Photochemistry and Photophysics of Octahedral Ruthenium Complexes

A Thesis

Presented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in the Graduate School of the Ohio State University

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2013

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ABSTRACT

The photo-induced ligand loss of the complexes [Ru(tpy)(AN)₃]²⁺ and cis-[Ru(tpy)(AN)₂Cl]⁺ (tpy = 2,2’:6’,2’’:terpyridine) and [Ru(tpy)(5CNU)₃]²⁺ was studied in water and in CH₂Cl₂ in the presence of chloride from tetrabutylammonium chloride (TBACl). [Ru(tpy)(5CNU)₃]²⁺ is not soluble in CH₂Cl₂. Photolysis in CH₂Cl₂ in the presence of chloride ions leads to the dichloro photoproduct trans-[Ru(tpy)(AN)Cl₂], and photolysis in water led to the diaqua photoproduct trans-[Ru(tpy)(AN)(H₂O)₂]²⁺ or trans-[Ru(tpy)(5CNU)(H₂O)₂]²⁺. The two axial ligands are replaced, while the equatorial ligand remains coordinated to the metal. For cis-[Ru(tpy)(AN)₃]²⁺ and [Ru(tpy)(5CNU)₃]²⁺ the axial ligands were replaced in a step-wise fashion, forming an intermediate with one axial acetonitrile ligand. All three complexes were shown to bind to DNA upon photolysis by gel electrophoresis, but not in the absence of light, indicating potential as anti-tumor agents for use in photodynamic therapy (PDT). cis-[Ru(tpy)(AN)₂Cl]⁺ has a higher quantum yield of ligand substitution and a lower energy metal to ligand charge transfer (MLCT) transition showing binding to DNA when irradiated at 650 nm, within the ideal PDT window of 600-850 nm.

The low temperature emission and photolysis of [Ru(bpy)₃]²⁺, cis-
[Ru(bpy)$_2$(AN)$_2$]$_2^{2+}$, cis-[Ru(bpy)$_2$(MeBN)$_2$]$_2^{2+}$, and cis-[Ru(bpy)$_2$(py)$_2$]$_2^{2+}$ was studied to explore their excited state properties. The emission of [Ru(bpy)$_3$]$^{2+}$ is known to take place from the $^3$MLCT state, with a temperature dependence resulting from a thermally accessible non-emissive triplet ligand field state ($^3$LF) higher in energy than the $^3$MLCT state. A decrease in emission quantum yield, $\Phi_{em}$, and comparable increase in the quantum yield of photolysis, $\Phi_{photo}$, is observed for [Ru(bpy)$_3$]$^{2+}$ with increasing temperature. This behavior led to the conclusion that the population of the $^3$LF from the $^3$MLCT state preceded photosubstitution.$^1$ The temperature dependence of the emission of the related compounds cis-[Ru(bpy)$_2$L$_2$]$^{2+}$, where L is AN, MeBN and py, was found to be different from the temperature dependence of the photolysis, suggesting that the photosubstitution proceeds through a different mechanism.$^2,3$ One possibility is that the $^3$LF state is populated directly from the initially excited state and does not require population through the $^3$MLCT state.
DEDICATION

My loving wife Paula
ACKNOWLEDGEMENTS

I would like to thank my advisor, Dr. Claudia Turro, for all of her help and guidance in my research and in writing this thesis. I would also like to thank the members of the Turro research group (2007-2012) for their assistance as well. The machine shop, electronics shop, and glass blower have also been invaluable towards my research here at Ohio State. I would also like to thank Dr. Danilov for his help with the cryostat for low temperature emission.
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CHAPTER 1
BACKGROUND

The most common example of a metal complex in cancer therapy is cis-diamminedichloroplatinum(II) (cisplatin). Since its discovery it and various analogs have been used to treat several types of cancer.\textsuperscript{4,5} The major mechanism by which cisplatin kills cancer cells is by binding to DNA and inhibiting cell replication.\textsuperscript{4,6,7} Upon entering the cell, water displaces the chloride ligands of cisplatin forming the cis-diamminediaquaplatinum(II) ion (Figure 1.1). The diaqua species binds primarily to the N7 position of adjacent guanine nucleotides in DNA, forming 1,2-intrastrand guanine-guanine bridges.\textsuperscript{6-8} This cross link kinks the DNA creating a bend of ~35-40 degrees towards the major groove preventing the cells from replicating.\textsuperscript{9} The cell is also prevented from repairing itself due to proteins with high mobility group (HMG) domains binding to the platinum adduct. This prevents the excision of the damaged DNA by the enzyme excinuclease and increases the toxicity of the drug.\textsuperscript{10-12}
Two major drawbacks of cisplatin and its analogs are its toxicity towards healthy cells and acquired resistance.\textsuperscript{13,14} There is little selectivity between healthy and cancerous cells with Cisplatin. Healthy cells are killed by the same mechanism as cancerous cells at nearly the same rate, limiting the possible dosage of the drug and decreasing its effectiveness. Second and third generation cisplatin complexes have been designed with lower toxicity, but none of these drugs have a significant selectivity for cancerous cells. This is because they are thermally activated, exchanging to the diaqua species upon entrance into the cells regardless of whether or not it is cancerous. Another problem is intrinsic and acquired resistance to cisplatin and its analogs.\textsuperscript{13-15} Cells with a high degree of excision repair tend to be resistant to cisplatin. A drug that is photo-activated, and not thermally activated, would have a significant advantage. Selectivity can be introduced by only irradiating tumors, greatly decreasing the side effects of the drugs and allowing for higher dosages, making resistance less of a problem.

Treatment of cancer by photo-activated drugs is generally known as photodynamic therapy (PDT). An ideal PDT drug is one that has a high quantum yield of photoaquation upon irradiation, absorbs strongly in the low energy visible-near infra red region of the electromagnetic spectrum (650-850nm), and possesses minimal dark toxicity. Human tissue is relatively transparent to...
light in the 650-850nm wavelength range, and a compound that absorbs light in this range would have maximum penetration inside the body. One class of PDT drugs that has been used successfully is porphyrins. Upon irradiation these compounds are excited to a singlet state, which can convert to a long lived triplet excited state through inter-system crossing (Figure 1.2). As shown in Figure 1.2, the triplet can undergo energy transfer producing singlet oxygen, $^1O_2$, which is highly reactive and damaging towards bio-molecules and other cellular components.

Photofrin is a PDT drug approved by the FDA that has been used for the treatment of lung cancer, esophageal cancer, and bladder cancer. Photofrin is composed of porphyrin derivatives (Figure 1.3). Although porphyrins have been effective in treating certain types of cancer, its lowest energy absorption band is at 630 nm, and it is not very strong.

**Figure 1.2** Jablonski diagram for production of singlet oxygen, showing (a) absorption of light (b) Fluorescence (c) non-radiative decay (d) Intersystem Crossing (e) Phosphorescence and (f) Singlet Oxygen Production.
In order to increase the wavelength and extinction coefficient of absorption, the π-
systems of the porphyrins were extended in phthalocyanine and naphthalocyanine
rings which can have absorbance bands ~750 nm (Figure 1.3). A metal atom can
be inserted inside of the rings, and axial ligands can be used to tune the solubility
of the compounds.\textsuperscript{16}

The major disadvantage of this type of PDT agent is the requirement of
oxygen for the action of the drug and resultant cell death. Cancer cells are usually
hypoxic, making a mechanism requiring oxygen less effective. A possible means
to address this drawback is a light activated cisplatin analogue, where the mode of
cell death is the same as in cisplatin, binding to DNA or other bio-molecules.
Such a species does not undergo conversion to the reactive diaqua species until it
is irradiated with light and thus still has selectivity. This type of PDT agent would
not depend on oxygen and could have improved toxicity in cancer cells that are
often hypoxic.
Two metals that have been studied extensively for use as anti-cancer agents are rhodium$^{17-28}$ and ruthenium$^{29-37}$. Complexes of these metals have been shown to bind to DNA upon irradiation of light, and to cause cell death through either singlet oxygen production or oxygen independent damage to DNA and other bio-molecules. Some of these complexes show improvements over FDA approved cisplatin and Photofrin in cell toxicity and in quantum yield of production of singlet oxygen.

One of the characteristics of a good PDT drug is absorbance in the near infrared spectral region. Dirhodium species of the type Rh$_2$(O$_2$CCH$_3$)$_3$ have low energy metal centered excitation of the rhodium-rhodium bond, making them a good candidate for PDT.$^{22}$ One such dirhodium compound, cis-[Rh$_2$(µ-O$_2$CCH$_3$)$_2$(CH$_3$CN)$_4$(H$_2$O)$_2$]$^{2+}$ (Figure 1.4), is a cisplatin analogue in that it loses ligands upon irradiation with light and binds to DNA. Upon irradiation with
light, two of the CH$_3$CN ligands are replaced by water, forming a complex that
binds to DNA. The cytotoxicity of cis-[Rh$_2$(μ-Ο$_2$CCH$_3$)$_2$(CH$_3$CN)$_4$(H$_2$O)$_2$]$^{2+}$
increases by a factor of 34 upon irradiation,\textsuperscript{17} several times greater than the 5 fold
increase measured for the key component of the drug Photofrin under the same
experimental conditions.

Figure 1.4 Schematic representation of cis-[Rh$_2$(μ-Ο$_2$CCH$_3$)$_2$(CH$_3$CN)$_4$(H$_2$O)$_2$]$^{2+}$.

Ruthenium complexes with labile ligands have been studied extensively as
potential pharmaceuticals.\textsuperscript{38} Three major mechanisms by which ruthenium can
undergo ligand loss and subsequent binding to DNA are thermal ligand loss,
activation by reduction, and photoinduced ligand loss. One compound known to
react thermally with DNA is Ru(azp)$_2$Cl$_2$ (azp = 2-(phenylazo)pyridine) shown in
Figure 1.5. Once inside the cell, ruthenium complexes with chloride ligands can
hydrolyze, replacing their chloride ligands with water in a similar way to
cisplatin.\textsuperscript{39,40} Ruthenium compounds with bidentate aromatic imine ligands such
as azp and bpy have better antitumor activity than other ruthenium chlorides such
as cis-Ru(DMSO)$_4$Cl$_2$.\textsuperscript{39,40} A possible reason is that the π-acceptor effect of the
imines decreases the rate of photolysis to the aqua species to a level that is similar
to cisplatin. Other possible reasons are increased hydrophobic interactions between the aromatic ligands and DNA, as well as geometric effects of the ligands effecting protein binding to DNA. Ruthenium diaqua species such as Ru(azp)$_2$(H$_2$O)$_2^{2+}$ and Ru(bpy)$_2$(H$_2$O)$_2^{2+}$ (bpy = 2,2’-dipyridine) have been shown to bind to DNA base adducts and do show cytotoxicity, presumably by binding to DNA. Table 1.1 shows the ID$_{50}$ values for Ru(azp)$_2$Cl$_2$, which undergoes thermal aquation to Ru(azp)$_2$(H$_2$O)$_2$, compared with cisplatin. Ru(azp)$_2$Cl$_2$ shows greater cell toxicity in several cases.

**Table 1.1** Comparison of inhibitory dose of 50% (ID$_{50}$, µM/L) of Ru(azp)$_2$Cl$_2$ compared with cisplatin.

<table>
<thead>
<tr>
<th>Cell line</th>
<th>MCF-7</th>
<th>EVSA-T</th>
<th>WIDR</th>
<th>IGROV</th>
<th>M19</th>
<th>A498</th>
<th>H266</th>
</tr>
</thead>
<tbody>
<tr>
<td>ID$_{50}$ Ru(azp)$_2$Cl$_2$</td>
<td>0.6</td>
<td>0.1</td>
<td>1.9</td>
<td>0.8</td>
<td>0.2</td>
<td>1.2</td>
<td>1.5</td>
</tr>
<tr>
<td>ID$_{50}$ Cisplatin</td>
<td>2.3</td>
<td>1.4</td>
<td>3.2</td>
<td>0.6</td>
<td>1.9</td>
<td>7.5</td>
<td>10.9</td>
</tr>
</tbody>
</table>

Binding to a model DNA base such as 9-ethylguanine has been observed in several ruthenium compounds with aromatic imine ligands including Ru(bpy)$_2$(H$_2$O)$_2^{2+}$, Ru(phen)$_2$(H$_2$O)$_2^{2+}$ (phen = 2-phenylpyridine) and Ru(tpy)(bpy)(H$_2$O)$_2^{2+}$ (tpy = 2,2’:6’,2”-terpyridine). The cytotoxicity in cells of the series Ru(bpy)$_2$Cl$_2$, Ru(bpy)(azp)Cl$_2$ and Ru(azp)$_2$Cl, which produce the above diaqua species in water, was studied and found to vary from the inactive Ru(bpy)$_2$Cl$_2$ to the highly cytotoxic Ru(azp)$_2$Cl$_2$ with Ru(azp)(bpy)Cl$_2$ showing intermediate cytotoxicity. The mechanism of cell death is thought to proceed through the diaqua species, and the difference in cytotoxicity may be due to the different electronic properties of azp compared to the bpy ligand. Due to the
high antitumor activity of Ru(tpy)Cl$_3$\(^{42}\), the binding of irradiated Ru(tpy)(apy)(AN) and Ru(tpy)(apy)Cl (apy = 2,2’-azobis(pyridine) Figure 1.5) to the DNA model base 9-ethylguanine has also been studied.\(^{33}\) Both compounds hydrolyzed to the aqua species and bound to 9-ethylguanine, with Ru(tpy)(apy)(AN) showing much faster binding.

![Structure of 2-(phenylazo)pyridine and 2,2’-azobis(pyridine)](image)

**Figure 1.5** Structure of (a) 2-(phenylazo)pyridine and (b) 2,2’-azobis(pyridine)

A second mechanism for cytotoxicity in ruthenium compounds is reduction upon entering the cell. Reduction of inert Ru(III) compounds activates them by conversion to Ru(II) in vivo, which can then thermally bind to DNA. In general, upon reduction to Ru(II), $\pi$-donating ligands become destabilized and hydrolyze. Two compounds that have been shown to operate by this mechanism are cis-[RuCl$_2$(NH$_3$)$_4$]Cl and [ImH]trans-[Ru(Im)$_2$Cl$_4$] (Im = imidazole). Activation by reduction has the advantage that tumor cells are generally more acidic than healthy cells and as a result have a lower electrochemical potential, making their interior more reducing.\(^{38}\) This difference between healthy and
cancerous cells adds selectivity to these compounds.

The third mechanism, phototinduced ligand loss, represents another way to achieve selective toxicity. Ruthenium complexes have high intensity metal to ligand charge transfer (MLCT) absorptions and long lived excited states making them good candidates for PDT. Photosubstitution is thought to occur from a ligand field state (LF) that is thermally accessible from the $^3$MLCT. Excitation with visible light can excite an electron to the $^1$MLCT which can access the $^3$MLCT through internal conversion. Second and third row transition metals undergo internal conversion very well due to spin-orbit coupling. For Ru(bpy)$_3^{2+}$ the process of going from the $^1$MLCT excited state to a $^3$MLCT lowest energy excited state was measured at $\sim 300$ fs, with intersystem crossing complete in $\sim 40$ fs. The processes are shown in Figure 1.6. Ru(tpy)(4-CO$_2$H-4’-Mebpy)(NO$_2$)$_2^+$, Ru(bpy)$_2$(NH$_3$)$_2^{2+}$, and Ru(bpy)$_2$(AN)$_2^{2+}$ are all known to undergo substitution to form the aqua species upon irradiation with light. Ru(tpy)(4-CO$_2$H-4’-Mebpy)(NO$_2$)$_2^+$ has an MLCT transition with a maximum at 475 nm, and has been observed upon irradiated to produce Ru(tpy)(4-CO$_2$H-4’-Mebpy)(AN)$_2^+$ in acetonitrile. It has also been shown to react with calf thymus DNA upon irradiation for 30 minutes in aqueous solution.
Figure 1.6 Jablonski diagram showing the general mechanism of photosubstitution of metal complexes.

Ru(bpy)$_2$(NH$_3$)$_2^{2+}$ has a low energy MLCT at 490 nm ($\varepsilon = 8,210$ M$^{-1}$cm$^{-1}$) and is known to lose the NH$_3$ ligands upon irradiation.$^{29}$ When irradiated at 400 nm in water, the NH$_3$ ligands are substituted with water molecules to form cis-Ru(bpy)$_2$(H$_2$O)$_2^{2+}$ with a quantum yield of $\Phi = 0.018.$$^{47}$ The compound has been shown to bind to the 15-mer single stranded oligonucleotide sequences 5’-TGCAAGCTTGGCACT-3’ and 5’-AGTGCCAAGCTTGCA-3’, and to double stranded DNA when irradiated at >345 nm.$^{29}$

Cis-Ru(bpy)$_2$(CH$_3$CN)$_2^{2+}$ has a higher energy MLCT transition with a maximum at 425 nm ($\varepsilon = 8,900$ M$^{-1}$cm$^{-1}$). When irradiated at 400 nm in water, it has been shown to undergo photoaquation in water with a quantum yield of $\Phi = 0.21,$$^{47,48}$ and to bind to double stranded DNA when irradiated at >345 nm.$^{47}$ The two complexes acted very similar towards DNA, the only major differences between them is that [Ru(bpy)$_2$(NH$_3$)$_2]$$_{2+}$ absorbs at a lower wavelength and [Ru(bpy)$_2$(CH$_3$CN)$_2]$$_{2+}$ has a higher quantum yield of photoaquation.
Acetonitrile is thought to have such a larger quantum yield of ligand loss because it binds to the metal center through both weak σ and π-back bonding. Excitation of the MLCT transition involves transfer of an electron from the metal to one of the bpy ligands, reducing the electron density on the metal and destabilizing the π-back bonding to acetonitrile. Table 1.2 compares the quantum yield of photoanation with chloride of a series of Ru(bpy)$_2$L$_2^{2+}$ compounds.

