

SYNTHESIS AND PHOTOPHYSICAL CHARACTERIZATION OF INORGANIC CHARGE-
TRANSFER CHROMOPHORES WITH EARTH-ABUNDANT METALS

By

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ABSTRACT

Fe(II) and Cu(I) charge transfer chromophores have the ability to solve the abundance problem associated with the use of Ru(II) in dye-sensitized solar cells. The use of molecular design can help bridge the gap in the performance for these more earth abundant alternatives. Previous work has highlighted the necessity of maximizing ligand field strength along with the avoidance of vibronic coupling to prevent the deactivation of MLCT excited states in Fe(II) compounds. Building upon this, this dissertation discusses the experimental and theoretical investigations into new design strategies for the charge transfer chromophores in a manner that is orthogonal to property maximization.

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“You cannot go on ‘seeing through’ things forever. The whole point of seeing through something is to see something through it. It is a good idea that the window should be transparent, because the street or garden beyond it is opaque. How if you saw through the garden too? It is no use to try to ‘see through’ first principles. If you see through everything, then everything is transparent. But a wholly transparent world is an invisible world. To ‘see through’ all things is the same as not to see.”

-C.S. Lewis, *The Abolition of Man*

“I never sleep, because sleep is the cousin of death.” -Nasir bin Olu Dara Jones

“Why should adoption of a new energy source [technology] be so slow?... It works by cultural diffusion-the spreading of ideas from one person to another- much like a disease epidemic...When zippers began replacing buttons, there were those who resisted the change because they believed zippers were sinful: they made it easier to disrobe.”

-Richard Rhodes, *Energy: A Human History*

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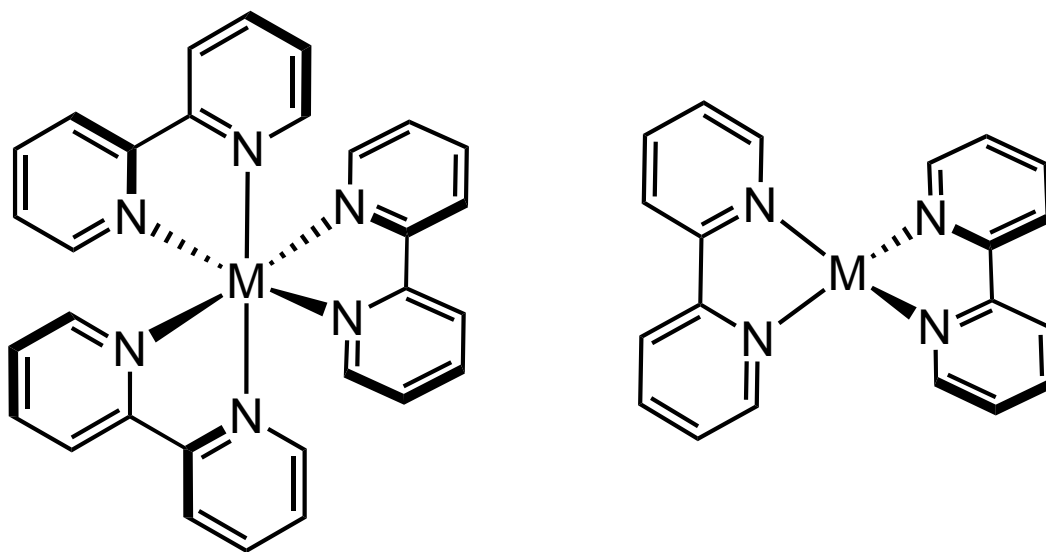
1) CHAPTER 1: INTRODUCTION TO THE DISSERTATION

1.1 INTRODUCTION

The push to decarbonize the energy sector has moved forwards in leaps and bounds over the past few decades.^{1,2} The main strategy has been a concerted push to decarbonize electricity generation through the use of low carbon renewables and decarbonize downstream processes like chemical manufacturing and green technology. However, the social capital generated by the label ‘green technology’ is often made the desired end, rather than the benefits a technology will bring.^{3,4} This so-called ‘green washing’ encompasses everything from use of coal fire to make solar panels, which increases the carbon break-even point with no guaranteed increase in product longevity, to the human rights violations occurring in the industrial and artisanal mining of cobalt in regions of central Africa which occurs on top of the intensive carbon emissions of the mining process. Acknowledgement of such misanthrope can make one cynical: cynical about the state of sustainability, cynical about the tools we use, cynical about humanity. I would argue however that cynicism, especially of the latter, was what contributed to the ‘green washing’ to begin with. To avoid such pitfalls, the cynicism as well as the green washing, the concerted strategy must be iteratively applied by individual researchers and society more broadly, while keeping in mind that all of this is being done to facilitate human flourishing.⁵⁸ The first practical question to ask is ‘where does this energy for this process come from?’ The second question to ask is ‘how can the release of carbon be minimized in this process?’

Inorganic charge-transfer chromophores (ICTC) can help answer both questions. These are molecular species that can capture solar energy and sensitize semiconductors in the dye-sensitized solar cell platform (DSSCs), which can in theory be used for grid-scale power generation. They can also sensitize molecular substrates and act as homogenous photoredox catalysts, which can reduce the temperature of some reactions and improve their atom economy

by leveraging light as a reagent, meaning they aid in minimizing the carbon released in primary processes.^{5,6} ICTCs commonly take the form of the structures pictured in scheme 1.1. Broadly speaking, these complexes interact with light in a way that creates useful excited states in which an electron-hole pair is created. This charge separated state is what facilitates the sensitization processes of DSSCs and photoredox catalysis. The scope of this chapter will discuss the use of ICTCs in the context of solar energy capture, however the impetus and molecular design principles discussed, in general apply equally to photoredox catalyst design.



Scheme 1.1: Structures of common classes of inorganic charge transfer chromophores. M=transition metal ion.

1.2 SOLAR ENERGY CAPTURE AND DYE-SENSITIZED SOLAR CELLS

Theoretically, the best sources of energy our society could have access to are derived from fusion. While fusion energy on a large scale is far off (with recent developments in mind), solar energy, derived from fusion is an abundant and underutilized resource society has access to now. Photovoltaic solar energy capture only represents 3% of the energy generated in the United States; however, it could make up a significantly larger portion, especially when coupled with technological advances in energy storage. While interest in solar energy has increased, there are

still hurdles related to the usability in certain climates, like that of Michigan, which has only an average solar irradiance between 3.0 and 3.5 kWh/m²/day. In part, the low solar fluence can however be compensated for by an increase in the total surface area of photovoltaic devices in a given region by their incorporation into existing infrastructure.

Polycrystalline solar cells, which dominate the PV market, are difficult to incorporate into existing infrastructure due to their rigidity.⁷ Thick and rigid device geometries are required for optimal performance. This is in part due to the indirect band gap of polycrystalline silicon, which amounts to a forbidden transition between valence and conduction bands of the semiconductor, that are promoted by lattice vibrations.⁸ This indirect band gap has advantages in current collection, for example it makes the CB→VB recovery process less favorable and thus prolongs the lifetime of a generated exciton. Ultimately, it makes crystalline silicon a relatively poor absorber of light and thus requires a significant thickness to generate the required current.

Other PV technologies have been devised to avoid rigid structures. These represent a class referred to generally as thin-film photovoltaics.^{9–12} These devices in general have improved light absorption capabilities and thus can be made amenable to flexible devices. One outgrowth of this regime of photovoltaics is the dye-sensitized solar cell (DSSC) or Grätzel cell named for the inventor.¹³ This system uses molecular charge transfer chromophores to sensitize a microporous semi-conductor electrode, which harvests the excited electrons.^{5,14–17} The molecular chromophores generally have strong absorptions in the visible spectrum and thus can be incorporated in smaller more flexible device volumes.

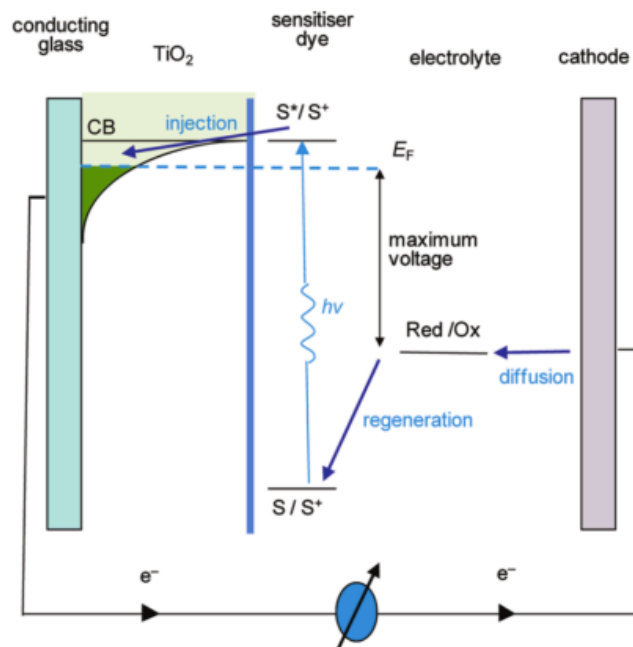


Figure 1.1: Schematic representation of a DSSC device. The excited sensitizer injects an electron into the semiconductor which collects electrons. The cathode reduces the redox couple in solution which regenerates the oxidized dye.

The semi-conductor/dye assemblies are immersed in an electrolyte, which contains some redox active molecular species. A schematic of a DSSC is presented in figure 1.1 with a description of the processes that facilitate its function. In many ways, the DSSC is more like modern Li-Ion battery in form, than other photovoltaics, due to the solution phase electron transfer processes. While the kinetic processes are highly interrelated, the first electron transfer step, called injection is critical for the device to function, as it involves the movement of electrons from the excited configuration of the a molecular dye into the conduction band of the semi-conductor electrode.¹⁸ The efficiency of this process is key for effective utilization in devices. Equation 1.1. illustrates the injection yield η_{inj} for this process assuming first order kinetics in the elementary steps:

$$\eta_{inj} = \frac{k_{inj}}{\sum_i k_i} = \frac{k_{inj}}{k_{inj} + k_{rec}} \quad 1.1$$

There are many processes possible for the excited state of the dye, in the equation above there are i such processes. However, for our purposes, the rate of recombination k_{rec} is sufficient to describe the unproductive reactions that are parasitic to the injection process. The best dyes, therefore, have a fast rate of injection and a slow rate of non-radiative decay. It is expected from equation 1.1 that a rate constant spread of 1 order of magnitude, will yield injection efficiencies of 90%.

Historically, inorganic dyes like $[\text{Ru}(\text{bpy})_3]^{2+}$ have been used because they sensitize DSSCs well.¹⁹ They exhibit strong transitions in the mid-visible, which yield charge transfer (CT) excited states which increases k_{inj} due to the reduced electronic coupling with the ground state upon the spatial separation of charge. Furthermore, these states persist for long periods of time suggesting decreased k_{rec} as it contains a component that depends on the non-radiative decay of the dye k_{nr} .²⁰ Separation of charge in the CT state delocalizes the excited state wavefunction onto anchoring moieties of the chromophore, giving proximity to the surface of the semiconductor and its conduction band, which is typically below the excited state energy of these chromophores leading to favorable electron transfer.^{21,22} Because of the increased electronic coupling of the MLCT excited state with the semiconductor and comparatively slow rates of excited state decay, CT dyes, particularly those incorporating Ru(II) perform extremely well as sensitizers in DSSCs. Figure 1.2 illustrates the distribution of charge in a model sensitizer, where the carboxylic acids are directed towards the semiconductor.

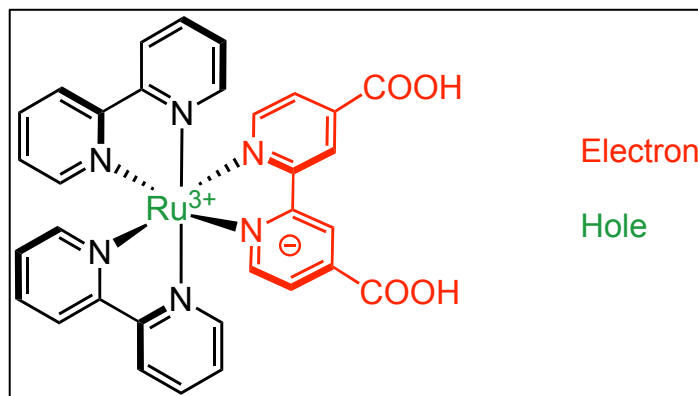


Figure 1.2: The distribution of the electron-hole pair of a localized MLCT excited state of Ru(II) sensitizer. Carboxylic acids are common anchoring groups for sensitizers.

1.3 THE ABUNDANCE PROBLEM AND ALTERNATIVES

While Ru(II) dyes may behave very well in devices, ruthenium metal is one of the rarest ores on earth.⁵⁷ This makes it impossible to generate photocurrent at scale with devices made from ruthenium. Alternatives have been sought to replace Ru(II). Typically, these alternatives are first row transition metals which tend to be more abundant than their second and third row congeners. Figure 1.3 illustrates the several orders of magnitude lower abundance of ruthenium compared with lighter first-row elements. Iron represents a seamless electronic comparison with ruthenium in a similar oxidation state. Like Ru(II), complexes of Fe(II) absorb visible light to populate MLCT states with similar intensity which are critical for a fast k_{inj} when sensitizing a semiconductor. Both ions have a d^6 electronic configuration, meaning the number and character of the electronic excited states are similar between the two species, assuming that symmetry is conserved between species.

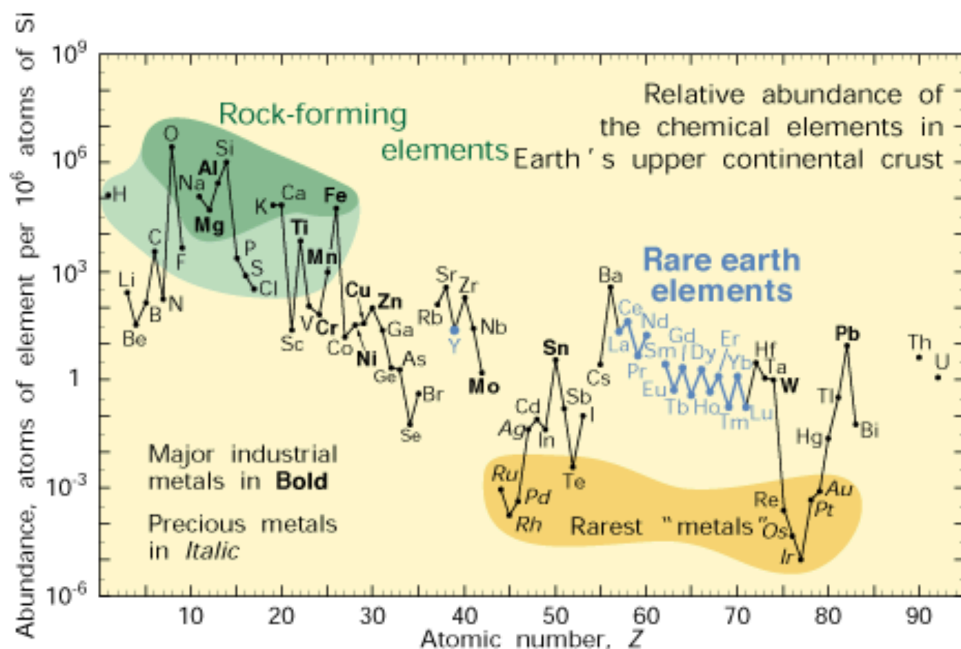


Figure 1.3: Crustal abundance of the elements of the periodic table. In general, first row transition metals are much more abundant than their third and fourth row counterparts. Compare the positions of iron and copper to that of ruthenium. Taken from reference 57.

Although the character of the excited states are the same, the ability for Fe(II) to act as a charge transfer sensitizer is quite poor. This is because Fe(II) has excited states which efficiently deactivate the MLCT manifold. In Ru(II) these ligand-field (LF) excited states occur at higher energy and thus do not deactivate the MLCT. Figure 1.4 illustrates these excited states and the respective decay pathways, which shows the lowest energy excited state in $[\text{Fe}(\text{bpy})_3]^{2+}$ is a $^5\text{T}_2$. Deactivation of the MLCT by the ligand field manifold was originally observed and proposed by Creutz and Sutin, using picosecond transient absorption (TA) spectroscopy and later validated independently.^{23,24} These spectroscopic observations are mirrored in the efficiency of devices employing Fe(II) chromophores. Ferrere and co-workers noted the extremely low current generation in DSSC devices utilizing a model complex that provided a 1:1 comparison with

standard Ru(II) sensitizers. The low injection efficiency is explained by increased k_{nr} relative to k_{inj} and is the primary reason for such poor performance.^{25,26}

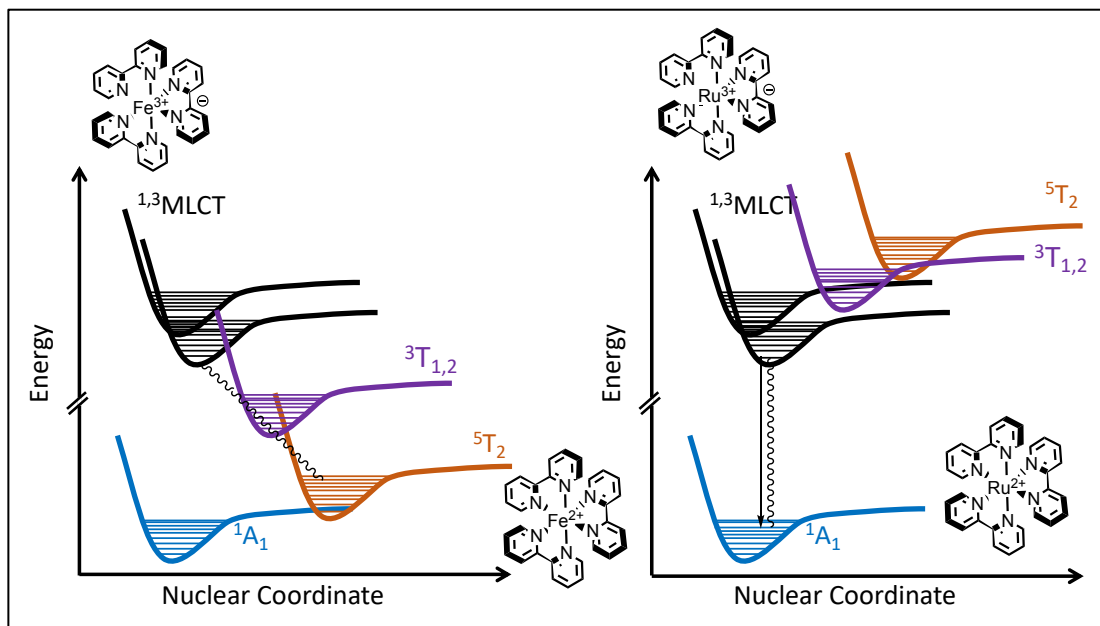


Figure 1.4: Potential energy surface diagrams for Fe(II) and Ru(II) for MLCT deactivation. Radiative (straight line) processes are present in Ru(II). Non-radiative processes (wavy) are present in both.

The reason for the increased density of excited states in $[\text{Fe}(\text{bpy})_3]^{2+}$ is because Fe(II) forms complexes with a weaker ligand field strength (LFS).²⁷ This weaker ligand field is manifest as differences in energy between the t_{2g} and e_g^* orbital manifolds. This energy separation in an octahedral field is called Δ_o . Figure 1.5 illustrates this for $[\text{Fe}(\text{bpy})_3]^{2+}$ on the left and $[\text{Ru}(\text{bpy})_3]^{2+}$ on the right, where the e_g^* manifold is destabilized relative to Fe(II). Thus, the higher orbital energy of Ru(II) suggests, to a first approximation, a higher energy excited state than in the state with the same configuration in the Fe(II) case.

Complexes of Fe(II) have lower ligand field strengths compared to Ru(II) because of fundamental differences in the electronic structure of 3d and 4d orbitals.²⁸ This difference is explained by the primogenic contraction of the 3d orbitals compared to the 4d orbitals. The primogenic effect is a product of the orthonormality of atomic wavefunctions in which the

maximum probability of the radial distribution function of the orbital in question is adjusted to maintain orthogonality with the other orbitals of similar angular momentum. As the 3d orbitals are the first to have $l=2$, the radial distribution function can minimize the orbital energy by contracting to some optimum. This primogenic contraction is not possible when the valence orbitals are of 4d character, because they must maintain strict orthonormality with the 3d orbitals. This manifests as a contraction in the probability densities of 3d orbitals compared to the 4d, by more than what would be expected from the increased n . This orbital contraction leads to an increased charge density around the atoms of the first transition series and increased ionicity in the bonding. Most importantly however, it reduces the orbital overlap between metal and ligand. This means that for every unit ability to destabilize a metal centered orbital a ligand has, Fe(II) will ‘feel’ a smaller portion of this than Ru(II) would. This translates directly into the smaller Δ_o of figure 1.5.

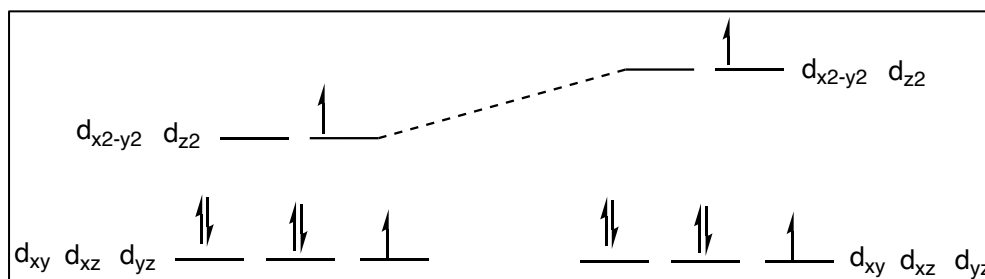


Figure 1.5: Electron configurations of d^6 octahedral complexes in an excited triplet state. The orbital energies of the Ru(II) case on the right are higher in energy compared to the Fe(II) case on the left. Note these are first order approximations.

This weak ligand field effects the energy of every metal centered (MC) excited state. This energy correlation with ligand field strength is best illustrated by the Tanabe-Sugano diagram for a d^6 complex of octahedral symmetry, illustrated in figure 1.6. As one moves from left to right, a break occurs, where the ground state electron configuration, changes from high spin ($S=2$) to low spin ($S=0$). In the low-spin regime, the energies of all MC states increase with increasing LFS.

1.4 THE SOLUTIONS

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increasing ligand field strength which happens through the increased donor ability of a ligand. Carbenes are the most common ligand type used for Fe(II) to achieve this end. Figure 1.7 illustrates, the effect of this approach on the PES of a MC state. Due to its displacement along the energy axis, this will be commonly referred to as the ‘y-axis’ strategy. Orthogonal to the thermodynamic approach is the kinetic approach, which involves the displacement of the PES minimum of a MC state along a specific nuclear coordinate with the goal of reducing the vibronic coupling between the CT and LF manifolds. In the Born-Oppenheimer approximation, the energy is a function of nuclear coordinates, as such this will be referred to as the ‘x-axis’ strategy and is illustrated in figure 1.7.

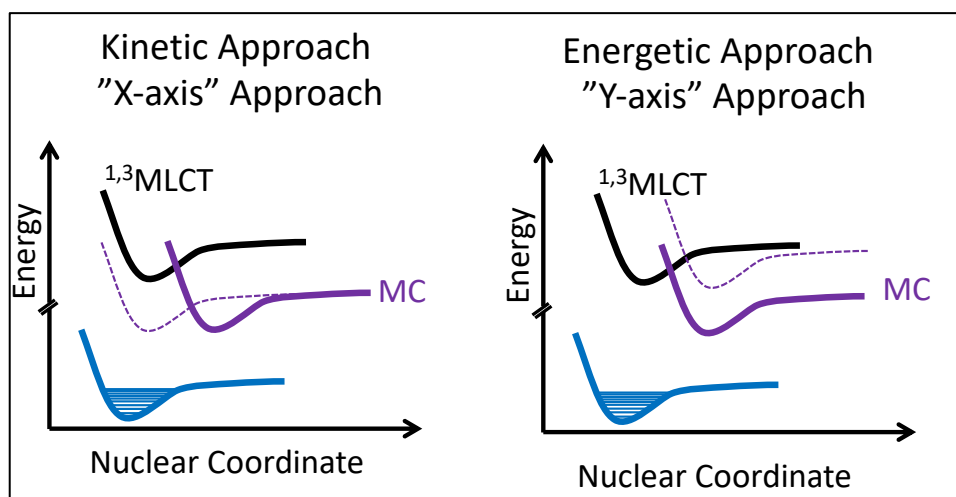


Figure 1.7: Illustration of the two orthogonal approaches converged in this thesis.

A third strategy is a convolution of these two orthogonal strategies and is called the entatic approach. This occurs when geometric constraints are placed upon a nuclear coordinate, which leads to an increase in free energy of a given MC excited state. Thus, restriction on the x-axis yields an increase in the y-axis. This type of description has been used to explain the photophysical and electrochemical properties of Cu(I) systems, which exhibit many correlations with entasis.²⁹ These three strategies will be covered in detail in the following sections.

1.4.1 The Thermodynamic Approach

The thermodynamic approach generally incorporates a strong σ -donor ligand that destabilizes metal-based orbitals of the same symmetry.³⁰ This ligand shifts the potential energy surface (PES) of a MC excited states above the zero-point energy of the $^3\text{MLCT}$ state, such that conversion to the ligand field is endergonic and unfavorable. This assumes the modifications made do not have any significant effect on the entropic component or vibronic coupling with the LF. Carbene ligands are superior to imine ligands in that they are better donors. Figure 1.8 illustrates this. The carbon atom of a carbene is less electronegative than the imine nitrogen, which allows it to overlap better (spatially and energetically) with the Fe center, compensating for primogenic contraction. This stabilizes the Fe-C σ -bonding orbital relative to the same orbital in the imine. This has the concurrent effect of destabilizing the σ -antibonding orbitals in the carbene. It is the occupation of these σ -antibonding orbitals in MC excited states that leads to their increase in energy. Figure 1.8 illustrates this for a ^3MC excited state.

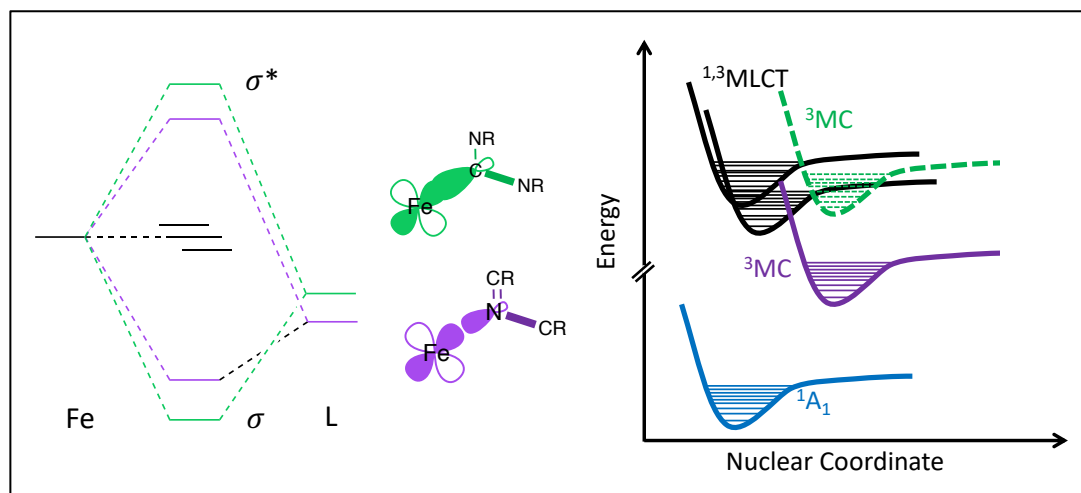
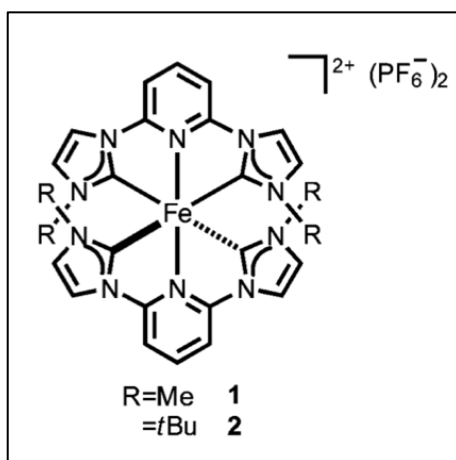


Figure 1.8: A comparison between a carbene and an imine bond, and how differences in bonding translate into differences in the zero-point energies of the PES. The increased orbital energies lead to an increase in state energies (to a first approximation).

The use of strongly donating ligands like carbenes has been a cornerstone of catalyst design since the inception of the first stable N-heterocyclic carbenes.^{31,32} It was inevitable that this strategy would make its way into the photosensitizer community. The use of strongly donating carbene ligands was first established as a viable strategy for longer lived Fe(II) MLCT states in the work of Wärnmark and coworkers who utilized the tetracarbene complex pictured in drawing 2.



Drawing 1.1: Structure of the Wärnmark complex. Taken from reference 33.

This pincer ligand framework had a heteroatomic first coordination sphere, where the carbene carbons are present in the axial sites and the pyridyl moieties are found equatorially. Transient absorption spectroscopy measured a radical anion absorption, which was prolonged compared to the pyridyl equivalent [Fe(terpy)₂]²⁺ (terpy=2,2':6,2''-terpyridine) with a lifetime of 9 ps.³³ Decomposition of the full spectral transient absorption data gave rise to two components with significant excited state absorption character. This led to the assignment of ¹MLCT→³MLCT→MC→GS, where the process of conversion to the MC state was rate limiting, making the GSR process untraceable by TA. Later studies using x-ray emission spectroscopy (XES) would go on to observe the ³MC, which decayed at a rate of 1.5 ps.³⁴ Furthermore, the fast absorptive component, originally assigned as ISC, was the formation of a kinetic branch

facilitated by a vibrationally hot MLCT state. Here, a portion of the excited population was modeled to convert ballistically to the ligand field.

The first Wärnmark complex was quickly surpassed by later varieties based on the carbene concept.^{30,35–37} Wärnmark again achieved a significant milestone by creating a homoleptic complex based on the meso-ionic ligand btz (btz =bis(1,2,3-triazol-5-ylidene)). This complex had a homoatomic inner coordination sphere which was the cited explanation for its 528 ps lifetime.³⁸ Quantum chemical calculations found that the lowest energy excited state was a ³MC and that the ⁵MC was displaced above the ³MLCT. The 528 ps species associated spectral (SAS) component was assigned implicitly by the observation that ³MC states often evolve much more quickly. Today, Fe(II) complexes with lifetimes over 1 ns are becoming more common.

Ligands other than carbenes have been developed for this strategy.^{39,40} Isocyanide ligands for example have been incorporated into complexes of several d⁶ metals of the first transition series like Cr(0) and Mn(I) which are plagued by similarly weak ligand fields. These ligands have yielded great results, including room temperature solution phase emission from charge transfer states.^{41–45} Another approach that falls outside of the increased ligand field strength paradigm is counterintuitive incorporation of π -donor character into the ligand framework, such that the highest occupied molecular orbital HOMO becomes ligand based. First pioneered by Herbert and coworkers, a neutral Fe(II) complex with an amido donor ligand was found to have a lifetime of 2 ns.⁴⁶ Only recently are the reasons for this phenomenon becoming apparent, which is intriguing as they seem to contradict intuitions developed about the spectrochemical series.^{47,48}

Much of the remainder of this dissertation will describe contributions into the use of the so called ‘y-axis strategy’ for improving the photophysics of Fe(II) compounds. Our prior work on this regime will be presented in detail in the introduction to chapter 2, which will discuss our

ongoing efforts to diagnose the mechanism of excited state decay in a diaminocarbene complex. Chapter 3 will discuss isocyanide complexes as strong field ligands on Fe(II) as well as their reactivity as precursors for the synthesis of novel carbene systems. Chapter 4 will delve into these novel carbene systems and present preliminary spectroscopic data. Chapter 5 will discuss the synthesis and characterization of several carbene and isocyanide systems which can function as strong field sensitizers.

1.4.2 The Kinetic Approach

The kinetic approach is less widely used than the thermodynamic approach is for Fe(II) systems. It involves the restriction of vibronic coupling between electronic states through ligand design, in which the motions that couple electronic states are restricted in such a way as to not facilitate deactivation. It is commonly referenced in the literature but is used in a ‘hand-wavy’ sense where bulky = rigidity = reduced k_{nr} , and it is generally used to explain results rather than as a design principle.⁴⁵ However, this strategy is intimately connected to non-radiative decay theory and semi-classical Marcus theory.

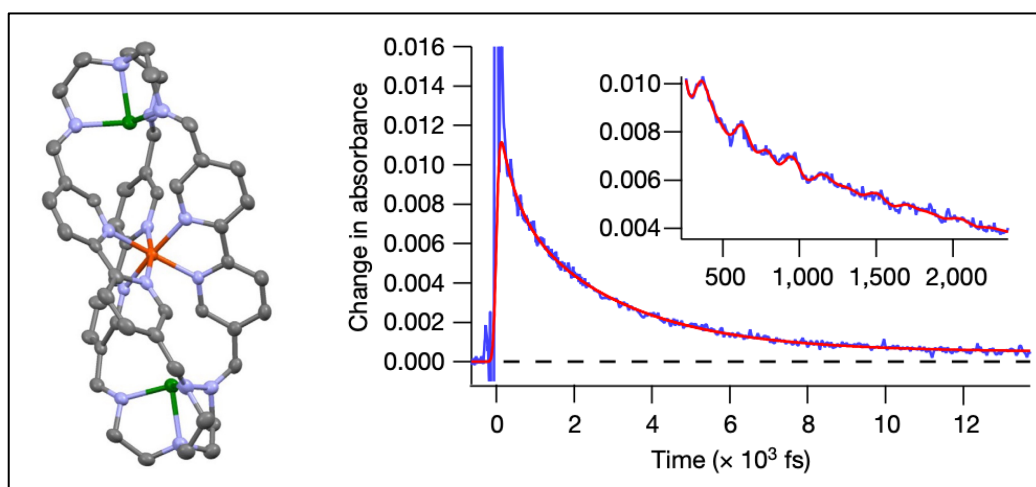


Figure 1.9: (left) Crystal structure of the Lehn-cage complex utilized to demonstrate the kinetic approach. Iron and copper atoms are orange and green respectively. (right) The decay of the

Figure 1.9 (cont'd) excited of the cage-complex with coherent oscillations superimposed upon the decay. Taken from reference 47.

The McCusker group has demonstrated the utility of this design strategy by utilizing an Fe(II) cage complex, with Cu(I) atoms as structural moieties. The complex, illustrated in figure 1.9, exhibited a 20-fold increase in lifetime when Cu(I) ions were incorporated, which locked the structure from reorganizing along a nuclear coordinate which was found relevant from the measurement of coherent oscillations, superimposed upon the kinetic decay traces.⁴⁹ These vibrations were then utilized as the basis for the targeting of synthetic modifications that would dampen these modes. This report was the first example of the use of vibronic coherences to improve upon the design of chromophores to enhance their utility in solar energy conversion.

While much of this dissertation is dedicated to the thermodynamic approach, chapter 7 describes a novel strategy for tracking computationally modeled vibrations across structural modifications. This is done in hopes of avoiding the ‘hand-wavy’ treatment that vibronic coupling is given in the synthetic literature.

1.4.3 The Entatic Approach

Entasis is a type of structure-reactivity relationship used in structural biology to describe fast kinetics of electron transfer in metalloproteins, whose active site is primed for the reaction by strict control of the geometry.^{50–53} Principles derived from the structural biology literature was applied to the well-known structural dependencies of Cu(I) excited state evolution.²⁹ In the language used above, this is a combined x and y- axis strategy, as steric effects (kinetics) prevent energy loss (thermodynamic) related to, in the case of Cu(I) MLCT excited states, the pseudo Jahn-Teller distortion. This is observed in the emission properties of Cu(I) polypyridyls, which show a blue shift in the emission maxima as the size of the steric groups increase. Figure 1.10 illustrates the difference between the entatic energy and the reorganization energy using PES

diagrams of Cu(I) polypyridyls with different degrees of substitution. Reorganization energy describes the energy required to make the geometry of a reactant state into the geometry of the product state. This considers the energy of a single compound's reactant and product states. The entatic energy considers the relationship of the potentials between different compounds, which makes the entatic concept more generalizable to systems of molecular substitutions by describing changes to the zero-point energy levels across a series.

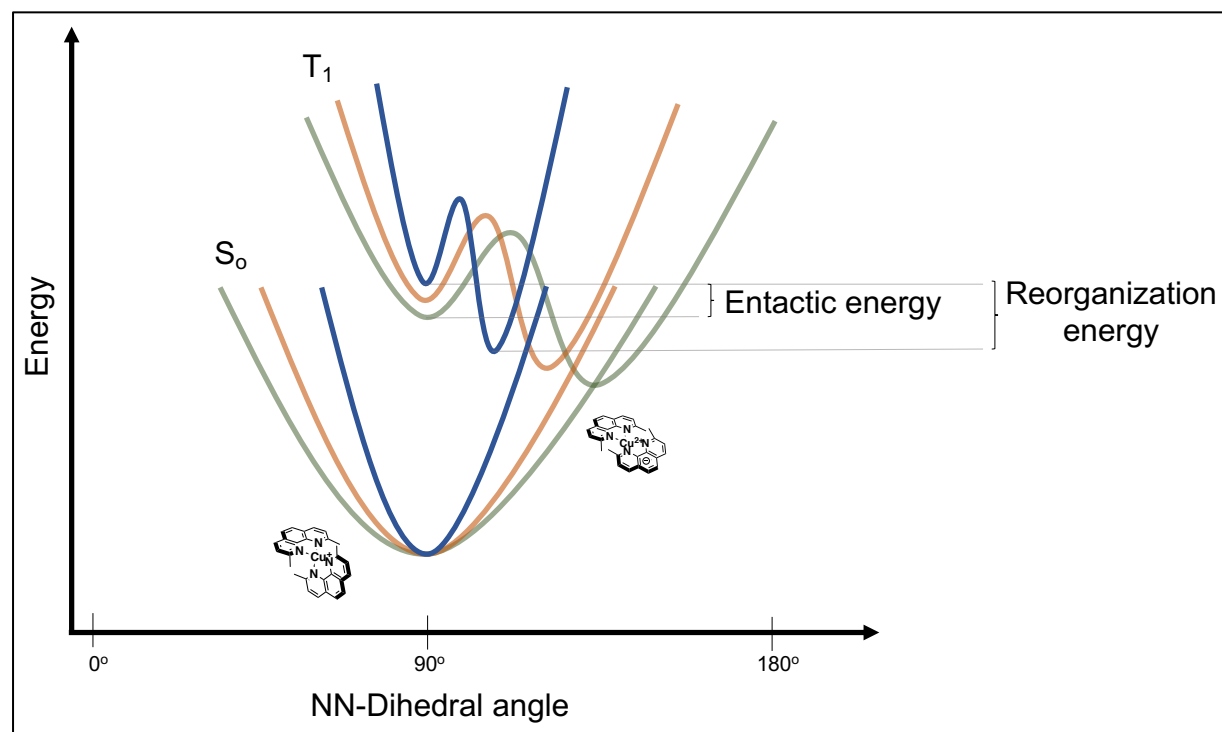


Figure 1.10: Illustration of the differences between the entatic energy and reorganization energy for the JT distortion on the T₁ surfaces of Cu(I) polypyridyls. Entatic energy is considered in reference to different species, whereas reorganization energy is considered in reference to different structural differences in the reactant and product states of the same complex. Green, orange, and blue traces are in the order of increasing steric bulk of the α -substitution.

The relationship between the rate of non-radiative decay and the zero-point energy difference between two states is described by the energy gap law (EGL) and is illustrated schematically in figure 1.11.⁵⁴ This ‘law’ applies only to systems whose potential energy surfaces are nested and the driving force is large relative to the size of the structural distortion

along the x-axis (i.e., the Marcus inverted regime). The EGL is a product of the energy dependence of the off-diagonal coupling elements of the vibrational wavefunction of two electronic states given by $\chi_{j,v}(E)$ for electronic state j and vibrational state v . As the energy difference increases the vibrational overlap decreases.⁵⁵ This decrease in overlap is explained by the quantum mechanical correspondence principle in which vibrational wavefunctions approach the expectation values of classical oscillators when $v \gg 0$, leaving a low probability near the equilibrium geometry. The entatic approach leverages this energy dependence as well as the functional dependence of the vibrational wavefunction on the coordinate Q . Figure 1.11 illustrates this principle in two concerted potential shifts, where the starting state (purple) has its motion along Q restricted, followed by the displacement vertically to state (green). The projections of both onto $v = 4$ of the ground state j is illustrated and shows the overlap in Q . This illustrates the larger overlap between the vibrational wavefunctions of the former compared with the latter. This figure illustrates the utility of the entatic approach as a design strategy as it incorporates both elements, x-axis, and y-axis strategies in one.

There are caveats to this. First is that the free energy gained must be in the form of recovered energy that would have otherwise been lost to some relaxation process. In Cu(I) MLCT states this relaxation process occurs via the pJT distortion. In the case of Fe(II) this could be applied to ³MC states, which are also expected to exhibit a JT distortion. The second caveat is that synthetic modifications do not lead to alternative pathways for vibrational deactivation. In the cases of Cu(I) complexes, while the motion of the alkyl groups are coupled to the decay process, this electronic coupling does not provide a lower energy pathway for deactivation and thus acts to enhance lifetimes.⁵⁶

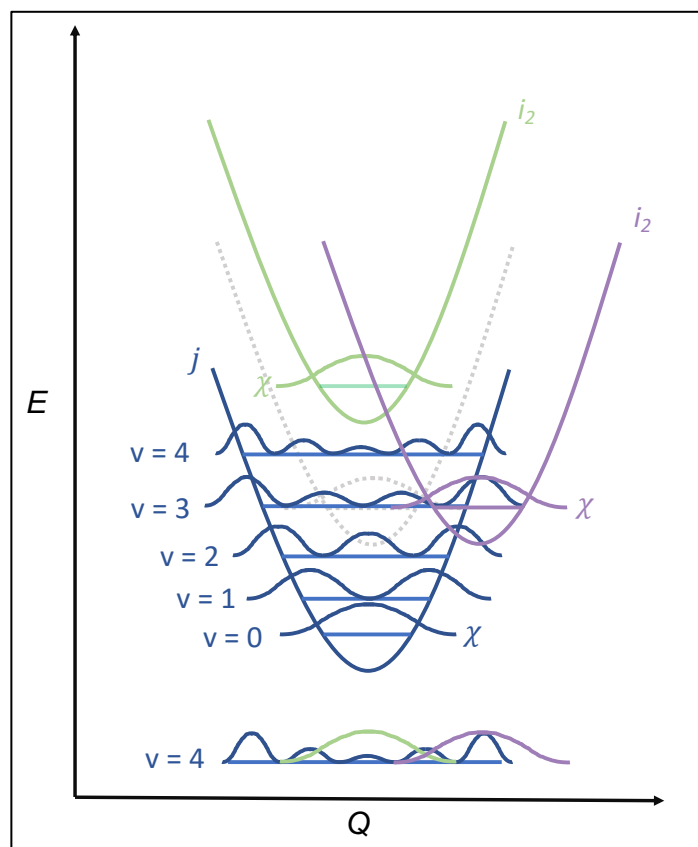


Figure 1.11: Illustrations of the orthogonal displacements of a potential energy surface along x and y-coordinate axes. Potential i_1 (purple) is constrained along the reaction coordinate Q to the position in grey, which leads to a reduction in non-radiative decay with state j . This state is then displaced vertically to the position represented in green leading to a reduction in non-radiative decay in accordance with the energy gap law. Projections of the $v=0$ vibrational wavefunctions of state i_2 with the $v=4$ vibrational wavefunction of state j is illustrated at the bottom of the figure to illustrate the benefit of constrained geometry.

The entatic approach will be considered in chapter 6 when the photophysics of Cu(I) complexes are described in more detail and the measurement of the reorganization energy of a Cu(I) model complex is performed. Opportunities to apply this strategy to other systems will be alluded to where appropriate.

1.5 CONTENTS OF THIS DISSERTATION

Chapter 2 will discuss the mechanism of excited state decay in an Fe(II) carbene complex utilizing time resolved spectroscopies and density functional theory calculations.

Chapter 3 will discuss the characterization new class of Fe(II) isocyanide complexes along with their behavior as precursors to carbene complexes and their reaction with amines.

Chapter 4 will discuss the characterization of a new class of Fe(II) carbene species and discuss the preliminary time resolved spectroscopic investigations.

Chapter 5 will discuss the study of a miscellaneous set of Fe(II) complexes which utilize the design principles laid out in this chapter.

Chapter 6 will discuss the temperature dependent emission properties of a Cu(I) sensitizer and the measurement of Marcus parameters associated with its ground state recovery process.

Chapter 7 will discuss a methodology for vibrational analysis for large, complex, asymmetric molecules.

Each section will discuss its own future works in their respective conclusions.

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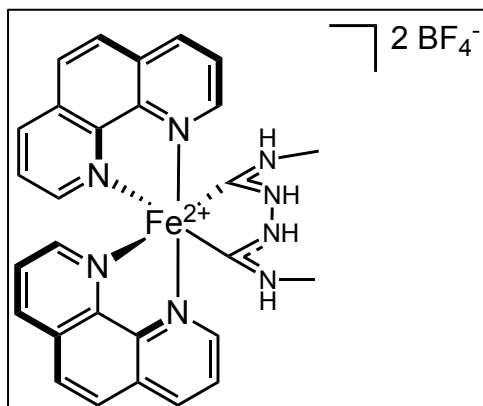
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**2) CHAPTER 2: PROBING THE EXCITED STATE
DEACTIVATION MECHANISM OF A HETEROLEPTIC
FE(II) CARBENE**

2.1 INTRODUCTION

The previous chapter discussed the need and the interest in studying molecular chromophores in the context of sensitizers in dye-sensitized solar cells, and the requirements of such photosensitizers to exhibit long MLCT excited state lifetimes. It was noted that carbene complexes could yield long-lived charge transfer lifetimes in Fe(II) chromophores due to their exceptional σ -donating ability.¹⁻⁵ This amounts to an energetic displacement of the metal centered (MC) excited states, facilitated by the increased covalency of bonding between Fe(II) and the carbene ligands. Stabilization of bonding orbitals due to increased bonding covalency increases the anti-bonding character of the e_g^* orbitals of the octahedral ligand field. High-spin states characterized by occupation of molecular orbitals with significant e_g^* character are thus destabilized relative to the ground and the MLCT manifold.



Drawing 2.1: Cation of 1 as the tetrafluoroborate salt.

Methods for addressing the problems associated with these first-row transition metal systems are not limited to the y-axis of the problem. Vibronic coupling of the charge transfer manifold to the ligand field is a fundamental driver of the decay cascade.⁶ Addressing these points separately is conceptually appealing as well as required for understanding orthogonal perturbations to each axis. Both approaches must be combined in a concerted fashion to make

meaningful progress. We believe that a heteroleptic platform will allow for the synthetic variability needed to address both x- and y-axes perturbations.

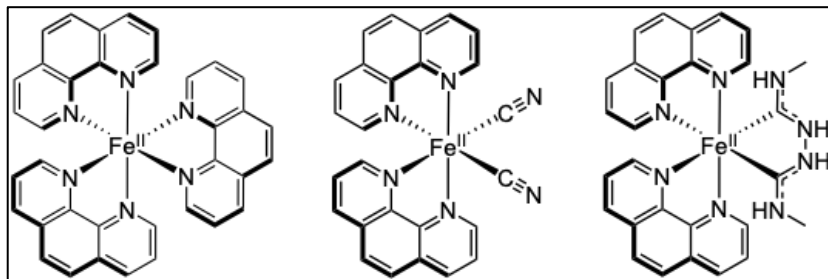
With this in mind our group decided to study a carbene complex $[\text{Fe}(\text{phen})_2(\text{C}_4\text{H}_{10}\text{N}_4)]^{2+}$ (**1**) in drawing 2.1 and alongside two other typical Fe(II) polypyridyls in drawing 2.2.⁷ This species was chosen for the modularity in its synthesis lending it a degree of tunability common in other diamino carbene ligands.^{8–11} Furthermore, acyclic diamino carbenes have been shown to be some of the strongest σ -donors. For example, bis(diisopropylamino)carbene was shown to be more basic than N-Heterocyclic carbene (NHC) ligands through its stabilization of CO stretching frequencies of a Rh(III) model complex.¹²

In our work, the superior σ -donor ability of the acyclic diamino functionality was leveraged in **1**, demonstrating a prolonged radical anion lifetime of about ~ 7.4 ps, an order of magnitude improvement from the typical polypyridyl. This prolonged radical anion absorption is consistent with literature observations in similar carbene systems which have been assigned as prolonged $^3\text{MLCT}$ excited state lifetimes.^{1,13} Notably, the acyclic diamino carbene **1**, with two carbon donors, achieved a lifetime increase on the same order as that of the $[\text{Fe}(\text{bmip})_2]^{2+}$ (where $\text{bmip} = 2,6\text{-bis}(3\text{-methyl-imidazole-1-ylidene})\text{-pyridine}$), which was observed to have a 9 ps radical anion absorption associated with a $^3\text{MLCT}$ that was hypothesized to be deactivated through a ^3MC state(s).¹³

2.1.1 A Modular Approach to Light-Capture

In our study mentioned above, the donor strength of several ligand architectures and their effects on the dynamics of excited state processes were observed. The ligand environment was modified only slightly for each system, illustrated in drawing 2.2. It was hypothesized that the ligand field strength (LFS) of each complex should be different and thus different kinetics.

$[\text{Fe}(\text{phen})_3]^{2+}$ should have a ligand environment consistent with standard polypyridyl systems. $\text{Fe}(\text{phen})_2(\text{CN})_2$ should have a different ligand environment, owing to the $-\text{CN}$ ligands increased π -acidity. Finally, $[\text{Fe}(\text{phen})_2(\text{C}_4\text{H}_{10}\text{N}_4)]^{2+}$ should act as a very strong σ -donor and behave differently than the other species. Transient absorption spectroscopy was utilized to measure the differences in kinetics of excited state deactivation.



Drawing 2.1: Complexes studied in reference 7. Complex 1 is on the right.

The control molecule, $[\text{Fe}(\text{phen})_3]^{2+}$, which has been well studied, was found to have an excited state absorption (ESA) lifetime of 180 fs with ground state recovery (GSR) occurring in ~ 1 ns. Full spectral transient absorptions at relatively long timescales ($\sim$ ps) showed no significant absorptions in the excited state and is dominated by a bleach of the ground state. This suggests the relaxation of the entire excited population into excited states with low oscillator strengths, a hallmark of metal based excited states. The kinetics and spectral features are consistent with those observed in the literature for the classic Fe(II) polypyridyl decay cascade.

Increasing ligand field strength involved substitution of a phenanthroline with cyanide ligands. This system exhibited a slight increase in the radical anion lifetime of ~ 250 fs and a decrease in the ground state recovery lifetime to 350 ps. Furthermore, the full spectral analysis showed no radical anion absorption at longer times ($\sim$ ps) shown in figure 2.1b. Interestingly, evolution-associated decay spectra (EADS) of the full spectra gave two components, suggestive of some processes occurring after decay of the MLCT, but before the recovery of the ground

state. These two spectra are consistent with vibrational cooling followed by ground state recovery on the 5T_2 surface. The increased LFS of the -CN ligand energy relative to phen, shortens the GSR lifetime, due to the increased driving force for recovery to the ground state. This is consistent with the dynamics from the 5T_2 occurring in the Marcus normal region, where an increase in driving force should increase the rate. This observation is consistent with the literature. Concurrently, an increased 3MLCT lifetime is observed, which may reflect the result of an increased driving force for GSR, namely a reduced driving force between the 3MLCT and 5T_2 . This could also be explained by the lowering of the 3MLCT lifetime, rather than a perturbation of the ligand field, as there is a significant redshift in the MLCT absorption manifold of $Fe(phen)_2(CN)_2$.

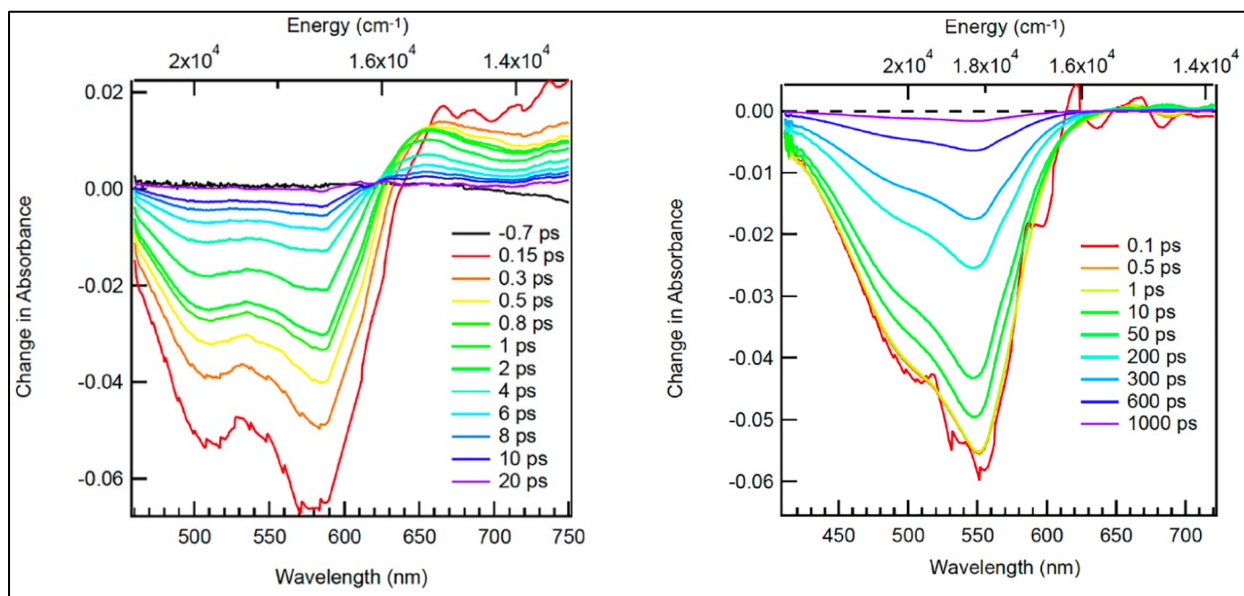


Figure 2.1: Full-spectral profile over the first 20 ps after laser excitation. (left) the spectrum of **1** indicates a radical anion absorption, which blue shifts on sub picosecond time scale. The GSB and ESA persist for the entire period. The ESA was interpreted as MLCT character being present. This spectrum agreed with the spectroelectrochemical measurement figure S22. (right) the ground state bleach of $Fe(phen)_2(CN)_2$, which lacks the excited state absorption feature usually associated with MLCT. Taken from reference 7.

Complex **1**, showed markedly different behavior as compared to the other two systems.

This is best shown in its contrast with the spectral profile $Fe(phen)_2(CN)_2$ in figure 2.1. The

absorption past 630 nm is indicative of a radical anion feature of a reduced phenanthroline, something that is not present in $\text{Fe}(\text{phen})_2(\text{CN})_2$ ($[\text{Fe}(\text{phen})_3]^{2+}$ not pictured however it resembles that of $\text{Fe}(\text{phen})_2(\text{CN})_2$) over the timescales studied. This profile matches the spectroelectrochemical measurements, suggesting MLCT character. The ground state bleach region recovers fully over the time window. This feature shifts blue at early times, decays to zero on a similar timescale as that of the bleach region. The associated time constants measured from triexponential fitting of a single wavelength kinetic trace were 230 fs, 3.4 ps and 7.4 ps. Component 1, was assigned to either solvent reorganization or intramolecular vibrational redistribution, as both processes have been shown to occur on similar timescales.¹⁴ The 3.4 ps component was assigned vibrational cooling on a relevant potential energy surface (PES). The 7.4 ps component described ground state recovery and as it exhibited a radical anion feature, it likely came from the MLCT manifold. This perturbation of the dynamics compared to the other two compounds is significant. However, the nature of its deactivation is still unclear. The absolute mechanism of decay in **1** was unable to be clarified due to the limits of the methods used, where ligand field states are generally unobservable.

The model of direct $^3\text{MLCT} \rightarrow ^1\text{A}_1$ was eliminated based on the magnitude of the lifetime for the GSR process. The radical anion which persists for this 7.4 ps, is several orders of magnitude faster than other non-radiative $^3\text{MLCT} \rightarrow ^1\text{A}_1$ processes. This suggests participation of a lower lying ligand field excited state or states or that structural aspects of **1** increase the degree of vibronic coupling with the ground state. It is likely however, that a ligand field state participates in the decay, consistent with other systems.^{1,13}

It was suggested that a triplet state was involved, as GSR of 7.4 ps was too short for a $\Delta S = 2$ transition, common for Fe(II) polypyridyls having lifetimes of the $^5\text{T}_2$ on the order of 1 ns.

The way in which this state participated depends on its energy relative to the MLCT among other things. Three possibilities were proposed to explain the mechanism of deactivation. The potential energy surfaces that describe the possibilities are presented in figure 2.2. Model 1 involves endergonic activation to $^3T_{1,2}$ state followed by fast transfer to the ground state. In this case the measured 7.4 ps time constant would correspond to the formation of this $^3T_{1,2}$ from the 3MLCT followed by fast deactivation to the ground state. This behavior is observed in a $[Ru(terpy)_2^{2+}]$ whose lifetime is several orders of magnitude shorter than $[Ru(bpy)_3]^{2+}$ and shows a temperature dependence in its emission properties consistent with multi-state kinetics.^{15,16} Model 2 involved a fast equilibrium between the 3MLCT and $^3T_{1,2}$ manifolds, giving spectral features associated with both manifolds (i.e. a radical anion) and the rate of decay associated with the fastest process i.e. $^3T_{1,2} \rightarrow ^1A_1$. Model 3 involved exergonic deactivation of the 3MLCT by the $^3T_{1,2}$ state which would be unobserved due to its exceptionally fast lifetime compared to the measured 7.4 ps. This model is like those proposed as the original assignments for the $[Fe(bmip)_2]^{2+}$ system.¹³ These three models are where the previous study left off.

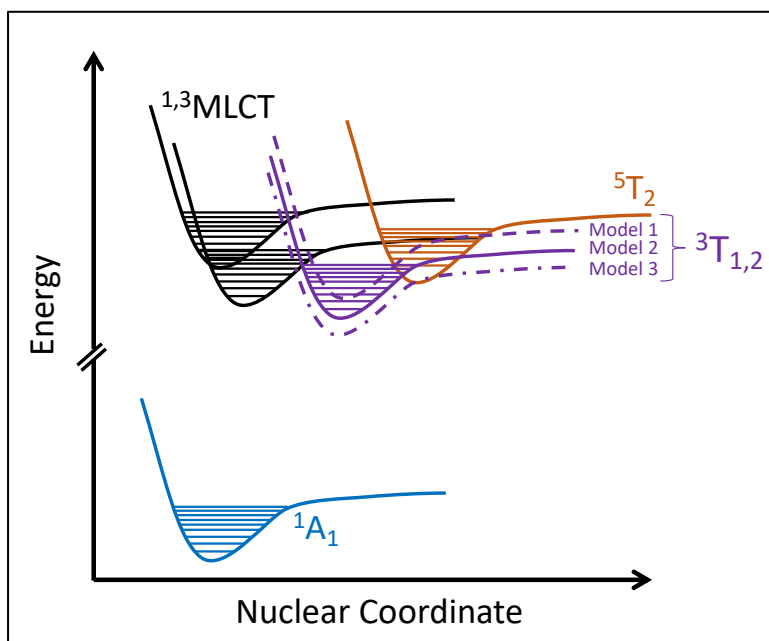


Figure 2.2: PES diagram for **1**. The models proposed depend highly on the energy orderings of the $^3\text{MLCT}$ and ^3T states relative to one another. The quintet state is not considered as a participant due to the speed of ground state recovery. Taken from Reference 7.

2.1.2 Diagnosis of the Excited State Decay Mechanism of **1**

The remainder of this chapter will provide more information about the specific nature of the excited state deactivation process in **1**. We employ three strategies to achieve these goals. The first is the use of time-resolved X-Ray Emission Spectroscopy (XES), which is sensitive to the spin-state and thus making the $^3\text{T}_{1,2}$ observable. The second strategy is the use of density functional theory (DFT) to compute the energies of the associated excited states to support experimental observations. Finally, variable temperature transient absorption (VT-TA) is used. Modulation of temperature allows for observation of kinetic barriers for processes that may not be observable in standard kinetic analysis. Furthermore, the parameters obtained will have some bearing on the character of the states involved. This methodology has been well established by our group to obtain this type of information for many systems.^{17,18} We can leverage data collected by these methods to obtain parametric data about the deactivation of **1** can enable mechanistic understanding.

Ultrafast transient absorption spectroscopy is a two-beam experiment, where a sample is excited with a high intensity ‘pump’ pulse and then probed with a lower intensity pulse usually in the form of white light. The time delay between pump and probe dictates the temporal position of the decay. Typically, a single probe frequency is examined by including a bandpass filter before the photodiode of the experiment. The absorption at some wavelength is given by equation 2.1, derived from Beer’s law.

$$\Delta A(t, \lambda) = \sum \Delta \epsilon_i(\lambda) b C \eta_i(t) \quad 2.1$$

The absorption is a function of all i species in solution. The difference $\Delta \epsilon_i(\lambda)$ is the molar absorptivity difference between the excited species i and the ground state of i at a given wavelength. The term b is the pathlength, C is the concentration of the ground state. $\eta_i(t)$ is the fraction of the total ground state species that were excited with the pump pulse. This factor is a function of time and is what gives rise to the decays measurable in $\Delta A(t, \lambda)$. This term can be expanded based on its definition to give:

$$\eta_i(t) = \frac{C_i(t)}{C} \quad 2.2$$

Where the ‘concentration’ of species i at a given time is given in the numerator, which is over the total concentration of species present. Incorporating equation 2.2 into 2.1 simplifies the equation to give:

$$\Delta A(t, \lambda) = \sum \Delta \epsilon_i(\lambda) C_i(t) \quad 2.3$$

The pathlength has been removed for clarity. The equation has been simplified to a set of differential absorption spectra multiplied by a set of concentration profiles for the same species. The concentration profiles depend on the mechanism in which the species i evolves by. Consider the case of a single first order process, in the case of **1**, it could be the unlikely case of

MLCT→GS, which happens with a rate constant given by k_1 . The expression for the difference amplitude as a function of time is given by:

$$\Delta A(t, \lambda) = \Delta \epsilon(\lambda) C_o e^{-k_1 t} \quad 2.4$$

In Fe(II) systems in the strong field domain, this rate constant is approximated well by k_{nr} . Considering this rate constant as a function of temperature will allow for a fit to the standard Arrhenius model which is given in the equation below.

$$k_{nr} = A e^{\left(-\frac{E_a}{k_b T}\right)} \quad 2.5$$

The activation energy E_a and prefactor A control the rate of conversion in a classical adiabatic system. These parameters are illustrated in figure 2.3 as they related to GSR process, where the reaction coordinate is pictured to move right to left. The activation energy is the barrier that must be traversed in the reaction. The pre-factor A , or frequency factor (units s^{-1}), represents the number of times the kinetic species approaches the barrier. In this adiabatic representation the conversion to the product state is 100% at the immediate left of the midpoint of the barrier.

Measuring k_{nr} as a function of temperature can give the parameters described above which can be used to describe the character of a particular kinetic process. This is however usually useful in reference to similar numbers generated in a similar way.

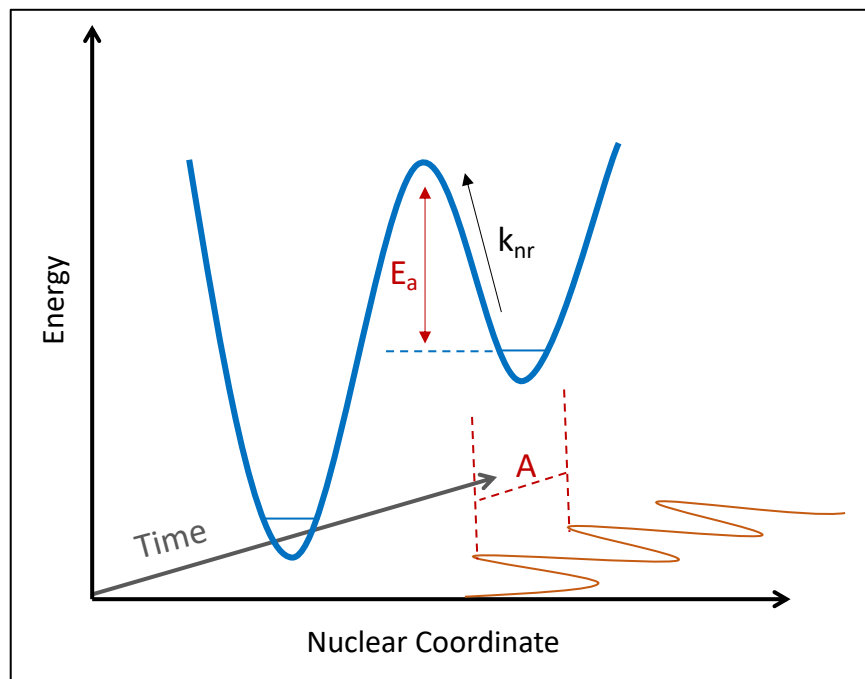


Figure 2.3: Arrhenius model describes the adiabatic potentials above, where products and reactants are on the left and right. The oscillation in time of the relevant nuclear degree of freedom is included to illustrate the frequency factor.

Semi-classical Marcus theory gives more meaningful parameters to characterize the non-radiative process.¹⁹ This model, originally designed for electron transfer, has also been applied as a description of non-radiative decay in the high temperature regime. There are several more complicated expressions that are derived from this; however, the semi-classical model is used throughout this work as all the works performed are in the high temperature domain. The equation that describes this rate constant non-radiative decay is below:

$$k_{nr} = \frac{2\pi}{\hbar} |H_{AB}|^2 \frac{1}{\sqrt{4\pi\lambda k_b T}} e^{\left(-\frac{(\lambda + \Delta G)^2}{4\pi k_b T}\right)} \quad 2.6$$

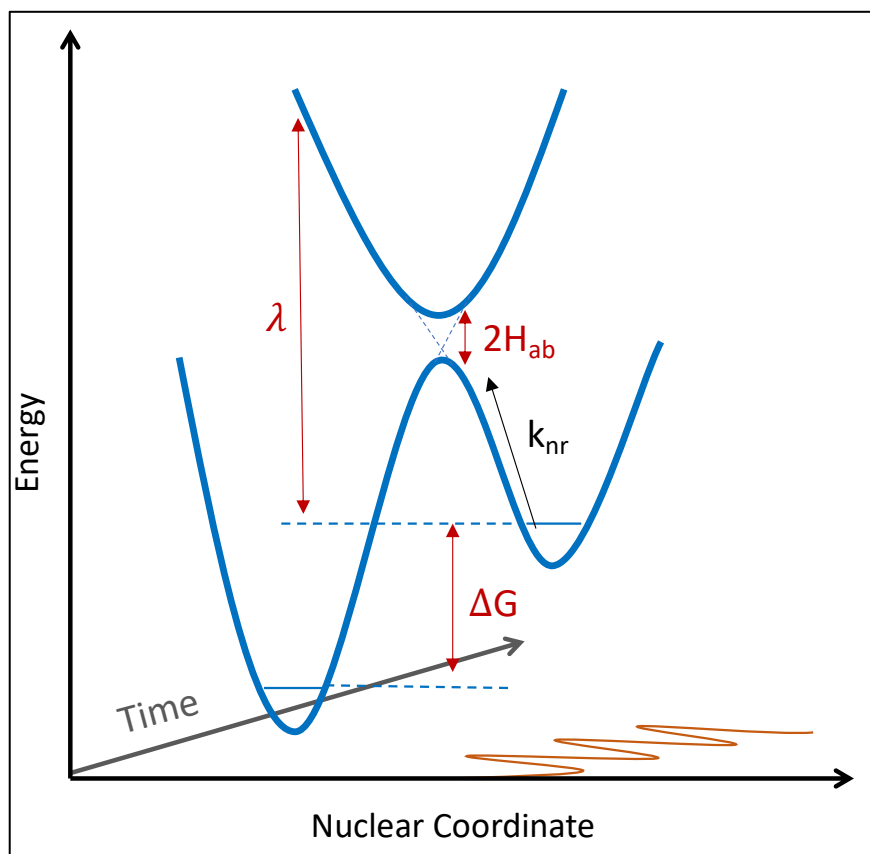


Figure 2.4: Depiction of the semi-classical Marcus model, where the reaction coordinate progresses from left to right. The oscillatory component is included and is highly dependent on the magnitude of the electronic coupling. It is important to note the likelihood of population transfer at the sinusoidal troughs is attenuated by the electronic coupling, compared to that in figure 2.3.

In the Marcus equation, H_{AB} , represents the electronic coupling, λ is the reorganization energy, and ΔG is the free energy difference between the reactant and product states, the left and right potentials respectively in figure 2.4. All other parameters are previously defined or have their usual meaning. Figure 2.4 illustrates how these relate to the potential energy surfaces. The reorganization energy, λ represents the magnitude of nuclear coordinate displacement between states. In practice this represents the amount of energy required to take the reactant geometry and make the product geometry without any free-energy changes associated with change in electronic configuration.

The similarities in both figures 2.3 and 2.4 are mirrored in the similarities of the Arrhenius and semi-classical Marcus expressions in equations 2.5 and 2.6, as they are both negative exponential functions in temperature. Calculation of the reorganization energy from the Arrhenius barrier is done through solving the quadratic expression in equation 2.7:

$$E_a = \frac{(\lambda + \Delta G)^2}{4\lambda} \quad 2.7$$

A root of the quadratic expression is the reorganization energy. With a measured activation energy, solving for λ requires independent measurement of ΔG . For Fe(II) complexes this can be done computationally or electrochemically, as emission spectroscopy is not usually an option (although this is changing). The magnitude of λ describes how displaced a reactant state is from the product state. In the case of ground state recovery, that reorganization energy describes the displacement of the excited state relative to the ground state. With the calculation of λ the electronic coupling can be calculated from the measured frequency factor with the equation:

$$A = \frac{2\pi}{\hbar} |H_{AB}|^2 \frac{1}{\sqrt{4\pi\lambda k_b T}} \quad 2.8$$

In this non-adiabatic picture of figure 2.4, there is a non-zero probability of continuing to belong on the reactant surface, this continuity is represented by the dashed lines between the upper and lower surfaces, in which the oscillating system continues its trajectory onto the upper surface. The magnitude electronic coupling is proportional to the inverse of this non-zero probability of population transfer between reactant and product. As an observable, the electronic coupling can describe the similarity between the electronic structures of both reactant and product states. For example, large values of H_{ab} occur when the transition is spin-allowed (singlet-singlet) and are small when the transition is spin-forbidden (singlet-triplet). While H_{ab}

describes relative similarity between states, it is limited in describing the absolute character of the states involved. For these, other methods are required.

2.1.3 X-ray Emission Spectroscopy

XES is a spin-state sensitive probe that detects emission that results after excitation of core-to-valence electronic transitions.^{20–22} These transitions are sensitive to spin and local oxidation state, which is the primary our group has used this in describing the deactivation cascades in Fe(II) systems.²³ The various types of emission are illustrated in figure 2.5. Like any other emission spectroscopy, the band is centered around a characteristic energy level and the transitions are distinguished by their transition energy and are labeled $K\alpha$ and $K\beta$ which describe emission from the second and third shells respectively. In the $K\beta$ manifold emission is derived from valence 3p orbitals. The similarity in energy of the 3p and 3d orbitals gives rise increased exchange coupling that make the emission energy sensitive to the occupation and spin of the 3d orbital, which occurs when LF states are occupied. As the valence to core emission is primarily dependent on the metal's spin-state, control molecules are used to calibrate the emission from a particular spin state. Figure 2.5.B. and 2.5.C. show these control spectra from

various compounds, that form a basis from which kinetic models of spin-state conversion can be modeled.

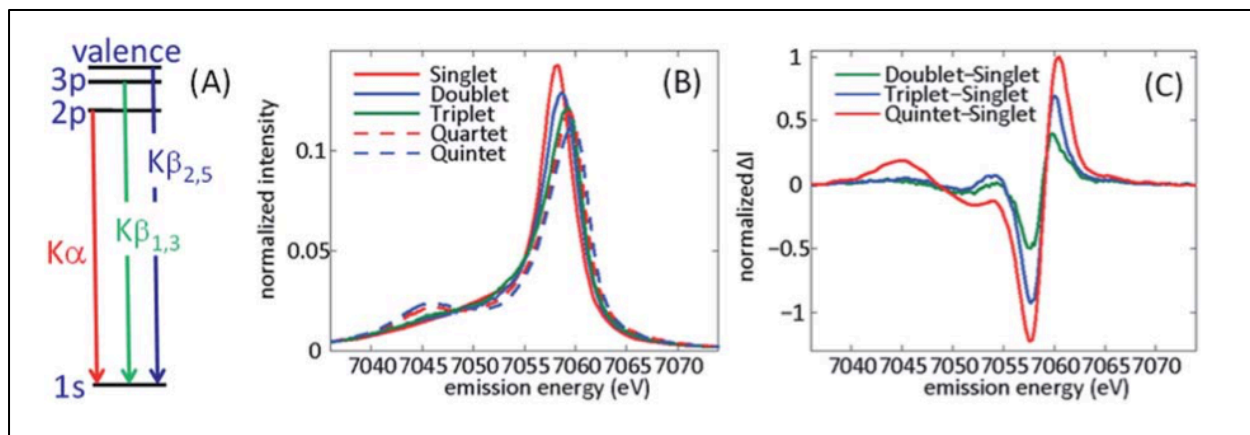


Figure 2.5: (A) schematic representation of the valence $\rightarrow$ core hole emission processes for the K-edge of Fe. (B) The emission profiles of several model complexes with various ground state spin configurations. (C) Normalized differential emission spectra of the relevant basis spectra in Fe(II) systems. Taken from reference 20.

Experimentally, the characters of the emitting states are highlighted by their differential emission spectra, which are calculated by the difference between the various basis spectra. Take, for example, the blue and red difference spectra in figure 2.5.B, where the former represents the difference spectrum of the triplet and singlet basis spectra, and the latter represents the difference between the quintet and singlet basis spectra. Triplet and quintet states can be clearly distinguished by the differences in signs in the region of 7055 eV as well as the broad feature near 7045 eV, which is present in the quintet case but not the triplet.

X-Ray solution scattering (XSS) is performed in concert with the XES experiment.²⁰ This experiment is utilized for measurements of the bonding environment, including bond lengths of the inner coordination sphere. Taken in concert XES/XSS experiments are incredibly information dense and are the ideal probe for the dynamics of the system we intend to study here however, the XSS data will not be presented here.

2.1.4 XES on Fe(II) carbenes

The use of XES to study iron carbene systems with 10s of ps lifetimes have been utilized to great effect in the diagnosis of excited state decay in Fe(II) systems. One notable example is the recent study of the $[\text{Fe}(\text{btz})_2(\text{bpy})]^{2+}$ ion. In the original report vibrational cooling was assigned to two time-constants 0.8 and 4.1 ps and decay of the ESA features assigned as $^3\text{MLCT}$ was 14.4 ps.¹ These models were corroborated by SVD and global analysis of the full spectral data. DFT calculations suggested the ground state recovery dynamics were facilitated by a ^3MC state which was calculated to lie below the $^3\text{MLCT}$ by 1 eV. This model is consistent with the progression:



Note that this model is analogous to model 3 proposed in our original report for **1**.

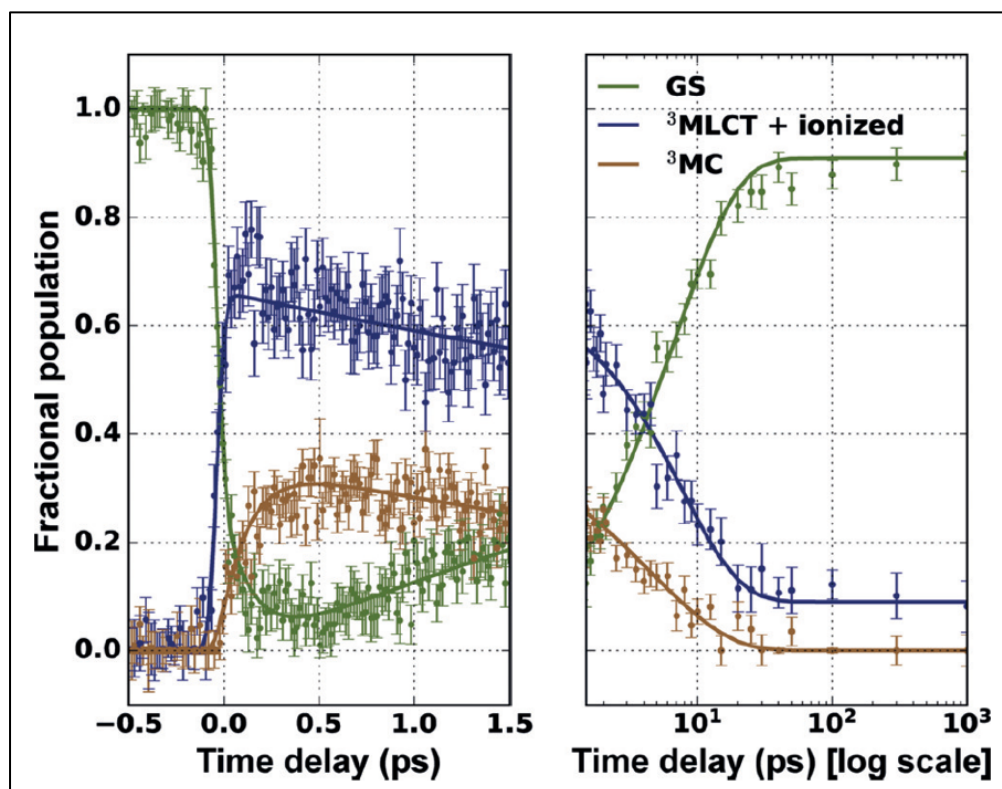
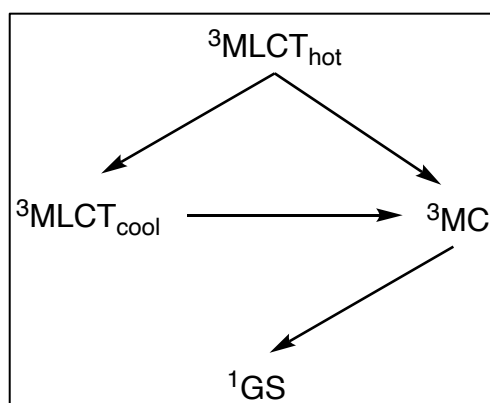


Figure 2.6: This figure shows the fractional population of excited $[\text{Fe}(\text{btz})_2(\text{bpy})]^{2+}$. The concurrent rise time of both the $^3\text{MLCT}$ and ^3MC states indicates branching. The state label

Figure 2.6 (cont'd) $^3\text{MLCT}$ +ionized means that a portion of the total CT population underwent oxidation and didn't fully recovery as indicated by the return to a steady state above baseline. Reproduced from reference 31.

The XES data of $[\text{Fe}(\text{btz})_2(\text{bpy})]^{2+}$ suggested a different mechanism. Here vibrationally hot $^3\text{MLCT}$ was observed to branch into a low-lying ^3MC state with a sub-picosecond lifetime and a cold $^3\text{MLCT}$ which eventually evolved, with a time-constant of 7.6 ps into the ^3MC , which decayed to the ground state on the order of 2.2 ps.²⁴ The total lifetime of the system was controlled by the $^3\text{MLCT}$'s lifetime, which made the 2.2 ps GSR process, kinetically unobservable in the original report assigned by TA spectroscopy. Scheme 2.3 illustrates this branching model after intersystem crossing from the $^1\text{MLCT}$.



