95 (m, 3H), 7.69 (m, 6H), 7.59 (m, 3H), 7.04 (m, 1H), 6.94 (m, 5H), 6.81 (m, 5H), 6.46 (VA, dd, 1 H, 17.49 and 10.84 Hz), 5.49 (VC, d, 1H, 17.60 Hz), 5.03 (VB, d, 1H, 10.87 Hz). UV-Vis $\epsilon_{287} = 4.24 \times 10^4$; $\epsilon_{290} = 1.13 \times 10^4$ CV 0.31 V vs. ferrocene (CH_2Cl_2 , 0.1M TBAH)

***mer*-[Ir(ppy) $_2$ (vppy)], 5'**

[Ir(ppy) $_2$ Cl] $_2$ (0.5g, 0.47 mmol, F.W. 1072.11 g·mol $^{-1}$), and silver triflate (0.13 g, 0.94 mmol, F. W. 256.06 g·mol $^{-1}$) were dissolved in acetone (40 mL) and refluxed under nitrogen for 2 hours. The cloudy yellow solution was cooled and gravity filtered to remove AgCl. To the filtrate was added vinylpyridine (vppyH) (0.35g, 1.9 mmol, F. W. 180.23 g·mol $^{-1}$) and triethylamine (0.5 mL). The solution was then stirred overnight at room temperature under nitrogen. After solvent-stripping to dryness the dark yellow solid was purified on a short silica gel column, eluting with dichloromethane. The first bright yellow/orange band was collected and solvent-stripped to dryness. The product was recrystallized by slow diffusion of hexanes into a concentrated dichloromethane solution, yielding a golden yellow microcrystalline solid [Ir(ppy) $_2$ (vppy)] 5' (220 mg, 0.33 mmol, 70% yield, F.W. 680.83 g·mol $^{-1}$).

Elemental analysis as the solvate $\text{C}_{35}\text{H}_{26}\text{N}_3\text{Ir} \cdot 0.2(\text{C}_6\text{H}_{14})$: %Calc'd C 62.29, H 4.16, N 6.02; %Found C 62.51, 4.56, 5.48).

^1H NMR (CD_2Cl_2 , 700 MHz): 8.14 (N₆, dd, 1H, 5.86 Hz and 1.59 Hz), 7.98 (N_v3, d, 1H, 8.25 Hz), 7.96 (N_v6, dd, 1H, 5.54 Hz and 1.60 Hz), 7.87 (N₃, N₃', d, 2H, 8.13 Hz), 7.77 (P_v3, d, 1H, 5.56 Hz), 7.75 (P₃, d, 1H, 7.56 Hz), 7.71 (P₃', dd, 1H, 7.89 Hz and 1.31 Hz), 7.68 (N_v4, ddd, 1H, 7.81 Hz, 7.78 Hz and 1.72 Hz), 7.65 (N₆', d, 1H 5.89 Hz),

7.61 (N4, ddd, 1H, 7.78 Hz, 7.76 Hz and 1.63 Hz), 7.57 (N4', ddd, 1H, 7.79 Hz, 7.76 Hz and 1.49 Hz), 7.12 (P_v4, dd, 1H, 8.10 Hz and 1.94 Hz), 7.01 (P4, ddd, 1H, 7.39 Hz, 7.53 Hz and 1.38 Hz), 6.96 (P5, ddd, 1H, 7.19 Hz, 7.21 Hz and 1.23 Hz), 6.94 (N_v5, ddd, 1H, 7.28 Hz, 5.82 Hz and 1.38 Hz), 6.93 (P4', ddd, 1H, 7.43 Hz, 7.31 Hz and 1.54 Hz), 6.91 (P_v6, d, 1H, 1.90 Hz), 6.86 (P5', ddd, 1H, 7.38 Hz, 7.36 Hz and 1.40 Hz), 6.81 (N5', ddd, 1H, 7.40 Hz, 5.99 Hz and 1.41 Hz), 6.80 (N5, ddd, 1H, 7.36 Hz, 5.96 Hz and 1.43 Hz), 6.61 (P6, dd, 1H, 7.20 Hz and 1.36 Hz), 6.51 (V_a, dd, 1H, 17.64 Hz and 10.892 Hz), 6.45 (P6', dd, 1H, 7.64 Hz and 1.21 Hz), 5.52 (V_c, dd, 1H, 17.63 Hz and 1.28 Hz), 5.06 (V_b, dd, 1H, 10.22 Hz and 1.27 Hz). ¹³C NMR (CD₂Cl₂, 176 MHz) 177.76 (P_v1), 175.18 (P1), 170.60 (N2), 168.10 (N_v2), 167.98 (N2'), 159.71 (P1'), 153.59 (N6), 151.61 (N_v6), 148.26 (N6'), 146.02 (P_v2), 145.26 (P2), 142.73 (P2'), 138.34 (VA), 138.22 (P_v5), 137.12 (N_v4), 136.35 (P_v6), 136.20 (N4), 134.78 (N4'), 132.96 (P6), 130.80 (P6'), 130.23 (P5), 129.92 (P5'), 124.84 (P_v3), 124.59 (P3), 124.44 (P3'), 122.83 (N_v5 or N5'), 122.69 (N5), 121.91 (N5' or N_v5), 121.35 (P4), 119.70 (N_v3), 119.51 (P_v4), 119.291 (P4'), 119.18 (N3 or N3'), 118.93 (N3 or N3'), 113.37 (VBC).

UV-Vis $\epsilon_{274} = 4.86 \times 10^4$; $\epsilon_{390} = 7.99 \times 10^3$, CV 0.25 V vs. ferrocene (CH₂Cl₂, 0.1M TBAH)

[Ir(ppy)₂(vacac)], 6

[Ir(ppy)₂Cl]₂ (0.5g, 0.47 mmol, F.W. 1072.11 g·mol⁻¹), and silver triflate (0.13 g, 0.94 mmol, F. W. 256.06 g·mol⁻¹) were dissolved in acetone (40 mL) and refluxed under nitrogen for 2 hours. The cloudy yellow solution was cooled and gravity filtered to remove AgCl. Allylacetoacetate (vacac) (174 μ L, 1.18 mmol, F. W. 142.16 g·mol⁻¹) and triethylamine (0.5 mL) were added to the filtrate. The solution was then stirred

overnight at room temperature under nitrogen. After solvent-stripping to dryness the dark yellow solid was purified on a short silica gel column, eluting with dichloromethane. The first bright yellow band was collected and solvent-stripped to dryness. The product was recrystallized by slow diffusion of hexanes into a concentrated dichloromethane solution, yielding a golden yellow microcrystalline solid $[\text{Ir}(\text{ppy})_2(\text{vacac})]$ **6** (330 mg, 0.514 mmol, 55% yield, F.W. $641.75 \text{ g}\cdot\text{mol}^{-1}$).

Elemental analysis as the semihydrate $\text{C}_{35}\text{H}_{26}\text{N}_3\text{Ir}\cdot 0.5\text{H}_2\text{O}$: %Calc'd C 53.53, H 4.03, N 4.30; %Found C 53.41, 3.83, 4.34).

^1H NMR (d^6 -acetone, 400 MHz): 8.64 (m, 2H), 8.08 (m, 2H), 7.93 (m, 2H), 7.65 (d, 2H, 8 Hz), 7.35 (m, 2H), 6.76 (t, 2H, 7.6 Hz), 6.60 (m, 2H), 6.23 (d, 2H, 7.6 Hz), 5.67 (V_B , m, 1H), 4.98 (V_A , m, 2H), 4.73 (V_2 , s, 1H), 4.25 (V_C , qtd, 2H, 12 Hz, 5.6 Hz, 1.5 Hz), 1.72 (V_1 , s, 3H). UV-Vis $\epsilon_{257} = 4.32 \times 10^4$; $\epsilon_{400} = 3.92 \times 10^3$; FTIR $\nu(\text{C}=\text{O})_{\text{acac}}$ 1605 cm^{-1} ; CV 0.47 vs. ferrocene (MeCN, 0.1M TBAH)

$[\text{Ir}(\text{C6})_2(\text{vacac})]$, **7**

$[\text{Ir}(\text{C6})_2\text{Cl}]_2$ (0.2 g, 0.17 mmol, F.W. $1154.20 \text{ g}\cdot\text{mol}^{-1}$), and silver triflate (0.09 g, 0.35 mmol, F.W. $256.06 \text{ g}\cdot\text{mol}^{-1}$) were dissolved in acetone (40 mL) and refluxed under nitrogen for two hours. The cloudy orange solution was cooled and gravity filtered to remove AgCl. Allylacetoacetate (vacac) (64 μL , 0.43 mmol, F. W. $142.16 \text{ g}\cdot\text{mol}^{-1}$) and triethylamine (0.5 mL) were added to the filtrate. The solution was stirred overnight at room temperature under nitrogen. Solvent-stripping to dryness yielded a deep orange solid which was purified using a short silica gel column, eluting with ether. The first bright orange band was collected and solvent-stripped to dryness. The product was

recrystallized by slow diffusion of hexanes into a concentrated dichloromethane solution, yielding red-orange X-ray quality crystals $[\text{Ir}(\text{C}_6)_2(\text{vacac})]$ **7** (120 mg, 0.12 mmol, 34% yield, F.W. 1032.23 $\text{g}\cdot\text{mol}^{-1}$).

Elemental analysis as the monosolvate $\text{C}_{35}\text{H}_{26}\text{N}_3\text{Ir}\cdot\text{CH}_2\text{Cl}_2$: %Calc'd C 51.61, H 4.06, N 5.02; %Found C 51.94, 4.02, 5.17).

^1H NMR (d^6 -acetone, 400 MHz): 7.98 (t, 2H, 8Hz), 7.58 (d, 1H, 8Hz), 7.46 (d, 1H, 8Hz), 7.23 (m, 4H), 6.19 (t, 2H, 2 Hz), 6.02 (dd, 2H, 9Hz, 2Hz), 5.91 (m, 2H), 5.65 (V_B , m, 1H), 4.97 (V_A , m, 2H), 4.38 (V_C , qtd, 2H, 17 Hz, 5 Hz, 1.5 Hz), 4.28 (V_2 , s, 1H), 3.21 (C6_{ethyl} , dq, 8H, 7 Hz, 2.6 Hz), 1.55 (V_1 , s, 3H), 0.90 (C6_{ethyl} , dt, 12H, 7 Hz, 2.5 Hz). UV-vis $\epsilon_{445} = 7.79 \times 10^4$ $\epsilon_{474} = 8.69 \times 10^4$; FTIR $\nu(\text{C}=\text{O})_{\text{C}_6}$ 1691 cm^{-1} , $\nu(\text{C}=\text{O})_{\text{vacac}}$ 1605 cm^{-1} ; CV 0.69 vs. ferrocene (CH_2Cl_2 , 0.1M TBAH)

$[\text{Ir}(\text{ppy})_2(\text{DMPSEpy})\text{Cl}]$, **8**

Dimethylphenylsilane (50 μL , 0.33 mmol, F.W. 136.27 $\text{g}\cdot\text{mol}^{-1}$) was added to a solution of **1** (100 mg, 0.16 mmol, F.W. 641.19 $\text{g}\cdot\text{mol}^{-1}$) in CH_2Cl_2 (12 mL) with Karstedt's catalyst (20 μL , 2.1% Pt solution in xylenes, ca. 1% relative to vinyl). The resultant solution was refluxed under nitrogen for 24 hours. The product was then slightly concentrated and precipitated into hexanes to remove unreacted silane. The yellow precipitate was collected by vacuum filtration and purified by column chromatography on silica gel using 2:1 hexanes/acetone as the mobile phase, collecting the first yellow band. The eluate was solvent stripped to dryness and the yellow product dried *in vacuo* $[\text{Ir}(\text{ppy})_2(\text{DMPSEpy})\text{Cl}]$ **8** (31 mg, 0.04 mmol, 25% yield, F.W. 777.46 $\text{g}\cdot\text{mol}^{-1}$).

Elemental analysis as the monohydrate $C_{37}H_{35}ClIrN_3Si \cdot H_2O$: %Calc'd C 55.87, H 4.69, N 5.28; %Found C 55.49, H 4.45, N 5.16.

1H NMR (CD_2Cl_2 , 400 MHz): 9.85 (N6, 1H, d, 5.2 Hz), 8.8 (V2,6, 2H, br), 8.10 (N6', 1H, d, 5.1 Hz), 7.92 (N3', 1H, d, 8.3 Hz), 7.78 (N3, 1H, m), 7.74 (N4', 1H, m), 7.72 (N4, 1H, m), 7.60 (P3', 1H, dd, 7.8 Hz), 7.54 (P3, 1H, dd, 7.7 Hz), 7.48 (Si-Ph, 1H, m), 7.34 (Si-Ph, 2H, m), 7.23 (N5, 1H, m), 7.07 (N5', 1H, m), 7.02 (V3,5, 2H, br), 6.88 (P4, 1H, ddd, 7.5 Hz), 6.84 (P4', 1H, ddd, 7.6 Hz), 6.78 (P5, 1H, ddd, 7.4 Hz), 6.72 (P5', 1H, ddd, 7.4 Hz), 6.33 (P6, 1H, d, 7.6 Hz), 6.16 (P6', 1H, d, 7.6 Hz), 2.54 (CH_2CH_2Si , 2H, m), 1.03 (CH_2CH_2Si , 2H, m), 0.26 (Si- CH_3 , 6H, s). ^{29}Si (d_6 -acetone, 80 MHz) -5.8 ppm. UV-vis ϵ_{262} 4.97×10^4 , ϵ_{399} 4.75×10^3 L·mol $^{-1}$ ·cm $^{-1}$.

[Ir(ppy) $_2$] $_2(\mu$ -oxalato) 14

6 (10 mg) was dissolved in 1 mL of d_6 -acetone and placed in an NMR tube. No attempt was made to exclude air from the tube. The tube was left sealed, but unshielded from light, for four weeks. Small, golden crystals of **14** were harvested from the NMR tube for X-ray crystallography. FTIR $\nu(C=O)_{oxalate}$ 1617 cm $^{-1}$.

3.2.2 Synthesis of Polymer Bound Iridium Complexes

i) Attachment of 3 to hydride terminated PDMS, yielding dye-attached polymer 9

A solution of **3** (50 mg, 0.08 mmol, F.W. 641.19 g·mol $^{-1}$) in CH_2Cl_2 (5 mL) was added to a solution of hydride terminated polydimethylsiloxane (PDMS) (4 g, 0.06 mmol,

Mn = 55-70 kDa) in CH_2Cl_2 (10 mL) with Karstedt's catalyst (10 μL , ca. 1% relative to vinyl). The resultant solution was stirred at reflux under nitrogen for 2 days and solvent stripped to dryness. The product was dissolved in a small volume of hexanes and was filtered sequentially through 1.0 μm and 0.45 μm Gelman Acrodiscs™ to remove unreacted complex. A clear, yellow solid was obtained by dropwise addition of the filtered solution to rapidly stirring methanol. Precipitation of concentrated hexanes solutions into methanol were performed two or three times. The supernatant liquors typically appear colourless. When this was not the case, serial precipitations were continued until a colourless supernatant was obtained.

ii) Attachment of 4 to hydride terminated PDMS, yielding dye-attached polymer 10

A solution of 4 (38 mg, 0.056 mmol, F.W. 682.80 $\text{g}\cdot\text{mol}^{-1}$) in CH_2Cl_2 (5 mL) was added to a solution of aminopropyl terminated polydimethylsiloxane (PDMS) (3 g, 0.11 mmol, Mn=27 kDa) in CH_2Cl_2 (10 mL). The resultant solution was stirred at reflux under nitrogen for 2 days and solvent stripped to dryness. The product was dissolved in a small volume of hexanes and was filtered sequentially through 1.0 μm and 0.45 μm Gelman Acrodiscs™ to remove unreacted complex. A clear, red-orange solid was obtained by dropwise addition of the filtered solution to rapidly stirred methanol. Precipitation of concentrated hexanes solutions into methanol were performed three times. The colour of the supernatant liquors were faint red initially and colourless after the final precipitation.

iii) Attachment of 5 to hydride terminated PDMS, yielding dye-attached polymer 11

Preparation of dye-attached polymer 11 based on compound 5 was done in a similar manner as for 9.

iv) Attachment of 6 to hydride terminated PDMS, yielding dye-attached polymer 12

Preparation of dye-attached polymer 12 based on compound 6 was done in a similar manner as for 9.

v) Attachment of 7 to hydride terminated PDMS, yielding dye-attached polymer 13

Preparation of dye-attached polymer 13 based on compound 7 was done in a similar manner as for 9.

3.2.3 Mechanical Mixtures of Iridium Complexes and Polymers**Dissolution/precipitation of dye and PDMS**

A mixture of any dye and hydride- or aminopropyl-terminated PDMS were dissolved in CH_2Cl_2 to form a homogeneous solution which was subsequently solvent stripped to dryness resulting in a cloudy yellowish suspension of complex in polymer. Dissolution of the mixture in hexanes resulted in a cloudy solution which was filtered through a 1.0 μm Gelman Acrodisc™. A clear, colourless siloxane fluid was obtained after solvent-stripping.

3.2.4 Evaluation of 3-8 and 9-13 as Oxygen Sensors

The oxygen sensitivity of the attached and unattached luminophores was compared by evaluating samples of **3-8** (dispersed in PDMS, PS, or a 1:1 PDMS/PS blend) with samples **9-13** (alone or in PS blends). Samples of **3-8** were combined such that the concentration of luminophore by weight of polymer was equal to that in the related attached system. Where blends with polystyrene (or additional PDMS) were made all components were dissolved to make a homogeneous solution in a single solvent before application.

A solution of the sample was applied to an aluminum plate previously covered with a layer of Tristar Starpoxy™ fluid resistant white epoxy primer (DHMS C4.01 Ty3) using a conventional airbrush and compressed nitrogen as the propellant. The painted plate was then mounted in an in-house designed pressure chamber. Pressure was controlled via a Scanivalve Corp model PCC100 Pressure Calibrator/Controller in manual mode, and the temperature of the mounting plate was controlled via a thermoelectric cooler coupled to a model LFI-3551 Temperature Controller using a model TCS650 thermistor in the 10 μ A range, both from Wavelength Electronics. Excitation in the UV was provided by a Hamamatsu Lightningcure™ LC5 200W model L8333 Hg/Xe source via a 10 m $\times$ 8 mm Oriel UV-Vis Liquid Light Guide (transmission window 300-650 nm). The source was equipped with 011FG09 and 300FS40 filters by Melles-Griot, transmitting approximately in the range 280-320 nm. Excitation in the blue was provided by a Photonics Research Systems PRS100B blue LED lamp equipped with a 420-500 nm bandpass filter (03-FIV-28, Melles Griot). Emission was measured with a 512x512 Photometrics CH350 12 bit CCD camera with an appropriate filter: e.g. for 3

and **9** a 500 ± 40 nm bandpass filter (500FS80-50, Melles Griot); for **7** and **13** a 600 ± 40 nm bandpass filter (03-FIB-012, Melles Griot). Measurements were taken at various pressures in the range 0.05-45 psi and at various temperatures in the range 10-30 °C. At each pressure, multiple measurements were taken to ensure the oxygen concentration in the film had come to equilibrium. The time required for equilibration provided a qualitative measure of response time. A second reading was obtained at 15 psi at the end of each experiment to determine whether photodegradation had occurred on the time scale of the experiment. Backgrounds were measured on a section of the primed plate. Spectra were also collected for various calibrations using an Acton Research Corporation Spectrums CCD Detection System consisting of a SpectraPro-150 Imaging Dual Grating Monochromator/Spectrograph with a 16 bit Hamamatsu 1024×256 CCD. The spectral signal was captured using a fiber optic equipped with a 450 nm cutoff filter (Kodak #3 long-pass filter). Excitation for the pulsed-lifetime measurements was provided by the Photonics Research Systems PRS100B blue LED lamp equipped with an Agilent 33120A waveform generator and monitored with a Fluke PM3380A combiscope.

3.3 Results and Discussion Part I: Ir (III) Luminophores

3.3.1 Synthesis of starting materials

Dimers **1** and **2** (see Scheme 3.4) were used as starting materials for all luminophores and were prepared using the methods of Watts and Nonoyama⁵⁸ and Thompson^{54b}.

Scheme 3.4: Synthesis of metal precursors

Ligands were commercially available with the exception of vinyl phenylpyridine (vppyH), which was synthesized via a Wittig reaction using 4-(2-pyridyl)benzaldehyde as shown in Scheme 3.5. Yields in this reaction were noticeably affected by the reaction conditions. When *n*-butyllithium was used as the base, in a ratio of carbonyl to phosphonium salt to base of 1:1:1, the yield was low, only 20%. Changing the base to potassium *t*-butoxide, and having a ratio of carbonyl to phosphonium salt to base of 1:2:4 resulted in more than twice the yield (47%).⁶¹

Scheme 3.5: Wittig reaction for the preparation of vppyH.

Successful synthesis of vppyH was confirmed by ^1H NMR, IR, and mass spectrometry. The ^1H NMR spectrum of vppyH (see Figure 3.5) showed the appropriate chemical shifts and integration for the phenyl and pyridyl protons. The three resonances associated with the three vinyl protons were clearly visible with an expected quartet, doublet, doublet splitting pattern. The infrared spectrum of the ligand was relatively simple, with an absorbance at 1627 cm^{-1} representative of the $\nu(\text{C}=\text{C})_{\text{vinyl}}$. The molecular weight of vppyH was confirmed by the mass spectrum, which exhibited an intense molecular ion peak at 181 m/z .

Figure 3.5: ^1H NMR spectrum (400 MHz) of vppyH in CD_2Cl_2 . Resonances associated with the vinyl group are highlighted.

Figure 3.6: Electron-Impact mass spectrum of vppyH. The molecular ion peak is at 181 m/z .

Figure 3.7: Infrared spectrum (neat) of vppyH. The $\nu(\text{C}=\text{C})$ is shown at 1627 cm^{-1} .

3.3.2 Synthesis and characterization of luminophores

All the luminophore syntheses involved breakage of the dimers **1** or **2** (with or without the use of a silver salt) and the coordination of a ligand capable of attachment to a silicone polymer. Schemes 3.6 and 3.7 outline the luminophore syntheses.

Scheme 3.6: Synthesis of complexes 3, 4, 5, 5', and 6 from dimer 1.

Scheme 3.7: Synthesis of complex 7 from dimer 2.

The first complex prepared was the non-ionic iridium complex **3**, $[\text{Ir}(\text{ppy})_2(\text{vpy})\text{Cl}]$ (vpy = 4-vinylpyridine). This complex was readily synthesized in high yield (70%) by cleaving the iridium dimer **1** with vinylpyridine, which provides the reactive site for the hydrosilation reaction.

Complexes **4** and **5** were both synthesized from **1** in 2-ethoxyethanol at elevated temperatures (95°C), using silver triflate to cleave the chloride bridged dimer.⁶² While acceptable yields were obtained for **4** (51 %), the low yield of **5** (18%) prompted a modification of the reaction conditions. The solvent was changed to acetone and triethylamine was added to help deprotonate the vppyH ligand. These new reaction conditions lead to the synthesis of the novel complex **5'** in good yield (70%). The possibility that **5** and **5'** were analogous to the facial and meridional isomers of $\text{Ir}(\text{ppy})_3$ was explored.

Tris-complexes with asymmetric ligands present the possibility of preparing either facial (*fac*) or meridional (*mer*) isomers. *Mer* and *fac* isomers based on the 2-phenylpyridyl ligand are expected to have markedly different behaviour due to the dissimilarity of the anionic phenyl and neutral pyridyl ligand. To date, there has only been one study of *mer* isomers of d^6 trischelates. In this case, high temperatures (refluxing glycerol ~200°C) were required to synthesize the *fac* isomer, while the *mer* isomer could be prepared using glycerol at 140-145°C.⁶³

The structure of the chloride bridged dimer used to synthesize the complexes has been shown to have the Ir-N bonds trans to one another.⁶⁴ Thus, if a third ligand is to be cyclometalated without causing any isomerization, it should lead to the meridional isomer. This is seen in the synthesis of **5'**, which is carried out at low temperature,

suggesting that this is the kinetically favoured product. The higher reaction temperature used in 2-ethoxyethanol allows for the *fac* isomer, the thermodynamically favoured product, to be formed. The *fac* isomer has all three phenyl ligands on the same face of the molecule, trans to a pyridyl nitrogen. This is likely the more thermodynamically favoured structure due to the strong trans influence of the anionic phenyl ligand. A full comparison of the two isomers is described in the sections on NMR spectroscopy, cyclic voltammetry, and photophysical studies.

6 and **7** were synthesized in a similar fashion from **1** and **2**, respectively. In both cases, silver triflate was used to cleave the iridium dimer, and the vinyl-bearing ligand used was allylacetoacetate (vacac). Acceptable yields were obtained in both cases (55% for **6**, 34% for **7**)

3.3.2.1 NMR spectroscopy

In all cases, successful syntheses of the complexes were monitored by the appearance in the proton NMR spectrum of characteristic resonances for the ligand, i.e. vinyl protons for **3**, **5**, **5'**, **6**, **7**, and an aldehyde proton for **4**. Complexes **3**, **4**, **5**, **5'**, also showed increased complexity in the aromatic region, while **6** and **7** each showed a new methyl resonance as a result of the vacac ligand.

