CONCERTED BOND FORMATION WITH ELECTRON TRANSFER TO RUTHENIUM POLYPYRIDYL EXCITED STATES

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Abstract

Electronic excited states possess an empty electron orbital at a lower energy than the ground state compound and therefore may participate in redox reactions that are energetically unfavorable for the ground state compound. These photo-initiated one-electron redox reactions often result in unstable compounds that undergo subsequent bond breakage or bond formation through a stepwise mechanism. However, some reactions that are energetically favorable overall are hindered due to a high energy product of the initial electron transfer step. In these cases, a concerted mechanism, where bond breakage or formation is coincident with electron transfer, may provide an alternative low-energy pathway for the reaction to follow. In the case of bond formation, ion-pairing in a low-dielectric solvent enables the simultaneous encounter between the two reactants and the photo-oxidant. Several ruthenium and osmium polypyridyl compounds were studied as excited-state photo-oxidants for halide ions. Reactions fell into one of three zones depending on the reduction potentials of both the halide and the excited-state compound. Combinations of transition metal compounds and halides in Zone 1 were known to proceed through the stepwise mechanism and suspected to also proceed through the concerted mechanism in a low-dielectric solvent. Combinations in Zone 2 were found to react only through the Concerted mechanism. Time-resolved spectroscopy indicated the simultaneous disappearance of reactants and appearance of products. In Zone 3 both mechanisms were energetically unfavorable and the photophysical effects of ion-pairing were studied that were otherwise masked by redox chemistry.
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Chapter 1

Introduction

1.1 Energy Demand

Professor Richard Smalley, one of the 1996 Nobel Laureates in Chemistry for the discovery of buckminsterfullerene, listed in 2003 the top ten problems facing humanity.\(^1\)

His list was:

1. Energy
2. Water
3. Food
4. Environment
5. Poverty
6. Terrorism and War
7. Disease
8. Education
9. Democracy
10. Population

At the top of the list is energy which is also listed as one of the five “Grand Challenges” that should be addressed by scientific research, and in particular, with nanotechnology. The energy problem, however, is not monolithic but consists of many overlapping issues such as supply (including source location, politics, energy independence, environmental impact, economic impact, sustainability and public acceptance), demand (including conservation, public policy, public opinion and economic impact) and technology (including conservation, specific applications, scale, public policy and improvements in
harvesting fossil fuels as well as alternative energy sources). Energy is used to grow and transport food to feed an ever increasing world population as well as drive industrial processes that provide our current quality of life. One of the main facets to the energy problem is this rising demand, due to both population growth and expanding industrialization of the developing world. As Figure 1.1 shows, the world population has been steadily increasing since the black plague in the early to middle 1300’s and it is currently estimated to be 7.2 billion people and is expected to rise to 9 billion by the year 2042.\textsuperscript{2,3} The explosion in population after the industrial revolution of the 18\textsuperscript{th} and 19\textsuperscript{th} centuries is also clearly evident and most troubling. Industrialization not only brings about an increase in population but each person now consumes a greater amount of energy, as seen in Figure 1.2 where the world’s energy consumption is growing at an even faster rate than the world’s population. Due to the combined effects of increases in both population and per capita energy use, humanity’s energy demand has now reached a rate of 17.5 terawatts (TW) as of 2010.\textsuperscript{4} In the United States alone, in 2012 energy was consumed at a rate of 3.3 TW or 18% of the global total. This large demand for energy must be met in order to maintain our current post-industrial society, including the supply of food for large urban populations.

\section*{1.2 Energy Supply}

In the United States in 2013, energy was supplied from a variety of sources with 84% from domestic sources, 13% from net imports (imports minus exports) and 3% from stock adjustments.\textsuperscript{5} Fossil fuels accounted for 82% of the energy supply while less than 10% came from renewable sources, Figure 1.3. Biomass is not completely renewable
Figure 1.1: Estimated world population based on data from the US Census.
Figure 1.2: Comparison of the estimated world population with the estimated world energy consumption since 1980 with data from references 2 and 4.
Figure 1.3: Energy Sources for the United States in 2013 with data from reference 5. Percentages may not total 100% due to independent rounding.
since more biomass is consumed than is regrown. The large dependence on fossil fuels is widely known to suffer from several major issues such as the finite reserves remaining, the hostile politics of many petroleum exporting countries towards the United States and the pollution of the atmosphere. The world’s proven reserves of petroleum, natural gas and coal are listed in Table 1.1 where “proven” indicates that there is at least a 90% chance of recovering that resource given the current technological, economic, and political situation. The proven reserves have actually been increasing slightly in recent years due to the economic and technological changes that have brought about oil extraction from the tar sands of Canada and, to a much lesser extent, Venezuela as well as “fracking”. If, for each energy source, the proven world reserves is divided by the current usage, then a very rough, order-of-magnitude estimate of the remaining years of each resource can be obtained. This calculation overestimates the years remaining because it ignores increases in population and energy use while it underestimates the years remaining because it ignores technological improvements in fossil fuel recovery, technological improvements in alternative energy sources, conservation and economic factors. As these resources become more scarce they become more expensive. A second problem with continued reliance on fossil fuels is that many of the largest reserves are located in countries that are politically hostile to the United States, Table 1.2. Even though significant reserves of fossil fuels may remain available for use, these may be withheld from the United States for their own country’s use or put on the market at extremely high prices for political or economic gain, both of which are obviously detrimental to our quality of life.

And lastly, the combustion of fossil fuels releases a large amount of carbon dioxide
### Table 1.1: Years of fossil fuel supply remaining. Values from reference 4 converted to terawatt-years (TW-yr) and terawatts (TW). The Years Remaining column is Proved Supply divided by Current Usage. It is intended as a rough gauge and not an accurate prediction.

<table>
<thead>
<tr>
<th>Fuel Type</th>
<th>“Proved” Supply (TW-yr)</th>
<th>Current Usage (TW)</th>
<th>Years Remaining</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil</td>
<td>320</td>
<td>6</td>
<td>53</td>
</tr>
<tr>
<td>Natural Gas</td>
<td>235</td>
<td>4</td>
<td>59</td>
</tr>
<tr>
<td>Coal</td>
<td>680</td>
<td>5</td>
<td>136</td>
</tr>
<tr>
<td>Petroleum</td>
<td>Natural Gas</td>
<td>Coal</td>
<td></td>
</tr>
<tr>
<td>-----------</td>
<td>-------------</td>
<td>------</td>
<td></td>
</tr>
<tr>
<td>Country</td>
<td>Reserves (10^9 bbl)</td>
<td>Country</td>
<td>Reserves (10^{12} Ft^3)</td>
</tr>
<tr>
<td>Venezuela</td>
<td>298</td>
<td>Russia</td>
<td>1688</td>
</tr>
<tr>
<td>Saudi Arabia</td>
<td>268</td>
<td>Iran</td>
<td>1187</td>
</tr>
<tr>
<td>Canada</td>
<td>173</td>
<td>Qatar</td>
<td>890</td>
</tr>
<tr>
<td>Iran</td>
<td>155</td>
<td>United States</td>
<td>308</td>
</tr>
<tr>
<td>Iraq</td>
<td>141</td>
<td>Saudi Arabia</td>
<td>288</td>
</tr>
<tr>
<td>Kuwait</td>
<td>104</td>
<td>Turkmenistan</td>
<td>265</td>
</tr>
<tr>
<td>United Arab Emirates</td>
<td>98</td>
<td>United Arab Emirates</td>
<td>215</td>
</tr>
<tr>
<td>Russia</td>
<td>80</td>
<td>Venezuela</td>
<td>195</td>
</tr>
<tr>
<td>Libya</td>
<td>48</td>
<td>Nigeria</td>
<td>182</td>
</tr>
<tr>
<td>Nigeria</td>
<td>37</td>
<td>Algeria</td>
<td>159</td>
</tr>
</tbody>
</table>

**Table 1.2:** Top ten countries with proved reserves of selected fuel types. Data is from reference 4. Data for petroleum and for natural gas is from 2013 while data for coal is from 2011.
and pollutants such as nitrogen oxides and sulfur dioxide, Figure 1.4. This has led to a steep rise in the measured atmospheric CO$_2$ concentrations. Since 1958 the atmospheric CO$_2$ concentration has been measured at the Mauna Loa observatory in Hawaii and just recently in April of 2014 a new CO$_2$ concentration milestone of 400 parts per million (ppm) was surpassed.\textsuperscript{6} However, fossil fuels are not the only energy sources with problems, which is why alternative energy sources are not yet used on a larger scale.

Nuclear fission is not a renewable energy source but there is enough uranium and thorium to last well into the future even if the world’s energy needs came solely from nuclear energy. However, events such as Three Mile Island, Chernobyl, and Fukushima Daiichi loom large in public opinion. If the number of nuclear reactors in the United States was increased dramatically, then the potential for an accident or major disaster to occur would also increase. For these reasons, the last time construction on a new nuclear reactor was started in the United States was in 1977 and the last completed construction of an operational reactor was in 1996.\textsuperscript{7} There is a long lead time of at least ten years to build and certify a new nuclear reactor.

Within the renewable energy sources, biomass provides about half of the energy. However, in the United States, most biomass comes from wood rather than fast-growing crops and the carbon released from burning these trees is not taken up by new trees for many years. According to the Partnership for Public Policy, the 115 new biomass burning power plants in the United States will burn the equivalent of 650,000 acres of clear-cut forest per year by 2014.\textsuperscript{8} Additionally, biomass burning plants release 1.5 times as much CO$_2$ into the atmosphere per energy unit as a coal burning plant and 3 to 4 times as much CO$_2$ as a natural gas facility. In addition, biomass usage for fuel can create competition
Figure 1.4: Total World \( \text{CO}_2 \) Emissions. Data is from reference 8.
for food crops such as corn. Therefore, biomass in the United States is not truly carbon-neutral and although it is classified as a renewable resource by the federal government for tax incentives, it is not a renewable resource in the usual sense of the word.

Hydroelectric power suffers from being a limited resource. In 2013, 86 gigawatts (GW) of power were produced by hydroelectric plants in the United States accounting for approximately 2.5% of the total energy consumed. The Department of Energy estimates that an additional 65 GW could be harnessed with 12 GW coming from the 80,000 existing non-powered dams.\(^9\) Even if all the potential hydroelectric power were tapped, it would still only be able to supply 4.6% of the energy demand. Furthermore, new dams are expensive to build and the resulting lakes formed may displace existing towns, families and businesses as well as cause environmental damage such as changing the water table. Of course, this is not to say that one should not pursue hydroelectric power, because the energy solution is likely to be a mix of many energy sources just as current energy needs are met by a mixture of sources.

In 2013, wind power in the United States generated 53 GW of power or 1.6% of the total energy demand. Despite this current small contribution, according to a Department of Energy report, continental on-shore wind power has the potential to supply 10.5 TW with another 4 TW possible from off-shore windmills.\(^10\) This well exceeds the current 3.3 TW demand. Two important drawbacks of wind power are that current windmills cause the death of approximately 250,000 birds per year, including endangered species, and that the windmills necessarily extract energy from the wind and the climatic impact of large-scale wind power production has not been fully studied.

In 2013, geothermal power accounted for 0.2% of the total energy demand with the
potential for existing technologies to expand that to 0.8% of the total energy demand. However, more recently developed “Enhanced Geothermal Systems” can extract energy from a much larger number of sites, increasing the resource potential to somewhere between 1 and 12 TW. The first attempt to use this technology by the Los Alamos Laboratory started in 1974 at Fenton Hill, NM but was shut down in 1992, never achieving a net gain in energy. This technology, though, is still being researched and developed.

Solar energy, including thermal and photovoltaic systems, provided 10.3 GW to the United States in 2013. One advantage of both wind and solar power is the possibility for smaller-scale distributed production, rather than limiting production to large systems at specific sites such as the case with geothermal, hydroelectric, biomass and fossil fuels. According to a Department of Energy study, solar energy has the potential to produce 0.09 TW from rooftop systems, 0.25 TW from urban utility systems and 32 TW from rural utility systems, which is the highest of any renewable energy source. There are many different types of solar cells and their historical and current record efficiencies are shown in Figure 1.5 from NREL. These record efficiencies are for solar cells made in the laboratory; mass produced cells have lower efficiencies. Also, efficiency is only one parameter to be considered. The cost of production, reliability, life span and performance at various temperatures and light levels needs to be considered. In order to meet the energy demands of the future, engineering and scientific research continues with regard to all of the energy sources discussed here. One area of intense research concerns Dye-Sensitized Solar Cells which are inexpensive to fabricate and have a good efficiency.
Figure 1.5: Historical laboratory-based efficiencies of various solar cell types. Chart is from reference 12.
1.3 Dye-Sensitized Solar Cells

An attractive alternative to silicon based solar cells is the relatively low-cost Dye-Sensitized Solar Cell (DSSC) which have recently reached a record 15% power-conversion efficiency.\textsuperscript{13} Like any photoelectrochemical cell, the typical DSSC employs two electrodes that can be connected to an external circuit to make use of the electrical power that is generated, Figure 1.6. Glass slides coated on one side with fluorine-doped tin-oxide (FTO) are used as electrodes because they conduct electricity and also because they are transparent to visible light, allowing light to reach the interior of the DSSC. A semiconductor is fixed to the anode so that an electron that has been photo-excited to a high energy level can delocalize from its source atom, achieving charge separation, and travel through the semiconductor’s conduction band to the FTO electrode and then through the electric circuit. The most efficient DSSCs utilize anatase titanium dioxide (TiO\textsubscript{2}) as the semiconductor which has a band gap of 3.2 eV. Excitation of an electron from the valence band to the conduction band is evidenced by light absorption in the UV region below 390 nm. The TiO\textsubscript{2} is transparent to visible light. Therefore, a sensitizer (S), which adsorbs visible light is adsorbed to the TiO\textsubscript{2}. The standard reduction potential for the oxidized sensitizer and the excited state, typically $E^\circ(3+/2+^*)$, is more negative than the TiO\textsubscript{2} conduction band edge, $E_{CB}$, providing a favorable free energy change for excited state electron transfer to the conduction band, leaving the oxidized sensitizer behind. An acetonitrile solution that contains mixtures of iodine and iodide is typically the redox mediator that shuttles charge between the oxidized sensitizer and a platinum coated electrode. The iodide redox chemistry that occurs at the sensitized TiO\textsubscript{2} electrode is of direct relevance to this thesis work.
Figure 1.6: Dye-Sensitized Solar Cell
There are several measurements used to characterize the performance of DSSCs. The first is the Incident-Photon-to-Current Efficiency (IPCE) which measures the ratio of the number of photons incident on a DSSC to the number of electrons flowing through the external circuit. The IPCE is measured at various wavelengths of incident light and the resulting spectrum usually matches the absorbance spectrum of the sensitized TiO\textsubscript{2} electrode. The second, more critical measurement is a current-voltage, i-v, curve where the DSSC is typically illuminated with simulated sunlight. A sample i-v curve is shown in Figure 1.7 where \( J_{SC} \) is the short-circuit current and \( V_{OC} \) is the open-circuit voltage.\textsuperscript{14} The maximum current is attained at short-circuit conditions when resistance to current flow is minimized. The maximum voltage is attained at open circuit conditions (\( V_{OC} \)) when the resistance between the two electrodes is infinite and represents the difference of the quasi-Fermi levels of the two electrodes. The power produced by the DSSC is the product of the voltage difference between the two electrodes and the current flowing through the external circuit, plotted as the magenta line in Figure 1.7. The Power Point (PP) is the point of maximum power output from the DSSC and \( J_{PP} \) and \( V_{PP} \) are the current and voltage at the power point, respectively. The Fill Factor (FF) is the ratio of the power at the power point and the theoretical power that would be obtained at \( V_{OC} \) and \( J_{SC} \), as shown in Equation 1.1.

\[
FF = \frac{J_{PP} \cdot V_{PP}}{J_{SC} \cdot V_{OC}} \tag{1.1}
\]

The efficiency of a DSSC (\( \eta \)) is the ratio of the output power to the input power and it is calculated from Equation 1.2 below where \( A \) is the geometric area of the DSSC and the standard power input, \( P_{INPUT} \), is typically the 1 Sun condition of approximately 1000 watts per square meter.

\[
\eta = \frac{P_{OUTPUT}}{P_{INPUT}} = \frac{J_{SC} V_{OC} FF \cdot A}{1000 \text{ W/m}^2} \tag{1.2}
\]

The next few sections will look more closely at the TiO\textsubscript{2} semiconductor, the sensitizer molecules and the redox mediator.
Figure 1.7: Typical I-V curve for a DSSC. $J_{sc}$ is the short-circuit current, $V_{oc}$ is the open-circuit voltage and $J_{pp}$ and $V_{pp}$ are the current and voltage at the power point. Figure taken from reference 14.
1.3.1 Titanium Dioxide Semiconductor

In 1991 Professor Michael Grätzel published a seminal paper in which mesoporous, nanocrystalline anatase TiO$_2$ semiconductor thin films were utilized in DSSCs in place of planar TiO$_2$ electrodes. This greatly increased DSSC efficiencies. An SEM image of the TiO$_2$ surface is shown in Figure 1.8. The thin films were approximately 6-10 μm thick and were comprised of fused nanocrystalline particles approximately 20 nm in diameter with a 50-70% porosity. The porous structure resulted in surface areas that were approximately 1000 times larger than the geometric area. This provided a larger number of surface sites for the sensitizer molecules and therefore a much greater fraction of the incident light was absorbed and converted to electrical power. Titanium dioxide is inexpensive and abundant and the semiconductor thin film is inert, stable and capable of accepting electrons and transporting them to the FTO substrate. It is also relatively easy to fabricate.

1.1.1 Sensitizers

Ruthenium (II) polypyridyl transition metal complexes are typically used as sensitizers in DSSCs due to their superior performance, however ruthenium is both expensive and rare and DSSCs with sensitizers based on more abundant metals are an active area of research. The chemical structures of selected ruthenium (II) sensitizers are depicted in Scheme 1.1. The sensitizer molecules will bind to the TiO$_2$ surface through either a carboxylic acid or phosphonate functional group where ester-type surface linkages have been proposed. By far the most common ligand used to anchor sensitizers to the TiO$_2$ surface is called dcb which is 4,4’-(COOH)$_2$-2,2’-bipyridine. Chapter 4 of this thesis work
Figure 1.8: SEM of a mesoporous nanocrystalline (anatase) TiO$_2$ thin film surface.
Scheme 1.1: Chemical structures of selected sensitizers.
describes alternative ambidentate ligands that serve as viable substitutes for dcb. Photo-excitation with visible light usually results in a Metal-to-Ligand Charge Transfer (MLCT) from a metal based d orbital to a ligand based π* orbital.\textsuperscript{19-21} Formal spin states cannot be assigned due to heavy atom spin-orbit coupling, however, the Franck-Condon excited state is predominately singlet in character (labeled \(^1\)MLCT) and it is converted rapidly (40 ± 15 fs) and with a quantum yield near unity through intersystem crossing to a manifold of closely spaced states (< \(kT\) separation in energy) that are predominately triplet in character (labeled \(^3\)MLCT).\textsuperscript{22-25} Three factors lead to electron injection into the semiconductor on the picosecond and faster timescales: the \(^1\)MLCT and \(^3\)MLCT states have good energetic overlap with the conduction band of TiO\(_2\), the adsorbed sensitizer has good spatial overlap with the conduction band orbitals, and the d\(\pi\) symmetry of the empty Ti\(^{IV}\) orbitals of the semiconductor conduction band have the same symmetry as the π* ligand orbitals.\textsuperscript{14}

### 1.3.2 Redox Mediator

Electrons at the cathode must be transported through the solution phase to the oxidized sensitizer that is anchored to the TiO\(_2\) semiconductor. This is accomplished with redox mediators dissolved in the solution. The most pervasive and effective redox mediator used in DSSCs is comprised predominately of iodide and triiodide. The oxidized sensitizer is reduced by iodide, returning the sensitizer to its original state (Ru\(^{II}\)) and producing iodine atoms, Error! Reference source not found.. The iodine atoms then react with a second iodide anion, forming diiodide (I\(_2^-\)) as depicted in Error! Reference source not found. below.\textsuperscript{26} The diiodide then disproportionates to form triiodide and iodide,
Error! Reference source not found., and the triiodide is reduced at the cathode to iodide. Overall there is no net chemistry, with all the species returning to their original states after photon absorption.

$$\text{Ru}^{III}(\text{bpy})_3/\text{TiO}_2 + \text{I}^- \rightarrow \text{Ru}^{II}(\text{bpy})_3/\text{TiO}_2 + \text{I} \cdot \quad \text{Equation 1.3}$$

$$\text{I} \cdot + \text{I}^- \rightarrow \text{I}_2^- \quad \text{Equation 1.4}$$

$$2 \text{I}_2^- \rightarrow \text{I}_3^- + \text{I}^- \quad \text{Equation 1.5}$$

1.4 Iodide Oxidation in Solution

Studies of the iodide/triiodide redox mediator in a functioning DSSC are greatly complicated by the heterogeneous nature of interactions between the redox mediator in the solution phase and the sensitizer adsorbed to the solid phase TiO$_2$ semiconductor. Another complication arises from the multiple pathways available to the injected electrons. They can travel to the FTO electrode and through the external circuit or they can recombine with an oxidized sensitizer or they can reduce the oxidized form of the redox mediator, triiodide. Any kinetic study of electron transfer reactions from the TiO$_2$ is complicated by electron transport through the nanocrystalline mesoporous thin film. Also, in a functioning DSSC, experimental parameters cannot be varied greatly without affecting the overall functioning of the DSSC which further complicates the analysis. One route to avoid these complications is to study the sensitizers and the redox mediator in fluid solution and to relate the results qualitatively to a functioning DSSC. Chapters 2 and 3 will focus exclusively on such solution studies.

In chromophore solutions, the ruthenium polypyridyl complexes are known to absorb ultraviolet light at approximately the same energy as the free ligand in a ligand-based
π→π* transition that quickly relaxes to the ground state with no detectable photoluminescence (PL). These transition metal complexes also absorb visible light, typically promoting a metal based d-electron to a ligand-based π* orbital (MLCT) leaving a hole in the formally d⁵ metal center. As mentioned before, because of the heavy-atom effect due to the ruthenium atom, spin is not a good quantum number for these complexes, however, the Franck-Condon excited state has mostly singlet character, \(^1\)MLCT. The excited state then undergoes intersystem crossing with a quantum yield of approximately 1 to a comparatively long-lived excited state that is mostly triplet in character, \(^3\)MLCT, before relaxing back to the ground state through either a radiative or non-radiative pathway with a lifetime of approximately 1 μs. **Figure 1.9** shows the UV-visible absorption spectrum and the PL spectrum for the [Ru(bpy)₃]²⁺, the prototype for ruthenium chromophores.

Acetonitrile has a relative dielectric constant of 36.6 and a permanent dipole of 3.92 D at 20 °C whereby it dissolves the salts at the concentrations used and there is very little ion-pairing\(^{29}\). On the other hand, dichloromethane has a relative dielectric constant of only 8.9 and a permanent dipole of 1.60 D at 25 °C resulting in a high degree of ion-pairing even at low salt concentrations. Accordingly, when moderate amounts of tetrabutylammonium iodide (TBAI) is added to acetonitrile solutions of a ruthenium polypyridyl compound, there are no visible changes to the ground state UV-Vis spectrum. However, in dichloromethane the ground-state UV-Vis spectrum is altered considerably and these changes are reversible upon addition of excess TBAPF₆ which is consistent with an ion-pairing between the ruthenium complex and iodide that is competitively supplanted by ion-pairing with PF₆⁻, **Figure 1.10**
Figure 1.9: [Ru(bpy)$_3$] (PF$_6$)$_2$ in room temperature acetonitrile UV-visible spectrum displaying MLCT absorption (1) and $\pi$$\rightarrow$$\pi^*$ absorption (2) in black and photoluminescence spectrum in red.
Figure 1.10: Changes in the electronic absorption spectrum of [Ru(deeb)_3]^{2+} upon addition of TBAI to dichloromethane solution. Isosbestic points, 458 and 477 nm, were maintained as the concentration of iodide was increased. (inset) Data obtained in acetonitrile solution over a similar TBAI concentration range showing no visible spectral changes. Figure and caption from reference 30.
The MLCT excited states of ruthenium polypyridyl compounds are both stronger reductants, due to the ligand-based photoexcited electron, and stronger oxidants, due to the low-lying metal-based hole, than the ground state compound. The excited states of a number of these compounds have been shown to efficiently oxidize iodide in both acetonitrile and dichloromethane solvents, reductively quenching the excited state.\(^{30-37}\) In acetonitrile, time-resolved PL experiments with added TBAI revealed only dynamic quenching of the excited state PL, **Figure 1.11**. Single exponential decays of the PL at all moderate iodide concentrations indicated a quenching process that was first order in excited state ruthenium complex. The resulting Stern-Volmer plots were linear, indicating a quenching process that is also first-order in iodide concentration, with quenching rate constants between \(5.7 \times 10^9\) and \(6.6 \times 10^{10}\text{ M}^{-1}\text{s}^{-1}\).\(^{33}\)

In dichloromethane, both static and dynamic quenching of excited state PL were evident. A Stern-Volmer plot of the static component gave an ion-pairing equilibrium constant of \(K_{SV} = 59,700\text{ M}^{-1}\) for \([\text{Ru(bpy)}_2(\text{deeb})]^2^+\) and \(K_{SV} = 41,000\text{ M}^{-1}\) for \([\text{Ru(deeb)}_3]^2^+\).\(^{33,36}\) Static quenching also supports the idea of ion-pairing in dichloromethane since diffusion would no longer be required and after the excitation light pulse, electron transfer, and therefore excited state quenching, can occur within the instrument response time. In dichloromethane with added iodide, PL decays of \([\text{Ru(deeb)}_3]^2^+\) were single exponential and a quenching rate constant of \(1.9 \times 10^{10}\text{ M}^{-1}\text{s}^{-1}\) was calculated. However, with \([\text{Ru(bpy)}_2(\text{deeb})]^2^+\) the PL decays were biexponential and meaningful quenching rate constants were not extracted. The difference in behavior is probably due to differences in excited state reduction potentials (vida infra); \(E^\circ(\text{I•}/\text{I}^-) = 0.99\text{ V, } [\text{Ru(bpy)}_2(\text{deeb})]^2^+ E^\circ(2^+*/+) = 0.99\text{ V, and } [\text{Ru(deeb)}_3]^2^+ E^\circ(2^+*/+) = 1.21\text{ V}\)
Figure 1.11: Time-resolved photoluminescence decays monitored at 620 nm for [Ru(deeb)$_3$]$^{2+*}$ in acetonitrile (A) and dichloromethane (B) as a function of increased [TBAI]. (inset A) A Stern-Volmer plot for lifetime quenching. (inset B) A Stern-Volmer plot for both lifetime (black) and amplitude (red) quenching components. The figure and caption are from reference 30.
versus SCE at room temperature.\textsuperscript{33} Additionally, when [Ru(bpy)$_2$(deeb)]$^{2+}$ was dissolved in CH$_2$Cl$_2$ with 100 mM TBAPF$_6$ and 40 to 400 μM TBAI, where the excess TBAPF$_6$ competitively ion-pairs with the ruthenium complex, only dynamic quenching was evident indicating that the ion-pairing is required for static quenching.

Nanosecond time-scale transient absorption measurements have also been made for various ruthenium polypyridyl compounds in both acetonitrile and dichloromethane. Authentic spectra of TBAI, TBAI$_3$, I$_2^-$, and the dicationic and singly reduced ruthenium compounds were used to analyze the changes in absorption Figure 1.12. Typically, the excited state was evidenced by a strong bleach in the 450 nm region while the reduced compound produced an absorption peak in the 500 nm region and diiodide gave a long-wavelength peak near 750 nm and a shortwavelength peak near 400 nm. After the rapid excited state decay, the remaining delta absorbance could typically be fit to a 1:1 linear combination of the spectra for the reduced compound and diiodide, Figure 1.13. In acetonitrile, after the initial laser pulse excitation, the reduced compound is formed at approximately the same rate as the excited-state decay, indicating that the reduced compound is a primary product of the excited-state quenching process. The rate of formation of the reduced compound increased with increasing driving force for the electron transfer from iodide to the excited-state ruthenium complex. Diiodide was formed 2-3 times more slowly than the reduced ruthenium compound, with an average rate of 2.4 x 10$^{10}$ M$^{-1}$s$^{-1}$ largely independent of the ruthenium species used, indicating that it is the product of a second, follow-on reaction.\textsuperscript{33} Once the reduced ruthenium compound is formed, together with diiodide inside the solvent cage, it is highly energetically
Figure 1.12: UV-Vis absorption spectra of TBAI, TBAI$_3$, and I$_2$ in acetonitrile (top). Extinction coefficient spectra of [Ru(bpy)$_2$(deeb)]$^{2+}$ and [Ru(bpy)$_2$(deeb)$^-$] in acetonitrile. The reduced compound was generated by steady state photolysis of the dication in the presence of triethylamine. Figure and caption are from references 32 and 34.
Figure 1.13: Transient absorption spectrum (black dots) 1 μs after pulsed laser excitation of 35 μM [Ru(bpy)$_2$(deeb)]$^{2+}$ and 7.8 mM TBAI in acetonitrile. The blue line is the simulation of a 1:1 mixture of reduced compound and diiodide. (Inset) Extinction coefficient spectra of the singly reduced compound minus the dicationic form (black) and diiodide (red). Figure and caption from reference 34.
favorable ($\Delta G^o = 1.5 - 2 \text{ eV}$) for the reduced ruthenium compound to reduce diiodide to two iodide ions (back transfer). For this reason, the cage escape of the reduced compound and diiodide is low, often less than 5%. For [Ru(bpy)$_2$(deeb)]$^{2+}$ plus TBAI in acetonitrile, back transfer occurred with a rate constant of $2.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ which was approximately 10 times faster than the rate of disproportionation of two molecules of diiodide into triiodide and iodide, $3.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.\textsuperscript{31,33-35}

The experimental data above is consistent with the reaction of excited-state ruthenium complexes with iodide to form the reduced ruthenium complex and iodine atoms. Iodine atoms then react with iodide to form diiodide, Scheme 1.2, where [Ru$^{II}$(LL)$_3$]$^{2+}$ is any of the ruthenium polypyridyl compounds studied, such as [Ru(bpy)$_2$(deeb)]$^{2+}$. In acetonitrile, there is effectively no ion-pairing and the oxidation of iodide is controlled by diffusion, whereas in dichloromethane iodide oxidation occurs within the instrument response time due to substantial ion-pairing. In either case, this will be called the “Stepwise” mechanism, with two distinct reactions, Scheme 1.2. In dichloromethane, [Ru(bpy)$_2$(deeb)]$^{2+}$ displayed nonexponential decay of the excited state at higher iodide concentrations where the possibility of a dicaticon ruthenium complex could be ion-paired with two iodides. This fact suggests the possibility of a second mechanism that was proposed to be the “Concerted” mechanism, Scheme 1.2. However, at these iodide concentrations, both the reduced ruthenium compound and diiodide were formed within the instrument response time and it was not possible to determine whether the Concerted mechanism or a fast Stepwise mechanism (due to the elevated iodide concentrations) had occurred.
Scheme 1.2: Iodide oxidation by ruthenium polypyridyl excited states: Stepwise pathway (top) and Concerted pathway (bottom).
In previous studies, all but one of the ruthenium compounds had excited-state reduction potentials that were equal to or more positive than $E^\circ(I^*/I^-)$ while the one remaining compound had a potential only 40 mV more negative than $E^\circ(I^*/I^-)$. Since the oxidation of a single iodide is thermodynamically favorable for these compounds (except for the one compound), it should not be a surprise that the stepwise mechanism was occurring, especially in acetonitrile where the lack of ion-pairing requires a termolecular collision for the concerted mechanism to function. Even in dichloromethane with two iodides ion-paired to the ruthenium complex, one can imagine that the concerted mechanism would require a specific geometry between the two iodides and the ruthenium complex, however, no such restriction, or at least a much more flexible restriction, would govern the single iodide oxidation in the stepwise mechanism. Therefore, in order to further investigate iodide oxidation, and especially the concerted mechanism, studies should include ruthenium complexes with different excited-state reduction potentials to control which mechanism is occurring and make use of different solvents to control the extent of ion-pairing.