**Table 1.2** Quantum yields of photoanation ($\Phi_{\text{Cl}}$) with tetrabutylammoniumchloride (TBACl) in CH$_2$Cl$_2$. (A) taken from reference 49.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\Phi_{\text{Cl}}$</th>
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<tr>
<td>Ru(bpy)$_2$(AN)$_2^{2+}$</td>
<td>0.31 mol/Einstein</td>
</tr>
<tr>
<td>Ru(bpy)$_2$(CO)$_2^{2+}$</td>
<td>0.05 mol/Einstein</td>
</tr>
<tr>
<td>Ru(bpy)$_2$(py)$_2^{2+}$</td>
<td>0.20 mol/Einstein</td>
</tr>
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CHAPTER 2

EXPERIMENTAL

2.1 Materials

2.1.1 Commercial Materials

Water used in all reactions and measurements was deionized using a Barnstead Fi-stream filter system to 18 MΩ. H₂SO₄, Et₂O, and N(Et)₃ purchased from Fisher, CHCl₃ and MeOH purchased from Mallinckrodt, and CH₃CN and EtOH absolute purchased from Acros, and Decon labs, respectively were used without further purification. RuCl₃ trihydrate, Bu₄NPF₆, NH₄PF₆, 2,2’-dipyridyl, N,N-dimethylformamide, 2,2’:6’,2”-terpyridine, 2,3-diaminopyridine, sodium dithionite, loading buffer (0.05% (w/v) bromophenol blue, 40% (w/v) sucrose, 0.1 M EDTA (pH = 8.0, 0.5% (w/v) sodium lauryl sulfate), and ethidium bromide were purchased from Aldrich, Bu₄NCl and 1,10-phenanthroline were purchased from Fluka, LiCl was purchased from J. T. Chemical Co. and used as received. Sodium acetate trihydrate was purchased from Sigma, (NH₄)₃[Fe(C₂O₄)₃] trihydrate was purchased from Riedel-de Haën, and (NH₄)₂OsCl₆ and 5-cyanouracil was purchased from Alfa Aesar and used as received. The pUC19 plasmids were purchased from Bayou Biolabs and purified using the QIAprep miniprep spin system from Qiagen. Sma I and RExact 4 buffer were purchased
from Invitrogen, and the removal of Sma I was performed with the QIAquick gel extraction kit from Qiagen.

2.1.2 Synthesis and Characterization

The ligands dipyrido[3,2-α:2′,3′-c]phenazine (dppz)\(^{50}\) and 1,10-phenanthroline-5,6-dione\(^{51,52}\) were synthesized from literature procedures.

**Ru(tpy)Cl\(_3\).** Ru(tpy)Cl\(_3\) was synthesized by a method previously reported.\(^{53}\) A mixture of 476.2 mg (1.82 mmol) RuCl\(_3\)·3H\(_2\)O, 399.9 mg (1.71 mmol) 2,2′:6′:2′′-terpyridine, and 130 mL of absolute ethanol was stirred under reflux for 3 hours. The solution was filtered and washed with three 30 mL portions of absolute ethanol to remove Ru(tpy)\(^{2+}\), three 30 mL portions of diethyl ether to remove excess tpy, and air dried. Yield: 606 mg (80%). \(^1\)H NMR (400 MHz, \(CD_3CN\)) \(\delta\)(ppm): 8.3 (d, 2H), 8.2 (m, 2H), 7.8 (m, 2H), 7.7 (t, 2H), 7.6 (t, 3H).

**Ru(tpy)(AN)Cl\(_2\).** Ru(tpy)(AN)Cl\(_2\) was prepared according to a literature procedure.\(^{54}\) A mixture of 122.7 mg (0.278 mmol) Ru(tpy)Cl\(_3\), 1 mL acetonitrile, and 1 mL of triethyl amine was refluxed for 1.5 hours in 30 mL of chloroform. The solution was cooled to room temperature, filtered, and 30 mL of ethanol was added. The solution was condensed to ~20 mL, filtered, and air dried. Yield: 96.7 mg (78%). \(^1\)H NMR (250 MHz, \(CDCl_3\)) \(\delta\)(ppm): 9.17 (d, J= 5.82 Hz, 2H), 8.05 (dd, J = 13.30, 7.75 Hz, 4H), 7.78 (t, J=7.70 Hz, 2H), 7.63 (t, J=7.90 Hz, 1H), 7.46 (t, J=7.05 Hz, 2H), 2.85 (s, 3H) shown in Figure 2.2.

**[Ru(tpy)(AN)\(_2\)Cl](PF\(_6\)).** Ru(tpy)(AN)\(_2\)Cl was prepared following a literature procedure.\(^{54}\) A mixture of 138.9 mg (0.315 mmol) Ru(tpy)Cl\(_3\) and 3 mL acetonitrile was refluxed for 9 hours in 1:1 (v/v) ethanol : water. The solution
was condensed to ~10 mL and NH₄PF₆(aq) was added. The solution was filtered and chromatographed on an alumina I (basic) column using 1:1 (v/v) dichloromethane/acetone as the eluent. Yield: 21.6 mg (11%). ¹H NMR (400 MHz, acetone) δ(ppm): 9.12 (ddd, J = 5.47, 1.51, 0.76 Hz, 2H), 8.57 (m, 4H), 8.13 (m, 3H), 7.74 (ddd, J = 7.60, 5.46, 1.32 Hz, 2H), 2.94 (s, 3H), 2.13 (s, 3H) shown in Figure 2.3.

[Ru(tpy)(AN)₃](PF₆)₂. Ru(tpy)(AN)₃ was prepared following a literature procedure.⁵⁴ A mixture of 138.9 mg (0.315 mmol) Ru(tpy)Cl₃ and 3 mL acetonitrile was refluxed for 9 hours in 1:1 (v/v) ethanol : water. The solution was condensed to ~10 mL and NH₄PF₆(aq) was added. The solution was filtered and chromatographed on an alumina I (basic) column using 1:1 (v/v) dichloromethane/acetone as the eluent. Yield: 36.2 mg (15%). ¹H NMR (400 MHz, d₆-acetone) ppm 9.15 (dd, J = 5.42, 0.72 Hz, 2H), 8.69 (dd, J = 8.07, 1.74 Hz, 4H), 8.33 (m, 3H), 7.87 (ddd, J = 7.62, 5.46, 1.26 Hz, 2H), 2.92 (s, 3H), 2.16 (s, 3H) shown in Figure 2.4.

The chloride salts [Ru(tpy)(AN)₃]Cl₂ and [Ru(tpy)(AN)₂Cl]Cl were prepared by adding an acetone solution of N(Bu)₄Cl to the PF₆ salt of each compound dissolved in acetone. The solutions were filtered and the solid product was air dried.

[Ru(tpy)(5CNU)₃](PF₆)₂. Ru(tpy)Cl₃ (0.114 mmol, 50 mg) was suspended in 10 mL of ethanol. To this brown mixture Ag(CF₃SO₃) (0.341 mmol, 88 mg) was added and the mixture quickly turned purple. The solution was filtered and 5-cyanouracil (1.14 mmol, 156 mg) and 2 mL of H₂O were
added. The solution was refluxed under N\textsubscript{2} for 24 hr. The solvent was removed, and the crude product was dissolved in boiling H\textsubscript{2}O and a saturated solution of NH\textsubscript{4}PF\textsubscript{6} was added. The solution was placed in a freezer over night to aid in precipitation of the product. The solid was collected and washed with cold water and ether. The chloride salt was formed by running the \((\text{PF}_6)^{-}\) salt through an Amberlite\textsuperscript{®} exchange column. Elemental analysis calculated. For \([\text{Ru}(C_{15}H_{11}N_3)(C_5H_3N_3O_2)_3]\text{Cl}_2\cdot6.5\text{H}_2\text{O}: \text{C}, 39.0\%; \text{H}, 2.9\%; \text{N}, 18.2\%. \text{Found:} \text{C}, 29.3\%; \text{H}, 3.3\%; \text{N}, 18.1\%. \text{H NMR (400 MHz, } d_2\text{-water}) \text{ppm 9.09 (d, } J = 5.95 \text{ Hz, 2H), 8.72 (s, 1H), 8.50 (t, } J = 9.36, 9.36 \text{ Hz, 4H), 8.33-8.22 (m, 3H), 8.01 (s, 2H), 7.82 (t, 2H) shown in Figure 2.5.}

\textbf{Cis-Ru(bpy)}\textsubscript{2}\text{Cl}_2. \text{Cis-Ru(bpy)}\textsubscript{2}\text{Cl}_2 \text{was synthesized by a method previously reported.}^{55} \text{A mixture of 891.2 mg (1.84 mmol) RuCl}_3\cdot3\text{H}_2\text{O, 1.0266 g (6.57 mmol) 2,2'}\text{-dipyridyl and 1.0799 g (25.5 mmol) LiCl was refluxed for 8 hours under nitrogen in 2:5 (v/v) N,N-dimethylformamide/methanol. 35 mL of acetone was added and the solution was cooled in a freezer overnight. The solid was filtered and dissolved in CH}_2\text{Cl}_2 \text{and [Ru(bpy)}\textsubscript{3}\text{]}^{2+} \text{was extracted with water until no [Ru(bpy)}\textsubscript{3}\text{]}^{2+} \text{could be seen in the water layer. The CH}_2\text{Cl}_2 \text{was evaporated and the solid collected. Yield: 630.3 mg (40%).}

\textbf{[Ru(bpy)}\textsubscript{3}\text{]}\text{Cl}_2. \text{[Ru(bpy)}\textsubscript{3}\text{]}\text{Cl}_2 \text{was extracted as a by-product of the synthesis of cis-Ru(bpy)}\textsubscript{2}\text{Cl}_2 \text{shown above. [Ru(bpy)}\textsubscript{3}\text{]}\text{Cl}_2 \text{was extracted from the mixture by water and the solvent was removed.}^1 \text{H NMR (400 MHz, } d_3\text{-acetonitrile}) \text{ppm 8.49 (d, } J = 8.07 \text{ Hz, 6H), 8.05 (dt, } J = 8.13, 7.95, 1.48 \text{ Hz, 6H), 7.72 (m, 6H), 7.39 (ddd, } J = 7.54, 5.64, 1.31 \text{ Hz, 6H) shown in Figure}
Cis-[Ru(bpy)$_2$(AN)$_2$(PF$_6$)$_2$. Cis-[Ru(bpy)$_2$(AN)$_2$(PF$_6$)$_2$ was synthesized by a method previously described.$^{48}$ A mixture of 218.3 mg (0.45 mmol) cis-Ru(bpy)$_2$Cl$_2$ and 30 mL of 1:1 (v/v) acetonitrile:water was refluxed under nitrogen for 2 hours. The solution was hot filtered and allowed to cool. The product was precipitated by the addition of NH$_4$(PF$_6$)(s) and collected by filtration. Yield: 299.5 mg (85%). $^1$H NMR (400 MHz, d$_2$-water) ppm 9.40 (dd, $J$ = 5.58, 0.75 Hz, 2H), 8.59 (d, $J$ = 8.12 Hz, 2H), 8.43 (d, $J$ = 8.06 Hz, 2H), 8.31 (dt, $J$ = 8.08, 1.49 Hz, 2H), 7.97 (dt, $J$ = 8.05, 1.44 Hz, 2H), 7.93-7.84 (m, 2H), 7.70 (dd, $J$ = 5.67, 0.75 Hz, 2H), 7.31-7.21 (m, 2H), 2.35 (s, 6H), shown in Figure 2.7

Cis-[Ru(bpy)$_2$(BN)$_2$(PF$_6$)$_2$. Cis-[Ru(bpy)$_2$(BN)$_2$(PF$_6$)$_2$ was synthesized by a method previously described.$^{56}$ A mixture of 18.5 mg (0.0382 mmol) cis-Ru(bpy)Cl$_2$ and 4 mL (4.38 mmol) benzonitrile was refluxed under nitrogen in 1:1 (v/v) methanol:water for 2 hours. The methanol was evaporated and excess benzonitrile ligand was extracted with 3X30 mL ether. The product was precipitated by addition of NH$_4$(PF$_6$) and collected by filtration. The compound was chromatographed on an alumina I (basic) column using 1:1 (v/v) dichloromethane/acetonitrile as the eluent. The second fraction was collected and dissolved in minimal acetone and precipitated by addition of ether. Yield: 3.6 mg (10%). $^1$H NMR (400 MHz, d$_6$-acetone) ppm 9.80 (d, $J$ = 5.05 Hz, 2H), 8.89 (d, $J$ = 8.10 Hz, 2H), 8.75 (d, $J$ = 8.06 Hz, 2H), 8.48 (dt, $J$ = 8.01, 1.24 Hz, 2H), 8.18 (dt, $J$ = 8.10, 8.01, 1.21 Hz, 2H), 8.06 (dd, $J$ = 12.62, 6.23 Hz, 4H)
7.84-7.72 (m, 6H), 7.58 (t, $J = 7.87$ 7.87 Hz, 4H) 7.55-7.46 (m, 2H), shown in Figure 2.8

Cis-[Ru(bpy)$_2$(4-Me-BN)$_2$](PF$_6$)$_2$. Cis-[Ru(bpy)$_2$(4-Me-BN)$_2$](PF$_6$)$_2$ was synthesized by a procedure analogous to that of Cis-[Ru(bpy)$_2$(BN)$_2$](PF$_6$)$_2$ except 4-methylbenzonitrile was used in place of benzonitrile. Yield: 17.1 mg (17%). $^1$H NMR (400 MHz, $d_6$-acetone) ppm 9.77 (dd, $J = 4.92, 0.70$ Hz, 2H), 8.88 (d, $J = 8.04$ Hz, 2H), 8.74 (d, $J = 7.95$ Hz, 2H), 8.47 (t, $J = 7.92, 7.92$ Hz, 2H), 8.16 (t, $J = 7.87, 7.87$ Hz, 2H), 8.04 (dd, $J = 12.93, 5.99$ Hz, 4H), 7.64 (d, $J = 8.10$ Hz, 4H), 7.50 (t, $J = 7.21, 7.21$ Hz, 2H), 7.39 (d, $J = 8.46$ Hz, 4H), 2.40 (s, 6H) shown in Figure 2.9

Cis-[Ru(bpy)$_2$(py)$_2$](PF$_6$)$_2$. A quantity of 8 mg (0.00854 mmoles) of cis-[Ru(bpy)$_2$(4-Me-BN)$_2$](PF$_6$)$_2$ was dissolved in 5 mL of pyridine and allowed to reflux under nitrogen for 6 hours. The compound was crashed out of solution by the addition of 10 mL of ether and filtered. $^1$H NMR (400 MHz, $d_6$-acetone) ppm 9.34 (dd, $J = 5.61, 0.64$ Hz, 2H), 8.72-8.65 (m, 6H), 8.60 (d, $J = 8.00$ Hz, 2H), 8.36-8.21 (m, 4H), 8.09 (dt, $J = 8.09, 7.92, 1.45$ Hz, 2H), 8.01-7.92 (m, 4H), 7.58-7.51 (m, 2H), 7.45 (ddd, $J = 7.60, 5.23, 1.35$ Hz, 4H) shown in Figure 2.10

Cis-Os(bpy)$_2$Cl$_2$. Cis-Os(bpy)$_2$Cl$_2$ was prepared following a published procedure.$^{57,58}$ A mixture of 242.4 mg (0.55 mmoles) (NH$_4$)$_2$OsCl$_6$ and 169.9 mg (1.09 mmoles) 2,2′-bipyridine was refluxed in 10 mL ethylene glycol under nitrogen for 1 hour. The solution was kept in a freezer overnight to help precipitation and filtered. The solid obtained was added to a solution of 3.5 g sodium dithionite (Na$_2$S$_2$O$_4$, 20 mmoles) in 20 mL water. The solution
was cooled for 30 minutes in a freezer, filtered, and washed with water and ether. Yield: 189 mg (60%).

**Pryido[2',3': 5,6]pyrazino[2,3-f][1,10]phenanthroline (dppp2).** The dppp2 ligand was synthesized by the condensation of 1,10-phenanthroline-5,6-dione and 2,3-diaminopyridine in an analogous method to similar ligands. A solution of 506.5 mg 1,10-phenanthroline-5,6-dione (2.41 mmoles) and a solution of 279.5 mg 2,3-diaminopyridine (2.52 mmoles) dissolved in hot ethanol were prepared separately. The solutions were then combined and refluxed under nitrogen for six hours. The solvent was evaporated and the resulting solid was added to ethanol and filtered. The solid was collected. Yield: 215.8 mg (32%). 1H NMR (400 MHz, d6-dimethylsulfoxide) ppm 9.57 (ddd, J = 16.62, 8.10, 1.69 Hz, 2H), 9.42 (dd, J = 4.00, 1.88 Hz, 1H), 9.29-9.23 (m, 2H), 8.86 (dd, J = 8.48, 1.86 Hz, 1H), 8.08 (dd, J = 8.48, 4.03 Hz, 1H), 7.99 (ddd, J = 8.11, 6.31, 4.44 Hz, 2H) shown in Figure 2.11.

**Cis-[Os(bpy)2(dppz)](PF6)2.** Cis-[Os(bpy)2(dppz)](PF6)2 was synthesized following a literature procedure for Cis-[Os(bpy)2LL](PF6)2 where LL is a phenanthroline derivative. A mixture of 15.8 mg of cis-Os(bpy)2Cl2 and 8 mg dppz in ethylene glycol was refluxed under nitrogen for four hours. Excess (NH4)(PF6) in 15 mL water was added and the solution was filtered. The solid was chromatographed on an alumina I (basic) column using 1:1 (v/v) dichloromethane : acetone as the first eluent and acetonitrile as a second eluent. 1H NMR (500 MHz, d6-acetone) ppm 9.56 (dd, J = 8.18, 1.23 Hz, 2H), 8.85 (dd, J = 18.20, 7.99 Hz, 4H), 8.56-8.47 (m, 4H), 8.25-8.19 (m, 2H), 8.10 (ddd, J
= 9.53, 7.89, 3.83 Hz, 4H), 8.05-7.95 (m, 6H), 7.61-7.55 (m, 2H), 7.33 (ddd, J = 7.38, 5.83, 1.32 Hz, 2H) shown in Figure 2.12.

Cis-[Os(bpy)$_2$(dppp2)](PF$_6$)$_2$. Cis-[Os(bpy)$_2$(dppp2)](PF$_6$)$_2$ was synthesized in an analogous procedure to cis-[Os(bpy)$_2$(dppz)](PF$_6$)$_2$ with dppp2 replacing dppz. Yield 5 mg (27%). $^1$H NMR (500 MHz, $d_6$-acetone) ppm 9.57-9.48 (m, 3H), 8.92 (dd, J = 8.54, 1.92 Hz, 1H), 8.84 (ddd, J = 17.69, 8.17, 0.79 Hz, 4H), 8.52 (ddd, J = 5.46, 3.41, 1.20 Hz, 2H), 8.19 (dd, J = 8.54, 3.99 Hz, 1H), 8.09 (ddd, J = 9.43, 6.85, 1.10 Hz, 4H), 8.04-7.95 (m, 6H), 7.57 (ddd, J = 7.36, 5.74, 1.31 Hz, 2H), 7.35-7.29 (m, 2H) shown in Figure 2.13.

