**Luminescent Water-Soluble Oxygen-Sensor Films and Their
Application in Pressure Sensitive Paints**

by

Arezoo Habibagahi, M.Sc.

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in partial fulfillment of the requirements for the degree of
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Abstract

Luminescent water-soluble oxygen sensors have been prepared by bonding iridium complexes to inexpensive water-soluble polymers, such as poly(ethylene glycol) methyl ether-aldehyde (PEGME-Aldehyde) or Silamine D208-EDA. The luminescent iridium complexes, $[\text{Ir}(\text{fppy})_2(t\text{-Bu-iCN})_2][\text{CF}_3\text{SO}_3]$, $[\text{Ir}(\text{C}_6)_2(\text{acacacid})]$, $[\text{Ir}(\text{ppy})_2(\text{amppy})\text{Cl}]$, $[\text{Ir}(\text{ppy})_2(\text{phendiald})][\text{PF}_6]$, where $\text{fppy} = 4\text{-(2-pyridyl)benzaldehyde}$, $t\text{-Bu-iCN} = \text{tert-butyl isocyanide}$, $\text{C}_6 = 3\text{-(2'-benzothiazolyl)-7-N,N-diethylaminocoumarin}$, $\text{acacacid} = 4,6\text{-dioxoheptanoic acid}$, $\text{ppy} = 2\text{-phenylpyridine}$, $\text{amppy} = 5\text{-aminomethyl-2-phenylpyridine}$, and $\text{phendiald} = 1,10\text{-phenanthroline-2,9-dicarboxaldehyde}$, have been synthesized and characterized by nuclear magnetic resonance, absorption and emission spectroscopies. These complexes along with $[\text{Ir}(\text{tpy})_2(t\text{-Bu-iCN})_2][\text{CF}_3\text{SO}_3]$ and $[\text{Ir}(\text{ppy})_2(\text{fppy})]$, where $\text{tpy} = 2\text{-(p-tolyl)pyridine}$, were dispersed in or covalently attached to functionalized water-soluble polymers by reductive amination or coupling reactions. Aqueous blends of these water-soluble luminophores with colloidal microcrystalline cellulose (MC) were used to prepare oxygen sensor films, otherwise known as pressure sensitive paints (PSPs). Oxygen sensitivities of these PSPs were determined as a function of blended MC and obeyed Stern-Volmer kinetics. These novel materials offer an environmentally friendly alternative to non-aqueous PSP formulations and provide improved workplace safety, and lower contamination.

Oxygen quenching sensitivity data (slope of a linear fit to the modified Stern-Volmer plot) for water-soluble luminophores composed of Silamine-attached $[\text{Ir}(\text{fppy})_2(t\text{-}$

$\text{Bu-iCN})_2][\text{CF}_3\text{SO}_3]$ and $[\text{Ir}(\text{ppy})_2(\text{fppy})]$ are between 0.4 and 0.5, which are appropriate for pressure sensitive paint applications. Investigation of luminescence microscopy and solid state lifetime measurements revealed that the preferential binding of the luminophore to MC increased its luminescence lifetime and was primarily responsible for the improved oxygen quenching sensitivity of PSP films that include MC.

The temperature dependence of luminescence was examined between 10 to 40 °C for a number of PSPs and gave temperature sensitivities (percent emission intensity loss per degree) of between -0.8% and -1.6% °C⁻¹ at 1 bar atmospheric pressure.

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List of Abbreviations

acac	Acetylacetonate
acacacid	4,6-Dioxoheptanoic acid
AIBN	Azobisisobutyronitrile
amppy	5-Aminomethyl-2-phenylpyridine
bpy	2,2'-Bipyridine
C ₆	3-(2'-Benzothiazolyl)-7-N,N-diethylaminocoumarin
CN- <i>t</i> -Bu	tert-butyl isocyanide
COSY	Correlation spectroscopy
DCC	N,N'-dicyclohexylcarbodiimide
DEAD	Diethylazodicarboxylate
dpp	diphenylphenanthroline
Φ	Luminescence quantum yield
FIB	Poly(hexafluoroisopropyl- <i>co</i> -heptafluoro- <i>n</i> -butyl methacrylate)
fppy	4-(2-Pyridyl)benzaldehyde
H ₂ TMpyp-4	5,10,15,20-tetrakis(1-methyl-4-pyridyl)-21H,23H-porphine
HOMO	Highest occupied molecular orbital
k_l	Radiative decay (luminescence) rate
k_{nr}	Non-radiative decay rate
k_q	Bimolecular quenching constant
K_{SV}	Stern-Volmer quenching constant

LEC	Light-emitting electrochemical cell
LUMO	Lowest unoccupied molecular orbital
MC	Microcrystalline cellulose
MLCT	Metal-to-ligand charge-transfer
OEP	Octaethylporphine
OEPK	Octaethylporphyrin ketones
OLED	Organic light-emitting diode
OTf	Trifluoromethanesulfonate
PBA	1-Pyrenebutyric acid
PDMS	Poly(dimethylsiloxane)
PDMS-based copolymer	Dimethylsiloxane-(60% propylene oxide- 40% ethylene oxide) block polymer
PEGME	Poly(ethylene glycol) methyl ether
phendiald	1,10-Phenanthroline-2,9-dicarboxaldehyde
ppy	2-Phenylpyridine
PSP	Pressure sensitive paint
PVA	Polyvinylalcohol
Q_s	Oxygen quenching sensitivity
τ	Luminescence lifetime
TFPP	Tetrakis(pentafluorophenyl) porphyrin
Tg	Glass transition temperature
TMpyp-4	5,10,15,20-Tetrakis(1-methyl-4-pyridyl)-porphine
TMS	Tetramethylsilane

TMSP	1-Trimethylsilyl-1-propyne
tpy	2-(<i>p</i> -Tolyl)pyridine

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Chapter 1

Introduction

1.1 Optical Oxygen Sensors

Various oxygen measurement techniques have been described in the literature including amperometric,¹ paramagnetic,² thermoluminescence,³ and chemiluminescence⁴ methods. Clark electrodes offer a standard and trusted technique for oxygen measurement. The method is based on the reduction of oxygen at the cathode. However, parameters affecting diffusion of oxygen, and electrical interference can lead to inaccuracy in the measurements. Furthermore, since oxygen is consumed, the method can be inappropriate for a number of practical applications. Another disadvantage of these sensors is their limited lifetime due to the consumption of the electrolyte by the oxygen being reduced. Therefore, improvement of novel non-destructive oxygen measurement methods is of considerable interest. Paramagnetic sensors exploit the fundamental magnetic field distortion by oxygen, and are applied in gas analysis.² One of the current techniques in the field is optical oxygen sensors. Reduction of luminescence intensity of organic luminophores in presence of oxygen was first reported and the mechanism of emission loss explained in 1935.⁵ Research in optical oxygen sensors has found application in a variety of fields including in vivo imaging,⁶ aerodynamics,⁷ environmental analysis,⁸ analytical chemistry,⁹ food industry,¹⁰ and biochemistry.¹¹ Data

are sent out as emitted light signals in these sensors. Optical oxygen sensors are required to be low-cost and easy to apply with no electrical interference.

1.2 Photophysical Properties of Oxygen Sensor Luminophores

Spontaneous emission of light or photoluminescence is generated in particular compounds after excitation, as illustrated in the Jablonski diagram (Figure 1.1). Vertical lines symbolize that molecular nuclei are stationary during electronic transitions. Absorption of light with appropriate wavelength results in several radiative and non-radiative processes. Usually the luminophore is excited to a higher vibrational level of an electronic singlet excited state, S₁. Relaxation to the lowest vibrational level may happen by internal conversion. Once the excited molecule restores to the ground state, it emits a longer wavelength light compared to the initial light. A short-lived emission from a singlet (spin-paired electrons) excited state is fluorescence. Because there is no change in spin multiplicity in transition from the excited singlet state to the ground state, the lifetime of an excited singlet state and consequently the decay time of spin-allowed fluorescence are normally short (10^{-9} to 10^{-7} s). Intersystem crossing from the singlet excited state to the triplet state can also take place. The transition from the first excited triplet state to the ground state has a low probability, as long-lived phosphorescence (10^{-5} to 10 s)¹² is associated with a change in electron spin. The presence of an atom with a high atomic number can enhance the rate of the spin-forbidden transitions by “heavy atom effect” which is due to spin-orbit coupling of the excited molecule.

Phosphorescence appears at longer wavelengths compared with fluorescence, which is due to the relative energies of the excited states.

The energy difference between absorption and emission is called Stokes shift. It occurs when excited vibrational levels of the excited state is populated. Internal conversion to the zeroth vibrational level of the excited state decreases the energy of the excited state and so emission occurs at significantly lower energies than absorption.

An excited molecule may also undergo non-radiative decay from an excited state to a ground state which is basically the conversion of electronic excitation into vibrational and rotational energies in the molecule or its environment. The probability of intramolecular energy transfer between two electronic states is inversely proportional to the energy gap, ΔE , between the two states (energy gap law). Therefore, the non-radiative rate constant is reduced by the size of the energy gap between the two states.

Figure 1.1: Jablonski diagram

The average time the molecule remains in its excited state prior to emitting a photon is termed luminescence lifetime which is an important parameter for sensor applications. The excited state de-population rate is the sum of all radiative and non-radiative processes and the luminescence lifetime is the inverse of the decay rate:

$$\tau = \frac{1}{k_l + k_{nr}} \quad (1.1)$$

where k_l is the radiative decay (luminescence) rate and k_{nr} is the non-radiative decay rate. The efficiency of the luminescence is shown by the luminescence quantum yield, which is the ratio of the number of photons emitted to the number of photons absorbed.

$$\Phi = \frac{\text{Number of photons emitted}}{\text{Number of photons absorbed}} \quad (1.2)$$

The luminescence quantum yield can be determined by the excited state decay rates as well:

$$\Phi = \frac{k_l}{\sum_i k_i} \quad (1.3)$$

where k_l is the radiative decay (luminescence) rate and k_i is any radiative or non-radiative excited state decay rate.

1.3 Energy Transfer Mechanisms and Luminescence Quenching

Theodor Förster proposed a mechanism for energy transfer between different molecules.¹³ Initially, the light is absorbed by the luminophore. Due to internal conversion, this “donor” luminophore relaxes to an excited electronic state that can resonance with an excited state of an "acceptor" molecule. In this mechanism, energy transfer is determined by three parameters. Overlapping of the luminescence spectrum of the donor and the absorption spectrum of the acceptor, termed as Förster’s overlap integral, is one of the factors controlling the probability of energy transfer. Another parameter is the distance between the donor and the acceptor molecules, since the interaction between molecules is a dipole-dipole interaction. The third factor is the orientation of the dipoles of the two molecules. The rate of energy transfer is represented in terms of an effective distance, R_0 , the distance between the donor and the acceptor (r), and the luminescence lifetime of the donor (τ_l):

$$k_{ET} = \frac{1}{\tau_l} \left(\frac{R_0}{r} \right)^6 \quad (1.4)$$

Another energy transfer mechanism is the Dexter mechanism.¹⁴ As is shown in Figure 1.2, when the interaction energy between the two molecules is high and the molecules are in close proximity, it is possible that the excited electron is exchanged between the donor and acceptor molecules. The relative energies of the HOMO and LUMO of the two molecules are shown in Figure 1.2.

Figure 1.2: Dexter energy transfer, where D is the donor and A is the acceptor molecule.

Excited state quenching can be collisional and static. When energy transfer from the excited luminophore to the quencher occurs through molecular collisions, it is called collisional quenching. As shown in Scheme 1.1, the luminophore is relaxed to its ground state by a non-radiative decay process and both the luminescence quantum yield and lifetime decrease consequently.¹⁵

Scheme 1.1: Schematic explanation of dynamic quenching

In static quenching a non-luminescent complex is formed between the luminophore and the quencher. Scheme 1.2 describes the static quenching process. In this case, the luminescence lifetime of the uncomplexed luminophore is unchanged.

Non-luminescent

Scheme 1.2: Schematic explanation of static quenching.

Long-lived triplet state excited molecules are principally subject to interactions with other molecules. Diffusion-limited collisional oxygen quenching is described by the Stern-Volmer relationship, in which both luminescence lifetime and intensity are applicable.

$$\frac{I_0}{I} = \frac{\tau_0}{\tau} = 1 + k_q \tau_0 [O_2] = 1 + K_{SV} (p_{O_2}) \quad (1.5)$$

where I_0 and I are the luminescence intensities, and τ_0 and τ are the lifetimes in the absence and presence of oxygen, respectively, k_q is the bimolecular quenching constant, and K_{SV} is the Stern-Volmer constant. k_q is described by a modified Smoluchowski equation¹⁶:

$$k_q = 4\pi N_p (D_A + D_B) \times 10^3 \quad (1.6)$$

where N is Avogadro's number, p is a factor representing the probability of a collision resulting in quenching and relates to the radius of interaction between the donor (luminophore) and the acceptor (oxygen), and D_A and D_B are the diffusion coefficients of the donor and acceptor, respectively. Normally, k_q is considered constant under defined experimental conditions.

In describing static quenching, the complex formation equilibrium constant for the non-luminescent complex is taken into account:

$$K_s = \frac{[D \cdot Q]}{[D][Q]} \quad (1.7)$$

where $[D \cdot Q]$, $[D]$, and $[Q]$ are the complex, luminophore, and quencher concentrations, respectively. The luminescence intensity is dependent on the uncomplexed luminophore concentration ($[D]$). Considering:

$$[D \cdot Q] = [D_0] - [D] \quad (1.8)$$

where $[D_0]$ is the total concentration of luminophore, and replacing it into equation (1.7) results in:

$$K_s = \frac{[D_0]}{[D][Q]} - \frac{1}{[Q]} \quad (1.9)$$

Substituting luminophore concentrations with luminescence intensities gives:

$$\frac{I_0}{I} = 1 + K_s [Q] \quad (1.10)$$

Equation (1.10) has the same form as that of equation (1.5) which is defined for collisional quenching.

For quenching by oxygen, a single luminophore environment results in a linear plot of I_0/I or τ_0/τ vs. $[O_2]$. When the luminophore happens to be in multiple quenching environments, curvature may appear in the Stern-Volmer plot. Luminophores in the most accessible environments are easily quenched at low pressures, while those luminophores in less accessible environments will be quenched at higher pressures. Each environment therefore has its own quenching dependence (K_{SV}) and so curvature in the plot results. A model explaining multiple quenching accessibilities can be utilized (equation 1.11).^{15, 17}

$$\frac{I}{I_0} = \frac{\tau}{\tau_0} = \frac{1}{\frac{f_1}{1 + K_{SV1}[O_2]} + \frac{f_2}{1 + K_{SV2}[O_2]} + \frac{f_3}{1 + K_{SV3}[O_2]} + \dots} \quad (1.11)$$

where $f_1, f_2, f_3 \dots$ are the fractions of total unquenched luminescence intensity from different environments and $K_{SV1}, K_{SV2}, K_{SV3} \dots$ are the Stern-Volmer constants for those environments. An adequate approximation would be taking only two terms in equation 1.11, representing double quenching in heterogeneous polymers, called a two-site model.^{15, 17}

1.4 Oxygen Quenching

Gijzeman et al.¹⁸ described the mechanism of oxygen quenching of the aromatic excited triplet state, in which the relative contributions of the two mechanisms depend on the solvent. Studies on oxygen quenching of the excited metal to ligand charge transfer states of luminescent complexes of ruthenium (II), osmium (II), and iridium (III) assigned the process to energy transfer.¹⁹ However, the electron transfer process was found possible in which the quenching rate constants inversely correlate with the excited state energy, and correlate with the oxidation potentials of the complexes.¹⁹

The Stern-Volmer relationship (equation 1.5) can be utilized to correlate luminescence intensity with oxygen pressure in oxygen quenching sensors. However, calibrations at zero oxygen pressure, especially in wind tunnel tests, are not practical. Provided that Henry's law is applicable to oxygen concentration in pressure sensitive materials (equation 1.12, where p is the partial pressure of oxygen, c is molar concentration of oxygen, and k is the Henry's law constant), it is expected that the oxygen concentration will change with global air pressure.

$$P = kc \quad (1.12)$$

In order to make the Stern-Volmer relation more practical, it is possible to substitute oxygen concentration with air pressure and do reference measurements at 1 atm pressure. This will yield equation (1.13):

$$\frac{I_{ref}}{I} = \frac{\tau_{ref}}{\tau} = C + Q_s \frac{P}{P_{ref}} \quad (1.13)$$

where P_{ref} is the reference pressure (generally 1 atm) at which the luminescent compound's intensity is I_{ref} and C is normally 1- Q_s if temperature is constant. Oxygen quenching sensitivity (Q_s) is obtained from the slope of a linear fit to the modified Stern-Volmer plot (equation 1.13). However, since the pressure sensitive method (section 1.5) is applied to solid phases, deviations from linearity can happen (see eqn 1.11).

1.5 Pressure Sensitive Paints

In the field of aerodynamics, conventional pressure distribution measurement requires the use of pressure taps or transducers. The primary disadvantage of this technique is that since the pressure taps are placed at separate spots on the model, pressure data are only provided at those points. In addition, minimization of flow intrusion by taps and transducers requires considerable time and expense when installing these devices. In the pressure sensitive paint (PSP) technique, an oxygen-sensor luminophore is incorporated in paint formulations whose photophysical properties change with changing air pressure.^{7b, 20} PSPs have several advantages over discrete pressure taps

including high spatial resolution, less time consumption, surface-flow visualization, simplicity and versatility.²¹ This technique is shown in Figure 1.3.

Figure 1.3: Schematic picture of pressure sensitive paint coated model surface.

It is possible to design oxygen sensors for specific practical applications.²² Since highly pressure sensitive sensors with large values of Q_s cause large decrease in intensity for a pressure increase, detection difficulties may arise. For pressure sensitive paints used in the range of 0–1 atm, values of 0.4–0.8 for Q_s result in good accuracy.²³

Ideally, a PSP would only respond to oxygen concentration. However, temperature affects the luminescence of PSPs by increasing the non-radiative decay rate of the luminophore. It can also change the oxygen permeability of the binder according to equation (1.14):

$$P = P_0 \exp\left(\frac{-E_p}{RT}\right) \quad (1.14)$$

where P is the permeability coefficient, P_0 is a pre-exponential factor, E_p the activation energy of permeation, R the gas constant, and T the temperature in Kelvin. It is desirable for the permeability coefficient of PSP binders to be largely independent of temperature. A possible solution is a dual luminophore PSP formulation which contains an oxygen sensitive luminophore and a temperature sensitive luminophore that is not quenched by oxygen. This formulation can provide temperature versus pressure data that can be used to correct for the temperature sensitivity of the luminophore being quenched by oxygen.^{20u-v, 24, 21a}

1.6 Materials for Optical Oxygen Sensors

Several requirements are needed to be met by luminophores before being used in sensors. These include practical excitation wavelengths, large molar absorption coefficients, photostability, long lifetimes, and high quantum yields. Polymers are required to dissolve the luminophore and have good mechanical properties and high oxygen permeabilities.

Thickness of films of soft and deformable polymers would change under changing pressure, leading to unreliable data. Because of this, polymers possessing the mechanical properties of environmental stress crack resistance, resistance to flow, and low compressibility are optimal for PSP applications.

Oxygen permeation through flawless polymeric matrix happens by successive steps of dissolution of oxygen and diffusion of the dissolved oxygen. The permeation rate is determined by oxygen permeability coefficient P which is calculated as

$$P = DS \quad (1.15)$$

where D and S are the oxygen diffusion constant and oxygen solubility coefficient, respectively.

1.6.1 Luminescent Probes for PSPs

Not many luminescent compounds are appropriate for pressure sensitive paint applications, since they are expected to meet several conditions including: photostability, long lifetime (for improved quenching efficiency), large Stokes shift, high emission quantum yield (in order to increase ease of measurement), and stability against singlet oxygen. In addition, visible excitation would eliminate safety concerns. Practically, there is no perfectly appropriate luminescent compound for all PSP calibrations.

Luminophores utilized in PSPs include organic dyes,²⁵ polycyclic aromatic hydrocarbons,²⁶ and organometallic compounds.²⁷ Organic dyes usually suffer from short excited state lifetimes.

Polycyclic aromatic hydrocarbons are quenched by oxygen and have been utilized in optical oxygen sensors. As an example, pyrene with an excited-state lifetime of 400 ns has been studied for oxygen sensing. However, its photostability limits the

applicability.^{26e, 28} Associating a polymer ligated cobaltporphyrin with 1-pyrenebutyric acid, a dual-mode and non-Stern–Volmer oxygen pressure sensitive film has been developed.²⁹ Another example of polycyclic aromatic hydrocarbons is decacyclene as an oxygen sensor luminophore for which a blue excitation can be used.^{26g}

Organometallic compounds demonstrate large Stokes shifts and efficient and long-lived emissions and are often utilized as optical oxygen pressure sensors. Varying the metallic centre or ligands, a library of compounds with different properties can be prepared. Basically, the energy and characteristics of the lowest excited state define the luminophore's properties, since emission is generated from this level.³⁰ For efficient energy transfer to oxygen, the proper energy for the lowest excited state is $\geq 95 \text{ kJmol}^{-1}$. Because d-d states of the metallic centre are not luminescent, the lowest excited state should be a charge-transfer or a ligand $\pi\text{-}\pi^*$. Also, in order to avoid thermal population of the d-d states and rapid decay and large temperature sensitivity as a consequence, they should be well separated from the emitting level.

Transition metal polypyridyl compounds of ruthenium, rhenium, osmium, and iridium and metalloporphines of platinum and palladium are especially used in oxygen sensors. One of the extensively used polypyridyl complexes utilized in the field is Ru(dpp)_3 (dpp = diphenylphenanthroline).^{27a} The photophysical properties have been increased by expanded conjugation of the diimine ligand (from bipyridine to phenanthroline to diphenylphenanthroline). A thermally populated d-d state in ruthenium complexes, especially Ru(bpy)_3^{2+} results in deactivation and temperature sensitivity consequences.³⁰ More photostable osmium polypyridyl complexes with excitation in the red region of visible spectrum are reported to show similar sensitivities as ruthenium

complexes.^{27b} Normally, ionic transition metal polypyridyl compounds are insoluble in organic polymers. However, intensely luminescent iridium complexes are soluble in organic polymers (due to similar polarities) and show long lifetimes (order of μs) and high quantum yields. Therefore, iridium complexes are desirable candidates as oxygen sensors.^{27c-f, 27i-j, 31}

Platinum and palladium porphyrins display strong room temperature luminescence with long lifetimes (order of hundreds of μs) and high quantum yields.^{27a} PtOEP has been used in several optical oxygen sensor studies in which it displayed photobleaching at continuous illumination conditions. PtTFPP (Pt(II) tetrakis(pentafluorophenyl) porphyrin) shows enhanced stability due to the presence of electron-withdrawing fluorine atoms.^{27h} Platinum and palladium octaethylporphyrin ketones (OEPK) are reported as photostable optical sensors.^{27g, i}

Other luminescent transition metal complexes investigated for oxygen sensing applications include compounds based on copper,³² zirconium,³³ lanthanides,³⁴ and gold.³⁵

1.6.2 Polymers for PSPs

Binders' properties are considerably important in oxygen sensors. Normally, a good binder for luminescent probe immobilization should be easy to prepare, photostable, mechanically strong, soluble in an appropriate solvent, stable against singlet oxygen, have appropriate oxygen permeability, dissolve the luminophore well, and have little or no impact on photophysical properties of the luminescent probes.

Generally, luminophores are immobilized in binders by covalent attachment or embedding technology. Covalent attachment prevents luminophore aggregation (and the subsequent self-quenching) due to poor solubility. Furthermore, it can control luminophore distribution between the different components of the paint.^{36, 7c} Ruthenium complexes have been covalently attached to polythionylphosphazenes and silicon-dioxide polymers.^{36c, 37} Derosa et al. synthesized polymer-bound iridium complexes by hydrosilation reaction.^{7c, 36d} Attachment of palladium or platinum porphyrin to poly(trimethylsilylpropyne) has also been studied.³⁸

Organic binders are commonly used in PSP application.³⁹ Normally, the luminophore is dispersed in a polymeric solution. Different organic polymers have been considered in oxygen sensors owing to their distinctive oxygen permeabilities.⁴⁰ Cellulose derivatives, fluoropolymers, silicone polymers and organic glassy polymers including polystyrene and poly(methylmethacrylate) can be named.^{26g} Cellulose derivatives such as ethyl cellulose and cellulose acetate produce mechanically strong films. Introducing a plasticizer to cellulose derivatives provides highly oxygen permeable films.^{31d} Fluoropolymers such as poly(hexafluoroisopropyl-*co*-heptafluoro-*n*-butyl methacrylate) (known as FIB) and poly(2,2,2-trifluoroethyl-*co*-isobutyl methacrylate) are photostable oxygen permeable polymers.⁴¹ The American standard polymeric binder in PSPs, FIB, necessitates hazardous solvent (α,α,α -trifluorotoluene) application.⁴² Poly(dimethylsiloxane)s (PDMS) have large oxygen permeabilities,⁴³ but they suffer from poor mechanical properties. Cross-linking would improve mechanical properties, but may result in different luminophore environments due to film non-uniformity.⁴⁴ Furthermore, because of high hydrophobicity of these polymers, aggregate and

microcrystallite formation in them have been reported.⁴⁵ Poly(1-trimethylsilyl-1-propyne) (poly(TMSP)) is reported to have higher gas permeability compared with PDMS while producing durable porous films.⁴⁶ Organic glassy polymers have lower oxygen permeabilities compared with fluoropolymers or silicon polymers but provide good mechanical properties.³⁹

Avnir et al. immobilized rhodamine 6G into an organic ceramic presenting the sol-gel method.⁴⁷ This method has applications in oxygen sensor technology, however, the films were brittle and inadequate for oxygen diffusion due to the high polarity of the film.⁴⁸

Organic-inorganic hybrid films are used in oxygen sensors,^{48a, 49} which are grouped into two types: type I in which van der Waals forces or hydrogen bonds exist between organic and inorganic molecules, and type II in which covalent bonds exist between organic and inorganic parts.⁵⁰ Commonly, inorganic particles improve the mechanical properties of the polymeric film, and increase the surface area.^{17e, 51} Metal oxides including Al_2O_3 , Fe_2O_3 , Sb_2O_3 , and ZrO_2 have been dispersed on the surface of cellulose and its derivatives.⁵² Nanostructured materials such as aluminum oxide embedded into polyvinylalcohol (PVA) were also studied as possible matrices for organometallic compounds.^{51, 53} Consistent films of ormosil have been prepared, in which organic parts are assembled in silicon-oxide networks.⁵⁴ $[\text{Ru}(\text{dpp})_3]^{2+}$ immobilized in fluorinated xerogels consisting of n-propyltrimethoxysilane and 3,3,3-trifluoropropylmethoxysilane has been investigated and detected as highly oxygen sensitive sensors.⁵⁵ The films are even, uniform, and durable.

1.6.3 Electrochemical Adsorption of Luminophores

Binders increase the response time by decreasing the luminophore's access to oxygen. A method has been developed to electrochemically anodize aluminum surfaces and omit binders in order to decrease the response time. A uniform porous surface is produced which adsorbs the luminophore. In this method, the luminescence lifetime of the luminophore defines the response time.^{20t, 56} However, this method is only applicable to aluminum surfaces and some luminophores are not easily adsorbed.

1.7 Water-Soluble Pressure Sensitive Paints

PSP formulations in current use are based in organic solvents and their application and recycling engender workplace safety and contamination concerns. These concerns could be eliminated by using an entirely aqueous PSP formulation that possesses acceptable performance compared to commercial PSPs. Furthermore, the surface of the paint will be smooth after evaporation of the relatively high boiling water.

Oglesby and Ingram developed a water-based PSP that incorporated non-volatile organic solvents, an emulsion polymer and a platinum porphyrin luminescent compound.⁵⁷

Luminescent iridium complexes have been used in PSPs because of their large quantum yields of emission under room temperature and normal pressure, and efficient quenching of the photoexcited triplet state by molecular oxygen. However, their solubility is poor in aqueous solution. The poor solubility can be overcome by covalent

attachment to a water-soluble polymer. It can also prevent aggregation or leaching of the luminophore. Polydimethylsiloxane is used in oxygen sensors^{44, 58} as a well known oxygen permeable polymer, the mechanical properties of which need to be improved for practical applications. Polyethylene glycol is a polar rubbery polymer with oxygen permeability of $0.5 \times 10^{-13} \text{ cm}^3\text{cm}/\text{cm}^2\cdot\text{S}\cdot\text{Pa}$ in the semi-crystalline and $6.1 \times 10^{-13} \text{ cm}^3\text{cm}/\text{cm}^2\cdot\text{S}\cdot\text{Pa}$ in the amorphous phase (at 35°C; MW = approx. 1,000,000), which is independent of pressure.⁵⁹ It has been used in cellulose-based films as a plasticizer to change barrier and physical properties, thus making more flexible films.⁶⁰

1.8 Reductive Amination

Reductive amination of carbonyl compounds became an important and practical route in synthesis of amines, after the presentation of a method using cyanoborohydride,⁶¹ for in situ reductive amination reaction. However, this method has usage difficulties due to the toxicity of the reagent.

In situ reductive amination with methanolic pyridine-borane⁶² presents a conveniently mild process for covalent attachment of carbonyl functionalized and amine functionalized compounds. Pyridine-borane is commercially available, relatively stable in air, and easy to use. Molecular sieves are utilized in situ to imine formation to absorb water. It has been reported⁶² that the intermediate imine is reduced during the reaction, not the acidic workup.

Inexpensive water-soluble amine-functionalized siloxane polymer, Silamine,⁶³ is commercially available, to which a carbonyl functionalized luminophore can be attached.

Also, poly(ethylene glycol) methyl ether (PEGME) can be oxidized to PEGME-aldehyde by a copper-catalyzed procedure under mild conditions.⁶⁴ In this approach an amine functionalized luminophore will provide the appropriate reaction site. Reductive amination reaction between a carbonyl functionalized luminophore and Silamine is demonstrated in Scheme 1.3.

Scheme 1.3: Reductive amination reaction between a carbonyl functionalized luminophore (L) and water-soluble amine-functionalized polymer Silamine.

In case of double-functionalized luminophores, the attachment can be of cross-linked Silamine chains, as shown in Scheme 1.4.

Scheme 1.4: Reductive amination reaction between a double carbonyl functionalized luminophore (L) and two cross-linked water-soluble amine-functionalized polymer Silamine.

Using mono-functionalized luminophores can prevent this problem. However, as long as the solubility of the product in water is satisfactory, this would not affect the practicality of the method.

1.9 Amide Formation Reaction

Utilizing the coupling agent dicyclohexylcarbodiimide⁶⁵ introduced an effective method for peptide or in general, amide bond formation. In this method, a carboxyl and an amino functional group couple in high yield at room temperature. Furthermore, it can be conducted in aqueous solution, due to insensitivity to water. N,N'-dicyclohexylurea is the by-product which is simply separated, since it has a very low solubility in water and most organic solvents.