1.5 Stepwise and Concerted Mechanisms

Iodide oxidation excited states of ruthenium polypyridyl compounds can occur through a stepwise or a concerted mechanism. In the concerted mechanism two iodides and the excited-state ruthenium complex are within the solvent cage and the I-I bond formation is coincident with the electron transfer. In the extreme case, electron transfer and bond formation are “coincident” or “at the same time” if they occur within the relevant bond vibration period. However, in this work, “coincident” or “at the same time” have the
meaning of “within the resolution of the instrumentation”. The transient absorption instrument in the Meyer laboratory measures a data point every 2.5 ns. However, the instrument response time after the initial laser pulse is approximately 20 ns.

The stepwise and concerted pathways are depicted in Scheme 1.2. The pathway taken is a function of the metal complex’s excited state reduction potential, the iodide concentration, and the extent of ion-pairing based on the solvent polarity/dielectric constant. The redox potentials for several halides and hydroxide are shown in Scheme 1.3 where it can be seen that the oxidation of two anions to the dimer occurs more easily, at a potential that is approximately 300 mV more negative. This work will focus on iodide, which the most easily oxidized anion and the one used in DSSCs. For instance, the one-electron reduction potential for iodine atom in acetonitrile is +990 mV while the one-electron reduction of diiodide to two iodide ions is at +690 mV. Therefore, the transition metal complexes can be divided into three zones based on their excited state reduction potentials, Scheme 1.3. The divisions between the three zones are more conceptual and not hard barriers that cannot be crossed, rather, in accordance with the Nernst equation, they are the point, at standard conditions, where the activities of the reduced and oxidized species are equal. Oxidation or reduction occurs to a greater or lesser extent as the potential is moved away from this value. So there is considerable overlap of the three zones. At standard conditions, within 59 mV of the dividing line can be considered a “borderline” case while >59 mV from the dividing line only gives a vanishingly small amount of the other zone and will be considered to be cleanly within the one zone.

In Zone one the ruthenium complex’s excited state reduction potential is more positive
<table>
<thead>
<tr>
<th>Potential (V)</th>
<th>Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.69</td>
<td>I_{2}^- / 2 I^-</td>
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<tr>
<td>0.99</td>
<td>I^-</td>
</tr>
<tr>
<td>1.4</td>
<td>Br_{2}^- / 2 Br^-</td>
</tr>
<tr>
<td>1.6</td>
<td>H_{2}O_{2}^- / 2 OH^-</td>
</tr>
<tr>
<td>1.7</td>
<td>OH^-</td>
</tr>
<tr>
<td>1.7</td>
<td>Br^-</td>
</tr>
<tr>
<td>2.0</td>
<td>Cl_{2}^- / 2Cl^-</td>
</tr>
<tr>
<td>2.3</td>
<td>Cl^-</td>
</tr>
</tbody>
</table>

+ $E^0$ vs. SCE

**Scheme 1.3:** (left) Reduction potentials of the indicated species. Iodine atom and diiodide potentials are in ACN, others are aqueous. (right) Three Zones defining the mechanistic pathway for excited state halide oxidation based on reduction potentials. See the text for more details.
than both the iodine atom reduction potential and the diiodide reduction potential so that both the stepwise and the concerted mechanisms are possible. However, the stepwise pathway only requires a two-body collision while the concerted pathway requires three entities to simultaneously collide. This can occur through a three-body collision, which is statistically improbable, or it can occur through a two-body collision if two of the entities are previously ion-paired or it can occur through the rearrangement and decay of a single entity if two iodide anions are previously ion-paired with the ruthenium complex. The concerted pathway is energetically favored by 300 mV but can be effectively shut off by use of a solvent with a high dielectric constant which limits the degree of ion-pairing.

In Zone 2, the stepwise pathway is energetically uphill and should not occur to a significant amount. However, the concerted pathway is still energetically downhill but requires at least one iodide to be ion-paired in order to avoid the necessity of a three-body collision.

In Zone 3, both the stepwise pathway and the concerted pathway are energetically unfavorable and should not occur. There should not be any redox chemistry. The specific potentials that define these three zones depend on the reductant utilized (chloride, iodide, etc.). For chloride, bromide and hydroxide, four ruthenium compounds that fall within Zone 3 were tested. Two osmium compounds with excited state reduction potentials in Zone 3 for iodide were also tested. Measurements in Zone 3 can be used to investigate the photophysical effects of ion-pairing an anion with the transition metal complex without the interference of redox chemistry.
1.6 References


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Chapter 2

Ion-Pairing with Ru(II) and Os(II) Compounds in Dichloromethane

2.1 Introduction

Chemists have been fascinated by ion-pairs for some time, particularly when one or more of the ions is a transition metal coordination compound.\textsuperscript{1-5} Such ion-pairs have practical importance in catalysis\textsuperscript{6-8} and chromatography\textsuperscript{9} as well as in some types of batteries\textsuperscript{10} and solar cells.\textsuperscript{11,12} Their behavior is also of fundamental importance in its own right. A variety of techniques including X-ray crystallography, electrical conductivity, NMR spectroscopy, and UV-Visible spectroscopy have been used to characterize a wide range of ion-pairs. Spectroscopic assays have also been utilized to determine whether ion-pairing occurs at specific sites within the cation and/or anion. In one particularly novel study, regiospecific reactivity of a cobalt coordination compound with chloride was observed.\textsuperscript{13} The compound $p$-[Co(tren)(NH$_3$)$_2$OH$_2$]$^{3+}$ underwent dissociative anation through a 5-coordinate intermediate that would normally be accompanied by loss of stereochemistry. However, the site of chloride ion-pairing detected with X-ray Crystallography and $^1$H NMR spectroscopy positioned the chloride so that the original stereochemistry was retained. In this thesis chapter studies of ion-pairing with dicationic Ru(II) and Os(II) polypyridyl compounds in dichloromethane (DCM) are described. These studies were designed to identify whether preferred ion-pairing sites exist and the influence of such interaction on excited state decay.

Contact ion-pairs between redox active ions can result in outer-sphere charge transfer
absorption bands that are of great utility for fundamental electron transfer studies that can also be exploited for improved solar light harvesting. It was recently reported that ion-pairing was evident in the oxidation of iodide by the metal-to-ligand charge transfer (MLCT) excited states of Ru(II) polypyridyl compounds in dichloromethane. Ion-pair formation was found to greatly facilitate iodide photo-oxidation relative to that measured in more polar acetonitrile solutions where ion-pairing appeared to be absent. X-ray crystallographic studies provided evidence for specific iodide adducts in the solid state that could give rise to new mechanisms for iodide oxidation and I-I bond formation. However, analysis of the solution UV-visible absorption spectra was complicated by what appeared to be outer-sphere charge transfer transitions that overlapped in energy with a highly perturbed MLCT absorption. It was therefore difficult to assign the absorption changes that accompanied iodide ion-pairing.

The reduction potential for the transition metal compound as well as the anion must be known in order to predict any redox chemistry that may occur. The experimental details and calculation of excited state reduction potentials (2+/+) for the ruthenium compounds are detailed in Appendix 3 while the excited state potential (2+/+) for [Os(bpy)_3](PF_6)_2 is from Kober, et al. For chlorine, bromine and the hydroxyl radical, both the monomer and dimer reduction potentials, (X*/X⁻) and (X_2⁻, 2X⁻) respectively, are much more positive than the excited state potential (2+/+) of the four ruthenium compounds used in this chapter, Scheme 2.1 (left). Chloride, bromide and hydroxide were therefore expected to be redox inactive under these conditions. Likewise, the reduction potentials for iodine, (I*/I) and (I_2⁻, 2I⁻), are more positive than the excited state potential (2+/+) of the osmium compounds used, Scheme 2.1 (right), and iodide is expected to be redox
inactive with these compounds. These ruthenium and osmium compounds are hence within the Zone 3 described in Chapter 1 and Scheme 1.3. Any changes in photophysical properties measured in a low dielectric solvent such as dichloromethane upon addition of a salt such as TBAI or TBACl should be the result of ion-pairing with the anionic species. Ion-pairing will also be present for transition metal compounds in Zones 1 and 2 in dichloromethane, but the effects will be masked by the redox chemistry. The effects of ion-pairing can be used to probe the interactions between these positively charged transition metal complexes and anions. Thus we undertook a study to characterize ion-pairing with these anions whose formal reduction potential precludes the appearance of outer-sphere charge transfer bands in the visible region or excited state electron transfer chemistry.

The series of four Ru(II) and two Os(II) polypyridyl compounds based on 2,2’-bipyridine (bpy) and/or 4,4’-(CO$_2$CH$_2$CH$_3$)$_2$-2,2’-bipyridine (deeb), Scheme 2.2, were synthesized and characterized. Ion-pairing was found to have a significant influence on the UV-Vis absorption spectra of the compounds in dichloromethane. These ions were also found to significantly influence the MLCT excited state lifetime, quantum yield, and radiative and non-radiative rate constants. Specific sites for ion-pairing were identified that exchanged rapidly on the NMR time scale. Similar results were found for all four anions and for all six transition metal complexes that were tested.
Scheme 2.1: (left) Excited state reduction potentials for four ruthenium compounds (0.1 M TBAClO$_4$/DCM) in relation to chloride, bromide and hydroxide aqueous potentials. (right) Excited state reduction potentials for osmium compounds (0.1 M TBAPF$_6$/ACN) in relation to iodide potentials (ACN).
Scheme 2.2: Ligand structures, abbreviations and carbon atom numbering used.
2.2 Experimental

Materials. Argon gas (Airgas, 99.99%), [Ru(bpy)$_3$]Cl$_2$$\cdot$6H$_2$O (Aldrich, 99.95%), ammonium hexafluorophosphate (Acros, 99.5%), tetrabutylammonium chloride (TBACl; Fluka, >97%), tetrabutylammonium bromide (TBABr; Aldrich, 99%), tetrabutylammonium iodide (TBAI; Fluka, >97%), tetrabutylammonium hexafluorophosphate (TBAH, Fluka, >98%), potassium hydroxide (Fischer, >87%), 18-Crown-6 (Aldrich, 99%), triethylamine (TEA; Fluka, >99.5%), and dichloromethane (DCM; EMD, >99.8%) were used as received without further purification. [Ru(bpy)$_3$](PF$_6$)$_2$ was prepared by ion exchange of [Ru(bpy)$_3$]Cl$_2$$\cdot$6H$_2$O with NH$_4$PF$_6$. [Ru(bpy)$_2$(deeb)](PF$_6$)$_2$, [Os(bpy)$_3$](PF$_6$)$_2$, and [Os(bpy)$_2$(deeb)](PF$_6$)$_2$ were available from previous studies. $^{15,16,20,21}$ [Ru(deeb)$_2$(bpy)](PF$_6$)$_2$ and [Ru(deeb)$_3$](PF$_6$)$_2$ were prepared by a modified literature method. $^{22}$

Measurements. Steady State Absorption. UV–Vis absorption spectra were obtained on a Varian Cary 50 UV–Vis spectrophotometer at room temperature. Ten scans at approximately 1 nm resolution were averaged. The spectra were volume corrected for the addition of salt solutions. Typically 10 to 300 µL of salt solution were added to 5.00 mL of ruthenium or osmium compound solution. Job plot measurements were conducted with 1.00 mL of solution in a cuvette with a 0.20 cm path length.

Nanosecond Transient Absorption. Argon purged DCM solutions of approximately 20 µM ruthenium or osmium compound both with and without TBACl or TBAI were measured at room temperature as described previously. $^{23}$ The responses to 40 laser pulses were averaged with a fluence of approximately 2 mJ/cm$^2$. 

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Steady State Photoluminescence. A Spex Fluorolog with a 450 W Xe lamp was utilized for steady-state PL measurements. PL spectra were acquired at 25.0 ± 0.1 °C in argon purged DCM and corrected for lamp intensity fluctuations and detector response. Samples were illuminated at the MLCT peak wavelength. Five scans at 2 nm resolution were averaged. Comparative actinometry using [Ru(bpy)₃]Cl₂ in water (φ_em = 0.042) was used to measure PL quantum yields.²⁴

Time-Resolved Photoluminescence. Excited-state lifetimes were measured using a nitrogen-dye laser system described previously with a 532 nm excitation wavelength.²³ PL intensity was monitored at the PL maximum wavelength. Argon purged DCM solutions of approximately 20 μM ruthenium or osmium compound at 25.0 ± 0.1 °C were measured as various anions in argon purged DCM were titrated into the sample solution.

¹H NMR. Ruthenium compound was dissolved in approximately 0.50 mL CD₂Cl₂ with added tetramethylsilane to make an approximately 3 mM solution and spectra were recorded as aliquots of TBACl in CD₂Cl₂ were added. Spectra were measured on a Bruker Avance 400 MHz FT-NMR spectrometer at 298 ± 0.3 K. The mole ratio of ruthenium compound to TBACl was calculated using the integration of the ester methylene peak and the terminal methyl peak from tetrabutylammonium.

X-Ray Crystallography. Crystals of [Ru(bpy)₂(deeb)]Cl₂ were grown by addition of a 10-fold molar excess of tetrabutylammonium chloride to [Ru(bpy)₂(deeb)](PF₆)₂ in DCM. The solution was placed in an open vial inside a larger vial with diethylether. After 7 days, red-orange plate-like crystals had grown. A suitable crystal was mounted in oil on the end of a glass fiber and used for X-ray crystallographic analysis. All reflection intensities were measured at 100(2) K using a SuperNova diffractometer (equipped with
Atlas detector) with Cu Kα radiation (mirror optics, λ = 1.54178 Å) under the program CrysAlisPro (Version 1.171.36.24 Agilent Technologies, 2012). The same program was used to refine the cell dimensions and for data reduction. The structure was solved with the program SHELXS-97 (Sheldrick, 2008) and was refined on $R^2$ with SHELXL-97 (Sheldrick, 2008). Analytical numeric absorption corrections based on a multifaceted crystal model were applied using CrysAlisPro (Version 1.171.36.24 Agilent Technologies, 2012). The temperature of the data collection was controlled using the system Cryojet (manufactured by Oxford Instruments). The H atoms (unless specified) were placed at calculated positions using the instructions AFIX 23, AFIX 43 or AFIX 137 with isotropic displacement parameters having values 1.2 or 1.5 times $U_{eq}$ of the attached C atoms.

2.3 Results with Chloride, Bromide and Hydroxide

The chloride salt of [Ru(bpy)$_2$(deeb)]$^{2+}$ was characterized by X-ray crystallography, Table 2.1. The Mercury 3.1 program$^{25}$ was used to determine all the chloride ions located within the sum of the van der Waals radii$^{26}$ to [Ru(bpy)$_2$(deeb)]$^{2+}$. The distances from the chloride ions to the closest point on the ruthenium compound are listed in Table 2.2. It was found that the closest chloride counterion was situated approximately 2.5 and 2.8 Å from the bpy C-3H and C-3’H respectively and the next closest chloride ions were located approximately 2.8 Å from the deeb C-6H. On the other hand, the deeb carbonyl carbon atoms were located approximately 5.5 Å from the nearest chloride, and this chloride was only 2.7 Å from the deeb C-6H. Chloride adducts with bpy C-3H and C-3’H are in agreement with other literature reports for tris-bipyridyl type compounds.$^{13,27-29}$
| Table 2.1: Crystal parameters for [Ru(bpy)$_2$(deeb)] Cl$_2$ |
|-----------------|-----------------|
| **Empirical Formula** | C$_{36}$Cl$_2$H$_{32}$N$_6$O$_4$Ru |
| **Formula Weight** | 1124.35 |
| **Crystal Color** | orange-red plate |
| **Habit** | $0.51 \times 0.28 \times 0.03$ mm$^3$ |
| **Temperature** | 100 K |
| **Radiation** | Cu Kα $\lambda = 1.54178$ Å |
| **Space Group** | monoclinic, P2/c (no. 13) |
| **Unit Cell Dimensions** | |
| a | 11.8518(3) |
| b | 12.9483(3) |
| c | 17.0261(6) Å |
| $\beta$ | 112.244(4)$^\circ$ |
| **Z** | 2 |
| **Calculated Density** | 1.544 g cm$^{-3}$ |
| **Absorbance Coefficient** | $\mu = 8.086$ mm$^{-1}$ |
| **R1/wR2 [I > 2σ(I)]** | 0.0578/0.1551 |
| **R1/wR2 [all refl.]** | 0.0642/0.1607 |
Table 2.2: Distances from Chlorides within Sum of van der Waals Radii.

<table>
<thead>
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<th>Atoms</th>
<th>Distance (Å)</th>
<th>Atoms</th>
<th>Distance (Å)</th>
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<td>Bpy C5H</td>
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<td>Bpy C-5'</td>
<td>3.439</td>
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</table>
The distances to the bpy C-3H and C-3’H refer to the same chloride, as seen in Figure 2.1, while all the other entries refer to separate chloride ions.

The $^1$H NMR spectra and peak assignments for three compounds, [Ru(bpy)$_3$](PF$_6$)$_2$, [Ru(bpy)$_2$(deeb)](PF$_6$)$_2$ and [Ru(deeb)$_3$](PF$_6$)$_2$, are detailed in Appendix 1. The $^1$H NMR spectra were then measured for [Ru(bpy)$_3$]$^{2+}$ and [Ru(deeb)$_3$]$^{2+}$ with one equivalent of added TBACl. For [Ru(bpy)$_3$]$^{2+}$, the C-3H peak was significantly shifted downfield, however, for [Ru(deeb)$_3$]$^{2+}$ the C-6H peak was shifted downfield, while the other hydrogens displayed only minor shifts, Figure 2.2. The $^1$H NMR spectra were also measured for [Ru(bpy)$_2$(deeb)]$^{2+}$ as TBACl was titrated into the solution, from 0 to 42 equivalents. The maximum shifts of all the hydrogens, upon addition of 1 or 42 equivalents of TBACl, are shown in Figure 2.3. As with the homoleptic compounds, the bpy C-3H peak shifted significantly downfield upon addition of TBACl while the deeb C-3H peak did not shift appreciably, Figure 2.4. Additionally, the change in chemical shift ($\Delta$ppm) for the bpy C-3H and the deeb C-6H are plotted in Figure 2.5.

Two equilibria were used to model the results, Equation 2.1 and Equation 2.2, where $R^{2+}$ is [Ru(bpy)$_2$(deeb)]$^{2+}$, $R_0$ is the initial concentration of [Ru(bpy)$_2$(deeb)]$^{2+}$ before ion-pairing and $X^-$ is Cl$. The system of four equations (two equilibria equations, mass balance of ruthenium compound and mass balance of chloride) was solved for the four concentration variables [$R^{2+}$, $[X]$, [$R^{2+}$,$X^-$] and [$R^{2+}$, 2$X^-$]] using assumed values for $K_1$ and $K_2$. The NMR shifts were fit to Equation 2.3 where $\Delta\delta_{\text{max}}$ is the asymptotic maximum shift observed by varying $K_1$ and $K_2$. In order to reduce the number of free-floating variables, it was assumed that the singly ion-paired species produced half the change in chemical shift as the doubly ion-paired species. The equilibrium constants.
Figure 2.1: ORTEP diagram for $[\text{Ru(bpy)}_2(\text{deeb})]^{2+}$ showing the closest four chloride ions. The interactions of the chlorides (light green dashed lines) with the bpy C-3H hydrogens are more clearly seen in the viewing angle on the left and the interactions with the deeb C-6H are more clearly seen in the view on the right. Ellipsoids drawn at the 50% probability level. Note: the electrically neutral compound only has two chlorides.
Figure 2.2: The $^1$H NMR shifts upon addition of one equivalent of TBACl to (A) [Ru(bpy)$_3$] (PF$_6$)$_2$ or (B) [Ru(deeb)$_3$] (PF$_6$)$_2$ in CD$_2$Cl$_2$. A positive shift is downfield and a negative shift is upfield.
Figure 2.3: The $^1$H NMR shifts upon addition of one equivalent (top numbers) or 42 equivalents (bottom numbers) of TBACl to [Ru(bpy)$_2$(deeb)]($\text{PF}_6$)$_2$ in CD$_2$Cl$_2$. A positive shift is downfield and a negative shift is upfield.
Figure 2.4: The $^1$HNMR spectrum of [Ru(bpy)$_2$(deeb)](PF$_6$)$_2$ in CD$_2$Cl$_2$. (A) The bpy C-3 proton shifted with added TBACl. (B) The deeb C-3 proton did not shift.
Figure 2.5: Changes in the $^1$H NMR spectral peaks for bpy C-3H (black squares) and deeb C-6H (red triangles) of approximately 3 mM [Ru(bpy)$_2$(deeb)] (PF$_6$)$_2$ in CD$_2$Cl$_2$ as TBACl is titrated into the solution. The calculated fit is depicted as a green line. (A) Full plot. (B) Close-up of the first 1.0 mM of added TBACl.
extracted were $K_1 = 480 \text{ M}^{-1}$ and $K_2 = 70 \text{ M}^{-1}$. The NMR shifts at low concentrations, Figure 2.5(B), did not satisfactorily fit this or any of the attempted models.

\[
\begin{align*}
R^{2+} + X^- & \overset{K_1}{\rightleftharpoons} [R^{2+}, X^-] & \text{Equation 2.1} \\
[R^{2+}, X^-] + X^- & \overset{K_2}{\rightleftharpoons} [R^{2+}, 2X^-] & \text{Equation 2.2} \\
\Delta ppm = \frac{\Delta \delta_{\text{max}}}{2} \left[ \frac{[R^{2+}, X^-]}{R_0} \right] + \Delta \delta_{\text{max}} \left[ \frac{[R^{2+}, 2X^-]}{R_0} \right] & \text{Equation 2.3}
\end{align*}
\]

The electronic absorption spectra (UV-Vis) of the ruthenium compounds in dichloromethane were altered when TBACl was added, as seen in Figure 2.6(A). The metal-to-ligand charge transfer (MLCT) absorption maximum of $[\text{Ru(bpy)}_2(\text{deeb})]^{2+}$ at 478 nm was red-shifted and decreased in intensity while absorbances at approximately 425 nm displayed a slight growth and those at 362 nm were red shifted with small changes in intensity. The deeb $\pi \rightarrow \pi^*$ and the bpy $\pi \rightarrow \pi^*$ absorption bands in the ultraviolet region both decreased in intensity without a shift in energy (data not shown). The MLCT absorption spectra changed monotonically with added chloride and the isosbestic points were lost at the highest concentrations used. These spectral changes plateaued at higher Cl$^-$ concentrations such that the spectra measured with 7 and 10 equivalents of Cl$^-$ were very similar. The spectral changes observed with TBACl were reversed when a 10-fold excess of TBAPF$_6$ was added. The presence of 10 equivalents of
Figure 2.6: (A) The UV-Vis absorption spectrum of a 26 μM [Ru(bpy)$_2$(deeb)](PF$_6$)$_2$ solution in CH$_2$Cl$_2$ titrated with TBACl. The red arrows indicate the direction of change with added TBACl. The inset shows the absorbance change measured at 448 nm with an overlaid fit to a modified Benesi-Hildebrand analysis from which an equilibrium constant of $K_{obs} = 17,600 \pm 700$ M$^{-1}$ was abstracted (left). (B) Job plot for [Ru(bpy)$_2$(deeb)](PF$_6$)$_2$ with TBACl. The red line is a calculated plot based on two equilibria with $K_1 = 130,000$ M$^{-1}$ and $K_2 = 60,000$ M$^{-1}$. 
TBAPF$_6$ in a solution of just [Ru(bpy)$_2$(deeb)]$^{2+}$ produced only negligibly small changes in intensity without any measureable wavelength shifts. There were qualitatively similar changes for [Ru(bpy)(deeb)$_2$]$^{2+}$ and [Ru(deeb)$_3$]$^{2+}$. However, [Ru(bpy)$_3$]$^{2+}$ displayed smaller changes and a net blue shift in the MLCT maximum with increased TBACl. Specific details of these spectral changes, as well as related spectral data observed with added TBABr and KOH, are listed in the Supporting Information.

Benesi and Hildebrand have previously described how spectroscopic titration data can be analyzed to abstract equilibrium constants.$^{30}$ In its original form, the Benesi-Hildebrand equation assumed a large excess of one of the constituents which was not a valid assumption for this study. Therefore, the relation was reformed as described below. An analysis of the chloride titration data with [Ru(bpy)$_2$(deeb)]$^{2+}$ is shown as the inset of Figure 2.6(A). Due to the lack of structure in the data, a single equilibrium was assumed, Equation 2.4. The terms in the equilibrium equation can be reformed and then solved for the concentration of the ion-paired species, Equation 2.5, where $R_0$ is the initial concentration of [Ru(LL)$_3$]$^{2+}$, $X_0$ is the initial concentration of the added anion, and $K_{obs}$ is the equilibrium constant for ion-pairing; only one of the roots of the quadratic makes physical sense. The derivation of Equation 2.4 and 2.5 is shown in Appendix 7.
Using **Equation 2.5** the Benesi-Hildebrand equation then becomes

**Equation 2.6** where $\Delta A$ is the change in absorbance at 448 nm and $\Delta \varepsilon$ is the difference in extinction coefficients between $[\text{Ru(bpy)}_2(\text{deeb})]^{2+}$ and the ion-paired species and $\ell$ is the path length. The experimental data were fit using a least squares analysis to find the best values of $K_{\text{obs}}$ and $\Delta \varepsilon$. The equilibrium constants for ruthenium compounds and anions are listed in **Table 2.3**.

In order to determine the stoichiometry of ion-pairing, a Job plot$^{31}$ was constructed for the addition of TBACl to $[\text{Ru(bpy)}_2(\text{deeb})]^{2+}$, **Figure 2.6(B)**, where the sum of the concentrations of $[\text{Ru(bpy)}_2(\text{deeb})]^{2+}$ and TBACl was kept constant at 207 ± 11 $\mu$M. The maximum change in absorbance at 448 nm was at a $[\text{Ru(bpy)}_2(\text{deeb})]^{2+}$ mole fraction of approximately 0.3 which corresponds to a 1:2 ratio for $[\text{Ru(bpy)}_2(\text{deeb})]^{2+}$:TBACl. For comparison, the solid red line is a calculated plot based on two equilibria with $K_1= 130,000$ M$^{-1}$ and $K_2 = 60,000$ M$^{-1}$.

Light excitation into the MLCT absorption band resulted in room temperature PL **Figure 2.7(A)**. The PL intensity decreased, red shifted, and became sharper with increased chloride concentration. For example, the PL maximum red-shifted by 36 mV when 10 equivalents of TBACl were added. Similar behavior was observed for $[\text{Ru(bpy)}(\text{deeb})_2]^{2+}$, however, light excitation of $[\text{Ru(bpy)}_3]^{2+}$ and $[\text{Ru(deeb)}_3]^{2+}$ resulted in net photochemistry, as evidenced by the appearance of long wavelength absorption bands in solutions that had undergone prolonged irradiance, and were therefore not studied further. Pulsed light excitation of $[\text{Ru(bpy)}_2(\text{deeb})]^{2+}$ and $[\text{Ru(bpy)}(\text{deeb})_2]^{2+}$ resulted in PL decays that were well described by a first-order kinetic model. The addition of excess salts resulted in decreased excited state lifetimes. Typical data for the
Table 2.3: Photophysical Results.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Anion</th>
<th>Ground State&lt;sup&gt;(a)&lt;/sup&gt;</th>
<th>Excited State&lt;sup&gt;(b)&lt;/sup&gt;</th>
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</thead>
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<tr>
<td></td>
<td></td>
<td>Abs λ&lt;sub&gt;max&lt;/sub&gt; (nm)</td>
<td>Δ ε (M&lt;sup&gt;-1&lt;/sup&gt; cm&lt;sup&gt;-1&lt;/sup&gt;)</td>
</tr>
<tr>
<td>[Ru(bpy)&lt;sub&gt;3&lt;/sub&gt;] (PF&lt;sub&gt;6&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sup&gt;-&lt;/sup&gt;</td>
<td>Cl&lt;sup&gt;-&lt;/sup&gt;</td>
<td>453</td>
<td>1500 ± 20</td>
</tr>
<tr>
<td>[Ru(bpy)&lt;sub&gt;2&lt;/sub&gt;(deeb)] (PF&lt;sub&gt;6&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sup&gt;-&lt;/sup&gt;</td>
<td>Cl&lt;sup&gt;-&lt;/sup&gt;</td>
<td>448</td>
<td>2340 ± 20</td>
</tr>
<tr>
<td>[Ru(bpy)(deeb)&lt;sub&gt;2&lt;/sub&gt;] (PF&lt;sub&gt;6&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sup&gt;-&lt;/sup&gt;</td>
<td>Cl&lt;sup&gt;-&lt;/sup&gt;</td>
<td>479</td>
<td>1500 ± 30</td>
</tr>
<tr>
<td>[Ru(deeb)&lt;sub&gt;3&lt;/sub&gt;] (PF&lt;sub&gt;6&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sup&gt;-&lt;/sup&gt;</td>
<td>Cl&lt;sup&gt;-&lt;/sup&gt;</td>
<td>448</td>
<td>1800 ± 60</td>
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<td>Br&lt;sup&gt;-&lt;/sup&gt;</td>
<td>448</td>
<td>1430 ± 30</td>
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<tr>
<td>[Ru(bpy)&lt;sub&gt;2&lt;/sub&gt;(deeb)] (PF&lt;sub&gt;6&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;OH&lt;sup&gt;-&lt;/sup&gt;</td>
<td>OH&lt;sup&gt;-&lt;/sup&gt;</td>
<td>448</td>
<td>1650 ± 50</td>
</tr>
</tbody>
</table>

<sup>(a)</sup> Values derived from analysis of ground state UV-Vis data.

<sup>(b)</sup> Equilibrium constants estimated by analysis of excited state lifetime data with added iodide.

