Two-Photon Applications of Transition Metal Polypyridyl Complexes

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<tbody>
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<td>1PA</td>
<td>One Photon Absorption</td>
</tr>
<tr>
<td>2PA</td>
<td>Two Photon Absorption</td>
</tr>
<tr>
<td>B3LYP</td>
<td>Beke-3 term Lee, Yang, Parr exchange</td>
</tr>
<tr>
<td>DCM</td>
<td>Dichloromethane</td>
</tr>
<tr>
<td>DFT</td>
<td>Density Functional Theory</td>
</tr>
<tr>
<td>DMSO</td>
<td>Dimethyl sulfoxide</td>
</tr>
<tr>
<td>DP</td>
<td>Dye Precursor</td>
</tr>
<tr>
<td>ECP</td>
<td>Effective Core Potential</td>
</tr>
<tr>
<td>ESA</td>
<td>Excited-State Absorption</td>
</tr>
<tr>
<td>$f_{\text{os}}$</td>
<td>Oscillator strength</td>
</tr>
<tr>
<td>FRET</td>
<td>Förster Resonance Energy Transfer</td>
</tr>
<tr>
<td>fs</td>
<td>Femtosecond</td>
</tr>
<tr>
<td>GM</td>
<td>Goeppert-Mayer units</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest Occupied Molecular Orbital</td>
</tr>
<tr>
<td>ILCT</td>
<td>Intra Ligand Charge Transfer</td>
</tr>
<tr>
<td>IR</td>
<td>Infra-Red</td>
</tr>
<tr>
<td>LC</td>
<td>Ligand Centred</td>
</tr>
<tr>
<td>LLCT</td>
<td>Ligand to Ligand Charge Transfer</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest Unoccupied Molecular Orbital</td>
</tr>
<tr>
<td>MALDI</td>
<td>Matrix Assisted Laser Desorption/Ionisation</td>
</tr>
<tr>
<td>MC</td>
<td>merocyanine</td>
</tr>
<tr>
<td>MLCT</td>
<td>Metal to Ligand Charge Transfer</td>
</tr>
<tr>
<td>MS</td>
<td>Mass Spectrometry</td>
</tr>
<tr>
<td>NIR</td>
<td>Near Infra-Red</td>
</tr>
<tr>
<td>NLO</td>
<td>Non-Linear Optics</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>ns</td>
<td>Nanosecond</td>
</tr>
<tr>
<td>PCM</td>
<td>Polarised Continuum Model</td>
</tr>
<tr>
<td>PDT</td>
<td>Photodynamic Therapy</td>
</tr>
<tr>
<td>phen</td>
<td>1,10-Phenanthroline</td>
</tr>
<tr>
<td>ppy</td>
<td>2-Phenylpyridine</td>
</tr>
<tr>
<td>pq</td>
<td>Benzo-[H]-quinoline</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>ps</td>
<td>Picosecond</td>
</tr>
<tr>
<td>PS</td>
<td>Photosensitizer</td>
</tr>
<tr>
<td>PSS</td>
<td>Photo Stationary State</td>
</tr>
<tr>
<td>Rh</td>
<td>Rhodamine (dye)</td>
</tr>
<tr>
<td>ROS</td>
<td>Reactive Oxygen Species</td>
</tr>
<tr>
<td>S&lt;sub&gt;0&lt;/sub&gt;</td>
<td>Singlet electronic ground state</td>
</tr>
<tr>
<td>S&lt;sub&gt;1&lt;/sub&gt;</td>
<td>First singlet electronic excited state</td>
</tr>
<tr>
<td>S&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Second singlet electronic excited state</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
</tr>
<tr>
<td>SO</td>
<td>Spiroxazine</td>
</tr>
<tr>
<td>SP</td>
<td>Spiropyran</td>
</tr>
<tr>
<td>T&lt;sub&gt;1&lt;/sub&gt;</td>
<td>First triplet electronic excited state</td>
</tr>
<tr>
<td>TPIP</td>
<td>Two Photon Induced Polymerisation</td>
</tr>
<tr>
<td>SHG</td>
<td>Second Harmonic Generation</td>
</tr>
<tr>
<td>TD-DFT</td>
<td>Time Dependent Density Functional Theory</td>
</tr>
<tr>
<td>TPEF</td>
<td>Two-photon excited fluorescence</td>
</tr>
<tr>
<td>UV</td>
<td>Ultra Violet</td>
</tr>
<tr>
<td>UV-vis</td>
<td>Ultra Violet-visible</td>
</tr>
<tr>
<td>XRD</td>
<td>X-Ray Diffraction</td>
</tr>
<tr>
<td>ε</td>
<td>Extinction coefficient</td>
</tr>
<tr>
<td>ε&lt;sub&gt;r&lt;/sub&gt;</td>
<td>Dielectric constant</td>
</tr>
<tr>
<td>λ&lt;sub&gt;max&lt;/sub&gt;</td>
<td>Maximum absorption wavelength</td>
</tr>
<tr>
<td>λ&lt;sub&gt;em&lt;/sub&gt;</td>
<td>Maximum emission wavelength</td>
</tr>
<tr>
<td>μ</td>
<td>Dipole Moment</td>
</tr>
<tr>
<td>μs</td>
<td>Microsecond</td>
</tr>
<tr>
<td>σ&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Two photon cross section</td>
</tr>
<tr>
<td>τ</td>
<td>Luminescence lifetime</td>
</tr>
<tr>
<td>Φ</td>
<td>Quantum yield</td>
</tr>
<tr>
<td>WORM</td>
<td>Write Once Read Many</td>
</tr>
</tbody>
</table>
Abstract

Materials that undergo two-photon absorption (2PA), the simultaneous absorption of two photons, are finding increasing use in many applications including 3D fluorescence microscopy, 3D data storage, and photodynamic therapy (PDT). For efficient use, a large two-photon cross-section is desired which can arise from centrosymmetric charge transfer in push-pull electron donor-acceptor (D-A) diads. These structural motifs have been applied to the construction of organic-based chromophores yielding materials with remarkably high two-photon absorption cross-sections, yet, few metal based examples have been studied. Hence, this thesis concerns research into enhanced two photon absorption and emission properties of d^6 transition metal complexes bearing suitably structurally modified polypyridyl chromophores using a combination of experimental and theoretical data.

Two polar tolyterpyridyl-stilbene amine ligands, where NR_2 = methyl and phenyl (1a and 1b respectively) have been synthesised and coordinated to a range of d^6 transition metals as D-π-A-π-D motifs (Ru^{II} and Ir^{III}) or D-π-A variations (Re^{I} and Pt^{II}). A single crystal X-ray structure of ligand (1b) was obtained. Spectroscopic analysis indicated successful synthesis of all compounds. One photon luminescence spectroscopy indicated ligand centred emissions for all compounds. Unfortunately, 2PA measurements were unsuccessful for the compounds due to their weak emission and likely small cross-sections too low for the equipment available. Attempts at cis-trans isomerisation of the stilbene bond in the ligands 1a and 1b by UV irradiation were successful, and the isomerisation process was monitored by both UV-visible spectroscopy and ^1H NMR spectroscopy.

Two 5-substituted-1,10-phenanthroline ligands bearing fluorenyl units (7 and 8) were successfully coordinated to Ir^{III} cyclometallated with phenylpyridine (ppy) and benzo-[H]-quinoline (pq). A single crystal X-ray structure was obtained for [Ir(ppy)_2(7)][PF_6] (7a). The complexes demonstrated strong emission originating from a triplet metal to ligand charge transfer (3MLCT) excited states due to their long lived luminescent lifetimes measured up to 2 μs. Quantum yields were measured up to 22 % and their triplet oxygen quenching efficiencies were established by their Stern-Volmer quenching constants, K_{SV} that were determined to be ca. 40 bar^{-1} and 60 bar^{-1} for the ppy complexes of 7 and 8 respectively. Preliminary in vitro experiments performed with C6 Glioma cells treated with [Ir(ppy)_2(7)][PF_6] (7a) show efficient sensitization for triplet oxygen (3O_2) by two-photon excitation at 740 nm resulting in photodynamic effects which led to localised cell damage and death. This complex also demonstrated relatively high two-photon absorption cross-sections ranging from 50-80 Goeppert-Mayer units (GM) between 750 and 800 nm.

Two new Re^{I} complexes have been synthesised utilising the ligands 7 and 8 (7e and 8e). A single crystal X-ray structure was obtained for Re(CO)_3(7)Cl. (7c) These complexes also exhibited relatively long luminescence lifetimes of ca. 300 ns originating from a 3MLCT state, but emission quantum yields were much lower than corresponding Ir^{III} complexes. The Stern-Volmer quenching analysis demonstrated much less efficient quenching by 3O_2 with K_{SV} values of around 8 bar^{-1} for both compounds.

A ligand containing a fluorenyl linker between two 5-substituted-1,10-phenanthroline units (9) has been utilised as a bridge for Ir^{III}-Re^{I} (9a) and Ir^{III}-Ru^{II} (9b) complexes. Emission in these complexes arises from 3MLCT excited states and both exhibit dual component long lived luminescent lifetimes up to 1.3 μs and quantum yields around 22 %. K_{SV} constants were measured at 23 and 41 bar^{-1} for Ir-Re (9a) and Ir-Ru (9b) respectively. Furthermore, the Ir-Ru complex demonstrated a markedly large two-photon cross-section of 350 GM at 730 nm.
Declaration
I declare that no portion of the work referred to in this thesis has been submitted in support of an application for another degree or qualification of this or any other university or other institute of learning with the exception of selected results reported in Chapters 3 and 5 which are also submitted in the thesis of Elizabeth Boreham as some experiments in this work were conducted jointly, the details of which are stated in Chapters 3 and 5.

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1 Chapter 1: Introduction

Materials that undergo two-photon excitation (2PE) are the focus of a vast amount of research in recent years due to their use in many applications. Such applications include 3-D optical imaging, microfabrication, 3-D optical data storage and photodynamic therapy (PDT) amongst others. 2PE is a relatively new field and as such research is lacking into examples of inorganic materials utilised in these applications.

1.1 Luminescence

Luminescence is the emission of ultraviolet, visible or near infrared light from an electronically excited state. There are many difference processes by which luminescence can occur such as chemiluminescence, in which light is emitted as a result of a chemical reaction, and photoluminescence, where absorption of photons leads to re-radiation of photons. The Jablonski diagram (Figure 1) illustrates the processes occurring during the photoluminescence process.

![Jablonski diagram](https://example.com/jablonski-diagram.png)

**Figure 1: Jablonski diagram illustrating the processes occurring during photoluminescence (adapted from reference 4)**

Absorption of a photon (process A) leads to the excitation of a molecule from the ground-state singlet ($S_0$) to an excited vibrational state of the excited-state singlet ($S_2$). The Born-Oppenheimer approximation states nuclei are much larger than electrons and hence an electronic transition takes place much faster than the nuclei can respond. Because of this, transitions are represented as a vertical line. Upon reaching the excited states, the molecule
relaxes vibronically to the lowest excited singlet state ($S_1$). This is the process of internal conversion (IC), a non-radiative decay process. The molecule is now able to relax to the ground-state singlet with the emission of a photon, known as fluorescence (F). This is a spin allowed process and it occurs rapidly. Alternatively, from the excited singlet state ($S_1$) the molecule can convert to a triplet state ($T_2$) by means of intersystem crossing (ISC). Again this is a non-radiative decay process and happens readily in the presence of a heavy metal atom due to spin-orbit coupling effects; this is known as the ‘heavy atom effect’. Vibronic relaxation by internal conversion (IC) occurs, the electron lies in the lowest energy triplet state ($T_1$) and then can relax to the ground-state by means of phosphorescence (P). Unlike fluorescence, phosphorescence is a spin forbidden process (but it can be observed because of vibronic and spin-orbit coupling) as governed by the Pauli Exclusion Principle. For this reason phosphorescence is a much longer process (up to seconds for deactivation of the excited state compared to nanoseconds in fluorescence deactivation processes). Furthermore, the energy of the emission is less than the energy of excitation, and this is due to the non-radiative decay processes (IC and ISC). The difference in this energy is known as the Stokes shift.

Due to the non-radiative decay processes occurring (IC and ISC) and other non-radiative competing processes, some excited molecules will not return to the $S_0$ state through radiative processes. The fraction of excited molecules that fluoresce is known as the quantum yield of fluorescence, $\Phi_f$ which is given by:

$$\Phi_f = \frac{k_f}{k_f + k_{nr}}$$

Where $k_f$ is the rate constant for fluorescence and $k_{nr}$ is the rate constant of radiationless processes. $\Phi_f$ is therefore the fraction of excited molecules that relax to the ground state by means of fluorescence, hence the closer to unity the more intense the emission. Along with quantum yield, the lifetime ($\tau$) is important. $\tau$ is defined as the average time the excited molecule spends in the lowest excited singlet state before emission and is given by:

$$\tau = \frac{1}{k_f + k_{nr}}$$

When studying a chromophore these are important factors to consider. Typically organic compounds exhibit fluorescence lifetimes in the nanosecond domain. In general, applications of fluorescent compounds require a strong emission, therefore highly extended
conjugated π-systems and transition metal complexes have been actively researched for their luminescence properties.

### 1.1.1 Transition Metal Luminescence

Luminescence from transition metal based systems, particularly those of the platinum group metals can result in marked electronic spectral shifts from the spectra of their free ligands.\(^5\)\(^,\)\(^8\) Excitation of a molecule from the metal to the ligand (d-π\(^*\)) can now occur. This is known as metal to ligand charge transfer (MLCT). Figure 2 illustrates this process.

![Figure 2: Simplified Jablonski diagram for a MLCT process (adapted from reference 4)](image)

The complex is excited to the singlet MLCT state, and this complex can convert to a triplet \(^3\)MLCT state by intersystem crossing and then decays back to the ground-state by phosphorescence. As previously discussed phosphorescence is a spin forbidden process and therefore results in long emission lifetimes. Widely studied transition metal complexes involve diimine ligands with ruthenium (Ru\(^{II}\)), rhenium (Re\(^{I}\)) or osmium (Os\(^{II}\)) and iridium (Ir\(^{III}\)) which are all d\(^6\) systems.\(^9\) This is because d\(^6\) ions give rise to intense spin allowed MLCT transitions. Additionally, ligand to metal charge transfer (LMCT) and d-d transitions can occur. However, many transition metal systems with luminescent aromatic ligands do not fluoresce or phosphoresce. In the majority of non-transition metal the MLCT process cannot happen, however the positive polarization at the ligand coordination site induces spectral shifts of the ligand centred emission.\(^8\)
1.2 Two-Photon Absorption

Multi-photon absorption, the simultaneous absorption of two or more photons, was first proposed by Maria Goeppert-Mayer in 1931.\textsuperscript{10} It was not until 1961, following the invention of the laser, that the theory was verified experimentally. Frankel \textit{et al.} found that ruby laser light, of wavelength $\lambda_{em} = 694$ nm, propagating through a quartz crystal will produce light at the second harmonic frequency with a wavelength of $\lambda/2$.\textsuperscript{11} Kaiser and Garrett followed this with the first publication on two-photon absorption (2PA) and the resulting fluorescence of a europium-doped crystal.\textsuperscript{12}

The emission spectra following 2PA should look the same as those of one-photon absorption (1PA) because only one photon is emitted in de-excitation as the same excited state is populated as in 1PA. The result of this is that two photons, of half the energy of 1PA, are absorbed simultaneously \textit{via} a virtual state, and one photon of a higher energy is emitted (Figure 3).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{jablonski_dia.png}
\caption{Simplified Jablonski diagram for 2PA (adapted from reference 4)}
\end{figure}

\textit{Figure 3: Simplified Jablonski diagram for 2PA (adapted from reference 4)}

Figure 3 shows the higher energy photon (1PA) is showed to be half of the energy of the two lower energy photons, however this is not strictly true. In 2PA different vibrational states can be populated due to differences in parity. Furthermore it is important to note that the virtual state is not real, and the two photons are absorbed in the same quantum event.

2PA is a 3\textsuperscript{rd} order non-linear optical process (NLO), meaning a material can possess often interesting (and unusual) optical properties that are modified under an intense photon flux. The result of this is that the absorption depends non-linearly upon the strength of the incident light, unlike 1PA where there is a linear dependency.\textsuperscript{13} So, in 2PA there is a quadratic dependence upon intensity and so can be denoted as non-linear. Therefore it can
be said that if the power (intensity) of the source is increased two-fold, the resulting emission sees a four-fold increase (intensity is proportional to the power squared).\textsuperscript{14}

This relationship can be plotted as a graph of the natural logarithm of the integrated emission intensity vs. the natural logarithm of the power of the laser source, and for 2PA the gradient of the graph will be two. Furthermore, this can be extended into three photon absorption (3PA) where intensity will be proportional to the power cubed, and the gradient of the graph will be three.

The higher order dependency on the incident intensity of light is a great advantage of 2PA in comparison to 1PA. As stated previously, 1PA is linearly dependent on the light intensity, this results in absorption in the focal plane in solution, hence absorbance is constant across the cuvette. In 2PA, the dependence of absorption on the square of the intensity of the light source means that the observed absorbance is no longer constant over the cuvette and the focal volume is small where the laser flux is most intense, as shown in Figure 4. This small excitation focal volume theoretically allows for 3-D control over the absorbance (i.e. excitation, not just in the $xy$ plane, but also along the $z$ direction) leading to the numerous applications of two-photon techniques.\textsuperscript{15}

\textbf{Figure 4:} Comparison of one- and two-photon absorption using femtosecond (fs) lasers, image taken from the now non-existent website of Kevin Belfield, University of Central Florida

In 1PA, the molar absorption coefficient ($\varepsilon$) is measured, as per the Beer Lambert Law, which is measured in M$^{-1}$ cm$^{-1}$ (or sometimes dm$^3$ mol$^{-1}$ cm$^{-1}$ or cm$^2$ mol$^{-1}$). This can be understood as the probability of an electronic transition occurring and in spectral terms, the
area over which a single molecule absorbs light. When applied to 2PA processes, the equivalent absorption coefficient becomes the two-photon cross-section ($\sigma_2$). $\sigma_2$ is the probability of 2PA process occurring, which reflects the efficiency by which a compound can undergo a two-photon process. The units of $\sigma_2$ are given in Goeppert-Mayer units (GM), where $1\ \text{GM} = 10^{-50}\ \text{cm}^4\ \text{s photon}^{-1}$. There are many different experimental methods by which two-photon cross-sections can be measured and these will be discussed in Section 1.3.1.

1.3 Examples of 2PA Cross-sections

The theory of 2PA shows the requirements for a molecule to exhibit an effectual cross-section to be long $\pi$-conjugated chains with co-planarity. This is due to the resultant high values of dipole moments of the ground, final, and intermediate states that occur during absorption.\textsuperscript{16} For this same reason, the Donor-Acceptor-Donor (D-A-D) motif is favourable. Experimental data also confirm the same requirements and thus enables synthetic design for effective 2PA cross-sections. There are numerous research efforts into improving the 2PA cross-sections of organic molecules, however when it comes to inorganic compounds the research is comparatively lacking. It is also important to note that although a high 2PA cross-section is favourable for many of the applications of two-photon processes, molecules with conformational rigidity and strong $\pi$ conjugation tend to have small $S_0$-$S_1$ energy gaps and rapid internal conversion processes, leading to reduced emission quantum yields.

1.3.1 Measurement of 2PA Cross-Sections

There are two widely used methods of measuring $\sigma_2$, the $z$-scan method and two-photon excited fluorescence (TPEF). In the $z$-scan method the sample is moved along the path of a focused laser beam, and a detector measures the light as a function of its position along the $z$-axis as shown in Figure 5.\textsuperscript{17} The $z$-scan detector can either be “closed-aperture” or “open-aperture” in setup. In a “closed-aperture” setup the detector has a narrow aperture, resulting in the output being sensitive to intensity-dependent changes in the refractive index, which in turn leads to self-focusing or defocusing of the beam. In the “open-aperture” setup, the detector collects all the light from the sample, and the output only reflects the intensity-dependent transmission, which can be used to measure 2PA cross-
sections. However, in the open-aperture z-scan experiments, light can be lost due to self-defocusing or non-linear scattering, resulting in extra contributions to non-linear absorption. Furthermore, excited-state absorption (ESA) can occur due to a build-up of excited-state populations. These phenomena can contribute to the apparent 2PA cross-sections measured.\textsuperscript{18}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{z-scan_setup.png}
\caption{z-scan experimental set up (adapted from reference 15)}
\end{figure}

In TPEF the emission intensity following two-photon absorption provides direct information on 2PA efficiency. This method uses a reference compound with a known 2PA spectrum, most commonly rhodamine B or coumarin, to which the one- and two-photon excited fluorescence excitation spectra is compared under identical conditions.\textsuperscript{19} The calculation of $\sigma_2$ is given by:

$$\frac{\sigma_2^S \phi^S}{\sigma_2^R \phi^R} = \frac{\eta^R n^S C^S F^S P^R}{\eta^S n^R C^R F^R P^S}$$

Where $\phi$ is the quantum yield of fluorescence, $\eta$ accounts for the wavelength-dependent collection efficiency of the fluorescence, $n$ is the refractive index of the solvent, $C$ is the concentration, $F$ is the integrated fluorescence signal from the recorded spectrum, $P$ is the excitation power and $S$ and $R$ refer to sample and reference. Recent optimisation of the TPEF method by Rebane \textit{et al.} has led to reported accurate reference 2PA spectra for a wide range of commercially available dyes making TPEF an attractive method.\textsuperscript{20}

It is important to note that experimentally, the 2PA cross-sections from z-scan measurements often appear larger when compared to the TPEF values.\textsuperscript{21} Furthermore, there are several other techniques available for measurement of 2PA cross-sections which are less effective or less widely used, such as degenerate four-wave mixing (DFWM),\textsuperscript{22} and the white-light continuum method (fs-WLC).\textsuperscript{23}
1.3.2 Examples of Organic Compound Cross-sections

Organic chromophores have been extensively studied for their two-photon cross-sections, and numerous design strategies have been implemented and reviewed. Marder et al. compared a trans-stilbene (1) and its derivatives with varying para-substituent donor groups (2,3). Figure 6 shows the cross-section values for each of the molecules, and it is evident that variation of the R group drastically alters the cross-section values. These prominent data lead to the design of 2PA chromophores with either terminal donor, or acceptor moieties linked by a π-conjugated bridge, due to the centrosymmetric charge transfer transitions that can occur within them.

![Figure 6: Two-photon cross-section values for D-π-D molecules](image)

Commonly used donor groups include dialkyl and diaryl amino donor groups, but others have been studied. For example compound 4 (Figure 6) has an oxygen donor terminal group, and its two photon cross-section of 110 GM is over ten times less that its nitrogen counterpart 5. The A-π-A motif has also been studied, however data show that the D-π-D motifs are generally more effective. This is illustrated by compounds 6 and 7 (Figure 7), where the terminal donating group -NHex₂ (Hex = hexyl) possesses a two photon cross section of nearly ten times the value when the terminal group is an electron acceptor (-SO₂CF₃).

![Figure 7: Comparison of 2PA cross-sections of D-π-D and A-π-A motifs](image)

Further to terminal donors, changing the central bridge of a compound has been studied in order to tune 2PA properties. The D-π-A-π-D structures, with electron-deficient cores lead to increased cross-sections. Compounds 8 and 9 (Figure 8) indicate the addition of electron
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deficient moiety to the central core of the molecule can increase the cross-section.\textsuperscript{26} Compound \textbf{10} possesses a huge cross-section of 27000 GM, this squaraine dye has a highly efficient electron accepting core. However, these molecules tend not to be stable in normal aerobic environments.\textsuperscript{27}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure8.png}
\caption{Examples of two-photon cross-sections of molecules containing electron deficient cores.\textsuperscript{26,27}}
\end{figure}

Research also indicates the extension of the $\pi$-conjugation is a useful way of increasing the 2PA efficiency. Extension of the $\pi$-conjugation can lead to difficulties in comparison of the resulting cross-section values and therefore the normalised cross-section, ratio of cross-section and number of $\pi$-electrons ($\sigma_2/N_e$), should be considered.\textsuperscript{16} For example compound \textbf{10} (Figure 8) has a normalised cross-section of 750 GM per $\pi$ electron. Furthermore, the nature of the $\pi$-bridge needs to be considered. Rebane \textit{et al.} showed that a vinylene-linked porphyrin (\textbf{11}) has a lower cross-section than the ethynylene-linked porphyrin (\textbf{12}) illustrated in Figure 9.\textsuperscript{28}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure9.png}
\caption{Comparison of the type of $\pi$-linker on 2PA cross-sections\textsuperscript{28}}
\end{figure}

Another example of a class of molecules that exhibit large two photon absorption cross-sections are illustrated by porphyrin-like systems. These large, $\pi$-conjugated macrocycles possess high transition dipole moments. Compound \textbf{13} (Figure 10) possesses a very high $\sigma_2$ of 2300 GM.\textsuperscript{4} Compounds \textbf{14} and \textbf{15} (Figure 10) further illustrate how large cross-sections can be achieved with expanded porphyrin systems.\textsuperscript{29} Furthermore, the four fold
decrease in overall cross-section from compound 14 to compound 15 is due to an overall two electron reduction within the macrocyclic π system (Figure 10).

Figure 10: Examples of two-photon cross-section of porphyrin based chromophores

Further design features of efficient 2PA chromophores are trigonal branched octupolar systems. This is illustrated well by compounds 16-18 (Figure 11), which have an electron-deficient triazine core and a differing number of electron-rich side arms. Upon increasing the number of branches, an increase in the cross-section and the normalised cross-section is observed.
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Figure 11: Illustration of varying two-photon cross-section with increasing the branches of an electron deficient triazine core

The above examples show a variety of synthetic approaches for increasing $\sigma_2$, which are based upon increasing the $\pi$-conjugation. The donor acceptor pair and the conjugation bridge is demonstrated to be very important. Furthermore, theoretical calculations on a variety of octupolar molecules have been performed and supported the experimental observations. 

1.3.3 Examples of Two-Photon Cross-Sections of Inorganic Chromophores

Research into the area of inorganic 2PA cross-sections is lacking in examples of effective cross-sections, with the exception of porphyrin based systems. Compound 19 (Figure 12) exhibits a large cross-section of 8200 GM, whereas 20 (Figure 12) possesses a much lower cross-section (60 GM). This again shows the importance of chromophore design, where changing the vinylene bridge to an ethynyl bridge results in disruption of communication between the two porphyrin rings. Compound 21 (Figure 12), developed by Osuka et al. is an azulene-fused system which demonstrates efficient two photon absorption with a large two-photon cross-section of 7200 GM (at 1380 nm excitation). The \textit{trans}-porphyrin-
perinaphthothioindigo dye 22 (Figure 12) also displays a high cross-section of 2000 GM at 850 nm excitation.\textsuperscript{34}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figures.png}
\caption{Examples of two-photon cross-sections of inorganic complexes with porphyrin ligands\textsuperscript{33,34}}
\end{figure}

Feuvrie et al. studied a series of octupolar tris(bipyridyl)metal complexes for their two-photon properties.\textsuperscript{35} Their studied system, Figure 13, indicates the important role of the metallic core of a molecule for its participation in the non-linear optical activity, and it also indicates the importance of sigma donor conjugated substituents and intra-ligand charge transfer (ILCT) and MLCT transitions to enhance the two-photon absorption properties of such chromophores. The highest cross-section is shown by the Ru\textsuperscript{II} derivative followed closely by the Fe\textsuperscript{II} counterpart, both of which are d\textsuperscript{6} metals which are known to be effective in NLO processes.\textsuperscript{36}
In a more recent publication, Natraj et al. studied several Ir$^{III}$ and Ru$^{II}$ complexes with polar terpyridyl stilbene chromophores that result in chromophores containing a D-$\pi$-A-$\pi$-D system (Figure 14).\textsuperscript{37}

Each of the complexes was studied for their one and two-photon photophysical properties. As shown in Table 1, the Ir$^{III}$ complexes exhibit long luminescent lifetimes in the microsecond domain which are assumed to be a result of excited state mixing between ligand centred (LC), MLCT, and $\pi$-$\pi^*$ ILCT in character. In comparison, the Ru$^{II}$ counterparts have much shorter lifetimes. This difference has been attributed to a lack of metal based emission character in the Ru$^{II}$ complexes. It is also possible to see that the $\sigma_2$ values of the iridium complexes measured by TPEF are approximately six times as large as the ruthenium analogues. Furthermore, these values of $\sigma_2$ are much larger than any other
heteroleptic polypyridyl transition metal complexes. These results show promise in the development of multi-photon active materials.

Table 1: RuII and IrIII bis terpyridyl stilbene D-π-A-π-D complexes with associated lifetimes quantum yields and cross sections.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\tau_{\text{MeCN}}$ (ns)</th>
<th>$\tau_{\text{MeOH}}$ (ns)</th>
<th>$\phi_{\text{MeCN}}$</th>
<th>$\sigma_2$ (GM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ir(tpy stilbene)$_2$3PF$_6$</td>
<td>1346</td>
<td>1428</td>
<td>0.0059</td>
<td>67</td>
</tr>
<tr>
<td>Ir(ttpyene anisole)$_2$3PF$_6$</td>
<td>1536</td>
<td>1513</td>
<td>0.0026</td>
<td>58</td>
</tr>
<tr>
<td>Ru(tpy stilbene)$_2$2PF$_6$</td>
<td>5</td>
<td>5</td>
<td>0.0059</td>
<td>12</td>
</tr>
<tr>
<td>Ru(ttpyene anisole)$_2$2PF$_6$</td>
<td>5</td>
<td>5</td>
<td>0.0029</td>
<td>11</td>
</tr>
</tbody>
</table>

Lifetimes quoted at 405 nm excitation, subject to ±10 % error. Quantum yields determined relative to quinine sulphate in 1M $\text{H}_2\text{SO}_4$ at 350 nm excitation, estimated error ±20 %. Two photon cross section, $\sigma_2$, at 740 nm, $GM = 10^{-50}$ cm$^4$ s photon$^{-1}$; estimated error ±30 %. More recently several more examples have been published, Sun et al. have studied several platinum complexes with terpyridyl ligands. The ligands have a nitrogen donor, fluorenyl linker, and then are varied by a different spacer group (Figure 15). Both the ligands and their corresponding PtII complexes were studied for their one and two photon properties. Notably, the ligands possess much longer emissive lifetimes and larger fluorescence quantum yields than their corresponding platinum complexes.
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Figure 15: Ligands and corresponding platinum complexes studied for their two photon cross-sections reported by Sun et al.\textsuperscript{41}

The measured $\sigma_2$ values of the ligands were carried out by TPEF, and $\mathbf{25}$ shows the highest 2PA cross-section of 448 GM, which from the previously discussed molecules, is expected. The Pt$^{\text{II}}$ complexes were studied for their two-photon absorption cross-sections. However using TPEF, data could not be obtained (presumably because the emission response was too weak to be detected); and so the cross-sections were measured using the open-aperture $z$-scan method. Complex $\mathbf{26}$ (Figure 15) showed the highest value of $\sigma_2$ at 2000 GM, $\mathbf{24}$ exhibited a $\sigma_2$ of 850 GM, and a value could not be recorded for $\mathbf{28}$. However as previously discussed, there are several shortcomings with the $z$-scan method and the values obtained from it may not be representative of the true 2PA cross section.
Table 2: Two-photon cross-sections and optical properties of the diphenyl amino fluorenyl terpyridyl ligands and their respective PtII complexes reported by Sun et al.\textsuperscript{41}

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\tau_{\text{DCM}}$ (ns)</th>
<th>$\tau_{\text{MeCN}}$ (ns)</th>
<th>$\Phi_{\text{DCM}}$</th>
<th>$\sigma^2$ GM</th>
</tr>
</thead>
<tbody>
<tr>
<td>23</td>
<td>12 (26 %), 102 (74 %)</td>
<td>not measured</td>
<td>0.59</td>
<td>142\textsuperscript{a}</td>
</tr>
<tr>
<td>25</td>
<td>12 (23 %), 91 (76 %)</td>
<td>not measured</td>
<td>0.70</td>
<td>448\textsuperscript{a}</td>
</tr>
<tr>
<td>27</td>
<td>33 (41 %), 112 (59 %)</td>
<td>not measured</td>
<td>0.42</td>
<td>204\textsuperscript{a}</td>
</tr>
<tr>
<td>24</td>
<td>not measured</td>
<td>0.048 (29 %), 2.241 (71 %)</td>
<td>0.00047</td>
<td>850±50\textsuperscript{b}</td>
</tr>
<tr>
<td>26</td>
<td>not measured</td>
<td>0.086 (2 %), 3.683 (98 %)</td>
<td>0.00035</td>
<td>2000±200\textsuperscript{b}</td>
</tr>
<tr>
<td>28</td>
<td>not measured</td>
<td>0.150 (8 %), 2.976 (92 %)</td>
<td>0.00019</td>
<td>Unobserved</td>
</tr>
</tbody>
</table>

Lifetimes quoted at 375 nm excitation, subject to ±10 % error. Quantum yields determined relative to [Ru(bpy)$_3$]Cl$_2$ at 350 nm (ligands) and 436 nm (complexes) excitation. Two photon cross section, $\sigma_2$, GM = 10$^{-50}$ cm$^4$ s photon$^{-1}$; estimated error ±30 % for TPEF. \textsuperscript{a} Determined by TPEF, \textsuperscript{b} determined by open aperture z-scan.

Beeby \textit{et al.} studied various cyclometallated iridium complexes for their two photon properties (Figure 16).\textsuperscript{42} All of the compounds studied were shown to have a quadratic dependence on the intensity (gradient of Log(P) vs Log (I) ~ 2). The $\sigma_2$ values range from 9.5 to 44 GM, which are of a similar magnitude to those measured for the Ir(terpy-stilbene)$_2$ derivatives reported by Natrajan \textit{et al.} although they are slightly lower. The difference can be attributed to limited $\pi$ conjugation in the cyclometallated complexes compared to the terpyridine derivatives and a change in the nature of the excited states involved in the emission (predominantly MLCT vs. ILCT respectively). Interestingly, this is in spite of the fact the cyclometallated derivatives exhibit much larger emissive quantum yields.
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Figure 16: Iridium cyclometallated complexes and their corresponding two-photon cross-sections reported by Beeby et al.\textsuperscript{42}

Goswami \textit{et al.} were able to synthesise inorganic auxochromatic compounds with extremely large $\sigma_2$ values using Pt\textsuperscript{II} and Au\textsuperscript{I} (Figure 17).\textsuperscript{43} The complexes contain a 2,1,3-benzothiadiazole core with thienylene and ethynylene linkers to Pt\textsuperscript{II} or Au\textsuperscript{I} centres. The reported TPEF $\sigma_2$ values of the gold complexes 34 and 35 were approaching 150 GM at 775 nm, whereas measured $\sigma_2$ values for the Pt\textsuperscript{II} complexes 36 and 37 were significantly higher with values of near 1000 GM at 760 nm. This large increase in $\sigma_2$ values is attributed to a larger change in dipole moment upon excitation in the Pt\textsuperscript{II} complexes when compared to Au\textsuperscript{I} complexes. Additionally, DFT calculations provided evidence for a larger Pt\textsuperscript{II} metal orbital contribution in the HOMO than in the Au\textsuperscript{I} derivatives, this metal orbital contribution leads to higher polarizability in the platinum complexes.

Figure 17: Inorganic auxochromes studied by Goswami \textit{et al.}\textsuperscript{43}
Although the number of compounds being researched is increasing there is still a need for inorganic compounds with cross-sections comparable to the organic compounds discussed previously since they possess many attractive features including long emission lifetimes, resistance to photobleaching (which is a major problem in both commercial and novel organic dyes) and quenching by triplet oxygen.

1.4 Applications of 2PA

1.4.1 Imaging – Tracers, Sensors and Probes

There are numerous advantages of utilising two-photon processes in optical imaging. Firstly, use of a near infra-red laser source (usually a fs pulsed Ti:Sapphire laser), can achieve high penetration of near infrared light into biological tissues where there is little absorption by the tissue and water themselves.\textsuperscript{8,44} Further advantages of using near infrared light is little or no background fluorescence is seen. Since endogenous biomolecules including flavoproteins and NAD(P)H have very low 2PA cross sections in the order of $10^{-2}$ GM in the nIR window,\textsuperscript{45} less tissue damage occurs, and the sample will scatter light significantly less (scattering is proportional to the fourth power of wavelength).\textsuperscript{6,14,46} Furthermore only molecules in the focal point of the laser pulse will be receiving sufficient intensity to undergo 2PA. The improved signal-to-noise ratio enables a much higher sensitivity in results.\textsuperscript{47}

The cyclometallated Pt\textsuperscript{II} complex (38) exhibits a strong two photon-induced emission with a relatively high cross-section ($\sigma_2 = 20.8$ GM) for an inorganic molecule. It also exhibits good live cell internalisation properties and fast bioaccumulation, with a low cytotoxicity. These factors and its ability to exhibit two-photon luminescence makes it a useful bioimaging probe (Figure 18).\textsuperscript{48} It is interesting to note however, that similar cyclometallated bis pyridyl Pt\textsuperscript{II} complexes that possess a $\sigma_2$ value of ca. 4 GM are more than sufficiently emissive under two photon excitation for cell microscopy purposes by taking advantage of the long phosphorescent lifetimes of Pt\textsuperscript{II} polypyridyl complexes using two photon time resolved emission imaging microscopy (TREM).\textsuperscript{49}
Chong et al. have developed a two-photon Cd$^{2+}$ probe, 39 (Figure 19).$^{50}$ In vitro and in vivo studies have been carried out. The probe is shown to be Cd$^{2+}$ selective, and displays a large red shift upon binding and an eightfold emission increase; there is also a large increase in $\sigma_2$ upon binding to Cd$^{2+}$. The 2PEF imaging shows cell permeability and localisation of the bound complex within HeLa cells (Figure 19). Furthermore cytotoxicity was low with nearly 90% of cells still viable after treatment with 10 μM of 39 and after a long incubation time (24 hours).

