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Chemical And Physical Studies Of Charge Transfer Excited States Of Ruthenium Complexes With Aromatic Ligands

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CHEMICAL AND PHYSICAL STUDIES OF CHARGE TRANSFER EXCITED STATES OF RUTHENIUM COMPLEXES WITH AROMATIC LIGANDS

by

MARIM KHALIFA ALNAED

DISSERTATION

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Approved By:

Advisor Date
Advisor Date
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Advisor Date
DEDICATION

My dissertation is dedicated to my husband, kids, and family
ACKNOWLEDGMENTS

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mM, PH 7.4 and 10% DMSO solvent using 337 N nm pulsed excitation monitored at 543 and 631. (A) [MH-3-110] at 77 K; (B) [MH-3-55] at 77 K. (C) [MH-3-110] at ambient condition. (D) [MH-3-55] at ambient condition. The mono exponential fit (black) and the extracted data (pink) are indistinguishable; residuals are in red. The samples were probably microcrystalline at 77K. A fast decay component with about 10% of the substrate amplitude was probably mostly due to the instrument response to scattered excitation light, but it could also contain contribution from heterogeneities or impurities. Exponential decay fittings performed in Origin; IRF= 12 ns. ................................................................. 114
CHAPTER 1. GENERAL INTRODUCTION

Over the past several decades there have been increasingly sophisticated studies that attempt to develop a scientific understanding of the chemical and physical properties of the lowest triplet states ($^3\text{MLCT}$) of nd$^6$ transition metal complexes. This strong interest has been stimulated both by the important applications of these complexes and by the challenges presented by excited state electronic configurations that differ significantly from those known for ground state complexes. For example, these materials have been used as sensitizers in dye-sensitized solar cells, $^3$-$^6$ in photodynamic therapy, etc.$^7$-$^9$

Many of the potential applications involve the lowest energy triplet state and the understanding of the properties of these lowest energy triplet states ($^3\text{MLCT}$) are much more poorly understood than for those of pure organic materials. The chemical properties of molecules depend on their electronic structures and the descriptions of the electronic configurations of $^3\text{MLCT}$ excited states are most often based on idealized models in which light absorption results in oxidation of a metal center and reduction of a ligand moiety of the complex. Emission spectroscopy and contemporary density functional theory techniques have relatively recently shown that such primitive models of electronic structure are not always appropriate.

The lowest energy triplet metal-to-ligand-charge-transfer ($^3\text{MLCT}$) excited states of ruthenium(II) have been of interest for some time largely due to their facile excited state electron transfer reactions or to facile excited state-ligand substitution reactions. In order to design efficient photosensitizers, it is necessary to understand the molecular properties that will optimize these efficiencies.
In addition to the previously mentioned importance of understanding the properties of the charge transfer excited state, understanding the requirement for photoionized electrons to the solvent will be important in biology, solution chemistry and electrochemistry. The solvent plays important role in affecting the outcome and efficiency of the reactions, and light absorption by the ground state of the substrate, a charge transfer to solvent transition (CTTS) state may be generated and this corresponding to the formation of photoionized species. In case of iodide the formation of the CTTS state is accompanied by the formation of \( \{S^+,e^-\}_{IP} \) ion pairs. This kind of intermediate has not been reported for the photoionization of transition metal complexes.

The most obvious requirements for an effective excited state photosensitizer are: (a) its chemical integrity during the time of the sensitized reaction; and (b) that it is sufficiently reactive that the rate determining step of the sensitized reaction has a lifetime that is more or less comparable to its excited state lifetime. The chemical integrity of the excited state depends on its various intrinsic decay pathways (including those that are thermally activated) and on its susceptibility to photodecomposition if it absorbs some of the light used in its generation. These factors can be altered to various extents by mixing of the photo-sensitizer excited state with other electronic excited states that have similar energies. Transition metal complexes typically have a large number of electronic excited states whose energies differ only a little from that of their lowest energy excited states. As a result, many excited states can be populated by light absorption with many different relaxation pathways and some mixing among the states with different electronic configurations is expected. The lowest energy excited states of transition metal complexes
are difficult to characterize because: (a) these states have short lifetimes so that standard thermochemical and structural characterization techniques cannot be used; and (b) there are a several excited states that are close in energy and mix to alter the electronic configuration of the lowest energy excited state and the shape of its potential energy surface.

It is theoretically reasonable to expect that the configurational mixing (CI) between different excited states with the same spin multiplicity generally larger than the spin-orbit coupling (SOC) mediated mixing between states with different spin multiplicities for the same energy differences between the mixed states, although there is little direct experimental confirmation of this. Such mixing appears to be important in [ruthenium(II)−(aromatic ligand)] based photo-sensitizers. Balzani and his co-workers\textsuperscript{10} have surveyed the synthesis and the photochemical, photophysical, and electrochemical properties of a large number of complexes of the Ru-polypyridine family and the properties of the lowest energy excited states of monobipyridine [(L)\textsubscript{4}Ru(bpy)]\textsuperscript{m+} complexes have been extensively examined.\textsuperscript{11-15} These complexes provide much important information on the properties of metal to ligand charge transfer excited states of potential transition metal sensitizers in which CI seems to be small to moderate.

Over the last decade, many potential photosensitizers have been identified based on metal donors and aromatic ligand acceptors; however, there is insufficient information to explain all the parameters that may lead to an understanding of either the photoionization phenomena and/or help design synthesis of complexes with longer lifetimes. Therefore, the design a system which enables optimization of sensitizer efficiencies for solar energy
conversion or other important applications requires an understanding of the changes in the molecular and electronic properties of the excited states when their coordination environments are changed.
CHAPTER 2. CHEMICAL SCAVENGING OF SHORT-LIVED PRODUCTS FROM THE VISIBLE LIGHT PHOTOIONIZATION OF THE TRIS-BIPYRIDINE-RUTHENIUM(II) TRIPLET METAL-TO-LIGAND CHARGE-TRANSFER EXCITED STATE

Photoionization is among the simplest possible kinds of excited state decomposition and the basic physical principles governing it have been understood for a long time: 16 (a) photoionization occurs once the energy of an absorbed photon exceeds a threshold energy; (b) the threshold energy is a molecular property; (c) the energy of the photon that exceeds the threshold energy appears as kinetic energy in the photo-generated electron. This process is complicated in solutions because the electron’s kinetic energy can be transferred to the solvent molecules and this can give rise to a number of electron-containing species. Acid scavenger experiments play a role in the characterization of the intermediate species that are generated from the excitation of a substrate in solution. Since there is relatively little detailed information available about the photoionization of transition metal cationic complexes it is useful to first consider some of the observations on iodide photoionization.

Solution phase photoionization of I− 17 has been extensively investigated using both H+ scavenging for the electron and short pulse laser transient absorption spectroscopy 18. The excitation of iodide ion leads to the generation of charge transfer to solvent transition (CTTS) absorption, and the irradiation of this band give rise to the formation of the neutral iodine atom and the solvated electron. These species undergo a series of reactions in H2O to form I2 and H2 gas. Stein and co-workers1, 19-20 used H+ to scavenge for electrons and alcohols as H-atom scavengers. In addition, they demonstrated that the photogeneration of
electrons did not react with H\(^+\) ions in simple manner, which lead them to postulate that the CTTS state decays into a solvated electron and iodine atom in a solvent cage. Later, Dainton and Logan and co-workers\(^{21-23}\) used N\(_2\)O as electron scavenger to characterize the intermediate that formed, and they were trying to understand how electrons were formed, how the CTTS state decays and what is the quantum yield efficiency of the electron scavenging. Bradforth and co-workers\(^{17}\) have studied the photoionization of iodide CTTS system and their results confirmed the formation of short and long-range photo-ejection caged pair \(\{I^\bullet,e^-\}\) intermediate.

This previous work on I\(^-\) has suggested that there are three main spatial regimes that are important in the photoionization process:\(^{17}\), (a) a contact ion pair \(\{I^\bullet,e^-\}\) where this solvent caged pair are still in contact with one another and ‘‘Primary recombination’’ of these pairs form the iodide ion is in the fs time regime and chemical scavenging is impossible; (b) ion pairs in which the photo-products are separated by one or more solvent molecules and ‘‘Secondary recombination’’ is slower (ps time regime) so that some chemical scavenging is possible; (c) the pairs have diffused so far apart that ‘‘Combination’’ of the photo-products is in the ns time regime so that the free solvated electrons can be scavenged at lower acid concentrations. These processes are schematically illustrated in Figure 1.
Figure 1: A qualitative illustration of the scavenging yield obtained from the formation of the caged pairs as the scavenger concentration is varied. The “geminate recombination”, which describes the caged pairs that successfully react, either through primary or secondary recombination. The time regimes for primary and secondary recombination are probably in the fs and ps, respectively. Only higher acid concentration can compete with the primary and secondary recombination processes. At lower acid concentration, free solvated electrons are scavenged in the ns time regime.

The photoionization of iodide illustrates the basis for the interpretation of our observations.\textsuperscript{17} Although information on the photoionization of anions is readily available, there are few studies on photoionization \textsuperscript{24-29} of cations, or more specifically, transition metal cationic complexes in solution. In previous work, the photoionization \textsuperscript{25-29} of \([\text{Ru(bpy)}_3]^{2+}\) in solution has been based on the spectroscopic detection of free electrons, not associated with \([\text{Ru(bpy)}_3]^{3+}\) in the bulk solution. This is in contrast to the interpretations of the photoionization of iodide in solutions summarized above.\textsuperscript{1,17,30-31} Our approach was to use chemical scavengers to probe the photoionization of the \([\text{Ru(bpy)}_3]^{2+}\)
complex in aqueous solution. One of the most important issues in characterizing the photoionization process is the value of the threshold energy, \( E_{\text{th}} \), which can be based on thermodynamic parameters, and the nature of the photo-products formed. Photoionization of molecules occurs for photons with energy \( h \nu > E_{\text{th}} \) and the excess photon energy, \( E_{\text{xs}} = (h \nu - E_{\text{th}}) > 0 \), in vacuum appears mostly as kinetic energy of the electron. This kinetic energy can be largely dissipated in solutions by means of interactions with solvent.

The rarity of the detailed reports on CTTS absorptions for cationic species may be due to competing absorptions of some states that are characteristic of these complexes since their absorption may obscure the CTTS absorptions. Our expectations were that the photoionization of these cationic complexes would lead to the generation of ion pairs and free solvated electrons as has been found in the photoionization of the iodide ion. Due to the electrostatic interactions of the photo-products, the separation of the photoionization products is likely to be more difficult for these cations than for \( \Gamma^- \), the photo-generated electrons are likely to have shorter recombination lifetimes for similar separation distances and electron/Ru\(^{3+}\) product attractions probably extend over a greater distance for cationic than for anionic substrates.

Matsubara and Ford studied the photoionization of the hexaamine ruthenium(II) complex, \([\text{Ru(NH}_3)_6]^{2+}\) and they were able to efficiently scavenge for free solvated electron, \( e^{-}_{aq} \) within an acid range of 0.001-0.01 M H\(^+\). A significant optical absorption band of \([\text{Ru(NH}_3)_6]^{2+}\) has been assigned as (CTTS) transition\(^{32, 34-35}\) at 275 nm (4.5 eV). This corresponds to the energy required for a photon to promote an electron into the solvation sphere of the complex with the ground state nuclear coordinates fixed, but it
does not correspond to the minimum energy required to ionize the complex. The irradiation of the [Ru(NH$_3$)$_6$]$^{2+}$ CTTS absorption (at 254 nm) generates [Ru(NH$_3$)$_6$]$^{3+}$ and the solvated electron with a quantum yield of 0.36$^{33}$. In our study, we used H$^+$ ion as electron scavenger and find moderate acid dependent quantum yields for 405 nm photoionization of the [Ru(bpy)$_3$]$^{2+}$ MLCT excited state in aqueous solution under ambient condition.

2.1 Experimental

2.1.1. Compound preparation

The following commercial chemicals were purchased from Sigma-Aldrich and used without further purification: tris-(2,2'-bipyridine)ruthenium(II) chloride; 2-Propanol (≥99.5%); high purity trifluoromethylsulfonic acid (≥99.5%). Spectroscopic grade acetone (≥99.5%) and trifluoroacetic acid (≥99.5%) were purchased from Alfa-Aesar. The [Ru-tris-1,10-phenanthroline](PF$_6$)$_2$ (95% purity) was purchased from Strem Chemical INC. Lithium carbonate, [{Ru(bpy)$_2$}$_2$(2, 3-dpp)](PF$_6$)$_4$ was synthesized as reported previously$^{36}$ (a sample was also provided by Prof. Y. J. Chen).

In most of the photolysis experiments we used solutions of 10$^{-4}$ M [Ru(bpy)$_3$]$^{2+}$, various trifluoroacetic acid (TFA) or triflic acid (HOTf) ranging from 10$^{-4}$ – 4 M and 0.1 M 2-propanol prepared in deionized water and transferred to the photolysis cell by means of a syringe. Samples were renewed after each irradiation sequence. All samples were deaerated with argon through the solution mixture using stainless steel needles, serum capped vessels and the effluent gas was vented through water in a beaker for 30 min. All the photolysis solutions were prepared in the dark. Photolysis experiments were performed
with individual 405 or with superimposed 405 and 532 nm irradiations of solutions in a 2 mm id cylindrical cell or/and 3 mm fluorescence cuvette cell.

**Synthesis of [(bpy)$_2$Ru(dpp)Ru(bpy)$_2$](PF$_6$)$_4$**

A solution of 0.42 g, 0.867 mmol, [Ru(bpy)$_2$Cl$_2$].2 H$_2$O and 0.1 g, 0.426 mmol, of 2,3-dpp were refluxed in 30 mL of deareated 95% ethanol for 72 h. After this time the reaction mixture was filtered and evaporated to dryness. The solid was dissolved in a minimum of deareated water and a saturated solution of NH$_4$PF$_6$ was added. The solid was isolated after washing with a little water and then with ether. The resulting material was dissolved in the smallest amount of 5:3(v/v) water/acetone, and the resulting solution was chromatographed on Sephadex-C-25 ion-exchange resin. Elution with 0.3 M NaCl gave the desired purple band. The solution was partly evaporated in vacuo, and solid NH$_4$PF$_6$ was added until the precipitation was completed. The product was recovered as a purple solid, dissolved in acetonitrile and precipitated with ethanol. It was then washed several times with ethanol and then once with ether, and eventually dried in vacuo. Typical yield ~ 56%. For C$_{54}$H$_{38}$N$_{12}$P$_4$F$_{24}$Ru$_2$ (calcd): C, 39.92 (39.61); H, 2.10 (2.32); N, 10.64 (10.26)%

### 2.2 Instrumentation

2.2.1 Ambient and 77 K Emission and absorption spectrophotometers

Ambient absorption spectra were determined with a Shimadzu UV-2101PC spectrophotometer (1 Nishinokyo Kuwabara-cho, Nakagyo-ku, Kyoto 604-8511, Japan). An Andor Shamrock 500 spectrometer with an Andor Newton DU920-BV CCD detector was used for the ambient and 77 K emission spectra. The Andor spectrometer was calibrated using an Oriel Model 6045 calibrated Xe pen lamp.
emission lines and a NIST traceable Oriel model 63966 Quartz Tungsten Halogen (QTH) lamp for intensity. The Andor Newton detector was used for visible light detection in the wavelength range of 385 - 900 nm. The spectrometer was equipped with three gratings: 150 l/mm, 3001/mm; 800 nm blaze; 500 nm blaze; 1200 nm. Light was captured with ‘‘1’’ plano-convex optic and focused to an F/# matcher by a Thorlabs 3 mm Core Liquid Light Guide LLG0338-4. The function of F/# matcher is to match the emitted light to the optics of the Andor SR500i and has 6.5, numerical aperture (NA) of 0.077, acceptance angle of 8.8º and 2.9 magnification. The use of the liquid light guide and detector together resulted in a limit of 395 nm for the shortest wavelength of spectral detection.

2.2.2. Electrochemistry

Synthesized complexes were characterized in part with cyclic voltammetry. The electrochemical measurements were performed with several different solvents, all solutions were purged with argon, 0.1 M Bu₄NPF₆ was used as the electrolyte, sample concentrations ranged from 10⁻⁴-10⁻⁵ M. Tetrabutylammonium hexafluorophosphate was used as an electrolyte in a BAS 100B electrochemical system with a three-electrode system: Ag/AgCl reference electrode, a Pt wire counter electrode, and a Pt disk working electrode. 1μM diamond polish was used to polish the working electrode on a Buehler polishing cloth. A scan rate was 150 mV/s, solutions were purged with argon. The measurements started from zero and swept in the negative direction, ferrocene was used as an internal reference.

2.2.3. Lifetime measurements

The ambient and 77 K emission lifetimes were determined using a Spectra Physics VSL-337ND-S nitrogen laser-pumped DUO-210 Dye laser system and a Jobin-Yvon H-
10 spectrometer for detection with PMT output digitized using a PC with a National Instruments NI PCI-5154, 2 GS/s, 1 GHz digitizer with 8 MB/ch on board memory PC card as described previously.\textsuperscript{37-38} For photolysis experiments, emission decay lifetimes were determined for aerated, deaerated, or oxygen saturated samples with the sample concentration of $10^{-4}$ M. The Dewar was only used in the 77 K lifetime measurements.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{Ambient and 77K Lifetime measurements setup}
\end{figure}
Figure 3. An example of the lifetime instrument response to scattered laser light with no sample. The instrument response function was determined prior to the lifetime measurements and it was determined to be about 11-12 ns.

2.2.4. Proton Nuclear Magnetic Resonance Spectroscopy ($^1$H NMR)

$^1$H NMR spectra were obtained with an Oxford 400 MHz magnet fitted with a default Varian 1H/19F/13C/31P PFG Auto Switchable 5mm, VT (-20°C to +80°C) probe in the Lumigen Instrumentation Center at Chemistry department, Wayne State University. The samples were dissolved in deuterated solvents, dimethylsulfoxide (C$_2$D$_6$SO), acetonitrile (CD$_3$CN), water (D$_2$O), and acetone (C$_2$D$_6$CO). The aliphatic protons of the complexes were spread in the upfield region and aromatic rings (bpy), (dpp), and quinoline ligands. Protons were found in the downfield region of the spectra. The pure synthesized complexes were further characterized with other analytical techniques.

2.2.5. Light Sources used for photolysis experiments

Most irradiations were performed using continuous wave diode laser modules: (a) 405 nm (nominally $\geq$ 50 mW; Power Technologies, Inc.); (b) and/or 532 nm (nominally $\geq$80 mW; Laserglow Technology); 470 nm excitation nominally $\geq$ 10 mW; Changchun
New Industries Optoelectronics Tech.Co., Ltd. Laser output power was measured using a Coherent Fieldmate Laser Power meter; part number 1067353 with OM 10 Powermax sensor (provided by Professor Wen Li) and the output power of the 405 and 532 nm lasers was measured as 46±2 and 139±5 mW, respectively. Some irradiations were performed using the broad band output of an Oriel model 63966 Quartz Tungsten Halogen (QTH) lamp.

2.2.6. Photolysis cells and holders

Several different photolysis cells have been used: (a) A 3 mm id square fluorescence cell with internal dimensions of 3x3 mm (Starna catalog # 3-3.30-SOG-3). This cell was securely mounted on a specially designed cell holder to minimize the effects of building vibrations, and the cell holder was made of aluminum and was fixed securely by anchoring to the optical table, the shape of the cavity was square with a dimension of 0.4 cm for each side, and the depth of this cavity was 0.3 cm. The cell was fixed to a stack of 5 two inch of aluminum blocks bolted together and fixed to the Newport optical table; Figure 4 (b) A 2 mm id cylindrical fluorescence cell: This cell was also mounted on a specifically designed holder with holes in the top and the bottom, the diameters of the top hole is 0.3 cm and the bottom one is 0.2 cm, the depth of the top hole is about 3 cm and the bottom one is about 2 cm, this design allowed the 2 mm cell to be set tightly in the base of the holder and the holder was anchored in the table; Figure 5 (c) A Starna model 18-SOG-10 cuvette with internal dimensions of 10x4 mm mounted in a fabricated 1-cm cuvette holder.
The designed holder for 3 mm cuvette cell

Sample in 3 mm cuvette cell

Figure 4: Schematic diagram shows the cell holder we designed to hold 3 mm cuvette cell for the ambient condition photolysis experiment.

Figure 5. Schematic diagram shows the cell holder designed to hold 2 mm cylindrical cell for the ambient condition photolysis experiment.

2.2.7 Experimental set up for ambient photolysis study of various ruthenium complexes

The experiments employed a cut-off filter which only transmits wavelengths longer than 558 nm in the front of the liquid light guide to remove most of the scattered excitation light. A concentration of $10^{-4}$ M $[\text{Ru(bpy)}_3]^{2+}$ was used to ensure uniform absorption of the
laser light through the cell. The emitted light was collected at approximately 90° to the excitation beam(s).

All the photolysis solutions were prepared in the dark. Most of the basic characterizations of the [Ru(bpy)$_3$]$^{2+}$ photolysis were performed with 405 nm irradiations of solutions in a 2 mm id cylindrical cell. The two photon nature of the [Ru(bpy)$_3$]$^{2+}$ photolysis was further characterized using superimposed 405 and 532 nm laser beams with sample solutions in a 3 mm id cuvette. For these studies the 532 and 405 nm lasers beams were aligned so that they were superimposed in solution with angles in the range of 137°-180° between their beams which were incident on opposite sides of the cell see Figure 6. This arrangement enabled the separation of the $^3$MLCT generation step, by single photon 532 nm absorption, and its subsequent photolysis with 405 nm radiation. There was some uncertainty in the exact alignment of the laser beams inside the various cells we used. The diode laser radiation sources had 1 mm beam diameters. As a consequence, the volume of the photolysis region was smaller than the total solution volume and small volume cells to minimize the volume difference. 2 mm cylindrical cells were used in the characterization of the photochemical process because diffusion complications were relatively small. We used the 3 mm cuvette cell for quantum yield determinations.
Figure 6: Schematic diagram of the photolysis experimental set up showing the relative positions of the 532 nm and 405 nm lasers and spectrophotometer used.

Figure 7: Experimental setup for the QTH lamp output; the sample cell was angled at 45 degrees to minimize the scatter light.
2.2.8. Data analysis

Emission intensity and absorption spectral data were transferred from the Andor Solis or Shimadzu data files, respectively, to a computer EXCEL file. For experiments in which intensity data were collected in the kinetic mode, the intensity data were converted to the fraction of intensity decrease, \( F_t = (I_{t=0} - I_t)/I_{t=0} \), (where \( F_t \) is the fraction of photoproducts formed at time \( t \); \( I_{t=0} \) is the emission intensity at zero time; and \( I_t \) is the emission intensity at time \( t \)) plotted as a function of the irradiation time, \( t \). Since the time for opening the manual shutter was significant compared to the initial photolysis times, we estimated \( I_{t=0} \) by extrapolating the initial intensities to the time at which the shutter was half open. The variations in \( F_t \) with irradiation time were fitted to eq 1.

\[
F_t = F_\infty (1 - \exp(- k (t - t_0)))
\]  

(1)

where the parameters \( F_\infty, k \) and \( t_0 \) were obtained by non-linear Least Square Fit (LSQ) fitting routines in either PariPLOT or Origin. Equation 1 consistently gave excellent fits to the data obtained in each experiment when the kinetic plots were significantly curved. For most of the experiments, the fitted data were used to determine the “initial rate”, \( R_{\text{init}} \), as \( R_{\text{init}} = F_\infty \times k \), since \( F_t \xrightarrow{t \to 0} F_\infty \times k \). Linear least squares fits were used for the initial slopes of \( F_t \) when the \( F \) vs. \( t \) plots had very little curvature.

