

PROBING VIBRATIONAL RELAXATION DYNAMICS IN CHARGE-TRANSFER
EXCITED STATES: SYNTHESIS, PHYSICAL, AND PHOTOPHYSICAL
CHARACTERIZATION OF CYANO-SUBSTITUTED POLYPYRIDYL
COMPLEXES OF RU(II)

By

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ABSTRACT

PROBING VIBRATIONAL RELAXATION DYNAMICS IN CHARGE-TRANSFER EXCITED STATES: SYNTHESIS, PHYSICAL, AND PHOTOPHYSICAL CHARACTERIZATION OF CYANO-SUBSTITUTED POLYPYRIDYL COMPLEXES OF RU(II)

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Photo-induced charge separation is the physical phenomenon underlying virtually all schemes geared toward the conversion of light into chemical, electrical, and/or mechanical energy. Charge separation is typically effected in a molecular system through charge-transfer excited states, in which photon absorption causes charge redistribution within the chromophore: maintaining, amplifying, or, in the least favorable circumstances, destroying the resulting chemical potential depends on dynamics that occur within the chromophore immediately following the absorptive event. In transition metal complexes a majority of excited state energy is dissipated through non-radiative decay. Despite the prominent role it plays in the deactivation of charge-transfer excited states, there is relatively known about the mechanism of non-radiative decay in charge transfer complexes.

Probing vibrational relaxation in transition metal complexes is not always a straightforward process. Often times information about vibrational relaxation from the initially excited Franck-Condon state to the long lived excited state is inferred from transient electronic absorption spectroscopy. Infrared spectroscopy is more direct way to probe the vibrational state of an electronic excited state.

This dissertation investigates the fundamental photophysics of ruthenium polypyridyl complexes, in particular the non-radiative decay between the initial excited Franck-Condon state and the long lived excited state. The complexes studied in this dissertation incorporate cyanide groups as infrared tags in order to use infrared transient absorption spectroscopy, coupled with visible transient absorption spectroscopy, to probe the vibrational relaxation dynamics in ruthenium polypyridyl complexes.

Before ultrafast dynamics can be interpreted it is critical to have a solid understanding of the properties of both the initial Franck-Condon excited state and the long lived excited state. Nanosecond time-resolved spectroscopic techniques which can be used to probe the long lived excited state of transition metal complexes are discussed. These techniques are used to characterize the long lived excited states of a series of cyano-substituted ruthenium(II) bipyridine and terpyridine complexes. A combination of ultrafast infrared and visible absorption spectroscopies are used to probe the excited state dynamics in the series of cyano-substituted ruthenium(II) bipyridine complexes. By combining the two techniques it can be conclusively shown that small amplitude changes in the time resolved electronic absorption spectra on a ~ 1 -10 ps time scale are due to vibrational relaxation on the lowest energy excited state potential surface. The large energy difference between the cyano substituted bipyridine ligand and the unsubstituted bipyridine ligand allows for selectively localizing the initial excited state on either the cyano-substituted or unsubstituted bipyridine ligands. This potentially allows the dynamics associated with intramolecular vibrational redistribution to be decoupled from the dynamics associated with interligand electron transfer.

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KEY TO ABBREVIATIONS AND SYMBOLS

ΔQ	Nuclear displacement of excited state relative to the ground state
$\Delta\bar{\nu}_{0,1/2}$	Spectral bandwidth
$\hbar\omega_M$	Average vibrational mode
Φ	Quantum yield
acac	Acetylacetonate
bpy	2,2'-bipyridine
CCD	Charge coupled device
Cl-Me-bpy	4,4'-dichloro-5,5'-dimethyl-2,2'-bipyridine
Cl-tpy	4-chloro-2,2':6',2''-terpyridine
CN-Me-bpy	4,4'-dicyano-5,5'-dimethyl-2,2'-bipyridine
CN-tpy	4-cyano-2,2':6',2''-terpyridine
CS	Charge separated state
CV	Cyclic voltammetry
DPV	Differential pulse voltammetry
E_0	Zero point energy difference
IC	Internal conversion
IL	Intraligand transition
ILET	Interligand electron transfer
IRF	Instrument response function
ISC	Intersystem crossing
IVR	Intramolecular vibrational redistribution
LF	Ligand field
LMCT	Ligand-to-metal charge transfer
MLCT	Metal-to-ligand charge transfer
MMCT	Metal-to-metal charge transfer
OPO	Optical parametric oscillator

phen.....	1,10-phenanthroline
PMT	Photomultiplier tube
S_M	Huang-Rhys factor
SSIR	Step-scan infrared
TBAPF ₆	Tetrabutylammonium hexafluorophosphate
tpy	2,2':6',2''-terpyridine
TR ²	Transient resonance Raman
TR ³	Time-resolved resonance Raman
TRIR	Time-resolved infrared
VR.....	Vibrational relaxation

Chapter 1: Introduction to Photophysical Properties of Ruthenium Polypyridyl Complexes

1.1 Introduction

This dissertation investigates the fundamental photophysics of ruthenium polypyridyl complexes, in particular the non-radiative decay between the initial excited Franck-Condon state and the long lived excited state. The complexes studied in this dissertation incorporate cyanide groups as infrared tags in order to use infrared transient absorption spectroscopy, coupled with visible transient absorption spectroscopy, to probe the vibrational relaxation dynamics in ruthenium polypyridyl complexes. This chapter highlights what is known in the literature about the excited state dynamics of $[\text{Ru}(\text{bpy})_3]^{2+}$ as a model for all ruthenium(II) polypyridyl complexes with emphasis on topics relevant to the work in this dissertation. Examples of applications for ruthenium(II) polypyridyl complexes are also highlighted.

1.2 Ground State Properties of $[\text{Ru}(\text{bpy})_3]^{2+}$

The discovery of emission from $[\text{Ru}(\text{bpy})_3]^{2+}$, the first example of charge transfer emission, over 50 years ago was the beginning of research interest in the photophysics of ruthenium polypyridyl complexes.¹ In addition to being (relatively) highly emissive the long lived excited states and reversible oxidation and reduction chemistry makes this class of compounds useful in many different applications and drives research into understanding their fundamental photophysical behavior.²

In the ground state electronic absorption spectrum of ruthenium(II) complexes, there are generally three types of transitions that can be observed. These transitions are defined by the nature of the initial and final orbitals involved

in the transitions, as shown in the molecular orbital diagram in Figure 1-1. The intraligand (IL) transition is a transition between two ligand based orbitals, the ligand field (LF) transition (also referred to as a d-d or metal centered transition) is a transition between two metal based orbitals, and the metal-to-ligand charge transfer (MLCT) transition is a transition from a metal based orbital to a ligand

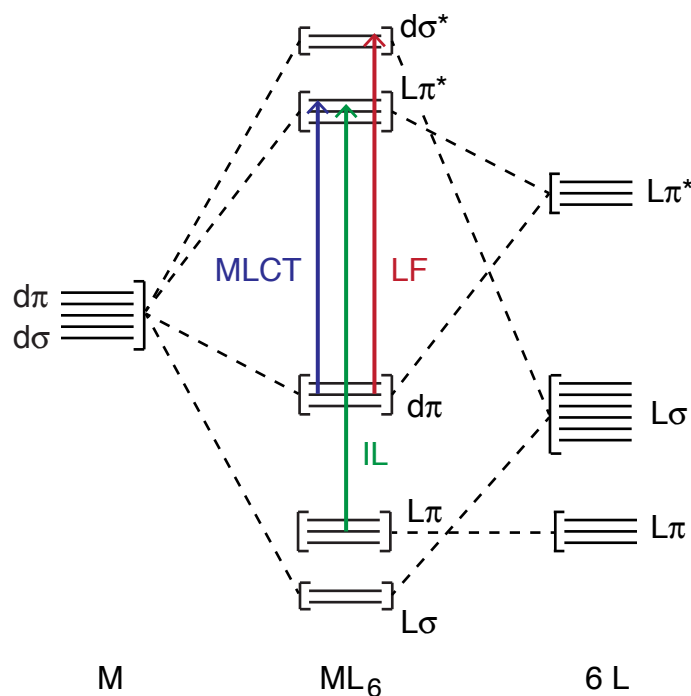


Figure 1-1: Simplified molecular orbital diagram showing the interactions between a π acceptor ligand and metal d orbitals in O_h symmetry. For a low spin d^6 metal center the possible transitions in the electronic absorption spectrum are shown by the arrows. MLCT (blue arrow) is a metal to ligand charge transfer transition from a filled metal orbital to an empty π^* ligand orbital. IL (green arrow) is an intraligand transition from a filled ligand π orbital to an empty π^* ligand. LF (red arrow) is a ligand field transition from a filled metal d orbital to an empty metal d orbital. For interpretation of the references to color in this and all other figures, the reader is referred to the electronic version of this dissertation.

based orbital. The ligand field strength, redox properties of the metal and ligand(s), as well as the intrinsic properties of the ligand(s) are the three major factors in determining the relative energies of these three transitions. The electronic absorption spectrum of $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$, the prototypical ruthenium polypyridyl complex, is shown in Figure 1-2. The intense absorption at 285 nm has been assigned as an intraligand transition by consideration of the extinction coefficient and comparison to the absorption spectrum of the protonated bipyridine ligand³ and the small shoulders on the IL band at approximately 320 nm and 350 nm have been tentatively assigned as ligand field absorptions.⁴

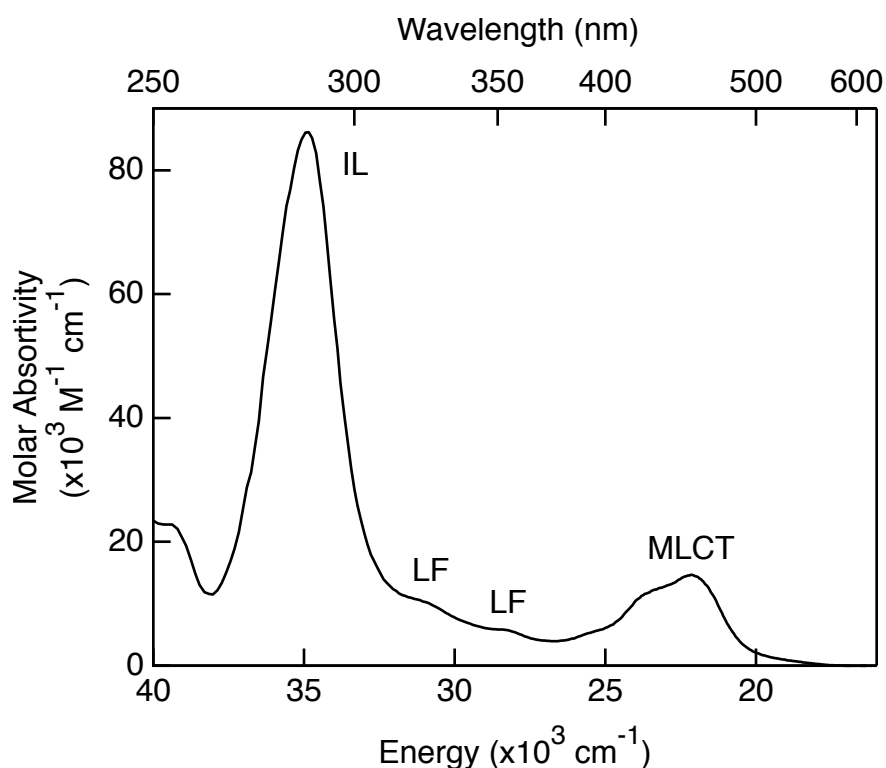


Figure 1-2: Electronic absorption spectrum of $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ in CH_3CN solution. MLCT is the metal-to-ligand charge transfer absorption band, LF is the ligand field absorption bands, and IL is the intraligand $\pi \rightarrow \pi^*$ absorption band.

The absorption band at 450 nm has been assigned as the metal-to-ligand charge transfer absorption manifold based on extinction coefficient and electrochemical data. An MLCT transition can be thought of as the simultaneous oxidation of the metal center and reduction of the ligand. Therefore, to a reasonable approximation, the energy of a metal-to-ligand charge transfer absorption is the sum of the energy required to oxidize the metal and reduce the ligand i.e. $E(\text{MLCT}) \approx |E(\text{M} \rightarrow \text{M}^+)| + |E(\text{L} \rightarrow \text{L}^-)|$.⁵ Figure 1-3 shows the cyclic voltammogram of $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$; the $\text{Ru}^{\text{II/III}}$ oxidation can be seen at +0.91 V and the first $\text{bpy}^{0/-}$ reduction is at -1.70 V versus the ferrocene/ferrocenium redox couple. According the approximation above, this

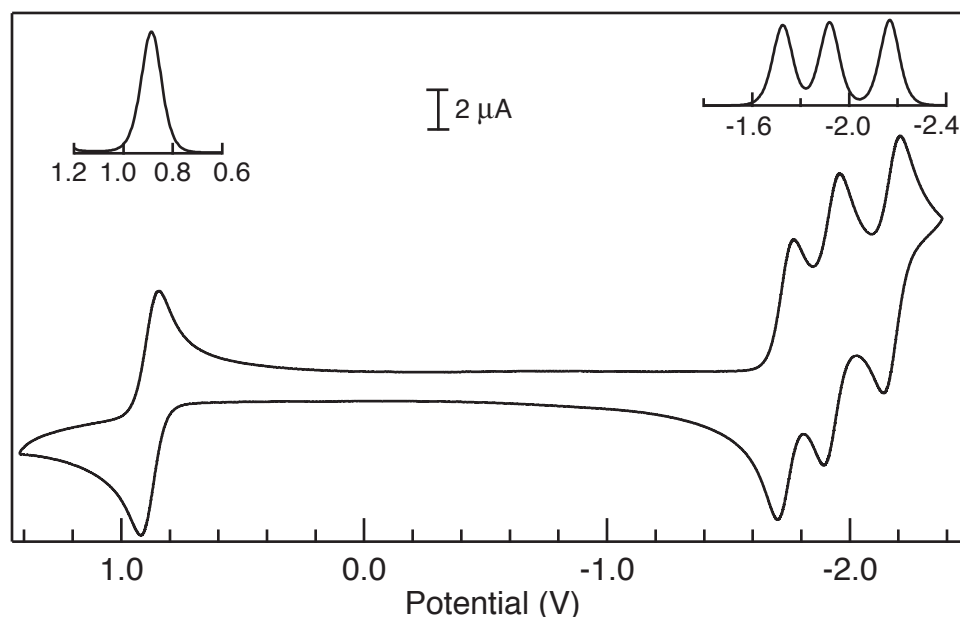


Figure 1-3: Cyclic voltammogram of $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ in CH_3CN with 0.1 M TBAH as the electrolyte. The spectrum was collected using the standard three electrode setup with a platinum working electrode, graphite counter electrode, and a Ag/AgCl reference electrode. The spectrum is referenced to the ferrocene/ferrocenium redox couple, which was added as an internal standard. The differential pulse voltammograms are shown in the insets.

electrochemical data predicts that the metal-to-ligand charge transfer transition in $[\text{Ru}(\text{bpy})_3]^{2+}$ should occur at 2.61 eV (475 nm) which is fairly close to the experimentally observed 450 nm, especially considering this model does not account for solvation energy or electron correlation effects.⁵

While there are rare examples of ruthenium(II) polypyridyl-like complexes where the lowest energy excited state is a ligand field state or an intraligand state,⁶⁻⁸ a vast majority of these complexes have photophysical properties which are comparable to the $[\text{Ru}(\text{bpy})_3]^{2+}$ prototype. Because of this, lessons learned from studying $[\text{Ru}(\text{bpy})_3]^{2+}$ can be applied to a wide range of systems.

1.3 Long Lived Excited State of $[\text{Ru}(\text{bpy})_3]^{2+}$

The long lived emissive state in $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ has been identified as being $^3\text{MLCT}$ in nature⁹ and over the years, many different spectroscopic techniques have been used to characterize the $^3\text{MLCT}$ state of $[\text{Ru}(\text{bpy})_3]^{2+}$. Variable temperature emission experiments have shown that the lowest energy $^3\text{MLCT}$ is actually split into a set of three closely spaced ($\sim 80 \text{ cm}^{-1}$) states.¹⁰⁻¹² These states have differing amounts of mixing with higher energy singlet states and therefore different ground state recovery kinetics. The dynamics observed at room temperature represent a Boltzmann average of the three states, but at low temperature the energies and dynamics of the three individual states can be resolved.

In addition to emission spectroscopy many other spectroscopic techniques have been used to observe the long lived excited state in $[\text{Ru}(\text{bpy})_3]^{2+}$ and other related molecules. Results of resonance Raman,^{13,14} time-resolved infrared,¹⁵ time-resolved electron paramagnetic resonance,¹⁶ and other techniques all show that the emissive state in ruthenium(II) polypyridyl complexes is localized on a single ligand rather than being evenly delocalized over all three ligands.

Upon absorption of a photon, $[\text{Ru}(\text{bpy})_3]^{2+}$ is excited into a $^1\text{MLCT}$ state, which rapidly relaxes into a long lived $^3\text{MLCT}$ state via a combination of intersystem crossing (ISC) and vibrational relaxation (Figure 1-4). This long lived excited state decays back to the ground state via radiative and non radiative decay. Ground state recovery in most ruthenium polypyridyl complexes lies in the Marcus inverted region and non-radiative decay can be modeled with the energy gap law.¹⁷⁻¹⁹

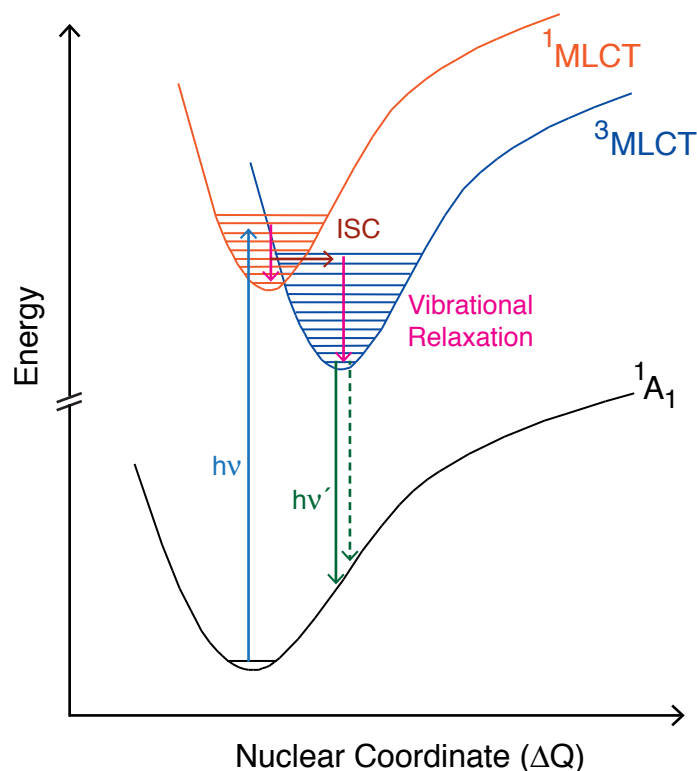


Figure 1-4: Potential energy diagram for $[\text{Ru}(\text{bpy})_3]^{2+}$. The $^1A_1$ ground state can be excited with visible light into a $^1\text{MLCT}$ state. This initial $^1\text{MLCT}$ state rapidly intersystem crosses to form the $^3\text{MLCT}$ state, which is the long lived excited state. The $^3\text{MLCT}$ state can relax back to the ground state through radiative and non-radiative decay.

1.4 Ultrafast Dynamics of $[\text{Ru}(\text{bpy})_3]^{2+}$

The advent of ultrafast spectroscopic techniques has allowed for studying shorter timescale dynamics; i.e. the relaxation from the initially excited state to the long lived excited state. Three general questions or themes investigated are: What is the timescale of intersystem crossing between the $^1\text{MLCT}$ state and the $^3\text{MLCT}$ state? What is the timescale and mechanism of vibrational relaxation on the long lived $^3\text{MLCT}$ surface? Are the initial and long lived excited states delocalized over the entire molecule or localized on a single ligand?

1.4.1 Intersystem Crossing

Differential absorption spectroscopy has been used perviously in our group to infer a formation time of approximately 100 fs for the $^3\text{MLCT}$ state,²⁰ but there is not necessarily a difference between the absorption spectrum of a $^1\text{MLCT}$ state and a $^3\text{MLCT}$ state, so this technique is not ideal for differentiating between singlet and triplet states. Fluorescence upconversion is an experimental technique that is uniquely suited to monitor intersystem crossing. In the upconversion experiment, sum frequency generation is used to mix the emitted light with a gate pulse to create a unique frequency of light to be detected. This is a non-linear process, so it is selective for spin allowed fluorescence because of the large k_f value (and high photon flux) and discriminates against spin forbidden phosphorescence because of the small k_f value (and low photon flux).

Because of this, the $^3\text{MLCT}$ phosphorescence, which dominates the steady state emission, can be excluded in the fluorescence upconversion experiment. The $^1\text{MLCT}$ fluorescence, which is undetectable in the steady state can be selectively monitored. Okada and coworkers used this technique in 2002 on $[\text{Ru}(\text{bpy})_3]^{2+}$ and saw a 40 ± 15 fs decay of the $^1\text{MLCT}$ emission and a 500 fs to 1 ps decay component that they tentatively assigned to emission from a

vibrationally excited $^3\text{MLCT}$ state.²¹ In 2006, Chergui and coworkers also used fluorescence upconversion to study the intersystem crossing dynamics of $[\text{Ru}(\text{bpy})_3]^{2+}$ and observed a 15 ± 10 fs decay of the $^1\text{MLCT}$ fluorescence but saw no signature for vibrational relaxation.²² Using femtosecond stimulated Raman spectroscopy coupled with fluorescence upconversion, Mathies and coworkers have developed a three state model to describe the early time dynamics in $[\text{Ru}(\text{bpy})_3]^{2+}$ (Figure 1-5).²³ This model states that the initially excited $^1\text{MLCT}$ state very rapidly ($\tau < 30$ fs) decays to a lower energy $^1\text{MLCT}$ state which is stabilized by excited state solvent interactions. This lower energy $^1\text{MLCT}$ state then intersystem crosses to the long lived $^3\text{MLCT}$ state with a time constant of approximately 110 fs.

Together, all of these results show that despite its spin forbidden nature, intersystem crossing occurs very rapidly in ruthenium polypyridyl systems. The classic rules developed through the study of organic photophysics state that vibrational relaxation is the fastest relaxation process, followed by internal conversion, and intersystem crossing is the slowest relaxation process ($k_{\text{VR}} > k_{\text{IC}} > k_{\text{ISC}}$). The results above, along with similar results for other transition metal systems,²⁴⁻²⁷ show that the classic rules don't necessarily apply to inorganic systems and inorganic photophysics are fundamentally different than organic photophysics.

1.4.2 Vibrational Relaxation

The study of the vibrational relaxation dynamics in ruthenium(II) polypyridyl complexes is the primary focus of the work in this dissertation. In the literature previous studies on $[\text{Ru}(\text{bpy})_3]^{2+}$ and other similar complexes has yielded some conflicting results regarding vibrational relaxation in these complexes.

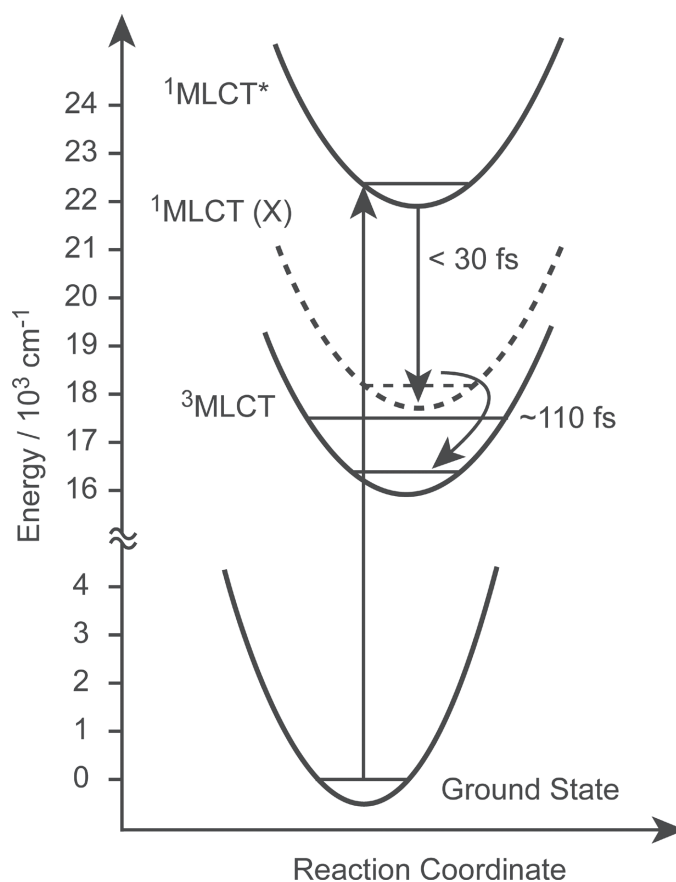


Figure 1-5: Three state model for intersystem crossing in $[\text{Ru}(\text{bpy})_3]^{2+}$ developed by Mathies and coworkers. Reproduced from reference 23.

As briefly mentioned above, previous work in our group using ultrafast differential absorption spectra of $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ showed that by 500 fs after a 480 nm excitation, the absorption spectrum was identical to the spectrum of the thermalized $^3\text{MLCT}$ state obtained by nanosecond transient absorption spectroscopy.²⁰ This suggests a formation time of approximately 100 fs for thermalized $^3\text{MLCT}$ state, which includes contributions from intersystem crossing and vibrational relaxation. The work of Chergui and Mathies, discussed above,

also shows very rapid formation of the thermalized $^3\text{MLCT}$ state, again suggesting that vibrational relaxation in the $^3\text{MLCT}$ state is occurring on the same ultrafast timescale as intersystem crossing from the initially excited $^1\text{MLCT}$ state.^{22,23}

In contrast to the results above, previous work from our group on the related $[\text{Ru}(\text{dmb})_3](\text{PF}_6)_2$ (dmb = 4,4'-dimethyl-2,2'-bipyridine) showed an additional decay signal ($\tau = 5 \pm 0.5$ ps) in the transient absorption spectra when exciting the molecule at 400 nm (compared to 480 nm for the previous $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ study).²⁸ This picosecond decay component was assigned as vibrational relaxation on the $^3\text{MLCT}$ surface. Browne, McGarvey, and coworkers recently used picosecond resonance Raman spectroscopy to monitor the growth of vibrations of the bipyridine radical anion in the thermalized $^3\text{MLCT}$ state.²⁹ In contrast to the work of Mathies, Browne and McGarvey see the thermalized triplet grow in over ~ 20 ps. Vibrational relaxation in many different transition metal systems occurs on a picosecond timescale,^{25,30-34} which suggests that the vibrational relaxation in ruthenium polypyridyl complexes most likely takes place on a similar timescale. The conflicting conclusions in the literature highlight the need for further study.

1.4.3 Localization or Delocalization of the Excited State

A metal-to-ligand charge transfer excited state can be describe as a localized state, i.e., $\{[\text{Ru}^{3+}(\text{bpy})_2(\text{bpy}^-)]^{2+}\}^*$ or as a delocalized state, i.e., $\{[\text{Ru}^{3+}(\text{bpy}^{-1/3})_3]^{2+}\}^*$. As discussed in Chapter 1.3, there is a consensus that on longer (nanosecond) timescales the long lived $^3\text{MLCT}$ state of ruthenium bipyridyl complexes is localized on a single ligand, even in homoleptic complexes such as $[\text{Ru}(\text{bpy})_3]^{2+}$. The question remains, is the initial Franck-Condon state localized and, if it is, is that localization maintained throughout the relaxation

process?

Using Stark effect spectroscopy, Oh and Boxer showed that there was an 8.8 D change in the dipole moment of $[\text{Ru}(\text{bpy})_3]^{2+}$ upon excitation. As the ground state is D_3 symmetry and has no permanent dipole this result means that the initial excited state has a significant dipole moment and therefore must be localized rather than being evenly delocalized over the three bipyridine ligands.³⁵ Ground state resonance Raman experiments³⁶ and variable solvent absorption spectroscopy³⁷ among other experiments also confirm that the initial excited state is localized on a single ligand in $[\text{Ru}(\text{bpy})_3]^{2+}$.

Ultrafast polarized absorption measurements show a very rapid decrease in the anisotropic signal from the excited state. Work from our group showed that the timescale of this anisotropy decay was dependent on solvent and theorized that it was due to the transition from a delocalized state to a localized state that is driven by solvent interactions.³⁸ Hammarström and coworkers suggest that the excited state very rapidly (< 300 fs) randomizes, but it is unclear whether this randomization is due to the formation of a delocalized state or interligand electron transfer.³⁹ Recently, Chergui and coworkers have used molecular dynamics calculations to study the lowest energy triplet state of $[\text{Ru}(\text{bpy})_3]^{2+}$. In the gas phase calculations, the triplet state remained delocalized over all three ligands for the entire simulation. However, in calculations done in a water dielectric continuum the triplet state localized very quickly and oscillated between being localized on one or two bipyridine ligands.⁴⁰

As of now there is no clear consensus in the literature about the localized or delocalized nature of the excited state of $[\text{Ru}(\text{bpy})_3]^{2+}$. There is an abundant amount of experimental evidence to show that the long lived excited state is localized on a single bipyridine ligand. There is also strong experimental evidence to show that the initial Franck-Condon state is also localized on a single

bipyridine ligand. What is still unclear is the evolution of the initial excited state into the long lived excited state; anisotropy absorption measurements and molecular dynamics simulations suggest that the initial localization of the excited state isn't maintained. This randomization could be due to the formation of a delocalized state that will randomly re-localize on a single ligand or it could be a result of very rapid intramolecular transfer. The idea of excited state localization vs delocalization and techniques to differentiate between delocalization and rapid interligand electron transfer will be discussed further in Chapter 4.

1.5 Applications of Ruthenium Polypyridyl Complexes

One reason why ruthenium polypyridyl complexes are so highly studied are their applications in many areas of chemistry.⁴¹ Dye sensitized solar cells often use ruthenium polypyridyl complexes as dye molecules.⁴²⁻⁴⁷ The dye molecule absorbs light and is excited into a metal-to-ligand charge transfer excited state. If this excited state is above the conduction band edge, it can inject an electron into the conduction band. In these systems vibrational relaxation competes with electron injection; in cases where the long lived excited state lies above the conduction band vibrational relaxation represents a loss of potential (or driving force for electron injection) for each electron and in cases where the long lived excited state lies below the conduction band edge the electron injection must outcompete the excited state deactivation in order to get a high injection yield.

As shown previously, ruthenium polypyridyl complexes exhibit reversible oxidation and reduction behavior. Because of this ruthenium polypyridyl complexes are also often used as redox or photoredox catalysts. One of the most famous is the ruthenium blue dimer developed by Meyer and coworkers in the 1980's, which was the first example of a molecular catalyst able to split water.^{48,49} The blue dimer is an oxo bridged ruthenium(III) dimer with the formula

cis,cis-[(bpy)₂(H₂O)Ru^{III}ORu^{III}(OH₂)-(bpy)₂]⁴⁺ (Figure 1-6). The blue dimer can electrochemically catalyze the 4-electron and 4-proton splitting of water in the presence of cerium(IV) as a sacrificial oxidant.

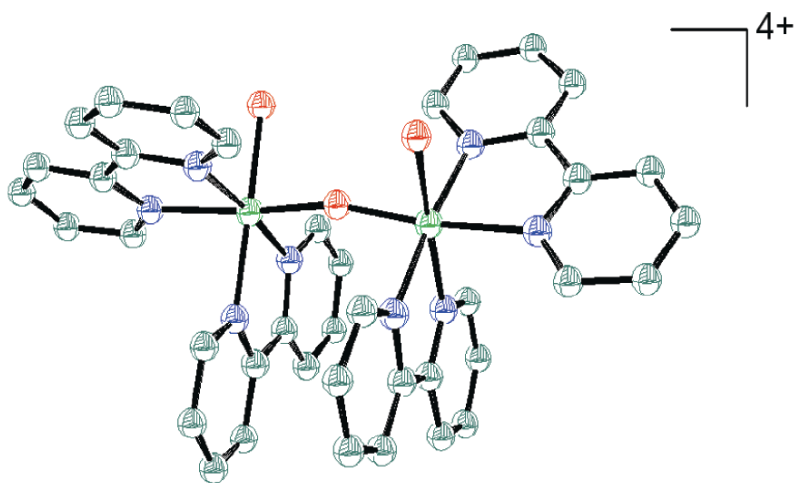


Figure 1-6: Structure of the ruthenium blue dimer, *cis,cis*-[(bpy)₂(H₂O)Ru^{III}ORu^{III}(OH₂)-(bpy)₂]⁴⁺. Reproduced from reference 49

The work of MacMillan and coworkers is another example of using ruthenium polypyridyl complexes as catalysts.⁵⁰ In their proposed catalytic cycle photoexcited [Ru(bpy)₃]²⁺ acts as both an oxidant and a reductant in two discrete single electron transfer steps, creating two reactive radical species. These two reactive radicals then combine to form new carbon-carbon bonds. This is different from most carbon-carbon bond forming reactions, which require a two electron oxidation and/or reduction.

1.6 Dissertation Outline

The work described in this dissertation is primarily focused on studying vibrational relaxation in ruthenium(II) polypyridyl complexes. This involves the synthesis and characterization of series both of cyano substituted bipyridine and

cyano substituted terpyridine ligands followed by an ultrafast transient absorption study of the bipyridine complexes. An outline of this dissertation is below:

- **Chapter 2** is a discussion of the different nanosecond time-resolved spectroscopic techniques commonly used to study photophysical and photochemical processes in transition metal complexes. These techniques include time-resolved emission, transient absorption, time-resolved infrared methods, time-resolved electron paramagnetic resonance, and time-resolved X-ray spectroscopy. The experimental requirements for each technique and examples from the literature of how each is used are covered.
- **Chapter 3** discusses the synthesis and characterization of a series of cyano-substituted bipyridine complexes. The properties of the ground state and long lived excited state are investigated by spectroscopic and computational methods.
- **Chapter 4** focuses on the ultrafast dynamics of the cyano-substituted bipyridine complexes introduced in Chapter 3. Both visible and infrared transient absorption spectroscopy are used to monitor the vibrational relaxation process between the initially excited state and the long lived excited state as a function of excitation wavelength. Time dependent DFT calculations are used to identify the initial excited state for each of the excitation wavelengths used. Possible future applications of these complexes to study excited state delocalization will also be discussed.
- **Chapter 5** reports studies on a series of cyano-substituted terpyridine complexes. The properties of the ground state and long lived excited state are investigated by spectroscopic methods and possible future directions on these systems are discussed.

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Chapter 2: The Application of Nanosecond Time-Resolved Spectroscopies to the Study of Inorganic Photophysics and Photochemistry

2.1 Introduction

Nanosecond time-resolved spectroscopic methods are becoming more accessible to the average inorganic chemist. Unlike ultrafast spectroscopic techniques, nanosecond systems are generally reasonably affordable and do not require extensive training and expertise to operate. This chapter discusses time-resolved nanosecond spectroscopic techniques that are most commonly used to investigate photochemical and photophysical processes in inorganic systems. The necessary equipment and experimental requirements for each technique will be discussed and examples of how they are used in the literature will be given.

2.2 Time-Resolved Emission Spectroscopy

2.2.1 Experimental Setup

Time-resolved emission is the simplest of the nanosecond time-resolved experiments. The time-resolved emission experiment consists of three main parts; an excitation source, monochromator, and detector. The excitation source is generally a pulsed laser, such as a Q-switched Nd:YAG laser (Figure 2-1). This can either be used alone to excite the sample with a limited number of fundamental and harmonic frequencies (1064 nm, 532 nm, 355 nm, or 266 nm for Nd:YAG) or it can be coupled to an optical parametric oscillator (OPO) to generate a continuous range of frequencies across the UV, visible, and/or infrared. In some cases, flashlamps, which excite the sample with a temporally short polychromatic light pulses, are also used as an excitation source. This practice was far more common before pulsed lasers and OPO's were as widely available as they are today.

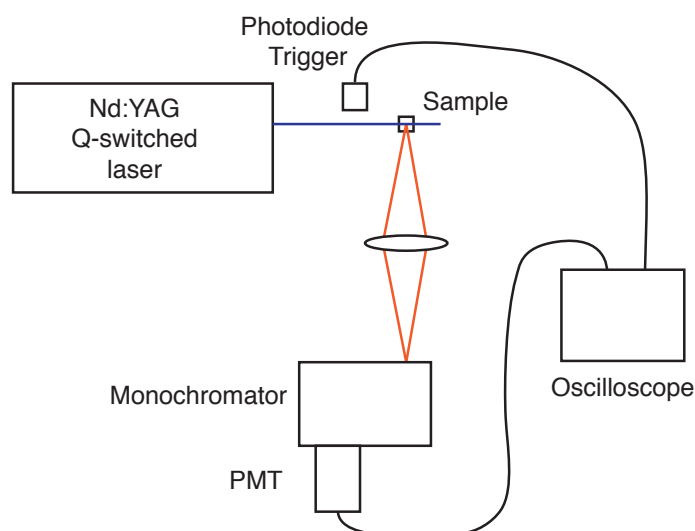


Figure 2-1: Example optical layout of a time-resolved emission spectrometer. A pulsed Nd:YAG laser excites the sample and a fraction of the emission is collected and focused into a monochromator. The emission decay is monitored in real time at a single wavelength. A photodiode trigger synchronized data collection with sample excitation.

The sample is excited with the pulsed laser source. While the peak power of a nanosecond laser pulse is much less than in picosecond or femtosecond laser pulses, two photon absorption of the sample is still a possibility in some circumstances. For this experiment, as well as the the others discussed in this chapter, two photon processes can be easily avoided by checking that the emission intensity responds linearly with changes in pump energy before each experiment. When the sample is excited, emission occurs non-coherently in all directions, so lenses are used to capture a fraction of the emitted light at 90° to the excitation beam to minimize interference and scatter from the excitation beam. The collected emission is focused into a monochromator and the emission decay at a single wavelength is monitored and recorded in real time. A trigger is used to synchronize the sample excitation and data collection

In the emission experiment, a signal is measured against a dark background. The ideal detector for emission will be able to reliably measure a small signal with a minimal amount of background noise. The detector that is most commonly used in the emission experiment is the photomultiplier tube (PMT). Alternatively, an array detector, such as a charge coupled device (CCD), and spectrograph can be used in order to probe the entire emission spectrum as a function of time rather than probing the emission decay at a single wavelength. While there may be an advantage to probing the entire emission spectrum rather than a single wavelength, the higher cost of the array detector leads to the PMT being far more commonly used.

The temporal resolution of any time-resolved experiment is determined by the temporal width of the excitation pulse, the bandwidth or response time of the detector and the bandwidth of any other electronics used to read and/or record the detector signal. These factors combined are the instrument response function (IRF) for a particular experiment. In practice, the ~ 10 ns laser excitation pulse is generally what limits the temporal resolution of the time resolved emission experiment.

When choosing a sample for a time-resolved emission experiment, a few factors should be considered. One clear requirement is the sample must be emissive and lifetime must be long enough (at least 3 times the IRF) to be accurately measured. Other experimental techniques are available to measure emission on picosecond and femtosecond timescales, but they will not be discussed here. The sample should also be optically dilute, an absorbance of 0.1 to 0.2 at the excitation wavelength, to avoid intramolecular interactions and possible self quenching. Because emission is measured against zero background, it is an incredibly sensitive technique. This can be a great advantage with quenched or weakly emitting systems, but also makes the

experiment vulnerable to emissive impurities, which can dominate the spectrum even when present in trace amounts that are undetectable by other characterization methods. This can be a particular problem with covalently attached donor-acceptor complexes, where any complex dissociation will result in a (relatively) highly emissive, unquenched fluorophore.^{1,2}

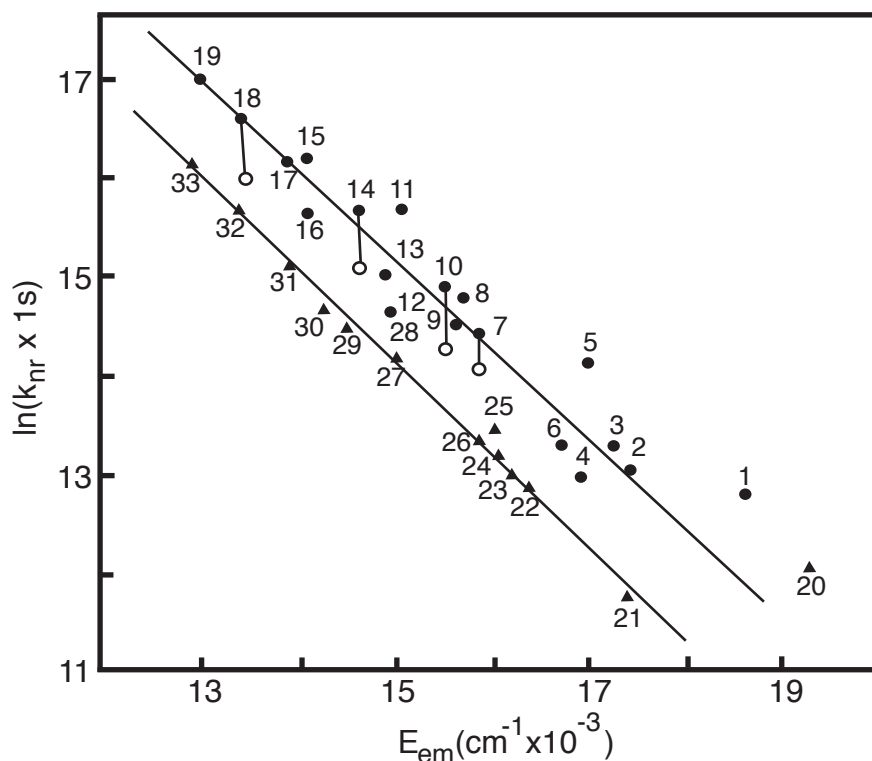


Figure 2-2: Plot of the observed value of $\ln(k_{nr})$ vs. E_{em} , the emission maximum in acetonitrile solution. Complexes have the general formula $[\text{Os}(\text{bpy}')_2(\text{L})]^{2+}$, where L is one bidentate or two monodentate ligands and bpy' is bpy ($\bullet$), $\text{bpy}-d_8$ ($\circ$), or phen ($\blacktriangle$). The drawn lines indicate the separate linear correlations for the bpy and phen series, both with slopes of $(1,100 \text{ cm}^{-1})$. Reproduced from reference 3.

2.2.2 Examples

Coupled with quantum yield measurements, the radiative and non-radiative decay contributions to the observed lifetime (τ_{obs}) can be calculated using Equations 2-1 and 2-2. Unlike using the quantum yield (Φ) or lifetime alone,

$$\Phi = \frac{k_r}{k_{\text{obs}}} \quad 2-1$$

$$k_{\text{obs}} = k_r + k_{\text{nr}} \quad 2-2$$

trends in k_r and k_{nr} across a series of molecules can give insight into changes in transition moment dipole or excited state geometry distortion.⁴ In 1986 Meyer and coworkers measured the emission lifetimes and quantum yields across a large series of osmium(II) polypyridyl complexes. Using this data, they were able to show, for the first time, that non-radiative decay from the long-lived excited state back to the ground state in transition metal complexes follows the energy gap law (Figure 2-2).³

Measuring the emission lifetime of a system as a function of temperature and fitting the data to a Boltzmann model will give the energy difference between two or more states in thermal equilibrium; fitting to an Arrhenius type model can give activation energy of a quenching reaction. Variable temperature emission lifetime measurements (Figure 2-3) were a critical piece of evidence that Harrigan and Crosby used to identify that the emissive $^3\text{MLCT}$ state in $[\text{Ru}(\text{bpy})_3]^{2+}$ is actually a set of three closely spaced triplet states.⁵ The same experimental technique has since been applied to additional ruthenium and other d^6 transition metal complexes in order to study the energy splitting within the emissive $^3\text{MLCT}$ state and what effect it has on the photophysical properties of the complexes.⁶⁻⁹

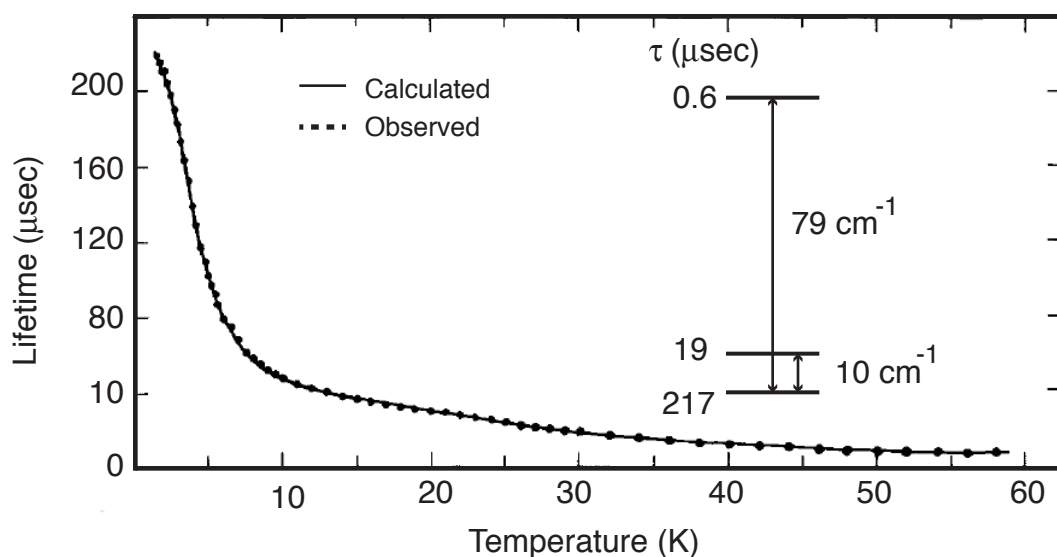


Figure 2-3: Plot of emission lifetime vs temperature for $[\text{Ru}(\text{bpy})_3](\text{SO}_4)_2$ doped in $[\text{Zn}(\text{bpy})_3](\text{SO}_4)_2$ (1:1000). The solid line the result of fitting the data to a modified Boltzmann type model. The energy level diagram to the right shows the energy separations and intrinsic emission lifetimes resulting from the fit. Reproduced from reference 5.

Time-resolved emission is a valuable tool for identifying and quantifying quenching of an emissive state by electron or energy transfer. Emission lifetimes alone are not sufficient to distinguish between an energy or electron transfer quenching processes but by comparison to an appropriate non-quenched model complex the rate of the quenching process can be determined. An example from our group compares a series of iron(III)-rhenium(I) donor-acceptor complexes of the general formula $[\text{Fe}(\text{pyacac})_3(\text{Re}(\text{bpy}')(\text{CO})_3)_3]^{3+}$ (pyacac = 3-(4-pyridyl)-acetylacetonate) with their analogous aluminum(III)-rhenium(I) control complexes.² In the aluminum complexes, the emissive state of the rhenium(I) is unquenched because there is no possibility of energy or electron transfer from the Re^{I} to the Al^{III} . Emission lifetime measurements on these control complexes

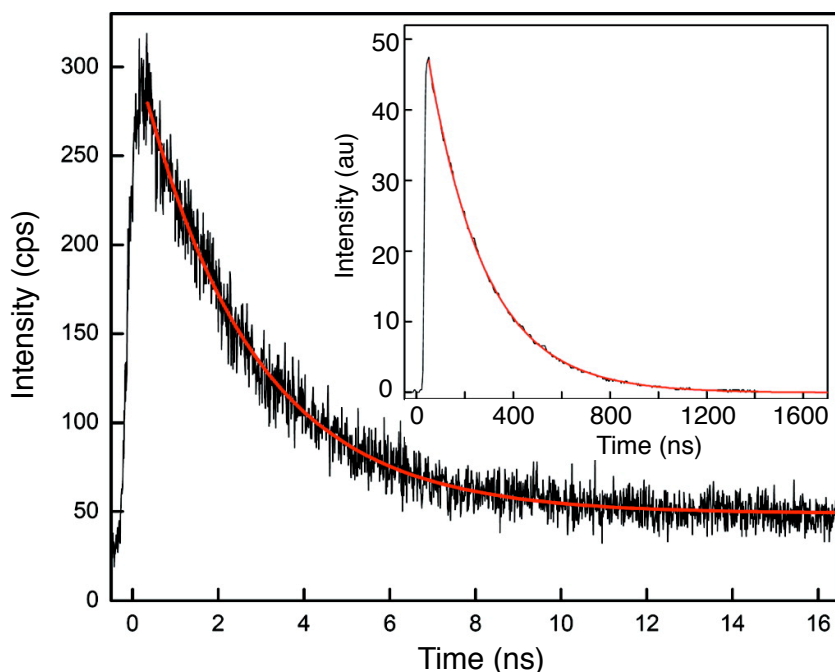


Figure 2-4: Time-resolved emission data for $[\text{Fe}(\text{pyacac})_3(\text{Re}(\text{deeb})(\text{CO})_3)_3](\text{OTf})_3$ (deeb = 4,4'-diethylester-2,2'-bipyridine). The emission was monitored at $\lambda_{\text{probe}} = 624 \text{ nm}$ following excitation at $\lambda_{\text{pump}} = 430 \text{ nm}$. The solid red line corresponds to a fit to a single-exponential decay model with $\tau_{\text{obs}} = 2.5 \pm 0.1 \text{ ns}$. The inset shows time-resolved emission data for the corresponding model complex, $[\text{Al}(\text{pyacac})_3(\text{Re}(\text{deeb})(\text{CO})_3)_3](\text{OTf})_3$ with $\tau_{\text{obs}} = 235 \pm 20 \text{ ns}$. Reproduced from reference 2.

give the intrinsic radiative and non-radiative decay rates of the emissive rhenium center in the absence of any quenching kinetics (Figure 2-4). In the iron complexes the emissive state of the Re^{I} is quenched by the Fe^{III} center. The observed emission decay rates of the iron(III)-rhenium(I) complexes were collected by time correlated single photon counting emission spectroscopy (TCSPC) due to their short lifetimes. The kinetics in the iron(III)-rhenium(I) complexes are a combination of the intrinsic decay kinetics of the rhenium center and the quenching kinetics introduced by replacing aluminum with iron, i.e. $k_{\text{obs}} =$

$k_r + k_{nr} + k_q$. By using the values of k_r and k_{nr} from the aluminum model complexes, the rate of quenching in the iron(III)-rhenium(I) complexes can be calculated.

The idea of using time-resolved emission to monitor quenching reactions has been used by the Gray group, among others, as a method to probe protein folding dynamics.¹⁰ This works by attaching a fluorophore and quencher onto a protein such that when the protein is unfolded, the two are far apart and the fluorophore is unquenched, but when the protein folds, the fluorophore and quencher are close to each other and the fluorophore is quenched. Measuring the the emission lifetime and intensity of the fluorophore over time then gives kinetic information about protein folding.

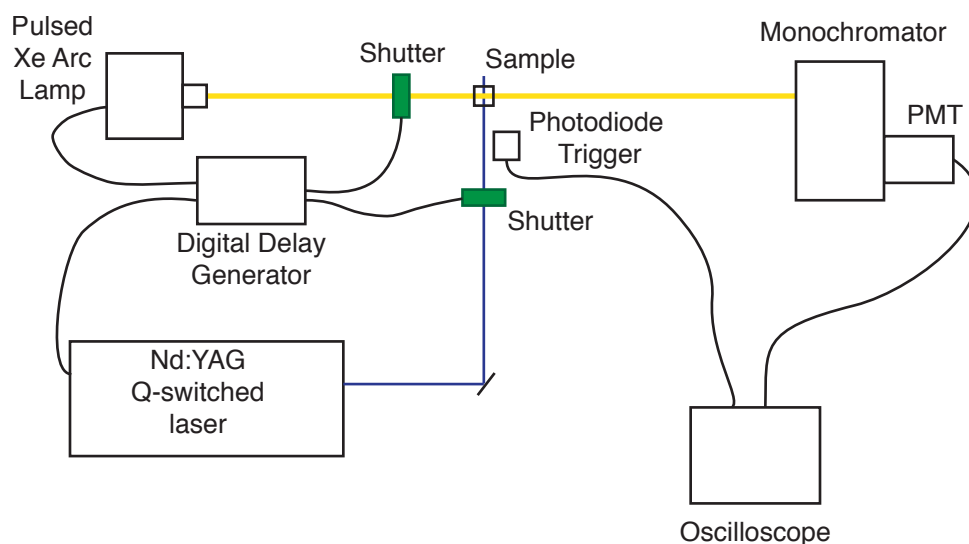


Figure 2-5: An example optical layout of a transient absorption spectrometer. A pulsed Nd:YAG laser excites the sample and a pulsed Xe arc lamp probes the sample. Shutters and a digital delay generator control the timing of the laser and white light pulses. The intensity of the probe beam is measured at a single wavelength before and after the sample is excited. A photodiode trigger synchronizes data collection with sample excitation.

2.3 Time-Resolved Absorption Spectroscopy

2.3.1 Experimental Setup

Time-resolved absorption spectroscopy, also referred to as transient absorption or flash photolysis, can be used with nearly any sample unlike time-resolved emission, which can only be used on emissive samples. Much of the transient absorption experimental setup is similar to that of the time-resolved emission. An example of a typical time-resolved absorption spectrometer can be seen in Figure 2-5. Just like in the time-resolved emission experiment, the sample is excited with a pulsed laser, either alone or coupled with an OPO. A white light source, often a xenon arc lamp, is used as the probe beam. Generally, but not always, the arc lamp is pulsed. This dramatically increases the lamp output, especially in the UV region of the spectrum, but it limits the frequency of data collection. The typical Q-switched Nd:YAG laser operates at 10 Hz whereas the typical arc lamp pulser operates at 1 Hz. Therefore, in this example, only 1 out of every 10 laser pulses can be used for data collection. Shutters are used to block the unused pulses from hitting the sample, and a digital delay generator is used to synchronize the laser Q-switch, arc lamp pulser, and shutters.

The white light probe beam passes through the sample at 90° to the pump beam to minimize scatter and is focused into a monochromator (or spectrograph for full spectra) and the change in intensity of the white light is monitored in real time at a single wavelength. A photodiode trigger is used to synchronize data collection and recording to the laser excitation pulse. Detection for time-resolved absorption spectroscopy is more challenging than in time-resolved emission. Instead of measuring a small signal against a dark background, transient absorption measures small differences in large signals. While this makes transient absorption far less sensitive than time-resolved emission, it also makes

the experiment much less susceptible to trace impurities. As with time-resolved emission, the spectra can be collected in single wavelength traces by using a monochromator and PMT or other similar detector or the entire spectrum can be collected as a function of time using a spectrograph and array detector such as a CCD. With single wavelength decay traces from a PMT detector, a full spectrum can be constructed by plotting the initial amplitude of each decay trace, as determined by a single exponential fit, versus wavelength. This only works when all the experimental conditions are kept constant (*vide infra*).

2.3.2 Analysis and Interpretation of Time-Resolved Absorption Spectra

In transient absorption spectroscopy, the intensity of the transmitted probe beam is measured without the pump beam present to give baseline (ground state) transmittance of the sample, I_0 . Then the intensity of the probe beam is measured as a function of time after sample excitation to give the transient transmittance of the sample, I_t . In wavelength regions where the sample is emissive, an emission decay trace, I_{em} , is collected by blocking the probe beam and exciting the sample with the pump beam, as in the time-resolved emission experiment. The change in absorbance for the sample is calculated from Equation 2-3.

$$\Delta A = -\log \left[\frac{(I_t - I_{em})}{I_0} \right] \quad 2-3$$

The magnitude and sign of the ΔA signal depends on Equation 2-4, which is

$$\Delta A = \Delta \epsilon \cdot b \cdot [c]^{gs} \cdot \eta_{ex} \quad 2-4$$

derived from Beer's Law, where ΔA is the change in absorbance of the sample before and after excitation, $\Delta \epsilon$ is the difference between the ground state and excited state extinction coefficients, b is the pathlength, $[c]^{gs}$ is the ground state

concentration, and η_{ex} is the fraction of ground state molecules that are excited into the excited state. The ground state sample concentration and the cell pathlength are both constant over the course of an experiment. In order to get any chemical information from a transient absorption spectrum the η_{ex} must also stay constant over the course of the experiment. Many factors go into η_{ex} . Some of the most important are the extinction coefficient of the sample at the excitation wavelength, the power of the excitation beam, and the overlap between the pump and probe beams. The extinction coefficient of the sample at the excitation wavelength represents the probability that a molecule will absorb a photon and become excited. This is a fundamental property of the molecule, so while it plays a role in determining η_{ex} , it cannot play a role in the η_{ex} varying over the course of an experiment. The power of the excitation beam and the overlap between the pump and probe beams are the major contributors to variation in η_{ex} so it critical to keep these two constant during the course of an experiment.