[Os(dppp2)$_3$](PF$_6$)$_2$. Os(dppp2)$_3$(PF$_6$)$_2$ was synthesized according to a literature procedure for Os(LL)$_3^{2+}$ complexes.$^{60}$ A mixture of 11.0 mg (NH$_4$)$_2$[OsCl$_6$] and 21.7 mg dppz in ethylene glycol was refluxed for two hours under nitrogen. Excess (NH$_4$)$_2$(PF$_6$) in 10 mL of water was added and the solution was filtered. The solid was chromatographed on an alumina 1 (basic) column using acetonitrile as the eluent. The compound was recrystallized by addition of ether to a solution of the compound in methanol. Yield 25 mg (75%). $^1$H NMR (500 MHz, $d_4$-methanol) ppm 9.66 (ddd, J = 21.19, 8.11 Hz, 6H), 9.54 (ddd, J = 4.15, 1.88 Hz, 3H), 9.03 (ddd, J = 8.63, 1.86 Hz, 3H), 8.46-8.39 (m, 6H), 7.97-7.89 (m, 3H), 8.21 (ddd, J = 8.64, 4.19 Hz, 6H) shown in Figure 2.14.

2.2 Instrumentation

$^1$H NMR spectra were obtained on a 250, 400, or 500 MHz Bruker system. Electronic absorption spectra were performed on a Hewlett-Packard Diode Array Spectrometer (HP 8453) equipped with HP 8453 Win System software.
Emission and excitation spectra were recorded on a HoribaJobinYvon Fluoromax-4 spectrometer with a 150W xenon arc lamp as the excitation source. Sample solutions were contained in a 1 cm quartz cell in air unless otherwise noted. Irradiation was done using a 150W Xe arc lamp from Photon Technology International with an LPS-220 lamp power supply unless otherwise specified. The ethidium bromide stained agarose gels were imaged using a GelDoc 2000 transilluminator (BioRad) equipped with Quantity One (v. 4.0.3) software. Cyclic voltammetry measurements were carried out on a CV-50W voltammetric analyzer from Bioanalytical Systems Inc. Temperatures for temperature dependent photolysis near room temperature were maintained by circulating water with a NESLAB RTE-100 circulator connected to a jacketed cuvette holder. Temperatures for temperature dependent emission and photolysis at low temperatures were maintained with a Cryodyne model M22CP cryostat from CTI Cryogenics attached to a model SC(air-cooled) compressor also from CIT Cryogenics, a model DRC-70C temperature controller from Lakeshore Cryotronics Inc., and a Sargent-Welch Direct-Torr vacuum pump model 8814 A. The cryostat was fit with a copper sample holder made in house to fit a 1 cm x 1cm cuvette.

2.3 Methods

2.3.1 Quantum Yields of Photolysis

Photolysis reactions were carried out on a 150 W Xe arc lamp. The light beam was filtered through a Newport 400 nm band pass filter model 10BPF10-400 with a FWHM = 10 nm. The absorption of the compounds at the irradiation
wavelength was >0.7 to ensure 100% light absorption. The intensity of the incident light was measured by ferrioxalate actinometry. Ferric oxalate has a well characterized photochemical reaction through which the iron(III) is reduced to iron(II). The ligand 1,10-phenanthroline coordinates almost exclusively with iron(II) over iron(III) to form a metal complex, Fe(phen)$_3^{2+}$, which absorbs in the visible region. This allows the reaction to be monitored by UV-Vis spectroscopy. The quantum yield of the iron oxalate reaction is known for a wide range of irradiation wavelengths, which allows the calculation of the intensity of the lamp via equation 1. All solutions were degassed by bubbling nitrogen for 10 minutes prior to photolysis. The quantum yields were calculated from equation 1,

$$
\Phi = \frac{MV}{It}
$$

where $M$ is the change in molarity of the reactant, $V$ is the volume of the irradiated sample, $I$ is the intensity of the lamp, and $t$ is the irradiation time. Once the intensity of the lamp is known, equation 1 can be used to calculate the quantum yield of any species. A graph of the concentration of the reactant vs. irradiation time was constructed, and the quantum yield was determined from the initial slope of the graph. The reactant concentration during the photolysis is determined by equation 2, the simultaneous solution of Beer’s law for the reactant and product species, where $A_x$ is the absorbance at wavelength $x$, $\varepsilon_{p,x}$ is the molar extinction coefficient of the product at wavelength $x$, and $\varepsilon_{r,x}$ is the molar extinction coefficient of the reactant at wavelength $x$. 
2.3.2 Quantum Yields of $^1\text{O}_2$ production.

Quantum yields of singlet oxygen production were performed by monitoring the change in emission intensity at 475 nm of 1,3-diphenylisobenzofuran (DPBF) when irradiated with a singlet oxygen producing species. Singlet oxygen reacts rapidly with DPBF producing a non-emitting species, as shown in Figure 2.1. The rate of the decrease of emission of DPBF is inversely proportional to the quantum yield of the singlet oxygen producing species in solution.

$$M_R = \frac{\varepsilon_{P,400} A_{549} - \varepsilon_{P,549} A_{400}}{\varepsilon_{P,400} \varepsilon_{R,549} - \varepsilon_{P,549} \varepsilon_{R,400}}$$

**Figure 2.1.** Reaction of 1,3-diphenylisobenzofuran with singlet oxygen.

Samples were irradiated at 460 nm using the 150W xenon arc lamp in the fluorometer as the irradiation source. Ru(bpy)$_3^{2+}$ was used as a standard with a known quantum yield of singlet oxygen of 0.81. Concentrations of 20 µM of DPBF were used in each sample, and concentrations of standard and unknown solutions were chosen to give equal absorption at the irradiation wavelength, 460 nm. Absorbance at the irradiation wavelength was always less than 0.1. Graphs of
emission intensity at 475 nm vs. irradiation time were constructed for both the standard and the unknown and the slopes were found. Quantum yields were calculated by multiplying 0.81 by the ratio of the slope of the unknown to the slope of the standard.

2.3.3 Low Temperature Emission and Photolysis

Emission at 77 K was taken by dissolving the compound in 4:1 ethanol:methanol and placing in an NMR tube. The NMR tube is then placed in a double walled cuvette with a vacuum space between designed in house. The cuvette is then filled with liquid nitrogen submerging the sample and bringing it to 77 K. Temperature dependent emission in the range 20 K – 330 K was taken by dissolving the samples in 4:1 ethanol:methanol and degassing by bubbling nitrogen for 10 minutes. The temperatures were maintained using the cryostat previously described.

Low temperature photolysis was done by monitoring the decrease in the emission of the samples with irradiation time. The complexes were dissolved in 4:1 ethanol:methanol and degassed by bubbling nitrogen for 10 minutes. The temperature was maintained using the cryostat previously described. The experiment was done entirely in the fluorometer using it as the irradiation source as well for monitoring the amount of product remaining. Emission spectra were taken with the $\lambda_{ex}$ equal to the absorption maxima of the lowest energy $^1\text{MLCT}$ transition of the complex and the slits = 4.0 nm. Irradiation was done by opening the slits to 10.0 nm with the $\lambda_{ex}$ equal to the absorption maxima of the lowest energy $^1\text{MLCT}$ transition.
2.3.4 DNA Binding Agarose Gels

DNA binding experiments were carried out using a 20 µL total sample volume in 0.5 mL transparent Eppendorf tubes containing 50 µM linearized pUC19 plasmid and various concentrations of each metal complex and 10 mM sodium phosphate buffer, pH = 8.3. After irradiation, 4 µL of the DNA gel loading buffer was added to each 20 µL sample. The electrophoresis was carried out using a 1% agarose gel in TBE buffer (40 mM Tris-acetate, 1 mM EDTA, pH = 8.2). The gels were then soaked for 30 minutes in 0.5 µg/mL ethidium bromide in water and imaged.
Figure 2.2. Molecular structure with proton numbering scheme and \(^1\)H NMR spectrum of trans-Ru(ppy)(AN)Cl\(_2\) in \(d\)-chloroform. Assignments from reference 54.
Figure 2.3. Molecular structure with proton numbering scheme and $^1$H NMR spectrum of cis-[Ru(tpy)(AN)$_2$Cl]$^+$ in $d_2$-dichloromethane. Assignments from reference 54.
Figure 2.4. Molecular structure with proton numbering scheme and $^1$H NMR spectrum of [Ru(tpy)(AN)$_3$]$^{2+}$ in $d_6$-acetone. Assignments from reference 54.
Figure 2.5. Molecular structure and $^1$H NMR spectrum of $[\text{Ru(tpy)(5CNU)}_3]^{2+}$ in $d_2$-water.
Figure 2.6 Molecular structure and $^1$H NMR spectrum of [Ru(bpy)$_3$]$^{2+}$ in d$_3$-acetonitrile
Figure 2.7 Molecular structure and \(^1\)H NMR spectrum of cis-[Ru(bpy)\(_2\)(AN)\(_2\)]\(^{2+}\) in d\(_2\)-water
Figure 2.8 Molecular structure and $^1$H NMR spectrum of cis-$[\text{Ru(bpy)}_2(\text{NCPh})_2]^{2+}$ in $d_6$-acetone
**Figure 2.9** Molecular structure and $^1$H NMR spectrum of cis-[Ru(bpy)$_2$(4-Me-NCPh)$_2$]$^{2+}$ in d$_6$-acetone
Figure 2.10 Molecular structure and $^1$H NMR spectrum of cis-[Ru(bpy)$_2$(py)$_2$]$^{2+}$ in d$_6$-acetone
Figure 2.11 Molecular structure and $^1$H NMR spectrum of dppp2 in $d_6$-dimethylsulfoxide
Figure 2.12 Molecular structure and $^1$H NMR spectrum of [Os(bpy)$_2$(dppz)](PF$_6$)$_2$ in d$_6$-acetone
Figure 2.13 Molecular structure and $^1$H NMR spectrum of [Os(bpy)$_2$(dppp2)](PF$_6$)$_2$ in d$_6$-acetone
Figure 2.14 Molecular structure and $^1$H NMR spectrum of [Os(dppp)$_3$(PF$_6$)$_2$] in d$_4$-methanol
CHAPTER 3

Ruthenium Terpyridine Compounds

3.1 Background

Two important features of a photodynamic therapy agent are a low energy MLCT transition and a high quantum yield of photoaquation. Low energy MLCT transitions are desirable because organic tissue becomes more transparent in the near infrared wavelengths. The increased $\pi$-conjugation of the 2,2':6',2''-terpyridine (tpy) results in a lower MLCT transition as compared to 2,2'-dipyridyl (bpy), as shown in Figure 3.1. For this reason, Ru(tpy)L$_3$ complexes were chosen for study as possible PDT agents. The ligand, L, was chosen for maximum quantum yield of photostititution in order to get maximum conversion to the activated aqua species. Comparing known Ru(bpy)$_2$L$_2$ complexes, the highest quantum yield of photoanation is when the ligand, L, is acetonitrile (Table 1.2).$^{47,49}$ For these reasons, [Ru(tpy)(AN)$_3$]$^{2+}$ and cis-[Ru(tpy)(AN)$_2$Cl]$^+$ were studied as possible agents for photodynamic therapy. Photolysis of these compounds causes photosubstitution of the acetonitrile ligands forming an aqua species in water that will bind to DNA bases. [Ru(tpy)(5CNU)$_3$]$^{2+}$ (5CNU = 5-cyanouracil, Figure 3.15) was also studied as a possible dual action drug. Upon photolysis [Ru(tpy)(5CNU)$_3$]$^{2+}$ undergoes photolysis to the diaqua
species, analogous to \([\text{Ru(tpy)(AN)}_3]^{2+}\), however it also releases free 5-
cyanouracil into the cell which has biological properties of its own and can inhibit
cell replication.\(^{64,65}\)

![UV-VIS spectra](image)

**Figure 3.1** UV-VIS spectra of \([\text{Ru(bpy)}_3]^{2+}\) (solid line) and \([\text{Ru(tpy)}_2]^{2+}\) (dashed line) in acetonitrile.

### 3.2 Absorption and emission of Ru(tpy)XYZ compounds

The electronic absorption spectra of \([\text{Ru(tpy)(AN)}_3]^{2+}\), cis-
[\text{Ru(tpy)(AN)}_2\text{Cl]}^+, and trans-Ru(tpy)(AN)Cl\(_2\) have been previously reported, and
are shown in Figure 3.2.\(^{54}\) The absorption of \([\text{Ru(tpy)(5CNU)}_3]^{2+}\) is shown in
Figure 3.3. The absorbance maxima and molar extinction coefficients for each
compound are listed in Table 3.1. The absorption spectra of all of the compounds
show ligand centered \(^1\pi\pi^*\) transitions on the tpy ligand with maxima at \(~300\) nm.
\([\text{Ru(tpy)(AN)}_3]^{2+}\) and cis-[\text{Ru(tpy)(AN)}_2\text{Cl]}^+ exhibit singlet metal to ligand charge
transfer \(^1\text{MLCT}\) transitions from the ruthenium \(t_{2g}\) state to the \(\pi^*\) orbital on the
tpy ligand, with maxima at 434 nm and 485 nm respectively. Trans-
Ru(tpy)(AN)Cl$_2$ has two $^1$MLCT transitions at 400 and 549 nm. 
[Ru(tpy)(5CNU)$_3$]$^{2+}$ has a higher energy $^1$MLCT transition at 420 nm. Upon excitation of the $^1$MLCT the complexes quickly go to the $^3$MCLT and can undergo non-radiative relaxation, phosphorescence or ligand loss.

It has been previously reported that neither [Ru(tpy)(AN)$_3$]$^{2+}$, cis-[Ru(tpy)(AN)$_2$Cl]$^+$, nor trans-Ru(tpy)(AN)Cl$_2$ exhibit room-temperature emission.$^{54}$ [Ru(tpy)(5CNU)$_3$]$^{2+}$ also shows no room temperature emission. This could be due to solvent quenching, since emission of ruthenium terpyridine complexes has been related to the ability of solvent molecules to access pockets between ligands.$^{44}$ It is from the $^3$MLCT state, or a state that is thermally accessible from the $^3$MLCT state, that photo substitution occurs.$^{43,66}$

Figure 3.2 Absorption of [Ru(tpy)(AN)$_3$]$^{2+}$ (solid line) cis-[Ru(tpy)(AN)$_2$Cl]$^+$ (dashed line) and trans-Ru(tpy)(AN)Cl$_2$ (dotted line) in CH$_2$Cl$_2$. 

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Figure 3.3 Absorption of [Ru(tpy)(5CNU)$_3$]$^{2+}$ in water

Table 3.1 Absorption and emission maxima of Ru(tpy)L$_3$ compounds. a, from ref 54.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\lambda_{max}$, nm ((\varepsilon), M$^{-1}$cm$^{-1}$) in CH$_2$Cl$_2$</th>
<th>$\lambda_{max}$, nm ((\varepsilon), M$^{-1}$cm$^{-1}$) in water</th>
<th>$\lambda_{em}$, nm at 77K in 4:1 ethanol:methanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ru(tpy)(AN)$_3$]$^{2+}$</td>
<td>434 (4400)</td>
<td>434 (4000)</td>
<td>550, 590</td>
</tr>
<tr>
<td>Cis-[Ru(tpy)(AN)$_3$Cl]$^+$</td>
<td>485 (4600)</td>
<td>450 (4000)</td>
<td>665</td>
</tr>
<tr>
<td>Trans-Ru(tpy)(AN)Cl$_2$</td>
<td>400 (5300)</td>
<td>NA</td>
<td></td>
</tr>
<tr>
<td>[Ru(tpy)(5CNU)$_3$]$^{2+}$</td>
<td>NA</td>
<td>420 (4500)</td>
<td>550, 590</td>
</tr>
</tbody>
</table>

Low temperature emission at 77 kelvin was done in 4:1 ethanol : methanol glass. The spectrum of [Ru(tpy)(AN)$_3$]$^{2+}$ and [Ru(tpy)(5CNU)$_3$]$^{2+}$ are very similar, both showing peaks at 550 and 590 nm. Cis-[Ru(tpy)(AN)$_3$Cl]$^+$ has a
lower energy emission peak at 665nm, as would be expected from the lower energy \(^1\)MLCT in the absorption spectrum. The emission and excitation spectra for each compound are shown in Figures 3.4 and 3.5. The excitation and absorbance spectra are shown as well. Although there is more vibrational structure to the excitation spectra, since they are taken at 77 K, they match the absorption spectra indicating that the emission is not from an impurity. For \([\text{Ru(tpy)(AN)}_3]^{2+}\) and \([\text{Ru(tpy)(5CNU)}_3]^{2+}\) emission spectra were taken with an irradiation wavelength of 435 nm, and excitation spectra were taken with the emission detector set to 550 nm. The emission spectrum of cis-\([\text{Ru(tpy)(AN)}_2\text{Cl}]^{+}\) was taken with an irradiation wavelength of 480 nm, and the excitation spectrum were taken looking at the emission at 665 nm.

![Graph showing emission and excitation spectra](image)

**Figure 3.4** Low temperature emission and excitation shown with room temperature absorbance of cis-\([\text{Ru(tpy)(AN)}_2\text{Cl}]^{+}\) in 4:1 ethanol:methanol

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Figure 3.5 Low temperature Emission and excitation shown with room temperature absorption for (a) [Ru(tpy)(AN)$_3$]$^{2+}$ and (b) [Ru(tpy)(5CNU)]$^{2+}$ in 4:1 ethanol:methanol

3.3 Photoanation of Complexes in CH$_2$Cl$_2$. 

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3.3.1 \([\text{Ru(tpy)(AN)}_3]^{2+}\)

Irradiation of the \(^1\)MLCT transition of \([\text{Ru(tpy)(AN)}_3]^{2+}\) or cis-
\([\text{Ru(tpy)(AN)}_2\text{Cl}^+]\) initiates ligand loss of acetonitrile as previously reported.\(^{54}\)
The acetonitrile ligand is replaced by either a coordinating anion in solution or a solvent molecule. The photolysis of 130 \(\mu\)M \([\text{Ru(tpy)(AN)}_3]^{2+}\) in the presence of chloride ions was followed by UV-Vis spectroscopy and is shown in Figure 3.6. The compound was irradiated with 400 nm light in \(\text{CH}_2\text{Cl}_2\) with \(\sim10\ \text{mM}\) tetrabutlyammonium chloride (TBACl). As the acetonitrile ligands are replaced by chloride, the absorbance of the \(^1\)MLCT state becomes red shifted. This is due to the decreased ligand field splitting of the chloride ligand compared to the acetonitrile ligand. The product of the photolysis is trans-\text{Ru(tpy)(AN)Cl}_2\), as is apparent from comparing the UV-Vis spectrum of photolyzed \([\text{Ru(tpy)(AN)}_3]^{2+}\) to that of synthesized trans-\text{Ru(tpy)(AN)Cl}_2\). (Figure 3.8).