The iodometric experiments involved measurements of small differences in absorbance determined in a partly filled semi-micro cuvette and there were occasional baseline problems. In order to minimize these, we adjusted the sample absorbancies in EXCEL to average zero in the 650-700 nm range. When the absorption of the KI solution was significantly different from zero at the shorter wavelengths it was subtracted from the
spectra of samples treated with KI. The depletion of \([\text{Ru(bpy)}_3]^{2+}\) was determined from the difference in the absorption at 452 nm of the photolyzed and unphotolyzed solutions; the recovery was determined from the difference at 452 nm of these solutions after addition of an equal volume of aqueous KI.

2.3. Results

2.3.1. Characterization of experimental systems

a. The distortion of the laser beams by the walls of the photolysis cells has been examined by the beam shape at various distances after the cell. The observations are summarized in Table 1. The 3 mm cuvette does not distort the beam significantly, but the 2 mm cylindrical cell does.

| Table 1. Contrast in 405 nm laser beam modification by photolysis cells |
|-----------------------------|--------------------------|
| Distance past the cell      | Diameter of the laser beam after the photolysis cell |
| 2 mm cylindrical cell       |                          |
| 0.5 cm                      | Almost 1 mm              |
| 7 cm                        | 1.2 cm (horizontal line) |
| 17 cm                       | 6.5 cm (horizontal line) |
| 3 mm cuvette                |                          |
| 1 cm                        | 1 mm                     |
| 6 cm                        | 1.2 mm                   |
| 14 cm                       | 1.5 mm                   |
b. **Estimation of initial intensity.** Since the time required to open the manual shutter was significant it was necessary to estimate the initial intensity by extrapolation to the time when it was about half open as illustrated in Figure 8.

![Figure 8](image)

**Figure 8:** Typical extrapolation of the observed emission intensity, $I_0$, to an “effective intensity at zero-time”, $I_0$ in the photolysis of [Ru(bpy)$_3$]$_2^{2+}$. The gray rectangle indicates the time where the shutter was partially opened.

c. **An example of intensity increased by 532 nm irradiation**

Small increases in emitted emission intensity was observed for 532 nm irradiations in aerated solutions as shown in Figure 9. No significant changes were observed for 532 nm irradiations of deaerated solutions of [Ru(bpy)$_3$]$_2^{2+}$.
Figure 9. Illustrating the small increase in the emission intensity for 532 nm irradiation of $10^{-4}$ M $\text{[Ru(bpy)}_3\text{]}^{2+}$ with 0.1 M 2-propanol and 0.5 M trifluoroacetic acid in aqueous solution (ambient conditions).

d. General observations of the 405 nm irradiation of $\text{[Ru(bpy)}_3\text{]}^{2+}$ and illustration of data obtained in the kinetic observation mode.

The 405 nm irradiation of the $\text{[Ru(bpy)}_2\text{]}^{2+}$ MLCT excited state resulted in an efficient substrate decomposition while 532 nm irradiations alone did not show any photodecomposition. There are no significant changes in the $\text{[Ru(bpy)}_2\text{]}^{2+}$ emission energy maximum or bandshape for the irradiation periods used; see Figure 10 for the observations. The calculated initial rates from these observations are based on the integrated intensities of the spectral scans obtained using the kinetic mode. Aqueous hydrogen ion, $\text{H}^+$, was used for an electron scavenger and 2-propanol to scavenge H-atoms in order to observe significant photodecompositions. Strong acids were used whose anions are relatively unreactive towards the solvated electron.
Figure 10: Example of the Andor Solis operating software readout using the kinetic mode: ambient condition photolysis experiment showing the changes in the emission intensity as a result of 405 nm irradiation of \([\text{Ru(bpy)}_3]^{2+}\) in a 2 mm id cylindrical cell. The right panel shows the superimposed variations of the spectral scans at different irradiation times and the left shows the spectral scan variations displayed as the kinetic mode output. The solution contained 0.5 M acid, 0.1 M 2-propanol and 1.0×10^{-4} M \([\text{Ru(bpy)}_3]^{2+}\). The spectral scans shown start at 117 s (which excludes the time for opening the shutter), have 39 s intervals and 13 min the time of irradiation.

e. Illustration of selection of points for LSQ treatment

The linear least squares fitting method was used for initial rate estimates when the observed intensity variations had little curvature as illustrated in Figure 11.
Figure 11. Procedure for selection of the initial points for LSQ fits; y-axis is the fractional change of emission after the designated period of photolysis and the x-axis is the irradiation time in seconds. The red line indicates the initial points that we used for the initial rate calculations.

f. Variations of $R_{\text{init}}$ with the variation of [2-propanol] concentration. $R_{\text{init}}$ increased with the increases of [2-propanol] $> 0.1$ M. The rate constant for the H$^*/$2-propanol reaction is reported to be $7.4 \times 10^7$ M$^{-1}$s$^{-1}$, and this reaction should have about a 140 ns mean lifetime in 0.1 M 2-propanol. Thus, 0.1 M 2-propanol is a good scavenger for the free H-atom. At [2-propanol] $\leq 0.1$ M $R_{\text{init}}$ is independent of [2-propanol] concentration which illustrates that the reactions of the free aqueous H-atom with either the substrate or with the [Ru(bpy)$_3$]$^{3+}$ photoproduct do not greatly complicate our observations. However, for [2-propanol] $> 0.1$ M the $R_{\text{init}}$ was found to increase possibly as a result of a significant amount of 2-propanol in the solvation sphere of the substrate leading to either: (a) a smaller energy difference between the $^3$MC and $^3$MLCT excited states than with purely water solvation
and an enhancement of ligand substitution; or (b) that the H• that is formed in the [Ru(bpy)₃]³⁺ solvation sphere might reduce it to [Ru(bpy)₃]²⁺.

Table 2. Dependence of initial photolysis rates on 2-propanol concentration.

<table>
<thead>
<tr>
<th>[2-propanol], M</th>
<th>k, s⁻¹×10⁴</th>
<th>F₇</th>
<th>R₀, s⁻¹×10⁴</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>...</td>
<td>...</td>
<td>15±1b</td>
</tr>
<tr>
<td>0.1</td>
<td>35±1</td>
<td>0.40±0.01</td>
<td>14±3</td>
</tr>
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<td>...</td>
<td>...</td>
<td>14±1b</td>
</tr>
<tr>
<td>1</td>
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<td>0.79±0.02</td>
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</tr>
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</tr>
<tr>
<td>3</td>
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<td>0.72±0.01</td>
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</tbody>
</table>

a Irradiated at 405 nm in a 2 mm id cylindrical cell; deaerated solutions contained 1.0×10⁻⁴ M [Ru(bpy)₃]²⁺ and 0.5 M HOTf; fitted to eq 1 except as indicated. b Linear LSQ fit of the initial data points. Error limits are standard deviation of replicate determination.

2.3.2 Fraction of [Ru(bpy)₃]³⁺ photodecomposition with irradiation time

532 nm irradiation did not result in [Ru(bpy)₃]²⁺ photodecomposition, however, there was a small increase in the emission intensity which arises from increases in the ³MLCT photostationary state concentration as [O₂] is decreased (due to local heating and/or electron scavenging). The 532 nm irradiations can be used to generate the ³MLCT excited state that can then be photolyzed by 405 nm irradiation. The 405 nm irradiations also generate the ³MLCT excited state from the ground state of the [Ru(bpy)₃]²⁺. The rate of the photodecomposition was approximately doubled when we used superimposed 405 and 532 nm laser irradiation compared to the sum of the individual laser contributions; see Figure 12.
Figure 12. The contrasts between the photolysis rates in a 2 mm cylindrical cell of [Ru(bpy)$_3$]$^{2+}$ using superimposed 532 & 405 nm irradiation or individual 405 or 532 irradiations. The individual 532 nm irradiation is represented by G; and that at 405 nm is represented by B. The fraction of product formed when the two laser beams were superimposed is represented by B&G. The circles are the fractions of product formed ($F_t = (I_{em(t=0)} - I_{em(t)})/I_{em(t=0)}$) in the separate photolysis experiments. The squares correspond to the individual laser photolyses with F adjusted for the fraction of the intensity that each individual laser contributed to the observed emission in the dual laser experiment (both lasers produce emitting $^3$MLCT excited states); in the dual laser experiment $I_{em(B&G)} = f_B I_{em(B)} + f_G I_{em(G)}$ where the experimental values are $f_B = 0.57$ and $f_G = 0.43$. The solid lines are fits to eq 1: for this set of experiments $R_{init}(B&G) = (38\pm2)$, $R_{init}(B(adj)) = (17\pm1)$ and $R_{init}(G(adj)) = (-1.1\pm0.1)$ s$^{-1}$/10$^{-4}$ (B(adj) and G(adj) have been adjusted to account for the fractional contributions of the respective lasers to the observed emission); the open squares are for (B(adj) + G(adj)). The difference between $R_{init}(B&G)$ and $R_{init}(B(adj) + G(adj))$, see the arrow in the figure, is $\Delta R_{init}$ for 405 nm photolysis of that portion of the $^3$MLCT excited state that was generated by absorption of 532 nm light. The ratio of the two lasers used in these experiments were calculated from taking the differences in intensities between the two lasers when we irradiation the sample in 3 mm cuvette cell with the superimposed two lasers and the 405 nm irradiation was blocked each 3 minutes for several times.
Table 3. Laser intensity ratios based on measured emission intensities

<table>
<thead>
<tr>
<th>Segment/Experiment</th>
<th>( \frac{I_t(B&amp;G)}{I_t(G)} )</th>
<th>( \frac{I_t(B&amp;G)}{I_t(B)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.34</td>
<td>2.20</td>
</tr>
<tr>
<td>2</td>
<td>2.54</td>
<td>1.69</td>
</tr>
<tr>
<td>3</td>
<td>2.12</td>
<td>1.93</td>
</tr>
<tr>
<td>4</td>
<td>2.41</td>
<td>1.68</td>
</tr>
<tr>
<td>5</td>
<td>2.09</td>
<td>1.68</td>
</tr>
<tr>
<td>Experiment Average</td>
<td>2.4±0.2</td>
<td>1.84±0.24</td>
</tr>
<tr>
<td>Overall average</td>
<td>2.34±0.23</td>
<td>1.74±0.21</td>
</tr>
</tbody>
</table>

In the correction of \( R_{\text{obs}} \text{(B\&G)} \) for intensity contributions of the individual lasers, \( f_B = 0.57±1.8 \) and \( f_G = 0.43±0.13 \).

2.3.3. The dependence of initial rates on light intensity

The photodecomposition induced by 405 nm irradiation of \([\text{Ru(bpy)}_3]^{2+}\) complex for our experimental conditions is second order in light intensity as illustrated by Figure 13.

![Figure 13](image)

Figure 13. The dependence of the initial photodecomposition rate, \( R_{\text{init}} \), of \([\text{Ru(bpy)}_3]^{2+}\) on the square of the incident intensity of 405 nm radiation; the error bars correspond to standard deviations of replicate determinations. The sample contained a degassed solution of 0.5 M \([\text{H}^+]\), 0.1 M isopropanol and \(10^{-4}\) M substrate. The samples were irradiated in 2 mm id cylindrical cells for 6 min and stacks of microscope slides were used as filters. The dashed line is the LSQ fit (\( r^2 = 0.95 \)): \( R_{\text{init}} \times 10^4 = (56±5)(I_n/I_0)^2 + 0.4±2.4 \).
Table 4 shows the relative intensity of 405 nm irradiation that was absorbed by
[Ru(bpy)$_3$]$^{2+}$ complex, this intensity was calculated as the intensity observed for
the complex when there were no slides divided by the intensity observed when there are
different numbers of the microscope slides in the front of 405 nm lasers.

**Table 4. Average relative intensity of 405 nm radiation absorbed by [Ru(bpy)$_3$]$_2^{2+}$.**

<table>
<thead>
<tr>
<th>Slides in stack</th>
<th>I(scattered light)</th>
<th>I(Ru emission)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>0.8</td>
</tr>
<tr>
<td>3</td>
<td>0.72</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>0.67</td>
</tr>
<tr>
<td>7</td>
<td>0.66</td>
<td>0.66</td>
</tr>
<tr>
<td>10</td>
<td>0.34</td>
<td>0.34</td>
</tr>
<tr>
<td>Average Intensity abs./slide</td>
<td>0.07</td>
<td>0.07</td>
</tr>
</tbody>
</table>

$^a$From Table 5.

The data was fit using equation 1 for the acid concentration > 0.01 and LQS fits was used
to fit the data for the acid concentration < 0.001 and the summary of fitting parameters are
shown in Table 5.
Table 5. Fitting parameters of the initial rates of [Ru(bpy)$_3$]$_2^{2+}$ photodecomposition using 405 nm irradiations in 2 mm cylindrical cell with different light intensities.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>I$_{0, \text{counts}}$</th>
<th>Filter</th>
<th>I$<em>{\text{abs, Filter}}$ + I$</em>{\text{abs, no Filter}}$</th>
<th>Exponential fit; $F$= $F_\infty(1-\exp(-kt_0))$</th>
<th>$F_\infty$</th>
<th>$k$</th>
<th>$t_0$</th>
<th>$R_{\text{obs}} \times 10^4$, s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MA274</td>
<td>11200</td>
<td>none</td>
<td>1.00±0.04</td>
<td>$F_\infty$</td>
<td>0.68(1) $^a$</td>
<td>0.076(2)</td>
<td>52±3</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$k$</td>
<td>0.65(4)</td>
<td>0.0081(1)</td>
<td>28(1)</td>
<td>53±4</td>
</tr>
<tr>
<td>Averages</td>
<td></td>
<td></td>
<td>1.00±0.04</td>
<td>$t_0$</td>
<td></td>
<td></td>
<td></td>
<td>52±4</td>
</tr>
<tr>
<td>MA300</td>
<td>16000</td>
<td>2 slides</td>
<td>0.88±0.14</td>
<td>$F_\infty$</td>
<td>0.95(15) $^a$</td>
<td>0.0040(3)</td>
<td>38±6</td>
<td></td>
</tr>
<tr>
<td>MA318</td>
<td>13000</td>
<td></td>
<td></td>
<td>$k$</td>
<td>0.59(1)</td>
<td>0.0067(3)</td>
<td>10(2)</td>
<td>40±6</td>
</tr>
<tr>
<td>MA317</td>
<td>13000</td>
<td></td>
<td></td>
<td>$t_0$</td>
<td>0.63(9)</td>
<td>0.0061(2)</td>
<td>13(1)</td>
<td>38±6</td>
</tr>
<tr>
<td>Averages</td>
<td></td>
<td></td>
<td>0.88±0.14</td>
<td>$R_{\text{obs}}$</td>
<td>66(3)</td>
<td>0.0078(3)</td>
<td></td>
<td>39±6</td>
</tr>
<tr>
<td>MA301</td>
<td>14100</td>
<td>4 slides</td>
<td>0.79±0.07</td>
<td>$F_\infty$</td>
<td>0.73(5) $^a$</td>
<td>0.0045(4)</td>
<td>32±8</td>
<td></td>
</tr>
<tr>
<td>MA315</td>
<td>11000</td>
<td></td>
<td></td>
<td>$k$</td>
<td>0.56(1) $^a$</td>
<td>0.0062(3)</td>
<td></td>
<td>32±7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$t_0$</td>
<td>0.55(2)</td>
<td>0.0069(6)</td>
<td>3(4)</td>
<td></td>
</tr>
<tr>
<td>MA316$^a$</td>
<td>11750</td>
<td>4 slides</td>
<td>0.79±0.07</td>
<td>$F_\infty$</td>
<td>0.63(1) $^a$</td>
<td>0.0058(2)</td>
<td>36±6</td>
<td></td>
</tr>
<tr>
<td>MA316$^b$</td>
<td>12000</td>
<td></td>
<td></td>
<td>$k$</td>
<td>0.59(1)</td>
<td>0.0069(4)</td>
<td>-3(3)</td>
<td>41±4</td>
</tr>
<tr>
<td>MA328</td>
<td>10600</td>
<td></td>
<td></td>
<td>$t_0$</td>
<td>0.86(5)</td>
<td>0.0024(2)</td>
<td>16(3)</td>
<td>21±4</td>
</tr>
<tr>
<td>Averages</td>
<td></td>
<td></td>
<td>0.79±0.07</td>
<td>$F_\infty$</td>
<td>0.6(1)</td>
<td>0.006(1)</td>
<td></td>
<td>32±6</td>
</tr>
<tr>
<td>MA273</td>
<td>8250</td>
<td>6 slides</td>
<td>0.6±0.07</td>
<td>$F_\infty$</td>
<td>0.23(1) $^a$</td>
<td>0.050(3)</td>
<td>22±10</td>
<td></td>
</tr>
<tr>
<td>MA302</td>
<td>12500</td>
<td></td>
<td></td>
<td>$k$</td>
<td>0.57(4)</td>
<td>0.006(10)</td>
<td>22(14)</td>
<td>22±9</td>
</tr>
<tr>
<td>MA313</td>
<td>10500</td>
<td></td>
<td></td>
<td>$t_0$</td>
<td>1.1(3) $^a$</td>
<td>0.0020(6)</td>
<td></td>
<td>19±2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$R_{\text{obs}}$</td>
<td>0.9</td>
<td>0.002(1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MA313</td>
<td>11600</td>
<td></td>
<td></td>
<td>$F_\infty$</td>
<td>0.56(1)</td>
<td>0.0048(4)</td>
<td>1(3)</td>
<td>27±4</td>
</tr>
<tr>
<td>MA329</td>
<td>10600</td>
<td></td>
<td></td>
<td>$k$</td>
<td>1.1(2)</td>
<td>0.0016(5)</td>
<td>10(5)</td>
<td>18±6</td>
</tr>
<tr>
<td>MA330</td>
<td>11000</td>
<td></td>
<td></td>
<td>$t_0$</td>
<td>0.74(4)</td>
<td>0.0030(2)</td>
<td>23(2)</td>
<td>22±3</td>
</tr>
<tr>
<td>Averages</td>
<td></td>
<td></td>
<td>0.6±0.07</td>
<td>$F_\infty$</td>
<td>0.7(3)</td>
<td>0.004(2)</td>
<td></td>
<td>22±6</td>
</tr>
<tr>
<td>MA545$^a$</td>
<td>2500</td>
<td>8 slides</td>
<td>0.52±0.10</td>
<td>$F_\infty$</td>
<td>0.36(6)</td>
<td>0.0028(8)</td>
<td>12(7)</td>
<td>3±2</td>
</tr>
<tr>
<td>MA545$^b$</td>
<td>2100</td>
<td></td>
<td></td>
<td>$k$</td>
<td>0.122(1)</td>
<td>0.0021(8)</td>
<td>-15(5)</td>
<td>2.6±0.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$t_0$</td>
<td>0.52±0.10</td>
<td>0.24(12)</td>
<td>0.0026(8)</td>
<td>6±4</td>
</tr>
<tr>
<td>MA275</td>
<td>11200</td>
<td>9 slides</td>
<td>0.45±0.03</td>
<td>$F_\infty$</td>
<td>0.46(4)</td>
<td>0.0036(7)</td>
<td>20(10)</td>
<td>13±5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$k$</td>
<td>0.46(4)</td>
<td>0.0036(7)</td>
<td></td>
<td>13±5</td>
</tr>
<tr>
<td>MA546$^a$</td>
<td>2800</td>
<td>10 slides</td>
<td>0.30±0.15</td>
<td>$F_\infty$</td>
<td>0.16(1) $^a$</td>
<td>0.0078(8)</td>
<td>66±5</td>
<td>12±1</td>
</tr>
<tr>
<td>MA546</td>
<td>2500</td>
<td></td>
<td></td>
<td>$k$</td>
<td>0.11(1) $^a$</td>
<td>0.0030(2)</td>
<td>120±15</td>
<td>3±1</td>
</tr>
<tr>
<td>Averages</td>
<td></td>
<td></td>
<td>0.30±0.12</td>
<td>$F_\infty$</td>
<td>0.14(2)</td>
<td>0.0054(20)</td>
<td></td>
<td>8±5</td>
</tr>
</tbody>
</table>

$^a$ Fitted to $F = F_\infty(1 - \exp(-kt_0))$. $^b$LSQ fits.
2.3.4. Iodometry

The relative yields of the Ru(III) photoproducts that were generated from the 405 nm laser irradiations were determined by the oxidation of iodide at various acid concentrations with various irradiation times. The solutions used consisted of $10^{-4}$ M $[\text{Ru(bpy)}_3]^{2+}$ and 0.1 M 2-propanol and $10^{-3}$- 4 M acid. The samples were deaerated with argon and irradiated with 405 nm for various times. The absorbance at 452 nm ($\varepsilon_{\text{max}} = 14,600$ M$^{-1}$cm$^{-1}$) was used to determine the concentration of $[\text{Ru(bpy)}_3]^{2+}$ before and after photolysis and with and without KI added to the photolyzed solution after photolysis. The results are shown in Figure 14 and the summary of the recovered yield of Ru$^{2+}$ for those experiments are shown in Table 6. Figure 14 also shows that most of the bleached $[\text{Ru(bpy)}_3]^{2+}$ absorption was recovered as a result of the $[\text{Ru(bpy)}_3]^{3+}$ oxidation of iodide. These observations demonstrate that most of the photo-oxidized product is $[\text{Ru(bpy)}_2]^{3+}$ and the overall average of the recovered absorption of $[\text{Ru(bpy)}_2]^{2+}$ over an acid variation was calculated to be 80±20%. There could be a minor photosubsitution reaction pathway (16±10%; Table 6) even at higher acid concentration where our uncertainties are relatively small.
Figure 14. The figure shows the changes in the absorption of $[\text{Ru(bpy)}_3]^{2+}$ that result from 405 nm irradiation (upper panel) and the recovery of $\text{Ru}^{2+}$ absorbance after adding an equal volume of 0.01 M KI to the photolyte (compared to the unphotolyzed solution absorbance after adding KI) (lower panel). The black area are the unphotolyzed solutions absorbance and red area is the photolyzed solution absorbance in both figures. The solutions contained of $1 \times 10^{-4}$ M $[\text{Ru(bpy)}_3]^{2+}$ and the acid concentration was 4 M. The solution was irradiated with 405 nm for 30 min. The dilution errors were determined from comparisons of the unphotolyzed solution absorbance with and without KI and averaged to be about 10%. The generation of the photo-product ($[\text{Ru(bpy)}_3]^{3+}$) was accompanied by the oxidation of $\Gamma^-$, and we were not able to determine the stoichiometric relationship between them due to the background absorbancies in the UV region. In addition, the photolysis resulted in a small blue shift in the bpy-$\pi\pi^*$ absorption at about 250-300 nm.
Table 6. Summary of iodometric yield determinations