Scheme 2.2: Branching model found common in Fe(II) carbenes.

These branching dynamics occurred with a ratio of 70:30 for the $^3\text{MLCT}_{\text{cool}}/^3\text{MC}$ and ^3MC state formed with a time constant on the order of 150 fs. The model of the excited state populations was obtained by global analysis of the XES spectra by fitting linear combinations of model complex basis spectra as a function of time. These data are pictured in figure 2.6. This shows a nearly concurrent rise time for both $^3\text{MLCT}$ (blue) and ^3MC (orange) states. While the fractional populations differ, they do recover on a similar timescale suggesting they are coupled in some manner. Other examples of the advantages of XES compared to room temperature TA were shown with the complex $[\text{Fe}(\text{bmip})_2]^{2+}$.²⁵ This system also exhibited branching dynamics

when analyzed by XES, which was not kinetically observable in the original report for similar reasons as those described above.¹³

The remainder of this work will describe the confluence of both robust experimental methods, XES and VT-TA in conjunction with quantum chemical calculations. Mechanistic insight will be provided that will help in narrowing down the decay mechanism of complex **1**. This work will support future studies of carbene complexes derived from this complex platform.

2.2 EXPERIMENTAL

2.2.1 General

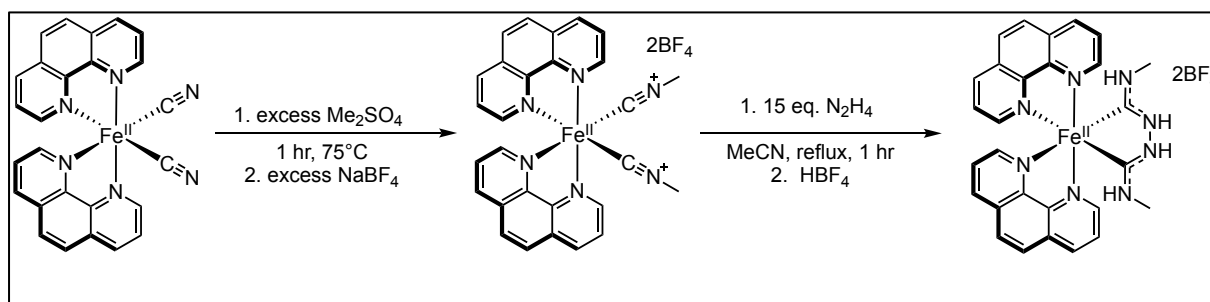
Spectrophotometric grade methanol was used for all spectroscopic measurements and was purchased from Sigma Aldrich. The precursor complexes were synthesized according to modified literature procedures.⁷ NMR spectra were collected at the Max T. Rodgers institute at MSU on an Agilent 500 MHz NMR spectrometer. Structural characterization methods were described previously.⁷

All variable temperature measurements were performed with a setup described previously.¹⁷ The samples were made with an absorption of 0.65 at 500 nm and excited at this wavelength. The temperature of the system was lowered, and measurements were made starting from the lowest temperature first, increasing in 10 K increments. The data was processed in Igor Pro where it was fit to a double exponential model. MATLAB was used for some data visualization.

2.2.2 Synthesis

Synthesis of Fe(phen)₂(CN)₂·4H₂O: 2.184 g (5.47 mmol, 1 eq) of Fe(NH₄)₂(SO₄)₂·6H₂O was dissolved in 60 mL water followed by 2.96 g (16.4 mmol, 3 eq) of 1,10-phenanthroline, upon which a bright red solution was formed. This was stirred and heated in open air until ~90

°C was reached, whereupon 5.48 g (84 mmol, 15.4 eq) of KCN was added in crystalline form with an solids funnel and the flask was immediately sealed under nitrogen and stirred while boiling for ~10 minutes. Solids precipitate which becomes complete upon cooling to room temperature and then to 0 °C. The solids were filtered and washed with significant amounts of water. **Note, all filtrates were neutralized with 30% bleach, which was also used to wash all glassware.** The solids were dried for a time on the funnel, where they were washed with diethyl ether. The solids were heated *en vacuo* overnight. The dark purple/brown solid was isolated. Yield, 2.651 g 96%. Results consistent with that previously reported.^{7,26} ¹H NMR (500 MHz, Methanol-*d*₄) δ 9.98 (dd, *J* = 5.2, 1.3 Hz, 1H), 8.67 (dd, *J* = 8.2, 1.3 Hz, 1H), 8.43 (dd, *J* = 8.1, 1.3 Hz, 1H), 8.20 (d, *J* = 8.9 Hz, 1H), 8.11 (d, *J* = 8.9 Hz, 1H), 8.01 (dd, *J* = 8.2, 5.2 Hz, 1H), 7.50 (dd, *J* = 5.2, 1.4 Hz, 1H), 7.45 (dd, *J* = 8.0, 5.2 Hz, 1H). ¹³C NMR (126 MHz, Methanol-*d*₄) δ 159.58 (axial, α-C), 152.53 (equatorial, α-C), 151.04 (axial, α'-C), 149.88 (equatorial, α'-C), 136.60 (axial, γ-C), 136.48 (equatorial, γ-C), 131.14 (axial, δ-C), 131.12 (equatorial, δ-C), 128.61 (equatorial, ε-C), 128.39 (axial, ε-C), 126.26 (axial, β-C), 125.93 (equatorial, β-C).



Scheme 2.3: Synthesis of relevant complexes. Only the carbene complex **1** is considered in significant detail in this chapter. Aqueous fluoro-boric acid use.

Synthesis of [Fe(phen)₂(CNMe)₂](BF₄)₂: 30 mL of dimethyl sulfate was added to a round bottomed flask, with a magnetic stir bar. To this was added 1.051 g of Fe(phen)₂(CN)₂ (2.08 mmol). This turns the solution a yellow color which darkens after a time. The temperature was raised to ~75 °C and was heated for an hour, after which an orange color persists. The solution

was cooled on ice and then extracted with ether/water until the organic layer is colorless. The orange solid was precipitated with NaBF₄ and allowed to cool overnight in at 5°C. This was filtered and the filtrate was separated. The solids were washed with dichloromethane leaving a small amount of red solid on the frit. This filtrate was slowly precipitated with diethyl ether, forming a yellow/orange solid which was filtered and dried overnight *en vacuo*. Yield, 1.221 g 82%. Results consistent with that previously reported.^{7,10} ¹H NMR (500 MHz, acetonitrile-*d*₃) δ 9.44 (dd, *J* = 5.2, 1.3 Hz, 2H), 8.85 (dd, *J* = 8.3, 1.3 Hz, 2H), 8.57 (dd, *J* = 8.2, 1.3 Hz, 2H), 8.27 (d, *J* = 8.9 Hz, 2H), 8.19 (d, *J* = 8.9 Hz, 2H), 8.10 (dd, *J* = 8.3, 5.2 Hz, 2H), 7.52 (dd, *J* = 8.2, 5.3 Hz, 2H), 7.35 (dd, *J* = 5.3, 1.3 Hz, 2H), 3.46 (s, 6H). ¹³C NMR (126 MHz, methanol-*d*₄) δ 159.03 (axial, α-C), 152.75 (equatorial, α-C), 149.47 (axial, α'-C), 148.32 (equatorial, α'-C), 139.15 (axial, γ-C), 138.86 (equatorial, γ-C), 131.40 (axial, δ-C), 131.20 (equatorial, δ-C), 128.73 (equatorial, ε-C), 128.57 (axial, ε-C), 127.34 (axial, β-C), 126.74 (equatorial, β-C), 32.21 (methyl).

Synthesis of [Fe(*phen*)₂(C₄H₁₀N₄)](BF₄)₂ (**1**): 1.355 g (1.88 mmol, 1 eq) of the methyl isocyanide complex was dissolved in 25 mL of dry acetonitrile. To this was added 15 mL (28 mmol, 15 eq) of neat hydrazine, which darkened the solution upon addition. After 4 hours of heating at 50 °C the purple solution was cooled to room temperature. 6 mL of 48% HBF₄ in water was added turning the solution a red color. This was stirred for 1 hour. The volume was reduced by rotatory evaporation to approximately 10 mL, where water was slowly added yielding blocky crystals. These were dried *en vacuo*. Yield, 1.127 g 80%. Results consistent with that previously reported.^{7,10} ¹H NMR (500 MHz, acetonitrile-*d*₃) δ 9.65 (s, 1H), 8.68 (dd, *J* = 5.2, 1.2 Hz, 1H), 8.61 (dd, *J* = 8.2, 1.3 Hz, 1H), 8.41 (dd, *J* = 8.2, 1.3 Hz, 1H), 8.18 (d, *J* = 8.9 Hz, 1H), 8.12 (d, *J* = 8.9 Hz, 1H), 7.84 (dd, *J* = 8.2, 5.2 Hz, 1H), 7.41 (dd, *J* = 8.2, 5.2 Hz, 1H), 7.19

(dd, $J = 5.2, 1.3$ Hz, 1H), 5.80 (d, $J = 5.8$ Hz, 1H), 2.15 (s, partially obscured by solvent). ^{13}C NMR (126 MHz, methanol- d_4) δ 231.20 (carbene C), 157.15 (axial, α -C), 152.06 (equatorial, α -C), 150.25 (axial, α' -C), 148.68 (equatorial, α' -C), 136.88 (axial, γ -C), 136.63 (equatorial, γ -C), 131.64 (axial, δ -C), 131.54 (equatorial, δ -C), 128.98 (equatorial, ϵ -C), 128.70 (axial, ϵ -C), 126.73 (axial, β -C), 126.62 (equatorial, β -C), 31.36 (methyl).

2.2.3 Computational

Quantum chemical calculations were performed with Gaussian 16 at the High-Performance Computing Center (HPCC) at MSU.³⁷ The structure was optimized with density functional theory (DFT) using the B3LYP+GD2 functional primarily, but with modifications in the functional including differences in HF exchange.^{27,38-41} PBEO functional was used in addition for some comparisons. All final calculations were performed with the 6-311G* basis set for light elements and a pseudopotential on the Fe atom for optimizations.⁴²⁻⁴⁶ High-spin structures were calculated with uB3LYP and modifications thereof. The calculated vibrational frequencies were all found to be real confirming an energy minimum. Time-dependent density functional theory (TD-DFT) was used for simulation of vertical excitations spectra of the ground and triplet states. All calculations were performed in with the polarized continuum model simulating methanol as a dielectric.⁴⁷

2.3 RESULTS AND DISCUSSION

A reduction of symmetry in **1** compared to the standard polypyridyl environment, makes the use of symmetry labels less useful. As such the discussion that follows will use generic spin labels like ^3MC or ^5MC to describe excited states localized on the metal center. In cases with multiple states, subscript numerals will be used in ascending order of energy. For example, $^3\text{MC}_1$

is the lowest energy triplet state in the ligand field manifold. It will be assumed that all ground state species are singlets.

2.3.1 Preliminary Considerations of Time-resolved X-Ray Emission data

Time resolved XES was performed by collaborators at the SLAC National Accelerator Laboratory. Preliminary data on **1** is given in Figure 2.7 which shows the differential spectra of $K\beta$ emission. The 3MC basis spectrum is overlain in blue and is in good agreement except for the region just below 7055 eV where the basis spectrum of the 3MC over predicts the intensity. It must be noted this region is most diagnostic in differentiating 3MC and 3MLCT . This can be seen in figure 2.5 where the latter is represented by the doublet-singlet difference spectrum. The ambiguity in the data makes it difficult to ascertain whether the decay occurs exclusively by 3MC . However, in consult with figure 2.5, the participation of the 5MC can be cautiously eliminated from possibility due to the lack of the broad and intense signal around 7045 eV coupled to a drop of signal near 7055 eV.

The $K\beta$ time domain trace in figure 2.7 was fit to a mono-exponential with a lifetime of 3.49 ps. Interesting to note is that it does not come back to baseline over the experimental period, suggesting the presence of a longer lived, albeit low amplitude component. Such a component was not observed in the original report where the full amplitude had recovered to baseline by this time.⁷ We would like to highlight again that these are only preliminary analyses. These data suggests that a single carbene ligand has pushed past the quintet/triplet crossing point of the octahedral d^6 Tanabe-Sugano diagram.

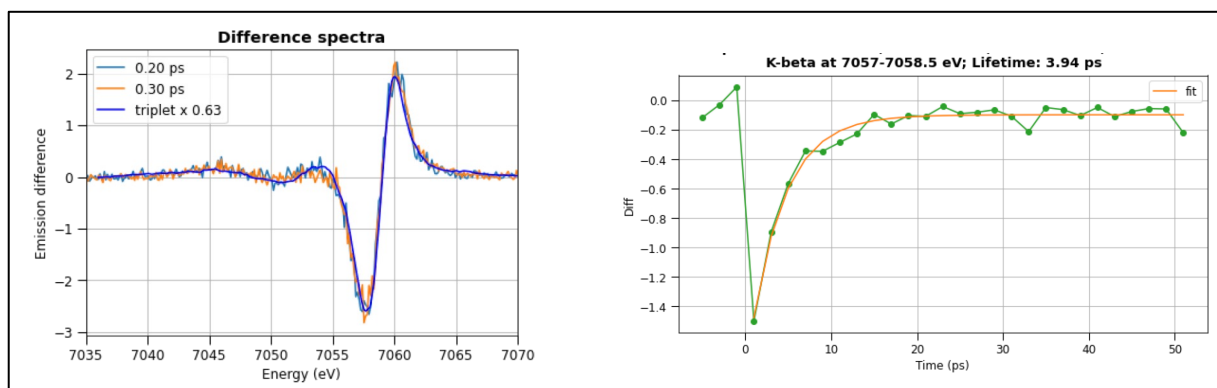


Figure 2.7: (left) XES difference spectra at 0.2 ps and 0.3 ps time delays which are overlain with the basis spectrum for the triplet state. (right) decay of $K\beta$ emission fit to a mono-exponential function which is clearly underfit. Data were collected and worked up by Hyeongtaek Lim at SLAC.

2.3.2 Ligand Field State Energy Calculations

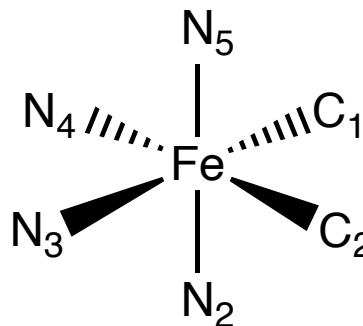
DFT calculations were performed to find the energy minima for the states likely involved. Unfortunately, $^3\text{MLCT}$ calculations did not converge in time for this report. The geometries and energies of the ground and high spin-states were calculated using uB3LYP and uBLYP*.²⁸

The calculated bond lengths are found from these states. The ground state values are in error with the ground state crystal structure by ~ 0.2 Å. The structure of the lowest energy triplet state was found by optimizing from the ground state geometry on the triplet surface. A noticeable bond elongation is observed for the axial nitrogen atoms of about 0.2 Å. Such an isotropic elongation is expected for Jahn-Teller (JT) distorted state like ^3MC . The HOMO, illustrated in figure 2.17, shows a slight anti-bonding interaction with both the carbene and phenanthroline ligands. The reduced occupation of this orbital in an MLCT should yield a decrease in bond lengths which is supplemented by the columbic attraction of the separated charges. It is for this reason the computed geometry is assigned to ^3MC . The ^5MC state also behaves as expected, a

symmetric lengthening is observed for all bonds due to the occupation of anti-bonding orbitals in the ligand field.

Table 2.1: Calculated bond lengths with (u)B3LYP.

Bonds	GS (Å)	³ MC (Å)	⁵ MC (Å)
Fe-C1	1.947	1.984	2.172
Fe-C2	1.948	1.984	2.172
Fe-N3	2.040	2.075	2.223
Fe-N4	2.040	2.075	2.222
Fe-N2	2.004	2.266	2.216
Fe-N5	2.004	2.268	2.216



The energies of the relaxed spin state were calculated. The quintet and triplet reorganize from the Frank-Condon geometry by about 11,400 cm⁻¹ and 4,500 cm⁻¹ respectively, which agrees with the expectation of increasing bond lengths associated with these states. This is verified in a later section. When considering different functionals, there is a significant difference in quintet energies between functionals. These data confirm that a metal centered triplet is the lowest energy LF excited state (likely lowest energy period). The observation that the fast GSR dynamics in **1** is driven by a $\Delta S = 1$ transition is thus strengthened and is in line with the participation of ³MC throughout the entire process. However, this does not rule out participation of the quintet state in deactivation, but rather suggests it must be a minor component the population of which is through kinetic control. The calculated energy difference between ³MC and ⁵MC (with B3LYP) is 539 cm⁻¹ meaning it could be accessible at room temperature.

Table 2.2: State energies relative to the ground state. FC is the Frank-Condon geometry.

State	uB3LYP (cm ⁻¹)	uBLYP* (cm ⁻¹)
Ground state	0	0
³ MC (FC)	11689	-
³ MC	7189	8024
⁵ MC (FC)	19171	-
⁵ MC	7728	11653

Interesting to note is the energy pinning for the ³MC state with uBLYP* compared to that of the [Fe(btz)₃]²⁺ complex, which was calculated with a similar functional that has a similar triplet energy compared to those calculated above. This system however exhibits a 528 ps MLCT lifetime. This drastic difference in lifetime must be controlled by reduced energy gap between the ³MLCT and the ³MC state compared to **1**.²⁹ The small ³MLCT/³MC energy gap, of approximately 1,600 cm⁻¹ is facilitated by the decreased reduction potential of the BTZ ligand framework compared to phen. This does suggest that the single diamino carbene ligand in **1**, has the same a similar ability to destabilize the ligand field as a hexacarbene complex with distorted symmetry, from a computational perspective.

2.3.3 Dushinsky Displacement Vectors and the Linear-Reaction Pathway

The computations support the notion that ³MC is the lowest energy excited state, which suggests it participates in the ground state recovery process. Establishing a reaction coordinate for this process as well as the other possible processes (i.e. ³MC→⁵MC, ⁵MC→GS) will be useful. A linear reaction pathway will allow for this and has been used in the past by our group and others to establish what vibrational modes are relevant for excited state deactivation.^{30–32}

The linear reaction pathway was computed by a MATLAB program written by Dr. Bryan Paulus, a copy of which can be found in his dissertation. The program uses the coordinates of the reactant and product, as well as the Hessian matrix of the reactant state. The reorganization energies are computed from the components of the Dushinsky Rotation matrix, the details of

which are covered elsewhere. Please note that the computations were performed in a methanol dielectric for all species. However, the author believes that the polarized continuum should contribute as its effects are implicit in the Hessian matrix. It is therefore assumed that the reorganization energy found from the Dushinsky rotation is the total reorganization energy.

Table 2.3: Total reorganization energies of some possible processes calculated from the LRP. Includes the ratios of the computed reorganization energy and the driving force of the processes.

Process	λ (cm ⁻¹)	$\lambda / \Delta G$
Triplet to Ground	5,258	0.73
Triplet to Quintet	6,493	12.05
Quintet to Ground	10,687	1.38

Three processes were examined: $^3\text{MC} \rightarrow \text{GS}$, $^3\text{MC} \rightarrow ^5\text{MC}$, and $^5\text{MC} \rightarrow \text{GS}$. The table 2.3 includes the total reorganizing energy for each of these processes. The $^3\text{MC} \rightarrow \text{GS}$ process is found to be around 5,285 cm⁻¹ and the $^5\text{MC} \rightarrow \text{GS}$ process was found to be 10,687 cm⁻¹, which is consistent with the magnitude of the bond increases found computationally. They are in approximate agreement with the energy difference between the computed FC geometries and the relaxed geometries of each state *vide supra*. The conversion between excited states, has a relatively large λ of 6,493 cm⁻¹.

The Marcus region for each process can be found from the ratio of computed $\lambda / \Delta G$. The energies calculated with uB3LYP were used. A ratio below 1 will have inverted kinetics and a

ratio above 1 will be a normal process. The ground state recovery process is inverted in the $^3\text{MC} \rightarrow \text{GS}$ case and normal in the $^5\text{MC} \rightarrow \text{GS}$ case.

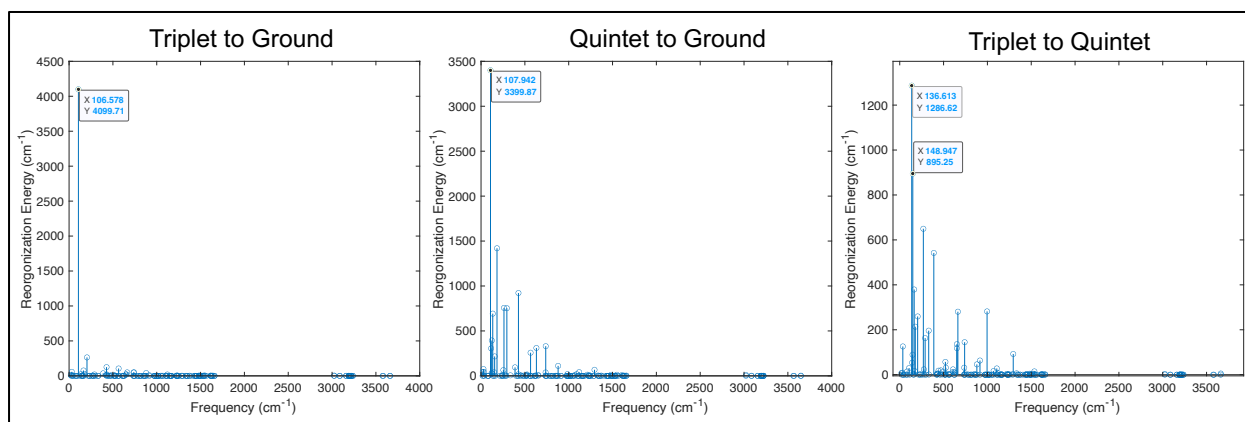


Figure 2.8: Plots of calculated reorganization energies of individual normal modes of vibration labeled by their frequencies. The most relevant modes are labeled with data tips. The 4,099 cm^{-1} reorganization energy of the 106 cm^{-1} mode suggests there is very little distortion in this excited state, except along this one coordinate.

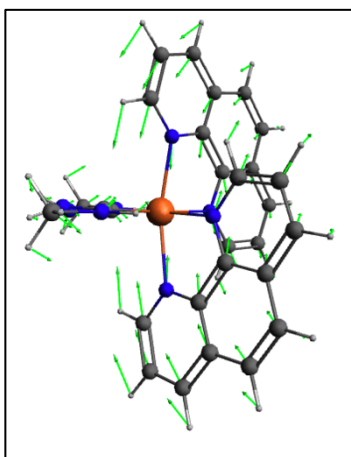


Figure 2.9: Vibrational mode with 106 cm^{-1} in the triplet state.

The contributions of each normal mode to the total reorganization energy included in the calculation. Figure 2.8 shows the plot of λ vs. frequency for each of the processes examined, the figures include data tips of the dominant contributions to the reorganization energy. The $^3\text{MC} \rightarrow \text{GS}$ process is dominated by the 106 cm^{-1} mode, accounting for 77% of λ . Compare this to dominant modes of $^5\text{MC} \rightarrow \text{GS}$ and $^3\text{MC} \rightarrow ^5\text{MC}$ accounting for 31% and 19% respectively. If the 106 cm^{-1} mode is visualized, it clearly shows an elongation of the axial Fe-N bonds. This is

consistent with the nuclear trajectory for the JT distortion, suggesting that it plays a significant role in the kinetics of the deactivation of **1**.

Table 2.4: Measured vibronic coherences versus those calculated with DFT. Measurements made by Dr. Bryan Paulus.

Measured (cm ⁻¹)	Calculated (cm ⁻¹)
66	71
103	106
115	113
159	160
163	164
225	232
408	421

Coherence measurements on **1** were made previously by Dr. Bryan Paulus. These data are reported in table 2.4 and are compared with computed frequencies. The measured 103 cm⁻¹ mode is in reasonable agreement with the calculations and indicate that this frequency may be a probe of deactivation of the triplet state and can be compared with similar measurements made on structural derivatives. While this does not prove the participation of the 103 cm⁻¹ mode in the ground state recovery process, it is highly likely this is the case, due to the dominance of this mode in the reorganization energy. This assumes the dominant decay pathway is through ³MC.

2.3.4 Room Temperature Kinetics

Ultrafast TA was performed on the cation in methanolic solution. The data were fit to bi-exponential models. This is surprising as a tri-exponential fit was found optimal for this species in the original report. Figure 2.10 below shows the quality of the biexponential fits for both the GSB and ESA. Figure 2.11 shows the GSB fit to mono-exponential and tri-exponential functions. The mono-exponential function is not a good fit. Although less obvious, the tri-exponential is also not great as its third component is ~20 ps with a 7 ps margin of error. This component is also very low amplitude. These combine to suggest that the trace is overfit with the tri-exponential model.

The differences between these values and the original report could be explained by the utilization of global analysis (GA) in the latter. The full spectral data utilized for GA is presented in figure 2.1.⁷ It was suggested by the XES measurements that a minor long component may be at play in the data, but that it was low amplitude. This may be true for the TA data as well and the tri-exponential fit captures this, but due to the limited scan window for these data, it is in significant error (~35%). Exploration of the longer component is put into the category of future works.

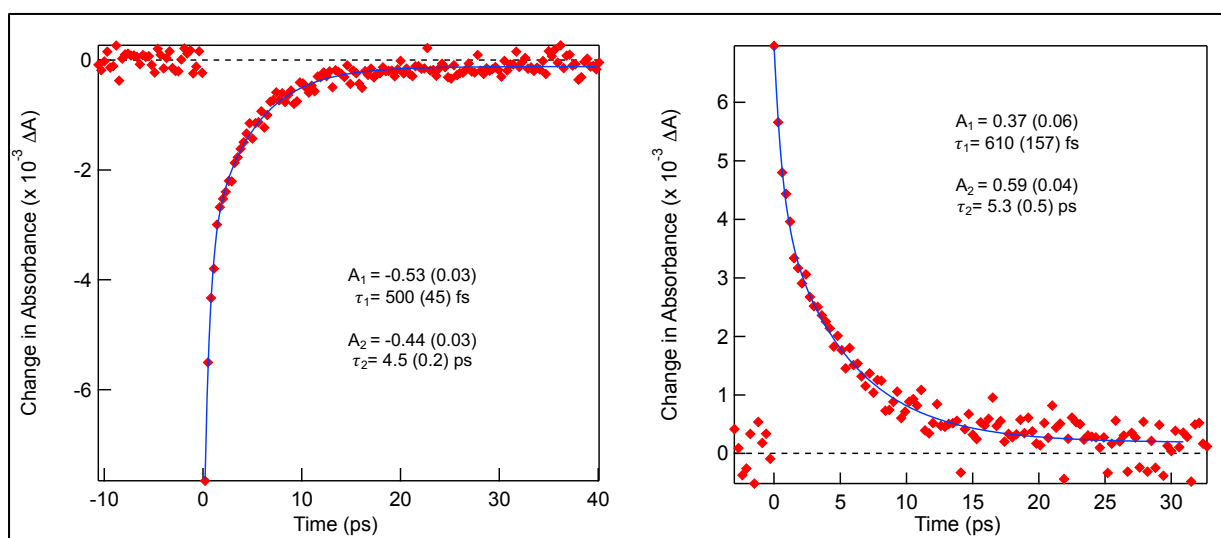


Figure 2.10: Kinetic traces measured at 295 K (left) ground state bleach recovery monitored at 580 nm. (right) excited state absorption recovery monitored at 680 nm. The errors reported in parenthesis are the errors associated with the fits.

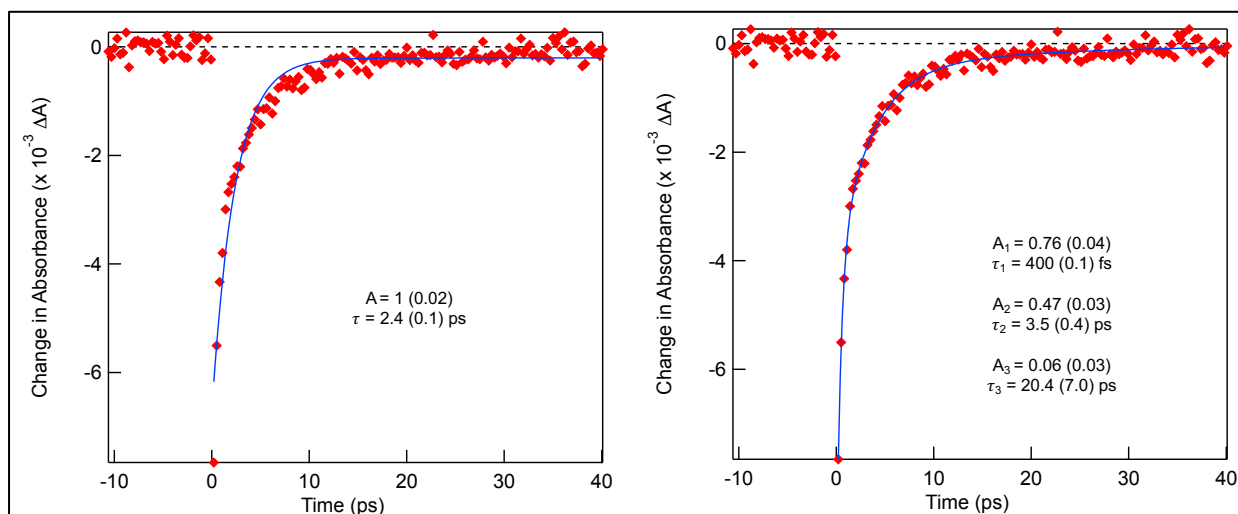


Figure 2.11: Mono and tri-exponential fits of the ground state bleach in figure 5. Both fittings lead to significant errors. (left) the fitting error is seen explicitly. (right) The error for τ_3 is 35% of the measured lifetime. This coupled with its low amplitude suggestive of overfitting of this data set.

The first time-constant for both the ESA and GSB are on the order of ~ 500 fs and each are within error of one another. The errors for the 680 nm case are larger due to the decreased signal to noise. In the original report a ~ 250 fs component accompanied a blue shift in the spectrum. It is likely that the components measured here also represent a similar shift in the spectrum. The long components are 4.1 and 5.2 ps (from table 3) for GSB and ESA respectively. They are shorter than the longest component (7.4 ps) measured in the original report, which also included a ~ 3 ps second component. Furthermore, the preliminary analysis of the $K\beta$ emission decay occurred on the order of 3.9 ps. The proximity of all these values, albeit statistically different, suggest some continuity between the measurements and likely describe the same process.

2.3.5 Variable-Temperature Transient-Absorption

VT-TA was performed on methanolic samples of **1**, over a temperature range of 295 K-235 K in 10-degree steps for both ESA and GSB. The data reported here are averages of two runs. The data quality was gauged by fitting errors in Igor. Note the reported error for the time

constants for probe 680 nm and 255 K and 265 K are their fitting errors due to an inability to collect these two temperature points for one of the two runs. The long component for each fit increases throughout the temperature range. This suggests the rate of non-radiative decay decreases as the temperature is dropped. The sensitivity to temperature suggests that the ground state recovery process is derived from a thermalized excited state. The noise in the data makes it difficult to determine if recovery to baseline is observed, however in the case of the ESA, it is clearly not returning to baseline at lower temperatures. The necessity of an increased scan window has been addressed above. The individual traces with their fits are given in the appendix to this chapter.

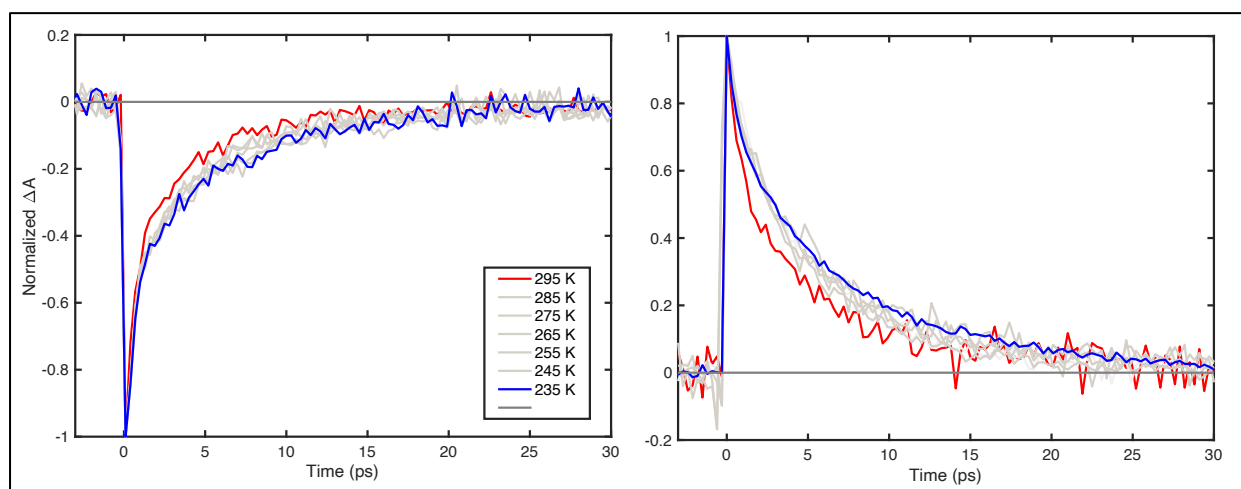


Figure 2.12: VT-TA data for both probe regions (left) 580 nm, (right) 680 nm. The individual spectra are included in the appendix to this chapter.

Table 2.5: Associated time constants for each wavelength region and each temperature. The numbers in parenthesis are the errors. *Indicates reported errors are fitting errors and not from an average of two runs as is the case with all others.

Temperature (K)	τ_1^{580} (ps)	τ_2^{580} (ps)	τ_1^{680} (ps)	τ_2^{680} (ps)
235	0.77 (0.13)	6.91 (0.19)	0.78 (0.16)	6.94 (0.65)
245	0.80 (0.10)	6.36 (0.43)	0.57 (0.10)	6.64 (0.15)
255	0.77 (0.22)	5.86 (0.16)	0.76 (0.10)*	6.40 (0.21)*
265	0.94 (0.10)	5.73 (0.50)	0.90 (0.10)*	6.36 (0.23)*
275	1.02 (0.10)	5.19 (0.13)	0.67 (0.10)	5.93 (0.30)
285	1.12 (0.23)	4.96 (0.13)	0.66 (0.10)	5.59 (0.47)
295	0.69 (0.12)	4.13 (0.16)	0.50 (0.10)	5.24 (0.10)

The time constants are reported in the table 2.5. The reported errors are averages of multiple datasets. The temperature dependence is clear in the long components (τ_1) at both wavelengths. This is not observed with the short components (τ_2), which show no statically relevant trend in the temperature dependence. As the time resolution on our picosecond system is approximately 100 fs FWHM, we must be cautious about deriving significant meaning from the data on this timescale.

These results can be understood by considering that these describe the amplitudes of the kinetic traces in a bi-exponential model. The lack of temperature dependence in the measured normalized average amplitudes suggests the initial populations of each form by some temperature independent process. This is consistent with the original model proposed, where the MLCT was formed by some fast and likely, non-equilibrium process. This lack of temperature dependence eliminates the equilibrium model, except in cases with a very low energy barrier.

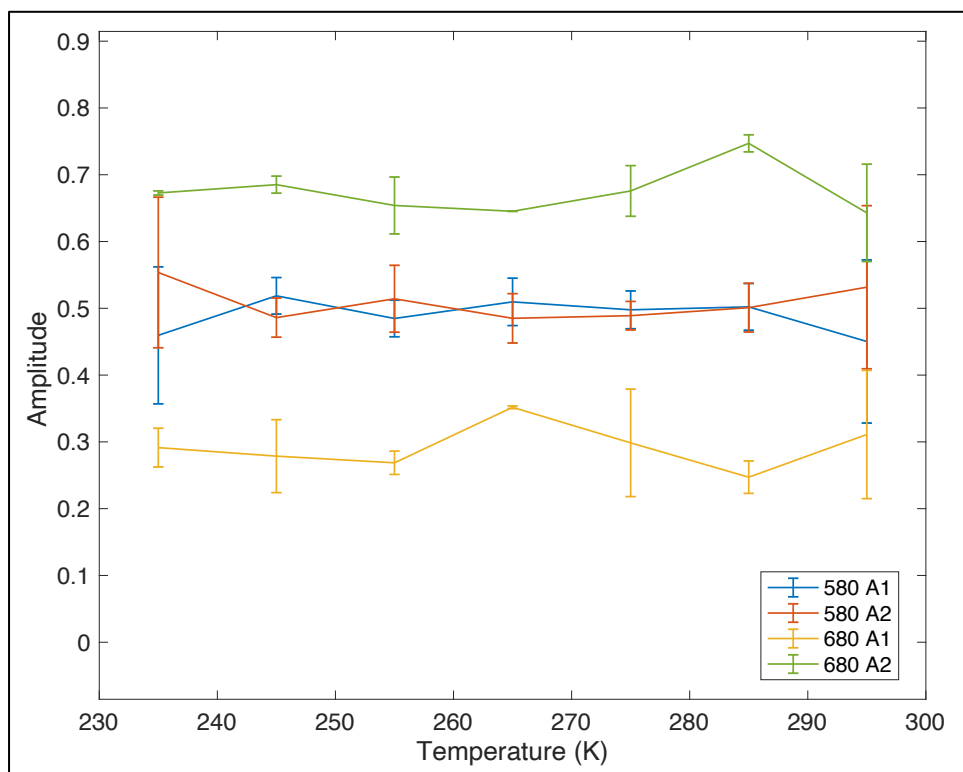


Figure 2.13: Normalized fitting amplitudes for the bi-exponential decay models at both probe regions. Errors in the short components are higher, which is expected due to the time resolution of the instrument. Virtually no temperature dependence is observed in these data, suggesting temperature independent process dictate initial populations of the terminal configuration.

To simplify the discussion for variable temperature, the expression will only consider the second time constant which is temperature dependent. As has been noted this corresponds to the observed ground state recovery rate, which should encompass all unmeasurable rates of decay for this process is tentatively assigned as $S \rightarrow {}^3MC \rightarrow GS$, where S describes a state that exhibits the excited state absorption, which includes the 3MLCT as a likely possibility due to the agreement with spectroelectrochemical measurements. An equation that describes the time dependent amplitudes as a function of wavelength are given as the following:

$$\Delta A(t, \lambda) = \Delta \epsilon_S(\lambda) C_S(t) + \Delta \epsilon_{MC}(\lambda) C_{MC}(t) \quad 2.10$$

As mentioned, the form of this equation is justified by the presence of the low lying 3MC state and its participation in the XES data. The form this expression takes depends on the mechanism.

A set of differential equations can be proposed for the two-state system, which considers only the decay after the formation of the ESA and equilibration of the ³MLCT.

$$S' = -k_1 S \quad 2.11$$

$$MC' = k_1 S - k_2 MC \quad 2.12$$

The solution for the first differential is a single exponential. From the knowledge that the process k_2 is unobserved and therefore larger than k_1 which is common.^{24,25} The change in the population of this negligible throughout the process approximating a steady state, which simplifies its rate expression into the following.

$$MC(t) = \frac{k_1 S(t)}{k_2} \quad 2.13$$

These can be substituted into the expression for the amplitudes in equation 2.10.

$$\Delta A(t, \lambda) = \Delta \epsilon_S(\lambda) C_S e^{-k_1 t} + \Delta \epsilon_{MC}(\lambda) \frac{k_1 MLCT(t)}{k_2} \quad 2.14$$

This expression describes the probe dependence of the observed decay when $k_2 \gg k_1$. When probing at 580 nm, both terms $\Delta \epsilon_S$ and $\Delta \epsilon_{MC}$ have a non-zero amplitude and thus both contribute to the observed signal. The $\Delta \epsilon_{MC}$ term should exhibit spectral behavior like the EADS observed for the non-carbene species, with low amplitude past 650 nm.⁷ Thus, when probing at 680 nm the second term (expected for MC states) goes to zero and the observed decay depends only upon the first term. This naturally extend to the temperature dependence of the non-radiative processes describe by k_1 and k_2 , which explains the differences in the rate constants for the probe regions.

2.3.6 Arrhenius Analysis

Arrhenius analysis of the VT data was carried out by the method described in the introduction to this chapter. The Arrhenius plots for each wavelength are given in figure 2.14.

Only the longer component at each wavelength was analyzed as the short components exhibited no obvious temperature dependence. Analysis of the bleach region (580 nm) yields an activation energy (E_a) of $462 \pm 45 \text{ cm}^{-1}$ and a frequency factor (FF) of $(1.73 \pm 0.42) \times 10^{13} \text{ s}^{-1}$. The probe of the ESA gives a measured barrier of $310 \pm 18 \text{ cm}^{-1}$ with a frequency factor of $(6.82 \pm 0.86) \times 10^{12} \text{ s}^{-1}$. The difference of these parameters is in line with the observed probe dependence consistent with equation 2.14.

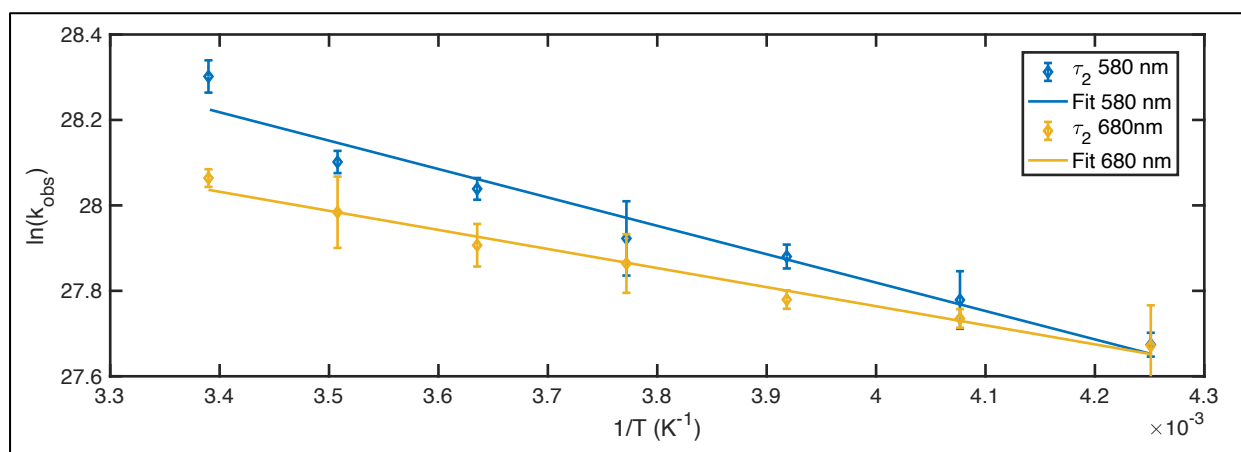


Figure 2.14: The Arrhenius plots for the long components of both probe regions. Different slopes likely indicate slightly different state contributions to the decay of each feature.

The frequency factors (FF) indicate the lifetime of the system in the absence of a barrier. Without a barrier to traverse, conversion between the reactant and product states would occur in one period of an oscillation of the nuclear coordinate.^{17,19} This means that when no barrier is present, nuclear motion drives conversion between electronic states occurs with 100% efficiency. The Born-Oppenheimer approximation relies on this concept to describe adiabatic movement on electronic potential energy surfaces, as the barriers between electronic configurations at nuclear coordinates Q and $Q + \Delta Q$ are zero thus approximating continuous evolution in Q . In the absence of a barrier, the electronic orthonormality between reactant and product wavefunctions will control the magnitude of this measured factor. This dictates the ‘allowedness’ of a transformation and is a measure of the type of conversion observed. It is therefore critical to compare the

frequency factors measured above with those observed previously for electronic transitions of known character.

Table 2.6: Arrhenius parameters measured for the two probe regions.

Probe Wavelength	580 nm	680 nm
E_a (cm ⁻¹)	462 (45)	310 (18)
A (x10 ¹² s ⁻¹)	17.3 (4.2)	6.82 (0.68)

This analysis has been done by our group previously for benchmark compounds. [Fe(bpy)₃]²⁺ for example has a measured frequency factor of 4.34x10⁹ s⁻¹ for its ~1 ns long component.¹⁷ This component represents the ⁵T₂→¹A₁ ground state recovery process and a spin-change of $\Delta S = 2$. This seems to be the proper order of magnitude for many pyridyl complexes that undergo this quintet to singlet transition.^{17,18} The values in table 4 are several orders of magnitude faster (~7x10¹² s⁻¹ and ~2x10¹³ s⁻¹) in the case of both the ESA and GSB features of **1**. This suggests that a $\Delta S=1$ process must at least occur. If the probe at 680 nm represents the observed decay without the influence of the ³MC state, it represents the FF of the ³MLCT→³MC process a spin allowed pathway.

The Arrhenius plots are linear consistent with only one measurable barrier for each probe region. The measured activation energies for the GSB and the ESA are 462±45 cm⁻¹ and 310±18 cm⁻¹ respectively. Like its frequency factor, the measured barrier for the ESA is for the ³MLCT→³MC process. Implicit in the barrier for the GSB region is the barrier which is traversed for the ³MC→GS process. While these cannot be separated it is consistent with a more temperature sensitive process which depends upon the two non-radiative processes in the last term of equation 2.14.

2.3.7 Application of the Marcus Equation

The measured Arrhenius parameters can be used to calculate the Marcus parameters alluded to in the introduction. Separate measurement of the driving force is typically utilized or calculated. As there is no information about the ZPE of the $^3\text{MLCT}$ and thus the driving force between the $^3\text{MLCT}$ and ^3MC state cannot be calculated. This means the Marcus parameters cannot be derived explicitly.

It is possible to parametrically calculate λ and H_{ab} from a range of possible ΔG values that could reasonably represent the energy gap between the $^3\text{MLCT}$ and ^3MC . As the excitation into the MLCT occurs around $20,000\text{ cm}^{-1}$, the driving force must lie between this and $7,100\text{ cm}^{-1}$ which is the calculated ^3MC energy. The large boundary of this range $12,900\text{ cm}^{-1}$ which corresponds to the situation in which the $^3\text{MLCT}$ energy is equal to the excitation energy (this is not the case but is included for completeness). The small boundary is 0, which corresponds to a condition in which the two excited states are degenerate.

The range of ΔG and the measured Arrhenius parameters ($E_a = 310\text{ cm}^{-1}$ and $A = 6.82 \times 10^{12}\text{ s}^{-1}$) and equations 2.7 and 2.8, a set of reorganization energies and coupling constants can be created which are depicted in figure 2.15. Improved specificity can be achieved by considering recent studies of Co(III) polypyridyls. These have demonstrated that GSR occurs out of ^3MC states located in the Marcus inverted region. VT-TA measurements have found the reorganization energy of the $^3\text{MC} \rightarrow ^1\text{GS}$ process to be around $5,500\text{ cm}^{-1}$. This is in very good agreement with the Dushinsky derived reorganization energy of **1** of around $5,200\text{ cm}^{-1}$. Making the common assumption that the MLCT and GS manifolds are sufficiently nested, this number for GSR can be taken as the reorganization energy of $^3\text{MLCT} \rightarrow ^3\text{MC}$ process as well.

In figure 2.15 illustrates that when $\lambda = 5,500 \text{ cm}^{-1}$ the driving force is just under 8,000 cm^{-1} . This value pair implies the process is in the Marcus normal region, however, the curve derived from the Arrhenius parameters, ensures that nearly all possible ordered pairs would belong to the inverted region. This driving force yields an electronic coupling of over 140 cm^{-1} . Compare this for the process of ground state recovery in $[\text{Fe}(\text{bpy})_3]^{2+}$ of about 4 cm^{-1} .¹⁷ The larger values the larger value is expected for the spin-allowed transition of the $^3\text{MLCT} \rightarrow ^3\text{MC}$.

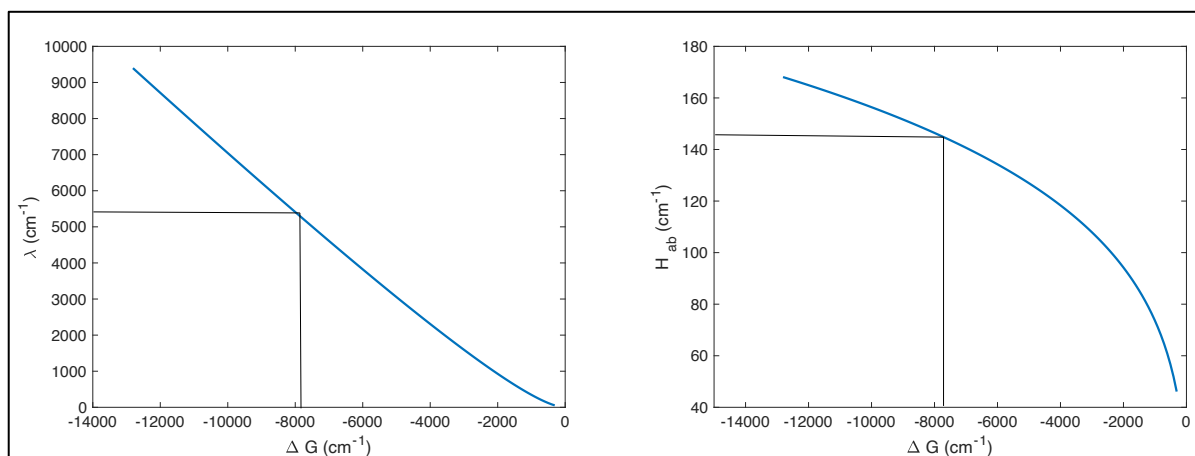


Figure 2.15: Marcus parameters from for the $^3\text{MLCT} \rightarrow ^3\text{MC}$ process as a function of driving force and the measured Arrhenius parameters. (left) Reorganization energy calculated from a set of reasonable driving forces. A driving force of just under 8,000 cm^{-1} is found by assuming $\lambda = 5,500 \text{ cm}^{-1}$. The activation energy of 310 cm^{-1} ensures that nearly the entire range is in the Marcus inverted region. (right) Electronic coupling element calculated from a set of reasonable driving forces and $A = 6.8 \times 10^{12} \text{ s}^{-1}$. The driving force approximated in the left panel gives $H_{ab} \sim 145 \text{ cm}^{-1}$.

2.3.8 Mechanism Summary

In the last four sections, data was presented that suggests the participation of a short-lived ligand field state likely deactivates the state responsible for the absorption feature past 650 nm. The presence of an excited state absorption is a signature of MLCT character. The preliminary XES data however does not indicate exclusive participation of a spin-doublet associated with such an excited state. While this doesn't exclude MLCT participation alternative explanations for this spectral feature may be useful. Furthermore, assuming the XES and TA spectral assignments

are correct, prompt formation ^3MC (~ 250 fs) could indeed occur within the data at hand. In the introduction, it was noted that a population branch occurs in the evolution of a vibrationally hot MLCT manifold in similar carbene complexes among other Fe(II) complexes.³³ A portion of that population relaxes to a cool MLCT state, and the remainder fast conversion into a ^3MC state on a timescale of a similar order to that observed in this work for the short component (~ 100 fs). These non-equilibrium dynamics are expected to be temperature independent. This study does not rule the possibility of this process out. If this is indeed the case, the non-equilibrium dynamics branch to form two kinetic channels: a thermalized pathway and a non-thermalized pathway. This explanation allows for both a prompt ^3MC formation and the observed temperature dependence of the transient absorption spectra along with the temperature independent normalized amplitudes. This model would mean that the temperature dependent dynamics discussed in the last sections occur during the deactivation of the vibrationally cool $^3\text{MLCT}$ state, which is facilitated by the lower lying ^3MC state. This branching mechanism changes the global kinetic model, however the set of differential equations which describe the thermalized pathway should not change, as the state S could represent any state with a radical anion absorption. Thus, the non-equilibrium dynamics and the steady-state approximation made previously is still valid, given the different magnitudes of the time constants for each process. A potential mechanism is illustrated in figure 2.16 and is discussed in further detail below.

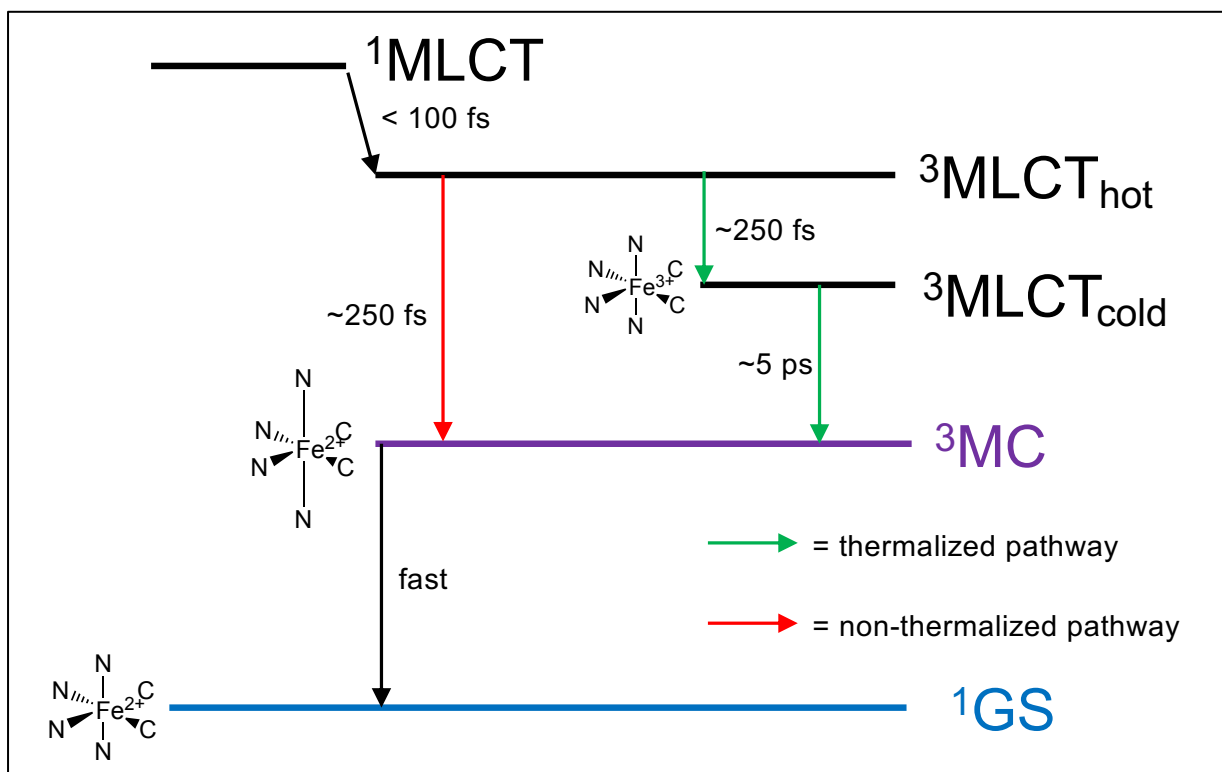


Figure 2.16: A Jablonski-like diagram illustrating a possible decay mechanism in **1**. This figure highlights the two decay channels: the thermalized pathway and non-thermalized pathway. The thermalized pathway was examined using VT-TA and established the presence of some lower lying triplet state.

2.3.9 An analysis of possible decay channel 1: non-thermalized pathway

Much of this report has examined the thermalized pathway. Discussing some basic parameters of the non-thermalized pathway should be done even if such a pathway is not definitively established. The process of $\text{hot-}^3\text{MLCT} \rightarrow ^3\text{MC}$ is likely a strongly coupled vibronic process, which has a high probability of population transfer in any given vibrational period. In the case of injection into a semiconductor for example, delocalization of the excited state wavefunction is so severe that its electron is now deemed to belong to a separate species. In a similar way, strong coupling between the MLCT and the ligand field can be illustrated by considering the orbital partitioning of the populated orbitals. The electronic structure then provides some insight into the nature of electronic coupling between states and species when the order of symmetry of the system overall changes.

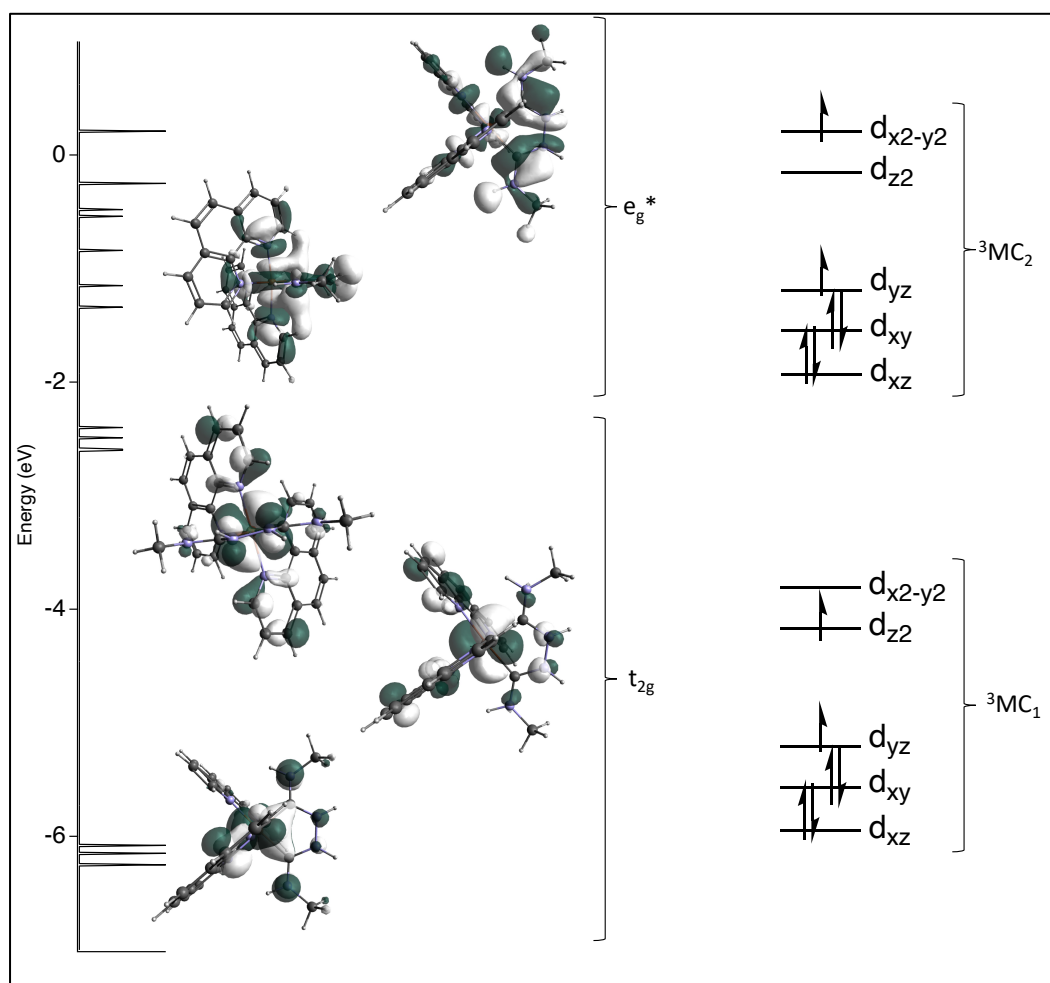


Figure 2.17: Broken symmetry of the system lends itself to a highly non-degenerate ligand field manifold. (left) Ligand field molecular orbitals calculated with B3LYP functional. The sticks on the energy axis are elongated when the MO is represented. From the top, orbitals are in descending order of energy. There are clearly π -bonding interactions that stabilize the lowest energy MO. The highest energy orbital clearly shows the anti-bonding character and nodal structure of the orbital of $d_{x^2-y^2}$ origin. (right) Electron configurations of two possible triplet states both of which are expected to undergo a JT distortion. They are labeled 3MC_2 and 3MC_1 in descending order.

The electronic structure of the ligand field-based orbitals given in ground state is shown in figure 2.17. The electronic degeneracies associated with d^6 octahedral complexes are gone, a result of the broken symmetry of the ligand framework. This is clearly due to the π functionality of the carbene ligand itself. MO1 shows a π bonding effect that stabilizes the orbital of appropriate symmetry to a significant degree. Likewise, a π anti-bonding effect destabilizes the orbital of appropriate symmetry. A non-bonding interaction splits the difference and acts like a

Barycenter. Compare this broken degeneracy to that found for the LF orbitals of $[\text{Fe}(\text{phen})_3]^{2+}$ in the appendix to this chapter, which is minimal and can likely be easily described by assuming pseudooctahedrality. The antibonding orbitals of σ -symmetry are even less degenerate. The highest in energy is the $d_{x^2-y^2}$ orbital, which shows a lot of ligand contribution but definitively represents an M-L antibonding interaction. The d_{z^2} orbital is lower in energy and does appear to be stabilized by a bonding interaction with the phenanthroline ligand. When considering excited configurations of the e_g^* orbital sets, the difference in energy suggests the need to distinguish between the two. The configuration when $d_{x^2-y^2}$ is occupied will be called ${}^3\text{MC}_2$ and the configuration when d_{z^2} is occupied will be called ${}^3\text{MC}_1$. The electron configurations of the LF are given on the right-hand side of figure 2.17. From optimized DFT structures, the ${}^3\text{MC}_1$ state is found to be the lowest energy excited state.

Transitions arising from this ground state configuration were found from natural transition orbitals (NTOs) generated from TD-DFT calculations. The calculated absorption spectrum is overlain with the absorption spectrum in figure 2.18. The two bunches of sticks represent the two broad absorption bands seen in the experimental spectrum, which are in reasonable agreement in that they are within 0.5 eV. Natural transition orbitals were calculated

for the 8 transitions of lowest intensity. The inset shows particle and hole orbitals of the 7th calculated transition.

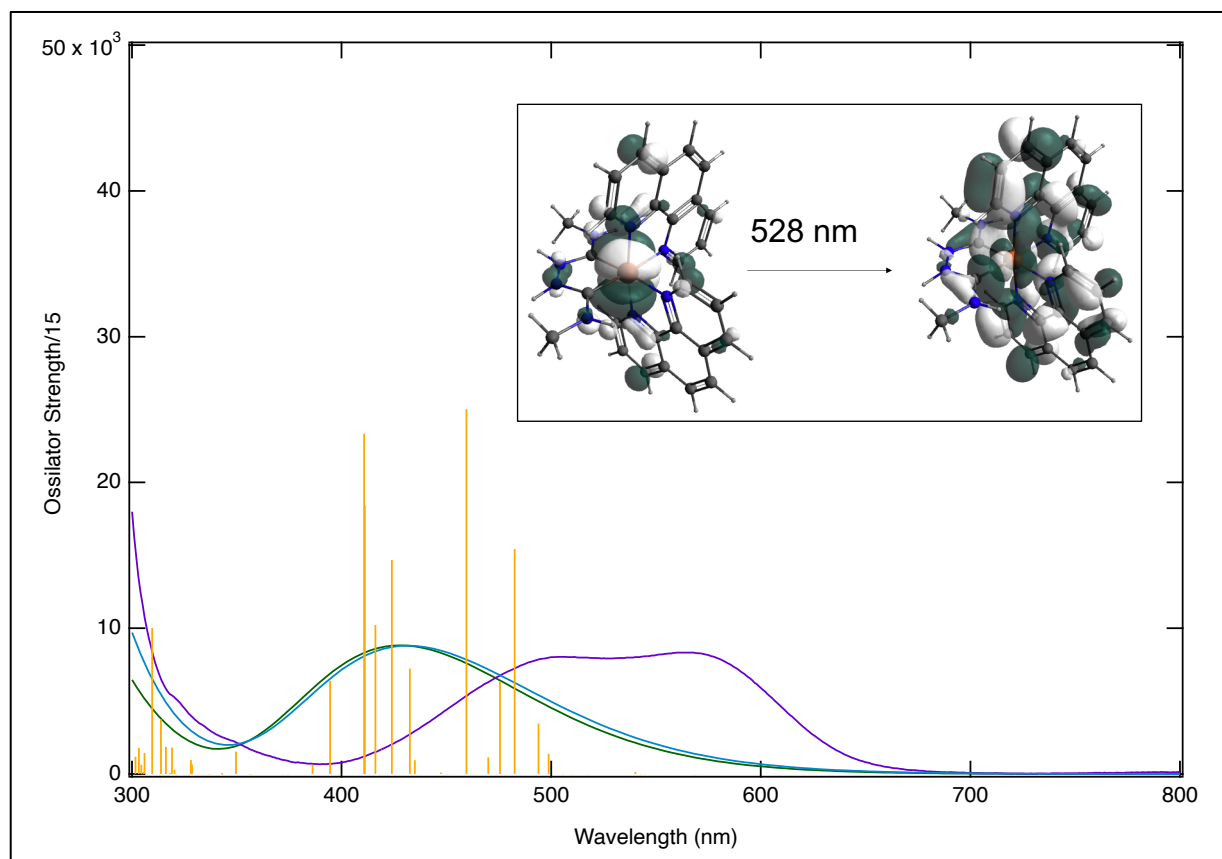


Figure 2.18: Calculated UV-Vis spectra from both B3LYP (cyan) and the associated transitions (scaled by 15) and BLYP* (green). They are overlaid on the empirical absorption spectrum in methanol. (inset) Natural transition orbital number 7 which includes significant metal character along with its delocalization along the phenanthroline ligands. The red sticks represent relevant transitions that have a calculated oscillator strength of zero. Their absolute intensity is arbitrary.

While other transitions are easily assignable as d-d or MLCT in nature. Transition 7 shows the movement of a localized metal-based orbital (of π symmetry) in the ground state to a very delocalized excited state with a transition energy of 528 nm. This ending state has the phen character of an MLCT, but unmistakably has the σ^* anti-bonding character of a state that could be described by 3MC_2 . It is not hard to image a state with such an orbital configuration facilitating deactivation of the MLCT manifold due to the similarity in orbital composition and the resultant magnitude of the off-diagonal coupling elements. Or at the very

least, give a ^3MC excited state which has strongly allowed $\pi\pi^*$ transitions on the ligand. This ambiguity is also seen in NTO 8 to some degree. This increased electronic coupling could facilitate the fast transfer associated with the non-thermalized pathway.

Along with the electronic coupling, vibrational aspects likely play a critical role in the non-thermalized pathway. This is common for species that expect a (pseudo) Jahn-Teller Effect ((p)JTE), a likely driver of the non-radiative decay of Cu(I) polypyridyls. Something like this must occur in the triplet LF manifold in this complex: an illustration of this is the axial bond distortion of the lowest energy triplet state *vide supra*. This distortion likely attenuates the strength of a given carbene ligand, by providing a ‘pressure release valve’ through which the energy of the system can be minimized.

This is likely not unique to **1**, but is likely a feature of carbene complexes of Fe(II). Thus, as triplet states are found to be the lowest energy excited states in these systems, design principles tailored to the features of these states must be devised. The entatic strategy discussed in the introduction of this dissertation could be applied to these types of systems. This would take the form of joining the carbene and pyridyl ligands to increase rigidity: specifically, along the axial Fe-N bond. Illustrated in figure 2.9. The reduced magnitude along the distortion of this coordinate would favor a decrease in non-radiative decay. Furthermore, this should raise the energy of the $^3\text{MC}_1$ excited state, minimizing the degree that ‘pressure release’ of the JT distortion provides. While not cited explicitly, this is likely the reason for the emissive complex of Berkefeld and coworkers.³⁴

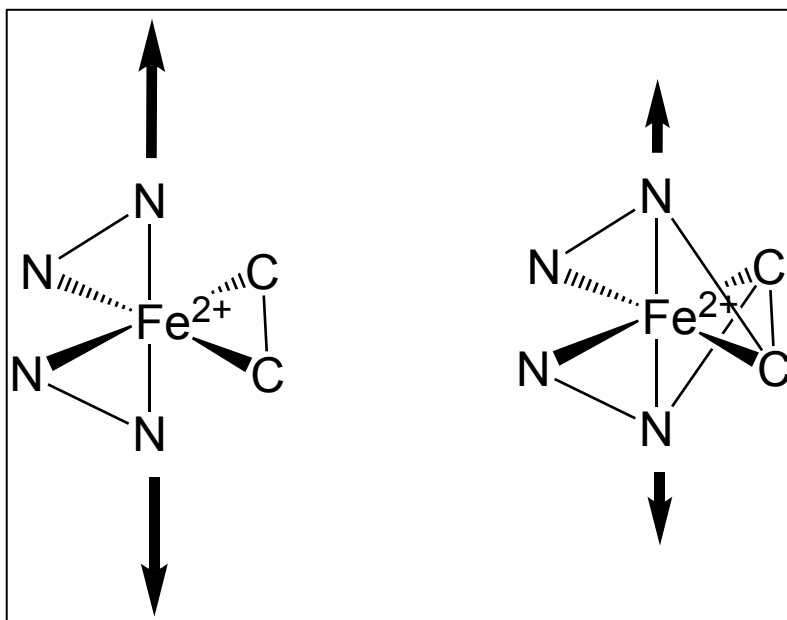


Figure 2.19: Illustration of the DOF a which could be leveraged to incorporate the entatic strategy into the next generation ligand design.

2.4 CONCLUSIONS AND FUTURE WORKS

In this chapter we have computationally determined the lowest energy excited state is a ^3MC . The assignment of the ^3MC state agrees with preliminary XES measurements which show that participation of this state begins promptly. The lack of quintet character as the dominant deactivation feature suggests we have pushed past the triplet/quintet crossing point on the Tanabe-Sugano diagram for the d^6 pseudo-octahedral ligand field. This is quite remarkable in that, a single ligand has destabilized ^3MC past that of the hexacarbene complex $[\text{Fe}(\text{btz})_3]^{2+}$ (6700 cm^{-1} vs. 7200 cm^{-1}).²⁹ It was found using VT-TA that the bleach and absorption features of the transient spectrum have different temperature dependencies. This probe dependence illustrates confirms the participation of a second, non-absorbing state in the decay of the MLCT manifold. A partial Marcus analysis was performed on Arrhenius data measured for the ESA region where a possible range of driving forces were used to calculate a range of reorganization energies and coupling constants. Along with the prompt formation of the ^3MC signal in XES, a

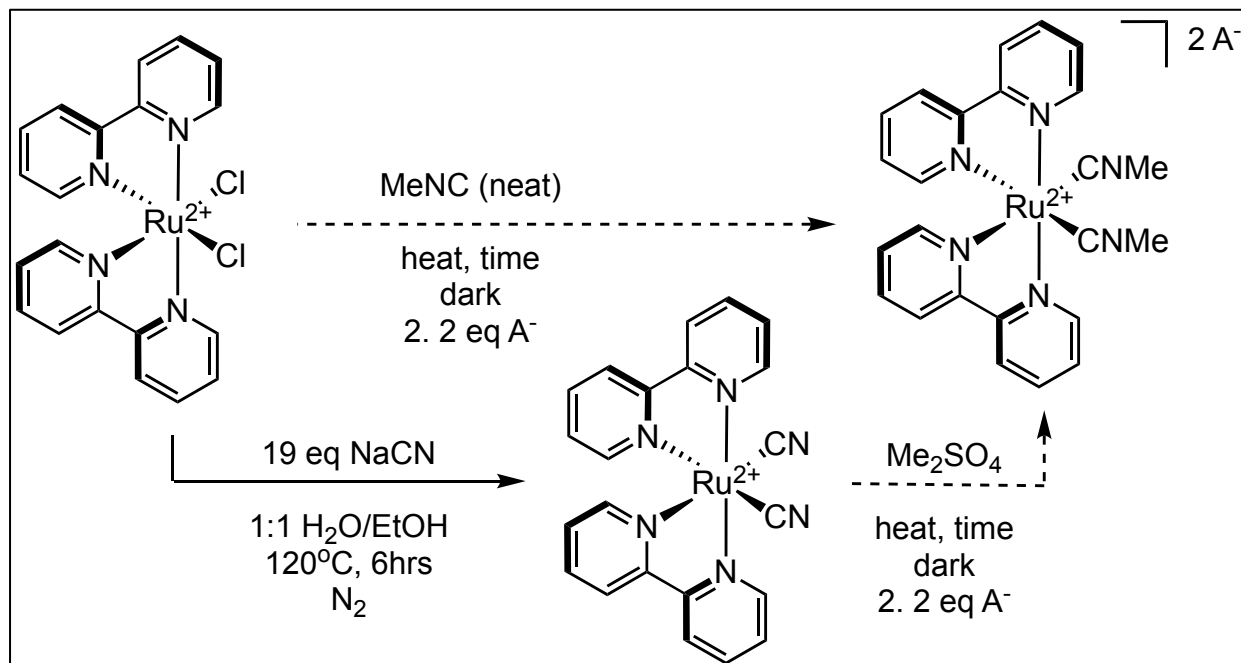
mechanism was proposed with two channels, a thermalized pathway, which involves the states examined by VT-TA, and a non-thermalized pathway or the prompt formation of a ^3MC state.

Several things are needed to tighten the analysis. First, the radical anion absorption should be definitively assigned as belonging to a CT state. XES data is not conclusive to confirm this. TD-DFT calculations can be performed on the ^3MC state to verify the nature of possible transitions, which may have strong $\pi\pi^*$ character. Another step is finding the ZPE of the $^3\text{MLCT}$. Calculations are currently underway for this and would help in performing a full Marcus analysis. Even better would be the synthesis of a Ru(II) version of **1** which would help shed light on the energetics of the MLCT states in these systems, as it can be assumed that ground state recovery process involves an emissive $^3\text{MLCT}$ (which is the case in similar species). The energy could be measured from emission fitting by well-known procedures.³⁵ Furthermore, the reorganization energy of this Ru(II) species could be measured by variable temperature emission spectroscopy using methods like those described in chapter 6 of this dissertation.

The synthesis of a Ru(II) carbene complex could be performed as illustrated in scheme 2.5. The cyanation is based on modified literature procedures, however the desired product could not be isolated.³⁶ No further optimization was performed. This cyanated derivative could then undergo the methylation step to form the *bis*-isocyanide whereupon it could be reacted to form the desired carbene with hydrazine. A more direct route however would be by isocyanation, which may leverage the insolubility of alkali metal chloride salts in organic solvents to drive product formation.

Future studies that could leverage this work could be the observation of the dynamics of **1** in a glass. The large geometric changes, induced by the JT distortion could be frozen out and thus made unfavorable, using a similar concept as the ligand design in the previous section. This

may tune the dynamics of the two proposed pathways and perhaps the change the normalized fitting amplitudes relative to those found in fluid solution. A full analysis of the XES and XSS data would be helpful for a more detailed assignment of the dynamics. Chapter 4 of this work highlights a homologous series to **1**, that have aryl functionalities and changes in the carbene backbone structure.



Scheme 2.4: Proposed route to an equivalent Ru(II) carbene species. Cyanation was attempted but unsuccessful. The cyanation path is from reference 36.

This work lays the foundation for future ligand structures that incorporate all aspects of the design principles laid out in the introduction, while keeping an eye on modularity and orthogonalization of the processes and parameters required for a well-performing photosensitizer.

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APPENDIX

2.6.1 Computations

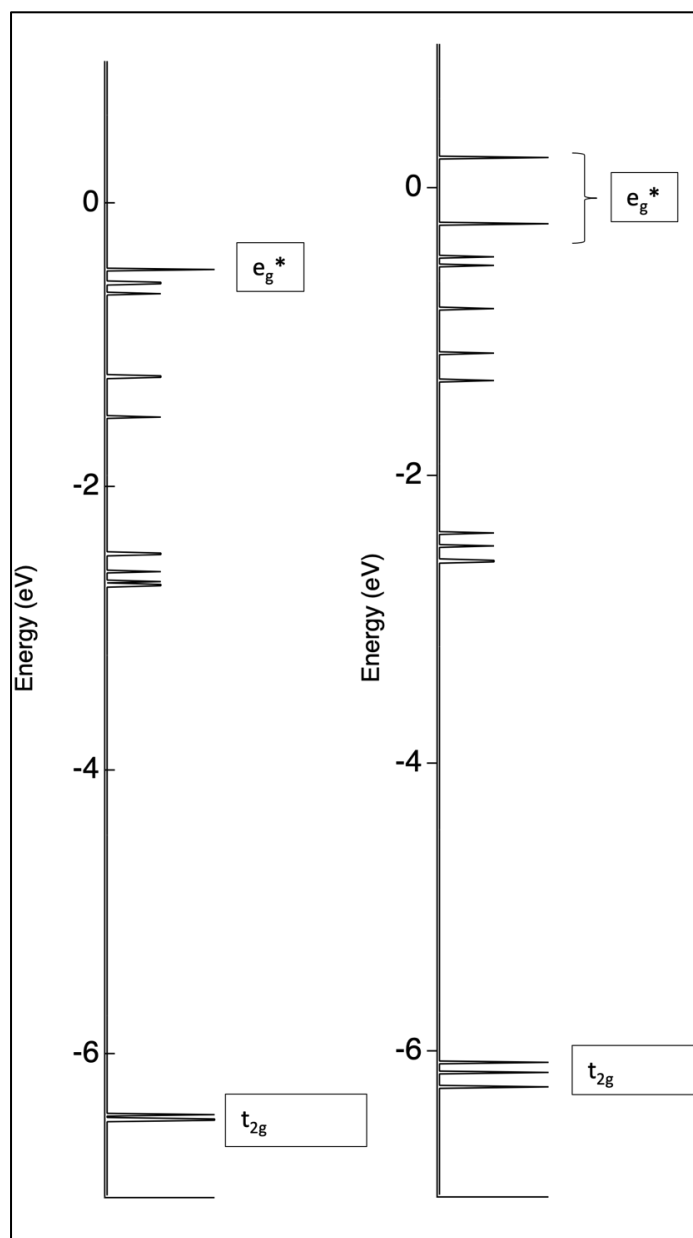


Figure S2.20: Orbital energies of (left) $[\text{Fe}(\text{phen})_3]^{2+}$ and (right) **1**. Showing that symmetry breaking is energetically important and must be considered in analyses of the electronic structure.

Table S2.7: First 8 natural transition orbitals in ascending order of their transition energies.