Use of 1-D and 2-D techniques allowed for assignment of each hydrogen of both phenylpyridine ligands and the vinylpyridine ligand on **3**. The following series of experiments were required in order to label the molecule.

Chart 1. Structure of $[\text{Ir}(\text{ppy})_2(\text{vpy})\text{Cl}]$, **3**, indicating the numbering scheme used in assigning the ^1H NMR. All resonances are assigned in the experimental section.

Figure 3.8: ^1H NMR spectrum (700 MHz) of **3** in CD_2Cl_2 . The resonances corresponding to the vinyl moiety are highlighted.

In addition to a standard ^1H NMR experiment (Figure 3.8), COSY (correlated spectroscopy, Figure 3.9) was used to assign groups of neighbouring protons. ^{13}C NMR

(Figure 3.10) in conjunction with DEPT135 (Distortionless enhancement by polarization transfer, Figure 3.11) was used to distinguish quaternary carbons signals (no signal in DEPT), CH carbon signals (pointing upward) and the vinyl CH₂ carbon signal (pointing downward).

Figure 3.9: COSY (700 MHz) of **3** in CD₂Cl₂.

Figure 3.10: ^{13}C NMR spectrum (175 MHz) of **3** in CD_2Cl_2 .

Figure 3.11: DEPT135 (175 MHz) of **3** in CD_2Cl_2 .

Heteronuclear multiple quantum coherence (HMQC, Figure 3.12) displays carbon-hydrogen ^1J correlations and was used to assign carbon-hydrogen pairs. The heteronuclear multiple bond coherence (HMBC, Figure 3.13) experiment displays longer range carbon-hydrogen correlations. This experiment was used along with the COSY results to assign the groups of hydrogens and carbons that make up the individual rings (*i.e.* P, P', N, N', V) and to link the corresponding phenyl and pyridyl groups (*i.e.* P to N, P' to N'). While these experiments allowed for assignment of all the protons, it was not possible to determine which ppy (primed or unprimed) was *trans* to vpy, due to the partial rotation of the vinylpyridine ligand even at lower temperature.

Figure 3.12: HMQC spectrum (700 MHz) of **3** in CD_2Cl_2 .

Figure 3.13: HMBC (700 MHz) of **3** in CD_2Cl_2 .

Of particular interest is the NMR analysis of **5** and **5'**, the facial and meridional isomers of $\text{Ir}(\text{ppy})(\text{vppy})$. The effective C_3 symmetry of the *fac* isomer leads to a simpler ^1H NMR spectrum, while the C_1 symmetry of the *mer* isomer yields a much more complicated pattern. As it was not possible to determine the solid-state structures of these two isomers using X-ray crystallography, a collaboration with researchers at Health Canada was formed to explore whether 2D NMR techniques on their 700 MHz instrument would confirm the identity of the two isomers.

Unfortunately, the spectral overlap present in the *fac* isomer precluded complete NMR analysis. The ^1H and ^{13}C NMR spectra of **5** can be found in Figures 3.14 and 3.15.

Figure 3.14: ^1H NMR spectrum (700 MHz) of 5 in CD_2Cl_2 . The resonances corresponding to the vinyl moiety are highlighted.

Figure 3.15: ^{13}C NMR spectrum (175 MHz) of 5 in CD_2Cl_2 .

The resonances of the *mer* isomer were sufficiently resolved to allow for individual assignment of each proton. This was accomplished in the same manner as was described for the analysis of **3**. Figures 3.16 and 3.17 show the 1-D ^1H and ^{13}C NMR spectra of **5'**. Once again, DEPT135 (Figure 3.18) was used to distinguish between the different types of carbons. COSY (Figure 3.19), TOCSY (total correlated spectroscopy, Figure 3.23), HMQC (Figure 3.20), and HMBC (Figure 3.21) were all employed to assign the groups of carbons and hydrogens that make up the rings and to link the bicyclic systems.

Chart 2. Structure of *mer*-[Ir(ppy)₂(vppy)], **5'**, indicating the numbering scheme used in assigning the ^1H NMR. All resonances are assigned in the experimental section.

Figure 3.16: ^1H NMR spectrum (700 MHz) of **5'** in CD_2Cl_2 . The resonances corresponding to the vinyl moiety are highlighted.

Figure 3.17: ^{13}C NMR spectrum (175 MHz) of **5'** in CD_2Cl_2 .

Figure 3.18: DEPT135 spectrum (700 MHz) of 5' in CD_2Cl_2 .

Figure 3.19: COSY spectrum (700 MHz) of 5' in CD_2Cl_2 .

Figure 3.20: TOCSY spectrum (700 MHz) of **5'** in CD_2Cl_2 .

Figure 3.21: HMQC spectrum (700 MHz) of **5'** in CD_2Cl_2 .

Figure 3.22: HMBC spectrum (700 MHz) of 5' in CD_2Cl_2 .

Once all resonances were assigned, it was then possible to use ROESY experiments (rotating frame overhauser spectroscopy) to determine through space inter-ring interactions. In order for a correlation to exist, the two interacting protons must be within 5 Å of one another.⁶⁵ Using this technique, the following interactions could be established: N6 with P6' and P_v6, P6 with N6' and N_v6. These interactions can only occur in the meridional structure shown in Chart 3, and its mirror image.

Figure 3.23: ROESY spectrum (700 MHz) of 5' in CD_2Cl_2 .

Chart 3: Structure of **5'** based on 2-D NMR analysis. Only hydrogens at the 6 positions are shown. Dashed green and red lines indicate inter-ring correlations.

Now, with confirmation that the complicated splitting pattern in the phenyl and pyridyl region is indicative of a *mer* configuration, inspection of the ^1H NMR of **4**, suggests that this complex is also the less symmetrical *mer* isomer. The phenyl and pyridyl ring regions of the spectrum display similar complexity as is noted in **5'**. As **4** was synthesized using the same reaction conditions as **5** (2-ethoxyethanol at elevated temperatures), it indicates that there may be a larger kinetic barrier to isomerization in this case. All attempts to synthesize the *fac* isomer have as yet been unsuccessful.

Figure 3.24: ^1H NMR spectrum (400 MHz) of **4** in CD_2Cl_2 . The resonances corresponding to the vinyl moiety are highlighted.

The NMR spectra of **6** and **7** are much simpler to interpret and are very similar due to the presence of the vacac ligand. The allyl group (V_A , V_B , V_C ; see Chart 3 and 4) in each case displays three peaks of expected integration and chemical shift (around 4–5.75 ppm). The other vacac protons (V_1 and V_2) are singlets found below 2 ppm and above 4 ppm, respectively, in both **6** and **7**. The phenyl and pyridyl region of **6** is very simple, with the expected 8 resonances for the protons of a single ppy ligand, indicating that the two ppy ligands are magnetically equivalent. Similarly, **7** exhibits the expected 7 resonances for identical C6 ligands, as well as one set of ethyl resonances.

Chart 4. Structure of $[\text{Ir}(\text{ppy})_2(\text{vacac})]$, **6**, indicating the numbering scheme used in assigning the ^1H NMR. Vacac ligand resonances are assigned in the experimental section.

Figure 3.25: ^1H NMR spectrum (400 MHz) of **6** in d_6 -acetone. The resonances corresponding to the allyl moiety are highlighted.

Chart 5. Structure of $[\text{Ir}(\text{C6})_2(\text{vacac})]$, **7**, indicating the numbering scheme used in assigning the ^1H NMR. The second C6 ligand is represented by a semicircle for simplicity. Vacac ligand resonances and the C6 ligand ethyl resonances are assigned in the experimental section.

Figure 3.26: ^1H NMR spectrum (400 MHz) of **7** in d_6 -acetone. The resonances corresponding to the allyl moiety are highlighted.

3.3.2.2 X-ray crystallography

Single crystals of **3** and **7** were grown by diffusion of hexanes into concentrated dichloromethane solutions and their structures were unambiguously confirmed by X-ray crystallography. The ORTEPs of **3**·(CH_3CH_2)₂O and **7**·(CH_2Cl_2) are given as Figures 3.27 and 3.28, respectively. Tables of crystallographic data and selected bond lengths and angles can be found in Tables 3.1-3.4. Complete tables of atomic coordinates, bond lengths and angles for each complex are given in Appendix A.

Figure 3.27. ORTEP of **3**·(CH_3CH_2)₂O with thermal ellipsoids depicted at 30% probability. The diethyl ether molecule of solvation and all hydrogen atoms have been omitted for clarity.

Table 3.1: X-ray Crystallographic Data for $3 \cdot (\text{CH}_3\text{CH}_2)_2\text{O}$.

Empirical formula	$\text{C}_{33}\text{H}_{33}\text{ClIrN}_3\text{O}$
Formula weight	715.27
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	$a = 16.4774(19) \text{ \AA}$ $b = 10.7471(13) \text{ \AA}$ $c = 17.489(2) \text{ \AA}$ $\beta = 113.210(2)^\circ$
Volume	$2846.4(6) \text{ \AA}^3$
Calculated Density	1.669 g/cm^3
Temperature	203(2) K
λ	$0.71073 \text{ \AA}$
R1(Fo2)	0.0354
wR2(Fo2)	0.1099
Z	4
Absorption coefficient	4.816 mm^{-1}

Table 3.2: Selected Bond Lengths ($\text{\AA}$) and Angles (deg.) for $3 \cdot (\text{CH}_3\text{CH}_2)_2\text{O}$. Standard deviations are given in parentheses.

Ir-Cl	2.5045(12)	Cl-Ir-N3	177.94(17)
Ir-C1	2.004(5)	Cl-Ir-C12	177.41(14)
Ir-N1	2.042(4)	Cl-Ir-N1	88.11(11)
Ir-N3	2.203(4)	Cl-Ir-N2	97.04(11)
C28-C29	1.317(8)	Cl-Ir-N3	90.19(12)
N1-Ir-C1	80.29(18)	C25-C28-C29	125.9(6)
N1-Ir-N2	173.27(15)	N1-Ir-C12	93.83(18)

Figure 3.28: Molecular Structure (top) and ORTEP (bottom) of $7 \cdot (\text{CH}_2\text{Cl}_2)$. The dichloromethane molecule of solvation and all hydrogen atoms have been omitted for clarity.

Table 3.3: X-ray Crystallographic Data for $7 \cdot (\text{CH}_2\text{Cl}_2)$.

Empirical formula	$\text{C}_{48}\text{H}_{45}\text{Cl}_2\text{IrN}_4\text{O}_7\text{S}_2$
Formula weight	1117.10
Crystal system	Monoclinic
Space group	$P21/c$
Unit cell dimensions	$a = 14.5249(9) \text{ \AA}$ $b = 17.4530(11) \text{ \AA}$ $c = 22.1208(14) \text{ \AA}$ $\beta = 124.978(10)^\circ$
Volume	$4594.8(5) \text{ \AA}^3$
Calculated Density	1.615 Mg/m^3
Temperature	$173(2) \text{ K}$
λ	$0.71073 \text{ \AA}$
$R1(F_o^2)$	0.0434
$wR2(F_o^2)$	0.1034
Z	4
Absorption coefficient	3.169 mm^{-1}

Table 3.4: Selected Bond Lengths ($\text{\AA}$) and Angles (deg.) for $7 \cdot (\text{CH}_2\text{Cl}_2)$. Standard deviations are given in parentheses.

Ir-C41	1.9912(13)	Ir-O64	2.1404(17)
Ir-C11	1.981(2)	O61-Ir-O64	87.68(6)
Ir-N1	2.0488(14)	N1-Ir-O61	82.74(5)
Ir-N31	2.0386(14)	C41-Ir-O61	172.37(7)
Ir-O61	2.1246(11)	C11-Ir-N1	80.29(7)

In both these structures, the iridium is octahedrally coordinated with the nitrogen atoms of the two cyclometalated ligands *trans* to one another. In $3 \cdot (\text{CH}_3\text{CH}_2)_2\text{O}$, the Ir-N

and Ir-C bond lengths for the ppy ligands are in accord with similar species containing an $[\text{Ir}(\text{ppy})_2]$ fragment.^{54a, 62} The vpy Ir-N bond is considerably longer than the Ir-N bonds for the ppy ligands, as expected since the vpy nitrogen is *trans* to the anionic phenyl ligand and is not part of a metallocycle. The vpy Ir-N bond is slightly longer (by ca. 0.07 Å) than a ppy Ir-N bond length for a nitrogen *trans* to a carbon atom.⁶² The intraligand C-N and C-C bond lengths are all within the normal range. The structure of $7 \cdot (\text{CH}_2\text{Cl}_2)$ shows Ir-O bond lengths (2.1404(17) Å and 2.1246(11) Å) that are longer than the mean Ir-O value of 2.088 Å listed in the Cambridge Crystallographic database, due once again to the strong trans influence of the anionic phenyl groups. This corresponds well with similar cyclometalated Ir(III) acetylacetonate (acac) complexes.^{54a}

In an interesting aside, while attempting to grow X-ray quality crystals of **6** from a solution in d_6 -acetone, golden yellow crystals of the dimer $[\text{Ir}(\text{ppy})_2]_2(\mu\text{-oxalato})$ **14** were isolated (see Figure 3.29 and Tables 3.3-3.4).

Figure 3.29: Molecular Structure of $14 \cdot 0.8$ (*acetone*). All acetone molecules and hydrogen atoms have been omitted for clarity.

Table 3.5: X-ray Crystallographic Data for 14.

Empirical formula	C _{53.15} H _{38.31} Ir ₂ N ₄ O _{6.39}
Formula weight	1219.54
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 9.9708(5) Å b = 13.0403(7) Å c = 19.3556(10) Å α = 103.383(10)° β = 99.003(10)° γ = 98.203(10)°
Volume	2375.9(2) Å ³
Calculated Density	1.705 Mg/m ³
Temperature	173(2) K
λ	0.71073 Å
R1(F _o ²)	0.0420
wR2(F _o ²)	0.1010
Z	2
Absorption coefficient	5.650 mm ⁻¹

Table 3.6: Selected Bond Lengths (Å) and Angles (deg.) for 14. Standard deviations are given in parentheses.

Ir(2)-O(1)	2.2004(18)	Ir(2)-N(3)	2.033(2)
Ir(2)-O(2)	2.1938(16)	Ir(2)-N(4)	2.022(2)
Ir(2)-C(13)	1.989(2)	O(2)-Ir(2)-O(1)	76.32(6)
Ir(2)-C(14)	1.977(3)	C(13)-Ir(2)-N(4)	80.97(10)

Oxalate was not added to the reaction mixture, and the crystals of 14 would not form in any other solvent or if under an argon atmosphere. Our initial assumption was that the oxalate was formed by the reductive coupling of two CO₂ molecules. This reduction has been accomplished electrochemically⁶⁶ and via metal complexation⁶⁷. However, all attempts to repeat this result using carbonate or bicarbonate as the CO₂ source^{67b} were unsuccessful. Since acetone was required for the synthesis of the oxalate dimer, a mechanism where oxidative cleavage takes place on a substrate formed by an aldol condensation between the enolate acac anion and acetone was postulated (see Scheme 3.8).

Scheme 3.8: Aldol condensation between the vacac ligand and acetone.

Once A is formed, dehydration of the aldol could lead to the formation of a double bond that then could react with singlet oxygen to form an unstable dioxetane. As 6 was assumed to be a singlet oxygen photosensitizer, the possibility that it was also a chemical quencher of singlet oxygen is not unreasonable.^{8, 57, 68} Cleavage of the dioxetane could then lead to the formation of a tricarbonyl species (Scheme 3.9).

Scheme 3.9: Dioxetane-based mechanism for the synthesis of the tricarbonyl.

However, singlet oxygen is an electrophilic species, and may not react with the electron deficient double bond formed by the dehydration of the aldol.⁶⁹ Instead, molecular oxygen could be taken up by A to form a hydroperoxide that can then dehydrate to form the tricarbonyl species.⁷⁰

Scheme 3.10: Hydroperoxide-based mechanism for the synthesis of the tricarbonyl.

In any case, the tricarbonyl species can be easily hydrated to the *geminal*-diol and further hydrolysis can form the aldehyde ester.⁷⁰ Hydrolysis of allyl ester and air oxidation of the aldehyde gives the oxalate molecule (Scheme 3.11).

Scheme 3.11: Cleavage of the tricarboxyl and formation of the oxalate ligand.

No matter which mechanism is invoked, the formation of **14** is indicative that **6** (and possibly **7**, as it is based on the same vacac ligand) is subject to decomposition and may be a quencher of singlet oxygen. This may have implications in sensor photostability.

3.3.2.3 Infrared spectroscopy

The infrared spectra of complexes **3-7** are shown in Figures 3.30-3.35. Infrared spectroscopy is of limited use for the characterization of these complexes, as the $\nu(\text{C}=\text{C})_{\text{vinyl}}$ stretch is generally weak if observed at all⁷¹, and is potentially masked by the more intense $\nu(\text{C}=\text{C})_{\text{phenyl}}$. In **4**, the presence of an $\nu(\text{C}=\text{O})_{\text{aldehyde}}$ stretch at 1682 cm^{-1} is further evidence of the successful synthesis of the complex. Also, in **6** and **7**, the $\nu(\text{C}=\text{O})_{\text{vacac}}$ is seen at 1605 cm^{-1} .

Figure 3.30: Infrared spectrum (KBr pellet) of 3.

Figure 3.31: Infrared spectrum (KBr pellet) of 4. The $\nu(\text{C}=\text{O})$ at 1682 cm^{-1} is highlighted.

Figure 3.32: Infrared spectrum (KBr pellet) of 5.

Figure 3.33: Infrared spectrum (KBr pellet) of 5'.

Figure 3.34: Infrared spectrum (KBr pellet) of 6.

Figure 3.35: Infrared spectrum (KBr pellet) of 7.

3.3.2.4 Cyclic voltammetry

All complexes showed quasi-reversible oxidations in acetonitrile or dichloromethane (see Figure 3.36, for example, and Table 3.7) that range from 0.25 to 0.69 vs. the ferrocene/ferrocenium redox couple, in agreement with literature data.^{54a, 54b,}

⁶³ Oxidation of Ir(III) cyclometalated compounds tend to be reversible when iridium centred, while oxidation of HOMOs with considerable σ -bond orbital contributions are irreversible.⁷² Thus, these oxidations are assigned to the iridium (IV/III) couple. The trend in the electrochemistry data corresponds well with the emission data for the complexes with predominantly MLCT based emission (3-6) (see section on solution electronic spectroscopy).

Mer-Ir(III) tris-cyclometalates have been shown to be easier to oxidize than their facial analogues by 50-100 mV.⁶³ The electrochemistry of **5** and **5'** (Figure 3.36) concur with these findings with a 60 mV difference in Ir(IV/III) couples. A possible explanation for this difference in electrochemistry is suggested to be due to the difference in ligand field strength of the two isomers. In the *mer* isomer, the two anionic phenyl ligands are *trans* to one another. This can lead to a lengthening of the Ir-C bonds, destabilizing the HOMO, allowing for more facile oxidation of the metal centre.

Table 3.7: CV data for complexes 3-7

Complex	$E_{1/2}$ (V) (vs. Fc/Fc^+)	ΔE_p (mV)
$\text{Ir}(\text{ppy})_2(\text{vpy})\text{Cl}$ 3	0.59 ^a	60
$\text{Ir}(\text{ppy})_2(\text{fppy})$ 4	0.41 ^a	60
<i>fac</i> - $\text{Ir}(\text{ppy})_2(\text{vppy})$ 5	0.31 ^b	75
<i>mer</i> - $\text{Ir}(\text{ppy})_2(\text{vppy})$ 5'	0.25 ^b	75
$\text{Ir}(\text{ppy})_2(\text{vacac})$ 6	0.47 ^a	60
$\text{Ir}(\text{C6})_2(\text{vacac})$ 7	0.69 ^a	150

^a in acetonitrile (0.1M TBAH) ^b in CH_2Cl_2 (0.1M TBAH)

Figure 3.36 Cyclic voltammogram of **5'** (A) and **5** (B) in CH_2Cl_2 (0.1 M TBAH) using Pt working and counter electrodes, a silver wire pseudo-reference (ferrocene internal reference) at 100 mV/s scan rate.

3.3.2.5 Electronic Spectroscopy

All spectroscopic data have been placed in Table 3.8, and spectra are given in Figures 3.37-3.42. The absorption spectra of **3-6** were assigned by analogy to similar phenylpyridine-based complexes,^{54a, 54b, 58a, 62} and show intense spin-allowed phenyl- and pyridyl-based π - π^* bands from 260-290 nm with metal-to-ligand (MLCT) transitions from 380-474 nm. The MLCT transitions consist of the spin-allowed 1 MLCT at higher energies and the formally spin forbidden 3 MLCT at lower energies. The extinction coefficients for the two are comparable in all cases, since the 3 MLCT can 'steal' intensity from the 1 MLCT through spin-orbit coupling induced by the heavy iridium centre. Comparison of the absorption spectra of the facial and meridional isomers **5** and **5'** reveals several differences. The π - π^* absorbance in **5** is less intense than in **5'** and shows a more pronounced shoulder at lower energy. The MLCT band envelope of **5** is also more sharply defined. These differences mirror those seen in the literature for Ir(III) *fac* and *mer* isomers.⁶³ The absorbance spectrum of complex **7** is considerably different from the other complexes. The spectrum is characterized by two intense ligand-based absorbances in the blue region.

Solution emission spectra of **3-7** show λ_{max} in the green from 506-570nm. The trend in emission energy for complexes **3-6** resembles the trend in redox potentials: the higher the redox potential, the higher the emission energy. This suggests the emissive state in these complexes has a large contribution of MLCT character, a reasonable assumption since the emissive states of similar Ir(III) complexes tend to be chiefly MLCT based.^{62, 73} Emission bands from predominantly $^3(\pi$ - $\pi^*)$ ligand-based excited

states show more structured emission with vibronic features, while emission from purely MLCT states tend to be broad and unstructured.⁶² The emission spectra of **3** and **6** are very broad and lack any noticeable structure, thus are assigned to predominantly MLCT based emission. Complexes **4**, **5**, and **5'** show more structured emission, thus may have some ligand contribution to the emissive state. This is especially seen in the case of **5**, whose emission profile is markedly different from Ir(ppy)₃.^{49b} The vinyl-group in vinylphenylpyridine leads to greater conjugation in this ligand, thus its ³(π - π^*) excited state should be at slightly lower energy than in the phenylpyridine system, and may contribute to emissive state. This explanation is supported by the effect of attachment on the solution emission spectrum of **11** (**5** attached to PDMS), however, thin film emission data suggest that the changes in the emission profile may be a result of aggregation (see section 3.4.4.2). The emission spectrum of the *mer* isomer **5'** is less structured than that of **5**, and its highest energy feature is red-shifted.

The emissive state of complex **7** is C6 ligand-based. The C6 ligand is a fluorescent laser dye that emits green fluorescence with high efficiencies at room temperature and shows no noticeable phosphorescence. By cyclometalating C6 with Ir to produce complex **7**, the emission energy shifts from 500 nm for the free dye to 568. Intersystem crossing into the triplet levels of the ligand, assisted by the presence of the heavy iridium centre, can lead to ligand based phosphorescence. A similar energy red-shift is seen in other C6 complexes.^{54b}

Table 3.8: Solution absorption and emission data for complexes 3-7

	3	4	5	5'	6	7
$\lambda_{\max}$ $\pi-\pi^*$ ^a (ϵ) ^b	261 ^g (4.00×10^4)	290 ^e (3.60×10^4)	287 ^f (4.24×10^4)	274 ^g (4.86×10^4)	257 ^g (4.32×10^4)	445 ^g (7.79×10^4), 474 ^g (8.69×10^4)
$\lambda_{\max}$ MLCT (ϵ)	396 ^g (4.44×10^3) 442 ^g (2.01×10^3)	379 ^e (7.40×10^3) ^d 454 ^e (2.60×10^3)	384 ^f (1.13×10^4) 440 ^f (3.90×10^3)	390 ^g (7.99×10^3) 445 ^g (3.86×10^3)	400 ^g (3.92×10^3) 448 ^g (2.76×10^3)	
$\lambda_{\max}$ Emission	506 ^f	510 ^e	514 ^e 542 ^e	535 ^g	520 ^f	568 ^g
$\lambda_{\max}$ Emission ^c		540 ^e	580 ^e	572 ^e		613 ^g

^a wavelengths in nm ^b ϵ has units of $\text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ ^c low-energy shoulder ^d broad ^e in toluene ^f in acetonitrile ^g in dichloromethane.

Figure 3.37: Electronic absorption spectrum in dichloromethane (left) and emission spectrum (uncorrected) in acetonitrile (right) of 3.

Figure 3.38: Electronic absorption spectrum in toluene (left) and emission spectrum (uncorrected) in toluene (right) of 4.

Figure 3.39: Electronic absorption spectrum in acetonitrile (left) and emission spectrum (uncorrected) in toluene (right) of 5.

Figure 3.40: Electronic absorption spectrum in dichloromethane (left) and emission spectrum (uncorrected) in toluene (right) of 5'.

Figure 3.41: Electronic absorption spectrum in dichloromethane (left) and emission spectrum (uncorrected) in acetonitrile (right) of 6.

Figure 3.42: Electronic absorption spectrum in dichloromethane (left) and emission spectrum (uncorrected) in dichloromethane (right) of 7.