The presence of an intermediate can be seen in the photoanation of \([\text{Ru(tpy)(AN)}_3]^{2+}\) in Figure 3.6 by the formation a peak at \(\sim485\text{nm}\) at 2 minutes, and its subsequent disappearance around 8 minutes. The lack of constant isosbestic points throughout the photolysis also indicates an intermediate. The intermediate is identified as cis-\([\text{Ru(tpy)(AN)}_2\text{Cl}^+]\) by the location of the peak at \(\sim485\text{nm}\) and as previously reported.\(^{54}\) The photolysis reaction is shown in equation 1, and has been previously described.\(^{54}\) Since the intermediate is a stable compound that can be isolated, the overall reaction is most likely a two photon process, requiring one photon for the formation of cis-\([\text{Ru(tpy)(AN)}_2\text{Cl}^+]\), and a
second photon for the formation of trans-Ru(tpy)(AN)Cl₂.

**Scheme 1.** Photolysis of \([\text{Ru(tpy)(AN)}]^{2+}\) with in CH₂Cl₂ TBACl

The axial acetonitrile ligands are replaced by chloride ions, while the equatorial acetonitrile ligand trans to the tpy ligand remains coordinated to the metal. The difference in reactivity of axial and equatorial acetonitrile ligands can be explained by the trans effect; both acetonitrile and chloride have a stronger trans effect than pyridine, and therefore the ligand trans to the terpyridine ring is less likely to be substituted. Figure 3.8 compares the absorption spectra of the photoproducts of \([\text{Ru(tpy)(AN)}]^{2+}\) and cis-[Ru(tpy)(AN)₂Cl]⁺ with that of synthesized trans-Ru(tpy)(AN)Cl₂. It can be seen that the photo product of both species is in fact trans-Ru(tpy)(AN)Cl₂. It is necessary to de-gas the solutions of cis-[Ru(tpy)(AN)₂Cl]⁺ prior to photolysis. In the presence of air, a different photolysis product is obtained. No \(^1\)H NMR signal could be detected for this photolysis product and it is therefore most likely an oxidized paramagnetic ruthenium(III) compound.
3.3.2 Cis-[Ru(tpy)(AN)$_2$Cl]$^+$

The photolysis of cis-[Ru(tpy)(AN)$_2$Cl]$^+$ results in the loss of the axial acetonitrile ligand. The acetonitrile is replaced by either a coordinating anion in solution or a solvent molecule, as shown in equation 2. Figure 3.7 shows the photolysis of 250 µM cis-[Ru(tpy)(AN)$_2$Cl]$^+$ in CH$_2$Cl$_2$ with ~10 mM TBACl.

![Scheme 2. Photolysis of cis-[Ru(tpy)(AN)$_2$Cl]$^+$ in CH$_2$Cl$_2$ with TBACl](image-url)
TBACl. The compound was irradiated at 450nm, and the photolysis product was trans-Ru(tpy)(AN)Cl$_2$ as previously reported$^{54}$ and characterized by UV-Vis spectroscopy. Figure 3.8 compares the photoproduct of cis-[Ru(tpy)(AN)$_2$Cl]$^+$, photolyzed in the presence of Cl$^-$, to that of synthesized trans-Ru(tpy)(AN)Cl$_2$. The axial ligand is replaced while the equatorial acetonitrile ligand remains bound to the metal. The difference in the reactivity of the two acetonitrile ligands can also be explained by the trans effect analogously to the case of [Ru(tpy)(AN)$_3$]$^{2+}$ described above.

![Graph](image.png)

**Figure 3.7** Photolysis of 250 µM cis-[Ru(tpy)(AN)$_2$Cl]$^+$ in dichloromethane in the presence of ~10 mM chloride ions from TBACl. 150W lamp 450 nm band pass filter.
Figure 3.8 Electronic absorption spectrum of the photolysis products of $[\text{Ru(tpy})(\text{AN})_3]^{2+}$ (dotted line) and cis-$[\text{Ru(tpy)}(\text{AN})_2\text{Cl}]^+$ (dashed line) photolyzed in the presence of Cl$^-$ compared with the spectrum of trans-$\text{Ru(tpy)}(\text{AN})\text{Cl}$ (solid line) synthesized from a literature procedure.$^{54}$

3.4 Photoaquation

$\text{Ru(tpy)(AN)}_3^{2+}$, cis-$\text{Ru(tpy)}(\text{AN})_2\text{Cl}^+$, and $\text{Ru(tpy)}(5\text{CNU})_3^{2+}$ undergo photolysis in water to produce the a product with $\lambda_{\text{max}}= 475$ nm. The photoproduct was characterized by electronic absorption spectroscopy and NMR as trans-$\text{Ru(tpy)}(\text{H}_2\text{O})_2(\text{AN})^{2+}$ or $\text{Ru(tpy)}(\text{H}_2\text{O})_2(5\text{CNU})^{2+}$. Just as with photoanation in $\text{CH}_2\text{Cl}_2$, the nitrile ligand trans to the tpy ligand is not photolabile. During the synthesis of cis-$[\text{Ru(tpy)}(\text{AN})_2\text{Cl}]^+$ and trans-$\text{Ru(tpy)}(\text{AN})\text{Cl}$, no trace of the isomers trans-$[\text{Ru(tpy)}(\text{AN})_2\text{Cl}]^+$ or cis-$\text{Ru(tpy)}(\text{AN})\text{Cl}$ could be detected, indicating these species do not generally form. The photolysis product was not $[\text{Ru(tpy)}(\text{H}_2\text{O})_3]^{2+}$, as it is a known species with a $\lambda_{\text{max}}= 532$ nm,$^{66}$ which does not match the absorption of the photoproduct.
3.4.1 $[\text{Ru(tpy)(AN)}_3]^{2+}$

The changes to the absorption spectra during the photoaquation of Ru(tpy)(AN)$_3^{2+}$ in water are shown Figure 3.9. Figure 3.10 shows the photolysis followed by $^1$H NMR spectroscopy in D$_2$O. Although it is not clear in the absorption spectra, the $^1$H NMR spectra shows an intermediate species forming during the reaction, most likely cis-$[\text{Ru(tpy)(AN)}_2(\text{H}_2\text{O})]^{2+}$.

![Absorption Spectra](image)

**Figure 3.9** Photolysis of $[\text{Ru(tpy)(AN)}_3]^{2+}$ in water. 150W lamp 395 nm long pass filter.

In the $^1$H NMR spectra, the highest field aromatic peak at 9 ppm and the peak corresponding to the equatorial acetonitrile at 2.9 ppm are the most informative because they shift the most. They both shift up field by about 0.1 ppm early in the photolysis, corresponding to the formation of the intermediate, and then shift up field again by an additional ~0.2 ppm and split into two peaks.
In fact, every peak in the spectrum of [Ru(tpy)(AN)\(_3\)]\(^{2+}\) splits into two peaks when the photolysis is complete. Comparing the \(^1\)H NMR spectra of [Ru(tpy)(AN)\(_3\)]\(^{2+}\) to that of the photoproduct in D\(_2\)O after 19 hours, the integration of the aromatic peaks remains the same, indicating no reaction with the tpy ligand. The equatorial acetonitrile peaks of the photoproduct also integrate to 3 hydrogens. The peak corresponding to the axial acetonitrile ligands also shifts up field, but only by a total of 0.1 ppm, and it does not split. The lack of splitting indicates that the axial acetonitrile is no longer coordinated to the metal complex, and its peak position of 2.1 ppm has been identified as free acetonitrile in D\(_2\)O.\(^{48}\) The integration of the free acetonitrile peak is six hydrogens, indicating all of the axial acetonitriles were exchanged. The splitting of the product peaks suggests that there may be more than one photoproduct, possibly from formation of hydroxide from one of the bound waters. The photolysis reaction is shown in equation (3).

\[\text{Scheme 3. Photolysis of [Ru(tpy)(AN)\(_3\)]}^{2+}\text{ in water}\]
Figure 3.10 Photolysis of [Ru(tpy)(AN)$_3$]$^{2+}$ in D$_2$O 150W lamp 395 long pass filter (A) benzene added for reference (b) Solvent peak (c) equatorial acetonitrile (d) axial acetonitrile (e) free acetonitrile.

3.4.2 cis-[Ru(tpy)(AN)$_2$Cl]$^+$

Cis-[Ru(tpy)(AN)$_2$Cl]$^+$ undergoes photoaquation to the same photoproduct as [Ru(tpy)(AN)$_3$]$^{2+}$. The photolysis followed by UV-Vis spectroscopy is shown in Figure 3.11. The photolysis of Ru(tpy)(AN)$_2$Cl$^+$ in D$_2$O was also followed by $^1$H NMR and is shown in Figure 3.12, with a comparison of the photoproducts of [Ru(tpy)(AN)$_3$]$^{2+}$ and cis-[Ru(tpy)(AN)$_2$Cl]$^+$ in D$_2$O shown in Figure 3.13. The exchange of the chloride ligand happens thermally and is immediate when placed in water. This is apparent from the large differences in the absorption spectra of trans-[Ru(tpy)(AN)$_2$Cl]$^+$ in CH$_2$Cl$_2$ and water with a $\lambda_{\text{max}}$ of the $^1$MLCT of 485...
nm and 450 nm respectively. [Ru(tpy)(AN)₃]²⁺ has no such shift, with a λ_max of 434 nm in both CH₂Cl₂ and water. Cis-[Ru(tpy)(AN)₂Cl]⁺ underwent photoaquation at wavelengths as long as 590 nm with comparable speed to that of 400 nm. This approaches the ideal PDT window of 700-900 nm. The photolysis reaction is shown in equation 4.

Figure 3.11 Photolysis of [Ru(tpy)(AN)₂Cl]⁺ in water. 150W lamp 395 nm long pass filter

Scheme 4. Photolysis of cis-[Ru(tpy)(AN)₂Cl]⁺ in water
Figure 3.12 Photolysis of cis-[Ru(tpy)(AN)$_2$Cl]$^+$ in D$_2$O 150W lamp 395 nm long pass filter. (a) benzene added as reference (b) solvent peak (c) equatorial acetonitrile (d) acetone as second reference (e) axial acetonitrile (f) free acetonitrile

Figure 3.13 Comparison of photolysis products of [Ru(tpy)(AN)$_3$]$^{2+}$ in D$_2$O (top) and cis-[Ru(tpy)(AN)$_2$Cl]$^+$ in D$_2$O (bottom).
3.4.3 \([\text{Ru(tpy})(5\text{CNU})_3]^{2+}\)

\([\text{Ru(tpy})(5\text{CNU})_3]^{2+}\) undergoes photolysis in water to lose two of the 5CNU ligands forming trans-\([\text{Ru(tpy)}(5\text{CNU})(\text{H}_2\text{O})_2]^{2+}\). The photolysis followed by UV-Vis spectroscopy is shown in Figure 3.14. The presence non-constant isosbestic points indicates there is an intermediate, likely cis-\([\text{Ru(tpy)}(5\text{CNU})_2(\text{H}_2\text{O})]^{2+}\), with a maximum around 450 nm. The photolysis of \([\text{Ru(tpy)}(5\text{CNU})_3]^{2+}\) in D$_2$O by $^1$H NMR also shows the presence of an intermediate (Figure 3.16). The complex doesn’t have any peaks below 7.5 ppm, and only 7-10 ppm is shown. Figure 3.15 shows the structure of the 5CNU ligand. The only peak from the ligand that is visible in the NMR spectrum is the hydrogen bound to the carbon atom, which is starred in the figure. The axial 5CNU ligands show up at \(~7.9\) ppm, while the equatorial ligand appears at \(~8.7\) ppm. Only the axial ligands are exchanged, analogous to \([\text{Ru(tpy)}(\text{AN})_3]^{2+}\), and the free ligand comes in at \(~8.3\) ppm. Benzene was added as a reference and can be seen at 7.5 ppm.
Figure 3.14 Photolysis of \([\text{Ru(tpy})(5\text{CNU})_3]^2+\) in water. 150W lamp 395 long pass filter

Figure 3.15 Structure of 5-cyanouracil. The starred hydrogen is the peak that is visible in the NMR spectrum
3.5 Quantum Yields

The Quantum yield of photoanation with chloride and photoaquation in water were measured for both [Ru(tpy)(AN)₃]²⁺ and [Ru(tpy)(AN)₂Cl⁺] with $\lambda_{irr} = 400$ nm. The quantum yield of [Ru(tpy)(5CNU)₃]²⁺ was measured only
in water at $\lambda_{\text{irr}} = 400$ nm since it is not soluble in CH$_2$Cl$_2$. The quantum yield was measured from the slope of the decrease in concentration of the reactant with irradiation time. Such a graph for the photoanation of [Ru(tpy)(AN)$_3$]$^{2+}$ is shown in Figure 3.17. The quantum yields for the compounds are listed in Table 3.2. The quantum yield of photoanation with chloride was independent of the chloride concentration. An excess of chloride ions with concentrations from ~5-15 mM were used.

![Figure 3.17](image-url)

**Figure 3.17.** Concentration of [Ru(tpy)(AN)$_3$]$^{2+}$ vs. irradiation time. Photolysis was done in CH$_2$Cl$_2$ in the presence of ~10 mM TBACl, 150W lamp 400nm band pass filter. Initial concentration of [Ru(tpy)(AN)$_3$]$^{2+}$ = 250 $\mu$M.
Table 3.2 Quantum yields of photoaquation and photoanation. $\lambda_{\text{irr}} = 400$ nm.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\Phi_{\text{Cl}}$ in CH$_2$Cl$_2$</th>
<th>$\Phi_{\text{water}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ru(tpy)(AN)$_3$]$^{2+}$</td>
<td>0.040 ± 0.001</td>
<td>0.035 ± 0.001</td>
</tr>
<tr>
<td>Cis-[Ru(tpy)(AN)$_2$Cl]$^+$</td>
<td>0.12 ± 0.01</td>
<td>0.12 ± 0.01</td>
</tr>
<tr>
<td>[Ru(tpy)(5CNU)$_3$]$^{2+}$</td>
<td>NA</td>
<td>0.022 ± 0.002</td>
</tr>
</tbody>
</table>

The quantum yields of photoanation with chloride have been previously reported at $\lambda_{\text{irr}} = 436$ nm.\textsuperscript{54} The quantum yields measured at $\lambda_{\text{irr}} = 400$ nm agree within error of the reported values for $\lambda_{\text{irr}} = 436$ nm.

3.6 Dark Reactions

In order to study the photolysis of ruthenium terpyridine compounds, the reactivity in the absence of light had to be investigated to make sure there were no dark reactions affecting the measurement of the quantum yields. The stability of all three photoactive complexes in water, and [Ru(tpy)(AN)$_3$]$^{2+}$ and [Ru(tpy)(AN)$_2$Cl]$^+$ in CH$_2$Cl$_2$ with TBACl, were studied in the dark. The solutions were degassed by bubbling N$_2$ through them for 10 min, and allowed to sit for at least 1 day in the dark. The UV-Vis spectrum of each dark reaction is shown in Figures 3.18-3.20. In every case the $\lambda_{\text{max}}$ of the compound is unchanged indicating that there was no reaction. In some of the spectra, the absorbance taken after one day has a higher intensity then the initial absorbance due to evaporation of the solvent. This is especially prevalent for cis-[Ru(tpy)(AN)$_2$Cl]$^+$ in CH$_2$Cl$_2$. 

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Figure 3.18 Electronic absorption spectrum of (a) [Ru(tpy)(AN)]_{3}^{2+} and (b) cis-[Ru(tpy)(AN)_{2}Cl]^{+} in water at time = 0 (solid line) and 25 hours (dashed line) kept in the dark at 25°C.
Figure 3.19 Electronic absorption spectrum of (a) [Ru(tpy)(AN)₃]²⁺ and (b) cis-[Ru(tpy)(AN)₂Cl]⁺ in CH₂Cl₂ with TBACl at t = 0 (solid line) and 25 hours (dashed line) kept in the dark at 25°C.
Figure 3.20 Electronic absorption spectrum of $[\text{Ru(tpy)(5CNU)$_3$}]^{2+}$ in water at $t = 0$ (solid line) and 24 hours (dashed line) kept in the dark at 25°C.

3.7 DNA Binding Studies

Agarose gel electrophoresis studies were performed to test the binding of the complexes to DNA. Cisplatin has been previously shown to bind to double stranded DNA through agarose gel electrophoresis, as have complexes requiring photoinitiated binding. The binding of complexes to the DNA decreases its mobility on the agarose gel. The mobility gels for $[\text{Ru(tpy)(AN)$_3$}]^{2+}$, cis-$[\text{Ru(tpy)(AN)$_2$Cl}]^+$, and $[\text{Ru(tpy)(5CNU)$_3$}]^{2+}$ are shown in Figure 3.21. Lanes 1 and 8 are 1 kb DNA molecular weight standard, and lanes 2 and 7 have only 50 µM linearized pUC 19 plasmid without any complex present. Lanes 2-6 have increasing concentration of complex irradiated in the presence of ds-DNA with
$\lambda_{\text{irr}} \geq 395$ nm light for 5 minutes for \([\text{Ru(tpy}(\text{AN})_3)_2]^{2+}\) and \(\text{cis-}[\text{Ru(tpy}(\text{AN})_2\text{Cl}]]^{+}\), and for 15 minutes for \([\text{Ru(tpy}(\text{5CNU})_3)_2]^{2+}\). The concentrations for \([\text{Ru(tpy}(\text{AN})_3)_2]^{2+}\) and \(\text{cis-}[\text{Ru(tpy}(\text{AN})_2\text{Cl}]]^{+}\) are 1, 2.5, 5, and 10 $\mu$M in lanes 3-6 respectively. The concentration of \([\text{Ru(tpy}(\text{5CNU})_3)_2]^{2+}\) is 5, 10, 25, and 50 $\mu$M in lanes 3-6 respectively. The DNA can be seen to not move as far along the gel for increased concentrations of the complexes, indicating binding to the DNA. The increased irradiation time required for \([\text{Ru(tpy}(\text{5CNU})_3)_2]^{2+}\) is likely due to its decreased quantum yield of photoaquation. Agarose gel electrophoresis was also carried out without irradiating the samples. Figure 3.22 shows the mobility gels for all three complexes without irradiation. Lanes 3-6 match the control lanes 2 and 7 in every case, indicating there is no DNA binding in the dark.