Recently, Xu synthesised a Ru$^{II}$ terpyridine complexes containing glycol-nanoparticles (Ru-GNPs) which were able to demonstrate efficient 2PA in the near infrared (NIR).$^{51}$ The measured $\sigma_2$ values of 0.2-22.4 GM at excitation wavelengths of 720-880 nm were deemed sufficient for TPEF imaging. The Ru-GNPs were shown to localise in both the cytoplasm
and nucleus of KB cells (derived from carcinoma of nasopharynx) (Figure 20) and have a low cytotoxicity which shows promise of this construct for applications in TPEF imaging and labelling.

![Figure 20: KB cell images using Ru-GNPs for a) two-photon excited fluorescence, b) bright-field and c) two-photon excited fluorescence and bright-field overlay images, taken from reference 51.](image)

### 1.4.2 Photoactivation and Drug Delivery

Rapid and concentrated release of biologically active agents in the body by deprotection of bioactive molecules can be initiated by two-photon techniques. Such molecules include neurotransmitters, proteins or ions.\(^{16}\) In general, the chromophores used have very small 2PA \(\sigma_2\) values which is due to the adaptation of these dyes from traditional 1PA dyes, and as such they have not yet been fully optimised for non-linear excitation. Glutamine is an example of a widely used neurotransmitter that has been utilised for this technique. A glutamine derivative, 4-methoxy-7-nitroindolino glutamate has led to significant advances in understanding neuron signalling, despite its very small 2PA \(\sigma_2\) value of 0.06 GM.\(^{52}\) Photolabile masked glutamates have been explored based on coumarin, for example compound 40, as shown in Scheme 1.\(^{53}\)

![Scheme 1: Uncaging of glutamic acid, \(\sigma_2 = 50\) GM at 740 nm.](image)

The two photon initiated release of calcium ions is also a vital process for analysing signal synapses. The calcium ions can be selectively released using 2PA whilst avoiding
excitation of surrounding biomolecules. Again, the compound utilised for this purpose (41) has small 2PA cross section (0.6 GM) but still shows great promise as a caged calcium releasing agent, as shown in Scheme 2.\(^{54}\)

![Scheme 2: Uncaging of calcium ions, \(\sigma_2 = 0.6\) GM at 720 nm\(^{54}\)](image)

Branda \textit{et al.}, developed a system containing a dialkoxybenzoin photocage and a diarylethene photo-switch designed undergoes sequential photoreactions (Scheme 3), first the release of acetic acid by photoactivated bond breaking in the dialkoxybenzoins and then ring closure in the diarylethene for an photoisomerically pure chromophore.\(^{55}\) The successful release and visual reporting of this system using the same wavelength of light demonstrates a good architecture for future research into their use in biological environments with more biomedically relevant species.

![Scheme 3: UV light liberates caged acetic acid and generates a photoresponsive diarylethene molecular switch. UV light then converts the colourless isomer into its coloured form to visually report on the uncaging event.\(^{55}\)](image)

1.4.3 Optical Power Limiting

Materials that exhibit intensity-dependent absorption can be said to possess optical limiting properties which are highly useful for protection against high intensity lasers. These optical limiting materials respond on an ultrafast timescale on exposure to growing intensity of light.\(^{56}\) Optical power limiting is usually a result of excited-state absorption (ESA) in which absorption of light produces an excited state with the ability to absorb more strongly
than the ground state, as shown by the Jablonski diagram in Figure 21. ESA demonstrated by singlet states is short-lived however ESA of excited triplet states leads to much longer lived effects.\textsuperscript{57,58}

![Simplified Jablonski diagram demonstrating optical power limiting by 1PA (red arrow) and 2PA (blue arrows) processes. ESA (cyan arrows) is shown for both singlet and triplet energy levels.](image)

The use of 2PA in optical power limiting is advantageous due to high transmission at low laser intensities, instant response times and saturation effects being limited.\textsuperscript{44} Furthermore the use of transition metal complexes, such as Ru\textsuperscript{II}, have shown great promise in this area due to their long-lived MLCT excited states.\textsuperscript{59,60} Humphrey \textit{et al.} synthesised a family of tri-Ru\textsuperscript{II} organometallic carbonyl chalcogenide clusters with power limiting abilities measured using a z-scan technique. Examples of gallium and indium porphyrin based complexes have been recently published by Miao \textit{et al.}\textsuperscript{61} These demonstrated that a heavy central metal enhances spin-orbit coupling and results in better optical power limiting behaviour.

1.4.4 Microfabrication and Lithography

Two photon lithography (microfabrication and more recently nanofabrication) is a rapidly expanding field and is increasingly being used to fabricate 3-D microscopic structures with sub-micrometre resolution.\textsuperscript{2} Photoinititated polymerization or depolymerisation reactions lead to a contrast in solubility, which is the basis of many lithographic processes. Utilising two-photon processes for microfabrication leads to photochemistry inside the focal
volume, unlike one-photon microfabrication which is outside the focal volume leading to loss of lithographic contrast and definition. Figure 22 shows the result of microfabrication, in which a polymerisation reaction has been controlled using two-photon techniques to create a propeller shape.

![SEM image of a polymeric object obtained by microfabrication, image taken from reference 62](image)

**Figure 22:** SEM image of a polymeric object obtained by microfabrication, image taken from reference 62

More recently efforts have been made to improve the quality of the two photon induced polymerisation (TPIP) with great success. Li *et al.* worked towards improving the 2PA cross-section of the photo initiators and the photoreactivity. With a cross-section of 440 GM at 800 nm 42, has been used to create complex 3D structures which demonstrate the advantages of TPIP such as high spatial resolution and definition (Figure 23).

![Complex 3D images created using TPIP with 42 as the photo-initiator, images taken from reference 63](image)

**Figure 23:** Complex 3D images created using TPIP with 42 as the photo-initiator, images taken from reference 63
1.4.5 3-D Optical Data Storage

Presently optical data storage devices, such as DVDs and Blu-ray, use one photon processes to read and write information on a two dimensional surface. The highly localised 2PA excitation volume and high discrimination against the surrounding background allows for data to be stored in a 3-D medium. This 3-D storage ability leads to a huge increase in the data density. At present a proto-type exists which has the ability to hold 1 TB of data, which is a gargantuan increase from that of a conventional DVD (4.7 GB) or Blu-ray (20 GB). The design of the prototype is compact, with a 120 mm diameter and 1.2 mm thickness, and 200 layers of information within the volume of the disk (Figure 24). However, it was found that the write speed of this proto-type was 3 MB s\(^{-1}\) and so it would take 4 days to fill. When comparing to that of a domestic DVD-R, this is approximately 20 times slower.

![Schematic of prototype disc, with SEM images of the multiple layers](image)

The above example utilises an irreversible photochemical reaction upon writing, and hence is a write once read many (WORM) disc. The layers contain a dye precursor (DP), which is colourless and stable in neutral media, but in the presence of acid it converts to rhodamine 700 (Rh-700) dye which is coloured and strongly fluorescent. In order to write a light sensitive photoacid generator is incorporated into the layers so that upon irradiation it can react with the DP to generate the Rh-700 thus forming ‘spots’ at the laser focal point and hence data bits.

A more recent example of a WORM system with 10 layers, utilises gold nano-particles. In this system data are stored as a fluorescent pattern by a two-photon induced reduction of
Au$^{III}$ nano particles and subsequent interaction between rhodamine B (Rh-B) and Au$^{3+}$ to form reduced Au$^0$. The disc is read by field enhanced surface plasmon resonance occurring on reduced Au nanoparticles with good signal to noise ratio. The device has been shown to record binary data without significant cross talk from adjacent layers. Furthermore, after 0.12 million readouts 80 % of the signal intensity remained, and after 1 year at room temperature there was no decrease in signal intensity.

For this process, an effective 2PA cross-section is desired from a molecule with photo-isomerisation properties, required for binary data storage. For example compound 22, discussed previously, generates a stable cis isomer at room temperature, and the porphyrin ring results in a large cross-section that allows rapid switching between isomers on ideal time scales for working memory.\textsuperscript{16} The two forms of the dye together make up the ‘1’ and ‘0’ binary numbers needed for data storage, but the issue with the system is that at present it is write once, read many (WORM). Hence, the discs are not re-writable. For efficient re-writable discs materials need to be developed where the two forms have clear differences in their fluorescence spectra.

Hu et al. have recently demonstrated the use of two-photon-induced reversible birefringence for erasable and re-writable polarization storage.\textsuperscript{68} The diazobenze chromophore used (Figure 25) shows promise in the application of high density data storage due to its evident polarization dependence and good re-writability. However, the research was only studied in one layer, and hence multi-layered experiments are needed to attempt to increase the storage density.

![Figure 25 - Diazobenzene/MMA copolymer, 43, used for re-writable polarization storage\textsuperscript{68}](image)

Re-writable data storage has also been studied using coumarin based copolymers, 44 (Figure 26).\textsuperscript{69} The copolymers are doped onto glass slides and written using two-photon
irradiation and then this is read using second harmonic generation (SHG) efficiency mapping. The two-photon irradiation forms $44'$, and this is a reversible process and so further irradiation using 250 nm UV light, is able to erase. This process and the process of re-writing was demonstrated (Figure 26).

Figure 26: Molecule 44 used for 3-D data storage using SHG and SHG read out images at 800 nm, a) after line written at 700 nm, b) after irradiation using 250 nm light and c) SHG image after new line written perpendicular to the first line, images taken from reference 69.

Mariz et al. developed a two-photon absorbing polymer with alternating acceptor and donor cores to use with a known photochromic switch of the diarylethene family inducing switching via Förster resonance energy transfer (FRET). The polymer demonstrated a large 2PA cross-section of 6930 GM at 740 nm. The desired multilayer data storage was demonstrated using 1s exposure times and 1 mW laser power at 740 nm as shown in Figure 27. Although this was successful the FRET efficiency was lower than anticipated and it
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was concluded that incorporating the photochromic unit into the polymer would be more effective.

![3D image of data recorded in 3 layers by 2PE at 740 nm irradiation and read out at the same wavelength. Layers are separated by 15 μm. Image taken from reference 70.](image)

**Figure 27:** 3D image of data recorded in 3 layers by 2PE at 740 nm irradiation and read out at the same wavelength. Layers are separated by 15 μm. Image taken from reference 70.

### 1.4.6 Photodynamic Therapy (PDT)

Cancers of the skin and in hollow organs are often treated using one-photon photodynamic therapy (PDT). This technique employs a photosensitiser which is unable to cause harm in the absence of light, but induces damage upon optical irradiation. This phototoxicity is produced by the singlet oxygen generated by transfer of energy from a triplet excited electronic state of a sensitiser to the triplet ground state molecular oxygen.\(^\text{16}\) Due to the ability to confine the excitation of the photosensitiser to the focal volume and the use of longer-wavelength light required, two-photon PDT (especially using transition metal complexes) is of particular interest in cancer therapy, neurology and ophthalmology.\(^\text{71}\)

Watcher *et al.* successfully utilised 2PA-PDT with a psoralen-based drug to kill *Salmonella typhimurium* bacteria.\(^\text{72}\) Furthermore porphyrin derivatives have been clinically approved, and demonstrate two-photon-excited destruction of eukaryote cells and blood capillaries in chicken embryos.\(^\text{73,74}\)

Collins *et al.* have successfully demonstrated the use of a phototoxic porphyrin dimer, 45, which demonstrated a high one photon PDT potency, rapid uptake by cells and high cross-section and was therefore studied for its potential in two photon PDT.\(^\text{75}\) Collins *et al.* were able to occlude blood vessels in a mouse using this molecule and continual irradiation at 920 nm light after only 12 mins of continual irradiation (Figure 28).
The porphyrin-based photosensitizers discussed, although successful, are not without disadvantages such as poor water solubility, slow clearance from the body and weak photostability.\textsuperscript{76} This has led to recent developments utilising Ru\textsuperscript{II} polypyridyl complexes due to these types of complexes demonstrating attractive properties for 2PE-PDT therapies.\textsuperscript{77,78} Such properties include high water solubility, high $\sigma_2$ values, efficient production on singlet oxygen ($^{1}\text{O}_2$) and good photostability.\textsuperscript{79} Chao et al.\textsuperscript{77} and Lui et al.\textsuperscript{78} both demonstrated the successful treatment of HeLa cells with polypyridyl Ru\textsuperscript{II} molecules as 2PE-PDT photosensitisers; water soluble positively charged [Ru\textsuperscript{II}-tris(bipyridyl-bisamine)]\textsuperscript{3+} and [Ru\textsuperscript{II}-(bis-phenanthroline-bis-phenyl)(lophine)]\textsuperscript{3+} complexes respectively.

1.5 Photo-isomerisation

Compounds able to undergo a reversible transformation between two distinct forms induced by absorption of electromagnetic radiation are of particular interest for their numerous applications, such as 3-D data storage. At present there is a large number of research accounts detailing photo-isomerisation induced by 1PA, however the field of 2PA is lacking in examples. There are numerous different photochromic groups that have been studied which are suitable candidates for 2PA; several of these are outlined below.
1.5.1 Stilbene Isomerisation

Stilbene is a well known molecule that can interconvert between \textit{trans} and \textit{cis} isomers photochemically. The \textit{cis} form can also undergo a 6π electrrocyclisation, forming a closed ring system, which disrupts the aromaticity.\textsuperscript{80} This is also a reversible reaction, however further oxidation can occur forming a phenanthrene, which limits the repeated switchability of this molecule required for a read many system (Scheme 4).

![Scheme 4: Isomerisation of stilbene](image)

The mechanism of switching is thought to proceed via a perpendicular conformation, where the stilbene has twisted to 90°, however there is a large activation barrier preventing this twist and so excitation to a singlet excited state is needed.\textsuperscript{81} In the singlet excited state for the \textit{trans} conformer there is a smaller barrier to torsional motion and the excited perpendicular state is the potential energy minimum. Furthermore the \textit{cis} excited state has little or no barrier to torsional motion. By internal conversion the excited perpendicular state can relax to the ground state and either re-form the \textit{trans} isomer, or isomerise to the \textit{cis} isomer, for which there is an equal probability. In the case of substituents that are able to promote intersystem crossing, a triplet pathway can occur (Figure 29).\textsuperscript{82}
Mac et al. studied compound 46 for its photo-isomerisation.\textsuperscript{83} The trans isomer was irradiated at 365 nm, and this showed significant decrease in the first absorption band and a simultaneous increase of the absorption at 39000 cm\textsuperscript{-1}, showing the formation of the cis isomer. Further irradiation at 313 nm led to the recovery of the trans isomer. The efficiency of switching is given by a quantum yield of trans-cis isomerisation which is 35\% in acetonitrile. The time-scales for irradiation were not given.

Figure 30: Molecule 46 studied for isomerisation, results of which are shown in UV-vis spectra. The irradiation wavelengths are given on each spectra. Images taken from reference 83.
Yam et al. have studied the 1PA isomerisation properties of rhenium(I) diimine complexes with stilbene type ligands.\textsuperscript{84} Compound 47 (Figure 31) was one of the first studied complexes, which was irradiated at 366 nm for 4 h to reach the photostationary state, at which point there were no more changes in the UV-vis spectra. This compound was also studied by luminescence spectroscopy, which showed a large increase in intensity for the MLCT emission and a 35 fold increase in the luminescence quantum yield.

![Figure 31: Example of photoswitchable rhenium complex\textsuperscript{84}](image)

The majority of the research into the isomerisation of stilbenes occurs from trans to cis, following irradiation, however synthesis of the thermodynamically less stable cis isomer is also possible. Nishirara et al. synthesised a Fe\textsuperscript{II} complex of a cis-stilbene molecule 48 (Scheme 5), and irradiated the complex in acetone with 436 nm light corresponding to the MLCT absorption band.\textsuperscript{85} It was shown that over time the intensity of the MLCT band increased and it was confirmed that the trans isomer had no photoreaction with 436 nm light. Interestingly, this compound was able to undergo isomerisation by photoirradiation in the solid state.

![Scheme 5: cis-trans isomerisation of 48.\textsuperscript{85}](image)
1.5.2 Diarylethenes

Diarylethenes, diarylperfluorocyclopentenes, are an extension of a stilbene system. They isomerise from an open form (cis stilbene) to a closed form via a \(6\pi\) electrocyclisation like stilbene (Figure 29). In general the open form is colourless and the closed form is coloured, these isomers are shown in Figure 32. One of the most attractive properties of diarylethenes is that the isomerisation process in the majority of derivatives is thermally irreversible and are fatigue-resistant.\(^8\)  

![Figure 32: General photoisomerisation of diarylethenes](image)

A diarylethene based molecular switch containing fluorenyl units was studied for its photochromic properties with 2PA by Luchita et al.\(^8\) The photochromic transformation demonstrated a quantum yield of close to 100 % when studied by 2PA, with measured \(\sigma_2\) values of 450-600 GM for \(49b\) and 50-70 GM for \(49a\) attributed to the extension of the \(\pi\)-conjugation upon cyclisation, Figure 33. Furthermore this structure was shown to have potential for optical data storage after preliminary two-photon data recording and readout experiments.
Figure 33: Structure of open form diarylethene 49a and its closed form 49b. The graph shows the 2PA spectra of 49 (1), 49a (2) and the one-photon absorption spectra of 49 (3) and 49a (4). The inset shows the scaled 2PA spectra of 49. Image taken from reference 87.

1.5.3 Azo Dyes

One group of compounds that has been extensively researched using 1PA techniques is that of azobenzene dyes. The photochemistry predominantly involves the reversible photo-isomerisation of a thermally stable trans structure to a cis form. The back reaction occurs both photochemically and thermally. Unlike the stilbene mechanism, where isomerisation occurs solely by twisting, azobenzene can isomerise via several different mechanisms. This is known since the sum of the quantum yields (trans-cis and cis-trans) does not equal 1. There are 4 proposed mechanisms for the switching of azobenzene. Rotation, where the N=N π-bond breaks allowing free rotation about the bond. Inversion, which proceeds via an sp hybridization of the azo-nitrogen atom. Concerted inversion, via a linear transition state with no net dipole moment, and inversion-assisted rotation. These processes are all shown in Figure 34. From all of the mechanisms, relaxation to the ground state geometry can occur to either the cis or trans isomer, and hence all mechanisms give photostationary states.
Azobenzene (AB) isomerisation occurs with irradiation of the $\pi-\pi^*$ transition (320 nm) with a photostationary state (PSS) containing 20 % trans-AB, or the $n-\pi^*$ (450 nm) but the latter is much weaker and gives a PSS containing 90 % trans-AB.\textsuperscript{93} Substitution can drastically change the absorption and therefore the isomerisation properties of ABs. For example, dimethyl yellow exhibits *trans-cis* isomerisation by irradiation with UV and blue light, as shown in Scheme 6.

The above photo-isomerisation has been studied using 1-D $^1$H NMR spectroscopy by Tait \textit{et al.} They were able to show that the forward reaction occurs with irradiation at 457 nm, and using the $^1$H NMR of both the \textit{cis} and \textit{trans} isomers the photostationary state (PSS) was determined. At the PSS the system has reached equilibrium, and in this example the percentage of \textit{cis} isomer present in the PSS at 457 nm was 66 %.\textsuperscript{94}
Magennis et al. also studied an azo dye (Scheme 7), however, they were able to study both the one- and two-photon isomerisation properties. The one- and two-photon isomerisation properties were studied at 475 nm and 740 nm excitation respectively, and the forward reaction was followed by $^1$H NMR spectroscopy. Results indicate that upon irradiation by both methods the isomerisation occurred and that the two-photon process was similar to that of the one-photon process. For the one-photon process the PSS contained 58 % of the cis form and the two-photon process contained 54 % of the cis form at the PSS. In order to confirm that at 720 nm photo-isomerisation occurred by two-photons, mode locked and continuous wave studies were used. Furthermore they were able to show a non-linear quadratic dependence on the intensity of the absorption.

\[ \text{Scheme 7: Isomerisation studied by Magennis et al. } R = \text{Me, and } R' \text{ corresponds to a typical reactive group for attachment of the dye to textile fabrics}. \]

### 1.5.4 Spiropyrans

Another well studied class of compound for its photo-isomerisation properties is that of spiropyrans, Scheme 8. Upon irradiation the C-O bond of the colourless spiropyran (SP) breaks and the subsequent isomerisation leads to the coloured open photomerocyanine (MC). The MC can isomerise back to the initial SP form both thermally or photochemically. This has further been extended to the derivative spiroxazine (SO). Importantly, this photochemical reaction can occur in quantitative yield.

\[ \text{Scheme 8: Photo-isomerisation of spiro compounds. } X = \text{CH spiropyran, } X = N \text{ spiroxazine} \]
Buback et al. recently studied the photo-isomerisation of a di-nitro substituted spiropyran. They reported that the quantum yields of ring-closing and ring-opening are tuneable, but either ring closure can be achieved with high quantum yield at the cost of the quantum efficiency of ring opening, and *vice versa*. Figure 35, shows the absorption spectra of both the ring closed SP and ring-opened MC. The ring-closed SP can be opened with light from the UV region, and MC can be closed with light from either the UV or visible spectral region.

![Absorption spectra of both SP and MC](image)

*Figure 35: Absorption spectra of both SP and MC, image taken from reference 98*

Zhu et al. have studied SP for both its one and two-photon isomerisation properties. One-photon excitation of SP was carried out using < 420 nm light in order to convert this to the MC form. The two-photon isomerisation was carried out using 700-840 nm light. They concluded that in the two-photon process, isomerisation from SP to MC occurred and then further excitation of the MC lead to emission of red fluorescence. However, in the one-photon process the SP form was isomerised to the MC form but returned back to the SP form, switching off the red fluorescence (Figure 36). Furthermore, they have been able to apply this two-photon induced isomerisation in advanced bioimaging.
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Figure 36: Photo-isomerisation of SP and fluorescence excitation of MC by one- and two-photon processes, image taken from reference 99

1.6 Aims of the PhD

The investigative aim of the project is to find suitable inorganic complexes for potential applications using 2PA. Namely, these applications will be 3-D data storage and PDT. For 3-D data storage to be effective a molecule with a large two-photon cross-section and an efficient photo-isomerisation profile is needed, whereas PDT requires a high efficiency production of cytotoxic singlet oxygen.

The ligand systems investigated herein, are focused on polypyridyl ligands, more specifically tridentate terpyridine systems and bidentate phenanthroline systems. As discussed, achieving an effective two photon cross-section requires a D-π-A-π-D system, that is planar with a long conjugated chain. For data storage, the design of these ligands will have an electron donating group such as –NR₂ (R = Me, Ph etc.), then photo-isomerisation moiety (stilbene), and a polypyridyl group for co-ordination to the desired metal centres which act as an acceptor. The metal centres chosen for this research are a range of d⁶ transition metals, these include Ru^{II}, Ir^{III} for D-π-A-π-D and Re¹ and d⁸ Pt^{II} for D-π-A diads. As discussed, d⁶ metals are targeted since they lend themselves well to non-linear optics, and have been shown to exhibit long lived phosphorescence from ³MLCT states.
Chapter 2: Investigating Metal Terpyridyls Containing a Stilbene Moiety For Potential use in 3-D Data Storage Devices

2.1 Introduction

3-D optical data storage using two-photon processes has become a growing field due to the desire for greater capacity storage and to reduce power consumption. There is a vast range of examples utilising two-photon irradiation to write information. A recent prototype developed by Fuji film has demonstrated the ability to record large amounts of data on a twenty layer medium. The prototype utilises a photochromic material for two-photon recording, and the data is read using one-photon fluorescence signals.

For effective 3-D optical data storage, molecules with large 2PA cross-sections are required along with photo-isomerisation properties. Stilbene is well known for its photochemical interconversion between trans and cis isomers. Photoisomerisation of stilbene derivatives are widely studied for one-photon isomerisation properties, yet two-photon isomerisation of stilbene derivatives is lacking. Moreover, there is a distinct lack of inorganic examples of stilbene derivatives able to undergo photo-isomerisation by two-photon processes.

2.2 Results and Discussion

2.2.1 Synthesis and Characterisation

2.2.1.1 Ligands

The push-pull D-π-A ligands chosen for this study are based on a terpyridine-stilbene motif that are functionalised in the para position of the terminal aryl group. Here, R = NMe$_2$ and NPh$_2$, compounds 1a and 1b respectively, which have previously been reported for their non-linear properties. However, their use as ligands with Re, Ru, Ir and Pt complexation and their two photon properties have not yet been reported. There are many different synthetic routes to the formation of C=C double bonds, such as the Wittig, Julia, Peterson and palladium cross coupling reactions such as the Heck reaction. The route chosen followed a synthesis by Natrajan et al. forming the C=C double bond via a Wittig reaction.
In order to synthesize the target terpyridyl based ligands a series of starting materials were synthesised. There are numerous synthetic routes to syntheses terpyridines, most utilising a Kröhnke type synthesis. Hanan et al. successfully synthesised a range of aryl substituted terpyridine molecules in good yields using very mild conditions. The reaction proceeds via an aldol condensation and Michael addition to form the 1,5 diketone intermediate, which is soluble under these reaction conditions and so the central pyridine ring can form with an aqueous ammonia source. Two equivalents of 2-acetylpyridine, were mixed with one equivalent of the desired aldehyde, with two equivalents of KOH and 2.5 equivalents of NH₄OH.

\[ \text{Scheme 9: General synthetic route to terpyridine stilbene derivatives employing the Wittig reaction} \]

\[ \text{Scheme 10: Synthetic route to ligands 1a and 1b} \]
The synthesis of 4’-(p-tolyl)-2,2’:6,2”-terpyridine (ttpy) required stirring at room temperature for 24 h, at which time the precipitate was filtered to give a pale yellow powder, which contained some dark green crystals. Recrystallisation from hot EtOH, yielded pale yellow needles in high purity and moderate yield (19 %). 1H NMR spectroscopic analysis shows the desired product (Figure 37). This was further confirmed by ES+ MS and elemental analysis.

![Figure 37: 1H NMR spectrum of the expanded aromatic region of ttpy (CDCl3, 298 K, 400 MHz)](image)

The formation of 4’-(4-(bromomethyl)phenyl)-2,2’:6,2”-terpyridine was undertaken by N-Bromosuccinimide (NBS) radical bromination under mercury lamp irradiation. An equimolar amount of ttpy and NBS, and a catalytic amount of dibenzoylperoxide was heated to reflux temperature in CCl4 for 4 hours. The resulting reaction mixture was filtered to remove the succinimide residue and the filtrate was evaporated to dryness under reduced pressure. The crude oil was triturated in MeOH giving the desired product in high yield (70 %). 1H NMR spectroscopic analysis (Figure 38) showed a downfield shift of the methyl group of ttpy from 2.44 ppm to 4.58 ppm. The formation of the desired product was further indicated by ES+ MS showing the {M+H}+ peak at 403 amu.
Figure 38: $^1\text{H}$ NMR spectrum of the expanded aromatic region of 4’-(4-(bromomethyl)phenyl)-2,2’:6’,2”-terpyridine and an inset of the methylene peak (CDCl$_3$, 298 K, 400 MHz)

The synthesis of (4-([2,2’:6’,2”-terpyridin]-4’-yl)benzyl)triphenylphosphonium bromide was then undertaken by heating equimolar amounts of 4’-(4-(bromomethyl)phenyl)-2,2’:6’,2”-terpyridine with PPh$_3$ in toluene to reflux temperature for 7 h. Upon cooling in ice, a precipitate formed which was filtered and washed with toluene. $^1\text{H}$ NMR spectroscopic (Figure 39) analysis showed the desired appearance of the PPh$_3$ resonances with correct integration, the methylene hydrogen peak has also shifted to 5.30 ppm. Mass spectrometry (MALDI and ES) was inconclusive in the indication of formation of the desired product, however, elemental analysis is consistent with the $^1\text{H}$ NMR data.
Upon successful synthesis of (4-((2,2′:6′,2″-terpyridin)-4′-yl)benzyl)triphenylphosphonium bromide, the Wittig reaction was carried out with 4-dimethylaminobenzaldehyde and 4-(dimethylphenyl)benzaldehyde. The phosphonium ylid was formed by deprotonation of the terpy-benzyl triphenylphosphonim bromide with potassium tert-butoxide (t-BuOK) at 0 °C in THF to give a bright orange solution. The desired benzaldehyde was added and the solution was left to stir for 48 h until the solution was no longer orange, indicating that the ylid had been consumed. Both ligands 1a and 1b were isolated as yellow powders in analytically pure form following evaporation of all volatiles, and trituration in methanol.

Figure 39: $^1$H NMR spectrum of the expanded aromatic region of (4-((2,2′:6′,2″-terpyridin)-4′-yl)benzyl)triphenylphosphonium bromide (DMSO-d$_6$, 298 K, 400 MHz)

The $^1$H NMR spectrum of ligands 1a (Figure 40) and 1b show the appearance of roofed doublets at 7.1 and 6.9 ppm with large coupling constants (16.4 Hz) which are indicative...
of the formation of a \textit{trans} C-C double bond. The MS and elemental analyses were further conclusive that the desired products had been synthesised.

A single crystal X-ray structure was obtained for the NPh$_2$ ligand (1b). A representation of the molecular structure is shown in Figure 41 and selected geometric parameters are shown in Table 3. For crystallographic data and refinement details see Appendix A.

Table 3: Selected Interatomic Distances and Angles for the ligand 1b

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond Length / Å</th>
<th>Bond</th>
<th>Angle / deg</th>
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<td>117.4(2)</td>
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<tr>
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<td>C11-N3-C15</td>
<td>116.9(2)</td>
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<td>117.6(2)</td>
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Figure 41: Representation of the molecular structure of 1b (50 % ellipsoids)

The molecular structure of 1b shows near coplanarity of the terpyridyl unit, with a dihedral angle of 1.5(1)$^\circ$. The aryl ring bonded to the terpyridine (C$_{16}$-C$_{21}$) however, is twisted out of the plane of the terpyridyl unit with a dihedral angle of 31.7(1)$^\circ$ around C$_8$ and C$_{16}$. A slightly larger twist is seen between the N-phenyl substituent and aryl rings with respect to
Chapter 2: Investigating Metal Terpyridyls Containing a Stilbene Moiety

the stilbene plane where the dihedrals are measured to be 32.5(1)° and 51.0(1)° which is likely a result of steric hindrance from the phenyl rings.

2.2.1.2 Platinum Complex Synthesis and Characterisation

Platinum complexes were synthesised by heating one equivalent of the corresponding ligands in acetonitrile with two equivalents of Pt(DMSO)$_2$Cl$_2$ to reflux temperature for 48 h (Scheme 11). Over the course of the reactions the solutions turned from yellow to intensely deep purple (2a) and dark red (2b). Upon cooling the reaction mixtures a precipitate formed which was isolated by filtration. The precipitates were washed and to remove any impurities and the compounds were dissolved in warm DMSO and filtered. The complex in the filtrate was reprecipitated by addition of diethyl ether. The reaction yields were 74 % for 2a and 78 % for 2b. The products exhibited intense colour in comparison to the yellow ligands which can be attributed to a large charge transfer from the NR$_2$-donor of the ligand to the Pt-acceptor.

![Scheme 11: Synthesis of Pt$^{II}$ complexes 2a and 2b](image)

The $^1$H NMR spectrum of 2b recorded in DMSO-d$_6$ is shown in Figure 42, exhibited the expected peaks. The roofed doublets resonating at 7.15 and 7.38 ppm exhibited coupling constants of 16.14 and 16.26 Hz respectively corresponding to the trans stilbene bond. The same features were exhibited in 2a, with the trans stilbene bond at slightly lower chemical shifts (7.06 and 7.36 ppm). It is important to note that the $^1$H NMR data of the complex could not be compared directly to the corresponding ligand $^1$H NMR spectra due to differences in solubility. Both complexes showed the correct M-Cl$^-$ molecular ion peaks in their ES$^+$ mass spectra. The elemental analysis is further consistent with the formulation of the compounds.
2.2.1.3 Rhenium Complex Synthesis and Characterisation

The required rhenium starting material, rheniumpentacarbonyl chloride, was synthesised from the dimer dirhenium decacarbonyl, Re₂(CO)₁₀, and sulfuryl chloride. The complexes were synthesised by heating equimolar amounts of the ligands 1a and 1b and Re(CO)₅Cl to reflux temperature in toluene for 14 hours (Scheme 12). Upon cooling of the mixture the product precipitated and was filtered. The products were synthesised in very high yields of 92 % and 89 % for 3a and 3b respectively.

The ¹H NMR spectrum of 3b is shown in Figure 43. Both 3a and 3b show much more complicated spectra than the uncomplexed ligands due to the change in magnetic equivalency in the ligand because only two of the pyridyl groups are coordinated to the...
metal centre. Both spectra appear to be quite broad and some peaks are not well resolved, likely due to the incomplete solubility of the complex in the NMR solvent. It is still possible to observe the trans stilbene roofed doublets at 7.24 and 7.43 ppm in 3b, and at 7.09 and 7.37 ppm in 3a. The coupling constants are indicative of trans stilbene at around 16 Hz in each complex.

![NMR spectrum of 3b](image)

*Figure 43: $^1$H NMR spectrum of 3b (DMSO, 298 K, 400 MHz)*

The complex has a distinct lack of symmetry ($C_1$), hence three carbonyl stretches are expected in its infrared spectrum. Figure 44 shows the recorded infrared spectrum, with the asterisked peaks identifying the carbonyl stretches of 3b. The values of $\nu$(CO) for each rhenium complexes is shown in Table 4, and these are typical for $\nu$(CO) of metal-carbonyl complexes.\textsuperscript{104}
Table 4: ν(CO) frequencies for compounds 3a and 3b

<table>
<thead>
<tr>
<th>Compound</th>
<th>ν(CO) / cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>2017</td>
</tr>
<tr>
<td></td>
<td>1910</td>
</tr>
<tr>
<td></td>
<td>1878</td>
</tr>
<tr>
<td>3b</td>
<td>2019</td>
</tr>
<tr>
<td></td>
<td>1920</td>
</tr>
<tr>
<td></td>
<td>1821</td>
</tr>
</tbody>
</table>

Figure 44: Infrared spectrum of 3b run as a solid sample. The asterisked peaks correspond to the carbonyl stretching frequencies

2.2.1.4 Ruthenium Complex Synthesis and Characterisation

The chemistry used for the synthesis of the ruthenium complexes 4a and 4b is shown in Scheme 13. Firstly one equivalent of the chosen ligand is coordinated to ruthenium, forming an insoluble ruthenium-terpyridine trichloride complex. The next step is to abstract the chlorides using silver triflate, which replaces the chlorides with the more labile triflate anion. This can now accept another terpyridyl ligand, by heating to reflux temperature in EtOH for 3 days. During this time the ruthenium is reduced from Ru³⁺ to Ru²⁺. Finally the
counter ions are replaced with hexafluorophosphate. After repeated recrystallisations the products were isolated in low-moderate yields of 52 and 46 % for 4a and 4b respectively.

Scheme 13: Synthetic route to ruthenium complexes 4a and 4b
Characterisation of 4a and 4b by $^1$H NMR spectroscopy (Figure 45) was carried out in acetone-$d_3$. Both gave well resolved spectra with only one of the trans stilbene protons showing in 4b due to overlapping signals. Again, direct comparison to the ligands cannot be made due to differences in solubility. Mass spectral and elemental analysis also showed that the correct products had been synthesised.
2.2.1.5 Iridium complexes

The iridium(III) complexes of ligands 1a and 1b were synthesised by heating two equivalents of the ligand with IrCl$_3$·xH$_2$O in ethylene glycol at 100 °C for 3 hours at which point the temperature was further raised to 195 °C for a further 2 hours, as shown in Scheme 14. Upon cooling and addition of aqueous NH$_4$PF$_6$ for 3 hours, the temperature was then raised to 195 °C for a further 2 hours. Upon cooling and addition of aqueous NH$_4$PF$_6$, the crude products were isolated. The complexes were recrystallised multiple times from acetone/diethyl ether.

Scheme 14 Synthesis of Ir$^{III}$ complexes 5a and 5b

The complexes 5a and 5b were studied by $^1$H NMR spectroscopy in $d_3$-acetone. The resulting spectra showed the desired peaks, however they were not very well resolved.
Further recrystallisations did not have any effect on repeated \(^1\)H NMR spectra. Elemental analysis was also carried out, which indicated the compounds were not analytically pure.

### 2.2.2 Single Photon Absorption and Luminescence Analysis

Each of the ligands and the corresponding compounds have been studied by optical spectroscopy. Absorption, emission and excitation spectra were recorded along with lifetimes and quantum yields in MeCN, are given in Table 5. All emission spectra and quantum yields were measured from the highest wavelength excitation maxima, and the excitation spectra were measured from the emission maxima. The lifetimes were measured with 375 nm excitation.