Scheme 1.5: Amide formation reaction between a carboxyl and an amine.

1.10 Imine Attachment

Another reaction that can be used in covalent attachment of luminophores to polymers is imine formation reaction between carbonyl and amine functionalized moieties.⁶⁶ Normally, this method is acid-catalyzed, in which the reactants are refluxed, in the presence of an azeotroping reagent if needed. Imines can be produced quantitatively from highly reactive aromatic aldehydes with no need to eliminate the by-product water during the reaction.

Scheme 1.6: Imine attachment reaction between an aldehyde and an amine.

Carbonyl functionalized iridium complexes have been utilized to cross-link L-alanine, avidin, and biotin,⁶⁷ as well as to covalently attach to amine-terminated polymers.⁶⁸

1.11 Cyclometalated Iridium Complexes

Luminescent iridium complexes possess high quantum yields due to small non-radiative decay rates. The excited state of these complexes is ligand-based and, by varying the substituents on the ligands, the emission wavelengths can be systematically varied. Cyclometalated iridium complexes are neutral or ionic compounds with strong photophysical properties, which have been investigated in different studies, including biological labeling,^{67a, 69} sensors,^{7c, 27c, 27j, 70} light-emitting electrochemical cells (LECs),⁷¹ organic light-emitting diodes (OLEDs),⁷² and sensitizers of luminescence.⁷³ Examples of iridium-complex applications in the field of sensors are homocysteine, metal cations, and oxygen sensors. The coordinating arrangement around the Ir atom contains disposition of a 5 or 6 membered metallocycle, with 2-phenylpyridine (ppy) being the most common ligand. Facial Ir(ppy)₃ was the first iridium complex studied as an oxygen sensor in polystyrene.^{27d} The conventional synthesis of an Ir(III) complex is performed by a two-step method. In the first step a chloro bridged dinuclear Ir(III) dimer is prepared.^{72c, 74} By substituting the chloro ligands with a third ligand (usually bidentate), the luminescent

compound forms. Most of the cyclometalating ligands have one neutral and one anionic coordinating site, e.g. in ppy, the phenyl ring provides the anionic site. The Ir–C bond between the Ir(III) metal and ppy-based ligands is strong, comparable to covalent bonds. Therefore, these complexes are thermally stable, while having electronic interactions between orbitals of iridium centre and the ligands.

Basically, four transitions can be observed in these complexes: singlet and triplet metal-to-ligand charge transfer ($^1\text{MLCT}$ and $^3\text{MLCT}$) and singlet and triplet ligand-centered (^1LC and ^3LC) transitions, with energetic order of: $^1\text{LC} > ^1\text{MLCT} > ^3\text{MLCT} \geq ^3\text{LC}$. Generally, it is believed that the phosphorescent state is a mixed state of MLCT and LC transition states, originated from spin-orbit coupling.⁷⁵

There is efficient energy transfer from the long-lived triplet excited state of luminescent iridium(III) complexes to the triplet ground state of molecular oxygen, leading to luminescence quenching and singlet oxygen production.^{36d} Therefore, these compounds can be used as oxygen sensors in different areas.^{7c, 43a, 53, 76}

In order to acquire solid state sensors, it is essential for the iridium luminophore to be compatible with the matrix.^{70b, 77} Fluorinated polyacrylates, PDMS, poly(thionylphosphazene)s, and polystyrene have been used as the matrix.^{58, 78} Covalent attachment of these luminophores to the polymeric binder has been the favorable method. DeRosa et al. have described the synthesis and characterization of polymer bound luminescent iridium complexes.^{36d, 36e, 58} Employing polystyrene led to desirable oxygen sensors with good mechanical properties.

1.12 Research Approach

In this project, completely water-soluble pressure sensitive paints will be synthesized and characterized as environmentally friendly alternatives to non-aqueous paint formulations, in order to improve workplace safety, and lower contamination.

Inexpensive water-soluble polymers will be utilized in developing appropriate matrices for dissolving luminophores. Providing spray-able formulations with good mechanical properties as well as high oxygen permeabilities will be the challenges to overcome.

Novel functionalized luminescent iridium complexes will be used, in order to benefit from their large quantum yields of emission and efficient quenching of the excited triplet state by molecular oxygen. The poor solubility of the complexes will be overcome by their covalent attachment to water-soluble polymers.

Producing water-soluble luminescent polymers by covalent attachment to commercially available or synthesized functionalized water-soluble polymers will be investigated. Reductive amination, amide formation, and imine attachment reactions will be studied as practical covalent bonding methods.

Photophysical properties, oxygen quenching sensitivity, and matrix composition impact on the sensitivity of the formulations will be explored.

Chapter 2

Experimental

2.1 Starting Materials

2.1.1 Reagents

Iridium (III) chloride hydrate (Pressure Chemical), 4-(2-pyridyl)benzaldehyde (fppy) ($\geq 97\%$, Aldrich), 2-phenylpyridine (ppy) (98%, Aldrich), silver trifluoromethanesulfonate (AgOTf) (99+%, Aldrich), tert-butyl isocyanide (CN-*t*-Bu) ($\geq 97\%$, Aldrich), 4,6-Dioxoheptanoic acid (acacacid) (Aldrich), triethylamine ($\geq 99.5\%$, Fluka), hydrochloric acid (ACS Reagent grade, Anachemia), 5-aminomethyl-2-chloro pyridine (97%, Aldrich), acetylchloride (98%, Aldrich), phenylboronic acid (95%, Aldrich), tetrakis (triphenylphosphine) palladium (0) (99%, Aldrich), sodium carbonate (ACS Reagent grade, $\geq 99.5\%$, Aldrich), sodium hydroxide (lab grade, Anachemia), potassium hexafluorophosphate (98%, Aldrich), 5,10,15,20-tetrakis(1-methyl-4-pyridyl)-21H,23H-porphine, tetra-*p*-tosylate salt ([H₂TMpyp-4][OTs]₄) (Aldrich), palladium chloride (dry, Fisher), sodium tetrafluoroborate ($\geq 97\%$, Aldrich), ammonium hexafluorophosphate (95+%, Aldrich), copper (I) chloride (ACS Reagent grade, $\geq 90\%$, Aldrich), 1,10-phenanthroline (99+%, Aldrich), potassium carbonate (ACS Reagent grade, $\geq 99\%$, Aldrich), diethyl azodicarboxylate (Aldrich), poly(ethylene glycol) methyl ether-550 (M_n~550, Aldrich), pyridine-borane (Aldrich), N,N'-dicyclohexylcarbodiimide

(99%, Aldrich), Silube CS-1 (MW 3000, acid value 44-52, Siltech Corp.), polyethylene glycol (PEG) (average M_n Ca. 200; Aldrich), (hydroxypropyl) methyl cellulose (Aldrich), dimethylsiloxane-(60% propylene oxide- 40% ethylene oxide) block polymer (PDMS-based copolymer) (MW 30,000, Gelest), and 1-pyrenebutyric acid (97%, Aldrich) were used as received without further purification. Silamine D208 EDA (MW 2475, amine value 30, Siltech Corp.) was heated to 80 °C under vacuum for 30 minutes before use in reductive attachment reaction. 1,10-Phenanthroline-2,9-dicarboxaldehyde was prepared according to Chandler.⁷⁹

2.1.2 Solvents

Dichloromethane (Technical, ACP chemicals) was dried over calcium hydride (90-95%, Aldrich) and distilled and stored under argon before use. Methanol (HPLC Grade, J. T. Baker), diethyl ether (Anhydrous ACS, Fisher Scientific), hexanes (Spectro grade, Caledon), tetrahydrofuran (Certified, Fisher Scientific), ethanol (Anhydrous, Commercial Alcohols), ethyl acetate (Reagent grade, Caledon), methyl tert-butyl ether (Reagent grade, Aldrich), N,N'-dimethylformamide (Reagent grade, Caledon), chloroform (Reagent grade, Caledon), and toluene (Reagent grade, Caledon) were used as received. Acetone (ACS Reagent grade, Anachemia) was distilled before use. 2-Ethoxyethanol (ReagentPlusTM, Aldrich) was distilled and dried over $MgSO_4$ ($\geq 97\%$, Aldrich). For absorption and emission spectroscopies, acetonitrile (Spectrograde, Fisher Scientific) and dichloromethane (Spectro grade, Caledon) were used as received. For NMR spectroscopy, chloroform-*d* (99.8 atom % D, CDN Isotopes), dimethyl-*d*₆ sulfoxide

(99.9 atom % D, CDN Isotopes), deuterium oxide (99.9 atom % D, CDN Isotopes), acetone- d_6 (99.9 atom % D, CDN Isotopes), and tetramethylsilane (99.9+%, Aldrich) were used as received.

2.1.3 Compressed Gas

Argon (ultra high purity, Praxair) was used as received.

2.1.4 Ion Exchange Resin, Drying Agent, and PSP Additive

Dowex[®] 1-X10 anion exchanger ionic form Cl^- (200-400 mesh, J. T. Baker Chemical), 4 Å molecular sieves (activated, Aldrich), and Cellulose (colloidal microcrystalline, Aldrich) were used as received.

2.1.5 Starting Complexes

Starting materials $[\text{Ir}(\text{fppy})_2\text{Cl}]_2$, $[\text{Ir}(\text{C}_6)_2\text{Cl}]_2$, and $[\text{Ir}(\text{ppy})_2\text{Cl}]_2$ were synthesized using the methods of Lo,^{67a} Thompson,^{72c} and Watts and Nonoyama.⁷⁴

2.2 Synthesis of Iridium Complexes

[Ir(tpy)₂(*t*-Bu-iCN)₂][CF₃SO₃], 1

[Ir(tpy)₂(*t*-Bu-iCN)₂][CF₃SO₃] was prepared according to Li et al.⁷⁵

[Ir(fppy)₂(*t*-Bu-iCN)₂][CF₃SO₃], 2

[Ir(fppy)₂Cl]₂ (0.14 g, 0.12 mmol, F.W. 1184.15 g.mol⁻¹) was dissolved in dichloromethane (15 mL) and a solution of AgOTf (0.07 g, 0.27 mmol, F.W. 256.94 g.mol⁻¹) in methanol (15 mL) was added and the resultant solution was stirred for 1 hour and then filtered. To the orange filtrate was added CN-*t*-Bu (0.25 g, 3.0 mmol, F.W. 83.13 g.mol⁻¹) and the resultant solution was stirred for 2 days at room temperature. The reaction mixture was evaporated to dryness under vacuum and the yellow product was filtered and grown as crystals by ether diffusion into a dichloromethane solution of it. [Ir(fppy)₂(*t*-Bu-iCN)₂][CF₃SO₃] (0.15 g, 0.17 mmol, 72% yield, F.W. 871.95 g.mol⁻¹)

Elemental analysis as the monosolvated C₃₅H₃₄IrN₄O₅F₃S·CH₂Cl₂ Calcd (%): C 45.19, H 3.79, N 5.86. Found: C 45.13, H 3.78, N 5.74.

¹H NMR (CDCl₃, 300 MHz): 9.70 (Ald., 1H, s), 9.20 (N6, 1H, d, 5.7 Hz), 8.13 (N3,4, 2H, m), 7.82 (P3, 1H, d, 8.0 Hz), 7.69 (N5, 1H, td, 6.3 Hz), 7.53 (P4, 1H, dd, 8.0 Hz), 6.61 (P6, 1H, s), 1.37 (*t*-Bu, 9H, s) ppm. UV-vis (CH₃CN) ε₂₃₁ (3.07 × 10⁴), ε₂₅₈ (2.51 × 10⁴), ε₂₇₆ (Shoulder) (2.24 × 10⁴), ε₃₀₆ (2.42 × 10⁴), ε₃₁₆ (2.64 × 10⁴), ε₃₅₃ (6.92 × 10³ L.mol⁻¹.cm⁻¹).

[Ir(C₆)₂(acacacid)], 3

[Ir(C₆)₂Cl]₂ (0.15 g, 0.13 mmol, F.W. 1154.20 g.mol⁻¹) was dissolved in dichloromethane (25 mL) and a solution of AgOTf (0.07 g, 0.31 mmol, F.W. 256.06 g.mol⁻¹) in methanol (5 mL) was added and refluxed under argon for 2 hours. The cloudy orange solution was cooled to room temperature and gravity filtered to remove AgCl. 4,6-Dioxoheptanoic acid (acacacid) (0.05 g, 0.32 mmol, F.W. 158.16 g.mol⁻¹) and triethylamine (0.7 mL) were added to the filtrate. The solution was stirred overnight at room temperature under argon. After solvent-stripping to dryness, the orange solid was precipitated out of a dichloromethane solution using hexanes. It was then dissolved in tetrahydrofuran (10 mL) and hydrochloric acid solution (1.27 mL, 0.01 M) was added. The organic solvent was evaporated followed by introducing dichloromethane (20 mL). The solution was washed with distilled water and the bright orange organic layer was separated. The reaction mixture was then evaporated to dryness and the orange product was recrystallized by addition of hexanes to a concentrated dichloromethane solution of it. [Ir(C₆)₂(acacacid)] (0.10 g, 0.10 mmol, 38% yield, F.W. 1048.23 g.mol⁻¹)

Elemental analysis as the semihydrate C₄₇H₄₃IrN₄O₈S₂·0.5H₂O Calcd (%): C 53.40, H 4.19, N 5.30. Found: C 53.41, H 4.05, N 5.26.

¹H NMR (DMSO-*d*₆, 300 MHz): 12.02 (ac₅, bs, 1H), 8.15 (m, 2H), 7.39 (m, 6H), 6.35 (m, 2H), 6.00 (m, 4H), 4.98 (ac₂, s, 1H), 3.26 (C6_{ethylene}, q, 8H, 6.8 Hz), 2.22 (m, 2H), 2.08 (m, 2H), 1.69 (ac₁, s, 3H), 0.94 (C6_{methyl}, q, 12H, 6.9 Hz) ppm. UV-vis (CH₂Cl₂) ε₄₄₇ (6.51 × 10⁴), ε₄₇₄ (7.54 × 10⁴ L.mol⁻¹.cm⁻¹).

5-Aminomethyl-2-phenylpyridine amppy

To a solution of 5-aminomethyl-2-chloropyridine (1.0 g, 7.01 mmol, F.W. 142.59 g mol^{-1}) in dichloromethane (15 mL) at 0° C was added triethylamine (1.1 mL, 7.71 mmol) followed by acetylchloride (0.55 mL, 7.71 mmol). The reaction was allowed to warm to room temperature and was stirred overnight. It was poured into water (15 mL) and the layers were separated. The organic layer was treated with charcoal (0.8 g), heated to reflux, filtered over Celite, and concentrated to an oil. The oil was dissolved in dichloromethane and crystallized by addition of diethylether. The solids were filtered to afford 5-acetadimomethyl-2-chloro pyridine (1.14 g, 6.18 mmol, 88% yield, F.W. 184.63 g mol^{-1})

^1H NMR (CDCl_3 , 300 MHz): 8.31 (1H, d, 2.1 Hz), 7.65 (1H, dd, 8.3 Hz, 2.7 Hz), 7.31 (1H, d, 8.4 Hz), 6.0 (1H, bs), 4.44 (2H, d, 6.0 Hz), 2.06 (3H, s), FTIR (KBr pellet): $\nu(\text{N-H})_{\text{acetamide}}$ 3281 cm^{-1} , $\nu(\text{C=O})_{\text{acetamide}}$ 1649 cm^{-1} , MS (EI) $\text{M}^+ = 184$

5-acetadimomethyl-2-chloro pyridine (0.34 g, 1.84 mmol, F.W. 184.63 g mol^{-1}) and PhB(OH)_2 (0.34 g, 2.79 mmol, F.W. 121.93 g mol^{-1}) were dissolved in a mixture of toluene (25 mL) and ethanol (10 mL). The mixture was flushed with argon three times and stirred at room temperature for 10 minutes. Then $\text{Pd(PPh}_3)_4$ (0.11 g, 0.095 mmol, F.W. 1,155.58 g mol^{-1}) was added. It was stirred for 15 minutes followed by addition of a solution of Na_2CO_3 (0.39 g, 3.68 mmol, F.W. 105.99 g mol^{-1}) in water (10 mL). The reaction mixture was then degassed twice more and refluxed overnight. It was cooled to room temperature, filtered, and the layers were separated. The aqueous layer was

extracted with ethyl acetate, and the organic extracts were combined and evaporated to dryness. The crude solid was dissolved in methanol (30 mL), filtered, and concentrated. Hydrochloric acid (0.6 mL) was added. The solution was concentrated to a low volume, washed with tetrahydrofuran, and dried. The product was then triturated in tetrahydrofuran and filtered to afford 5-acetamidomethyl-2-phenyl pyridine hydrochloride (0.39 g, 1.30 mmol, 71% yield, F.W. 299.20 g mol^{-1}).

^1H NMR ($\text{DMSO-}d_6$, 400 MHz): 8.73 (1H, s), 8.31 (2H, m), 8.11 (2H, m), 7.62 (3H, m), 5.56 (3H, bs), 4.44 (2H, m), 1.92 (3H, s), FTIR (KBr pellet): $\nu(\text{N-H})_{\text{acetamide}}$ 3362 cm^{-1} , $\nu(\text{C=O})_{\text{acetamide}}$ 1649 cm^{-1} , MS (EI) $\text{M}^+ = 226$

To a solution of 5-acetamidomethyl-2-phenyl pyridine hydrochloride (0.14 g, 0.53 mmol, F.W. 262.74 g mol^{-1}) in methanol (5 mL) was added concentrated hydrochloric acid (2.5 mL). The reaction mixture was heated to reflux overnight and concentrated to a low volume. Tetrahydrofuran (50 mL) was added and the white precipitate was filtered to afford 5-aminomethyl-2-phenyl pyridine hydrochloride (0.12 g, 0.47 mmol, 89% yield, F.W. 257.16 g mol^{-1}).

^1H NMR (D_2O , 300 MHz): 8.80 (1H, s), 8.52 (1H, dd, 8.5 Hz, 1.8 Hz), 8.24 (1H, d, 8.5 Hz), 7.82 (2H, m), 7.61 (3H, m), 4.37 (2H, s) FTIR (KBr pellet): $\nu(\text{N-H})_{\text{ammonium}}$ 2855 cm^{-1} , MS (EI) $\text{M}^+ = 184$

5-aminomethyl-2-phenyl pyridine hydrochloride (0.61 g, 2.80 mmol, F.W. 257.16 g mol^{-1}) was dissolved in water (25 mL) and filtered. The pH was adjusted to ~ 12 with concentrated aqueous sodium hydroxide. It was then diluted with methyl *tert*-butyl ether

(25 mL). The organic layer was separated to afford 5-aminomethyl-2-phenyl pyridine (0.31 g, 1.68 mmol, 60% yield, F.W. 184.24 g mol⁻¹).

¹H NMR (CDCl₃, 300 MHz): 8.66 (1H, d, 1.1 Hz), 8.00 (2H, m), 7.76 (2H, m), 7.50 (3H, m), 3.97 (2H, s), 1.48 (2H, s) FTIR (KBr pellet): $\nu(\text{N-H})_{\text{amine}}$ 3437 and 3269 cm⁻¹, $\nu(\text{N-H})_{\text{amine}}$ 1602 cm⁻¹, MS (EI) M⁺=184

[Ir(ppy)₂(amppy)Cl], 4

[Ir(ppy)₂Cl]₂ (0.5g, 0.47 mmol, F.W. 1072.11 g mol⁻¹) was dissolved in dichloromethane (40 mL) and a solution of AgOTf (0.24 g, 0.94 mmol, F.W. 256.06 g.mol⁻¹) in methanol (10 mL) was added and the resultant solution was refluxed under argon for 2 hours. The cloudy yellow solution was cooled to room temperature and gravity filtered to remove AgCl. Amppy (0.22g, 1.2 mmol, F.W. 184.24 g mol⁻¹) and triethylamine (0.3 mL) were added and the resultant solution was stirred overnight at room temperature under argon. The reaction mixture was evaporated to dryness and the yellow product was grown as diamond shaped crystals by hexanes diffusion into a dichloromethane solution of it. [Ir(ppy)₂(amppy)Cl] (0.53 g, 0.74 mmol, 79% yield, F.W. 720.30 g.mol⁻¹)

Elemental analysis as the monosolvated C₃₄H₂₈IrN₄Cl·CH₂Cl₂ Calcd (%): C 52.21, H 3.76, N 6.96. Found: C 51.88, H 3.58, N 7.05

¹H NMR (CDCl₃, 300 MHz): 9.93 (d, 1H, 5.6 Hz), 8.54 (d, 1H, 5.5 Hz), 8.19 (d, 1H, 1.7 Hz), 7.81 (m, 6H), 7.44 (m, 8H), 7.19 (m, 1H), 6.79 (m, 4H), 6.34 (d, 1H, 7.5 Hz), 6.17 (dd, 1H, 7.5 and 0.69 Hz), 3.36 (m, 2H), 1.62 (s, 2H) ppm. UV-vis (CH₂Cl₂) ϵ_{259} (3.38 × 10⁴), ϵ_{392} (1.78 × 10³ L.mol⁻¹.cm⁻¹), ϵ_{431} (1.31 × 10³ L.mol⁻¹.cm⁻¹).

[Ir(ppy)₂(fppy)], 5

[Ir(ppy)₂(fppy)] was prepared according to Evans et al.⁶⁸

[Ir(ppy)₂(phendiald)][PF₆], 6

[Ir(ppy)₂Cl]₂ (0.11 g, 0.10 mmol, F.W. 1072.11 g.mol⁻¹) was dissolved in methanol/dichloromethane (30 mL, 1:1 v/v) and 1,10-phenanthroline-2,9-dicarboxaldehyde (0.05 g, 0.21 mmol, F.W. 236.23 g.mol⁻¹) was added and the resultant solution was stirred at reflux under argon for 4 hours. The orange solution was cooled to room temperature and KPF₆ (0.037 g, 0.20 mmol, F. W. 184.07 g.mol⁻¹) was added. It was then evaporated to dryness and the orange product was recrystallized by addition of hexanes to a concentrated dichloromethane solution of it. [Ir(ppy)₂(phendiald)][PF₆] (0.15 g, 0.17 mmol, 85% yield, F.W. 881.80 g.mol⁻¹)

¹H NMR (acetone-*d*₆, 300 MHz): 9.70 (Ald., 2H, s), 9.11 (m, 2H), 8.51 (m, 2H), 8.37 (d, 2H, 8.3 Hz), 8.21 (m, 2H), 7.93 (m, 6H), 6.98 (m, 4H), 6.86 (dd, 2H, 15.7 and 8.2 Hz), 6.27 (m, 2H) ppm. UV-vis (CH₂Cl₂) ε₂₅₇ (3.75 × 10⁴), ε₂₉₃ (4.55 × 10⁴), ε₃₈₄ (8.53 × 10³ L.mol⁻¹.cm⁻¹), ε₅₀₈ (1.28 × 10³).

2.3 Synthesis of Palladium Complex

[PdTMpyp-4][PF₆]₄, 7

The synthesis was carried out following a modified procedure of Pasternack⁸⁰ as follows:

N,N'-Dimethylformamide (5 mL) was brought to reflux and 5,10,15,20-tetrakis(1-methyl-4-pyridyl)-21H,23H-porphine,tetra-*p*-tosylate salt (0.05 g, 0.04 mmol, F.W. 1363.63 g.mol⁻¹) was added. The resultant mixture was stirred for 1 minute in order to allow for complete dissolution and then palladium chloride (0.007 g, 0.04 mmol, F.W. 177.33 g.mol⁻¹) was added. The resultant solution was stirred at reflux overnight after which it was evaporated to dryness and then dissolved in water (15 mL). The deep red-orange solution was filtered through Celite and NaBF₄ (1.6 g, 0.01 mol, F.W. 109.79 g.mol⁻¹) was added to the filtrate. The resultant mixture was centrifuged (2000 rpm, 15 minutes) and the resultant red solid was suspended in water with anion exchange resin Dowex[®] 1-X10 in the chloride form (0.22 g). The mixture was stirred for 1 hour and was then filtered to remove the anion exchange resin. NH₄PF₆ (0.96 g, 5.9 mmol, F.W. 163 g.mol⁻¹) was added to the filtrate to precipitate the product which was then dissolved by addition of adequate amount of acetone. The purple product was acquired by slow evaporation of the solvent. It was filtered, washed with methanol and ether, and dried in vacuo. [PdTMpyp-4][PF₆]₄ (0.034 g, 0.025 mmol, 62% yield, F.W. 1363.10 g.mol⁻¹)

Elemental analysis as C₄₄H₃₆F₂₄N₈P₄Pd Calcd (%): C 38.77, H 2.66, N 8.22. Found: C 38.88, H 2.78, N 7.83.

UV-vis absorption data was matched with reference 81.

2.4 Synthesis of Functionalized Water-Soluble Polymer

i) Copper-Catalyzed Oxidation of Poly(Ethylene Glycol) Methyl Ether (PEGME) to PEGME-Aldehyde

CuCl (0.05g, 0.51 mmol, F.W. 99.00 gmol⁻¹) and 1,10-phenanthroline (0.09g, 0.50 mmol, F.W. 180.21 gmol⁻¹), and K₂CO₃ (2.75g, 0.02 mol, F.W. 138.21 gmol⁻¹) were added to toluene (80 mL) and the mixture was stirred for 30 minutes at room temperature. Diethylazodicarboxylate (DEAD) (0.09g, 0.52 mmol, F.W. 174.15 gmol⁻¹) and poly(ethylene glycol) methyl ether-550 (11g, 0.02 mol, typical M_n 550) were added successively, and the mixture was heated for 3 hours on an oil bath at 80°C while air was gently bubbled through the reaction mixture. The catalyst was then filtered and the product was precipitated by addition of anhydrous diethyl ether followed by leaving in freezer, filtering and washing with cold anhydrous diethyl ether (~ -6°C). It was then dried and PEGME-Aldehyde was isolated as a colorless semisolid.

IR (KBr pellet): $\nu(\text{C=O})_{\text{aldehyde}}$ 1719 cm⁻¹, $\nu(\text{C-H})_{\text{aldehyde}}$ 2724 cm⁻¹

2.5 Synthesis of Water-Soluble Oxygen Sensors

i) Reductive Attachment of **2** to Silamine D208-EDA to Synthesize **8**

To Silamine D208-EDA (1.5 g, 0.6 mmol, pre-dried by heating at 80 °C under vacuum for 30 minutes) was added dichloromethane (24 mL). The solution was degassed with argon for 10 minutes and then 0.53 g of activated 4 Å molecular sieves and **2** (0.09 g, 0.1 mmol) were added followed by pyridine-borane (0.01 mL, 0.099 mmol). After the solution was stirred at room temperature under argon for 16 hours, methanol (10 mL) was added and the resultant solution was treated with 6 N HCl (10 mL) for 15 minutes, and then pH was adjusted to 12 using concentrated aqueous NaOH solution. NaCl was precipitated by addition of diethyl ether (100 mL) and filtered off. The filtrate was solvent stripped and the residue dissolved in a small volume of acetone which was filtered sequentially through 1.0 µm and 0.45 µm Gelman acrodiscs. The filtered solution was added dropwise to rapidly stirred hexanes yielding a clear, yellow polymer fluid.

ii) Covalent Attachment of **3** to Silamine D208-EDA to Synthesize **9**

To Silamine D208-EDA (1.0 g, 0.4 mmol) was added ethyl acetate (5 mL). **3** (0.07 g, 0.07 mmol) dissolved in ethyl acetate (5 mL) was added followed by N,N'-dicyclohexylcarbodiimide (0.04g, 0.19 mmol, F.W. 206.33 g mol⁻¹) dissolved in ethyl acetate (1 mL). After the solution was stirred at room temperature for 6 hours, it was solvent stripped and the residue dissolved in a small volume of water which was filtered

sequentially through 1.0 μm and 0.45 μm Gelman acrodiscs. A clear, orange polymer fluid was obtained after solvent stripping.

iii) Dispersion of 4 in Silube CS-1 to Produce 10

To Silube CS-1 (0.3 g, 0.1 mmol) was added ethyl acetate (1 mL). **4** (0.02 g, 0.03 mmol) dissolved in ethyl acetate (3 mL) was added and the solution was stirred at room temperature for 6 hours. It was then solvent stripped and the residue dissolved in a small volume of water which was filtered sequentially through 1.0 μm and 0.45 μm Gelman acrodiscs. A clear, yellow polymer fluid was obtained after solvent stripping.

iv) Covalent Attachment of Amppy to PEGME-Aldehyde

Amppy (0.33g, 1.79 mmol, F.W. 184.24 g mol^{-1}) was dissolved in chloroform (10 mL) and added to a solution of PEGME-Aldehyde (1.0g, 1.82 mmol, typical M_n 550) in chloroform (10 mL). The resultant solution was stirred at reflux under argon for 2.5 days. It was then solvent stripped, dissolved in water, filtered through 1.0 μm and 0.45 μm Gelman AcrodiscsTM, and evaporated.

v) Synthesis of PEGME Attached Ir-amppy Dimer

Iridium trichloride hydrate (0.13g, 0.44 mmol, F.W. 298.58 g mol^{-1}) was combined with PEGME-amppy (1.0g, ~ 0.87 mmol amppy), dissolved in a mixture of 2-

ethoxyethanol (10 mL) and water (5 mL), and refluxed for 24 hours under argon. The deep orange solution was filtered and the filtrate was evaporated to dryness. It was then dissolved in methanol (30 mL), filtered, and used in the next step.

vi) Synthesis of PEGME Attached [Ir(amppy)₂(*t*-Bu-iCN)₂][CF₃SO₃], 11

To the methanolic solution of PEGME attached Ir-amppy dimer acquired from the previous step was added AgOTf (0.13g, 0.51 mmol, F.W. 256.94 g.mol⁻¹) to yield a cream-colored slurry. After the slurry was stirred for 1 hour, it was filtered and CN-*t*-Bu (0.25 g, 3.0 mmol, F.W. 83.13 g.mol⁻¹) and dichloromethane (20 mL) were added to it. The resultant solution was stirred for 2 days at room temperature. The reaction mixture was evaporated to dryness under vacuum and the residue was dissolved in acetone, filtered through 1.0 µm and 0.45 µm Gelman AcrodiscsTM, and evaporated. The filtered solution was added dropwise to rapidly stirred hexanes, yielding a clear, yellow polymer fluid.

vii) Covalent Attachment of 5 to Silamine D208-EDA to Synthesize 12

A solution of **5** (34mg, 0.05 mmol, F.W. 682.80 g.mol⁻¹) in dichloromethane (5 mL) was added to a solution of Silamine D208-EDA (0.25g, 0.10 mmol, M.W. 2400) in dichloromethane (10 mL). The resultant solution was stirred at reflux under argon for 2 days. It was solvent stripped to dryness and the product was dissolved in acetone (5 mL)

and filtered through 1.0 μm and 0.45 μm Gelman AcrodiscsTM. The filtered solution was added dropwise to rapidly stirred hexanes, yielding a clear, yellow polymer fluid.

viii) Reductive Attachment of 5 to Silamine D208-EDA to Synthesize 13

To Silamine D208-EDA (1.5g, 0.6 mmol, M.W. 2400, pre-dried by heating at 80 °C under vacuum for 30 minutes) was added dichloromethane (24 mL). The solution was degassed with argon for 10 minutes and then 0.53 g of activated 4 Å molecular sieves and **5** (0.08 g, 0.12 mmol, F.W. 682.80 g.mol⁻¹) were added followed by pyridine-borane (0.01 mL, 0.099 mmol). After the solution was stirred at room temperature under argon for 16 hours, methanol (10 mL) was added and the resultant solution was treated with 6 N HCl (10 mL) for 15 minutes, and then pH was adjusted to 12 using concentrated aqueous NaOH solution. NaCl was precipitated by addition of diethyl ether (100 mL) and filtered off. The filtrate was solvent stripped and the residue dissolved in a small volume of acetone which was filtered sequentially through 1.0 μm and 0.45 μm Gelman Acrodiscs. The filtered solution was added dropwise to rapidly stirred hexanes, yielding a clear, yellow polymer fluid.

ix) Reductive Attachment of 6 to Silamine D208-EDA to Synthesize 14

To Silamine D208-EDA (1.5 g, 0.6 mmol, pre-dried by heating at 80 °C under vacuum for 30 minutes) was added dichloromethane (24 mL). The solution was degassed with argon for 10 minutes and then 0.53 g of activated 4 Å molecular sieves and **6** (0.09

g, 0.1 mmol) were added followed by pyridine-borane (0.01 mL, 0.099 mmol). After the solution was stirred at room temperature under argon for 16 hours, methanol (10 mL) was added and the resultant solution was treated with 6 N HCl (10 mL) for 15 minutes, and then pH was adjusted to 12 using concentrated aqueous NaOH solution. NaCl was precipitated by addition of diethyl ether (100 mL) and filtered off. The filtrate was solvent stripped and the residue dissolved in a small volume of acetone which was filtered sequentially through 1.0 μm and 0.45 μm Gelman acrodiscs. The filtered solution was added dropwise to rapidly stirred hexanes, yielding a clear, orange polymer fluid.

x) Covalent Attachment of 1-Pyrenebutyric Acid (PBA) to Silamine D208-EDA to Synthesize 15

To Silamine D208-EDA (1.0 g, 0.4 mmol) was added ethyl acetate (5 mL). PBA (0.001 g, 0.003 mmol, F.W. 288.35 g mol^{-1}) dissolved in ethyl acetate (5 mL) was added followed by N,N'-dicyclohexylcarbodiimide (0.04g, 0.19 mmol, F.W. 206.33 g mol^{-1}) dissolved in ethyl acetate (1 mL). After the solution was stirred at room temperature for 6 hours, it was solvent stripped and the residue dissolved in a small volume of water which was filtered sequentially through 1.0 μm and 0.45 μm Gelman acrodiscs. A clear polymer fluid was obtained after solvent stripping.