Table 3.9 lists luminescence lifetimes and quantum efficiencies for complexes 3-7. Owing to the extremely low luminescence intensity of 3, deconvolution of the decay profile was difficult, and the lifetime given in Table 3.9 for this complex must be considered approximate. Based on the lifetime and quantum yield, complexes 4, 5, and 7 are the most promising luminophore candidates. As expected, the meridional isomer 5' has a shorter luminescence lifetime and a lower quantum yield compared to its facial analogue 5. The poorer photophysical properties of 5' could be partially attributed to higher non-radiative rate constants caused by dissociation of the Ir-C bond in the excited

state.⁶³ Despite the fact that **4** is considered to be the *mer* isomer, based on NMR evidence, its long luminescence lifetime and acceptable quantum efficiency make it a good luminophore candidate. Judging by the improvement in the photophysical properties of **5** over **5'**, the facial isomer of **4** would in all likelihood be an ideal luminophore. While **5** possesses a high quantum efficiency and long lifetime compared to the other phenylpyridine based complexes in this study, its photophysical properties are less ideal compared to those of Ir(ppy)₃. Excited state reactions of the vinyl group are possibly responsible for an increase in non-radiative decay. Compound **7** has not only the longest lifetime and highest quantum efficiency of all complexes, it also enjoys the added advantages of a sizeable Stokes shift (3500 cm⁻¹) and intense absorption in the visible which should allow for efficient excitation at longer wavelengths.

Table 3.9: Photophysical data (lifetime and quantum yield in toluene) for complexes **3-7**

	3	4	5	5'	6	7
$\tau(\mu\text{S})$ 298K	0.06 ^a	0.9	0.4	0.2	0.1	6.0
ϕ	0.06	0.05	0.2	0.03	0.02	0.22

^a approximate (see text)

3.3.3 Summary of Part I: Ir(III) Luminophores

A series of luminescent cyclometalated Ir(III) complexes with suitable pendent ligands for polymer attachment has been synthesized and characterized spectroscopically (absorption and emission, NMR, and IR), electrochemically (cyclic voltammetry) and by

X-ray crystallography. On the basis of the photophysical properties of the luminophores in solution, sensors based on complexes **4**, **5**, and **7** are the most promising candidates for PSP studies.

3.4 Result and Discussion Part II: Polymer-bound Ir(III) Luminophores

3.4.1 Model complex synthesis and characterization:

Proof of the feasibility of the hydrosilation reaction was first achieved by the synthesis of a model complex **8** via the reaction of **3** with dimethylphenylsilane (see Scheme 3.12).

Scheme 3.12: Hydrosilation of **3** with dimethylphenylsilane to form the model **8**.

Complex **8** provides an opportunity to spectroscopically probe the effects of hydrosilation on the properties of the luminophore. Complex **8** exhibits a single resonance in the ²⁹Si NMR at −5.8 ppm (Figure 3.44), as well as an absence of vinyl resonances in its ¹H NMR spectrum (Figure 3.43), suggesting the successful formation of the anticipated Si-C bond from reaction of the vinyl and Si-H moieties.

Figure 3.43: ^1H NMR of **8** in CD_2Cl_2 . Two new CH_2 resonances and the loss of the vinyl resonances as a result of the hydrosilation reaction are highlighted.

Figure 3.44: ^{29}Si NMR of **8** in d_6 -acetone referenced to TMS.

The electronic spectrum of **8** (see Figure 3.45) is very similar to that of **3**, with one exception. The molar absorptivity of the π - π^* transition in **8** is significantly larger than in **3**. A similar increase in intensity of this π - π^* transition can be effected by the addition of dilute HCl to a solution of **3**, presumably due to acid hydrolysis of the double bond. The loss of the vinyl group and consequently reduced conjugation of the monodentate pyridyl ligand results in a simplification of electronic transitions, which could explain the decrease in bandwidth and increase in intensity.

Figure 3.45: Electronic absorption spectrum in CH_2Cl_2 (left) and emission spectrum (uncorrected) in acetonitrile (right) of **8**.

The emission spectrum of **8** (also shown in Figure 3.45) shows a maximum at 509 nm and a low-energy shoulder at 537 nm, which is more defined than the emission of **3** (see Figure 3.37). The photophysical properties of the luminophore also change upon reaction with the silane. The luminescence lifetime of **8** in solution is 430 ns and its quantum efficiency is 0.07, noticeably larger than those found for **3** in solution. If

excited state reactions involving the vinyl group are responsible for non-radiative decay in **3**, the reaction with the silane moiety to yield a saturated linker may justify the improved properties.

3.4.2 PDMS-bound luminophore synthesis and characterization

The successful synthesis of the model complex **8** suggested that hydrosilation would be an effective method for preparing polymer bound iridium luminophores. Thus, the reactions of complexes **3**, **5**, **6**, and **7** with hydride-terminated PDMS ($M_n = 55$ -70 kDa) were attempted, resulting in luminophore-end-functionalized polymers, **9**, **11**, **12**, and **13**. Scheme 3.13 illustrates the hydrosilation reactions to yield **9**, **11**, **12**, and **13**.

Scheme 3.13: Attachment reactions for the various polymer-bound luminophores.

Attachment yields were calculated using the electronic spectrum of the luminophore-functionalized polymer. To illustrate, **9** is used as an example. If **9** is treated as a solution of **3** in PDMS, the maximum concentration range at complete luminophore loading is 35.3 – 27.7 mM (23000 - 18000 ppm). The actual concentration of attached luminophore was assessed spectroscopically using the molar absorptivity of the π - π^* transition of **8** to model the attached luminophore. **9** was found to be 3.6 mM (2400 ppm) in luminophore. From the reaction stoichiometry, 100% attachment would have resulted in a luminophore concentration of 18.9 mM (12500 ppm). The hydrosilation reaction yield is therefore approximately 19%. Attachment yields for the other hydrosilation reactions are listed in Table 3.10.

Table 3.10: Hydrosilation attachment yields

Complex / Luminophore- functionalized polymer	Luminophore concentration (ppm; mmol)	Maximum Luminophore concentration (mmol)	Attachment yield (%)
3 / 9	2400; 3.6	18.9	19
5 / 11	4700; 4.4	17.7	25
6 / 12	1900; 2.7	18.9	14
7 / 13	2300; 3.5	11.7	30

Yields for the attachments were low, ranging from 14 to 30%, however all reactions generated intensely yellow-coloured polymers. In an attempt to explore other attachment reactions, complex **4** was reacted with aminopropyl terminated PDMS (25-30 kDa) to prepare **10** as illustrated in Scheme 3.14. As described in the introduction, an imine linker is readily formed between aldehyde and amino functional groups, without need for a catalyst or extreme reaction conditions.

Scheme 3.14: Attachment of **4** to aminopropyl-terminated PDMS via an imine linker to form **10**.

Attachment yield for this reaction was calculated in the same manner as described for the hydrosilation reactions. **10** was found to be 12000 ppm or 17 mM in **4** and the overall yield was 94%, a large improvement over the hydrosilation reaction. In this case, the resultant polymer was deep orange in colour. Because of the lower molecular weight of this polymer (avg. 27 kDa), the maximum attachment possible is 78 mM.

3.4.2.1 Proof of attachment

Due to the low attachment yields for these systems, NMR spectroscopy could not be used to probe the attached luminophore directly. Luminophore attachment was, however, evident by the different behaviour of the polymer bound systems relative to dispersions of the luminophores in PDMS. For example, while PDMS and the PDMS-bound systems are both soluble in hexanes, the dyes themselves are not. Samples of **9-13** can thus be wholly dissolved in hexanes, whereas with dispersions of **3-8** in PDMS (prepared by solvent stripping a dichloromethane solution of the two components to dryness) only the polymer dissolves, leaving behind a suspension of the luminophore.

IR spectroscopy was also found to be an effective tool to prove luminophore attachment in **10**, due in part to its high luminophore loading. The $\nu(\text{C}=\text{O})$ band at 1690 cm^{-1} is strong in the unattached complex **4**, while reaction with the amino-terminated PDMS would result in a red-shifted and weaker $\nu(\text{C}=\text{N})$, which would potentially be masked by the pyridine $\nu(\text{C}=\text{N})$. The IR spectrum of PDMS was subtracted from the spectrum of **10** and that of **4** dispersed in the PDMS. The IR spectrum of **10** revealed a loss of the $\nu(\text{C}=\text{O})$, with preservation of the other absorbances at 1601, 1582, 1560, and

1471 cm^{-1} assigned to phenyl and pyridyl $\nu(\text{C}=\text{C})$ and $\nu(\text{C}=\text{N})$. In contrast, the IR spectrum of the **4** in PDMS showed conservation of the $\nu(\text{C}=\text{O})$. See Figure 3.46.

Figure 3.46: Infrared spectra of **4** dispersed in PDMS (top-black) and **10** (bottom-red) indicating the absence of the $\nu(\text{C}=\text{O})$ in the attached sample.

Other evidence of successful attachment is discussed below in the sections on electronic spectroscopy and oxygen sensitivity.

3.4.2.2 Electronic spectra and Photophysical Data

Absorption spectra of **9-13** were all very similar to the unattached complexes, and the λ_{max} values are listed in Table 3.11.

Table 3.11: Electronic solution absorption (dichloromethane) and emission (toluene) data for **8** to **13**

	8	9	10	11	12	13
$\lambda_{\max} \pi\text{-}\pi^*{}^a$ (ϵ) ^b	262 (4.97×10^4)	265	290	290	260	445 474
$\lambda_{\max}$ MLCT (ϵ)	399 (4.75×10^3)	396	380 455	385 440	400 450	
$\lambda_{\max}$ Emission	509	509	513 546	510	518	567
$\lambda_{\max}$ Emission ^c	537	537		540		611

^a Wavelengths in nm ^b ϵ has units of $\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ^c low-energy shoulder

Emission spectra of the polymer systems did show perceptible differences from the unattached systems. The spectra are shown in Figure 3.47-3.51 and the $\lambda_{\max}$ values are listed in Table 3.11.

The solution emission spectrum of **9** (Figure 3.47) and the model complex **8** (Figure 3.44) exhibit identical bandshapes and energy. The emission spectra of **10** and **11** are quite dramatically different from those of **4** and **5**. The solution emission of **10** bears a remarkable resemblance to that of **5** (Figure 3.39). A possible explanation for this is that the C=N linker is more energy matched with the conjugation of the phenylpyridine ligand than was the carbonyl, making **10** more similar to **5** in terms of the ligand energy. As a result, **10** has a greater ligand-based contribution to its emissive state. The solution emission of complex **11**, in contrast, is now more similar to $\text{Ir}(\text{ppy})_3$, perhaps as a result of the loss of conjugation. Spectra of **12** and **13** are virtually unchanged from those of **6** and **7**, evidence that the vacac ligand offers little or no contribution to the emissive state.

Figure 3.47: Solution emission (toluene; uncorrected) spectra of **9**.

Figure 3.48: Solution emission spectrum (uncorrected; toluene) of **10**.

Figure 3.49: Solution emission spectrum (toluene; uncorrected) of 11.

Figure 3.50: Solution emission spectrum (uncorrected; toluene) of 12.

Figure 3.51: Solution emission spectrum (uncorrected; toluene) of **13**.

Table 3.12: Photophysical data for **8** to **13**

	8^a	9^b	10^b	11^b	12^b	13^b
τ (μ s)	0.43	0.20	0.09, 0.70 ^c	1.0	0.2	8.0
ϕ	0.07	0.32	0.05	0.5	0.03	0.2

^a in acetonitrile ^b in toluene ^c fitted to two exponentials

The luminescence lifetimes along with quantum yields for all dye-attached systems (**8-13**) can be found in Table 3.12. All systems with the exception of **10** exhibit longer lifetimes and similar or improved quantum efficiencies in comparison with the free luminophores. Improved photophysical properties upon attachment may arise from a reduction in the luminophore's freedom of movement, or from a decrease in non-radiative decay through excited state reactions with the pendent functional groups.

The emission spectra of thin films of the polymer-bound luminophores **9-13** and dispersions of the free dyes **3-8** are very dependent on the film composition. Figures 3.52-3.54 are illustrative of this point. As with the solution spectra, the thin film emission bandshape of **9** is similar to that of **8**, and very different from that of **3**. When PS is used as a blend polymer to rigidify the thin films (PS was chosen based on its commercial availability and low cost), changes occur in both band shape and energy, resulting in similar emission profiles for all three species. The emission bandshapes of **3** (Figure 3.52) suggest that the luminophore partitions into the PS phase when a 1:1 PDMS/PS blend is used as the matrix. In PDMS, the emission spectrum is broad and featureless whereas in PS it exhibits a distinct low energy shoulder. When dispersed in a 1:1 PDMS/PS blend, the emission profile is identical to that of **3** in PS, with no broadening or shifting to lower energy, which would be expected if a significant proportion of the luminophore was in the PDMS phase. The emission spectra of thin films of **8** dispersed in PDMS, PS, and a 1:1 PDMS/PS blend similarly indicate partitioning of the luminophore into the PS phase (see Figure 3.53). A similar, but slightly less extensive change can be observed in the spectra of **9** and its PS blends (Figure 3.54). The spectral narrowing and changes in bandshape that occur in the presence of PS can be attributed to different luminophore solvation microenvironments in PS relative to PDMS, and may also be due in part to solvent viscosity effects that have been noted for the $^3\text{MLCT}$ emissions of similar species.⁶²

Figure 3.52. Thin film emission spectra **3** dispersed in PDMS (blue line), 1:1 PDMS/PS (black line), and PS (red line). The spectra have been rescaled to fit the picture, and no significance should be given to the relative spectral intensities.

Figure 3.53. Thin film emission spectra **8** dispersed in PDMS (blue line), 1:1 PDMS/PS (black line), and PS (red line). The spectra have been rescaled to fit the picture, and no significance should be given to the relative spectral intensities.

Figure 3.54. Thin film emission spectra of **9** (blue line), 1:1 **9**/PS (black line), and 1:9 **9**/PS (red line). The spectra have been rescaled to fit the picture, and no significance should be given to the relative spectral intensities.

The effect of the matrix on the emission spectra of **3**, **8**, and **9** is representative of what is seen with the other systems. All luminophores exhibit some change in emission bandshape and/or energy depending on the surrounding environment. The emission spectrum of compound **4** exhibits a red-shift in energy with no change in bandshape when PS is blended with the PDMS film (Figure 3.55). When **10** is blended with PS, a blue-

shift in energy is noted (Figure 3.56). Both **4** and **10**, however, prefer to be solvated by the less oxygen permeable PS environment, as can be seen by the similarity of the 1:1 PS and pure PS (or 1:9 PS) emission spectra. Compounds **6** and **12**, as well as **7** and **13**, (Figures 3.57-3.60) also show evidence of preferential solvation within the PS environment. In all cases, the aromatic ligands surrounding the iridium centre in these luminophores may lead to increased solubility in the unsaturated PS environment relative to the saturated siloxane polymer.

Figure 3.55. Thin film emission spectra **4** dispersed in PDMS (blue line), 1:1 PDMS/PS (black line), and PS (red line). The spectra have been rescaled to fit the picture, and no significance should be given to the relative spectral intensities.

Figure 3.56. Thin film emission spectra of 10 (blue line), 1:1 10/PS (black line), and 1:9 10/PS (red line). The spectra have been rescaled to fit the picture, and no significance should be given to the relative spectral intensities.

Figure 3.57. Thin film emission spectra **6** dispersed in PDMS (blue line), 1:1 PDMS/PS (black line), and PS (red line). The spectra have been rescaled to fit the picture, and no significance should be given to the relative spectral intensities.

Figure 3.58. Thin film emission spectra of 12 (blue line), 1:1 12/PS (black line), and 1:9 12/PS (red line). The spectra have been rescaled to fit the picture, and no significance should be given to the relative spectral intensities.

Figure 3.59. Thin film emission spectra 7 dispersed in PDMS (blue line), 1:1 PDMS/PS (black line), and PS (red line). The spectra have been rescaled to fit the picture, and no significance should be given to the relative spectral intensities.

Figure 3.60. Thin film emission spectra of **13** (blue line), 1:1 **13**/PS (black line), and 1:9 **13**/PS (red line). The spectra have been rescaled to fit the picture, and no significance should be given to the relative spectral intensities.

Figure 3.61 shows the dramatic effect that matrix has on the thin film emission spectra of dispersions of **5**. Once again, a preference for solvation by the PS environment is revealed. In thin films of compound **11** (Figure 3.62), with or without PS, emission bandshape and energy is largely unchanged. Dilution of **11** with additional PDMS,

however, yielded an emission spectrum more resembling that of **11** in solution. This is perhaps evidence of aggregation within the film.

Figure 3.61. Thin film emission spectra **5** dispersed in PDMS (blue line), 1:1 PDMS/PS (black line), and PS (red line). The spectra have been rescaled to fit the picture, and no significance should be given to the relative spectral intensities.

Figure 3.62. Thin film emission spectra of 11 (blue line), 1:1 11/PS (black line), 1:9 11/PS (red line), and 1:9 11/PDMS (green line). The spectra have been rescaled to fit the picture, and no significance should be given to the relative spectral intensities.

The tendency for these luminophores to partition within the less oxygen permeable PS phase will have implications on sensor properties such as oxygen sensitivity and response time. These findings confirm the need for covalent attachment to ensure that the dye remains in close proximity to the oxygen permeable PDMS environment. Further corroboration of the advantage of covalent attachment is found in the next section on oxygen sensitivity (3.4.2.3).

3.4.2.3 Oxygen Sensitivity

Quenching sensitivity (Q_S) data were obtained from CCD experiments and have been placed in Tables 3.13-3.17. Where curvature in the Stern-Volmer plots did not allow an acceptable linear fit ($r^2 > 0.98$) to the data, Q_S values were obtained within constrained pressure ranges that did give linear data fits. Q_S values calculated from spectral band maxima are listed in the captions of figures showing spectral response to changes in pressure. Stern-Volmer plots using the intensity of the spectral band maxima tend to give higher Q_S values than the CCD data, as the CCD data are believed to slightly under represent oxygen sensitivity due to the presence of scattered light from the excitation source that could not be completely blocked by the camera's filters.

i) Sensors 3, 8, and 9/ Sensors 6 and 12

Oxygen sensitivity of **9** was measured on thin films of **9** itself as well as on films of **9** blended with PS in both 1:1 and 1:9 ratios. These data were compared with

measurements on **3** and **8** dispersed in PDMS, in PS, and in a 1:1 PDMS/PS blend. Figures 3.63-3.67 show the effect of pressure on the emission spectra of **3** and **9** in different matrices. The dispersed systems (Figures 3.63-3.65) show very little sensitivity to changes in air pressure. In the attached systems (Figures 3.66-3.67) it is clear that the sensitivity of emission intensity to oxygen is greatest at low pressures. This is more quantitatively represented by the Stern-Volmer plots found in Figure 3.68. The oxygen quenching data in Table 3.13 support the luminophore partitioning suggested by the electronic spectra.

Table 3.13 - Oxygen Sensitivity CCD Data for **3, **8**, and **9****

Sensor	Matrix/Blend	Q_s (r^2)
3	in PDMS ^f	0.117 ^b ; 0.031 ^e (0.990)
	in 1:1 PDMS/PS ^f	0.067 ^a (0.990)
	in PS ^f	0.08 (0.990)
8	in PDMS ^g	0.033 ^a (0.993)
	in 1:1 PDMS/PS ^g	0.168 ^a (0.993)
	in PS ^g	0.136 ^a (0.9997)
9	no blend ^f	0.634 ^b ; 0.155 ^c (0.995); 0.08 ^d (0.998)
	1:1 with PS ^f	0.561 ^b ; 0.120 ^e (0.990)
	1:9 with PS ^f	0.587 ^b ; 0.152 ^e (0.990)

^a0.05-45 psi; ^b0.05-5 psi; ^c10-20 psi; ^d25-45 psi; ^e10-45 psi; ^fvery stable (0-0.5% decomposition/hour illuminated); ^gmoderately stable (0.5-1% decomposition/hour illuminated); ^hunstable (>1% decomposition/hour illuminated)

Figure 3.63. Spectra of a thin film of **3** in PDMS showing the loss of intensity with increasing total air pressure. Spectra were taken at 5 psi increments over the range 0.05 – 45 psi and have been corrected for background. Q_S from band maxima are 0.08 ($r^2 = 0.96$) in the range 10 – 45 psi.

Figure 3.64. Spectra of a thin film of **3** in 1:1 PDMS/PS showing the loss of intensity with increasing total air pressure. Spectra were taken at 5 psi increments over the range 0.05 – 45 psi and have been corrected for background. Q_S from band maxima are 0.08 ($r^2 = 0.99$) in the range 10 – 45 psi.

Figure 3.65. Spectra of a thin film of **3** in PS showing the loss of intensity with increasing total air pressure. Spectra were taken at 5 psi increments over the range 0.05 – 45 psi and have been corrected for background. Q_s from band maxima are 0.09 ($r^2 = 0.98$) in the range 10 – 45 psi.

Figure 3.66. Spectra of a thin film of **9** showing the loss of intensity with increasing total air pressure. Spectra were taken at 5 psi increments over the range 0.05 – 45 psi and have been corrected for background. Q_s from band maxima are 0.578 (0-5 psi); 0.145 (10-20 psi, $r^2 = 0.98$); 0.06 (25-45 psi, $r^2 = 0.998$).

Figure 3.767. Spectra of a thin film of 1:9 9/PS showing the loss of intensity with increasing total air pressure. Spectra were taken at 5 psi increments over the range 0.05 – 45 psi and have been corrected for background. Q_s from band maxima are 0.556 (0 – 5 psi) and 0.187 ($r^2 = 0.9938$) in the range 10 – 45 psi.

As shown in the Stern-Volmer analysis in Figure 3.68, the quenching sensitivity of a thin film of **9** is greater than the sensitivity of dispersions of **3** or **8** in PDMS. In light of the lifetime data, the greater sensitivity of **9** may be ascribed to a decreased tendency for the luminophore to aggregate within this material. The Ir complex in **9** has, by virtue of its being bound to a long PDMS chain, greatly reduced mobility. This inability of the luminophore to move independently of the polymer chain may lead to its diminished tendency to aggregate.

Figure 3.68: Stern-Volmer calibration curves from CCD data for **3**, **8** and **9**. Green diamonds = 1:9 **9**/PS; Blue triangles = **8** in 1:1 PDMS/PS; Yellow circles = **9**; Black squares = **3** in PS; Black stars = **8** in PDMS; Red circles = **3** in PDMS.

The blending of PS with **9** to increase the mechanical properties of the film has resulted in a further increase in oxygen sensitivity compared to the film made up of **9** alone. This unexpected albeit gratifying result is suggested to arise from a further increase in luminescence lifetime of the luminophore because of a reduction in its freedom of movement.

The marked downward curvature of the Stern-Volmer plots is indicative of a range of luminophore microenvironments having differing oxygen sensitivity. The degree of curvature in the Stern-Volmer plots decreases as the proportion of high T_g polymer is increased, presumably due to the limited mobility of the luminophore molecules in the more rigid matrix. This is apparent in the data for **9** and a 1:9 **9**/PS blend shown in Figure 3.68, and may suggest that the luminophore in the polystyrene blend is solvated by PS at the interface of the two polymers.

While sensor response times for all systems were only measured qualitatively (see experimental section), the “dispersed in PS” sensors exhibited markedly longer response times to changes in pressure (on the order of tens of seconds) relative to the “dispersed in PDMS” sensors (which responded as quickly as the pressure could be changed). In the attached system, blending with PS did not adversely affect response time, a distinct advantage brought about by the attachment of the luminophore.

Similar results were found for sensors **6** and **12** as shown in Table 3.14 and Figures 3.69-3.74. The main difference involved the photostability of the sensors during illumination, which is an important consideration for PSPs. Dispersed samples of **6** were highly unstable during illumination, with greater than 1% intensity loss throughout the course of the experiment. This instability could have been predicted as **6** was suspected

of being a singlet oxygen quencher (see Crystallography section). Upon attachment, however, the stability of the sensors improved, particularly when blended with PS. Limiting luminophore movement by polymer attachment and the addition of rigidifiers may be not only decrease luminophore aggregation but also luminophore reactivity.

Table 3.14 - Oxygen Sensitivity CCD Data for 6 and 12.

Sensor	Matrix/Blend	Q_s (r^2)
6	in PDMS ^h	0.178 ^b ; 0.066 ^c (0.999); 0.047 ^d (0.993)
	in 1:1 PDMS/PS ^h	0.193 ^a (0.999)
	in PS ^h	0.200 ^a (0.994)
12	no blend ^g	1.020 ^b ; 0.166 ^c (0.992); 0.075 ^d (0.991)
	1:1 with PS ^f	0.742 ^b ; 0.265 ^c (0.998); 0.214 ^d (0.999)
	1:9 with PS ^f	0.626 ^b ; 0.236 ^c (0.998); 0.173 ^d (0.999)

^a0.05-45 psi; ^b0.05-5 psi; ^c10-20 psi; ^d25-45 psi; ^e10-45 psi; ^fvery stable (0-0.5% decomposition/hour illuminated); ^gmoderately stable (0.5-1% decomposition/hour illuminated); ^hunstable (>1% decomposition/hour illuminated)

Figure 3.69: Spectra of a thin film of **6** in PDMS showing the loss of intensity with increasing total air pressure. Spectra were taken at 5 psi increments over the range 0.05 – 45 psi and have been corrected for background. Q_s from band maxima are 0.18 (0-5 psi); 0.05 (10-45 psi, $r^2=0.99$).