**Table 5: Data from photophysical measurements of compounds 1-5.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Abs / ( \lambda_{\text{max}} (\varepsilon / \text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}) )</th>
<th>( \lambda_{\text{em}} / \text{nm} )</th>
<th>( \lambda_{\text{ex}} / \text{nm} )</th>
<th>( \tau / \text{ns} )</th>
<th>( \phi / % )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>232 (17100), 305 (19300), 400 (17100)</td>
<td>595</td>
<td>280, 370</td>
<td>2</td>
<td>19</td>
</tr>
<tr>
<td>1b</td>
<td>298 (16100), 380 (15100)</td>
<td>568</td>
<td>300, 380</td>
<td>5</td>
<td>51</td>
</tr>
<tr>
<td>2a</td>
<td>281 (13100), 331 (17500), 456 (11300)</td>
<td>481</td>
<td>368</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>2b</td>
<td>444 (14800), 337 (21900), 301 (17900), 285 (18000)</td>
<td>487</td>
<td>369</td>
<td>4</td>
<td>6</td>
</tr>
<tr>
<td>3a</td>
<td>424 (12700), 314 (13100)</td>
<td>554</td>
<td>288, 375</td>
<td>2</td>
<td>&lt;1</td>
</tr>
<tr>
<td>3b</td>
<td>418 (14200), 304 (17900)</td>
<td>564</td>
<td>292, 378</td>
<td>2</td>
<td>&lt;1</td>
</tr>
<tr>
<td>4a</td>
<td>281 (87700), 310 (87700), 495 (46000)</td>
<td>600</td>
<td>250, 275, 380 (4600)</td>
<td>5</td>
<td>&lt;1</td>
</tr>
<tr>
<td>4b</td>
<td>310 (90000), 501 (61000)</td>
<td>561</td>
<td>228, 298, 383</td>
<td>8</td>
<td>&lt;1</td>
</tr>
<tr>
<td>5a</td>
<td>254 (57700), 282 (57100), 320 (44900) (sh), 375 (27500) (sh), 515 (11371) (sh)</td>
<td>505</td>
<td>350</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5b</td>
<td>289 (110000), 375 (89024), 476 (48394)</td>
<td>497</td>
<td>341</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

*All measurements were carried out in deoxygenated MeCN. Emission spectra were measured at the excitation maxima. Excitation spectra were taken at the emission maxima. Lifetimes measured using a ps pulsed 375 nm diode laser, subject to ±10% error. Quantum yields determined using an integrating sphere, estimated error ±3%.*

The absorption maxima and corresponding extinction coefficients are given in Table 5 and UV-visible spectra are given in Figure 46. The ligands 1a and 1b exhibit strong absorptions at 400 and 380 nm attributed to \( \pi-\pi^* \) LC and ILCT transitions respectively.\(^{36}\) The absorption spectra of the complexes all demonstrate spin allowed ligand centred (LC) \( \pi-\pi^* \) transition in the UV region (below 350 nm). The complexes exhibit low energy
transitions typical of a intraligand charge transfer (ILCT) transitions. Furthermore the Ru$^{II}$ complexes also exhibit low energy $^1$MLCT absorption bands (~ 500 nm).

![UV-Vis spectra](image)

**Figure 46:** UV-Vis spectra of ligands and corresponding complexes, a) ligands 1a (red) and 1b (black), b) complex 2a (red) and 2b (black), c) complex 3a (red) and 3b (black), d) complex 4a (red) and 4b (black) and e) complex 5a (red) and 5b (black)

The uncomplexed ligand spectra of 1a and 1b are shown in Figure 47. The features of both the excitation and emission spectra are similar for both ligands, with 1a exhibiting a slight red shift from 1b in its emission spectrum and a slight blue shift from 1b in the excitation spectrum. The lifetimes of both uncomplexed ligands are relatively short, with lifetimes in the nanosecond domain typical of ligand fluorescence (2 and 5 ns for 1a and 1b).
respectively). The fluorescence quantum yields of the uncomplexed ligands are large at 19 and 51 % for 1a and 1b respectively. The longer lifetime and higher quantum yield in 1b can most likely be attributed to the presence of the phenyl groups, further stabilisation of the charge transfer excited state and fewer competitive non-radiative decay pathways. The obtained data are comparable to those of terpyridine ligands in the literature.\textsuperscript{105}

Figure 47: Emission and excitation plots of a) 1a excitation (red) and emission (black) and b) 1b excitation (red) and emission (black)
The Pt$^{II}$ complex emission and excitation spectra that are shown in Figure 48, exhibit very similar features. An emission at 500 nm from excitation at \(~370\) nm is produced for both complexes. The radiative lifetimes of the complexes are very short at 3 and 4 ns for 2a and 2b respectively, indicating the emission originates from an \(3^{{ILCT}}\) state and there is not contribution from a \(3^{{MLCT}}\) state in this complex. The quantum yields of 2 and 6 % are relatively low but consistent with ligands 1a and 1b reported previously. The quantum yields for 2b is slightly larger than that of 2a, which is also in line with reduced competitive excited state quenching mechanisms as a result of the phenyl groups.$^{105}$ Notably, these measured quantum yields are relatively high in comparison to those measured for similar compounds with measured quantum yields ranging from 0.019 to 1 %.$^{106,41}$
The Re\textsuperscript{I} complexes 3\textit{a} and 3\textit{b} exhibit very weak emission as expected with the chloride ligand being well known for photoinduced electron transfer processes quenching the luminescence.\textsuperscript{107} The emission and excitation spectra of both complexes, shown in Figure 49, are similar to those of the free ligands. The lifetimes of both are again very short at 2 ns. Furthermore the quantum yields were measured as less than 1 % indicating that the
ligand centred processes are dominant over any MLCT emission in these complexes and thus the emission can be attributed to $^1$LC process.

Figure 49: Emission and excitation plots of a) $3\text{a}$ excitation (red) and emission (black) and b) $3\text{b}$ excitation (red) and emission (black)

Emission spectra of the Ru$^{\text{II}}$ complexes $4\text{a}$ and $4\text{b}$, shown in Figure 50, show similar emission to that of the ligands and is thus likely to be mainly a ligand centred transition.\textsuperscript{37} The excitation spectra interestingly show an additional high energy peak in both spectra.
when compared to the uncomplexed ligands and show no contribution from the MLCT absorption at lower energy ca. 500 nm. The lifetimes are again short at 5 and 8 ns for the 4a and 4b respectively, again with the diphenylamino analogue being slightly longer. The quantum yields are extremely low at less than 1 % for both compounds. In comparison to those measured by Natrajan et al. the lifetimes and quantum yields are very similar for the stilbene and anisole analogues. This would suggest that moving from no donor (stilbene) to oxygen donor (anisole) and finally nitrogen donor does not have an effect on the lifetime or quantum yield but rather the additional conjugation of the dimethylamino donor does. The short lifetimes and low quantum yields can be attributed to the ligand centred emission, since the $^3$MLCT, is known to be efficiently quenched in solution. This $^3$MLCT is quenched due to an equilibration with low lying high-spin d-d metal centred (MC) states due to a small energy gap between them.
Figure 50: Emission and excitation plots of a) 4a complex excitation (red) and emission (black and b) 4b complex excitation (red) and emission (black)

Emission spectra of the Ir$^{III}$ complexes 5a and 5b, shown in Figure 50, both show a broad featureless emission around 500 nm. Attempted measurement of lifetimes yielded no results, this is remarkably different to the analogous complexes studied by Natrajan et al. which demonstrated long lived lifetimes in the microsecond domain. Quantum yields were
also not obtained due to extremely weak emission. This is likely due to the fact that the complexes were analytically impure as shown by the elemental analysis.

Figure 51: Emission and excitation plots of a) 5a excitation (red) and emission (black) and b) 5b excitation (red) and emission (black)
2.2.3 Two-Photon luminescence analysis

Preliminary attempts to measure the two photon spectra of the ligands and complexes was carried out. Unfortunately, it was not possible to measure the two photon emission of the complexes. It is likely that these compounds have very low cross-sections, similar to those measured by Natrajan et al. which are too low for the capabilities of the current laser set up. Furthermore, the short lifetimes and low quantum yields may contribute to the inability to measure with the capabilities of the detector used.

2.2.4 Isomerisation and Photoswitching Studies

The ligands synthesised and thus the compounds contain a stilbene unit that should undergo isomerisation upon irradiation with UV light. These can be followed by $^1$H NMR spectroscopy due to the differences in coupling constant for the stilbene protons in the cis and trans isomers. Furthermore they can be followed by UV-vis spectroscopy.

The ligands, 1a and 1b, were irradiated using 360 nm light from a high pressure Hg lamp equipped with focussing lenses and bandpass filters in order to induce a trans-cis isomerisation. Absorbance was monitored after 5 min periods of irradiation of $2.5 \times 10^{-5}$ M solutions. The UV-vis spectra (Figure 52) show a decrease in the lowest energy absorbance and a hypsochromic shift of the higher energy peak. A clear isosbestic point is seen in both spectra at 292 nm and 300 nm in 1a and 1b respectively. The photostationary state (PSS) was reached in 1a after 1 h 25 mins mins of irradiation and in 1b the PSS was reached after 40 mins. Upon reaching the PSS the sample was left in the dark and spectra measured at 10 min intervals, however in both cases no change was seen after 1h indicating a thermally stable mixture. Attempts to recover the trans isomer were made by irradiation with 254 nm and 340 nm light, however no changes were seen in the spectra. With stilbenes in literature, the recovery of the trans isomer was found when the sample was irradiated at 313 nm, however this wavelength was inaccessible with the experimental set up used.
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Figure 52: UV-vis monitored irradiation of 1b in MeCN at a concentration of $2.5 \times 10^{-5}$M with mercury lamp fitted with a 360 nm filter. The arrows indicate the direction of the spectral changes upon irradiation.

It was also possible to follow this reaction by $^1$H NMR spectroscopy for 1a. In 1b the NPh$_2$ $^1$H NMR resonances of the phenyl groups masked any changes in the molecule along with the stilbene roofed doublets. The sample was irradiated with 360 nm light for 3 hours until the PSS was reached and a $^1$H NMR spectrum was recorded every 15 minutes. This took a lot longer to reach than in the UV-vis experiment likely due to the higher optical density from the increased concentration of approximately 0.02 M, which is required for $^1$H NMR spectroscopy. Figure 53 shows the spectra for 1a from each hour, and they show the inclusion of 3 new resonances and a decrease in the intensity of the trans-stilbene doublets. The changes are only moderate even at the PSS and integration of the ratio of the resonances showed that 35 % of the trans has been converted into the cis. As in the UV-vis experiment the cis form was found to be both thermally and photo stable in the absence of further irradiation in the UV.
Figure 53: $^1H$ NMR spectral switching analysis of 1a (CDCl$_3$, 298K, 400 MHz). Before switching (blue), after 1 hour irradiation (green), after 2 hours of irradiation (grey) after 3 hours irradiation (pink).

Each complex described in this chapter was also irradiated and monitored by UV-visible spectroscopy. No complex showed any changes upon irradiation with a variety of bandpass filters (340, 360, 410, 450 and 540 nm). Here, it is possible that the presence of absorption bands that appear in both the cis and trans isomer means that irradiation may well induce both the forward and the backwards reaction. It is therefore reasonable to assume that the rate of both of these isomerisation processes is apparently the same, resulting in no net observable change in absorption. Of course, this effect is dependent on the molar absorption extinction coefficient of the individual cis and trans isomer absorption bands and the actual rates of the forward and backwards reactions.

### 2.2.5 Computational Chemistry

To aid better understanding of the electronic and optical properties of the complexes described in this chapter, TD-DFT calculations have been carried out on both ligands and complexes using Gaussian 09\textsuperscript{10}. Geometry optimisation of ligands 1a and 1b were conducted using the B3LYP functional and a 6-311G++\textsuperscript{11} basis set. Geometry
optimisation of the Pt, Ru and Ir complexes were carried out at the B3LYP level, with cc-PVQZ-pp\textsuperscript{112,113} basis set and SDD\textsuperscript{114} pseudopotential on the metal centres and a 6-311G++ basis set on all other atoms. Geometry optimisation of the Re complexes were carried out at a B3LYP level, with a LANL2DZ\textsuperscript{115} basis set and pseudo potential on the metal centre with a 6-311G++ basis set on all other atoms. TD-DFT calculations were performed at the CAM-B3LYP\textsuperscript{116} level, due to this functional being able to estimate charge transfer excitations with a larger degree of accuracy than B3LYP. Both trans and cis isomers were studied. Solvent effects were accounted for in the TD-calculations by using a solvent continuum model (CPCM)\textsuperscript{117,118} with acetonitrile. The first 50 states were calculated for each compound and the UV-visible spectra and transition information were simulated using the GaussSum\textsuperscript{119} program.

### 2.2.5.1 Absorption

The calculated and experimental UV-visible spectra of ligands 1b is shown in Figure 54. Predicted transition energies of ligands 1a and 1b are given in Table 6 and selected orbitals are shown in Figure 55. The low energy bands for 1a and 1b (ca. 350 nm) are calculated to be a result of one transition, with the higher energy bands being a result of multiple transitions. Both calculated spectra show a poor match with the experimental spectra, with deviations of ca. 50 nm from the experimental low energy peaks.
Figure 54: TD-DFT (blue) and experimental (green) UV-visible spectra of a) 1a and b) 1b in MeCN. The \( \varepsilon \) axis refers to the experimental data only and the vertical axes of the calculated spectra are scaled to match the low energy experimental absorbance. The oscillator strength axes refers to the individual calculated transitions (red).
Table 6: Data from TD-DFT Calculations based on B3LYP/6-31G++ geometries of ligands 1a and 1b

<table>
<thead>
<tr>
<th>Compound</th>
<th>Transition</th>
<th>$\Delta E / \text{nm (eV)}$</th>
<th>$f_{\text{os}}$</th>
<th>Major contributions</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1a</strong></td>
<td>1</td>
<td>358.23 (3.46)</td>
<td>1.92</td>
<td>HOMO $\rightarrow$ LUMO (71 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO $\rightarrow$ LUMO+2 (19 %)</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>266.84 (4.65)</td>
<td>0.36</td>
<td>HOMO-2 $\rightarrow$ LUMO (40 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO $\rightarrow$ LUMO+1 (35 %)</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>254.61 (4.86)</td>
<td>0.16</td>
<td>HOMO-2 $\rightarrow$ LUMO+1 (32 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO-7 $\rightarrow$ LUMO+1 (19 %)</td>
</tr>
<tr>
<td></td>
<td></td>
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<td></td>
<td>HOMO-9 $\rightarrow$ LUMO (12 %)</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>254.31 (5.00)</td>
<td>0.22</td>
<td>HOMO-2 $\rightarrow$ LUMO+1 (44 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO-9 $\rightarrow$ LUMO+1 (12 %)</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>240.21 (5.16)</td>
<td>0.34</td>
<td>HOMO-5 $\rightarrow$ LUMO+1 (42 %)</td>
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<td></td>
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<td>HOMO-2 $\rightarrow$ LUMO+3 (19 %)</td>
</tr>
<tr>
<td><strong>1b</strong></td>
<td>1</td>
<td>358.63 (3.46)</td>
<td>2.01</td>
<td>HOMO $\rightarrow$ LUMO (68 %)</td>
</tr>
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<td>HOMO $\rightarrow$ LUMO+2 (18 %)</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>280.26 (4.42)</td>
<td>0.11</td>
<td>HOMO $\rightarrow$ LUMO+5 (48 %)</td>
</tr>
<tr>
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<td>HOMO-1 $\rightarrow$ LUMO (18 %)</td>
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<tr>
<td></td>
<td>3</td>
<td>279.95 (4.43)</td>
<td>0.17</td>
<td>HOMO-2 $\rightarrow$ LUMO (46 %)</td>
</tr>
<tr>
<td></td>
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<td></td>
<td></td>
<td>HOMO-2 $\rightarrow$ LUMO+2 (15 %)</td>
</tr>
<tr>
<td></td>
<td></td>
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<td></td>
<td>HOMO-1 $\rightarrow$ LUMO+1 (10 %)</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>272.21 (4.55)</td>
<td>0.30</td>
<td>HOMO $\rightarrow$ LUMO+6 (83 %)</td>
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</tr>
<tr>
<td></td>
<td>8</td>
<td>261.00 (4.75)</td>
<td>0.27</td>
<td>HOMO $\rightarrow$ LUMO+1 (45 %)</td>
</tr>
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<td></td>
<td>HOMO-2 $\rightarrow$ LUMO (17 %)</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO-1 $\rightarrow$ LUMO+1 (62 %)</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>257.01 (4.82)</td>
<td>0.21</td>
<td>HOMO $\rightarrow$ LUMO+2 (21 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO $\rightarrow$ LUMO (16 %)</td>
</tr>
<tr>
<td></td>
<td></td>
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<td></td>
<td>HOMO-1 $\rightarrow$ LUMO+2 (13 %)</td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td>HOMO-2 $\rightarrow$ LUMO+1 (11 %)</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>253.84 (4.88)</td>
<td>0.16</td>
<td>HOMO-2 $\rightarrow$ LUMO+1 (34 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO $\rightarrow$ LUMO+9 (21 %)</td>
</tr>
</tbody>
</table>

In both 1a and 1b the transition that results in the lowest energy absorption band is largely due to a HOMO-LUMO transition with a small contribution from a HOMO-LUMO+2 transition. Both LUMOs are $\pi$-antibonding across the stilbene moiety. Furthermore both transitions are largely $\pi - \pi^*$ transitions from the donor NMe$_2$ group to the terpyridyl unit.
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Figure 55: TD-DFT derived orbitals involved in the low energy transition of 1a (isosurface value 0.03 au).

The calculated and experimental UV-visible spectra for Pt$^{II}$ complexes 2a and 2b are shown together in Figure 56. Selected transition energy data are given in Table 7 and selected orbitals are shown in Figure 57 and Figure 58. The TD-DFT profiles show a blue shift from the experimental data in the lower energy bands of approximately 25 nm for both complexes but the higher energy bands show a reasonable match with the experimental data, although the relative intensities of the profiles are quite different with respect to the oscillator strength of the transitions. The low energy bands contain a single transition, whereas, the higher energy bands consist of multiple transitions, a few of which are more dominant.
Figure 56: TD-DFT (blue) and experimental (green) UV-visible spectra of a) 2a and b) 2b in MeCN. The $\varepsilon$ axis refers to the experimental data only and the vertical axes of the calculated spectra are scaled to match the low energy experimental absorbance. The oscillator strength axes refers to the individual calculated transitions (red).
Table 7: Data from TD-DFT Calculations based on B3LYP/6-31G++/cc-pVQZ-pp geometries of 2a and 2b

<table>
<thead>
<tr>
<th>Compound</th>
<th>Transition</th>
<th>ΔE / nm (eV)</th>
<th>f_{0s}</th>
<th>Major contributions (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>1</td>
<td>435.86 (2.84)</td>
<td>1.44</td>
<td>HOMO → LUMO (73 %)</td>
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<td>HOMO → LUMO+2 (12 %)</td>
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<td></td>
<td>3</td>
<td>339.01 (3.65)</td>
<td>0.12</td>
<td>HOMO-2 → LUMO (41 %)</td>
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<td>HOMO-1 → LUMO (20 %)</td>
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<td></td>
<td></td>
<td>HOMO → LUMO+2 (20 %)</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>327.89 (3.78)</td>
<td>0.62</td>
<td>HOMO → LUMO+2 (37 %)</td>
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<td>HOMO → LUMO (22 %)</td>
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<td>HOMO-2 → LUMO (12 %)</td>
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<td></td>
<td>11</td>
<td>285.30 (4.34)</td>
<td>0.36</td>
<td>HOMO-8 → LUMO (52 %)</td>
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<td>HOMO-7 → LUMO+5 (16 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO-2 → LUMO+1 (12 %)</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>284.90 (4.35)</td>
<td>0.12</td>
<td>HOMO-1 → LUMO (40 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO-2 → LUMO (20 %)</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>278.67 (4.45)</td>
<td>0.17</td>
<td>HOMO-7 → LUMO+5 (62 %)</td>
</tr>
<tr>
<td></td>
<td>18</td>
<td>263.01 (4.71)</td>
<td>0.23</td>
<td>HOMO-4 → LUMO+1 (76 %)</td>
</tr>
<tr>
<td>2b</td>
<td>1</td>
<td>417.54 (2.97)</td>
<td>1.66</td>
<td>HOMO → LUMO (60 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO → LUMO+2 (17 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO-1 → LUMO (13 %)</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>327.911 (3.78)</td>
<td>0.50</td>
<td>HOMO → LUMO (32 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO → LUMO+2 (29 %)</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>285.56 (4.34)</td>
<td>0.37</td>
<td>HOMO-12 → LUMO (54 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO-10 → LUMO+5 (13 %)</td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>273.29 (4.53)</td>
<td>0.30</td>
<td>HOMO → LUMO+8 (83 %)</td>
</tr>
<tr>
<td></td>
<td>19</td>
<td>263.48 (4.70)</td>
<td>0.23</td>
<td>HOMO-5 → LUMO+1 (75 %)</td>
</tr>
<tr>
<td></td>
<td>23</td>
<td>253.27 (4.90)</td>
<td>0.25</td>
<td>HOMO-12 → LUMO+1 (53 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO-13 → LUMO (18 %)</td>
</tr>
</tbody>
</table>

The low energy band for the Pt^{II} complex 2a consists of one transition corresponding to contributions from a HOMO → LUMO and a HOMO → LUMO+2 as seen in the ligands. The HOMO displays π character on the aniline moiety and the stilbene, almost identical to the HOMO of the corresponding ligand. The LUMO is π antibonding across the terpyridyl fragment with some contribution from the Pt^{II} metal. The LUMO+2 is largely π-antibonding and based around the stilbene and terpyridine moiety. This low energy band can thus be attributed to ILCT and LMCT transitions. The band around 300-350 nm results from a couple of transitions with the same contributions discussed above along with contributions from the HOMO-2 which has significant π character on the double bond and has large Pt(d) and Cl(p) character. These transitions can therefore be assigned to be MLCT/LLCT in character.
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As with 2a the low energy band in 2b also consists of only one transition. The transition has a large contribution from a HOMO → LUMO transition with smaller contributions from the HOMO → LUMO+2 and HOMO-1 → LUMO transitions. The HOMO is again located mostly over the stilbene and diphenyl aniline part of the molecule and is largely \(\pi\) bonding. The LUMO is largely \(\pi\)-antibonding across the terpyridyl moiety with small contributions from the platinum d orbitals. The HOMO-1 orbitals are concentrated around the stilbene moiety with some electron density around the aniline moiety and the LUMO+2 is largely \(\pi\)-antibonding around the stilbene. As with 1a the lowest energy transition can assigned to an ILCT with some LMCT involved.

![Derived orbitals](image)

**Figure 57**: TD-DFT derived orbitals involved in the low energy transitions of 2a (isosurface value 0.03 au).
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Figure 58: TD-DFT derived orbitals involved in the low energy transitions of 2b (isosurface value 0.03 au).

The calculated and experimental UV-visible spectra of the Re\textsuperscript{I} complexes 3a and 3b are shown together in Figure 59. Selected transition energy data are given in Table 8 and selected orbitals are shown in Figure 60 and Figure 61. In both 3a and 3b the calculated profiles consist of 2 peaks, the lowest energy band in each is a result of one strong transition and the higher energy band is a result of multiple transitions. The calculated data are slightly blue shifted from the experimental data by approximately 25 nm in both compounds. Furthermore the relative intensities of the peaks are reversed.
Figure 59: TD-DFT (blue) and experimental (green) UV-visible spectra of a) 3a and b) 3b in MeCN. The ε axis refers to the experimental data only and the vertical axes of the calculated spectra are scaled to match the low energy experimental absorbance. The oscillator strength axes refer to the individual calculated transitions (red).
In both 3a and 3b the transition that results in the lowest energy band is predominately HOMO → LUMO with a smaller contribution from a HOMO → LUMO+1 transition. For both molecules the HOMO is localised on the aniline and stilbene portion of the molecule and is predominately π-bonding in character. The LUMO is located across the coordinated portion of the terpyridine and is largely π-antibonding. The LUMO+1 shows similar electron density to the LUMO with an extension of electron density on the uncoordinated portion of the terpyridyl unit. In both molecules these MOs show no contribution from the metal, and thus the transitions are a result of an ILCT in agreement with the assignments from the experimental data. In 3a the HOMO-1 and HOMO-2 are both calculated to be largely Re(d) in character with π-backbonding into the carbonyl ligand, and the HOMO-3 is calculated to contain a large contribution from the rhenium centre with some π-bonding electron density over the stilbene portion of the ligand. Weak MLCT transitions from these orbitals into the LUMO are seen at 344 and 329 nm. Similarly, in 3b the HOMO-2 and

<table>
<thead>
<tr>
<th>Compound</th>
<th>Transition</th>
<th>ΔE / (nm) eV</th>
<th>f_0s</th>
<th>Major contributions</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>1</td>
<td>393.62 (3.15)</td>
<td>1.85</td>
<td>HOMO → LUMO (62 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO → LUMO+1 (14 %)</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>339.46 (3.65)</td>
<td>0.02</td>
<td>HOMO-1 → LUMO (65 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO-2 → LUMO (14 %)</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>325.89 (3.80)</td>
<td>0.01</td>
<td>HOMO-2 → LUMO (65 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO-3 → LUMO (14 %)</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>309.24 (4.01)</td>
<td>0.18</td>
<td>HOMO → LUMO+1 (40 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO → LUMO (22 %)</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>278.83 (4.45)</td>
<td>0.12</td>
<td>HOMO-5 → LUMO (17 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO → LUMO+2 (12 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO → LUMO+1 (11 %)</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>268.54 (4.62)</td>
<td>0.14</td>
<td>HOMO-3 → LUMO (30 %)</td>
</tr>
<tr>
<td>3b</td>
<td>1</td>
<td>386.10 (3.21)</td>
<td>1.98</td>
<td>HOMO → LUMO (52 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO → LUMO+1 (15 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO-1 → LUMO (12 %)</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>343.94 (3.60)</td>
<td>0.02</td>
<td>HOMO-2 → LUMO (69 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO-3 → LUMO (73 %)</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>329.44 (3.76)</td>
<td>0.01</td>
<td>HOMO-3 → LUMO (23 %)</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>307.75 (4.03)</td>
<td>0.14</td>
<td>HOMO-4 → LUMO (15 %)</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>284.90 (4.35)</td>
<td>0.35</td>
<td>HOMO-7 → LUMO (28 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO-1 → LUMO (20 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO → LUMO (11 %)</td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>271.03 (4.57)</td>
<td>0.34</td>
<td>HOMO → LUMO+9 (79 %)</td>
</tr>
<tr>
<td></td>
<td>21</td>
<td>251.34 (4.51)</td>
<td>0.12</td>
<td>HOMO-14 → LUMO+1 (12 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO-13 → LUMO (11 %)</td>
</tr>
</tbody>
</table>

Table 8: Data from TD-DFT Calculations based on B3LYP/6-31G++/LANL2DZ geometries of 3a and 3b
HOMO-3 can be described as Re(d) in character with π backbonding into the carbonyl ligands. Again these exhibit very weak MLCT transitions into the LUMO.

Figure 60: TD-DFT derived orbitals of 3a involved in lowest energy transition (isosurface value 0.03 a.u.)
The calculated and experimental UV-visible spectra of the RuII complexes, 4a and 4b, are shown together in Figure 62. Selected transition energy data are given in Table 9 and selected orbitals are shown in Figure 63 and Figure 64. The calculated spectra for 4a and 4b show an overall poor match with the experimental data. Neither calculated spectrum produces the required low energy transitions (500 nm), with deviations of approximately...
75 nm in each case. The lowest calculated peaks in both cases show a reasonable overlap with the lower energy experimental peaks especially in the case of 4b. The calculated band around 425 nm in both is a result of one large transition and is broadened by a few weaker transitions, the shoulder on these bands (ca. 375 nm) is also a result of one strong transition and a few weak transitions.

To attempt to overcome the poor match between the experimental and calculated band positions the calculations were run with a range of basis sets and pseudopotentials (Def2\textsuperscript{120}, LANL2DZ\textsuperscript{115} and Stuttgart-Koeln\textsuperscript{113}). However, it was found that cc-PVQZ-pp/SDD was the most successful for both compounds without vastly overestimating the lowest energy transitions.
Figure 62: TD-DFT (blue) and experimental (green) UV-visible spectra of a) 4a and b) 4b in MeCN. The ε axis refers to the experimental data only and the vertical axes of the calculated spectra are scaled to match the low energy experimental absorbance. The oscillator strength axes refers to the individual calculated transitions (red).
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Table 9: Data from TD-DFT Calculations based on B3LYP/6-31G++/cc-PQVZ geometries of 4a and 4b

<table>
<thead>
<tr>
<th>Compound</th>
<th>Transition</th>
<th>ΔE / nm (eV)</th>
<th>$f_{os}$</th>
<th>Major contributions (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a</td>
<td>1</td>
<td>428.53 (2.89)</td>
<td>2.59</td>
<td>HOMO-2 $\rightarrow$ LUMO (28 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO-3 $\rightarrow$ LUMO+1 (23 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO $\rightarrow$ LUMO (18 %)</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>420.04 (2.95)</td>
<td>0.02</td>
<td>HOMO-4 $\rightarrow$ LUMO (90 %)</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>419.51 (2.96)</td>
<td>0.02</td>
<td>HOMO-4 $\rightarrow$ LUMO+1 (89 %)</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>373.49 (3.32)</td>
<td>1.47</td>
<td>HOMO-3 $\rightarrow$ LUMO+1 (14 %)</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>363.30 (3.41)</td>
<td>0.04</td>
<td>HOMO-1 $\rightarrow$ LUMO+1 (13 %)</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>340.60 (3.64)</td>
<td>0.04</td>
<td>HOMO-4 $\rightarrow$ LUMO+3 (38 %)</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>324.70 (3.81)</td>
<td>0.00</td>
<td>HOMO-3 $\rightarrow$ LUMO+2 (29 %)</td>
</tr>
<tr>
<td></td>
<td>17</td>
<td>320.73 (3.87)</td>
<td>0.00</td>
<td>HOMO-1 $\rightarrow$ LUMO+3 (12 %)</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>310.18 (3.99)</td>
<td>0.09</td>
<td>HOMO-1 $\rightarrow$ LUMO + 60%</td>
</tr>
<tr>
<td>4b</td>
<td>1</td>
<td>422.19 (2.94)</td>
<td>2.47</td>
<td>HOMO-2 $\rightarrow$ LUMO (30 %)</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>420.58 (2.95)</td>
<td>0.02</td>
<td>HOMO-4 $\rightarrow$ LUMO (90 %)</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>392.38 (3.16)</td>
<td>0.00</td>
<td>HOMO $\rightarrow$ LUMO+1 (17 %)</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>372.20 (3.33)</td>
<td>2.06</td>
<td>HOMO-1 $\rightarrow$ LUMO (17 %)</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>362.96 (3.41)</td>
<td>0.00</td>
<td>HOMO-1 $\rightarrow$ LUMO+1 (17 %)</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>360.20 (3.44)</td>
<td>0.04</td>
<td>HOMO-2 $\rightarrow$ LUMO+3 (16 %)</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>359.79 (3.45)</td>
<td>0.05</td>
<td>HOMO-3 $\rightarrow$ LUMO+3 (16 %)</td>
</tr>
</tbody>
</table>

The transitions that result in the lowest energy band and the shoulder band in 4a are a result of one strong transition which is made up of many orbital contributions. The orbitals involved are HOMO, HOMO-1, HOMO-2, HOMO-3, LUMO and LUMO-1. HOMO-3
and HOMO-2 are degenerate in energy, and visually they differ with the orientation of the large d orbital contribution on the Ru\textsuperscript{II} metal, and inversion of the orbital coefficient sign on one terpyridyl ligand. The same can be said of the HOMO-1 and HOMO, which are \(\pi\)-bonding in character across the stilbene and to the nitrogen with the reflection of the MOs on one side of the molecule. The LUMO and LUMO+1 are visually similar, with \(\pi\)-antibonding character around the terpyridyl portion of the molecule and Ru(d) contributions but have marginally different energies. The transitions from HOMO-2/HOMO-3 \(\rightarrow\) LUMO can be said to be largely MLCT in character. The HOMO \(\rightarrow\) LUMO and HOMO-1 \(\rightarrow\) LUMO+1 transitions exhibit both a ILCT and LMCT character.

A very similar picture is seen in complex \textbf{4b}. The strong transition that results in the lowest energy band is mainly a result of 3 contributions from HOMO \(\rightarrow\) LUMO, HOMO-2 \(\rightarrow\) LUMO and HOMO-3 \(\rightarrow\) LUMO+1. As with \textbf{4a} the HOMO/HOMO-1, HOMO-2/HOMO-3 and LUMO/LUMO+1 are degenerate pairs, furthermore the MOs are the same in \textbf{4a} and \textbf{4b}. The shoulder peak ca. 375 nm also includes transition from HOMO \(\rightarrow\) LUMO+5 and HOMO-1 \(\rightarrow\) LUMO+4. The LUMO+4 and LUMO+5 are again degenerate in energy, and the charges are reversed on one terpyridyl ligand. They are both \(\pi\) antibonding across the stilbene molecule with a very small amount of electron density on the terpyridyl portion of the molecule.
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Figure 63: TD-DFT derived orbitals of $4a$ involved in selected transitions (isosurface value 0.03 a.u.)

Figure 64: TD-DFT derived orbitals of $4b$ involved in selected transitions (isosurface value 0.03 a.u.)
The Ir$^{III}$ complexes, 5a and 5b, calculated and experimental UV-visible spectra are shown together in Figure 65. Selected transition energy data are given in Table 10 and selected orbitals are shown in Figure 66. The calculated spectrum for 5a shows an overall poor profile match and the lowest energy peak in the experimental having a red shift of approximately 50 nm, the computed higher energy peaks match quite well with shoulder bands in the experimental with difference around 25 nm. Complex 5b shows a better profile match, although shifted by approximately 30 nm for most peaks, with the relative intensities differing, i.e. the strength of the lowest energy band being vastly overestimated as with the other compounds described in this chapter. The lowest energy calculated transition in both Ir$^{III}$ complexes are a result of one very strong transition and a few weak transitions. The next highest energy bands are both due to one strong transition and a few weaker transition. The highest energy bands are due to multiple transitions.
Figure 65: TD-DFT (blue) and experimental (green) UV-visible spectra of a) 5a and b) 5b in MeCN. The ε axis refers to the experimental data only and the vertical axes of the calculated spectra are scaled to match the low energy experimental absorbance. The oscillator strength axes refers to the individual calculated transitions (red).
Table 10: Data from TD-DFT Calculations based on B3LYP/6-31G++/cc-PQVZ geometries of 5a and 5b

<table>
<thead>
<tr>
<th>Compound</th>
<th>Transition</th>
<th>ΔE / nm (eV)</th>
<th>f_0s</th>
<th>Major contributions</th>
</tr>
</thead>
<tbody>
<tr>
<td>5a</td>
<td>1</td>
<td>463.96 (2.67)</td>
<td>2.96</td>
<td>HOMO → LUMO (39 %)</td>
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<td>2</td>
<td>451.88 (2.74)</td>
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<td>HOMO-1 → LUMO+1 (37 %)</td>
</tr>
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<td></td>
<td>3</td>
<td>377.03 (3.29)</td>
<td>0.00</td>
<td>HOMO-1 → LUMO+1 (49 %)</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>338.78 (3.66)</td>
<td>1.59</td>
<td>HOMO → LUMO+5 (24 %)</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>312.06 (3.97)</td>
<td>0.10</td>
<td>HOMO-8 → LUMO (53 %)</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>311.85 (3.98)</td>
<td>0.10</td>
<td>HOMO-8 → LUMO+1 (53 %)</td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>310.32 (4.00)</td>
<td>0.20</td>
<td>HOMO-2 → LUMO (31 %)</td>
</tr>
<tr>
<td>5b</td>
<td>1</td>
<td>441.85 (2.80)</td>
<td>3.32</td>
<td>HOMO → LUMO (17 %)</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>431.70 (2.87)</td>
<td>0.00</td>
<td>HOMO-1 → LUMO+1 (16 %)</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>339.13 (3.66)</td>
<td>1.41</td>
<td>HOMO → LUMO+4 (12 %)</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>322.58 (3.84)</td>
<td>0.30</td>
<td>HOMO-2 → LUMO (20 %)</td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>312.41 (3.97)</td>
<td>0.10</td>
<td>HOMO-16 → LUMO (45 %)</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>312.25 (3.97)</td>
<td>0.09</td>
<td>HOMO-16 → LUMO+1 (45 %)</td>
</tr>
</tbody>
</table>

In the case of both 5a and 5b, the molecular orbitals are the same as the RuII complexes which is consistent with the emission data. There is again degeneracy between the HOMO-1/HOMO and the LUMO/LUMO+1 pairs. One major difference seen is that the transitions that result in the lowest energy band no longer exhibit a metal character in the IrIII complex, thus there is no MLCT character predicted and the transition is predominantly LMCT and ILCT.
2.2.5.2 Calculated Isomerisation

Using TD-DFT, both the *trans* and *cis* forms can be assessed. The spectra gained from these calculations can be plotted together in order to visualise the potential changes upon experimental photo-isomerisation.