2.6 PSP Formulations

For each PSP formulation, a solution of dye in MeOH or H₂O was added to another solution that was prepared by mixing water-soluble polymer in H₂O. The combined solutions were filtered through a 1.0 μ m Gelman Acrodisc and then mixed with microcrystalline cellulose in H₂O.

2.7 Physical Measurements

2.7.1 Elemental Analyses

Elemental analyses were performed by Canadian Microanalytical Service, Ltd. of Delta, BC, Canada.

2.7.2 X-ray Structural Determination

The x-ray structures of **2** and **4** were performed by Dr. Glenn P. A. Yap at the University of Delaware. The following experimental description was written by Dr. Yap.

For **2**·0.25(CH₂Cl₂): A crystal was mounted using viscous oil onto a glass fiber and cooled to the data collection temperature. Data were collected on a Brüker-AXS APEX CCD diffractometer with graphite-monochromated Mo-K α radiation (λ =0.71073 Å). Unit cell parameters were obtained from 60 data frames, 0.3° ω , from three different sections of the Ewald sphere. No symmetry higher than triclinic was observed and

solution in the centrosymmetric space group option yielded chemically reasonable and computationally stable results of refinement. The data set was treated with SADABS absorption corrections based on redundant multiscan data.⁸² The structure was solved using direct methods and refined with full-matrix, least-squares procedures on F^2 . Two symmetrically unique but chemically equivalent ion pairs are located in the asymmetric unit. One disordered methylene chloride molecule of crystallization per unit cell was located away from the ion pairs. The disordered triflate anions and methylene chloride molecule were treated as diffused contributions (Squeeze/Platon).⁸³ Two *t*-Bu-iCN ligands (one on each cation) and one fppy ligand were located disordered in two positions with refined site occupancies of 65/35, 80/20 and 54/46, respectively. The structure displays disorder that cannot be satisfactorily modeled because of the subtle differences (<1 Å) in atomic positions leading to larger than ideal $U_{eq_{max}}/U_{eq_{min}}$ ranges, low C-C precision and Hirshfeld test failures. All bonds were restrained as rigid bonds with common U_{ij} values within standard deviation. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. Structure factors are contained in the SHELXTL 6.12 program library.^{82a} The structure has been deposited at the Cambridge Crystallographic Data Centre under CCDC 717607.

For 4: A data crystal was selected and mounted on a glass fiber using viscous oil flash-cooled to the data collection temperature. Data were collected on a Brüker-AXS APEX CCD diffractometer with graphite-monochromated Mo-K α radiation ($\lambda=0.71073$ Å). Unit cell parameters were obtained from 60 data frames, $0.3^\circ \omega$, from three different sections of the Ewald sphere. The systematic absences in the data and the unit cell

parameters were uniquely consistent to the reported space group. The data-sets were treated with SADABS absorption corrections based on redundant multiscan data.^{82b} The structures were solved using direct methods and refined with full-matrix, least-squares procedures on F^2 . A methylene chloride solvent molecule was found cocrystallized. The hydrogen atoms on the amine nitrogen atom were located from the electron density difference map and refined with N-H distance = 0.95 Å and with $U_{iso} = 1.2 U_{ij}$ of the nitrogen atom. All non-hydrogen atoms were refined with anisotropic displacement parameters. All other hydrogen atoms were treated as idealized contributions. Atomic scattering factors are contained in the SHELXTL 6.12 program library.^{82a}

2.7.3 Spectroscopic Measurements

All 1-D and 2-D NMR spectra were performed on a Bruker 300 spectrometer at ambient temperatures using NORELL XR-55 sample tubes and were referenced to TMS.

Absorption spectra were acquired on a Varian Cary 5 UV-vis-NIR spectrophotometer at ambient temperatures using 1.000 cm path length quartz cells (Wilmad). Scans were performed at 500 nm/min vs. solvent backgrounds, with a spectral bandwidth of 2.00 nm, a signal averaging time of 0.033 s, and a data interval of 1.000 nm.

Steady-state emission spectra were acquired on a Shimadzu RF-1501 spectrofluorophotometer at ambient temperatures using quartz fluorimeter cells (Wilmad) of 1.000 cm path length.

To obtain time-resolved fluorescence decays, the samples were excited with the third harmonic of a Continuum Surelite 2 Nd:YAG laser generating pulses at 355 nm of 6 ns duration and 15 mJ energy. The signals from the monochromator/photomultiplier system were initially captured by a Tetrax TDS 2012 oscilloscope and transferred to a Macintosh PC clone computer with software LFP V3.0 developed in the LabVIEW environment from Luzchem. A total of 10 shots were averaged to obtain the decay traces. All solution lifetime experiments were done in static $1.0 \times 1.0 \text{ cm}^2$ fused silica cuvettes, following purging with inert gas for 30 min. Each thin-film lifetime measurement was acquired on a plain microscope slide (Globe Scientific Inc.), sprayed with the paint using a conventional airbrush and mounted in a pressure chamber described elsewhere.^{36d, e}

For the quantum yield determinations, the samples were optically matched to solutions of Coumarin 1 (Laser grade, Fisher) in ethanol ($\rho = 0.73$)⁴⁸ at room temperature using a Shimadzu RF-1501 spectrofluorophotometer. Quartz fluorimeter cells (Wilma) of 1.000 cm path length were used in quantum yield measurements.

Electron Impact Mass Spectrometry (EI-MS) was performed at the University of Ottawa Mass Spectrometry centre.

Infrared spectroscopy was performed on a Varian 1000-FT-IR spectrometer as KBr pellets. Data was analyzed using Varian resolutions 4.1.0.101 software.

2.7.4 Determination of Oxygen Quenching Sensitivity (Q_s)

The oxygen sensitive paints were calibrated. Each PSP formulation was applied to a primed aluminum plate with a Tristar Starpoxy fluid resistant white epoxy primer

(DHMS C4.01 Ty3) using a conventional airbrush and compressed argon as the propellant. It was then mounted in a pressure chamber described elsewhere.^{36d, e} The average film thickness was estimated to be $2 \pm 1 \mu\text{m}$ by a Positector 6000 model thickness gauge. Excitation in the UV was provided by a Hamamatsu Lightningcure LC5 200W (model L8333 Hg-Xe) source by a $10 \text{ m} \times 8 \text{ mm}$ Oriel UV-vis liquid light guide. Several optical filters in parallel were placed inside the lamp, before the light guide, to block wavelengths greater than 400 nm (Rapp Optoelectronic UV-1 and Hamamatsu A7028-05 filter). Excitation in the blue was provided by a Photonics Research Systems PRS100B blue LED lamp coupled with a 420-500 bandpass filter (03-FIV-28, Melles Griot). Thin-film emission spectra were collected using an Acton Research Corporation SpectruMM CCD detection system. A fiber optic lightguide (LG-455-020), equipped with a Kodak Wratten Gelatin 3 filter absorbing ultraviolet radiations passed the emission through a SpectraPro-150 imaging dual grating monochromator/spectrograph onto a 16-bit Hamamatsu 1024×256 CCD. Following the dark current subtraction, the spectra were normalized by the maximum intensity at atmospheric pressure to produce the spectra variations with pressure. Data for the Stern-Volmer plots were obtained by integrating the spectra over wavelengths between 460 and 560 nm. These measurements were taken at 24 °C, between 0.007 and 45 psi. A Scanivalve Corp. pressure calibrator/controller and a thermoelectric cooler coupled to a temperature controller were used to control pressure and temperature, respectively. Measurements at the reference pressure of 14.7 psi were taken two times during the calibration in order to estimate the photostability of the paints. The excitation light source stability was monitored with a temperature controlled Oriel 7123 photodiode.

The decrease in emission intensity with increasing air pressure relative to the emission intensity at 1 atm pressure was treated according to Stern-Volmer kinetics and modified Stern-Volmer plots were acquired. Oxygen quenching sensitivity (Q_s) data were calculated from linear fits to the Stern-Volmer plots with $r^2 > 0.95$. Multiple quenching processes arising from heterogeneous luminophore environments could result in curvature in the Stern-Volmer plots of thin films. In these cases criteria for acceptable range of P/P_{ref} was considered as $r^2 > 0.95$. Measurements were repeated at least three times and the error in reported Q_s data was estimated at ± 0.01 .

2.7.5 Luminescence Microscopy

All microscopy was performed at Agriculture Canada. PSP films were sprayed on plain microscope slides (Globe Scientific Inc.). The luminescence images were observed in air using a confocal microscope Carl Zeiss LSM510 Meta (405 nm, 42.6% laser intensity) with an ECPlan-Neofluar 40x/1.30 Oil Dic M27 objective exciting at 405 nm and collecting image data at 505 nm. The observed images were analyzed with LSM510 V.4.0 SP2.

Chapter 3

Results and Discussion

3.1 Initial Choice of Matrix

The first challenge in this project was acquiring water-soluble matrices that dissolve luminophores and have good mechanical properties and high oxygen permeabilities. To start, a copolymerization reaction was developed in order to produce copolymers of water-soluble poly(N-vinyl pyrrolidone) or poly(N,N-dimethylacrylamide) and oxygen permeable poly(2, 2, 2-trifluoroethyl methacrylate). While some water-soluble copolymers were successfully prepared via radical polymerization using AIBN as the initiator, the synthesis was not pursued due to low oxygen permeabilities and practical problems in sprayed films of them. The problems occurred during pressure sensitivity calibrations, when the films cracked under changing pressures. Therefore, commercially available polyethylene glycol (PEG) (average M_n Ca. 200), (hydroxypropyl) methyl cellulose, and a water-soluble copolymer of the well known oxygen permeable polymer, polydimethylsiloxane (dimethylsiloxane-(60% propylene oxide- 40% ethylene oxide) block polymer (PDMS-based copolymer) (MW 30,000) were utilized as the initial matrices to develop water-based PSP formulations. The mechanical properties of these polymers need to be improved for practical applications. To compensate for the poor mechanical properties of the water-soluble polymers, microcrystalline cellulose (MC) was included in the formulations. MC was decided on, since it is a semicrystalline

polymer with a low chemical reactivity and has been used widely as binder in tableting technology in order to improve compactibility.

3.2 Initial Choice of Luminophore

Luminescent iridium complexes have been used in PSPs because of their large quantum yields of emission under room temperature and normal pressure, and efficient quenching of the photoexcited triplet state by molecular oxygen. The first iridium complex studied in water-based PSP formulations was the charged complex **1** which is soluble in water-methanol mixtures containing up to 75 volume percent of water.

3.3 Characterization of Initial Pressure Sensitive Paint (PSP) Films

The pressure-dependent film emission spectra of **1** in different matrices were studied. Figure 3.1 shows a representative example. Films of **1** displayed an intense yellow-white luminescence with UV irradiation under low pressure conditions. The decrease in emission intensity with increasing air pressure relative to the emission intensity at 1 atm pressure can be treated according to Stern-Volmer kinetics (See Experimental) and Figure 3.2 shows modified Stern-Volmer plots of **1** in three PEG-based formulations.

Oxygen quenching sensitivity (Q_s) data for various thin films were calculated from linear fits to the Stern-Volmer plots with $r^2 > 0.95$ and have been placed in Table 3.1. Multiple quenching processes arising from heterogeneous luminophore

environments could result in curvature in the Stern-Volmer plots of thin films. In these cases appropriate linear fits with $r^2 > 0.95$ were not acquired. Constrained pressure ranges presenting linear fits to the plots were chosen to find Q_s data.

Figure 3.1: Effect of pressure on thin film luminescence of **1** in PDMS-based copolymer. The decrease of intensity with increasing the air pressure is displayed. Spectra were acquired at 1.3 mbar (black), 0.34 bar (red), 0.68 bar (green), 1 bar (purple), 1.36 bar (blue), 1.70 bar (grey), 2.04 bar (dark red), 2.38 bar (dark green), 2.72 bar (dark blue), and 3.06 bar (dark purple). Background correction has been performed.

Figure 3.2: Stern-Volmer plots of **1** in PEG, ○; in 1:1 PEG: MC, ●; and in 1:9 PEG: MC, ●.

Table 3.1: PSP films oxygen sensitivity data for **1**.

Luminophore	Matrix	$Q_s(r^2)$
1	(Hydroxypropyl) Methyl Cellulose	0.38 (0.987) ^a
	PEG	0.41 (0.991) ^a
	1:1 PEG: MC	0.43 (0.990) ^a
	1:9 PEG: MC	0.08 (0.985) ^b
	PDMS-based Copolymer	0.36 (0.983) ^b
	1:1 PDMS-Cop.: MC	0.45 (0.991) ^b
	1:9 PDMS-Cop.: MC	0.31 (0.987) ^c

^a0.007-45 psi; ^b5-45 psi; ^c10-45 psi

Oxygen sensitivity as well as mechanical properties of the film is increased as a consequence of the blending of MC with luminophores compared with the film composed

of the polymer with low glass transition temperature. It is suggested that this effect originates from a decrease in the luminophore's freedom of motion and consequentially an increase in its luminescence lifetime. Moreover, the preferential binding of luminophore to MC could lead to de-aggregation and a decrease in self-quenching.

3.4 Synthesis of Water-Soluble Oxygen Sensor 8

3.4.1 Functionalizing Ir (III) Complex

In order to overcome the poor solubility of complex **1** in aqueous solutions, the covalent attachment of the analogous functionalized complex **2** to water soluble polymers was investigated.

3.4.1.1 Synthesis

Starting material $[\text{Ir}(\text{fppy})_2\text{Cl}]_2$ (Scheme 3.1) was prepared according to Lo.^{67a}

Scheme 3.1: Synthesis of starting functionalized iridium dimer.

Complex **2**, $[\text{Ir}(\text{fppy})_2(t\text{-Bu-iCN})_2][\text{CF}_3\text{SO}_3]$ (fppy = 4-(2-pyridyl)benzaldehyde, and *t*-Bu-iCN = *tert*-butyl isocyanide), was synthesized in a high yield (72%) by cleaving the iridium dimer $[\text{Ir}(\text{fppy})_2\text{Cl}]_2$ with silver triflate followed by coordination of the *tert*-butyl isocyanide ligand (shown in Scheme 3.2).

Scheme 3.2: Synthesis of **2**

The pyridylbenzaldehyde ligands provide the reactive sites for the reductive amination reaction.

3.4.1.2 X-ray Crystallography

Structure of **2** was confirmed by X-ray crystallography on its single crystals grown from dichloromethane solutions by diffusion of ether. It was shown that two symmetrically unique but chemically equivalent ion pairs are located in the asymmetric unit of **2**. The ORTEP drawing of $\mathbf{2} \cdot 0.25(\text{CH}_2\text{Cl}_2)$ is shown in Figures 3.3. Crystallographic data and some selected bond lengths and angles are given in Tables 3.2-3.3. Full data of atomic coordinates, bond lengths and angles for the complex can be found in Appendix A.

Table 3.2: X-ray Crystallographic Data and Refinement Details for $2 \cdot 0.25(\text{CH}_2\text{Cl}_2)$.

Empirical formula	$\text{C}_{35}\text{H}_{34}\text{F}_3\text{IrN}_4\text{O}_3\text{S} \cdot 0.25(\text{CH}_2\text{Cl}_2)$
M_r	861.15
Cryst syst	Triclinic
Space group	$P\bar{1}$
unit cell dimensions	$a = 15.164(5) \text{ \AA}$ $b = 17.083(6) \text{ \AA}$ $c = 17.242(6) \text{ \AA}$ $\alpha = 117.569(5)^\circ$ $\beta = 104.876(5)^\circ$ $\gamma = 100.075(5)^\circ$
V	$3595(2) \text{ \AA}^3$
D_x	1.591 g cm^{-3}
T	$120(2) \text{ K}$
λ	$0.71073 \text{ \AA}$
$R[F^2 > 2\sigma(F^2)]$	0.0498
$wR(F^2)$	0.1343
Z, Z'	4, 2
μ	3.864 mm^{-1}

Table 3.3: Selected Bond Lengths ($\text{\AA}$) and Angles ($^\circ$) for $2 \cdot 0.25(\text{CH}_2\text{Cl}_2)$.^a

Ir1—N1	2.049(5), 2.039(10)	N1—Ir1—N2	170.7(2), 165.2(6)
Ir1—N2	2.047(5), 2.051(5)	C25—Ir1—C30	91.9(4), 89.1(3)
Ir1—C7	2.046(6), 2.057(11)	C7—Ir1—N1	80.1(2), 80.0(5)
Ir1—C25	2.037(8), 2.062(6)	C19—Ir1—N2	80.3(2), 79.9(2)
C12—O1	1.147(9), 1.148(14)	C25—Ir1—C30	91.94(4), 89.1(3)
C24—O2	1.202(8), 1.193(7)	N3—C25	1.138(10), 1.157(8)
N3—C26	1.515(13), 1.457(10)	N4—C30	1.164(8), 1.118(8)
N4—C31	1.487(9), 1.464(8)		

^a The second value is for chemically equivalent bonds in the second symmetrically unique cation. In case of disordered fragments, only the major contributor is represented.

In $2 \cdot 0.25(\text{CH}_2\text{Cl}_2)$, iridium occupies a distorted octahedral coordination sphere of four carbon and two nitrogen donor atoms in which *tert*-butyl isocyanide ligands are *cis* to each other. In this stereochemistry, the bidentate pyridylbenzaldehyde ligands are expected to be coordinated to iridium with pyridine nitrogens *trans* to each other because that is the geometry of the reagent dimer complex.⁸⁴ This is confirmed in Figure 3.3 and by the Ir-N bond lengths (Table 3.3) which are similar to those of analogous complexes possessing the bis(pyridylbenzaldehyde)iridium fragment.^{83, 85} Figure 3.3 also shows that the *tert*-butyl isocyanide ligands are slightly bent with Ir1-C30-N4 and C30-N4-C31 bond angles of $176.8(6)^\circ$ and $173.2(7)^\circ$ respectively. This is similar to that observed in crystal structures of other *tert*-butyl isocyanide iridium complexes.⁸⁶

3.4.1.3 NMR Spectroscopy

The successful synthesis of **2** was confirmed by displaying characteristic resonances of *tert*-butyl protons of the ligand in the proton NMR spectrum. Moreover, the ^{13}C NMR (Figure 3.4) spectrum of **2** showed all twelve aromatic and aldehyde carbon peaks between 120 to 195 ppm as well as the characteristic quaternary carbon signal of *tert*-butyl at 59 ppm.

Chart 1: Structure of $[\text{Ir}(\text{fppy})_2(\text{t-Bu-iCN})_2][\text{CF}_3\text{SO}_3]$, **2**, with the numbering used in assigning the ^1H NMR.

Figure 3.4: ^{13}C NMR spectrum (300 MHz) of **2** in CDCl_3 .

In order to assign hydrogens of pyridyl benzaldehyde ligands, 1-D and 2-D techniques of ^1H NMR (Figure 3.5) and COSY (correlation spectroscopy, Figure 3.6) were used.

Figure 3.5: ^1H NMR spectrum (300 MHz) of **2** in CDCl_3 .

The COSY spectrum of **2** is shown in Figure 3.6. Spatially, the P6 proton of **2** is isolated from other protons by at least four bonds and appears as a singlet. No other aromatic hydrogen signals are easily identifiable based on multiplicity. To further interpret this COSY spectrum, it is necessary to analyze a model of the molecule graphically and determine possible interactions between protons. For example, the P4

proton has a potential interaction with P3 over three bonds. The expected result is a doublet for P4. Mutual interactions are between P3 and P4, N3 and N4, N4 and N5, and N5 and N6.

The aromatic region of proton spectrum in Figure 3.5 is grouped into six regions. In order to simplify the discussion, letters are used to represent each region. For example “A” refers to the singlet at 6.61 ppm, “B” refers to the peaks centered at 7.53 ppm and so on. Utilizing this method, a simplified COSY spectrum can be created as shown in Figure 3.7. The goal is to assign each region to a specific proton. Region C can be assigned to N4 or N5 due to interactions with two other groups of peaks E and F. Since assigning region F to N6 is more reasonable than N3, the C area resonances are therefore assigned to N5 proton. It follows that regions B and D must be due to the P3 and P4 protons, respectively.

Figure 3.6: COSY spectrum (300 MHz) of **2** in CDCl_3 .

	F (9.20)	E (8.13)	D (7.82)	C (7.69)	B (7.53)	A (6.61)
A (6.61)						AA
B (7.53)			BD		BB	
C (7.69)	CF	CE		CC		
D (7.82)			DD		DB	
E (8.13)		EE		EC		
F (9.20)	FF			FC		

Figure 3.7: Simplified representation of COSY spectrum of **2** in CDCl_3 .

3.4.1.4 Infrared Spectroscopy

The infrared spectrum of complex **2** is shown in Figure 3.8 in which the $\nu(\text{C}\equiv\text{N})_{\text{isocyanide}}$ is seen at 2177 cm^{-1} .

Figure 3.8: Infrared spectrum (KBr pellet) of **2** with $\nu(\text{C}\equiv\text{N})$ at 2177 cm^{-1} .

3.4.1.5 Electronic Spectroscopy

The room-temperature quantitative UV-Vis and emission spectra have been collected for **2** and are shown in Figure 3.9. Assignments are made by comparing the absorption spectrum of **2** with analogous complexes.^{67a, 75}

Three characteristic types of well-resolved absorption bands are observed in **2**. Intense absorption bands below 320 nm ($\epsilon \sim 3.0 \times 10^4 \text{ cm}^{-1} \text{ M}^{-1}$) are assigned to allowed $\pi\text{-}\pi^*$ transitions of the fppy ligand.^{67a} The weaker band appearing at 353 nm ($\epsilon = 6920 \text{ cm}^{-1} \text{ M}^{-1}$) can be assigned to Ir $\rightarrow$ fppy charge-transfer transitions.^{72k, 84} The aldehyde group of the fppy ligand appears to decrease the extinction coefficient of the MLCT band and to shift it to longer wavelengths compared to the MLCT band of its non-functionalized analogue **1**.⁷⁵ The decrease in MLCT intensity reflects a decrease in metal-ligand coupling⁸⁷ and the shift to longer wavelengths, particularly for emission, is consistent with a stabilization of the π^* orbitals of fppy by a conjugated electron-withdrawing substituent. The emission band shows a vibronic progression that has been previously analyzed for a series of Ir(tolylpyridine)₂ complexes, assuming a dominant vibrational stretch.⁸⁴ The relative intensities of these vibronic components is evidently substituent dependent as shown by the emission spectrum of **2**, compared with **1** and **8** (**2** attached to Silamine) (see section 3.4.2), but this was not investigated further.

Figure 3.9: Solution electronic absorption and emission spectra of **2**. The absorption spectrum was acquired in CH₃CN and the emission spectrum was acquired in CH₂Cl₂.

Complex **2** is strongly luminescent (quantum yield $\phi = 0.35$) with a long luminescence lifetime ($\tau = 17.3 \mu\text{s}$) at room temperature. Emission is suggested to be originating from a triplet excited state, based on the long lifetime and similarity of quantum yield to that of *fac*-Ir(*tpy*)₃ reported in the literature.⁷⁵ In addition, it benefits from a large Stokes shift (7100 cm⁻¹).

3.4.2 Synthesis of Water-Soluble Oxygen Sensor **8** by Reductive Attachment of **2** to Silamine D208-EDA and Spectroscopic Characterization

Reductive amination reaction between **2** and the water-soluble amine-functionalized Silamine D208-EDA gave the luminophore-functionalized Silamine, **8**, as shown in Scheme 3.3.

Scheme 3.3: Reductive amination of **2** with Silamine D208-EDA to make **8**.

The yield of the reaction in Scheme 3.3 was estimated by assuming that the electronic absorption properties of the iridium complex in **8** were the same as those of free complex **1**. The electronic spectrum of **8** was used to calculate attachment yield considering **8** as a solution of **1** in Silamine. Thus, a quantitative solution of **8** in CH₂Cl₂ showed a π - π^* absorption band at 263 nm that was assumed to possess the same extinction coefficient as the π - π^* absorption band of **1** ($\lambda = 260$ nm, $\varepsilon = 3.35 \times 10^4$ M⁻¹ cm⁻¹). Using the molar absorptivity of the π - π^* transition of **1** as the Silamine-attached luminophore model complex, the actual concentration of luminophore was determined. The calculated concentration of iridium complex in **8** indicated quantitative attachment of **2** to Silamine.

The attachment of **2** shown in Scheme 3.3 is of cross-linked Silamine chains. However, it is also possible for **2** to bind to a single Silamine chain by one or two methyl-amine links. **2** dispersed in Silamine shows an aldehyde proton chemical shift in the ¹H NMR at approx. 9.58 ppm (Figure 3.12). There was no evidence of unreacted aldehyde in the ¹H NMR of **8** (see Figures 3.10-3.13), which may indicate a complete condensation reaction or reduction of the aldehyde group by pyridine-borane. Unfortunately, ¹H NMR chemical shift of phenylpyridine protons overlaps with an imine proton that may be present. This, together with the large molecular weight of **8**, makes an assignment of the chemical shift of an imine proton ambiguous. Nevertheless, the similarity of **8** and **1**'s photophysical properties and electronic absorption spectroscopy (see Figure 3.15, compare with reference 75) suggests that imine linkages were reduced to methyl-amines by pyridine- borane. This was desired in order to closely

match the electronic and photophysical properties of the Silamine bound iridium complex **8** to those of complex **1**.

Figure 3.10: ^1H NMR spectrum (300 MHz) of Silamine D208-EDA in CDCl_3 .

Figure 3.11: ^1H NMR spectrum (300 MHz) of **2** dispersed in Silamine D208-EDA in CDCl_3 .

Figure 3.12: Aromatic range of ^1H NMR spectrum (300 MHz) of **2** dispersed in Silamine in CDCl_3 . Note the aldehyde proton chemical shift at 9.58 ppm

Figure 3.13: ^1H NMR spectrum (300 MHz) of **8** in CDCl_3 . The loss of the aldehyde peak due to the condensation reaction is labeled.

Luminophore attachment in **8** was proved by using IR spectroscopy as well. The IR spectrum of the iridium complex **2** in Silamine shows $\nu(\text{C}=\text{O})$ as a strong band at 1686 cm^{-1} , whereas **8** displays no aldehyde $\text{C}=\text{O}$ band (see Figure 3.14). Complete reaction with Silamine gives rise to the disappearance of the $\nu(\text{C}=\text{O})$ in the IR spectrum of **8**, while bands at 1609 , 1591 , 1564 , and 1454 cm^{-1} , corresponding to cyclometalating ligands $\text{C}=\text{C}$ and $\text{C}=\text{N}$ vibrational stretches, are retained.

Figure 3.14: Infrared spectra (thin films) of **2** in Silamine (top) and **8** (bottom) displaying no aldehyde C=O band in the polymer bound luminophore.

Room temperature absorption and emission spectra data for **8** are shown in Figure 3.15, which are very similar to those of **1**. Three characteristic absorption bands

are observed; the band at $\lambda = 258$ nm is assigned to fppy ligand $\pi-\pi^*$ transitions, whereas the band $\lambda = 367$ nm is assigned to iridium to fppy metal-to-ligand charge-transfer (MLCT) transitions.^{67a, 72k, 84}

Figure 3.15: Solution electronic absorption and emission spectra of **8**. The absorption spectrum was acquired in CH₃CN and the emission spectrum was acquired in CH₂Cl₂. For **8**, the extinction coefficient at $\lambda = 255$ nm was assumed to be identical with that of **1** at 260 nm.⁷⁵

The relative intensities of vibronic components of the emission band is shown to be substituent dependent (see Figure 3.16), however any additional analysis was not performed.

Figure 3.16: Qualitative solution emission spectra of **1** (red), **2** (blue), and **8** (black) in CH_3CN .