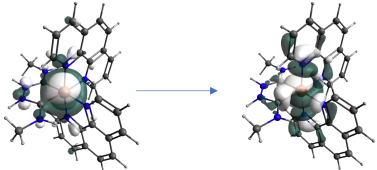
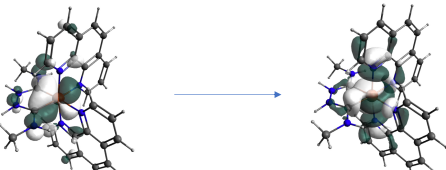
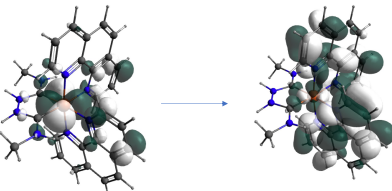
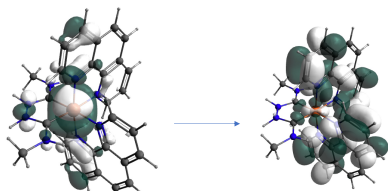
NTO	Sum of Contributions	Contributions	Asg.	E (eV/c m ⁻¹)
1		136 ->139 0.11833 136 ->147 0.54016 136 ->150 -0.14515 137 ->147 0.37070 136 <-147 0.11542	³ MC ₁	1.5150 /12219
2		135 ->139 0.10883 135 ->147 0.63575 135 ->150 -0.16615 136 ->148 0.14667 135 <-147 0.11411	³ MC ₂	1.7934 /14465
3		133 ->147 0.11031 136 ->139 -0.10527 136 ->147 -0.34691 137 ->139 0.19952 137 ->147 0.51877 137 ->150 -0.13788	³ MC ₃	1.8184 /14666
4		135 ->147 -0.10238 137 ->138 -0.23437 137 ->144 0.15178 137 ->148 0.60175 137 ->152 0.11722	³ MC ₄	2.0944 /16892
5		136 ->139 -0.26275 136 ->147 0.10750 137 ->139 0.59016 137 ->147 -0.19792	³ MLCT ₁	2.2205 /17909
6		135 ->138 -0.21651 136 ->139 0.51520 136 ->140 0.24800 136 ->147 -0.12772 137 ->139 0.25352	³ MLCT ₂	2.3339 /18824

Table S2.7 (cont'd)

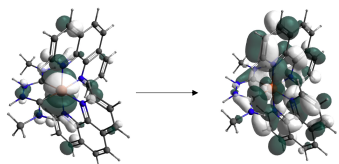
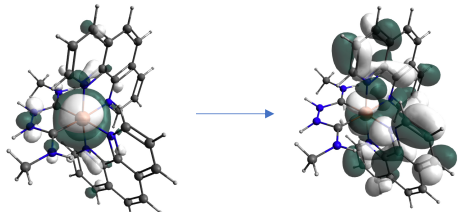
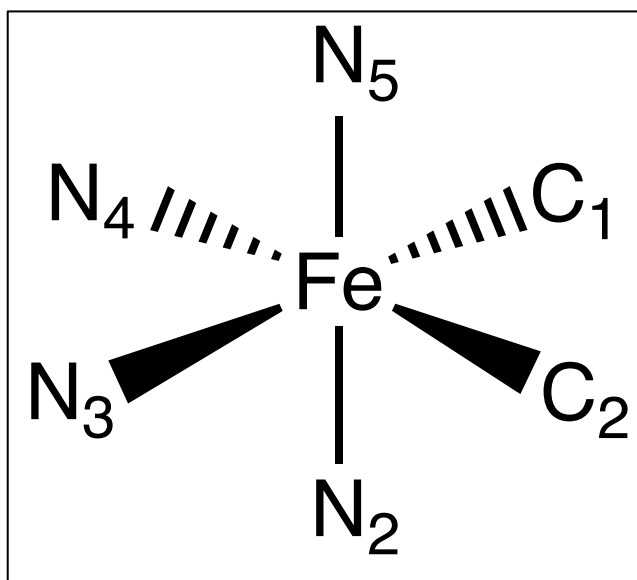
7		135 ->139 -0.19049 135 ->147 0.15898 136 ->138 0.45952 136 ->148 -0.39411 137 ->138 -0.10732	$^3\text{MLCT}_3$	2.3466 /18927
8		136 ->139 0.41472 136 ->147 0.37452 137 ->139 0.31622 137 ->147 0.18976	$^1\text{MLCT}_1$	2.3502 /18956

Table S2.8: Computed bond lengths of the ground state compared to crystal structure.

^aOptimized from the crystal structure z-matrix input. ^bNo empirical dispersion included.

Bonds (Å)	X-Ray ⁷	Vac B3LYP ^a	<u>B3LYP</u>	B3LYP ^a	BLYP-15	PBEO ^b
Fe-C ₁	1.917	1.949	1.946	1.947	1.957	1.938
Fe-C ₂	1.916	1.949	1.946	1.948	1.957	1.938
Fe-N ₃	2.012	2.045	2.048	2.040	2.056	2.032
Fe-N ₄	2.024	2.045	2.047	2.040	2.056	2.032
Fe-N ₂	1.97	2.017	2.012	2.004	2.017	1.992
Fe-N ₅	1.969	2.017	2.012	2.004	2.017	1.992



2.6.2 Time-Resolved Spectroscopy

Kinetic Decay Traces 580 nm:

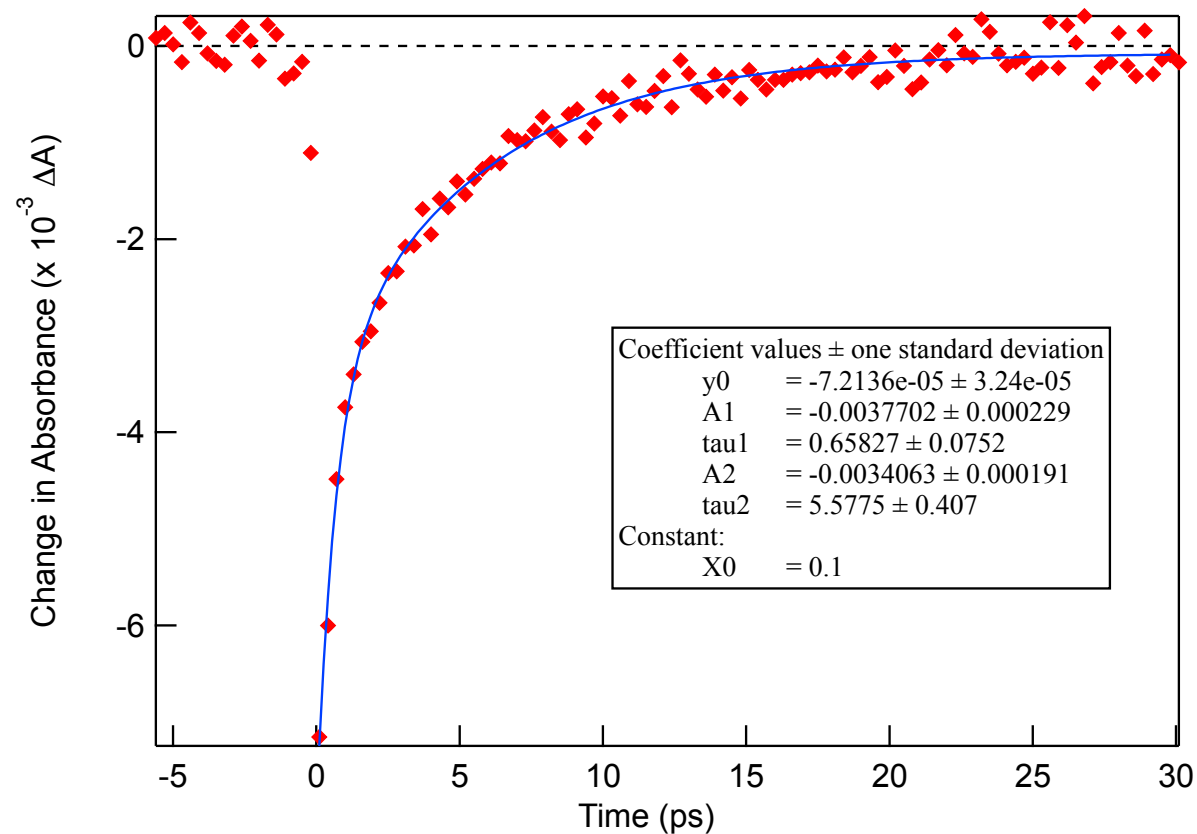


Figure S2.21: Kinetic trace of **1** in methanol. Exemplary 580 nm probe at 285 K.

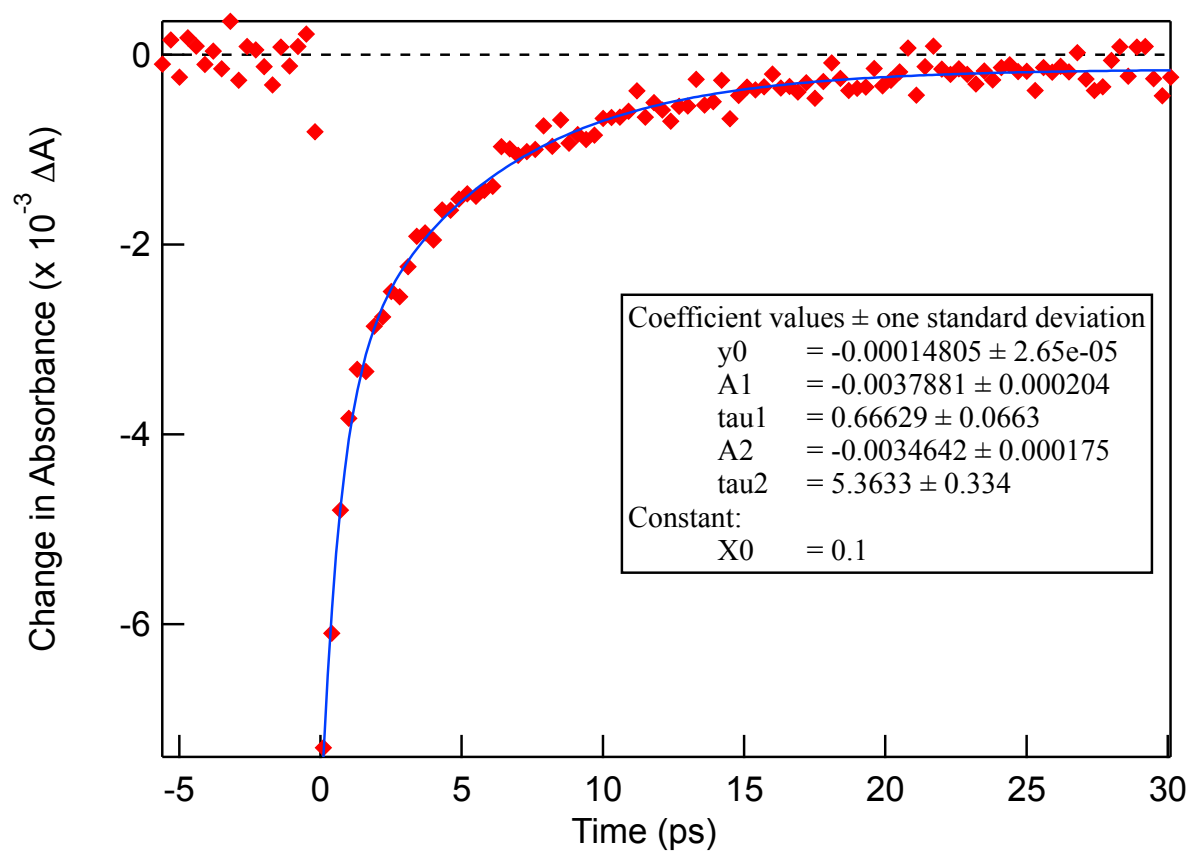


Figure S2.22: Kinetic trace of **1** in methanol. Exemplary 580 nm probe at 275K.

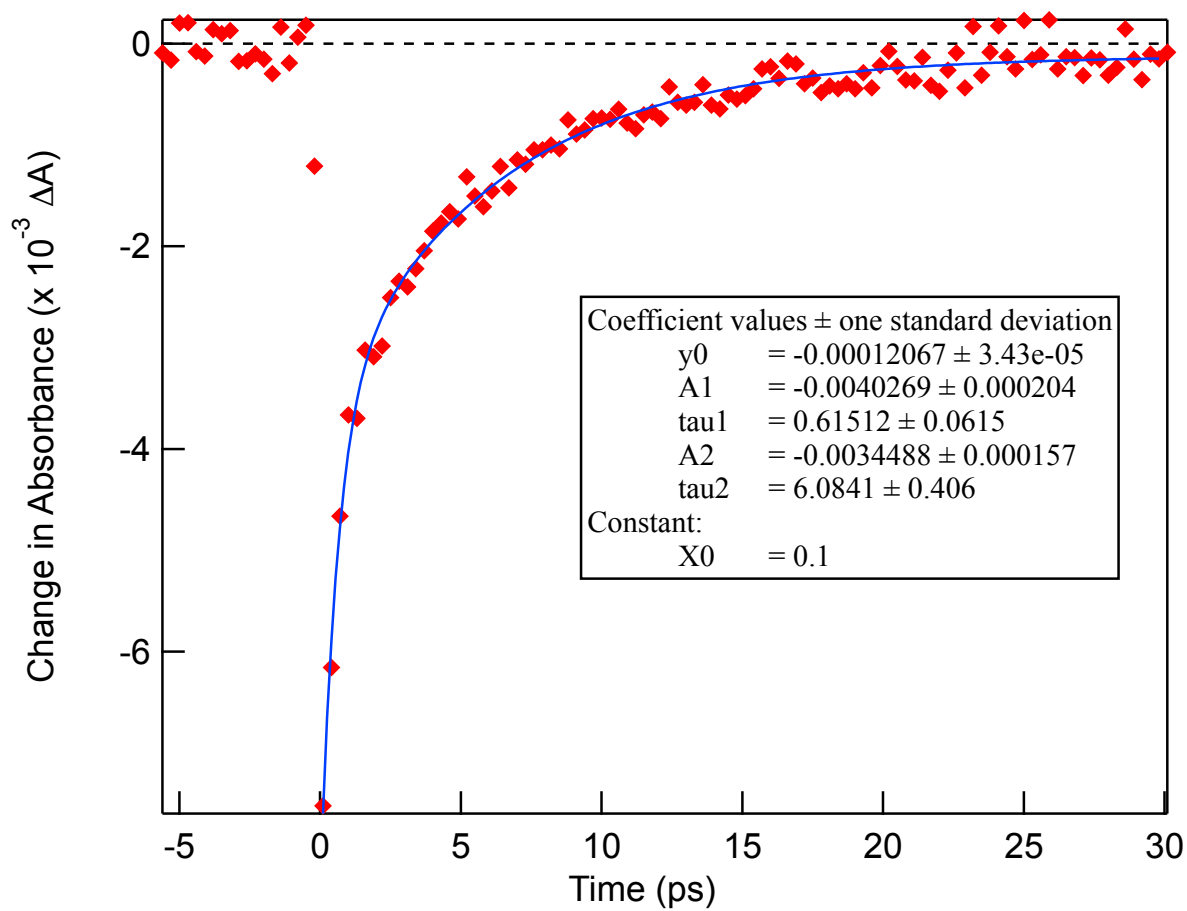


Figure S2.23: Kinetic trace of **1** in methanol. Exemplary 580 nm probe at 265K.

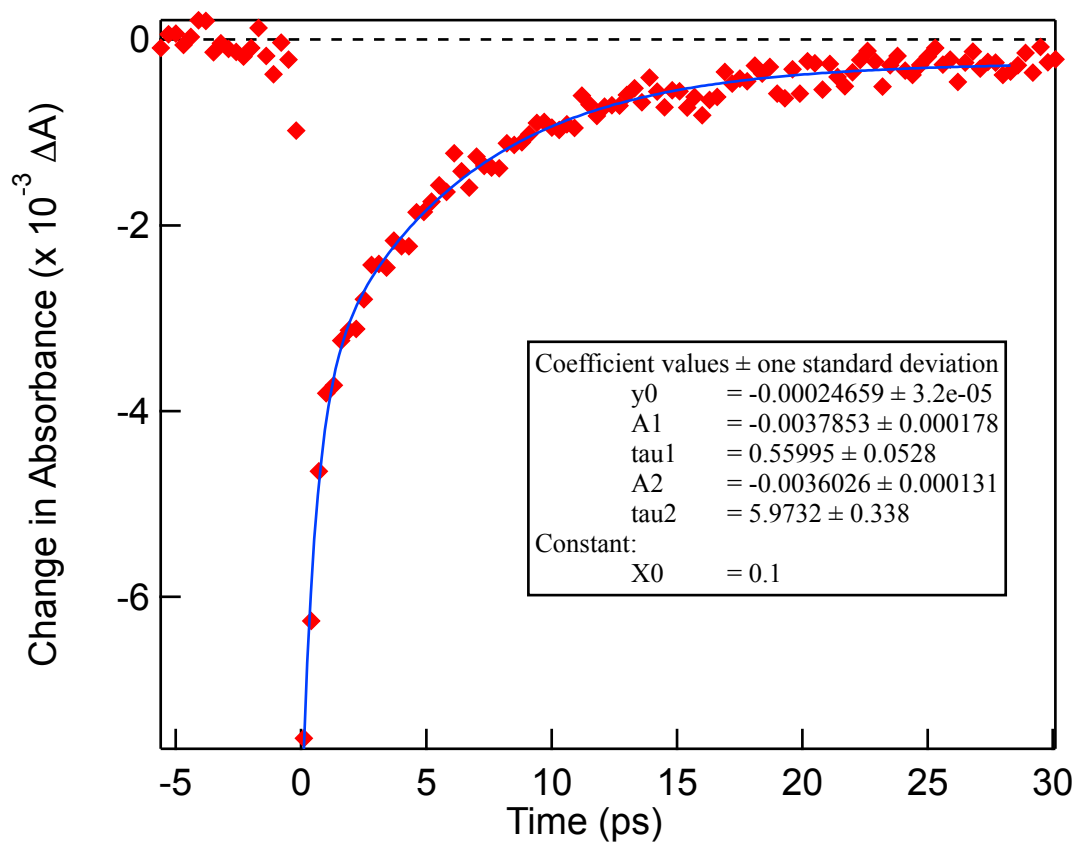


Figure S2.24: Kinetic trace of **1** in methanol. Exemplary 580 nm probe at 255K.

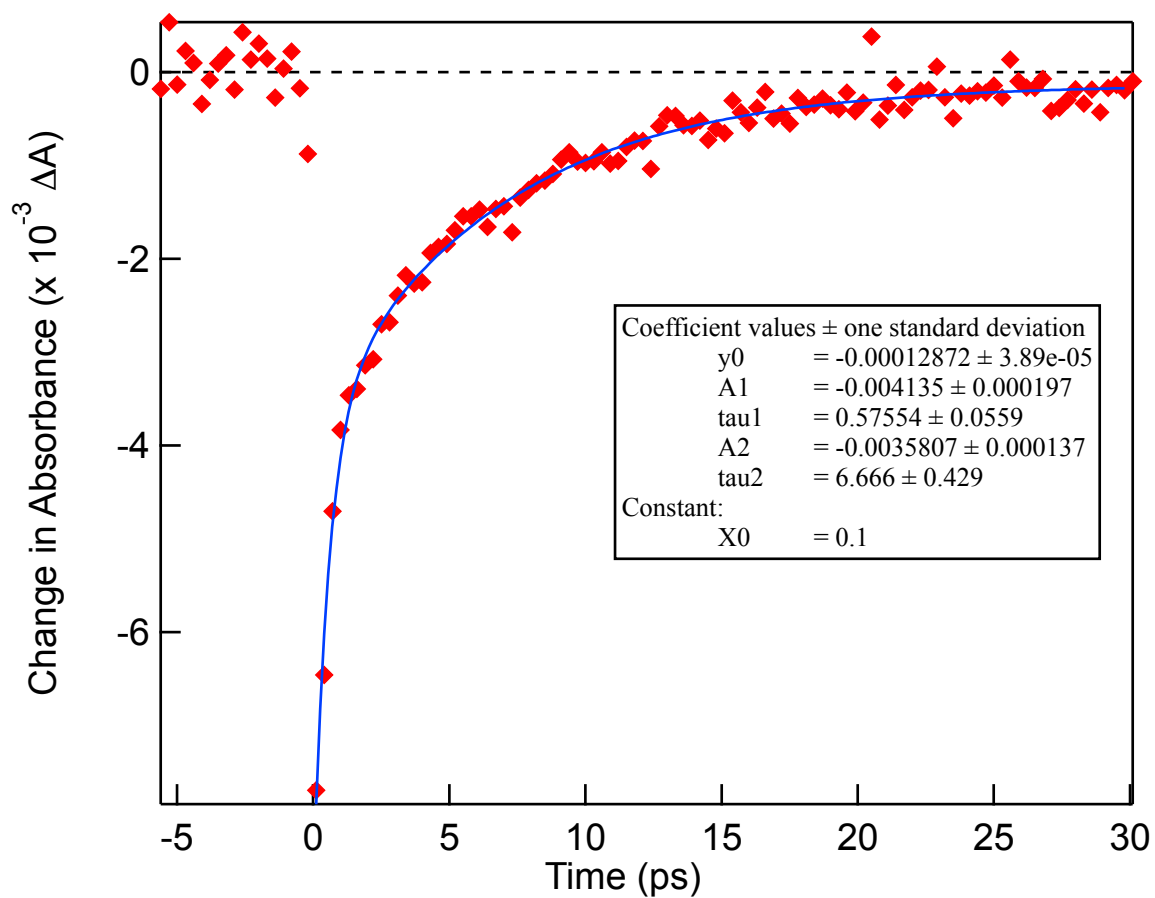


Figure S2.25: Kinetic trace of **1** in methanol. Exemplary 580 nm probe at 245K.

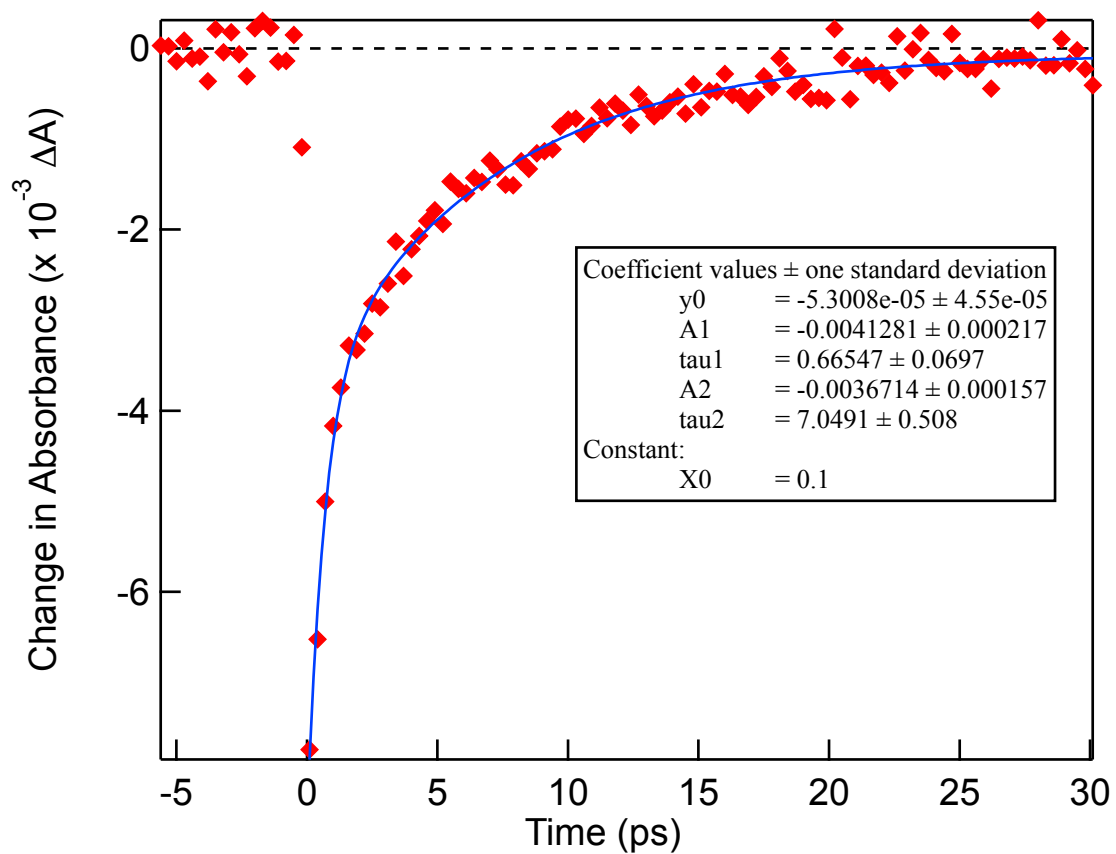


Figure S2.26: Kinetic trace of **1** in methanol. Exemplary 580 nm probe at 235K.

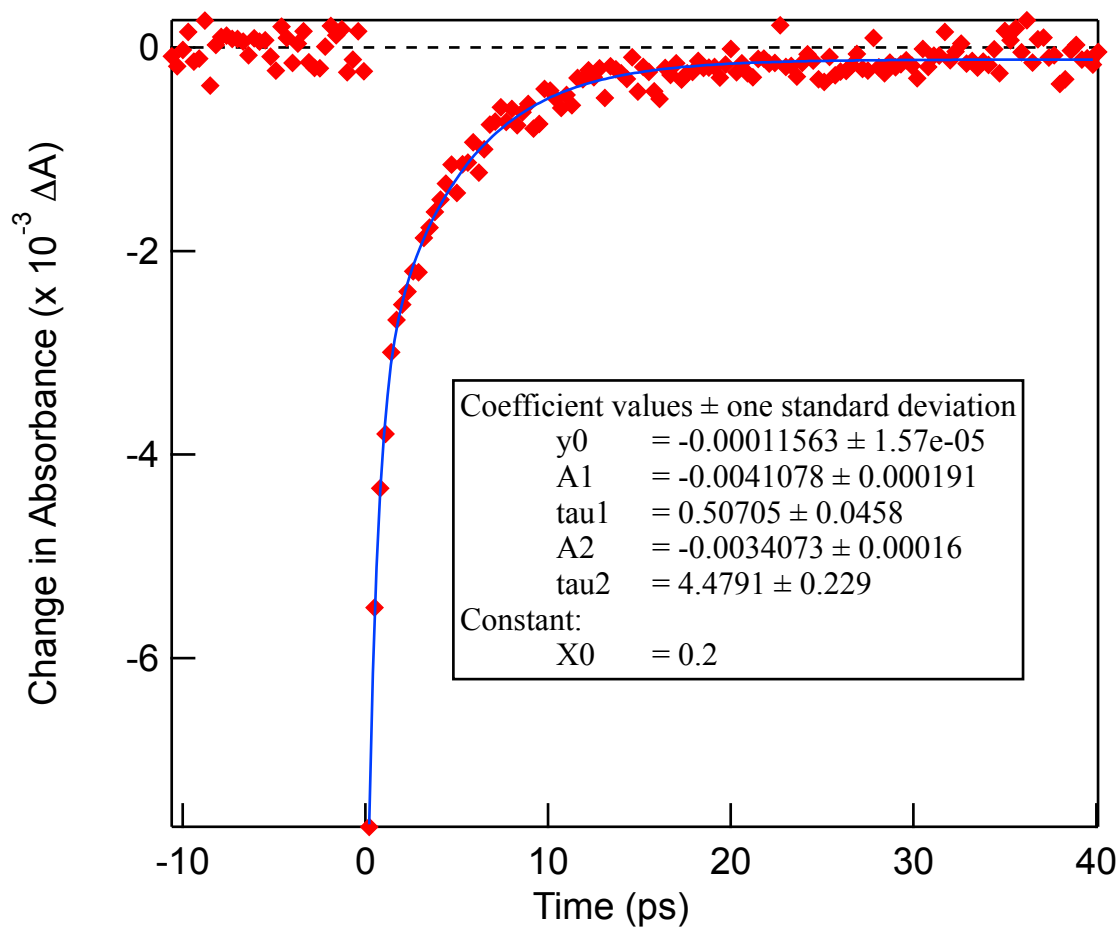


Figure S2.27: Kinetic trace of **1** in methanol. Exemplary 580 nm probe at 295K.

Kinetic decay traces 680 nm

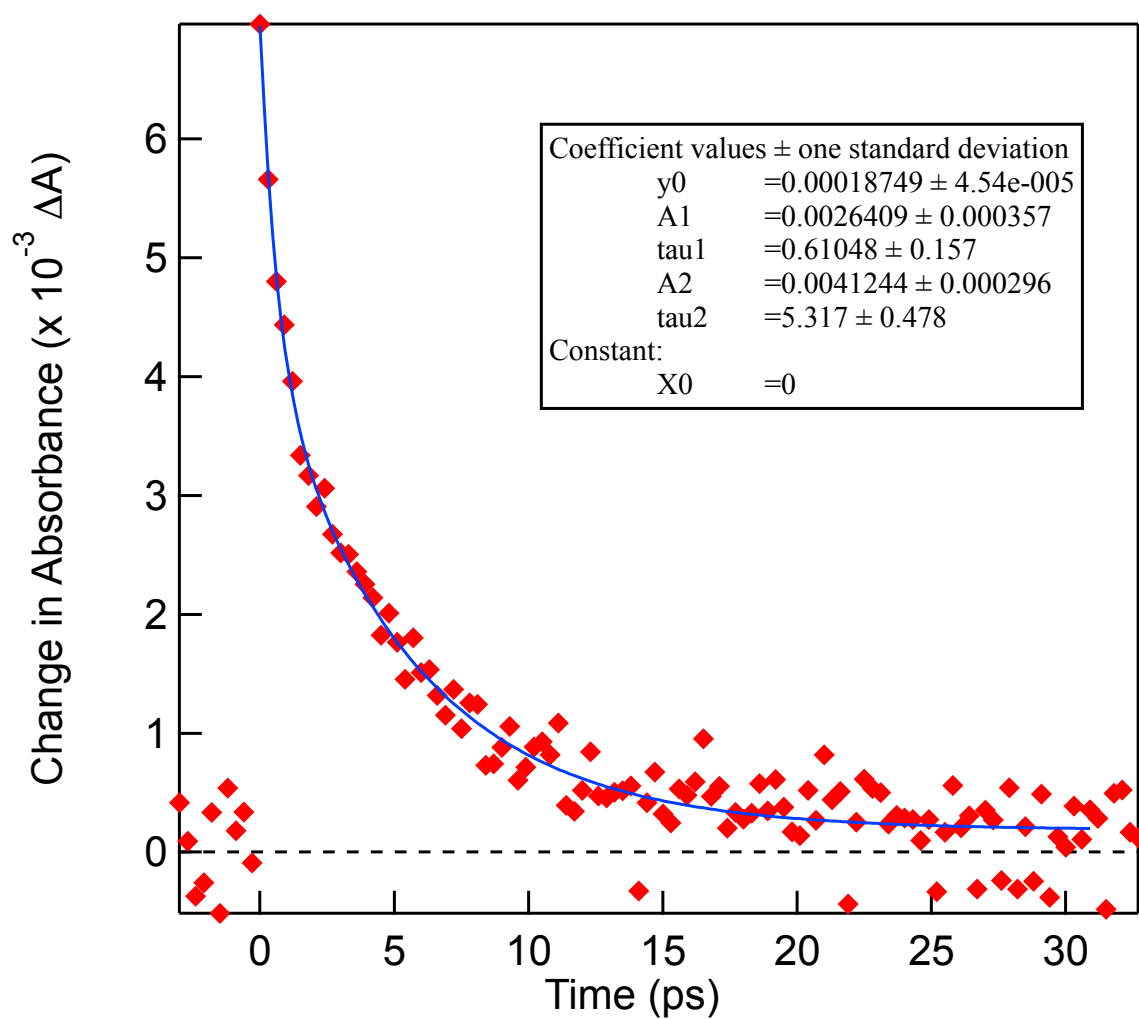


Figure S2.28: Kinetic trace of **1** in methanol. Exemplary 680 nm probe at 295K.

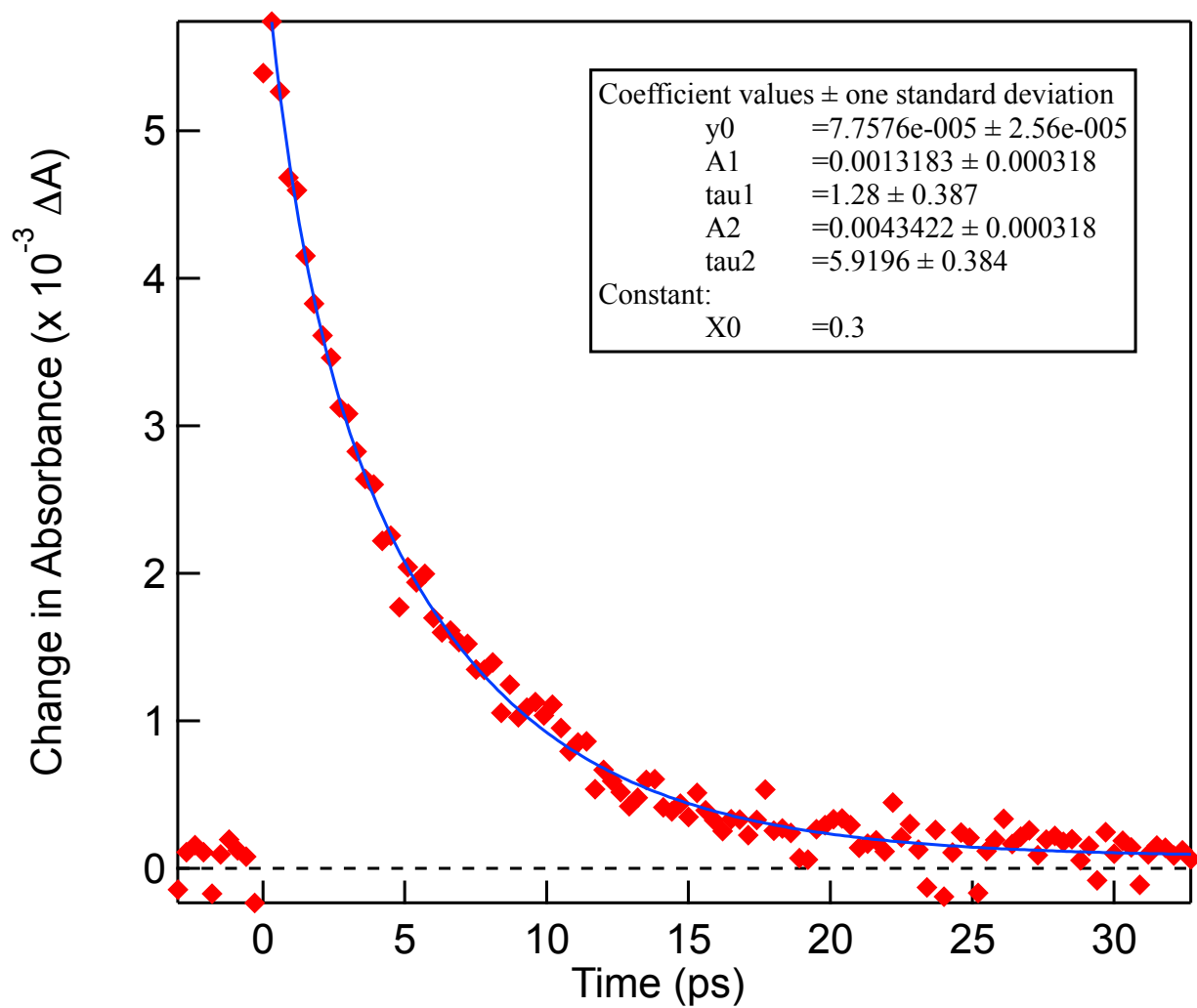


Figure S2.29: Kinetic trace of **1** in methanol. Exemplary 680 nm probe at 285K.

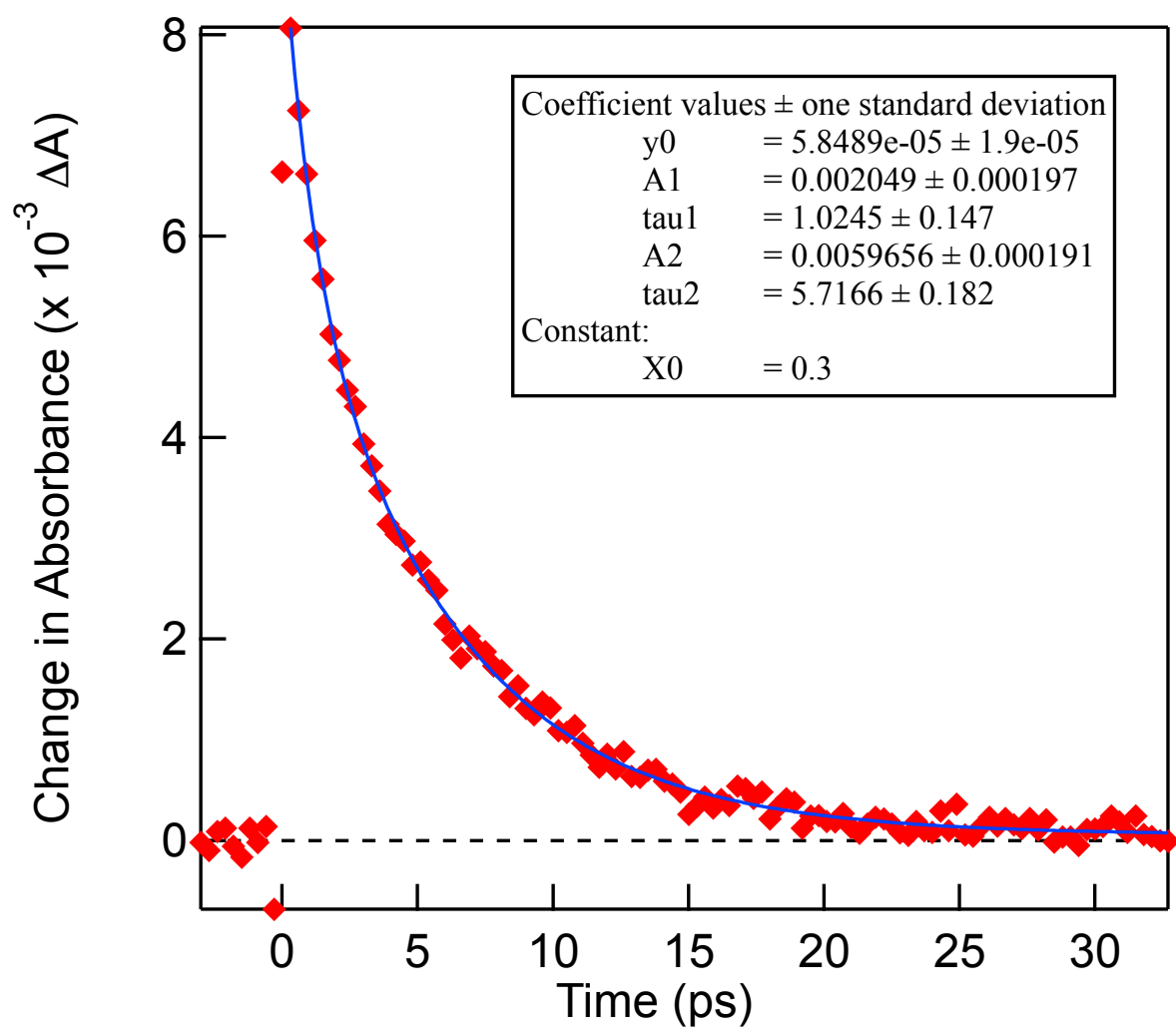


Figure S2.30: Kinetic trace of **1** in methanol. Exemplary 680 nm probe at 275K.

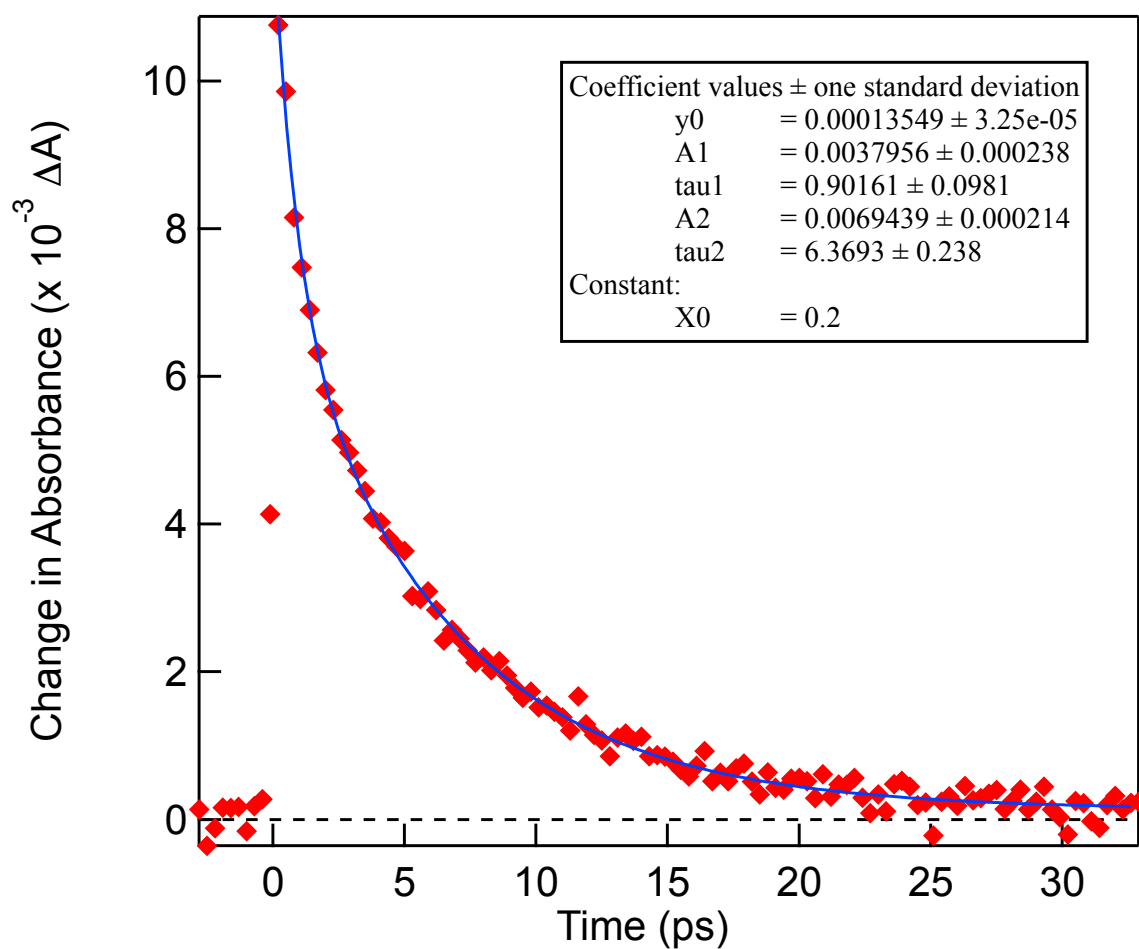


Figure S2.31: Kinetic trace of **1** in methanol. Exemplary 680 nm probe at 265K.

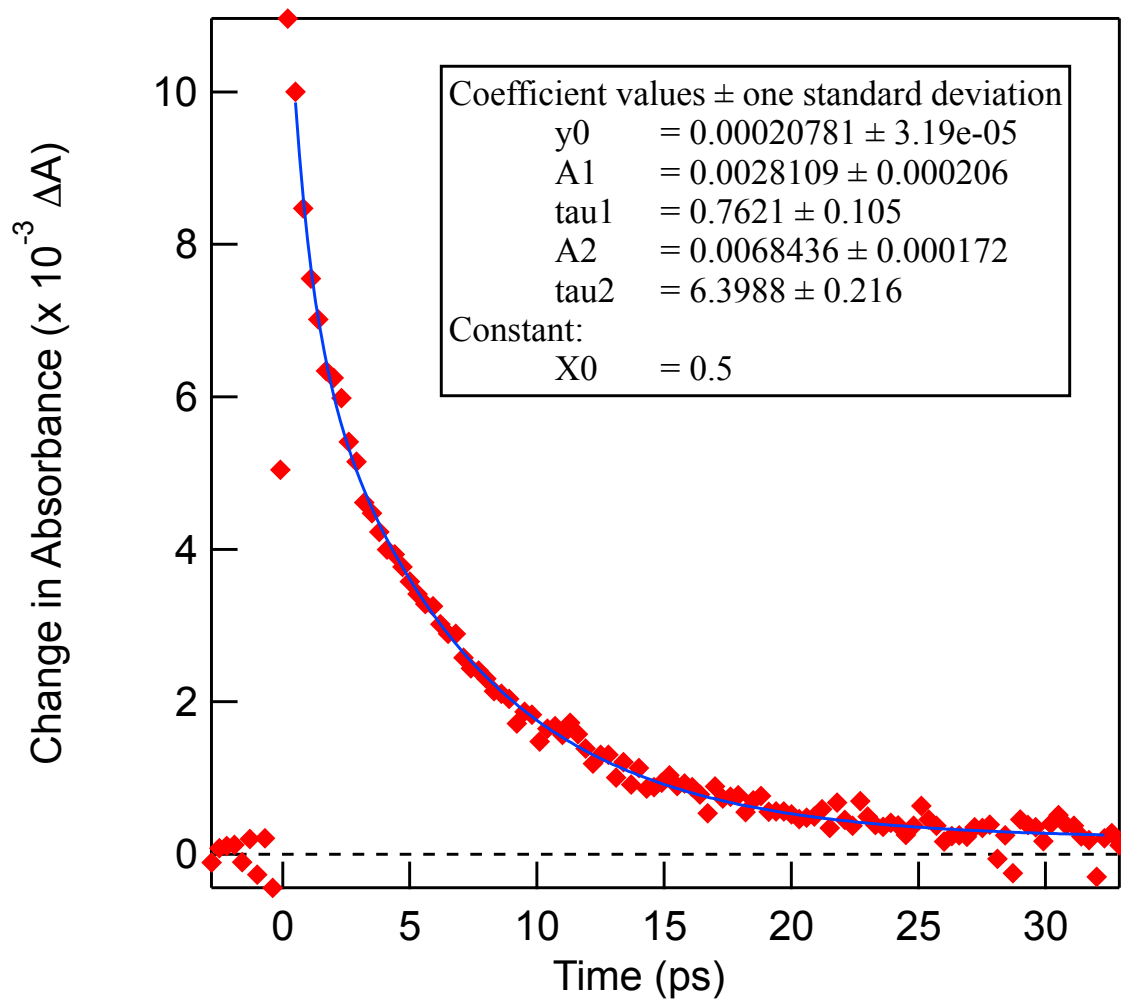


Figure S2.32: Kinetic trace of **1** in methanol. Exemplary 680 nm probe at 255K.

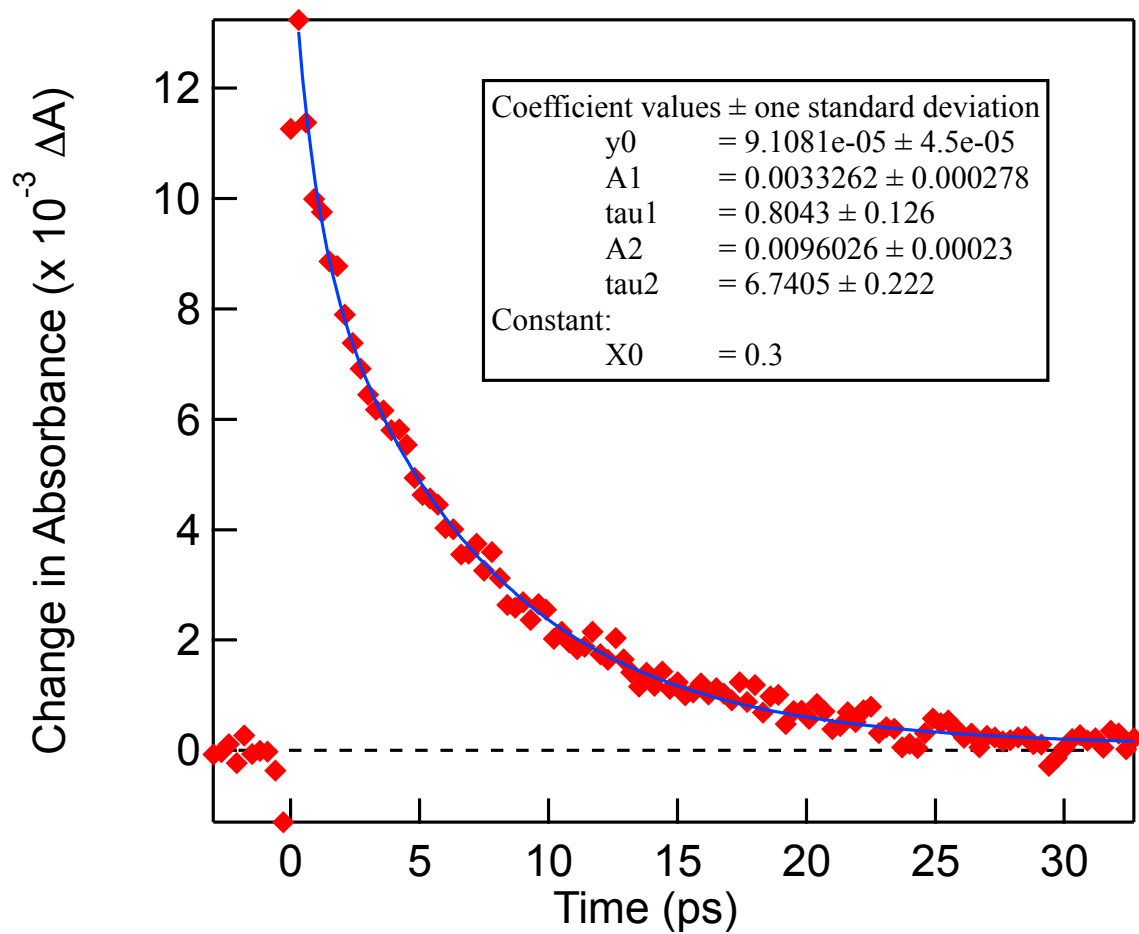


Figure S2.33: Kinetic trace of **1** in methanol. Exemplary 680 nm probe at 245K.

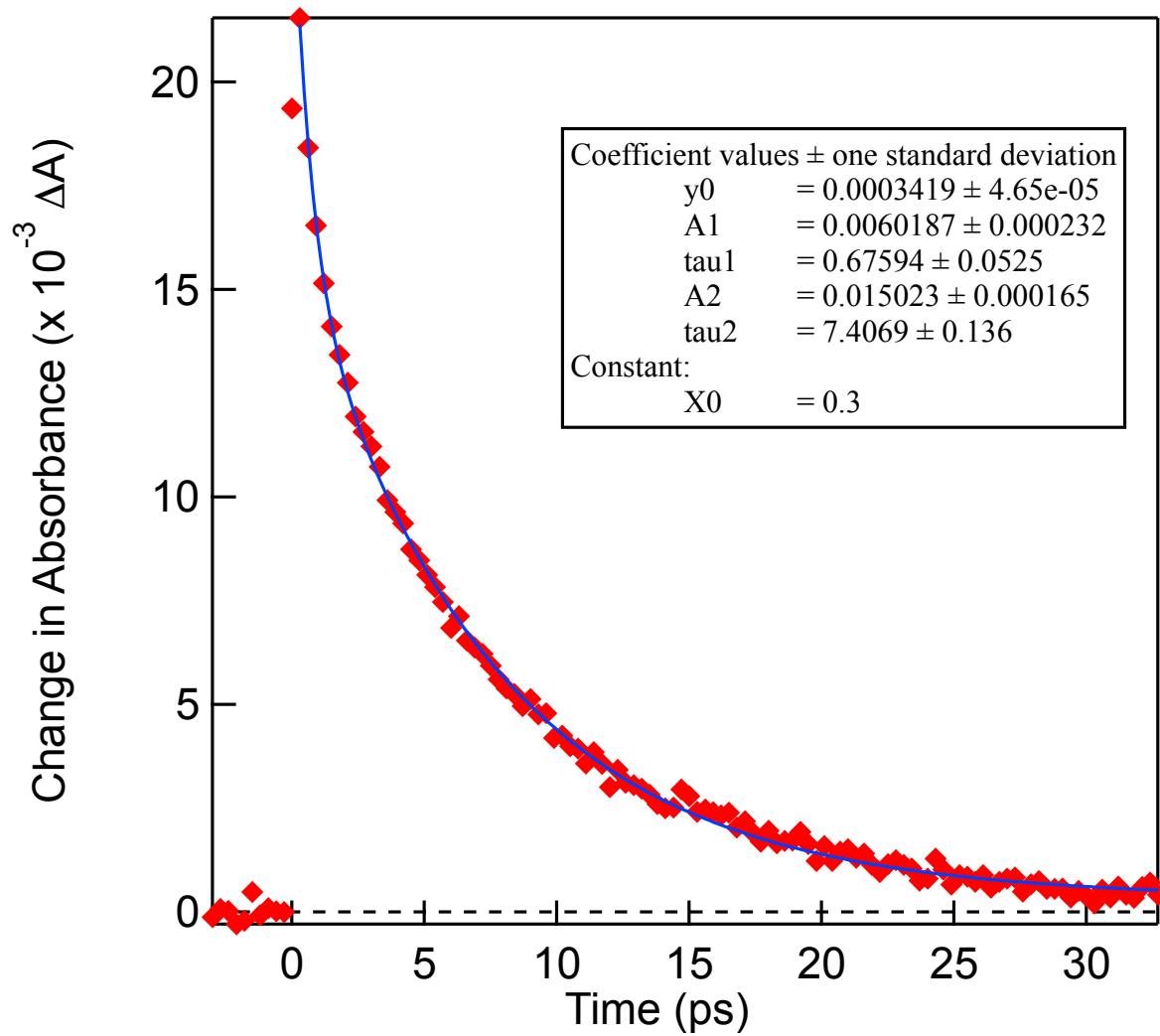


Figure S2.34: Kinetic trace of **1** in methanol. Exemplary 680 nm probe at 235K.

2.6.3 NMR spectroscopy

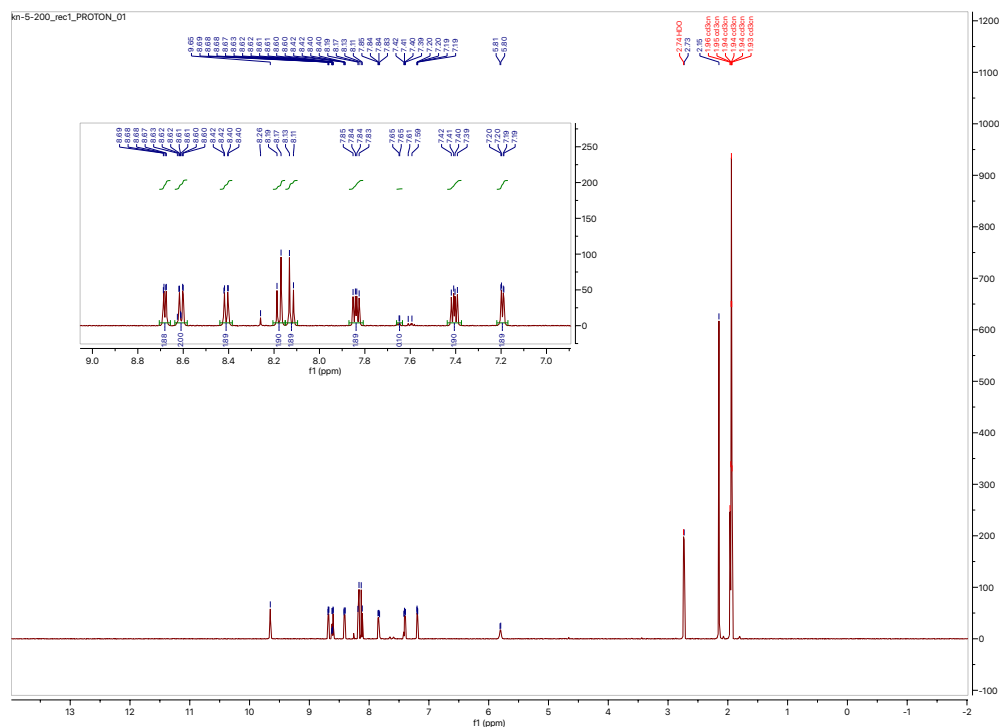


Figure S2.35: ^1H NMR of **1** in $d_3\text{-MeCN}$. < 1% Fe(phen)_3^{2+} impurity.

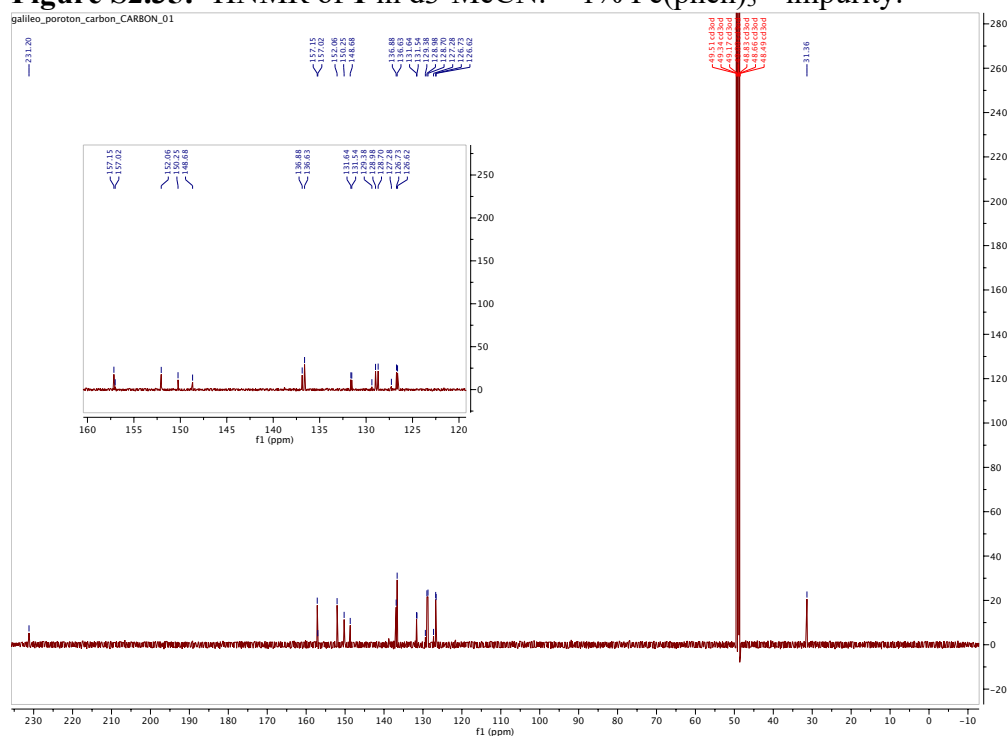


Figure S2.36: ^{13}C NMR of **1** in $d_3\text{-MeCN}$ < 1% Fe(phen)_3^{2+} impurity.

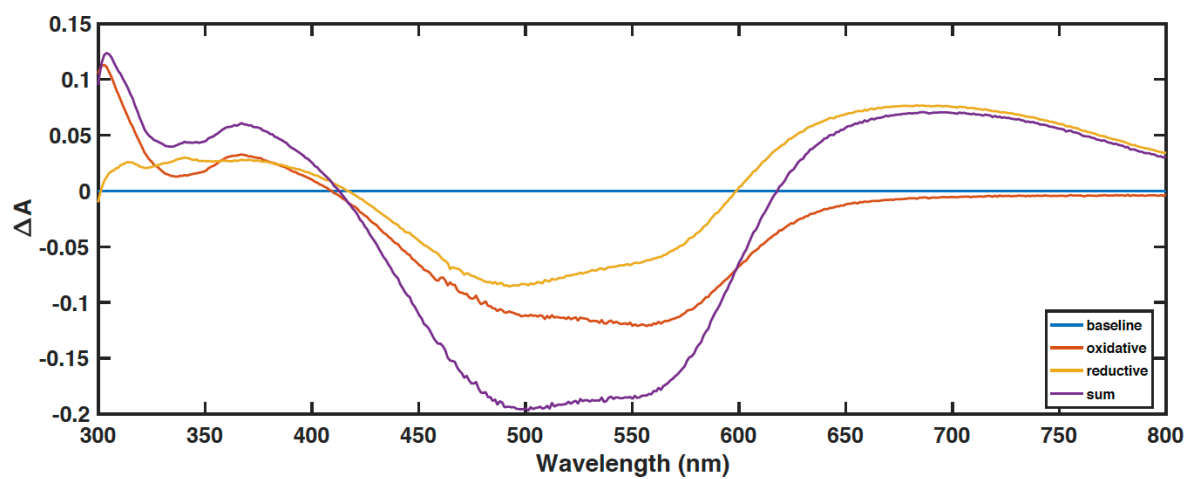


Figure S2.41: Spectroelectrochemistry of **1**. Taken from reference 7. The details on the procedure of its generation are reported therein.

**3) CHAPTER 3: THE SYNTHESIS, CHARACTERIZATION,
AND REACTIVITY OF NOVEL HETEROLEPTIC FE(II)
ISOCYANIDE COMPLEXES FOR HIGH ENERGY CHARGE
TRANSFER EXCITED STATES AND PRECURSORS FOR
DIAMINO CARBENES**

3.1 INTRODUCTION

The introductory chapter discussed the use of carbene ligands in a modular, heteroleptic Fe(II) complexes. Strong field ligands like carbenes destabilize ligand field states, which has been referred to as the thermodynamic approach. Other ligand systems can be used for similar purposes. For example, an isocyanide ligand framework is interesting in that it can act both as good σ -donors while also being strong π -acceptors.^{1,2} Figure 3.1 illustrates the relevant bonding molecular orbitals of this type of ligand. In this case, the two π -antibonding orbitals are non-degenerate. The in-plane p-orbitals are raised in energy due presumably to their repulsion with electron density in the plane of the benzene ring. In the ligand field context, the σ -symmetry orbitals destabilize metal based e_g^* orbitals and while orbitals of π -symmetry stabilize the t_{2g} orbitals in the limit of an octahedral ligand field.

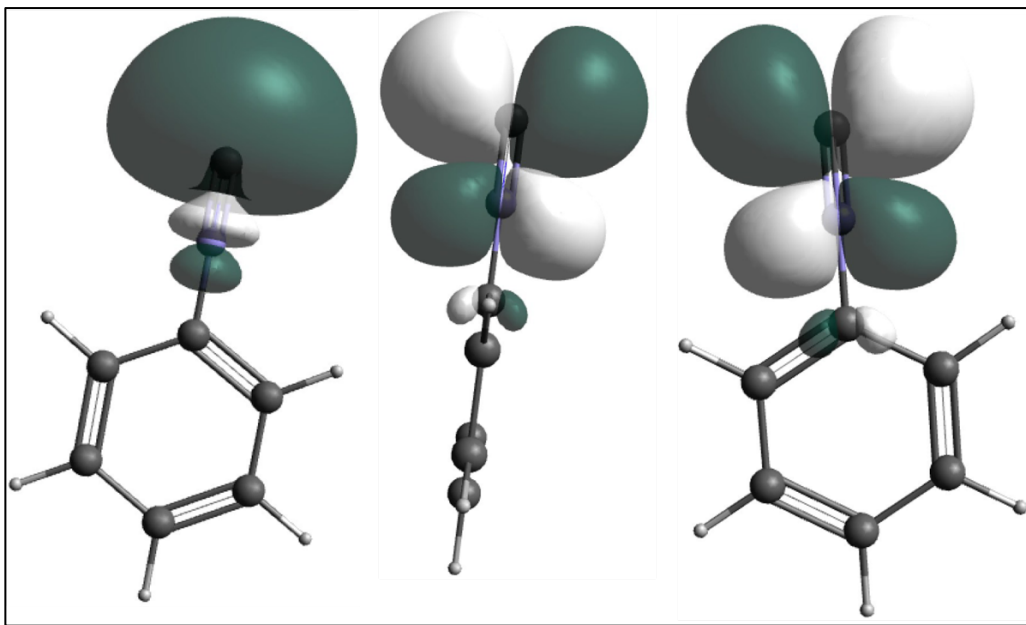


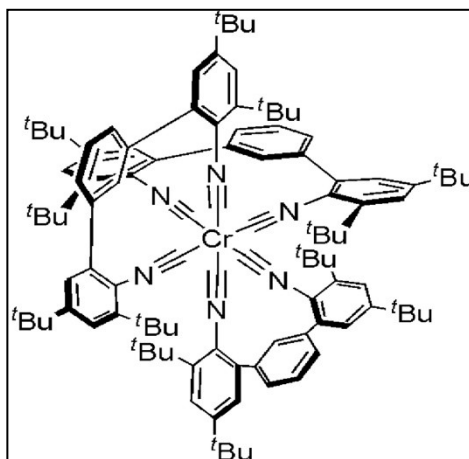
Figure 3.1: Optimized structure of phenylisocyanide (CNPh) and the orbitals relevant for bonding with the metal ion. In the free form the orbital of σ - symmetry is lowest in energy followed by the π -symmetry perpendicular to the phenyl and then coplanar to the phenyl group.

Isocyanides are isoelectronic to the prototypical strong-field ligand carbon monoxide (CO) suggesting chemical similarity in their effects as ligands. Isocyanides, however, have the added

benefit over CO of being synthetically tunable. The typical formula of this neutral donor is CNR, where R can be aliphatic, aromatic, or heteronuclear. This in theory can tune the donor/acceptor ability of the ligand and thus provide a quasi-continuous electronic perturbation upon the ligand field. This diversity in structure and property provides a path for experimentation and optimization of the ligand field such that the goals outlined in the introductory chapter are achieved.

3.1.1 Isocyanides for Luminescent First-Row Transition Metal Complexes

This ligand class is the most exciting in the development of luminescent, first-row transition metal complexes.^{3,4} This work has been pioneered by Wenger and co-workers in a report on a luminescent d⁶ analogue to Fe(II) polypyridyl systems which exhibited room temperature phosphorescence.⁵ The flagship complex Cr(CN^{tBu}Ar₃NC)₃ (where CN^{tBu}Ar₃NC = 3",5,5"-tetra-*tert*-butyl-2,2"-diisocyano-1,1':3,1"-terphenyl) was based a bis-chelating isocyanide ligand utilizing an aryl spacer.⁶ The inclusion of *t*-butyl groups in proximity to the inner sphere of coordination, allowed for a rigid ligand environment, paired with strong-field isocyanides to destabilize ligand-field electronic states, an example of a combined approach leveraging both electronic and steric effects to control non-radiative decay. Biexponential kinetics were observed from emission decay at room temperature. This decay was on the same order as that observed with transient absorption (TA) spectroscopy. While no charge separation was noted in this system's TA, it interacted with an anthracene in an excited triplet state to quench the emission observed, implying triplet character of the emitting state.⁵ This report was the first to show the utility of the isocyanide ligand in creating long lived photoexcited states in first row transition metals.



Drawing 3.1: $\text{Cr}(\text{CN}^{\text{tBu}}\text{Ar}_3\text{NC})_3$ taken from reference 5.

A follow up study examined the same general complex motif with a pyrene moiety appended to the to the phenyl spacer.⁷ The study noted a solvent dependence on emission, consistent with longer charge-transfer (CT) dipole, provided by the pyrene, confirming its nature as CT. A bell-shaped solvent dependence was observed, suggestive of participation of higher lying ligand field states, the coupling to which becomes stronger with a smaller energy gap, due to a less-stabilized MLCT in non-polar solvents. This study shows how isocyanide ligands can act in destabilizing metal centered states to a significant degree and are affected by the dielectric environment.

Most recently, this group published a study on two Mn(I) complexes incorporating bidentate and tridentate ligand environments.⁸ The 0.05% quantum-yield of the bidentate variety was observed at room temperature, a novel observation for a first-row d^6 ion. This improvement is in part due to the increased oxidation number of Mn(I) compared with Cr(0), where better orbital overlap is facilitated by the increased columbic portion of the M-L bond. The oxidation state did reduce the back bonding, however. This was established by considering the -55 cm^{-1} shift of the CN stretch that occurs when going from the free ligand to the complexed ligand indicates there is still significant back bonding from metal to ligand, contributing the ligand field

strength (LFS) of this complex (compare to the -158 cm^{-1} shift for the Cr(0) complex). The increasing oxidation state of d^6 ions yields improved photophysical properties, what happens when this trend continues across the first row? Does the increased charge density around Fe(II) lead to even better orbital overlap and thus superior ligand field stabilization? Or does the benefit of increased oxidation number end with Mn(I)?

3.1.2 Fe(II) Isocyanide Systems

The use of isocyanides with Fe(II) systems is not unheard of, however reports are few and far between. The first report of the $[\text{Fe}(\text{CNMe})_6]^{2+}$ complex cation is over 100 years old.³³ This species is synthesized by the serial methylation of ferrocyanide using neat methyl sulfate. The workup of the corresponding bright white powder yields Prussian blue-like compound if exposed to significant amounts of water. The first crystal structure of this compound is reported in figure 3.2. The C-N-C angles indicate the magnitude of back bonding. There is significant linearity, suggesting an electron deficient metal center, which is not unexpected for a hexacoordinate isocyanide complex. This complex is thermally stable, however can undergo photo-substitution in acetonitrile solution after irradiation with UV- light. The kinetics of this process were demonstrated by Costanzo and coworkers.⁹

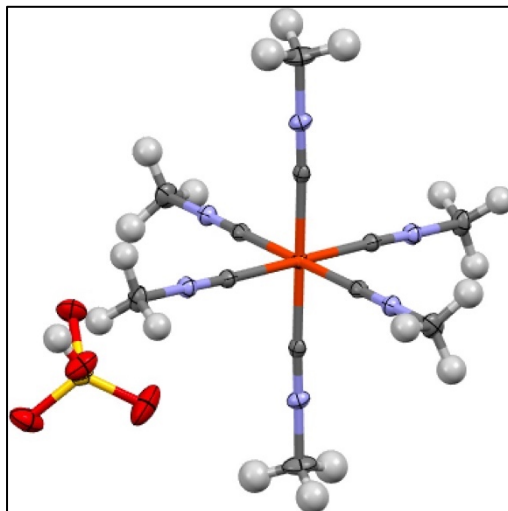


Figure 3.2: Crystal Structure of $\text{Fe}(\text{CNMe})_6(\text{HSO}_4)_2$. Collected and solved by Dr. R.J. Staples. Equatorial Fe-C: 1.901 Å; Axial Fe-C: 1.895 Å.

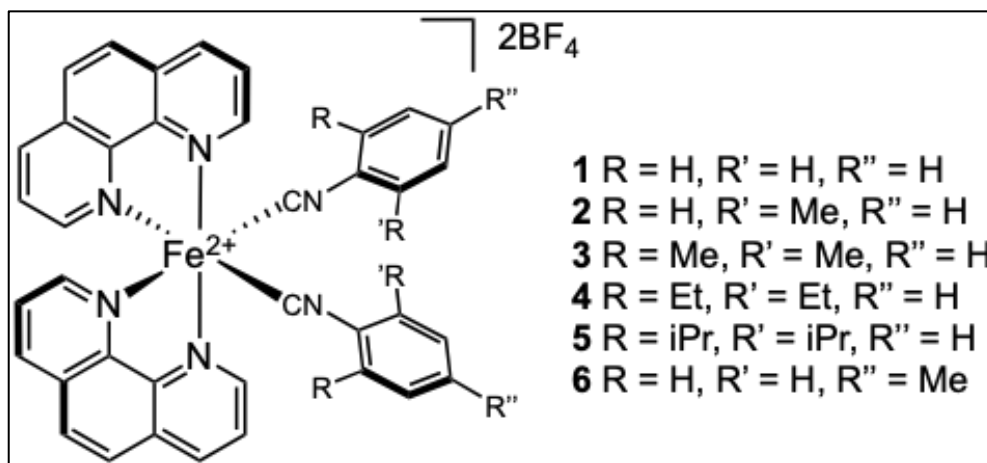
Miller et. al. utilized a similar method of methylation from the $\text{Fe}(\text{phen})_2(\text{CN})_2$ complex to yield a bis-methylisocyanide complex, the modified synthesis we discussed in a recent publication by our group.¹⁰ The isocyanide $[\text{Fe}(\text{phen})_2(\text{CNMe})_2]^{2+}$,¹¹ were found to be precursors to carbene complexes. It was not studied further however but was used as a precursor to the synthesis of the $[\text{Fe}(\text{phen})_2(\text{C}_4\text{H}_{10}\text{N}_4)^{2+}]$ cation (see chapter 1 experimental). The orange isocyanide complex quickly reacts with amines due to the electrophilic activation of the isocyanides upon complexation. This is a typical trend in the reactivity of isocyanides and further highlights the structural diversity for these systems. Understanding mechanistic properties of these systems will be key and are highlighted in the following section.

3.1.3 Isocyanides as precursors to carbenes

Costnazo et. al. has conducted the most comprehensive kinetic study of the formation of Fe(II) aryl amino carbenes from isocyanides.^{9,12–15} The study of the formation of the $[\text{Fe}(\text{phen})_2(\text{C}_4\text{H}_{10}\text{N}_4)]^{2+}$ cation is particularly important. The kinetics of hydrazine bridging were tracked using electronic absorption spectroscopy. The rate of the reaction was found to be first order in hydrazine and the first step included a concerted protonation and nucleophilic attack on

the isocyanide nitrogen and carbon respectively. The second amine of the bound hydrazine followed a similar mechanism but was not observable due to its rapidity. Deprotonation by excess hydrazine to the imine form of the carbene backbone was found to be reversible, consistent with the re-protonation from previous reports using 15 equivalents of hydrazine.¹⁶

The reactivity of a complex is proportional to the electrophilicity of the isocyanide carbon. The electrophilicity of the isocyanide carbon is proportional to the amount of electron density at the carbon atom, modulated by its π -acidity. This is in turn, dependent upon the interaction between the metal center and the ligand. For example, Teets and coworkers' syntheses of blue-emitting iridium(III) complexes required strongly electron withdrawing, $-\text{NO}_2$ and $-\text{CF}_3$, groups on an aryl ring for the reaction with a severe excess of hydrazine to proceed.^{17,18} While the examples of Costanzo et. al. on Fe(II) isocyanides interacting productively with amines, diverse ligand structures cannot be assumed to work *a priori*.



Drawing 3.2: Diagram of the species synthesized and studied for this chapter.

The goals of this chapter are twofold: the first is to establish some intuition about the metal-ligand interaction in a series of heteroleptic isocyanides through structural and computational analyses. Drawing 3.2 highlights some of the varieties studied in this chapter. The second is to treat these species as precursors to the formation of carbene complexes, through

their reaction with hydrazine. The dual nature as ligands, both donors and acceptors, as well as nucleophiles and electrophiles, mean that isocyanides are excellent tools to have in the toolbox for making diverse heteroleptic complexes, but this complexity requires understanding of the limitations of their use in specific contexts. This chapter intends to shed light upon these limitations.

3.2 EXPERIMENTAL

All substituted anilines were purchased from either Sigma Aldrich, Alfa Aesar, or Oakwood Chemical. 1,10-phenanthroline was purchased from Oakwood chemical. $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ was purchased from Sigma Aldrich. Ferrous ammonium sulfate was purchased from Spectrum Chemical. Phosphorus oxychloride was purchased from Sigma Aldrich. Sodium tetrafluoroborate (NaBF_4) was purchased from Sigma Aldrich. All solvents were dried on an alumina column and degassed unless otherwise specified. The synthesis of free isocyanides from the corresponding anilines were performed in two steps according to modified literature procedures without purification.^{19,20} All NMRs were performed on a 500 MHz instrument in the Max T. Rodgers NMR facility at MSU and Uv-Vis spectroscopy was performed on a Cary 50 spectrophotometer. X-Ray structures were collected at the Center for Crystallographic Research at Michigan State University and solved with the ShelX algorithm.²¹

3.2.1 Synthesis of bis-aryl isocyanides:

*Synthesis of $[\text{Fe}(\text{phen})_2(\text{CNPh})_2][\text{BF}_4]_2$ (**1**):* 5.551 g (31 mmol, 2.8 eq) of 1,10-phenanthroline was added to a solution of 4.183 g (11 mmol, 1 eq) of ferrous ammonium sulfate in 200 mL of water. The clear solution turned a bright and vibrant red, which was heated to reflux temperature in open air. 5.440 g (53 mmol, 5 eq) of phenylisocyanide was added quantitatively to the stirred solution with a methanol wash and heating was continued under nitrogen to contain the strong

odor. After 1 hour, no color change was observed, except for the meniscus which had turned an orange color. The reaction was cooled. The aqueous solution was extracted several times with an equal volume of diethyl ether until the yellow color of the organic impurities is no longer visible. The aqueous layer was treated with an excess of NaBF₄. The resulting precipitate was filtered, washed with water, and dried *en vacuo*. The solid was recrystallized by slow cooling from a solution of 10:1 toluene/acetonitrile in a covered flask wrapped with insulation. The solid was dried again giving 4.114 g of a red/orange solid. Yield, 48%. ¹H NMR (500 MHz, acetonitrile-*d*₃) δ 9.55 (dd, *J* = 5.2, 1.3 Hz, 2H), 8.88 (dd, *J* = 8.3, 1.3 Hz, 2H), 8.61 (dd, *J* = 8.2, 1.3 Hz, 2H), 8.28 (d, *J* = 8.9 Hz, 2H), 8.21 (d, *J* = 8.9 Hz, 2H), 8.13 (dd, *J* = 8.3, 5.2 Hz, 2H), 7.57 (dd, *J* = 8.2, 5.3 Hz, 2H), 7.48 – 7.36 (m, 12H). ¹³C NMR (126 MHz, acetonitrile-*d*₃) δ 159.16, 152.57, 149.10, 147.97, 139.68, 139.32, 131.60, 131.40, 131.11, 130.45, 128.78, 128.61, 127.85, 127.68, 126.97. FTIR: 1032 cm⁻¹ (BF₄ stretch), 1431 cm⁻¹, 1486 cm⁻¹, 1586 cm⁻¹, 2136 cm⁻¹ (-CN, asym), 2165 cm⁻¹ (-CN, sym), 3070 cm⁻¹.

*Synthesis of [Fe(phen)₂(CN-*o*Tol)₂][BF₄]₂ (2):* This complex was synthesized analogously to that described for **1**. It crystallizes as two conformers, with methyl groups parallel and anti-parallel configurations. Yield, not available. ¹H NMR (500 MHz, acetonitrile-*d*₃) δ 9.56 (dd, *J* = 5.3, 1.3 Hz, 2H), 8.87 (dd, *J* = 8.3, 1.2 Hz, 2H), 8.63 (dd, *J* = 8.2, 1.3 Hz, 2H), 8.28 (d, *J* = 8.9 Hz, 2H), 8.22 (d, *J* = 8.9 Hz, 2H), 8.11 (dd, *J* = 8.3, 5.2 Hz, 2H), 7.59 (dd, *J* = 8.2, 5.3 Hz, 2H), 7.53 – 7.45 (m, 4H), 7.32 (td, *J* = 7.5, 1.5 Hz, 2H), 7.29 – 7.20 (m, 4H), 1.75 (s, 6H). ¹³C NMR (126 MHz, acetonitrile-*d*₃) δ 159.16, 152.81, 149.07, 147.96, 139.74, 139.41, 136.59, 131.62, 131.47, 131.44, 131.04, 128.85, 128.62, 127.89, 127.80, 127.28, 127.05, 17.80.

Synthesis of [Fe(phen)₂(CNDMP)₂][BF₄]₂ (3): 0.555 g (3.1 mmol, 2.8 eq) of 1,10-phenanthroline were added to a solution of 0.381 g (1.1 mmol, 1 eq) of Fe(BF₄)₂•6H₂O in 10 mL of methanol.

The clear solution turned a bright and vibrant red, which was heated to reflux temperature in open air. 0.742 g (5.6 mmol, 5 eq) of 2,6-dimethylphenylisocyanide was added quantitatively to the stirred solution and reflux was continued under nitrogen. Red/orange solids formed overnight. The solution was cooled to room temperature and the solids were filtered. The solid was washed with water followed by di-ethyl ether. The solid was recrystallized with slow cooling from a solution of 10:1 toluene/acetonitrile followed by drying *en vacuo*. Isolated 0.793 g of orange/yellow solid. Yield, 84%. Crystals suitable for x-ray diffraction were obtained by the slow evaporation of acetonitrile from toluene to form orange/yellow blocks. ¹H NMR (500 MHz, acetonitrile-*d*₃) δ 9.54 (dd, *J* = 5.2, 1.2 Hz, 2H), 8.87 (dd, *J* = 8.3, 1.2 Hz, 2H), 8.65 (dd, *J* = 8.2, 1.3 Hz, 2H), 8.28 (d, *J* = 8.9 Hz, 2H), 8.23 (d, *J* = 8.9 Hz, 2H), 8.11 (dd, *J* = 8.3, 5.2 Hz, 2H), 7.61 (dd, *J* = 8.1, 5.2 Hz, 2H), 7.56 (dd, *J* = 5.3, 1.3 Hz, 2H), 7.18 (dd, *J* = 8.2, 7.1 Hz, 2H), 7.13 – 7.02 (m, 4H), 1.96 (s, 14H). ¹³C NMR (126 MHz, Acetonitrile-*d*₃) δ 159.09, 152.98, 149.11, 148.08, 139.83, 139.57, 136.29, 131.76, 131.52, 130.56, 128.96, 128.96, 128.75, 128.05, 127.19, 18.39. FTIR: 1018 cm⁻¹ (BF₄ stretch), 1428 cm⁻¹, 1584 cm⁻¹, 2134 cm⁻¹ (-CN, asym), 2160 cm⁻¹ (-CN, sym), 3069 cm⁻¹.