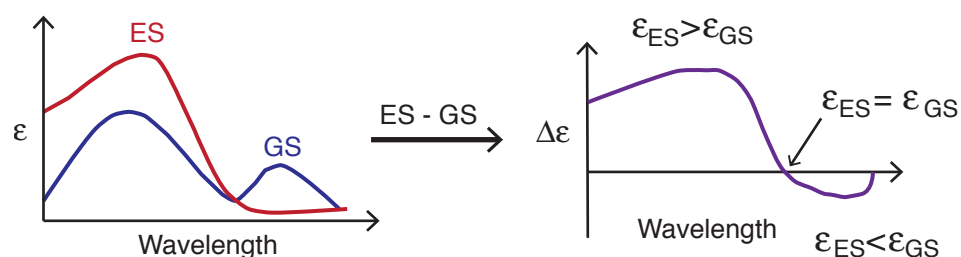


Figure 2-6: Cartoon showing a theoretical ground state absorption (GS) and excited state absorption (ES) (left graph). The transient absorption experiment measures the difference in the extinction coefficients of these two states (right graph), leading to the possibility of both positive and negative features in the transient spectrum. Reproduced from reference 11.

All other things being constant, changes in the magnitude and sign of ΔA across a spectrum reflect changes in $\Delta \epsilon$. Figure 2-6 shows an illustrative example of how changes in relative extinction coefficients of the ground and excited states of a sample effect the observed transient absorption. Areas of the spectrum where the extinction coefficient of the excited state is greater than that of the ground state the transient absorption spectrum will have a net absorption. Areas of the spectrum where the ground state extinction coefficient is larger than the excited state extinction coefficient transient absorption spectrum will have a net negative feature, or bleach. Areas of the spectrum where the extinction coefficients of the ground state and excited state are exactly the same the transient absorption spectrum will be zero (an isosbestic point).

If the excited state that is being probed by transient absorption is charge transfer in nature, then spectroelectrochemistry is a useful tool for the qualitative prediction or interpretation of the charge transfer differential absorption spectrum. For a metal complex $[M(L)_6]^{n+}$, a charge transfer transition can be written as $[M^{(n+1)+}(L)_5(L^-)]^{n+}$ for a metal-to-ligand charge transfer transition (MLCT) or $[M^{(n-1)+}(L)_5(L^+)]^{n+}$ for a ligand-to-metal charge transfer transition (LMCT). In both of these cases, the excited state absorption qualitatively will be a superposition of the absorption spectrum of the oxidized (or reduced) metal and the reduced (or oxidized) ligand. This technique can be used to identify features in the transient absorption spectrum¹² or as a method to determine the nature of the long lived excited state.¹³ Further discussion and examples of this can be found in Chapter 3.

2.3.3 Examples

Time-resolved absorption spectroscopy is a more versatile experiment than time-resolved emission. Time-resolved absorption can be used to detect

"dark states", non emissive states, as well as products of photochemical reactions. Steiner and coworkers use transient absorption as well as time-resolved infrared absorption spectroscopy to monitor isomerization and ligand loss in Fisher carbene complexes with the formula $(\text{CO})_5\text{W}=\text{C}(\text{OMe})\text{Ph}$.¹⁴ By monitoring the transient absorption spectra of the carbene complex in the presence of CO or other coordinating ligand the authors were able to determine that CO loss and isomerization are two competing processes out of the excited carbene rather than occurring stepwise as was previously thought (Figure 2-7).

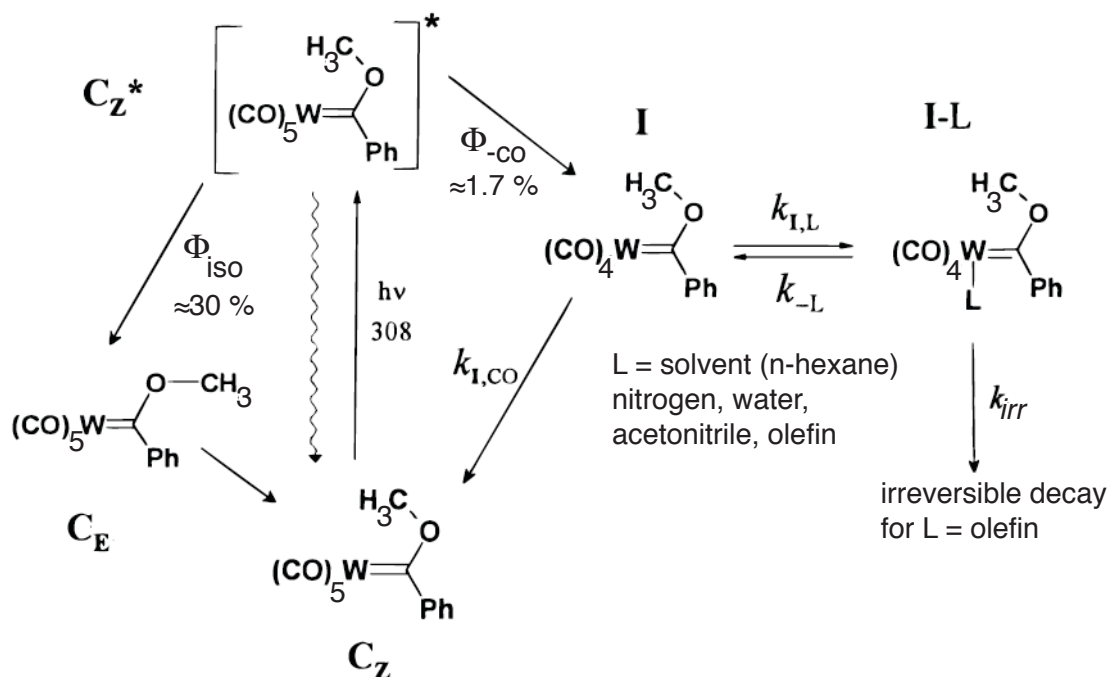
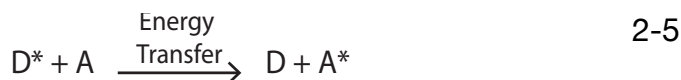


Figure 2-7: Reaction pathways available for the photoexcited Fisher carbene complex $(\text{CO})_5\text{W}=\text{C}(\text{OMe})\text{Ph}$ as determined by time resolved absorption spectroscopy. The excited state of the carbene can decay non-radiatively back to the ground state, lose a CO ligand to form the tetracarbonyl complex, or isomerize from syn (C_Z) to anti (C_E). Reproduced from reference 14.

The experiments showed that CO loss occurred from a higher energy ligand field state. That ligand field state relaxes rapidly to the lowest energy excited state which is charge transfer in nature. This rapid deactivation of the ligand field states explains the low yield for CO loss. The lowest energy charge transfer state is the state which undergoes the isomerization reaction.

Time-resolved absorption spectroscopy can be especially useful in identifying electron transfer reactions and detecting charge separated intermediates. Bernhardt, Hauser, and coworkers have used nanosecond and femtosecond transient absorption spectroscopy to study the metal-to-metal charge transfer (MMCT) excited state of a cyano-bridged, mixed-valence dimer of the formula $[\text{LCo}^{\text{III}}\text{NCFel}^{\text{II}}(\text{CN})_5]^-$, where L is a pentadentate macrocyclic pentaamine ligand.¹⁵ In the ground state, both the cobalt(III) and iron(II) centers are in the low spin state. Photoexcitation generates the low spin MMCT excited state, $\text{Co}^{\text{II}}(\text{l.s.})\text{-Fe}^{\text{III}}(\text{l.s.})$, which is too short lived to be detected on the nanosecond timescale. The MMCT state can undergo intersystem crossing to form $\text{Co}^{\text{II}}(\text{h.s.})\text{-Fe}^{\text{III}}(\text{l.s.})$, which relaxes back to the low spin ground state on a nanosecond timescale.

In an energy transfer reaction (Equation 2-5) the donor returns to the ground state and the acceptor is in an excited state. In an electron transfer reaction



(Equation 2-6) the donor is oxidized and the acceptor is reduced. Time-resolved absorption spectroscopy of an energy transfer reaction will show the complete decay of the donor excited state absorption features and the (possible) growth of

acceptor excited state absorption features. In the case of an electron transfer, reaction time-resolved absorption spectroscopy will show only partial recovery of the donor excited state absorption features, as shown in Figure 2-8. Previous work from our group has used nanosecond transient absorption spectroscopy to differentiate between an electron and energy transfer quenching mechanism in a bimolecular quenching reaction between ruthenium(II) polypyridyl complexes and iron(III) dimers.¹⁶ Figure 2-8 shows the change in absorbance versus time at

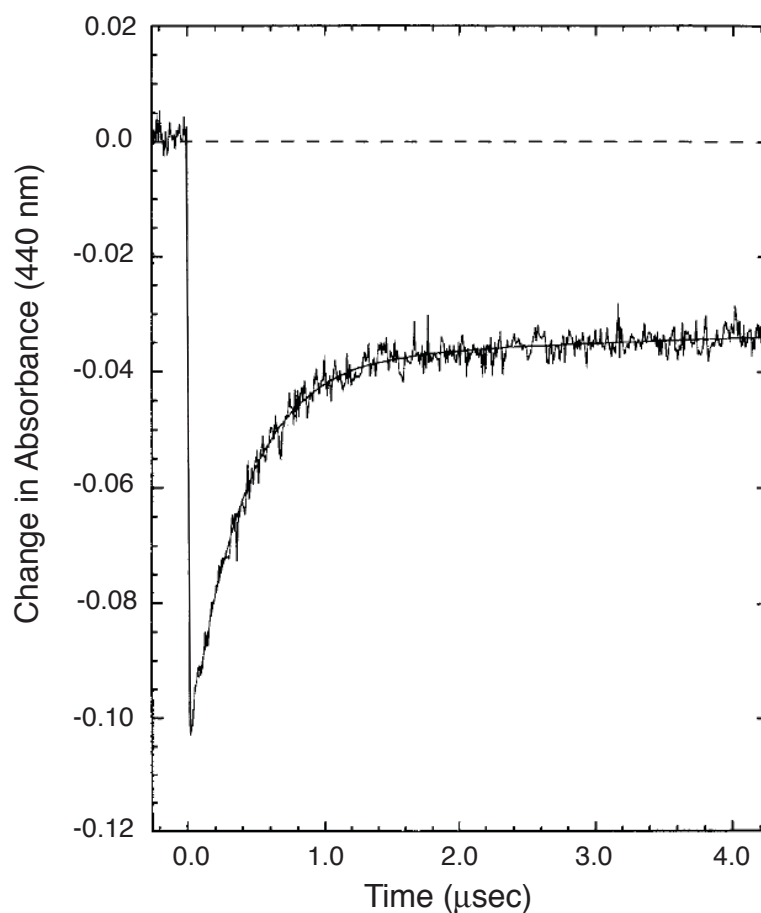


Figure 2-8: Plot of the excited-state differential absorbance of a CH_3CN solution containing $[\text{Ru}(\text{dmb})_3]^{2+}$ and $[\text{Fe}_2(\text{OH})(\text{O}_2\text{CCH}_3)_2(\text{Tp})_2]^+$ at 440 nm following 10 ns excitation at 450 nm. The solid line indicates a fit to a biexponential kinetic model. Reproduced from reference 16.

440 nm which is probing the loss of the MLCT absorption in the excited state. This trace shows the partial recovery of the MLCT bleach which indicates the quenching is an electron transfer reaction.

2.4 Time-Resolved Vibrational Spectroscopy

Two major techniques are used for nanosecond time-resolved vibrational spectroscopy: time-resolved resonance Raman spectroscopy (TR³) and time-resolved infrared spectroscopy (TRIR). Both techniques have their advantages and disadvantages. TR³ uses visible light to both excite and resonantly scatter off of the excited state. Consequently, only those vibrational modes which are vibronically coupled to the excited electronic transition will be enhanced. This vastly simplifies the spectrum and makes interpretation much easier, but it only shows a small subset of the entire excited state vibrational spectrum. Because visible light is used as the probe, emission from the sample can interfere with the data collection. This can make collecting TR³ data on highly emissive molecules a challenge.

Time-resolved infrared spectroscopy uses visible light to excite the sample and probes the excited state with a broadband infrared source. In this way, the entire infrared allowed excited vibrational spectrum can be measured. This could make interpretation of the spectra difficult, especially with heteroleptic complexes. However, it does allow for probing vibrations that are not directly coupled to the excited state, like the CO stretch in [Re(bpy)(L)(CO)₃]⁺ complexes. Solvents are not completely transparent in the infrared which poses another challenge in the collection and interpretation of TRIR spectra. Very thin pathlength cells (0.5 or 0.2 mm are most common) are used to minimize solvent absorptions. As a consequence of the thinner cell, much higher concentrations of sample ($\sim 10^{-2}$ - 10^{-3} M for TRIR vs $\sim 10^{-5}$ M for TR³) are necessary, which can

cause difficulty for samples with low solubility. There are several recent reviews of time-resolved vibrational spectroscopy that discuss applications of both TR³ and TRIR¹⁷⁻²¹.

2.4.1 Experimental Setup

The time-resolved resonance Raman experiment uses visible excitation and probe beams. There are two different ways the experiment can be done: the one-color, transient resonance Raman (TR²), experiment or the two-color, time-resolved resonance Raman (TR³), experiment. In the TR² experiment, a single laser pulse is used to both excite the molecule and resonantly scatter off of that excited state. In order for this technique to succeed, both the ground state and the excited state have to absorb at the same wavelength. For ruthenium(II) polypyridyl complexes, a 355 nm pulse is generally used because both ground state and bipyridine radical anion absorb strongly at that wavelength. Also, since a single laser pulse is acting as both the pump and probe, there is no way to vary the time delay between the pump and probe. Consequently, the TR² experiment only shows a snapshot of the excited state and doesn't give any information about excited state dynamics.

In the TR³ experiment, two different laser pulses, from two different lasers, are used for the pump and probe beams. An example of a TR³ spectrometer can be seen in Figure 2-9. The major advantage of the TR³ experiment is the ability to independently vary the pump and probe wavelengths to best suit the sample being studied. Also, independent pump and probe pulses mean the time delay between pump and probe pulses can be varied to get a true time resolved spectrum and look at excited state dynamics. The clear disadvantage to TR³ is that it requires two lasers, which adds considerable cost and complexity to the

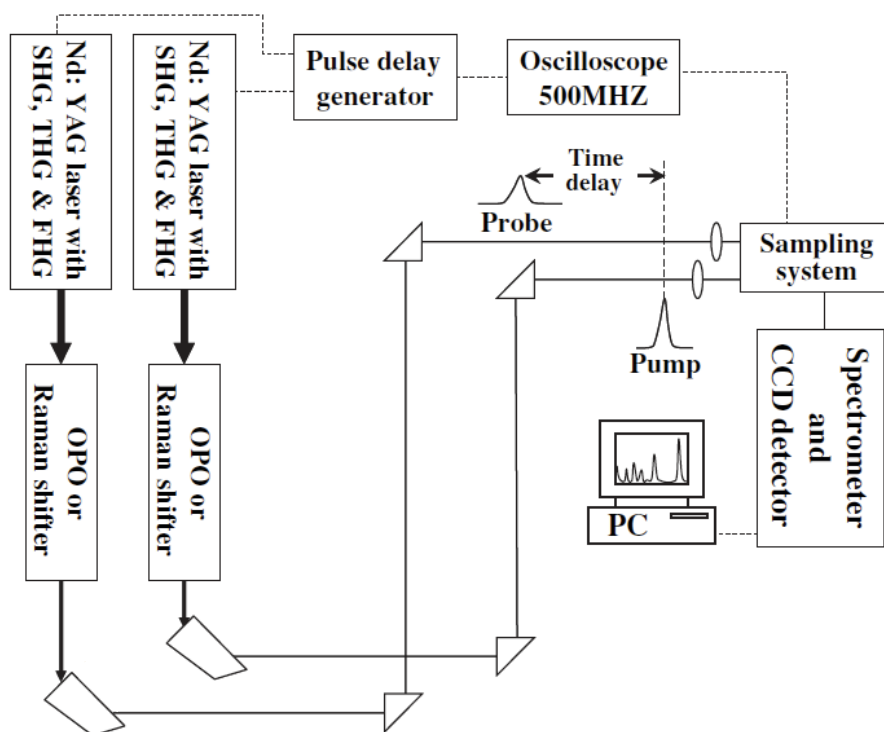


Figure 2-9: Example optical layout for two-color time-resolved resonance Raman spectrometer. There are two pulsed lasers to independently pump and probe the sample. A pulse delay generator controls the time between the pump and probe pulses. Raman scatter is collected at 90°, dispersed with a spectrograph and the full spectrum is collected with a CCD array. Reproduced from reference 19.

experiment. For both the TR² and TR³ methods, the scattered light is collected, generally at 90° to minimize scatter, and focused into a monochromator. Using double or triple monochromator will exclude more Rayleigh scatter and other stray light. It will also increase the experimental resolution and allow for the detection of lower frequency vibrations. Depending on the probe wavelength used, notch filters can also be used to exclude Rayleigh scatter. The scattered light is then dispersed onto an array detector such as a CCD or photodiode to record the full resonance Raman spectrum.

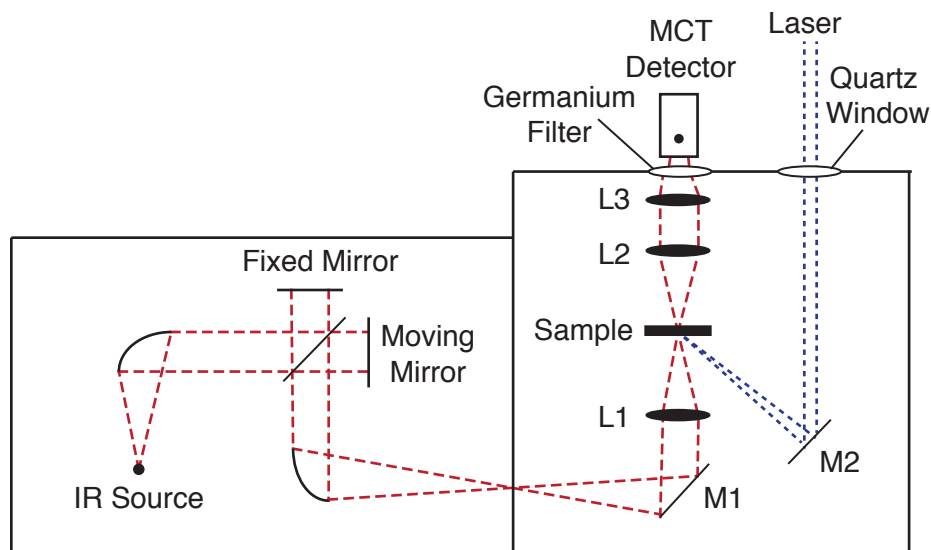


Figure 2-10: Example optical layout of a time-resolved step-scan FTIR spectrometer. Reproduced from reference 22.

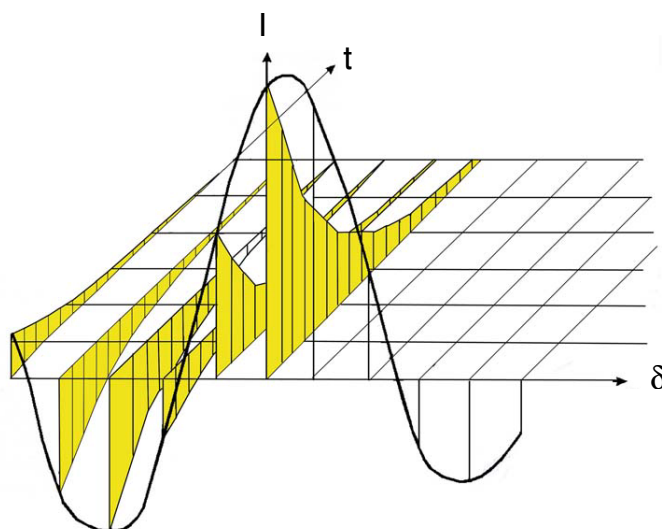


Figure 2-11: Data collection process in SSIR experiment. Decay traces (I vs t) are collected at each fixed mirror position δ . After data collection, interferograms (I vs δ) are generated for every time t , and these interferograms are used for further data analysis. Reprinted from reference 23.

Nanosecond time resolved infrared spectroscopy generally uses a step-scan IR (SSIR) spectrometer, which can be seen in Figure 2-10. The step-scan IR spectrometer is a modification of the standard FTIR instrument²⁴. In the standard rapid scan FTIR instrument, such as the reactIR, the moving mirror in the interferometer is constantly moving. The time resolution is determined by how fast the mirror can move back and forth through all the positions (ms- μ s resolution). In the step-scan IR instrument, the moving mirror steps to a fixed position and a decay trace is collected while the mirror is held in that position. The mirror then steps to the next position and another decay trace is collected. This is shown graphically in Figure 2-11. Using this method, the time resolution of the experiment is limited by the temporal width of the excitation pulse and the bandwidth of the detector and any other electronics used in data collection ($\sim$ ns resolution).

The excitation source is generally a pulsed laser source, such as a Q-switched Nd:YAG, and the probe beam is generated by a broadband source (Hg lamp for the far IR, globar for the mid IR, or tungsten lamp for the near IR) and Michelson interferometer. The angle between the pump and probe beams is kept as small as practically possible (approaching collinear) to maximize the volume of overlap between the pump and probe beams in the sample. The probe beam is then detected by the appropriate detector such as MCT photovoltaic for far to mid infrared or an InGaAs photodiode for the near infrared. The detector is separated from the sample chamber by a germanium window to block visible light such as laser scatter from reaching the detector and saturating or possibly damaging it. Detectors used for this experiment will generally have both a DC and AC coupled output. The DC coupled output is used to measure the ground state spectrum of the sample. The AC coupled output contains only

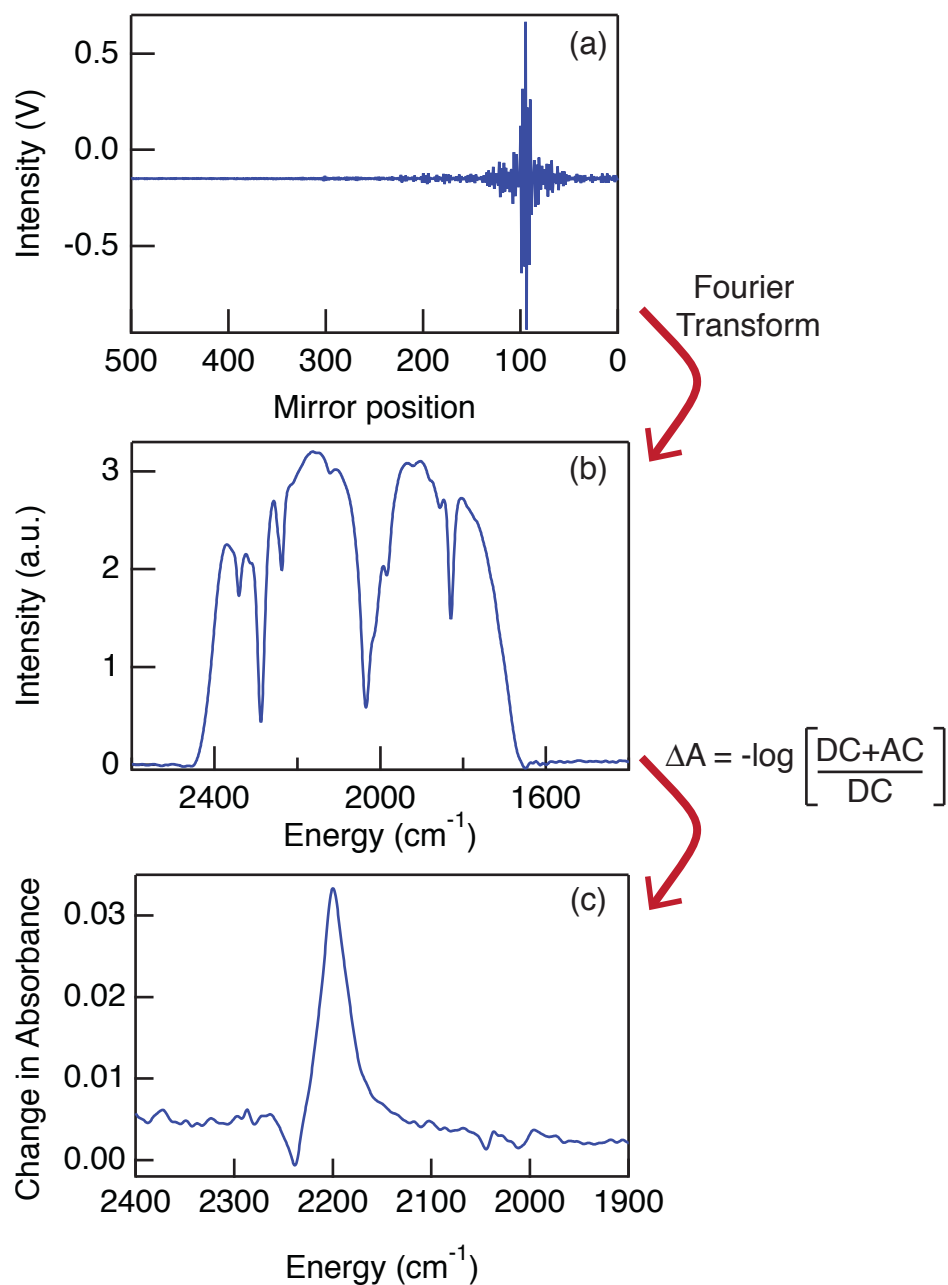


Figure 2-12: Example of data processing in the SSIR experiment. The interferogram (a) is Fourier transformed to generate the single channel spectrum (b). The ΔA spectrum (c) is calculated from the AC and DC coupled single channel spectra. A single two dimensional slice of the three dimensional spectra has been shown for simplicity.

the portion of the signal which changes over time, so it is used to measure the excited state spectrum of the sample. Because the excited state signal has a much smaller amplitude than the ground state, the AC signal is generally amplified before it is recorded.

As mentioned above, the moving mirror is stepped to discrete positions, and decay traces (I vs t) are collected while the moving mirror is held those fixed positions. The number of positions will depend on the spectral range and the resolution of the experiment. After decay traces are collected at each mirror position δ interferograms, plots of I vs δ , are generated for each time t and the final ΔA spectra are then calculated from these interferograms (Figure 2-12). Each 3D interferogram (I vs δ vs t) is converted to a 3D single channel spectrum (I vs cm^{-1} vs t) via a Fourier transform. It is important to note that in order to avoid introducing artifacts when generating the single channel spectrum, the spectrum must return to zero at both ends. Often, filters are used to isolate the spectral region of interest and minimize the necessary data collection time. The 3D ΔA spectrum is calculated from the ground state (DC coupled) spectrum and the excited state (AC coupled) by Equation 2-7²⁵, after accounting for any amplification of the AC signal.

$$\Delta A = -\log \left[\frac{\text{AC} + \text{DC}}{\text{DC}} \right] \quad 2-7$$

Depending on the number of spectra averaged per mirror position and the resolution and spectral window of the experiment, collecting a single full spectrum can take thousands or tens of thousands of laser shots over an hour or more of collection time. This means that the photochemical or photophysical process being monitored must be repeatable and reproducible over that period of time and that number of laser shots. Monitoring photochemical reactions by

step-scan IR is thus challenging, but flowing the solution to ensure that each laser shot is exciting fresh sample is one way to avoid problems with photostability and reproducibility. A more detailed description of the data acquisition process for the Bruker IFS 66/S can be found in Appendix C.

2.4.2 Examples

2.4.2.1 Time-Resolved Resonance Raman

Time-resolved resonance Raman spectroscopy was one of the many pieces of evidence that showed that the long lived excited state of $[\text{Ru}(\text{bpy})_3]^{2+}$ was localized on a single bpy ligand on the nanosecond timescale.²⁶ Dallinger, Woodruff, and coworkers compared the TR² spectra of $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$ collected in a one-color experiment, exciting at 355 nm, to the ground state resonance Raman spectra of the free bipyridine radical anion and $[\text{Ru}^{\text{III}}(\text{bpy})_3]^{3+}$. They found that the excited state spectrum of $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$ was essentially a superposition of the bpy^- and the $[\text{Ru}^{\text{III}}(\text{bpy})_3]^{3+}$ resonance Raman spectra, which supports describing the excited state as $\{[\text{Ru}^{\text{III}}(\text{bpy})_2(\text{bpy}^-)]^{2+}\}^*$. They also compared the TR³ spectra of $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$ and $[\text{Ru}^{\text{II}}(\text{bpy})_2(\text{en})]^{2+}$ (en=ethylenediamine). The shift between the ground state and excited state bipyridine stretches was the same in both complexes, which is also evidence for a localized excited state. If the excited state was delocalized, the shift between the ground state and the excited state for $[\text{Ru}^{\text{II}}(\text{bpy})_2(\text{en})]^{2+}$ would be larger than for $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$ because the excited electron would be delocalized over two rather than three bipyridine ligands.

Kim, Yoon, and coworkers used TR² to study copper(II) porphyrins in aqueous and non-aqueous environments.²⁷ In the excited state, copper(II) porphyrins can form an exciplex with solvent molecules, i.e. the solvent

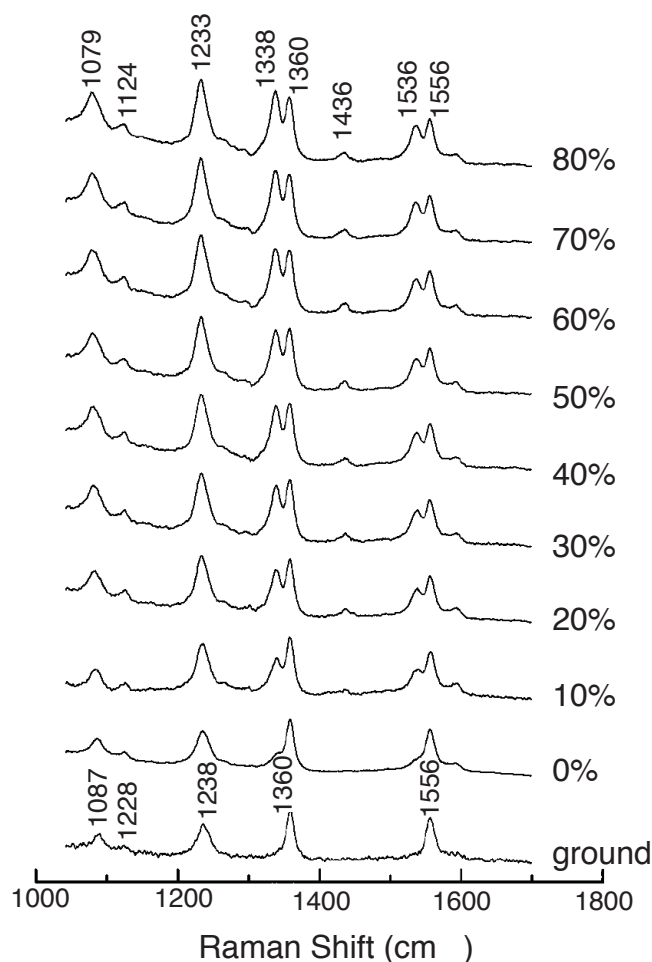


Figure 2-13: Nanosecond transient resonance Raman spectra of Cu^{II} TSPP in dioxane/ water solvent mixture. Percentages show the increasing fraction of dioxane in the solvent mixture. Reproduced from reference 27

coordinates to the copper center to form a five-coordinate complex. This exciplex formation leads to a rapid deactivation of the excited state. Figure 2-13 shows the transient resonance Raman spectrum of Cu^{II} TSPP (TSPP = tetrakis(*p*-sulfonatophenyl)porphyrin) collected in mixtures of water and dioxane. In these spectra two sets of peaks are seen: one for the four-coordinate species and one for the five-coordinate species. Monitoring the ratio between the

intensities of the four- and five-coordinate species as a function of solvent mixture allows the authors to infer relative concentrations of five-coordinate species, and therefore relative binding energies of the different solvents to the copper center.

2.4.2.2 Step-Scan IR

One major advantage of TRIR over TR³ is that all (infrared allowed) excited state vibrations will appear in the spectrum rather than only the subset of vibrations which are Raman allowed and are resonantly enhanced by coupling to the excited electronic transition. Schoonover, Meyer, and coworkers have used this idea to build on the work of Dallinger, Woodruff, and coworkers mentioned above; using TRIR to assign the full mid-infrared excited state vibrational spectra of [Ru(bpy)₃](PF₆)₂ and [Ru(phen)₃](PF₆)₂.^{22,28} They compared the nanosecond step-scan IR spectra of [Ru^{II}(L)₃]²⁺ to electrochemically generated [Ru^{III}(L)₃]³⁺ and [Ru^{II}(L)₂(L⁻)]⁺ (L = 2,2'-bipyridine or 1,10'-phenanthroline). They also used heteroleptic complexes [Re(bpy)(CO)₃(4-Etpy)]⁺ and [Os(phen)(DAS)₂]²⁺ (4-Etpy = 4-ethyl-pyridine and DAS = 1,2-bis(diphenylarsino)ethane) as comparisons as well because the excited state is forced to be localized to a single ligand in these examples. Like the resonance Raman experiment discussed above, these experiments showed that the long lived excited state in [Ru(bpy)₃]²⁺ and [Ru(phen)₃]²⁺ are both localized on a single ligand. In the case of [Ru(bpy)₃]²⁺, it was also possible to determine which vibrational mode(s) were contributing to each observed peak by comparison to the previous normal coordinate analysis of the ground state IR and resonance Raman spectra of [Ru(bpy)₃]²⁺.²⁹

Dattelbaum, Schoonover, and coworkers used time-resolved step-scan IR to study a series of rhenium(I) carbonyl complexes such as the one pictured in

Figure 2-11 that have low energy charge separated (CS) and intraligand (IL) states in competition with the $^3\text{MLCT}$ state.³⁰ This is one example of a study which would not be possible with TR³ because the CO vibrations are not directly coupled to a charge transfer excitation and are therefore not enhanced in

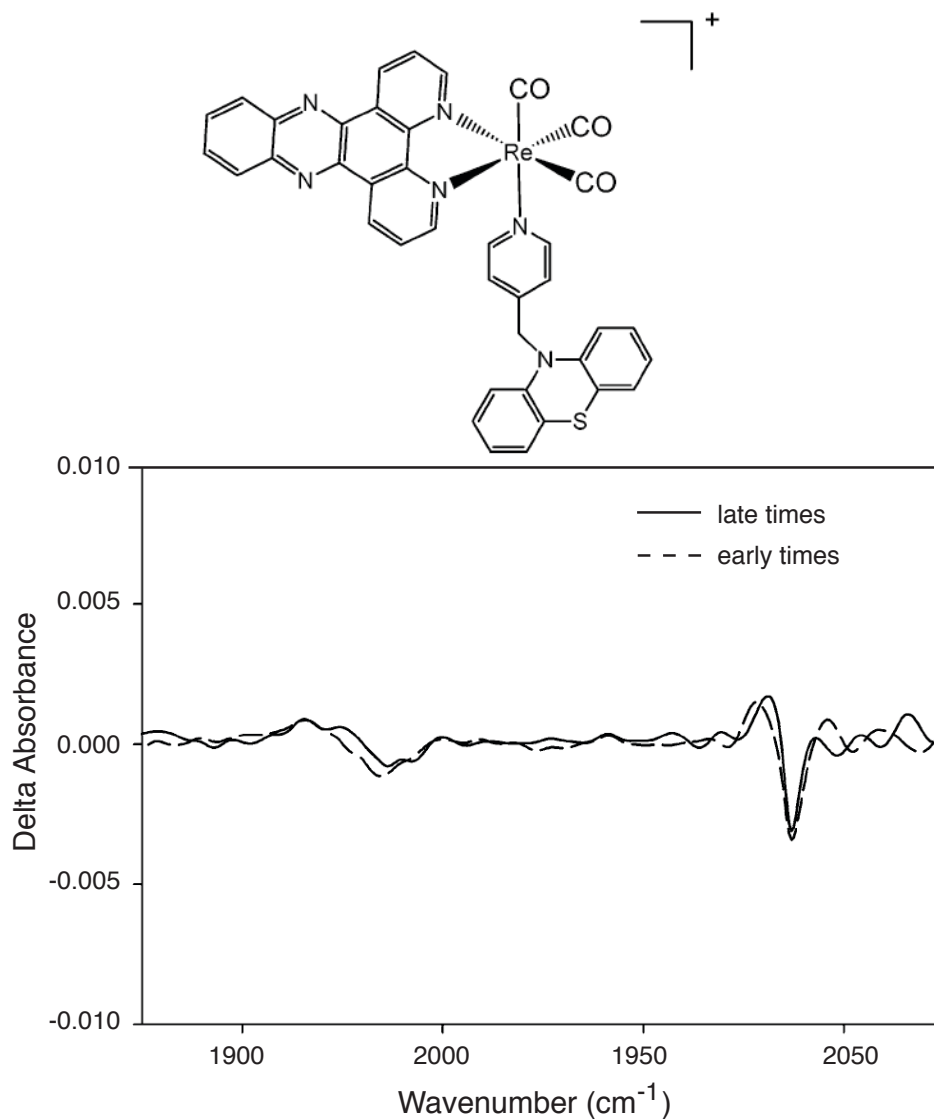


Figure 2-14: TRIR spectra of $fac\text{-[Re(dppz)(CO)}_3\text{(py-PTZ)]}^{+}$ (pictured above) separated into early and late time average spectra. At early times (<300 ns, dashed line), the charge separated state dominates. At later times (>300 ns, solid line), the IL state dominates and the ground-to-excited-state shifts in $\nu(\text{CO})$ decrease. Reproduced from reference 30

resonance Raman or TR³ spectroscopy. While the CO vibrations are not directly coupled to the excited state, they are very sensitive to the electron density at the rhenium center which makes them a very useful indirect reporter of excited state dynamics.

Figure 2-14 shows the early and late time TRIR spectra of *fac*-[Re^I(CO)₃(dppz)(py-PTZ)]⁺ (dppz = dipyrido-[3,2-a:2',3'-c]phenazine and py-PTZ = 10-(4-picoly)phenothiazine). The early time spectra shows the CO vibrations in the CS state, where the excited electron is transferred to the phenothiazine. Because of the methylene linkage, there is little overlap between the phenothiazine and the rhenium center and the rhenium is best described as Re^{II}. The later time spectrum shows the CO vibrations in the IL state of the phenazine ligand. Because the phenazine ligand is directly bound to the rhenium center, there is overlap and mixing between the phenazine and rhenium orbitals and to a small extent the IL state is also delocalized onto the rhenium center, making it not fully oxidized to Re^{II}. This is reflected in the smaller change in CO stretching frequency vs ground state than is seen in the CS state.

2.5 Time-Resolved X-ray Spectroscopy

2.5.1 Experimental Setup

Unlike the other techniques discussed in this chapter, there is not a commercially available bench-top instrument for time-resolved X-ray spectroscopy. Like the other techniques discussed, the excitation source for the time resolved X-ray experiment is usually a pulsed laser source. The difficulty in the time resolved X-ray experiment lies in the probe source. In order to achieve short data averaging times and reasonable time resolution, the high brightness and temporally short pulses of a synchrotron X-ray source are necessary. An

example of a time resolved X-ray spectrometer can be seen in Figure 2-15.

There are two different methods of collecting time-resolved X-ray spectroscopy. The diffraction of X-rays through a crystal is described by Bragg's Law (Equation 2-8), where n is an integer, λ is the wavelength, d is the space

$$n\lambda = 2d \sin\theta \quad 2-8$$

between layers in the crystal lattice, and θ is the angle of the incoming X-rays. In the monochromatic method, λ is constant and θ is varied by rotating the crystal. In the polychromatic (Laue) method the crystal is kept in a fixed position and probed with a polychromatic X-ray beam.

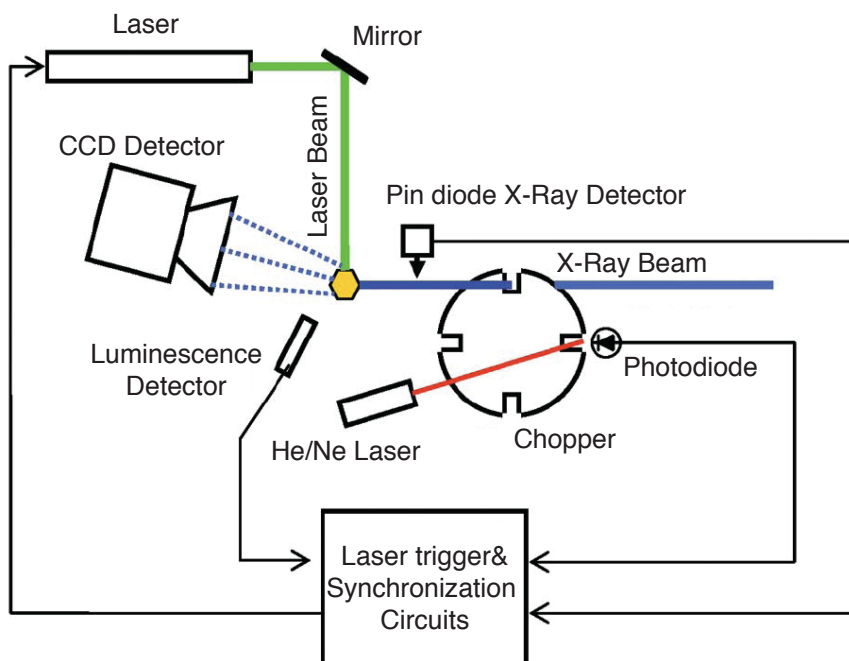


Figure 2-15: Schematic diagram of a time-resolved X-ray diffraction experiment at the Advanced Photon Source, Argonne National Lab. Reproduced from reference 31.

The monochromatic method is the same as method that is used in laboratory single crystal diffractometer and is most often used in small molecule spectroscopy. A monochromatic X-ray beam probes the sample crystal and the crystal is rotated to collect a sufficient number of reflections. In order to do this experiment in a time resolved manner, a pump probe technique, similar to other experiments discussed previously, is used. Synchrotron X-ray sources have very high repetition rates (100's of kHz). In order to most efficiently use the synchrotron source, the excitation source is a high repetition rate laser like the Nd vanadate laser, which can operate at a 20 kHz repetition rate with sufficient power to generate a significant excited state population in the crystal. Even with the Nd vanadate laser, there is still a large mismatch between the repetition rate of the laser excitation and the synchrotron source. Consequently shutters or choppers are used to select the X-ray pulses and synchronize them with the laser excitation. The data collection process is similar to that in SSIR. At each position the crystal is excited with the laser pump, probed with the X-ray pulse, and the diffracted X-rays are collected by CCD detector. Then, the crystal is probed without laser excitation as a background. The crystal then rotates to the next position and the process repeats. Much like SSIR, this experiment requires that the structural change being monitored is reversible and reproducible over many pump-probe cycles. Crystal integrity creates an additional difficulty in time resolve X-ray spectroscopy. Repeated structural changes can put strain on the crystal lattice and cause the long range order of the crystal to break down.

The Laue method is an alternate method that is most often used for macromolecular structures such as proteins or other biological molecules. This technique uses a polychromatic X-ray beam and keeps the crystal stationary during data collection. This results in an overall shorter collection time, which minimizes damage to fragile biological crystals. The Laue method is also a good

option for irreversible structural changes or photochemical reactions because a complete set of reflections can be collected from a single shot of the pump and probe beams. There are several recent reviews that cover both small molecule and macromolecular time resolved X-ray spectroscopy.³¹⁻³⁴

2.5.2 Examples

Moffat and coworkers used the Laue method to monitor the structural changes that accompany substrate binding in myoglobin.³⁵ When crystals of a carbon monoxide complex of myoglobin, where the CO is bound axially to the iron heme center, are photoexcited the CO dissociates from the iron center. Over time, the CO ligand re-coordinates to the iron heme center and the structural changes that occur as the CO re-coordinates are monitored by X-ray probe. The structure was probed at six different time delays (4 ns, 1 μ s, 7.5 μ s, 50.5 μ s, 350 μ s, and 1.9 ms). The most prominent features seen in the electron density difference plots was the loss of CO at the iron center, which recombines in $\sim$ 100 μ s, and the iron moving out of the heme plane and towards the axially coordinated histidine ligand when the CO ligand dissociates. The iron returns to the plane of the heme ring as the CO ligand re-coordinates.

Coppens and coworkers used time resolved X-ray spectroscopy to observe structural changes that occur upon photexcitation in a copper(I) phenanthroline complex, $[\text{Cu}(\text{dmp})(\text{dppe})]^+$ (dmp = 2,9-dimethyl-1,10-phenanthroline and dppe = 1,2-bis(diphenylphosphino)-ethane).³⁶ In the ground state, four coordinate copper(I) complexes favor tetrahedral geometries. In an MLCT excited state the copper(I) is (at least partially) oxidized to copper(II), which tend to favor square planar geometries. This means that once a copper(I) complex is excited into an MLCT excited state it will distort and flatten to a more square planar geometry. Figure 2-16 shows an overlay of the ground state and distorted excited state

structures in $[\text{Cu}(\text{dmp})(\text{dppe})]^+$. The structures show the rocking and the out of plane bending of the phenanthroline ligand in the excited state.

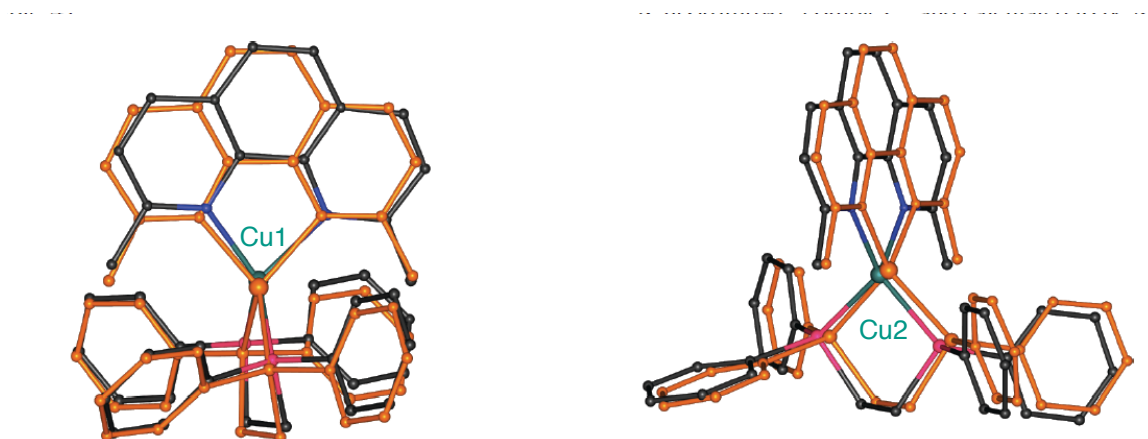


Figure 2-16: ES geometries (orange) of $[\text{Cu}(\text{dmp})(\text{dppe})]^+$ superimposed on the GS of the complex (Cu, green; C, black; P, purple; N, blue). The different views are shown to illustrate the change in rocking distortion (left) and the displacement of the phenanthroline ligand from its GS plane (right) upon excitation. Reproduced from reference 36

2.6 Concluding Comments

Nanosecond time resolved spectroscopy can be a valuable and versatile tool for any inorganic chemist. Unlike ultrafast spectroscopic techniques, the nanosecond spectroscopic techniques do not require specialized training and expertise. Commercial benchtop spectrometers are available for many of the techniques discussed, with the exception of the time-resolved X-ray spectroscopy. Nanosecond time resolved spectroscopic techniques can be used to investigate a wide range of inorganic systems and give insight to many chemical questions.

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Chapter 3: Synthesis and Spectroscopic Characterization of Cyano-Substituted Bipyridyl Complexes of Ruthenium(II)

3.1 Introduction

Photo-induced charge separation is the physical phenomenon underlying virtually all schemes geared toward the conversion of light into chemical, electrical, and/or mechanical energy. For example, in photosynthesis absorption of light by either the light harvesting complex or the reaction center itself sets the stage for the creation of a trans-membrane potential gradient: this ultimately provides the chemical energy for ATP synthase.^{1,2} In materials science, where semiconductors are the functional element of the vast majority of commercial photovoltaic devices, irradiation leads to the formation of electron-hole pairs that establish an electric potential. The well-known Grätzel cell, which has arguably helped to redefine research on photovoltaics over the past two decades,³⁻⁶ essentially combines molecular and semiconductor photophysics to create a functional device with overall conversion efficiencies that now exceed 11%^{7,8}. In all of these cases, absorption of light and the resulting redistribution of energy within the chromophoric system represent the primary steps for solar energy conversion.

Charge separation is typically effected in a molecular system through charge-transfer excited states, in which photon absorption causes charge redistribution within the chromophore: maintaining, amplifying, or, in the least favorable circumstances, destroying the resulting chemical potential depends on dynamics that occur within the chromophore immediately following the absorptive event. Transition metal complexes having intense charge-transfer features have long been exploited to achieve the goal of creating reactive excited states for photochemical energy conversion.^{9,10} Formation of the desired reactive state

then relies on a sequence of events: excitation into an upper level having significant radiative coupling to the ground state, followed by relaxation to the lower energy state(s). A host of dynamic processes are potentially involved in this process, among them intersystem crossing (ISC), internal conversion (IC), vibrational relaxation (VR) and/or intramolecular vibrational redistribution (IVR), as well as solvation dynamics. In general, all of these fundamental processes can be categorized as either radiative or non-radiative in nature. With regard to intramolecular dynamics, with the notable exception of certain highly emissive compounds,¹¹⁻¹³ energy dissipation in the vast majority of transition metal-based charge-transfer systems occurs primarily through vibrational relaxation. Despite being the dominant contribution to excited-state relaxation – and in practical terms an important competing process for the efficient conversion of absorbed energy into more productive reaction pathways – there is relatively little known concerning the mechanism(s) by which vibrational relaxation occurs.

Probing vibrational relaxation in transition metal complexes is not always a straightforward process. Often times information about vibrational relaxation from the initially excited Franck-Condon state to the long lived excited state is inferred from transient electronic absorption spectroscopy.¹⁴ The number and energy of the possible Franck-Condon transitions changes as the molecule goes from a vibrationally hot excited state to a thermalized excited state, which can lead to changes in bandshape and/or peak position in the electronic absorption spectra. These changes are usually seen as a red shifting and narrowing of an absorption feature over time, but the nature of the change depends on the relative displacement and slope of the two excited state potential energy surfaces. Infrared spectroscopy is more direct way to probe the vibrational state of an electronic excited state. In infrared spectroscopy, vibrational relaxation generally manifests itself as a narrowing and blue shifting of the excited state

vibrational peak.^{15,16} This is because the Franck-Condon excitation creates a distribution of vibrationally excited states which all relax to a single $v' = 0$ vibrational state which causes the spectrum to narrow and the anharmonic nature of the potential surface means the vibrational spacing is smaller at the top of the potential well and larger at the bottom, leading to a blue shift. Browne, McGarvey, and coworkers have used time-resolved resonance Raman to monitor the formation of the thermalized $^3\text{MLCT}$ state in $[\text{Ru}(\text{bpy})_3]^{2+}$ by monitoring the growth of ring stretching and bending vibrations assigned to the bipyridyl radical anion.^{17,18}

While the results of Browne, McGarvey, and coworkers are significant because it is the first time that vibrational relaxation has been directly probed in a ruthenium(II) polypyridyl complex, using vibrations in the fingerprint region is less than ideal. The disadvantage of using these vibrations to probe vibrational relaxation in the excited state is that there are many overlapping vibrational modes in this region of the spectrum, which can mask the subtle changes in the peak shape and energy that accompany vibrational relaxation. In the fingerprint region interference from solvent vibrations can also cause significant interference. In the case of heteroleptic complexes, the complexity of the vibrational spectrum in the fingerprint region dramatically increases. This makes even distinguishing the vibrations of the different ligands difficult at best.¹⁹ An alternative is to use an infrared tag to probe the vibrational state of an excited chromophore. The ideal infrared tag is a functional group which has a vibration which is spectrally isolated, is not overlapping with other vibrations of the molecule or solvent, has a significant change in frequency from ground to excited state, and is located where the charge transfer excited state is localized. Many studies have used the CO stretch in metal carbonyl complexes as an infrared tag, however many of these complexes are not photostable and the the CO

stretch is used to monitor photodissociation reactions.²⁰⁻²² In cases where no photochemistry is occurring, such as in $\text{Re}(\text{bpy})(\text{L})(\text{CO})_3$ type complexes, the CO is an ancillary ligand, and is not directly coupled to the bpy MLCT excited state²³. The cyano group is a less frequently used alternative to the carbonyl group. The CN stretching frequency is sensitive to local environment and well isolated from other molecular and solvent vibrations, so cyano substituted amino acids have been used to probe secondary structure and environment in proteins.²⁴ The terminal CN in metal dimers can be used to monitor electron transfer reactions.²⁵⁻²⁷ Vlček and coworkers used the CN stretch of 4-cyano-pyridine to assign the nature of the charge transfer transitions in $\text{W}(\text{CO})_5(4\text{-CN-py})$.¹⁵

Combining the features of the charge-transfer character of Ru^{II} -polypyridyls with the vibrational properties of 4-cyanopyridine takes advantage of benefits of both systems. Specifically, we felt that incorporating CN groups into the bipyridyl ligand would introduce a vibrationally well-isolated infrared tag into the chromophore. Moreover, placing the CN group at the 4 and/or 4' positions of the rings would result in direct coupling of the CN group to the π^* system of the bipyridine ring; the presence of an electron in the π^* orbital should result in a significant shift in the CN stretching frequency, thereby allowing us an unambiguous probe for vibrational processes associated with the charge-transfer state. This chapter describes the synthesis and spectroscopic characterization of such a system and provides the foundation for the detailed study of vibrational relaxation dynamics in a prototypical MLCT chromophore which is discussed in Chapter 4.

3.2 Experimental Section

3.2.1 General.

All chemicals and solvents were obtained from Fisher or Aldrich Chemical Co.

and used without further purification unless otherwise stated. $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$, tris(benzylideneacetone)dipalladium(0) ($\text{Pd}_2(\text{dba})_3$), and diphenylphosphinoferrocene (dppf) were purchased from Strem Chemicals, Inc. and C18 reversed phase silica gel was purchased from SiliCycle. NMR spectra were collected on Varian Inova-300 (300 MHz) or Varian UnityPlus-500 (500 MHz) spectrometers. Ground state infrared spectra ($4000\text{--}400\text{ cm}^{-1}$) were measured as KBr pellets using a Mattson Galaxy series 3000 FTIR spectrophotometer. Mass spectra were obtained through the Michigan State University Mass Spectrometry Facility. Elemental analyses were obtained through the analytical facilities at Michigan State University or from Columbia Analytics. Solvent included in calculated elemental analysis percentages was included to give the best fit based on solvents identified by NMR and IR.

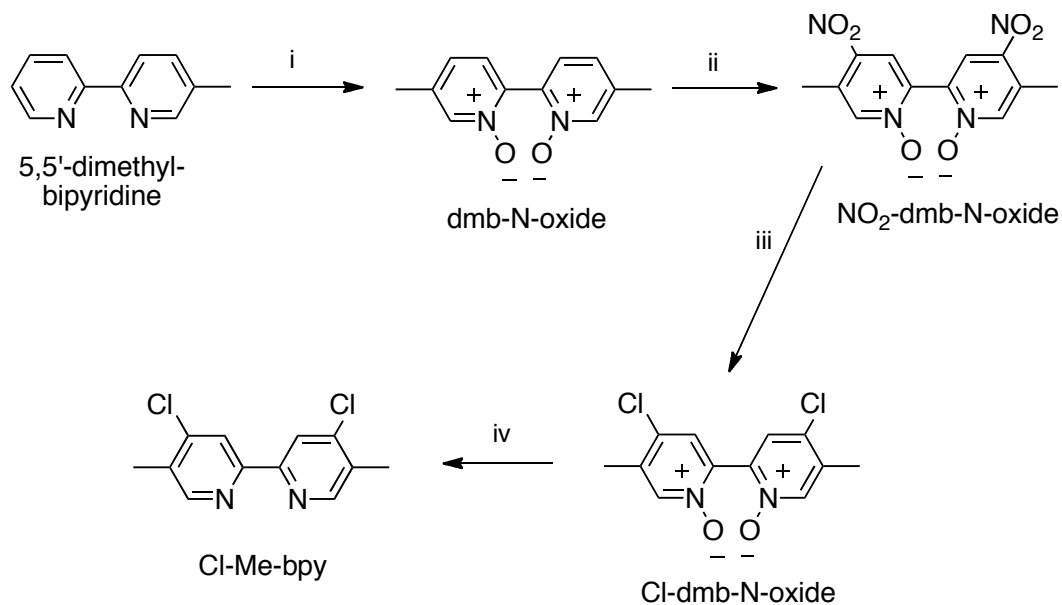


Figure 3-1: Synthesis of 4,4'-dichloro-2,2'-bipyridine. (i) Acetic acid and 30% hydrogen peroxide, refluxed. (ii) Sulfuric acid and fuming nitric acid, gentle heating. (iii) Acetyl anhydride refluxed in acetic acid (iv) PCl_3 refluxed in acetonitrile

3.2.2 Ligand Synthesis

5,5'-dimethyl-2,2'-bipyridine-N,N'-dioxide

*dmb-N-oxide*²⁸

5,5'-dimethyl-2,2'-bipyridine (5.0 g) was dissolved in 35 mL of glacial acetic acid and 7.0 mL of 30% hydrogen peroxide were slowly added. After heating the solution to 70-80 °C for 4 hours, an additional 4.0 mL of 30% hydrogen peroxide were added and the reaction mixture was heated overnight. The product was isolated by pouring the cooled solution over approximately 400 mL of acetone and reducing the volume under vacuum until a white precipitate formed. The white precipitate was collected by vacuum filtration, rinsed sparingly with acetone and ether, and then dried further under vacuum. Yield: 4.76 g (81%). ¹H NMR (300 MHz, D₂O): δ 8.19 (s, 2H), 7.57 (d, J=8.0 Hz, 2H), 7.14 (d, J=8.0 Hz, 2H), 2.35 (s, 6H).