<sup>(c)</sup> Not determined due to irreversible photochemistry.
Figure 2.7: (A) Steady-State photoluminescence spectra of argon purged 6 μM [Ru(bpy)$_2$(deeb)]$^{2+}$ with the indicated TBACl concentrations. (B) Time resolved PLI decay measured after 532 nm pulsed light excitation of an argon purged 31 μM [Ru(bpy)$_2$(deeb)]$^{2+}$ dichloromethane solution with added TBACl.
addition of chloride to [Ru(bpy)$_2$(deeb)]$^{2+}$ is shown in Figure 2.7(B). Stern-Volmer plots$^{32}$ were constructed from the calculated lifetimes, Figure 2.8(A). With excess TBAPF$_6$ the lifetime decreased by up to 9%, while the other salts resulted in decreases of 25-30%. The Stern-Volmer plots were non-linear as the lifetimes became independent of the salt concentration at high salt concentrations. There was no clear evidence of static quenching as the PL amplitudes immediately following the laser pulse displayed no discernible dependence on salt concentration. The equation for the average lifetime of a mixture of two photoluminescent species, was reformed into Equation 2.7.$^{32}$ Using Equation 2.5 for the concentration of the ion-paired species, the changes in lifetime were fit to Equation 2.7 and an equilibrium constant for ion-pairing with the excited state, K$_{obs, ES}$, was extracted. Table 2.3 compares the equilibrium constants obtained from UV-Vis and lifetime measurements.

\[
<\tau> = \frac{\alpha_1 \tau_1^2 + \alpha_2 \tau_2^2}{\alpha_1 \tau_1 + \alpha_2 \tau_2}
\]

\[
\alpha_1 = \frac{[R^{2+}]}{R_0} \quad \alpha_2 = \frac{[R^{2+}, X^-]}{R_0}
\]

$\tau_1$ is the lifetime without added anion

$\tau_2$ is the asymptotic lifetime as infinite anion concentration

\[
<\tau> = \frac{R_0 \tau_1^2 + \left(\tau_2 - \tau_1\right)[R^{2+}, X^-]}{R_0 \tau_1 + \left(\tau_2 - \tau_1\right)[R^{2+}, X^-]}
\]

The relative PL quantum yield was calculated using Equation 2.8 below where $\phi$ is the PL quantum yield, $A$ is the absorbance of the sample compound at the excitation wavelength, $\eta$ is the refractive index of the solvent and $D$ is the integrated PL.$^{33,34}$ The
Figure 2.8: (A) Stern-Volmer plots of lifetimes of approximately 20 μM [Ru(bpy)$_2$(deeb)](PF$_6$)$_2$ solutions in CH$_2$Cl$_2$ with added TBAPF$_6$ (black squares), TBACl (red circles), TBABr (green triangles), KOH (dark blue upside down triangles) and [Ru(bpy)(deeb)]$_2$(PF$_6$)$_2$ with added TBACl (light blue diamonds). (B) Ratios of the quantum yield ($\phi$), $k_r$ and $k_{nr}$ for a 6 μM [Ru(bpy)$_2$(deeb)](PF$_6$)$_2$ solution in CH$_2$Cl$_2$ measured with the indicated TBACl concentration.
subscripts R and x refer to the reference compound and the unknown respectively. The literature value for [Ru(bpy)$_3$]Cl$_2$ in water was used as the reference$^{24}$ ($\phi_r = 0.042$) and the refractive indices of water and CH$_2$Cl$_2$ used were 1.3387 and 1.4242, respectively.$^{35}$

$$\phi_x = \phi_R \left( \frac{A_R}{A_x} \right) \left( \frac{\eta_x}{\eta_R} \right)^2 \left( \frac{D_x}{D_R} \right)$$  \hspace{1cm} \text{Equation 2.8}

The PL quantum yield ($\phi$) values and the excited state lifetimes ($\tau$) were used to calculate radiative ($k_r$) and non-radiative ($k_{nr}$) rate constants using Equation 2.9 and Equation 2.10.$^{32}$ The values of $\phi_0/\phi_r$, $k_{r,0}/k_r$ and $k_{nr}/k_{nr,0}$ were plotted in Figure 2.8(B). Note that both $\phi$ and $k_r$ decreased with added salt while $k_{nr}$ increased. Therefore, the ratio shown in Figure 2.8(B) for $k_{nr}$ was inverted.

$$k_r = \frac{\phi_{em}}{\tau}$$ \hspace{1cm} \text{Equation 2.9}

$$k_{nr} = \frac{1}{\tau} - k_r$$ \hspace{1cm} \text{Equation 2.10}

As TBACl was added, the energy gap decreased as evidenced by the red shift of the PL spectra. The radiative rate constant is often related to this energy gap ($E$) and the transition moment integral ($\mu$),$^{36}$ Equation 2.11, where $\varepsilon_0$ is the permittivity of free space and $c$ is the speed of light.

$$k_r = \frac{E^3}{3\pi \varepsilon_0 h^4 c^3} \mu^2 \quad \mu^2 = \left| \psi_{gr} | \hat{\mu} | \psi_{es} > \right|^2$$ \hspace{1cm} \text{Equation 2.11}

The non-radiative rate constant is often related to the Energy Gap Law which can be given in the simplified form of Equation 2.12, where $E$ is taken to be the PL maximum, $S_M$ is the Huang-Rhys factor, $\omega_m$ is a medium frequency vibration and C is a collection of other terms.$^{2,37-44}$
\[
\ln k_{nr} = C - \frac{\gamma_0 E}{\hbar \omega_m} \quad \gamma_0 = \ln \left( \frac{E}{S_M \hbar \omega_m} \right) - 1 \quad \text{Equation 2.12}
\]

In Figure 2.9(A), the natural logarithm of the non-radiative rate constant was plotted against the energy gap and fit to a straight line with a slope of \(-15.4 \text{ eV}^{-1}\) that gave a Huang-Rhys factor of 0.4 based on an average medium frequency vibration of 1300 cm\(^{-1}\). This Huang-Rhys factor is considerably less than that for [Ru(bpy)]\(_3\)\(^{2+}\) and indicates an excited state geometry that is less distorted from the ground state than for [Ru(bpy)]\(_3\)\(^{2+}\).\(^{45}\)

In Figure 2.9(B) the radiative rate constant is plotted against the cube of the energy gap for PL and fit to a straight line using a least squares analysis with a slope of \(1.2 \times 10^5 \text{ s}^{-1} \text{eV}^{-3}\).

Nanosecond transient absorbance measurements of [Ru(bpy)\(_2\)(deeb)]\(^{2+}\) with and without 10 mM TBACl were measured, Figure 2.10 (B) and Figure 2.10 (A), respectively. Difference spectra measured under both conditions were typical of MLCT excited states with a bleach of the visible absorption band and intense transitions in the ultraviolet region. With excess TBACl, isosbestic points were maintained at 400 nm and 528 nm; the subtle spectral changes measured in comparison to that measured without chloride, were correlated to the changes in the ground state spectra. The spectra measured at different delay times after pulsed light excitation were found to be the same when normalized indicating that one excited state was generated within the 10 ns instrument response time. There was no evidence for permanent photochemistry or for production of the reduced ruthenium compound.
Figure 2.9: \([\text{Ru}(\text{bpy})_2(\text{deeb})] (\text{PF}_6)_2\) with added TBACl.

(A) The natural logarithm of the non-radiative rate constant as a function of the energy gap. (B) The radiative rate constant as a function of the cube of energy gap.
Figure 2.10: Transient absorption data for argon purged [Ru(bpy)$_2$(deeb)] (PF$_6$)$_2$ in (A) neat CH$_2$Cl$_2$ and (B) 10 mM TBACl CH$_2$Cl$_2$. The pink solid lines at the bottom are the ground state absorption spectra.
2.4 Results with Iodide

[Os(bpy)_3](PF_6)_2 has an excited state reduction potential more negative than the diiodide (I$_2$/2I) and iodine atom (I•/I$^-$) reduction potentials. Therefore, it was expected that both [Os(bpy)$_3$]$^{2+}$ and [Os(bpy)$_2$(deeb)]$^{2+}$ would not be redox active with added iodide in dichloromethane solution. The electronic absorption spectra (UV-Vis) of the osmium compounds in dichloromethane were altered when TBAI was added, as seen in Figure 2.11. The longest wavelength MLCT absorption peak at 480-500 nm decreased in intensity and was red-shifted for [Os(bpy)$_2$(deeb)]$^{2+}$ while absorbances at 320-400 nm displayed a slight growth. The bpy $\pi$$\rightarrow$$\pi^*$ peak at 291 nm and the deeb $\pi$$\rightarrow$$\pi^*$ peak at 311 nm essentially did not change with added iodide (data not shown). Iodide was also added to a dichloromethane solution of the neutral complex [Os(bpy)$_2$Cl$_2$]. In this case, within instrumental error, no spectral changes were seen, Figure 2.11 (bottom).

Light excitation into the [Os(bpy)$_3$]$^{2+}$ MLCT absorption band resulted in room temperature PL. Pulsed light excitation resulted in PL decays that were well described by a first-order kinetic model. The addition of TBAI salts resulted in a decrease in the lifetime. A Stern-Volmer plot was constructed from the calculated lifetimes and PL amplitudes immediately following light excitation. The Stern-Volmer lifetime plot was qualitatively similar to the plots for ruthenium compounds with added chloride in the previous section, Figure 2.12. They were non-linear as the lifetimes became independent of the TBAI concentration at high TBAI concentrations with the maximum $\tau_0/\tau$ reaching a value of approximately 1.3. The initial amplitudes were corrected for the change in [Os(bpy)$_3$]$^{2+}$ concentration due to the change in volume as TBAI was added to the solution. The amplitude Stern-Volmer plot showed a decreasing initial amplitude with
Figure 2.11: UV-Vis spectra of [Os(bpy)$_3$](PF$_6$)$_2$, [Os(bpy)$_2$(deeb)](PF$_6$)$_2$, and [Os(bpy)$_2$Cl$_2$] in dichloromethane with the indicated concentrations of added TBAI.
Figure 2.12: Stern-Volmer plot of lifetime and initial amplitude measurements for \([\text{Os(bpy)}_3]^2+\) with added TBAI in CH$_2$Cl$_2$ after pulsed 532 nm laser excitation.
increasing TBAI concentration where the ruthenium compounds in the previous section showed no amplitude quenching with added salts. The lifetime Stern-Volmer plot was fit to Equation 2.7 (previous section) and the amplitude Stern-Volmer plot was fit to Equation 2.13 below. An equilibrium constant for ion-pairing with the excited state, $K_{\text{obs,ES}}$, was extracted from each fit with $K_{\text{eq}} = 154,000$ from the lifetime quenching data and $K_{\text{eq}} = 38,000$ from the amplitude data.

$$\frac{A_0}{A} = \frac{A_0 R_0}{A_0 R_0 - (A_0 - A')RX}$$  \text{Equation 2.13}

Nanosecond transient absorbance measurements of $[\text{Os(bpy)}_3]^{2+}$ and $[\text{Os(bpy)}_2(\text{deeb})]^{2+}$ with and without 3 equivalents of TBAI were measured, Figure 2.13 and Figure 2.14. Difference spectra measured under both conditions were typical of osmium polypyridyl MLCT excited states with a bleach of the visible absorption band and growth of absorbance at both longwavelengths and in the ultraviolet region. Without added TBAI $[\text{Os(bpy)}_3]^{2+}$ maintained isosbestic points at 413 and 686 nm but with added TBAI the isosbestic points shifted to 415 and 696 nm. For $[\text{Os(bpy)}_2(\text{deeb})]^{2+}$ the isosbestic points were at 407 and 406 nm, without and with added TBAI respectively. The isosbestic points and the fact that the normalized spectra at different delay times after pulsed light excitation were essentially superimposable indicated that only one process had occurred: excited state decay to the ground. There was no evidence for permanent photochemistry or for production of the reduced osmium compounds.
Figure 2.13: TA spectra of 48 μM [Os(bpy)$_3$](PF$_6$)$_2$ without (top) and with (bottom) 142 μM TBAI in CH$_2$Cl$_2$ at the indicated delay times after pulsed 532 nm laser excitation.
Figure 2.14: TA spectra of 25 μM [Os(bpy)$_2$(deeb)](PF$_6$)$_2$ without (top) and with (bottom) 75 μM TBAI in CH$_2$Cl$_2$ at the indicated delay times after pulsed 532 nm laser excitation.
2.5 Discussion.

Chloride ion-pairing with the series of four ruthenium compounds in dichloromethane was found to have a significant influence on the metal-to-ligand charge transfer (MLCT) excited states. Studies of the homoleptic compounds, \([\text{Ru(deeb)}_3]^{2+}\) and \([\text{Ru(bpy)}_3]^{2+}\) were complicated by the well documented appearance of ligand loss photochemistry,

\[
\text{Equation 2.14}^{38,39}
\]

\[
\left[\text{Ru(bpy)}_2\right]\text{Cl}_2 + h\nu \rightarrow \text{Ru(bpy)}_2\text{Cl}_2 + \text{bpy}
\]

Interestingly, this photochemistry was far less efficient for the heteroleptic compounds. While the origins of this very disparate photochemistry for homo- versus hetero-leptic compounds are not well understood, it was not explored in more detail herein.\(^{24,40,46,47}\)

The inefficient photochemistry was exploited as it enabled a more detailed characterization of the excited state properties of the heteroleptic compounds. The site(s) of adduct formation between chloride and the ruthenium compounds was quantified by \(^1\text{H NMR studies and in the solid state with a crystal structure of } [\text{Ru(bpy)}_2(\text{deeb})]\text{Cl}_2.\)

Ion-pairing was shown for the first time to influence both the radiative and non-radiative rate constants of MLCT excited states. Below we discuss these and relevant literature results in more detail.

2.5.1 Ion Pair Interactions

Chloride titration studies with \(^1\text{H NMR spectroscopy has provided new insights into the site(s) of ion-pairing in this important class of ruthenium polypyridyl compounds. As chloride was added to the solution, several NMR resonances were shifted considerably
downfield while others remained essentially at the same position. The downfield shift can be rationalized as a coulombic attraction between the hydrogen and the negatively charged chloride that elongates the C-H bond and thereby lowers the electron density around the hydrogen atom. The chloride is much farther away than the carbon atom and any electron density provided by the chloride’s more diffuse orbitals does not compensate for the loss. When one equivalent of TBACl was added to the homoleptic complexes \([\text{Ru(bpy)}_3]^{2+}\) and \([\text{Ru(deeb)}_3]^{2+}\), the greatest peak shifts occurred for resonances associated with C-3H and C-6H respectively, indicating the preferred site of interaction for each of those ligands.

When 42 equivalents of TBACl were added to the heteroleptic \([\text{Ru(bpy)}_2(\text{deeb})]^{2+}\), the bpy C-3H shifted almost 6 times as far as when one equivalent of TBACl was added to \([\text{Ru(bpy)}_3]^{2+}\), Table 2.4. In contrast, the deeb C-6H shifted less than when one equivalent was added to \([\text{Ru(deeb)}_3]^{2+}\). Additionally, the deeb C-6H are located directly above the aromatic ring of the adjacent bpy ligand and in the case \([\text{Ru(bpy)}_2(\text{deeb})]^{2+}\) the shift in the deeb C-6H appeared to be a secondary effect from chloride association with the bpy C-3H. However, one would then expect the C-6H in \([\text{Ru(bpy)}_3]^{2+}\) to be influenced by this secondary effect and they were not. In any case, the primary site of interaction with \([\text{Ru(bpy)}_2(\text{deeb})]^{2+}\) is the bpy C-3H. Interestingly, the addition of only 0.1 equivalents of chloride to \([\text{Ru(bpy)}_2(\text{deeb})]^{2+}\) resulted in a significant shift in these resonances without broadening or the appearance of new peaks. Since a single chloride simultaneously interacting with 40 hydrogens on 20 bpy ligands is not possible on steric grounds alone, the chloride ion must be exchanging sites between the ligands on the NMR time scale. The titration data is also consistent with an equilibrium with a rapid exchange.
Table 2.4: Selected $^1$H NMR Changes

<table>
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<tr>
<th>Sample</th>
<th>Change in Chemical Shift</th>
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<tr>
<td></td>
<td>bpy C-3H</td>
</tr>
<tr>
<td>$[\text{Ru(bpy)}_3]^{2+}$ plus 1 equiv. TBACl</td>
<td>0.135</td>
</tr>
<tr>
<td>$[\text{Ru(deeb)}_3]^{2+}$ plus 1 equiv. TBACl</td>
<td>---</td>
</tr>
<tr>
<td>$[\text{Ru(bpy)}_2(\text{deeb})]^{2+}$ plus 42 equiv. TBACl</td>
<td>0.761</td>
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Although the $^1$H NMR spectra and the crystal structure describe the [Ru(bpy)$_2$(deeb)]$^{2+}$ complex in two distinct phases, a comparison provides several interesting points which illuminate the atomic level interactions between the ruthenium compound and halide ions:

(1) In the crystal structure, the closest chlorides to the ruthenium compound are situated near the two bpy C-3H and the deeb C-6H and in solution phase these are also the hydrogens that undergo the largest shift in the $^1$H NMR spectrum. In addition, a previously reported$^{14}$ crystal structure of [Ru(bpy)$_2$(deeb)]$^{2+}$I$_2$ was reanalyzed and it was found that the closest iodides were located 3.0-3.2 Å from the two bpy C-3H in that structure as well.

(2) The chloride near the bpy C-3H is coplanar with the bipyridine ligand, both of the C--H--Cl angles are 171° and the H-Cl distance is approximately 2.5 and 2.8 Å, which is less than the sum of the van der Waals radii (2.95 Å).$^{26}$ These criteria support what has previously been described as a carbon-hydrogen-chloride hydrogen bond.$^{48}$ In the $^1$H NMR spectrum, the bpy C-3H are the most acidic hydrogens (most downfield) in the complex except for the deeb C-3H which do not display any indication of interaction with the chlorides. On this basis the ion-pair interaction can be described as an acid-base adduct.

(3) In the crystal structure the ethyl ester groups are rotated away from the deeb C-3H and it may be that the oxygen lone pair electrons coulombically repel any chloride ions. Alternatively, space filling models show that in solution phase, it is possible for the ethyl ester groups to rotate and sterically block the deeb C-3H from interacting with chloride.
Either one of these or a combination of both may explain why there is no interaction with the deeb C-3H.

(4) Even though it is reasonable to expect that the chlorides would interact with the ethyl ester carbonyl carbon atoms, there is a conspicuous lack of evidence in both the crystal structure and the \(^1\)H NMR data for any significant interaction.

Overall, the crystal structure and NMR data for \([\text{Ru(bpy)}_2(\text{deeb})]^{2+}\) indicate that upon ion-pairing, there is a significant interaction between the chlorides and the bpy C-3H, as well as possibly the deeb C-6H, that perturbs the electronic structure of the complex and could well be described as an acid-base adduct.

Further indication of the perturbed electronic structure can be seen in the photophysical data. In the UV-Vis spectra, both peak positions in energy and oscillator strengths were reversibly perturbed, indicating an interaction that alters energy levels and/or transition integrals without permanent chemistry. The excited state absorption spectrum with added chloride was only altered in a manner consistent with the ground state UV-Vis changes. The excited state spectrum measured with transient absorption returned to baseline with approximately the same lifetime as that measured by PL, indicating that no photochemistry or redox chemistry was occurring.

The spectral shifts in the peak maximum for steady-state PL were correlated with similar shifts in the absorbance. Both absorption and PL involve the same electronic ground state, however, for PL, the upper level was the \(^3\)MLCT thermally equilibrated excited (thexi) state and for absorbance the upper level was the \(^1\)MLCT Franck-Condon state. Upon addition of 10 equivalents of chloride the PL energy was perturbed less (36 mV) than the absorbance (48 mV). Therefore, the \(^3\)MLCT thexi state was probably
located farther from the chloride than the $^1$MLCT. This presumably results from the coulombic repulsion of chloride ions with the ligand in which the excited state was localized upon in the $^3$MLCT thexi state. Interestingly, both the absorbance and PL energies were decreased by 1.9 % on addition of 10 equivalents of chloride. These minor changes to the steady-state PL spectrum, excited-state lifetimes, and quantum yields for PL as TBACl was titrated into the solution were all consistent with a perturbed electronic structure in the excited state.

A chloride adduct with the bpy C-3H’s of $[\text{Ru(bpy)}_3]^{2+}$ would inductively raise the energy levels of delocalized bpy $\pi^*$ orbitals to a greater extent than the metal based d-orbitals, consistent with the observed blue shift in the MLCT absorption for $[\text{Ru(bpy)}_3]^{2+}$. On the other hand, a chloride adduct with the bpy C-3H’s of $[\text{Ru(bpy)}_2(\text{deeb})]^{2+}$ would inductively raise the energy levels of the metal-based orbitals more than the deeb $\pi^*$ orbitals. This would cause the observed red-shift in the PL and absorbance spectra from or to a ligand localized orbital, consistent with previous reports.49

2.5.2 Excited State Relaxation

The decrease in integrated steady-state PL and excited state lifetime were fundamentally related to changes in the radiative and non-radiative rate constants for excited state decay.2 The radiative rate constant decreased with the cube of the energy gap, indicating qualitative agreement with the theoretical treatment of Strickler and Berg.36 On the other hand, as the energy gap decreased, the number of available vibration modes increased and the non-radiative rate constant ($k_{nr}$) increased in accordance with the Energy Gap Law.2,37-39,41,43,44 The increase in $k_{nr}$ far exceeded the decrease in $k_r$, causing a
decrease in steady-state PL, excited state lifetime and quantum yield of PL with the addition of chloride. In summary, the significant changes in $k_r$ and $k_{nr}$ with chloride resulted from the energy level changes due to ion-pairing.

### 2.5.3 Equilibrium Constants

In CH$_2$Cl$_2$ solutions it is known that TBA$^+$ and Cl$^-$ will ion-pair and the data described herein show that these ruthenium compounds also ion-pair with chloride, bromide and hydroxide. Therefore, in a solution of [Ru(bpy)$_2$(deeb)](PF$_6$)$_2$ and TBACl, it is reasonable to describe the ground state equilibria with the equations in Scheme 2.3. Additionally, there is no reason to assume that the excited state equilibrium constants would be the same as the ground state equilibrium constants. Experimentally, the UV-Vis spectrum and $^1$H NMR reported on the ground state equilibrium while the PL and transient absorption reported on the excited state equilibrium. The fact that the normalized transient absorption spectra were independent of the observation time and returned cleanly to the ground state with the same lifetime measured by PL indicated that the excited state equilibrium was fully established within approximately 10 ns. Interestingly, the equilibrium constants for the excited state obtained from lifetime measurements were much greater than the corresponding equilibrium constants obtained from ground state UV-Vis measurements.

In the MLCT excited state of ruthenium polypyridyl compounds with a coordinated deeb ligand, the excited state is localized on the deeb ligand. For example, with [Ru$^{II}$(bpy)$_2$(deeb)]$^{2+}$, the more Lewis acidic metal center in the excited state, [Ru$^{III}$(bpy)$_2$(deeb$'$)]$^{2+}$, will inductively attract electron density from the bpy ligands. This
### Scheme 2.3: Equilibria in CH₂Cl₂ solution with [Ru(bpy)₂(deeb)](PF₆)₂ and TBACl.

\[
\begin{align*}
[Ru(LL)_3]^{2+} + Cl^- & \rightleftharpoons [Ru(LL)_3]^{2+}, Cl^- \quad K_1 \\
[Ru(LL)_3]^{2+}, Cl^- + Cl^- & \rightleftharpoons [Ru(LL)_3]^{2+}, 2 Cl^- \quad K_2 \\
[Ru(LL)_3]^{2+} + PF_6^- & \rightleftharpoons [Ru(LL)_3]^{2+}, PF_6^- \quad K_3 \\
[Ru(LL)_3]^{2+}, PF_6^- + PF_6^- & \rightleftharpoons [Ru(LL)_3]^{2+}, 2 PF_6^- \quad K_4 \\
[Ru(LL)_3]^{2+}, Cl^- + PF_6^- & \rightleftharpoons [Ru(LL)_3]^{2+}, Cl^-PF_6^- \quad K_5 \\
[Ru(LL)_3]^{2+}, PF_6^- + Cl^- & \rightleftharpoons [Ru(LL)_3]^{2+}, Cl^-PF_6^- \quad K_6 \\
TBA^+ + Cl^- & \rightleftharpoons [TBA^+, Cl^-] \quad K_8 \\
TBA^+ + PF_6^- & \rightleftharpoons [TBA^+, PF_6^-] \quad K_9
\end{align*}
\]
in turn increases the acidity of the bpy C-3H, forming a stronger adduct with chloride and resulting in a larger equilibrium constant. Whereas the actual solution dynamics are an interplay of all the equilibria, the first two are expected to be the most relevant for the experimental effects described herein. However, even though two equilibria were expected, the presence of all three species, the dicationic ruthenium complex, the singly ion-paired monocation and the doubly ion-paired neutral species, could not be detected spectroscopically. Only a single set of isosbestic points were observed in the UV-Vis spectra until reaching the highest chloride concentrations where no isosbestic points were seen. Additionally, the Benesi-Hildebrand analysis of the absorption changes associated with ion-pairing were found to be well described by a single equilibrium constant whose magnitude increased with the number of deeb ligands present on the ruthenium compound.

The changes in the excited state photophysical properties (excited state lifetime and PL quantum yield) also did not contain sufficient structure to model two equilibria and therefore each experiment yielded only a single, “observed” equilibrium constant that presumably represents a weighted combination of the actual equilibrium constants. Based on coulombic considerations the first equilibrium constant is expected to be significantly greater than the second. The experimental $K_{\text{obs}}$ varied from 480 M$^{-1}$ to 118,000 M$^{-1}$, probably due to the complex equilibria mentioned above and the varied effects each species has on the measured quantities. Using Bjerrum ion-pairing theory,$^1$ the first equilibrium constant was calculated to be $K_1 = 290,000$ M$^{-1}$ while using the Eigen-Fuoss equation$^{51,52}$ the calculations resulted in $K_1 = 117,000$ and $K_2 = 500$. The experimental and theoretical equilibrium constants are at least of a similar order of magnitude.
The Job plot provided the clearest evidence for the expected 1:2 cation to anion ratio. Additionally, the $^1$H NMR data point to chloride-hydrogen-carbon hydrogen bonds in the ion-paired state which would require two chlorides to form adducts with the two bpy ligands and in this case a two equilibria model was used. Deviations from the modeled fit at low TBACl concentrations can be attributed to water in the solution that was evident in the NMR spectra that would preferentially pair with the chlorides.

Chloride, bromide and hydroxide can be thought as redox inactive analogs for iodide that is used extensively as a redox mediator in Dye-Sensitized Solar Cells (DSSCs). The data reported herein measured in the low dielectric constant solvent dichloromethane may have some relevance to DSSCs. While the spectral changes associated with ion-pairing were significant, they were small. For example, the subtle changes to the visible absorption spectra reported herein could easily be missed in an operational solar cell where interfacial heterogeneity is thought to play a key role. The influence of ion-pairing on excited state injection should be negligible, unless the excited state was very short lived or was remote to the semiconductor surface or both. The ~ 30% change in excited state lifetime would not be expected to influence injection rates that are often found to occur on picosecond and shorter time scales. Ion-pairing between the oxidized sensitizer and iodide has in fact been invoked to rationalize rapid regeneration under some conditions. Unfortunately the oxidized sensitizer formed after excited state injection is often assumed to be a ‘cation’ even though the charge of the ground state dye molecule is generally unknown and is rarely neutral or cationic. Nevertheless, the electric field generated by injected electrons certainly influences the interfacial dielectric constant.
and the data described herein show that careful absorption measurements may yield direct
evidence for ion-pairing.

2.5.1 Ion-Pairing with Iodide

Iodide ion-pairing with [Os(bpy)$_3$](PF$_6$)$_2$ and [Os(bpy)$_2$(deeb)](PF$_6$)$_2$ were used to
determine if the ion-pairing results could be extended to osmium polypyridyl compounds
and to ion-pairing with iodide. The ground state UV-Vis changes, the PL lifetime
quenching and the transient absorption changes upon the addition of iodide were
qualitatively similar to those for the ruthenium compounds with added chloride. Although
the similarity of the osmium and ruthenium compounds and the similarity of the anions
would predict these results, it is instructive that the size or the polarizability of the iodide
ions did not alter the ion-pairing effects. Additionally, the UV-Vis spectra of
[Os(bpy)$_2$Cl$_2$] with added TBAI were measured and essentially no changes in the spectra
were seen. Even though this compound has two bpy ligands with C-3 hydrogens capable
of interacting with an iodide ion, the lack of a positive charge on the complex precluded
effective ion-pairing with iodide. Therefore, the ion-pairing is mostly an electrostatic
phenomenon with the C-3H interaction only determining the preferred site of interaction.

The only difference between ion-pairing of the osmium compounds with iodide and the
ruthenium compounds with chloride was the appearance of PL initial amplitude
quenching with added iodide. At the highest iodide concentration tested, the initial
amplitude of PL was only 72% of the amplitude without any iodide. The source of this
amplitude quenching remains undetermined. The initial amplitudes were corrected for
changes in [Os(bpy)$_3$]$^{2+}$ concentration as volumes of TBAI were added, but the
concentration of [Os(bpy)$_3$]$^{2+}$, determined from UV-Vis spectra, was an additional 5%
lower after the experiment. However, there was no indication in the UV-Vis spectra of any permanent photochemistry and this is much less than the reduction in initial PL amplitude. Another possible source was the amount of laser light absorbed, however, the ground state absorbance at 532 nm is small and does not change with added iodide. It remains possible that an unnoticed instrumental condition, such as diminishing laser power, was the cause of this effect.

2.6 Conclusion

The data suggests that chloride preferentially formed adducts with the hydrogen atoms in the 3 and 3’ positions of bpy in the low dielectric solvent dichloromethane. This preference suggests that the sites of ion-pairing can be controlled in heteroleptic Ru$^{2+}$ compounds. The ion-pairing produced a perturbation in the electronic structure such that various photophysical properties were altered in a measurable and predictable manner. Changes to the radiative and non-radiative rate constants were in accordance with known theoretical equations for the radiative rate constant and the Energy Gap Law and suggest that these photophysical effects are due to changes in energy levels. Observed equilibrium constants were extracted that were in general agreement with Bjerrum and Eigen-Fuoss equations.
2.7 References


(51) Fuoss, R. M. *Journal of the American Chemical Society* 1958, 80, 5059-5061.


Chapter 3

Concerted Diiodide Bond Formation and Electron Transfer

3.1 Introduction

Bond breakage or bond formation is often associated with single electron transfer events. The electron transfer can occur before or after bond breakage/formation in a “Stepwise” mechanism or at the same time in a “Concerted” mechanism. The electron transfer may be either reductive or oxidative with respect to the molecule of interest and may be either thermal or photo-induced. Reductive cleavage of alkyl and aryl halides is one example that can proceed through either the Stepwise or Concerted mechanism. In fact, there are many examples of bond breakage accompanying electron transfer in a Concerted mechanism, although bond formation in conjunction with electron transfer is much less common. However, there have been several studies on the thermal oxidation of iodide and thiocyanide with Fe(III), Os(III) and Ir(IV) transition metal complexes. Nord and Stanbury proposed the Stepwise and Concerted pathways based on pseudo-first-order observed rate constants that were first order in oxidant and first and/or second order in anion concentration. Transition state enthalpies and entropies were also found and it was shown that the Franck-Condon barrier for concerted bond formation and electron transfer was not prohibitively high. One drawback of these previous studies is that only one reactant or product transition metal compound was monitored spectroscopically and the Concerted mechanism was proposed based solely on kinetic analyses that were second-order in reductant concentration. Herein a photoinitiated system is studied where, for the concerted mechanistic step, one of the reactants and both products were all three monitored spectroscopically.
In a photo-initiated system electron transfer involves reduction or oxidation of the excited state of the light-absorbing species. For example, the excited states of ruthenium(II) polypyridyl compounds are often strong enough oxidants to remove an electron from iodide, forming an iodine atom and thereafter diiodide through a Stepwise mechanism. Alternatively, if two iodides and the excited-state ruthenium complex are all within the solvent cage, the excited state might remove an electron and simultaneously form an I-I covalent bond through a Concerted mechanism, Scheme 3.1. Ruthenium polypyridyl compounds with excited-state reduction potentials within Zone 1 (Scheme 3.2) are strong enough oxidants for either the Stepwise or the Concerted mechanism, however, in a high dielectric (non-ion-pairing) solvent the Stepwise mechanism will be preferred due to the requirement for a three-body collision for the Concerted mechanism. The Stepwise mechanism may also be preferred in a low dielectric (ion-pairing) solvent due to the geometric requirements for bond formation coincident with electron transfer. Hence, both the redox potentials of the reactant species and the solvating ability of the solvent must be considered.

In order to isolate the concerted mechanism, advantage was taken of the 300 mV difference in standard reduction potentials between iodine atoms and diiodide that form the limits of Zone 2 for iodide: $E^\circ(I^*/I^-) = 0.99 \text{ V}$ and $E^\circ(I_2^-/2I^-) = 0.69 \text{ V}$. Therefore, ruthenium(II) polypyridyl compounds were chosen that were strong enough photo-oxidants to react with two iodides through the Concerted mechanism, but were too weak to oxidize a single iodide through the Stepwise mechanism.