Synthesis of [Fe(phen)₂(CNDEP)₂][BF₄]₂ (4): This complex was synthesized in an analogous manner to that of **3** but using 2,6-diethylphenylisocyanide. Poor crystallization occurred with the solvent systems tried including the slow evaporation from an acetonitrile/toluene system and variations on a dichloromethane/ether system with slow addition and vapor diffusion. Isolated 1.842 g of orange solid. Yield, 85%. ¹H NMR (500 MHz, acetonitrile-*d*₃) δ 9.54 (dd, *J* = 5.2, 1.2 Hz, 2H), 8.89 (dd, *J* = 8.3, 1.2 Hz, 2H), 8.66 (dd, *J* = 8.2, 1.3 Hz, 2H), 8.30 (d, *J* = 8.9 Hz, 2H), 8.25 (d, *J* = 8.9 Hz, 2H), 8.13 (dd, *J* = 8.3, 5.2 Hz, 2H), 7.62 (dd, *J* = 8.2, 5.3 Hz, 2H), 7.55 (dd, *J* = 5.3, 1.3 Hz, 2H), 7.27 (t, *J* = 7.7 Hz, 2H), 7.11 (d, *J* = 7.7 Hz, 4H), 2.34 (q, *J* = 7.6 Hz, 8H),

0.76 (t, $J = 7.6$ Hz, 12H). ^{13}C NMR (126 MHz, acetonitrile- d_3) δ 159.04, 153.06, 149.12, 148.05, 142.02, 139.96, 139.64, 131.80, 131.58, 131.09, 129.07, 128.80, 128.05, 127.41, 127.28, 25.96, 13.81. FTIR: 1032 cm^{-1} (BF_4 stretch), 1429 cm^{-1} , 2124 cm^{-1} (-CN, asym), 2156 cm^{-1} (-CN, sym), 2967 cm^{-1} , 3073 cm^{-1} .

*Synthesis of $[\text{Fe}(\text{phen})_2(\text{CNDiPP})_2][\text{BF}_4]_2$ (**5**):* This complex was synthesized in an analogous manner to that of **3** but using 2,6-diisopropylphenylisocyanide. Isolated 2.532 g of orange product. Yield, 70%. ^1H NMR (500 MHz, acetonitrile- d_3) δ 9.53 (dd, $J = 5.2, 1.2$ Hz, 2H), 8.92 (dd, $J = 8.3, 1.2$ Hz, 2H), 8.67 (dd, $J = 8.2, 1.3$ Hz, 2H), 8.32 (d, $J = 8.9$ Hz, 2H), 8.26 (d, $J = 9.0$ Hz, 2H), 8.14 (dd, $J = 8.2, 5.3$ Hz, 2H), 7.62 (dd, $J = 8.2, 5.3$ Hz, 2H), 7.55 (dd, $J = 5.3, 1.3$ Hz, 2H), 7.33 (t, $J = 7.8$ Hz, 2H), 7.16 (d, $J = 7.8$ Hz, 4H), 2.73 – 2.64 (m, 4H), 0.85 (dd, $J = 11.1, 6.9$ Hz, 23H). ^{13}C NMR (126 MHz, acetonitrile- d_3) δ 159.06, 153.17, 149.11, 148.00, 146.23, 140.00, 139.64, 131.78, 131.59, 131.33, 129.15, 128.80, 127.98, 127.31, 124.60, 30.66, 22.53, 22.50. FTIR: 1044 cm^{-1} (BF_4 stretch), 1430 cm^{-1} , 2123 cm^{-1} (-CN, asym), 2162 cm^{-1} (-CN, sym), 2964 cm^{-1} , 3071 cm^{-1} .

*Synthesis of $[\text{Fe}(\text{phen})_2(\text{CNp-tol})_2][\text{BF}_4]_2$ (**6**):* This complex was synthesized in a similar manner to **1**, but using 4-methylphenylisocyanide. Isolated 1.456 g of orange product. Yield, 31%.

Crystals suitable for x-ray diffraction were grown from the slow evaporation of acetonitrile from toluene. ^1H NMR (500 MHz, acetonitrile- d_3) δ 9.52 (dd, $J = 5.2, 1.3$ Hz, 1H), 8.86 (dd, $J = 8.3, 1.3$ Hz, 1H), 8.59 (dd, $J = 8.2, 1.3$ Hz, 1H), 8.27 (d, $J = 8.9$ Hz, 1H), 8.20 (d, $J = 8.9$ Hz, 1H), 8.11 (dd, $J = 8.3, 5.2$ Hz, 1H), 7.55 (dd, $J = 8.2, 5.3$ Hz, 1H), 7.40 (dd, $J = 5.3, 1.3$ Hz, 1H), 7.33 – 7.27 (m, 2H), 7.25 – 7.19 (m, 2H), 2.33 (s, 3H), 2.15 (s, 3H), 0.58 (s, 2H). FTIR: 1033 cm^{-1} (BF_4^- stretch), 2130 cm^{-1} (-CN, asym), 2157 cm^{-1} (-CN, sym), 3069.

3.2.2 Equilibrium studies:

NMR equilibrium studies were performed in deuterated acetonitrile that had been dried with 3 Å molecular sieves in a nitrogen glovebox. Samples were kept at a volume of 1 mL between runs and solvent volume was adjusted to compensate. Several equivalents of hydrazine solution were titrated into NMR tubes containing the Fe(II) sample. Samples were mixed thoroughly and allowed to equilibrate for 30 minutes. ¹H NMR spectra were then taken on 500 MHz instrument.

3.2.3 In-Situ Infrared spectroscopy:

Reaction kinetics at a preparatory scale were monitored using a Perkin-Elmer, ReactIR in dichloromethane solutions. A three-neck flask was fit with two septa and the IR probe, using a 14/20 Teflon adapter. The rate of stirring was adjusted to allow for full immersion of the probe. The orange solution which contained 0.099g (0.12 mmol, 1eq) of **3** and 8 mL of DCM was warmed to ~35 °C. The control of temperature was prioritized, and a thermal equilibrium was found. To this was added 0.108 mL (3.47 mmol, 30 eq) of hydrazine was added with a syringe with stirring, and the probe was blanked. Scans were taken every 30 seconds for a period of two hours. The resulting spectra were zeroed around 1800 cm⁻¹ as there is a continual increase in baseline for these experiments. Time traces were corrected with a smoothing function on the ReactIR software. The full spectral data was decomposed using the single value decomposition (SVD) written in a MATLAB program.

3.2.4 Computational Details:

Quantum chemical calculations were performed using density functional theory on the Gaussian 16 package at the High-Performance Computing Center at Michigan State University.³⁴ The B3LYP+ GD2 functional and empirical dispersion was used along with the 6-311G* basis

set for the light atoms and the SDD pseudopotential for the metal atom.³⁵⁻⁴³ Energy calculations were performed with the pseudopotential removed. An acetonitrile polarized continuum was used in all cases.⁴⁴ Natural bond orbital calculations we performed using NBO 6.0 with standard input.^{22,23}

3.2.5 *Electrochemistry*

Electrochemistry was performed in an argon filled glovebox using a potentiostat from CH-instruments. The 0.1 M TBAPF₆ acetonitrile supporting electrolyte immersed the three-electrode setup which included a glassy carbon working electrode, platinum wire counter electrode, and a silver wire pseudo-reference electrode. A ferrocene internal standard was used, and all results are reported to this potential. Cyclic voltammetry (CV) experiments were run with 100 mV/s scan rate for oxidations and 500 mV/s for the reductions. Experiments started on the far ends of the electrochemical waves. Differential pulse voltammetry (DPV) was performed in conjunction with CV.

3.3 RESULTS AND DISCUSSION

3.3.1 *Synthesis*

A quick note on safety, production of any small molecule isocyanide should be done in a fume-hood with the sash height raised to a minimum. All used gloves should be kept in the hood. Trace vapors are very unpleasant and toxic.

There are several methods to produce isocyanides.^{19,20} The formylation method was chosen. This involves the reaction of an amine formic acid which is dehydrated with phosphorus oxychloride and base to form the corresponding isocyanide, usually as a dark oil. Due to the toxicity and general unpleasantness of working with isocyanides, workup was not taken any

further than necessary and thus precluded purification of the oils. The formylation method is ideal because the purity of the oil is reasonable and does not require sublimation.

Complexes were synthesized from the corresponding free isocyanides. This likely occurred by substitution process. The formation of the tris-polypyridyl complex is followed by the substitution with excess isocyanide, due the formation of a blood red color before the addition. Less than molar equivalents of phenanthroline were used to limit the excess of free phenanthroline upon substitution with the isocyanide. Workup to remove residual organic material is done with diethyl ether extraction. In many cases, after the precipitation from methanol, some residual $[\text{Fe}(\text{phen})_3]^{2+}$ remains. It can be removed by dissolving the red/orange solids in small portions of dichloromethane and filtering off the red solids. The filtrate can be precipitated the slow addition of diethyl ether with gentle stirring. Recrystallization by slow cooling of acetonitrile and toluene yields good purity crystalline material.

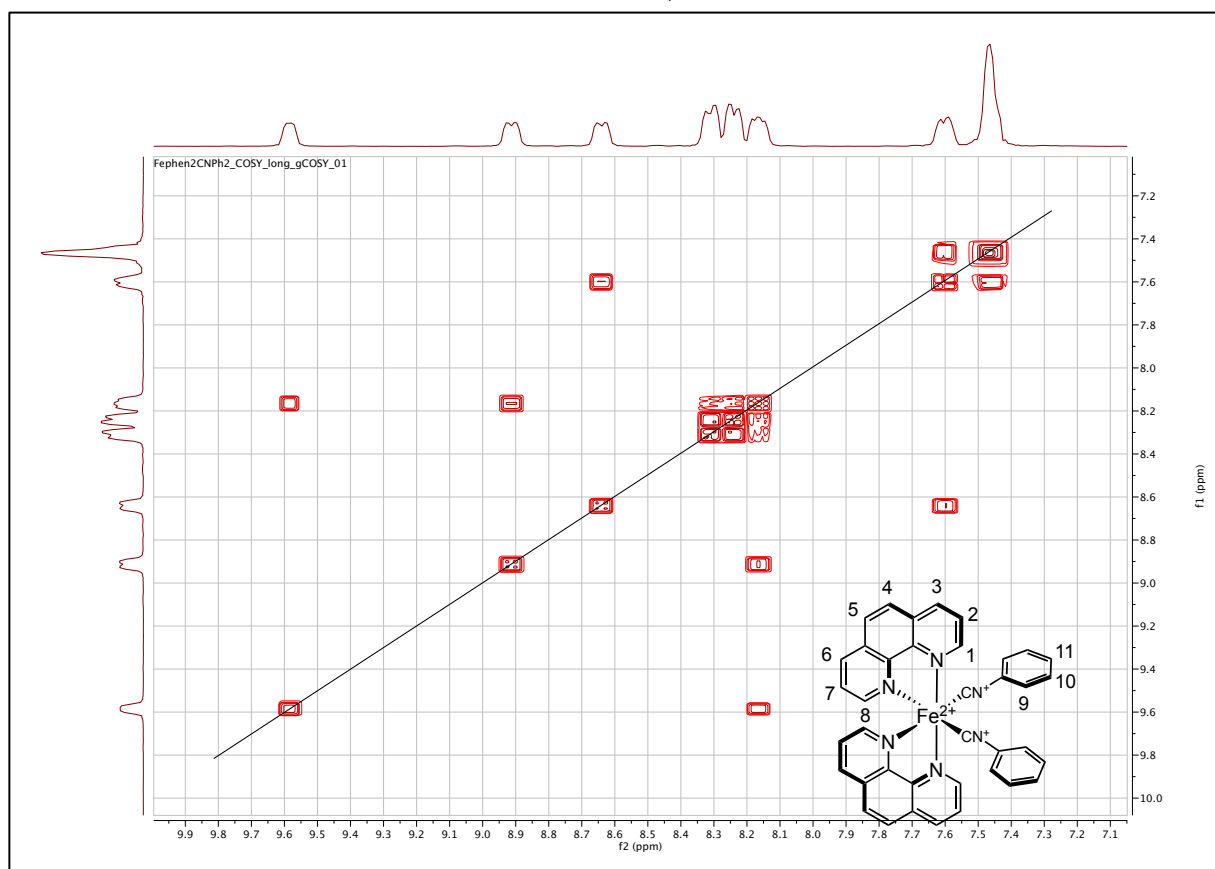


Figure 3.3: gCOSY spectrum of **1**. The assignments are as follows: 9.58 ppm, 1; 8.92 ppm, 3; 8.64 ppm, 6; 8.31 ppm, 4; 8.24 ppm, 5; 8.17 ppm, 2; 7.60 ppm, 7; Protons 8-11 occur in the poorly resolved resonance centered at 7.45 ppm.

The original method devised for the synthesis of these was based on the work of Schilt, using aqueous conditions. This was the method used for the synthesis of **1**, **2**, and **6** starting from ferrous ammonium sulfate. Due to the reasonable reactivity of free isocyanides with water and the relative insolubility of the more substituted aryl isocyanides, methanol was used instead. It is highly recommended for future synthesis to modify the procedures for the synthesis of **1**, **2**, and **6** to be in line with the methanolic route. There is room for optimization with other solvents which are aprotic which would likely allow for a decrease in the needed equivalence of aryl isocyanide.

Establishing robust NMR assignments is key not just for this series but all the nominally C₂ symmetry species reported here. This was done with gCOSY. The spectrum of **1** can be used to establish the specific resonances of this series, in figure 3.3. The most downfield resonance is assigned as proton 1 in the figure. This proton couples with a triplet at 8.17 ppm, this is assigned to proton 2. These couple to proton 3 giving the resonance at 8.92 ppm. Two coupled doublets are seen in the NMR spectrum, which can be assigned to the bridging ethynyl group in phenanthroline, these are not resolved in the gCOSY spectrum and thus their assignments are tentative and based on their position above or below the isocyanide plane. Protons 6 and 7 correspond to the resonances at 8.64 and 7.60 respectively. These couple to a resonance buried in the range of 7.40-7.50 ppm, which must correspond to proton 8. This shift up field is consistent with a resonance shielded by the π -system in which it is directed at. Ring currents arise in some other ways as well. For example, the strong shielding of the methyl protons in **4** and **5** which occur below 1 ppm. This may also explain the coupling constant of 11.1 Hz in the case of the methyl protons in **5**. A corresponding coupling constant is not observed for any other resonance.

The ¹³C-NMR spectra are missing two signals across all the aryl-isocyanide complexes where such spectra are available. The missing carbons are likely due to the isocyanide functional group next to a metal center. This environment is highly electron deficient and could increase the rate of relaxation beyond the instrument response function. Other systems?

3.3.2 X-Ray Crystallography

Only a handful of complexes were able to be grown as single crystals. We examine the structures of these in this section. Selected bond lengths of **1-3** are included in table 3.1. Complex **1** crystalizes with two complexes in the asymmetric unit. A result likely due to the low energy barriers between rotational isomers of the isocyanide. This can be shown by the different

torsional angles between the axial (perpendicular to isocyanide plane) Fe-N bonds and the plane of the phenyl groups which differ by 38°. These are oriented different in the other formula unit (not pictured). The Fe-C bond lengths are 1.847(4) and 1.854(4) Å highlighting the strength of the bonding interaction. There is a notable destabilization on the equatorial nitrogen atoms but is quite minor with the bond being almost < 2 Å. The axial bond lengths are 1.969(3) and 1.991(3) Å. Interesting to note is their relative asymmetry to one another as well as the fact that this asymmetry manifests axially and not equatorially (i.e. in the bonds *trans* to the Fe-C bond) as we would expect in a complex with *trans*-influence, where a correspondingly shorter Fe-C bond should manifest in a relatively longer Fe-N bond *trans* to it, all else being equal (see Chapter 3). While this doesn't rise to the level of a *cis*-influence, as these are within the normal range of Fe-N bonding, it is curious nonetheless as *cis*-effects should not be driven by strong donor or acceptor ligands like the isocyanide.

Table 3.1: Selected bond lengths for complexes **1-3**.

Bond (Å)	1	2	3
Fe-N _{trans1}	2.009(3)	2.008(2)	2.012(2)
Fe-N _{trans2}	2.005(3)	2.006(2)	2.007(2)
Fe-N _{cis1}	1.969(3)	1.968(2)	1.986(2)
Fe-N _{cis1}	1.991(3)	1.985(2)	1.985(2)
Fe-C ₁	1.847(4)	1.846(3)	1.863(2)
Fe-C ₂	1.854(4)	1.858(3)	1.869(2)

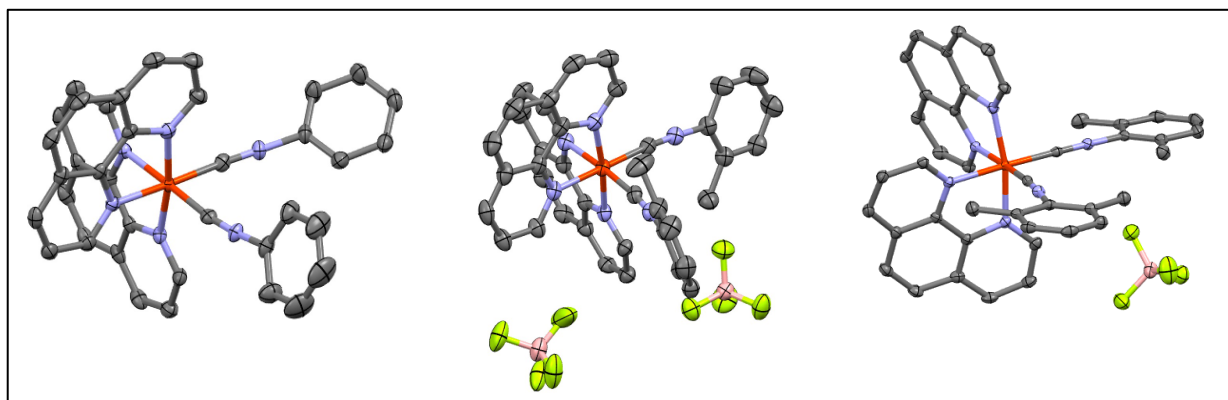


Figure 3.4: (left) Crystal structure of **1**. (center) Crystal Structure for **2**, solved by Dr. R.J. Staples. (right) Crystal structure of **3**. Orange: iron, purple: nitrogen, grey: carbon, pink: boron, yellow: fluorine. Hydrogen atoms removed for clarity. Thermal ellipsoids at 50% probability.

The α -hydrogen on phenanthroline, is 3 Å from the plane of the adjacent phenanthroline ligand close to be susceptible to some above plane ring current, explaining the chemical shift to 9.6 ppm in the NMR spectrum above. The CN bond lengths are 1.15 Å consistent with a formal triple bond along with a significant linearity. Compare these with monodentate W(0) complexes whose lack of linearity in the isocyanides are clear.^{24–28} This may be related to the donor ability of the metal ion, which is expected to be reduced in the doubly valent state.

Complex **2** crystalizes with two formula units, each methyl group pointing parallel or anti-parallel. This suggests that each conformer is approximately equal in energy; however we will consider the trans-configuration as it would likely be the lowest energy in a vacuum or dielectric. The Fe-C bonds have a length of 1.858(3) and 1.846(3) Å, a slight elongation compared to the phenyl derivative described above due to the disruption of the bond by the methyl group. Again, there is a *trans*-influence although minor as well as an asymmetry manifesting in the axial imine bonds.

Complex **3** crystalizes with only a single conformer in the asymmetric unit suggesting rigidity in the cyanide bond axis upon addition of a second methyl group. It exhibits approximately coplanar phenyl groups likely due to packing forces. Comparison with the o-tolyl

derivative is fruitful. The Fe-C bond lengths have increased slightly by approximately 15 pm outside the error for each. Interestingly the *trans*-influence increases compared to the MMP derivative. Furthermore, the asymmetry in the Fe-C bonding manifests in the imine bond *trans* to them rather than in the *cis* configuration. The linearity of the isocyanide nitrogen has increased by $\sim 6^\circ$ which must be due to rigidity imparted by the second methyl groups.

Crystallization conditions for complexes **4** and **5** in the series have not been found to yield crystals suitable for X-ray diffraction. This could be due to the increased alkane complexity in these species. A dramatic change from the standard acetonitrile/toluene that works extremely well for these species may be necessary along with a change in the counter-anion to BPh₄⁻ or similar.

3.3.3 Quantum Chemical Calculations

DFT calculations were performed on **1**. Bond lengths for the Fe-N bonds are well predicted using the B3LYP+GD2 functional in acetonitrile polarized continuum. Bond lengths are within $\sim 2\%$ of that measured in the crystal structure, where there is a clear lifting of bond asymmetries due to packing forces within the molecule. Orbital picture is comparable to the carbene systems, in that C₂ symmetry lends itself to non-degenerate metal centered orbitals. Noticeable is the ligand character in the t_{2g} manifold. These are significantly π -antibonding and AOm_{ix}^{29,30} calculations on the optimized ground state geometry show (performed by Jonathan Yarranton) that the HOMO to HOMO-2 appear to have significant ligand character, with the 31% of HOMO-1 being localized on the isocyanides. Orbitals 139 and 141 represent the d_{x²-y²} and d_{z²} sigma bonding orbitals respectively. MOs 150 to 152 are derived from the t_{2g} set of orbitals of iron. The molecular orbitals are pictured in figure 3.5 and are ordered with their corresponding energies.

Table 3.2: Computationally derived bond lengths for **1** compared against the crystal structure.

Bond (Å)	1	B3LYP	% Error
Fe-N _{trans1}	2.009(3)	2.036	1.3
Fe-N _{trans2}	2.005(3)	2.036	-
Fe-N _{cis1}	1.969(3)	2.018	2.4
Fe-N _{cis1}	1.991(3)	2.018	-
Fe-C ₁	1.847(4)	1.888	2.1
Fe-C ₂	1.854(4)	1.888	-

Natural bond orbital (NBO) calculations were performed to shed light on the nature of the bonding interactions between the metal and the ligands. A set of selected NBOs are given in the tables in figure 3.5. The fractional occupancies are listed for the corresponding NBO. The lone pair on the isocyanide carbon has a lower fractional occupancy than the lone pair of Fe (the full d-orbitals). The isocyanide carbons were found to be the lowest in energy followed by the iron lone pairs. The lone valences (LV) on iron show over a half an electron has been transferred from all sources. These represent the e_g^* orbitals of the ligand field. The BD* NBOs represent the anti-bonding π -orbitals of the isocyanide ligands (only showing 2) which are the highest in energy. A third LV is observed for Fe (II) which is described primarily as an orbital of s-character.

Consider the relevant second order perturbation theory (SOPT) interactions derived from NBO output in the table 3.3. SOPT quantifies donor-acceptor interactions in a molecule.²³ Lewis NBOs (LPs, BDs) are donors and non-Lewis NBOs (LV, BD*) are acceptors. There are hundreds of these interactions, but only the high energy interactions between the metal and isocyanide fragments are considered. The energy is proportional to the energy separation

between donor and acceptor as well as their overlap. These values are reported in the last three columns of table 3.3.

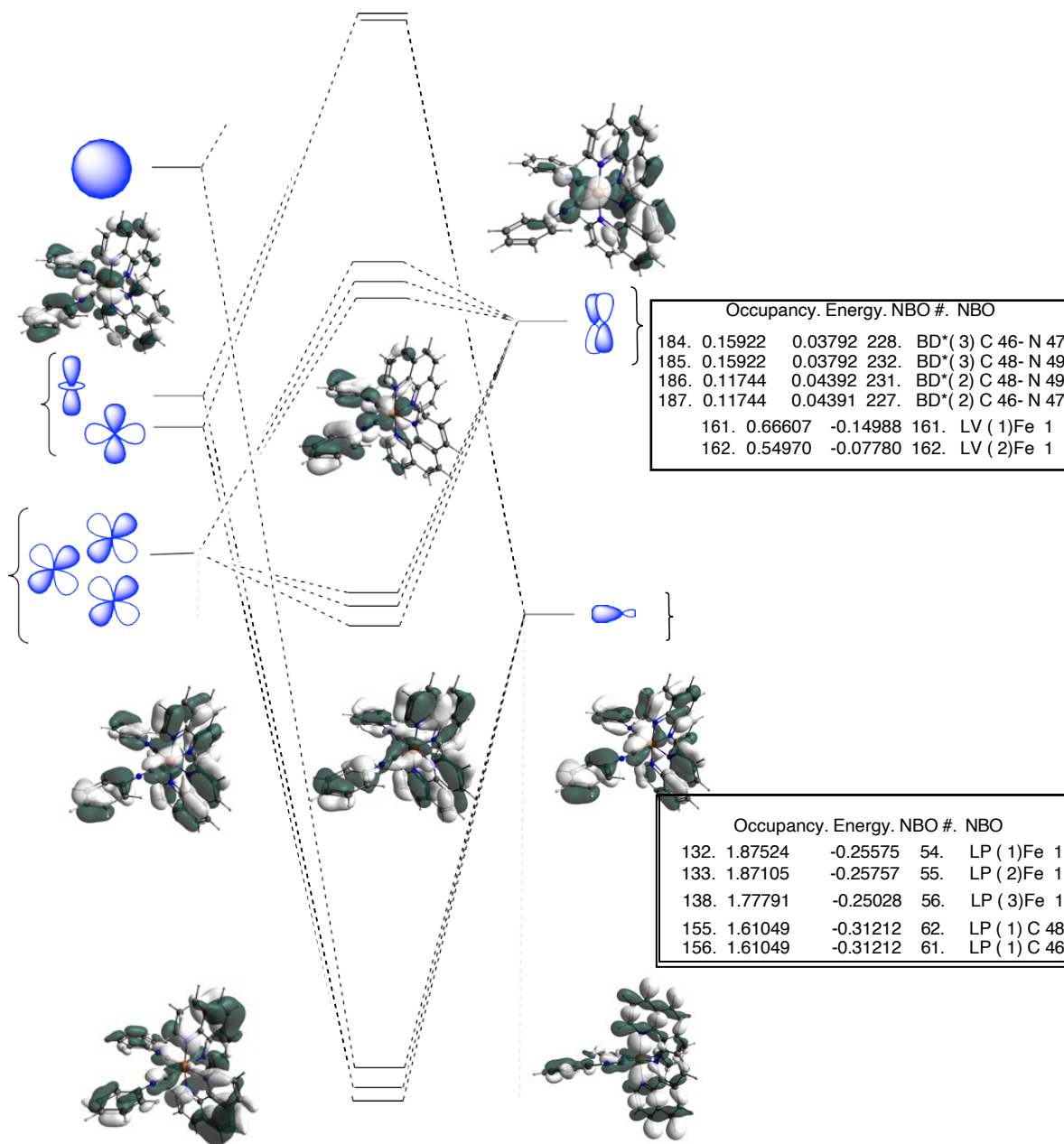


Figure 3.5: Molecular orbital diagram for the bonding in the ligand field of 1. The information in boxes give the energy ordering of the NBOs which are then stabilized by their corresponding SOPT stabilization energy, as given in table 3.3. The MOs are presented in ascending order of energy as they are ordered from computational output.

The dominant isocyanide-iron bonding interaction is the donation of carbon lone pair, donating into a metal-based LVs which corresponds to two pure d and s-orbitals. The interaction with the d-orbitals is 100 kcal/mol. This interaction holds the molecule together. The energy separation is narrow except for the s-orbital which is large. The increased overlap in this orbital is what compensates for the energy gap however, which is expected for a centrosymmetric orbital. Surprisingly back bonding interactions ($LP \rightarrow BD^*$) from a metal based lone pair to π^* -orbitals of the CN bond are very small. In total it represents at most, 9% of the stabilization energy of the LP-LV interactions. Isocyanides are good donors and good acceptors, however the former is highlighted here. The donor-acceptor overlap can be cited as a reason for this however it is not immediately obvious why this would be the case. This lack of π -acidity is consistent with the crystal structures too which exhibit nearly linear CN-R bonds, indicating a lack of back bonding, at least in relative terms.

Table 3.3: Relevant second-order perturbation theory analysis from NBO output of **1**.

	Donor		Acceptor	E2(kcal/mol)	E(A)-E(D)	F(D,A)
LP	(1) C 46	LV	(2)Fe 1	101.40	0.23	0.138
LP	(1) C 48	LV	(2)Fe 1	101.39	0.23	0.138
LP	(1) C 48	LV	(1)Fe 1	100.66	0.16	0.114
LP	(1) C 46	LV	(1)Fe 1	100.64	0.16	0.114
LP	(1) C 46	LV	(3)Fe 1	98.91	1.25	0.314
LP	(1) C 48	LV	(3)Fe 1	98.91	1.25	0.314
LP	(3)Fe 1	BD*	(2) C 46- N 47	9.14	0.29	0.046
LP	(3)Fe 1	BD*	(2) C 48- N 49	9.14	0.29	0.046
LP	(2)Fe 1	BD*	(3) C 46- N 47	5.21	0.30	0.035
LP	(2)Fe 1	BD*	(3) C 48- N 49	5.20	0.30	0.035
LP	(1)Fe 1	BD*	(3) C 48- N 49	4.62	0.29	0.033
LP	(1)Fe 1	BD*	(3) C 46- N 47	4.61	0.29	0.033

The SOPT analysis can be correlated with our MOs for construction of a molecular orbital diagram that mirrors the relative energy orderings found in the calculated molecular orbitals. Metal orbitals from the e_g^* manifold are used to accept electron density from the lone pairs on the isocyanide carbon and are represented as bonding orbitals given by MOs 139 and 141. The most stabilized orbital is the $d_{x^2-y^2}$ due to its excellent overlap with the isocyanide lone pairs is represented in MO 139, which shows axial symmetry in the orbital structure. A similar stabilization is observed in MO 141 but for d_{z^2} . The π bonding interactions represent a stabilization of 5-10 kcal/mol from the Fe lone pairs, which are nearly pure d-orbitals. We can then assume that the non-Lewis CN BD* orbitals destabilize to a similar degree. These represent an anti-bonding interaction given by MOs 158, 159, and 160 as described above. From AOMix calculations, these MOs are mostly metal based, which is not reflected in the diagram above, which would suggest the orbitals are mostly ligand based. The diagram neglects to include donor interactions from the phenanthroline ligands. The overall occupancy of the metal based lone pairs is in line with AOMix calculations.

3.3.4 Absorption Spectra and Electrochemistry

The electronic absorption spectrum of this class of compounds gives absorptions blue of 400 nm in acetonitrile. The figure on the right for **3** is characteristic of this class of complexes. This blue shift likely represents the stabilization of π orbitals associated with both the metal center and isocyanide ligands. As expected, the electrochemistry reflects this too. Electrochemical oxidation occurs at very positive potentials. Across the homologues, oxidation potential increases by 100 mV. The reduction potentials, which change by approximately 30 mV in no particular order. The difference in potentials highlights this increase better and follows the trend set forth in the oxidations. The bulkier complex is harder to oxidize. This could be due to

an increased reorganization energy with larger alkyl substituents directed at the metal center, which is further supported by contradicting an electronic explanation as the **5** should be less deactivating.

Table 3.4: Results of electrochemistry experiments. The voltammograms are presented in the supplementary information.

Complex	E_{ox} (V vs. Fc/Fc ⁺)	E_{red} (V vs. Fc/Fc ⁺)	$E_{\text{ox}}-E_{\text{red}}$ (eV)	I_c/I_a	E_p (V)
1	1.256	-1.596	2.852	2	0.064
3	1.272	-1.620	2.892	4	0.074
4	1.336	-1.592	2.928	8	0.078
5	1.340	-1.604	2.944	13	0.080

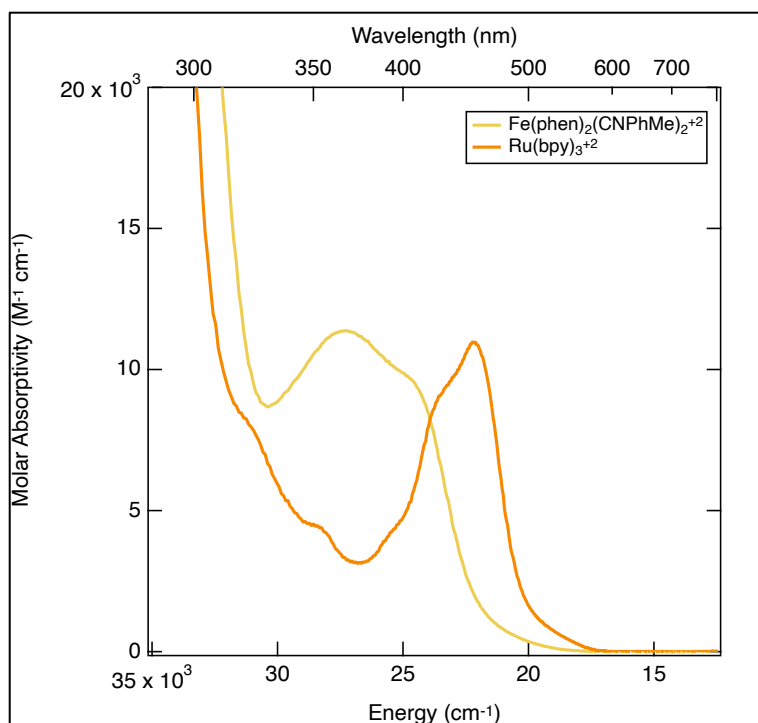


Figure 3.6: Electronic absorption spectrum of **3** overlain with [Ru(bpy)₃](PF₆)₂ in MeCN solution. The absorption of this MLCT surpasses that of the ruthenium complex, and is uncommon of Fe(II) complexes.

This increased reorganization energy could only be modeled as a Fe-C bond contraction, as there is very little evidence of back bonding in the Fe(II) structures. This bond contraction moves the alkyl substituents closer to the metal center, which is less favorable with larger

substituents, which must reorganize themselves to facilitate bonding. This increased reorganization energy slows the rate of electron transfer at the metal center, thus requiring overpotential. The difference in peak separation is consistent with this hypothesis, given that the sweep rate is fixed to 100 mV/s. This is clearly not present in the reduction case. In the series, the Fe(III) ion should have approximately the same Lewis acidity without a significant basicity increase of the isocyanide. Because the Fe-C bond is destabilized by bulkier groups explains the chemical irreversibility of the cathodic/anodic current ratios, which increase across the series.

3.3.5 Reaction with amines

The reaction of isocyanide ligands with amines, leads to the formation of electron rich carbenes in plenty of varieties. Rules have been formulated that correlate the electrophilicity of the carbon atom to its IR stretching frequency.³¹ Thus, the ability of a complex to react with amines depends on the shift in CN stretching frequency between free and complexed isocyanides. A shift to a higher energy (i.e. $\Delta\nu = \nu_{bound} - \nu_{free} > 0$) is indicative of electrophilic activation and thus will lead to reaction. In contrast, a negative value will not react. In the latter case when the metal center acts as a strong π -base, the electron density is too high to favor productive interactions with the nucleophile. This has led researchers like Teets and co-workers to use electron-withdrawing substituents in deactivated Ir(III) systems in order to form stable carbenes, when less deactivating varieties did not work.¹⁸ Table 3.5 reports the stretching frequencies of several of the systems under consideration. Due to their general unpleasantness and the public nature of the ATIR spectrometer, the free isocyanides were not characterized but were found from literature sources. The positive $\Delta\nu$ suggests all can react with amines. The lack of back bonding is consistent with this increased electrophilicity.

Table 3.5: Isocyanide stretching frequencies for relevant complexes.

Complex	ν_{asym} (cm ⁻¹)	ν_{sym} (cm ⁻¹)
1	2136	2165
3	2132	2159
4	2123	2155
5	2126	2160

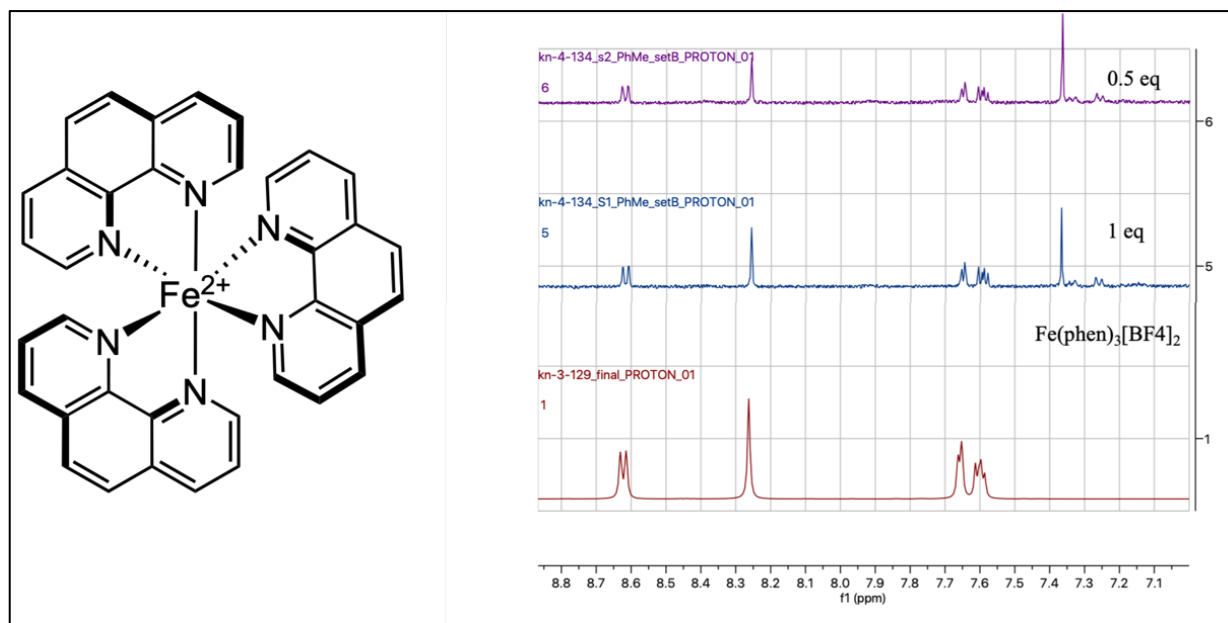


Figure 3.7: (left) structure of the $[\text{Fe}(\text{phen})_3]^{2+}$ cation. (right) The NMR spectrum of the described titration of $[\text{Fe}(\text{phen})_2(\text{CNPhMe})_2](\text{BF}_4)_2$. Note that even at 0.5 equivalents of hydrazine the reaction still proceeds to form the tris-phenanthroline complex. This was performed for several more equivalents (not shown) including 2, 5, and 10 eq.

When reacting **6** with 0.5 equivalents of hydrazine the starting material is quantitatively decomposed to form the D_3 symmetry complex and some aromatic material. Note the sharp resonance at 7.37 is not part of free isocyanide but rather some derivative thereof and is inversely correlated with hydrazine equivalence. The complete loss of starting material at 0.5 eq hints at a reaction of hydrazine with isocyanide with at least a 2:1 ratio.

When complex **3** was utilized however, which has methyl groups adjacent to the CN functionality, the starting material is stable to hydrazine as shown in the NMR. At 0.5 equivalents a small amount of product is formed which increases with successive equivalents.

Also in there is a significant density of under resolved resonances around 7.25 ppm, the region commonly associated with the free isocyanide. In the 1 and 2 equivalent cases, a resonance grows at 9.15 ppm, assigned to the deprotonated carbene. Resonances downfield of 9 ppm are generally not associated with carbene species. At two equivalents, most of the starting material has been reacted. The growth of a resonance around 6.8 ppm accompanied the loss of starting material. While this is not well resolved and does not align well with the free isocyanide but could be related to some breakdown product. Interestingly, the resonance at 7.38 ppm occurs here too. The similarity between experiments suggests this species is likely due to a salt of hydrazine, which would be consistent between experiments. This is expected from Costanzo et. al. who observed the slow attack of the isocyanide followed by a fast acid/base equilibrium. A similar experiment was performed for the methyl isocyanide species $[\text{Fe}(\text{phen})_2(\text{CNMe})_2]^{2+}$. The loss of starting material occurs much more slowly and there is no increase in any signal that could be described as a side product. At two equivalents, the product and starting material are roughly equal in concentration. This is best illustrated by the methyl resonances around 3.45 ppm. The sharp resonance at 7.38 ppm shows up again but only minorly consistent with the reduce amount of acidic carbene species present.

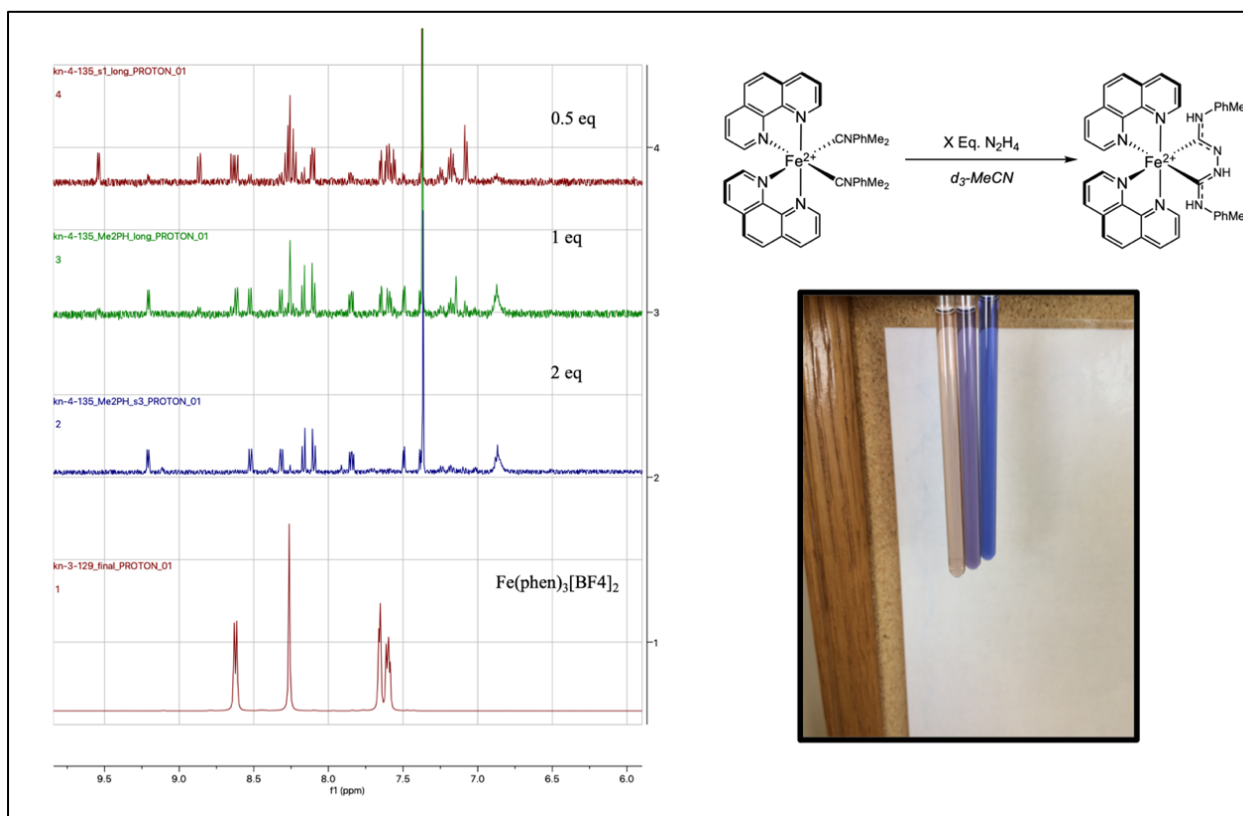


Figure 3.8: (left) NMR spectrum of the hydrazine titration of **3** which includes the spectrum of $[\text{Fe}(\text{phen})_3]^{2+}$ complex for comparison. The reaction is depicted on the right along with the resulting-colored solutions for both 0.5, 1, and 2 equivalents respectively.

The results above highlight several important things for understanding the reactivity of these species. First, that the decomposition occurs somewhere along the path of carbene formation. This supported by the increased rate of starting material loss in the aryl varieties compared to that of the alkyl variety. The more electropositive isocyanide carbon of the aryl groups should favor a faster reaction with hydrazine compared to the alkyl variety. This makes the forward reaction more likely to outcompete any other reactions that could diverge off the main reaction path. Second, the pathway of decomposition is related to differences in the structures. The complexes **6** and **3** likely have similar propensities to degrade, but the presence of the methyl groups provide stability.

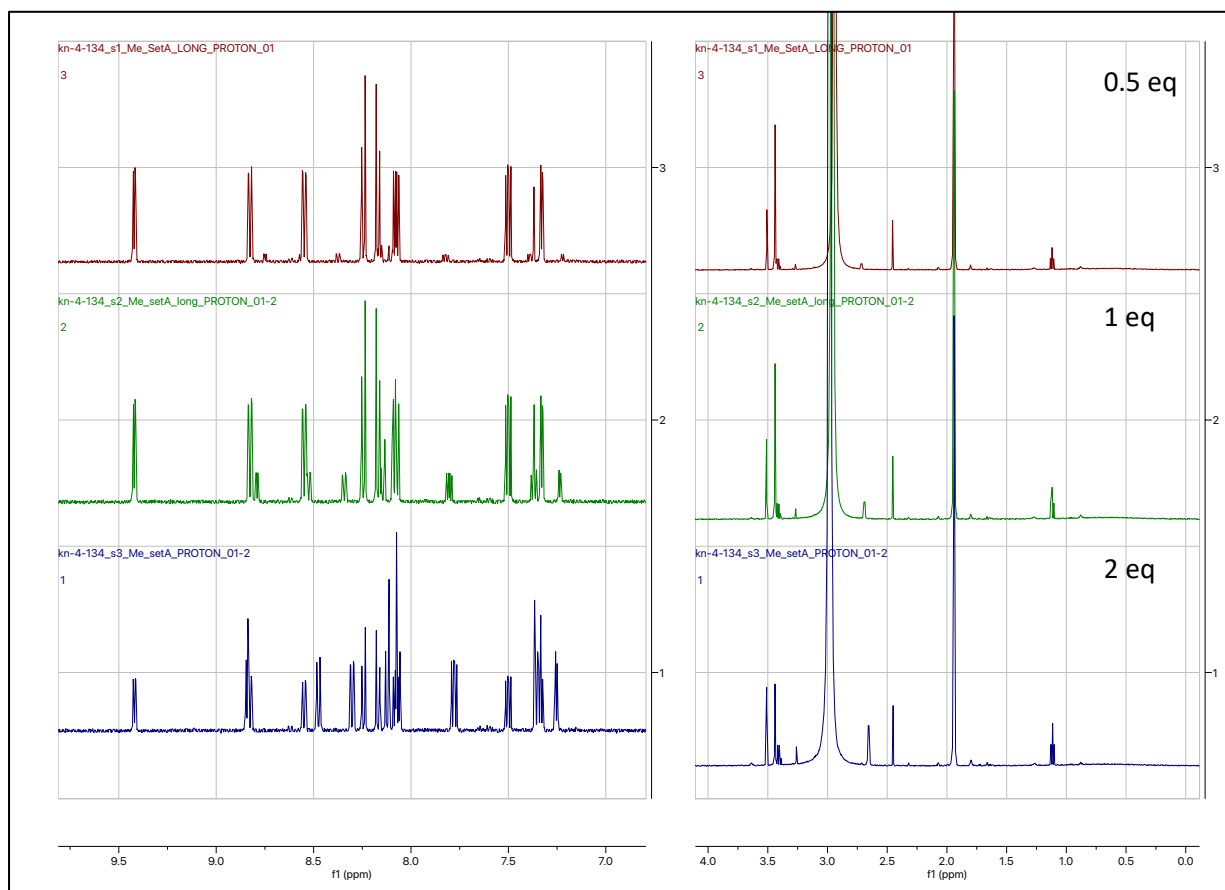


Figure 3.9: Titration experiment of $\text{Fe}(\text{phen})_2(\text{CNMe})_2[\text{BF}_4]_2$ with hydrazine in 0.5, 1, and 2 equivalents. Aromatic region shows the growth of the product carbene species. The aliphatic region shows proportional changes of the deshielded methyl protons around 3.5 ppm.

To address the mechanism of decomposition further, time resolved IR was performed. This, however, represents a work in progress and the data and some preliminary analyses are described in the appendix.

3.4 CONCLUSION AND FUTURE WORKS

Several novel $\text{Fe}(\text{II})$ isocyanides were synthesized. Structural analysis showed minor differences in bond lengths but large similarities in the configuration of the isocyanides themselves. NBO calculations suggest that the main bonding character is the donation of the isocyanide lone pair to the metal center, with very little back bonding compared to other species, indicated by the isocyanide bond angle C-N-R of $\sim 175^\circ$ of all species from x-ray structural

analyses. Reactivity of the complexes with hydrazine was found to require substitutions in the positions α to the isocyanides to avoid quantitative decomposition to unwanted side products. The optimized synthesis of the carbenes derived from **3**, **4**, and **5** are discussed in the next chapter. This dissociation is consistent with a bonding configuration that is primarily σ -covalent which is then prone to displacement upon formation of the first carbene.

The observations in this report allude to some of the limitations of isocyanides as ligands for the purposes of the y-axis strategy. Although photophysical characterization has not been performed in any robust manner, the structural features of the complexes studied here suggest that the dual nature of the isocyanides, which can in theory act as both σ -donors and π -acceptors, does not seem to be the case for Fe(II). This can be further illustrated by considering the balance between columbic attraction and the oxidation potential of a metal, which are inversely correlated.

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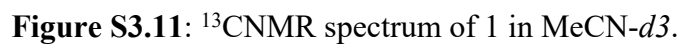
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3.6.1 NMRs of Compounds Discussed



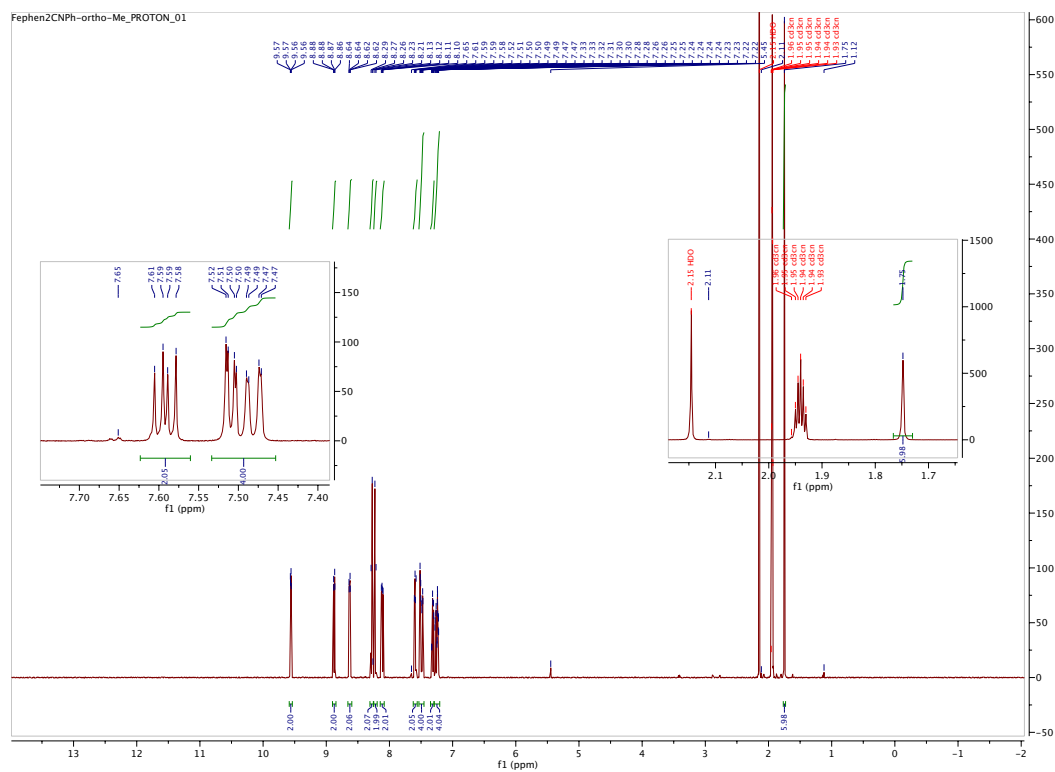


Figure S3.12: ^1H NMR spectrum of 2 in MeCN- d_3 .

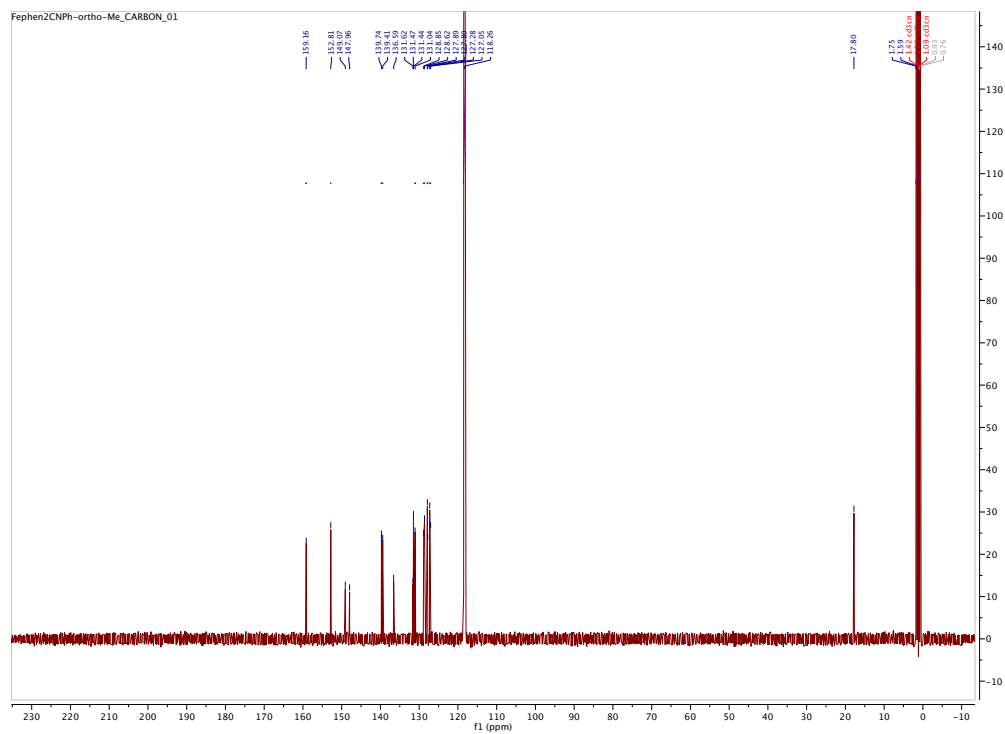


Figure S3.13: ^{13}C NMR spectrum of **2** in MeCN- d_3 .

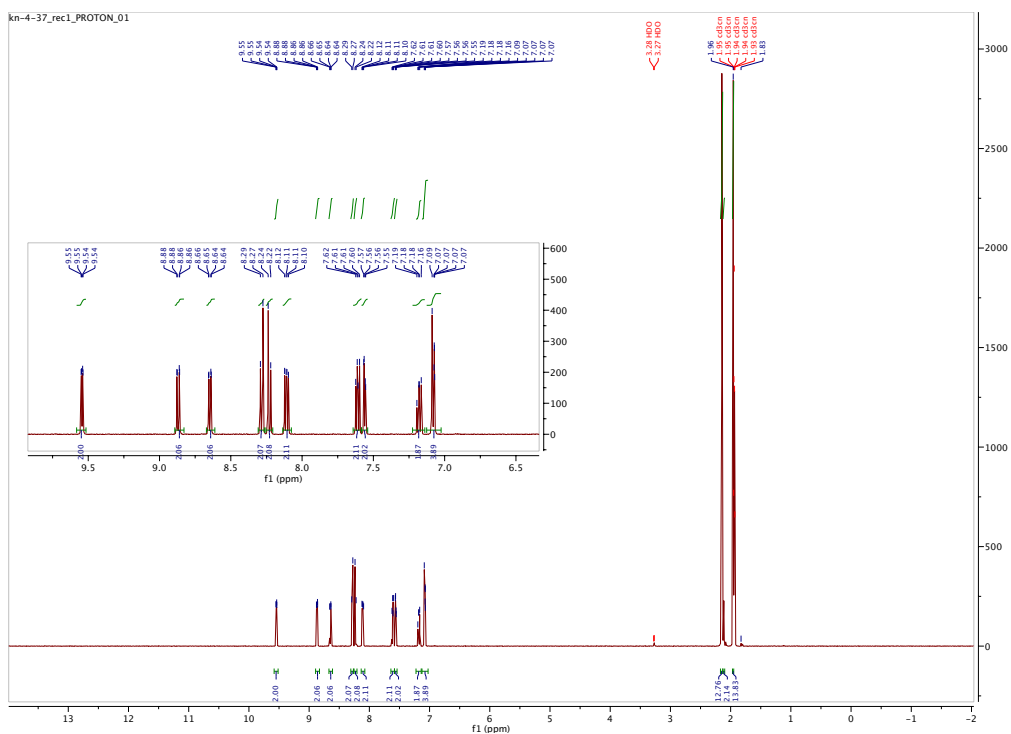


Figure S3.14: ^1H NMR spectrum of **3** in $\text{MeCN-}d_3$.

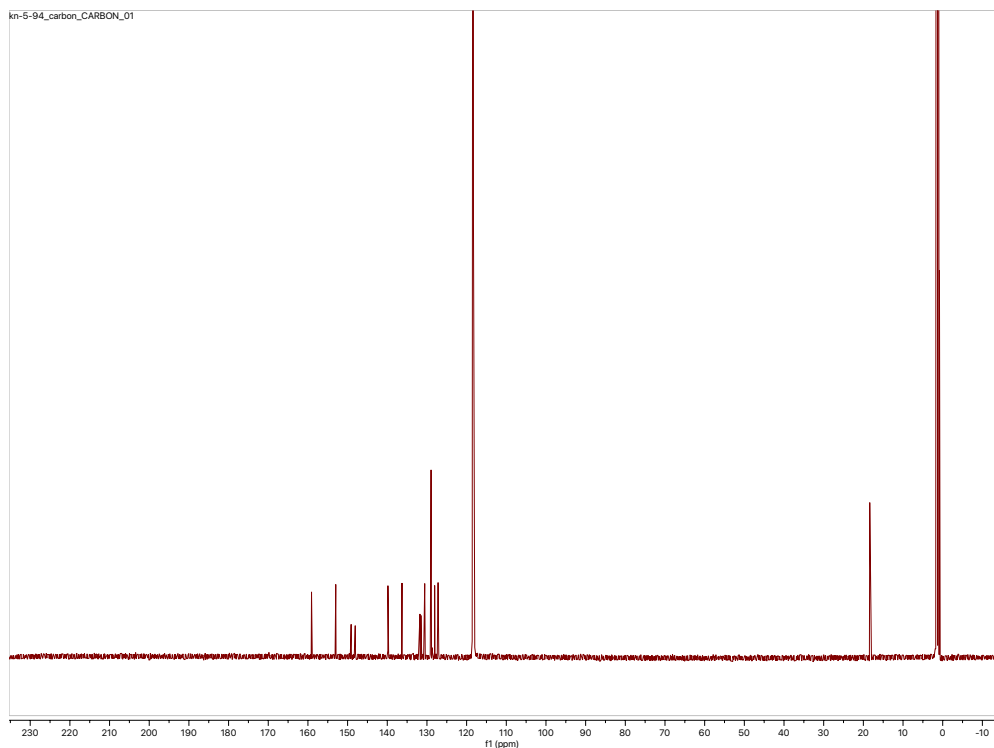


Figure S3.15: ^{13}C NMR spectrum of **3** in $\text{MeCN-}d_3$.

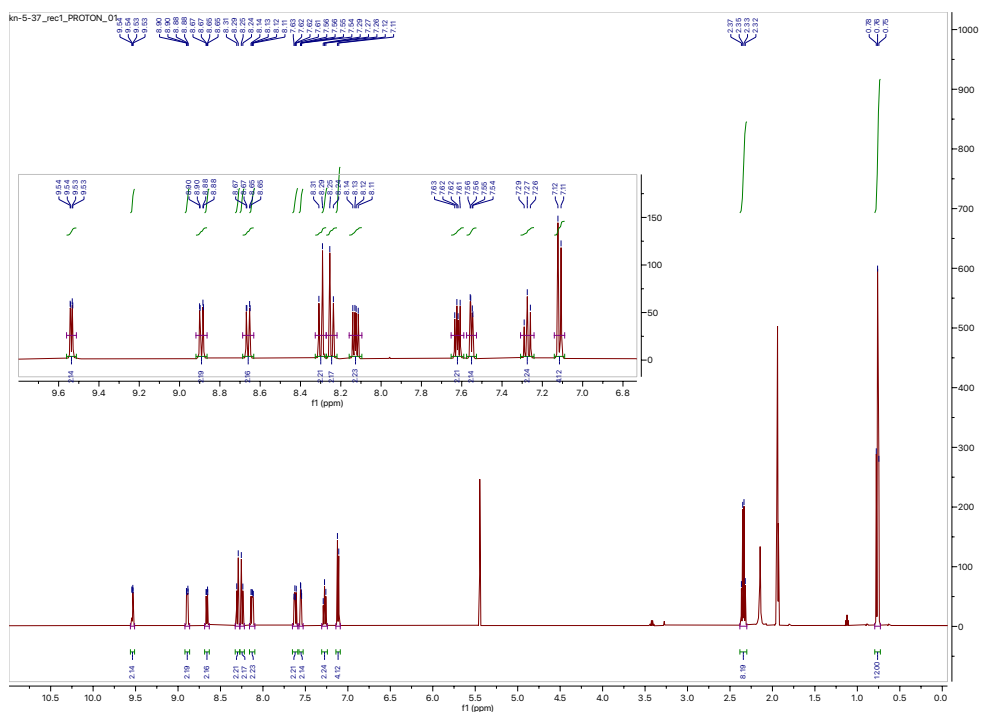


Figure S3.16: ^1H NMR spectrum of **4** in $\text{MeCN-}d_3$. Spectrum includes some residual dichloromethane from attempted recrystallizations.

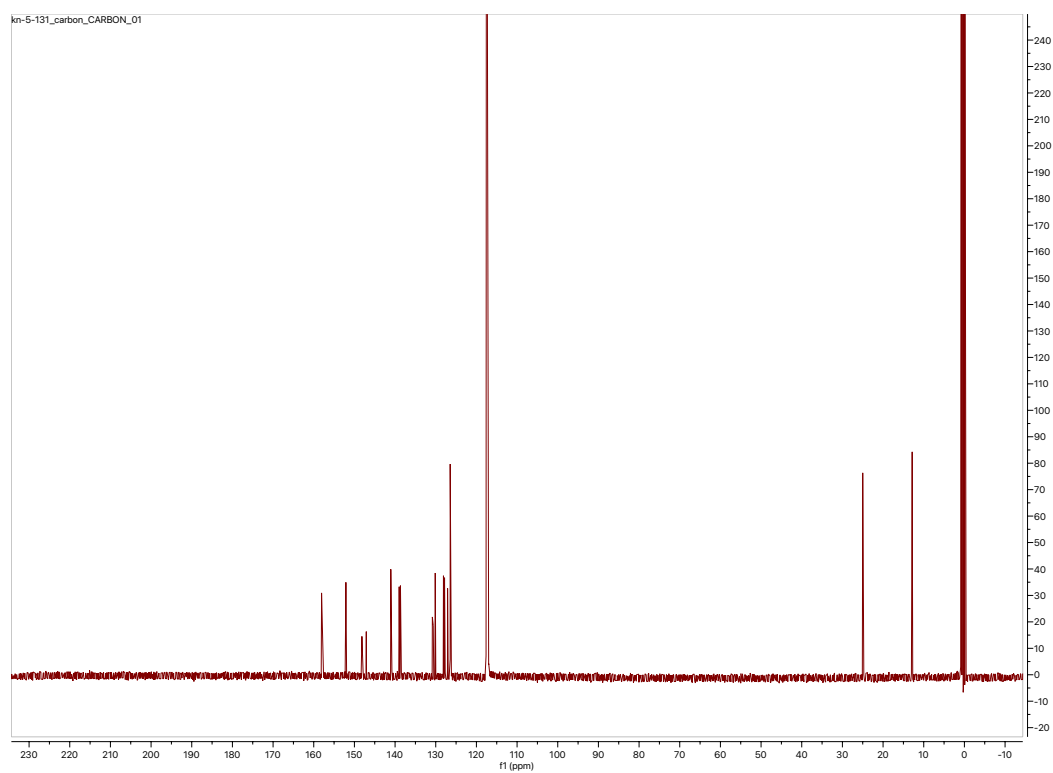


Figure S3.17: ^{13}C NMR spectrum of **4** in $\text{MeCN-}d_3$.

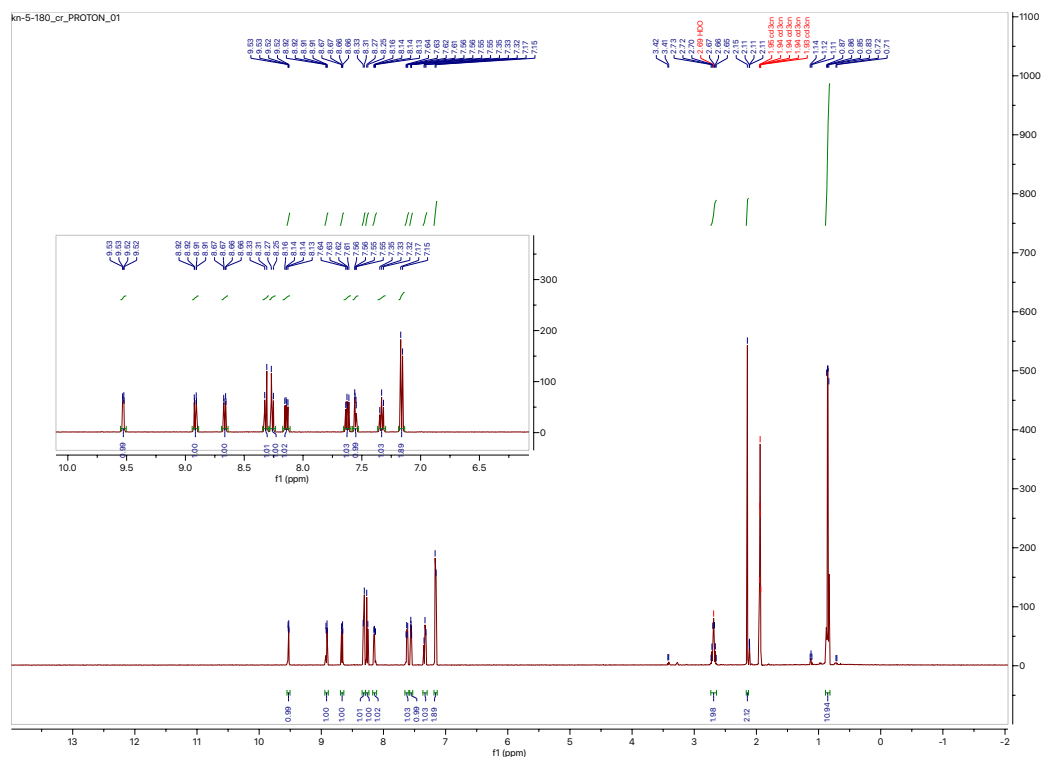


Figure S3.18: ^1H NMR spectrum of 5 in $\text{MeCN-}d_3$.

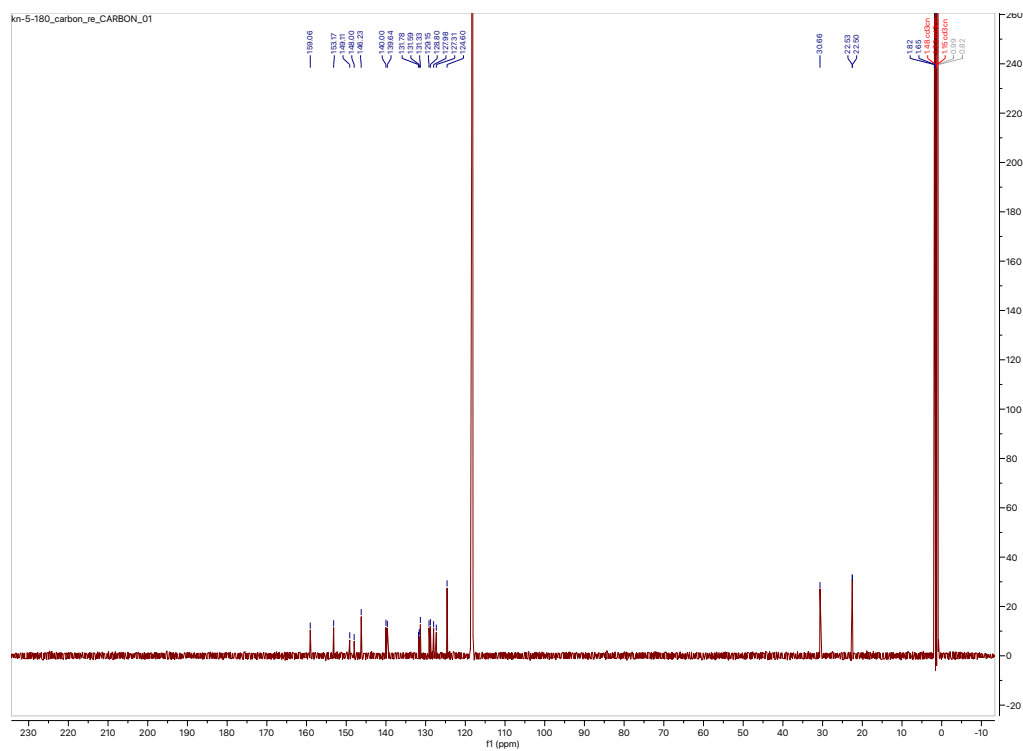
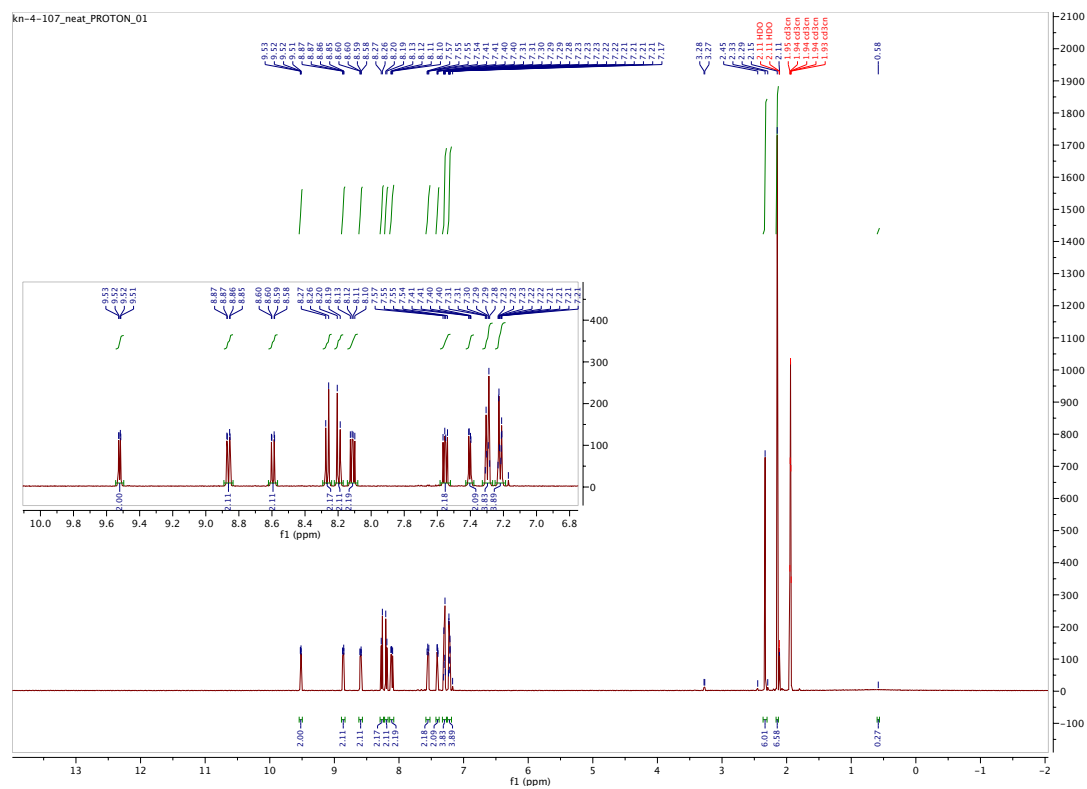


Figure S3.19: ^{13}C NMR spectrum of 5 in $\text{MeCN-}d_3$.



3.6.2 FTIR of Some Compounds Discussed

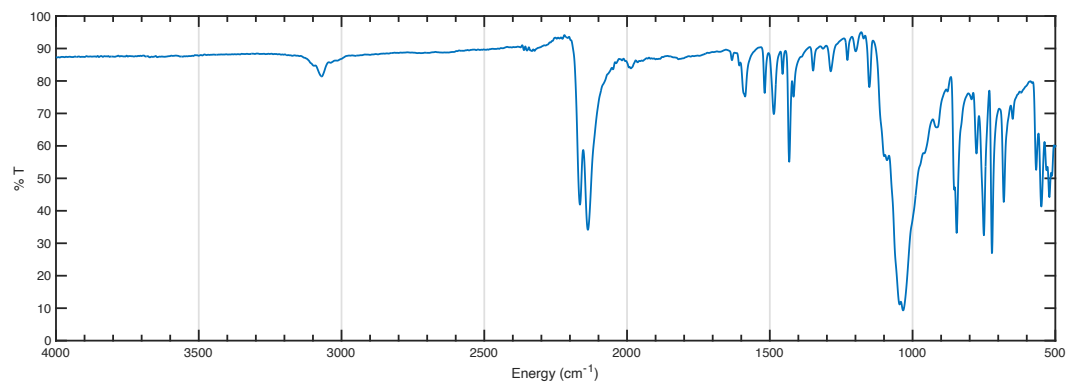


Figure S3.21: FTIR spectrum of 1.

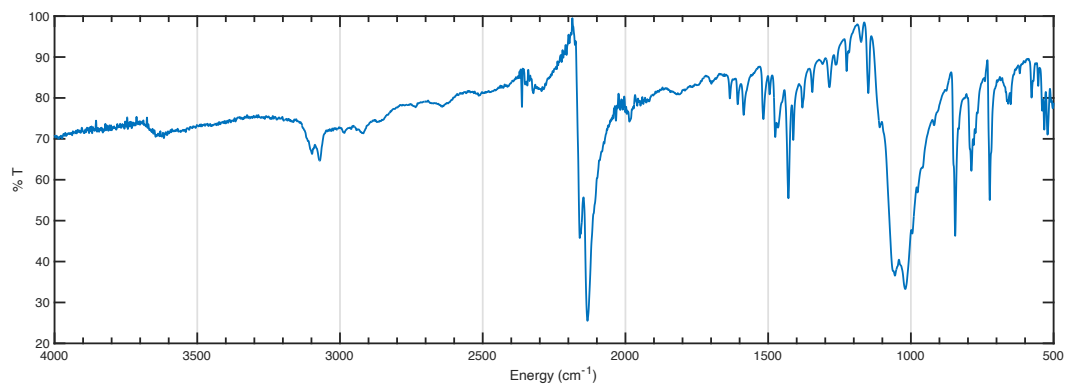


Figure S3.22: FTIR spectrum of 3.

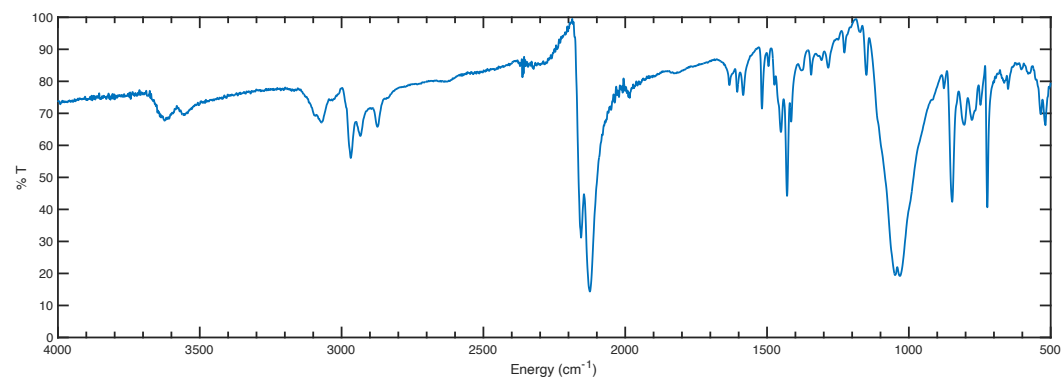


Figure S3.23: FTIR spectrum 4.

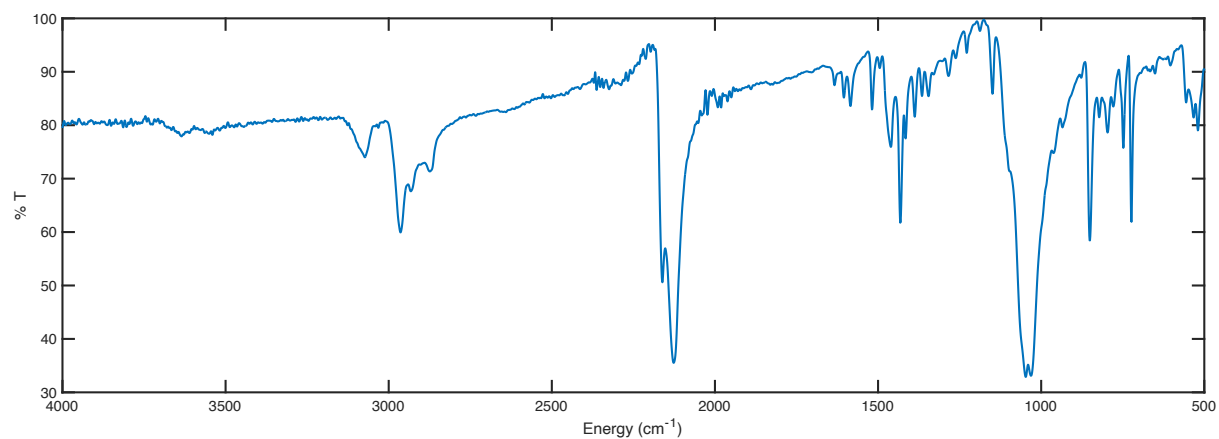


Figure S3.24: FTIR spectrum of 5.

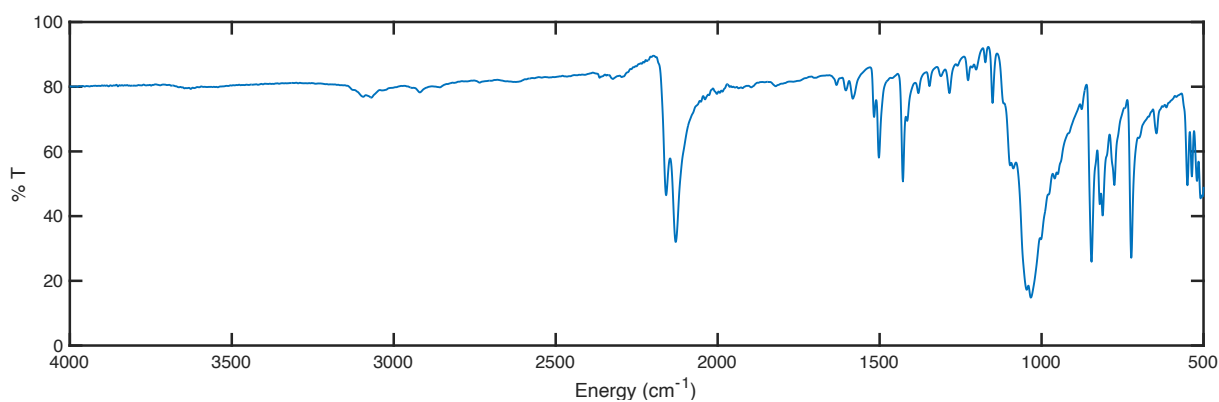


Figure S3.25: FTIR spectrum of 6.