Figure 3.70: Spectra of a thin film of **6** in 1:1 PDMS/PS showing the loss of intensity with increasing total air pressure. Spectra were taken at 5 psi increments over the range 0.05 – 45 psi and have been corrected for background. Q_s from band maxima is 0.206 ($r^2=0.9991$).

Figure 3.71: Spectra of a thin film of 6 in PS showing the loss of intensity with increasing total air pressure. Spectra were taken at 5 psi increments over the range 0.05 – 45 psi and have been corrected for background. Q_s from band maxima is 0.217 ($r^2=0.9994$).

Figure 3.72: Spectra of a thin film of 12 showing the loss of intensity with increasing total air pressure. Spectra were taken at 5 psi increments over the range 0.05 – 45 psi and have been corrected for background. Q_s from band maxima are 1.02 (0-5 psi); 0.158 (10-20 psi, 0.99); 0.07 (25-45 psi, $r^2=0.98$)

Figure 3.73: Spectra of a thin film of 1:9 12/PS showing the loss of intensity with increasing total air pressure. Spectra were taken at 5 psi increments over the range 0.05 – 45 psi and have been corrected for background. Q_s from band maxima are 0.2555 $r^2=0.9597$

Figure 3.74: Stern-Volmer calibration curves from CCD data for 6 and 12. Green diamonds = 1:9 12/PS; Black squares = 6 in PS; Yellow circles = 12; Red circles = 6 in PDMS.

Sensors 9 and 12 demonstrate the benefits of luminophore attachment: improved sensitivity, maintenance of short response times in presence of PS, and improved photostability. Unfortunately, the Q_s values found for these systems are too low for application in wind-tunnel testing. Thus, the sensor performance of the systems based on more promising luminophores (10, 11, and 13) was investigated.

ii) Sensors 4 and 10

Results of oxygen sensitivity experiments for thin films of 4 and 10 can be found in Table 3.15 and in Figures 3.75-3.81.

Table 3.15 - Oxygen Sensitivity CCD Data for 4 and 10

Sensor	Matrix/Blend	Q_s (r^2)
4	in PDMS ^h	0.118 ^a (0.998)
	in 1:1 PDMS/PS ^g	0.135 ^a (0.999)
	in PS ^g	0.149 ^a (0.999)
10	no blend ^f	0.165 ^a (0.990)
	1:1 with PS ^f	0.160 ^a (0.997)
	1:9 with PS ^f	0.187 ^a (0.992)

^a0.05-45 psi; ^b0.05-5 psi; ^c10-20 psi; ^d25-45 psi; ^e10-45 psi; ^fvery stable (0-0.5% decomposition/hour illuminated); ^gmoderately stable (0.5-1% decomposition/hour illuminated); ^hunstable (>1% decomposition/hour illuminated)

Figure 3.75: Spectra of a thin film of **4** in PDMS showing the loss of intensity with increasing total air pressure. Spectra were taken at 5 psi increments over the range 0.05 – 45 psi and have been corrected for background. Q_s from band maxima are 0.132 ($r^2 = 0.998$).

Figure 3.76: Spectra of a thin film of 4 in 1:1 PDMS/PS showing the loss of intensity with increasing total air pressure. Spectra were taken at 5 psi increments over the range 0.05 – 45 psi and have been corrected for background. Q_s from band maxima are 0.147 ($r^2 = 0.9994$).

Figure 3.77: Spectra of a thin film of **4** in PS showing the loss of intensity with increasing total air pressure. Spectra were taken at 5 psi increments over the range 0.05 – 45 psi and have been corrected for background. Q_S from band maxima are 0.156 ($r^2 = 0.997$).

Figure 3.78: Spectra of a thin film of **10** showing the loss of intensity with increasing total air pressure. Spectra were taken at 5 psi increments over the range 0.05 – 45 psi and have been corrected for background. Q_S from band maxima is 0.144 (0 – 45 psi; $r^2 = 0.99$).

Figure 3.79: Spectra of a thin film of 1:1 10/PS showing the loss of intensity with increasing total air pressure. Spectra were taken at 5 psi increments over the range 0.05 – 45 psi and have been corrected for background. Q_s from band maxima is 0.166 (0 – 45 psi; $r^2 = 0.998$).

Figure 3.80: Spectra of a thin film of 1:9 10/PS showing the loss of intensity with increasing total air pressure. Spectra were taken at 5 psi increments over the range 0.05 – 45 psi and have been corrected for background. Q_s from band maxima is 0.204 (0 – 45 psi; $r^2 = 0.994$).

Sensor 10 exhibited the highest luminophore loading of all attached systems. All Stern-Volmer plots shown in Figure 3.81 are considerably more linear than those seen in other systems. This seems counterintuitive as greater luminophore loading should likely increase the possibility of aggregation. However, more exhaustive attachment of the luminophore could lead to a more homogeneous matrix, as evidenced by more linear Stern-Volmer plots.

Figure 3.81: Stern-Volmer calibration curves from CCD data for **4** and **10**. Green diamonds = 1:9 **10**/PS; Black squares = **4** in PS; Yellow circles = **10**; Red circles = **4** in PDMS.

The effect of attachment on oxygen sensitivity and on photostability mirrors what has been seen for the previously described systems. The oxygen sensitivity of **10** is greater than that obtained for a dispersion of **4** in PDMS. The addition of polystyrene for improved film properties again leads to improved sensitivity without any adverse effect on response time. The photostability of the system also improved upon attachment.

The Q_s values for **10** and its PS blends, while larger than those of **9** and **12** are still too small for wind-tunnel applications. However, the high luminophore loading of the system and the linearity of the Stern-Volmer plots suggests that the use of imine linkers for the covalent attachment of luminophores is a viable strategy. Compound **4** is a meridional isomer, which tend to have poorer photophysical properties relative to the

facial analogue. Thus, the synthesis and attachment of the facial isomer of **4** warrants further investigation.

iii) Sensors **5** and **11**

Complex **5** exhibited very promising photophysical characteristics and thus its sensitivity to oxygen as a dispersed luminophore and in the attached system **11** were of great interest. Table 3.16 lists the oxygen sensitivity data for **5** and **11** and dispersed Ir(ppy)₃ for comparison.

Table 3.16- Oxygen Sensitivity CCD Data for **5 and **11****

Sensor	Matrix/Blend	Q _s (r ²)
5	in PDMS ^h	0.197 ^a (0.992)
	in 1:1 PDMS/PS ^h	0.149 ^a (0.999)
	in PS ^h	0.126 ^a (0.999)
11	no blend ^f	1.272 ^b ; 0.578 ^c (0.998); 0.376 ^d (0.997)
	1:1 with PS ^f	1.309 ^b ; 0.511 ^c (0.997); 0.364 ^d (0.998)
	1:9 with PS ^f	1.233 ^b ; 0.517 ^c (0.997); 0.367 ^d (0.999)
	1:9 with PDMS ^f	1.227 ^b ; 0.666 ^c (0.997); 0.399 ^d (0.997)
Ir(ppy)₃	in PDMS ^h	0.235 ^a (0.998)
	in 1:1 PDMS/PS ^h	0.207 ^a (0.999)
	in PS ^h	0.245 ^a (0.999)

^a0.05-45 psi; ^b0.05-5 psi; ^c10-20 psi; ^d25-45 psi; ^e10-45 psi; ^fvery stable (0-0.5% decomposition/hour illuminated); ^gmoderately stable (0.5-1% decomposition/hour illuminated); ^hunstable (>1% decomposition/hour illuminated)

Dispersions of **5** are slightly less oxygen sensitive relative to dispersions of Ir(ppy)₃. Ir(ppy)₃ exhibits a longer lifetime and quantum yield in solution photophysical

measurements compared to **5**, so this difference could be anticipated. Sensor **11**, alone or with blend polymer, is markedly more sensitive and more photostable than dispersions of either **5** or Ir(ppy)₃. This is easily seen by comparing the effect of air pressure on emission spectra as illustrated in Figures 3.82-3.88 and examining the Stern-Volmer plots found in Figure 3.89.

Figure 3.82: Spectra of a thin film of **5** in PDMS showing the loss of intensity with increasing total air pressure. Spectra were taken at 5 psi increments over the range 0.05 – 45 psi and have been corrected for background. Q_S from band maxima are 0.2 (0-5 psi) and 0.11 (10 – 45 psi; $r^2 = 0.996$).

Figure 3.83: Spectra of a thin film of 5 in 1:1 PDMS/PS showing the loss of intensity with increasing total air pressure. Spectra were taken at 5 psi increments over the range 0.05 – 45 psi and have been corrected for background. Q_s from band maxima is 0.12 (0 – 45 psi; $r^2 = 0.9998$).

Figure 3.84: Spectra of a thin film of **5** in 1:9 PDMS/PS showing the loss of intensity with increasing total air pressure. Spectra were taken at 5 psi increments over the range 0.05 – 45 psi and have been corrected for background. Q_s from band maxima is 0.14 (0 – 45 psi; $r^2 = 0.9993$).

Figure 3.85: Spectra of a thin film of **11** showing the loss of intensity with increasing total air pressure. Spectra were taken at 5 psi increments over the range 0.05 – 45 psi and have been corrected for background. Q_s from band maxima is 0.6065 (0 – 45 psi; $r^2 = 0.96$).

Figure 3.86: Spectra of a thin film of 1:1 11/PS showing the loss of intensity with increasing total air pressure. Spectra were taken at 5 psi increments over the range 0.05 – 45 psi and have been corrected for background. Q_s from band maxima are 1.36 (0-5 psi) and 0.483 (10-45 psi; $r^2 = 0.99$).

Figure 3.87: Spectra of a thin film of 1:9 11/PS showing the loss of intensity with increasing total air pressure. Spectra were taken at 5 psi increments over the range 0.05 – 45 psi and have been corrected for background. Q_s from band maxima are 1.34 (0-5 psi) and 0.49 (10 – 45 psi; $r^2 = 0.99$).

Figure 3.88: Spectra of a thin film of 1:9 **11**/PDMS showing the loss of intensity with increasing total air pressure. Spectra were taken at 5 psi increments over the range 0.05 – 45 psi and have been corrected for background. Q_s from band maxima is 0.892 (0 – 45 psi; $r^2 = 0.9922$).

Evidence for aggregation in thin films of **11** can be found in Figure 3.85. As the air pressure over the film is increased, a marked decrease in emission intensity is noted. However, the bandshape of the emission is changed, with an increase in the relative intensity of the low energy shoulder, indicating that this portion of the emission spectrum is more difficult to quench. This implies the presence of different luminophore environments, which again could be attributed to aggregation. When **11** is diluted with either PS (Figures 3.86 and 3.87) or PDMS (Figure 3.88), the effect, although still present, is diminished.

Figure 3.89: Stern-Volmer calibration curves from CCD data for 5 and 11. Blue triangles = 1:9 11/PDMS; Green diamonds = 1:9 11/PS; Yellow circles = 11; Red circles = 5 in PDMS; Black squares = 5 in PS.

Despite these aggregation problems, the Stern-Volmer plots of 11 (Figure 3.89) reveal improved linearity, in comparison to 9 and 12, as well as large Q_s values that are within the desired range for wind-tunnel applications. Once again, attachment has led to improved sensitivity and photostability over simple dispersions. Linearity and sensitivity are further enhanced upon blending with PS or upon dilution with additional PDMS, while response times remain unaffected. Since this sensor appeared to be very promising for PSP applications, its temperature sensitivity was investigated (see Figure 3.90 and Figure 3.91). Stern-Volmer plots of 11 show very little variation with temperature (Figure 3.90). A plot of the change in emission intensity with temperature

(at 1 atm) revealed a temperature dependence of -0.6 % per °C (Figure 3.91), comparable to the widely used PSP Pt(II)tetra(pentafluorophenyl)porphyrin in FIB.^{21a}

Figure 3.90: Stern Volmer plots of 11 at different temperatures (1 atm). Unfilled black diamond (30°C); Unfilled black square (20°C); Unfilled black circle (10°C)

Figure 3.91: Effect of temperature on intensity for 11 (1 atm). Slope indicates a 0.6% change per °C.

iv) Sensors 7 and 13

Based on solution luminescence lifetime and quantum efficiency measurements, 7 and 13 are arguably the most promising of all systems in this study for use in oxygen sensing. Oxygen sensitivity data for 7 and 13 are listed in Table 3.17 and some counterintuitive results are evident. In this case, 7 dispersed in polystyrene is more sensitive to changes in air pressure than the PDMS-bound system 13. In fact, 13 shows virtually no sensitivity to oxygen, while 7 dispersed in 1:1 PDMS/PS has the largest Q , value of any of the systems described in this study. The addition of rigidifying PS to 13, however, yields very pressure-sensitive films. This finding is further demonstration of the effect of matrix rigidity on pressure sensitivity. The effect of air pressure on emission intensity is illustrated in Figures 3.92-3.97.

Table 3.17 - Oxygen Sensitivity CCD Data for 7 and 13.

Sensor	Matrix/Blend	Q_s (r^2)
7	in PDMS ^h	0.216 ^a (0.990)
	in 1:1 PDMS/PS ^f	0.499 ^a (0.999)
	in PS ^f	0.467 ^a (0.999)
13	no blend ^f	0.089 ^a (0.993)
	1:1 with PS ^f	0.427 ^a (0.994)
	1:10 with PS ^f	0.452 ^a (0.996)

^a0.05–45 psi; ^b0.05–5 psi; ^c10–20 psi; ^d25–45 psi; ^e10–45 psi; ^fvery stable (0–0.5% decomposition/hour illuminated); ^gmoderately stable (0.5–1% decomposition/hour illuminated); ^hunstable (>1% decomposition/hour illuminated)

Figure 3.92: Spectra of a thin film of 7 in PDMS showing the loss of intensity with increasing total air pressure. Spectra were taken at 5 psi increments over the range 0.05 – 45 psi and have been corrected for background. Q_s from band maxima are 0.19 (0–5 psi) and 0.17 (10 – 45 psi; $r^2 = 0.992$).

Figure 3.93: Spectra of a thin film of 7 in 1:1 PDMS/PS showing the loss of intensity with increasing total air pressure. Spectra were taken at 5 psi increments over the range 0.05 – 45 psi and have been corrected for background. Q_S from band maxima are 0.50 (0 – 45 psi; $r^2 = 0.9997$).

Figure 3.94: Spectra of a thin film of 7 in PS showing the loss of intensity with increasing total air pressure. Spectra were taken at 5 psi increments over the range 0.05 – 45 psi and have been corrected for background. Q_s from band maxima are 0.49 (0 – 45 psi; $r^2 = 0.9994$).

Figure 3.95: Spectra of a thin film of **13** showing the loss of intensity with increasing total air pressure. Spectra were taken at 5 psi increments over the range 0.05 – 45 psi and have been corrected for background. Q_S from band maxima are 0.09 (0 – 45 psi; $r^2 = 0.993$).

Figure 3.96: Spectra of a thin film of 1:1 **13**/PS showing the loss of intensity with increasing total air pressure. Spectra were taken at 5 psi increments over the range 0.05 – 45 psi and have been corrected for background. Q_S from band maxima are 0.439 (0 – 45 psi; $r^2 = 0.994$).

Figure 3.97: Spectra of a thin film of 1:9 **13**/PS showing the loss of intensity with increasing total air pressure. Spectra were taken at 5 psi increments over the range 0.05 – 45 psi and have been corrected for background. Q_S from band maxima are 0.605 (0 – 45 psi; $r^2 = 0.96$).

Figure 3.98: Stern-Volmer calibration curves from CCD data for 7 and 13. Black squares = 7 in PS; Green diamonds = 1:9 13/PS; Red circles = 7 in PDMS; Yellow circles = 13.

By examination of the Stern-Volmer plots in Figure 3.98, roughly equivalent behaviour can be inferred for 1:9 13/PS and PS dispersions of 7. Nevertheless, the polymer-bound system has advantages. Akin to the aforementioned systems, polystyrene blends of 13 display faster response times than their dispersed analogues. The sensor 7 in polystyrene formed a very hard film that delaminated toward the end of the experiment. Upon inspection of the primed plate after the PS film had been removed, it was noted that some 7 had leached onto the plate, as evidenced by a noticeable orange colour. The unimolecular nature of 13 precludes any leaching problems, and no indication of leaching into the primer layer was noted after the film of 13 was carefully removed from the plate.

Despite the presence of the vacac ligand, which apparently leads to photostability problems in 6, only 7 in PDMS displays any noticeable decomposition during the course

of the experiment. The temperature sensitivity of a 1:1 blend of **13** with PS was examined and the results are shown in Figures 3.99 and 3.100. This system is slightly more sensitive to temperature changes, with a measured intensity change of -1% per °C.

Figure 3.99: Stern Volmer plots of 1:1 **13**/PS at different temperatures (1 atm). Black diamond (30°C); Unfilled black square (25°C); Unfilled red triangle (20°C); Black x (15°C); Unfilled black circle (10°C)

Figure 3.100: Effect of temperature on intensity for 1:1 13/PS(1 atm). Slope indicates a -1% change/ °C

7 and 13 have another advantage over the other systems of this study as they could be efficiently excited in the blue region of the visible spectrum, allowing for lifetime-based measurements to be taken using a pulsed blue LED. The effects of both pressure and temperature on luminescence decay are shown in Figures 3.101 and 3.102 (for a thin film of 7 in PS) and 3.104 and 3.105 (for a 1:1 13/PS blend). All decay data required a double exponential fit (and therefore, two luminophore lifetimes) to achieve acceptable results, further confirmation that two limiting luminophore environments exist within these sensors. Notably, in both cases, the average lifetime within the thin film is very close to the solution lifetime of that system, *i.e.* $\tau_{\text{solution}} 7 = 6 \mu\text{s}$, $\tau_{\text{film}}^{\text{avg}} 7 \text{ in PS} = 5.3 \mu\text{s}$; $\tau_{\text{solution}} 13 = 8 \mu\text{s}$, $\tau_{\text{film}}^{\text{avg}} 1:1 13/\text{PS} = 8.1 \mu\text{s}$.

Figure 3.101: Luminescence decay curves of 7 in PS after an excitation pulse at different air pressures (20 °C) . The data are fitted at each pressure to a double exponential fit. Pressures (in psi) are 14.7 (dark blue), 11.3 (orange), 7.4 (mauve), 3.6 (green), 0.058 (pale blue).

Figure 3.102: Luminescence decay curves of 7 in PS after an excitation pulse at different temperatures (14.7 psi). The data are fitted at each pressure to a double exponential fit. Temperatures (in °C) are 40 (orange), 30 (mauve), 20 (green), 10 (pale blue). Data indicates a 0.49% change per °C.

Figures 3.101 and 3.102 indicated that the luminescence lifetime of 7 in PS is sensitive to pressure, but relatively insensitive to temperature (only -0.49% change per °C). Figure 3.103 compares luminescence lifetime based Stern-Volmer plots with luminescence intensity based data. As described in the introduction, this is a useful method for determining if static quenching is taking place within a system. Very little difference is noted between the lifetime-based and intensity-based measurement, suggesting that there is little or no contribution from static quenching.

Figure 3.103: Stern-Volmer calibration curves of 7 in PS. Unfilled squares = lifetime method ($\tau_{ref1} = 3.78 \mu s$; $\tau_{ref2} = 7.67 \mu s$; $\tau_{avg} = 5.33 \mu s$. $Q_s = 0.51$ $r^2 = 0.992$) Filled diamonds = luminescence intensity method ($Q_s = 0.52$; $r^2 = 0.998$).

Figures 3.104 and 3.105 illustrate the pressure and temperature sensitivity, respectively, of 13 blended with PS. The luminescence lifetime results parallel intensity based measurements for both temperature sensitivity (0.7-1% loss per °C) and pressure sensitivity (Figure 3.104). Once again, quenching in this system can be largely attributed to dynamic quenching (Figure 3.106).

Figure 3.104: Luminescence decay curves of 1:1 13/PS after an excitation pulse at different air pressures (20 °C) . The data are fitted at each pressure to a double exponential fit. Pressures (in psi) are 14.7 (dark blue), 11.3 (orange), 7.4 (mauve), 3.6 (green), 0.058 (pale blue).

Figure 3.105: Luminescence decay curves of 1:1 **13** / PS after an excitation pulse at different temperatures (14.7 psi). The data are fitted at each pressure to a double exponential fit. Temperatures (in °C) are 40 (orange), 30 (mauve), 20 (dark blue), 10 (pale blue). Data indicate a -0.7% change per °C.

Figure 3.106: Stern-Volmer calibration curves of 1:1 13/PS. Unfilled squares = lifetime method ($\tau_{ref1} = 3.23 \mu\text{s}$; $\tau_{ref2} = 11.55 \mu\text{s}$; $\tau_{avg} = 8.11 \mu\text{s}$. $Q_s = 0.34$ $r^2 = 0.98$) Filled diamonds = luminescence intensity method ($Q_s = 0.34$; $r^2 = 0.99$).

3.4.3 Summary Part II: Polymer-bound Ir(III) Luminophores

In this study, unimolecular luminescent oxygen sensors were developed based on the covalent attachment of iridium complexes onto hydride- or aminopropyl-terminated PDMS. Attachment via hydrosilation was confirmed first by the synthesis and characterization of the model complex **8**, and then by the preparation and study of **9**, **11**, **12**, and **13**. The use of an imine linker was also proven to be a viable attachment approach by the synthesis of **10**. In general, photophysical properties of the systems, such as luminescence lifetimes and quantum yields, were improved upon attachment.

Thin films of **3-7** dispersed in a polymer matrix, as well as films of **9-13**, alone or with blends, were examined for oxygen sensitivity. The results clearly indicate that binding an iridium luminophore to a polymer improves the oxygen sensitivity of a pressure sensitive paint. In addition, the advantage of having the iridium luminophore covalently bound to a polymeric compound is further demonstrated by the improvement in the sensor behaviour upon blending with polystyrene. Not only is the oxygen sensitivity of the unimolecular systems greater than that of the dispersed systems, but the physical properties of the sensor film can be improved by blending without compromising sensor behaviour. Blends with PS yielded robust films which exhibited improved oxygen sensitivity, while maintaining short response times to changes in oxygen concentration. This is in direct contrast to the effect of blending on the response times of the dispersed-luminophore sensors. Improved photostability and the absence of leaching are ancillary benefits of luminophore attachment.

While **9**, **10**, and **12** demonstrated certain benefits of luminophore-attached sensors, the systems **11** and **13** based on the more promising free luminophores (**5** and **7**) have Q_s values that are well within the range of applicable PSPs ($0.4 \leq Q_s \leq 0.5$). Sensor **11** has the added advantage of low temperature sensitivity, while blends of **13** in PS can be efficiently excited at longer wavelengths (in the blue).

Comparing the oxygen sensitivity results of this study with those in literature can be difficult, as it is important to compare systems with similar matrices and luminophores with similar photophysical properties. In any case, the luminophore-attached sensors of this study compare favourably both in sensitivity and versatility with dispersed sensors utilizing transition metal coordination complexes having similar structures and excited state lifetimes (*e.g.* $Q_s = 0.47$ for $[\text{Ru}(\text{dpp})_3]^{2+}$ in polythionylphosphazene-poly(THF) copolymer¹⁶).

3.5 Future Work

Two of the sensor systems described in this study are very promising candidates for wind tunnel applications. Unfortunately, aggregation continues to be a problem despite luminophore attachment, particularly for **11**. To eliminate or at least attenuate this problem, a 'star' complex (tris-vppy complex) could be synthesized and attached to PDMS. If all three vinyl groups undergo hydrosilation with the hydride terminated PDMS, then the luminophores should be effectively shielded from one another, inhibiting aggregation.

As the hydrosilation reaction suffered from low attachment yields, it may be worthwhile to examine other attachment reactions. Attachment via an imine linker was demonstrated to be a very effective method for the covalent tethering of luminophores to a polymer. Now that this method has been shown to be successful, it should be attempted using a luminophore with more ideal photophysical characteristics. For example, synthesis and attachment of the facial isomer of 4 would likely yield an oxygen sensor with improved properties. The low attachment yield for hydrosilation, however, could allow for the attachment of a second, temperature sensitive luminophore to the polymer matrix.

Further improvements could be achieved through the use of fluorinated acrylates, such as FIB, as blend polymers. These blend polymers can serve to add structural rigidity without compromising oxygen permeability. Covalent attachment of the luminophores to this polymer may indeed yield an ideal sensor.

3.6 References

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Chapter 4:

A PDMS-bound Ru(II) complex for electrochromic applications

4.1 Introduction

4.1.1 Chemically-modified electrodes

One of the key aims of an electrochemist is the control of reactivity at the electrode surface. As a result, chemically-modified electrodes have attracted considerable attention over the past three decades due to their potential as electrochemical sensors, electrocatalytic materials, and electrochromic films for information displays and storage devices.¹

Some of the earliest work in this area was accomplished by Lane and Hubbard who studied the electrochemistry of a number of olefin species chemisorbed onto platinum electrodes.² Although adsorption is a simple method for the modification of an electrode, it suffers from small surface coverage (usually not more than a monolayer) and poor stability due to the desorption of species. To circumvent the desorption problem, the covalent anchoring of redox centres to an electrode was first demonstrated by Murray and co-workers, who exploited the reactivity of silane reagents with surface hydroxy groups on metal oxide electrodes, yielding a redox-active monolayer.³ This strategy has since been applied to immobilize a variety of reagents onto conventional and transparent electrodes for electrochemical and liquid crystal applications.⁴ The self-assembly of a monolayer onto a metal surface has been extensively studied as a means of surface modification.⁵ The affinity of thiols for gold and pyridine moieties for platinum has been exploited for the assembly of transition metal complex monolayers onto electrodes.