The four ruthenium compounds used in this thesis chapter are listed in Scheme 3.3, where the ligand structures and carbon atom numbering are also displayed. These
**Scheme 3.1:** An example of the Stepwise and Concerted pathways. Reactant ion-pairing prior to light excitation has not been considered here.

<table>
<thead>
<tr>
<th>Stepwise pathway:</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Ru(LL)}_3]^{2+} \xrightarrow{\text{hv}} [\text{Ru(LL)}_3]^{2+*} \xrightarrow{+ I^-} [\text{Ru(LL)}_3]^+ + I^-$</td>
</tr>
<tr>
<td>$I^- + I^- \rightarrow I_2^-$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Concerted pathway:</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Ru(LL)}_3]^{2+} \xrightarrow{\text{hv}} [\text{Ru(LL)}_3]^{2+*} \xrightarrow{+ 2I^-} [\text{Ru(LL)}_3]^+ + I_2^-$</td>
</tr>
</tbody>
</table>
Scheme 3.2: (left) Reduction potentials of the indicated species. Iodine atom and diiodide potentials are in ACN, others are aqueous. (right) Three Zones defining the mechanistic pathway for excited state halide oxidation based on reduction potentials. See chapter 1 text for more details.
Scheme 3.3: List of Zone 2 compounds used, ligand structures and numbering of carbon atoms.
compounds were studied in three solvent systems: acetonitrile (ACN), acetone (DMK) and dichloromethane (DCM). The solvent properties relevant to ion-pairing for these solvents are listed in Table 3.1. Acetonitrile has a large dielectric constant and easily solvates the salts used herein resulting in low concentrations of the ion-paired species creating, in general, the necessity of three-body collisions to utilize the Concerted mechanism. At the other end of the scale, DCM is known to dissolve the salts but retain a large amount of ion-pairing, including the dicationic ruthenium complex ion-paired with two iodides. In this case, with all three reactants within the solvent cage, the difference between the Concerted mechanism and the Stepwise mechanism could not be distinguished experimentally because both the Stepwise and Concerted mechanisms were suspected to occur within the instrument response time. However, a solvent with an intermediate dielectric constant, such as DMK may preferentially ion-pair with only one iodide, allowing the measurement of the diffusion controlled reaction with a second iodide.

3.2 Experimental

Materials.
Argon gas (Airgas, 99.99%), RuCl$_3$$\cdot$2H$_2$O (Aldrich), [Ru(bpy)$_3$]Cl$_2$$\cdot$6H$_2$O (Aldrich, 99.95%), [Ru(phen)$_3$]Cl$_2$$\cdot$6H$_2$O (Aldrich, 99.95%), ammonium hexafluorophosphate (Acros, 99.5%), tetrabutylammonium iodide (TBAI; Fluka, >97%), tetrabutylammonium triiodide (TBAI$_3$; Aldrich, >97%), tetrabutylammonium hexafluorophosphate (TBAH, Fluka, >98%), 4-4'-dimethyl-2-2'-bipyridine (dmb; Aldrich, 99%), acetonitrile (Burdick and Jackson, spectroscopic grade) and dichloromethane (DCM; EMD, >99.8%) were
<table>
<thead>
<tr>
<th>Solvent</th>
<th>Dielectric Constant</th>
<th>Dipole Moment (D)</th>
<th>Gutmann Donor Number (kcal/mol)</th>
<th>Gutmann Acceptor Number (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DCM</td>
<td>9</td>
<td>1.60</td>
<td>1</td>
<td>20.4</td>
</tr>
<tr>
<td>DMK</td>
<td>21</td>
<td>2.88</td>
<td>17</td>
<td>12.5</td>
</tr>
<tr>
<td>MeOH</td>
<td>33</td>
<td>1.70</td>
<td>19</td>
<td>41.5</td>
</tr>
<tr>
<td>ACN</td>
<td>37</td>
<td>3.92</td>
<td>14.1</td>
<td>18.9</td>
</tr>
<tr>
<td>H₂O</td>
<td>80</td>
<td>1.85</td>
<td>18</td>
<td>54.8</td>
</tr>
</tbody>
</table>
used as received without further purification. \([\text{Ru(bpy)}_3](\text{PF}_6)_2\) and \([\text{Ru(phen)}_3](\text{PF}_6)_2\) were prepared by ion exchange, dissolving the chloride salt of the ruthenium complex in distilled water, adding a 10-fold excess of \(\text{NH}_4\text{PF}_6\), collecting the precipitate and recrystallizing from acetonitrile/diethylether. \([\text{Ru(bpy)}_2(\text{phen})](\text{PF}_6)_2\) was available from previous studies.\(^9\)\(^{10}\) Acetone (Pharmco-AAPER, HPLC-UV grade) was purged with argon for 30 minutes, dried for a minimum of 16 hours over non-indicating Drierite and decanted. 

\([\text{Ru(dmb)}_3](\text{PF}_6)_2\): A modification of the procedure by McCusker was used.\(^1\)\(^1\) \(\text{RuCl}_3 \cdot 2\text{H}_2\text{O} (0.2414 \text{ g, 1.0 mmol})\) and 4,4′-dimethyl-2,2′-bipyridine (dmb) (0.6080 g, 3.3 mmol) were placed in 50 mL of ethanol and heated to reflux. The solution began to change to a dark red color almost immediately. Small aliquots were removed occasionally and the UV-Vis spectrum recorded. After 8 hours there was still some trace of what may be \(\text{Ru(dmb)}_2\text{Cl}_2\) present indicated by an absorbance peak at 675 nm. \(\text{Ag(NO}_3\) (0.5096 g, 3.0 mmol) was then added to remove the chloride and after one further hour of reflux the solution was a bright red color and the longwavelength peak at 675 nm had disappeared. The solution was filtered and 1.70 g of \(\text{NH}_4\text{PF}_6\) was added and stirred. The solution became cloudy with red-orange particles. The solution was cooled to \(\sim 5 \degree\)C for 15 minutes resulting in a clear solution and red-orange precipitate. The precipitate was collected in a filter, washed 3x with water, washed 3x with diethyl ether and dried resulting in a 58% yield. \(^1\)\(^H\) NMR in \(\text{CD}_3\text{CN}\): 2.515s, 3H, methyl; 7.202ddd, 1H, \(J = 5.8, 1.8, 0.8\) Hz, bpy-C5H; 7.515d, 1H, \(J = 5.8\) Hz, bpy-C6H; 8.319dd, 1H, \(J = 1.0, 0.7\) Hz, bpy-C3H.
Measurements.

Steady State Absorption. UV–Vis absorption spectra were obtained on a Varian Cary 50 UV–Vis spectrophotometer at room temperature. For extinction coefficient and Benesi-Hildebrand measurements ten scans at approximately 1 nm resolution were averaged. All spectra were volume corrected for added salt solution, if applicable. Typically 10 to 300 μL of TBAI salt solution were added to 5.00 mL of the appropriate ruthenium compound solution.

Nanosecond Transient Absorption. Argon purged solutions of approximately 20–40 μM ruthenium compound both with and without TBAI were measured at room temperature as described previously.\(^\text{12}\) Briefly, a Nd:YAG laser with a doubling crystal provided pulsed 532 nm light (1 Hz, 8 ns FWHM, 2-10 mJ/cm\(^2\) per pulse) to create the initial concentration of excited states. A pulsed 150 watt Xenon arc lamp was aligned perpendicular to the laser beam and was used to measure the sample absorbance. A Spex 1702/04 monochrometer was used for wavelength selection and transmitted light was detected by a Hamamatsu R-928 photomultiplier tube. The responses to either 30 or 40 laser pulses were collected and averaged with a LeCroy 9450 oscilloscope.

Steady State Photoluminescence. A Spex Fluorolog with a 450 W Xe lamp was utilized for steady-state PL measurements in argon purged solvent at 25.0 ± 0.1 °C using a water bath and pump that circulated through the sample holder. All spectra were corrected for lamp intensity fluxuations. Unless otherwise noted, samples were illuminated at the MLCT peak wavelength.

Time-Resolved Photoluminescence. Excited-state lifetimes were measured using a nitrogen-dye laser system described previously with a 532 nm excitation wavelength.\(^\text{12}\)
PL intensity was monitored at the PL maximum wavelength. Argon purged solutions of approximately 20 μM ruthenium compound at 25.0 ± 0.1 °C were measured as TBAI in argon purged solvent was titrated into the sample solution.

Electrochemistry. The appropriate ruthenium compound was dissolved in 0.1 M TBAPF$_6$ in the selected solvent. Cyclic voltammetry was measured using a BASi CV-50W potentiostat with a three electrode configuration at a scan rate of 100 mV/s. The working electrode was a glass slide with fluorine-doped tin-oxide on one side (FTO) that was approximately 0.5 cm x 2 cm in area. The counter electrode was a platinum mesh and the reference electrode was Ag/AgCl in saturated KCl(aq). The reference electrode was calibrated before and after all measurements using ferrocene in 0.2 M LiClO$_4$/ACN with platinum disk working and counter electrodes, $E_{1/2}(\text{Fc}^+/\text{Fc}) = +310$ mV versus SCE.

$^1$H NMR. The ruthenium compound was dissolved in approximately 1 mL of deuterated solvent with added tetramethylsilane (TMS) to make an approximately 3 mM solutions and spectra were recorded as aliquots of TBAI in deuterated solvent were added. Spectra were measured on a Bruker Avance 400 MHz FT-NMR spectrometer at 298 ± 0.3 K. The mole ratio of ruthenium compound to TBAI was calculated using integration of the resulting spectra.

3.3 Results

The four ruthenium polypyridyl compounds used in this study, $[\text{Ru(bpy)}_3]^{2+}$, $[\text{Ru(bpy)}_2(\text{phen})]^{2+}$, $[\text{Ru(phen)}_3]^{2+}$ and $[\text{Ru(dmb)}_3]^{2+}$, were red-orange solids at room temperature and were soluble in acetonitrile, acetone and dichloromethane but only slightly soluble in water. $^1$H NMR spectra for the four complexes in deuterated acetone
were in agreement with literature reports. Spectra and peak assignments are given in Appendix 1. The NMR spectra showed no indication of impurities except for a small amount of residual solvent from the recrystallization (acetonitrile and/or diethyl ether) and a small amount of water.

The excited state reduction potentials for these four compounds were determined from measurements of the first reduction potential using cyclic voltammetry and the PL spectrum at both 77K and 25.0 °C. The details of determining the excited state reduction potentials are in Appendix 3. In DCM all four compounds fell within Zone 2, Figure 3.1, although [Ru(dmb)3]2+ is on the border. In DMK the excited state reduction potentials were 70-100 mV more negative than in DCM. While [Ru(bpy)3]2+, [Ru(phen)3]2+, and [Ru(bpy)2(phen)]2+ were still within Zone 2, the excited-state reduction potential of [Ru(dmb)3]2+ is probably more negative than 0.69 V vs. SCE. The source of the difference in reduction potentials between the two solvents, DCM and DMK, was evenly split between differences in the first reduction potential and differences in the excited state energy, E_{00}, calculated from the PL spectra (Appendix 3).

UV-Vis ground state absorbance spectra of the ruthenium compounds in ACN, DCM and DMK showed the expected peaks at approximately 450 nm corresponding to MLCT transitions as well as peaks at 250-300 nm corresponding to ligand localized π→ π* transitions, Figure 3.2. The series of compounds allowed the bpy and dmb π→ π* peaks to be identified at 287 nm and the one for phen at 264 nm. Peaks < 320 nm in DMK and < 220 nm in DCM were masked by the solvent. UV-Vis spectra for the four ruthenium compounds with various concentrations of added TBAI were measured in ACN, DMK
Figure 3.1: Electrochemical potential scale highlighting Zone 2 and the excited state reduction potential for the listed compounds, $E^0 (2^+* / +)$. 

<table>
<thead>
<tr>
<th>Compound</th>
<th>DMK</th>
<th>DCM</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Ru(dmb)}_3]^{2+}$</td>
<td>0.70</td>
<td></td>
</tr>
<tr>
<td>$[\text{Ru(bpy)}_3]^{2+}$</td>
<td>0.76</td>
<td>0.83</td>
</tr>
<tr>
<td>$[\text{Ru(bpy)}_2(\text{phen})]^{2+}$</td>
<td>0.77</td>
<td>0.84</td>
</tr>
<tr>
<td>$[\text{Ru(phen)}_3]^{2+}$</td>
<td>0.79</td>
<td>0.89</td>
</tr>
</tbody>
</table>
Figure 3.2: Molar extinction coefficient spectra for the four compounds used in ACN (top), DMK (middle) and DCM (bottom).
and DCM. Similar results were found for all four compounds. The spectra for [Ru(bpy)$_3$](PF$_6$)$_2$, Figure 3.3, and [Ru(dmb)$_3$](PF$_6$)$_2$, Figure 3.4 are representative. The difference spectra (the spectrum at the indicated TBAI concentration minus the spectrum without added iodide) are also included. For [Ru(bpy)$_3$](PF$_6$)$_2$ in ACN there was almost no spectral change except for the iodide peak at 245 nm and a small peak at 325 nm that was roughly proportional to the added iodide concentration at low iodide concentrations and then became independent of iodide concentration. In DMK there was some additional absorbance along the red edge of the MLCT peak as well as additional absorbance between the solvent peak at 320 nm and 400 nm. In DCM the MLCT was shifted more to the red than in DMK, there was more absorbance in the 330-400 nm range and a larger peak formed at 302 nm. All of the new absorbance peaks were roughly proportional to added iodide concentration through 0.3 mM TBAI (~7.5 equivalents) and then became iodide concentration independent as more TBAI was added. For [Ru(dmb)$_3$](PF$_6$)$_2$, the spectra in all three solvents were qualitatively the same, with spectral changes increasing in magnitude as the solvent polarity decreased.

Because UV-Vis effects of ion-pairing in DCM were thoroughly investigated in Chapter 2 of this thesis and because UV-Vis effects were mostly absent in ACN, the focus was turned to acetone solvent. As in Chapter 2 of this thesis, the Benesi-Hildebrand analysis was reformed into Equation 3.1 based on a single equilibrium and without the simplifying assumption of a large excess of one species. In this equation $R_0$ is the initial concentration of [Ru(LL)$_3$]$^{2+}$, $X_0$ is the initial concentration of the added anion, $K_{obs}$ is the equilibrium constant for ion-pairing, $\Delta \varepsilon$ is the difference in extinction coefficients between the ion-paired and not ion-paired species and $\ell$ is the path length. Only one of
Figure 3.3: UV-Vis spectra of \([\text{Ru(bpy)}_3]^{2+}\) plus TBAI in ACN (top), DMK (middle) and DCM (bottom). On the left side are the full spectra. On the right side are the difference spectra.
Figure 3.4: UV-Vis spectra of [Ru(dmb)$_3$](PF$_6$)$_2$ plus TBAI in ACN (top), DMK (middle) and DCM (bottom). On the left side are the full spectra. On the right side are the difference spectra.
the roots of the quadratic makes physical sense. Benesi-Hildebrand plots were constructed for the spectral data at selected wavelengths for \([\text{Ru(bpy)}_3\text{(PF}_6\text{)}_2\) and \([\text{Ru(bpy)}_2\text{(phen)}\text{(PF}_6\text{)}_2\), Figure 3.5 and Figure 3.6 respectively. The experimental data were fit using a least squares analysis to find the best values of \(K_{\text{obs}}\) and \(\Delta\varepsilon\). Only at low iodide concentrations was the data satisfactorily fit by Equation 3.1. The equilibrium constant was extracted from the fit for each of the selected wavelengths, Table 3.2.

Iodide solutions in organic solvents often contain a small level of triiodide, so the UV-Vis spectrum of \([\text{Ru(bpy)}_3\text{(PF}_6\text{)}_2\) with added triiodide was measured in DMK, Figure 3.7(top). The difference spectra were also calculated, Figure 3.7(bottom). The difference spectrum exactly matched a normalized authentic spectrum of triiodide in DMK that was measured separately. No spectral changes were evident other than the linear combination of the \([\text{Ru(bpy)}_3\text{]}^{2+}\) and triiodide spectra.

In order to ascertain the details of any interaction between TBAI and the ground state ruthenium complexes, \(^1\text{H}\) NMR spectra were recorded for each ruthenium compound with various concentrations of added TBAI in acetone-\(d_6\), Figure 3.8 through Figure 3.11. \(^1\text{H}\) NMR spectra without added iodide and peak assignments are given in Appendix 1. For \([\text{Ru(bpy)}_3\text{(PF}_6\text{)}_2\), Figure 3.8, essentially the only spectral change observed upon
Figure 3.5: Benesi-Hildebrand plots for [Ru(bpy)$_3$]$^{2+}$ plus TBAI in DMK.
Figure 3.6: Benesi-Hildebrand plots for [Ru(bpy)$_2$(phen)]$^{2+}$ plus TBAI in DMK.
**Table 3.2:** Equilibrium constants based on fits of Benesi-Hildebrand plots for the indicated compound in acetone.

<table>
<thead>
<tr>
<th>Compound</th>
<th>[Ru(bpy)$_3$] (PF$_6$)$_2$</th>
<th>[Ru(bpy)$_2$(phen)] (PF$_6$)$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{eq}$ ($\lambda$)</td>
<td>7,500 M$^{-1}$ (301 nm)</td>
<td>16,300 M$^{-1}$ (305 nm)</td>
</tr>
<tr>
<td>$K_{eq}$ ($\lambda$)</td>
<td>5,900 M$^{-1}$ (365 nm)</td>
<td>16,300 M$^{-1}$ (361 nm)</td>
</tr>
<tr>
<td>$K_{eq}$ ($\lambda$)</td>
<td>12,600 M$^{-1}$ (475 nm)</td>
<td>37,200 M$^{-1}$ (449 nm)</td>
</tr>
</tbody>
</table>
Figure 3.7: (top) Ground state absorption spectrum of $[{\text{Ru(bpy)}_3}]({\text{PF}_6})_2$ with added TBAI$_3$ in DMK. (bottom) Difference absorption spectrum with and without added triiodide.
Figure 3.8: (top) $^1$H NMR spectrum of 0.9 mM [Ru(bpy)$_3$] (PF$_6$)$_2$ in acetone-d$_6$ with the indicated concentration of TBAI. (bottom) Shifts in the C3-H $^1$H NMR peak upon addition of TBAI (black dots) and the calculated fit (black line).
addition of TBAI was a 0.12 ppm downfield shift of the C3-H peak. In contrast the C5-H peak was only shifted slightly downfield, 0.007 ppm or 6% of the C3-H shift. The C4-H and C-6H peaks were shifted slightly upfield, 0.012 ppm (11% of the C3-H shift) and 0.002 ppm (2% of the C3-H shift). The change in the downfield position of the C3-H peak (Δppm) was plotted versus the concentration of added TBAI, Figure 3.8 (bottom), and the results fit using Equation 3.2 where R²⁺ is the ruthenium polypyridyl compound, [R²⁺]₀ is the concentration of ruthenium compound added to the solution, [I⁻]₀ is the concentration of iodide added to the solution and [R²⁺, X⁻] is the concentration of the ion-paired species. The equilibrium constant calculated from the fit was 440 M⁻¹.

\[
\text{Equation 3.2}
\]

\[
\Delta \text{ppm} = \Delta \delta_{\text{max}} \frac{[R^{2+}, X^-]}{R_0} \quad R_0 = [R^{2+}] + [R^{2+}, X^-]
\]

\[
[R^{2+}, X^-] = \frac{1}{2} \left[ \left( [R^{2+}]_0 + [I^-]_0 + \frac{1}{K_{eq}} \right)^2 - \sqrt{ \left( [R^{2+}]_0 + [I^-]_0 + \frac{1}{K_{eq}} \right)^2 - 4[R^{2+}]_0 [I^-]_0} \right]
\]

For [Ru(phen)₃](PF₆)₂, Figure 3.9, essentially no shifts in peak position were evident. However, a considerable amount of orange precipitate was evident after just 0.6 equivalents of TBAI were added and after 2.0 equivalents were added 83% of the ruthenium compound (and 83% of the iodide) had precipitated, giving an approximate solubility product constant for [Ru(phen)₃]I₂ of 10⁻⁸ M².

For [Ru(bpy)₂(phen)](PF₆)₂, Figure 3.10, the bpy C3-H peak was shifted the most, by far while at the other extreme the bpy C4-H and C6-H were barely shifted at all. The other peaks were shifted by varying degrees. For comparison purposes, the maximum
Figure 3.9: $^1$H NMR spectrum of 9 mM [Ru(phen)$_3$] (PF$_6$)$_2$ in acetone-d$_6$ with the indicated concentrations of TBAI.
Figure 3.10: (top) $^1$H NMR spectrum of 9 mM [Ru(bpy)$_2$(phen)] (PF$_6$)$_2$ in acetone-d$_6$ with the indicated concentration of TBAI. (bottom) Shifts in the downfield location of the indicated peaks upon addition of TBAI. The shifts of the two complimentary bpy peaks are often superimposable.
shift in the bpy C3-H peak was normalized to a shift of 1.00 and the maximum shift for each of the other peaks was calculated as a percentage of that value, Table 3.3. Next to the bpy C3-H peak, all the phenanthroline peaks were shifted the most. Even though the Ru(II) compound concentrations for both the [Ru(phen)₃](PF₆)₂ and [Ru(bpy)₂(phen)](PF₆)₂ trials were 9 mM, there was no perceptible precipitation of [Ru(bpy)₂(phen)](PF₆)₂ with added iodide, even at 47.3 mM TBAI.

For [Ru(dmb)₃](PF₆)₂, Figure 3.11, the shifts in peak position were barely noticeable, but again with this compound, a large degree of precipitation occurred. After 2 equivalents of TBAI were added, approximately 98% of the red-orange [Ru(dmb)₃]I₂ had precipitated, giving an approximate solubility product constant of 7 x 10⁻¹² M².

Light excitation of acetone and dichloromethane solutions of the ruthenium compounds resulted in room temperature PL, Figure 3.12. The wavelength dependent PL spectra were broad and featureless. In both solvents [Ru(phen)₃]²⁺ displayed the highest energy transition while [Ru(bpy)₃]²⁺ and [Ru(bpy)₂(phen)]²⁺ gave PL maxima at nearly the same wavelength. Pulsed light excitation of all four compounds in acetonitrile or acetone solvent resulted in PL decays that were well described by a first-order kinetic model. A lifetime, τ = 1/k, as well as the initial photoluminescence amplitude was calculated for each iodide concentrations from a single exponential fit of the data. The PL maxima and lifetime data for each of the compound/solvent combinations without added iodide are reported in Table 3.4.

The lifetimes were also measured as TBAI was added to the solution and Stern-Volmer plots were constructed. In acetonitrile, Stern-Volmer plots for all four compounds tested were flat, indicating a lack of both static or dynamic quenching, Figure 3.13. In acetone,
Figure 3.11: (top) $^1$H NMR spectrum of the aromatic region for 6 mM [Ru(dmb)$_3$](PF$_6$)$_2$ in acetone-$d_6$ with the indicated concentration of TBAI added. (bottom) Shifts in methyl side chain $^1$H NMR peak with the indicated concentration of TBAI added.
Table 3.3: Comparison of $^1$H NMR peak shifts for $[\text{Ru(bpy)}_2(\text{phen})](\text{PF}_6)_2$ with added TBAI in acetone-d$_6$

<table>
<thead>
<tr>
<th>Peak Designation</th>
<th>Max Shift (Δppm)</th>
<th>Max Shift (% of bpy C3-H max shift)</th>
</tr>
</thead>
<tbody>
<tr>
<td>bpy C3-H</td>
<td>0.1913</td>
<td>100 %</td>
</tr>
<tr>
<td>phen C4-H</td>
<td>0.0603</td>
<td>32 %</td>
</tr>
<tr>
<td>phen C5-H</td>
<td>0.0452</td>
<td>24 %</td>
</tr>
<tr>
<td>phen C2-H</td>
<td>0.0294</td>
<td>15 %</td>
</tr>
<tr>
<td>phen C3-H</td>
<td>0.0295</td>
<td>15 %</td>
</tr>
<tr>
<td>bpy C5-H</td>
<td>0.0238</td>
<td>12 %</td>
</tr>
<tr>
<td>bpy C4-H</td>
<td>-0.0059</td>
<td>-3 %</td>
</tr>
<tr>
<td>bpy C6-H</td>
<td>0.011</td>
<td>6 %</td>
</tr>
</tbody>
</table>
Figure 3.12: Steady-state PL spectrum of the indicated compounds in acetone (top) and CH$_2$Cl$_2$ (bottom) at room temperature. Light excitation was at 510 nm for acetone solutions and at the MLCT maximum for CH$_2$Cl$_2$ solutions.
Table 3.4: Photophysical properties.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$<a href="%5Ctext%7BPF%7D_6">\text{Ru(bpy)}_3</a>_2$</th>
<th>$<a href="%5Ctext%7BPF%7D_6">\text{Ru(bpy)}_2(\text{phen})</a>_2$</th>
<th>$<a href="%5Ctext%7BPF%7D_6">\text{Ru(phen)}_3</a>_2$</th>
<th>$<a href="%5Ctext%7BPF%7D_6">\text{Ru(dmb)}_3</a>_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda_{\text{max}}(\text{em})$ (ACN)</td>
<td>615 nm</td>
<td>608 nm</td>
<td>584 nm</td>
<td></td>
</tr>
<tr>
<td>$\lambda_{\text{max}}(\text{em})$ (DMK)</td>
<td>618 nm</td>
<td>611 nm</td>
<td>598 nm</td>
<td></td>
</tr>
<tr>
<td>$\lambda_{\text{max}}(\text{em})$ (DCM)</td>
<td>600 nm</td>
<td>597 nm</td>
<td>582 nm</td>
<td>613 nm</td>
</tr>
<tr>
<td>$\tau_0$ (ACN)</td>
<td>$836 \pm 6$ ns</td>
<td>$813 \pm 3$ ns</td>
<td>$394 \pm 5$ ns</td>
<td>$927 \pm 4$ ns</td>
</tr>
<tr>
<td>$\tau_0$ (DMK)</td>
<td>$884 \pm 4$ ns</td>
<td>$848 \pm 6$ ns</td>
<td>$447 \pm 2$ ns</td>
<td>$900 \pm 4$ ns</td>
</tr>
<tr>
<td>$\tau_0$ (DCM)</td>
<td>$609 \pm 8$ ns</td>
<td>$486 \pm 1$ ns</td>
<td>$139 \pm 2$ ns</td>
<td>$963 \pm 3$ ns</td>
</tr>
</tbody>
</table>
Figure 3.13: Stern-Volmer plots for the indicated ruthenium compounds plus TBAI in acetonitrile at room temperature. Lifetime quenching is indicated in black and initial amplitude quenching in red.
the Stern-Volmer plot for [Ru(dmb)$_3$]$^{2+}$ also showed no static or dynamic quenching while the other three compounds tested displayed dynamic quenching but no static quenching, Figure 3.14. The dynamic quenching curve of $\tau_0/\tau$ versus iodide concentration was fit to a straight line at the lower iodide concentrations. The slope of the line was the Stern-Volmer constant, $K_{SV}$, which permitted the calculation of the quenching rate constant, $k_q$, where $\tau_0$ is the lifetime without any added iodide.

$$K_{SV} = k_q \tau_0$$

The quenching rate constants varied from $2.17 \pm 0.13 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$ for [Ru(bpy)$_2$(phen)]$^{2+}$ to $4.5 \pm 0.2 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$ for [Ru(phen)$_3$]$^{2+}$. In DCM the PL decays were first-order at low iodide concentrations but then a second process became more and more dominant as increasing amounts of iodide were added. Figure 3.15 shows log plots of the PL intensity versus time after 532 nm pulsed laser irradiation of samples containing TBAI. With 0 or 0.4 equivalents of added TBAI, any non-linearity was indistinguishable from the noise in the plot. However, by 0.6 equivalents of added TBAI the non-linearity could clearly be seen in the first 500 ns as some of the excited states decay through a faster process. As increasing amounts of TBAI were added the fraction of excited states decaying through the faster process also increased. Stern-Volmer plots for DCM were constructed for the fast component lifetime, the slow component lifetime and for the total initial amplitude, Figure 3.16. As with the other two solvents, [Ru(dmb)$_3$]$^{2+}$ in DCM displayed no static or dynamic quenching for all iodide concentrations tested. Both [Ru(bpy)$_3$]$^{2+}$ and [Ru(bpy)$_2$(phen)]$^{2+}$ underwent dynamic quenching without any static quenching of the total PL. Quenching rate constants in DCM were $2.1 \pm 0.2 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$ and $1.55 \pm 0.02 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$ for [Ru(bpy)$_3$]$^{2+}$ and
Figure 3.14: Stern-Volmer plots for the indicated ruthenium compounds plus TBAI in acetone at room temperature. Lifetime quenching is indicated in black and initial amplitude quenching in red.
Figure 3.15: PL decay for $[\text{Ru(bpy)}_2(\text{phen})]^2^+ \text{ in DCM with the indicated concentration of TBAI after 532 nm pulsed laser excitation. The growth of the second exponential with increasing TBAI concentration is evident in the series.}$
Figure 3.16: Stern-Volmer plots for the indicated ruthenium compound plus TBAI in CH₂Cl₂ at room temperature. Total initial amplitude quenching is indicated in black, the slow component lifetime quenching in red and the fast component lifetime in green.
[Ru(bpy)$_2$(phen)]$^{2+}$ respectively. Both the slow and fast component lifetimes and the total initial amplitude quenching for [Ru(phen)$_3$]$^{2+}$ in DCM gave slightly upward sloping Stern-Volmer plots with ratio maxima of approximately 1.3. From the initial PL amplitudes of the slow and fast components, the fraction of excited states that decay through each process was calculated and plotted in Figure 3.17.

The transient absorption spectra of each of the four compounds was measured in acetone. In order to analyze the transient absorption spectra, though, authentic spectra of the individual species likely to be found in the solution were needed. The Ru(II) transition metal compounds, iodide and triiodide are all stable compounds and their ground state spectra have already been given. Other species that were considered likely were the Ru(II) excited state, Ru$^{2+*}$, the singly reduced form of the ruthenium compound, and diiodide. The UV-Vis extinction coefficient spectra for diiodide, the MLCT excited states and the reduced ruthenium compounds are given in Appendices 4, 5 and 6 respectively. For reference, the molar extinction coefficient spectra of iodide, diiodide and triiodide in acetone solvent are given in Figure 3.18. Iodide absorbed at approximately 245 nm in other organic solvents so its lowest energy electronic absorption was obscured by the solvent. The excited state spectra of [Ru(bpy)$_3$]$^{2+}$, [Ru(bpy)$_2$(phen)]$^{2+}$, [Ru(phen)$_3$]$^{2+}$ and [Ru(dmb)$_3$]$^{2+}$, tops of Figures 3.19, 3.20, 3.21 and 3.22 respectively, displayed a bleach of the MLCT absorption band in the neighborhood of 450 nm, the formation of a new absorbance peak at 350-400 nm and a small amount of absorbance at long wavelengths. The ground state absorption is included as a magenta line at the bottom of the graph, so the excited state bleach can be compared to the ground
state MLCT absorbance. All of the excited state changes returned to baseline concomitantly.