As noted earlier \(\text{cis-}[\text{Ru(tpy}(\text{AN})_2\text{Cl}]]^{2+}\) undergoes photolysis in water at $\lambda_{\text{irr}} \geq 590$ nm at a comparable speed to $\lambda_{\text{irr}} \geq 395$ nm. To test for binding near the ideal photodynamic therapy window agarose gel electrophoresis was performed for \(\text{cis-}[\text{Ru(tpy}(\text{AN})_2\text{Cl}]]^{+}\) with $\lambda_{\text{irr}} \geq 645$ nm. An increased irradiation time of 30 minutes was used to account for the low absorption of the complex at that wavelength. Figure 3.23 shows the mobility gel for \(\text{cis-}[\text{Ru(tpy}(\text{AN})_2\text{Cl}]]^{+}\) irradiated for 30 minutes and the dark control. The complex shows DNA binding even at $\lambda_{\text{irr}} \geq 645$ nm, approaching the ideal window of 700-900 nm.
Figure 3.21 Agarose electrophoresis gels of 50 mM linearized pUC19 plasmid (10mM phosphate buffer, pH = 8.3) irradiated at $\lambda_{irr} \geq 395$ nm with (a) $[\text{Ru(tpy)}(\text{AN})_3]^{2+}$ (b) cis-$[\text{Ru(tpy)}(\text{AN})_2\text{Cl}]^+$ ($t_{irr} = 5$ min) and (c) $[\text{Ru(tpy)}(5\text{CNU})_3]^{2+}$ ($t_{irr} = 15$ min). Lanes 1 and 8 are 1 kb DNA molecular weight standard. Lanes 2 and 7 are linearized plasmid alone. Lanes 3-6 have complex concentrations of 1, 2.5, 5, and 10 $\mu$M respectively for a, and b; and concentrations of 5, 10, 25, and 50 $\mu$M respectively for c.
Figure 3.22 Agarose electrophoresis gels of 50 mM linearized pUC19 plasmid (10mM phosphate buffer, pH = 8.3) with (a) [Ru(tpy)(AN)Cl]^{2+} (b) cis-[Ru(tpy)(AN)_2Cl]^+ and (c) [Ru(tpy)(5CNU)_3]^{2+} not irradiated. Lanes 1 and 8 are 1 kb DNA molecular weight standard. Lanes 2 and 7 are linearized plasmid alone. Lanes 3-6 have complex concentrations of 1, 2.5, 5, and 10 µM respectively for a, and b; and concentrations of 5, 10, 25, and 50 µM respectively for c.
Figure 3.23 Agarose electrophoresis gels of 50 mM linearized pUC19 plasmid (10mM phosphate buffer, pH = 8.3) with cis-[Ru(tpy)(AN)₂Cl]⁺ (a) irradiated at λ_{irr} ≥ 645 nm for 30 minutes and (b) kept in the dark for 30 minutes. Lanes 1 and 8 are 1 kb DNA molecular weight standard. Lanes 2 and 7 are linearized plasmid alone. Lanes 3-6 have complex concentrations of 1, 5, 10, and 10 µM respectively.

3.8 Electrochemistry

Cyclic voltammetry measurements were conducted on [Ru(tpy)(AN)₃]²⁺, cis-[Ru(tpy)(AN)₂Cl]⁺, and [Ru(tpy)(5CNU)₃]²⁺. The oxidation and reduction potentials are listed in Table 3.3. Measurements of [Ru(tpy)(AN)₃]²⁺ and
cis-[Ru(tpy)(AN)2Cl]+ were done in CH2Cl2 with 0.1 M tetrabutylammonium hexafluorophosphate (TBA(PF6)) as the electrolyte. Measurements of [Ru(tpy)(5CNU)3]2+ were done in acetonitrile with 0.1 M TBA(PF6) since the complex is not soluble in CH2Cl2. Both [Ru(tpy)(AN)3]2+ and [Ru(tpy)(5CNU)3]2+ have oxidation potentials of 1.8 vs. NHE and a reduction potential at -1.2 vs. NHE as would be expected from there similar structures. The oxidation potential represents Ru3+/2+ oxidation and agrees well with previously reported results for [Ru(tpy)(AN)3]2+. The reduction potential is attributed to the reduction of the tpy ligand and is close to that measured for similar Ru(tpy)L32+ complexes. [Ru(tpy)(5CNU)3]2+ has a second irreversible reduction potential at -0.9 vs. NHE and is attributed to the reduction of the 5CNU ligand. Although it is lower in potential than the reduction attributed to the tpy ligand, the lowest un-occupied molecular orbital is still believed to be localized on the tpy ligand due to the similarity in the absorption and emission spectra. The lower reduction potential of the 5CNU ligand could be due to a proton-coupled reduction process. The oxidation potential of cis-[Ru(tpy)(AN)2Cl]+ is at 1.2 vs. NHE with a reduction potential at -1.3 vs. NHE. These values are also consistent with previous reports. The lower oxidation potential of cis-[Ru(tpy)(AN)2Cl]+ is expected from its lower energy 1MLCT absorption due to the π-donating nature of the chloride ligand which destabilizes the Ru(dπ) orbitals making them easier to oxidize. The cyclic voltammograms for the complexes are shown in Figures 3.24-3.26.
Table 3.3 Redox potentials of [Ru(tpy)(AN)₃]²⁺, cis-[Ru(tpy)(AN)₂Cl]⁺, and [Ru(tpy)(5CNU)₃]²⁺ vs. NHE with 0.1 M TBA(PF₆). [Ru(tpy)(AN)₃]²⁺ and cis-[Ru(tpy)(AN)₂Cl]⁺ done in CH₂Cl₂, [Ru(tpy)(5CNU)₃]²⁺ done in NCCH₃.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Redox potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ru(tpy)(AN)₃]²⁺</td>
<td>+1.80, -1.20</td>
</tr>
<tr>
<td>[Ru(tpy)(5CNU)₃]²⁺</td>
<td>+1.82, -0.88, -1.18</td>
</tr>
<tr>
<td>Cis-[Ru(tpy)(AN)₂Cl]⁺</td>
<td>+1.18, -1.30</td>
</tr>
</tbody>
</table>

Figure 3.24 Cyclic voltammogram of [Ru(tpy)(AN)₃]²⁺ in CH₂Cl₂ with 0.1 M TBA(PF₆). Spectrum taken vs. AgCl reference electrode; ferrocene used as reference.
Figure 3.25 Cyclic voltammogram of [Ru(tpy)(5CNU)_3]^{2+} in acetonitrile with 0.1 M TBA(PF_6). Spectrum taken vs. AgCl reference electrode; ferrocene used as reference.

Figure 3.26 Cyclic voltammogram of cis-[Ru(tpy)(AN)_2Cl]^+ in CH_2Cl_2 with 0.1 M TBA(PF_6). Spectrum taken vs. AgCl reference electrode; ferrocene used as reference.
3.9 Conclusion

Ruthenium compounds bound to tpy ligands exhibit a lower energy MLCT transition compared to those with coordinated bpy ligands (Figure 2.4). In conjunction with acetonitrile ligands, these complexes exhibit large quantum yield of photosubstitution. For these reasons \([\text{Ru(tpy)(AN)}_3]^{2+}\), \([\text{Ru(tpy)(5CNU)}_3]^{2+}\), and \([\text{cis-Ru(tpy)(AN)}_2\text{Cl}]^{+}\) were chosen and studied as possible candidates for PDT agents. All of compounds were shown to photolyze to the diaqua product upon irradiation with visible light. \([\text{cis-Ru(tpy)(AN)}_2\text{Cl}]^{+}\) has a lower energy MLCT, and photolysis can be achieved with irradiation wavelengths as low as 645 nm. It exhibits a greater quantum yield of photosubstitution in water (0.12) compared to 0.035 for \([\text{Ru(tpy)(AN)}_3]^{2+}\) and 0.022 for \([\text{Ru(tpy)(5CNU)}_3]^{2+}\) under similar irradiation conditions. As such \([\text{Ru(tpy)(AN)}_2\text{Cl}]^{+}\) is the most likely candidate for PDT as a cisplatin analog. \([\text{Ru(tpy)(5CNU)}_3]^{2+}\) could be viable due to the release of 5CNU which has biological properties of its own and can inhibit cell replication.\(^{69,70}\)
CHAPTER 4

Ultra-fast Ligand Exchange in Octahedral Ruthenium Compounds

4.1 Background

Photoinduced ligand exchange is a process that has seen applications in a variety of fields including photodynamic therapy (PDT), solar energy conversion, molecular switches, and C-H activation. The first step of the process is the excitation of a molecule into an excited state. Once excited, the molecule can undergo a variety of processes such as vibrational cooling, internal conversion, and intersystem crossing to achieve the lowest energy excited state (Figure 4.1). In organic molecules, these processes are assumed to happen with the relative speeds $k_{vc} > k_{ic} > k_{isc}$. However, the presence of a metal increases $k_{isc}$ significantly through spin-orbit coupling exerted by the metal. In the complex $[\text{Ru(bpy)}_3]^{2+}$ (bpy = 2,2'-bipyridine) intersystem crossing from an initial singlet metal-to-ligand charge transfer ($^1\text{MLCT}$) excited state to the corresponding triplet $^3\text{MLCT}$ lowest energy excited state was measured to be ~40 fs.

The emission of $[\text{Ru(bpy)}_3]^{2+}$ has been thoroughly studied and is known to take place from the $^3\text{MLCT}$ state, with a temperature dependence resulting from a thermally accessible non-emissive triplet ligand field state ($^3\text{LF}$) higher in energy than the $^3\text{MLCT}$ state. A decrease in emission quantum yield, $\Phi_{em}$, and comparable increase in the quantum yield of photolysis, $\Phi_{\text{photo}}$, is observed for
[Ru(bpy)$_3$]$^{2+}$ with increasing temperature. This behavior led to the conclusion that the population of the $^3$LF from the $^3$MLCT state preceded photosubstitution, as shown in Figure 1.6. The temperature dependence of emission of the related compounds cis-[Ru(bpy)$_2$L$_2$]$^{2+}$, where L is a photo-labile ligand such as pyridine or acetonitrile, was found to fit the same model, but the value of $\Phi_{\text{photo}}$ of photosubstitution of such complexes exhibits very little increase with temperature, suggesting that the photosubstitution proceeds through a different mechanism.

One possibility is that the $^3$LF state is populated directly from the initially excited state and does not require population through the $^3$MLCT state, as suggested by the modified Jablonski diagram shown in Figure 4.1. In order to determine which model better describes the events that lead to the observed photochemistry, Figure 1.6 or Figure 1.4, the temperature dependence of the emission of cis-[Ru(bpy)$_3$]$^{2+}$, cis-[Ru(bpy)$_2$(AN)$_2$]$^{2+}$ (AN = acetonitrile), cis-[Ru(bpy)$_2$(py)$_2$]$^{2+}$ (py = pyridine), and cis-[Ru(bpy)$_2$(MeBN)$_2$]$^{2+}$ (MeBN = 4-methylbenzonitrile) was compared to the temperature dependence of the quantum yield of photosubstitution with Cl$^-$ ions, $\Phi_{\text{Cl}}$. 


Figure 4.1 Jablonski diagram showing population of $^3$LF state directly from the initially excited singlet states. $k_R$ is the rate constant for radiative decay, $k_{NR}$ for nonradiative decay, and $k_{ISC}$ for intersystem crossing.

4.2 Absorption

The electronic absorption spectra of $[\text{Ru(bpy)}_3]^{2+}$ and cis-$[\text{Ru(bpy)}_2(\text{AN})_2]^{2+}$ are shown in Figure 4.2. The electronic absorption spectra of cis-$[\text{Ru(bpy)}_2(\text{py})_2]^{2+}$ and cis-$[\text{Ru(bpy)}_2(\text{MeBN})_2]^{2+}$ are shown in Figure 4.3. All of the compounds exhibit a ligand centered $1\pi\pi^*$ transitions at 280-290 nm localized on the bpy ligands. The compounds also show a Ru$(t_{2g})\rightarrow\text{bpy}(p^*)$ $1\text{MLCT}$ transition with maxima at 420 nm for both cis-$[\text{Ru(bpy)}_2(\text{AN})_2]^{2+}$ and cis-$[\text{Ru(bpy)}_2(\text{MeBN})_2]^{2+}$ which shifts to 451 nm in for cis-$[\text{Ru(bpy)}_3]^{2+}$, and 460 nm in cis-$[\text{Ru(bpy)}_2(\text{py})_2]^{2+}$. The absorption maxima and extinction coefficients are listed in Table 4.1 and are consistent with previously reported values.\textsuperscript{78-81}

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**Figure 4.2** Electronic absorption spectra of cis-[Ru(bpy)$_2$(AN)$_2$]$^{2+}$ (solid line) and [Ru(bpy)$_3$]$^{2+}$ (dashed line) in water.

**Figure 4.3** Electronic absorption spectra of cis-[Ru(bpy)$_2$(MeBN)$_2$]$^{2+}$ (solid line), and cis-[Ru(bpy)$_2$(py)$_2$]$^{2+}$ (dashed line) in water.
Table 4.1 Absorption maxima and extinction coefficients of Ru(II) compounds in water.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Absorption $\lambda_{\text{max}}$, nm ($\varepsilon$, M$^{-1}$cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-[Ru(bpy)$_2$(AN)$_2$]$^{2+}$</td>
<td>420 (8900)</td>
</tr>
<tr>
<td>cis-[Ru(bpy)$_2$(py)$_2$]$^{2+}$</td>
<td>460 (9200)</td>
</tr>
<tr>
<td>cis-[Ru(bpy)$_2$(MeBN)$_2$]$^{2+}$</td>
<td>420 (6500)</td>
</tr>
<tr>
<td>[Ru(bpy)$_3$]$^{2+}$</td>
<td>451 (14800)</td>
</tr>
</tbody>
</table>

4.3 Emission

All solutions were degassed prior to emission measurements by bubbling with nitrogen for 10 minutes. The absorption, emission, and excitation spectra of [Ru(bpy)$_3$]$^{2+}$ in acetonitrile at room temperature are shown in Figure 4.4. [Ru(bpy)$_3$]$^{2+}$ has strong emission with a maximum at 615 nm that is well established in the literature.\textsuperscript{78}

All of the compounds exhibit low temperature emission. The spectra collected in 4:1 ethanol:methanol or acetonitrile at 77 K and are shown in Figures 4.4-4.8. The spectrum of [Ru(bpy)$_3$]$^{2+}$ at 77 K is similar to that obtained at room temperature, with maximum at 590 nm. The vibronic progression is more apparent, and the emission maximum is blue shifted due to the prominent E$_{00}$ transition afforded by the compound being frozen in a solid matrix. Cis-[Ru(bpy)$_2$(AN)$_2$]$^{2+}$ and cis-[Ru(bpy)$_2$(MeBN)$_2$]$^{2+}$ exhibit emission spectra similar to that of [Ru(bpy)$_3$]$^{2+}$ but with maxima at higher energy, 575 nm. This shift in the emission is expected since the absorption maxima of these complexes are also at higher energy. The emission spectrum of cis-[Ru(bpy)$_2$(py)$_2$]$^{2+}$ is
almost identical to that of [Ru(bpy)$_3$]$^{2+}$ with a maximum at 590 nm. This can be attributed to the similar structures of the complexes, and can also been seen in the similarity of the absorption spectra. The major difference between [Ru(bpy)$_3$]$^{2+}$ and cis-[Ru(bpy)$_2$(py)$_2$]$^{2+}$ is the lack of room temperature emission from cis-[Ru(bpy)$_2$(py)$_2$]$^{2+}$.

**Figure 4.4** Room temperature absorption, emission, and excitation of [Ru(bpy)$_3$]$^{2+}$ in acetonitrile.
Figure 4.5 Emission and excitation spectra (77 K) and room temperature absorption spectrum of \([\text{Ru(bpy)}_3]^{2+}\) in acetonitrile.

Figure 4.6 Emission and excitation spectra (77 K) and room temperature absorption spectrum of cis-\([\text{Ru(bpy)}_2(AN)]^{2+}\) in 4:1 ethanol:methanol.
Figure 4.7 Emission and excitation spectra (77 K) and room temperature absorption spectrum of cis-[Ru(bpy)$_2$(MeBN)$_2$]$^{2+}$ in 4:1 ethanol:methanol.

Figure 4.8 Emission and excitation spectra (77 K) and room temperature absorption spectrum of cis-[Ru(bpy)$_2$(py)$_2$]$^{2+}$ in 4:1 ethanol:methanol.
Table 4.2 lists the emission maxima of the cis-[Ru(bpy)₂L₂]²⁺ complexes and [Ru(bpy)₃]²⁺. Excitation wavelengths for emission experiments were chosen to coincide with the absorption maximum of each compound and emission wavelengths for excitation experiments were chosen to coincide with the emission maximum of each compound.

Table 4.2 Emission maxima at room temperature and 77 K of cis-[Ru(bpy)₂L₂]²⁺ compounds a) acetonitrile and b) 4:1 ethanol: methanol.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Emission λ_{max}, nm Room Temperature</th>
<th>Emission λ_{max}, nm 77 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-[Ru(bpy)₂(AN)₂]²⁺</td>
<td>NA</td>
<td>575 nm^b</td>
</tr>
<tr>
<td>cis-[Ru(bpy)₂(py)₂]²⁺</td>
<td>NA</td>
<td>590 nm^b</td>
</tr>
<tr>
<td>cis-[Ru(bpy)₂(MeBN)₂]²⁺</td>
<td>NA</td>
<td>575 nm^b</td>
</tr>
<tr>
<td>cis-[Ru(bpy)₃]²⁺</td>
<td>615 nm^a</td>
<td>590 nm^a</td>
</tr>
</tbody>
</table>

4.4 Temperature Dependence of Emission

In order to calculate the energy gap between the emissive ³MLCT state and the non-emissive ³LF state, the dependence of the emission intensity on temperature was measured for each compound. Neither cis-[Ru(bpy)₂(AN)₂]²⁺, cis-[Ru(bpy)₂(MeBN)₂]²⁺, nor cis-[Ru(bpy)₂(py)₂]²⁺ exhibit any room temperature emission. The temperature dependence of the emission of cis-[Ru(bpy)₂(py)₂]²⁺ was previously reported resulting in a calculated ³MLCT-³LF energy gap of 2758 cm⁻¹, which is smaller than the 3850 cm⁻¹ gap reported for [Ru(bpy)₃]²⁺.⁷⁷

The changes of the emission spectrum of each compound with temperature
are shown in Figures 4.9-4.12. The luminescence of \([\text{Ru(bpy)}_3]^{2+}\) was measured over the temperature range of 270-330 K since it exhibits room temperature emission. Below 270 K \([\text{Ru(bpy)}_3]^{2+}\) shows negligible change in emission intensity with temperature. Each compound has a different temperature range that produces the largest change in emission intensity, and this range was chosen for the experiments described herein. Cis-\([\text{Ru(bpy)}_2(\text{py})_2]^{2+}\) was measured over the temperature range of 180-210 K, and cis-\([\text{Ru(bpy)}_2(\text{AN})_2]^{2+}\) and cis-\([\text{Ru(bpy)}_2(\text{MeBN})_2]^{2+}\) at 140-180 K.