Bonding with Silamine slightly perturbs the photophysical properties of the luminophore. The excited MLCT state for **8** has a smaller emission quantum efficiency (0.23) but a longer lifetime (20.6 μs) compared to those of **2** ($\phi = 0.35$ and $\tau = 17.3 \mu\text{s}$).

Figures 3.17-3.19 give the emission spectra of thin films of luminophores **1**, **2**, and **8**. It appears that in case of **1** and **2**, the emission spectra depend highly on the thin film formulation. Due to low mechanical properties of Silamine D208-EDA, MC was

blended with PSPs before spraying them into films. The emission band shapes are more or less similar and the shift of the maxima in **2** relative to **1** and **8** has been decreased compared to what was seen in solution emission spectra. There are two kinds of matrix effects on emission spectra. Effects arising from the refractive index and dielectric constant are general effects which are essentially defined by the Lippert equation.⁸⁸ Effects resulting from specific chemical interactions between the luminophore and matrix are specific matrix effects.⁸⁸ Also, the shift can be attributed to aggregate formation due to a higher solubility of the luminophore in MC. As is displayed in Figure 3.18, it is proposed that once MC proportion in the film formulation is increased, the luminophore distributes in MC. Increasing MC concentration in the film, sharpens the low-energy shoulder of the emission spectrum. The emission spectra of thin films of **1** in 9:1 Silamine: MC, 1:2 Silamine: MC, and 1:5 Silamine: MC matrices also exhibit this effect (Figure 3.17). As illustrated in Figure 3.19, the thin film emission spectra of **8** show small changes by increasing MC proportion.

Figure 3.17: Effect of matrix on thin film luminescence of **1**. Matrices compositions are: 9:1 Silamine: MC (black), 1:2 Silamine: MC (red), and 1:5 Silamine: MC (green). For each formulation, the spectrum at 14.7 psi is shown, which is normalized to its maximum emission intensity.

Figure 3.18: Effect of matrix on thin film luminescence of **2**. Matrices compositions are: 9:1 Silamine: MC (black), 5:1 Silamine: MC (red), 1:1 Silamine: MC (green), 1:2 Silamine: MC (yellow), and 1:5 Silamine: MC (blue). For each formulation, the spectrum at 14.7 psi is shown, which is normalized to its maximum emission intensity.

Figure 3.19: Effect of matrix on thin film luminescence of **8**. Matrices compositions are: 5:1 Silamine: MC (black), 1:1 Silamine: MC (red), and 1:5 Silamine: MC (green). For each formulation, the spectrum at 14.7 psi is shown, which is normalized to its maximum emission intensity.

3.5 Synthesis of Water-Soluble Oxygen Sensor 11

3.5.1 Copper-Catalyzed Oxidation of Poly(ethylene glycol) Methyl Ether (PEGME) to PEGME-Aldehyde

In order to oxidize PEGME into PEGME-Aldehyde a practical copper-catalyzed procedure under mild conditions, invented by Markó et al.⁶⁴ was followed. Air was used in the catalytic method in which water is the only generated by-product. To increase the lifetime of the catalyst and the reaction rate, diethylazodicarboxylate was utilized. Insoluble K_2CO_3 adsorbs the heterogeneous catalyst. It is suggested that initially an alkoxide-bound azo-copper complex is produced which is transformed to a carbonyl-bound hydrazino-copper complex by a hydrogen-transfer reaction (Scheme 3.4). A binuclear copper (II) peroxide is then formed due to reaction with oxygen which is converted to a hydroxyl Cu(I) complex after homolytic cleavage and hydrogen atom abstraction from the hydrazine. The catalyst is restored by exchange between PEGME and the OH ligand, releasing a water molecule.

Scheme 3.4: Mechanism of copper-catalyzed oxidation of PEGME to PEGME-Aldehyde, $m = n - 1$

In PEGME-Aldehyde infrared spectrum, the $\nu(\text{C}=\text{O})_{\text{aldehyde}}$ is seen at 1719 cm^{-1} (Figure 3.20), indicating the successful oxidation.

Figure 3.20: Infrared spectrum (thin film) of PEGME-Aldehyde with $\nu(\text{C}=\text{O})$ at 1719 cm^{-1} .

3.5.2 Synthesis of Aminomethyl Phenylpyridine

Aminomethyl phenylpyridine (amppy) was synthesized by a Suzuki coupling reaction as shown in Scheme 3.5. 5-aminomethyl-2-chloro pyridine was first protected as the acetamide then the palladium mediated coupling proceeded efficiently with subsequent cleavage of the acetamide using HCl.⁸⁹

Scheme 3.5: Preparation of amppy by Suzuki coupling reaction.

Oxidative addition of the acetadimomethyl pyridine chloride to the palladium(0) complex generates a palladium (II) intermediate. This then undergoes a transmetallation with phenylboronic acid, expelling the product by reductive elimination and regenerating the palladium (0) catalyst. Sodium carbonate is the base used in order to accelerate the transmetallation step.

Scheme 3.6: Intermediates in amppy preparation by Suzuki coupling reaction.

^1H NMR, IR, and mass spectrometry confirmed successful synthesis of amppy. Chemical shifts and integration of the ^1H NMR spectrum of amppy (Figure 3.21) were appropriate for the phenyl and pyridyl protons. The expected singlet methylene and broad amine protons peaks were clearly visible. The infrared spectrum of the ligand showed representative absorbances of the $\nu(\text{N-H})_{\text{amine}}$ at 3437, 3269, and 1602 cm^{-1} . Mass spectrum confirmed the molecular weight of amppy with a molecular ion peak at 184 m/z.

Figure 3.21: ^1H NMR spectrum (300 MHz) of amppy in CDCl_3 .

Figure 3.22: Infrared spectrum (KBr pellet) of amppy with $\nu(\text{N-H})$ at 3437, 3269, and 1602 cm^{-1} .

3.5.3 Coupling of Ampy to PEGME-Aldehyde and Spectroscopic Characterization

$$\text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{Ph} + \text{O}=\text{C}-\text{CH}_2-\text{O}-[\text{CH}_2-\text{CH}_2-\text{O}]_m-\text{CH}_3 \longrightarrow \text{Ph}-\text{C}_6\text{H}_4-\text{CH}_2-\text{N}=\text{CH}-\text{O}-[\text{CH}_2-\text{CH}_2-\text{O}]_m-\text{CH}_3$$

Scheme 3.7: Coupling reaction of amppy with PEGME-Aldehyde

The aromatic region of the ^1H NMR spectrum of PEGME-Aldehyde and PEGME-attached amppy is illustrated in Figures 3.24-25. Whereas PEGME-Aldehyde shows an aldehyde peak at 9.6 ppm, PEGME-attached amppy shows peaks as follows: 8.69 (1H, d, 1.8 Hz), 8.27 (1H, dd, 2.1, 8.4 Hz), 8.07 (1H, d, 8.4 Hz), 7.85 (2H, dd, 3.0, 6.7 Hz), 7.56 (3H, m).

Figure 3.24: Aromatic region of the ^1H NMR spectrum (300 MHz) of PEGME-Aldehyde in D_2O showing the aldehyde chemical shift at 9.6 ppm.

Figure 3.25: Aromatic region of the ^1H NMR spectrum (300 MHz) of PEGME-attached amppy in D_2O showing amppy chemical shifts.

The calculated concentration of amppy in PEGME-attached amppy (see section 3.4.2) revealed quantitative attachment of amppy to PEGME-Aldehyde.

3.5.4 PEGME Attached Ir-Amppy Dimer Synthesis and Spectroscopic Characterization

PEGME-amppy is metallated easily using a method similar to Watts and Nonoyama⁷⁴ reactions. It reacts with iridium trichloride to give the PEGME attached Ir-

ampy dimer characterized by spectroscopic methods. This iridium dimer is an important reagent polymer that could lead to an entire family of water-based PSP formulations.

Proton NMR data for the PEGME attached amppy dimer of Ir(III) in D₂O is shown in Figure 3.26. The non-quantitative aromatic region peaks suggests that the environment is not homogeneous.

Figure 3.26: ¹H NMR spectrum (300 MHz) of PEGME-attached Ir-ampy dimer in D₂O.

The absorption and luminescence spectra of PEGME attached Ir-ampy dimer are shown in Figure 3.27. The intense ultraviolet absorption band observed at 279 nm is

assigned to an intraligand transition. Several transitions between 300 and 500 nm can be assigned to MLCT transitions. It displays a relatively intense emission at 460 nm.

Figure 3.27: Solution electronic absorption and emission spectra of PEGME attached Ir-ampy dimer. Both spectra were acquired in CH_2Cl_2 . The extinction coefficient was assumed to be identical with that of $[\text{Ir}(\text{ppy})_2\text{Cl}]_2$.

3.5.5 Synthesis of Water-Soluble Oxygen Sensor 11 - PEGME Attached [Ir(ampyy)₂(t-Bu-iCN)₂][CF₃SO₃] – Synthesis and Spectroscopic Characterization

The PEGME attached [Ir(ampyy)₂(t-Bu-iCN)₂][CF₃SO₃] complex was prepared from PEGME attached amppy dimer by chloride abstraction with AgOTf followed by complexation with CN-*t*-Bu (shown in Scheme 3.8).

Scheme 3.8: Synthesis of **11**

The room temperature absorption and emission spectra displayed by **11** is shown in Figure 3.28. The attachment of the complex to PEGME results in little change in the photophysical properties of the [Ir(ampyy)₂(t-Bu-iCN)₂][CF₃SO₃] complex relative to **8**. The three typical absorption bands are found as amppy ligand π - π^* transition band at $\lambda = 253$ nm, and iridium to amppy metal-to-ligand charge-transfer (MLCT) transition band at $\lambda = 371$ nm.

Figure 3.28: Solution electronic absorption and emission spectra of **11**. The absorption spectrum was acquired in CH_3CN and the emission spectrum was acquired in CH_2Cl_2 . For **11**, the extinction coefficient at $\lambda = 253 \text{ nm}$ was assumed to be identical with that of **1** at 260 nm .⁷⁵

3.6 Characterization of Pressure Sensitive Paint (PSP) Films of **2**, **8**, and **11**

Among PSPs incorporating **2**, **8**, and **11**, the completely water-soluble film formulations are those of **8** and **11**. To compensate for the poor mechanical properties of Silamine D208-EDA, microcrystalline cellulose (MC) was included in the formulations. The pressure-dependent film emission spectra of **2**, **8**, and **11** in different matrices were studied and are represented in Figures 3.29-3.31. Films of **8** displayed an intense yellow-white luminescence with UV irradiation under low pressure conditions, while films of **2**

showed a noticeably reduced luminescence despite having the same concentration of luminophore and a higher emission quantum yield. This suggests that **2** aggregates and self-quenches in the film formulations used in this study. Various thin films oxygen sensitivities were measured and compared in Table 3.4. It is evident that the oxygen sensitivity of emission intensity is linear in the pressure range of 0.007-45 psi (Figure 3.32). Figure 3.32 shows modified Stern-Volmer plots of **1**, **2**, and **8** in two Silamine:MC formulations.

Figure 3.29: Effect of pressure on thin film luminescence of **2** in 1:1 Silamine: MC. The decrease of intensity with increasing the air pressure is displayed. Spectra were acquired at 1.3 mbar, 0.34 bar, 0.68 bar, 1 bar, 1.36 bar, 1.70 bar, 2.04 bar, 2.38 bar, 2.72 bar, and 3.06 bar. Background correction has been performed.

Figure 3.30: Effect of pressure on thin film luminescence of **8** in 1:1 Silamine: MC. The decrease of intensity with increasing the air pressure is displayed. Spectra were acquired at 1.3 mbar, 0.34 bar, 0.68 bar, 1 bar, 1.36 bar, 1.70 bar, 2.04 bar, 2.38 bar, 2.72 bar, and 3.06 bar. Background correction has been performed.

Figure 3.31: Effect of pressure on thin film luminescence of **11** in 4:1 PEG: MC. The decrease of intensity with increasing the air pressure is displayed. Spectra were acquired at 1.3 mbar, 0.34 bar, 0.68 bar, 1 bar, 1.36 bar, 1.70 bar, 2.04 bar, 2.38 bar, 2.72 bar, and 3.06 bar. Background correction has been performed.

Oxygen quenching sensitivity of **8** in 1:1 Silamine: MC is the greatest compared with sensitivities of films of **1**, **2**, or **11**, (see Figure 3.32 and Table 3.4).

Figure 3.32: Stern-Volmer plots of **1** in 9:1 Silamine: MC, $\square$; **1** in 1:1 Silamine: MC, $\bullet$; **2** in 9:1 Silamine: MC, $\circ$; **2** in 1:1 Silamine: MC, $\square$; **8** in 9:1 Silamine: MC, $\bullet$; **8** in 1:1 Silamine: MC, $\circ$; **11** in 4:1 PEG: MC, $\bullet$.

Table 3.4: PSP films oxygen sensitivity data for **1**, **2**, **8**, and **11**.

Luminophore	Matrix	$Q_s(r^2)$
1	9:1 Silamine: MC	0.26 (0.992) ^b
	5:1 Silamine : MC	0.28 (0.991) ^b
	1:1 Silamine: MC	0.30 (0.980) ^b
	1:2.3 Silamine: MC	0.26 (0.981) ^b
	1:5 Silamine: MC	0.26 (0.975) ^b
2	9:1 Silamine: MC	0.24 (0.973) ^b
	5:1 Silamine : MC	0.25 (0.977) ^b
	1:1 Silamine: MC	0.29 (0.974) ^b
	1:2.3 Silamine: MC	0.27 (0.970) ^b
	1:5 Silamine : MC	0.24 (0.974) ^b
8	9:1 Silamine: MC	0.28 (0.976) ^b
	5:1 Silamine : MC	0.28 (0.955) ^b
	1:1 Silamine: MC	0.50 (0.989) ^a
	1:2.3 Silamine: MC	0.44 (0.975) ^a
	1:5 Silamine: MC	0.33 (0.982) ^b
11	4:1 PEG: MC	0.20 (0.986) ^a

^a0.007-45 psi; ^b5-45 psi

Oxygen sensitivity as well as mechanical properties of the film is increased as a consequence of the blending of MC with luminophores compared with the film composed of the polymer with low glass transition temperature. It is suggested that this effect originates from a decrease in the luminophores freedom of motion and consequentially an increase in its luminescence lifetime. Moreover, the preferential binding of luminophore to MC could lead to de-aggregation and a decrease in self-quenching.

Increasing the MC content in PSP formulations of **8**, results in decrease in downward curvature of the Stern-Volmer plots. This is supposed to be owing to the increased rigidity of the matrix and the confined movement of the luminophore molecules. This is evident in Figure 3.32 for **8** in 9:1 Silamine: MC and a 1:1 Silamine: MC blend. Several low Tg polymer: MC ratios were used for luminophores in order to

determine the conditions for optimum PSP performance. As seen from Figure 3.32 and the data in Table 3.4, quenching sensitivity (particularly for **8**) is dependent upon microcrystalline cellulose concentration. To help understand this, the luminescence microscopy of films of **8** was examined, and the results are shown in Figure 3.33.

Figure 3.33: Luminescence microscopy of films of **8** performed under ambient conditions: A, 9:1 Silamine:MC; B, 5:1 Silamine:MC; C, 1:1 Silamine:MC; D, 1:2.3 Silamine:MC; E, 1:5 Silamine:MC. The scale in red is 10 μm .

In Figure 3.33 A, luminescence microscopy shows that at low concentration of MC, the luminescence from the film is largely dispersed with some local enhancement around particles of MC. This localization of luminescence around MC particles becomes even more obvious in Figure 3.33 C, the film that gives the best oxygen sensor performance. In Figure 3.33 E, the film that has the greatest concentration of MC, an overall loss of luminescence intensity has obviously occurred which is attributed to light scattering by MC particles but there is still evidence of luminophore association with MC. It is suggested that the positively charged iridium luminophore in **8** is electrostatically attracted to the polar hydroxyl groups on the surface of MC.

Lifetime measurements of 9:1, 1:1 and 1:5 Silamine:MC films of **8**, under ambient pressure and vacuum, are compiled in Table 3.5. Emission decay was fitted with a double exponential assuming two luminophore environments: **8** in Silamine polymer and **8** associated with the MC surface. The data show an increase in lifetime with increasing MC fraction which can be due to a decrease in non-radiative decay of the excited molecule.

Table 3.5: Luminescence lifetime data in μs (with pre-exponential factors in parentheses) of **8** in Silamine:MC films

Silamine:MC film	Vacuum			Ambient pressure		
	τ_1	τ_2	R^2	τ_1	τ_2	R^2
9:1	0.5 (0.7)	5.9 (0.3)	0.990	0.3 (0.9)	4.9 (0.1)	0.986
1:1	0.6 (0.8)	17.6 (0.2)	0.995	0.6 (0.7)	12.9 (0.3)	0.997
1:5	3.2 (0.8)	25.8 (0.2)	0.993	0.5 (0.9)	15.3 (0.1)	0.984

Quenching sensitivity Q_s is dependent upon both lifetime and the quenching rate constant k_q (Eqn 1.5 and 1.13) and so the observation of an optimum Q_s value (see Table

3.4) with MC fraction suggests that the quenching rate constant, or more specifically the diffusion of oxygen, must decrease with increasing fraction of MC. The optimum PSP formulation in Table 3.4 is **8** in 1:1 Silamine:MC which gave an oxygen sensitivity of 0.50, with good linear behavior in a pressure range of 0.007 to 45 psi.

The temperature dependence of emission intensity of **1**, **2** and **8** in 1:1 Silamine:MC films were examined in the temperature range of 10 to 40 °C under vacuum and 1 bar atmospheric pressure. The emission intensities were normalized to that at 10 °C and the results plotted in Figure 3.34.

Figure 3.34: Temperature versus emission intensity ratio (I_{ref} is the intensity at 10 °C) of **1** in 1:1 Silamine: MC: vacuum ▲ and P = 1bar ●, **2** in 1:1 Silamine: MC: vacuum ● and P = 1bar ▼, and **8** in 1:1 Silamine: MC: vacuum ■ and P = 1bar .

In Figure 3.34, the data for the temperature dependence of emission gave good linear least-squares fits passing through or at least closely approaching the normalization value at 10 °C. The temperature sensitivities (percent intensity loss per degree) of the films were determined to be -1.1% and -1.3% °C⁻¹ for **1**, -1.5% and -1.6% °C⁻¹ for **2**, and -1.1% and -1.4% °C⁻¹ for **8** at vacuum and 1 bar atmospheric pressure, respectively. The increase in temperature sensitivity at 1 bar atmospheric pressure relative to that at vacuum can be ascribed to the temperature dependence of bimolecular oxygen quenching and is expected but the significant temperature sensitivities of the films of **1**, **2** and **8** in vacuum are not. Luminescent decay of Ir(C_s)(acac)₂, where C_s is 3-benzothiazol-2-yl)-7-(diethylamino)-coumarin and acac is acetylacetonate, showed very little dependence on temperature from 1 to 50 °C in vacuum.^{36d} Similarly, PSP's using osmium complex luminophores have shown a range of temperature sensitivities varying from -0.11 to -1.00 %°C⁻¹ in vacuum^{20c} which suggests that the nature of the coordination sphere plays a critical role in determining temperature sensitivity. In any case, the temperature sensitivity of **8** in 1:1 Silamine:MC films must be compensated for to obtain correct barometric data and this can be achieved by using a temperature sensitive calibrant as in a dual-luminophore oxygen and temperature sensor film.^{20u}

3.7 Other Functionalized Ir (III) Complexes

3.7.1 Synthesis

Starting materials $[\text{Ir}(\text{C}_6)_2\text{Cl}]_2$ and $[\text{Ir}(\text{ppy})_2\text{Cl}]_2$ (Scheme 3.9) were prepared according to Thompson,^{72c} and Watts and Nonoyama.⁷⁴

Scheme 3.9: Synthesis of starting iridium dimers.

Commercially unavailable ligand 1,10-phenanthroline-2,9-dicarboxaldehyde was prepared according to Chandler.⁷⁹

Synthesis of iridium complexes involved breaking of starting dimers using silver triflate (except for **6**) followed by coordination of the second ligand (shown in Schemes 3.10, 3.11, and 3.12).

Scheme 3.10: Synthesis of **3**

Scheme 3.11: Synthesis of **4**

Scheme 3.12: Synthesis of **6**

Complex **3** was synthesized from $[\text{Ir}(\text{C}_6\text{H}_5)_2\text{Cl}]_2$ using silver triflate to cleave the iridium dimer, and the acid functionalized ligand used was 4,6-dioxoheptanoic acid (acacacid). An acceptable yield was obtained (38%).

The non-ionic complex **4** was synthesized from $[\text{Ir}(\text{ppy})_2\text{Cl}]_2$ at room temperature using silver triflate to cleave the chloride bridged dimer.⁹⁰ The amine group of amppy coordinates to iridium preventing the cyclometalation of phenylpyridine. A high yield (79%) was obtained.

6 was synthesized from $[\text{Ir}(\text{ppy})_2\text{Cl}]_2$ and 1,10-phenanthroline-2,9-dicarboxaldehyde in a high yield (85%).

3.7.2 X-ray Crystallography

Structure of **4** was confirmed by X-ray crystallography on its single crystals grown from dichloromethane solutions by diffusion of hexanes. The ORTEP drawing of

$4 \cdot \text{CH}_2\text{Cl}_2$ is shown in Figure 3.35. Crystallographic data and some selected bond lengths and angles are given in Tables 3.6-3.7. Full data of atomic coordinates, bond lengths and angles for the complex can be found in Appendix A.

Figure 3.35: ORTEP of $4 \cdot \text{CH}_2\text{Cl}_2$. The methylene chloride solvent molecule and aromatic-ring hydrogen atoms are omitted for clarity.

Table 3.6: X-ray Crystallographic Data and Refinement Details for **4**·CH₂Cl₂.

Empirical formula	C ₃₄ H ₂₈ IrN ₄ Cl·CH ₂ Cl ₂
M _r	805.18
Cryst syst	Monoclinic
space group	<i>P</i> 2(<i>1</i>)/ <i>c</i>
unit cell dimensions	<i>a</i> = 10.4363(15) Å <i>b</i> = 25.923(4) Å <i>c</i> = 11.7427(17) Å α = 90.00 ° β = 100.315(2) ° γ = 90.00 °
<i>V</i>	3125.5(8) Å ³
<i>D</i> _x	1.711 g cm ⁻³
<i>T</i>	200(2) K
λ	0.71073 Å
R[<i>F</i> ² > 2σ(<i>F</i> ²)]	0.0305
wR(<i>F</i> ²)	0.0684
<i>Z</i>	4
μ	4.560 mm ⁻¹

Table 3.7: Selected Bond Lengths (Å) and Angles (°) for **4**·CH₂Cl₂.

Ir1—N1	2.040(3)	N4—Ir1—Cl1	82.56(9)
Ir1—N2	2.047(3)	C28—N4—Ir1	119.0(2)
Ir1—C11	1.994(3)	C11—Ir1—N1	80.62(13)
Ir1—C22	1.997(3)	C22—Ir1—N2	80.27(14)
Ir1—Cl1	2.4894(9)	C25—Ir1—C30	91.94(4), 89.1(3)
Ir1—N4	2.222(3)		

In **4**·CH₂Cl₂ iridium is octahedrally coordinated with one chlorine, two carbon, and three nitrogen donor atoms in which aminomethyl phenylpyridine and chlorine ligands are *cis* to each other. The Ir-N and Ir-C bond lengths (Table 3.7) are similar to those of analogous complexes possessing the bis(phenylpyridine)iridium fragment.^{84, 91} Being the amppy nitrogen *trans* to the anionic phenyl ligand and not part of a

metallocycle, the amppy Ir-N bond length is greater than the ppy Ir-N bonds. It is longer by ca. 0.09 Å than that of an analogous complex possessing ppy ligands with nitrogens *trans* to carbon atoms.⁹¹

3.7.3 NMR Spectroscopy

The successful syntheses of the iridium complexes were confirmed by displaying characteristic resonances of the ligand in the proton NMR spectrum. These characteristic chemical shifts are new methyl, methylene, and carboxylic acid protons for **3**, a more complicated spectrum in the aromatic region, and new amine and methylene protons for **4**, and aldehyde protons for **6**.

In the NMR spectrum of **3**, the carboxylic acid group (5, Chart 2) displays a downfield broad peak of an integration of one (12.02 ppm). 1 and 2 protons are singlets found at 1.69 ppm and 4.98 ppm, respectively and 3 and 4 protons are found as multiplets at 2.22 and 2.08 ppm. The aromatic region shows four multiplet resonances for C6 ligands. C6 ethyls appear at 3.27 and 0.94 ppm.

Chart 2: Structure of $[\text{Ir}(\text{C}_6)_2(\text{acacacid})]$, **3**, with the numbering used in assigning the ^1H NMR.

Figure 3.36: ^1H NMR spectrum (300 MHz) of **3** in $\text{DMSO}-d_6$.

The splitting pattern of the ^1H NMR of **4** exhibits complexity in the phenyl and pyridyl region.

Figure 3.37: ^1H NMR spectrum (300 MHz) of **4** in CDCl_3 .

The aldehyde protons of **6** display a peak at the expected chemical shift (9.70 ppm).

Chart 3: Structure of $[\text{Ir}(\text{ppy})_2(\text{phendiald})][\text{PF}_6]$, **6**.

Figure 3.38: ^1H NMR spectrum (300 MHz) of **6** in acetone- d_6 . The aldehyde resonance is labelled.

3.7.4 Infrared Spectroscopy

The infrared spectra of complexes **3**, **4**, and **6** are shown in Figures 3.39-3.41, respectively. For **3**, Figure 3.39, shows two $\nu(\text{C=O})_{\text{acacacid}}$ stretches appear at 1680 cm^{-1} (lactone) and 1607 cm^{-1} (carboxylic acid). For **4**, Figure 3.40, the $\nu(\text{N-H})_{\text{amine}}$ is seen at 3281 cm^{-1} . Also, in **6** a $\nu(\text{C=O})_{\text{phendiald}}$ stretch is shown at 1729 cm^{-1} .

Figure 3.39: Infrared spectrum (KBr pellet) of **3** with $\nu(\text{C=O})$ at 1680 and 1607 cm^{-1} .

Figure 3.40: Infrared spectrum (KBr pellet) of **4** with $\nu(\text{N-H})$ at 3281 cm^{-1} .

Figure 3.41: Infrared spectrum (KBr pellet) of **6** with $\nu(\text{C}=\text{O})$ at 1729 cm^{-1} .

3.7.5 Electronic Spectroscopy

The room-temperature quantitative UV-Vis and emission spectra have been collected for all the complexes and are shown in Figures 3.42-3.44. All spectroscopic data are given in Table 3.8 and assignments made by comparing the absorption spectra with those of analogous complexes.^{36e, 67a, 72c, 92} **4**, and **6** exhibit ultraviolet intense absorption bands below 300 nm ($\epsilon \sim 3.0\text{-}4.0 \times 10^4\text{ cm}^{-1}\text{ M}^{-1}$) which are assigned to allowed $\pi\text{-}\pi^*$ transitions of the aromatic ligands. Weaker bands located at longer

wavelengths can be assigned to MLCT transitions consisting of $^1\text{MLCT}$ and $^3\text{MLCT}$ transitions.

Two intense $\pi\text{-}\pi^*$ transitions of the C6 ligand are observed in the absorbance spectrum of complex **3**. C6 is a common fluorescent laser dye with a green fluorescence in solution and high quantum efficiency at room temperature. It does not show any detectable phosphorescence.^{72c} The emission maximum appears at 500 nm which shifts to 570 nm in **3** as a result of coordination to Ir, which is similar to the non-functionalized complex, $(\text{C6})_2\text{Ir}(\text{acac})$. This is an indication of intersystem crossing prompted by the vicinity of the heavy Ir atom.^{72c} A vibronic fine structure is also shown in the structured luminescent spectrum of **3**, thus the emission is from a ligand-based excited state.

The absorption spectrum of **4** exhibits intense phenyl- and pyridyl-based $\pi\text{-}\pi^*$ band at 259 nm with $^1\text{MLCT}$ transitions at 392 nm and $^3\text{MLCT}$ transitions at 431 nm. No peak is observed at wavelengths longer than 470 nm. The solution emission spectrum of **4** shows a single broad band with a maximum at 531 nm and no clear low-energy shoulder; hence the emission is from a mainly MLCT-based excited state.⁹¹

Complex **6** exhibits intense high-energy absorption bands at 257 nm ($\epsilon = 3.75 \times 10^4 \text{ cm}^{-1} \text{ M}^{-1}$) and 293 nm ($\epsilon = 4.55 \times 10^4 \text{ cm}^{-1} \text{ M}^{-1}$) and a weaker broad absorption band at 384 nm in the electronic absorbance spectrum, which are assigned to intraligand $\pi\text{-}\pi^*$ and spin-allowed MLCT transitions, respectively. A weaker absorption tail is also displayed around 473-555 nm in the spectrum, characteristic of spin-forbidden MLCT transitions. It shows an intense, broad, structureless orange-yellow luminescence with maximum at 584 nm in dichloromethane solution at room temperature. Based on

literature,⁹³ the emission is assigned to be originating from a charge-transfer triplet excited state involving low-lying π^* orbitals of the coordinated phenaldiol ligand as the acceptor orbital.⁹²

Table 3.8: Solution absorption and emission data for complexes 1-6

	1^c	2	3	4	5^f	6
$\lambda_{\max}^*$ $\pi-\pi^*$ (nm)(ϵ) ^a	260 (3.35×10^4)	258 ^d (2.51×10^4)	447 ^e (6.51×10^4)	259 ^c (3.38×10^4)	290 ^g (3.60×10^4)	257 ^c (3.75×10^4)
$\lambda_{\max}$ MLCT (nm) (ϵ)	348 (1.21×10^4)	367 ^d (6.92×10^3)	474 ^c (7.54×10^4)	392 ^c (1.78×10^3) 431 ^e (1.31×10^3)	379 ^g (7.40×10^3) ^h 454 ^g (2.60×10^3)	384 ^c (8.53×10^3) 508 ^e (1.28×10^3)
$\lambda_{\max}$ emission (nm)	458	496 ^e 534 ^e	570 ^c	531 ^e	510 ^g	584 ^e
$\lambda_{\max}$ emission (nm) ^b		573 ^e	619 ^c		540 ^g	

^a units of $M^{-1}cm^{-1}$, ^b low-energy shoulder, ^c from reference 75, ^d CH_3CN , ^e CH_2Cl_2 , ^f from reference 68, ^g toluene, ^h broad

Figure 3.42: Solution electronic absorption and emission spectra of **3**. Both the absorption and emission spectra were acquired in CH_2Cl_2 .

Figure 3.43: Solution electronic absorption and emission spectra of **4**. Both the absorption and emission spectra were acquired in CH_2Cl_2 .