5,5'-dimethyl-4,4'-dinitro-2,2'-bipyridine-N,N'-dioxide

NO₂-dmb-N-oxide^{29,30}

4.5 g of dmb-N-oxide was dissolved in 21 mL of sulfuric acid and 9.0 mL of fuming nitric acid were slowly added to the solution. The solution was gently heated to 90-100° C for 4 hours. During the course of the reaction the mixture became yellow and a brown gas formed above the solution. The solution was cooled to room temperature and slowly poured over ice formed by mixing 75 mL of water with excess liquid nitrogen. Additional liquid nitrogen was added, while stirring, to form a yellow slush. As the slush melted, a yellow precipitate was collected by vacuum filtration, rinsed thoroughly with water and ether, and then dried under vacuum. Yield: 3.75 g (59%). ¹H NMR (500 MHz, DMSO-d₆): δ 8.65 (s, 2H), 8.53 (s, 2H), 2.58 (s, 6H).

4,4'-dichloro-5,5'-dimethyl-2,2'-bipyridine-N,N'-dioxide

*Cl-dmb-N-oxide*³¹

NO₂-dmb-N-oxide (3.75 g) was suspended in 55.0 mL of glacial acetic acid and 45.0 mL of acetyl chloride. The suspension was refluxed for two hours, during which time the solution became a clear yellow color. The solution was cooled to room temperature and slowly poured over approximately 500 mL of ice. The resulting clear yellow solution was neutralized with concentrated sodium hydroxide, resulting in the formation of a white precipitate. The white solid was collected by vacuum filtration, rinsed with water and ether, and dried under vacuum. Yield: 3.13 g (90%). ¹H NMR (300 MHz, DMSO-d₆): δ 8.45 (s, 2H), 7.86 (s, 2H), 2.31 (s, 6H).

4,4'-dichloro-5,5'-dimethyl-2,2'-bipyridine

*Cl-Me-bpy*³²

Cl-Me-bpy-N-oxide (3.13 g) was suspended in 460 mL of dry acetonitrile and 21.0 mL of phosphorus trichloride were slowly added to the mixture. The suspension was refluxed under nitrogen for four hours, after which the solution became a clear yellow color. The solution was cooled to room temperature and slowly poured over approximately 500 mL of ice. The solution was made basic (pH >11) with the addition of concentrated sodium hydroxide resulting in the formation of a white precipitate. The white solid was collected by vacuum filtration, rinsed with water and dried under vacuum. Concentrating the filtrate yielded additional product. Yield: 2.57 g (92%). ¹H NMR (500 MHz, CDCl₃): δ 8.47 (s, 2H), 8.37 (s, 2H), 2.42 (s, 6H). ¹³C NMR (500 MHz, CDCl₃): δ 154.51, 150.85, 145.45, 132.44, 121.46, 16.94.

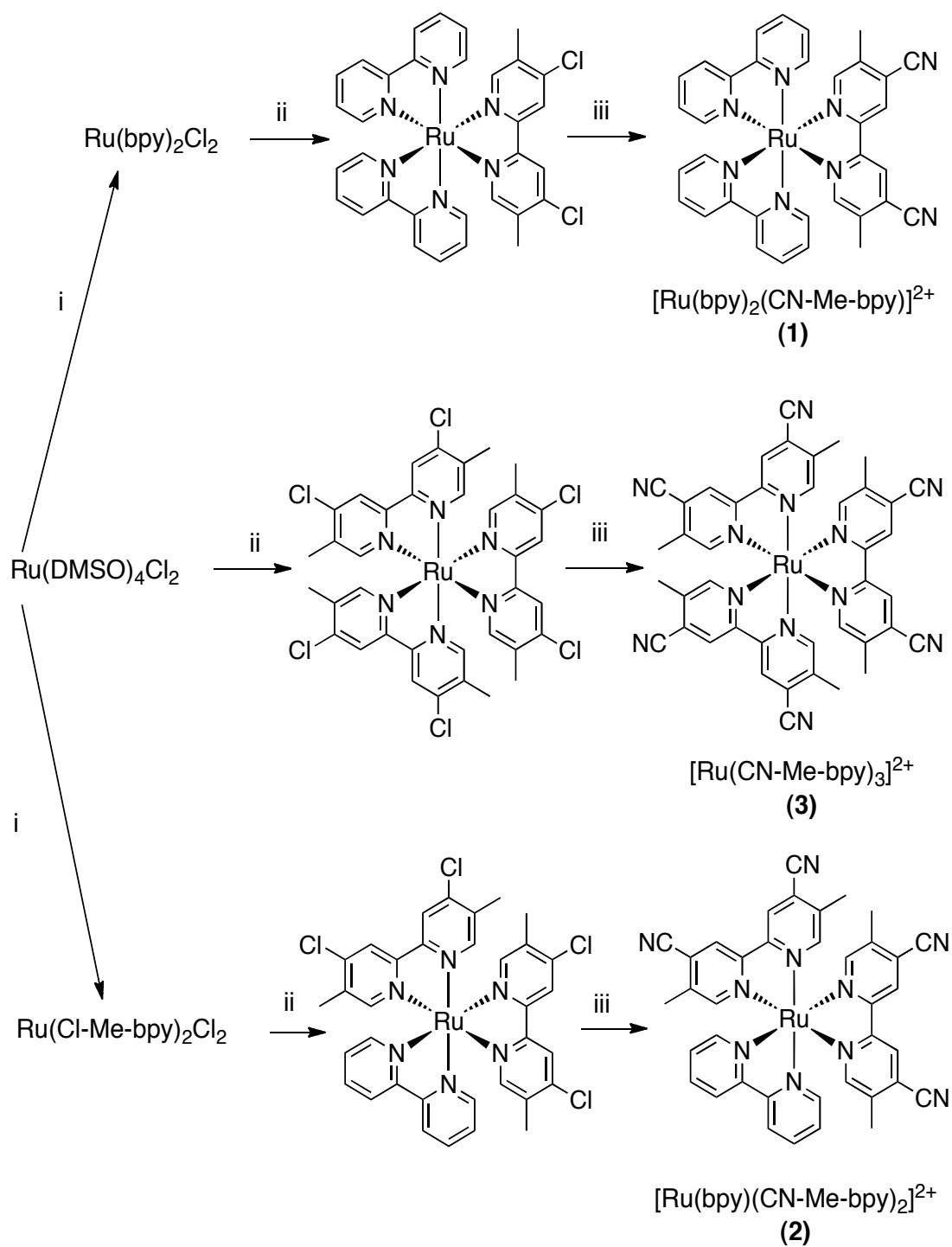


Figure 3-2: Synthesis of complexes **1-3**. (i) bpy or Cl-Me-bpy and LiCl refluxed in DMF. (ii) bpy or Cl-Me-bpy refluxed in ethanol for 48 hrs. (iii) $\text{Pd}_2(\text{dba})_3$, dppf, ZnCN, and zinc dust heated in DMA. See text for details.

3.2.3 Synthesis of [Ru(bpy)₂(CN-Me-bpy)](PF₆)₂, (1)

Dichlorotetrakis(dimethyl sulfoxide)ruthenium(II)



Ru(DMSO)₄Cl₂ was prepared by a modified version of the reported literature method.³³ Dimethyl sulfoxide (25.0 mL) was bubble degassed with nitrogen for 15 minutes, after which time 1.50 g of RuCl₃·xH₂O were added to the solution. The reaction was gently heated under nitrogen for 30-45 minutes until the dark black-red solution became dark yellow-orange in color. The solution was cooled to room temperature, poured over 100 mL of acetone, and cooled in the freezer overnight to precipitate the product. The yellow microcrystalline solid was collected by vacuum filtration, rinsed once with acetone, rinsed three times with ether, and dried under vacuum. Yield: 2.20 g. Anal. Calcd (Found) for C₈H₂₄Cl₂O₄S₄Ru·0.25 (CH₃)₂SO: C, 20.26 (20.14); H, 5.10 (5.23).

Bis(2,2'-bipyridine)dichlororuthenium(II)



Ru(bpy)₂Cl₂ was prepared from a modified version of the reported literature method, using Ru(DMSO)₄Cl₂ rather than RuCl₃·xH₂O.³⁴ Freshly distilled DMF (35.0 mL) was bubble degassed with nitrogen for 15 minutes and 1.60 g of Ru(DMSO)₄Cl₂, 1.10 g of 2,2'-bipyridine, and 7.30 g of LiCl were added to the solution. The solution was shielded from light using aluminum foil and heated to reflux under nitrogen for approximately 4 hours; the progress of the reaction was monitored using thin layer chromatography (silica, 10% acetone in dichloromethane). The dark purple reaction mixture was then cooled slightly after which the warm solution was poured over approximately 400 mL of acetone and cooled overnight in the freezer to precipitate the product. The dark precipitate was collected by vacuum filtration and rinsed with water to remove

excess LiCl and a side product of $[\text{Ru}(\text{bpy})_3]^{2+}$ until the filtrate was colorless. The remaining purple-green solid was rinsed three times with ether and dried under vacuum. Yield: 0.989 g (60%). Anal. Calcd (Found) for $\text{C}_{20}\text{H}_{16}\text{Cl}_2\text{N}_4\text{Ru}\cdot 1.0 \text{ H}_2\text{O}$: C, 47.82 (47.71); H, 3.61 (3.56); N, 11.15 (10.90). ^1H NMR (500 MHz, DMSO-d_6): δ 9.97 (d, $J=5.0$ Hz, 2H), 8.65 (d, $J=8.1$ Hz, 2H), 8.49 (d, $J=8.0$ Hz, 2H), 8.07 (dt, $J=7.8, 1.26$ Hz, 2H), 7.77 (dt, $J=6.6, 1.0$ Hz, 2H), 7.68 (dt, $J=7.8, 1.1$ Hz, 2H), 7.52 (d, $J=5.6$ Hz, 2H), 7.10 (dt $J=6.6, 1.1$ Hz, 2H).

*Bis(2,2'-bipyridine)(4,4'-dichloro-5,5'-dimethyl-2,2'-bipyridine)ruthenium(II)
hexafluorophosphate*



Ethanol (30.0 mL) was bubble degassed with nitrogen for 15 minutes and 0.59 g of $\text{Ru}(\text{bpy})_2\text{Cl}_2$ and 0.33 g of Cl-Me-bpy were added to the solution. The solution was shielded from light and heated to reflux overnight under nitrogen. The solution was cooled to room temperature and excess NaPF_6 dissolved in 50 mL of water was added to the solution to precipitate a red powder. The precipitate was collected by vacuum filtration, rinsed well with water and ether, and dried under vacuum. The solid was recrystallized once by acetonitrile/ether diffusion. Yield: 0.849 g (73%). Anal. Calcd (Found) for $\text{C}_{32}\text{H}_{27}\text{Cl}_2\text{F}_{12}\text{N}_6\text{P}_2\text{Ru}\cdot 0.5 \text{ H}_2\text{O}$: C, 39.81 (39.60); H, 2.82 (2.80); N, 8.70 (8.63). ^1H NMR (500 MHz, CD_3CN): δ 8.51 (s, 2H), 8.48 (t, $J=8.5$ Hz, 4H), 8.05 (m, $J=7.9$ Hz, 4H), 7.75 (d, $J=5.6$ Hz, 2H), 7.65 (d, $J=5.6$ Hz, 2H), 7.51 (s, 2H), 7.41 (dt, $J=6.6, 1.3$ Hz, 2H), 7.37 (dt $J=6.7, 1.3$ Hz, 2H), 2.20 (s, 6H). ^{13}C NMR (500 MHz, CD_3CN): δ 158.38, 158.33, 156.32, 153.86, 153.18, 152.98, 146.90, 139.19, 139.17, 138.52, 128.96, 128.77, 125.78, 125.65, 125.64, 17.71. MS [ESI (CH_3CN), m/z (rel. int.)]: 333.1 (100) $[\text{M}-2\text{PF}_6]^{2+}$, 811.2 (68) $[\text{M}-\text{PF}_6]^{1+}$.

Bis(2,2'-bipyridine)(4,4'-dicyano-5,5'-dimethyl-2,2'-bipyridine)ruthenium(II)
hexafluorophosphate
[Ru(bpy)₂(CN-Me-bpy)](PF₆)₂, (1)

This synthesis is a modified version of the reported synthesis for 4'-cyano-2,2':6',2"-terpyridine complexes of ruthenium.³⁵ Anhydrous dimethylacetamide (DMA) was degassed using freeze-pump-thaw techniques prior to use. [Ru(bpy)₂(Cl-Me-bpy)](PF₆)₂ (0.500 g), zinc cyanide (0.740 g), Pd₂(dba)₃ (0.045 g), dppf (0.060 g), zinc dust (0.200 g), and DMA (80.0 mL) were combined in an inert atmosphere glovebox. The solution was transferred from the glovebox to a Schlenk line, shielded from light, and heated slowly under nitrogen. The progress of the reaction was monitored by electronic absorption spectroscopy. After the reaction was complete (i.e., when no further changes in the absorption spectrum were noted ca. 1 hour) the solution was cooled to room temperature and filtered through celite. The filtrate was evaporated to near dryness under vacuum and the dark red-orange residue was dissolved in acetonitrile and precipitated with ether. The resulting orange solid was collected by vacuum filtration and washed with ether. The solid was recrystallized once by acetonitrile/ether diffusion and then purified twice by column chromatography using neutral alumina and C-18 reverse phase silica gel with 7:1 acetonitrile:aqueous KNO₃ as the eluent for both columns. After the column purification the product was recrystallized a final time by acetonitrile/ether diffusion to remove excess nitrate salts from the column eluent. Yield: 0.309 g (63%). Anal. Calcd (Found) for C₃₄H₂₆F₁₂N₈P₂Ru: C, 43.55 (43.40); H, 2.79 (2.85); N, 11.95 (11.84); Ru, 10.78 (10.11). ¹H NMR (500 MHz, CD₃CN): δ 8.69 (s, 2H), 8.49 (t, J=7.8 Hz, 4H), 8.08 (m, J=7.9, 1.5 Hz, 4H), 7.78 (s, 2H), 7.64 (dd, J=12.6, 5.5 Hz, 4H), 7.41 (m, J=7.08, 1.3 Hz, 4H), 2.38 (s, 6H). ¹³C NMR (500 MHz, CD₃CN): δ 156.88, 156.56, 154.54, 153.52, 151.95, 151.54, 140.52,

138.49, 138.41, 127.90, 127.60, 126.21, 124.57, 124.54, 121.22, 114.80, 17.12. MS [ESI (CH₃CN), *m/z* (rel. int.)]: 324.0 (95) [M-2PF₆]²⁺, 793.1 (100) [M-PF₆]¹⁺. MS [HR-ESI (CH₃CN)] *m/z* 793.0973 [M-PF₆]¹⁺, calcd. (C₃₄H₂₆N₈F₆PRu) 793.0966. FTIR (selected frequencies in KBr pellet, cm⁻¹) 3117(w), 2234(m), 1605(m), 1467(s), 1447(s), 1241(m), 839(vs), 762(s), 557(vs). Electronic absorption (CH₃CN) λ, nm (ε, M⁻¹ cm⁻¹): 285 (63,800) 318 (36,700), 420 (13,400) 479 (14,000).

3.2.4 Synthesis of [Ru(bpy)(CN-Me-bpy)₂](PF₆)₂, (2)

This molecule was synthesized in the same manner as [Ru(bpy)₂(CN-Me-bpy)](PF₆)₂, starting from the appropriate Cl-Me-bpy ruthenium complex.

Bis(4,4'-dichloro-5,5'-dimethyl-2,2'-bipyridine)dichlororuthenium(II)

Ru(Cl-Me-bpy)₂Cl₂

Freshly distilled DMF (20.0 mL) was bubble degassed for 15 minutes and 0.810 g of Ru(DMSO)₄Cl₂, 0.850 g of Cl-Me-bpy, and 8.00 g of LiCl were added to the solution. The solution was shielded from light with aluminum foil and heated to reflux under nitrogen for 2 hours. The dark purple reaction mixture was then cooled slightly after which the warm solution was poured over approximately 400 mL of acetone and cooled overnight in the freezer to precipitate the product. The dark precipitate was collected by vacuum filtration and rinsed with water to remove excess LiCl and a side product of [Ru(Cl-Me-bpy)₃]²⁺ until the filtrate was colorless. The remaining dark purple solid was rinsed with ether and dried under vacuum. The product was recrystallized once by dichloromethane/ether diffusion. Yield: 0.747 g (66%). ¹H NMR (500 MHz, DMSO-d₆): δ 9.72 (s, 2H), 8.89 (s, 2H), 8.75 (s, 2H), 7.53 (s, 2H), 2.53 (s, 6H), 2.10 (s, 6H).

(2,2'-bipyridine)bis(4,4'-dichloro-5,5'-dimethyl-2,2'-bipyridine)ruthenium(II)
hexafluorophosphate
 $[Ru(bpy)(Cl-Me-bpy)_2](PF_6)_2$

30.0 mL of ethanol were bubble degassed with nitrogen for 15 min and 0.500 g of $Ru(Cl-Me-bpy)_2Cl_2$ and 0.120 g of 2,2'-bipyridine were added to the solution. The reaction was shielded from light and heated to reflux, under nitrogen, overnight. The solution was cooled to room temperature and excess $NaPF_6$ dissolved in 50.0 mL of water was added to precipitate a red powder. The precipitate was collected by vacuum filtration, rinsed well with water and ether, and dried under vacuum. The red powder was recrystallized once by acetonitrile/ether diffusion. Yield: 0.681 g (88%). Anal. Calcd (Found) for $C_{34}H_{28}Cl_4F_{12}N_6P_2Ru \cdot 0.50 H_2O$: C, 38.43 (38.74); H, 2.75 (2.87); N, 7.91 (8.13). ^1H NMR (500 MHz, CD_3CN): δ 8.51 (s, 2H), 8.49 (s, 2H), 8.47 (d, J=7.9 Hz 2H), 8.06 (dt, J=7.9, 1.3 Hz, 2H), 7.70 (d, J=5.7 Hz, 2H), 7.55 (s, 2H), 7.41 (s, 2H), 7.39 (dt, J=6.6, 1.3 Hz, 2H), 2.25 (s, 6H), 2.18 (s, 6H). ^{13}C NMR (500 MHz, CD_3CN): δ 158.43, 156.42, 156.40, 154.03, 153.84, 153.23, 147.07, 147.04, 139.34, 138.59, 138.56, 128.91, 125.89, 125.80, 17.84, 17.67. MS: [ESI, m/z (rel. int.)]: 382.1 (100) $[M-2PF_6]^{2+}$, 909.1 (67) $[M-PF_6]^{1+}$.

(2,2'-bipyridine)bis(4,4'-dicyano-5,5'-dimethyl-2,2'-bipyridine)ruthenium(II)
hexafluorophosphate
 $[Ru(bpy)(CN-Me-bpy)_2](PF_6)_2$, **(2)**

$[Ru(bpy)(CN-Me-bpy)_2](PF_6)_2$ was synthesized in the same manner as $[Ru(bpy)_2(CN-Me-bpy)](PF_6)_2$ using 0.300 g of $[Ru(bpy)(Cl-Me-bpy)_2](PF_6)_2$, 0.400 g of zinc cyanide, 0.051 g of $Pd_2(dba)_3$, 0.063 g of dppf, 0.300 g of zinc dust, and 60.0 mL of DMA. Yield: 0.116 g (40%). Anal. Calcd (Found) for $C_{38}H_{28}F_{12}N_{10}P_2Ru \cdot 1.5 H_2O$: C, 43.77 (43.89); H, 2.99 (2.72); N, 13.43 (13.20);

Ru, 9.69 (8.94). ^1H NMR (500 MHz, CD_3CN): δ 8.70 (s, 2H), 8.68(s, 2H), 8.50 (d, $J=7.9$ Hz, 2H), 8.12 (dt, $J=7.9$ Hz, 1.5, 2H), 7.68 (t, $J=0.7$ Hz, 2H), 7.64 (t, $J=0.7$ Hz, 2H) 7.58 (d, $J=5.3$ Hz, 2H), 7.42 (dt, $J=6.7$, 1.3 Hz, 2H), 2.41 (s, 6H), 2.37 (s, 6H). ^{13}C NMR (500 MHz, CD_3CN): δ 157.90, 155.74, 155.45, 155.10, 154.80, 153.21, 142.25, 142.15, 140.34, 129.26, 127.77, 127.76, 126.22, 123.36, 123.27, 116.04, 116.02, 18.65, 18.44. MS [ESI (CH_3CN), m/z (rel. int.)]: 363.1 (100) $[\text{M}-2\text{PF}_6]^{2+}$, 871.1 (48) $[\text{M}-\text{PF}_6]^{1+}$. MS [HR-ESI (CH_3CN)] m/z 871.1166 $[\text{M}-\text{PF}_6]^{1+}$, calcd ($\text{C}_{38}\text{H}_{28}\text{N}_{10}\text{F}_6\text{PRu}$) 871.1184. FTIR (selected frequencies in KBr pellet, cm^{-1}) 3117(w), 2920(w), 2236(s), 1607(m), 1478(s), 1384(s), 1241(m), 841(vs), 765(m), 562(vs). Electronic absorption (CH_3CN) λ , nm (ϵ , $\text{M}^{-1} \text{cm}^{-1}$): 284 (37,000) 317 (55,200), 367 (12,800), 440 (12,600), 477 (16,700).

3.2.5 Synthesis of $[\text{Ru}(\text{CN-Me-bpy})_3](\text{PF}_6)_2$, (3).

This molecule was synthesized in the same manner as $[\text{Ru}(\text{bpy})_2(\text{CN-Me-bpy})](\text{PF}_6)_2$, starting from the appropriate Cl-Me-bpy ruthenium complex.

Tris(4,4'-dichloro-5,5'-dimethyl-2,2'-bipyridine)ruthenium(II) hexafluorophosphate
 $[\text{Ru}(\text{Cl-Me-bpy})_3](\text{PF}_6)_2$

Ethanol (30 mL) was bubble degassed with nitrogen for 15 minutes and 0.260 g of $\text{Ru}(\text{DMSO})_4\text{Cl}_2$ and 0.530 g of Cl-Me-bpy were added to the solution. The reaction was shielded from light and heated to reflux for 48 hours under nitrogen. The solution was cooled to room temperature and excess NaPF_6 , dissolved in 50.0 mL of water, was added to precipitate a red powder. The precipitate was collected by vacuum filtration, rinsed well with water and ether, and dried under vacuum. The solid was recrystallized once by acetonitrile/ether diffusion. Yield: 0.385 g (63%). Anal. Calcd (Found) for $\text{C}_{36}\text{H}_{30}\text{Cl}_6\text{F}_{12}\text{N}_6\text{P}_2\text{Ru}$: C, 37.59 (37.17); H, 2.63 (2.62); N, 7.31 (7.25). ^1H NMR (500 MHz, CD_3CN): δ 8.49 (s, 2H), 7.48 (s, 2H), 2.23 (s, 6H). ^{13}C NMR (500 MHz, CD_3CN): δ 156.33, 153.88, 147.11,

138.57, 125.91, 17.68. MS [ESI, m/z (rel. int.)]: 430.1 (100) $[M-2PF_6]^{2+}$, 1005.1 (55) $[M-PF_6]^{1+}$.

Tris(4,4'-dicyano-5,5'-dimethyl-2,2'-bipyridine)ruthenium(II) hexafluorophosphate
 $[Ru(CN-Me-bpy)_3](PF_6)_2$, (**3**)

$[Ru(CN-Me-bpy)_3](PF_6)_2$ was synthesized in the same manner as $[Ru(bpy)_2(CN-Me-bpy)](PF_6)_2$ using 0.630 g of $[Ru(Cl-Me-bpy)_3](PF_6)_2$, 1.90 g of zinc cyanide, 0.160 g of $Pd_2(dba)_3$, 0.180 g of dppf, 0.500 g of zinc dust, and 125 mL of DMA. Yield: 0.117 g (20%). Anal. Calcd (Found) for $C_{42}H_{30}F_{12}N_{12}P_2Ru \cdot 1.75 CH_3CN$: C, 46.89 (47.29); H, 3.05 (2.77); N, 16.52 (16.11); Ru, 8.67 (8.29). ^1H NMR (500 MHz, CD_3CN): δ 8.71 (s, 2H), 7.59 (s, 2H), 2.41 (s, 6H). ^{13}C NMR (500 MHz, CD_3CN): δ 155.33, 154.99, 142.50, 128.01, 123.83, 115.95, 18.51. MS [ESI (CH_3CN), m/z (rel. int.)]: 402.1(100) $[M-2PF_6]^{2+}$, 949.1 (10) $[M-PF_6]^{1+}$. MS [HR-ESI (CH_3CN)] m/z 949.1413 $[M-PF_6]^{1+}$, calcd ($C_{42}H_{30}N_{12}F_6PRu$) 949.1402. FTIR (selected frequencies in KBr pellet, cm^{-1}) 3050(w), 2235(m), 1631(m), 1477(s), 1385(s), 1242(m), 842(vs), 558(vs). Electronic absorption (CH_3CN) λ , nm (ϵ , $M^{-1} cm^{-1}$): 315 (78,800), 458 (23,000).

3.2.6 Physical Measurements

Electrochemistry and Spectroelectrochemistry.

Electrochemical measurements were carried out in a Ar-filled drybox (Vacuum Atmospheres) using a CHI 630B electrochemical analyzer. A standard three-electrode arrangement was used consisting of a Pt working electrode, a graphite counter electrode, and a Ag/AgCl reference electrode (Cypress Systems). Measurements were carried out in spectrophotometric grade CH_3CN , which was freeze-pump-thaw degassed before use, and using 0.1 M

tetrabutylammonium hexafluorophosphate (TBAPF₆) as the supporting electrolyte. Data were acquired by cyclic voltammetry (CV) and differential pulse voltammetry (DPV); the scan rate for the CV measurements was 50 mV/s and the scan rate and pulse width for the DPV measurements were 20 mV/s and 50 mV, respectively. Values for $E_{1/2}$ obtained by the two techniques were comparable. All oxidation and reduction waves were reversible over several consecutive scans. Potentials are listed versus the ferrocene/ferrocenium couple, which was used as an internal standard, and quoted as $E_{1/2}$ values as calculated from the DPV peak potentials.³⁶

UV-visible spectroelectrochemical experiments were performed in a 1 mm pathlength spectroelectrochemical cell (CH Instruments) with Ag/AgCl reference electrode inside an Ar filled glovebox. Measurements were carried out in spectrophotometric grade CH₃CN, which was freeze-pump-thaw degassed before use, and using 0.1 M TBAPF₆ as the supporting electrolyte. Samples were dissolved in the electrolyte solution to give an absorbance of 0.3-0.5 at the maximum of the main absorption band in the visible region. Difference spectra were collected on a SI440 CCD spectrometer in ca. 30 second intervals as the samples were oxidized or reduced. Oxidative spectra were collected at a potential 100 mV more positive than $E_{1/2}^{\text{ox}}$; reductive spectra were collected at a potential 100 mV more negative than $E_{1/2}^{\text{red1}}$ or halfway between $E_{1/2}^{\text{red1}}$ and $E_{1/2}^{\text{red2}}$, whichever was less reducing.

Electronic Steady-State and Time-Resolved Spectroscopies.

All spectra were collected in spectrophotometric grade CH₃CN unless otherwise noted. For steady state emission and time-resolved measurements, the solvent was freeze-pump-thaw degassed before use. Electronic absorption spectra for all compounds were acquired using a Cary 50 spectrophotometer.

Steady-state emission spectra were acquired using a Spex Fluoromax fluorimeter and corrected for instrumental response using a NIST standard of spectral irradiance (Optronic Laboratories, Inc., OL220 M tungsten quartz lamp). Samples were prepared in an inert atmosphere glovebox in 1 cm quartz cuvettes and measured under optically dilute conditions (o.d. 0.1-0.2). The resulting emission spectra were fit with an asymmetric double sigmoidal function using IGOR pro. This function has no mathematical significance but it is able to accurately reproduce the shape of the entire emission curve and thereby capture the small area (< 10%) that lies outside of the detector range thereby providing for a more accurate estimate of the integrated spectrum. Relative radiative quantum yields (Φ_r) were determined using $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ as a standard ($\Phi_{\text{std}} = 0.095$ in degassed CH_3CN ³⁷). Quantum yields were calculated using Equation 3-1, where Φ_{unk} is the relative radiative quantum yield of the sample, I_{unk} and I_{std} are the integrated areas of the corrected emission spectra of the

$$\Phi_{\text{unk}} = \Phi_{\text{std}} \left(\frac{I_{\text{unk}}}{A_{\text{unk}}} \right) \left(\frac{A_{\text{std}}}{I_{\text{std}}} \right) \left(\frac{\eta_{\text{unk}}}{\eta_{\text{std}}} \right)^2 \quad 3-1$$

sample and standard respectively, A_{unk} and A_{std} are the absorbances of the sample and the standard at the excitation wavelength, and η_{unk} and η_{std} are the indexes of refraction of the respective solvents (taken to be equal to the neat solvents in both cases). Low-temperature emission spectra were collected using a Janis SVT-100 optical cryostat as described previously.³⁸ Measurements were taken at 80 K in a 9:2 mixture of butyronitrile and propionitrile, both of which were freeze-pump-thaw degassed before use. Estimates of the zero point energy gap (E_0), Huang-Rhys factor (S_M), energy of the average vibrational mode coupling the ground and excited states ($\hbar\omega_M$), and spectral bandwidth ($\Delta\bar{\nu}_{0,1/2}$) were determined by a single mode fit of the steady-state emission spectra to Equation

3-2 as described by Claude and Meyer.³⁹ The correction of Parker and Rees was applied to all spectra when converting from wavelength to energy units.⁴⁰

$$I(\bar{\nu}) = \sum_{v_M=0}^5 \left\{ \left(\frac{E_0 - v_M \hbar \omega_M}{E_0} \right)^3 \frac{S_M^{v_M}}{v_M!} \cdot \exp \left(-4(\ln 2) \left(\frac{\bar{\nu} - E_0 + v_M \hbar \omega_M}{\Delta \bar{\nu}_{0,1/2}} \right)^2 \right) \right\} \quad 3-2$$

Nanosecond time-resolved emission and transient absorption experiments were carried out using a Nd:YAG laser spectrometer that has been described previously.^{41,42} Time-resolved emission was collected on the same samples used to acquire the room-temperature steady-state emission spectra (*vide supra*). Samples for time-resolved absorption measurements were prepared with an absorbance in the range of 0.3-0.5 at the excitation wavelength (500 nm for **1** and **2** and 480 nm for **3**) and sealed under an Ar atmosphere in 1 cm quartz cuvettes. Data corresponds to a 15 shot average (0.2 Hz) of the signal and baseline as well as background sample emission with 1-3 mJ of power at the sample. The baseline and emission were subsequently subtracted from the signal and the data analyzed using a program of local origin. All data were checked for linearity with respect to pump power. In addition, absorption spectra were measured before and after all time-resolved absorption experiments to ensure the integrity of the sample. Laser power was periodically monitored to ensure constant pump power over the course of the experiment. Data acquired at each probe wavelength was fit to a single exponential kinetic model; the amplitudes for each of these fits were plotted to produce the differential absorption spectra reported herein.

Nanosecond Time-Resolved Infrared Spectroscopy.

Nanosecond time-resolved step-scan infrared (SSIR) absorption spectra were measured on a step-scan modified Bruker IFS66 FTIR spectrometer with a standard globar source and nitrogen purge. Nitromethane was used as the solvent in these experiments; emission measurements on complex **1** in CH₃CN and CH₃NO₂ showed no significant differences in the emission profile or lifetime. The compounds were dissolved in dried CH₃NO₂ to give a ground state infrared absorption of 0.2-0.6 for the $\bar{\nu}(\text{CN})$ band (10-20 mM). All solutions were deoxygenated by bubbling with nitrogen for 15 min. Spectra were measured in a demountable CaF₂ cell with a 0.5 mm or 1 mm Teflon spacer (Specac). Samples were excited using an OPOTEK Vibrant Nd:YAG laser (~3-4 mJ/pulse, 10 Hz). Excitation wavelengths within the lowest energy visible absorption feature were chosen such that the absorbance was less than 2 in order to ensure uniform excitation of the sample. An AC/DC-coupled photovoltaic Kolmar Technologies mercury cadmium telluride (PV MCT) detector with a 20 MHz preamplifier was used to sample the transmitted IR probe beam. The detector's AC signal was further amplified (25X) with a 350 MHz fast preamplifier (Stanford Research SR445A) before being directed to a 100/200 MHz PAD82a transient digitizer board. The interferogram response before and after laser excitation was collected in 10 ns time slices, with 30 laser shots averaged at each mirror position. For each scan, folding limits of 2600 and 1000 cm⁻¹ at 4 cm⁻¹ resolution resulted in 1332 mirror positions. The DC signal was collected separately and used to check for sample decomposition as well as for phase correction of the AC signal. Bruker Instruments' Opus 5.5 software was used to process the recorded data. Differential absorbance spectra were calculated from the AC and DC single channel spectra as described previously.⁴³ The differential excited state absorption spectra reported herein represent an average

of 4-8 scans, ground-state spectra correspond to an average of 30 (rapid) scans.

Calculations.

Calculations on complex **1** were performed using the Gaussian 03 software package.⁴⁴ Geometry optimizations were done on both the ground state and the lowest energy triplet state using a spin unrestricted formalism at the B3LYP/LANL2DZ level of theory.^{45,46} No symmetry restrictions were placed on the geometry optimizations. The effects of the acetonitrile solvent environment were included by using the polarizable continuum model (PCM). Frequency calculations were performed on both the singlet and triplet optimized structures to ensure that these geometries corresponded to global minima. No imaginary frequencies were obtained for either of the optimized geometries. The highest energy CN-Me-bpy π bonding orbital of the ground state optimized geometry and the lowest energy CN-Me-bpy π^* antibonding orbital of the lowest energy triplet optimized geometry were visualized with GaussView. The cartesian coordinates for the optimized geometries can be found in Appendix D.

3.3 Results and Discussion

I have synthesized a series of cyano substituted ruthenium polypyridyl complexes with the general form $[\text{Ru}(\text{bpy})_{3-n}(\text{CN-Me-bpy})_n](\text{PF}_6)_2$, as shown in Figure 3-2. These complexes have been designed to combine the well documented charge transfer properties of the ruthenium polypyridyl complexes with the cyanide infrared tag in order to study the vibrational relaxation process in charge transfer excited states. This chapter describes the synthesis of the three complexes as well as the spectroscopic characterization of the long lived $^3\text{MLCT}$ state; this study will provide the necessary foundation for the detailed study of vibrational relaxation dynamics in a MLCT chromophore in Chapter 4.

3.3.1 Synthesis

The synthesis of ruthenium complexes is well established, versatile, and can be used with bipyridine ligands with electron withdrawing groups such as such as nitro, trifluoromethyl, and ethyl ester.⁴⁷⁻⁵¹ However, initial attempts to synthesize ruthenium complexes of 4,4'-dicyano-2,2'-bipyridine (CN-bpy) using a variety of reaction conditions led to only trace amounts of the desired products even with extended (weeks to months) reaction time. The fact that examples of ruthenium complexes containing cyano substituted bipyridine ligands exist in the literature suggests that $[\text{Ru}(\text{bpy})_{3-n}(\text{CN-bpy})_n]^{2+}$ ($n=1-3$) complexes are thermodynamically stable and kinetic factors are likely responsible for the low yields of the CN-bpy complexes.^{52,53} If this is true, a change in reaction mechanism could beneficially alter the reaction kinetics, and (potentially) increase product yield.

One alternate pathway to form ruthenium complexes of CN-bpy is to carry out the cyanide functionalization after the ligand is bound to the metal center. There are many examples of such transformations in the literature, circumventing difficult purifications, insoluble intermediates, and/or kinetically unfavorable reactions.⁵⁴⁻⁵⁹ In particular palladium catalysts have proven effective in converting aryl halides to cyanides in high yields;^{60,61} Hanan, Campagna, and coworkers have demonstrated that this reaction can also be used on ruthenium complexes.³⁵ Starting from the chloro-substituted ruthenium bipyridine complexes, I was able to synthesize ruthenium complexes of 4,4'-dicyano-2,2'-bipyridine, proving that the desired complexes are indeed thermodynamically stable. Unfortunately, these complexes were highly susceptible to hydrolysis to form the corresponding amide, especially during column chromatography as well as subsequent to reduction during electrochemical measurements. In order to increase the basicity of the nitrogens and (hopefully) increase the stability of the complexes, electron donating methyl groups were added to the 5 and 5' positions

of the bipyridine ring. This approach proved to be successful, yielding the final $[\text{Ru}(\text{bpy})_{3-n}(\text{CN-Me-bpy})_n]^{2+}$ ($n=1-3$) complexes, shown in Figure 3-2, that could withstand column chromatography as well as exhibiting reversible electrochemistry.

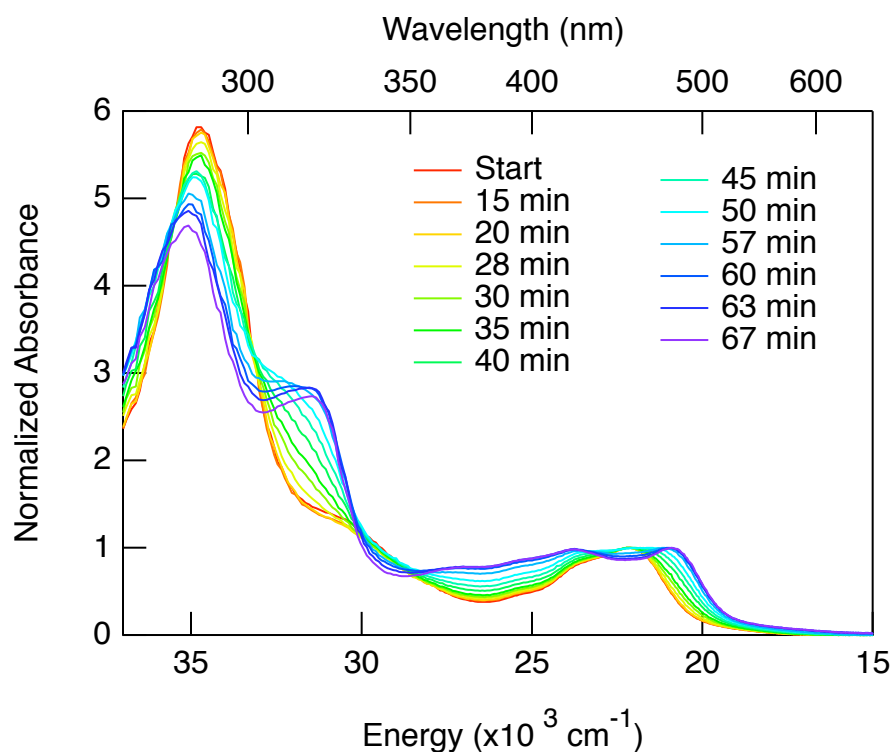


Figure 3-3: Electronic absorption spectra of the conversion of $[\text{Ru}(\text{bpy})_2(\text{Cl-Me-bpy})]^{2+}$ to $[\text{Ru}(\text{bpy})_2(\text{CN-Me-bpy})]^{2+}$. The inset indicates the time following initiation of the reaction that each aliquot was taken. See text for further details.

The synthesis of the desired complexes took place in three parts. First, the Cl-Me-bpy ligand was synthesized via the nitro-substituted intermediate using the literature procedure reported for 4,4-dichloro-2,2'-bipyridine.²⁸⁻³² The ruthenium complexes of the Cl-Me-bpy ligand were then synthesized using well-established literature methods. For the final step of synthesizing the CN-Me-bpy ruthenium complexes, the procedure Hanan, Campagna, and coworkers reported for

$[\text{Ru}(\text{tpy})(\text{CN-tpy})]^{2+}$ and $[\text{Ru}(\text{CN-tpy})_2]^{2+}$ (CN-tpy = 4'-cyano-2,2':6',2''-terpyridine) had to be modified for these bipyridine based reactions. The amount of palladium catalyst and ligand were kept the same as reported (5 and 10 mol% per CN group respectively), however I found that an excess of zinc cyanide (as opposed to the stoichiometric amount used for the tpy-based systems) was necessary to form the bipyridine complexes. In addition, the 6-12 hour reaction time necessary for the terpyridine complexes had to be truncated to 1-2 hours for the bipyridine analogs to avoid the formation of side products which were not easily removed by recrystallization or column chromatography. The ideal reaction time differed depending on the exact rate of heating ($\sim 1^\circ\text{C}/\text{minute}$ was used), so monitoring the reaction progress by UV-vis spectroscopy, as shown in Figures 3-3, A-2, and A-4, was essential for determining when the reaction had reached completion. Even under the best of conditions, the separation achieved by column chromatography was less than ideal; multiple fractions were collected and evaluated by UV-vis and NMR. Attempts to grow single crystals were unsuccessful, so the identity and purity of the final complexes were ultimately determined by NMR, high resolution ESI/MS, and elemental analysis.

3.3.2 Ground State Spectroscopic Properties

The ground state absorption spectra of the three complexes and $[\text{Ru}(\text{bpy})_3]^{2+}$ are shown in Figure 3-4. Metal bipyridyl complexes typically exhibit both intraligand as well as charge transfer transitions. Based on extinction coefficients as well as other ruthenium polypyridyl complexes, the UV absorption features in complexes **1-3** can be assigned as $\pi \rightarrow \pi^*$ absorptions of the bipyridine ligands whereas the somewhat weaker visible features are as metal-to-ligand charge transfer (MLCT) in nature. The variation in composition across the series is reflected in the spectra. For example, in complex **3** there is a single UV

absorption at 315 nm which can be readily assigned as a $\pi \rightarrow \pi^*$ absorption(s) of the CN-Me-bpy ligand. Complexes **1** and **2** also have UV absorptions at 318 and 317 nm, respectively, which are likewise also assigned to $\pi \rightarrow \pi^*$ absorptions of the CN-Me-bpy ligand. In the heteroleptic complexes there is also

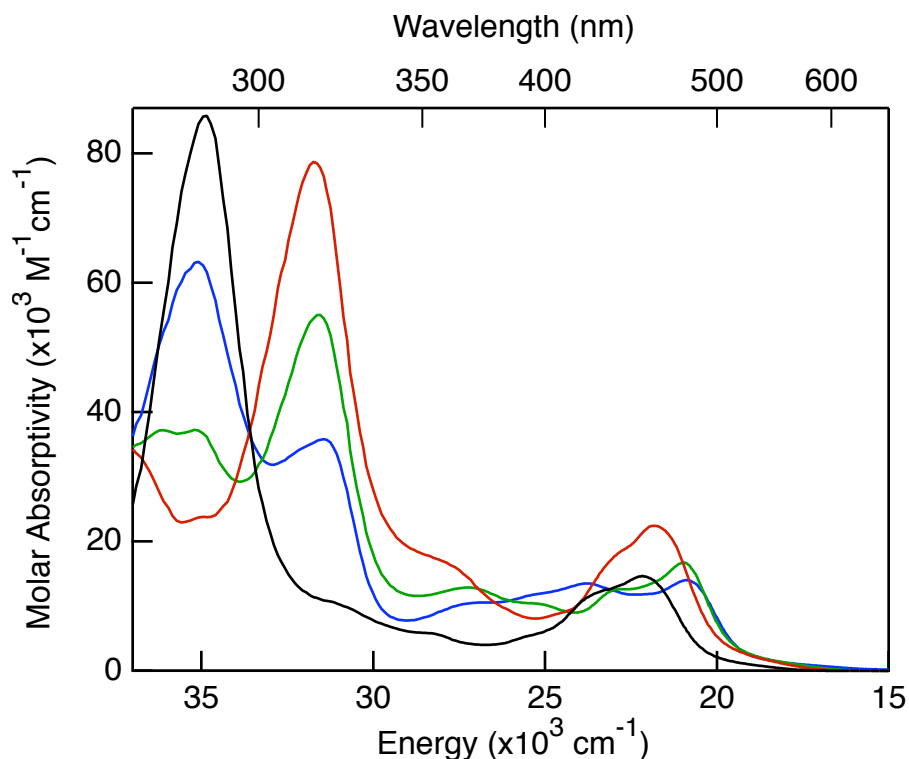


Figure 3-4: Electronic absorption spectra of $[\text{Ru}(\text{bpy})_2(\text{CN-Me-bpy})](\text{PF}_6)_2$ (**1**, blue line), $[\text{Ru}(\text{bpy})(\text{CN-Me-bpy})_2](\text{PF}_6)_2$ (**2**, green line), $[\text{Ru}(\text{CN-Me-bpy})_3](\text{PF}_6)_2$ (**3**, red line), and $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ (black line) in CH_3CN solutions.

a higher energy UV absorption that is not present in complex **3**, but is in $[\text{Ru}(\text{bpy})_3]^{2+}$: this is most likely associated with the unsubstituted bipyridine ligand which is not present in complex **3**. The change in relative intensity of the two bands going from complexes **1** to **3** is consistent with this assignment, as are the relative energies of the two absorption features given the additional

conjugation of the π system of the CN-Me-bpy ligand compared to the unsubstituted bipyridine. Assignments within the charge transfer band are not a straight forward, but can be clarified using electrochemistry. To a reasonable approximation the energy of a metal-to-ligand charge transfer band can be thought of in terms of the energy required to oxidize the metal and reduce the ligand i.e. $E(\text{MLCT}) \approx E(\text{M} \rightarrow \text{M}^+) + E(\text{L} \rightarrow \text{L}^-)$ for $\text{M-L} \rightarrow \text{M}^+ \cdot \text{L}^-$.⁶² For two ligands bound to the same metal, the energy of the MLCT states will therefore correlate with the reduction potential of the ligands. The electrochemical properties of complexes **1-3** have been investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV), the results of which are shown in Figure 3-5 and listed in Table 3-1.

The electron-withdrawing nature of the cyano group is immediately apparent in the trends in the ruthenium oxidation potential across the series. Starting with $[\text{Ru}(\text{bpy})_3]^{2+}$, each successive replacement of 2,2'-bipyridine by CN-Me-bpy in the coordination sphere systematically shifts the oxidation potential of the metal center positive by ca. 130 mV. This electropositive shift in charge density at the ruthenium indicates the generally poorer electron donating ability of the CN-Me-bpy relative to the unsubstituted ligand. For the ligand reductions, first compare the reduction potentials of complex **3** and $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ where there is no question of which ligand is being reduced. The CN-Me-bpy ligand is more easily reduced than the bpy ligand by 480 mV and in both complexes the three reduction potentials are evenly spaced, with 150 to 250 mV between them. Next we compare the two heteroleptic complexes (**1** and **2**) to the two homoleptic complexes. In complex **1** the first reduction potential is much closer in energy to that of complex **3** whereas the second and third reduction potentials are much closer to those of $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$, this combined with the large energy splitting between the first and second reductions show that the first reduction potential is

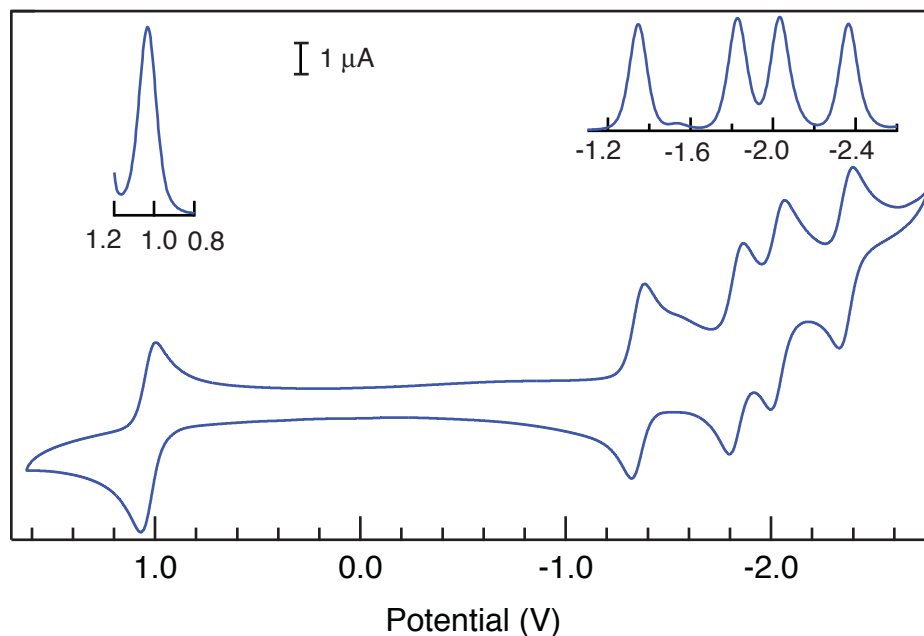


Figure 3-5: Cyclic voltammogram of complex **1** in CH₃CN with 0.1 M TBAPF₆ as the electrolyte. Spectrum was collected using the standard three electrode setup with a platinum working electrode, graphite counter electrode, and a Ag/AgCl reference electrode and is referenced to the ferrocene/ferrocenium redox couple, which was added as an internal standard. The differential pulse voltammogram is shown in the insets.

Table 3-1: Electrochemical Data for Complexes **1-3** and [Ru(bpy)₃](PF₆)₂^a

Complex	E _{1/2} ^{ox}	E _{1/2} ^{red1}	E _{1/2} ^{red2}	E _{1/2} ^{red3}	ΔE (eV) ^b	E ₀ (eV) ^c
[Ru(bpy) ₃](PF ₆) ₂	+0.91	-1.70	-1.89	-2.14	2.61	2.03
(1)	+1.01	-1.38	-1.86	-2.06	2.45	1.82
(2)	+1.13	-1.33	-1.52	-1.99	2.46	1.91
(3)	+1.29	-1.25	-1.40	-1.61	2.54	1.99

^aPotentials are reported in V versus the ferrocene/ferrocenium couple in acetonitrile solution as described in the experimental section.

^bΔE = (E_{1/2}^{ox} - E_{1/2}^{red1}). ^cE₀ from Table 3-3 (page 82).

the reduction of the CN-Me-bpy ligand and the second and third reductions are those of the unsubstituted bpy ligands. A similar comparison can be made for complex **2** which shows that the first and second reductions are the reductions of the two CN-Me-bpy ligands and the third reduction is the reduction of the unsubstituted bpy ligand.

With the electrochemical results in hand, it is now straightforward to assign the features in the electronic absorption spectrum. Specifically, for complex **1**, the lower energy absorption at 479 nm can be assigned to an MLCT transition associated with the CN-Me-bpy ligand whereas the higher energy portion of the absorption band near 420 nm are charge-transfer features coupled to the unsubstituted bpy ligands. The same is true for complex **2**, the lowest energy visible absorption feature is an MLCT transition to the CN-Me-bpy ligands and the higher energy visible absorption is an MLCT transition to the unsubstituted bpy ligand. In complex **3** there is a single visible absorption at 458 nm which obviously corresponds to MLCT transitions to the CN-Me-bpy ligand. It is interesting to note that the MLCT absorption in the symmetric tris complex is much narrower and appears at higher energy than its counterpart in the heteroleptic complexes **1** and **2**. This phenomenon has been seen in other series of heteroleptic ruthenium complexes and the change in breadth of the absorption band is most likely due to the reduction of symmetry (i.e. from nominally D₃ to C₂) while the difference in energy is primarily due to ancillary ligand effects.^{19,50,63}

3.3.3 Steady-State and Time-Resolved Emission Spectroscopies

The room temperature emission spectra for all three complexes are plotted in Figure 3-6a. The emission maxima for [Ru(bpy)₂(CN-Me-bpy)](PF₆)₂, [Ru(bpy)(CN-Me-bpy)₂](PF₆)₂, and [Ru(CN-Me-bpy)₃](PF₆)₂ are at 686 nm, 658

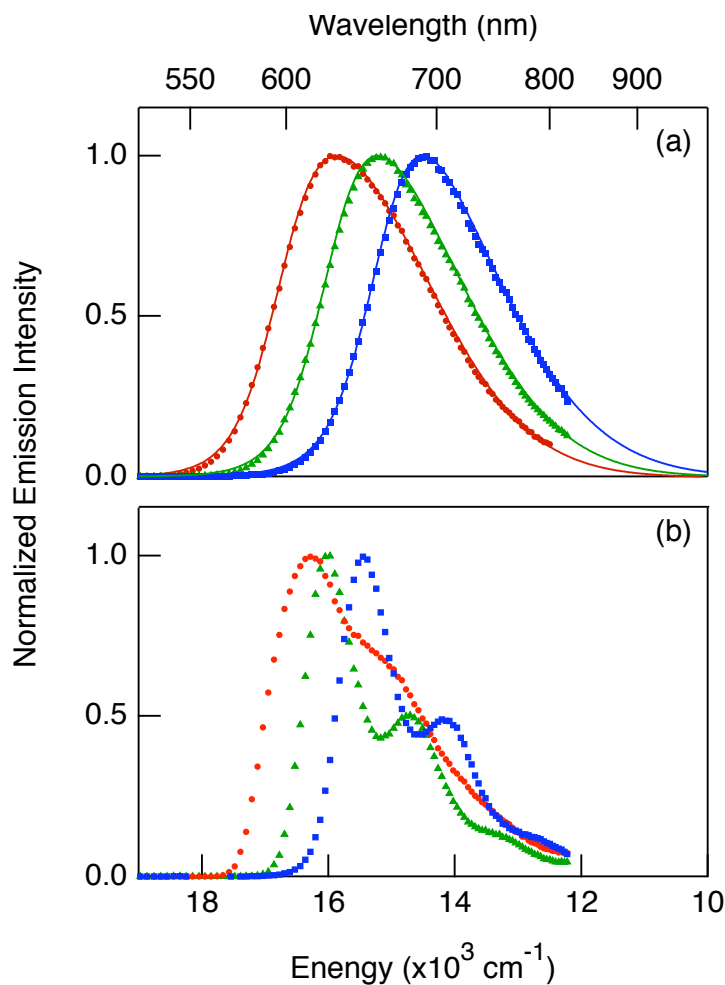


Figure 3-6: Steady-state emission spectra of $[\text{Ru}(\text{bpy})_2(\text{CN-Me-bpy})](\text{PF}_6)_2$ (**1**, blue squares), $[\text{Ru}(\text{bpy})(\text{CN-Me-bpy})_2](\text{PF}_6)_2$ (**2**, green triangles), and $[\text{Ru}(\text{CN-Me-bpy})_3](\text{PF}_6)_2$ (**3**, red circles). (a) Room-temperature spectra acquired in deoxygenated CH_3CN solution. The solid lines correspond to fits to an asymmetric double sigmoidal function – see text for further details. (b) Emission spectra acquired in a 9:2 butyronitrile/propionitrile glass at 80 K.

nm and 626 nm respectively following the same trend as the ruthenium oxidation potentials across the series. Radiative quantum yields for complexes **1-3** were determined relative to the $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ standard, and are listed in Table 3-2. As the emission energy increases the quantum yield of the complexes also

Table 3-2: Photophysical Data for Complexes **1-3** and [Ru(bpy)₃](PF₆)₂

Complex	λ_{em} (nm)	Φ^a	k_{obs}^b ($\times 10^5 \text{ s}^{-1}$)	$k_r^{a,c}$ ($\times 10^4 \text{ s}^{-1}$)	$k_{\text{nr}}^{a,d}$ ($\times 10^5 \text{ s}^{-1}$)
[Ru(bpy) ₃](PF ₆) ₂	618	0.095 ± 0.003	10.5 ± 0.10	10.0 ± 0.30	$9.53 \pm .08$
(1)	686	0.13 ± 0.004	6.41 ± 0.08	8.33 ± 0.25	5.58 ± 0.17
(2)	658	0.27 ± 0.008	3.82 ± 0.06	10.3 ± 0.31	2.79 ± 0.08
(3)	626	0.40 ± 0.012	2.86 ± 0.04	11.4 ± 0.35	1.71 ± 0.05

^a Error bars based on the 3% uncertainty in the [Ru(bpy)₃](PF₆)₂ quantum yield standard. ^b Uncertainty determined by the standard deviation of multiple measurements. ^c $k_r = \Phi_r \cdot k_{\text{obs}}$. ^d $k_{\text{nr}} = k_{\text{obs}} - k_r$.

increases, going from 13% in **1** to 40% in **3**. While these quantum yields may seem unusually large for ruthenium polypyridyl complexes (especially that of complex **3**), many ruthenium tris bipyridine⁴¹ and tris phenanthroline⁴⁷ complexes containing aromatic substituents exhibit radiative quantum yields on this order. In addition the recent correction in the absolute value for Φ_r from 6.2% to 9.5% for [Ru(bpy)₃](PF₆)₂ must be borne in mind when comparing values in the literature.³⁷

To obtain more quantitative insights into the ³MLCT excited states of this system we carried out a single mode spectral fitting analysis using Equation 2 as described by Meyer and coworkers.^{39,64} The room temperature emission spectra are typical of molecules in this class, showing virtually no vibrational fine structure; the spectra can be fit equally well with a wide range of the four parameters (E_0 , S_M , $\hbar\omega_M$, and $\Delta\bar{\nu}_{0,1/2}$). We therefore acquired low temperature emission spectra (Figure 3-6b) which exhibit sufficient fine structure to yield well-

defined values for all four parameters. Following the example of Claude and Meyer, the value of $\hbar\omega_M$ was assumed to be temperature independent, so the room temperature spectra were refit using the low temperature value of $\hbar\omega_M$ as a fixed value. Using this approach, well defined (<10% variation) values for $^3\text{MLCT}$ zero-point energy (E_0), Huang-Rhys factor (S_M), and the spectral bandwidth ($\Delta\bar{\nu}_{0,1/2}$) could be determined for the room-temperature spectra. Spectral fitting parameters for complexes **1-3** and $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ are listed in Table 3-3.

