

DISSERTATION

REEVALUATING THE PHOTOPHYSICS AND ELECTRONIC STRUCTURE OF CR(III)
AND V(II) COMPLEXES: THE IMPLICATIONS OF DISTORTION ON THE EXCITED
STATE MANIFOLD

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Romeo I. Portillo

Department of Chemistry

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Doctoral Committee

Advisor: Matthew P. Shores

Anthony K. Rappé
Eugene Y.-X. Chen
Christopher Peterson

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ABSTRACT

REEVALUATING THE PHOTOPHYSICS AND ELECTRONIC STRUCTURE OF CR(III) AND V(II) COMPLEXES: THE IMPLICATIONS OF DISTORTION ON THE EXCITED STATE MANIFOLD

Presented in this dissertation are investigations into the electronic structure of chromium and vanadium complexes targeted towards photocatalysis. These studies have focused on two primary features in the excited state manifold: the energy of the excited state and the relative distortion of the excited state to the ground state.

Chapter 1 provides a background on how the study of electron transfer led to the development of inorganic photocatalysis. The chapter includes the progression of photocatalysts design from $[\text{Ru}(\text{bpy})_3]^{2+}$ to modern alternatives focusing on Earth-abundant reagents. Additionally, I provide my perspective on these advances and criticism of prevalent methodologies.

Chapter 2 discusses the synthesis and characterization of polypyridyl-containing Cr(III) complexes. Each complex exhibits spectroscopic signatures of an unusual $^4(^3\text{IL})$ excited state, a mixed excited state between a paramagnetic ligand and metal center. Calculations provide insight into the character of this excited state, suggesting this $^4(^3\text{IL})$ excited state may be the lowest spin-allowed excited state in some of these complexes. The minimal distortion in these excited states limit the degrees of freedom for non-radiative decay compared to the metal-based $^4\text{T}_2$ excited state.

Chapter 3 discusses the synthesis and characterization of two V(II) polypyridyl complexes. Here, I reevaluate the proposed excited state manifold in the literature which claims that the

$^4\text{MLCT}$ is the lowest energy excited state. Spectroelectrochemical and picosecond-resolved spectroscopic techniques reveal a short-lived excited state, presumably $^2\text{MLCT}$. A new excited state manifold is presented, suggesting doublet excited states are relevant to the understanding of V(II) photophysics.

Chapter 4 discusses the differences in the electronic structure of isoelectronic V(II) and Cr(III) polypyridyls. While several factors contribute to these differences, the identity and energies of the relevant excited states lead to a completely different excited state manifold between the two systems. The chapter summarizes the work of Chapters 2 and 3.

Chapter 5 discusses the synthesis and electronic structure of a tripodal ligand scaffold bound to V(II) and V(III). The differences between the hexacoordinate V(II) and heptacoordinate V(III) further our understanding of the apical nitrogen's role on the electronics of the complex. Additionally, we exploit the utility of the SHAPE program to quantify structural distortion and correlate to the species' electronic structure.

Chapter 6 discusses the electronic structure of a similar vanadium tripodal complex, $[\text{V}((5\text{-CO}_2\text{Me})\text{py})_3\text{tren}]^{2+}$. This complex displays spectroscopic signals of both a V(II) complex with a neutral ligand and V(III) complex with a ligand radical. Different phenomena are proposed, but neither provide a complete explanation of the results.

Chapter 7 summarizes the investigations into V(II) and Cr(III) photophysics. Additionally, I discuss how SHAPE may be used in other fields and identify important structural motifs through machine learning.

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DEDICATION

To Cristobal Portillo and Dr. Cassandra Welch

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Chapter 1: A Tutorial on Inorganic Photochemistry

1.1 Foreword

This chapter is intended to be an advanced tutorial for new inorganic students interested in photocatalysis. Photocatalysis is a collaborative effort that *typically* requires knowledge of organic, catalysis, physical, computational, and inorganic chemistry. Trends in inorganic photocatalysis focus on the electronic structure of a new molecule, organic transformations via photo-induced electron transfer (PIET), and optimizing reactivity through ligand design. Ultimately, inorganic photocatalysis is an application of electrochemistry, thermodynamics and photochemistry.

My undergraduate experience has tailored this tutorial differently than other resources. Frequently, photocatalysis is introduced with the catalytic cycle and discussion of the catalyst's photophysical properties. Logically, this makes sense as absorbance of a photon is the initial step in the cycle. However, this introduction presents a model to the inorganic student rather than engage them in addressing a fundamental goal in the field: electron and/or energy transfer. In my undergraduate courses, my professors reinforced the importance of thermodynamics in advanced courses before discussing special topics. This activation of prior knowledge allowed me to appreciate topics such as electrochemistry, which were presented as applications of thermodynamics. In a similar fashion, inorganic photocatalysis can be viewed as an application of electrochemistry, or fundamental thermodynamics of electron processes.

In this advanced tutorial, it is assumed that the inorganic photochemist has been introduced to the field in the typical manner through discussion of the photocatalytic cycle. General topics are outlined to provide a foundation and encourage the use of available resources to further this knowledge. This tutorial will begin with the electron transfer and end with inorganic photocatalysis.

1.2 From Electron-Transfer to Photoredox catalysis

The fundamental study of electron transfer continues to drive new discovery in all fields of chemistry. Generally, electron transfer is the movement of an electron from one atom/molecule to another. From the fundamental work by Marcus¹ and Hush² to calculating the energy generated in galvanic cells³, understanding electron movement allows for the manipulation of chemical transformations from molecules to materials.

First, it is important to distinguish one-electron and two-electron transfer processes due to differences in reaction mechanisms. Two-electron processes are more common in organic reactions, for example, where lone pairs perform S_N2 reactions or a palladium center undergoes reductive elimination in a Suzuki cross-coupling reaction. Single-electron processes are observed in self-exchange with transition metal complexes and polymerization reactions. The radical reaction pathway allows new opportunities in synthesis such as hydrogen atom transfer as the final step in natural product synthesis.⁴ Classical sources of radicals include azobisisobutyronitrile⁵, samarium(II) iodide⁶, and tributyltin hydride,⁷ all of which are unstable under ambient conditions and quite toxic. Due to the potential hazards to one's health and the environment, efforts towards sustainable initiators have been pursued. I will focus on single-electron processes because they are primarily tunable thermodynamic processes.

To begin, let us consider how we characterize single-electron transfer in redox-based catalysis. First, the prepared compound should show reversible electrochemistry. The electrochemical reversibility is usually determined with cyclic voltammetry, with an anodic and cathodic peak being of equal magnitude. Quasi-reversible redox events may lead to bottlenecks in reaction mechanisms such as incomplete reactions or low turn-over. Second, the peak to peak

separation will determine the number of electrons involved in that redox process. For example, the Nernst equation at room temperature is

$$E_{cell} = E_{cell}^0 - \frac{RT}{nF} \ln Q \quad 1.1$$

where n is the number of electrons in the process. If $n = 1$, then the peak to peak separation should be 59 mV in an ideal system at 25 °C. However, the peak to peak separation is usually greater due to the solvent's diffusion limitations. Third, one may assume that the species is unsuited for electrocatalysis when processes are irreversible or quasi-reversible. One must consider that upon electrochemical reduction that the species may undergo a chemical transformation (EC reaction). Thus, increased scan rates typically show increased reversibility as there is less time for chemical transformations to occur. All these factors are taken into consideration when determining the catalyst's potential performance.

Now, *photoredox* catalysis allows for this redox-based single electron transfer mechanism through the use of light. This process tends to occur from benign reagents compared to classic radical initiators. The photocatalyst is electronically excited with light, followed by the transfer of a single electron to another molecule. This generates a radical on the substrate molecule, which leads to other reactions based on this single-electron transfer. Admittedly, attempts are being made towards two-electron transfer but the field has not reached this goal as of the time of writing. Additionally, energy transfer is relevant in photocatalysis but we will not be discussing it for sake of brevity. In order to fully understand photoredox catalysis, we must shift our focus on to the importance of photophysics and photochemistry.

Light as a reagent in chemical reactions has been documented, especially in the context of breaking chemical bonds. For example, a ketone excited state may lead to a Norrish Type II

reaction where intramolecular hydrogen atom abstraction occurs on the ketone. The selectivity of this photoreaction has led to improved yields in the preparation of an intermediate towards the total synthesis of ouabagenin.⁸ Thus, it is advantageous to incorporate light as a reaction parameter in the formation of new chemical bonds.

Visible light carries enough energy to break chemical bonds, another advantage of photoredox catalysis. When we consider visible absorbance (400-700 nm), the energy ranges from 43 to 75 kcal/mol (Figure 1.1). Within this energy range falls certain chemical bonds such as the O-O bond in peroxides (50 kcal/mol, or 600 nm). In theory, a 600 nm photon could break an O-O bond such as the bond in hydrogen peroxide. However, peroxides do not absorb this 600 nm wavelength of light (Grotthuss-Draper law, first law of photochemistry) and other nonradiative decay pathways exist beyond bond breaking. Now, consider a metal-ammonia bond. The bond energies may range from 30.59 kcal/mol (980 nm) to 93.04 kcal/mol (322 nm) for a first-row transition metal.⁹ These molecules absorb light at these wavelengths, which leads to the possibility of photodecomposition in solution. Considering the lability of first row transition metals, there are competing factors to keep the molecule together.¹⁰ Thus, it is an important assumption to consider, as photoexcitation could distort the metal-ligand bonds or break the molecule entirely. This assumption will be further discussed in later sections.

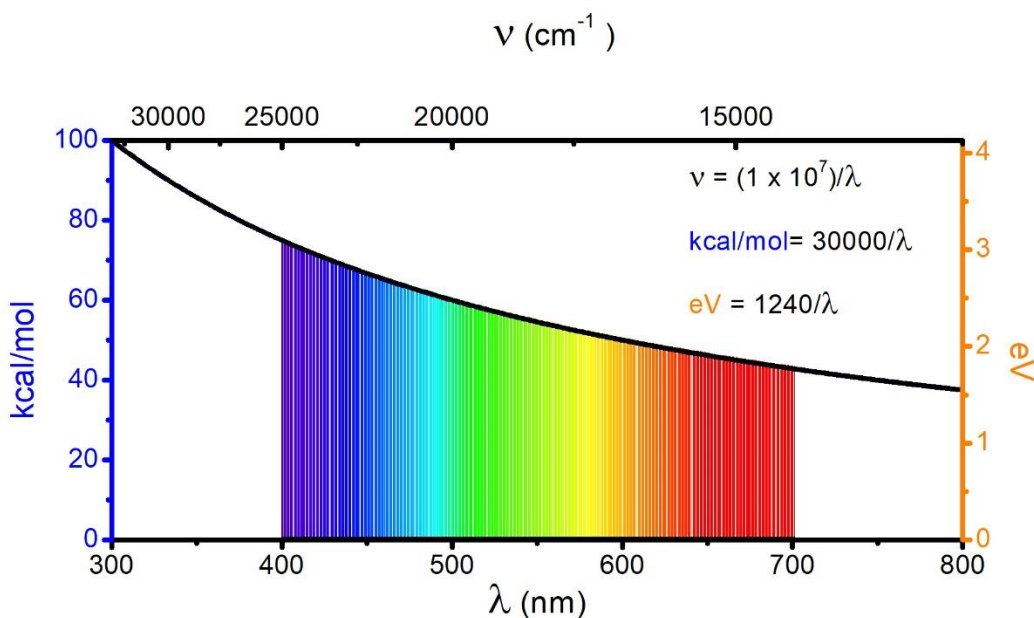


Figure 1.1 Relationship between wavelength (nm) and energy

Quantification of the electronic transition may help with assignment of electronic structure and the excited state. Our generic photocatalyst begins in a ground state, with limited reactivity. Upon excitation, our photocatalyst absorbs a photon of $E = h\nu$ and populates an excited state. The efficiency of that excitation depends on the extinction coefficient ϵ (units) of the transition, which has numerous dependencies, such as spin allowedness and symmetry. The typical extinction coefficients of such processes are summarized in Table 1.1. Several exceptions exist, but these ranges serve as a first approximations for characterization.

Table 1.1 Molar extinction coefficients for relevant electronic transitions

Transition	Spin-Forbidden	Spin-Allowed (d-d)	Spin-Allowed d-d (No inversion center)	Charge Transfer	$\pi-\pi^*$
$\epsilon, \text{ M}^{-1} \text{ cm}^{-1}$ (order of magnitude)	$(1 \times 10^{-4}) - 10^0$	$10^1 - 10^2$	10^2	$10^3 - 10^4$	$10^5 - 10^6$

Upon excitation of the initial excited state, the molecule attempts to alleviate the excess energy through several pathways. These potential pathways include chemical transformations, vibrational modes, and emission of a photon (Figure 1.2). Vibrational processes are thermal processes where energy is dissipated either inter- or intramolecularly. A vibrational mode allows the molecule to transfer that energy to its environment. Internal conversion is the nonradiative decay between excited states with the same spin multiplicity, whereas intersystem crossing is nonradiative decay between different spin multiplicities. Emission is radiative transfer from an excited state to the ground state. Fluorescence refers to emission between states with identical multiplicity. Phosphorescence refers to the emission of a photon to change between states with different multiplicities. Generally, the excited state lifetime is greater in phosphorescence due to the requirement of a spin-flip to access the ground state. This assumption does not always hold true in metal-based chromophores due to vibronic coupling.

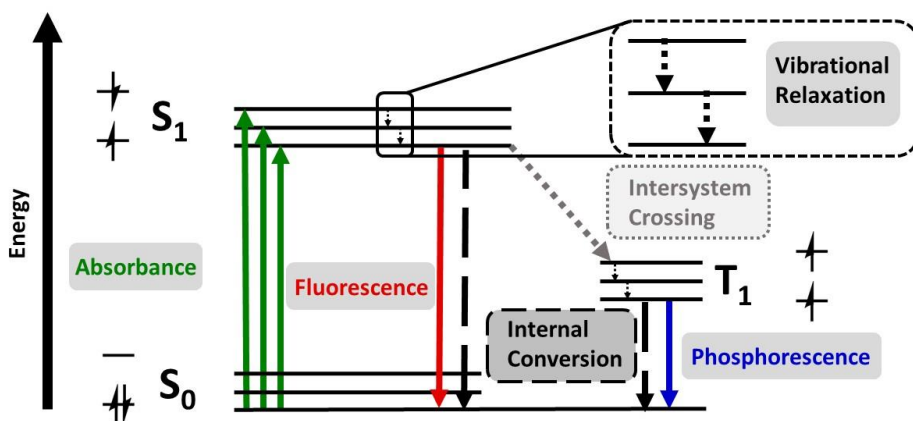


Figure 1.2 Representative Jablonski diagram for a diamagnetic organic molecule. S_0 represents the singlet ground state, S_1 represents the singlet excited state, and T_1 represents the triplet excited state.

With understanding of both the electrochemical and photophysical processes of our photocatalyst, we can discern their roles in photoredox processes. Unfortunately, there is no direct method to measure the excited state redox potential. However, we can estimate the excited state reduction potential based on the Rehm-Weller equation (Equation 1.2-1.3).

$$E_{1/2}(\text{PC}^+/\text{PC}^*) = E_{1/2}(\text{PC}^+/\text{PC}) - E_{00} \quad 1.2$$

$$E_{1/2}(\text{PC}^*/\text{PC}^-) = E_{1/2}(\text{PC}/\text{PC}^-) - E_{00} \quad 1.3$$

For photoinduced electron transfer to occur, the change in Gibbs free energy for the process must be negative. Recall that $\Delta G = -nFE^\circ$ where $E^\circ = E_{1/2}(\text{Reduced species}) - E_{1/2}(\text{Oxidized species})$. Thus, $E_{1/2}(\text{Sub}/\text{Sub}^-)$ must be greater than $E_{1/2}(\text{PC}^+/\text{PC})$ in order for photoreduction to occur. For photooxidation, $E_{1/2}(\text{PC}^*/\text{PC}^-)$ must be greater than $E_{1/2}(\text{Sub}/\text{Sub}^+)$. These are summarized in Figure 1.3.

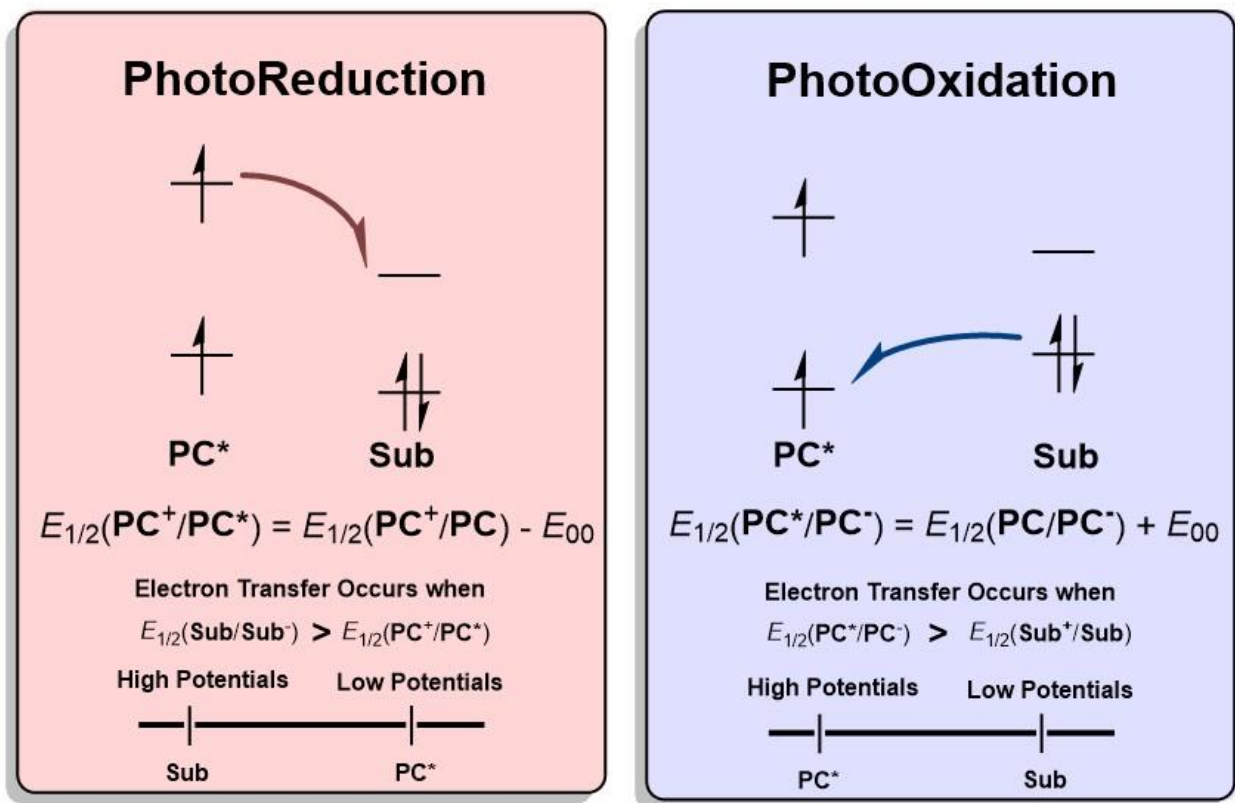


Figure 1.3 Comparison of photoreduction and photooxidation.

Additionally, the kinetic requirements must also be addressed beyond just the thermodynamic requirements. For a bimolecular reaction, the photoexcited chromophore and substrates must interact in solution. This reaction is dependent on the diffusion coefficient, k_{diff} , of the solvent based on the equation

$$k_{\text{diff}} \ll k_r [A] \quad 1.4$$

where k_r is the radiative decay constant of the excited state and $[A]$ is the concentration of the photocatalyst. Typically, photoinduced electron transfer will occur if the excited state lifetime is greater than 2 ns. Coincidentally, two nanoseconds is the instrument response time for most fluorometers. Here, $\tau = RC$ where τ is the response time, R is the resistance and C is the capacitance. While a molecule may be constantly irradiated in a fluorometry experiment, the

instrument cannot distinguish an emitted photon from noise in 2 ns. Thus, a molecule with an excited state lifetime less than 2 ns will not show any emission on these fluorometers.

In the following section, I will highlight key photocatalysts/photo-initiators which have pushed the field towards new sustainable alternatives.

1.3 Survey of Diamagnetic Photocatalysis

1.3.1 Ruthenium

Ruthenium remains a staple in photoredox due to being well characterized. Initial experiments by Meyer and Whitten revealed electron transfer was possible between $[\text{Ru}(\text{bpy})_3]^{2+}$ and methyl viologen (MV).^{11–13} Importantly, these processes were photoinduced and single electron transfer. Upon excitation of the MLCT band, the excited state of $[\text{Ru}(\text{bpy})_3]^{2+}$ would reduce methyl viologen by a single electron. Beyond the initial discovery of photoinduced electron transfer, the new $[\text{Ru}(\text{bpy})_3]^{3+}$ and $[\text{MV}]^+$ species were then potent enough reagents to oxidize water into dioxygen and reduce protons to dihydrogen.¹³ At this point, photoinduced electron transfer allowed new possibilities in mechanisms of various applications.

$[\text{Ru}(\text{bpy})_3]^{2+}$ exhibits a number of characteristics which allows it to perform photoinduced electron transfer (PIET) efficiently.¹⁴ These include, but are not limited to:

- 1) Long-lived excited state
- 2) High energy excited state
- 3) Tunable redox potentials
- 4) Efficient population of excited state (High triplet conversion?)
- 5) High molar absorptivity

1.3.2 Iridium

After the initial studies with ruthenium, it was a while before researchers discovered the possibility of iridium-based photoredox processes.¹⁵ The absorbance profiles of relevant complexes iridium may vary from ligand-based to charge-transfer transitions, typically a complex mixture of the two excited states.¹⁶ The absorbance in the visible region is a shoulder of these transitions, with relatively high molar absorptivities. It shares much of the same properties as ruthenium, except that its redox properties are better suited to photoreduction.^{17–19}

1.3.3 Organic

Once photoredox reemerged as a viable method for single electron transfer, efforts focused on sustainable alternative photocatalysts. In particular, ruthenium and iridium are precious metals with limited quantities in the Earth's crust. Organic photocatalysts were designed to mimic the properties of the transition metal counterparts, and work to a large degree.^{20,21} Additionally, the limited number of excited states allows for easier characterization of their photochemistries and limit the extent of non-radiative decay. While ideal in several cases, some limitations for organic sensitizers include:

- 1) Tunable absorbance in the visible spectra
- 2) Reversible electrochemistry

1.4 Towards sustainably-sourced inorganic chromophores

1.4.1 Iron

Once $[\text{Ru}(\text{bpy})_3]^{2+}$ was identified as an efficient photocatalyst, other transition metal complexes were developed to compete with the state-of-the-art. In particular, first row transition metals were sought as sustainable alternatives to ruthenium(II). Iron(II) is isoelectronic to ruthenium(II) and exhibits much of the same ground state properties, including a high molar

absorptivity and tunable redox potentials. However, early studies failed to produce signals on nanosecond spectrometers. It was later revealed that the “long-lived” excited state was only picoseconds long, and was not the initially populated excited state. This “long-lived” excited state was the 5A state which arose from intersystem crossing from a singlet ground state. Upon excitation, the molecule would distort and elongate the M-N bonds^{22,23}. The initially populated singlet MLCT converted to a triplet MLCT, followed by a triplet metal-centered (MC) state, and eventually a quintet MC state (Figure 1.4). This transformation mimics spin-crossover, such that this has been called photoinduced spin state switching. As the molecule continues to distort, the excited state manifold changes and lowers in energy to ~ 0.5 V.²³ At this point, the excited state is low enough that vibrational modes allow for non-radiative decay to the ground state. Based on this lower energy excited states, first row transition metals have often failed to yield long-lived excited states. In short, the multiple low-lying excited states become populated and lead to non-radiative decay within picoseconds.

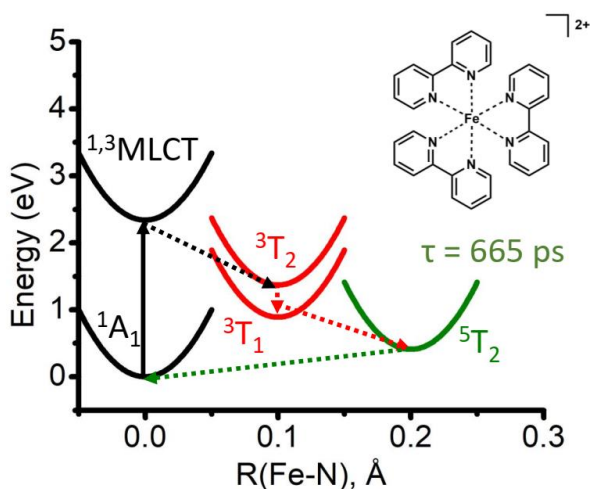


Figure 1.4 Distortion pathway for the excited states of $[\text{Fe}(\text{bpy})_3]^{2+}$

1.4.2 Copper

Despite the failures of iron(II), copper(I) has achieved remarkable success due to a different line of thinking. Tetrahedral copper(I) is d^{10} , which eliminates the possibility of low-energy d-d excited states. Upon excitation of the MLCT, the copper is formally d^9 , which allows for population of low energy excited states. Additionally, the molecule begins to distort from tetrahedral to square planar. Through ligand design with steric bulk, copper(I) species have been found with nanosecond lifetimes and act as efficient photoreductants of organohalides²⁴.

1.5 The Unknown Impact of Spin Multiplicity in Photocatalysis

In the cases presented thus far, the relevant photophysical states have all been singlets and triplets. The ground state for each case has always been diamagnetic, whether low-spin d^6 in Fe(II)/Ru(II)/Ir(III), d^{10} in Cu(I), or S_0 with organophotocatalysts. A practical reason to study diamagnetic compounds is the ability to perform NMR experiments and elucidate mechanisms of electron transfer. However, it is worth considering excited state implications arising from a paramagnetic ground state: what happens if the ground state is paramagnetic? By extension, what is the importance of the spin multiplicity in photophysics/photochemistry/photocatalysis? A limited number of paramagnetic complexes, particularly some Cr(III) and lanthanide complexes, exhibit long-lived excited states. In these cases, the change in multiplicity is argued as the reason for a long-lived excited state since the electron must undergo a spin-flip. If such is the case, more electrons that require a spin-flip should lead to a longer-lived excited state.

Generally, an excited state with different multiplicity than its ground state is long-lived. The requirement to reorient spins slows down the process, relative to spin-allowed processes. For example, a triplet organic molecule will have a longer-lived excited state than its singlet analogue. However, these long-lived species are less common at room temperature due to a low quantum

yield of intersystem crossing from the singlet excited state to the triplet excited state and release of energy through vibrational relaxation. In the case of inorganic photophysics, a similar assumption is made. The ability to achieve an excited state with a greater difference in multiplicity than the ground state could lead to an even longer excited state. For example, the 5T_2 excited state in $[\text{Fe}(\text{bpy})_3]^{2+}$ is an $S = 2$ difference relative to the 1A_1 ground state. Then, why does the 5T_2 excited state decay in less than 1 ns? Once again, non-radiative decay pathways are accessible and even more pronounced in these systems.

As disheartening as some of this seems, there is still a need to understand the excited state manifold towards the design of new photocatalysts. A common method of non-radiative decay is vibrational motion. Within the field of inorganic photochemistry, this seems to be the most prevalent pathway for candidate chromophores to avoid emitting a photon. Typically, we assume the electrons move between different excited states independent of nuclear motion due to the Born-Oppenheimer approximation. However, this approximation fails in the presence of vibronic or spin-orbit coupling which are very prevalent in inorganic photophysics and photochemistry. Here, it is much more difficult to distinguish the parameters which lead to rapid intersystem crossing or specific vibrational modes responsible for relaxation. While some may point to single parameters such as spin-orbit coupling for long-lived excited states, this is but one variable in the delicate design of new photocatalysts. The spin-orbit coupling in Os(II) is greater than that of Ru(II), but the excited state lifetime is shorter due to changes in the excited state energies. Ultimately, many things are system-dependent and the best we can do is address our assumptions. Now, let us examine some paramagnetic systems that have demonstrated long-lived excited state lifetimes with continued potential for growth.

1.6 Paramagnetic inorganic chromophores

1.6.1 Potential of Lanthanides

Photocatalyst candidates with paramagnetic ground states are largely unexplored. Lanthanide complexes, except La(III) and Lu(III), exhibit paramagnetic ground states and display a range of emission wavelengths.²⁵ These metal-centered excited states range in multiplicity, and have recently been investigated for photocatalysis. Schelter and colleagues have utilized earth-abundant Ce(III) complexes, which exhibits a doublet excited state manifold.^{26,27} Recently, Eu(II) has been explored with other developments expected to follow.²⁸

1.6.2 Chromium

Early Cr(III) photochemistry focused on Werner compounds with six monodentate ligands and short-lived excited states. These molecules were interesting as they exhibited a sharp emission at ~640 to 800 nm. This sharp emission is assigned to the $^2E \rightarrow ^4A_2$ transition due to its independence from ligand field based on Tanabe-Sugano diagrams and lack of strong dependence on the ligand electronics. Additionally, the 2E energy will not shift as a function of M-N distance with less vibrational modes. Thus, it will have narrow full-width half-max (FWHM) of the emission. The ability to observe an emission demonstrated promise for this first-row transition metal, but experiments at 77 K proved less ideal for electron transfer applications. At room temperatures, the excited state lifetimes were typically less than 2 ns.

Serpone, Hoffman, and Jamieson later improved on this field by preparing and studying Cr(III) polypyridyl complex salts. Here a jump in excited state lifetime is observed from picoseconds to microseconds! Notably, these compounds represent the longest-lived excited states for transition metal chromophores. These molecules exhibit several of the properties for PIET except high molar absorptivity in the visible region. Despite all of these ideal conditions,

development of Cr(III) photochemistry remained largely dormant after Endicott²⁹, Kirk^{30,31}, and Forster³² retired.

It was not until our group and collaborators first published in 2010 when opportunities for Cr(III) in photoredox catalysis were exploited. In 2015, C-CLEAR was initiated as the Catalysis Collaboratory for Light-activated Earth Abundant Reagents. As photoredox began to popularize organic transformation, our group collaborated within the network to demonstrate a Diels-Alder cyclization with chromium photocatalysis.^{33,34} Later on, we discovered that Cr(III) exhibits a unique $^4(^3\text{IL})$ excited state which leads to energy transfer pathways.³⁵ New discoveries relevant to chromium photophysics have been pursued by several investigators, focusing on different strategies for various applications.^{36–39}

1.6.3 Vanadium

In an effort to understand Cr(III), C-CLEAR sought to use isoelectronic V(II) as an alternative photocatalyst. Shah and Maverick previously investigated V(II) as an alternative to Cr(III), assuming the excited state manifold to be the same as Cr(III). They observed an increased molar absorptivity in the visible region^{40,41}, yet the lowest energy excited state is observed for ~1.5 ns. This work has remained dormant since 1988 where it was assigned to be $^4\text{MLCT}$ due to the rapid decay.^{42,43} C-CLEAR had decided to revisit this assignment of excited states, which will be detailed in later chapters.

1.7 Future of Inorganic Photochemistry

Currently, there are two dominant methodologies focused on replacing Ru(II)/Ir(III) photocatalysts with earth abundant reagents. The first focuses on developing new sensitizers, adding new candidates to perform photo-induced electron transfer. Underexplored systems such as d^0 Zr(IV), d^3 Mn(IV), d^5 Fe(III), and d^6 Co(III) represent new opportunities for photoredox with

earth-abundant reagents. The second approach focuses on the tuning the photophysics of existing systems through understanding and changing electronic structure. Such efforts focus on raising the low energy metal-centered excited states with strong field ligands, which is expected to increase the excited state lifetimes based on the energy gap law.

Admittedly, these methodologies are an overgeneralization of efforts in the field, but highlight a self-imposed limitation to new developments. For years, the focus on replacing Ru(II) and Ir(III) with “cheaper alternatives” has ironically led to multistep ligand syntheses, which cost just as much to prepare and afford decreased yields of product in photocatalytic reactions. These methodologies only stagnate the field and slow down the discovery of a “holy grail” of a cheap, earth-abundant reagent, with ideal photochemical properties for photocatalysis.

A paradigm shift is required to truly advance the field and approach this “holy grail” in a more timely fashion. For example, several older papers reach conclusions appropriate at the time due to limitations in instrumentation or theories. Now, the field is highly collaborative with a collective knowledge to make these goals attainable. Rather than focus on the development of new compounds, in my view it is just as worthwhile to revisit older hypotheses and verify their accuracy with modern techniques.

1.8 Organization of the Dissertation

In this dissertation, I will be focusing on the electronic structures of Cr(III) and V(II) systems and their relevance to photocatalysis. Each chapter is summarized here for convenience.

In chapter 2, we investigate various Cr(III) species with polypyridyl ligands in order to understand the $^4(^3\text{IL})$ excited state. A combination of spectroscopic results and computations support this $^4(^3\text{IL})$ excited state as a triplet ligand coupled to a paramagnetic metal center. The excited state is part of a Heisenberg spin-ladder with a doublet, quartet, and sextet progression.

The minimal distortion within the first coordination sphere promotes an excited state progression to a microsecond-long excited state compared to picosecond-long excited states. Computational work and insight were provided by Collette Nite and Anthony Rappé.

In chapter 3, we reevaluate the assignments of excited states in V(II) polypyridyl complexes. We utilize a combination of measurements, including spectroelectrochemistry and picosecond transient absorption spectroscopy. Here, we observe a short-lived (3-5 ps) excited state which converts to a longer-lived (500 -1800 ps) excited state. We simulate a $^2\text{MLCT}$ with spectroelectrochemistry, which qualitatively agrees with the short-lived state. We postulate the long-lived state to be a ^2MC (metal-centered) excited state, resembling a ^2E state (Figure 1.5). We attempt photoreduction of phenacyl bromide to acetone, but observe detrimental effects when $[\text{V}(\text{phen})_3](\text{OTf})_2$ is present. Ultrafast spectroscopy measurements were performed by Ryan Dill and Sam Shepard at CU-Boulder; computational work was provided by Collette Nite and Anthony Rappé.

In chapter 4, we re-evaluate the assumption that V(II) will behave similarly to isoelectronic Cr(III). We increase our scope to other V(II) polypyridyl complexes and confront some synthetic challenges. Overall, these compounds support our initial claims of the electronic structure established in the previous section. Additionally, calculations suggest that the increased size of the V(II) d orbitals increases the covalency between the metal and ligand. As a result, spin density bleeds onto the ligand, which allows for vibrational modes to alleviate the excess energy. Computational work was provided by Collette Nite and Anthony Rappé.

In chapter 5, we examine a tripodal ligand scaffold bound to V(II) and V(III). The differences between the hexacoordinate V(II) and heptacoordinate V(III) further our understanding of the apical nitrogen's role on the electronics of the complex. Additionally, we exploit the utility

of the SHAPE program to quantify structural distortion and correlate to the species' electronic structure. Computational work was provided by Justin Joyce and Anthony Rappé.

In chapter 6, I discuss preliminary work on a vanadium tripodal complex with an ambiguous electronic structure. A solid-state structure suggests this complex to be a V(III) complex with a ligand radical yet solution-based experiments suggests otherwise. Hypotheses ranging from speciation to valence-tautomerism will be discussed, along with future directions to address its electronic structure.

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Chapter 2: The Lowest Spin-Allowed Transition in Cr(III): 4T_2 vs $^4(^3IL)$

2.1 Introduction

The resurgence of photoredox catalysis has motivated several groups to investigate new candidates for these organic transformations. Ru(II) and Ir(III) have seen the most widespread use, being fully incorporated into academic and industrial applications.^{1,2} However, the scarcity of these metals have motivated several groups to pursue earth-abundant alternatives to sustain these processes.³

Cr(III) is a great option for photoredox since it's a stronger photooxidant than Ru(II), abundance, and access to a long-lived excited state. Cr(III) has been studied for decades, with the photophysical properties of $[Cr(bpy)_3]^{3+}$ initially proposed by Konig and Herzog.⁴ Notable contributions by Serpone,⁵ Hoffman, Jamieson, Endicott,⁶ Kirk,⁷ and Forster⁸ have advanced our current understanding of this system and shaped our interpretation of these spectra. For example, most studies discuss the 4T_2 excited state as the first spin-allowed transition but several Cr(III) polypyridyl complexes have unique shoulders in the NUV. These shoulders are greater than the expected ligand field molar absorptivity and less than a charge transfer transition. Some have argued that a reduction in symmetry for the increased absorptivity,⁹ whereas others have proposed a complicated intraligand transition coupled to the metal center.¹⁰

Recently, our group has endorsed the intraligand transition coupled to the metal as the NUV transition in Cr(III) polypyridyl complexes.¹¹ Some of us have shown this NUV transition may perform energy transfer using single-wavelength experiments.¹² Computation models suggest a triplet on the ligand can transfer energy to an associated substrate to generate a triplet on the substrate. This energy transfer mechanism requires the excited state to incorporate the ligand, and

not be entirely metal-centered. In order to describe this spin-allowed transition, we must consider spin states of both the metal and ligands. The notation hence forward is based on the work of Eric Juban and James McCusker, who previously attempted to assign these excited states.¹³ In intraligand transitions (IL), the singlet ^1IL ground state becomes a triplet ^3IL excited state. When bound to a metal, the Cr(III) metal center is predominantly quartet during this transition. Thus, the overall transition appears as $^4(^1\text{IL})$ to $^4(^3\text{IL})$ where the molecule's spin-state remains as a quartet but the ligand exhibits character change from ^1IL to ^3IL .

While the application of this transition is unique, I became interested in how this may impact the excited state manifold. **Specifically, why do some Cr(III) species have a long-lived ^2E excited state and some are short (< 2 ns)?** In this study, I chose 3 different polypyridyl-containing Cr(III) complexes with various excited state lifetimes. As will be shown here, these complexes all exhibit a $^4\text{A}_{2g} \rightarrow ^4(^3\text{IL})$ electronic transition. The role of this excited state to the longevity of the ^2E excited state will be explored, particularly in how non-radiative decay pathways are minimized. We'll investigate what the NUV transition is, looking at 3 different auxiliary ligands to tune the electronic properties. This work is designed to answer three dominant questions:

- 1) what does a $^4(^3\text{IL})$ excited state look like?
- 2) which spectroscopic techniques help identify it?
- 3) what are the implications of the $^4(^3\text{IL})$ excited state for Cr(III) photophysics?

2.2 Diversion of Labor

The work in this chapter was done by Romeo Portillo, Collette M. Nite, Anthony K. Rappé, and Jacob M. Nite. Romeo Portillo prepared and characterized compounds **2.1-2.3**, including synthesis, electronic absorbance, electrochemistry, emission spectroscopy, and spectroelectrochemistry experiments. Collette M. Nite and Anthony K. Rappé calculated the

optimized structures for all complexes, as well as the TDDFT excited states, absorption spectra, Franck-Condon analysis and NEVPT2 calculations.¹⁴ Jacob M. Nite calculated the vibrational distortion plots, including the structure alignments.

2.3 Experimental Section

2.3.1 Preparation of compounds

The starting materials $[\text{Cr}(\text{en})_2(\text{phen})]\text{Cl}_3$ ¹⁵ and $[\text{Cr}(\text{acac})_2]$ ¹⁶ were prepared according to a previous literature reports. $[\text{Cr}(\text{phen})_3]\text{OTf}_3$, $[\text{Cr}(\text{Me}_2\text{phen})_3]\text{OTf}_3$, and $[\text{Cr}(\text{Ph}_2\text{phen})_3]\text{OTf}_3$ were prepared according to previous literature reports.¹⁷

$[\text{Cr}(\text{bpy})_3](\text{OTf})_3$ (2.1)

The compound was prepared according to a previous literature report.¹⁷

$[\text{Cr}(\text{en})_2(\text{phen})](\text{OTf})_3 \cdot \text{CH}_3\text{CN}, \text{H}_2\text{O}$ (2.2 $\cdot \text{CH}_3\text{CN}, \text{H}_2\text{O}$)

Silver(I) triflate (153 mg, 0.595 mmol) was added to beaker of a stirring solution of $[\text{Cr}(\text{en})_2(\text{phen})]\text{Cl}_3$ (84 mg, 0.183 mmol) in water (15 mL). Immediately, silver(I) chloride precipitated out of solution as the reaction mixture continued to stir for 30 min. The solution was filtered through a nylon membrane. The filtrate was dried *in vacuo*, dissolved in CH_3CN , and filtered in order to remove all residual silver salts. The solution was concentrated via rotary evaporation, and set to crystallize via diffusion of diisopropyl ether into the concentrated solution: after ~24 hours, this yielded 116 mg of orange plate crystals, which were collected by filtration and washed with diethyl ether (0.135 mmol, 74%). UV-vis (CH_3CN) $\lambda_{\text{max}}/\text{nm}$ ($\epsilon_{\text{M}}/\text{M}^{-1} \text{ cm}^{-1}$): 205 (35500), 223 (28200), 272 (16900), 302sh (6240), 319sh (3520), 334sh (1080), 350sh (623), 426 (68), 461 (69). $m/z = 590.00$ (**1** – en – OTf), 649.91 (**1** – OTf[−]). Anal. Calcd For $\text{C}_{38}\text{H}_{26}\text{F}_6\text{N}_6\text{O}_7\text{S}_2\text{V}$ (**1**): C, 29.37; H, 3.40; N, 11.42. Found: C, 29.12; H, 3.35; N, 11.49.

[Cr(acac)₂(bpy)](PF₆) (2.3)

Under an inert atmosphere, a solution of [Cr(acac)₂] (93 mg, 0.372 mmol) and 2,2-bipyridine (61 mg, 0.391 mmol) was stirred in 8 mL of acetonitrile for 1 hour to form a dark, brown solution. Addition of AgPF₆ (105 mg, 0.415 mmol) caused the solution color to change to purple and precipitation of a grey solid. The mixture continued to stir for 1 hour. Once completed, the solution was filtered in air through Celite, concentrated, and set to crystallize via diisopropyl ether diffusion into a concentrated solution over 24 hours to yield 139 mg of pink plate crystals (0.252 mmol, 68% yield). UV-vis (CH₃CN) λ_{max} /nm ($\epsilon_{\text{M}}/\text{M}^{-1} \text{ cm}^{-1}$): 211 (32300), 250 (18100), 304 (14400), 390sh (683), 420sh (381), 539 (72). $m/z = 432.25$ (**2** – PF₆). Anal. Calcd For C₂₀H₂₂CrF₆N₂O₄P: C, 43.57; H, 4.02; N, 5.08. Found: C, 43.65; H, 4.12; N, 4.85.

[Cr(NH₃)₄(bpy)](BF₄)₃ (2.4)

The computed structure was calculated and optimized by Collette Nite and Anthony K. Rappé.¹⁴

2.3.2 Electrochemical Studies

Voltammograms were recorded with a CH Instruments 1230A potentiostat in a glovebox under a dinitrogen atmosphere. All experiments used 0.1 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) solution in acetonitrile with a 0.25 mm carbon working electrode, Ag wire quasi-reference electrode, and a Pt wire auxiliary electrode. Reported potentials are referenced to the ferrocenium/ferrocene ([C₅H₅)₂Fe]⁺/[(C₅H₅)₂Fe], Fc^{+ / 0}) redox couple and were determined by adding ferrocene as an internal standard at the conclusion of each electrochemical experiment.

2.3.3 Photophysical Studies

Electronic absorption spectra were obtained with either a Hewlett-Packard 8453 or Ocean Optics DH-2000-spectrophotometer in a quartz cuvette with a 1 cm path length; experiments were performed at room temperature, unless specified. Elemental analyses were performed by Midwest Microlabs (Minneapolis, MN).

2.3.4 Crystallographic Measurements

Key structural data for compound **2.2** are provided in Table 2.1. Crystals were coated in Paratone oil, supported on Cryoloops, and mounted on a Bruker D8 Quest ECO with a Photon 50 CMOS diffractometer under a stream of cold nitrogen. All data collections were performed with Mo K α radiation and a graphite monochromator. Initial lattice parameters were determined from a minimum of 310 reflections harvested from 24 frames; these parameters were later refined against all data. Data sets were collected targeting full coverage and fourfold redundancy. Data were integrated and corrected for absorption effects with the APEX 3 software packages. Structures were solved by direct methods and refined with the SHELXTL software package. Displacement parameters for all non-hydrogen atoms were refined anisotropically. All hydrogens were assigned to ideal positions and refined using a riding model with an isotropic thermal parameter 1.2 times that of the attached carbon atom.

Table 2.1 Crystallographic parameters for **2.2**

	2.2·CH₃CN, H₂O
Formula	C ₂₁ H ₂₉ CrF ₉ N ₇ O ₁₀ S ₃
FW	930.73
Color, habit	Orange plates
T, K	120(2)
Space group	<i>C2/c</i>
Z	8
<i>a</i> , Å	40.69(3)
<i>b</i> , Å	9.536(7)
<i>c</i> , Å	19.702(14)
<i>A</i> , deg	90
<i>β</i> , deg	115.69(3)
<i>γ</i> , deg	90
<i>V</i> , Å ³	6889(9)
<i>d</i> _{calc} , g/cm ³	1.656
GOF	1.171
<i>R</i> ₁ (<i>wR</i> ₂), %	5.61 (17.80)
Δ <i>ρ</i> _{max,min} /e Å ⁻³	1.12, -0.82

2.3.5 Other Physical Methods

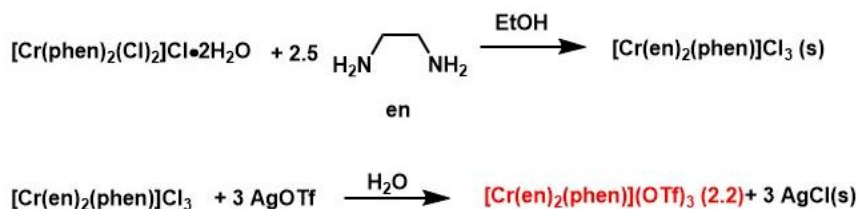
Infrared spectra were measured with either a Nicolet 380 FT-IR or Bruker TENSOR II spectrometer. Mass spectrometry measurements were performed in either the positive ion or negative ion mode on a Thermo-Finnigan LTQ mass spectrometer equipped with an analytical electrospray ion source using a 2.5 V spray voltage and 175 °C capillary temperature.

2.4 Results & Discussion

2.4.1 Synthesis

The synthesis of $[\text{Cr}(\text{en})_2(\text{phen})](\text{ClO}_4)_3$ has been reported¹⁵, and was modified to yield the triflate salt **2.2**. Scheme 2.1 demonstrates the optimized reaction conditions. The bis-polypyridyl starting material, $[\text{Cr}(\text{phen})_2\text{Cl}_2]\text{Cl}$, undergoes ligand exchange in the presence of ethylenediamine, and the yellow mono-polypyridyl $[\text{Cr}(\text{en})_2(\text{phen})]\text{Cl}_3$ precipitates from a purple solution. Unfortunately, this reaction is restricted to electron-rich polypyridyls and chloride salts. Attempts to use electron-deficient polypyridyls failed, such as bathophenanthroline (Ph_2phen) and dimethyl [2,2'-bipyridine]-4,4'-dicarboxylate ($(\text{CO}_2\text{Me})_2\text{bpy}$). These failures are likely due to the increased solubilities of both the starting material and product, preventing isolation of the desired product and allowing for further ligand exchange. Additional attempts to prepare heteroleptic complexes using other amines such as tetramethylethylenediamine (TMEDA) and tris(2-aminoethyl)amine (tren) also failed using these electron-deficient polypyridyls.

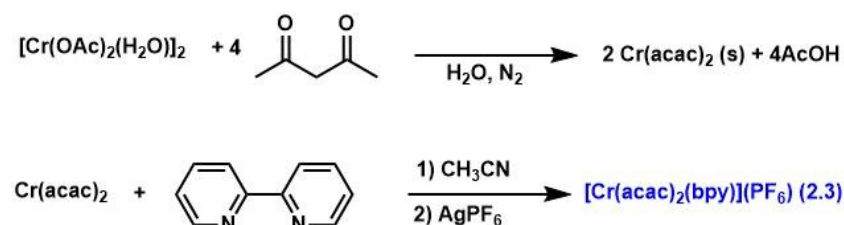
Scheme 2.1 Synthesis of **2.2**



The mechanism for ligand exchange between $[\text{Cr}(\text{phen})_2\text{Cl}_2]\text{Cl}$ and ethylenediamine is unknown, but we can infer a few components. First, and to the best of our knowledge, $[\text{Cr}(\text{phen})_2(\text{en})]^{3+}$ is neither isolated nor observed in the reaction. Second, using increased amounts of ethylenediamine does not appear to increase the yield nor rate of this reaction. This suggests a dissociation mechanism rather than an associative one. Third, a purple $[\text{Cr}(\text{en})_2(\text{H}_2\text{O})_2]\text{Cl}_3$ by-product is observed in the filtrate.^{18,19} When the solvent is exchanged for dichloromethane, $[\text{Cr}(\text{en})_2(\text{H}_2\text{O})_2]\text{Cl}_3$ precipitates out of solution. These observations suggest $[\text{Cr}(\text{phen})_2\text{Cl}_2]\text{Cl}$ to be a better starting material for syntheses of heteroleptic ammine/polypyridyl complexes.

The synthesis of $[\text{Cr}(\text{acac})_2(\text{bpy})]^+$ has been previously reported²⁰, and was modified to yield the tetrafluoroborate salt **2.3**. The synthesis is based on work by Ghosh and Wieghardt, where $[\text{Cr}(\text{acac})_2]$ is treated with one equivalent of ligand followed by oxidation. Additionally, this synthesis allows for different salts.

Scheme 2.2 Synthesis of **2.3**



2.4.2 Crystallography:

While the synthesis of $[\text{Cr}(\text{en})_2(\text{phen})]^{3+}$ has been reported previously, the work in this dissertation represents the first crystallographic report of this complex salt.¹⁵ Compound **2.2** crystallizes via diffusion of diethyl ether into a concentrated solution of acetonitrile in air. Crystals

form with cocrystallized acetonitrile and water molecules as shown in the crystal structure and elemental analysis results (Figure 2.1).

Single crystal XRD data for **2.2**·CH₃CN, H₂O are shown in Table 2.1. Here, we see that the complex is best described as Cr(III) with neutral ligands. Both Cr-N_{en} and Cr-N_{phen} bonds average to 2.068 Å, on par with their homoleptic analogues.^{21,22} Additionally, the phenanthroline C-C bond is the expected length for a neutral ligand.²¹

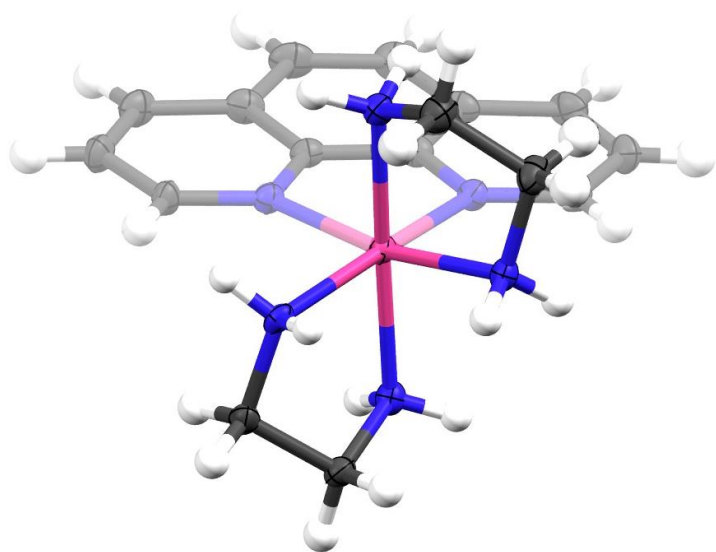


Figure 2.1 Crystal structure of the chromium complex in compound **2.2**. Solvent, hydrogen, and anion atoms are omitted for clarity. Ellipsoids are set to 40%.

2.4.3 Electronic Absorbance

The absorbance spectra of various Cr(III) complexes underlie the complexity of the putative ⁴(³IL) electronic transition. Spectra of **2.1-2.3** are shown in Figure 2.2. For example, compound **2.2** reveals two peaks in the visible region, one smooth ($\lambda = 462$ nm) and one sharp ($\lambda = 426$ nm). Substitution of 1,10-phenanthroline for 2,2-bipyridine resolves the smooth feature, similar to their homoleptic analogues (Figure A1.2).¹⁵ Compound **2.3** exhibits a smooth transition centered at $\lambda = 536$ nm. Based on the molar absorptivity and ligand field considerations, this

transition has been assigned as the Cr(III) $^4A_{2g} \rightarrow ^4T_{2g}$ transition for other Cr(III) diketonate polypyridyl species.^{20,23} However, a vibronic transition is observed ($\lambda > 450$ nm) with a molar absorptivity larger than expected for a ligand field transition and smaller than expected for a charge transfer transition. This vibronic progression also appears in compound **2.1**, albeit at slightly lower energies. If one assumes a reduction from octahedral (O_h) to lower symmetry, then the lack of an inversion center may increase the allowedness of the ligand field transition. However, this does not explain the multiple transitions nor the progression of these transitions based on a d^3 Tanabe-Sugano diagram regarding ligand field strength. Closer inspection reveals that these transitions are resolved by $\sim 1500\text{ cm}^{-1}$, approximately equal to a ligand C=C or C=N vibration. Thus, we infer that the ligands are involved.

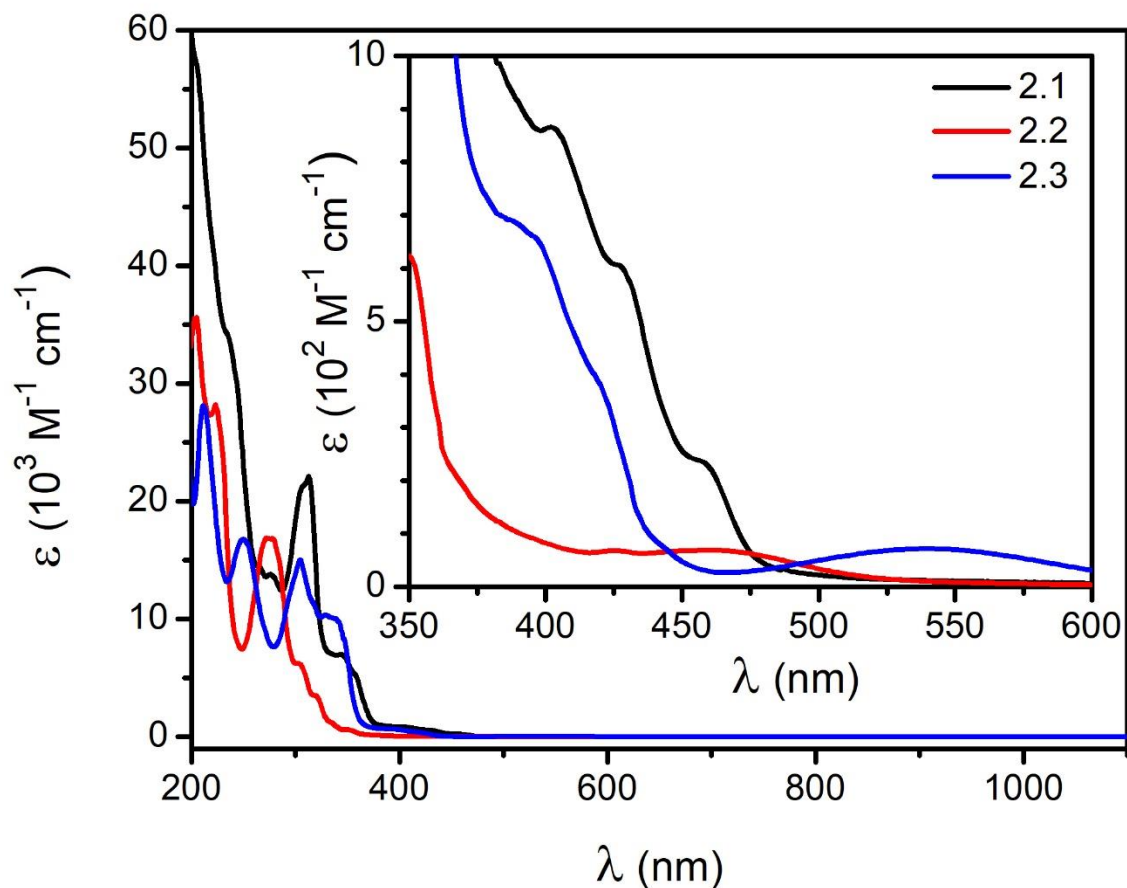


Figure 2.2 Electronic absorbance spectra of **2.1-2.3** in CH₃CN.

To further probe the possibility of vibronic participation in the electronic absorption, we have investigated other homoleptic Cr(III) species also showing this absorbance. At room temperature, the transitions are much more resolved in bipyridine systems compared to phenanthroline. Additionally, 4,4'-substitution with electron donating groups (such as 4,4'-Me₂bpy) better resolve these transitions. Upon cooling to 77 K, these transitions are distinct for the investigated homoleptic Cr(III) polypyridyl complexes and allow for precise assignment of the peak absorbances (Figure A1.5).

2.4.4 Emission from 2E Excited State

Compounds **2.1-2.3** display emission in the infrared, consistent with emission from the 2E excited state. Previously reported emission data for **2.1** and **2.2**¹⁵ are consistent with our measurements (Figure 2.3). Excitation of the lowest energy transitions produces a narrow peak at 727 and 692 nm for **2.1** and **2.2**, respectively. This peak is assigned as the $^2E \rightarrow ^4A_2$ emission; the $^2T_1 \rightarrow ^4A_2$ emission appears as a higher energy peak. In the case of **2.2**, the $^2T_1 \rightarrow ^4A_2$ transition is close in energy to the $^2E \rightarrow ^4A_2$ emission and appears as a shoulder off the $^2E \rightarrow ^4A_2$ emission peak.

Ligand-based emission of **2.3** has been reported at room temperature, but no emission in the near-IR was reported.²⁰ At room temperature, we observe no emission for **2.3** in the presence or absence of oxygen. Cryogenic emission in a 4:5 (v:v) propionitrile:butyronitrile solvent glass reveals a peak at 818 nm, and a shoulder at ~775 nm. These peaks are assigned as the $^2E \rightarrow ^4A_2$ and $^2T_1 \rightarrow ^4A_2$, based on their positions and intensities.

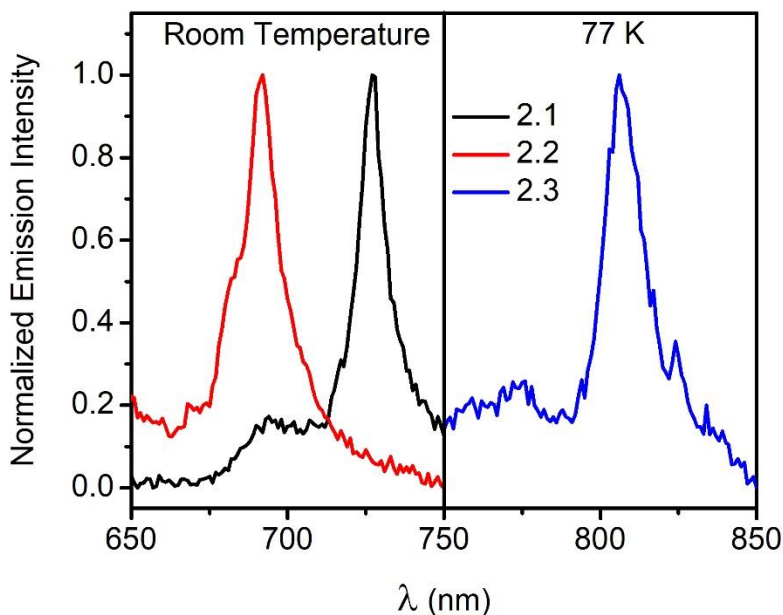


Figure 2.3 Emission spectra of **2.1-2.3**. Spectra for **2.1** and **2.2** were collected in CH₃CN at room temperature under atmospheric conditions. The spectrum for **2.3** was collected in a 4:5 (v:v) propionitrile:butyronitrile solvent glass at 77 K.

2.4.5 Natural Transition Orbitals Reveal “Triplet Ligand” Transitions: The $^4(^3IL)$ Excited State

Due to the ambiguity in the absorbance spectra of **2.1**, calculations were performed with the model compound **2.4**.¹⁴ Compound **2.4**, $[\text{Cr}(\text{NH}_3)_4\text{bpy}]^{3+}$, represents the simplest Cr(III) species with a N_6 first coordination sphere and a polypyridyl ligand. Attempts to perform calculations on **2.2** have occasionally failed due to decreased Franck-Condon overlap between the ground state and excited state. These small distortions forced some calculations to fail, complicating discussions of the photophysics of **2.2**. Since compound **2.4** resembles the electronic structure of **2.2**, we will continuously refer to it due to their similarities. The calculated spectra with time-dependent density functional theory (TDDFT) matches the expected energies best with the APF-D functional, compared to $\omega\text{B97X-D}$ (Figure A1.3). The electronic transition at 435 nm in compound **2.4**, the lowest energy spin allowed excited state, resembles the broad peak at 461 nm in compound **2.2** (Figure 2.4). Admittedly, neither contain the vibronic features present in **2.1**. Utilizing the excited at 435 nm for compound **2.4**, the vibronic features are present using Franck-Condon-Herzberg-Teller analysis (Figure A1.4).²⁴

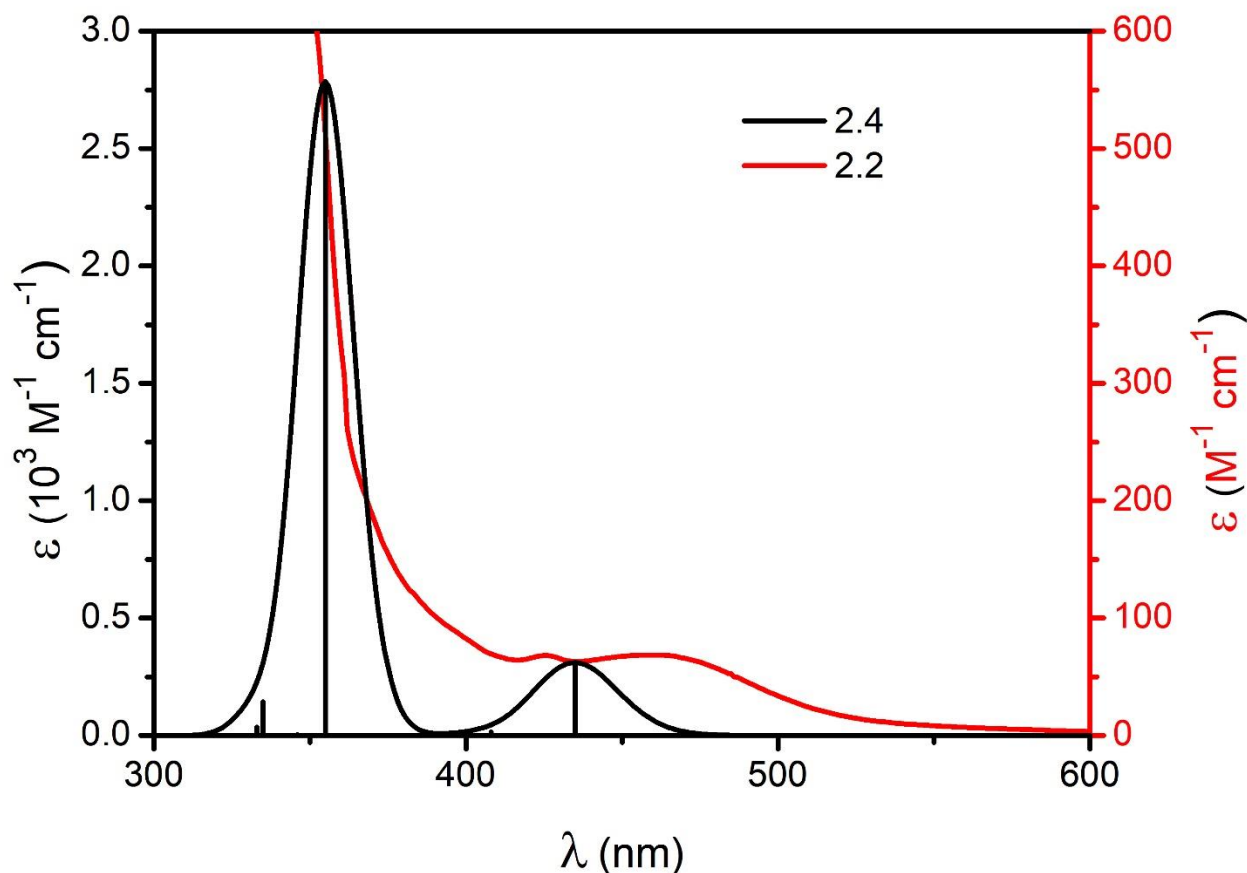


Figure 2.4 Comparison of the calculated absorbance spectra of compound **2.4** (black) and experimental absorbance spectra of **2.2** (red). The absorbance spectra of compound **2.4** was calculated with TDDFT (APF-D/6-311+G*). The absorbance spectra of **2.2** was measured in CH₃CN.

In order to gain more insight, natural transition orbitals utilizing the 435 nm excited state in compound **2.4** were calculated. We were surprised to see a ligand-based transition as the lowest energy, spin-allowed transition (Figure 2.5).¹⁴ We performed calculations on the free ligand, bpy, to gain further insight. The lowest energy transition represents a $^1A_g \rightarrow ^3B_2$, consistent with other calculations showing a $^1\pi \rightarrow ^3\pi^*$ transition.²⁵ We note that these transitions are also observed in the homoleptic species **2.1**. Overall, electron density is shifted on the ligand but there is more contribution from the metal centered orbitals in **2.1** than **2.4**. Thus, the transition in **2.1** could be characterized as a $\pi \rightarrow \pi^* + d$ transition. There is likely some coupling between Cr(III) and bpy which allows for the singlet-to-triplet transition to become spin-allowed.

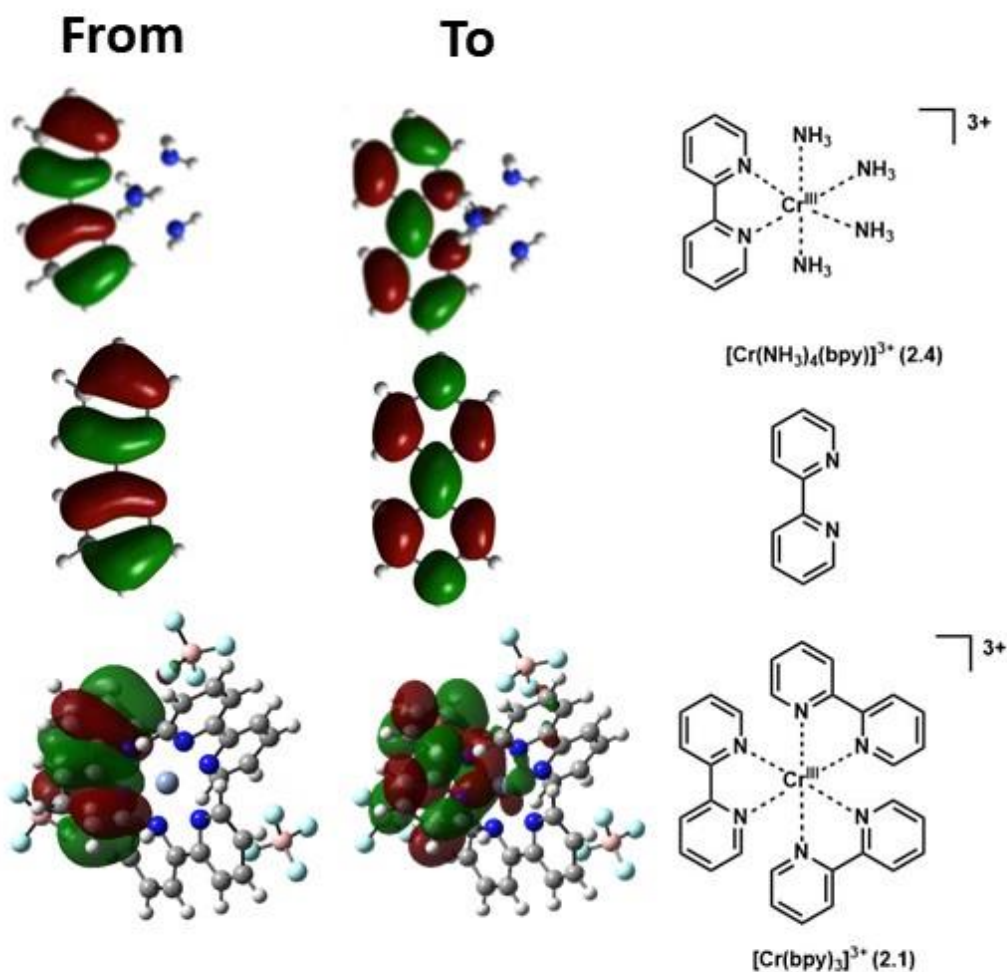


Figure 2.5 Natural transition orbitals of **2.4** (top), bpy (middle), and **2.1** (bottom).

Admittedly, it is difficult to consider how this $^4(^3\text{IL})$ does not violate rules for photophysics. Classically, singlet to triplet transitions are typically described as two photon processes where a molecule 1) absorbs a photon and excites to a singlet excited state and 2) undergoes intersystem crossing to a lower-lying triplet excited state. Direct excitation into spin-forbidden transitions are possible but have low molar absorptivities/oscillator strengths. In some instances, spin-orbit coupling helps with excited mixing to increase the molar absorptivity/oscillator strength, as

exemplified in tetraphenyl lead.²⁶ These are all possibilities that are well documented and generally accepted within the photophysical research community. However, most characterized systems in the community focus on diamagnetic ground states whereas our system is always paramagnetic. Thus, we must consider the importance of the paramagnetic metal center and not restrict discussion to classically accepted rules based on diamagnetic species.

2.4.6 Mechanism for $^4(^3IL)$ Transition as a Single Photon Phenomena

In order to describe the $^4(^3IL)$ excited state, we utilized CASSCF/NEVPT2 calculations to understand the spin-states involved. CASSCF calculations are performed within a 5 electron, 7 orbital complete active space. Since the states are always paramagnetic, these calculations require delicate handling to avoid nonsensical solutions and program crashes. Admittedly, the modest basis set does not reproduce experimental energies but does provide a description of the excited state. Coefficients of the spin-determinants from the seventh quartet state are shown in

Table 2.2. Within the 5 electron-7 orbital calculation, there are no electrons observed in the metal e_g^* antibonding orbitals. Thus, the lowest lying transitions are not ${}^4A_{2g} \rightarrow {}^4T_{2g}$. The first and last entry show a β electron in the π and π^* with coefficients of approximately -0.5. Combined, these two represent a $(\alpha\beta + \beta\alpha)$ state which is the $M_s = 0$ $\hbar$ state of a triplet. Interestingly, the β is not confined to the ligand orbitals but appears in the t_{2g} set as well. The excited state may be summarized with the wavefunction equation 2.1:

$$(\alpha\beta + \beta\alpha)\alpha + \alpha\alpha\beta)_{t_{2g}} - (\alpha\beta + \beta\alpha)_{\pi\pi^*} \quad 2.1$$

Table 2.2 Spin determinant components and coefficients that comprise the seventh quartet state. Each row represents a single spin-determinant with their corresponding coefficient

π	t_{2g}	t_{2g}	t_{2g}	π^*	e_g	e_g	coefficient
β	α	α	α	α	0	0	-0.516963949
α	β	α	α	α	0	0	0.348638985
α	α	β	α	α	0	0	0.346837396
α	α	α	β	α	0	0	0.356099333
α	α	α	α	β	0	0	-0.534611765

Expanding the calculation reveals a series of similar transitions. A lower lying doublet exhibits a similar series with the β electron delocalized unto both metal and ligand-based orbitals. (Table 2.3). Again, no electrons are observed in the e_g orbitals. Finally, a higher energy sextet is calculated in the NEVPT2 calculations. Together, this series of doublet, quartet, and sextet states is characteristic of a Heisenberg antiferromagnetic spin ladder.

Table 2.3 Spin-determinant components for the eight doublet state. Each row is representative of a single spin-determinant with their corresponding coefficient.

π	t_{2g}	t_{2g}	t_{2g}	π^*	e_g	e_g	coefficient
β	β	α	α	α	0	0	0.222742025
β	α	β	α	α	0	0	0.222069413
α	β	β	α	α	0	0	-0.218220048
β	α	α	β	α	0	0	0.216607890
α	β	α	β	α	0	0	-0.222355890
α	α	β	β	α			-0.220843389
β	α	α	α	β			-0.661419327
α	β	α	α	β			0.217833914
α	α	β	α	β			0.216994025
α	α	α	β	β			0.226591389

Molecular species exhibiting a Heisenberg spin-ladder typically require two paramagnetic species. Here, the ligand is only paramagnetic upon excitation of NUV light which complicates characterization. To the best of our knowledge, this is the first explicit written report of a Heisenberg spin ladder generated upon photoexcitation.²⁷ Additionally, this excited state is short-lived as it readily converts to the 2E excited state within a few picoseconds. Femtosecond resolution would be required in order to observe a triplet-state ligand, which is beyond our capabilities.

The coupling of ligand-based transitions to metal centers has been reported previously, albeit in large aromatic systems such as porphyrins. Gouterman and colleagues have investigated a series where NIR transitions were assigned as triplet ligand coupled to various multiplicities of Cr(III).²⁸ Additionally, the molar absorptivity of these NIR transitions in Cr(III) porphyrins is

significantly higher compared to other paramagnetic centers such as Ti(III) or vanadyls. It has been hypothesized that the closeness in energy of these transitions to charge transfer excited states would allow for increased spatial overlap, increasing the mixing of these states and the allowedness of the transitions. Ohno, Kato, Kaizaki, and Hanazaki previously assigned the $^4(^3\text{IL})$ in other aromatic Cr(III) systems while estimating the oscillator strength for that transition.¹⁰ The oscillator strength and coupling energy between the ligand and metal center were estimated based on the proximity of ligand and metal center excited state energies. In both models, approximations of the coupling rely solely on ground state properties, which don't provide accurate descriptions of the excited states. Probing these models are difficult endeavors and require thorough characterization of the $^4(^3\text{IL})$ excited state. Previous attempts to observe the $^4(^3\text{IL})$ excited state proved difficult due to the quick relaxation to the ^2E state within 2 ps.¹³ Thus, this computational work provides more insight into the nature of mixed states in Cr(III) systems rather than an experimental model.

2.4.7 Spectroscopic Identity of ^3IL and $^4(^3\text{IL})$

Should the ligand be involved, we must consider the photophysical properties of the ligand to gain insight to this set of electronic transitions in Cr(III)-containing complexes. The electronic absorbance spectrum of 2,2'-bipyridine collected at room temperature reveals high-energy $\pi\text{-}\pi^*$ transitions and no features in the near-UV/visible regions. Emission studies performed on the free ligand show a bright $^1\pi\rightarrow^1\pi^*$ with some vibronic structure. The small Stokes shift supports the assignment of a $^1\pi\rightarrow^1\pi^*$ transition, but the energy is higher than the transitions in Cr(III). Upon cooling to 77 K, the $^3\pi\text{-}\pi^*$ transition is observed at lower energy in the near-UV/visible region. Interestingly, the low energy shoulder in Cr(III) almost overlaps with the ν_{00} transition for the $^1\pi\rightarrow^3\pi^*$ emission (Figure A1.7).