3.6.3 UV-Vis Spectra of Some of the Complexes Discussed

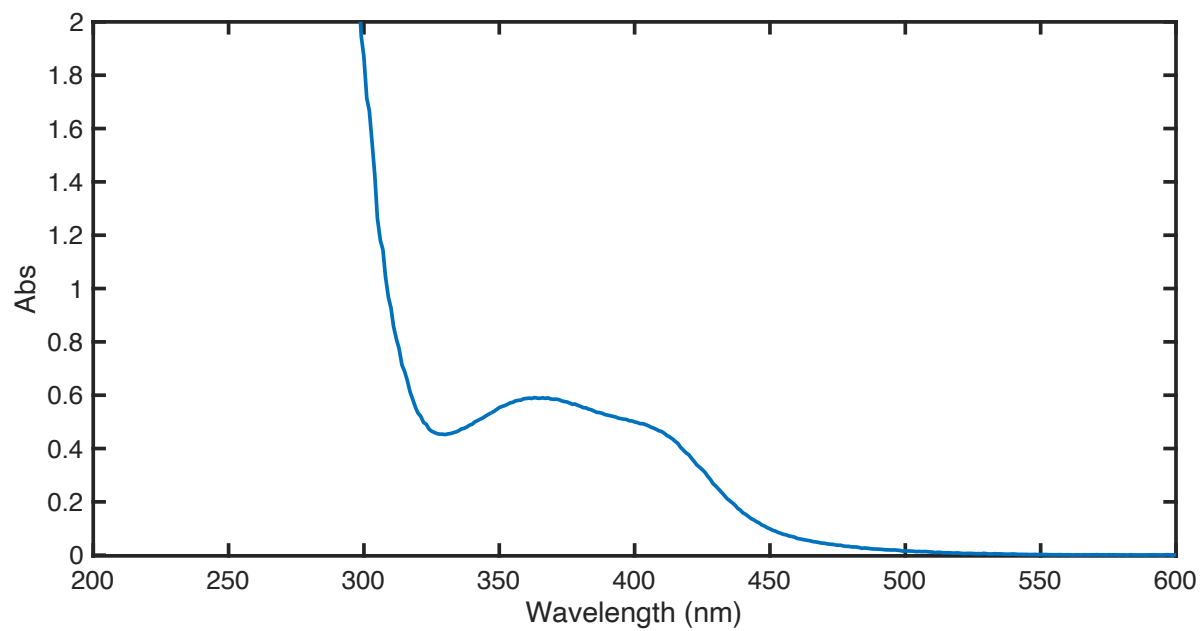


Figure S3.26: UV-Vis spectrum of 1 in acetonitrile.

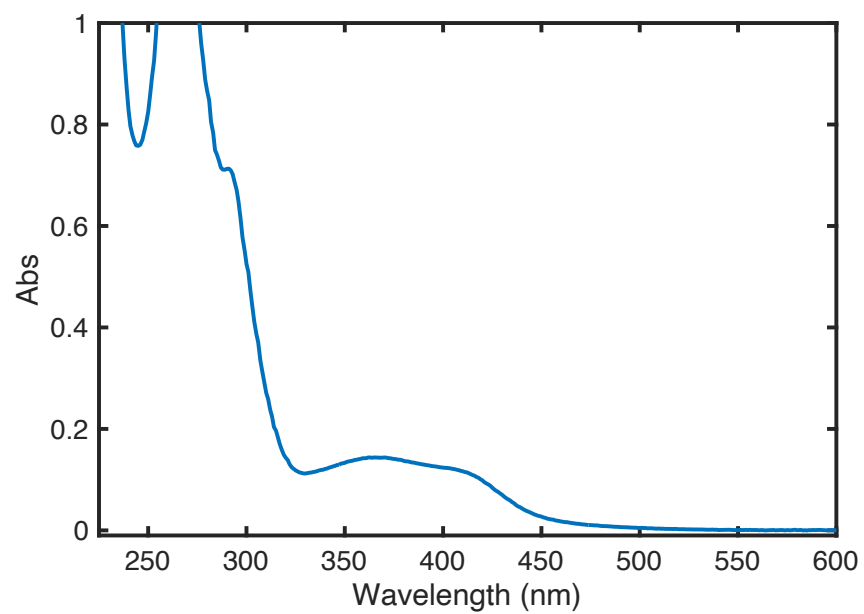


Figure S3.27: UV-Vis spectrum of 4 in acetonitrile.

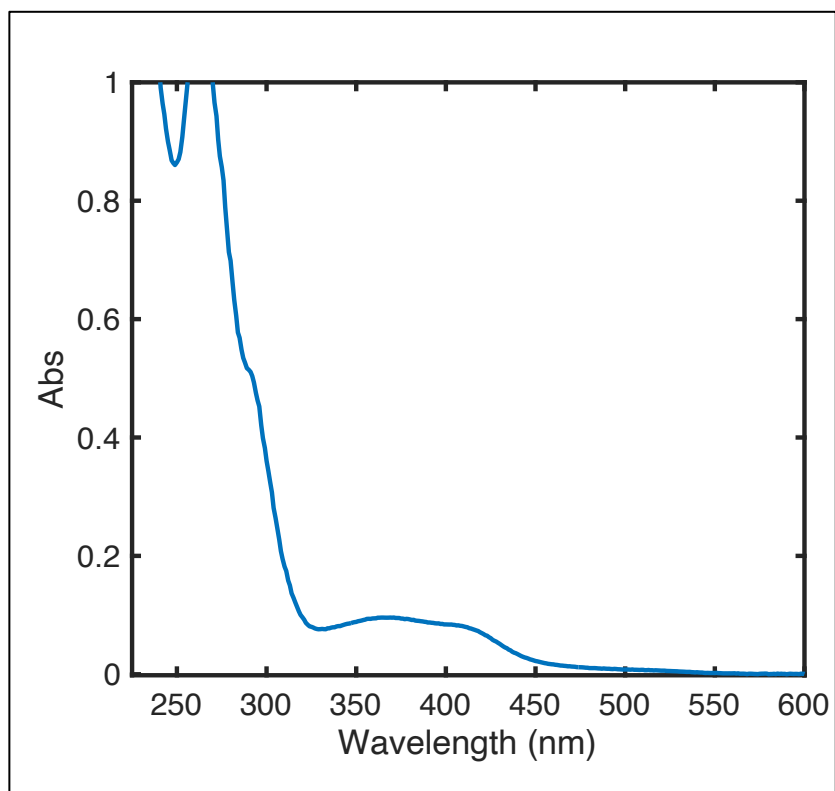


Figure S3.28: UV-Vis spectrum of 5 in acetonitrile.

3.6.4 Crystal Structures of some Complexes Discussed

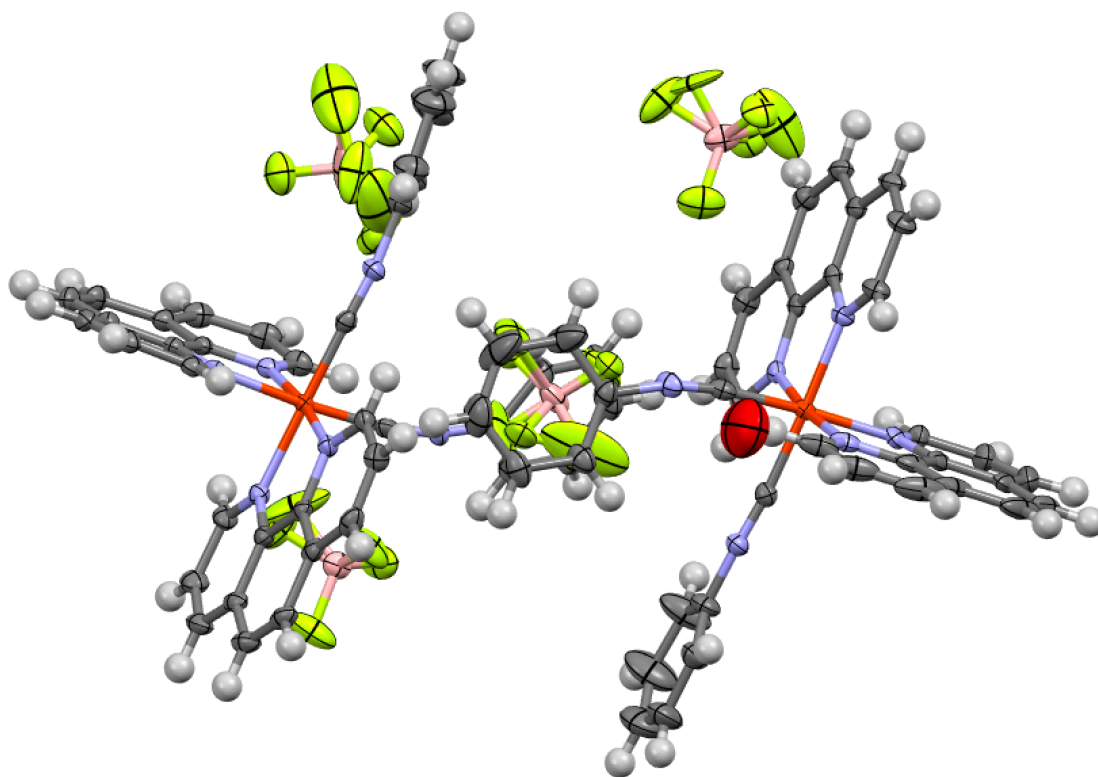


Figure S3.29: Crystal Structure of **1**. Orange: iron, purple: nitrogen, grey: carbon, pink: boron, yellow: fluorine, hydrogen: white, oxygen: red. Thermal ellipsoids at 50% probability.

Table S3.6: Crystal Structure and refinement for **1**

Identification code	kn-5-121
Empirical formula	C ₇₆ H _{52.5} B ₄ F ₁₆ Fe ₂ N ₁₂ O _{0.24}
Formula weight	1596.58
Temperature/K	100.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	10.4981(2)
b/Å	17.1814(4)
c/Å	20.9703(4)
α /°	80.605(2)
β /°	85.477(2)
γ /°	72.994(2)
Volume/Å ³	3566.61(13)
Z	2
ρ_{calc} /g/cm ³	1.487
μ /mm ⁻¹	4.102
F(000)	1621.0
Crystal size/mm ³	0.104 × 0.076 × 0.046
Radiation	Cu K α (λ = 1.54184)
2 Θ range for data collection/°	5.438 to 154.208
Index ranges	-13 ≤ h ≤ 12, -21 ≤ k ≤ 20, -17 ≤ l ≤ 26
Reflections collected	46467
Independent reflections	14320 [R_{int} = 0.0324, R_{sigma} = 0.0341]
Data/restraints/parameters	14320/0/1081
Goodness-of-fit on F ²	1.132
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0718, wR_2 = 0.1806
Final R indexes [all data]	R_1 = 0.0769, wR_2 = 0.1832
Largest diff. peak/hole / e Å ⁻³	0.77/-0.51

Table S3.7: Bond Lengths for **1** is available upon request.

Table S3.8: Bond Angles for **1** is available upon request.

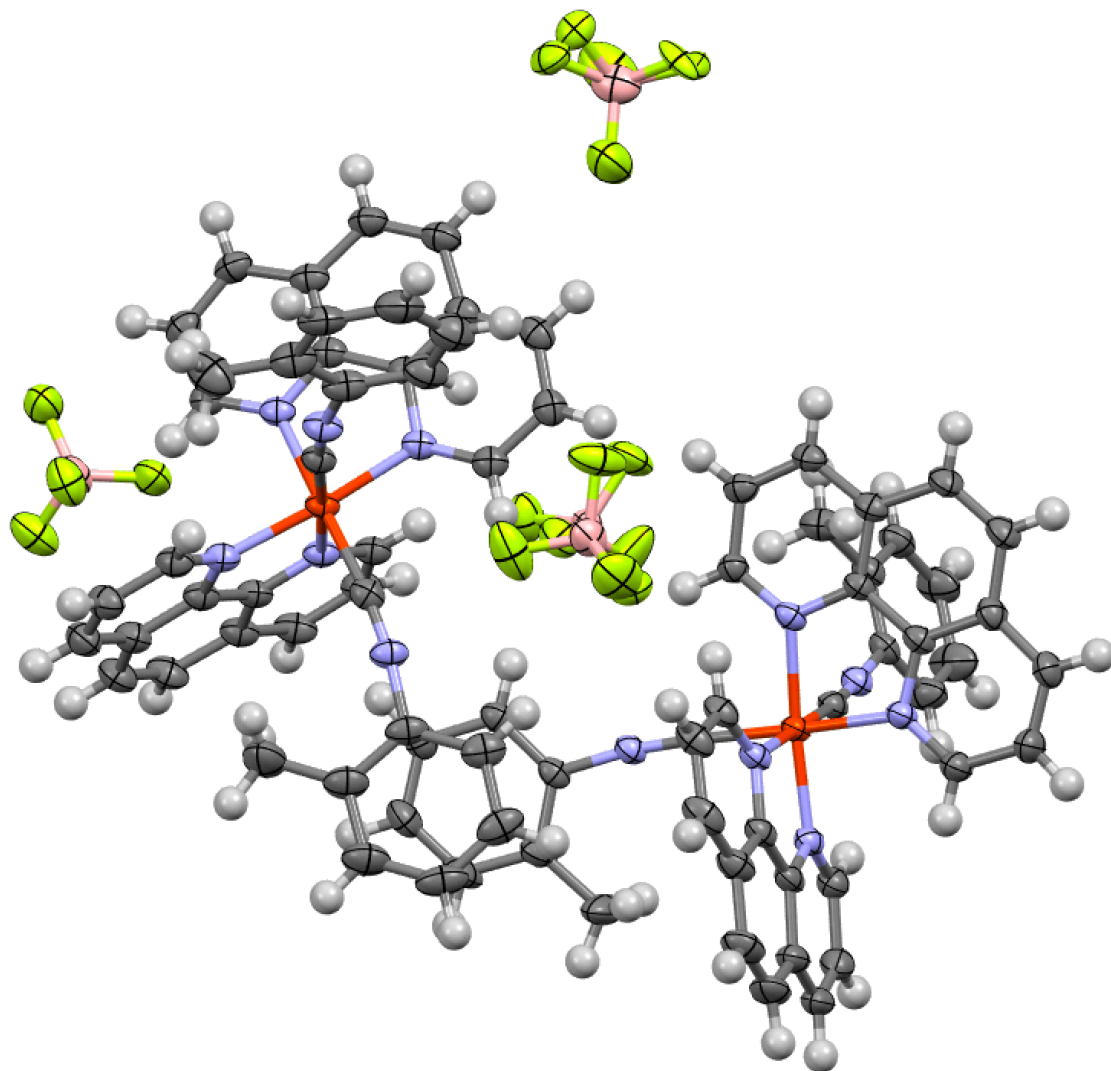


Figure S3.30: Crystal Structure of **2**. Orange: iron, purple: nitrogen, grey: carbon, pink: boron, yellow: fluorine, hydrogen: white, oxygen: red. Thermal ellipsoids at 50% probability.

Table S3.9: Crystal data and structure refinement of **2**. Note some atoms are split.

Identification code	kn-4-152_auto
Empirical formula	C _{45.71} H _{34.29} B _{2.29} F _{9.09} Fe _{1.14} N _{6.85}
Formula weight	940.74
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	P2 ₁ /n
a/Å	18.0085(2)
b/Å	21.7285(2)
c/Å	18.8066(2)
α /°	90
β /°	98.2360(10)
γ /°	90
Volume/Å ³	7283.08(13)
Z	7
ρ_{calc} /g/cm ³	1.501
μ /mm ⁻¹	4.031
F(000)	3356.0
Crystal size/mm ³	0.286 × 0.24 × 0.126
Radiation	Cu K α (λ = 1.54184)
2 Θ range for data collection/°	6.252 to 153.77
Index ranges	-17 ≤ h ≤ 22, -25 ≤ k ≤ 26, -23 ≤ l ≤ 21
Reflections collected	59581
Independent reflections	14518 [R_{int} = 0.0385, R_{sigma} = 0.0324]
Data/restraints/parameters	14518/0/1077
Goodness-of-fit on F ²	1.039
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0557, wR_2 = 0.1597
Final R indexes [all data]	R_1 = 0.0625, wR_2 = 0.1655
Largest diff. peak/hole / e Å ⁻³	1.12/-0.48

Table S3.10: Bond Lengths for **2** is available upon request.

Table S3.11: Bond Angles for **2** is available upon request.

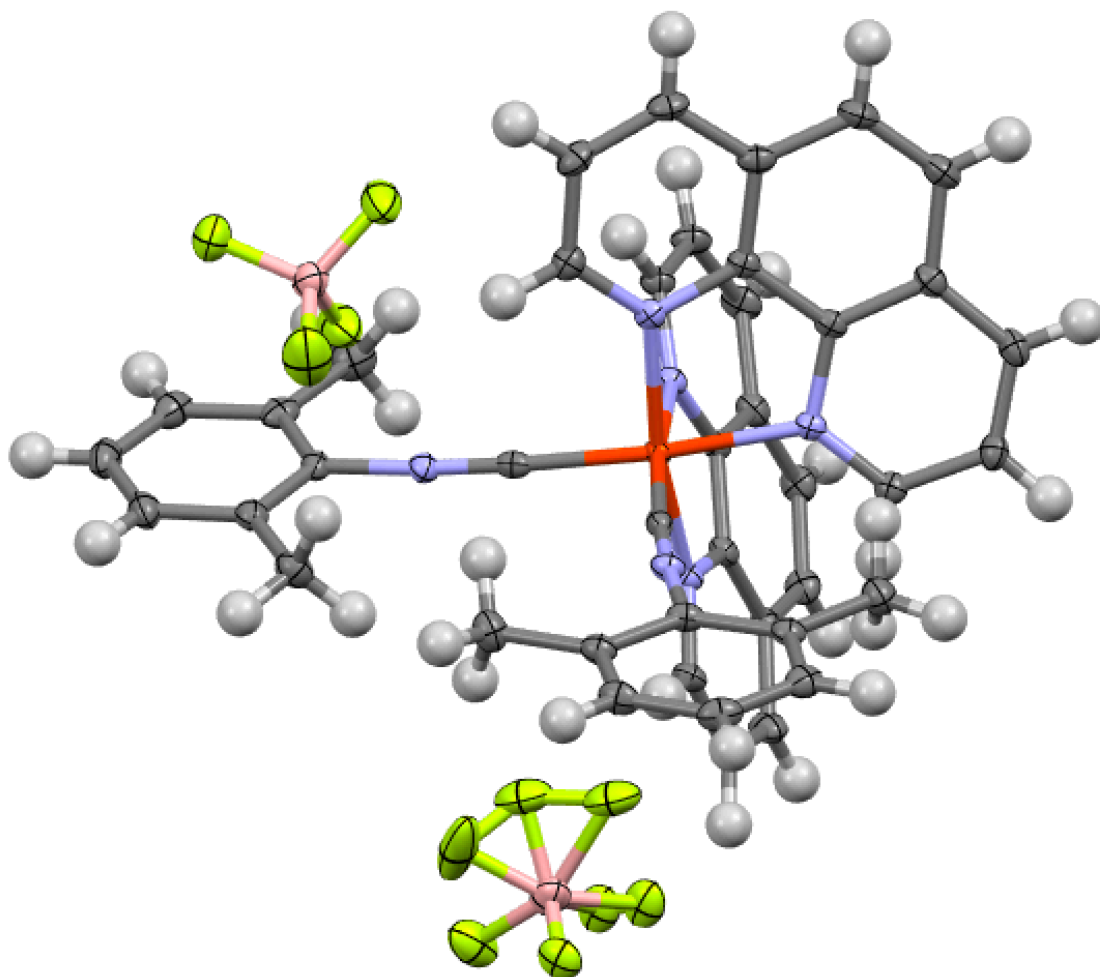


Figure S3.31: Crystal Structure of **3**. Orange: iron, purple: nitrogen, grey: carbon, pink: boron, yellow: fluorine, hydrogen: white, oxygen: red. Thermal ellipsoids at 50% probability.

Table S3.12: Crystal data and structure refinement of **3**.

Identification code	exp_395
Empirical formula	C ₄₂ H ₃₄ B ₂ F ₈ FeN ₆
Formula weight	852.22
Temperature/K	100.01(10)
Crystal system	triclinic
Space group	P-1
a/Å	8.83501(14)
b/Å	12.93210(15)
c/Å	18.2922(2)
$\alpha/^\circ$	101.9966(11)
$\beta/^\circ$	95.3655(12)
$\gamma/^\circ$	108.4700(12)
Volume/Å ³	1910.22(5)
Z	2
$\rho_{\text{calc}}/\text{g cm}^{-3}$	1.482
μ/mm^{-1}	3.864
F(000)	872.0
Crystal size/mm ³	0.386 × 0.274 × 0.141
Radiation	Cu K α (λ = 1.54184)
2 θ range for data collection/ $^\circ$	5.014 to 154.728
Index ranges	-10 ≤ h ≤ 11, -16 ≤ k ≤ 16, -23 ≤ l ≤ 17
Reflections collected	42662
Independent reflections	7835 [R_{int} = 0.0513, R_{sigma} = 0.0316]
Data/restraints/parameters	7835/15/552
Goodness-of-fit on F ²	1.066
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0395, wR_2 = 0.1047
Final R indexes [all data]	R_1 = 0.0408, wR_2 = 0.1056
Largest diff. peak/hole / e Å ⁻³	1.05/-0.53

Table S3.13: Bond Lengths for **3** is available upon request.**Table S3.14:** Bond Angles for **3** is available upon request.

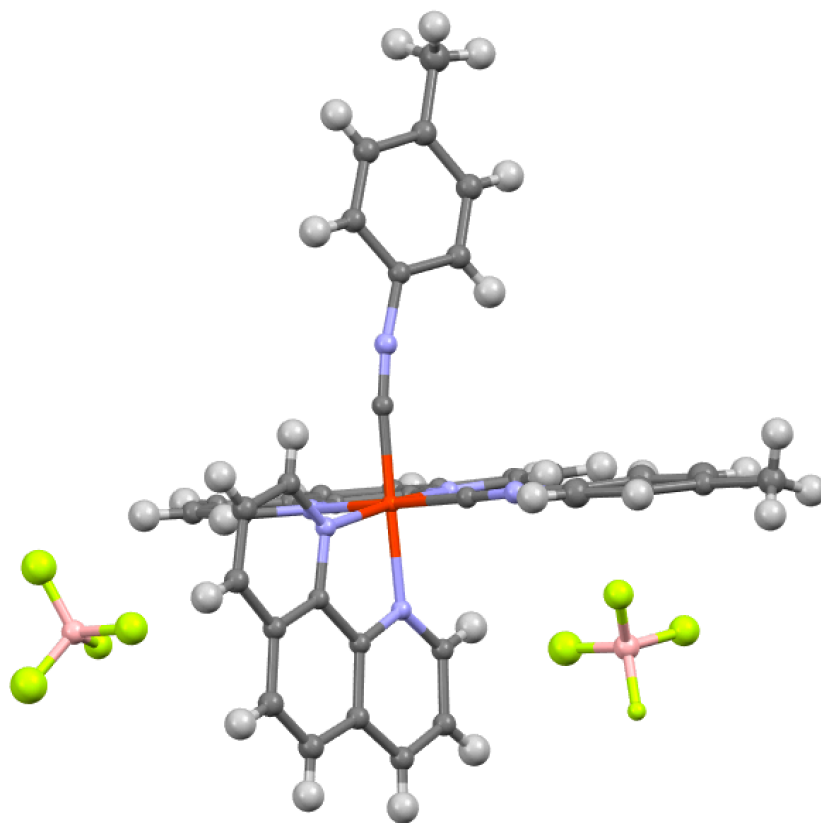


Figure S3.32: Crystal structure of **6**. Orange: iron, purple: nitrogen, grey: carbon, pink: boron, yellow: fluorine, hydrogen: white, oxygen: red. Thermal ellipsoids at 50% probability.

Table S3.15: Bond Lengths for **6** is available upon request.

Table S3.16: Bond Angles for **6** is available upon request.

3.3.5 Electrochemistry

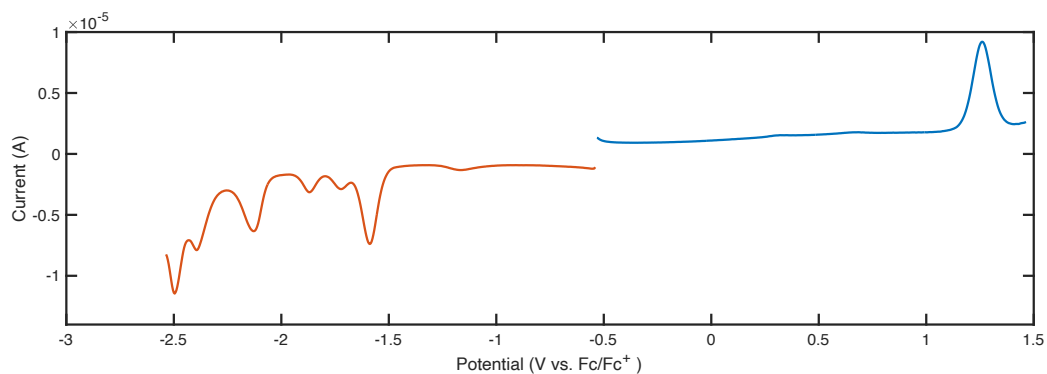


Figure S3.33: Differential pulse voltammogram for 1.

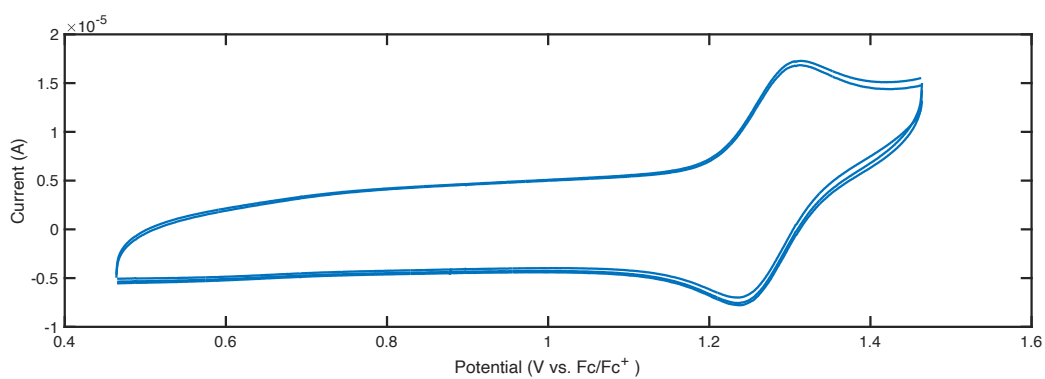


Figure S3.34: Oxidative cyclic voltammogram for 1. Scan rate 100 mv/s.

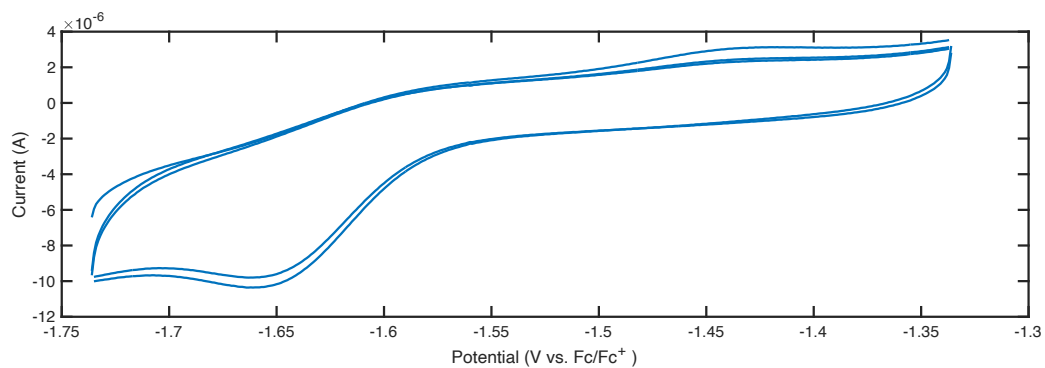


Figure S3.35: Reductive cyclic voltammogram for 1. Scan rate 500 mv/s.

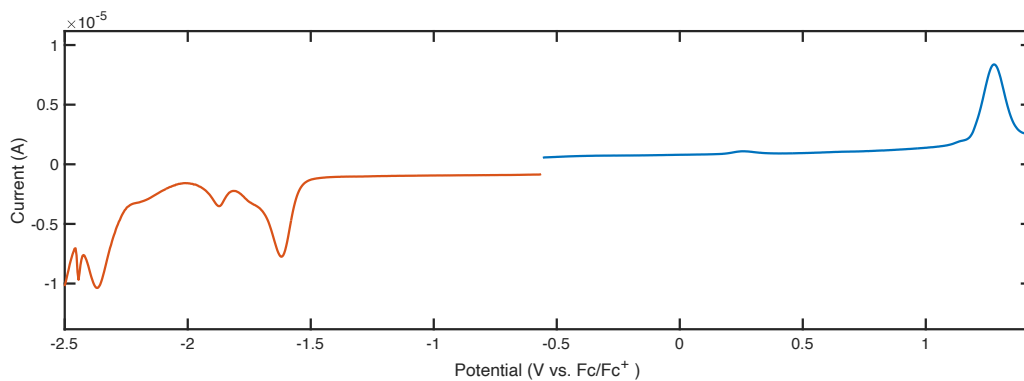


Figure S3.36: Differential pulse voltammogram for 3.

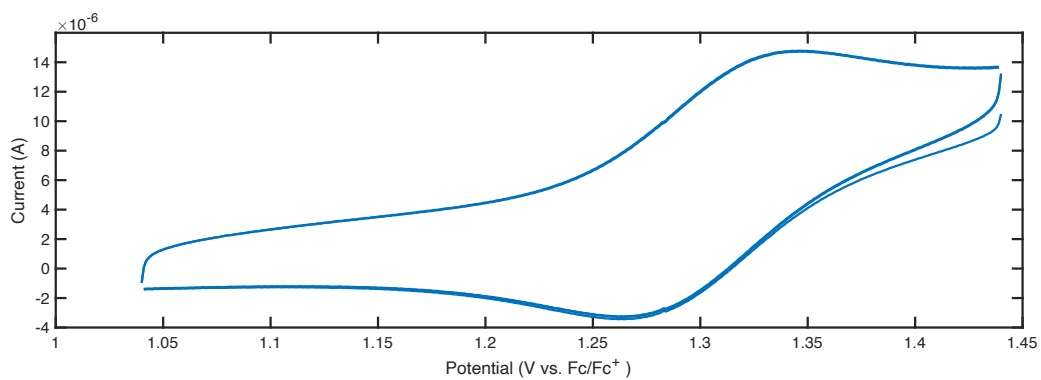


Figure S3.37: Oxidative cyclic voltammogram for 3. Scan rate 100 mv/s.

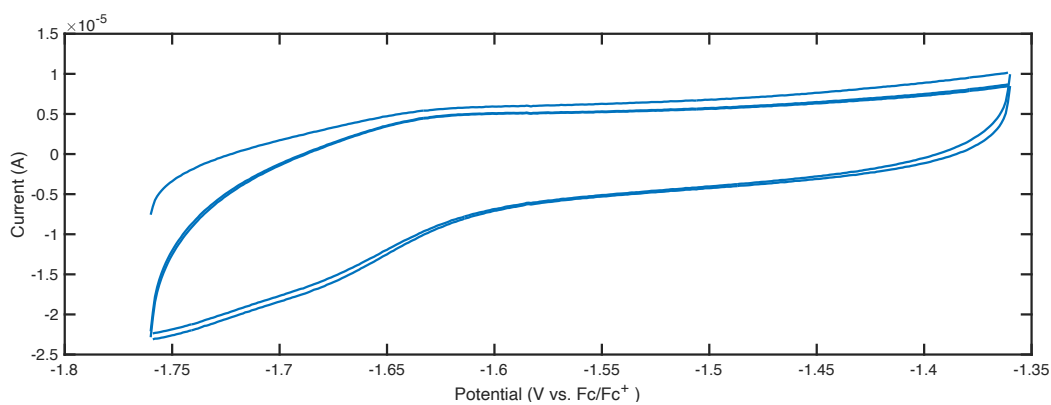


Figure S3.38: Reductive cyclic voltammogram for 3. Scan rate 500 mv/s.

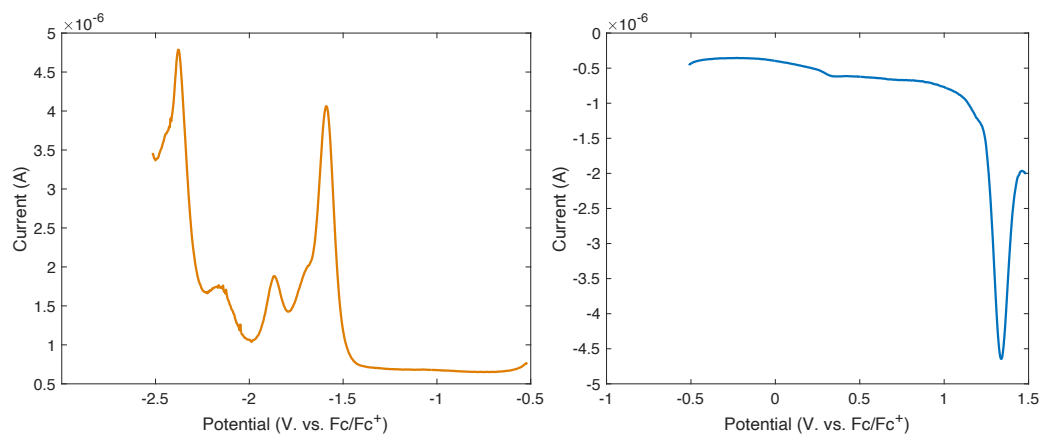


Figure S3.39: Differential pulse voltammogram of 4.

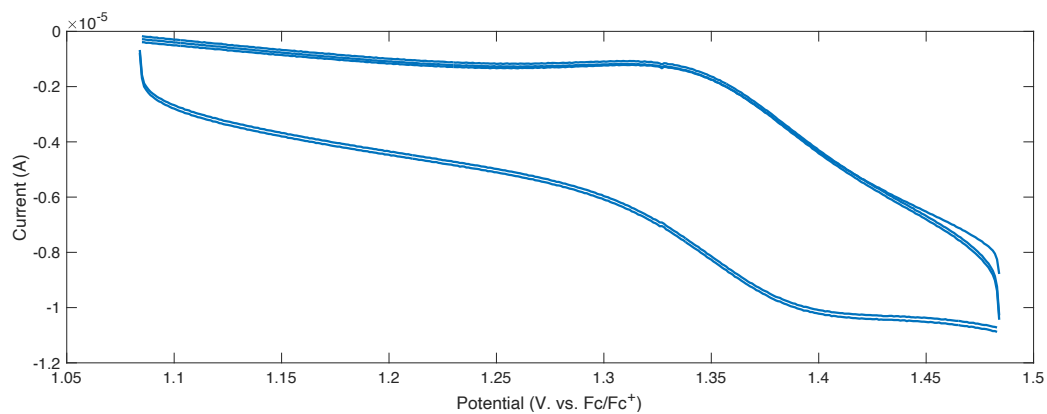


Figure S3.40: Oxidative cyclic voltammogram for 4. Scan rate 100 mv/s.

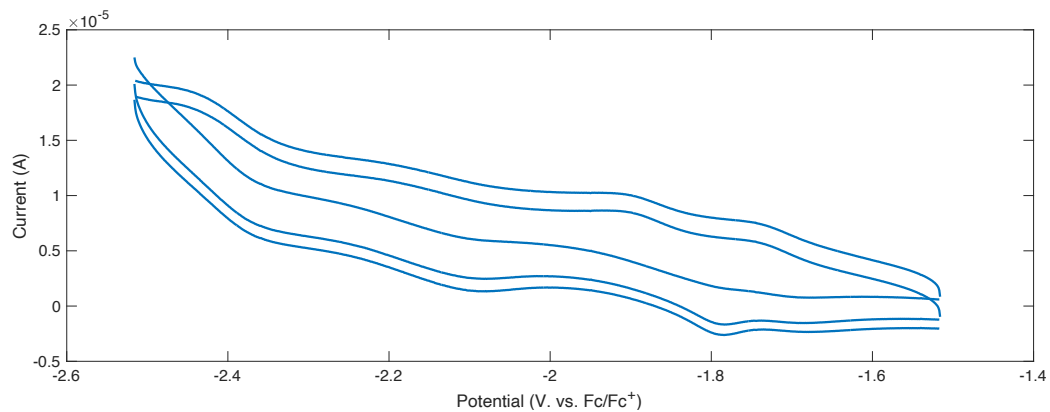


Figure S3.41: Reductive cyclic voltammogram for 4. Scan rate 100 mv/s.

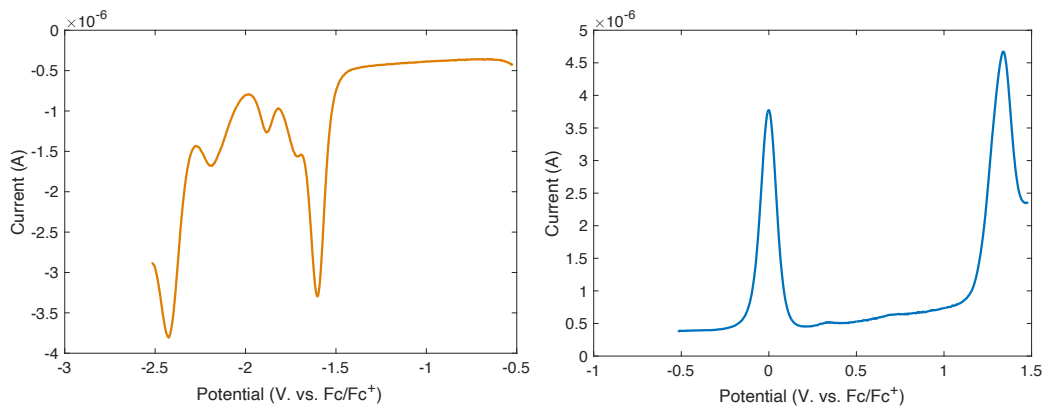


Figure S3.42: Differential pulse voltammogram of **5**. Includes ferrocene/ferrocenium couple.

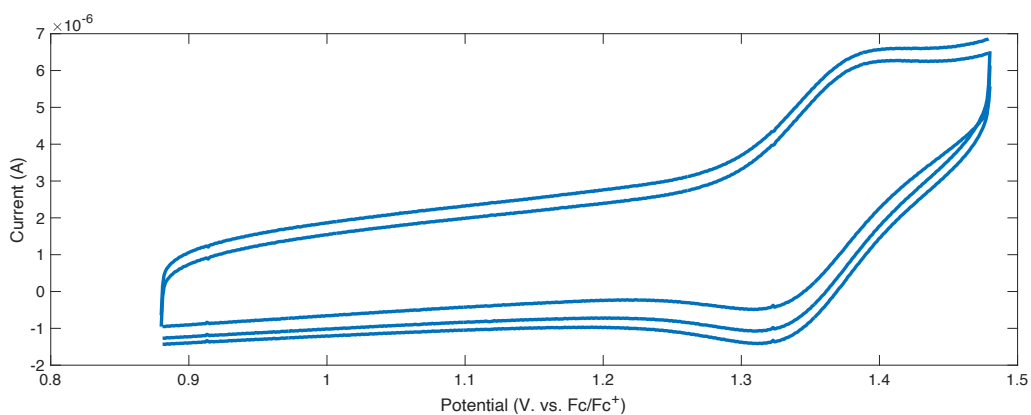


Figure S3.43: Oxidative cyclic voltammogram for **5**. Scan rate 100 mv/s.

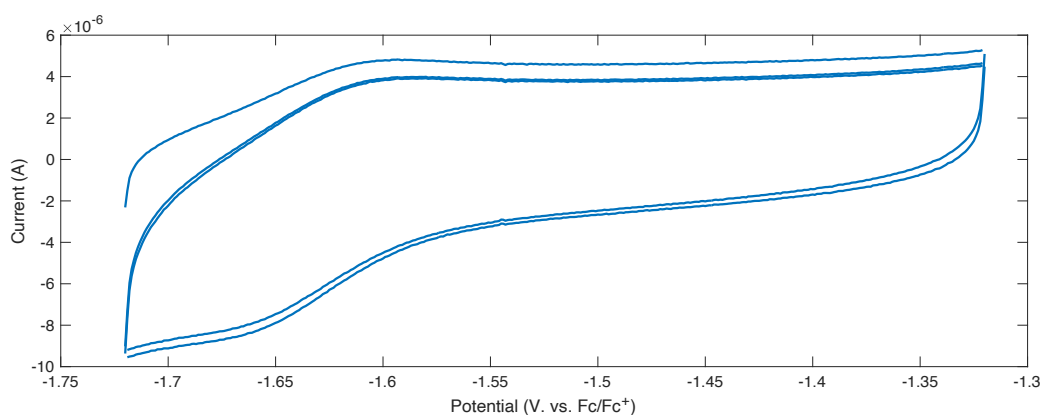


Figure S3.44: Reductive cyclic voltammogram for **5**. Scan rate 100 mv/s

3.6.6 Time-Resolved IR data

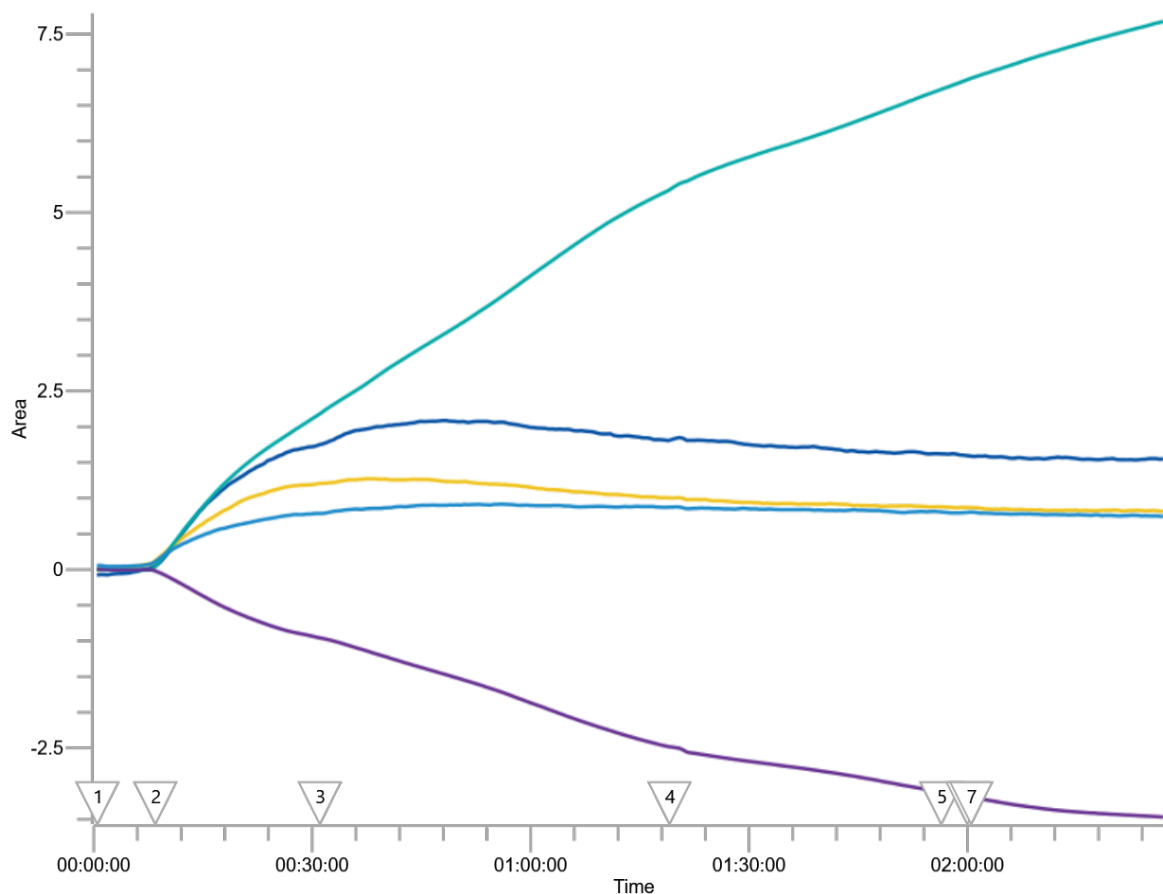


Figure S3.45: Temporal profile of selected peaks measured in the ReactIR software. Areas were calculated by integration to zero.

Table S3.17: Frequencies that were tracked over the course of the experiments. The intensity was generated by integrals from the peak to zero.

Trend	Color	Units
Peak at 2159 cm ⁻¹		Area
Peak at 2022 cm ⁻¹		Area
Peak at 1608 cm ⁻¹		Area
Peak at 1240 cm ⁻¹		Area
Peak at 1974 cm ⁻¹		Area

3.6.7 *In Situ* IR data from the reaction of $\text{Fe}(\text{phen})_2(\text{CNDMP})_2^{2+}$ with hydrazine.

The reaction of **3** with hydrazine was studied with *in situ* IR at a preparatory scale. This experiment tracked the differential absorption of IR radiation between 500 cm^{-1} and 3000 cm^{-1} over a period of two hours. The spectral range above 2500 cm^{-1} is not well resolved due to noise. The ground state spectrum of **1** is included which was obtained after the DCM solution was blanked. It is expected the spectrum of **3** is similar. Absorption in the positive direction is associated with the complex. The band just above 1000 cm^{-1} is associated with the BF_4^- anion of the complex. The isocyanide stretching frequencies of the complex are observed along with a band suggesting the presence of free isocyanide. This suggests that lysis of the isocyanide is occurring in solution. This is not observed in NMR spectra however, however. This suggests that the lysis could be due to photo-dissociation of the isocyanides in this experiment. An interesting observation is the band around 2095 cm^{-1} , which does not describe the complexed isocyanides ($\sim 2140\text{ cm}^{-1}$) or free isocyanides ($\sim 2000\text{ cm}^{-1}$). The presence of bleaching could be the result of a baseline offset by the addition of new material. The peaks outlined in red of figure S3.45 correspond to those of the solvent. The NIST spectrum of DCM is also pictured. This change is in proportion to the addition of the compound, which could reduce the concentration of DCM at the probe, resulting in the bleach. The concentration of DCM is $\sim 15.6\text{ M}$ which would correspond to a 0.6% drop in mole fraction when a 0.01 M solution of **3** is made, which is the case for the basis spectrum. Such a small change is unlikely to be measurable and thus is likely due to some solute/solvent reaction. The nature of which is uncertain, however it could be due to the lysis of the isocyanide from the main complex. This would have the effect of increasing total solute, while at the same time liberate a reactive functional group which could participate in some activity with the solvent.

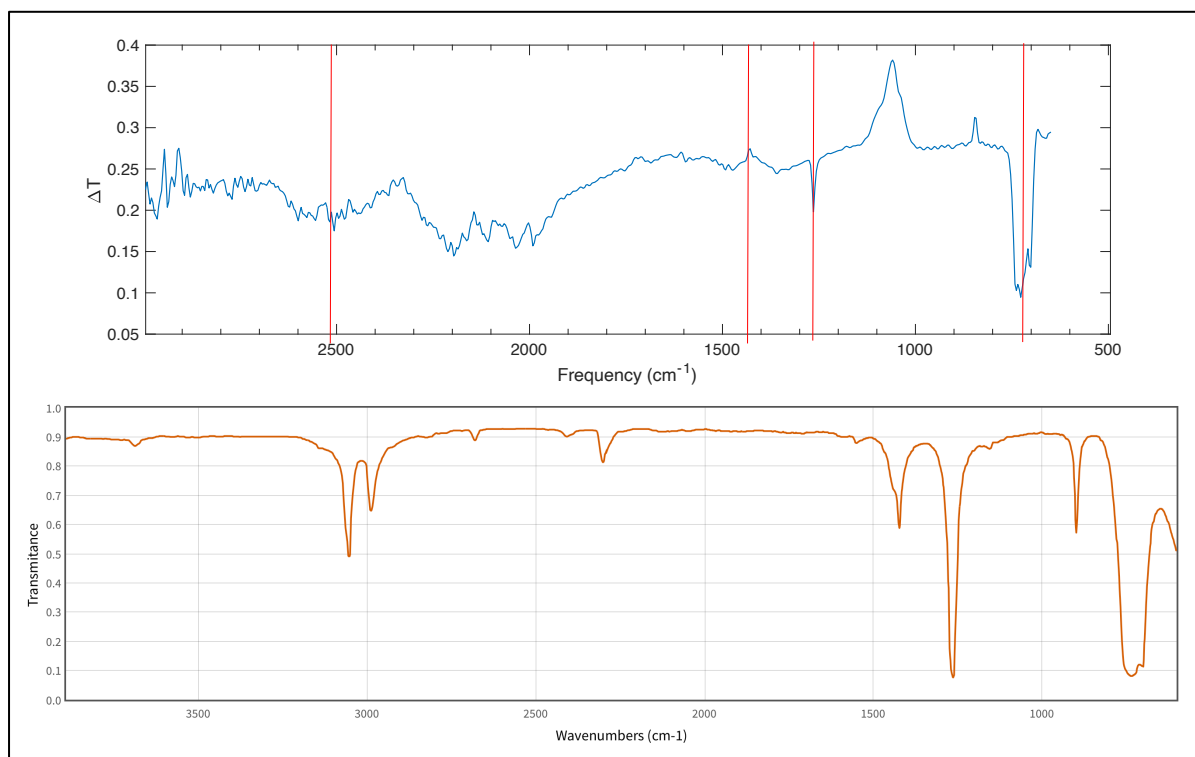


Figure S3.46: (top) IR spectrum of **1** in DCM solution. Red lines indicate vibrations found in the solvent. (bottom) IR spectrum of liquid DCM from the NIST database.

The basis spectrum for **3** will likely look a similar way. The reaction with **3** was performed in DCM solutions, where both starting materials, **3** and hydrazine were blanked. The full spectral data, viewed along the time axis is presented in figure S3.46. The growth of a large band dominates the landscape around 1000 cm^{-1} . Concurrent with this is the growth of a band at 1611 cm^{-1} , which is wide and has a fat shoulder. The positive amplitude of the band at 2159 cm^{-1} is interesting a suggests the formation of some terminal complexed isocyanide. The bleaches occur at frequencies associated with the solvent, which supports the notion of solvent reactivity.

The growth of the large band around 1000 cm^{-1} is interesting. This could be due to several factors including a red-shifted $\nu\text{-N-N}/\delta\text{-N-H}$ related to the final product, or to some form of the BF_4^- hydrazinium salt, both of which could be correlated with the final product. As precipitates

are often observed in the reaction mixture, which are likely hydrazinium salts, the former assignment is likely. While this region dominates the spectrum, its ambiguity limits its utility and will not be considered much in this analysis.

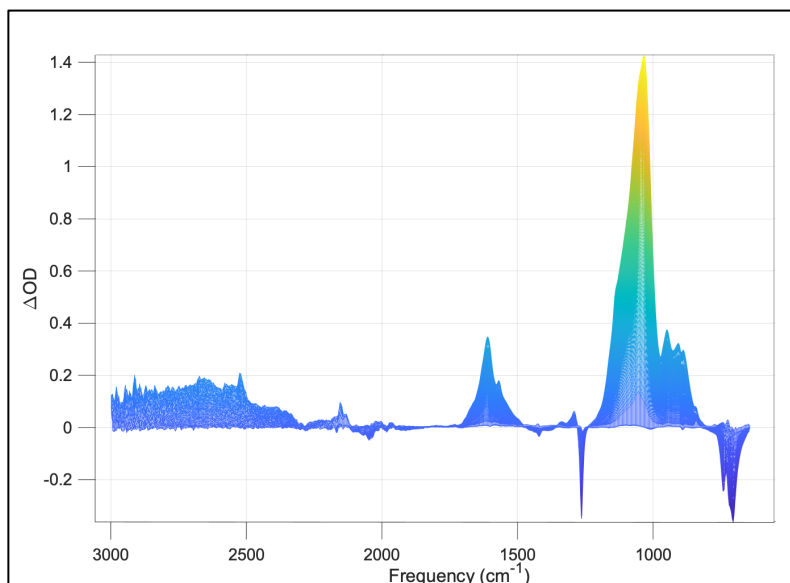


Figure S3.47: Frequency domain of the 2D data. Spectrum is set to zero around 1800 cm^{-1} . Only data at a lower energy than 2500 cm^{-1} were considered due to signal-to-noise at wavelengths higher than this.

Table S3.18: Assignment of transitions observed in the full spectral data.

Frequency (cm^{-1})	Species/assignment	Calculated 3c
701	Solvent	-
1044	3c ν -N-N/ δ -N-H or $\text{N}_2\text{H}_5^+\text{BF}_4^-$	1011 cm^{-1}
1264	Solvent	-
1566	3c δ -N-H	1502 and 1508 cm^{-1}
1611	3c δ -N-H	1565 – 1569 cm^{-1}
2159	Complexed ν -CN	

The band which grows in at 1611 cm^{-1} has a small sharp shoulder at 1566 cm^{-1} . These are likely due the formation of some δ -N-H mode of a terminal amine species. DFT frequency

calculations of the terminal imine complex show two separate bands of these δ -N-H motions separated by about 60 cm^{-1} in good agreement with the 45 cm^{-1} separation measured. The width of the bands is consistent with the presence of several transitions. These vibrations are coupled with the C=N stretches of the backbone. Table S3.18 summarizes these tentative assignments.

The kinetic traces of selected wavelengths are included in figure S3.47. Most of which grow in to give some equilibrium concentration at the end of the experiment which suggests the formation of some terminal configuration different than the starting materials. The resonance at 2159 cm^{-1} is unique in that it peaks at early times and begins to move back toward baseline, but eventually comes to some equilibrium value. The fact it does not react further suggests an inability to react with hydrazine or an incomplete bridging reaction. These possibilities will be discussed later in detail.

A set of possible reactions are proposed in scheme S3.2. The core reactions, include the formation of the carbene, compound **3b** in the scheme followed by its deprotonation to give complex **3c** and a hydrazinium salt $\text{N}_2\text{H}_5\text{BF}_4$. This species could also undergo a breakdown to lower order products. This decomposition path is in the lower right corner of the scheme 3.S2. The pathway is not favorable due to the differences in pKas of the hydrazinium and fluoroborate ions (~ 8 vs ~ 1 for $\text{N}_2\text{H}_5\text{BF}_4$ and HBF_4 respectively) but is included because of the likely large heat the reaction associated with the hydrazine/flouoroborane complex. It is important to highlight that the reactions with the solvent are not included in the scheme, making it incomplete.

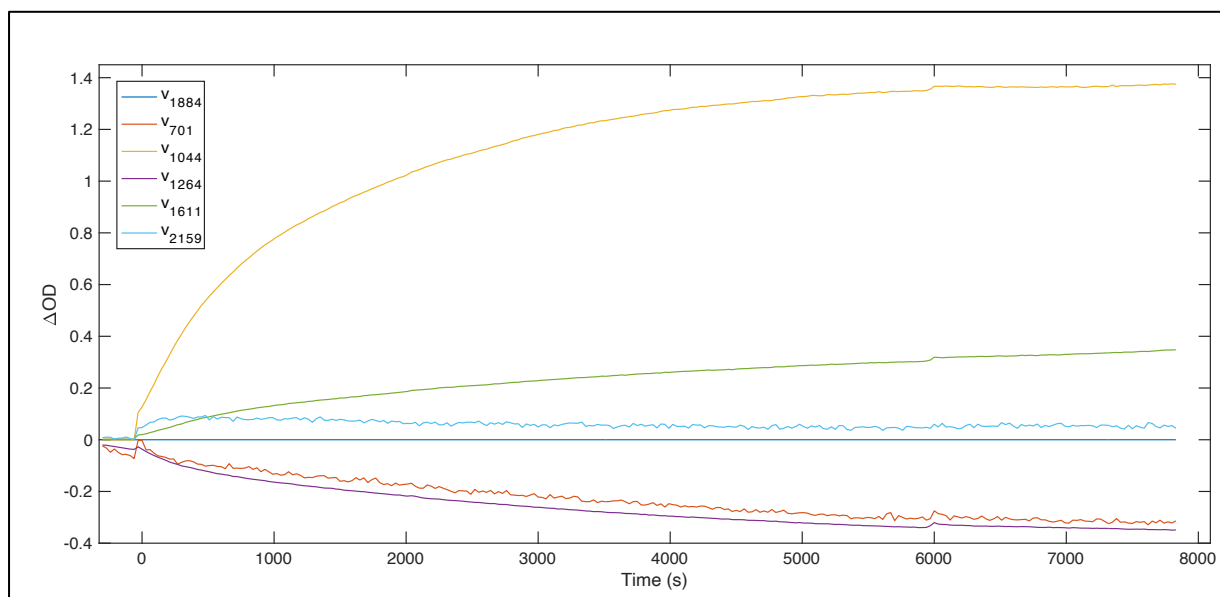
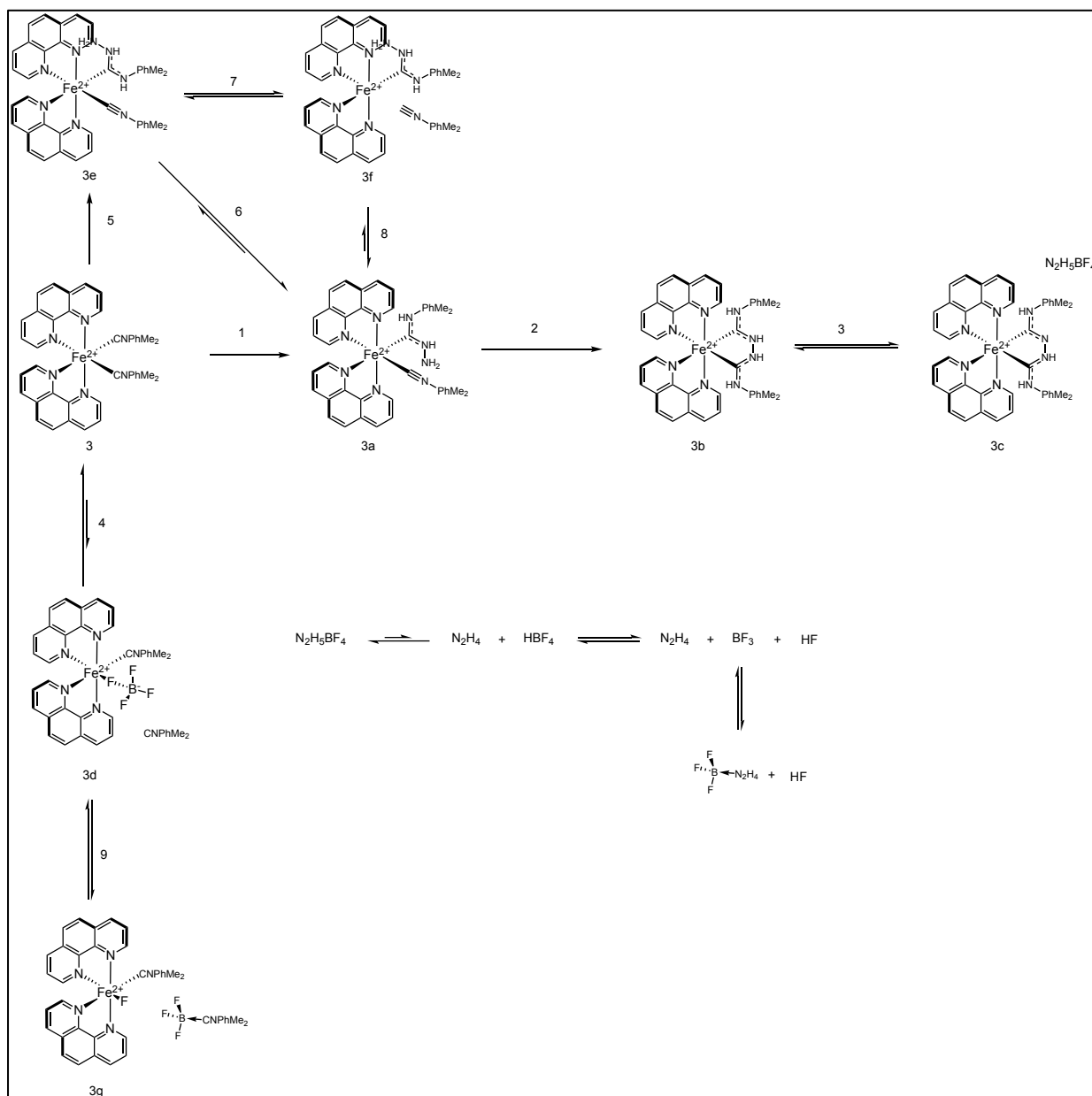


Figure S3.48: Time domain spectra of selected frequencies after the addition of hydrazine to **3** which is set to zero at time zero.

There are several possible reactions that occur off this main pathway. The first off path reaction is the dissociation of the isocyanide of **3** by some means, whether it be thermal or photochemical to form the species **3d**, in which the open position left by the isocyanide is taken by the fluoroborate ion. This is consistent with the observation of the $\sim 2000\text{ cm}^{-1}$ resonance in the basis spectrum, in figure S3.45. This species could in theory eliminate neutral trifluoroborate, to make the fluoride adduct of the Fe(II) complex, **3g**. The mechanism of this likely leans heavily towards the association of the borate ion upon photoexcitation rather than dissociation. A dissociative mechanism would have to pass through a pentacoordinate transition state. Pentacoordinate iron isocyanide species are known; however, they are generally d^8 . This may be an explanation for why the methyl groups are important, to slow the access of the counter anion to the metal center, even if there is still a propensity for isocyanide liberation. In unsubstituted varieties this would much more readily, as should occur in proportion to the basicity of the isocyanide carbon.



Scheme S3.1: Some reactions which could be occurring upon starting the reaction. (1) The desired forward reaction in which hydrazine attacks the isocyanide from the interior parallel the C₂ axis. (2) The reaction which forms the bis-carbene. (3) Acid/base equilibrium between the observed final product and the carbene, this likely occurs through the reaction with hydrazine. (4) Dissociation of the isocyanide and coordination of the fluoroborate anion. This behavior is observed in the spectrum in figure 11. (5) Reaction in the attack of hydrazine from outside the C₂ axis. The size of the ligand makes rotation about the carbene bond difficult. (6) Rotation of the carbene bond to the interior. (7) Persistence of the mono-carbene would lead to a dissociative equilibrium. (8) Re-association of the isocyanide to favor nucleophilic attack. (9) Release of fluoroborane to make the fluoride adduct. The acid base chemistry with free acid in solution is unlikely but could lead to a strong hydrazine/borane complex.

Another pathway considers the reaction of **3** with hydrazine by its approach relative to the C₂ rotation axis. If the hydrazine were to approach from the outside of the complex, as opposed to the inside of the two monodentate ligands, a carbene could form in which the free amine is on the outside of the C₂ axis. The large bulky aryl group will likely slow the rotation of the amine of the now planar monodentate towards the C₂ axis. In Costanzo et. al. no extra rotary component was found and the step from the attack of the first isocyanide to the bridge was treated as fast and unmeasurable. Rotation could be avoided by the dissociation of the isocyanide and its re-coordination passing from species **3f** to **3a**. In the dissociation case, the counter anion or the dangling hydrazine could take the place of the isocyanide. The latter is more likely for kinetic reasons; however, both could end in terminal side products. For example, the deprotonation of the amine donor could lead to an amido complex. The basic environment virtually assures that an intermediate like this is terminal but could still react further. This could in part explain the benefit of the alkyl groups which could slow either anion coordination or amine deprotonation.

If the dangling amine is uncoordinated, this intermediate could react either through deprotonation to form a hydrazone or the free amine could react with other electrophiles to form azines, or both. This would occur quickly as hydrazones are difficult to isolate. In the synthesis of acetohydrazone for example, acetone azine is made quantitatively from one equivalent of hydrazine, which is then lysed with the addition of a second equivalent in a separate step.³² This is also the reason why the process 2 for the reaction of **3a** is so quick.

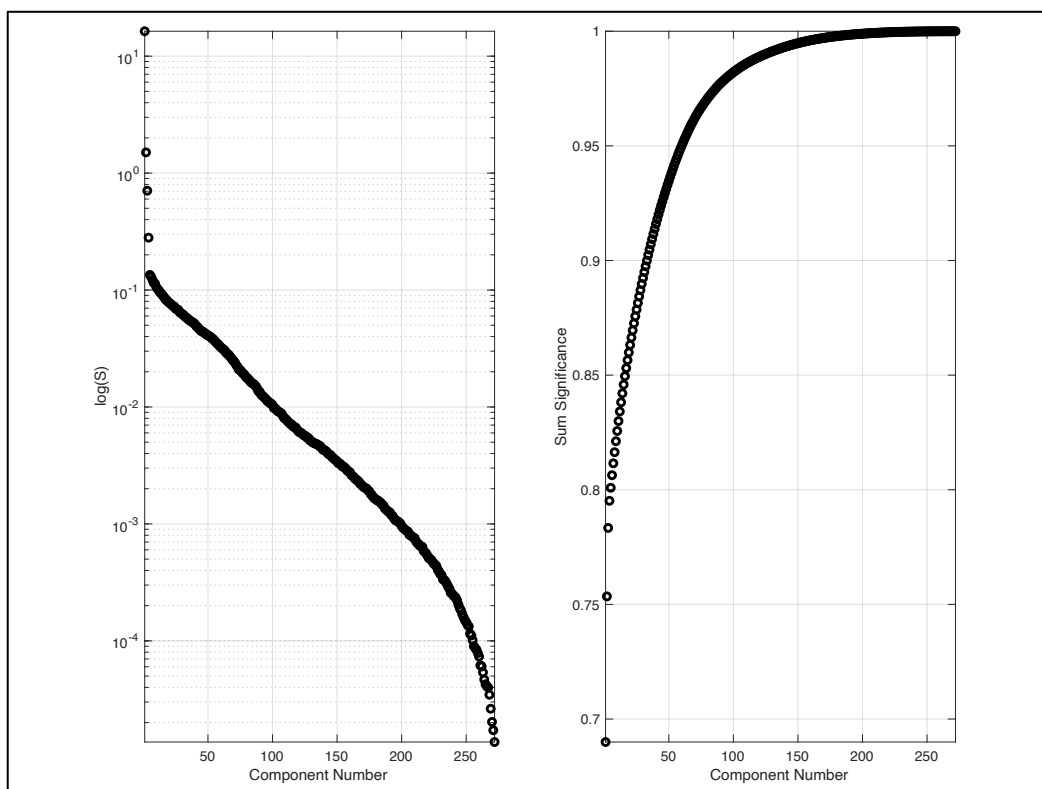


Figure S3.49: Skree plot for the singular value decomposition of the 2D matrix for the spectral range cm^{-1} . The first four components describe most of the spectral density.

The complexity of the scheme can be reduced by single value decomposition (SVD) of the full spectral data was performed in MATLAB. The singular values shown in figure S3.48. Four components are clearly set apart from the rest. This suggests that, to a first approximation, four processes describe the evolution in this system. However, when considering the sum of the significance plots, the first four components only make up around 83% of the data. There is a high density of points of similar relevance. This is not surprising as the density of information for an IR experiment is very high. The full spectral data was remade with only four components and the residuals were calculated ($y_{\text{rec}} - y_{\text{exp}}$) after normalization of both experimental and recreated spectra. The result is given in figure S3.49. While this does not describe the data perfectly, particularly in the regions greater than 2000 cm^{-1} , it gives at most 3% error. Clearly the

region around 1000 cm^{-1} has a multitude of processes which are not described in the first four components, suggesting some BF_4^- chemistry may be neglected.

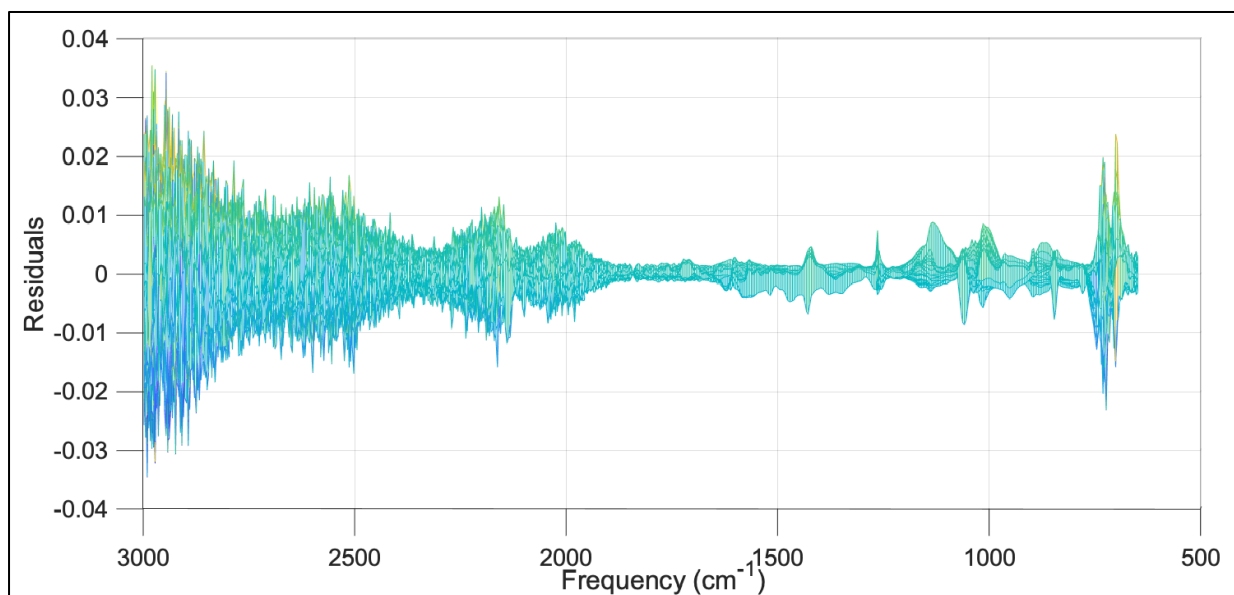


Figure S3.50: Residuals of the synthetic dataset after recreation with the first four singular values. Most of the error is in the high energy domains but no more than 3%.

The right and left eigenvectors of the first four components are presented in figure S3.50. The fourth component in purple is dotted for clarity. A break in the time vector is observed in the small components, due to an attempted sampling of the solution during the reaction. This minor effect in the data is magnified in the lower order components. Component 1 (C1) represents the terminal configuration shown by the plot of its right eigenvector with time. The left eigenvector of C1 effectively show no amplitude in the isocyanide region consistent with the formation of the final imine product. C2 in orange, has a temporal profile that peaks around 1500 s, whereupon it decays at a slower rate than it was formed. It crosses negative, around 4500 s. This crossing point illustrates when the basis spectrum goes from an absorptive feature to a bleach feature and suggests that the configuration that evolves with C2 is an intermediate species.

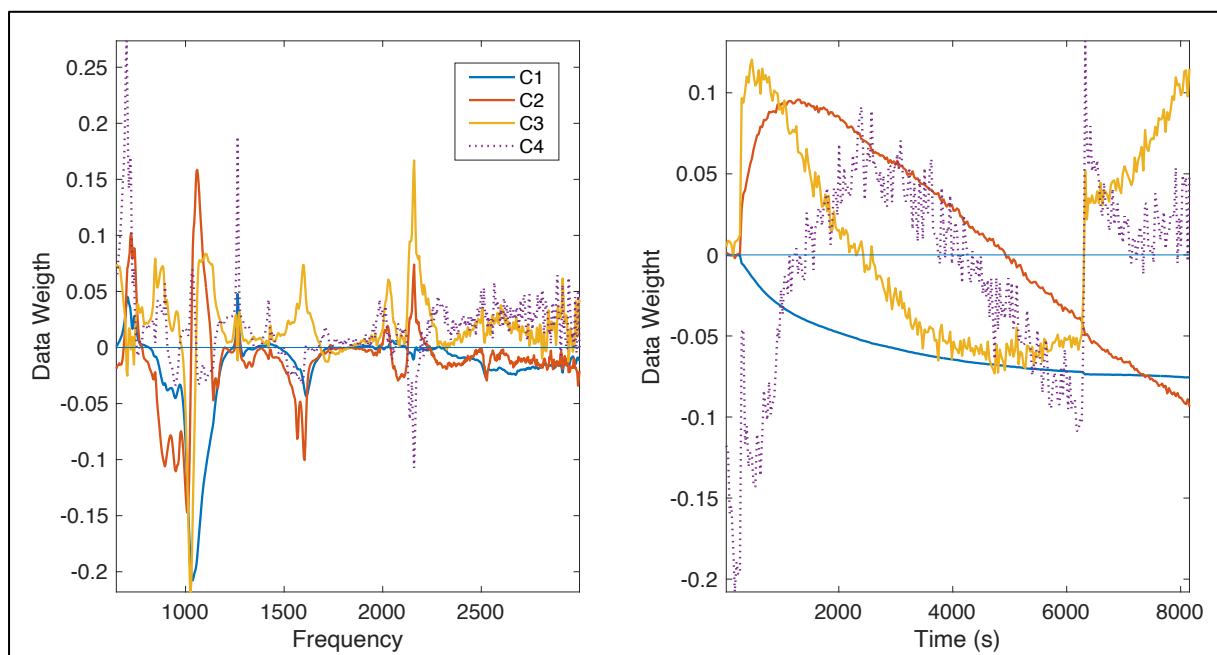


Figure S3.51: Right and left eigenvectors of the 2D data for the full 600-3000 cm^{-1} range.

C3 in yellow grows quickly, peaks early, and changes over time more slowly than when it formed. It crosses zero before the second component, but levels off to an approximately constant value until the break in the spectrum. The spectral regions associated with this process around 1600 cm^{-1} and the free-isocyanide and complexed isocyanide regions, both would have absorptions at early times, but eventually decay to a bleach. The fourth component's time vector, in dotted purple, starts negative heads positive and crosses the zero line around 1500s. It peaks positive, and then goes negative again. The spectral regions associated for this process, around 2150 cm^{-1} suggests this region loses intensity with time where it eventually bleaches. This region does become an absorption later times in the experiment.

3.6.8 Tentative Assignments of the Processes Involved

The tentative mechanism derived from inspection of the SVD data is presented in scheme S3.3. Component 4 likely describes the dissociation process of **3**. It is present before the addition of the hydrazine, and it describes a loss in the frequencies associated with **3** and an increase in

the region related to free isocyanide. The reaction of **3** with hydrazine occurs from the side quickly, compared to the attack from the middle, and forms the mono-carbene complex with a dangling amine. This monocarbene undergoes a fast equilibrium between its associated and dissociated forms. The dissociated form is likely stabilized by the coordination of the dangling amine to the metal center, which can be easily displaced in the re coordination of the isocyanide. C3 shows a consistent loss of amplitude in both the coordinated, un-coordinated isocyanide regions along with 1600 cm⁻¹ region, a decaying δ -N-H mode, which would accompany the formation of the mono-carbene. This process then describes the rotation of the monocarbene in plane to form **3a** that quickly forms the *bis*-carbene **3b** which is unobserved. The fast equilibrium of the monocarbene undergoes a second process described by C2, which shows the reduced amplitudes of the free and complexed isocyanides, reacting to form two sharp features around 1590 cm⁻¹ as well as a broad feature just below 2100 cm⁻¹. This is consistent with the formation of an ammonium ion. It then likely describes the protonation of an amine to form the ammonium, which is further illustrated by the crossing point which occurs at long times, where there is expected to be significant acid present. The scheme shows this as the protonation of the dangling amine of **3e** to make the primary ammonium of **3g**. This species can either break down or persist in solution. The kinetic trace at 2159 cm⁻¹ in figure 3.12 suggests that the latter might be the case. C1 is clearly the formation of the terminal product. There is very little amplitude to suggest a region which is bleached over this reaction. Therefore, it is likely this is the deprotonation step of the carbene, species which should only change slightly in the δ -N-H region.

providing a coarse-grained complement to the fine-grained analysis of the IR spectroscopy experiment. IR was performed because it could be done on a preparatory scale, to optimize the workflow, such an experiment with visible absorption could not be done on a preparatory scale.

To validate the model a kinetic analysis should be performed. A global analysis program was written to do just this. This is presented in the next section. Global analysis commonly assumes first-order or pseudo first-order kinetics when considering relaxation processes that are performed in many time-resolved spectroscopies. The functional form of the rate-laws cannot be assumed to be first order. Figure S3.50 shows this to be true. The program was written to account for this: it solves a system of non-linear differential equations which can then be utilized in an optimization to find the kinetic parameters buried in the 2D spectra. The program utilizes the SVD data presented above. However, the program was not applied effectively to these data which could be due to many reasons.