Table 3-3: Spectral Fitting Results for Complexes **1-3** and $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$

Complexes	Low Temperature ^{a,b}			
	E_0 (cm ⁻¹)	S_M	$\hbar\omega_M$ (cm ⁻¹)	$\Delta\bar{\nu}_{0,1/2}$ (cm ⁻¹)
(1)	15409 ± 40	0.67 ± 0.06	1288 ± 40	985 ± 60
(2)	15969 ± 50	0.69 ± 0.05	1286 ± 40	950 ± 50
(3)	16335 ± 70	0.84 ± 0.07	1365 ± 90	1316 ± 90
$[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$	17220 ± 50	1.05 ± 0.06	1345 ± 40	948 ± 60
	Room Temperature ^{b,c}			
	E_0 (cm ⁻¹)	S_M	$\hbar\omega_M$ (cm ⁻¹) ^d	$\Delta\bar{\nu}_{0,1/2}$ (cm ⁻¹)
(1)	14653 ± 50	0.65 ± 0.1	1288	1676 ± 110
(2)	15409 ± 50	0.73 ± 0.09	1286	1674 ± 120
(3)	15972 ± 70	0.79 ± 0.11	1365	1813 ± 150
$[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$	16366 ± 50	1.01 ± 0.08	1345	1742 ± 120

^a Fitting results for 80 K emission spectra in 9:2 butyronitrile:propionitrile.

^b Error bars represent an approximate range of visually equivalent fits. ^c Fitting results for room temperature emission spectra in CH₃CN, using a fixed value of $\hbar\omega_M$ based on the low temperature data. See text for details.

The fitted values for E_0 for all three complexes are very close to the observed emission maxima, indicating that the $v^* = 0 \rightarrow v = 0$ transition is the dominant contribution to the observed emission spectrum. The Huang-Rhys factor is a measure of the vibrational overlap between the excited state and the ground state and is proportional to $(\Delta Q)^2$, where ΔQ is the nuclear displacement between the excited state and the ground state. This makes S_M a useful parameter for gauging the amount of structural distortion in the excited state relative to the ground state.⁴¹ Comparing the room temperature Huang-Rhys factor for complexes **1** - **3** it is difficult to draw any conclusions concerning the differences across the series since the variations in S_M are within the uncertainties of the fits.

What is important to note, however, is that all three complexes have S_M values that are significantly lower than for $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$. This is not simply a consequence of the value of $\hbar\omega_M$ since the fitted value of $\hbar\omega_M$ for complex **3** is actually slightly larger than for $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ yet still exhibits a smaller value of S_M . This result indicates that the three cyano substituted complexes have excited states which are less displaced relative to the ground state compared to $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$, which is evidence that the emissive $^3\text{MLCT}$ excited state is strongly coupled on to the peripheral cyano group.

The lifetimes of complexes **1-3** were also determined using nanosecond time-resolved emission. From the lifetimes and quantum yields, radiative and non-radiative decay rates for all three complexes were calculated (Table 3-2). The most significant difference between the complexes is the value of k_{nr} . As predicted by the energy gap law⁶⁴, we see an inverse relationship between the zero-point energy differences and the rate of non-radiative decay back down to the ground state. The smaller non-radiative decay rate in the cyano substituted complexes as compared to $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ suggests that the excited state in

these complexes is delocalized onto the cyano group leading to a smaller excited state geometry distortions and less vibrational overlap between the long lived excited state and the ground state; this is wholly in agreement with the smaller values of S_M for complexes **1-3** compared to $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ discussed above. The differences in radiative decay rate (k_r) are less dramatic than what is observed for k_{nr} . Radiative decay theory specifies a proportionality between k_r and the product $\mu^2 \cdot E_0^3$ where μ is the transition dipole moment and E_0 is the energy gap.⁶⁵ In this context we note that, for complexes **1** through **3**, as the energy gap increases the radiative rate constant also increases, which is consistent with radiative decay theory. We also note that the energy gap for $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ is slightly larger than complex **3**, yet the radiative decay rate is smaller than that in complex **3**. This apparent discrepancy can be explained by considering the transition moment dipole in each complex. As discussed above, the charge transfer excited state in $[\text{Ru}(\text{CN-Me-bpy})_3](\text{PF}_6)_2$ is most likely delocalized onto the cyano group: this would also give rise to a larger transition dipole moment for emission from this state. This conclusion is consistent with the larger extinction coefficients for the $^1A_1 \rightarrow ^1\text{MLCT}$ absorption for this series as compared to $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ (Figure 3-4). Previous work from our lab on a series of aryl-substituted ruthenium (II) polypyridyl complexes revealed similar trends in k_r and k_{nr} that were attributed to an extended π system in the MLCT manifold.⁴¹

3.3.4 Time-Resolved Electronic Absorption Spectroscopy

Nanosecond transient absorption spectroscopy is another important tool for characterizing the lowest energy excited state in transition metal complexes, particularly as a precursor to ultrafast spectroscopic measurements.⁶⁶ Transient absorption spectra of complexes **1-3** acquired following $^1A_1 \rightarrow ^1\text{MLCT}$ excitation

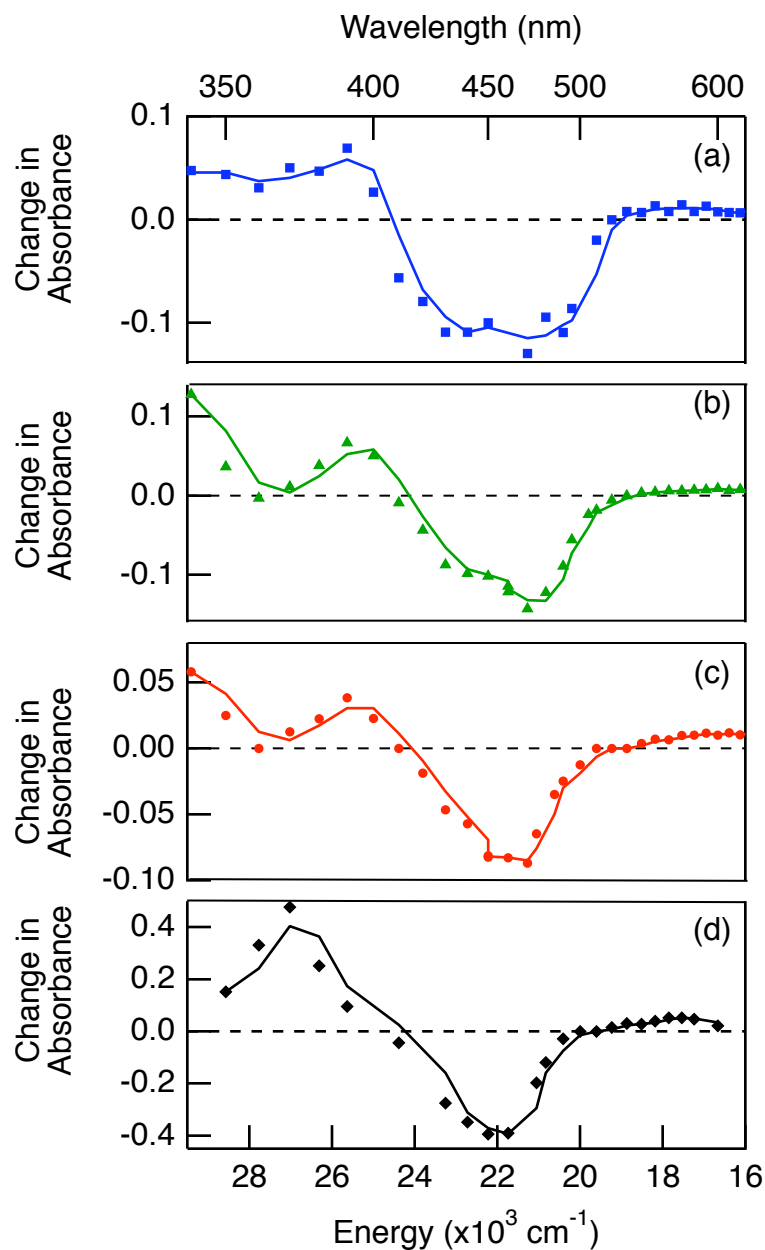


Figure 3-7: Nanosecond time-resolved differential absorption spectra acquired in room-temperature CH_3CN solution for (a) $[\text{Ru}(\text{bpy})_2(\text{CN-Me-bpy})](\text{PF}_6)_2$ (**1**), (b) $[\text{Ru}(\text{bpy})(\text{CN-Me-bpy})_2](\text{PF}_6)_2$ (**2**), (c) $[\text{Ru}(\text{CN-Me-bpy})_3](\text{PF}_6)_2$ (**3**), and (d) $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$. The individual points correspond to the amplitudes of fits of the kinetics data to single-exponential decay models; a smoothed solid line has been included in each plot to guide the eye.

are shown in Figure 3-7. The most striking aspect of Figure 3 is the similarity among the three CN-Me-bpy complexes as compared to $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$, especially in the near UV region of the spectrum. While changes in the transient absorption spectrum are affected by both differences in the ground state and excited state absorption, regions of positive absorption are dominated by the excited state absorption. The red shift of the near UV absorption in complexes **1-3** relative to $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ suggests that the nature of the excited state in complexes **1-3** is different from that found in $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$. This is in agreement with the electrochemical data, which showed that CN-Me-bpy was the lowest energy ligand in complexes **1-3**. There are three principle features observed in the spectra: a strong net absorption in the near-UV, a strong bleach in the mid-visible, and a weak absorption extending into the red. This overall pattern is typical of what is observed for the excited state spectra of Ru^{II} polypyridyl complexes. Since an MLCT excited state can be thought of in terms of an oxidized metal and a reduced ligand (*vide supra*), spectroelectrochemistry can be quantitatively used as a guide to determine the specific origins of each of these signals.

The change in absorbance upon oxidation of complex **1** is shown in Figure 3-8b. When the Ru^{2+} is oxidized to Ru^{3+} , the dominant feature in the differential absorption spectrum is the loss of the MLCT absorption band in the visible. The $\pi \rightarrow \pi^*$ absorption of the CN-Me-bpy ligand, which occurs at ~ 315 nm in the ground state spectrum (Figure 3-4) shifts to ~ 340 nm when coordinated to Ru^{3+} . The weak absorption at 725 nm shown in the inset can be assigned as an LMCT absorption based on comparison to other reported Ru^{3+} polypyridyl complexes.⁶⁷

When the CN-Me-bpy ligand is reduced (Figure 3-8c) strong absorptions associated with the radical anion of the ligand are seen across the UV and visible portions of the spectrum. A small bleach is also seen in the mid-visible due to

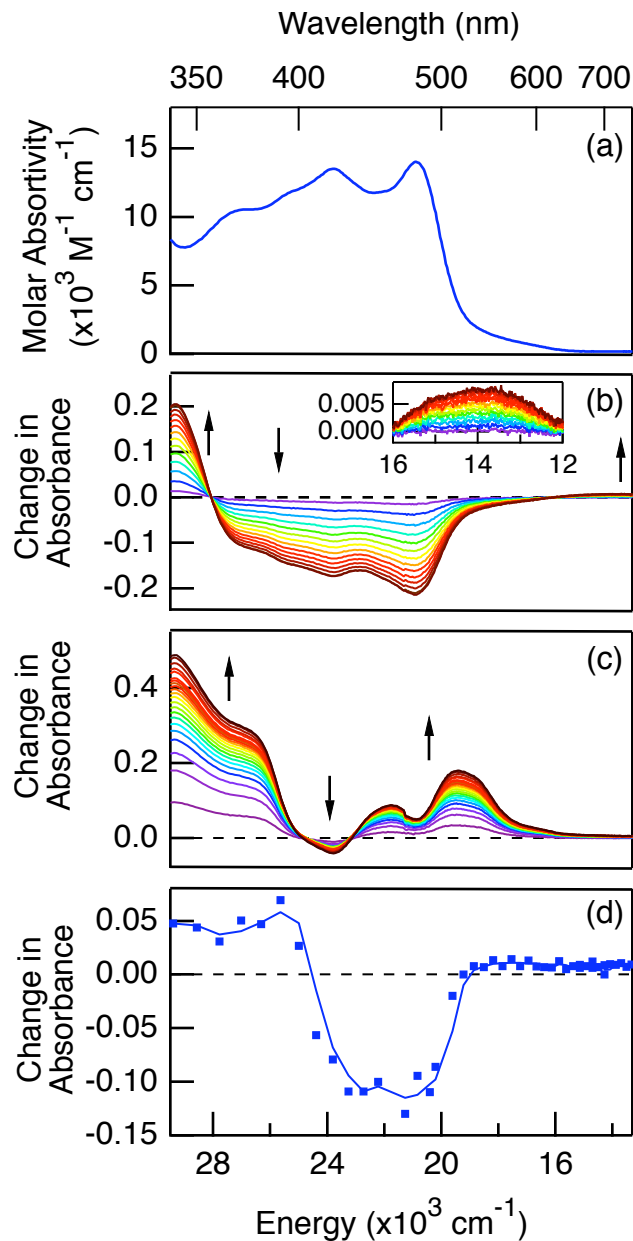


Figure 3-8: (a) Ground state absorption spectrum for $[\text{Ru}(\text{bpy})_2(\text{CN-Me-bpy})](\text{PF}_6)_2$ (**1**) in room-temperature CH_3CN solution. (b) Oxidative difference spectra acquired at an applied potential of +1.55 V versus Ag/AgCl. The inset corresponds to an expanded view of the low-energy portion of the spectrum. (c) Reductive difference spectra acquired at an applied potential of -1.05 V versus Ag/AgCl. (d) Time-resolved differential absorption spectrum of compound **1** following ca. 10 ns excitation at 500 nm.

the loss of the charge transfer transition to the CN-Me-bpy that has undergone reduction.

The transient absorption spectrum of complex **1** in Figure 4d can now be qualitatively compared to the oxidative and reductive spectra to identify the origins of the different transitions. The spectroelectrochemical spectra cannot be quantitatively combined to give the transient absorption spectrum but a comparison between the features of the spectroelectrochemical spectra and the transient absorption spectra can offer insight to the origin of the features of the transient absorption spectra. In the mid visible region of both the oxidative and reductive spectra there is a negative feature that correspond to the loss of metal-to-ligand charge transfer absorption band(s). The negative feature in the transient absorption spectrum is, therefore due to the loss of metal-to-ligand charge transfer absorption features in the excited state. The negative bleach feature in the time resolved differential absorption spectrum in the 430 to 520 nm region indicates that the ground state extinction coefficient is larger than the CN-Me-bpy radical absorption in that wavelength region. The intense absorption in the UV region of the transient absorption spectrum is due to the CN-Me-bpy radical anion. The fact that the time resolved differential absorption spectrum is a net absorption in this region indicates that the extinction coefficient of the CN-Me-bpy excited state absorption is significantly larger than the ground state MLCT absorption features in the region of 360 to 410 nm. For probe wavelengths blue of 360 nm both the oxidative and reductive contributions give rise to a positive absorption feature. Finally, wavelengths red of the ground state/excited state isosbestic point at 520 nm has contributions from both the CN-Me-bpy radical anion as well as LMCT transition(s) from the ancillary bpy ligands. Corresponding data for complexes **2** and **3** can be found in Figures S4 and S5 in the supporting information. While there are qualitative differences in the spectra,

due to differences in the ground state absorption spectra, the same conclusions can be drawn for the transient absorption spectra of complexes **2** and **3**.

3.3.5 Nanosecond Step-Scan Time-Resolved Infrared Spectroscopy

As mentioned in the introduction, the primary goal in developing this series of compounds was to use them as probes for vibrational relaxation dynamics in charge-transfer excited states. Similar to our protocol for studying the ultrafast absorption spectroscopy of transition metal chromophores,⁶⁶ it is important to fully characterize the spectroscopic properties of the long lived excited state as a foundation for interpreting data acquired on shorter timescales. For vibrational spectroscopy, both time-resolved resonance Raman (TR³) and time-resolved infrared (TRIR) methods have been developed; each technique has advantages and disadvantages. In TR³ visible light is used to create as well as resonantly scatter off the excited state. The resonance condition means that only those vibrations which are coupled to the excited electronic transition are enhanced. This can vastly simplify the spectrum and assigning the nature of the excited state, but at the same time gives only a partial picture of the excited state vibrational structure. From a technical perspective, interference from emission can make using this technique on highly emissive compounds challenging. With TRIR the entire vibrational spectrum of the excited state is sampled using an infrared probe beam: this provides a more complete picture of the excited-state vibrational structure but can make interpretation more difficult. TRIR has been used to characterize the vibrational structure of long lived excited states under a variety of circumstances.⁶⁸⁻⁷⁰ Previous work from our group employed TRIR on a series of heteroleptic ruthenium polypyridyl complexes to identify on which ligand the emissive excited state was localized.¹⁹ Relevant to the present study, Meyer, Palmer, and coworkers examined a series of ruthenium polypyridyl

Table 3-4: Step-Scan IR and DFT Results for Complexes 1-3

Step-Scan IR	$\bar{\nu}(\text{CN})_{\text{GS}} (\text{cm}^{-1})^a$	$\bar{\nu}(\text{CN})_{3\text{MLCT}} (\text{cm}^{-1})^b$	$\Delta\bar{\nu} (\text{CN}) (\text{cm}^{-1})^c$
(1)	2238	2200	-38
(2)	2238	2200	-38
(3)	2239	2202	-37
DFT	$\bar{\nu}(\text{CN})_{\text{GS}} (\text{cm}^{-1})^{d,e}$	$\bar{\nu}(\text{CN})_{3\text{MLCT}} (\text{cm}^{-1})^{e,f}$	$\Delta\bar{\nu} (\text{CN}) (\text{cm}^{-1})^c$
(1)	2272.01 (as)	2216.06 (as)	-56 (as)
	2272.73 (s)	2237.52 (s)	-35 (s)

^a Ground state absorption maximum in CH_3NO_2 solution (4 cm^{-1} resolution).

^b Excited state differential absorption maximum in CH_3NO_2 solution (4 cm^{-1} resolution). ^c $\Delta\bar{\nu} (\text{CN}) = \bar{\nu}(\text{CN})_{3\text{MLCT}} - \bar{\nu}(\text{CN})_{\text{GS}}$. ^d Frequency calculation results on the ground state optimized geometry. ^e (s) is the totally symmetric CN stretching frequency, (as) is the asymmetric CN stretching frequency.

^f Frequency calculation results on the lowest energy triplet state optimized geometry.

complexes substituted with diethyl ester and diethyl amide groups as infrared tags.^{71,72} These works were able to demonstrate localization of the long-lived excited state on a single bipyridine ligand for both the heteroleptic and homoleptic complexes. Interestingly their data and analysis clearly showed that in the case of 4-monosubstituted bipyridine ligands, the long-lived excited state was primarily localized on the substituted pyridine ring rather than being symmetrically distributed across the entire ligand.

The nanosecond step-scan IR spectra of complex **1** are shown in Figure 3-9. The ground state exhibits a single CN band at 2238 cm^{-1} . A group theoretical analysis indicates that both the A_1 (symmetric) and B_2 (asymmetric) CN vibrations of the CN-Me-bpy ligand should be IR active. Ground state DFT frequency calculations on complex **1** (Table 3-4) does predict two bands, but they are calculated to be separated by < 1 cm^{-1} . The single, fairly sharp feature in

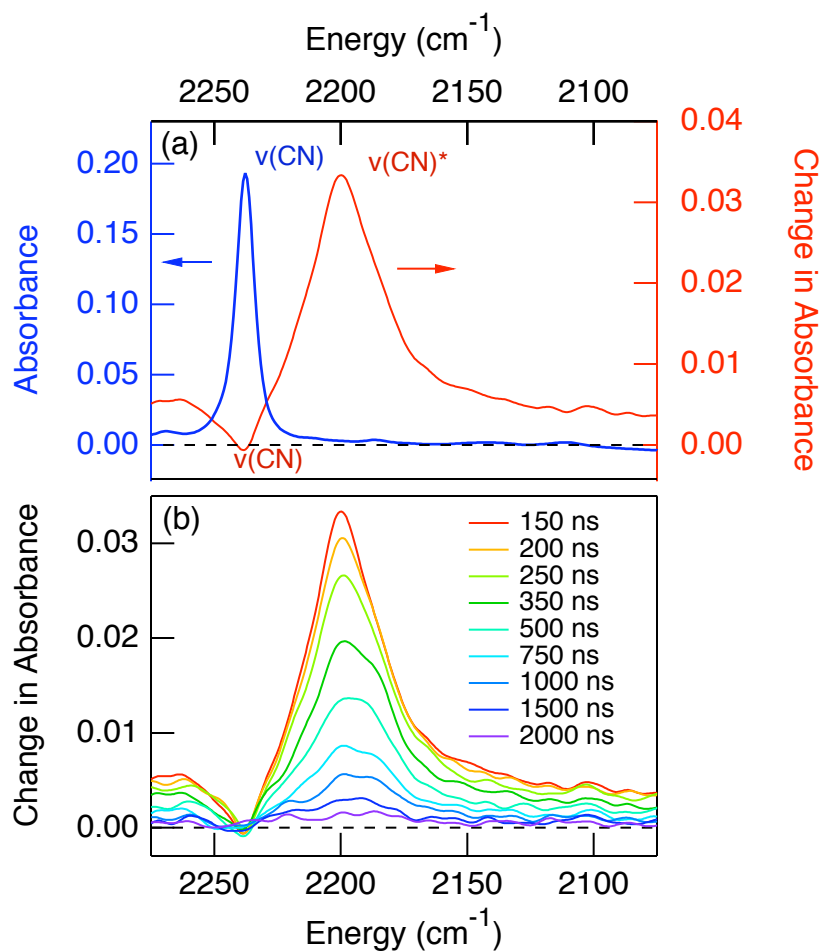


Figure 3-9: Steady-state and time-resolved infrared absorption data for [Ru(bpy)₂(CN-Me-bpy)](PF₆)₂ (**1**) in room-temperature CH₃NO₂ solution. (a) Comparison of the ground-state (blue line) and step-scan infrared differential absorption data acquired at a time delay of 150 ns following ca. 10 ns excitation at 540 nm (red line). The ~ 40 cm⁻¹ red-shift in the CN stretching frequency reflects the presence of an electron in the π^* orbital of the CN-Me-bpy ligand in the ³MLCT excited state. (b) Nanosecond step-scan infra-red spectra as a function of time following ca. 10 ns excitation at 540 nm. The kinetics describing the decrease in amplitude of the excited-state infrared absorption signal are within experimental error of the time-resolved emission and absorption data for compound **1** and are therefore assigned to relaxation of the ³MLCT excited state.

Figure 3-9a therefore presumably contains both of these vibrations; their accidental degeneracy is an indication of (relatively) weak coupling of these two modes in the ground state. This is in stark contrast to the vibrational spectra in the $^3\text{MLCT}$ excited state. The CN stretching frequency is observed to shift 38 cm^{-1} lower in energy relative to the ground state. Moreover the band is significantly broadened. The bathochromic shift is consistent with the population of a π^* antibonding orbital, which if coupled to the cyano group should reduce the CN bond order; the magnitude of the shift is comparable to those seen by Meyer and coworkers for amide and ester substituted systems.^{71,72}

The increased breadth of the absorption suggests that the coupling between the two cyano groups is greater in the excited state, leading to a larger difference in energy between the symmetric and asymmetric stretches. This interpretation is supported by DFT frequency calculations on the lowest energy triplet state of complex **1** which show that $\Delta\bar{\nu}$ has increased to $\sim 20\text{ cm}^{-1}$ in the emissive $^3\text{MLCT}$ state. This can be explained by considering the interaction of the π -type orbitals of the cyanide groups with the π -type orbitals of the bipyridine ring. For complex **1**, Figure 3-10 shows the highest energy π bonding orbital and lowest energy π^* antibonding orbital localized on the CN-Me-bpy ligand. Figure 3-10a shows that the π bonding orbitals of the cyanide groups have little or no interaction with the π bonding orbital of the bipyridine ring and therefore there is little coupling between the cyanide groups and the bipyridine ring and between the two cyanide groups in the ground state. Figure 3-10b shows that the π^* antibonding orbitals of the cyanide groups interact much more strongly with the π^* antibonding orbital on the bipyridine ring, leading to an increased coupling between the cyanide groups and the bipyridine ring and between the two cyanide groups in the excited state. The difference in mixing is consistent with the energies of the π bonding and π^* antibonding orbitals on the cyanide group. The

C≡N bond is significantly stronger than the C=C (and C=N) bonds within the bipyridine ring. While the cyanide π^* antibonding orbital is of an appropriate energy and symmetry to mix well with the π^* orbital on the bipyridine ring, the π bonding orbital of the cyanide is lower in energy than the π orbital on the bipyridine ligand, which leads to weaker (or no) mixing between the two.

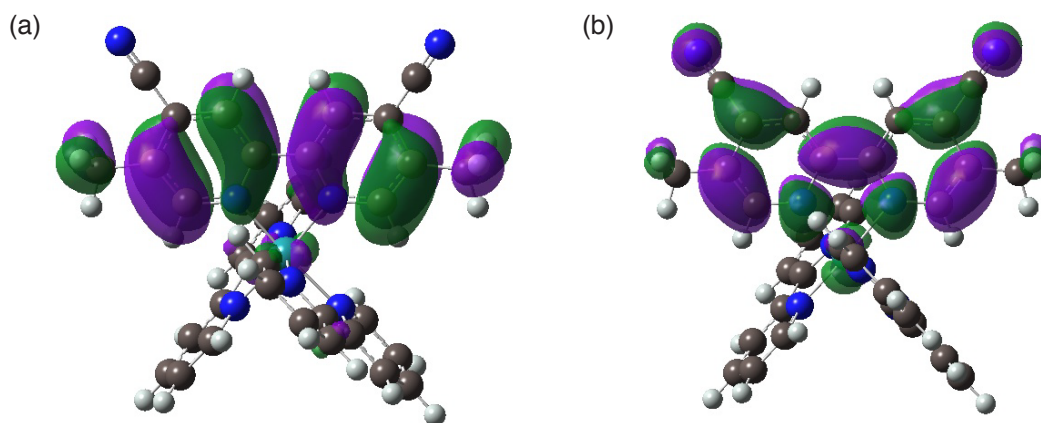


Figure 3-10: (a) Highest energy π bonding orbital on CN-Me-bpy in the geometry optimized ground state of complex **1**. (b) Lowest energy π^* antibonding orbital on CN-Me-bpy in the geometry optimized lowest energy triplet state of complex **1**.

The SSIR results for complexes **2** and **3** are summarized in Table 3-4; the spectra can be found in Figures A-8 and A-9. Within experimental error the ground state and excited state absorption maxima are at the same energy in all three complexes. This is compelling evidence that the long-lived excited state is localized on a single CN-Me-bpy ligand in all three complexes rather than being delocalized over multiple ligands in complexes **2** and **3**. This is in agreement with previous step-scan IR studies^{71,72} as well other experimental evidence showing a localized long lived excited state in ruthenium polypyridyl systems.

3.4 Concluding Comments.

This work describes the synthesis and spectroscopic characterization of a series of cyano substituted ruthenium polypyridyl complexes. While these complexes could not be synthesized in reasonable amounts by combining the ligand and ruthenium starting material under standard conditions, the chemistry-on-the-complex approach proved useful. By first synthesizing the chloro substituted ruthenium complexes and using a palladium catalyzed cyanation reaction it was possible to prepare and isolate all three CN-containing members of the $[\text{Ru}(\text{bpy})_{3-n}(\text{CN-Me-bpy})_n](\text{PF}_6)_2$ series with reasonable yield and of a high degree of purity.

The ground- and $^3\text{MLCT}$ -state properties of the $[\text{Ru}(\text{bpy})_{3-n}(\text{CN-Me-bpy})_n]^{2+}$ series have been characterized using electrochemical, optical, and infrared spectroscopies. As expected, the CN stretch of the CN-Me-bpy ligand sits in a well-isolated region of the infra-red, allowing for an unambiguous analysis of its behavior in the ground and excited state(s) of these compounds. The data we have presented definitively show that the lowest energy charge-transfer states in all three compounds are localized on the CN-containing ligand. In particular, time-resolved electronic and infra-red absorption spectroscopies reveal an identical optical signature for the $^3\text{MLCT}$ state for each compound in the series; in the case of the infra-red measurements, the common shift in the CN stretching frequency indicates that (a) the CN group is strongly coupled to the π^* system of the bipyridyl ligand, and (b) that the $^3\text{MLCT}$ state is localized on a single ligand on the vibrational time scale, even in the case of the tris-homoleptic complex $[\text{Ru}(\text{CN-Me-bpy})_3]^{2+}$. The unexpected increase in spectral bandwidth of the CN vibration(s) further revealed that the two CN groups of the ligand are more strongly coupled to each other in the $^3\text{MLCT}$ state relative to the ground state.

All of the features just enumerated underscore the potential utility of these

compounds as probes of vibrational dynamics in charge-transfer excited states. With the ground- and excited-state spectroscopic features of this series fully characterized, we believe that an examination of vibrational relaxation as well as the more elusive process of intramolecular vibrational redistribution will now be accessible through the combined application of femtosecond time-resolved electronic and infra-red absorption spectroscopies. Studies along these lines are currently underway.

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Chapter 4: Probing Vibrational Relaxation Dynamics With Ultrafast Electronic and Infrared Absorption Spectroscopy

4.1 Introduction

A number of important photophysical and photochemical processes occur on ultrafast timescales.¹⁻⁵ The very rapid rates of these reactions suggest that they are occurring from vibrationally excited "hot" states and are possibly in competition with vibrational relaxation of that hot state. In most charge transfer complexes, a majority of the energy from an absorbed photon is dissipated non-radiatively and the relaxation from the initially excited state to the long lived excited state is entirely a non-radiative process.

Despite its important role in excited state dynamics, there has not been much investigation into the mechanism of non-radiative decay in charge transfer excited states of transition metal complexes. As discussed in Chapter 1, there is even question as to the timescale for ruthenium(II) polypyridyl systems. Chergui and coworkers conclude from their fluorescence upconversion study on $[\text{Ru}(\text{bpy})_3]^{2+}$ that the thermalized $^3\text{MLCT}$ state is formed within 15 ± 10 fs and that vibrational relaxation occurs by very rapid IVR to low frequency vibrational modes, such as metal ligand bond stretches, followed by slower transfer to solvent.⁶ Contradicting this, Browne and McGarvey monitored the growth of vibrational features of the thermalized $^3\text{MLCT}$ state in $[\text{Ru}(\text{bpy})_3]^{2+}$ with time resolved resonance Raman. Their experiments showed that the formation of the thermalized $^3\text{MLCT}$ state was complete after 20 ps.⁷ A picosecond rate of vibrational relaxation has also been observed in many other transition metal complexes,⁸⁻¹³ which suggests that the interpretation of Browne, McGarvey and coworkers is the correct one

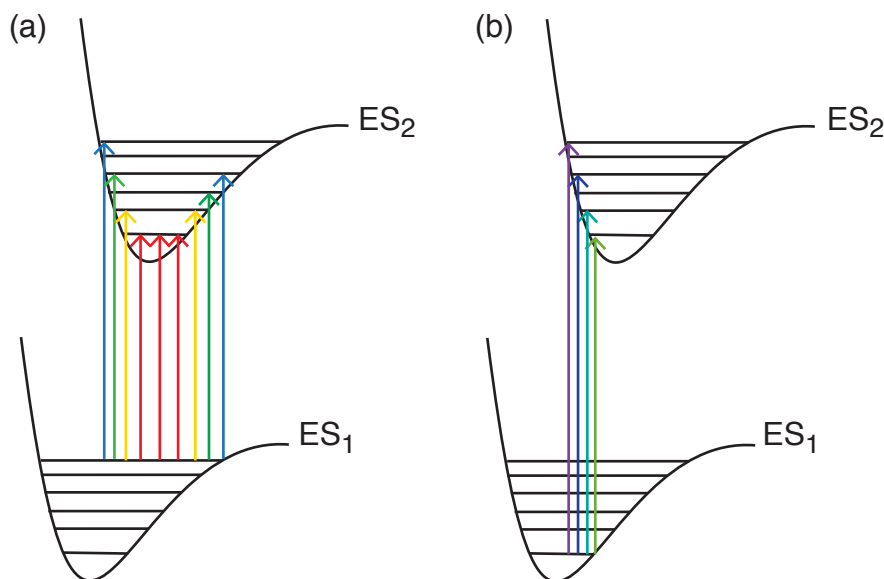


Figure 4-1: Potential energy surfaces illustrating the available Franck-Condon transitions between the optically prepared excited state (ES_1) and a higher lying excited state (ES_2) when (a) ES_1 is in a excited vibrational (hot) state and (b) ES_1 is in a thermalized vibrational (cooled) state

In ultrafast spectroscopy, information about vibrational relaxation from the initially excited Franck-Condon state to the long lived excited state is generally inferred from small changes in electronic absorption spectroscopy.¹² After all possible electronic transitions are assigned, small changes in the spectrum over time can be assigned to vibrational relaxation. These changes are usually seen as a narrowing of an absorption feature over time, but the nature of the change depends on the relative displacement and slope of the two excited state potential energy surfaces (Figure 4-1). A more direct way to monitor the vibrational relaxation is to use infrared spectroscopy, where the vibrational state of the molecule is directly monitored. With infrared spectroscopy, vibrational relaxation is generally observed as a narrowing and blue shifting of the infrared spectrum.

This is because the Franck-Condon excitation creates a distribution of vibrationally excited states which all relax to a single $v' = 0$ vibrational state which causes the spectrum to narrow and the anharmonic nature of the potential surface means the vibrational spacing is smaller at the top of the potential well and larger at the bottom, leading to a blue shift. Because transitions are occurring within a single electronic state, rather than between two electronic states, the nature of the signal is only a function of a single electronic state.

Electronic absorption and infrared spectroscopy can offer complementary information about excited state dynamics. For example, work in our group on the ultrafast absorption spectroscopy of $\text{Cr}(\text{acac})_3$ (acac = acetylacetonate) showed that upon excitation into the $^4\text{T}_2$ ligand field state, the ^2E state was formed very rapidly (>100 fs).¹² Monitoring excited state absorptions of the vibrational relaxation time on ^2E surface was 1.1 ± 0.01 ps and ground state recovery was ~ 700 ps. Maçôas and coworkers studied $\text{Cr}(\text{acac})_3$ by ultrafast infrared spectroscopy, monitoring the excited state ligand C=C and C=O stretches, and found biexponential ground state recovery kinetics.¹⁴ A majority of the excited state population (70-85%) had a ground state recovery time of 15 ps and a small fraction has a ground state recovery rate of 700-900 ps. Using the results from the electronic absorption spectroscopy above, the authors theorized that the 15 ps component was ground state recovery from the $^4\text{T}_2$ state, which was formed through back intersystem crossing, and the 700-900 ps component was the same ground state recovery from the ^2E state seen in the electronic absorption spectroscopy.

Maçôas and coworkers have also collected time-resolved infrared data on $\text{Fe}(\text{acac})_3$.¹³ Unlike the chromium system, there was not any reported time-resolved electronic absorption available for the iron system. Without any information about the electronic excited state(s) involved, the authors were

unable to definitively assign any of the kinetic features beyond ground state recovery. These examples show that time-resolved electronic absorption and time-resolved infrared absorption are complementary experimental techniques. When used together, the two techniques can give more information about the excited state dynamics than either technique alone can provide.

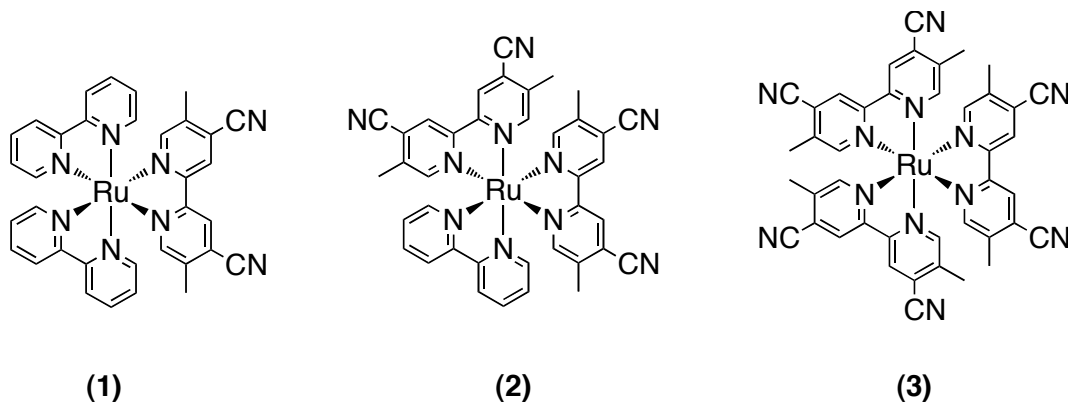


Figure 4-2: The series of cyano-substituted ruthenium(II) complexes investigated in this chapter.

This chapter discusses vibrational relaxation in the series of cyano-substituted ruthenium(II) bipyridine complexes introduced in Chapter 3, shown in Figure 4-2. Computational methods are used to identify the nature of the initially excited Franck-Condon state and the long lived, thermalized $^3\text{MLCT}$ states of the three complexes have been characterized in Chapter 3. In this chapter, both ultrafast electronic absorption and infrared absorption are used monitor the relaxation process from the initially excited state to the long lived excited state.

4.2 Experimental

4.2.1 Calculations

Calculations on complexes **1-3** were performed using the Gaussian 03 software package.¹⁵ Geometry optimizations were done on the ground state using a spin unrestricted formalism at the B3LYP/LANL2DZ level of theory.^{16,17} No symmetry restrictions were placed on the geometry optimizations. The effects of the acetonitrile solvent environment were included by using the polarizable continuum model (PCM). Frequency calculations were performed on the optimized structures to ensure that these geometries corresponded to global minima. No imaginary frequencies were obtained for any of the optimized geometries. The first 80 electronic transitions (singlets and triplets) of the optimized structures were calculated by time dependent DFT using spin unrestricted B3LYP/LANL2DZ. The orbitals contributing to each transition were visualized using GaussView. The cartesian coordinates for the optimized geometries can be found in Appendix D.

4.2.2 Time-Resolved Spectroscopic Measurements

Time-resolved infrared absorption data was collected by Professor Antonín Vlček at the Rutherford Appleton Laboratory. A description of the experimental setup and data collection can be found in the literature^{18,19}. Samples were prepared by dissolving the complexes in nitromethane so that, in a 0.1 mm pathlength cell, the absorbance was approximately 0.7 at the excitation wavelength. This resulted in a ground state infrared absorption of 0.005 to 0.01 for the CN vibration. The samples were excited at two wavelengths: 400 nm and 490 (**1** and **2**) or 475 (**3**). The raw data was background corrected with a spline function in IGOR pro. The energy axis was calibrated using Equation 4-1, where d is dispersion, a and b are pixels, and $\bar{\nu}_a$ and $\bar{\nu}_b$ are the energies (in cm^{-1}) of

pixels a and b and Equation 4-2, where $\bar{\nu}_i$ is the energy (in cm^{-1}) of pixel i, λ_a is the wavelength of pixel a (in cm). Kinetic traces were created by plotting the peak intensity or peak area vs time.

$$d = \frac{\frac{1}{\bar{\nu}_a} - \frac{1}{\bar{\nu}_b}}{b - a} \quad 4-1$$

$$\bar{\nu}_i = \frac{1}{[\lambda_a + d(a - i)]} \quad 4-2$$

Time resolved electronic absorption data was collected by Allison Brown here at Michigan State University. A general description of the experimental setup and data collection and processing has previously been published.^{12,20} Spectrophotometric grade acetonitrile, which had been freeze-pump-thaw degassed prior to use, was used as the solvent. Samples were prepared with an absorbance of 0.4 - 0.7 at the excitation wavelength in air-free 1 mm pathlength cells. Stability of the samples was monitored by electronic absorption spectroscopy before and after each measurement. Compounds **1** and **2** showed no changes in their UV-visible absorption spectra and no other signs of decomposition, so the samples were used for several days before replacing. Compound **3** showed a small change in the UV-vis spectrum over a two day period, so a fresh sample of **3** was prepared each day.

4.3 Results and Discussion

4.3.1 Time Dependent DFT

In the heteroleptic complexes (**1** and **2**) it is possible for the Franck-Condon state to be localized on either of the two ligands. Interpretation of the spectroscopic data requires knowledge of where the initial excited state is localized for each excitation wavelength. Initial attempts to use resonance

Raman spectroscopy to answer this question were unsuccessful because of interference from the sample emission. Instead, time dependent DFT calculations were used to visualize the orbital contributions to each transition. The ground state geometries for each complex were first optimized in an acetonitrile dielectric continuum as described in Chapter 3. These optimized geometries were used as the starting point for the time dependent DFT calculations. For each structure the first 80 transitions (singlets and triplets) were calculated. Figure 4-3 shows the results for complex **1**. The blue squares are the calculated singlet transitions, the red triangles are the calculated triplet transitions, which have a calculated oscillator strength of 0 due to their formally spin forbidden nature, and the black line is the experimental electronic absorption spectrum measured in acetonitrile.

The first thing to notice is how well the calculated transitions align with the experimental absorption spectrum without any of the corrections that are sometimes necessary for calculations of this sort.¹⁶ This excellent agreement with experimental results is evidence for the accuracy of the TD-DFT calculation. The calculations show that the predictions from electrochemistry in Chapter 3 are correct and the lowest energy absorption band is a metal-to-ligand charge transfer to the CN-Me-bpy. The orbital pictures for that transition shows that the transition is from a (mostly) metal based orbital to a (mostly) ligand based orbital. The selected higher energy MLCT transition has two approximately equal contributions, one from a metal based orbital to an orbital localized on the two bpy ligands and one from a metal based orbital to an orbital that is somewhat delocalized over all three ligands, but mostly localized onto the two bipyridine ligands. The third major absorption band is an intraligand transition. The dominant orbital contribution to that transition is from a CN-Me-bpy π bonding orbital to a CN-Me-bpy π^* antibonding orbital. This means that with the 490 nm

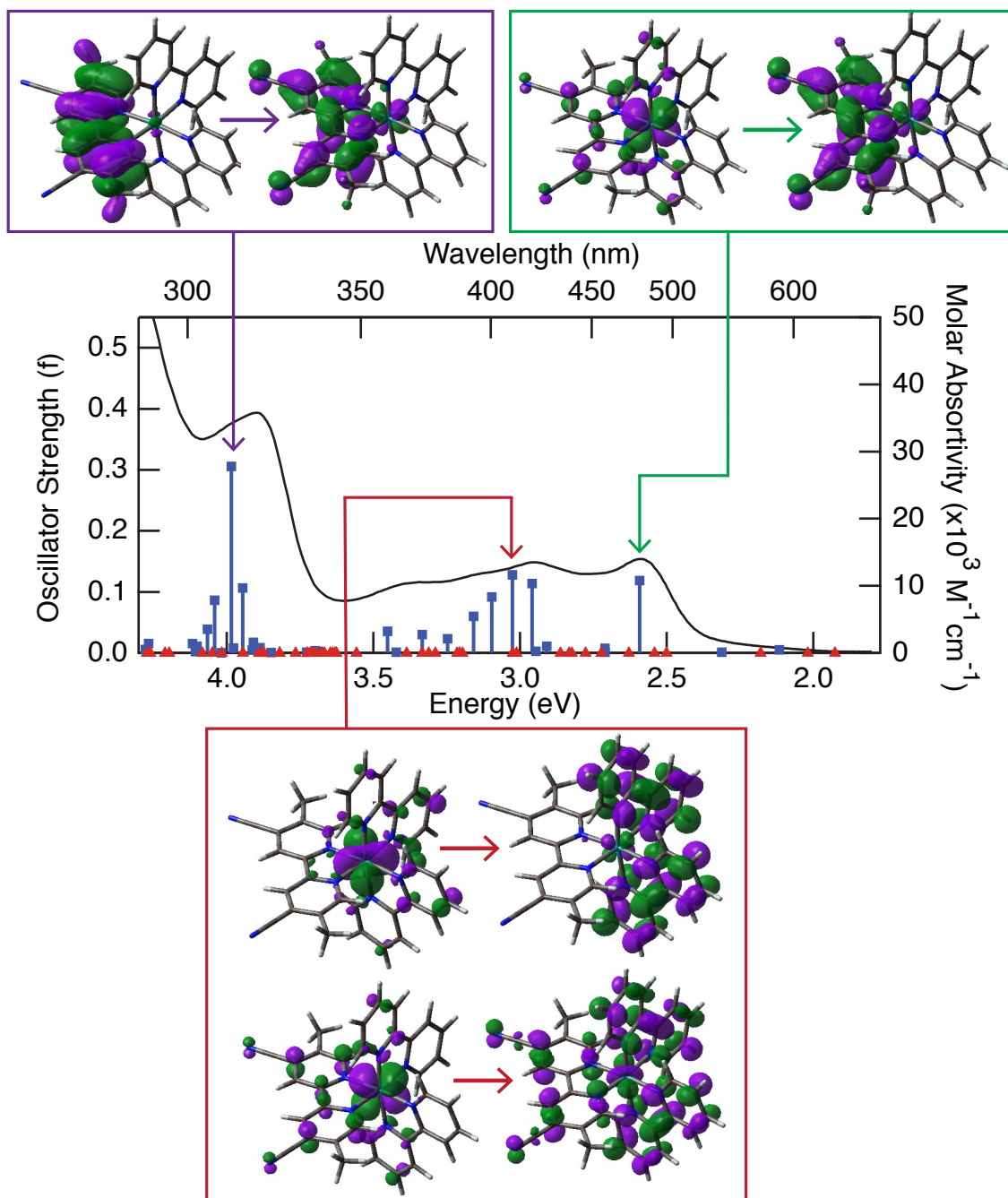


Figure 4-3: TD-DFT results for complex **1** calculated using a spin unrestricted formalism at the B3LYP/LANL2DZ level of theory. Acetonitrile solvent environment was modeled with the polarizable continuum model (PCM). The red triangles are calculated triplet transitions the blue squares are calculated singlet transitions, and the black line is the experimental electronic absorption spectrum in CH_3CN . Pictured orbitals are the major contributions to the selected transitions.

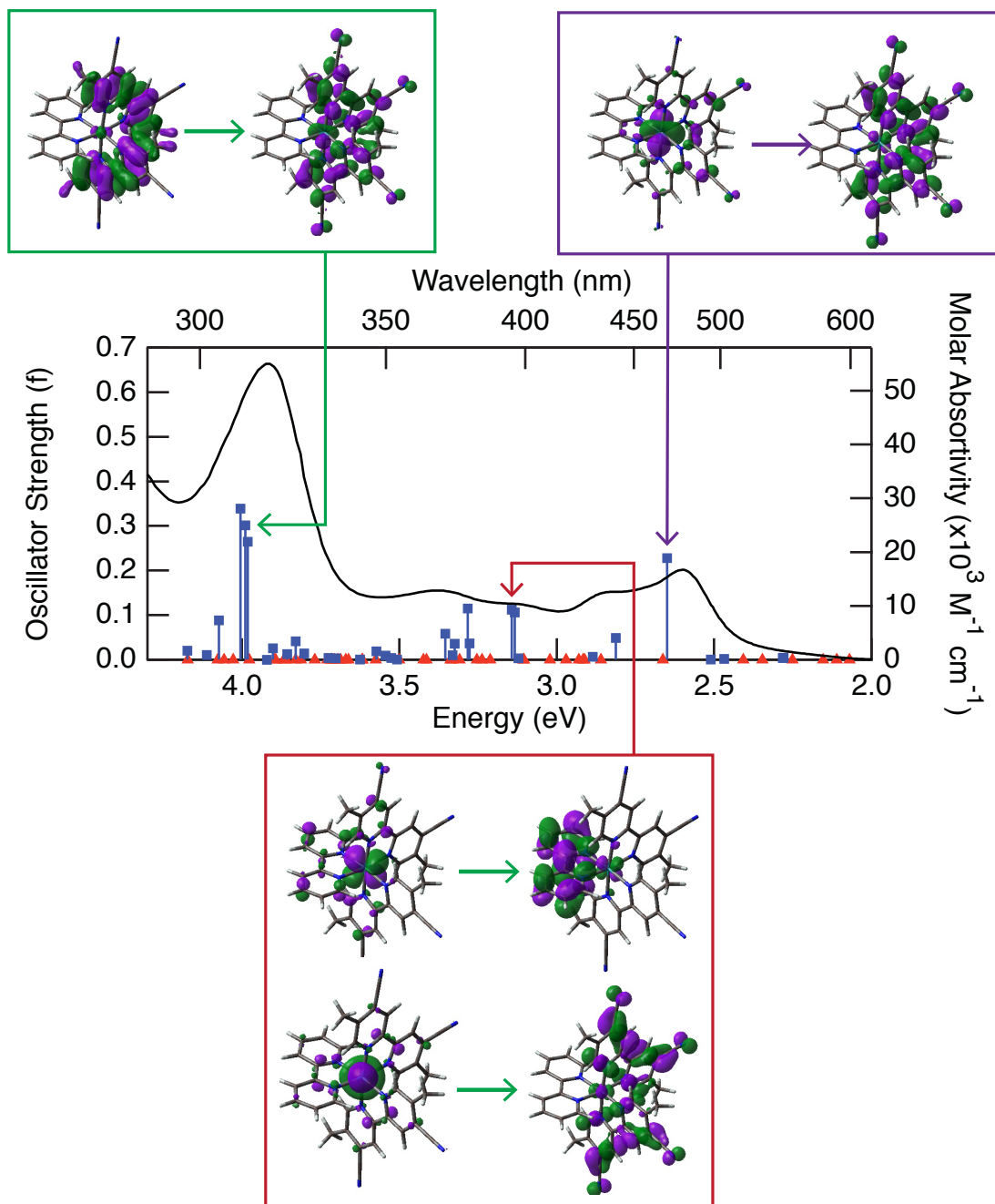


Figure 4-4: TD-DFT results for complex **2** calculated using a spin unrestricted formalism at the B3LYP/LANL2DZ level of theory. Acetonitrile solvent environment was modeled with polarizable continuum model (PCM). The red triangles are calculated triplet transitions the blue squares are calculated singlet transitions, and the black line is the experimental electronic absorption spectrum in CH₃CN. Pictured orbitals are the major contributions to the selected transitions.

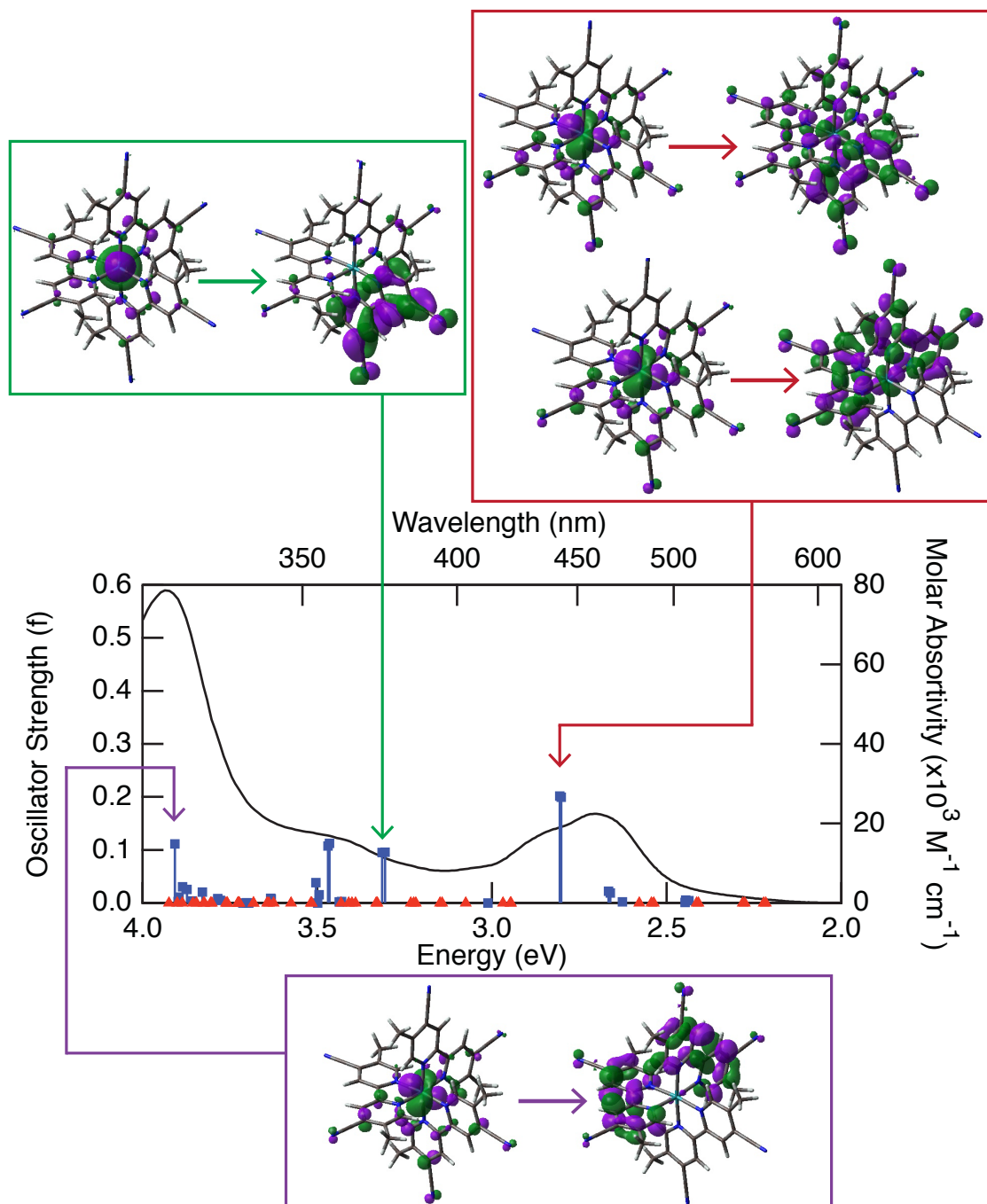


Figure 4-5: TD-DFT results for complex **3** calculated using a spin unrestricted formalism at the B3LYP/LANL2DZ level of theory. Acetonitrile solvent environment was modeled with polarizable continuum model (PCM). The red triangles are calculated triplet transitions the blue squares are calculated singlet transitions, and the black line is the experimental electronic absorption spectrum in CH_3CN . Pictured orbitals are the major contributions to the selected transitions.

excitation wavelength the Franck-Condon state will be localized on the CN-Me-bpy. The higher energy excitation wavelengths, 400 nm for the infrared absorption and 425 for the visible absorption, will generate a Franck-Condon state primarily localized on the unsubstituted bipyridine ligand(s). Calculations on complex **2** (Figure 4-4) show similar results. In complex **3** there is only one possible ligand for the initial excited state to be localized on. The computational results (Figure 4-5) show that both the high and low energy excitation will generate metal-to-ligand charge transfer states localized on either one or two of the CN-Me-bpy ligands.

4.3.2 Time-Resolved Infrared Spectroscopy

Vibrational relaxation in transition metal complexes can appear in different ways in vibrational spectroscopy. In complexes with a low density of vibrational states, like the $W(CO)_5L$ complexes studied by Vlček and coworkers, vibrational relaxation is seen as a narrowing and blueshifting of the excited state absorption.¹⁰ The spectrum narrows because multiple Franck-Condon transitions are allowed, creating a distribution of vibrational levels in the initial excited state which all relax to a single $v' = 0$ vibrational level. The anharmonic nature of the potential surface means that the vibrational spacing is smaller at the top of the potential well and larger at the bottom, which leads to the vibrational transition shifting to higher energy as the system cools. In these types of low density vibrational density metal complexes, each excited state absorption generally corresponds to a single vibrational mode. In complexes with higher densities of vibrational states, the observed absorption features are often a superposition of many closely spaced vibrational modes. The work of Browne, McGarvey, and coworkers on the time resolved resonance Raman spectroscopy of $[Ru(bpy)_3]^{2+}$ shows vibrational relaxation in a system with high density of

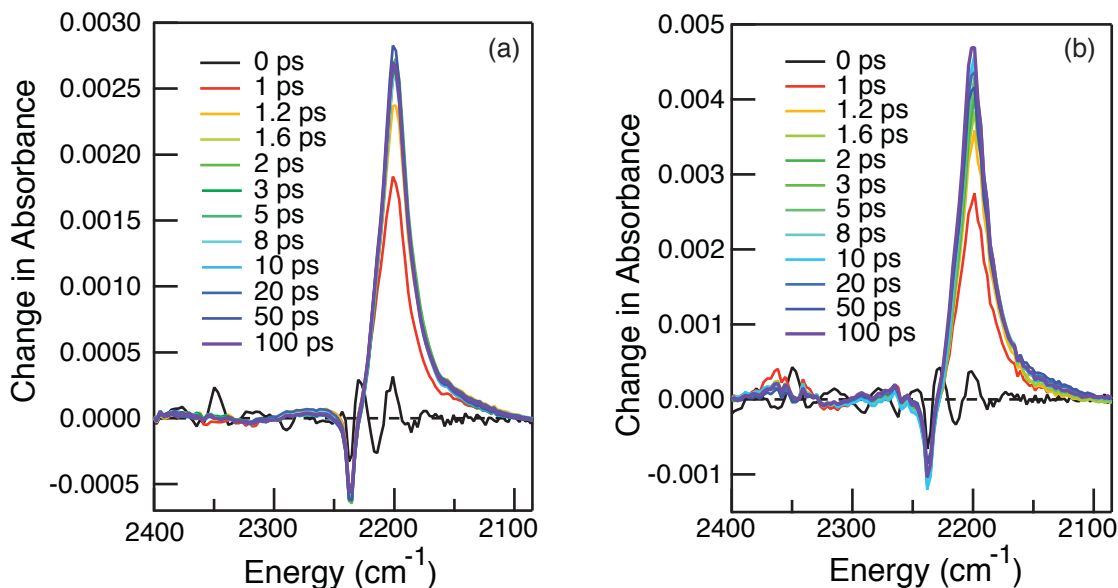


Figure 4-6: Time resolved infrared spectra collected for complex **1** in a nitromethane solution. (a) 490 nm excitation wavelength where the initial excited state is localized on the CN-Me-bpy ligand (b) 400 nm excitation wavelength where the initial excited state is localized on the unsubstituted bpy ligand.

vibrational states. The authors observe a increase in peak intensity over time without any significant changes in the peak shape or energy.