**Figure 3.17:** Fractions of fast and slow components of the excited state relaxation as a function of added TBAI.
Figure 3.18: UV-Vis molar extinction coefficient spectra for TBAI, diiodide and triiodide in acetone.
Figure 3.19: Transient absorption spectra of [Ru(bpy)$_3$](PF$_6$)$_2$ in acetone without (top) and with (bottom) added TBAI.
Figure 3.20: Transient absorption spectra of [Ru(bpy)$_2$(phen)](PF$_6$)$_2$ in acetone without (top) and with (bottom) added TBAI.
Figure 3.21: Transient absorption spectra of \([\text{Ru(phen)}_3]^2+\) in DMK in acetone without (top) and with (bottom) added TBAI.
Figure 3.22: TA spectrum $[\text{Ru(dmb)}_3](\text{PF}_6)_2$ with and without 5 Eq TBAI in DCM
After iodide was added to the solutions, the transient absorption spectra were very different except for \([\text{Ru(dmb)}_3](\text{PF}_6)_2\) which still showed a simple excited state spectrum and return to baseline, bottoms of Figures 3.19, 3.20, 3.21 and 3.22. Immediately after light excitation of the other three compounds, there was essentially an excited state spectrum that decayed to baseline as additional absorbance in the 390 nm and 500 nm regions appeared. The absorbance peak at 500 nm returned to baseline more slowly than the excited state and the 390 nm absorbance peak returned to baseline even more slowly. At long wavelengths (> 700 nm) the excited state absorbance decay was interrupted by the growth of additional absorbance that returned very slowly to baseline. The spectra displayed for 8 μs returned to baseline very slowly.

As a control, the transient absorption spectrum of just the solvent (acetone) and the solvent plus TBAI were measured, Figure 3.23. No transient absorption increases can be seen but the PL of acetone was evidenced by the bleach in absorbance below 500 nm. It should be noted that the transient absorption spectra in Figure 3.23 were measured with 355 nm pulsed laser light that was directly absorbed by acetone while the experiments with the ruthenium compounds utilized 532 nm laser excitation where there was no measurable acetone absorption. Acetone is known to phosphoresce and the steady-state PL spectrum of acetone, with continuous 355 nm illumination, was recorded, Figure 3.24 (top). Interestingly, acetone used as received showed little PL while acetone that had been dried over argon purged Drierite displayed strong PL and the addition of iodide and triiodide increased the emission intensity even more. The time-resolved measurement of the emission from acetone, Figure 3.23 (bottom), indicated that the PL was essentially finished by 200 ns after an excitation pulse.
Figure 3.23: Transient absorption of just acetone solvent (top) and with added 295 μM TBAI.
Figure 3.24: (top) Steady-state photoluminescence spectrum of acetone as received (red), acetone dried over Drierite (green) and a TBAI/TBAI₃ solution in acetone(black) using 355 nm excitation. (bottom) Time-resolved emission from acetone at indicated wavelengths following 355 nm pulsed laser excitation.
It has previously been found that solutions of iodide in organic solvents generate a small amount of triiodide by unknown mechanism(s). Therefore, the transient absorption spectrum of \([\text{Ru(bpy)}_3](\text{PF}_6)_2\) in acetone with various concentrations of added triiodide was also measured, **Figure 3.25** (top). There were no indications of any absorbing species except the excited state - the transient spectra were essentially superimposable on the spectra recorded without the addition of triiodide. The triiodide did quench the excited state, however. The excited state lifetime, as measured by the return to baseline of the bleach at 450 nm, decreased with increasing triiodide concentration, **Figure 3.25** (bottom), and the quenching rate constant was calculated to be \(9.2 \pm 0.4 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}\) was calculated.

As noted earlier, after approximately 5 μs, the transient absorption spectra match a normalized diiodide spectrum with a peak at approximately 390 nm and residual absorbance at long wavelengths. In order to investigate the source of this long-lived species, the absorbance changes at 390 nm were monitored for samples with various concentrations of \([\text{Ru(bpy)}_3](\text{PF}_6)_2\) and TBAI, **Figure 3.26**. When the iodide concentration was varied there was no change in the transient absorption at 390 nm. However, the magnitude of the absorption did change with respect to the concentration of ruthenium compound. The Delta Absorbance from 4 - 10 μs was fit to a straight line and when that was plotted versus the concentration of \([\text{Ru(bpy)}_3]^{2+}\), a straight line was obtained with an intercept near zero and a slope of 207 M\(^{-1}\), **Figure 3.27**. If the absorption at 390 nm is assumed to be wholly diiodide, then the Delta Absorption can be converted to concentration of diiodide, giving a slope of \(0.026 \text{ M(I}_2^\text{−}) / \text{M(Ru}^{\text{II}})\).
Figure 3.25: Transient absorption of [Ru(bpy)$_3$](PF$_6$)$_2$ in acetone with added triiodide. (bottom) Stern-Volmer plot of $\tau_0/\tau$ as a function of triiodide concentration based on transient absorption decay at 450 nm after 532 nm pulsed laser excitation.
Figure 3.26: (top) Transient absorbance at 390 nm of 35 μM [Ru(bpy)$_3$](PF$_6$)$_2$ in DMK with the indicated concentration of TBAI. (bottom) Transient absorbance at 390 nm of 359 μM TBAI in DMK with the indicated concentration of [Ru(bpy)$_3$](PF$_6$)$_2$. 
Figure 3.27: Plot of average transient absorbance at 390 nm from 4-10 μs after pulsed 532-nm laser excitation of 359 μM TBAI in DMK as a function of the concentration of added [Ru(bpy)$_3$](PF$_6$)$_2$. 

\[
\Delta \text{Abs(390 nm)} \text{ for } [\text{Ru(bpy)}_3](\text{PF}_6)_2 \text{ in DMK} \\
68 \mu\text{M TBAI} \\
\text{Incpt} = -0.0006 \pm 0.0002 \text{ mOD} \\
\text{Slope} = 207 \pm 7 \text{ M}^{-1} \\
\quad = 0.026 \text{ M (I$_2$) / M(Ru$^\delta$)}
\]
3.4 Discussion

The photo-initiated Concerted mechanism is a means of creating chemical bonds simultaneously with electron transfer to or from an excited state compound. Ruthenium compounds with excited state reduction potentials in Zone 1 (Scheme 3.2) were suspected of undergoing reductive quenching of their excited states by both the Stepwise and Concerted mechanisms at higher iodide concentrations, however, firm spectroscopic evidence was lacking. From a thermodynamic point of view, the Concerted mechanism had approximately 300 mV more driving force and would therefore seem to be the favored reaction pathway. However, when both the Stepwise and Concerted mechanisms were thermodynamically favorable, even if high iodide concentrations were used in a highly ion-pairing solvent, the reaction with one iodide (Stepwise) may have been statistically more favorable than the reaction with two iodides (Concerted) due to the geometric requirement for the two iodides to be in a position for both bond formation and electron transfer, and the Coulombic repulsion of the iodide ions. Whether the reaction pathway was determined by thermodynamics or statistics was not determined. It was predicted, though, that compounds in Zone 2 may restrict the Stepwise mechanism while still allowing the Concerted mechanism.

Using parameters from electrochemical and photophysical measurements, the excited state reduction potentials for three of the four compounds, [Ru(bpy)3](PF6)2, [Ru(bpy)2(phen)](PF6)2 and [Ru(phen)3](PF6)2 in ACN, DMK and DCM were found to be within Zone 2 while the excited state reduction potentials for [Ru(dmb)3](PF6)2 were on the border or slightly within Zone 3, Figure 3.28. Therefore, it should have been thermodynamically favorable for the three compounds to react through the Concerted
Figure 3.28: Excited-state reduction potentials of Zone 2 compounds in ACN, DMK and DCM.
mechanism but unfavorable to react through the Stepwise mechanism and both mechanisms should have been thermodynamically unfavorable for \([\text{Ru(dmb)}_3](\text{PF}_6)_2\). In accordance with the Nernst equation for these single electron redox reactions, every 59 mV of driving force results in a power of ten difference in the equilibrium position. Since most of the compounds were not near the diiodide or iodine atom reduction potentials, the Concerted mechanism is highly favored and the Stepwise mechanism is highly disadvantaged. A complication arose because the iodine atom and diiodide reduction potentials were measured in ACN and the method used to measure them could not be reproduced due to poor solubility. So exact thermodynamic energy differences could not be calculated.

The other major factor determining the reaction pathway is the solvent, specifically the degree of ion-pairing in a particular solvent. Without ion-pairing, the Concerted mechanism requires a three-body collision which is comparatively rare. A solvent with a large dielectric constant, such as ACN, is predicted to have little ion-pairing and reactions would only proceed through the Stepwise mechanism. A solvent with a low dielectric constant, such as DCM, is predicted to have a high degree of ion-pairing, including two iodides ion-paired with the same dicationic ruthenium complex.

Reversible changes in the ground state UV-Vis spectra of the ruthenium compounds as iodide is added to the solution reported on the degree of ion-pairing. Acetonitrile solutions showed no clear evidence for ion-pairing at the concentrations studied. Addition of iodide to DCM solutions revealed large spectral changes consistent with a large degree of ion-pairing and addition to DMK solutions revealed smaller, yet measurable, absorption changes indicating an intermediate degree of ion-pairing, Scheme 3.4.
Scheme 3.4: Degree of ion-pairing in each solvent based on UV-Vis ground state spectra with added iodide.
Equilibrium constants for ion-pairing in acetone derived from a Benesi-Hildebrand analysis were dependent on the wavelength monitored. However, 10,000 M$^{-1}$ is probably a good estimate of the true equilibrium constant. Since the spectral changes in DMK are so much smaller than those in DCM, it would be reasonable to assign this as the equilibrium constant for the first iodide ion-pairing. However, the difference in magnitude of the spectral changes could also be due to variations in how DMK and DCM solvate the ruthenium compounds. The UV-Vis spectra of [Ru(bpy)$_3$](PF$_6$)$_2$ with added triiodide in DMK produced spectra that were the simple addition of the two compounds and did not show any indications of ion-pairing despite the opposite charges on the ions. Perhaps the distribution of the negative charge over the three atoms makes triiodide a weaker Lewis base incapable of displacing solvent molecules. Alternatively, if the absorbance changes with added iodide are in fact charge transfer from iodide in nature, one would not expect triiodide to give those charge transfer bands.

The $^1$H NMR spectra of [Ru(bpy)$_3$](PF$_6$)$_2$ and [Ru(bpy)$_2$(phen)](PF$_6$)$_2$ in deuterated acetone (acetone-d$_6$) underwent slight shifts in peak positions as a function of added TBAI concentration. This implied that changes in electron density near the hydrogen atoms had occurred, perhaps due to ion-pairing, but no chemical reaction had taken place. The spectra revealed the strongest interaction with iodide occurred at the bpy-C3-H’s, just as $^1$H NMR and crystal structures indicated with chloride in chapter 2. Because the bpy-C3-H peak position is the most downfield, it had the lowest electron density and could therefore be considered the most acidic proton on the bpy structure. If an iodide ion approached the two bpy-C3-H’s it could coordinate with both of them, forming what has been called a carbon-hydrogen-iodide hydrogen bond, Figure 3.29 (top). The addition
Figure 3.29: (top) Single iodide ion coordinating with bot bpy-C3-H atoms. (bottom) Iodide ion pulling hydrogen nucleus away from carbon resulting in lower electron density.
of iodide caused downfield shifts in most, if not all, the peak positions. This is consistent with the approach of an iodide ion to the hydrogens, thereby coulombically attracting them and pulling them slightly farther from the carbon nucleus and to an area of lower electron density. Any increased electron density from the diffuse 5p orbitals of the iodide ion did not offset the loss from the smaller carbon 2sp² orbitals. The amount of peak position shift would therefore be dependent on the acidity of the hydrogen atom and the affinity that position has for ion-pairing. It should also be noted that if there was inner sphere coordination of iodide to the ruthenium center, the bpy-C6-H from the pyridyl ring no longer coordinated to ruthenium would experience a large shift in peak position since in the coordinated position it is pointing directly at the aromatic π-ring of an adjacent ligand, which noticeably affects its peak position.

In contrast to the bpy containing compounds, [Ru(phen)₃](PF₆)₂ and [Ru(dmb)₃](PF₆)₂ did not show any signs of ion-pairing, but there was very little iodide actually in the solutions because of the precipitation of [Ru(phen)₃]I₂ and [Ru(dmb)₃]I₂. The more intriguing question is why two of the compounds precipitated with added iodide and two did not. The two compounds with bpy ligands provided the preferred C3-H and C3’-H sites for iodide ion-pairing and it is possible that this coordination provided the means for effective solvation. [Ru(phen)₃]²⁺ does not have two hydrogens that point towards a central region such as the bpy-C3-H’s and [Ru(dmb)₃]²⁺ may inhibit ion-pairing at the C3-H site due to steric interference from the methyl groups. It should be noted that the ¹H NMR experiments required a much higher concentration of ruthenium compound than the spectroscopic experiments and while two of the compounds formed precipitates during the NMR experiment, precipitates were rarely seen during spectroscopic
experiments. In fact, all four compounds displayed approximately the same magnitude of UV-Vis spectral changes upon addition of iodide signifying approximately equal degrees of ion-pairing.

Stern-Volmer plots for [Ru(dmb)$_3$](PF$_6$)$_2$ in all three solvents showed no static or dynamic quenching, signaling that its excited state reduction potential must be more negative than the diiodide reduction potential or there is some other factor preventing the reaction. The Stern-Volmer plots of the other three compounds provide strong evidence that the Concerted mechanism is the primary pathway for reductive quenching of these compounds. In ACN, previous researchers have shown dynamic quenching with Zone 1 compounds indicating a diffusional process, and further transient absorption data clearly supported a Stepwise mechanism. The Zone 2 compounds tested in this study, however, were not quenched in ACN, presumably because reduction by a single iodide was thermodynamically inhibited and three body collisions did not appreciably occur.

In DMK there was dynamic quenching, but no static quenching. The lack of static quenching indicates that there was a limited concentration of doubly ion-paired species and that any singly ion-paired species were not directly quenched. Also, at all iodide concentrations the PL decay was satisfactorily fit by a single exponential function, indicating that at the pseudo-first order conditions of these experiments, the quenching reaction was first order in ruthenium compound. The linear Stern-Volmer plot versus the TBAI concentration indicates that the quenching reaction is also first-order in iodide concentration. Put together with the ACN results where a single iodide does not react, and the most likely explanation is that one iodide is ion-paired with the ruthenium complex and a second iodide was encountered diffusationally, followed by the Concerted
pathway reaction.

In DCM the situation is more complicated, probably because there is a mixture of singly and doubly ion-paired species present at the moment of light excitation. The excited state decays were satisfactorily fit by a biexponential model with a slow and a fast component at moderate and high iodide concentrations. Without any iodide and at the lowest concentrations tested, the excited states exhibit a single exponential decay with a lifetime that decreases with increasing iodide concentration (slow component). This slower component gives a linear Stern-Volmer plot at low to moderate iodide concentrations with a quenching rate constant near the diffusion limit at approximately $2 \times 10^{10} \text{M}^{-1}\text{s}^{-1}$. Results at these lower iodide concentrations are similar to the data obtained in acetone and can be modeled by a single iodide ion-pairing with the ruthenium complex before laser excitation and a second iodide diffusing to the excited-state ion-pair. As the iodide concentration was increased, a faster component became evident in the PL decays. This faster process had a rate constant that was independent of the iodide concentration and was approximately 50 ns for all three compounds. Moreover, the UV-Vis spectra before and after the experiment showed that no permanent chemical change had occurred with the ruthenium compounds, and because this phenomenon was not seen in the solvents with higher dielectric constants, it is plausible that the second, fast component species, is the result of double ion-pairing with two iodides. If both iodides were ion-paired prior to light excitation, one would predict a reaction rate that is independent of iodide concentration and no dynamic quenching would be seen, consistent with the experimental results. The rate constant itself could be a reflection of the requirement for
the two iodides within the solvent cage to meet the geometrical requirements for bond formation in concert with electron transfer.

The transient absorption spectra in acetone were first analyzed at various time slices to identify which species may be present at that time, Figure 3.30. At 50 ns after the laser pulse, the spectra were satisfactorily modeled by the excited state spectrum alone. At 500 ns, combinations of excited state, reduced compound and diiodide were evident. By 8 μs, almost all of the reduced compound has decayed and the spectra were satisfactorily modeled by the diiodide spectrum with an additional loss of absorbance below 400 nm.

In order to evaluate the complex overlap of spectra, a matrix analysis was used. Following Beer’s Law, \( A = \varepsilon C \ell \), matrices were used for the absorbance, concentration and extinction coefficients as outlined in Scheme 3.5. The path length of 1 cm is omitted from here forward. The extinction coefficient matrix had a column for each species and a row for each wavelength. The species considered were the ground state, the excited state, the singly reduced compound, diiodide and triiodide. The ground state ruthenium compound was eliminated by using difference spectra for the excited state and the singly reduced compound spectra because all of the ruthenium molecules were in one of those three forms. The values for the extinction coefficient matrix were taken from measurements of the authentic spectra as detailed in the appendices to this thesis. The absorbance matrix has a row for each wavelength and a column for each time slice measured from the laser excitation pulse. The absorbance matrix values were taken from the transient absorption experimental measurements. Beer’s Law was rearranged, solving for concentration, Equation 3.3. The pseudo-inverse of the extinction coefficient matrix was used because it was a rectangular matrix where a simple inverse could have been
Figure 3.30: Modeling of experimental TA spectra of [Ru(bpy)$_3$](PF$_6$)$_2$ + TBAI in DMK at 50 ns (top), 500 ns (middle), and 8 μs (bottom). See text for details.
Scheme 3.5: Matrix definitions for matrix analysis of transient absorption data.
used with a square matrix. The concentration matrix was calculated where each row was a list of values for the concentration of a particular species over time. Plots of the concentrations of excited state, reduced compound and diiodide were constructed and a representative example for each compound is shown in Figures 3.31, 3.32 and 3.33. The matrix analysis often resulted in slightly negative values for the excited state concentration so these values were artificially constrained to be non-negative.

If the time-dependent concentration of each species is simply fit to the simplest mathematical form possible for each species, the rate of appearance of diiodide is slower than the rate of appearance of the reduced compound. That would indicate that the Stepwise mechanism is being utilized. However, the other experiments, particularly Time-Resolved Photoluminescence, clearly point to a Concerted mechanism. Therefore, the simplest type of analysis was discarded.

In order to fit the time-dependent concentration data to a more complex, but still relatively simple, kinetic analysis, a mechanistic model was required, Scheme 3.6. A single equilibrium for ion-pairing one iodide was included for the ground state with the excited state dynamically pairing with a second iodide ion. The concerted electron transfer/bond formation then produced the singly reduced ruthenium compound and diiodide ion-paired within the solvent cage. Diiodide and the reduced compound would then recombine to give ground state reactants. This recombination is relatively slow.

\[
\varepsilon \cdot \Delta C = \Delta A
\]
\[
\Delta C = \varepsilon^{-1} \cdot \Delta A \quad \text{Equation 3.3}
\]
29 µM [Ru(bpy)$_3$](PF$_6$)$_2$
+ 281 µM TBAI
in DMK     P = 10 mW

Figure 3.31: Time dependent concentration of excited state, singly reduced compound and diiodide for [Ru(bpy)$_3$] (PF$_6$)$_2$ + TBAI in DMK.
Figure 3.32: Time dependent concentration of excited state, singly reduced compound and diiodide for [Ru(bpy)$_2$(phen)](PF$_6$)$_2$ + TBAI in DMK.
Figure 3.33: Time dependent concentration of excited state, singly reduced compound and diiodide for \([\text{Ru(bpy)}_2(\text{phen})](\text{PF}_6)_2 + \text{TBAI}\) in DMK.

\[
42 \, \mu\text{M} \ [\text{Ru(phen)}_3](\text{PF}_6)_2 + 212 \, \mu\text{M} \text{TBAI in DMK} \quad P = 10 \, \text{mW}
\]
Scheme 3.6: Concerted mechanism with single iodide ion-pairing in the ground state and a dynamic reaction with a second iodide producing the singly reduced compound and diiodide.
because the electron transfer reaction has a very large driving force and is far into the Marcus inverted region. Diiodide should be produced in a 1:1 ratio with the singly reduced compound but additional diiodide was produced and after all the reduced compound was consumed, there was a similar amount of diiodide remaining. So a second, unknown source of diiodide was included. Based on the fact that the rate of appearance of this extra diiodide is slower than the appearance of diiodide attributed to the reductive quenching from the primary reaction, it is possible that some unknown oxidant reacts with iodide to produce iodine atoms that then react with another iodide to produce diiodide. The kinetic equations for the model were solved, giving the expressions in Scheme 3.7 (top). The derivation of these equations is given in Appendix 7. Collections of kinetic parameters were combined into the abbreviated equations for fitting the experimental data, Scheme 3.7 (bottom).

The time dependent concentration of the excited state, singly reduced compound and diiodide could each be satisfactorily fit to the kinetic equations to obtain rate constants or combinations of rate constants, Figure 3.34 and Figure 3.35. The concentration of excited state was well fit by a single exponential decay with a lifetime that was within error the same as that from emission data from the TA experiment, Table 3.5 and Table 3.6. There was no static formation of diiodide or the reduced compound. The time-dependent concentration data for the singly reduced compound and diiodide were also satisfactorily fit by the derived kinetic equations. Both the singly reduced compound and diiodide were formed with nearly identical rate constants that were similar to the excited state decay, indicating that they were both primary products of reductive quenching. The results are similar for all three of the four compounds that were quenched by iodide. Both
Scheme 3.7: (top) Kinetic equations for the concentration of ion-paired plus not ion-paired (total) excited state ([R*]ₜ), singly reduced compound ( [R⁺] ), and diiodide. The derivation of these equations is in Appendix 7. (bottom) Abbreviated equations used to fit the experimental data.
Figure 3.34: Kinetic fits of time-dependent concentration data for 48 μM [Ru(bpy)₂(phen)](PF₆)₂ + 249 μM TBAI in DMK.
Figure 3.35: Kinetic fits of time-dependent concentration data for 30 μM [Ru(phen)$_3$](PF$_6$)$_2$ + 304 μM TBAI in DMK.
Table 3.5: Parameters from kinetic fits for 48 μM [Ru(bpy)$_2$(phen)](PF$_6$)$_2$ + 249 μM TBAI in DMK. Highlighted values were fixed to match the values from the reduced compound fits.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Emission</th>
<th>Ex. State</th>
<th>Reduced</th>
<th>Diodide</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_0 + k_q[I]$</td>
<td>s$^{-1}$</td>
<td>$1.0 \times 10^7$</td>
<td>$1.0 \times 10^7$</td>
<td>$9.6 \times 10^6$</td>
<td>$9.6 \times 10^6$</td>
</tr>
<tr>
<td>$k_q$</td>
<td>s$^{-1}$</td>
<td>$3.5 \times 10^{10}$</td>
<td>$3.5 \times 10^{10}$</td>
<td>$3.4 \times 10^{10}$</td>
<td>$3.4 \times 10^{10}$</td>
</tr>
<tr>
<td>$k_3$</td>
<td>s$^{-1}$</td>
<td></td>
<td>$4.1 \times 10^5$</td>
<td></td>
<td>$5.1 \times 10^5$</td>
</tr>
<tr>
<td>$k_9$</td>
<td>s$^{-1}$</td>
<td></td>
<td></td>
<td></td>
<td>$3.0 \times 10^6$</td>
</tr>
</tbody>
</table>

$k_0 = 1.18 \times 10^6$ s$^{-1}$ \hspace{1cm} [TBAI] = 249 μM

$k_q$ (TRPL) = $2.2 \times 10^{10}$ s$^{-1}$ \hspace{1cm} $\varphi_{ce} = 0.30$
Table 3.6: Parameters from kinetic fits for 30 μM [Ru(phen)$_3$](PF$_6$)$_2$ + 304 μM TBAI in DMK. Highlighted values were fixed to match the values from the reduced compound fits.

<table>
<thead>
<tr>
<th></th>
<th>Units</th>
<th>Emission</th>
<th>Ex. State</th>
<th>Reduced</th>
<th>Diiodide</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_0 + k_q[\Pi]$</td>
<td>s$^{-1}$</td>
<td>1.5 x 10$^7$</td>
<td>1.5 x 10$^7$</td>
<td>1.4 x 10$^7$</td>
<td>1.4 x 10$^7$</td>
</tr>
<tr>
<td>$k_q$</td>
<td>s$^{-1}$</td>
<td>4.2 x 10$^{10}$</td>
<td>4.2 x 10$^{10}$</td>
<td>3.9 x 10$^{10}$</td>
<td>3.9 x 10$^{10}$</td>
</tr>
<tr>
<td>$k_3$</td>
<td>s$^{-1}$</td>
<td></td>
<td>2.4 x 10$^{5}$</td>
<td>2.6 x 10$^{5}$</td>
<td></td>
</tr>
<tr>
<td>$k_9$</td>
<td>s$^{-1}$</td>
<td></td>
<td></td>
<td>2.9 x 10$^{6}$</td>
<td></td>
</tr>
</tbody>
</table>

$k_0 = 2.24 \times 10^6$ s$^{-1}$  \quad [\text{TBAI}] = 304$\mu$M

$k_q$ (TRPL) = 4.5 x 10$^{10}$ s$^{-1}$ \quad $\varphi_{ce} = 0.31$
the reduced compound and the diiodide attributable to reductive quenching decayed as a first-order process with similar rate constants \((k_3)\), consistent with the proposed mechanism of recombination of diiodide with reduced compound. It is suggested that the remaining diiodide disproportionate slowly to form triiodide and iodide.

The analysis given above is somewhat less than satisfying due to the extra diiodide produced from an unknown source. Also, it was noticed that the transient absorption spectra at wavelengths below 400 nm did not satisfactorily match the diiodide spectrum at long times. There was too little absorption at these wavelengths. Possible causes include the consumption of triiodide or the loss of ion-pairing for all the excited state molecules. Both of these sources were not fully investigated in this work and may be the focus of future work.

Lastly, the importance of the Concerted mechanism is that it provides a low-energy pathway for some reactions. For any reaction involving coupled electron transfer with bond formation, Compounds in Zone 1 will react through either pathway while compounds in Zone 3 will not react at all, **Scheme 3.8**. For reactions involving compounds in Zone 2, the Stepwise pathway contains a high-energy intermediate where electron transfer has occurred but bond formation has not yet occurred. In these cases, the Concerted mechanism can bypass this high-energy intermediate and allow the reaction to proceed at an acceptable rate. In this study a series of compounds that spanned all three zones could be used in order to elucidate the chemistry that was occurring. However, it is envisioned that in other systems of practical value a Zone 2 reaction may not proceed through the Stepwise pathway and by switching to an ion-pairing solvent, the Concerted
mechanism can be accessed and provide the low-energy pathway for the reaction to occur.

Scheme 3.8: Low energy pathway to reaction products utilizing the Concerted pathway.
3.5 Conclusions

Three ruthenium polypyridyl compounds were tested that have excited state reduction potentials in-between that of the iodine atom and diiodide. All three displayed evidence of increased ion-pairing with iodide as the dielectric constant of the solvent was decreased. Time-Resolved PL studies in ACN demonstrated that the Stepwise mechanism could not be accessed in that solvent. Similar studies in DMK resulted in dynamic reductive quenching that could be explained by a model where a single iodide ion-pairs with the ruthenium complex prior to light excitation and a second iodide then reacts with the ion-pair through the Concerted mechanism. In DCM, reductive quenching of the excited state by iodide resulted in a bi-exponential decay of photoluminescence. A slower process proceeded at a rate that was dependent on the iodide concentration to the first power while the faster process proceeded at a rate that was independent of the iodide concentration and the fraction of ruthenium molecules reacting through the faster process increased with increasing iodide concentration. Taken together, these results are consistent with single iodide ion-pairing at low iodide concentrations that reacts diffusionally through the Concerted mechanism and a double iodide ion-pairing at higher concentrations that reacts at a fixed rate through the Concerted mechanism. Transient absorption data supports the Concerted mechanism for all three ruthenium compounds where the reduced compound and diiodide both appeared at the same rate as the excited state disappeared supporting a mechanism in which reductive quenching by iodide leads
directly to both products. The Concerted mechanism provides a low-energy pathway for Zone 2 reactions to proceed in low-dielectric solvents.

3.6 References


(2) In this discussion, “at the same time” theoretically means within one vibrational period, but practically is limited by the experimental instrument response time of approximately 20 ns.


Chapter 4

A New Dicarboxylic Acid Bipyridine Ligand for Ruthenium Polypyridyl Sensitization of TiO$_2$


4.1 Introduction

Over thirty years ago, Goodenough and coworkers reported the use of 4,4’-(CO$_2$H)$_2$-2,2’-bipyridine, dcb, as an ambidentate ligand for coordination to Ru$^{II}$ and metal oxide semiconductors.$^1$ To this day dcb remains the most efficient and widely utilized ligand for applications in dye sensitized solar cells (DSSCs).$^2$ The t$_2$-orbital parentage of the TiO$_2$ conduction band was expected to bond strongly with the $\pi^*$ orbitals of ruthenium bipyridine excited state through carboxylic-acid derived surface linkages, but not for SnO$_2$ that has a conduction band orthogonal to the $\pi^*$ system.$^1$ There now exists some experimental evidence that supports this proposal. Strong electronic coupling between the MLCT excited states of dcb-containing Ru compounds and TiO$_2$ has been inferred from femtosecond transient absorption spectroscopy,$^3$ and the rate constants abstracted from such data are more rapid than those measured at SnO$_2$ interfaces.$^4,5$

However, ultrafast measurements usually show evidence for slower picosecond components$^4$ to excited state injection that are detrimental for short lived MLCT excited states, like those of iron diimine compounds,$^6-8$ and for driving reactions from upper excited states relevant to exceeding the well-known Schockley-Queisser limit.$^9$ While the origin of the slower injection processes remains speculative, experimental studies
have suggested that surface heterogeneity\textsuperscript{10} and/or interligand hopping contribute to the complex kinetics.\textsuperscript{11} Theoretical calculations indicate that a coplanar arrangement of the carboxyl and the pyridine ring is most optimal for excited state injection; the interfacial electronic interactions decrease markedly when the carboxyl group becomes orthogonal to the pyridine ring.\textsuperscript{12} This suggests that ultrafast injection occurs from those excited states where the carboxyl and pyridine ring are co-planar and slower injection from those that deviate from planarity.

In this thesis chapter a new bipyridine ligand (dfm) with a dicarboxylic acid group conjugated to the pyridine rings through an olefin group is described, Scheme 4.1. Conjugated linkers to carboxylic acid functional groups have previously been employed for Ru(II) coordination compounds. Most notable are the ’rigid rod’ linkers based on oligophenyleneethynylene spacers between carboxylic acid functional groups and the pyridine rings of bipyridine.\textsuperscript{13} However, it is well known that rotation about the phenyl-ethyne bond dramatically alters electronic coupling much like that proposed above for excited state injection. In contrast, the sp\textsuperscript{2} hybridization of the olefin linker in dfm prevents rotation and ensures a planar orientation of the olefin spacer with the pyridine rings. In addition, closely related malonic acid binding groups have been utilized to functionalize a variety of metal oxide surfaces with molecular compounds.\textsuperscript{14-17} The 3,3’ bridge that connects the two pyridine rings in the dfm ligand resulted in long Ru-N\textsubscript{dfm} bond lengths that had the undesirable effect of stabilizing ligand field excited states. Nevertheless, transient absorbance excited state injection yields and photocurrent measurements with a ruthenium compound based on this ligand indicate nearly quantitative excited state injection yields.
Scheme 4.1: Chemical structures of the two ligands dcb and dfm.
4.2 Experimental

Materials. All chemicals were reagent grade or better unless otherwise specified and were used without further purification. The following reagents and substrates were used as received from the indicated commercial suppliers: ruthenium(III) chloride hydrate (Aldrich); potassium thiocyanate (Acros); acetonitrile (Burdick & Jackson, spectrophotometric grade); toluene (OmniSolv, 99.99 %); lithium perchlorate (Aldrich, 99.99 %); \( n \)-tetrabutylammonium perchlorate (TBAP; Fluka, > 99.9 %); argon gas (Airgas, > 99.998 %); nitrogen gas (Airgas, > 99.999 %); oxygen gas (Airgas, industrial grade); titanium(IV) isopropoxide (Sigma–Aldrich, 97 %); fluorine-doped \( \text{SnO}_2 \)-coated glass (FTO; Hartford Glass Co., Inc., 2.3 mm thick, 15 Ohm/□); and microscope slides (Fisher Scientific, 1 mm thick).