<table>
<thead>
<tr>
<th>[H(^+)], M</th>
<th>[Ru(^{III})B(<em>{3})](</em>{init}), µM</th>
<th>Photolyte Vol., mL</th>
<th>Abs. 405 nm</th>
<th>Irradiation time, min</th>
<th>(\Delta[\text{Ru}(^{III})B(<em>{3})](</em>{dec}), µM (^a)</th>
<th>(\Delta[\text{Ru}(^{III})B(<em>{3})](</em>{rec}), µM (^b)</th>
<th>Fraction Recovered (^c)</th>
<th>(\sim 2[\text{I}^-], \mu\text{M} (^d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.0</td>
<td>76</td>
<td>0.30</td>
<td>0.63</td>
<td>30</td>
<td>32</td>
<td>27</td>
<td>0.85</td>
<td>≥17</td>
</tr>
<tr>
<td>4.0</td>
<td>74</td>
<td>0.30</td>
<td>0.62</td>
<td>30</td>
<td>28</td>
<td>23</td>
<td>0.82</td>
<td>≥18</td>
</tr>
<tr>
<td>4.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.84±0.02</td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>35</td>
<td>0.30</td>
<td>0.25</td>
<td>30</td>
<td>14</td>
<td>12</td>
<td>0.86</td>
<td>≥11</td>
</tr>
<tr>
<td>2.0</td>
<td>41</td>
<td>0.30</td>
<td>0.34</td>
<td>30</td>
<td>18</td>
<td>12</td>
<td>0.67</td>
<td>≥11</td>
</tr>
<tr>
<td>2.0</td>
<td>42</td>
<td>0.30</td>
<td>0.28</td>
<td>30</td>
<td>8</td>
<td>8</td>
<td>1.0</td>
<td>≥4</td>
</tr>
<tr>
<td>2.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.84±0.17</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>72</td>
<td>0.30</td>
<td>0.57</td>
<td>5</td>
<td>7</td>
<td>9</td>
<td>1.3</td>
<td>≥2</td>
</tr>
<tr>
<td>0.5</td>
<td>97</td>
<td>0.30</td>
<td>0.71</td>
<td>10</td>
<td>15</td>
<td>13</td>
<td>0.9</td>
<td>4</td>
</tr>
<tr>
<td>0.5</td>
<td>88</td>
<td>0.30</td>
<td>0.68</td>
<td>20</td>
<td>35</td>
<td>40</td>
<td>1.1</td>
<td>≥8</td>
</tr>
<tr>
<td>0.5</td>
<td>65</td>
<td>0.30</td>
<td>0.51</td>
<td>20</td>
<td>7</td>
<td>5</td>
<td>0.7</td>
<td>≥4</td>
</tr>
<tr>
<td>0.5</td>
<td>55</td>
<td>0.30</td>
<td>0.41</td>
<td>30</td>
<td>13</td>
<td>15</td>
<td>1.1</td>
<td>≥9</td>
</tr>
<tr>
<td>0.5</td>
<td>94</td>
<td>0.30</td>
<td>0.73</td>
<td>30</td>
<td>7</td>
<td>10</td>
<td>1.4</td>
<td>≥1</td>
</tr>
<tr>
<td>0.5</td>
<td>55</td>
<td>0.30</td>
<td>0.40</td>
<td>30</td>
<td>18</td>
<td>18</td>
<td>1</td>
<td>≥8</td>
</tr>
<tr>
<td>0.5</td>
<td>98</td>
<td>0.60</td>
<td>0.74</td>
<td>30</td>
<td>9</td>
<td>10</td>
<td>1.1</td>
<td>≥3</td>
</tr>
<tr>
<td>0.5</td>
<td>92</td>
<td>0.30</td>
<td>0.77</td>
<td>60</td>
<td>20</td>
<td>12</td>
<td>0.6</td>
<td>≥13</td>
</tr>
<tr>
<td>0.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.0±0.3</td>
<td></td>
</tr>
<tr>
<td>0.20</td>
<td>58</td>
<td>0.30</td>
<td>0.44</td>
<td>30</td>
<td>5</td>
<td>3</td>
<td>0.6</td>
<td>≥5</td>
</tr>
<tr>
<td>0.20</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>0.10</td>
<td>91</td>
<td>0.60(^y)</td>
<td>0.70</td>
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<td>0.75</td>
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<td>≥12</td>
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<tr>
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<td>0.45</td>
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</tr>
<tr>
<td>0.010</td>
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<td></td>
<td></td>
<td></td>
<td>0.6±0.3</td>
<td></td>
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\(^a\)The determination of the amount of the photodecomposition from the differences in the amplitude of 452 nm 3MLCT absorption maxima in the spectra of the initial solution and the photolyzed solution. \(^b\) The amount of Ru\(^{II}\) recovery calculated from the difference between 452 nm 3MLCT absorption maxima in the spectra of the initial solution and the photolyzed solution after added 0.3 ml of KI solution; \(\epsilon_{\text{max}} = 14,500 \text{ M}^{-1}\text{cm}^{-1}\). \(^c\) The difference between 350 nm MLCT absorption maxim of I\(_3^-\) (\(\epsilon_{\text{max}} = 23,200\text{M}^{-1}\text{cm}^{-1}\)) in the spectra of the initial solution and the photolyzed solution after each was mixed with an equal volume of 0.010 M KI was used for crude estimate of [I\(_3^-\)]; the 350 nm absorbance in the absence if I\(_3^-\) is not the same before and after photolysis.
2.3.5. Acid dependence of photodecomposition rate

The initial rate of the photodecomposition was acid dependent for \([\text{Ru}(\text{bpy})_3]^{2+}\) photolysis experiments that were performed under ambient conditions. The photolysis rate, \(R_{\text{init}}\), increased about 10-fold when the acid concentration was increased from \([\text{H}^+] = 0.001\) M to \([\text{H}^+] = 4\) M. In addition, the observations of the changes of the initial rate with acid concentration were similar to those in 3mm cuvette and in a 2 mm i.d. cylindrical cell, but the initial rate \(R_{\text{init}}\) was larger in the cylindrical cell than in the 3 mm cuvette; see Figures 15 and 16 and Table 7. The acid dependence of the initial rate for photodecomposition of \([\text{Ru}(\text{phen})_3]^{2+}\) showed similar trend but \(R_{\text{init}}\) was smaller compared to \([\text{Ru}(\text{bpy})_3]^{2+}\), with \((R_{\text{init}})_{(\text{Ru-phen})} \approx R_{\text{init}}(\text{Ru-bpy})/3\). However, the photodecomposition rate of \([{(\text{bpy})_2\text{Ru}}_2\text{pz}]^{4+}\) complex was acid independent for the range of the acid concentrations used.
Figure 15. The dependence of the photodecomposition rate on, $R_{\text{init}}$, on acid concentration for various Ru$^{\text{II}}$ complexes in ambient aqueous solutions with 0.1 M 2-propanol in a 2 mm cylindrical cell: The green circles is for [Ru(bpy)$_3$]$^{2+}$, the red squares are for [Ru(phen)$_3$]$^{2+}$ and the black diamonds are for [{Ru(bpy)$_2$}$_2$(2,3-dpp)] with the 532 nm irradiation and the light blue diamonds for 405 nm irradiation. The errors are the standard deviations of replicate determinations. The dashed curve is the non-linear least squares fit of eq 2 to the [Ru(bpy)$_3$]$^{2+}$ data and the red-dashed curve is the fit of eq 3 for a large number of scavengerable ion pair species. The best fit in both cases required a small positive intercept. The data are for from Table 8.

Two models were used for the H$^+$/e$^-$ scavenging for acids concentration ([H$^+$] > 0.1 M; section 2.6 1B): The first model for only one ion-pair species scavenged; and the second model for many ion-pair species scavenged. The competition kinetics of the first model predicts that the initial rate of product formation from the H$^+$/e$^-$ scavenging has the algebraic form in eq 2,

$$R_{\text{init}} \approx \left( \phi_u G(\lambda) \right) \frac{[H^+]}{f_{R,h} + [H^+]} + C$$  (2)
Fit to eq 2: \((\phi_U G_\lambda) \times 10^4 = 114 \pm 8 \text{ s}^{-1}\), \(f_{R,h} = 0.7 \pm 0.2 \text{ M}\) and \(C \times 10^4 = 6 \pm 4 \text{ s}^{-1}\); where \(f\) is the ratio of recombination and scavenging rate constants; \(\phi_U\) is the photoionization quantum yield; \(G(\lambda) = \frac{k_{S(\lambda)} k_{E(\lambda)}}{k_{obsd}}\); \(k_{S(\lambda)} = \varepsilon_{S(\lambda)} d_{\text{ph}} I_{\lambda}^\text{ph}\); \(k_{E(\lambda)} = \varepsilon_{E(\lambda)} d_{\text{ph}} I_{\lambda}^\text{ph}\).

The origin of this equation is shown in section 2.6. The second idealized model, model 2 considers the possibility that the chemical scavenger used can react with several ion pair species with different recombination rates by treating \(f_{R,h}\) as a variable and integrating eq 2 from \(f_{R,h} = 0\) to \(f_{R,h} = f_{\text{max}}\) resulting in eq 3. The parameters \(f_{U G_\lambda}, f_{\text{max}}, C\) found for the fit to eq 3 (red dashed curve) shown in Figures 15 and 16 are \((\phi_U G_\lambda) \times 10^4 = 59 \pm 14 \text{ s}^{-1}\), \(f_{\text{max}} = 2.6 \pm 0.6 \text{ M}\) and \(C \times 10^4 = 5 \pm 4 \text{ s}^{-1}\).

\[
R_{\text{init}} = \phi_U G_\lambda [H^+][H^+] \ln \left( \frac{f_{\text{max}} + [H^+]}{[H^+]^2} \right) + C
\]  

(3)

Figure 16 expands the low acid range from Figure 15 and the fit to eq 2. That the best fit requires an intercept is consistent with more than one species being scavenged. The initial rate dependence of acid \([H^+]\) for \([\text{Ru(phen)}_3]^{2+}\), Figure 15, was similar to that of \([\text{Ru(bpy)}_3]^{2+}\), however, the initial rate of \(R_{\text{init}}\) was about 30\% of those of the Ru-bpy complex; and this illustrates that \([H^+] / (B + [H^+])\) is about the same for both complexes while \(\phi_U G_\lambda\) is significantly smaller for the Ru-phen complex. This is consistent with the scavenging behavior being dependent only on the radicals scavenged and not on their origin. In contrast, the initial rate of the photodecomposition of \([\{(bpy)_2\text{Ru}\}_2\text{dpp}]^{4+}\) was acid independent when we irradiate the sample with either 405 or 532 nm lasers which suggests that this complex was not photoionized, and the yield of the product was higher.
with 532 nm than with 405 nm irradiation. Thus, this complex might photodecompose through an excited state thermal substitution.

Figure 16. The photodecomposition of [Ru(bpy)$_3$]$_{2+}$ at low acid concentration. See the caption of Figure 15 for details.

The scavenging model and the kinetic analysis shown in 2.6 indicates that R$_{\text{init}}$ is independent of diffusion and the extrapolation to $t = 0$ eliminates the problems associated with product formation. However, the parameters $F_\infty$ and $k$, that result from the fittings to the experimental data by eq 1, are diffusion dependent (section 2.5, eq B19).

$$k \approx R_{\text{init}} + k_D$$ and $$F_\infty \approx \frac{R_{\text{init}}}{k_D + R_{\text{init}}}$$

Table 7 shows the average experimental value $k_D = (k - R_{\text{init}})$ that was calculated from the experimental observation of the irradiations of [Ru(bpy)$_3$]$_{2+}$ in a 2 mm id cell in the acid range of 0.001- 4 M; the diffusion rate values were independent for the $[H^+] \geq 0.01$ with $k_{D(\text{ave})} = 25\pm7 \text{ s}^{-1}$. 
Table 7. Initial rates of [Ru(bpy)_3]^{2+} photodecomposition resulting from the 405 nm irradiation in acidic 2-propanol solutions in a 2 mm cylindrical cell.

<table>
<thead>
<tr>
<th>[H^+] , M</th>
<th>k_0, s^{-1} x 10^4</th>
<th>F_0</th>
<th>R_{init} = k x F_0 x 10^4, s^{-1}</th>
<th>k_D = k - R_{ob}</th>
<th>(2\pm1) c</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0001</td>
<td>LSQ fit</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>0.001</td>
<td>13±1</td>
<td>0.5±0.1</td>
<td>4±2</td>
<td>6±3</td>
<td></td>
</tr>
<tr>
<td>0.01</td>
<td>34±5</td>
<td>0.28±0.03</td>
<td>8±2</td>
<td>26±7</td>
<td></td>
</tr>
<tr>
<td>0.05</td>
<td>30±4</td>
<td>0.52±0.02</td>
<td>16±2</td>
<td>18±6</td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>46±5</td>
<td>0.57±0.04</td>
<td>26±3</td>
<td>20±8</td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td>64±9</td>
<td>0.58±3</td>
<td>37±6</td>
<td>27±15</td>
<td></td>
</tr>
<tr>
<td>0.3</td>
<td>51±10</td>
<td>0.72±0.07</td>
<td>37±7</td>
<td>14±17</td>
<td></td>
</tr>
<tr>
<td>0.4</td>
<td>69±8</td>
<td>0.66±0.01</td>
<td>46±6</td>
<td>23±15</td>
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</tr>
<tr>
<td>0.5</td>
<td>80±16</td>
<td>0.65±0.03</td>
<td>52±10</td>
<td>28±26</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>114±5</td>
<td>0.69±0.01</td>
<td>77±4</td>
<td>34±9</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>120±30</td>
<td>0.79±0.02</td>
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<td>25±56</td>
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</tr>
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<td></td>
</tr>
<tr>
<td>4</td>
<td>143±34</td>
<td>0.80±0.12</td>
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a Data were fitted to eq 1, and the values reported are the averages of several determinations; for the experiments that show very little curvature, the F_t vs. t plots fitting using this equation did not converge and we used linear least squares (LSQ) fits. b The results based on our kinetic model in section 2.6. The empirical parameter related to the rate of diffusional replacement of the photolyte by bulk solution is expressed as k_D = k_{init} + k_D, our fits resulted in (k_D)_{ave} = 25±7 s^{-1} for [H^+] ≥ 0.01 M. c The slope of LQS fits.

Table 8. Summary of the fitting\(^a\) parameters for the acid dependent [Ru(bpy)_3]^{2+} photodecomposition rate in various aqueous acidic solutions in a 2 mm cylindrical cell with 405 nm radiation (Ar deaerated).

<table>
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<tr>
<th>Laser Wavelength, nm</th>
<th>[H^+] , M</th>
<th>t_0, s</th>
<th>k, s^{-1} x 10^4</th>
<th>F_0</th>
<th>Initial Intensity, I_{t=0}, counts</th>
<th>R_{obs} = k x F_0 x 10^4, s^{-1}</th>
<th>LSQ fits R_{obs} x 10^4, s^{-1}</th>
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<td>35000</td>
<td>2</td>
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<td></td>
<td></td>
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</tr>
<tr>
<td>405 E-4</td>
<td>35000</td>
<td>2.5</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>405 E-4</td>
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<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>405 E-3</td>
<td>59</td>
<td>14±10</td>
<td>0.41±0.22</td>
<td>20300</td>
<td>6±5</td>
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</table>

2±1
<p>| | | | | | |</p>
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<td>E-3</td>
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</tr>
</tbody>
</table>
Photodecomposition data fitted to eq 1; aLSQ fits in parentheses.

2.3.6. Superimposed dual laser irradiations

a. Irradiation with dual 405 & 532 nm irradiation in 2 mm cylindrical cell

The observed rate the photodecomposition of \([\text{Ru(bpy)}_3]^{2+}\) 532 and 405 nm lasers superimposed is much larger than the 405 nm alone or the weighted sum of photolysis rates found for the individual lasers. The calculated values of \(R_{\text{int}}\) obtained in 2 mm i.d. cylindrical cells were about 5 times larger than those obtained in the 3 mm i.d. cuvette. Argon gas dearation resulted in doubling of the initial rate, \(R_{\text{int}}\), which is in proportion to the increase in the photo-stationary state concentration of \(^3\text{MLCT}\). Greater rate of intensity decrease observed for the superimposed lasers resulted from the two-photon dependence of the photodecomposition. The larger values of \(R_{\text{init}}\) and the cylindrical cell were a result of curvature which resulted in some focusing of the laser beam width, decreasing the effective photolysis volume and increasing the photon density within the photolysis volume.
Figure 17. The changes in $^3$MLCT emission intensity that accompany irradiation of [Ru(bpy)$_3$]$^{2+}$ with superimposed 405 & 532 nm laser beams. The left panel shows the superimposed variations of the spectral scans as a function of irradiation time and the right panel shows the spectral scan variations displayed as the kinetic mode output. The solutions contained 0.5 M acid, 0.1 M 2-propanol and initial concentrations of [Ru(bpy)$_3$]$^{2+}$ = 1.0×10$^{-4}$ M. The irradiation times represented start at 117 s (which excludes the time for opening the shutter; the kinetic mode timing is internal in the spectrometer software) with spectral scans at 39 s intervals and 13 min total time of irradiation. The experimental data points were obtained as the intensities of the kinetic mode spectral scans.

An example of the observed changes in the [Ru(bpy)$_2$]$^{2+}$ emission spectrum with irradiation time using overlapped 405 and 532 nm lasers in 3 mm cuvette cell is shown in Figure 18. The emission energy maximum or the band shape do not change when the intensity changed. Also displayed in Figure 18 are the emission spectral intensity changes that are observed for this complex using 405 nm excitation only. The emission intensity (in counts per second) on the Y- axis was determined in EXCEL as the average intensity of each spectral scan, $I_{ave} = \left( \frac{\sum I_\lambda}{N_\lambda} \right)$ ($I_\lambda$ the intensity recorded at wavelength $\lambda$; $N_\lambda$ the number of wavelength increments, about every 3 nm, in the EXCEL record of the scan).
Figure 18: Experiments illustrating the contrasting fractional decreases in $^3$MLCT emission intensity induced by the simultaneous 532 and 405 nm laser irradiations of [Ru(bpy)$_3$]$^{2+}$ in ambient acidic solution with those of the 405 nm laser alone in a 3 mm id cuvette (13 min total irradiation time): superimposed 532 and 405 nm laser beams in the left panel and 405 nm laser only in the right panel. The conditions and procedures are as described in the caption of Figure 17.
Table 9. Summary of the calculated initial rate of the photodecomposition of [Ru(bpy)$_3$]$_2^{2+}$ in a 3 mm id cuvette cell with individual 405 and 532 or the laser beams superimposed.

<table>
<thead>
<tr>
<th>Complex$^a$</th>
<th>Conditions</th>
<th>λ Irradiation, nm</th>
<th>Average $10^4$$\times$R$_{\text{int}}$ b s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ru(bpy)$_3$]$^{2+}$</td>
<td>[TFA], M</td>
<td>[2-propanol], M</td>
<td>other</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
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<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Ru(bpy)$_3$]$^{2+}$</td>
<td>0.5</td>
<td>0.1</td>
<td>30% L$_c^c$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Ru(bpy)$_3$]$^{2+}$</td>
<td>0</td>
<td>0</td>
<td>0.5 M acetone</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Ru(bpy)$_3$(CN)$_2$]</td>
<td>0</td>
<td>0</td>
<td>0.5 M acetone</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Ambient solutions in a 3 mm square fluorescence cell with [Ru(bpy)$_3$]$^{2+}$ = 1.0×10$^{-4}$ M except as indicated. The measured cw laser power outputs were 46±2 mW (405 nm laser) and 139±5 mW (532 nm laser). $^b$ Average calculated initial using LSQ fits. $^c$ 30% neutral density filter. $^d$0.55×10$^{-4}$ M [Ru(bpy)$_3$]$^{2+}$.

The initial photolysis rates for these experiments were calculated using the least square fits, the initial few points of the fraction of the product formed after the shutter was open up to 300 second were chosen for the fits.
2.3.7. Ambient condition photolysis of $[\text{Ru(bpy)}_3]^{2+}$ with the quartz halogen tungsten lamp (QTH) lamp

An example of the emission changes of $[\text{Ru(bpy)}_2]^{2+}$ with the QTH lamp in ambient condition in a 3 mm cuvette cell, a cut off filter that cuts before 558 nm was used in the front of liquid light guide. The cell was placed at about 45° to the laser beam to minimize the scattered light. The result of this irradiation is shown in Figure 19. The initial rates of the photodecomposition calculated from least square fits are shown in Table 10.

Table 10. Summary of the calculated initial rate of the photodecomposition of $[\text{Ru(bpy)}_3]^{2+}$ in a 3 mm cuvette using QTH as irradiation source under ambient condition.

<table>
<thead>
<tr>
<th>Code</th>
<th>Laser Wavelength, nm</th>
<th>Initial Intensity, $I_{t=0}$ counts/s</th>
<th>Initial rate $10^4 x dF/dt$, s$^{-1}$</th>
<th>r$^2$</th>
<th>Special Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>MA145</td>
<td>QTH</td>
<td>8,320</td>
<td>2.6±0.4</td>
<td>[0.92]</td>
<td>RuB$_3$</td>
</tr>
<tr>
<td>MA146</td>
<td>QTH w/uv filter</td>
<td>10,870</td>
<td>0.6±0.03</td>
<td>[0.99]</td>
<td>RuB$_3$</td>
</tr>
</tbody>
</table>

Figure 19. Observed photochemistry of $10^{-4}$ $[\text{Ru(bpy)}]^{2+}$ in aqueous solution with 0.5 M trifluoroacetic acid and 0.1 M 2-propanol using QTH lamp as irradiation source at ambient condition. Red line is the variation of the emission intensity with a < 558
nm cut off filter. The black line is the variation of the emission intensity without using the cut off filter.

2.3.8. Comparison of the absorption spectra of the \([\text{Ru(bpy)}_3]^{2+}\) ground state and \(^3\text{MLCT}\) excited state to the relative intensity distributions in the global solar spectrum and QTH lamp spectra

The net photoionization yields are more significant when a combination of long and short wavelength visible radiation is used, the relative amounts of QTH radiation absorbed by the ground state; less than ten percent of the light absorbed by the \([\text{Ru(bpy)}_3]^{2+}\) \(^3\text{MLCT}\) excited state results in most of the photoionization, and the visible radiation can be absorbed by the ground state to generate more \(^3\text{MLCT}\) that can be ionized by 405 nm radiation. Thus, it should be possible to achieve a significant photoionization with any broadband irradiation of a substrate such as \([\text{Ru(bpy)}_3]^{2+}\) if the absorption of both the ground and excited state overlap with that radiation; see Figure 20.
Figure 20. Comparison of the absorption spectra of the ground state and $^3$MLCT excited state of $[\text{Ru(bpy)}_3]^{2+}$ to the relative intensity distributions in the global solar and QTH lamp spectra. The green triangles represent the 532 nm and blue is for 405 nm. The amplitudes of the spectra have been adjusted for convenient comparison; the $^3$MLCT absorptivity at 405 nm is about three times that of the ground state. The standard global solar spectrum was downloaded from PVEDucation.org, ([www.pveducation.org/pvcdrom/appendices/standard-solarspectra](http://www.pveducation.org/pvcdrom/appendices/standard-solarspectra)) as an EXCEL file.