The time resolved infrared absorption spectra for all three complexes were collected at two different excitation wavelengths, 490 (**1** and **2**) or 475 (**3**) and 400 nm. The Franck-Condon state with the 400 nm excitation (for complexes **1** and **2**) will be localized on the unsubstituted bipyridine ligand and the lower energy excitation will create a Franck-Condon state that is localized on the CN-Me-bpy ligand. The data for complex **1** can be seen in Figure 4-6. The most notable observation is that there is little or no difference between the 490 nm and the 400 nm spectra. In both spectra, there is an increase in the intensity of the excited state absorption feature without any measurable change in the energy or shape of the peak, similar to what Browne, McGarvey and coworkers observed

for $[\text{Ru}(\text{bpy})_3]^{2+}$. A kinetic analysis shows that the rise time of the peak in both spectra is approximately 2 ps. Figure 4-9 shows the change in excited state absorption peak intensity over time for the 400 nm spectra and similar results are seen for the 490 nm data.

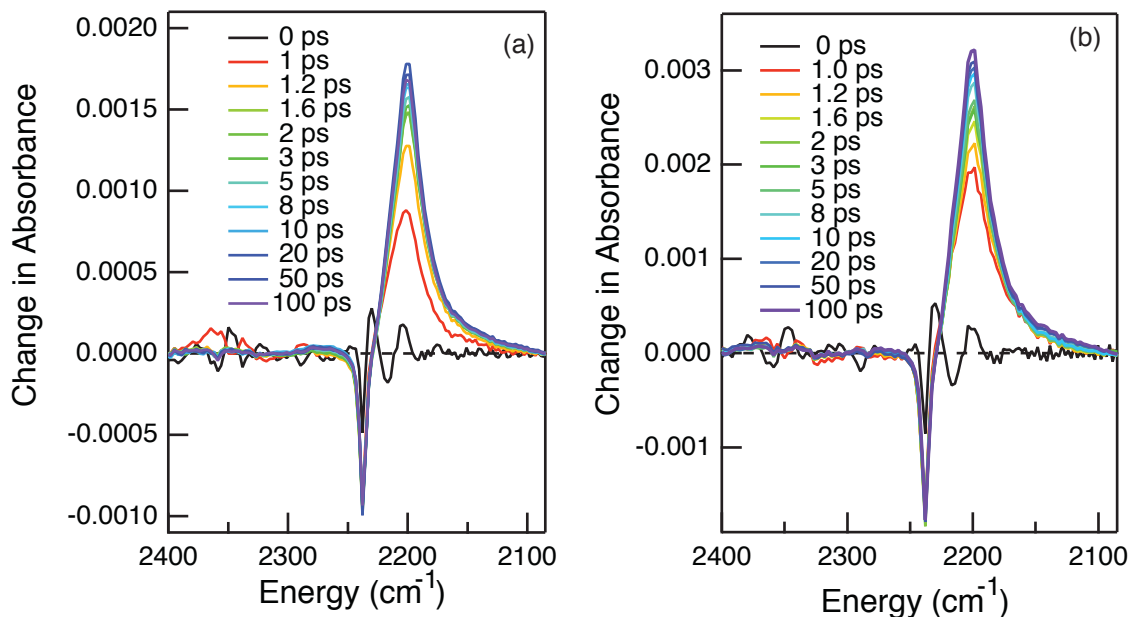


Figure 4-7: Time resolved infrared measurements on complex **2**. in a nitromethane solution. (a) 490 nm excitation wavelength where the initial excited state is localized on the CN-Me-bpy ligand (b) 400 nm excitation wavelength where the initial excited state is localized on the unsubstituted bpy ligand.

As discussed in Chapter 3, when the excited state is localized on the CN-Me-bpy ligand the excited electron is in a π^* antibonding orbital of the CN-Me-bpy ligand. The cyanide group is conjugated into the π system of the bipyridine rings, so populating a π^* antibonding orbital leads to a weaker CN bond and lower frequency vibration. When the excited state is localized on the unsubstituted bipyridine ligand, the excited state cyanide stretching frequency would be

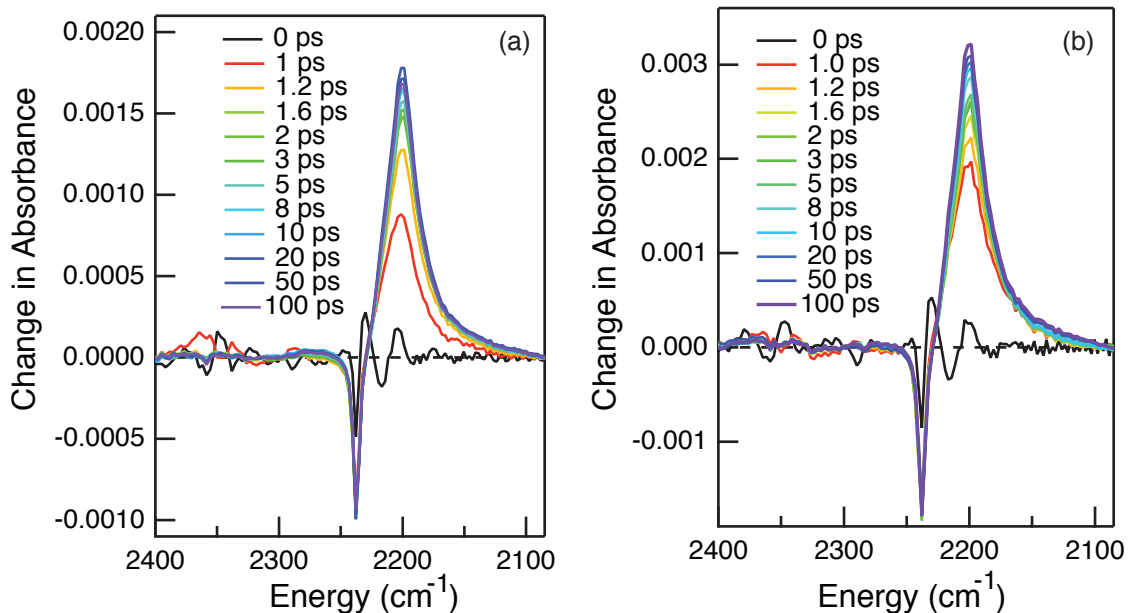


Figure 4-8: Time resolved infrared measurements on complex **3**. in a nitromethane solution. (a) 475 nm excitation wavelength where the initial excited state is localized on the CN-Me-bpy ligand (b) 400 nm excitation wavelength where the initial excited state is localized on the CN-Me-bpy bpy ligand.

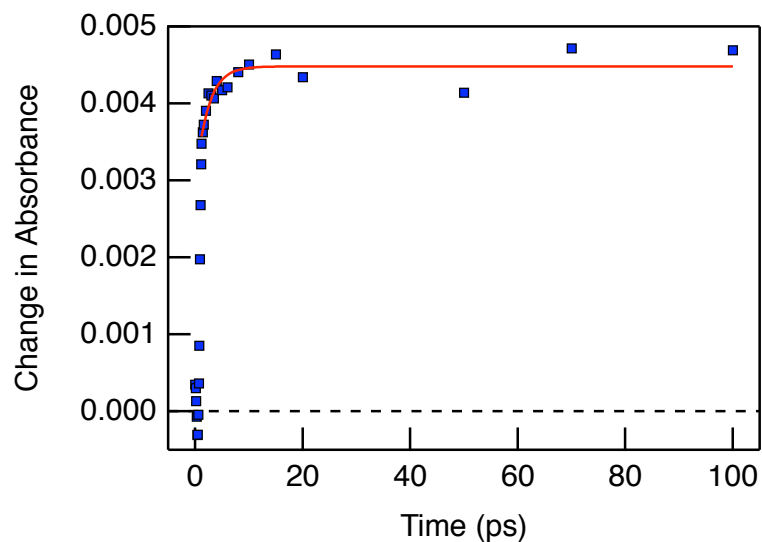
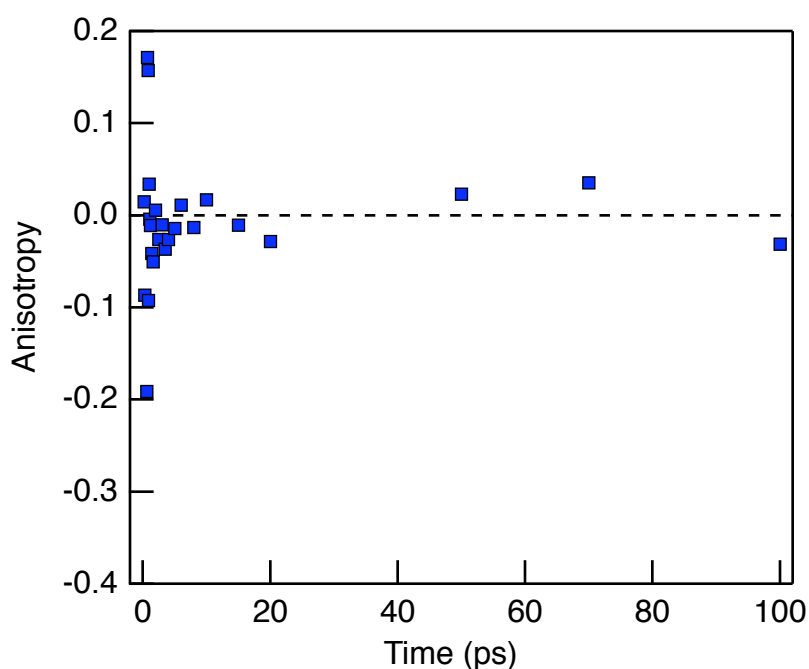


Figure 4-9: Kinetic trace of the absorption maximum (2200 cm^{-1}) for complex **1** excited at 400 nm. The red line is the result of a single exponential fit of the data yielding a time constant of $2.29 \pm 0.7\text{ ps}$

somewhat higher in energy relative to the ground state because the backbonding interaction between the ruthenium and CN-Me-bpy will be weaker in the excited state (where the ruthenium is formally Ru^{3+}), which leads to a stronger CN bond and higher frequency vibration in the excited state. This suggests that on the picosecond timescale of this measurement, the excited state in both cases is already localized on the CN-Me-bpy ligand and the interligand electron transfer rate from the unsubstituted bpy to the CN-Me-bpy ligand is much less than a picosecond.



the parallel and perpendicular spectra using Equation 4-3, where r is the

$$r = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + 2I_{\perp}} \quad 4-3$$

anisotropy, $I_{\parallel}$ is the parallel transient absorption signal, and $I_{\perp}$ is the perpendicular transient absorption signal. The time dependence of the anisotropic signal for complex **1** with 400 nm excitation is shown in Figure 4-10. The lack of any anisotropic signal shows that the excited state is completely randomized on this time scale, again suggesting that the ILET rate is much less than 1 ps.

A comparison of Figures 4-6 - 4-8 shows that the spectra for the three complexes are more or less identical. The fact that the excited state absorption maximum is the same for all three complexes shows that the amount of excited state delocalization is also the same. The absorption maximum is also the same as what is observed in the nanosecond step-scan IR experiment. Therefore, in all three complexes, the excited state must be localized on a single CN-Me-bpy ligand and the increase in the peak intensity is due to vibrational relaxation on the long lived excited state potential energy surface. Like the $[\text{Ru}(\text{bpy})_2(\text{CN-Me-bpy})](\text{PF}_6)_2$, the only kinetic feature seen in the other two complexes is the growth of the excited state absorption maximum. For all three complexes, at both excitation wavelengths, the growth could be fit with a single exponential to yield time constants from ~1 to 8 ps, which is similar to the vibrational relaxation time measured by Browne, McGarvey and coworkers.⁷

4.3.3 Time-Resolved Electronic Absorption Spectroscopy

As a complement to the infrared data, time-resolved visible absorption spectra were also collected on the three complexes, exciting at two different wavelengths. Like the infrared data, the two excitation wavelengths were chosen

so that at the lower energy wavelength (490 nm) the initial excited state would be localized on the CN-Me-bpy ligand and at the higher energy wavelength (425 nm) the initial excited state in complexes **1** and **2** would be localized on the unsubstituted bipyridine ligand.

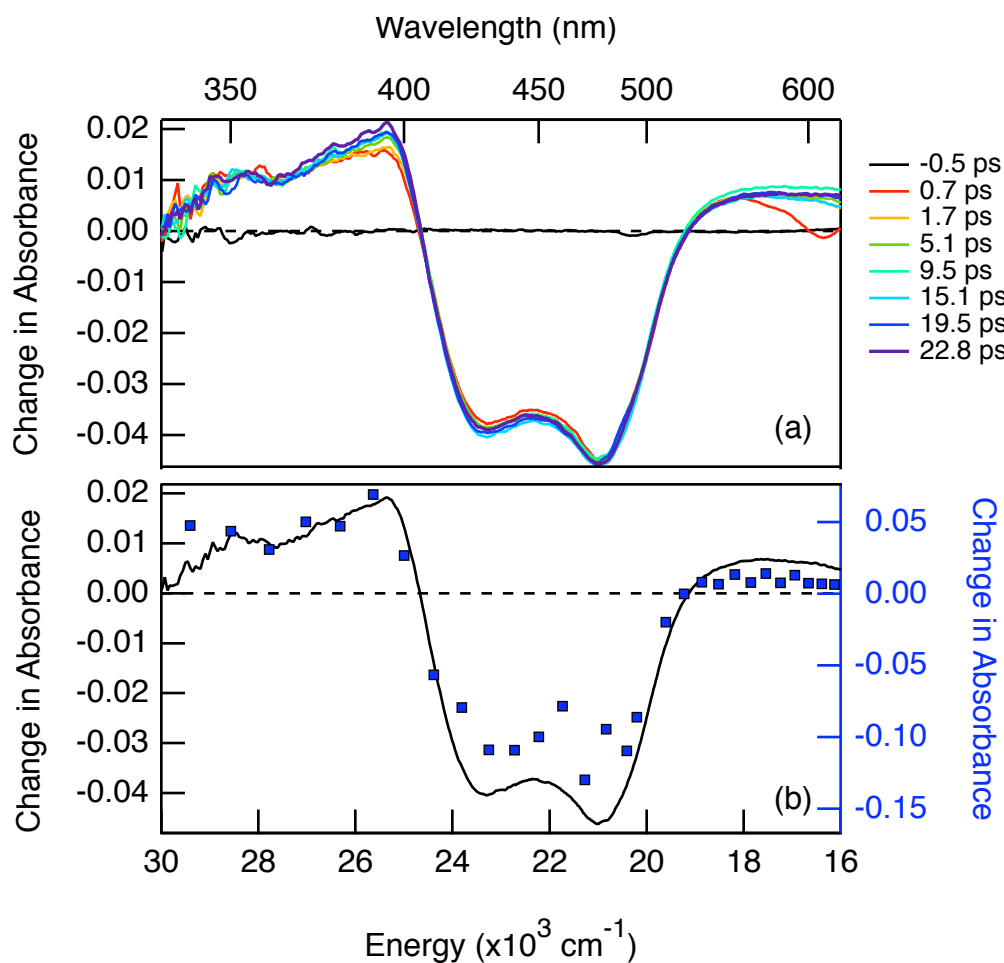


Figure 4-11: Full spectra for compound **1** excited at 490 nm (a) probed in 1 ps steps. (b) Overlay of the 15 ps spectrum (black line) with the nanosecond transient absorption spectrum (blue squares)

4.3.3.1 Low Energy Excitation

As a parallel to the time resolved infrared spectra, Figure 4-11a shows the full spectra of $[\text{Ru}(\text{bpy})_2(\text{CN-Me-bpy})](\text{PF}_6)_2$ after 490 nm excitation, collected in

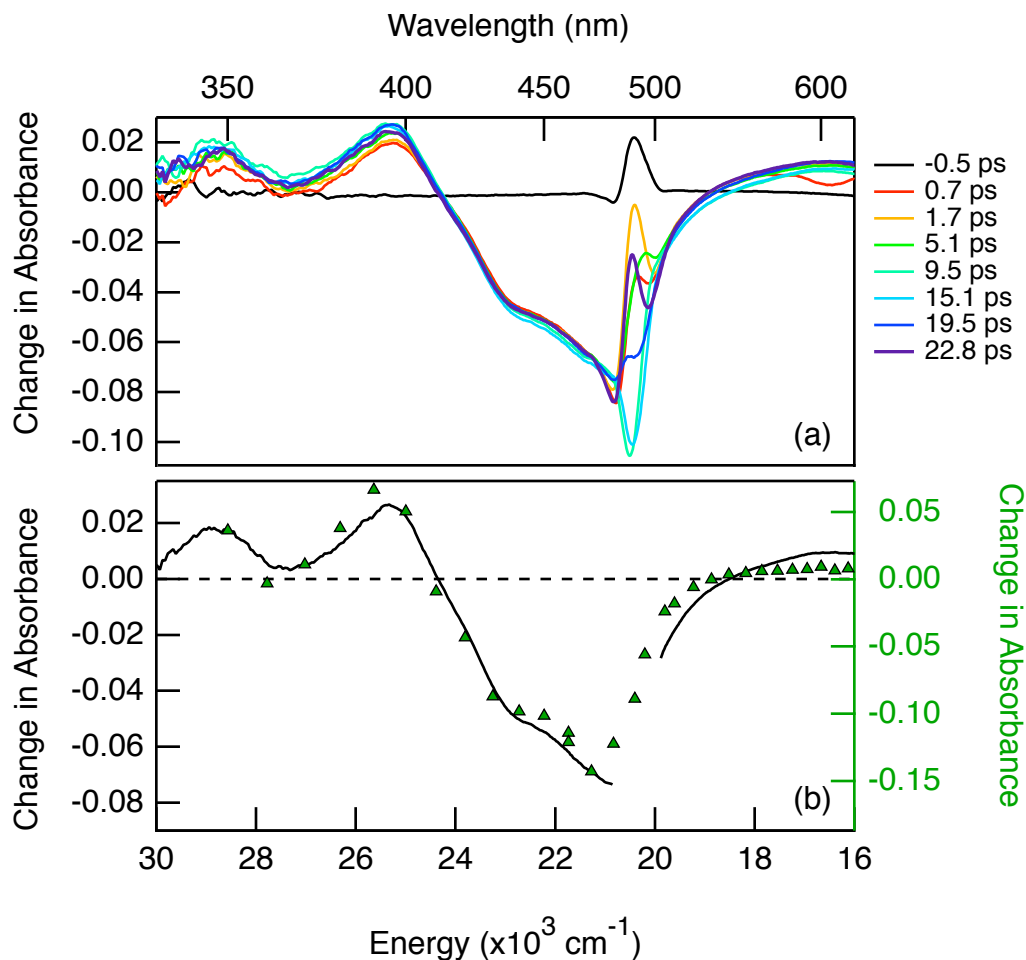


Figure 4-12: Full spectra for compound **2** excited at 490 nm (a) probed in 1 ps steps. (b) Overlay of the 15 ps spectrum (black line) with the nanosecond transient absorption spectrum (green triangle). The scatter at 490 pump wavelength was removed for a better comparison.

1 ps steps. This spectrum shows a slight rise in the CN-Me-bpy radical absorption over time, without any significant change in the peak position or shape. This mirrors the behavior seen in the infrared spectra. By 15 ps the spectrum matches the spectrum seen on the nanosecond timescale (Figure 4-11b). This shows that the thermalized long lived triplet state, which is present on a nanosecond timescale, is formed within 15 ps. Complexes **2** and **3**

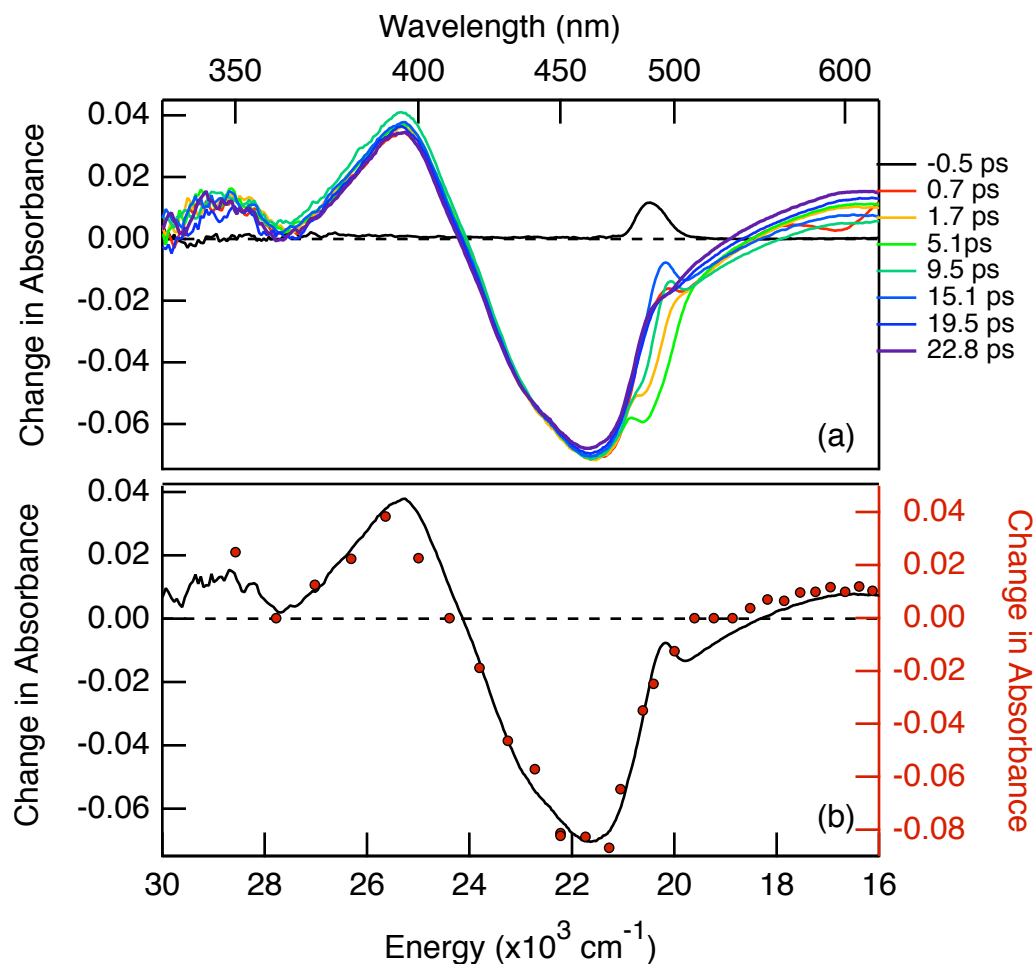


Figure 4-13: Full spectra for compound **3** excited at 490 nm (a) probed in 1 ps steps. (b) Overlay of the 15 ps spectrum (black line) with the nanosecond transient absorption spectrum (red circle)

(Figures 4-12 and 4-13) show a similar rise in the CN-Me-bpy radical absorption over time.

To get a more accurate estimate of the timescale of the peak increase, single wavelength traces were measured for all three complexes (Figures 4-14 - 4-16). For each complex, a single wavelength trace was collected at the CN-Me-bpy radical absorption (370 nm), the isosbestic point between the radical absorption

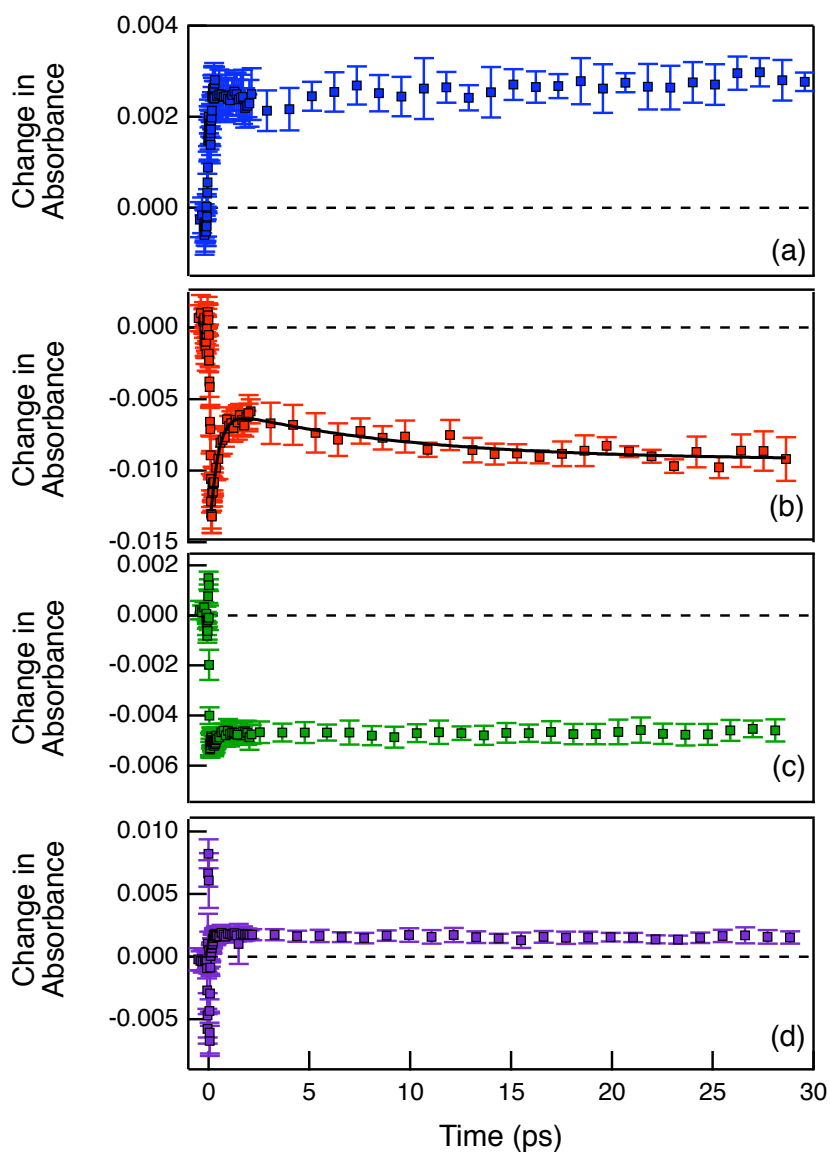


Figure 4-14: Single wavelength kinetics for complex **1** after 490 nm excitation. Probe wavelengths are (a) 370 nm (blue), (b) 400 nm (red), (c) 460 nm (green), and (d) 540 nm (purple). The black line is the result of a double exponential fit, yielding lifetimes of 0.42 ± 0.05 ps and 9.20 ± 2.5 ps.

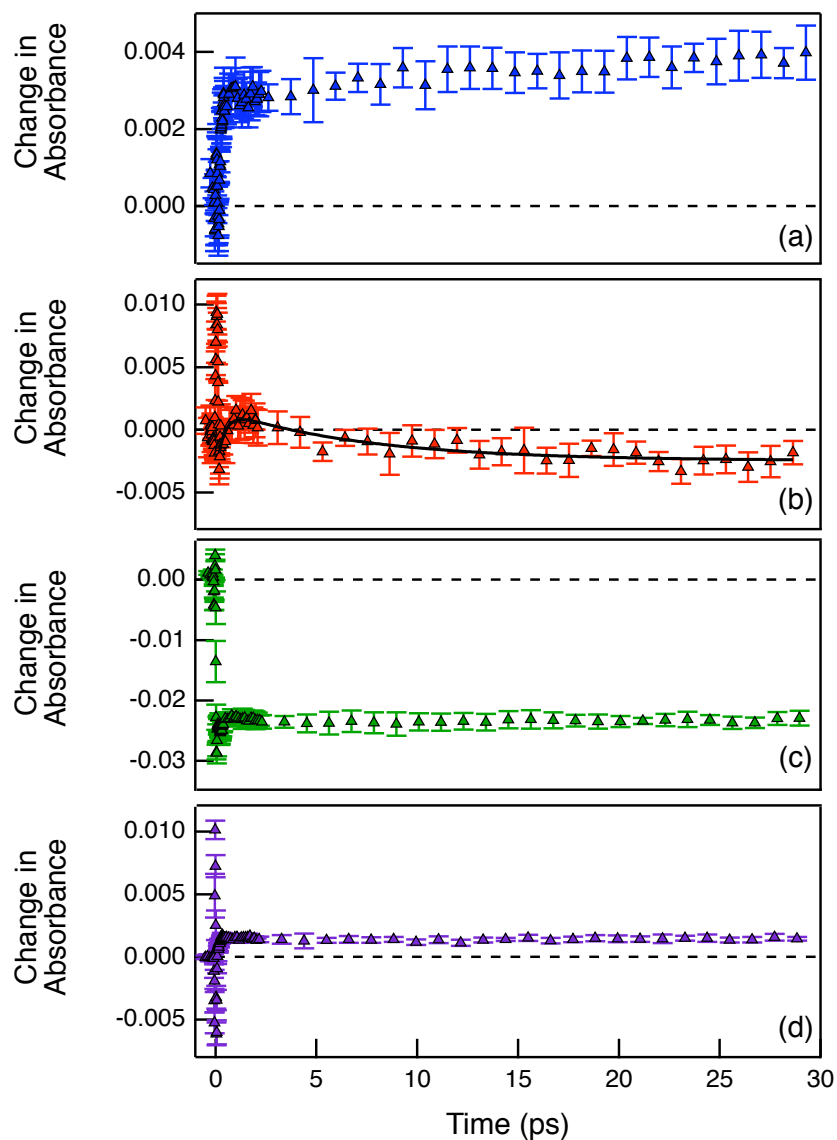


Figure 4-15: Single wavelength kinetics for complex **2** after 490 nm excitation. Probe wavelengths are (a) 370 nm (blue), (b) 410 nm (red), (c) 460 nm (green), and (d) 540 nm (purple). Black line is the results of a double exponential fit, yielding lifetimes of 0.39 ± 0.13 ps and 7.16 ± 2.1 ps.

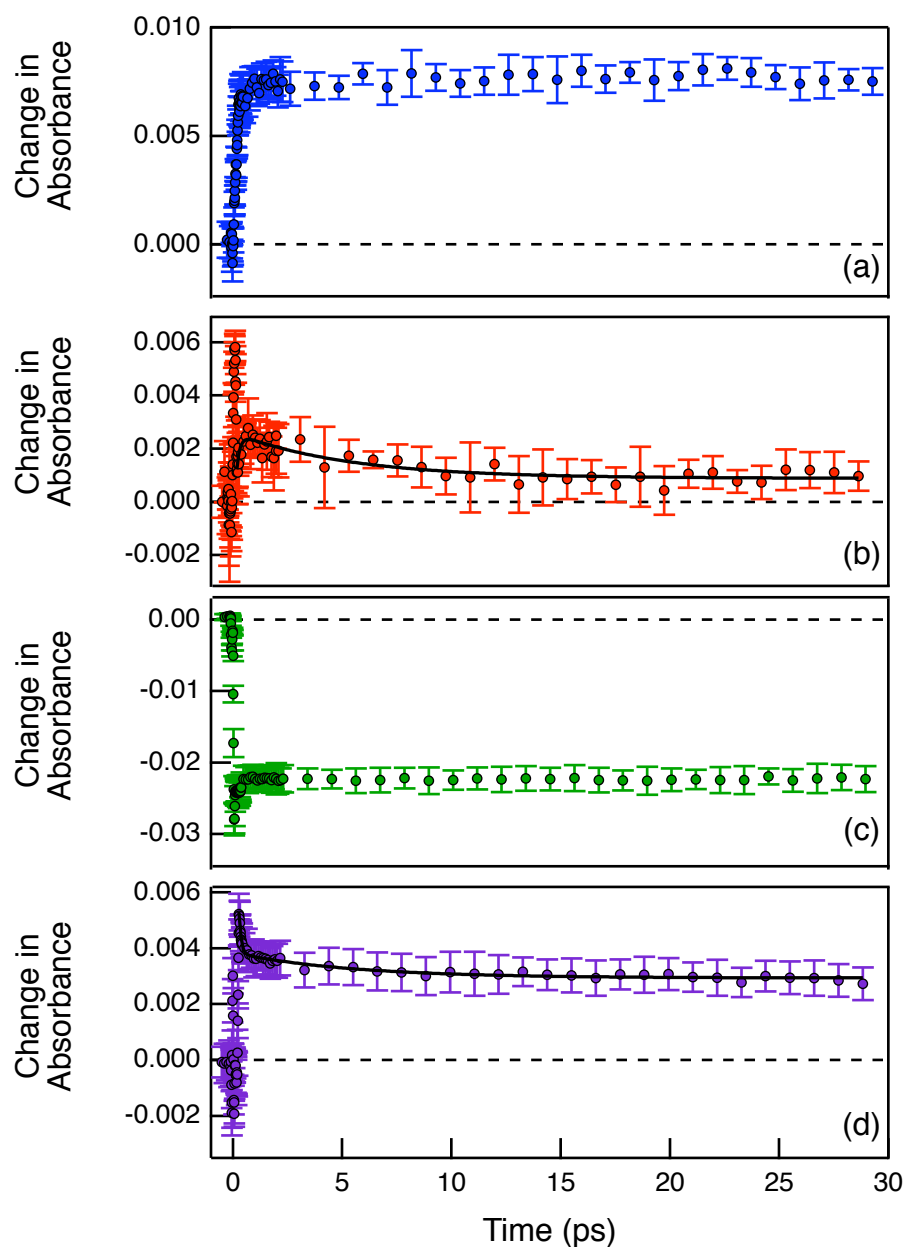


Figure 4-16: Single wavelength kinetics for complex **3** after 490 nm excitation. Probe wavelengths are (a) 370 nm (blue), (b) 410 nm (red), (c) 460 nm (green), and (d) 540 nm (purple). Black lines are the results of double exponential fits, yielding lifetimes of 0.15 ± 0.07 ps and 5.25 ± 1.5 ps for 410 nm and $0.10 \pm .01$ ps and 5.45 ± 0.87 ps for 540 nm.

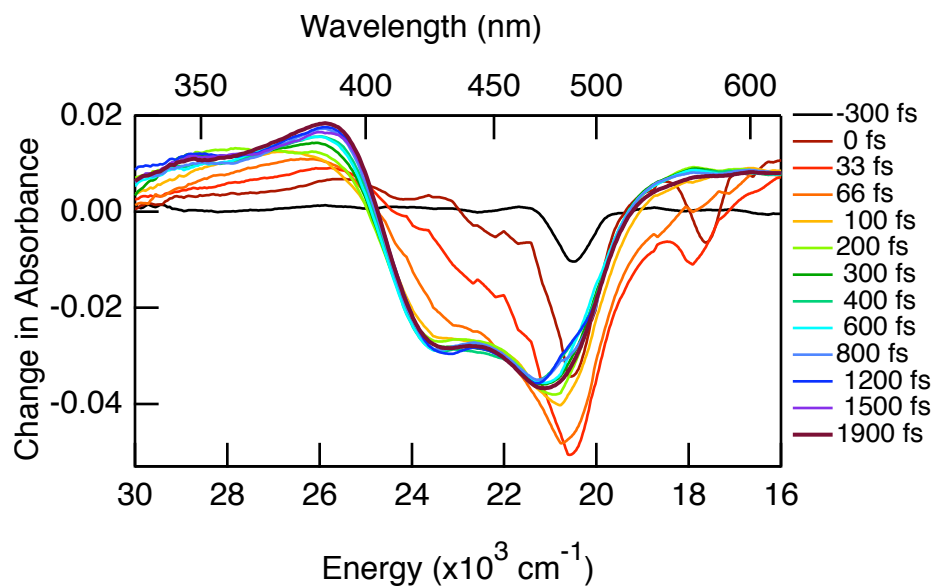


Figure 4-17: Full spectra for compound **1** excited at 490 nm, probed in 33 fs steps.

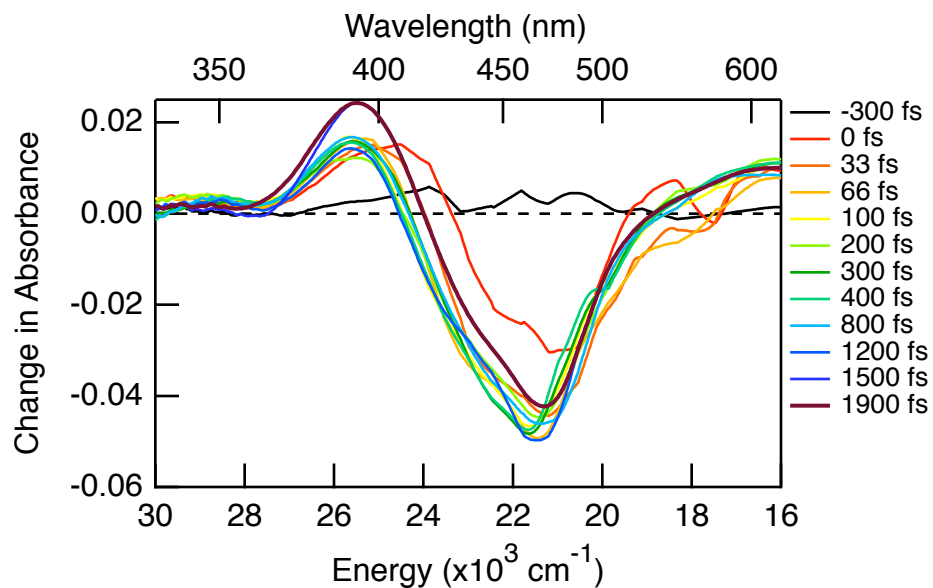


Figure 4-18: Full spectra for compound **2** excited at 490 nm, probed in 33 fs steps.

and bleach features (390 or 410 nm), the MLCT bleach (460 nm), and the red absorption (540 nm). The single wavelength trace collected at the isosbestic point on all three complexes shows a fast increase (100-500 fs) followed by a slower (5-10 ps) decay. This is in agreement with previous work in our group on $[\text{Ru}(\text{dmb})_3]^{2+}$ and $[\text{Ru}(\text{dpb})_3]^{2+}$ (dmb = 4,4'-dimethyl-2,2'-bipyridine and dpb = 4,4'-diphenyl-2,2'-bipyridine).²¹ By comparison to those previous results and the infrared results above, the slower component can be assigned as vibrational relaxation within the lowest energy $^3\text{MLCT}$ state. This result confirms the assumption that the subtle, small amplitude changes in the time resolved electronic absorption spectrum do correspond to vibrational relaxation dynamics.^{12,21,22}

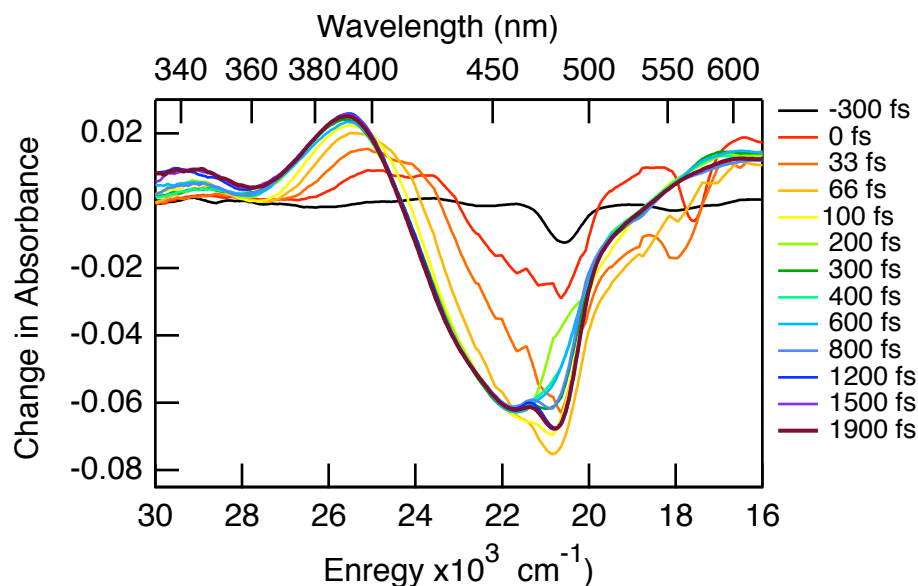


Figure 4-19: Full spectra for compound **2** excited at 490 nm, probed in 33 fs steps.

The origin of the faster component is more uncertain. In order to get a better picture of the origin of the faster component full spectra were collected in 33 fs steps. The shorter time spectra of complex **1**, (Figure 4-17) shows some shifting of the CN-Me-bpy radical absorption and a growing in of the MLCT bleach over ~200 fs. With the 490 nm excitation both the initial and long lived excited state are localized on the CN-Me-bpy ligand. This means that interligand electron transfer can be eliminated as the origin of the fast kinetic component. In other ruthenium tris bipyridyl complexes, such as $[\text{Ru}(\text{bpy})_3]^{2+}$, $[\text{Ru}(\text{dmb})_3]^{2+}$ and $[\text{Ru}(\text{dpb})_3]^{2+}$ (dpb = 4,4'-diphenyl-2,2'-bipyridine) a similar fast kinetic component

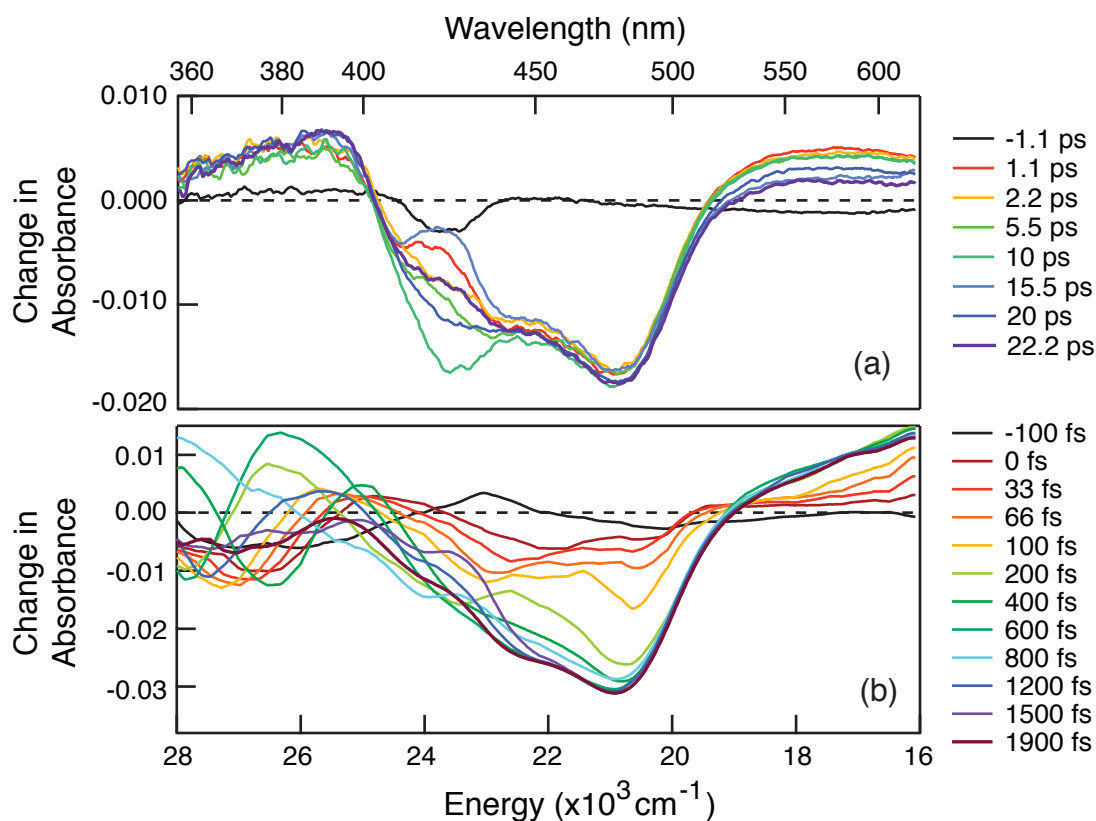


Figure 4-20: Full spectra for $[\text{Ru}(\text{bpy})_2(\text{CN-Me-bpy})](\text{PF}_6)_2$ (**1**) after 425 nm excitation, probed in (a) 1 ps steps and (b) 33 fs steps

on the order of 100 fs has been observed.^{21,23,24} In the literature this fast component has been assigned as the formation of the ³MLCT state. The slow growth in of the bleach feature, however, may suggest that the observed kinetic component is due to intramolecular vibrational redistribution (IVR). Similar behavior is seen for complexes **2** and **3** (Figures 4-18 and 4-19).

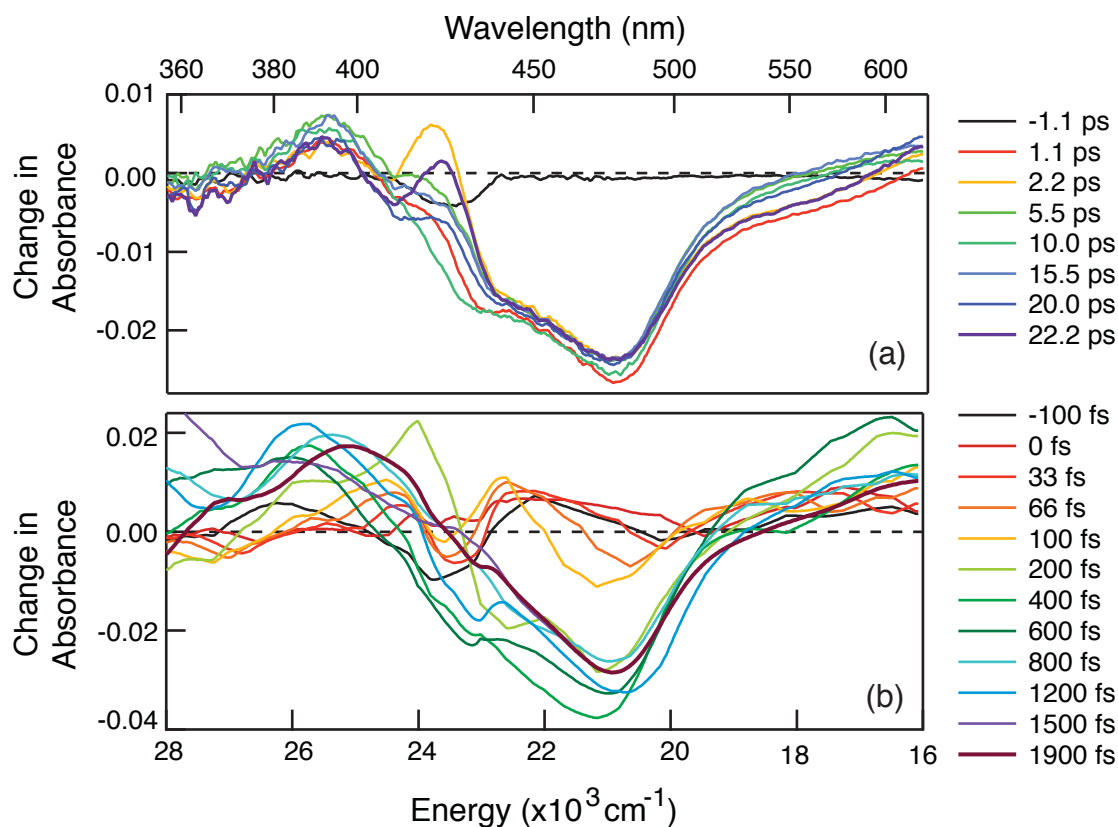


Figure 4-21: Full spectra for compound **2** with 425 nm excitation probed in (a) 1 ps intervals and (b) 33 fs intervals.

4.3.2.2 High Energy Excitation

To mirror the time-resolved infrared experiments, time-resolved electronic absorption spectra were collected after excitation at higher energy (425 nm).

With the 425 nm excitation, the TD-DFT calculations show that the initial excited state is localized on the unsubstituted bipyridine ligand(s) in complexes **1** and **2**. This opens up the possibility of interligand electron transfer. Figure 4-20 shows the full spectra of $[\text{Ru}(\text{bpy})_2(\text{CN-Me-bpy})](\text{PF}_6)_2$ after 425 nm excitation. At this excitation wavelength, the initial excited state is localized on the unsubstituted bipyridine ligand(s). In the long time spectra, collected in 1 ps steps, there is an increase in the ligand radical absorption over time without a significant change in the energy or shape of the peak. This is the same behavior that was seen in the spectra collected after 490 nm excitation. This is not surprising, considering the time resolved infrared spectra showed no differences between 400nm excitation

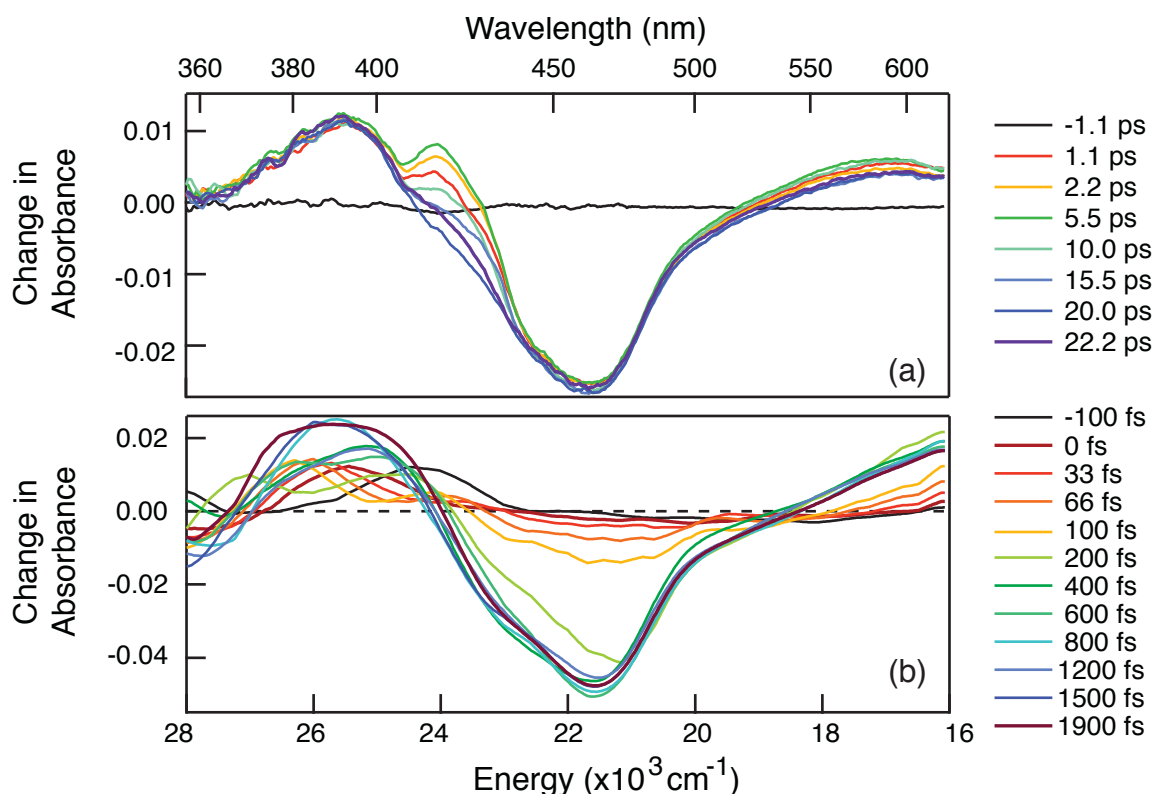


Figure 4-22: Full spectra for compound **3** with 425 nm excitation probed in (a) 1 ps intervals and (b) 33 fs intervals.

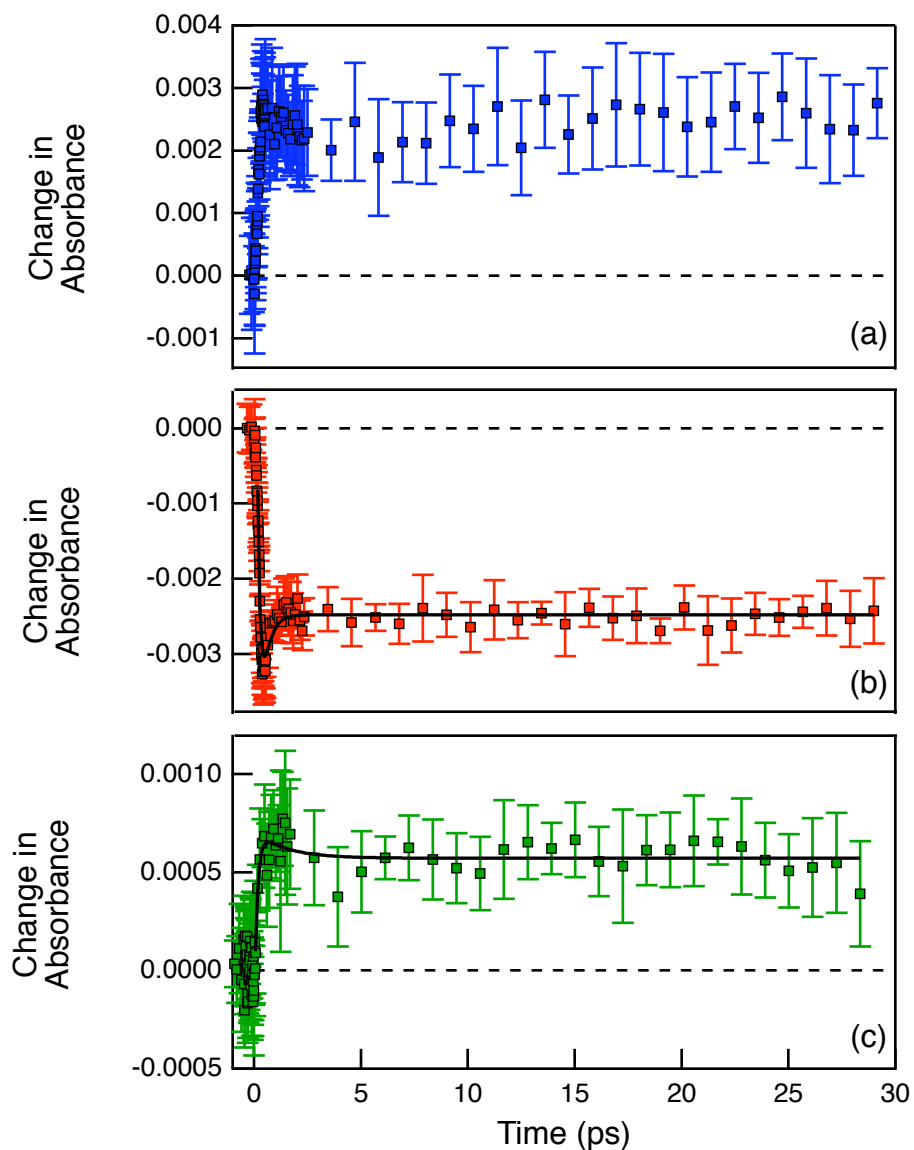


Figure 4-23: Single wavelength kinetics for complex **1** after 425 nm excitation. Probe wavelength are (a) 370 nm (blue), (b) 460 nm (red), and (c) 520 nm (green). The black lines on the 460 nm and 520 nm traces are the results of biexponential fits, yielding lifetimes of $0.12 \pm .03$ ps and 0.33 ± 0.13 ps for 460 nm and $0.14 \pm .07$ ps and 1.46 ± 2.3 ps for 540 nm.