Figure 3.44: Solution electronic absorption and emission spectra of **6**. Both the absorption and emission spectra were acquired in CH_2Cl_2 .

Luminescence lifetime and quantum yields for complexes **1-6** are tabulated in Table 3.9. Complex **3** has an emission quantum yield of 0.01 with 1.76 μs lifetime. The phosphorescent transition quantum yield is different from that of the fluorescent transition of *C6* ligand. Higher non-radiative rate constants can be resulted from excited state reactions of the carboxylic acid group. Complex **6** has a luminescence lifetime of 2.3 μs at room temperature. Complexes **2** and **3** were found to be the most favorable luminophores, according to the lifetime and quantum yield data. Among all complexes, **2** has the longest lifetime and highest emission quantum yield. For **3**, its strong absorbance in the visible region means that efficient excitation is possible using long-wavelength radiation.

Table 3.9: Luminescence quantum yields and lifetimes for complexes **1-7**

	1^a	2	3	4	5^b	6	7^c
ϕ	0.28	0.35	0.01	0.004	0.05	0.007	0.006
τ (μ s)	35.6	17.3	1.76	0.20	0.9	2.3	144

^a from reference 75, ^b from reference 68, ^c from reference 81

3.8 Other Water-Based PSP Formulations

3.8.1 Criteria for Attachment

Comparing water-soluble polymer bound oxygen sensors with dispersions of the luminophores in water-soluble polymers, the altered behavior proved the bindings between luminophores and polymers. For example, polymer bound luminophores are water-soluble, whereas trying to dissolve polymer dispersed luminophores in water, crystallized the luminophores out of solutions. Moreover, electronic absorption and emission, and oxygen sensitivity of the polymer bound sensors would be different from dispersions.

3.8.2 Synthesis of 9 by Coupling of 3 to Silamine D208-EDA and Spectroscopic Characterization

The covalent attachment of complex 3 to Silamine D208-EDA occurred at room temperature by the use of coupling agent dicyclohexylcarbodiimide.⁶⁵ The coupling agent has been often used in peptide synthesis⁹⁴ and its mechanism is shown below:

The acid anhydride of 3, as shown in Step 5 reacts with the amine groups of the Silamine polymer, giving 9. Using the method explained in section 3.4.2, the attachment yield of the orange polymer was 83%.

9 displays room temperature absorption and emission spectra shown in Figure 3.45. The Silamine attachment causes only subtle changes in the photophysical characteristics of the luminophore, suggesting that the carboxylic group of the acacacid does not influence the excited state.

Figure 3.45: Solution electronic absorption and emission spectra of **9**. Both spectra were acquired in CH_2Cl_2 . For **9**, the extinction coefficient at $\lambda = 445$ nm was assumed to be identical with that of **3** at 447 nm. See Table 3.8 data.

3.8.3 Preparation and Spectroscopic Characterization of 10

The dispersion of complex **4** in Silube CS-1 was tried in order to develop water-soluble luminophore **10**. The formulation of **10** is shown in Scheme 3.13.

Scheme 3.13: Dispersing **4** in Silube CS-1 to make **10**.

The absorption and emission spectra of **10** are shown in Figure 3.46. The intense absorption band in ultraviolet region at 255 nm is assigned to intraligand transition while absorption bands at 396 nm and 457 nm can be assigned to $^1\text{MLCT}$ and $^3\text{MLCT}$ transitions, respectively. A single broad band is observed in the solution emission spectrum of **10** with a maximum at 525 nm.

Figure 3.46: Solution electronic absorption and emission spectra of **10**. Both spectra were acquired in CH_2Cl_2 .

3.8.4 Synthesis of **12** by Coupling of **5** to Silamine D208-EDA and Spectroscopic Characterization

In order to study **5** in a water-soluble formulation, it was bound to Silamine as illustrated in Scheme 3.14. An imine is formed by the reaction between amine functionalized polymer and the aldehyde group followed by an elimination of water.

Scheme 3.14: Coupling reaction of **5** with Silamine D208-EDA to make **12**.

Attachment yield of the yellow polymer was calculated, (section 3.4.2), to be 97%.

The absorption and emission spectra of **12** are shown in Figure 3.47. The intraligand transition appears as an intense absorption band in ultraviolet region at 285

nm while MLCT transitions are shown as transitions between 360 and 490 nm. The emission is displayed at 528 nm.

Figure 3.47: Solution electronic absorption and emission spectra of **12**. Both spectra were acquired in CH₂Cl₂. For **12**, the extinction coefficient at $\lambda = 285$ nm was assumed to be identical with that of **5** at 290 nm.⁶⁸

3.8.5 Synthesis of 13 by Reductive Attachment of 5 to Silamine D208-EDA and Spectroscopic Characterization

The luminophore-functionalized Silamine, **13**, was produced by reductive amination reaction between **5** and the water-soluble amine-functionalized Silamine D208-EDA, as shown in Scheme 3.15.

Scheme 3.15: Reductive amination of **5** with Silamine D208-EDA to make **13**.

Using the method explained in section 3.4.2, the attachment yield of the yellow polymer was 96%.

The electronic absorption and emission spectra of **13** are similar to those of **5**⁶⁸ and **12** and are shown in Figure 3.48.

Figure 3.48: Solution electronic absorption and emission spectra of **13**. Both spectra were acquired in CH_2Cl_2 . For **13**, the extinction coefficient at $\lambda = 282$ nm was assumed to be identical with that of **5** at 290 nm.⁶⁸

3.8.6 Synthesis of **14** by Reductive Attachment of **6** to Silamine D208-EDA and Spectroscopic Characterization

Reductive amination reaction between **6** and the water-soluble amine-functionalized Silamine D208-EDA gave the luminophore-functionalized Silamine, **14**, as shown in Scheme 3.16.

The attachment yield of the orange polymer was calculated, (see section 3.4.2) to be 63%.

As shown in Scheme 3.16, it is possible for **6** to cross-link Silamine chains, or bind to a single Silamine chain by one or two methyl-amine links.

Figure 3.49 shows the electronic absorption and emission spectra of **14**. This water-soluble polymer-bound luminophore exhibits an intense high-energy absorption band at 269 nm which is assigned to intraligand $\pi\text{-}\pi^*$ transitions. Spin-allowed MLCT transitions appear as a weaker absorption shoulder at 400 nm while spin-forbidden MLCT transitions are displayed as a weaker absorption tail around 478-496 nm. At room temperature, **14** in dichloromethane solution shows a broad orange-yellow luminescence at 504 nm with a low-energy shoulder at 527 nm which is assigned to be originating from a MLCT triplet excited state involving low-lying π^* orbitals of the coordinated phenoidal ligand as the acceptor orbital.⁹² The emission spectrum does not vary when the excitation wavelength is changed in the region above 360 nm, suggesting that only the single, lower energy component is excited at these wavelengths.

Figure 3.49: Solution electronic absorption and emission spectra of **14**. Both spectra were acquired in CH_2Cl_2 . For **14**, the extinction coefficient at $\lambda = 269$ nm was assumed to be identical with that of **6** at 257 nm. See Table 3.8 data.

3.8.7 Synthesis of **15** by Coupling of 1-Pyrenebutyric Acid (PBA) to Silamine D208-EDA and Spectroscopic Characterization

Pyrene-based PSPs have lower temperature sensitivities compared with other PSPs.^{20b} However, pyrene sublimation is a disadvantage.⁹⁵ Since Silamine has a large number of amine functionalities, an appropriate concentration of pyrene can be obtained by coupling it with PBA in order to acquire excimer emission which is more sensitive to oxygen compared with monomer emission. In addition, the sublimation of pyrene is

prevented by polymer attachment. The coupling reaction was used for acquiring **15**, in the same manner utilized for synthesizing **9**, and is shown in Scheme 3.17.

Scheme 3.17: Coupling reaction of **PBA** with Silamine to make **15**.

Attachment yield of the colourless polymer was calculated, as explained in section 3.4.2. and indicated a quantitative attachment of **PBA** to Silamine.

The absorption and emission spectra of **15** are shown in Figure 3.50. The α -band appears at 345 nm and the p -bands are shown in ultraviolet region at 267, 277, and 329 nm. **15** shows two characteristic emission peaks: a blue monomer fluorescence in solution at 381, and 399 nm and excimer peak at 479 nm.

Figure 3.50: Solution electronic absorption and emission spectra of **15**. Both spectra were acquired in CH_2Cl_2 . For **15**, the extinction coefficient at $\lambda = 344$ nm was assumed to be identical with that of **PBA** at 341 nm.⁹⁶

3.8.8 Electronic Spectroscopy

The room-temperature UV-Vis and emission data of **8-15** are given in Table 3.10 and the luminescence lifetimes and quantum yields for all of luminophores **8-15** are

listed in Table 3.11. Comparing each polymer bound oxygen sensor with the original dye, (**8** and **2**, **9** and **3**, **12** and **5**, **13** and **5**, **14** and **6**, compare Tables 3.11 and 3.9), reveals that upon attachment to a polymer, each luminophore shows an increase in excited state lifetime. Interactions of excited state with the functional groups can give rise to non-radiative decay which might have been reduced in case of attached dyes. The increase in lifetime can also originate from a decrease in the dyes motion in the polymeric matrix. In **10**, the luminophore is not attached to the polymer and in **14**, the presence of the unreacted aldehyde functional groups can still result in non-radiative decay.

Table 3.10: Solution absorption and emission data for **8-15**.

	8	9	10	11	12	13	14	15
$\lambda_{\max} \pi\text{-}\pi^*$ (nm)	239,263, 317 ^b	445 ^c	255 ^c	253, 268, 310 ^b	285 ^c	282 ^c	270 ^c	345 ^c
$\lambda_{\max}$ MLCT (nm)	359 ^b	473 ^c	396 ^c 457 ^c	371 ^b	360 ^{c, d} 444 ^c	350 ^{c, d} 463 ^c	400 ^c 487 ^c	
$\lambda_{\max}$ emission (nm)	461 ^c	567 ^c	525 ^c	463 ^c	528 ^c	523 ^c	504 ^c	380 ^c
$\lambda_{\max}$ emission (nm) ^a		606 ^c			597 ^c	575 ^c	527 ^c	

^a low-energy shoulder, ^b CH₃CN, ^c CH₂Cl₂, ^d broad**Table 3.11:** Luminescence quantum yields and lifetimes for **8-15**

	8^a	9^a	10^a	11^b	12^a	13^a	14^a	15^a
ϕ	0.23	0.01	0.01	0.003	0.03	0.03	0.02	0.06
τ (μ s)	20.6	10.02	0.03, 0.18 ^c	4.10	1.4	3.0	1.9	0.14

^a CH₂Cl₂, ^b CH₃CN, ^c fitted with a double exponential

The effect of matrix on thin film luminescence of **9**, **10**, **12**, **13**, and **14** is presented in Figures 3.51-3.55. Small variation in thin film emission spectrum due to matrix change is displayed.

Figure 3.51: Effect of matrix on thin film luminescence of **9**. Matrices compositions are: Silamine (black), 1:1 Silamine: MC (red), and 1:5 Silamine: MC (green). For each formulation, the spectrum at 14.7 psi is shown, which is normalized to its maximum emission intensity.

Figure 3.52: Effect of matrix on thin film luminescence of **10**. Matrices compositions are: Silube (black), 5:1 Silube: MC (red), 1:1 Silube: MC (green), and 1:5 Silube: MC (yellow). For each formulation, the spectrum at 14.7 psi is shown, which is normalized to its maximum emission intensity.

Figure 3.53: Effect of matrix on thin film luminescence of **12**. Matrices compositions are: 2.3:1 Silamine: MC (black), 1:1 Silamine: MC (red), and 1:9 Silamine: MC (green). For each formulation, the spectrum at 14.7 psi is shown, which is normalized to its maximum emission intensity.

Figure 3.54: Effect of matrix on thin film luminescence of 13. Matrices compositions are: 2.3:1 Silamine: MC (black), 1:1 Silamine: MC (red), and 1:9 Silamine: MC (green). For each formulation, the spectrum at 14.7 psi is shown, which is normalized to its maximum emission intensity.

Figure 3.55: Effect of matrix on thin film luminescence of **14**. Matrices compositions are: 5:1 Silamine: MC (black), 1:1 Silamine: MC (red), and 1:2.3 Silamine: MC (green). For each formulation, the spectrum at 14.7 psi is shown, which is normalized to its maximum emission intensity.

3.8.9 Characterization of Pressure Sensitive Paint (PSP) Films

3.8.9.1 PSP 9

9 benefits from absorbance in the visible region and efficient excitation using long-wavelength radiation. Results for oxygen sensor **9** are given in Figures 3.56-3.58 and Table 3.12.

Figure 3.56: Effect of pressure on thin film luminescence of **9** in Silamine. The decrease of intensity with increasing the air pressure is displayed. Spectra were acquired at 1.3 mbar, 0.34 bar, 0.68 bar, 1 bar, 1.36 bar, 1.70 bar, 2.04 bar, 2.38 bar, 2.72 bar, and 3.06 bar. Background correction has been performed.

Figure 3.57: Effect of pressure on thin film luminescence of **9** in 1:1 Silamine: MC. The decrease of intensity with increasing the air pressure is displayed. Spectra were acquired at 1.3 mbar, 0.34 bar, 0.68 bar, 1 bar, 1.36 bar, 1.70 bar, 2.04 bar, 2.38 bar, 2.72 bar, and 3.06 bar. Background correction has been performed.

Among three film compositions, oxygen quenching sensitivity of **9** in Silamine is the greatest, which is displayed in the Stern-Volmer plots in Figure 3.58.

Figure 3.58: Stern-Volmer plots of **9** in Silamine, ●; in 1:1 Silamine: MC, ●; and in 1:5 Silamine: MC, ●.

Table 3.12: PSP films oxygen sensitivity data for **9**.

Luminophore	Matrix	$Q_s(r^2)$
9	Silamine	0.12 (0.974) ^b
	1:1 Silamine: MC	0.08 (0.972) ^b
	1:5 Silamine: MC	0.10 (0.957) ^d

^b5-45 psi; ^d5-40 psi

3.8.9.2 PSP 10

Oxygen sensitivity calibration results for oxygen sensor films of **10** are presented in Figures 3.59-3.62 and Table 3.13.

Figure 3.59: Effect of pressure on thin film luminescence of **10** in Silube. The decrease of intensity with increasing the air pressure is displayed. Spectra were acquired at 1.3 mbar, 0.34 bar, 0.68 bar, 1 bar, 1.36 bar, 1.70 bar, 2.04 bar, 2.38 bar, 2.72 bar, and 3.06 bar. Background correction has been performed.

Figure 3.60: Effect of pressure on thin film luminescence of **10** in 5:1 Silube: MC. The decrease of intensity with increasing the air pressure is displayed. Spectra were acquired at 1.3 mbar, 0.34 bar, 0.68 bar, 1 bar, 1.36 bar, 1.70 bar, 2.04 bar, 2.38 bar, 2.72 bar, and 3.06 bar. Background correction has been performed.

Figure 3.61: Effect of pressure on thin film luminescence of **10** in 1:1 Silube: MC. The decrease of intensity with increasing the air pressure is displayed. Spectra were acquired at 1.3 mbar, 0.34 bar, 0.68 bar, 1 bar, 1.36 bar, 1.70 bar, 2.04 bar, 2.38 bar, 2.72 bar, and 3.06 bar. Background correction has been performed.

Figure 3.62: Effect of pressure on thin film luminescence of **10** in 1:5 Silube: MC. The decrease of intensity with increasing the air pressure is displayed. Spectra were acquired at 1.3 mbar, 0.34 bar, 0.68 bar, 1 bar, 1.36 bar, 1.70 bar, 2.04 bar, 2.38 bar, 2.72 bar, and 3.06 bar. Background correction has been performed.

Among four film compositions, oxygen quenching sensitivity of **10** in 1:5 Silube: MC is the greatest, which is displayed in the Stern-Volmer plots in Figure 3.63.

Figure 3.63: Stern-Volmer plots of **10** in Silube, ●; in 5:1 Silube: MC, ●; in 1:1 Silube: MC, ●; and in 1:5 Silube: MC, ●.

Table 3.13: PSP films oxygen sensitivity data for **10**.

Luminophore	Matrix	$Q_s(r^2)$
10	Silube	0.13 (0.992) ^a
	5:1 Silube : MC	0.13 (0.995) ^a
	1:1 Silube: MC	0.16 (0.978) ^a
	1:5 Silube: MC	0.17 (0.964) ^a

^a0.007-45 psi

As displayed in Figure 3.63, all Stern-Volmer plots are fairly linear, an indication of a uniform matrix and little self-aggregation.

Blending MC with **10** once again results in increase in both oxygen sensitivity and mechanical properties of the film (Figure 3.63 and the data in Table 3.13). This

suggests that the lifetime must be increasing with increasing fraction of MC in case of Silube polymer.

However, the oxygen quenching sensitivity data for **10** in the above mentioned matrices are inadequate for wind tunnel applications, although larger than those of **9**. Nevertheless, coupling reaction offers a suitable procedure for producing polymer bound oxygen sensors. It is worth to perform more research on the synthesis of other amine-functionalized iridium complexes with favorable lifetimes and quantum yields.

3.8.9.3 PSPs 5, 12, and 13

Oxygen sensitivities of **5**, **12** and **13** were studied in order to compare luminophore linkages. Thin films oxygen sensitivities were measured and compared in Table 3.14.

The pressure-dependent emission spectra of **5**, **12**, and **13** in different film matrices are shown in Figures 3.64-3.69.

The coupling **5** with Silamine to form **12** resulted in an increase in oxygen quenching sensitivity. According to solution luminescence lifetime data, (Tables 3.9 and 3.11), the extended lifetime of **12** is known to be responsible for this effect. Films of **13** displayed increased oxygen quenching sensitivities compared with **5** or **12** as shown by Figure 3.70.

Figure 3.64: Effect of pressure on thin film luminescence of **5** in 2.3:1 Silamine: MC. The decrease of intensity with increasing the air pressure is displayed. Spectra were acquired at 1.3 mbar, 0.34 bar, 0.68 bar, 1 bar, 1.36 bar, 1.70 bar, 2.04 bar, 2.38 bar, 2.72 bar, and 3.06 bar. Background correction has been performed.

Figure 3.65: Effect of pressure on thin film luminescence of **5** in 1:1 Silamine: MC. The decrease of intensity with increasing the air pressure is displayed. Spectra were acquired at 1.3 mbar, 0.34 bar, 0.68 bar, 1 bar, 1.36 bar, 1.70 bar, 2.04 bar, 2.38 bar, 2.72 bar, and 3.06 bar. Background correction has been performed.

Figure 3.66: Effect of pressure on thin film luminescence of **12** in 2.3:1 Silamine: MC. The decrease of intensity with increasing the air pressure is displayed. Spectra were acquired at 1.3 mbar, 0.34 bar, 0.68 bar, 1 bar, 1.36 bar, 1.70 bar, 2.04 bar, 2.38 bar, 2.72 bar, and 3.06 bar. Background correction has been performed.

Figure 3.67: Effect of pressure on thin film luminescence of **13** in 2.3:1 Silamine: MC. The decrease of intensity with increasing the air pressure is displayed. Spectra were acquired at 1.3 mbar, 0.34 bar, 0.68 bar, 1 bar, 1.36 bar, 1.70 bar, 2.04 bar, 2.38 bar, 2.72 bar, and 3.06 bar. Background correction has been performed.

Figure 3.68: Effect of pressure on thin film luminescence of **13** in 1:1 Silamine: MC. The decrease of intensity with increasing the air pressure is displayed. Spectra were acquired at 1.3 mbar, 0.34 bar, 0.68 bar, 1 bar, 1.36 bar, 1.70 bar, 2.04 bar, 2.38 bar, 2.72 bar, and 3.06 bar. Background correction has been performed.

Figure 3.69: Effect of pressure on thin film luminescence of **13** in 1:9 Silamine: MC. The decrease of intensity with increasing the air pressure is displayed. Spectra were acquired at 1.3 mbar, 0.34 bar, 0.68 bar, 1 bar, 1.36 bar, 1.70 bar, 2.04 bar, 2.38 bar, 2.72 bar, and 3.06 bar. Background correction has been performed.

Figure 3.70: Stern-Volmer plots of **5** in 2.3:1 Silamine: MC, ●; **5** in 1:1 Silamine: MC, ●; **12** in 2.3:1 Silamine: MC, *; **12** in 1:1 Silamine: MC, ; **13** in 2.3:1 Silamine: MC, ●; **13** in 1:1 Silamine: MC, ●.

Table 3.14: PSP films oxygen sensitivity data for **5**, **12**, and **13**.

Luminophore	Matrix	$Q_s(r^2)$
5	2.3:1 Silamine: MC	0.35 (0.993) ^a
	1:1 Silamine: MC	0.25 (0.994) ^a
	1:9 Silamine: MC	0.15 (0.950) ^c , 0.05 (0.980) ^f
12	2.3:1 Silamine: MC	0.38 (0.988) ^a
	1:1 Silamine: MC	0.24 (0.973) ^a
	1:9 Silamine: MC	0.66 ^d , 0.12 (0.966) ^c
13	2.3:1 Silamine : MC	0.39 (0.989) ^a
	1:1 Silamine: MC	0.32 (0.991) ^a
	1:9 Silamine: MC	0.23 (0.980) ^a

^a0.007-45 psi; ^b5-45 psi; ^c10-45 psi; ^d0.007-5 psi; ^e5-14.7 psi; ^f20-45 psi

In order to increase the mechanical properties of the film, MC was blended with luminophores which resulted in decrease in oxygen sensitivity compared with the film

composed of a lower proportion of low T_g polymer (the effect being the least for **13**). This is shown in Figure 3.70 and the data in Table 3.14 in which the optimum PSP formulation is **13** in 2.3:1 Silamine:MC which gave an oxygen sensitivity of 0.39, with good linear behavior in a pressure range of 0.007 to 45 psi.

The luminescence microscopy of films of **13** was examined, and the results are shown in Figure 3.71.

Figure 3.71: Luminescence microscopy of films of **13** performed under ambient conditions: A, 9:1 Silamine: MC; B, 5:1 Silamine: MC; C, 1:1 Silamine: MC; D, 1:5 Silamine: MC. The scale in red is 10 μm .

In Figure 3.71 A, luminescence microscopy shows that at low concentration of MC, the luminescence from the film is largely dispersed with little evidence of association around particles of MC unlike that seen for **8** (Figure 3.33). Increasing MC concentration results in a slight increase in luminescence which suggests that while there

is a weak association of the luminophore with MC, the resulting increase in lifetime is insufficient to compensate for the decrease in oxygen diffusion.

The temperature dependence of emission intensity of **5** and **13** in 2.3:1 Silamine:MC films were examined in the temperature range of 10 to 40 °C under 1 bar atmospheric pressure. The emission intensities were normalized to that at 10 °C and the results plotted in Figure 3.72.

Figure 3.72: Temperature versus emission intensity ratio (I_{ref} is the intensity at 10 °C) of **5** in 2.3:1 Silamine: MC: 1bar ● **13** in 2.3:1 Silamine: MC: 1bar ▼.

In Figure 3.72, the data for the temperature dependence of emission gave good linear least-squares fits passing through or at least closely approaching the normalization value at 10 °C. The temperature sensitivities (percent intensity loss per degree) of the films were determined to be $-1.3\% \text{ } ^\circ\text{C}^{-1}$ for **5** and $-0.8\% \text{ } ^\circ\text{C}^{-1}$ for **13** at 1 bar atmospheric pressure. Although the temperature sensitivity of **13** in 2.3:1 Silamine: MC film is

improved compared to **5** and **8** (see section 3.6), it still must be compensated for by using a temperature sensitive calibrant to obtain correct barometric data.

3.8.9.4 PSP 14

Table 3.15 lists oxygen quenching sensitivity data for **14** and the effect of air pressure on emission intensity is illustrated in Figures 3.73-3.75. Modified Stern-Volmer plots of **14** in three Silamine: MC formulations are shown in Figure 3.76.

Figure 3.73: Effect of pressure on thin film luminescence of **14** in 5:1 Silamine: MC. The decrease of intensity with increasing the air pressure is displayed. Spectra were acquired at 1.3 mbar, 0.34 bar, 0.68 bar, 1 bar, 1.36 bar, 1.70 bar, 2.04 bar, 2.38 bar, 2.72 bar, and 3.06 bar. Background correction has been performed.

Figure 3.74: Effect of pressure on thin film luminescence of **14** in 1:1 Silamine: MC. The decrease of intensity with increasing the air pressure is displayed. Spectra were acquired at 1.3 mbar, 0.34 bar, 0.68 bar, 1 bar, 1.36 bar, 1.70 bar, 2.04 bar, 2.38 bar, 2.72 bar, and 3.06 bar. Background correction has been performed.

Figure 3.75: Effect of pressure on thin film luminescence of **14** in 1:2.3 Silamine: MC. The decrease of intensity with increasing the air pressure is displayed. Spectra were acquired at 1.3 mbar, 0.34 bar, 0.68 bar, 1 bar, 1.36 bar, 1.70 bar, 2.04 bar, 2.38 bar, 2.72 bar, and 3.06 bar. Background correction has been performed.

Figure 3.76: Stern-Volmer plots of **14** in 5:1 Silamine: MC, ●; **14** in 1:1 Silamine: MC, ●; **14** in 1:2.3 Silamine: MC, ●.

Table 3.15: PSP films oxygen sensitivity data for **14**.

Luminophore	Matrix	$Q_s(r^2)$
14	5:1 Silamine : MC	0.27 (0.969) ^a
	1:1 Silamine: MC	0.28 (0.981) ^a
	1:2.3 Silamine: MC	0.27 (0.977) ^a

^a0.007-45 psi

As shown in Figure 3.76 and the data in Table 3.15, blending MC with **14** has a subtle effect on oxygen sensitivity and the PSP formulations exhibit good linear behavior in a pressure range of 0.007 to 45 psi.

The temperature dependence of emission intensity of **14** in 5:1 Silamine:MC films was examined in the temperature range of 10 to 40 °C under vacuum. The emission intensities were normalized to that at 10 °C and the results plotted in Figure 3.77.

Figure 3.77: Temperature versus emission intensity ratio (I_{ref} is the intensity at 10 °C) of **14** in 5:1 Silamine: MC: vacuum •.

The film was found to have a temperature sensitivity of $-1.3\% \text{ } ^\circ\text{C}^{-1}$ at vacuum.

3.8.9.5 PSP 15

As illustrated in Figure 3.78, the excimer emission of **15** is insignificantly quenched by oxygen with a pressure sensitivity of 10.6%/bar in a pressure range of 0.007 to 14.7psi.

Figure 3.78: Effect of pressure on thin film luminescence of **15** in 9:1 Silamine: MC. The decrease of intensity with increasing the air pressure is displayed. Spectra were acquired at 1.3 mbar (black) and 1 bar (red).

While some pyrene derivatives (including PBA) exhibit poor oxygen quenching sensitivities in silicon matrices,⁹⁷ there exists promising compound 1-decyl-4-(1-pyrenyl) butanoate with high oxygen sensitivity. Since preparation of a pyrene-based water-

soluble formulation with appropriate excimer emission intensity was successful, it would be worthwhile to make a new water-soluble pyrene derivative with high oxygen quenching sensitivity. Synthesis of 4-(1-pyrenyl) butanal from PBA and attempt to bound it to Silamine by coupling or reductive attachment is proposed.

3.8.9.6 Luminophore 7

The cationic palladium porphyrin dispersed in PDMS-based Copolymer showed very broad red phosphorescence illustrated in Figure 3.79 the intensity of which was not very sensitive to the air pressure.

Figure 3.79: Effect of pressure on thin film luminescence of **7** in 9:1 PDMS-based Copolymer: MC. Spectra were acquired at 1.3 mbar (black) and 1 bar (red).

Porphyrins tend to aggregate resulting in oxygen insensitive dimers and higher aggregates⁹⁸ which can be an explanation for the oxygen sensitivity behavior of **7**.

Chapter 4

Conclusions and Future Studies

4.1 Summary of Water-Soluble PSP films

Completely water-soluble pressure sensitive paints for visualizing air pressure are presented here. Using inexpensive water-soluble polymers and microcrystalline cellulose, spray-able PSP formulations were prepared. These paints offer an environmentally friendly alternative to non-aqueous PSP formulations and provide improved workplace safety, and lower contamination.

The first challenge was acquiring water-soluble matrices that dissolve luminophores and have good mechanical properties and high oxygen permeabilities. To achieve this goal, polyethylene glycol and water-soluble copolymers of the well known oxygen permeable polymer, polydimethylsiloxane, were used. The mechanical properties of these polymers need to be improved for practical applications. To compensate for the poor mechanical properties of the water-soluble polymers, microcrystalline cellulose was included in the formulations.

Luminescent iridium complexes have been used in PSPs because of their large quantum yields of emission under room temperature and normal pressure, and efficient quenching of the photoexcited triplet state by molecular oxygen. However, their solubility is poor in aqueous solution. The poor solubility was overcome by covalent attachment to water-soluble polymers.

Producing water-soluble luminescent polymers by covalent attachment to the water-soluble amine-functionalized polymer Silamine D208-EDA by reductive amination was confirmed in **8**, **13**, and **14**. In addition, it was shown that utilizing coupling reactions in synthesis of **9**, **11**, **12**, and **15** is a practical covalent bonding method. Normally, polymer bound oxygen sensors show extended lifetimes compared with original dyes.

Oxygen quenching sensitivities of PSP films composed of **1**, **2**, **5**, **7**, and **10** dispersed in water-soluble polymer matrices, and **8**, **9**, **11**, **12**, **13**, **14**, and **15** in different film compositions were tested. Blending MC improved both oxygen quenching sensitivities and mechanical properties of the PSP films. It is suggested that this effect originates from a decrease in the luminophores freedom of motion and consequentially an increase in its luminescence lifetime. Moreover, the preferential binding of luminophore to MC could lead to de-aggregation and a decrease in self-quenching.

The optimum PSP formulations are **12** in 2.3:1 Silamine:MC, **13** in 2.3:1 Silamine:MC, and **8** in 1:1 Silamine:MC, which gave oxygen sensitivities of 0.379, 0.385, and 0.502, respectively, and are appropriate for pressure sensitive paint applications.

4.2 Future Work

Among water-soluble PSPs reported in this research, three sensors, **8**, **12**, and **13**, are favourable with potential wind tunnel applications. In order to achieve even more sensitive water-soluble paints, it may be worthwhile to examine **7**, as a sensor with an

increased lifetime, trying to eliminate aggregation using molecular carriers, such as cyclodextrin or calixarene, which monomerize or solubilize the aggregate and form non-covalent supramolecular complexes with porphyrins.⁹⁸ Synthesis of new water-soluble oxygen permeable polymers (e. g. copolymerizing water-soluble polymer poly(vinyl pyrrolidone) with fluoropolymers) may result in highly sensitive water-soluble PSPs. Fluoropolymers such as poly(hexafluoroisopropyl-*co*-heptafluoro-*n*-butyl methacrylate) (known as FIB) and poly(2,2,2-trifluoroethyl-*co*-isobutyl methacrylate) are photostable oxygen permeable polymers.⁴¹ These copolymers can provide improved mechanical properties as well as oxygen permeability.