2.3.9. Estimates of photoionization quantum yields. We were able to estimate the quantum yields of scavengeable electrons and the fits of eqs 2 and 3 provide slightly different estimates of $(\phi_e)G(\lambda)$, these estimates are in Table 11; the parameters used in these estimates are in Table 12.
Table 11. Photoionization quantum yield estimates

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Model</th>
<th>Single Ion Pair</th>
<th>Many Ion Pairs</th>
</tr>
</thead>
<tbody>
<tr>
<td>f&lt;sub&gt;R,h&lt;/sub&gt;, M</td>
<td></td>
<td>0.7±0.2&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2.1±0.6&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>φ&lt;sub&gt;U&lt;/sub&gt; ([H&lt;sup&gt;+&lt;/sup&gt;]= 0.5 M)</td>
<td></td>
<td>0.026±0.002&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.013±0.006&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>φ&lt;sub&gt;free&lt;/sub&gt; (free only)</td>
<td></td>
<td>~0.003</td>
<td>~0.001</td>
</tr>
</tbody>
</table>

<sup>a</sup> Value used in calculation from fit of eq 2 to data in Table 8. <sup>b</sup> Value used in calculation from fit of eq 3 to data in Table 8. <sup>c</sup> From R<sub>init</sub> in a 3 mm cuvette (Table 9) and (eq 2). <sup>d</sup> From R<sub>init</sub> in a 3 mm cuvette (Table 9) and (eq 2). <sup>e</sup> Based on the ratio of the average of R<sub>init</sub> for [H<sup>+</sup>] = 0.001 and 0.01 M (R<sub>ave</sub> = 0.0006 s<sup>-1</sup>) to R<sub>init</sub> = 0.0052 s<sup>-1</sup> for [H<sup>+</sup>] = 0.5 M (data from Table 8).

Table 12. Parameters for quantum yield estimate of [Ru(bpy)<sub>3</sub>]<sup>2+</sup>

<table>
<thead>
<tr>
<th>Parameter</th>
<th>S&lt;sub&gt;532&lt;/sub&gt;</th>
<th>3&lt;sup&gt;MLCT&lt;/sup&gt;</th>
<th>532</th>
<th>405</th>
<th>532</th>
<th>405</th>
</tr>
</thead>
<tbody>
<tr>
<td>I&lt;sub&gt;0&lt;/sub&gt;, ein s&lt;sup&gt;-1&lt;/sup&gt;×10&lt;sup&gt;7&lt;/sup&gt;</td>
<td>6.3</td>
<td>1.56</td>
<td>6.3</td>
<td>1.56</td>
<td></td>
<td></td>
</tr>
<tr>
<td>V&lt;sub&gt;phot&lt;/sub&gt;, µL&lt;sup&gt;b&lt;/sup&gt;</td>
<td>2.4</td>
<td>≈2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>I&lt;sub&gt;0&lt;/sub&gt;, ein/L·s&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.065</td>
<td>0.32</td>
<td>0.09</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ε&lt;sub&gt;λ&lt;/sub&gt;, M&lt;sup&gt;-1&lt;/sup&gt;cm&lt;sup&gt;-1&lt;/sup&gt;&lt;sup&gt;d&lt;/sup&gt;</td>
<td>1330</td>
<td>7330</td>
<td>&lt;1000</td>
<td>22,200</td>
<td></td>
<td></td>
</tr>
<tr>
<td>d&lt;sub&gt;phl&lt;/sub&gt;, cm</td>
<td>0.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>k&lt;sub&gt;obsd&lt;/sub&gt;, µ&lt;sup&gt;s&lt;sup&gt;d&lt;/sup&gt;&lt;/sup&gt;</td>
<td>2.6 (aerated)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Irradiation at:</td>
<td>405 nm only</td>
<td>(405 + 532)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>k&lt;sub&gt;M(SH)&lt;/sub&gt;, s&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>140</td>
<td>(130)&lt;sup&gt;f&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>k&lt;sub&gt;M(EH)&lt;/sub&gt;, s&lt;sup&gt;-1&lt;/sup&gt;&lt;sup&gt;e&lt;/sup&gt;</td>
<td>&lt;90</td>
<td>500</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G(λ)&lt;sup&gt;g&lt;/sup&gt;</td>
<td>0.027</td>
<td>0.025&lt;sup&gt;f&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R&lt;sub&gt;init&lt;/sub&gt;, s&lt;sup&gt;-1&lt;/sup&gt;×10&lt;sup&gt;4&lt;/sup&gt; (0.5 M H&lt;sup&gt;+&lt;/sup&gt;)&lt;sup&gt;h&lt;/sup&gt;</td>
<td>4±1</td>
<td>8±2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ΔR, s&lt;sup&gt;-1&lt;/sup&gt;×10&lt;sup&gt;4&lt;/sup&gt; (0.5 M H&lt;sup&gt;+&lt;/sup&gt;)&lt;sup&gt;h&lt;/sup&gt;</td>
<td>5±2&lt;sup&gt;i&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Solutions contain \([H^+] = 0.5\), and 0.1 M 2-propanol. \(^b\) The intersection volume of photolysis: the 405 nm laser beam volume that passed through the cell and the intersection volume of the two beams in the dual beam experiments. \(^c\) The photons/sec in the photolysis volume. \(^d\) From \([\text{Ru(bpy)}_3]^{2+}\) absorption spectrum and analysis of excited state spectra.\(^{41}\)

\[ e^{\kappa_{\lambda}(X)} = \varepsilon_{\lambda}(\lambda) d_{\text{ph}} \] \(^e\) For the superimposed lasers. \(^f\) From Table 9.

For the amount of \(^{3}\text{MLCT}\) generated by 532 nm irradiation and photolyzed by 405 nm radiation.

\[ \phi_U(h) = \left( \frac{f_{R,h} + [H^+]}{[H^+]} \right) \frac{R_{\text{init}}}{G(\lambda)} ; f_{R,h} \approx 1. \]

2.3.10. Preliminary observations of the photolysis of various ruthenium complexes under ambient conditions.

Some preliminary photochemical studies of the \([\text{Ru(phen)}_3]^{2+}\), \([\{\text{bpy}\}_2\text{Ru}\}_{2\text{dpp}}^{4+}\) (dpp = 2,3-(dipyridyl)pyrazine) and \([\text{Ru(bpy)}_2(\text{CN})_2]\) complexes were made with the same photolysis procedure as in section 2.3.6 (a) in the experimental, and the acid concentrations ranging from \(10^{-3}\) - 4 M for the first two complexes. No acid was used in the photolysis of \([\text{Ru(bpy)}_2(\text{CN})_2]\). The photodecomposition yields were found to be small for all complexes, but behavior similar to that of \([\text{Ru(bpy)}_3]^{2+}\) was found only for the \([\text{Ru(phen)}_3]^{2+}\) complex; the Ru-dpp complex shows an acid independent photochemistry. The photolysis rates of Ru-dpp complex were larger for 532 nm than for 405 nm irradiations, see Figure 21 for the observations. The initial rate data are summarized in Tables 13 and 14.
Figure 21. Ambient condition photolysis of [Ru(bpy)_2(CN)_2], [{Ru(bpy)_2}$_2$(2, 3-dpp)] (PF6)$_4$, and Tris(1,10-phenanthroline) ruthenium(II). The photolysis solution contained 2×10$^{-4}$M [Ru(bpy)$_2$(CN)$_2$], 0.5 M acetone. The photolysis of [{Ru(bpy)$_2$}$_2$(2, 3-dpp)] (PF6)$_4$, and Tris(1,10-phenanthroline) ruthenium(II) contain 10×10$^{-4}$M complex and 0.1 M 2-Propanol, and 0.5 M triflic acid. The irradiation of [Ru(bpy)$_2$(CN)$_2$] was done in 3 mm cuvette, while the irradiation of [{Ru(bpy)$_2$}$_2$(2, 3-dpp)] (PF6)$_4$, and Tris(1,10-phenanthroline) ruthenium(II) were done in a 2 mm cell.
2.3.11. Fitting parameters of other complexes

Table 13. Summary of fitting parameters for Tris(1,10-phenanthroline) ruthenium(II) photodecomposition rate in various aqueous acidic solutions in a 2 mm cylindrical cell with 405 nm radiation (Ar deaerated).a

<table>
<thead>
<tr>
<th>Code</th>
<th>λ, nm</th>
<th>[H+]i, M</th>
<th>k, s⁻¹×10⁴</th>
<th>F∞</th>
<th>kxF∞×10⁴, a s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>MA620D</td>
<td>405</td>
<td>0.001</td>
<td>123±4</td>
<td>0.0707±0.005</td>
<td>8.7±0.4</td>
</tr>
<tr>
<td>[Ru(phen)₃]²⁺</td>
<td>405</td>
<td>0.001</td>
<td>123±2</td>
<td>0.0707±0.005</td>
<td>8.7±0.4</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MA615 (A)</td>
<td>405</td>
<td>0.1</td>
<td></td>
<td>LSQ</td>
<td>(5±1)</td>
</tr>
<tr>
<td>MA615 (B)</td>
<td>405</td>
<td>0.1</td>
<td>23±2</td>
<td>0.55±0.08</td>
<td>12±1</td>
</tr>
<tr>
<td>[Ru(phen)₃]²⁺</td>
<td>405</td>
<td>0.1</td>
<td>23±2</td>
<td>0.55±0.08</td>
<td>12±1</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MA376</td>
<td>532</td>
<td>0.5</td>
<td>82±3</td>
<td>0.160±0.003</td>
<td>13±1</td>
</tr>
<tr>
<td>MA342</td>
<td>405</td>
<td>0.5</td>
<td>53±6</td>
<td>0.243±0.002</td>
<td>13±2</td>
</tr>
<tr>
<td>MA616 (A)</td>
<td>405</td>
<td>0.5</td>
<td>20±2</td>
<td>0.55±0.04</td>
<td>11±2</td>
</tr>
<tr>
<td>MA616 (B)</td>
<td>405</td>
<td>0.5</td>
<td>33±2</td>
<td>0.37±0.01</td>
<td>12±3</td>
</tr>
<tr>
<td>[Ru(phen)₃]²⁺</td>
<td>405</td>
<td>0.5</td>
<td>26±6</td>
<td>0.46±0.09</td>
<td>12±3</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MA617 (A)</td>
<td>405</td>
<td>2</td>
<td>94±4</td>
<td>0.380±0.004</td>
<td>36±4</td>
</tr>
<tr>
<td>MA617 (B)</td>
<td>405</td>
<td>2</td>
<td>106±3</td>
<td>0.247±0.002</td>
<td>26±3</td>
</tr>
<tr>
<td>[Ru(phen)₃]²⁺</td>
<td>405</td>
<td>2</td>
<td>100±6</td>
<td>0.31±0.07</td>
<td>31±10</td>
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<tr>
<td>Average</td>
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</tr>
<tr>
<td>MA627A</td>
<td>405</td>
<td>4</td>
<td>104±3</td>
<td>0.437±0.003</td>
<td>45±3</td>
</tr>
<tr>
<td>MA627B</td>
<td>405</td>
<td>4</td>
<td>80±3</td>
<td>0.389±0.003</td>
<td>31±2</td>
</tr>
<tr>
<td>[Ru(phen)₃]²⁺</td>
<td>405</td>
<td>4</td>
<td>92±12</td>
<td>0.413±0.024</td>
<td>38±7</td>
</tr>
</tbody>
</table>

a Data fitted to: \( F = F_\infty [1 - \exp(-k(t - t_0))] \); LSQ fits in parentheses.
Table 14. Fits of photodecomposition rates found for 405 and 532 nm irradiations of [(bpy)$_2$Ru$_2$(2,3-(dipyridyl)pyrazine)]$^{4+}$a

<table>
<thead>
<tr>
<th>Code</th>
<th>$\lambda$, nm</th>
<th>[H$^+$], M</th>
<th>k</th>
<th>$F_{\infty}$</th>
<th>t$\theta$</th>
<th>$R_{init}$ b</th>
</tr>
</thead>
<tbody>
<tr>
<td>62ob</td>
<td>532</td>
<td>0.001</td>
<td>163(4)</td>
<td>0.0715(3)</td>
<td>28</td>
<td>12±1</td>
</tr>
<tr>
<td>62oc</td>
<td>532</td>
<td>0.001</td>
<td>123(4)</td>
<td>0.0707(5)</td>
<td>27</td>
<td>9±1</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>10±2</td>
</tr>
<tr>
<td>623b</td>
<td>405</td>
<td>0.1</td>
<td>391(111)</td>
<td>0.015(1)</td>
<td>28</td>
<td>6±2</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>6±2</td>
</tr>
<tr>
<td>243</td>
<td>405</td>
<td>0.5</td>
<td>52(5)</td>
<td>0.0309(5)</td>
<td>107</td>
<td>1.6±0.2</td>
</tr>
<tr>
<td>623a</td>
<td>405</td>
<td>0.5</td>
<td>166(17)</td>
<td>0.0223(1)</td>
<td>16</td>
<td>3.7±0.4</td>
</tr>
<tr>
<td>623c</td>
<td>405</td>
<td>0.5</td>
<td>169(13)</td>
<td>0.0211(6)</td>
<td>26</td>
<td>2.6±0.3</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.6±0.7</td>
</tr>
<tr>
<td>242</td>
<td>532</td>
<td>0.5</td>
<td>89(7)</td>
<td>0.099(1)</td>
<td>75</td>
<td>9±1</td>
</tr>
<tr>
<td>615</td>
<td>532</td>
<td>0.5</td>
<td>206(8)</td>
<td>0.0756(3)</td>
<td>17</td>
<td>16±1</td>
</tr>
<tr>
<td>615</td>
<td>532</td>
<td>0.5</td>
<td>174(4)</td>
<td>0.0752(3)</td>
<td>30</td>
<td>13±1</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>13±2</td>
</tr>
<tr>
<td>616a</td>
<td>532</td>
<td>2</td>
<td>149(5)</td>
<td>0.077(4)</td>
<td>25</td>
<td>11±1</td>
</tr>
<tr>
<td>616b</td>
<td>532</td>
<td>2</td>
<td>118(4)</td>
<td>0.80(1)</td>
<td>35</td>
<td>9.5±0.3</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>10±1</td>
</tr>
<tr>
<td>620</td>
<td>532</td>
<td>4</td>
<td>179(3)</td>
<td>0.0588(19)</td>
<td>29</td>
<td>10.5±0.8</td>
</tr>
<tr>
<td>620d</td>
<td>532</td>
<td>4</td>
<td>150(5)</td>
<td>0.0684(5)</td>
<td>32</td>
<td>10±1</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>10±1</td>
</tr>
<tr>
<td>250</td>
<td>532</td>
<td>5</td>
<td>165(14)</td>
<td>0.085(1)</td>
<td>12</td>
<td>14±1</td>
</tr>
</tbody>
</table>

a We have used equation 1 for the fits summarized in this table, and LSQ fits for those experiments that show small curvature. b Expected ratio for 1$^{st}$ order in light intensity:

$$
\frac{R_{532}}{R_{405}} = \frac{(1 - e^{-Abs(532)})}{(1 - e^{-Abs(405)})} \times \frac{I_{532}}{I_{405}} = \frac{(1 - e^{-0.392})}{(1 - e^{-0.216})} \times \frac{139}{46} = \frac{0.324}{0.194} \times \frac{139}{46} = 5.0.
$$

Observed ratio for [H$^+$] = 0.5 M: $\frac{R_{532}}{R_{405}} \approx \frac{13}{2.6} = 5 \pm 3$

If the observed acid-independent photodecomposition of the Ru-dpp complex were first order in light intensity and due to a $^3$MLCT thermal reaction, then the relative rates at 532 and 405 nm should be equal to the ratio of the intensities of light absorbed at the two wavelengths.
2.3.12. Absorption spectra of ruthenium complexes.

a. Ambient absorption of [Ru-Tris-1, 10-((1,10-phenanthroline)] complex

Figure 22 represents the ambient UV-vis absorption for the $10^{-4} \text{M} \ [\text{Ru-Tris-1, 10-}\text{(phenanthrene)}]$ complex in aqueous solution, 0.5 M triflic acid and 0.1 M Iso-propanol, this complex has $^3\text{MLCT}$ absorption has band at 470nm.

![Absorption spectrum](image)

**Figure 22:** Ambient absorption of $10^{-4} \ [\text{Ru-Tris-1, 10-}\text{(phenanthrene)}$ in 0.5 M triflic acid and 0.1 M Iso-propanol in 4:1 Ethanol: Methanol.

b. Ambient absorption of [(Ru(bpy)$_2$)$_2$-2, 3-dpp] complex

The ambient UV-vis absorption for the $10^{-4} \text{M} \ [(\text{Ru(bpy})_2]_2\text{-2, 3-dpp}]$ complex in butironitrile, this complex has $^3\text{MLCT}$ absorption band at 530 nm.
2.3.13. Emission spectra of ruthenium complexes.

a. 77 K emission spectrum of [(Ru(bpy)$_2$)$_2$-2,3-dpp]$^{4+}$

The 77 K emission of [(Ru(bpy)$_2$)$_2$-2,3-dpp]$^{4+}$ contains vibronic structure at 790 nm and this vibronic band is well resolved at 77K; this vibronic structure is not resolved in the ambient emission.
2.3.14. Excited state lifetimes

a. Ambient and 77 K lifetimes

The ambient emission decay for [Ru(bpy)$_3$]$^{2+}$ in various aqueous solutions is shown in Figure 25. The decay measurement was done with mono exponential fit. In this experiment we used a control of aqueous solution of $10^{-4}$ [Ru(bpy)$_3$]$^{2+}$ and we varied the acid and 2-Propanol concentrations in some experiments to compare the effect of the scavengers on the life-times of the complex. All measurements were done using cut off filter that cuts <470 nm excitation, and the emission decay was monitored at 610 nm. The lifetime of the three measurements was averaged the same to each individual measurement.
Example of the observed emission decays are shown in Figure 25-27 and summarized in Tables 15 and 16.

![Figure 25. Emission decay of [Ru(bpy)$_3$]$^{2+}$ in aqueous solution using 337 nm pulsed excitation monitored at 610 nm. The monoexponential fit (black) and the extracted data (pink) are indistinguishable; residuals are in red, the raw data shows in blue. (a) monoexponential fit for an aqueous solution of $10^{-4}$ [Ru(bpy)$_3$]$^{2+}$ in 0.1 M 2-Propanol and 0.5 M trifluoroacetic acid; (b) fits for an aqueous solution of $10^{-4}$ [Ru(bpy)$_3$]$^{2+}$ (control); (c) emission decay fits for an aqueous solution of $10^{-4}$ [Ru(bpy)$_3$]$^{2+}$ with 0.1 M 2-Propanol.](image-url)
Figure 26. Ambient Emission decay of $10^{-4}$ M [Ru-Tris-1,10-phenanthroline] in 0.5 M aqueous acidic solution and 0.1 M Iso-propanol, emission decay was monitored at 470 nm.

The ambient emission life-times of [Ru-tris-1,10-phenanthorine] were quite long in solutions deroated with argon, and the decays were fitted to single exponentials. All measurements were done using a cut-off filter in the front of the PMT that cuts < 470 nm excitation and the emission decay was monitored at 610 nm. The solution conditions are shown in the caption of Figure 26.
The 77 K emission decay of [(Ru(bpy)$_2$)$_2$(2,3-dpp)] in acetonitrile is shown in Figure 27. The decay measurement was done with mono exponentials fit, cut off filter was used to cut the excitation wavelength and the emission decay was monitored at 710 nm.

b. The effect of oxygen on the observations. The effects of dissolve oxygen on the observations were investigated. Based on the observed results, it was found that the dissolved O$_2$ quenched the $^3$MLCT excited state and reduced its lifetime. The results are summarized in Table 15.
Table 15. Initial photodecomposition rates and emission lifetimes for solutions of [Ru(bpy)_3]^{2+} in a 2 mm cylindrical cell with different amounts of oxygen.\textsuperscript{a}

<table>
<thead>
<tr>
<th>( R_{\text{obs}} \times 10^4 ), s(^{-1} )</th>
<th>( \tau_{\text{obs}}, \text{ns} )</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>45±5 \textsuperscript{b}</td>
<td>534±2</td>
<td>deareated</td>
</tr>
<tr>
<td>22±4</td>
<td>380±1</td>
<td>aerated</td>
</tr>
<tr>
<td>−5±3 \textsuperscript{c}</td>
<td>179±1</td>
<td>( \text{O}_2 ) saturated</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Aqueous solutions with 1.0\times10^{-4} \text{ M} [Ru(bpy)_3]^{2+}, 0.5 \text{ M} TFA, 0.1 \text{ M} 2-propanol

c. Medium dependence of the lifetime

Table 16. Life-time data for [Ru(bpy)_3]^{2+} and [Ru(bpy)_2(CN)]\(_2\) for the experimental conditions employed.

<table>
<thead>
<tr>
<th>Complex</th>
<th>[TFA], M</th>
<th>[2-propanol], M</th>
<th>( \tau_{\text{ave}(X)}, \mu\text{s} \textsuperscript{b} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ru(bpy)_3]^{2+} \textsuperscript{a}</td>
<td>0</td>
<td>0</td>
<td>0.377(4)</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>0.1</td>
<td>0.392(4)</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>0.1</td>
<td>0.373(4)</td>
</tr>
<tr>
<td>Overall Average:</td>
<td></td>
<td></td>
<td>0.38(1)</td>
</tr>
<tr>
<td>[Ru(bpy)_2(CN)](_2) \textsuperscript{c}</td>
<td>0</td>
<td>0</td>
<td>0.17(1) \textsuperscript{d}</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Dye laser excitation wavelength at 470 nm; monitored at 610 nm; aqueous solutions with 10^{-4} \text{ M} [Ru(bpy)_3]^{2+}. \textsuperscript{b} Average of three life-time determinations; standard deviation (in the last digit) in parenthesis. \textsuperscript{c} Dye laser excitation wavelength was 431 nm; aqueous solutions with 1.2\times10^{-4} \text{ M} [Ru(bpy)_2(CN)]\(_2\). \textsuperscript{d} Overall average of 3 determinations.
Table 17. Summary of the initial rates determined for superimposed 532 and 405 nm, individual 405 and 532 nm laser irradiations in 3 mm cuvette using the linear fit for [Ru(bpy)2(CN)]2 complexes in aqueous solutions; ambient conditions.