3.6.9 Attempted Non-exponential Global Analysis Program

A global analysis program for the global optimization of the 2D *in situ* IR data was attempted using the script below. Efforts were unsuccessful however the program is included for future reference as this type of analysis will be highly useful when properly implemented.

```
% This script is used for solving differential-algebraic expressions.
% Details for modifications can be found in the documentation:
https://www.mathworks.com/help/symbolic/solve-differential-algebraic-equations.html

%creates symbolic math expression based on the kinetic model
clc,clear

syms A(t) B(t) C(t) D(t) E(t) k1 k2 k3 K1

eq1 = diff(A,t) == -k1*A
eq2 = diff(B,t) == k1*A-k2*B-k3*Bs
eq3 = diff(C,t) == k2*B-K1*C
```

```

eq4 = 0 == K1*C-D
eq5 = diff(E,t) == k3*B

vars = [A(t)];
origVars = length(vars);

eqns= [eq1,eq2,eq3,eq4,eq5];

vars = [A(t),B(t),C(t),D(t),E(t)];
origVars = length(vars);

M=incidenceMatrix(eqns,vars);

[eqns,vars] =reduceDifferentialOrder(eqns,vars);

isLowIndexDAE(eqns,vars); %could create a function which runs index redux.

[DAEs,DAEvars] = reduceDAEIndex(eqns,vars);

%converts symbolic DAE systems into matlab functions
pDAEs = symvar(DAEs);
pDAEvars = symvar(DAEvars);
extraParams = setdiff(pDAEs,pDAEvars);

f = daeFunction(DAEs,DAEvars,k1,k2,k3,K1);

%
% %this begins the optimization
open full_spectrum_workspace.mat;

time = ans.time;
freq = ans.freq;
U = ans.U;
S = ans.S;
V = ans.V;

```

```
[opt_spectrum] =  
eigenvector_optim(optim_trace,U(:,1:5),S(1:5,1:5),V,freq,time,f);  
  
mesh(time,freq,optim_trace)  
  
mesh(time,freq,opt_spectrum)  
  
mesh(time,freq,(opt_spectrum-optim_trace))
```

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```

%     mesh(time1,freq,yst(yopt)-y);
%
%     xlabel('time');
%     ylabel('residuals');
%     zlabel('Residuals')
%
%
k1 = yopt(1);
k2 = yopt(2);
k3 = yopt(3);
k4 = yopt(4);
K1 = yopt(5);
If = [k1,k2,k3,k4,K1];
opt_spectrum = yst(yopt);

end

function [composite] = diff_make(f,I,time1,U,S)
%needs to go step five and onwards

%defines differential function F in terms of current crop of
parameters
F = @(t,in2,in3) f(t,in2,in3,I(1),I(2),I(3),I(4));

y0est = [1.45E-2,0,0,0,0];
yp0est = zeros(5,1);

opt = odeset('RelTol', 10.0^(-7), 'AbsTol',10.0^(-7));

[y0,yp0] = decic(F,0,y0est,[],yp0est,[],opt);

sol = ode15i(F,[0 10000],y0,yp0,opt);
transfer = [];
for n = 1:length(time1)
    search = time1(n);
    transfer = [transfer deval(sol,n)];
end

[composite,C] = OD_simulator(U,S,transfer,I);
end

function [composite,C] = OD_simulator(U,S,transfer,I)

```

```
    P =  
    [I(5),I(6),I(7),I(8),I(9);I(10),I(11),I(12),I(13),I(14);I(15),I(16),I(17),  
    I(18),I(19);I(20),I(21),I(22),I(23),I(24);I(25),I(26),I(27),I(28),I(29)];  
    C = transfer';  
  
    Vstar = C*P;  
  