In an effort to better resolve the vibronic absorbance in these compounds, we looked at the cryogenic excitation spectra of these compounds as an appropriate substitute. Originally, absorbance spectra taken in solvent glasses required a non-ideal set-up. Compounds were prepared under an inert atmosphere, submerged in liquid nitrogen until a solvent glass formed, and immediately measured on a spectrometer. Typically, atmospheric moisture condensed on the sides of the cuvette which required multiple measurements until a suitable spectrum was collected (Figure A1.5). However, our fluorometer can “mimic” an absorbance spectrum with an excitation spectrum of the 2E emission. While an emission spectrum is the measurement of photons at a constant excitation wavelength, an excitation spectrum is the converse where the excitation wavelength varied with a constant emission wavelength. If a single species exists in solution, the “excitation spectrum represents the relative emission of the fluorophore at each excitation wavelength. For most fluorophores, the quantum yields and emission spectra are independent of excitation wavelength. [Thus], an excitation spectrum can be superimposable on its absorbance spectrum.”²⁹ Lovaasen and colleagues have also observed improved resolution with this technique at room temperature compared to the room temperature absorbance.³⁰

Here, we build off the use of excitation spectra by performing measurements at cryogenic temperatures for better resolution. Thus, we were able to collect excitation spectra at cryogenic temperatures in lieu of cryogenic absorbance spectra. This technique greatly resolved broad absorbance features into numerous individual peaks. For instance, $[\text{Cr}(\text{Ph}_2\text{phen})_3](\text{BF}_4)_3$ exhibits a broad visible absorbance spectra with mild shoulders hinting at the $^4(^3\text{IL})$ excited state. The excitation spectra of the 2E emission greatly resolves the broad absorbance to reveal 3 distinct peaks reminiscent of other Cr(III) polypyridyl complexes. (Figure A1.7). For compound **2.2**, the broad peak centered at 461 nm is resolved into multiple peaks (Figure 2.6). When compared to the

vibronic spectrum of **2.4**, several high energy peaks in **2.4** qualitatively match peaks in **2.2**. This observation further supports that the lowest spin-allowed electronic transition in **2.2** is the $^4(^3\text{IL})$ excited state.

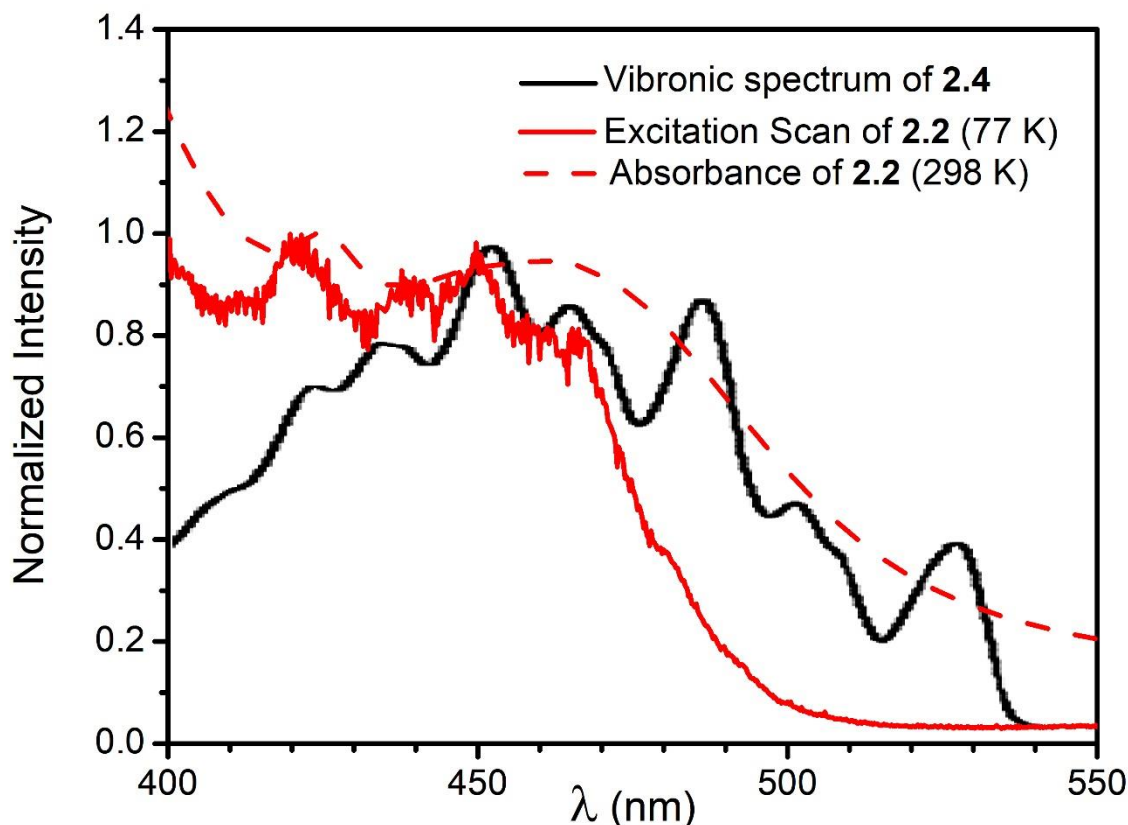


Figure 2.6. The vibronic spectrum of **2.4** (black), visible absorbance spectra of **2.2** in CH_3CN at 298 K (dashed red), and excitation spectra of the $^2\text{E} \rightarrow ^4\text{A}_2$ emission ($\lambda_{\text{em}} = 691 \text{ nm}$) for **2.2** (solid red) in 1:4 methanol:ethanol at 77 K. The excitation spectra of **2.2** resolves the shoulder features in the 298 K absorbance spectra, providing more accurate assignment of the vibronic $^4(^3\text{IL})$ excited state.

Additionally, the d^{10} species $[\text{Zn}(\text{bpy})_2(\text{OTf})_2]$ was investigated in an attempt to understand the effects of chelation. The diamagnetic metal center does not exhibit any ligand field excited states, thus any emission must be ligand-based. $[\text{Zn}(\text{bpy})_2(\text{OTf})_2]$ was prepared *in-situ* in a 1:4 methanol:ethanol solution with $[\text{Zn}(\text{OTf})_2]$ and 3 equivalents of bpy followed by dilution to the desired concentration. Admittedly, I attempted to prepare the tris-analogue $[\text{Zn}(\text{bpy})_3]\text{OTf}_2$ only

to latter learn that the triflate coordinate to the metal center based on crystallographic data.³¹ Thus, there is little difference between the emissions of free ligand and the zinc analogue, possibly due to free ligand in solution. However, similar emission spectra are observed with other metals such as Be²⁺, Al³⁺, and Rh³⁺.³² In these systems, the vibronic peaks appear at the same energy but the oscillator strength of the transitions are varied by coordination to the metal ions. Preparation of the tris species with an appropriate anion, such as SO₄⁻ would rectify my error.³³

2.4.8 Minimizing Geometric Distortion of Excited State: ⁴(³IL) vs ⁴T₂

Computational data suggest that the ⁴(³IL) excited state exhibits minimized distortion in relation to the metal center. First, the free bpy ligand was computationally investigated in the cis-conformation. The neutral ligand in its ¹A state exhibits a C-C bond length of 1.493 Å, consistent with a neutral bpy ligand (Figure 2.7). Once excited to a triplet state, the bridge contracts to 1.388 Å, which is a difference of 0.105 Å. Additionally, adjacent bonds lengthen ~0.05 Å as seen in Figure 2.7. Upon chelation to Cr(III) in compound **2.4**, the neutral ligand exhibits similar bond lengths. The Cr-N_{bpy} distance is calculated as 2.021 Å, which is close to the observed bond length in **2.2**. When excited to the ⁴(³IL) state, the bpy bridge C-C distance contracts as the adjacent bonds elongate, similar to the free ligand. However, the Cr-N_{bpy} bond length does not significantly change. This is remarkable as the geometric distortion is localized on the ligand with little effect on the metal center.

The minimized geometric distortion has often been attributed to short-lived excited states in a number of molecules.^{34–37} Large geometric distortions often lead to “vibrationally hot” excited states which undergo internal conversions to the ground state rather than emit a photon. This is particularly important in first-row transition metal ions, such as Fe(II), where nonradiative decay pathways compete with possible emission from lower lying ligand field excited states. As will be

demonstrated in Chapter 5, geometric distortion may change the relative energies of these ligand field excited states, which leads to new non-radiative decay pathways.

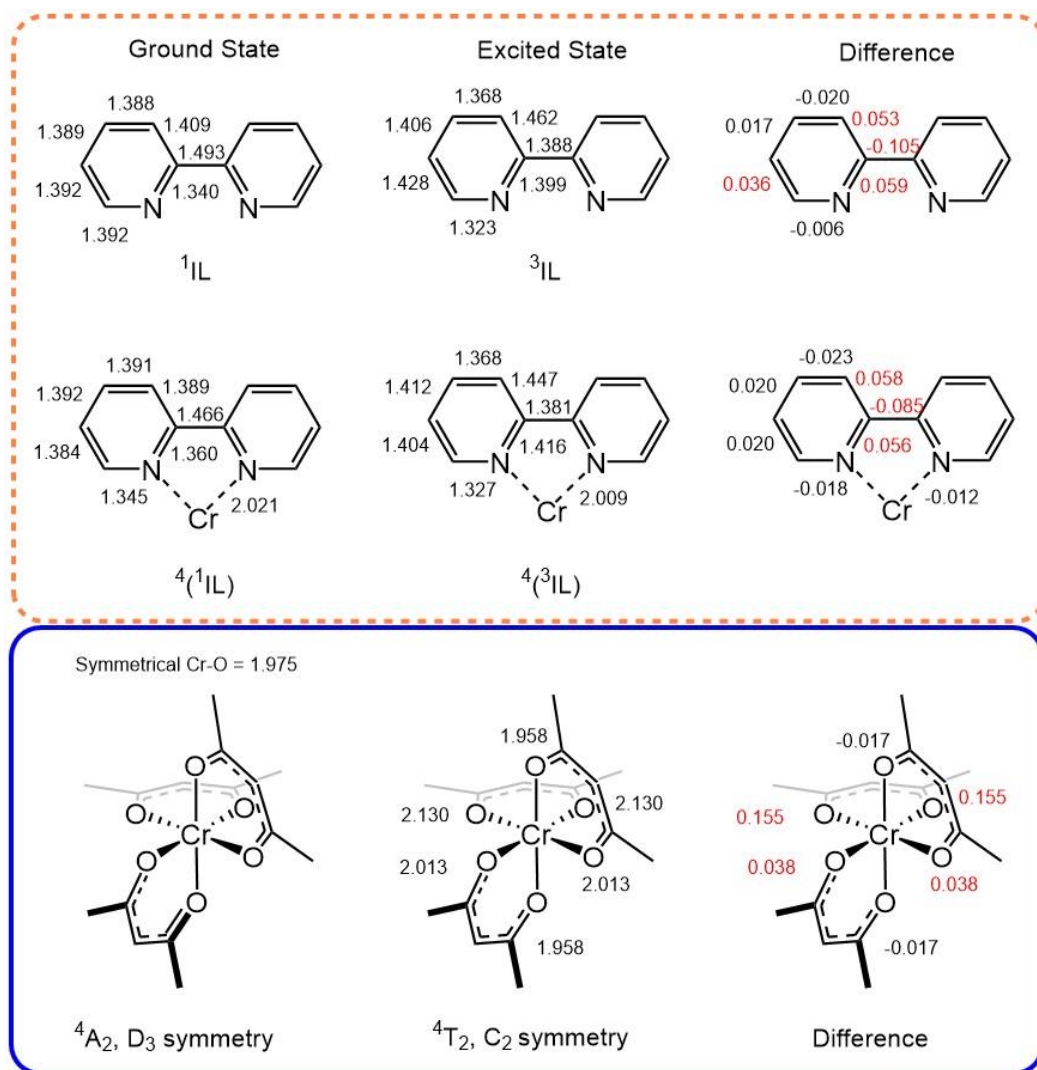


Figure 2.7 Computationally-determined bond length changes for bpy (top row), **2.4** (middle), and [Cr(acac)₃] (bottom). Bond lengths for the ground state(left), relevant excited state(middle), and difference (right) are shown. Differences in red represent absolute bond length changes larger than 0.03 Å.

The geometric distortion for the $^4(^3\text{IL})$ excited state of **2.4** is minimal compared to the $^4\text{T}_{2g}$ excited state of [Cr(acac)₃]. Previous calculations by Sato and colleagues for [Cr(acac)₃] model the $^4\text{A}_2$ ground state as D_3 -symmetric with Cr-O bonds equal to 1.975 Å;³⁸ this model is in good agreement with the crystallographic data. Upon excitation to the $^4\text{T}_2$ ligand field excited state, the molecule exhibits Jahn-Teller distortion as one acac ligand expands out. The Cr-O bond increases

by 0.155 Å, while the other acac ligands exhibit minor changes in the primary coordination sphere (Figure 2.7). This large distortion allows for access to more vibrational modes with nonradiative decay pathways to the ground state, shortening the excited state lifetime of the overall complex.

The importance of geometric distortion on relative energies of excited states is illustrated for **2.1-2.3** in Figure 2.8. In all complexes, the polypyridyl ligands contribute to the $^4(^3\text{IL})$ state; thus, this $^4(^3\text{IL})$ excited state is at approximately the same energy. In compound **2.1-2.2**, the $^4\text{A}_2 \rightarrow ^4\text{T}_2$ transition is not discernable by spectroscopic techniques; thus, these energies are based on the computed structures. For instance, the $^4\text{A}_2 \rightarrow ^2\text{E}$ transition for **2.1** is computed to be 764 nm, which is only $\sim 540\text{ cm}^{-1}$ lower than experimental. The $^4\text{A}_2 \rightarrow ^4\text{T}_2$ transition is computed to occur at 354 nm, an area obscured by ligand-based transitions in the absorbance spectrum. While we cannot observe this transition, the good agreement between experimental and calculations for the $^4\text{A}_2 \rightarrow ^2\text{E}$ transition suggests similar agreement. For **2.2**, the $^4\text{A}_2 \rightarrow ^4\text{T}_2$ is calculated to occur at $\sim 426\text{ nm}$, which is the sharp peak in the absorbance spectra. For **2.3**, the $^4\text{A}_2 \rightarrow ^4\text{T}_2$ transition is observed at 536 nm, consistent with previous reports.²³ This is slightly higher in energy than neutral $[\text{Cr}(\text{acac})_3]$ ($\lambda = 560\text{ nm}$), and shows an increased ligand field strength due to the bipyridine ligand. In regards to the $^4(^3\text{IL})$ transition, the $^4(^3\text{IL})$ excited state is the lower in energy than the $^4\text{T}_2$ state, and populates the (μs) ^2E excited state in **2.1** and **2.2**. The first coordination spheres of these excited states are all similar, and thus have minimal changes in the reaction coordinate diagrams. These excited states exhibit good Franck-Condon overlap and are nested, factors which help preserve the long-lived excited state. Complex **2.3** exhibits a short-lived (ps) ^2E excited state. Excitation into the lower energy $^4\text{T}_2$ distorts the first coordination sphere, generating non-radiative decay pathways. If the $^4(^3\text{IL})$ were excited at higher energy, it would still lead to population of the $^4\text{T}_2$ which is lower in energy and shares the same multiplicity as the populated excited state.

As an aside, these energies do not follow obvious ligand field energies. For example, compound **2.2** has a lower ligand field compared to **2.3**; however, the Racah parameter for **2.2** is larger than **2.3** (Figure A1.10). Additionally, the Racah parameter does not correlate to the charge of the molecule (Table A1.1). These results are based on a cursory survey of complexes where the $^4A_2 \rightarrow ^4T_2$ transition was correctly distinguished from the $^4A_2 \rightarrow ^4(^3IL)$ transition.

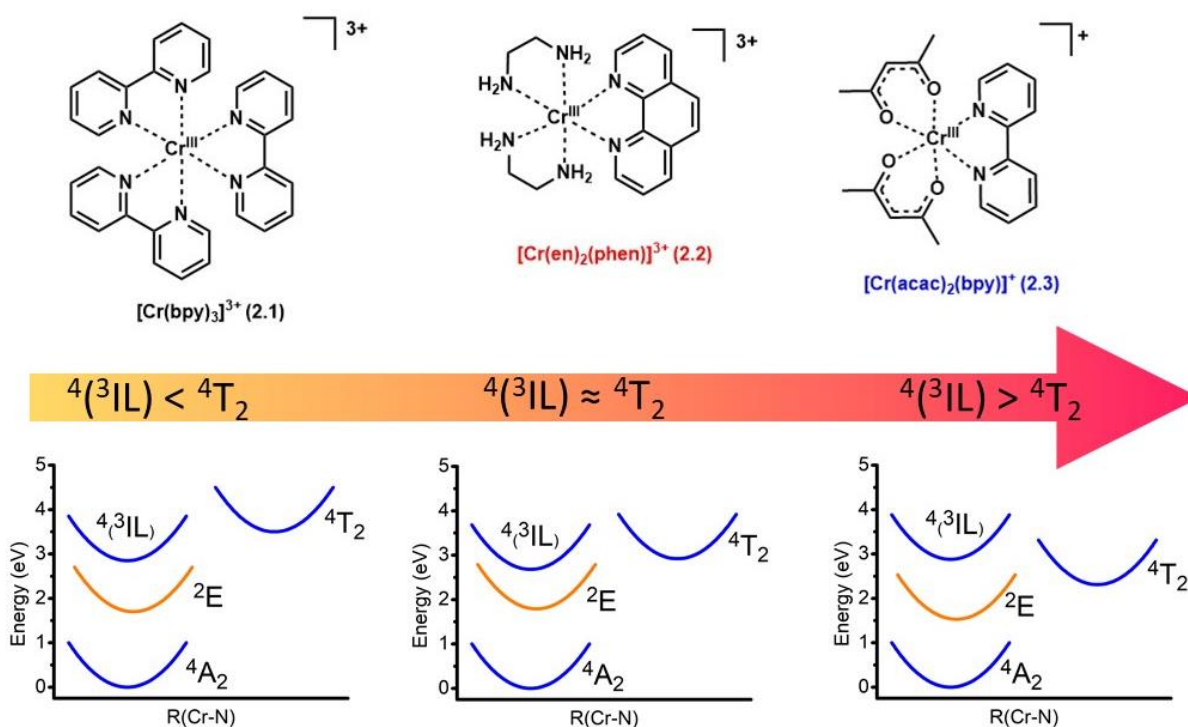


Figure 2.8 Potential energy wells for relevant excited states for **2.1-2.3**. The energy of the $^4(^3IL)$ excited state is compared to the energy of the 4T_2 via inequalities.

2.4.9 Lingering Questions

Admittedly, there are several unaddressed questions within this system: 1) the exchange coupling and mechanism of coupling between the triplet ligand and Cr(III) ion 2) the variable molar absorptivity for the $^4(^3IL)$ transition 3) the energy differences for the excited states in the

absorbance spectra. I will briefly propose a few possible explanations and possible experiments which may address these questions. At the moment of writing, these claims are speculative.

1) Exchange coupling and mechanism between the triplet ligand and Cr(III) ion

As previously stated, earlier models try to approximate the coupling between the ligand and Cr(III) ion based on inaccurate ground state properties.^{10,28} These models rely on approximations of angular orbital coefficients, spin-orbit coupling, and assignment of charge-transfer excited states. In order to quantify exchange coupling between the metal and ligand, one might expect magnetometry to provide a suitable solution. For the complex $[\text{Cr}(\text{tBu}_2\text{bpy})_3]^{2+}$, the ligand radical strongly couples to the metal center as $J \sim -730 \text{ cm}^{-1}$.³⁹ While we could suggest that this value as a starting point to understand the variable $^4(^3\text{IL})$ oscillator strength, this approximation relies on ground state energies for excited state dynamics. Ultimately, future work would require the use of new methods in magnetic circular dichroism⁴⁰ or ultrafast spectroscopy²⁷ towards obtaining accurate exchange coupling values.

Based on the assignment of a $^4(^3\text{IL})$ excited state in the Heisenberg spin-ladder, there is possibility of “energy transfer” between the Cr(III) ion and bipyridine ligand. There are two mechanisms for energy transfer, Förster and Dexter energy transfer. Förster energy transfer is a two-electron exchange process arising through the overlap of frontier orbitals. Dexter energy transfer is defined as “a through space [process] resulting from the interaction of an oscillating dipolar electric field ...[which] induces an electric oscillation of [another species].”⁴¹ For both mechanisms, a photon would initially excite a metal based $^4\text{A}_{2g} \rightarrow ^4\text{T}_{2g}$ transition. In a Förster energy transfer mechanism, the excited electron would transfer to the lowest unoccupied molecular orbital (LUMO) of the ligand as the ligand simultaneously transfers an electron to the t_{2g} metal

orbitals on Cr(III). In a Dexter energy transfer mechanism, the dipole generated from the $^4T_{2g}$ excited state would induce a dipole on the ligand and lead to a triplet ligand. Ultimately, both mechanisms would be two-step processes rather than a single step/photon process. Experimentally, the mechanism might be addressed with femtosecond-resolved spectroscopic techniques. The 2E excited state is populated within a picosecond, requiring a faster laser pulse to see spectroscopic signs of a metal based excited and/or triplet ligand.¹³ If a two-step process existed, population of the $^4T_{2g}$ excitation would precede a 3bpy response. Two kinetic traces would support either mechanism, but not immediately address which is operative. Additionally, this would suggest this behavior is common in other paramagnetic metal complexes whereas this has currently been suggested in Cr(III) complexes.²⁸ Again, these systems are unique and our interpretations should not be limited to conventional knowledge which has already failed to describe the photophysics thus far *vide infra*.

2) The variable molar absorptivity for the $^4(^3IL)$ transition

There is quite an increase in visible absorbance in these Cr(III) complexes going from one bipyridine to three bipyridine ligands. Synthetically, it is difficult to prepare $[Cr(bpy)_2(en)]^{3+}$ as discussed earlier. However, an electronically similar $[Cr(bpy)_2(NH_3)_2]^{3+}$ species has been reported by Josephsen and Schäffer.⁴² In that report, the molar absorbance increases as a function of number of bipyridine ligands. If someone prepares similar Cr(III) containing species, they will need to be wary of ligand exchange during experiments. This complication may create difficulty during various experiments such as electrochemistry.

Nevertheless, the exchange between the metal and ligand in the $^4(^3IL)$ excited state may be calculated. These methods involve monitoring the degree of excited state mixing via magnetic

circular dichromism (MCD), a technique developed by Kirk and Schultz.^{40,43} MCD resolves the vibronic peaks in the $^4A_{2g} \rightarrow ^4(^3IL)$ transition, and the coupling may be calculated by monitoring changes as a function of magnetic field.

3) The energy differences for the excited states in the absorbance spectra

The vibronic progression in the absorbance of Cr(III) polypyridyl complexes is variable with no distinguishable trends. One method to possibly manipulate the energy spacing is by preparing bipyridine ligands with different isotopes of hydrogen, carbon, and nitrogen. Changes to the mass of these atoms would change the stretching frequencies of the ligand, possibly changing the vibronic progression in the absorbance. Admittedly, the changes upon deuteration are minimal and probably indistinguishable in an absorbance spectra. The changes would be $\sim 40\text{ cm}^{-1}$, but a typical spectrophotometer is set to every nm which is $\sim 50\text{ cm}^{-1}$ at the low energy range. Since the expected change is smaller than the spectrometer resolution, changes may not be visible. Calculations by Ohno and colleagues suggest the shift may be upwards of 69 cm^{-1} , but again these are small changes.

2.4.10 Implications for Energy Transfer

One implication of understanding the exchange mechanism between the Cr(III) center and ligand is to utilize this towards catalyst design with energy transfer. In the energy transfer mechanism between $[\text{Cr}(\text{Ph}_2\text{phen})_3]^{3+}$ and chalcone, association between the ligand chalcone facilitate the energy transfer between the ligand and substrate.¹¹ In those results, the $^6(^3IL)$ excited state was partly responsible for energy transfer leading to regioselectivity. Attempts to prepare similar π - π stacking species such as $[\text{Cr}(\text{en})_2(\text{Ph}_2\text{phen})]^{3+}$ failed when following procedures analogous to compound **2.2**. However, internal results within are group have shown association

for small Cr(III) aromatics with chalcone based on NMR shifts.¹² These molecules display a short-lived 2E excited state, as no emission is observed at room temperature. Thus, new Cr(III) photocatalysts may not require a long-lived 2E excited state in new organic transformations.

Another implication of this $^4(^3IL)$ excited state is the order of the Heisenberg spin ladder. Is the $^2(^3IL)$ or $^6(^3IL)$ excited state the lowest in the series? Here, our results suggests the $^2(^3IL)$ excited state is lowest based on calculated energies. Others may argue that the ferromagnetically coupled $^6(^3IL)$ excited state must be lowest based on the “Pauli principle forbidding unpaired electrons... [from approaching] each other and occupying the same region of space.”^{27,41} This is beyond the scope of this dissertation, as I focus on identifying these Heisenberg spin ladder excited states. What point is discussion of the relative energies of the Heisenberg spin ladder if the community rejects its existence?

Once again, these future directions are predicated on the current understanding of the $^4(^3IL)$ excited state. Your results may vary.

2.5 Conclusion

In this work, we assign and characterize an unusual $^4(^3IL)$ excited state found in Cr(III) polypyridyl complexes. The $^4(^3IL)$ state represents a mixed excited state between a paramagnetic ligand and metal center, which is ultimately spin-allowed relative to the 4A_2 ground state. This $^4(^3IL)$ excited state is present in every polypyridyl species here, with variable resolution of peaks. NTOs reveal the transitions to be predominantly ligand based, as a singlet to triplet excitation. CASSCF calculations further support this electronic transition at the lowest energy quartet excited state. Additionally, other ligand based excited states are observed but as doublets and sextets. These states create a Heisenberg spin ladder, a combination of eigenstates based on coupling between a triplet ligand and quartet metal center. We can use cryogenic temperatures to resolve

the peaks in the absorbance spectra, via excitation scans in fluorometry. Finally, the minimal distortion in these excited states limit the degrees of freedom for non-radiative decay.

Along these lines, we encourage others to re-evaluate their assignment of these “shoulders” in Cr(III) polypyridyl complexes as metal-based transitions. Further studies are needed to address several points such as:

- 1) the exchange coupling and mechanism of exchange coupling between the triplet ligand and Cr(III) ion
- 2) the variable molar absorptivity for the $^4(^3\text{IL})$ transition
- 3) the energy differences for the excited states in the absorbance spectra

These results will, hopefully, lead to efficient photocatalysts with these excited states. Ideally, other systems may be designed to show a triplet ligand coupled to a paramagnetic metal center. These long-lived excited states would then be capable of undergoing photo-induced electron transfer.

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Chapter 3: Long-lived Antiferromagnetically-Coupled MLCT States in V(II) Bipyridine and Phenanthroline Complexes

3.1 Introduction

Long-lived excited states with Cr(III) motivates investigations into similar d^3 systems. In Chapter 2, we showed that Cr(III) polypyridyl complexes exhibit long-lived excited states due to involvement of a $^4(^3\text{IL})$ excited state. The minimal distortion within the first coordination sphere limits non-radiative decay pathways, leading to microsecond-long excited state lifetimes. This unique excited state manifold begs the question: do isoelectronic analogues display similar excited state manifolds?

Recently, a d^3 Mn(IV) complex has been reported with a ^2E excited state lifetime of 1.5 μs .¹ In this system, the $^4\text{LMCT}$ is excited which eventually leads to the ^2E excited state. These preliminary results suggests more investigations into the system, especially the progression of excited states in this d^3 system.

Unfortunately, isoelectronic V(II) complexes have not shown a long-lived excited state. Maverick and Shah reported a short-lived excited state for V(II) polypyridyl complexes (0.5-2.0 ns), due to a low energy $^4\text{MLCT}$ relative to the ^2E .² This reasoning was made based on two assumption: 1) $^4(^3\text{IL})$ transitions in $[\text{Cr}(\text{bpy})_3]^{3+}$ were interpreted as ligand field (d-d) transitions and 2) ligand field strength is the same between Cr(III) and V(II). The first assumption was addressed in Chapter 2, and the second assumption will be discussed more thoroughly in Chapter 4. Here, we will use V(II) starting materials to prepare V(II) polypyridyl complexes in a straightforward synthesis. We will present the results of new spectroscopic techniques (ultrafast transient absorbance and spectroelectrochemistry) and discuss how these results differ than those

presented by Shah and Maverick. We will reassign the long-lived excited state in V(II) polypyridyl complexes and propose a new description to the excited state manifold. Ultimately, we find the excited state progression to be $^4A_{2g} \rightarrow ^4MLCT \rightarrow ^2MLCT \rightarrow ^2MC(^2E_g \text{ mixed with other metal-centered states})$. Finally, we attempted to use a V(II) polypyridyl complex in a photocatalytic reaction.

3.2 Division of Labor

This work was done by Romeo Portillo, Michael Nguyen, Sam Shepard, and Ryan Dill. Romeo Portillo prepared and characterized **3.1-3.2**, including synthesis, electronic absorbance, electrochemistry, and spectroelectrochemistry experiments. Michael Nguyen began research into the literature of V(II) polypyridyl complexes, performed initial studies on **3.1B**, and collected the crystal structure. Sam Shepard collected initial transient absorption spectra of **3.1B**. Ryan Dill performed transient absorption experiments on **3.1-3.2**, kinetic fits of excited state lifetimes for **3.1-3.2**, and preliminary stability studies of **3.1B**.

3.3 Experimental Section

3.3.1 Preparation of Compounds

The starting materials $[V(CH_3CN)_3Cl_3]$,³ $[V(CH_3CN)_6](OTf)_2$,⁴ and $[V(CH_3CN)_6](BPh_4)_2$ ^{5,6} were prepared according to a previous literature report. Tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) was recrystallized twice from ethanol before use. Ferrocene was sublimed before use.

$[V(bpy)_3](OTf)_2$ (3.1A)

A solution of $[V(CH_3CN)_6](OTf)_2$ (218 mg, 0.366 mmol) and 2,2'-bipyridine (179 mg, 1.15 mmol) in 5 mL of acetonitrile was stirred for 6 hours. The blue solution was dried *in vacuo* and washed with diethyl ether (3×3 mL). Diffusion of diethyl ether into a concentrated solution of the crude product in acetonitrile afforded 166 mg (0.203 mmol, 55% yield) of dark blue plate

crystals. UV-vis (CH₃CN) $\lambda_{\text{max}}/\text{nm}$ ($\epsilon_{\text{M}}/\text{M}^{-1} \text{ cm}^{-1}$): 246 (28800), 298 (36100), 404 (3460), 643 (5890). IR (KBr pellet): $\nu_{\text{C=N}}$ 1600 cm^{-1} . ESI-MS(+) (CH₃CN): $m/z = 257.67$ (**3.1A** – 2OTf[−])²⁺. Anal. Calcd For C₃₂H₂₄F₆N₆O₆S₂V (**3.1A**): C, 47.01; H, 2.96; N, 10.47. Found: C, 46.73; H, 2.98; N, 10.42.

[V(bpy)₃](BPh₄)₂ (**3.1B**)

A solution of [V(CH₃CN)₆](BPh₄)₂ (95 mg, 0.102 mmol) and 2,2'-bipyridine (49 mg, 0.314 mmol) in 5 mL of acetonitrile was stirred for 6 hours. The blue solution was dried *in vacuo* and washed with diethyl ether (3 × 3 mL). Diffusion of diethyl ether into a concentrated solution of the crude product in acetonitrile yielded 51 mg (0.044 mmol, 43% yield) of blue plate crystals. UV-vis (CH₂Cl₂) $\lambda_{\text{max}}/\text{nm}$ ($\epsilon_{\text{M}}/\text{M}^{-1} \text{ cm}^{-1}$): 299 (36600), 404 (3780), 643 (5820). IR (KBr pellet): $\nu_{\text{C=N}}$ 1599 cm^{-1} . ESI-MS(+) (CH₃CN): $m/z = 257.67$ (**1** – 2BPh₄[−]). Anal. Calcd For C₇₈H₆₄B₂N₆V (**1**): C, 80.90; H, 5.56; N, 7.26. Found: C, 80.51; H, 5.86; N, 7.47.

[V(phen)₃](OTf)₂ (**3.2**)

A solution of [V(CH₃CN)₆](OTf)₂ (268 mg, 0.450 mmol) and 1,10-phenanthroline (251 mg, 1.39 mmol) in 5 mL of acetonitrile was stirred for 6 hours. The solution was dried *in vacuo* and washed with diethyl ether (2 × 3 mL). Crystals were grown from a diethyl ether diffusion into a concentrated solution in acetonitrile to yield 306 mg (0.344 mmol, 76% yield) of dark purple plate crystals. UV-vis (CH₃CN) $\lambda_{\text{max}}/\text{nm}$ ($\epsilon_{\text{M}}/\text{M}^{-1} \text{ cm}^{-1}$): 226 (88700), 266 (66200), 349 (3300), 640 (7940). IR (KBr pellet): $\nu_{\text{C=N}}$ 1646 cm^{-1} . ESI-MS(+) (CH₃CN): $m/z = 295.67$ (**2** – 2OTf[−]). Anal. Calcd For C₃₈H₂₄F₆N₆O₆S₂V: C, 51.30; H, 2.72; N, 9.45. Found: C, 51.15; H, 2.83; N, 9.29.

3.3.2 Electrochemical Studies

Voltammograms were recorded with a CH Instruments 1230A potentiostat in a glovebox under a dinitrogen atmosphere. All experiments used 0.1 M tetrabutylammonium

hexafluorophosphate (Bu_4NPF_6) solution in acetonitrile with a 0.25 mm carbon working electrode, Ag wire quasi-reference electrode, and a Pt wire auxiliary electrode. Reported potentials are referenced to the ferrocenium/ferrocene ($[(\text{C}_5\text{H}_5)_2\text{Fe}]^+ / [(\text{C}_5\text{H}_5)_2\text{Fe}]$, $\text{Fc}^{+/0}$) redox couple and were determined by adding ferrocene as an internal standard at the conclusion of each electrochemical experiment.

3.3.3 Photophysical Studies

Absorption spectra were obtained with a Hewlett-Packard 8453 spectrophotometer in a quartz cuvette with a 1 cm path length; all experiments were performed at room temperature. Steady-state emission measurements were performed on a Horiba Jobin-Yvon FluoroLog-3 spectrophotometer in an air-free quartz cuvette. All samples were set to have an absorbance between 0.10 and 0.20 AU at the excitation wavelength. Slit widths were set to 4 mm for the excitation wavelength and 1 mm for the emission wavelengths.

3.3.4 Transient Absorption Spectroscopy

Samples were prepared in 2 mm quartz cuvettes with Kontes HI-VAC® vacuum-valves in a dinitrogen-filled glovebox in solvent that was sparged with argon. All samples were set to have an absorbance between 0.1 and 0.4 AU at the excitation wavelength. Steady state absorption spectra were taken immediately after preparation of the sample and after experiments to check the degree of decomposition. In the case of **3.1B** in acetonitrile, experiments were terminated if the absorbance dropped below 10% of the initial level.

Ultrafast visible TA spectroscopy was performed on a homebuilt spectrometer which has been described elsewhere. Briefly, the output of a Ti:sapphire multi-pass amplifier (~800nm, ~1mJ/pulse at 1 kHz repetition rate, Quantronix Odin) is split into two paths, one of which is directed into a homebuilt noncollinear optical parametric amplifier (NOPA), the design of which

has been described elsewhere[refs]. The NOPA output (center wavelength 560-650 nm, FWHM ~30nm) is compressed to ~35-50 fs with a prism-pair compressor. Pulse durations are measured using SHG autocorrelation. Pump pulses are mechanically chopped at 500Hz and then focused just before the sample so that the pump spot size in the sample (measured using knife-edge method, ~120-200 μ m) is >~3 times the size of the probe spot size (~30-60 μ m). The excitation pulse polarization is set to magic angle (54.7°) relative to the probe pulse to minimize the contribution to dynamics that results from rotational diffusion.

Near infrared transient absorption spectroscopy was performed using a Helios IR (Ultrafast Systems) under care of the Dukovic laboratory (CU-Boulder).

The visible probe supercontinuum is generated by focusing a small fraction (~1 μ J/pulse) of the split 800nm beam into a 3mm CaF₂ window (Thorlabs) which is continuously actuated in an elliptical pattern by a pair of linear actuators (Zaber T-series) to prevent damage to the window. This beam is then focused into the sample with a 250mm focal length concave mirror, after which the residual 800nm light is removed by a short-pass filter. The resulting signal beam is coupled into a spectrograph (Chromex 250 IS) and detected at 1 kHz with a CCD (charge coupled device, Andor Newton DU920P-OE) in full vertical binning mode. The experiment is controlled by software written in-house in LabVIEW (National Instruments). Data processing procedure has been described elsewhere.⁷

Decay fitting was performed using a Matlab global fitting script written in-house to simultaneously fit data from all wavelengths to the same exponential decay models.

3.3.5 Crystallographic Measurements

Key structural data for compounds **3.1B-3.2** are provided in Table 3.1. Crystals were coated in Paratone oil, supported on Cryoloops, and mounted on either a Bruker Kppa Apex 2 with a CCD diffractometer (**3.1B**) or a Bruker D8 Quest ECO with a Photon 50 CMOS diffractometer (**3.2**) under a stream of cold nitrogen. All data collections were performed with Mo K α radiation and a graphite monochromator. Initial lattice parameters were determined from a minimum of 310 reflections harvested from 24 frames; these parameters were later refined against all data. Data sets were collected targeting full coverage and fourfold redundancy. Data were integrated and corrected for absorption effects with the APEX 3 software packages. Structures were solved by direct methods and refined with the SHELXTL software package. Displacement parameters for all non-hydrogen atoms were refined anisotropically. All hydrogens were assigned to ideal positions and refined using a riding model with an isotropic thermal parameter 1.2 times that of the attached carbon atom.

Table 3.1 Crystallographic Data for **3.1B** and **3.2**

	3.1B	3.2
Formula	VB ₂ C ₇₈ H ₆₄ N ₆	VC ₄₄ H ₃₈ F ₆ O ₇ S ₂
FW	1157.97	991.87
Color, habit	Dark blue plate	Dark purple plate
T, K	120(2)	110(2)
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>Cc</i>
Z	4	4
<i>a</i> , Å	12.3773(7)	21.5063
<i>b</i> , Å	14.6602(9)	14.6080

c , Å	34.086(2)	17.3663
A , deg	90	90
β , deg	98.180(2)	126.351
γ , deg	90	90
V , Å ³	6122.09	4394.16
d_{calc} , g/cm ³	1.256	1.345
GOF	1.099	1.086
R_1 (wR_2), %	3.73 (14.76)	5.49 (15.25)

3.3.6 Other Physical Methods

Infrared spectra were measured with either a Nicolet 380 FT-IR or Bruker TENSOR II spectrometer. Mass spectrometry measurements were performed in either the positive ion or negative ion mode on a Thermo-Finnigan LTQ mass spectrometer equipped with an analytical electrospray ion source using a 2.5 V spray voltage and 175 °C capillary temperature. Spectroelectrochemical measurements were performed with a Pine Research Instrumentation gold honeycomb electrode connected to a Gamry Reference 600 potentiostat and an Ocean Optics DH-2000-BAL spectrophotometer. Spectra were collected within 2 minutes of equilibration.

3.4 Results

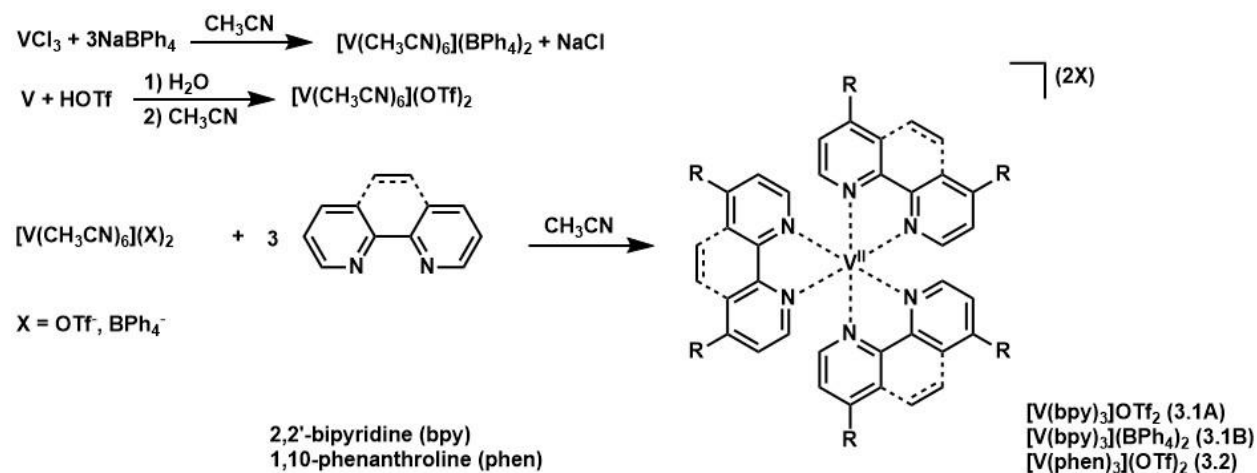
3.4.1 Synthesis of V(II) polypyridyl complexes

Due to the limited number of V(II) starting materials available to us, we prepared $[\text{V}(\text{CH}_3\text{CN})_6]^{2+}$ as the OTf^- and BPh_4^- salts. Spectroscopically, both yield identical complexes in solution. We note that our syntheses for these compounds have been performed in both argon and nitrogen atmospheres. While there are concerns for nitrogen activation with low-valent vanadium

species, we observed no differences in the syntheses of these samples in either environment.^{8–10} The synthetic routes vary as V(0) is oxidized by triflic acid and V(III) is reduced by an unknown mechanism (Scheme 3.1 Preparation of 3.1-3.2. Reactions for starting material are not-balanced. See text for details.). The reaction with HOTf is based on a previous report by Bechlars using a 1:1 mole ratio of triflic acid to V(0). In the reaction with NaBPh₄, acetonitrile has been proposed as a reductant, although we could not identify any by-products beyond NaCl and an acidic supernatant.^{5,11} A complete discussion of the different synthetic routes appears in the Discussion section of this chapter. We found that the BPh₄[−] salts were unstable after a few hours in solution, which is exemplified by poor elemental analyses and difficulty to be isolated as single crystals.

The tris(bidentate) compounds **3.1B** are prepared using a slight excess of ligand in the presence of [V(CH₃CN)₆](BPh₄)₂. Compounds **3.1A** and **2** are purified via crystallization.

Scheme 3.1 Preparation of 3.1-3.2. Reactions for starting material are not-balanced. See text for details.



3.4.2 Structural Analyses via Single-Crystal X-Ray Diffraction

Here, we present the first crystal structures of homoleptic V(II) polypyridyl complexes. The crystal structure of **3.1B** was collected and the relevant data are summarized in Table 1. The

presence of two BPh_4^- anions suggests an overall dicationic species. The bipyridine ligands exhibit typical $\text{C}_{\text{pyridine}}\text{-C}_{\text{pyridine}}$ bond lengths for a neutral ligand, averaging 1.479(5) Å, via comparison to $[\text{Cr}(\text{bpy})_3](\text{PF}_6)_3$.¹² This average $\text{C}_{\text{pyridine}}\text{-C}_{\text{pyridine}}$ bond length is also longer than the reported 1.438(6) Å distance reported in $[\text{V}(\text{Me}_2\text{bpy})_3]$, which exhibits two radical anionic ligands around the V(II) metal center.¹³ Additionally, the V-N bond lengths average 2.136(5) Å which suggests a dicationic species. When compared to the bis-bidentate analogue, $[\text{V}(\text{bpy})_2\text{SO}_4]^0$, the V-N bond lengths, 2.113(5), are in qualitative agreement.¹⁴

Compound **3.2** crystallizes with a disordered solvent molecule. The $[\text{V}(\text{phen})_3]^{2+}$ cation is split along the crystallographic C_2 axis, generating no crystallographically unique phenanthroline ligands. This structure resembles a previously reported $[\text{V}(\text{Me}_2\text{phen})_3]^0$, albeit with longer $\text{C}_{\text{pyridine}}\text{-C}_{\text{pyridine}}$ and V-N bond lengths.¹⁵ Should a ligand radical exist in our system, this crystallographic symmetry constraint limits the assignment between a localized and delocalized radical. Notwithstanding, all ligand interatomic distances are found within the expected values for a neutral phenanthroline.

The disordered diisopropyl ether solvent in **3.2** caused complications during the refinement of the crystal structure. The solvent is partially split along the C_2 axis, with the oxygen atom residing closest to that axis. As a result, the unit cell displays two oxygen atoms for the diisopropyl ether solvent and adds to error in the crystal structure. Here, we solved the structure in the Cc to better model the diisopropyl ether. Additionally, *SQUEEZE* performed on the Cc crystallographic model decreases the overall error, with no significant residual electron density elsewhere. PLATON found 498 electrons in the unit cell, equating to 124.5 electrons in the asymmetric void. Diisopropyl ether contains 58 electrons, thus ~4 diisopropyl ethers are expected in the unit cell ie.

1 solvent per asymmetric unit. The void of 588 Å³ with 588/30 atoms that can fill the void or ~20 atoms. This is approximately 1 diisopropyl ether which further supports this claim.

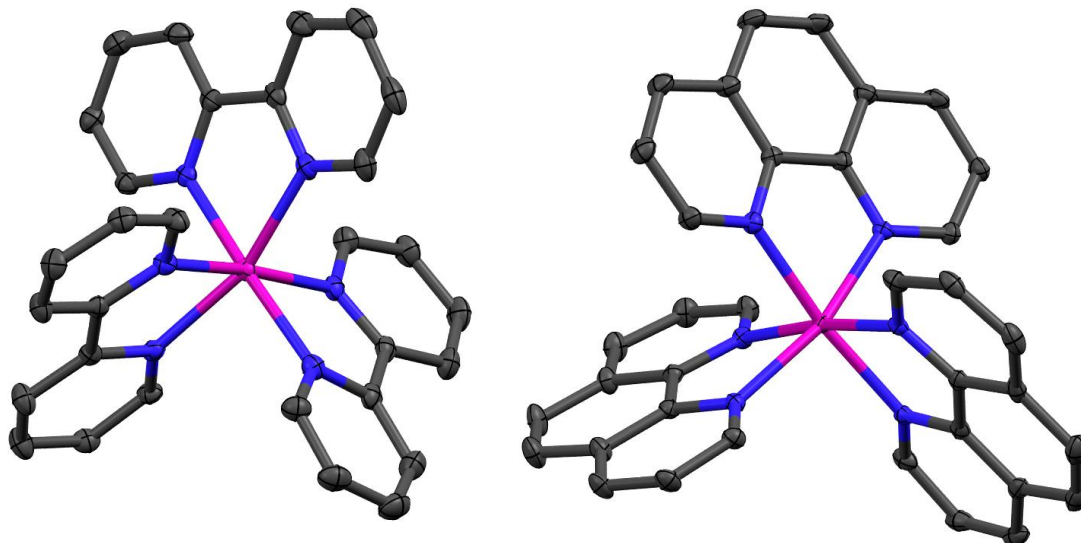


Figure 3.1 Crystal structure of **3.1B** and **3.2**. Hydrogens, anions, and co-crystallized solvent are omitted for clarity. Ellipsoids are set to 40%.

3.4.3 Electronic Absorbance

Electronic absorbance spectra of **3.1-3.2** show significant transitions in the visible region (Figure 3.2). The metal-to-ligand charge transfer (MLCT) bands are assigned at lower energies ($\lambda > 550$ nm) due to the relatively high ($1000 \text{ M}^{-1} \text{ cm}^{-1}$) extinction coefficients, shifts in λ_{max} from the substituent groups, and qualitative agreement with electrochemical data. First, the large extinction coefficient is consistent with a Laporte-allowed, spin-allowed transition for an electron in the metal t_{2g} orbital to a ligand π^* orbital. Second, the difference between the $E_{1/2}(3+/2+)$ and $E_{1/2}(2+/1+)$ couples is similar in energy to the proposed transition. This difference in electrochemical potential suggests metal-to-ligand charge transfer and is consistent with similar M(II) polypyridyl complexes. The bands at higher wavelength ($\lambda < 450$ nm) are likely charge transfer, although it is not possible to assign it as either MLCT or LMCT.

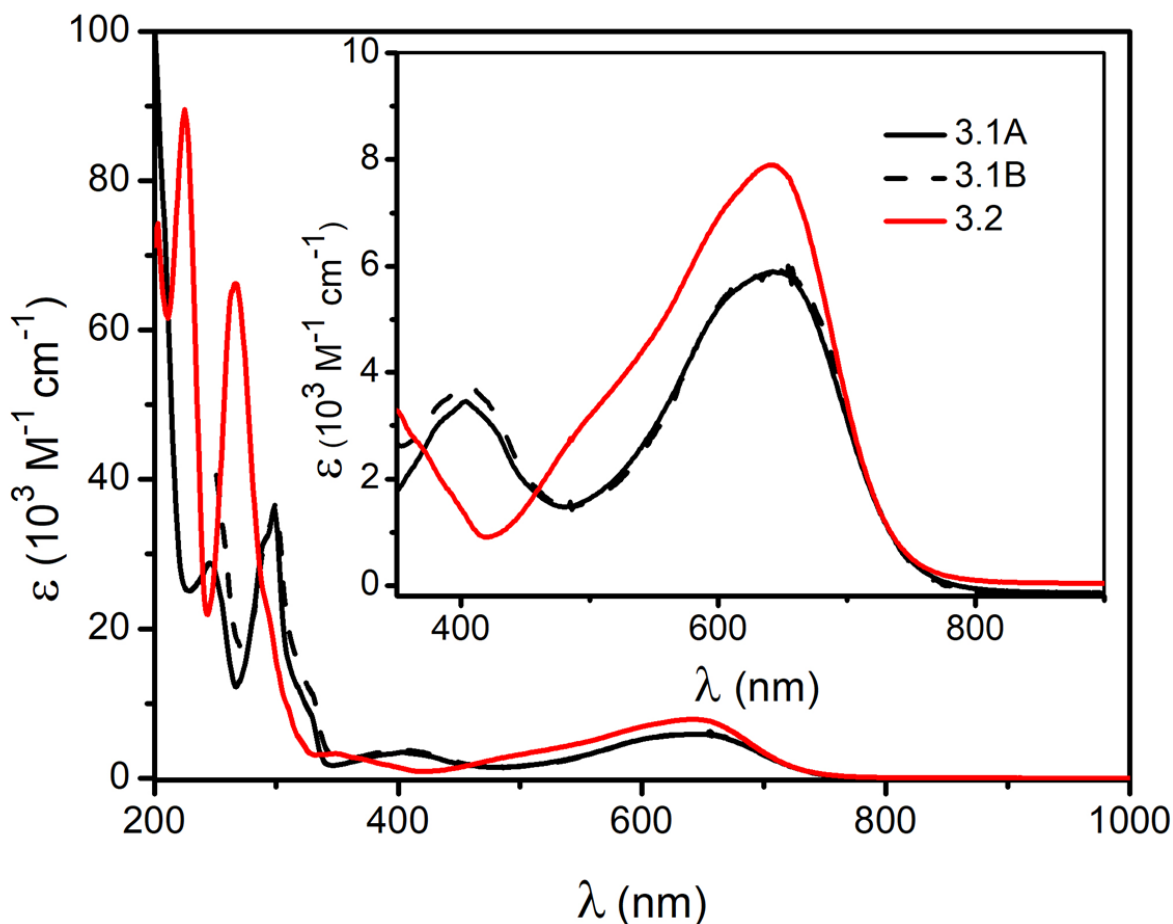


Figure 3.2 Electronic absorption spectra of **3.1A** and **3.2** in CH₃CN. The spectrum of **3.1B** was measured in CH₂Cl₂.

Spectroscopically, there is no significant difference between **3.1A** in CH₃CN and **3.1B** in CH₂Cl₂ (Table 3.2). These similarities suggest that both yield the same species in solution, [V(bpy)₃]²⁺ and counter anions. The increased absorbance at $\lambda \sim 250$ nm in **3.1B** is a result of absorbance from the BPh₄⁻ ion and the solvent CH₂Cl₂.¹⁶ Unfortunately, compound **3.1B** is susceptible to decomposition in CH₃CN. Our collaborators observed $\sim 50\%$ decomposition in solution in the dark over 6 hours (Figure A2.1). In lab verification confirmed decomposition, although the changes were $\sim 10\%$ overnight (Figure A2.1 and Figure A2.2). This likely occurs via dissociation of the bipyridine ligand(s), due to the lability of V(II) ions in solution.¹⁷ Additionally,

there is no isosbestic point or detectable intermediate observed via UV-Vis at $\sim 200 \mu\text{M}$.¹⁸ Regardless, these results and other *vide infra* pushed us to investigate **3.1A** rather than **3.1B**.

Table 3.2. Metal-to-ligand charge transfer absorbance

3.1A	3.1B	3.2
643 nm ($5890 \text{ M}^{-1} \text{ cm}^{-1}$)	643 nm ($5820 \text{ M}^{-1} \text{ cm}^{-1}$)	640 nm ($7980 \text{ M}^{-1} \text{ cm}^{-1}$)

3.4.4 Electrochemistry of **3.1-3.2**

Cyclic voltammograms for **3.1-3.2** show different reversibility based on the ligand scaffold (Figure 3.3 and Table 3.3). In **3.1A**, all observed redox events are reversible at scan rates of 100 mV/s in a 0.1 M Bu_4NPF_6 CH_3CN solution. The open circuit potential lies between one oxidation and three reduction events. The first two reductions are in close proximity, separated by 120 mV, typical of 2,2'-bipyridine reduction.¹⁹ The oxidation at 0.08 V vs Fc^+/Fc^0 is assigned to the 3+/2+ couple.

The cyclic voltammogram of **3.1B** resembles **3.1A**, albeit with some complications. At potentials more anodic than +0.5 V versus Fc^+/Fc^0 , the tetraphenylborate anion is oxidized, producing a cationic borane and biphenyl via two-electron oxidation.^{20,21} This redox process suppresses the detection of the 3+/2+ couple for **3.1B** via cyclic voltammogram. Thus, square wave voltammetry was used to assign this redox event for **3.1B** in Table 1, which is in close agreement to **3.1A** (Figure A2.4).

The cyclic voltammogram of **3.2** exhibits quasi-reversible behavior in comparison to **3.1A**. The first two reductions are quasi-reversible, with increased current on the reduction scan. At 100 mV/s scan rates, the peak-to-peak separation for each event is less than 59 mV, which is less than the expected difference for a one-electron Nernstian process. This would suggest a two-electron process, based on the relation $\Delta E = 0.059 \text{ V}/n$, where n = the number of for the redox event. At

scan rates as high as 500 mV/s, the reversibility is increased as well as the peak to peak difference (Figure A2.5). Additionally, the change from phenanthroline to bipyridine should not significantly change the electrochemical behavior, as the ligand electronics are very similar. As a result, the peak-to-peak separations are omitted for the 2+/1+ and 1+/0 redox couples. Finally, the 3+/2+ couple is quasi-reversible with a preference towards oxidation.

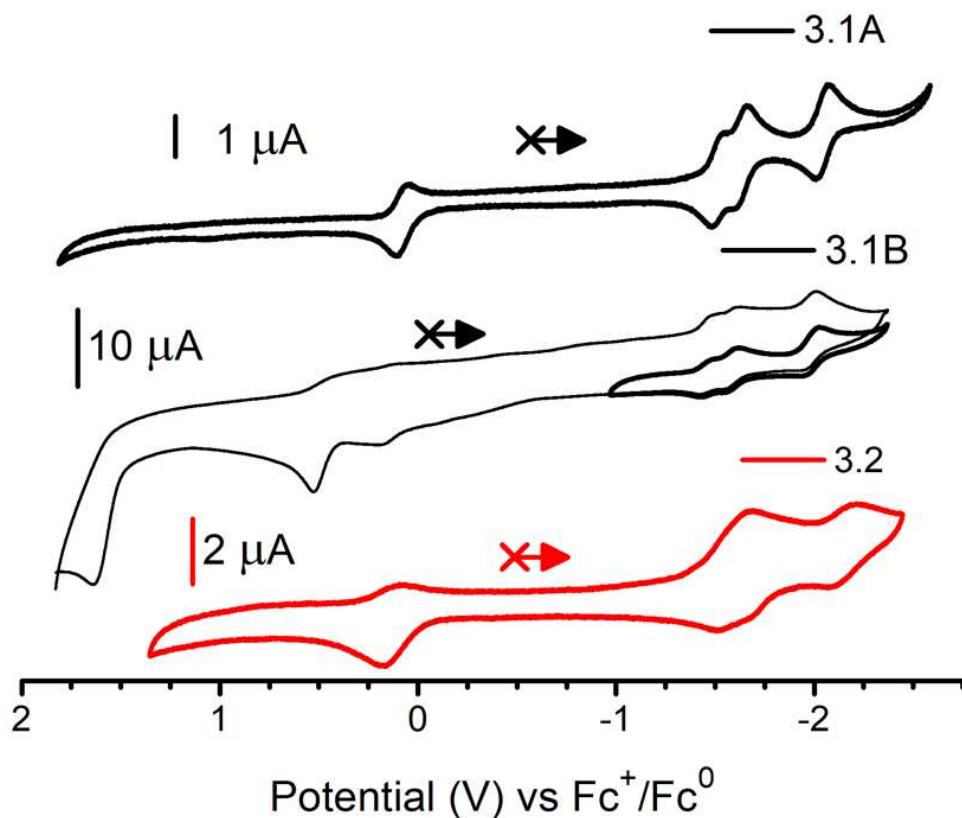


Figure 3.3 Cyclic voltammograms (0.100 V/s) of the cathodic reduction potentials for **3.1-3.2** in 0.1 M Bu_4NPF_6 in CH_3CN . Reduction potentials are tabulated in Table 1. Arrows indicate scan direction and the open circuit potential before each experiment.

Table 3.3 Ground state reduction potentials for **3.1A** and **3.2**.

Redox Event ^a	$E_{1/2}$ 3+/2+	$E_{1/2}$ 2+/1+	$E_{1/2}$ 1+/0	$E_{1/2}$ 0/1-
[V(bpy) ₃] ²⁺ (3.1A)	0.08 (59)	-1.46 (60)	-1.58 (66)	-1.99 (72)
[V(phen) ₃] ²⁺ (3.2)	0.13 (83)	-1.53	1.68	-2.16 (90)

^aPotentials reported in V vs Fc^{+/0} (ΔE_p in mV). Experiments were performed in 0.1 M Bu₄NPF₆ in CH₃CN utilizing a carbon working electrode, platinum counter electrode, and a pseudo silver wire reference electrode which was referenced to Fc^{+/0} at a 100 mV/s scan rate.

3.4.5 Attempts to observe lowest energy excited state

Fluorescence spectra collected for **3.1A** and **3.2** show no observable emission at room temperature. Excitation of the charge transfer bands between 400 and 700 nm produced no peaks attributed a V(II) excited state between 650-850 nm at room temperature. Additional experiments utilizing a NIR detector (up to 1600 nm) did not show any peaks either. As a result, there are no experimental values for the excited state energies.

3.4.6 Ultrafast Spectroscopy

Sub-picosecond transient absorbance spectroscopy of **3.1A** and **3.2** have revealed two distinct excited states within 16 ps. Excitation of the ⁴A_{2g} → ⁴MLCT transition between 560-700 nm produced identical results within the resolution (0.3 ps) of these experiments. In compound **3.1A**, strong photoinduced absorption (PA) signals are observed from 350-520 nm and 800-1600 nm while ground state bleach (GSB) is observed from 520-700 nm (Figure 3.4). Breaks in the spectra represent the pump wavelength (~650 nm) and change to a NIR detector (~800 nm). Within 16 ps, this initial transient species evolves into a final transient species. The PA signal at ~450 nm is red shifted to ~530 nm and a new PA signal emerges at ~1200 nm. Eventually, the signal decays

within ~500 ps. Similar behavior is observed with compound **3.2**, although the intensity of the signal are much larger.

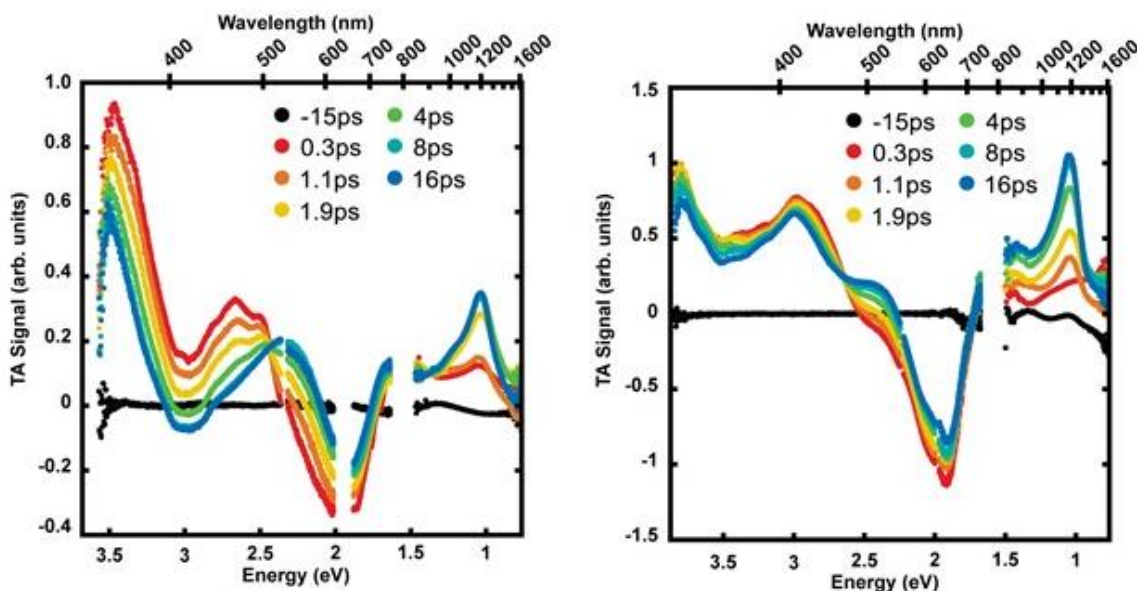


Figure 3.4 Transient absorption spectra of **3.1A** (left) and **3.2** (right) in CH_3CN .

Global fits of these transient absorbance spectra suggest 2 distinct excited states, although another process may exist in solution. There are two regions, 1-10 ps and 10-1000 ps based on the rates of the absorbance changes. Upon first inspection, we expected a 2 exponential decay fit for **3.1A** and **3.2**. Fits performed on the PA signal as a function of time are satisfactorily fit with two exponentials (Figure A2.7), but fits performed on the peak wavelength as a function of time require a third exponential (Figure A2.8). Subtle wavelength-dependent behavior is observed in the fit residual, requiring the addition of a 55 ps intermediate. This intermediate component is likely associated with changes such as vibrational relaxation and solvent reorganization. This intermediate exponential (55 ps) does not significantly change the initial component (3.3 ps) when included (2.6 ps) but does suggest the initial state is undergoing non-electronic changes in solution. The presented excited states lifetime in Table 3.4 represent a 3 exponent fit, with the intermediate

component being 55 ps (Figure A2.9 and Figure A2.10). Thus, we will use two exponentials to describe the excited states but refer to the presence of the intermediate component when describing solution dynamics.

Table 3.4. Excited state lifetimes of **3.1A** and **3.2** in CH₃CN

	τ_1 (ps)	τ_2 (ps)
3.1A	2.5	430
3.2	3.0	1710

3.4.7 Simulating a ²MLCT Excited State with Spectroelectrochemistry

In an attempt to assign an excited state in our transient absorption data, we employed spectroelectrochemical measurements to elucidate an excited MLCT state. Here, the metal is formally oxidized while the ligand is reduced; this has been previously described as “light induced intramolecular redox” process (Scheme 3.2).²²

Scheme 3.2. Top: Representation of MLCT as intramolecular redox. Bottom: Selected equations demonstrating calculated transient absorbance of ⁴MLCT excited state.



$$\Delta A_{\text{Oxidized}} = [A_{[\text{V}(\text{bpy})_3]^{3+}}] - [A_{[\text{V}(\text{bpy})_3]^{2+}}] \quad 3.1$$

$$\Delta A_{\text{Reduced}} = [A_{[\text{V}(\text{bpy})_3]^+}] - [A_{[\text{V}(\text{bpy})_3]^{2+}}] \quad 3.2$$

$$\Delta {}^2\text{MLCT} = \Delta A_{\text{Oxidized}} - \Delta A_{\text{Reduced}} \quad 3.3$$

Spectroelectrochemical measurements were attempted on **3.1B** but the close proximity between the 3+/2+ redox event and the oxidation of BPh₄⁻ complicates these results. Thus, **3.1A**

was used for spectroelectrochemical measurements. Oxidation of **3.1A** results in loss of the MLCT band in the visible region (Figure 3.5). Reduction of **3.1A** also shows loss of the MLCT band along with increased absorbance at other wavelengths. I observed formation of the doubly reduced $[V(bpy)_3]$ complex after an extended period of time, based on the increased absorbance at 597 nm.^{23,24} This complication arises from the close proximity of the 2+/1+ and 1+/0 redox events. Thus, I found that the absorbance spectra of the monocationic species must be taken quickly (within 2 min of equilibrating) before $[V(bpy)_3]^0$ is generated. Compound **3.2** exhibits very similar behavior to **3.1A**. (Figure 3.5)

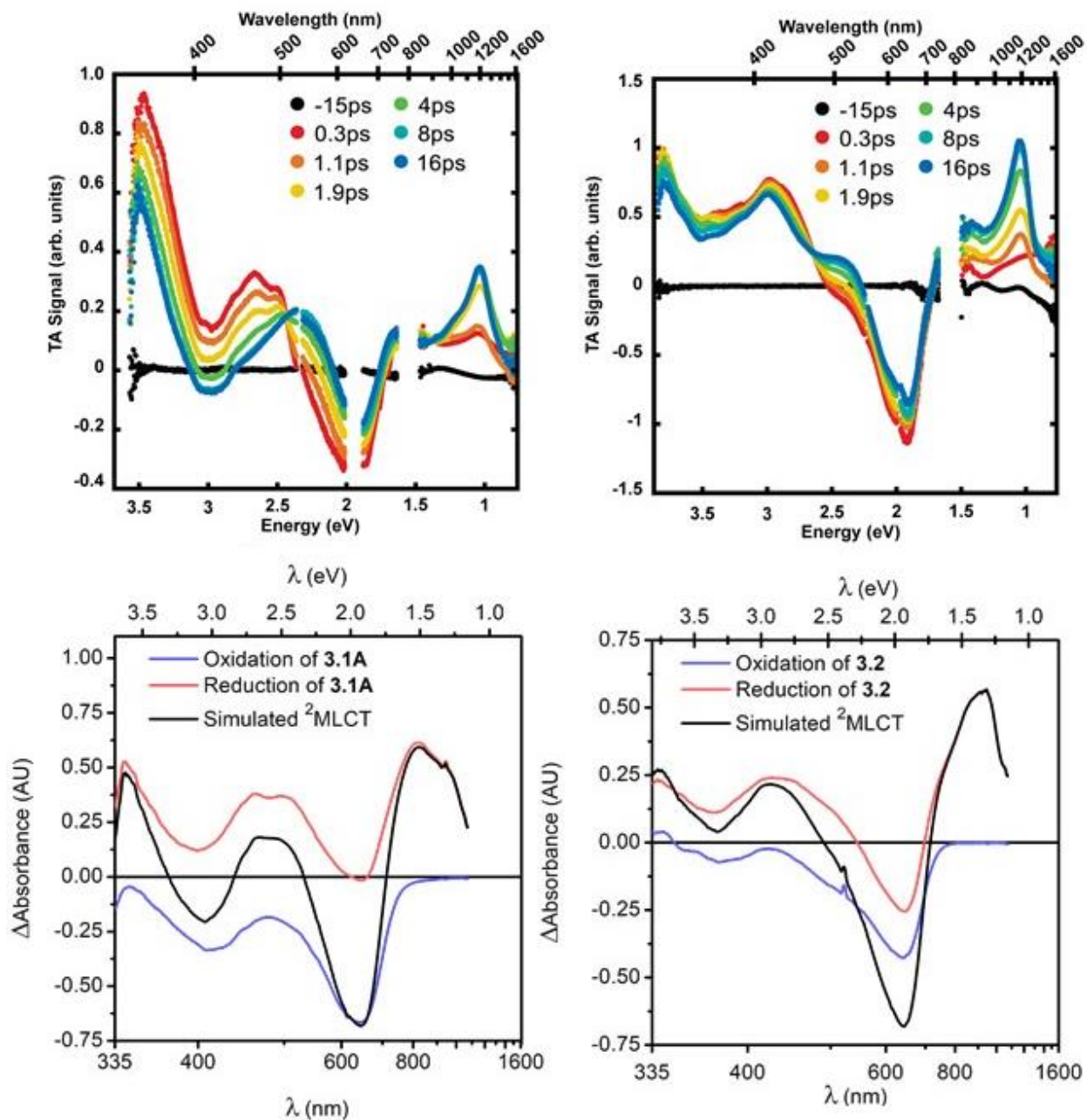


Figure 3.5. Comparison of transient absorption difference spectra and spectroelectrochemical difference spectra. Top left: Transient absorption difference spectra of **3.1A**. Top right: Transient absorption difference spectra of **3.2**. Bottom left: Spectroelectrochemical difference spectra of **3.1A**. Bottom right: Spectroelectrochemical difference spectra of **3.2**.

3.4.8 Attempted Photooxidation Reactions

Despite difficulty assigning the exact nature of the longest-lived excited state (τ_2), the lifetime of the state suggests feasibility in using it for reactions, so we performed preliminary studies into the photoreductive chemistry of **3.2**. The long-lived excited state persists for 1.7 ns, thus the radiative decay constant equals $5.8 \times 10^8 \text{ s}^{-1}$ (Equation 3.4).

$$k_r = \frac{1}{1.7 \times 10^{-9} \text{ s}} = 5.9 \times 10^8 \text{ s}^{-1} \quad 3.4$$

In order to participate in bimolecular quenching reactions, the diffusion constant (k_{diff}) must be less than the product of the radiative decay constant and concentration (Equation 3.5).

$$k_{diff} \ll k_r [A] \quad 3.5$$

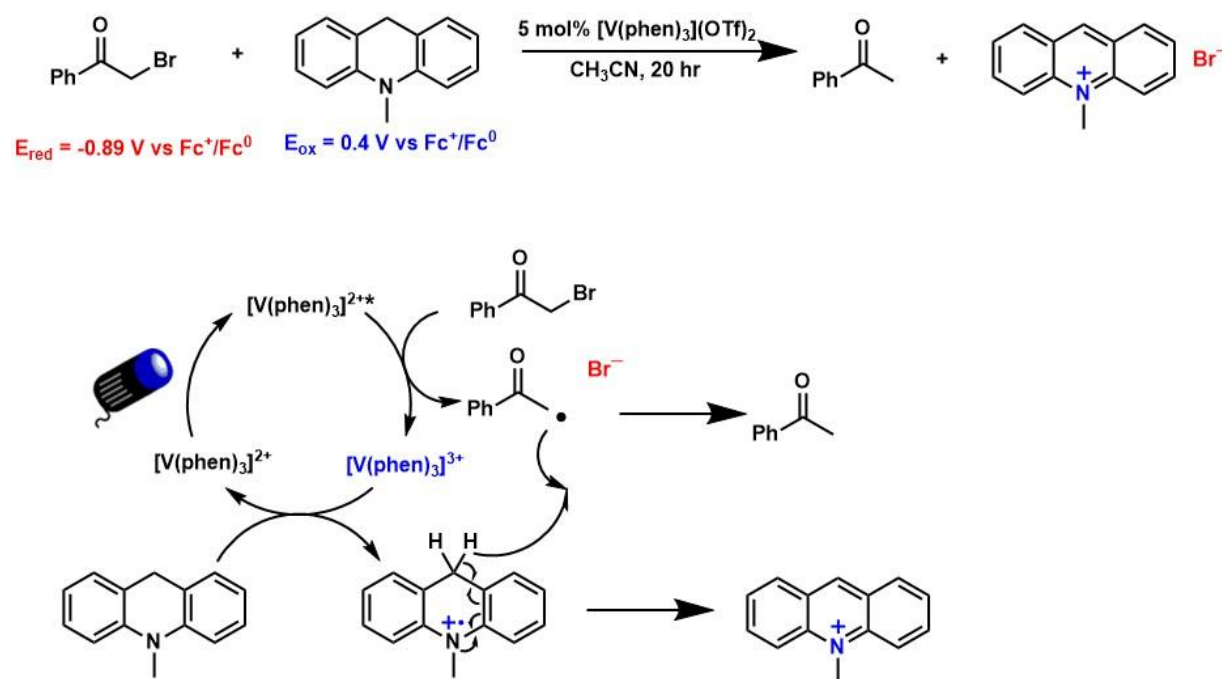
This equation assumes a diffusion limited energy/electron transfer process. Thus, we expect **3.2** may still exhibit photocatalytic properties at high concentration.

Due to the unknown energy of the longest-lived excited state, we attempted to back calculate the energy through reactivity studies. We began our investigations with two biaryl species, methyl viologen and 4,4'-dinitrobenzene (Scheme 3.3). These substrates have been previously studied with $[\text{Ru}(\text{bpy})_3]^{2+}$ in order to determine the limits for photoredox.²⁵ The reduction potential for methyl viologen is -0.85 V vs Fc^+/Fc^0 , and the reduction potential of 4,4'-dinitrobenzene is -1.40 V vs Fc^+/Fc^0 .²⁵ Additionally, both species are colorless in solution and deeply colored when reduced due to $\pi^*-\pi^*$ transitions. In the presence of **3.2** and light, methyl viologen is reduced (Figure A2.6); 4,4'-dinitrobenzene is not reduced in the presence of **3.2** and light. This suggests $E_{1/2}^{3/2*}$ ranges between -0.85 V to -1.40 V and the energy of the lowest excited state (E_{00}) to range between 0.98 eV (1265 nm) and 1.53 eV (810 nm), based on the Rehm-Weller formalism (Equation 3.6)

$$\text{Photoreduction: } E_{1/2}^{3/2*} = E_{1/2}^{3/2} - E_{00} \quad 3.6$$

Where $E_{1/2}^{3/2*}$ is the reduction potential of the excited state, and E_{00} is the energy of the lowest lying excited state.