Metal complexes such as ferrocene, metalloporphyrins and metallophthalocyanines, and ammine, pyridine, bipyridine, and terpyridine complexes of ruthenium and osmium have all been examined.⁶

Of late, focus in this field has shifted from monolayers to adsorbed redox polymer films, which are generally more easily prepared, more stable, and display larger signals. There are a number of well-established approaches to the preparation of electroactive metallopolymer films on a variety of electrodes:^{1a} the adsorption of a preformed redox polymer onto an electrode, the addition of a redox-active species to polymer-coated electrode, or the electropolymerization of redox-active monomers. It is perhaps useful at this point to differentiate between redox polymers and conducting polymers. Conducting polymers, such as polythiophene and polypyrrole, contain delocalized electronic states. Conversely, redox polymers are composed of localized redox centres either covalently or electrostatically bound to a polymer. In these cases, the polymer serves only as a structural support. As the literature in chemically-modified electrodes is substantial, this chapter will focus only on redox polymers, and more specifically, those with redox-active transition metal species.

Electropolymerization is one effective technique for the modification of electrode surfaces. The reductive electropolymerization of vinyl-containing metal species, such as vinylpyridine, vinylbipyridine, vinylterpyridine and related complexes of ruthenium, osmium, iron, and cobalt is well known.⁷ This process is not limited to monomer species as was demonstrated by the electropolymerization of the ruthenium polypyridyl modified styrene oligomer $[\text{PS-CH}_2\text{CH}_2\text{NHCO-Ru}^{\text{II}}_{18}]^{36+}$, prepared by amide coupling of

aminoethyl-terminated polystyrene and Ru(II)polypyridyl complexes with terminal carboxylic acid groups.⁸

The coordination of metal complexes to a polymer backbone via ligand-exchange reactions has been investigated by Oyama and Anson for the tethering of ruthenium ammine and ruthenium EDTA complexes onto polyvinylpyridine- and polyacrylonitrile-coated graphite electrodes.⁹ Meyer's early work in this area investigated the attachment reaction of $[\text{Ru}(\text{trpy})(\text{bpy})(\text{H}_2\text{O})]^{2+}$ with polyvinylpyridine to yield polymer bound $[\text{Ru}(\text{trpy})(\text{bpy})(\text{py})]^{2+}$.¹⁰ This work has been extended to include polymeric materials of ruthenium, osmium, rhenium, and other transition metals.¹¹ Meyer and coworkers have also covalently attached polystyrene-modified ruthenium (II) polypyridyl complexes to a sol gel which was subsequently cast onto an indium-tin-oxide electrode (ITO).¹² As a result of the covalent anchoring of the metal centre, these composites are stable against leaching, unlike dispersed metal-sol gel systems.¹³ An alternate approach to attaching metal-containing redox polymers involves the reaction of metal complexes, containing ligands with pendent amino groups, to *p*-chlorosulfonated polystyrene, forming the stable sulfonamide linkage. A variety of ruthenium, iron, osmium, and nickel complexes have been incorporated onto electrodes using this methodology.¹⁴ The synthesis of metallodendrimers for the modification of electrodes has also been investigated. Wang and coworkers have developed ruthenium-containing dicarbonyldrazide cross-linked dendrimers, using triisocyanate as a cross-linker to deposit the redox film onto ITO.¹⁵ More recently, a "layer-by-layer" approach to chemically-modified electrodes has been elaborated, which affords a great deal of control over the thickness and composition of the redox film.¹⁶ In this method, a charged substrate is exposed alternately to solutions of

a polycation and a polyanion to form a polyelectrolyte thin film. This technique has been used to create a film of a ruthenium (II) dendrimer and polystyrene sulfonate on glassy carbon.¹⁷

4. 1. 2. Electrochemistry of Modified Electrodes

The current response of a chemically modified electrode can be quite different from that seen in conventional solution experiments¹⁸ and thus warrants some explanation. An ideal cyclic voltammogram for an electrode coated with a monolayer is shown in Figure 4.1. Unlike the CV of an analyte in solution, an electrochemically reversible system will exhibit symmetrical current peaks, $\Delta E_p = 0$, and a linear dependence of peak current on scan rate. The full width at half maximum (FWHM) in a reversible monolayer system should be $90.6/n$, where larger values are indicative of repulsion between redox centres, or a distribution of redox centre environments. In general, most immobilized redox species display symmetric waveshapes and small ΔE_p values.

Figure 4.1: Model cyclic voltammogram of a monolayer-coated electrode surface.

In the case of polymeric redox films on an electrode surface, more complex behaviour and a wide range of waveshapes have been reported. Typically, larger surface coverages are possible with a polymer film, and as such, a number of aspects must be considered when describing the response of a redox polymer modified electrode, particularly electron transport mechanisms through the film and the movement of solvent and electrolyte through the polymer. There are two possible mechanisms for charge transfer through a redox polymer: physical motion of the redox centres and electron transfer between neighboring redox centres or “electron-hopping”.¹⁸ In covalently-bound redox polymer systems, physical motion of the centres is not possible (ignoring any limited polymer motion) and thus, the electron-hopping mechanism is dominant. This process, first described by Kaufmann and co-workers, can be depicted as a series of self-exchange steps between neighbouring redox groups (see Figure 4.2).¹⁹

Figure 4.2: Schematic of electron-hopping mechanism for charge transfer through a redox polymer (X = oxidized group, Y = reduced group)

The two-step process entails, first, charge injection at the polymer-electrode interface, which involves the redox sites closest to the surface, and second, the

percolation of charge through the film. The relationship between the rate of self exchange (R_{SE}) and electron transfer (k_{ET}) processes is as follows:

$$R_{SE} = k_{ET}[ox][red]. \quad (4.1)$$

In a polymer film with a fixed amount of redox species (*i.e.*, $[ox] + [red] = [tot]$), the self-exchange rate will reach a maximum when the concentration of both species is equal, *i.e.*, $[ox] = [red]$, which occurs at E° . To a first approximation, charge transport behaviour through these redox films tends to obey the laws of diffusion.^{1a} The diffusion layer (δ), the area closest to electrode surface where the concentrations differ from those in the bulk, and the film thickness (ϕ) can therefore affect the current response of a redox film. When $\phi \gg \delta$, (semi-infinite behaviour), the current response tends to mimic that of a solution redox species. The alternative case where $\phi \ll \delta$ (thin-layer behaviour), current response is similar to that of a monolayer. δ is dependent on the parameter $D_{\alpha}\tau/\phi^2$, where D_{α} is the charge transport diffusion coefficient and τ is the timescale of the experiment (dictated by the scan rate in CV). When $D_{\alpha}\tau/\phi^2 \gg 1$, which would be the case for a large D , a thin film, or a long timescale, monolayer type behaviour is observed. For this reason, in cyclic voltammetry experiments of redox films, slow scan rates (10 $\text{mV}\cdot\text{s}^{-1}$) are generally necessary in order to observe thin-layer behaviour.¹⁸ Alternatively, for cases of small D , a thick film, or a short time scale ($D_{\alpha}\tau/\phi^2 \ll 1$), solution or semi-infinite behaviour is typically observed.

The movement of counterion through the polymer film to maintain electroneutrality is also an important consideration. The mechanism by which solvent and counterions penetrate into the polymer film has been ascribed to local segmental

motions of the polymer backbone.¹⁹ While there have been cases where a change in the counterion has a dramatic effect on the observed electrochemistry of the films, it is often the case that counterion exchange between the polymer and the solution tends to be faster than the rate of electron transfer, and therefore has little effect on current response.¹⁸

4.1.3. Electrochromism in chemically-modified electrodes

Electrochromism is defined as the reversible change in transmittance (or reflectance) caused by an electrochemically-induced oxidation or reduction.^{1b} This change can manifest itself by switching between a bleached (transparent) state and a coloured state, or between two coloured states.

A number of inorganic-based electrochromic materials have been investigated. Transition metal oxides have been known to be electrochromic for some time.²⁰ These films require sophisticated techniques for their deposition, such as sputtering, chemical vapour deposition, etc.^{1b} Thin films of Prussian Blue, formed by the electrochemical reduction of solutions containing iron (III) and hexacyanoferrate (III) ions have also been investigated for electrochromism.²¹ Metal phthalocyanines, particularly Lutetium bis(phthalocyanine), have been extensively studied for their multicolour electrochromism.^{1b, 22} These films are typically prepared by vacuum sublimation, but electropolymerization of metal 4,4',4'',4'''-tetraaminophthalocyanines has also been successfully attempted. Recently, chemisorbed films of cyano-bridged ruthenium and iron dinuclear complexes have been shown to display electrochromism in the visible and the near infrared.²³ While inorganic materials tend to exhibit dramatic changes in

absorption upon change of redox state, at present, polymer-based electrochromic materials, *e.g.* based on polypyrrole, polythiophene, and polyaniline, are preferred, mainly for their ease of preparation, improved processibility, and reduced cost.^{1b} Transition-metal redox polymers are therefore ideally suited for electrochromic applications, as they enjoy the advantages of both families of materials: the spectroscopic and redox properties of transition metal complexes, as well as the tractability of polymers.²⁴

4.1.4 Applications of electrochromic materials

Materials that display electrochromism have a wide variety of potential applications.¹ “Smart windows”, for example, are devices which allow the electrochemically-driven control of light absorption/transmission and can be envisaged for use in the improvement of energy efficiency in buildings or glare reduction in eyeglasses and car windshields. Electrochromic displays (ECDs) compare well with current liquid crystal display (LCD) technology, and have added advantages in the ease of preparation, and that the display does not depend on viewing angle.^{1b}

Non-visible electrochromic materials are also notable, particularly for use in optical information processing. Silica fibers used for optical data transmission have absorption minima at *ca.* 1300 and 1550 nm, thus, near infrared (NIR) electrochromic materials that are active in this region can have applications as variable optical attenuators (VOAs) for telecommunications.²⁵ Dinuclear oxo-molybdenum (V)

complexes, asymmetric ferrocenyl-oxomolybdenum (V) dimers, and ruthenium dendrimers, have been investigated for this application.^{15, 26}

Dinuclear ruthenium complexes of the 1,4-dicyanamidobenzene ligand (dicyd²⁻) have been studied for some time by the Crutchley group for their metal-metal coupling in the mixed-valence state. Spectroelectrochemical studies of dinuclear dicyd²⁻-bridged ruthenium pentaammine, tetraammine pyridine, triammine bipyridine, and terpyridine bipyridine complexes show the appearance of a NIR absorption ($\lambda_{\text{max}} = 1100\text{-}1600\text{ nm}$; $\epsilon = 10^3\text{-}10^4\text{ M}^{-1}\cdot\text{cm}^{-1}$) upon reduction to the mixed-valence state.²⁷ Similarly, mononuclear complexes of the formula $[\text{Ru}(\text{trpy})(\text{bpy})(\text{L})]^{2+/3+}$, where L = phenylcyanamide and substituted derivatives, show intense ligand-to-metal (LMCT) transitions from 1000-1150 nm upon oxidation to Ru (III).²⁸ It is evident that this family of complexes could find applications in NIR electrochromic materials.

4.1.5 Research Strategy

Transition-metal catalyzed hydrosilation has been demonstrated in Chapter 3 to be an effective method for the attachment of a neutral metal complex onto a polymer for use in oxygen sensing applications. The goal of this project is to demonstrate that this approach can also be applied to the preparation of novel redox polymers for electrochromic applications. The objectives of this project are as follows:

- 1) Synthesis and characterization of a neutral, electrochromic ruthenium complex with a pendent vinyl group. The complex, $[\text{Ru}(\text{trpy})(\text{vpy})\text{Cl}_2]$, where trpy is

2,2':6',2''-terpyridine, and vpy is 4-vinylpyridine, was chosen as the model complex.

- 2) Attachment of the complex to hydride-terminated polydimethylsiloxane (PDMS) via hydrosilation to form a novel redox polymer.
- 3) Evaluation of the electrochromic properties of the redox polymer via spectroelectrochemistry.

4.1.4. Materials and Methods

All reagents were used as received unless otherwise stated. Ruthenium (III) chloride hydrate was purchased from Pressure Chemical company, tetrabutylammonium hexafluorophosphate (TBAH), 4-vinylpyridine (vpy), 2,2':6',2''-terpyridine (trpy), and triethylamine were purchased from Aldrich, Karstedt's catalyst (platinum divinyltetramethyldisiloxane complex in xylene, 2.1-2.4% Pt), and hydride terminated polydimethylsiloxane (Mn 25,000 – 35,000) were purchased from Gelest. $\text{Ru}(\text{trpy})\text{Cl}_3$ was synthesized according to literature procedures.²⁹ Tetrabutylammonium hexafluorophosphate was twice recrystallized from 1:1 ethanol/ dH_2O and dried *in vacuo* at 110°C overnight. Solvents were purified as follows: dichloromethane (Laboratory grade, Caledon) and acetonitrile (Reagent grade, Caledon) were dried over calcium hydride and were distilled under nitrogen before use. Chloroform (Laboratory grade, Caledon) and ethanol (95%, Commercial Alcohol Inc.) were used as received.

Absorption spectra were acquired in dry CH_2Cl_2 or dry acetonitrile on a Cary 5 UV-Vis-NIR spectrophotometer at ambient temperatures using quartz cells of either

1.000 (Wilmad) or 0.200 (Hellma) cm path length. NMR spectra were acquired on a Bruker AMX-400 at ambient temperatures using #512 sample tubes (Wilmad) in CD_2Cl_2 from Canadian Isotopes Limited, and were referenced to solvent resonances. Cyclic voltammetry was performed with a BAS CV-27 voltammograph and a BAS X-Y recorder. A double-jacketed cell was fitted with a Teflon lid incorporating the three-electrodes and an argon bubbler and was attached to a Haake D8-G circulating bath to maintain the temperature at 25 °C. Platinum disc working and counter electrodes (BAS, 1.6 mm diameter), a silver wire pseudo-reference with a ferrocene as an internal reference, and 0.1 M TBAH as the supporting electrolyte were used. Spectroelectrochemistry was performed using an OTTLE (Optically Transparent Thin-Layer Electrochemistry; see Appendix B for further details) cell based on Hartl³⁰ using ITO (Delta Technologies) on quartz (10 ± 2 ohm coating) working and counter electrodes (see appendix B for etching and preparation procedures) and a Ag/AgCl reference electrode (see appendix B for preparation). Potentials were controlled using the BAS CV-27. Spectra were obtained on the Cary 5 Spectrophotometer at a scan rate of 1800 nm/min after applying a given potential and the current had returned to its baseline level (0 μA). Elemental analyses were performed by Canadian Microanalytical Service, Ltd. of Delta, B.C., Canada.

4.2.1 Metal complex synthesis

Trans-[Ru(trpy)(vpy)Cl₂], 1

4-Vinylpyridine (2 mL, 20 mmol, F.W. 105.14 $\text{g}\cdot\text{mol}^{-1}$) was added to a solution of Ru(trpy)Cl₃ (1.0 g, 2.2 mmol, F.W. 440.66 $\text{g}\cdot\text{mol}^{-1}$) and triethylamine (8 mL) in

chloroform (100 mL), and the resultant solution was refluxed under nitrogen for 1.5 hours. After cooling the purple/blue solution to room temperature, the volume was reduced to 20 mL, and a black precipitate was crashed out of solution by the addition of diethyl ether (100 mL). The product was collected by vacuum filtration, recrystallized from warm ethanol and chloroform (1:1), and dried *in vacuo* for three days. $[\text{Ru}(\text{trpy})(\text{vpy})\text{Cl}_2] \cdot 0.5 \text{ H}_2\text{O}$, (0.7 g, 1.4 mmol, 70% yield, F.W. 519.40 $\text{g} \cdot \text{mol}^{-1}$).

Elemental analysis as the semihydrate: Calc'd(%) C, 50.87; H, 3.87; N, 10.79; Found(%) C, 51.37; H, 3.64; N, 10.35. ^1H NMR (CD_2Cl_2 , 400 MHz): 9.70 (2H, d, 5 Hz), 8.42 (2H, d, 5.5 Hz), 8.08 (4H, m), 7.72 (2H, dt, 8.0, 1.5 Hz), 7.59 (1H, t, 8 Hz), 7.54 (2H, d, 5 Hz), 7.35 (2H, t, 7 Hz), 6.83 (1H, dd, 18, 11 Hz), 6.14 (1H, d, 18 Hz), 5.60 (1H, d, 11 Hz) ppm; UV-vis $\epsilon_{409} 1.02 \times 10^4$, $\epsilon_{565} 5.79 \times 10^3 \text{ L} \cdot \text{mol}^{-1} \text{cm}^{-1}$.

***Trans*-[Ru(trpy)(vpy)(pcyd)Cl], 2**

$\text{Ru}(\text{trpy})(\text{vpy})\text{Cl}_2$ (0.2 g, 0.39 mmol, 519.4 $\text{g} \cdot \text{mol}^{-1}$) was added to 200 mL of chloroform and filtered. $\text{Ag}(\text{CF}_3\text{SO}_3)$ (0.1 g, 0.39 mmol, 256.93 $\text{g} \cdot \text{mol}^{-1}$) was added to the solution forming a purple-red precipitate. The mixture was heated to reflux under an argon atmosphere overnight, yielding a deep blue solution and a grey AgCl precipitate. The silver chloride was removed by filtration and phenylcyanamide (pcydH) (0.1 g, 0.8 mmol, 118.14 $\text{g} \cdot \text{mol}^{-1}$) and triethylamine (0.5 mL) were added to the filtrate. The solution was heated to reflux under an argon atmosphere overnight. Solvent-stripping to dryness yielded a deep blue solid which was purified by column chromatography (silica gel) using 10% methanol in chloroform as the mobile phase. A complex mixture of

products was evident by the number of bands present on the column. The second band (purple-red) was collected (after a blue band of starting material) and solvent-stripped to dryness. The product was recrystallized by hexanes diffusion into a concentrated chloroform solution, yielding a microcrystalline powder of $[\text{Ru}(\text{trpy})(\text{vpy})(\text{pcyd})\text{Cl}]\cdot 0.5 \text{H}_2\text{O}$, (40 mg, 0.07 mmol, 18 % yield, F.W. $601.07 \text{ g}\cdot\text{mol}^{-1}$).

Elemental analysis as the monohydrate: Calc'd(%) C,57.09; H,4.13; N,13.99; Found(%) C,57.38; H,3.98; N,13.99. ^1H NMR (CD_2Cl_2 , 400 MHz): 9.37 (2H, d, 7 Hz), 8.33 (2H, d, 5.5Hz), 8.09 (4H, m), 7.76 (2H, dt, 8.0, 1.5 Hz), 7.60 (1H, t, 8.0 Hz), 7.54 (2H, d, 7 Hz), 7.36 (2H, t, 7 Hz), 6.83 (1H, dd, 18, 11 Hz), 6.71 (2H, m), 6.36 (1H, t, 7 Hz), 6.13 (1H, d, 18 Hz), 5.99 (2H, m), 5.60 (1H, d, 11 Hz) ppm.

4.2.2 Synthesis of polymer-bound $\text{Ru}(\text{trpy})(\text{PDMS-py})\text{Cl}_2$, 3

A solution of 1 (10 mg, 0.02 mmol, F.W. $511.40 \text{ g}\cdot\text{mol}^{-1}$) in CH_2Cl_2 (20 mL) was added to a solution of hydride terminated PDMS (3 g, 0.06 mmol, $\text{Mn} = 25\text{-}35 \text{ kDa}$) in CH_2Cl_2 (10 mL) with Karstedt's catalyst (10 μL). The resultant solution was stirred at reflux under argon for 2 days and solvent stripped to dryness. The product was dissolved in a small volume of hexanes and was filtered through 1.0 μm Gelman Acrodisc™ to remove unreacted complex. A clear, dark blue viscous liquid was obtained by dropwise addition of the filtered solution to rapidly stirring methanol. Precipitation of concentrated hexanes solutions into methanol was performed three times, resulting in a colourless supernatant liquor.

4.2.3 Preparation, cyclic voltammetry, and spectroelectrochemistry of modified electrodes

A platinum-disc electrode was dip-coated from a 10% w/v solution of **3** in CHCl_3 and was left to dry for two hours under ambient conditions. The cyclic voltammetry of the film was studied using the standard setup, in a complex-free solution of 0.1 M TBAH in acetonitrile, using a platinum counter electrode, and silver wire pseudo-reference (ferrocene added as an internal reference) at a scan rate of 10-20 mV/sec.

A thin film of **3** was applied to a transparent ITO electrode from a 10% w/v solution using a conventional airbrush and compressed argon as the propellant. The ITO plate was masked prior to application of the film to ensure coverage of only the working electrode. The film was allowed to dry for two hours under ambient conditions. The spectroelectrochemistry of the film was studied in complex-free acetonitrile (0.1 M TBAH) using conventional OTTLE technique.

4.3 Results and Discussion

4.3.1 Synthesis and Characterization of **1**

The neutral complex $[\text{Ru}(\text{trpy})(\text{vpy})\text{Cl}_2]$ **1** was chosen as a model complex for this study, based on ease of synthesis, solubility in solvents appropriate for hydrosilation (*e.g.* CH_2Cl_2), and potential electrochromism. The synthetic strategy used to prepare **1** was adapted from the procedure used to synthesize $\text{Ru}(\text{trpy})(\text{py})\text{Cl}_2$.³¹ In this straightforward reaction, the $\text{Ru}^{\text{III}}(\text{trpy})\text{Cl}_3$ starting material is reduced using triethylamine in refluxing chloroform, in the presence of the vinylpyridine ligand to give **1** (see scheme 4.1) in good

yield (70%). The final product retained a great deal of solvent and it was necessary to dry the solid under vacuum for three days. Elemental analysis was consistent with a proposed stoichiometry of the semihydrate, $1 \cdot 0.5 \text{ H}_2\text{O}$.

Scheme 4.1: Synthesis of **1** from $\text{Ru}(\text{trpy})_3\text{Cl}_3$ and vinylpyridine.

^1H NMR of **1** in CD_2Cl_2 (see Figure 4.3) confirmed the successful synthesis and purity of the product. The relatively simple spectrum showed 8 resonances in the aromatic region (> 7 ppm) for the terpyridine and pyridine ligands and three resonances in the vinyl region (5.5-7 ppm) for the pendent vinyl group, all of which is consistent with a symmetrical complex. All resonances are of appropriate splitting pattern and integration. The presence of water in the ^1H NMR spectrum also confirmed the stoichiometry of the elemental analysis.

Figure 4.3: ^1H NMR of **1** in CD_2Cl_2 . Resonances of the three vinyl protons on the vinylpyridine ligand are highlighted.

Electronic absorption spectroscopy of **1** was performed in CH_2Cl_2 and is shown in Figure 4.4. The spectrum shows trpy $\pi\text{-}\pi^*$ transitions at 327 nm ($\epsilon = 2.08 \times 10^4$) and two lower energy bands at 409 nm ($\epsilon = 1.02 \times 10^4$) and 565 nm ($\epsilon = 5.79 \times 10^3$), which are assigned to a manifold of $d\pi\text{-}\pi^*(\text{trpy})$ metal-to-ligand charge transfer transitions. This spectrum is comparable to those in the literature for $[\text{Ru}(\text{trpy})(\text{py})\text{Cl}_2]$.^{31, 32}

Figure 4.4: Electronic absorption spectrum of **1** in CH₂Cl₂.

Cyclic voltammetry of **1** was performed in a 0.1 M TBAH solution in CH₂Cl₂ (see Figure 4.5). A redox couple at 0.01 vs. the ferrocene/ferrocenium couple was observed and assigned to the Ru (III/II) couple. No terpyridine reduction couples were observed, probably due to the limited range of the solvent. The Ru (III/II) couple showed equivalent anodic and cathodic waves, with a peak separation of 75 mV. The peak separation showed a slight dependence on scan rate (see Figure 4.5B). The anodic and cathodic peak current was proportional to the square root of the scan rate ($i \propto v^{1/2}$), as expected for the cyclic voltammogram for a solution species. These results compare well with those of the analogous complex [Ru(trpy)(py)Cl₂]³⁰, thus confirming that the addition of the pendent vinyl group has little effect on the redox properties of the complex

Figure 4.5: Cyclic voltammograms of **1** in CH_2Cl_2 (0.1 M TBAH electrolyte), using Pt working and counter electrodes, a silver wire pseudo-reference (ferrocene internal reference). A) at 100 mV/S scan rate B) from 50-500 mV/S scan rate.