*Figure 66: TD-DFT derived orbitals of 5a involved in selected transitions (isosurface value 0.03 a.u.)*
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Figure 67: Calculated trans (black) and cis (red) absorption spectra of a) ligand 1a and b) ligand 1b

Upon computational analysis of the trans and cis forms for the ligands, 1a and 1b it can be seen that there are only small changes in the absorption spectra. The proportions of the higher energy peaks (ca. 225-300 nm) are larger in the cis form, and the higher energy peak (ca. 350 nm) exhibits a blue shift of 20 nm when changing from trans to cis. This blue shift is slightly higher in the NPh₂ ligand. However the graphs show only the 100 % cis and trans forms, and experimental photo-isomerisation does not always exhibit 100 % conversion. This matches nicely with the experimental data for 1a and 1b (Figure 52), in which the lower energy peak decreases and the higher energy peak increases. Neither compound’s calculated spectra estimates the isosbestic point.
In the case of the complexes, there are very similar changes to that of the ligands. In the 
*cis*-platinum complexes, there is again a slight blue shift of the lower energy peaks and the 
oscillator strength of the transition is much lower compared to the *trans*-platinum complex. 
The higher energy peaks show an increase in oscillator strength. The *cis*-iridium 
complexes show a very small increase in oscillator strength for the higher energy 
transitions and a large decrease in intensity in the high energy peak compared to the *trans*- 
iridium complexes. Interestingly the *cis*-ruthenium complexes show a red shift from 270 – 
285 nm, and a decrease in oscillator strength of the lower energy peak in comparison to the *trans*- 
ruthenium complex. There is also a slight change in the profile between 325 nm and 
250 nm, where the shoulder in the *trans*-ruthenium complex is no longer present in *cis*- 
ruthenium isomer.

### 2.3 Conclusion

Photophysical characterisation by UV-vis absorption and luminescence spectroscopy 
displayed similar properties for all of the compounds involved suggesting ligand centred
transitions. Attempts at two-photon measurements were carried out with no avail, most likely due to the compounds having very small 2PA cross-sections that are too low for the capabilities of the equipment used. Ligands 1a and 1b were shown to undergo appreciable photoisomerisation (as shown by UV-vis and NMR spectroscopies) using 360 nm light affording thermally stable cis-configurations. However the transition metal derivatives of 1a and 1b did not isomerise using a range of wavelengths, suggesting that the ILCT based emission dominates the photophysical properties of the complexes under the irradiation wavelengths used and/or thermal isomerisation of any cis forms is extremely fast. Computational studies agree with the assignments of the UV-visible features, with the calculated low energy transitions exhibiting predominant ILCT character.

2.4 Further work

The compounds described within this chapter would not be suitable for 3-D data storage. For a better photoswitch, the absorption and emission need to have a larger spectral separation and so adaptation of ligands in order to red shift the ligand emission further from the metal emission is required. The compounds themselves maybe suitable as sensors (oxygen or ions). Experiments could be carried out to ascertain if any of the ligands or complexes are good for ion sensing and if so do any have a selectivity towards a particular ion. Further to this, the ReI complexes could be useful as pH probes, due to the pendant pyridyl that remains uncoordinated to the ReI centre. It would also be interesting to replace the chloride ligand in the ReI complexes with a triflate anion or solvent molecule such as MeCN or pyridine in order to further study the photophysical properties.
Chapter 3: \textit{d}^0 Metal Complexes for Applications in Two-Photon PDT

3.1 Introduction

The clinically used cancer treatment PDT currently uses one-photon techniques. The use of two-photon excitation in PDT is of particular interest, owing to advantages of the technique. Of particular interest are metal based systems which exhibit emission from triplet states such as Ru$^{II}$ or Ir$^{III}$ polypyridyl complexes. For efficient 2PE-PDT the photosensitiser needs an effective two-photon cross-section and efficient quenching by triplet oxygen.

Triplet oxygen is a known quencher of ligand centred and metal centred triplet excited states exhibited by inorganic complexes containing platinum group metals. Stern-Volmer analysis of the luminescence data of a compound can provide a measure of the efficiency of the quenching process occurring in these types of compounds. In a fluid solution the Stern-Volmer relationship is given by the Stern-Volmer equation:

\[
\frac{\tau_0}{\tau} = \frac{I_0}{I} = 1 + K_{SV}[O_2] = 1 + k_q \tau_0 [O_2] = 1 + k_q \tau_0 K_{H}^{Solv} p_{O_2}
\]

Where the \(\tau\) terms denote the luminescence lifetimes, I terms refer to the emission intensity, the subscript 0 refers to the quantities in the absence of the quencher, \(K_{SV}\) is the Stern-Volmer quenching constant, \(k_q\) is the bimolecular rate constant for quenching of the excited state, and \(K_{H}^{Solv}\) denotes the Henry constant of O$_2$ (gas) in a given solvent. From the given equation it is possible to see that plots of \(I_0/I\) and \(\tau_0/\tau\) vs the oxygen concentration will be linear with slopes equal to \(K_{SV}\).

Lemercier \textit{et al.} have previously reported 5-substituted-1,10-phenanthroline ligands containing a highly conjugated fluorenyl moiety coordinated to Ru$^{II}$. The fluorenyl lends itself well to the increase of a molecule’s two-photon cross-section, whereas functionalisation of the 5-membered ring is an attractive property for biological applications.
3.2 Results and Discussion

The work described in this chapter was conducted as a joint EPSRC/University of Manchester funded collaboration with Miss Elizabeth Boreham (also a PhD student in the group of Louise Natrajan, thesis in submission pending viva) within the group of Dr Gilles Lemercier (University of Reims, France). The work performed solely by the author of this thesis involves the synthesis and characterisation of complexes 7b and 7c, the photophysical measurements of these compounds and DFT calculations all performed in Manchester. The remainder of the work described herein was conducted with Elizabeth Boreham: synthesis and characterisation of compounds 7 and 7a from starting materials synthesised by Dr Gilles Lemercier, and the characterisation and photophysical measurements of these compounds (made in both Manchester and at the University of Reims). Single crystals for X-ray diffraction were obtained by the author, and the data solved by Simon Randall and Daniel Whittaker. Cell studies were performed by Christine Terryn at the University of Reims. Two-photon absorption cross-section measurements were performed by Elizabeth Boreham (in the laboratory of Mireille Blanchard-Desc at the University of Bordeaux, CNRS with the assistance of Vincent Hughes).

3.2.1 Synthesis and Characterisation of Ligands and Complexes

The synthetic route to the target ligand 7 is shown in Scheme 15. This first requires the synthesis of 5-bromo-1,10-phenanthroline (6) and then a Suzuki cross-coupling reaction with a fluorenyl boronic acid. The bromination of phenanthroline was carried out by heating one equivalent of 1,10-phenanthroline with 0.6 equivalents of elemental bromine in oleum in a pressurised vessel. Compound 6 was then reacted with the fluorenyl boronic acid in a palladium cross-coupling reaction utilising tetrakistriphenylphosphine palladium as the catalyst (Scheme 15).

Scheme 15: Synthetic scheme for the synthesis of 6 and 7
The synthesis of 5-bromo-1,10-phenanthroline required stirring 1,10-phenanthroline in oleum and bromine in a closed pressure vessel and heating to 135 °C and maintaining this temperature for 48 h. The reaction was quenched by pouring the reaction mixture over ice. The pH was adjusted to pH 7 with ammonium hydroxide and the product extracted into CHCl₃. The isolated product analysis showed both the desired product and a small amount of 5,6-dibromo-1,10-phenanthroline. The unwanted side product was removed by heating in diethyl ether, filtering through celite and evaporating to dryness and this process was repeated three times. The ¹H NMR spectra of both the crude and triply purified product are shown together in Figure 69. The purified product shows that the 5,6-dibromo-1,10-phenanthroline is still present but the ratio of products has been reduced from 1:3.3 to 1:10 and was of sufficient purity to successfully perform the next synthetic step. Further analysis was not carried out due to this being a known literature compound.
Figure 69: \(^1\)H NMR of the expanded aromatic region of compound 6 (CDCl\(_3\), 400 MHz, 298 K). The crude product is shown in the top spectrum and the triply purified product is the bottom spectrum.

Ligand 7 was synthesised by means of a Suzuki cross coupling reaction. Compound 6 and (9,9-dihexyl-9H-fluoren-2-yl)boronic acid (synthesized and supplied by Gilles Lemercier) were reacted in a one to one molar ratio in degassed toluene. Sodium carbonate was added as a base and a catalytic amount of tetrakis(triphenylphosphine)palladium(0) was used. After heating the reaction mixture to reflux temperature for 3 days, the organic phase was separated and the aqueous phase was extracted into DCM. The volatiles of the combined organics were evaporated to dryness and the crude product was purified using column chromatography on alumina with a mixed solvent system (DCM:acetone:triethylamine, 80:19:1). Compound 7 was isolated as a white solid in a low yield of 25 %. The \(^1\)H NMR
spectrum, shown in Figure 70, indicates the formation of the correct product. Analysis was further confirmed by mass spectrometry and elemental analysis.

![Figure 70: $^1$H NMR of the expanded aromatic region of 7 with an inset of the region associated with the hexyl chains present in the molecule (CDCl₃, 400 MHz, 298 K)](image)

In order to synthesise the desired cyclometalated iridium complexes with ligand 7 the corresponding cyclometallated iridium chloride dimers were synthesised as previously reported by Nonoyama and Yamasaki et al. It was then possible to break apart the dimer with the addition of ligand 7 producing the desired complex. The synthetic route to the dimer precursors and the corresponding cyclometalated complexes 7a and 7b is shown in Scheme 16.
Both the phenylpyridine (ppy) and benzo-[H]-quinoline (pq) complexes were synthesised by dissolving IrCl$_3$.xH$_2$O and the ppy or pq ligand in ethoxyethanol and water producing a purple solution and heating to reflux temperature for 24 h. During this time a yellow solid precipitated out and the suspension was cooled and filtered and washed with ethanol and acetone. This solid was then dissolved in DCM and toluene and hexane added and the solution was reduced to half the original volume and the resulting precipitate was isolated by filtration, giving yellow crystalline solids for both dimer syntheses. The synthesis of both Ir$^{III}$ dimers were successful with yields of around 70 %. $^1$H NMR spectroscopic analysis showed the desired products had been synthesised in both cases by matching with the literature.

The iridium(III) complexes 7a and 7b were synthesised by refluxing the corresponding cyclometallated iridium dimer in MeOH with 7 in DCM. Over time, the yellow solution turned bright orange, signifying the complexation of 7. After 18 h, the solution was cooled and the complexes were precipitated as the PF$_6$ salts. Complex 7a was produced in high yield and purity, as displayed by the $^1$H NMR spectrum in Figure 71. The spectrum

**Scheme 16: Synthetic route to 7a and 7b.**
exhibits the expected upfield aromatic resonances at 6.45 and 6.91 ppm for protons on the phenyl ring of the ppy ligand. These are similar to the resonances seen in cyclometallated dimer but cannot be compared due to different solvents being used. The resonances at 8.62, 8.37 and 8.23 ppm are all indicative of the phenanthroline protons adjacent to the coordinated nitrogen. Successful synthesis of 7a was further confirmed by $^{13}$C NMR spectroscopy, mass spectrometry and elemental analysis. Furthermore, crystals of 7a were grown by slow vapour diffusion of hexane into chloroform. Compound 7b was also produced in good yield and all analytical measurements showed the successful synthesis of the product.

Figure 71: $^1$H NMR spectrum of the aromatic region of 7a (CD$_2$Cl$_2$, 400 MHz, 298 K)

A rhenium complex was synthesised with ligand 7 as shown in Scheme 17. Equimolar amounts of rhenium(I)pentacarbonyl chloride and ligand 7 were heated to reflux temperature in toluene for 48 hr. The original clear solution developed into a yellow/orange slurry as the product was formed and precipitated from the reaction mixture. After cooling, the product was filtered and washed with toluene and hexane. The product was isolated in an 89 % yield as a yellow/orange crystalline solid.
The $^1$H NMR spectroscopic analysis (Figure 72) of 7c showed the desired peaks. The shifts show a slight upfield deviation when compared to that of the ligand. Confirmation of the desired product was also confirmed by ES+ MS and $^{13}$C NMR spectroscopy. Furthermore, a single crystal X-ray structure was obtained.

**Figure 72: $^1$H NMR of the expanded aromatic region of 7c (CDCl$_3$, 400 MHz, 298 K)**

### 3.2.2 Crystallographic Studies

A single crystal X-ray structure was obtained for 7c from vapour diffusion of hexane into a saturated chloroform solution. A representation of the molecular structure is shown in Figure 73 and selected geometric parameters are shown in Table 11. For crystallographic data and refinement details see Appendix A.
Table 11: Selected bond lengths and angles of 7c

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond Length / Å</th>
<th>Bond</th>
<th>Angle / deg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Re1-Cl</td>
<td>2.4640(9)</td>
<td>N1-Re1-Cl1</td>
<td>83.21(8)</td>
</tr>
<tr>
<td>Re1-N1</td>
<td>2.186(3)</td>
<td>N1-Re1-N2</td>
<td>75.49(11)</td>
</tr>
<tr>
<td>Re1-N2</td>
<td>2.171(3)</td>
<td>N1-Re1-C1</td>
<td>92.33(15)</td>
</tr>
<tr>
<td>Re1-C1</td>
<td>1.890(4)</td>
<td>C1-Re1-C2</td>
<td>92.15(17)</td>
</tr>
<tr>
<td>Re1-C2</td>
<td>1.917(4)</td>
<td>C2-Re1-C11</td>
<td>91.23(12)</td>
</tr>
<tr>
<td>Re1-C3</td>
<td>1.931(4)</td>
<td>C3-Re1-N1</td>
<td>89.84(15)</td>
</tr>
<tr>
<td>C1-O1</td>
<td>1.171(6)</td>
<td>C1-Re1-C1</td>
<td>175.52(13)</td>
</tr>
<tr>
<td>C2-O2</td>
<td>1.164(5)</td>
<td>C3-Re1-N2</td>
<td>171.56(16)</td>
</tr>
<tr>
<td>C3-O3</td>
<td>1.138(6)</td>
<td>C2-Re1-N1</td>
<td>171.81(14)</td>
</tr>
</tbody>
</table>

Figure 73: Representation of the molecular structure of 7c (50 % ellipsoids)

The structure of 7c shows a slightly distorted octahedral structure around the rhenium centre, with the phenanthroline unit being the cause of this distortion. The Re-Cl and Re-N(phen) bond lengths are typical for a Re(CO)₃(phen)Cl structure. The fluorenyl unit is twisted out of plane with a torsion angle of 62°.
A crystal structure was also obtained for 7a, again grown by slow vapour diffusion of hexane into chloroform. A representation of the molecular structure is shown in Figure 74 and selected geometric parameters are shown in Table 12. For crystallographic data and refinement details see Appendix A.

Table 12: Selected Interatomic Distances and Angles for 7a

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond Length / Å</th>
<th>Bond</th>
<th>Angle / deg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ir1-N1</td>
<td>2.017(15)</td>
<td>C12-Ir1-C24</td>
<td>78.7(8)</td>
</tr>
<tr>
<td>Ir1-C12</td>
<td>1.93(3)</td>
<td>N25-Ir1-N36</td>
<td>77.2(6)</td>
</tr>
<tr>
<td>Ir1-N13</td>
<td>2.053(14)</td>
<td>N13-Ir1-C24</td>
<td>79.6(6)</td>
</tr>
<tr>
<td>Ir1-C24</td>
<td>2.01(2)</td>
<td>C75-Ir2-N64</td>
<td>79.6(6)</td>
</tr>
<tr>
<td>Ir1-N25</td>
<td>2.087(18)</td>
<td>C87-Ir2-N76</td>
<td>80.8(6)</td>
</tr>
<tr>
<td>Ir1-N36</td>
<td>2.108(17)</td>
<td>N99-Ir2-N88</td>
<td>78.3(5)</td>
</tr>
<tr>
<td>Ir2-N64</td>
<td>2.041(15)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ir2-C75</td>
<td>1.986(16)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ir2-N76</td>
<td>2.063(13)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ir2-C87</td>
<td>2.018(15)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ir2-N88</td>
<td>2.142(12)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ir2-N99</td>
<td>2.112(11)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The solid state structure of 7a contains two molecules and PF$_6^-$ counterions within the asymmetric unit cell. There is a large amount of disorder within the crystal structure, especially in the hexyl chains. The Ir$^{III}$ centres are hexacoordinated by ligand 7 and two ppy ligands. The ppy ligands lie mutually cis to one another as expected. The hexacoordination is approximately octahedral in geometry with some distortion due to the phen and ppy ligands. The Ir-C and Ir-N bonds within the ppy ligands and ligand 7 are consistent with similar structures reported in literature.$^{126,127}$ The solid state structure exhibits dihedral angles of 48° (Ir1) and 52° (Ir2) between the phenanthroline unit and the fluorenyl unit on ligand 7.
3.2.3 Luminescence analysis

Solution state luminescence was carried out in MeCN for both 7a and 7b complexes, whereas 7c was studied in DCM due low solubility in MeCN. All compounds were studied in degassed solutions by excitation at 400 nm and the excitation spectra were recorded at the emission maxima. Lifetimes were measured at 405 nm and quantum yields were measured using 400 nm excitation. Measured data are given in Table 13.

Table 13: Data from photophysical measurements. 7a and 7b measured in deoxygenated MeCN, 7c measured in deoxygenated DCM. All emission and quantum yields were measured at 400 nm excitation. Excitation spectra were taken at the emission maximum. Lifetimes measured using a ps pulsed 405 nm diode laser.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Abs / $\lambda_{\text{max}}$ (ε / dm$^3$ mol$^{-1}$ cm$^{-1}$)</th>
<th>$\lambda_{\text{em}}$/nm</th>
<th>$\lambda_{\text{ex}}$/nm</th>
<th>$\tau$/ns</th>
<th>$\phi$/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>7a</td>
<td>270 (74800), 300 (32900), 330 (25000), 380 (9600)</td>
<td>593</td>
<td>275</td>
<td>966</td>
<td>18</td>
</tr>
<tr>
<td>7b</td>
<td>258 (35100), 326 (15600), 420 (2550)</td>
<td>606</td>
<td>264</td>
<td>823</td>
<td>22</td>
</tr>
<tr>
<td>7c</td>
<td>270 (96900), 342 (29300), 410 (8940)</td>
<td>624</td>
<td>260, 300, 342</td>
<td>339</td>
<td>4</td>
</tr>
</tbody>
</table>

Lifetimes subject to ±10% error. Quantum yields determined using an integrating sphere, estimated error ±3%.

The absorption spectra of complexes 7a – 7c are given in Figure 75. The spectra of the Ir$^{III}$ complexes 7a and 7b both exhibit a broad, weak band (380-420 nm) which can be attributed to a d-$\pi^*$ $^3$MLCT, consistent with data for similar cyclometallated Ir$^{III}$ complexes.$^{128}$ The absorption spectrum of the Re$I$ complex, 7c, also displays a weak, low energy band with a maximum absorbance at 410 nm also attributed to a MLCT transition. The absorption spectra of all three complexes also contain absorption bands in the UV region which are assigned to mainly ILCT and $\pi$-$\pi^*$ electronic transitions.
Figure 75: UV-vis data for complexes 7a (black), 7b (red) and 7c (green). Both 7a and 7b were recorded in MeCN and 7c was recorded in DCM.

In comparison, Ir(phen)$_3^{3+}$ data is given in Table 14. Ayala et. al found that there were three major peaks attributed to a π-π* transition, and three weaker peaks at longer wavelengths which were also assigned to a π-π* transition. This is consistent with the data found for iridium complexes 7a and 7b.

<table>
<thead>
<tr>
<th>Abs / $\lambda_{\text{max}}$ ($\epsilon$ / dm$^3$ mol$^{-1}$ cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>222 (94000), 273 (79000), 303 (21500), 332 (7440), 336 (5240), 354 (5500)</td>
</tr>
</tbody>
</table>

Excitation and emission spectra of 7a and 7b are shown in Figure 76. The emission is typical of an iridium centred triplet MLCT and LLCT transition indicated by a broad featureless emission at 593 nm and 606 nm for 7a and 7b respectively. The lifetimes, measured at 0.97 µs and 0.82 µs are typical of cyclometalated iridium complexes. These phosphorescent lifetimes are relatively short and typical of an excited state that follows the energy gap law, wherein the non-radiative decay increases with a decreasing energy gap.
The measured quantum yields indicate efficient luminescence and are again quite typical of a cyclometallated iridium complex.\textsuperscript{131,132}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig76.png}
\caption{Excitation (black), Emission (red) spectra of 7a (top) and 7b (bottom) in MeCN.}
\end{figure}

The emission and excitation spectra of 7c are shown in Figure 77. The emission is typical for that of a rhenium carbonyl complex.\textsuperscript{133} The lifetime of 339 ns and quantum yield of 4
% are very different to that of the iridium complexes. This is likely due to luminescence quenching from the chloride ligand present in the complex.\textsuperscript{134}

![Excitation (black), Emission (red) spectra of 7c in DCM.](image)

3.2.3.1 Triplet Oxygen Quenching

The potential of compounds 7a, 7b and 7c to show efficient triplet oxygen quenching were assess by recording their emission in deoxygenated fluid solution. Further to the deoxygenated data discussed each compound was also studied in aerated solutions and oxygen saturated solutions to determine the efficiency of triplet oxygen quenching on the luminescence. Emission spectra were measured along with the lifetimes and quantum yields in degassed, aerated and oxygenated solutions. These data are collated in Table 15.
Table 15: Lifetime and quantum yield data for degassed, aerated and oxygen saturated solutions of 7a, 7b and 7c. 7a and 7b measured in MeCN, 7c measured in DCM. Quantum yields were measured at 400 nm. Lifetimes measured with 405 ps pulsed diode laser.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Degassed $\tau$ / ns</th>
<th>Aerated $\tau$ / ns</th>
<th>Oxygenated $\tau$ / ns</th>
<th>Degassed $\phi$ / %</th>
<th>Aerated $\phi$ / %</th>
<th>Oxygenated $\phi$ / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>7a</td>
<td>966</td>
<td>75</td>
<td>19</td>
<td>18</td>
<td>4</td>
<td>1.0</td>
</tr>
<tr>
<td>7b</td>
<td>823</td>
<td>73</td>
<td>18</td>
<td>22</td>
<td>2</td>
<td>1.5</td>
</tr>
<tr>
<td>7c</td>
<td>339</td>
<td>157</td>
<td>45</td>
<td>4</td>
<td>2</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Lifetimes subject to $\pm 10\%$ error. Quantum yields determined using an integrating sphere, estimated error $\pm 3\%$.

Emission data and Stern-Volmer analysis for 7a are given in Figure 78. The emission plot of the degassed, aerated and oxygen saturated solutions of 7a show a large difference between the emission intensity in the absence of oxygen and in the air equilibrated solution and the emission intensity is even weaker in the oxygen saturated solution. The Stern-Volmer plots produce straight line correlations and the gradients were determined to be 43 and 39 bar$^{-1}$ for emission intensity and radiative lifetimes respectively. The values obtained are within error of each other and are consistent with the Stern-Volmer relationship. The values measured for 7a are significantly higher than similar complexes measured, for example LeMercier et al. measured [(phen)$_2$Ru(phenCOOH)]$^{2+}$ in water and found a $K_{SV}$ of 5 bar$^{-1}$.\textsuperscript{135}
Figure 78: a) Emission of 7a in MeCN. Degassed (black), aerated (red) and oxygen saturated (blue). b) Stern-Volmer plot from 7a luminescence intensity (blue) and lifetime (red). The y axis refers to $I_0/I$ for the intensity slope and $\tau_0/\tau$ for the lifetime slope. ±2% in all measurements and $R^2 = 0.99$ for both slopes.
The Stern-Volmer plot for 7b is given in Figure 79. Again the gradients of the slopes give values within error of each other. The measured values of $K_{SV}$ are 39 and 45 bar$^{-1}$ for $I_0/I$ and $\tau_0/\tau$ respectively. These are very similar to those measured for 7a, meaning that the efficiency of triplet oxygen quenching is almost the same for these compounds, suggesting that changing cyclometallated ligands from ppy to pq does not significantly affect the oxygen quenching efficiency of the complex.

![Stern-Volmer plot from 7b luminescence intensity (blue) and lifetime (red). The y axis refers to $I_0/I$ for the intensity slope and $\tau_0/\tau$ for the lifetime slope. ±2% in all measurements and $R^2 = 0.99$ for both slopes.](image)

Figure 79: Stern-Volmer plot from 7b luminescence intensity (blue) and lifetime (red). The y axis refers to $I_0/I$ for the intensity slope and $\tau_0/\tau$ for the lifetime slope. ±2% in all measurements and $R^2 = 0.99$ for both slopes.

The $K_{SV}$ values for complex 7c are calculated to be significantly lower than the iridium complexes as shown by the Stern-Volmer plot in Figure 80. The $I_0/I$ and $\tau_0/\tau$ gradients are measured as 8.0 and 6.5 bar$^{-1}$ respectively. This suggests that the rhenium complex is not very efficiently quenched by triplet oxygen when compared to its iridium counterparts, but in comparison to [(phen)$_2$Ru(phenCOOH)]$^{2+}$ the efficiency of quenching is very similar. The lower value of $K_{SV}$ is likely due to the competing quenching mechanism of photoinduced electron transfer in the Re$^1$ complex being more efficient than $^3$O$_2$ quenching. Furthermore there is already quenching of the luminescence in the absence of triplet oxygen as shown by differences in the quantum yields and lifetimes.
Figure 80: Stern-Volmer plot from 7c luminescence intensity (blue) and lifetime (red). The y axis refers to \( I_0/I \) for the intensity slope and \( \tau_0/\tau \) for the lifetime slope. ±2% in all measurements and \( R^2 = 0.99 \) for both slopes.

### 3.2.3.2 Two-photon analysis

Two-photon analysis for complex 7a was carried out at the University of Bordeaux. The nonlinear process of two-photon spectroscopy was confirmed by power dependence measurements that indicated a quadratic relation of the emission intensity induced by different laser powers. The 2PEF emission spectra shown in Figure 81 is identical to the one photon emission spectra, showing that the same excited state is accessed by both methods.
The 2PA cross section measurements were measured using TPEF with fluorescein in 0.01 M NaOH as a reference. The two-photon cross-section values are shown in Figure 82 along with the linear absorption spectra, which demonstrates a very similar absorption process as expected for two-photon absorption. Compound 7a exhibits a 2PA cross-section (\(\sigma_2\)) of around 10 GM over a broad excitation range (800–1000 nm) due to population of the intra-ligand excited states in addition to the MLCT. Increased IL character at shorter wavelengths results in an increase in the \(\sigma_2\) value from 10 to 80 GM between 700 and 800 nm. These cross-section values are similar to those measured for an analogous Ru\(^{II}\) complex [Ru(phen)_2(7)][PF_6]_2 which was measured to be 10 GM at 900 nm and 50 GM at 750 nm. The very weak resonant absorption band attributed to the \(^3\)MLCT is relatively large by a two-photon process. This likely due to the symmetry and/or spin character of this transition now being formally allowed by the selection rules for 2PA.
Figure 82: Two-photon excitation (marked squares) and linear excitation (solid line) spectra of 7a in degassed acetonitrile. (One-photon at $2 \times 10^{-5}$ M, two-photon measurement at a concentration of $4 \times 10^{-5}$ M, measured by two photon excited fluorescence (2PEF) referenced to fluorescein in 0.01 M NaOH, $1 \times 10^{-4}$ M)

Attempted measurements of complexes 7b and 7c were carried out at the University of Manchester but measurements were not successful due to limitations of the set up. These limitations include a filter than overlaps with the emission and a dichroic mirror that is inefficient at wavelengths required. Based on the observed one photon absorption and luminescent properties complex 7b would be expected to exhibit similar two-photon properties to that of 7a, whereas complex 7c would be expected to show a weaker two-photon emission that that of 7a.

3.2.3.3 PDT studies

The efficient quenching of compounds 7a and 7b by triplet oxygen indicate that they are good candidates for PDT. To this end, preliminary in vitro experiments were carried out using 7a. Confocal microscopy was utilised to evaluate 7a as a potential photosensitiser in the treatment of C6 Glioma cells under two-photon irradiation. Glioma cells are responsible for tumours originating in the brain or central nervous system and are accountable for approximately 80% of all malignant brain tumours. Glioma tumours are
rarely curable and are divided into two major categories of high-grade and low-grade glioma. The prognosis of high-grade gliomas is generally poor at around 1 year, whereas low-grade gliomas have a more optimistic prognosis of around 15 years. The aggressiveness of these tumours, and incurability makes glioma cells a target of PDT treatment.

The effectiveness of 7a as a photosensitiser can be monitored by the change in cell morphology under two-photon irradiation, where the cells should change from elongated (fibroblast) shape to round when they become unhealthy. Three separate cell samples were prepared, two treated with 7a dissolved in 1 % DMSO and taken up into water at concentration of 10 and 1 mM and a control sample where the cells were not treated with 7a. The cell samples were incubated at 37 °C for 1 hour. After incubation the treated cells were checked for any damage due to the presence of the complex by confocal microscopy; no significant damage was observed. Each cell sample was irradiated at 740 nm at a 5 % laser power (32.5 μW) for 5 minutes and the cells were monitored at 15 minute intervals. The control sample was irradiated for 5 minutes and after a 15 minute interval it was further irradiated for another 5 minutes.

Cell images before and after irradiations for each of the three samples are shown in Figure 83 (all cell images can be found in Appendix C). The control sample indicated limited damage to the cells, with only 7 % of irradiated cells showing a change in morphology after 10 min of irradiation and 30 min of monitoring and a 14 % change of morphology after 45 min. No further changes in cell morphology was seen after 1 hour of monitoring, hence the irradiation alone does not adversely affect the cells. The 10 mM treated cells underwent larger changes in cell morphology with 54 % of cells showing morphology changes after 15 mins of monitoring and 72 % showing changes after 30 min. There were no further changes after 45 min and 1 hour of monitoring. The 1 mM treated samples all showed similar effects to the higher concentration of 7a with a 70 % change in cell morphology after irradiation and 1 hour of monitoring.
Figure 83: Confocal microscopy images from before and after irradiation. The irradiated area is highlighted with a blue box. a) Control sample before irradiation, b) control sample after 10 min irradiation and 1 hour monitoring, c) zoom area of irradiation of the control sample before irradiation, d) zoom area of irradiation of the control sample after 10 min of irradiation, e) 10 mM doped cells before irradiation, f) 10 mM doped cells after 5 min irradiation and 1 hour of monitoring, g) zoom area of irradiation of 10 mM doped cells before irradiation, h) zoom area of irradiation of 10 mM doped cells after 5 min of irradiation, i) 1 mM doped cells before irradiation, j) 1 mM doped cells after 5 min, k) zoom area of irradiation of 1 mM doped cells before irradiation, l) zoom area of irradiation of 1 mM doped cells after 5 min irradiation.

3.2.4 Computational Studies

To aid better understanding of the electronic and optical properties of the complexes TD-DFT calculations have been carried out on the complexes 7a, 7b and 7c using Gaussian 09. The obtained crystal structures were used in the geometry optimisation of complexes 7a and 7c, and the input structure for complex 7b was modified from the structure obtained for complex 7a. The hexyl chains of the ligands have been replaced with methyl groups (denoted 7a', 7b' and 7c') to simplify calculations, making them less computationally expensive. Geometry optimisation was carried out at the B3LYP level, with cc-PQVZ-pp basis set and a relativistic SDD pseudopotential on the metal centres (Ir, Re) and 6-311G++ on all other atoms. TD-DFT was performed at the CAM-B3LYP level,
due to this functional being able to estimate charge transfer excitations with a larger degree of accuracy. Solvent effects were accounted for in the TD-calculations by using a solvent continuum model (CPCM)\textsuperscript{117,118} with acetonitrile and dichloromethane for Ir and Re respectively. The first 50 states were calculated for each compound and the UV-visible spectra and transition information were simulated using the GaussSum program.\textsuperscript{119}

### 3.2.4.1 Structures

In comparison to the X-ray crystal structure the optimised structure of 7a' shows slightly shorter bond lengths for the Ir-N (phen) and generally longer bond lengths for the Ir-ppy bonds, but none differ more than 0.1 Å from the crystal structure. The bond angles in 7a' differ by less than 1° when compared to the crystal structure. Optimisation of 7a' affords a dihedral angle of 55° between the phenanthroline and the fluorenyl unit of the ligand, which is slightly higher than in the crystal structure. The optimised structure of 7c' shows differences in bond lengths of no more than 0.07 Å when compared to the crystal structure and the N-Re-N bond angle differs only by 0.5°. The measured torsion angle between the phenanthroline and fluorenyl unit in 7c' of 52° differs from the crystal structure measured torsion angle of 62°.

### 3.2.4.2 Absorption Spectra

The calculated and experimental UV-visible spectra of 7a' and 7a are shown in Figure 84. Predicted transition energies are given in Table 16 and selected orbitals are shown in Figure 85. The predicted profile has an acceptable match with the experimental data at higher energies but it fails to predict the low energy shoulder bands below 350 nm. The experiential data shows a peak at 330 which matches with the calculated transition at 334 nm. The lowest energy band of the calculated spectra matches well with the shoulder peak at 305 nm in the experimental spectra. The low energy shoulder band (ca. 330 nm) are calculated to be a result of one transition, and the low energy peak (ca. 310 nm) is a result of multiple transitions. The higher energy peak is a result of the a vast number of transitions.
Figure 84: TD-DFT-calculated (blue) and experimental (green) UV-visible spectra of 7a and 7a’ in MeCN. The ε-axes refers to experimental data only and the vertical axes of the calculated data are scaled to match the main experimental absorbance. The oscillator strength axis refer to the individual calculated transitions (red).

Table 16: Selected transition data based on B3LYP/cc-QZVP-pp/SDD Geometries of 7a’

<table>
<thead>
<tr>
<th>Compound</th>
<th>Transition</th>
<th>ΔE / nm (eV)</th>
<th>f_os</th>
<th>Major contributions</th>
</tr>
</thead>
<tbody>
<tr>
<td>7a</td>
<td>1</td>
<td>355.55 (3.49)</td>
<td>0.00</td>
<td>HOMO → LUMO (91 %)</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>334.02 (3.71)</td>
<td>0.14</td>
<td>HOMO → LUMO+2 (85 %)</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>319.61 (3.88)</td>
<td>0.22</td>
<td>HOMO-4 → LUMO (32 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO-1 → LUMO (30 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO → LUMO+1 (12 %)</td>
</tr>
<tr>
<td>7</td>
<td>7</td>
<td>306.07 (4.05)</td>
<td>0.45</td>
<td>HOMO-1 → LUMO+1 (52 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO-3 → LUMO (17 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO-5 → LUMO (10 %)</td>
</tr>
<tr>
<td>9</td>
<td>9</td>
<td>279.47 (4.17)</td>
<td>0.15</td>
<td>HOMO-4 → LUMO+1 (45 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO-2 → LUMO+1 (15 %)</td>
</tr>
<tr>
<td>11</td>
<td>11</td>
<td>276.27 (4.49)</td>
<td>0.14</td>
<td>HOMO-3 → LUMO+2 (66 %)</td>
</tr>
<tr>
<td>14</td>
<td>14</td>
<td>271.62 (4.56)</td>
<td>0.16</td>
<td>HOMO-2 → LUMO+3 (29 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO-4 → LUMO+3 (17 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO-5 → LUMO+2 (12 %)</td>
</tr>
<tr>
<td>18</td>
<td>18</td>
<td>262.92 (4.72)</td>
<td>0.29</td>
<td>HOMO-1 → LUMO+4 (16 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO-9 → LUMO+1 (11 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO-1 → LUMO+5 (10 %)</td>
</tr>
<tr>
<td>20</td>
<td>20</td>
<td>261.68 (4.74)</td>
<td>0.25</td>
<td>HOMO-4 → LUMO+3 (36 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO-2 → LUMO+5 (17 %)</td>
</tr>
</tbody>
</table>
Chapter 3: \( d^6 \) Metal Complexes for Applications in Two-Photon PDT

The transitions at 334 nm has a major contribution from a HOMO to LUMO+2 transition. The HOMO shows \( \pi \) bonding over the ppy ligands with d-orbital contributions and the LUMO+2 is largely \( \pi^* \) antibonding over the ppy ligands. This transition is a result of MLCT and ILCT. The peak at 310 nm incorporates two strong transitions and two weaker transitions. The strong transitions are made up of contributions from the HOMO-5, HOMO-4, HOMO-3 and HOMO-1 all transitioning to the LUMO, along with contributions from the HOMO and HOMO-1 transitioning into the LUMO+1. The HOMO-5, HOMO-4 and HOMO-3 all exhibit Ir(d) character but differ in their location of \( \pi \) electron density. Both HOMO-5 and HOMO-3 feature their \( \pi \) electron density over the ppy ligands, whereas the HOMO-4 has pi character on the phenanthroline portion of ligand \( 7' \). In contrast the HOMO-1 consists of \( \pi \)-electron density over the fluorenyl portion of ligand \( 7' \). The LUMO and LUMO+1 are predominately \( \pi^* \) antibonding over the phenanthroline portion of ligand \( 7' \).
Figure 85: TD-DFT derived orbitals involved in the low energy transitions of complex 7a'.
(isosurface value 0.03 au)

The calculated and experimental UV-visible spectra of 7b' is shown in Figure 86. Predicted transition energies are given in Table 17 and selected orbitals are shown in Figure 87. The calculated spectrum displays some similarities to the experimental data but again fails to predict the low energy shoulder. The low energy structured band at 310 nm matches well with a shoulder peak on the experimental data and is predicted to encompass multiple transitions. The higher energy band at 260 nm is a result of multiple predicted transitions.
Chapter 3: d<sup>6</sup> Metal Complexes for Applications in Two-Photon PDT

Figure 86: TD-DFT-calculated (blue) and experimental (green) UV-vis spectra of 7b and 7b' in MeCN. The ε-axes refers to experimental data only and the vertical axes of the calculated data are scaled to match the main experimental absorbance. The oscillator strength axis refer to the individual calculated transitions (red).