Reductive amination and coupling reactions utilized in this work are presented as efficient procedures towards covalent binding of sensors to water-soluble polymers. A pyrene-based water-soluble formulation with appropriate excimer emission intensity was successfully prepared. While some pyrene derivatives (including PBA) exhibit poor oxygen quenching sensitivities in silicon matrices,⁹⁷ there exists promising compound 1-decyl-4-(1-pyrenyl) butanoate with high oxygen sensitivity. It would be worthwhile to make a new water-soluble pyrene derivative with high oxygen quenching sensitivity by synthesis of 4-(1-pyrenyl) butanal from PBA and attempt to bound it to Silamine by coupling or reductive attachment.

Response times of pressure sensitive paints to passing shockwaves are important in studying pressure changes in unsteady flows. Including pressure sensitive luminophores in polymeric microspheres could afford fast responding oxygen sensors. Films of a luminescent platinum (II) porphyrin in core-shell particles made of a polystyrene core and a poly(vinyl pyrrolidone) shell were prepared using the aqueous

dispersion of the sensor. The hydrogen bonds between poly(vinyl pyrrolidone) shell and aluminum surface provide the advantage of omitting the need for a binder polymer and its diffusional barrier, leading to desirable short response times. Response time of the films was approximately measured to be < 1 s.⁹⁹ Instrumentation for accurate measurements must be developed. Designing core-shell particles with tuned oxygen permeabilities could result in improved response times. Developing porous films would likely be beneficial in unsteady flow measurements.

The morphology and oxygen quenching sensitivities of blend films consisting of a linear poly(dimethylsiloxane) end-functionalized with a luminescent Ir(III) complex blended with polystyrene have shown the oxygen sensor response of the blend films with micrometer spatial resolution.⁵⁸ Studying the film morphologies in order to map the oxygen permeability of the films and investigating the correlation between morphology and sensitivity of the films would also provide more insight into sensor design.

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Appendix A: Crystallographic Data

Table 1: Crystal data and structure refinement for $2 \cdot 0.25(\text{CH}_2\text{Cl}_2)$

Computing details

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 2001); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2001).

Crystal data

$\text{C}_{35.25}\text{H}_{34.50}\text{Cl}_{0.50}\text{F}_3\text{IrN}_4\text{O}_3\text{S}$

$M_r = 861.15$

Triclinic, *P1*

$a = 15.164$ (5) Å

$b = 17.083$ (6) Å

$c = 17.242$ (6) Å

$\alpha = 117.569$ (5)°

$\beta = 104.876$ (5)°

$\gamma = 100.075$ (5)°

$V = 3595$ (2) Å³

$Z = 4$

$F_{000} = 1706$

$D_x = 1.591$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 439 reflections

$\theta = 1.6$ – 23.4°

$\mu = 3.86$ mm⁻¹

$T = 120$ (2) K

Plate, yellow

$0.25 \times 0.17 \times 0.08$ mm

Data collection

Bruker AXS APEX diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

Detector resolution: 836.6 pixels mm⁻¹

$T = 120$ (2) K

ω scans

Abs. corr.: multi-scan SADABS (Sheldrick, 2003)

$T_{\min} = 0.441$, $T_{\max} = 0.745$

38770 measured reflections

12670 independent reflections

9231 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.040$

$\theta_{\max} = 25.0^\circ$

$\theta_{\min} = 1.6^\circ$

$h = -18 \rightarrow 18$

$k = -20 \rightarrow 20$

$l = -20 \rightarrow 20$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.050$	H-atom parameters constrained
$wR(F^2) = 0.142$	
	$w = 1/[\sigma^2(F_o^2) + (0.0851P)^2]$
	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{\max} = 0.005$
12670 reflections	$\Delta\rho_{\max} = 2.78 \text{ e } \text{\AA}^{-3}$
811 parameters	$\Delta\rho_{\min} = -1.03 \text{ e } \text{\AA}^{-3}$
1632 restraints	Extinction correction: none
Primary atom site location: structure-invariant direct methods	

Special details

Experimental. Data collection is performed with four batch runs at $\varphi = 0.00^\circ$ (600 frames), at $\varphi = 90.00^\circ$ (600 frames), at $\varphi = 180^\circ$ (600 frames) and at $\varphi = 270^\circ$ (600 frames). Frame width = 0.30 $^\circ$ in ω . Data is merged, corrected for decay, and treated with multiscan absorption corrections.

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) etc. and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$) for $2 \cdot 0.25(\text{CH}_2\text{Cl}_2)$.

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Ir1	0.445091 (17)	0.217574 (17)	0.686611 (18)	0.05862 (11)	
Ir2	0.89507 (2)	0.219383 (18)	0.236746 (18)	0.06763 (12)	
N1	0.5671 (4)	0.1807 (4)	0.7003 (4)	0.0726 (14)	
C1	0.6587 (5)	0.2421 (7)	0.7557 (6)	0.097 (2)	
H1A	0.6690	0.3076	0.7882	0.117*	
C2	0.7379 (6)	0.2126 (8)	0.7665 (7)	0.112 (3)	

H2A	0.8018	0.2568	0.8058	0.135*	
C3	0.7217 (6)	0.1187 (7)	0.7195 (6)	0.101 (3)	
H3A	0.7752	0.0973	0.7268	0.121*	
C4	0.6299 (6)	0.0542 (7)	0.6618 (6)	0.090 (2)	
H4A	0.6198	-0.0111	0.6283	0.108*	
C5	0.5512 (5)	0.0865 (5)	0.6529 (5)	0.0672 (15)	
C6	0.4504 (4)	0.0276 (4)	0.5957 (4)	0.0621 (14)	
C11	0.4199 (6)	-0.0718 (5)	0.5399 (5)	0.0758 (18)	
H11A	0.4667	-0.1025	0.5361	0.091*	
C10	0.3245 (6)	-0.1227 (5)	0.4924 (5)	0.0802 (19)	
H10A	0.3042	-0.1894	0.4583	0.096*	
C9	0.2549 (5)	-0.0788 (4)	0.4927 (5)	0.0744 (17)	
C8	0.2856 (5)	0.0204 (4)	0.5454 (4)	0.0611 (15)	
H8A	0.2385	0.0504	0.5450	0.073*	
C7	0.3828 (4)	0.0747 (4)	0.5977 (4)	0.0558 (13)	
C12	0.1519 (6)	-0.1353 (6)	0.4409 (6)	0.101 (3)	
H12A	0.1343	-0.2017	0.4100	0.121*	
O1	0.0910 (6)	-0.1044 (6)	0.4353 (6)	0.152 (3)	
N2	0.3128 (4)	0.2348 (4)	0.6716 (4)	0.0659 (13)	
C13	0.2627 (5)	0.2537 (5)	0.6098 (5)	0.0783 (19)	
H13A	0.2924	0.2644	0.5718	0.094*	
C14	0.1721 (6)	0.2586 (6)	0.5985 (6)	0.093 (2)	
H14A	0.1391	0.2711	0.5530	0.112*	
C15	0.1298 (6)	0.2448 (6)	0.6552 (7)	0.099 (2)	
H15A	0.0669	0.2486	0.6495	0.119*	
C16	0.1778 (5)	0.2257 (5)	0.7196 (6)	0.087 (2)	
H16A	0.1481	0.2153	0.7578	0.104*	
C17	0.2706 (4)	0.2217 (4)	0.7287 (5)	0.0680 (16)	
C18	0.3318 (5)	0.2044 (5)	0.7941 (4)	0.0663 (16)	
C23	0.3008 (6)	0.1882 (6)	0.8572 (5)	0.089 (2)	
H23A	0.2387	0.1896	0.8583	0.107*	
C22	0.3600 (6)	0.1704 (7)	0.9172 (6)	0.103 (3)	
H22A	0.3396	0.1618	0.9612	0.124*	
C21	0.4506 (6)	0.1647 (6)	0.9143 (5)	0.084 (2)	
C20	0.4784 (5)	0.1785 (5)	0.8497 (4)	0.0672 (16)	
H20A	0.5398	0.1757	0.8475	0.081*	
C19	0.4193 (4)	0.1962 (4)	0.7882 (4)	0.0575 (13)	
C24	0.5094 (7)	0.1411 (7)	0.9775 (6)	0.103 (3)	
H24A	0.4876	0.1371	1.0230	0.123*	
O2	0.5835 (5)	0.1266 (5)	0.9742 (4)	0.1085 (19)	
N5	1.0363 (12)	0.293 (2)	0.2759 (10)	0.081 (2)	0.536 (8)
C35	1.0794 (13)	0.280 (2)	0.2142 (12)	0.095 (3)	0.536 (8)
H35A	1.0422	0.2345	0.1488	0.114*	0.536 (8)
C36	1.1761 (12)	0.3297 (16)	0.2418 (13)	0.108 (4)	0.536 (8)
H36A	1.2060	0.3163	0.1972	0.130*	0.536 (8)
C37	1.2274 (12)	0.3996 (15)	0.3367 (13)	0.109 (4)	0.536 (8)
H37A	1.2936	0.4352	0.3581	0.130*	0.536 (8)
C38	1.1813 (12)	0.4178 (15)	0.4010 (12)	0.100 (4)	0.536 (8)
H38A	1.2164	0.4654	0.4661	0.120*	0.536 (8)
C39	1.0845 (12)	0.3661 (19)	0.3691 (12)	0.087 (3)	0.536 (8)
C40	1.0280 (13)	0.373 (2)	0.4271 (11)	0.083 (3)	0.536 (8)

C45	1.0674 (13)	0.4397 (18)	0.5256 (11)	0.098 (4)	0.536 (8)
H45A	1.1327	0.4811	0.5550	0.117*	0.536 (8)
C44	1.0143 (13)	0.446 (2)	0.5796 (12)	0.102 (4)	0.536 (8)
H44A	1.0424	0.4881	0.6464	0.123*	0.536 (8)
C43	0.9162 (11)	0.3869 (19)	0.5330 (10)	0.089 (3)	0.536 (8)
C42	0.8774 (11)	0.328 (2)	0.4343 (9)	0.073 (3)	0.536 (8)
H42A	0.8092	0.2952	0.4035	0.087*	0.536 (8)
C41	0.9303 (16)	0.313 (3)	0.3786 (12)	0.073 (2)	0.536 (8)
C46	0.8574 (13)	0.3965 (16)	0.5900 (11)	0.099 (3)	0.536 (8)
H46A	0.8885	0.4456	0.6550	0.119*	0.536 (8)
O3	0.7784 (11)	0.3522 (9)	0.5660 (8)	0.124 (3)	0.536 (8)
N5'	1.0312 (13)	0.283 (3)	0.2506 (12)	0.081 (2)	0.464 (8)
C35'	1.0650 (16)	0.262 (3)	0.1808 (13)	0.095 (3)	0.464 (8)
H35B	1.0216	0.2130	0.1182	0.114*	0.464 (8)
C36'	1.1587 (14)	0.305 (2)	0.1935 (14)	0.108 (4)	0.464 (8)
H36B	1.1784	0.2882	0.1416	0.130*	0.464 (8)
C37'	1.2215 (14)	0.3733 (19)	0.2852 (14)	0.109 (4)	0.464 (8)
H37B	1.2851	0.4079	0.2975	0.130*	0.464 (8)
C38'	1.1914 (13)	0.3913 (19)	0.3592 (14)	0.100 (4)	0.464 (8)
H38B	1.2364	0.4350	0.4226	0.120*	0.464 (8)
C39'	1.0968 (14)	0.347 (2)	0.3425 (12)	0.087 (3)	0.464 (8)
C40'	1.0532 (15)	0.368 (3)	0.4125 (12)	0.083 (3)	0.464 (8)
C45'	1.1026 (14)	0.435 (2)	0.5108 (13)	0.098 (4)	0.464 (8)
H45B	1.1699	0.4689	0.5353	0.117*	0.464 (8)
C44'	1.0549 (15)	0.451 (2)	0.5712 (14)	0.102 (4)	0.464 (8)
H44B	1.0883	0.4990	0.6365	0.123*	0.464 (8)
C43'	0.9569 (14)	0.398 (2)	0.5368 (11)	0.089 (3)	0.464 (8)
C42'	0.9101 (13)	0.331 (2)	0.4389 (11)	0.073 (3)	0.464 (8)
H42B	0.8446	0.2923	0.4151	0.087*	0.464 (8)
C41'	0.9529 (19)	0.319 (4)	0.3771 (13)	0.073 (2)	0.464 (8)
C46'	0.9045 (15)	0.4099 (19)	0.5993 (11)	0.099 (3)	0.464 (8)
H46B	0.8404	0.3658	0.5685	0.119*	0.464 (8)
O3'	0.9266 (11)	0.4638 (10)	0.6803 (8)	0.124 (3)	0.464 (8)
N6	0.7658 (4)	0.1534 (3)	0.2328 (3)	0.0611 (12)	
C47	0.6797 (5)	0.1660 (5)	0.2035 (5)	0.0729 (17)	
H47A	0.6773	0.2049	0.1783	0.087*	
C48	0.5969 (5)	0.1257 (5)	0.2084 (5)	0.0750 (18)	
H48A	0.5388	0.1372	0.1880	0.090*	
C49	0.5997 (6)	0.0683 (5)	0.2435 (5)	0.0802 (19)	
H49A	0.5431	0.0391	0.2475	0.096*	
C50	0.6866 (5)	0.0531 (5)	0.2735 (5)	0.0707 (17)	
H50A	0.6891	0.0138	0.2982	0.085*	
C51	0.7683 (4)	0.0951 (4)	0.2671 (4)	0.0571 (13)	
C52	0.8623 (4)	0.0836 (4)	0.2922 (4)	0.0581 (14)	
C57	0.8803 (5)	0.0259 (4)	0.3277 (5)	0.0659 (16)	
H57A	0.8300	-0.0069	0.3362	0.079*	
C56	0.9697 (5)	0.0169 (5)	0.3499 (5)	0.0684 (16)	
H56A	0.9816	-0.0221	0.3737	0.082*	
C55	1.0437 (5)	0.0658 (4)	0.3372 (4)	0.0636 (15)	
C54	1.0266 (4)	0.1237 (4)	0.3036 (4)	0.0598 (15)	
H54A	1.0772	0.1567	0.2954	0.072*	

C53	0.9366 (4)	0.1339 (4)	0.2818 (4)	0.0577 (14)	
C58	1.1387 (5)	0.0521 (5)	0.3573 (5)	0.0751 (18)	
H58A	1.1449	0.0094	0.3774	0.090*	
O4	1.2085 (4)	0.0893 (4)	0.3510 (4)	0.0881 (15)	
N4	0.4673 (4)	0.2592 (4)	0.5293 (4)	0.0743 (15)	
N7	0.8304 (4)	0.0597 (5)	0.0212 (4)	0.0753 (15)	
N8	0.8316 (5)	0.3488 (4)	0.1651 (4)	0.0771 (16)	
N3	0.5483 (6)	0.4334 (5)	0.8495 (6)	0.089 (2)	0.808 (6)
C25	0.5097 (6)	0.3567 (6)	0.7895 (8)	0.071 (2)	0.808 (6)
C26	0.6023 (8)	0.5376 (8)	0.9202 (8)	0.116 (3)	0.808 (6)
C27	0.5223 (9)	0.5760 (8)	0.9472 (8)	0.139 (4)	0.808 (6)
H27A	0.5499	0.6446	0.9897	0.208*	0.808 (6)
H27B	0.4972	0.5485	0.9793	0.208*	0.808 (6)
H27C	0.4693	0.5593	0.8896	0.208*	0.808 (6)
C28	0.6780 (8)	0.5473 (9)	1.0024 (8)	0.142 (5)	0.808 (6)
H28A	0.7164	0.6139	1.0488	0.213*	0.808 (6)
H28B	0.7207	0.5132	0.9800	0.213*	0.808 (6)
H28C	0.6465	0.5211	1.0324	0.213*	0.808 (6)
C29	0.6489 (10)	0.5806 (10)	0.8724 (11)	0.155 (5)	0.808 (6)
H29A	0.6825	0.6483	0.9174	0.233*	0.808 (6)
H29B	0.5981	0.5698	0.8165	0.233*	0.808 (6)
H29C	0.6955	0.5509	0.8529	0.233*	0.808 (6)
N3'	0.6029 (19)	0.4168 (17)	0.814 (3)	0.089 (2)	0.192 (6)
C25'	0.540 (3)	0.3495 (17)	0.773 (3)	0.071 (2)	0.192 (6)
C26'	0.689 (2)	0.5064 (18)	0.879 (2)	0.116 (3)	0.192 (6)
C27'	0.654 (4)	0.579 (4)	0.945 (4)	0.139 (4)	0.192 (6)
H27D	0.7090	0.6370	0.9921	0.208*	0.192 (6)
H27E	0.6243	0.5542	0.9767	0.208*	0.192 (6)
H27F	0.6055	0.5924	0.9071	0.208*	0.192 (6)
C28'	0.764 (3)	0.483 (3)	0.935 (3)	0.142 (5)	0.192 (6)
H28D	0.8219	0.5394	0.9797	0.213*	0.192 (6)
H28E	0.7823	0.4336	0.8907	0.213*	0.192 (6)
H28F	0.7367	0.4610	0.9698	0.213*	0.192 (6)
C29'	0.718 (4)	0.529 (4)	0.813 (3)	0.155 (5)	0.192 (6)
H29D	0.7798	0.5819	0.8492	0.233*	0.192 (6)
H29E	0.6680	0.5459	0.7822	0.233*	0.192 (6)
H29F	0.7264	0.4739	0.7648	0.233*	0.192 (6)
C30	0.4604 (5)	0.2418 (5)	0.5858 (5)	0.0675 (16)	
C31	0.4789 (6)	0.2933 (6)	0.4661 (6)	0.0806 (19)	
C32	0.3832 (8)	0.3003 (10)	0.4236 (10)	0.162 (5)	
H32A	0.3877	0.3230	0.3814	0.243*	
H32B	0.3669	0.3443	0.4744	0.243*	
H32C	0.3326	0.2382	0.3873	0.243*	
C33	0.5489 (9)	0.3909 (7)	0.5272 (8)	0.142 (4)	
H33A	0.5577	0.4159	0.4876	0.212*	
H33B	0.6114	0.3913	0.5619	0.212*	
H33C	0.5238	0.4302	0.5724	0.212*	
C34	0.4989 (12)	0.2236 (9)	0.3904 (9)	0.178 (6)	
H34A	0.5063	0.2448	0.3478	0.267*	
H34B	0.4449	0.1637	0.3547	0.267*	
H34C	0.5589	0.2150	0.4176	0.267*	

C59	0.8570 (5)	0.1189 (5)	0.1001 (5)	0.0684 (16)	
C60	0.7890 (6)	−0.0148 (6)	−0.0785 (5)	0.087 (2)	
C61	0.7076 (9)	−0.0919 (9)	−0.0929 (8)	0.157 (5)	
H61A	0.7346	−0.1208	−0.0593	0.235*	
H61B	0.6737	−0.1397	−0.1608	0.235*	
H61C	0.6618	−0.0651	−0.0679	0.235*	
C62	0.8690 (7)	−0.0411 (7)	−0.1092 (7)	0.120 (3)	
H62A	0.8997	−0.0685	−0.0755	0.181*	
H62B	0.9176	0.0151	−0.0945	0.181*	
H62C	0.8420	−0.0872	−0.1777	0.181*	
C63	0.7445 (7)	0.0266 (7)	−0.1340 (6)	0.111 (3)	
H63A	0.6911	0.0442	−0.1167	0.166*	
H63B	0.7195	−0.0203	−0.2021	0.166*	
H63C	0.7942	0.0824	−0.1187	0.166*	
C64	0.8505 (6)	0.3044 (5)	0.1938 (5)	0.0762 (19)	
C65	0.8122 (6)	0.3966 (5)	0.1142 (5)	0.094 (2)	
C66	0.744 (2)	0.3290 (17)	0.0108 (11)	0.110 (4)	0.351 (16)
H66A	0.7821	0.3158	−0.0291	0.165*	0.351 (16)
H66B	0.6985	0.3572	−0.0076	0.165*	0.351 (16)
H66C	0.7081	0.2702	0.0024	0.165*	0.351 (16)
C67	0.9164 (13)	0.444 (2)	0.124 (2)	0.133 (4)	0.351 (16)
H67A	0.9624	0.4747	0.1893	0.199*	0.351 (16)
H67B	0.9145	0.4912	0.1064	0.199*	0.351 (16)
H67C	0.9371	0.3962	0.0811	0.199*	0.351 (16)
C68	0.776 (2)	0.4754 (19)	0.171 (2)	0.112 (4)	0.351 (16)
H68A	0.8311	0.5280	0.2274	0.168*	0.351 (16)
H68B	0.7285	0.4511	0.1909	0.168*	0.351 (16)
H68C	0.7454	0.4973	0.1313	0.168*	0.351 (16)
C66'	0.7018 (9)	0.3395 (10)	0.0442 (10)	0.110 (4)	0.649 (16)
H66D	0.6637	0.3292	0.0789	0.165*	0.649 (16)
H66E	0.6964	0.2788	−0.0078	0.165*	0.649 (16)
H66F	0.6770	0.3753	0.0184	0.165*	0.649 (16)
C67'	0.8798 (13)	0.3881 (14)	0.0638 (13)	0.133 (4)	0.649 (16)
H67D	0.9467	0.4253	0.1103	0.199*	0.649 (16)
H67E	0.8633	0.4114	0.0216	0.199*	0.649 (16)
H67F	0.8739	0.3220	0.0263	0.199*	0.649 (16)
C68'	0.8248 (13)	0.4986 (9)	0.1843 (11)	0.112 (4)	0.649 (16)
H68D	0.8932	0.5330	0.2276	0.168*	0.649 (16)
H68E	0.7846	0.4996	0.2208	0.168*	0.649 (16)
H68F	0.8049	0.5284	0.1493	0.168*	0.649 (16)

Table 3: Atomic displacement parameters ($\text{\AA}^2$) for $2 \cdot 0.25(\text{CH}_2\text{Cl}_2)$.

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ir1	0.05016 (16)	0.05415 (17)	0.06077 (18)	0.01560 (12)	0.00840 (12)	0.03014 (14)
Ir2	0.0775 (2)	0.05193 (17)	0.05900 (18)	0.01162 (14)	0.00037 (14)	0.03582 (14)
N1	0.064 (3)	0.093 (4)	0.069 (4)	0.031 (3)	0.023 (3)	0.049 (3)

C1	0.053 (4)	0.123 (6)	0.095 (6)	0.025 (4)	0.013 (4)	0.053 (5)
C2	0.066 (5)	0.169 (7)	0.099 (7)	0.046 (5)	0.022 (4)	0.072 (6)
C3	0.082 (5)	0.170 (8)	0.098 (6)	0.074 (5)	0.043 (5)	0.091 (6)
C4	0.095 (5)	0.144 (6)	0.093 (5)	0.078 (5)	0.052 (4)	0.088 (5)
C5	0.075 (4)	0.095 (4)	0.062 (4)	0.046 (3)	0.033 (3)	0.055 (3)
C6	0.081 (4)	0.071 (3)	0.055 (4)	0.038 (3)	0.029 (3)	0.044 (3)
C11	0.106 (5)	0.075 (4)	0.073 (5)	0.050 (4)	0.039 (4)	0.050 (4)
C10	0.122 (5)	0.056 (4)	0.076 (5)	0.034 (4)	0.039 (4)	0.043 (4)
C9	0.101 (4)	0.057 (4)	0.059 (4)	0.022 (3)	0.017 (4)	0.036 (3)
C8	0.075 (4)	0.058 (3)	0.047 (3)	0.023 (3)	0.010 (3)	0.033 (3)
C7	0.073 (3)	0.057 (3)	0.048 (3)	0.029 (3)	0.021 (3)	0.035 (3)
C12	0.111 (5)	0.075 (5)	0.076 (5)	0.007 (4)	-0.009 (5)	0.042 (4)
O1	0.119 (5)	0.120 (6)	0.161 (7)	0.000 (4)	-0.021 (5)	0.087 (6)
N2	0.055 (3)	0.049 (3)	0.071 (3)	0.018 (2)	0.008 (2)	0.024 (3)
C13	0.070 (4)	0.072 (5)	0.080 (5)	0.028 (4)	0.011 (4)	0.039 (4)
C14	0.075 (5)	0.075 (5)	0.110 (6)	0.036 (4)	0.010 (4)	0.044 (5)
C15	0.062 (5)	0.080 (5)	0.121 (7)	0.031 (4)	0.013 (4)	0.038 (5)
C16	0.061 (4)	0.079 (5)	0.095 (6)	0.022 (4)	0.020 (4)	0.033 (4)
C17	0.053 (3)	0.050 (4)	0.077 (4)	0.015 (3)	0.017 (3)	0.021 (3)
C18	0.067 (4)	0.056 (4)	0.053 (4)	0.025 (3)	0.023 (3)	0.011 (3)
C23	0.080 (5)	0.094 (6)	0.081 (5)	0.032 (4)	0.032 (4)	0.036 (4)
C22	0.100 (6)	0.134 (8)	0.077 (5)	0.043 (5)	0.041 (5)	0.052 (5)
C21	0.095 (5)	0.096 (6)	0.059 (4)	0.037 (4)	0.029 (4)	0.039 (4)
C20	0.065 (4)	0.068 (4)	0.048 (4)	0.021 (3)	0.014 (3)	0.021 (3)
C19	0.063 (3)	0.043 (3)	0.048 (3)	0.015 (3)	0.009 (3)	0.018 (3)
C24	0.114 (7)	0.138 (8)	0.066 (5)	0.052 (6)	0.036 (5)	0.058 (5)
O2	0.111 (5)	0.140 (5)	0.084 (4)	0.053 (4)	0.024 (4)	0.070 (4)
N5	0.082 (3)	0.073 (6)	0.089 (7)	0.012 (3)	0.001 (5)	0.064 (6)
C35	0.075 (6)	0.099 (10)	0.105 (8)	0.011 (5)	0.008 (7)	0.071 (9)
C36	0.085 (7)	0.106 (10)	0.114 (9)	-0.005 (6)	0.004 (8)	0.075 (10)
C37	0.094 (7)	0.095 (10)	0.118 (11)	-0.003 (6)	0.003 (7)	0.074 (10)
C38	0.092 (5)	0.077 (10)	0.113 (9)	0.010 (6)	0.000 (6)	0.064 (8)
C39	0.076 (5)	0.067 (9)	0.098 (7)	0.007 (5)	-0.011 (4)	0.058 (6)
C40	0.085 (7)	0.049 (5)	0.084 (5)	0.007 (8)	-0.014 (4)	0.042 (5)
C45	0.105 (9)	0.050 (5)	0.087 (5)	0.017 (9)	-0.021 (5)	0.032 (5)
C44	0.119 (10)	0.058 (6)	0.070 (5)	0.016 (10)	-0.025 (5)	0.027 (5)
C43	0.114 (9)	0.057 (6)	0.054 (4)	0.030 (9)	-0.017 (5)	0.023 (4)
C42	0.081 (8)	0.047 (4)	0.056 (3)	0.027 (8)	-0.014 (5)	0.022 (3)
C41	0.083 (8)	0.045 (6)	0.066 (3)	0.012 (7)	-0.007 (4)	0.034 (3)
C46	0.122 (10)	0.083 (7)	0.053 (5)	0.068 (9)	-0.009 (7)	0.017 (5)
O3	0.155 (8)	0.108 (7)	0.068 (5)	0.057 (6)	0.015 (5)	0.028 (5)
N5'	0.082 (3)	0.073 (6)	0.089 (7)	0.012 (3)	0.001 (5)	0.064 (6)
C35'	0.075 (6)	0.099 (10)	0.105 (8)	0.011 (5)	0.008 (7)	0.071 (9)
C36'	0.085 (7)	0.106 (10)	0.114 (9)	-0.005 (6)	0.004 (8)	0.075 (10)
C37'	0.094 (7)	0.095 (10)	0.118 (11)	-0.003 (6)	0.003 (7)	0.074 (10)
C38'	0.092 (5)	0.077 (10)	0.113 (9)	0.010 (6)	0.000 (6)	0.064 (8)
C39'	0.076 (5)	0.067 (9)	0.098 (7)	0.007 (5)	-0.011 (4)	0.058 (6)
C40'	0.085 (7)	0.049 (5)	0.084 (5)	0.007 (8)	-0.014 (4)	0.042 (5)
C45'	0.105 (9)	0.050 (5)	0.087 (5)	0.017 (9)	-0.021 (5)	0.032 (5)
C44'	0.119 (10)	0.058 (6)	0.070 (5)	0.016 (10)	-0.025 (5)	0.027 (5)
C43'	0.114 (9)	0.057 (6)	0.054 (4)	0.030 (9)	-0.017 (5)	0.023 (4)