Spectroelectrochemistry of the Ru (III/II) couple in CH_2Cl_2 was investigated to confirm the electrochromism of **1** (see Figure 4.6). At the outset of the experiment, the solution of **1** in dichloromethane is deep blue. Upon oxidation of the complex to Ru (III), the intensity of the MLCT bands at 409 and 565 nm is greatly reduced, leaving weak pyridine $\pi\text{r}-\text{d}\pi$ LMCT transitions. As a result of this bleaching, the solution of fully oxidized **1** is pale yellow. All spectral changes caused by a voltage up to a 0.7 V vs. Ag/AgCl are fully reversible (>95%), and spectral response to changes in potential is

rapid (10-20 seconds). The application of higher oxidation potentials causes some loss of reversibility (~90% reversible).

Figure 4.6: Partial oxidation of **1** in CH_2Cl_2 (0.1 M TBAH electrolyte) from 0.2-0.7 V vs. Ag/AgCl.

4.3.2 Synthesis and characterization of **2**

The ruthenium (II) complex **2** was synthesized due to the possibility that it could display NIR electrochromism when oxidized to ruthenium (III) by analogy with similar complexes²⁸ where the phenylcyanamide ligand-to-metal charge transfer band has a λ_{max} between 1000-1150 nm. The synthesis of **2** is illustrated in Scheme 4.2. In this synthetic sequence, one equivalent of Ag^+ is used to remove Cl^- from **1**, leaving an empty coordination site for the protonated phenylcyanamide ligand. The phenylcyanamide is deprotonated using triethylamine, yielding the neutral complex **2**. This complex is

soluble in a range of solvents, notably chloroform and dichloromethane which are both used as solvents for hydrosilation.

Scheme 4.2: Synthesis of 2 from 1 and phenylcyanamide (pcyd).

Unfortunately, this synthetic strategy generated a number of products, and the final yield of 2 was very low. Similar reactions on $\text{Ru}(\text{trpy})(\text{py})\text{Cl}_2$ have also been shown to produce a complex mixture of products.³² As a result, 2 was only partially characterized, and further study of its attachment and electrochromism will be left to future work.

Despite the low yield, both elemental analysis and ^1H NMR spectroscopy (see Figure 4.7) confirm the identity of 2. The NMR spectrum retained the terpyridine and vinyl pyridine resonances seen in the spectrum of 1, and showed additional peaks of appropriate chemical shift and integration for the phenyl protons on pcyd. The infrared

spectrum (Figure 4.8) shows an intense absorbance at 2169 cm^{-1} , a typical value for a $\nu(\text{NCN})$ band.³³

Figure 4.7: ^1H NMR of **2** in CD_2Cl_2 . Resonances of the three vinyl protons on the vinylpyridine ligand and the phenyl protons on phenylcyanamide are highlighted.

Figure 4.8: IR spectrum of **2** (KBr pellet). The energy of the $\nu(\text{NCN})$ has been highlighted.

4.3.3 Synthesis and characterization of **3**

The synthesis of the novel redox polymer $[\text{Ru}(\text{trpy})(\text{PDMS-py})\text{Cl}_2]$ **3**, was accomplished via a hydrosilation reaction between the vinyl moiety on **1** and hydride-terminated PDMS ($M_n = 25\text{--}35$ kDa), using the Karstedt's catalyst (platinum divinyltetramethyldisiloxane complex in xylene, 2.1–2.4% Pt) to catalyze the reaction (see Scheme 4.2). Successful attachment of **1** was evident by the different behaviour of the polymer bound system relative to unbound complex in PDMS, similarly shown in Chapter 3. While PDMS and **3** are soluble in hexanes, **1** is not. Filtering a hexanes solution of **3** through a 1 μm Acrodisc and repeated precipitations of the filtrate into methanol yielded a clear, dark blue solution. After solvent-stripping, the dark blue viscous solid showed no sign of unreacted complex.

Scheme 4.3: Hydrosilation reaction of **1** onto H-terminated PDMS to yield **3**.

Electronic spectroscopy of **3** in CH_2Cl_2 (Figure 4.7) and as a thin film (Figure 4.8) was performed for comparison with **1**. Both spectra are comparable to the solution spectrum of **1**, with only slight broadening of the bands.

Figure 4.9: Electronic absorption spectrum of **3** in CH_2Cl_2 .

Figure 4.10: Electronic absorption spectrum of a film **3** painted on a quartz cuvette.

Attachment yield was calculated using electronic spectroscopy as described in Chapter 3. The actual concentration of attached luminophore was assessed spectroscopically using the molar absorptivity of the MLCT band of **1** at 409 nm. **3** was found to be 1.3 mM (700 ppm) in luminophore. From the reaction stoichiometry, 100% attachment would have resulted in a luminophore concentration of 6.5 mM (3300 ppm). The hydrosilation reaction yield is therefore approximately 20 %. While the yield is low, this is consistent with results found for the attachment of neutral Ir (III) complexes in Chapter 3. For complete complex loading, the maximum concentration range in **3** is 78 – 55 mM (51000 – 28000 ppm). Thus, a more concentrated polymer could be prepared with an adjustment of the reaction conditions.

4.3.3.1 Cyclic voltammetry of 3

A platinum electrode dip-coated from a solution of **3** in chloroform was placed in a 0.1M TBAH solution of acetonitrile for cyclic voltammetry experiments (see Figure 4.9). **3** is insoluble in acetonitrile, but did show evidence of swelling when in contact with the solvent. No indication of leaching of the complex from the polymer was noted after the experiment. Figure 4.9 A shows the voltammogram for the adsorbed redox polymer at a scan rate of 20 mV/s. The single redox couple at -0.04 V vs. ferrocene/ferrocenium is attributed to the Ru (III/II) couple and is only slightly shifted from that of **1**. Although the cathodic and anodic currents are rather small, it is possible to discern that the peak heights are approximately equal, but the peaks themselves are not perfectly symmetrical, although perhaps more symmetric than seen in **1**. The peak separation for the couple is 40 mV, smaller than that noted for **1** in solution. Unfortunately, peak widths at half maximum were too difficult to measure for such a small current. While it is difficult to draw a relationship between peak current and scan rate when limited to only two different rates (10 and 20 mV/s) (see Figure 4.9 B), and when dealing with such a small current, the doubling of scan rate has led to a doubling of peak current, thus suggesting a linear relationship ($i \propto v$). Further study would be necessary to confirm this relationship. These results for the adsorbed film of **3** on the platinum electrode can be described as that for an intermediate case between thin-layer and semi-infinite behaviour, a case known as finite diffusion. Adsorbed redox polymers tend to fall under this description.¹⁸ All electrochemical results are compared to **1**, and to $[\text{Ru}(\text{trpy})(\text{py})\text{Cl}_2]$ in Table 4.1.

Table 4.1: Summary of electrochemical data and comparison to Ru(trpy)(py)Cl₂^{31,32}

	Ru(trpy)(py)Cl ₂	Ru(trpy)(vpy)Cl ₂	Ru(trpy)(PDMS-py)Cl ₂
$E_{1/2}$ vs. Fc/Fc ⁺	0.05 ^a , -0.03 ^b	0.01 ^b	-0.04 ^a
ΔE_p	75 mV	75 mV	40 mV
Current (i) proportional to	-	$v^{1/2}$	v

^a in acetonitrile (0.1 M TBAH) ^b in CH₂Cl₂ (0.1 M TBAH)

Figure 4.11: Cyclic voltammograms of **2** in acetonitrile (0.1 M TBAH electrolyte), using Pt working and counter electrodes, a silver wire pseudo-reference (ferrocene internal reference). A) at 20 mV/s scan rate B) at 10(blue)-20(black) mV/s scan rate .

4.3.3.2 Spectroelectrochemistry of 3

The spectroelectrochemistry of a film of **3** deposited on an optically transparent ITO electrode is shown in Figure 4.6. Prior to any electrochemistry, the film was pale blue. A potential of 0.6 V was applied to the cell and spectra were taken at two minute intervals. Bleaching of the MLCT transitions was observed as the Ru(II) complex was oxidized to Ru(III), resulting in a transparent film in the fully oxidized state. This behaviour mirrors that seen in the solution spectroelectrochemistry of **1**, with the exception of response time. Spectral response to potential changes was slow, taking ten minutes to display the fully oxidized spectrum and 10 minutes to return to the fully reduced spectrum (by applying a potential of -0.1V). All spectral changes were fully reversible ($>95\%$), thus the electrochromism is due entirely to the change of oxidation state at the metal centre, not to dissociation of the complex or decomposition of the polymer. Three consecutive oxidation and reduction cycles were attempted with no sign of decomposition. At oxidation potentials higher than 0.7 V vs. Ag/AgCl, however, some loss in reversibility was noted ($\sim 85\%$ reversible).

Figure 4.12: Partial oxidation of **3** in acetonitrile (0.1 M TBAH electrolyte, 0.6 V vs. Ag/AgCl).

4.4 Conclusions and Future Work

This study was an investigation into hydrosilation as a novel approach to the synthesis of electrochromic redox polymers. Complex **1** displayed electrochromism in the solution spectroelectrochemistry of its Ru (III/II) couple, with bleaching of the MLCT bands at 409 and 565 nm. The hydrosilation reaction of **1** with hydride-terminated PDMS was successful, yielding redox polymer **3**. Spectroelectrochemistry of thin films of **3** displayed electrochromism similar to that seen in **1**, indicating a capacity for charge percolation through the polymer. Based on these results, hydrosilation is found to be a viable methodology for the preparation of novel electrochromic materials. Now that this synthetic approach has been validated, future work will focus on the primary goal of this

project: a redox polymer based on a NIR absorbing ruthenium dicyd²⁻ or pcyd⁻ complex for use in VOAs. Present studies include the full characterization and hydrosilation of vinyl-terminated mononuclear phenylcyanamide **2** and dinuclear dicyd²⁻ complexes.

A problem remains that overall intensity and response time in our model system are sub-optimal. This could be addressed by more complete complex loading, leading to a deeper colour and more redox-active sites from which 'electron-hopping' can occur. Low attachment yields, however, could allow for the possibility of covalent attachment of these novel redox polymers to the transparent electrode, as it is statistically unlikely that the PDMS polymer chains are functionalized at both ends. This avenue could be investigated in order to improve communication between the electrode and the film. Experiments with polyelectrolyte blends in order to develop a solvent-free system are also worth exploring.

4.4 References

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Appendix A: Crystallographic Data

Table 1: Crystal data and structure refinement for [Ir(ppy)₂(vpy)Cl]

Empirical formula	C ₃₃ H ₃₃ Cl Ir N ₃ O	
Formula weight	715.27	
Temperature	203(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2 ₁ /n	
Unit cell dimensions	a = 16.4774(19) Å	α = 90°.
	b = 10.7471(13) Å	β = 113.210(2)°.
	c = 17.489(2) Å	γ = 90°.
Volume	2846.4(6) Å ³	
Z	4	
Density (calculated)	1.669 Mg/m ³	
Absorption coefficient	4.816 mm ⁻¹	
F(000)	1416	
Crystal size	0.20 x 0.20 x 0.30 mm ³	
Theta range for data collection	2.28 to 28.41°.	
Index ranges	-21 ≤ h ≤ 20, -0 ≤ k ≤ 14, 0 ≤ l ≤ 23	
Reflections collected	21529	
Independent reflections	6621 [R(int) = 0.0310]	
Completeness to theta = 29.62°	92.4 %	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	6621 / 0 / 352	
Goodness-of-fit on F ²	1.027	
Final R indices [I > 2σ(I)]	R ₁ = 0.0354, wR ₂ = 0.1099	
R indices (all data)	R ₁ = 0.0424, wR ₂ = 0.1125	
Largest diff. peak and hole	1.567 and -1.686 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Ir}(\text{ppy})_2(\text{vpy})\text{Cl}]$. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Ir	3806 (1)	7284 (1)	1223 (1)	24 (1)
Cl	5295 (1)	8056 (1)	1370 (1)	32 (1)
N(1)	4199 (3)	5538 (4)	1057 (2)	31 (1)
N(2)	3345 (2)	8932 (4)	1469 (2)	27 (1)
N(3)	3244 (3)	7885 (4)	-87 (2)	30 (1)
O(1)	1199 (4)	2895 (6)	9005 (7)	116 (3)
C(1)	4359 (3)	6725 (5)	2411 (3)	29 (1)
C(2)	4440 (4)	7410 (5)	3129 (3)	35 (1)
C(3)	4892 (4)	6912 (6)	3920 (3)	43 (1)
C(4)	5241 (3)	5741 (6)	4020 (3)	43 (1)
C(5)	5160 (3)	5026 (5)	3329 (3)	39 (1)
C(6)	4723 (3)	5527 (5)	2532 (3)	30 (1)
C(7)	4626 (3)	4861 (5)	1767 (3)	34 (1)
C(8)	4903 (4)	3676 (5)	1713 (4)	43 (1)
C(9)	4744 (4)	3144 (6)	955 (5)	56 (2)
C(10)	4320 (4)	3834 (6)	234 (4)	48 (1)
C(11)	4066 (4)	5016 (5)	318 (3)	39 (1)
C(12)	2622 (3)	6718 (5)	1147 (3)	29 (1)
C(13)	2249 (3)	5538 (5)	978 (3)	37 (1)
C(14)	1386 (4)	5331 (6)	880 (3)	45 (1)
C(15)	867 (3)	6298 (6)	964 (3)	44 (1)
C(16)	1207 (3)	7472 (6)	1147 (3)	39 (1)
C(17)	2089 (3)	7688 (5)	1246 (3)	31 (1)
C(18)	2523 (3)	8903 (5)	1466 (3)	29 (1)
C(19)	2157 (3)	9986 (5)	1661 (3)	38 (1)
C(20)	2633 (4)	11050 (6)	1867 (3)	44 (1)
C(21)	3492 (4)	11061 (5)	1882 (3)	45 (1)
C(22)	3816 (3)	10002 (5)	1680 (3)	33 (1)
C(23)	2435 (4)	7544 (5)	-618 (3)	34 (1)
C(24)	2014 (3)	8039 (5)	-1406 (3)	33 (1)
C(25)	2430 (3)	8921 (5)	-1699 (3)	34 (1)
C(26)	3292 (3)	9255 (5)	-1157 (3)	39 (1)
C(27)	3664 (3)	8732 (5)	-374 (3)	38 (1)
C(28)	1967 (4)	9546 (6)	-2497 (3)	45 (1)
C(29)	2184 (4)	10624 (7)	-2720 (4)	57 (2)
C(30)	1617 (7)	3852 (9)	8803 (7)	98 (3)
C(31)	981 (5)	4623 (13)	8246 (6)	138 (6)
C(32)	1804 (9)	2268 (10)	9801 (8)	114 (4)
C(33)	2338 (6)	1412 (9)	9626 (5)	87 (3)

Table 3. Bond lengths [Å] and angles [°] for [Ir(ppy)₂(vpy)Cl].

Ir-C(12)	1.999(5)	C(12)-Ir-C(1)	90.59(17)
Ir-C(1)	2.004(5)	C(12)-Ir-N(2)	80.90(18)
Ir-N(2)	2.040(4)	C(1)-Ir-N(2)	95.52(17)
Ir-N(1)	2.042(4)	C(12)-Ir-N(1)	93.83(18)
Ir-N(3)	2.203(4)	C(1)-Ir-N(1)	80.29(18)
Ir-Cl	2.5045(12)	N(2)-Ir-N(1)	173.27(15)
N(1)-C(11)	1.346(6)	C(12)-Ir-N(3)	91.21(16)
N(1)-C(7)	1.369(6)	C(1)-Ir-N(3)	177.94(17)
N(2)-C(18)	1.352(6)	N(2)-Ir-N(3)	85.77(15)
N(2)-C(22)	1.355(6)	N(1)-Ir-N(3)	98.58(15)
N(3)-C(23)	1.341(6)	C(12)-Ir-Cl	177.41(14)
N(3)-C(27)	1.354(6)	C(1)-Ir-Cl	88.06(13)
O(1)-C(30)	1.360(10)	N(2)-Ir-Cl	97.04(11)
O(1)-C(32)	1.514(13)	N(1)-Ir-Cl	88.11(11)
C(1)-C(6)	1.400(7)	N(3)-Ir-Cl	90.19(12)
C(1)-C(2)	1.417(6)	C(11)-N(1)-C(7)	118.7(5)
C(2)-C(3)	1.393(7)	C(11)-N(1)-Ir	125.3(4)
C(3)-C(4)	1.365(9)	C(7)-N(1)-Ir	116.0(3)
C(4)-C(5)	1.394(8)	C(18)-N(2)-C(22)	119.1(4)
C(5)-C(6)	1.400(7)	C(18)-N(2)-Ir	115.8(3)
C(6)-C(7)	1.470(7)	C(22)-N(2)-Ir	125.0(3)
C(7)-C(8)	1.369(7)	C(23)-N(3)-C(27)	116.2(4)
C(8)-C(9)	1.370(9)	C(23)-N(3)-Ir	122.4(3)
C(9)-C(10)	1.390(10)	C(27)-N(3)-Ir	121.0(3)
C(10)-C(11)	1.363(8)	C(30)-O(1)-C(32)	111.0(8)
C(12)-C(13)	1.390(7)		
C(12)-C(17)	1.416(7)		
C(13)-C(14)	1.382(7)		
C(14)-C(15)	1.389(9)		
C(15)-C(16)	1.366(8)		
C(16)-C(17)	1.413(7)		
C(17)-C(18)	1.466(7)		
C(18)-C(19)	1.413(7)		
C(19)-C(20)	1.351(8)		
C(20)-C(21)	1.405(8)		
C(21)-C(22)	1.362(7)		
C(23)-C(24)	1.382(7)		
C(24)-C(25)	1.381(7)		
C(25)-C(26)	1.408(7)		
C(25)-C(28)	1.464(7)		
C(26)-C(27)	1.380(7)		
C(28)-C(29)	1.317(8)		
C(30)-C(31)	1.389(12)		
C(32)-C(33)	1.388(13)		

C(6)-C(1)-C(2)	117.2(4)
C(6)-C(1)-Ir	115.2(3)
C(2)-C(1)-Ir	127.5(4)
C(3)-C(2)-C(1)	120.5(5)
C(4)-C(3)-C(2)	121.0(5)
C(3)-C(4)-C(5)	120.3(5)
C(4)-C(5)-C(6)	119.1(5)
C(5)-C(6)-C(1)	121.8(5)
C(5)-C(6)-C(7)	123.2(5)
C(1)-C(6)-C(7)	115.0(4)
C(8)-C(7)-N(1)	119.9(5)
C(8)-C(7)-C(6)	126.6(5)
N(1)-C(7)-C(6)	113.5(4)
C(7)-C(8)-C(9)	120.9(6)
C(8)-C(9)-C(10)	119.4(6)
C(11)-C(10)-C(9)	117.7(5)
N(1)-C(11)-C(10)	123.4(6)
C(13)-C(12)-C(17)	117.0(5)
C(13)-C(12)-Ir	129.0(4)
C(17)-C(12)-Ir	113.9(4)
C(14)-C(13)-C(12)	121.3(6)
C(13)-C(14)-C(15)	120.8(5)
C(16)-C(15)-C(14)	120.2(5)
C(15)-C(16)-C(17)	119.1(6)
C(16)-C(17)-C(12)	121.4(5)
C(16)-C(17)-C(18)	123.4(5)
C(12)-C(17)-C(18)	115.2(4)
N(2)-C(18)-C(19)	120.1(5)
N(2)-C(18)-C(17)	113.9(4)
C(19)-C(18)-C(17)	125.9(4)
C(20)-C(19)-C(18)	120.2(5)
C(19)-C(20)-C(21)	119.1(5)
C(22)-C(21)-C(20)	118.9(5)
N(2)-C(22)-C(21)	122.6(5)
N(3)-C(23)-C(24)	123.8(5)
C(23)-C(24)-C(25)	120.4(5)
C(24)-C(25)-C(26)	116.3(4)
C(24)-C(25)-C(28)	121.3(5)
C(26)-C(25)-C(28)	122.2(5)
C(27)-C(26)-C(25)	120.0(5)
N(3)-C(27)-C(26)	123.3(4)
C(29)-C(28)-C(25)	125.9(6)
O(1)-C(30)-C(31)	108.3(9)
C(33)-C(32)-O(1)	109.7(10)

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Ir}(\text{ppy})_2(\text{vpy})\text{Cl}]$. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U11	U22	U33	U23	U13	U12
Ir	21 (1)	31 (1)	22 (1)	-4 (1)	10 (1)	-5 (1)
Cl	23 (1)	39 (1)	35 (1)	-4 (1)	12 (1)	-6 (1)
N(1)	27 (2)	30 (2)	39 (2)	-11 (2)	18 (2)	-10 (2)
N(2)	23 (2)	31 (2)	26 (2)	-6 (2)	9 (2)	1 (2)
N(3)	24 (2)	36 (3)	28 (2)	-2 (2)	8 (2)	-2 (2)
O(1)	57 (4)	54 (4)	229 (9)	47 (4)	47 (5)	8 (2)
C(1)	27 (2)	32 (3)	28 (2)	-4 (2)	12 (2)	-8 (2)
C(2)	34 (3)	45 (3)	26 (2)	-6 (2)	11 (2)	-3 (2)
C(3)	43 (3)	61 (4)	28 (2)	-2 (2)	18 (2)	-6 (3)
C(4)	29 (3)	66 (4)	31 (2)	15 (2)	9 (2)	-1 (2)
C(5)	27 (3)	45 (3)	44 (3)	11 (2)	14 (2)	0 (2)
C(6)	18 (2)	34 (3)	36 (2)	2 (2)	10 (2)	-3 (2)
C(7)	26 (2)	31 (3)	45 (3)	-4 (2)	16 (2)	-6 (2)
C(8)	33 (3)	35 (3)	64 (3)	2 (3)	23 (3)	-2 (2)
C(9)	50 (4)	39 (3)	89 (5)	-16 (3)	38 (3)	-3 (3)
C(10)	52 (3)	45 (3)	57 (3)	-24 (3)	32 (3)	-15 (3)
C(11)	41 (3)	43 (3)	41 (3)	-14 (2)	23 (2)	-14 (2)
C(12)	27 (2)	38 (3)	21 (2)	1 (2)	9 (2)	-5 (2)
C(13)	34 (3)	49 (3)	31 (2)	-1 (2)	16 (2)	-9 (2)
C(14)	39 (3)	58 (4)	38 (3)	-3 (2)	16 (2)	-27 (3)
C(15)	24 (2)	74 (4)	33 (2)	4 (3)	11 (2)	-13 (3)
C(16)	22 (3)	64 (4)	31 (3)	4 (2)	11 (2)	1 (2)
C(17)	24 (2)	44 (3)	26 (2)	0 (2)	11 (2)	-2 (2)
C(18)	25 (2)	40 (3)	24 (2)	-1 (2)	11 (2)	2 (2)
C(19)	32 (3)	48 (3)	38 (3)	0 (2)	18 (2)	9 (2)
C(20)	43 (3)	47 (3)	44 (3)	-6 (2)	20 (2)	7 (3)
C(21)	56 (3)	35 (3)	45 (3)	-9 (2)	21 (3)	-3 (2)
C(22)	31 (3)	35 (3)	38 (2)	-6 (2)	19 (2)	-5 (2)
C(23)	32 (3)	39 (3)	34 (3)	-5 (2)	15 (2)	-9 (2)
C(24)	28 (2)	38 (3)	32 (2)	-8 (2)	11 (2)	-6 (2)
C(25)	27 (2)	45 (3)	29 (2)	-1 (2)	12 (2)	-1 (2)
C(26)	32 (3)	49 (3)	38 (3)	7 (2)	16 (2)	-8 (2)
C(27)	24 (2)	49 (3)	36 (2)	2 (2)	9 (2)	-7 (2)
C(28)	33 (3)	64 (4)	35 (3)	6 (2)	11 (2)	0 (3)
C(29)	51 (4)	69 (4)	47 (3)	21 (3)	14 (3)	-1 (3)
C(30)	100 (7)	75 (7)	149 (9)	18 (6)	79 (7)	-4 (5)
C(31)	46 (5)	227 (15)	128 (9)	121 (10)	21 (5)	23 (7)
C(32)	126 (11)	72 (7)	129 (10)	-22 (6)	33 (8)	8 (6)
C(33)	73 (5)	79 (6)	78 (5)	-8 (4)	-5 (4)	12 (5)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Ir}(\text{ppy})_2(\text{vpy})\text{Cl}]$

	x	y	z	U(eq)
H(2A)	4187	8206	3072	42
H(3A)	4957	7389	4391	51
H(4A)	5537	5416	4558	51
H(5A)	5395	4217	3397	46
H(8A)	5206	3221	2202	52
H(9A)	4921	2321	923	67
H(10A)	4212	3496	-293	58
H(11A)	3782	5491	-166	47
H(13A)	2591	4866	929	45
H(14A)	1146	4526	755	54
H(15A)	281	6144	895	53
H(16A)	858	8127	1206	47
H(19A)	1581	9967	1648	45
H(20A)	2392	11771	1999	53
H(21A)	3837	11787	2029	53
H(22A)	4389	10014	1687	40
H(23A)	2137	6932	-445	41
H(24A)	1441	7774	-1745	40
H(26A)	3614	9834	-1329	46
H(27A)	4238	8976	-23	45
H(28A)	1470	9140	-2886	54
H(29A)	2676	11063	-2352	69
H(29B)	1847	10956	-3248	69
H(30A)	2008	3530	8548	118
H(30B)	1974	4319	9304	118
H(31A)	1267	5313	8095	206
H(31B)	598	4941	8504	206
H(31C)	632	4155	7751	206
H(32A)	2171	2894	10191	137
H(32B)	1451	1844	10060	137
H(33A)	2724	1012	10138	131
H(33B)	2691	1836	9375	131
H(33C)	1972	789	9244	131

Table 7. Crystal data and structure refinement for Ir(C6)₂(vacac).