Table 17: Selected transition data based on B3LYP/cc-QVZP-pp/SDD Geometries of 7b'

<table>
<thead>
<tr>
<th>Compound</th>
<th>Transition</th>
<th>ΔE / nm (eV)</th>
<th>f&lt;sub&gt;os&lt;/sub&gt;</th>
<th>Major contributions</th>
</tr>
</thead>
<tbody>
<tr>
<td>7b'</td>
<td>1</td>
<td>355.71 (3.49)</td>
<td>0.00</td>
<td>HOMO → LUMO (87 %)</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>341.99 (3.63)</td>
<td>0.13</td>
<td>HOMO → LUMO+2 (72 %)</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>309.02 (4.01)</td>
<td>0.10</td>
<td>HOMO-3 → LUMO (33 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO-6 → LUMO (29 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO-1 → LUMO+1 (20 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO-1 → LUMO+1 (48 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO-3 → LUMO (19 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO-6 → LUMO (11 %)</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>306.14 (4.05)</td>
<td>0.43</td>
<td>HOMO-4 → LUMO+1 (21 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO → LUMO+4 (19 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO-4 → LUMO+3 (18 %)</td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>280.09 (4.43)</td>
<td>0.37</td>
<td>HOMO-2 → LUMO+4 (18 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO-3 → LUMO+3 (16 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO-4 → LUMO+6 (13 %)</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>278.65 (4.45)</td>
<td>0.12</td>
<td>HOMO-2 → LUMO+1 (11 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO-3 → LUMO+3 (11 %)</td>
</tr>
<tr>
<td></td>
<td>22</td>
<td>263.96 (4.70)</td>
<td>0.14</td>
<td>HOMO-2 → LUMO+1 (11 %)</td>
</tr>
</tbody>
</table>

The low energy band is predicted to originate from numerous transitions, the strongest of which are a mixture of HOMO-1, HOMO-3, and HOMO-6 to LUMO and LUMO+1. HOMO-1 has pi electron density localised over the fluorenyl unit of the ligand, HOMO-3
is largely pi in character on the pq ligands with Ir(d) character and HOMO-6 has Ir(d) character and pi electron density over the pq and phen portions of the molecule but also displays small amounts of electron density on the fluorenyl portion of the molecule. Both LUMOs are $\pi^*$ antibonding over the phenanthroline unit of the ligand. The calculated data indicates this band is a result of ILCT mixed with MLCT and a small LLCT component.

Figure 87: TD-DFT derived orbitals involved in the low energy transitions of complex 7b' (isosurface value 0.03 au)
The calculated and experimental UV-visible spectra of 7c is shown in Figure 88. Predicted transition energies are given in Table 18 and selected orbitals are shown in Figure 89. The predicted profile fails to calculate the weak absorbance band ca. 420 nm. The lowest energy peak is shifted by approximately 30 nm from the experimental spectra. The low energy peak in the experimental spectrum matches with the shoulder on the lowest energy peak of the calculated spectrum and is a result of one weak and one strong transition. The main body of the low energy peak in the spectrum is a result of a multiple transitions.

![Figure 88: TD-DFT-calculated (blue) and experimental (green) UV-vis spectra of 7c and 7c' in DCM. The ε-axes refers to experimental data only and the vertical axes of the calculated data are scaled to match the main experimental absorbance. The oscillator strength axis refer to the individual calculated transitions (red).](image)
**Table 18: Selected transition data based on B3LYP/cc-QVZP-pp/SDD Geometries of 7c’**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Transition</th>
<th>ΔE / nm (eV)</th>
<th>f_{os}</th>
<th>Major contributions</th>
</tr>
</thead>
<tbody>
<tr>
<td>7c’</td>
<td>1</td>
<td>349.59 (3.55)</td>
<td>0.00</td>
<td>HOMO-1 → LUMO (92 %)</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>340.76 (3.64)</td>
<td>0.18</td>
<td>HOMO-2 → LUMO (73 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO → LUMO (19 %)</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>313.18 (3.96)</td>
<td>0.08</td>
<td>HOMO-3 → LUMO (60 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO → LUMO (10 %)</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>310.60 (3.99)</td>
<td>0.36</td>
<td>HOMO → LUMO+1 (49 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO-3 → LUMO (16 %)</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>306.50 (4.05)</td>
<td>0.13</td>
<td>HOMO-1 → LUMO+1 (27 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO-5 → LUMO (19 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO → LUMO (13 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO → LUMO+1 (11 %)</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>299.02 (4.15)</td>
<td>0.04</td>
<td>HOMO-1 → LUMO+1 (65 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO → LUMO (13 %)</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>294.83 (4.21)</td>
<td>0.12</td>
<td>HOMO-2 → LUMO+1 (80 %)</td>
</tr>
</tbody>
</table>

The shoulder transitions have contributions from HOMO-2 and HOMO to LUMO transitions. The HOMO is largely π bonding over the fluorenyl unit of the ligand and the HOMO-2 is made up of a large Re(d) contribution with π-back bonding from the three carbonyl ligands and a Cl(p) contribution. The LUMO is π* antibonding over the phenanthroline unit of the ligand, thus the shoulder is a result of a MLCT transition with a small contribution from an ILCT component. The transition forming the main low energy peak result are similar to those of the shoulder with additional contributions from HOMO-1, HOMO-3 and HOMO-5 to LUMO and LUMO+1. HOMO-1 and HOMO-2 are very similar with a smaller contribution on the equatorial carbonyl group. HOMO-3 is largely Re(d) with π back bonding from the carbonyl groups *trans* to the ligand. The orbitals in HOMO-5 are largely π bonding, located over the phenanthroline and on the terminal aryl group of the fluorenyl moiety of the ligand.
Figure 89: TD-DFT derived orbitals involved in the transitions of complex 7e' (isosurface value 0.03 au)
3.3 Conclusion

A phenanthroline ligand bearing a fluorenyl unit has been synthesised and successfully coordinated to ppy and pq cyclometallated iridium(III) complexes as well as a rhenium(I) carbonyl complex. Ligand and complex syntheses were confirmed to be successful by $^1$H NMR spectroscopy, MS and elemental analysis. Absorption spectra indicated the presence of broad, weak MLCT transition bands at low energies and bands in the UV region attributed to ILCT transitions and $\pi-\pi^*$ transitions. These data were supported by TD-DFT calculations. Photophysical characterisations showed typical iridium and rhenium centred luminescence with all complexes exhibiting long lived luminescence lifetimes ($\mu$s domain) indicating emission from predominantly $^3$MLCT states in degassed solutions. Further evidence for $^3$MLCT character was found when lifetimes measured in aerated solutions were significantly decreased when compared to the degassed solutions. This demonstrated that the $^3$MLCT state is significantly quenched by $^3$O$_2$. The Stern-Volmer data calculated for both of the complexes 7a and 7b produced a $K_{SV}$ of around 40 bar$^{-1}$ indicating high efficiency $^3$O$_2$ sensitisation. By contrast, the rhenium complex exhibited a $K_{SV}$ of around 7 bar$^{-1}$, which still indicated $^3$O$_2$ quenching is taking place but it is not as efficient as in the Ir(III) derivatives.

Two photon analysis for compound 7a showed a quadric dependence on laser power and maximum cross-section measurement of 78 GM at 700 nm. This led to preliminary in vitro cell studies which indicated that 7a is a good candidate as a 2PE-PDT photosensitiser due to efficient cell damage in C6 Glioma cells treated with 7a after two-photon irradiation conditions. This was further confirmed the fact that by cells irradiated in the absence of the complex showed minimal changes in morphology. Two photon analysis of complexes 7b and 7c were unsuccessful due to limitations of the laser set-up available for these measurements.

In addition to potential applications of 7a as a PDT photosensitiser, all complexes investigated in this chapter could also be utilised for (cellular) oxygen sensing. This is based on the efficiency of luminescence quenching displayed by all complexes when in the presence of ground state oxygen triplet oxygen.
4 Chapter 4: An Extended bis Fluorenyl Chromophore for 2PA Applications

4.1 Introduction

Extension of the 5-substituted phenanthroline based fluorenyl unit of the previous chapter further demonstrated that increasing π-conjugation is vital in the design of ligands for 2PA. Upon adding an additional fluorenyl unit to the phenanthroline ligand, the corresponding Ru^{II} complexes exhibited a large increase in the two-photon cross-section.\(^\text{121}\)

4.2 Results and Discussion

The work described in this chapter was conducted as a joint EPSRC/University of Manchester funded collaboration within the group of Dr Gilles Lemercier (University of Reims, France). The synthesis of ligand 8 was carried out by Dr Gilles Lemercier. The remainder of the work in this chapter was performed solely by the author of this thesis.

4.2.1 Synthesis and Characterisation of Complexes

Ligand 8 (Scheme 18) is an extension of 7 in terms of an additional fluorenyl group. The ligand was synthesised and supplied by Gilles Lemercier, by means of a Suzuki cross coupling between 6 and \((9,9',9'-\text{tetrahexyl}-9H,9'H-[2,2'-\text{bifluoren}]-7-\text{yl})\)boronic acid.\(^\text{121}\)

In order to synthesise the bis-fluorenyl unit, the fluorenyl unit bearing a boronic acid was reacted with 2-iodo-7-bromo-9,9-dihexylfluorenyl due to the selectivity of the Suzuki cross-coupling for iodine over bromine. The bromine in the product was then converted to a boronic acid in order to synthesise the ligand 8 by means of a second Suzuki cross coupling reactions (Scheme 18).

\[
\text{Scheme 18: Synthetic route to the bis-fluorenyl-phenanthroline ligand 8}
\]

\[\text{Scheme 18: Synthetic route to the bis-fluorenyl-phenanthroline ligand 8}\]
The complexes in the chapter are analogous to the complexes in the Chapter 3 and were synthesised using the same methodology. Complex 8a and 8b (ppy and pq respectively) were synthesised by reacting the corresponding cyclometallated iridium dimer in MeOH with 8 in DCM at reflux temperature for 18 hours at which point the complexes were precipitated as the PF$_6$ salts and purified by trituration with hexane. Compounds 8a and 8b were successfully synthesized in high yield and purity, as confirmed by $^1$H NMR spectroscopy, mass spectrometry and elemental analysis. Complex 8c was synthesised by heating ligand 8 with rhenium(I)pentacarbonyl chloride in toluene to reflux temperature for 48 hrs whereby upon cooling, the product was isolated by filtration in a 92 % yield as a yellow crystalline solid. Analytical analysis of the complex by $^1$H NMR spectroscopy, mass spectrometry and elemental analysis confirmed successful synthesis and purity.

**Figure 90: Structures of complexes 8a, 8b and 8c**

### 4.2.2 Luminescence analysis

Solution state luminescence was carried out in MeCN for the complexes 8a and 8b. Compound 8c was studied in dichloromethane due to insolubility in MeCN. All compounds were studied in degassed solutions by excitation at 400 nm and the excitation spectra were recorded at the emission maxima. Luminescence lifetimes were measured at 405 nm with a picosecond pulsed diode laser and quantum yields were determined using 400 nm excitation. Measured data are shown in Table 19.
Table 19: Data from photophysical measurements. 8a and 8b measured in degassed MeCN, 8c measured in DCM. All emission spectra and quantum yields were measured at 400 nm, excitation spectra were taken at the emission maxima. Lifetimes measured with 405 diode laser

<table>
<thead>
<tr>
<th>Compound</th>
<th>Abs / λ&lt;sub&gt;max&lt;/sub&gt; (ε / dm&lt;sup&gt;3&lt;/sup&gt; mol&lt;sup&gt;-1&lt;/sup&gt; cm&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>λ&lt;sub&gt;em&lt;/sub&gt;/ nm</th>
<th>λ&lt;sub&gt;ex&lt;/sub&gt;/ nm</th>
<th>τ / μs</th>
<th>ϕ / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>8a</td>
<td>265 (57400), 334 (56900)</td>
<td>603</td>
<td>336</td>
<td>1.70</td>
<td>8</td>
</tr>
<tr>
<td>8b</td>
<td>215 (141000), 331 (64900)</td>
<td>601</td>
<td>332</td>
<td>1.97</td>
<td>22</td>
</tr>
<tr>
<td>8c</td>
<td>333 (45000)</td>
<td>620</td>
<td>335</td>
<td>0.25</td>
<td>2</td>
</tr>
</tbody>
</table>

Lifetimes subject to ± 10% error. Quantum yields determined using an integrating sphere, estimated error ± 3%.

The absorption spectra are shown in Figure 91. All complexes exhibit the broad/weak absorbance in the range 400-450 nm indicative of a 3MLCT transition and higher energy bands that can be attributed to ILCT transitions and π-π* transitions.

Figure 91: UV-vis data for complexes 8a (black), 8b (red) and 8c (green). Both 8a and 8b were recorded in MeCN and 8c was recorded in DCM

Excitation and emission spectra of 8a and 8b are given in Figure 92. Both compounds exhibit emission typical of an iridium centred 3MLCT transition indicated by the broad featureless emission at 603 and 601 nm for 8a and 8b respectively. The lifetimes of 1.70 μs (8a) and 1.96 μs (8b) are typical of cyclometalated iridium complexes. In contrast to the
lifetimes measured for 7a and 7b (0.97 and 0.82 μs respectively) these are much longer likely due to the increased conjugation from the additional fluorenyl unit. The emission quantum yield for 8a, measured as 8 % is much lower than that of 8b (22 %) suggesting a larger amount of non-radiative decay in 8a which may be attributed to the increased rigidity of the IrIII centre with the pq ligand in 8b. In comparison to the analogous compound 7a the quantum yield of 8a is much lower indicating again that there is a larger degree of competitive non-radiative decay processes in this molecule. By contrast, complex 8b, has a measured quantum yield identical to that of 7b of 22 %.
Figure 92: Excitation (black), and emission (red) spectra of 8a (top) and 8b (bottom) in MeCN at room temperature.

Figure 93 shows the emission and excitation spectra of 8c, which shows a broad featureless emission at 620 nm. The lifetime is shorter than that of the cyclometallated iridium complexes at 245 ns but typical of Re¹ polypyridyl complexes, and the quantum yield is
also much lower at 2%. In comparison to $7c$, the measured values are lower, suggesting more non-radiative decay processes with the more conjugated ligand in this system.

Figure 93: Excitation (black), and emission (red) spectra of $8c$ in MeCN.

### 4.2.3 Triplet Oxygen Quenching

Complexes $8a$, $8b$ and $8c$ were also studied in aerated and oxygenated solutions along with the degassed data in order to determine the degree of triplet oxygen quenching on the luminescence. Data for the lifetimes and quantum yields in degassed, aerated and oxygen saturated solutions are given in Table 20.

Table 20: Lifetime and quantum yield data for degassed, aerated and oxygen saturated solutions of $8a$, $8b$ and $8c$. $8a$ and $8b$ measured in MeCN, $8c$ measured in DCM. Quantum yields were measured at 400 nm. Lifetimes measured with a ps pulsed 405 diode laser

<table>
<thead>
<tr>
<th>Compound</th>
<th>Degassed $\tau$ / ns</th>
<th>Aerated $\tau$ / ns</th>
<th>Oxygenated $\tau$ / ns</th>
<th>Degassed $\phi$ / %</th>
<th>Aerated $\phi$ / %</th>
<th>Oxygenated $\phi$ / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>$8a$</td>
<td>1700</td>
<td>141</td>
<td>27</td>
<td>8</td>
<td>0.41</td>
<td>&gt;0.1</td>
</tr>
<tr>
<td>$8b$</td>
<td>1970</td>
<td>117</td>
<td>29</td>
<td>22</td>
<td>1.33</td>
<td>0.32</td>
</tr>
<tr>
<td>$8c$</td>
<td>250</td>
<td>78</td>
<td>26</td>
<td>2</td>
<td>0.45</td>
<td>&gt;0.1</td>
</tr>
</tbody>
</table>

Lifetimes subject to ±10 % error. Quantum yields determined using an integrating sphere, estimated error ±3 %.
Stern-Volmer analysis for 8a is given in Figure 94. Both Stern-Volmer plots produce a straight-line correlation with gradients of 66 and 62 bar\(^{-1}\) for emission intensity and radiative lifetimes respectively. These values are within error of each other and are consistent with the Stern-Volmer relationship. In comparison to the analogous complex 7a, 8a has much higher \(K_{SV}\) values. This would suggest that the increase in conjugation of the bis fluorenyl phenanthroline ligand in complex 8a has a significant effect on the efficiency of triplet oxygen quenching. This is possibly correlated to the increased lifetime of the emissive excited state in 8a compared to 7a. A similar result to this was found by Castellano with pyrenyl-ligands coordinated to a Ru\(^{ll}\) centre.\(^{136}\) Castellano describes that increasing the number of pyrenyl chromophores coordinated increases the excited state lifetime. This effect was attributed to the additional conjugation shifting the excited state equilibrium between the inorganic and organic chromophore in favour of the pyrene reservoir.

![Figure 94: Stern-Volmer plot from 8a luminescence intensity (blue) and lifetime (red). The y axis refers to \(I_0/I\) for the intensity slope and \(\tau_o/\tau\) for the lifetime slope. Estimated error \(\pm 2\%\) in all measurements and \(R^2 = 0.99\) for both slopes.](image)

All Stern-Volmer constants measured are given in Table 21. As with 7a and 7b the \(K_{SV}\) values of 8a and 8b are similar to each other showing there is very little difference between the use of a ppy or pq ligand on the efficiency of oxygen quenching. There are however
much higher $K_{SV}$ values measured when increased conjugation is used in the ligand in all iridium(III) compounds when compared to the analogous complexes of the previous chapter. The Re$^1$ complex, $8c$, data are very similar (within error) to the values obtained for $7c$, suggesting that the additional conjugation of ligand 8 does not affect the efficiency of the oxygen quenching in the rhenium complexes.

Table 21: Stern-Volmer constant data for complexes $8a$, $8b$ and $8c$ given in bar$^{-1}$ for both emission data and lifetime data from excitation at 400 nm measured at room temperature.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$K_{SV}$ Emission / bar$^{-1}$</th>
<th>$K_{SV}$ Lifetime / bar$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$8a$</td>
<td>66</td>
<td>62</td>
</tr>
<tr>
<td>$8b$</td>
<td>57</td>
<td>69</td>
</tr>
<tr>
<td>$8c$</td>
<td>7</td>
<td>8</td>
</tr>
</tbody>
</table>

*Estimated error ±2% in all measurements*

### 4.2.4 Two-photon Absorption

Attempted measurements of the complexes in this chapter were attempted with the two-photon set-up at the University of Manchester without success. As in the previous chapter the current laser set up was not sufficiently powerful for these complexes during the timeframe of the PhD. It would be expected that the two-photon cross-sections would be larger than measured for $7a$, due to the increased conjugation allowing for a larger absorption.

### 4.2.5 Computational Studies

To aid better understanding of the electronic and optical properties of the complexes TD-DFT calculations have been carried out on the complexes $8a$, $8b$ and $8c$ using Gaussian 09. The hexyl chains of the ligands have been replaced with methyl groups (denoted $8a'$, $8b'$ and $8c'$) to simplify calculations, making them less computationally expensive. Geometry optimisation was carried out at the B3LYP level, with cc-PQVZ-pp basis set and a relativistic SDD pseudopotential on the metal centres (Ir, Re) and 6-311G++ on all other atoms. TD-DFT was performed at the CAM-B3LYP level, due to this functional being able to estimate charge transfer excitations with a larger degree of accuracy. Solvent effects were accounted for in the TD-calculations by using a solvent continuum model (CPCM) with acetonitrile and dichloromethane for Ir and Re respectively. The first 50 states were calculated for each compound and the UV-visible spectra and transition information were simulated using the GaussSum program.
4.2.5.1 Absorption

The calculated and experimental UV-visible spectra of 8a' and 8a are shown in Figure 95. Predicted transition energies are given in Table 22 and selected orbitals are shown in Figure 96. The overall profile of the calculated spectra does not match the experimental data very well, however the low energy peak of the calculated data matches well with the shoulder at 334 nm in the experimental data. This low energy peak in the calculated spectra is a result of one strong transition and a few weaker transitions.

Figure 95: TD-DFT-calculated (blue) and experimental (green) UV-vis spectra of 8a and 8a' in MeCN. The ε-axes refers to experimental data only and the vertical axes of the calculated data are scaled to match the main experimental absorbance. The oscillator strength axis refer to the individual calculated transitions (red).
### Table 22: Selected transition data based on B3LYP/cc-QVZP-pp/SDD Geometries of $8a'$

<table>
<thead>
<tr>
<th>Compound</th>
<th>Transition</th>
<th>$\Delta E / \text{nm (eV)}$</th>
<th>$f_{os}$</th>
<th>Major contributions</th>
</tr>
</thead>
<tbody>
<tr>
<td>$8a'$</td>
<td>1</td>
<td>355.66 (3.48)</td>
<td>0.00</td>
<td>HOMO-1 $\rightarrow$ LUMO (90 %)</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>333.82 (3.71)</td>
<td>0.15</td>
<td>HOMO-1 $\rightarrow$ LUMO+2 (85 %)</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>324.39 (3.82)</td>
<td>1.60</td>
<td>HOMO $\rightarrow$ LUMO+1 (22 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO $\rightarrow$ LUMO+4 (18 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO-2 $\rightarrow$ LUMO (14 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO $\rightarrow$ LUMO (11 %)</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>317.46 (3.91)</td>
<td>0.35</td>
<td>HOMO-5 $\rightarrow$ LUMO (18 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO $\rightarrow$ LUMO+1 (16 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO-2 $\rightarrow$ LUMO (13 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO-1 $\rightarrow$ LUMO+1 (10 %)</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>294.41 (4.21)</td>
<td>0.51</td>
<td>HOMO $\rightarrow$ LUMO+4 (38 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO-2 $\rightarrow$ LUMO+1 (17 %)</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>275.95 (4.49)</td>
<td>0.13</td>
<td>HOMO-4 $\rightarrow$ LUMO+2 (65 %)</td>
</tr>
</tbody>
</table>

The strong transition in the lowest energy band is calculated to be a result of multiple orbitals contributions. It is the result of transitions from the HOMO to LUMO, LUMO+1 and LUMO+4 with a contribution from a transition from the HOMO-2 to the LUMO. Both the HOMO and HOMO-2 are largely $\pi$ bonding over both the fluorenyl units of the molecule with the HOMO-2 also containing a small orbital contribution from the iridium. The LUMO and LUMO+1 are both $\pi^*$ antibonding over the phenanthroline moiety of the ligand with a small iridium contribution exhibited by the LUMO and the LUMO+4 is $\pi^*$ antibonding over the fluorenyl unit. These transitions are all indicative of an ILCT. The weaker transitions which contribute to this low energy band are calculated to be a result of multiple transitions. The transition at 333 nm is an MLCT transition from the HOMO-1, which has a large Ir(d) character and $\pi$ electron density over the phenyl portion of the ppy ligand, to the LUMO+2, which is largely $\pi^*$ antibonding over the ppy ligands. The weak transition at 317 nm is a result of transitions from the HOMO-2 and HOMO-5 into the LUMO, and HOMO and HOMO-1 into the LUMO+1. The HOMO-5 exhibits orbital mixing from the Ir(d) with the coordinated carbons from the ppy ligand. These bands can be attributed to an MLCT transition with a small contribution from an LLCT transition.
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Figure 96: TD-DFT derived orbitals involved in the low energy transitions of complex 8a' (isosurface value 0.03 au)

The calculated and experimental UV-visible spectra of 8b' and 8b are shown in Figure 97. Predicted transition energies are given in Table 23 and selected orbitals are shown in Figure 98. The predicted profile matches well with the experimental data with the low
energy peaks being only slightly shifted from each other with a 10 nm difference. This low energy band is calculated to be a result of one strong transition and many weaker transitions.

Figure 97: TD-DFT-calculated (blue) and experimental (green) UV-vis spectra of 8b and 8b′ in MeCN. The ε-axes refers to experimental data only and the vertical axes of the calculated data are scaled to match the main experimental absorbance. The oscillator strength axis refers to the individual calculated transitions (red).
Table 23: Selected transition data based on B3LYP/cc-QVZP-pp/SDD Geometries of 8b′

<table>
<thead>
<tr>
<th>Compound</th>
<th>Transition</th>
<th>ΔE / nm (eV)</th>
<th>f_osc</th>
<th>Major contributions</th>
</tr>
</thead>
<tbody>
<tr>
<td>8b′</td>
<td>1</td>
<td>356.04 (3.48)</td>
<td>0.13</td>
<td>HOMO-1→LUMO (86 %)</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>342.00 (3.63)</td>
<td>0.13</td>
<td>HOMO-1→LUMO+2 (71 %)</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>324.30 (3.82)</td>
<td>1.65</td>
<td>HOMO→LUMO+1 (21 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO→LUMO+4 (19 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO-3→LUMO (14 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO→LUMO (11 %)</td>
</tr>
<tr>
<td>5</td>
<td>319.37 (3.88)</td>
<td>0.24</td>
<td></td>
<td>HOMO-1→LUMO+1 (61 %)</td>
</tr>
<tr>
<td></td>
<td>316.25 (3.92)</td>
<td>0.16</td>
<td></td>
<td>HOMO-3→LUMO (16 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO-6→LUMO (12 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO-1→LUMO+1 (11 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO-5→LUMO (11 %)</td>
</tr>
<tr>
<td>10</td>
<td>294.39 (4.21)</td>
<td>0.48</td>
<td></td>
<td>HOMO→LUMO+4 (38 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO-3→LUMO+1 (15 %)</td>
</tr>
<tr>
<td>14</td>
<td>280.05 (4.43)</td>
<td>0.37</td>
<td></td>
<td>HOMO-1→LUMO+5 (25 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO-5→LUMO+3 (20 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO-5→LUMO+1 (14 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO-4→LUMO+2 (13 %)</td>
</tr>
<tr>
<td>17</td>
<td>277.21 (4.47)</td>
<td>0.11</td>
<td></td>
<td>HOMO-4→LUMO+1 (23 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO-8→LUMO+1 (15 %)</td>
</tr>
</tbody>
</table>

The calculations show that the lowest energy peak originates from numerous transition, the strongest of which at 324 nm has a very large oscillator strength resulting in the peak maxima of the band. This is predicted to be a mixture of HOMO to LUMO, LUMO+1 and LUMO+4 transitions with a HOMO-3 to LUMO+1 transition also contributing. The HOMO and HOMO-3 are both π-bonding in character over the fluorenyl units with the HOMO-3 also containing a small Ir(d) contribution. The LUMO and LUMO+1 are largely π* antibonding character on the phenanthroline moiety with the LUMO also containing a small Ir(d) contribution. The LUMO+4 is π* antibonding over the fluorenyl unit of the fluorenyl ligand. Therefore this strong transition can be attributed to an ILCT transition. The weaker transitions that contribute to this band of the calculated spectra are calculated and can be assigned to a MLCT which can be seen in such transitions as HOMO-1, which has a large electron density around the Ir^{III} centre, to the LUMO+2 which exhibits π* antibonding character over the pq ligands.
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Figure 98: TD-DFT derived orbitals involved in the transitions of complex 8b' (isosurface value 0.03 au)

The calculated and experimental UV-visible spectra of 8c' and 8c are shown in Figure 99. Predicted transition energies are given in Table 24 and selected orbitals are shown in Figure 100. The lowest energy band in the predicted spectra is a close match to that of the experimental data with a slight shift between them of approximately 10 nm. This lowest
energy peak of the calculated spectrum is a result of multiple weak transitions and one strong transition. The overall profile of the calculated spectra fails to match well with the higher energy bands seen in the experimental data.

![Figure 99: TD-DFT-calculated (blue) and experimental (green) UV-vis spectra of 8c and 8c' in DCM. The ε-axes refers to experimental data only and the vertical axes of the calculated data are scaled to match the main experimental absorbance. The oscillator strength axis refer to the individual calculated transitions (red).](image)

**Table 24: Selected transition data based on B3LYP/cc-QVZ-pp/SDD Geometries of 8c'**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Transition</th>
<th>ΔE / nm (eV)</th>
<th>f_os</th>
<th>Major contributions</th>
</tr>
</thead>
<tbody>
<tr>
<td>8c'</td>
<td>1</td>
<td>349.59 (3.54)</td>
<td>0.00</td>
<td>HOMO-1→LUMO (91 %)</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>341.11 (3.63)</td>
<td>0.33</td>
<td>HOMO-2→LUMO (76 %)</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>324.32 (3.82)</td>
<td>1.53</td>
<td>HOMO→LUMO+1 (37 %)</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td></td>
<td></td>
<td>HOMO→LUMO+2 (27 %)</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>308.58 (4.02)</td>
<td>0.08</td>
<td>HOMO-2→LUMO (20 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO-4→LUMO (17 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO-8→LUMO (14 %)</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>299.42 (4.14)</td>
<td>0.21</td>
<td>HOMO-2→LUMO+1 (51 %)</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>291.15 (4.52)</td>
<td>0.18</td>
<td>HOMO-3→LUMO+1 (24 %)</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>290.24 (4.27)</td>
<td>0.05</td>
<td>HOMO-2→LUMO+4 (38 %)</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td></td>
<td></td>
<td>HOMO-3→LUMO+1 (14 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO-3→LUMO+4 (11 %)</td>
</tr>
</tbody>
</table>
The calculated band at 326 nm is a result of one strong transition, which has major contributions from the HOMO to the LUMO+1 and LUMO+2. The transition HOMO to LUMO+1 transition can be described as an ILCT where the HOMO is largely $\pi$ bonding over the fluorenyl units of the ligand and the LUMO+1 has electron density in $\pi^*$ antibonding orbitals over the phenanthroline portion of the molecule. The transition from HOMO to LUMO+2 can be assigned to a $\pi-\pi^*$ transition within the fluorenyl unit as the LUMO+2 is calculated to be $\pi^*$ antibonding in character over the fluorenyl unit of the molecule. There are also significant contributions to this low energy band resulting from weaker transitions that originate from the HOMO-2, which has Re(d) character and electron density in $\pi$-back bonding to the carbonyl ligands, and transition to the LUMO which can be described as $\pi^*$ antibonding in the phenanthroline portion of the ligand. This calculated low energy band can therefore be attributed to a strong ILCT with some MLCT character.
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4.3 Conclusion

A extended phenanthroline ligand bearing two fluorenyl units has been successfully coordinated to ppy and pq cyclometallated iridium(III) complexes as well as a rhenium(I) tris carbonyl chloride complex. The syntheses were confirmed to be successful by \(^1\)H NMR spectroscopy, MS and elemental analysis. Characterisation of the photophysical properties of the complexes \(8a\) and \(8b\) indicated typical iridium and centred luminescence with all complexes exhibiting long lived luminescence lifetimes (\(\mu\)s domain) showing emission that is typical of \(^3\)MLCT states when compared to previously reported compounds. These were compared to the analogous compounds from the previous Chapter to show that increasing fluorenyl chain length increases the luminescence lifetimes in all compounds. The \(^3\)MLCT character was also evident when measuring the complexes in deoxygenated and aerated
solutions for which the complexes showed a significant decrease in lifetimes in the presence of known quencher $^3\text{O}_2$. The Stern-Volmer data calculated for complexes $8\text{a}$ and $8\text{b}$ produced $K_{SV}$ values of around 60 bar$^{-1}$ indicating high efficiency for $^3\text{O}_2$ quenching. Compound $8\text{c}$ was also quenched by $^3\text{O}_2$ but with a lower efficiency as indicated by a calculated $K_{SV}$ of 8 bar$^{-1}$. When compared to the analogous compounds in the Chapter 3, both iridium complexes, $8\text{a}$ and $8\text{b}$, have much higher calculated $K_{SV}$ values than $7\text{a}$ and $7\text{b}$. This suggests that the larger conjugation has a large effect on the efficiency of quenching by $^3\text{O}_2$. By contrast, the rhenium complexes $8\text{c}$ and $7\text{c}$ both possess similar values. These data indicate that the iridium ppy and pq complexes of the ligand 8 may well exhibit enhanced properties in applications such as two-photon photodynamic therapy.

### 4.4 Future Work

The Ir$^{III}$ compounds contained in this Chapter and Chapter 3 are potential candidates for PDT therapies due to the efficiency of oxygen quenching demonstrated. The increase in $K_{SV}$ values in the extended chromophore in ligand 8 leads to the possibility of further extending the conjugation. Furthermore, introducing a donor group to the terminal fluorenyl unit in order to study changes to both the one and two-photon photophysical properties would be of interest. Additionally, the photophysical properties of the Re$^I$ complexes $7\text{c}$ and $8\text{c}$ could be enhanced via replacement of the chloride ligand...
Chapter 5: Heterobimetallic Compounds for Potential PDT Applications

5.1 Introduction

Substantial increases in the two-photon cross-sections of inorganic complexes has been achieved by synthesis of heteropolymetallic complexes. For example, the tri- and heptametallic Ru\textsuperscript{II}/Pt\textsuperscript{II} metal complexes which are connected by polypyridyl ligands (quaterpyridine) were synthesised and their non-linear optical properties were studied.\textsuperscript{137} Relatively large two-photon $\sigma_2$ values (z-scan) were measured at 301 and 523 GM for the RuPt\textsubscript{3} and RuPt\textsubscript{6} constructs. In addition, heterobimetallic Ru\textsuperscript{II}-Ir\textsuperscript{III} complexes have been synthesised with a varied length of an oligophenylene spacer unit as a potential molecular wire.\textsuperscript{138}

5.2 Results and Discussion

The work described in this chapter was conducted as a joint EPSRC/University of Manchester funded collaboration with Miss Elizabeth Boreham (also a PhD student in the group of Louise Natrajan, thesis submitted pending viva) within the group of Dr Gilles Lemercier (University of Reims, France). The work performed solely by the author of this thesis involves the synthesis and characterisation of complex 9a, the photophysical measurements of all compounds and DFT calculation performed in Manchester. The remainder of the work described herein was conducted with Elizabeth Boreham: synthesis and characterisation of 9b from starting materials provided by Dr Gilles Lemercier. Two-photon absorption cross-section measurements of 9b were performed by Elizabeth Boreham (in the laboratory of Mireille Blanchard-Desc at the University of Bordeaux, CNRS with the assistance of Vincent Hughes).\textsuperscript{123}

5.2.1 Synthesis and Characterisation of Complexes

Ligand 9 (Scheme 19) is a variation of ligand 7 with the ability to link two metal centres together. It was synthesised by Gilles Lemercier by means of a Suzuki cross-coupling reaction with 5-bromo-1,10-phenanthroline and a fluorenyl bearing two boronic acid
groups. The complex 9a is a heterobimetallic complex with a rhenium(I) centre and an iridium(III) centre for which the synthetic route is given in Scheme 19.

Scheme 19: Synthetic Route to heterobimetallic complex 9a

Ligand 9 was first heated to reflux temperature with rheniumpentacarbonyl chloride in toluene for 24 hours. The rhenium product that precipitated was isolated by vacuum filtration and then dissolved in DCM and mixed with the cyclometallated iridium dimer in methanol by heating to reflux temperature for 24 hours. The product was precipitated by addition of ammonium hexafluorophosphate and isolated by filtration. The crude product was purified by trituration in hexane. The complex 9a was produced in a high yield (70 %) and showed high purity by $^1$H NMR spectroscopy (Figure 101). The $^1$H NMR spectrum shows the expected resonance of 6.42 ppm corresponding to the protons adjacent to the metallated C of the ppy ligand. The usual singlet peak corresponding to the proton at the 6 position of the phenanthroline ring is masked by overlapping signals ca. 8.00 ppm.
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Figure 101: $^1$H NMR spectrum of 9a (CDCl$_3$, 298 K, 400 MHz)

The Ir$^{III}$-Ru$^{II}$ heterobimetallic complex 9b was synthesised by reacting a ruthenium complex containing ligand 9 with the cyclometallated iridium dimer, 8a. The ruthenium complex was synthesised and supplied by Gilles Lemercier and the heterobimetallic complex 9b was synthesised as shown in Scheme 20.
Complex 9b was synthesised successfully in a 74% yield as a deep orange crystalline solid following purification by trituration with hexane. Analysis of the $^1$H NMR spectrum indicated a good purity in the synthesis of complex 9b, with all the desired peaks (Figure 102). This was further confirmed by elemental analysis and mass spectrometry. The $^1$H NMR spectra displays broadening of the peaks which could be due to delta- and lambda isomerisation around the ruthenium centre.
5.2.2 Absorption and Luminescence Analysis

Solution state luminescence was carried out in MeCN for both 9a and 9b. The compounds were both studied in degassed solution by excitation at 400 nm and the excitation spectra was recorded at the emission maxima. Lifetimes were measured at 405 nm excitation and quantum yields were measured using 400 nm excitation. Measured data are shown in Table 25.