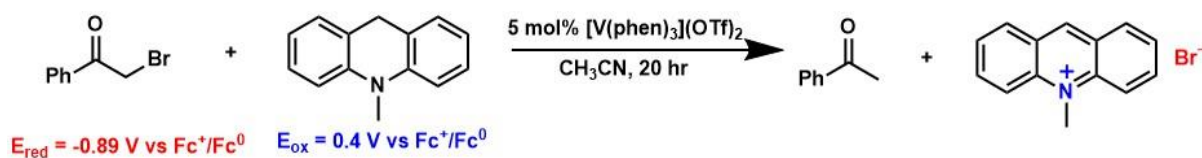
Scheme 3.3 Proposed mechanism for photoreduction of phenacyl bromide



Assuming a lower limit where $E_{1/2}^{3+/2+*} = -0.85 \text{ V}$, there are several potential substrates to be reduced by **3.2** in a photoexcited state.²⁶ Of those possible, electron-deficient sulfonyl chlorides, anhydrides, and aryl aldehydes/ketones are the most likely candidates for photoredox with **3.2**. The reported reduction potential of phenacyl bromide ($-0.89 \text{ V vs Fc}^+/\text{Fc}^0$) is very close to the lower limit estimated for **3.2** ($-0.85 \text{ V vs Fc}^+/\text{Fc}^0$), and this substrate has been previously reported with $[\text{Ru}(\text{bpy})_3]^{2+}$ in a photooxidative route to acetophenone, so we began photoreduction of phenacyl bromide as a preliminary substrate for photoredox studies. Here, we propose a

photoreductive route to acetophenone. Surprisingly, we found that the reaction is optimal with no **3.2** added (Scheme 3.4).

Scheme 3.4 Preliminary investigations into photoreduction of phenacyl bromide using **3.2**



Deviations from Standard Conditions	Results
Standard (0.1 M phenacyl bromide/N-methylacridan)	51%
2 mol N-methylacridan	48%
No catalyst	61%
No N-methylacridan	6.5%
100 mol% catalyst	6.3%
No light	4.2%
[Ru(bpy) ₃]Cl ₂	76%

3.5 Discussion

3.5.1 Syntheses of Compounds

In previous reports, V(II) polypyridyl complexes were prepared via reduction of isolated V(III) compounds.^{27,28} Recently, V(II) polypyridyl complexes were prepared by oxidizing a zero-valent $[\text{V}(\text{tBu}_2\text{bpy})_3]$ species.²³ We chose to use known V(II) starting materials, $[\text{V}(\text{CH}_3\text{CN})_6](\text{BPh}_4)_2$ and $[\text{V}(\text{CH}_3\text{CN})_6](\text{OTf})_2$, which are prepared reliably and are well-characterized. While the synthesis of these starting materials is reported, certain aspects of the characterization warrant explanation.

In the preparation of $[\text{V}(\text{CH}_3\text{CN})_6](\text{OTf})_2$, non-stoichiometric quantities are used in the reaction. This ultimately limits the theoretical yield to 50%, whereas the reported yield is 28%.²⁹ Synthetically, this yields pure product as unreacted V(0) is removed during the Soxhlet extraction step. Briefly, I pursued the synthesis of $[\text{V}(\text{THF})_4(\text{OTf})_2]$,³⁰ but preparation of the anhydrous $[\text{V}(\text{OTf})_3]$ salt was complicated by the presence of residual trifluoacetic acid, even after copious washes.³¹ Ultimately, I did not optimize these reactions.

In the literature, the starting material $[\text{V}(\text{CH}_3\text{CN})_6](\text{BPh}_4)_2$ is commonly prepared via the reduction of $[\text{V}(\text{CH}_3\text{CN})\text{Cl}_3]$ in the presence of CH_3CN and NaBPh_4 (Scheme 3.1). Despite numerous references, the reaction mechanism is unknown. Wilkinson and colleagues propose acetonitrile as the reductant, as previously proposed in their work involving ReCl_5 .¹¹ In their rhenium work, Wilkinson cites the reduction of VCl_5 to $[\text{V}(\text{CH}_3\text{CN})_3\text{Cl}_3]$ as precedence for acetonitrile-based reduction.³² Reduction of high-valent vanadium halides has been reported for V(IV) to V(III).³ If acetonitrile is a reductant, then an oxidized organic product is expected. Early transition metals are known to react with transition metal ions, such as tantalum(III), to reductively

couple acetonitrile.^{33,34} Wilkinson and colleagues did not note any oxidized organic product, but they did observe HCl gas evolution.

While understanding the mechanism of this reaction may lead to a better understanding of syntheses of low-valent vanadium complexes, it is beyond the scope of this project to focus on the mechanism for a sub-optimal starting material. The months (almost a year) spent investigating the mechanism of this $[V(CH_3CN)_6](BPh_4)_2$ starting material in order to prepare analytically pure **3.1B** were incredibly frustrating upon the realization that a month invested into preparing $[V(CH_3CN)_6](OTf)_2$ was far superior. Regardless, several previous students attempted to prepare electronically similar V(II) iminopyridines and would have appreciated any insight into low-valent vanadium chemistry. Thus, the following observations are included for any future student's stake.

The mechanism proposed by Wilkinson seems plausible but is not consistent with some preliminary investigations. In my experience preparing $[V(CH_3CN)_6](BPh_4)_2$, I noticed that the reaction mixture was acidic according to pH paper strips. This observation agrees with the generation of HCl observed by Wilkinson.⁵ Thus, special care is required when handling the supernatant. With this observation, it is not obvious why NaBPh₄ facilitates this reaction. In order to understand the role of NaBPh₄, I attempted to study the reaction via cyclic voltammetry. When $[V(CH_3CN)_3Cl_3]$ is dissolved in acetonitrile, a redox couple appears at -0.89 V vs Fc⁺/Fc⁰ in CH₃CN and only shifts slightly in the presence of NaBPh₄ (Figure A2.11). This redox event resembles the reported half reaction $V(III) + e^- \rightarrow V(II)$ (-0.266 V vs NHE in 0.5 M H₂SO₄; approximately -0.87 V vs Fc⁺/Fc⁰), although the results may be coincidental.

In regards to $[V(CH_3CN)_6](BPh_4)_2$, there are two synthetic routes reported by Wilkinson and Miller, respectively. Both employ the same $[V(CH_3CN)Cl_3]$ starting material, but have different levels of tolerances for its purity.³ In the Wilkinson synthesis of $[V(CH_3CN)_3Cl_3]$, VCl₃

is refluxed in acetonitrile “to completeness.”³ Both the starting material and product are slightly soluble in acetonitrile; thus, careful observation must be made that there is no purple VCl_3 remaining. Additionally, the precipitate formed is not always sufficiently pure for subsequent reactions. Based on these experiences, I recommend crystallizing $[\text{V}(\text{CH}_3\text{CN})_3\text{Cl}_3]$ via cooling a concentrated solution. In the Wilkinson route, crystalline $[\text{V}(\text{CH}_3\text{CN})_3\text{Cl}_3]$ gives reliable reproducibility whereas powders generate variable yields based on the crystallinity of the starting material. In the Miller route, the synthesis is tolerant of powder and crystalline material and yields high quality crystals. Unreacted $[\text{V}(\text{CH}_3\text{CN})_3\text{Cl}_3]$ and leftover byproducts are the primary contaminants, and the Miller route is ideal for purification of $[\text{V}(\text{CH}_3\text{CN})_6](\text{BPh}_4)_2$. However, the Miller route requires a minimum of 2 weeks to generate starting material, which was not efficient for synthesis.

Ultimately, the unresolved mechanism raises concern for how vanadium may interact under various solution conditions. The highly reactive nature of low-valent V(II) requires careful preparation and storage in order to preserve these molecules. As a result, I will do my best to address any discrepancies found between our system and those previously reported.

3.5.2 Previous Reports on the Photophysical Properties of V(II) polypyridyl complexes

Similar to our initial goals, others have proposed other d^3 systems as complements to Cr(III). Shah and Maverick investigated the photophysical properties of **3.1A** and **3.2**, reporting similar results to those presented here.²⁷ The reported lifetimes are within experimental error of those presented here, again shorter than 2.0 ns at room temperature. The authors proposed a $^4\text{MLCT}$ as the lowest lying excited state, which could vibrationally relax to the $^4\text{A}_2$ ground state.² This argument utilizes two assumptions, both which are further discussed in other chapters:

- 1) *The ligand field strengths of Cr(III) and V(II) are comparable:* Shah and Maverick present the ligand field strength of Cr(III) as a free ion, with an amine ligand set, and with a polypyridyl ligand set. Within this set, a modest increase in the ligand field strength is observed from the free-ion to $[\text{Cr}(\text{phen})_3]^{3+}$ (Table 5). Based on the comparison to the free-ion in a solid matrix, the ligand field strength is extrapolated for $[\text{V}(\text{phen})_3]^{2+}$ from this single value. This assumes the change in Δ_o and the Racah parameter B change in a similar fashion for the two d^3 ions, which is not the case when comparing Cr(III) to V(II). This assumption is discussed further in Chapter 4.
- 2) *The absorbance peaks ~450 nm for $[\text{Cr}(\text{bpy})_3]^{3+}$ are ligand field transitions.* The ligand field strength of $[\text{V}(\text{phen})_3]^{2+}$ is extrapolated from transitions observed in $[\text{Cr}(\text{phen})_3]^{3+}$. In the original assignments, the molar absorptivities are disregarded and the transitions are assigned as various ligand field transitions.³⁵ We believe these transitions are part of a Heisenberg spin ladder of intraligand triplet ($^3\pi$) coupled to the quartet metal center (4A_2), while the 4T_2 occurs at 375 nm and the ligand field strength is 43.3. This phenomenon is further discussed in Chapter 2.

Table 3.5 Ligand field transitions/strength of Cr(III) and V(II). Italicized values are extrapolated or incorrectly assigned, originally reported in reference 27 (see text for details).

	Cr(III), eV (nm)			V(II), eV (nm)		
	4T_2	2E	Δ_o/B	4T_2	2E	Δ_o/B
Ion Matrix	2.23 (556)	1.79 (693)	26.3	1.77 (699)	1.43 (870)	26.2
[M(en) ₃]	2.71 (457)	1.46 (668)	30.9	1.93 (641)		
[M(phen) ₃]	2.85 (435)	1.70 (730)	35.5	2.21 (562)	1.36 (909)	34.3

3.5.3 Development of Excited State Manifold: Assignment of a $^2\text{MLCT}$

Initially, **3.1** and **3.2** undergo a $^4\text{A}_{2g} \rightarrow ^4\text{MLCT}$ excitation near their peak absorbance. Due to the large molar absorptivity, emission from this state should be large and observed in a steady-state emission experiments or as stimulated emission in the transient absorbance spectra. The lack of any of these observations suggests the $^4\text{MLCT}$ excited state does not appear within the 0.3 ps resolution of the transient absorption spectra. Thus, we can propose it as the initial excited state but cannot assign any excited state lifetimes.

Our combined efforts in ultra-fast transient absorbance and spectroelectrochemistry suggest an early MLCT state, most likely a $^2\text{MLCT}$ excited state.

First, stimulated emission in the transient absorbance spectra would suggest the presence of a $^4\text{MLCT}$ excited state at the observed lifetime. Since the **3.1** and **3.2** are excited to their respective $^4\text{MLCT}$ excited state, we would expect $^4\text{MLCT}$ to be the initial excited state in each molecule. As such, stimulated emission should be observed given the large molar absorptivity of the $^4\text{A}_2 \rightarrow ^4\text{MLCT}$ would lead to efficient population of the $^4\text{MLCT}$ excited state. The lack of any observed stimulated emission suggests the $^4\text{MLCT}$ decays within the initial laser pulse (0.3 ps), leading to a different excited state. Thus, the lifetime of the $^4\text{MLCT}$ must be less than 0.3 ps. Second, spectroelectrochemistry does suggest the population of another MLCT excited state. In our spectroelectrochemical experiments, we reduce $[\text{V}(\text{bpy})_3]^{2+}$ and $[\text{V}(\text{phen})_3]^{2+}$ by a single electron to their monocationic form. The increased absorbance at NIR wavelengths suggest a ligand radical in the antibonding π^* orbital of one of the ligands. Additionally, the peak at ~380 nm is consistent with a bpy anion.^{19,36} Upon oxidation of **3.1-3.2**, the V(II) metal center is oxidized to V(III). As a result, the absorbance of the $^4\text{A}_2 \rightarrow ^4\text{MLCT}$ decreases in the visible region due to the higher ionization energy of V(III) compared to V(II). When the two spectra are referenced to the ground

state absorbance, a difference spectrum reveals the changes in absorbance at various wavelengths. In addition, the combination of the two spectra lead to a simulation of a MLCT as demonstrate in Scheme 3.2. These simulated spectra do qualitatively match the initial excited state observed in the transient absorbance spectra of **3.1** and **3.2**, suggesting a MLCT excited state within the first 3 ps. Third, a $^2\text{MLCT}$ excited state would address the population of a MLCT without any stimulated emission. When a single electron occupies the polypyridyl π^* orbital in **3.1-3.2**, this electron may either be ferromagnetic or antiferromagnetic in relation to the electrons in the t_{2g} orbitals of the metal center ion. While the best method to assign the coupling is through magnetic susceptibility of the monocationic species, these species quickly disproportionate into the dication and zero-valent species. Magnetic measurements require accurate knowledge of the identity of the investigated species; we have only been able to observe these species through *in-situ* experiments for short periods of time (less than 5 mins). In order to assign the spin-state, we are relying on the reported electronic structure of $[\text{V}(\text{tBu}_2\text{bpy})_3]$ by Bowman and colleagues.²³ This low-valent vanadium polypyridyl exhibits 2 ligand radicals based on a number of spectroscopic techniques.. Magnetic measurements in their system suggest a $S = 1/2$ system, which is possible with the two electrons on the ligand radical antiferromagnetically coupling to the three electrons on the V(II) metal center. This suggests a single ligand electron should also antiferromagnetically couple to the V(II) center generated during spectroelectrochemical experiments. Thus, our experiments would simulate a $^2\text{MLCT}$ rather than a $^4\text{MLCT}$. As previously addressed, the similarities between the first state in the transient absorbance spectra and the simulated $^2\text{MLCT}$ state lead us this assignment.

This new assignment of a $^2\text{MLCT}$ indirectly disagrees with the previously assigned $^4\text{MLCT}$ as the longest-lived excited state. First, we are exciting a ground state quartet ($^4\text{A}_2$) to a quartet

excited state. This quartet excited state is likely a $^4\text{MLCT}$, based on the large molar absorptivity and qualitative agreement of energy between spectroscopic and electrochemical data. Although we do not observe this state within the resolution of our transient absorption measurements (300 fs), first row transition metal ions are capable of quickly decaying from an initially-populated MLCT state. Second, this $^4\text{MLCT}$ would likely decay to another state of similar electronic structure. In the case of Fe(II) polypyridyl complexes, the initial $^1\text{MLCT}$ decays to a $^3\text{MLCT}$ within a few femtoseconds.³⁷ This precedence would support a $^4\text{MLCT}$ quickly decaying to a $^2\text{MLCT}$. In this case, the electron on the ligand would antiferromagnetically couple to the remaining two electrons on the metal t_{2g} orbitals. Thus, we would begin to describe the excited state manifold of V(II) polypyridyl complexes as a $^4\text{A}_2 \rightarrow ^4\text{MLCT} \rightarrow ^2\text{MLCT}$. Third, the transient absorbance spectra suggest another low-energy excited state which would not be the $^4\text{MLCT}$. Within 16 ps, a second excited state is populated as the absorbance spectra appears to red-shift. The isosbestic point found at ~500 nm for **3.1** and **3.2** suggests complete conversion to this state with no other intermediate state. Additionally, a PA signal at ~1200 nm strongly supports population of a new state as this spectroscopic signature is not observed in **3.1** and **3.2**. These observations are inconsistent with Shah and Maverick arguments that a $^4\text{MLCT}$ excited state being lower energy than a $^2\text{MLCT}$ or ^2MC excited state.² Once again, we argue that:

- 1) The first observed excited state is a $^2\text{MLCT}$ based on similarities between the transient absorbance spectra and spectroelectrochemical data (Figure 3.5)
- 2) The $^2\text{MLCT}$ is lower in energy than the $^4\text{MLCT}$ based on ground state magnetic susceptibility data in neutral V(II) polypyridyl complexes with ligand radicals^{15,23}

If we pursue an argument where $^4\text{MLCT}$ is lower energy than a doublet excited state consistent with these results, it becomes convoluted and suggests other observations. A long-lived $^4\text{MLCT}$

description would require the initial $^4\text{MLCT}$ to cross into a higher energy $^2\text{MLCT}$ state and back-intersystem cross to the same $^4\text{MLCT}$ state. This would require an additional source of energy, such as energy transfer through collision, require a longer-lived initial excited state (τ_1) to gain this additional energy via bimolecular collision, and show other spectroscopic signatures. Thus, we cannot describe the $^4\text{MLCT}$ as the lowest energy excited state.

Admittedly, we cannot prove the identity of the long-lived excited state (τ_2). Experimental methods require acquisition at the same-time scale of these excited states, which are picoseconds in these cases. Newer techniques such as picosecond and femtosecond XANES, edge spectroscopy, are all beyond our collaboration's current capabilities. Additionally, the air sensitivity of these samples further complicates these experiments. These resources are limited to a few experts in the world, who are still establishing the excited state manifold in better defined systems. These results will hopefully encourage other scientists to begin investigations in these newer systems, at which point new trends may be identified.

Here, we will temporarily propose a doublet metal center (^2MC) state as the long-lived excited state for **3.1** and **3.2** based on antiferromagnetism. We propose the $^4\text{MLCT}$ to be higher in energy than a $^2\text{MLCT}$ *vide supra*. No charge transfer is observed in the near infrared, thus we do not expect a $^4\text{LMCT}$ to be involved in our excited state manifold; by this extension, a $^2\text{LMCT}$ is likely not involved. If no metal-ligand excited states are further involved, we are left with the ligand and metal as the remaining possibilities. Ligand based excitation requires higher energy ($\lambda < 400\text{ nm}$) than the $^4\text{MLCT}$. Thus, a low energy metal-center excited state is likely involved in the excited state manifold and decay. These excited states have often been implicated in the short-lived excited states observed in first-row transition metal complexes. In the case of $[\text{Fe}(\text{bpy})_3]^{2+}$, the lowest excited state is a distorted ^5A state compared to the $^1\text{A}_1$ ground state. The quintet quickly

relaxes to the ground state, independent of the spin-multiplicity. Typically, one would expect the large difference in spin-multiplicity to extend the excited state lifetime as there are 2 spin-flips required to achieve the ground state. Ultimately, the excited state distortion allows for vibrational relaxation to the ground state. Thus, it is possible for a doublet to quickly decay to a quartet in our system. There are several low-energy doublet states for a d^3 metals, based on a Tanabe-Sugano diagram. While we cannot accurately point to a specific doublet state, we can propose a low energy 2MC state as the long-lived component (τ_2).

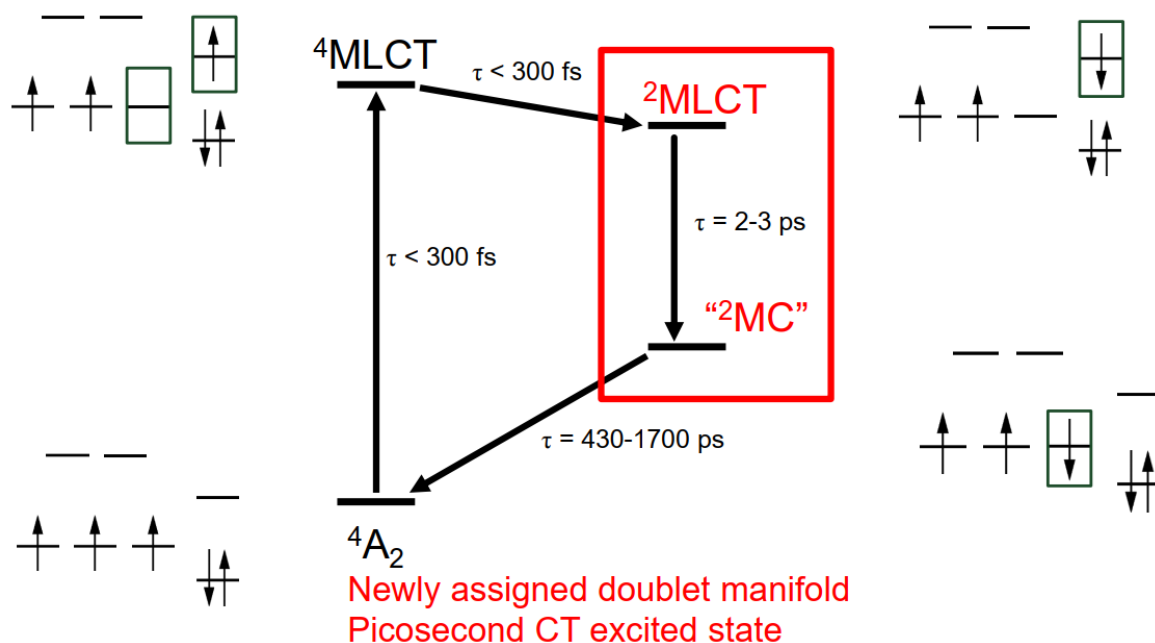


Figure 3.6 Proposed excited state manifold of V(II) polypyridyl complexes.

3.5.4 Estimating the energy for 2MC through photo-induced electron transfer

We can approximate the energy of the 2MC state through photo-induced electron transfer. Electron transfer is dependent of bimolecular quenching, which is diffusion limited based on the equation:

$$k_{diff} (M^{-1} s^{-1}) = \frac{8RT}{3000\eta} \quad 3.7$$

where R is the gas constant, η is the solvent viscosity, and T is temperature. The long-lived excited state of **3.2** ($\tau_2 = 1.7$ ns in CH₃CN) is borderline appropriate as an electron transfer reagent at high concentrations based on the equation **3.5**. Thus, the concentration of excited state **3.2** must be greater 0.03 M in acetonitrile for photoinduced-electron transfer to occur.

Next, we must choose appropriate substrates suitable for electron transfer with the excited state of **3.2**. Organic substrates are best due to strong spectroscopic signatures upon reduction. The $\pi^* \rightarrow \pi^*$ absorptions exhibit large molar absorptivities and occur in the visible/near-infrared spectrum. Both methyl viologen dichloride and 4,4'-dinitrobiphenyl are common organic substrates and have been used to estimate the excited state energy of [Ru(bpy)₃]²⁺.²⁵ After 50 minutes of irradiation, methyl viologen was reduced in the presence of **3.2**; there were no signs of reactivity with 4,4'-dinitrobiphenyl. Methyl viologen is easier to reduce ($E_{1/2} = -0.85$ V vs Fc⁺⁰) than 4,4'-dinitrobiphenyl ($E_{1/2} = -1.40$ V vs Fc⁺⁰), suggesting the excited state reduction potential of **3.2** to lie between -0.85 V and -1.40 V vs Fc⁺⁰ in CH₃CN. Thus, the energy of the unassigned ²MC state ranges between 1.1 V and 1.7 V vs Fc⁺⁰. Considering there has been no observed emission at room temperature in the visible spectrum, we can further reduce the range to 1.46 V (~850 nm) and 1.1 V (~1100 nm). This low-energy ²MC somewhat limits the utility of **3.2** as a photocatalysis, but the excited state can still reduce organic substrates.

3.5.5 Shortcomings of preliminary photoredox studies

The photoreduction of phenacyl bromide is theoretically possible with **3.2**. The reduction potential of phenacyl bromide ($E_{red} = -0.89$ V vs Fc⁺⁰ in CH₃CN) is very close to methyl viologen ($E_{1/2} = -0.85$ V vs Fc⁺⁰), thus we expect **3.2** ($E_{1/2}^{3+/2+*} < -0.97$ V vs Fc⁺⁰) to be competent to photoreduce phenacyl bromide. Phenacyl bromide may be reduced to acetophenone, allowing us

to gauge the efficiency of **3.2** to other photocatalysts. Tanaka and colleagues have reported a photooxidative route to acetophenone in the presence of N-methyl acridan, $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$, and light.³⁸ Photooxidation of N-methyl acridan serves as the initial electron-transfer step, followed by reduction of phenacyl bromide via $[\text{Ru}(\text{bpy})_3]^+$. In our system, we could theoretically perform photoreduction of phenacyl bromide as the initial step towards acetophenone.

Unfortunately, our proposed reaction towards acetophenone with **3.2** is non-ideal. Screening conditions for our reaction are summarized in Scheme 3.4. Under standard conditions, 51% conversion of phenacyl bromide to acetophenone is observed. The largest conversion (61%) is achieved in the absence of **3.2**. At 100% loading of **3.2**, a conversion of 6.3% is achieved. These results suggest **3.2** is detrimental to the proposed reaction compared to Tanaka's report. A control reaction of $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ achieved a conversion of 76%. The yield is bit lower than those reported by Tanaka (84%). In their reactions, monochromatic light ($\lambda = 452 \text{ nm}$) and higher concentrations of phenacyl bromide (0.3 M) were used. The use of monochromatic 452 nm light limits the absorption by the 10-methylacridinium ion ($\epsilon_{452} \sim 3000 \text{ M}^{-1} \text{ cm}^{-1}$ for 10-methylacridinium iodide)³⁹ compared to $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ ($\epsilon_{452} \sim 14000 \text{ M}^{-1} \text{ cm}^{-1}$).⁴⁰ Additionally, the increased concentration of phenacyl bromide increases the probability of bimolecular quenching with the excited $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ molecule. Overall, these differences likely increase the literature yield.

V(II) polypyridyl complexes appear to be poor candidates for photocatalysis due to their short-lived excited states and weak excited state reduction potentials. A short-lived excited state requires higher mole loadings to perform bimolecular quenching. In acetonitrile, the concentration of the excited state species must be greater than 0.03 M in order to perform photo-induced electron transfer as discussed *vide supra*. A high mole loading can interfere with subsequent steps of H-atom transfer and oxidation of the methyl acridanium intermediate. Additionally, high mole

loading will interfere with absorption in the reaction mixture. In a 1 cm diameter vial, a 0.05 M solution of **3.2** has an absorbance value of 400(!) AU at 640 nm. Thus, light will be absorbed at the surface of the vial but cannot penetrate the center of the reaction mixture. This results in a heterogeneous mixture where the substrate and excited state **3.2** occur only at the surface. In regards to the weak excited state reduction potential, it severely limits its utility as a photoreductant. Sulfonyl chlorides, anhydrides, and aryl aldehydes/ketones are susceptible to nucleophilic attacks under mild conditions. Additionally, phenacyl bromide decomposes in the presence of nucleophiles (atmospheric water). If the compound **3.2** could achieve some isomer selectivity, then its inefficiency may warrant some use in organic transformations. Finally, these electron-deficient substrates may be reduced with mild reagents. Elemental zinc serves as a stronger reductant (-1.4 V vs $\text{Fc}^{+/0}$), is earth abundant, and air stable. Compound **3.2** requires inert conditions, is not readily available in most labs, and likely decomposes after some time upon oxidation. Thus, there is no practical utility for **3.2** in photocatalysis.

An area of improvement not pursued here are kinetic studies to determine the excited state reduction potential of **3.2**. The energy of the putative ^2MC state was estimated to range between 1.1 V and 1.46 V vs $\text{Fc}^{+/0}$ through photoinduced electron transfer between aromatic substrates and detection limits of spectrometers. While we cannot experimentally observe this excited state within the spectroscopic window of our fluorometer ($\lambda < 850$ nm), we can extrapolate with electron transfer rate constants. A linear relationship between the natural logarithm of the rate constant and difference in redox potential would allow someone to back-calculate the excited state redox potential.²⁵ These studies are non-trivial and require studies of photooxidation and photoreduction of the **3.2** in order to solve for the unknown value of the excited state energy of **3.2**.

3.6 Conclusion

We reassign the excited state manifold in V(II) polypyridyl complexes, as summarized in Figure 5. Here, an initial $^4A_2 \rightarrow ^4MLCT$ excitation occurs followed by $^4MLCT \rightarrow ^2MLCT$ within 1 ps. The 2MLCT excited state was assigned based on similarities between spectroelectrochemical data simulating the 2MLCT excited state and the transient absorbance spectra. The 2MLCT quickly relaxes to a metal-centered excited state (2MC) and persists for 430 (**3.1A**) and 1700 (**3.2**) ps, respectively. The identity of the 2MC is complicated as we cannot experimentally simulate relevant doublet metal-centered excited states. Additionally, the 2MC energy was estimated based on the ability to reduce methyl viologen and not 4,4-dinitro-diphenyl. Future directions involve the assignment of the lowest energy excited state, along with exploring opportunities for **3.2** to perform photoreduction of substrates.

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Chapter 4: Differences in Photophysical Properties in Oh d3 Systems Based on Choice of Metal

4.1 Introduction

In previous chapters, we have reevaluated the photophysical properties of Cr(III) and V(II) polypyridyl systems. In Chapter 2, we showed that Cr(III) polypyridyl complexes exhibit long-lived excited states due to involvement of a $^4(^3\text{IL})$ excited state. The minimal distortion within the first coordination sphere limits non-radiative decay pathways, leading to microsecond-long excited state lifetimes. In Chapter 3, we observed a new picosecond $^2\text{MLCT}$ excited state and proposed an excited state manifold involving doublet states. This new assignment leads to population of a short-lived excited state ($\tau < 2$ ns) which is weakly photoreducing.

Despite Cr(III) and V(II) exhibiting the same d^3 electron configuration, these excited state lifetimes are quite different. Here, we will highlight the difference in the ground and excited state electronic structure. We will discuss these differences with the use of computational work in order to understand the differences in their excited state lifetimes. Ultimately, these computed results reveal that the differences in energies for relevant excited states allow for different decay pathways and why V(II) does not behave like Cr(III).

4.2 Division of Labor

Romeo Portillo has prepared and characterized all compounds presented in this work. Michael Nguyen prepared and collected preliminary data on compound **4.5**. Collette M. Nite calculated the optimized structures for all complexes including the V(II) and Cr(III) complexes with the 1,3-propanedionato(PDO) and bipyridine(bpy) ligands, calculated all TDDFT excited states and absorption spectra. Jacob M. Nite calculated the vibrational distortion plots, including the structure alignments, and performed all SORCI calculations.

4.3 Experimental

4.3.1 Preparation of Compounds

The starting materials $[\text{V}(\text{CH}_3\text{CN})_3\text{Cl}_3]$,¹ $[\text{V}(\text{CH}_3\text{CN})_6](\text{OTf})_2$,² and $[\text{V}(\text{CH}_3\text{CN})_6](\text{BPh}_4)_2$ ^{3,4} were prepared according to a previous literature report. Tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) was recrystallized twice from ethanol before use. Ferrocene was sublimed before use. Compounds **3.1A** and **3.2** from Chapter 3 are referenced throughout.

$[\text{Cr}(\text{bpy})_3](\text{BF}_4)_3$ (**4.1**)

This compound was prepared according to a previous literature report.⁵

$[\text{Cr}(\text{phen})_3](\text{BF}_4)_3$ (**4.2**)

This compound was prepared according to a previous literature report.⁵

$[\text{V}(\text{Me}_2\text{bpy})_3](\text{OTf})_2$ (**4.3**)

A solution of $[\text{V}(\text{CH}_3\text{CN})_6](\text{OTf})_2$ (41 mg, 0.069 mmol) and 4,4'-dimethyl-2,2'-bipyridine (38 mg, 0.206 mmol) in 5 mL of acetonitrile was stirred for 6 hours. The blue solution was dried *in vacuo* and washed with diethyl ether (3×3 mL). Diffusion of diethyl ether into a concentrated solution of the crude product in acetonitrile yielded 39 mg (0.043 mmol, 63% yield) of blue plate crystals. UV-vis (CH_2Cl_2) $\lambda_{\text{max}}/\text{nm}$ ($\epsilon_{\text{M}}/\text{M}^{-1} \text{ cm}^{-1}$): 249 (29000), 298 (37600), 424 (3860), 659 (6300). IR (KBr pellet): $\nu_{\text{C}=\text{N}}$ 1616 cm^{-1} . ESI-MS(+) (CH_3CN): $m/z = 301.83$ (**4.3** – 2OTf)²⁺. Anal. Calcd For $\text{C}_{38}\text{H}_{36}\text{F}_6\text{N}_6\text{O}_7\text{S}_2\text{V}$ (**1**): C, 50.61; H, 4.02; N, 9.32. Found: C, 50.33; H, 4.21; N, 9.55.

$[\text{V}(t\text{Bu}_2\text{bpy})_3](\text{OTf})_2$ (**4.4**)

A solution of $[\text{V}(\text{CH}_3\text{CN})_6](\text{BPh}_4)_2$ (95 mg, 0.102 mmol) and 4,4'-*tert*-2,2'-bipyridine (49 mg, 0.314 mmol) in 5 mL of acetonitrile was stirred for 6 hours. The blue solution was dried *in vacuo* and washed with diethyl ether (3×3 mL). Diffusion of diethyl ether into a concentrated solution

of the crude product in acetonitrile yielded 51 mg (0.044 mmol, 43% yield) of blue plate crystals. UV-vis (CH₃CN) $\lambda_{\text{max}}/\text{nm}$ ($\epsilon_{\text{M}}/\text{M}^{-1} \text{ cm}^{-1}$): 206 (119000), 296 (47500), 419 (5220), 652 (8240). IR (KBr pellet): $\nu_{\text{C=N}}$ 1612 cm⁻¹. ESI-MS(+) (CH₃CN): m/z = 856.50 (**1** – 2OTf)²⁺. Anal. Calcd For C₇₈H₆₄B₂N₆V (**1**): C, 58.27; H, 6.29; N, 7.28. Found: C, 57.95; H, 6.13; N, 7.18.

[V((CO₂Me)₂bpy)](OTf)₂ (4.5**)**

This compound was prepared in analogous method to compounds **4.3-4.4**. See “Difficulties with Electron-Deficient Polypyridyls” for details.

[V((CF₃)₂bpy)₃](OTf)₂ (4.6**)**

This compound was prepared in analogous method to compounds **4.3-4.4**. See “Difficulties with Electron-Deficient Polypyridyls” for details.

4.3.2 Electrochemical Studies

Voltammograms were recorded with a CH Instruments 1230A potentiostat under a dinitrogen atmosphere. All experiments used 0.1 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) solution in acetonitrile with a 0.25 mm carbon working electrode, Ag wire quasi-reference electrode, and a Pt wire auxiliary electrode. Reported potentials are referenced to the ferrocenium/ferrocene ([C₅H₅)₂Fe]⁺/[(C₅H₅)₂Fe], Fc^{+ / 0}) redox couple and were determined by adding ferrocene as an internal standard at the conclusion of each electrochemical experiment.

4.3.3 Photophysical Studies

Absorption spectra were obtained with a Hewlett-Packard 8453 spectrophotometer in a quartz cuvette with a 1 cm path length; all experiments were performed at room temperature. Steady-state emission measurements were obtained on a Horiba Jobin-Yvon FluoroLog-3 spectrophotometer. All sample concentrations were adjusted to give absorbance values between 0.10 and 0.20 AU at

the excitation wavelength in an air-free quartz cuvette. Slit widths were set to 4 mm for the excitation wavelength and 1 mm for the emission wavelengths.

4.3.4 Computational Methods

The structures of compound **4.1**, $[\text{V}(\text{bpy})_3](\text{BF}_4)_2$, $[\text{Cr}(\text{PDO})_3]$, and $[\text{V}(\text{PDO})_3]^-$ were optimized using DFT with the APF-D functional and the 6-311+G* basis set. The spin-density plots were calculated using Gausview using a course grain cube and an isovalue of 0.003 to insure optimal visualization of the differences between the chromium and vanadium complexes. All DFT calculations were computed using the Gaussian 09d software suite.⁶

Model complexes with the ligand 1,3-propanedionato (PDO) were studied to gain an insight into the excited state behavior of Cr(III) and V(II). The electronic states are referenced to an O_h point group to remain consistent with literature.⁷ The $^4A_{2g}$ ground states of $[\text{Cr}(\text{PDO})_3]$ and $[\text{V}(\text{PDO})_3]^-$ were optimized with the same DFT approaches. The lowest excited state structures were calculated corresponding to the Jahn-Teller distorted $^4T_{2g}$ state constrained to the C_2 symmetry point group. These structures are analogous to the $^4T_{2g}$ excited state of $[\text{Cr}(\text{acac})_3]$.⁷ The ground state and excited state structures were aligned to form a linear pathway and formed linearly interpolated structures along their path.⁸

The excited states of each structure along the distortion coordinate were calculated using the spectroscopy oriented configuration interaction (SORCI) method to construct the excited state pathways between the ground state and relaxed excited state. The initial wave function for each structure was calculated using the B3LYP functional with a cc-(p)VDZ basis set for all atoms except the metal center which used a cc-pCVTZ basis set. Each wave function was refined using a complete active space self-consistent field wave function (CASSCF) with a 3,5 active space and state averaging. All SORCI calculations utilizing the CASSCF wave functions were done

including additional core electrons beyond the CASSCF active space. The B3LYP DFT, CASSCF, and SORCI calculations were computed using the ORCA 3.0.3 electronic structure suite.⁹

The vibrational contributions to the difference between the ground state and excited states of $[\text{Cr}(\text{bpy})_3]^{3+}$ and $[\text{V}(\text{bpy})_3]^{2+}$ were calculated using a vibrational mode projection scheme used by Ando and colleagues.⁷ Briefly, the vibrational normal modes of both $[\text{Cr}(\text{bpy})_3]^{3+}$ and $[\text{V}(\text{bpy})_3]^{2+}$ calculated for the ground state geometry. The excited state structure was aligned to the ground state structure using the same criteria used for the linear reaction pathway in the SORCI calculations where any translational and angular momentum were removed from the structure. The excited state center of mass was translated to the center of mass of the ground state and the excited state structure was rotated by the Euler indices that satisfy the equation:

$$\sum_i m_j (\vec{R}_j^r \times \vec{R}_i^p) = 0 \quad 4.1$$

where i is over all atoms, m_i is the mass of atom i , and $\vec{R}_i$ is the Cartesian coordinates of atom i .⁸ The resulting structures were examined to ensure that the alignment did not contain any unphysical atom movements between the structures. This ensures that no vibrational modes are projected onto differential distortions due to translations or rotations of the whole complex.

The frequency calculation of the ground state includes the eigenvalues and eigenvectors of the diagonalized Hessian, which describe the vibrational energies and mode motion in terms of atom displacements, $\mathbf{L}_{\text{gs}}$. A Duschinsky vector, $\mathbf{K}_{\text{gs}}$, is calculated using the formula

$$\mathbf{K}_{\text{gs}} = \mathbf{M}\mathbf{L}_{\text{gs}}\mathbf{R}_{\text{d}} \quad 4.2$$

where $\mathbf{M}$ is a matrix containing the masses of each atom and, $\mathbf{R}_{\text{d}}$ is the difference vector of atomic coordinates between the ground and excited states.⁷ This results in a vector, $\mathbf{K}_{\text{gs}}$, that describes a relative amount of each vibrational mode resulting from the distortion between the ground and excited states.

4.3.5 Other Physical Methods

Infrared spectra were measured with either a Nicolet 380 FT-IR or Bruker TENSOR II spectrometer. Mass spectrometry measurements were performed in either the positive ion or negative ion mode on a Thermo-Finnigan LTQ mass spectrometer equipped with an analytical electrospray ion source using a 2.5 V spray voltage and 175 °C capillary temperature. Spectroelectrochemical measurements were performed with a Pine Research Instrumentation gold honeycomb electrode connected to a Gamry Reference 600 potentiostat and an Ocean Optics DH-2000-BAL spectrophotometer. Spectra were collected within 2 minutes of equilibration. Elemental analyses were performed by Midwest Microlabs (Minneapolis, MN).

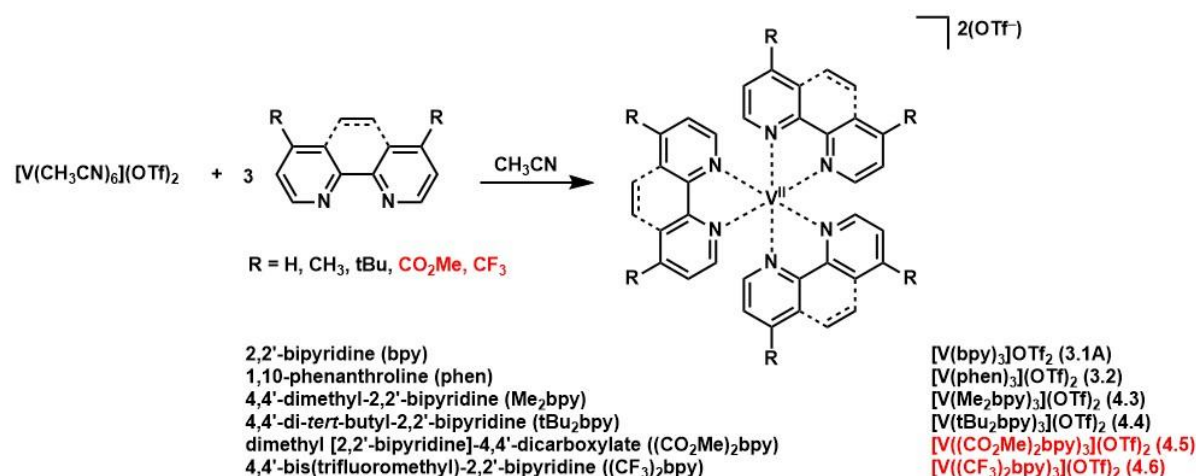
4.4 Results

4.4.1 Synthesis of V(II) polypyridyl complexes

V(II) polypyridyl complexes were prepared cleanly using ligands with electron donating groups (Scheme 1). Compounds **4.3** and **4.4** contain representative electron-donating methyl and t-butyl groups, respectively, and yield large crystals in good yield. Compound **4.3** has been previously reported, via a different synthetic route.¹⁰ Compound **4.4** has been prepared as a tetrafluoroborate salt.¹¹ In both instances, the compounds I prepared resemble the electronic structures provided in their previous reports. One advantage to the method reported here is the access to large diffraction-quality crystals. Attempts using polypyridyl ligands with electron-withdrawing groups were more challenging and did not yield pure products. Compound **4.5** has been attempted via other synthetic routes, but continues to be a challenge. In these characterization experiments, the color depends on the solvent identity and other data suggests bis-ligation *vide infra*. Compound **4.6** appears to be more stable in solution, with no distinguishable difference in

color based on solvent. However, it did not precipitate out of solution during preliminary studies which suggests impurities in the sample.

Scheme 4.1



4.4.2 Electronic Absorbance

Electronic absorbance spectra of V(II) polypyridyl complexes show significant absorbances in the visible region (Figure 4.1). The metal-to-ligand charge transfer (MLCT) bands are assigned at lower energies ($\lambda > 550$ nm) due to the relatively high ($1000 \text{ M}^{-1} \text{ cm}^{-1}$) extinction coefficients, shifts in λ_{max} from the substituent groups, and qualitative agreement with electrochemical data. First, the high extinction coefficient is consistent with a Laporte-allowed, spin-allowed transfer of an electron in the metal t_{2g} orbital to a ligand π^* orbital. Second, within the limited data set of prepared and known V(II) polypyridyl complexes, we observe that electron-donating groups shift the lowest energy absorbance peak towards higher energies. Finally, the difference between the $E_{1/2}(3+/2+)$ and $E_{1/2}(2+/1+)$ couples are similar in energy to the proposed transition. This difference in electrochemical potential suggests metal-to-ligand charge transfer and is consistent with similar M(II) polypyridyl complexes.

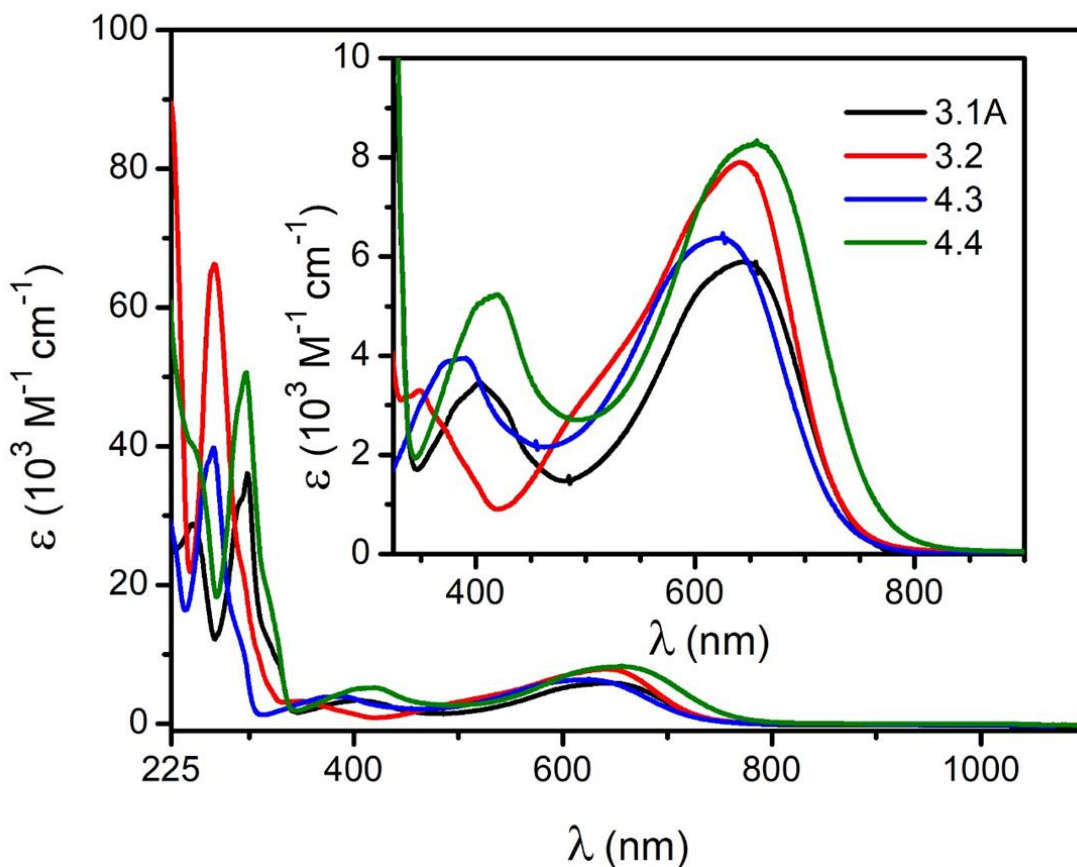


Figure 4.1 Electronic absorption spectra of V(II) polypyridyl complexes in CH₃CN.

V(II) polypyridyl complexes and their Cr(III) counterparts exhibit very different optical properties in the visible region (Figure 4.2). As previously discussed in Chapter 2, Cr(III) polypyridyl complexes exhibit unique absorbance spectra arising from a Heisenberg spin ladder involving coupling between a triplet ligand and paramagnetic Cr(III) metal center. The Heisenberg spin ladder is observed between 400 and 500 nm with a molar absorptivity less than $1000 \text{ M}^{-1} \text{ cm}^{-1}$ for compounds **4.1-4.2**. They appear yellow/orange in solution due to their higher energy absorbance (purple/blue wavelengths); the V(II) analogues are blue in solution due to their lower energy absorbance (yellow wavelengths).

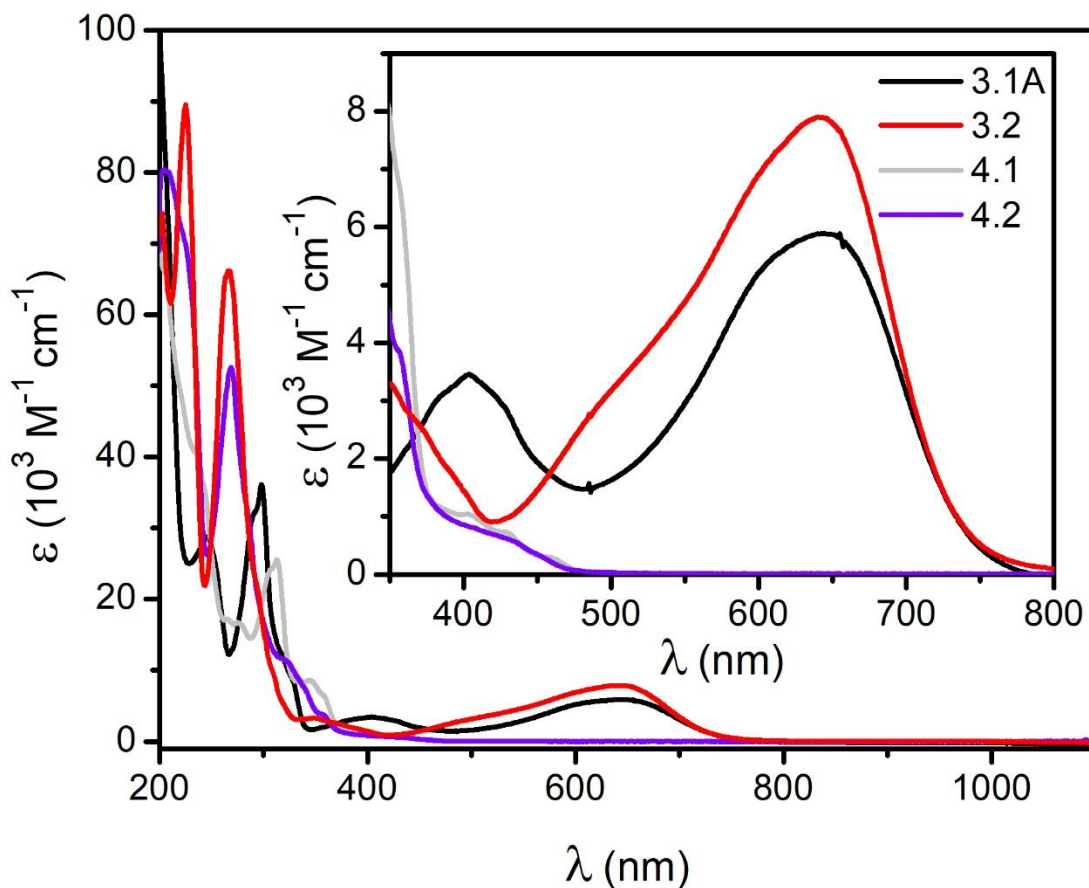


Figure 4.2 Comparison of electronic absorption spectra of V(II) and Cr(III) polypyridyl complexes in CH₃CN solvent.

4.4.3. Electrochemistry of V(II) polypyridyl complexes

V(II) polypyridyl complexes exhibit multiple, reversible redox events that shift based on the substituent groups (Figure M4.3 and Table 2). Compound **3.1A** exhibits perfect Nernstian, diffusion-limited reversibility for the assigned 3+/2+ couple as $\Delta E_p = 59$ mV. This redox event lies at 0.08 V vs Fc⁺/Fc⁰ in CH₃CN. When electron donating substituent groups are added to the polypyridyl ligand, such as in compounds **4.3** and **4.4**, the $E_{1/2}$ of the 3+/2+ couple shifts cathodically relative to **3.1** (Table 4.1). The same trend is observed for the $E_{1/2}$ of the 2+/1+ and 1+/0 redox couples.

Compound **4.4** exhibits anomalously large ΔE_p relative to the other V(II) polypyridyl complexes. Here, $\Delta E_p = 200$ mV for the 3+/2+ redox couple, which is quite large in CH₃CN. Cyclic voltammograms of compound **3.1A** in CH₂Cl₂ exhibit large ΔE_p around 150 mV presumably due to reorganization of the larger solvent molecules relative to CH₃CN. Compound **4.4** has been previously reported as the neutral species [V(*t*Bu₂bpy)₃]⁰ by Bowman and Weighardt.¹¹ In that work, $\Delta E_p \sim 100$ mV in tetrahydrofuran for the 3+/2+ couple. The 2+/1+ and 1+/0 redox events are less resolved in the oxidative return scan, but appear to have large ΔE_p . Additionally, an irreversible redox event has been reported at 0.80 V vs Fc⁺/Fc⁰; however, this event is not observed in our system and may be dependent on their experimental set-up. Regardless, the remaining redox couples are in proximity to the reduction potentials reported by Bowman and Wieghardt.

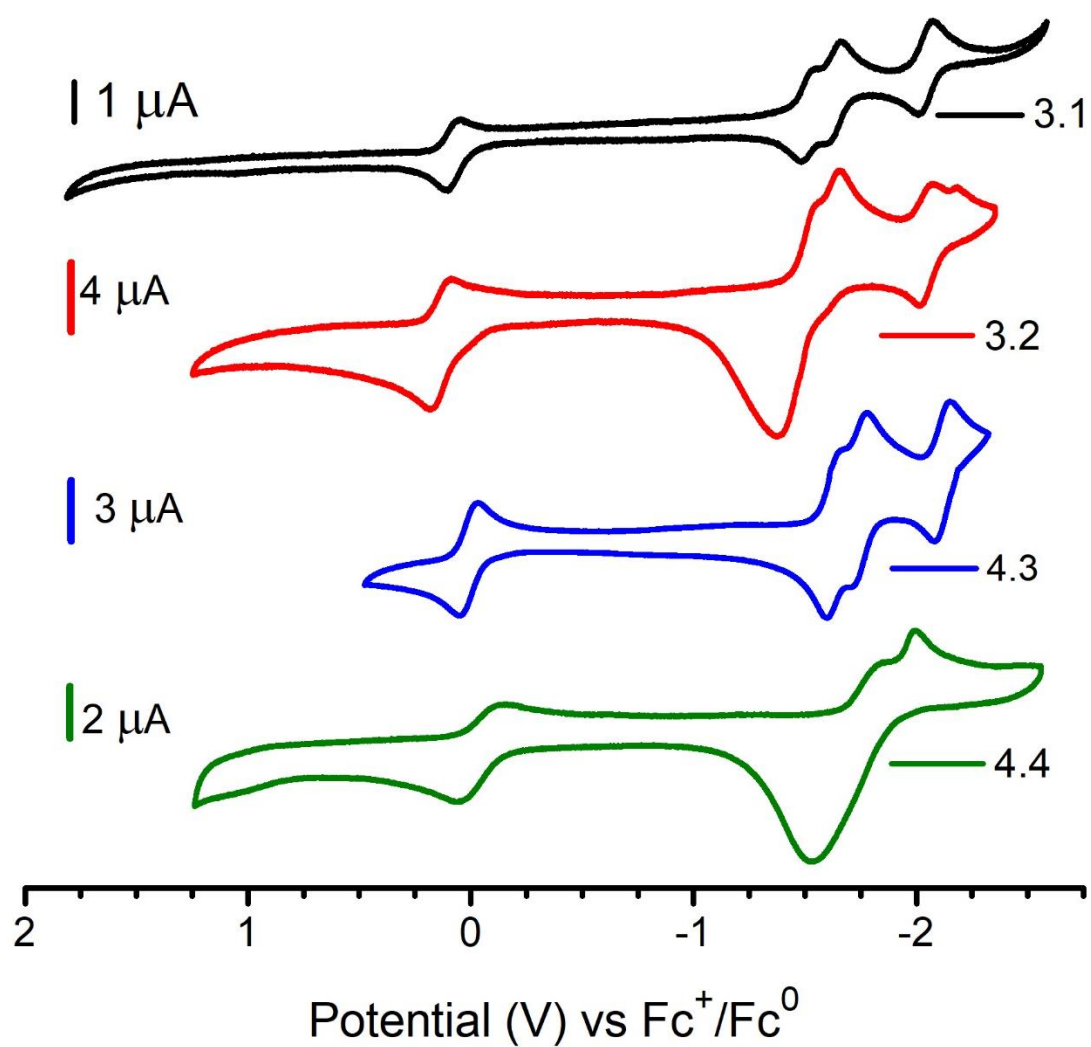


Figure 4.3 Cyclic voltammograms (0.1 V/s) of the cathodic reduction potentials for V(II) polypyridyl complexes in 0.1 M Bu₄NPF₆ in CH₃CN. Reduction potentials are tabulated in Table 1.

Table 4.1 Ground state reduction potentials for **1-4** and their Cr(III) analogues

Redox Event ^a	E _{1/2} 3+/2+	E _{1/2} 2+/1+	E _{1/2} 1+/0	E _{1/2} 0/1-	E _{1/2} 1-/2-	Reference
[V(bpy) ₃] ²⁺ (3.1A)	0.08 (59)	-1.46 (60)	-1.58 (66)	-1.99 (72)		Chapter 3
[Cr(bpy) ₃] ³⁺ (4.1)	-0.60 (84)	-1.12 (77)	-1.69 (77)	-2.31 (77)	-2.62 (84)	12
[V(phen) ₃] ²⁺ (3.2)	0.13 (83)	-1.53	1.68	-2.16 (90)		Chapter 3
[Cr(phen) ₃] ³⁺ (4.2)	-0.60 (84)	-1.12 (77)	-1.69 (77)			12

[V(Me ₂ bpy) ₃] ²⁺ (4.3)	0.01 (72)	-1.62 (59)	-1.74 (60)	-2.11 (75)		This Work
[Cr(Me ₂ bpy) ₃] ³⁺	-0.76(70)	-1.26 (77)	-1.79 (77)	-2.38 (77)	-2.66 (91)	12
[V(<i>t</i> Bu ₂ bpy) ₃] ²⁺ (4.4)	-0.04 (200)	-1.67 (240)	-1.86 (220)			This Work
[Cr(<i>t</i> Bu ₂ bpy) ₃] ³⁺	-0.79	-1.28	-1.81			11

^aPotentials reported in V vs Fc^{+/0} (ΔE_p in mV). Cyclic voltammetry of V and Cr complexes: experiments were performed in 0.1 M Bu₄NPF₆ in CH₃CN utilizing a Pt working electrode, platinum counter electrode, and a pseudo silver wire reference electrode which was referenced to Fc^{+/0} at a 0.100 mV/s scan rate.

4.4.4 Electron Structures of ⁴A₂ Ground State and ²E Excited State

Electronic structure calculations allow us to model both the ⁴A₂ ground state and ²E excited state for both V(II) and Cr(III) polypyridyl complexes. Spin density plots provide key insight into the distribution of unpaired electrons in these systems (Figure 4.4). First, both d³ polypyridyls show a cubic spin density centered around the metal center in their ⁴A₂ ground state. This cubic spin density is the result of 3 orthogonal α spins ie. three electrons populating the metal t_{2g} orbitals in a purely octahedral coordination geometry. The sum of the d_{xy}, d_{xz}, and d_{yz} yield a cube, suggestive of Cr(III) and V(II). Second, a small amount of β spin is observed on the bipyridine nitrogen atoms as the calculated α spin is not perfectly 3.00. However, V(II) reveals a small leak of α spin unto the bipyridine ring, whereas no significant leakage of this α spin is observed in Cr(III). Here, this suggests increased covalency between the V(II) ion and the bipyridine ligands. This phenomena may be expected, as the atomic radii of V(II) = 0.79 Å whereas Cr(III) = 0.615 Å. Third, both complexes show a nodal β spin for the ²E excited state. This leads to a net 1 unpaired spin, as expected for a ²E excited state. However, a key difference between the two plots is the leakage of β spin unto the ligand. The ²E state of V(II) reveals an appreciable leakage of spin density on the ligand compared to Cr(III). Overall, this leakage of spin density is a key difference observed in the electronic structure of both the ground and excited state.

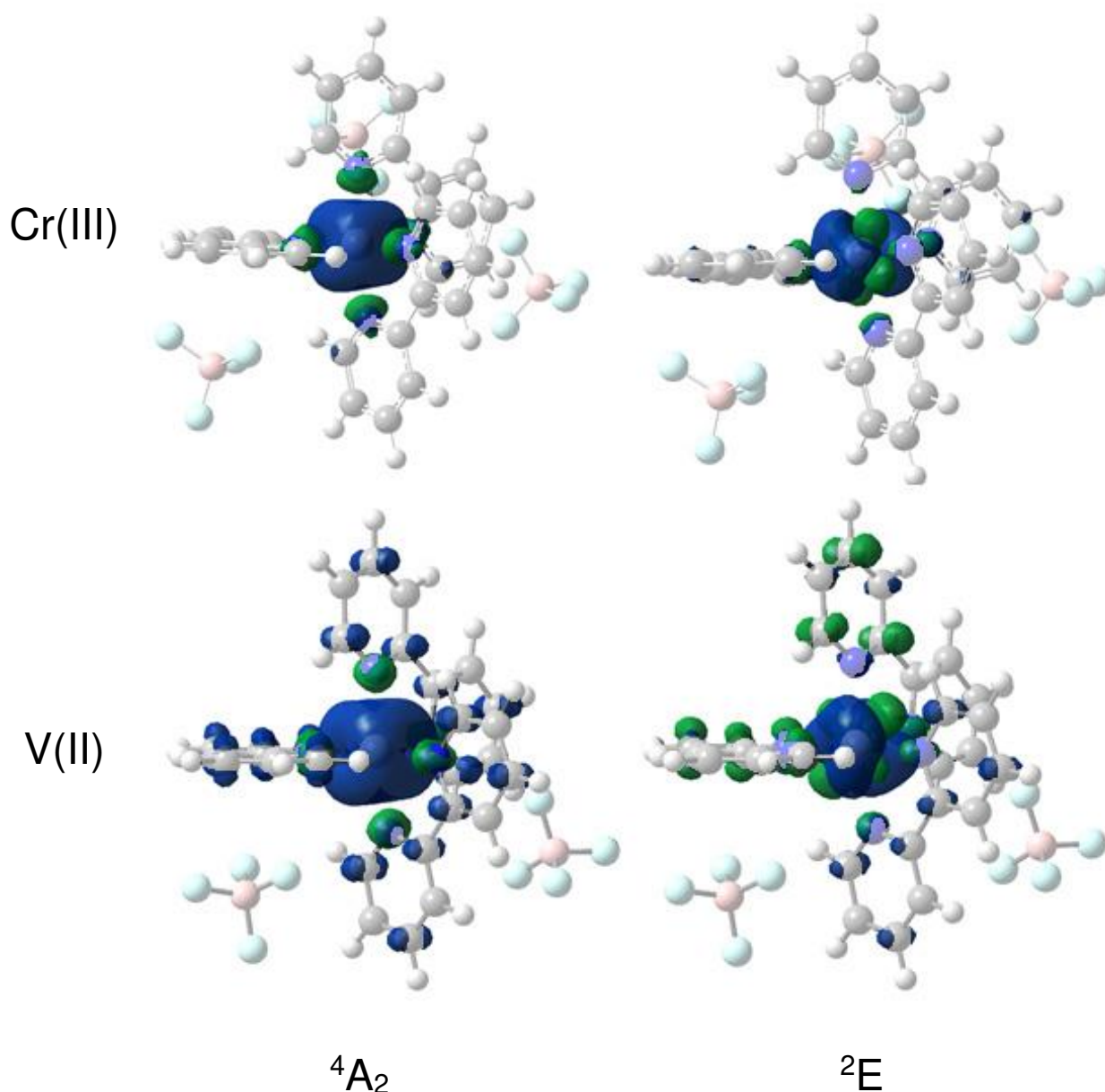


Figure 4.4 Spin density plots of 4A_2 and 2E states of compound **3.1** and $[V(bpy)_3](BF_4)_2$. See experimental 4.3.4 for details. Atoms in original figure (Figure A3.1) were shaded for clarity, in order to highlight spin density.

There is a significant decrease in the 2E energy for V(II) relative to Cr(III). In compound **4.1**, the doublet is calculated at 1.62 eV (765 nm) above the ground state whereas the doublet is 1.08 eV (1148 nm) in the isoelectronic V(II) analogue, a ratio representing a 33% decrease from Cr(III) to V(II). Coincidentally, this ratio is equivalent to the ratio for the $^4A_{2g} \rightarrow ^4T_{2g}$ energy for $[Cr(H_2O)_6]^{3+}$ (2.18 eV) to $[V(H_2O)_6]^{2+}$ (1.46 eV).¹³ The leakage of spin density also highlights an

underlying difference in energies between V(II) and Cr(III). In the case of the doublet state for V(II), the α and β electrons delocalize as much as possible. Additionally, the d orbitals on V(II) are much larger than the d orbitals of the Cr(III) metal center. This combination leads to weaker exchange between the α and β electrons, decreasing the energy of the 2E excited state relative to Cr(III). The combination of β electron density on the ligand and energy differences suggests that the doublet state is more stable for the V(II) complex, decreasing the available chemical potential to catalyze reactions.

The decrease in 2E energy is significant enough to limit the utility of V(II) as a potential photocatalyst. First, a low 2E allows for increased non-radiative decay rates. As the energy of the excited state decreases, vibrational modes and distortion become more important in their ability to alleviate energy. Thus, the excited state lifetime and quantum yield of a 2E state are expected to decrease relative to Cr(III). Second, a low 2E limits the utility of V(II). Based on the Rehm-Weller formalisms (Equation 1.2-1.3), a small E_{00} value will lead to less difference in energy between the excited state and ground state. Theoretically, compound **3.1A** has a $E_{1/2}(2+^*/1+) = -0.38$ V vs Fc^+/Fc^0 for photooxidation and $E_{1/2}(3+/2+^*) = -1.0$ V vs Fc^+/Fc^0 . While one may try to use compound **3.1A** based on the comparisons made to Cr(III), compound **3.1A** is such a poor photooxidant that it is better to use as a photoreductant (Figure 1.3). Even as a photoreductant, V(II) will be limited to photoreduction of easily reduced substrates. This limitation is seen directly with preliminary photoreduction studies with **3.2** in chapter 3.

4.4.5 Crossing of Potential Energy Curves in Cr(III), not V(II)

In an effort to better understand the excited state manifold of V(II) vs Cr(III), the excited states of each structure along the distortion coordinate were calculated using a SORCI method. Since these methods are very computationally expensive, we chose smaller molecules with

relevant photophysical properties. $[\text{Cr}(\text{acac})_3]$ represents a good candidate as the photophysical properties are well studied and has been previously studied with a similar method by Ando and colleagues.^{7,14} Additionally, the 42 atoms of the three acetylacetonate ligands can be reduced to 24 atoms by using 1,3-propanedionato ligands.

Plots of the linear distortion reaction coordinate reveal important distinctions between the presumed and computed excited state manifold (Figure 4.5). Presumably, excitation of the $^4\text{A}_2$ ground state leads to a $^4\text{T}_2$ excited state which then undergoes intersystem crossing to a ^2E excited state. For the Cr(III) complex, most of this behavior is observed in the plots. Excitation where the reaction coordinate is 0.0 (D_3 symmetry) most likely leads to the quartet state at ~ 2.75 eV. From here, the quartet splits to a few excited states with roughly constant to slight decreased energies as it distorts to the $^4\text{T}_2$ excited state (C_2 symmetry). At $R = 0.67$, the lowest excited quartet state crosses with the lowest doublets which is in agreement with previous reports.⁷ This provides a low energy barrier pathway to the $^2\text{E}_g$ state since the states in the crossing region do exhibit mixed doublet/quartet character when spin-orbit coupling contributions are included in the calculation (Figure A3.2). This leads to fast intersystem crossing to the $^2\text{E}_g$ state in $[\text{Cr}(\text{acac})_3]$. The excited states along the distortion coordinate show a different trend for the $[\text{V}(\text{PDO})_3]^-$ complex. The lowest excited quartets rise in energy with the doublets as the structure distorts towards the stable $^4\text{T}_{2g}$ state. This contrasts with the Cr(III) complex where the lowest excited quartets decrease in energy as a function of distortion. This causes no crossings between the excited quartets and doublets in the V(II) complex. While the difference between these two excited state pathways is not definitive proof that $[\text{V}(\text{PDO})_3]^-$ is unable to reach the $^2\text{E}_g$ state, it does suggest that V(II) complexes may be significantly less likely to reach a stable doublet state upon excitation compared to a Cr(III) analogue. Without a complete map of the potential energy surface, it is not known

whether other low barrier quartet to doublet transitions exist, but the most direct path does not contain one.

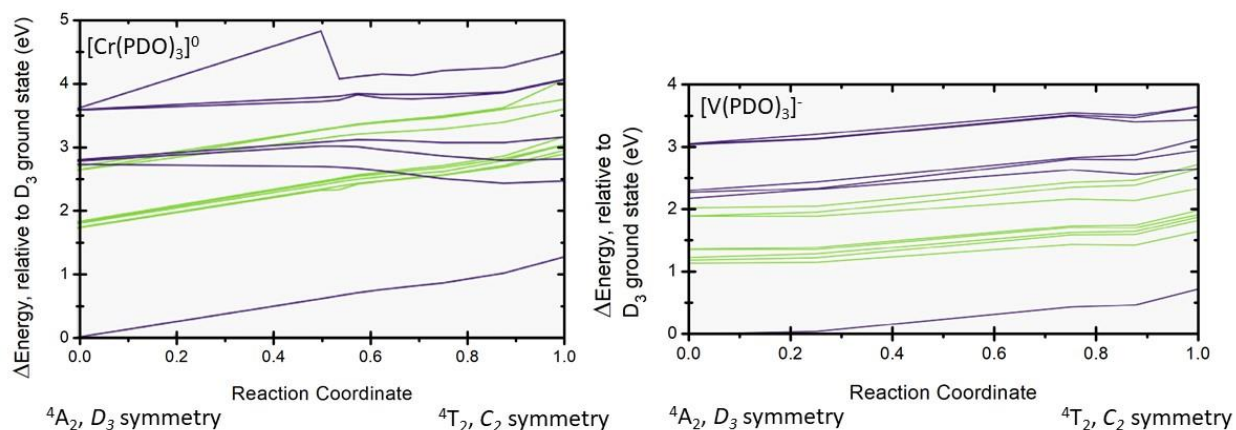


Figure 4.5 Plot of excited states of $[\text{Cr}(\text{PDO})_3]^0$ and $[\text{V}(\text{PDO})_3]^-$ along a linear distortion reaction coordinate between the $^4\text{A}_{2g}$ and $^4\text{T}_{2g}$ optimized geometries. The purple and green lines represent the quartet and doublet states, respectively.

4.5 Discussion

4.5.1 Discrepancies in assigning the electronic structure of $[\text{V}(\text{tBu}_2\text{bpy})_3]^{3+}$

Although compound **4.4** has been previously reported as a different salt, I chose to prepare it in order to support our discussion of the electronic structures of V(II) polypyridyl complexes. $[\text{V}(\text{tBu}_2\text{bpy})_3]^{2+}$ crystallizes here as a triflate salt, whereas the previously reported tetrafluoroborate salt yields microcrystals. A preliminary structure was collected for compound **4.4**, yielding a dicationic V(II) polypyridyl complex with two triflate counteranions (Figure A3.4). Complications, such as incomplete data collection of the space group due to misassignment of the crystal Laue class and icing on the crystal, during the collection process reduced the quality of the data. Qualitatively, the structure resembles compounds **3.1A** and **3.2**, which supports the electronic structure of V(II) polypyridyl complexes (Figure A3.3). It appears as triflate anions may be preferred for use in crystallization should other V(II) polypyridyl complexes require structural analyses.

While the identity of compound **4.4** agree with previous reports, the identity of $[\text{V}(\text{tBu}_2\text{bpy})_3]^{3+}$ is not straightforward. The trication is necessary in our spectroelectrochemical experiments which lead to assignment of the $^2\text{MLCT}$ in transient absorbance experiments. A two-electron reduction of compound **4.4** would yield a neutral $[\text{V}(\text{tBu}_2\text{bpy})_3]^0$ molecule, which has also been reported by Bowman and Wieghardt. In these spectroelectrochemical experiments, the *in-situ* absorbance spectra resemble their reported data. A slight shift in energy ($\nu < 300 \text{ cm}^{-1}$) is observed, due to choice of solvent. However, oxidation of $[\text{V}(\text{tBu}_2\text{bpy})_3]^{2+}$ in compound **4.4** yields a different spectrum than that reported by Bowman and Wieghardt. A loss of MLCT is observed in the visible spectra with peak at 528 nm, as previously reported. Air-oxidation of the spectrochemical sample ($\sim 5 \text{ mM}$ compound **4.4** in a 0.1 M Bu_4NPF_6) yields a pink solution with a peak at 528 nm (Figure A3.5). Chemical oxidation with AgBF_4 in the presence of air also yield this pink solution (Figure A3.6). Oxidation under other conditions resemble a dimeric V(III) species, which also has a peak at $\sim 530 \text{ nm}$.¹⁵ These data are confusing, and would lead to suspicion of our preparation. Chemical oxidation of compound **4.4** with AgOTf does not yield an isolated compound, requiring alternative routes to be required. When $[\text{V}(\text{tBu}_2\text{bpy})_3]^{3+}$ is prepared in a similar fashion to that reported by Bowman and Wieghardt, a red precipitate is observed. Residual ferrocenium triflate remains, as observed via absorbance spectroscopy. However, mass spectrometry displays peaks suggestive of $[\text{Fe}(\text{tBu}_2\text{bpy})_3]^{2+}$ rather than $[\text{V}(\text{tBu}_2\text{bpy})_3]^{3+}$ (Figure A3.7). Upon closer inspection, I find that the absorbance data correspond to the λ_{max} of $[\text{Fe}(\text{tBu}_2\text{bpy})_3]^{2+}$, which has a large molar absorptivity due to MLCT (Figure A3.8).^{16,17} If a small amount of $[\text{Fe}(\text{tBu}_2\text{bpy})_3]^{2+}$ were to exist in solution, it is plausible that the absorbance of that impurity would obscure a weakly absorbing $[\text{V}(\text{tBu}_2\text{bpy})_3]^{3+}$ species. Thus, I suggest our

spectrochemical *in-situ* data of $[\text{V}(\text{tBu}_2\text{bpy})_3]^{3+}$ to be a better description of its electronic structure rather than chemical isolations attempted here and previously reported.

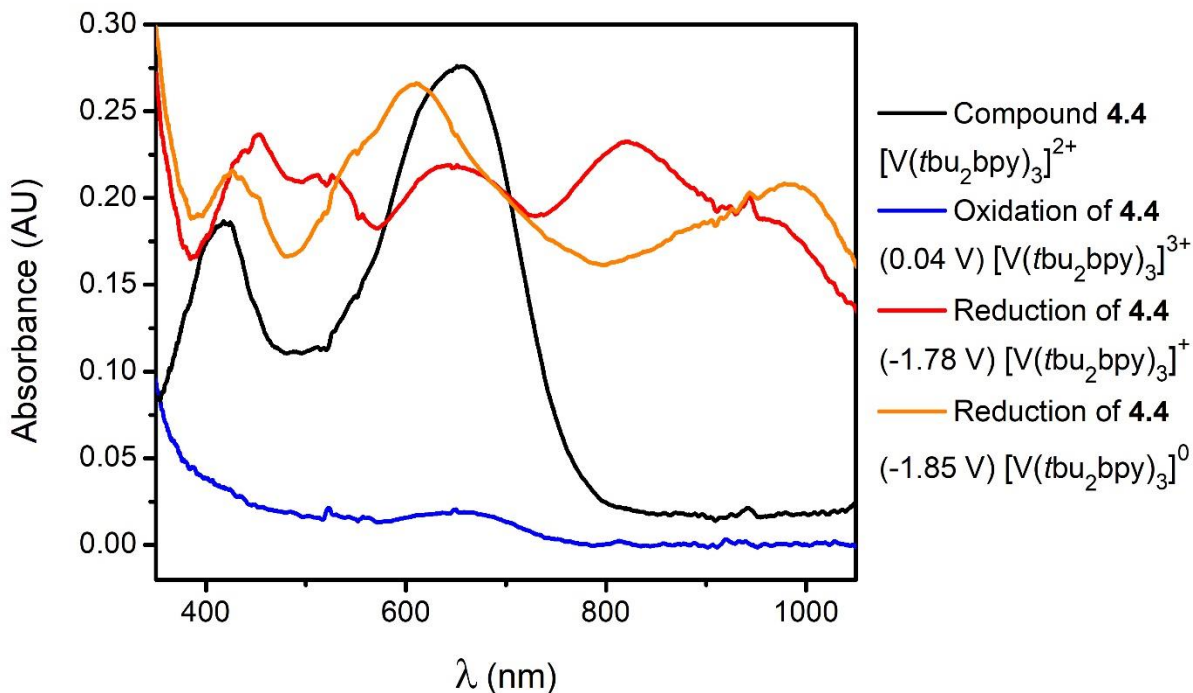


Figure 4.6 Spectroelectrochemical spectra of **4.4** at the rest potential (black), oxidation of **4.4** at 0.04 V vs Fc^+/Fc^0 (blue), reduction of **4.4** at -1.78 V vs Fc^+/Fc^0 (red), and reduction of **4.4** at -1.85 V (orange). The relevant electroactive species are included in the legend for convenience.