<table>
<thead>
<tr>
<th>Code</th>
<th>Laser Wavelength, nm</th>
<th>Initial Intensity, ( I_{t=0} ) counts/s</th>
<th>Initial rate ( 10^4 \text{d}F/\text{d}t ), s⁻¹</th>
<th>( r^2 )</th>
<th>Special Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>MA118</td>
<td>532</td>
<td>1,870</td>
<td>–0.22±0.05</td>
<td>[0.74]</td>
<td>RuB2(CN)2</td>
</tr>
<tr>
<td>MA117</td>
<td>405</td>
<td>10,300</td>
<td>7.9±0.3</td>
<td>[0.99]</td>
<td>RuB2(CN)2</td>
</tr>
<tr>
<td>MA119</td>
<td>532+405</td>
<td>8,300</td>
<td>12±1</td>
<td>[0.9]</td>
<td>RuB2(CN)2</td>
</tr>
</tbody>
</table>

\( ^a \) Fits performed in the Origin program. \( ^b \) In counts/sec. \( ^c \) LSQ = least squares fit, error limits are one standard deviation; Initial rate estimates based on fits of the initial points after the shutter is open. The numbers in the square brackets are the correlation coefficients (\( r^2 \)).

The initial rate of [Ru(bpy)2(CN)2] complex was calculated using the least square fits, the initial few points of the fraction of the product formed at time where the shutter was open to 300 second were chosen for the linear fits.

**2.3.15. Diffusion effects.**

The effect of diffusion has also been examined for photolysis in the 3 mm id cuvette (see Table 18). For the evaluation of the effect of diffusion in the 3 mm cuvette we used the observed emission intensities before (bef) and after (aft) shuttering the 405 nm laser: \( \Delta I_D = I_{\text{aft}} - I_{\text{bef}} \); \( I_{\text{bef}} \) was the last point of a regular photolysis sequence with time \( t_{\text{bef}} \); \( I_{\text{aft}} \) was the first point of the next regular photolysis sequence; \( \Delta t = t_{\text{aft}} - t_{\text{bef}} \); \( t_{\text{bef}} \) determined as time of the last reading before the shutter started to close; alternatively \( \Delta t \) was determined as the time interval between the half closed and half opened shutter as illustrated in this figure. It is assumed that the effect of diffusion is to replace the photodecomposed substrate and that the rate for this process (\( k_D \)) is directly proportional to the difference between the
concentration of substrate in the photolysis region and the bulk solution; this is determined in terms of the intensity differences, \( \Delta I_0 = (I_{t=0} - (I_{aft} + I_{bef})/2) \). The intensity \( I_{t=0} \), corresponding to the bulk solution [S] was determined by the extrapolation procedure. The intensity data used for \( \Delta I \) in this table were the last (or first) points of a regular, monotonic sequence of decreasing intensities; shuttered segments for which one or both of \( I_{aft} \) or \( I_{bef} \) deviated from a regular sequence were discarded.

**Table 18. Estimation of diffusion effects**

<table>
<thead>
<tr>
<th>Segm't</th>
<th>( \Delta I_0 )</th>
<th>( \Delta t )</th>
<th>( I_0 )</th>
<th>( I_{ave} )</th>
<th>( I_{ave} - (I_{ave})_{ave} )</th>
<th>( I_{ave} - (I_{ave})_{ave} )</th>
<th>( I_{ave} - (I_{ave})_{ave} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>1236</td>
<td>171</td>
<td>18,000</td>
<td>14,832</td>
<td>3168</td>
<td>13841</td>
<td>3119.00</td>
</tr>
<tr>
<td>4</td>
<td>1176</td>
<td>152</td>
<td>18,000</td>
<td>13,025</td>
<td>2975</td>
<td>13724</td>
<td>2547.00</td>
</tr>
<tr>
<td>2</td>
<td>454</td>
<td>300</td>
<td>11,600</td>
<td>9,321</td>
<td>1928</td>
<td>9824</td>
<td>1361.00</td>
</tr>
<tr>
<td>4</td>
<td>998</td>
<td>300</td>
<td>11,600</td>
<td>8,238</td>
<td>3362</td>
<td>8437</td>
<td>1396.00</td>
</tr>
<tr>
<td>2</td>
<td>544</td>
<td>300</td>
<td>11,400</td>
<td>9,964</td>
<td>1436</td>
<td>10273</td>
<td>1162.00</td>
</tr>
<tr>
<td>2</td>
<td>579</td>
<td>300</td>
<td>12,400</td>
<td>9,210</td>
<td>3190</td>
<td>9861</td>
<td>1879.00</td>
</tr>
<tr>
<td>4</td>
<td>611</td>
<td>300</td>
<td>12,400</td>
<td>7,974</td>
<td>4426</td>
<td>8406</td>
<td>1255.00</td>
</tr>
<tr>
<td>2</td>
<td>1532</td>
<td>300</td>
<td>12,000</td>
<td>10,235</td>
<td>1765</td>
<td>9804</td>
<td>1478.00</td>
</tr>
<tr>
<td>4</td>
<td>932</td>
<td>300</td>
<td>12,000</td>
<td>10,235</td>
<td>1865</td>
<td>10130</td>
<td>1743.00</td>
</tr>
</tbody>
</table>

**Summary:** Averages of \( \Delta I_0 / \Delta I_{ave(s-1)} \): (a) segment 2, 0.25 ± 0.13; (b) segment 4, 0.33 ± 0.13; (c) all segments, 0.29 ± 0.13.

a Experiments with superimposed 405 and 532 nm laser irradiations in which the 405 nm laser was shuttered for 1-3min (\( \Delta t \)). Segments numbered as below. b \( \Delta I_0 \) = the increase in emission intensity between the end of a dual photolysis segment and the beginning of the next one (before and after shuttering the 405 nm laser); see below. c \( \Delta t \) = photolysis time in the segment considered; see below. d \( \Delta I_{ave(s)} = I_0 - (I_{ave})_{ave} \); (\( I_{ave} \))_{ave} = average of the emission intensity between the end of a dual photolysis segment and the beginning of the next one. This assumes that the extent of diffusion is too small to dilute the bulk substrate concentration; thus, there is no statistically meaningful difference between the 2nd and 4th segments even though the net photolysis time is about twice as long for the latter. e For the linear part of the preceding segment. f Average of initial and final points of the linear part of the preceding segment. g Difference between the initial and final points of the linear part of the preceding segment. h \( \Delta I_{ave(s-1)} \) adjusted for segment time differences = \( \Delta I_{ave(s-1)} \times (\Delta t_s / \Delta t_{s-1}) \).
Figure 28. The parameters used in \( k_D \) calculations for the 3mm id cuvette. Segment numbers are circled. \( I_0 \) is selected as illustrated in this section 2.3 and/or by comparison to other experiments in the same series. The manual shutter opening (or closing) can complicate the initial intensity determination for a segment and when this happens, we used a short extrapolation as illustrated at the beginning of segment 3 (note that some photochemistry occurs during the opening and closing of the shutter).

2.3.16. An example of the effect of diffusion

Figure 29. An example of the effect of vibration and diffusion on the observed emission intensities. The anomaly at 400 s was generated by tapping the photolysis cell. The gray rectangle indicates the time during which the shutter was being opened.
2.4. DISCUSSION AND CONCLUSION

This study has used the acid concentration dependent initial photodecomposition rate of the \([\text{Ru(bpy)}_3]^{2+}\) $^3\text{MLCT}$ excited state with 405 nm irradiation to demonstrate that it is photoionized with high energy visible light and that the dominant photo-products are electron-containing, ion-pair precursors to the formation of free solvated electrons. Free energy considerations suggest that this should be the case and this work sets an upper limit of 3.06 eV for the photoionization energy of this complex. The net photoionization quantum yield is apparently of the order of 10% and much larger than previously suspected based on the spectroscopic detection of free electrons because the very rapid recombination reactions within the ion-pair species makes them very hard to detect. This kind of behavior is expected to be common for redox active substrates with long-lived, visible light absorbing excited states.

2.4.1. The Ru(bpy)$_3$]$_2^+$ $^3\text{MLCT}$ excited state photoionization

The observation that products of the 405 nm irradiation of the $^3\text{MLCT}$ excited state oxidizes iodide to regenerate most of the photo-decomposed substrate complements the spectroscopic observations of the free solvated electrons generated by its higher energy, short pulse irradiations.$^{43-45}$ That the predominant metal-containing photoproduct is [Ru(bpy)$_3$]$^{3+}$ for all acid concentrations in the 0.001-4 M range while the photodecomposition yield increases in a somewhat complex way by more than 10-fold in this range indicates that: (a) H$^+$ scavenges more than one electron containing species; and (b) back electron recombination with [Ru(bpy)$_3$]$_2^+$ is very rapid for the species that are scavenged at the higher acid concentrations. Since the free solvated electron reacts with H$^+$
in water with a diffusion limited rate constant of $2.3 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$, the scavengable short lived species is most likely an ion pair, [Ru(bpy)$_3$]$^{3+}$ and a solvated electron, trapped by their electrostatic attraction. The intermediacy of ion pairs has been well documented in the photoionization of the iodide ion.

### 2.4.2. Significance and implications of [H$^+$]-dependent photoionization yields

The acid dependent electron scavenging for the $^3$MLCT photoionization products is very similar in general form to that for the photoionization of I$^-$, as is shown in Figure 30. For this figure the initial rates from Table 8 have been converted to quantum yields relative to $\phi_{e^-} = 0.026$ for [H$^+$] = 0.5 M, scaled to make the comparison to the I$^-$ data easier and plotted vs. $-\log([\text{H}^+])$.

![Figure 30](image-url)

Figure 30. The initial rate of photodecomposition, $R_{\text{init}}$, replotted as function of $\log_{10}([\text{H}^+])$ for the photoionization of [Ru(bpy)$_3$]$^{2+\text{MLCT}}$ excited state (green circles) and estimated photoionization yields for the 254 nm irradiation of I$^-$ (white circles). The photoionization yields for the [Ru(bpy)$_3$]$^{2+\text{MLCT}}$ excited state were relative to $\phi$ for [H$^+$] = 0.5 M in Table 11 and were calculated as $\phi_{rel} = 3.4 \times R_{\text{init}} \times (0.026/52)$; $R_{\text{init}}$ data are from Table 7. The photoionization yields for I$^-$ are from Figure 1 of ref. 1.
The time regime for the $e^-/H^+$ reaction in aqueous solution is based on the rate constant, $k = 2.3 \times 10^{10}$ M s$^{-1}$ and $\tau_{\text{react}} = 1/(||H^+||)^2$.

The basic chemical reactions involved in these systems can be represented simply as (with $S_p = ^3\text{MLCT}$ or $I^-$; and $S_p^+ = [\text{Ru}(\text{bpy})_3]^3^+ + I^*$),

\[
[Ru(\text{bpy})_3]^{2^+} + \text{hv} \rightarrow S_p
\]

\[
S_p + \text{hv} \rightleftharpoons \{S_p^+, e^-\}_1
\]

\[
\{S_p^+, e^-\}_1 + H^+ \rightarrow S_p^+ + e_{\text{aq}}^-
\]

\[
e_{\text{aq}}^- + H^+ \rightarrow H^*
\]

\[
S_p^+ + e_{\text{aq}}^- \rightarrow S_p
\]

\[
H^* + (\text{CH}_3)_2\text{CH(OH)} \rightarrow H_2 + \text{radicals}
\]

The hydrogen ion/electron scavenging kinetics can be treated as a competition between the scavenging reaction, eqs 5 and/or 7, and the recombination reaction, eqs 6 and/or 8. This treatment is simplest for a single scavenging reaction, and for strongly acidic solutions the reactions in eqs 5 and 6 are dominant. For this condition the initial rate can be represented as eq 2 and $R_{\text{init}} \approx \phi_e G(\lambda) [H^+]/(f_{R,h} + [H^+])$. This equation represents the initial rate as the product of a factor, $\phi_e G(\lambda)$ that depends only on the properties of the substrate $S$ and a factor, $[H^+]/(f_{R,h} + [H^+])$, that depends on the details of the scavenging...
kinetics. The variable, \( f_{R,h} \) is the ratio of the first order rate constant for the recombination reaction to the second order rate constant for the reaction of \( \{S^+,e^-\} \) with \( H^+ \).

The different \([H^+]\) regimes for the scavenging of the photo-generation of electrons from \([Ru(bpy)_3]^{2+}\) and \( I^- \) illustrated in Figure 27 are a consequence of the large differences in values of \( f_{R,h} \) in the kinetic factor. Since \( k_h \) should be nearly the same in both systems, this contrast arises from differences in the recombination rate constants with \( k_R(\text{3MLCT}) \sim 10 \times k_R(I^-) \). This is in accord with the expectation that \( k_R(\text{3MLCT}) > k_R(I^-) \) due to the larger number of acceptor electronic states and the cationic charge of \([Ru(bpy)_3]^{3+}\). The large number of electronic states with different energies is important in determining \( k_R \) since the electron transfer rate constant depends strongly on the driving force for the reaction, \( \Delta G_{\text{et}} \): 

\[
 k_R = Z \exp\left(-\lambda_{\text{reorg}} [1 - (\Delta G_{\text{et}}/\lambda_{\text{reorg}})]^2 \right);
\]

\( \lambda_{\text{reorg}} \) is the reorganizational energy associated with the electron transfer process.\(^{47}\)

The kinetic competition between the scavenging and recombination rate as obtained from the rate equations, gives a simple dependence of \( R_{\text{init}} \) on \([H^+]\) when there is a single radical pair species involved: 

\[
 R_{\text{init}} \propto [H^+] / (f_{R,h} + [H^+]);
\]

section 2.5. The fits of the date in Table 8 to this function gave \( f_{R,h} \approx 0.7 \pm 0.2 \). This resulted in \( k_R \sim 0.7 \times 2.5 \times 10^{10} \text{ s}^{-1} = 180 \text{ ps}^{-1} \) in contrast to the value of \( k_{h,e} \) resulted in \( k_R \approx 0.02 \text{ ps}^{-1} \) for the bulk solution combination reaction. The recombination lifetime for the reaction of these species is much shorter than that of the solvated electrons reacting with this substrate (\( k_R \) is estimated to be greater than 150 ns for \( e^- \text{aq} \) when \([Ru(bpy)_3]^{3+} \) < 10\(^{-4} \) M ).\(^2,26\) in section 2.5, the mechanistic arguments and the fitting in Figure 12 (dashed line) shows that there is only
Based on CTTS recombination to generate the iodide in fs time regime\textsuperscript{17} it is likely that the ionized species formed close to $[\text{Ru(bpy)}_3]^{3+}$ complex recombined too efficiently (i.e., with $f_{R,h} > 4$ M) to be detected by the chemical scavenging that we used. Thus, we interpret that the fitted parameter $f_{R,h}$ representing an average of the contributions of the many species scavenged under our conditions and that the species detected are limited by the rate of H$^+$ diffusion.

\textbf{2.4.3. Photoionization yields and threshold energy.} We have estimated the quantum yield of scavengeable photoelectrons to be in the range of 0.01-0.03 based on the model used for $[\text{H}^+] = 0.5$ M (TABLE 11), and we were not able to determine the maximum scavenging yield because the rate of H$^+$ diffusion and maximum feasible [H$^+$] limit the lifetimes of scavengeable species to longer than 10 ps. The observations summarized in Table 19 suggest that the primary photoionization quantum yield is greater than 0.1. The yield inferred for free electrons from 405 nm irradiation is about 0.005, and smaller than Goez’s value of 0.02 for 355 nm irradiation which is consistent with $E_{\text{th}} \leq 3.06$ eV.

An important implication of these considerations and Figures 9 and 35 is that the net photoionization yield is much greater than implied by the detection of free solvated electrons: the largest values found for $R_{\text{init}}$ are about ten times larger than those attributed to $e^-_{\text{aq}}$ scavenging and chemical scavenging is unlikely to detect all of the $\{[\text{Ru(bpy)}_3]^{3+}, e^-\}_{\text{IP}}$ species.
2.4.4. Possible complications from the generation of photo-substitution products

Our 405 nm photodecomposition of [Ru(bpy)₃]²⁺ may have resulted in small percentages of photo-induced ligand substitution which is a well-known process for the \(^3\)MC excited state of this complexe. \(^26,48-60\) The reaction of \(e^-\) with [Ru(bpy)₃]³⁺ has been reported to result in the formation of \(^3\)MLCT and \(^3\)MC [Ru(bpy)₃]²⁺ excited states and substitution of a bpy ligand through such population of the \(^3\)MC excited state (eqs 7 and 8) is expected when the generated ion pair recombines. However, the [Ru(bpy)₃]³⁺ was found to be the dominant ruthenium product and we were not able to identify any other photoproduct that formed by the 405 nm irradiation even at low acid concentrations.

\[
\begin{align*}
[Ru(bpy)₃]^{3+},e^-\text{IP} & \rightarrow \quad ^3\text{MLCT} \\
 & \downarrow \quad ^3\text{MC} \\
MC & \rightarrow \quad ^3\text{MLCT} \\
 & \downarrow \quad [Ru^{II}(bpy)_2L_2]^{m+} + \text{bpy}
\end{align*}
\]

(7) (8)

Our observations indicate the photolysis of \([\{(bpy)₂Ru\}₂dpp]^{4+}\) did not result in the photoionization by either 405 or 532 nm irradiation. Since the ratio of the products of the substrate absorptivities and incident light intensities is close to the ratio of the photoproducts resulted from 532 and 405 nm irradiations, as result, the photoionization of this complex might result in ligand substitution.
2.4.5. Some other related considerations

This study was initiated because the values estimated for $E_{th}$ estimated for the [Ru(bpy)$_3$]$^{2+}$ photoionization was much larger than the values of $\Delta G_{th}$. Lever and coworkers$^{61-62}$ have discussed the relationships between electrochemical potentials and charge transfer absorption spectra to the substrate’s ionization and affinity energies. The energy requirements for the photoionization of chemical species is a matter of thermodynamics, and once the thermodynamic energy requirements are met the product yields depend on some system specific details such as the efficiencies of crossing from the potential energy (PE) surfaces of high energy excited states to the dissociative photoionization PE surface and/or the diffusive separation of products. However, the condensed phase photoionization process has been difficult to investigate because of the interactions of the electron with the solvent even for simple species like the iodide ion. The free energy parameters (electrode potentials) are available for a variety of redox active complexes and can be used to estimate of the photoionization threshold free energy, $\Delta G_{th}$. $E_{th}$ is more difficult to determine since the entropy contributions are often not available, but the entropy contributions seem to be relatively small in magnitude (T$\Delta S$ of a few hundred meV at 300 K)$^{2,63}$ Many divalent ruthenium complexes have comparable $\Delta G_{th}$ values to that of [Ru(bpy)$_3$]$^{2+}$. Contrary to that, $G_{th}$ tends to have smaller magnitude for ruthenium complexes with lower charges. In support of these points, the spectroscopic and electrochemical properties of [Ru(phen)$_3$]$^{2+}$ are very similar to those of [Ru(bpy)$_3$]$^{2+}$ and it shows a similar photoionization behavior but with 1/3 smaller values of $\phi G(\lambda)$ probably
because of a smaller 405 nm excited state absorptivity and/or photoionization quantum yield.

2.5. Basic mechanistic treatment (treatment by J. F. Endicott): (2.5.1) $^3$MLCT thermal reactions and (B) photoionization

Since the incident 405 nm light intensity is constant throughout the experiment and since the concentrations of intermediates (and of products) are necessarily extremely small for the short irradiation times where $R_{\text{init}}$ is determined, the photostationary state concentrations of these species are used to simplify the photolysis rate equations. For sufficiently small concentrations of a species X the absorbance of $X \ll 1$ and the intensity of radiation with a wavelength $\lambda$ that it absorbs is $I_{\lambda}(X) \approx \varepsilon_{X(\lambda)}d_{\text{ph}}[X]I_\lambda^0 = \kappa_{\lambda}(X)[X]$; where $\varepsilon_{X(\lambda)}$ = molar absorptivity of X at $\lambda$, $d_{\text{ph}}$ = effective pathlength of the radiation through the photolysis cell, and $I_\lambda^0$ = intensity of the radiation incident on the cell. For brevity, $S$ = Ru(II) substrate, $E$ = $^3$MLCT and $P$ = photo-reaction products. We assume that the quantum yield for forming the $^3$MLCT excited state by light absorption in the ground state is 1.0.\textsuperscript{64} We have express the photolysis rates in terms of the fraction of substrate decomposed, $F$, where: $F = ([S]_{t=0} - [S]_t)/[S]_{t=0}$; $[S]_{t=0}$ = initial substrate concentration; $t$ = irradiation time.

2.5.2. $^3$MLCT excited state reactions for generating a substitutional product: 1. The chemical equations representing the simplest mechanism for the formation of products directly from a $^3$MLCT thermal reaction are

$$ S + h\nu \rightarrow E \quad I_{\lambda(S)} \quad (A1) $$
2.5.3. The rate laws and photostationary states:

\[
\frac{d[S]}{dt} = -\kappa_{\lambda(S)}[S] + k_{\text{obs}}[E] \quad \kappa_{\lambda(S)} \approx \varepsilon_X(\lambda)d_{\text{path}} I_\lambda^o \tag{A4}
\]

\[
\frac{d[E]}{dt} = \kappa_{\lambda(S)}[S] - (k_{\text{obs}} + k_P)[E] \tag{A5}
\]

A very simple way to express the effect of diffusion on our observations is to represent it as a constant, \(k_D\), multiplied by the difference between the substrate concentration in the bulk and photolysis regions. Then

\[
\frac{d[P]}{dt} = k_P[E] - k_D[P] \tag{A6}
\]

If \(k_{\text{obs}} \gg k_P\), then the photostationary state (ps) approximation is

\[
\frac{d[E]}{dt} = \kappa_{\lambda(S)}[S] - (k_{\text{obs}} + k_P)[E] \approx 0 \tag{A7}
\]

\[
[E]_{\text{ps}} \approx \frac{k_{\lambda(S)}}{k_{\text{obs}} + k_P}[S] \tag{A8}
\]

\[
\frac{d[P]}{dt} \approx k_P \kappa_{\lambda(S)}[S] - k_D[P] \tag{A9}
\]

\[
\frac{d[F]}{dt} \approx k_P \kappa_{\lambda(S)}(1 - F) - k_D F = k_P \frac{k_{\lambda(S)}}{k_{\text{obs}} + k_P} - \left( k_D + k_P \kappa_{\lambda(S)} \right) F \tag{A10}
\]

This is of the form, \(\frac{d[F]}{dt} = A - BF\) with \(A = \frac{k_{\lambda(S)}}{k_{\text{obs}} + k_P}k_P\) and \(B = (k_D + A)\). For \(\lambda = 405\) nm in the 3 mm cuvette, \(\kappa_{405(S)} = \varepsilon_{S(405)}d_{\text{path}}I_\lambda^o = (7330)(0.3)(7.4 \times 10^{-2}) = 163 \text{ s}^{-1}\). The integral form
of eq A10 is \( \left( \frac{\ln(A - BF)}{-B} \right) = t \). Since \( F = 0 \) for \( t = 0 \) and in the absence of diffusion \( (k_D = 0) \) \( F = 1 \) at \( t = \infty \)

\[
F = \frac{A}{B} (1 - e^{-Bt}) = F_\infty (1 - e^{-kt}) \tag{A11}
\]

Or, \( F_\infty = A/B, k = B \).