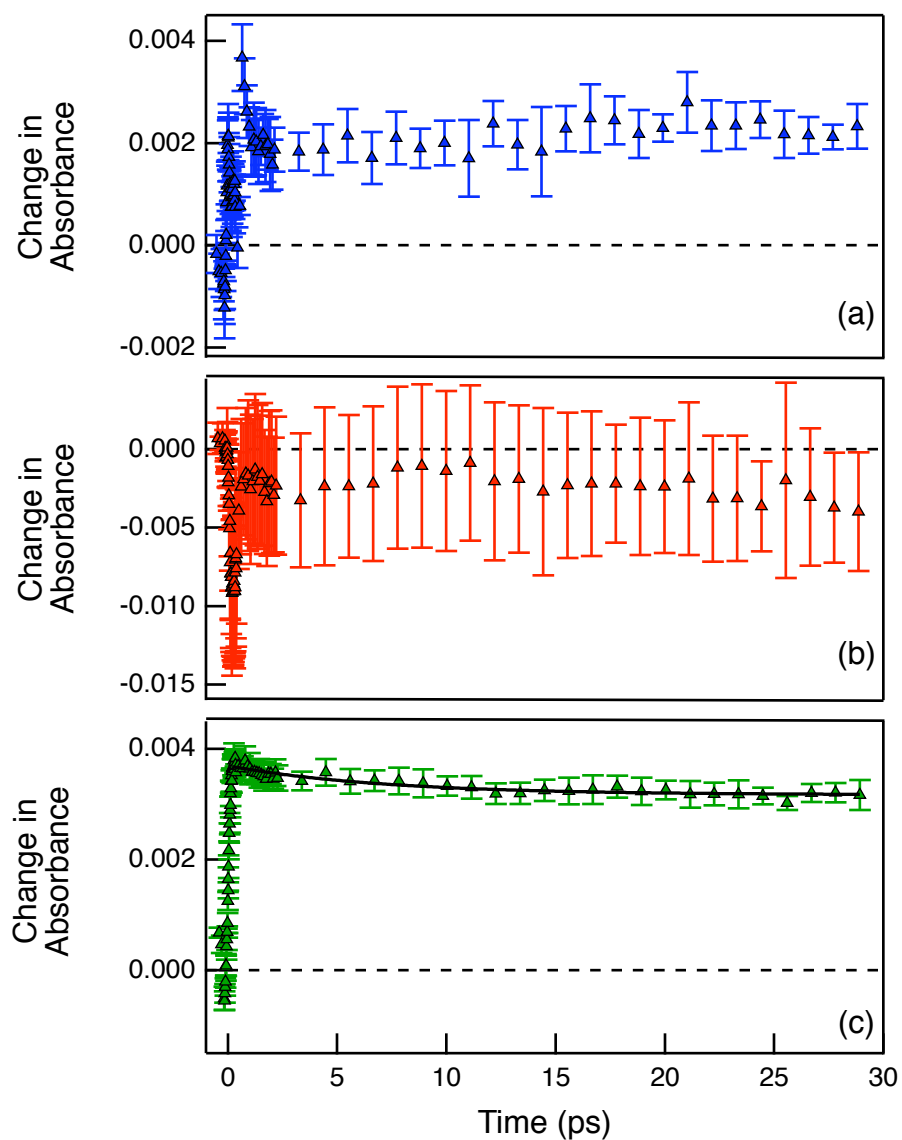


Figure 4-24: Single wavelength kinetics for complex **2** after 425 nm excitation. Probe wavelengths are (a) 370 nm (blue), (b) 460 nm (red), and (c) 520 nm (green). The black line on the 520 nm trace is the result of a single exponential fit yielding a lifetime of 7.25 ± 1.3 ps.

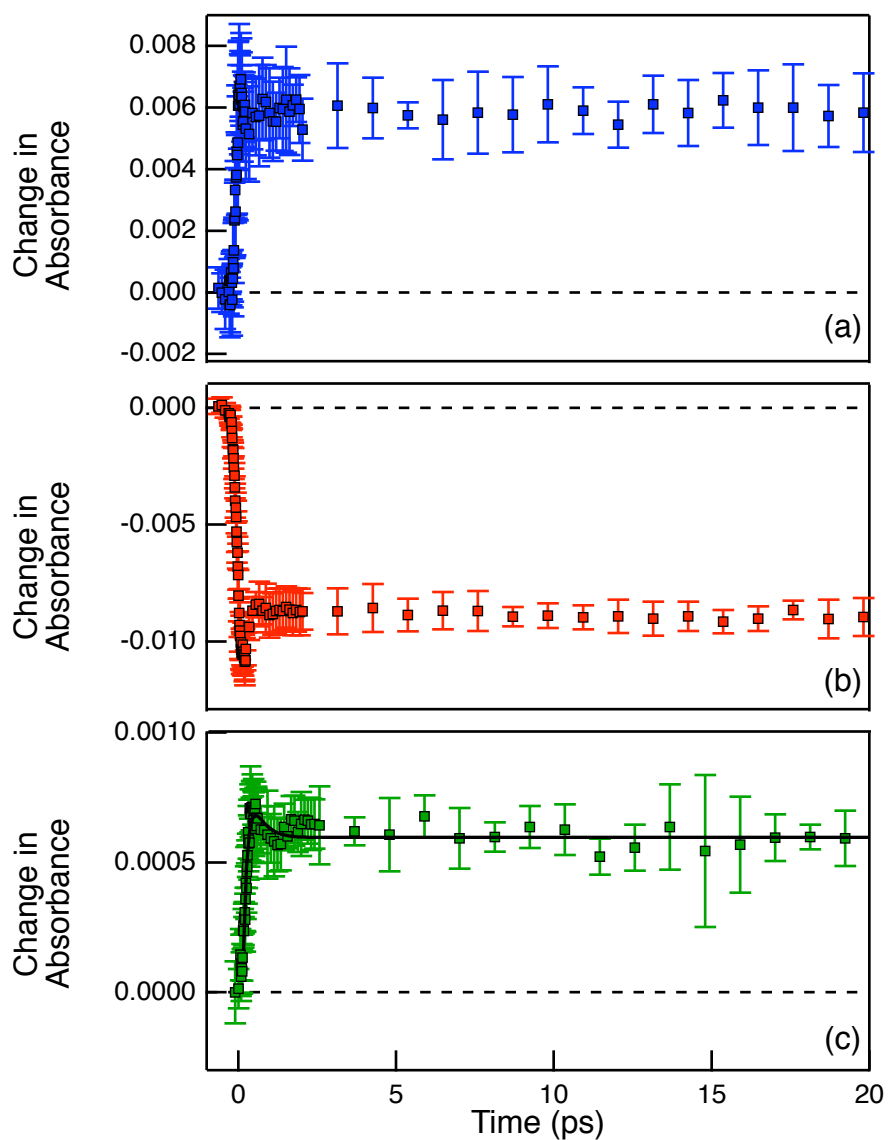


Figure 4-25: Single wavelength kinetics for complex **3** after 425 nm excitation. Probe wavelengths are (a) 370 nm (blue), (b) 460 nm (red), and (c) 540 nm (green). The black line on the 540 nm trace is the result of a biexponential fit yielding lifetimes of 0.15 ± 0.08 ps and 0.32 ± 0.27 ps.

and 490 nm excitation. In the shorter time spectra, however, the poor signal-to-noise ratio in the near UV region of the spectrum make it difficult to determine if there is any shifting of the ligand radical absorption band, as was seen in the spectra after 490 nm excitation. Similar results were seen for complexes **2** and **3** (Figures 4-21 and 4-22).

Again, to get a more accurate estimate of any kinetic processes, single wavelength traces were collected for all three complexes (Figures 4-23 - 4-25). For each complex, a single wavelength trace was collected at the CN-Me-bpy radical absorption (370 nm), the MLCT bleach (460 nm), and the isosbestic point between the MLCT bleach and the red absorption (520 or 540 nm). At the isosbestic points in complexes **1** and **2** there is a long component, ~ 1.5 ps and ~ 7 ps respectively, which most likely corresponds to vibrational relaxation in the lowest energy $^3\text{MLCT}$ state. All three complexes also show shorter dynamics, similar to those seen after 490 nm excitation. These possibly represent the formation of the $^3\text{MLCT}$ state. In the long time full spectra, it is clear that the long lived $^3\text{MLCT}$ is already established and the observed changes are due to the vibrational relaxation within that state. Unfortunately, the poor signal-to-noise of the shorter time full spectra make it difficult to determine whether the nature of the excited state is changing (through interligand electron transfer) or otherwise give clues as to what processes could be giving rise to the shorter kinetic components.

4.4 Future Works

4.4.1 Solvent Effects

Preliminary transient absorption spectra of $[\text{Ru}(\text{bpy})_2(\text{CN-Me-bpy})](\text{PF}_6)_2$ at longer times revealed an additional kinetic component (180 ± 30 ps) to the decay, which can be seen in Figure 4-26. The ground state recovery time in

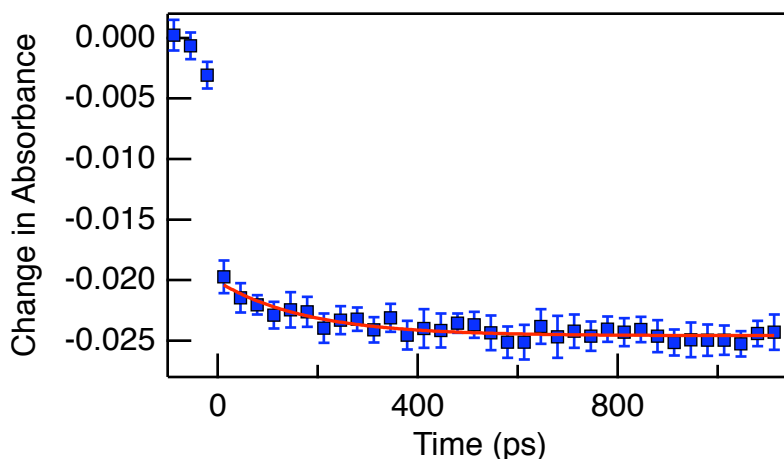


Figure 4-26: Single wavelength trace for $[\text{Ru}(\text{bpy})_2(\text{CN-Me-bpy})](\text{PF}_6)_2$ collected at 450 nm, following excitation at 490 nm. The red line is the result of a single exponential fit, resulting in a lifetime of 180 ± 30 ps.

complex **1** from Chapter 3 is around 1.5 μs , so this new component is far too short to be associated with ground state recovery. The ultrafast infrared and visible absorption spectroscopy show that the thermalized $^3\text{MLCT}$ state is formed within 15-20 ps (*vide supra*) and therefore the ~ 200 ps process must be occurring from the thermalized long lived $^3\text{MLCT}$ state. In related ruthenium(II) complexes of 4,4'-dicarboxy-2,2'-bipyridine (dcbpy) the carboxylate groups are mostly deprotonated in the ground state ($\text{pK}_a \approx 2$), but in the long lived $^3\text{MLCT}$ state they become more basic ($\text{pK}_a^* \approx 4$)^{25,26}. One result of this shift in pK_a is that the excited state on the complex can be protonated by the solvent (or water in the solvent). Work in our group has shown that this excited state protonation reaction most likely occurs with a time constant of hundreds of picoseconds.²⁷ Scandola and coworkers performed similar experiments with $\text{Ru}(\text{bpy})_2\text{CN}_2$ and showed that the cyanide groups have similar acid-base equilibria.²⁸

Like the carboxylate groups in the ruthenium(II) dcbpy complexes, the cyanide groups in complex **1** also have an increased electron density in the excited state, potentially making them more basic. It may be possible that the observed 180 ps decay component is due to an interaction between the excited state and the solvent (or residual water in the solvent). The solvatochromism of the lowest energy charge transfer feature, shown in Figure 4-27, is another indication that the excited state has a significant interaction with the solvent. Solvatochromism and what it implies about solvent-molecule interactions will be discussed in Chapter 5. A variable solvent time-resolved absorption study using non-polar, dipolar aprotic, and protic solvents is a way to either support or disprove this theory.

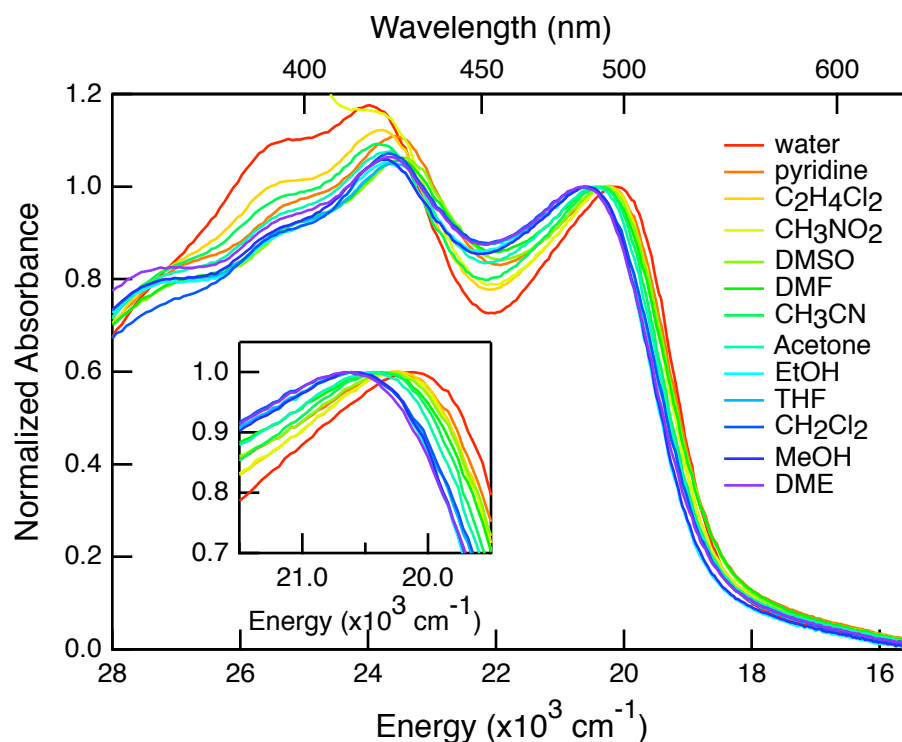


Figure 4-27: Electronic absorption spectra of $[\text{Ru}(\text{bpy})_2(\text{CN-Me-bpy})](\text{PF}_6)_2$ (**1**) in different solvents, showing the solvatochromatic behavior of the lowest energy MLCT absorption band. The inset shows an expanded view of the lowest energy absorption maxima.

4.4.2 ILET and Localization

As mentioned in Chapter 1, one of the major unresolved questions in ruthenium (II) photophysics is the localized or delocalized nature of the excited state. It is well established that the thermalized lowest energy $^3\text{MLCT}$ state is localized on a single ligand, even in homoleptic complexes.²⁹⁻³² A number of experiments also show that the initially excited Franck-Condon state is most likely also localized on a single ligand.³³⁻³⁵ The question remains, does the excited state stay localized on the same bipyridine ligand as it moves from the Franck-Condon state to the thermalized $^3\text{MLCT}$ state? Ultrafast polarized absorption spectra collected by Hammarström and coworkers show that the excited state in $[\text{Ru}(\text{bpy})_3]^{2+}$ is randomized in < 300 fs, meaning it has no memory of where the initial excited state was localized. It is unclear, however, whether this randomization is due to the formation of a delocalized state or very rapid interligand electron transfer (ILET).

The cyano-substituted ruthenium(II) bipyridine complexes offer a unique opportunity to resolve this question. By changing the ancillary bipyridine ligands, as shown in Figure 4-18, it is possible to design a series of compounds where the driving force for ILET varies across the series. In these examples, the energy difference between the two different bipyridine ligands is estimated by comparing the first reduction potentials for the respective homoleptic complexes. For example, the energy difference between $\text{CF}_3\text{-bpy}$ ($\text{CF}_3\text{-bpy}$ = 4,4'-bis(trifluoromethyl)-2,2'-bipyridine) and CN-Me-bpy in $[\text{Ru}(\text{CF}_3\text{-bpy})_2(\text{CN-Me-bpy})]^{2+}$ is estimated by comparing $[\text{Ru}(\text{CF}_3\text{-bpy})_3]^{2+}$ ($E_{\text{red}} = 0.77$ V vs SCE)³⁶ and $[\text{Ru}(\text{CN-Me-bpy})_3]^{2+}$ ($E_{\text{red}} = 0.85$ V vs SCE). This predicts that the $\text{CF}_3\text{-bpy}$ ligand is ~ 80 mV lower in energy than the CN-Me-bpy ligand so ILET from $\text{CF}_3\text{-bpy}$ to CN-Me-bpy would be a slightly uphill process.

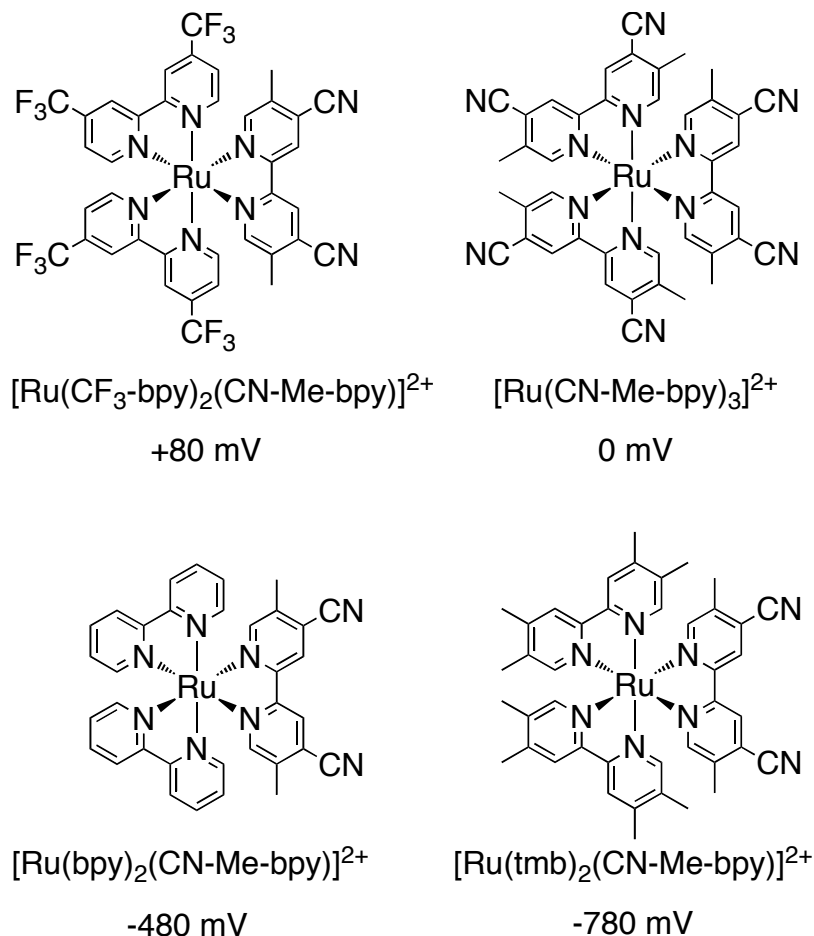


Figure 4-28: A series of $[\text{Ru}(\text{bpy}')_2(\text{CN-Me-bpy})](\text{PF}_6)_2$ complexes with varying energy differences between bpy' and CN-Me-bpy . Listed energy differences are estimated by the difference in the first reduction potential for the corresponding homoleptic complexes, i.e. $E_{\text{red}}\{[\text{Ru}(\text{CN-Me-bpy})_3]^{2+}\} - E_{\text{red}}\{[\text{Ru}(\text{bpy}')_3]^{2+}\}$.

Polarized absorption measurements, like those done by Hammarström and coworkers³⁷, will be able to measure the timescale of excited state randomization but cannot distinguish between delocalization and rapid ILET. The cyanide substituents in this series of complexes provide a way by which the two can be distinguished. The excited state stretching frequency of the cyanide group will be very different in a delocalized excited state compared to a localized excited state undergoing rapid ILET. Time resolved infrared measurements on $[\text{Ru}(\text{CN-Me-}$

$\text{bpy})_3]^{2+}$ on a nanosecond timescale show a $\sim 40 \text{ cm}^{-1}$ shift between the ground state and the excited state. As mentioned above, it is well established that the excited state is localized on a single ligand on a nanosecond timescale, so that 40 cm^{-1} shift represents a localized excited state. In the case of a delocalized excited state, the excited electron is delocalized over all three CN-Me-bpy ligands so the effect on the cyanide stretching frequency should be about a third of what it is in the localized state ($\sim 13 \text{ cm}^{-1}$). The difference between a 13 cm^{-1} shift and a 40 cm^{-1} shift should be easily detectable by time-resolved infrared spectroscopy or femtosecond stimulated Raman spectroscopy.

4.5 Concluding Comments

Both the time-resolved infrared and visible absorption experiments show evidence that vibrational relaxation occurs on 1-10 ps timescale in these complexes. Vibrational relaxation on this timescale has been observed in other ruthenium bipyridine systems, most notably in the work of Browne, McGarvey and coworkers on the time-resolved resonance Raman spectroscopy of $[\text{Ru}(\text{bpy})_3]^{2+}$. This is further evidence that the conclusions drawn by Chegui and coworkers, that the thermalized long lived $^3\text{MLCT}$ state in $[\text{Ru}(\text{bpy})_3]^{2+}$ is fully formed in 15 fs, is incorrect.

The time resolve infrared experiments also show that interligand electron transfer and/or intermolecular vibrational energy redistribution both occur much faster than the picosecond resolution of the experiment. Localizing the initial excited state on the CN-Me-bpy or unsubstituted bpy lead to identical spectra, meaning in both cases only the long live excited state, localized on a single CN-Me-bpy ligand was being probed. The time-resolved electronic absorption data also shows a $\sim 1\text{-}10 \text{ ps}$ vibrational relaxation time. The faster kinetic components of the electronic absorption spectra are most likely related to the formation of the

long lived $^3\text{MLCT}$ state, but without further experiments, it is unclear exactly which process (intersystem crossing, interligand electron transfer, intermolecular vibrational energy redistribution, etc.) corresponds to the observed rates.

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Chapter 5: Synthesis and Spectroscopic Characterization of Cyano-Substituted Terpyridyl Complexes of Ruthenium(II)

5.1 Introduction

Ruthenium tris bipyridine complexes have many properties, which have been discussed in Chapters 1 and 3, that make them ideally suited for a wide array of applications. Briefly, their lowest energy excited state is a $^3\text{MLCT}$ state that lives 100's of nanoseconds to microseconds. The charge transfer nature of the long lived excited state means that the excited state can reversibly act as either an oxidant or a reductant and the long lifetime of the excited state allows for bimolecular excited state reactions to occur. The relatively high quantum yields of this class of compound also makes them potentially useful as fluorescent dyes or sensors. The properties of ruthenium(II) bipyridine complexes, particularly $[\text{Ru}(\text{bpy})_3]^{2+}$, have been widely studied on all timescales and the excited state dynamics in these compounds is fairly well (but not completely) understood.

The geometry is one aspect of tris bipyridine complexes that is not ideal for many applications is the geometry. Many different applications, such as light harvesting systems or molecular arrays, are best served by well ordered linear geometries. With a tris bipyridine complex, there are many different ways to arrange two substituent around the metal center (a few of which can be seen in Figure 5-1), and any reaction will yield a mixture of these different isomers. In order to get a linear arrangement of substituents with only one isomer, it is necessary to move to a bis terpyridine framework.

While the geometry of bis(terpyridyl) ruthenium(II) complexes makes them perfectly suited for many applications, their photophysical properties are less than ideal. The bis(terpyridyl)ruthenium(II) systems have electrochemical properties that are similar to related bipyridine systems, so they can still act as

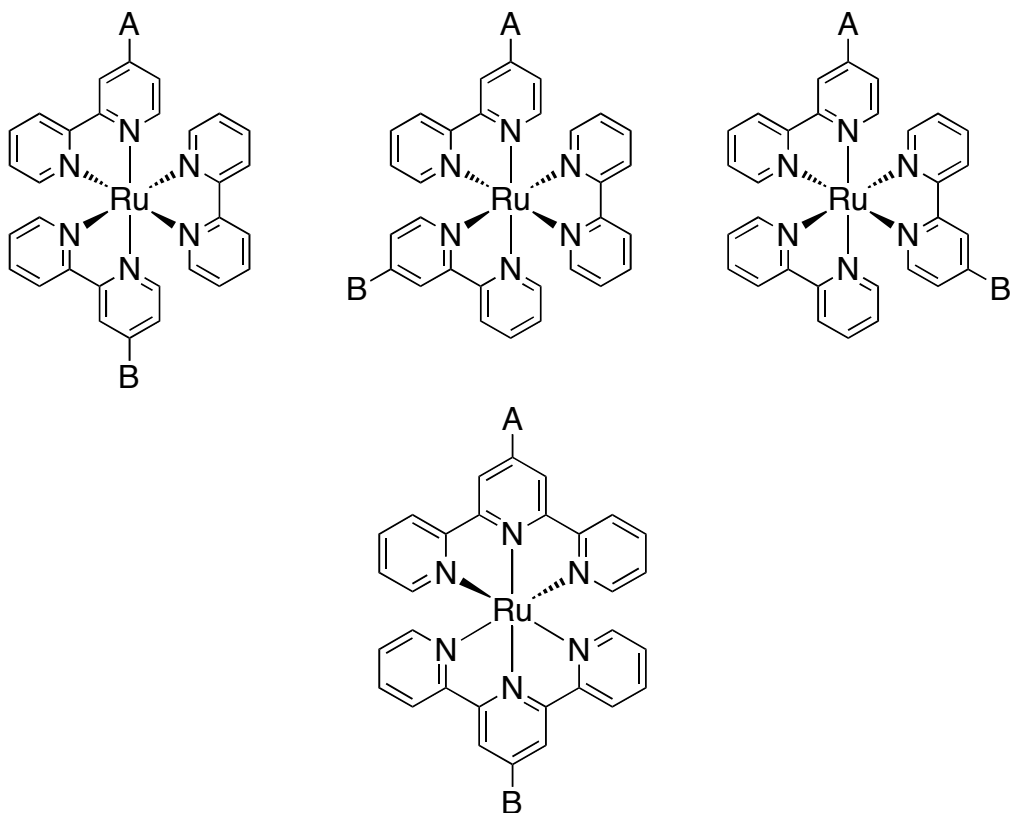


Figure 5-1: Examples of different isomers formed with two substituents (A and B) in a ruthenium tris(bipyridine) complex (top) and a ruthenium bis(terpyridine) complex (bottom)

both oxidants and reductants when photoexcited. The longest lived excited state is also charge transfer in nature. The problem is the terpyridine with the lifetime of the longest lived excited state; $[\text{Ru}(\text{tpy})_2]^{2+}$ has a lifetime of only 250 ps, compared to 950 ns for $[\text{Ru}(\text{bpy})_3]^{2+}$. The main reason for the difference in lifetimes is the difference in ligand field strength between bipyridine and terpyridine. The geometry of the terpyridyl ligand distorts the ruthenium center from an ideal octahedral coordination environment and weakens the ligand field strength of the terpyridine ligand. The weaker ligand field strength means that the ligand field states are lower in energy in terpyridine complexes than they are

in bipyridine. In $[\text{Ru}(\text{tpy})_2]^{2+}$ and other terpyridine complexes the ligand field states are low enough in energy that they are thermally accessible from the long lived excited state. In general, ligand field states couple to the ground state very efficiently through non-radiative decay, so thermal population of the ligand field states in ruthenium(II) terpyridine complexes leads to very rapid, non-radiative deactivation of the excited state.

Different approaches have been taken in attempt to lengthen the lifetime of bis(terpyridyl) ruthenium(II) complexes by increasing the energy between the charge transfer and ligand field states. Increasing the conjugation in the terpyridyl π system both lowers the energy of the charge transfer state, which increases the energy barrier between the charge transfer and ligand field states and makes the charge transfer state more nested, which lowers the rate of non-radiative decay directly from the charge transfer state to the ground state. The increased conjugation can also increase the transition dipole (μ), which increases k_r according to radiative decay theory, therefore increasing the extinction coefficient and the quantum yield. Harriman and coworkers used a phenylethynyl substituent to extend the lifetime to 44 ± 3 ns (compared to 250 ps for $[\text{Ru}(\text{tpy})_2]^{2+}$) and increased the room temperature quantum yield to 3.6×10^{-4} (compared to $< 5 \times 10^{-6}$ for $[\text{Ru}(\text{tpy})_2]^{2+}$).¹ Increasing the ligand field strength of the ligands bound to the ruthenium center will increase the energy of the ligand field states. Scandola and coworkers replaced one terpyridine ligand with strong field cyanide ligands in order to increase the energy separation between the charge transfer and ligand field states. The $[\text{Ru}(\text{tpy})(\text{CN})_3]^{1-}$ complex exhibited extended lifetimes but the results were highly solvent dependent, ranging from <1 ns to 49 ns in different solvents.² The most dramatic improvements in excited state lifetime and quantum yield come from modifying the terpyridine ligand to increase its flexibility and make the coordination environment around the

ruthenium center more octahedral.³ Johansson, Hammarström, and coworkers replaced terpyridine with 2,6-di(quinolin-8-yl)pyridine (Figure 5-2a).⁴ This change increased the bite angle of the ligand to 178° (from 158° for terpyridine) and resulted in a complex with a 3 μs lifetime and a quantum yield of 0.02, which is comparable to ruthenium tris bipyridine complexes. Schramm *et. al.* used a ketone bridged tripyridine ligand to form a perfectly octahedral coordination environment around the ruthenium center (i.e. bond angles of 180° and 90°).⁵ This bis(tripyridine)ruthenium(II) complex exhibited a 3.5 μs lifetime and a quantum yield of 30% (Figure 5-2b). This is actually an improvement over many tris(bipyridine)ruthenium(II) complexes. For example [Ru(bpy)₃]²⁺ has a 950 ns lifetime and a 9.5% quantum yield.

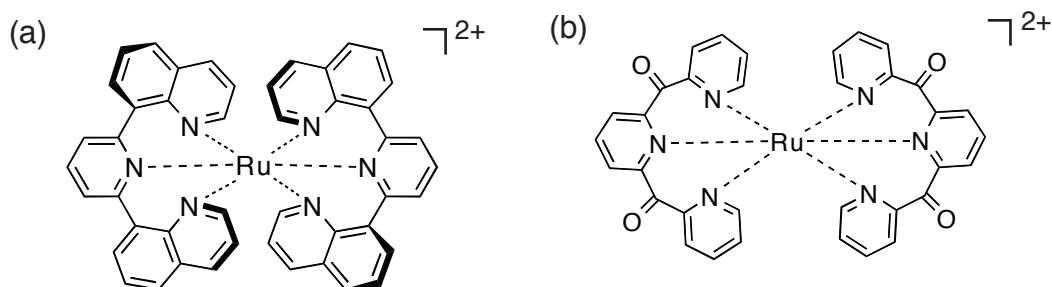


Figure 5-2: Examples of ruthenium(II) complexes with tridentate ligands having a near octahedral coordination geometry. (a) [Ru(dqp)₂]²⁺ (dqp = 2,6-di(quinolin-8-yl)pyridine) (b) [Ru(tripy)₂]²⁺ (tripy = 1,1'-(2,6-pyridinediyl)bis[1-(2-pyridinyl)methanone])

This chapter investigates the ground state and long lived excited states of a series of cyano-substituted terpyridine complexes (Figure 5-3). These complexes served as the synthetic inspiration for the bipyridine complexes discussed in Chapters 3 and 4. Compared to tris bipyridine complexes, there

has been relatively little work done to investigate the excited state dynamics in bis terpyridine complexes. The work in this chapter lays the groundwork for a wider study into the excited state dynamics of bis(terpyridyl)ruthenium(II) complexes.

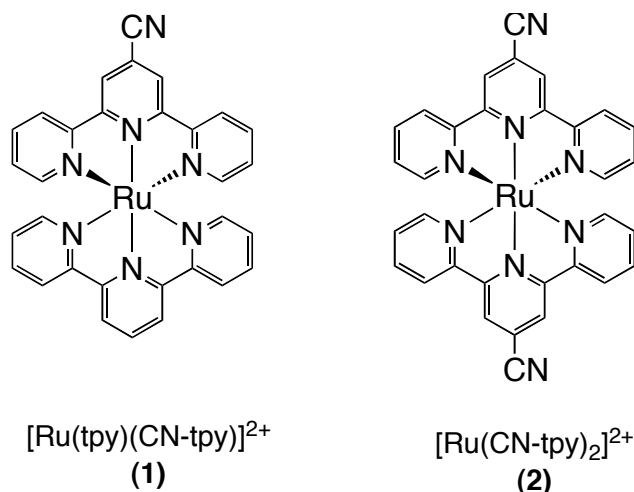


Figure 5-3: Structures of the cyano-substituted terpyridine ruthenium(II) complexes discussed in this chapter.

5.2 Experimental

5.2.1 General

All chemicals and solvents were obtained from Fisher or Aldrich Chemical Co. and used without further purification unless otherwise stated. Tris(benzylideneacetone)dipalladium(0) ($\text{Pd}_2(\text{dba})_3$), diphenylphosphinoferrocene (dppf), and 4'-chloro-2,2':6,6''-terpyridine were purchased from Strem Chemicals, Inc. NMR spectra were collected on the Varian UnityPlus-500 (500 MHz) spectrometer. Ground state infrared spectra ($4000\text{--}400\text{ cm}^{-1}$) were measured as KBr pellets using a Mattson Galaxy series 3000 FT-IR spectrophotometer. Mass

spectra were obtained through the Michigan State University Mass Spectrometry Facility. Elemental analyses were obtained through the analytical facilities at Michigan State University. Solvent included in calculated elemental analysis percentages was included to give the best fit based on solvents identified by NMR and IR.

5.2.2 Synthesis of $[\text{Ru}(\text{tpy})(\text{CN-tpy})](\text{PF}_6)_2$

Trichloro(terpyridine)ruthenium(III)

$\text{Ru}(\text{tpy})\text{Cl}_3$

$\text{Ru}(\text{tpy})\text{Cl}_3$ was synthesized as reported by Constable *et. al.*⁶ Briefly, 1.07 g of $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ and 0.96 g of 2,2':6',2''-terpyridine were refluxed in 200 mL of ethanol for one hour. The solution was cooled to room temperature and a brown solid was collected by vacuum filtration; rinsed with ethanol, water, and ether; and dried further under vacuum. The insolubility of the product prevented characterization by ESI/MS, NMR, or electronic absorption spectroscopy. Yield: 1.37 g

(4'-chloro-terpyridine)terpyridineruthenium(II) hexafluorophosphate

$[\text{Ru}(\text{tpy})(\text{Cl-tpy})](\text{PF}_6)_2$

$[\text{Ru}(\text{tpy})(\text{Cl-tpy})](\text{PF}_6)_2$ was synthesized as reported by Constable *et. al.*⁶ Briefly, 0.05 g of $\text{Ru}(\text{tpy})\text{Cl}_3$ and 0.03 g of 4'-chloro-terpyridine (Cl-tpy) were suspended in 20.0 mL of methanol. Five drops of N-ethylmorpholine were added and the solution was heated to reflux for one hour. After an hour the solution was cooled to room temperature and filtered through celite to remove any unreacted $\text{Ru}(\text{tpy})\text{Cl}_3$. Excess aqueous NH_4PF_6 was added to the filtrate to precipitate a red powder. The red solid was collected by vacuum filtration; rinsed once with cold methanol, three times with water and three times with ether; and

dried under vacuum. Product was recrystallized once by acetonitrile/ether diffusion. Yield: 0.08 g (75.5%) ^1H NMR (500 MHz, $(\text{CD}_3)_2\text{CO}$): δ 9.20 (s, 2H), 9.08 (d, $J=8.2$ Hz, 2H), 8.90 (d, $J=7.6$ Hz, 2H), 8.82 (d, $J=8.1$ Hz, 2H), 8.60 (t, $J=8.2$ Hz, 1H), 8.09 (m, 4H), 7.80 (d, $J=6.3$ Hz, 2H), 7.76 (d, $J=6.3$ Hz, 2H), 7.37 (t, $J=6.6$ Hz, 2H), 7.32 (t, $J=5.9$ Hz, 2H).

(4'-cyano-terpyridine)terpyridineruthenium(II) hexafluorophosphate
 $[\text{Ru}(\text{tpy})(\text{CN-tpy})](\text{PF}_6)_2$

$[\text{Ru}(\text{tpy})(\text{CN-tpy})](\text{PF}_6)_2$ was synthesized as reported by Hanan, Campagna, and coworkers.⁷ Briefly, 0.025 g of $[\text{Ru}(\text{tpy})(\text{Cl-tpy})](\text{PF}_6)_2$, 0.002 g of $\text{Zn}(\text{CN})_2$, 0.001 g of $\text{Pd}_2(\text{dba})_3$, 0.001 g of dppf, and a trace amount of zinc dust were combined with 5.0 mL of dimethylacetamide (DMA) in a inert atmosphere glovebox. The solution was transferred from the glovebox to a Schlenk line and heated to 120°C for six hours. After six hours, the warm solution was filtered through celite and the filtrate was evaporated to dryness. The red-brown residue was purified by column chromatography using silica gel and 7:1 CH_3CN :saturated aqueous KNO_3 . The purified product was recrystallized once by acetonitrile and ether diffusion. The purity of the product was confirmed by NMR and elemental analysis. Anal. Calcd (Found) for $\text{C}_{31}\text{H}_{21}\text{F}_{12}\text{N}_7\text{P}_2\text{Ru}\cdot 0.25$ CH_3CN : C, 42.38 (42.51); H, 2.46 (2.10); N, 11.37 (11.70). ^1H NMR (500 MHz, CD_3CN): δ 9.07 (s, 2H), 8.79 (d, $J=8.2$ Hz, 2H), 8.54 (d, $J=8.0$ Hz, 2H), 8.51 (d, $J=8.7$ Hz, 2H), 8.48 (t, $J=8.1$ Hz, 1H), 7.98 (t, $J=7.9$ Hz, 2H), 7.92 (t, $J=8.0$ Hz, 2H), 7.41 (d, $J=5.1$ Hz, 2H), 7.29 (t, $J=5.5$ Hz, 2H), 7.24 (t, $J=6.6$ Hz, 2H), 7.14 (t, $J=6.1$ Hz, 2H). FT-IR (selected frequencies in KBr pellet, cm^{-1}) 3116(m), 2240(m), 1602(s), 1449(s), 835(vs), 558(vs).

5.2.3 Synthesis of $[\text{Ru}(\text{CN-tpy})_2](\text{PF}_6)_2$

Trichloro(4'-chloro-terpyridine)ruthenium(III)

$\text{Ru}(\text{Cl-tpy})\text{Cl}_3$

$\text{Ru}(\text{tpy})\text{Cl}_3$ was synthesized as reported by Constable *et. al.*⁶ Briefly, 0.52 g of $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ and 0.55 g of 4'-chloro-2,2':6',2''-terpyridine were refluxed in 100 mL of ethanol for one hour. The solution was cooled to room temperature and a brown solid was collected by vacuum filtration; rinsed with ethanol, water, and ether; and dried further under vacuum. The insolubility of the product prevented characterization by ESI/MS, NMR, or electronic absorption spectroscopy. Yield: 0.78 g

Bis(4'-chloro-terpyridine)ruthenium(II) hexafluorophosphate

$[\text{Ru}(\text{Cl-tpy})_2](\text{PF}_6)_2$

$[\text{Ru}(\text{Cl-tpy})_2](\text{PF}_6)_2$ was synthesized as reported by Constable *et. al.*⁶ Briefly, 0.175 g of $\text{Ru}(\text{Cl-tpy})\text{Cl}_3$ and 0.099 g of 4'-chloro-terpyridine (Cl-tpy) were suspended in 60.0 mL of methanol. Fifteen drops of N-ethylmorpholine were added and the solution was heated to reflux for one hour. After an hour the solution was cooled to room temperature and filtered through celite to remove any unreacted $\text{Ru}(\text{Cl-tpy})\text{Cl}_3$. Excess aqueous NH_4PF_6 was added to the filtrate to precipitate a red powder. The red solid was collected by vacuum filtration; rinsed once with cold methanol; three times with water and three times with ether; and dried under vacuum. Product was recrystallized once by acetonitrile/ether diffusion. Yield: 0.13 g (38.2%) ^1H NMR (500 MHz, CD_3CN): δ 9.10 (s, 2H), 8.80 (d, $J=8.0$ Hz, 2H), 8.00 (td, $J=7.9, 1.5$ Hz, 2H), 7.74 (d, $J=5.6$ Hz, 2H), 7.26 (dt, $J=4.8, 1.3$ Hz, 1H).

Bis(4'-cyano-terpyridine)ruthenium(II) hexafluorophosphate

[Ru(CN-tpy)₂](PF₆)₂

[Ru(CN-tpy)₂](PF₆)₂ was synthesized as reported by Hanan, Campagna, and coworkers.⁷ Briefly, 0.108 g of [Ru(Cl-tpy)](PF₆)₂, 0.0162 g of Zn(CN)₂, 0.012 g of Pd₂(dba)₃, 0.013 g of dppf, and a trace amount of zinc dust were combined with 25.0 mL of dimethylacetamide (DMA) in a inert atmosphere glovebox. The solution was transferred from the glovebox to a Schlenk line and heated to 120°C for overnight. The warm solution was filtered through celite and the filtrate was evaporated to dryness. The red-brown residue was purified by column chromatography using silica gel and 7:1 CH₃CN:saturated aqueous KNO₃. The purified product was recrystallized once by acetonitrile and ether diffusion. After recrystallization, the solid was isolated as mixed salt. Elemental analysis suggests ~1.5 NO₃⁻ and 0.5 PF₆⁻ as the average counterion composition. The purity of the product was also confirmed by NMR and mass spectroscopy. Anal. Calcd (Found) for C₃₂H₂₀N₈Ru•1.5 NO₃ 0.5 PF₆: C, 49.08 (49.19); H, 2.57 (2.65); N, 16.99 (16.72). ¹H NMR (500 MHz, CD₃CN): δ 9.08 (s, 2H), 8.52 (d, J=8.1 Hz, 2H), 7.99 (td, J=7.9, 1.6 Hz, 2H), 7.35 (d, J=5.6 Hz, 2H), 7.22 (td, J=5.6, 1.3 Hz, 2H). MS [ESI (CH₃CN), *m/z* (rel. int.)]: 309.1 (100) [M-2PF₆]²⁺. MS [HR-ESI (CH₃CN)] *m/z* 309.0430 [M-2PF₆]²⁺, calcd. (C₃₂H₂₀N₈Ru) 309.0427. FT-IR (selected frequencies in KBr pellet, cm⁻¹) 3121(w), 2240(m), 1625(w), 1603(s), 1426(s), 1353(s), 831(vs), 558(vs).

5.2.4 Physical Measurements

Electrochemistry

Electrochemical measurements were carried out in a Ar-filled drybox (Vacuum Atmospheres) using a CHI 630B electrochemical analyzer. A standard three-electrode arrangement was used, consisting of a Pt working electrode, a

graphite counter electrode, and a Ag/AgCl reference electrode (Cypress Systems). Measurements were carried out in spectrophotometric grade CH₃CN, which was freeze-pump-thaw degassed before use, and using 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as the supporting electrolyte. Data were acquired by cyclic voltammetry (CV) and differential pulse voltammetry (DPV); the scan rate for the CV measurements was 50 mV/s and the scan rate and pulse width for the DPV measurements were 20 mV/s and 50 mV, respectively. Values for $E_{1/2}$ obtained by the two techniques were comparable. All oxidation and reduction waves were reversible over several consecutive scans. Potentials are listed versus the ferrocene/ferrocenium couple, which was used as an internal standard, and quoted as $E_{1/2}$ values as calculated from the DPV peak potentials.⁸

Electronic Steady-State and Time-Resolved Spectroscopies

All spectra were collected in spectrophotometric grade CH₃CN unless otherwise noted. For steady state emission and time-resolved measurements, the solvent was freeze-pump-thaw degassed before use. Electronic absorption spectra for all compounds were acquired using a Cary 50 spectrophotometer. Steady-state emission spectra were acquired using a Spex Fluoromax fluorimeter and corrected for instrumental response using a NIST standard of spectral irradiance (Optronic Laboratories, Inc., OL220 M tungsten quartz lamp). Samples were prepared in an inert atmosphere glovebox in 1 cm quartz cuvettes and measured under optically dilute conditions (o.d. 0.1-0.2). The resulting emission spectra were fit with an asymmetric double sigmoidal function using IGOR pro. This function has no mathematical significance but it is able to accurately reproduce the shape of the entire emission curve and thereby capture the small area (< 10%) that lies outside of the detector range thereby providing

for a more accurate estimate of the integrated spectrum. Relative radiative quantum yields (Φ_r) were determined using $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ or $[\text{Os}(\text{bpy})_3](\text{PF}_6)_2$ as a standard ($\text{Ru } \Phi_{\text{std}} = 0.095$ in degassed CH_3CN ⁹, $\text{Os } \Phi_{\text{std}} = 0.0077$ in degassed CH_3CN ^{10,11}). Quantum yields were calculated as described in Chapter 3, using Equation 5-1, where Φ_{unk} is the relative radiative quantum yield

$$\Phi_{\text{unk}} = \Phi_{\text{std}} \left(\frac{I_{\text{unk}}}{A_{\text{unk}}} \right) \left(\frac{A_{\text{std}}}{I_{\text{std}}} \right) \left(\frac{\eta_{\text{unk}}}{\eta_{\text{std}}} \right)^2 \quad 5-1$$

of the sample, I_{unk} and I_{std} are the integrated areas of the corrected emission spectra of the sample and standard, respectively, A_{unk} and A_{std} are the absorbances of the sample and the standard at the excitation wavelength, and η_{unk} and η_{std} are the indexes of refraction of the respective solvents (taken to be equal to the neat solvents in both cases). Low-temperature emission spectra were collected using a Janis SVT-100 optical cryostat as described previously.¹² Measurements were taken at 80 K in a 9:2 mixture of butyronitrile and propionitrile, both of which were freeze-pump-thaw degassed before use. Estimates of the zero point energy gap (E_0), Huang-Rhys factor (S_M), energy of the average vibrational mode coupling the ground and excited states ($\hbar\omega_M$), and spectral bandwidth ($\Delta\bar{\nu}_{0,1/2}$) were determined by a single mode fit of the steady-state emission spectra to Equation 5-2 as described by Claude and Meyer.¹³ The correction of Parker and Rees was applied to all spectra when converting from wavelength to energy units.¹⁴

$$I(\bar{\nu}) = \sum_{\nu_M=0}^5 \left\{ \left(\frac{E_0 - \nu_M \hbar\omega_M}{E_0} \right)^3 \frac{S_M^{\nu_M}}{\nu_M!} \cdot \exp \left(-4(\ln 2) \left(\frac{\bar{\nu} - E_0 + \nu_M \hbar\omega_M}{\Delta\bar{\nu}_{0,1/2}} \right)^2 \right) \right\} \quad 5-2$$

Nanosecond time-resolved emission and transient absorption experiments were carried out using a Nd:YAG laser spectrometer that has been described previously.^{15,16} Time-resolved emission was collected on the same samples used to acquire the room-temperature steady-state emission spectra (*vide supra*). Samples for time-resolved absorption measurements were prepared with an absorbance in the range of 0.3-0.5 at the excitation wavelength, 510 nm, and sealed under an Ar atmosphere in 1 cm quartz cuvettes. Data corresponds to a 15 shot average (0.2 Hz) of the signal and baseline as well as background sample emission with 1-3 mJ of power at the sample. The baseline and emission were subsequently subtracted from the signal and the data analyzed using a program of local origin. All data were checked for linearity with respect to pump power. In addition, absorption spectra were measured before and after all time-resolved absorption experiments to ensure the integrity of the sample. Laser power was periodically monitored to ensure constant pump power over the course of the experiment. Data acquired at each probe wavelength was fit to a single exponential kinetic model; the amplitudes for each of these fits were plotted to produce the differential absorption spectra reported herein.

5.3 Results and Discussion

I have synthesized and characterized the cyano-substituted terpyridine complexes that served as synthetic inspiration for the cyano-substituted bipyridine complexes discussed in the previous chapters. The properties of the long lived ³MLCT state in these terpyridine complexes, shown in Figure 5-3, are investigated and compared to the related bipyridine complexes. The focus of this chapter is the similarities and differences between the two families of molecules in the ground state and long-lived excited state.

5.3.1 Synthesis

Hanan, Campagna, and coworkers originally synthesized these complexes in the hope that the coordinating ability of the cyanide group would make them useful building blocks for more complex supermolecular assemblies.¹⁷ The authors used the unusual chemistry-on-the-complex approach to synthesize these complexes because, at the time, there was not a high yielding method available to synthesize the free 4'-cyano-2,2':6',2''-terpyridine (CN-tpy) ligand. Pre-coordinating the starting chloro-substituted ligand to the ruthenium center made the terpyridine more reactive to substitution and prevented it from coordinating to and deactivating the Pd catalyst. The starting Cl-tpy ruthenium complexes and final CN-tpy ruthenium products were synthesized exactly as reported in the literature, without any changes or modifications.

After recrystallization, $[\text{Ru}(\text{CN-tpy})_2]^{2+}$ complex was isolated with mixture of hexafluorophosphate and nitrate counterions. The elemental analysis results suggest the average formula is $[\text{Ru}(\text{CN-tpy})_2](\text{NO}_3)_{1.5}(\text{PF}_6)_{0.5}$. The infrared spectrum of the compound (Figure B-4) shows infrared stretches at 831 cm^{-1} and 558 cm^{-1} for PF_6 and a broad feature at $1300 - 1400\text{ cm}^{-1}$ which is most likely due to the nitrate ion. The identity of the counterion, however, will have no effect on the photophysical properties of the complex.

5.3.2 Ground State Spectroscopic Properties

The ground state absorption spectra of the two complexes and $[\text{Ru}(\text{tpy})_2](\text{PF}_6)_2$ are shown in Figure 5-4. The electronic absorption spectra of ruthenium terpyridyl complexes are qualitatively very similar to the ruthenium bipyridyl complexes discussed in Chapter 3. They exhibit both intraligand as well as charge transfer transitions, but unlike the bipyridine complexes there isn't an obvious distinction between the absorption features associated with the CN-tpy

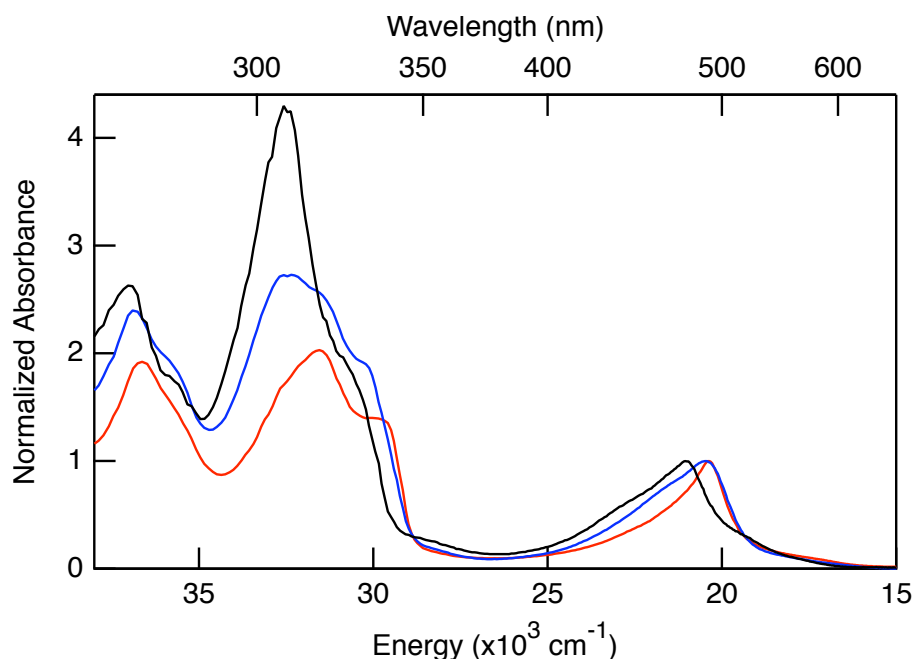


Figure 5-4: Normalized absorption spectra of $[\text{Ru}(\text{tpy})(\text{CN-tpy})]^{2+}$ (**1**, blue) and $[\text{Ru}(\text{CN-tpy})_2]^{2+}$ (**2**, red) and $[\text{Ru}(\text{tpy})_2]^{2+}$ (black) in acetonitrile solution. Spectra are normalized at the maximum of the MLCT absorption feature to better show the change in shape of the MLCT absorption band across the series.

and the unsubstituted tpy. Based on extinction coefficients as well as comparison to the cyano-substituted ruthenium bipyridine complexes, the UV absorption features in complexes **1-2** can be assigned as $\pi \rightarrow \pi^*$ absorptions of the terpyridine ligands whereas the somewhat weaker visible features are metal-to-ligand charge transfer (MLCT) in nature. In $[\text{Ru}(\text{tpy})_2](\text{PF}_6)_2$ there are two UV absorptions, one at 270 nm and one at 307 nm which can both be readily assigned as $\pi \rightarrow \pi^*$ absorptions of the terpyridine ligand by comparison to the reported absorption spectrum of $[\text{Zn}(\text{tpy})_2]^{2+}$.¹⁸ Complex **2** has two UV absorptions at 273 nm and 317 nm. These are assigned to the analogous $\pi \rightarrow \pi^*$ absorptions of the CN-tpy ligand. In complex **1**, the UV absorption features are at 271 nm and 309 nm, which fall between the absorption maxima of the two homoleptic complexes. These features are a superposition of absorption

features of the tpy ligand and the CN-tpy ligand; it is not possible to differentiate the contributions from the different ligands as in the bipyridine complexes.

Assignments within the charge transfer band are not straight forward but can be clarified using electrochemistry. As discussed in Chapter 3, the energy of a metal-to-ligand charge transfer band can be thought of in terms of the energy required to oxidize the metal and reduce the ligand.¹⁹ For two ligands bound to the same metal, the energy of the MLCT states will therefore correlate with the reduction potential of the ligands. The electrochemical properties of complexes **1** and **2** have been investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV), the results of which are shown in Figure 5-5 and listed in Table 5-1.

The electron-withdrawing nature of the cyano group is apparent in the trends in the ruthenium oxidation potential across the series, although the effect is not as dramatic as in the bipyridine complexes. Starting with $[\text{Ru}(\text{tpy})_2]^{2+}$, each successive replacement of 2,2':6',2''-terpyridine by CN-tpy in the coordination sphere systematically shifts the oxidation potential of the metal center positive by ca. 100 mV (compared to 130 mV for the bipyridine complexes). This shift in charge density at the ruthenium indicates the comparatively poorer electron donating ability of the CN-tpy relative to the unsubstituted terpyridine ligand.

To assign the ligand reductions, first compare the reduction potentials of complex **2** and $[\text{Ru}(\text{tpy})_2](\text{PF}_6)_2$. In these cases, there is no question of which ligand is being reduced. The CN-tpy ligand in complex **2** is more easily reduced than the tpy ligand in $[\text{Ru}(\text{tpy})_2]^{2+}$ by 380 mV which is significant, but less than the 480 mV seen in the bipyridine complexes. Next, compare the heteroleptic complex **1** to the two homoleptic complexes; the first reduction potential is much closer in energy to that of complex **2**, whereas the second reduction potential is much closer to the $[\text{Ru}(\text{tpy})_2]^{2+}$. This, combined with the larger energy splitting

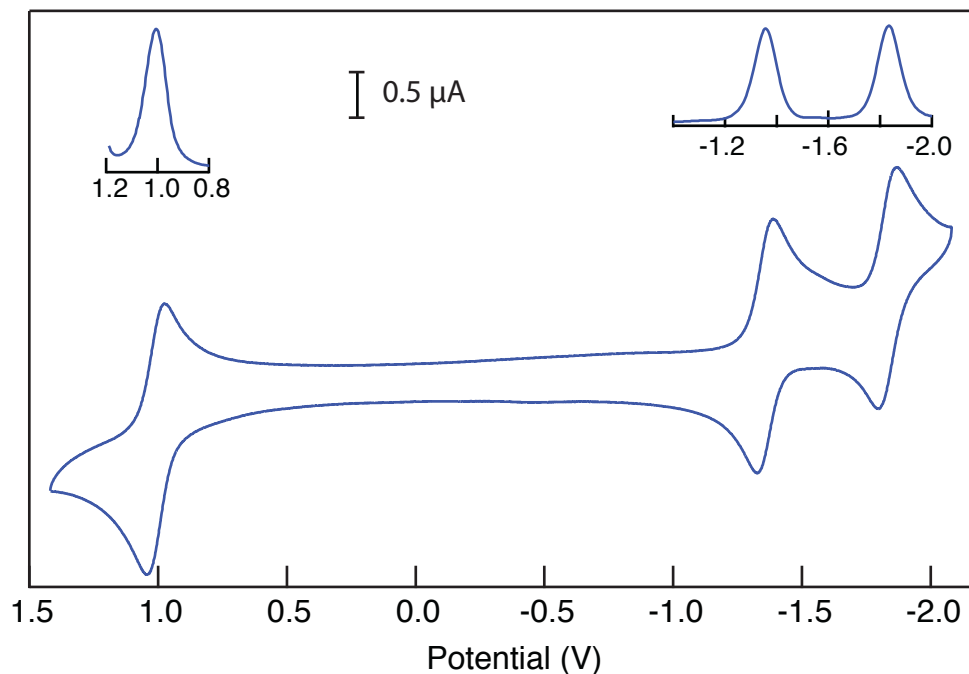


Figure 5-5: Cyclic voltammogram of $[\text{Ru}(\text{tpy})(\text{CN-tpy})](\text{PF}_6)_2$ (**1**) in CH_3CN with 0.1 M TBAPF_6 as the electrolyte. Spectrum was collected using the standard three electrode setup with a platinum working electrode, graphite counter electrode, and a Ag/AgCl reference electrode and is referenced to the ferrocene/ferrocenium redox couple, which was added as an internal standard. The differential pulse voltammogram is shown in the insets

Table 5-1: Electrochemical Data for Complexes **1-2** and $[\text{Ru}(\text{tpy})_2](\text{PF}_6)_2$ ^a

Complex	$E_{1/2}^{\text{ox}}$	$E_{1/2}^{\text{red1}}$	$E_{1/2}^{\text{red2}}$	ΔE (eV) ^b
$[\text{Ru}(\text{tpy})_2](\text{PF}_6)_2$	+0.92	-1.63	-1.88	2.55
$[\text{Ru}(\text{tpy})(\text{CN-tpy})](\text{PF}_6)_2$	+ 1.03	-1.34	-1.81	2.37
$[\text{Ru}(\text{CN-tpy})_2](\text{PF}_6)_2$	+1.13	-1.25	-1.53	2.38

^aPotentials are reported in V versus the ferrocene/ferrocenium couple in acetonitrile solution as described in the experimental section.