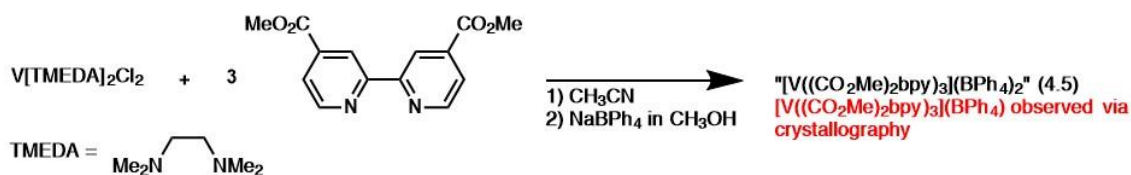
4.5.2 Difficulties with Electron-Deficient Polypyridyls

Previously, compound **4.5** was prepared via 2 two synthetic routes (Scheme 4.2). In the first route, one would expect a simple ligand exchange between the starting material $\text{V}(\text{TMEDA})_2\text{Cl}_2$ and available polypyridyl ligand. However, an *in-situ* reduction is observed and the monoreduced form of compound **4.5**, $[\text{V}((\text{CO}_2\text{Me})_2\text{bpy})_3]^+$, is generated. This species crystallizes out of solution in the presence of tetraphenylborate counterion, as reported by Michael Nguyen (Figure A3.9). The crystal structure supports an *in-situ* reduction of the molecule as a single tetraphenylborate anion exists per metal complex. This reduction process is peculiar, as preparation of compound **3.1** and **3.2** via this synthetic route do not yield a monoreduced species.

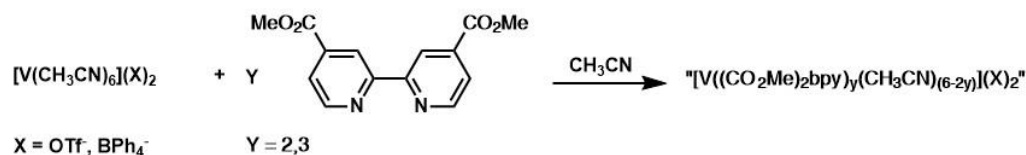
In the second route, another ligand substitution reaction occurs between the solvated V(II) ion and free polypyridyl ligands. This route does not appear to reduce the complex and appears to give a straightforward path to compound **4.5**.

Scheme 4.2 Attempted preparation of compound **4.5**

Route 1:



Route 2:



While route 2 appears to yield compound **4.5**, experiments to elucidate its electronic structure appear to suggest ligand dissociation. The solution turns green in CH₂Cl₂ and CH₃CN, suggestive of a red-shifted MLCT due to electron-withdrawing ligands. However, the reaction turns purple in O-donor solvents such as tetrahydrofuran, acetone, methanol, and dimethylformamide (Figure A3.10). Mass spectra obtained in any of the solvents show no signs of a tris-ligated species, but rather bis-polypyridyl species and solvated species. Electrochemical experiments reveal several poorly-resolved redox events in acetonitrile and dimethylformamide (Figure A3.11). The open-circuit potential lies at the peak of a cathodic redox event, suggestive of an equilibrium between compound **4.5** and its monoreduced analogue. Attempts to prepare [V((CO₂Me)₂bpy)₂(CH₃CN)₂]²⁺ were pursued in order to understand a bis-solvated species

(Scheme 4.2). In solution, both compounds appear the same based on electrochemistry (Figure A3.12). Computational studies of a bis-solvated species show no remarkable difference in the absorbance spectra between a tris polypyridyl V(II) species and a bis polypyridyl, bis solvated V(II) complex (Figure A3.13-Figure A3.14). Thus, the electronic structure of compound **4.5** is quite difficult to assign based on the multiple techniques described here and requires much more attention for an accurate description.

Compound **4.6** appears to be a better representative of V(II) polypyridyl complexes with electron-withdrawing substituent groups. In CH₃CN, the electrochemistry exhibits similar behavior to that of the other V(II) polypyridyl complexes (Figure A3.15). The open-circuit potential lies between two redox events at approximately -0.5 V vs Fc⁺/Fc⁰. The anodic event resembles a vanadium 3+/2+ couple based on its proximity to the potential for similar 3+/2+ couples, although additional anodic events are observed. The cathodic events are close together, separated by less than 200 mV, suggestive of ligand reduction. Square wave voltammetry reveals a large difference in current passed in the cathodic events compared to the anodic event. This suggests that an electron-deficient ligand is weak at stabilizing the V(III) metal center, requiring a larger reorganization in solution, and passing less current. Similar behavior of the amount of current passed is observed with compound **3.1B** compared to compound **3.1A** in Chapter 3. Overall, these behaviors agree with the electronic structure of V(II) polypyridyl complexes.

The absorbance spectrum of compound **4.6** exhibits an unexpected red-shift which may suggest the ligand is acting as a π -donor. Two distinct peaks appear in the visible region, similar to the other V(II) polypyridyl complexes (Figure A3.16). The low-energy transition is close in energy to the expected MLCT transition, with a slight shift towards higher energy wavelengths. This trend is quite unique, opposing the typical description of bipyridine as a π -acceptor ligand for

transition metals.¹⁸ A plot of the MLCT energy as a function of Hammett parameter σ_{para} ¹⁹ reveals a positive slope, an opposing trend relative to what is observed in Fe(II) polypyridyl complexes (Figure 4.7).¹⁸ Bipyridine ligands have recently been described as π -donors/acceptors, with the positive slope suggestive of increased π -donor character here.¹⁸

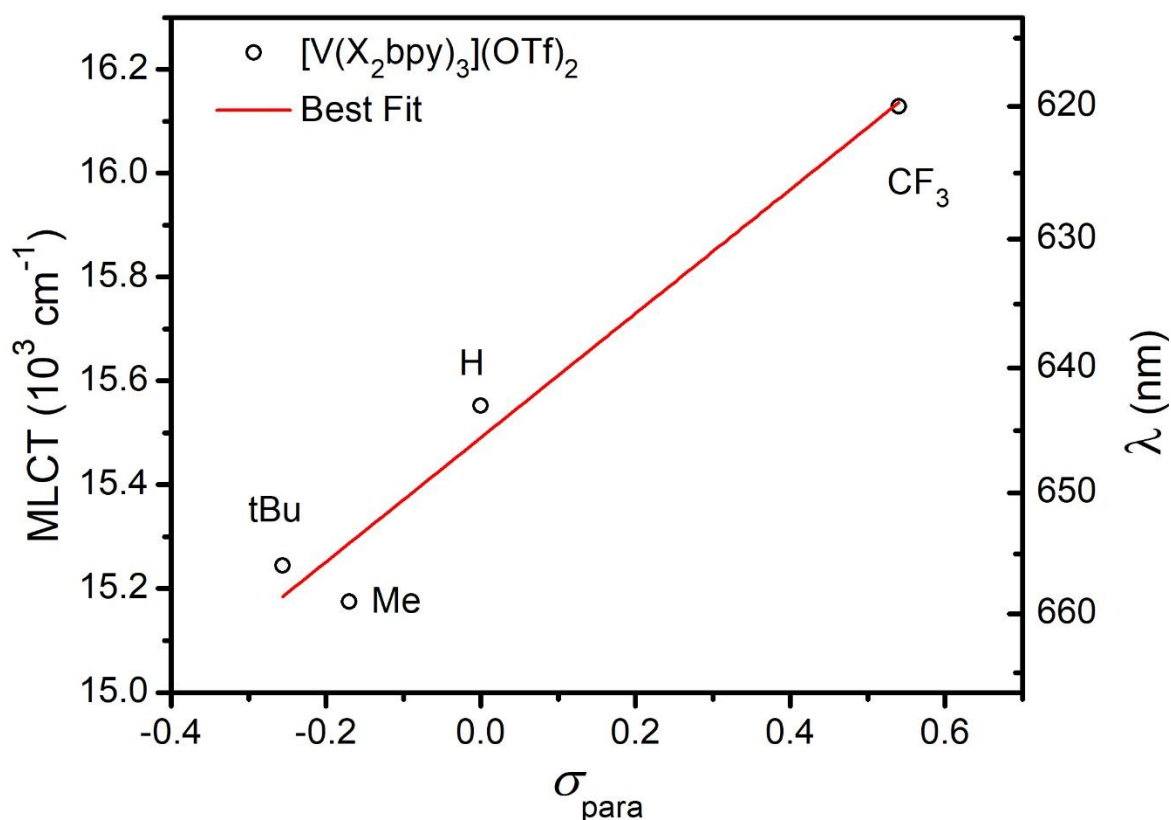


Figure 4.7 Plot of the MLCT energy for prepared V(II) polypyridyl complexes as function of σ_{para} . Line of best fit: $y = 1200 \times \sigma_{\text{para}} + 15500$. $R^2 = 0.94689$

4.5.3 Differences in oxidation state of metal center dictating electrochemical properties

The stark difference between the redox events of the V(II) and Cr(III) complexes reveals different stabilities of metal oxidation states. Wieghardt and colleagues have shown via electronic structure considerations a preference for a Cr(III) oxidation state in the bipyridyl system with reduced ligands. Here, it was argued that the *weak* π -acceptor nature of the bipyridine cannot

effectively stabilize reduction of Cr(III) to Cr(II) whereas reduction of $[\text{Cr}^{\text{III}}(\text{CN})_6]^{3-}$ affords a formal Cr(II) metal center.²⁰ In contrast, V(II) is the preferred oxidation state in a tris bipyridyl system with reduced ligands. Here, it was hypothesized that the exchange stabilization in d^3 vanadium is weaker and allows for this preferred oxidation state.¹¹ Overall, this suggests that forced spin-pairing by adding electrons to a d^3 system is not favorable. Additionally, these observations further suggest a preferred d^0 - d^3 redox series where these are the preferred electron configurations for the metal centers within these particular systems.²¹

4.5.4 Nature of the Lowest Lying Excited States in V(II) versus Cr(III)

Cr(III) emission has been well characterized, due to formation of the long-lived ^2E state that exists for microseconds in solution. However, the quantum yield of this ^2E state is very small ($\phi = 0.0025$ for $[\text{Cr}(\text{bpy})_3](\text{OTf})_3$ in deaerated CH_3CN),¹² meaning the rate of nonradiative decay is still large. The low quantum yield has been speculated to arise from several causes such as: 1) fluorescence from $^4\text{T}_2$ 2) inefficient intersystem crossing from $^4\text{T}_2$ to the long lived ^2E state or 3) internal conversion from the ^2E state. In the literature, the non-radiative decay has been attributed to internal conversion from the excited $^4\text{T}_2$ state.^{22,23}

In this work, we have gained further insight based on the identity of the $^4(^3\text{IL})$ excited state and SORCI calculations. First, the $^4(^3\text{IL})$ excited state is the lowest quartet excited state in compound **4.1-4.2** with minimal distortion. This excited state displays minimal distortion relative to the ground state, reducing non-radiative decay pathways. Additionally, this excited state is closely related to a $^2(^3\text{IL})$ excited state as these intraligand transitions compose part of a Heisenberg spin-ladder. Thus, intersystem crossing from the quartet into the doublet manifold could then lead to a relaxation to a lower lying doublet state such as $^2\text{T}_1$ or ^2E . Second, the $^4\text{T}_{2g}$ excited state can cross with the ^2E excited state in other Cr(III) systems. In Chapter 2, the heteroleptic compound

2.3, [Cr(acac)₂(bpy)] presents several similarities to homoleptic [Cr(PDO)₃] presented here. As shown in the SORCI plot (Figure A3.2), the ⁴T₂ and ²E excited states do cross as it approaches the geometry of the distorted ⁴T₂ excited state. While the ²E excited state lifetime is quite short ($\tau < 2$ ns in compound **2.3**), the excited state is still populated and observed. Altogether, these two pathways are accessible to Cr(III) complexes and lead to population of the ²E excited state.

When one considers isoelectronic V(II) complexes, the excited state manifold differs than Cr(III). First, V(II) complexes are easily oxidizable ($E_i = 14.618$ eV)²⁴ and typically show a MLCT band in the visible spectra. Due to their high molar absorptivity, the lowest quartet excited state is typically ⁴MLCT. Any relevant Cr(III) complex with studied photophysics do not exhibit a low energy ($\lambda > 500$ nm) charge transfer band due to their high ionization energy ($E_i = 30.96$ eV).²⁴ Since MLCT excited states involve oxidation of the metal and reduction of the ligand, the first coordination sphere is expected to undergo changes in geometry and/or bond lengths. These changes will change the electronic structure of the complex, energies of relevant excited states, and allow for non-radiative decay to reach their equilibrium excited state geometry. Second, SORCI calculations do not show a crossing between the ⁴T₂ and ²E excited state. If the metal centered states were lower energy than the charge transfer state, there is little likelihood that the ²E would be populated which may contribute to the lack of observed emission.

While the difference in excited state manifolds are important between Cr(III) and V(II), the differences in energy appear to be more worthwhile. For metal centered excited states, the energies for [Cr(bpy)₃]³⁺ are higher in energy than for [V(bpy)₃]²⁺. From a combination of multiple spectroscopic and computational techniques presented in previous chapters and here, we can summarize the relevant energies with Table 4.2. First, it is interesting to note the ⁴T₂ energies for both complexes compared to previous reports. These values of 3.28 eV for [Cr(bpy)₃]³⁺ and 2.86

for $[\text{V}(\text{bpy})_3]^{2+}$ are larger than those extrapolated by Shah and Maverick, 2.85 and 2.21 respectively (Table 3.5).¹⁰ These values scale differently as Cr(III) is ~15% larger than V(II) here whereas Shah and Maverick calculate Cr(III) to increase by 29% relative to V(II). Second, the ligand field strength, $\Delta_{\text{O}}/\text{B}$, are not equivalent for $[\text{Cr}(\text{bpy})_3]^{3+}$ and $[\text{V}(\text{bpy})_3]^{2+}$. Shah and Maverick assume Cr(III) and V(II) to have a similar $\Delta_{\text{O}}/\text{B}$ value of ~35, which would suggest the ^2E excited state to exist at 1.36 eV for $[\text{V}(\text{bpy})_3]^{2+}$. Their extrapolation is based on the reported values for Cr(III) and V(II) in an ion matrix which are nearly identical. Here, $\Delta_{\text{O}}/\text{B}$ for $[\text{Cr}(\text{bpy})_3]^{3+}$ is calculated as 43.3 based on the computed values and 41.3 for a combination of the two. For $[\text{V}(\text{bpy})_3]^{2+}$, $\Delta_{\text{O}}/\text{B} = 56.1$. Additionally, $\Delta_{\text{O}}/\text{B}$ calculates to ~33 and ~41 for $[\text{Cr}(\text{PDO})_3]$ and $[\text{V}(\text{PDO})_3]^-$ respectively. These results suggests the V(II) ion is much more susceptible to changes in ligand field strength than Cr(III). While I do not understand the reason for this behavior, these results hopefully underscore the misconception that isoelectronic Cr(III) and V(II) behave in similar fashion.^{10,11} Ultimately, that work will require thorough investigation into the electronic structure of more V(II) and Cr(III) complexes.

Table 4.2 Energy of Relevant Excited States in $[\text{Cr}(\text{bpy})_3]^{3+}$ and $[\text{V}(\text{bpy})_3]^{2+}$. Calculated values are in italicized.

Excited State	$[\text{Cr}(\text{bpy})_3]^{3+}$	$[\text{V}(\text{bpy})_3]^{2+}$
$^4\text{T}_{2g}$	<i>(3.28 eV)</i>	<i>(2.86 eV)</i>
$^4(^3\text{IL})$	2.71 (2.88 eV)	
$^4\text{MLCT}$		1.93 <i>(1.75 eV)</i>
$^2\text{MLCT}$		<i>(1.72 eV)</i>
^2E	1.70 eV <i>(1.62 eV)</i>	<i>(1.08 eV)</i>
$\Delta\text{o/B}$	41.3 (43.3)	<i>(56.1)</i>

4.6 Conclusions

Overall, the electronic structure of isoelectronic V(II) and Cr(III) polypyridyl complexes are quite different for both ground state and excited state properties. Within several chapters, we have shown differences in the electronic absorbance, electrochemistry, excited state energies/lifetimes, and excited state manifold between these two systems. These results are humbling as we attempted to achieve the photocatalytic properties observed in Cr(III) polypyridyl complexes with V(II), but observe subpar properties by switching the metal centers. While several factors contribute to these differences, the identity and energies of the relevant excited states lead to a completely different excited state manifold. In future work, consideration of the excited state manifold will likely lead to more efficient chromophores with potential photocatalytic properties.

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Chapter 5: The Impact of Reorganization Energy on the Excited State Manifold in V(II)

Tripodal Systems

5.1 Introduction

Cr(III) polypyridyls are great but have low absorptivity and possible ligand dissociation upon reduction. Cr(III) tripods could offer stability and better absorbance, but shorter excited state lifetimes so not useful for photoredox. In Chapter 2, I discussed how the $^4(^3\text{IL})$ absorbance is important for long-lived excited states in Cr(III). We attempted V(II) since it's isoelectronic to Cr(III), but would have an MLCT. Unfortunately, the excited state is too short-lived and weak for the V(II) analogues. In Chapter 3, I discussed how we successfully enter a doublet excited state manifold rather than remain in a quartet manifold. We looked closer to why isoelectronic V(II) does not behave like Cr(III). In Chapter 4, we realized the larger d-orbitals in V(II) allow for spin density to spill unto the ligand. This leads to lower excited state energies and more vibrational relaxation.

Here, we expect V(II) tripod **5.1** to exhibit short-lived excited states. Since we excite into an MLCT, the oxidized and reduced form could provide insight into the electronic structure of this excited state. We were lucky to isolate the oxidized form (**5.2**), which is structurally different than **5.1**. The large geometric differences yield large differences in the electronic structure. Low energy vibrational modes can lead to large changes in orbital energies. We look at the distortion of **5.2** relative to **5.1** using the continuous shape measure (CShMe), to quantify the differences between the two. In some preliminary models, large structural changes (CShMe ~ 1) between ground state and excited state proxy seem to lead to short-lived excited state. Thus, minimize structural distortion in the future.

5.2 Division of Labor

Romeo Portillo has prepared and characterized all compounds presented in this work. Justin P. Joyce calculated the optimized structures for **5.1-5.3**, the ligand strain, and NEVPT2/CASSCF calculations. Collette M. Nite calculated the original optimized structures for **5.1**, **5.3**, and the Cr(III) analogues, calculated their TDDFT excited states and absorption spectra. Ryan Dill performed transient absorption experiments on **5.1-5.2**.

5.3 Experimental Section

5.3.1 Preparation of Compounds

Manipulations and syntheses of all metal complexes were performed inside a dinitrogen-filled glovebox (MBRAUN Labmaster 130). All solvents were sparged with dinitrogen, passed over molecular sieves, and degassed prior to use. The compounds $[\text{V}(\text{CH}_3\text{CN})_3\text{Cl}_3]$, $[\text{V}(\text{C}_5\text{H}_8\text{O})_3\text{Cl}_3]$, $[\text{V}(\text{CH}_3\text{CN})_6](\text{BPh}_4)_2$, $[\text{V}(\text{CH}_3\text{CN})_6](\text{OTf})_2$,¹ py_3tren ,² $(5\text{-CO}_2\text{Mepy})_3\text{tren}$,³ $[\text{Cr}(\text{py})_3\text{tren}](\text{BF}_4)_3$,⁴ and $[\text{Zn}(\text{py})_3\text{tren}]\text{OTf}_2$ ⁵ were all prepared according to literature procedures.

$[\text{V}(\text{py})_3\text{tren}](\text{OTf})_2$ (**5.1**)

A green solution of $[\text{V}(\text{CH}_3\text{CN})_6](\text{OTf})_2$ (629 mg, 1.06 mmol) and $(\text{py})_3\text{tren}$ (444 mg, 1.08 mmol) in 8 mL of CH_3CN was stirred for 4 hours. The solution was dried *in vacuo* and washed with diethyl ether (3×3 mL). Dark green, plate crystals were grown from a diethyl ether diffusion into a concentrated solution of CH_3CN to yield 665 mg (0.872 mmol, 83% yield) of dark green plate crystals. UV-Vis (CH_3CN) $\lambda_{\text{max}}/\text{nm}$ ($\epsilon_{\text{M}}/\text{M}^{-1} \text{ cm}^{-1}$): 246 (28800), 298 (36100), 404 3460), 643 (5890). IR (KBr pellet): $\nu_{\text{C}=\text{N}}$ 1599 cm^{-1} . ESI-MS(+) (CH_3CN): $m/z = 232.09$ (**5.1** – 2OTf)²⁺. Anal. Calcd For $\text{C}_{26}\text{H}_{27}\text{F}_6\text{N}_7\text{O}_6\text{S}_2\text{V}$ (**5.1**): C, 40.95; H, 3.57; N, 12.86. Found: C, 40.87; H, 3.56; N, 12.84.

[V(py)₃tren](OTf)₃ (5.2)

A clear solution of AgOTf (129, 0.503 mmol) in 3 mL of CH₃CN was added to a solution of [V(py)₃tren]OTf₂ (383 mg, 0.502 mmol) in 8 mL of CH₃CN. Immediately, Ag precipitate was observed as the solution color changed from green to brown. The mixture was stirred for 1 hr. The reaction mixture was filtered through Celite to remove Ag metal, and the filtrate was concentrated in vacuo. Crystals were grown from diisopropyl ether into a concentrated CH₃CN solution to yield 303 mg (0.332 mmol, 66% yield) of brown needle crystals. UV-Vis (CH₃CN) $\lambda_{\text{max}}/\text{nm}$ ($\epsilon_{\text{M}}/\text{M}^{-1} \text{ cm}^{-1}$): 288 (15200), 369 (3760), 449 (788), 506 (351), 774 (26). IR (KBr pellet): $\nu_{\text{C=N}}$ 1605 cm⁻¹. ESI-MS(+) (CH₃CN): m/z = 154.75 (**5.2** – 3OTf)³⁺, 762.09 (**5.2** – OTf)²⁺. Anal. Calcd for C₂₇H₂₇F₉N₇O₉S₃V (**5.2**): C, 35.57; H, 2.99; N, 10.75 Found: C, 35.44; H, 3.01; N, 10.78

[V(5-CO₂Mepy)₃tren](OTf)₂ (5.3)

A solution of [V(CH₃CN)₆](OTf)₂ (242 mg, 0.406 mmol) and ligand (5-CO₂Mepy)₃tren (240 mg, 0.408 mmol) in 8 mL of CH₃CN was stirred for 4 hours. The solution was dried *in vacuo* and washed with diethyl ether (3 × 3 mL). Crystals were grown from a diethyl ether diffusion into a concentrated solution of methanol to yield 195 mg (0.208 mmol, 51% yield) of black plate crystals. UV-Vis (CH₃CN) $\lambda_{\text{max}}/\text{nm}$ ($\epsilon_{\text{M}}/\text{M}^{-1} \text{ cm}^{-1}$): 205 (55300), 236 (37500), 287 (29900), 396 (4620), 667 (3900), 785 (5440), 1024 (1210). IR (KBr pellet): $\nu_{\text{C=O}}$ 1725 cm⁻¹, $\nu_{\text{C=N}}$ 1600 cm⁻¹. ESI-MS(+) (CH₃CN): m/z = 319.25 (**5.3** - 2OTf)²⁺. Anal. Cald. for C₃₂H₃₃F₆N₇O₁₂S₂V (**5.3**): C, 41.03; H, 3.55; N, 10.47. Found C, 40.68; H, 2.72, N, 10.42.

[V(5-CO₂Mepy)₃tren](OTf)₃ (5.4)

A solution of AgOTf (54, 0.210 mmol) in 3 mL of CH₃CN was added to a solution of [V(5-CO₂Mepy)₃tren](OTf)₂ (195 mg, 0.208 mmol) in 8 mL of CH₃CN. Immediately, Ag precipitate was observed as the solution changed from green/black to brown. The mixture was stirred for 1

hr. The reaction mixture was filtered through Celite to remove Ag metal, and the filtrate was concentrated in vacuo. Crystals were grown from diisopropyl ether into a concentrated CH₃CN solution to yield 105 mg (0.097 mmol, 47% yield) of brown crystals. UV-Vis (CH₃CN) λ_{max} /nm ($\epsilon_{\text{M}}/\text{M}^{-1} \text{ cm}^{-1}$): 290 (18000), 373 (3120), 420sh (1730), 465sh (823), 524sh (397), 756 (52). IR (KBr pellet): $\nu_{\text{C=O}}$ 1733 cm^{-1} , $\nu_{\text{C=N}}$ 1608 cm^{-1} . ESI-MS(+) (CH₃CN): m/z = 212.66 (**5.4** - 2OTf⁻).

5.3.2 Electrochemical Studies

Voltammograms were recorded with a CH Instruments 1230A potentiostat in a glovebox under a dinitrogen atmosphere. All experiments used 0.1 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) solution in acetonitrile with a 0.25 mm carbon working electrode, Ag wire quasi-reference electrode, and a Pt wire auxiliary electrode. Reported potentials are referenced to the ferrocenium/ferrocene ([C₅H₅)₂Fe]⁺/[(C₅H₅)₂Fe], Fc⁺⁰) redox couple and were determined by adding ferrocene as an internal standard at the conclusion of each electrochemical experiment.

5.3.3 Photophysical Studies

Absorption spectra were obtained with a Hewlett-Packard 8453 spectrophotometer in a quartz cuvette with a 1 cm path length; all experiments were performed at room temperature. Steady-state emission measurements were performed on a Horiba Jobin-Yvon FluoroLog-3 spectrophotometer in an air-free quartz cuvette. All samples were set to have an absorbance between 0.10 and 0.20 AU at the excitation wavelength. Slit widths were set to 4 mm for the excitation wavelength and 1 mm for the emission wavelengths.

5.3.4 Transient Absorption Spectroscopy

Samples were prepared in 2 mm quartz cuvettes with Kontes HI-VAC® vacuum-valves in a dinitrogen-filled glovebox in solvent that was sparged with argon. All samples were set to have

an absorbance between 0.1 and 0.4 AU at the excitation wavelength. Steady state absorption spectra were taken immediately after preparation of the sample and after experiments to check the degree of decomposition.

Ultrafast visible TA spectroscopy was performed on a homebuilt spectrometer which has been described elsewhere. Briefly, the output of a Ti:sapphire multi-pass amplifier (~800nm, ~1mJ/pulse at 1 kHz repetition rate, Quantronix Odin) is split into two paths, one of which is directed into a homebuilt noncollinear optical parametric amplifier (NOPA), the design of which has been described elsewhere[refs]. The NOPA output (center wavelength 560-650 nm, FWHM ~30nm) is compressed to ~35-50 fs with a prism-pair compressor. Pulse durations are measured using SHG autocorrelation. Pump pulses are mechanically chopped at 500Hz and then focused just before the sample so that the pump spot size in the sample (measured using knife-edge method, ~120-200 μ m) is >~3 times the size of the probe spot size (~30-60 μ m). The excitation pulse polarization is set to magic angle (54.7°) relative to the probe pulse to minimize the contribution to dynamics that results from rotational diffusion.

5.3.5 Computational Procedure

The following were performed using the Gaussian 16 electronic structure package⁶: The structures were optimized with the B3LYP functional⁷ and 6-311+g(d) basis set^{8,9}. The associated D3 empirical dispersion correction was applied in which the a_2 parameter was reduced to 4.064¹⁰. The intermediate geometries were generated through a relaxed scan in which the separation between the metal center and bridgehead nitrogen was constrained. The strain of the ligand set was calculated with the detailed basis set at the Hartree-Fock level of theory. TD-DFT^{11,11} and the resulting natural transition orbitals (NTO's)¹² were generated with the ω B97X-D3BJ functional¹³ and a 6-311+g(2d) basis set. The kinetic and potential energy terms were calculated with a

Restricted or Unrestricted HF wavefunction and an aug-cc-pVTZ basis set⁹. The kinetic energy for the frontier orbitals were calculated at the same level of theory. The basis set superposition error (BSSE) was addressed through the counterpoise correction.¹⁴

The following were performed with the ORCA 4.1 electron structure package¹⁵. NEVPT2/CASSCF^{16–18} was performed on the V(II/III) structures. The active space was defined by the 3d-orbitals; (3,5) [10 doublets and 40 quartets] and (2,5) [10 singlets and 15 triplets]. The def2-TZVP basis set was used in conjunction with its RI-JK approximation¹⁹. *Ab initio* ligand field theory (AILFT) was performed to generate the eigenvalues of the active space and the associated Racah parameters²⁰.

5.3.6 Crystallographic Results

Key structural data for compounds **5.1-5.3** are provided in Table 5.1. Crystals were coated in Paratone oil, supported on Cryoloops, and mounted on either a Bruker Kappa Apex 2 with a CCD diffractometer (**5.1**) or a Bruker D8 Quest ECO with a Photon 50 CMOS diffractometer (**5.2-5.3**) under a stream of cold nitrogen. All data collections were performed with Mo K α radiation and a graphite monochromator. Initial lattice parameters were determined from a minimum of 310 reflections harvested from 24 frames; these parameters were later refined against all data. Data sets were collected targeting full coverage and fourfold redundancy. Data were integrated and corrected for absorption effects with the APEX 3 software packages. Structures were solved by direct methods and refined with the SHELXTL software package. Displacement parameters for all non-hydrogen atoms were refined anisotropically. All hydrogens were assigned to ideal positions and refined using a riding model with an isotropic thermal parameter 1.2 times that of the attached carbon atom.

Table 5.1 Crystallographic Data for **5.1-5.3**

	5.1	5.2	5.3
Formula	C ₂₆ H ₂₇ F ₆ N ₇ O ₆ S ₂ V	C ₂₇ H ₂₇ F ₉ N ₇ O ₉ S ₃ V	C ₃₂ H ₃₃ F ₆ N ₇ O ₁₂ S ₂ V
FW	762.08	864.81	963.71
Color, habit	Green, plates	Brown, needles	Black, plates
T, K	100	293	181
Space group	<i>P</i> 2 ₁ <i>c</i>	<i>P</i> 2 ₁ <i>m</i>	<i>P</i> 6 ₃
Z	0.71073	0.71073	0.71073
<i>a</i> , Å	15.2026	10.242	17.8364
<i>b</i> , Å	10.7668	43.98	17.8364
<i>c</i> , Å	19.9330	17.480	20.9311
<i>A</i> , deg	90.000	90	90
<i>β</i> , deg	109.618	90.901	90
<i>γ</i> , deg	90.000	90	120
<i>V</i> , Å ³	3073.31	7873	5766.8
<i>d</i> _{calc} , g/cm ³	1.65	0.730	1.618
GOF	1.069	1.618	0.992
R ₁ (<i>wR</i> ₂), %	8.2 (19.5)	12.51(37.33)	13.36 (29.39)

5.3.7 Other Physical Methods

Infrared spectra were measured with either a Nicolet 380 FT-IR or Bruker TENSOR II spectrometer. Mass spectrometry measurements were performed in either the positive ion or negative ion mode on a Thermo-Finnigan LTQ mass spectrometer equipped with an analytical electrospray ion source using a 2.5 V spray voltage and 175 °C capillary temperature.

Spectroelectrochemical measurements were performed with a Pine Research Instrumentation gold honeycomb electrode connected to a Gamry Reference 600 potentiostat and an Ocean Optics DH-2000-BAL spectrophotometer. Spectra were collected within 2 minutes of equilibration.

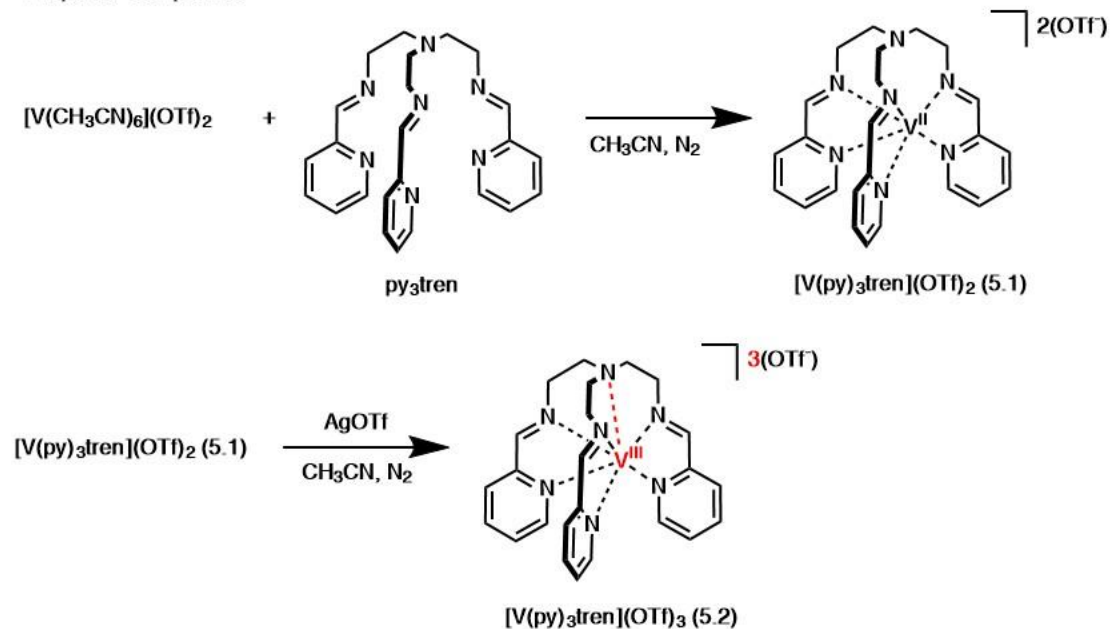
5.4 Results

5.4.1 Synthesis of V(II) Tripod

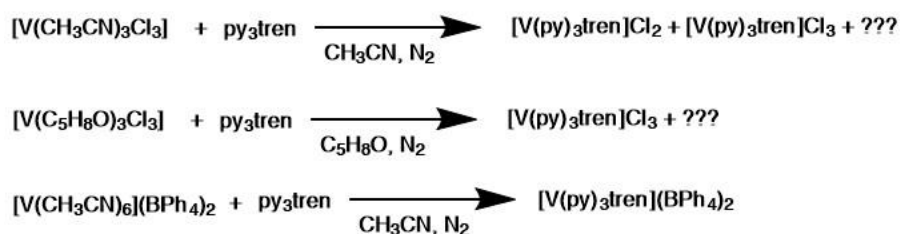
Compound **5.1** is generated under multiple conditions, although the starting material $[\text{V}(\text{CH}_3\text{CN})_6](\text{OTf})_2$ leads to pure product (Scheme 5.1). Preliminary studies with the V(III) starting material $[\text{V}(\text{CH}_3\text{CN})\text{Cl}_3]$ yield a green solution with the same absorbance as compound **5.1** in CH_3CN (Figure A4.2). However, other spectroscopic techniques reveal a mixture of compound **5.1** and **5.2** (Figure A4.1). When the reaction conditions are exchanged from acetonitrile to tetrahydrofuran, a brown product resembling compound **5.2** is produced. The yield increases with a decrease in temperature as -77°C affords ~88% of the crude brown precipitate (Figure A4.2). Due to these complications, V(II) starting materials were pursued with $[\text{V}(\text{CH}_3\text{CN})_6](\text{BPh}_4)_2$. Although $[\text{V}(\text{py})_3\text{tren}]^{2+}$ is present based on the absorbance spectra, the molar absorptivity is much lower than compound **5.1** in the same solvent. Eventually, we found compound **5.1** to be a readily prepared with the procedure in Scheme 5.1.

Scheme 5.1 Prepared and attempted procedures for V(II) and V(III) Tripod

Prepared Compounds



Attempted Procedures



The synthesis and electronic structure of compound **5.3** is much more complex. Compound **5.3**, $[\text{V}(\text{5-CO}_2\text{Me})\text{py})_3\text{tren}](\text{OTf})_2$ is prepared in an analogous method to compound **5.1**. Compound **5.4** is also prepared in a similar fashion to **5.2**. However, compound **5.3** displays solution dependent behavior and spectroscopic signatures of a ligand radical. In this chapter, discussion of **5.3** will be restricted to its crystallographic structure due to its relevance to this chapter's focus on chemical structures. Chapter 6 thoroughly investigates all other components of **5.3** which is referred to as compound **6.1** in that chapter.

5.4.2 Crystallography Results

Compound **5.1** crystallizes via slow diffusion of Et₂O into CH₃CN. The crystal structure exhibits two crystallographically unique triflate ions, supporting the assignment of a V(II) ion in the cation [V(py)₃tren]²⁺. The first coordination sphere is best described as a distorted octahedron compared to trigonal prismatic, based on the calculated shape measure.²¹ The trigonal twist angle, θ , averages to 48.06° which better resembles an octahedral (60°) compared to trigonal prismatic (0°) geometry (Table A4.1). The V-N_{imine} bonds average to 2.127(5) Å whereas the V-N_{py} bonds average 2.146(5) Å due to the geometric constraint within the tripodal ligand motif. These bond distances are consistent with a V(II) ion and a neutral ligand, as shown previously with [V(phen)₃](OTf)₂ (**3.2**). Although the ligand can be reduced to store an electron, the C-C bond distances of the iminopyridine suggests a neutral ligand. Thus, [V(py)₃tren]²⁺ is best described as a V(II) ion with a neutral ligand. Finally, the V-N_{bridge} distance is too large (3.151 Å) to be considered a coordinate covalent bond in the +2 oxidation state.

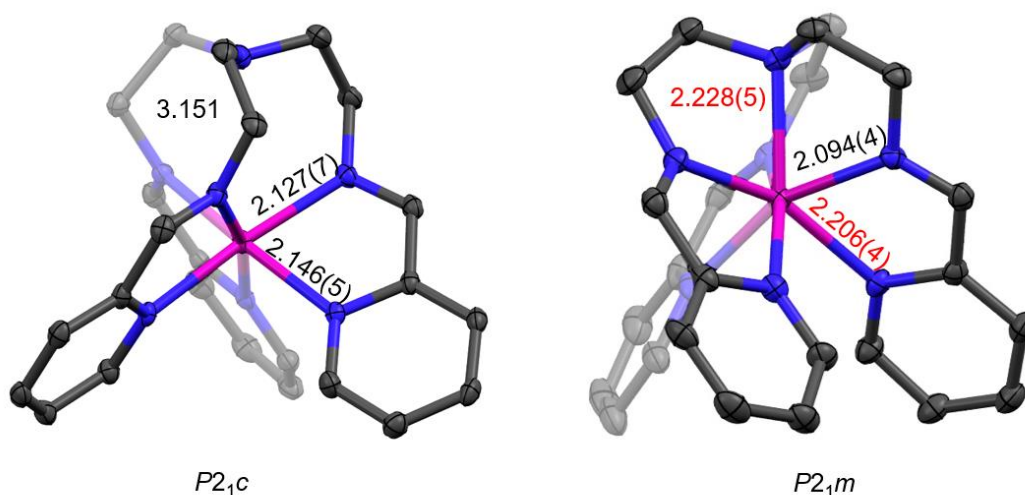


Figure 5.1 Crystal structure of the cationic complexes in compounds **5.1** (left) and **5.2** (right). Hydrogens, anions, and co-crystallized solvent are omitted for clarity. Ellipsoids are set to 40%.

Table 5.2 Continuous shape measure of the metal complexes **5.1-5.3**

Continuous Shape Measure (CShMe)	Octahedral (6)	Trigonal Prismatic (6)	Capped Octahedral (7)	Capped trigonal prismatic (7)
5.1 [V(py) ₃ tren] ²⁺	1.480	14.052		
5.2 [V(py) ₃ tren] ³⁺			0.792	2.439
5.3 [V((5-CO ₂ Me)py) ₃ tren] ²⁺			0.943	2.375

Upon oxidation, the hexacoordinate **5.1** undergoes rearrangement to heptacoordinate **5.2**. Here, the bridgehead nitrogen forms a bond with the metal center ($V-N_{\text{bridge}} = 2.228(5) \text{ \AA}$). This species exhibits the shortest $M-N_{\text{bridge}}$ bond distance for a tren-capped tripodal species, which has previously been held by Mn(II) tripodal species (shortest $Mn-N_{\text{bridge}} = 2.498(5) \text{ \AA}$).^{22,23} Heptacoordinate V(III) complexes have been previously reported, although few exhibit the capped octahedral geometry.^{24,25} Additionally, this tripodal ligand prefers capped-octahedral geometry compared to other multidentate systems.²⁶ In order to conform, the $M-N_{\text{imine}}$ bonds slightly compress to $2.094(4) \text{ \AA}$ whereas the $M-N_{\text{py}}$ bonds elongate to $2.206(4) \text{ \AA}$. Additionally, the average trigonal twist (51.68°) better resembles an octahedral geometry than **5.1**. This conformation highlights the importance of steric constraints in the top (tren) portion of this molecule.

Compound **5.3** exhibits a similar first coordination sphere to **5.2** but with a ligand radical (Figure 5.2). Again, the bridgehead nitrogen forms a bond ($V-N_{\text{bridge}} = 2.213(9) \text{ \AA}$) and best resembles a capped octahedral geometry. The bond lengths of the $V-N_{\text{py}}$ are also contracted relative to compound **5.1**, further suggesting a V(III) metal center. However, the bond lengths for each arm are not within error of each other. In fact, one arm has a number of bonds in the N-C-C-N-M metallocycle significantly shortened (Figure 5.2). In particular, the shortened C-C bond

distance is consistent with a monoreduced iminopyridine previously reported in a Cr(III) system with a monoreduced ((5-CO₂Me)py)₃tren ligand.³

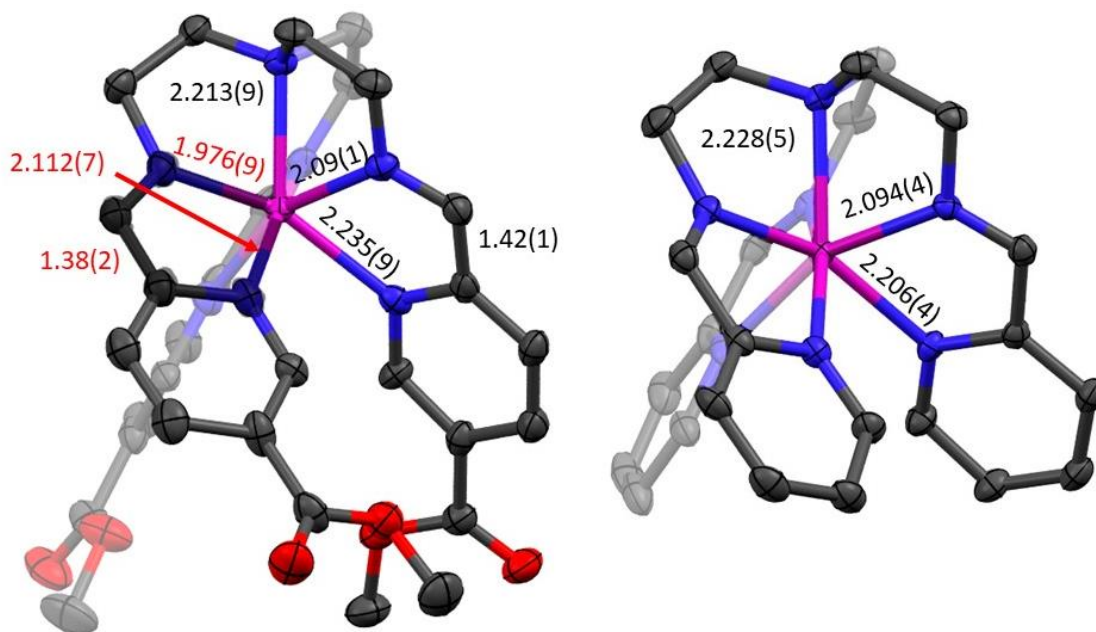


Figure 5.2 Crystal structure of the cationic complexes in compounds **5.3** (left) and **5.2** (right). Hydrogens, anions, and co-crystallized solvent are omitted for clarity. Ellipsoids are set to 40%.

5.4.3 UV-Vis Spectroscopy

Compound **5.1** is deeply colored due to the charge transfer excitation, dominant in the NIR. Due to the high molar absorptivity ($> 1000 \text{ M}^{-1} \text{ cm}^{-1}$) and plausibility to oxidize the metal and reduce the ligand *vide infra*, these excitations are assigned as metal-ligand charge transfer. Additionally, these transitions are red-shifted in reference to the tris-bidentate analogue suggestive of an interaction between the bridgehead nitrogen and the metal center. A similar trend has been previously reported with Cr(III) tripodal complexes.⁵

Compound **5.2** absorbs less visible light compared to **5.1** due to the loss of the charge transfer excitation. The smaller atomic radius of the V(III) ion reduces the orbital overlap between the metal and ligand, requiring higher energy excitation. Additionally, it is much more difficult to

oxidize V(III) to V(IV) compared to V(II) to V(III) based on their ionization energy.²⁷ Thus, the MLCT blue-shifts in these compounds from ~750 nm to ~375 nm.

Additionally, metal-based transitions are observed in the visible region for compound **5.2**. Two sets of transitions are observed with different magnitudes of molar absorptivities. At 774 nm, a weak d-d transition is observed with relatively low extinction coefficients ($26 \text{ M}^{-1} \text{ cm}^{-1}$). This transition is consistent with a spin-allowed, Laporte forbidden transition typical in O_h systems. However, another set of transitions are observed at 506 and 449 with higher extinction coefficients, 351 and $788 \text{ M}^{-1} \text{ cm}^{-1}$ respectively. The extinction coefficients are smaller than expected for a MLCT transition, suggesting these are another set of metal d-d transitions. In part, the reduced symmetry in C_{3v} removes the degeneracy of octahedral t_{2g} orbitals to a_1 and e .

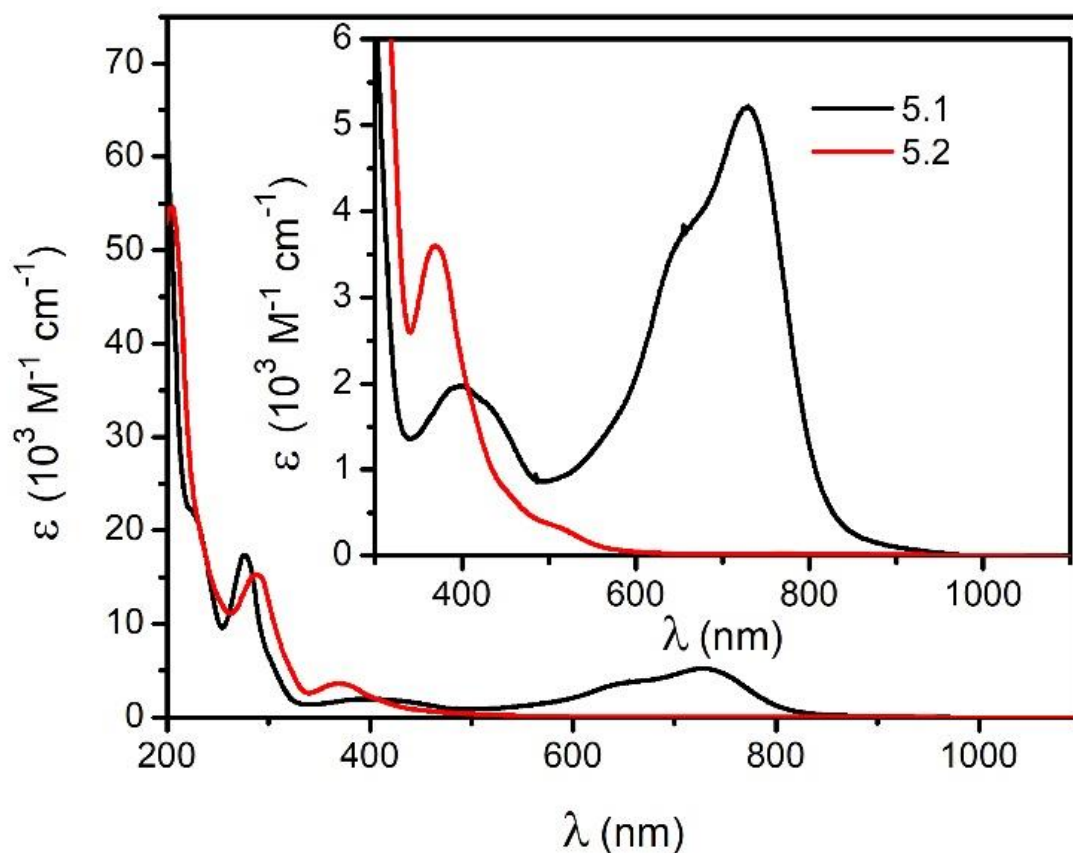


Figure 5.3 Absorbance spectra of **5.1** and **5.2** in CH₃CN.

5.4.4 Electrochemistry

To our surprise, the electrochemical behavior of these vanadium tripodal species resemble that of their Cr(III) analogue. For V(III) tripodal species, there are three reversible reductions and 1 quasi-reversible reduction that in the proximate vicinity of their Cr(III) analogue (Figure 5.4 and Table 5.3).⁴ Additionally, each redox event is well resolved by ~250 mV which should allow for the isolation of each species in the electrochemical series. Compared to previously reported first-row transition metal tripods and the best of our knowledge, this behaviour appears to be exclusive to these two metals.⁵ When the V(II) tripodal species is measured, the same peaks are observed suggesting that only the open-circuit potential of the solution changes. This indicates that the two

species are related by an electrochemical process and the peak is assigned to reduction of the V(III) to V(II). Randles-Sevcik analysis shows that the reduction generates a higher response compared to oxidation. Since both exhibit a linear response, they are indeed reversible transformations. When investigating the difference in the peak-to-peak difference as a function of scan rate, we find three regions in this plot (Figure A4.5 and Figure A4.6):

- 1) linear region when $\nu < 10 \text{ (mV/s)}^{1/2}$
- 2) a plateau region when $10 < \nu < 22.5 \text{ (mV/s)}^{1/2}$
- 3) an increase when $\nu > 22.5 \text{ (mV/s)}^{1/2}$.

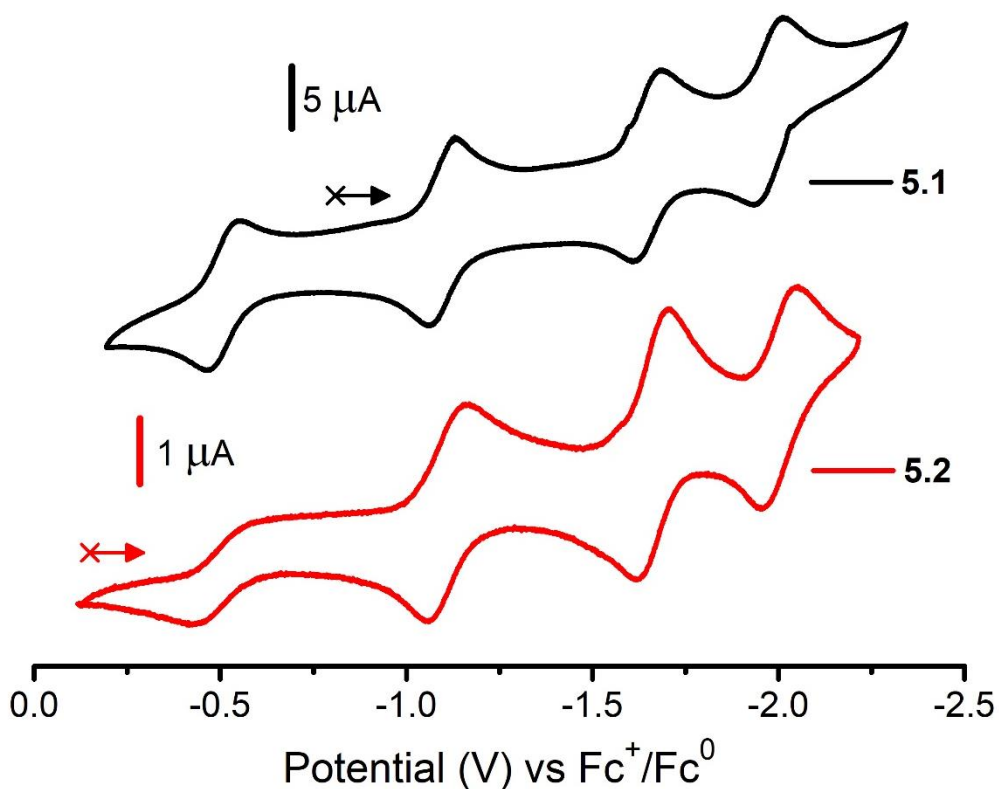


Figure 5.4 Cyclic voltammograms (0.1 V/s) of **5.1-5.2** in 0.1 M Bu₄NPF₆ in CH₃CN. Reduction potentials are tabulated in Table 1. Arrows indicate scan direction and the open circuit potential before each experiment. Compound **5.1** was measured with a Pt working electrode; compound **5.2** was measured with a glassy carbon working electrode.

Table 5.3 Ground state reduction potentials for **5.1** and its Cr(III) analogues.

Redox Event	$E_{1/2} 3+/2+$	$E_{1/2} 2+/1+$	$E_{1/2} 1+/0$	$E_{1/2} 0/1-$	Reference
5.1 - [V(py) ₃ tren] ²⁺	-0.51 (73)	-1.09 (75)	-1.64 (61)	-1.98 (66)	This work
[Cr(py) ₃ tren] ³⁺	-0.45 (71)	-0.93 (70)	-1.55 (77)	-2.44 (160) irr	4

5.4.5 Spectroelectrochemistry

Spectroelectrochemical data supports the reversibility of redox events for these complexes in solution. For compound **5.1**, oxidation exhibits the same absorbance peak seen in **5.2** at 391 nm. Reduction of **5.1** reveals a blue-shift in absorbance to the 660 nm followed by absorbance in the NIR. This is attributed to a ligand radical, as observed in the case of [Cr(5-CO₂Mepy)₃]²⁺.³ Despite incomplete oxidation/reduction in some of these measurements, the compounds exhibit no degradation nor disproportionation to other oxidation states as each redox event is well resolved from its redox neighbor. This allows for direct observation of the mono-reduced species [V(py)₃tren]⁺.

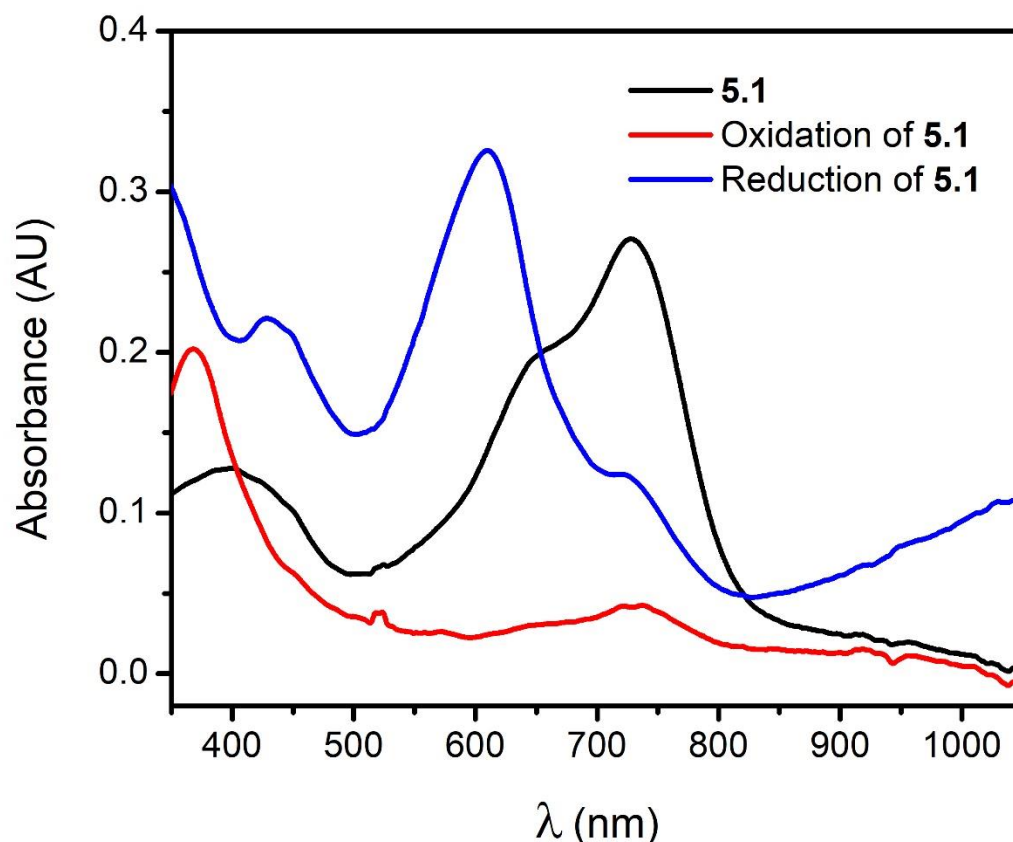


Figure 5.5 Absorbance spectra of **5.1** obtained during electrochemical measurements. Spectra were collected at the open-circuit potential (black), at -0.41 V vs Fc^+/Fc^0 (red), and at -1.19 V vs Fc^+/Fc^0 (blue).

5.4.6 Emission Spectroscopy

With the newly formed $\text{M-N}_{\text{bridge}}$ bond in compound **5.2**, we were optimistic of emission and a long-lived excited state for these species. Previously, tripodal complexes with Ru(II) and Cr(III) were found to display no metal-based emissions at room temperature compared to their tris-bidentate analogues.^{4,28,29} In each system, there are two possible nonradiative decay pathways: (1) the steric constraint of the hexadenate ligand, or (2) intramolecular quenching from the bridgehead nitrogen. Here, we have addressed the second component as a result of the $\text{V-N}_{\text{bridge}}$ bond in compound **5.2**. Due to the lack of emission at room temperature in the visible spectrum, the excited state was either too low in energy to be observed with a typical fluorometer with a

photomultiplier tube, or too short lived to be observed at room temperature. Upon cooling to 77 K in a glassing solvent of 4:1 ethanol:methanol, no emission was observed. Thus, the excited state is either too low in energy to be observable in the NIR, or extremely short lived.

In an attempt to further test these hypotheses, we measured $[\text{Cr}(\text{py})_3\text{tren}](\text{BF}_4)_3$ at 77 K. For Cr(III) iminopyridines, the ^2E excited state is essentially independent of ligand field as shown in d^3 Tanabe-Sugano diagrams. Thus, there emissions lie between 700 to 825 nm (14500-12000 cm^{-1}), which is within the range of a typical fluorometer. For this particular complex, the ^2E excited state is calculated at 810 nm. It should be noted that DFT has generally underestimated the ^2E excited state, thus placing the excited state well within the observable window of our fluorometer. Originally, some of us reported the lack of emission due to the “imposter states” from N_{bridge} that could quench the ^2E excited state.⁴ However, excitation at 355 nm generated a broad peak centered at ~835 nm (Figure A4.7). A similar peak was observed for the free ligand at 810 nm, upon excitation at 355 nm. Thus, this peak is likely a ligand centered emission. The shift in peak is likely due to the heavy atom effect exerted by the Cr(III) center, lowering the energy of the harmonic oscillator. Thus, we can assume that the lack of emission is due to an incredibly short lived excited state within these tripodal species.

5.4.7 Ultrafast Spectroscopy

Ultrafast spectroscopy reveals picosecond excited state lifetimes in compound **5.1**. Excitation of the MLCT at 800 nm initially reveals photoinduced absorption (PA) signals between 375 to 530 nm while a ground state bleach (GSB) is observed between 530 and 650 nm (Figure 5.6 and Figure A4.8). Within 0.4 ps, a new transient is observed as the PA signal is significantly decreased but red-shifted. This PA signal is observed across all wavelengths within the observed spectroscopic window. After 24 ps, the signal is gone and the ground state is recovered. These

excited state lifetimes are much too short to be considered for photoinduced electron transfer or to show emission for most fluorometers (Table 5.4). These results are consistent with the lack of metal-based emission observed in complexes with py₃tren ligands.^{4,29}

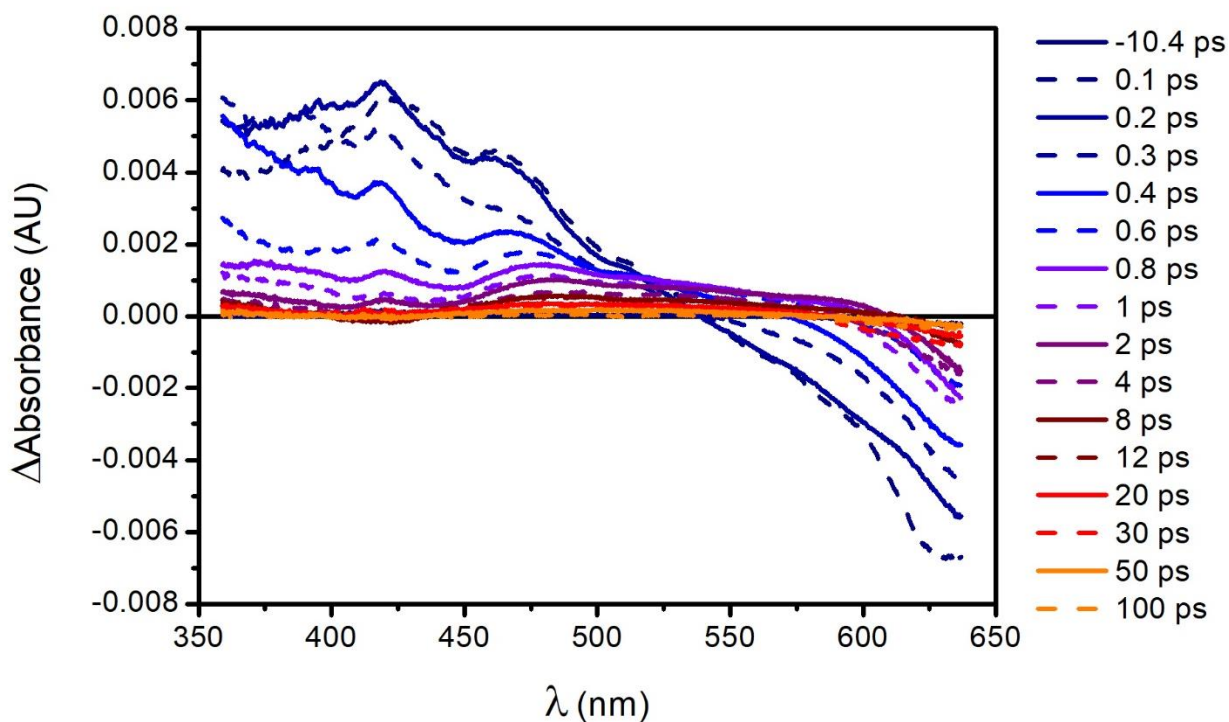


Figure 5.6 Transient absorption spectra of **5.1** in CH₃CN.

Table 5.4 Excited state lifetime of **5.1** in CH₃CN

	τ_1 (ps)	τ_2 (ps)
5.1 – [V(py) ₃ tren] ²⁺	0.4	24

Attempts to assign the excited states in compound **5.1** have failed with various simulations and models. First, we attempted to model the ²E PA signals with computations. We used the calculated visible absorbance spectra of the ground state(Figure A4.17) and excited state(Figure A4.18) to simulate a ΔA spectra for the ²E excited state(Figure 5.7). In this model, a peak PA

signal is expected ~560 nm along with shoulders at ~500 and 450 nm. Unfortunately, this does not adequately match with any of the experimental spectra. Second, we attempted to model a $^2\text{MLCT}$ excited state based on the same method described in chapter 3. A peak PA signal is expected at ~580 nm, along with positive PA signal until 620 nm. Again, the generated spectra does not match any experimental spectra. Third, we attempted to simulate a ligand-to-ligand charge transfer (LLCT) excited state. In a previous study, our group noted how the bridgehead nitrogen and iminopyridine display charge-transfer like absorbance in the NUV region.⁴ Thus, we chose $[\text{Zn}(\text{py})_3\text{tren}]\text{OTf}_2$ whose electrochemical behavior is ligand based. Upon reduction, increased absorbance is observed in the visible region but not in the NIR region (Figure A4.19). This is quite surprising since all investigated compounds in this dissertation display some NIR absorbance upon reduction. Upon oxidation, the absorbance peak is broadened. A $\Delta\text{LLCT}(\?)$ spectra exhibits peak absorbance at ~570 nm and positive PA signal until ~800 nm. Once again, this simulation does not match any computed spectra.

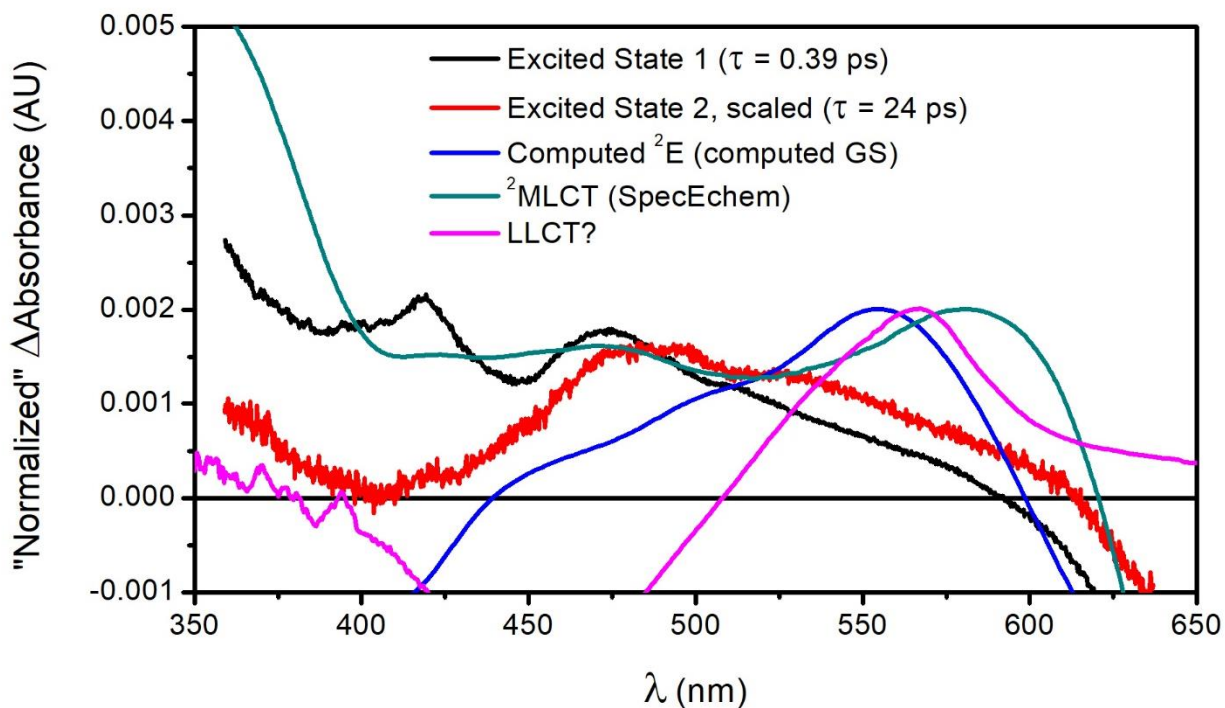


Figure 5.7 Experimental TA spectra (black and red) compared to simulated 2E (blue), 2MLCT (teal), and LLCT (pink) excited states.

Preliminary results of the excited state of compound **5.2** suggests the excited state lifetime is marginally longer. At the moment, the longest-lived excited state is approximately 200 ps compared to 24 ps in compound **5.1**. The low molar absorptivity at excitation in compound **5.2** have made experiments difficult, resulting in low signal and difficulties with further analysis. However, this result supports the lack of emission observed in the previous section.

5.4.8 Calculations

Initial calculations on complex **5.1** suggest a V(II) metal center with neutral ligands in an octahedral (O_h) ligand field. Spin density plots generated for the quartet ground state reveal a cubic α spin localized on the metal, suggesting 3 electrons in the metal t_{2g} orbitals. However, electron density spills unto the tripodal ligand (Figure A4.9). This plot resembles $[V(bpy)_3]^{2+}$ discussed in Chapter 4, where both α and β spin-polarization are seen on the ligand. Important to this tripodal

ligand motif, electron density exists on the apical nitrogen. This suggests interaction with the metal center, introducing “intruder” ligand based excited states as seen in Cr(III) tripods.⁴

Calculations for **5.2** strongly suggest a different electronic structure than **5.1**. With the bridgehead nitrogen acting as a seventh ligand, the first coordination sphere significantly distorts from octahedral(O_h) to capped octahedral (C_{3v}) symmetry. This reduction in symmetry splits the t_{2g} orbitals into a low-lying e and higher energy a_1 sets. The e orbitals are each singly occupied, supporting an $S = 1$ ground spin state. The unoccupied a_1 and e orbitals are initially calculated at 10308 and 15830 cm^{-1} , respectively. Further calculations recalculate these energies as 12900 cm^{-1} (1.60 eV) and 19800 cm^{-1} (2.45 eV) for the a_1 and e orbitals, respectively. Finally, the lower number of unpaired electrons make calculations of **5.2** easier compared to **5.1**. These implications will be discussed further *vide infra*.

With the introduction of the seventh ligand, we became curious about the relationship between the M-N_{bridge} distance and the electronic structure of the **5.2**. These calculations are summarized in Figure M5.5, highlighting the change from capped octahedral to octahedral. The calculations utilized the crystallographic data of **5.1** and **5.2** as the end points. Intermediate structures were geometry optimized with a fixed M-N_{bridge} distance. As M-N_{bridge} distance increases, there is a somewhat linear increase in the energies of the e^* orbitals and exponential decrease in the a_1^* orbital energy. When M-N_{bridge} equals 3.15 Å, the a_1^* orbital is nearly isoenergetic with the low-lying e orbitals. This electronic structure highlights how **5.1** is best described as octahedral. While the molecule still exhibits C_{3v} symmetry, the first coordination sphere once again resembles octahedral symmetry.

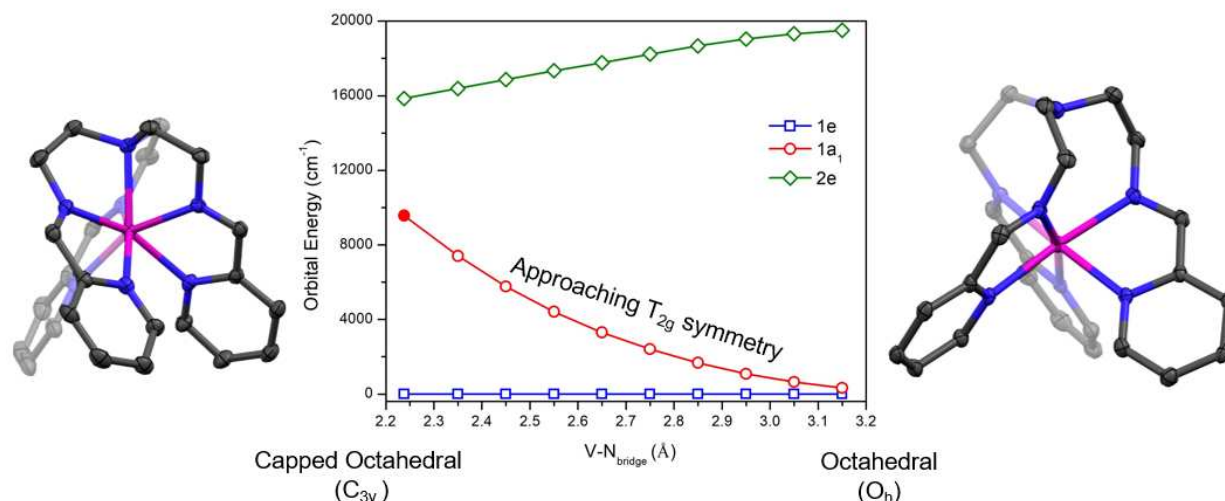


Figure 5.8 Orbital energies of **5.2** as a function of V-N_{bridge} distance.

Since $[\text{V}(\text{py})_3\text{tren}]^{3+}$ is best described as a capped octahedron, the orbital splitting has immediate implications for spin-allowed transitions. Converting from O_h to the C_{3v} point group, the t_{2g} non-bonding orbitals break down to a_1 and e due to loss of degeneracy. To a first approximation, the new orbital assignments are:

- 1) non-bonding $d\pi$ orbital (resembling d_{xz} and d_{yz})
- 2) an antibonding $d\sigma$ orbital (resembling d_{z^2})
- 3) an antibonding $d\sigma^*$ orbital (resembling $d_{x^2-y^2}$ and d_{xy}).

Based on the crystallographically-determined geometry, the energy for a_1^* orbital must be ~ 1.0 eV above the $d(\pi)$ set, and therefore the corresponding $e \rightarrow a_1^*$ (3E) transition must be ~ 1.0 eV.

Comparison of the spin-density plots reveal different degrees of interaction with the bridgehead nitrogen. First, Cr(III) displays interactions consistent with previous results. When the t_{2g} orbitals are splitting into $d\pi$ and $d\sigma$, the amount of spin-density on the ligand differs. In the $d\pi$ case, virtually no spin density is observed on the ligand (Figure A4.10); in the $d\sigma$ case, spin-density is observed on the bridgehead nitrogen (Figure A4.11). Spin density between the bridgehead nitrogen and Cr(III) metal center was previously observed, offering a benchmark for further

calculations.⁴ Second, compound **5.1** displays a large amount of spin-density on the ligand. In the $d\pi$ case, the spin density is largely on the iminopyridine arms (Figure A4.12). The nodes on the iminopyridine resemble those found in V(II) polypyridyls, suggesting the ligand to be acting as a π -donor rather than a π -acceptor.³⁰ In the $d\sigma$ case, the degree of spin density observed on the bridgehead nitrogen is less than that observed on Cr(III). In this case, lewis-acidity of Cr(III) compared to V(II) may lead to a stronger interaction in Cr(III). Third, compound **5.2** interacts more strongly with the ligand overall. In the $d\pi$ case, spin density is delocalized across the entire ligand (Figure A4.14); in the $d\sigma$ case, increased spin density is observed on the bridgehead nitrogen compared to compound **5.1**. The increased interaction between V(III) and the bridgehead nitrogen would suggest increased lewis basicity as the primary reason.