Synthesis: Diethyl(4,5-diazafluoren-9-ylidene) malonate (defm) was prepared as described previously.\(^{18}\) The (4,5-diazafluoren-9-ylidene) malonic acid (dfm) ligand was isolated as the lithium carboxylate salt from hydrolysis of the diethyl ester compound, defm. Briefly, approximately 3 mmol of the diester ligand dissolved in 50 mL of acetone was added to 19 mmol LiOH in 30 mL of water at room temperature. The reaction was stirred and allowed to proceed for 5 hours at which time a white solid was filtered, washed with acetone and then dried in vacuum overnight. The crude product was recrystallized from water with acetone. \(^{1}H\) NMR (400 MHz, D\(_2\)O): 8.43 (dd, 2H); 8.16 (dd, 2H); 7.32 (dd, 2H).
[Ru(bpy)$_2$(dfm)]Cl$_2$·6.75H$_2$O.  [Ru(bpy)$_2$]Cl$_2$ (0.30 g, 0.58 mmol) and dilithium (4,5-diazafluoren-9-ylidene) malonate (0.20 g, 0.71 mmol) were dissolved in 6 mL of water with stirring. 1 M HCl solution was then added dropwise until the stirred solution tested weakly acidic. 30 mL of ethanol was then added, and the flask purged briefly with Ar. After refluxing for 12 hours under Ar, the reaction mixture was filtered by gravity and taken to dryness. The solid residues were suspended in ca. 35 mL of 0.50 M HCl solution, heated and stirred to dissolve, and then the mixture was filtered. The filtrate was set aside to concentrate by slow evaporation for several days. Resulting crystalline solids were collected by suction filtration, washed with a small amount of 0.5 M HCl and then diethyl ether. Yield: 390 mg (90 %). $^1$H NMR (400 MHz, DMSO-d$_6$): 8.83 (m, 4H), 8.32 (dd, 2H), 8.15 (m, 4H), 8.05 (m, 2H), 7.81 (m, 2H), 7.63 (m, 2H), 7.59 (m, 2H), 7.52 (m, 4H). Elemental analysis: Calculated for RuC$_{34}$H$_{37.5}$O$_{10.75}$N$_6$Cl$_2$: C, 46.71; H, 4.32; N, 9.61; Cl, 8.11. Found: C, 46.91; H, 3.97; N, 9.63; Cl, 8.25.

[Ru(bpy)$_2$(dfm)]Cl$_2$·5CH$_3$OH. Crystals of the methanol solvate suitable for X-ray measurements were obtained by slow diffusion of diethyl ether into 2 – 3 mL concentrated methanol solution of the above product.

[Ru(bpy)$_2$(defm)](PF$_6$)$_2$·CH$_3$CN. 0.26 g (0.5 mmol) of [Ru(bpy)$_2$]Cl$_2$·2H$_2$O and 0.18 g (0.58 mmol) of defm were placed in a 50 mL RB flask with 25 mL of ethanol and refluxed 7 hours under Ar. After cooling to room temperature, the mixture was filtered by gravity and the filtrate was taken to dryness. The residue was taken up in minimum volume of water and loaded onto a column of Sephadex SP-C25. The column was eluted first with water, then with aqueous HCl in a concentration gradient ranging from 0.1-0.4M. A pale orange component eluted first, followed by main dark red component.
Collected fractions were analyzed using UV-Vis. Middle fractions with similar spectra were collected together and concentrated by rotary evaporation. Saturated NH$_4$PF$_6$ solution was added to precipitate the product. After cooling at 0°C overnight, solids were collected by centrifugation and the supernatant was decanted. The solids were washed 2x with water and dried overnight in vacuo. Yield: 350 mg (89%). The product was further purified by recrystallization from CH$_3$CN/Et$_2$O. $^1$H NMR (400 MHz, CD$_3$CN): 8.45 (dd, 4H), 8.28 (d, 2H), 8.03 (m, 6H), 7.82 (d, 2H), 7.54 (d, 2H), 7.40 (m, 6H), 4.44 (q, 4H), 1.33 (t, 6H). Elemental Analysis: Calculated for RuC$_{40}$H$_{35}$O$_4$N$_7$P$_2$F$_{12}$: C, 44.95; H, 3.30; N, 9.17; Found: C, 44.77; H, 3.31; N, 9.00.

The crystal used for the x-ray structure determination was obtained by recrystallization from CH$_3$CN/Et$_2$O, however no CH$_3$CN was located in the crystal structure. Evidently, the solvent is weakly bound within the crystals and is lost upon standing in air for several weeks without disrupting the crystalline structure.

**Sensitized Metal-Oxide Thin Film Electrodes.** Transparent TiO$_2$ nanocrystallites (anatase, ~15 nm in diameter) were prepared by hydrolysis of the Ti(i-OPr)$_4$ using a sol-gel technique previously described in the literature.$^{19}$ The sols were cast as mesoporous thin films (~10 μm thick) by doctor blading onto glass microscope slides for spectroscopic measurements, transparent FTO conductive substrates for electrochemical measurements, and microscope slides for transmission-mode spectroscopic measurements. Scotch tape was employed as a spacer. In all cases, the thin films were annealed at 420 °C for 30 min. under O$_2$ flow.

Sensitization was achieved by immersing the supported thin films in sensitizer acetonitrile solutions (μM concentrations) overnight. Films were then soaked in the neat
CH$_3$CN for 5 – 10 minutes followed by a thorough washing with the experimental solvent. Unless noted otherwise, the thin films were sensitized to roughly maximum surface coverage, $\Gamma \sim 7 \times 10^{-8}$ mol/cm$^2$, which was calculated by a modified Beer–Lambert Law formula: $A = \varepsilon \times \Gamma \times 1000$. The samples were then quickly transferred to a standard 1 cm square quartz cuvette containing the experimental solution and were positioned diagonally (for microscope slide-supported films) or parallel (for FTO-supported films) in the cuvette. For at least 30 minutes prior to transient absorption and electrochemical studies, the cuvettes containing the sample and electrolyte solution were purged with Ar gas which was pre-moistened with the same electrolyte solution.

**UV–Visible Absorption.** Steady-state UV–visible (Vis) absorbance spectra were obtained on a Varian Cary 50 spectrophotometer at room temperature. Nanosecond transient absorption measurements were obtained with an apparatus similar to that which has been previously described.$^{20}$ Briefly, samples were excited by a pulsed Nd:YAG laser (Quantel USA (BigSky) Brilliant B; 5 – 6 ns full width at half maximum (fwhm), 1 Hz, ~10 mm in diameter) tuned to 532 nm with the appropriate non-linear optics. The excitation fluence was measured by a thermopile power meter (Molelectron) and was typically 3 – 4 mJ/pulse so that the absorbed fluence was typically < 1 mJ/pulse, unless noted otherwise. A 150 W Xenon arc lamp (OSRAM; Applied Photophysics) served as the probe beam and was aligned orthogonal to the laser excitation light. For detection at sub-100 microsecond timescales the lamp was pulsed with 100 V. Detection was achieved with a Spex 1702/04 monochromator optically coupled to a Hamamatsu R-928 photomultiplier tube. The overall instrument response time was approximately 10 ns.

**Photoluminescence.** Steady-state PL measurements were obtained with a Spex Fluorolog
1681 spectrometer or 1682 double spectrometer. PL spectra were corrected for both irradiance fluctuations and the wavelength-dependent system detection by calibration with a traceable, 45 W tungsten–halogen irradiance-standard lamp.

**Infrared Absorption.** Attenuated Total Reflection (ATR) FTIR absorbance spectra were obtained using a Thermo Scientific Nicolet Nexus 670 spectrophotometer with a Golden Gate ATR accessory. The measurements were made under an N\textsubscript{2} atmosphere and the spectra were averaged for 256 scans with 4 cm\textsuperscript{-1} resolution.

**Electrochemistry.** A BAS model CV-50W or Epsilon electrochemical analyzer potentiostat was employed in a standard three-electrode arrangement with a glassy carbon working electrode, a Pt gauze counter electrode, and a Ag/AgNO\textsubscript{3} reference electrode.

### 4.3 Results

Crystals suitable for X-ray structure determination were prepared by diffusion of diethyl ether into a CH\textsubscript{3}CN solution of [Ru(bpy)\textsubscript{2}(defm)](PF\textsubscript{6})\textsubscript{2} or [Ru(bpy)\textsubscript{2}(dfm)]Cl\textsubscript{2} with methanol, Figure 4.1. Crystallographic data and selected bond angles/distances are given in Table 4.1 and Table 4.2, respectively. The N(5)-Ru-N(6) angle for dfm was 82.41°, and the analogous angles, N(2)-Ru-N(1) and N(3)-Ru-N(4) for the two bpy ligands were 78.94° and 79.84° respectively. The Ru-N(5) and Ru-N(6) distances for [Ru(bpy)\textsubscript{2}(dfm)]\textsuperscript{2+} were 2.115 Å and 2.108 Å respectively, whereas the four bpy Ru-N distances were 2.050 Å, 2.052 Å, 2.058 Å, and 2.063 Å. The dihedral angles between the pyridine rings were 4.10° and 3.55° for the two bipyridine ligands and 1.73° for dfm. The two carboxylic acid groups were not equal since the torsion angles for C(34)-C(32)-C(33)-O(1) and C(33)-C(32)-C(34)-O(4) were different (106.1° and 149.5° respectively).
Figure 4.1: Displacement ellipsoid plots (50% probability level) for the cations [Ru(bpy)$_2$(dfm)]$^{2+}$ (left) and [Ru(bpy)$_2$(defm)]$^{2+}$ obtained from their respective crystal structures. H-atoms were omitted for the sake of clarity.
Table 4.1: Crystallographic Data for [Ru(bpy)_2(dfm)]Cl_2·3CH_3OH and [Ru(bpy)_2(defm)](PF_6)_2.

<table>
<thead>
<tr>
<th></th>
<th>[Ru(bpy)_2(dfm)] Cl_2·5CH_3OH*</th>
<th>[Ru(bpy)_2(defm)] (PF_6)_2*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C_{37} H_{36} Cl_2 N_6 O_7 Ru*</td>
<td>C_{38} H_{32} N_6 O_4 P_2 F_{12} Ru*</td>
</tr>
<tr>
<td>Formula weight</td>
<td>848.69*</td>
<td>1027.70*</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>110</td>
<td>173</td>
</tr>
<tr>
<td>Wavelength (Å)</td>
<td>0.71073</td>
<td>0.71073</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2(1)/c</td>
<td>P2(1)/c</td>
</tr>
<tr>
<td>a (Å)</td>
<td>8.82563(16)</td>
<td>11.744(4)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>18.6217(4)</td>
<td>30.697(11)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>25.0098(4)</td>
<td>12.589(4)</td>
</tr>
<tr>
<td>β</td>
<td>95.5838(15)</td>
<td>113.201(9)</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>4090.81(13)</td>
<td>4171(3)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>D_{calc} (g/cm³)</td>
<td>1.473</td>
<td>1.636</td>
</tr>
<tr>
<td>Absorption coefficient (cm⁻¹)</td>
<td>0.566*</td>
<td>0.554*</td>
</tr>
<tr>
<td>F(000)</td>
<td>1736*</td>
<td>2064*</td>
</tr>
<tr>
<td>Crystal size (mm)</td>
<td>0.87 x 0.37 x 0.29</td>
<td>0.33 x 0.02 x 0.18</td>
</tr>
<tr>
<td>Theta max for data collection (°)</td>
<td>26.00</td>
<td>25.67</td>
</tr>
<tr>
<td>Final R indices [I&gt;2σ(I)]</td>
<td>R1 = 0.0407</td>
<td>R1 = 0.0489</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>wR2 = 0.1009</td>
<td>wR2 = 0.1277</td>
</tr>
</tbody>
</table>

* These data are given by excluding the contribution of the unresolved residual electron density via the Squeeze program by A.L. Spek, Acta Cryst. 2009, D65, 148-155.
**Table 4.2:** Selected bond distances and angles for [Ru(bpy)$_2$(dfm)]Cl$_2$·5CH$_3$OH and [Ru(bpy)$_2$(defm)] (PF$_6$)$_2$.

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Bond</th>
<th>Distance (Å)</th>
<th>Ligand</th>
<th>Bond</th>
<th>Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>bpy-1</td>
<td>Ru-N(1)</td>
<td>2.063(2)</td>
<td>bpy-1</td>
<td>Ru-N(4)</td>
<td>2.066(3)</td>
</tr>
<tr>
<td></td>
<td>Ru-N(2)</td>
<td>2.051(2)</td>
<td></td>
<td>Ru-N(3)</td>
<td>2.056(3)</td>
</tr>
<tr>
<td>bpy-2</td>
<td>Ru-N(3)</td>
<td>2.045(2)</td>
<td>bpy-2</td>
<td>Ru-N(1)</td>
<td>2.054(3)</td>
</tr>
<tr>
<td></td>
<td>Ru-N(4)</td>
<td>2.062(2)</td>
<td></td>
<td>Ru-N(2)</td>
<td>2.061(3)</td>
</tr>
<tr>
<td>dfm</td>
<td>Ru-N(5)</td>
<td>2.113(2)</td>
<td>defm</td>
<td>Ru-N(5)</td>
<td>2.125(3)</td>
</tr>
<tr>
<td></td>
<td>Ru-N(6)</td>
<td>2.107(2)</td>
<td></td>
<td>Ru-N(6)</td>
<td>2.119(3)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Points</th>
<th>Angle (°)</th>
<th>Ligand</th>
<th>Points</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>bpy-1</td>
<td>N(1)-Ru-N(2)</td>
<td>78.98(10)</td>
<td>bpy-1</td>
<td>N(3)-Ru-N(4)</td>
<td>79.17(13)</td>
</tr>
<tr>
<td>bpy-2</td>
<td>N(3)-Ru-N(4)</td>
<td>79.59(10)</td>
<td>bpy-2</td>
<td>N(1)-Ru-N(2)</td>
<td>79.02(12)</td>
</tr>
<tr>
<td>dfm</td>
<td>N(5)-Ru-N(6)</td>
<td>82.18(9)</td>
<td>defm</td>
<td>N(5)-Ru-N(6)</td>
<td>86.03(13)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Planes</th>
<th>Dihedral angle (°)</th>
<th>Planes</th>
<th>Dihedral angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>bpy-1 – bpy-2</td>
<td>83.24(9)</td>
<td>bpy-1 – bpy-2</td>
<td>86.24(12)</td>
</tr>
<tr>
<td>bpy-1 – dfm</td>
<td>86.80(8)</td>
<td>bpy-1 – defm</td>
<td>81.23(11)</td>
</tr>
<tr>
<td>bpy-2 - dfm</td>
<td>83.98(7)</td>
<td>bpy-2 - defm</td>
<td>84.30(11)</td>
</tr>
</tbody>
</table>
The electronic absorption spectra for \([\text{Ru(bpy)}_2(\text{dfm})]\text{Cl}_2\) and \([\text{Ru(bpy)}_2(\text{defm})](\text{PF}_6)_2\) in \(\text{CH}_3\text{CN}\) solution are shown in Figure 4.2. The expected MLCT transitions in the visible region were observed, as were the bpy-centered \(\pi-\pi^*\) transitions at 285 nm. The extinction coefficient for the \([\text{Ru(bpy)}_2(\text{dfm})]\text{Cl}_2\) compound was larger than the diester compound. The addition of 8 equivalents of \(\text{HClO}_4\) to the \([\text{Ru(bpy)}_2(\text{dfm})]\text{Cl}_2/\text{ACN}\) solution blue-shifted the MLCT peak by 4 nm and increased the oscillator strength of both the MLCT and ligand based transitions while the addition of 8 equivalents of triethylamine (TEA) resulted in a red shift of \(~3\) nm to the MLCT maximum, a decrease in oscillator strengths and the accentuation of a shoulder at approximately 325 nm. Room temperature time-resolved PL and transient absorption measurements revealed pulse-limited responses consistent with excited state lifetimes \(<10\) ns in fluid solution. However, in a 4:1 (v/v) \(\text{EtOH}:\text{MeOH}\) glass at 77 K, visible light excitation of \([\text{Ru(bpy)}_2(\text{dfm})]\text{Cl}_2\) alone or with added TEA led to steady state PL. The PL spectra displayed a vibrational spacing of \(~1300\) cm\(^{-1}\) typical of MLCT excited states, Figure 2. Both the ester and the protonated carboxylic acid forms were extremely weak emitters. Excited state decay observed after pulsed excitation of \([\text{Ru(bpy)}_2(\text{dfm})]\text{Cl}_2\) at 77 K was non-exponential but could be fit to a bi-exponential kinetic model, Table 3. With added TEA, first-order kinetics were observed, \(\tau = 5.94\) \(\mu\)s, while the excited state lifetimes of the protonated and ester forms could not be resolved, \(\tau < 10\) ns.
Figure 4.2: Room-temperature UV–Visible absorption spectra in CH$_3$CN (left) and steady-state photoluminescence spectra measured at 77 K in MeOH:EtOH glass (right), under the indicated conditions.

$\varepsilon \times 10^3$ (M$^{-1}$ cm$^{-1}$)

Wavelength (nm)

PL Intensity (a.u.)

Wavelength (nm)
Cyclic voltammetry revealed a Ru\textsuperscript{III/II} redox process at positive potentials that was termed quasi-reversible because although the anodic and cathodic currents were approximately equal, the peak-to-peak separation was typically 80 – 100 mV over scan rates of 10 – 100 mV/s.\textsuperscript{22,23} Cathodic excursions resulted in ligand-based reductions that were quasi-reversible for [Ru(bpy)\textsubscript{2}(dfm)](PF\textsubscript{6})\textsubscript{2} and irreversible for [Ru(bpy)\textsubscript{2}(dfm)]Cl\textsubscript{2}, Figure 4.3 and Table 4.3. The compounds were anchored to TiO\textsubscript{2} by overnight reactions in CH\textsubscript{3}CN. Both compounds were bound to TiO\textsubscript{2} with saturation surface coverages of 3 x 10\textsuperscript{-8} mol/cm\textsuperscript{2}, typical of Ru\textsuperscript{II} sensitizers with a dcb ligand. The sensitized films are abbreviated Ru(bpy)\textsubscript{2}(dfm)/TiO\textsubscript{2} and Ru(bpy)\textsubscript{2}(defm)/TiO\textsubscript{2} throughout.

Attenuated total reflection Fourier transform infra-red (ATR-FTIR) measurements of [Ru(bpy)\textsubscript{2}(dfm)]Cl\textsubscript{2} showed expected bipyridine ring vibrations and an intense peak at 1710 cm\textsuperscript{-1} with shoulders at 1721 cm\textsuperscript{-1}, 1704 cm\textsuperscript{-1}, and 1695 cm\textsuperscript{-1}. When anchored to TiO\textsubscript{2}, the absorptions in the 1695-1721 cm\textsuperscript{-1} region were replaced by a broad absorption centered at 1640 cm\textsuperscript{-1} and a peak at 1360 cm\textsuperscript{-1}. The solid [Ru(bpy)\textsubscript{2}(defm)](PF\textsubscript{6})\textsubscript{2} diethylester derivative showed an intense band at 1745 cm\textsuperscript{-1} that tailed to 1700 cm\textsuperscript{-1}, while intense peaks were observed at 1738 cm\textsuperscript{-1} and 1731 cm\textsuperscript{-1} on TiO\textsubscript{2}.

Pulsed 532 nm light excitation of Ru(bpy)\textsubscript{2}(dfm)/TiO\textsubscript{2} or Ru(bpy)\textsubscript{2}(defm)/TiO\textsubscript{2} thin films immersed in 0.1 M LiClO\textsubscript{4} CH\textsubscript{3}CN resulted in the instrument response limited appearance of spectral features reasonably assigned to oxidized sensitizer and an electron injected in TiO\textsubscript{2}, Figure 4.4. A bleach of the MLCT absorption band and a positive weak absorption in the red region were observed. Excited state injection yields estimated by comparative actinometry on a nanosecond time scale\textsuperscript{24} were $\phi_{\text{inj}} = 0.70 \pm 0.05$ for
Figure 4.3: Cyclic voltammograms of [Ru(bpy)$_2$(dfm)]Cl$_2$ (red) and [Ru(bpy)$_2$(defm)](PF$_6$)$_2$ (blue) dissolved in 0.1 M TBAP/CH$_3$CN. Measurements were made at room temperature at a scan rate of 100 mV/s.
### Table 4.3: Photophysical and electrochemical properties for the Ru(II) compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>UV- Vis Absorption$^a$</th>
<th>PL 77 K$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\lambda_{\text{max}}$/nm $\quad (\varepsilon/M^{-1}\text{cm}^{-1})$</td>
<td>$\lambda_{\text{max}}$/nm $\quad \tau/\mu$s</td>
</tr>
<tr>
<td>[Ru(bpy)$_2$(dfm)] Cl$_2$</td>
<td>285 (60500) $\quad$ 444 (11200)</td>
<td>578 $\quad$ 0.38</td>
</tr>
<tr>
<td>[Ru(bpy)$_2$(dfm)] Cl$_2$ + HClO$_4$</td>
<td>285 (64900) $\quad$ 440 (12600)</td>
<td>-- $\quad$ &lt; 0.01</td>
</tr>
<tr>
<td>[Ru(bpy)$_2$(dfm)] Cl$_2$ + TEA</td>
<td>286 (56500) $\quad$ 447 (10800)</td>
<td>576 $\quad$ 5.94</td>
</tr>
<tr>
<td>[Ru(bpy)$_2$(defm)] (PF$_6$)$_2$</td>
<td>285 (42700) $\quad$ 439 (8200)</td>
<td>-- $\quad$ &lt; 0.01</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>E/V (vs. Ag/AgNO$_3$)$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Compound</strong></td>
</tr>
<tr>
<td>[Ru(bpy)$_2$(dfm)] Cl$_2$</td>
</tr>
<tr>
<td>[Ru(bpy)$_2$(defm)] (PF$_6$)$_2$</td>
</tr>
<tr>
<td>[Ru(bpy)$_2$(dafo)] (PF$_6$)$_2$ $^c$</td>
</tr>
<tr>
<td>[Ru(bpy)$_3$]$^{2+}$ $^c$</td>
</tr>
</tbody>
</table>

$^a$ Measured in acetonitrile at room temperature. $^b$ Measured in 4:1 EtOH:MeOH glass.

$^c$ Measured in 0.1 M TBAClO$_4$/CH$_3$CN at room temperature. $^d$ Irreversible reduction.

$^e$ Data taken from reference 33.
Figure 4.4: Absorption difference spectra measured at the indicated times after pulsed 532 nm light excitation of Ru(bpy)$_2$(dfm)/TiO$_2$ (left) and Ru(bpy)$_2$(defm)/TiO$_2$ (right). The insets display single wavelength absorption transients at the indicated irradiances.
both sensitized materials. The instrument response-limited appearance of this product was consistent with an excited state injection rate constant, $k_{\text{inj}} > 10^8$ s$^{-1}$. Recombination of the injected electron with the Ru$^{\text{III}}$ metal center occurred quantitatively on a millisecond time scale that gave rise to absorption transients that cleanly returned to the baseline before the next laser pulse. The recombination kinetics were monitored over the first ten microseconds where recombination was observed to be significantly faster for the dfm compound relative to the diester, Figure 4.4 insets.

The incident photon-to-current efficiency (IPCE) was measured in regenerative solar cells with a 0.5 M LiI/0.05 M I$_2$/CH$_3$CN electrolyte. This electrolyte was found to result in significant desorption for Ru(bpy)$_2$(dfm)/TiO$_2$ that precluded quantitative measurements. For Ru(bpy)$_2$(dfm)/TiO$_2$, a sustained photocurrent was observed with a photocurrent action spectrum that closely resembled the absorptance spectrum, plotted as one minus the transmittance, T, of the sensitized thin film, Figure 4.5. The maximum IPCE value was 0.70 ± 0.05.

4.4 Discussion

A new ambidentate ligand useful for coordination to Ru$^{\text{II}}$ and binding to a metal oxide semiconductor was synthesized, characterized, and tested. The dfm ligand provides a 2,2’-bipyridine chelate for Ru$^{\text{II}}$ with an olefin bridge in the 3 and 3’ positions to two carboxylic acid groups. The coordinated ligand dramatically decreased the lifetime of the metal-to-ligand charge transfer (MLCT) excited states in fluid solution yet still efficiently sensitized TiO$_2$. In the following discussion, the MLCT excited state, redox properties,
Figure 4.5: The incident photon to current efficiency (IPCE) and absorptance spectra measured for Ru(bpy)$_2$(dfm)/TiO$_2$ in a regenerative solar cell with a 0.5 M LiI/0.05 M I$_2$ acetonitrile electrolyte.
surface binding, and injection yield are described and contrasted with the widely utilized dcbligand.

Crystallographic data for [Ru(bpy)$_2$(dfm)]$^{2+}$ revealed a distorted octahedral geometry around the Ru$^{II}$ metal center, with Ru-N$_{bpy}$ and Ru-N$_{dfm}$ bond lengths of about 2.050 and 2.115 Å, respectively. The elongated Ru-N$_{dfm}$ bonds are reasonably attributed to the slightly increased N-N bite angle of the dfm ligand that results from linking the two pyridine rings together. A convenient way of visualizing this is shown in Scheme 4.2, where the atomic coordinates from the crystal structures of [Ru(bpy)$_3$]$^{2+}$ and [Ru(bpy)$_2$(dfm)]$^{2+}$ are overlaid with the N-Ru-N atoms defining the plane of this text. From this viewpoint, one clearly sees that the olefin group has the effect of pulling the 3 and 3’ carbons closer and hence opening the Ru bite angle by about three degrees. The elongation of the Ru-N bond that results is also observed. In contrast, when crystallographic data for [Ru(dcb)(bpy)$_2$]$^{2+}$ and [Ru(bpy)$_3$]$^{2+}$ are overlaid in the same manner, right hand side of Scheme 2, there is no significant change evident in the bond angle or lengths. The structures are essentially superimposable. One might have anticipated that the electron withdrawing CO$_2$H group would influence the Ru-N$_{pyr}$ bond length. However, any inductive influence that decreases the basicity of the pyridyl nitrogens in dcb must be offset by enhanced back-bonding as there is no significant difference between dcb and bpy coordination to Ru$^{II}$ in the solid state. Scheme 4.3 provides a side-on view of the Ru(bpy), Ru(dcb), and Ru(dfm) fragments taken from the crystal structures of [Ru(bpy)$_3$]$^{2+}$, [Ru(bpy)$_2$(dcb)]$^{2+}$, and [Ru(bpy)$_2$(dfm)]$^{2+}$, respectively.
Scheme 4.2: Ru(dfm) overlaid on Ru(bpy) on the left and Ru(deb) overlaid on Ru(bpy) on the right.
The larger dihedral angle between the two pyridine rings of dcb relative to bpy in Scheme 4.3 was particular to these specific compounds and was not significant in a review of 11 crystal structures of ruthenium compounds with 17 coordinated dcb ligands.\textsuperscript{22,25-30} The dihedral angles ranged between 0.6 and 13 degrees for coordinated dcb and bpy ligands. The bridging olefin in the 3 and 3’ positions of dfm maintains planarity of the two pyridyl rings while a significant change in the out-of-plane orientation of the oxygen atoms of the carboxylic acid groups in dfm relative to dcb was clearly observed. The oxygen atoms of the ester groups in [Ru(bpy)]\textsubscript{2}(defm)]\textsuperscript{2+} were also significantly out of the pyridine plane. How the solid state crystal structures are related to those when the compounds are anchored to TiO\textsubscript{2} and how this might influence interfacial electron transfer is presently unknown. However, the influence on excited state behavior is evident. The elongated Ru-N\textsubscript{dfm} bond lengths measured in the solid state imply weaker bonds. Hence, 2,2’-bipyridine is expected to be a stronger field ligand than dfm. This is important as the presence of low-lying ligand field (LF) states are known to decrease MLCT excited state lifetimes and result in unwanted photochemistry.\textsuperscript{21} Indeed, previous photophysical data reported for 3,3’-bridged bipyridyl Ru\textsuperscript{II} compounds, based mainly on 4,5-diazafluoren-9-one and closely related derivatives, reveal short lived excited states consistent with MLCT → LF internal conversion.\textsuperscript{31-34}

Both [Ru(bpy)]\textsubscript{2}(dfm)]Cl\textsubscript{2} and [Ru(bpy)]\textsubscript{2}(defm)](PF\textsubscript{6})\textsubscript{2} displayed no significant PL at room temperature in acetonitrile solution with excited state lifetimes < 10 ns, behavior that is also reasonably assigned to MLCT excited state deactivation by low-lying LF states.
Scheme 4.3: Side-on view, perpendicular to the N-Ru-N plane, of the Ru(bpy), Ru(dcb), and Ru(dfm) fragments taken from the crystal structures of [Ru(bpy)$_3$]$^{2+}$, [Ru(bpy)$_2$(dcb)]$^{2+}$, and [Ru(bpy)$_2$(dfm)]$^{2+}$, respectively. Ruthenium atoms are magenta, carbon atoms are gray, oxygen atoms are red and nitrogen atoms are blue.
Cyclic voltammetry of $[\text{Ru(bpy)}_2(\text{dfm})]^{2+}$ displayed an irreversible reduction while reduction of the corresponding ester compound, $[\text{Ru(bpy)}_2(\text{defm})]^{2+}$, was reversible. Similarly, reduction of coordinated dcb ligands is irreversible while ester derivatives, such as $4,4'-(\text{CO}_2\text{Et})_2$-bpy, are reversible. The irreversible nature of dcb reductions has reasonably been attributed to hydrogen gas formation from the carboxylic acid protons.$^{35}$ The same may be true for $[\text{Ru(bpy)}_2(\text{dfm})]^{2+}$. Comparisons with literature data show that the first reduction of $[\text{Ru(bpy)}_2(\text{defm})]^{2+}$ is localized on the coordinated defm ligand. The coincidence of the irreversible reduction of $[\text{Ru(bpy)}_2(\text{dfm})]^{2+}$ and the reversible reduction of $[\text{Ru(bpy)}_2(\text{defm})]^{2+}$, indicates that the dfm ligand is also reduced first. For heteroleptic Ru$^{II}$ coordination compounds, DeArmond noted that the first ligand reduced electrochemically was the same ligand that the excited state localizes upon in the thermally equilibrated or 'thexi' excited state.$^{36}$ Therefore, the relaxed MLCT excited state is reasonably formulated as $[\text{Ru}^{III}(\text{bpy})_2(\text{dfm}^-)]^{2+*}$ and $[\text{Ru}^{III}(\text{bpy})_2(\text{defm}^-)]^{2+*}$. The equilibrated excited state is thus expected to be localized upon the ligand that binds to TiO$_2$.