Empirical formula	C ₄₈ H ₄₅ Cl ₂ Ir N ₄ O ₇ S ₂	
Formula weight	1117.10	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2 ₁ /c	
Unit cell dimensions	a = 14.5249(9) Å	α = 90°.
	b = 17.4530(11) Å	β = 124.978(10)°.
	c = 22.1208(14) Å	γ = 90°.
Volume	4594.8(5) Å ³	
Z	4	
Density (calculated)	1.615 Mg/m ³	
Absorption coefficient	3.169 mm ⁻¹	
F(000)	2240	
Crystal size	0.20 x 0.16 x 0.12 mm ³	
Theta range for data collection	1.62 to 29.62°.	
Index ranges	-20 ≤ h ≤ 20, -24 ≤ k ≤ 23, -30 ≤ l ≤ 30	
Reflections collected	57453	
Independent reflections	12904 [R(int) = 0.0577]	
Completeness to theta = 29.62°	99.6 %	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	12904 / 12 / 589	
Goodness-of-fit on F ²	1.012	
Final R indices [I > 2σ(I)]	R ₁ = 0.0434, wR ₂ = 0.1034	
R indices (all data)	R ₁ = 0.0766, wR ₂ = 0.1176	
Largest diff. peak and hole	1.781 and -0.807 e.Å ⁻³	

Table 8. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{Ir}(\text{C}_6)_2(\text{vacac})$. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U(\text{eq})$
Ir(1)	4137(1)	2251(1)	688(1)	32(1)
S(8)	5447(1)	662(1)	2594(1)	47(1)
S(38)	2436(1)	3803(1)	-1260(1)	44(1)
O(61)	5628(1)	2798(1)	1554(1)	46(1)
O(64)	4967(1)	2068(1)	154(1)	46(1)
O(49)	1115(1)	2448(1)	-2124(1)	56(1)
O(48)	933(1)	1390(1)	-1659(1)	51(1)
O(19)	4267(1)	1621(1)	3020(1)	48(1)
O(18)	2948(1)	2474(1)	2306(1)	38(1)
O(65)	6297(1)	2233(1)	-58(1)	67(1)
N(31)	3540(1)	3205(1)	39(1)	34(1)
N(50)	343(2)	-965(1)	-868(1)	76(1)
N(1)	4832(1)	1322(1)	1374(1)	34(1)
N(20)	-339(1)	3936(1)	736(1)	54(1)
C(63)	6660(2)	2752(1)	1018(1)	55(1)
C(6)	6544(2)	-384(1)	2230(1)	60(1)
C(12)	2534(1)	2826(1)	1114(1)	33(1)
C(11)	3465(1)	2373(1)	1249(1)	31(1)
C(42)	2195(1)	1096(1)	-348(1)	37(1)
C(45)	926(2)	-289(1)	-699(1)	57(1)
C(40)	2353(1)	2279(1)	-834(1)	38(1)
C(37)	3270(1)	4402(1)	-499(1)	40(1)
C(49)	1466(1)	2078(1)	-1565(1)	43(1)
C(35)	4111(1)	5542(1)	182(1)	50(1)
C(62)	6485(2)	2949(1)	1553(1)	51(1)
C(7)	5879(1)	262(1)	2070(1)	46(1)
C(34)	4604(1)	5136(1)	833(1)	49(1)
C(23)	-652(2)	3886(2)	1257(1)	67(1)
C(16)	1367(1)	3218(1)	1538(1)	35(1)
C(46)	648(2)	260(1)	-1238(1)	57(1)

C(9)	4741(1)	1366(1)	1934(1)	33(1)
C(32)	3796(1)	3980(1)	158(1)	35(1)
C(43)	2441(1)	546(1)	189(1)	44(1)
C(47)	1275(2)	913(1)	-1069(1)	44(1)
C(64)	5915(1)	2342(1)	367(1)	45(1)
C(66)	5554(2)	1876(2)	-738(1)	82(1)
C(13)	1775(1)	3226(1)	459(1)	42(1)
C(14)	844(1)	3595(1)	333(1)	45(1)
C(15)	611(1)	3599(1)	876(1)	41(1)
C(10)	4003(1)	1934(1)	1893(1)	33(1)
C(41)	2771(1)	1814(1)	-215(1)	34(1)
C(51)	704(2)	-1573(2)	-314(2)	78(1)
C(69)	7363(2)	3393(2)	2188(1)	74(1)
C(39)	2810(1)	3037(1)	-669(1)	37(1)
C(4)	6341(2)	-190(2)	1086(1)	61(1)
C(3)	5703(1)	455(1)	928(1)	49(1)
C(2)	5472(1)	688(1)	1435(1)	39(1)
C(36)	3442(1)	5184(1)	-486(1)	47(1)
C(33)	4447(1)	4351(1)	835(1)	42(1)
C(21)	-1182(2)	4291(2)	33(1)	88(1)
C(19)	3781(1)	1975(1)	2446(1)	36(1)
C(17)	2281(1)	2847(1)	1637(1)	32(1)
C(24)	-263(3)	4573(2)	1731(2)	114(2)
C(54)	-1753(2)	-598(2)	-1735(2)	105(1)
C(53)	-733(2)	-1065(2)	-1606(1)	86(1)
C(67)	5949(2)	1979(2)	-1226(2)	92(1)
C(5)	6760(2)	-608(2)	1728(1)	65(1)
C(44)	1852(2)	-120(1)	31(1)	55(1)
C(22)	-1994(2)	3707(3)	-499(2)	139(2)
C(52)	227(2)	-1454(2)	132(2)	101(1)
C(68)	6019(3)	1443(3)	-1660(2)	134(2)
C(501)	8434(6)	3605(8)	7584(3)	211(5)
Cl(1)	9463(2)	3226(1)	8436(1)	102(1)
Cl(2)	8785(2)	3706(1)	6934(1)	102(1)
C(601)	8329(6)	3481(6)	7808(5)	211(5)
Cl(3)	9295(4)	3351(4)	7574(3)	102(1)

Cl(4)	8664(4)	4292(3)	8359(3)	102(1)
C(500)	9149(6)	3403(7)	7776(4)	211(5)
Cl(5)	8332(3)	3503(3)	8130(2)	121(1)
Cl(6)	8476(3)	3985(3)	6994(2)	121(1)
C(600)	9121(8)	3128(6)	7631(4)	211(5)
Cl(7)	8123(3)	3865(3)	7311(2)	121(1)
Cl(8)	9552(4)	2882(3)	8530(2)	121(1)

Table 9. Bond lengths [Å] and angles [°] for Ir(C6)₂(vacac).

Ir(1)-C(11)	1.981(2)
Ir(1)-C(41)	1.9912(13)
Ir(1)-N(31)	2.0386(14)
Ir(1)-N(1)	2.0488(14)
Ir(1)-O(61)	2.1246(11)
Ir(1)-O(64)	2.1404(17)
S(8)-C(9)	1.7246(17)
S(8)-C(7)	1.747(3)
S(38)-C(39)	1.7259(19)
S(38)-C(37)	1.7492(17)
O(61)-C(62)	1.274(3)
O(64)-C(64)	1.266(2)
O(49)-C(49)	1.219(2)
O(48)-C(49)	1.378(3)
O(48)-C(47)	1.379(2)
O(19)-C(19)	1.210(2)
O(18)-C(19)	1.374(2)
O(18)-C(17)	1.3815(19)
O(65)-C(64)	1.352(3)
O(65)-C(66)	1.399(3)
N(31)-C(39)	1.3269(18)
N(31)-C(32)	1.387(2)
N(50)-C(45)	1.374(3)
N(50)-C(51)	1.472(3)
N(50)-C(53)	1.488(3)

N(1)-C(9)	1.323(3)
N(1)-C(2)	1.401(2)
N(20)-C(15)	1.363(3)
N(20)-C(21)	1.455(3)
N(20)-C(23)	1.465(4)
C(63)-C(62)	1.389(4)
C(63)-C(64)	1.403(3)
C(6)-C(5)	1.372(4)
C(6)-C(7)	1.393(3)
C(12)-C(17)	1.401(3)
C(12)-C(13)	1.404(2)
C(12)-C(11)	1.443(2)
C(11)-C(10)	1.397(2)
C(42)-C(43)	1.406(3)
C(42)-C(47)	1.410(2)
C(42)-C(41)	1.439(3)
C(45)-C(46)	1.397(3)
C(45)-C(44)	1.418(2)
C(40)-C(41)	1.396(2)
C(40)-C(49)	1.416(2)
C(40)-C(39)	1.431(3)
C(37)-C(36)	1.386(3)
C(37)-C(32)	1.401(2)
C(35)-C(36)	1.368(3)
C(35)-C(34)	1.379(3)
C(62)-C(69)	1.464(3)
C(7)-C(2)	1.387(3)
C(34)-C(33)	1.390(3)
C(23)-C(24)	1.474(4)
C(16)-C(17)	1.377(3)
C(16)-C(15)	1.396(2)
C(46)-C(47)	1.371(3)
C(9)-C(10)	1.424(3)
C(32)-C(33)	1.390(2)
C(43)-C(44)	1.365(3)
C(66)-C(67)	1.495(5)

C(13)-C(14)	1.376(3)
C(14)-C(15)	1.421(3)
C(10)-C(19)	1.434(3)
C(51)-C(52)	1.510(6)
C(4)-C(3)	1.370(3)
C(4)-C(5)	1.390(3)
C(3)-C(2)	1.403(3)
C(21)-C(22)	1.492(5)
C(54)-C(53)	1.566(5)
C(67)-C(68)	1.386(6)
C(501)-Cl(1)	1.730(7)
C(501)-Cl(2)	1.790(9)
C(601)-Cl(4)	1.746(10)
C(601)-Cl(3)	1.766(11)
C(500)-Cl(6)	1.744(9)
C(500)-Cl(5)	1.766(11)
C(600)-Cl(7)	1.755(11)
C(600)-Cl(8)	1.763(10)

C(11)-Ir(1)-C(41)	95.92(7)
C(11)-Ir(1)-N(31)	100.93(7)
C(41)-Ir(1)-N(31)	80.21(6)
C(11)-Ir(1)-N(1)	80.29(7)
C(41)-Ir(1)-N(1)	102.92(6)
N(31)-Ir(1)-N(1)	176.56(5)
C(11)-Ir(1)-O(61)	90.05(6)
C(41)-Ir(1)-O(61)	172.37(7)
N(31)-Ir(1)-O(61)	94.02(5)
N(1)-Ir(1)-O(61)	82.74(5)
C(11)-Ir(1)-O(64)	175.45(5)
C(41)-Ir(1)-O(64)	86.67(7)
N(31)-Ir(1)-O(64)	83.17(6)
N(1)-Ir(1)-O(64)	95.50(6)
O(61)-Ir(1)-O(64)	87.68(6)
C(9)-S(8)-C(7)	89.37(10)
C(39)-S(38)-C(37)	89.39(8)

C(62)-O(61)-Ir(1)	125.70(14)
C(64)-O(64)-Ir(1)	125.02(13)
C(49)-O(48)-C(47)	121.07(13)
C(19)-O(18)-C(17)	121.78(16)
C(64)-O(65)-C(66)	116.06(19)
C(39)-N(31)-C(32)	112.70(14)
C(39)-N(31)-Ir(1)	112.30(12)
C(32)-N(31)-Ir(1)	134.67(9)
C(45)-N(50)-C(51)	121.56(17)
C(45)-N(50)-C(53)	119.7(2)
C(51)-N(50)-C(53)	118.5(2)
C(9)-N(1)-C(2)	111.90(15)
C(9)-N(1)-Ir(1)	112.12(12)
C(2)-N(1)-Ir(1)	135.65(14)
C(15)-N(20)-C(21)	123.3(2)
C(15)-N(20)-C(23)	121.81(17)
C(21)-N(20)-C(23)	114.53(19)
C(62)-C(63)-C(64)	126.2(2)
C(5)-C(6)-C(7)	118.1(2)
C(17)-C(12)-C(13)	114.71(17)
C(17)-C(12)-C(11)	120.15(14)
C(13)-C(12)-C(11)	124.98(19)
C(10)-C(11)-C(12)	114.88(18)
C(10)-C(11)-Ir(1)	113.10(13)
C(12)-C(11)-Ir(1)	132.02(13)
C(43)-C(42)-C(47)	114.69(17)
C(43)-C(42)-C(41)	125.81(13)
C(47)-C(42)-C(41)	119.47(17)
N(50)-C(45)-C(46)	121.69(17)
N(50)-C(45)-C(44)	121.5(2)
C(46)-C(45)-C(44)	116.8(2)
C(41)-C(40)-C(49)	125.11(18)
C(41)-C(40)-C(39)	114.18(13)
C(49)-C(40)-C(39)	120.35(16)
C(36)-C(37)-C(32)	120.77(15)
C(36)-C(37)-S(38)	128.74(14)

C(32)-C(37)-S(38)	110.49(14)
O(49)-C(49)-O(48)	115.83(14)
O(49)-C(49)-C(40)	127.2(2)
O(48)-C(49)-C(40)	116.94(17)
C(36)-C(35)-C(34)	120.95(19)
O(61)-C(62)-C(63)	127.33(18)
O(61)-C(62)-C(69)	115.0(2)
C(63)-C(62)-C(69)	117.7(2)
C(2)-C(7)-C(6)	121.5(2)
C(2)-C(7)-S(8)	110.61(16)
C(6)-C(7)-S(8)	127.93(18)
C(35)-C(34)-C(33)	121.50(17)
N(20)-C(23)-C(24)	110.2(3)
C(17)-C(16)-C(15)	119.8(2)
C(47)-C(46)-C(45)	121.02(16)
N(1)-C(9)-C(10)	117.15(15)
N(1)-C(9)-S(8)	114.88(14)
C(10)-C(9)-S(8)	127.70(16)
N(31)-C(32)-C(33)	126.98(16)
N(31)-C(32)-C(37)	112.81(14)
C(33)-C(32)-C(37)	120.13(17)
C(44)-C(43)-C(42)	123.18(15)
C(46)-C(47)-O(48)	114.90(14)
C(46)-C(47)-C(42)	123.26(19)
O(48)-C(47)-C(42)	121.83(18)
O(64)-C(64)-O(65)	118.72(17)
O(64)-C(64)-C(63)	127.6(2)
O(65)-C(64)-C(63)	113.67(19)
O(65)-C(66)-C(67)	110.1(2)
C(14)-C(13)-C(12)	122.7(2)
C(13)-C(14)-C(15)	120.91(16)
N(20)-C(15)-C(16)	121.9(2)
N(20)-C(15)-C(14)	120.67(16)
C(16)-C(15)-C(14)	117.38(18)
C(11)-C(10)-C(9)	114.03(18)
C(11)-C(10)-C(19)	125.13(17)

C(9)-C(10)-C(19)	120.56(15)
C(40)-C(41)-C(42)	115.45(13)
C(40)-C(41)-Ir(1)	112.58(13)
C(42)-C(41)-Ir(1)	131.84(12)
N(50)-C(51)-C(52)	111.5(3)
N(31)-C(39)-C(40)	116.50(16)
N(31)-C(39)-S(38)	114.50(14)
C(40)-C(39)-S(38)	128.62(11)
C(3)-C(4)-C(5)	121.8(3)
C(4)-C(3)-C(2)	118.1(2)
C(7)-C(2)-N(1)	113.2(2)
C(7)-C(2)-C(3)	119.82(19)
N(1)-C(2)-C(3)	126.95(17)
C(35)-C(36)-C(37)	118.70(18)
C(34)-C(33)-C(32)	117.85(17)
N(20)-C(21)-C(22)	110.6(3)
O(19)-C(19)-O(18)	117.9(2)
O(19)-C(19)-C(10)	126.08(18)
O(18)-C(19)-C(10)	116.03(14)
C(16)-C(17)-O(18)	114.39(18)
C(16)-C(17)-C(12)	124.46(15)
O(18)-C(17)-C(12)	121.14(15)
N(50)-C(53)-C(54)	115.3(3)
C(68)-C(67)-C(66)	129.1(4)
C(6)-C(5)-C(4)	120.6(2)
C(43)-C(44)-C(45)	121.0(2)
Cl(1)-C(501)-Cl(2)	116.5(5)
Cl(4)-C(601)-Cl(3)	111.1(6)
Cl(6)-C(500)-Cl(5)	104.2(5)
Cl(7)-C(600)-Cl(8)	108.1(7)

Table 10. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{Ir}(\text{C}_6)_2(\text{vacac})$. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Ir(1)	35(1)	33(1)	34(1)	2(1)	22(1)	3(1)
S(8)	50(1)	53(1)	36(1)	14(1)	24(1)	23(1)
S(38)	50(1)	45(1)	44(1)	14(1)	32(1)	9(1)
O(61)	41(1)	50(1)	45(1)	0(1)	24(1)	-2(1)
O(64)	49(1)	52(1)	46(1)	3(1)	33(1)	6(1)
O(49)	70(1)	62(1)	36(1)	6(1)	30(1)	-1(1)
O(48)	61(1)	52(1)	33(1)	-6(1)	24(1)	-10(1)
O(19)	49(1)	59(1)	35(1)	11(1)	24(1)	18(1)
O(18)	39(1)	42(1)	33(1)	2(1)	22(1)	10(1)
O(65)	61(1)	87(1)	68(1)	11(1)	46(1)	4(1)
N(31)	44(1)	31(1)	35(1)	3(1)	27(1)	0(1)
N(50)	99(1)	53(1)	58(1)	-7(1)	34(1)	-33(1)
N(1)	32(1)	35(1)	33(1)	-1(1)	19(1)	4(1)
N(20)	46(1)	65(1)	55(1)	11(1)	31(1)	20(1)
C(63)	48(1)	63(1)	63(1)	6(1)	36(1)	-3(1)
C(6)	66(1)	57(1)	57(1)	14(1)	35(1)	31(1)
C(12)	32(1)	32(1)	36(1)	1(1)	21(1)	0(1)
C(11)	31(1)	27(1)	32(1)	-2(1)	17(1)	1(1)
C(42)	39(1)	39(1)	35(1)	-3(1)	23(1)	0(1)
C(45)	75(1)	44(1)	51(1)	-10(1)	35(1)	-17(1)
C(40)	42(1)	43(1)	37(1)	-1(1)	28(1)	3(1)
C(37)	43(1)	39(1)	55(1)	5(1)	37(1)	4(1)
C(49)	52(1)	47(1)	39(1)	-1(1)	31(1)	4(1)
C(35)	57(1)	34(1)	85(1)	4(1)	56(1)	2(1)
C(62)	47(1)	49(1)	56(1)	9(1)	29(1)	-1(1)
C(7)	45(1)	50(1)	42(1)	9(1)	24(1)	17(1)
C(34)	56(1)	42(1)	69(1)	-15(1)	48(1)	-8(1)
C(23)	57(1)	90(2)	64(1)	20(1)	41(1)	35(1)
C(16)	35(1)	36(1)	37(1)	-5(1)	22(1)	1(1)
C(46)	63(1)	58(1)	37(1)	-8(1)	21(1)	-14(1)

C(9)	34(1)	34(1)	26(1)	2(1)	13(1)	5(1)
C(32)	41(1)	33(1)	48(1)	1(1)	36(1)	1(1)
C(43)	48(1)	38(1)	43(1)	-2(1)	25(1)	-3(1)
C(47)	58(1)	43(1)	35(1)	-6(1)	29(1)	-3(1)
C(64)	44(1)	51(1)	54(1)	13(1)	36(1)	11(1)
C(66)	82(1)	102(2)	85(1)	0(1)	61(1)	-7(1)
C(13)	43(1)	45(1)	41(1)	8(1)	27(1)	8(1)
C(14)	46(1)	48(1)	45(1)	17(1)	28(1)	15(1)
C(15)	38(1)	40(1)	45(1)	3(1)	23(1)	8(1)
C(10)	34(1)	33(1)	33(1)	0(1)	20(1)	3(1)
C(41)	37(1)	36(1)	34(1)	-1(1)	23(1)	5(1)
C(51)	88(1)	51(1)	83(1)	-10(1)	41(1)	-17(1)
C(69)	47(1)	85(2)	85(1)	0(1)	35(1)	-15(1)
C(39)	45(1)	41(1)	37(1)	8(1)	31(1)	6(1)
C(4)	62(1)	71(1)	55(1)	1(1)	36(1)	26(1)
C(3)	49(1)	58(1)	41(1)	1(1)	27(1)	14(1)
C(2)	37(1)	40(1)	37(1)	0(1)	19(1)	9(1)
C(36)	49(1)	41(1)	68(1)	13(1)	45(1)	10(1)
C(33)	51(1)	39(1)	52(1)	-2(1)	38(1)	-2(1)
C(21)	78(1)	122(2)	87(1)	44(1)	60(1)	63(1)
C(19)	34(1)	42(1)	30(1)	1(1)	17(1)	4(1)
C(17)	31(1)	28(1)	34(1)	-3(1)	17(1)	0(1)
C(24)	114(2)	118(2)	74(2)	-9(2)	33(1)	52(2)
C(54)	101(2)	125(3)	80(2)	-14(2)	47(1)	-51(2)
C(53)	112(2)	72(2)	61(1)	-23(1)	43(1)	-47(1)
C(67)	84(1)	112(2)	81(1)	9(2)	48(1)	-3(2)
C(5)	64(1)	64(1)	64(1)	6(1)	35(1)	34(1)
C(44)	73(1)	39(1)	46(1)	-1(1)	30(1)	-7(1)
C(22)	65(2)	248(5)	61(2)	-27(2)	12(1)	44(2)
C(52)	110(2)	79(2)	120(2)	14(2)	70(1)	-6(2)
C(68)	108(2)	173(4)	128(2)	-36(3)	72(1)	-26(2)

Table 11. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{Ir}(\text{C}_6)_2(\text{vacac})$.

	x	y	z	U(eq)
H(63)	7349	2910	1100	66
H(6)	6840	-662	2675	72
H(35)	4238	6078	199	60
H(34)	5061	5400	1289	58
H(23A)	-311	3423	1567	80
H(23B)	-1479	3842	982	80
H(16)	1252	3215	1919	42
H(46)	15	179	-1730	68
H(43)	3046	643	686	52
H(66A)	4794	2101	-978	99
H(66B)	5505	1323	-661	99
H(13)	1910	3242	86	50
H(14)	349	3852	-123	54
H(51A)	1535	-1580	21	94
H(51B)	454	-2076	-565	94
H(69A)	7139	3492	2522	111
H(69B)	7470	3881	2016	111
H(69C)	8068	3103	2449	111
H(4)	6503	-356	747	73
H(3)	5425	736	487	59
H(36)	3102	5467	-932	56
H(33)	4774	4077	1285	51
H(21B)	-809	4543	-173	106
H(21A)	-1591	4688	111	106
H(24B)	-479	4533	2076	171
H(24C)	-607	5030	1424	171
H(24A)	557	4611	2009	171
H(54B)	-2419	-698	-2234	157
H(54A)	-1576	-49	-1680	157
H(54C)	-1900	-753	-1373	157

H(53B)	-933	-1616	-1677	103
H(53A)	-613	-915	-1987	103
H(67)	6185	2482	-1240	110
H(5)	7199	-1053	1821	78
H(44)	2064	-475	415	66
H(22B)	-2548	3955	-970	208
H(22C)	-2379	3468	-300	208
H(22A)	-1589	3313	-575	208
H(51A)	483	-1867	495	151
H(51B)	-595	-1457	-198	151
H(51C)	484	-960	388	151
H(68B)	5796	928	-1673	160
H(68A)	6289	1591	-1945	160
H(50A)	8226	4116	7664	253
H(50B)	7760	3275	7361	253
H(60A)	7562	3537	7352	253
H(60B)	8338	3024	8076	253
H(50C)	9930	3578	8140	253
H(50D)	9164	2863	7644	253
H(60C)	9774	3303	7637	253
H(60D)	8787	2677	7302	253

Table 12. Crystal data and structure refinement for $[\text{Ir}(\text{ppy})_2]_2(\mu\text{-oxalato})$

Empirical formula	C _{53.15} H _{38.31} Ir ₂ N ₄ O _{6.39}	
Formula weight	1219.54	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.9708(5) Å	α = 103.383(10)°.
	b = 13.0403(7) Å	β = 99.003(10)°.
	c = 19.3556(10) Å	γ = 98.203(10)°.
Volume	2375.9(2) Å ³	
Z	2	
Density (calculated)	1.705 Mg/m ³	
Absorption coefficient	5.650 mm ⁻¹	
F(000)	1181	
Crystal size	0.20 x 0.15 x 0.10 mm ³	
Theta range for data collection	1.10 to 29.59°.	
Index ranges	-13 ≤ h ≤ 13, -18 ≤ k ≤ 18, -26 ≤ l ≤ 26	
Reflections collected	30173	
Independent reflections	13194 [R(int) = 0.0435]	
Completeness to theta = 29.59°	98.9 %	
Absorption correction	Multiscan	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	13194 / 4 / 568	
Goodness-of-fit on F ²	1.032	
Final R indices [I > 2σ(I)]	R1 = 0.0420, wR2 = 0.1010	
R indices (all data)	R1 = 0.0652, wR2 = 0.1157	
Largest diff. peak and hole	2.452 and -1.148 e.Å ⁻³	