Table 25: Data from photophysical measurements. All measurements were carried out in deoxygenated MeCN. Emission spectra and quantum yields were measured at 400 nm excitation. Excitation spectra were taken at the emission maxima. Lifetimes measured using a ps pulsed 405 nm diode laser.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Abs / λ&lt;sub&gt;max&lt;/sub&gt; (ε / dm&lt;sup&gt;3&lt;/sup&gt; mol&lt;sup&gt;-1&lt;/sup&gt; cm&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>λ&lt;sub&gt;em&lt;/sub&gt; / nm</th>
<th>λ&lt;sub&gt;ex&lt;/sub&gt; / nm</th>
<th>τ / ns</th>
<th>Φ / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>9a</td>
<td>269 (89400), 340 (42500)</td>
<td>606</td>
<td>283, 335</td>
<td>315 (23 %)</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>897 (77 %)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9b</td>
<td>267 (83800), 330 (30600), 450 (10300)</td>
<td>605</td>
<td>259</td>
<td>784 (63 %)</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1320 (37 %)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Lifetimes subject to ±10 % error. Quantum yields determined using an integrating sphere, estimated error ±3 %.

The absorption spectra of 9a and 9b are shown together in Figure 103. The spectrum of the Ir<sup>III</sup>-Re<sup>I</sup> complex 9a consists of an intense high energy band with a maximum absorbance at 269 nm assigned to ILCT π-π* transitions. A weaker and broad band at a lower energy with a maximum absorbance at 340 nm with a small tail indicative of a very weak and
broad absorption band above 400 nm which can be attributed to a weak contribution from a spin-forbidden $^3$MLCT transition from the Ir$^{III}$ centre. The absorption spectra of 9b also exhibits broad and weak absorption bands from ca. 380 nm, comprising of two overlapping bands. These overlapping bands can be attributed to MLCT transitions from each metal centre. Furthermore, 9b exhibits a broad absorption band in the region of 300-370 nm likely due to Ir$^{III}$-based spin-allowed MLCT transitions and an intense sharp band with a maximum absorbance of 267 nm attributed to spin-allowed a combination of $\pi-\pi^*$ ILCT transitions.

![UV-vis spectra of 9a (black) and 9b(red) recorded in MeCN](image)

The excitation and emission spectra of 9a is shown in Figure 104. The broad featureless emission at 606 nm is likely due to a triplet MLCT transition which is likely iridium centred. In comparison to the emission maximum of the iridium and rhenium complexes with ligand 7, the emission maximum is similar to that of the iridium complexes. The lifetime has dual components likely due to emission from both metal centres. When comparing with previous compounds it is likely that the shorter, weaker lifetime component of 315 ns can be assigned to the emission from the rhenium centre, whereas the longer lifetime of 897 ns is likely due to emission from the iridium centre. The relative
intensity of these components in the kinetic profile of 23 % and 77 % are comparable with the difference in strength of emission seen in complexes 7a and 7c, where the iridium complexes show a much stronger emission than the rhenium. The measured fluorescence quantum yield of 18 % in 9a indicates efficient luminescence similar to that of complex 7a.

Figure 104: Excitation (black) and emission (red) spectra of 9a measured in MeCN at room temperature

The emission and excitation spectra of complex 9b are shown in Figure 105. The emission is again broad and featureless with a maximum of 605 nm, indicating a 3MLCT emissive state. When compared to values reported by Lemercier et al. for [Ru(7)3][PF6]2, which exhibited an emission maximum at 590 nm, the emission of 9b is slightly red shifted. However, the emission maximum demonstrated for [Ru(7)3][PF6]2 is similar to that of the [Ir(7)(ppy)2][PF6], which was measured to be 593 nm. The lifetime is again dual component as expected for a heterobimetallic complex, with lifetimes of 784 ns (63 %) and 1320 ns (37 %). It is likely that the lifetime of 784 ns can be assigned to emission from the IrIII centre due to similarities with the iridium complex of 7a, and the longer lifetime of 1320 ns is due to emission from the RuII metal centre. For [Ru(7)3][PF6]2 the lifetime component assigned to the ruthenium centre is similar to the measured lifetime of 1700 ns. The quantum yield was measured as 22 % which is slightly higher than that of 9a, likely owing to more efficient luminescence from the ruthenium centre when compared to that of
the rhenium centre. The complex [Ru(7)3][PF6]2 had a measured quantum yield of 9 %, however comparison is tentative as the relative method used to measure this value has a much larger error as the absolute method using an integrating sphere.

Figure 105: Excitation (black) and Emission (red) spectra of 9b measured in MeCN at room temperature

5.2.3 Two Photon Luminescence Studies

Two-photon analysis for compound 9b was carried out at the University of Bordeaux. The nonlinear process of two-photon spectroscopy was confirmed by power dependence measurements which showed a quadratic relation of the emission intensity induced by different laser powers. As with compound 7a the one photon emission spectrum and the 2PEF spectrum indicate that the same excited state is accessed by both methods.

The 2PA cross-section was measured relative to fluorescein in 0.01 M NaOH as a reference using TPEF. The two-photon cross-section measurements are shown alongside the linear absorption in Figure 106, which show that different absorbance is exhibited for both processes. The profile of the measured cross-section data is very similar to that measured for [Ru(phen)2(7)][PF6]2 suggesting that the RuII is dominant in the process of 2PA. The values of σ2 are between 50 - 70 GM for a broad excitation range (850 – 950) and these are relatively high for a two-photon process which as with 7a, is likely due to the
symmetry and/or spin character of this transition which is assigned to a $^3$MLCT state. The measured $\sigma_2$ increases from 70 GM to a maximum of 350 GM between 850 and 730 nm and showing a steady decrease to 300 GM at 700 nm. This is an incredibly high value compared 7a (80 GM) and $[\text{Ru(phen)}_2(7)][\text{PF}_6]_2$ (50 GM) and $[\text{Ru}(7)_3][\text{PF}_6]_2$ (40 GM).\textsuperscript{121}

![Graph showing absorption and emission spectra.](image)

*Figure 106: Two-photon excitation (blue squares) and linear excitation (black line) spectra of 9b in degassed acetonitrile at room temperature. (One-photon at $2 \times 10^{-5}$ M, two-photon measurement at a concentration of $4 \times 10^{-5}$ M, measured by two photon excited fluorescence (2PEF) referenced to fluorescein in 0.01 M NaOH, $1 \times 10^{-4}$ M)*

Attempted measurements of 9a in the University of Manchester were again unsuccessful due to the previously discussed limitations of the laser set up. It is expected that 9a would exhibit two-photon properties similar to that of complex 7a due to similarities in one-photon photophysical properties.

### 5.2.4 Triplet Oxygen Quenching

The emission plots for complex 9a and consequential Stern-Volmer plot are given in Figure 107. The emission plot shows a large difference in the intensity between the three measurements with an extremely weak emission in an oxygen saturated solution. The Stern-Volmer plot produces a straight line correlation with gradient calculated at 23 bar$^{-1}$. This value is almost half of the measured $K_{SV}$ for 7a but higher than 7c, which is to be
expected with the bimetallic nature of the compound. Furthermore it is almost an average of the values measured for 7a and 7c suggesting that there is little communication between the metal centres in the deactivation pathways.

The emission data and Stern-Volmer analysis for 9b is shown in Figure 108. As with 9b there is a linear decrease in the emission intensity from degassed to aerated and oxygenated.

Figure 107: a) Emission of 9a in MeCN. Degassed (red), aerated (blue) and oxygen saturated (blue). b) Stern-Volmer plot from 9a luminescence intensity. Estimated error ±2% in all measurements and $R^2 = 0.99$ for the slope.
solutions. This is shown in the Stern-Volmer plot where the slope has been calculated to be 41 bar$^{-1}$. This is much higher than exhibited by 9a due to the nature of the triplet states accessed by Ru (II) complexes being much closer in energy to that of $^3$O$_2$ and therefore is susceptible to a higher degree of quenching by triplet oxygen present in the solution.

Figure 108: a) Emission of 9b in MeCN. Degassed (red), aerated (blue) and oxygen saturated (blue). b) Stern-Volmer plot from 9b luminescence intensity. Estimated error ±2% in all measurements and $R^2 = 0.99$ for both plots
The deoxygenated and aerated lifetimes are given in Table 26. Due to the nature of the dual lifetimes exhibited by the heterobimetallic complexes oxygenated lifetimes were not measured. This is due to uncertainty of assigning the lifetime components to one of the metal centres for the aerated data in order to ascertain an overall combined degree of quenching.

Table 26: Comparison of the deoxygenated and aerated lifetimes of 9a and 9b measured at 405 nm with a ps pulsed diode laser in MeCN solution

<table>
<thead>
<tr>
<th>Compound</th>
<th>Degassed $\tau$ / ns</th>
<th>Aerated $\tau$ / ns</th>
</tr>
</thead>
<tbody>
<tr>
<td>9a</td>
<td>315 (63 %), 897 (27 %)</td>
<td>72 (95 %), 166 (5 %)</td>
</tr>
<tr>
<td>9b</td>
<td>784 (63 %), 1320 (37 %)</td>
<td>141 (59 %), 77 (41 %)</td>
</tr>
</tbody>
</table>

Lifetimes subject to ± 10 % error.

5.2.5 Computational Studies

To aid better understanding of the electronic and optical properties of the complexes TD-DFT calculations have been carried out on the complexes 9a and 9b using Gaussian 09. The hexyl chains of the ligands have been replaced with methyl groups (denoted 9a' and 9b') to simplify calculations, making them less computationally expensive. Geometry optimisation was carried out at the B3LYP level, with cc-PVQZ-pp basis set and a relativistic SDD pseudopotential on the metal centres (Ir, Re and Ru) and 6-311G++ on all other atoms. TD-DFT was performed at the CAM-B3LYP level, due to this functional being able to estimate charge transfer excitations with a larger degree of accuracy. Solvent effects were accounted for in the TD-calculations by using a solvent continuum model (CPCM) with acetonitrile as the solvent. The first 50 states were calculated for each compound and the UV-visible spectra and transition information were simulated using the GaussSum program.

5.2.5.1 Absorption

The calculated and experimental UV-visible spectra of 9a' and 9a are shown in Figure 109. Predicted transition energies are given in Table 27 and selected orbitals are shown in Figure 110 and Figure 111. The predicted spectra exhibits two bands much like the experimental spectra, and the peaks are calculated to be very similar energies to the experimental spectra, however the overall profile shape differs. The lowest energy band is calculated to have an absorbance maximum around 20 nm blue shifted from that of the experimental spectra, although there is a transition predicted close to the energy of the
experimental peak maxima. This low energy band is calculated to be a result of 5 strong transitions.

Figure 109: TD-DFT-calculated (blue) and experimental (green) UV-visible spectra of 9a and 9a′ in MeCN. The ε-axes refers to experimental data only and the vertical axes of the calculated data are scaled to match the main experimental absorbance. The oscillator strength axis refer to the individual calculated transitions (red)
The low energy peak is a combination of 5 relatively strong transitions. The lowest energy of this is an mixture of HOMO-1 and HOMO-3 to the LUMO. The HOMO-1 is largely \(\pi\)-bonding over the fluorenyl portion of the molecule, and the HOMO-3 is largely Re(d) in character with orbital mixing with the CO ligands, there is also Cl(p) and O(p) character. The LUMO in which these transitions terminate is \(\pi^*\) antibonding over the phenanthroline portion of ligand 9 which is coordinated to rhenium. This transition can be attributed to an MLCT with ILCT character. The remainder of this band is a result of transitions that can be attributed to a mixture of ILCT and MLCT transitions. The remainder of the transitions originate from HOMO and HOMO-6, which are largely Ir(d) in character. The HOMO also contains \(\pi\)-bonding character over the phenyl ring of the ppy ligand, and the HOMO-6 exhibits orbital mixing to the carbons of the ppy ligand and \(\pi\)-bonding character over the ppy ligands and the phenanthroline.
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Figure 110: Selected HOMO orbitals of 9a* (isosurface value 0.03 a.u)

The electronic transitions are assigned to a multitude of different LUMOs: LUMO, LUMO+1, LUMO+2, LUMO+3, LUMO+4 and LUMO+5. The LUMO is $\pi^*$ antibonding over the phenanthroline portion of ligand 9 which is coordinated to rhenium whereas the LUMO+1 is $\pi^*$ antibonding over the phenanthroline unit of ligand 9 which is bound to the iridium centre. LUMO+2 and LUMO+3 are very similar with the majority of their electron
density located over both of the phenanthroline unit coordinated to each metal centre. The LUMO+4 and LUMO+5 are degenerate molecular orbitals with their electron density in $\pi^*$ antibonding orbitals on the cyclometalating ppy ligands around the iridium centre.

![LUMO orbitals](image)

**Figure 111: Selected LUMO orbitals of 9a’ (isosurface value 0.03 a.u)**

The calculated and experimental UV-visible spectra of 9b’ and 9b are given in Figure 112. Predicted transition energies are given in Table 28 and selected orbitals are shown in Figure 113 and Figure 114. The overall profile of the predicted spectrum does exhibit some
similar features as the experimental spectrum, however it fails to accurately predict the weak absorbance at wavelengths below 400 nm. The calculated spectrum shows two major bands with a shoulder on the lowest energy peak. This shoulder peak of the calculated spectrum is an acceptable match with the shoulder exhibited in the experimental spectrum. However the larger peak at 315 nm does not match with the experimental spectrum. The highest energy peaks in both spectra overlay very well in energy, however the overall relative intensities are very different. It is important to note that the highest energy transitions calculated was at 255 nm but it would be too computationally expensive to calculate further states. Increasing the number of states calculated could change the overall profile of the higher energy band depending on the relative oscillator strengths of the transitions calculated.

Figure 112: TD-DFT-calculated (blue) and experimental (green) UV-visible spectra of 9b and 9b' in MeCN. The ε-axes refers to experimental data only and the vertical axes of the calculated data are scaled to match the main experimental absorbance. The oscillator strength axis refer to the individual calculated transitions (red)
### Table 28: Selected transition data based on B3LYP/cc-QZP-pp/SDD Geometries of 9b’

<table>
<thead>
<tr>
<th>Compound</th>
<th>Transition</th>
<th>ΔE / nm (eV)</th>
<th>$f_{os}$</th>
<th>Major contributions</th>
</tr>
</thead>
<tbody>
<tr>
<td>9b’</td>
<td>1</td>
<td>377.43 (3.28)</td>
<td>0.00</td>
<td>HOMO-4 → LUMO+2 (20 %)</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>363.27 (3.41)</td>
<td>0.06</td>
<td>HOMO-6 → LUMO+2 (31 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO-1 → LUMO+2 (11 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO-5 → LUMO+2 (10 %)</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>360.57 (3.44)</td>
<td>0.34</td>
<td>HOMO-6 → LUMO (20 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO-5 → LUMO (15 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO-1 → LUMO (12 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO-6 → LUMO+4 (10 %)</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>359.88 (3.44)</td>
<td>0.40</td>
<td>HOMO-5 → LUMO+4 (14 %)</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td>HOMO-5 → LUMO (11 %)</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td>HOMO-6 → LUMO+2 (10 %)</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>334.12 (3.71)</td>
<td>0.14</td>
<td>HOMO → LUMO+8 (85 %)</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>324.40 (3.82)</td>
<td>0.55</td>
<td>HOMO-1 → LUMO+1 (16 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO-6 → LUMO+1 (14 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO-6 → LUMO+4 (12 %)</td>
</tr>
<tr>
<td></td>
<td>17</td>
<td>320.32 (3.87)</td>
<td>0.76</td>
<td>HOMO-9 → LUMO+3 (18 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO-3 → LUMO+1 (10 %)</td>
</tr>
<tr>
<td></td>
<td>19</td>
<td>317.34 (3.91)</td>
<td>0.31</td>
<td>HOMO-4 → LUMO+5 (15 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO-4 → LUMO+7 (29 %)</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>316.22 (3.92)</td>
<td>0.14</td>
<td>HOMO-4 → LUMO+6 (66 %)</td>
</tr>
<tr>
<td></td>
<td>21</td>
<td>315.47 (3.93)</td>
<td>0.16</td>
<td>HOMO-4 → LUMO+6 (15 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO-4 → LUMO+7 (15 %)</td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td>HOMO → LUMO+9 (10 %)</td>
</tr>
<tr>
<td></td>
<td>29</td>
<td>303.37 (4.09)</td>
<td>0.39</td>
<td>HOMO-6 → LUMO+5 (17 %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO-5 → LUMO+6 (14 %)</td>
</tr>
<tr>
<td></td>
<td>48</td>
<td>265.48 (4.67)</td>
<td>0.50</td>
<td>HOMO-1 → LUMO+11 (13 %)</td>
</tr>
</tbody>
</table>

The calculated shoulder at 360 nm results from two strong transitions and one weaker transition, for which the calculated orbital contributions involved can be attributed to Ru$^{II}$ MLCT character with a small amount of ILCT. The MLCT transitions originate from the HOMO-5 or HOMO-6 orbitals which are both Ru(d) in character with very small amount of $\pi$ electron density on ligand 7 coordinated to ruthenium. The LUMOs in which these MLCT transitions terminate are LUMO, LUMO+2 and LUMO+4. These LUMOs all contain $\pi^*$ antibonding electron density around the phenanthrolines coordinated to the ruthenium centre. The transition from the HOMO-1, which is largely $\pi$-bonding in character over one of the ligand 7 coordinated to ruthenium, with a small contribution from Ru(d), into the LUMO. The band at 320 nm is also predominantly attributed to Ru$^{II}$ MLCT transitions, although there are some transitions with orbital contributions which can be attributed to iridium$^{III}$ MLCT character. These transitions originate in the HOMO, which
can be described as largely Ir(d) in character with π-bonding orbitals located over the ppy ligands, and the HOMO-9, which has a large Ir(d) contribution with π-backbonding to the coordinated carbons from the ppy ligands as well as π-bonding orbitals on the phenanthroline coordinated to Ir. The LUMO’s in which these transitions terminate are LUMO+3, which contains π* antibonding electron density on the phenanthroline coordinated to the iridium centre and the LUMO+8 which is largely π* antibonding over the ppy ligands surrounding the iridium.
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Figure 113: Selected HOMO orbitals involved in the low energy transition of 9b' (isosurface value 0.03 a.u.)
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5.3 Conclusion

Two new heterobimetallic complexes have been synthesised with a symmetric phenanthroline-fluorenyl-phenanthroline ligand. With this bridging ligand Ir\textsuperscript{III}Re\textsuperscript{I} (9a) and Ir\textsuperscript{III}Ru\textsuperscript{II} (9b) complexes have been successfully synthesised. Synthesis was confirmed by \textsuperscript{1}H NMR spectroscopy, MS and elemental analysis. Absorption spectroscopy of 9a indicates \textsuperscript{3}MLCT absorption owing to the Ir\textsuperscript{III} by the presence of broad, weak bands above 400 nm. TD-DFT calculations of 9a demonstrate a small contribution from the Re\textsuperscript{I} in the lowest energy absorption band, however they are predominantly Ir(d) in character which is consistent with the experimental data. Complex 9b exhibited a much more complex absorption in this low energy region attributed to overlapping bands of MLCT transitions from both the Ru\textsuperscript{II} and Ir\textsuperscript{III} metal centres. Due to the spin orbit coupling, it is likely that the
weaker band is due to a \(^1\)MLCT transition. Again TD-DFT was used to probe the excited states, and although the calculated spectrum does not match well with the experimental data, especially at the low energy region of the spectrum, the lowest energy calculated transitions consist of Ir\(^{III}\) and Ru\(^{II}\) MLCT transitions with the latter exhibiting much larger calculated oscillator strength. This suggests that the Ru\(^{II}\) MLCT excited state may well contribute more significantly to the overall emissive properties of the heterobimetallic 9b than the Ir\(^{III}\) excited states.

Photophysical characterisation of both complexes indicated metal centred emission with long lived luminescence lifetimes. The dual component lifetimes indicated differences in the emission from each metal centre. Stern-Volmer analysis of the emission intensity demonstrated emission from a \(^3\)MLCT state due to significant quenching by ground state \(^3\)O\(_2\). The calculated Stern-Volmer constants of 23 bar\(^{-1}\) and 41 bar\(^{-1}\) for 9a and 9b respectively indicate a high efficiency of quenching by \(^3\)O\(_2\). The value of K\(_{SV}\) is much lower in compound 9a due to the less efficient quenching of the Re\(^1\) centre.

Two-photon analysis of compound 9b indicated a quadratic dependence on laser power and a very large two-photon cross-section maximum of 350 GM at 730 nm. This value is much higher than that of 7a (78 GM) and [Ru(7)\(_3\)][PF\(_6\)]\(_2\) (40 GM). This indicates a great potential for the compound in two-photon applications. Two-photon analysis of 9a was unfortunately unsuccessful due to limitations of the laser set-up available.

5.4 Future Work

Worked contained in this chapter has the potential to be extended to a wider range of metal centres. Studies into the photophysical properties of a Re\(^1\)-Ru\(^{II}\) complex could give information into the components of the lifetimes measured. The ligand 9 could be used to synthesise homobimetallic compounds to compare photophysical properties. Furthermore, an extended link between the phenanthroline units and thus metallic centres would probe the communication between said metal centres.

Due to the successful Stern-Volmer experiments, and large two-photon cross-section measured for 9b, preliminary in vitro PDT using two-photon microscopy should be carried out and be the focus of future studies.
Chapter 6: Experimental Procedures

6.1 General

Acetonitrile (MeCN) and dichloromethane (DCM) were dried over CaH$_2$ and tetrahydrofuran (THF) dried over potassium/benzophenone and distilled and degassed prior to use. All other chemicals were obtained from Sigma Aldrich and used as supplied. All air sensitive manipulations were conducted in an Ar filled glove box (Innovative Technologies PE2) total O$_2$ and H$_2$O content was always below 0.1 ppm. All NMR spectra were recorded on a Bruker Advance 400 spectrometer, operating frequency 400 MHz ($^1$H) and 101 MHz ($^{13}$C). Mass spectra were obtained using MALDI from methanol solutions with an ALPHA matrix on a Micromass TOF Spec 2E spectrometer. Elemental Analyses were performed by the microanalytical services at the University of Manchester using a Carlo ERBA Instruments CHNS-O EA1108 elemental analyser (C, H and N analysis) and a Fisons Horizon elemental analysis ICP-OED spectrometer for P.

X-ray diffraction data were collected at 100 K with a Bruker APEX 2 diffractometer using graphite-monochromated Mo-K$_\alpha$ radiation. The structures were solved by direct methods and refined using OLEX-2 software.$^{139}$ The structure was completed by iterative cycles of $\Delta$F-syntheses and a full matrix least squares refinement. All non-H atoms were refined anisotropically and difference Fourier syntheses were employed in positioning idealised hydrogen atoms and were allowed to ride on their parent C or N-atoms. All refinements were against F2 and used OLEX-2.

UV-visible spectra were recorded on a Shimadzu UV-2600 spectrometer using quartz cuvettes with a path length of 1 cm. Steady state emission spectra were recorded in quartz cuvettes on an Edinburgh Instrument FP920 Phosphorescence Lifetime Spectrometer equipped with a 5 W microsecond pulsed xenon flashlamp and a 450 W continuous wave xenon lamp (with single 300 mm focal length excitation and emission monochromators in Czerny Turner configuration) and a red sensitive photomultiplier in peltier (air cooled) housing, (Hamamatsu R928P). Lifetime data were recorded following excitation with an EPL 405 picosecond pulsed diode laser (Edinburgh Instruments) using time correlated single photon counting (PCS900 plug-in PC card for fast photon counting). Lifetimes were obtained by tail fit on the data obtained and quality of fit judged by minimization of
reduced chi-squared. Absolute quantum yields were measured using an integration sphere (Edinburgh Instruments).

### 6.1.1 Nonlinear Optical measurements

The two-photon absorption spectra were determined in the 700–1000 nm range by investigating the two-photon excited luminescence (2PEL) in deoxygenated $10^{-4}$ mol dm$^{-3}$ acetonitrile solution in a 10 mm × 10 mm quartz cuvette. The measurements were performed using a Nd:YLF pumped Ti:sapphire oscillator generating 150 fs pulses at a rate of 76 MHz. The excitation was focused into the cuvette through a microscope objective (10 x, NA 0.25). The luminescence was detected in epifluorescence mode via a dichroic mirror (Chroma 675dcoxru) and a barrier filter (Chroma e650sp-2p) by a compact CCD spectrometer module, BWTek BTC112E. Total luminescence intensities were obtained by integrating the corrected emission spectra measured by this spectrometer. 2PA cross-sections ($\sigma_2$) were determined from the two-photon excited luminescence cross-sections ($\sigma_2\Phi$) and the luminescence emission quantum yield ($\Phi$). 2PEL cross-sections of $10^{-4}$ M solutions were measured relative to a $10^{-4}$ M solution of fluorescein in 0.01 M aqueous NaOH for the range 700–1000 nm, using the well-established method described by Xu and Webb$^{19}$ and the appropriate solvent-related refractive index corrections.$^{140}$ Data points between 700 and 715 nm were corrected. The quadratic dependence of the luminescence intensity on the excitation power was checked for each sample at all wavelengths indicating that the measurements were carried out in intensity regimes where saturation or photodegradation did not occur.

### 6.1.2 Stern-Volmer Measurements

Dry degassed acetonitrile and dichloromethane solutions were prepared in a glove box in a quartz cell equipped with a Young’s tap (10 mm × 10 mm) for the oxygen free measurements. The solutions were left open to equilibrate with the air for 1 hour to obtain an aerated sample and then bubbled with oxygen from an oxygen cylinder for 5 minutes to obtain an oxygen-saturated solution.
6.1.3 In vitro Cell experiments

C6 glioma cells were seeded at a density of $5 \times 10^3$ cells per well in 96-well plates and grown in Dulbecco’s Modified Eagle Medium F12, enriched with 10% fetal calf serum (FCS) and antibiotics (penicillin $50 \text{ U ml}^{-1}$, streptomycin $50 \text{ mg ml}^{-1}$). After 24 h, cells were treated with 7a at concentrations of 1 mM and 10 mM. A laser-scanning microscope LSM 710 NLO Zeiss (Iena, Germany) was used. Excitation was provided by a CHAMELEON femtosecond Titanium-Sapphire laser (Coherent, Santa Clara, USA) set at 740 nm with a photon flux of 0.025 mW cm$^{-2}$. Living cells were deposited in glass bottom box and were imaged with a 63 x 1.4 NA oil objective lens. The pathology of these cells was not affected by the presence of small quantities of DMSO.

6.2 Synthesis of 4’-(p-tolyl)-2,2′:6,2′″-terpyridine (ttpy)

![Diagram of 4’-(p-tolyl)-2,2′:6,2′″-terpyridine (ttpy)]

According to a modification of a literature procedure,$^{141}$ EtOH (200 mL) was added to a mixture of 2-acetylpyridine (9.68 g, 80.0 mmol), 4-methylbenzaldehyde (4.00 g, 40.0 mmol) and KOH (6.16 g, 80.0 mmol). Ammonia solution (120 mL) was added and the solution was stirred at room temperature for 24 h. The resulting precipitate was filtered and washed with cold EtOH. The crude product was recrystallised from a minimum volume of hot EtOH to give pale yellow needles (2.43 g, 19%). ES$^+$ MS (MeCN): $m/z$ 324 {M + H}$^+$ (85 %). $^1$H NMR (400 MHz, CDCl$_3$) $\delta_H$: 2.44 (s, 3H, CH$_3$), 7.31 - 7.37 (m, 4H, 4 x Ar-H), 7.83 (d, 2H, $^3J_{HH} = 8.15$ Hz, 2 x Ar-H), 7.87 (td, 2H, $^3J_{HH} = 7.74$, $^4J_{HH} = 1.77$ Hz, 2 x Ar-H), 8.68 (d, 2H, $^3J_{HH} = 7.96$ Hz, 2 x Ar-H), 8.73 (m, 2H, 2 x Ar-H), 8.74 (s, 2H, 2 x Ar-H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta_C$: 156.51, 149.08, 155.81, 150.11, 139.04, 135.42, 136.79, 129.60, 127.11, 123.73, 121.31, 118.56 ppm. UV-vis (MeCN) $\lambda_{\text{max}}$ ($\varepsilon / \text{mol}^{-1} \text{dm}^3 \text{cm}^{-1}$) = 280 (119,000). Anal calcd. for C$_{22}$H$_{16}$N$_3$: C 81.71, H 5.12, N 12.97. Found C 81.29, H 5.12, N 12.97.
6.3 Synthesis of 4'-(4-(bromomethyl)phenyl)-2,2':6',2''-terpyridine

According to a literature procedure, 4'-(p-tolyl)-2,2':6,2''-terpyridine (2.0 g, 6.2 mmol) was added to CCl₄ (20 mL) and stirred at room temperature. N-bromosuccinimide (NBS) (1.1 g, 6.2 mmol) and dibenzoylperoxide (25 mg) were then added and the solution was heated to reflux temperature for 4 h under UV-visible lamp irradiation. The solution was cooled to room temperature and filtered to remove the succinimide residues. The solvent was removed under reduced pressure to give a pale yellow oil. The oil was sonicated in EtOH and resulting precipitate was filtered to give a pale yellow solid (1.72 g, 70 %). ES⁺ MS (MeCN): m/z 403 {M + H}⁺ (12 %). ¹H NMR (400 MHz, CDCl₃) δH: 4.58 (s, 2H, CH₂), 7.35 - 7.39 (m, 2H, 2 x Ar-H), 7.52 - 7.58 (m, 2H, 2 x Ar-H), 7.87 - 7.92 (m, 4H, 4 x py-H), 8.68 (dt, ³JHH = 7.96, ⁴JHH = 0.95 Hz, 2H, 2 x py-H), 8.73 - 8.75 (m, 4H, 4 x py-H) ppm. Anal calcd. for C₂₂H₁₆N₃Br : C 65.68, H 4.01, N 10.16, Br 20.79. Found C 64.48, H 3.62, N 10.16, Br 20.79.

6.4 Synthesis of (4-(2,2':6',2''-terpyridin]-4'-(4-(bromomethyl)phenyl)triphenylphosphonium bromide

According to a literature procedure, ³⁶ 4'-(4-(bromomethyl)phenyl)-2,2':6',2''-terpyridine (1.0 g, 3.4 mmol) and PPh₃ (0.65 g, 3.4 mmol) were heated to reflux temperature in toluene for 24 h. The resulting solution was cooled to room temperature and further cooled in ice. The resulting solid was collected by filtration to give a pale yellow solid (1.1 g, 65 %).
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NMR (400 MHz, DMSO) δH: 5.30 (d, 2H, \(^{2}J_{HH} = 15.98\) Hz, CH\(_2\)), 7.53 (ddd, 3H, \(^{2}J_{HH} = 7.48\), \(^{4}J_{HH} = 4.77\) Hz, 3 x Ar-H), 7.70 - 7.85 (m, 15H, PPh\(_3\)-H), 7.91 - 7.96 (m, 3H, 3 x Ar-H), 8.04 (td, 2H, \(^{2}J_{HH} = 7.72\), \(^{4}J_{HH} = 1.80\) Hz, 2 x Ar-H), 8.66 (s, 2H, Ar-H), 8.72 - 8.76 (m, 2H, Ar-H) ppm. Anal calcd. for C\(_{40}\)H\(_{31}\)N\(_3\)BrP: C 72.79, H 4.70, N 4.74, Br 12.02, P 4.66. Found C 72.83, H 4.74, N 5.79, Br 11.05, P 4.27.

6.5 Synthesis of (E)-4-((4-[2,2':6',2''-terpyridin]-4'-yl)styryl)-N,N-dimethylaniline (1a)

According to a modification of a published procedure by the group, under N\(_2\), a flamed out Schlenk flask was loaded with (4-[2,2':6',2''-terpyridin]-4'-yl)benzyl)triphenylphosphonium bromide (300 mg, 0.456 mmol) and potassium tert-butoxide (79 mg, 0.684 mmol). The flask was immersed in an ice bath and dry THF (5 mL) was added via cannula. The resulting solution was stirred at 0 °C for 30 min during which the solution turned bright orange. 4-(dimethylamino)benzaldehyde (71 mg, 0.479 mmol) was added and the solution was slowly warmed to room temperature and stirred for a further 72 h. The solution was quenched by addition of ice water and solvents removed under reduced pressure. Methanol (20 mL) was added and the solution was stirred overnight at room temperature. The resulting yellow solid was isolated by vacuum filtration and washed with water and methanol to give a pale yellow solid (130 mg, 51%).

ES\(^{+}\) MS (MeCN): \(m/z\ 454\) \{M \+ H\}\(^{+}\) (89%). \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) δH: ppm 3.03 (s, 6H, CH\(_3\)), 7.00 (d, 1H, \(^{2}J_{HH} = 16.17\) Hz, trans-C=CH), 7.17 (d, 1H, \(^{2}J_{HH} = 16.17\) Hz, trans-C=CH) 7.38 (ddd, 2H, \(^{2}J_{HH} = 7.58\), \(^{4}J_{HH} = 4.80\), 1.26 Hz, 2 x Ar-H), 7.48 (d, 2H, \(^{2}J_{HH} = 8.84\) Hz, 2 x Ar-H), 7.63 (d, 2H, \(^{2}J_{HH} = 8.34\) Hz, 2 x Ar-H) 7.87 - 7.97 (m, 4H, 4 x Ar-H) 8.67 - 8.73 (m, 2H, 2 x Ar-H) 8.74 - 8.78 (m, 2H, 2 x Ar-H) 8.79 (s, 2H, 2 x Ar-H). UV-vis
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(MeCN) $\lambda_{\text{max}}$ (ε / mol$^{-1}$ dm$^3$ cm) : 232 (17100), 305 (19300), 400 (17100). Anal Calcd. for C$_{31}$H$_{26}$N$_4$ expected C 81.91 H 5.77 N 12.33. Found C 80.81 H 5.43 N 12.07.

6.6 Synthesis of (E)-4-(4-([2,2':6',2''-terpyridin]-4'-yl)styryl)-N,N-diphenylaniline (1b)

According to a modification of a published procedure by the group,$^{37}$ under N$_2$, a flamed out Schlenk flask was loaded with (4-([2,2':6',2''-terpyridin]-4'-yl)benzyl)triphenylphosphonium bromide (286 mg, 0.434 mmol) and potassium tert-butoxide (75 mg, 0.653 mmol). The flask was immersed in an ice bath and dry THF (5 mL) was added via cannula transfer. The resulting solution was stirred at 0 $^\circ$C for 30 min during which the solution turned bright orange. 4-(diphenylamino)benzaldehyde (125 mg, 0.457 mmol) was then added dropwise and the solution was slowly warmed to room temperature and stirred for a further 72 h. The solution was quenched by addition of ice water and solvents removed under reduced pressure. Methanol (20 mL) was added and the solution was stirred overnight at room temperature. The resulting yellow solid was isolated by vacuum filtration and washed with water and methanol to give a pale yellow solid (186 mg, 70%). ES$^+$ MS (MeCN): m/z 578 {M + H}$^+$ (94 %). $^1$H NMR (400 MHz, CDCl$_3$) δ$_H$: ppm 6.93 (d, 1 H, $^3$J$_{HH}$ = 7.82 Hz, Ar-H) 7.08 (d, 2 H, $^3$J$_{HH}$ = 14.67 Hz, trans-C=CH) 7.09-7.28 (m, 8H, Ar-H), 7.26 (q, J=7.38 Hz, 5 H, Ar-H) 7.36 (br. s., 2H, Ar-H) 7.40 - 7.50 (m, 2H, Ar-H), 7.79 - 7.97 (m, 4H, Ar-H) 8.61 - 8.78 (m, 6H, Ar-H). UV-vis (MeCN) $\lambda_{\text{max}}$ (ε / mol$^{-1}$ dm$^3$ cm): 298 (16100), 380 (15100). Anal Calcd. for C$_{41}$H$_{30}$N$_4$ expected C 85.09 H 5.23 N 9.68. Found C 84.97 H 5.31 N 9.69.
6.7 Synthesis of [Pt(1a)Cl]Cl (2a)

Pt(DMSO)$_2$Cl$_2$ (58 mg, 0.14 mmol) and 1a (31 mg, 0.07 mmol) were mixed in MeCN (10 mL). The resulting solution was heated to reflux temperature with stirring for 48 h. The resulting solution was cooled to room temperature and the solid removed by vacuum filtration, washed with MeCN (2 x 5 mL), and Et$_2$O (2 x 5 mL) to afford a dark purple solid (34 mg, 74%). ES$^+$ MS (MeCN) m/z 685 $\{\text{M} - \text{Cl}\}$ (100 %). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ ppm: 2.97 (br. s., 6H, 2 x CH$_3$), 6.72 (d, 2H, $^3$J$_{HH}$ = 7.46 Hz, Ar-H) 7.06 (d, 1H, $^3$J$_{HH}$ = 16.38 Hz, trans-C=CH), 7.36 (d, 1H, $^3$J$_{HH}$ = 16.26 Hz, trans-C=CH) 7.47 (d, 2H, $^3$J$_{HH}$ = 7.34 Hz, Ar-H), 7.74 (d, $^3$J$_{HH}$ = 6.85 Hz, 2 H) 7.87 - 8.85 (m, 4 H, Ar-H) 8.89 ppm. $^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$: 40.63, 120.63, 122.56, 123.78, 124.67, 125.62, 126.26, 126.22, 128.43, 129.28, 129.86, 130.76, 132.69 (q), 141.06 (q), 142.60, 146.98 (q), 147.53 (q), 151.29, 151.88 (q), 154.30 (q), 158.26 (q). UV-vis (MeCN) $\lambda_{max}$ (ε / mol$^{-1}$ cm$^{-1}$): 456 (11300), 331 (17500), 281 (13100). Anal calcd. For C$_{31}$H$_{26}$Cl$_2$N$_4$Pt expected C 51.67 H 3.64 N 7.78. Found C 51.57 H 4.06 N 7.34.