Multireference calculations were performed on the intermediate geometries to accurately determine the energy of metal-based excited states. The results shown in Figure 5.9 summarize the shift in excited state energies of **5.2** as a function of V-N_{bridge} distance. For **5.2** at its ground state geometry, many interesting features are observed. First, there is qualitative agreement between the observed spin-allowed d-d transitions and calculated energies. The $^3A_2 \rightarrow ^3E$ transition is calculated at ~800 nm whereas a d-d transition is observed at 775 nm. The $^3A_2 \rightarrow ^3A_1$ transition is calculated at ~570 nm whereas a d-d transition is observed at 506 nm. The lack of an inversion center removes the Laporte selection rule in these molecules, increasing the extinction coefficient for the $^3A_2 \rightarrow ^3A_1$ transition. Second, the position of the lowest energy singlet (1E) is very close in energy to the 3E excited state. This close proximity should allow for efficient intersystem crossing, especially since the 1E state sits just below the 3E excited state. However, the energy of the 1E excited state remains nearly constant across the intermediate geometries. Thus, vibrational modes may lead to back-intersystem crossing, repopulate the 3E excited state, remain in the triplet manifold, and

vibrationally relax to the ground state. Third, the energies of the 3E and 3A_1 excited states follow the change in energy of the $1a_1$ and $2e$ orbitals in Figure 5.9. These changes are expected since the spin-allowed transitions are ultimately based on the energies of the orbitals. Fourth, the final calculated geometry shows no crossing point between triplet and singlet excited states. The large gap in energy suggests no intersystem crossing through a metal-only excited state manifold. Altogether, these calculations highlight the importance of understanding the distortion of the molecule upon photoexcitation rather than focus on the static ground state.

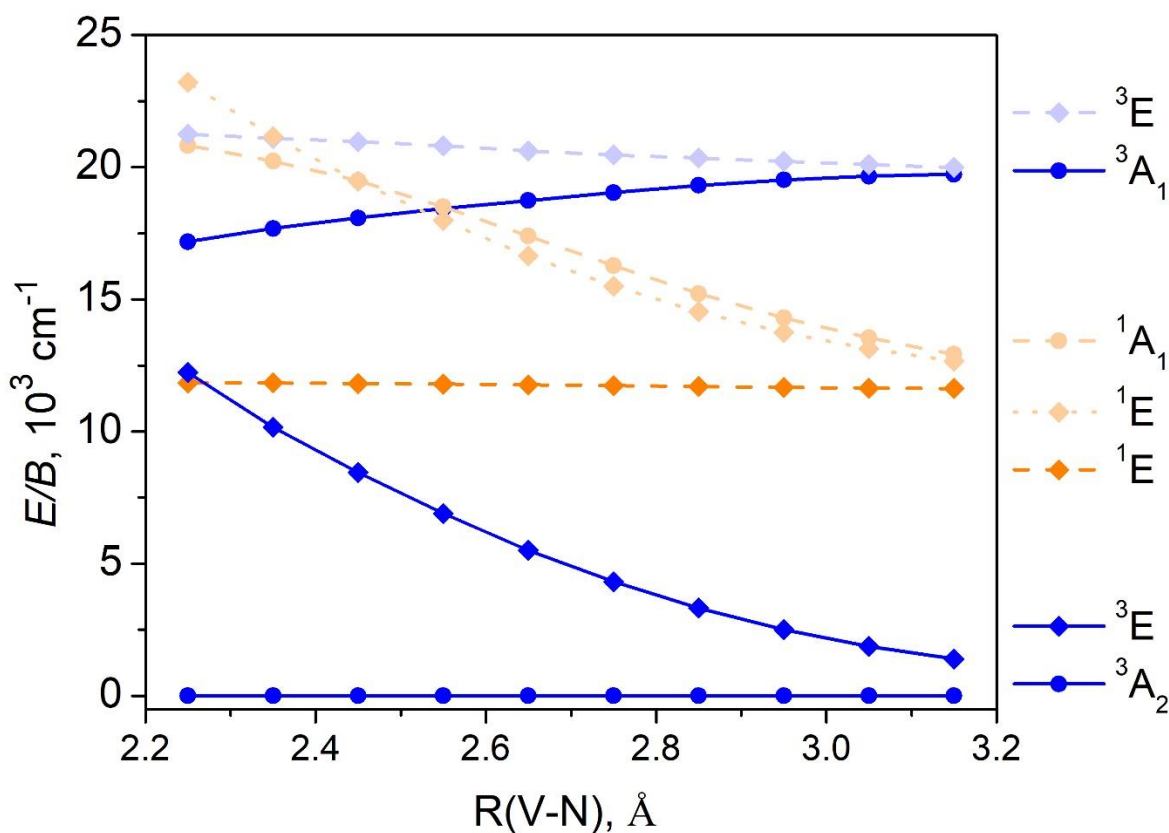


Figure 5.9 Calculated excited state energies of compound **5.2** as a function of V-N_{bridge} distance. The initial points at 2.23 Å represent calculated energies for compound **5.2**. All other points represent calculated geometries. Shaded lines represent excited states relevant to excited state decay.

5.4.9 Utility of SHAPE

We became interested in addressing why the bridgehead nitrogen acts as a seventh ligand for compound **5.2**. Specifically, we were interested in how SHAPE may be used as method to quantify the differences in structures rather than proximity to ideal geometries. Before we delve further, let us briefly discuss the SHAPE program.

SHAPE is designed as a tool to quantify the continuous shape measure for set of coordinates. For compound **5.1**, we start with the coordinates of the first coordination sphere (the 6 bound nitrogens). The program then compares these coordinates to the input geometry from a reference file, which is a set of Cartesian coordinates for that geometry. For an octahedron, these coordinates are (0,0,1), (0,1,0), (1,0,0), (0,0,-1), (0,-1,0), and (-1, 0, 0) for a unit geometry. These coordinates are oriented and scaled to resemble the input coordinates as much as possible. The program focuses on minimizing the distance between the input coordinates and reference coordinates until it generates a minimum value (continuous shape measure). While these values are minimized, it may be difficult to understand the deviation from an ideal geometry. First, the lower the continuous shape measure the better it resembles the input geometry. A continuous shape measure that perfectly matches the ideal geometry would yield a 0. For an arbitrary geometry, a continuous shape measure of 0.10 better resembles that geometry compared to a compound with a continuous shape measure of 1.00. Second, best practices compare two ideal geometries with a minimum distortion pathway. The minimum distortion pathway is a curved plot based on sum of square roots as shown in Equation 5.1, where Φ represents the continuous shape measure.

$$k_{12} = \sqrt{\Phi_1} + \sqrt{\Phi_2} \quad 5.1$$

With this plot, it is easier to visualize how the molecule better resembles one geometry over another geometry. This will be further highlighted in the next section. Third, continuous *shape*

measures are better indicators of distortion than continuous *symmetry* measures since the latter does not consider how the coordinates move in space. For example, a square bipyrdimal structure will generate the same value no matter how elongated the two axial coordinates are relative to the planar coordinates. Thus, the point group is less important than the deviation from a unit geometry.

Now, it is difficult for molecules to perfectly follow the minimal distortion pathway between two geometries. There is often some deviation from a minimal distortion, even for well-documented distortion pathways. Three factors ultimately contribute to the deviations: (1) stereochemistry and electronic preference for a given polyhedron, (2) tendency to maximize use of valence atomic orbitals, and (3) geometrical and steric constraints imposed by the ligands.³¹ In this chapter, I will focus on the ligand contributions as synthetic capabilities allow for manipulation of this parameter. Steric constraints may restrict distortion pathways and impart deviations from idealized paths. For example, an octahedral structure may distort to a trigonal prismatic geometry following a Bailar pathway. A Fe(II) species with 6 monodentate ligands is not limited by chelate rings and follows the Bailar path very closely (deviation average 4.2%). However, a tris-bidentate Fe(II) complex will deviate significantly if the ligand-imposed bite angle is too small.³¹ These restrictions may lead to other distortion pathways, and thus final geometries not easily predicted.

5.4.10 Utilizing SHAPE to map distortion in Extended Tripods

Ultimately, we are interested in modeling the distortion of **5.1** to **5.2** in order to gain insight to nonradiative relaxation pathways. One complication is that the primary coordination sphere of compound **5.1** is best described as a 6-coordinate octahedron, whereas **5.2** is best described as a 7-coordinate capped octahedron (COC). SHAPE may generate distortion pathways between 2 geometries, if they have the same number of vertices (ligands). Thus, we prepared a 7-coordinate “tren-capped octahedron”(tren) shape to describe **5.1** (Scheme A4.1). This shape utilizes the

coordinates of an ideal octahedron but adds another vertex ~1.47 units away from the center, mimicking the distances in $[\text{Fe}(\text{py})_3\text{tren}]^{2+}$. This new reference geometry allows for a shape map between Φ_{COC} and Φ_{TREN} . Unfortunately, the values for **5.1** and **5.2** do not sit along the minimal distortion pathway between capped octahedral and “tren-capped octahedral.” (Figure 5.10). Additionally, the intermediate geometries calculated through constrained optimization procedure (*vide supra*) do not lie on the minimal distortion pathway, but resemble a similar curvature to the minimal distortion pathway. Thus, the steric constraints of the ligands generate deviation from the minimal distortion pathway which range from 28 to 43% based on the various geometries. Again, if we only concern ourselves with distortion between **5.1** and **5.2** then the continuous shape measure from **5.1** may quantify that distortion pathway. The primary coordination sphere and apical nitrogen in compound **5.1** were used as vertices for the reference geometry. Continuous SHAPE measure were plotted against the V-N_{bridge} distance (Figure 5.11). Interestingly, the plot resembles the increase in orbital energy for $1a_1$ in Figure 5.8.

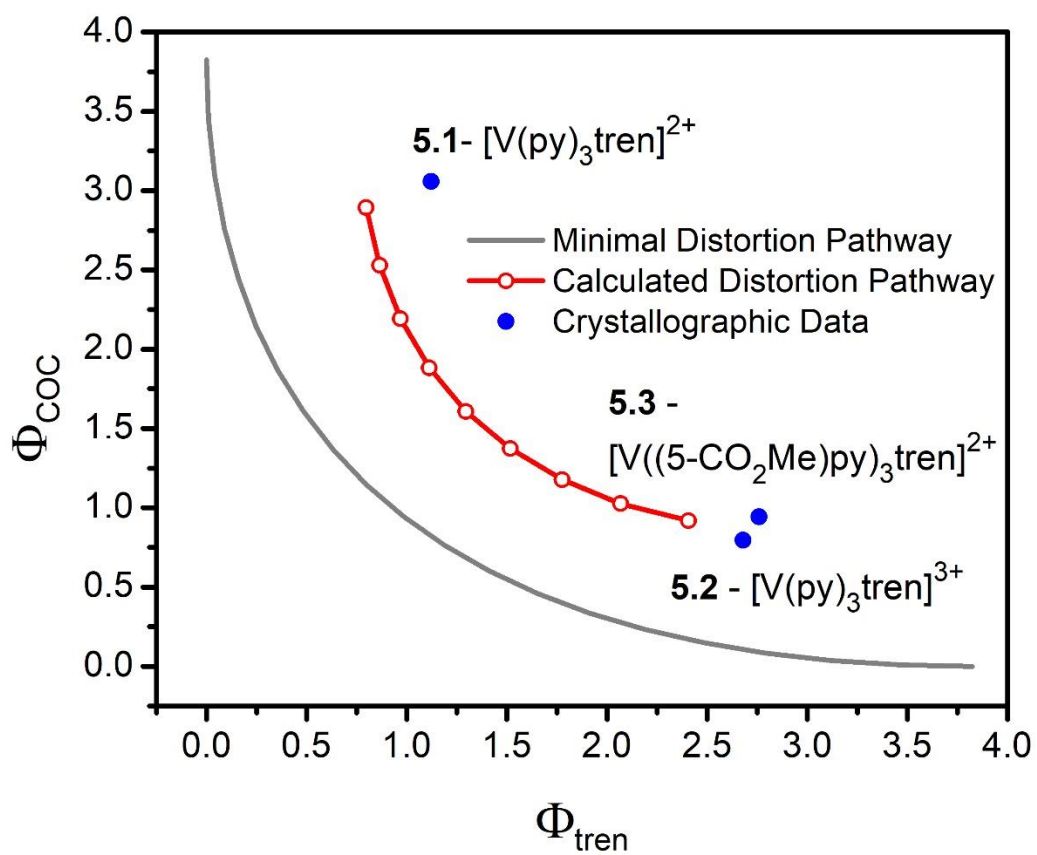


Figure 5.10 Continuous shape measure of capped octahedral (Φ_{coc}) and tren-capped octahedral (Φ_{tren}) for **5.1** and **5.2**. The minimal distortion pathway (grey) and calculated distortion pathway (red) are plotted for comparison.

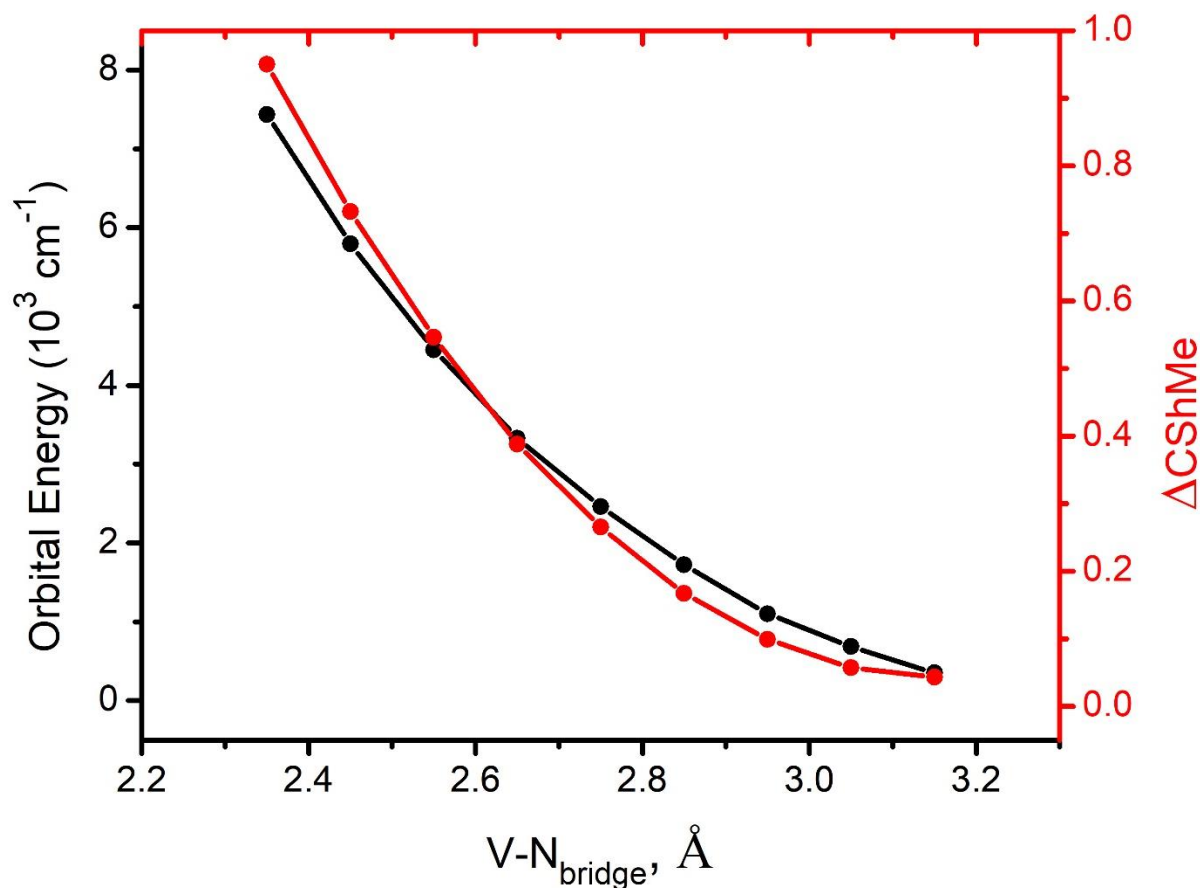


Figure 5.11 Orbital energy of **5.2** at intermediate geometries and continuous shape measure relative to **5.1** as a function of the V-N_{bridge} distance.

5.4.11 Quantifying Distortion in Other Excited State Proxies

Previous reports by Alvarez and colleagues have successfully correlated geometry to several physicochemical properties in [FeN₆]²⁺ complexes.³¹ In one study, the LS ground state and transient HS excited state collected through picosecond X-ray absorption spectroscopy were shown to model similar trends.³² Their results suggested that this methodology could be applied to other systems such as Cu(I) photosensitizers. In tetrahedral Cu(I), MLCT excitation induces Jahn-Teller distortion towards a square-planar Cu(II) complex with a ligand radical.³³

We propose that understanding the electronic structure of the two geometries is the best predictor of distortion and determination of routes for non-radiative decay. We utilized SHAPE to

quantify the differences between the ground state and excited state proxy, generating a reference geometry based on the first coordination sphere of the ground state. For the excited state proxies, we considered models that reasonably mimic the expected distortion. For example, a low-spin, singlet Fe(II) complex will distort to a high-spin, quintet Fe(II) species upon photoexcitation. Thus, crystallographic data of the low-spin and high-spin structures from a spin-crossover Fe(II) complex could serve as an ideal model in our studies. We utilized both computed structures and crystallographic data, when available, to understand these distortions (Table 5.5). The results suggests that complexes with a short excited state lifetime tend to have large continuous shape measures ($\Delta\text{CShMe} > 1$). Naturally, a compound that significantly distorts from the ground state will undergo several vibrational modes of relaxation. The converse of this result - if long-lived excited states, then small distortion - is not always true with the models used here. These results highlights the competition between electronic and steric effects when understanding the excited state manifold.

Table 5.5 summarizes a cursory attempt to correlate excited state lifetimes to geometric distortion. Some of us have investigated SCO in Fe(II) tripodal systems, attempting to prepare SCO complexes with different substituent groups.³⁴ This SHAPE analysis was performed on the computed HS $[\text{Fe}(\text{py})_3\text{tren}]^{2+}$ relative to its LS state, generating a continuous shape measure of 1.281. For $[\text{Fe}(\text{py})_3\text{tren}]^{2+}$, the short excited state ($\tau = 8$ ps) is attributed to the change in spin-state brought about by structural distortion.³⁵ Additionally, $[\text{Ru}(\text{bpy})_3]^{2+}$ is a common photosensitizer with a long-lived $^3\text{MLCT}$ excited state ($\tau = 890$ ns) with two different proxies for our analysis. First, we consider $[\text{Ru}(\text{bpy})_3]^{3+}$ in the same vein we chose **5.2** as a proxy for **5.1**. The differences in the continuous shape measure are negligible as $\Delta\text{CShMe} \sim 0$. Second, we considered a computed $^3\text{MLCT}$ excited state structure where the ligand radical shortens the Ru-N bond distance in one

arm.³⁶ In This change distorts the O_h coordination sphere towards C_{2v} symmetry. Again, the changes based on the continuous shape measure are still minimal (0.086) with this new proxy.

Table 5.5 Changes in continuous shape measure between ground state and excited state proxy

Ground State	Excited State Proxy	$\Delta CShMe$	τ (ns)	Distortion	References
$[V(py)_3tren]^{2+}$	$[V(py)_3tren]^{3+}$	1.115	0.029	$O_h \rightarrow C_{3v}$	This work
$[Ru(bpy)_3]^{2+}$	$[Ru(bpy)_3]^{3+}$	0.014	890		37
	3MLCT	0.08618	890	$O_h \rightarrow C_{2v}$	36
$[Fe(py)_3tren]^{2+}$	HS $[Fe(py)_3tren]^{2+}$	1.281	0.008	$O_h \rightarrow C_{3v}$	34

Predicting the excited state geometry appears to generally depend on the distortion on the metal center rather than changes on the ligand. In the case of compound **5.1**, we have been using **5.2** as an excited state proxy for the 2MLCT excited state. The 2MLCT does contain a V(III) metal center but also a ligand radical on the iminopyridine. Compound **5.3**, $[V(5-CO_2Mepy)_3tren]OTf_2$ contains a V(III) metal center and ligand radical on the iminopyridine based on the crystallographic data. The first coordination sphere is best described as a capped octahedral (0.943), with a similar V- N_{bridge} bond distance (2.213(9) Å). The electronic structure of this compound is quite complicated and will be discussed further in Chapter 6. For the moment, compound **5.3** demonstrates that our method to proxy the excited of **5.1** with compound **5.2** is reasonable. This further supports our hypothesis that understanding the changes to the first coordination sphere will advance our knowledge of the excited state manifold.

However, we must remember that these values are qualitative measures of the distortion within the molecule. SHAPE scales the coordinates of the reference geometry to lower the continuous shape measure during a fit. Thus, the effects of bond elongation/contraction are minimized and the value will be lower than expected. This effect is particularly difficult with first-row transition metal ions, which tend to undergo a change in their ionic radii upon changes in

oxidation state or spin-state. Thus, these values offer qualitative insight into the geometric distortion in these excited states.

5.5 Discussion

5.5.1 Electronic Structure of Heptacoordination vs Hexacoordination

Originally, we were very surprised to reach the heptacoordinate species **5.2** in this tripodal iminopyridine ligand scaffold. The apical nitrogen has often been considered as a possible ligand, but the distance to the metal center has always been larger than the sum of their van der Waal radii. This result demonstrates that the apical nitrogen can bond to the metal center, and is not restricted due to steric constraints of the ligand. Cadmium(II) tren-capped sarcophagenes are another example where all the nitrogens are bond to the metal center.³⁸ This opens up the possibility of tuning the ability to bind by changing the hybridization in the ligand backbone (Figure 5.12).

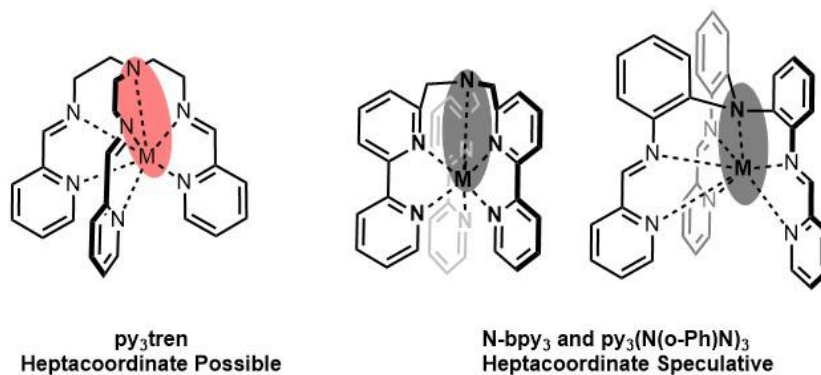


Figure 5.12 Nitrogen-capped tripodal complexes where the nitrogen has questionable interactions with the metal center

This system allows for the direct comparison of a complex between a hexacoordinate and heptacoordinate analogue, to identify structural motifs that enable such changes in the first coordination sphere. First, let us consider other tripodal Schiff base ligands. In these systems, the ability for the bridgehead nitrogen to form a bond is largely dependent on the metal center. Metal

centers such as LS Fe(II) exhibit a preference for octahedral geometry whereas HS Fe(II) do not. The electronic preference based on the metal center appears to be an important indicator on the preferred geometry but not the ability to form a bond with the bridgehead nitrogen. Even at its shortest distance (3.048 Å),³⁹ the Fe-N_{bridge} distance is much too large to be considered a chemical bond. Now, one may argue that the expansion of Fe(II) between LS to HS limits the ability to form a bond with the bridgehead nitrogen. Indeed, the ionic radii increases from 0.61 Å to 0.78 Å from LS to HS. However, HS Mn(II) exhibits a short Mn-N_{bridge} distance of 2.489(5) Å,²² despite having a larger ionic radii (0.830 Å) than HS Fe(II).⁴⁰ Altogether, the choice of the metal center appears most important whether a bond will form between the bridgehead nitrogen.

Now, let us consider systems where the bridgehead nitrogen may interact to form a chemical bond with the metal center. In other ligand sets, the bridgehead nitrogen have been speculated to interact with the metal center and lead to unexpected properties. For example, N-bpy in Figure 5.12 does not show an emission at room temperature when chelated to Ru(II) or Cr(III).²⁸ This is unexpected as the electronic properties are similar to the tris-bidentate analogue, suggesting that the bridgehead nitrogen is involved in a nonradiative decay pathway. Unfortunately, no crystal structure exists to determine the proximity of the bridgehead nitrogen to the metal center and how it may interact. Additionally, we may speculate how another ligand set such as py₃(N(o-Ph)N)₃ may/not interact with the metal center. When one compares the limited number of py₃(N(o-Ph)N)₃ complexes to their py₃tren analogue, the M-N_{bridge} distances are ~0.15 Å longer.⁴¹ Here, the steric constraint of the aromatic carbons in the capping ligand may restrict the proximity of the N_{bridge} to the metal center. Thus, it would be interesting to investigate the crystal structure of the V(III) analogues and see whether a bond forms with the N_{bridge}. The distance may provide information

into the strain on the capping ligand imposed by the V(III) metal center attempting to form a 7th bond.

5.5.2 Addressing assumptions when using 5.2 as a proxy for the excited state of 5.1

In an octahedral environment, there are numerous similarities between the d² and d³ metal-centered ligand field states (Figure A4.16). A Tanabe-Sugano diagram of d² systems reveals the lowest spin-allowed and spin-forbidden transition to be ³T_{2g} and ¹E_g, respectively. In the d³ system, the lowest spin-allowed and spin-forbidden transitions are ⁴T_{2g} and ²E_g. In both cases, the spin-allowed transition, ³T_{2g} and ⁴T_{2g}, increase linearly as a function of ligand field whereas the spin-forbidden transition, ¹E_g and ²E_g, are constant across ligand field strengths. These similarities and the reduced number of microstates, compared to other transition metals, make **5.2** optimal for understanding the effect of coordination geometry in light-absorbing materials.

I note that compound **5.2** does not consider the effects the ligand radical may have in the ²MLCT, whereas **5.3** does, and thus the latter might be a better proxy for a charge transfer excited state. In compound **5.2**, each V-N_{Imine} and V-N_{Py} distance is similar enough to be considered C_{3v} symmetrical. In compound **5.3**, the anionic ligand radical draws one arm towards the V(III) core and reduces the symmetry to C_{2v}. The reason **5.2** and **5.3** display similar differences in the continuous shape measure relative to **5.1** is due to the differences between “tren-capped octahedral” and capped octahedral. In a scenario where the metal center retains the same coordination geometry, then this assumption becomes important. As seen with [Ru(bpy)₃]²⁺ in Table 5.5, ΔCShMe may range from 0.01 to 0.08. Larger data sets may help reveal what is a statistically significant difference between different coordination spheres and better appreciation of the quantitative degree of distortion. At the moment, our attempts to understand these differences are qualitative descriptors of the importance of geometry in excited state dynamics.

5.5.3 Implications of the continuous shape measure and possible correlation to reorganization energy

As previously stated, a limit of SHAPE is the scaling of the reference geometry to the investigated structure. At the moment, there is no method to turn-off the scaling function in the program. Should a feature exist in a future update, SHAPE would provide a quick, first approximation to calculate the reorganization energy of transition metal complexes.

Here, we used the two crystal structures of **5.1** and **5.2** to approximate the reorganization energy between capped octahedral and octahedral geometries in these tripodal systems. Typically, the reorganization energy of a compound may be calculated from the self-exchange reaction of the two species with 2D EXSY⁴²; however, the fast nuclear relaxation in these species makes assignment of peaks futile. Typically, solvent peaks are observed while peaks associated with the compound are not present. The reorganization energy of a molecule (λ_{in}) may be calculated using the following equations:

$$\Delta G_{in}^* (mdyn \text{ \AA}) = \frac{\lambda_{in}}{4} \quad 5.2$$

$$\lambda_{in} (mdyn \text{ \AA}) = \frac{1}{2} \sum k_i (\Delta d_0)^2 \quad 5.3$$

$$k (mdyn \text{ \AA}^{-1}) = 5.89 \times 10^{-7} v^2 m_L \quad 5.4$$

In equation 5.3, k represents the force constant of the vibrational mode under investigation and Δd_0 (Å) represents the changes in bond-length. In equation 5.4, v (cm⁻¹) represents the frequency of the vibrational mode and m_L (amu) represents the mass of the moved atom. In our system, $m_L = 14$ amu (the mass of a nitrogen atom) and $v = 231$ cm⁻¹ for the reduced average value of the vibrational modes in compound **5.1** distorting towards capped octahedral. Thus, $f = 0.44$ mdyn Å⁻¹. During the vibrational mode, the V-N_{bridge} distance changes by 0.35 Å while the other

V-N distances are essentially unchanged. This results in $\lambda_{\text{in}} = 0.027$ mdy $\text{\AA}$ based on equation 5.3. Finally, we compute that $\Delta G_{\text{in}} = 0.0067$ mdy $\text{\AA} = 4.033$ kJ mol⁻¹ for this vibrational mode.

The total reorganization energy for the conversion from compound **5.1** to **5.2** was calculated using the four-point method.⁴³ First, the total energy of **5.1** and **5.2** are calculated at their optimized geometry (**5.1**_{initial} and **5.2**_{initial}). Second, we consider **5.2** as an excited state to **5.1** and calculate the total energy of **5.1** at the geometry of **5.2** (**5.1**_{final}) to mimic a vertical transition. Afterwards, we calculate the total energy of **5.2** at the optimized geometry of **5.1** (**5.2**_{final}). These two new points, **5.1**_{final} and **5.2**_{final}, represent vibrational states for their corresponding potential energy surface. The energy differences for **5.1** (**5.1**_{final} – **5.1**_{initial}) and **5.2** (**5.2**_{final} – **5.2**_{initial}) are summed to yield the total reorganization energy. Here, the total reorganization energy equals 28.22 kJ mol⁻¹, a value relatively low compared to change in the coordination number.⁴² While this value is a bit on the low end, the implications on the electronic structure are still quite large.

5.5.4 Excited state dynamics in tripodal systems

Despite various spectroscopic techniques at our disposal, no technique has adequately identified any excited states in compound **5.1**. We were fortunate in chapter 3 to assign a ²MLCT excited state using spectroelectrochemistry and propose the population of a doublet excited state manifold. Here, the proposed doublet excited states (²MLCT and ²E) do not match any of the experimental spectra. We cannot prove or disprove whether ISC is present and a doublet excited state manifold exists in this complex. As a result, the excited state dynamics of this tripodal system is severely underdeveloped.

However, we can propose a relaxation pathway by understanding the distortion pathway between compound **5.1** to **5.2** (Figure 5.13). First, we can expect compound **5.1** to distort from an octahedral geometry towards capped octahedral. We base this hypothesis as MLCT excitation

would yield a V(III) metal center and ligand radical. Compound **5.3**, which resembles a V(III) metal center with a ligand radical, is best described as capped octahedral for its first coordination sphere. Additionally, compound **5.2** shares a similar first coordination sphere to compound **5.1**. While compound **5.1** is distorted from its ground state geometry, the system is “spring loaded” in this MLCT excited state. While the excited molecule may possibly release this energy as a photon, it chooses to vibrationally relax to its original geometry. This change in geometry requires at least $28.22 \text{ kJ mol}^{-1}$ (0.29 eV) in reorganization energy, but is significantly less energy than emitting a photon of higher energy.

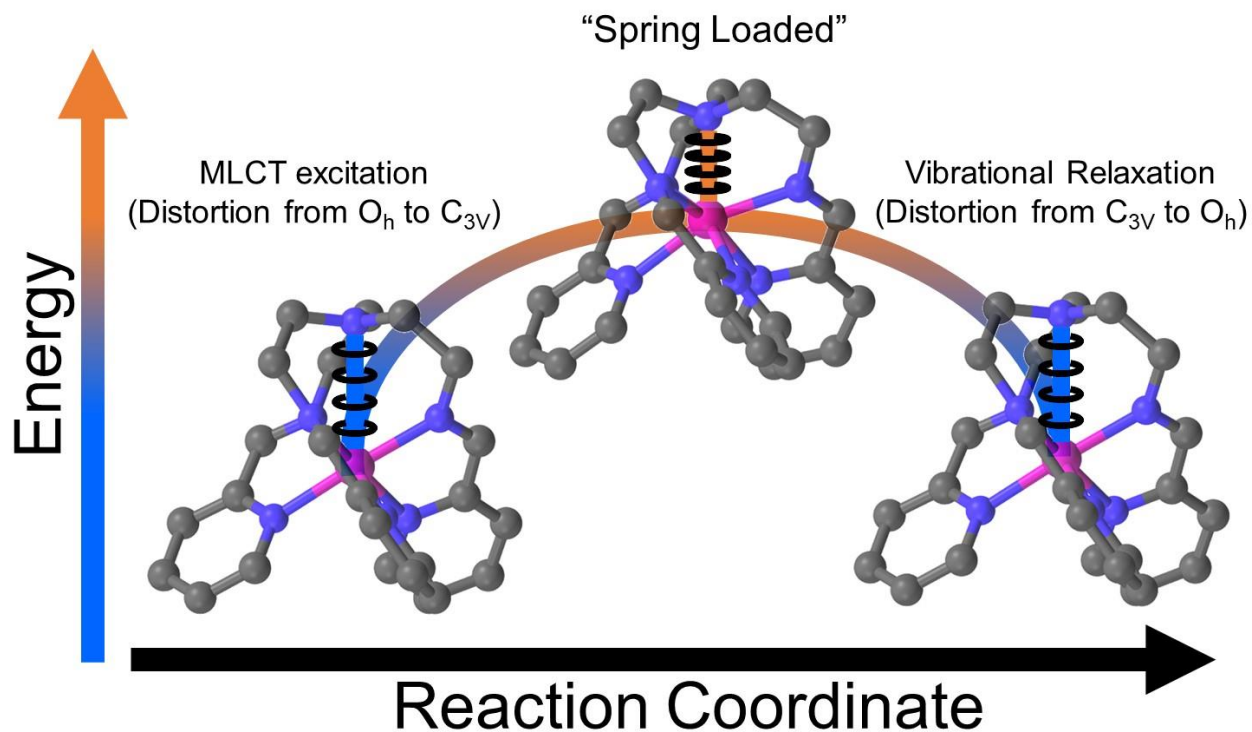


Figure 5.13 Proposed reaction coordinate diagram for compound **5.1** upon MLCT excitation

5.6 Conclusion

Here, we have attempted to understand the photophysical properties of the hexacoordinate compound **5.1** by using the heptacoordinate compound **5.2** as a proxy for the excited state. The bridgehead nitrogen in these tripodal systems will act as a seventh ligand based on the electronic

preferences of the metal center. These results suggests that this ligand is not limited by steric constraints to be heptacoordinate.

Additionally, we utilized the SHAPE program to help model the excited distortion to a first approximation, and quantify the distortion. First, the distortion pathway for our user-defined “tren-capped octahedral” towards capped octahedral resembles the same curvature in the minimal distortion pathway. This difference may provide a qualitative description of the steric constraint in the ligand from a minimized distortion pathway. Second, we used SHAPE to quantify the distortion between 2 different crystal structures. When we choose appropriate crystal (or computed) structures to proxy for the ground state and excited state of various chromophores, we were able to quantify the distortion between these two structures. If the distortion is too large ($\Delta\text{CShMe} \sim 1$), it is best to work to understand the excited state geometry rather than the ground state to determine excited state dynamics. Third, SHAPE can also serve as an approximation for reorganization energy in transition metal complexes. Since the electronic properties are dependent on the geometry of the first coordination sphere, this simple provides a qualitative description of the reorganization energy. Large differences in continuous shape measures yields large reorganization energies. As a result, large reorganization energies leads to more non-radiative decay pathways and an overall lower excited state lifetime. This last feature is currently system dependent and will require calibration for each metal center to provide a more quantitative description.

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Chapter 6: Efforts Towards Understanding the Electronic Structure of $[V((5\text{-CO}_2\text{Me})\text{py})_3\text{tren}]^{2+}$

6.1 Introduction

Electronic structure helps design efficient materials in areas such as catalysis, sensing, and magnetism. In Chapter 5, the electronic structure of a V(II) tripodal complex with ester substituent groups (**5.3**) was not well-defined due to conflicting results between experiments. Here, we will discuss the spectroscopic signals of **5.3** under various conditions and propose two possible explanations of these results: speciation or valence tautomerism.

6.2 Division of Labor

All work in this chapter was performed by Romeo Portillo.

6.3 Experimental Section

6.3.1 Preparation of Compounds

Manipulations and syntheses of all metal complexes were performed inside a dinitrogen-filled glovebox (MBRAUN Labmaster 130). All solvents were sparged with dinitrogen, passed over molecular sieves, and degassed prior to use. The compounds $[V(\text{CH}_3\text{CN})_6](\text{OTf})_2$,¹ py_3tren ,² and $(5\text{-CO}_2\text{Mepy})_3\text{tren}$ ³ were prepared according to literature procedures.

$[V(5\text{-CO}_2\text{Mepy})_3\text{tren}](\text{OTf})_2$ (**6.1**)

Please refer to compound **5.3** for preparation of this compound. Due to the different forms observed in solution, the distinction **6.1A** or **6.1B** will be used as a shorthand description of the form being discussed. Form **6.1A** will refer to a V(II) metal with neutral ligand; form **6.1B** will refer to a V(III) metal with a ligand radical

$[V(5\text{-CO}_2\text{Mepy})_3\text{tren}](\text{OTf})_3$ (**6.2**)

Please refer to compound **5.4** for preparation of this compound.

6.3.2 Electrochemical Studies

Voltammograms were recorded with a CH Instruments 1230A potentiostat in a glovebox under a dinitrogen atmosphere. All experiments used 0.1 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) solution in acetonitrile with a 0.25 mm carbon working electrode, Ag wire quasi-reference electrode, and a Pt wire auxiliary electrode. Reported potentials are referenced to the ferrocenium/ferrocene ([C₅H₅)₂Fe]⁺/[(C₅H₅)₂Fe], Fc⁺⁰) redox couple and were determined by adding ferrocene as an internal standard at the conclusion of each electrochemical experiment.

6.3.3 Photophysical Studies

Electronic absorption spectra were obtained with either a Hewlett-Packard 8453 or Ocean Optics DH-2000-spectrophotometer in a quartz cuvette with a 1 cm path length; experiments were performed at room temperature, unless specified.

6.3.4 Magnetic Measurements

Solid-state magnetic property data for compound **6.1** were collected using a Quantum Design MPMS XL SQUID magnetometer. Powdered microcrystalline samples were loaded into polyethylene bags and inserted into a straw before transportation to the magnetometer. The presence of ferromagnetic impurities was probed by a variable field analysis (0 to 10 kOe) of the magnetization at 100 K (Figure A5.6). Lack of curvature in the M vs H plots for **6.1** indicate the absence of significant ferromagnetic impurities. Magnetic susceptibility data were collected at temperatures ranging from 2 to 300 K. Data were corrected for the diamagnetic contributions of the sample holder and bag by subtracting empty containers; corrections for the sample were calculated from Pascal's constants.⁴ The magnetic susceptibility data were fit to the spin Hamiltonian of general form described in equation 6.1, using the program PHI.⁵

$$\hat{H} = -2(\hat{S}_i \cdot \hat{S}_j) \quad 6.1$$

6.3.5 Other Physical Methods

Infrared spectra were measured with either a Nicolet 380 FT-IR or Bruker TENSOR II spectrometer. Mass spectrometry measurements were performed in either the positive ion or negative ion mode on a Thermo-Finnigan LTQ mass spectrometer equipped with an analytical electrospray ion source using a 2.5 V spray voltage and 175 °C capillary temperature. Spectroelectrochemical measurements were performed with a Pine Research Instrumentation gold honeycomb electrode connected to a Gamry Reference 600 potentiostat and an Ocean Optics DH-2000-BAL spectrophotometer. Spectra were collected within 2 minutes of equilibration.

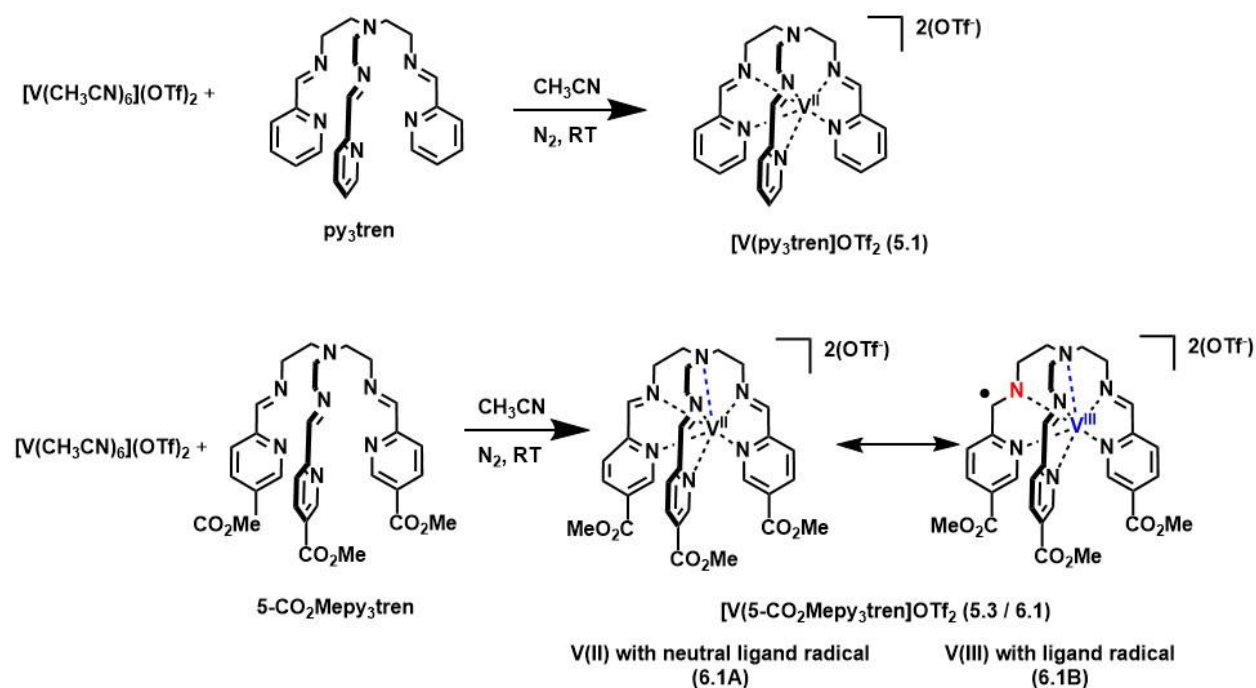
6.4 Results and Discussion

6.4.1 Syntheses of Compounds 6.1-6.2

Compounds **6.1** and **6.2** were prepared in a similar fashion to their parent compounds **5.1** and **5.2**. The V(II) starting material is stirred in a solution of the ligand, as shown in Scheme 6.1. In the case of **5.1**, the solution becomes deep green whereas **6.1** turns a black. Diffraction quality crystals of **6.1** were obtained via diffusion of diethyl ether into a concentrated methanol solution. Aprotic mother liquors such as CH₃CN and CH₂Cl₂ failed to yield diffraction quality crystals. Additionally, compound **6.1** is not very soluble in ethanol, limiting the concentrations at which cryogenic spectroscopic techniques may be performed.

Compound **6.2** was prepared via oxidation with AgOTf, as the metal precipitate can be separated via filtration over Celite. Direct synthesis of **6.2** with a V(III) starting material has not been attempted but may provide a useful alternative with an increased yield.

Scheme 6.1 Preparation of **5.1** and **6.1**



6.4.2 Crystallographic Results

Crystallographic data of **6.1** provides the strongest evidence to suggest a V(III) ion bound to a singly reduced ligand (Figure 6.1). The geometry best resembles a capped octahedral geometry similar to compound **5.2**. The bridgehead nitrogen forms a bond with the vanadium, suggesting a V(III) metal center rather than a V(II) core. The implications of a V(III) core would suggest three charge balancing anions in the crystal structure which is not observed. Only two triflate anions are observed per metal complex. Rather than third anion, the ligand displays shortened bond distances suggesting a radical. When one compares the V-N bond distances, the bond distances are $\sim 0.1 \text{ \AA}$ shorter compared to the other arms (Figure 6.1). Additionally, the C-C bond between the imine and pyridine carbon is $\sim 0.04 \text{ \AA}$ than the other arms. Similar bond contraction have been observed in the chromium analogue, further suggesting a monoreduced iminopyridine arm.³ It is important to note that the structure of **6.1** was taken at 181 K. Due to instrument limitations at the time of

collection, the structure could not be collected at lower temperatures. Thus, in the event of valence tautomerization this structure is not fully **6.1A** with some mixture of **6.1B**.

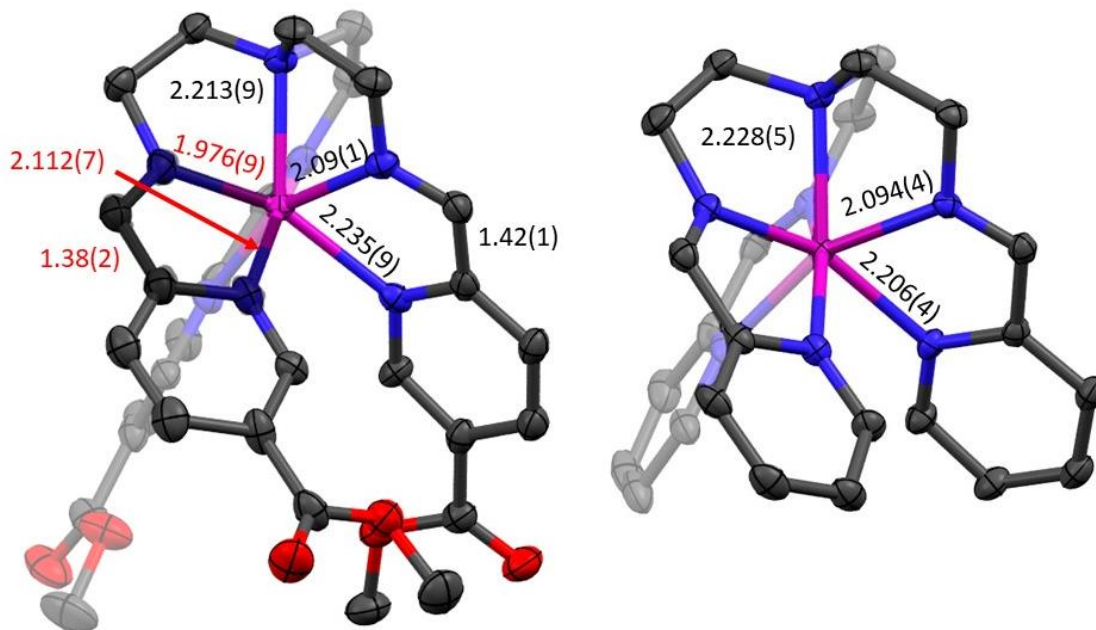


Figure 6.1 Crystal structure of the cationic complexes in compounds **6.1** (left) and **5.2** (right). Hydrogens, anions, and co-crystallized solvent are omitted for clarity. Ellipsoids are set to 40%.

6.4.3 Electronic Absorbance

The absorbance of compound **6.1** shows signatures of both a V(II) species and a ligand radical. The MLCT of **6.1** peaks at 756 nm (1.64 eV) which is approximately the same energy as **5.1** (Figure 6.2). Here, the ester withdrawing group red-shifts the MLCT suggesting the iminopyridine behaves as a π -acceptor. Interestingly, this agrees with several reports of metal iminopyridines/bipyridine complexes but disagrees with our observations of V(II) polypyridyl complexes discussed in Chapter 4. With this similarity, we would initially describe **6.1** as a V(II) species (form **6.1A**). However, ligand radical behavior is seen in the NIR. A broad peak is observed at 1024 nm (1.21 eV) with an extinction coefficient greater than $1000 \text{ M}^{-1} \text{ cm}^{-1}$. This lower energy electronic absorbance is consistent with ligand based $\pi^* \rightarrow \pi^*$ transitions. As an aside, the

analogous $[\text{Cr}(\text{5-CO}_2\text{Mepy})_3\text{tren}]^{2+}$ displays a $\pi^* \rightarrow \pi^*$ at 1068 nm (1.16 eV) which further supports the existence of a ligand radical (form **6.1B**). Ultimately, these two features complicate the electronic structure of **6.1**. If a ligand radical exists, then the expected electronic structure should be a V(III) complex with a ligand radical (**6.1B**).

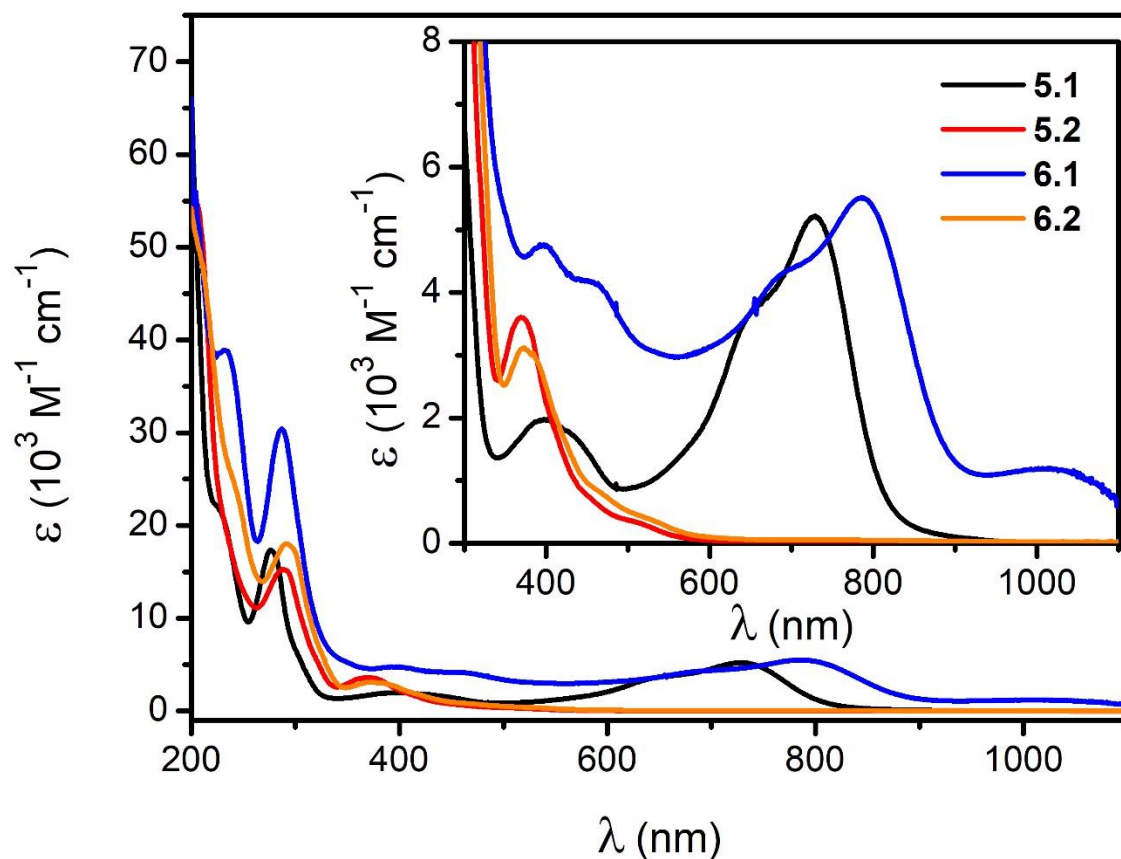


Figure 6.2 Electronic absorbance spectra of **5.1-5.2**, **6.1-6.2** in CH_3CN at room temperature.

The absorbance of **6.2** resembles the features in its parent compound **5.2**, best described as a V(III) complex with a neutral ligand. The loss of a low energy MLCT transition is expected, as oxidation of V(III) is more difficult compared to V(II). The peak at 373 nm (3.32 eV) is slightly red-shifted to the peak in **5.1**. Since that peak was best described as a MLCT in Chapter 5, we assign the peak at 373 nm as a MLCT absorbance. Additionally, shoulders persist in the visible

region similarly to **5.1**. Likewise, the description of d-d transitions would be consistent in a capped octahedral V(III) complex.

6.4.4 Electrochemistry

Electrochemical measurements of **6.1** resemble the parent compound **5.1**, along with expected shifts in energy due to the ester substituents. First, several reversible redox events lie within “close” proximity of each other (Figure 6.3). This result is consistent with the parent compound **5.1** and Cr(III) analogue where subsequent redox events are within 1 V of each other. No reversible peaks are observed past 1.0 V, likely irreversible oxidation of the ligand and decomposition of the complex (Figure A5.2). Second, the open circuit potential lies nested between two close redox events. Importantly, the open circuit potential does not sit at the $E_{1/2}$ of the observed peaks. This assures there is no impurity of a reduced/oxidized species and one predominant species exists in solution. Thus, the prepared dicationic tripod species $[V(5\text{-CO}_2\text{Mepy})_3\text{tren}]^{2+}$ is oxidized at -0.39 V and reduced at -0.73 V vs Fc^+/Fc^0 . Initially, we assumed **6.1** to be a V(II) species with a neutral ligand. If we assume the same electronic structure as **5.1**, the first oxidation would be the $\text{V}^{3+}/\text{V}^{2+}$ redox event and the first reduction would be a ligand-based reduction. By extension, the MLCT would be expected at 3600 nm (0.34 eV). This approximation would imply the nonsensical result that the MLCT (2700 cm^{-1}) is lower in energy than the C-H vibrational modes in the complex (Figure A5.1). Third, the ester withdrawing group shifts the redox events and increases the number of observed events. The $E_{1/2 3+/2+}$ and $E_{1/2 2+/1+}$ redox events in compound **6.1** are 0.12 V and 0.34 V anodic to the parent compounds, respectively (Table 6.1). Additionally, five reversible redox events are observed in the 0.1 M NBu₄PF₆ in CH₃CN solution. This suggests the electron-deficient substituent group stabilizes additional charges compared to the parent compound.

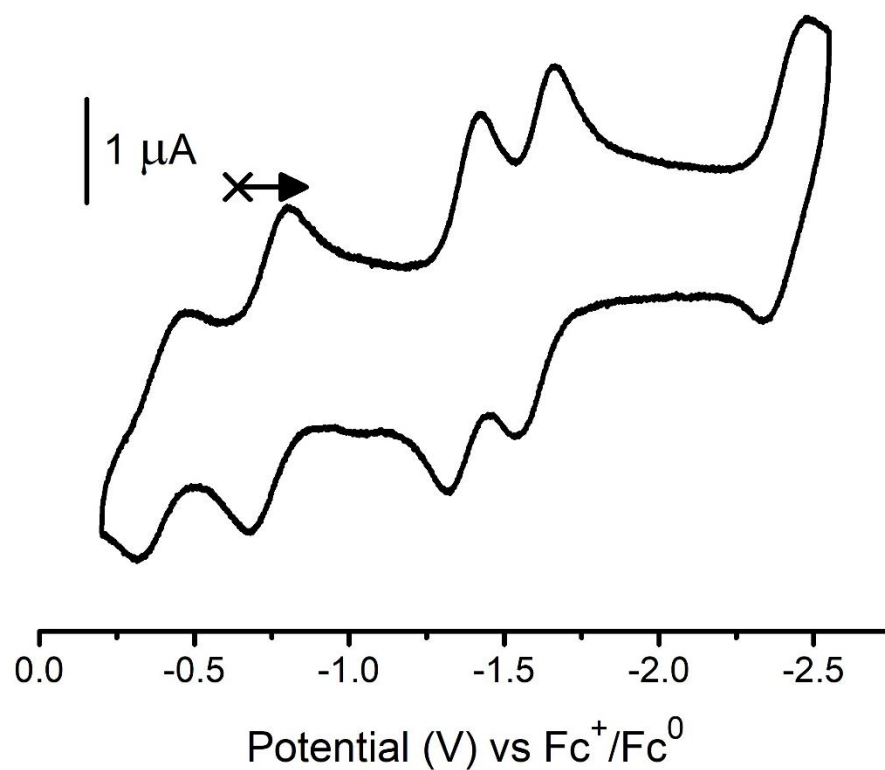


Figure 6.3 Cyclic voltammograms (0.1 V/s) of **6.1** in 0.1 M Bu₄NPF₆ in CH₃CN. Reduction potentials are tabulated in Table 1. Arrows indicate scan direction and the open circuit potential before each experiment. Compound **6.1** was measured with a glassy carbon working electrode.

Table 6.1 Ground state reduction potentials for 5.1, 6.1, and their Cr(III) analogues

Redox Event	$E_{1/2}^a$ 3+/2+	$E_{1/2}$ 2+/1+	$E_{1/2}$ 1+/0	$E_{1/2}$ 0/1-	$E_{1/2}$ 1-/2-	Reference
5.1 - [V(py) ₃ tren] ²⁺	-0.51 (73)	-1.09 (75)	-1.64 (63)	-1.97 (70)		Chapter 5
[Cr(py) ₃ tren] ³⁺	-0.45 (71)	-0.93 (70)	-1.55 (77)	-2.44 (irr)		6
6.1 - [V(5-CO ₂ Mepy) ₃] ²⁺	-0.39 (72)	-0.73 (60)	-1.37 (62)	-1.60 (59)	-2.41 (66)	This work
[Cr(5-CO ₂ Mepy) ₃] ³⁺	-0.25 (71)	-0.67 (71)	-1.12 (71)	-1.89 (81)	-2.18 (86)	3

Randles-Sevcik analysis of **6.1** exhibits different behavior compared to the previously analyzed compound **5.2**. First, oxidation generates a higher response compared to reduction (Figure A5.3). This preference is approximately twice that of reduction, along with a more linear response. Second, the differences in the peak to peak potential do not exhibit any significant changes as a function of scan rate. The small changes are minimal, with a poor R^2 of ~ 0.4 , suggesting no overall change. Experimentally, scans began at the open circuit potential for each compound but directions differed. Compound **6.1** was initially swept oxidatively, whereas compound **5.2** was initially swept reductively. Additionally, compound **6.1** contains the dicationic complex whereas **5.2** contains the tricationic complex. These experimental differences may bias the results of **6.1** and **5.2** in opposite directions for Randles-Sevcik analyses.

6.4.5 Spectroelectrochemistry

Spectroelectrochemical data of **6.1** support an electronic structure like the parent **5.1**, albeit with some unexpected differences. First, the NIR absorbance of the initial **6.1** is red-shifted in the 0.1 M NBu₄PF₆ in CH₃CN solution (Figure 6.4). In the electronic absorbance spectra, the NIR absorbance peaks at 1024 nm; in the spectroelectrochemistry experiments, the peak is shifted outside of the detector window. This not a limit of the spectrophotometer, as the detector is not saturated at these wavelengths (Figure A5.5). In fact, the spectrometer signal is above 100 CPS at these wavelengths, ensuring quality response in the NIR region. These results suggest solvatochromism where the solution environment shifts the charge-transfer absorbance. To my knowledge, organic-based transitions are more susceptible to solvatochromism whereas MLCT transitions are not. Thus, the ligand based $\pi^* \rightarrow \pi^*$ transition in the NIR may be shifted based on solution environment among other competing factors.⁷ Second, oxidation of **6.1** resembles the spectra of **6.2**. The similarities reassure the electronic structure **6.2** as a V(III) complex with a

neutral ligand. Third, reduction of **6.1** by one electron displays similar behavior to reduction of compound **5.1**. A peak at 667 nm and increased absorbance in the NIR are consistent with the parent complex, with a slight red-shift for both peaks. The intensity of the peak at 667 nm would suggest a molar absorptivity over $9000 \text{ M}^{-1} \text{ cm}^{-1}$, a substantial increase when compared to the reduction of compound **5.1**. Absorbance above 475 nm is unreliable at which point the detector is saturated and can produce a false peak (Figure A5.5). Subsequent reduction of **6.1** better displays this detector saturation at 400 nm. However, a NIR peak is shifted to the spectrometer window at $\sim 960 \text{ nm}$.

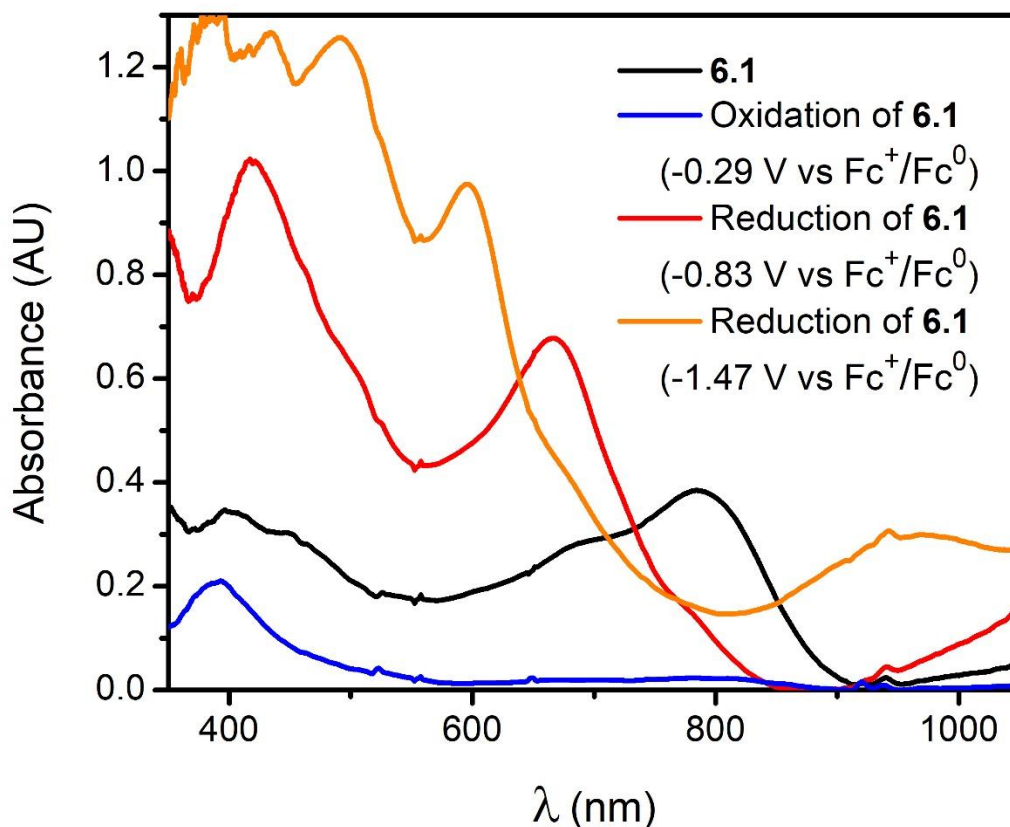


Figure 6.4 Absorbance spectra of **6.1** obtained during electrochemical measurements. Spectra were collected at the open-circuit potential (black), at $-0.29 \text{ V vs Fc}^+/\text{Fc}^0$ (blue), $-0.83 \text{ V vs Fc}^+/\text{Fc}^0$ (red) and at $-1.47 \text{ V vs Fc}^+/\text{Fc}^0$ (orange).

6.4.6 Preliminary Magnetometry Experiments

SQUID magnetometry was attempted to elucidate the electronic structure of **6.1**, suggesting valence tautomerism-like behavior. Field dependence of magnetization at 100 K confirm no ferromagnetic purity, as a linear response with a coefficient of determination ~ 1 is observed (Figure A5.6). Magnetic susceptibility was measured as a function of temperature, yielding an unexpected response (Figure 6.5). At low temperatures, the magnetic susceptibility suggests a $S = \frac{1}{2}$ ground state with a single unpaired electron. The data appears linear above 50 K for both measurements at 1 kOe and 10 kOe. Typically, a logarithmic response is expected as most first-row octahedral complex achieve a saturated paramagnetic response at room temperature. Additionally, $1/\chi$ only displays a linear response at low temperatures (Figure A5.7). The curve at higher temperatures suggests diamagnetic impurities, but elemental analysis are within acceptable ranges. The result is odd, resembling the response from a second/third row d^2 octahedral complex.⁸ A similar result has been shown by Clark, where the results were attributed to temperature-independent paramagnetism (TIP) response.⁹ The observed TIP was an order of magnitude larger than expected (ie. 1000×10^{-6} emu K mol⁻¹), but no fits were provided. Since the ground state resembles $S = \frac{1}{2}$, TIP becomes significant and may be overcompensated in these fits. Linear regressions were performed with the data, with satisfactory simulation with this simple fit (Figure A5.8). Fits to the various magnetic parameters were performed, suggesting a similarly high TIP (Table 6.2). For the remainder of these discussions, magnetic susceptibility will be referred to the values at 10 kOe. Additionally, the g-factor (g_{iso}) minimizes to the lowest constraints which affects the fits for the TIP and exchange coupling (J). Truncation of the data ($T < 50$ K is ignored) shows the same behavior, where g_{iso} is minimized to yield the best fit.

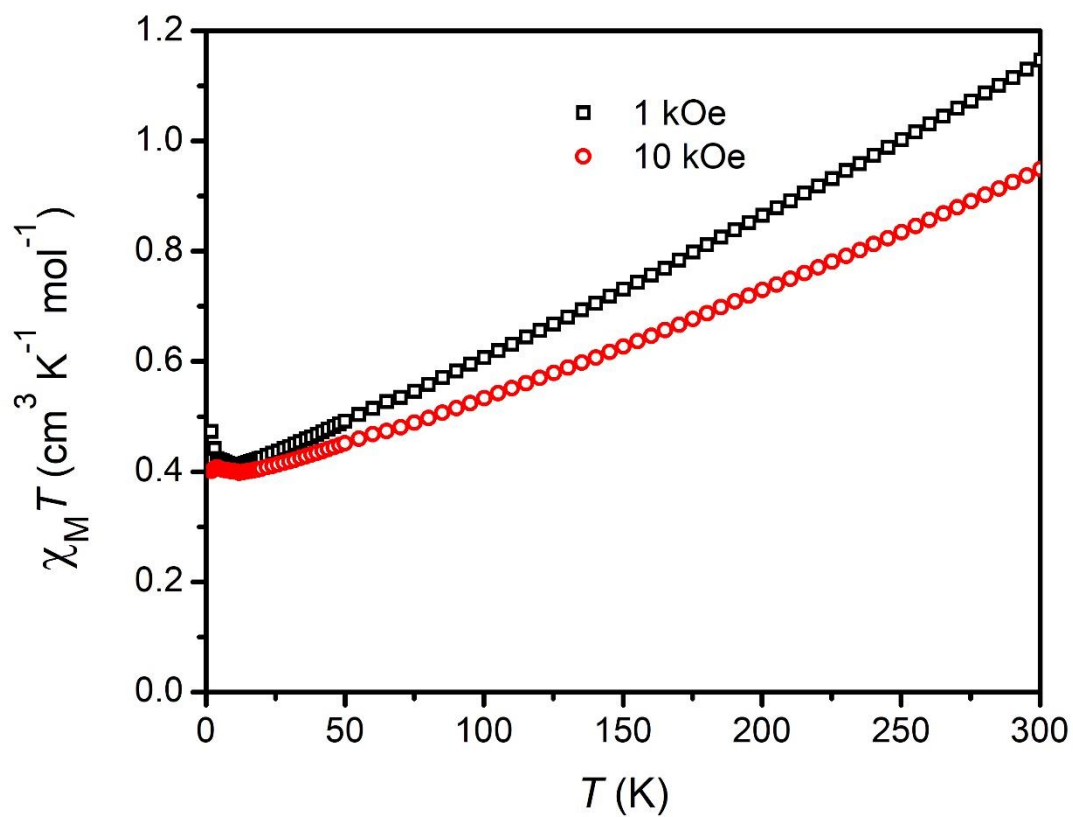


Figure 6.5 Solid-state magnetic susceptibility of compound 6.1.

Table 6.2 Results of fits for **6.1** utilizing PHI

Truncation					T < 50 K	T < 50 K	T < 50 K
g_{iso}	1.80	1.80	1.70	1.90	1.70	1.70	1.80
$J \text{ (cm}^{-1}\text{)}$	-117	-210	-94	-400	-110	-113	-108
TIP ($\times 10^{-6} \text{ emu K mol}^{-1}$)	1000*	1822	772	200	598	1040	430
S = 1 Impurity (%)	17.59	13.68	22.31	5.32	12.78	25.19	11.18
f	0.02166	0.00661	0.01698	0.02207	0.00428	0.00283	0.00524

While the behavior is quite odd to interpret, the data is consistent with other experiments. First, the crystallographic data suggests a $S = \frac{1}{2}$ ground state which was collected at 181 K. The $X_M T = 0.69$, suggestive of a primarily $S = \frac{1}{2}$ state where 79% of all species are in this $S = \frac{1}{2}$ ground state (form **6.1B**). Second, the electronic absorbance at room temperature displays spectroscopic signals of form **6.1B** and **6.1A**. At 300 K, the magnetic susceptibility is 0.96 which suggests 61% is in a $S = \frac{1}{2}$ electronic state ie. form **6.1B**.

6.4.7 Solvent dependent absorbance spectra

Cryogenic absorbance spectroscopy was performed to elucidate the electronic structure at low temperatures. Compound **6.1** is slightly soluble in a 1:4 (v:v) methanol:ethanol solvent mixture, a convenient solvent that readily glasses at 77 K. Surprisingly, the room temperature absorbance resembles the reduction of **6.1** (-0.83 V vs Fc^+/Fc^0) absorbance spectra (Figure 6.6). Upon cooling to 77 K, the spectrum is predominantly identical to the room temperature spectra. In principle, the cryogenic absorbance spectra at 77 K would be 93% **6.1B** with the remaining 7% be **6.1A**. Due to similarities at room temperature and 77 K, the results here are inconclusive.

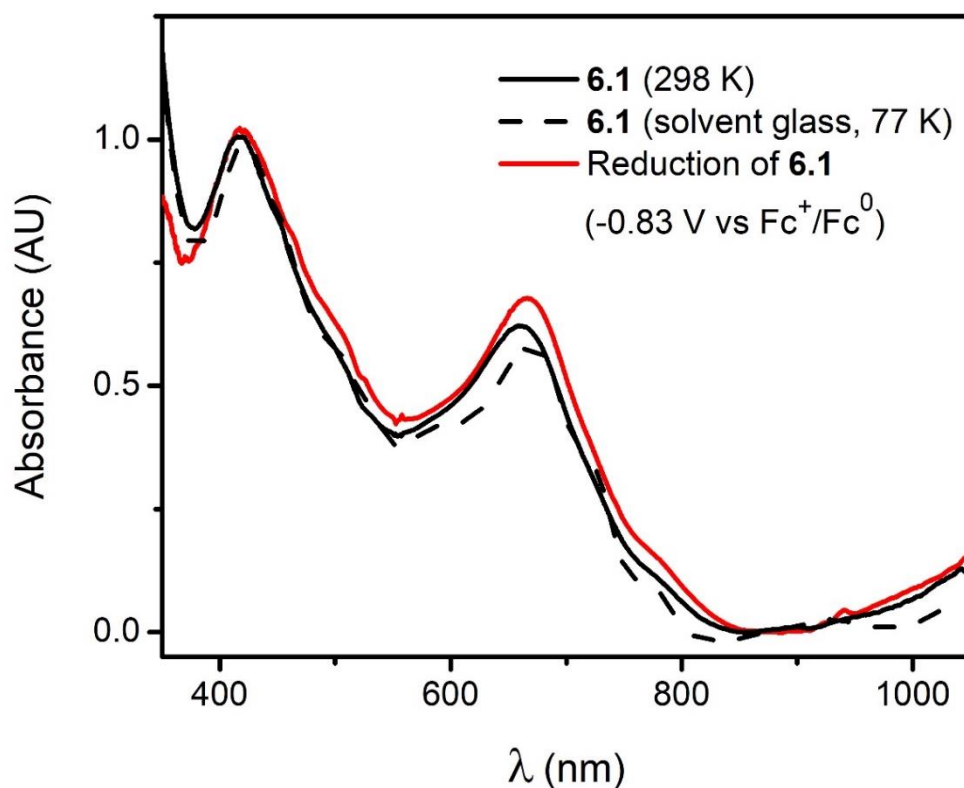


Figure 6.6 Electronic absorbance spectra of **6.1** in a 1:4 methanol:ethanol solution at room temperature (solid black) and 1:4 methanol:ethanol solvent glass at 77 K (dashed black). The spectra of the reduction of **6.1** in CH₃CN (red) is included for comparison.

Solvent dependent studies of **6.1** were attempted but did not yield any meaningful insight. Spectra were collected in the following order as shown in Figure 6.7: tetrahydrofuran, methanol, dichloromethane, acetonitrile, nitromethane, dimethylformamide, and pyridine. Compound **6.1** is not soluble in tetrahydrofuran, yielding a baseline response. The NIR peak for each spectrum is outside the detector window, which would provide the ideal signal to monitor changes. Attempts to track shifts of the peak/shoulder at ~680 and ~780 nm did not correlate well to changes in dielectric constant (Figure A5.10). However, a better correlation is observed with donor number of the solvent albeit small changes (Figure A5.10). Expected changes would be yield a linear response over a range of 1000+ cm⁻¹. Ultimately, this system is challenging to describe with spectroscopic techniques.

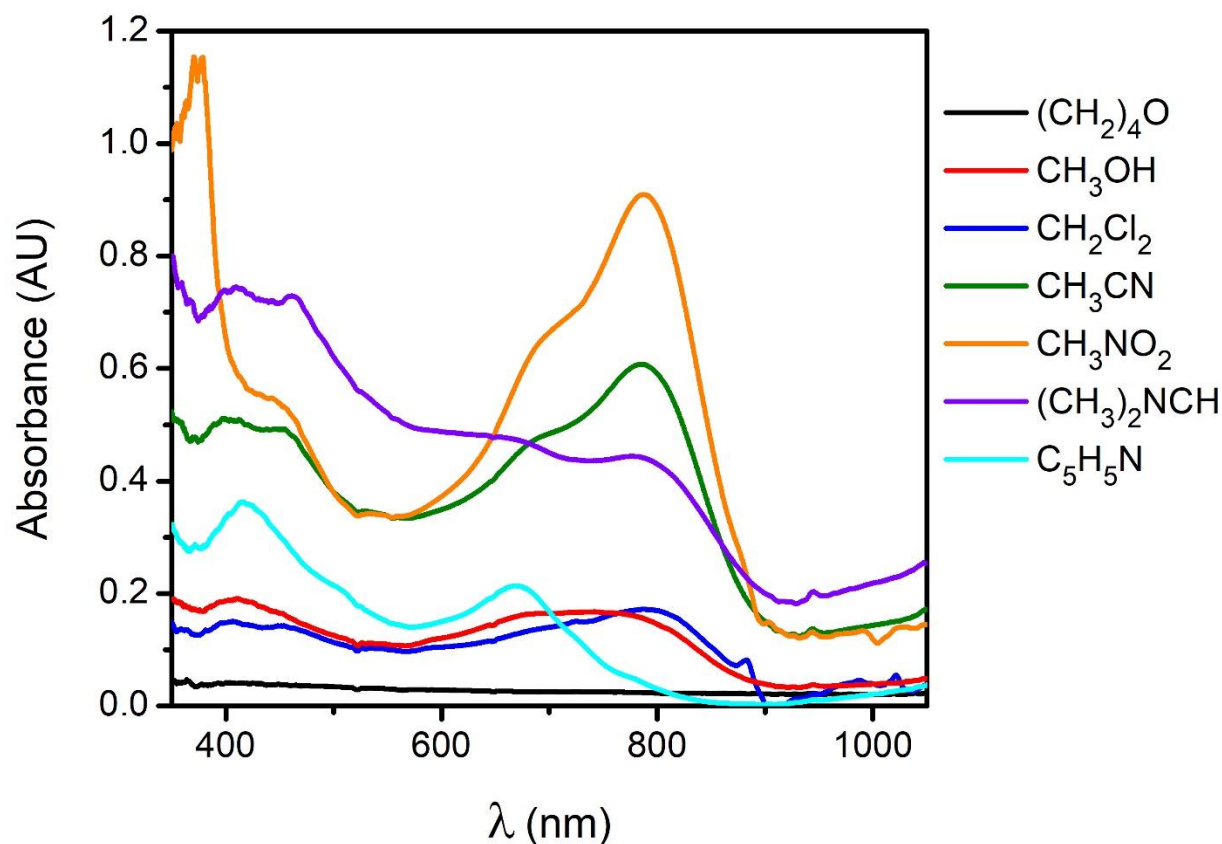


Figure 6.7 Electronic absorbance spectra of **6.1** in tetrahydrofuran (black), methanol (red), dichloromethane (blue), acetonitrile (green), nitromethane (orange), dimethylformamide (purple), and pyridine (teal).