C42'	0.081 (8)	0.047 (4)	0.056 (3)	0.027 (8)	-0.014 (5)	0.022 (3)
C41'	0.083 (8)	0.045 (6)	0.066 (3)	0.012 (7)	-0.007 (4)	0.034 (3)
C46'	0.122 (10)	0.083 (7)	0.053 (5)	0.068 (9)	-0.009 (7)	0.017 (5)
O3'	0.155 (8)	0.108 (7)	0.068 (5)	0.057 (6)	0.015 (5)	0.028 (5)
N6	0.079 (3)	0.048 (3)	0.039 (3)	0.019 (2)	0.008 (2)	0.018 (2)
C47	0.086 (4)	0.071 (4)	0.054 (4)	0.034 (4)	0.008 (3)	0.035 (3)
C48	0.083 (4)	0.089 (5)	0.063 (4)	0.039 (4)	0.025 (4)	0.048 (4)
C49	0.090 (5)	0.085 (5)	0.076 (5)	0.041 (4)	0.037 (4)	0.044 (4)
C50	0.092 (4)	0.063 (4)	0.065 (4)	0.033 (4)	0.028 (4)	0.039 (3)
C51	0.075 (3)	0.043 (3)	0.036 (3)	0.015 (3)	0.006 (3)	0.018 (3)
C52	0.077 (3)	0.046 (3)	0.043 (3)	0.016 (3)	0.013 (3)	0.023 (3)
C57	0.079 (4)	0.058 (4)	0.064 (4)	0.023 (3)	0.021 (3)	0.038 (3)
C56	0.081 (4)	0.059 (4)	0.060 (4)	0.019 (3)	0.013 (3)	0.037 (3)
C55	0.079 (4)	0.048 (3)	0.046 (3)	0.017 (3)	0.008 (3)	0.022 (3)
C54	0.066 (3)	0.049 (3)	0.051 (3)	0.008 (3)	0.008 (3)	0.027 (3)
C53	0.070 (3)	0.046 (3)	0.040 (3)	0.011 (3)	0.005 (3)	0.022 (3)
C58	0.078 (4)	0.074 (5)	0.066 (4)	0.023 (4)	0.009 (4)	0.043 (4)
O4	0.076 (3)	0.100 (4)	0.094 (4)	0.028 (3)	0.018 (3)	0.065 (3)
N4	0.077 (4)	0.068 (4)	0.080 (4)	0.024 (3)	0.020 (3)	0.046 (3)
N7	0.075 (4)	0.081 (4)	0.066 (3)	0.022 (3)	0.016 (3)	0.045 (3)
N8	0.099 (4)	0.068 (4)	0.059 (3)	0.028 (3)	0.009 (3)	0.040 (3)
N3	0.062 (4)	0.063 (3)	0.091 (5)	0.023 (3)	-0.004 (3)	0.022 (3)
C25	0.050 (5)	0.062 (3)	0.080 (5)	0.013 (3)	0.005 (4)	0.035 (3)
C26	0.095 (6)	0.065 (5)	0.115 (8)	0.014 (4)	-0.013 (5)	0.026 (5)
C27	0.141 (9)	0.072 (6)	0.110 (8)	0.047 (6)	-0.016 (6)	0.010 (6)
C28	0.101 (8)	0.085 (8)	0.128 (9)	0.018 (6)	-0.034 (6)	0.020 (6)
C29	0.126 (10)	0.091 (9)	0.175 (11)	-0.008 (7)	0.010 (8)	0.058 (8)
N3'	0.062 (4)	0.063 (3)	0.091 (5)	0.023 (3)	-0.004 (3)	0.022 (3)
C25'	0.050 (5)	0.062 (3)	0.080 (5)	0.013 (3)	0.005 (4)	0.035 (3)
C26'	0.095 (6)	0.065 (5)	0.115 (8)	0.014 (4)	-0.013 (5)	0.026 (5)
C27'	0.141 (9)	0.072 (6)	0.110 (8)	0.047 (6)	-0.016 (6)	0.010 (6)
C28'	0.101 (8)	0.085 (8)	0.128 (9)	0.018 (6)	-0.034 (6)	0.020 (6)
C29'	0.126 (10)	0.091 (9)	0.175 (11)	-0.008 (7)	0.010 (8)	0.058 (8)
C30	0.056 (4)	0.057 (4)	0.072 (4)	0.012 (3)	0.011 (3)	0.032 (3)
C31	0.100 (5)	0.076 (4)	0.084 (5)	0.033 (4)	0.032 (4)	0.056 (4)
C32	0.116 (7)	0.222 (14)	0.210 (13)	0.054 (7)	0.033 (7)	0.177 (12)
C33	0.155 (9)	0.104 (6)	0.153 (9)	0.005 (6)	0.032 (7)	0.087 (6)
C34	0.361 (19)	0.142 (8)	0.144 (9)	0.140 (11)	0.155 (12)	0.112 (7)
C59	0.073 (4)	0.075 (4)	0.062 (3)	0.023 (3)	0.016 (3)	0.046 (3)
C60	0.083 (5)	0.087 (5)	0.063 (4)	0.013 (4)	0.011 (4)	0.035 (4)
C61	0.156 (9)	0.142 (9)	0.091 (7)	-0.047 (7)	0.007 (7)	0.056 (6)
C62	0.125 (7)	0.106 (7)	0.089 (6)	0.054 (6)	0.031 (6)	0.023 (5)
C63	0.118 (7)	0.139 (8)	0.070 (5)	0.047 (6)	0.018 (5)	0.061 (6)
C64	0.087 (5)	0.067 (4)	0.067 (4)	0.023 (4)	0.010 (4)	0.042 (4)
C65	0.131 (6)	0.079 (5)	0.060 (4)	0.033 (4)	0.000 (4)	0.048 (4)
C66	0.149 (8)	0.084 (6)	0.062 (6)	0.021 (7)	-0.009 (6)	0.045 (5)
C67	0.167 (9)	0.146 (13)	0.102 (11)	0.039 (7)	0.038 (8)	0.091 (9)
C68	0.139 (11)	0.062 (6)	0.081 (7)	0.025 (7)	-0.020 (9)	0.034 (5)
C66'	0.149 (8)	0.084 (6)	0.062 (6)	0.021 (7)	-0.009 (6)	0.045 (5)
C67'	0.167 (9)	0.146 (13)	0.102 (11)	0.039 (7)	0.038 (8)	0.091 (9)
C68'	0.139 (11)	0.062 (6)	0.081 (7)	0.025 (7)	-0.020 (9)	0.034 (5)

Table 4: Geometric parameters (Å, °) for $2 \cdot 0.25(\text{CH}_2\text{Cl}_2)$.

Ir1—C25'	2.009 (17)	C46—O3	1.148 (14)
Ir1—C30	2.022 (8)	N5'—C35'	1.349 (13)
Ir1—C25	2.037 (8)	N5'—C39'	1.378 (12)
Ir1—C7	2.046 (6)	C35'—C36'	1.392 (13)
Ir1—N2	2.047 (5)	C36'—C37'	1.378 (14)
Ir1—N1	2.049 (5)	C37'—C38'	1.384 (14)
Ir1—C19	2.061 (6)	C38'—C39'	1.387 (13)
Ir2—C59	2.010 (8)	C39'—C40'	1.454 (12)
Ir2—C41'	2.026 (12)	C40'—C41'	1.408 (12)
Ir2—N5	2.039 (10)	C40'—C45'	1.414 (12)
Ir2—C64	2.049 (7)	C45'—C44'	1.368 (14)
Ir2—N6	2.051 (5)	C44'—C43'	1.402 (13)
Ir2—N5'	2.056 (11)	C43'—C42'	1.404 (12)
Ir2—C41	2.057 (11)	C43'—C46'	1.458 (14)
Ir2—C53	2.062 (6)	C42'—C41'	1.343 (13)
N1—C1	1.350 (8)	C46'—O3'	1.172 (13)
N1—C5	1.364 (8)	N6—C47	1.365 (7)
C1—C2	1.384 (10)	N6—C51	1.375 (7)
C2—C3	1.358 (11)	C47—C48	1.365 (9)
C3—C4	1.370 (10)	C48—C49	1.370 (9)
C4—C5	1.402 (8)	C49—C50	1.402 (8)
C5—C6	1.446 (8)	C50—C51	1.376 (8)
C6—C7	1.409 (7)	C51—C52	1.455 (7)
C6—C11	1.417 (8)	C52—C53	1.396 (7)
C11—C10	1.347 (9)	C52—C57	1.410 (7)
C10—C9	1.398 (9)	C57—C56	1.367 (8)
C9—C8	1.412 (8)	C56—C55	1.405 (8)
C9—C12	1.459 (10)	C55—C54	1.387 (7)
C8—C7	1.382 (8)	C55—C58	1.479 (8)
C12—O1	1.147 (9)	C54—C53	1.383 (8)
N2—C13	1.344 (8)	C58—O4	1.193 (7)
N2—C17	1.381 (8)	N4—C30	1.164 (8)
C13—C14	1.360 (9)	N4—C31	1.487 (9)
C14—C15	1.380 (10)	N7—C59	1.157 (8)
C15—C16	1.369 (10)	N7—C60	1.453 (10)
C16—C17	1.392 (8)	N8—C64	1.118 (8)
C17—C18	1.444 (8)	N8—C65	1.464 (8)
C18—C19	1.383 (8)	N3—C25	1.138 (10)
C18—C23	1.406 (9)	N3—C26	1.515 (13)
C23—C22	1.371 (10)	C26—C28	1.496 (12)
C22—C21	1.406 (9)	C26—C29	1.548 (13)
C21—C20	1.386 (8)	C26—C27	1.550 (12)
C21—C24	1.476 (9)	N3'—C25'	1.114 (18)
C20—C19	1.387 (8)	N3'—C26'	1.50 (2)
C24—O2	1.202 (8)	C26'—C29'	1.505 (16)

N5—C35	1.340 (12)	C26'—C27'	1.527 (16)
N5—C39	1.376 (12)	C26'—C28'	1.528 (16)
C35—C36	1.390 (13)	C31—C34	1.450 (13)
C36—C37	1.386 (14)	C31—C33	1.483 (12)
C37—C38	1.403 (14)	C31—C32	1.501 (12)
C38—C39	1.386 (12)	C60—C62	1.502 (12)
C39—C40	1.454 (12)	C60—C61	1.514 (12)
C40—C45	1.408 (12)	C60—C63	1.528 (11)
C40—C41	1.412 (12)	C65—C67'	1.490 (11)
C45—C44	1.362 (13)	C65—C66	1.519 (12)
C44—C43	1.408 (13)	C65—C68'	1.532 (11)
C43—C42	1.397 (11)	C65—C68	1.546 (13)
C43—C46	1.463 (13)	C65—C67	1.575 (13)
C42—C41	1.368 (12)	C65—C66'	1.585 (11)
C25'—Ir1—C30	81.8 (17)	C42—C43—C44	119.0 (12)
C25'—Ir1—C25	17.4 (14)	C42—C43—C46	122.8 (11)
C30—Ir1—C25	91.9 (4)	C44—C43—C46	118.0 (12)
C25'—Ir1—C7	163.8 (13)	C41—C42—C43	124.8 (12)
C30—Ir1—C7	95.5 (2)	C42—C41—C40	114.3 (10)
C25—Ir1—C7	172.4 (4)	C42—C41—Ir2	132.5 (9)
C25'—Ir1—N2	103.8 (13)	C40—C41—Ir2	113.2 (9)
C30—Ir1—N2	94.9 (2)	O3—C46—C43	128.1 (15)
C25—Ir1—N2	88.9 (3)	C35'—N5'—C39'	117.4 (11)
C7—Ir1—N2	92.3 (2)	C35'—N5'—Ir2	126.7 (11)
C25'—Ir1—N1	84.0 (13)	C39'—N5'—Ir2	115.3 (10)
C30—Ir1—N1	91.3 (2)	N5'—C35'—C36'	125.0 (14)
C25—Ir1—N1	97.9 (3)	C37'—C36'—C35'	116.6 (15)
C7—Ir1—N1	80.1 (2)	C36'—C37'—C38'	119.7 (14)
N2—Ir1—N1	170.7 (2)	C37'—C38'—C39'	121.2 (14)
C25'—Ir1—C19	98.7 (17)	N5'—C39'—C38'	119.6 (12)
C30—Ir1—C19	175.2 (2)	N5'—C39'—C40'	113.5 (11)
C25—Ir1—C19	87.4 (4)	C38'—C39'—C40'	126.5 (13)
C7—Ir1—C19	85.4 (2)	C41'—C40'—C45'	118.7 (12)
N2—Ir1—C19	80.3 (2)	C41'—C40'—C39'	116.2 (11)
N1—Ir1—C19	93.5 (2)	C45'—C40'—C39'	125.1 (12)
C59—Ir2—C41'	171.7 (13)	C44'—C45'—C40'	121.0 (14)
C59—Ir2—N5	102.9 (5)	C45'—C44'—C43'	120.1 (13)
C41'—Ir2—N5	70.1 (6)	C44'—C43'—C42'	117.5 (12)
C59—Ir2—C64	89.1 (3)	C44'—C43'—C46'	121.9 (12)
C41'—Ir2—C64	95 (2)	C42'—C43'—C46'	120.6 (13)
N5—Ir2—C64	90.1 (12)	C41'—C42'—C43'	123.4 (13)
C59—Ir2—N6	89.4 (2)	C42'—C41'—C40'	118.8 (13)
C41'—Ir2—N6	97.0 (6)	C42'—C41'—Ir2	126.3 (12)
N5—Ir2—N6	165.2 (6)	C40'—C41'—Ir2	113.8 (10)
C64—Ir2—N6	98.5 (3)	O3'—C46'—C43'	132.1 (19)
C59—Ir2—N5'	93.3 (5)	C47—N6—C51	117.9 (6)
C41'—Ir2—N5'	80.0 (6)	C47—N6—Ir2	125.7 (4)
N5—Ir2—N5'	10.3 (8)	C51—N6—Ir2	116.3 (4)
C64—Ir2—N5'	86.4 (14)	C48—C47—N6	123.8 (6)
N6—Ir2—N5'	174.5 (12)	C47—C48—C49	118.3 (7)
C59—Ir2—C41	174.8 (15)	C48—C49—C50	119.5 (7)

C41'—Ir2—C41	9.9 (7)	C51—C50—C49	120.2 (6)
N5—Ir2—C41	80.0 (5)	N6—C51—C50	120.3 (5)
C64—Ir2—C41	95.2 (18)	N6—C51—C52	113.2 (5)
N6—Ir2—C41	87.2 (5)	C50—C51—C52	126.5 (5)
N5'—Ir2—C41	89.9 (6)	C53—C52—C57	120.1 (6)
C59—Ir2—C53	91.7 (3)	C53—C52—C51	117.5 (5)
C41'—Ir2—C53	84 (2)	C57—C52—C51	122.5 (5)
N5—Ir2—C53	91.3 (12)	C56—C57—C52	120.4 (6)
C64—Ir2—C53	178.2 (3)	C57—C56—C55	119.4 (6)
N6—Ir2—C53	79.9 (2)	C54—C55—C56	120.3 (6)
N5'—Ir2—C53	95.2 (14)	C54—C55—C58	120.8 (6)
C41—Ir2—C53	83.9 (18)	C56—C55—C58	118.9 (6)
C1—N1—C5	119.6 (6)	C53—C54—C55	120.6 (6)
C1—N1—Ir1	124.6 (5)	C54—C53—C52	119.2 (5)
C5—N1—Ir1	115.7 (4)	C54—C53—Ir2	128.0 (4)
N1—C1—C2	122.0 (8)	C52—C53—Ir2	112.8 (4)
C3—C2—C1	118.2 (8)	O4—C58—C55	126.7 (7)
C2—C3—C4	121.5 (8)	C30—N4—C31	173.1 (7)
C3—C4—C5	118.8 (8)	C59—N7—C60	175.3 (8)
N1—C5—C4	119.9 (7)	C64—N8—C65	169.8 (8)
N1—C5—C6	114.7 (5)	C25—N3—C26	172.9 (12)
C4—C5—C6	125.5 (7)	N3—C25—Ir1	176.9 (10)
C7—C6—C11	121.1 (6)	C28—C26—N3	107.0 (9)
C7—C6—C5	116.1 (5)	C28—C26—C29	111.2 (9)
C11—C6—C5	122.9 (6)	N3—C26—C29	109.2 (10)
C10—C11—C6	119.8 (6)	C28—C26—C27	112.4 (9)
C11—C10—C9	120.9 (6)	N3—C26—C27	103.7 (8)
C10—C9—C8	119.2 (6)	C29—C26—C27	112.9 (9)
C10—C9—C12	119.9 (7)	C25'—N3'—C26'	173 (5)
C8—C9—C12	120.8 (7)	N3'—C25'—Ir1	169 (4)
C7—C8—C9	121.4 (6)	N3'—C26'—C29'	104 (3)
C8—C7—C6	117.5 (5)	N3'—C26'—C27'	107 (3)
C8—C7—Ir1	129.1 (4)	C29'—C26'—C27'	114.0 (14)
C6—C7—Ir1	113.3 (4)	N3'—C26'—C28'	106 (3)
O1—C12—C9	123.9 (9)	C29'—C26'—C28'	114.0 (14)
C13—N2—C17	117.9 (6)	C27'—C26'—C28'	111.4 (13)
C13—N2—Ir1	126.4 (5)	N4—C30—Ir1	176.8 (6)
C17—N2—Ir1	115.6 (4)	C34—C31—C33	119.1 (10)
N2—C13—C14	124.1 (7)	C34—C31—N4	108.5 (7)
C13—C14—C15	117.8 (8)	C33—C31—N4	107.3 (7)
C16—C15—C14	120.4 (7)	C34—C31—C32	108.6 (10)
C15—C16—C17	119.6 (8)	C33—C31—C32	105.9 (9)
N2—C17—C16	120.1 (6)	N4—C31—C32	106.7 (7)
N2—C17—C18	113.2 (5)	N7—C59—Ir2	176.6 (7)
C16—C17—C18	126.7 (7)	N7—C60—C62	109.4 (7)
C19—C18—C23	119.9 (6)	N7—C60—C61	108.0 (7)
C19—C18—C17	118.4 (6)	C62—C60—C61	117.7 (10)
C23—C18—C17	121.5 (6)	N7—C60—C63	106.8 (7)
C22—C23—C18	120.0 (7)	C62—C60—C63	106.5 (8)
C23—C22—C21	120.8 (7)	C61—C60—C63	107.9 (8)
C20—C21—C22	118.0 (7)	N8—C64—Ir2	173.1 (8)

C20—C21—C24	123.5 (7)	N8—C65—C67'	106.6 (9)
C22—C21—C24	118.4 (7)	N8—C65—C66	112.5 (13)
C19—C20—C21	122.0 (6)	C67'—C65—C66	77.4 (11)
C18—C19—C20	119.1 (6)	N8—C65—C68'	109.6 (9)
C18—C19—Ir1	112.3 (4)	C67'—C65—C68'	113.5 (9)
C20—C19—Ir1	128.6 (5)	C66—C65—C68'	130.8 (15)
O2—C24—C21	123.1 (8)	N8—C65—C68	107.3 (17)
C35—N5—C39	119.8 (11)	C67'—C65—C68	135.5 (18)
C35—N5—Ir2	123.3 (10)	C66—C65—C68	114.2 (11)
C39—N5—Ir2	116.6 (9)	C68'—C65—C68	26.2 (12)
N5—C35—C36	122.8 (13)	N8—C65—C67	102.8 (13)
C37—C36—C35	117.7 (14)	C67'—C65—C67	35.8 (11)
C36—C37—C38	119.9 (13)	C66—C65—C67	111.3 (10)
C39—C38—C37	119.8 (13)	C68'—C65—C67	82.3 (13)
N5—C39—C38	119.6 (11)	C68—C65—C67	108.0 (11)
N5—C39—C40	113.7 (10)	N8—C65—C66'	103.3 (7)
C38—C39—C40	126.3 (12)	C67'—C65—C66'	113.1 (7)
C45—C40—C41	121.9 (11)	C66—C65—C66'	35.8 (11)
C45—C40—C39	121.9 (11)	C68'—C65—C66'	110.2 (8)
C41—C40—C39	116.1 (10)	C68—C65—C66'	86.0 (11)
C44—C45—C40	121.5 (13)	C67—C65—C66'	144.9 (12)
C45—C44—C43	117.8 (12)		
C25'—Ir1—N1—C1	3.0 (18)	C64—Ir2—N5'—C35'	−82 (4)
C30—Ir1—N1—C1	84.6 (7)	N6—Ir2—N5'—C35'	125 (8)
C25—Ir1—N1—C1	−7.5 (7)	C41—Ir2—N5'—C35'	−177 (5)
C7—Ir1—N1—C1	179.9 (7)	C53—Ir2—N5'—C35'	99 (4)
N2—Ir1—N1—C1	−143.9 (12)	C59—Ir2—N5'—C39'	−165 (3)
C19—Ir1—N1—C1	−95.4 (6)	C41'—Ir2—N5'—C39'	10 (4)
C25'—Ir1—N1—C5	179.4 (18)	N5—Ir2—N5'—C39'	−5(12)
C30—Ir1—N1—C5	−99.0 (5)	C64—Ir2—N5'—C39'	106 (3)
C25—Ir1—N1—C5	168.9 (5)	N6—Ir2—N5'—C39'	−46 (13)
C7—Ir1—N1—C5	−3.7 (5)	C41—Ir2—N5'—C39'	11 (4)
N2—Ir1—N1—C5	32.5 (16)	C53—Ir2—N5'—C39'	−73 (3)
C19—Ir1—N1—C5	81.0 (5)	C39'—N5'—C35'—C36'	−7(7)
C5—N1—C1—C2	−0.3 (12)	Ir2—N5'—C35'—C36'	−178 (4)
Ir1—N1—C1—C2	176.0 (7)	N5'—C35'—C36'—C37'	2(6)
N1—C1—C2—C3	0.0 (14)	C35'—C36'—C37'—C38'	4(5)
C1—C2—C3—C4	0.8 (14)	C36'—C37'—C38'—C39'	−5(5)
C2—C3—C4—C5	−1.3 (13)	C35'—N5'—C39'—C38'	6(6)
C1—N1—C5—C4	−0.2 (10)	Ir2—N5'—C39'—C38'	178 (3)
Ir1—N1—C5—C4	−176.8 (5)	C35'—N5'—C39'—C40'	178 (4)
C1—N1—C5—C6	−179.9 (6)	Ir2—N5'—C39'—C40'	−9(5)
Ir1—N1—C5—C6	3.5 (7)	C37'—C38'—C39'—N5'	0(5)
C3—C4—C5—N1	1.0 (10)	C37'—C38'—C39'—C40'	−172 (4)
C3—C4—C5—C6	−179.4 (7)	N5'—C39'—C40'—C41'	1(6)
N1—C5—C6—C7	−0.9 (8)	C38'—C39'—C40'—C41'	174 (5)
C4—C5—C6—C7	179.5 (6)	N5'—C39'—C40'—C45'	−175 (4)
N1—C5—C6—C11	178.7 (6)	C38'—C39'—C40'—C45'	−3(7)
C4—C5—C6—C11	−0.9 (10)	C41'—C40'—C45'—C44'	2(7)
C7—C6—C11—C10	−4.1 (10)	C39'—C40'—C45'—C44'	178 (4)
C5—C6—C11—C10	176.3 (6)	C40'—C45'—C44'—C43'	3(6)

C6—C11—C10—C9	3.9 (11)	C45'—C44'—C43'—C42'	−3(5)
C11—C10—C9—C8	−1.5 (11)	C45'—C44'—C43'—C46'	177 (3)
C11—C10—C9—C12	−179.8 (7)	C44'—C43'—C42'—C41'	−3(6)
C10—C9—C8—C7	−0.8 (10)	C46'—C43'—C42'—C41'	177 (5)
C12—C9—C8—C7	177.5 (7)	C43'—C42'—C41'—C40'	8(8)
C9—C8—C7—C6	0.6 (9)	C43'—C42'—C41'—Ir2	175 (4)
C9—C8—C7—Ir1	−175.2 (5)	C45'—C40'—C41'—C42'	−8(8)
C11—C6—C7—C8	1.8 (9)	C39'—C40'—C41'—C42'	176 (5)
C5—C6—C7—C8	−178.6 (5)	C45'—C40'—C41'—Ir2	−176 (4)
C11—C6—C7—Ir1	178.3 (5)	C39'—C40'—C41'—Ir2	7(6)
C5—C6—C7—Ir1	−2.1 (7)	C59—Ir2—C41'—C42'	−140 (8)
C25'—Ir1—C7—C8	−170 (6)	N5—Ir2—C41'—C42'	−174 (6)
C30—Ir1—C7—C8	−90.7 (6)	C64—Ir2—C41'—C42'	98 (6)
C25—Ir1—C7—C8	104 (2)	N6—Ir2—C41'—C42'	−1(6)
N2—Ir1—C7—C8	4.5 (6)	N5'—Ir2—C41'—C42'	−177 (6)
N1—Ir1—C7—C8	179.0 (6)	C41—Ir2—C41'—C42'	8(18)
C19—Ir1—C7—C8	84.6 (6)	C53—Ir2—C41'—C42'	−80 (6)
C25'—Ir1—C7—C6	14 (6)	C59—Ir2—C41'—C40'	27 (17)
C30—Ir1—C7—C6	93.4 (4)	N5—Ir2—C41'—C40'	−6(4)
C25—Ir1—C7—C6	−72 (2)	C64—Ir2—C41'—C40'	−95 (5)
N2—Ir1—C7—C6	−171.5 (4)	N6—Ir2—C41'—C40'	166 (4)
N1—Ir1—C7—C6	3.0 (4)	N5'—Ir2—C41'—C40'	−9(5)
C19—Ir1—C7—C6	−91.4 (4)	C41—Ir2—C41'—C40'	175 (27)
C10—C9—C12—O1	−177.3 (10)	C53—Ir2—C41'—C40'	87 (5)
C8—C9—C12—O1	4.4 (14)	C44'—C43'—C46'—O3'	5(5)
C25'—Ir1—N2—C13	83.9 (18)	C42'—C43'—C46'—O3'	−174 (3)
C30—Ir1—N2—C13	1.2 (6)	C59—Ir2—N6—C47	−86.0 (5)
C25—Ir1—N2—C13	92.9 (7)	C41'—Ir2—N6—C47	99 (2)
C7—Ir1—N2—C13	−94.6 (6)	N5—Ir2—N6—C47	128 (4)
N1—Ir1—N2—C13	−130.1 (13)	C64—Ir2—N6—C47	3.0 (6)
C19—Ir1—N2—C13	−179.5 (6)	N5'—Ir2—N6—C47	155 (10)
C25'—Ir1—N2—C17	−98.8 (18)	C41—Ir2—N6—C47	97.8 (19)
C30—Ir1—N2—C17	178.5 (5)	C53—Ir2—N6—C47	−177.9 (5)
C25—Ir1—N2—C17	−89.7 (6)	C59—Ir2—N6—C51	97.2 (4)
C7—Ir1—N2—C17	82.8 (5)	C41'—Ir2—N6—C51	−77 (2)
N1—Ir1—N2—C17	47.2 (15)	N5—Ir2—N6—C51	−49 (4)
C19—Ir1—N2—C17	−2.1 (4)	C64—Ir2—N6—C51	−173.7 (4)
C17—N2—C13—C14	−1.7 (11)	N5'—Ir2—N6—C51	−21 (10)
Ir1—N2—C13—C14	175.6 (6)	C41—Ir2—N6—C51	−78.9 (19)
N2—C13—C14—C15	1.2 (12)	C53—Ir2—N6—C51	5.4 (4)
C13—C14—C15—C16	−0.8 (13)	C51—N6—C47—C48	1.6 (10)
C14—C15—C16—C17	1.0 (13)	Ir2—N6—C47—C48	−175.1 (5)
C13—N2—C17—C16	1.8 (10)	N6—C47—C48—C49	−0.9 (11)
Ir1—N2—C17—C16	−175.8 (5)	C47—C48—C49—C50	0.3 (11)
C13—N2—C17—C18	−178.3 (6)	C48—C49—C50—C51	−0.4 (11)
Ir1—N2—C17—C18	4.1 (7)	C47—N6—C51—C50	−1.6 (8)
C15—C16—C17—N2	−1.5 (11)	Ir2—N6—C51—C50	175.4 (5)
C15—C16—C17—C18	178.6 (7)	C47—N6—C51—C52	177.5 (5)
N2—C17—C18—C19	−4.6 (9)	Ir2—N6—C51—C52	−5.5 (6)
C16—C17—C18—C19	175.4 (7)	C49—C50—C51—N6	1.1 (9)
N2—C17—C18—C23	−179.2 (6)	C49—C50—C51—C52	−177.9 (6)

C16—C17—C18—C23	0.8 (11)	N6—C51—C52—C53	2.0 (7)
C19—C18—C23—C22	4.3 (12)	C50—C51—C52—C53	-179.0 (6)
C17—C18—C23—C22	178.8 (8)	N6—C51—C52—C57	-179.2 (6)
C18—C23—C22—C21	-2.3 (14)	C50—C51—C52—C57	-0.2 (10)
C23—C22—C21—C20	0.5 (14)	C53—C52—C57—C56	-1.6 (9)
C23—C22—C21—C24	-177.3 (9)	C51—C52—C57—C56	179.6 (6)
C22—C21—C20—C19	-0.9 (12)	C52—C57—C56—C55	0.1 (10)
C24—C21—C20—C19	176.8 (8)	C57—C56—C55—C54	0.8 (9)
C23—C18—C19—C20	-4.6 (10)	C57—C56—C55—C58	-177.3 (6)
C17—C18—C19—C20	-179.2 (6)	C56—C55—C54—C53	-0.2 (9)
C23—C18—C19—Ir1	177.4 (5)	C58—C55—C54—C53	177.9 (6)
C17—C18—C19—Ir1	2.8 (7)	C55—C54—C53—C52	-1.3 (9)
C21—C20—C19—C18	2.9 (10)	C55—C54—C53—Ir2	177.1 (5)
C21—C20—C19—Ir1	-179.5 (5)	C57—C52—C53—C54	2.2 (9)
C25'—Ir1—C19—C18	102.3 (14)	C51—C52—C53—C54	-179.0 (5)
C30—Ir1—C19—C18	8(3)	C57—C52—C53—Ir2	-176.4 (5)
C25—Ir1—C19—C18	89.0 (5)	C51—C52—C53—Ir2	2.4 (7)
C7—Ir1—C19—C18	-93.5 (5)	C59—Ir2—C53—C54	88.4 (6)
N2—Ir1—C19—C18	-0.4 (4)	C41'—Ir2—C53—C54	-84.4 (7)
N1—Ir1—C19—C18	-173.3 (5)	N5—Ir2—C53—C54	-14.5 (7)
C25'—Ir1—C19—C20	-75.5 (15)	C64—Ir2—C53—C54	-154 (8)
C30—Ir1—C19—C20	-170 (3)	N6—Ir2—C53—C54	177.5 (6)
C25—Ir1—C19—C20	-88.8 (6)	N5'—Ir2—C53—C54	-5.0 (8)
C7—Ir1—C19—C20	88.8 (6)	C41—Ir2—C53—C54	-94.3 (7)
N2—Ir1—C19—C20	-178.1 (6)	C59—Ir2—C53—C52	-93.1 (5)
N1—Ir1—C19—C20	9.0 (6)	C41'—Ir2—C53—C52	94.1 (6)
C20—C21—C24—O2	-4.4 (16)	N5—Ir2—C53—C52	164.0 (6)
C22—C21—C24—O2	173.3 (10)	C64—Ir2—C53—C52	24 (8)
C59—Ir2—N5—C35	9(4)	N6—Ir2—C53—C52	-4.0 (4)
C41'—Ir2—N5—C35	-175 (4)	N5'—Ir2—C53—C52	173.5 (7)
C64—Ir2—N5—C35	-80 (3)	C41—Ir2—C53—C52	84.2 (6)
N6—Ir2—N5—C35	154 (3)	C54—C55—C58—O4	2.8 (11)
N5'—Ir2—N5—C35	-11 (12)	C56—C55—C58—O4	-179.1 (7)
C41—Ir2—N5—C35	-175 (4)	C26—N3—C25—Ir1	128 (17)
C53—Ir2—N5—C35	101 (3)	C25'—Ir1—C25—N3	-79 (18)
C59—Ir2—N5—C39	-177 (3)	C30—Ir1—C25—N3	-133 (18)
C41'—Ir2—N5—C39	-2(3)	C7—Ir1—C25—N3	33 (20)
C64—Ir2—N5—C39	93 (3)	N2—Ir1—C25—N3	132 (18)
N6—Ir2—N5—C39	-32 (7)	N1—Ir1—C25—N3	-42 (18)
N5'—Ir2—N5—C39	162 (17)	C19—Ir1—C25—N3	52 (18)
C41—Ir2—N5—C39	-2(3)	C25—N3—C26—C28	-128 (7)
C53—Ir2—N5—C39	-85 (3)	C25—N3—C26—C29	-7(8)
C39—N5—C35—C36	8(6)	C25—N3—C26—C27	113 (7)
Ir2—N5—C35—C36	-179 (3)	C26'—N3'—C25'—Ir1	-105 (44)
N5—C35—C36—C37	-4(5)	C30—Ir1—C25'—N3'	-63 (27)
C35—C36—C37—C38	0(4)	C25—Ir1—C25'—N3'	172 (33)
C36—C37—C38—C39	0(4)	C7—Ir1—C25'—N3'	18 (33)
C35—N5—C39—C38	-8(5)	N2—Ir1—C25'—N3'	-156 (27)
Ir2—N5—C39—C38	179 (3)	N1—Ir1—C25'—N3'	29 (27)
C35—N5—C39—C40	178 (4)	C19—Ir1—C25'—N3'	122 (27)
Ir2—N5—C39—C40	5(4)	C25'—N3'—C26'—C29'	164 (37)