Infrared analysis of the surface bound sensitizers were consistent with carboxylate binding. Deacon and Philips have examined the Raman and infrared spectroscopy of x-ray crystallographically characterized metal carboxylate compounds and reported a correlation between the nature of the carboxylate-metal coordination mode and the energy separation between the antisymmetric and symmetric CO stretches, $\Delta = v_{\text{assym}}(\text{CO}_2^-) - v_{\text{sym}}(\text{CO}_2^-)$. This $\Delta$ parameter has been used as an indirect measure of the surface linkage that results from the reaction of carboxylic acid containing compounds with heterogeneous metal oxide surfaces.$^{38-40}$ In this study, ATR-FTIR analysis of
Ru(bpy)$_2$(dfm)/TiO$_2$ sensitized films yielded a $\Delta = 280$ cm$^{-1}$ that is most consistent with a surface linkage where each carboxylate oxygen is linked to a single surface site, presumably Ti$^{IV}$. In previous studies of malonic acid binding to DeGussa P-25 TiO$_2$ particles, Dolamic and Bürgi proposed similar carboxylate binding for one of the $\text{-CO}_2$ groups with a monodentate/H-bonding mode for the other.$^{41}$ We note that DeGussa P25 is known to be a mixture of anatase and rutile TiO$_2$ polymorphs and this may underlie the different binding modes observed. The vibrational spectrum of Ru(bpy)$_2$(defm)/TiO$_2$ showed no evidence for hydrolysis of the ester groups and easily desorbed from TiO$_2$. Notably absent in the ATR-FTIR data of either sensitized material was any evidence for ring-opening of the central five membered ring as had been previously noted after TiO$_2$ surface reactions with [Ru(bpy)$_2$(dafo)]$^{2+}$, where dafo is 4,5-diazofluoren-9-one.$^{42}$

Excited state injection into TiO$_2$ was observed to occur with a quantum yield of 0.7 for both sensitizers on a nanosecond time scale. The incident photon-to-current efficiency also reached 0.7 in regenerative solar cells. As electron injection from ligand field states is unprecedented, sub-nanosecond injection from the MLCT excited state is expected. For other Ru$^{II}$ and Fe$^{II}$ compounds with low-lying ligand field states there is compelling evidence that non-radiative decay and/or spin trapping by high spin states competes kinetically with excited state injection thereby lowering the quantum yield; the observation of an excitation wavelength dependence to excited state injection was consistent with electron transfer from non-thermally equilibrated excited states.$^{6-8}$ However, in the present study, the high IPCE measured for Ru(bpy)$_2$(dfm)/TiO$_2$ in regenerative solar cells closely followed the absorbance spectrum of the sensitized film consistent with wavelength independent excited state injection.
4.5 Conclusion

A new ambidentate dicarboxylic acid ligand, dfm, that provides a continuous conjugation pathway from 2,2’-bipyridine (bpy) to a metal oxide surface was synthesized and coordinated to [Ru(bpy)₂] for sensitization of TiO₂. Even though the [Ru(bpy)₂(dfm)]²⁺ MLCT excited state lifetime was < 10 ns, efficient interfacial electron transfer to TiO₂ was observed with φᵢᵣᵢ = 0.70 ± 0.05. The shortened MLCT excited state was attributed to the bridging olefin that increased the N-Ru-N bite angle in the dfm ligand, thereby elongating the Ru-N bonds and stabilizing anti-bonding ligand field excited states. The dfm ligand provides a new alternative to the commonly utilized dcb ligand for the coordination of transition metal compounds to metal oxide surfaces.

4.6 References

(5) Benkoe, G.; Myllyperkioe, P.; Pan, J.; Yartsev, A. P.; Sundstroem, V. Journal of the American Chemical Society 2003, 125, 1118-1119.


Appendix 1: $^1$H NMR Spectra

The $^1$H NMR spectra of the ruthenium polypyridyl compounds used in Chapter 2 of this thesis were measured in deuterated dichloromethane (CD$_2$Cl$_2$) and those compounds used in Chapter 3 of this thesis were measured in deuterated acetone (acetone-d$_6$). For each compound the spectrum is displayed above the peak assignment data in its respective figure.

The $^1$H NMR spectra of $[\text{Ru(bpy)}_3]^{2+}$, $[\text{Ru(bpy)}_2(\text{deeb})]^{2+}$ and $[\text{Ru(deeb)}_3]^{2+}$ in CD$_2$Cl$_2$ solution were measured and peak assignments were made. For $[\text{Ru(bpy)}_3]^{2+}$, Figure A1.1, the two doublets at 7.716 and 8.425 ppm were assigned to C-3H and C-6H with only one adjacent hydrogen each. The literature value for the coupling constant between hydrogens at position C-3 and C-4 (notated as (3,4)) in pyridine is 7-9 Hz while for (5,6) the literature value is 5-6 Hz. Therefore, the peak at 8.425 ppm was assigned to C-3H and the peak at 7.716 ppm was assigned to C-6H. Since the pyridine (3,4) and (4,5) coupling constants are both 7-9 Hz, it was expected that the peak for C-4H would be split by approximately the same amount by both C-3H and C-5H, thereby producing a triplet pattern, whereas the (4,5) and (5,6) coupling constants were significantly different, producing a doublet of doublets pattern. Therefore, the peak at 7.474 ppm was assigned to C-5H and the peak at 8.074 ppm to C-4H.

For $[\text{Ru(deeb)}_3]^{2+}$, Figure A1.2, the peak at 8.993 ppm had two coupling constants that were too small to be assigned to adjacent hydrogens, therefore, this peak was assigned to C-3H. The (5,6) is approximately 6 Hz and the peak with the larger second coupling constant (1.7 Hz) was assigned to the hydrogen closer to C-3H, so this peak was assigned to C-5H and the smaller second coupling constant (0.6 Hz) was assigned to C-
6H. The literature pyridine values for (3,5) and (3,6) are 1-2 Hz and 0-1 Hz, in agreement with this analysis.¹

As expected, the analogous peaks in the spectrum of [Ru(bpy)₂(deeb)]²⁺ were only shifted slightly from the homoleptic [Ru(bpy)₃]²⁺ and [Ru(deeb)₃]²⁺ spectra and the same assignment process as above was used, Figure A1.3. However, with [Ru(bpy)₂(deeb)]²⁺, symmetric hydrogens on the same bpy ligand, but different pyridyl rings, were no longer equivalent and had slightly different chemical shifts. Crosspeaks in an NOE spectrum indicated that the peak for bpy C-6H, where the bpy C-6 to bpy C-6H bond points at the center of a bpy pyridyl ring, was probably downfield of the bpy C-6’H, which points at a deeb pyridyl ring. Likewise, the bpy C-5H was probably downfield of the bpy C-5’H. The NOE data did not differentiate bpy C-4H from bpy C-4’H.

The ¹H NMR spectra of [Ru(bpy)₃]²⁺, [Ru(bpy)₂(phen)]²⁺, [Ru(phen)₃]²⁺ and [Ru(dmb)₃]²⁺ in acetone-d₆ solution were measured and peak assignments were made. For [Ru(bpy)₃]²⁺, Figure A1.4, the same reasoning as for [Ru(bpy)₃]²⁺ in CD₂Cl₂ was used to assign the peaks. The peak positions in acetone-d₆ were in the same sequence as in CD₂Cl₂ but with all the peaks shifted downfield from 0.1 to 0.4 ppm; the C-3H and C-6H peaks were shifted the most. This effect is consistent with the lone pair electrons on acetone pulling the hydrogens slightly away from the bonded carbon atoms and thus to an area of lower electron density.

For [Ru(phen)₃]²⁺, the singlet at 8.4122 ppm was assigned to C-5H as this is the only position that should appear as a singlet. Likewise, the doublet of doublets (dd) peak at 7.8060 ppm was assigned to C-3H as this is the only position that should be split by two different adjacent hydrogens. Using the predicted coupling constants for pyridine,¹ C-2H
with a predicted coupling constant of 5-6 Hz was assigned to the peak at 8.4046 ppm and C-4H with a predicted coupling constant of 7-8 Hz was assigned to the peak at 8.7897 ppm.

For [Ru(bpy)$_2$(phen)]$^{2+}$, Figure A1.6, analogous hydrogens on opposite pyridyl rings of the same bpy ligand are no longer equivalent, just as for [Ru(bpy)$_2$(deeb)]$^{2+}$ above. The paired hydrogen positions are labeled “a” and “b” in Figure A1.6 such that all the “a” hydrogens have the larger downfield shift. It is not known whether these hydrogens are on the same pyridyl ring or not. Each couple of paired peaks have the same splitting pattern and were assigned to the bpy ligands while the four peaks that could not be paired were assigned to the phen ligand. The same reasoning as for [Ru(phen)$_3$]$^{2+}$ above was used to assign the peaks to the phen ligand hydrogens. The coupling constants and splitting patterns were also used to assign the bpy hydrogens. The bpy-C6-H is predicted to be split by the bpy-C5-H by 5-6 Hz, bpy-C4-H by 1-2 Hz and bpy-C3-H by 0-1 Hz and is assigned to the peaks at 7.8935 and 8.1850 ppm. The bpy-C5-H is predicted to be split by the bpy-C6-H by 5-6 Hz, bpy-C4-H by 7-8 Hz and bpy-C3-H by 1-2 Hz and is assigned to the peaks at 7.3904 and 7.6387 ppm. The bpy-C4-H is predicted to be split by the bpy-C5-H and bpy-C3-H by 7-8 Hz in a triplet pattern and by the bpy-C6-H by 1-2 Hz and is assigned to the peak at 8.1454 and 8.2602 ppm. The bpy-C3-H is predicted to be split by the bpy-C4-H by 7-8 Hz, bpy-C5-H by 1-2 Hz and bpy-C6-H by 01-Hz and is assigned to the peaks at 8.8137 and 8.8575 ppm. Because the coupling constants for bpy-C5-H and bpy-C6-H are similar, the peaks appear as a doublet of triplets (dt) rather than a doublet of doublets of doublets (ddd).

For [Ru(dmb)$_3$]$^{2+}$, Figure A1.7, the singlet peak at 2.5643 ppm was immediately
assigned to the methyl hydrogens. The C3-H is the only aromatic hydrogen predicted to be a singlet and was assigned to the peak at 8.6637 ppm. The C3-H peak was also the most downfield peak for the bpy and deeb ligands. The C5-H and C6-H hydrogens were assigned using the same sequence as for the bpy ligand with C5-H as the most upfield aromatic hydrogen peak. The differentiation between these two hydrogen positions is somewhat uncertain.
Figure A1.1: $^1$H NMR spectrum of [Ru(bpy)$_3$](PF$_6$)$_2$ in CD$_2$Cl$_2$. The C-5H peak was the internal standard for integration.
Figure A1.2: $^1$H NMR spectrum of [Ru(deeb)$_3$](PF$_6$)$_2$ in CD$_2$Cl$_2$. The ester CH$_3$ peak was the internal standard for integration.
Figure A1.3: $^1$H NMR spectrum of [Ru(bpy)$_2$(deeb)](PF$_6$)$_2$ in CD$_2$Cl$_2$. The ester CH$_2$ peak was the internal standard for integration.
Figure A1.4: $^1$H NMR spectrum of [Ru(bpy)$_3$](PF$_6$)$_2$ in acetone-$d_6$. 
Figure A1.5: $^1$H NMR spectrum of [Ru(phen)$_3$](PF$_6$)$_2$ in acetone-d$_6$. 

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<td>8.4046</td>
<td>6 H</td>
<td>d</td>
<td>J = 6.1</td>
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<tr>
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<td>7.8060</td>
<td>6 H</td>
<td>dd</td>
<td>J = 8.3, 5.3</td>
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<td>8.7897</td>
<td>6 H</td>
<td>d</td>
<td>J = 8.1</td>
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</tr>
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<td>C5-H</td>
<td>8.4122</td>
<td>6 H</td>
<td>s</td>
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</table>
**Figure A1.6:** $^1$H NMR spectrum of [Ru(bpy)$_2$(phen)](PF$_6$)$_2$ in acetone-$d_6$. The bpy hydrogen atoms on the two pyridyl rings are not equivalent because one is near the second bpy ligand and the other is near the phen ligand. For each bpy hydrogen position, the upfield and downfield peaks are labelled (a) and (b) respectively. All the (a) peaks, or all the (b) peaks, are not necessarily on the same pyridyl ring.
Figure A1.7: $^1$H NMR spectrum of [Ru(dmb)$_3$](PF$_6$)$_2$ in acetone-d$_6$. 
References:

Appendix 2: Molar Extinction Coefficients

The research presented in this thesis required that the molar extinction coefficients are known so that solution concentrations could be determined using UV-Vis absorbance measurements and Beer’s Law, Equation A2.1. Most literature reports do not include the extinction coefficients used, probably due to the inherent errors discussed below. Despite this general lack of reporting, extinction coefficients can be found for many ruthenium polypyridyl compounds in acetonitrile solutions, a few can be found for dichloromethane solutions and there is almost a complete absence of data for acetone solutions.

\[ A = \varepsilon C \ell \] Equation A2.1

All the ruthenium polypyridyl compounds measured were salts with PF_6^- as the counterion. The compounds were recrystallized from acetonitrile/diethylether, filtered and dried under vacuum. The mass of approximately 20 mg of ruthenium compound was measured to an accuracy of ± 0.1 mg (~0.5 %). The compound was dissolved in 50.0 ± 0.1 mL of solvent in a volumetric flask. Then 5.00 mL of solvent was placed in a quartz cuvette. Aliquots from the ruthenium solution were added to the cuvette using a 100-μL syringe in the difference mode and 10 UV-Vis scans were averaged. Typically, eight different concentrations were measured with an absorbance at the MLCT maximum between 0.1 and 1.0. A plot of absorbance at the MLCT maximum versus concentration gave a straight line with a slope equal to the extinction coefficient, Figure A2.1. The extinction coefficients measured in DMK and DCM are listed in Table A2.1 along with literature values in ACN and water.
Figure A2.1: UV-vis absorption spectra of various concentrations of $[\text{Ru(phen)}_3] \,(\text{PF}_6)_2$ in DMK (top). Plot of absorbance at $\lambda_{\text{max}}$ (446 nm) versus the concentration of $[\text{Ru(phen)}_3] \,(\text{PF}_6)_2$ in DMK with a slope equal to the extinction coefficient.
**Table A2.1:** Molar extinction coefficients (M$^{-1}$cm$^{-1}$) in various solvents. Values in black are measured in this work while values in green are from the indicated literature report and usually contained a counterion other than PF$_6^-$. The MLCT maximum wavelength is given in parentheses.

<table>
<thead>
<tr>
<th>Compound</th>
<th>DCM</th>
<th>DMK</th>
<th>ACN</th>
<th>H$_2$O</th>
</tr>
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<tbody>
<tr>
<td>Ru(bpy)$_3$</td>
<td>16,300 ± 150 (453 nm)</td>
<td>16,200 ± 100 (452 nm)</td>
<td>14,600 (452 nm)$^1$</td>
<td>14,600 (452 nm)$^2$</td>
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<tr>
<td>Ru(bpy)$_2$(deeb)</td>
<td>14,700 ± 300 (477 nm)</td>
<td>16,000 (478 nm)$^3$</td>
<td></td>
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</tr>
<tr>
<td>Ru(bpy)(deeb)$_2$</td>
<td>17,100 ± 200 (477 nm)</td>
<td>18,000 (477 nm)$^3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ru(deeb)$_3$</td>
<td>26,500 ± 300 (463 nm)</td>
<td>22,000 (467 nm)$^3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ru(bpy)$_2$(phen)</td>
<td>17,100 ± 300 (451 nm)</td>
<td>16,600 ± 200 (450 nm)</td>
<td>15,740 ± 30 (449 nm)</td>
<td>16,000 (452 nm)$^4$</td>
</tr>
<tr>
<td>Ru(phen)$_3$</td>
<td>21,300 ± 200 (447 nm)</td>
<td>20,200 ± 100 (446 nm)</td>
<td>18,400 (447 nm)$^5$</td>
<td>19,000 (447 nm)$^2$</td>
</tr>
<tr>
<td>Ru(dmb)$_3$</td>
<td>13,720 ± 140 (460 nm)</td>
<td>13,270 ± 80 (458 nm)</td>
<td>13,960 ± 180 (458 nm)</td>
<td>14,300 (460 nm)$^2$</td>
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<tr>
<td>TBAI</td>
<td>15,900 ± 500 (245 nm)</td>
<td>Obscured by solvent</td>
<td>16,300 (246nm)$^6$</td>
<td></td>
</tr>
<tr>
<td>TBAI$_3$</td>
<td>25,700 ± 400 (363 nm)</td>
<td>21,600 ± 400 (363 nm)</td>
<td>22,200 (361nm)$^6$</td>
<td></td>
</tr>
<tr>
<td>I$_2$</td>
<td>909 (503 nm)</td>
<td></td>
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</tbody>
</table>
The margin of error listed for the extinction coefficients was based on the least-squares fit of the absorbance versus concentration data. However, as long as the compound obeyed Beer’s Law at the concentrations tested, the reported error only reflects random errors in the various measurements: mass of the compound, absorbance, volumes of ruthenium compound solution added and total volume. Error in the calculated molecular weights were negligible. In fact, a rigorous propagation of error analysis for one of the compounds resulted in a predicted error of $\pm 200 \ \text{M}^{-1}\text{cm}^{-1}$, a value very similar to the least-squares values listed in Table A2.1. However, a systematic error due to impurities in the solid compound are not included. Impurities could be in the form of salts, free ligand or solvent left over from the synthesis or the recrystallization.

It should also be noted that the X-ray crystal structures of PF$_6^-$ salts of the ruthenium polypyridyl compounds often do not contain solvent molecules and the $^1$H NMR spectra of these compounds do not show any free ligand. Any impurity in the solid compound would make the absorbance less for a given mass of compound and the extinction coefficient would likewise be smaller. Therefore, the reported extinction coefficients in Table A2.1 are lower limits of the true extinction coefficients and are reported as the values used in this thesis.
References:


Appendix 3: Excited State Reduction Potentials

The MLCT excited states of ruthenium polypyridyl compounds consist, formally, of a Ru(III) metal center and a reduced ligand with the excited state electron in a π* orbital. The excited electron is a better reductant than the ground state and the hole left on the metal center is a better oxidant than the ground state. For photo-initiated oxidation of anions such as iodide, it is useful to know the excited state reduction potentials, however, these potentials could not be measured directly. Instead, they were calculated using data from three experiments, the PL spectra at 77K and at room temperature and the first reduction potential.

The PL spectra of the four ruthenium compounds used in chapter 2 and the four compounds used in chapter 3 of this thesis were measured in a 4:1 EtOH/MeOH glass at 77 K, Figure A3.1 (top). All of the spectra were consistent with the large body of literature of ruthenium polypyridyl compounds and exhibited a major peak at the highest energy as well as smaller vibronic peaks. The spectra were measured as a function of wavelength and then converted to wavenumbers following the procedure in Parker and Rees.¹ The spectra were modeled assuming two vibrational modes, a medium frequency mode in the range of 1500 cm⁻¹ and a low frequency mode in the range of 300 cm⁻¹. The spectra were fit to Equation A3.1 where I(E) is the PL intensity as a function of the PL energy, E₁ and E₂ are medium and low frequency vibrational mode energies with their respective quantum numbers n₁ and n₂ and Huang-Rhys factors S₁ and S₂, Δν₁/₂ is the full-width at half maximum (FWHM), E₀₀ is the energy difference between the vibrational ground state of the first excited electronic state (e₁=1, n₁=0, n₂=0) and the electronic and vibrational ground state (e₁=0, n₁=0, n₂=0) and E is the PL energy.² The
summation was over the lowest six vibrational quantum numbers for each mode and all energies were in wavenumbers. An example of the fit is shown in Figure A3.1 (bottom) for [Ru(phen)_3] (PF_6)_2. The parameters derived from the fits are displayed in Table A3.1.

**Equation A3.1:**

\[
I(E) = \sum_{n1=0}^{5} \sum_{n2=0}^{5} \left[ \frac{E_{00} - n_1E_1 - n_2E_2}{E_{00}} \right]^3 \left( \frac{S_{n1}^1}{n_1!} \right) \left( \frac{S_{n2}^2}{n_2!} \right) \exp \left\{ -4\ln(2) \left( \frac{E - E_{00} + n_1E_1 + n_2E_2}{\Delta\nu_{1/2}} \right) \right\}^2 \]

The PL spectra of the four compounds were also measured in acetone and in dichloromethane at room temperature, Figure A3.2 (top). All the compounds gave a broad peak with a Stokes shift of 152-213 nm for the compounds tested in acetone and 139-172 nm for the compounds tested in DCM. The room temperature PL spectra were also fit to Equation A3.1. An example of the fit is shown in Figure A3.2 (bottom) for [Ru(phen)_3] (PF_6)_2. However, the featureless spectra at room temperature cannot be fit to a unique set of seven parameters. Therefore the vibration mode energies, E_1 and E_2, were fixed at the values taken from fits of the 77K spectra. The derived parameters from the room temperature fits for both solvents are listed in Table A3.1 for the four compounds used in chapter 2 of this thesis and Table A3.2 for the four compounds used in chapter 3.

The energy stored in the thermally relaxed excited state (E_{00}) is the only parameter used in the calculation of the excited state reduction potential.

The oxidation and reduction potentials for the ground-state compounds were determined in acetone and dichloromethane using cyclic voltammetry. An example of the results is shown in Figure A3.3 for [Ru(bpy)_2(phen)](PF_6)_2 in both acetone and dichloromethane. In acetone the first metal-based oxidation, E^0(3+/2+), can be seen at
positive potentials while the successive reduction of each ligand, $E^0(2+/+)$, $E^0(+/0)$ and $E^0(0/-)$, can be seen at increasing negative potentials. In DCM the oxidizing and reducing excursions were measured separately and only the first one or two reductions could be obtained. In both solvents the oxidation and reductions were electrochemically reversible. The $E_{1/2}$ values are listed in Table A3.3.

The excited state reduction potential is given by Equation A3.2 where $E^0(2+/+)$ is the first reduction potential and $E_{00}$ is the energy stored in the excited state, taken from the room temperature data in Tables A3.1 and A3.2. The calculated excited state reduction potentials are listed in Table A3.4.

$$E^0(2+*+/+) = E^0(2+/+) + E_{00}$$  

Equation A3.2
Figure A3.1: (top) PL spectra of all four compounds in 4:1 EtOH/MeOH glass at 77K. (bottom) 77K PL spectrum of [Ru(phen)$_3$](PF$_6$)$_2$ (black dots) and the calculated fit (red line).
Figure A3.2: (top) Room temperature steady-state PL spectra in DMK. (bottom) Room temperature steady-state PL spectrum of [Ru(phen)₃]PF₆ in DMK (black dots) and the calculated fit (red line).
Table A3.1: PL parameters from fits at 77K and room temperature for compounds used in chapter 2 of this thesis.

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<th>Room Temp</th>
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<td>Ru(bpy)$_3$ in EtOH/MeOH</td>
<td>Ru(bpy)$_3$(deeb) in EtOH/MeOH</td>
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<tr>
<td>E$_00$ (cm$^{-1}$)</td>
<td>17168 ± 2</td>
<td>15972 ± 8</td>
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<td>E1 (cm$^{-1}$)</td>
<td>1410 ± 3</td>
<td>1443 ± 5</td>
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<tr>
<td>S1</td>
<td>0.62 ± .01</td>
<td>.43 ± 0.1</td>
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<tr>
<td>E2 (cm$^{-1}$)</td>
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<td>640 ± 14</td>
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<tr>
<td>S2</td>
<td>0.39 ± .01</td>
<td>.62 ± .02</td>
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<tr>
<td>FWHM (cm$^{-1}$)</td>
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<td>.84 ± .01</td>
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<tr>
<td>E$_00$ (cm$^{-1}$)</td>
<td>16887 ± 5</td>
<td>15403 ± 11</td>
<td>15693 ± 11</td>
<td>16186 ± 5</td>
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<td>E0 (mV)</td>
<td>2094 ± 1</td>
<td>1910 ± 1</td>
<td>1946 ± 1</td>
<td>2007</td>
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<td>E1 (cm$^{-1}$)</td>
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<td>0.481 ± .005</td>
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<td>FWHM (cm$^{-1}$)</td>
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<td>N</td>
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<td>0.652 ± .007</td>
<td>0.81 ± .01</td>
<td>0.811 ± .005</td>
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Table A3.2: PL parameters from fits at 77K and room temperature for compounds used in chapter 3 of this thesis.

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<th>[Ru(bpy)$_3$]$^{2+}$</th>
<th>[Ru(bpy)$_2$(phen)]$^{2+}$</th>
<th>[Ru(phen)$_3$]$^{2+}$</th>
<th>[Ru(dmb)$_3$]$^{2+}$</th>
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<tr>
<td>$E_{00}$ (cm$^{-1}$)</td>
<td>17168 ± 2</td>
<td>17345 ± 4</td>
<td>17652 ± 4</td>
<td>16862 ± 2</td>
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<td>$E_1$ (cm$^{-1}$)</td>
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<td>1387 ± 4</td>
<td>1386 ± 3</td>
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<td>S1</td>
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Figure A3.3: Cyclic Voltammetry of [Ru(bpy)$_2$(phen)](PF$_6$)$_2$ and 0.1 M TBAPF$_6$ in DMK (top) and DCM (bottom) at a scan rate of 100 mV/s.
Table A3.3: \( E_{1/2} \) values (mV) for various ruthenium polypyridyl compounds in 0.1 M TBAPF\(_6\) in DMK at 100 mV/s scan rate and 0.1 M TBAClO\(_4\) in DCM at 500 mV/s scan rate. Literature values in ACN are included for comparison. (a) Values taken from Caspar and Meyer in 0.1 M TEAClO\(_4\). (b) Values taken from Wacholtz et al in TBAPF\(_6\) electrolyte. (c) Values taken from Tokel-Takvoryan et al in 0.1 M TBABF\(_4\).

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**Table A3.4:** Excited state reduction potentials in acetone, dichloromethane and acetonitrile. Potentials are vs. SCE.

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<th>$E_{1/2}^{+2^* / +}$ (mV)</th>
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References:


Appendix 4: Diiodide Absorption Spectrum and Selected Kinetics

One of the products of iodide oxidation by excited states of ruthenium polypyridyl compounds, whether through the Stepwise or the Concerted pathway, was diiodide. So in order to properly analyze the transient absorption (TA) results, the extinction coefficient spectrum of diiodide was required. Although the diiodide spectrum was known in acetonitrile\(^1\) and THF\(^2\), the possibility of differences based on solvent necessitated the determination of the spectrum in the same solvent as the TA experiment, namely acetone (DMK) and dichloromethane (DCM). Kinetic rate constants could also be measured in this simpler system for comparison.

Actinometry was performed with 9,10-dibromoanthracene (DBA) in toluene, following the procedure of Gardner, et al. using parameters from Darmanyan.\(^1,3\) After 355 nm irradiation (3 mJ per pulse at 1 Hz) of a 54.64 μM solution of DBA, a long-lived excited state of DBA was formed with a quantum yield (\(\phi\)) of 0.7. The excited state concentration was quantified by extrapolation of the delta absorbance (\(\Delta A\)) at 427.5 nm back to time = 0, Figure A4.1. At 427.5 nm the excited state had an extinction coefficient (\(\varepsilon\)) of 48,000 M\(^{-1}\)cm\(^{-1}\) and the ground state had a negligible extinction coefficient of ~ 50 M\(^{-1}\)cm\(^{-1}\). The concentration of DBA Franck-Condon excited states was calculated using Equation A4.1 where \(\Delta A_0\) is the extrapolated delta absorbance at time zero and \(\ell\) is the path length (1 cm).

\[
C(DBA^*) = \left(\frac{1}{\phi}\right) \left(\frac{\Delta A_0}{\varepsilon \ell}\right)
\]

Equation A4.1
Figure A4.1: UV-vis spectrum of DBA in DMK (top). Delta absorbance at 427.5 nm of solution of DBA in DMK after 355 nm pulsed irradiation (bottom).
The $I_2^-$ spectrum was found by irradiating an argon purged solution of tetrabutyl ammonium triiodide (TBAI$_3$) and excess tetrabutylammonium iodide (TBAI) with 355 nm laser pulses and measuring the absorbance changes.$^1$ In acetone, triiodide has an absorbance peak at 363 nm and the iodide absorbance is masked by the solvent (< 320 nm) so that the only non-negligible absorbing species in the solution at the irradiation wavelength of 355 nm is triiodide, Figure A4.2 (top right).

After pulsed laser excitation the change in absorbance at selected wavelengths was measured. Triiodide and iodide do not absorb at 720 nm and the delta absorbance at that wavelength can be directly related to diiodide concentration, Figure A4.2. The change in absorbance at 720 nm can be divided into three phases and previous authors have assigned these phases to the mechanism in Equations A4.2, A4.3 and A4.4.$^{4,5}$ The first two phases produce a fast and then slow rise in absorbance with each producing approximately the same change in absorbance (equal change in diiodide concentration). The first phase occurs within the laser pulse (20 ns) and corresponds to the photoinitiated dissociation of triiodide, Equation A4.2. The second phase is associated with the
Figure A4.2: (top and bottom left) Change in absorbance at 720 nm for a solution of 21 μM TBAI$_3$ and 21 μM TBAI in DMK irradiated at 355 nm. The top graph is on a short time scale while the bottom graph is on a much longer time scale. (top right) UV-vis absorption spectrum of sample solution. (bottom right) Delta absorbance for the same sample at 370 nm on a short time scale.
reaction of iodine atoms with iodide, **Equation A4.3** and the third phase, a much slower return to baseline, corresponds to the disproportionation of diiodide into triiodide and iodide, **Equation A4.4**. At short wavelengths (λ ≤ 400 nm) the first phase produces a bleach in absorbance, because the first reaction step, **Equation A4.2**, consists of the loss of one molecule of triiodide and the formation of one molecule of diiodide and at these wavelengths the molar extinction coefficient of triiodide is greater than that of diiodide.

In determining the molar extinction coefficient of diiodide, a large excess of TBAI (1.00 mM) was used to minimize unwanted photochemistry and to drive the conversion of iodine atoms to diiodide to completion by approximately 0.5 μs. Based on the approximately equal change in absorbance in phases one and two, it was assumed that all of the iodine atoms produced reacted with excess iodide to make a second diiodide per photon absorbed. Because the disproportionation of diiodide was slow, the change in absorption after 0.5 μs could be fit to a straight line and extrapolated back to time zero (the center of the laser pulse), **Figure A4.3 (top)**. The resulting uncorrected spectrum, **Figure A4.3 (bottom)** (black line), was then corrected for the bleach in absorbance due to the loss of triiodide **Figure A4.3 (bottom)** (red line), to give the corrected spectrum **Figure A4.3 (bottom)** (green line). The concentration of photoexcited triiodide was calculated using **Equation A4.5** where C is concentration and α is the absorptance of the given species and C(DBA*) was calculated using **Equation A4.1**. The bleach in

\[
C(\text{I}_3^-*) = C(\text{DBA}^*) \frac{\alpha(\text{I}_3^-, 355\text{nm})}{\alpha(\text{DBA}, 355\text{nm})}
\]

**Equation A4.5**

\[
\Delta A_\lambda(\text{I}_3^-) = C(\text{I}_3^-*) \varepsilon_\lambda(\text{I}_3^-) \ell = \varepsilon_\lambda \ell C(\text{DBA}^*) \frac{\alpha(\text{I}_3^-, 355\text{nm})}{\alpha(\text{DBA}, 355\text{nm})}
\]

**Equation A4.6**
**Figure A4.3:** (top) ΔA at 415 nm of 10.11 μM TBAI$_3$ and 1.00 mM TBAI in DMK. (bottom) Time zero amplitude of uncorrected diiodide spectrum calculated from fit of ΔA at each wavelength (black), calculated ΔA due to loss of I$_3^-$ (red) and corrected diiodide spectrum (green).
absorbance due to the loss of triiodide was calculated using Equation A4.6. Then using Equation A4.7, the concentration of photoexcited triiodide from Equation A4.5 was used to convert the corrected diiodide Delta Absorbance spectrum into an extinction coefficient spectrum based on the stoichiometric formation of two molecules of diiodide per photon absorbed.

\[
\varepsilon_\lambda = \frac{\Delta A_\lambda}{C(I_2)} = \frac{\Delta A_\lambda}{2 \cdot C(I_3^*)}
\]

Equation A4.7

The same procedure was also performed in dichloromethane solution with similar results. Figure A4.4 displays the molar extinction coefficient spectra for diiodide in acetone and in dichloromethane. The spectra in acetonitrile (ACN)\(^1\) and tetrahydrofuran (THF)\(^2\) are also included for reference. The spectra in ACN and THF are nearly identical while the spectra in DMK and DCM show the short wavelength peak blue shifted 30-40 nm and the peak at long wavelengths is much less intense. The molar extinction coefficients for the four solvents are listed in Table A4.1.
Figure A4.4: Molar extinction coefficient spectrum of diiodide in acetonitrile (black), tetrahydrofuran (red), acetone (green) and dichloromethane (blue).
Table A4.1: Molar extinction coefficients of diiodide in four solvents.