6.4.8 Determining the underlying electronic structure of **6.1**: Speciation or valence tautomerism?

Overall, the results thus far suggest either speciation or valence tautomerism in compound **6.1**. Both phenomena have been observed in vanadium complexes, albeit at different oxidation states.

Speciation may address the inconsistencies observed in the crystal structure compared to the solution-based behavior. Compound **6.1** crystallizes from a concentrated solution of methanol via diffusion of diethyl ether. The crystal structure is predominately form **6.1B** based on the short V-N_{bridge} distance and ligand radical observed on an iminopyridine arm. We'd expect a mixture of form **6.1B** and **6.1A** in the crystal structure, since the crystal structure was collected at 181 K

(approximately 80:20 of **6.1B**:**6.1A** based on solid-state magnetometry). Methanol may predispose compound **6.1** to adopt form **6.1B** and influence subsequent experiments. Since the complex is crystallized from methanol, residual solvent on the crystal may be producing signals of the “ $S = \frac{1}{2}$ ” state in other solvents. Finally, the solid-state structure may differ than the structure in solution. In solution, the ligand may delegate from the metal center and allow for coordination of solvent to the open-coordination sites. No absorbance spectra were performed in both the solid-state and solution, thus we cannot disprove this possibility. Additionally, the ester substituents may undergo chemical changes in solution. In methanol, the absorbance spectra is the same at 77 and 298 K. If changes were reversible, then spectroscopic signals of the form **6.1A** should be present at room temperature. A V(IV/V) dinuclear compound has shown different oxidation states on the metal center based on ligation/deligation of solvent molecules.¹⁰ Thus, speciation may address many inconsistencies observed between the crystal structure and solution.

Valence tautomerism may address inconsistencies in the magnetic measurements, independent of solution. The solid-state magnetic susceptibility data suggests a $S = \frac{1}{2}$ ground state at 2 K, consistent with form **6.1B**. At room temperature, the solid-state magnetic susceptibility lies between 0.375 ($S = 1/2$) and below $1.875 \text{ cm}^3 \text{ K}^{-1} \text{ mol}^{-1}$ ($S = 3/2$). Magnetic measurements in both CH_3CN and CH_3OH at room temperature are consistent with this result, suggesting the same species in both the solid-state and solution. This intermediate value would agree the “intramolecular electron transfer between the ligand and metal center” in valence tautomerism.¹¹ Valence tautomerism has been reported in a V(IV) system between a $S = 1/2$ and $3/2$ system, although the values are a bit off in that report.⁹ Since the bridgehead nitrogen is bound in the crystal structure of **6.1**, the interaction between this seventh ligand and metal center may be generate these odd changes. Coordination-induced valence tautomerism has been reported in a cobalt dioxolene

complex, changing the electronic structure based on the coordination number of the complex.¹² Thus, a change between an $S = 1/2$ and $3/2$ system may occur based on external stimuli such as temperature and solvent.

Although speciation and valence tautomerism may explain different phenomena, both can address other observations. First, both speciation and valence tautomerism may explain solvent dependent absorbance spectra. Speciation was proposed for compound **5.5** which contained ester substituents on the ligand. In **5.5**, the absorbance spectra differ whether the solvent is an N vs O donor. Here, we do not see any obvious trend between solvents such as protic vs aprotic solvents or solvent donicity. Valence tautomerism would allow for small interactions to influence the absorbance spectra. Changes, such as addition of the salt Bu_4NPF_6 , which would not affect the primary coordination sphere of **6.1** may influence the second coordination sphere and impart some changes in energy. Here, the NIR absorbance would shift based on these changes such as addition of salt. Ultimately, both phenomena do not provide a full explanation of the electronic structure of compound **6.1** as summarized by Figure 6.8.

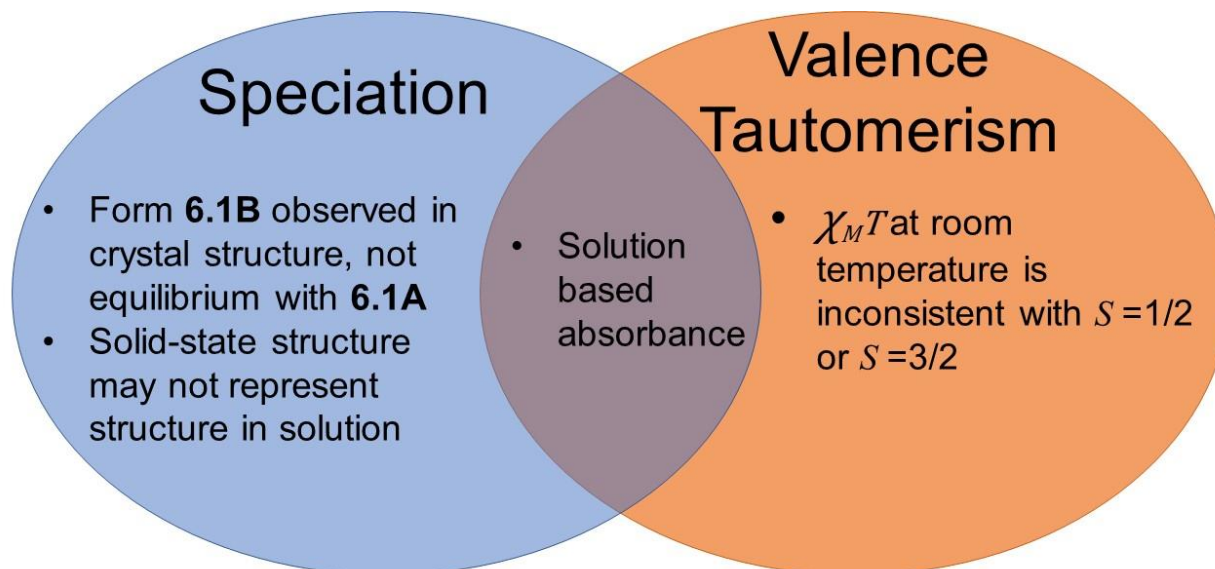


Figure 6.8 Venn-diagram comparing possible speciation and valence tautomerism in compound **6.1**

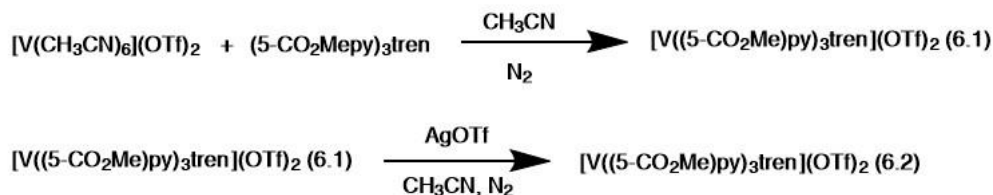
6.4.9 Future Directions

Although the results here are still inconclusive, investigations into compound **6.2** may reveal the electronic structure of compound **6.1**. First, we must establish the electronic structure of compound **6.2** using crystallography. Compound **6.2** did not crystallize under multiple conditions, suggesting the triflate anion may not be ideal in this system. In this case, tetraphenylborate may be substituted for triflate (Scheme 6.2). Either option, whether switching the syntheses to include BPh_4^- or anion exchange between **6.2** and NaBPh_4 in methanol, would be easy to perform within our group's laboratory (Scheme 6.2). In the event these options do not yield crystals of $[\text{V}(\text{5-CO}_2\text{Mepy})_3\text{tren}](\text{BPh}_4)_3$, other synthetic routes are available. For example, compound $[\text{V}((\text{5-CO}_2\text{Me})\text{py})_3\text{tren}]^{3+}$ may be prepared with a V(III) starting material. Direct synthesis between the ligand and V(III) trifluoroacetate, $[\text{V}(\text{OCH}_2\text{CF}_3)]$, may result in a product that readily crystallizes. Additionally, different anions could be exchanged with the starting material V(III) trifluoroacetate (Scheme 6.2). As an aside, this alternative may allow **6.1** to crystallize in other solvents. Finally, compound **6.2** using a V(III) chloride starting material. Preliminary experiments in Chapter 5 with

the parent ligand, py₃tren, suggest it is possible to prepare the V(III) tripodal complex in tetrahydrofuran at cold temperatures. If impurities may be removed from the product, then anion exchange with the halide may yield clean product (Scheme 6.2).

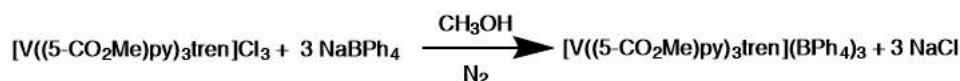
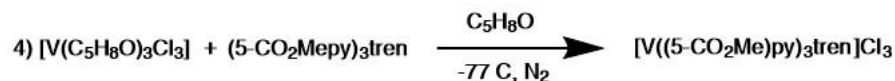
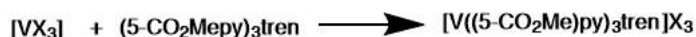
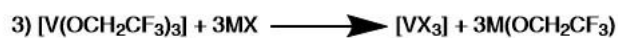
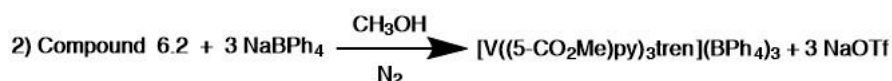
Scheme 6.2 Preparation of **6.1-6.2** and alternative synthetic routes to [V((5-CO₂Me)py)₃tren]³⁺

Preparation of Compounds **6.1** and **6.2**



Alternative Routes to [V((5-CO₂Me)py)₃tren]³⁺

1) Exchange [V(CH₃CN)₆](OTf)₂ and AgOTf with [V(CH₃CN)₆](BPh₄)₂ and AgBPh₄



Additionally, NIR absorbance may allow for better characterization of **6.1** under various conditions. These experiments require spectroelectrochemical measurements of **6.2** under atmospheric conditions, limiting some variables such as absence of salt and certain solvents. Upon reduction of **6.2**, a NIR band should be present at energies outside the spectroscopic window of our Ocean Optics or Agilent spectrometer. Our Bruker TENSOR II allows for measurements from 909 nm to 2000 nm, a large window to observe the NIR band. Characterization of this band may

allow for further analyses, such as using the molar absorptivity to quantify the concentration of form **6.1A** and **6.1B** in solution.

6.5 Conclusion

Ultimately, the electronic structure of **6.1** is complex and requires further characterization. While speciation and valence tautomerism may address some inconsistencies between experiments, they do not provide a complete description of **6.1**. Future direction may address these differences by crystallizing the $[V((5\text{-CO}_2\text{Me})\text{py})_3\text{tren}]^{2+}$ ion in different solvents or monitoring the specie *in-situ* using an appropriate NIR spectrometer.

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Chapter 7: Closing Remarks and Future Directions

7.1 Conclusion of photophysical measurements

The results in Chapters 2-4 demonstrate the importance of reevaluating previous hypotheses with modern techniques. First, the $^4(^3\text{IL})$ excited state in Cr(III) complexes has been identified using cryogenic spectroscopic techniques in tandem with computational models. These results demonstrate that the $^4(^3\text{IL})$ is the lowest excited state in long-lived Cr(III) chromophores, an attractive motif to pursue in other paramagnetic systems. Second, a doublet excited state manifold has been identified in V(II) complexes. These results contradict the literature claim that a quartet excited state is the lowest energy excited state in this system. Third, isoelectronic V(II) chromophores does not behave as Cr(III) chromophores. The decrease in energy, increased spin-density on the ligand, and relative distortion in their excited states are all contributors to the differences in excited state lifetimes.

In Chapter 5, the program SHAPE quantified the geometric distortion in V(II) excited states using other relevant structures as proxies. Large differences in continuous shape measure between the ground state and excited state, $\Delta\text{CShMe} \sim 1$, suggests large changes in electronic structure upon photoexcitation. Thus, it is equally important to understand the electronic structure at the excited state geometry in order to fully understand the excited state manifold.

7.2 Use of SHAPE in other fields

After looking at SHAPE in the context of photocatalysis, I began to wonder how this parameter could be used in other fields. By identifying an appropriate geometry for the first coordination sphere, one may conclude the assumed electronic structure of a molecule. Admittedly, a single continuous shape measure does not provide enough detail of a system as it requires other data to give a whole description of electronic structure. Thus, a large dataset

including the continuous shape measure may be a useful tool to screen new compounds for any field.

I investigated a small dataset to investigate the relationship of structure and spin-crossover through basic machine learning. I began with the published structures of tripodal iminopyridines, which are available free of charge through the Cambridge Crystallographic Data Center (CCDC). This resource is commonly used to help assign the spin-state for Fe(II) diimines, such as the Fe-N bond lengths and torsion angle. However, this resource is underused as a source to motivate research in computational studies. The Cambridge Structural Database (CSD) is a licensed software which efficiently scans the one million published crystal structures based on parameters set by the user. In the data science community, organized data can be an impeding step towards effective machine learning. Here is an opportunity to use preexisting big data along with free open-source code to guide future studies of the secondary coordination sphere's effect on electronic structure in spin-crossover Fe(II) complexes.

Originally, I used measurements commonly used in the community to assign spin-state such as Fe-N bond lengths and torsion angles. The spin-state of each structure are assigned based on the author's investigations into their electronic structure through various techniques. This dataset represents a multi-class classification problem where molecule were either low-spin Fe(II), high-spin Fe(II), or spin-crossover Fe(II). Six different statistical algorithms were tested using published code by Dr. Jason Brownlee (Scheme A6.1).¹ A linear discriminant analysis (LDA) was effective method under several preliminary test to distinguish low spin Fe(II) from the other two classifications. However, this algorithm could not distinguish a molecule locked into a high-spin state compared to one exhibiting spin-crossover.

In order to address the previous limitation, an open-source decision tree classifier was used based on Classification and Regression Trees (CART) which classifies each spin-state after a series of Boolean statements. The open-source published by Josh Gordon demonstrated improvements in identifying key parameters relevant to classifying the spin-state in Fe(II) tripodal complexes (Scheme A6.2).² Due to the automation achieved in our programs, the dataset was refined to include unexplored parameters for spin-crossover analysis. First, several atomic distances were gathered such as the distance between the metal center and imine carbon. Surprisingly, this measurement appears in the decision tree as an effective method to classify spin-state in these systems (Figure 7.1). To the best of my knowledge, this measurement has never been used to classify spin-state leading investigations into its relevance in spin-crossover. Occurrences like this may guide research into the role of the 5 membered ring “metallocycle” and its possible role to assign (and eventually predict) spin-state. Second, the continuous shape measure of the first coordination sphere was incorporated into the CART program. I used the coordinate file of these crystal structures (through the CSD), to quantify how closely it resembles a perfect octahedron and our user defined “TREN” geometry. Once again, this measurement proves to be effective in our algorithm as the continuous shape measure is based on a number of bond-distances which reduces the number of nodes in our decision tree (Figure 7.1). These investigations require troubleshooting with more robust machine learning algorithms, while expanding the dataset to other Fe(II) tris diimines.

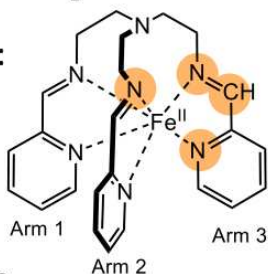
$[\text{Fe}(\text{py})_3\text{tren}]^{2+}$ SCO Decision Tree

Initial Dataset:

11 High Spin

23 Low Spin

22 SCO



Φ_{TREN} = Continuous Shape Measure for Octahedron(6) with 7th N Ligand

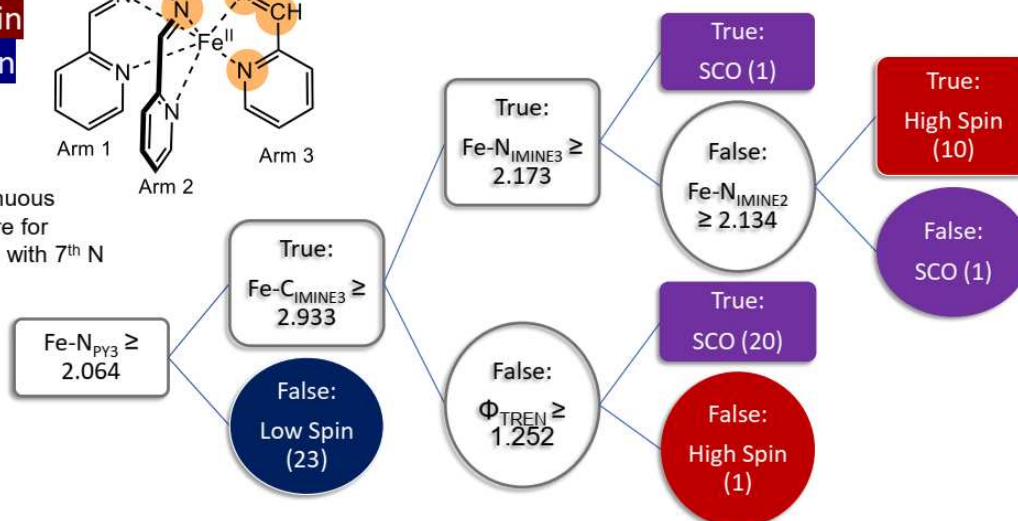


Figure 7.1 Decision tree to distinguish spin-state in Fe(II) tripodal complexes

References

- 1 Your First Machine Learning Project in Python Step-By-Step, <https://machinelearningmastery.com/machine-learning-in-python-step-by-step/>, (accessed 27 March 2020).
- 2 tutorials/decision_tree.ipynb at master · random-forests/tutorials · GitHub, https://github.com/random-forests/tutorials/blob/master/decision_tree.ipynb, (accessed 27 March 2020).

APPENDIX 1: Supporting Information for Chapter 2

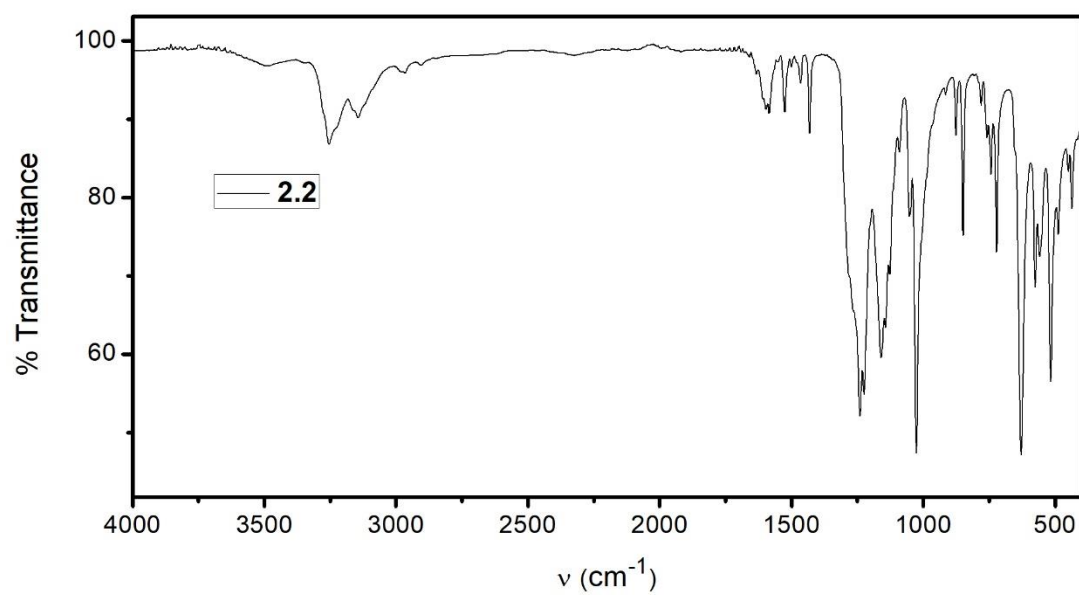


Figure A1.1 FTIR spectrum of **2.2**

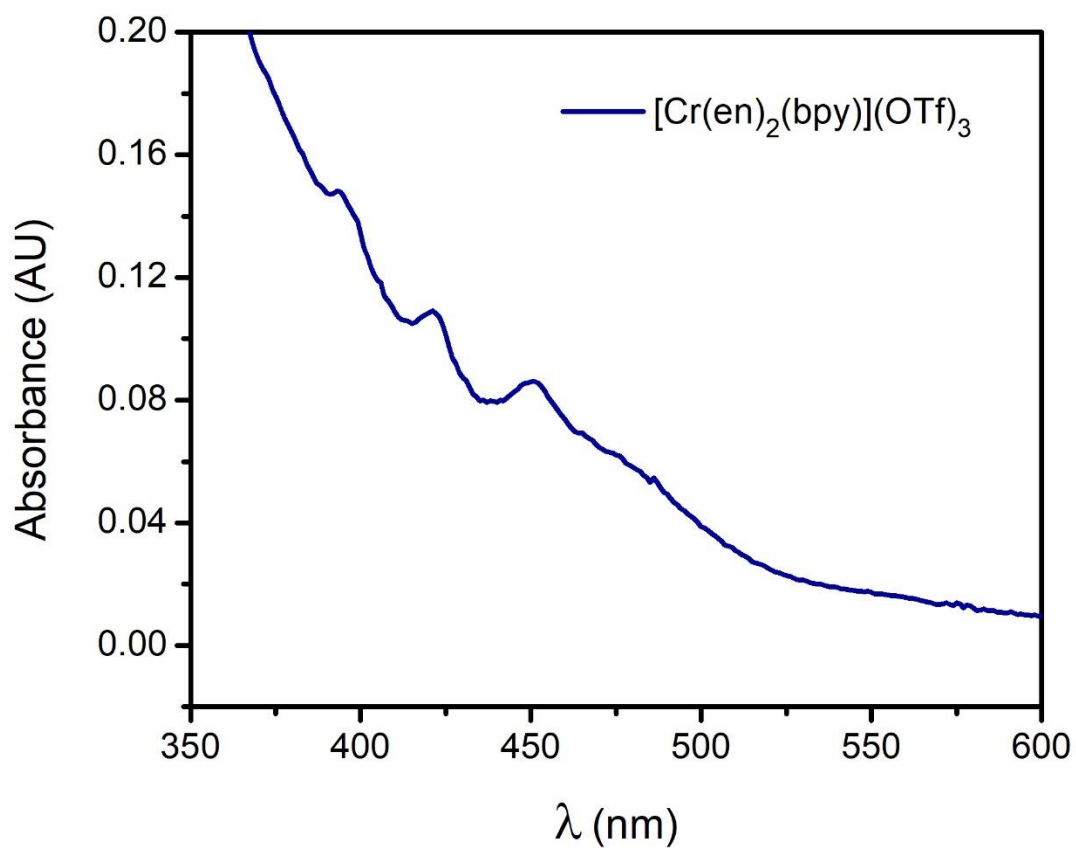


Figure A1.2 Absorbance spectra of $[\text{Cr}(\text{en})_2(\text{bpy})](\text{OTf})_3$ in CH_3CN . $[\text{Cr}(\text{en})_2(\text{bpy})](\text{OTf})_3$ was prepared in an analogous method to **2.2**, consistent with previous reports of the absorbance spectra.¹⁵

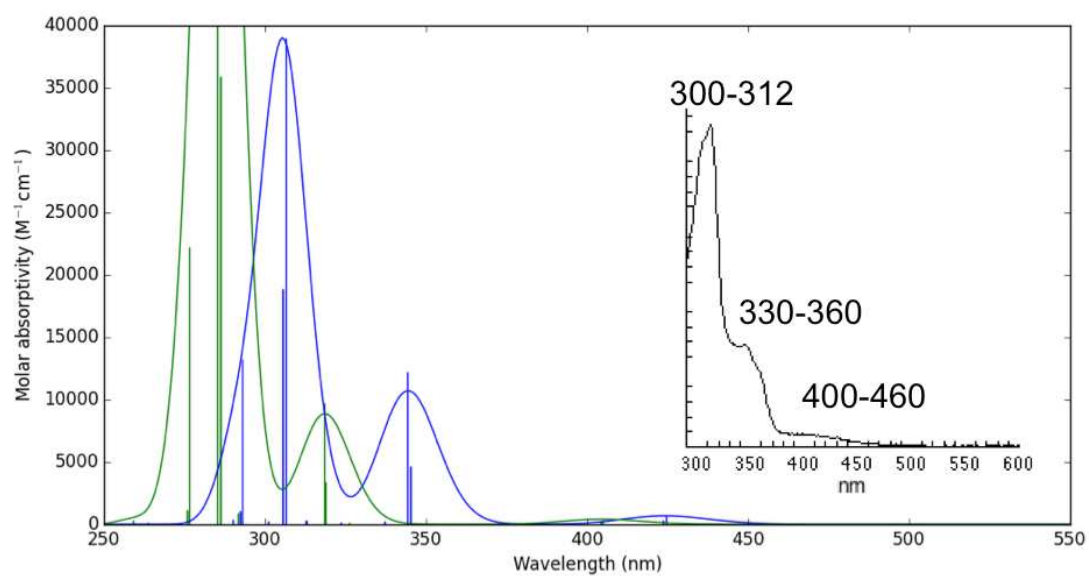


Figure A1.3 TDDFT absorbance spectra of $[\text{Cr}(\text{bpy})_3]^{3+}$ with APF-D (blue) and $\omega\text{B97X-D}$ (green) XC functional with basis set 6-311+G*.¹⁴

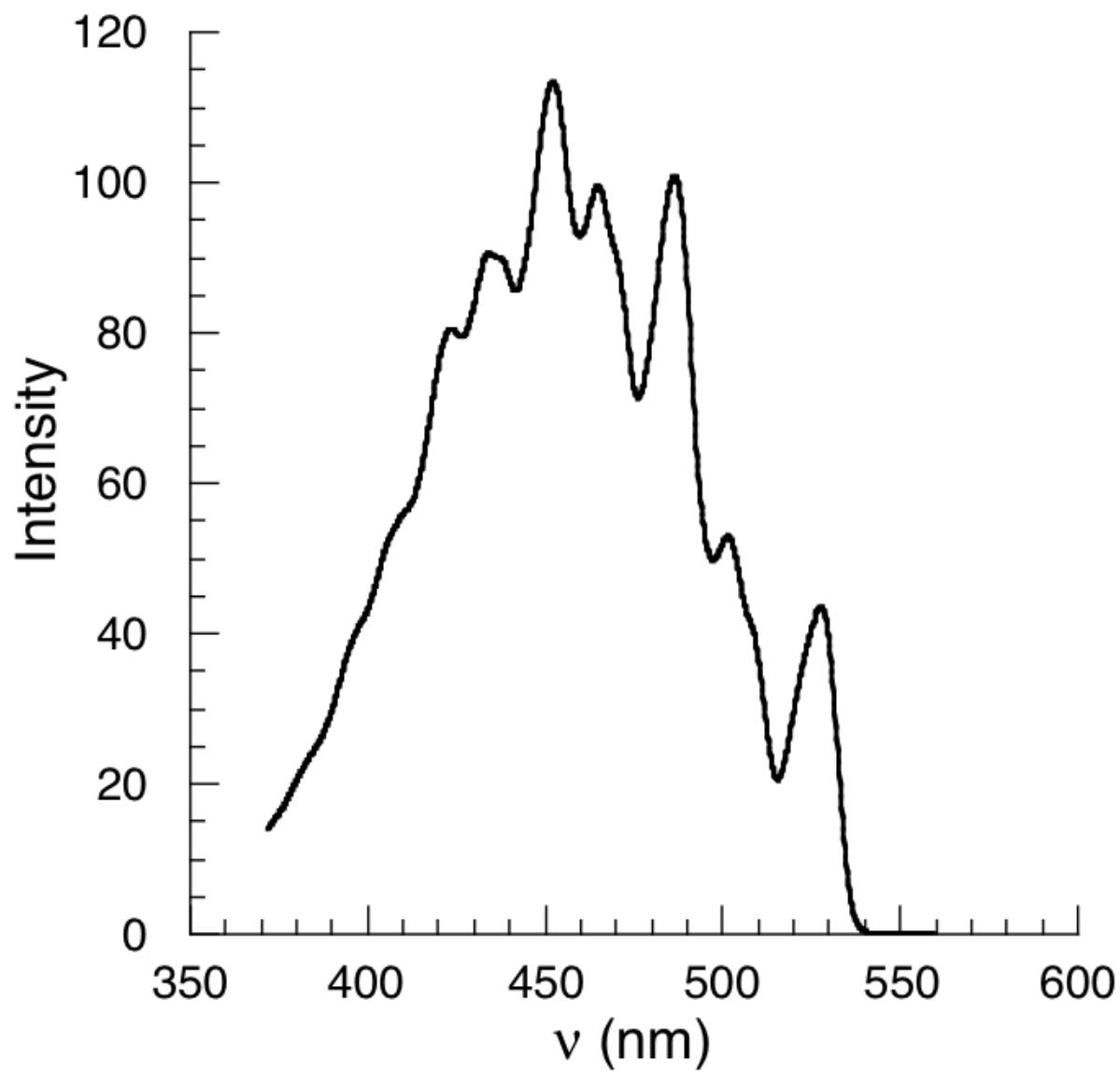


Figure A1.4 The vibronic spectrum of the first excited state $\text{Cr(III)(NH}_3)_4(\text{bpy})$ as calculated using DFT/TDDFT(APF-D/6-311+G*) with a Franck-Condon-Herzberg Teller analysis.¹⁴

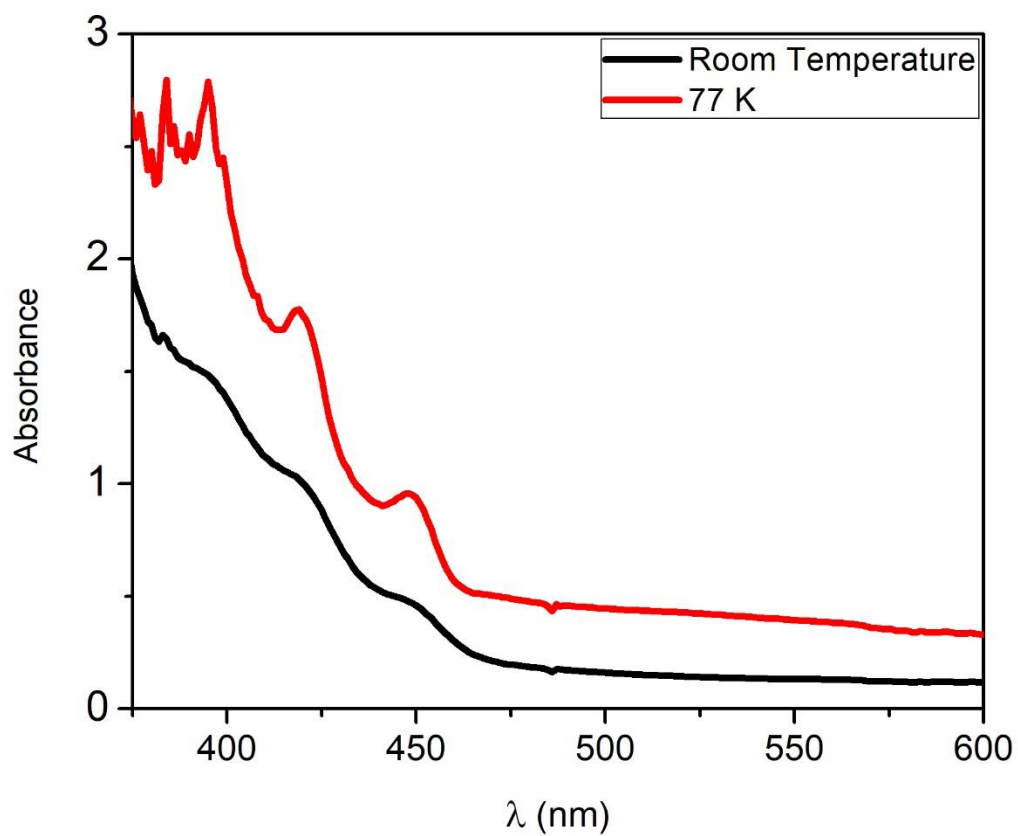


Figure A1.5 Absorbance spectra of [Cr(Me₂bpy)₃](OTf)₃. Spectra were collected in 1:4 methanol:ethanol mixture. Scattering is observed in the 77 K sample due to frost on the cuvette.

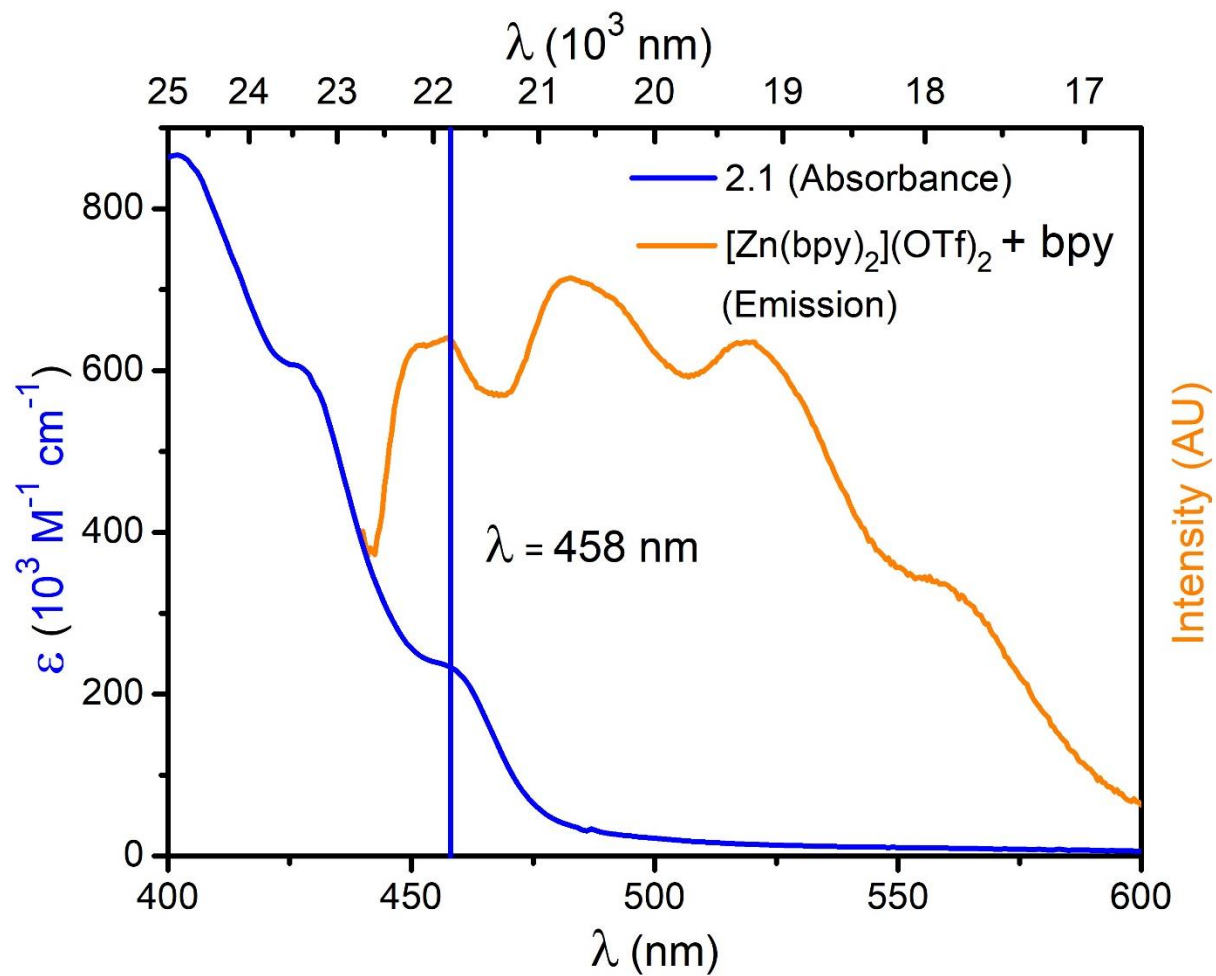


Figure A1.6 Minimal Stokes shift for ^3bpy . The absorbance of $[\text{Cr}(\text{bpy})_3](\text{BF}_4)_3$ ie. ^3bpy is taken at room temperature in CH_3CN . The emission of $[\text{Zn}(\text{phen})_2(\text{OTf})_2]$ ie. $^3\text{phen}$ is taken at 77 K in a 1:4 methanol:ethanol solvent glass.

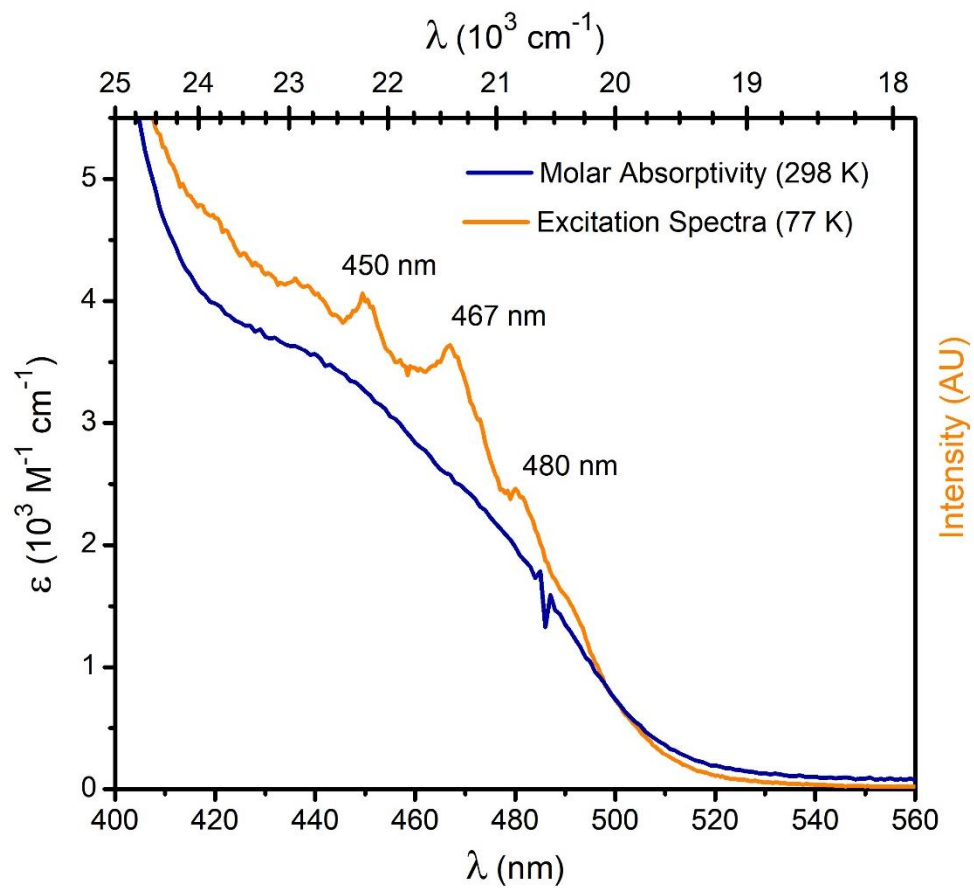


Figure A1.7 Room temperature absorbance spectra of $[\text{Cr}(\text{Ph}_2\text{phen})_3](\text{BF}_4)_3$ in CH_3CN (blue) and the excitation spectra of the ^2E emission in a 4:5 propionitrile:butyronitrile solvent glass at 77 K.

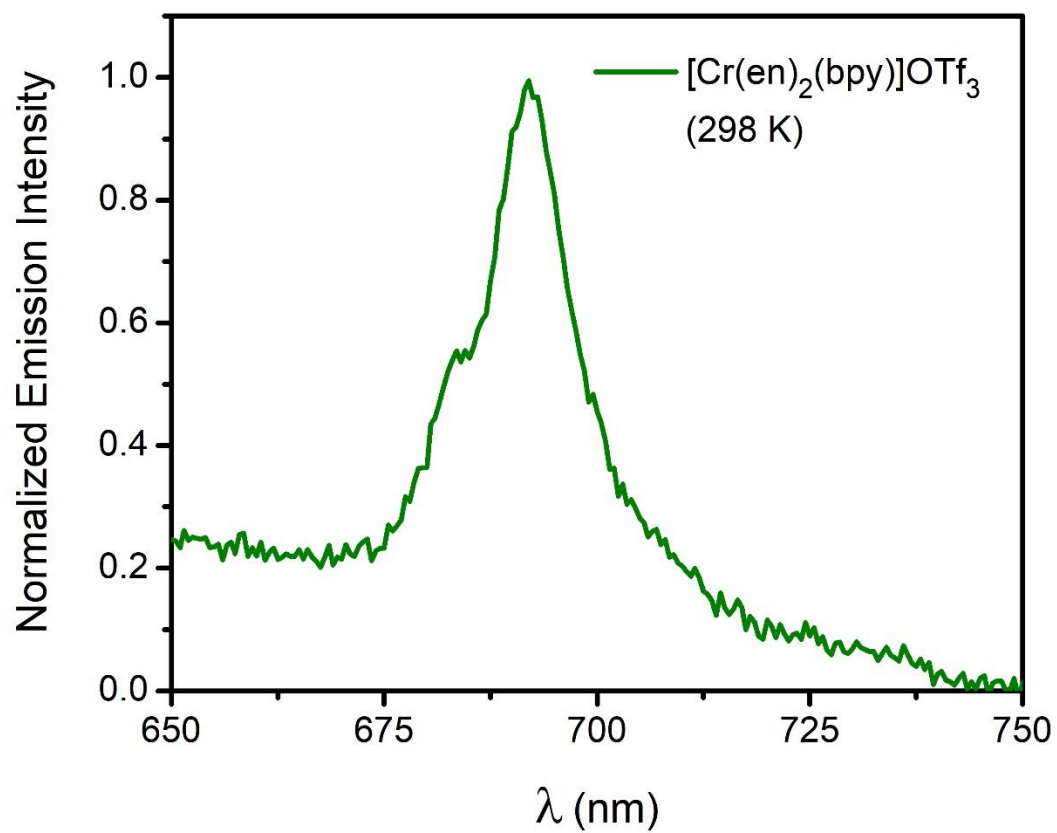


Figure A1.8 Emission spectra of $[\text{Cr}(\text{en})_2(\text{bpy})]\text{OTf}_3$ in CH_3CN at 298 K.

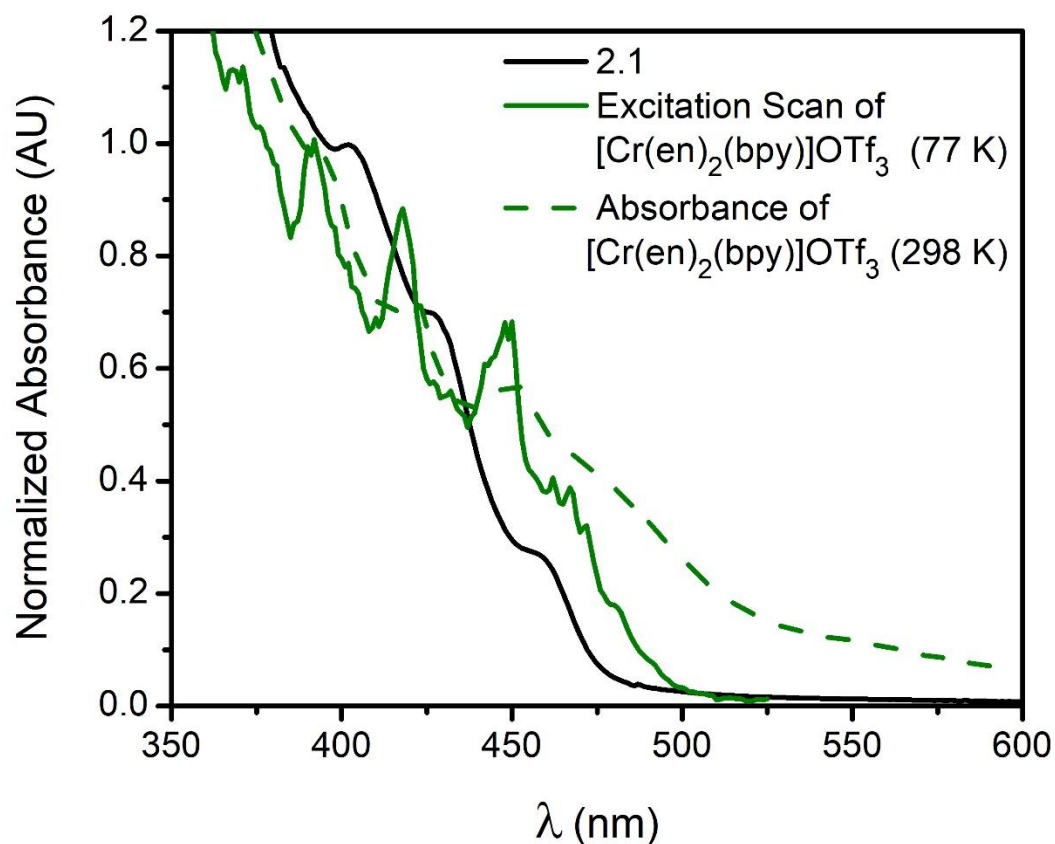


Figure A1.9 Comparison of absorbance spectrum of **2.1** (black), visible absorbance spectrum of $[\text{Cr}(\text{en})_2(\text{bpy})](\text{OTf})_3$ in CH_3CN at 298 K (dashed green), and excitation spectra of the ${}^2\text{E} \rightarrow {}^4\text{A}_2$ emission ($\lambda_{\text{em}} = 691 \text{ nm}$) for $[\text{Cr}(\text{en})_2(\text{bpy})](\text{OTf})_3$ (solid green) in 1:4 methanol:ethanol at 77 K. The excitation spectra of $[\text{Cr}(\text{en})_2(\text{bpy})](\text{OTf})_3$ resolves the shoulder features in the 298 K absorbance spectra, providing more accurate assignment of the vibronic ${}^4({}^3\text{IL})$ excited state.

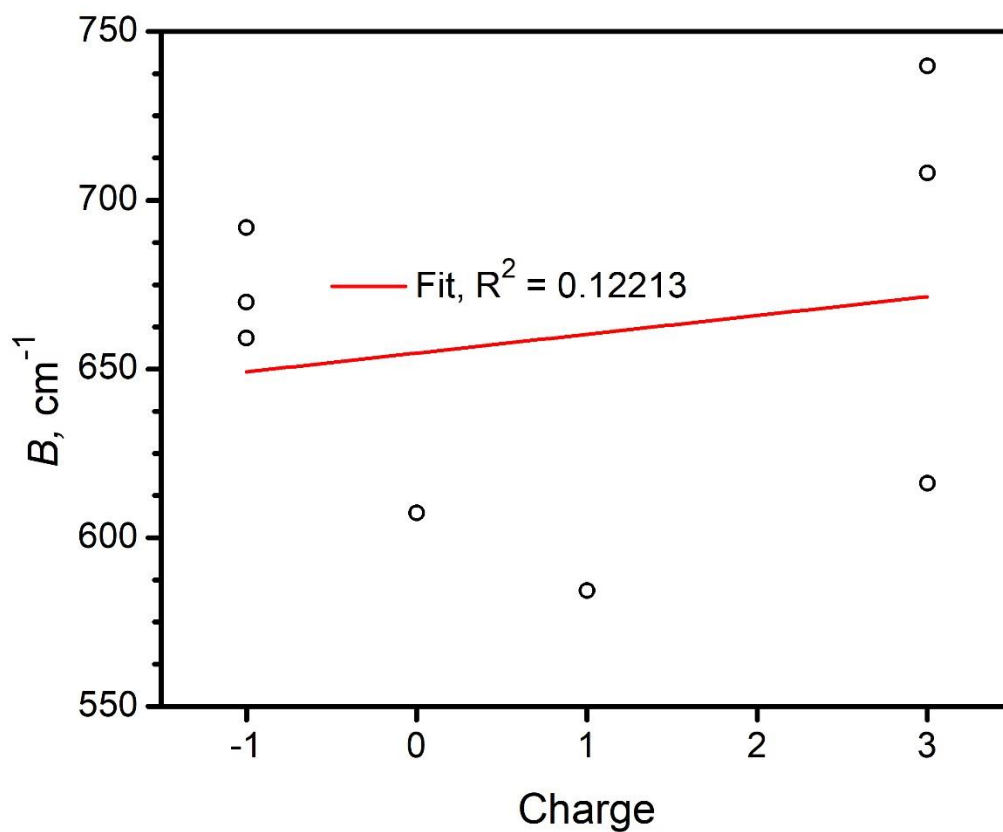


Figure A1.10. Plot of charge vs Racah parameter. See **Table A1.1** below.

Table A1.1. Calculation of Racah parameter for some Cr(III) species

Compound	4T_2 , cm ⁻¹ (nm)	2E , cm ⁻¹ (nm)	Δ/B	B, cm ⁻¹	Charge	Reference
[Cr(acac) ₃]	17860 (560)	12820 (780)	29.4	607	0	⁴⁴
[Cr(acac) ₂ bpy] ⁺	18660 (536)	12420 (805)	31.9	584	+1	This work
[Cr(bpy) ₃] ³⁺	26670 (375)	13720 (729)	43.3	616	+3	This work
[Cr(en) ₃] ³⁺	21880 (457)	14970 (668)	30.9	708	+3	¹⁵
[Cr(en) ₂ (phen)] ³⁺	23470 (426)	14470 (691)	31.7	740	+3	This work

$[\text{Cr}(\text{ox})_2(\text{phen})]^-$	18500 (541)	14100 (709)	27.6	670	-1	45
$[\text{Cr}(\text{ox})_2(\text{bpy})]^-$	18300 (546)	13900 (719)	27.80	659	-1	45
$[\text{Cr}(\text{ox})_2(\text{en})]^-$	20300 (493)	14600 (685)	29.3	692	-1	45

APPENDIX 2: Supporting information for chapter 3

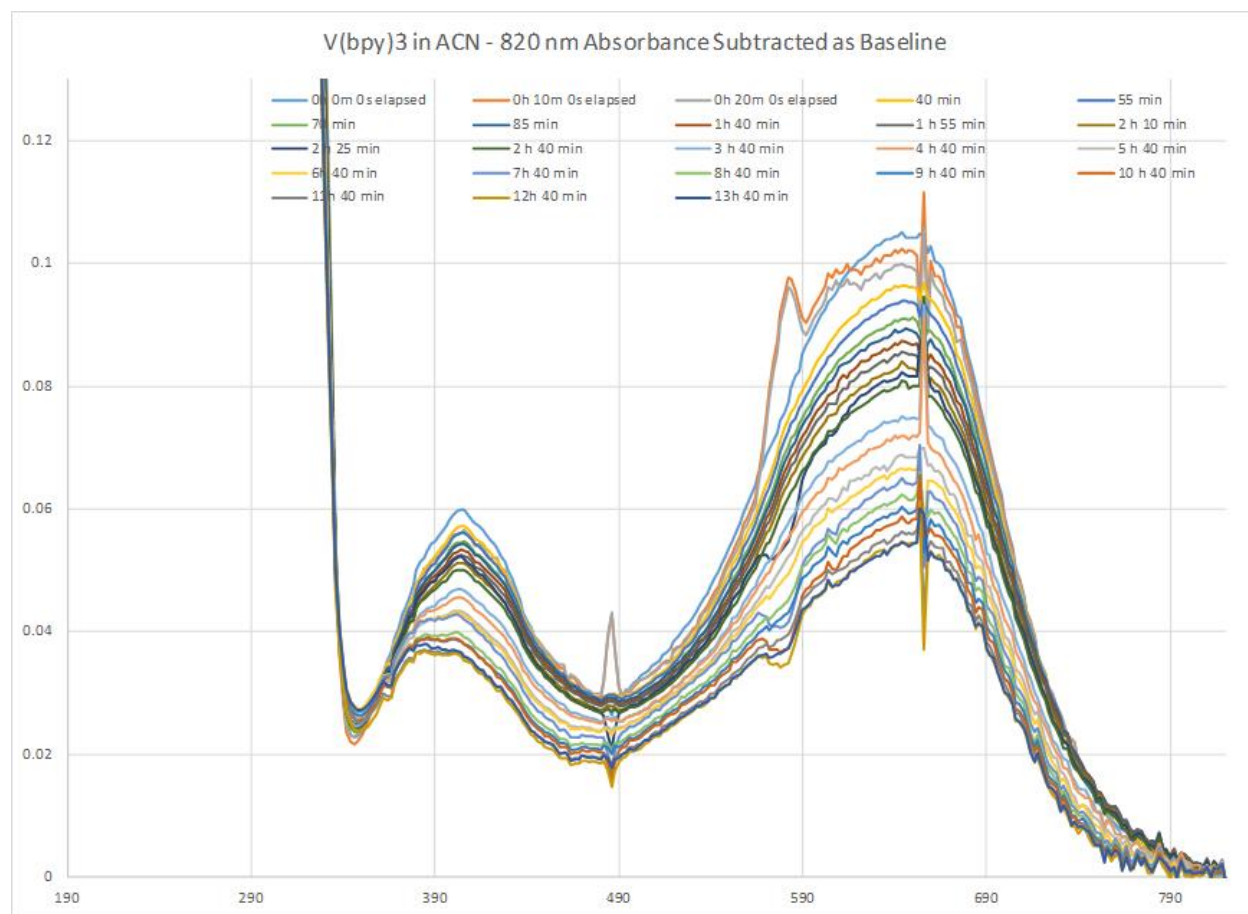


Figure A2.1 Visible absorbance spectra of $\sim 20 \mu\text{M}$ **3.1B** in CH_3CN performed by the Damrauer group.

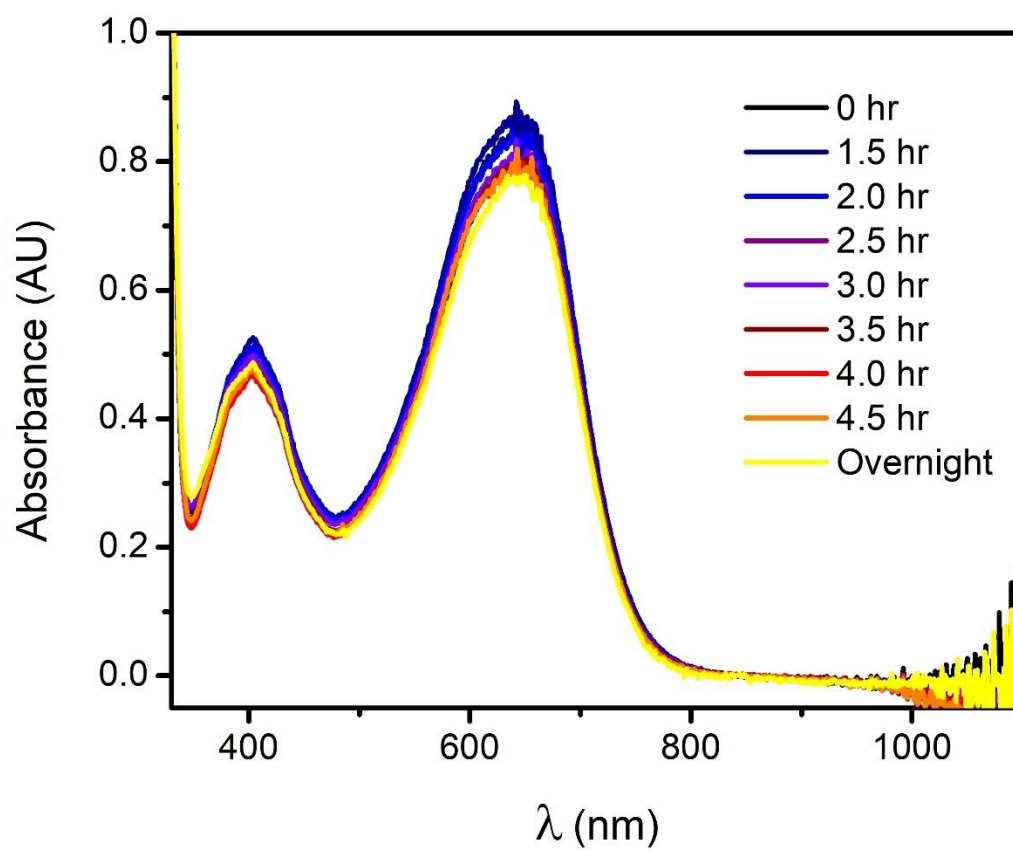


Figure A2.2 Visible absorbance spectra of ~200 μ M of **3.1B** in CH₃CN measured in the Shores laboratory.

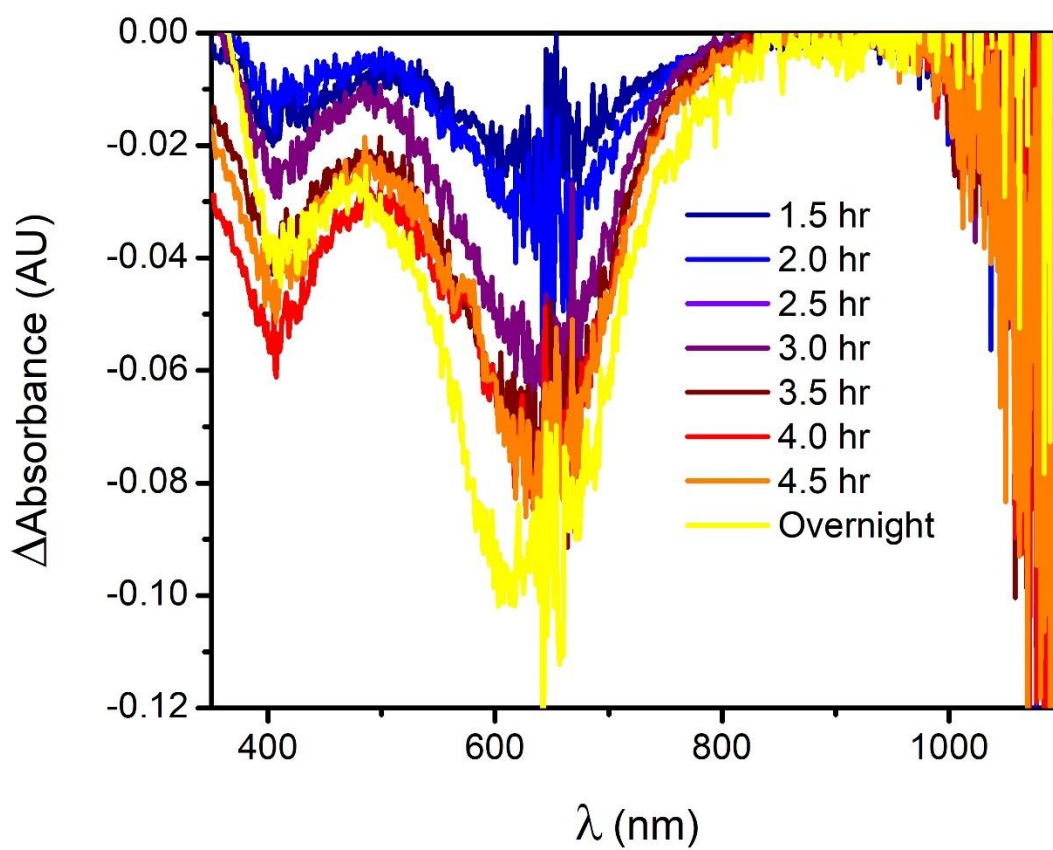


Figure A2.3 Difference spectra of $\sim 200 \mu\text{M}$ of **3.1B** in CH_3CN measured in the Shores laboratory.

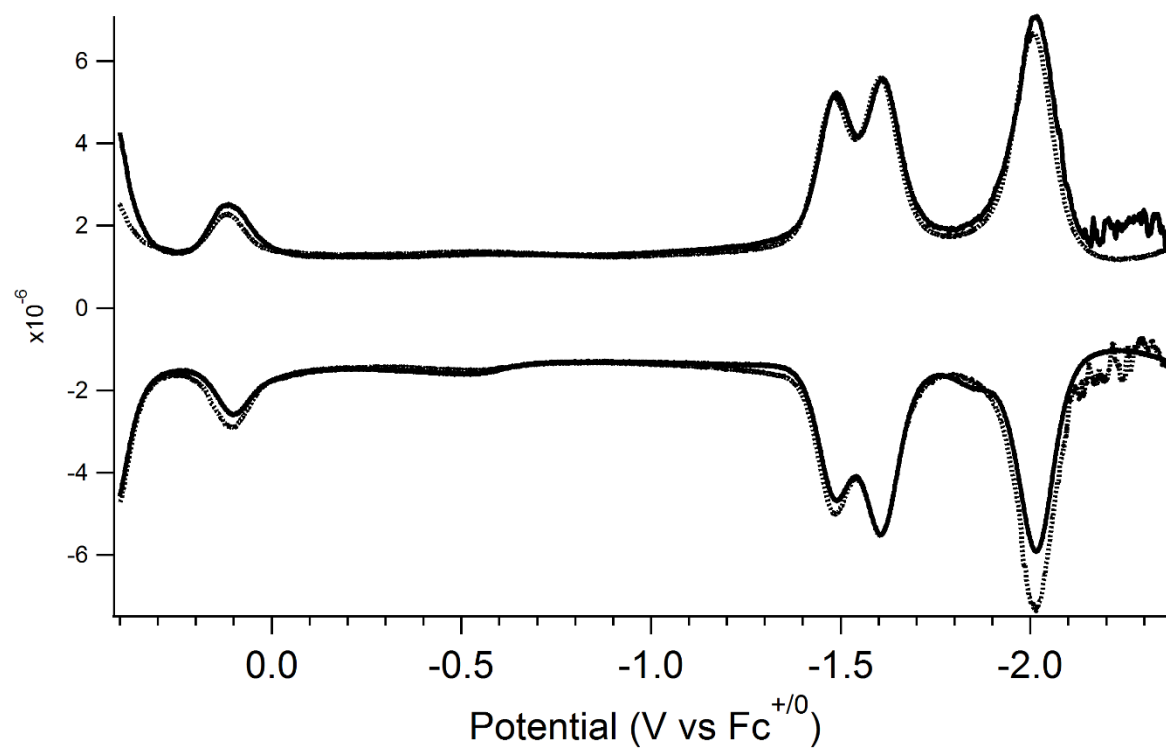


Figure A2.4 Square wave voltammogram of **3.1B** in CH_3CN . The peak at 0.11 V vs Fc^+/Fc^0 is attributed to the $3+/2+$ redox couple.

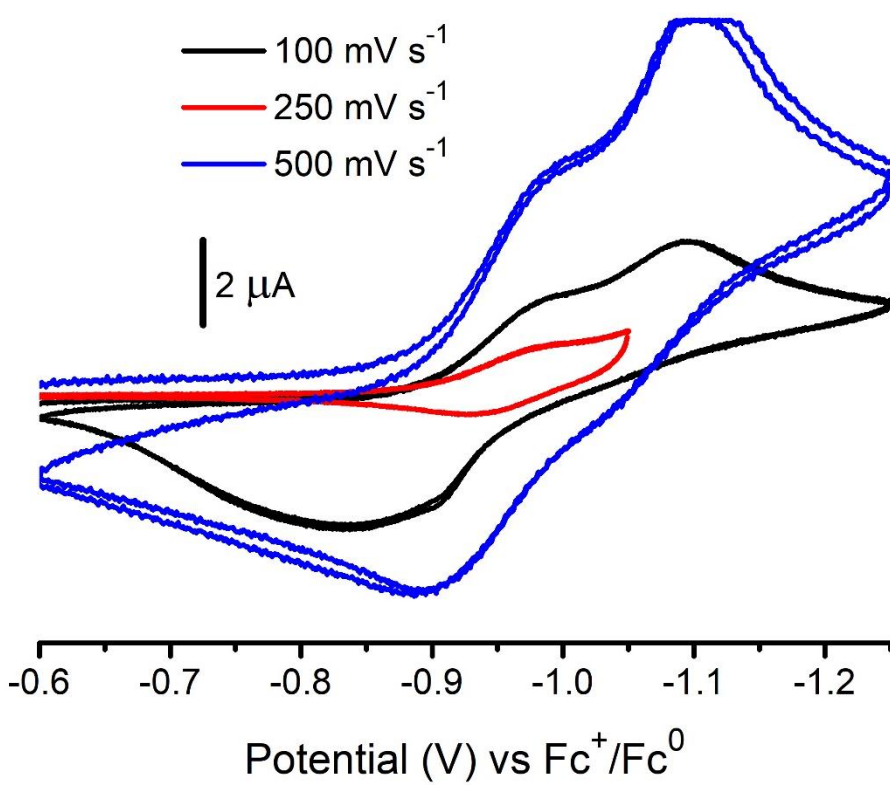


Figure A2.5 Cyclic voltammograms of **3.2** in CH₃CN taken at different scan rates.

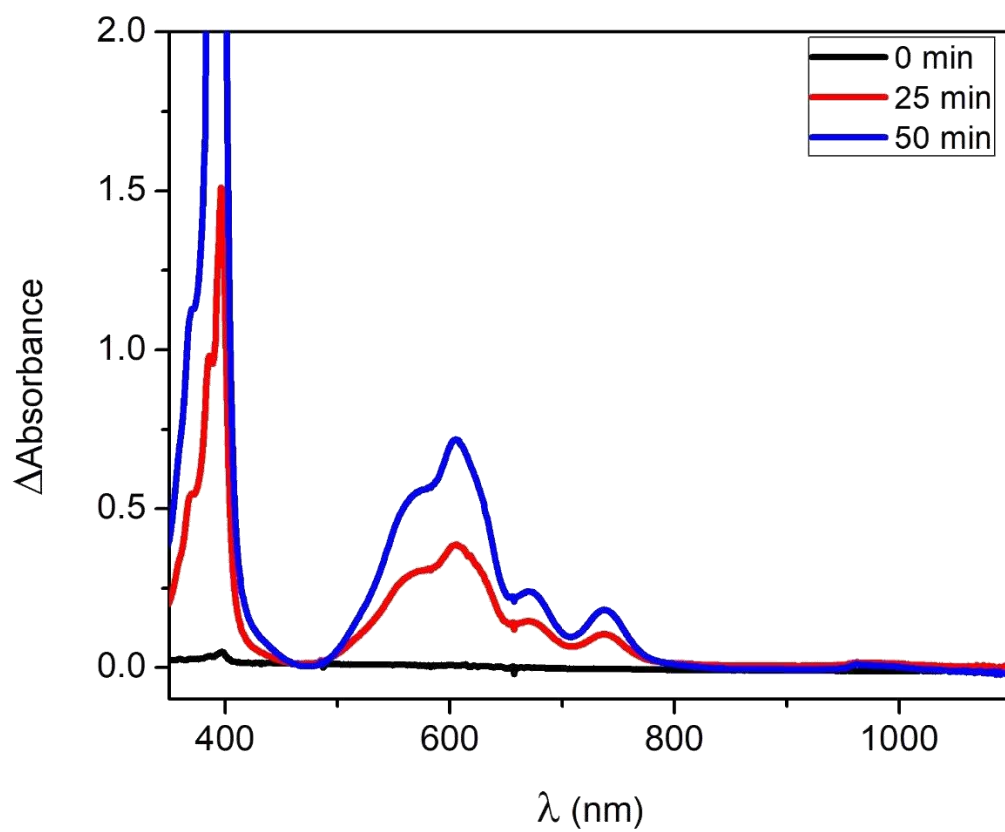


Figure A2.6 Difference in absorbance spectra for reaction mixture of **3.2** and methyl viologen. The increased absorbance is attributed to the growth of reduced methyl viologen.

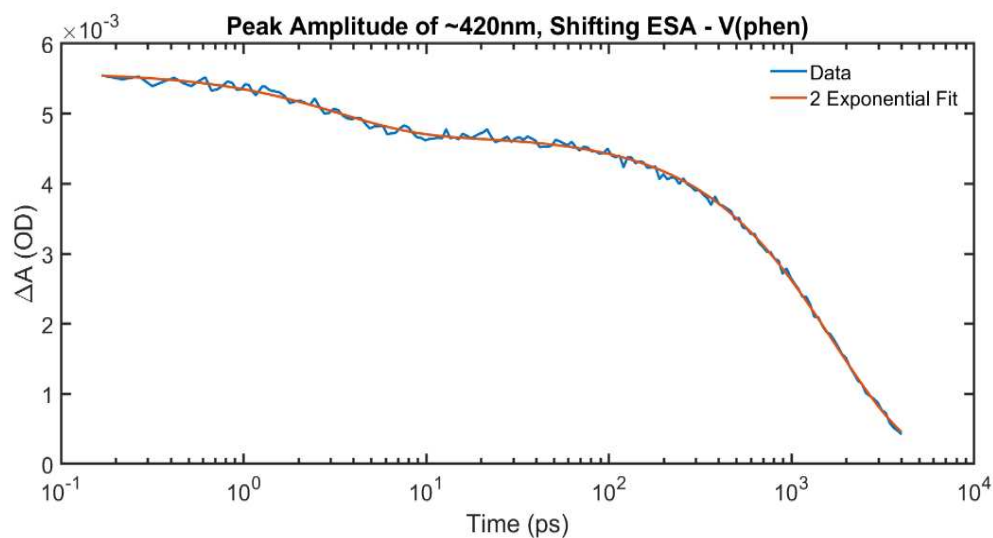


Figure A2.7 Fit of the 420 nm PA peak amplitude as a function of time in compound **3.2**. $\tau_1 = 3.3$ ps, $\tau_2 = 1710$ ps, $R^2 = 0.9985$

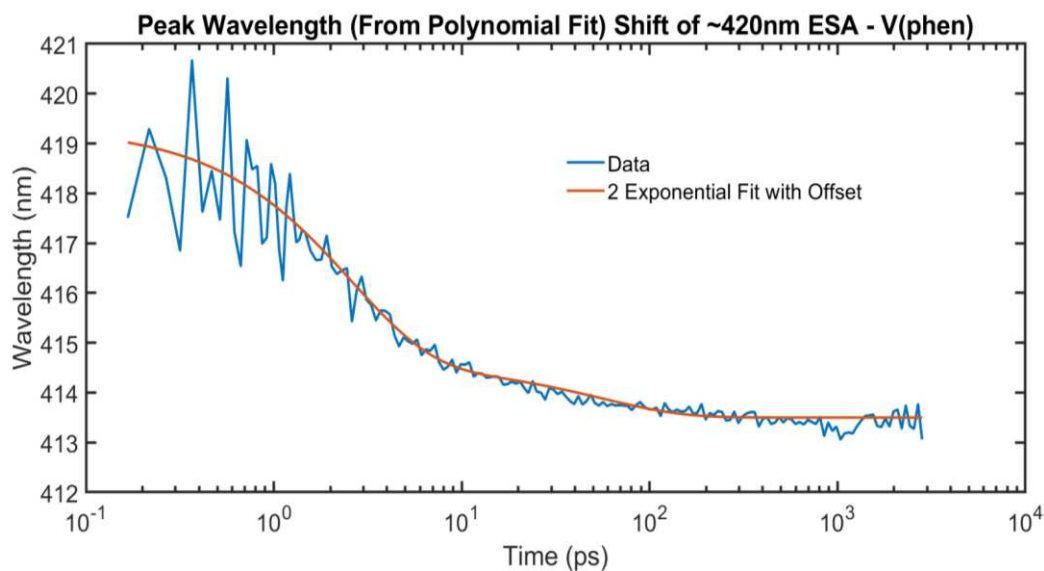


Figure A2.8 Fit of peak wavelength as a function of time in compound **3.2**. $\tau_1 = 2.6$ ps, $\tau_2 = 55$ ps, $R^2 = 0.9899$

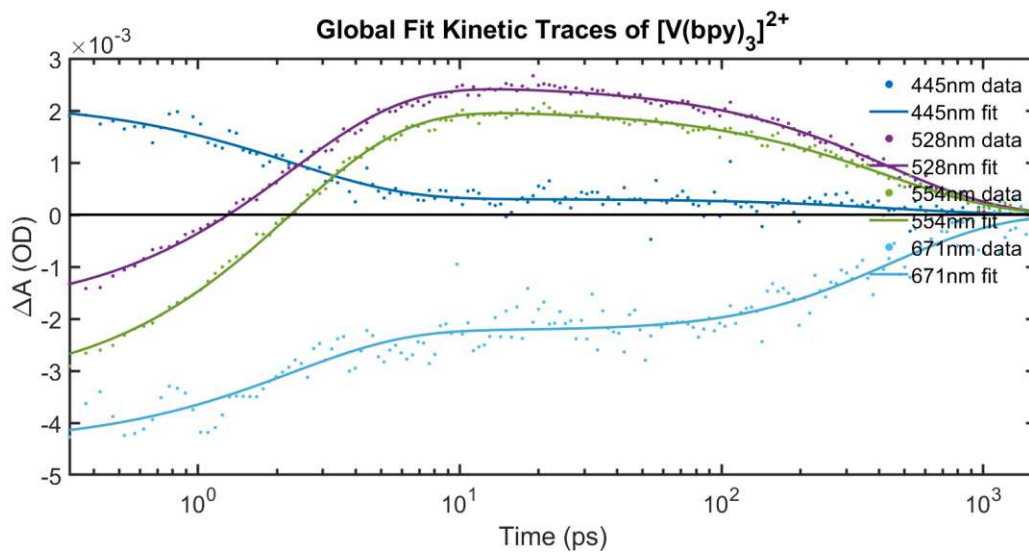


Figure A2.9 Kinetic fits to single wavelength time traces obtained from a global fit using 3 exponential decay components.

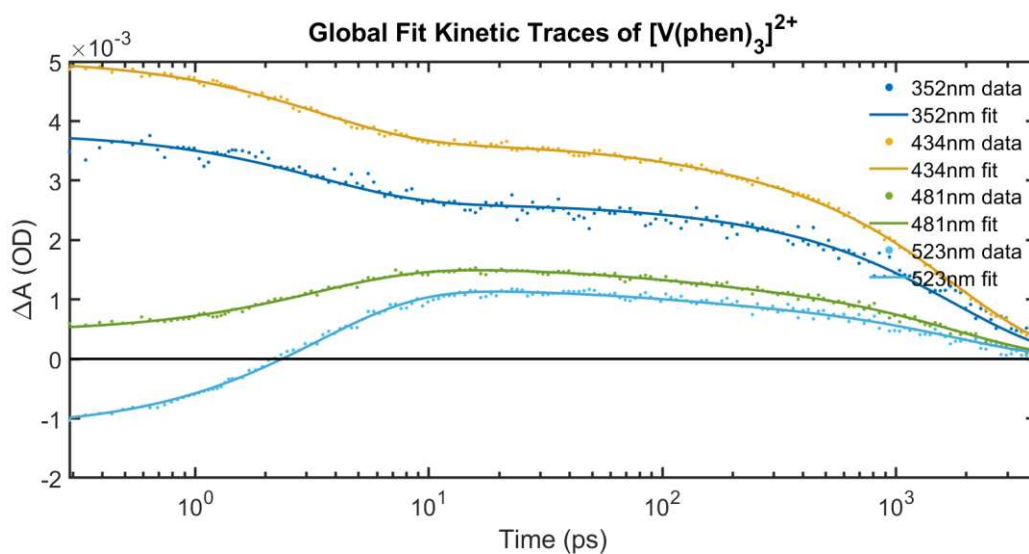


Figure A2.10 Kinetic fits to single wavelength time traces obtained from a global fit using 3 exponential decay components.