![Graph showing emission of \([\text{Ru(bpy)}_3]^{2+}\) in 4:1 ethanol:methanol from 330K – 220K; \(\lambda_{ex} = 450\) nm](image)

**Figure 4.9** Emission of \([\text{Ru(bpy)}_3]^{2+}\) in 4:1 ethanol:methanol from 330K – 220K; \(\lambda_{ex} = 450\) nm
Figure 4.10 Emission of cis-[Ru(bpy)$_2$(py)$_2$]$^{2+}$ in 4:1 ethanol:methanol from 220K–150K; $\lambda_{ex} = 450$ nm

Figure 4.11 Emission of cis-[Ru(bpy)$_2$(AN)$_2$]$^{2+}$ in 4:1 ethanol:methanol from 180K – 120K; $\lambda_{ex} = 425$ nm
Figure 4.12 Emission of cis-[Ru(bpy)$_2$(MeBN)$_2$]$^{2+}$ in 4:1 ethanol:methanol from 160K–120K; $\lambda_{ex}$ = 425nm

The energy gap between the $^3$MLCT and $^3$LF states was calculated for each compound from the relative quantum yields of emission. Quantum yield of emission can be defined as

$$\Phi_{em} = \frac{k_r}{k_r + k_{nr} + k_{nr2}} e^{-\frac{\Delta E}{RT}} \quad (1)$$

Where $\Phi_{em}$ is the quantum yield of emission, $\Delta E$ is the energy gap between the $^1$MLCT and the $^3$LF states, $T$ is temperature, $R$ is the gas constant, and $k_r$, $k_{nr}$, and $k_{nr2}$ are as defined in Figure 4.1. Equation 1 can be re-written as

$$\frac{1}{\Phi_{em}} = A + Be^{-\frac{\Delta E}{RT}} \quad (2)$$

The integrated emission in Figures 4.9–4.12, which is proportional to the quantum yield of emission, was graphed vs. $1/T$ and fitted to the exponential equation 2.
The energy difference, $\Delta E$, was extracted from the data by an exponential fit.

Figures 4.13-4.16 show the fits to equation 2 for each compound. The fits match literature values for $[\text{Ru(bpy)}_3]^{2+}$ and cis-$[\text{Ru(bpy)}_2(\text{py})_2]^{2+}$.

Figure 4.13 Exponential fit of emission for $[\text{Ru(bpy)}_3]^{2+}$

Figure 4.14 Exponential fit of emission for cis-$[\text{Ru(bpy)}_2(\text{py})_2]^{2+}$

Figure 4.15 Exponential fit of emission for cis-$[\text{Ru(bpy)}_2(\text{AN})_2]^{2+}$
**Figure 4.16** Exponential fit of emission for cis-[Ru(bpy)$_2$(MeBN)$_2$]$^{2+}$

**Table 4.3** Energy gap between the $^3$MLCT and $^3$LF states for cis-[Ru(bpy)$_2$L]$^{2+}$ compounds in 4:1 ethanol:methanol.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta E$/cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cis-[Ru(bpy)$_3$]$^{2+}$</td>
<td>3850</td>
</tr>
<tr>
<td>Cis-[Ru(bpy)$_2$(py)$_2$]$^{2+}$</td>
<td>2040</td>
</tr>
<tr>
<td>Cis-[Ru(bpy)$_2$(AN)$_2$]$^{2+}$</td>
<td>1310</td>
</tr>
<tr>
<td>Cis-[Ru(bpy)$_2$(MeBN)$_2$]$^{2+}$</td>
<td>910</td>
</tr>
</tbody>
</table>

**4.5 Dependence of the Photolysis on Temperature**

**4.5.1 Room Temperature Photolysis**

Irradiation of the $^1$MLCT transition of cis-[Ru(bpy)(L)$_2$]$^{2+}$, where L is a photolabile ligand, results in the ligand exchange of L with solvent or coordinating ligand in solution as previously reported for L = acetonitrile, pyridine and ammonia.$^{48,49}$ The photolysis of cis-[Ru(bpy)$_2$(AN)$_2$]$^{2+}$, cis-[Ru(bpy)$_2$(MeBN)$_2$]$^{2+}$, and cis-[Ru(bpy)$_2$(py)$_2$]$^{2+}$ at 25°C in the presence of chloride results in changes to the electronic absorption spectrum of each complex,
as shown in Figures 4.18-4.20. The complexes were irradiated with 400 nm light in CH$_2$Cl$_2$. For the complexes cis-[Ru(bpy)$_2$(AN)$_2$]$^{2+}$ and cis-[Ru(bpy)$_2$(MeBN)$_2$]$^{2+}$, ~10 mM tetrabutylammonium chloride (TBACl) was added. The source of chloride ions for cis-[Ru(bpy)$_2$(py)$_2$]$^{2+}$ was from the counter ion of the complex. The $\Phi_{\text{Cl}}$ for cis-[Ru(bpy)$_2$(py)$_2$]$^{2+}$ is independent of chloride concentration, as has been reported for similar compounds. As the monodentate ligands are replaced by chloride ions, the $^1\text{MLCT}$ absorption maximum red shifts. This is due to the decreased ligand field splitting introduced by the chloride ligand as compared to acetonitrile, pyridine, and 4-methylbenzonitrile. The final product of the photolysis is cis-[Ru(bpy)$_2$]$^2_+$. The complex cis-[Ru(bpy)$_2$(AN)Cl]$^+$ has a $^1\text{MLCT}$ absorption maximum of 480 nm, and is an intermediate in the photocatalysis of cis-[Ru(bpy)$_2$(AN)$_2$]$^{2+}$. An intermediate peak of ~480 nm can be seen in the photocatalysis of each cis-[Ru(bpy)$_2$L$_2$]$^{2+}$ compound, as shown in Figure 4.17 for the photolysis of cis-[Ru(bpy)$_2$(MeBN)$_2$]$^{2+}$ in the presence of TBACl. During the first 8 minutes of the photolysis an absorption maximum grows in around 480 nm, attributed to the $^1\text{MLCT}$ of the intermediate species cis-[Ru(bpy)$_2$(MeBN)Cl]$^+$, along with a smaller absorption maximum at 555 nm that matches the $^1\text{MLCT}$ for the product cis-[Ru(bpy)$_2$]$^2_+$. Photolysis beyond 8 minutes results in the decrease of the absorption maximum at 480 nm and an increase in the absorption maximum at 555 nm (Figure 4.17b). The photolysis reaction is shown in Scheme 1. Since in each case the intermediate is a stable compound that can be isolated, the overall reaction is most likely a two photon process, requiring one photon.
for the formation of cis-[Ru(bpy)_2LCl]^+, and a second photon for the formation of cis-Ru(bpy)_2L_2. For the case of cis-[Ru(bpy)_2(AN)_2]^{2+}, the process has been shown to require two photons to generate the final dichloro product. The dependence of photolysis on temperature of cis-[Ru(bpy)_2(MeBN)_2]^{2+} was also conducted in water and is shown in Figure 4.21. The results are similar to the photolysis in CH_2Cl_2 with TBACl.

Scheme 4.1 Photolysis of cis-[Ru(bpy)_2(AN)_2]^{2+} in CH_2Cl_2 with TBACl

The quantum yield for ligand substitution of each compound was measured at six temperatures; every five degrees from 5° to 30°C. The Φ_{Cl} was measured by the decrease of the reactant, and corresponds to the formation of the monochloride intermediate cis-[Ru(bpy)_2LCl]^{2+}. Table 4.4 lists the quantum yield of each compound at each temperature.
Figure 4.17 Photolysis of cis-[Ru(bpy)$_2$(MeBN)$_2$]$^{2+}$ in CH$_2$Cl$_2$ with ~10 mM TBACl. 150 W lamp, 400 nm band pass filter (a) 0-8 minutes (b) 8-135 minutes
Figure 4.18 Photolysis of cis-[Ru(bpy)$_2$(AN)$_2$]$^{2+}$ in CH$_2$Cl$_2$ with ~10 mM Cl$^-$. 150W lamp, 400 nm band pass filter.

Figure 4.19 Photolysis of cis-[Ru(bpy)$_2$(MeBN)$_2$]$^{2+}$ in CH$_2$Cl$_2$ with ~10 mM Cl$^-$. 150W lamp, 400 nm band pass filter.
Figure 4.20 Photolysis of cis-[Ru(bpy)$_2$(py)$_2$]Cl$_2$ in CH$_2$Cl$_2$. 150W lamp, 400 nm band pass filter.

Figure 4.21 Photolysis of cis-[Ru(bpy)$_2$(MeBN)$_2$]$^{2+}$ in water. 150W lamp, 400 nm band pass filter.
Table 4.4 Quantum yields of photolysis of cis-[Ru(bpy)$_2$L$_2$]$^{2+}$ (L = AN, MeBN, py) with TBACl in CH$_2$Cl$_2$ at six different temperatures from 5-30°C, and in water at four different temperatures from 10-40°C.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>cis-[Ru(bpy)$_2$(AN)$_2$]$^{2+}$ ± 0.02</th>
<th>cis-[Ru(bpy)$_2$(py)$_2$]$^{2+}$ ± 0.01</th>
<th>cis-[Ru(bpy)$_2$(MeBN)$_2$]$^{2+}$ In CH$_2$Cl$_2$ ± 0.02</th>
<th>cis-[Ru(bpy)$_2$(MeBN)$_2$]$^{2+}$ In Water ± 0.01</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.27</td>
<td>0.13</td>
<td>0.28</td>
<td>NA</td>
</tr>
<tr>
<td>10</td>
<td>0.27</td>
<td>0.17</td>
<td>0.31</td>
<td>0.22</td>
</tr>
<tr>
<td>15</td>
<td>0.29</td>
<td>0.15</td>
<td>0.33</td>
<td>NA</td>
</tr>
<tr>
<td>20</td>
<td>0.32</td>
<td>0.17</td>
<td>0.31</td>
<td>0.24</td>
</tr>
<tr>
<td>25</td>
<td>0.31</td>
<td>0.17</td>
<td>0.34</td>
<td>NA</td>
</tr>
<tr>
<td>30</td>
<td>0.34</td>
<td>0.18</td>
<td>0.35</td>
<td>0.26</td>
</tr>
<tr>
<td>40</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>0.27</td>
</tr>
</tbody>
</table>

The quantum yield of photolysis, $\Phi_{\text{photo}}$, is proportional to the rate constant of the photolysis reaction, and an Arrhenius equation can be set up relating $\Phi_{\text{photo}}$ to the temperature such that the activation energy of the reaction may be calculated according to equation 3. Figure 4.22 depicts an energy well diagram for the $^3$MLCT and $^3$LF states and the activation energy calculated. An activation energy similar to that determined from the luminescence experiments indicates that the photolysis reaction proceeds through the $^3$MLCT state. In contrast, a difference between the two would indicate that the photolysis reaction doesn’t proceed through the $^3$MLCT state. Graphs of the ln($F_{\text{photo}}$) vs. 1/T are shown for each complex in Figure 4.23. Table 4.5 lists the activation energy of the photolysis reactions and compares them with the energy gap between the $^3$MLCT and $^3$LF states obtained from the temperature dependence of the emission of each compound.
\[
\ln(\Phi_{\text{photo}}) = \ln(A) - \frac{E_a}{RT} \quad (3)
\]

**Figure 4.22** Energy well diagram depicting the activation energy between the \(^3\)MLCT and \(^3\)LF states.

**Figure 4.23** Arrhenius plot of quantum yield of photolysis vs. temperature for cis-[Ru(bpy)_2(MeBN)_2]^{2+} (squares), cis-[Ru(bpy)_2(AN)_2]^{2+} (triangles), and cis-[Ru(bpy)_2(py)_2]^{2+} (exes) with TBACl in CH₂Cl₂, and cis-[Ru(bpy)_2(MeBN)_2]^{2+} in water (diamonds).
Table 4.5 Comparison of activation energies of photoanation and energy gap between $^3\text{MCLT}$ and $^3\text{LF}$ states for Cis-[Ru(bpy)$_2$L$_2$]$^{2+}$ for L = AN, MeBN, and py. Activation energies are of photoanation with TBACl in CH$_2$Cl$_2$ except the value in parenthesis which is activation energy of photoaquation. Energy gaps from Table 4.3.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$E_a$/cm$^{-1}$</th>
<th>$\Delta E$/cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cis-[Ru(bpy)$_2$(AN)$_2$]$^{2+}$</td>
<td>550</td>
<td>1310</td>
</tr>
<tr>
<td>Cis-[Ru(bpy)$_2$(MeBN)$_2$]$^{2+}$</td>
<td>450 (400)</td>
<td>910</td>
</tr>
<tr>
<td>Cis-[Ru(bpy)$_2$(py)$_2$]$^{2+}$</td>
<td>600</td>
<td>2040</td>
</tr>
</tbody>
</table>

The changes in the quantum yields of photolysis with temperature are only slightly larger than the error of the measurements, as can be seen in Table 4.4. The activation energies listed in Table 4.5 therefore have large errors, up to ± 200 cm$^{-1}$. Activation energies for the photolysis of cis-[Ru(bpy)$_2$(AN)$_2$]$^{2+}$ and cis-[Ru(bpy)$_2$(py)$_2$]$^{2+}$ in CH$_2$Cl$_2$ with TBACl has been previously reported as 700 cm$^{-1}$.83 Despite the large error the activation energies are still definitely smaller than the energy gaps measured by emission, which is an indication that the photolysis reactions do not proceed through the $^3\text{MLCT}$ state.

4.5.2 Low Temperature Photolysis

Table 4.5 compares the energy barriers measured from the temperature dependence of the photolysis and the emission for each compound. A possible point of concern is that the measurements were made at different temperatures. The quantum yield of photolysis for each complex was measured from 278 K to 293 K, while the emission experiments were collected at significantly lower
temperature, 120 K – 220 K, depending on the compound. In order to get a better comparison, the photolysis was measured at low temperatures to match the temperatures at which the emission was taken. The low temperature photolysis was measured by monitoring the decrease of emission of the complexes with irradiation since only the starting material emits at the wavelength monitored (Scheme 2). Figures 4.24 and 4.25 show graphs of the relative emission intensity vs. irradiation time for cis-[Ru(bpy)$_2$(AN)$_2$]$^{2+}$ and cis-[Ru(bpy)$_2$(py)$_2$]$^{2+}$ from 130 K – 170 K and 180 K – 230 K respectively. The photolysis was conducted in 4:1 ethanol methanol with ~20 mM TBACl. The rate of photolysis can be seen to decrease as the temperature decreases for both compounds. It is evident that no photolysis occurs at 180 K for cis-[Ru(bpy)$_2$(py)$_2$]$^{2+}$, but cis-[Ru(bpy)$_2$(AN)$_2$]$^{2+}$ shows some photolysis even at 130 K. This suggests a greater activation barrier for cis-[Ru(bpy)$_2$(py)$_2$]$^{2+}$ as compared to cis-[Ru(bpy)$_2$(AN)$_2$]$^{2+}$.

\[
\begin{align*}
[Ru(bpy)_2L_2]^{2+} \xrightarrow{hv} & \quad [Ru(bpy)_2(L)Cl]^+ \\
Emissive at & \quad 550-650 \text{ nm} \\
\downarrow & \\
\text{Not Emissive at} & \quad 550-650 \text{ nm}
\end{align*}
\]  

(2)

An absolute quantum yield was not possible to calculate, but a relative rate of the reaction can be inferred from the relative emission. An Arrhenius-like equation can be set up in the form

\[
\ln(1 - I_{rel}) = \ln(A) - \frac{E_a}{RT}
\]

Where \(I_{rel}\) is the relative emission, \(E_a\) is the activation energy, \(T\) is the
temperature, and $R$ is the gas constant. Arrhenius plots for the low temperature photolysis at 2 minutes, 4 minutes, and 6 minutes of irradiation are shown in Figures 4.26 and 4.27. The activation energies average to $515 \pm 100\ \text{cm}^{-1}$ for cis-$[\text{Ru(bpy)_2(AN)}_2]^{2+}$ and to $940 \pm 85\ \text{cm}^{-1}$ for cis-$[\text{Ru(bpy)_2(py)}_2]^{2+}$. The photolysis rate changes much more drastically over the temperature range 130 K– 170 K than from 278 K – 298 K, decreasing the error in the measurement.

**Figure 4.24** Relative emission of cis-$[\text{Ru(bpy)_2(AN)}_2]^{2+}$ vs. irradiation time at 130, 140, 150, 160, and 170 K in 4:1 ethanol:methanol with ~20 mM TBACl.
Figure 4.25 Relative emission of cis-[Ru(bpy)$_2$(py)$_2$]$^{2+}$ vs. irradiation time at 180, 190, 200, 210, 220, and 230 K in 4:1 ethanol:methanol with ~20 mM TBACl.

Figure 4.26 Arrhenius plot for photolysis of cis-[Ru(bpy)$_2$(AN)$_2$]$^{2+}$ with Cl$^-$ vs. temperature.
The lowest temperature data point (180 K) for the photolysis of cis-[Ru(bpy)$_2$(py)$_2$]$^{2+}$ does not match the rest of the data at any of the irradiation times and was not included in the line of best fit, this is likely because no photolysis occurs at this temperature. Table 4.6 compares the activation energy from low temperature photolysis studies with the energy gap between the $^3$MLCT and the $^3$LF states measure from emission over the same temperature range.

**Table 4.6** Comparison of activation energies of photoanation measured by temperature dependent photolysis and energy gap between $^3$MCLT and $^3$LF states measured by temperature dependent emission for Cis-[Ru(bpy)$_2$L$_2$]$^{2+}$ (L = AN and py). Photolysis measurements are for photoanation in 4:1 ethanol:methanol with ~20 mM TBACl. Experiments conducted over the same temperature range.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_a$ /cm$^{-1}$</th>
<th>$\Delta E$ /cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cis-[Ru(bpy)$_2$(AN)$_2$]$^{2+}$</td>
<td>515 ± 100</td>
<td>1310</td>
</tr>
<tr>
<td>Cis-[Ru(bpy)$_2$(py)$_2$]$^{2+}$</td>
<td>940 ± 85</td>
<td>2040</td>
</tr>
</tbody>
</table>
4.5.3 Dark Reactions

In order to study the photolysis of ruthenium bipyridine compounds, the reactivity in the absence of light had to be investigated to make sure there were no dark reactions affecting the measurement of the quantum yields. The stability of all three photoactive complexes in CH$_2$Cl$_2$ with TBACl, and cis-[Ru(bpy)$_2$(MeBN)$_2$]$^{2+}$ in water, were studied in the dark. The solutions were degassed by bubbling N$_2$ through them for 10 min, and allowed to sit for at least one hour in the dark at the highest temperature at which photolysis was measured. The absorbance spectrum of each dark reaction is shown in Figures 4.28-4.31. In every case the absorption spectrum of the compound is unchanged indicating that there was no reaction.