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In a separate experiment it was possible to measure the rate constants $k_2$ and $k_3$ from Equation A4.3 and A4.4. Approximately 20 μM TBAI$_3$ and from 1 to 10 equivalents of TBAI in either DMK or DCM were used. Since PL from the acetone solvent interfered with measurements at the blue end of the spectrum, the kinetics were measured with changes in absorbance at 720 nm, Figure A4.5. The first step in the reaction, dissociation of I$_3^-$, is complete within the instrument response time (~20 ns). At that time the concentration of diiodide and iodine atoms are equal to the initial concentration of excited state triiodide, $[I_2^-] = [I^•] = [I_3^-]_0$. The rate law for the second step is:

$$\frac{d[I_2^-]}{dt} = k_2[f•][I^-]$$

The concentration of iodine atoms produced by the first step is approximately 3 μM and the TBAI concentration varied between 20 and 200 μM. Given the excess TBAI, pseudo-first order conditions were applied and the rate law was expressed as a first-order process in iodine atom concentration:

$$\frac{d[I^-]}{dt} = -\frac{d[I^•]}{dt} = k_{OBS}[I^•] \quad k_{OBS} = k_2[I^-]$$

The integrated rate law for iodine atoms was: $[I^•] = [I^•]_0 \exp(-k_{OBS}t)$

The integrated rate law for the second equation in terms of diiodide was therefore:

$$[I_2^-] = [I^-]_0[1-\exp(-k_{OBS}t)] = [I_2^-]_0[1-\exp(-k_{OBS}t)]$$

Adding the diiodide concentrations from the first and second steps of the reaction gave Equation A4.8, which was used to fit the ΔA versus time trace for each TBAI concentration.

$$[I_2^-] = [I_2^-]_0 \left(2 - e^{-k_{OBS}t}\right) \quad \text{Equation A4.8}$$
Figure A4.5: (top left) Delta absorbance at 720 nm for 23 μM TBAI$_3$ and 20 μM TBAI in DMK after pulsed 355 nm laser irradiation. The red line is the calculated fit. (top right) ΔA at 720 nm for 23 μM TBAI$_3$ and the indicated TBAI concentrations. (bottom left) $k_{OBS}$ vs. TBAI concentration in DMK giving $k_2$ as the slope. (bottom right) $k_{OBS}$ vs. TBAI concentration in DCM giving $k_2$ as the slope.
The observed rate constants \( (k_{\text{OBS}}) \) were then plotted against the TBAI concentration and fit to a straight line. The slope of that fit gives \( k_2 \), Figure A4.5 (bottom).

By 10 \( \mu \text{s} \) the second step of the reaction is essentially complete and the only process remaining is third step, the disproportionation of diiodide into triiodide and iodide, Equation A4.4. The loss of absorbance at 720 nm for the lowest concentration of TBAI, approximately 20 \( \mu \text{M} \) in both TBAI\(_3\) and TBAI, is shown in Figure A4.6 (top). The data could not be satisfactorily fit with an exponential decay but was accurately modeled with bimolecular kinetics, Equation A4.9, which agrees with the proposed diiodide disproportionation reaction. The delta absorbance decay was measured with various TBAI concentrations (1-10 fold the concentration of TBAI\(_3\)) and the calculated rate constant was plotted versus TBAI concentration, Figure A4.6 (bottom). The observed rate constant is nearly constant with respect to TBAI concentration, as expected from the proposed reaction step, and the average value was calculated for each solvent. The rate constants \( k_2 \) and \( k_3 \) in DCM and DMK are listed in Table A4.2 along with literature values in water and acetonitrile. While the rate of the iodine atom/iodide reaction to form diiodide \( (k_2) \) is fairly independent of solvent and appears to be diffusion controlled, the diiodide disproportionation \( (k_3) \) is strongly solvent dependent. The source of the stability of diiodide in acetone is unknown.

\[
\begin{align*}
[I_2^-] &= \frac{[I_2^-]_0}{1 + 2 \left[ I_2^- \right]_0 k_3 t} \\
\text{Equation A4.9}
\end{align*}
\]
Figure A4.6: (top) Delta absorbance at 720 nm after pulsed 355 nm laser irradiation of a DMK solution (23 μM TBAI3 and 20 μM TBAI), left, and DCM solution (24 μM TBAI3 and 23 μM TBAI), right. The red lines are the calculated fits. (bottom) $k_{OBS}$ vs. TBAI concentration in DMK (left) and DCM (right). The red lines are the average value.
Table A4.2: Rate constants for reaction steps following photodissociation of triiodide. Values in water and acetonitrile are from the indicated literature references.

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<td>3.8 ± 0.8 (4) 2.3 (7)</td>
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<td>2.3 (6) 2.5 ± 0.4 (1)</td>
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Appendix 5: Excited State Absorption Spectra

In order to fully and properly analyze the transient absorption spectra of the photoinitiated reactions used in this thesis, an authentic absorption spectrum of any absorbing species present during the reaction must be known. Because the reactions are photoinitiated, excited states will surely exist in the solution. After 532 nm light absorption by the ruthenium and osmium compounds, a metal-based electron is promoted to a ligand-based \( \pi^* \) orbital in a Metal-to-Ligand Charge Transfer (MLCT). The Franck-Condon excited state is mostly singlet in character and undergoes intersystem crossing to an MLCT excited state that is mostly triplet in character and subsequent thermal relaxation on the femtosecond time-scale.\(^1\)\(^2\) The intersystem crossing and relaxation processes are complete well within our instrument response time, so the excited-state spectra referred to in this thesis is that of the thermally relaxed \(^3\)MLCT. After light excitation, the excited-state exists in the solution until it either decays to the ground state (radiatively or non-radiatively) or further reacts.

The excited-state spectrum was obtained using transient absorption spectroscopy with solutions of the transition metal compounds. After light excitation, the change in absorption at various wavelengths was measured and the extinction coefficient at each wavelength was quantified with actinometry. It was deemed that the only absorbing species observed were the ground state and the excited state of the transition metal compound because no change was observed in the ground state UV-Vis before and after the experiment, the transient absorbance lifetime was similar at all wavelengths measured and the transient absorption spectra at various time intervals were normalizable. Additionally, the transient absorbance lifetime was consistent with the lifetime measured
with Time-Resolved Photoluminescence Spectroscopy. The transient absorbance decay at each wavelength was fit to a single exponential equation as a function of time and the time = 0 intercept was taken as the initial absorbance value. The mid-point in the rise of the transient absorption signal was taken as time = 0.

The initial absorbance at each wavelength was converted to a molar extinction coefficient using Beer’s Law, where $C^*$ is the excited-state concentration at time = 0, $\Delta A$ is the absorption change at time = 0, $\varepsilon$ and $\varepsilon^*$ are the ground state and excited-state extinction coefficients at that wavelength respectively, and $\ell$ is the 1.00 cm path length.

$$\Delta \varepsilon = \frac{\Delta A}{\ell C^*} \quad \Delta \varepsilon = \varepsilon^* - \varepsilon$$

The excited-state concentration at time = 0 was measured by comparative actinometry using [Ru(bpy)$_3$](PF$_6$)$_2$ in ACN that has a known $\Delta \varepsilon = 10,000$ M$^{-1}$ cm$^{-1}$ at 450 nm. In the following equation S is the sample being measured, R is [Ru(bpy)$_3$](PF$_6$)$_2$ in ACN and $\alpha$ is absorptance.

$$C^*(S) = C^*(R) \frac{\alpha(S)}{\alpha(R)} \quad C^*(R) = \frac{\Delta A(R)}{\ell \Delta \varepsilon(R)}$$

The ground state and excited state extinction coefficient spectra for each compound used in chapter 3 of this thesis are shown in Figures A5.1, A5.2, A5.3 and A5.4. The molar extinction coefficients for each compound and solvent measured are listed in Table A5.1.
Figure A5.1: Ground and excited state UV-Vis spectra of [Ru(bpy)$_3$](PF$_6$)$_2$ in DCM (top) and DMK (bottom).
Figure A5.2: Ground and excited state UV-Vis spectra of \([\text{Ru(bpy)}_2(\text{phen})](\text{PF}_6)_2\) in DCM (top) and DMK (bottom).
Figure A5.3: Ground and excited state UV-Vis spectra of [Ru(phen)$_3$](PF$_6$)$_2$ in DCM (top) and DMK (bottom).
Figure A5.4: Ground and excited state UV-Vis spectra of [Ru(dmb)₃](PF₆)₂ in DCM (top) and DMK (bottom).
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Appendix 6: Spectra of Singly Reduced Ruthenium Compounds

The ruthenium compounds utilized in chapter 3 of this thesis all contained a transition metal complex with a +2 charge (dicationic). Reductive quenching by iodide of the excited states of these compounds produced the singly reduced ruthenium compounds that consisted of a formally Ru(II) metal center and one ligand that is reduced by one electron, such as bpy$. An authentic absorption spectrum of the singly reduced compound was necessary to properly analyze the transient absorption spectra. The singly reduced forms were produced using electrochemical reduction of the dicationic compound. Typically, an argon purged, stirred acetone solution of the ruthenium compound (~ 50 μM) and 0.1 M TBAPF$_6$ was used in a three electrode configuration with a platinum mesh counter electrode, an FTO slide with an approximate area of 0.5 x 3.0 cm working electrode, and a Ag/AgCl(sat. KCl$_{(aq)}$) reference electrode that was calibrated against ferrocene/0.2 M LiClO$_4$/ACN.$^1$ The counter electrode was in a separate compartment isolated by a fine frit with only the electrolyte and solvent. Reduction potentials from Table A3.3 in Appendix 3 were used to set the potential of the working electrode in between E$_{1/2}$ for first and second reductions of the ruthenium compound. UV-Vis spectra were recorded until a steady-state condition was reached. The working electrode was then set to an oxidative potential (typically + 500 mV vs SCE) and the solution was opened to air. Typically, the UV-Vis spectra quickly changed to approximately match the original spectrum of the dicationic ruthenium compound. The reduced spectra for three of the are shown in Figure A6.1. The reduced spectrum of [Ru(dmb)$_3$]$^{2+}$ was not measured because this compound did not undergo reductive quenching.
The molar extinction coefficient spectra were calculated for each reduced compound based on the initial concentration of the dicationic compound. Then the difference spectrum was calculated as the spectrum of the singly reduced compound minus the spectrum of the dicationic compound. The extinction coefficient spectrum for the dicationic compound came from the Molar Extinction Coefficient experiments (see Appendix 2). The extinction coefficients at selected wavelengths for the difference spectra are listed in Tables A6.1 and A6.2.
Figure A6.1: UV-Vis spectra of the indicated singly reduced ruthenium compounds in acetone.
**Table A6.1:** Molar extinction coefficients (M$^{-1}$cm$^{-1}$) for the difference spectrum (singly reduced compound minus dicationic compound) for the indicated ruthenium compounds, 800 - 400 nm.

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<tr>
<td>480</td>
<td>7238</td>
<td>6922</td>
<td>12585</td>
</tr>
<tr>
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<td>2125</td>
<td>2676</td>
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<td>460</td>
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<td>-503</td>
<td>-1047</td>
</tr>
<tr>
<td>400</td>
<td>2070</td>
<td>1305</td>
<td>-341</td>
</tr>
</tbody>
</table>
Table A6.2: Molar extinction coefficients (M\(^{-1}\)cm\(^{-1}\)) for the difference spectrum (singly reduced compound minus dicationic compound) for the indicated ruthenium compounds, 390 - 330 nm.

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>[Ru(bpy)(_3)](^{2+})</th>
<th>[Ru(bpy)(_2)(phen)](^{2+})</th>
<th>[Ru(phen)(_3)](^{2+})</th>
</tr>
</thead>
<tbody>
<tr>
<td>390</td>
<td>4631</td>
<td>1916</td>
<td>480</td>
</tr>
<tr>
<td>380</td>
<td>7959</td>
<td>2911</td>
<td>2319</td>
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<tr>
<td>370</td>
<td>12001</td>
<td>4538</td>
<td>4381</td>
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<td>360</td>
<td>15372</td>
<td>6356</td>
<td>7098</td>
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<tr>
<td>350</td>
<td>15795</td>
<td>7334</td>
<td>9908</td>
</tr>
<tr>
<td>340</td>
<td>16128</td>
<td>6952</td>
<td>12071</td>
</tr>
<tr>
<td>330</td>
<td>13608</td>
<td>6441</td>
<td>13689</td>
</tr>
</tbody>
</table>
References:

Appendix 7: Derivations

1. Derivation of the Equation for Benesi-Hildebrand Analysis

From the equilibrium expression:

\[ \text{R} + \text{X} \rightleftharpoons [\text{R}, \text{X}] \quad \text{R} = [\text{Ru(LL)}]^2^+ \]

\[ K_{eq} = \frac{[RX]}{[R][X]} \]

\[ R_0 = [R] + [RX] \quad X_0 = [X] + [RX] \]

\[ K_{eq} = \frac{[RX]}{(R_0 - [RX]) (X_0 - [RX])} \]

\[ (R_0 - [RX]) (X_0 - [RX]) = \frac{[RX]}{K_{eq}} \]

\[ [RX]^2 - \left( R_0 + X_0 + \frac{1}{K_{eq}} \right) [RX] + R_0 X_0 = 0 \]

Using the quadratic formula:

\[ [RX] = \frac{\Delta A}{\Delta \varepsilon} = \frac{1}{2} \left( R_0 + X_0 + \frac{1}{K_{eq}} \right) - \sqrt{\left[ \frac{1}{2} \left( R_0 + X_0 + \frac{1}{K_{eq}} \right) \right]^2 - R_0 X_0} \]

From Beer's Law:

\[ A_R = [R] \varepsilon R \ell \quad A_{RX} = [RX] \varepsilon_{RX} \ell \quad A_0 = R_0 \varepsilon R \ell \]

From mass balance:

\[ R_0 = [R] + [RX] \]

\[ A_{\text{soln}} = A_R + A_{RX} \]

\[ \Delta A = A_R + A_{RX} - A_0 = [R] \varepsilon R \ell + [RX] \varepsilon_{RX} \ell - R_0 \varepsilon R \ell = ([R] - R_0) \varepsilon R \ell + [RX] \varepsilon_{RX} \ell \]
Substituting: \[ [R] - R_0 = -[RX] \]
\[ \Delta A = -[RX] \varepsilon R \ell + [RX] \varepsilon_{RX} \ell = [RX] (\varepsilon_{RX} - \varepsilon R) \ell \]
\[ \Delta A = [RX] \Delta \varepsilon \ell \]

2. Derivation of the Equation for PL Lifetime Analysis

The average lifetime of a two component system is as follows.\(^2\)
\[ < \tilde{\tau} > = \frac{\alpha_1 \tau_1^2 + \alpha_2 \tau_2^2}{\alpha_1 \tau_1 + \alpha_2 \tau_2} \]
\[ \alpha_1 = \frac{[R]}{R_0} \quad \alpha_2 = \frac{[RX]}{R_0} \quad R_0 = [R] + [RX] \]
\[ < \tau > = \frac{\alpha_1 \tau_1^2 + \alpha_2 \tau_2^2}{\alpha_1 \tau_1 + \alpha_2 \tau_2} = \frac{[R]}{R_0} \frac{\tau_1^2 + [RX]}{\tau_1 + [RX]} \frac{R_0}{R_0} \tau_2^2 = \left( \frac{[R]}{R_0} \right) \frac{\tau_1^2 + [RX]}{\tau_1 + [RX]} \frac{R_0}{R_0} \tau_2^2 \]
\[ < \tau > = \frac{R_0 - [RX]}{(R_0 - [RX]) \tau_1 + [RX] \tau_2} \frac{\tau_1^2 + [RX] \tau_2^2}{\tau_1 + [RX]} = \frac{R_0 \tau_1^2 - (\tau_1^2 - \tau_2^2) [RX]}{R_0 \tau_1 - (\tau_1 - \tau_2) [RX]} \]

By forming the equation in terms of \([RX]\), the result from the previous derivation can be used to express the average lifetime as a function of initially added concentrations \(R_0\) and \(X_0\), the measured quantity \(\tau_1\), and the fitted parameters \(K_{eq}\) and \(\tau_2\).

\[ [RX] = \frac{\Delta A}{\Delta \varepsilon} = \frac{1}{2} \left( R_0 + X_0 + \frac{1}{K_{eq}} \right) - \sqrt{\left[ \frac{1}{2} \left( R_0 + X_0 + \frac{1}{K_{eq}} \right) \right] - R_0 X_0} \]

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3. Derivation of the Equation for Excited State Actinometry

For the TA sample and the laser pulse:

The ground state absorption at 532nm follows

\[ A = - \log \frac{I}{I_0} \quad \frac{I}{I_0} = 10^{-A} \]

Light intensity is power per square meter, or total energy per second per square meter:

\[ I = \frac{P}{L^2} = \frac{E_t}{t L^2} \quad E_t = I t L^2 \]

The number of photons is the total energy divided by the energy of one photon:

\[ n_p = \frac{E_t}{E_p} = \frac{E_t}{h \nu} = \frac{I t L^2}{h \nu} \]

The number of excited state molecules equals the number of photons absorbed which equals the number of photons in the laser pulse before passing through the sample minus the number of photons in the laser pulse after passing through the sample.

\[ n^* = n_{p_0} - n_p = \frac{I_0 t L^2}{h \nu} - \frac{I t L^2}{h \nu} = (I_0 - I) \frac{t L^2}{h \nu} \]

The concentration of excited state molecules is:

For the reference compound, [Ru(bpy)_3](PF_6)_2 in ACN (R)

\[ C^* (R) = \frac{n^*}{V} = (I_0 - I) \frac{t L^2}{h \nu V} = \left( 1 - \frac{I}{I_0} \right) \frac{I_0 t L^2}{h \nu V} = \frac{(1 - 10^{-A}) I_0 t L^2}{h \nu V} \]

\[ \frac{I_0 t L^2}{h \nu V} = \frac{C^* (R)}{(1 - 10^{-A})} \]
For the unknown sample compound (S)

\[
\frac{I_0 t L^2}{h \nu V} = \frac{C^*(R)}{1 - 10^{-A(R)}} = \frac{C^*(S)}{1 - 10^{-A(S)}} \quad C^*(S) = C^*(R) \left( \frac{1 - 10^{-A(S)}}{1 - 10^{-A(R)}} \right)
\]

For the reference compound, Ru(bpy)_3(PF_6)_2 in ACN

\begin{align*}
A_0, C_0 &= \text{absorbance / concentration of Ru(2+) before laser pulse} \\
A_1, C_1 &= \text{absorbance / concentration of Ru(2+) after laser pulse} \\
A^*, C^* &= \text{absorbance / concentration of Ru(2+*) after laser pulse} \\
\varepsilon_1 &= \text{extinction coefficient for Ru(2+)} \\
\varepsilon^* &= \text{extinction coefficient for Ru(2+*)}
\end{align*}

\[
A_0 = \varepsilon_1 C_0 \\
A_1 = \varepsilon_1 C_1 = \varepsilon_1 (C_0 - C^*) \\
A^* = \varepsilon^* C^*
\]

\begin{align*}
A(\text{pre-laser pulse}) &= A_0 = \varepsilon_1 C_0 \\
A(\text{post-laser pulse}) &= A_1 + A^* = \varepsilon_1 (C_0 - C^*) + \varepsilon^* C^* = \varepsilon_1 C_0 - \varepsilon_1 C^* + \varepsilon^* C^* \\
\Delta A = A(\text{post}) - A(\text{pre}) &= \varepsilon_1 C_0 - \varepsilon_1 C^* + \varepsilon^* C^* - \varepsilon_1 C_0 = \varepsilon^* C - \varepsilon_1 C_2 = \Delta \varepsilon C^* \\
C^* &= \frac{\Delta A}{\Delta \varepsilon}
\end{align*}

For Ru(bpy)_3(PF_6)_2 in ACN, \(\Delta \varepsilon = 10,000\) at 450 nm

Use \(\Delta A(R)\) and \(\Delta \varepsilon(R)\) to get \(C^*(R)\)

Use \(C^*(R), A(R)_{532}\) and \(A(S)_{532}\) to get \(C^*(S)\)

Then calculate the \(\Delta \varepsilon\) spectrum for (S) using \(\Delta \varepsilon(S)_\lambda = \Delta A(S)_\lambda / C^*(S)\)

The excited state spectrum can then be calculated from the \(\Delta \varepsilon\) and the ground state spectrum.
4. Derivation of the Kinetics Equations for the Unknown Oxidant Model

**Ground-state equilibria**

\[
K_{g1} = \frac{k_{g1}}{k_{-g1}} = \frac{[R^{2+}, I^{-}]}{[R^{2+}] [I^{-}]} \quad [R^{2+}, I^{-}] = K_{g1} [I^{-}] [R^{2+}]
\]

\[
R_I = [R^{2+}]_0 + [R^{2+}, I^{-}]_0 = [R^{2+}]_0 Z_{GS} \quad Z_{GS} = (1 + K_{g1} [I^{-}]) \quad \phi_0 = \frac{1}{Z_{GS}} \quad \phi_1 = \frac{K_{g1} [I^{-}]}{Z_{GS}}
\]

**Excited State equilibria**

\[
K_1 = \frac{k_1}{k_{-1}} = \frac{[R^*, I^{-}]}{[R^*] [I^{-}]} \quad K_2 = \frac{k_2}{k_{-2}} = \frac{[R^*, 2I^{-}]}{[R^*],1[-] [I^{-}]}
\]

\[
[R^*, I^{-}] = K_1 [R^*][I^{-}] \quad [R^*, 2I^{-}] = K_2 [R^*,1[-]][I^{-}] = K_1 K_2 [I^{-}]^2 [R^*]
\]

**Excited State concentrations after excited state equilibria are established (fast):**

Here it is assumed that the equilibria are established within the instrument response time.

\[
R^*_{I0} = [R^*]_0 + [R^*, I^{-}]_0
\]

\[
R^*_{I0} = [R^*]_0 + K_1 [I^{-}], [R^*]_0
\]

\[
R^*_{I0} = [R^*]_0 (1 + K_1 [I^{-}]) = [R^*]_0 Z \quad Z = \{1 + K_1 [I^{-}]\}
\]

\[
\phi_0^* = \frac{[R^*]_0}{R^*_{I0}} = \frac{1}{Z} \quad \phi_1^* = \frac{K_1 [I^{-}]}{Z} \quad \phi_2^* = \frac{K_1 K_2 [I^{-}]^2}{Z}
\]

\[
[R^*]_0 = \phi_0^* R^*_{I0} \quad [R^*, I^{-}]_0 = \phi_1^* R^*_{I0} \quad [R^*, 2I^{-}]_0 = \phi_2^* R^*_{I0}
\]
The excited state decay as measured with Time-resolved PL decay, emission on the TA or a fit of excited state ΔAbs is always first-order throughout. Therefore, all excited state species decay with approximately the same numerical rate constant.

\[
[R^*] = \phi_0^* R_{r_0}^* \exp\left(-a^* t\right) \quad \text{where} \quad a = k_0 + k_q[I-]
\]

\[
k_q = \frac{k_2(k_0 + k_{et})}{k_{-2} + k_{et} + k_0} \approx K_2(k_0 + k_{et})
\]

\[
[R^*, I-] = \phi_1^* R_{r_0}^* \exp\left(-a^* t\right)
\]

\[
[R^*, 2I-]_{SS} = \phi_2^* R_{r_0}^* \exp\left(-a^* t\right)
\]

**Steady-state approximation for [Ru^{2+*}, 2I]:**

\[
\frac{d[R^*, 2I-]_{SS}}{dt} = 0 = k_2[I-][R^*, I-] - k_{-2}[R^*, 2I-]_{SS} - k_{et}[R^*, 2I-]_{SS} - k_0[R^*, 2I-]_{SS}
\]

\[
[R^*, 2I-]_{SS} = \frac{k_2[I-]}{(k_{-2} + k_{et} + k_0)} [R^*, I-] = \frac{k_2[I-]}{(k_{-2} + k_{et} + k_0)} \phi_1^* R_{r_0}^* \exp\left(-a^* t\right)
\]

According to the calculations:

\[
k_2 = 2.0 \times 10^9 \text{ s}^{-1} \quad \quad k_{et} = 2.1 \times 10^7 \text{ s}^{-1} \quad \quad k_0 = 1.0 \times 10^6 \text{ s}^{-1}
\]

Therefore, to within \( \sim 1\% \) error:

\[
[R^*, 2I-]_{SS} \approx \frac{k_2[I-]}{k_{-2}} [R^*, I-] = K_2[I-][R^*, I-]
\]

Which is another way of saying that the equilibrium is fast and maintained throughout.
Singly ion-paired excited-state, after excited state equilibrium is established

\[
\frac{d[R^*, I^-]}{dt} = k_1[I^-][R^*] + k_2[R^*, 2I^-] - k_0[R^*, I^-] - k_{-1}[R^*, I^-] - k_2[I^-][R^*, I^-]
\]

\[
= k_1[I^-][R^*, I^-] + k_2 \frac{k_2[I^-]}{(k_{-2} + k_{et} + k_0)}[R^*, I^-] - k_0[R^*, I^-] - k_{-1}[R^*, I^-] - k_2[I^-][R^*, I^-]
\]

\[
= [R^*, I^-]\left[-k_0 - k_{-1} - k_2[I^-]\right]
\]

\[
= [R^*, I^-]\left[-\left(k_0 + \frac{k_2(k_0 + k_{et})}{(k_{-2} + k_{et} + k_0)}[I^-]\right)\right]
\]

where \( k_q = \frac{k_2(k_0 + k_{et})}{(k_{-2} + k_{et} + k_0)} \approx K_2(k_0 + k_{et}) \)

\[
[R^*, I^-] = [R^*, I^-]_0 \exp[-(k_0 + k_q[I^-])t] = \phi_1^* R_{I7,0}^* \exp(-a^*t) \quad \text{where} \quad a = k_0 + k_q[I^-]
\]

Doubly ion-paired excited-state, after excited state equilibrium is established

\[
[R^*, 2I^-] = \phi_2^* R_{I7,0}^* \exp(-a^*t) \quad \text{where} \quad a = k_0 + k_q[I^-]
\]

Ion-paired reduced compound:

Assuming there is no cage escape - the reduced compound and diiodide recombine relatively slowly inside the solvent cage because the electron transfer is very far into the Marcus inverted region. This assumption is necessary because both the reduced compound and the diiodide attributable to the reduction of the excited state decay as a first order process. This can only be possible if there is just one species that is decaying, the ion-paired reduced compound/diiodide.
Solve the first-order differential equation.

\[
\frac{d[R^+, I_2^-]}{dt} = k_{et}[R^+, 2I -] - (k_{-et} + k_3)[R^+, I_2^-]
\]

\[
\frac{d[R^+, I_2^-]}{dt} + (k_{-et} + k_3)[R^+, I_2^-] = k_{et} \phi_2^* R_0^* \exp(-a^* t)
\]

Diiodide (ion-paired and extra):

The diiodide concentration from the reduction of the ruthenium compound excited state is the same as the concentration of the reduced compound. The term with \( A_0 \) is an unknown source of diiodide.

\[
[R^+, I_2^-] = \frac{k_{et} \phi_2^* R_0^*}{(a - k_3 - k_{-et})} \left[ \exp\left(-k_3 t\right) - \exp\left(-a t\right) \right] + A_0 \left[ 1 - \exp\left(-k_3 t\right) \right]
\]

References:


Appendix 8: Curriculum Vitae

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EDUCATION

*Johns Hopkins University*, Baltimore, Maryland
  - Ph.D. in Inorganic Chemistry (specialization in spectroscopy) 2014
  - M.S. in Chemistry 2011

*Montgomery College*, Rockville, Maryland
  - Alternative Certification for Effective Teachers 2007

*University of Delaware*, Newark, Delaware
  - B.S. in Chemistry 1985

AWARDS and HONORS

- William Hooper Grafflin Fellowship 2012
- Emmet and Elsie Buhle Fellowship Award for academic excellence 2010
- First Place in Biochemical Div./Intercollegiate Student Chemists Convention 1985

PUBLICATIONS


RESEARCH EXPERIENCE

*Johns Hopkins University*, Baltimore, MD 2009-2014

Research adviser: Dr. Jerry Meyer

- Experimental techniques: UVV steady state and nanosecond time-scale transient absorption, steady-state and time resolved photoluminescence, FTIR-ATR, ¹H and ¹⁹F NMR, ESI-MS, electrochemistry, spectroelectrochemistry, inorganic synthesis and liquid nitrogen cryostat
- Photochemical formation of iodine-iodine bonds
- Mechanism and kinetics of iodide oxidation, the primary redox mediator in Dye-Sensitized Solar Cells
• Effects of halide ion-pairing with ruthenium polypyridyl compounds in the low dielectric solvent dichloromethane
• Photophysical properties of ruthenium polypyridyl chromophores used in Dye-Sensitized Solar Cells in solution and adsorbed to TiO₂ semiconductor surfaces
• Assisted in the writing and submission of DOE and NSF grant proposals

*University of Delaware*, Newark, DE 1983-1985
Research adviser: Dr. Colin Thorpe

• Synthesis, characterization and testing of long chain alkynoyl-Coenzyme A inhibitors to General Acyl-CoA Dehydrogenase.

**TEACHING EXPERIENCE**

*Johns Hopkins University*, Baltimore, MD 2009-present

• **Mentor**: Undergraduate research, 1 student

• **Instructor**: Introductory Chemistry and Introductory Chemistry Lab
  • Taught or co-taught seven classes, 291 students total, during summer sessions
  • Supervised two laboratory Teaching Assistants
  • Student End-of-Course evaluations rated the teaching effectiveness and usefulness of feedback above the Arts and Sciences school average

• **Substitute Instructor**: Introductory Chemistry
  • Developed and presented lectures for three weeks during spring semester
• **Teaching Assistant**: Introductory Chemistry, Physical Chemistry, Physical Chemistry Lab

*Magruder High School*, Rockville, MD 2006-2009

• Taught Chemistry, Honors Chemistry, Introduction to Engineering and Aerospace Engineering

*United States Air Force*

• **Air Campaign Planning Instructor**: Combat Plans 2001 - 2002
• **Flight Instructor**: F-111F and F-15E aircraft 1990 - 2000

*ESL Teacher*: Church volunteer 2011 - 2013

**PREVIOUS ACCOMPLISHMENTS**

*United States Air Force Officer* 1985 - 2005

• Squadron Commander  (Lieutenant Colonel)  Wiesbaden, Germany  2003-2005
  • Supervised 80 personnel at 3 locations; achieved 100% of training and career development goals
  • Directed movement of all personnel and equipment to Kuwait and then to Baghdad for 14 months;
  • Accomplished 100% of the mission, all personnel and equipment returned safely
- Directed successful maintenance program for $20 Million worth of vehicles and equipment
- Responsibly administered $400K annual budget; consistent savings used to upgrade equipment

**SKILLS**
- Origin and Mathematica computer programs, programming in C++, visual basic and LabVIEW
- Intermediate level German and Romanian languages
- Saxophone, flute and guitar