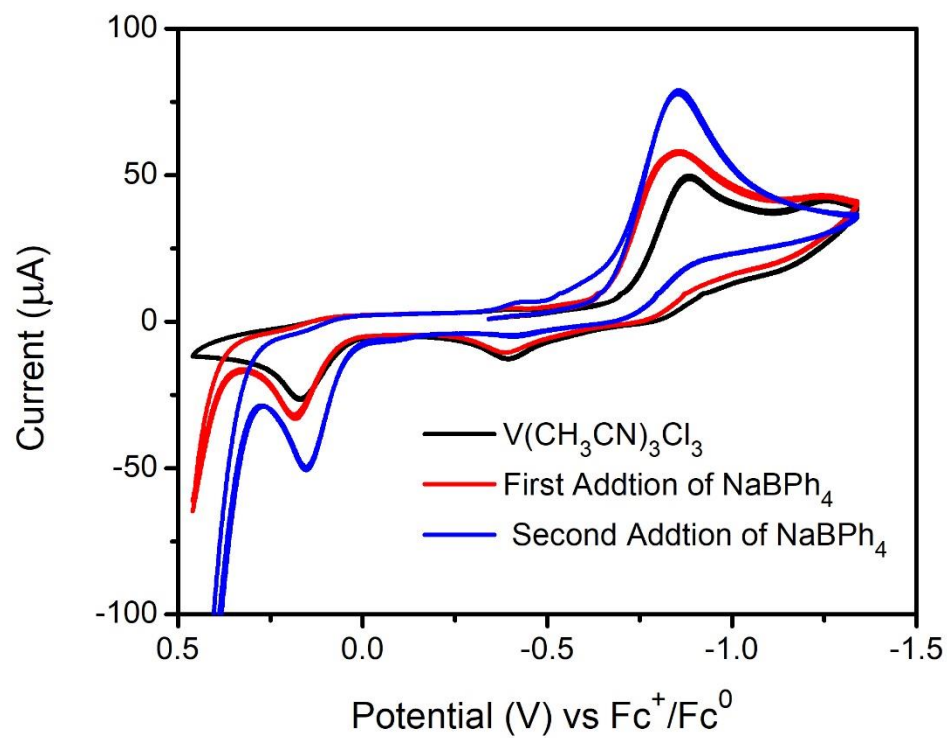


Figure A2.11 Cyclic voltammogram of $[\text{V}(\text{CH}_3\text{CN})_3\text{Cl}_3]$ performed in 0.1 M Bu_4NPF_6 in CH_3CN . NaBPh_4 was added in two, spatula tip portions.

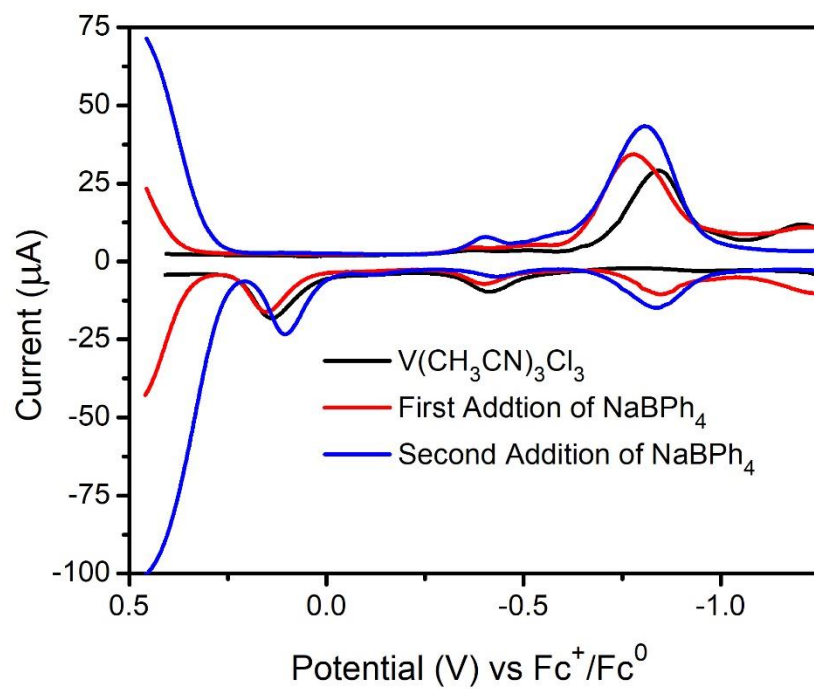


Figure A2.12 Square wave voltammogram of $[V(CH_3CN)_3Cl_3]$ performed in 0.1 M Bu_4NPF_6 in CH_3CN . $NaBPh_4$ was added in two portions.

APPENDIX 3: Supporting Information for Chapter 4

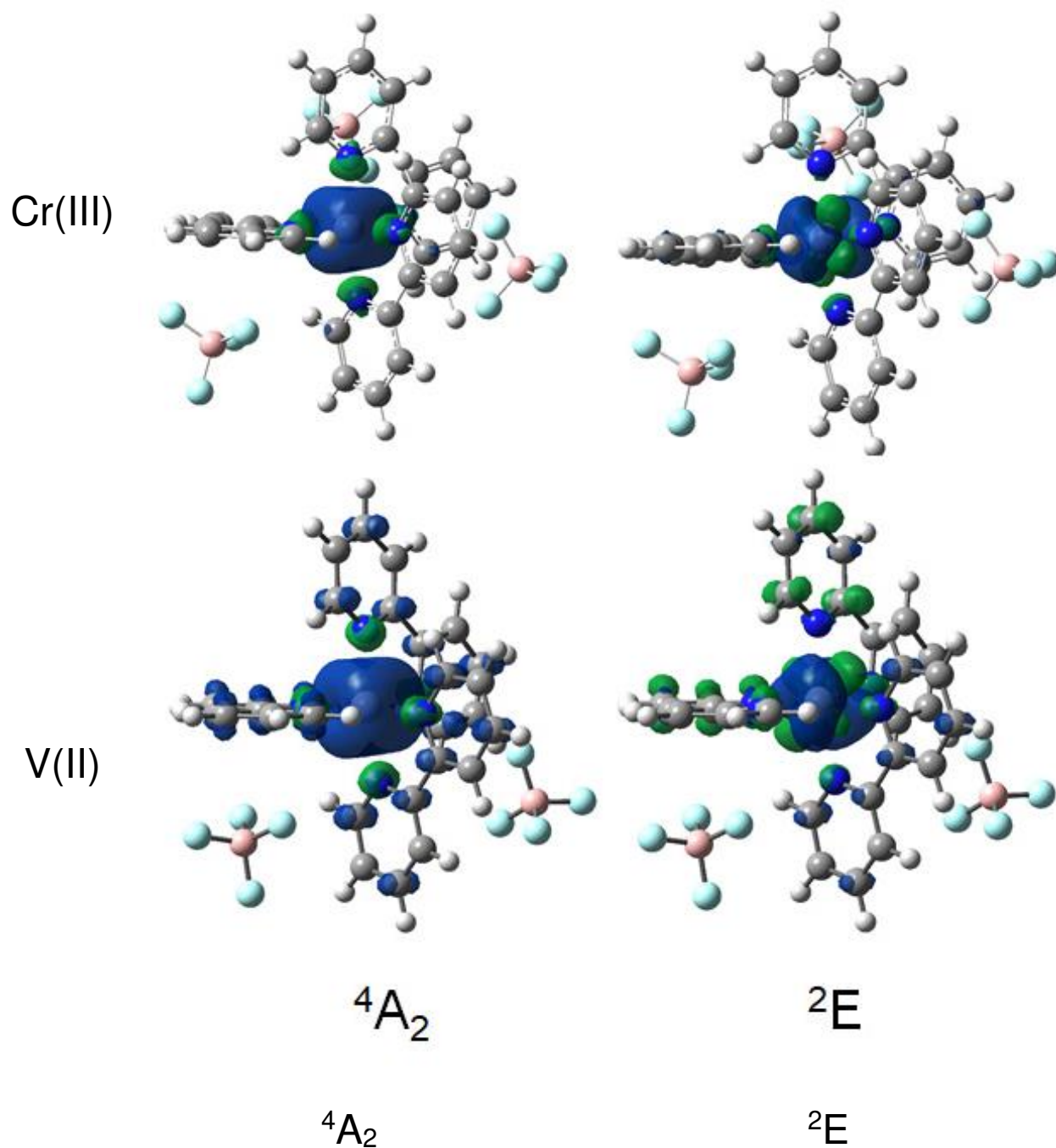


Figure A3.1 Original spin density plots of 4A_2 and 2E states of compound **4.1** and $[V(bpy)_3](BF_4)_2$.

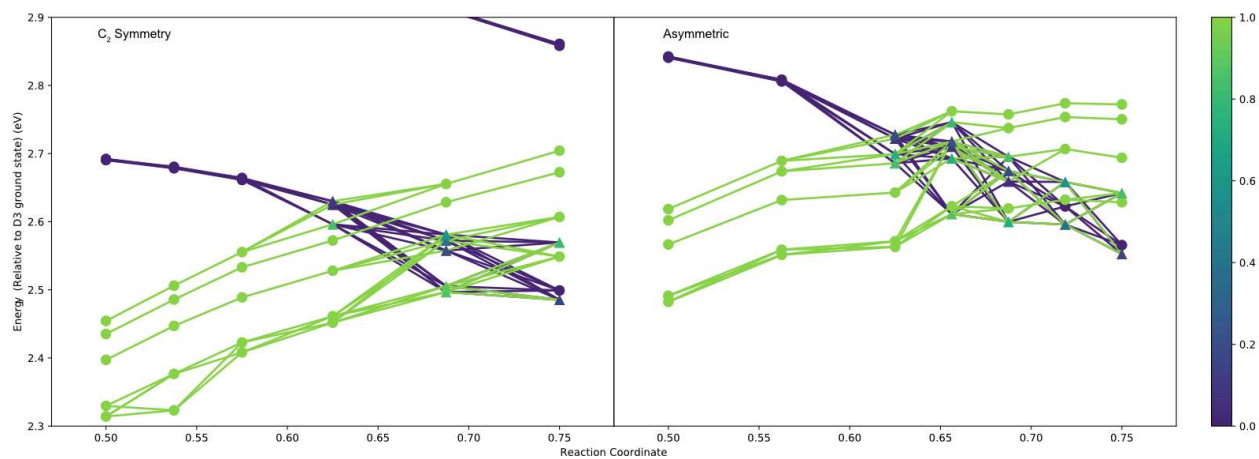


Figure A3.2 SORCI excited state calculations including SOC contributions for the reaction coordinate range 0.5 to 0.75 for the linear paths formed from the C₂ constrained structure and the vibrational minimum structure. The y-axis range has been limited to 2.3-2.9 eV for better clarity in the lowest crossing region. The lines are colored purple for quartet states and green for doublet states. Each circle represents a pure doublet/quartet state while the triangles represent a state of mixed character whose mixture corresponds to the color bar.

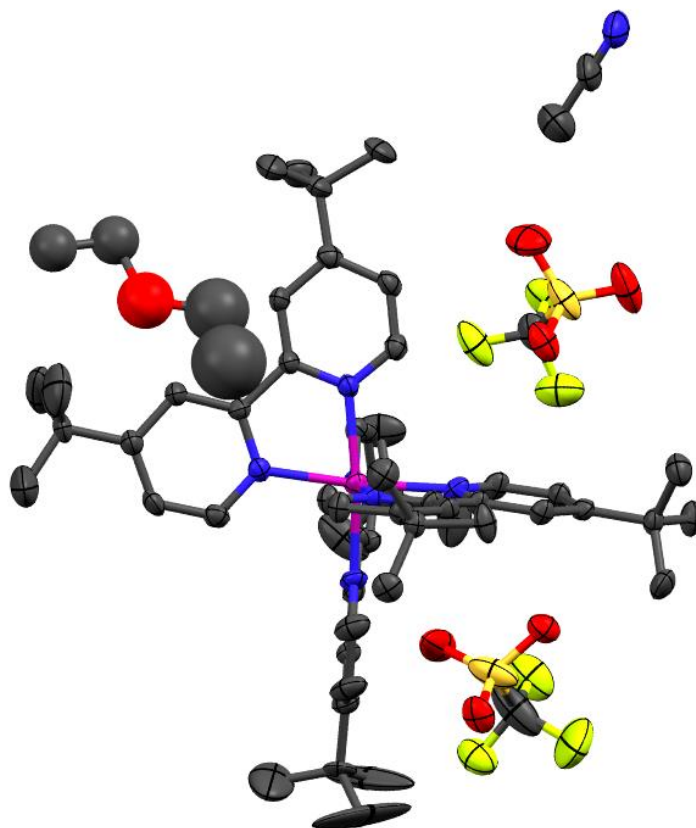


Figure A3.3 Crystal structure of compound **4.4**. Hydrogen atoms are omitted for clarity. Ellipsoids are set to 40%.

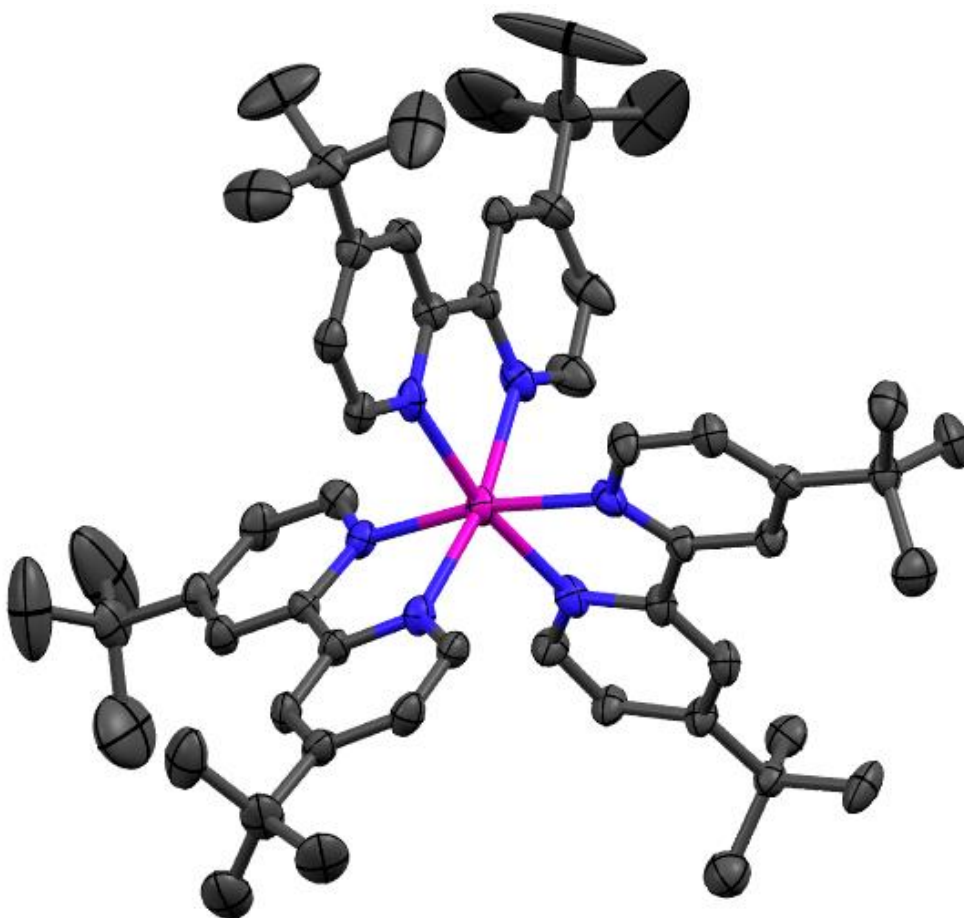


Figure A3.4 Crystal structure of the V(II) complex in compound **4.4**. Solvent, hydrogen, and anion atoms are omitted for clarity. Ellipsoids are set to 40%.

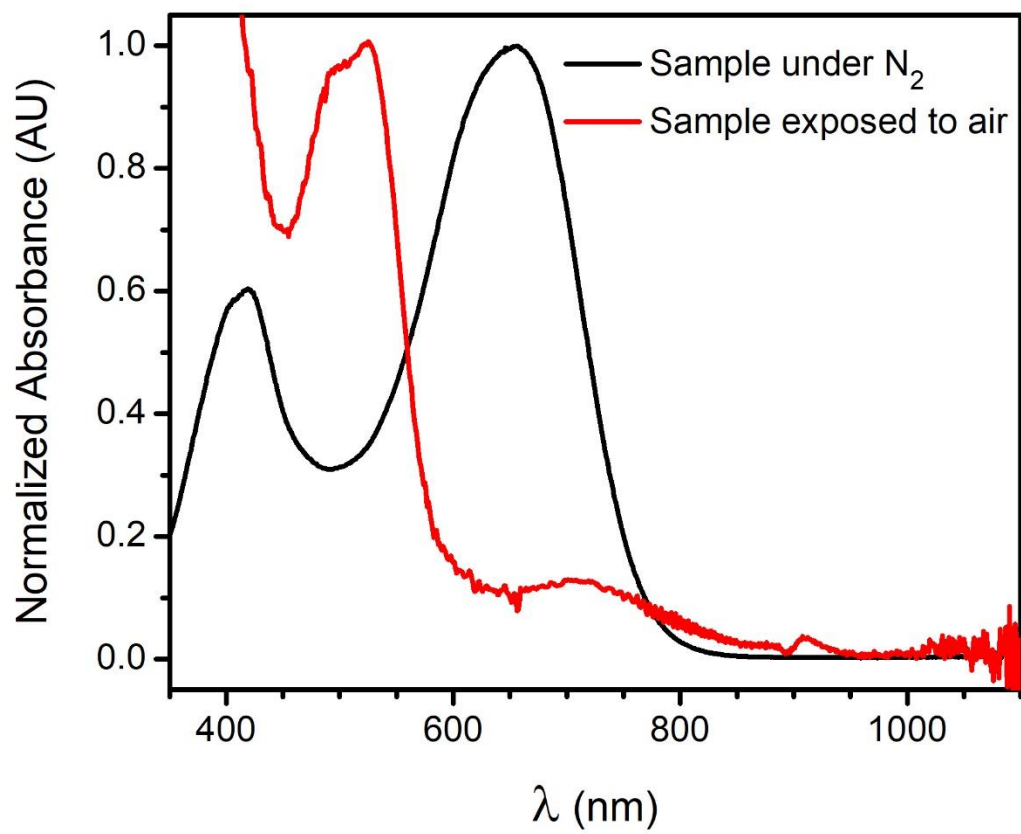


Figure A3.5 Compound **4.4** in 0.1 M Bu₄NPF₆ in CH₃CN under an inert atmosphere(black) and exposed to air(red)

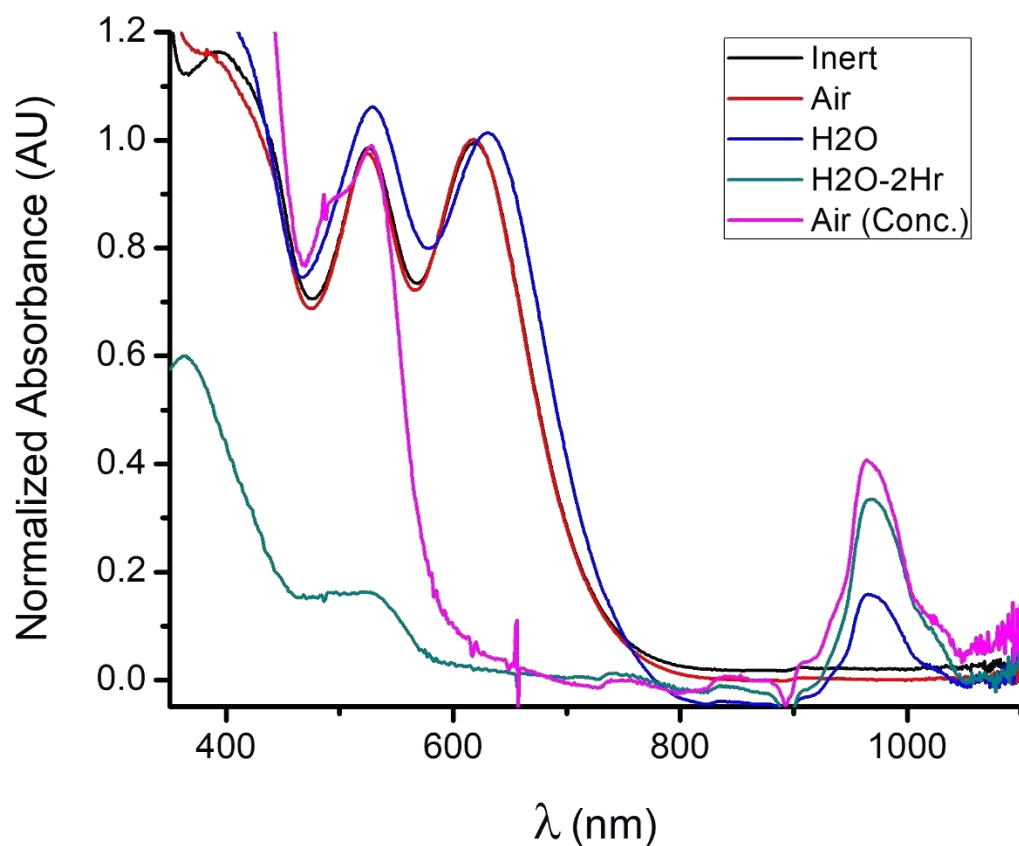


Figure A3.6 Compound **4.4** and its attempted oxidation with stoichiometric AgBF_4 under inert (black), atmospheric (red), atmospheric and wet (blue) conditions. The sample under atmospheric and wet conditions was measured once more after 2 hours (teal). A concentrated sample exposed to AgBF_4 and atmospheric conditions was also measured (pink).

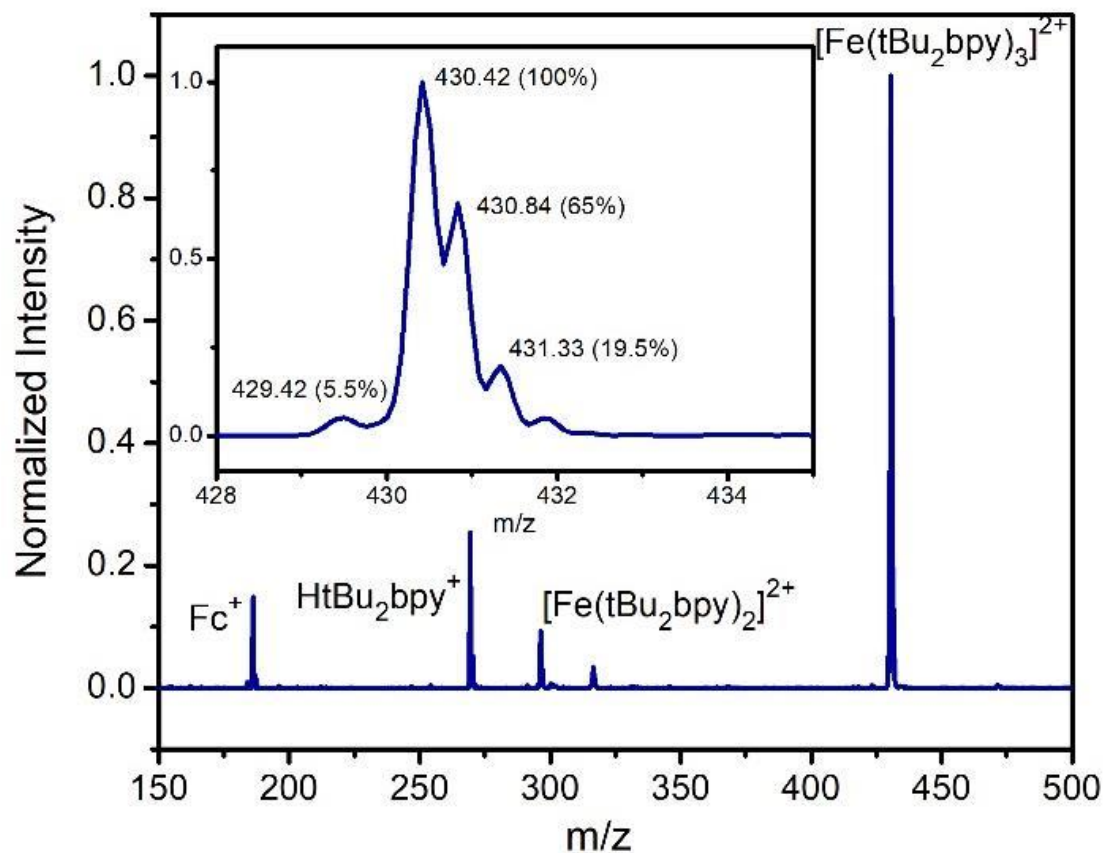


Figure A3.7 Mass spectrometry plot of $[\text{V}(\text{tBu}_2\text{bpy})_3](\text{BF}_4)_3$ as prepared according to the procedure by Bowman and Wieghardt.¹¹

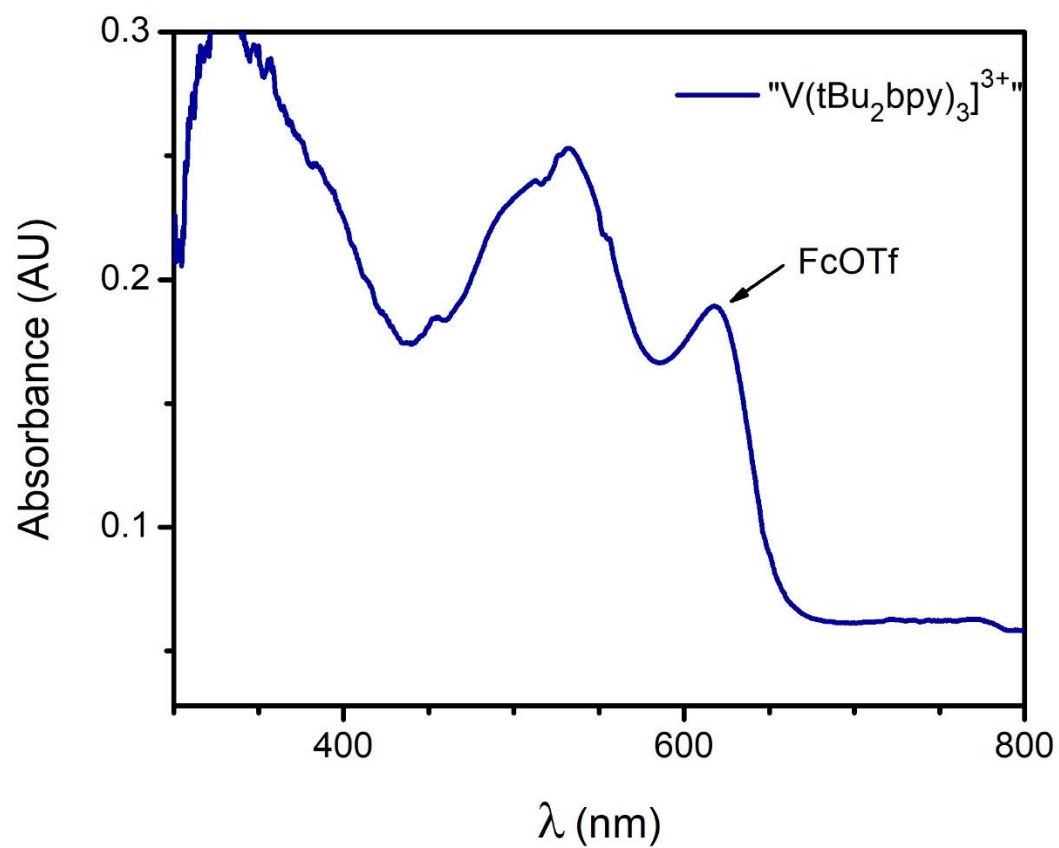


Figure A3.8 Absorbance spectra of $[V(tBu_2bpy)_3](OTf)_3$ in CH_3CN prepared in analogous method according to the procedure by Bowman and Wieghardt.¹¹ Residual FcOTf is present based on the absorbance peak at 618 nm.

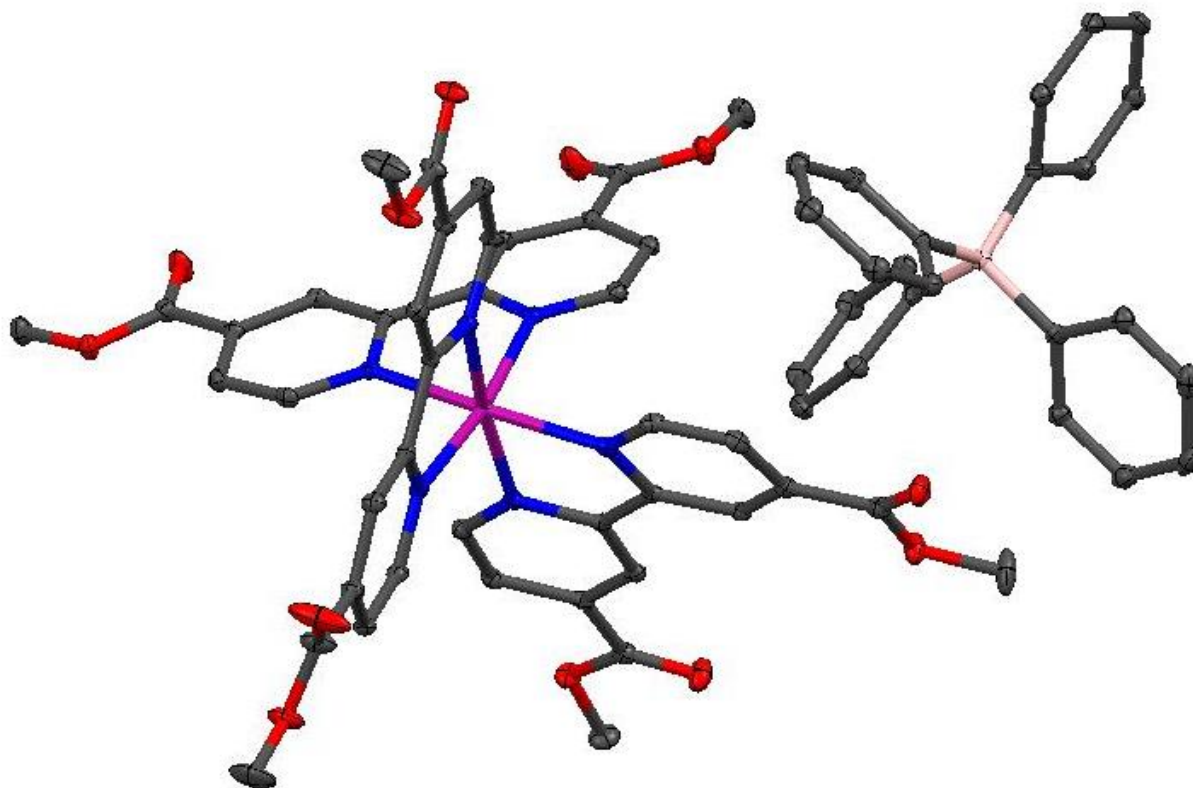


Figure A3.9 Crystal structure of $[V((CO_2Me)_2bpy)_3]BPh_4$. Hydrogen atoms are omitted for clarity. Ellipsoids are set to 40%.

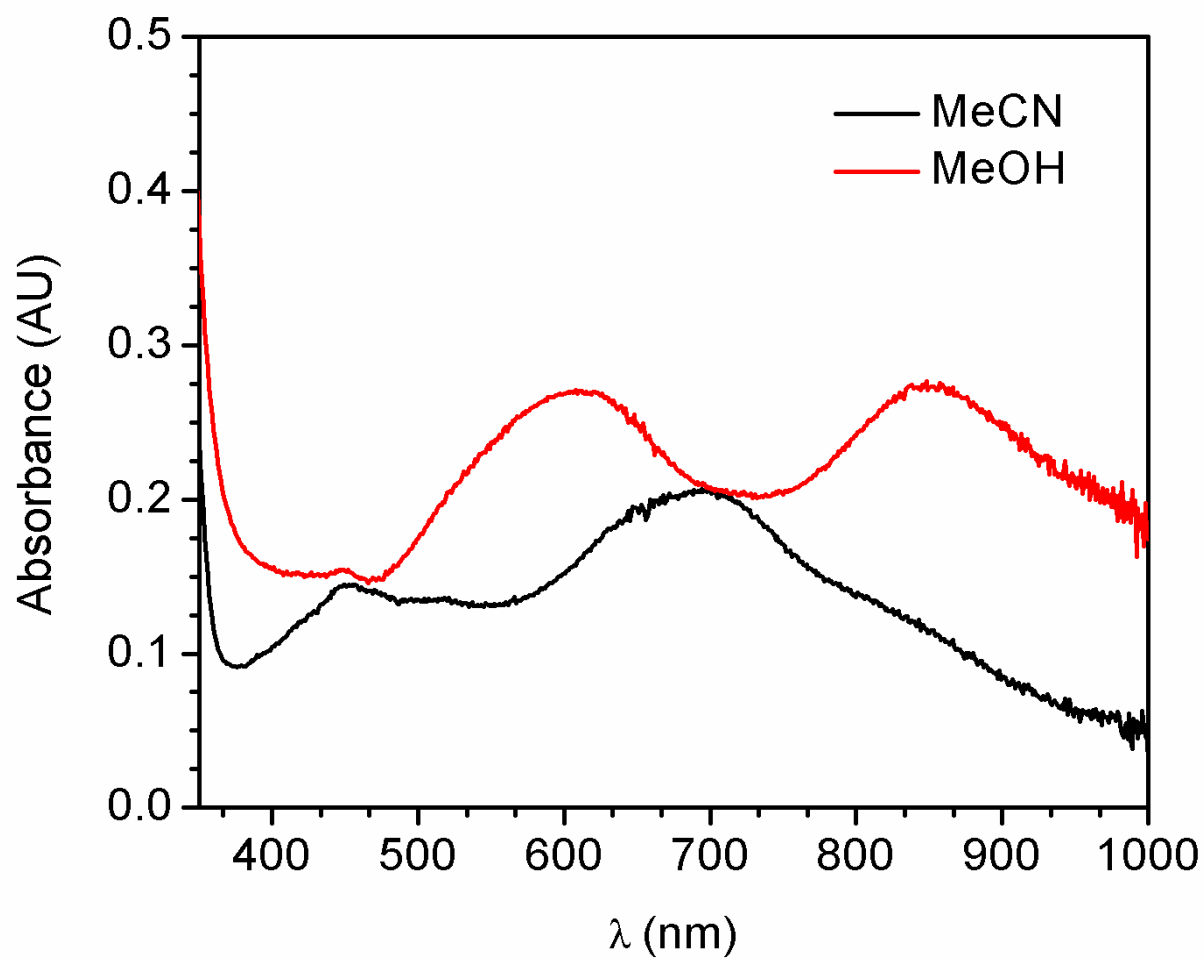


Figure A3.10 Representative absorbance spectra of **4.5** in a N-donor solvent (acetonitrile) and O-donor solvent (methanol).

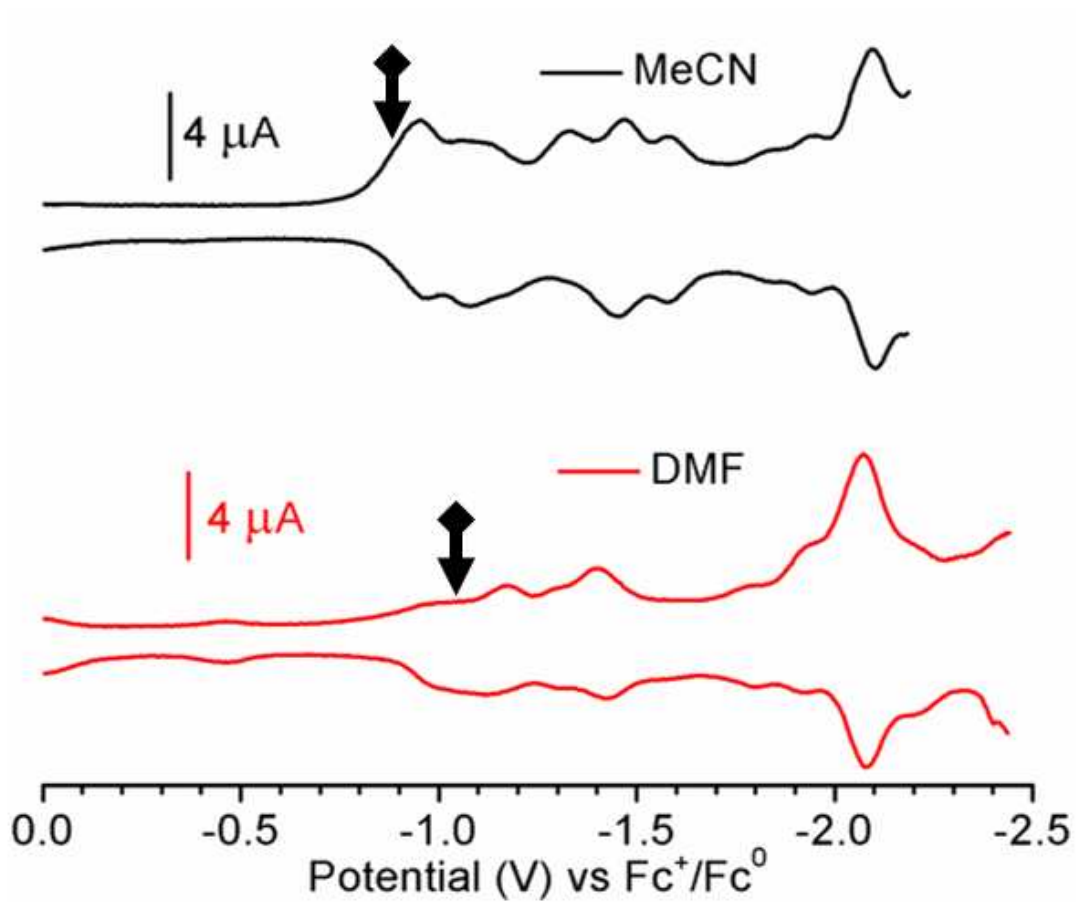


Figure A3.11 Square wave voltammogram of **4.5** measured in 0.1 M Bu₄NPF₆ in acetonitrile (black) and dimethylformamide (red). Arrows denote the open circuit potential before the scans.

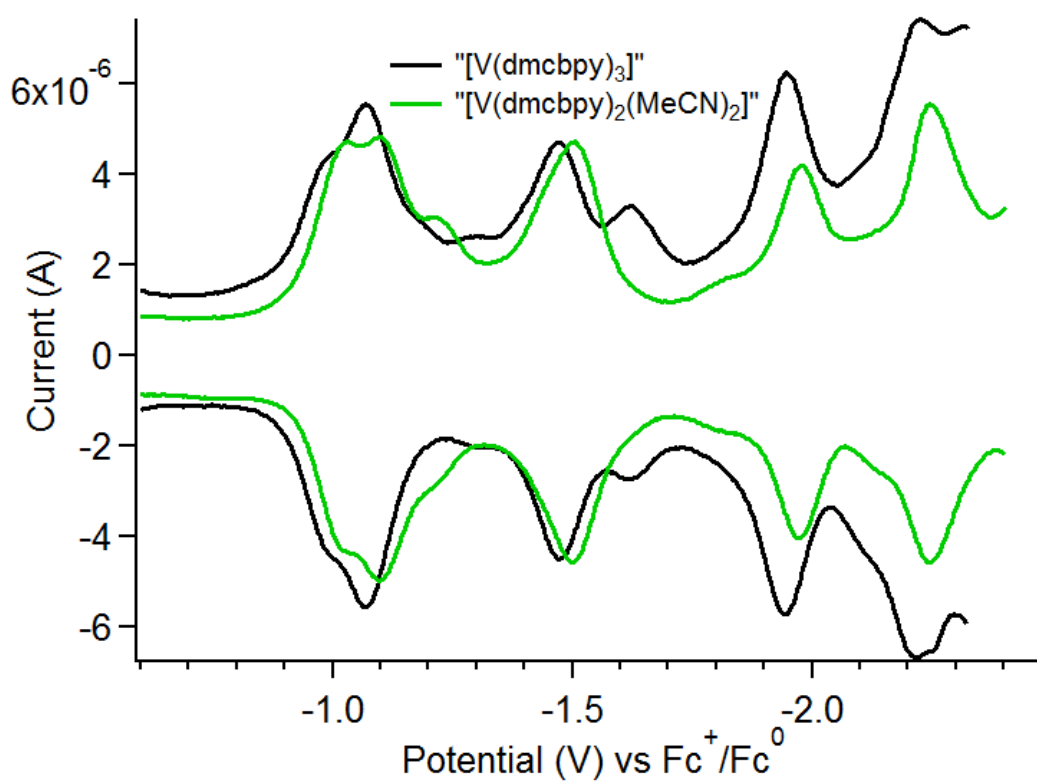


Figure A3.12 Square wave voltammogram of the attempted product $[\text{V}((\text{CO}_2\text{Me})_2\text{bpy})_3]^{2+}$ (black) and $[\text{V}((\text{CO}_2\text{Me})_2\text{bpy})_2(\text{CH}_3\text{CN})_2]^{2+}$ (green) in 0.1 M Bu_4NPF_6 in CH_3CN .

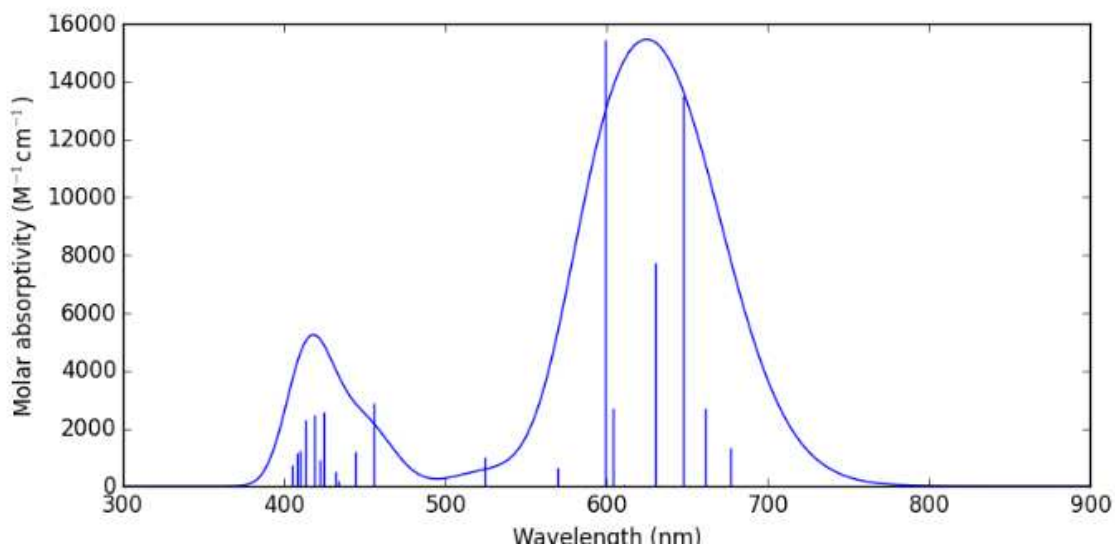


Figure A3.13 Calculated absorbance spectra of $[\text{V}(\text{bpy})_3](\text{BF}_4)_2$.

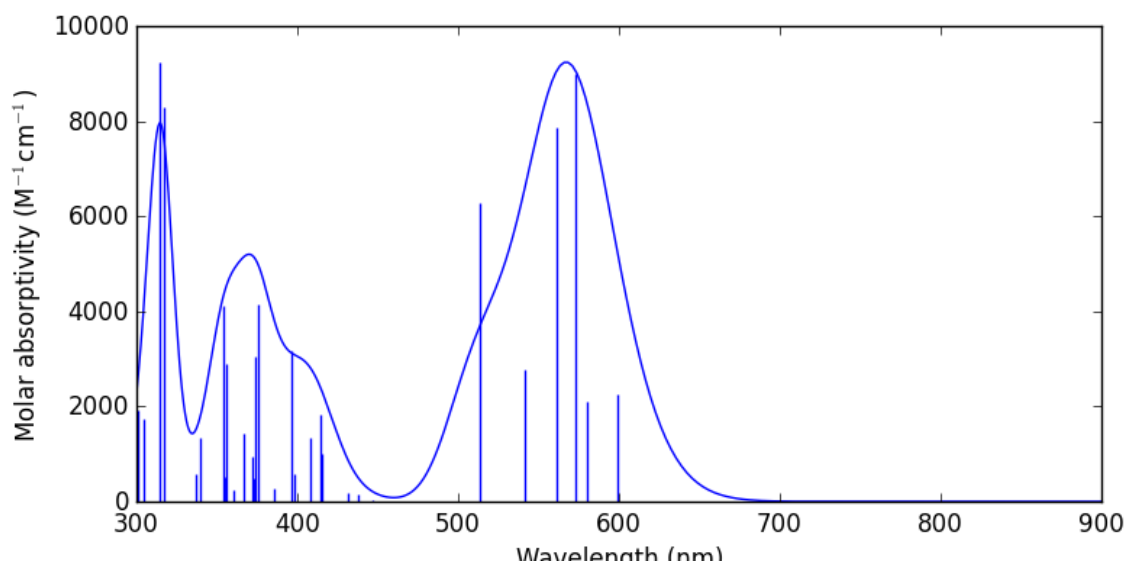


Figure A3.14 Calculated absorbance spectra of $[\text{V}(\text{bpy})_2(\text{CH}_3\text{CN})_2](\text{BF}_4)_2$.

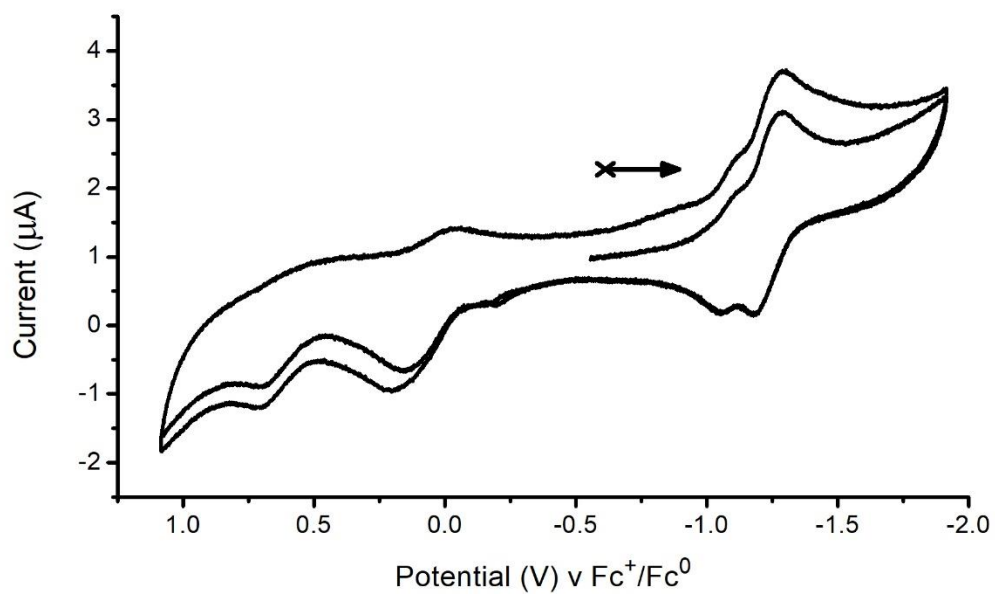


Figure A3.15 Cyclic voltammograms (0.1 V/s) of the cathodic reduction potentials for compound **4.6** in 0.1 M Bu_4NPF_6 in CH_3CN . The arrow indicate scan direction and the open circuit potential before each experiment.

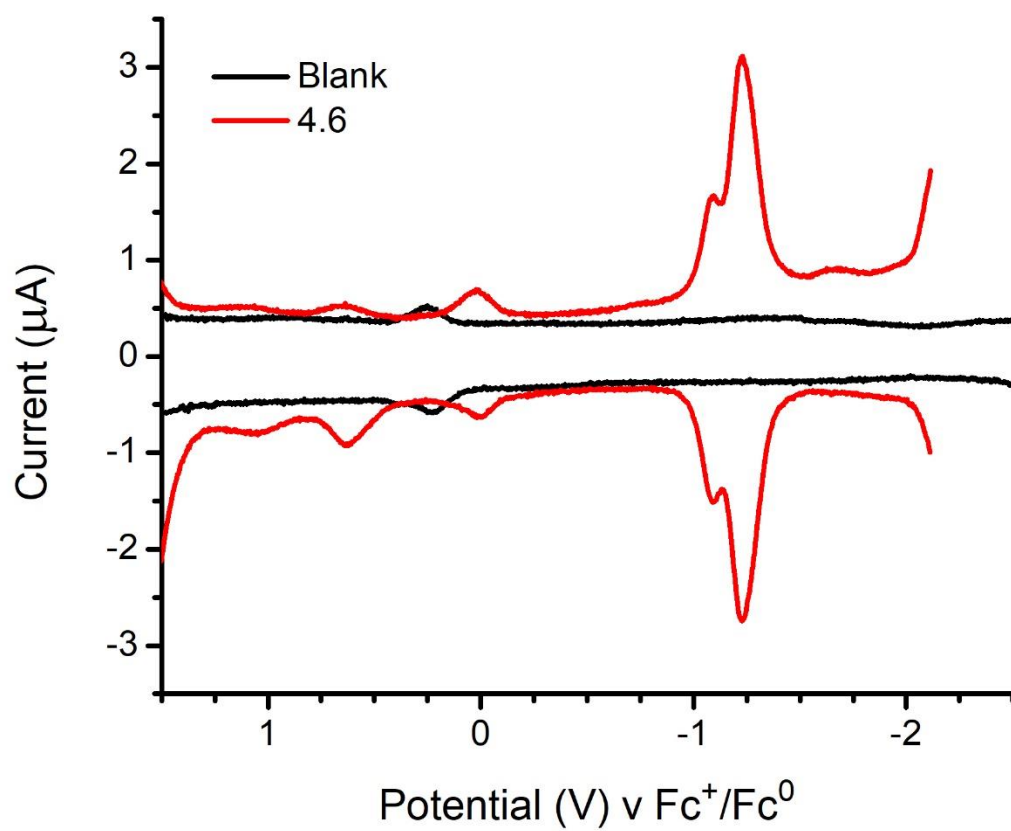


Figure A3.16 Square wave voltammogram of compound **4.6** in 0.1 M Bu₄NPF₆ in CH₃CN.

APPENDIX 4: Supporting Information for Chapter 5

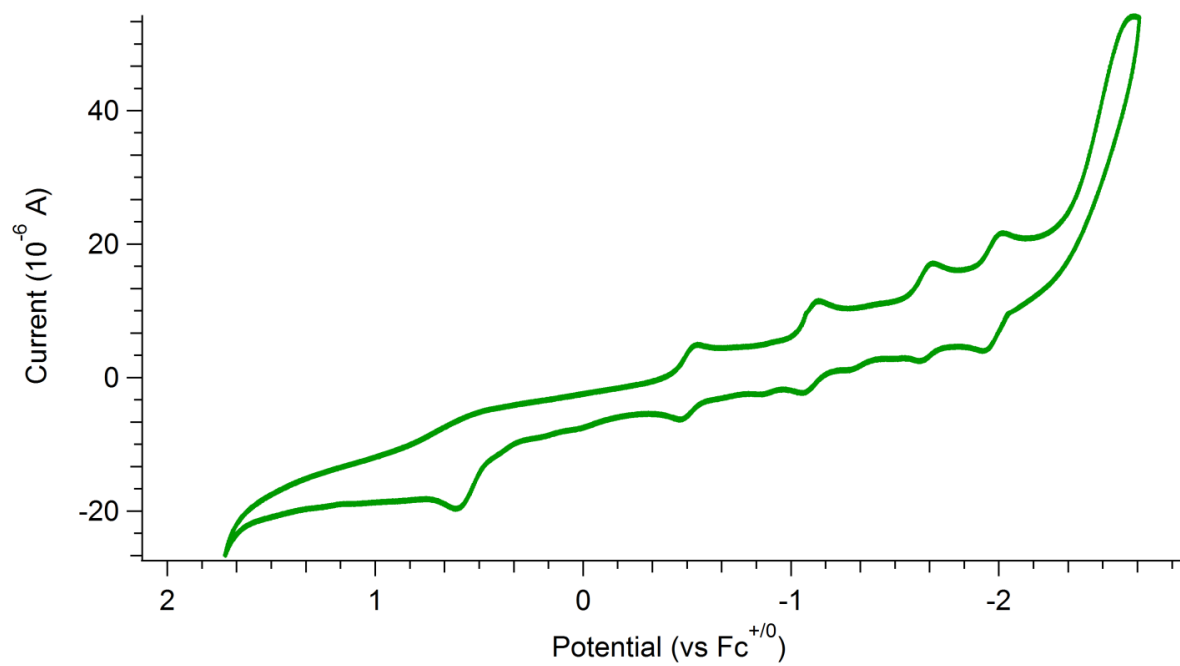


Figure A4.1 Cyclic voltammogram of the attempted

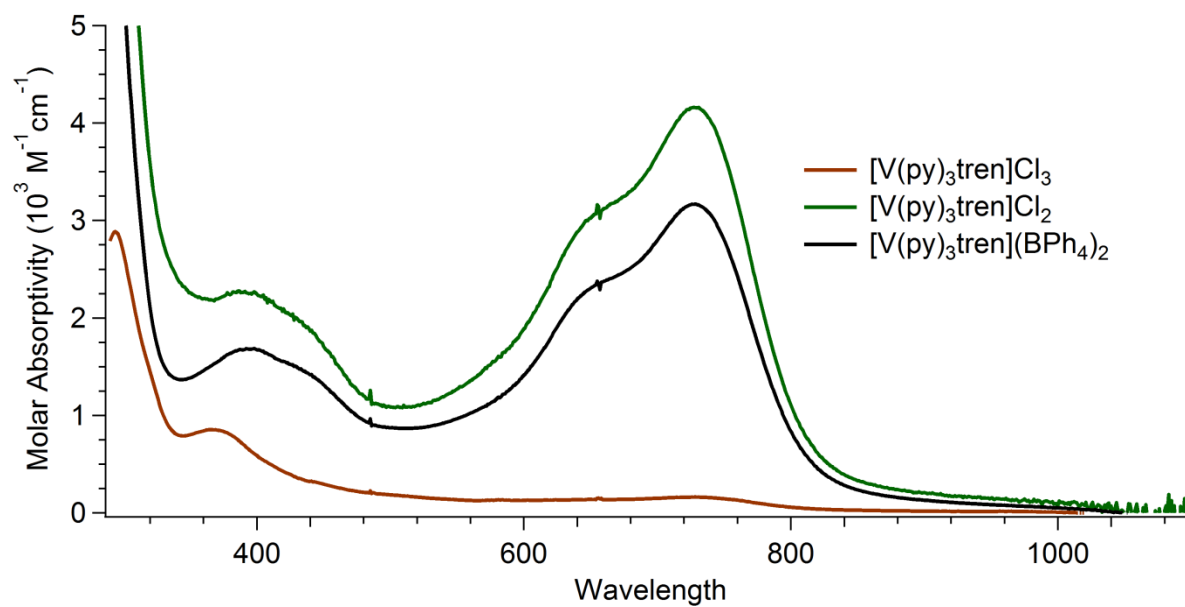


Figure A4.2 Absorbance spectra of the attempted products in Scheme 1

Table A4.1 Average bond-lengths and angels in compounds **5.1-5.3**

Compound	M-N _{Imine} , Å	M-N _{py} , Å	M-N _{tren} , Å	θ, °
5.1	2.127(7)	2.146(5)	3.151	48.06 (47.72, 47.82, 48.65)
5.2	2.094(4)	2.206(4)	2.228(5)	51.68 (51.31, 51.62, 52.12)
5.3	2.055	2.173	2.213	51.36 (51.93, 51.61, 50.55)

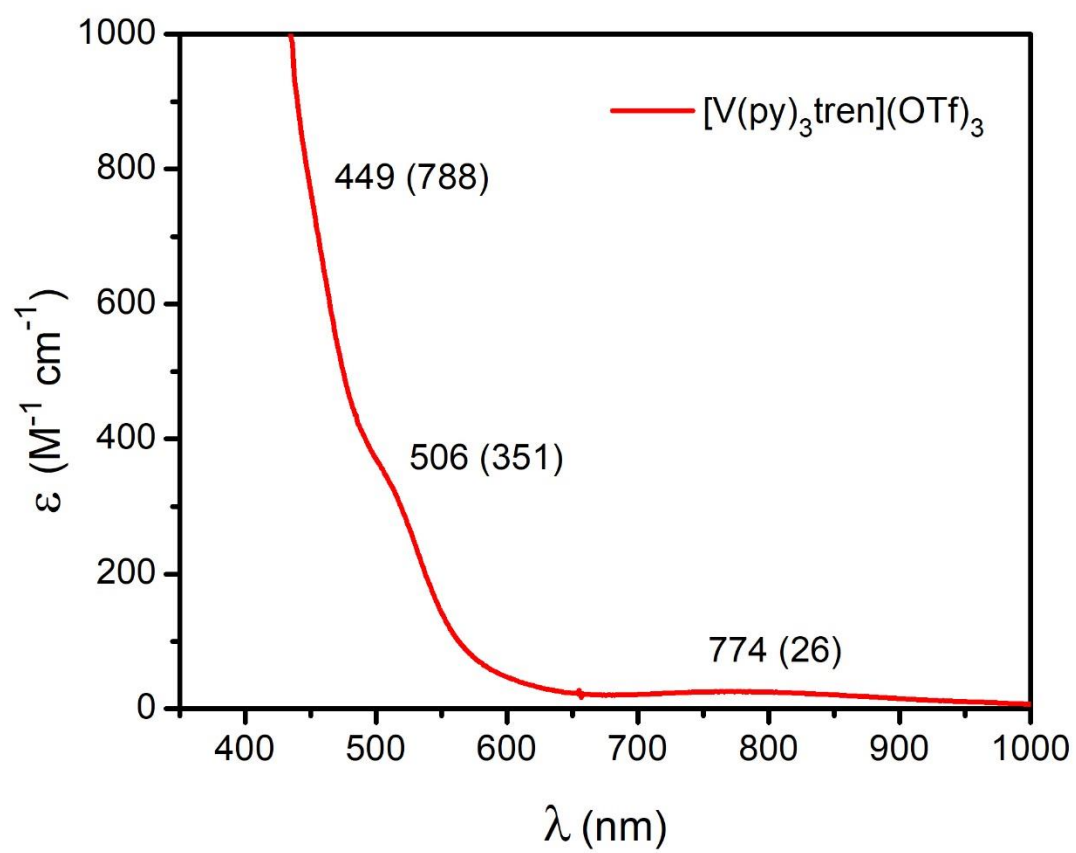


Figure A4.3 Absorbance spectra of compound **5.2**, highlighting metal-based transitions.

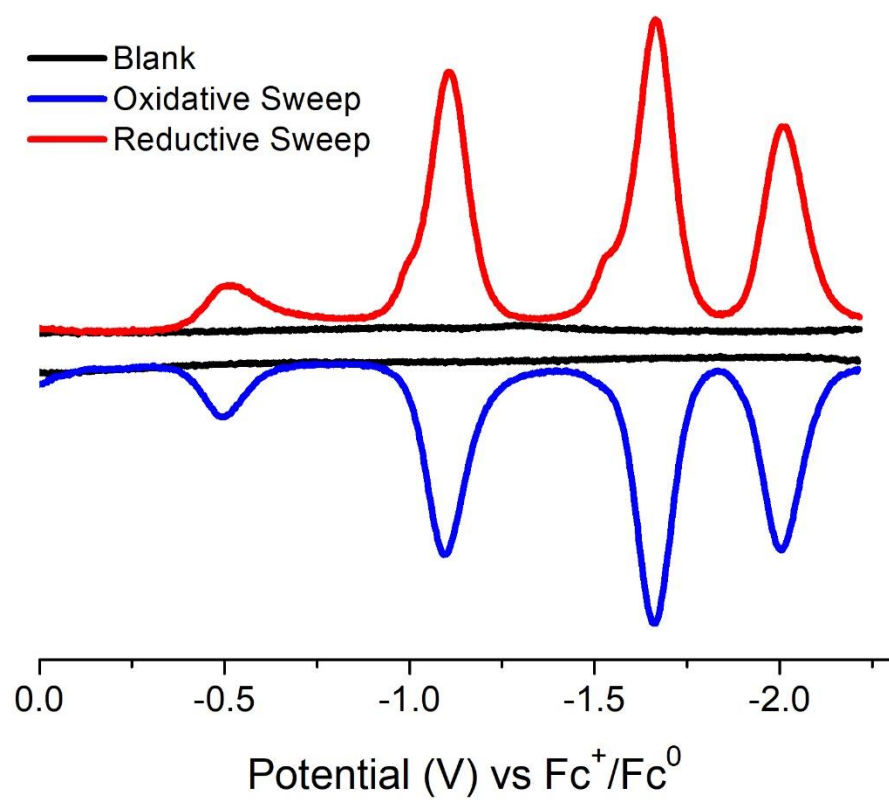


Figure A4.4 Square wave voltammogram of **5.2**

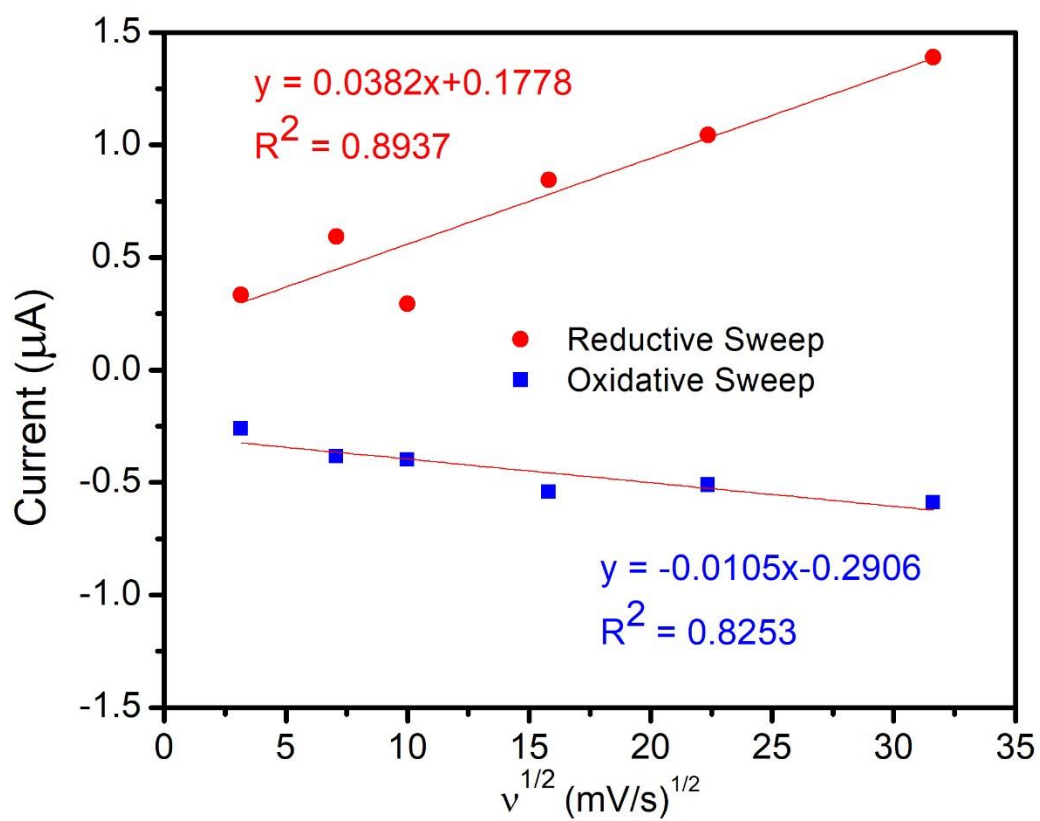


Figure A4.5 Randles-Sevcik analysis of 5.2

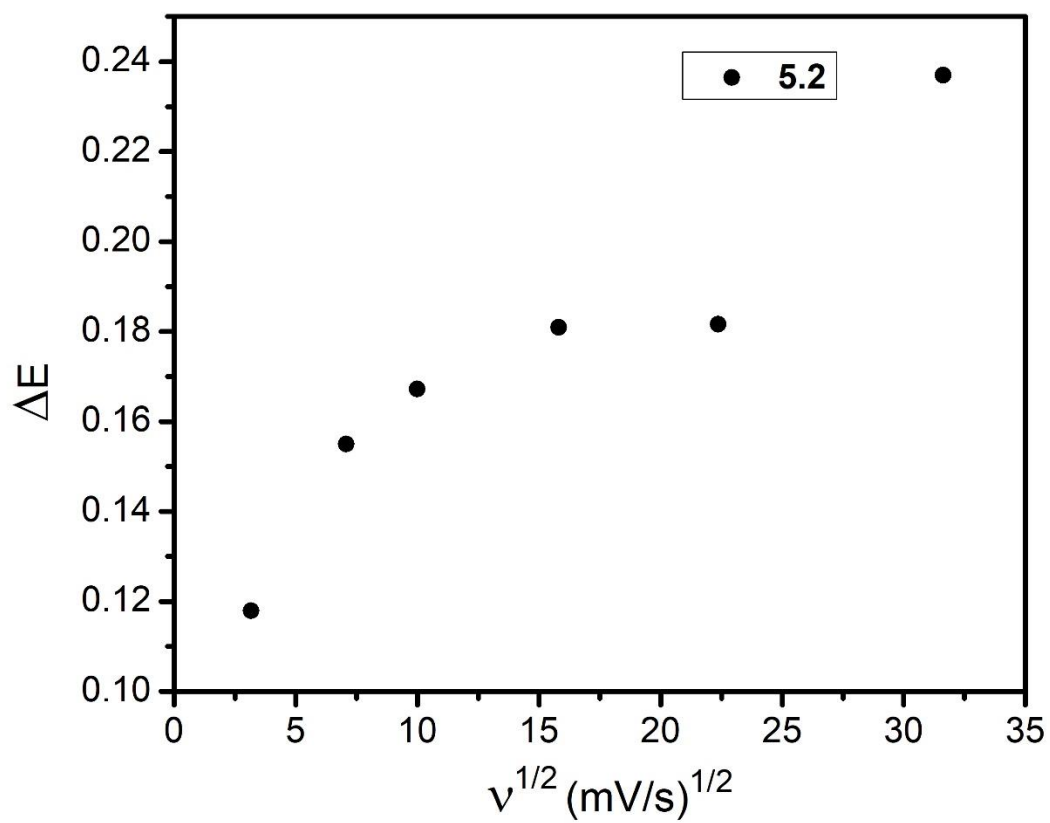


Figure A4.6 Peak to Peak separation(ΔE) of $E_{1/2}3+/2+$ redox couple in **5.2** as a function of the square root of scan rate.

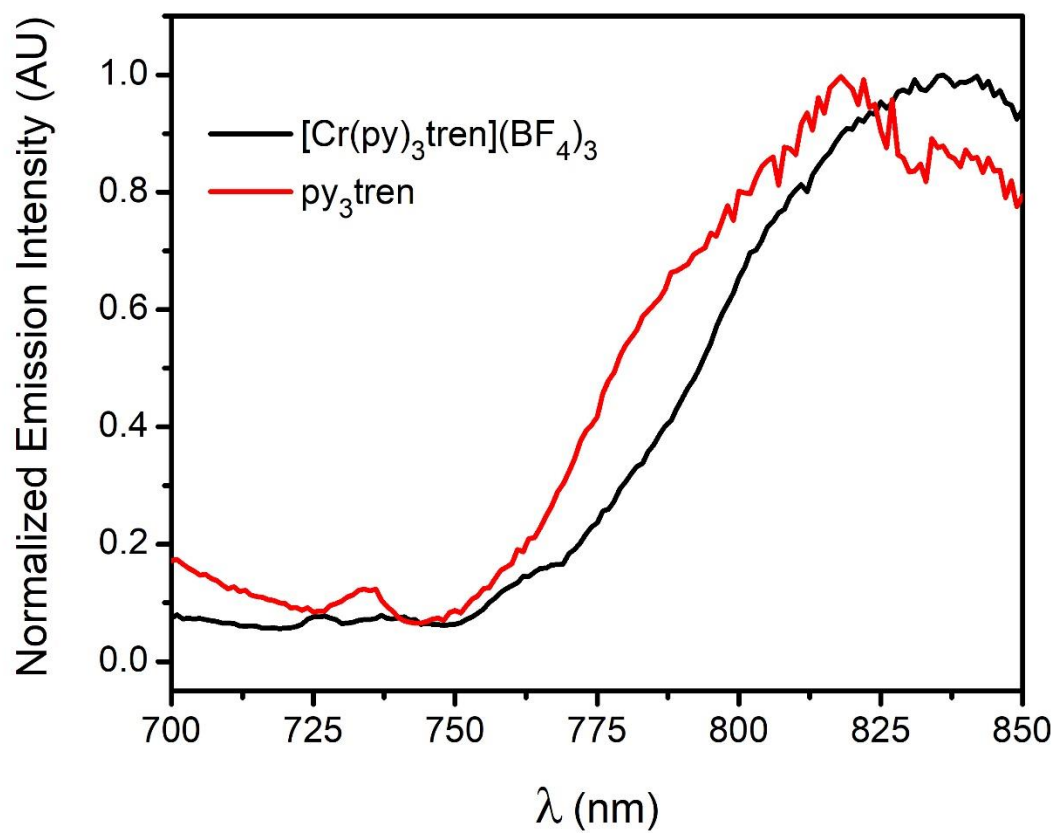


Figure A4.7 Emission spectra of [Cr(py)₃tren](BF₄)₃ and py₃tren in a 1:4(v:v) methanol:ethanol glass at 77 K. Excitation was performed at 355 nm. See experimental section for general details.

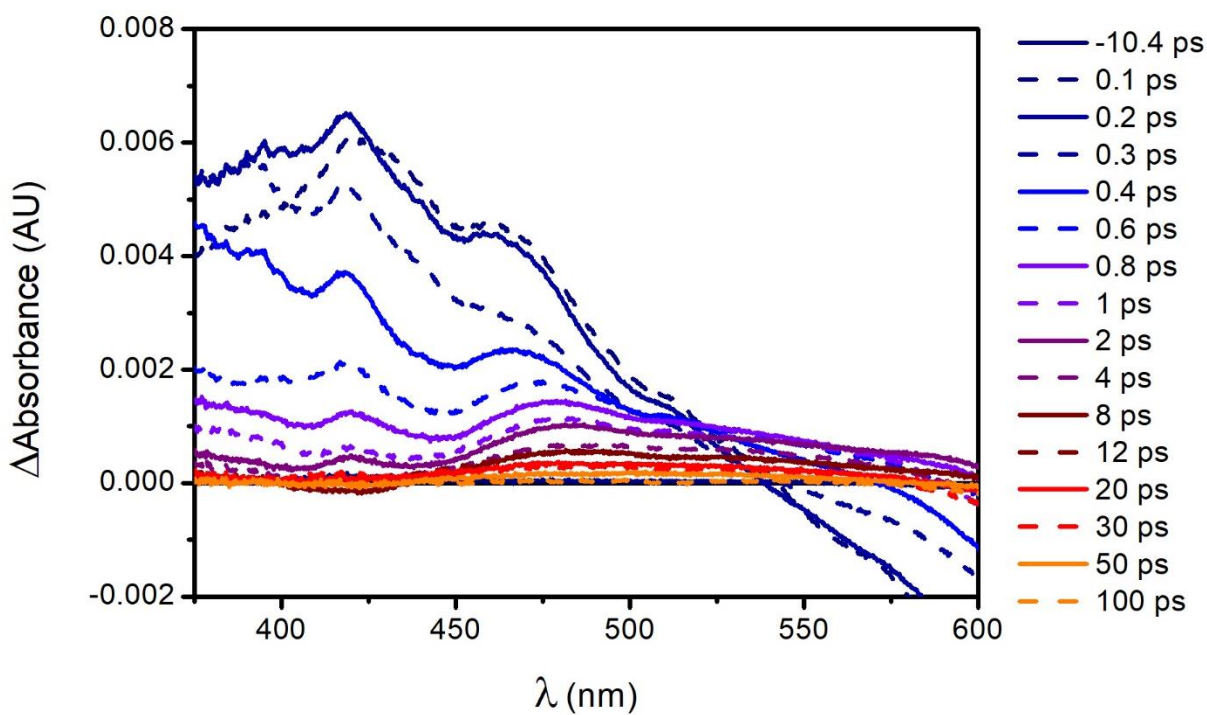


Figure A4.8 Transient absorption spectra of **5.1** in CH₃CN.