    composite = U*S*Vstar';  
end
```

4) CHAPTER 4: PRELIMINARY STUDIES OF ARYLATED CARBENE HETEROLEPTICS OF Fe(II)

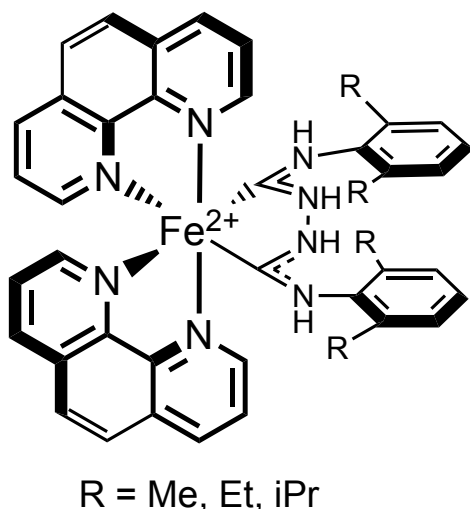
4.1 INTRODUCTION

The bulk of this work looks to interrogate the kinetic and thermodynamic approaches for the improvement of light capture capabilities of Fe(II) chromophores for use in DSSCs, laid out in the introduction of this thesis. This is done in practice by considering a modular and orthogonal approach to the design of novel chromophores which is centered around the $[\text{Fe}(\text{phen})_2(\text{C}_4\text{H}_{10}\text{N}_4)]^{2+}$ platform, studied previously by our group.¹

The work in chapter 2 was dedicated to interrogating the photophysics of the diamino carbene $[\text{Fe}(\text{phen})_2(\text{C}_4\text{H}_{10}\text{N}_4)]^{2+}$ complex utilizing variable temperature transient absorption spectroscopy (VT-TA) in conjunction with x-ray emission spectroscopy (XES). Kinetic traces from TA were found to fit to a biexponential model with a short and long time constant about ~ 500 fs and ~ 5 ps respectively. Arrhenius analysis suggested a different set of kinetic parameters of the excited state absorption region compared with the ground state bleach region of the time resolved spectrum. This suggested participation of a lower lying excited state, unobserved by TA that participated in the ground state recovery process. XES found that prompt formation of a triplet metal centered excited state, ^3MC , was present at time delays on the order of the shorter time component. This led to two proposed channels: a thermalized pathway which describes the temperature dependence and long-lived ESA and a non-thermalized pathway which gives rise to the early ^3MC signal.

The work in chapter 3 discussed the synthesis and characterization of aryl isocyanide complexes. These complex's reactivity with hydrazine was also studied. Achievement of stable carbene species was found to occur when the isocyanide ligands incorporated alkyl groups adjacent to the -NC functionality. This is likely due to the protection of intermediate species in the mechanism from bis-isocyanide to bis-carbene.

This chapter focuses on studying the carbene species derived from the isocyanides discussed in chapter 3. The general structure of the complexes discussed in this chapter are given in drawing 4.1. Complex **1** is substituted with methyl in the 2,2' positions of its aryl group, which was found to be required for its stability, discussed in the previous chapter. While required for synthesis, it posed an interesting opportunity for examining kinetic effects in the carbene platform, i.e., x-axis perturbations along with any donor effects the ligands may imparted on the complexes. As such, complexes, **2** with ethyl, and **3** with isopropyl were synthesized.



Drawing 4.1: General framework for the complexes studied in this chapter. **1**: R=Me, **2**: R=Et, and **3**: R= iPr.

It was hypothesized that this series could isolate kinetic aspects from electronic perturbations making it an ideal series to study these effects. This was driven by the rotation of the aryl groups to orthogonal to the carbene plane making the inductive π -effects essentially zero. Electronic isolation is key in making the argument that observables, like excited state lifetime, are not a product of electronic effects but instead entirely due to structural and/or steric factors. This must be established in a separate experiment. For example, the lack of electronic perturbation by the addition of Cu(I) ions as structural elements in the Fe(II) cage [Fe(cage)Cu₂] complex was determined with a ground state absorption spectrum and a Zn(II) analogue

[Zn(cage)Cu₂]. The spectrum of the [Fe(cage)Cu₂] was a virtual superposition of the two native spectra and the Zn(II) analogue, suggesting that only minor electronic coupling between the metal centers. It was in-part upon these grounds that the increase in lifetime was attributed to vibronic aspects.²

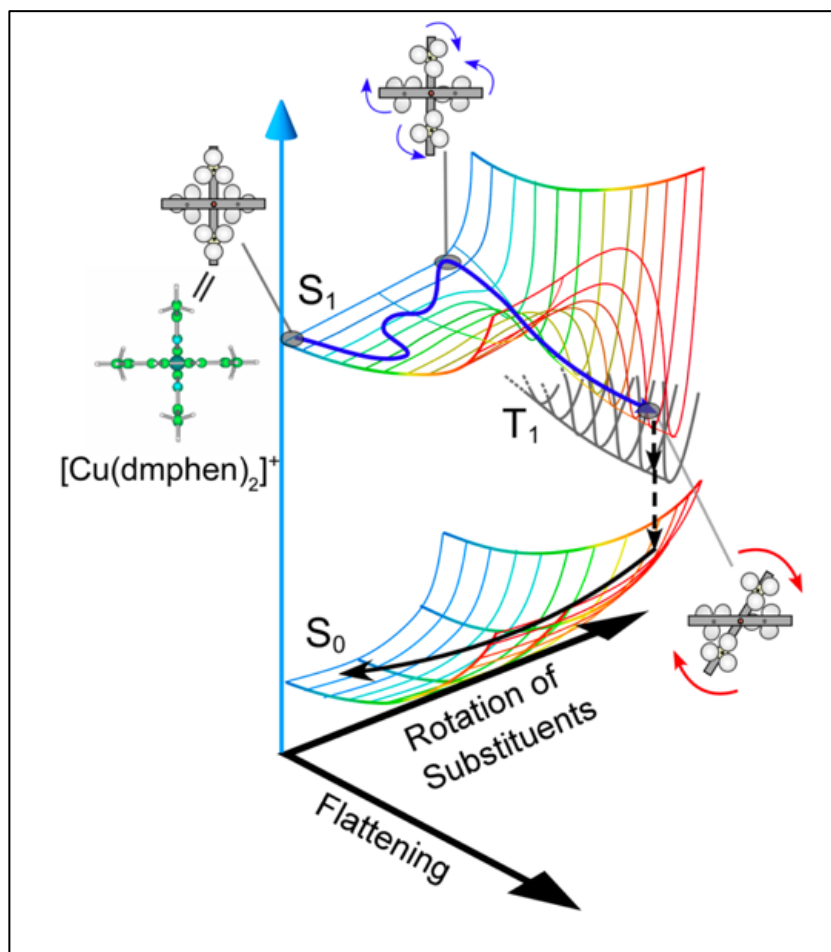


Figure 4.1: Illustration of the random walk of [Cu(dmp)₂]⁺ on the S₁ surface. Taken from reference 4.

The systems **1-3** are however exhibit structural modifications different from the cage in that they will likely act more as an ‘outer-sphere’ degree of freedom coupled to some ‘internal’ degree of freedom which drives the relaxation process. These pseudo-outer sphere effects can play a role in many different types of chemistries. In this way they are expected to behave more like Cu(I) polypyridyl systems than the Fe(II) cage system. Tahara and coworkers proposed the

two-coordinate relaxation pathway illustrated in figure 4.1, where an adiabatic relationship exists between substituent rotation and flattening.^{3,4} Here the coupling of this rotational coordinate to the flattening coordinate explained the threefold increase in the relaxation time of the structure from tetrahedral to square planar in $[\text{Cu}(\text{dmp})_2]^+$ compared to $[\text{Cu}(\text{phen})_2]^+$ (dmp = 2,9-dimethyl-1,10-phenanthroline). While substitution could have electronic effects, it is easy to neglect these compared to the systems of **1-3** whose decay is highly dependent on the presence of LFS, which are not generally seen as an issue for Cu(I) systems.

This work seeks to test the relative electronic isolation of the aryl groups as well as determine the degree the donor ability of the ligand changes across the series. The quasi-outer sphere interactions of the substituted aryl groups and their modular increase in size means that the kinetics of the system can be perturbed in a monotonic fashion.

4.2 EXPERIMENTAL

4.2.1 General Synthesis:

The syntheses of the relevant precursor compounds were discussed in the previous chapter. Compounds were synthesized under an inert atmosphere and all solvents were degassed and dried by an alumina column dry-still. Hydrazine was purchased from Millipore-Sigma and stored at -20 °C in an inert atmosphere glove box. NMRs were collected on a 500 MHz spectrometer at the Max T. Rodgers NMR facility at MSU. ESI-MS was performed at the Metabolomics Core at MSU. X-Ray structures were collected at the Center for Crystallographic Research at MSU, using the ShelX protocol in Olex.⁵

*Synthesis of $\text{Fe}(\text{phen})_2(\text{DMP_carbene})[\text{BF}_4]_2$ (**1**):* In an inert atmosphere glove box 0.154 g (0.17 mmol, 1 eq) of $\text{Fe}(\text{phen})_2(\text{CNDMP})_2[\text{BF}_4]_2$ was dissolved in 10 mL of dichloromethane in a pressure tube. To this was added 86 μL (2.6 mmol, 15 eq) of hydrazine. The color darkened

immediately and formed a rich green color while stirring at room temperature for 1 hour. This was removed from the box and brought past reflux for 1 hour. After this the tube was cooled to room temperature and brought into the box once more. 0.37 mL (2.7 mmol, 16 eq) of $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ complex was added and an immediate color change from blue to red was observed and stirred for 5 minutes. Precipitated salts were filtered through cealite and the complex in the filtrate was precipitated by the slow addition of diethyl ether. This red powder was filtered outside of the glovebox in air. The red powder was recrystallized from 5% HBF_4 in acetonitrile and water, where a red/purple oil forms, whereupon a secondary application of heat allows for shiny black/purple crystals to form. These were filtered off 0.085g (52% yield). Crystals suitable for X-Ray diffraction were grown by the slow evaporation of acetonitrile from aqueous solution. ^1H NMR (500 MHz, acetonitrile- d_3) δ 9.14 (s, 2H), 8.93 – 8.88 (m, 2H), 8.73 (dd, J = 8.2, 1.2 Hz, 2H), 8.47 (dd, J = 8.1, 1.2 Hz, 2H), 8.26 (d, J = 8.9 Hz, 2H), 8.19 (d, J = 8.9 Hz, 2H), 7.96 (dd, J = 8.3, 5.2 Hz, 2H), 7.46 (dd, J = 8.1, 5.2 Hz, 2H), 7.40 (dd, J = 5.2, 1.3 Hz, 2H), 7.12 (d, J = 7.6 Hz, 2H), 7.09 (t, J = 7.4 Hz, 2H), 7.04 (s, 2H), 6.88 (d, J = 7.4 Hz, 2H), 2.35 (s, 6H), 0.70 (s, 6H). ^{13}C NMR (126 MHz, acetonitrile- d_3) δ 230.35, 157.21, 152.63, 149.82, 148.32, 137.28, 137.13, 136.93, 136.25, 135.15, 131.67, 131.43, 129.76, 129.63, 128.89, 128.59, 126.97, 126.78, 18.57, 16.12. ESI-MS: $[\text{M}-\text{H}]$ calcd. 709.2486, anal. 709.2543 M-H. EA: calcd. C: 57.07% ; H: 4.33% ; N: 12.67%; anal. C: 57.07% ; H: 4.35% ; N: 12.77%;

Synthesis of $\text{Fe}(\text{phen})_2(\text{DEP_carbene})[\text{BF}_4]_2$ (2): In an inert atmosphere glove box 0.115 g (0.13 mmol, 1 eq) of $\text{Fe}(\text{phen})_2(\text{CNDEP})_2[\text{BF}_4]_2$ was dissolved in 5 mL of dichloromethane in a pressure tube. To this was 121 μL (3.8 mmol, 30 eq) of hydrazine. The color darkened immediately and formed a rich green color while stirring at room temperature for 1 hour. Removed from the box and brought to reflux for 10 hours. This was cooled to room temperature

and pumped into the glove box. Whereupon 0.822 mL (5.08 mmol, 40 eq) of $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ was added changing color from vibrant blue to a red solution. The white precipitates which formed were filtered through cealite. The volume of the filtrate was dried. The red film was dissolved up into a 1:1 Ethyl acetate/DCM solution and extracted with 5% aqueous HBF_4 . The organic layer was dried with MgSO_4 . This was filtered and the filtrate was layered in batches with dry diethyl ether while being stored at 5°C . Black/red crystals form, suitable for X-ray diffraction were obtained. 0.063 g was filtered off (53% yield). ^1H NMR (500 MHz, acetonitrile- d_3) δ 9.19 (s, 2H), 8.91 (dd, $J = 5.2, 1.2$ Hz, 2H), 8.78 (dd, $J = 8.3, 1.2$ Hz, 2H), 8.47 (dd, $J = 8.1, 1.3$ Hz, 2H), 8.27 (d, $J = 8.9$ Hz, 2H), 8.20 (d, $J = 8.9$ Hz, 2H), 8.01 (dd, $J = 8.2, 5.2$ Hz, 2H), 7.47 (dd, $J = 8.1, 5.2$ Hz, 2H), 7.38 (dd, $J = 5.2, 1.3$ Hz, 2H), 7.20 (t, $J = 7.4$ Hz, 2H), 7.17 (dd, $J = 7.6, 1.9$ Hz, 2H), 7.08 (s, 2H), 6.93 (dd, $J = 7.3, 1.9$ Hz, 2H), 2.78 – 2.65 (m, 4H), 1.25 (t, $J = 7.6$ Hz, 6H), 1.19 (dt, $J = 15.0, 7.5$ Hz, 2H), 0.85 – 0.73 (m, 2H), 0.16 (t, $J = 7.6$ Hz, 6H). ^{13}C NMR (126 MHz, acetonitrile- d_3) δ 230.20, 156.98, 152.60, 149.91, 148.31, 142.65, 142.10, 137.33, 137.28, 133.96, 131.68, 131.58, 130.17, 128.99, 128.64, 128.14, 128.02, 126.95, 126.90, 25.54, 23.80, 15.21, 14.17. ESI-MS: $[\text{M}-\text{H}]$ calcd. 765.3184, anal. 765.3150. EA: calcd. C: 58.75% ; H: 4.93% ; N: 11.92%; anal. C: 58.01% ; H: 5.02% ; N: 11.67% ;

Synthesis of $\text{Fe}(\text{phen})_2(\text{DiPP_carbene})[\text{BF}_4]_2$ (3): 0.167 g (0.17 mmol, 1 eq) of $[\text{Fe}(\text{phen})_2(\text{CNDiPP})_2](\text{BF}_4)_2$ was dissolved in 5.86 mL of dichloromethane in a pressure tube, followed by 0.329 mL (10.2 mmol, 60 eq) of hydrazine was added and the solution became yellow/green in color. This was removed from the glovebox and warmed to reflux temperatures. After 4 days, the reaction was cooled to room temperature. The purple-colored organic layer was increased in volume was extracted with water 2 times and dried with MgSO_4 and filtered. Dry ether was slowly added, which precipitated golden/brown and white precipitates. The solid was

subsequently filtered yielding a vibrantly blue filtrate which was dried, brought into the glovebox and dissolved in minimal dichloromethane whereupon 0.082 g (0.51 mmol, 3 eq) of $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ was added and stirred forming a red-colored solution. A solid was precipitated by layering in batches with dry diethyl ether while being stored at 5 °C. Black/red crystals formed suitable for x-ray diffraction. 0.103 g was filtered off (61 % yield). ^1H NMR (500 MHz, acetonitrile- d_3) δ 9.23 (s, 1H), 8.87 (dd, J = 5.2, 1.3 Hz, 2H), 8.80 (dd, J = 8.3, 1.2 Hz, 2H), 8.49 (dd, J = 8.2, 1.3 Hz, 2H), 8.28 (d, J = 8.9 Hz, 2H), 8.21 (d, J = 8.9 Hz, 2H), 8.02 (dd, J = 8.3, 5.2 Hz, 2H), 7.49 (dd, J = 8.1, 5.2 Hz, 2H), 7.43 (dd, J = 5.3, 1.3 Hz, 2H), 7.27 (t, J = 7.6 Hz, 2H), 7.22 (dd, J = 7.7, 1.6 Hz, 2H), 7.09 (s, 2H), 6.98 (dd, J = 7.6, 1.6 Hz, 2H), 3.30 – 3.18 (m, 2H), 1.39 (d, J = 7.0 Hz, 6H), 1.14 (d, J = 6.9 Hz, 6H), 0.90 – 0.80 (m, 3H), 0.69 (d, J = 6.9 Hz, 6H), -0.00 (d, J = 6.8 Hz, 6H). ^{13}C NMR (126 MHz, acetonitrile- d_3) δ 229.59, 156.65, 152.80, 149.90, 148.30, 147.11, 146.38, 137.31, 132.21, 131.72, 131.60, 130.51, 129.06, 128.97, 128.78, 128.62, 128.58, 126.93, 126.88, 125.30, 29.44, 28.20, 24.37, 23.78, 23.63, 22.76. ESI-MS: $[\text{M}-\text{H}]$: calcd: 821.3732, anal. 821.3764.

Synthesis of $[\text{Fe}(\text{phen})_2(\text{DiPP_C}_2\text{H}_3\text{N}_4)]\text{BPh}_4$ (4): A methanolic solution of equimolar $[\text{Fe}(\text{phen})_2(\text{CNDiPP})_2](\text{BF}_4)_2$ and NaBPh_4 was made and heated for ~1 hour, the yellow precipitate was filtered and washed with methanol. This was brought into an inert atmosphere glovebox. A dichloromethane (13.0 mL) solution of $[\text{Fe}(\text{phen})_2(\text{CNDiPP})_2](\text{BPh}_4)_2$ (0.366 g, 0.3 mmol, 1 eq) was made. To this was added 0.491 g (15.4 mmol, 60 eq) of hydrazine. The synthesis was continued in the same manner for complex **3** but did not include the addition of acid after purification. The purification was performed as described above, where successive precipitates were filtered off, and the ether addition was continued until a blue powdery precipitate was obtained with a mass of 0.79 g. Yield, 34%. ^1H NMR (500 MHz, acetonitrile- d_3)

8 9.22, 8.58, 8.32, 8.30, 8.20, 8.18, 8.11, 8.09, 7.88, 7.51, 7.50, 7.39, 7.07, 6.84, 1.38, 1.37, 1.27, 1.14, 1.12, 1.11, 0.64, -0.06, -0.07. Note these represent chemical shift of broadened peaks and thus multiplets are not available. No other characterization is available.

4.2.2 Computational methods:

All computations were performed using the Gaussian 16 suite coupled to Avogadro for molecular visualizations.¹⁷ Calculations were performed in a methanol polarized continuum.²⁷ Using density functional theory (DFT) with the B3LYP-GD2 and uB3LYP-GD2 functionals for low and high-spin states respectively, with empirical dispersion.¹⁸⁻²¹ The 6-311G* basis set were used for all atoms, except Fe, which utilized the pseudo-potential SDD during optimizations.²²⁻²⁶ NBO6 was utilized as an additional module for Gaussian 16.^{6,7} NBO output was parsed using a homebrewed python program reported in the appendix of this chapter. Orbital partitioning was calculated with AO mix software by Jon Yarranton.¹⁶

4.2.3 Transient Absorption Spectroscopy

All TA measurements were performed on a system described previously.^{8,9} Spectrophotometric grade methanol was used for all measurements. Optical density was maintained around 0.6 for all measurements. Samples were excited at 510 nm and 550 nm in successive experiments. 580, 600, and 620 nm probe wavelengths were used.

4.2.4 Electrochemistry

Electrochemistry was performed in an argon filled glovebox using a potentiostat from CH-instruments. The 0.1M TBAPF₆ acetonitrile supporting electrolyte immersed the three-electrode setup which included a glassy carbon working electrode, platinum wire counter electrode, and a silver wire pseudo-reference electrode. A ferrocene internal standard was used, and all results are reported therein. Cyclic voltammetry (CV) experiments were run with 100

mV/s scan rate for oxidations and 500 mV/s for the reductions. Experiments started on the far ends of the electrochemical waves. Differential pulse voltammetry (DPV) was performed in conjunction with CV.

4.3 RESULTS AND DISCUSSION

4.3.1 *Synthesis:*

The synthesis of the complexes was discussed in the previous chapter. Their sensitivity to running in reaction conditions like acetonitrile was noted very quickly and DCM was chosen to be the solvent of choice for prep-scale reactions however we acknowledge that this may not be the optimal solvent. Further, the importance of having blocking groups adjacent to the isocyanide functionality was noted. These groups protect the functionality from side reactions likely derived from the protonation of an intermediate species generated by some acid in solution. The proton release of the final product is the likely driver.

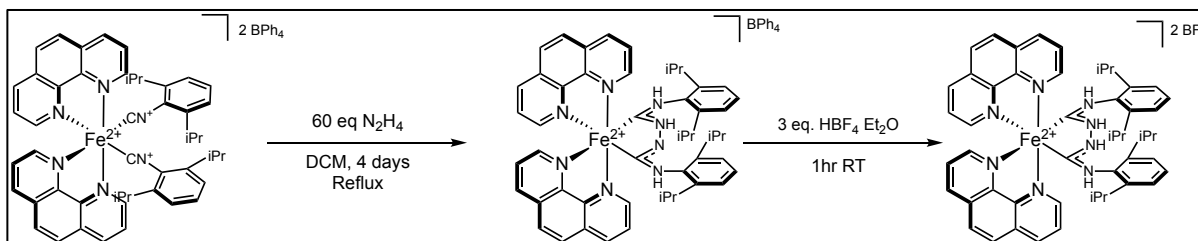
In the syntheses of **2** and **3**, for example, no formation of $[\text{Fe}(\text{phen})_3]^{2+}$ is observed, which does still occur to some degree in the synthesis of **1**. The size of these groups protects the intermediates and the imine functionality. These groups slow the productive reaction considerably, however. Consider the fact that in the case of complex **3**, completion is not reached and there is commonly starting material still present after 4 days of reaction time. However, the stability imparted by the larger alkyl functionality in **2** and especially **3**, makes purification easier.

While less time was spent on the optimization of the synthesis of **3** the benefits of this protection are clear. The isopropyl groups facilitate the stability of the deprotonated imine form meaning that removal of hydrazine and its associated salts could be done through aqueous extraction. This also meant that the intermediate could be isolated and characterized as its own

species and purified from the starting material based on charge differences. Chapter 5 will address the preliminary investigations of this imine form. It is unlikely that the aqueous extraction method can be used for **1** and as such the amount of acid required for protonation is determined by amount of hydrazine present. In this report, 16 equivalents of acid were added to the solution of **1** to neutralize the ~13 equivalents of hydrazine remaining and to protonate the complex to give the carbene form. The precipitated salts are removed by filtration in a nitrogen glovebox. While, likely more tolerant to the aqueous extraction, isolation of **2** was performed in a similar manner to **1**, however with an increased ratio of amine to speed the reaction.

In the synthesis of **3**, the phenyl borate salts of the isocyanide precursor were used as it was found to be easier to remove from the intermediate imine form. The complex was converted to the fluoroborate upon the addition of the fluoroboric acid to make the carbene form, confirmed by the lack of the phenyl borate signal in proton NMR. Trouble shooting this reaction was not as in-depth as it was for the species **1** and **2**. As such the optimization to drive the reaction to completion, and eliminate the remaining starting material was not performed. However, due to its protective properties, different solvent conditions and thus higher temperatures would facilitate the complete conversion to the final product. Furthermore, this could lead to the

reduction in the hydrazine required, meaning less water for extraction, and thus less decomposition.



Scheme 4.1: Synthetic scheme for **3**. All reactions were performed under a nitrogen atmosphere. (Yield, 31%). Complexes **1** and **2** were synthesized in a similar manner with different reaction times and hydrazine equivalents.

The ability to isolate the imine form of **3**, opens the system to a whole world of reactivity. For example, alkylation of the imine nitrogen could be achieved in a straightforward manner, for example MeI, which would preferentially react with excess amine, if solutions of the intermediate imine forms of **1** or **2** were dosed. Methylation of this backbone position could have electronic and steric effects that could yield 1:1 comparison with **3**. Discussion on the nature of the deprotonated form of **3** will be done at the end of this chapter.

4.3.2 X-Ray Crystallography and Structural Analysis

Quantification of the electronic effects imparted by the structural modifications can be interrogated with structural analysis by examining the *trans*-influence of the carbene ligand. Furthermore, the hybridization of the carbene carbon can be determined and should give some insight on electronegativity difference across the series in accordance with Bent's rule. Single

crystals were grown of **1-3** and their x-ray structures were collected. The structures are given in the following figures.

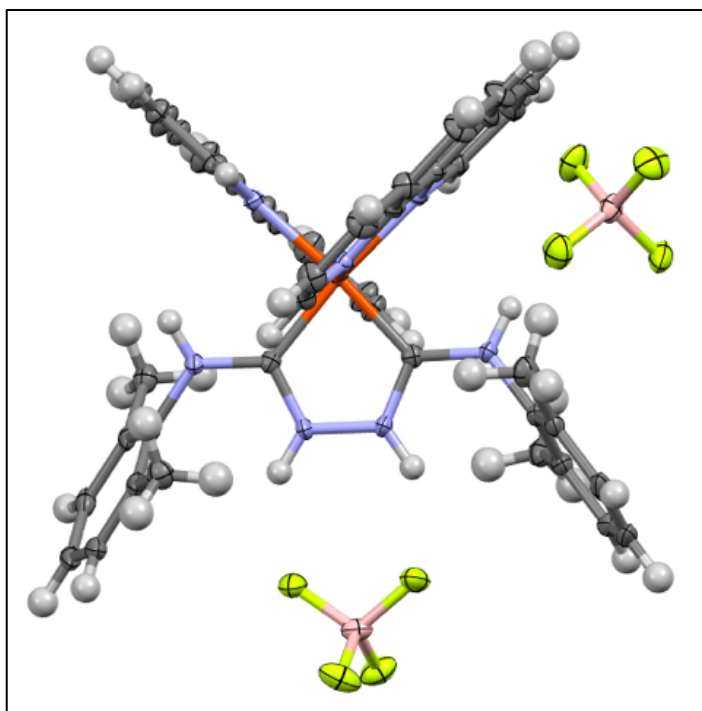


Figure 4.2: X-Ray structure of **1**. Orange: Iron; Purple: nitrogen; Grey: carbon; White: hydrogen; pink: boron; yellow: fluorine. Thermal ellipsoids at 50% probability.

The crystal structure of **1** indicates an interesting hydrogen bonding interaction with the BF₄⁻ anion through the two proximal protonated nitrogen (proximal to the C₂ axes of rotation). The distance is 2.026 Å, in line with many BF₄⁻ H-bonding complexes.¹⁰ The inner coordination sphere exhibits a nominal C₂ symmetry, as expected for this configuration. The Fe-C bond lengths are 1.914(2) Å and 1.921(2) Å, outside the margin of error of 2 pm. This gives an average of 1.917 Å in very good agreement with [Fe(phen)₂(C₄H₁₀N₄)]²⁺.¹ This asymmetry is likely due to crystal packing forces in the lattice although it may be biased by a minor H-bonding interaction with the second BF₄⁻ anion. The influence of the carbene moieties is observed in the Fe-N bond lengths in the *trans*-position with bond lengths of 2.011(2) Å and 2.023(2) Å with an average bond length of 2.017 Å. Consider the *trans*-influence in [Fe(phen)₂(C₄H₁₀N₄)]²⁺ which

has an equivalent average bond length of 2.018 Å. As the magnitude of the *trans*-influence depends on the donor ability of the ligand, there is no statistical difference in donor ability between **1** and $[\text{Fe}(\text{phen})_2(\text{C}_4\text{H}_{10}\text{N}_4)]^{2+}$. The axial nitrogen's have bond lengths of 1.969(2) Å and 1.970(2) Å, there equivalence speaks to the fact that the bond asymmetry is an in-plane effect. These values are equivalent to those observed for $[\text{Fe}(\text{phen})_2(\text{C}_4\text{H}_{10}\text{N}_4)]^{2+}$. These are also in line with the Fe-C bond lengths seen in other heteroleptic carbenes.¹¹

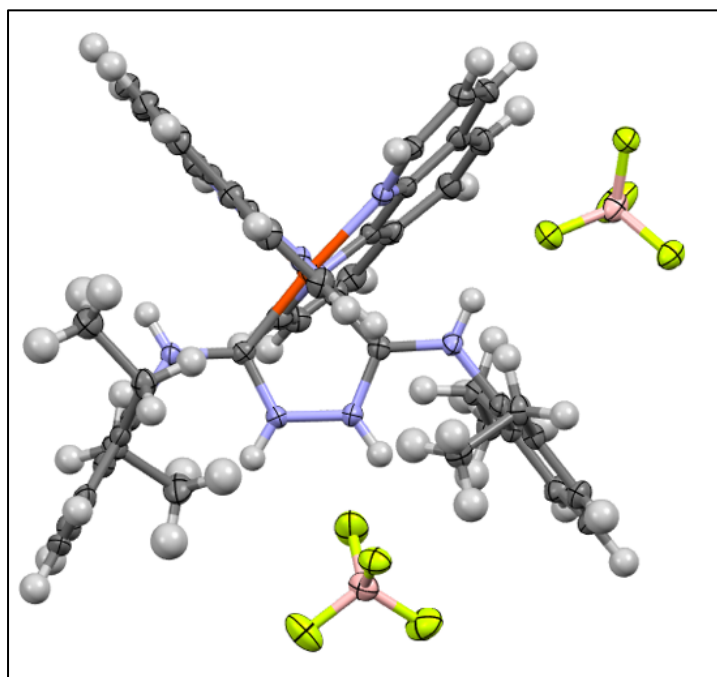


Figure 4.3: X-Ray structure of **2**. Orange: Iron; Purple: nitrogen; Grey: carbon; White: hydrogen; pink: boron; yellow: fluorine. Thermal ellipsoids at 50% probability.

The bulkier compound **2** shows a structure like the methyl derivative but with a few obvious differences. For example, the tetrafluoroborate anion does not hydrogen bond with both proximal hydrogens but rather H-bonds with one, having a longer F---H bond of 2.081 Å. This is a superficial difference however, as the inner coordination sphere is not however disrupted by the bulky groups, where the Fe-C bond lengths are 1.909(3) Å and 1.919(3) Å for an average of 1.914 Å. It is very similar to the methyl derivative, however just outside error for the former Fe-C bond. The inequivalence, again is likely due to crystal packing

forces. While both exhibiting the *trans*-influence, one Fe-N bond *trans* to the carbene is significantly different than the methyl derivative with bond lengths of 2.004(3) Å and 2.013(2) Å an average of 2.009 Å compared to the average of 2.017 Å in **1**. This suggests, the force experienced by the ligand field in **2** is weaker than in **1**. Even though the Fe-C bond length is shorter in the former, it is not necessarily statistically relevant. Oddly enough, the *trans*-influence is larger in the case of the longer Fe-C bond. The reason for this unclear. The axial Fe-N bonds are equivalent at 1.970(3) Å and 1.974(3) Å almost both within error of the same bonds in **1**.

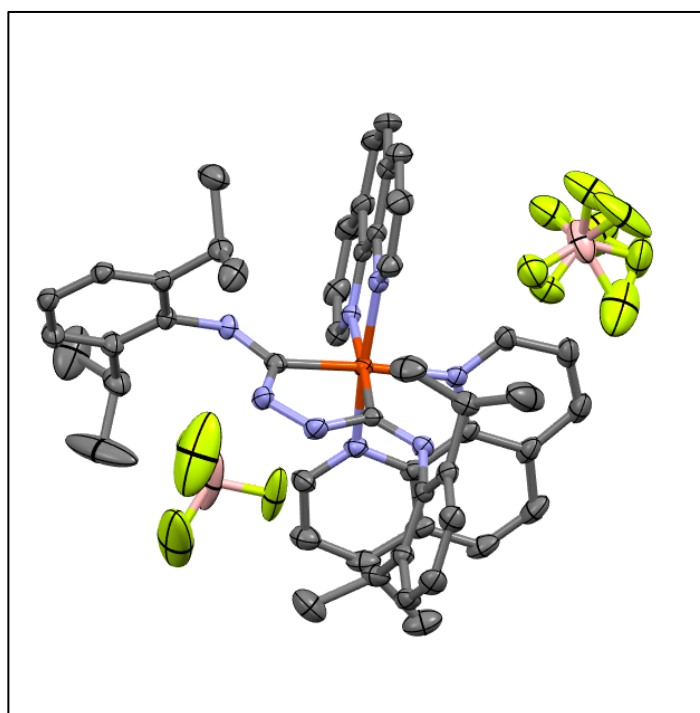


Figure 4.4: X-Ray structure of **3**, with hydrogens removed for clarity. Orange: Iron; Purple: nitrogen; Grey: carbon; pink: boron; yellow: fluorine. Thermal ellipsoids at 50% probability.

Compound **3** is expected to be the bulkiest. The crystal structure shows some significantly disordered hydrogens in some of the isopropyl groups and anions; however, the rest of the structure is well resolved. A hydrogen bonding interaction with 2.119 Å is observed for the counter anion. The bonding in the inner coordination sphere is standard. The Fe-C bond lengths are 1.920(2) Å and 1.918(2) Å are slightly longer than the other two systems. The *trans*-

influence is observed in this system, resulting in Fe-N bond lengths of 2.005(2) Å. When taken as a gauge of donor strength the destabilization is smaller than in **1** and **2**, suggesting that **3** is the weakest donor. Note that the asymmetry in the Fe-C and Fe-N_{trans} bonds is not observed in **3** suggesting that perhaps structural rigidity and packing forces are distributed into other degrees of freedom. The axial nitrogens are equivalent and in agreement with the other systems.

Table 4.1: Selected bond lengths for the series obtained from x-ray crystallography.

Bond	1	2	3
Fe-C1	1.9142 (17)	1.909 (3)	1.918 (2)
Fe-C2	1.9206 (18)	1.919 (3)	1.920 (2)
Fe-Nax1	1.9691 (15)	1.968 (3)	1.967 (2)
Fe-Nax2	1.9703 (15)	1.974 (3)	1.967 (2)
Fe-Neq1	2.0114 (15)	2.004 (3)	2.005 (2)
Fe-Neq2	2.0227 (14)	2.013 (2)	2.005 (2)

The carbene in **1** appears to be the strongest donor and **3** the weakest based on the *trans*-influence destabilization of bond lengths. This can be explained by steric effects as this runs counter to the expectation that the isopropyl derivative should exhibit the better donor ability based purely on inductive arguments. Utilizing a valence bond approach, this can be tested across the series, with the understanding that hybrid orbital composition is a function of orbital stabilization in bonding (i.e. Bents rule). Utilizing Coulson directionality and Sum rule, the hybrid bonding orbital composition of the carbene carbons was found by solving a system of equations which are given in the appendix. The bond angles in table 4.2 was utilized as inputs and the scheme included is the key for the table, where N_{in} represents the nitrogens near the rotational axis. Average hybridizations are included table 3 which includes the NBO calculated hybridizations for **1**.

Table 4.2: Carbene bond angles for the series from crystal structures. The groups (not in bold) are illustrated in the legend on the right hand side. Both carbenes, which are inequivalent are described.

Species	1	2	3
Group	Angle (degrees)	Angle (degrees)	Angle (degrees)
1	114.41	115.00	114.21
2	130.29	129.88	128.81
3	115.03	114.98	116.52
1	114.89	115.39	114.36
2	129.62	130.47	129.25
3	115.2	114.09	116.15

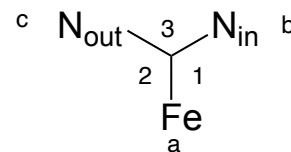


Table 4.3: Bonding hybrid averages calculated from the data in table 4.2. The groups which each hybrid is directed to are illustrated in the figure therein. The table also includes the average CNCN-torstional angles which gauges planarity of the carbene ligand.

Species	1	2	3	1
Group	Hybridization	Hybridization	Hybridization	NBO Calc.
a	1.58	1.56	1.69	1.55
b	3.70	3.59	3.48	2.29
c	1.51	1.56	1.48	2.17
CNCN-torsion	11.70	8.61	4.55	-

The bonding hybrids show an interesting p-character polarization towards the inner nitrogen which are nearly sp^4 hybrids, where the remining two bonds compensate in the other direction in being sub sp^2 hybrid orbitals. This is contrasted with the NBO calculations which exhibit a hybridization more in line with the expected sp^2 character of a carbene. This cannot be explained by anion effects in the crystal as the bond angles in the NBO calculations are approximately the same as for the crystals. It more likely has to do with the planarity of the ligand in the crystals, which is relieved in computations. The agreement with the Fe-C bonding hybrid, however, is consistent between measured and calculated, suggesting it is higher in s-character that would be expected for a traditional carbene of sp^2 hybridization.

Across the series, it appears that the derivative **2** has the most s-character in the Fe-C bond. Bent's rule suggests s-character accumulates in hybrids directed at electropositive species and p-character accumulates in hybrids directed at electronegative species. The s-character of the bonding hybrids should be proportional to the difference in electronegativity of the Fe(II) atom and the carbene carbon. A similar statement should apply to the s-character of the other hybrids as well. If we accept that inductive effects are in play, and that we should expect an increase in basicity in the order **1** Me < **2** Et < **3** iPr, however a monotonic change in the bonding hybrid composition with donor ability is not observed. Therefore, inductive effects alone describe electronegativity differences. Interestingly, there is a monotonic change for the C-N_{in} bonding hybrids in the order in the order **1** Me > **2** Et > **3** iPr. This can be explained by steric effects of the different alkyl groups and their imposition of planarity in the carbene backbone. Table 4.3 includes the average CNCN-torsion angle (C_{ph}-N_{out}-C-N_{in}) which decreases with increasing size of the alkyl group. This forced planarity increases the s-character of the C-N_{in} bonding hybrid, which explains the drop in hybridization across the series. This removes s-character which can be used for the Fe-C hybrid.

This observation is not in line with the observed *trans*-influence, of which **3** was found to have the lowest and **1** the highest *trans*-influence. This, along with the slightly longer Fe-C bond lengths of **3** suggests that steric effects do play a role in weakening the interaction of **3** with the metal center compared to those observed for the other two derivatives. As this likely translates into energies of the ligand field states, this should have a discernable effect upon the dynamics of the species.

An important distinction is to be made between steric effects which change the donor ability of the ligand, like those steric effects that forced planarity of the carbene, from those

steric effects which are leveraged in the x-axis strategy. The former can be thought of as being somewhat independent from the inner workings of the ligand field to the degree they do not change DOF which drive vibronic coupling between ligand field states. This does not mean that they are not important, utilizing such steric interactions could be leveraged for the purposes of the y-axis strategy insofar as the steric effects change the donor ability of the ligand. However, establishing a steric effect, does not imply the systems are isolated from electronic perturbation.

4.3.3 Steady state absorption and electrochemistry

Steady state absorption spectra in methanol are reported in figure 4.5. It shows the MLCT absorption bands for each species in the visible region with a molar absorptivity for each between 8,000 and 10,000 $\text{cm}^{-1}\text{M}^{-1}$. There are several similarities between the spectra. Notably is their similar absorptivity and onset of their main band which peaks around 17,000 cm^{-1} . Furthermore, their main feature seems to be two bands, consistent with that observed for $[\text{Fe}(\text{phen})_2(\text{C}_4\text{H}_{10}\text{N}_4)]^{2+}$. However, the relative intensities of these bands differ. For example, the two bands of **1** (in blue) are approximately equal, which is not the case of the band shape for **2** and **3**, in which have their leading band has a higher absorptivity. Interestingly **2** and **3** have a shoulder around 15,000 cm^{-1} as well as a proportional loss of the absorption band around 20,000 cm^{-1} . While this could be due to the increased allowedness of some absorption transitions, due to geometry changes inducing novel vibronic couplings, this is likely due to the incomplete protonation of the carbene backbone or proton release, in the cases of the bulkier substituents. This deprotonation event redshifts the absorption by a significant degree. Figure 4.14 illustrates this absorption for $[\text{Fe}(\text{phen})_2(\text{C}_4\text{H}_{10}\text{N}_4)]^{2+}$ upon deprotonation with triethylamine. None of this impurity is seen in the ^1H -NMR spectra, however due to its diastereotopic proton environment in the basic form, the NMR signals broaden which would be difficult to detect in low

concentrations. Elemental analysis confirms the purity of **2** as a solid. This suggests the sample is related to proton release in solution. Future studies will require some buffered system in order to maintain specificity.

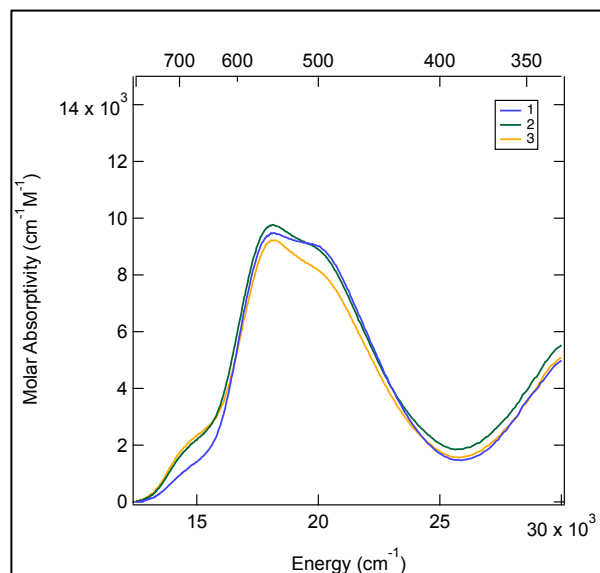


Figure 4.5: Absorption spectra in methanol of the complexes studied in this chapter.

This poses a problem for the transient absorption measurements, as pumping at a given wavelength, will likely excite both protonated and unprotonated species, leading to complicated kinetics. An attempt was made to reduce this complexity by exciting **2** and **3** only at 510 nm to minimize the contribution of the deprotonated species to the data.

Electrochemical analysis by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) was performed. The results are similar for the series. Three oxidations occur in the electrochemical window. The first oxidation is around 320-360 mV vs. Fc/Fc^+ and are quasi-reversible (see appendix). This was taken to be the $\text{Fe}^{2+/3+}$ in that it is in reasonable agreement with the oxidation of $[\text{Fe}(\text{phen})_2(\text{C}_4\text{H}_{10}\text{N}_4)]^{2+}$. The DiPP complex is shifted positive by 40 mV. This likely corresponds to an over-potential required for the bulkier derivative that may require some rotation about the isopropyl bond with the aryl group to allow for contraction of the inner coordination sphere in the more Lewis acidic Fe^{3+} state. This is supported by the divergence from

unity, of the peak currents for the oxidation, which implies irreversibility across the series. This irreversibility could be due to chemical stability of the oxidation products or slower kinetics across the series. As we would expect chemical stability to increase with a more rigid system as in **3**, an asymmetry in the kinetics of oxidation and reduction is the only explanation, which gets larger with the size of the alkyl group. The second waves are approximately 400 mV and 1000 mV more positive than the first oxidation and are irreversible. The potentials change with the species, suggesting it is not some common impurity, but is related to the structure of the complex. Its presence in every case suggest it is not related to the protonation state of the carbene, which would lead to a different profile between **1** and the other two species. These other oxidations could be due to the broken degeneracy of the t_{2g} manifold illustrated in chapter 1.

Table 4.4: Electrochemical parameters of the complexes studied.

Complex	E_{ox} (V vs. Fc/Fc ⁺)	E_{ox} (V vs. Fc/Fc ⁺)	$E_{ox}-E_{red}$ (eV)	I_c/I_a (ox)	ΔE_p (V)
1	0.32	-1.778	2.098	1.29	0.077
2	0.328	-1.8	2.128	1.7	0.082
3	0.36	-1.772	2.132	1.86	0.085

Further, addition of amine ligands makes this system incredibly electron rich, and thus could mean these are related to the oxidation of the ligand backbone. There are two distinct electron rich regions in the ligand, the proximal and distal nitrogen atoms and thus could represent any of these higher energy oxidations. There is, however, a great chance that electronic reorganization of the ligand backbone occurs and these distinct regions breakdown. Important to note is the distinct oxidation potential of the most positive wave compared with the isocyanide derivatives which occur at a different voltage and are reversible, suggesting the less positive oxidations do not lead to the oxidation of hydrazine to N₂.

Reductive electrochemistry is generally irreversible even at a scan rate 2000 mV/s, except for the **3** which shows a distinct voltammogram in the reductive region with 500 mV/s. The insensitivity of the reduction chemistry is consistent with the lack of any structural dependence upon its potential. The increased reversibility in the case of **3** hints at the chemical irreversibility of the reductive chemistry in the other two species.

Structural dependence of the first oxidation indicates the bulk of the *-iPr* group impacts the process, in this case acting as an over-potential for oxidation. Like the hybridization parameters, species **1** and **2** group together in their first oxidation potentials compared to **3**, suggesting the steric effect in the overpotential of oxidation acts as a shelf, which is not large enough in the cases of **1** and **2** but does matter in the case of **3**.

Spectroelectrochemistry was not performed on these compounds. It is assumed that the spectral profile of the charge transfer manifold will be like what was previously reported.¹ This can be considered necessary future works.

4.3.4 Fitting of Preliminary Transient Absorption Spectroscopy Data

Preliminary TA experiments were performed on **1-3**. Different exponential models were tested to describe each species. The following is a discussion of these models for the GSB and ESA regions along with their implication. It is assumed that the general features of the transient spectra are analogous to those for $[\text{Fe}(\text{phen})_2(\text{C}_4\text{H}_{10}\text{N}_4)^{2+}]$ whose full spectrum is presented in figure 2.1. Therefore, similar spectral regions were probed.

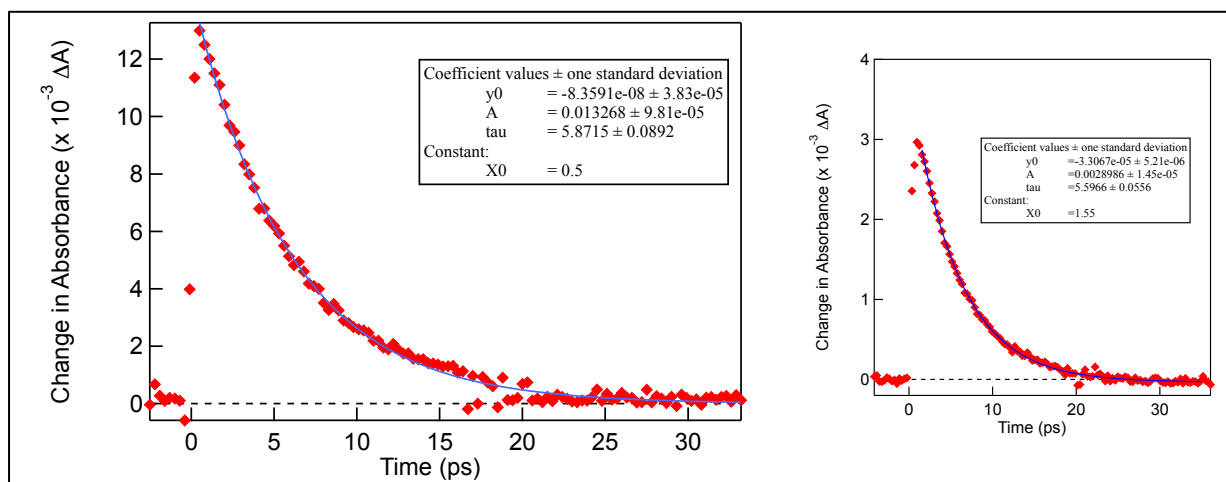


Figure 4.6: (right) decay profile of **1** at 620 nm after excitation at 510 nm. (left) 620 nm probe with 550 nm excitation.

The excited state absorption features at 620 nm were fit to single exponential functions with very low error. These gave time constants of 5.9 ps, 5.9 ps, and 5.8 ps for **1-3** respectively. Figures 4.6 and 4.7 show the fits of these decays for **1** and **2-3** respectively. There is a rise-time associated with each ESA feature too, which can be fit with a second exponential to around 500 fs in the case of **1** and **2**, however the accuracy of the rise times are limited due to the temporal resolution of the instrument. These double exponential fits are in the appendix of this chapter. An isosbestic point forms at 600 nm for **1** and **2** at a rate like the rise time observed at 620 nm. The growth and monotonic decay of the feature at 620 nm and the monotonic decay at 600 nm suggests that we are observing the shift in the isosbestic point which first occurs at 620 nm. This feature is lost as the ESA shifts leading to the recovery of a GSB at 600 nm at a similar rate. The blue shift in the ESA has been noted previously.¹ This suggests that the decay of the ESA is in accordance with the data measured in chapter 2. To determine if there are any relevant structural trends in the data, several more experiments would need to be run, especially at improved time resolutions. There does not seem to be any structural dependences on the kinetics of the ESA features of each complex. If the analysis of chapter 2 holds, which describes the decay of the

ESA corresponding to a $^3\text{MLCT} \rightarrow ^3\text{MC}$ pathway, then the structural modifications between **1-3** do not significantly change the rate at which this occurs.

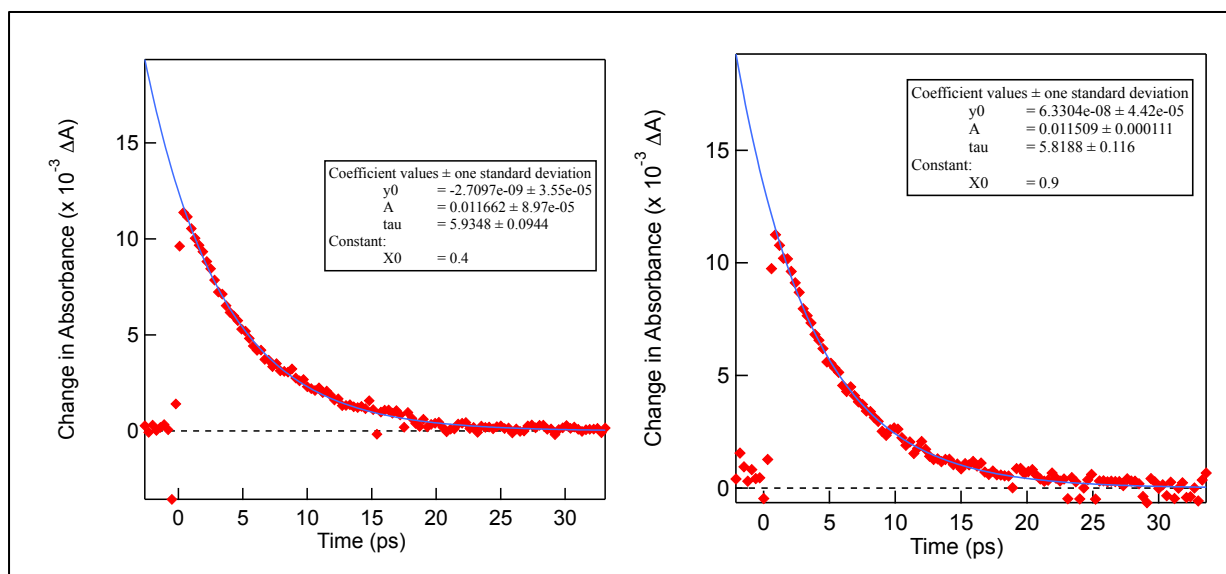


Figure 4.7: (left) decay profile of **2** at 620 nm after excitation at 510 nm. (right) decay profile of **3** at 620 nm after excitation at 510 nm.

The GSB region is more difficult to fit. There does seem to be a species dependence as well. For example, fitting **1** gave the best fit with three time-constants. The trace, the fit, and its residuals are given in figure 4.8. The red crosses indicate data that is neglected by the fit. This gave the time constants of 0.3 ± 0.10 ps, 2.7 ± 0.3 ps, and 16.3 ± 4 ps. The error on the longest component is about 25%. The residuals are small compared to the biexponential fit, which is pictured in the appendix. The normalized fitting amplitudes in of each component in ascending order are 0.28, 0.6, and 0.12, suggesting that the ~ 3 ps component dominates the kinetics. An increase in the lifetime of the ^3MC is a plausible explanation for the increased lifetime of component 3 compared to the largest component of $[\text{Fe}(\text{phen})_2(\text{C}_4\text{H}_{10}\text{N}_4)]^{2+}$.

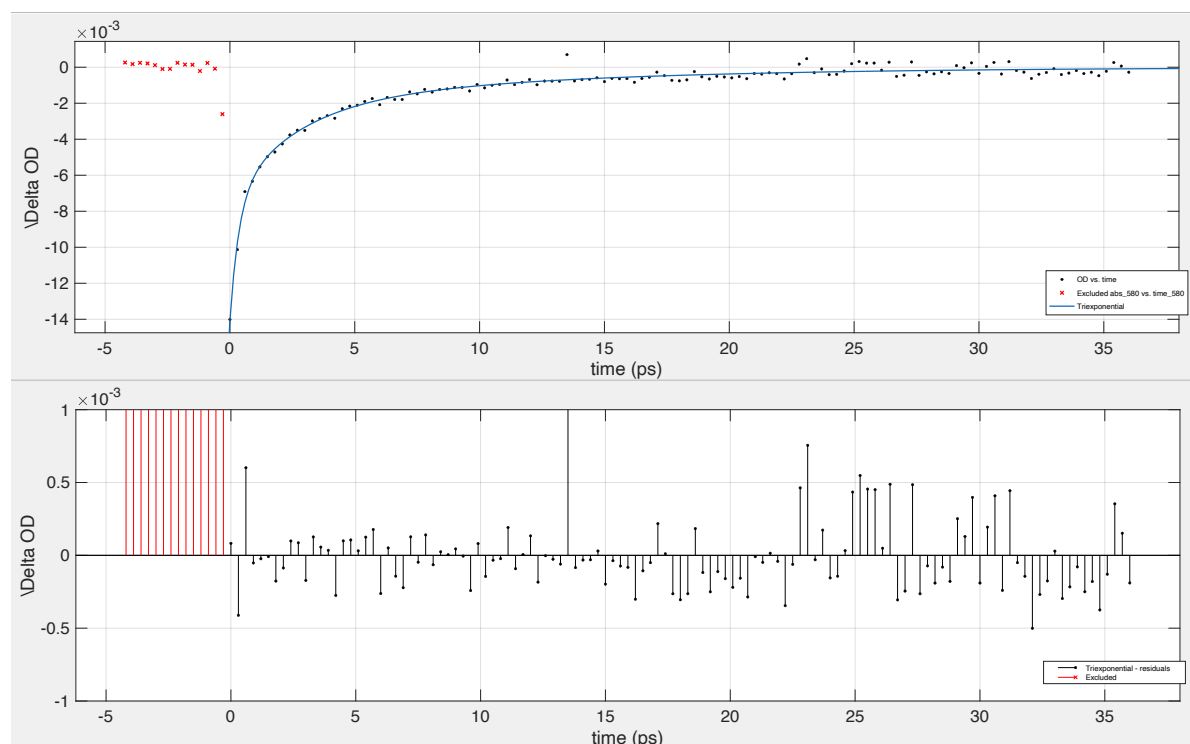


Figure 4.8: decay profile of **1** at 580 nm after excitation at 510 nm and the associated residuals to a fit of a triexponential function.

The triexponential fit of **2** gave time constants of 0.8 ± 0.3 ps, 3.7 ± 2.6 ps, and 18.4 ± 16 ps, which had poor fits for the long component ($\sim 100\%$ error). The fit was improved by excluding the first two points and a fitting to a biexponential function which is shown in figure 4.9. This fit gave time constants of 1.6 ± 0.2 ps and 11.5 ± 2 ps. This led to a fit with approximately the same magnitude of residuals as the tri-exponential fit. The fitting amplitude for the ~ 1 ps component still dominates the decay suggesting a continuity between these data and **1**. It should be emphasized that the fit to a biexponential model should only be considered a placeholder. This model is presented purely based on the improved margin of error of the fits. The triexponential fit of species **2** is presented in the appendix of this chapter.

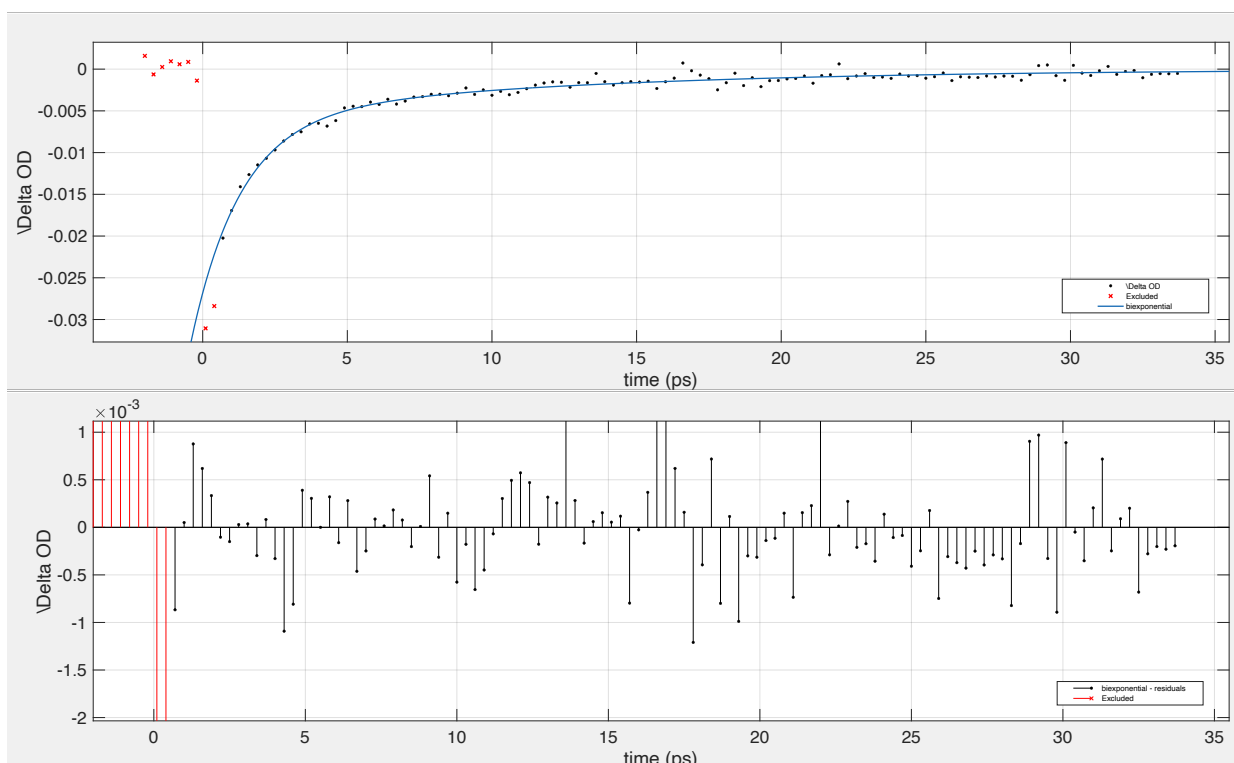


Figure 4.9: Decay profile of **2** at 580 nm after excitation at 510 nm and the associated residuals to a fit of a biexponential function.

The triexponential fit of **3** gave poor fits ($>25\%$) for the long component although but are tolerable. This is depicted in figure 4.10. The time constants for this fit were 0.6 ± 0.4 ps, 2.4 ± 0.9 ps, and 23.7 ± 6 ps. Removing the early data did not yield an improvement in fitting results. This is likely a triexponential function as the errors were much worse with biexponential model. One notable feature of the data in figure 4.10 is that it does not return to baseline. Thus the time domain was increased to 80 ps, shown in figure 4.11 (for these data the laser was tuned to 550 nm so the data are not a 1:1 comparison with the previous). The trace almost returns to baseline. This gives a set of time constants of 0.6 ± 0.1 ps, 3.8 ± 0.3 ps, and 44.8 ± 6 ps. The reduction in the error of the third component suggests this wider scan window will be required for future studies

of **3** and that the significant errors of the largest components are a likely result of this. It can be assumed that this will also be required for compounds **1** and **2** as well.

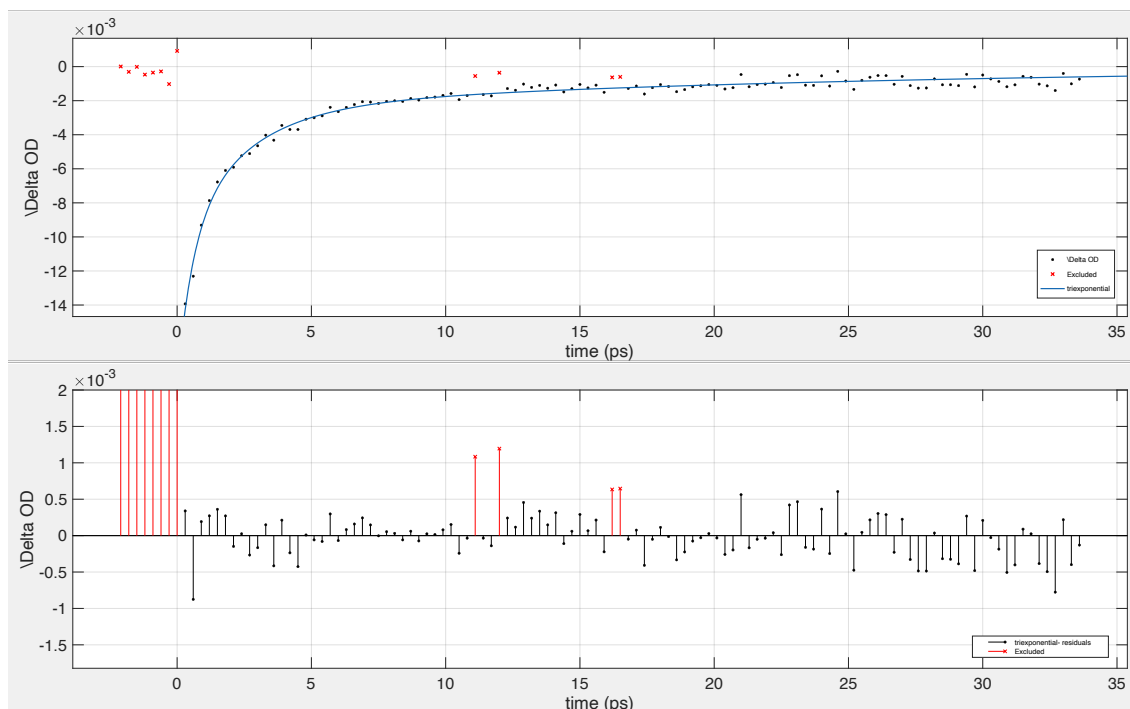


Figure 4.10: Triexponential fit of the GSB at 580 nm of **3** and the corresponding residuals after excitation at 510 nm. The fitting parameters were $A = 0.008$, $\tau_1 = 0.6$, $B = 0.008$, $\tau_2 = 2.4$ ps, $C = 0.002$, $\tau_3 = 23.7$ ps. The scan window was limited to 34 ps. The fits clearly do not return to baseline.

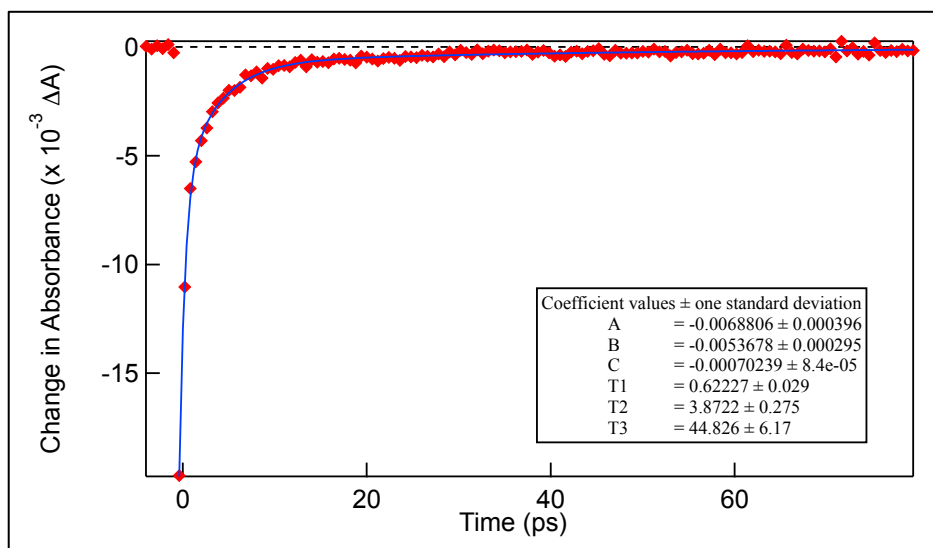


Figure 4.11: Triexponential fit of the GSB at 580 nm of **3** after excitation at 550 nm. The fitting parameters were $A = 0.006$, $\tau_1 = 0.6$, $B = 0.005$, $\tau_2 = 3.9$ ps, $C = 0.001$, $\tau_3 = 44.8$ ps. The scan window was extended to 80 ps.

Table 4.5: Summary of the preliminary spectroscopic data discussed above.

Pump	Probe Region	620 nm	580 nm		
	Species	τ_1 (ps)	τ_1 (ps)	τ_2 (ps)	τ_3 (ps)
510 nm	1	5.9 ± 0.1	0.3 ± 0.1	2.7 ± 0.3	16.3 ± 4
	2	5.9 ± 0.1	-	1.6 ± 0.2	11.5 ± 2
	3	5.8 ± 0.1	0.6 ± 0.4	2.4 ± 0.9	23.7 ± 6
550 nm	1	5.6 ± 0.1	0.4 ± 0.1	2.6 ± 1.2	11.0 ± 4
	3*	-	0.6 ± 0.1	3.8 ± 0.3	44.8 ± 6

*Time window extended to 80 ps.

A summary of the preliminary fitting data are presented in table 4.5. While we stress again the data is preliminary, there are some indications the synthetic modifications did perturb the dynamics. For example, in $[\text{Fe}(\text{phen})_2(\text{C}_4\text{H}_{10}\text{N}_4)]^{2+}$ the ground state recovery process occurs at a similar rate as the loss of the excited state absorption. The data here would suggest that that the ESA lifetime is shorter than the GSR process. If the model presented in chapter 1 is correct and holds for these systems, where deactivation along the thermalized pathway occurs by $^3\text{MLCT} \rightarrow ^3\text{MC} \rightarrow \text{GS}$: then the increased time to GSR is likely due to a prolonged lifetime of the ^3MC excited state. This prolonged lifetime cannot be explained by an increase in the LFS of the

carbene in **3** as it was observed that the *trans*-influence in **3** compared to **1** and $[\text{Fe}(\text{phen})_2(\text{C}_4\text{H}_{10}\text{N}_4)^{2+}]$ is small, and thus suggests it is a weaker donor (due primarily to steric reasons). The prolonged lifetime cannot be explained by the reduced donor ability of **3** which should lead to a faster rate of recovery, assuming Marcus inverted kinetics (which have been loosely established in chapter 2 for $[\text{Fe}(\text{phen})_2(\text{C}_4\text{H}_{10}\text{N}_4)]^{2+}$). A reduced electronic coupling could indeed explain the effect, which cannot be rule out at this time. The more likely explanation is due reorganization energy considerations and kinetic effects.

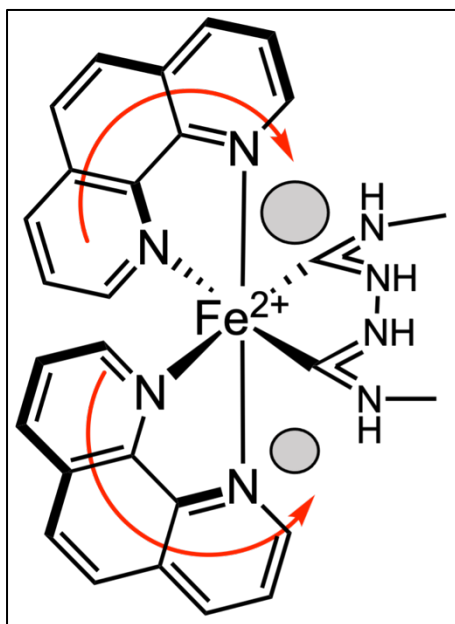


Figure 4.12: Chomping motion of the axial Fe-N bonds. The space that should be occupied by steric groups is shown as grey circles.

Kinetic effects are not ruled out from the data above. Consider the chomping motion depicted in figure 4.12 which was found to be the normal mode which described a significant majority of the reorganization energy for the $^3\text{MC} \rightarrow \text{GS}$ process in $[\text{Fe}(\text{phen})_2(\text{C}_4\text{H}_{10}\text{N}_4)]^{2+}$ highlighted in the Dushinsky calculations. Large bulky groups such as those present in the derivative **3** could couple to this motion and thus interrupt the ground state recovery process. The steric groups present in the series will occupy the space highlighted by the grey ovals in figure

4.12. The $^3\text{MLCT} \rightarrow ^3\text{MC}$ process, while it can traverse a similar coordinate, it likely has other options to reach the required minimum geometry of the lowest energy triplet state.

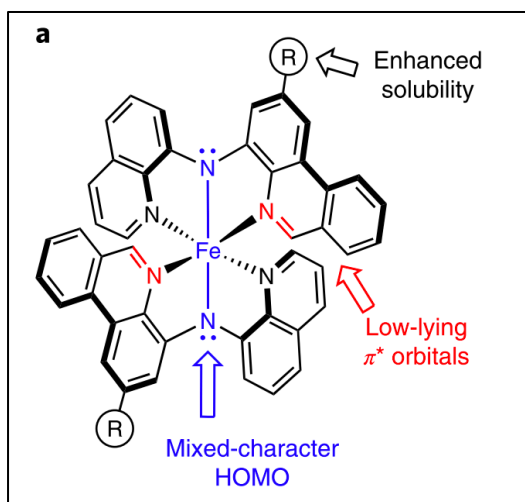


Figure 4.13: Illustration of the Herbert complex. Taken from reference 13.

There does not seem to be a structural dependence on the ESA as each species has the same lifetime of ~ 5.9 ps, the assignment with the most confidence in these compounds. Interestingly there does seem to be a pump dependence in the lifetime of the ESA, where excitation at 550 nm, leads to a shorter component in **1**. This will need verification in future studies; however, this probe dependence does show up in the long component of the GSB feature but leaves the shorter two components with no relevant change. A probe dependence in the ESA should translate to a probe dependence of the GSR if the mechanism in chapter 1 is applicable to these compounds. The lack of overlap between the measured time constants of the ESA and the mid-range component in the GSB is cause for concern and must be explored further.

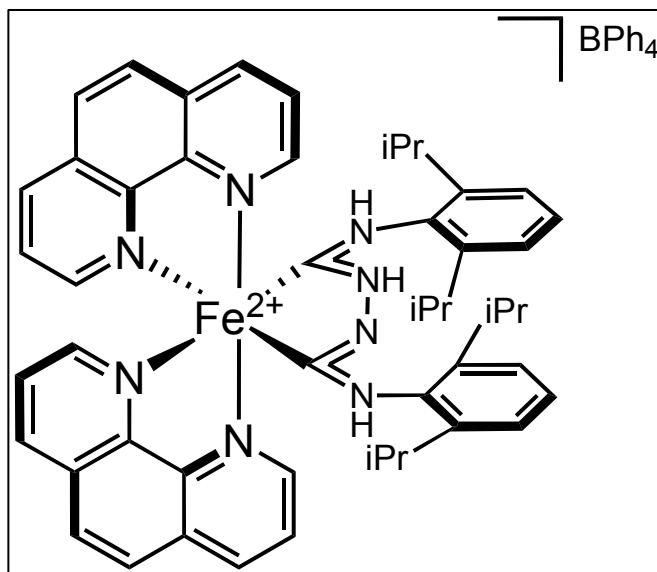
No probe dependence can be spoken to for **2** and **3**, although experiments were performed at the 550 nm excitation wavelength. The absorption spectra of these species in figure 4.5 suggest that probing at 550 nm would lead to excitation of multiple species. Other data which

include the data for **2** and **3** excited at 550, the biexponential fits of **1** and **3**, and the kinetics of the isosbestic point formation are presented in the appendix to this chapter.

4.3.4 HOMO-inversion in deprotonated carbene species

The spectral changes observed for the partially deprotonated complexes in figure 4.5 illustrate the drastic change in the absorption spectrum upon deprotonation, which are illustrated fully in figure 4.14. We would like to understand the change in the absorption spectrum from a perspective of a design strategy that has led to successful chromophore designs. Recent theoretical and experimental work have demonstrated that the concept of HOMO-inversion can increase the molar-absorptivity and extend the charge transfer lifetimes of Fe(II) chromophores.^{12–15} This phenomenon describes a smearing of orbital character across a metal and ligand system, a result of ligand π -donation into the metal. This orbital mixing increases the number of transitions leading to panchromatic absorptions, the type of behavior observed when **3** is deprotonated to complex **4** shown in drawing 4.2. Recently the Herbert group synthesized a complex that exhibited HOMO inversion that utilized a nitrogen lone pair to act as a π -donor. The compound is pictured in figure 4.13. This complex was found to have a 2 ns lifetime. Quantum chemical computations on this complex explained this superior lifetime was a product a lowest energy triplet state (deemed from vertical excitation of the ground state) with some charge transfer character. An increase in the molar absorptivity upon forming $[\text{Fe}(\text{phen})_2(\text{C}_4\text{H}_9\text{N}_4)]^+$ along with the increase in the absorptions blue of $25,000\text{ cm}^{-1}$ is observed suggests a similar thing is occurring here. Such a drastic change in the absorption spectrum

indicates a vastly different electronic structure, one that is likely to only perturb the HOMO orbitals of the ground state.



Drawing 4.2: Representation of **4**. Note the missing proton on the carbene. The connectivity is otherwise the same as that of **3**.

The attempted isolation of the complex $[\text{Fe}(\text{phen})_2(\text{C}_4\text{H}_9\text{N}_4)]^+$ unsuccessful. It was found that utilizing the aryl carbenes **1-3** had increased stability in its deprotonated form and were able to be isolated. The bulky *i*Pr- monocation complex was able to be isolated with reasonable purity which was used for spectroscopic studies and the decoronated version of **1** was utilized for computations as the convergence of the derivatives with larger alkyl groups did not converge on an energy minimum in time for this work. Thus, the remainder of this chapter discusses the computational and spectroscopic studies into the nature of these ligands and whether the observed red shift is due to HOMO inversion or some other phenomenon and whether this phenomenon translates into longer excited state lifetimes.

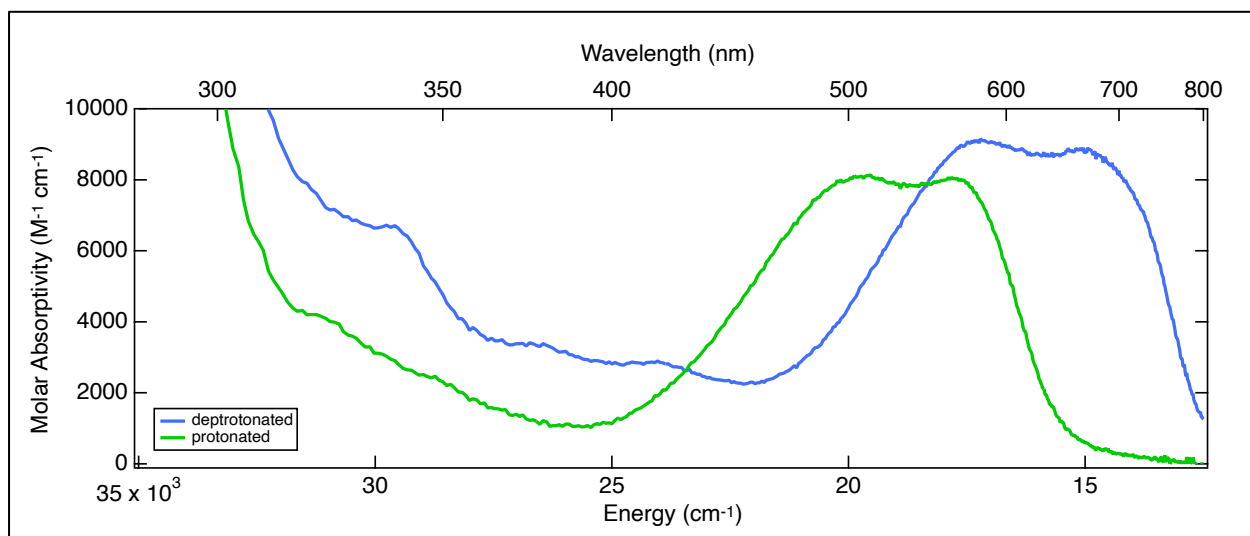


Figure 4.14: Absorption spectrum of $[\text{Fe}(\text{phen})_2(\text{C}_4\text{H}_{10}\text{N}_4)]^{2+}$ in dichloromethane (green) with the addition of a slight excess of triethylamine to form $[\text{Fe}(\text{phen})_2(\text{C}_4\text{H}_9\text{N}_4)]^+$. This process can be reversed by addition of excess acid.

4.3.5 Synthesis and Proton Transfer in Solution

The isopropyl complex studied in this chapter was synthesized and purified by precipitation. It was not characterized as robustly as the other species in this report. However, there is ^1H NMR evidence it exists but is fluxional in solution. This is indicated by the line-broadening of a crude mixture of **4** as the fluoroborate salt in figure 4.15. This broadening is likely due to proton transfer between the two diastereotopic forms of the compound. It is likely due to steric reasons as this behavior is not observed in the $[\text{Fe}(\text{phen})_2(\text{C}_4\text{H}_9\text{N}_4)]^+$ complex which should be less sterically encumbered. Temperature dependent ^1H NMR indicated a loss of signal due to broadening at higher temperatures suggesting a more complex picture than just proton transfer between diastereomers, which should sharpen with increased temperature. The spectra are included in the appendix to this chapter however no further analysis was performed. Future studies should examine proton transfer coupling to large amplitude ligand motion.

Formation of x-ray quality crystals of **4** was attempted in dry dichloromethane/toluene mixtures by evaporation in open air and as such there is no guarantee water did not penetrate the

sealed vial. This led to the formation of orange crystals, which corresponded to the isocyanide complex, which suggests **4** is unstable over time and leads to the elimination of hydrazine, likely as N₂ gas. Other methods for obtaining crystals other than that described above, was not attempted.

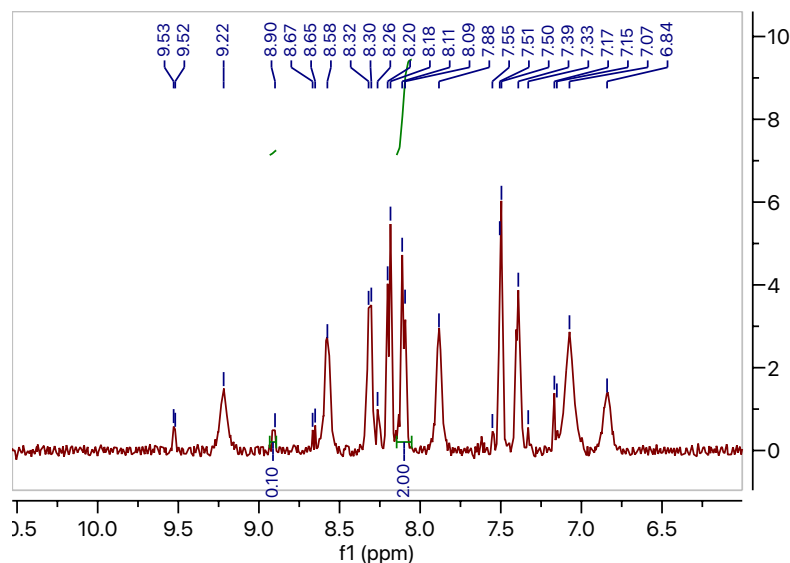


Figure 4.15: Proton NMR of **4**. Signal around 9.50 ppm is associated with the starting material. The signals related to the product are broadened. The integrations show a ~5% impurity likely isocyanide.

4.3.6 Computational evidence for HOMO inversion:

The hallmark of HOMO inversion is the increased ligand contribution of the frontier orbital which raises its energy, leading to a red shift in the absorption. Orbital partitioning of the both the carbene and the imine HOMOs are shown figure 4.16 along with the colors of a DCM solution associated with their protonation state. The deprotonated complex clearly exhibits a significant ligand character and there is a noticeable reduction in the metal center contribution. Interestingly the deprotonation leads to an asymmetric orbital environment. The nodal structure along the carbene bond prevents the interaction of the metal center with the carbene carbon which could be deemed a metal-ligand anti-bonding interaction. However, there is a minor M-L bonding interaction that uses p-orbitals of the peripheral nitrogen atoms of the imine ligand

backbone. This can be explained by the increased delocalization of this p-orbital in the carbene ligand. The metal likely makes up for this deficiency by forming a quasi- σ bond with this nitrogen.

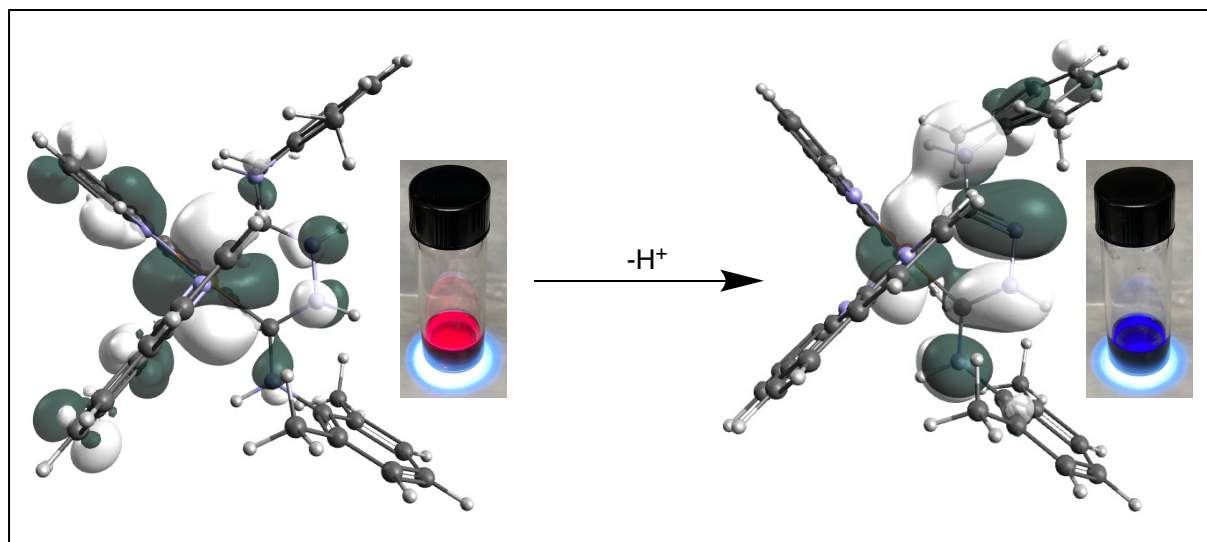


Figure 4.16: HOMO orbitals of acid base pair **3** and **4** computed with DFT. Metal contribution between the conformers is attenuated in the deprotonated flavor. The color of each complex in DCM solution are given in the figures next to the structures.

It is curious to note the orbital structure of the protonated carbene variety, which does show some metal-ligand anti-bonding interactions with the orbitals of phenanthroline that are in the carbene plane. This suggests the carbene ligand polarizes the orbitals of the phenanthroline ligands to some degree and could also be qualified as ‘HOMO-inversion’.