^b $\Delta E = (E_{1/2}^{\text{ox}} - E_{1/2}^{\text{red1}})$.

between the first and second reductions show that the first reduction potential is the reduction of the CN-tpy ligand and the second reduction is of the unsubstituted tpy ligand.

With the electrochemical results, assigning the electronic absorption features is now simplified. First, start with the two homoleptic complexes, complex **1** and $[\text{Ru}(\text{tpy})_2]^{2+}$. In complex **2** the narrow charge transfer absorption feature at 491 nm is solely due to metal-to-ligand charge transfer transitions to the CN-tpy ligand and in $[\text{Ru}(\text{tpy})_2]^{2+}$ the MLCT transition to the terpyridine ligand is blue-shifted to 475 nm due in part to the higher reduction potential of the terpyridine

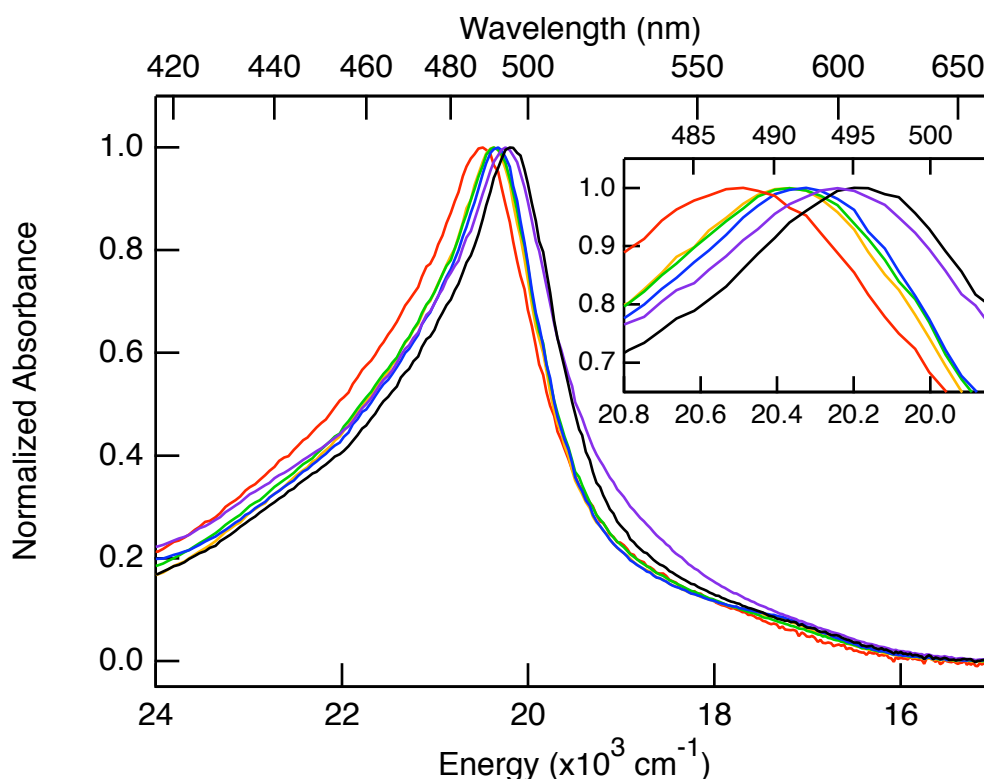


Figure 5-6: Electronic absorption spectra of $[\text{Ru}(\text{CN-tpy})_2]^{2+}$ (**2**) in methanol (red line, $\lambda_{\text{max}} = 488$ nm), acetonitrile (orange line, $\lambda_{\text{max}} = 491$ nm), acetone (green line, $\lambda_{\text{max}} = 491$ nm), nitromethane (blue line, $\lambda_{\text{max}} = 492$ nm), DMF (purple line, $\lambda_{\text{max}} = 494$ nm), and DMSO (black line, $\lambda_{\text{max}} = 495$ nm). The inset shows an expanded view of the absorption maxima.

ligand. Complex **1** will have both MLCT transitions to CN-tpy and to tpy. Unlike the bipyridine complexes, there is no clear distinction between the two absorption features. Comparison of the band shapes in complexes **1** and **2** does suggest some differentiation between the CN-tpy and tpy absorption features. The MLCT absorption feature in complex **1** has a definite shoulder on the blue edge of the absorption band that is not present in the homoleptic complex. This broadening of the charge transfer manifold in complex **1** is due to the addition of tpy charge transfer transitions to the absorption feature.

Solvatochromism is an important feature of some cyanide-containing compounds. In ruthenium(II) cyanide complexes such as $[\text{Ru}(\text{bpy})\text{CN}_4]^{2-}$ the absorption spectrum can shift over 6800 cm^{-1} ($\sim 150\text{ nm}$) by changing solvents.^{20,21} Molecular donor-acceptor systems that incorporate $[\text{Ru}(\text{bpy})\text{CN}_4]^{2-}$ can change the direction of energy transfer by changing the solvent.²²⁻²⁴ While the solvatochromatic response for complexes **1** and **2** is not nearly as dramatic as the ruthenium cyanide complexes (*vide supra*) there is a definite shift in the MLCT absorption maximum as a function of solvent, which can be seen in Figures 5-6 and B-6. There have been many different scales (donor number, acceptor number, dipole moment, and Z-values for example) used to quantify the effect a solvent has on electronic absorption.²⁵⁻²⁷

The trends seen in solvatochromism can also give insight to the electronic structure of the ground state and/or the excited state and how they interact with solvent. The solvatochromatic shift in the ruthenium cyanide complexes is a function of the solvent acceptor number, which is the electron accepting strength of the solvent. Solvents that are good electron acceptors shift the absorption maximum to higher energy and solvents that are poor electron acceptors shift the absorption maximum to lower energy.²¹ This trend shows that the solvent is specifically interacting with the molecule and accepting electron density,

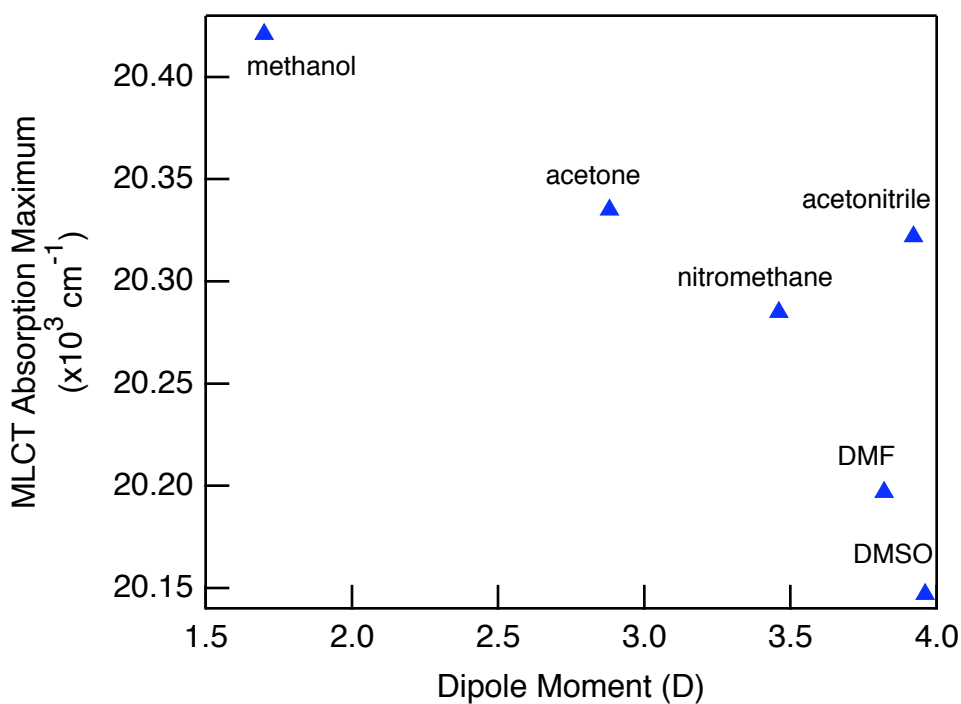


Figure 5-7: Plot of MLCT absorption maximum vs solvent dipole moment for $[\text{Ru}(\text{CN-tpy})_2]^{2+}$ in various solvents (see Figure 5-6). The plot shows a correlation between the absorption maximum and the solvent dipole moment, suggesting the solvatochromatic response is caused by the charged excited state being stabilized by solvent dipole interactions.

therefore stabilizing it. The fact that the strongest electron acceptors give the highest energy absorption features indicates that the solvent interaction is strongest in the ground state and that the ground state is stabilized more than the excited state. As seen in Figure 5-7, the solvatochromatic response for complex **2** is correlated with the solvent dipole moment; solvents with a large dipole shift the spectrum lower in energy and solvents with a small dipole moment shift the spectrum to higher energy. This indicates that, unlike the ruthenium cyanide complexes, the solvent has no specific interactions with the molecule and the solvatochromatic shift is due to a dipole interaction. The absorption maximum is

shifted to lower energy in more polar solvents; this suggests that the solvent is primarily stabilizing the excited state and lowering its energy. This phenomenon is seen in charge transfer excited states with and without cyanide groups. This behavior is another confirmation that the initial excited state has a significant dipole, and is therefore localized on a single ligand.²⁸

5.3.3 Steady-State and Time-Resolved Emission Spectroscopies

The room temperature emission spectra for the two complexes are plotted in Figure 5-8a. The emission maxima for complexes **1** and **2** are at 696 nm and 688 nm respectively, following the same trend as the ruthenium oxidation potentials across the series. Radiative quantum yields for complexes **1-2** were determined relative to both the $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ ⁹ and $[\text{Os}(\text{bpy})_3](\text{PF}_6)_2$ ^{10,11} standards, and are listed in Table 5-2. The quantum yield values for these complexes may seem small in comparison to the ruthenium bipyridine complexes in Chapter 3, but when compared to other ruthenium terpyridine complexes, they are actually quite large; for example, $[\text{Ru}(\text{ph-tpy})_2]^{2+}$ (ph-tpy = 4'-phenyl-2,2':6'2"-terpyridine) has a quantum yield of 4×10^{-5} and $[\text{Ru}(\text{tpy})_2]^{2+}$ has a quantum yield of less than 5×10^{-6} .²⁹

To obtain more quantitative insights into the ³MLCT excited states of this system, I carried out a single mode spectral fitting analysis using Equation 5-2 as described by Meyer and coworkers and the procedure described in Chapter 3.^{13,30} Briefly, the low temperature emission spectra (Figure 5-8b) was fit to yield well defined values for the four parameters (E_0 , S_M , $\hbar\omega_M$, and $\Delta\bar{\nu}_{0,1/2}$). The value of $\hbar\omega_M$ was assumed to be temperature independent, so the room temperature spectra were fit using the low temperature value of $\hbar\omega_M$ as a fixed value. Using this approach, well defined (<10% variation) values for the ³MLCT zero-point energy (E_0), Huang-Rhys factor (S_M), and the spectral bandwidth

($\Delta\bar{\nu}_{0,1/2}$) could be determined for the room-temperature spectra. Spectral fitting parameters for complexes **1** and **2** are listed in Table 5-3.

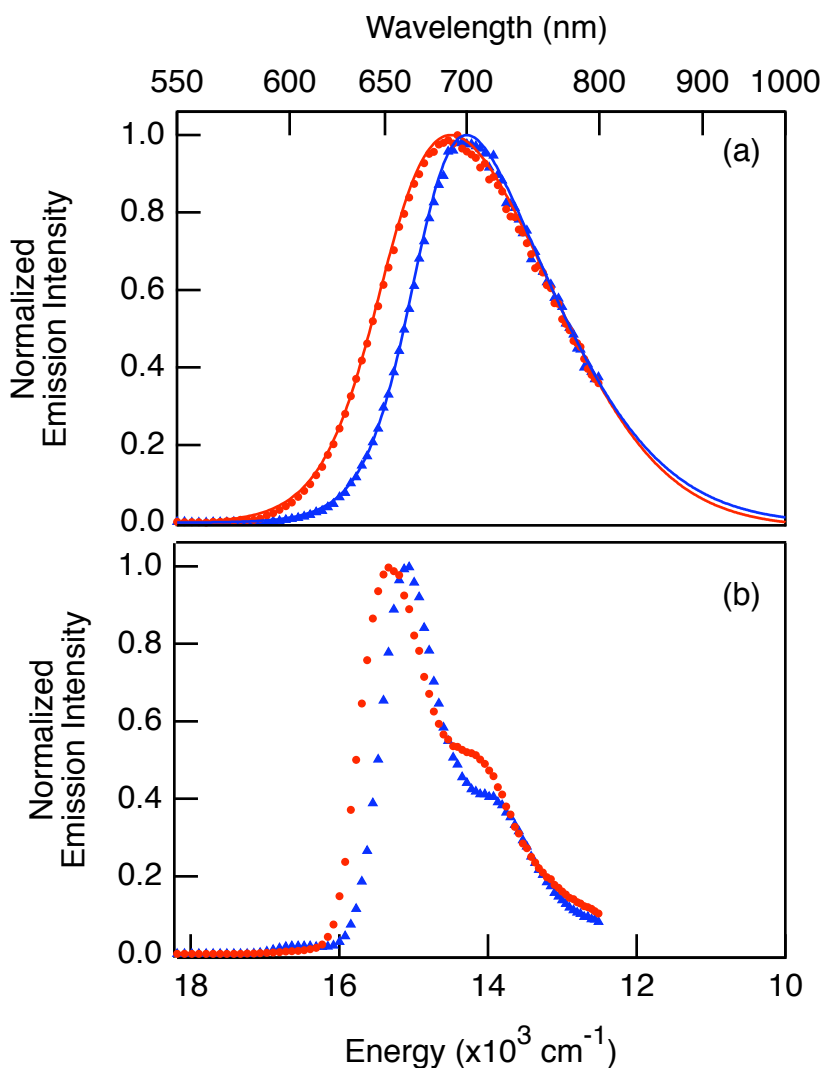


Figure 5-8: Steady-state emission spectra of [Ru(tpy)(CN-tpy)](PF₆)₂ (**1**, blue triangles) and [Ru(CN-tpy)₂](PF₆)₂ (**2**, red circles) (a) Room-temperature spectra acquired in deoxygenated CH₃CN solution. The solid lines correspond to fits to an asymmetric double sigmoidal function – see text for further details. (b) Emission spectra acquired in a 9:2 butyronitrile/propionitrile glass at 80 K

Table 5-2: Photophysical Data for Complexes **1** and **2**

Complex	λ_{em} (nm)	Φ^a ($\times 10^{-3}$)	k_{obs}^a ($\times 10^7 \text{ s}^{-1}$)	$k_r^{a,b}$ ($\times 10^4 \text{ s}^{-1}$)	$k_{\text{nr}}^{a,c}$ ($\times 10^7 \text{ s}^{-1}$)
$[\text{Ru}(\text{tpy})(\text{CN-tpy})]^{2+}$	696	1.9 ± 0.2	1.25 ± 0.03	2.38 ± 0.24	1.25 ± 0.03
$[\text{Ru}(\text{CN-tpy})_2]^{2+}$	688	1.7 ± 0.2	1.82 ± 0.09	3.09 ± 0.37	1.82 ± 0.09

^a Error bars determined by the standard deviation of multiple measurements.

^b $k_r = \Phi_r \cdot k_{\text{obs}}$. ^c $k_{\text{nr}} = k_{\text{obs}} - k_r$.

The fitted values for E_0 for all three complexes are very close to the observed emission maxima, indicating that the $v^* = 0 \rightarrow v = 0$ transition is the dominant contribution to the observed emission spectrum and that the ground state and excited state potential surfaces are fairly nested. The Huang-Rhys factor is a measure of the vibrational overlap between the excited state and the ground state and is proportional to $(\Delta Q)^2$, which makes S_M a useful parameter for gauging the amount of structural distortion in the excited state relative to the ground state.¹⁵ As with the bipyridine complexes, is difficult to draw any conclusions from the differences in the room temperature S_M value since the variations in S_M are within the uncertainties of the fits. The values for the terpyridine are very similar to those of the bipyridine complexes. When compared to $[\text{Ru}(\text{bpy})_3]^{2+}$ ($S_M = 1.01 \pm 0.08$), the Huang-Rhys factors for the terpyridine complexes are significantly smaller, which indicates an increase in delocalization. This increased delocalization could be due to the addition of the cyanide group but it just as easily be due to the additional pyridine ring in the terpyridine ligand. Unfortunately the more informative comparison to $[\text{Ru}(\text{tpy})_2]^{2+}$ is not possible because $[\text{Ru}(\text{tpy})_2]^{2+}$ is not measurably emissive in a room temperature solution.

The lifetimes of complexes **1** and **2** were also determined using nanosecond time-resolved emission (Figure 5-9). Radiative and non-radiative decay rates for both complexes were calculated from the lifetimes and quantum yields (Table 5-2).

Table 5-3. Spectral Fitting Results for Terpyridine Complexes

Complexes	Low Temperature ^{a,b}			
	E_0 (cm ⁻¹)	S_M	$\hbar\omega_M$ (cm ⁻¹)	$\Delta\bar{\nu}_{0,1/2}$ (cm ⁻¹)
[Ru(tpy)(CN-tpy)] ²⁺	15045 ± 50	0.55 ± 0.04	1135 ± 40	910 ± 60
[Ru(CN-tpy) ₂] ²⁺	15274 ± 60	0.67 ± 0.05	1161 ± 40	1000 ± 60
	Room Temperature ^{b,c}			
	E_0 (cm ⁻¹)	S_M	$\hbar\omega_M$ (cm ⁻¹) ^d	$\Delta\bar{\nu}_{0,1/2}$ (cm ⁻¹)
[Ru(tpy)(CN-tpy)] ²⁺	14445 ± 70	0.68 ± 0.1	1135	1510 ± 100
[Ru(CN-tpy) ₂] ²⁺	14820 ± 80	0.82 ± 0.12	1161	1795 ± 140

^a Fitting results for 80 K emission spectra in 9:2 butyronitrile:propionitrile.

^b Error bars represent an approximate range of visually equivalent fits. ^c Fitting results for room temperature emission spectra in CH₃CN, using a fixed value of $\hbar\omega_M$ based on the low temperature data. See text for details.

The results in Table 5-2 clearly show that the deactivation of the ³MLCT state in the terpyridine complexes is dominated by non-radiative decay, which is very different from what is seen in the bipyridine complexes. In ruthenium(II) terpyridine complexes, the major deactivation pathway is through the lowest energy ligand field state(s). Terpyridine is a weaker field ligand than the bipyridine, mostly due to its unfavorable bite angle. This means that the ligand field states in terpyridine complexes are lower in energy and therefore closer in

energy to the MLCT excited states. For comparison, the energy barrier between the lowest energy triplet state and the ligand field states in $[\text{Ru}(\text{bpy})_3]^{2+}$ is approximately 4000 cm^{-1} whereas in $[\text{Ru}(\text{tpy})_2]^{2+}$ it is only 1500 cm^{-1} .³¹ In terpyridine complexes, the long lived $^3\text{MLCT}$ state can thermally populate the ligand field manifold, which decays very rapidly down to the ground state non-radiatively. This means that the rate of non-radiative decay in terpyridine complexes cannot be predicted by the energy gap law (i.e. the ΔE and ΔQ between the excited state and the ground state) like it can in bipyridine complexes.³⁰ Instead, it is a function of the energy difference between the $^3\text{MLCT}$ and ^3LF states.

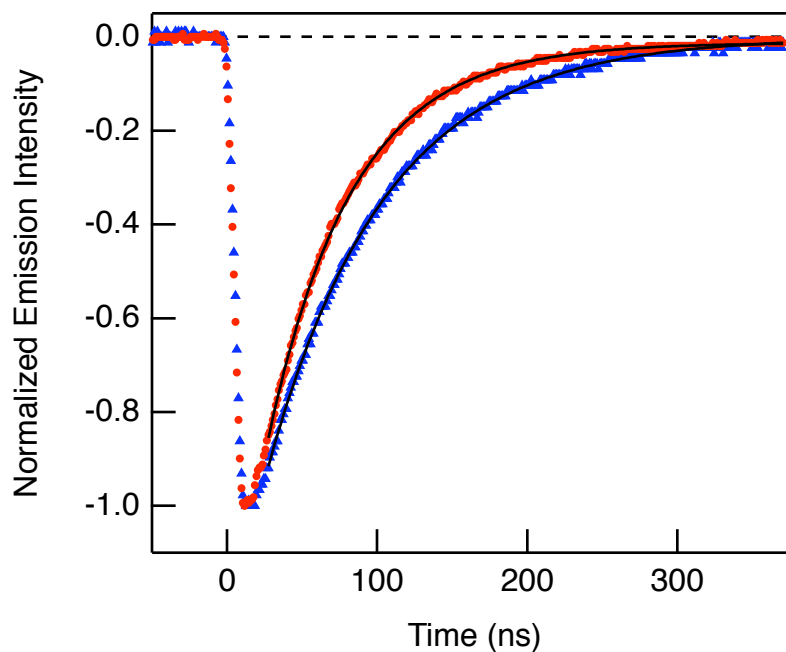


Figure 5-9: Time resolved emission decay traces for $[\text{Ru}(\text{tpy})(\text{CN-tpy})](\text{PF}_6)_2$ (**1**, blue triangle) and $[\text{Ru}(\text{CN-tpy})_2](\text{PF}_6)_2$ (**2**, red circle). Black lines are single exponential fits of the emission decay.

The results in Table 5-2 show that complex **1** has a slower rate of non-radiative decay than complex **2**, which suggests that the energy barrier between the $^3\text{MLCT}$ and ^3LF states for complex **1** is larger than for complex **2**. At first, it may seem counterintuitive that a heteroleptic complex would have a higher energy ligand field state than its corresponding homoleptic complex but work by Maestri *et. al.* has shown that to be true. The authors studied a series of homoleptic and heteroleptic bis(terpyridyl)ruthenium(II) complexes with electron donor and acceptor substituents and found that the complexes with the longest lifetimes were the heteroleptic complexes with one electron donor and one electron acceptor.²⁹ Their results (Figure 5-10) show that electron donor

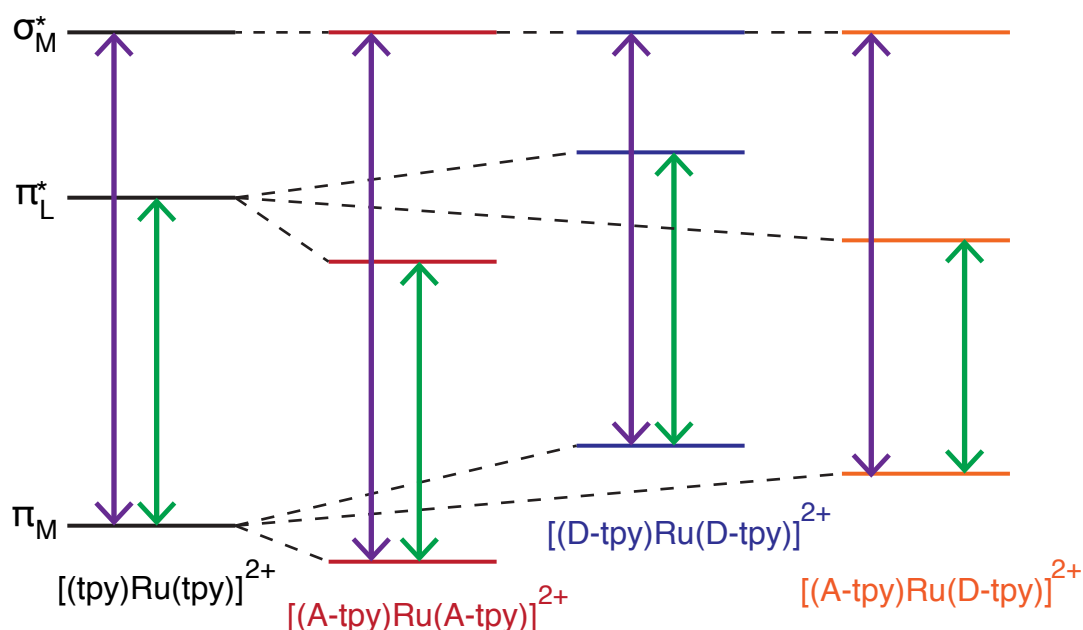


Figure 5-10: Schematic representation of the effect of electron accepting (A) and electron donating (D) substituents on the energy of the HOMO (π_M) and LUMO (π_L^*) orbitals in $[\text{Ru}(\text{tpy}')_2]^{2+}$ complexes. Purple arrows represent ligand field transitions and green arrows represent metal-to-ligand charge transfer transitions. Reproduced from reference 29.

substituents primarily destabilize the HOMO (π_M) orbital, lowering both the MLCT and LF energies and electron acceptor substituents primarily stabilizes the LUMO (π_L) orbital, lowering the MLCT energy and (slightly) raising the LF energy. In a heteroleptic complex with both donor and acceptor substituents the HOMO will be destabilized and the LUMO will be stabilized, leading to a slightly lower LF state and a much lower MLCT state. Experimentally, the heteroleptic complexes in the study had the largest energy barrier between the MLCT and LF states and the longest lifetimes.

The values for the radiative decay rate (k_r) in complexes **1** and **2** are similar to those seen in the bipyridine complexes in Chapter 3. The difference in k_r between the two complexes can be explained by radiative decay theory, which specifies a proportionality between k_r and the product $\mu^2 \cdot E_0^3$ where μ is the transition dipole moment and E_0 is the energy gap.³² This means the higher radiative decay rate in complex **2** can be explained by the larger energy gap between the ground state and the excited state.

5.3.4 Time-Resolved Electronic Absorption Spectroscopy.

Nanosecond transient absorption spectroscopy is another important tool for characterizing the lowest energy excited state in transition metal complexes.³³ The transient absorption spectra of complexes **1** and **2** acquired following $^1A_1 \rightarrow ^1MLCT$ excitation at 510 nm are shown in Figure 5-11. Like the bipyridine complexes in Chapter 3, the most striking aspect of Figure 5-11 is the similarity between the differential absorption spectra for the two complexes; this is in agreement with the notion anticipated from the electrochemistry data that the character of the long-lived ^3MLCT excited state is the same in both complexes. There are three principle features observed in the spectra: a strong net absorption in the near-UV, a strong bleach in the mid-visible, and a weak

absorption extending into the red. This overall pattern is typical of what is observed for the excited state spectra of Ru^{II} polypyridyl complexes.

By comparison to the bipyridine complexes in Chapter 3 the spectra can be tentatively assigned as follows: the strong absorption in the near UV is primarily due to the absorption of the terpyridyl radical anion in the excited state, the bleach in the mid visible is due to the loss of the ground state MLCT absorption, and the weaker absorption in the red is due to a combination of absorption of the terpyridyl radical anion and an excited state LMCT transition.

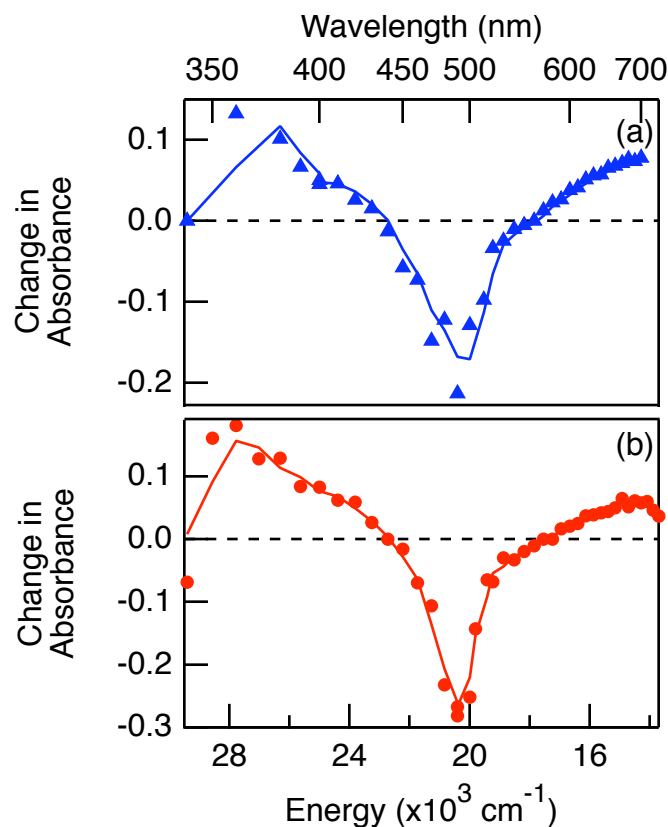


Figure 5-11: Nanosecond time-resolved differential absorption spectra acquired in room-temperature CH₃CN solution for (a) [Ru(tpy)(CN-tpy)](PF₆)₂ (**1**) and (b) [Ru(CN-tpy)₂](PF₆)₂ (**2**). The individual points correspond to the amplitudes of fits of the kinetics data to single-exponential decay models; a smoothed solid line has been included in both plots to guide the eye.

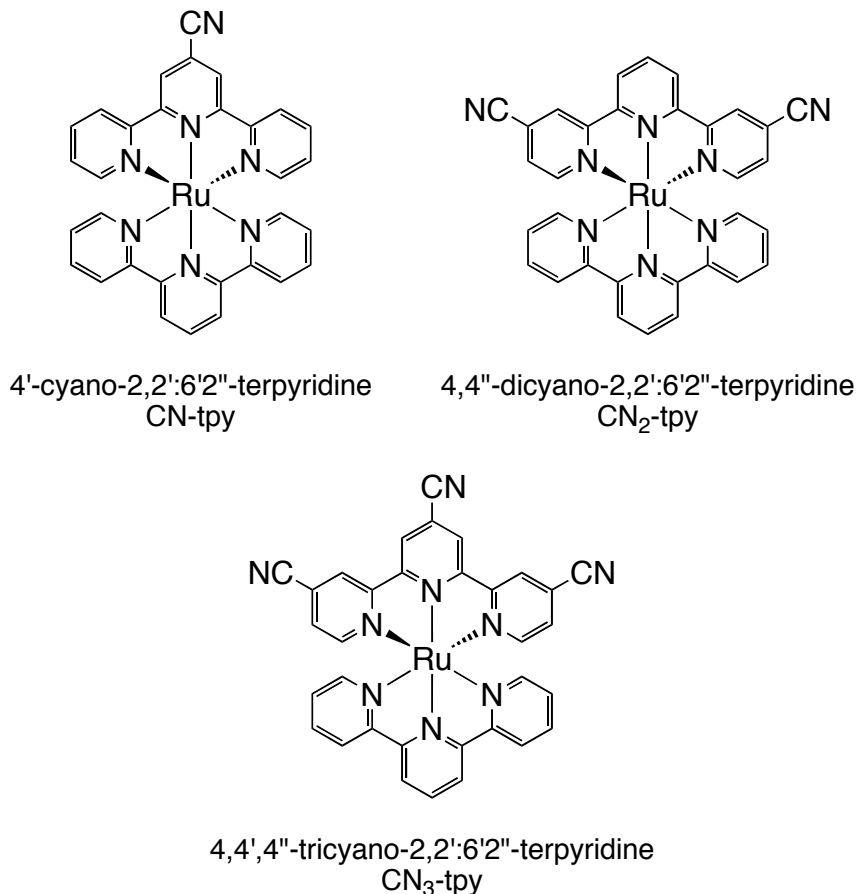


Figure 5-12: A series of ruthenium(II) terpyridyl incorporating an increasing number of electron withdrawing cyanide groups.

5.4 Concluding Comments and Future Directions

The study of complexes **1** and **2** discussed in this chapter has laid the groundwork for a wider study of the photophysical properties of ruthenium(II) terpyridyl complexes. While there have been some systematic studies of ruthenium(II) terpyridyl complexes, in general they are less studied and not as well understood as the related bipyridine complexes. Systematically increasing the number of cyanide groups on the terpyridine ligands, as shown in Figure 5-12, will increase the electronic asymmetry in the complexes. This increased

asymmetry should, according to the model developed by Maestri *et. al.*, lengthen the lifetime and increase the quantum yield of these complexes by increasing the energy gap between the $^3\text{MLCT}$ and ^3LF states. Measuring the $^3\text{MLCT}$ lifetime and quantum yield for the expanded series of complexes as well using variable temperature emission to determine the energy barrier between the $^3\text{MLCT}$ and ^3LF states will give additional experimental evidence that increasing asymmetry increases the energy difference between the $^3\text{MLCT}$ and ^3LF states in a series of complexes where the nature of the substituent does not change across the series.

The meridional binding in bis terpyridine complexes places the two terpyridine ligands orthogonal to each other. NMR spectroscopy shows that the identity of one terpyridine has no effect in the ^1H or ^{13}C shifts for the other terpyridine ligand in a heteroleptic complex, meaning the NMR spectrum of a heteroleptic ruthenium(II) bis terpyridal complex is identical to the superposition of the NMR spectra of the respective heteroleptic complexes. This suggests that there is little communication between the two ligands in the ground state.⁶ It is not clear if this is the case in the excited state as well. Harriman and coworkers have identified a ~single picosecond rate of interligand electron transfer in a porphyrin-substituted osmium(II) bis terpyridine complex.³⁴ This relatively rapid electron transfer suggests that there is communication between the two terpyridine ligands in the excited state of the osmium complex. While there are quite a few similarities between osmium(II) and ruthenium(II) polypyridyl complexes, the ligand field states in an osmium complex are higher in energy than the analogous ruthenium complex. Since the ligand field states play a very important role in the excited state dynamics of ruthenium(II) terpyridine complexes, the excited state behavior of an osmium(II) terpyridine complex is not necessarily a good predictor of the behavior in a ruthenium(II) complex.

With the series of complexes in Figure 5-11, it may be possible to measure the interligand electron transfer rate, which has not yet been done for a bis(terpyridyl)ruthenium(II) complex. The increased asymmetry in these complexes should increase the separation between the two metal-to-ligand charge transfer manifolds and hopefully allow for the selective excitation of the higher energy, unsubstituted terpyridine ligand. The interligand electron transfer and/or excited state delocalization can be monitored by excited state absorption anisotropy and infrared spectroscopy as described in Chapter 4. Understanding the communication (or lack thereof) between terpyridine ligands in ruthenium(II) bis terpyridine complexes is key for incorporating these types of complexes into light harvesting antenna arrays, molecular wires, or other super-molecular donor-acceptor systems.

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5.5 References

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APPENDICES

Appendix A: Additional Figures for Chapter 3

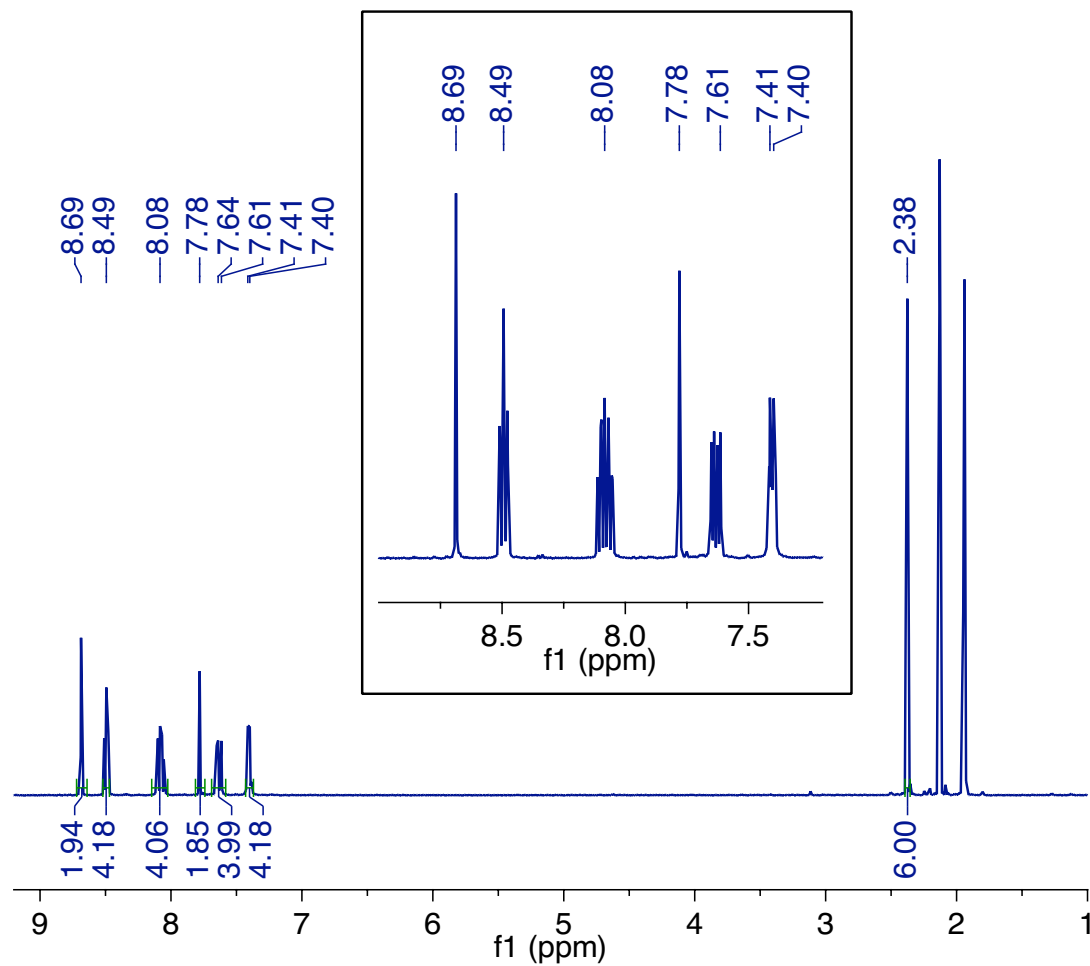


Figure A-1: ^1H -NMR of $[\text{Ru}(\text{bpy})_2(\text{CN-Me-bpy})](\text{PF}_6)_2$ in CD_3CN . Inset shows an expanded view of the aromatic region.

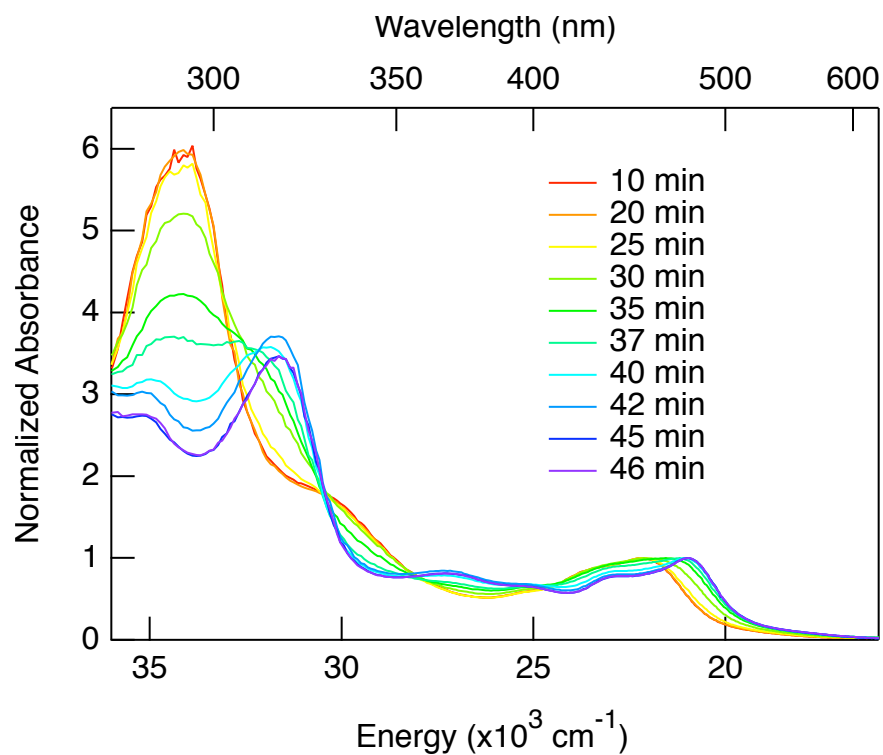


Figure A-2: Electronic absorption spectra of the conversion of $[\text{Ru}(\text{bpy})(\text{Cl-Me-bpy})_2]^{2+}$ to $[\text{Ru}(\text{bpy})(\text{CN-Me-bpy})_2]^{2+}$. The inset indicates the time following initiation of the reaction that each aliquot was taken. See text for further details.

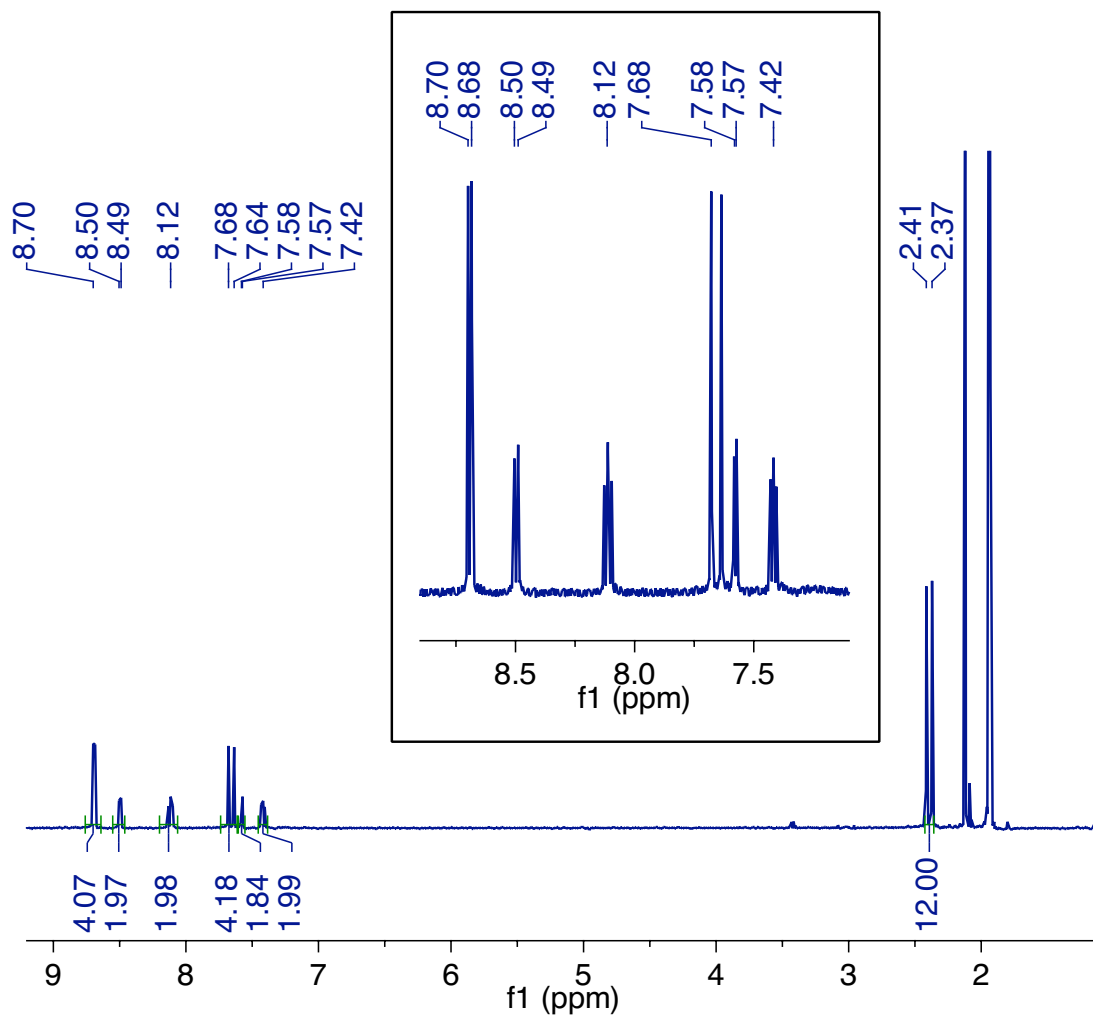


Figure A-3: ^1H -NMR of $[\text{Ru}(\text{bpy})(\text{CN-Me-bpy})_2](\text{PF}_6)_2$ in CD_3CN . Inset shows an expanded view of the aromatic region.

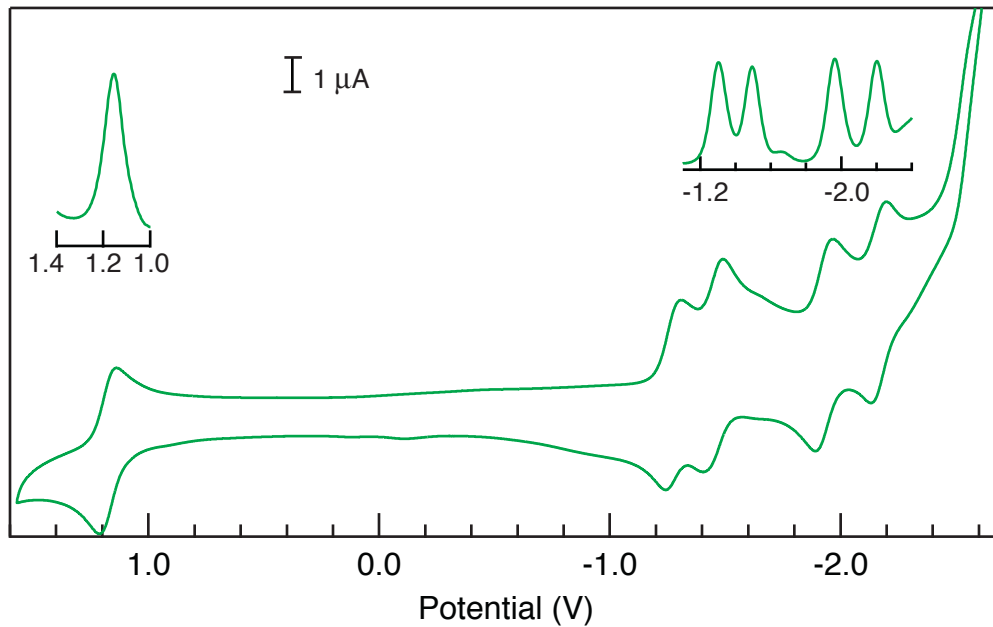


Figure A-4: Cyclic voltammogram of $[\text{Ru}(\text{bpy})(\text{CN-Me-bpy})_2](\text{PF}_6)_2$ in CH_3CN with 0.1 M TBAH as the electrolyte. Spectrum was collected using the standard three electrode setup with a platinum working electrode, graphite counter electrode, and a Ag/AgCl reference electrode and is referenced to the ferrocene/ferrocenium redox couple, which was added as an internal standard. The differential pulse voltammogram is shown in the insets.

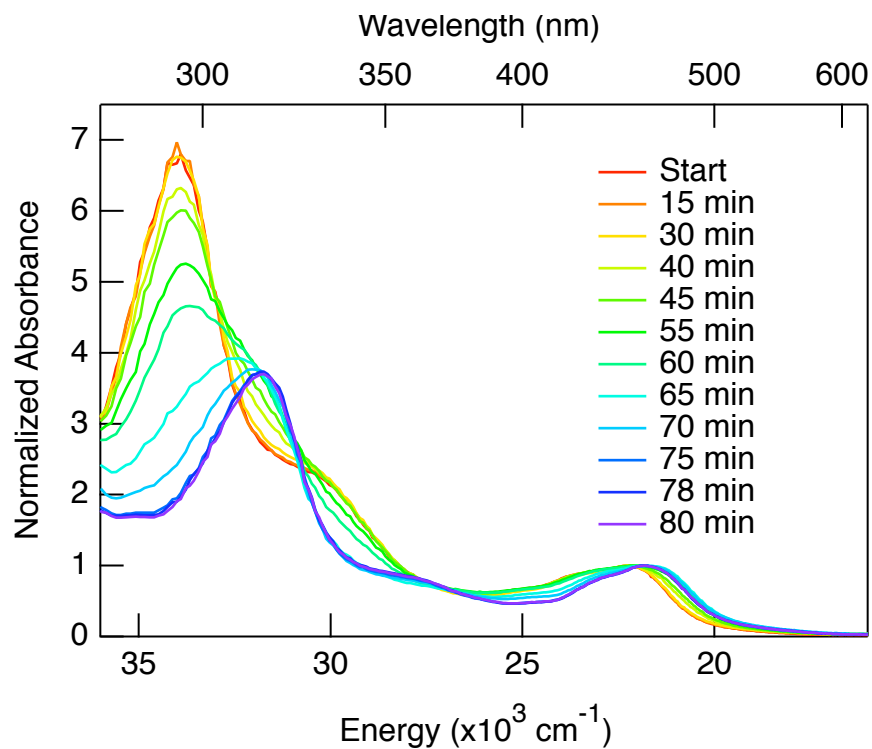


Figure A-5: Electronic absorption spectra of the conversion of $[\text{Ru}(\text{Cl-Me-bpy})_3]^{2+}$ to $[\text{Ru}(\text{CN-Me-bpy})_3]^{2+}$. The inset indicates the time following initiation of the reaction that each aliquot was taken. See text for further details.

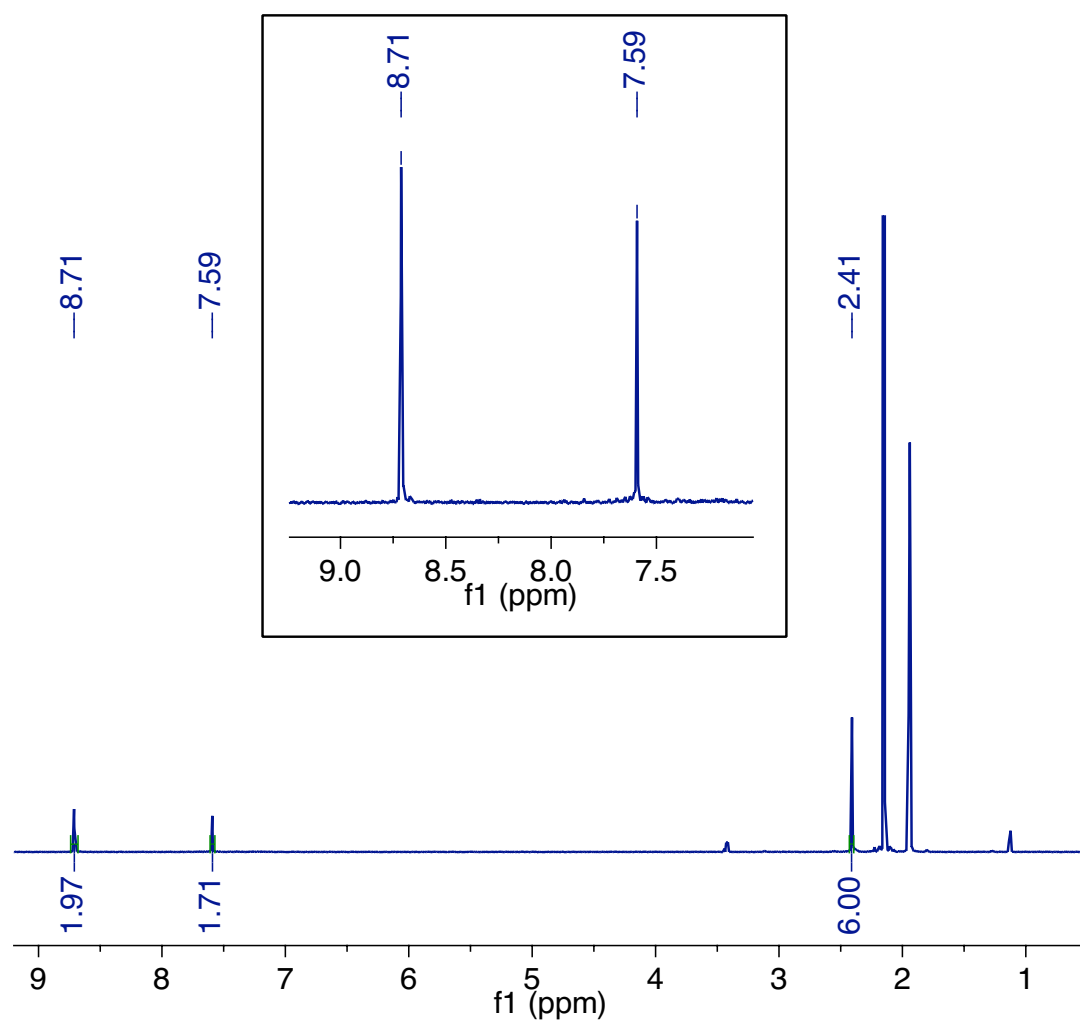


Figure A-6: ^1H -NMR of $[\text{Ru}(\text{CN-Me-bpy})_3](\text{PF}_6)_2$ in CD_3CN . Inset shows an expanded view of the aromatic region.

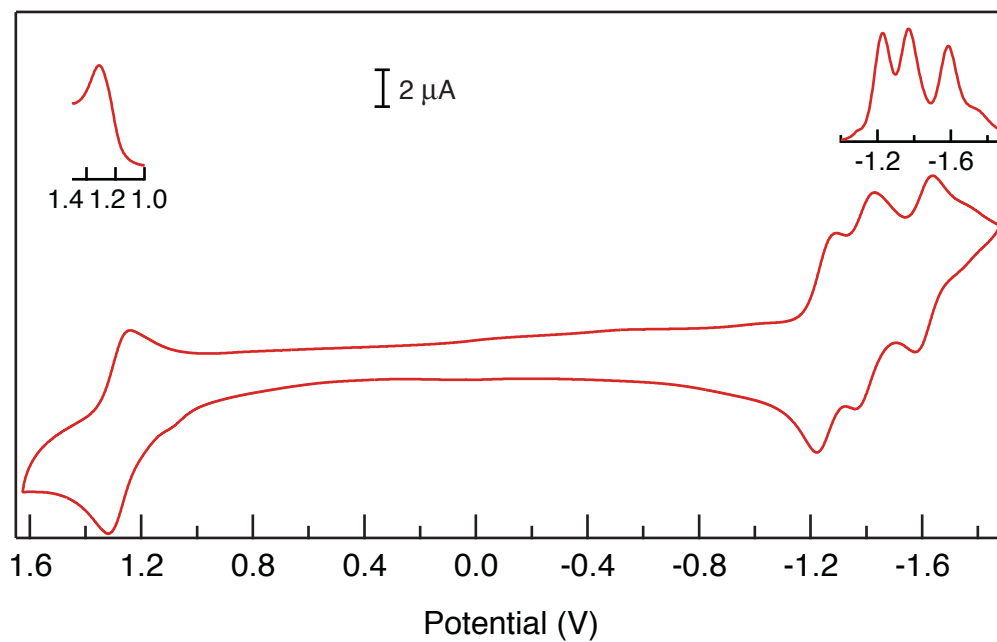


Figure A-7: Cyclic voltammogram of $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ in CH_3CN with 0.1 M TBAH as the electrolyte. Spectrum was collected using the standard three electrode setup with a platinum working electrode, graphite counter electrode, and a Ag/AgCl reference electrode and is referenced to the ferrocene/ferrocenium redox couple, which was added as an internal standard. The differential pulse voltammogram is shown in the insets.

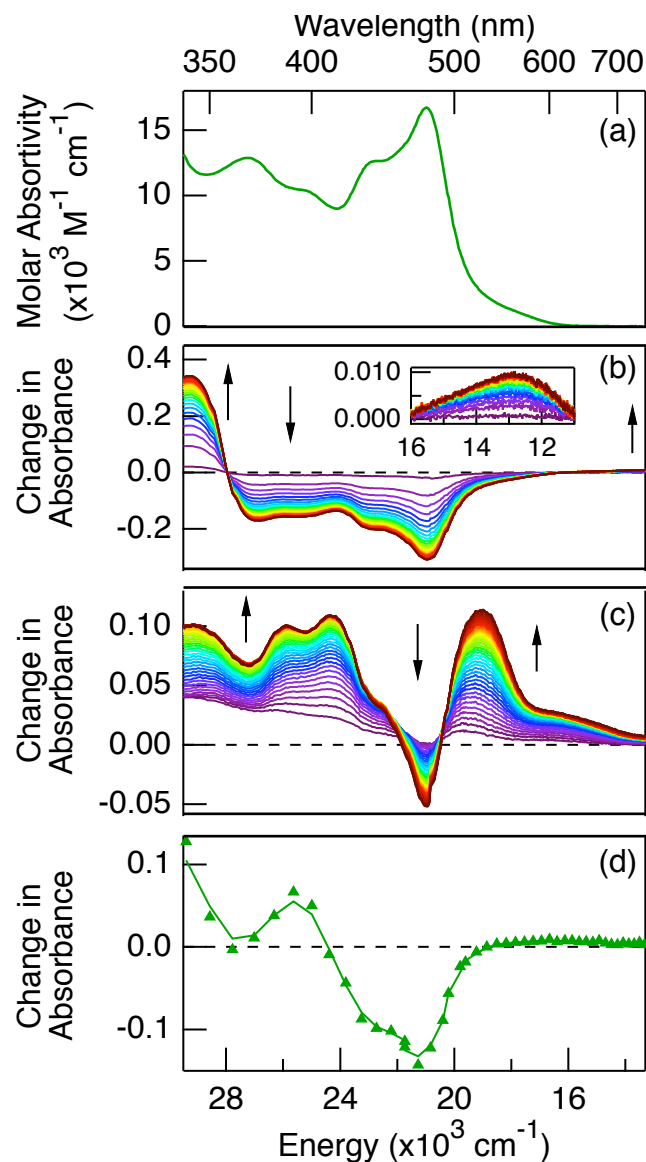


Figure A-8: (a) Ground state absorption spectrum for $[\text{Ru}(\text{bpy})(\text{CN-Mebpy})_2](\text{PF}_6)_2$ (**2**) in room-temperature CH_3CN solution. (b) Oxidative difference spectra acquired at an applied potential of +1.68 V versus Ag/AgCl. The inset corresponds to an expanded view of the low-energy portion of the spectrum. (c) Reductive difference spectra acquired at an applied potential of -0.980 V versus Ag/AgCl. (d) Time-resolved differential absorption spectrum of compound **1** following ca. 10 ns excitation at 500 nm.