**Figure 4.28** Electronic absorption spectra of cis-[Ru(bpy)$_2$(AN)$_2$]$^{2+}$ in CH$_2$Cl$_2$ with excess TBACl at t = 0 minutes, 30 minutes, and 60 minutes. Kept in the dark at 30°C.
Figure 4.29 Electronic absorption spectra of cis-[Ru(bpy)$_2$(py)$_2$]$^{2+}$ in CH$_2$Cl$_2$ with excess TBACl at t = 0 minutes, 30 minutes, and 60 minutes. Kept in the dark at 30°C.

Figure 4.30 Electronic absorption spectra of cis-[Ru(bpy)$_2$(MeBN)$_2$]$^{2+}$ in CH$_2$Cl$_2$ with excess TBACl at t = 0 minutes and 60 minutes. Kept in the dark at 30°C.
Figure 4.31 Electronic absorption spectra of cis-[Ru(bpy)$_2$(MeBN)$_2$]$^{2+}$ in water at $t = 0$ minutes, 30 minutes, and 60 minutes. Kept in the dark at 30°C.

4.5.4 Viscosity of 4:1 Ethanol:Methanol

When measuring the photolysis at very low temperatures one concern is changes to the viscosity of the solvent as a function of temperature is affecting the observed reaction rate. An increase in viscosity could decrease the rate of photolysis affecting the measurements at low temperature. The viscosity of 4:1 ethanol:methanol was measured using 9-(2,2-dicyanovinyl)julolidine (DCV) as a viscosity probe (shown in Figure 4.32). Upon increasing viscosity, the emission of DCV increases due to hindrance to molecular rotations which decreases non-radiative decay. The concentration of DCV was such that the optical density at 450 nm was 0.10. An excitation wavelength of 450 nm was chosen and the integrated emission was measured from 460-600 nm every ten degrees from 180 K to 60 K and the results are shown in Figure 4.33.
There are three distinct segments in Figure 4.33. There is a small increase in emission from 180-140 K, a sharp non-linear increase in luminescence from 130-90 K, and a linear increase from 90-60 K. The 180-140 K segment is consistent with a temperature dependence of the emission of DCV. The 130-90 K segment begins the phase change of the solvent and the increase in emission intensity is due to an increase in viscosity as the mixture freezes. The 90-60K segment is consistent with temperature dependence to the emission of DCV frozen in a matrix. This matches previously reported values of ~125 K for the start of the glass transition of 4:1 ethanol:methanol, and ~95 K for the mixture to be completely as glass.

Figure 4.34 compares the temperature dependence of the emission of DCV with that of [Ru(bpy)$_3$]$^{2+}$, cis-[Ru(bpy)$_2$(AN)$_2$]$^{2+}$, and cis-[Ru(bpy)$_2$(py)$_2$]$^{2+}$ in the range 180-130 K. Cis-[Ru(bpy)$_2$(AN)$_2$]$^{2+}$ shows a very large increase in emission intensity in this temperature range because this is where the emission for this complex turns on. Both [Ru(bpy)$_3$]$^{2+}$ and cis-[Ru(bpy)$_2$(py)$_2$]$^{2+}$ show strong emission above 180 K and there is very little increase in emission intensity at
these temperatures. The compound DVC show strong emission above 180 K, and the increase in relative emission above \([\text{Ru(bpy)}_3]^{2+}\) and cis-\([\text{Ru(bpy)}_2(\text{py})_2]^{2+}\) is due to an increase in viscosity. The 4:1 ethanol:methanol mixture is not frozen at 130 K, the lowest temperature that photolysis experiments were conducted.

**Figure 4.33** Relative emission vs. temperature for 9-(2,2-dicyanovinyl)julolidine (DCV) in 4:1 ethanol:methanol

**Figure 4.34** Relative emission vs. temperature for DCV and Ru(II) complexes

4.6 Conclusion

\([\text{Ru(bpy)}_3]^{2+}\) has been reported to have a decrease in \(\Phi_{\text{em}}\) and
an increase in $\Phi_{\text{photo}}$ upon increasing temperature with similar values for the energy gap between the $^3\text{MLCT}$ and $^3\text{LF}$ states and the activation energy of photolysis. This led to the conclusion that the population of the $^3\text{LF}$ state from the $^3\text{MLCT}$ state preceded photo substitution as shown in Figure 1.6.\textsuperscript{86} However, compounds of the type cis-[Ru(bpy)$_2$L$_2$]$^{2+}$ (L = AN, MeBN, py) have different values for the energy gap measured from emission and the activation energy measured from photolysis (Table 4.5 and 4.6). This suggests that the $^3\text{LF}$ state is populated directly from the initially excited $^1\text{MLCT}$, as shown in Figure 4.1.
CHAPTER 5

Solvent Dependent Emission of Os(bpy)$_2$L Compounds

5.1 Background

In addition to applications as potential PDT agents for treating cancer, ruthenium polypyridyl complexes are extensively studied for their applications in solar energy conversion, sensing and signaling, and information storage. Luminescence based sensing in ruthenium compounds is particularly promising because of their high sensitivity, ease of synthesis and modification, and simplicity of use. Ruthenium(II) compounds containing ligands with an extended π structure, such as dppz and dppp2 (dppz = dipyrido[3,2-a:20,30-c]phenazine, dppp2 = dipyrido[2′,3′:5,6]pyrazino[2,3-f][1,10]phenanthroline) show a strong solvent dependent emission. Compounds of ruthenium(II) containing the dppz ligand are known to have a $^3$MLCT state localized on the phenazine portion of the dppz ligand (distol to the metal) as the lowest energy excited state, with the $^3$MLCT state localized on the bpy portion of the dppz ligand (proximal to the metal) at a higher energy (Figure 5.1). Emission comes from the higher energy proximal $^3$MLCT state.
Figure 5.1 Structure of $[\text{Ru(bpy)}_2(\text{dppz})]^ {2+}$ showing the proximal (black) and distol (grey) portions of the dppz ligand.

The relative energies of proximal and distol $^3$MLCT states is dependent on environment, giving a large solvent dependence to the intensity of the emission. $[\text{Ru(bpy)}_2(\text{dppp2})]^ {2+}$ additionally shows a large change in the energy of emission in different solvents, while $[\text{Ru(bpy)}_2(\text{dppz})]^ {2+}$ does not show such a change. The complex $[\text{Ru(bpy)}_2(\text{dppp2})]^ {2+}$ has an emission maxima of 653 nm in dichloromethane, and 752 nm in acetonitrile. To further study the solvent dependence of the emission energy, the compounds $[\text{Os(bpy)}_2(\text{dppz})]^ {2+}$, $[\text{Os(bpy)}_2(\text{dppp2})]^ {2+}$, and $[\text{Os(dppp2)}_3]^ {2+}$ were synthesized and their emission was studied.

5.2 Absorption

The electronic absorption spectra of $[\text{Os(bpy)}_2(\text{dppz})]^ {2+}$, $[\text{Os(bpy)}_2(\text{dppp2})]^ {2+}$, and $[\text{Os(dppp2)}_3]^ {2+}$ are shown in Figure 5.2. The absorbance maxima and molar extinction coefficients for each compound are listed in Table 5.1. The absorption spectra of $[\text{Os(bpy)}_2(\text{dppz})]^ {2+}$ and $[\text{Os(bpy)}_2(\text{dppp2})]^ {2+}$ show ligand centered $^1\pi\pi^*$ transitions with maxima at
~290 nm while the absorption spectrum of [Os(dppp2)3]^{2+} shows a ligand centered \(1\pi\pi^*\) transition with a maximum at 270 nm. Both [Os(bpy)2(dppp2)]^{2+} and [Os(dppp2)3]^{2+} and have distinctive peaks at 345 and 360 nm that are not seen in [Os(bpy)2(dppz)]^{2+} and are attributed to \(1\pi\pi^*\) transitions in the dppp2 ligand. The ruthenium complexes [Ru(bpy)_{3-n}(dppp2)_n]^{2+} (n = 1-3) also show these peaks. [Os(bpy)2(dppz)]^{2+} and [Os(bpy)2(dppp2)]^{2+} exhibit \(1\text{MLCT}\) transitions resulting in a peak with two maxima at 435 nm and 475 nm. [Os(dppp2)3]^{2+} has a single broad peak centered on 470 nm attributed to a \(1\text{MLCT}\) transition. All three compounds have a large tail extending to ~700 nm corresponding to absorption directly into the \(3\text{MLCT}\) state of the complexes made possible by the large spin-orbit coupling of osmium.

![Absorption spectra of [Os(bpy)2(dppz)]^{2+}, [Os(bpy)2(dppp2)]^{2+}, and [Os(dppp2)3]^{2+} in acetonitrile.](image)

**Figure 5.2** Absorption spectra of [Os(bpy)2(dppz)]^{2+}, [Os(bpy)2(dppp2)]^{2+}, and [Os(dppp2)3]^{2+} in acetonitrile.
5.3 Emission

The absorption, emission and excitation spectra of \([\text{Os(bpy)}_2(\text{dppp2})]^2+\) and \([\text{Os(bpy)}_2(\text{dppz})]^2+\) in dichloromethane are shown in Figures 5.3 and 5.4. The osmium complexes have emission maxima of 740 nm and 725 nm for \([\text{Os(bpy)}_2(\text{dppp2})]^2+\) and \([\text{Os(bpy)}_2(\text{dppz})]^2+\) respectively. The emission in acetonitrile is much less intense, similar to what is seen for the ruthenium analogs.\(^{96}\) Figures 5.5 and 5.6 show the emission spectra of \([\text{Os(bpy)}_2(\text{dppp2})]^2+\) and \([\text{Os(bpy)}_2(\text{dppz})]^2+\) in dichloromethane as well as 9:1, 2:1, and 1:1 dichloromethane : acetonitrile. The emission maximum for \([\text{Os(bpy)}_2(\text{dppp2})]^2+\) shifts from 740 nm in dichloromethane to 715 nm in 1:1 dichloromethane : acetonitrile, while the emission maximum for \([\text{Os(bpy)}_2(\text{dppz})]^2+\) shifts from 725 nm in dichloromethane to 740 nm in 1:1 dichloromethane : acetonitrile. The complex \([\text{Ru(bpy)}_2(\text{dppp2})]^2+\) showed a change in emission maximum from 653 nm to 705 nm under similar conditions.\(^{96}\) Although \([\text{Os(bpy)}_2(\text{dppp2})]^2+\) shows a change in the energy of emission with solvent, the change is less then was found for \([\text{Ru(bpy)}_2(\text{dppp2})]^2+\) and in the opposite direction. \([\text{Ru(bpy)}_2(\text{dppp2})]^2+\) exhibits lower energy emission in acetonitrile compared to dichloromethane, whereas \([\text{Os(bpy)}_2(\text{dppp2})]^2+\) exhibits higher energy emission in acetonitrile compared to dichloromethane. In addition, \([\text{Os(bpy)}_2(\text{dppz})]^2+\) shows a shift in energy of the emission comparable to \([\text{Os(bpy)}_2(\text{dppp2})]^2+\) but in the opposite direction.
Table 5.1 Absorption and emission maxima of $[\text{Ru(bpy)}_2(\text{dppp}_2)]^{2+}$, $[\text{Os(bpy)}_2(\text{dppp}_2)]^{2+}$, $[\text{Os(bpy)}_2(\text{dppz})]^{2+}$, and $[\text{Os(dppp}_2)_3]^{2+}$. A) in acetonitrile. B) from reference 96. C) done in 3:2 CH$_2$Cl$_2$:NCCH$_3$.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Absorption$^a$ $\lambda_{\text{max}}$, nm ($\varepsilon$, M$^{-1}$cm$^{-1}$)</th>
<th>Emission $\lambda_{\text{max}}$, nm CH$_2$Cl$_2$</th>
<th>Emission $\lambda_{\text{max}}$, nm 1:1 CH$_2$Cl$_2$:NCCH$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Ru(bpy)}_2(\text{dppp}_2)]^{2+}$</td>
<td>440 (11,700)</td>
<td>653</td>
<td>705$^c$</td>
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<tr>
<td>$[\text{Os(bpy)}_2(\text{dppp}_2)]^{2+}$</td>
<td>435 (12,500) 475 (13,500)</td>
<td>740</td>
<td>715</td>
</tr>
<tr>
<td>$[\text{Os(bpy)}_2(\text{dppz})]^{2+}$</td>
<td>435 (12,000) 475 (13,000)</td>
<td>725</td>
<td>740</td>
</tr>
<tr>
<td>$[\text{Os(dppp}_2)_3]^{2+}$</td>
<td>470 (13,000)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 5.3 Absorption, emission, and excitation spectra of $[\text{Os(bpy)}_2(\text{dppp}_2)]^{2+}$ in dichloromethane.
Figure 5.4 Absorption, emission, and excitation spectra of \([\text{Os}(\text{bpy})_2(\text{dppz})]^{2+}\) in dichloromethane.

Figure 5.5 Emission spectra of \([\text{Os}(\text{bpy})_2(\text{dppp2})]^ {2+}\) in dichloromethane and 9:1, 2:1, and 1:1 dichloromethane : acetonitrile.
Figure 5.6 Emission spectra of [Os(bpy)$_2$(dppz)]$^{2+}$ in dichloromethane and 9:1, 2:1, and 1:1 dichloromethane : acetonitrile.
CHAPTER 6

Photophysical and Photochemical Properties of Ruthenium Polypyridyl Compounds

5.1 Background

A series of ruthenium compounds were received from Dr. Randolph Thummel at the University Houston in Houston, Texas and the photochemical and photophysical properties of the compounds were tested for possible applications in photodynamic therapy (PDT). The four compounds studied were trans-[Ru(bnap)(AN)₂(H₂O)]²⁺ (bnap = 4-tert-butyl-2,6-di(1‘,8‘-naphthryl-2’-yl)pyridine), [Ru(pydppn)(aazp)Cl]⁺ (pydppn = 3-(pyrid-2’-yl)-4,5,9,16-tetraazadibenzo[a,c]naphthacene; aazp = 2-(p-N,N-Dimethylaminophenylazo)pyridine), [Ru(pydppn)(AN)₃]²⁺, and [Ru(pyq)(AN)₃]⁺ (pyq = 2-(2’-Pyridyl)-8-hydroxyquinoline). The structures are shown in Figure 6.1.
Figure 6.1 Structure of (a) trans-[Ru(bnap)(AN)\textsubscript{2}(H\textsubscript{2}O)]\textsuperscript{2+} (b) [Ru(pyq)(AN)\textsubscript{3}]\textsuperscript{+} (c) [Ru(pydpnn)(aazp)Cl]\textsuperscript{+} and (d) [Ru(pydpnn)(AN)\textsubscript{3}]\textsuperscript{2+}
6.2 Trans-[Ru(bnap)(AN)$_2$(H$_2$O)]$^{2+}$

6.2.1 Absorption and Emission

The electronic absorption spectrum of [Ru(bnap)(AN)$_2$(H$_2$O)]$^{2+}$ in acetonitrile is shown in Figure 6.2. The absorbance maxima and molar extinction coefficients are listed in Table 6.1. The absorption spectrum exhibits ligand centered $^1\pi\pi^*$ transitions with maxima at ~315 nm and 368 nm. $^1$MLCT transitions can be seen with maxima at 450, 500, and 550 nm with a tail that extends to ~650 nm, into the ideal PDT window of 600-850 nm. The compound shows emission with a maximum of 735 nm in acetonitrile (Figure 6.2) and a maximum of 720 nm in dichloromethane (Figure 6.3). In both cases the excitation spectrum appears red shifted compared to the absorption spectrum. The affect is less pronounced in dichloromethane.

![Figure 6.2 Absorption, emission, and excitation spectra of trans-[Ru(bnap)(AN)$_2$(H$_2$O)]$^{2+}$ in acetonitrile.](image)

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Figure 6.3 Absorption, emission, and excitation spectra of trans-[Ru(bnap)(AN)2(H2O)]2+ in dichloromethane.

6.2.2 Dark Reaction

Trans-[Ru(bnap)(AN)2(H2O)]2+ undergoes a reaction in dichloromethane in the absence of light. Upon dissolving in dichloromethane, the 1MLCT peak at 450 nm shifts to 460 nm, while the peak at 500 nm shifts to 535 nm and increases in intensity. The reaction is complete in 45 minutes. If the resulting compound is re-dissolved in acetonitrile, the absorption spectrum undergoes a change back to the original spectrum. The reaction is reversible and likely consists of the substitution of one or both of the axial acetonitrile ligands with coordinated solvent molecules. The excitation spectrum better resembles the absorption in dichloromethane, suggesting that the emitting species is not the di-acetonitrile complex. The changes in the electronic absorption spectra in the dark are shown in Figures 6.4 and 6.5.
Figure 6.4 Electronic absorption spectra of trans-[Ru(bnap)(AN)₂(H₂O)]²⁺ in dichloromethane at t = 0, 10, 20, 30, and 45 minutes, kept in the dark at 25°C.

Figure 6.5 Electronic absorption spectra of the photoproduct of the dark reaction of trans-[Ru(bnap)(AN)₂(H₂O)]²⁺ in dichloromethane upon re-dissolving in acetonitrile. Spectra taken in acetonitrile at t = 0, 10, 20, and 30 minutes kept in the dark at 25°C.
The complex does not exhibit a change in the electronic absorption spectrum with time when dissolved in water indicating that either it is not reactive or that the substitution happens rapidly, before the spectrum is measured. There is no change in the absorption spectrum upon photolysis in water (Figure 6.6).

![Absorption spectrum of trans-[Ru(bnap)(AN)\(_2\)(H\(_2\)O)]\(^{2+}\) in water. 150W lamp, 550 nm long pass filter.](image)

**Figure 6.6** Photolysis of trans-[Ru(bnap)(AN)\(_2\)(H\(_2\)O)]\(^{2+}\) in water. 150W lamp, 550 nm long pass filter.

### 6.3 [Ru(pyq)(AN)\(_3\)]\(^+\)

#### 6.3.1 Absorption and Emission

The electronic absorption spectrum of [Ru(pyq)(AN)\(_3\)]\(^+\) in acetonitrile is shown in Figure 6.7. The absorbance maxima and molar extinction coefficients are listed in Table 6.1. The absorption spectrum shows a ligand centered \(^1\pi\pi^*\) transition with a maximum at 300 nm. \(^1\)MLCT transitions can be seen with maxima at 410 and 463 nm. There is a long tail to the \(^1\)MLCT transition that
extends past 650 nm absorbing into the ideal PDT window. The absorption in water is significantly different from the absorption in acetonitrile, and is also shown in Figure 6.7. The $^1$MLCT in water has maxima of 389 and 453 nm. There is also a difference in the $^1$H NMR of [Ru(pyq)(AN)$_3$]$^+$ in d$_3$-acetone and in D$_2$O, shown in Figure 6.8. The $^1$H NMR spectrum in d$_3$-acetone shows 7 aromatic peaks corresponding to the pyq ligand, 1 peak corresponding to the equatorial acetonitrile, and 1 peak corresponding to the axial acetonitriles. In D$_2$O, both the equatorial and axial acetonitrile peaks are split into two peaks. There are also 10 signals in the aromatic region, showing splitting there as well. The NMR spectrum indicates a mixture of two different species when the complex is dissolved in water. However, there is no peak for free acetonitrile and therefore the thermal substitution of the acetonitriles is not happening. The compound does not show any emission.