2.5.4. The reduced initial rates. From eq A11, \( R_{\text{init}} = A = F_\infty \times k \). Note that \( k \) is a pseudo-first order rate constant for the observed process (including diffusion, as in B below) for the observed process and \( (A/B) \times B = R_{\text{init}} \) is the first order or pseudo-first order rate constant for the chemically important process (such as \( k_p \) in eq A3); for conciseness we have referred to \( R_{\text{init}} \) as the “initial rate”.

\[
R_{\text{init}} \approx \frac{k_{\lambda(S)}}{k_{obs} + k_p} k_p; \tag{A12}
\]

Rearranging eq A12:

\[
k_p \approx \frac{k_{obs}}{k_{\lambda(S)} - R_{\text{init}}} R_{\text{init}}
\]

Thus,

\[
F_\infty \approx \frac{k_p k_{\lambda(S)}}{k_{obs} + k_p} = \frac{k_{\lambda(S)} k_p}{k_D (k_{obs} + k_p) + k_p k_{\lambda(S)}} \tag{A13}
\]

and,

\[
k \approx k_D + \frac{k_p k_{\lambda(S)}}{k_{obs} + k_p} = \frac{k_D (k_{obs} + k_p) + k_p k_{\lambda(S)}}{k_{obs} + k_p} = k_D + R_{\text{init}} \tag{A14}
\]

From A14 and for \( F << 1.0 \) (as for the \([(\text{bpy})_2\text{Ru}]_2\text{dppt}]^{4+} \) photodecomposition) and for \( k_{obs} >> k_p, k_p k_{\lambda(S)} << k_D (k_{obs} + k_p) \) and

\[
F_\infty \approx \frac{k_p k_{\lambda(S)}}{k_D k_{obs}} \tag{A15}
\]
For the other limit, $k_{\text{obs}} \ll k_P$,

$$F_{\infty} \approx \frac{\kappa_{\lambda(S)}}{k_p + \kappa_{\lambda(S)}} \sim 1$$  \hspace{1cm} (A16)

2.5.5 Quantum yield. For $k_{\text{obs}} \gg k_P$ and $\kappa_{\lambda(S)} \gg R_{\text{init(d)}}$ in eq A12,

$$\phi_p = \frac{dP}{d[	ext{photons}]} \approx \frac{k_p \left( \frac{\kappa_{\lambda(S)}}{k_{\text{obs}} + k_p} \right) [S]}{\kappa_{\lambda(S)} [S]} \approx \frac{R_{\text{init}}}{\kappa_{\lambda(S)}}$$  \hspace{1cm} (A17)

2.6. Acid dependent, two photon photoionization and the photoionization quantum yield expressed in terms of experimental rate parameters.

2.6.1. Some general considerations and simplifying assumptions:

We consider only the acid dependent processes leading to products. Since the total ruthenium species ($S + P + \ldots$; $P =$ the electron product species) is orders of magnitude smaller than $[\text{H}^+]$ in strongly acidic solutions ($[\text{H}^+] \geq 0.01 \text{ M}$), the diffusion limited $e^-/P$ and $e^-/S$ reactions of the “free” solvated electron would not be competitive with the $e^-/\text{H}^+$ reaction. The increases of $R_{\text{obs}}$ with increasing acid for $[\text{H}^+] > 0.01 \text{ M}$, where the predominant Ru-containing photoproduct species can be reduced by $I^-$ results in the recovery of most of the photo-bleached $[\text{Ru(bpy)}_3]^{2+}$ absorbance leads us to postulate that the proton-dependent photodecomposition of $[\text{Ru(bpy)}_3]^{2+}$ in highly acidic solutions predominately results from some proton scavenging of $\{P.e^-\}_{\text{IP}}$ species, similar to related observations for $I^-$.\textsuperscript{1,28} For this limit, the excited state photolysis products that contribute to the initial rate can be formulated as an associated pair of product species (or as an “ion pair”).
In principle the H$^+$ scavenging of the $\{P,e^-\}_{IP}$ species could involve either the direct scavenging of the ion pair (as appears to be the case for the $(I^*,e^-)_{IP}$ ion pair)$^{17}$ and/or scavenging of the electrons that escape from it (eqs B3 and B4). Our experiments do not distinguish between these or other details of ion pair behavior and we develop only the general aspects of the competition kinetics. Similarly, the treatment below assumes that the 2-propanol scavenging for the free aqueous proton is complete, that the radicals produced do not complicate the rate of photodecomposition of the substrate and we ignore any very fast reaction of H-atoms which are produced adjacent to the oxidized substrate and react by electron transfer to regenerate the substrate (which will be convoluted into a simple rate parameter, $k_R$). We consider a simple scavenging limit in which the only process that competes with the H$^+$/electron scavenging results is the regeneration of the substrate either directly or by means of a series of chemical steps.

The mechanistic algebra applicable to the proton scavenging of the free solvated electron, at least for simple mechanisms, is summarized below.

2.6.2. Basic reactions ($S = [Ru(bpy)_3]^{2+}$; $E = [Ru(bpy)_3]^{3+}$) and kinetic parameters; for the proton induced photodecompositions of $[Ru(bpy)_3]^{2+}$ observed at high acid concentrations ([H$^+$] > 0.1 M):

\[
S + h\nu \rightarrow E \quad \text{I}_{abs(S)} \quad (A1)
\]

\[
E \rightarrow S \quad k_{obs} \quad (A2)
\]

\[
E + h\nu \rightarrow \{P,e^-\}_{ip} \quad \phi I_{abs(E)} \quad (B1)
\]

\[
\{P,e^-\}_{ip} \rightarrow S, E, ^3\text{MC,} \quad k_a, k_b, k_c \quad (B2)
\]
\[
\{P,e^-\}_{ip} + H^+ \rightarrow P + H^* \quad k_h \quad (B3)
\]

\[
\{P,e^-\}_{ip} \rightarrow P + e^- \quad k_s \quad (B4)
\]

\[
H^+ + e^- \rightarrow H^* \quad k_{H} \quad (B5)
\]

\[H^* + \text{scavenger} \rightarrow \text{Radical Products}\]

Where \( k_a, k_h, \) and \( k_c \) are the rate constants for electron/Ru(III) recombination reactions that regenerate the substrate and different excited states (\( E \) and \( ^3MC \)) and \( Y^- \) is some reduced species such as \([\text{Ru(bpy)}_3]^+\) or \( \text{O}_2^-\). For simplicity we consider only one \( \{P,e^-\}_{ip} \) species, but one expects several, probably not easily distinguished electron /[Ru(bpy)_3]^+ “ion pair” species, each with a different recombination rate constant(s). Reactions B4-B5 are not considered further here.

Slower back reactions of the type B6 and B7 where \( Y \) is some species, such as S, propyl radicals, etc., can in principle complicate the long term kinetic details. Since we deal with the initial rate behavior, such reactions will not be considered here.

\[
e^- + Y \rightarrow Y^- \quad k_f \quad (B6)
\]

\[
Y^- + P \rightarrow S + Y \quad k_t \quad (B7)
\]

2.6.3. Rate equations. Our observations in strongly acidic solution correspond to the limit in which the contributions of reaction B5 are much smaller than those of B3 and we will only treat this limit. The rate equations for electron scavenging of the intermediate, \( \{P,e^-\}_{ip} = U, \quad (k_R = k_a + k_h + k_c + k_s) \) are

\[
\frac{d[S]}{dt} = -k_{s(b)}[S] + k_{\text{obsd}}[E] + k_a[U] \quad (B8)
\]
These reactions are a very simple expression of the photoionization behavior of this system. It has been reported that the free solvated electron/[Ru(bpy)$_3$]$^{3+}$ favors the regeneration of MLCT and MC excited states over [Ru(bpy)$_3$]$^{2+}$ in its ground state$^{25-26}$ and this possibility has been included in eqs B1, B9 and B10, with the assumption that the MC excited state populations mostly relax to the $^3$MLCT excited state.$^{26,65}$ Neglecting eqs B4 and B5,

$$\frac{d[P]}{dt} \approx k_h[H^+][U] - k_D(P)$$  \hspace{1cm} (B11)

Since $[S] >> [E] >> [U]$, we use the photostationary states (ps) in [E] (eq A8) and [U]:

$$[E]_{ps} \approx \frac{\kappa_{\lambda(S)}[S]}{k_{obsd}}$$  \hspace{1cm} (A8)

$$\frac{d[U]_{ps}}{dt} = \phi_U \kappa_{\lambda(E)} [E]_{ps} - k_R[U]_{ps} - k_h[H^+][U]_{ps} \approx 0$$  \hspace{1cm} (B12)

Equation B12 can be combined with eq A8 to obtain,

$$[U]_{ps} \approx \frac{\phi_U \kappa_{\lambda(E)} [E]_{ps}}{k_R + k_h[H^+]} \approx \frac{\phi_U \kappa_{\lambda(S)} \kappa_{\lambda(E)} [S]}{k_{obsd} \left(k_R + k_h[H^+]\right)}$$  \hspace{1cm} (B13)

Therefore, combining eqs B11 and B13,

$$\frac{d[P]}{dt} \approx k_h[H^+] \frac{\phi_U \kappa_{\lambda(S)} \kappa_{\lambda(E)} [S]}{k_R + k_h[H^+]} - k_D(P)$$  \hspace{1cm} (B14)

Setting $F = [P]/[S]_{t=0}$ and $[S] = (1 - F)[S]_{t=0}$, eq B14 leads to
Rearranging eq B15,

\[
\frac{d[F]}{dt} \approx k_h \left[ H^+ \right] \frac{\phi_U \kappa_{\lambda(E)}}{k_R + k_h \left[ H^+ \right]} \frac{\kappa_{\lambda(S)} (1 - F)}{k_{\text{obsd}}} - k_D F
\]  

(B15)

Setting \( G(\lambda) = \frac{\kappa_{\lambda(S)} \kappa_{\lambda(E)}}{k_{\text{obsd}}} \), which is a constant for each experiment, the reduced rate of product formation is expressed as,

\[
\frac{d[F]}{dt} \approx \frac{\kappa_{\lambda(S)} \phi_U \kappa_{\lambda(E)} k_h \left[ H^+ \right]}{k_{\text{obsd}} (k_R + k_h \left[ H^+ \right])} - \left( k_D + \frac{\kappa_{\lambda(S)} \phi_U \kappa_{\lambda(E)} k_h \left[ H^+ \right]}{k_{\text{obsd}} (k_R + k_h \left[ H^+ \right])} \right) F
\]

(B16)

It is convenient to further simplify eq B17 by setting \( k_R/k_h = f_{R,h} \),

\[
\frac{d[F]}{dt} \approx \phi_U G(\lambda) \frac{k_h \left[ H^+ \right]}{\left( f_{R,h} + \left[ H^+ \right] \right)} - \left( k_D + \frac{\phi_U G(\lambda) k_h \left[ H^+ \right]}{\left( f_{R,h} + \left[ H^+ \right] \right)} \right) F
\]

(B17)

This is in the same algebraic form as eqs A10 and A11 and leads to

\[
F_{\infty} \approx \frac{\phi_U G(\lambda) \left[ H^+ \right]}{f_{R,h} + \left[ H^+ \right]}, \quad k \approx k_D + \phi_U G(\lambda) \frac{\left[ H^+ \right]}{f_{R,h} + \left[ H^+ \right]}
\]

(B18)

In order to exhibit an acid independent plateau \( [H^+]_{F(\infty)} > f_{R,h} \) and

\[
F_{\infty} \approx \frac{\phi_U G(\lambda)}{k_D + \phi_U G(\lambda)}
\]

(B20)
Note that eq B20 corresponds to the limit for relatively high acid concentrations where $k_h[H^+] > k_R$, and it is applicable in the region where $[H^+]$ variations do not result in significant variations in $R_{\text{init}}$. More generally,

$$R_{\text{init}} = A \approx \phi_U G(\lambda) \frac{[k_h H^+]}{(k_R + k_h[H^+])} = \phi_U G(\lambda) \frac{[H^+]}{(f_{R,h} + [H^+]^\dagger)}$$

(B21)

and

$$F_{\infty} \approx \frac{R_{\text{init}}}{k_D + R_{\text{init}}}$$

2.6.4. **Quantum yields.** The representation of the quantum yield in terms of measurable quantities for the photoionization processes discussed here is not simple. The absorption of photons whose energies exceed $E_{\text{th}}$ will generate electrons distributed in solvent regions of the substrate’s solvation sphere of the substrate and the bulk solvent. By analogy with the photoionization of $I^-$,\(^{31}\) those electrons that are generated in the solvent immediately adjacent to the oxidized substrate (in a CTTS “state”) are expected to recombine in the fs time regime and would not be detectable with a diffusion limited chemical scavenger. In contrast, ns lifetimes are expected for free solvated electrons in bulk solution\(^ 2\) and these species are readily scavengeable with moderately dilute acids.\(^ 1,33\) Clearly there is a wide range of oxidized substrate/photo-generated electron species with a correspondingly wide range of recombination lifetimes so the definition of the quantum yield for these species generally depends on the experimental approach used for their determination. These considerations indicate that the parameters in eq B21 are averages over a range of $e^-$ species
scavenged. With these points in mind, the photoionization quantum yield based on H⁺/e⁻ scavenging with $G(\lambda) = \frac{K_r^{(S)} K_r^{(E)}}{k_{obsd}}$ and $[H^+] > 0.1$ M is,

$$\phi_{U(h)} = \left( f_{R.h} + \frac{[H^+]}{[H^+]} \right) \frac{R_{init}}{G(\lambda)}$$  \hspace{1cm} (B22)

2.7. Conclusions

Our 405 nm irradiations resulted in moderate photoionization of $^3\text{MLCT}$ excited state of $[\text{Ru(bpy)}_3]^{2+}$ at ambient condition in aqueous solution. In addition, the initial rate, $R_{init}$, of the photodecomposition increases as the acid concentration increases and our $[H^+]$ scavenger may intercept the electrons at an early stage of its evolution where it is still associated with $[\text{Ru(bpy)}_3]^{3+}$. In addition, the calculated initial rate of the photodecomposition was almost doubled when the superimposed of 405 and 532 nm laser beams were used.

The photoionization quantum yield of $[\text{Ru(bpy)}_3]^{2+}$ is much larger and its threshold energy corresponds to much longer wavelengths than it was previously believed. Similar low energy photoionization threshold energies are predicted for the $^3\text{MLCT}$ excited states of many (RuII-bpy)$^{2+}$ chromophores since many divalent ruthenium complexes have values of $\Delta G_{th}$ comparable to that of $[\text{Ru(bpy)}_3]^{2+}$. 
CHAPTER 3. STUDIES OF THE PHYSICAL AND CHEMICAL EXCITED STATE PROPERTIES OF RUTHENIUM (II) COMPLEXES CONTAINING AROMATIC LIGANDS

[Collaborative project with Jeremy Kodanko’s lab]

3.1. INTRODUCTION

Ruthenium(II) complexes with aromatic ligands (Ar) that have long-lived $^3$MLCT excited states have been very important as photosensitizers; for example, these complexes often have been utilized in dye-sensitized solar cells$^{13, 66}$ and photodynamic therapy.$^{67, 68, 69, 70}$ To efficiently promote electron transfer from or to the sensitizer’s excited state, other competing decay pathways must be minimized. These competing decay pathways determine the lifetimes of the complexes and this issue has been extensively studied and reported in the literature.$^1$−$^15$ Despite the large number of previous reports the choices of ligands that give rise to the desired excited state properties are most often based on extrapolations from the well characterized ground state species using idealized, often one electron models, and various empirical and/or trial and error approaches. Such approaches are not efficient, and they are often misleading. The problems arise in part because this class of transition metal complexes typically contain a few dozen electronic excited states with different molecular orbital distributions of electrons within a relatively narrow energy range. The actual electronic configurations of these excited states often has to be described in terms of mixtures of the extrapolated, idealized configurations. This mixing results in excited states with a corresponding mixture of the idealized chemical and physical properties that might be expected based on experience with electronic ground states. However, the excited state electronic configurations can be unique with few or no
ground state precedents so that properties extrapolated from those of ground states can be unreliable. The preferred approach is to model the excited state electronic configurations using a high level density functional theory calculation and to correlate the observed excited state properties with this model. While the transition metal electronic excited states are short lived species, usually with sub-millisecond lifetimes even at low temperatures, and therefore not easily characterized using conventional ground state-based methods, the characterization of these excited states can be approached in a systematic way by using a combination of emission spectroscopy and density functional theory modeling.

Many of the most investigated potential sensitizers involve a Ru$^{II}$ center and at least one aromatic acceptor ligand and have a low energy electronic excited state which is most simply described as having an electronic configuration in which an electron has been promoted from the highest energy filled molecular orbital (HOMO), a mostly non-bonding Ru$^{II}$ centered “dπ” orbital to the lowest energy unoccupied aromatic ligand orbital (LUMO). This simple, idealized electronic configuration is referred to as a metal-to-ligand charge transfer excited state (MLCT). The chemical and physical properties of the lowest energy MLCT excited states are generally discussed in terms of this idealized model, sometimes with small perturbation theory-based corrections to it. In most cases the triplet ($^3$MLCT) excited states emit in the visible or near infrared spectral region, and their emission bands often have resolved vibronic sidebands.$^{71-78}$ The relative intensities of these vibronic sidebands are correlated with excited state molecular distortions with the most intense vibronic sidebands corresponding the most distorted bond lengths or bond angles in the excited state; thus, the vibronic sidebands of an emission spectrum contain
information about the molecular structure of the emitting excited state and the excited state distortions are related to the molecular moieties which differ in excited state and ground state electron density. The distribution of excited state electron density and the associated bond distortions can be modeled using DFT approaches\textsuperscript{58, 79-82} and this can be compared to the structural implications of the vibronic sidebands of the emission spectrum. So far this approach has only been used on a number of complexes with relatively simple aromatic ligands.\textsuperscript{58, 79-82} Complexes with relatively long excited state lifetimes have been of some interest as potential sensitizers in some applications, but the strategies for their synthesis have relied mostly on extrapolations of experience with ground state systems and there has been very little systematic study of the ligand properties that might give rise to such behavior. There have been suggestions that ligands with extensively delocalized electron density in their LUMOs might result in increased $^3$MLCT excited state lifetimes and we have undertaken the study of the excited state properties of some Ru$^{II}$ complexes with quinoline-based ligands in order to find out how such excited state electronic delocalization affects the physical properties of Ru-quinoline $^3$MLCT excited states.\textsuperscript{58, 79-85}

Most Ru-Ar complexes with a wide variety of ancillary and acceptor ligands can be easily synthesized. Previous work from this laboratory, partly in collaboration with Professor Y. J. Chen’s lab, has involved systematic emission spectroscopic studies and DFT modeling of Ru-bpy and Ru-MDA chromophores (MDA = monodentate aromatic ligand such as pyridine, phenylpyridine, pyrazine, etc.).\textsuperscript{38, 58, 79-84} The Ru-bpy and Ru-MDA chromophores have distinctly different 77 K emission characteristics which can be attributed to differences in their $^3$MLCT excited state mixing with other excited states:
(a) The vibronic sidebands of the Ru-bpy chromophores increase in relative intensity with increasing $^3$MLCT excited state energy. This feature correlates with increased $(^3\text{MLCT})_{\text{ideal}}/\pi\pi^*$ configurational mixing in the triplet manifold.\textsuperscript{79, 84, 86} The radiative rate constants, $k_{\text{RAD}}$, for these chromophores are also energy dependent and in the range of $(0.5-8) \times 10^4$ s$^{-1}$.

(b) The vibronic sidebands of the Ru-MDA chromophores have not been resolved at 77 K and $k_{\text{RAD}} \approx (3\pm2) \times 10^3$ s$^{-1}$ is nearly energy independent in the range examined. The 77 K emission lifetimes for this class of chromophores are slightly longer than those of the Ru-bpy chromophores at the same energy.

3.2. EXPERIMENTAL SECTION

3.2.1. Compounds prepared for the study of the chemical and physical properties of $^3$MLCT excited states of ruthenium quinoline complexes

Potassium phthalimide, 1-(chloromethyl)isoquinoline, and hydrazine monohydrate, were purchased from Oakwood Chemical (West Columbia, South Carolina, SC) and used without further purification. Ethyl acetate and hexane ($\geq 99\%$) were purchased from Fisher Scientific (Pittsburgh, Pennsylvania, PA) for spectroscopic experiments. The $[1$ or $3$-$\text{Ru(iso-TQA)(X)}_2]$ complexes were provided by Professor Jeremy Kodanko’s research group; tris (isoquinolin-1-ylmethyl) amine (TQA) was synthesized as described elsewhere\textsuperscript{87} and $[1$-$\text{Ru(TQA)(CN)}_2]$ was synthesized using a literature procedure.\textsuperscript{88} Chlororpentaamineruthenium(III) chloride 98% was obtained from Strem. The isoquinoline ligand was obtained from Oakwood Chemical. The $[\text{Ru(NH}_3)_5$-isoquinoline]
complex was synthesized using literature procedures. \(^{89}\) \[(\text{Ru(bpy)}_2(2, 3\text{-dpp})](\text{PF}_6)_4\] was synthesized as reported previously. \(^{36}\)

Syntheses of these compounds were done under a flow of argon gas using a Schlenk line in the dark. Vapor diffusion and recrystallizations of these complexes were the main purification techniques. Column chromatography (Al\(_2\)O\(_3\)) techniques were also used.

![Chemical structures](image)

**Figure 31. Synthesis of 1-iso TQA**

**Synthesis of N-(1-isoquinolylmethyl) phthalimide (2)\(^{87}\)**

To the DMF solution (11 mL) of 1- (265 mg, 1.49 mmol) potassium phthalimide (278 mg, 1.50 mmol) was added and stirred overnight at room temperature. After the addition of chloroform, the organic layer was washed with water and 10% NaOH. The organic layer was dried, evaporated, and washed with hot ethanol to give 2 as white powder. Yield: 303 mg (1.05 mmol, 70%). \(^1\)H NMR (CDCl\(_3\)): \(\delta\) (d, \(J=5.7\)Hz, 1H), 8.21 (d, \(J=7.8\)Hz, 1H), 7.90–7.93 (m, 2H), 7.83 (d, \(J=8.4\) Hz, 1H), 7.65–7.76 (m, 4H), 7.52 (d, \(J=5.7\) Hz, 1H), 5.54 (s, 2H). \(^{13}\)C NMR (CDCl\(_3\)): \(\delta\) 168.5, 153.0, 141.9, 136.1, 133.9, 132.5, 130.1, 127.5, 125.9, 123.7, 123.5, 120.3, 40.7.
Synthesis of 1-Aminomethylisoquinoline (3)\textsuperscript{87}

To the methanol solution (11 mL) of N-(1-isoquinolylmethyl) phthalimide (2) (132 mg, 0.46 mmol) hydrazine monohydrate (0.38 mL, 7.8 mmol) was added and refluxed for 1.5 h. After the addition of water, the insoluble materials were filtered off. The filtrate was acidified with hydrochloric acid and filtered. The filtrate was neutralized with aqueous NaOH and extracted with ethyl acetate. The organic layer was dried and evaporated to give 3 as yellow oil. Yield: 6 mg (0.29 mmol, 63%). \textsuperscript{1}HNMR(CDCl\textsubscript{3}): \(\delta\) 8.45 (d, J=5.4 Hz, 1H), 8.08 (d, J=8.1 Hz, 1H), 7.81 (d, J = 7.8 Hz, 1H), 7.50–7.70 (m, 3H), 4.49 (s, 2H). \textsuperscript{13}C NMR (CDCl\textsubscript{3}): \(\delta\) 159.9, 141.2, 135.7, 129.7, 127.1, 127.0, 125.7, 123.8, 119.6, 44.6.