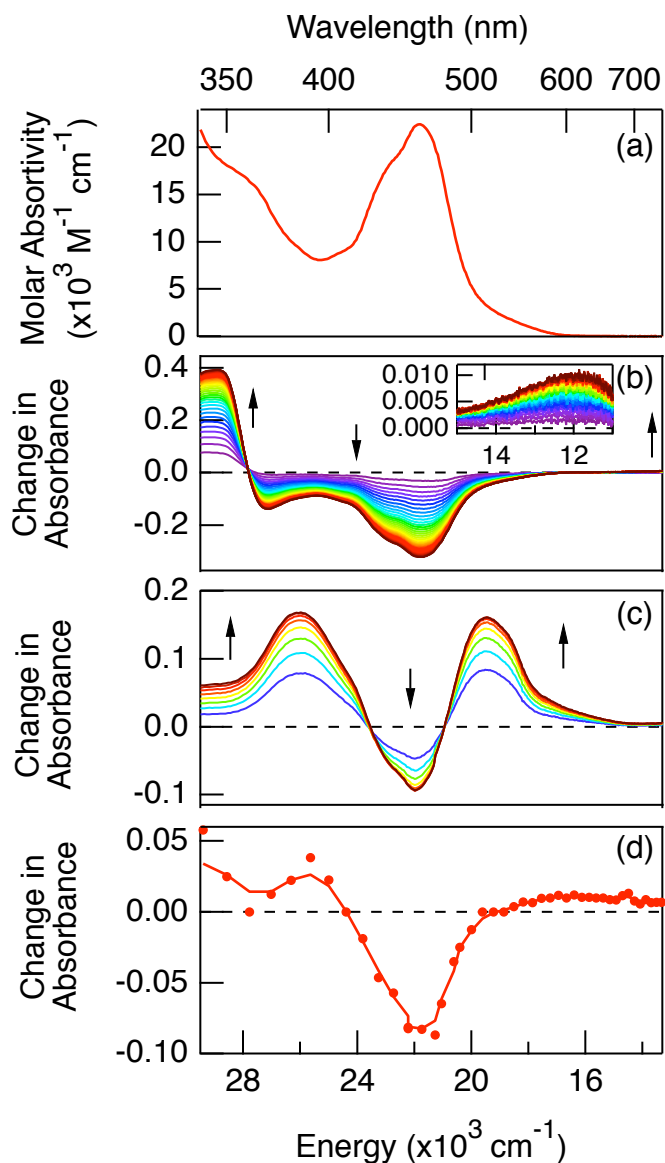


Figure A-9: (a) Ground state absorption spectrum for $[\text{Ru}(\text{CN-Me-bpy})_3](\text{PF}_6)_2$ (**3**) in room-temperature CH_3CN solution. (b) Oxidative difference spectra acquired at an applied potential of +1.85 V versus Ag/AgCl. The inset corresponds to an expanded view of the low-energy portion of the spectrum. (c) Reductive difference spectra acquired at an applied potential of -0.900 V versus Ag/AgCl. (d) Time-resolved differential absorption spectrum of compound **1** following ca. 10 ns excitation at 500 nm.

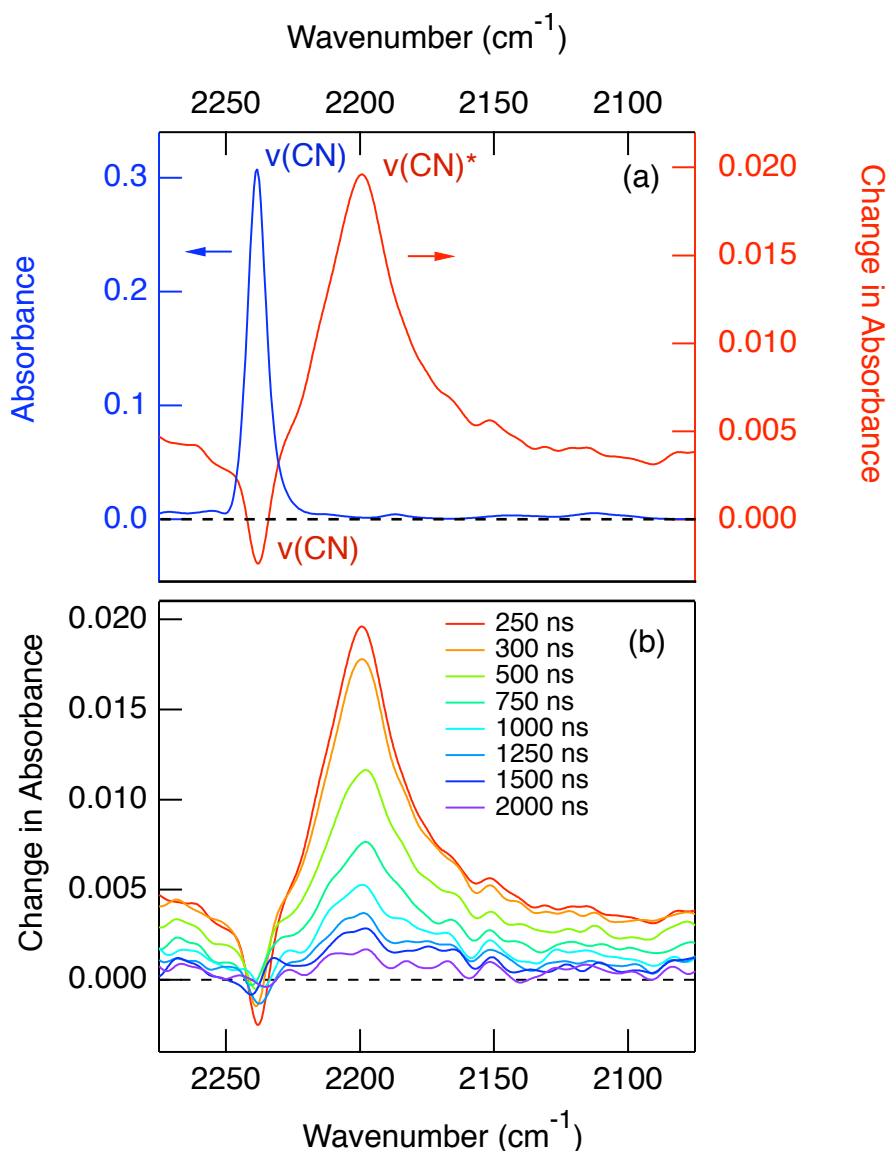


Figure A-10: Steady-state and time-resolved infra-red absorption data for **2** in CH_3NO_2 solution. (a) Comparison of the ground-state (blue line) and step-scan infrared differential absorption data acquired at a time delay of 150 ns following ca. 10 ns excitation at 540 nm (red line). The $\sim 40 \text{ cm}^{-1}$ red-shift in the CN stretching frequency reflects the presence of an electron in the π^* orbital of the CN-Me-bpy ligand in the $^3\text{MLCT}$ excited state. (b) Nanosecond step-scan infrared spectra as a function of time following ca. 10 ns excitation at 540 nm.

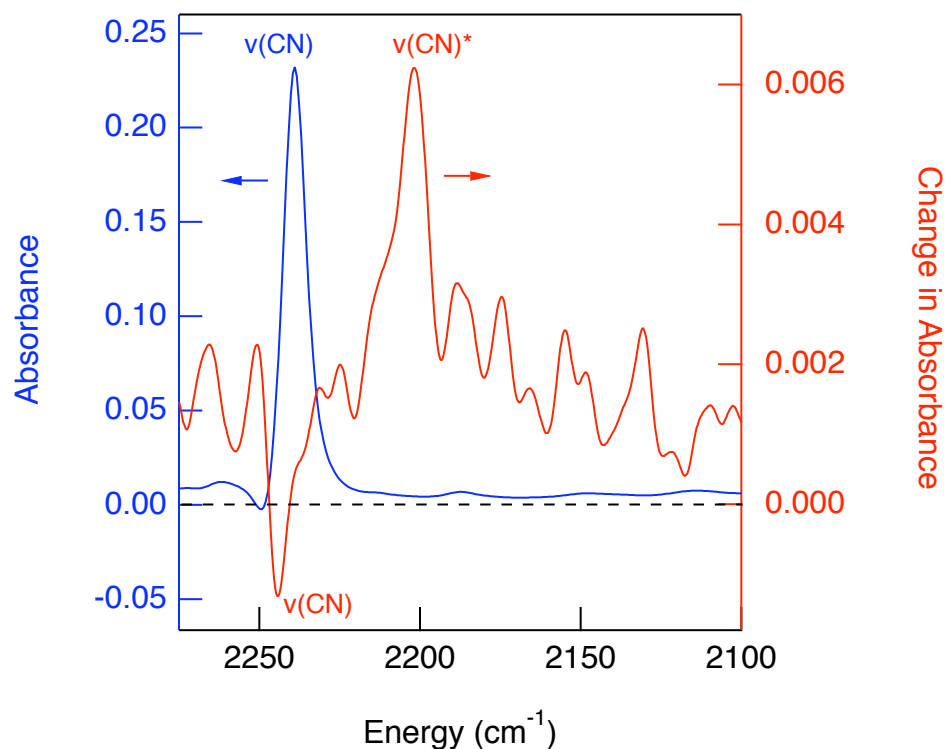


Figure A-11: Steady-state and time-resolved infra-red absorption data for **3** in CH_3NO_2 solution. Comparison of the ground-state (blue line) and step-scan infrared differential absorption data acquired at a time delay of 150 ns following ca. 10 ns excitation at 500 nm (red line). The $\sim 40 \text{ cm}^{-1}$ red-shift in the CN stretching frequency reflects the presence of an electron in the π^* orbital of the CN-Me-bpy ligand in the $^3\text{MLCT}$ excited state. Low signal to noise is primarily due to the lower solubility of complex **3**.

Appendix B: Additional Figures for Chapter 5

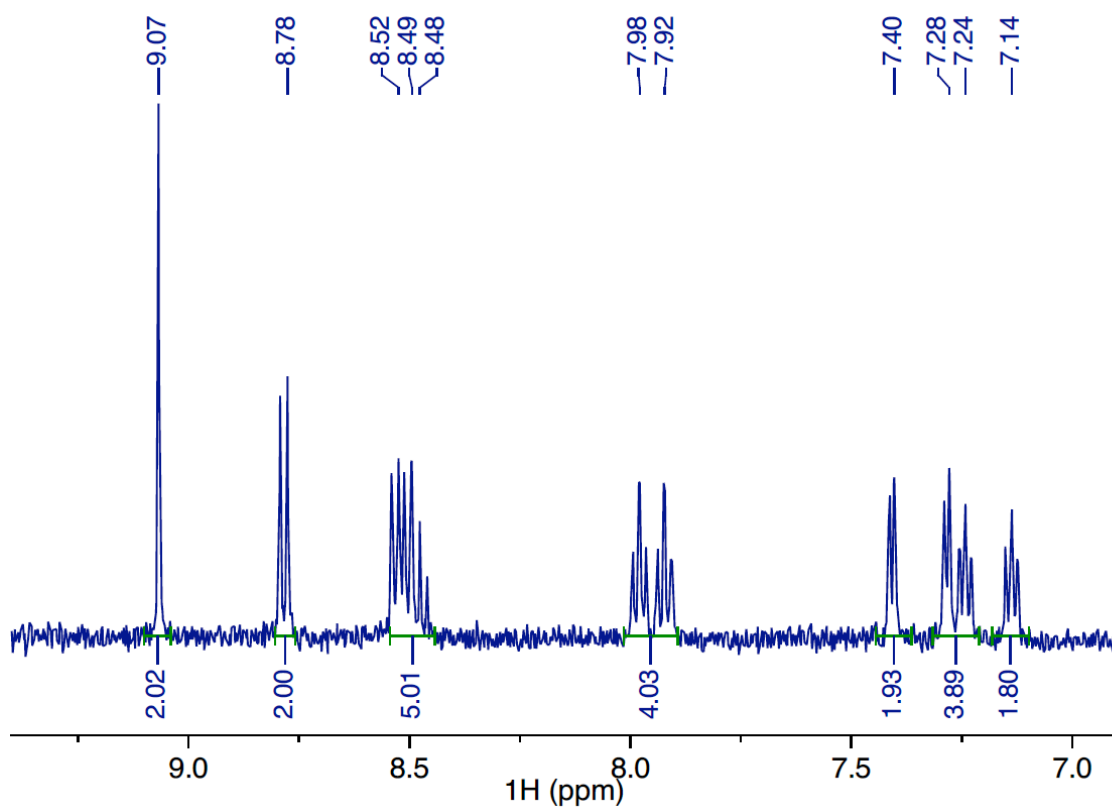


Figure B-1: ^1H NMR spectrum of $[\text{Ru}(\text{tpy})(\text{CN-tpy})](\text{PF}_6)_2$ in CD_3CN .

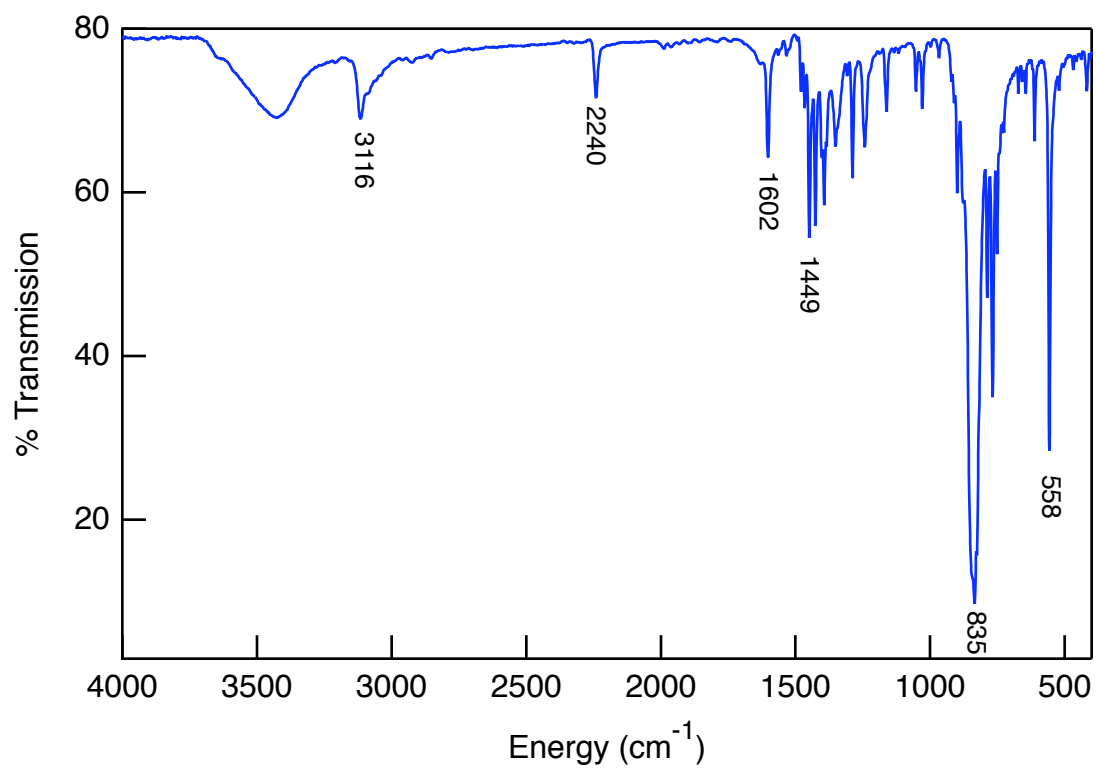


Figure B-2: Infrared spectrum of [Ru(tpy)(CN-tpy)](PF₆)₂ (**1**) in a KBr pellet

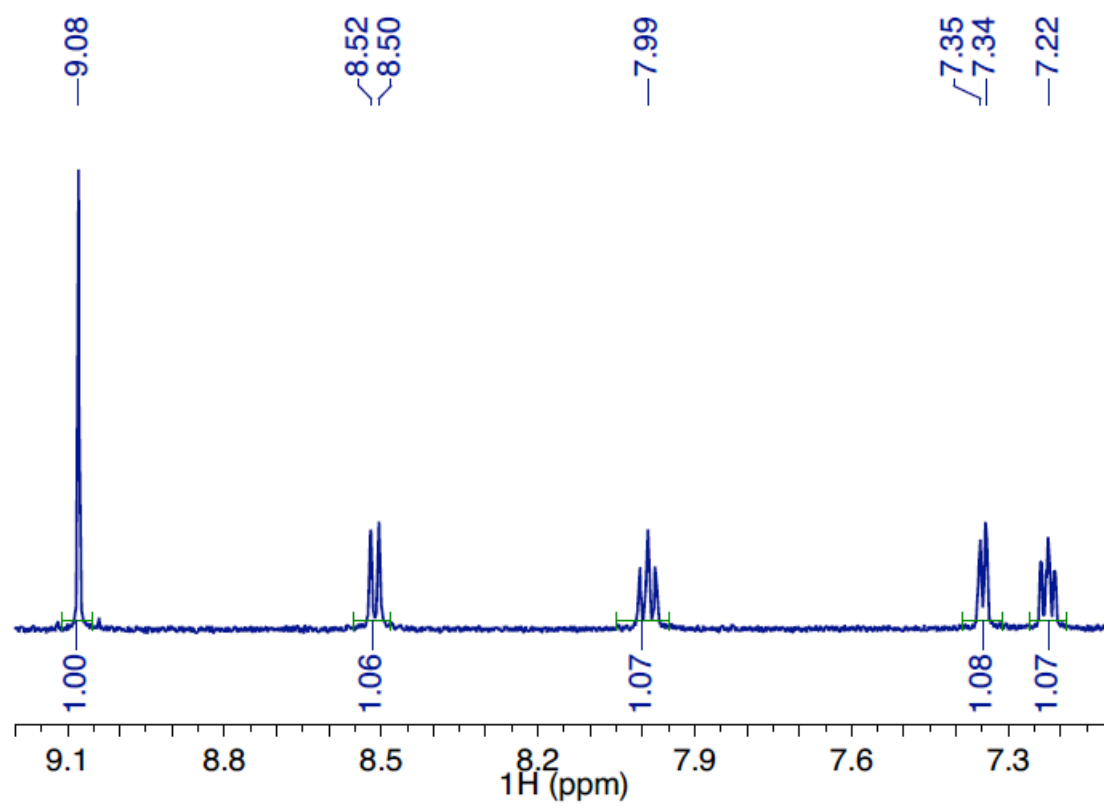


Figure B-3: ^1H NMR spectrum of $[\text{Ru}(\text{CN-tpy})_2]^{2+}$ in CD_3CN .

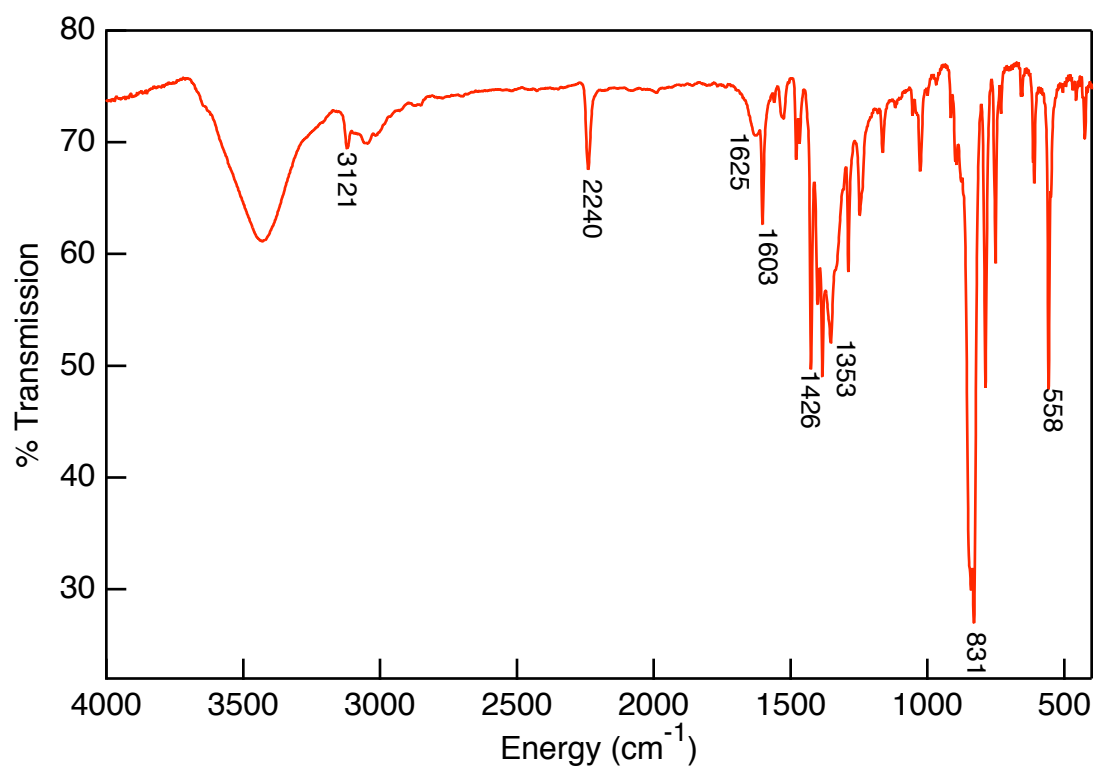


Figure B-4: Infrared spectrum of $[\text{Ru}(\text{CN-tpy})_2](\text{NO}_3)_{1.5}(\text{PF}_6)_{0.5}$ (**2**) in a KBr pellet

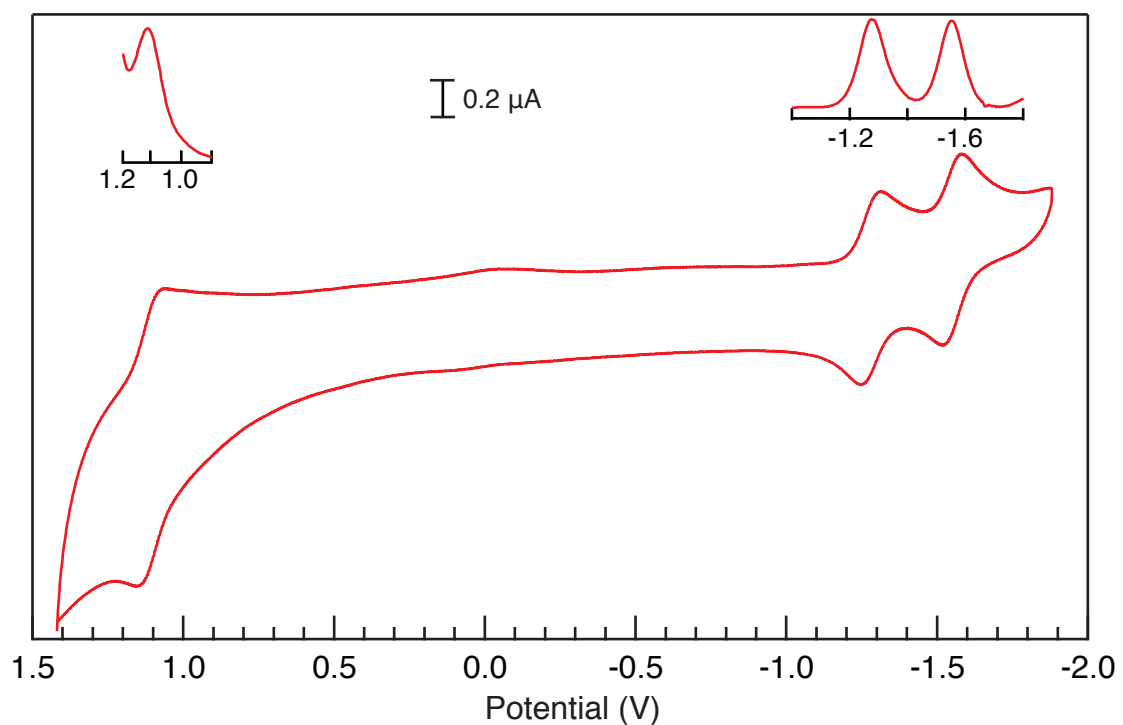


Figure B-5: Cyclic voltammogram of $[\text{Ru}(\text{CN-tpy})_2]^{2+}$ (**2**) in CH_3CN with 0.1 M TBAH as the electrolyte. Spectrum was collected using the standard three electrode setup with a platinum working electrode, graphite counter electrode, and a Ag/AgCl reference electrode and is referenced to the ferrocene/ferrocenium redox couple, which was added as an internal standard. The differential pulse voltammogram is shown in the insets

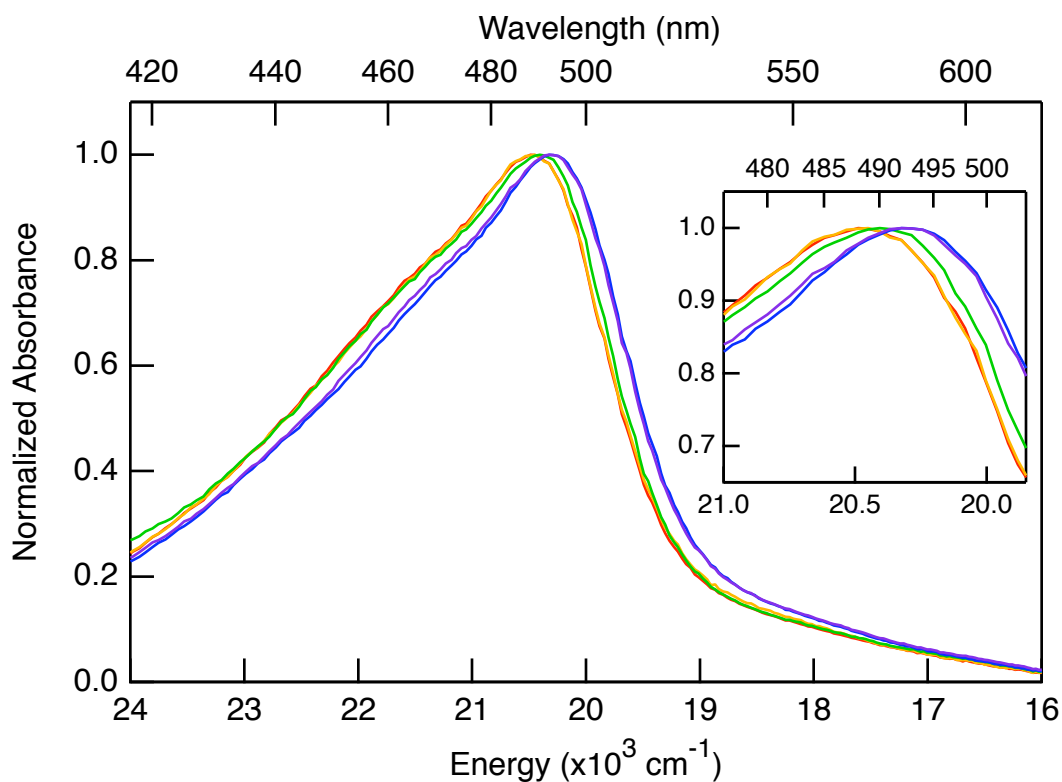


Figure B-6: Electronic absorption spectra of $[\text{Ru}(\text{tpy})(\text{CN-tpy})](\text{PF}_6)_2$ in acetonitrile (red line, $\lambda_{\text{max}} = 488 \text{ nm}$), acetone (orange line, $\lambda_{\text{max}} = 488 \text{ nm}$), nitromethane (green line, $\lambda_{\text{max}} = 490 \text{ nm}$), DMSO (blue line, $\lambda_{\text{max}} = 492 \text{ nm}$), and pyridine (purple line, $\lambda_{\text{max}} = 492 \text{ nm}$). The inset shows an expanded view of the absorption maxima.

Appendix C: Instructions for the Collection Step Scan IR Data on the Bruker IFS66/S

C.1 Instrument Warm Up Procedure

1. If it isn't on already, turn on the step scan instrument and globar source on the front of the SSIR power supply. A green light should light up on the MIR source button. The globar will need about an hour or two to warm up.
2. Turn on the laser by turning the key on the front of the laser power supply and turning on the switch on the back of the laser. Open the OPOTEK control software and wait for the temperature to reach 35°C (temperature can be checked on the remote or under laser status in the software). This will take ~15-20 minutes. Once the correct temperature is reached turn on the flashlamps by clicking the lamp button. Choose your wavelength and click the tune button. Set Laser energy to 100 and turn on the Q switch by clicking the Laser button (make sure the beam block is in front of the laser). Let the laser warm up ~30-45 min before using.

C.2 Collection of the Ground State Spectrum

1. Float the table by opening the rightmost valve all the way and increasing the pressure to ~70 psi. Adjust the flow to the SSIR (left valve) so there is sufficient flow to move the interferometer mirror (the light on the front of the instrument will be blinking green). The table will take a couple minutes to pressurize and float.
2. Open the cover to the detector compartment and fill the detector with liquid nitrogen. Close the cover and connect the DC output on the cover to the detector X input on the SSIR.

3. Open the OPUS 5.5 software (the password is OPUS) and then open the Advanced Measurement dialog box from the Measure menu and fill in all the necessary information (See below for example list of settings)
4. Go to the Check Signal tab. You should see the detector signal in the window. Adjust the three knobs on the parabolic mirror focusing light into the detector (it can be accessed from the sample compartment) to maximize the signal. It is easiest to change the display from interferogram to counts to do this.
5. Once the signal is maximized close the sample compartment and purge the sample chamber with N₂ using the middle valve and purge the rest of the instrument by increasing the purge flow to 1000-1500 L/hr on the instrument regulator. After purging 5-10 min the signal intensity will stabilize. Run the Auto Align sequence to make adjustments to the mirrors in the interferometer.
6. Fill the cell with your solvent of choice and put it in the sample holder facing the interferometer.
7. Vary the aperture setting (Optic tab) to make the signal as large as possible without saturating the detector. The detector is saturated when the interferogram is asymmetric (positive peak larger or smaller than the negative one). Collect a solvent scan with the sample single channel button.
8. Remove the cell and replace the solvent with the sample solution. Place the cell back in the sample holder and purge the sample compartment for 5 minutes.
9. Collect a molecule scan with the sample single channel button.

10. Calculate the absorbance spectrum by:

- Divide sample spectrum by solvent spectrum with the spectrum calculator (in toolbar or Manipulate menu) to get the transmission spectrum.
- Convert the transmission to absorbance using the AB $\leftrightarrow$ TR conversion. If it's not automatically selected, just drag the transmission block into the files to be converted box.
- The absorbance of the vibrations of interest should be ~ 0.3 to 0.7 .

C.3 Collection of the DC Coupled (Ground State) Step-Scan Spectra

1. The step scan experiment is noise and vibration sensitive, so turn off any music and speak quietly while the experiment is in progress.
2. Open the Advanced Measurement box and go to the check signal tab. Connect the DC output of the detector to the oscilloscope. Set divisions to 500 mV and 200 μ s.
3. The signal going to the external digitizer has to be smaller than ± 1 V. Vary the aperture to make sure the DC signal is within ± 1 V. Change the scope to ground mode to find where 0 V is. If the signal is less than 2 V peak-to-peak but is offset from zero use a small screwdriver in the hole on top of the detector to adjust the bias voltage (and the offset of the signal).
4. Connect the DC output of the detector to channel A of the digitizer. Terminate the AC output of the detector and channel B of the digitizer.
5. Turn off the purge to the sample compartment and turn the flow for the instrument purge down to ~ 500 L/hr
6. Open the Time Resolve Step Scan dialog box in the Measure menu

7. Fill in the appropriate settings. Most settings should transfer from the Advanced Measurement dialog box. See below for example settings. Note the interferogram size. This is the number of mirror positions needed to collect the spectra. The scan progress bar at the bottom of the screen will count number of mirror positions.
8. Collect the DC spectrum by clicking the Start Step Scan Time Resolved Measurement button
9. The resulting spectra should show an identical interferogram at all time points. Sometimes the 3D viewing window will only show the positive half of the interferogram.

C.4 Collection of the AC Coupled (Excited State) Step-Scan Spectra

1. Purge the instrument and sample compartment for 5-10 minutes while setting up.
2. Using the power meter, tune the laser with the two knobs on the back to get the maximum power.
3. Measure the power as close to the sample as possible. The desired power will vary by molecule, but usually ~3-4 mJ per pulse at the sample is a good power. If the power is too high adjust it using the laser energy slider in the OPOTEK control software.
4. Turn on the trigger and connect it to the oscilloscope. The trigger signal needs to be 4-5 V in intensity and at least 200 ns wide. Adjust the trigger position to meet these requirements. Disconnect from the scope and connect to the trigger channel of the digitizer.

5. Connect the DC output of the detector to channel B of the digitizer. Connect the AC output of the detector to the amplifier and connect the amplifier output to channel A of the digitizer. Turn on the amplifier.
6. Unblock the laser and verify that the laser is going through the glass window and hitting the center of the sample.
7. Turn off the sample compartment purge and return the instrument flow to ~500 L/hr
8. Collect the AC spectrum by clicking the Start Step Scan Time Resolved Measurement button
9. The progress bar at the bottom will keep track of the number of mirror positions measured. A typical scan will take 60-90 min but that will depend on the number of mirror positions and the number of laser shots per mirror position.
10. Depending on how strong the signal is, 4-6 or more spectra will need to be averaged together to get reasonable signal to noise. Be sure to purge 5-10 minutes between spectra and refill the detector with liquid nitrogen after 6-8 hours (It has an ~8 hour hold time and will automatically shut off to protect the electronics if the liquid nitrogen runs out). Also monitor the laser power before collecting each spectra to ensure the power stays constant.
11. The DC spectrum collected in the second channel is a way to monitor the sample stability. Any changes in in the DC spectrum over time indicate some change in the sample like decomposition or evaporation.

C.5 Data Analysis

The OPUS software will sometimes crash if data analysis and data collection happen at the same time. The OPUS software is also installed on the nanosecond computer, so its safer to transfer files to the nanosecond computer and analyze the data there if you want to collect and analyze data at the same time.

1. Open the DC step scan spectrum and right click in the 3D display window to open the extract spectra dialog box
 - In the Select files tab fill in the file name and save location
 - In the Extraction range tab select from beginning of file to end of file and uncheck use block list
 - In the Extraction mode tab select Store Average block and Load extracted files
 - Click the extract button
2. Select the averaged DC interferogram in the 2D display window (it should now have both the negative and positive portion of the signal)
3. Open the Interferogram to spectrum dialog box from the toolbar or the manipulate menu
 - In the Select files tab drag the file icon into the box if it is not already listed in the box
 - In the Store tab the first frequency is 5000 and the last is 0. Select the store phase box
 - In the Apodization tab select the Blackman-Harris 3-term function and 8 as a zerofilling factor

- In the Limit data tab uncheck both boxes and set direction and datapoints to both
 - In the Phase correction tab select Mertz as the phase correction mode
 - In the Non Linearity tab uncheck the box for non linearity correction
 - In the Peak search tab choose absolute largest value as the peak search mode. Put 0 as the number of positions to test and choose automatic as the symmetry of the interferogram
 - Calculate the single channel spectrum by clicking the convert button
4. Open the AC step scan spectra in the 3D display window
 5. Open the Interferogram to spectrum dialog box from the toolbar or the manipulate menu
 - Keep settings the same as for the DC spectrum EXCEPT:
 - Uncheck store phase in Store tab
 - Select Mertz/Stored phase option in the Phase correction tab and drag the phase block of the DC spectrum into the box
 - Select Take from Stored phase as the peak search mode in the Peak search tab
 - Click the convert button to calculate the single channel spectrum
 6. Use the spectrum calculator to calculate the change in absorbance spectrum from the AC and DC single channel spectra
 - To get the change in transmission: $((AC/50)+DC)/DC$
 - Use the AB<->TR conversion tool to convert to the change in absorbance spectrum
 7. Repeat for all AC step scan spectra

8. In order to improve signal to noise the AC ΔA spectra need to be averaged together, but in the software only 2D spectra can be averaged. To get around this:
 - Right click in the 3D display to open the Extract spectra dialog box
 - Fill in a file name and path
 - Choose the beginning and end of file as the extraction range. Check Use block list box and fill in the block you want to extract (for 10 ns steps block # x10 = time). It is best to do one at a time because the software will sometimes crash or extract the wrong blocks when extracting multiple blocks.
 - Choose series of single blocks as the extraction mode
 - Repeat for all desired times and for all AC spectra
9. Use Averaging (from the toolbar or the manipulate menu) to average all of the AC spectra at the same time delay together.
 - Choose the select by symbol option and drag all of the extracted AC spectra from the first time point into the box and click the average button
 - The file will by default be named Av.# and saved in the OPUS work folder. Use save as to rename and change save location
 - Repeat for all time points
10. In order to open the files in another program (Excel, Igor, Origin, etc) they must be saved as text files. In the Mode tab of the Save as Dialog box choose Data point table and in the Data point table tab make sure the save all data points option is selected.

C.6 Instrument Shut Down Procedure

1. Turn off the laser with the OPOTEK control software. Click the laser and the lamp buttons to turn them off and then exit the program. Leave the power supply on for ~5-10 min to allow the water to cool. Move the beam block in front of the laser.
2. Turn off the amplifier and disconnect it from the instrument
3. Open the Advanced Measurement box and click on the check signal tab to switch the instrument back to scan mode (the light on the front of the instrument should go from red to blinking green) and exit the OPUS program
4. If the instrument will be used again within a few weeks or a month it is better to leave the global on, but if the instrument won't be used again soon shut it off with switch on the power supply and turn off the water circulator by unplugging it from the power strip
5. Turn the nitrogen pressure down to ~20 psi and close the right and middle valves. Open the left valve all the way to keep nitrogen purging in the instrument
6. Turn off the trigger, scope and power meter and shut down the computer.

C.7 Example Advanced Measurement Settings

1. Basic
 - Fill in appropriate sample information
2. Advanced
 - Fill in file name and path
 - Resolution : 4 or 6

- Sample scan time: 30 scans
- Background scan time: 1 scan
- Save data from: Depends on region of interest, but MUST be 0 at ends.
For 5100 nm LP filter use 2600 to 1000. For the 4000 nm LP filter use 2250 to 1000
- Result spectrum: Transmittance
- Data blocks to be saved: Single channel and Sample interferogram

3. Optic

- Source: MIR
- Beamsplitter: KBr
- Aperture setting: start with 4 mm. Adjust as necessary depending on sample.
- Measurement channel: Front
- Background meas. channel: Front
- Detector setting: Ex3
- Scanner velocity: 8; 40.0 KHz
- Sample signal gain: 1
- Background signal gain: 1
- Switch gain: ON
- Delay after device change: 0
- Delay before measurement: 0
- Window in points: 350

4. Acquisition

- Wanted high and low frequency limit: use the same as Save data from

- Low pass filter: Open
- Acquisition mode: Single sided
- Correlation mode: No

5. FT

- Phase resolution: 8 x Resolution
- Phase correction mode: Mertz
- Apodization function: Blackman-Harris 3-Term
- Zerofilling factor: 8

C.8 Example Step Scan Time Resolved Measurements Settings

1. Basic

- Same as advanced measurement. Most settings should transfer over

2. Recorder setup

- Device: PAD82A (external 10 ns digitizer)
- Time resolution: 10 ns
- Number of timeslices: Depends on the lifetime of the molecule. 200 will give a 1990 ns window
- Timebase: Linear timescale
- Input range: $\pm 1V$
- Repetition/coadd count: 30
- Trigger mode: Internal for DC and External Positive Edge for AC
- Pre/Post trigger: 0 points
- Experiment recovery time: 0
- Stabilization delay after stepping: 40 ms
- Second Channel: Unused for DC and Save for AC
- Second Channel input range: $\pm 1V$ (AC only)

3. Advanced

- Fill in file name and path
- Resolution: Same as Advanced Measurement
- Save data from: Same as Advanced Measurement
- Data blocks to be saved: Sample inteferogram

4. Optic

- Source: MIR
- Beamsplittler: KBr
- Aperture: Start with 4mm, adjust as necessary
- Measure channel: Front
- Detector Setting: Ex3
- Scanner Velocity: 8; 40.0 KHz
- Sample signal gain: 1
- Delay after device change: 0
- Delay before measurement: 0

5. Acquisition

- Wanted High and Low frequency: Same as save data from
- Acquisition mode: Single sided

6. FT

- Settings don't matter because FT will be done separate from data collection

Appendix D: Cartesian Coordinates for Optimized Geometries of CN-Me-bpy Ruthenium(II) Complexes

D.1 [Ru(bpy)₂(CN-Me-bpy)](PF₆)₂ Optimized Ground State Geometry

N	1.09287500	1.26210500	0.41525600
Ru	-0.51128700	0.00061600	0.00202000
N	-2.01409000	-1.42715100	-0.32194800
N	-0.65890200	0.90551800	-1.88557100
N	-0.63482600	-0.90745800	1.89131400
N	-2.02639500	1.41234300	0.33677600
N	1.10046500	-1.24774400	-0.42178800
H	-2.53819400	3.38615000	-3.27365800
C	-1.79044500	2.60085900	-3.19533000
C	0.11005500	0.60296800	-2.96742100
C	-1.60747700	1.90031200	-1.98939900
C	-0.99643100	2.28377600	-4.30949800
C	-0.02981700	1.26728500	-4.19314600
C	-4.06509400	-3.33799400	-0.50568200
H	0.88526700	-5.05640200	-1.60684100
H	2.34678200	5.51781200	0.67420600
H	0.84244000	-0.18643600	-2.84824700
H	2.36911200	-5.49649100	-0.73776300
C	-3.42435800	3.10869400	-0.68225500
C	-2.68463700	1.59746200	1.51435000
C	-2.38529000	2.16381800	-0.76171900
C	-4.10352300	3.29299600	0.53306900
C	-3.72460400	2.52650600	1.65119400
C	-3.37671700	-3.14811500	0.70349000
H	0.65854800	-0.98371000	5.02502900
H	2.45552600	-4.99478400	-2.43100800
H	-2.36760500	0.99454600	2.35609500
H	-2.38408200	-1.00554300	-2.33641700
H	-4.86117300	-4.07794700	-0.57256000
H	-3.64328900	-3.74324200	1.57336600
H	-4.21305200	-2.67621900	-2.58144300
H	-1.12996200	2.81997500	-5.24781900
C	3.50862600	-1.45190200	-0.41506900
C	1.00691900	-2.54420200	-0.82405200
C	2.34524400	-0.69433500	-0.21547500
C	3.39898000	-2.79270100	-0.82651400
C	2.11874600	-3.37289500	-1.04271700

C	-2.35091200	-2.18841200	0.77667500
C	4.59006000	-3.57484600	-1.02514400
C	1.94288200	-4.80680800	-1.47844600
H	0.00679300	-2.92848800	-0.97850900
H	-4.22017500	2.63908300	2.61340600
C	0.01928300	-1.26920600	4.19197300
C	-1.56580400	-1.91850300	1.99829900
C	0.13750100	-0.59624800	2.96866100
C	-0.92809200	-2.30349000	4.31077000
C	-1.72619800	-2.62865300	3.20182000
H	0.85482000	0.20652500	2.84755700
H	-1.04386300	-2.84721800	5.24710800
H	0.60774100	0.98876000	-5.02986500
C	-3.70931600	-2.56068400	-1.62383900
H	4.48674200	1.04150600	0.26455900
C	3.50027400	1.47592800	0.41874100
C	0.99219600	2.56319700	0.80048800
C	2.34108100	0.71235300	0.21882100
C	3.38318400	2.82074500	0.81448600
C	2.09959300	3.39940000	1.01330300
C	-2.68268100	-1.61605100	-1.49314500
C	4.57018800	3.60915000	1.01181900
C	1.91626400	4.83986600	1.42318500
H	-0.01031400	2.94588700	0.94321200
H	-4.91017700	4.02093400	0.60477900
H	4.49248800	-1.01542000	-0.25044300
H	-3.70869200	3.69610000	-1.55178000
H	-2.45918800	-3.42751900	3.28247000
N	5.56230000	-4.22529400	-1.19071900
N	5.53921700	4.26466700	1.17624000
H	2.42053200	5.04570500	2.37654200
H	0.85698900	5.08881700	1.53848900

D.2 [Ru(bpy)₂(CN-Me-bpy)](PF₆)₂ Optimized Lowest Energy Triplet State Geometry

N	-1.06879600	-1.23035100	0.47965100
Ru	0.53024400	-0.00187900	-0.00164500
N	2.08412800	1.37408800	-0.37387200
N	0.59167000	-1.02924400	-1.82587500
N	0.62255900	1.02419000	1.82163500
N	2.05967700	-1.40703800	0.36201900
N	-1.05257900	1.25141900	-0.47091900
H	2.35225100	-3.63588200	-3.12617400
C	1.62551000	-2.82944200	-3.06287200
C	-0.23223200	-0.77819500	-2.87949900
C	1.51903500	-2.04641800	-1.90164300
C	0.78024800	-2.56638600	-4.15441300
C	-0.16167700	-1.52474300	-4.06244600
C	4.15657800	3.23683400	-0.62877900
H	-0.82469800	5.08093200	-1.65730700
H	-2.39137700	-5.47409000	0.87424000
H	-0.94166400	0.03302600	-2.77244800
H	-2.33158500	5.51265500	-0.82505200
C	3.36678900	-3.20367700	-0.59103600
C	2.76988800	-1.50615600	1.51837600
C	2.34516300	-2.24455000	-0.69450000
C	4.09561300	-3.31089000	0.60560900
C	3.79153400	-2.45142800	1.67782400
C	3.43192200	3.14482800	0.57144800
H	-0.77721500	1.30750100	4.89078100
H	-2.37539800	4.99401000	-2.51442900
H	2.51144800	-0.83099800	2.32605200
H	2.51261600	0.79002500	-2.34063100
H	4.96261800	3.96295300	-0.72506600
H	3.68185200	3.79931600	1.40299200
H	4.36592300	2.42434000	-2.64497200
H	0.85566600	-3.16731700	-5.05966400
C	-3.47548300	1.47532900	-0.46805800
C	-0.95315700	2.56561800	-0.86947300
C	-2.32054400	0.69316200	-0.24385900
C	-3.35667600	2.80120100	-0.89351200
C	-2.04634200	3.38562300	-1.10203200
C	2.39300100	2.20511000	0.68123800
C	-4.53687100	3.58293700	-1.11392500
C	-1.88217000	4.81842100	-1.54847200
H	0.04979400	2.94749000	-1.01983700

H	4.33194000	-2.50332000	2.62083400
C	-0.10489900	1.52986500	4.06459100
C	1.57183500	2.02117900	1.89386700
C	-0.19961500	0.78864700	2.87998400
C	0.86046900	2.54998900	4.15357700
C	1.70386000	2.79754500	3.05709200
H	-0.92870500	-0.00542300	2.77518200
H	0.95551400	3.14613600	5.06010800
H	-0.83395600	-1.28974600	-4.88515600
C	3.82962200	2.38340300	-1.69908300
H	-4.47531300	-0.99177200	0.28167600
C	-3.49409600	-1.42891600	0.45977100
C	-0.98673300	-2.54110900	0.89335200
C	-2.32926700	-0.66034800	0.23967500
C	-3.39275500	-2.75095100	0.90120800
C	-2.09050200	-3.34628400	1.12799000
C	2.78978500	1.45923300	-1.53428500
C	-4.58285200	-3.51732900	1.12268000
C	-1.94541700	-4.77467100	1.59488900
H	0.01083100	-2.93205700	1.05544000
H	4.88772900	-4.05276500	0.69719600
H	-4.46263700	1.04718300	-0.30119600
H	3.59942700	-3.86246900	-1.42418000
H	2.44843500	3.58774200	3.11762200
N	-5.50596700	4.23858300	-1.29994700
N	-5.56018900	-4.16032700	1.30976600
H	-2.45325800	-4.93337500	2.55610500
H	-0.89188600	-5.04525900	1.72135100

D.3 [Ru(bpy)(CN-Me-bpy)₂](PF₆)₂ Optimized Ground State Geometry

N	0.60851200	1.04407900	1.33300300
Ru	-0.00317700	-0.44699600	0.00260800
N	-0.41959900	-2.06875400	-1.26635200
N	-0.59387600	1.05501900	-1.32464400
N	0.39326700	-2.07607000	1.26822400
N	-2.05126600	-0.33862700	0.39627800
N	2.04458700	-0.36119400	-0.39694500
H	-3.51578500	2.60466900	-2.12932600
C	-2.45322400	2.36588700	-2.13733800
C	0.23828200	1.75467100	-2.14109600
C	-1.93768900	1.35571100	-1.31177600
C	-0.19272000	2.78473700	-2.99322200
C	-1.00428000	-4.37803400	-2.75309600
H	4.03520100	-2.62807700	-3.01890600
H	-0.73905300	4.58635500	3.65310400
H	1.28487000	1.47911500	-2.11402900
H	5.49376000	-2.65714400	-2.00795900
C	-4.14470400	0.67994200	-0.25210600
C	-2.72104400	-1.11092800	1.29361600
C	-2.75240800	0.55985300	-0.37732900
C	-4.11192600	-1.05392000	1.48303600
C	-0.54938600	-4.48232300	-1.42840100
H	1.46927000	-2.99973200	4.34839300
H	5.30802700	-1.41342800	-3.25081600
H	-2.12270300	-1.79604100	1.88005800
H	-0.96972900	-0.97732600	-2.96604000
H	-1.23192600	-5.27567100	-3.32622000
H	-0.42790100	-5.46425300	-0.97759700
H	-1.50806100	-2.97389000	-4.34767200
C	4.14880800	0.64561000	0.23317800
C	2.70309200	-1.14267300	-1.29464200
C	2.75684300	0.53461400	0.36940600
C	4.81971700	-0.17089600	-0.69545100
C	4.09321700	-1.09748300	-1.49225800
C	-0.26021700	-3.31502300	-0.69892900
C	6.24850300	-0.06608300	-0.83200600
C	4.76400100	-1.99941800	-2.49841200
H	2.09611900	-1.82611900	-1.87402200
C	1.12086000	-3.12142300	3.32462400
C	0.22064400	-3.31923200	0.69806800
C	0.83370600	-1.98706000	2.55388200
C	0.95179500	-4.39480500	2.75021900

C	0.49690600	-4.49121600	1.42511600
H	0.95339200	-0.99438400	2.97034000
H	1.16971200	-5.29604800	3.32144300
C	-1.16017300	-3.10165400	-3.32448200
H	3.54780800	2.57038400	2.11921500
C	2.48359400	2.33946600	2.13488900
C	-0.21154400	1.74513700	2.16068900
C	1.95440800	1.33537300	1.31044500
C	1.62518100	3.05785100	2.98681900
C	0.23382900	2.76868000	3.01337400
C	-0.86018500	-1.97210400	-2.55134500
C	2.16386700	4.09226300	3.83017000
C	-0.73108500	3.51627700	3.89952300
H	-1.26017500	1.47637100	2.14165400
H	4.71411500	1.35115000	0.84058500
H	-4.70096500	1.38749600	-0.86542500
H	0.36546300	-5.47074700	0.97186500
N	7.42091800	0.01223900	-0.95152400
N	2.59648300	4.94297000	4.52598800
H	-0.44491400	3.42747700	4.95569300
H	-1.75094900	3.13524000	3.78988800
C	-4.79462600	-1.94339300	2.49224900
H	-5.33743600	-1.34764500	3.23782700
H	-5.52729600	-2.59891400	2.00315000
H	-4.07315300	-2.57389900	3.02069000
C	0.78546300	3.53133900	-3.86570800
H	1.80241700	3.14554000	-3.74592500
H	0.51091500	3.44733300	-4.92536400
H	0.79513900	4.60049100	-3.61548100
C	-6.25569900	-0.01132000	0.80465800
N	-7.42813700	0.07609200	0.91753900
C	-2.10736500	4.12194200	-3.82420200
N	-2.52859300	4.97743500	-4.52115200
C	-4.82720500	-0.12739600	0.67606500
C	-1.58264100	3.08156800	-2.97935800

D.4 [Ru(CN-Me-bpy)₃](PF₆)₂ Optimized Ground State Geometry

N	-1.31324000	1.23583100	1.05759400
Ru	0.00279700	0.00032700	-0.00136100
N	1.46240900	-1.06381700	-1.05999700
N	-1.64997500	-0.72399900	-1.06328800
N	1.73407700	0.51076800	1.05912900
N	-0.41949900	-1.76080900	1.04744700
N	0.19985200	1.80359500	-1.04719600
H	-3.74888300	-3.39302800	-0.80967700
C	-3.32008500	-2.46466200	-1.18520200
C	-2.23450700	-0.10734100	-2.12549900
C	-2.18388900	-1.90056000	-0.58705200
C	-3.37431200	-0.60272800	-2.78167300
H	2.88242200	4.17969700	-3.68198500
H	-3.62630700	1.80242300	4.82772400
H	-1.77660900	0.81364800	-2.46294900
H	1.58325100	3.76350000	-4.80496600
C	-1.84019500	-3.71017700	1.16077000
C	0.29031300	-2.23160100	2.10758900
C	-1.48340600	-2.49044100	0.56700600
C	0.00233800	-3.44303200	2.75926300
C	3.80642700	-1.63151600	-1.18162700
H	2.62904300	2.48690900	-4.15124000
H	1.11659800	-1.61960400	2.44685400
H	0.19881700	-1.94118800	-2.46318800
H	4.82444400	-1.53977700	-0.80752800
C	-0.48187500	4.11840700	-1.15474700
C	1.03288800	2.01346200	-2.10145400
C	-0.55893700	2.84706800	-0.56682600
C	0.38298600	4.32454700	-2.24500300
C	1.17232100	3.25392200	-2.74725800
C	2.74715900	-0.93553800	-0.58041100
C	0.46991000	5.62824400	-2.84806000
C	2.11877900	3.42385300	-3.90859400
H	1.60796300	1.16112400	-2.44019700
C	2.96969900	1.70552600	2.78704300
C	2.90152500	-0.04021800	0.57986300
C	1.78119300	1.35278200	2.12592200
C	4.13230900	0.25909300	1.18298000
H	0.83628800	1.75884000	2.46409300
C	2.22707400	-2.60760700	-2.78449200
H	-2.40020000	4.45162100	0.80181500
C	-2.30835600	3.43323400	1.17741700

C	-2.07621700	0.84743700	2.11474800
C	-1.42189800	2.52340700	0.58253000
C	-3.09418000	3.02079100	2.26906900
C	-2.98938600	1.69326900	2.76712800
C	1.22513600	-1.87493800	-2.12560000
C	-4.01041200	3.94998100	2.87568800
C	-3.81138600	1.19767600	3.93012700
H	-1.95420300	-0.17447200	2.45036100
H	-1.07841000	4.94736900	-0.77570900
H	-2.67932200	-4.29243100	0.78261300
H	5.06094000	-0.16913600	0.81001100
N	0.54842200	6.69424300	-3.34985700
N	-4.76496100	4.70545800	3.37989400
H	-3.58160500	0.15481400	4.16844500
H	-4.88433700	1.26889800	3.70749400
C	2.95420200	2.64903100	3.96308900
H	1.93782300	2.97635500	4.20176100
H	3.37815800	2.17044200	4.85574800
H	3.56011900	3.54093100	3.75524100
C	1.89682900	-3.49539200	-3.95757400
H	0.83133400	-3.45608800	-4.20317300
H	2.46465600	-3.19658100	-4.84852700
H	2.15906100	-4.53969100	-3.74168600
C	5.43166900	1.44241200	2.90387800
N	6.46218300	1.70396400	3.41760200
C	4.63400100	-3.18973300	-2.89529000
N	5.51667300	-3.78596100	-3.40486500
C	4.16977500	1.13117700	2.28636900
C	3.54978800	-2.46858800	-2.28279500
C	0.83186300	-3.91288100	3.92752900
H	1.62557600	-3.19947800	4.16842900
H	0.20945900	-4.04728200	4.82203400
H	1.29889100	-4.88249700	3.70938200
C	-3.97978800	0.13246800	-3.95058400
H	-3.41605800	1.03898700	-4.19084600
H	-4.00165200	-0.50360500	-4.84530700
H	-5.01652400	0.42256800	-3.73412700
C	-1.45852700	-5.44304500	2.86362800
N	-1.74643200	-6.47082400	3.36867400
C	-5.08858100	-2.38915900	-2.89282300
N	-6.04930300	-2.85021100	-3.40149400
C	-1.09849800	-4.18902500	2.25629200
C	-3.91795300	-1.81716000	-2.28144700