6.8 Synthesis of [Pt(1b)Cl]Cl (2b)

Pt(DMSO)$_2$Cl$_2$ (58 mg, 0.140 mmol) and 1b (40 mg, 0.069 mmol) were mixed in MeCN (10 mL). The resulting solution was heated to reflux temperature with stirring for 48 h. The resulting solution was cooled to room temperature and the solid removed by vacuum filtration, washed with MeCN (2 x 5 mL), and Et$_2$O (2 x 5 mL) to afford a dark purple solid (34 mg, 74%). ES$^+$ MS (MeCN) m/z 685 $\{\text{M} - \text{Cl}\}$ (100 %). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ ppm: 2.97 (br. s., 6H, 2 x CH$_3$), 6.72 (d, 2H, $^3$J$_{HH}$ = 7.46 Hz, Ar-H) 7.06 (d, 1H, $^3$J$_{HH}$ = 16.38 Hz, trans-C=CH), 7.36 (d, 1H, $^3$J$_{HH}$ = 16.26 Hz, trans-C=CH) 7.47 (d, 2H, $^3$J$_{HH}$ = 7.34 Hz, Ar-H), 7.74 (d, $^3$J$_{HH}$ = 6.85 Hz, 2 H) 7.87 - 8.85 (m, 4 H, Ar-H) 8.89 ppm. $^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$: 40.63, 120.63, 122.56, 123.78, 124.67, 125.62, 126.26, 127.20, 128.22, 128.43, 129.28, 129.86, 130.76, 132.69 (q), 141.06 (q), 142.60, 146.98 (q), 147.53 (q), 151.29, 151.88 (q), 154.30 (q), 158.26 (q). UV-vis (MeCN) $\lambda_{max}$ (ε / mol$^{-1}$ cm$^{-1}$): 456 (11300), 331 (17500), 281 (13100). Anal calcd. For C$_{31}$H$_{26}$Cl$_2$NaPt expected C 51.67 H 3.64 N 7.78. Found C 51.57 H 4.06 N 7.34.
filtration, washed with MeCN (2 x 5 mL), and Et₂O (2 x 5 mL) to afford a dark purple solid (39 mg, 78 %). ES⁺ MS (MeCN) m/z 809 {M - Cl}(100 %). ¹H NMR (400 MHz, DMSO-d₆) δ ppm: 6.93 (d, 3J_HH = 7.95 Hz, 2H, Ar-H) 6.98 - 7.10 (m, 5H, Ar-H) 7.15 (d, 1H, 2J_HH = 16.14 Hz, trans-C=CH) 7.30 (t, 3J_HH = 7.40 Hz, 4H, Ar-H) 7.38 (d, 2J_HH = 16.26 Hz, 1 H trans-C=CH) 7.51 (d, 3J_HH = 7.95 Hz, 2 H, Ar-H) 7.73 (d, 3J_HH = 7.82 Hz, 2 H, Ar-H) 7.80 (d, 3J_HH = 5.75 Hz, 2 H, Ar-H) 8.12 (d, 3J_HH = 7.70 Hz, 2 H Ar-H) 8.40 (t, 3J_HH = 7.52 Hz, 2 H Ar-H) 8.86 (d, 4J_HH = 3.55 Hz, 2 H, Ar-H) 8.75 (d, 3J_HH = 7.70 Hz, 2 H Ar-H) 8.82 (br, 2 H, Ar-H). ¹³C NMR (101 MHz DMSO-d₆) δ ppm: 39.51 120.42, 122.36, 123.58, 124.47, 125.42, 126.06, 127.00, 128.01, 128.23, 129.08, 129.65, 130.56, 132.49 (q), 140.86 (q), 142.70, 146.77 (q), 147.33 (q), 151.09, 151.68 (q), 154.10 (q), 158.06 (q). UV-vis (MeCN) λ_max (ε / mol⁻¹ cm⁻¹): 444 (14800), 337 (21900), 301 (17900), 285 (18000).

6.9 Synthesis of Re(1a)(CO)₃Cl (3a)

Rhenium pentacarbonyl chloride (23 mg, 0.065 mmol) and 1a (29 mg, 0.065 mmol) were mixed in toluene (10 mL) and the resulting solution was heated to reflux temperature for 14 hours. The solution was cooled to room temperature and filtered. The filtrate was washed with Et₂O (3 x 5 mL) to afford a bright orange solid (45 mg, 92 %). ES⁺ MS (MeCN) m/z 725 {M – Cl}⁺ (14 %). ¹H NMR (400 MHz, DMSO-d₆) δ ppm: 2.96 (s, 6H, 2 x CH₃), 6.75 (d, 2H, 3J_HH = 7.58 Hz, Ar-H), 7.09 (d, 1H, 3J_HH = 16.87 Hz, trans-C=CH), 7.37 (d, 1H, 3J_HH = 17.12 Hz, trans-C=CH), 7.50 (d, 2H, 3J_HH = 7.21 Hz, Ar-H), 7.77 (m, 4H, Ar-H), 7.92 (m, 1H, Ar-H), 8.06 (m, 1H, Ar-H), 8.22 (m, 2H, Ar-H), 8.40 (m, 1H, Ar-H), 8.80 (m, 1H, Ar-H), 9.09 (d, 4H, 3J_HH = 16.63 Hz, Ar-H). ν_max/cm⁻¹ 2017 (C=O), 1910 (C=O), 1878 (C=O). UV-vis (MeCN) λ_max (ε / mol⁻¹ cm⁻¹): 424 (12700), 314 (13100).
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Anal calcd for C$_{34}$H$_{26}$ClN$_4$O$_3$Re expected C 53.71 H 3.45 N 7.37. Found C 53.73 H 3.27 N 7.05.

6.10 Synthesis of Re(1b)(CO)$_3$Cl (3b)

Rhenium pentacarbonyl chloride (23 mg, 0.065 mmol) and 1b (38 mg, 0.065 mmol) were mixed in toluene (10 mL) and the resulting solution was heated to reflux temperature for 14 hours. The solution was cooled to room temperature and filtered. The precipitate that had formed was washed with Et$_2$O (3 x 5 mL) to afford a bright orange solid (50 mg, 89 %). ES$^+$ MS (MeCN) m/z 849 {M – Cl}$^+$ (27 %). $^1$H NMR (400 MHz, DMSO-d$_6$) $\delta$ ppm 6.98 (d, 2H, $^3$$J_{HH}$ = 7.21 Hz, Ar-H), 7.06 (d, 6H, $^3$$J_{HH}$ = 7.21 Hz, Ar-H) 7.24 (d, 1H $^3$$J_{HH}$ = 16.02 Hz, trans-C=CH), 7.29 – 7.38 (m, 4H, Ar-H), 7.43 (d, 1H, $^3$$J_{HH}$ = 15.65 Hz, trans-C=CH), 7.52 – 7.67 (m, 4H, Ar-H), 7.81 (d, 2H, $^3$$J_{HH}$ = 6.85 Hz, Ar-H) 7.91 (d, 1H, $^3$$J_{HH}$ = 7.21 Hz, Ar-H), 8.06 (br. s., 1H, Ar-H) 8.25 (d, 2H, $^3$$J_{HH}$ = 9.54 Hz, Ar-H), 8.40 (br. s., 1H, Ar-H), 8.80 (br. s., 1H, Ar-H), 9.02 – 9.21 (m, 2H, Ar-H). $\nu_{\text{max}}$/cm$^{-1}$ 2019 (C=O), 1920 (C=O), 1821 (C=O). UV-vis : 418 (14600), 306 (18500). Anal calcd for C$_{44}$H$_{30}$ClN$_4$O$_3$Re.H$_2$O expected C 58.56 H 3.57 N 6.21. Found C 58.46 H 3.14 N 5.81.
6.11 Synthesis of [Ru(1a)2][PF6]2 (4a)

Under N2, RuCl3.xH2O (54 mg, 0.26 mmol) was dissolved in ethanol (10 mL) and 1a (65 mg, 0.143 mmol) was added. The resulting solution was heated to reflux temperature for 15 h. After this time, the precipitated solid was isolated by vacuum filtration, washed with H2O (2 x 5 mL), EtOH (5 x 5 mL) and CH2Cl2 (2 x 5 mL) and dried to yield Ru(ttpy-ene-NMe2).Cl3 as an insoluble brown powder (82 mg, 48%). Ru(1b).Cl3 (60 mg, 0.091 mmol) was stirred in a mixture of EtOH-acetone (12 mL, 1:4 v:v). This was placed under N2 and in the dark and AgOTf (82 mg, 0.32 mmol) was added. The solution was heated to reflux temperature and this temperature was maintained for 24 h. The resulting dark red solution was filtered through a pad of celite, and all volatiles were removed under reduced pressure. The residual solid was dissolved in EtOH (10 mL) and 1a (42 mg, 0.091 mmol) was again added. The resulting slurry was heated at reflux temperature for 3 days. After this time all the volatiles were removed under reduced pressure and the solid residue was dissolved in MeOH (15 mL) and filtered through a pad of celite. A saturated aqueous solution of NH4PF6 was added to precipitate the product as the PF6 salt. The precipitate was isolated by vacuum filtration and recrystallised three times from MeCN-Et2O to give Ru(ttpy-ene-NMe2)2.2PF6 (4a) as a red powder (62 mg, 52%). ES+ MS (MeCN) m/z 505 {M – 2[PF6]}2+ (100 %), 1155 {M - [PF6]}+ (7 %). 1H NMR (400 MHz, acetone-d6) δH: 3.03 (s, 6H, 2 x C6H3), 6.81 (d, 2H, 3JHH = 8.31 Hz, Ar-H), 7.18 (d, 1H, 3JHH = 16.02 Hz, trans-C=C=H), 7.28 - 7.46 (m, 3H, overlapping signals, 2 x Ar-H, 1 x trans-C=CH), 7.55 (d, 2H, 3JHH = 7.82 Hz, 2 x Ar-H), 7.69 - 7.94 (m, 2H, Ar-H), 8.10 (d, 2H, 3JHH = 6.48 Hz, Ar-H), 8.22 - 8.43 (m, 2H, Ar-H), 9.08 (d, 2H, 3JHH = 8.44 Hz), 9.20 - 9.58 (m, 4H, 4 x Ar-H).

UV-vis (MeCN) λmax (ε / mol⁻¹ dm³ cm): 281 (87700), 310 (87700), 495 (46000). Anal. Calc. for C62H52N8RuP2F12.1.5CCl2H2 Expected C 53.43 H 3.88 N 7.85. Found C 53.57 H 3.64 N 7.61.
6.12 Synthesis of [Ru(1b)\textsubscript{2}][PF\textsubscript{6}]\textsubscript{2} (4b)

Under N\textsubscript{2}, RuCl\textsubscript{3}.xH\textsubscript{2}O (54 mg, 0.26 mmol) was dissolved ethanol (10 mL) and ligand 1b (100 mg, 0.173 mmol) was added. The resulting solution was heated to reflux temperature for 15 h. After this time, the precipitated solid was isolated by vacuum filtration, washed with H\textsubscript{2}O (2 x 5 mL), EtOH (5 x 5 mL) and CH\textsubscript{2}Cl\textsubscript{2} (2 x 5 mL) and dried to yield Ru(tpy-ene-NPh\textsubscript{2}).Cl\textsubscript{3} as an insoluble brown powder (124 mg, 61 %). Ru(1b).Cl\textsubscript{3} (92 mg, 0.117 mmol) was stirred in a mixture of EtOH-acetone (12 mL, 1:4 v:v). This was placed under N\textsubscript{2} and in the dark and AgOTf (105 mg, 0.41 mmol) was added. The solution was heated to reflux temperature for 24 h. The resulting dark red solution was filtered through a pad of celite, and all volatiles were removed under reduced pressure. The residual solid was dissolved in EtOH (10 mL) and 1b (68 mg, 0.12 mmol) was added. The resulting slurry was heated at reflux temperature for 3 days. After this time all the volatiles were removed under reduced pressure and the solid residue was dissolved in MeOH (15 mL) and filtered through a pad of celite. A saturated aqueous solution of NH\textsubscript{4}PF\textsubscript{6} was then added to precipitate the product as the PF\textsubscript{6} salt. The precipitate was isolated by vacuum filtration and recrystallised three times from MeCN-Et\textsubscript{2}O to give Ru(tpy-ene-NPh\textsubscript{2})\textsubscript{2}.2PF\textsubscript{6} (4b) as a red powder (38 mg, 46 %). 

ES\textsuperscript{+} MS (MeCN) m/z 629 \{M – 2[PF\textsubscript{6}]\}\textsuperscript{2+} (100 %), 1403 \{M - [PF\textsubscript{6}]\}\textsuperscript{+} (3 %). \textsuperscript{1}H NMR (400 MHz, acetone-d\textsubscript{6}) \textdelta\text{ppm} 7.02 - 7.17 (m, 7H, Ar-H), 7.36 (t, 6H, \textit{J}HH = 7.03 Hz, Ar-H), 7.49 (d, 1H, \textit{J}HH = 16.38 Hz, trans-C=CH), 7.61 (d, 4H, \textit{J}HH = 7.70 Hz, Ar-H), 7.85 (d, 2H, \textit{J}HH = 5.26 Hz, Ar-H), 7.97 (d, 2H, \textit{J}HH = 7.58 Hz, Ar-H), 8.12 (t, 2H, \textit{J}HH = 7.46 Hz, Ar-H), 8.38 (d, 2H, \textit{J}HH = 7.82 Hz, Ar-H), 9.08 (d, 2H, \textit{J}HH = 8.07 Hz, Ar-H) 9.48 (s, 2H, Ar-H). \textsuperscript{13}C NMR (101 MHz d\textsubscript{3}-Acetone) \textdelta\text{C}: 121.95, 123.92, 124.47, 125.64, 125.76, 126.68, 128.29, 128.74, 128.82, 129.00, 130.47, 131.15, 132.19 (q), 135.94 (q), 139.18, 141.21 (q), 148.48, (q) 148.75 (q), 148.94 (q), 153.61, 156.77 (q), 159.61 (q). UV-vis (MeCN) \lambda_{\text{max}} (\epsilon / \text{mol}^{-1} \text{ dm}^{-3} \text{ cm}): 310 (90000), 501 (61000) Anal Calc for C\textsubscript{82}H\textsubscript{60}N\textsubscript{8}RuP\textsubscript{2}F\textsubscript{12} Expected C 63.61 H 3.91 N 7.24. Found C 62.57 H 3.73 N 6.85.
6.13 Synthesis of [Ir(1a)]_2[PF_6]_3 (5a)

According to a literature procedure, under N_2, IrCl_3.xH_2O (19.5 mg, 0.065 mmol) and ttpy-ene-NMe_2 (1a) (59 mg, 0.130 mmol) were added to ethylene glycol (7 mL). The resultant solution was heated at 100 °C for 3 hours after which the temperature was raised to 195 °C and maintained for a further 1.5 hours. The solution was cooled to room temperature and a saturated solution of aqueous NH_4PF_6 was added to precipitate the complex as the PF_6 salt. The precipitate was isolated by vacuum filtration and washed with H_2O (3 x 5 mL), MeOH (3 x 5 mL) and Et_2O (3 x 5 mL). The product was recrystallised 3 times from acetone-Et_2O to afford a dark purple powder (27 mg, 27 %). ^1H NMR (400 MHz, MeCN-d_3) δ_H ppm 3.06 (s, 6H 2 x CH_3), 6.96 (d, 2H, Ar-H), 7.26 (d, 1H, J_HH = 16.7 Hz, trans-C=CH), 7.46-7.70 (m, 3H, overlapping signal, Ar-H, trans-C=CH), 7.85 (d, 2H, J_HH = 7.46 Hz, Ar-H), 7.92 (d, 2H, J_HH = 7.32 Hz, Ar-H), 8.07-8.42 (m, 4H, Ar-H), 8.70-8.81 (m, 4H, Ar-H), 9.17 (s, 2H, Ar-H). UV-vis (MeCN) λ_max (ε / mol^-1 dm^3 cm): 254 (57700), 282 (57100), 320 (44900)(sh), 375 (27500)(sh), 515 (11371)(sh). Reliable CHN data could not be obtained due to the likely presence of residual iridium.

6.14 Synthesis of [Ir(1b)]_2[PF_6]_3 (5b)

According to a literature procedure, under N_2, IrCl_3.xH_2O (16.0 mg, 0.054 mmol) and ttpy-ene-NPh_2 (ligand 1b) (64.7 mg, 0.122 mmol) were added to ethylene glycol (7 mL). The resultant solution was heated at 100 °C for 3 hours after which the temperature was raised to 195 °C and maintained for a further 1.5 hours. The solution was cooled to room temperature and a saturated solution of aqueous NH_4PF_6 was added to precipitate the PF_6
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6.15 Synthesis of 5-(9,9-Dihexyl-9H-fluoren-2-yl)-1,10-phenanthroline (7)

Under an inert (Ar) atmosphere, 5-bromo-1,10-phenanthroline\textsuperscript{142} (243.5 mg, 2.24 mmol) and 9,9-dihexyl-9H-fluoren-2-yl)boronic acid\textsuperscript{121} (847.5 mg, 2.24 mmol) were dissolved in toluene (10 mL). The solution was degassed and aqueous sodium carbonate (1 M, 12 mL) was added. Tetrakis(triphenylphosphine) palladium(0) (99.0 mg, 0.086 mmol) was added. The solution was heated to reflux temperature for 72 hours. Upon cooling, the organic phase was separated and the aqueous phase was extracted into dichloromethane. The organic phases were combined and all volatiles were removed under reduced pressure. The resulting residue was purified by column chromatography on alumina (DCM:acetone:triethylamine, 80:19:1) to give 5-(9,9-dihexyl-9H-fluoren-2-yl)-1,10-phenanthroline, 7 (290 mg, 25 %) as a white powder. \textsuperscript{1}H NMR (250 MHz, CDCl\textsubscript{3}) \( \delta_H \): 0.78 (t, 10H, \( ^3J_{HH} = 6.69 \) Hz, alkyl-H), 1.02 - 1.17 (m, 12H, Hz, alkyl-H), 1.95 - 2.09 (m, 4H, Hz, alkyl-H), 7.34 - 7.44 (m, 3H, \( H_{14}, H_{15}, H_{16} \)) 7.47 - 7.54 (m, 2H, \( H_{11}, H_{17} \)) 7.59 (dd, \( ^3J_{HH} = 8.32, 4.30 \) Hz, \( H_8 \)), 7.69 (dd, 1H, \( ^3J_{HH} = 8.03, ^4J_{HH} = 4.40 \) Hz, \( H_3 \)), 7.75 - 7.87 (m, 1H, \( H_{13} \)), 7.89 (s, 1H, \( H_6 \)) 7.90 - 7.92 (m, 1H, \( H_{12} \)), 8.33 (td, 2H, \( ^3J_{HH} = 8.08, ^4J_{HH} = 1.63 \) Hz, \( H_4, H_7 \)) 9.24 (m, 2H, \( H_2, H_9 \)) Anal calcd. for C\textsubscript{37}H\textsubscript{40}N\textsubscript{2}: C 85.17, H 7.92, N 5.37. Found C 85.13, H 8.01, N 5.23.
6.16 Synthesis of bis(μ-chloro)bis[bis[2-(pyridin-2-yl)phenyl-C,N]iridium]

According to a literature procedure,\textsuperscript{124} iridium trichloride hydrate, IrCl$_3$.xH$_2$O (278.3 mg, 0.932 mmol) and 2-phenylpyridine (361.6 mg, 2.30 mmol) were dissolved in 2-ethoxyethanol (30 mL) and water (10 mL) and heated to reflux temperature for 24 hours. The solution was cooled and then filtered. The resulting solid was washed with ethanol (60 mL) and acetone (60 mL). The solid was then dissolved in DCM (75 mL) and toluene (25 mL) and then hexane (10 mL) was added. The solvent was reduced to half the volume under reduced pressure and the solution was filtered to give yellow crystals of bis(μ-chloro)bis[bis[2-(pyridin-2-yl)phenyl-C,N]iridium] (350 mg, 70 %). $^1$H NMR (250 MHz, CDCl$_3$) $\delta$: 5.93 (d, 2H, $J = 7.84$ Hz, Ar-H), 6.56 (t, 2H, $^3J_{HH} = 7.46$ Hz Ar-H), 6.68-6.85 (m, 4H, Ar-H), 7.49 (d, 2H, $^3J_{HH} = 7.84$ Hz, py-H), 7.68-7.80 (m, 2H, py-H), 7.87 (d, 2H, $^3J_{HH} = 7.07$ Hz, py-H), 9.24 (d, 2H, $^3J_{HH} = 5.35$ Hz, Ar-H).


According to a literature procedure,\textsuperscript{124} iridium trichloride hydrate, IrCl$_3$.xH$_2$O (215 mg, 0.72 mmol) and benzo[h]quinoline (322 mg, 1.80 mmol) were dissolved in 2-ethoxyethanol (20 mL) and water (7 mL) and heated to reflux temperature for 24 hours. The solution was cooled and then filtered. The collected solid was washed with ethanol (60 mL) and acetone (60 mL). The solid was then dissolved in DCM (75 mL) and toluene (25 mL) and then hexane (10 mL) was added. The solvent was reduced to half the volume under reduced pressure and the solution was filtered to give yellow crystals of
tetakis(benzo[h]quinolin-10-yl-C,N)di-μ-chloro-di-iridium (350 mg, 70 %). $^1$H NMR (400 MHz, CDCl$_3$) δH: 5.94 (d, 1H, $^3$J$_{HH}$ = 7.79 Hz, Ar-H), 6.83 (m, 1H, Ar-H), 7.11-7.28 (m, 2H, Ar-H), 7.82 (s, 2H, Ar-H), 8.42 (d, 2H, $^3$J$_{HH}$ =7.14, Py-H), 9.31 (d, 2H, $^3$J$_{HH}$ = 7.14 Hz, py-H).

6.18 Synthesis of [Ir(ppy)$_2$(7)]$[PF_6]$ (7a)

[Ir(ppy)$_2$(μ-Cl)$_2$]$_2$ (149 mg, 0.139 mmol) was dissolved in MeOH (20 mL). This solution was added slowly to a solution of ligand 7 (150 mg, 0.293 mmol) in DCM (15 mL). The resulting mixture was heated to reflux temperature for 18 h. The solution was cooled to room temperature and a saturated methanolic solution of ammonium hexafluorophosphate (5 mL) was added. The solution was stirred for a further 30 minutes. The solvent was reduced to half the volume under reduced pressure and the resultant precipitate filtered, washed with MeOH (10 mL) and Et$_2$O (10 mL), and dried to give orange crystals (243.3 mg, 75 %). MALDI MS (alpha): m/z 1014 {M$-$PF$_6$}$^+$ (100%). $^1$H NMR (400 MHz, DCM-d$_2$) δH: 0.68 - 0.79 (m, 10H, alkyl-H) 0.99 - 1.18 (m, 12H, alkyl-H) 1.98 - 2.11 (m, 4H, alkyl-H) 6.45 (ddd, 2H, $^3$J$_{HH}$ = 7.64, $^4$J$_{HH}$ = 2.59, 0.88 Hz, Ar-H), 6.91 (td, 2H, $^3$J$_{HH}$ = 6.13, 1.14 Hz, Ar-H) 7.02 (tt, 2H, $^3$J$_{HH}$ = 7.45, $^4$J$_{HH}$ = 1.39 Hz, Ar-H) 7.14 (tdd, 2H $^3$J$_{HH}$ = 7.52, $^4$J$_{HH}$ = 3.54, 1.14 Hz, Ar-H), 7.38 - 7.46 (m, 6H, Ar-H) 7.54 - 7.61 (m, 2H, Ar-H) 7.68 - 7.90 (m, 8H, Ar-H), 7.95 (d, 1H, $^3$J$_{HH}$ = 8.08 Hz, Ar-H) 7.97 - 8.04 (m, 2H, Ar-H) 8.20 (s, 1H, Ar-H), 8.37 (ddd, 2H, $^3$J$_{HH}$ = 8.97, 5.05, $^4$J$_{HH}$ = 1.39 Hz, Ar-H), 8.62 (ddd, 2H, $^3$J$_{HH}$ = 14.27, 8.34, $^4$J$_{HH}$ = 1.39 Hz, Ar-H). $^{13}$C NMR (101 MHz, CDCl$_3$) δC: 14.61(CH$_3$), 23.35 (CH$_2$), 24.72 (CH$_2$), 30.44 (CH$_2$), 32.34 (CH$_2$), 41.02 (CH$_2$), 56.23 (q), 120.72 (CH), 120.96 (CH), 121.04 (CH), 123.70 (CH), 123.97 (CH), 124.07 (CH), 125.30 (CH), 125.79 (CH) 127.10 (CH), 127.87 (CH), 128.71 (CH), 129.65 (CH), 131.59 (CH), 131.81 (q).
132.63 (CH), 135.74 (q) 137.95 (CH), 140.93 (q), 142.70 (q), 143.07 (q), 144.70 (q), 146.94 (q), 148.16 (q), 149.45 (CH), 150.09 (q), 150.49 (q), 151.84 (CH), 152.57 (q), 154.97 (q), 168.68 (q). UV-vis (MeCN) \( \lambda_{\text{max}} (\epsilon / \text{mol}^{-1} \text{dm}^{3} \text{cm}) : 319 \) (25700).

6.19 Synthesis of [Ir(pq)\(_{2}(7)\)\[PF_{6}\]] (7b)

[Ir(pq)\(_{2}(\mu-\text{Cl})\)]\(_{2}\) (60 mg, 0.051 mmol) was dissolved in MeOH (15 mL). This solution was added slowly to a solution of ligand 7 (55.3 mg, 0.108 mmol) in DCM (10 mL). The resulting mixture was heated to reflux temperature for 18 h. The solution was cooled to room temperature and a saturated methanolic solution of ammonium hexafluorophosphate (3 mL) was added. The solution was stirred for a further 30 minutes. The solvent was then reduced to half the volume and the resultant precipitate filtered, washed with MeOH (10 mL) and Et\(_{2}\)O (10 mL), and dried to give orange crystals of 7b (86 mg, 70 %). ES+ MS: m/z 1062 \{M-PF\(_{6}\)\}\(^{+}\) (100%). \(^{1}\)H NMR (400 MHz, CDCl\(_{3}\)) \( \delta_{\text{H}} \): 0.74 (dt, 10H, alkyl-H), 0.95 - 1.21 (m, 12H, alkyl-H), 1.57 (s, 4H, alkyl-H), 6.47 (t, 2H, \(^{3}\)J\(_{HH} = \) 7.15 Hz, Ar-H), 7.18 - 7.30 (m, 8H, Ar-H), 7.33 - 7.49 (m, 7H, Ar-H), 7.50 - 7.64 (m, 7H, Ar-H), 7.66 - 7.79 (m, 5H, Ar-H) 7.82 - 7.93 (m, 6H, Ar-H) 7.96 (d, 1H, \(^{3}\)J\(_{HH} = \) 4.77 Hz, Ar-H), 8.17 (s, 1H, Ar-H), 8.21 - 8.35 (m, 5H, Ar-H) 8.52 - 8.65 (m, 2H, Ar-H). UV-vis (MeCN) \( \lambda_{\text{max}} (\epsilon / \text{mol}^{-1} \text{dm}^{3} \text{cm}) : 258 \) (35100), 326 (15600), 420 (2550). Anal. Calcd. For C\(_{62}\)H\(_{63}\)F\(_{6}\)IrN\(_{4}\)P: C 63.45 H 5.08 N 4.48 P 2.48. Found C 62.97 H 5.03 N 4.57 P 2.41
6.20 Synthesis of Re(7)(CO)₃Cl (7c)

Rhenium pentacarboxylchloride (27 mg, 0.073 mmol) and ligand 7 (37 mg, 0.073) were dissolved in toluene (20 mL) and heated to reflux temperature for 18 hours. The reaction mixture was cooled to room temperature and all solvents were removed under reduced pressure. The resultant solid was recrystallised by THF:hexane vapour diffusion to give yellow crystals of 7c (58 mg, 99 %). ES+ MS: m/z 819 {M+H}⁺ (100%). ¹H NMR (400 MHz, CDCl₃) δH: 0.74 - 0.84 (m, 10H, alkyl-H), 1.02 - 1.18 (m, 13H, alkyl-H), 1.26 (s, 4H, alkyl-H), 7.38 - 7.54 (m, 6H, Ar-H) 7.77 - 7.85 (m, 2H, Ar-H), 7.89 - 7.95 (m, 2H, Ar-H), 8.04 (s, 1H, Ar-H), 8.60 (dd, 2H, 3JHH = 8.38, 4JHH = 1.04 Hz, Ar-H), 9.44 (ddd, 2H, 3JHH = 9.60, 5.01, 4JHH = 1.16 Hz, Ar-H). ¹³C NMR (101 MHz, CDCl₃) δC: 14.34 (CH₃), 22.86 (CH₂), 24.21 (CH₂), 29.94 (CH₂), 30.01 (CH₂), 31.81 (CH₂), 40.53 (CH₂), 55.66 (q), 120.49 (CH), 120.55 (CH), 123.39 (CH), 124.80 (CH), 125.77 (CH), 126.37 (CH), 127.19 (CH), 127.43 (CH), 128.26 (CH), 128.91 (CH), 130.58 (q), 131.11 (q), 135.11 (q), 137.40 (CH), 138.18 (CH), 141.78 (q), 146.73 (q), 151.31 (q), 152.02 (q), 153.00 (CH), 153.16 (CH). UV-vis (DCM) λmax (ε / mol⁻¹ dm³ cm): 270 (96900), 342 (29300), 410 (8940). Anal. Calcd. For C₄₀H₄₀ClReN₂O₃: C 58.70 H 4.93 N 3.42. Found C 58.38 H 5.86 N 2.77.
6.21 Synthesis of [Ir(ppy)$_2$(8)][PF$_6$] (8a)

[Ir(ppy)$_2$(μ-Cl)$_2$] (61 mg, 0.057 mmol) was dissolved in MeOH (15 mL). This solution was added slowly to a solution of ligand 8 (61 mg, 0.120 mmol) in DCM (10 mL). The resulting mixture was heated to reflux temperature for 18 h. The solution was cooled to room temperature and a saturated methanolic solution of ammonium hexafluorophosphate, NH$_4$PF$_6$ (5 mL) was added. The solution was stirred for a further 30 minutes. The solvent was reduced to half volume and the precipitate that formed filtered, washed with MeOH (10 mL) and Et$_2$O (10 mL), and dried to give an orange crystalline solid (58 mg, 68%).

MALDI MS (alpha): m/z 1345 {M-PF$_6$}$^+$ (100%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta_H$: 0.66 - 0.86 (m, 20H, alkyl-H), 1.03 - 1.20 (m, 24H, alkyl-H), 1.58 (s, 8H, alkyl-H), 6.35 (t, 1H, $^3$J$_{HH}$ = 7.83 Hz, Ar-H), 6.65 (t, 1H, $^3$J$_{HH}$ = 8.56 Hz, Ar-H), 7.32 - 7.41 (m, 4H, Ar-H) 7.44 - 7.51 (m, 4H, Ar-H) 7.55 (dd, 2H, $^3$J$_{HH}$ = 7.52, $^4$J$_{HH}$ = 1.41 Hz, Ar-H), 7.59 - 7.83 (m, 18H, Ar-H), 7.84 - 8.02 (m, 6H, Ar-H), 8.05 - 8.13 (m, 1H, Ar-H), 8.20 (d, 1H, $^3$J$_{HH}$ = 8.31 Hz, Ar-H), 8.28 (dd, 2H, $^3$J$_{HH}$ = 12.04, 4.59 Hz, Ar-H), 8.59 (dd, 1H, $^3$J$_{HH}$ = 6.30, $^4$J$_{HH}$ = 2.14 Hz, Ar-H), 8.64 - 8.71 (m, 2H, Ar-H). UV-vis (MeCN) $\lambda_{max}$ (ε / mol$^{-1}$ dm$^3$ cm): 265 (57400), 334 (56900). Anal. Calcd. For C$_{62}$H$_{63}$IrN$_4$F$_6$P: C 67.67 H 5.95 N 3.76. Found C 66.51 H 5.56 N 3.92
6.22 Synthesis of [Ir(pq)₂(8)][PF₆] (8b)

[Ir(pq)₂(μ-Cl)]₂ (60 mg, 0.051 mmol) was dissolved in MeOH (15 mL). This solution was added slowly to a solution of 8 (55.3 mg, 0.108 mmol) in DCM (10 mL). The resulting mixture was heated to reflux temperature for 18 h. The solution was cooled to room temperature and a saturated methanolic solution of ammonium hexafluorophosphate, NH₄PF₆ (3 mL) was added. The solution was stirred for a further 30 minutes. The solvent was then reduced to half the volume and the precipitate filtered, washed with MeOH (10 mL) and Et₂O (10 mL), and dried to give an orange crystalline solid (86 mg, 70 %). ES+ MS: m/z 1538 {M-PF₆}⁺ (100%). ¹H NMR (400 MHz, CDCl₃) δH: 0.69 - 0.81 (m, 20H, alkyl-H), 0.98 - 1.23 (m, 24H, alkyl-H), 1.96 - 2.21 (m, 8H, alkyl-H), 6.48 (t, 2H, ³J_HH = 7.70 Hz, Ar-H), 7.24 (d, 2H, ³J_HH = 7.95 Hz, Ar-H), 7.31 - 7.40 (m, 3H, Ar-H), 7.41 - 7.51 (m, 4H, Ar-H), 7.51 - 7.57 (m, 3H, Ar-H), 7.58 - 7.72 (m, 10H, Ar-H), 7.73 - 7.78 (m, 2H, Ar-H), 7.78 - 7.83 (m, 2H, Ar-H), 7.84 - 7.93 (m, 4H, Ar-H), 7.97 (d, 1H, ³J_HH = 7.13 Hz, Ar-H), 8.19 (s, 1H, Ar-H), 8.21 - 8.28 (m, 3H, Ar-H), 8.31 (d, 1H, ⁴J_HH = 3.91 Hz, Ar-H), 8.61 (dd, 2H, ³J_HH = 10.58, 9.11 Hz, Ar-H). UV-vis (MeCN) ⁶λ_max (ε / mol⁻¹ cm⁻¹): 215 (141000), 331 (64900). Anal. Calcd. For C₈₈H₈₈F₆IrN₄P: C 68.68 H 5.76 N 3.64. Found: C 67.33 H 5.76 N 3.53.
6.23 Synthesis of Re(8)(CO)_3Cl (8c)

Rhenium pentacarbonylchloride (31 mg, 0.085 mmol) and ligand 8 (44 mg, 0.085 mmol) were dissolved in toluene (20 mL) and heated to reflux temperature for 18 hours. The reaction mixture was cooled to room temperature and solvents were removed under reduced pressure. The resultant solid was recrystallised by THF:hexane vapour diffusion to give a yellow crystalline solid 79 mg, (81 %). ES+ MS: m/z 1153 {M+H}^+ (100%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 0.72 - 0.85 (m, 20H, alkyl-H), 1.05 - 1.22 (m, 24H, alkyl-H), 1.98 - 2.19 (m, 8H, alkyl-H), 7.31 - 7.41 (m, 3H, Ar-H), 7.45 - 7.59 (m, 6H, Ar-H), 7.63 - 7.71 (m, 5H, Ar-H), 7.72 - 7.79 (m, 2H, Ar-H), 7.80 - 7.85 (m, 2H, Ar-H), 7.87 - 7.98 (m, 3H, Ar-H), 8.06 (s, 1H, Ar-H), 8.62 (td, 2H, $^3$J$_{HH} = 8.65$, $^4$J$_{HH} = 1.16$ Hz, Ar-H), 9.45 (ddd, 2H, $^3$J$_{HH} = 11.28$, 5.04, $^4$J$_{HH} = 1.28$ Hz, Ar-H). UV-vis (DCM) $\lambda_{\text{max}}$ (ε / mol$^{-1}$ dm$^{3}$ cm): 333 (32900). For C$_6$H$_7$ClReN$_2$O$_3$: C 67.65 H 6.55 N 2.43 Cl 3.07. Found C 67.40 H 6.42 N 2.14 Cl 3.25.
6.24 Synthesis of [Ir(ppy)$_2$(μ-9)Re(CO)$_3$Cl][PF$_6$] (9a)

Rhenium pentacarbonylchloride (26 mg, 0.072 mmol) in toluene (10 mL) was added dropwise to a solution of PFP, 9 (50 mg, 0.072 mmol) in toluene (20 mL). The resultant solution was heated to reflux temperature for 18 h. Solvents were removed under reduced pressure. The product was then washed with pentane and dried (57 mg, 78%). [Re(9)CO)$_3$Cl] (57 mg, 0.057 mmol) was dissolved in DCM (10 mL) and [Ir(ppy)$_2$(μ-Cl)]$_2$ (30 mg, 0.028 mmol) dissolved in EtOH (10 mL) was added dropwise. The solution was heated to reflux temperature for 18 h. The reaction mixture was cooled to room temperature and a saturated methanolic solution of NH$_4$PF$_6$ (5 mL) was added. All solvents were removed under reduced pressure, and the resulting solid was extracted into DCM, washed with water, dried over magnesium sulphate and evaporated to dryness. The Ir-Re complex 9a was obtained as an orange solid (83 mg, 91%). ES+ MS m/z 1497 {M-PF$_6$}$^+$ (100%).