Synthesis of Tris(1-isoquinolylmethyl)amine (1-isoTQA)\textsuperscript{87}

To the acetonitrile solution (90 mL) of 1-chloromethylisoquinoline (1) (501 mg, 2.82 mmol) and 1-aminomethylisoquinoline (3) (223 mg, 1.41 mmol) potassium carbonate was added (1.05 g, 7.60 mmol) and stirred for 4 days under reflux. After removal of the solvent, the residue was extracted with a chloroform/water mixture. The organic layer was dried, evaporated, and washed with acetonitrile to give 1-iso-TQA as white powder. Yield: 70 mg (0.39 mmol, 27%). \textsuperscript{1}HNMR(CDCl\textsubscript{3}): \(\delta\) 8.49 (d, J=5.7 Hz, 3H), 7.75 (d, J=8.4 Hz, 3H), 7.58 (d, J = 6.0 Hz, 3H), 7.47 (dd, J = 6.9, 8.1 Hz, 3H), 6.98 (d, J = 8.7 Hz, 3H), 6.58 (dd, J = 6.9, 8.4 Hz, 3H), 4.35 (s, 6H). \textsuperscript{13}C NMR (CDCl\textsubscript{3}): \(\delta\) 158.0, 141.4, 136.0, 129.5, 127.3, 126.5, 125.9, 120.6, 60.0.
Synthesis of [Ru (tris(isoquinolin-1-ylmethyl)amine)(NC)₂]^2⁺

TQA (47.2 mg, 0.11 mmol), which was prepared by a known procedure was dissolved in 10 mL of dry MeOH under inert atmosphere in a pressure flask. To this Ru(DMSO)₄Cl₂ (52.0 mg, 0.11 mmol) was added and the solution was purged with Argon for 10 min at room temperature. The reaction mixture was refluxed for 5 h. The reaction mixture changed in color from pale yellow to dark red. The dark red reaction mixture was cooled to room temperature and concentrated under reduced pressure. To the flask NaCN (53.9 mg, 1.1 mmol) and 1:1 mixture of EtOH: H₂O (10 mL) were added and the mixture was refluxed for 16 h under inert atmosphere. Ice cold water (20 mL) was then added to the reaction mixture which resulted in the formation of dark red precipitate which was filtered, washed with ice cold water (300 mL), stirred with Et₂O, filtered and dried under reduced pressure to give the title complex as a dark red solid (39 mg, 61%): mp = 194 °C (decomp); ¹H NMR (400MHz (CD₃)₂SO) δ 9.64 (d, 1H, J = 6.0 Hz), 8.66 (d, 2H, J = 6.4 Hz), 8.14-8.16 (m, 2H), 7.90-7.82 (m, 3Hz), 7.77-7.70 (m, 6H), 7.65-7.62 (m, 3H), 7.51 (t, 1H, J = 8.0 Hz), 5.94 (d, 2H, J = 15.6 Hz), 5.54-5.49 (m, 4H); IR (KBr) νmax (cm⁻¹) 3852, 3744, 3726, 3673, 3528, 3432, 3252, 2994, 2947, 2891, 2063, 2043, 1693, 1650, 1594, 1553, 1503, 1453, 1394, 1376, 1317, 1294, 1262, 1236, 1198, 1145, 1099, 955, 827, 748, 679, 668, 660; UV-vis λmax = 470 nm (ε = 9600 M⁻¹cm⁻¹); LR-ESMS Calcd for C₃₂H₂₅N₆O₃Ru m/z = 595, Found 595; Anal. Calcd for C₃₄H₃₁N₁₂ORu: (2·0.5 H₂O·0.5 Et₂O) C, 63.74; H, 4.88; N, 13.12. Found: C, 63.49; H, 4.54; N, 13.29.
Figure 32. Synthesis of [Ru (TQA)(CN$_2$)]

**Synthesis of [dicyno-bis-(2,2'-bipridine) ruthenium (II)dihydrate]**

[Ru(CN)$_2$(bpy)$_2$.2H$_2$O]

The complex Ru(bpy)$_2$Cl$_2$.2H$_2$O (0.320 g) in methanol (10 mL) and water (10mL) was heated under reflux with sodium cyanide (2g). The purple solution turned orange and after 1 h was filtered and methanol evaporated using rotary evaporator. The orange solid was washed with cold water and diethyl ether, respectively and then dried in vacuum overnight to realize a pure orange compound suitable for analysis. Yield: 0.300g.

$^1$H NMR (400MHz, methanol-d$_4$): $\delta$ 9.64, 8.51, 8.45, 8.07, 7.91, 7.65, 7.59, 7.28. $^1$H NMR (400MHz, methanol-d$_4$): $\delta$ 158.6, 157.1, 156.3, 155.1, 148.9, 137.1, 136.2, 126.5, 126.2, 123.3, 122.8. CV in butyronitrile. $E_{1/2}$ mV ($\Delta$Ep, mV): +841(54), 1573(50). Ferrocene/ferrocenium {+464 mV (60 mV)}. Absorption in ethanol/methanol (1:1 v/v): MLCT absorption at 462 nm (21645 cm$^{-1}$).

**Synthesis of 2-(chloromethyl)nicotinonitrile**

To 2-methylnicotinonitrile (2.0 g, 16.9 mmol) in chloroform (30 mL) at reflux was added trichloroisocyanuric acid (1.57 g, 6.75 mmol) and the mixture was heated at reflux overnight. After cooling, the mixture was filtered, and the filtrate was diluted with dichloromethane, washed with sodium hydroxide.
solution and then brine, dried (MgSO₄), and evaporated to give 1.5 g of pure product, which by NMR contained ~19% starting material and 7% dichlorinated product: ¹H NMR (360 MHz, CDCl₃) δ 4.85 (2H, s), 7.43 (1H, dd, J = 7.9 and 4.9 Hz), 8.02 (1H, dd, J = 7.9 and 1.7 Hz), 8.81 (1H, dd, J = 4.9 and 1.7 Hz).

Synthesis of [Ru(NH₃)₅(iso-quinoline)](PF₆)₂⁸⁹

A 0.2-g sample of the [Ru³⁺(NH₃)₃Cl]Cl₂ starting material in 5 mL of H₂O was reduced by 1 g zinc amalgam in the dark with argon-bubbling agitation for 30 min and then transferred to an argon-degassed solution of 1.2 eq of the ligand, (iso-quinoline, L), in 10 mL of water. After 2 h, filter the mixture and the crude [Ru²⁺(NH₃)₅(L)](PF₆)₂, product was precipitated by adding 5 mL of a saturated solution of (NH₄)PF₆ in water to the filtrate. Yields were typically 60-70%. This material was purified in the following manner: The crude product was dissolved in a minimum volume (ca. 1 mL) of either Spectro quality or reagent grade acetone and cooled to 0°C in the freezer. On top of this was then carefully layered 2-3 mL of anhydrous ether, or until turbidity just started to occur in the upper part of the acetone layer. The resulting double-layered system was allowed to stand quietly and mix by diffusion in the ice bath for at least 12 h, at which point more ether was added if no solid had precipitated. For optimum purity, a recovery of no more than 40-50% was attempted. A second crop of reasonable quality could be obtained by repeating this procedure on the mother liquor after the first crop of dark, semicrystalline material had been collected. ¹H NMR (360 MHz, CDCl₃) δ 2.1 (s, 2H), δ 2.8 (d, 2H), δ 3.3 (s, 1H), δ 7.8 (m, 3H), δ 8.0 (m, 2H), δ 8.6 (s, 1H), δ 9.6 (s, 1H).
3.2.2 Light sources for the study of the chemical and physical properties of $^3$MLCT of ruthenium quinoline complexes

In these experiments we used the same light sources, except for the QTH lamp, that are described in Chapter II in addition to a 470 nm diode laser, which has a power nominally $\geq 10$ mW (Changchun New Industries Optoelectronics Tech.Co., Ltd).

3.2.3. Instrumental system used for 77 K Emission spectroscopy set up for ruthenium quinoline complexes

The techniques used for emission spectroscopy have been described in Chapter II. The major modification for low temperature emission is that the sample in a 2 mm id cylindrical fluorescence cell was immersed in liquid nitrogen contained in a Dewar flask as shown in Figure 34.
3.2.4. Instrumental system used for low temperature absorption spectroscopy of Ru-quinoline chromophores

In order to determine quantum yields at low temperatures it is necessary to know the substrate’s absorptivity at low temperatures. The absorption spectra of transition metal complexes are temperature dependent largely due to the temperature dependence of component bandwidths. The determinations of absorptivity are most readily determined in a cuvette, but rapid cooling of a cuvette, as happens when it is immersed in liquid nitrogen in a Dewar flask, causes the cuvette to break. However, it is possible to achieve reasonably low temperatures (87-90 K) for samples in a cuvette by slow cooling in a cryostat. The spectra of both ambient and low temperature absorptions were obtained using NSG Precision Cells, Inc. cryogenic square 1 cm quartz cuvettes with an ANDOR Shamrock
500 spectrometer in an Oxford Instruments OptistatCF Static Exchange Gas Continuous Flow Cryostat. Both detector and the liquid light guide and the Newton array detector contributed to a shortest wavelength spectral detection limit of $\lambda_{\text{obsd}} \geq 350$ nm.

Figure 35: 90 K absorption spectroscopy set up for ruthenium quinoline complexes

The low temperature absorption spectra were collected using an Oxford Instruments OptistatCF Static Exchange Gas Continuous Flow Cryostat with liquid nitrogen as the cryogen was used at 90 K with NSG Precision Cells, Inc.). The system used for this purpose is represented in Figure 35.

The temperature in the cryostat was controlled by an Oxford Instruments Intelligent Temperature Controller (ITC) 503S. Temperature was gradually decreased from ambient temperature to 90 K to prevent the quartz cuvette from fracturing and solvent-glass cracking. The cryostat requires two pumps: 1) Roughing pump (1 x 10^{-4} torr) for the inner
vacuum chamber (IVC) and 2) Turbo-pump \((10^{-3} \text{ – } 10^{-5} \text{ mbar})\) for the outer vacuum chamber. The outer vacuum chamber is continuously pumped during the experiments for temperature stability.

### 3.3 RESULTS

#### 3.3.1 Proton Nuclear Magnetic Resonance Spectroscopy (\(^1\)H NMR)

The \(^1\)H NMR spectra of the ruthenium pentaamine isoquinoline complex investigated is shown in Figure 36, 37; this spectrum was taken in acetone-D6. In this spectrum, the ammonia ligand peaks are split into a pseudo-doublet; this could be \(H_2O\) in the up-field region with the centermost (largest) peak at 2.8 ppm. The \(^1\)H NMR spectrum of ammonia should be a triplet (N has a nuclear spin of 1), but these are rarely resolved in complexes due to disorder in the relative proton coordinates in solution and other effects. In principle a complex with \(C_{4v}\) point group symmetry should have two peaks whose intensities are in a 4:1 ratio as a result of the different environments, however, the low symmetry quinoline ligand will reduce the complex symmetry and this might result in more peaks. The ratio of intensities of all the peaks assigned as ammonia to those of the quinoline peaks in the spectrum below is 3:1 and it should be about 2:1. This suggests that the sample has some \([Ru^{II}(NH_3)_5L]^{m+}\) impurity where L is not quinoline. In view of the instability (especially the photochemical instability) of this complex this is not surprising. Likewise, the multiplet that corresponds to the isoquinoline protons are shifted downfield at 7.6-8 ppm with two singlets that were pushed further in the downfield region. The pure isoquinoline ligand spectrum in Figure 37 shows all the aromatic protons in the down field region between 7.5-9.7 ppm.
**Figure 36: $^1$H NMR of [Ru(NH$_3$)$_5$-ISO-Quinoline]**

**Figure 37: $^1$H NMR of [ISO-Quinoline]**
3.3.2. Absorption Spectra

a. Ambient and 90 K absorption spectra of [Ru(1-iso-TQA)(X)₂] Series of complexes

The ambient and 90 K UV-vis absorption spectra for both isomers of [Ru(iso-TQA)(X)₂] based complexes are shown in Figures 38 and 39. The lowest energy relatively intense absorption band of [Ru(1-iso-TQA)(CH₃CN)₂] is at 500 nm, while that of [Ru(1-iso-TQA)(CN)₂] is at 440 nm and for [Ru(1-iso-TQA)(SCN)₂] this band is at 470 nm. The lowest energy absorption bands of the 3-iso-TQA complexes are at somewhat higher energy with absorption maxima at: 440 nm for [Ru(3-iso-TQA)(CH₃CN)₂], and 450 nm for [Ru-3-iso-TQA-(CN)₂].

The ambient spectra are unusually broad and are clearly the result of the convolution of several similarly intense absorption bands. The component contributions are much better resolved in the 90 K absorption spectrum.
Figure 38. The normalized ambient and 90 K absorption spectra of [Ru(1-iso-TQA)(X)_2] series. Top left is the spectrum for [Ru(1-iso-TQA)(CH_3CN)_2]; top right is for [Ru(1-iso-TQA)(SCN)_2], middle bottom is for [Ru(1-iso-TQA)(CN)_2]. The black line represents the ambient condition absorption while the red line represents the 90 K absorption, all the absorption spectrum were taken in 4:1 Ethanol: Methanol.
b. Ambient and 90 K Absorption spectra of [Ru(3-iso-TQA)(X)₂] complexes

![Absorption spectra graph](image)

Figure 39: Ambient and 90 K UV-vis absorption comparison of [Ru(3-iso-TQA)(NCCH₃)₂]²⁺ left, [Ru(1-iso-TQA)(CN)₂] right, in 4:1 ethanol: methanol. Black is the ambient spectrum and red is 90 K spectrum, spectra were determined in 4:1 Ethanol: Methanol.

c. Ambient and 77 K absorption of various ruthenium complexes

The ambient condition absorption spectrum of [Ru(NH₃)₅(isoquinoline)] is shown in the black curve in Figure 40. The maximum absorption of this complex is at 470 nm spectrum and there is a weaker peak at about 380 nm. The red spectrum is for the pure isoquinoline ligand which shows an absorption shoulder at about 450 nm.
3.3.3. 77 K emission spectra

This section is shown the photophysical measurements of all complexes investigated in this project.

a. Comparison of the emission spectra of the [Ru(1-iso-TQA)(X)₂] and [Ru(3-iso-TQA)(X)₂] series of complexes.

The normalized 77 K emission spectra of the two isomers of [Ru(1-iso-TQA)(X)₂] series in alcohol are compared in Figures 41 and 42. These emission spectra all have unusually intense vibronic sidebands. The complexes of these two isomers have qualitatively similar emission envelopes, but quite different emission decay lifetimes.
Figure 41. Normalized 77 K emission spectra of \([\text{Ru(1-iso-TQA)(NCCH}_3]_2^{2+}\), \([\text{Ru(1-iso-TQA)(CN)}_2]\) and \([\text{Ru(1-iso-TQA)(NCS)}_2]\). The emission spectra were in 4:1 Ethanol: Methanol
Figure 42. Normalized 77 K emission spectra of \([\text{Ru}(3\text{-iso-TQA})(\text{NCCH}_3)_2]^2+\), \([\text{Ru}(3\text{-iso-TQA})(\text{CN})_2]\) and \([\text{Ru}(3\text{-iso-TQA})(\text{NCS})_2]\). The emission spectra were obtained in 4:1 Ethanol: Methanol.

b. 77 K emission spectra of \([\text{Ru}(\text{NH}_3)_5(\text{isoquinoline})]^2+\) complex

(i) The 77 K photochemistry of \([\text{Ru}(\text{NH}_3)_5(\text{isoquinoline})]^2+\).

This complex was very difficult to work with: it is difficult to purify, it emits very weakly, its emission overlaps with that of the free isoquinoline ligand and it photodecomposes at 77 K. Figure 43 shows typical 77 K emissions obtained in a butyronitrile solution after 8 min of 470 nm irradiation. These complicated spectra (compare the general bandshape with those above) illustrate the difficulties of working with this complex. The results are qualitatively similar in 77 K DMSO/water, butyronitrile and ethanol/methanol glasses. A few of these observations are presented here. For these emission measurements, the spectrometer had to be set so that it took 1 min of spectral
accumulation to capture an emission spectrum. The observation from the 
[Ru(NH$_3$)$_5$(isoquinoline)]$^{2+}$ in butironitrile shows that the free ligand emission intensity 
increases significantly during the irradiation time.

![Emission Spectrum](image)

**Figure 43:** 77 K Emission of 6.2E-4 M[Ru(NH$_3$)$_5$(isoquinoline] in butironitrile using 470 excitation
77 K emission spectra of [Ru(NH$_3$)$_5$-isoquinoline] are shown in Figure 44.

![Emission spectra of [Ru(NH$_3$)$_5$-isoquinoline]](image)

**Figure 44:** Emission spectra observed at 470 nm irradiation of [Ru(NH$_3$)$_5$-(isoquinoline)] complex in butyronitrile at 77 K

The pure iso-quinoline ligand was found to emit at energies very close to the complex’s emission. Figure 45 shows this emission in two different solvents.

![Emission spectra of iso-quinoline ligand](image)

**Figure 45.** 470 nm 77 K irradiation of isoquinoline ligand in 4:1 ethanol : methanol, (i) and butyronitrile (ii)
The \([\text{Ru(NH}_3\text{)}_5(\text{isoquinoline})]^{2+}\) excited state emission in ethanol : methanol is shown in Figure 46.

![Figure 46](image)

**Figure 46.** Comparison of the complex and free ligand emissions in ethanol: methanol. Black line represents the 77 K emission using 470 nm excitation; red line represents the 77 K emission of the isoquinoline free ligand at 405 nm excitation; blue line represents the 77 K of the free ligand using 470 nm excitation.

### 3.3.4. 77 K life-time measurements

The 77 K emission decay for the two isomers of \([\text{Ru(iso-TQA)(X)}]^{2+}\) in alcohol are shown in Figures 47 and 48. The decay measurements were done with mono exponential fits, the residuals are shown in red. In Figure 47 the longest lifetime was recorded for \([\text{Ru-(1-isop-TQA)(CH}_3\text{CN)}]^{2+}\) where the mean decay lifetime was determined to be 145 µs, the next longest lifetimes were determined to be 94, and 77.5 µs for \([\text{Ru(3-isop-TQA)(CN)}]^{2+}\) and \([\text{Ru(1-isop-TQA)(CN)}]^{2+}\), respectively. In addition, the lifetimes were determined to be 25 and 17.6 µs for \([\text{Ru(3-isop-TQA)(SCN)}]^{2+}\) and \([\text{Ru(1-isop-TQA)(SCN)}]^{2+}\), respectively. The shortest lifetime was determined to be 3.6 µs for \([\text{Ru(3-isop-TQA)(Cl)}]^{2+}\). The observations are summarized in Table 19.
Figure 47. 77 K Lifetime measurements of $\text{[Ru(1-iso-TQA)(NCCH}_3\text{)]}_2$] top left, $\text{[Ru(iso- TQA)(CN)]}_2$] top right, $\text{[Ru(1-iso-TQA)(NCS)]}_2$] bottom left, and $\text{[Ru(1-iso-TQA)(Cl)]}_2$] bottom right.
Figure 48. 77 K Lifetime Measurements for $[\text{Ru}(3\text{-iso-TQA})(L)_2]^{m+}$ Series in 4:1 ethanol: methanol. Top left is the emission decay for $[\text{Ru}(3\text{-iso-TQA})(CN)_2]^{m+}$, $[\text{Ru}(3\text{-iso-TQA})(SCN)_2]^{m+}$ top right, and bottom is the emission decay for $[\text{Ru}(3\text{-iso-TQA})(\text{CH}_3\text{CN})]^{m+}$.

3.3.5. Comparison of the spectroscopic properties of the triplet metal to ligand charge transfer ($^3\text{MLCT}$) various Ru-aromatic complexes.
### Table 19. Quantum yields, radiative and non-radiative rate constants of various [Ru(TQA)(X)₂],[ Ru(NH₃)₅(isoquinoline)], and [Ru(NH₃)₅(phenyl-pyridine)]

<table>
<thead>
<tr>
<th>Complex</th>
<th>hv&lt;br&gt;abs(max)</th>
<th>hv&lt;br&gt;em(max)</th>
<th>k&lt;br&gt;abs 77 K</th>
<th>Quantum yields at 77 K</th>
<th>k&lt;br&gt;RAD, ms⁻¹</th>
<th>k&lt;br&gt;NRD, ms⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru(1(ISO-TQA)(NCCH₃)₂)²⁺⁺</td>
<td>23.8</td>
<td>18.3</td>
<td>0.0069</td>
<td>0.452±0.01</td>
<td>3.1</td>
<td>3.8</td>
</tr>
<tr>
<td>[Ru(3-ISO-TQA)(NCCH₃)₂]²⁺⁺</td>
<td>19.1</td>
<td>0.1136</td>
<td>0.52</td>
<td>59</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>[Ru(1-ISO-TQA)(CN)]²⁺⁺</td>
<td>21.3</td>
<td>17.3</td>
<td>0.0129</td>
<td>0.26±0.049</td>
<td>3.4</td>
<td>9.5</td>
</tr>
<tr>
<td>Ru(3-ISO-TQA)(CN)²⁺⁺</td>
<td>18.3</td>
<td>0.01064</td>
<td>0.21</td>
<td>2.23</td>
<td>8.4</td>
<td></td>
</tr>
<tr>
<td>[Ru(1-ISO-TQA)(SCN)]²⁺⁺</td>
<td>20.8</td>
<td>16</td>
<td>0.0568</td>
<td>0.499±0.06</td>
<td>28</td>
<td>29</td>
</tr>
<tr>
<td>Ru(3-ISO-TQA)(SCN)²⁺⁺</td>
<td>16.9</td>
<td>0.04</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>[Ru(NH₃)₅isoQ]²⁺⁺</td>
<td>14</td>
<td>~30</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Ru(NH₃)₅(phpy)]²⁺⁺₉¹</td>
<td>22.32</td>
<td>13.02</td>
<td>1.8</td>
<td>0.00044(4)</td>
<td>0.8 ± 0.1</td>
<td>1,800</td>
</tr>
</tbody>
</table>

 kemₗ· 1/τ₁/²  b4:1 Ethanol :Methanol, this work c Butyronitile; dTQA = tris(isoquinolin-1- ylmethyl)amine.

### 3.4. DFT Modeling

#### 3.4.1 Calculated bond dissociation energies of pentaammine-RuⅢ complexes with monodentate quinolone ligands

Since we unable to synthesize [Ru(NH₃)₅(quinolone)] after many trials with different synthetic procedures, DFT calculations were done to investigate whether there were any issues with the coordination sphere or bond energy of the target complexes. The
DFT calculations indicated that the Ru-quinoline bond disassociation energy (BDE) was about -5 kcal/mol smaller than the Ru-py BDE of the [Ru(NH$_3$)$_5$py] complex.