C37—C38—C39—N5	4(4)	C25'—N3'—C26'—C27'	-75 (38)
C37—C38—C39—C40	177 (3)	C25'—N3'—C26'—C28'	43 (38)
N5—C39—C40—C45	176 (4)	C31—N4—C30—Ir1	36 (15)
C38—C39—C40—C45	3(6)	C25'—Ir1—C30—N4	-63 (11)
N5—C39—C40—C41	-6(5)	C25—Ir1—C30—N4	-49 (11)
C38—C39—C40—C41	-180 (4)	C7—Ir1—C30—N4	133 (11)
C41—C40—C45—C44	3(6)	N2—Ir1—C30—N4	40 (11)
C39—C40—C45—C44	-180 (4)	N1—Ir1—C30—N4	-147 (11)
C40—C45—C44—C43	-3(5)	C19—Ir1—C30—N4	32 (13)
C45—C44—C43—C42	-2(4)	C30—N4—C31—C34	158 (6)
C45—C44—C43—C46	-177 (3)	C30—N4—C31—C33	29 (6)
C44—C43—C42—C41	9(5)	C30—N4—C31—C32	-85 (6)
C46—C43—C42—C41	-176 (4)	C60—N7—C59—Ir2	16 (18)
C43—C42—C41—C40	-9(6)	C41'—Ir2—C59—N7	155 (16)
C43—C42—C41—Ir2	172 (4)	N5—Ir2—C59—N7	-173 (10)
C45—C40—C41—C42	3(7)	C64—Ir2—C59—N7	-83 (10)
C39—C40—C41—C42	-174 (4)	N6—Ir2—C59—N7	15 (10)
C45—C40—C41—Ir2	-177 (3)	N5'—Ir2—C59—N7	-169 (11)
C39—C40—C41—Ir2	5(6)	C41—Ir2—C59—N7	63 (17)
C59—Ir2—C41—C42	-58 (17)	C53—Ir2—C59—N7	95 (10)
C41'—Ir2—C41—C42	179 (28)	C59—N7—C60—C62	-179 (100)
N5—Ir2—C41—C42	177 (6)	C59—N7—C60—C61	-50 (9)
C64—Ir2—C41—C42	88 (5)	C59—N7—C60—C63	66 (9)
N6—Ir2—C41—C42	-10 (5)	C65—N8—C64—Ir2	21 (9)
N5'—Ir2—C41—C42	175 (5)	C59—Ir2—C64—N8	-50 (6)
C53—Ir2—C41—C42	-90 (5)	C41'—Ir2—C64—N8	123 (6)
C59—Ir2—C41—C40	123 (9)	N5—Ir2—C64—N8	53 (6)
C41'—Ir2—C41—C40	0(20)	N6—Ir2—C64—N8	-140 (6)
N5—Ir2—C41—C40	-2(4)	N5'—Ir2—C64—N8	43 (6)
C64—Ir2—C41—C40	-91 (4)	C41—Ir2—C64—N8	132 (6)
N6—Ir2—C41—C40	171 (4)	C53—Ir2—C64—N8	-168 (6)
N5'—Ir2—C41—C40	-5(4)	C64—N8—C65—C67'	-28 (5)
C53—Ir2—C41—C40	91 (4)	C64—N8—C65—C66	55 (5)
C42—C43—C46—O3	9(4)	C64—N8—C65—C68'	-151 (4)
C44—C43—C46—O3	-176 (3)	C64—N8—C65—C68	-179 (100)
C59—Ir2—N5'—C35'	7(4)	C64—N8—C65—C67	-65 (5)
C41'—Ir2—N5'—C35'	-178 (5)	C64—N8—C65—C66'	91 (4)
N5—Ir2—N5'—C35'	166 (18)___		

Table 5: Crystal data and structure refinement for 4·CH₂Cl₂C₃₅H₃₀Cl₃IrN₄ $M_r = 805.18$ Monoclinic, $P2_1/c$ $a = 10.4363 (15) \text{ \AA}$ $b = 25.923 (4) \text{ \AA}$ $c = 11.7427 (17) \text{ \AA}$ $\beta = 100.315 (2)^\circ$ $F(000) = 1584$ $D_x = 1.711 \text{ Mg m}^{-3}$ Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 1021 reflections

 $\theta = 2.5\text{--}25.6^\circ$ $\mu = 4.56 \text{ mm}^{-1}$ $T = 200 \text{ K}$

$V = 3125.5 (8) \text{ \AA}^3$
 $Z = 4$

Block, Yellow
 $0.16 \times 0.12 \times 0.08 \text{ mm}$

Data collection

Bruker AXS APEX diffractometer	7764 independent reflections
Radiation source: fine-focus sealed tube graphite	6685 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.042$
Detector resolution: $836.6 \text{ pixels mm}^{-1}$	$\theta_{\text{max}} = 28.3^\circ$, $\theta_{\text{min}} = 1.9^\circ$
ω scans	$h = -13 \rightarrow 13$
Abs. corr.: Multi-scan <i>SADABS</i> (Sheldrick, 2003)	$k = -34 \rightarrow 34$
$T_{\text{min}} = 0.533$, $T_{\text{max}} = 0.712$	$l = -15 \rightarrow 15$
42578 measured reflections	

Refinement

Refinement on F^2	Primary atom site location: Structure-invariant direct methods
Least-squares matrix: Full	Secondary atom site location: Difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.031$	Hydrogen site location: Inferred from neighbouring sites
$wR(F^2) = 0.072$	H atoms treated by a mixture of independent and constrained refinement
$S = 1.01$	$w = 1/[\sigma^2(F_o^2) + (0.0362P)^2 + 2.425P]$
	where $P = (F_o^2 + 2F_c^2)/3$
7764 reflections	$(\Delta/\sigma)_{\text{max}} = 0.002$
395 parameters	$\Delta\rho_{\text{max}} = 1.42 \text{ e \AA}^{-3}$
2 restraints	$\Delta\rho_{\text{min}} = -0.44 \text{ e \AA}^{-3}$

Special details

Experimental. Data collection is performed with four batch runs at $\varphi = 0.00^\circ$ (600 frames), at $\varphi = 90.00^\circ$ (600 frames), at $\varphi = 180^\circ$ (600 frames) and at $\varphi = 270^\circ$ (600 frames). Frame width = 0.30° in ω . Data is merged, corrected for decay, and treated with multi-scan absorption corrections.

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry.

An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2 , conventional R-factors R are based on F, with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Table 6: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$) for $4 \cdot \text{CH}_2\text{Cl}_2$

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Ir	−0.029066 (12)	0.116314 (5)	0.520128 (10)	0.02764 (5)
Cl1	−0.20236 (9)	0.05028 (3)	0.51964 (8)	0.03644 (19)
Cl2	0.41938 (12)	0.05228 (5)	0.41176 (12)	0.0637 (3)
Cl3	0.38311 (16)	0.13280 (6)	0.23797 (13)	0.0770 (4)
N1	−0.0424 (3)	0.14712 (11)	0.6775 (2)	0.0325 (6)
N2	−0.0165 (3)	0.09606 (11)	0.3540 (2)	0.0317 (6)
N3	0.2863 (4)	0.00873 (17)	0.9927 (4)	0.0674 (12)
N4	0.0952 (3)	0.05553 (12)	0.6173 (3)	0.0358 (7)
H4	0.116 (4)	0.0264 (11)	0.576 (3)	0.043*
H5	0.045 (3)	0.0426 (15)	0.671 (3)	0.043*
C1	−0.1251 (4)	0.13120 (16)	0.7454 (3)	0.0405 (9)
H1A	−0.1798	0.1025	0.7214	0.049*
C2	−0.1335 (4)	0.15501 (19)	0.8487 (4)	0.0517 (11)
H2A	−0.1933	0.1429	0.8949	0.062*
C3	−0.0548 (5)	0.19644 (19)	0.8841 (4)	0.0572 (12)
H3A	−0.0586	0.2134	0.9551	0.069*
C4	0.0289 (4)	0.21282 (17)	0.8154 (4)	0.0517 (11)
H4A	0.0838	0.2415	0.8392	0.062*
C5	0.0359 (4)	0.18851 (14)	0.7110 (3)	0.0350 (8)
C6	0.1243 (4)	0.20093 (14)	0.6319 (3)	0.0360 (8)
C7	0.2183 (4)	0.24000 (15)	0.6518 (4)	0.0463 (10)
H7A	0.2229	0.2619	0.7173	0.056*
C8	0.3040 (4)	0.24680 (15)	0.5767 (4)	0.0458 (10)
H8A	0.3677	0.2734	0.5901	0.055*
C9	0.2972 (4)	0.21486 (15)	0.4815 (4)	0.0438 (9)
H9A	0.3575	0.2192	0.4305	0.053*
C10	0.2024 (4)	0.17623 (14)	0.4596 (3)	0.0386 (8)
H10A	0.1990	0.1548	0.3935	0.046*
C11	0.1130 (3)	0.16859 (13)	0.5328 (3)	0.0301 (7)
C12	0.0633 (4)	0.06022 (15)	0.3235 (3)	0.0397 (9)

H12A	0.1182	0.0417	0.3828	0.048*
C13	0.0694 (5)	0.04901 (19)	0.2102 (4)	0.0560 (12)
H13A	0.1269	0.0232	0.1913	0.067*
C14	-0.0114 (5)	0.0767 (2)	0.1235 (4)	0.0644 (14)
H14A	-0.0108	0.0695	0.0443	0.077*
C15	-0.0903 (5)	0.11359 (19)	0.1534 (4)	0.0587 (12)
H15A	-0.1437	0.1330	0.0947	0.070*
C16	-0.0945 (4)	0.12355 (15)	0.2698 (3)	0.0397 (9)
C17	-0.1748 (4)	0.16218 (15)	0.3129 (3)	0.0418 (9)
C18	-0.2668 (4)	0.19326 (18)	0.2407 (4)	0.0549 (12)
H18A	-0.2774	0.1903	0.1589	0.066*
C19	-0.3412 (5)	0.22792 (18)	0.2902 (5)	0.0645 (14)
H19A	-0.4025	0.2492	0.2422	0.077*
C20	-0.3267 (5)	0.23166 (18)	0.4085 (5)	0.0609 (13)
H20A	-0.3788	0.2554	0.4416	0.073*
C21	-0.2374 (4)	0.20141 (15)	0.4799 (4)	0.0453 (10)
H21A	-0.2291	0.2046	0.5615	0.054*
C22	-0.1578 (3)	0.16568 (13)	0.4334 (3)	0.0346 (8)
C23	0.2425 (5)	0.0421 (2)	0.9032 (4)	0.0633 (14)
H23A	0.1975	0.0724	0.9189	0.076*
C24	0.2609 (4)	0.03336 (15)	0.7922 (3)	0.0428 (9)
C25	0.3255 (5)	-0.01098 (18)	0.7753 (4)	0.0546 (11)
H25A	0.3396	-0.0190	0.6996	0.066*
C26	0.3699 (4)	-0.04387 (15)	0.8627 (3)	0.0433 (10)
H26A	0.4148	-0.0743	0.8477	0.052*
C27	0.3511 (3)	-0.03381 (15)	0.9703 (3)	0.0355 (8)
C28	0.2155 (4)	0.07060 (16)	0.6936 (4)	0.0494 (10)
H28A	0.2027	0.1050	0.7266	0.059*
H28B	0.2851	0.0740	0.6468	0.059*
C29	0.4680 (4)	-0.11446 (15)	1.0485 (4)	0.0465 (10)
H29A	0.4780	-0.1232	0.9720	0.056*
C30	0.5178 (5)	-0.14675 (17)	1.1397 (4)	0.0592 (12)
H30A	0.5628	-0.1773	1.1253	0.071*
C31	0.5031 (5)	-0.13524 (19)	1.2499 (4)	0.0599 (13)
H31A	0.5356	-0.1580	1.3118	0.072*
C32	0.4413 (5)	-0.0906 (2)	1.2707 (4)	0.0589 (13)
H32A	0.4324	-0.0821	1.3476	0.071*
C33	0.3915 (4)	-0.05781 (18)	1.1807 (4)	0.0489 (10)
H33A	0.3485	-0.0270	1.1965	0.059*
C34	0.4033 (4)	-0.06922 (15)	1.0680 (3)	0.0375 (8)
C35	0.4843 (6)	0.1089 (2)	0.3663 (6)	0.0815 (19)
H35A	0.5729	0.1022	0.3507	0.098*
H35B	0.4911	0.1352	0.4283	0.098*

Table 7: Atomic displacement parameters ($\text{\AA}^2$) for $4 \cdot \text{CH}_2\text{Cl}_2$.

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ir	0.03067 (8)	0.02483 (7)	0.02505 (7)	0.00162 (5)	-0.00140 (5)	-0.00120 (5)
Cl1	0.0382 (5)	0.0310 (4)	0.0391 (5)	-0.0031 (3)	0.0041 (4)	-0.0046 (3)
Cl2	0.0617 (7)	0.0543 (7)	0.0715 (8)	0.0009 (6)	0.0024 (6)	0.0075 (6)
Cl3	0.0902 (10)	0.0703 (8)	0.0801 (9)	0.0238 (7)	0.0413 (8)	0.0198 (7)
N1	0.0324 (15)	0.0328 (15)	0.0302 (15)	0.0031 (12)	0.0002 (12)	-0.0041 (12)
N2	0.0341 (16)	0.0317 (15)	0.0282 (15)	-0.0067 (12)	0.0023 (12)	-0.0031 (12)
N3	0.069 (3)	0.082 (3)	0.051 (2)	0.026 (2)	0.009 (2)	0.001 (2)
N4	0.0394 (18)	0.0343 (16)	0.0312 (16)	0.0076 (13)	-0.0003 (13)	0.0004 (13)
C1	0.040 (2)	0.046 (2)	0.037 (2)	-0.0030 (17)	0.0072 (16)	-0.0057 (17)
C2	0.047 (2)	0.069 (3)	0.040 (2)	-0.006 (2)	0.0113 (19)	-0.013 (2)
C3	0.055 (3)	0.071 (3)	0.048 (3)	-0.004 (2)	0.014 (2)	-0.028 (2)
C4	0.049 (3)	0.051 (3)	0.053 (3)	-0.009 (2)	0.006 (2)	-0.023 (2)
C5	0.0342 (19)	0.0334 (18)	0.0346 (19)	0.0023 (15)	-0.0013 (15)	-0.0049 (15)
C6	0.037 (2)	0.0309 (18)	0.0364 (19)	0.0030 (15)	-0.0028 (15)	-0.0040 (15)
C7	0.054 (3)	0.035 (2)	0.046 (2)	-0.0079 (18)	-0.0035 (19)	-0.0085 (17)
C8	0.046 (2)	0.033 (2)	0.055 (3)	-0.0112 (17)	-0.0027 (19)	0.0000 (18)
C9	0.040 (2)	0.041 (2)	0.048 (2)	-0.0021 (17)	0.0018 (18)	0.0124 (18)
C10	0.042 (2)	0.0344 (19)	0.0358 (19)	0.0013 (16)	-0.0029 (16)	0.0019 (15)
C11	0.0287 (17)	0.0293 (16)	0.0288 (17)	0.0041 (13)	-0.0041 (14)	0.0018 (13)
C12	0.042 (2)	0.039 (2)	0.038 (2)	-0.0018 (17)	0.0094 (17)	-0.0049 (16)
C13	0.055 (3)	0.068 (3)	0.047 (3)	-0.004 (2)	0.015 (2)	-0.020 (2)
C14	0.067 (3)	0.097 (4)	0.032 (2)	-0.012 (3)	0.015 (2)	-0.015 (2)
C15	0.063 (3)	0.075 (3)	0.034 (2)	-0.003 (2)	0.001 (2)	0.004 (2)
C16	0.043 (2)	0.043 (2)	0.0290 (18)	-0.0092 (17)	-0.0036 (16)	0.0029 (15)
C17	0.042 (2)	0.038 (2)	0.039 (2)	-0.0042 (16)	-0.0096 (17)	0.0066 (16)
C18	0.055 (3)	0.056 (3)	0.043 (2)	-0.003 (2)	-0.020 (2)	0.009 (2)
C19	0.052 (3)	0.048 (3)	0.081 (4)	0.009 (2)	-0.022 (3)	0.012 (2)
C20	0.048 (3)	0.044 (2)	0.083 (4)	0.011 (2)	-0.008 (2)	0.001 (2)
C21	0.038 (2)	0.035 (2)	0.058 (3)	0.0044 (17)	-0.0016 (19)	-0.0021 (18)
C22	0.0337 (19)	0.0271 (17)	0.039 (2)	-0.0018 (14)	-0.0048 (15)	0.0026 (14)
C23	0.057 (3)	0.076 (3)	0.054 (3)	0.032 (3)	0.002 (2)	-0.003 (2)
C24	0.040 (2)	0.038 (2)	0.043 (2)	0.0021 (17)	-0.0136 (17)	-0.0048 (17)
C25	0.071 (3)	0.052 (3)	0.036 (2)	0.013 (2)	-0.004 (2)	-0.0002 (19)
C26	0.059 (3)	0.036 (2)	0.0306 (19)	0.0182 (18)	-0.0018 (18)	-0.0001 (15)
C27	0.0279 (18)	0.042 (2)	0.0338 (18)	-0.0001 (15)	-0.0017 (14)	-0.0017 (15)
C28	0.042 (2)	0.044 (2)	0.055 (3)	-0.0040 (18)	-0.0129 (19)	0.0041 (19)
C29	0.051 (3)	0.042 (2)	0.045 (2)	-0.0009 (18)	0.0025 (19)	-0.0013 (17)
C30	0.063 (3)	0.038 (2)	0.071 (3)	-0.001 (2)	-0.002 (2)	0.010 (2)
C31	0.058 (3)	0.057 (3)	0.058 (3)	-0.013 (2)	-0.009 (2)	0.024 (2)
C32	0.053 (3)	0.083 (4)	0.037 (2)	-0.013 (3)	-0.003 (2)	0.010 (2)
C33	0.045 (2)	0.062 (3)	0.038 (2)	-0.001 (2)	0.0027 (18)	-0.0012 (19)
C34	0.035 (2)	0.040 (2)	0.0337 (19)	-0.0045 (16)	-0.0021 (15)	0.0002 (16)
C35	0.059 (3)	0.052 (3)	0.128 (6)	0.002 (2)	0.002 (3)	0.020 (3)

Table 8: Geometric parameters (Å, °) for 4·CH₂Cl₂.

Ir—C11	1.994 (3)	C10—C11	1.391 (5)
Ir—C22	1.997 (3)	C12—C13	1.375 (6)
Ir—N1	2.040 (3)	C13—C14	1.397 (7)
Ir—N2	2.047 (3)	C14—C15	1.350 (7)
Ir—N4	2.222 (3)	C15—C16	1.399 (6)
Ir—Cl1	2.4894 (9)	C16—C17	1.454 (6)
Cl2—C35	1.741 (5)	C17—C22	1.397 (5)
Cl3—C35	1.789 (6)	C17—C18	1.414 (5)
N1—C1	1.341 (5)	C18—C19	1.381 (7)
N1—C5	1.363 (5)	C19—C20	1.374 (7)
N2—C12	1.339 (5)	C20—C21	1.381 (6)
N2—C16	1.364 (5)	C21—C22	1.417 (5)
N3—C27	1.344 (5)	C23—C24	1.370 (6)
N3—C23	1.375 (6)	C24—C25	1.365 (6)
N4—C28	1.459 (5)	C24—C28	1.517 (5)
C1—C2	1.378 (5)	C25—C26	1.351 (5)
C2—C3	1.371 (6)	C26—C27	1.338 (5)
C3—C4	1.358 (6)	C27—C34	1.494 (5)
C4—C5	1.392 (5)	C29—C30	1.385 (6)
C5—C6	1.458 (5)	C29—C34	1.392 (6)
C6—C7	1.400 (5)	C30—C31	1.363 (7)
C6—C11	1.422 (5)	C31—C32	1.368 (7)
C7—C8	1.375 (6)	C32—C33	1.384 (6)
C8—C9	1.383 (6)	C33—C34	1.382 (5)
C9—C10	1.398 (5)		
C11—Ir—C22	91.49 (14)	C10—C11—Ir	128.5 (3)
C11—Ir—N1	80.62 (13)	C6—C11—Ir	114.4 (3)
C22—Ir—N1	93.55 (14)	N2—C12—C13	123.0 (4)
C11—Ir—N2	94.09 (13)	C12—C13—C14	118.0 (4)
C22—Ir—N2	80.27 (14)	C15—C14—C13	119.4 (4)
N1—Ir—N2	171.81 (11)	C14—C15—C16	120.8 (4)
C11—Ir—N4	94.93 (13)	N2—C16—C15	119.6 (4)
C22—Ir—N4	173.52 (13)	N2—C16—C17	114.4 (3)
N1—Ir—N4	86.61 (12)	C15—C16—C17	126.0 (4)
N2—Ir—N4	100.14 (12)	C22—C17—C18	121.3 (4)
C11—Ir—Cl1	175.90 (10)	C22—C17—C16	114.9 (3)
C22—Ir—Cl1	90.98 (10)	C18—C17—C16	123.7 (4)
N1—Ir—Cl1	95.97 (9)	C19—C18—C17	119.4 (4)
N2—Ir—Cl1	89.55 (8)	C20—C19—C18	120.2 (4)
N4—Ir—Cl1	82.56 (9)	C19—C20—C21	121.0 (5)
C1—N1—C5	119.1 (3)	C20—C21—C22	121.0 (4)
C1—N1—Ir	125.0 (3)	C17—C22—C21	117.1 (3)

C5—N1—Ir	115.8 (2)	C17—C22—Ir	115.2 (3)
C12—N2—C16	119.2 (3)	C21—C22—Ir	127.6 (3)
C12—N2—Ir	125.6 (3)	C24—C23—N3	122.7 (4)
C16—N2—Ir	115.2 (3)	C25—C24—C23	115.7 (4)
C27—N3—C23	118.4 (4)	C25—C24—C28	121.4 (4)
C28—N4—Ir	119.0 (2)	C23—C24—C28	122.9 (4)
N1—C1—C2	122.4 (4)	C26—C25—C24	122.2 (4)
C3—C2—C1	119.2 (4)	C27—C26—C25	120.4 (4)
C4—C3—C2	118.7 (4)	C26—C27—N3	120.6 (4)
C3—C4—C5	121.5 (4)	C26—C27—C34	120.7 (3)
N1—C5—C4	119.2 (4)	N3—C27—C34	118.7 (3)
N1—C5—C6	113.8 (3)	N4—C28—C24	114.5 (3)
C4—C5—C6	126.9 (4)	C30—C29—C34	120.5 (4)
C7—C6—C11	121.1 (4)	C31—C30—C29	120.7 (5)
C7—C6—C5	123.9 (3)	C30—C31—C32	119.4 (4)
C11—C6—C5	115.0 (3)	C31—C32—C33	120.5 (5)
C8—C7—C6	120.2 (4)	C34—C33—C32	120.9 (4)
C7—C8—C9	119.7 (4)	C33—C34—C29	117.8 (4)
C8—C9—C10	120.7 (4)	C33—C34—C27	121.4 (4)
C11—C10—C9	121.3 (4)	C29—C34—C27	120.8 (4)
C10—C11—C6	117.1 (3)	Cl2—C35—Cl3	110.3 (3)
C11—Ir—N1—C1	−177.8 (3)	C16—N2—C12—C13	−1.0 (6)
C22—Ir—N1—C1	91.3 (3)	Ir—N2—C12—C13	−178.6 (3)
N2—Ir—N1—C1	132.1 (7)	N2—C12—C13—C14	0.2 (7)
N4—Ir—N1—C1	−82.2 (3)	C12—C13—C14—C15	1.1 (7)
Cl1—Ir—N1—C1	0.0 (3)	C13—C14—C15—C16	−1.6 (8)
C11—Ir—N1—C5	5.4 (2)	C12—N2—C16—C15	0.4 (5)
C22—Ir—N1—C5	−85.5 (3)	Ir—N2—C16—C15	178.3 (3)
N2—Ir—N1—C5	−44.8 (9)	C12—N2—C16—C17	−178.7 (3)
N4—Ir—N1—C5	101.0 (3)	Ir—N2—C16—C17	−0.8 (4)
Cl1—Ir—N1—C5	−176.9 (2)	C14—C15—C16—N2	0.9 (7)
C11—Ir—N2—C12	87.2 (3)	C14—C15—C16—C17	179.9 (4)
C22—Ir—N2—C12	178.0 (3)	N2—C16—C17—C22	1.1 (5)
N1—Ir—N2—C12	136.6 (7)	C15—C16—C17—C22	−178.0 (4)
N4—Ir—N2—C12	−8.6 (3)	N2—C16—C17—C18	−177.0 (4)
Cl1—Ir—N2—C12	−90.9 (3)	C15—C16—C17—C18	3.9 (7)
C11—Ir—N2—C16	−90.5 (3)	C22—C17—C18—C19	0.2 (6)
C22—Ir—N2—C16	0.3 (3)	C16—C17—C18—C19	178.2 (4)
N1—Ir—N2—C16	−41.1 (9)	C17—C18—C19—C20	−0.7 (7)
N4—Ir—N2—C16	173.8 (3)	C18—C19—C20—C21	0.6 (8)
Cl1—Ir—N2—C16	91.4 (2)	C19—C20—C21—C22	0.1 (7)
C11—Ir—N4—C28	20.6 (3)	C18—C17—C22—C21	0.4 (6)
C22—Ir—N4—C28	−151.2 (11)	C16—C17—C22—C21	−177.7 (3)
N1—Ir—N4—C28	−59.6 (3)	C18—C17—C22—Ir	177.3 (3)
N2—Ir—N4—C28	115.7 (3)	C16—C17—C22—Ir	−0.8 (4)
Cl1—Ir—N4—C28	−156.1 (3)	C20—C21—C22—C17	−0.6 (6)

C5—N1—C1—C2	−0.4 (6)	C20—C21—C22—Ir	−177.1 (3)
Ir—N1—C1—C2	−177.1 (3)	C11—Ir—C22—C17	94.2 (3)
N1—C1—C2—C3	−0.1 (7)	N1—Ir—C22—C17	174.9 (3)
C1—C2—C3—C4	0.3 (7)	N2—Ir—C22—C17	0.3 (3)
C2—C3—C4—C5	0.0 (7)	N4—Ir—C22—C17	−93.9 (12)
C1—N1—C5—C4	0.6 (5)	C11—Ir—C22—C17	−89.1 (3)
Ir—N1—C5—C4	177.7 (3)	C11—Ir—C22—C21	−89.3 (3)
C1—N1—C5—C6	178.1 (3)	N1—Ir—C22—C21	−8.6 (3)
Ir—N1—C5—C6	−4.9 (4)	N2—Ir—C22—C21	176.8 (4)
C3—C4—C5—N1	−0.4 (7)	N4—Ir—C22—C21	82.6 (12)
C3—C4—C5—C6	−177.5 (4)	C11—Ir—C22—C21	87.4 (3)
N1—C5—C6—C7	−176.4 (3)	C27—N3—C23—C24	0.8 (8)
C4—C5—C6—C7	0.8 (6)	N3—C23—C24—C25	0.3 (7)
N1—C5—C6—C11	0.9 (5)	N3—C23—C24—C28	−178.5 (4)
C4—C5—C6—C11	178.1 (4)	C23—C24—C25—C26	−0.8 (7)
C11—C6—C7—C8	−1.8 (6)	C28—C24—C25—C26	178.0 (4)
C5—C6—C7—C8	175.4 (4)	C24—C25—C26—C27	0.3 (7)
C6—C7—C8—C9	−0.1 (6)	C25—C26—C27—N3	0.9 (7)
C7—C8—C9—C10	1.2 (6)	C25—C26—C27—C34	−178.3 (4)
C8—C9—C10—C11	−0.4 (6)	C23—N3—C27—C26	−1.4 (7)
C9—C10—C11—C6	−1.4 (5)	C23—N3—C27—C34	177.8 (4)
C9—C10—C11—Ir	−179.6 (3)	Ir—N4—C28—C24	154.1 (3)
C7—C6—C11—C10	2.5 (5)	C25—C24—C28—N4	79.8 (5)
C5—C6—C11—C10	−174.9 (3)	C23—C24—C28—N4	−101.4 (5)
C7—C6—C11—Ir	−179.1 (3)	C34—C29—C30—C31	0.8 (7)
C5—C6—C11—Ir	3.6 (4)	C29—C30—C31—C32	−1.6 (7)
C22—Ir—C11—C10	−93.1 (3)	C30—C31—C32—C33	1.3 (7)
N1—Ir—C11—C10	173.5 (3)	C31—C32—C33—C34	−0.2 (7)
N2—Ir—C11—C10	−12.8 (3)	C32—C33—C34—C29	−0.6 (6)
N4—Ir—C11—C10	87.8 (3)	C32—C33—C34—C27	−179.4 (4)
C11—Ir—C11—C10	139.8 (12)	C30—C29—C34—C33	0.3 (6)
C22—Ir—C11—C6	88.6 (3)	C30—C29—C34—C27	179.0 (4)
N1—Ir—C11—C6	−4.7 (2)	C26—C27—C34—C33	176.1 (4)
N2—Ir—C11—C6	169.0 (3)	N3—C27—C34—C33	−3.1 (6)
N4—Ir—C11—C6	−90.4 (3)	C26—C27—C34—C29	−2.6 (6)
C11—Ir—C11—C6	−38.4 (15)	N3—C27—C34—C29	178.2 (4)