$^1$H NMR (400 MHz, CDCl$_3$) δH: 0.65 - 0.85 (m, 10H, alkyl-\(H\)), 1.02 - 1.24 (m, 12H, alkyl-\(H\)), 2.10 (d, $^3$\(J_{HH} = 5.99\) Hz, 4H, alkyl-\(H\)), 6.40 - 6.48 (m, 2H, Ar-\(H\)), 6.94 - 7.13 (m, 6H, Ar-\(H\)), 7.42 (t, 1H, $^3$\(J_{HH} = 6.85\) Hz, Ar-\(H\)), 7.52 - 7.58 (m, 3H, Ar-\(H\)), 7.58 - 7.62 (m, 1H, Ar-\(H\)), 7.64 - 7.79 (m, 8H, Ar-\(H\)), 7.80 - 7.88 (m, 2H, Ar-\(H\)), 7.89 - 7.97 (m, 4H, Ar-\(H\)), 7.98 - 8.06 (m, 2H, Ar-\(H\)), 8.08 (d, 1H, $^3$\(J_{HH} = 4.28\) Hz, Ar-\(H\)), 8.20 (d, 1H, $^3$\(J_{HH} = 6.97\) Hz, Ar-\(H\)), 8.27 - 8.35 (m, 2H, Ar-\(H\)), 8.58 - 8.69 (m, 4H, Ar-\(H\)), 9.39 - 9.49 (m, 2H, Ar-\(H\)). UV-vis (MeCN) $\lambda$$_{max}$ (\(\varepsilon / \text{mol}^{-1} \text{dm}^3 \text{cm}^{-1}\)): 269 (89400), 340 (42500). Anal. Calcd. For C$_{74}$H$_{62}$ClF$_6$IrN$_6$O$_3$PRe: C 54.12 H 3.81 N 5.12. Found C 53.97 H 4.01 N 4.87.
6.25 Synthesis of [Ir(ppy)$_2$(μ-9)Ru(7)$_2$][(PF$_6$)$_3$] (9b)

[Ru(7)$_2$(PFP)][PF$_6$]$_2$ (58 mg, 0.0275 mmol) was dissolved in DCM (10 mL) and [Ir(ppy)$_2$(μ-Cl)$_2$] (15 mg, 0.014 mmol) dissolved in EtOH (10 mL) was added dropwise. The solution was heated to reflux temperature for 18 h. The reaction mixture was cooled to room temperature and a saturated methanolic solution of NH$_4$PF$_6$ (5 mL) was added. All solvents were removed under reduced pressure, and the resulting solid was extracted into DCM, washed with water, dried over magnesium sulphate and evaporated to dryness. The Ir-Ru complex was obtained as an orange solid (46 mg, 74 %). ES+ (MeCN): 1231.99 {M-PF$_6$} 89 %. $^1$H NMR (400 MHz, CDCl$_3$) δH: 0.65 (s, 30H, H$_{alkyl}$) 1.01 (s, 36H, H$_{alkyl}$) 1.83-2.12 (s, 12H, H$_{alkyl}$), 6.35 (t, 2H, $^3$J$_{HH}$ = 6.41 Hz, Ar-H) 6.78-7.05 (m, 8H, Ar-H) 7.19 (s, 4H, Ar-H), 7.32 (br. s., 6H, Ar-H), 7.40 - 7.94 (m, 29H, Ar-H), 8.00 - 8.29 (m, 10H, Ar-H), 8.35 - 8.64 (m, 6H, Ar-H). UV-vis (MeCN) $\lambda_{max}$ (ε / mol$^{-1}$ dm$^3$ cm): 267 (83800), 330 (30600), 450 (10300) Anal. Calcd. For C$_{145}$H$_{142}$F$_{18}$IrN$_{10}$P$_3$Ru: C 63.26 H 5.20 N 5.09. Found C 63.63 H 5.43 N 5.01.
Appendix A

X-Ray Crystallography

Crystallographic data and refinement details for compounds 1b, 7a and 7c are given in Table 29.

Table 29: Crystallographic Data and Refinement Details for the ligand 1b and the complexes 7a and 7c.

<table>
<thead>
<tr>
<th></th>
<th>1b</th>
<th>7a</th>
<th>7c</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C41H30N4</td>
<td>CoH5IrN4F3P</td>
<td>CoH5ClIrN5O3Re</td>
</tr>
<tr>
<td>M</td>
<td>578.69</td>
<td>1158.24</td>
<td>818.40</td>
</tr>
<tr>
<td>Crystal System</td>
<td>Monoclinic</td>
<td>Triclinic</td>
<td>Triclinic</td>
</tr>
<tr>
<td>a (Å)</td>
<td>44.548(15)</td>
<td>13.5173(9)</td>
<td>11.1417(4)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>9.560(7)</td>
<td>20.6494(13)</td>
<td>12.5724(4)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>22.941(8)</td>
<td>20.9242(14)</td>
<td>14.6245(5)</td>
</tr>
<tr>
<td>α (°)</td>
<td>90</td>
<td>102.854(6)</td>
<td>66.305(1)</td>
</tr>
<tr>
<td>β (°)</td>
<td>142.56(3)</td>
<td>97.805(5)</td>
<td>86.379(1)</td>
</tr>
<tr>
<td>γ (°)</td>
<td>90</td>
<td>90.954(5)</td>
<td>71.513(1)</td>
</tr>
<tr>
<td>Space Gp.</td>
<td>C1 2/c 1</td>
<td>P-1</td>
<td>P-1</td>
</tr>
<tr>
<td>Z</td>
<td>8</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>T (K)</td>
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<td>150</td>
<td>150</td>
</tr>
<tr>
<td>μ (mm⁻¹)</td>
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<td>7.702</td>
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<tr>
<td>Reflns. Measd</td>
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<td>16167</td>
<td>6497</td>
</tr>
<tr>
<td>Reflns. Obsd</td>
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<td>15463</td>
<td>6169</td>
</tr>
<tr>
<td>R₁ (obsd)</td>
<td>0.0515</td>
<td>0.1099</td>
<td>0.0319</td>
</tr>
<tr>
<td>wR²(all data)</td>
<td>0.1211</td>
<td>0.2906</td>
<td>0.0833</td>
</tr>
</tbody>
</table>
Appendix B

Theoretical Calculations

All DFT and TD-DFT calculations were carried out using the Gaussian 09 suite of programs. The UV-visible absorption spectra were simulated using the GaussSum program. Where possible, the crystallographic coordinates were used from the crystallographic information files (.cif files) prior to structure optimisation, in all other cases, the molecules were drawn in Gaussian 09 and used as a model for structural optimisation.

Chapter 2

Structure optimisation was conducted on ligands 1a and 1b using the B3LYP functional and 6-311G++ basis set. For ligand 1b the crystallographically determined geometry was used. TD-DFT calculations were carried out at the CAM-B3LYP level with a CPCM solvent model (acetonitrile). The first 50 excited states calculated, covering wavelength ranges of ca. 216-454 nm (1a) and 185-358 nm (1b). Structure optimisation were conducted on complexes (2a, 2b, 4a, 4b, 5a and 5b) using the B3LYP functional with cc-PVQZ-pp basis set and SDD pseudopotential on the metal centres and 6-311G++ on all other atoms. Structure optimisations were conducted on complexes 3a and 3b with a LANL2DZ basis set and pseudopotential on the metal centres and 6-311G++ on all other atoms. The TD-DFT calculations were performed at the CAM-B3LYP level with a CPCM solvent model (acetonitrile). The first 50 excited states calculated, the approximate wavelengths covered are given in Table 30.

Table 30: Approximate wavelengths covered in TD-DFT calculation of the first 50 states of complexes from chapter 2

<table>
<thead>
<tr>
<th>Complex</th>
<th>Wavelengths Covered / nm</th>
<th>Complex</th>
<th>Wavelengths Covered / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>200-435</td>
<td>2b</td>
<td>208-417</td>
</tr>
<tr>
<td>3a</td>
<td>205-394</td>
<td>3b</td>
<td>213-386</td>
</tr>
<tr>
<td>4a</td>
<td>246-428</td>
<td>4b</td>
<td>256-422</td>
</tr>
<tr>
<td>5a</td>
<td>244-464</td>
<td>5b</td>
<td>248-442</td>
</tr>
</tbody>
</table>

Structure optimisations of the cis isomers for compounds in Chapter 2 were also carried out with subsequent TD-DFT calculations were carried out using the using the B3LYP functional and with cc-PVQZ-pp basis set and SDD pseudopotential on the metal centres
and 6-311G++ on all other atoms. The first 50 states were calculated in order to visualise potential changes upon photo-isomerisation.

Chapter 3

Structure optimisation and subsequent TD-DFT calculations were conducted on models of complexes 7a, 7b, and 7c (denoted 7a’, 7b’ and 7c’) at the B3LYP level using cc-PQVZ-pp basis set and a relativistic SDD pseudopotential on the metal centres (Ir, Re) and 6-311G++ on all other atoms. The structure of compounds 7a’ and 7c’ were based upon crystallographically determined geometries of complexes 7a and 7b respectively, and complex 7b’ was based on a modified structure of the crystallographic data for complex 7a. TD-DFT calculations were based on the optimised geometries and conducted with at the CAM-B3LYP level using a CPCM solvent model (acetonitrile/chloroform). The first 50 excited states were calculated, covering wavelengths of 223-348 nm (7a’), 232-349 nm (7b’) and 198-350 nm (7c’).

Chapter 4

Structure optimisation was conducted on models of complexes 8a, 8b, and 8c (denoted 8a’, 8b’ and 8c’) at the B3LYP level using cc-PQVZ-pp basis set and a relativistic SDD pseudopotential on the metal centres (Ir, Re) and 6-311G++ on all other atoms. Subsequent TD-DFT calculations were conducted on the optimised geometries at the CAM-B3LYP level using a CPCM solvent model (acetonitrile/chloroform). The first 50 excited states were calculated covering wavelengths of 229-349 nm (8a’), 237-349 nm (8b’) and 205-350 nm (8c’).

Chapter 5

Structure optimisation was conducted on models of complexes 9a, and 9b (denoted 9a’ and 9b’) at the B3LYP level using a split cc-PQVZ-pp/6-311G++ basis set and a relativistic SDD pseudopotential on the metal centres (Ir, Re and Ru). Subsequent TD-DFT calculations were conducted on the optimised geometries at the CAM-B3LYP level using a CPCM solvent model (acetonitrile). The first 50 excited states were calculated covering wavelengths of 243-345 nm (9a’), 266-377 nm (9b’).
Appendix C
Cell Imaging

Three preliminary *in-vitro* cell experiments with C6-Glioma cells were carried out. The cell images obtained by two photon confocal microscopy for the control experiment are given in Figure 115, the cell images for irradiation with 1 mM of compound 7a are given in Figure 116 and cell images for irradiation with 10 mM of compound 7a are given in Figure 117.

Figure 115: Cell images for the control experiment. The irradiated area is highlighted with a blue box. a) Before irradiation, b) after 5 mins irradiation, c) after 5 mins irradiation and 15 mins of monitoring, d) after 10 mins 13 s irradiation and 30 mins of monitoring, e) after 10 mins 13 s irradiation and 45 mins of monitoring, f) after 10 mins 13 s irradiation and 1 hour of monitoring, g) zoom area before irradiation, h) zoom area after 10 min 13 s of irradiation.
Figure 116: Cell images for the 1 mM doped experiment. The irradiated area is highlighted with a blue box. a) Before irradiation, b) after 5 mins irradiation, c) after 5 mins irradiation and 15 mins of monitoring, d) after 5 mins irradiation and 30 mins of monitoring, e) after 5 mins irradiation and 45 mins of monitoring, f) after 5 mins irradiation and 1 hour of monitoring, g) zoom area before irradiation, h) zoom area after 5 mins of irradiation.

Figure 117: Cell images for the 10 mM doped experiment. The irradiated area is highlighted with a blue box. a) Before irradiation, b) after 5 mins irradiation, c) after 5 mins irradiation and 15 mins of monitoring, d) after 5 mins irradiation and 30 mins of monitoring, e) after 5 mins irradiation and 45 mins of monitoring, f) after 5 mins irradiation and 1 hour of monitoring, g) zoom area before irradiation, h) zoom area after 5 mins of irradiation.
Appendix D
Publications Resulting from the Thesis Work

A cyclometallated fluorenlyl Ir(III) complex as a potential sensitizer for two-photon excited photodynamic therapy (2PE-PDT)

Elizabeth M. Boreham, Lucy Jones, Adam N. Swinburne, Mireille Blanchard-Descée, Vincent Hughes, Christine Teryn, Fabien Mionandre, Gilles Lemercier and Louise S. Nattrass

A new Ir(III) cyclometallated complex bearing a fluorenlyl 5-substituted-1,10-phenanthroline ligand ([Ir(ppy)2(ppy)2]) is presented which exhibits enhanced triplet oxygen sensing properties. The efficacy of this complex to act as a photosensitizer for altering the morphology of C6 Gloma cells that represent malignant tumours has been evaluated. The increased heavy metal effect and related spin–orbit coupling parameters on the photophysical properties of this complex are evidenced by comparison with Ru(II) analogues. The complex ([Ir(ppy)2(ppy)2]) is shown to exhibit relatively high two-photon absorption efficiencies for the lowest energy MLCT electronic transitions with two-photon absorption cross sections that range from 50 to 80 Geoerget–Mayer units between 750 to 800 nm. Quantum yields for the complex were measured up to 23% and the Stern–Volmer quenching constant, Kn, was determined to be 40 bar−1 in acetonitrile solution, confirming the high efficiency of the complex as a triplet oxygen sensitizer. Preliminary in vitro experiments with C6 Gloma cells treated with ([Ir(ppy)2(ppy)2]) show that the complex is an efficient sensitizer for triplet oxygen, producing cytotoxic singlet oxygen (O2) by two-photon excitation at 740 nm resulting in photodynamic effects that lead to localised cell damage and death.

Introduction
Cyclometalated Ir(n) complexes are robust, synthetically versatile and both photochemically and thermally stable. Ir(n) has also attracted attention as it facilitates very efficient intersystem crossing (ISC) due to its large spin–orbit coupling value, ultimately leading to quantitative population of the molecule's triplet excited state. This long-lived triplet metal-to-ligand charge transfer excited state (MLCT) can be populated either directly via energy redistribution from excited singlet states located on the surrounding organic ligand. The spin–orbit nature of the radiative decay process is slightly relaxed due to partial triplet character of the ground state, resulting in high phosphorescence quantum efficiency from the lowest triplet excited state. This results in a large Stokes shift between excitation and emission and provides an efficient mechanism for triplet–triplet energy transfer (Förster mechanism) to the ground state of O2, so generating cytotoxic O2. Additionally, Ir(n) polypyridyl based complexes enable broader tuning of the intrinsically photophysical properties when compared to the lighter group congeners Fe(n) or Ru(n). This is principally due to increased ligand-field stabilization energy and pronounced decoupling of the MLCT excited states with those that are metal-centred; these are essentially thermally inaccessible under ambient conditions. For instance, homoleptic Ir(n) complex, such as the related compound Ir(ppy)3, possess desirable spectroscopic properties including long-lived electronic emitting states and high photo-luminescence quantum yield.
Appendix D

We reported previously the interest of 5-substituted-1,10-phenanthroline ligand-embedded Ru(II) complexes for their linear and nonlinear optical properties, and their potential application in optical power limiting and as photosensitizers for ZPF-PDT. The 5-fluorophenyl-substituted 1,10-phenanthroline ligand, L1 (see Fig. 1 for the molecular structure) was chosen for its distinctive optical properties and its ability to complex heavy transition metals. It has been shown that the two-photon absorption cross section (α2) of Ru(II) phenanthroline (phen) complexes is increased by coordination of the fluorine pendant at the fifth position of phen in [Ru(phen)(L1)]2+ compared to the unsubstituted 1,10-phenanthroline ligand in [Ru(phen)]2+. (from 20 to 40 GM at around 740 nm) Additionally, the non-planar geometry of this ligand can prevent aggregation, which may limit conjugation induced self-quenching and crosstalk formation at higher localized concentrations in addition to affecting the biological distribution of the compound in a more potential bio-applications are concerned.

Control of the solubility of the complex is afforded by substitution of the alkyl chain e.g. with triethylene glycol (TEG) for water solubility, with no detrimental effect on the photophysical properties. Previously, a homoleptic Ru(II) complex with three coordinated L1 ligands featuring the TEG functionality was reported as a fairly efficient photosensitizer proposed for two-photon PDT; a 2PA cross-section σ2PA around 40 GM was determined at 740 nm which corresponds to the wave-length used in the two-photon biological experiments.

In this work, a heteroleptic Ru(II) complex has been synthesised involving two cyclometalating 2-phenylpyridine (ppy) ligands and 5-fluoro-1,10-phenanthroline (L1) as the third ligand ([Ir(ppy3)L1]PF6); This complex is assessed as a two-photon absorber, and for its potential as a triplet O2 sensitiser; its effectiveness as a 2PA-PDT therapeutic agent is evaluated by preliminary in vitro tests with C6 glioma cells.
Appendix D

Results and discussion

Synthesis
The complex [Ir(ppy)2(L1)][PF6] (IrppyL1) was synthesised according to literature precedent from [Ir(ppy)2(acat)][PF6] by heating a dichloromethane : methanol solution of the dimer to reflux temperature with two equivalents of L1\textsuperscript{1+} (see Fig. 1). The complex is fully characterised by \textsuperscript{1}H NMR, mass spectrometry, elemental analysis and single crystal X-ray diffraction (see Experimental section).

Single crystals of IrppyL1 for structural analysis were grown by slow vapour diffusion of n-hexane into a dichloromethane : acetone solution of the complex at room temperature. In the solid state, the complex crystallises with two molecules of [Ir(ppy)2(L1)][PF6] in the asymmetric unit cell. As expected, the PF\textsubscript{6}\textsuperscript{-} counterions remain unbound to the metal centre. Each Ir(n) cation is hexacoordinated by two ppy ligands that lie in a mutually cis arrangement and one L1 ligand providing an approximate octahedral coordination geometry about each Ir(n) ion (see Fig. 2). The average C-Ir and N-Ir bond lengths of 2.02(3) Å and 2.03(2) Å in the ppy ligands respectively and marginally longer N-Ir bond distances from the phen mass spectra of 3.11(2) Å are consistent with those reported in the literature for similar Ir(ppy)(phen) compounds. In the solid state, the dihedral angles between the fluorenyl substituent and the phen unit are measured as 48° in the molecule containing Ir(1) and 57° in the molecule labelled with Ir(2).

One-photon absorption and emission
The absorption spectrum of IrppyL1 is composed of a broad, weak band in the 420–480 nm range attributed to triplet d\textsubscript{0}lu\textsuperscript{15+} metal-to-ligand charge-transfer (MLCT; Fig. 1 and see ESI† for expanded graph). This is in accordance with previous assignments for this type of Ir(n) complex involving ppy and poly-pyridyl ligands.\textsuperscript{15,11} A broad and more intense band between 370 and 420 nm (I\textsubscript{max} around 400 nm), is assigned to the \textsuperscript{1}MLCT, and finally bands at shorter wavelengths than 350 nm which are mainly ascribed to intra-ligand charge-transfer (ILCT) and n-\pi\textsuperscript{*} electronic transitions centred on aromatic rings. These features are also reproduced in the emission spectrum (see Fig. 2).

The emission maximum wavelength is around 600 nm in acetonitrile. Given that the radiative decay-time of IrppyL1 is of microsecond order, (see Table 1), the principal emissive excited state in the complex can be mainly ascribed as arising from the 3MLCT state.

The absolute value of the quantum yield was measured at 400 nm excitation, in degassed acetonitrile using an integrating sphere and found to be 23% (see Table 1), the corresponding value in aerated and oxygenated solvent was found to be much lower (3 and 1%, respectively). In the solid state, the luminescence quantum yield was determined to be 40%.

Due to the envelope of absorption transitions at higher energy and the fact that the MLCT state is the principle constituent, the lowest energy absorption bands are best described as an admixture of ligand to ligand charge transfer (LLCT) and ligand-centred (LC) transitions. This is in agreement with the observed photophysics indicating the long range of the charge transfer transitions, as desired for nonlinear and especially two-photon absorption properties.

Computational study
In order to further elucidate the nature of the electronic transitions, density functional theory (DFT) calculations were per-
formed on a simplified structure of the complex. The coordinates of the crystal structure were first altered to rotate the hexyl chains with methyl groups for computational simplicity, as they do not contribute electronically. This structure was then optimised using DFT in Gaussian09 using the B3LYP functional and the 6-31G** basis set for C, H and N atoms and the Stuttgart relativistic basis set and effective core potential (ECP) for F.

The optimised structure was then used for time-dependent DFT (TD-DFT) calculations with the same basis sets and the CAM-B3LYP functional, which describes charge-transfer transitions more accurately. Table 2 lists the orbital contributions for the first singlet transitions, which support our assignments of the low energy, weak bands to MLCT transitions and the higher energy, more strongly absorbing bands to intraligand transitions, in particular from the phenanthroline moiety.

There are six triplet states calculated before the first singlet state, the lowest of these, T1, S0 is described as a mixture of MLCT from the Ir(III) d orbitals to the phen (30%) and intraligand transitions located on L1 (50%) the remainder is made up of many smaller contributions.

Electrochemistry
In order to examine the effect of the charge transfer electronic transitions in the complex, the redox potential of Ir(m) in Ippy11 and the electrochemical properties of the system were investigated. One reversible, one-electron oxidation with the half-wave redox potential at 0.87 V (av. Fe3+/Fe2+) was observed for Ippy11 by cyclic voltammetry (CV) (see Fig. 4), characteristic of the oxidation of Ir(m) to Ir(m).

This experiment was conducted in a classical cell at 1 mM concentration in acetonitrile with tetrabutylammonium hexafluorophosphate as the electrolyte. In addition, the redox potential was also measured in a tailored spectro-electrochemical cell, which allows monitoring of the emission intensity upon an electrochemical signal. The emission can be partially switched off by oxidation of the metal from Ir(n) to Ir(n) as shown in Fig. 5. This shows that the removed electron is responsible for the emissive transition and supports the assignment of MLCT character for this transition. Unfortunately it has not been possible to restore the luminescence upon re-reduction, possibly because of oxygen production at the counter electrode acting as a quencher.

Stern-Volmer studies
Since ground state (triplet) oxygen is a very efficient dynamic or collisional quencher of triplet excited states in platinum group complex, Stern-Volmer analysis can provide a measure of the efficiency of this quenching process in terms of the quenching constant Kq. In this regard, the potential of Ippy11 to act as a triplet oxygen sensitizer, was assessed by determining both the emission intensity and phosphorescent lifetime in degassed, air equilibrated and oxygen-saturated acetonitrile solutions. The resulting relative lifetimes (t(T)/t(0)) and intensities (I(T)/I(0)) were then determined and plotted against the partial pressure of oxygen in solution to give the slope as Kq, the Stern-Volmer quenching constant of triplet O2 in this system (see Fig. 6).
In fluid solution, the dependence of emission intensity and lifetime with quencher concentration is given by the Stern-Volmer equation (eqn (1)):

\[
I = I_0 \left(1 + \frac{K_{sv}[Q]}{I_0}\right) = 1 + K_{sv} \tau_0 Q,
\]

where the \( I \) parameters are emission intensities, the \( \tau \) are lifetimes, \( K_{sv} \) is the Stern-Volmer quenching constant, \( \tau_0 \) is the bimolecular rate constant for quenching of the excited state, and, \( [Q] \), the Henry constant of \( Q \) (gas) in a given solvent. The subscript 0 denotes the values of the quantity in the absence of the quencher. Plots of \( \frac{I}{I_0} \) or \( \frac{\tau}{\tau_0} \) vs. oxygen concentration will be linear with identical slopes equal to \( K_{sv} \) if there is a single class of luminesophores that are all equally accessible to the quencher. This is what is observed in the case of **Irppy3L1** for both \( \frac{I}{I_0} \) and \( \frac{\tau}{\tau_0} \) representations. The gradient of the correlation line was determined to be 43 and 38 hbar\(^{-1}\) for the emission intensity and radiative lifetime respectively. The similar values obtained in terms of both emission intensity and lifetime value are consistent with the mechanism proposed for this energy transfer and oxygen sensitizing.

Interestingly, the values of \( K_{sv} \) are significantly higher in **Irppy3L1** than in the analogous triphenylamine derived ruthenium(ii) complexes that we studied recently, where for example, the value of 5 was found for \( K_{sv} \) of complex **[Ir(phen)Ru(phen)COD)]\(^{2+}\)** in water.

The elevated Stern-Volmer constant for triplet oxygen quenching in **Irppy3L1** when compared to that of unsubstituted Ru(II) based 1,10-phenanthroline complexes may arise from a higher phosphorescence quantum yield of the cyclometallated Ir(III) centre \( (\Phi_{MLCT} = 23\% \leq 9\% \text{ for } [Ru(1113)]^{2+}) \) and the relaxed spin-forbidden transition caused by increased SOC. When the rate constants for radiative and non-radiative decay are considered alongside \( \Phi_0 \) (\( \Phi_0 \) and \( \Phi_{MLCT} \) see Table 1), k\( _S \) is similar for **Irppy3L1** in all three solutions (around 3.3 \( \times 10^{9} \text{ s}^{-1} \)) whereas \( k_{nr} \) is an order of magnitude greater in the aerated solution compared to the deoxygenated solution, and higher again in the oxygen saturated (9.1, 133 and 525 \( \times 10^{9} \text{ s}^{-1} \), respectively) thereby confirming the presence of fast non-radiative relaxation pathways in the presence of oxygen. We were unable to measure the singlet oxygen quantum yield for **Irppy3L1**, but for comparison, the experimentally measured values for the closely related systems **[Ir(ppy)(bipy)]** and **[Ir(ppy)(phen)]** are 0.97 and 0.93 respectively.

### Two-photon absorption studies

The emission profile of **Irppy3L1** was shown to be identical to the one-photon emission profile following non-resonant two-photon excitation with 150 fs nIR laser pulses (700-1000 nm), indicating that the same excited state is accessed by either method as anticipated (see ESIF). This inference is corroborated by the fact that the two-photon excitation spectrum at half the wavelength is superimposable upon the one photon excitation spectrum. The occurrence of a two-photon nonlinear process was further confirmed by power dependence measurements that showed a quadratic relationship of the two-photon induced emission intensity on laser power; this method has been described previously. The 2PA cross-section was determined with reference to fluorescein in 0.01 M NaOH, for which \( \sigma_2 \) is well known. The complex **Irppy3L1** exhibits a 2PA cross-section \( (\sigma_2) \) of around 10 GM over a broad excitation range (800-1000 nm) due to non-resonant absorption populating the intra-ligand excited states in addition to the MLCT. Due to an increase in the IL character at shorter wavelengths, (supported by TDHF) the \( \sigma_2 \) value then increases from 10 to 80 GM between 700 and 800 nm. These values are comparable to those obtained for the analogous Ru(ii) complex **[Ru(phen)LL]PPy]**. 

It is remarkable that the very weak resonant absorption band attributed to the \(^{2}MLCT\) is relatively large by two-photon process (same average value for the 2PA cross-section at 960 and 800 nm, see Fig. 7); the symmetry and/or spin characteristics of this transition may well lie at the origin of this observation.

### In vitro experiments

In preliminary in vitro experiments, confocal microscopy was used to evaluate C6 Glioma cell damage induced by photodynamic effects in the presence of **Irppy3L1** under two-photon irradiation. The cell morphology is observed to change from an elongated (fibroblast) shape to round when they become unhealthy. C6 cells are a model of Glioma which represents a type of malignant tumour that originate in the brain, spine and nervous system. They may be considered to be the cause of aggressive primary brain tumours, which renders both C6 and Glioma cells attractive targets for PDT.

As a control experiment, a sample of cells in the absence of **Irppy3L1**, was irradiated at 740 nm (32.5 \( \mu \text{W} \)) for 5 minutes (which corresponds to two cycles of irradiation). After this time, there was limited damage to the cells and only 7% of the total number of cells underwent a change in morphology.
Conclusions

A new Ir(III) cyclometallated complex bearing the fluorene-
phenanthroline ligand (L1) has been synthesised and fully charac-
terised. The complex [Irppy] (L1) has an photoluminescent lifetime of
748 ns and a quantum yield of 23% in oxygen free solution,
which are dramatically decreased in the presence of O2. The
triplet-triplet energy transfer process is extremely efficient
with a Stern-Volmer quenching constant, Ksv of 60 bar−1 in
solution. The 2PA cross-section, α2, at 740 nm was determined
to be 46 GM. These values make the complex a good candidate
for a 2PE-PDT photosensitizer and in vitro studies with C6
Gloma cells showed efficient cell damage where cells were
treated with Irppy and irradiated under two-photon con-
ditions with 740 nm fs pulsed light, while cells irradiated
with no complex were unchanged. The change in morphology
of the cells observed may be an indication that additional photo-
dynamic cellular responses are occurring resulting from the
presence of Irppy and we are currently investigating the
mechanism(s) of cell damage in the presence of this and
related photosensitisers. In addition to its (two-photon
induced) photodynamic therapy, due to the high efficiency of
luminescence quenching in the presence of oxygen, the
complex could also be utilised for oxygen sensing in other
applications.37

Experimental section

General

Acetonitrile was dried over CaH2 and distilled prior to use. All
other chemicals were obtained from Sigma-Aldrich and used
as supplied. All air sensitive manipulations were conducted in
an Ar filled glove box (Innovative Technologies PE2) total O2
and H2O content was always below 0.1 ppm. All NMR spectra
were recorded on a Bruker Avance 500 spectrometer, operating
centre frequency 490 MHz (1H) and 116 Hz (13C). Mass spectra
were obtained using MALDI from methanol solutions with an
ALPHA matrix on a Micromass TOF Spec 2E spectrometer.

Elemental Analyses were performed by the microanalytical ser-
services at the University of Manchester using a Carlo ERBA
Instruments CHNS-O EA1110 elemental analyser (C, H and N
analysis) and a Perkin Elmer Elemental analysis ICP-OES
spectrometer for P.

X-ray diffraction data for [Irppy] were collected at 100 K
with a Bruker APEX 2 diffractometer using graphite-monochro-
mated Mo-Kα radiation. The structure was solved by direct
methods and refined using OLEX2 software. The structure
was completed by iterative cycles of ΔF-syntheses and a full
matrix least squares refinement. All non-H atoms were refined
anisotropically and difference Fourier syntheses were
employed in positioning idealised hydrogen atoms and were
allowed to ride on their parent C or N-atoms. All refinements
were against F2 and used OLEX2.
Appendix D

Synthesis of [(ppp)2Li][PF6]

[(ppp)2Li][PF6] (119 mg, 0.139 mmol) was dissolved in methanol (20 mL). This solution was added slowly to a solution of LiCl (150 mg, 2.53 mmol) in dichloromethane (15 mL). The resulting mixture was refluxed for 18 h. The solution was cooled to room temperature and a methanolic solution of ammonium hexafluorophosphate (5 mL) was added. The solution was stirred for a further 30 min. The solvent was reduced to half volume and the precipitate filtered, washed with methanol (10 mL) and ether (10 mL) and dried to give orange crystals (243.3 mg, 25%). MALDI MS (alpha): m/z 1018 (M – PF6) (100%). 1H NMR (400 MHz, CD3OD): 8.62 (s, 6H, JH, phen), 8.37 (s, 6H, JH, phen), 8.17 (dd, JH, phen) = 5.1 Hz, JH, phen = 4.1 Hz, 2H, phen), 8.23 (s, 1H, phen), 8.01 (s, 1H, fluorenyl), 7.84 (s, 1H, 2 phen), 7.4 (s, 1H, 4 phen), 7.08 (s, 1H, 1 fluorenyl), 7.42 (s, 1H, 1 fluorenyl), 7.46 (s, 1H, 2 phen), 7.42 (s, 1H, 1 fluorenyl), 7.17 (add, JH, phen = 7.5 Hz, JH, phen = 3.5 Hz, JH, phen = 1.1 Hz, 2H, 2 phen), 7.6 (t, JH, phen = 7.5 Hz, JH, phen = 1.4 Hz, 2H, 2 phen), 6.95 (dd, JH, phen = 6.1 Hz, JH, phen = 2.7 Hz, JH, phen = 0.9 Hz, 2H, 2 phen), 6.49 (dd, JH, phen = 7.6 Hz, JH, phen = 2.7 Hz, JH, phen = 0.9 Hz, 2H, 2 phen), 2.08 (s, 3H, 1.3 (1.23)), 0.79 (m, 10H), 12C NMR (136 Hz, CDCl3) 8.14 (CH3), 23.35 (CH3), 24.72 (CH3), 10.44 (CH3), 32.34 (CH3), 41.02 (CH3), 56.23 (q, 120.72 (CH), 120.56 (CH), 121.04 (CH), 123.70 (CH), 123.97 (CH), 124.07 (CH), 125.30 (CH), 125.79 (CH), 127.10 (CH), 127.87 (CH), 128.71 (CH), 128.65 (CH), 131.59 (CH), 131.81 (q), 132.63 (CH), 135.74 (q), 137.95 (CH), 139.10 (CH), 140.91 (q), 144.70 (q), 144.84 (q), 146.94 (q), 148.16 (q), 149.45 (CH), 150.69 (q), 150.69 (q), 151.84 (CH), 152.57 (q), 154.97 (q), 168.64 (q). UV/vis (acetone).

Photophysical characterization

UV-visible spectra were recorded on a Shimadzu UV-2600 spectrometer using quartz cuvettes with a path length of 1 cm. Steady state emission spectra were recorded on a quartz cuvette on an Edinburgh Instrument FP920 Phosphoroscope. Lifetime Spectrometer equipped with a 5 W microsecond pulsed xenon flashlamp (with single 100 ns focal length excitation and emission monochromators in Crimey Turner configuration) and a red sensitive photomultiplier in a light-tight housing. (Hamamatsu R928). Lifetime data was recorded following excitation with EPL 405 picosecond pulsed diode laser (Edinburgh Instruments) using time correlated single photon counting (PC5900 plug-in PC card for fast photon counting). Lifetimes were obtained by tail fit on the data obtained and quality of fit judged by minimisation of reduced chi-squared. Absolute quantum yields were measured using an integration sphere (Edinburgh Instruments).

Stokes–Volmer analysis

A dry degassed acetonitrile solution of [trpypp]I was prepared in a glass bottle in a quartz cell equipped with a Young’s cap (10 mm × 10 mm) for the oxygen-free measurement. This solution was left open to equilibrate with the air for 1 hour to obtain an aerated sample and then bubbled with oxygen for 5 minutes to obtain an oxygen-saturated solution.

Electrochemistry

Measurements were performed on N3 degassed acetonitrile solutions of 1 mm concentration, and tetrabutylammonium hexafluorophosphate was used as the electrolyte salt. Cyclic voltammetry was performed in a three-electrode cell with a platinum anode (Micro-STATA, Princeton Applied Research) driven by a PC. Platinum disk was used as the working electrode, with platinum wire as the counter and Ag wire as the reference electrode.

Electrochemical monitoring of the luminescence was performed in a tailored thin layer spectrophotocellectrochemical cell coupled to a Fluorolog 3 (Horiba) spectrofluorimetre through optical fibers and driven by a CHI6040 potentiostat.

In vitro cell experiments

Two-photon microscopy: C6 glioma cells were seeded at a density of 5 × 10^4 cells per well in 96-well plates and grown in Dulbecco’s Modified Eagle Medium (F12), enriched with 10% fetal calf serum (FCS) and antibiotics (penicillin 50 U ml^{-1}, streptomycin 50 mg ml^{-1}). After 24 h, cells were treated with [trpypp]I at concentrations of 1 mM and 10 mM. A laser-scanning microscope LSM 710 NLO (Zeiss, Jena, Germany) was used. Excitation was provided by a CHAMELEON femtosecond Titanium Sapphire laser (Coherent, Santa Clara, USA) set at 740 nm with a photon flux of 0.025 mW cm^{-2}. Living cells were deposited in glass bottom box and were imaged with a 63 × 1.4 NA objective lens. The pathology of these cells is not affected by the presence of small quantities of DMSO.

Nonlinear optical measurements

The two-photon absorption spectra of the [trpypp]I complex was determined in the 700-1000 nm range by recording its two-photon excited luminescence (2PEL) in degenerated 10^{-4} M L^{-1} acetonitrile solution in a 10 mm × 10 mm quartz cuvette. The measurements were performed using a Nd:YLF pumped Ti:sapphire oscillator generating 150 fs pulses at a rate of 76 MHz. The excitation was focused into the cuvette through a microscope objective (10x, NA 0.25). The luminescence was detected in epifluorescence mode via a dichroic mirror (Chroma 67314r) and a barrier filter (Chroma 60501-p) by a compact CCD spectrometer module, BWTek R7212R. Total luminescence intensities were obtained by integrating the corrected emission spectra measured by this spectrometer. 2PA cross-sections (σ_2) were determined from the two-photon excited luminescence cross-sections (σ_2) and the luminescence emission quantum yield (Φ). 2PEL cross-sections of 10^{-4} M solutions were measured relative to a 10^{-3} M solution of fluorescein in 0.01 M aqueous NaOH for the range 700-1000 nm, using the well-established method described by Xu and Webb and the appropriate solvent-related refractive index corrections. 15 Data points between 700 and 715 nm were corrected. The quadratic dependence of the luminescence
intensity on the excitation power was checked for each sample at all wavelengths, indicating that the measurements were carried out in intensity regimes where saturation or photodegradation did not occur.

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Notes and references
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