Table 20. Calculation of The Bond Energies of [Ru-(NH$_3$)$_5$L], L = Quinoline or Iso-Quinoline $^a$

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Complex</th>
<th>Dissociation energy of ligand (kcal/mol)</th>
<th>(Dissociation energy relative to py), $\Delta$E (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyridine</td>
<td>[Ru(NH$_3$)$_5$-py]</td>
<td>25.05</td>
<td>0.0</td>
</tr>
<tr>
<td>Quinoline</td>
<td>[Ru(NH$_3$)$_5$-Q]</td>
<td>19.97</td>
<td>-5.08</td>
</tr>
<tr>
<td>Iso-Quinoline</td>
<td>[Ru(NH$_3$)$_5$-Iso-Q]</td>
<td>25.06</td>
<td>0.01</td>
</tr>
</tbody>
</table>

$^a$ Calculations done in collaboration with Dr. Yi-Jung Tu.

3.4.2. Excited state modeling done for this project by Dr. Yi-Jung Tu.

(a) Singlet MLCT excited states. The TD-DFT calculations for singlet excitation of ground-state of [RuTQA(ACN)$_2$] were performed with the B3PW91 functional and the results are summarized in Table 21. The calculated and experimental absorption spectra are compared in Figure 50.
Figure 49. Comparison of calculated (lower “UV-Vis Spectrum”) and experimental (upper; black curve at 300 K and red curve at 90 K) spectra for Ru(TQA)(ACN)$_2$. The calculated energies are about 0.5 eV higher energy than the observed peaks.

The bandshapes of the observed and calculated spectra are very different. Part of this arises from a difference in the observed and assumed (for the calculated spectra) bandwidths. There may be an issue with the relative oscillator strengths calculated for multi-transition absorption bands. The calculated energy differences between the calculated transitions with the largest oscillator strengths have much larger energy differences than those between the observed absorption peaks. Possible assignment of the 90 K peaks: Lowest energy MLCT transition with the electron in the excited state acceptor.
SOMO delocalized over the equivalent (more or less) quinoline moieties; the central band is likely an MLCT transition with the electron in an excited state acceptor SOMO that is localized on the unique quinoline moiety; and the highest energy band is likely an inter-quinoline ligand CT transition (mixed with a small amount of MLCT character. The dominant, lowest energy transition seems to have a metal-centered $d_{xy}$-type of orbital. All of the components of the observed “MLCT” absorption appear to be mixtures of different diabatic electronic configurations.
Table 21. Calculated $^1$MLCT energies, oscillator strengths and Natural transition orbitals of the SOMOs for the $S_0 \rightarrow S_n$ transitions of $[\text{Ru(TQA)(ACN)}_2]$ transitions.

<table>
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<tr>
<th>Excited state</th>
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<th>nm</th>
<th>f</th>
<th>Orbital transition Donor</th>
<th>Orbital transition Acceptor</th>
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- $0.68990$
- $0.13354$
- $0.69059$
- $0.69059$
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<td>14</td>
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<td>20</td>
<td>4.1601</td>
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(b) Triplet excited states Natural transition orbitals of the SOMOs.

The NTOs for triplet excited states of \([\text{Ru(TQA)(ACN)}_2]\) with the \(^3\text{MLCT}\) geometry are shown in Figure 50. All the triplet states appear to be more complex than the singlet states in Figure 50. The \(T_0\) state is the most important of these since it would correspond to the emitting state and it appears to be a remarkable nearly 1:1 mixture of idealized diabatic MLCT and \(\pi\pi^*\) excited states and its metal centered partly vacant orbital has approximately \(d_{xz}\) symmetry.
$T_0$: 1.7793 eV  696.80 nm  $f=0.0000$

Donor  \hspace{50pt} \vdash \hspace{50pt} \text{Acceptor}

$><0.99235$

$><0.02879$

$T_1$: 2.4407 eV  507.98 nm  $f=0.0000$

$><0.71338$

$><0.19158$
$T_2: 2.5136 \text{ eV } 493.25 \text{ nm } f=0.0000$

$0.04902$

$0.63174$

$0.29678$

$0.03546$
Figure 50. Calculated triplet excited state energies, oscillator strengths and Natural transition orbitals of the SOMOs of [Ru(TQA)(ACN)_2]

(c) Some comparisons of the calculated triplet state electronic structures of [Ru(TQA)(X)_2] complexes with different ancillary ligands.

In a classical organic chromophore the emitting state is typically the lowest energy excited state. However, in Ru-Ar complexes this is not always the case and there are often states with lower energies than the ones whose emission is detected, \(^{16,17,23,33}\) These are often metal-centered excited states (MC) as found in the DFT modeling summarized in Figure 51 and Table 22.\(^{38, 57-58, 80}\)

Figure 51. Comparison of donor SOMOs (isovalue=0.03 a.u.) and orbital contributions (%) for the lowest energy CT state of TQA and bpy Ru complexes with the ancillary ligands: A) [Ru(TQA)(MeCN)_2]^{2+}; B) [Ru(TQA)(CN)_2]; C) [Ru(bpy)_2(MeCN)_2]^{2+}; D) [Ru(bpy)_2(CN)_2] in the \(^3\)CT optimized geometries
Table 22. lists the relative energies of the $^3$MLCT and the $^3$MC states. The $^3$MC energies calculated for the cyanide complexes were close to or slightly higher than those of the $^3$MLCT states, while the MeCN complexes have significantly lower energy $^3$MC states.

Table 22. Relative energies of the $^3$MLCT and $^3$MC states and orbital contributions (%) of Ru and ligands to the SOMOs of A) [Ru(TQA)(MeCN)$_2$]$^{2+}$; B) [Ru(TQA)(CN)$_2$]; C) [Ru(bpy)$_2$(MeCN)$_2$]$^{2+}$; D) [Ru(bpy)$_2$(CN)$_2$]

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<th>$^3$MC</th>
<th>$^3$MC</th>
<th>$^3$MC</th>
<th>$^3$MC</th>
<th>$^3$MC</th>
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<tr>
<td></td>
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<td>(T$_0$)</td>
<td>(T$_1$)</td>
<td>(T$_2$)</td>
<td>(T$_3$)</td>
<td>(T$_0$)</td>
<td>(T$_1$)</td>
<td>(T$_2$)</td>
</tr>
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<td><strong>B)</strong></td>
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<td>22</td>
<td>2</td>
<td>2</td>
<td>22</td>
<td>22</td>
</tr>
</tbody>
</table>

$^a$ Energies of the $^3$MLCT states are set to be zero. Energies of the $^3$MC states are compared to those of the $^3$MLCT states. $^b$ Ligand = TQA or bpy.

Previous calculations of Mazumder, et al.$^{92}$ for [Ru(MeCN)$_4$]bpy]$^{2+}$ found that the energy barrier for the internal conversion can be small so that the $^3$MC states can be thermally accessed at ambient temperature. These results are consistent with the difficulty in finding an ambient emission from these complexes and with the previous work of CH$_3$CN photodissociation from [Ru(TQA)(MeCN)$_2$]$^{2+}$ at room temperature.$^{93}$
3.5. Ambient and 77 K Life-time measurements of cathepsin L (CSTL) inhibitors bearing Re(I) and Ru(II)

This work was done to characterize the $^3$MLCT of cathepsin L (CSTL) inhibitors bearing Re(I) and Ru(II), work done with professor corporation with Jeremy Kodanko group.

Figure 52: Emission decay of [MH-3-110] and [MH-3-55] concentration 47.5 µM and 4.09 µM respectively at ambient and 77 K (frozen solution) in potassium phosphate buffer 50 mM, PH 7.4 and 10% DMSO solvent using 337 N nm pulsed excitation monitored at 543 and 631. (A) [MH-3-110] at 77 K; (B) [MH-3-55] at 77 K. (C) [MH-3-110] at ambient condition. (D) [MH-3-55] at ambient condition. The mono exponential fit (black) and the extracted data (pink) are indistinguishable; residuals are in red. The samples were probably microcrystalline at 77K. A fast decay component with about 10% of the substrate amplitude was probably mostly due to the instrument response to scattered excitation light, but it could also contain contribution from heterogeneities or impurities. Exponential decay fittings performed in Origin; IRF= 12 ns.
Table 23: 77 K and ambient condition lifetime measurements of [MH-3-110] and [MH-3-55] with 337 nm\(^a\) excitation in potassium phosphate buffer 50 mM, PH 7.4 and 10% DMSO solvent monitored 543 and 631 respectively.

<table>
<thead>
<tr>
<th>Complex(^b)</th>
<th>Lifetime (µs)(^c)</th>
<th>Initial amplitude (A)(^d)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>77K</td>
<td>Ambient condition</td>
</tr>
<tr>
<td>[MH-3-110]</td>
<td>9.5±0.02(^c)</td>
<td>0.6±0.02</td>
</tr>
<tr>
<td>[MH-3-110]</td>
<td>9.5±0.02</td>
<td>0.6±0.02</td>
</tr>
<tr>
<td>[MH-3-110]</td>
<td>9.5±0.02</td>
<td>0.6±0.02</td>
</tr>
<tr>
<td>[MH-3-55]</td>
<td>0.9±0.1</td>
<td>0.06±0.02</td>
</tr>
<tr>
<td>[MH-3-55]</td>
<td>0.9±0.1</td>
<td>0.06±0.02</td>
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<tr>
<td>[MH-3-55]</td>
<td>0.9±0.1</td>
<td>0.06±0.02</td>
</tr>
</tbody>
</table>

\(^a\) Nitrogen laser excitation wavelength was 337 nm; \(^b\) complex names were abbreviated as [MH-3-110] for and [MH-3-55]; \(^c\) lifetime measurements were determined three times and recorded in microseconds; \(^d\)(A) is the initial amplitude; \(^e\) Standard errors.

3.6. DISSCUSSION AND CONCLUSIONS

The Ru-quinoline chromophores have some unique spectroscopic and photophysical properties. Thus, the lowest energy absorption bands of the Ru-TQA complexes are not typical MLCT absorptions, but appear to be the convolution of several different, near in energy absorption bands, while the vibronic “sidebands” dominate the emission spectra of the Ru-TQA complexes with the highest energy emissions. This has little if any precedent among reported MLCT emission spectra. DFT modeling suggests that the Ru-TQA excited states that involved in the lowest energy absorption component
and in the observed emission have very different electronic configurations and that the emitting excited state has at least as much quinolone-ππ* character as (Ru-quinoline)-MLCT character. Such an electronic configuration of the emitting state is consistent with the unusually intense vibronic sidebands.

Since the Ru-quinoline complexes with high energy emissions seemed to have such unusual spectroscopic properties and since the configurational mixing between 3MLCT and 3ππ* excited states is strongly dependent on the 3MLCT energies in Ru-bpy complexes,38, 79, 83, 86 a spectroscopic comparison between the Ru-TQA complexes one or more complexes with lower energy emissions is likely to provide a useful perspectives of the Ru-quinoline excited state properties. The [Ru(NH₃)₅(quinoline)]²⁺ complexes were selected for this purpose. While these complexes were more difficult to handle than anticipated, the observed spectra provide some useful perspectives.

3.6.1 Absorption spectroscopy and the singlet excited states.

The very broad absorption bands observed for the Ru-TQA chromophores at room temperature are partially resolved into 2-5 components at 90 K. The DFT modeling of the [Ru(3-iso-TQA)(NCCH₃)₂]²⁺ complex indicates that the observed visible-UV absorptions arise from a mixture of MLCT, intra-TQA ligand and inter-TQA ligand absorptions. For the 3-iso-TQA complexes the 90 K spectra show three at least partly resolved absorption bands. Since the DFT modeling found many transitions in this region, not all of the observed absorptions can be simply described, but the lowest energy transition of [Ru(3-iso-TQA)(NCCH₃)₂]²⁺ is readily assigned as a nearly classical S₀→¹MLCT transition with the two equivalent quinolone moieties of the complex acting as acceptors. This is the basis
for assigning the transitions of the remaining complexes; see Table 24. The higher energy transitions of the 3-iso-TQA complexes are difficult to assign with confidence, but they must involve significant ligand→ligand contributions. The calculated spectrum shown in Figure 50 does not clearly show the expected three dominant transitions that are observed and it is spread over a significantly larger energy range than is observed. Thus, it appears that the calculated S₀→ligand transition energies differ more from those observed than do the calculated S₀→MLCT energies. This might be a consequence of the functional used for the calculation.

Table 24. Summary of absorption spectra of the complexes

<table>
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<tr>
<th>Acceptor Ligand</th>
<th>Ancillary Ligands</th>
<th>Abs. Max. nm</th>
<th>Probable Assignment</th>
<th>Calc. Max., nm</th>
<th>Aprox. Ru Orbital in SOMO</th>
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</thead>
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<td>3-iso-TQA</td>
<td>(AN)₂</td>
<td>541</td>
<td>MLCT (S₁)</td>
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<td>(dπ)ₓz</td>
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<td></td>
<td></td>
<td>505</td>
<td>MLCT (S₃)</td>
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<td></td>
<td></td>
<td>469</td>
<td>MLCT, Inter(Q), Intra(Q) (S₁₁₄, S₋₁₄, S₁₈)</td>
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</tr>
<tr>
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<td>(NCS⁻)₂</td>
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<td>(CN⁻)₂</td>
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<td>MLCT</td>
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<td>(517)ₛₙ</td>
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The 90 K [Ru(1-iso-TQA)(X)\textsubscript{2}]\textsuperscript{m+} absorption spectra also show multiple components, but with more significant low and high energy shoulders. Since there are so many possible transitions in the TQA complexes, the observation of absorption shoulders is not surprising. The lowest energy dominant absorption is assigned as predominantly an S\textsubscript{0}→\textsuperscript{1}MLCT transition analogous to [Ru(3-iso-TQA)(NCCH\textsubscript{3})\textsubscript{2}]\textsuperscript{2+}.

The [Ru(NH\textsubscript{3})\textsubscript{5}(1-iso-quinoline)]\textsuperscript{2+} absorption spectrum is simpler than those of the TQA complexes, at least partly because there are no inter-ligand transitions. That two absorption bands are observed for this complex suggests that some internal quinoline-ligand transitions contribute, but this is not yet established.

The free ligand also absorbs in the high energy visible region and a weak shoulder is observed at 435 nm which is almost certainly the n→π* absorption that is typical of this class of aromatic imines.\textsuperscript{94} When the quinoline ligand is coordinated to Ru\textsuperscript{II} the nitrogen “non-bonding” electron pair of the ligand form a donor-acceptor bond to the metal and the n→π* transition is expected to be at higher energy.

**3.6.2 Emission spectroscopy and the triplet excited states.**

The DFT modeling of the lowest energy [Ru(3-iso-TQA)(NCCH\textsubscript{3})\textsubscript{2}]\textsuperscript{2+} triplet excited state indicates that the emitting state has an extended aromatic electronic configuration that can be approximated as a nearly equal combination of MLCT and ππ* character. The unusually large ligand contribution to the electronic configuration of this excited state provides a very reasonable explanation for the observation that the vibronic contributions to the emission spectrum are much larger than is usually observed for \textsuperscript{3}MLCT emissions. Thus, in contrast to the Ru-TQA complexes, the Ru(bpy)\textsubscript{2} species show less
contribution (11-19%) from the bpy ligand in the metal-centered SOMOs as illustrated in Figure 51, and the 3MLCT states of Ru-(bpy) chromophores have much smaller contributions from the ππ* states.\textsuperscript{79} Since the ππ* state is a longer-lived than a pure 3MLCT state, this greater configurational mixing could be the reason behind the longer excited state lifetimes for the Ru-TQA species. Among the four complexes studied by DFT, [Ru(TQA)(MeCN)\textsubscript{2}]\textsuperscript{2+} displays the highest mixing, has the most prominent vibronic sidebands and has the highest energy emission. If the energy of the acceptor ligand ππ* excited state is only a very weak function of the ancillary ligands, then the amount of mixing, which will increase as the energy difference between the MLCT and ππ* states decreases; that it will increase as the 3MLCT energy increases as has been observed for the Ru-bpy chromophores.\textsuperscript{38, 79, 83-84, 86} This effect is clearest for the [Ru(NH\textsubscript{3})\textsubscript{5}isoquinoline]\textsuperscript{2+} complex which is the lowest energy emitter of the Ru-quinoline chromophores.

3.6.3 Triplet excited state emission quantum yields, relaxation rates and excited state properties.

The emission spectra of the Ru-TQA chromophores are relatively well resolved, their emission yields are relatively large and their lifetimes are relatively long for Ru-Ar complexes despite the DFT-based excited states being lower in energy. This is fairly common with the Ru-Ar class of complexes and it apparently arises because the 3MC states are so much more distorted than the Ru-bpy, Ru-MDA, etc., complexes with their distortions in different nuclear coordinates so that the higher energy, usually 3MLCT excited state potential energy surface is not usually much distorted by mixing between these states and the barriers to crossing between them are large at 77 K.\textsuperscript{58, 80} On the other
hand these barriers are often small enough that crossing is rapid at 300 K, consistent with the difficulty in finding an ambient emission from these complexes and with the previous work of CH$_3$CN photodissociation from [Ru(TQA)(MeCN))$_2$]$^{2+}$ at room temperature.\textsuperscript{93}

The $^3$MLCT emission of these complexes has a very small radiative rate constants. The radiative rate constants span the range observed for Ru-bpy and Ru-MDA complexes.

3.7. **Overview: summary of significance and implications**

The DFT modeling and the observed variations in vibronic sideband contributions have led to a model of the Ru-Ar triplet charge transfer excited states in which the HOMO of the aromatic ligand radical anion, Ar$^-\pi^*$, mixes with the partly occupied d$\pi$(Ru$^{III}$) orbital to form the donor-SOMO. The resulting excited state interactions can be qualitatively addressed in terms of a simple Huckel-level treatment in which the MLCT/$\pi\pi^*$ excited state mixings are treated in terms of the mixings between the Ar$^-\pi^*$-HOMO, the Ar$^-\pi^*$-SOMO and the partly occupied d$\pi$(Ru$^{III}$) orbital where only the d$\pi$ orbital mixings are important and result in stabilization energies $\varepsilon_a$.
Then the ground and triplet excited state energies for a four electron system are: \( E_G = 2E_a \) and \( E_E = 2E_a + E_b - \varepsilon_a \). Thus, the observed excited state energy varies as \( \Delta E = (E_E - E_G) = E_b - \varepsilon_a + 2\varepsilon_b \). The stabilization energies are the square of the appropriate matrix element divided by the energy difference between the mixed states so that as \( E_a \to 0 \) or for \( E_a < H_a \), \( E_a \to H_a \) and the \( \pi \) and \( d\pi \) orbitals are totally mixed.

This simple model for excited state electronic mixing is qualitatively consistent with the energy relationships observed for these complexes. In the limit of weak configurational mixing between the acceptor ligand states and the electronic states of the metal the stabilization energies will be small compared to the energy differences between electronic states so that \( \varepsilon_x << (E_a \text{ or } E_b) \) so that \( \Delta E(\text{weak}) \approx (E_b - E_a) \). Within this context, the free energy difference between the one electron oxidation and reduction of the ground state is also approximately equal to \( E_b \). Thus, in the weak mixing limit one expects a nearly 1:1 correspondence between the electrochemically determined oxidation and reduction free energies, \( -F\Delta E_{1/2} \), for a series of closely related complexes and their emission band origins (which are usually very close to \( h\nu_{\text{max}}(\text{emis}) \) for these complexes). This has been found to be very close to the case for Ru-bpy chromophores,\(^{61-62, 95}\) although the slopes of the correlations may be closer to 0.8:1.\(^{96}\) For \( E_a << E_b \) and/or very strong excited state mixing, \( \Delta E \approx E_b \) while the electrochemical relationships will be unchanged so that the emission band origin would be expected at energies much greater than those expected based on a 1:1 electrochemical correlation. This is consistent with our observations on the Ru-quinoline chromophores.
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ABSTRACT

CHEMICAL AND PHYSICAL STUDIES OF CHARGE TRANSFER EXCITED STATES OF RUTHENIUM COMPLEXES WITH AROMATIC LIGANDS

by

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The $^3$MLCT excited states generated from tris-bipyridineruthenium(II), [Ru(bpy)$_3$]$^{2+}$ and related complexes were ionized by 405 nm irradiation in ambient, acidic aqueous solutions. The photoionization product was Ru(bpy)$_3$$^{3+}$ and an electron with a quantum yield of about 0.04±0.02 in 0.5 M acid. However, 532 nm radiation does not induce photoionization, but it generates the $^3$MLCT excited state that can be photoionized by 405 nm irradiation. Dramatic decreases in [Ru(bpy)$_3$]$^{2+}$ emission intensities were observed when dual laser irradiations were used for 10-30 min in 0.5 M H$^+$. The proton is a very good electron scavenger, and the rate of photoionization of the $^3$MLCT excited state was determined to be acid dependent and it increased about ten-fold for acid concentrations between 0.001 and 4 M when 0.1 M isopropanol was used to scavenge hydrogen atoms. The increase in photoionization rate at acid concentration greater than 0.1 M indicate that the proton scavenges electron containing ion pair species in highly acidic solutions. The minimum free energy required to ionize the [Ru(bpy)$_3$]$^{2+}$ $^3$MLCT excited state is about 2
eV (620 nm). Such thermodynamic considerations also indicate that photoionization processes are possible for many of the electron donors whose excited states might be considered for use as photosensitizers. This suggests that the shorter wavelength visible light could lead to their degradation through reactions of the resulting free radicals and other product species when they are used in long term applications.

Ru-quinoline chromophores of the general formula [Ru(iso-TQA)L₂]ⁿ⁺, where TQA is tris(isoquinolin-1-ylmethyl)amine, and L is MeCN, CN or SCN, and n = 0 or 2, have some unique spectroscopic and photophysical properties. DFT modeling suggests that the Ru-TQA excited states have very different electronic configurations where the emitting excited state has the same contribution from quinolone-ππ* character as MLCT. In addition, the lowest energy absorption bands of the Ru-TQA complexes are not typical MLCT absorptions, it contains a convolution of several near in energy absorption bands. Furthermore, those complexes were determined to have a long lifetime and large quantum yields at 77 K and the vibronic structure of those complex are large and that might arise from ³MLCT/³ππ* mixing.
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Presentations

"Visible Light Photoionization of the tris-Bipyridine-Ruthenium(II) Triplet Metal to Ligand Charge Transfer Excited State: Observations and Implications" Talk - The ACS Central Regional Meeting, Dearborn, MI, June 2017
"The Photo-Generation of Electrons (and Hydrogen-atoms) from the Near-Ultraviolet Irradiation of tris-(bipyridine) Ruthenium(II)" Poster - Chemistry Department Symposium, Wayne State University, Detroit, MI, 2015

Publications

Alnaed, M. K.; J. F. Endicott, ‘‘The Visible Light Photoionization of the tris-Bipyridine-Ruthenium(II) Triplet Metal-to Ligand Charge-Transfer Excited State: Chemical Scavenging Probes of the Threshold Energy and Short-Lived Intermediates,’’ manuscript will be submitted soon.


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