Figure 6.7 Electronic absorption spectrum of [Ru(pyq)(AN)$_3$]$^{2+}$ in acetonitrile (solid line) and water (dashed line).
Figure 6.8 $^1$H NMR spectrum of [Ru(pyq)(AN)$_3$]$^+$ in d$_3$-acetone (top) and D$_2$O (bottom). The peak corresponding to the equatorial acetonitrile is marked with a triangle; the peak corresponding to the axial acetonitriles is marked with a diamond.

6.3.2 pH Dependence

A possible cause of the difference in the electronic absorption and $^1$H NMR spectra of [Ru(pyq)(AN)$_3$]$^+$ in water and acetonitrile is the protonation of the oxygen atom of the pyq ligand while in water. To test this, the pH dependence of the electronic absorption spectrum was investigated. The absorption spectrum changes reversibly with pH and is shown in Figure 6.9. The pH was changed by addition of either HCl or NaOH to the aqueous solution and the pH was measured with pH paper. All spectra were normalized to the maximum of the 453 nm peak. The spectrum taken in pure water is very close to the spectrum taken in pH 5, as might be expected. Upon increasing pH, the peak at 389 nm grows in intensity,
along with low energy peaks centered at 560 and 600 nm. The absorbance in acetonitrile is much closer to the absorbance in pH 9 water than it is in pure water, except for the unidentified low energy peaks at 560 and 600 nm (Figure (6.10).

The \(^1\)H NMR was also taken under basic conditions. Figure 6.11 shows the \(^1\)H NMR spectrum of [Ru(pyq)(AN)\(_3\)]\(^{2+}\) in D\(_2\)O with saturated NaCO\(_3\) giving the solution a pH of approximately 11. The \(^1\)H NMR spectrum shows essentially no splitting of the acetonitrile peaks, and only has seven signals in the aromatic region as opposed to ten different signals in D\(_2\)O without NaCO\(_3\). The NMR spectrum in basic D\(_2\)O is similar to the spectrum in acetonitrile. This supports the theory that the complex is protonated in water.

![Graph showing reversible change in absorption spectrum of [Ru(pyq)(AN)\(_3\)]\(^{1+}\) in water.](image)

**Figure 6.9** Reversible change in absorption spectrum of [Ru(pyq)(AN)\(_3\)]\(^{1+}\) in water.
Figure 6.10 Comparison of absorption spectrum of \([\text{Ru(pyq)(AN)}_3]^+\) in acetonitrile (solid line) and in water at pH 9 (dashed line).

Figure 6.11 $^1$H NMR of \([\text{Ru(pyq)(AN)}_3]^+\) in D$_2$O with saturated NaCO$_3$, pH ~ 11. The peak corresponding to the equatorial acetonitrile is marked with a triangle; the peak corresponding to the axial acetonitriles is marked with a diamond.

6.3.3 Photolysis

The photolysis of \([\text{Ru(pyq)(AN)}_3]^+\) in water with a 150 W lamp and a 395 nm long pass filter is shown in Figures 6.12 and 6.13. The solution was degassed by bubbling with nitrogen for 10 minutes. Upon photolysis, the peak at 453 nm
disappears and two new peaks at 384 nm and 533 nm grow in. An intermediate can be seen forming in the first two minutes with a peak at 555 nm (Figure 6.12). Photolysis was found to occur with wavelengths as high as 715 nm. Figure 6.14 shows the photolysis with a 150 W lamp and a 715 nm long pass filter. The photolysis is much slower, and after 20 hours the spectrum appears to be almost exclusively the intermediate product.

Figure 6.12 Photolysis of [Ru(pyq)(AN)$_3$]$^+$ in water, 0 - 2 minutes. 150 W lamp; 395 nm long pass filter
Figure 6.13 Photolysis of [Ru(pyq)(AN)₃]⁺ in water, 2 - 15 minutes. 150 W lamp; 395 nm long pass filter

Figure 6.14 Photolysis of [Ru(pyq)(AN)₃]⁺ in water. 150 W lamp; 715 nm long pass filter
The photolysis was also followed by $^1$H NMR. Figure 6.15 shows the photolysis of $[\text{Ru}(\text{pyq})(\text{AN})_3]^+$ in deuterated acetonitrile with a 150 W lamp and a 395 nm long pass filter. Dichloromethane was added as a reference. The axial acetonitriles can be seen at 2.12 ppm and are substituted first, being mostly gone after only 15 minutes of irradiation and completely gone after 1 hour. The peak for the equatorial acetonitrile can be seen at 2.71 ppm and does not lose any intensity in the first hour. After 19.5 hours it is at about a third of its original value. This is similar to the $[\text{Ru}(\text{tpy})(\text{AN})_3]^{2+}$ complex discussed in chapter 3 in that the equatorial acetonitrile is much harder to photolyze. The aromatic region remains unchanged.

The photolysis was also done in D$_2$O on a 150 W lamp with a 715 nm long pass filter and monitored by $^1$H NMR (Figure 6.16). Acetone was added as a reference and can be seen at 2.22 ppm. The photolysis at long wavelengths of irradiation is very slow, mirroring the absorption photolysis. Free acetonitrile can be seen forming at 2.06 ppm within the first hour. Another peak can be seen growing in at 2.8 ppm, most likely the mono substituted species cis-$[\text{Ru}(\text{pyq})(\text{AN})_2(\text{D}_2\text{O})]^+$. 
Figure 6.15 Photolysis of [Ru(pqy)(AN)]^+ in d_3-acetonitrile followed by ^1H NMR. 150 W lamp 395 nm long pass filter. Dichloromethane added as a reference. The peaks corresponding to equatorial acetonitrile, axial acetonitriles, and free acetonitrile are marked with a triangle, diamond, and star respectively.

Figure 6.16 Photolysis of [Ru(pyq)(AN)]^+ in D_2O followed by ^1H NMR. 150 W lamp 715 nm long pass filter. Acetone added as a reference. The peaks corresponding to equatorial acetonitrile, axial acetonitriles, and free acetonitrile are marked with a triangle, diamond, and star respectively.
6.3.4 Dark Reaction

In order to study the photolysis of \([\text{Ru(pqy)(AN)}_3]^+\), the reactivity in the absence of light had to be investigated to make sure there were no dark reactions affecting the measurements. The stability of the complex in water is shown in Figure 6.17. The absorption spectrum of the compound is unchanged after 44 hours indicating that there was no reaction.

![Absorption spectrum](image)

**Figure 6.17** Electronic absorption spectra of \([\text{Ru(pqy)(AN)}_3]^+\) in water at t = 0, 1 hour, and 44 hours, kept in the dark at 25°C.

6.4 \([\text{Ru(pydppn)(aazp)Cl}]^+\)

6.4.1 Absorption, Emission and Photolysis

The electronic absorption spectrum of \([\text{Ru(pydppn)(aazp)Cl}]^+\) in acetonitrile is shown in Figure 6.18. The absorbance maxima and molar extinction coefficients are listed in Table 6.1. The absorption spectrum shows
ligand centered $^1\pi\pi^*$ transitions with a maximum at 340 nm. $^1\text{MLCT}$ transitions can be seen with maxima at 503 and 580 nm with a tail that extends past 700 nm, into the ideal PDT window. The Compound does not exhibit any emission. When irradiated in water with a 150 W lamp and a 305 nm long pass filter the absorption spectrum showed no change over 30 minutes. The stability under irradiation is expected since the only monodentate ligand the compound has is chloride, which is not a photo labile ligand.

Figure 6.18 Electronic absorption spectrum of [Ru(pydppn)(aazp)Cl]$^+$ in acetonitrile

6.4.2 Singlet Oxygen Production

The octahedral ruthenium compounds [Ru(tpy)(pydppn)]$^{2+}$ and [Ru(pydppn)$_2$]$^{2+}$ are known to produce singlet oxygen under irradiation from a $^3\text{LC}$ state on the pydppn ligand, with high quantum yields of 0.92(2) and 1.07(7)
respectively.\textsuperscript{30} For this reason the quantum yield of singlet oxygen production of 
[Ru(pydpnn)(aazp)Cl]\textsuperscript{+} was investigated. Quantum yields were measured in 
methanol using [Ru(bpy)\textsubscript{3}]\textsuperscript{2+} as a standard (Φ = 0.81 in methanol) and 1,3-
diphenylisobenzofuran (DPBF) as a $^1$O\textsubscript{2} trapping agent, as described in section 
2.3.2. Samples were irradiated at 460 nm, and emission measurements were taken 
with $\lambda_\text{irr} = 405$ nm. The emission intensity of DPBF was graphed versus the 
irradiation time and is shown in Figures 6.19-6.21. Three trials were done of 
DPBF only, and six trials each of DPBF with [Ru(bpy)\textsubscript{3}]\textsuperscript{2+} and DPBF with 
[Ru(pydpnn)(aazp)Cl]\textsuperscript{+}. The quantum yield of singlet oxygen production was 
calculated from the following equation

$$\Phi_S = \frac{0.81}{S_R} \cdot S_S \cdot \frac{A_R}{A_S}$$

Where $\Phi_S$ is the quantum yield of the sample, $S_R$ is the slope from the graph of 
DPBF with the reference compound [Ru(bpy)\textsubscript{3}]\textsuperscript{2+}, $S_S$ is the slope from the graph 
of DPBF with the sample compound [Ru(pydpnn)(aazp)Cl]\textsuperscript{+}, and $A_R$ and $A_S$ are 
the absorbance of the reference and sample, respectively, at the irradiation 
wavelength of 460 nm. The quantum yield of singlet oxygen production for 
[Ru(pydpnn)(aazp)Cl]\textsuperscript{+} was measured to be 0.036 ± 0.01. This is significantly 
lower than Ru(tpy)(pydpnn)\textsuperscript{2+} and [Ru(pydpnn)\textsubscript{2}]\textsuperscript{2+}, and is probably related to the 
lack of emission seen in [Ru(pydpnn)(aazp)Cl]\textsuperscript{+}. The lack of emission indicates 
that the lowest energy excited state of [Ru(pydpnn)(aazp)Cl]\textsuperscript{+} does not last long 
enough to efficiently produce singlet oxygen.
Figure 6.19 Emission vs. irradiation time for DPBF in methanol.

Figure 6.20 Emission vs. irradiation time for DPBF and [Ru(bpy)$_3$]$^{2+}$ in methanol.
Figure 6.21 Emission vs. irradiation time for DPBF and [Ru(pydpnn)(aazp)Cl]⁺ in methanol

6.5 [Ru(pydpnn)(AN)₃]²⁺

6.5.1 Absorption and Emission

The electronic absorption spectrum of [Ru(pydpnn)(AN)₃]²⁺ in acetonitrile is shown in Figure 6.22. The absorbance maximum and molar extinction coefficient is listed in Table 6.1. The absorption spectrum shows ligand centered ¹ππ⁺ transitions with a maximum at 340 nm. A broad ¹MLCT transition can be seen with maximum at 445 nm and a tail that extends past 650 nm. The Compound does not show any emission.
Figure 6.22 Electronic absorption spectrum of [Ru(pydppn)(AN)₃]²⁺ in acetonitrile

Table 6.1 Absorption maxima and extinction coefficients of ruthenium(II) compounds in acetonitrile.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Absorption λₘₐₓ, nm (ε, M⁻¹ cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ru(bnap)(AN)₂(H₂O)]²⁺</td>
<td>450 (4000), 500 (4,250), 550 (3,250)</td>
</tr>
<tr>
<td>[Ru(pyq)(AN)₃]²⁺</td>
<td>410 (5,500), 463(3,750)</td>
</tr>
<tr>
<td>[Ru(pydppn)(aazp)Cl⁺]</td>
<td>503 (23,500), 580 (20,000)</td>
</tr>
<tr>
<td>[Ru(pydppn)(AN)₃]²⁺</td>
<td>445 (11,250)</td>
</tr>
</tbody>
</table>

6.5.2 Photolysis

The photolysis of [Ru(pydppn)(AN)₃]²⁺ in water with a 150 W lamp was conducted with 305 nm, 395nm, and 495nm long pass filters and is shown in Figures 6.23-6.25. The solutions were degassed by bubbling with nitrogen for 10 minutes. The absorption spectrum of [Ru(pydppn)(AN)₃]²⁺ shows no change upon photolysis with a 495 nm long pass filter. Photolysis with a 395 nm long
pass filter causes a decrease in the peak at 445 nm with an increase at 550 nm. However, the photolysis is relatively slow photolysis, taking approximately 2 hours. This is unexpected since acetonitrile is known to have a high quantum yield of photolysis\(^{47,49}\) and the \(^1\)MLCT peak extends well past 495 nm. Upon photolysis with a 305 nm long pass filter, the broad \(^1\)MLCT peak decreases without any product peak forming. This suggests that the compound is degrading, as substitution with water should cause a red shift of the \(^1\)MLCT.

The photolysis was also done in dichloromethane with tetrabutylammonium chloride (TBACl) and a 305 nm long pass filter (Figure 6.26). The photolysis shows a decrease in the initial peak at 445 nm with product peaks forming at 550 and 650 nm. There is also a rise of two peaks at 395 and 420 nm.
Figure 6.23 Photolysis of [Ru(pydppn)(AN)]^{2+} in water 150 W lamp 305 nm long pass filter.

Figure 6.24 Photolysis of [Ru(pydppn)(AN)]^{2+} in water 150 W lamp 395 nm long pass filter.
Figure 6.25 Photolysis of [Ru(pydppn)(AN)]\textsuperscript{3+} in water 150 W lamp 495 nm long pass filter.

Figure 6.26 Photolysis of [Ru(pydppn)(AN)]\textsuperscript{3+} in dichloromethane and ~10 mM TBACl. 150 W lamp 305 nm long pass filter.
The photolysis of [Ru(pydppn)(AN)$_3$]$^{2+}$ was also followed by NMR in 5 mL $d_6$-DMSO with 0.1 mL D$_2$O and is shown in Figure 6.27. The photolysis was conducted in DMSO for solubility reasons. The compound was degassed by bubbling nitrogen for 10 minutes and was photolyzed with a 395 nm long pass filter. The equatorial and axial acetonitriles can be seen at 2.90 ppm and 2.02 ppm respectively. A peak corresponding to free acetonitrile can be seen at 2.06 ppm at the earliest photolysis times. As the free acetonitrile peak rises, the axial acetonitrile peak decreases while the equatorial acetonitrile peak remains constant. This is analogous to [Ru(tpy)(AN)$_3$]$^{2+}$ in that the equatorial acetonitrile is not photo-active.
Figure 6.27 Photolysis of $[\text{Ru(pydppn)(AN)}_3]^{2+}$ in 5 mL $d_6$-DMSO with 0.1 mL $D_2O$ followed by NMR. 150 W lamp 395 nm long pass filter. The peaks corresponding to equatorial acetonitrile, axial acetonitriles, and free acetonitrile are marked with a triangle, diamond, and star respectively.

6.5.3 Singlet Oxygen Production

The quantum yield of singlet oxygen production was investigated for $[\text{Ru(pydppn)(AN)}_3]^{2+}$ as well. Quantum yields were measured in methanol using $[\text{Ru(bpy)}_3]^{2+}$ as a standard ($\Phi = 0.81$ in methanol) and 1,3-diphenylisobenzofuran (DPBF) as a $^{1}O_2$ trapping agent, as described in section 2.3.2. Samples were
irradiated at 460 nm, and emission measurements were taken with $\lambda_{\text{irr}} = 405$ nm. The emission intensity of DPBF was graphed versus the irradiation time and is shown in Figures 6.28-6.30. Three trials were done of DPBF by itself, DPBF with cis-[Ru(bpy)$_3$]$^{2+}$ and DPBF with [Ru(pydppn)(AN)$_3$]$^{2+}$. The quantum yield of singlet oxygen production was calculated as described in section 6.4.2 for [Ru(pydppn)(aazp)Cl]$^{+}$. The quantum yield of singlet oxygen production for [Ru(pydppn)(AN)$_3$]$^{2+}$ was measured to be 0.26 ± 0.01. This singlet oxygen production could explain the decrease in photolysis seen at longer wavelengths. The quantum yield of singlet oxygen production is significantly lower than that for the related compounds [Ru(tpy)(pydppn)]$^{2+}$ and [Ru(pydppn)$_2$]$^{2+}$, and may be related to the lack of emission seen in [Ru(pydppn)(AN)$_3$]$^{2+}$, or the photolysis reaction.

Figure 6.28 Emission vs. irradiation time for DPBF in methanol.

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Figure 6.29 Emission vs. irradiation time for DPBF and [Ru(bpy)$_3$]$^{2+}$ in methanol.

Figure 6.30 Emission vs. irradiation time for DPBF and [Ru(pydppn)(AN)$_3$]$^{2+}$ in methanol.
6.6 Conclusion

The photophysical and photochemical properties of the octahedral ruthenium complexes trans-[Ru(bnap)(AN)\(_2\)(H\(_2\)O)]\(^{2+}\), [Ru(pydppn)(aazp)Cl]\(^+\), [Ru(pydppn)(AN)\(_3\)]\(^{2+}\), and [Ru(pyq)(AN)\(_3\)]\(^+\) were studied for potential applications such as photodynamic therapy (PDT). The compounds were studied for their production of singlet oxygen and for their ability to photosubstitute with water to form cisplatin analogs. Neither trans-[Ru(bnap)(AN)\(_2\)(H\(_2\)O)]\(^{2+}\) nor [Ru(pydppn)(aazp)Cl]\(^+\) exhibited ligand substitution upon irradiation nor significant singlet oxygen production and are not promising candidates. [Ru(pydppn)(AN)\(_3\)]\(^{2+}\) exhibited both ligand dissociation, when irradiated with 395 nm light, and singlet oxygen production upon irradiation with 460 nm light. Although the quantum yield of singlet oxygen production was only 0.26 ± 0.01 and the ligand dissociation was much slower than seen with other octahedral ruthenium compounds with acetonitrile ligands, [Ru(pydppn)(AN)\(_3\)]\(^{2+}\) does have potential as a dual mode PDT agent acting as both a cisplatin analog and a singlet oxygen producer. [Ru(pyq)(AN)\(_3\)]\(^+\) is promising as a cisplatin analog, showing photolysis at wavelengths as long as 715 nm, inside the ideal PDT window of 600-850 nm.
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