Table 13. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Ir}(\text{ppy})_2]_2(\mu\text{-oxalato})$. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U(\text{eq})$
Ir(1)	3334(1)	1335(1)	4463(1)	28(1)
Ir(2)	3628(1)	6272(1)	951(1)	34(1)
O(1)	5412(2)	6379(1)	414(1)	39(1)
O(2)	3477(2)	4626(1)	301(1)	37(1)
O(3)	3710(2)	599(1)	5367(1)	33(1)
O(4)	5112(2)	569(1)	4275(1)	32(1)
N(1)	1901(2)	6(2)	3930(1)	33(1)
N(2)	4756(2)	2710(2)	4930(1)	34(1)
N(3)	2281(2)	6576(2)	153(1)	42(1)
N(4)	4914(2)	6070(2)	1806(1)	40(1)
C(01)	2179(3)	-869(2)	3487(1)	40(1)
C(02)	5362(3)	8953(2)	2728(2)	52(1)
C(03)	-917(3)	2301(2)	5012(2)	54(1)
C(04)	1174(3)	-1734(2)	3121(2)	56(1)
C(05)	3971(4)	9680(2)	1908(2)	61(1)
C(6)	1647(2)	1853(2)	4705(1)	31(1)
C(06)	4858(3)	9823(2)	2555(2)	56(1)
C(07)	3282(3)	3160(2)	2578(2)	53(1)
C(08)	-44(4)	6673(2)	-291(2)	64(1)
C(13)	4041(2)	7771(2)	1570(1)	39(1)
C(14)	1901(3)	6017(2)	1318(1)	40(1)
C(16)	414(2)	1069(2)	4463(1)	35(1)
C(17)	3209(2)	2006(2)	3641(1)	33(1)
C(19)	715(3)	6147(2)	874(2)	47(1)
C(20)	5557(2)	5501(2)	36(1)	33(1)
C(21)	6101(3)	4225(2)	4733(2)	52(1)
C(22)	4606(2)	4(2)	5314(1)	29(1)
C(24)	1524(3)	2874(2)	5104(1)	39(1)
C(27)	5024(2)	3346(2)	4493(1)	38(1)
C(28)	6861(3)	4483(2)	5428(2)	58(1)

C(29)	5433(2)	6975(2)	2366(1)	41(1)
C(30)	-602(3)	5982(3)	1063(2)	63(1)
C(32)	3530(3)	8666(2)	1402(2)	50(1)
C(33)	5299(3)	5126(2)	1848(1)	44(1)
C(34)	4938(2)	7919(2)	2235(1)	40(1)
C(35)	2347(3)	1619(2)	2959(1)	43(1)
C(41)	4115(3)	2988(2)	3770(1)	38(1)
C(42)	-841(3)	1306(2)	4623(2)	45(1)
C(43)	5511(2)	2955(2)	5606(1)	40(1)
C(46)	414(3)	5511(3)	2122(2)	60(1)
C(47)	577(2)	48(2)	4019(1)	36(1)
C(48)	6345(3)	6914(2)	2978(2)	45(1)
C(49)	2658(4)	6921(2)	-414(2)	58(1)
C(52)	-463(3)	-823(2)	3667(2)	54(1)
C(53)	6744(3)	5942(3)	3005(2)	53(1)
C(56)	945(3)	6473(2)	229(2)	49(1)
C(61)	6224(3)	5032(3)	2439(2)	50(1)
C(65)	1729(3)	5682(2)	1948(2)	49(1)
C(66)	4150(3)	3550(2)	3240(2)	53(1)
C(67)	346(4)	7010(3)	-840(2)	75(1)
C(68)	-158(3)	-1718(2)	3217(2)	61(1)
C(74)	2389(3)	2186(2)	2429(2)	52(1)
C(75)	1708(4)	7145(3)	-920(2)	72(1)
C(77)	-719(3)	5675(3)	1692(2)	67(1)
C(80)	6554(3)	3845(2)	5873(2)	49(1)
C(85)	273(3)	3086(2)	5251(2)	52(1)
O(101)	8233(4)	4214(2)	3525(2)	110(1)
C(101)	9843(4)	3118(4)	3249(3)	100(2)
C(102)	8491(4)	3319(3)	3307(2)	73(1)
C(103)	7362(5)	2377(3)	3072(3)	96(2)
O(111)	8948(7)	10693(5)	1557(3)	203(2)
C(111)	7673(10)	9055(7)	1332(5)	203(2)
C(112)	8816(11)	9783(8)	1367(4)	203(2)
C(113)	9966(10)	9208(7)	1237(5)	203(2)
O(121)	4750(16)	7823(12)	8716(8)	270
C(123)	7149(9)	8225(11)	9505(9)	270

C(122)	5718(8)	8544(7)	9366(5)	270
C(121)	4737(12)	9341(9)	9594(9)	270

Table 14. Bond lengths [Å] and angles [°] for [Ir(ppy)₂]₂(μ-oxalato).

Ir(1)-C(17)	1.982(3)
Ir(1)-C(6)	1.982(2)
Ir(1)-N(1)	2.0288(17)
Ir(1)-N(2)	2.0402(17)
Ir(1)-O(3)	2.1901(18)
Ir(1)-O(4)	2.1935(16)
Ir(2)-C(14)	1.977(3)
Ir(2)-C(13)	1.989(2)
Ir(2)-N(4)	2.022(2)
Ir(2)-N(3)	2.033(2)
Ir(2)-O(2)	2.1938(16)
Ir(2)-O(1)	2.2004(18)
O(1)-C(20)	1.249(3)
O(2)-C(20)#1	1.253(3)
O(3)-C(22)	1.264(3)
O(4)-C(22)#2	1.241(3)
N(1)-C(01)	1.352(3)
N(1)-C(47)	1.364(3)
N(2)-C(27)	1.345(4)
N(2)-C(43)	1.345(3)
N(3)-C(56)	1.354(4)
N(3)-C(49)	1.362(4)
N(4)-C(33)	1.356(4)
N(4)-C(29)	1.376(3)
C(01)-C(04)	1.365(3)
C(02)-C(06)	1.392(5)
C(02)-C(34)	1.423(4)
C(03)-C(42)	1.360(4)
C(03)-C(85)	1.390(4)
C(04)-C(68)	1.372(4)

C(05)-C(06)	1.372(4)
C(05)-C(32)	1.414(4)
C(6)-C(24)	1.409(3)
C(6)-C(16)	1.420(3)
C(07)-C(66)	1.370(4)
C(07)-C(74)	1.384(4)
C(08)-C(67)	1.331(6)
C(08)-C(56)	1.391(5)
C(13)-C(34)	1.403(3)
C(13)-C(32)	1.422(4)
C(14)-C(19)	1.405(4)
C(14)-C(65)	1.413(4)
C(16)-C(42)	1.395(4)
C(16)-C(47)	1.453(3)
C(17)-C(35)	1.395(3)
C(17)-C(41)	1.403(3)
C(19)-C(30)	1.419(4)
C(19)-C(56)	1.448(5)
C(20)-O(2)#1	1.253(3)
C(20)-C(20)#1	1.553(5)
C(21)-C(28)	1.377(4)
C(21)-C(27)	1.389(3)
C(22)-O(4)#2	1.241(3)
C(22)-C(22)#2	1.546(5)
C(24)-C(85)	1.374(4)
C(27)-C(41)	1.476(3)
C(28)-C(80)	1.367(5)
C(29)-C(48)	1.402(4)
C(29)-C(34)	1.449(4)
C(30)-C(77)	1.382(5)
C(33)-C(61)	1.393(4)
C(35)-C(74)	1.399(4)
C(41)-C(66)	1.394(4)
C(43)-C(80)	1.381(3)
C(46)-C(77)	1.369(5)
C(46)-C(65)	1.404(4)

C(47)-C(52)	1.384(3)
C(48)-C(53)	1.391(5)
C(49)-C(75)	1.366(5)
C(52)-C(68)	1.388(4)
C(53)-C(61)	1.387(4)
C(67)-C(75)	1.381(6)
O(101)-C(102)	1.225(5)
C(101)-C(102)	1.426(6)
C(102)-C(103)	1.472(5)
O(111)-C(112)	1.140(11)
C(111)-C(112)	1.357(13)
C(112)-C(113)	1.479(14)
O(121)-C(122)	1.487(16)
C(123)-C(122)	1.543(12)
C(122)-C(121)	1.564(13)

C(17)-Ir(1)-C(6)	89.67(10)
C(17)-Ir(1)-N(1)	95.05(8)
C(6)-Ir(1)-N(1)	80.61(8)
C(17)-Ir(1)-N(2)	80.70(9)
C(6)-Ir(1)-N(2)	99.39(8)
N(1)-Ir(1)-N(2)	175.75(9)
C(17)-Ir(1)-O(3)	173.80(8)
C(6)-Ir(1)-O(3)	96.13(8)
N(1)-Ir(1)-O(3)	88.09(7)
N(2)-Ir(1)-O(3)	96.13(7)
C(17)-Ir(1)-O(4)	98.11(8)
C(6)-Ir(1)-O(4)	171.31(8)
N(1)-Ir(1)-O(4)	94.79(7)
N(2)-Ir(1)-O(4)	85.75(7)
O(3)-Ir(1)-O(4)	76.26(6)
C(14)-Ir(2)-C(13)	89.42(10)
C(14)-Ir(2)-N(4)	96.76(10)
C(13)-Ir(2)-N(4)	80.97(10)
C(14)-Ir(2)-N(3)	80.49(10)
C(13)-Ir(2)-N(3)	94.81(10)

N(4)-Ir(2)-N(3)	175.03(9)
C(14)-Ir(2)-O(2)	96.91(8)
C(13)-Ir(2)-O(2)	172.19(8)
N(4)-Ir(2)-O(2)	93.69(8)
N(3)-Ir(2)-O(2)	90.77(7)
C(14)-Ir(2)-O(1)	172.27(7)
C(13)-Ir(2)-O(1)	97.64(9)
N(4)-Ir(2)-O(1)	87.49(8)
N(3)-Ir(2)-O(1)	95.72(8)
O(2)-Ir(2)-O(1)	76.32(6)
C(20)-O(1)-Ir(2)	114.08(15)
C(20)#1-O(2)-Ir(2)	114.14(14)
C(22)-O(3)-Ir(1)	113.80(15)
C(22)#2-O(4)-Ir(1)	113.85(15)
C(01)-N(1)-C(47)	119.96(19)
C(01)-N(1)-Ir(1)	124.15(16)
C(47)-N(1)-Ir(1)	115.84(15)
C(27)-N(2)-C(43)	119.3(2)
C(27)-N(2)-Ir(1)	115.78(15)
C(43)-N(2)-Ir(1)	124.61(18)
C(56)-N(3)-C(49)	119.8(3)
C(56)-N(3)-Ir(2)	116.0(2)
C(49)-N(3)-Ir(2)	124.1(2)
C(33)-N(4)-C(29)	119.8(2)
C(33)-N(4)-Ir(2)	124.46(16)
C(29)-N(4)-Ir(2)	115.77(19)
N(1)-C(01)-C(04)	122.2(3)
C(06)-C(02)-C(34)	119.5(3)
C(42)-C(03)-C(85)	119.4(3)
C(01)-C(04)-C(68)	118.7(3)
C(06)-C(05)-C(32)	122.2(3)
C(24)-C(6)-C(16)	116.4(2)
C(24)-C(6)-Ir(1)	128.67(16)
C(16)-C(6)-Ir(1)	114.85(16)
C(05)-C(06)-C(02)	119.9(3)
C(66)-C(07)-C(74)	119.6(3)

C(67)-C(08)-C(56)	119.5(3)
C(34)-C(13)-C(32)	119.1(2)
C(34)-C(13)-Ir(2)	114.1(2)
C(32)-C(13)-Ir(2)	126.83(18)
C(19)-C(14)-C(65)	117.7(3)
C(19)-C(14)-Ir(2)	114.6(2)
C(65)-C(14)-Ir(2)	127.6(2)
C(42)-C(16)-C(6)	121.1(2)
C(42)-C(16)-C(47)	124.4(2)
C(6)-C(16)-C(47)	114.4(2)
C(35)-C(17)-C(41)	117.0(2)
C(35)-C(17)-Ir(1)	128.12(19)
C(41)-C(17)-Ir(1)	114.86(17)
C(14)-C(19)-C(30)	121.1(3)
C(14)-C(19)-C(56)	115.5(3)
C(30)-C(19)-C(56)	123.4(3)
O(1)-C(20)-O(2)#1	124.7(2)
O(1)-C(20)-C(20)#1	117.7(3)
O(2)#1-C(20)-C(20)#1	117.7(2)
C(28)-C(21)-C(27)	120.6(3)
O(4)#2-C(22)-O(3)	124.8(2)
O(4)#2-C(22)-C(22)#2	118.2(3)
O(3)-C(22)-C(22)#2	117.0(3)
C(85)-C(24)-C(6)	121.2(2)
N(2)-C(27)-C(21)	120.0(2)
N(2)-C(27)-C(41)	113.6(2)
C(21)-C(27)-C(41)	126.4(3)
C(80)-C(28)-C(21)	118.8(3)
N(4)-C(29)-C(48)	119.8(3)
N(4)-C(29)-C(34)	113.1(2)
C(48)-C(29)-C(34)	127.2(2)
C(77)-C(30)-C(19)	119.3(3)
C(05)-C(32)-C(13)	118.5(3)
N(4)-C(33)-C(61)	122.5(2)
C(13)-C(34)-C(02)	120.8(3)
C(13)-C(34)-C(29)	116.1(2)

C(02)-C(34)-C(29)	123.1(2)
C(17)-C(35)-C(74)	121.3(2)
C(66)-C(41)-C(17)	121.4(2)
C(66)-C(41)-C(27)	123.8(2)
C(17)-C(41)-C(27)	114.8(2)
C(03)-C(42)-C(16)	120.7(2)
N(2)-C(43)-C(80)	122.4(3)
C(77)-C(46)-C(65)	120.9(3)
N(1)-C(47)-C(52)	119.3(2)
N(1)-C(47)-C(16)	113.95(18)
C(52)-C(47)-C(16)	126.6(2)
C(53)-C(48)-C(29)	119.6(2)
N(3)-C(49)-C(75)	121.2(3)
C(68)-C(52)-C(47)	119.9(3)
C(61)-C(53)-C(48)	120.5(3)
N(3)-C(56)-C(08)	119.7(3)
N(3)-C(56)-C(19)	113.4(3)
C(08)-C(56)-C(19)	126.9(3)
C(53)-C(61)-C(33)	117.9(3)
C(46)-C(65)-C(14)	120.3(3)
C(07)-C(66)-C(41)	120.5(3)
C(08)-C(67)-C(75)	121.8(4)
C(04)-C(68)-C(52)	119.9(3)
C(07)-C(74)-C(35)	120.2(3)
C(49)-C(75)-C(67)	117.9(4)
C(46)-C(77)-C(30)	120.7(3)
C(28)-C(80)-C(43)	118.9(3)
C(24)-C(85)-C(03)	121.2(3)
O(101)-C(102)-C(101)	123.8(4)
O(101)-C(102)-C(103)	119.8(4)
C(101)-C(102)-C(103)	116.4(4)
O(111)-C(112)-C(111)	126.7(11)
O(111)-C(112)-C(113)	123.8(10)
C(111)-C(112)-C(113)	108.7(9)
O(121)-C(122)-C(123)	114.0(10)
O(121)-C(122)-C(121)	97.5(9)

C(123)-C(122)-C(121) 148.5(9)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z #2 -x+1,-y,-z+1

Table 15. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Ir}(\text{ppy})_2]_2(\mu\text{-oxalato})$.The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Ir(1)	24(1)	25(1)	34(1)	6(1)	5(1)	4(1)
Ir(2)	31(1)	34(1)	33(1)	0(1)	7(1)	2(1)
O(1)	36(1)	36(1)	39(1)	2(1)	7(1)	-1(1)
O(2)	32(1)	37(1)	37(1)	0(1)	8(1)	1(1)
O(3)	26(1)	35(1)	38(1)	9(1)	7(1)	6(1)
O(4)	26(1)	33(1)	38(1)	8(1)	9(1)	5(1)
N(1)	29(1)	31(1)	40(1)	12(1)	5(1)	3(1)
N(2)	30(1)	29(1)	41(1)	3(1)	8(1)	4(1)
N(3)	43(1)	34(1)	39(1)	-3(1)	5(1)	4(1)
N(4)	29(1)	49(1)	38(1)	5(1)	12(1)	-3(1)
C(01)	36(1)	33(1)	48(1)	6(1)	11(1)	1(1)
C(02)	36(1)	54(2)	53(1)	-7(1)	17(1)	-6(1)
C(03)	38(1)	61(2)	71(2)	17(1)	23(1)	26(1)
C(04)	51(2)	35(1)	69(2)	-5(1)	15(1)	-2(1)
C(05)	79(2)	43(2)	55(2)	0(1)	23(1)	7(1)
C(6)	33(1)	28(1)	31(1)	10(1)	4(1)	5(1)
C(06)	58(2)	44(2)	61(2)	-1(1)	23(1)	-2(1)
C(07)	67(2)	51(1)	53(1)	28(1)	19(1)	16(1)
C(08)	58(2)	51(2)	70(2)	2(2)	-11(2)	18(1)
C(13)	34(1)	39(1)	40(1)	-1(1)	11(1)	4(1)
C(14)	39(1)	31(1)	41(1)	-7(1)	10(1)	-1(1)
C(16)	29(1)	32(1)	44(1)	11(1)	5(1)	5(1)
C(17)	30(1)	32(1)	40(1)	10(1)	10(1)	10(1)
C(19)	34(1)	37(1)	58(2)	-8(1)	5(1)	3(1)
C(20)	30(1)	36(1)	27(1)	3(1)	3(1)	1(1)

C(21)	50(1)	33(1)	64(2)	4(1)	15(1)	-12(1)
C(22)	24(1)	27(1)	32(1)	6(1)	3(1)	0(1)
C(24)	36(1)	37(1)	42(1)	7(1)	7(1)	7(1)
C(27)	31(1)	31(1)	46(1)	-1(1)	11(1)	-2(1)
C(28)	35(1)	40(1)	81(2)	-7(1)	7(1)	-5(1)
C(29)	28(1)	49(1)	37(1)	1(1)	10(1)	-6(1)
C(30)	36(1)	54(2)	80(2)	-13(2)	9(1)	1(1)
C(32)	54(1)	40(1)	54(1)	4(1)	21(1)	5(1)
C(33)	44(1)	48(1)	43(1)	12(1)	17(1)	3(1)
C(34)	31(1)	47(1)	37(1)	2(1)	11(1)	0(1)
C(35)	45(1)	44(1)	39(1)	13(1)	4(1)	7(1)
C(41)	42(1)	31(1)	44(1)	10(1)	15(1)	5(1)
C(42)	29(1)	46(1)	61(2)	16(1)	10(1)	2(1)
C(43)	31(1)	42(1)	42(1)	-1(1)	9(1)	5(1)
C(46)	57(1)	56(2)	59(2)	-4(1)	31(1)	-10(1)
C(47)	28(1)	33(1)	47(1)	12(1)	6(1)	6(1)
C(48)	32(1)	57(2)	42(1)	10(1)	8(1)	-4(1)
C(49)	70(2)	49(2)	47(2)	6(1)	2(1)	11(1)
C(52)	34(1)	43(1)	72(2)	-1(1)	10(1)	-5(1)
C(53)	39(1)	77(2)	44(1)	23(1)	9(1)	1(1)
C(56)	43(1)	38(1)	54(2)	-7(1)	0(1)	4(1)
C(61)	43(1)	63(2)	44(1)	16(1)	11(1)	1(1)
C(65)	44(1)	50(2)	47(1)	-2(1)	18(1)	-1(1)
C(66)	64(2)	33(1)	65(2)	14(1)	22(1)	3(1)
C(67)	78(2)	61(2)	75(2)	13(2)	-19(2)	24(2)
C(68)	40(1)	44(2)	81(2)	-6(2)	11(1)	-13(1)
C(74)	61(2)	49(1)	46(1)	13(1)	6(1)	9(1)
C(75)	92(2)	75(2)	48(2)	22(1)	-5(2)	23(2)
C(77)	43(1)	63(2)	77(2)	-13(2)	28(1)	-9(1)
C(80)	37(1)	44(1)	48(2)	-10(1)	-2(1)	2(1)
C(85)	50(1)	44(1)	62(2)	6(1)	17(1)	18(1)
O(101)	132(2)	71(2)	127(3)	13(2)	18(2)	43(2)
C(101)	59(2)	111(3)	131(4)	45(3)	2(2)	10(2)
C(102)	79(2)	61(2)	77(2)	20(2)	1(2)	23(2)
C(103)	102(3)	58(2)	117(3)	21(2)	-1(3)	8(2)

Table 16. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Ir}(\text{ppy})_2]_2(\mu\text{-oxalato})$.

	x	y	z	U(eq)
H(01)	3105	-883	3428	48
H(03)	-1774	2458	5119	64
H(04)	1393	-2335	2806	67
H(07)	3293	3555	2223	64
H(08)	-990	6570	-254	77
H(21)	6316	4653	4415	63
H(24)	2321	3425	5275	46
H(28)	7585	5092	5595	69
H(30)	-1395	6080	761	76
H(35)	1719	957	2853	51
H(42)	-1651	767	4459	55
H(43)	5319	2499	5910	48
H(46)	309	5277	2544	72
H(49)	3601	7007	-457	69
H(52)	-1385	-809	3733	64
H(65)	2507	5571	2255	59
H(66)	4780	4210	3340	64
H(67)	-330	7162	-1187	90
H(68)	-870	-2318	2976	73
H(74)	1804	1902	1966	63
H(75)	1974	7386	-1314	87
H(77)	-1595	5578	1827	80
H(80)	7051	4011	6358	58
H(85)	220	3783	5521	62
H(10A)	10505	3798	3409	150
H(10B)	9853	2773	2743	150
H(10C)	10099	2645	3554	150
H(10D)	6481	2609	3120	144
H(10E)	7525	1882	3374	144
H(10F)	7330	2013	2565	144

H(11A)	6887	9420	1384	305
H(11B)	7839	8700	1724	305
H(11C)	7468	8518	864	305
H(11D)	10774	9718	1219	305
H(11E)	9685	8656	776	305
H(11F)	10199	8869	1631	305
H(12A)	7135	7533	9169	405
H(12B)	7368	8167	10004	405
H(12C)	7851	8773	9429	405
H(12D)	3806	9058	9301	405
H(12E)	5086	10039	9516	405
H(12F)	4703	9427	10107	405

Appendix B: Techniques

1) ITO preparation and etching

Etching of the ITO plate was performed as follows: The ITO plates were first cleaned by placing the plate in a 20% by weight solution of ethanolamine in deionized water in an ultrasonic bath for 20 minutes. The areas of ITO that were to remain intact were first protected using nailpolish and the plate was left to dry overnight. The plate was then placed in a beaker containing an aqueous solution of 20% HCl, 5% HNO₃, and a few drops of liquid detergent. The solution was heated to between 50 and 60 °C for approximately five minutes. The plate is then rinsed in a 10% aqueous solution of Na₂CO₃. The resistance of the etched portions of the plate was then tested, and the procedure was repeated, if necessary, until a maximum resistance (20 MΩ) was measured using a multimeter. The masking was then removed from the protected portions using acetone.

2) OTTLE experiment with ITO electrode: Troubleshooting

When an ITO (on quartz) plate is used in the OTTLE experiment, an interference pattern is sometimes noted in the UV-vis spectrum. The appearance of a “rainbow” effect in the cell can be noted visually and the pattern in the electronic spectrum consists of a wavy line of varying amplitude. This interference pattern could not be removed by background subtraction and was only found to occur when the ITO plate was placed directly on the bottom quartz plate in the OTTLE cell. To avoid this interference pattern, the bottom quartz plate was removed, and was replaced with a plastic spacer of the same thickness with an opening of appropriate size to allow for the transmission of light through the cell.

3) Ag/AgCl reference electrode preparation

Two strips of silver wire with known diameter and length were twisted together. The wire was soaked in 3M HNO₃ for five minutes and rinsed with deionized water. A standard H-cell with working, counter, and reference electrodes was set up using the coiled silver wire as the working electrode and 0.1 M HCl as the electrolyte. The current of the cell was adjusted such that the current density is 0.4 mA/cm² of silver wire, and the cell was left for thirty minutes. The Ag/AgCl electrode was then rinsed with deionized water and left to dry.

4) Glove box indicator preparation

Titanocene (500 mg) was dissolved in a small volume of toluene (dried and distilled; 50 mL) and was poured into a small dropper bottle containing zinc powder (500 mg). The mixture changed colour from red/orange to deep blue/green over a period of a few days. Two drops of the indicator were placed on a watch glass in the glove box. If the solution remained blue/green while the toluene evaporated, then the glove box environment was acceptable (oxygen free). If the colour returned to orange, a glove box regeneration was necessary.