Scheme A4.1 User-defined reference shape for “tren-capped octahedron”

tren

tren-Octahedron

C3v

```

0.00000000  0.00000000 -1.00000000
1.00000000  0.00000000  0.00000000
0.00000000  1.00000000  0.00000000
-1.00000000  0.00000000  0.00000000
0.00000000 -1.00000000  0.00000000
0.00000000  0.00000000  1.00000000
0.85440000  0.85440000  0.85440000
0.00000000  0.00000000  0.00000000

```

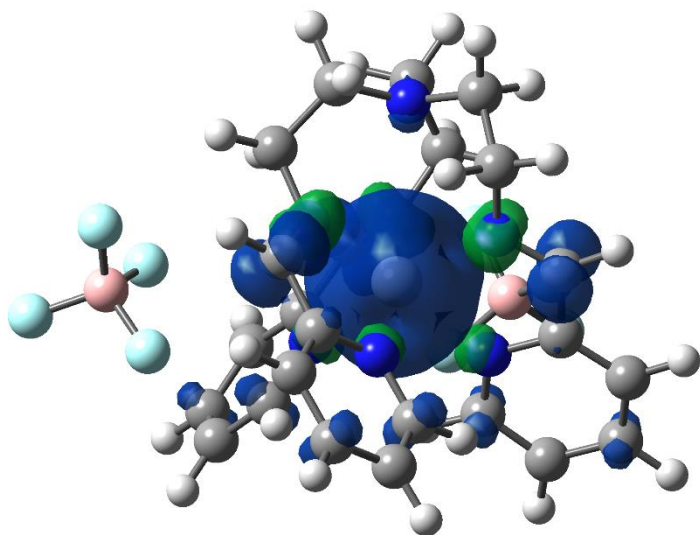


Figure A4.9 Spin density plot of **5.1**

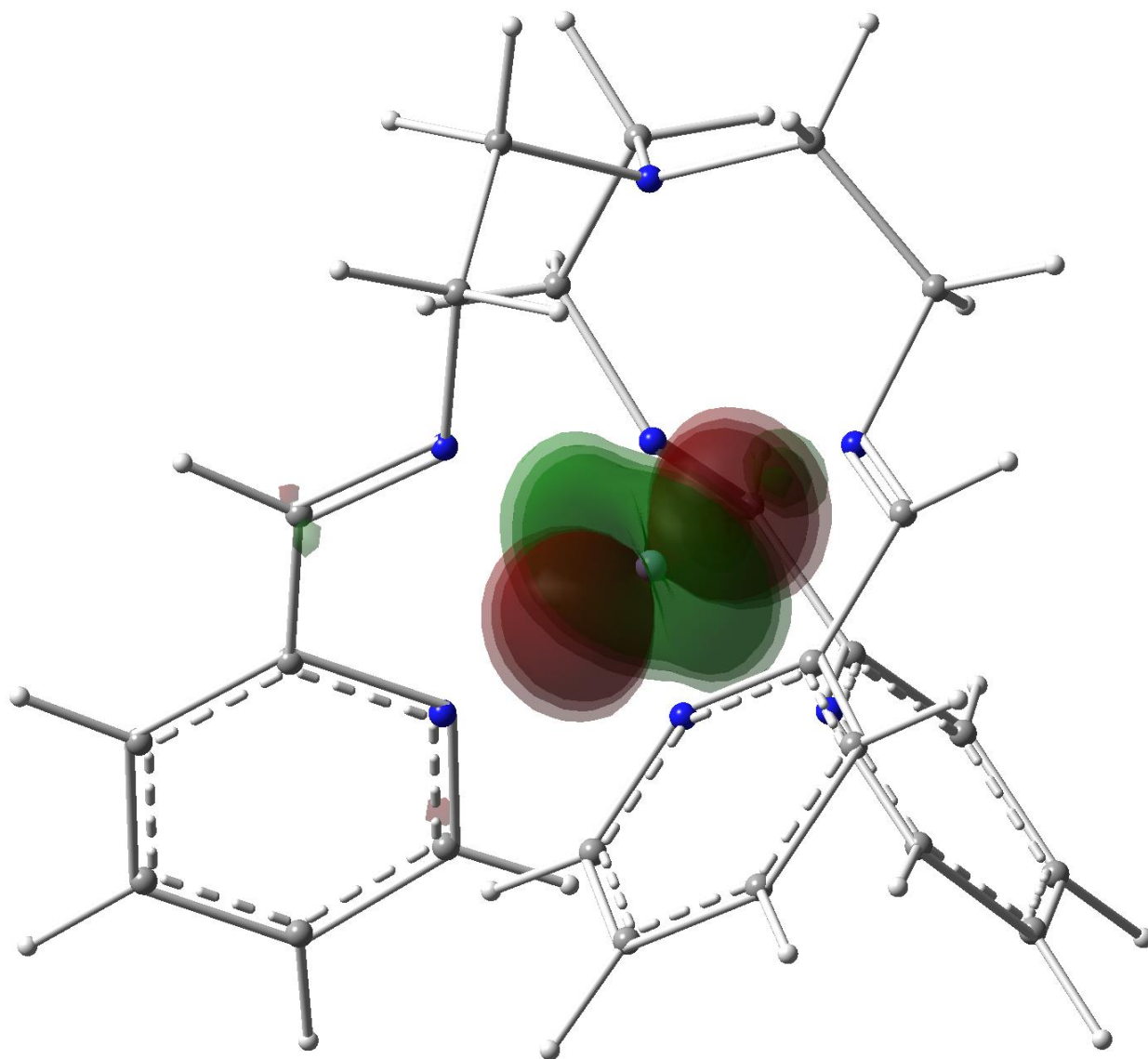


Figure A4.10 Spin density of d π orbitals in [Cr(py₃tren)]³⁺

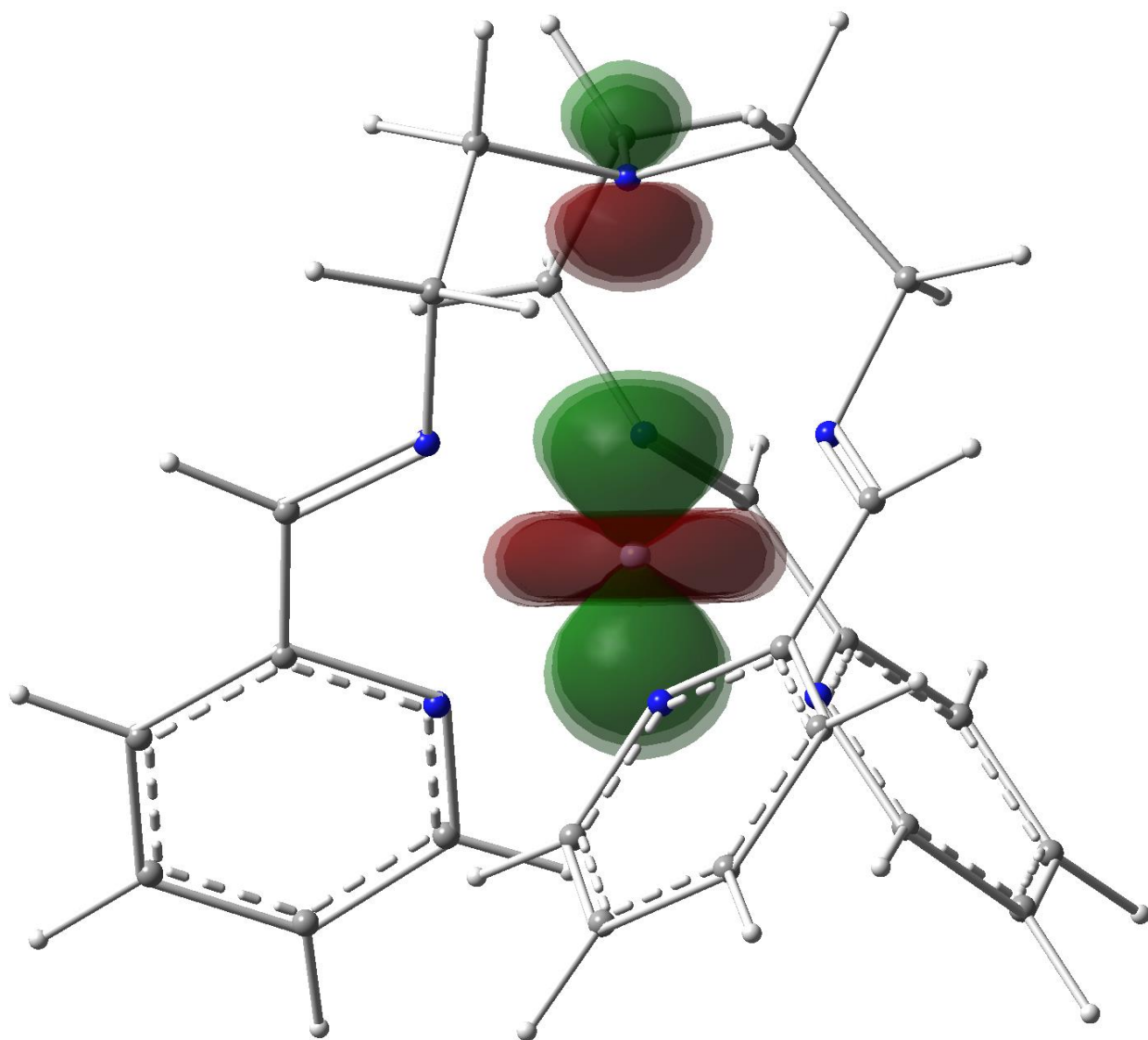


Figure A4.11 Spin density of dσ orbitals in [Cr(py₃tren)]³⁺

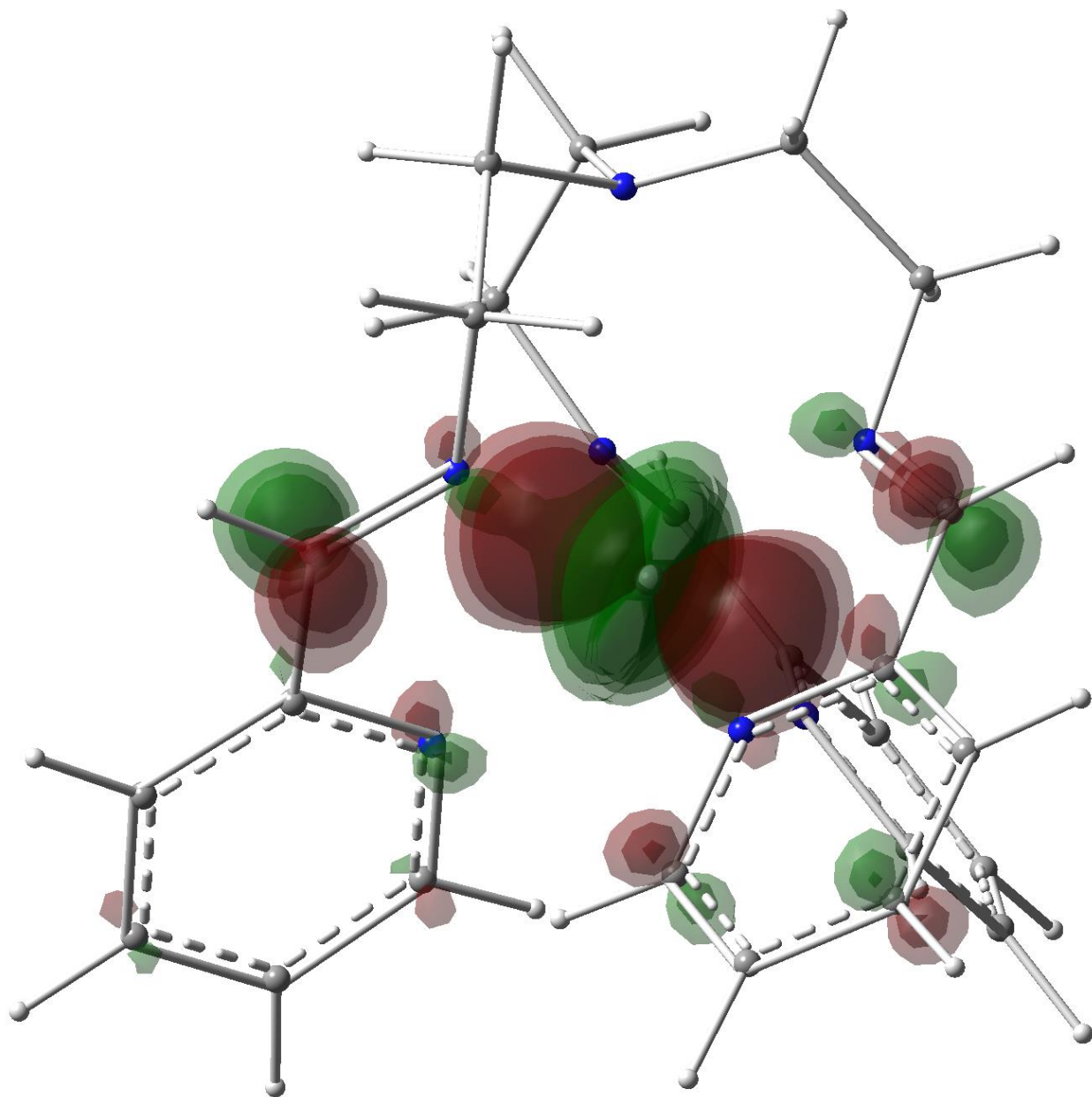


Figure A4.12 Spin density of $d\pi$ orbitals in **5.1**

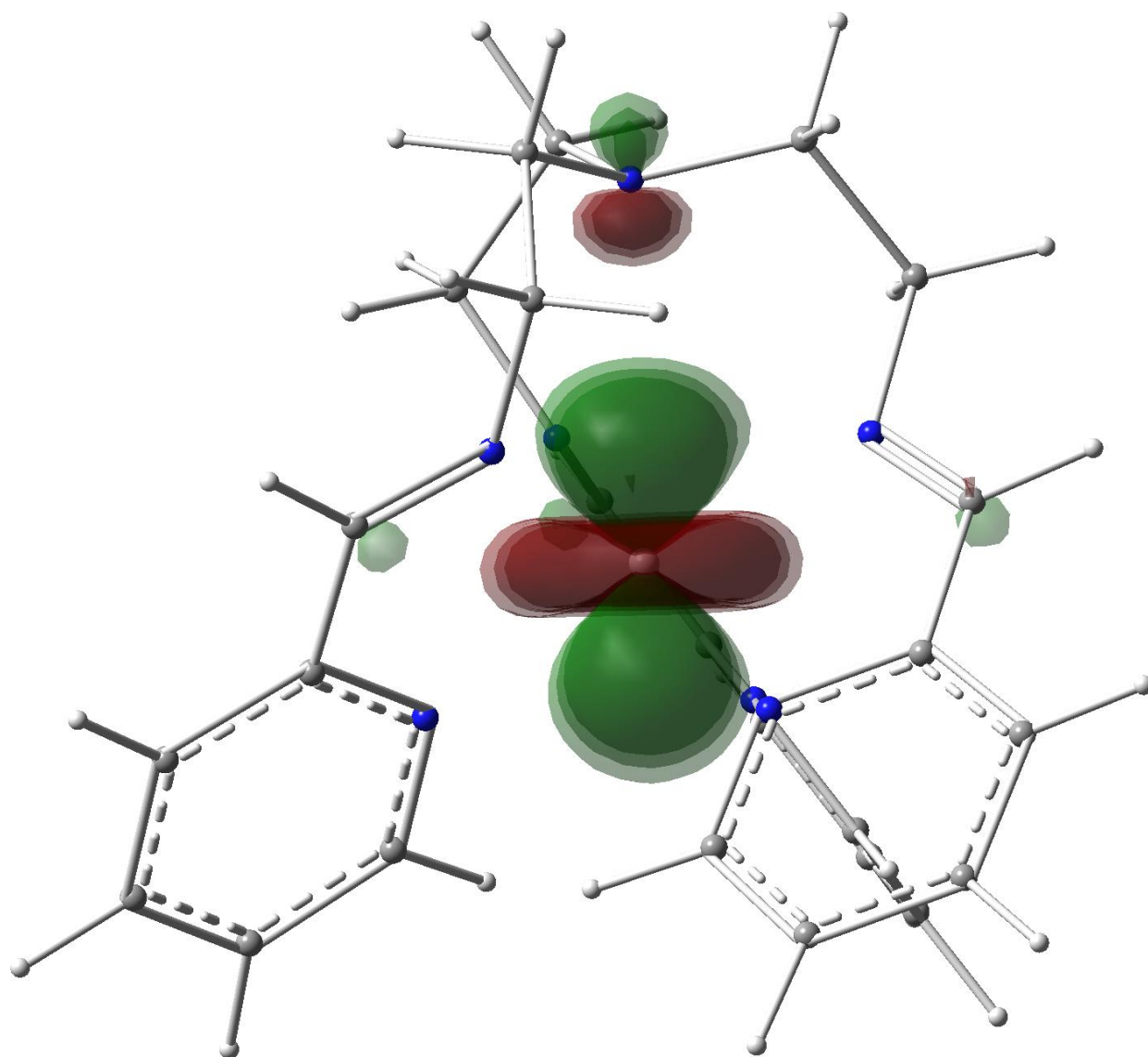


Figure A4.13 Spin density of $d\sigma$ orbitals in **5.1**

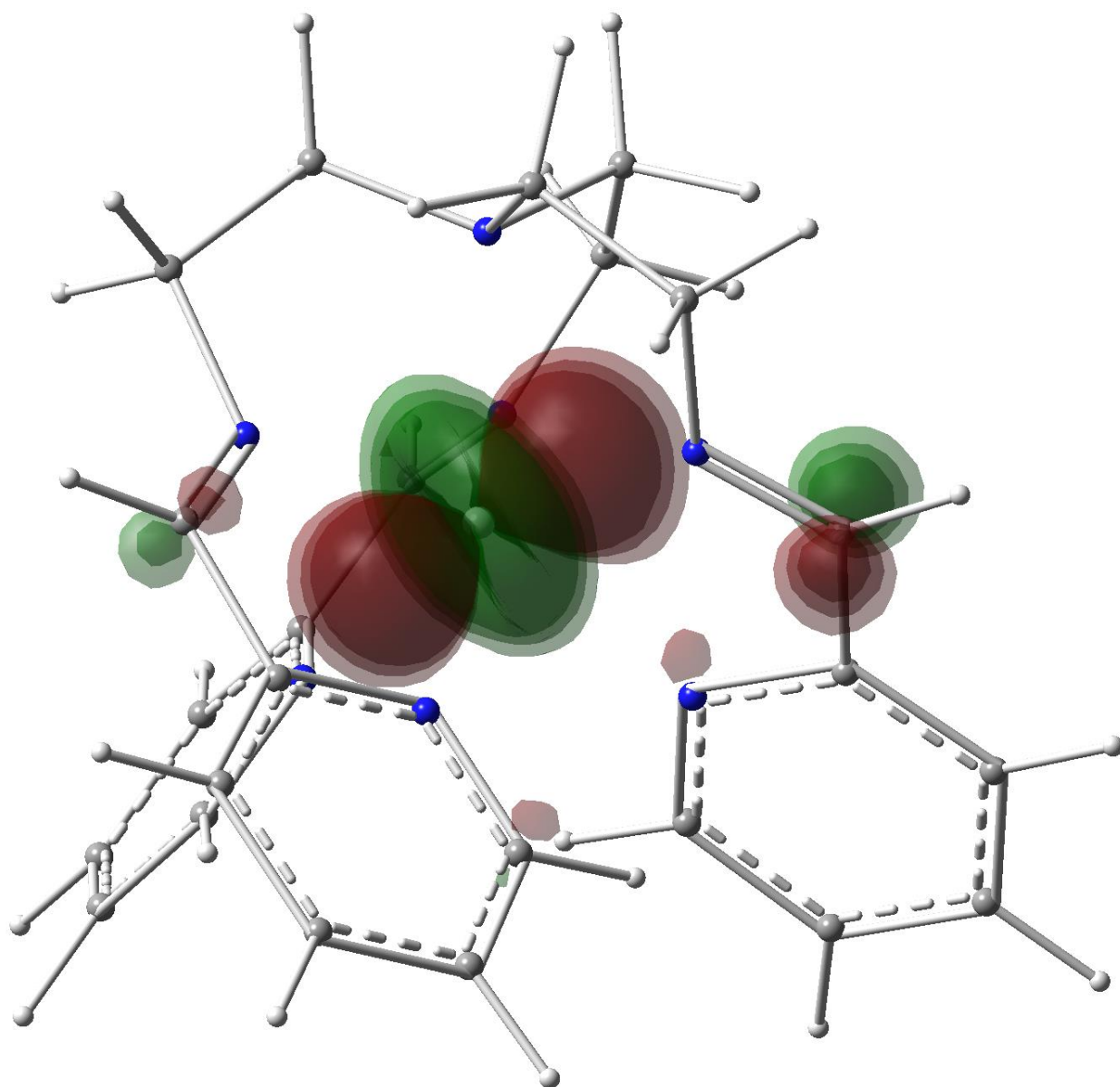


Figure A4.14 Spin density of $d\pi$ orbitals in **5.2**

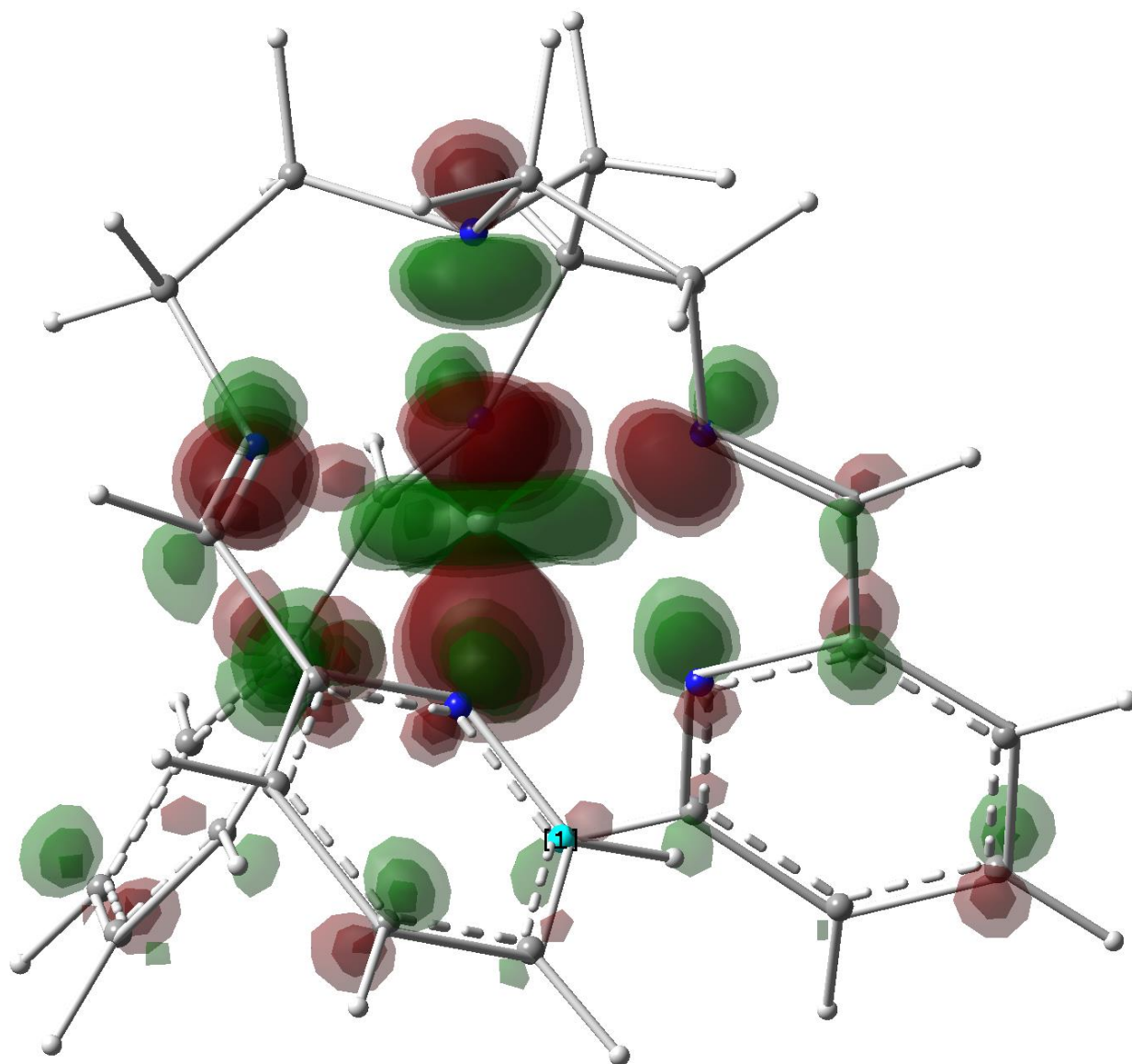


Figure A4.15 Spin density of $d\sigma$ orbitals in **5.2**

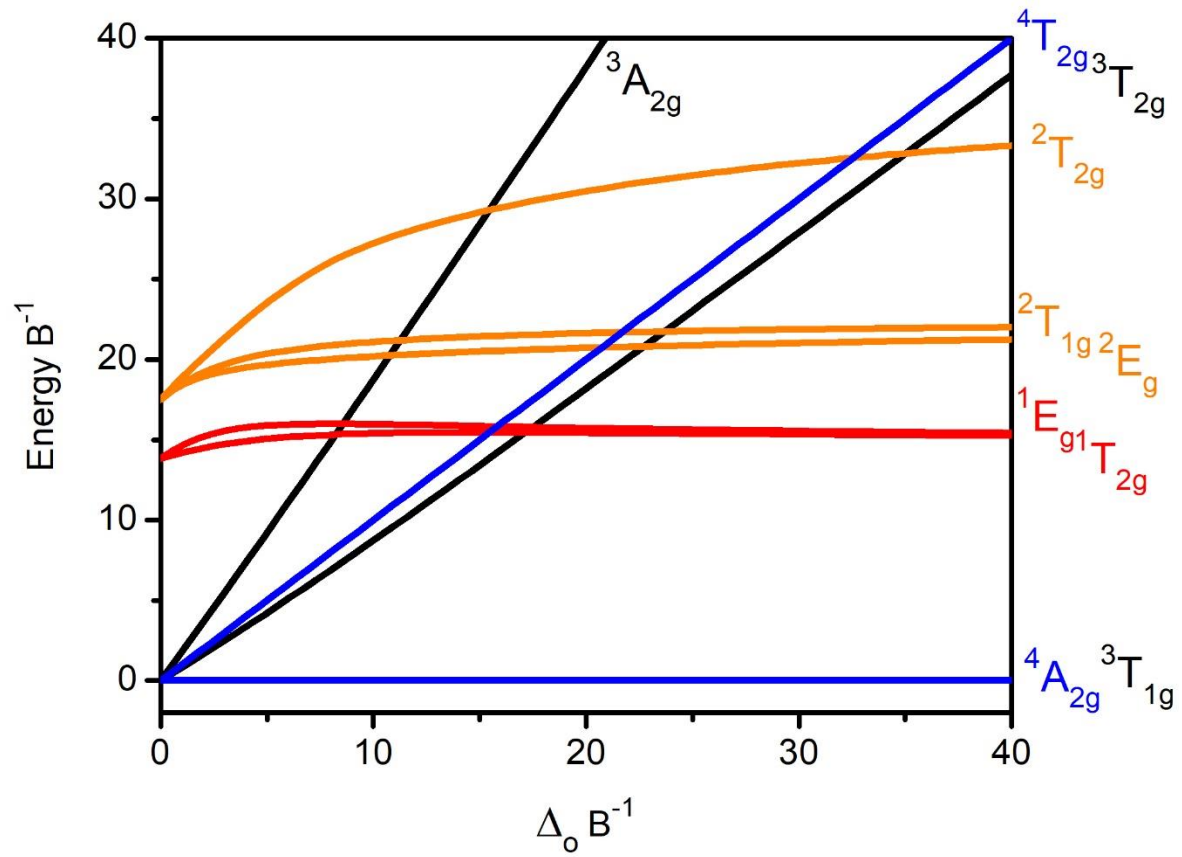


Figure A4.16 Tanabe-Sugano diagram of relevant O_h d^2 and d^3 ligand field states. d^2 states are shown in black (triplet) and red (singlet). d^3 states are shown in blue (quartet) and orange (doublet)

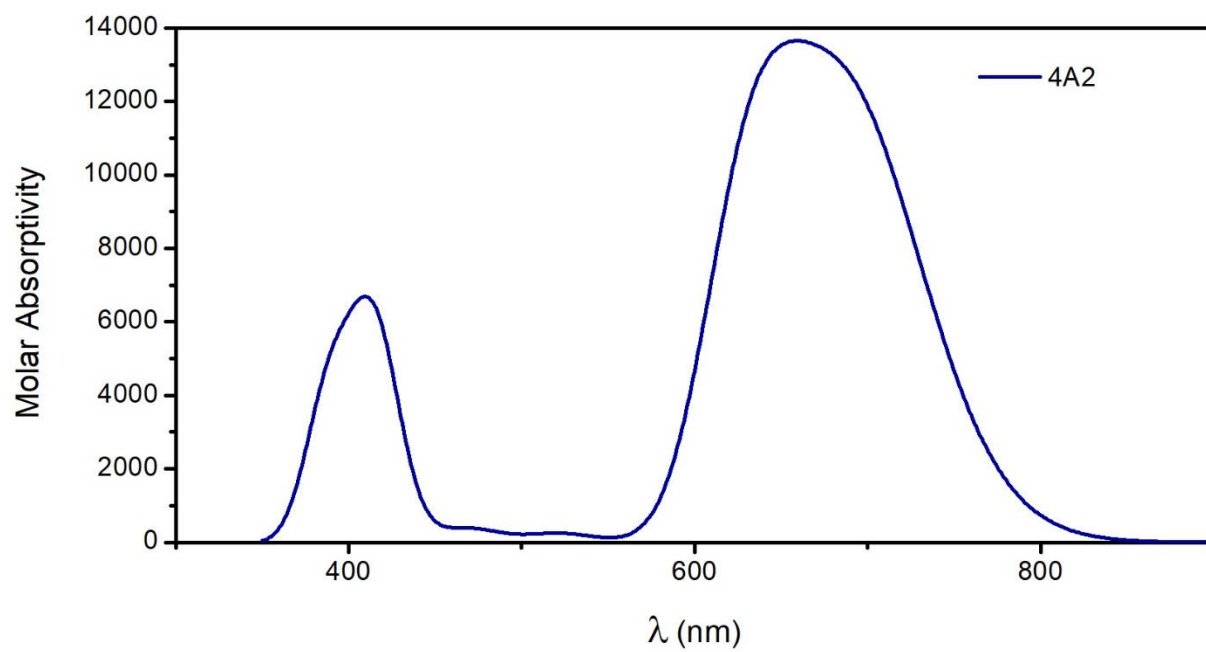


Figure A4.17 Calculated ground state absorbance for compound 5.1

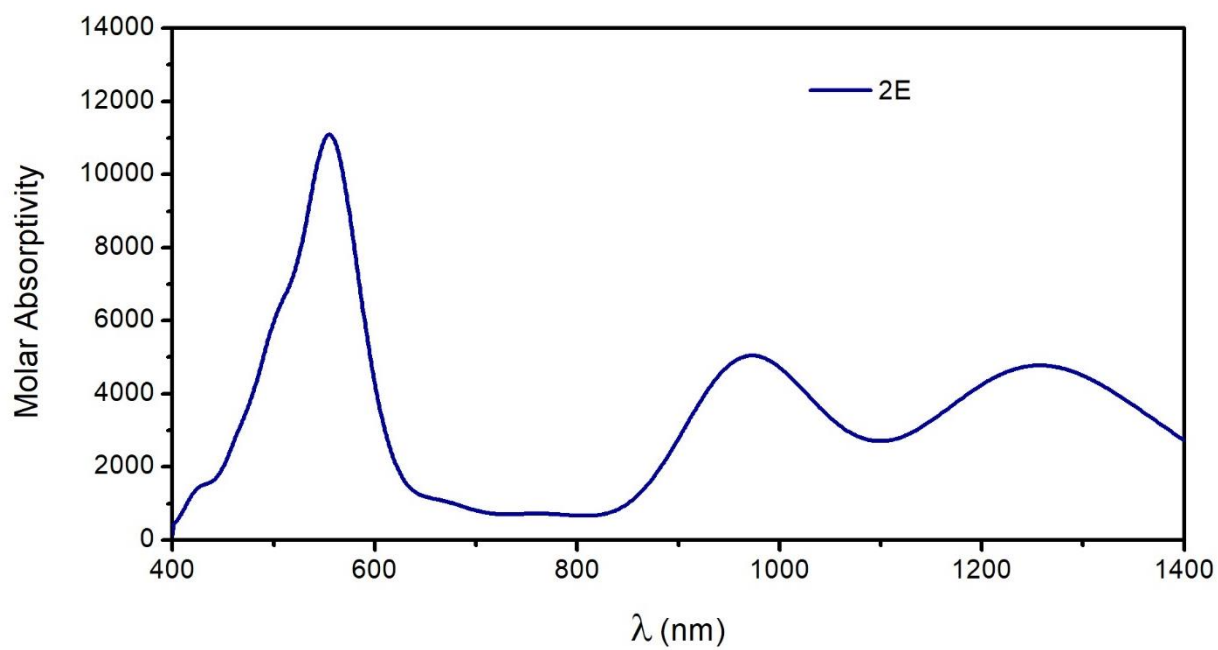


Figure A4.18 Calculated 2E excited state absorbance for compound 5.1

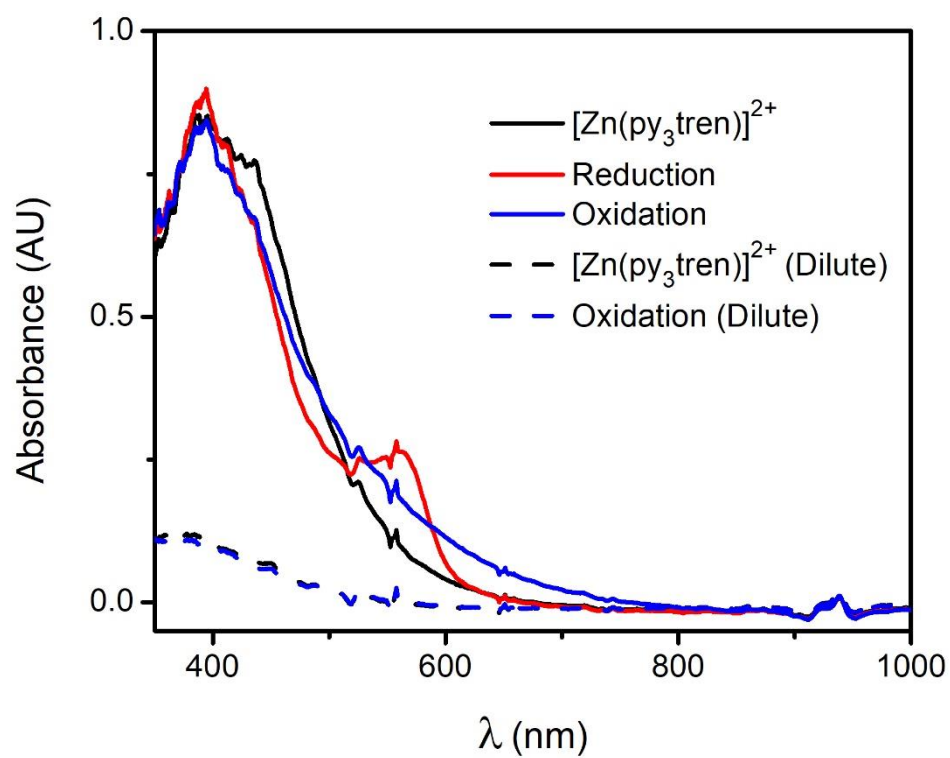


Figure A4.19 Spectroelectrochemistry spectra of [Zn(py)₃tren]OTf₂ in 0.1 M Bu₄NPF₆ in CH₃CN

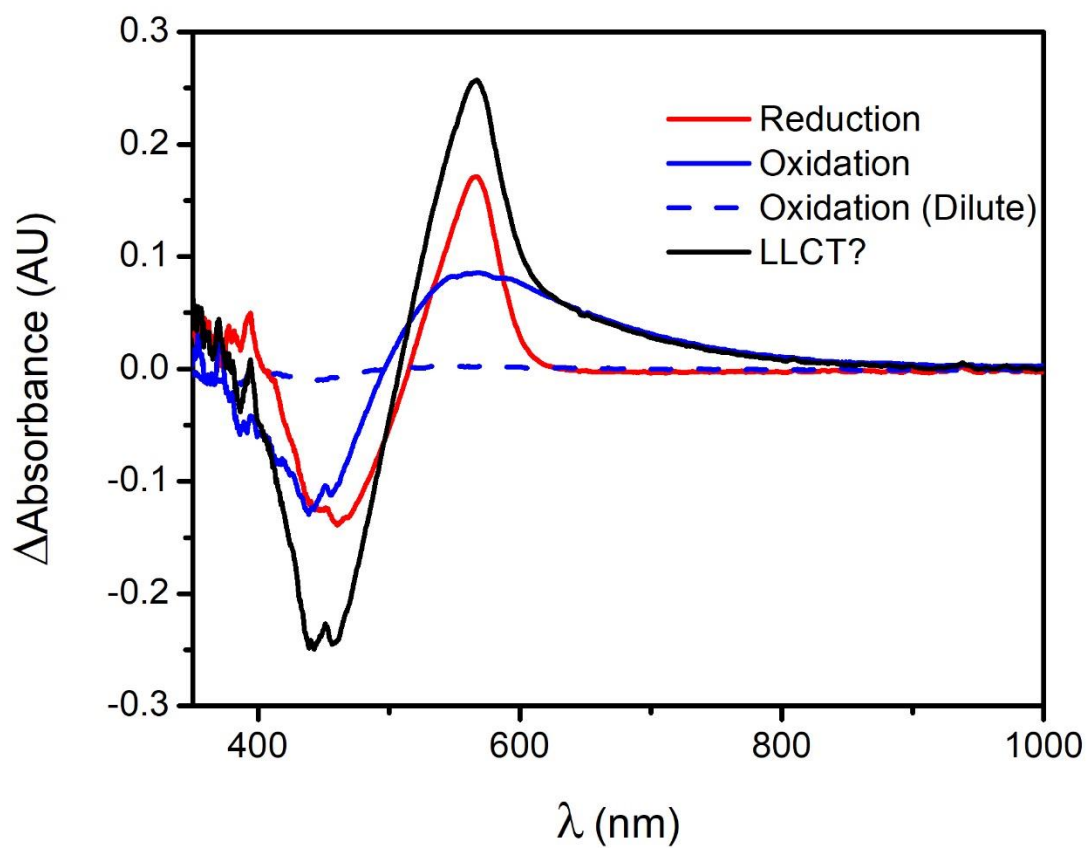


Figure A4.20 Spectroelectrochemistry difference spectra of [Zn(py)₃tren]OTf₂ in 0.1 M Bu₄NPF₆ in CH₃CN

APPENDIX 5: Supporting Information for Chapter 6

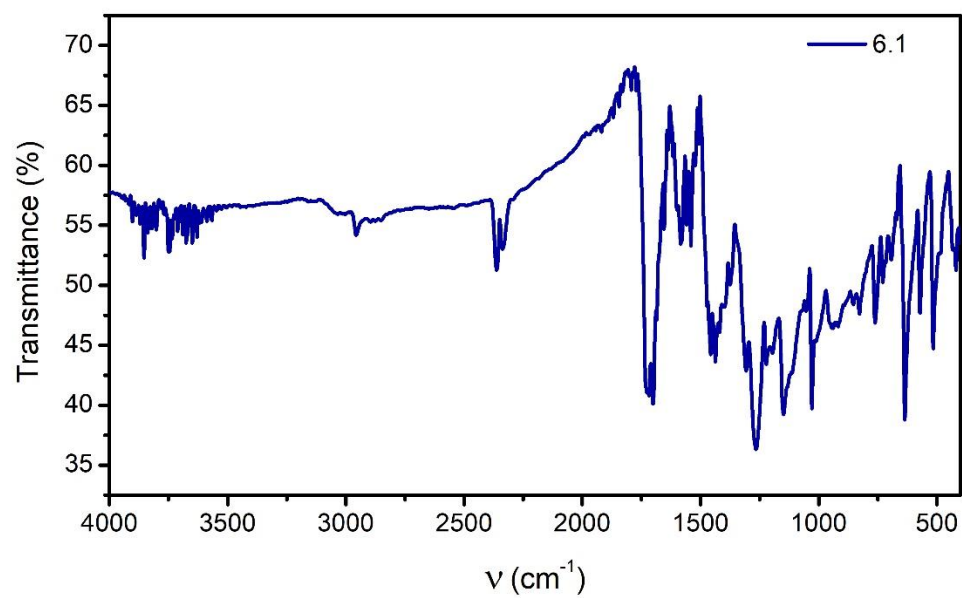


Figure A5.1 FT-IR transmittance spectra of **6.1** suspended in a KBr pellet.

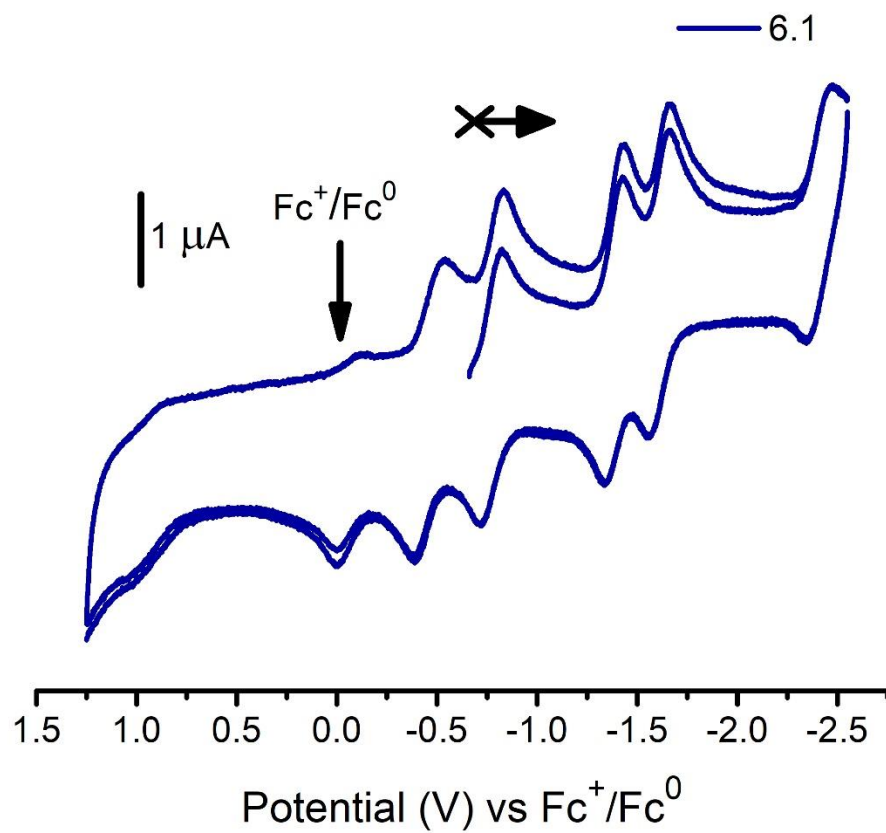


Figure A5.2 Cyclic voltammogram of compound **6.1** in 0.1 Bu_4NPF_6 in CH_3CN .

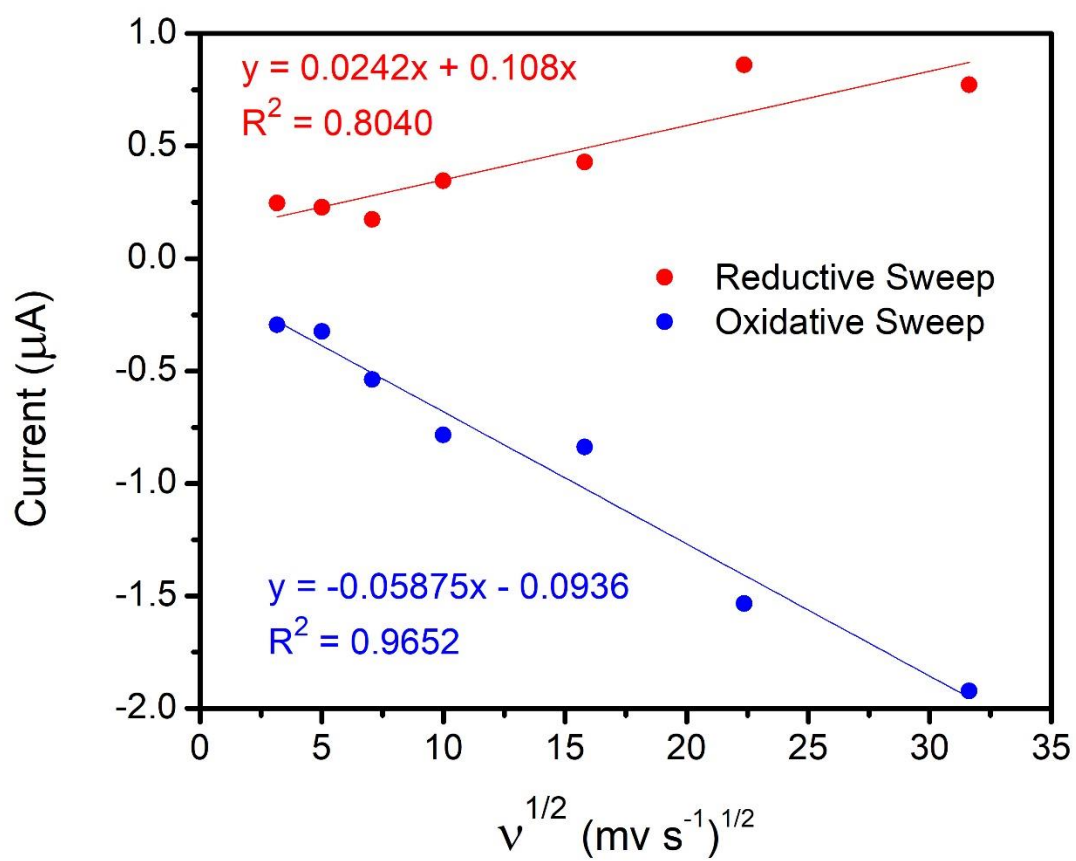


Figure A5.3 Randles-Sevcik plot of the 3+/2+ redox in compound **6.1**. Electrochemical measurements were taken in 0.1 Bu_4NPF_6 in CH_3CN .

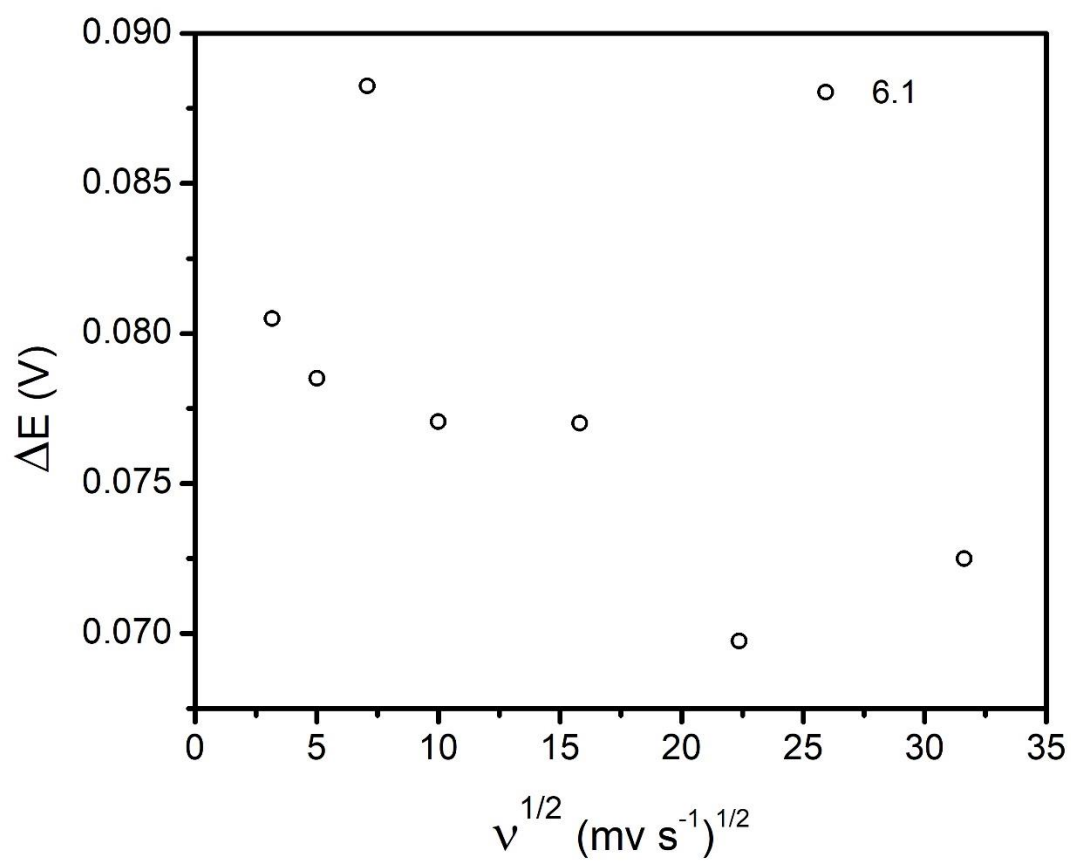


Figure A5.4 Peak to peak separation of the 3+/2+ redox in compound **6.1**. Electrochemical measurements were taken in 0.1 Bu₄NPF₆ in CH₃CN.

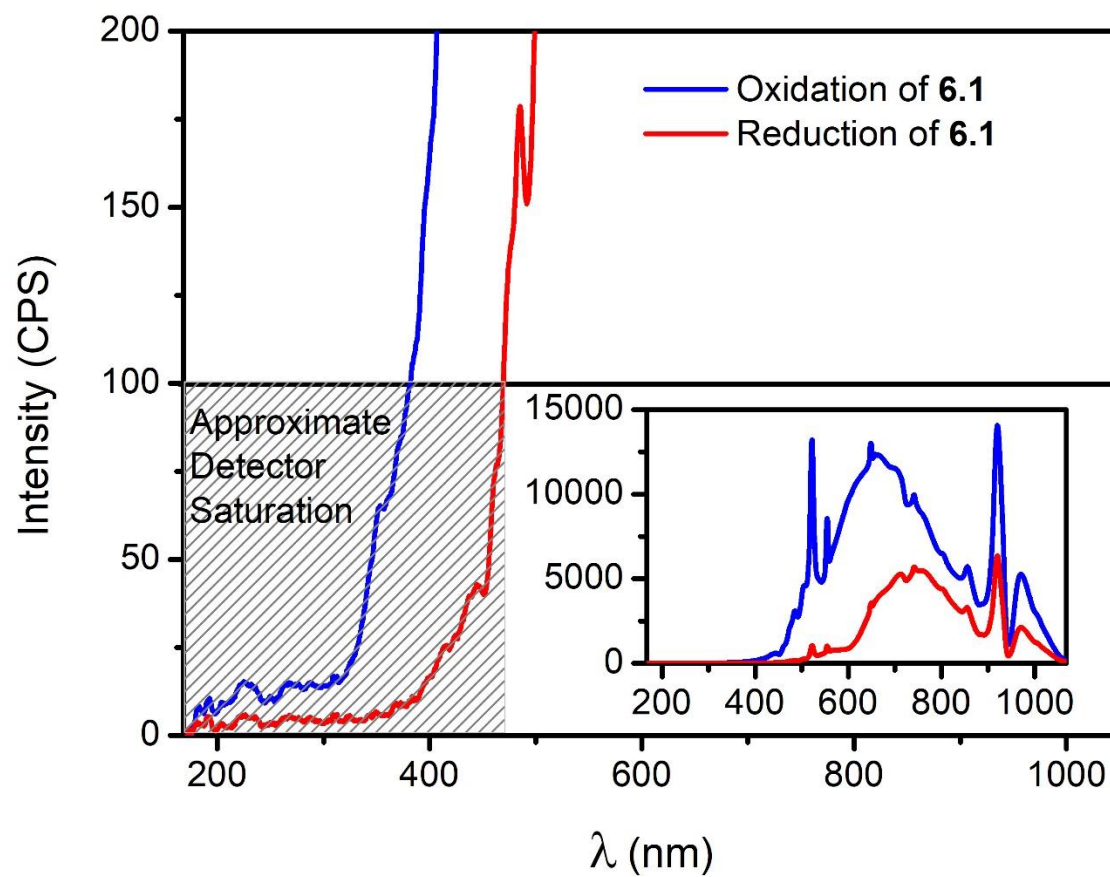


Figure A5.5 Acquisition window for Ocean-Optics spectrometer during spectroelectrochemistry experiments. The greyed out region between 168 and 475 nm represents detector saturation during reduction of compound **6.1**.

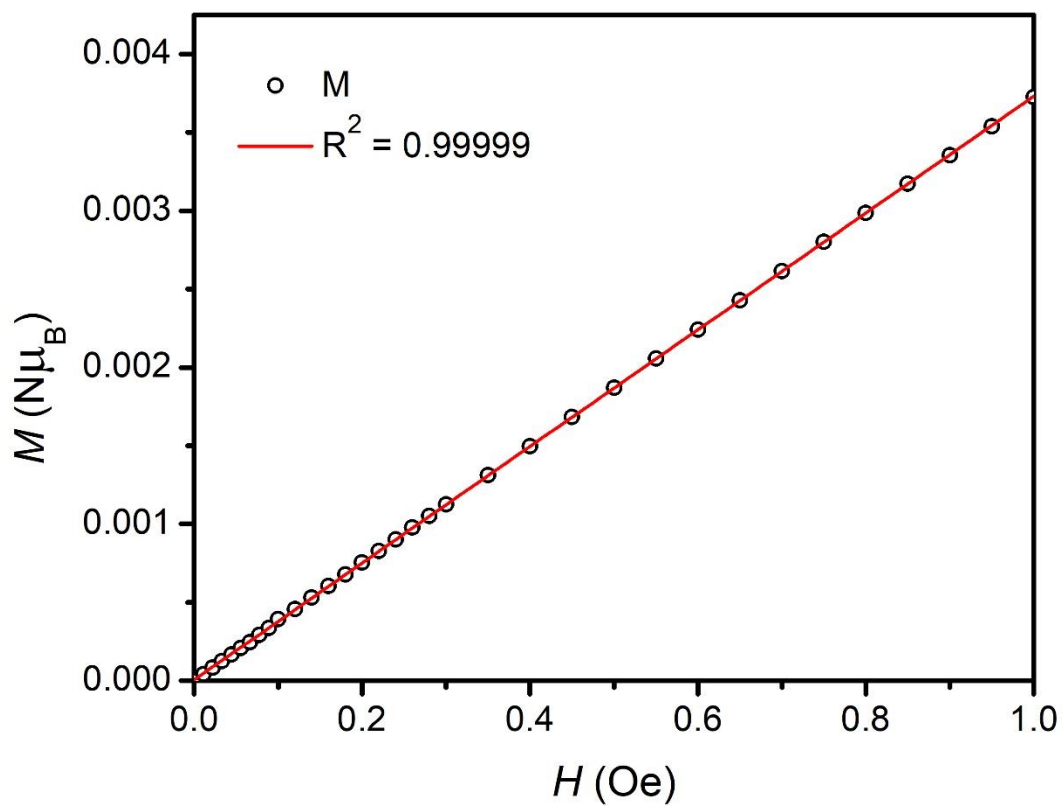


Figure A5.6 Field dependence of magnetization of compound 6.1 collected at 100 K. Fit:

$$y = 3.73 \times 10^{-3} (x) + 5.50975 \times 10^{-6}.$$

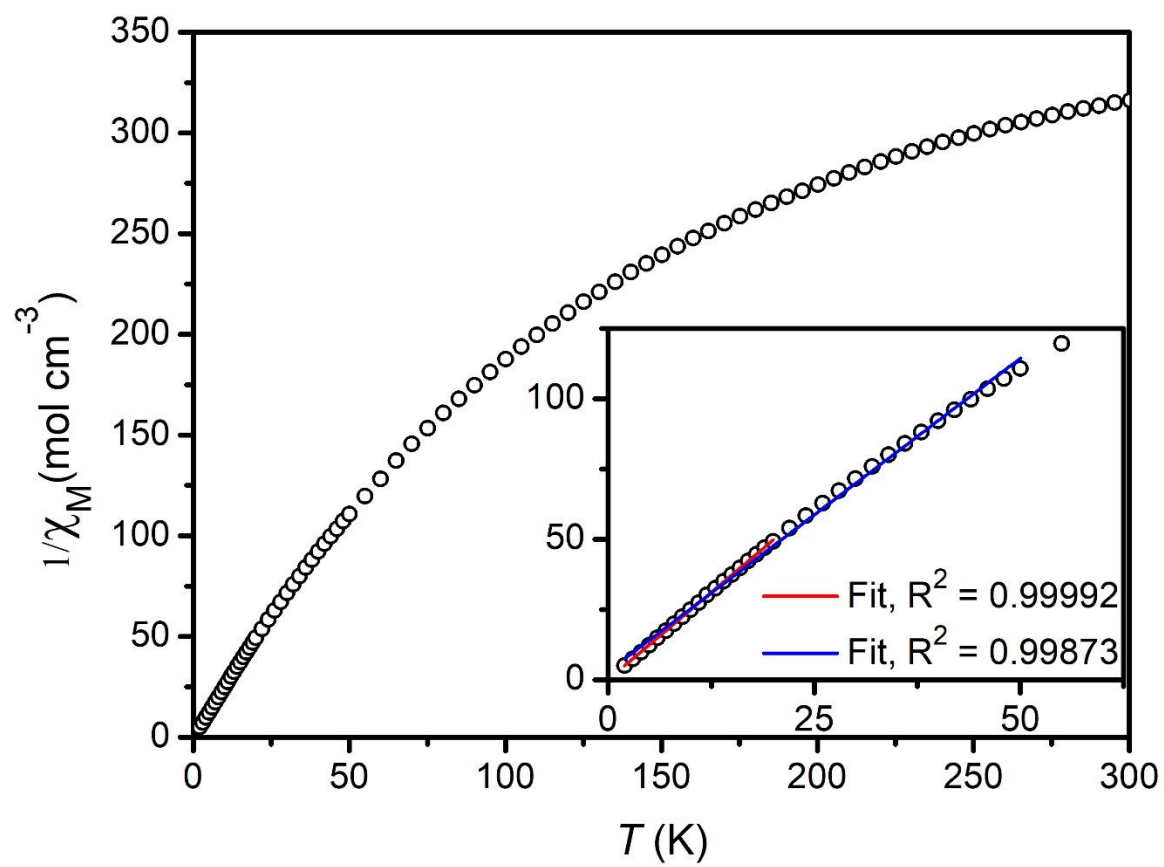


Figure A5.7 Temperature dependence of the inverse magnetic susceptibility for 6.1, collected at 10 kOe.

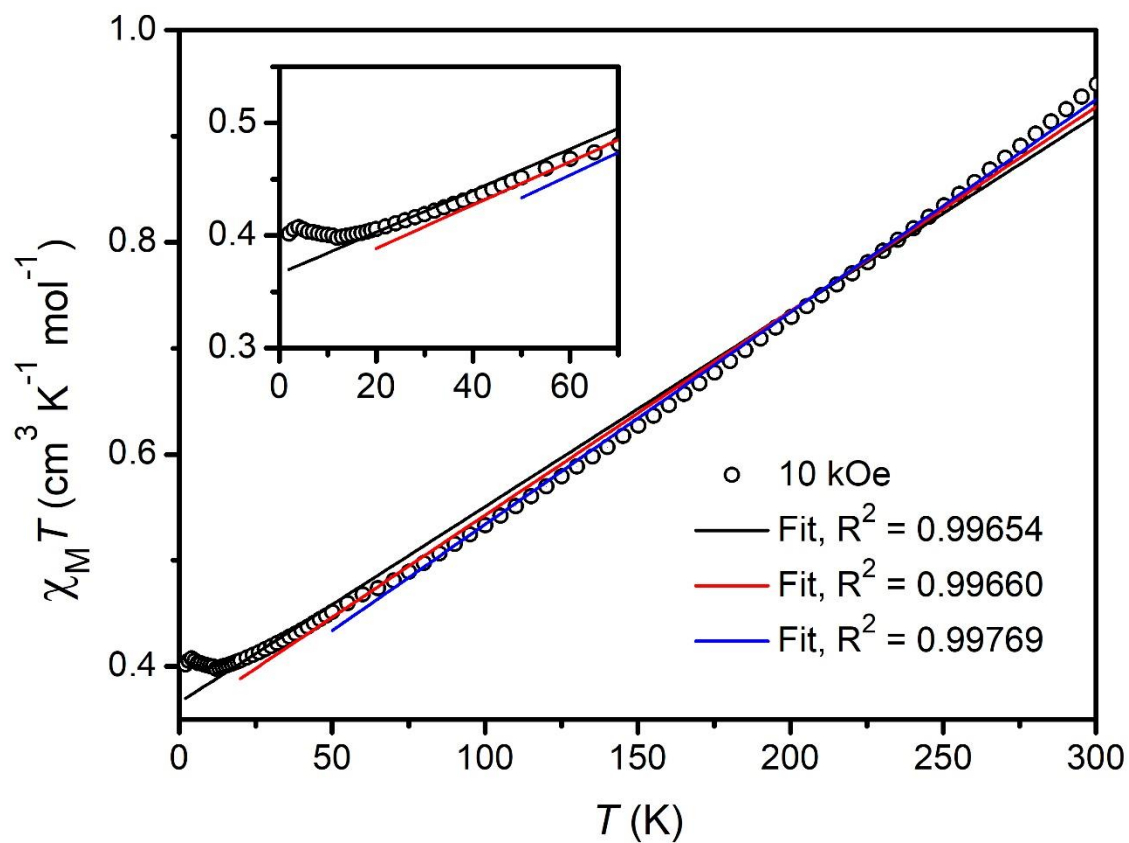


Figure A5.8 Solid state magnetic susceptibility of compound **6.1** collected at 10 kOe. Linear fits were attempted with truncation of the lower temperature at 2 K (black), 20 K (red), and 50 K (blue).

Fit ($T > 2$ K, black): $y = 1.85 \times 10^{-3} (x) + 0.36612$

Fit ($T > 20$ K, red): $y = 1.92 \times 10^{-3} (x) + 0.35016$

Fit ($T > 50$ K, blue): $y = 2.0 \times 10^{-3} (x) + 0.33356$

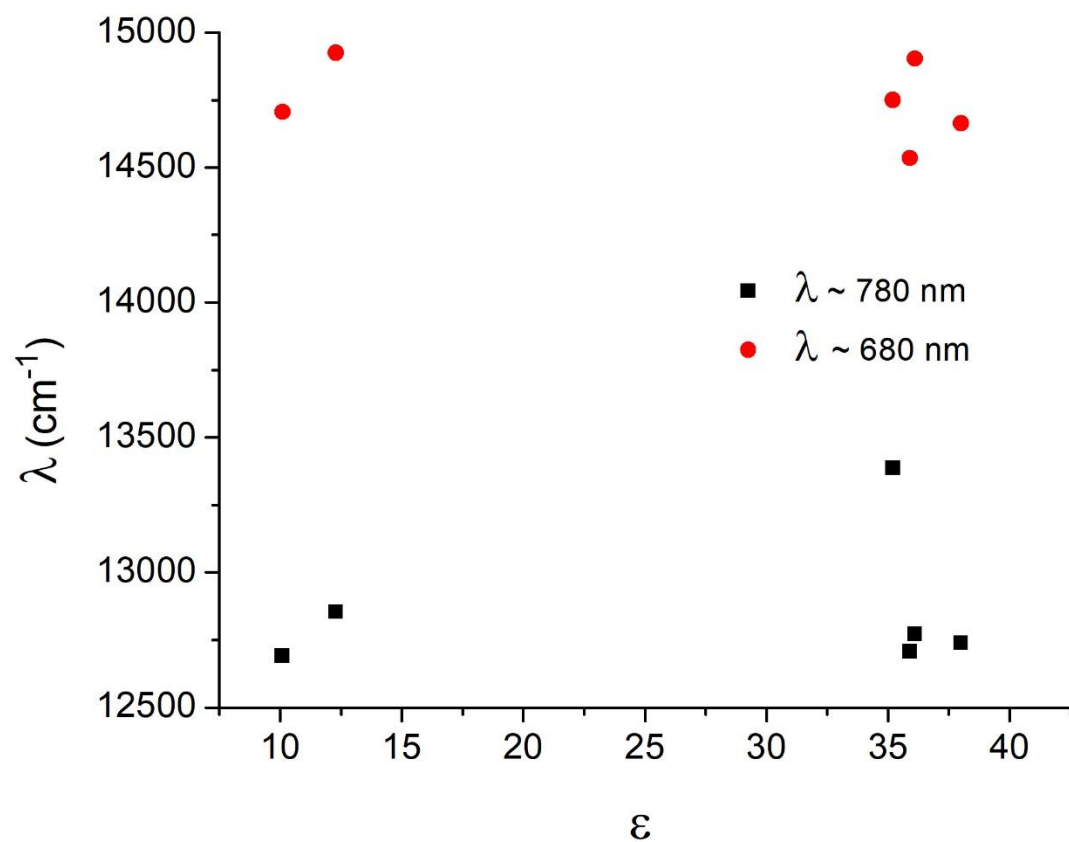


Figure A5.9 Change in MLCT peak of compound **6.1** as a function of solvent dielectric constant. Due to the solvent dependent absorbance spectra, two peaks were monitored in each solution

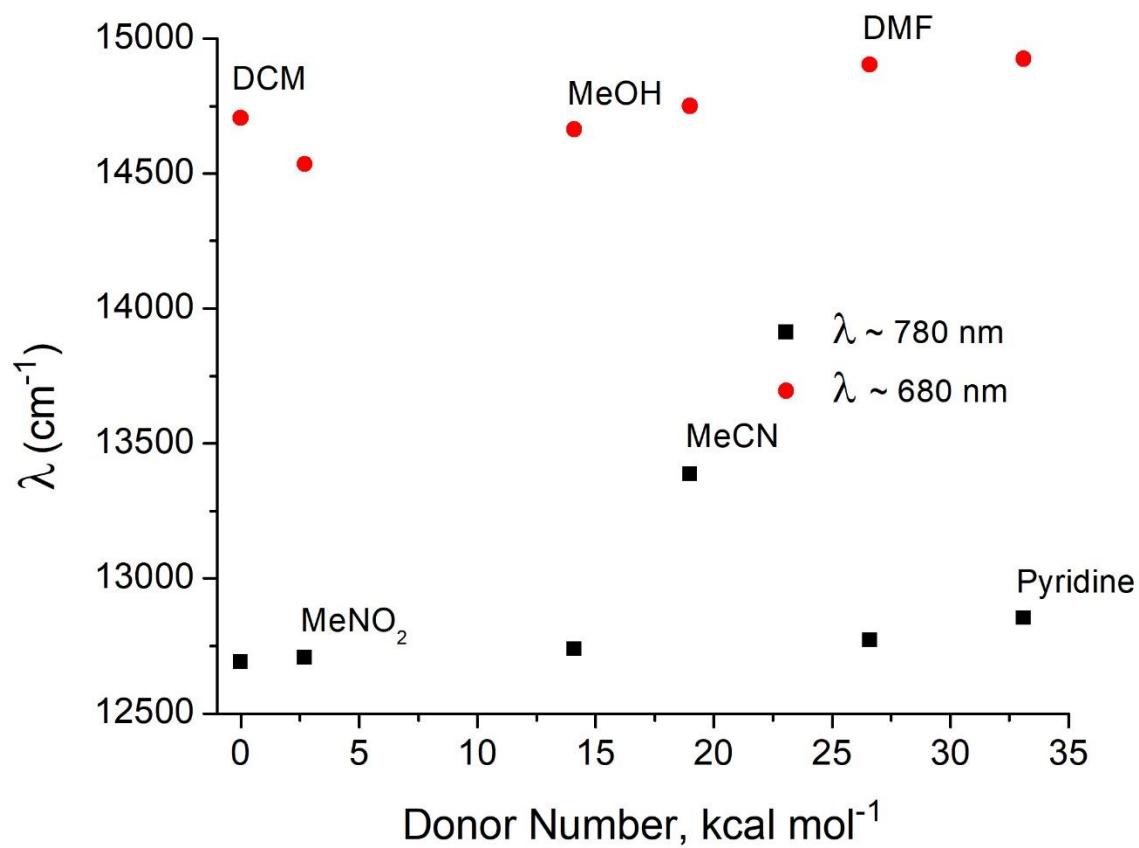


Figure A5.10 Change in MLCT peak of compound **6.1** as a function of solvent donor number. Due to the solvent dependent absorbance spectra, two peaks were monitored in each solution.

APPENDIX 6: Supporting Information for Chapter 7

Scheme A6.1 Modified python code for machine learning using statistical models

```
#import libraries for machine learning
from pandas.plotting import scatter_matrix
import matplotlib.pyplot as plt
from sklearn import model_selection
from sklearn.metrics import classification_report
from sklearn.metrics import confusion_matrix
from sklearn.metrics import accuracy_score
from sklearn.linear_model import LogisticRegression
from sklearn.tree import DecisionTreeClassifier
from sklearn.neighbors import KNeighborsClassifier
from sklearn.discriminant_analysis import LinearDiscriminantAnalysis
from sklearn.naive_bayes import GaussianNB
from sklearn.svm import SVC

#import data
data2 = pd.read_csv('Fepy3tren SCO Dist Geo.csv')

#see number of classified samples
print(data2.groupby('Spin-State').size())

data2.plot(kind='box', subplots=True, layout=(4,8), sharex=False, sharey=False, figsize=(20,10))
plt.show()

scatter_matrix(data2, figsize=(30,20))
plt.show()

#array size is size-1
limit = data2.shape[1]-1
array = data2.values
X = array[:,1:limit]
Y = array[:,limit]
validation_size = 0.3
seed = 2
X_train, X_validation, Y_train, Y_validation = model_selection.train_test_split(X, Y,
test_size=validation_size, random_state=seed)

# Test options and evaluation metric
seed = 2
scoring = 'accuracy'

# Spot Check Algorithms
models = []
```

```

models.append(('LR', LogisticRegression(solver='liblinear', multi_class='ovr')))
models.append(('LDA', LinearDiscriminantAnalysis()))
models.append(('KNN', KNeighborsClassifier()))
models.append(('CART', DecisionTreeClassifier()))
models.append(('NB', GaussianNB()))
models.append(('SVM', SVC(gamma='auto')))
# evaluate each model in turn
results = []
names = []
for name, model in models:
    kfold = model_selection.KFold(n_splits=10, random_state=seed)
    cv_results = model_selection.cross_val_score(model, X_train, Y_train, cv=kfold,
scoring=scoring)
    results.append(cv_results)
    names.append(name)
    msg = "%s: %f (%f)" % (name, cv_results.mean(), cv_results.std())
    print(msg)

# Compare Algorithms
fig = plt.figure()
fig.suptitle('Algorithm Comparison ' + str(seed))
ax = fig.add_subplot(111)
plt.boxplot(results)
ax.set_xticklabels(names)
plt.show()

# Make predictions on validation dataset
lda = LinearDiscriminantAnalysis()
lda.fit(X_train, Y_train)
predictions = lda.predict(X_validation)
print(accuracy_score(Y_validation, predictions))
print(confusion_matrix(Y_validation, predictions))
print(classification_report(Y_validation, predictions))

```

Scheme A6.2 Modified python code for Fe(II) tripodal complex spin-state decision tree

```
import pandas as pd
```

```
#import data
data2 = pd.read_csv('Fepy3tren SCO Total No Ref.csv')
training_data = data2.values.tolist()
```

```
# Column labels.
# These are used only to print the tree.
header = data2.columns.values.tolist()
```

```
def unique_vals(rows, col):
    """Find the unique values for a column in a dataset."""
    return set([row[col] for row in rows])
```

```
def class_counts(rows):
    """Counts the number of each type of example in a dataset."""
    counts = {} # a dictionary of label -> count.
    for row in rows:
        # in our dataset format, the label is always the last column
        label = row[-1]
        if label not in counts:
            counts[label] = 0
        counts[label] += 1
    return counts
```

```
class_counts(training_data)
```

```
def is_numeric(value):
    """Test if a value is numeric."""
    return isinstance(value, int) or isinstance(value, float)
```

```
class Question:
    """A Question is used to partition a dataset.
```

This class just records a 'column number' (e.g., 0 for Color) and a 'column value' (e.g., Green). The 'match' method is used to compare the feature value in an example to the feature value stored in the question. See the demo below.

```
"""
```

```
def __init__(self, column, value):
    self.column = column
    self.value = value
```

```
def match(self, example):
```

```

    # Compare the feature value in an example to the
    # feature value in this question.
    val = example[self.column]
    if is_numeric(val):
        return val >= self.value
    else:
        return val == self.value

def __repr__(self):
    # This is just a helper method to print
    # the question in a readable format.
    condition = "=="
    if is_numeric(self.value):
        condition = ">="
    return "Is %s %s %s?" % (
        header[self.column], condition, str(self.value))

def partition(rows, question):
    """Partitions a dataset.

    For each row in the dataset, check if it matches the question. If
    so, add it to 'true rows', otherwise, add it to 'false rows'.
    """
    true_rows, false_rows = [], []
    for row in rows:
        if question.match(row):
            true_rows.append(row)
        else:
            false_rows.append(row)
    return true_rows, false_rows

def gini(rows):
    """Calculate the Gini Impurity for a list of rows.

    There are a few different ways to do this, I thought this one was
    the most concise. See:
    https://en.wikipedia.org/wiki/Decision\_tree\_learning#Gini\_impurity
    """
    counts = class_counts(rows)
    impurity = 1
    for lbl in counts:
        prob_of_lbl = counts[lbl] / float(len(rows))
        impurity -= prob_of_lbl**2
    return impurity

def info_gain(left, right, current_uncertainty):

```

```
"""Information Gain.
```

```
The uncertainty of the starting node, minus the weighted impurity of  
two child nodes.
```

```
"""
```

```
p = float(len(left)) / (len(left) + len(right))  
return current_uncertainty - p * gini(left) - (1 - p) * gini(right)
```

```
def find_best_split(rows):
```

```
    """Find the best question to ask by iterating over every feature / value  
    and calculating the information gain."""
```

```
    best_gain = 0 # keep track of the best information gain  
    best_question = None # keep track of the feature / value that produced it  
    current_uncertainty = gini(rows)  
    n_features = len(rows[0]) - 1 # number of columns
```

```
    for col in range(n_features): # for each feature
```

```
        values = set([row[col] for row in rows]) # unique values in the column
```

```
        for val in values: # for each value
```

```
            question = Question(col, val)
```

```
            # try splitting the dataset  
            true_rows, false_rows = partition(rows, question)
```

```
            # Skip this split if it doesn't divide the  
            # dataset.  
            if len(true_rows) == 0 or len(false_rows) == 0:  
                continue
```

```
            # Calculate the information gain from this split  
            gain = info_gain(true_rows, false_rows, current_uncertainty)
```

```
            # You actually can use '>' instead of '>=' here  
            # but I wanted the tree to look a certain way for our  
            # toy dataset.  
            if gain >= best_gain:  
                best_gain, best_question = gain, question
```

```
    return best_gain, best_question
```

```
class Leaf:
```

```
    """A Leaf node classifies data.
```

This holds a dictionary of class (e.g., "Apple") -> number of times it appears in the rows from the training data that reach this leaf.
"""

```
def __init__(self, rows):
    self.predictions = class_counts(rows)
```

```
class Decision_Node:
    """A Decision Node asks a question.
```

This holds a reference to the question, and to the two child nodes.
"""

```
def __init__(self,
             question,
             true_branch,
             false_branch):
    self.question = question
    self.true_branch = true_branch
    self.false_branch = false_branch
```

```
def build_tree(rows):
    """Builds the tree.
```

Rules of recursion: 1) Believe that it works. 2) Start by checking for the base case (no further information gain). 3) Prepare for giant stack traces.
"""

```
# Try partitioning the dataset on each of the unique attribute,
# calculate the information gain,
# and return the question that produces the highest gain.
gain, question = find_best_split(rows)
```

```
# Base case: no further info gain
# Since we can ask no further questions,
# we'll return a leaf.
if gain == 0:
    return Leaf(rows)
```

```
# If we reach here, we have found a useful feature / value
# to partition on.
true_rows, false_rows = partition(rows, question)
```

```
# Recursively build the true branch.
true_branch = build_tree(true_rows)
```

```

# Recursively build the false branch.
false_branch = build_tree(false_rows)

# Return a Question node.
# This records the best feature / value to ask at this point,
# as well as the branches to follow
# depending on the answer.
return Decision_Node(question, true_branch, false_branch)

def print_tree(node, spacing=""):
    """World's most elegant tree printing function."""

    # Base case: we've reached a leaf
    if isinstance(node, Leaf):
        print (spacing + "Predict", node.predictions)
        return

    # Print the question at this node
    print (spacing + str(node.question))

    # Call this function recursively on the true branch
    print (spacing + '--> True:')
    print_tree(node.true_branch, spacing + " ")

    # Call this function recursively on the false branch
    print (spacing + '--> False:')
    print_tree(node.false_branch, spacing + " ")

#attempt to print gain
def print_tree(node, spacing=""):
    """World's most elegant tree printing function."""

    # Base case: we've reached a leaf
    if isinstance(node, Leaf):
        print (spacing + "Predict", node.predictions)
        return

    # Print the question at this node
    print (spacing + str(node.question))

    # Call this function recursively on the true branch
    print (spacing + '--> True:')
    print_tree(node.true_branch, spacing + " ")

    # Call this function recursively on the false branch

```

```
print (spacing + '--> False:')
print_tree(node.false_branch, spacing + " ")

my_tree = build_tree(training_data)
print_tree(my_tree)
```