Confirmation of the HOMO-inversion character of **4** was done by using AO-mix a computational program that portions molecular orbital character into structural bins.¹⁶ These bins correspond to different groups in the complex. In this case the metal center was treated as a fragment, along with the two phenanthroline ligands and the imine backbone. The calculated percentages describe the portion each fragment contributes to a particular molecular orbital. The results for the first four occupied orbitals of **4** are listed in table 4.6. The calculations were performed by Jon Yarranton.

Table 4.6: AO-Mix results for the first four orbitals of **6** from the PBEO functional. The HOMO-1 to -3 can all be considered traditional in that they primarily occupy the metal center. The HOMO orbital shows inversion to a significant degree. These values are rounded.

Fragment	HOMO-3	HOMO-2	HOMO-1	HOMO
Fe	71%	70%	76%	20%
2 Phen	11%	11%	16%	1%
Imine	18%	19%	7%	78%

The HOMO-3 to -1 orbitals are metal-based and represent the orbital configuration present in the carbene complex. There is significant ligand character in the HOMO. Nearly 80% of the HOMO is localized on the imine ligand. This orbital partition is on the far end of the mixed ligand/metal profile of the complexes studied by Herbert et. al. The orbital portioning along with the increased intensity of absorptive transitions in the ground state suggests that this class of compounds exhibit HOMO inversion. Whether this translates to increased lifetimes will be examined in the next section.

4.3.7 Time Resolved Spectroscopy of **4**

The original discussions of HOMO inversion did not suggest its ability to achieve long lifetimes.¹² Rather it was proposed as a method for increasing the absorption cross section of Fe(II) complexes for use as sensitizers in dye sensitized solar cells the benefit of which is an increased photocurrent. The presence of the prolonged lifetime of the Herbert complex was a pleasant surprise. To validate the statement: ‘HOMO inversion leads to long excited state lifetimes’, preliminary transient absorption experiments were performed on **4**.

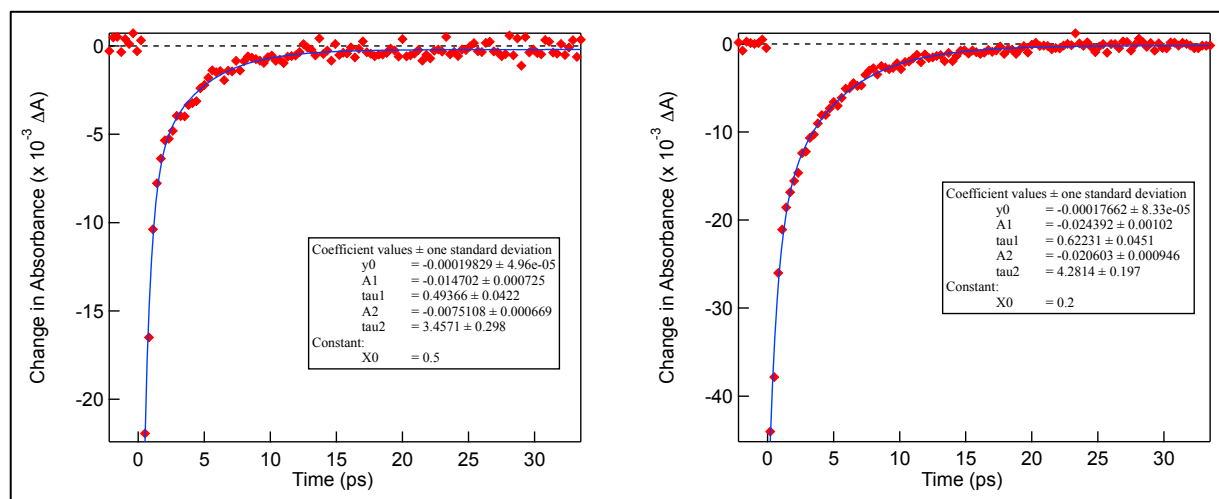


Figure 4.17: Preliminary transient absorption decay traces after excitation of DCM solutions of **4** at 510 nm. (left) GSB at a probe wavelength of 690 nm. (right) GSB at a probe wavelength of 620 nm.

Dichloromethane solutions of **4** were excited at 510 nm, the blue edge of the absorption manifold. The bleach regions were probed at 620 nm and 690 nm. The presence of any excited state absorptions remains to be seen as spectroelectrochemistry has not been performed on this set of compounds. The decay traces were fit with two time-constants shown in figure 14. The long components are statistically different between probe wavelengths but are on the same order observed for the carbene complex. These clearly fit very well to biexponential models. The exponential for the bleach at 620 nm recovers to baseline clearly, this is less clear in the 690 nm case as there is more noise in the baseline. The probe dependent lifetimes along with the similar time constant for decay suggest a similar mechanism of decay as that established in chapter 1. This similarity could be in part to the excitation wavelength, which is high in energy compared to the entire absorption manifold. Pumping the sample at a lower energy may lend different excited state kinetics. As the HOMO-3 to -1 orbitals should exhibit MLCT transitions analogous to those found in the carbene systems, excitation at 510 nm likely leads to the formation of these

states. It is therefore advised to conduct future experiments at lower energy excitation wavelengths.

4.4 CONCLUSION AND FUTURE WORKS

This chapter was concerned with the kinetic aspects of the deactivation of our heteroleptic carbene platform. Structural aspects of the series were discussed. For example, **1** was found to have the largest *trans*-influence compared to the others, suggesting it had the best orbital overlap. This should translate to effects on the ligand field; however these effects were not able to be established here. Furthermore, preliminary transient absorption studies implied a consistency with the data measured for $[\text{Fe}(\text{phen})_2(\text{C}_4\text{H}_{10}\text{N}_4)]^{2+}$ giving lifetimes of a similar order of magnitude. However, triexponential fits to the GSB were in better agreement with these data here as well as the ESA fitting to a single exponential. The latter is likely a probe dependent phenomenon and probing near 680 nm should exhibit a second component, consistent with that observed for $[\text{Fe}(\text{phen})_2(\text{C}_4\text{H}_{10}\text{N}_4)]^{2+}$.

While the ESA features of species **1-3** show no dependence on structure, the long components of the GSB region do show a dependence on structure. This is likely due to kinetic effects related to the ability of the alkyl substituted aryl groups to disrupt the ground state recovery process. It should be noted that the entire series should be studied on a longer time scale as it was demonstrated that the GSB recovers to baseline definitively with a time constant of 44 (6) ps in the case of **3**. The structural dependence on the long component of the GSB can be confirmed using VT-TA which should see structurally dependent barriers.

There are coherent artefacts in some of the kinetic traces *vide infra*, which suggest the necessity of shorter timescale experiments and coherence measurements. Coherent dephasing times for early components could help establish the degree to which kinetic effects play a role

across the series. Furthermore, full transient spectra can be collected to probe the differences in the number of components required to fit the decay, as well as the difference in the time constants for the ESA and mid-range lifetimes of the GSB. Full spectral analysis will allow for force the congruence of these components if they are indeed descriptions of the same process.

In this section we have shown that the diamino ligand platform exhibits HOMO-inversion when deprotonated. This is shown by the increased breadth of the absorption manifold as well as its concurrent increase in molar extinction coefficient. Computational modeling suggests that there are significant ligand contributions to the HOMO orbital, having 80% of its character located on the deprotonated ligand. Time-resolved spectroscopy does not suggest a stupendous increase in lifetime that is observed with some other complexes that exhibit HOMO-inversion. As the increased lifetime of the Herbert complex was not expected based on theory, it is reasonable to assume that using ‘HOMO inversion’ as a design strategy will likely require a more refined understanding of the structure-property relationships of this class of compounds. The platform presented in this chapter could serve as a crucible for this kind of experimentation.

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APPENDIX

4.6.1 NMR characterization

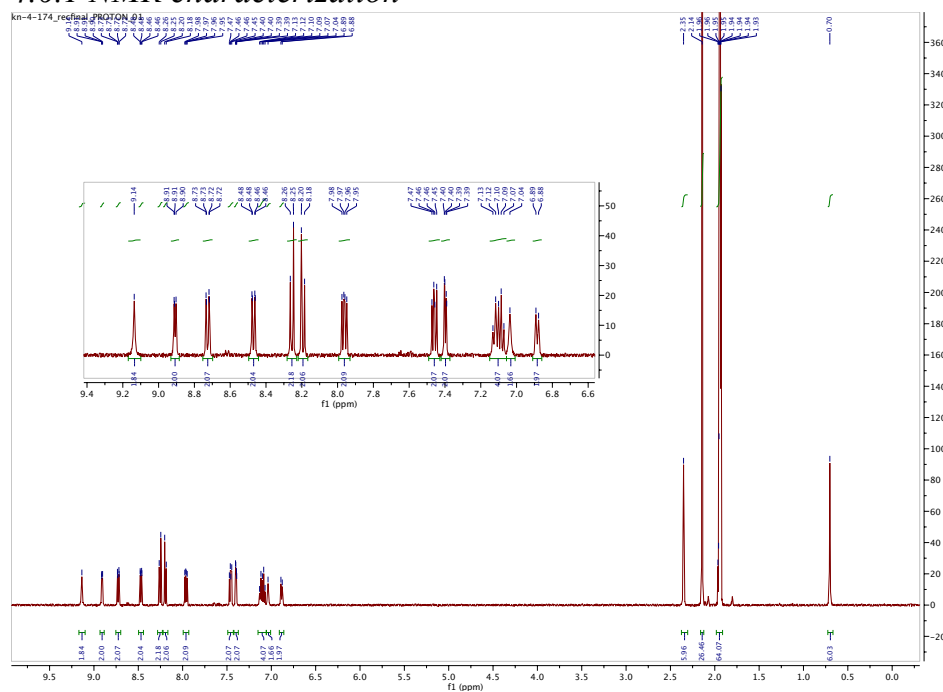
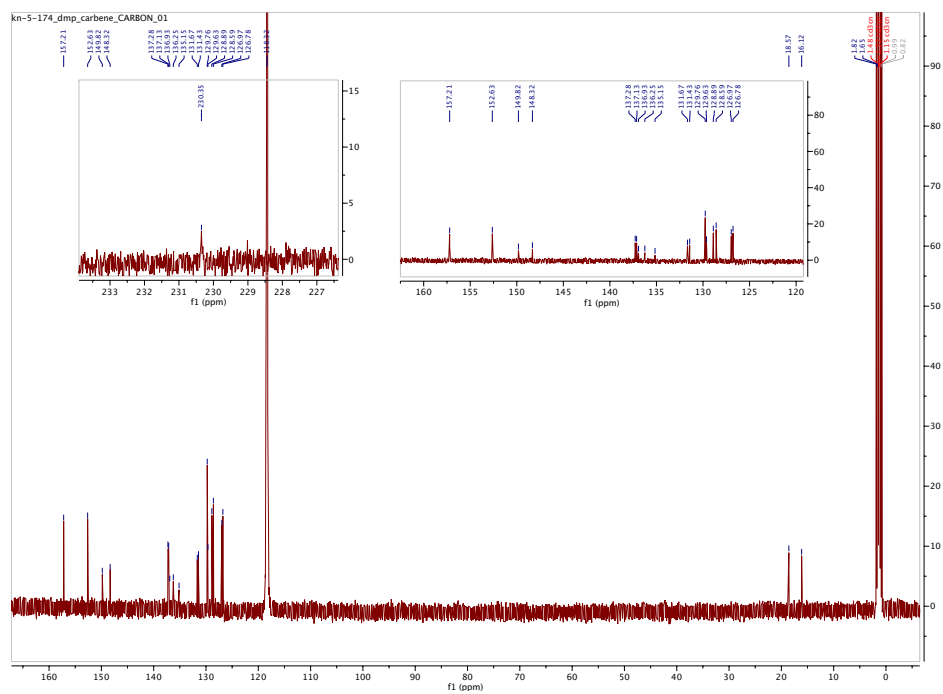
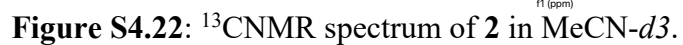


Figure S4.18: ^1H NMR spectrum of **1** in $\text{MeCN-}d_3$.





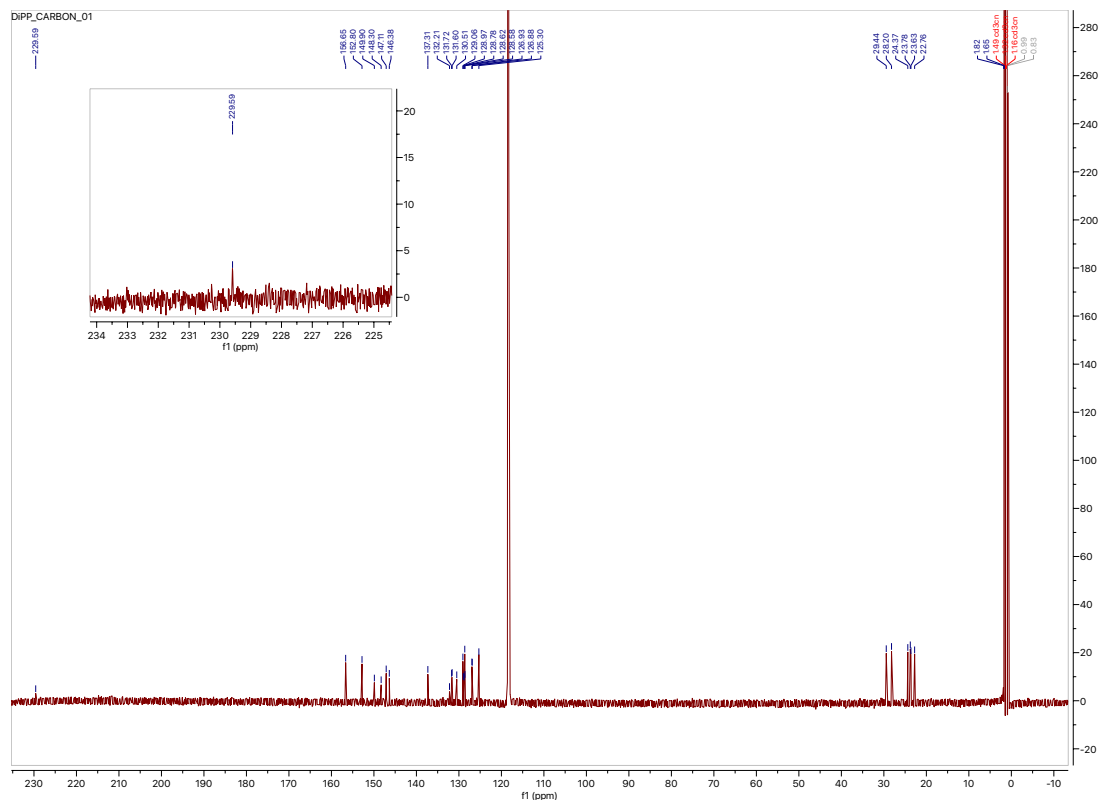


Figure S4.24: ^{13}C NMR spectrum of **3** in $\text{MeCN-}d_3$.

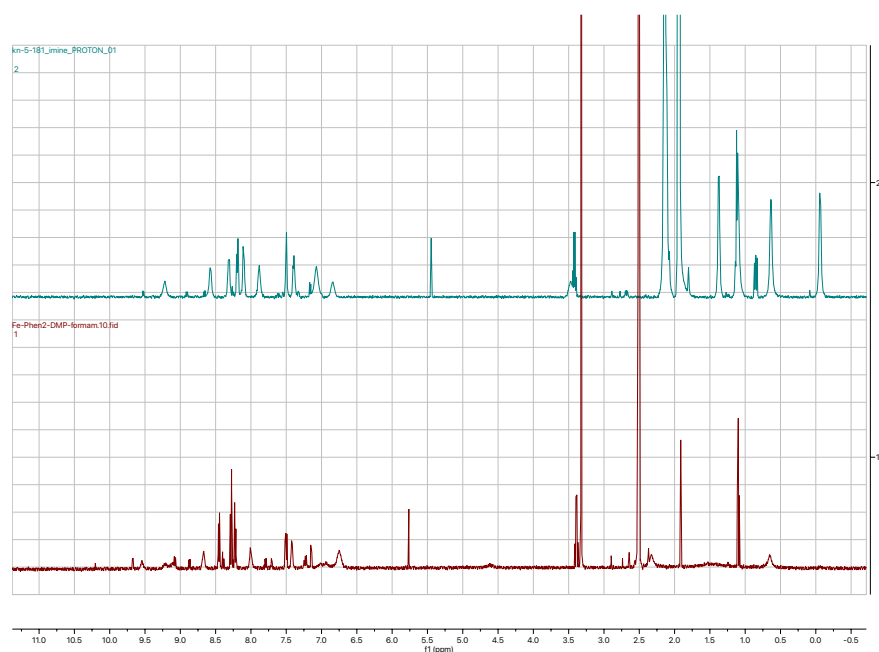


Figure S4.25: ^1H NMR spectra of **4** in various solvents. Room temperature in acetonitrile (sea green) and high temperature ($\sim 80^\circ\text{C}$) DMSO. Shows the disappearance of the aliphatic region, likely due to breakdown.

4.6.2 Electrospray ionization mass-spectrometry

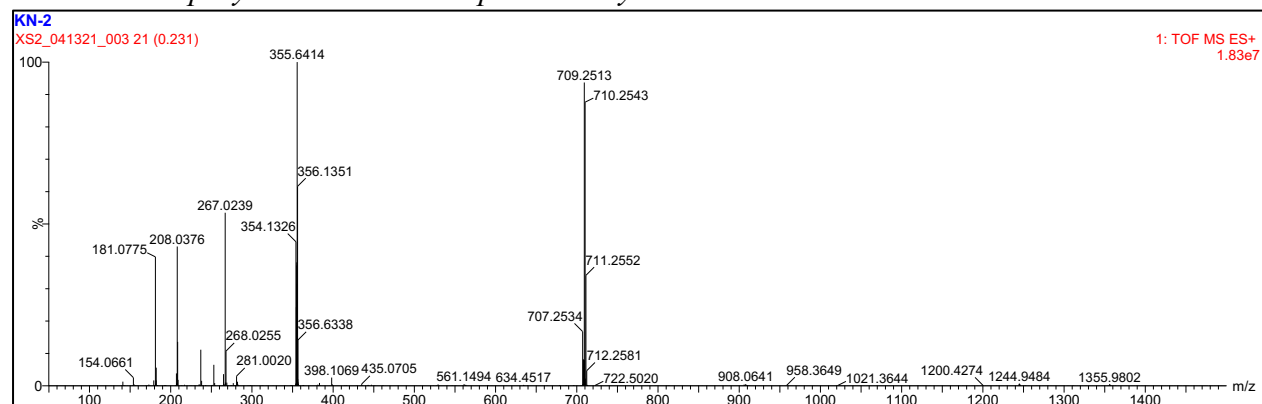


Figure S4.26: ESI-MS of 1. [M-H]: 709.2513, calcd: 709.2504.

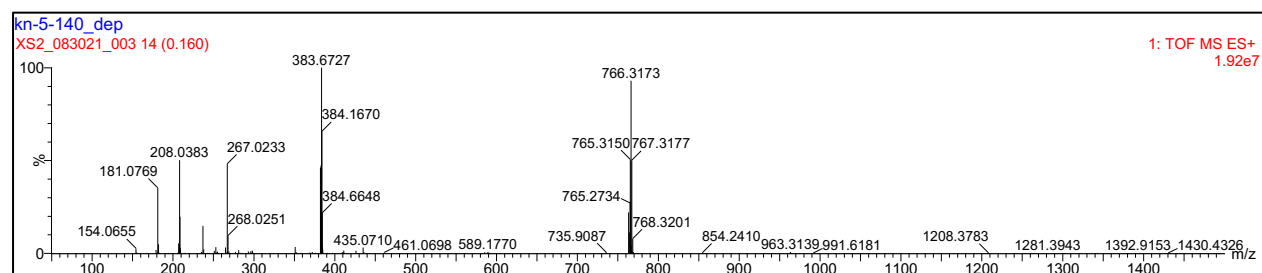


Figure S4.27: ESI-MS of 2. [M-H]: 765.3150, calcd: 765.3184.

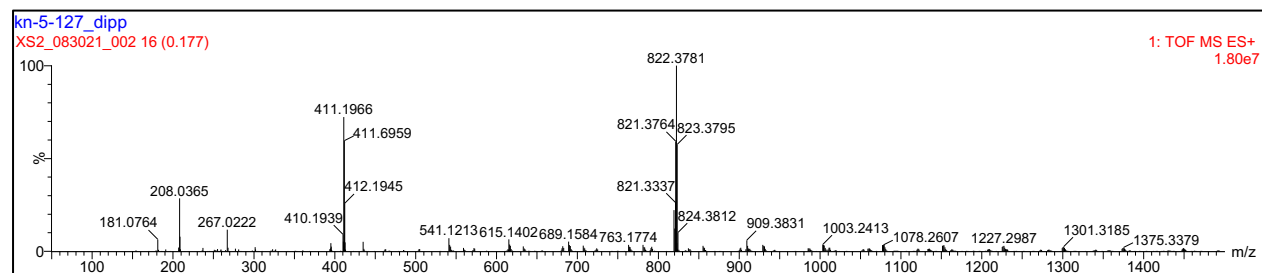


Figure S4.28: ESI-MS of 3. [M-H]: 821.3764, calcd: 821.3732.

4.6.3 X-Ray Crystal Structures

Table S4.7: Crystal Data and Structure Refinement for **1**.

Identification code	kn-4-174
Empirical formula	C ₄₂ H ₃₈ B ₂ F ₈ FeN ₈
Formula weight	884.27
Temperature/K	100.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	11.32912(14)
b/Å	11.88950(15)
c/Å	15.33627(14)
α/°	103.0273(9)
β/°	92.4624(9)
γ/°	94.3997(10)
Volume/Å ³	2002.80(4)
Z	2
ρ _{calc} /g/cm ³	1.466
μ/mm ⁻¹	3.720
F(000)	908.0
Crystal size/mm ³	0.323 × 0.213 × 0.141
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.926 to 154.154
Index ranges	-14 ≤ h ≤ 14, -15 ≤ k ≤ 12, -12 ≤ l ≤ 19
Reflections collected	25621
Independent reflections	7946 [R _{int} = 0.0321, R _{sigma} = 0.0330]
Data/restraints/parameters	7946/0/555
Goodness-of-fit on F ²	1.064
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0356, wR ₂ = 0.0900
Final R indexes [all data]	R ₁ = 0.0382, wR ₂ = 0.0913
Largest diff. peak/hole / e Å ⁻³	1.07/-0.36

Table S4.8: Bond Lengths of **1**.

Atom1	Atom2	Length (Å)	Atom1	Atom2	Length (Å)
Fe1	N21	1.970(1)	C28	C27	1.371(3)
Fe1	N35	2.011(2)	C28	C29	1.407(3)
Fe1	N25	2.023(2)	C55	H55	0.95
Fe1	N39	1.969(1)	C55	C56	1.387(3)
Fe1	C47	1.921(2)	C55	C54	1.381(3)
Fe1	C50	1.914(2)	C27	H27	0.95
N21	C20	1.370(2)	C44	H44	0.95
N21	C12	1.333(2)	C44	C43	1.388(3)

Table S4.8 (cont'd)

N35	C26	1.328(2)	C29	C30	1.437(3)
N35	C34	1.369(2)	C41	C42	1.398(3)
N25	C19	1.369(2)	C41	C60	1.507(3)
N25	C22	1.330(2)	C24	H24	0.95
N39	C36	1.335(2)	C24	C23	1.366(2)
N39	C33	1.370(2)	C43	H43	0.95
N49	H49	0.88	C43	C42	1.385(3)
N49	N48	1.396(2)	C13	H13	0.95
N49	C50	1.332(2)	C13	C14	1.375(3)
N48	H48	0.88	C42	H42	0.95
N48	C47	1.333(2)	C15	C16	1.437(3)
N51	H51	0.88	C15	C14	1.403(3)
N51	C50	1.344(3)	C23	H23	0.95
N51	C52	1.440(2)	C56	H56	0.95
N46	H46	0.88	C61	H61A	0.98
N46	C47	1.344(3)	C61	H61B	0.98
N46	C40	1.442(2)	C61	H61C	0.98
C20	C19	1.419(3)	C16	H16	0.95
C20	C15	1.405(2)	C16	C17	1.353(3)
C36	H36	0.95	C59	H59A	0.98
C36	C37	1.399(3)	C59	H59B	0.98
C19	C18	1.400(3)	C59	H59C	0.98
C26	H26	0.95	C14	H14	0.95
C26	C27	1.402(3)	C37	H37	0.95
C33	C34	1.419(2)	C37	C38	1.369(3)
C33	C32	1.401(2)	C30	H30	0.95
C40	C45	1.402(2)	C30	C31	1.352(3)
C40	C41	1.391(2)	C32	C38	1.405(3)
C22	H22	0.95	C32	C31	1.437(3)
C22	C23	1.407(3)	C60	H60A	0.98
C34	C29	1.401(3)	C60	H60B	0.98
C12	H12	0.95	C60	H60C	0.98
C12	C13	1.398(2)	C54	H54	0.95
C52	C57	1.397(2)	C17	H17	0.95
C52	C53	1.394(3)	C38	H38	0.95
C57	C56	1.393(3)	C31	H31	0.95
C57	C59	1.507(3)	C58	H58A	0.98
C45	C44	1.390(3)	C58	H58B	0.98
C45	C61	1.507(3)	C58	H58C	0.98

Table S4.8 (cont'd)

C53	C54	1.397(3)	F2	B3	1.411(3)
C53	C58	1.503(3)	F4	B3	1.379(3)
C18	C24	1.406(3)	F5	B3	1.408(3)
C18	C17	1.438(2)	F6	B3	1.377(2)
C28	H28	0.95	F7	B8	1.388(3)
			F9	B8	1.388(2)
			F10	B8	1.396(3)
			F11	B8	1.386(3)

Table S4.9: Crystal Data and Structure Refinement of **2**.

Identification code	kn-5-142
Empirical formula	C ₄₆ H ₄₆ B ₂ F ₈ FeN ₈
Formula weight	940.42
Temperature/K	99.9(4)
Crystal system	monoclinic
Space group	P2 ₁ /n
a/Å	10.4332(2)
b/Å	20.4000(4)
c/Å	20.5510(4)
α/°	90
β/°	100.045(2)
γ/°	90
Volume/Å ³	4306.97(16)
Z	4
ρ _{calc} /g/cm ³	1.450
μ/mm ⁻¹	0.430
F(000)	1944.0
Crystal size/mm ³	? × ? × ?
Radiation	Mo Kα (λ = 0.71073)
2θ range for data collection/°	5.672 to 61.882
Index ranges	-12 ≤ h ≤ 14, -26 ≤ k ≤ 27, -25 ≤ l ≤ 26
Reflections collected	48157
Independent reflections	10998 [R _{int} = 0.0515, R _{sigma} = 0.0433]
Data/restraints/parameters	10998/0/599
Goodness-of-fit on F ²	1.121
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0639, wR ₂ = 0.1335
Final R indexes [all data]	R ₁ = 0.1047, wR ₂ = 0.1591
Largest diff. peak/hole / e Å ⁻³	0.77/-0.54

Table S4.10: Bond Lengths of **2**.

Atom1	Atom2	Length	Atom1	Atom2	Length
Fe1	N21	2.012(3)	C31	C30	1.433(4)
Fe1	N25	1.968(3)	C23	H23	0.95
Fe1	N35	1.974(3)	C23	C24	1.400(5)
Fe1	N39	2.005(2)	C19	H19	0.95
Fe1	C47	1.909(3)	C19	C18	1.369(5)
Fe1	C50	1.919(3)	C19	C20	1.399(5)
N21	C12	1.367(4)	C41	C40	1.396(5)
N21	C20	1.332(4)	C41	C42	1.386(4)
N25	C13	1.370(4)	C41	C62	1.511(5)

Table S4.10 (cont'd)

N25	C24	1.333(4)	C33	H33	0.95
N35	C26	1.370(4)	C33	C34	1.404(5)
N35	C34	1.332(4)	C54	H54	0.93(4)
N51	H51	0.88	C37	H37	0.95
N51	C52	1.440(4)	C37	C36	1.402(4)
N51	C50	1.346(4)	C37	C38	1.370(5)
N46	H46	0.88	C45	C40	1.405(4)
N46	C47	1.339(4)	C45	C64	1.514(5)
N46	C40	1.443(4)	C30	H30	0.95
N48	H48	0.88	C30	C29	1.355(5)
N48	N49	1.397(3)	C18	H18	0.95
N48	C47	1.337(4)	C34	H34	0.95
N49	H49	0.88	C36	H36	0.95
N49	C50	1.339(4)	C64	H64A	0.99
N39	C27	1.364(4)	C64	H64B	0.99
N39	C36	1.338(4)	C64	C65	1.529(5)
C52	C57	1.406(4)	C38	H38	0.95
C52	C53	1.393(5)	C43	H43	0.95
C57	C56	1.390(5)	C43	C42	1.388(5)
C57	C60	1.514(5)	C59	H59A	0.98
C53	C58	1.512(5)	C59	H59B	0.98
C53	C54	1.394(5)	C59	H59C	0.98
C27	C26	1.427(4)	C24	H24	0.95
C27	C28	1.396(4)	C29	H29	0.95
C26	C31	1.401(4)	C16	H16	0.95
C12	C17	1.403(5)	C16	C15	1.356(5)
C12	C13	1.421(5)	C20	H20	0.95
C56	H56	0.95	C42	H42	0.95
C56	C55	1.388(5)	C62	H62A	0.99
C17	C18	1.410(5)	C62	H62B	0.99
C17	C16	1.433(5)	C62	C63	1.531(5)
C55	C54	1.375(5)	C60	H60A	0.99
C55	H55	0.97(4)	C60	H60B	0.99
C58	H58A	0.99	C60	C61	1.519(5)
C58	H58B	0.99	C15	H15	0.95
C58	C59	1.526(4)	C63	H63A	0.98
C32	H32	0.95	C63	H63B	0.98
C32	C31	1.408(4)	C63	H63C	0.98
C32	C33	1.369(4)	C61	H61A	0.98

Table S4.10 (cont'd)

C22	H22	0.95	C61	H61B	0.98
C22	C14	1.401(5)	C61	H61C	0.98
C22	C23	1.373(5)	C65	H65A	0.98
C28	C38	1.411(4)	C65	H65B	0.98
C28	C29	1.434(5)	C65	H65C	0.98
C14	C13	1.408(4)	F2	B3	1.381(4)
C14	C15	1.434(5)	F4	B3	1.421(4)
C44	H44	0.95	F5	B3	1.397(4)
C44	C45	1.392(4)	F6	B3	1.383(5)
C44	C43	1.374(5)	F7	B4	1.419(5)
C31	C30	1.433(4)	F13	B4	1.378(5)
C23	H23	0.95	B4	F15	1.390(4)
C23	C24	1.400(5)	B4	F14	1.375(4)

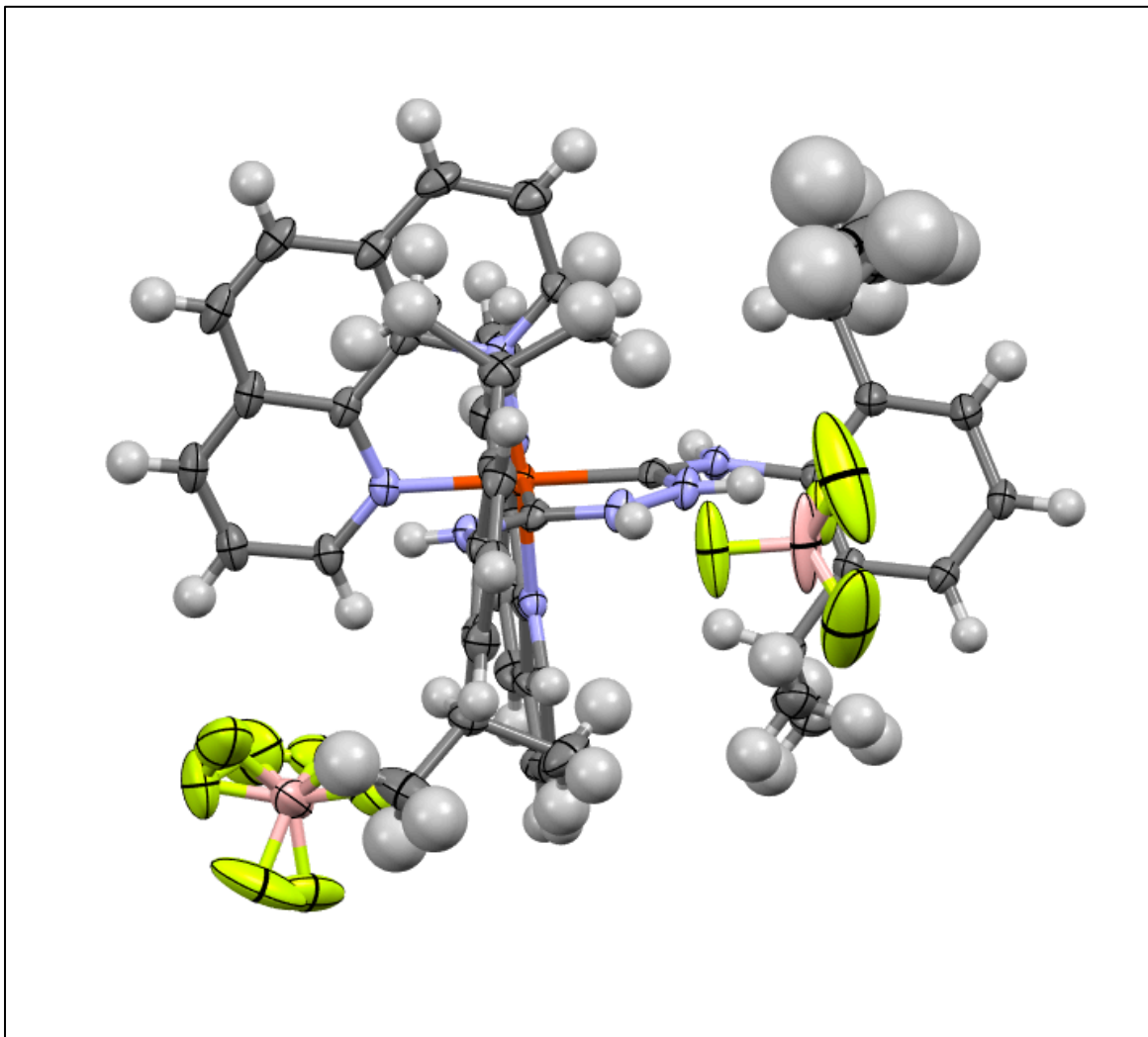


Figure S4.29: Crystal Structure of **3**. Orange: Iron; Purple: nitrogen; Grey: carbon; White: hydrogen; pink: boron; yellow: fluorine. Thermal ellipsoids at 50% probability.

Table S4.11: Crystal Data and Structure refinement of **3**.

Identification code	ov_kn-5-127_new
Empirical formula	C ₅₁ H ₅₈ B ₂ Cl ₂ F ₈ FeN ₈ O
Formula weight	1099.42
Temperature/K	100.15
Crystal system	monoclinic
Space group	P2 ₁ /n
a/Å	13.40180(10)
b/Å	21.1962(2)
c/Å	18.8103(2)
α/°	90
β/°	100.1470(10)
γ/°	90
Volume/Å ³	5259.81(9)
Z	4
ρ _{calc} /g/cm ³	1.388
μ/mm ⁻¹	3.868
F(000)	2280.0
Crystal size/mm ³	? × ? × ?
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	6.338 to 155.946
Index ranges	-16 ≤ h ≤ 16, -26 ≤ k ≤ 26, -23 ≤ l ≤ 21
Reflections collected	96186
Independent reflections	10966 [R _{int} = 0.0799, R _{sigma} = 0.0321]
Data/restraints/parameters	10966/0/666
Goodness-of-fit on F ²	1.030
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0574, wR ₂ = 0.1500
Final R indexes [all data]	R ₁ = 0.0607, wR ₂ = 0.1528
Largest diff. peak/hole / e Å ⁻³	0.83/-0.57

Table S4.12: Bond Lengths for **3**.

Atom1	Atom2	Length (Å)	Atom1	Atom2	Length (Å)
FE01	N005	2.0054	C015	C01S	1.5187
FE01	N006	1.967	C016	H016	0.95
FE01	N007	1.9665	C016	C01B	1.3932
FE01	N008	2.0048	C017	C01H	1.4071
FE01	C00G	1.9201	C017	C01K	1.4291
FE01	C00O	1.9181	C018	H018	0.95
N005	C00J	1.3288	C018	C01H	1.366
N005	C00M	1.3676	C019	H019	0.95
N006	C00L	1.375	C019	C01E	1.3711
N006	C00R	1.3261	C01A	H01A	0.95
N007	C00I	1.3727	C01A	C01J	1.3775
N007	C011	1.334	C01B	C01O	1.5239
N008	C00T	1.3683	C01C	H01C	0.95
N008	C00Y	1.331	C01E	H01E	0.95
N009	H009	0.88	C01F	H01F	0.95
N009	C00G	1.3388	C01F	C01M	1.3483
N009	C00P	1.4438	C01G	H01G	0.95
N00B	H00B	0.88	C01H	H01H	0.95
N00B	N00D	1.3965	C01I	H01I	0.95
N00B	C00G	1.3368	C01I	C01K	1.3485
N00C	H00C	0.88	C01J	H01J	0.95
N00C	C00O	1.3394	C01K	H01K	0.95
N00C	C00W	1.448	C01L	H01L	1
N00D	H00D	0.88	C01L	C01Q	1.5387
N00D	C00O	1.3357	C01L	C01R	1.531
C00H	H00H	0.95	C01M	H01M	0.95
C00H	C00N	1.3891	C01N	H01B	0.98
C00H	C016	1.3846	C01N	H01D	0.98
C00I	C00T	1.4134	C01N	H01N	0.98
C00I	C00V	1.4074	C01O	H01O	1
C00J	H00J	0.95	C01O	C01Z	1.5408
C00J	C00Z	1.4009	C01O	C020	1.4918
C00K	C00N	1.3928	C01P	H01P	0.98
C00K	C00W	1.4006	C01P	H01Q	0.98
C00K	C015	1.5169	C01P	H01R	0.98
C00L	C00M	1.4137	C01Q	H01S	0.98
C00L	C010	1.4053	C01Q	H01T	0.98
C00M	C013	1.4058	C01Q	H01U	0.98

Table S4.12 (cont'd)

C00N	H00N	0.95	C01R	H01V	0.98
C00P	C00Q	1.3963	C01R	H01W	0.98
C00P	C00U	1.4073	C01R	H01X	0.98
C00Q	C012	1.3944	C01S	H01Y	0.98
C00Q	C014	1.523	C01S	H	0.98
C00R	H00R	0.95	C01S	HA	0.98
C00R	C019	1.4025	C01W	H01Z	0.98
C00T	C017	1.4132	C01W	HB	0.98
C00U	C00X	1.394	C01W	HC	0.98
C00U	C01L	1.5139	C01Z	H01	0.98
C00V	C01A	1.4058	C01Z	HD	0.98
C00V	C01I	1.4354	C01Z	HE	0.98
C00W	C01B	1.3993	C020	H02A	0.98
C00X	H00X	0.95	C020	H02B	0.98
C00X	C01C	1.3807	C020	H02C	0.98
C00Y	H00Y	0.95	F15	B22	1.4127
C00Y	C018	1.4022	F15	F22	1.0575
C00Z	H00Z	0.95	F16	B22	1.3122
C00Z	C01G	1.3751	F16	F17A	0.5849
C010	C01E	1.401	F14	B22	1.3965
C010	C01F	1.4373	F14	F14A	0.8362
C011	H011	0.95	F17	B22	1.3515
C011	C01J	1.4058	F17	F16A	1.1762
C012	H012	0.95	F17	F22	1.2349
C012	C01C	1.3881	B22	F14A	1.3418
C013	C01G	1.4002	B22	F17A	1.4325
C013	C01M	1.4383	B22	F16A	1.6101
C014	H014	1	B22	F22	1.2619
C014	C01N	1.5305	F18	B23	1.356
C014	C01W	1.5173	F19A	B23	1.381
C015	H015	1	B23	F20	1.3941
C015	C01P	1.5414	B23	F21	1.31

4.6.4 Hybridization Calculations

Calculation of orbital hybrids were performed by solving a system of linear equations according to Coulson's directionality theorem in the form of $Ax=b$.

$$\begin{pmatrix} -\cos \omega_{12} & 0 & 0 \\ 0 & -\cos \omega_{13} & 0 \\ 0 & 0 & -\cos \omega_{23} \end{pmatrix} \begin{pmatrix} \sqrt{\lambda_1 \lambda_2} \\ \sqrt{\lambda_1 \lambda_3} \\ \sqrt{\lambda_2 \lambda_3} \end{pmatrix} = \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix} \quad \text{S4.1}$$

The individual values for lambda were solved for algebraically.

Table S4.13: Calculation of orbital hybrids for **1**.

DMP 1											
Angle	Degrees	Funct.	A			b	A ⁻¹			A ⁻¹ *b	(A ⁻¹ *b) ²
1	114.41	Cos	-0.41	0.00	0.00	-1	-2.42	0.00	0.00	2.42	5.86
2	130.29	Cos	0.00	-0.65	0.00	-1	0.00	-1.55	0.00	1.55	2.39
3	115.03	Cos	0.00	0.00	-0.42	-1	0.00	0.00	-2.36	2.36	5.59

Bond	Hybridization	s-orbital sum rule	p-orbital sum rule
a	1.58	1.00	3.02
b	3.70		
c	1.51		

Table S4.14: Calculation of carbene orbital hybrids for **2**.

DEP 2											
Angle	Degrees	Funct.	A			b	A ⁻¹			A ⁻¹ *b	(A ⁻¹ *b) ²
1	115	Cos	0.42	0.00	0.00	1	2.37	0.00	0.00	2.37	5.60
2	129.88	Cos	0.00	0.64	0.00	1	0.00	1.56	0.00	1.56	2.43
3	114.98	Cos	0.00	0.00	0.42	1	0.00	0.00	2.37	2.37	5.61

Bond	Hybridization	s-orbital sum rule	p-orbital sum rule
a	1.56	0.98	3.02
b	3.59		
c	1.56		

Table S4.15: Calculation of carbene orbital hybrids for **3**.

DiPP 3											
Angle	Degrees	Funct.	A			b	A ⁻¹			A ⁻¹ *b	(A ⁻¹ *b) ²
1	114.36	Cos	-0.41	0.00	0.00	-1	-2.42	0.00	0.00	2.42	5.88
2	129.25	Cos	0.00	-0.63	0.00	-1	0.00	-1.58	0.00	1.58	2.50
3	116.15	Cos	0.00	0.00	-0.44	-1	0.00	0.00	-2.27	2.27	5.15

Table S4.15 (cont'd)

Bond	Hybridization	s-orbital sum rule	p-orbital sum rule
a	1.69	1.00	3.01
b	3.48		
c	1.48		

4.6.5 ATIR spectra

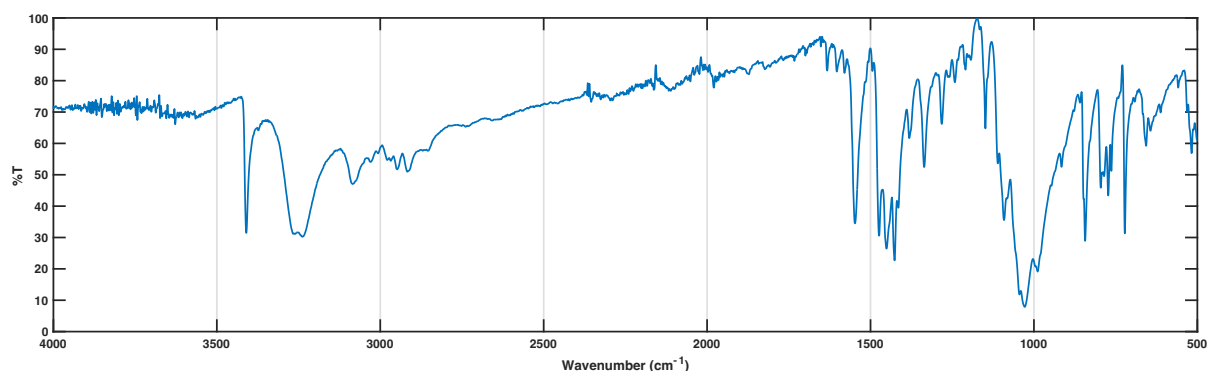


Figure S4.30: ATIR spectrum of **1**.

4.6.6 Electrochemistry

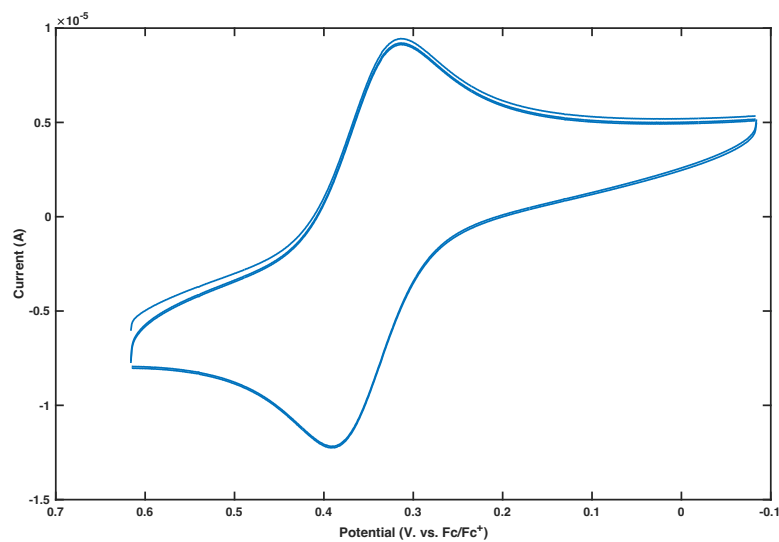


Figure S4.31: Oxidative CV of **1** at 100 mV/s.

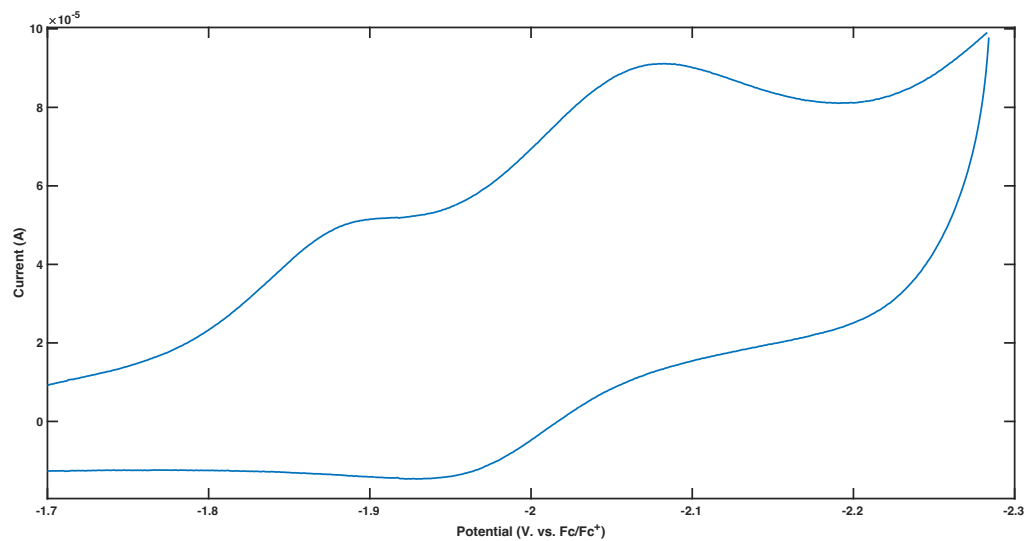


Figure S4.32: Reductive CV of **1** at 2000 mV/s. 2 sweeps.

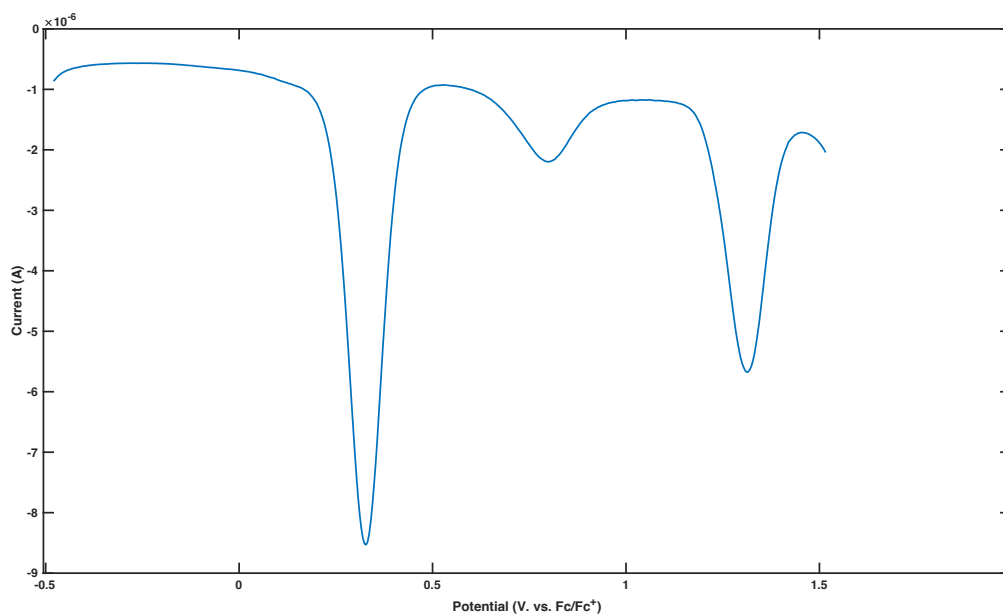


Figure S4.33: Oxidative DPV of **1**.

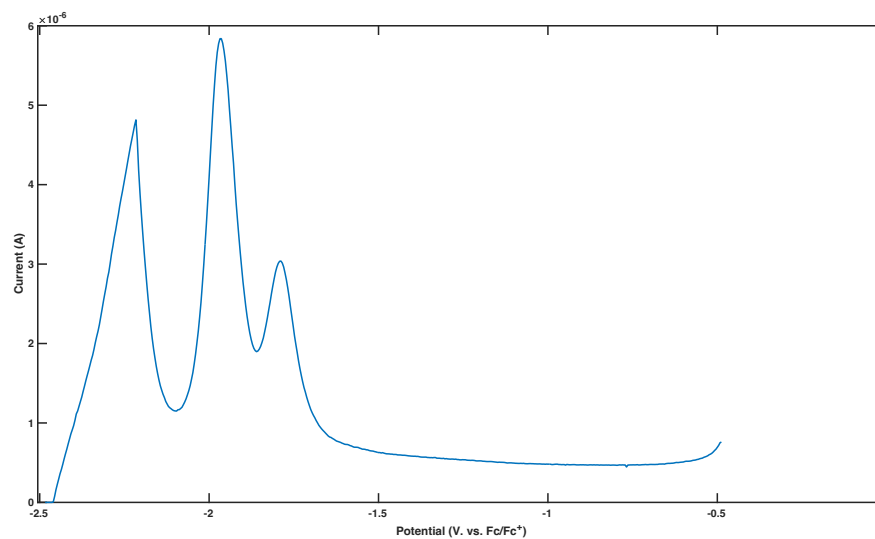


Figure S4.34: Reductive DPV of **1**.

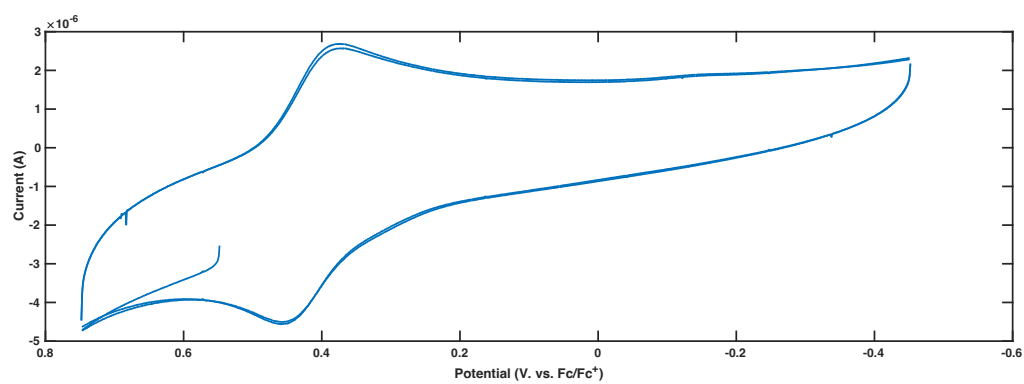


Figure S4.35: Oxidative CV of **2** at 100 mV/s.

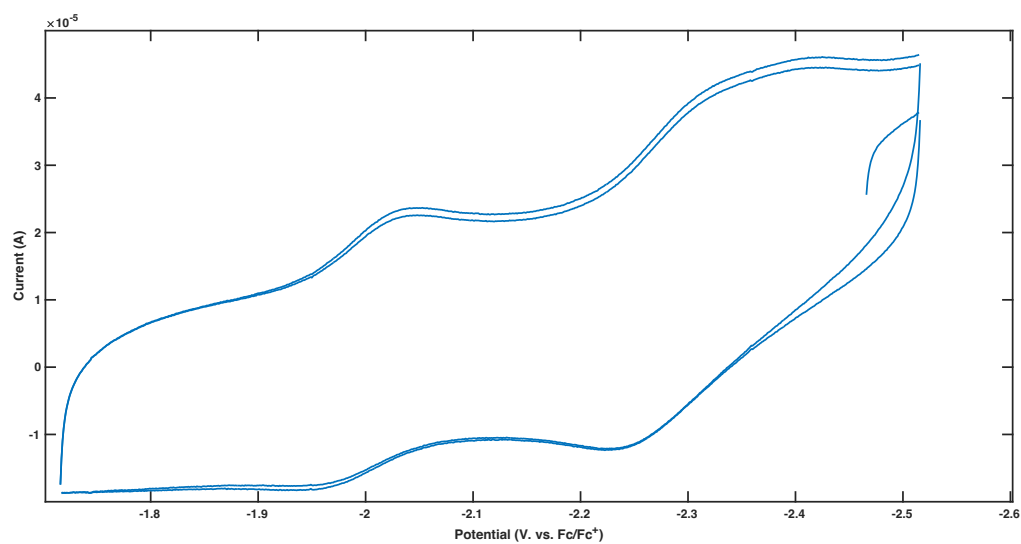


Figure S4.36: Reductive CV of **2** at 2000 mV/s

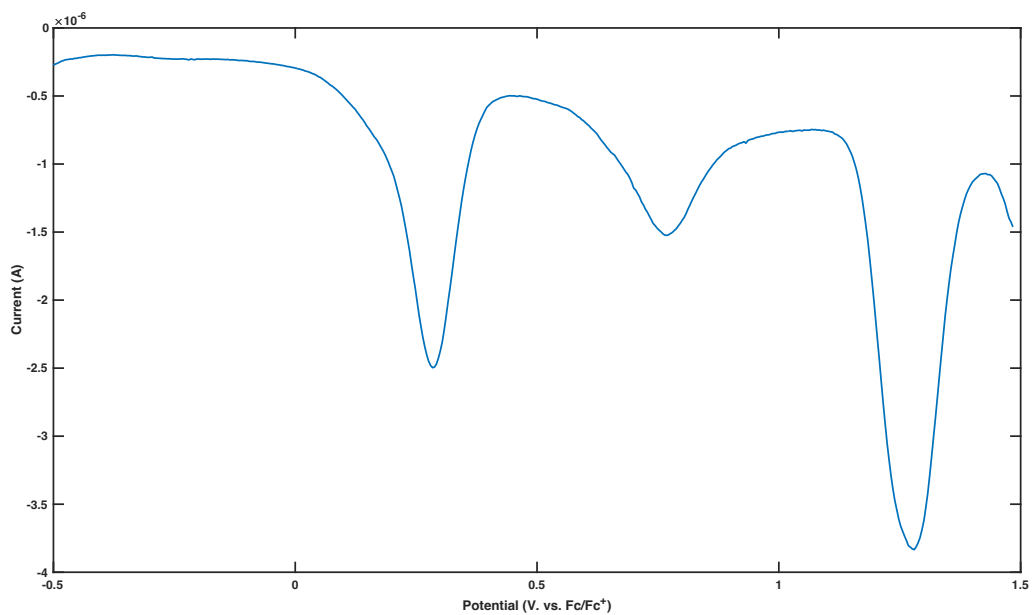


Figure S4.37: Oxidative DPV of **2**.

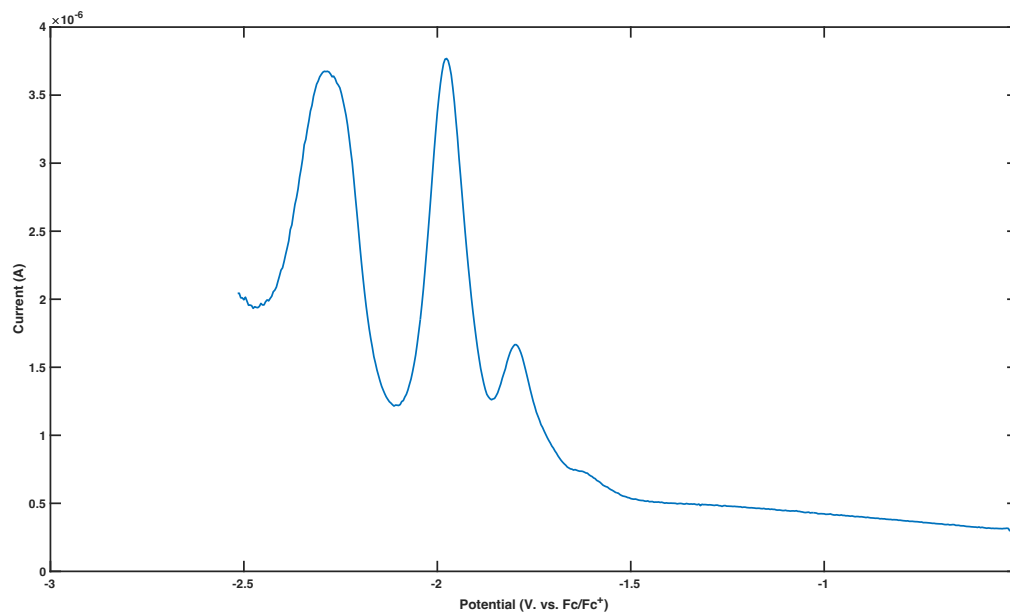


Figure S4.38: Reductive DPV of **2**.

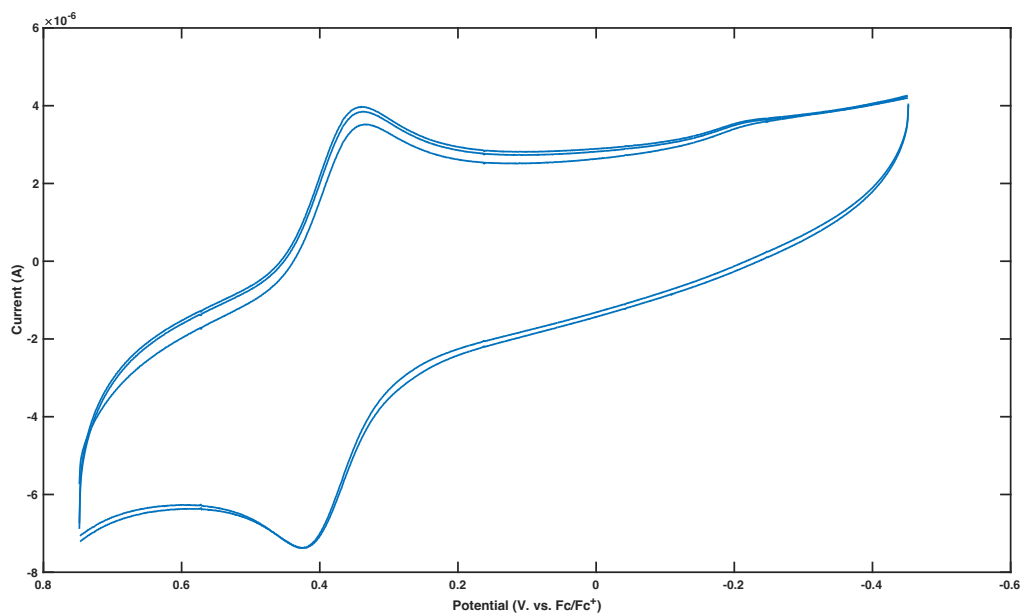


Figure S4.39: Oxidative CV of **3** at 100 mV/s.

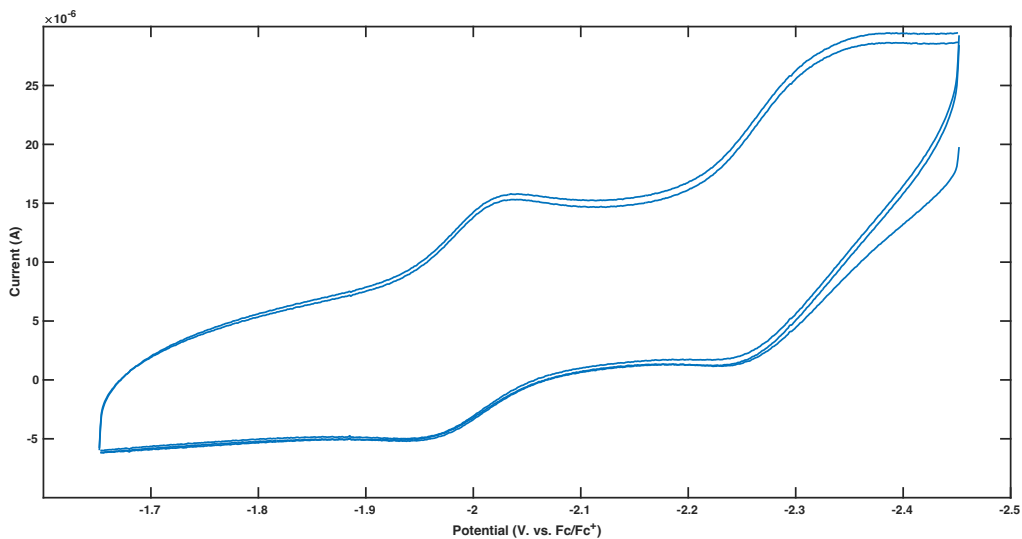


Figure S4.40: Reductive CV of **3** at 500 mV/s.

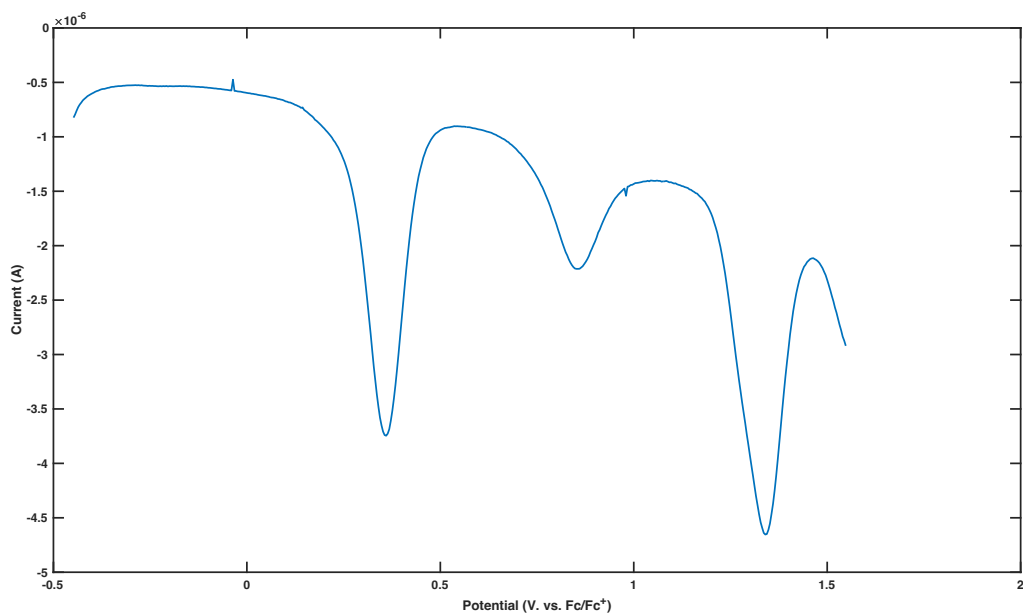


Figure S4.41: Oxidative DPV of **3**.

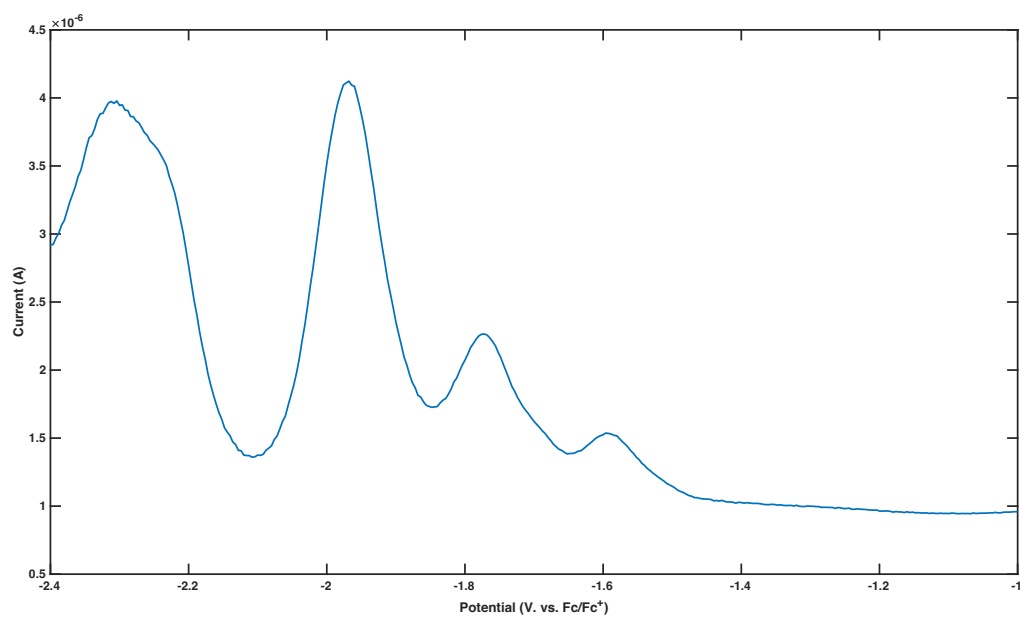


Figure S4.42: Reductive DPV of **3**.

4.6.7 Transient Absorption Spectroscopy 550 nm Probe Experiments

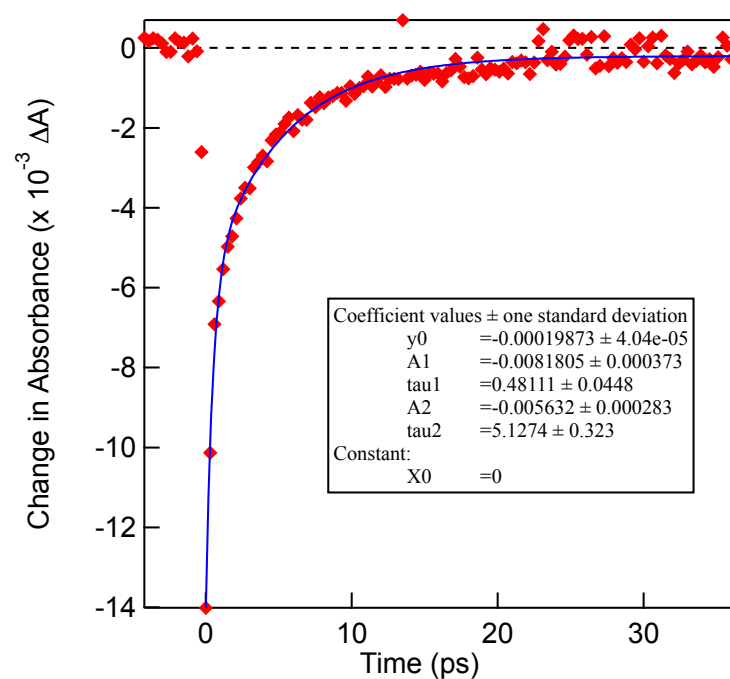


Figure S4.43: GSB recovery of **1** at 580 nm after excitation of 550 nm.

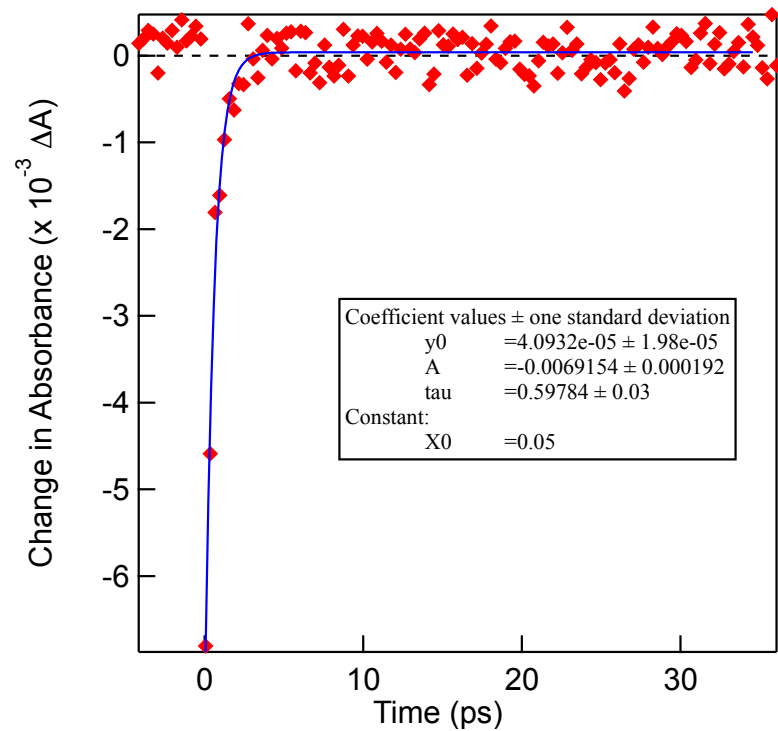


Figure S4.44: Formation of an isosbestic point in **1** at 680 nm after excitation with 550 nm.

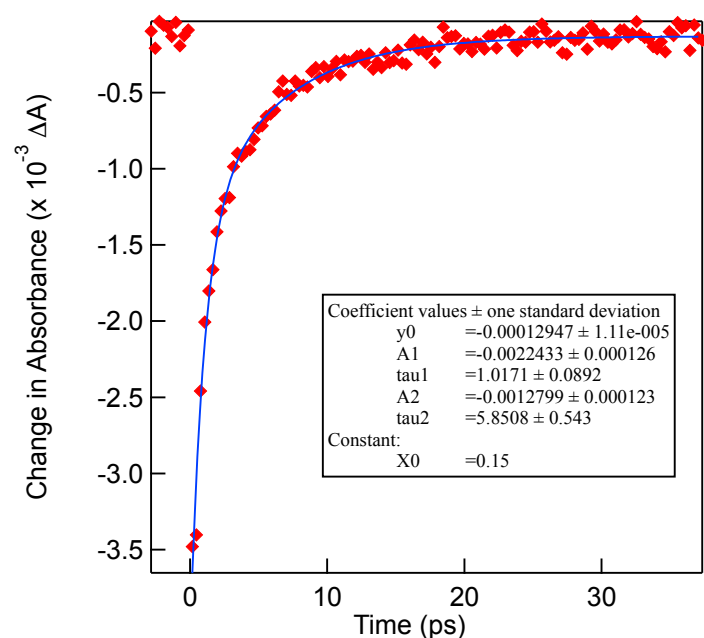


Figure S4.45: GSB recovery of **2** at 580 nm after excitation of 550 nm.

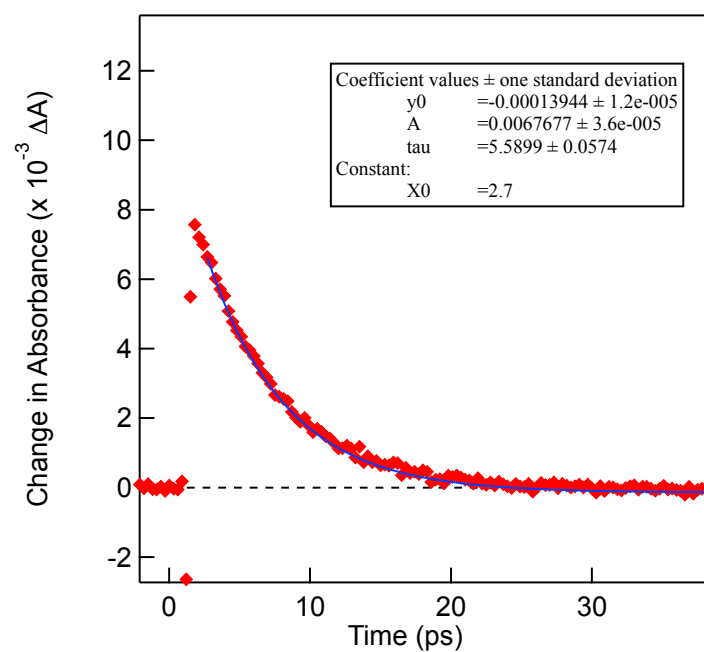


Figure S4.46: ESA decay of **2** at 620 nm after excitation of 550 nm.

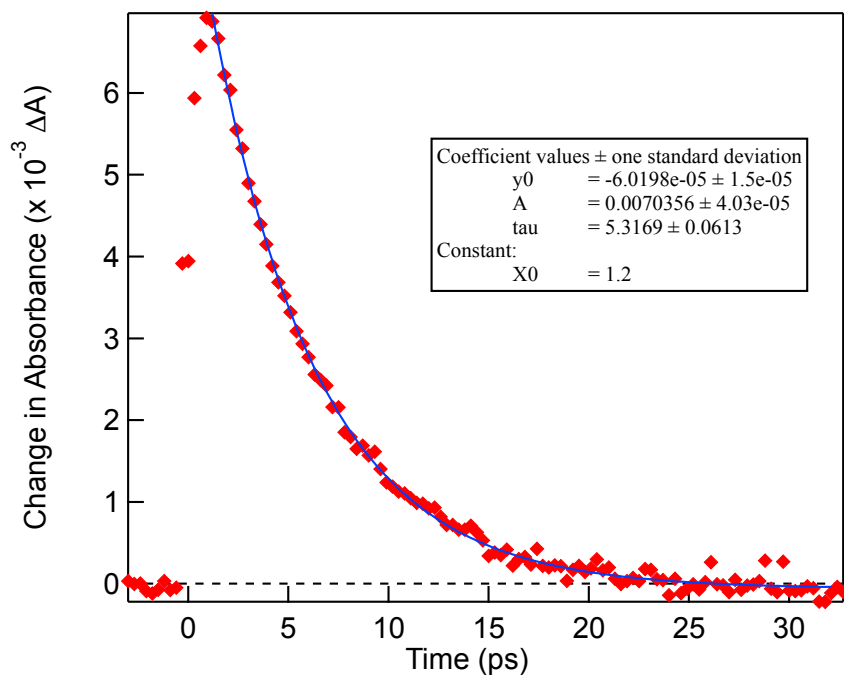


Figure S4.47: ESA decay of **3** at 620 nm after excitation of 550 nm.

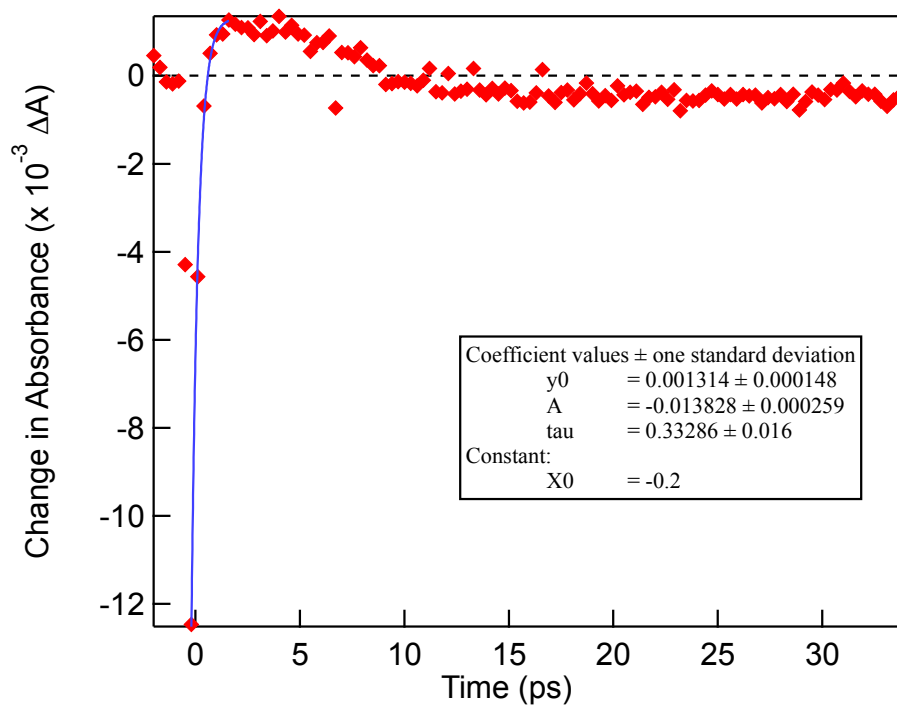


Figure S4.48: Complicated kinetics of **3** at 600 nm after excitation of 550 nm.

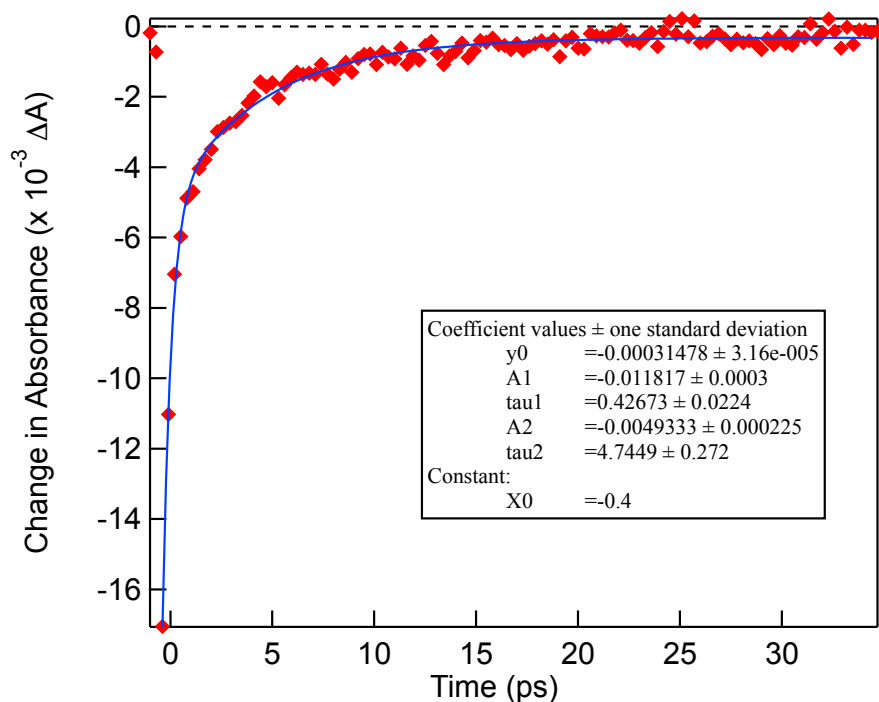


Figure S4.49: GSB recovery of **3** at 580 nm after excitation of 550 nm.

4.6.8 Alternative Fitting of 510 nm TA Spectra

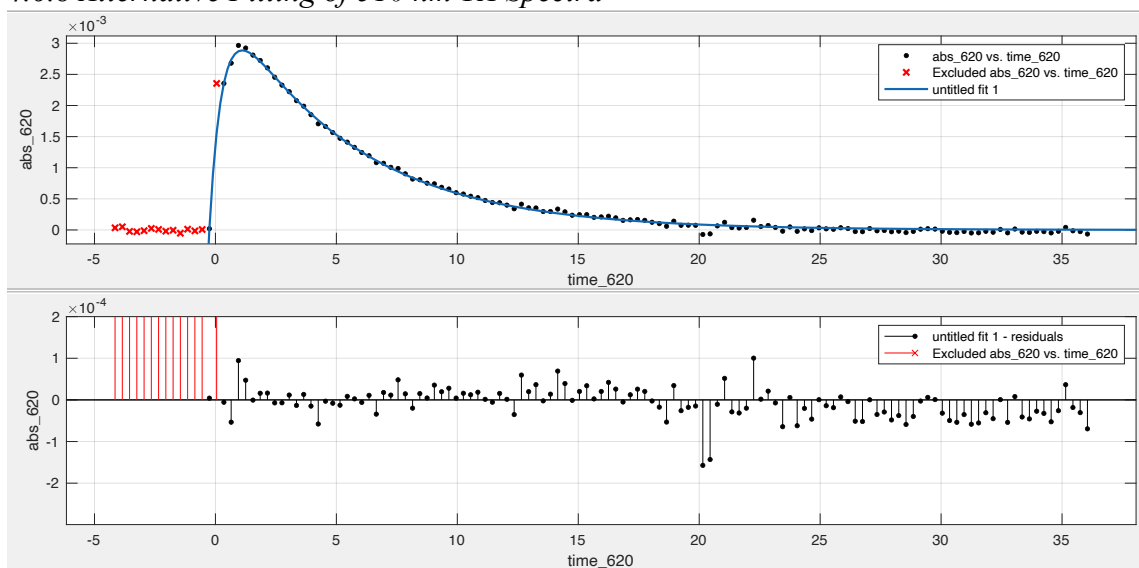


Figure S4.50: Species **1**. Biexponential fit to rise and decay of the ESA feature at 620 nm after excitation with 510 nm light. Parameters are in the text immediately after this figure.

General model:

$$f(x) = a \cdot \exp(-x/T1) + b \cdot \exp(-x/T2)$$

Coefficients (with 95% confidence bounds):

$$T1 = 0.5361 \text{ (0.5076, 0.5646)}$$

$$T2 = 5.238 \text{ (5.139, 5.336)}$$

a = -0.002604 (-0.002714, -0.002494)

b = 0.003973 (0.003898, 0.004048)

Goodness of fit:

SSE: 1.765e-07

R-square: 0.9977

Adjusted R-square: 0.9976

RMSE: 3.884e-05

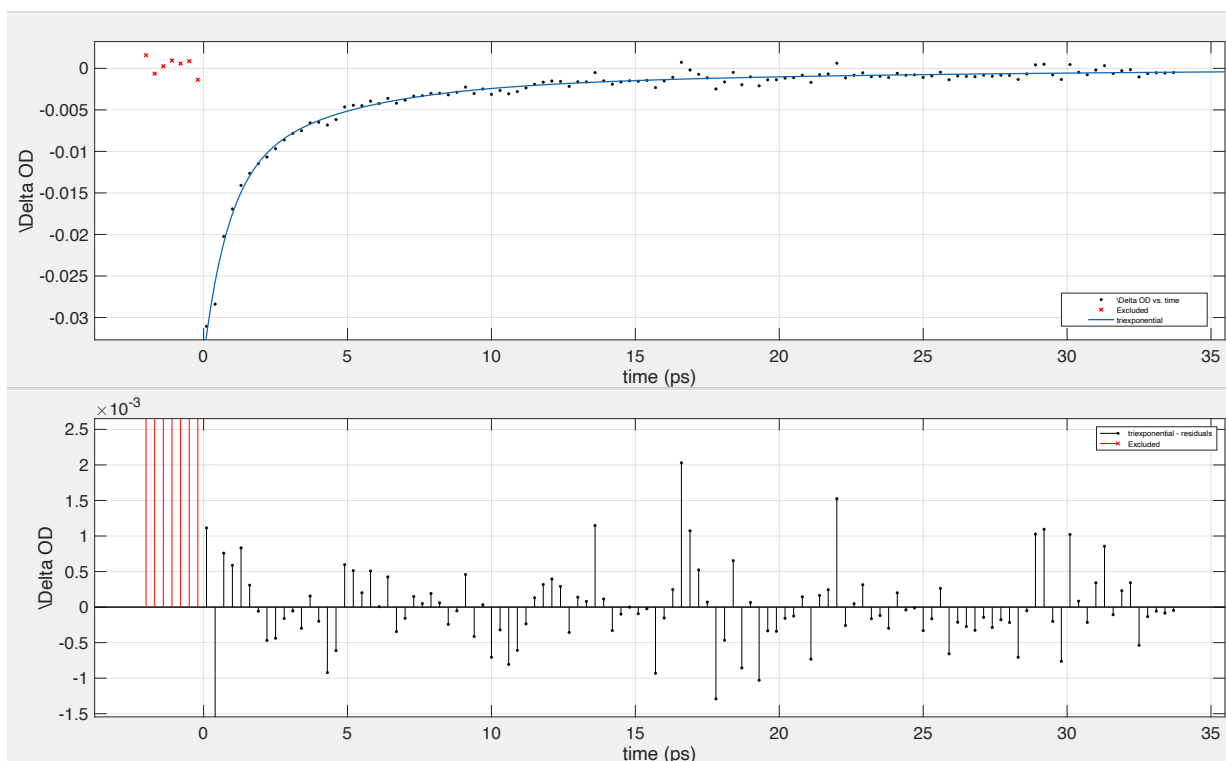


Figure S4.51: Species **2** Triexponential fit and associated residuals at 580 nm after excitation with 510 nm light. Parameters are in the text immediately after this figure.

General model:

$$f(x) = a \cdot \exp(-(x/T1)) + b \cdot \exp(-(x/T2)) + c \cdot \exp(-(x/T3))$$

Coefficients (with 95% confidence bounds):

T1 = 0.8344 (0.5695, 1.099)

T2 = 3.709 (1.113, 6.304)

T3 = 18.46 (1.627, 35.29)

a = -0.02079 (-0.02669, -0.01488)

b = -0.01117 (-0.01546, -0.006888)

c = -0.002875 (-0.006423, 0.0006733)

Goodness of fit:

SSE: 3.839e-05

R-square: 0.9863

Adjusted R-square: 0.9856

RMSE: 0.000599

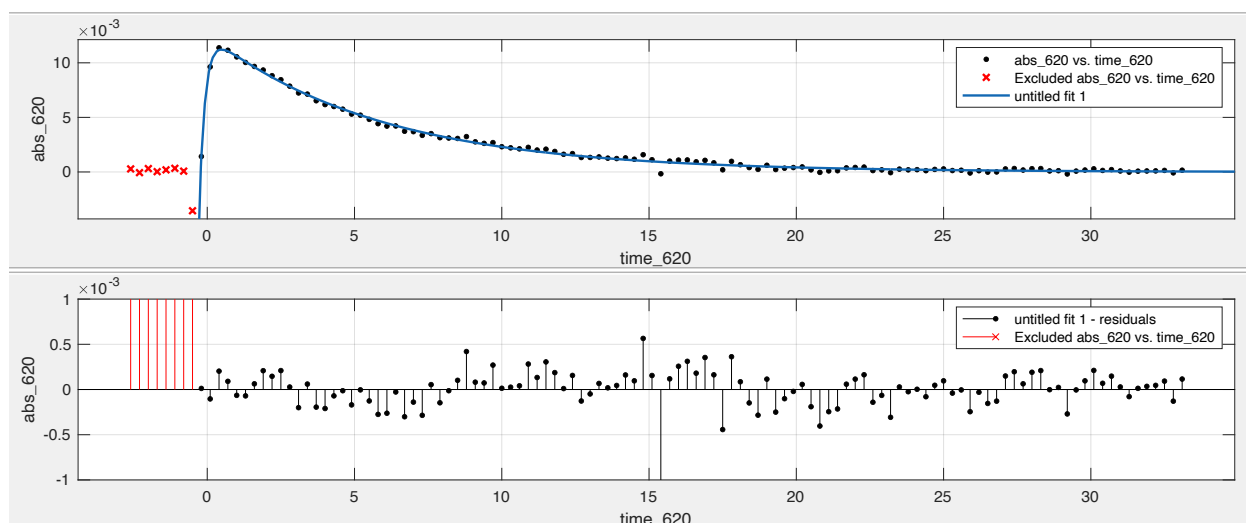


Figure S4.52: Species 2 Biexponential fit to rise and decay of the ESA feature at 620 nm after excitation with 510 nm light. Parameters are in the text immediately after this figure.

General model:

$$f(x) = a \cdot \exp(-x/T1) + b \cdot \exp(-x/T2)$$

Coefficients (with 95% confidence bounds):

$$T1 = 5.874 \text{ (5.738, 6.01)}$$

$$T2 = 0.2037 \text{ (0.1806, 0.2268)}$$

$$a = 0.01262 \text{ (0.01239, 0.01285)}$$

$$b = -0.004364 \text{ (-0.004897, -0.003831)}$$

Goodness of fit:

SSE: 4.648e-06

R-square: 0.9952

Adjusted R-square: 0.9951

RMSE: 0.0002074

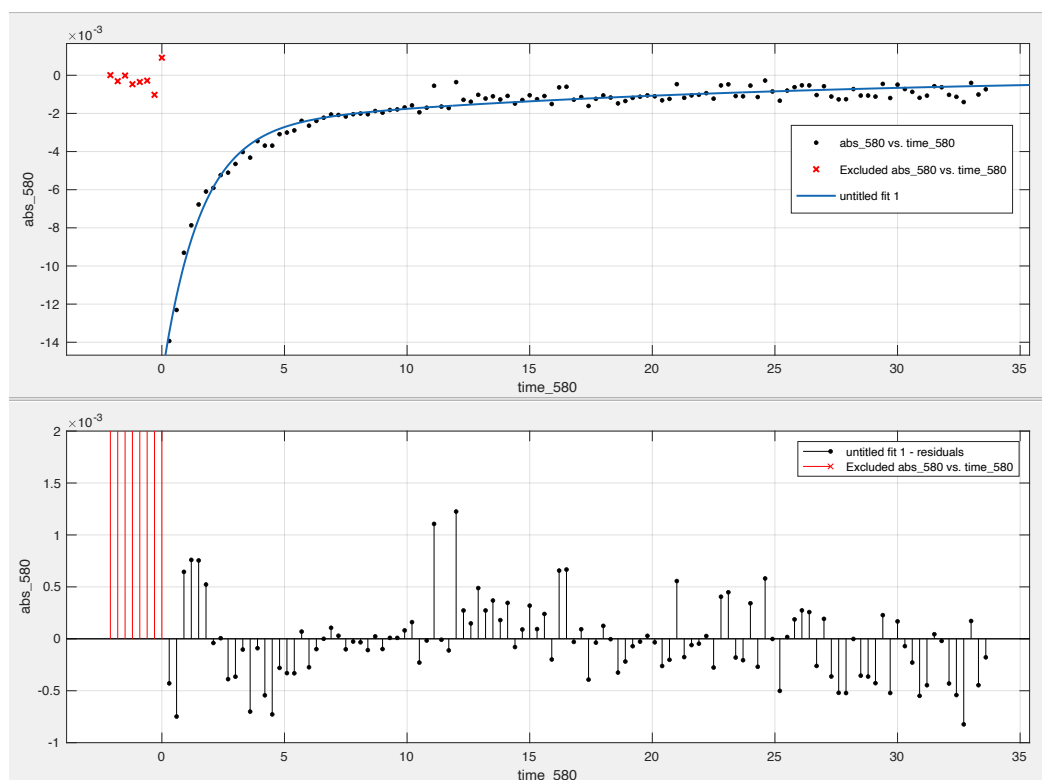


Figure S4.53: Biexponential fit of the data from **3** and associated residuals probing at 580 nm after excitation with 510 nm light. The parameters are in the following text.

General model:

$$f(x) = a \cdot \exp(-x/T1) + b \cdot \exp(-x/T2)$$

Coefficients (with 95% confidence bounds):

$$T1 = 1.535 \text{ (1.355, 1.714)}$$

$$T2 = 20.68 \text{ (16.69, 24.66)}$$

$$a = -0.01304 \text{ (-0.01386, -0.01222)}$$

$$b = -0.002821 \text{ (-0.003244, -0.002398)}$$

Goodness of fit:

SSE: 1.507e-05

R-square: 0.9712

Adjusted R-square: 0.9704

RMSE: 0.0003736

**5) CHAPTER 5: CONTINUED SYNTHETIC DESIGN FOR
LONG-LIFETIME Fe(II) CHARGE-TRANSFER
CHROMOPHORES AND FUTURE DIRECTIONS**

INTRODUCTION

In the introductory chapter the need to consider orthogonality in our approach to modify the structures of coordination complexes along both nuclear coordinate (x-axis) and the excited state energetics (y-axis) was established. It was posited that a great method for doing this is by heteroleptic complex synthesis. This is because each ligand can perform a unique function along a particular dimension (x or y) and the summation of which leads to a complex with the desired properties, which include broad intense absorptions, stability, and long MLCT lifetimes. In this chapter this idea is expanded upon in terms of syntheses of heteroleptic Fe(II) complexes, that are within this design purview. This can be thought of as a summary of the various synthetic procedures developed and modified over the years in development of this platform.

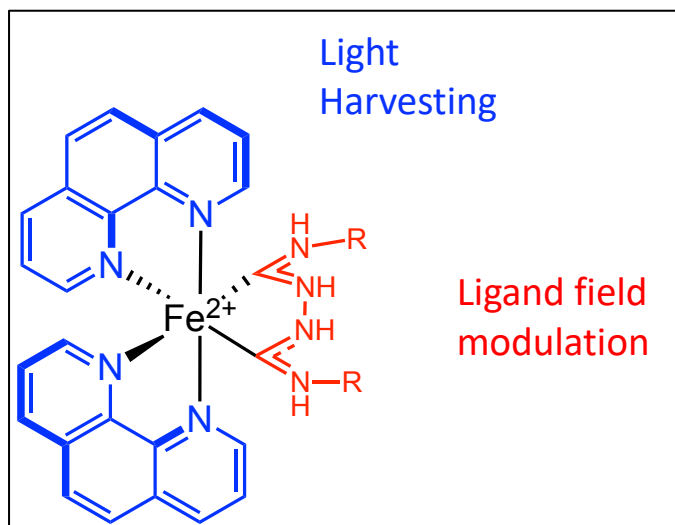


Figure 5.1: The general design principles of the species in this dissertation. This chapter expands on some of these concepts and introduces new possibilities.

It has been established in chapter 1 that a single diamino carbene ligand can destabilize the ligand field (LF) past the triplet/quintet crossing point. This means that this ligand can itself do the work, that the polypyridyls cannot. It is more prudent to use the 1,10-phenanthroline ligand (phen) for what it is good at, namely absorbing light. It is treated as an antenna to localize the charge separated state, and the carbene ligand takes on the role of LF destabilization.

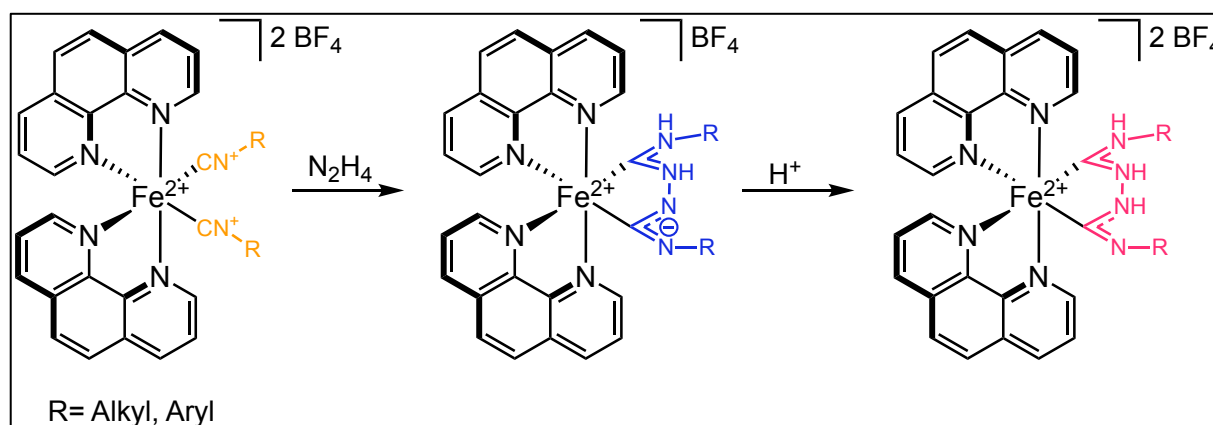


Figure 5.2: Small structural modifications to this heteroleptic platform dial in severe electronic perturbations. The colors of each ligand are associated with their respective colors in dilute solution.

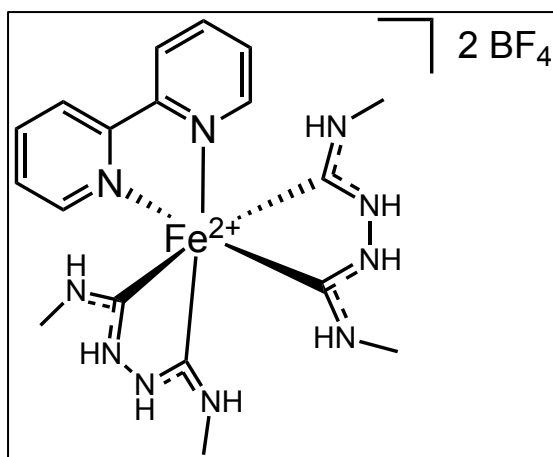
The diamino carbene platform has a multitude of opportunities to explore different structures and ligand types with only minor modification. Figure 5.2 illustrates this, in which isocyanide, imine, and carbene functionalities can be accessed in a few steps but exhibit absorption properties over a span of 100 nm. These small changes represent a very coarse tuning of absorption properties; more granular tuning can be achieved through small modifications to the structure (ex. changing R, substituting phen, etc.). Each of these *bis*-phenanthroline heteroleptics could in theory be converted into *mono*-phenanthroline complexes and still fall within the light harvesting framework of figure 5.1. Leveraging the versatility of this platform will be the cornerstone of future works. We will discuss several modifications that can be made to this general structure in the following sections as well as some of the empirical and computational properties of interesting species, which fall into the design scheme, along the way.

The goal of this chapter is to describe a region of chemical space to mine, probing new systems for interesting structure/property relationships for a desirable sensitizer. Therefore, this chapter will be organized differently, in that it will be presented in parts. Introductions will discuss the reasoning behind syntheses and any previous work done in this regard. Much of this work is considered a ‘work in progress’ and the flow will reflect this, sometimes abruptly.

PART 1: PROGRESS TOWARDS THE SYNTHESIS OF A HETEROLEPTIC BIS-DIAMINO CARBENE COMPLEX

1. Introduction

The basics formulation of ligand field theory describes a linear combination of ligand orbitals that mix with metal-based orbitals to generate new bonding and anti-bonding orbitals. A general result of these linear combinations is that ligand effects are additive. Thus, addition of a second diamino carbene ligand to the platform in figure 5.1 is a valid strategy to maximize the LFS, pushing the system further into the strong field regime. The system we wish to consider in this first part is shown in drawing 5.1. This part of the chapter describes the steps implemented in attempts at its successful isolation.



Drawing 5.1: Representation of complex 1 discussed in this chapter.

2. Experimental

4.2.1 Synthesis

General synthesis. All compounds were synthesized in a nitrogen atmosphere and with degassed and dried solvents unless otherwise specified. Potassium cyanide, iron powder, dimethyl sulfate, and sodium tetrafluoroborate was obtained from Sigma Aldrich, 2,2'-bipyridine was obtained from Oakwood Chemical, iron(II) chloride was obtained from Tokyo Chemical

Industries (TCI). Quinoline was obtained from TCI and purified by distillation over zinc dust. P-toluene sulfonyl chloride was obtained from Jade Scientific, N-methyl formamide was obtained from Beantown Chemical. Methyl isocyanide was synthesized according to literature procedures.¹ The synthesis of $\text{Fe}(\text{bpy})_2(\text{CN})_2 \cdot 3\text{H}_2\text{O}$ and $\text{K}_2\text{Fe}(\text{bpy})(\text{CN})_4 \cdot 4\text{H}_2\text{O}$ were prepared from modified literature procedures.^{2,3} $\text{Fe}(\text{bpy})\text{Cl}_2$ was synthesized according to literature procedures using a Schlenk filter under nitrogen.⁴ Method 1 for the synthesis of **3** and **5** was modified from literature procedures.⁵ NMRs were collected on a 500 MHz spectrometer at the Max T. Rodgers NMR facility at MSU. ESI-MS was performed at the Metabolomics Core at MSU. X-Ray structures were collected at the Center for Crystallographic Research at MSU, using the ShelX protocol.⁶ d

*Synthesis of $[\text{Fe}(\text{bpy})(\text{CNMe})_4](\text{BF}_4)_2$ (**3a**):* (method 1) In air, 0.252 g of $\text{K}_2\text{Fe}(\text{bpy})(\text{CN})_4 \cdot 4\text{H}_2\text{O}$ (0.54 mmol, 1 eq) was added to excess dimethyl sulfate (15 mL) and heated to 80°C after purging with N_2 . After 3 hours, the color of the solution was murky yellow. Heating was continued overnight (~18 hours) after which the flask was cooled to room temperature and 15 mL of diethyl ether was added. The organic layer was then extracted with water (3x ~10 mL). NaBF_4 was added to the combined aqueous extracts and the volume was reduced by rotary evaporation until a yellow precipitate formed with solid white impurities. The remaining aqueous solution was separated from the solid with filtration. Into a separate flask, the filter cake was washed with acetonitrile, leaving the white solids behind. The yellow filtrate was quickly precipitated with diethyl ether and collected by filtration as a microcrystalline yellow solid. Several washes with ether followed. Solids were dried in air, over a two-day period. 0.212 g, 71% yield. ^1H NMR (500 MHz, acetonitrile- d_3) δ 8.91 (ddd, $J = 5.6, 1.5, 0.7$ Hz, 2H), 8.38 (dt,

$J = 8.0, 1.2 \text{ Hz, 2H}$), $8.21 \text{ (td, } J = 7.9, 1.5 \text{ Hz, 2H)}$, $7.71 - 7.65 \text{ (m, 2H)}$, 3.66 (s, 6H) , 3.25 (s, 6H)).

*Synthesis of $[\text{Fe}(\text{bpy})(\text{CNMe})_4](\text{BF}_4)_2$ (**3a**):* (method 2): **Procedures were carried out in a fume hood with the sliding doors closed and taped, the sash was kept at minimum height.**

To a nitrogen purged pressure tube was added 3 mL of methylisocyanide, which was freshly prepared but had matured into a red/orange color upon warming to room temperature. To this was added 1.053 g (3.7 mmol, 1 eq) of $\text{Fe}(\text{bpy})\text{Cl}_2$ as an orange solid, the dissolution of which did not change the color of the solution. This flask was closed and stirred at room temperature for 1 hour whereupon goldenrod-colored solids formed. At this point the flask was heated, behind a blast shield to 90°C . The solids dissolved and the solution color reverted to its dark-red color. Heating was continued for 5 hours. After cooling, the flask was allowed to sit and stir overnight. A 1:1 water/methanol solution was added, and this was extracted with diethyl ether. To the aqueous layer was added excess NaBF_4 which precipitated a yellow solid that was collected by filtration. Into a separate flask, the filter cake was redissolved in MeCN leaving behind white solids. The filtrate was precipitated with diethyl ether and washed several times with the same solvent. It was dried on a watch glass overnight. Crystals suitable for x-ray diffraction were obtained by slow cooling in ethanol as the monohydrate. 1.641 g, 80% yield. ^1H NMR (500 MHz, acetonitrile- d_3) δ 8.92 (ddd, $J = 5.6, 1.5, 0.8 \text{ Hz, 2H}$), 8.39 (dt, $J = 8.1, 1.1 \text{ Hz, 2H}$), 8.21 (td, $J = 7.9, 1.5 \text{ Hz, 2H}$), 7.68 (ddd, $J = 7.4, 5.7, 1.3 \text{ Hz, 2H}$), 3.66 (s, 6H), 3.25 (s, 6H). EA: calcd. C: 38.07%, H: 3.91%, N: 14.80%. Anal. C: 38.43%, H: 3.70%, N: 14.76%.

*Synthesis of $[\text{Fe}(\text{phen})(\text{CNMe})_4](\text{BF}_4)_2$ (**3b**):* 0.199 g (0.5 mmol, 1 eq) of $\text{K}_2\text{Fe}(\text{phen})(\text{CN})_4 \cdot 4\text{H}_2\text{O}$ reacted according to method 1 for the synthesis of **3a**. 0.192 g of a yellow solid was isolated. Yield, 70%. ^1H NMR (500 MHz, acetonitrile- d_3) δ 9.24 (dd, $J = 5.2,$

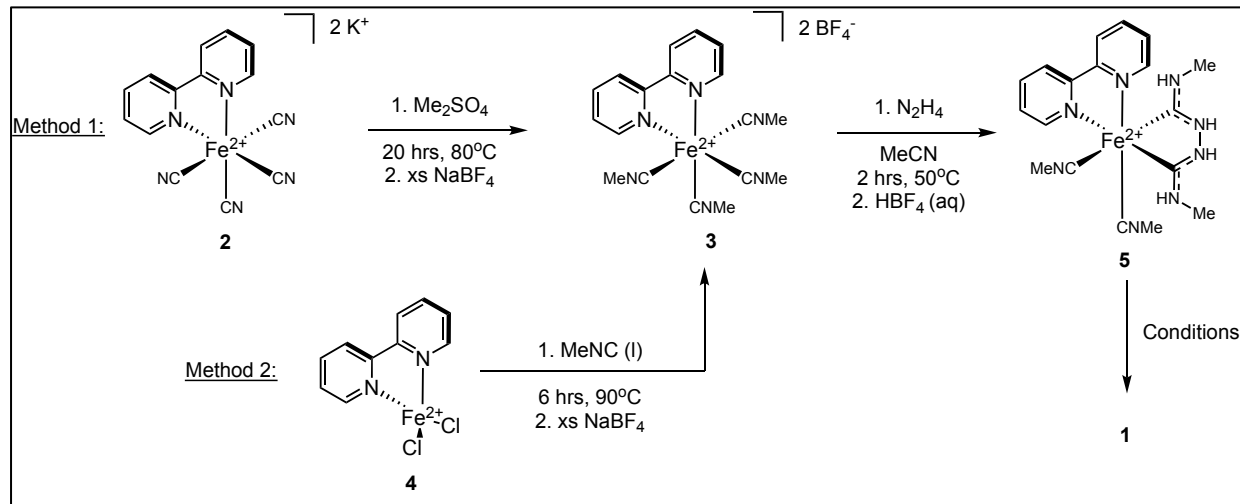
1.3 Hz, 2H), 8.77 (dd, $J = 8.3, 1.3$ Hz, 2H), 8.20 (s, 2H), 8.01 (dd, $J = 8.3, 5.2$ Hz, 2H), 3.72 (s, 6H), 3.14 (s, 6H).

*Synthesis of $[Fe(bpy)(CMMMe)_2(C_4H_{10}N_4)](BF_4)_2$ (**5a**):* 0.523 g (0.95 mmol, 1 eq) **3a** was dissolved in 12 mL acetonitrile in a glass round bottom flask. To this was added 0.095 mL of hydrazine hydrate (1.9 mmol, 2 eq). Color darkens upon addition. It was heated for 2 hours at 50°C after which the color turns red. This was cooled and 0.53 mL (1.03 mL/g) of 48% HBF₄ in water was added where the color changed from dark-red to orange. 25 mL of a 5% HBF₄ aqueous solution was added and washed with ether. The volume of this aqueous layer was reduced by rotary evaporation which precipitated microcrystalline orange/red solids which were collected by filtered. This solid was heated overnight *en vacuo*. 0.47 g, 85% yield. ¹H NMR (500 MHz, acetonitrile-*d*₃) δ 9.32 (s, 1H), 9.26 (s, 1H), 8.99 (ddd, $J = 5.5, 1.5, 0.8$ Hz, 1H), 8.34 (dt, $J = 8.3, 1.1$ Hz, 1H), 8.30 (dt, $J = 8.0, 1.1$ Hz, 1H), 8.20 (ddd, $J = 5.7, 1.6, 0.8$ Hz, 1H), 8.12 (td, $J = 7.9, 1.5$ Hz, 1H), 8.03 (td, $J = 7.9, 1.5$ Hz, 1H), 7.63 (ddd, $J = 7.6, 5.5, 1.3$ Hz, 1H), 7.47 (ddd, $J = 7.5, 5.6, 1.4$ Hz, 1H), 3.46 (s, 3H), 3.21 (s, 3H), 2.55 (d, $J = 5.1$ Hz, 3H).

4.2.2 Computations

All computations were performed using the Gaussian 16 B.01 suite.¹⁶ Calculations were performed in a methanol or acetonitrile polarized continuum (PCM) using density functional theory (DFT) with the B3LYP functional and GD2 empirical dispersion.^{17-20,26} The 6-311G* basis set were used for all atoms, except Fe, which utilized the pseudo-potential SDD during optimizations.²¹⁻²⁵ NBO6 was utilized as an additional module for Gaussian 16.^{7,8} NBO output was parsed using a homebrewed python program reported in the appendix of this chapter.

3. Results and Discussion



Scheme 5.1: Synthetic scheme for the synthesis of **1**. Method 1 involved the cyanation of $\text{Fe}(\text{bpy})_2\text{CN}_2$ to make **2**. Reaction of **2** with dimethyl sulfate occurred with a yield of 71%. A limiting factor for this route is the scalability of the cyanation routes. Method 2 involved reacting **4** with neat isocyanide which was freshly synthesized for a yield of 80%. The tetra-isocyanide precursor **3** was reacted with 2 equivalents of hydrazine in acetonitrile to give **5** in a yield of 85%. This was used to optimize the synthesis of **1**.

The synthesis of precursor isocyanides proceeded by two different routes shown in scheme 5.1. Literature precedent utilizes the tetracyano species which is methylated. This was achieved in good yield, however, uses 250 equivalents of KCN to make the substitution of a bipyridine ligand in $\text{Fe}(\text{bpy})_2\text{CN}_2$ ligand favorable. This meant that only small batches of precursors could be synthesized at any given time to avoid large absolute quantities of cyanide salts. This, combined with the long reaction time (> 4 days) in the case of the 1,10-phenanthroline ligand makes this route unsustainable.

Method 2 was chosen as a workaround in that it avoided the pitfalls of the previous methodology. This started from a low coordinate iron precursor which is well-known, **4** was prepared from literature procedures.⁴ This was dissolved in methylisocyanide. Upon heating a yellow product form with good yield. Method 2 represents a novel route to the synthesis of $[\text{Fe}(\text{bpy})(\text{CNMe})_4]^{2+}$ cation.

hydrogen bonding interactions shown in the figure with the hydrogens of the isocyanide group. This further suggests a very electron deficient metal center and may explain the sensitivity of these types of complexes to base. Water too is hydrogen bonded to the axial isocyanide and in the crystal likely orients its other hydrogen, towards the adjacent BF_4^- ion. The presence of water is not wholly unsurprising as the ethanol of recrystallization was not strenuously dried.

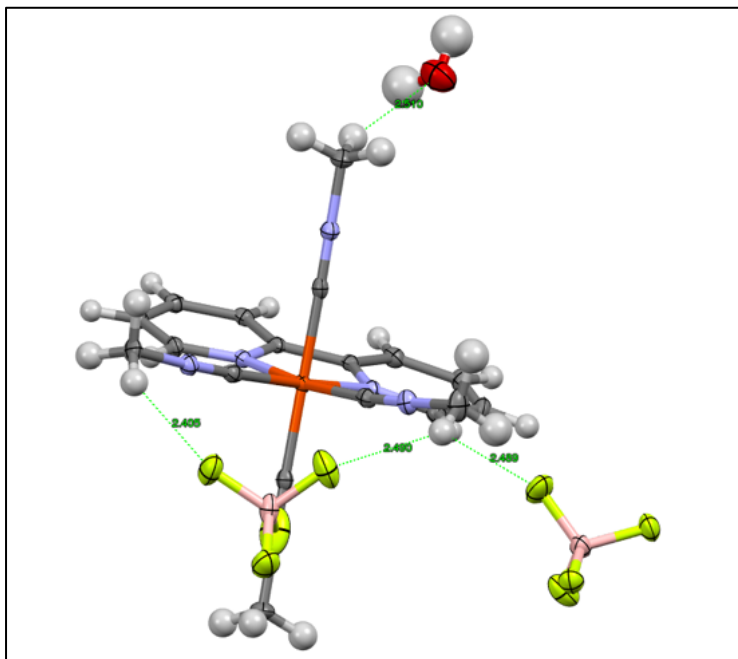
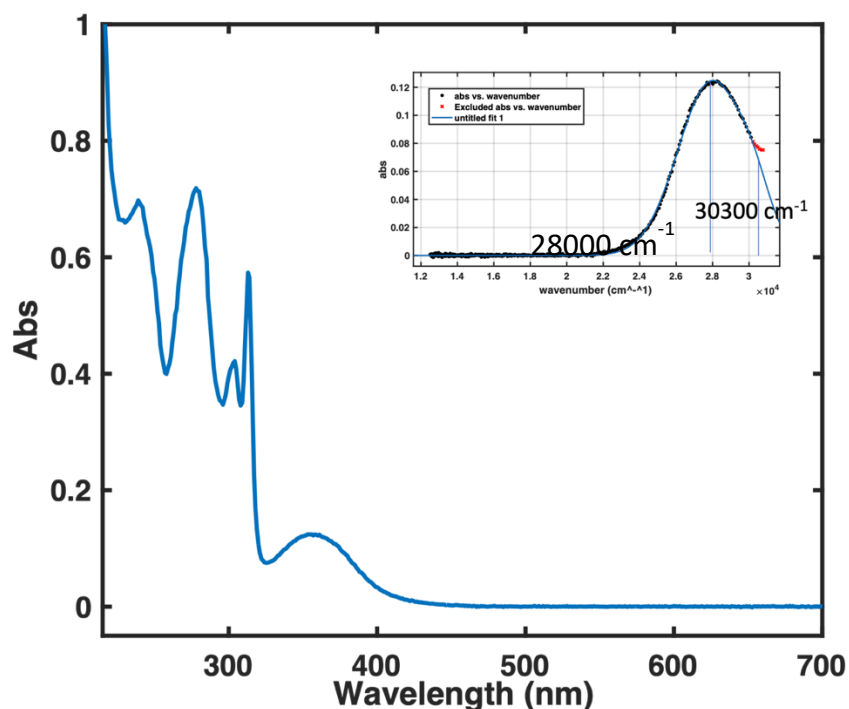


Figure 5.4: X-ray crystal structure of **3**. A notable hydrogen bonding interaction is present between the equatorial methyl protons and the counter anions. Orange: iron, purple: nitrogen, grey: carbon, pink: boron, yellow: fluorine, red: oxygen. Thermal ellipsoids at 50% probability.

The absorption spectrum of **3** in figure 5.5 is interesting as it absorbs in the near UV regions consistent with its light-yellow color. A single Gaussian is fit when the spectrum is deconvolved consistent with a single donor-acceptor pair of the metal center and bipyridine ligand. The sharp transition around 315 nm is likely due to a ligand-to-ligand transition, the donor of which has a very tight ground state potential (i.e. little broadening). Thus, this likely describes the CN π to bipyridine π^* .

Table 5.1: Selected bond lengths of compounds **3** and **5**.

Bond	3 (Å)	Bond	5 (Å)
Fe-N ₁	1.9957(15)	Fe-N _{carbene}	2.019
Fe-N ₂	1.9959(16)	Fe-N _{isocyanide}	2.005
Fe-C _{ax1}	1.9120(2)	Fe-C _{ax,carbene}	1.948
Fe-C _{ax2}	1.9030(2)	Fe-C _{ax,isocyanide}	1.906
Fe-C _{eq1}	1.8703(19)	Fe-C _{eq,carbene}	1.922
Fe-C _{eq2}	1.8790(19)	Fe-C _{eq,isocyanide}	1.846

**Figure 5.5:** UV-Vis spectrum of **3** in acetonitrile showing a transition blue of 400 nm, consistent with its pale yellow color. (inset) Gaussian deconvolution of the transition, suggests a single transition centered at 28,000 cm⁻¹.

3 was dissolved in acetonitrile and 2 equivalents of hydrazine were added with heating, a modification of the 20 equivalents called for in literature procedure.⁹ This reaction is very clean and the light yellow to blood-red color change is very descriptive. The red color disappears upon protonation to form an orange solution. This blueshift upon protonation is consistent with spectral changes observed in the other carbene species studied in this report. The crystal structure of **5** in its phenanthroline flavor is presented in figure 5.6. The table of selected bond lengths for

5 are included in table 5.1. A *trans*-influence in the Fe-N bond across from the carbene is observed. Compare this to the Fe-N bond trans from the axial isocyanide, which shows very little difference from the same bonds in **3**. This is consistent with the carbene being a better donor. This however should influence the bonding of the isocyanides, however both isocyanide bonds are equal and shorter than equivalent bonds in **3**. This would seem to suggest some compensatory bonding interaction is occurring.

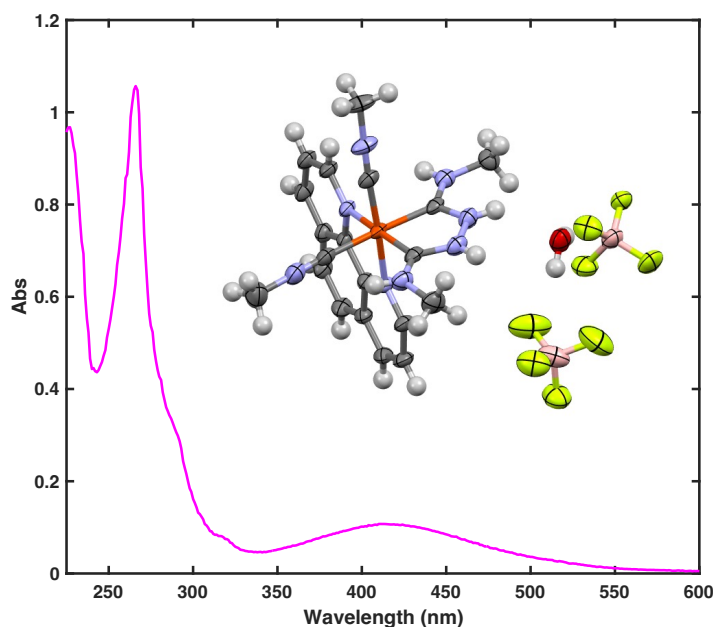


Figure 5.6: UV-vis spectrum of **5** in acetonitrile. MLCT absorption manifold is broadened and redshifted compared to its precursor. Inset: Crystal structure of **5** with 1,10-phenanthroline as the counter ligand Thermal ellipsoids at 50% probability. Solved by Dr. R.J. Staples.

This compensatory bonding interaction was illustrated with natural bond orbital (NBO) calculations. The natural resonance structure (NRS) is depicted in figure 5.7, which depicts a bonded core of carbene and isocyanide ligands (group 1) made with metal sd^2 hybrid orbitals. The free isocyanide and bipyridine make up groups 2 and 3 respectively. Note NRT calculations were not performed, however the dominant resonance structure is included in the standard NBO output.^{7,8} These latter moieties are included in the structure through dative resonance

interactions, the energies of which can be found from second order perturbation theory in the NBO output. The highest energy interactions are included in table 5.2. The isocyanide lone pair, acts as a donor with multiple acceptors, notably all Fe-C σ -bonds in group 1. The delocalization of this NBO to these acceptors alone accounts for about 350 kcal/mol in resonance stabilization. These appear to be driven by the orbital mixing factor, itself dependent on orbital overlap. This is demonstrated by the highest energy interaction, in which the LP donates to the Fe-C σ -bond *trans* to it, making a three center four electron bond. It is likely that the other resonance contributor of this 3-c-4-e bond (isocyanide covalent bond with carbene as LP donor) has a similar energy. On top of this bond, the lone pair interacts with the other σ -bonds where orbital mixing is reduced considering the bonding interactions are orthogonal to the isocyanide LP axis. However, taken together these interactions have a huge effect on the bonding and could function as the compensatory bonding interaction that explains the lack of a *trans*-influence in the isocyanide. Like the NBOs in other chapters, the back bonding interaction with the isocyanides is miniscule (~5 kcal/mol).

Table 5.2: Second-order perturbation theory analysis ordered by energetic contribution. Relevant interactions to the argument of a compensating bonding interactions are greyed. The script for extracting this is printed in the appendix to this chapter.

Order	NBO	Donor Group (L)	NBO	Acceptor Group (NL)	E2(kcal/mol)	E(NL)-E(L)	F(L,NL)
1*	42.	LP (1) C 42	111.	BD* (1)Fe 1- C 26	239.17	0.78	0.385
2	38.	LP (1) N 25	108.	LV (1) C 24	179.32	0.16	0.149
3	39.	LP (1) N 27	109.	LV (1) C 26	176.33	0.16	0.15
4	40.	LP (1) N 28	109.	LV (1) C 26	114.59	0.2	0.134
5	41.	LP (1) N 29	108.	LV (1) C 24	114.48	0.2	0.133
6	36.	LP (1) N 18	112.	BD* (1)Fe 1- C 43	63.06	1.03	0.227
7*	42.	LP (1) C 42	112.	BD* (1)Fe 1- C 43	61.85	0.92	0.213
8	37.	LP (1) N 19	110.	BD* (1)Fe 1- C 24	60.3	0.86	0.204
9	44.	BD (1)Fe 1- C 26	110.	BD* (1)Fe 1- C 24	56.94	0.82	0.193
10	44.	BD (1)Fe 1- C 26	112.	BD* (1)Fe 1- C 43	56.19	0.99	0.21
11*	42.	LP (1) C 42	110.	BD* (1)Fe 1- C 24	55.54	0.76	0.183

Table 5.2 (cont'd)

12	43.	BD	(1)Fe 1- C 24	111.	BD*	(1)Fe 1- C 26	51.62	0.85	0.188
13	43.	BD	(1)Fe 1- C 24	112.	BD*	(1)Fe 1- C 43	46.42	1	0.385

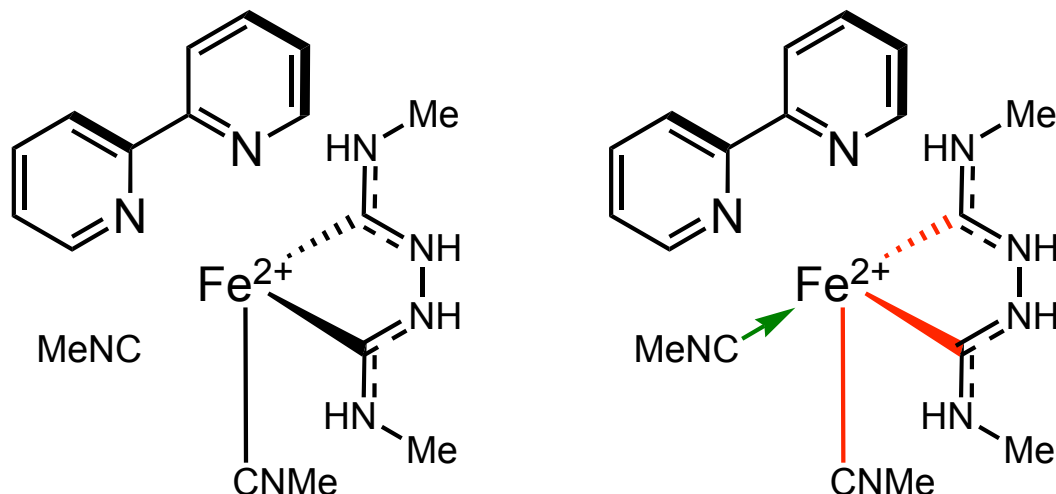


Figure 5.7: Partial natural resonance structure (NRS) of **5** computed from NBO calculations. Group 1 includes the carbene and isocyanide. Groups 2 and 3 correspond to the bipyridine and methylisocyanide respectively. (right) The isocyanide LP (green) in group 3 donates to the BD* interactions (red) in group 1. Note these structures only considers Fe-L delocalizations and thus are partial NRSs.

Quantum chemical calculations were performed on **5** as its structure is fascinating in that it combines a carbene, two isocyanides, and a pyridyl ligand in one platform. Orbital analysis suggests a d-orbital manifold that contains four molecular orbitals in place of the three degenerate non-bonding orbitals of the t_{2g} set. The other MO is of ligand origin. Two are non-bonding and two of which can only be described as π -bonding with the carbene ligand. Such a bonding interaction may change the nature of the excited state transitions in **5**. These molecular orbitals are visualized in figure S5.18 in the appendix of this chapter.

To interrogate this system further, TD-DFT was performed on **5** and the calculated UV-Vis spectrum is in figure 5.8 along with the measured absorption spectrum. A single transition dominates the region near $27,000\text{ cm}^{-1}$ which is expected for a single acceptor. The natural

transition orbital (NTO) for this is pictured in the inset of figure 5.8. It shows a particle/hole pair that is consistent with MLCT character. An electron in a definitively metal-based orbital transfers to an orbital of π -symmetry on the phenanthroline ligand. This suggests that the design principle presented in figure 5.1 still holds, that the pyridyl moiety acts as an antenna for light capture, the metal a unitary donor and the other ligands likely act to perturb the energetics of the system. This last point however has not been rigorously established.

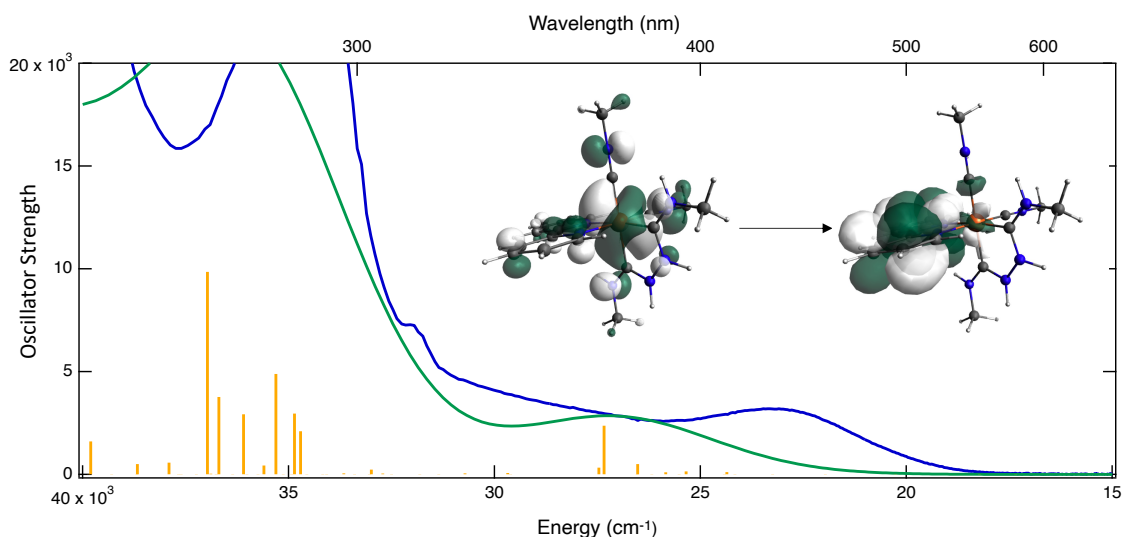
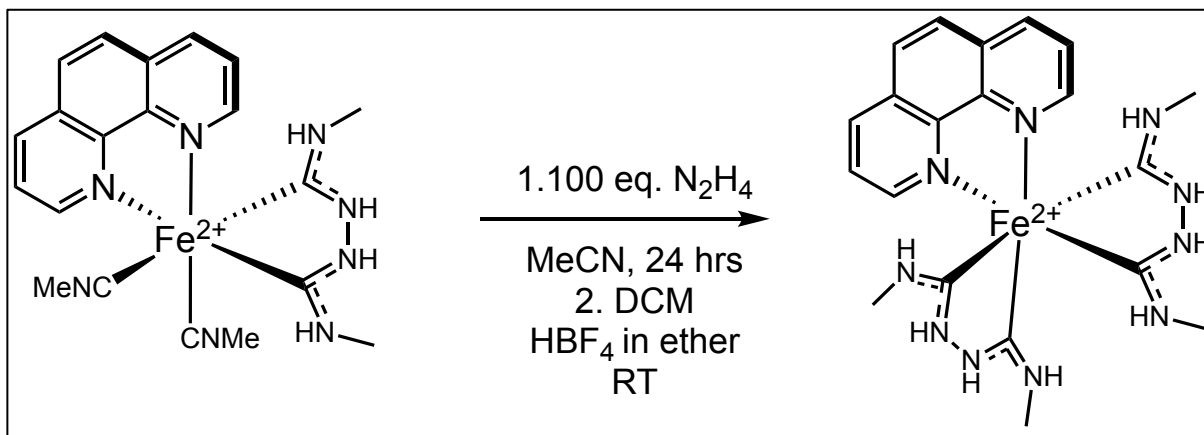


Figure 5.8: Calculated UV-Vis spectrum overlain with the empirical spectrum. A single transition is dominant in the near visible region which corresponds to NTO 15 which is illustrated in the inset. This particle/hole pair suggests MLCT character which localizes on the phenanthroline ligand.

Complex **5** was used as a precursor for the synthesis of the target compound **1**.

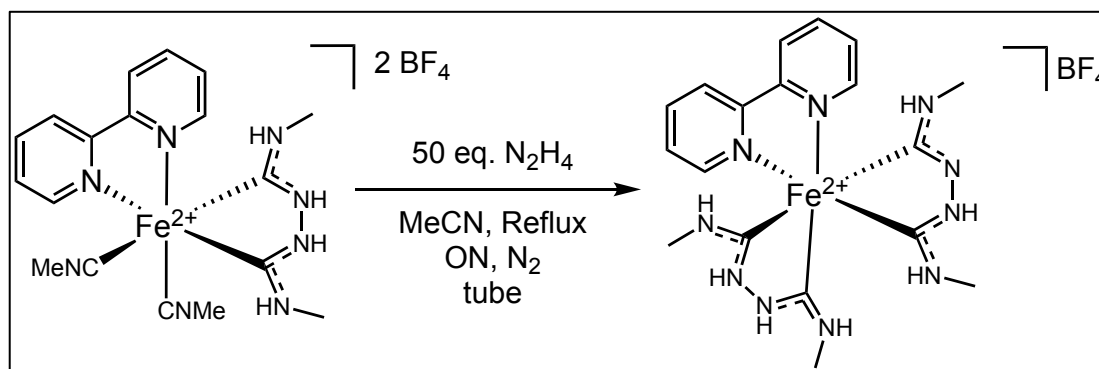
Previous investigations into the synthesis of bis-carbenes through amine addition speak on the inability to induce the formation of a second carbene. For example, Balch was only able to form a mono-carbene from the $[\text{Fe}(\text{CNMe})_6]^{2+}$ precursor.¹⁰ This larger activation barrier, which could be considered as disputing the bonding interactions in table 5.2, likely slows down the reaction to form the second carbene. Therefore, during the investigations into the synthesis of **1**, a 100-fold excess of hydrazine was used in a small volume of acetonitrile with excessive heating. Upon the

addition of hydrazine, the solution would turn orange to red. This color was recoverable by the addition of acid, suggesting that the monocation is reacting. After an extended period of reaction, solutions would form a black/purple solution which would change color to an orange color upon interaction with air. Electrospray ionization mass-spectrometry was used to deconvolve the complicated mixtures. Demethylation of the isocyanides were observed in some cases.



Scheme 5.2: Prototypical reaction scheme for both the bipyridine and phenanthroline varieties. No yield has been found for the reaction.

It was deemed likely that the black sludge like material obtained was due to reduction products from heating with excess amine. The amount of hydrazine used, and the time spend under reflux was reduced. In one experiment in scheme 5.3 yielded a dark solution. Upon filtration of the small amount of solid material, a purple filtrate was isolated and analyzed by ESI-MS. The mass spectrum of this filtrate is shown in figure 5.9. It includes the target compound, as well as some other species which suggest demethylation of the isocyanides. This spectrum suggests that the synthesis of **1** is indeed possible, which runs counter to the investigations of Balch et. al.^{10,11} This was unable to be isolated however as precipitation with non-polar organic solvents led to layer separations with hydrazine and aqueous extraction led to product breakdown.



Scheme 5.3: Reaction scheme which was found to produce the desired product.

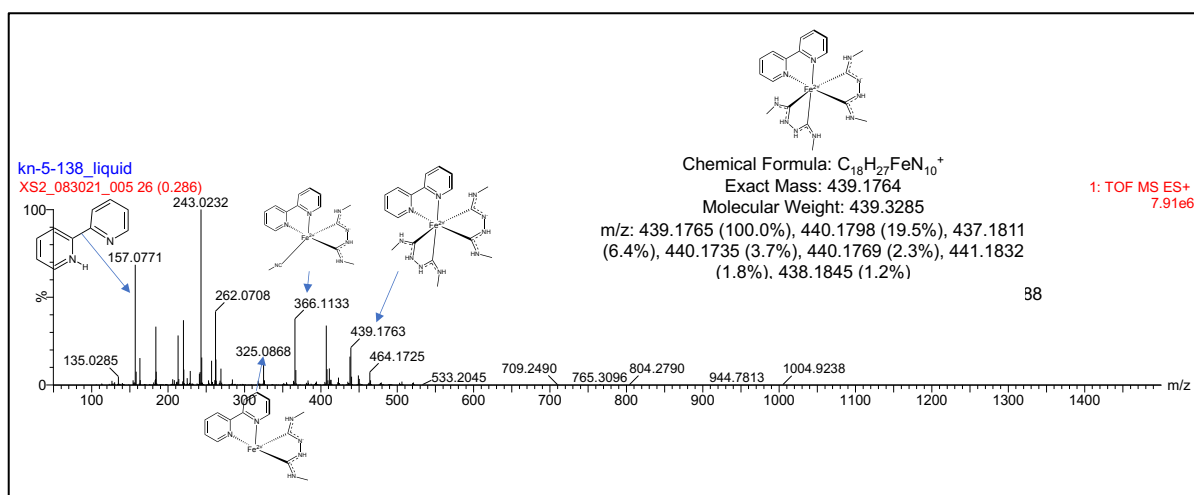
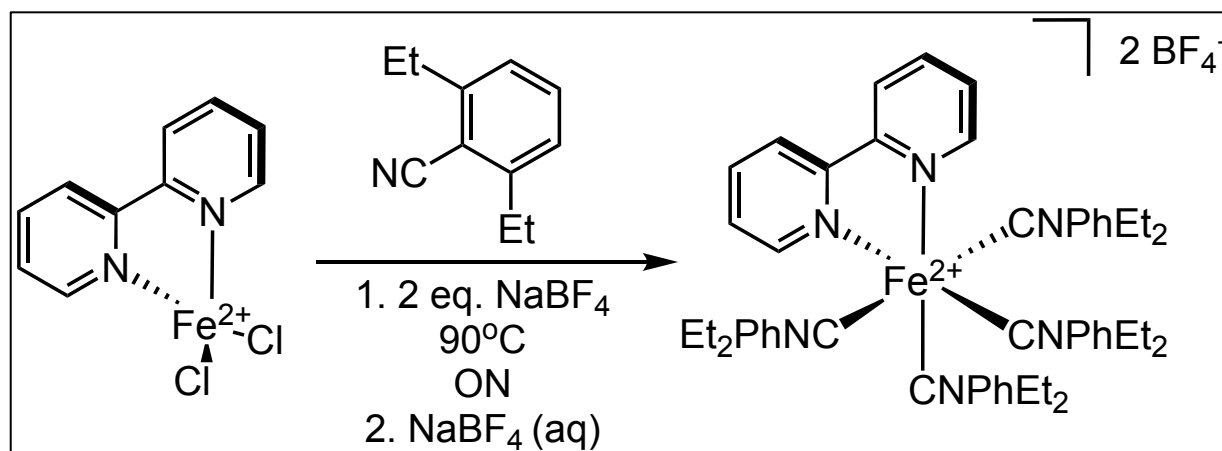


Figure 5.9: Mass spectrum of the reaction mixture from scheme 4.3. The mixture contains the desired product, some lysed starting material as well as some unresolved peaks. MSMS has not been performed on this system. Computed analytical results are included in the inset.

Optimization of the procedure for increased yield and the removal of excess hydrazine impurities will be critical for the next steps in the synthesis of this type of complex. For example, less heat and longer reaction times may prove useful at reacting the remaining starting material. However, the stability of the target compound is indeterminate. As such, longer reactions may prove detrimental, which is consistent with the earlier investigations. One potentially advantageous strategy would utilize the selective precipitation of the product by changing the formal charge through the acid/base chemistry of the carbene backbone. In moderately non-polar solvents, where the doubly deprotonated form is expected to be more soluble, inclusion of a

$\text{N}_2\text{H}_4/\text{N}_2\text{H}_5\text{X}$ (where X is some solubilizing counter anion) buffer system could help selectively precipitate the doubly protonated form. The key requirement is that the hydrazinium complex and starting material are both soluble enough to undergo reaction. The buffer system can be made *in situ* as to not require the isolation of solid hydrazine salts in air.

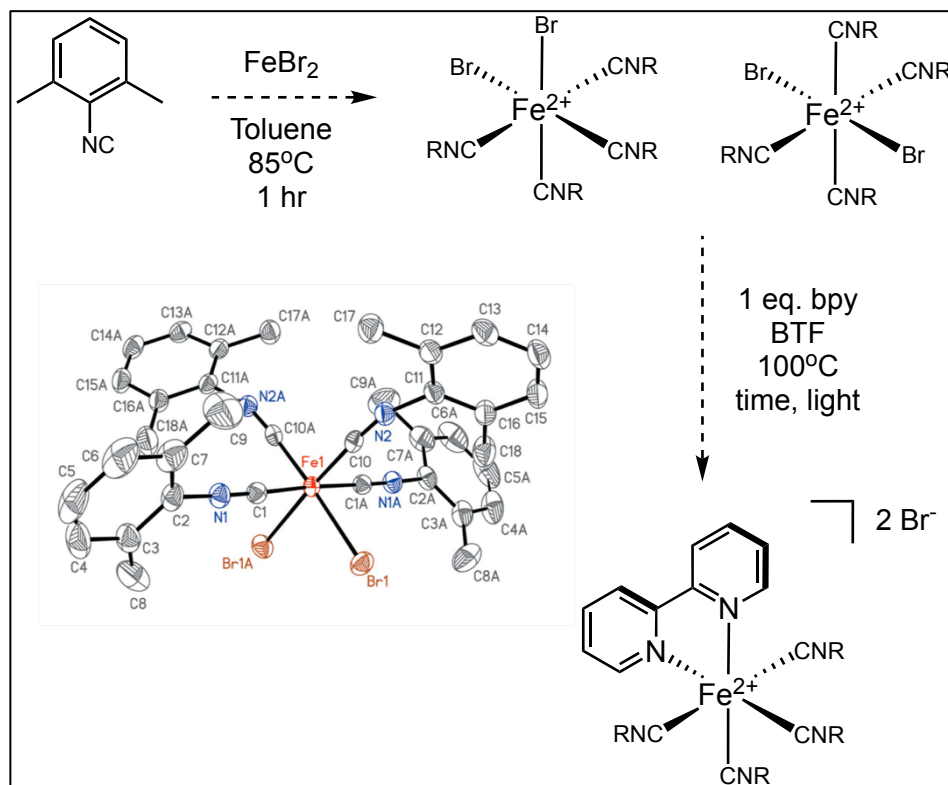
The decreased reactivity of the isocyanides upon the first carbene formation is likely the limiting factor in the synthesis of their bis-carbene analogues, using different isocyanides may change this reactivity. For example, trifluoromethyl isocyanide could be utilized to increase the reactivity the complex for reaction with hydrazine. This could be achieved by the method 2 for tetrakisocyanide synthesis by the *in-situ* dehalogenation of the dibromo-trifluoromethanimines with Mg in THF or by method 1 and reaction of tetracyanides with trifluoromethyl iodide.¹² These were not attempted however.



Scheme 5.4: Reaction scheme for the synthesis of tetra-aryl isocyanides. Compound was unable to be isolated however there was an intriguing color change.

Attempts to make tetra-isocyanides from aryl-isocyanides has been attempted utilizing **4** as a starting material. The DEPNC isocyanide was used for convenience and not for any optimal withdrawing ability. Attempts to make the corresponding tetrakisocyanide compound is depicted in scheme 5.4. The reaction was run in a matured solution of the isocyanide. Included were two equivalents of sodium tetrafluoroborate to make it possible for anion exchange and

avoid free chlorides. There was no evidence this worked, however. A yellow precipitate was formed, which is consistent with the color of species **3** in this report. ^1H -NMR was taken of this solid however and the spectrum was consistent with the free isocyanide. No further investigations were performed.



Scheme 5.5: Proposed route to tetra-aryl isocyanides inspired by reference 11. The second reaction proposition is novel. Structure taken from reference 11.

Tetraarylisocyanides starting from FeX_2 are known.¹³ This complex could be reacted with 1 eq of chelating polypyridyl which should favor substitution of the chloride over time. In the presence of light this would likely favor the formation of the *cis*-complex. An illustration of such a reaction is included in scheme 5.5.

4. Conclusions

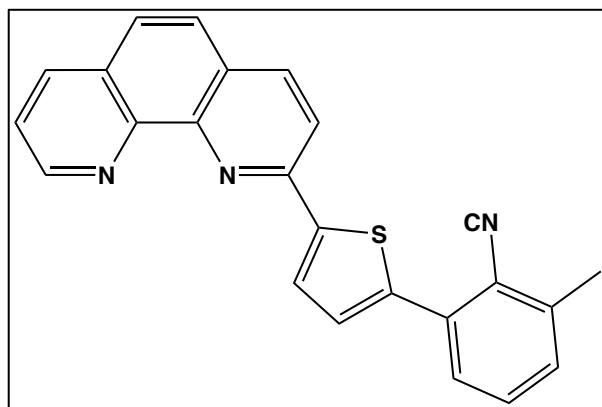
Investigations into the synthesis of a *bis*-carbene system was discussed. A novel synthetic procedure was found for precursor isocyanide compounds **3** and **5**, which avoided the

cyanation route, which can be scaled up without absurd amounts of cyanide salts. Structural analysis of the crystal structure of precursor **5** revealed little *trans*-influence induced by the carbene compared to **3**. NBO calculations revealed this was likely due to compensatory donor-acceptor interactions with other parts of the complex. The precursor was utilized in the synthesis of target compound **1**. The synthesis proved difficult; however, it was demonstrated by mass spec to exist when reacted with a super excess of hydrazine and ~8 hour reaction times. This runs contrary to expectations of bis-carbene species synthesized by the metal template method in previous literature. Some strategies to improve the yield of its synthesis and an alternative route to a *bis*-carbene system was also proposed.

PART 2: IMPORTANT FUTURE WORKS

Recent work by Berkefeld and co-workers describes the synthesis of an Fe(II) cyclometalate that exhibits NIR emission in solution.¹⁴ This was attributed to the strong ligand field imparted by the aryl ligands. The lowest energy excited state was found from vertical excitation of the ground state to be ³MLCT in nature.

This system shares a similar coordination environment to the complexes studied here, however the dynamics are drastically different. The work in chapter 1 suggests that a JT distortion occurs in the lowest energy ³MC state and it is likely to drive non-radiative decay. The Berkefeld complex likely suppresses this distortion by utilizing a bis-tridentate ligand framework, in accordance with the x-axis strategy discussed previously.



Drawing 5.2: A possible isocyanide ligand design that could be converted to tridentate carbene systems.

Therefore, it would be prudent incorporate a tri-dentate design into the systems described in this work. One example is illustrated in scheme 5.2, where a thiophene group links a phenanthroline and an aryl isocyanide. This ligand is inspired by the work of Wenger and coworkers who have leveraged this type of ligand design into isocyanides.¹⁵ This ligand could in theory undergo the metal templated reactions described throughout this work to make a carbene system that suppresses the axial JT distortion. This ligand was inspired by the *bi*- and *tri*- dentate isocyanide ligands made by the Wenger group. Simple molecular mechanics energy minimization of an iron complex using the ligand in drawing 5.2 suggests bond lengths would correspond to a high-spin ground state and thus may be unworthy to pursue, therefore a linker which facilitates an appropriate geometry is highly desirable. The system could be further examined in the context of CT delocalization, where the linker group and isocyanide could aid in the delocalization of the excited wavefunction into the aryl group's π -system.

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5.7.1 NMR spectra



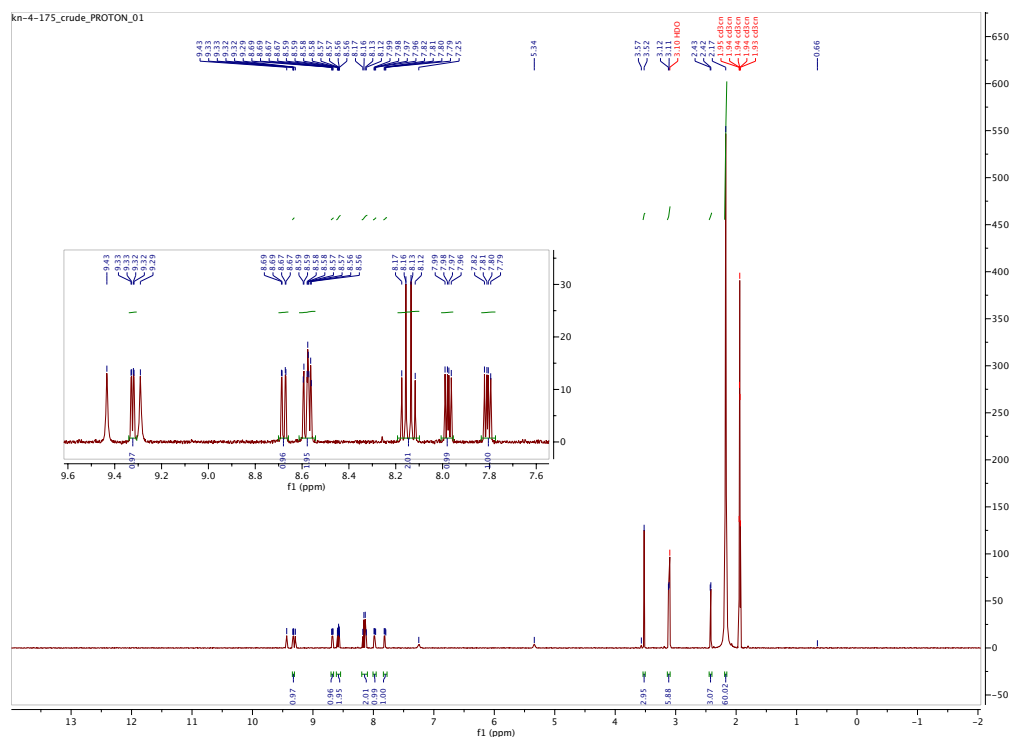


Figure S5.12: ^1H NMR spectrum of 5b in $\text{MeCN-}d_3$

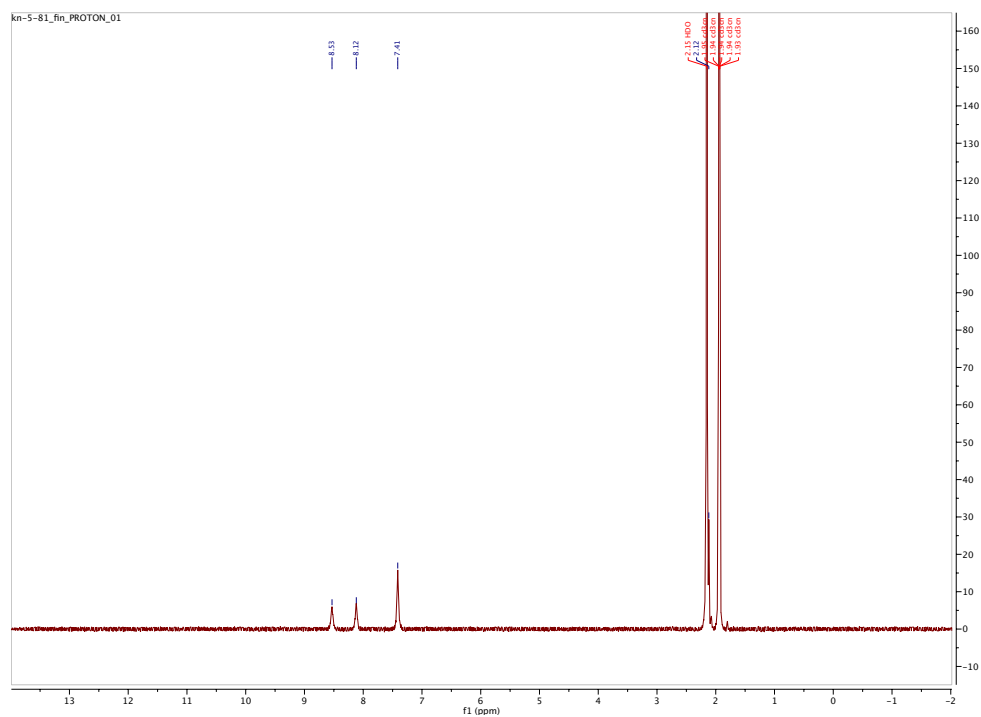
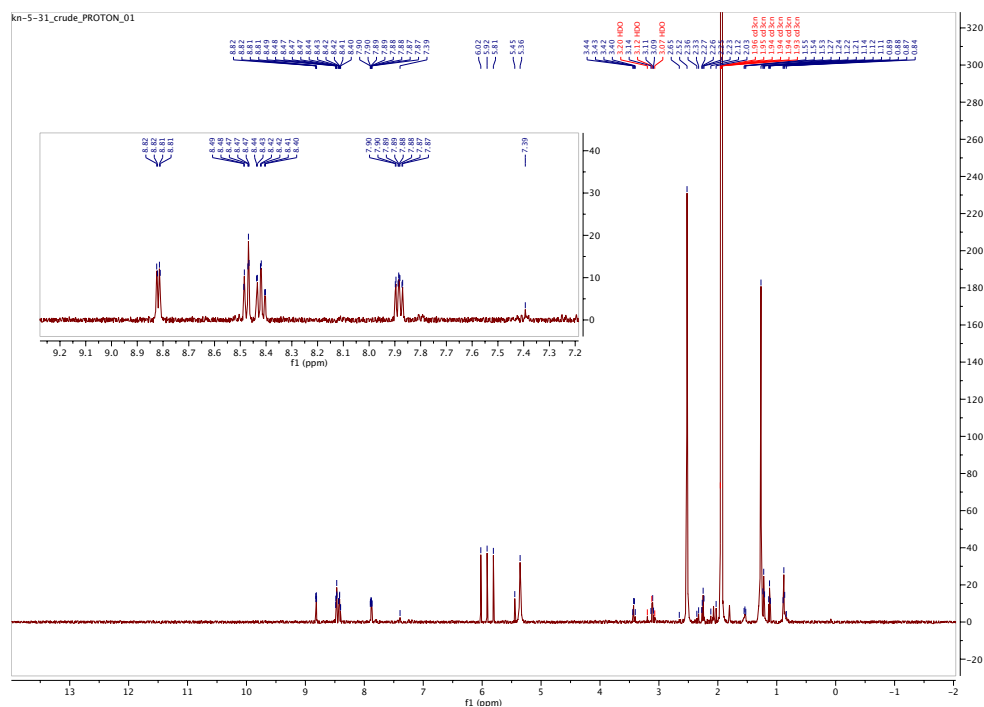


Figure S5.13: ^1H NMR spectrum of 4 in $\text{MeCN-}d_3$.



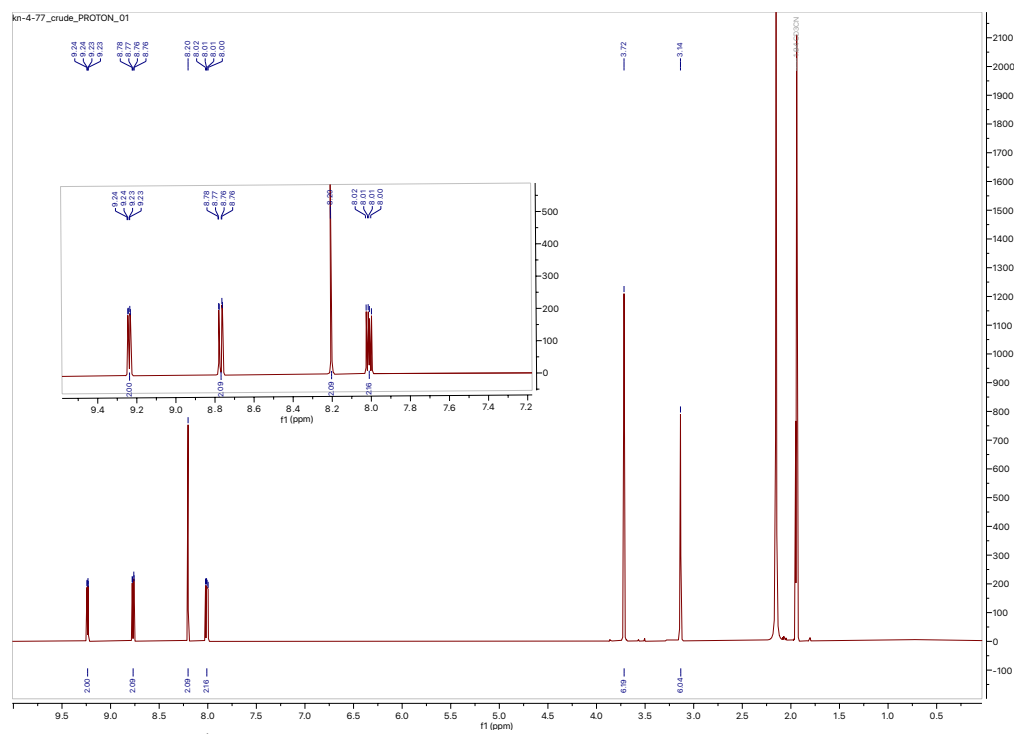


Figure S5.16: ^1H NMR spectrum of **3b** in $\text{MeCN-}d_3$.

5.7.2 Crystal Structures

Table S5.3: Crystal Data and structure refinement for **3**.

Identification code	kn-5-7
Empirical formula	C ₁₈ H _{20.3} B ₂ F ₈ FeN ₆ O _{0.15}
Formula weight	552.57
Temperature/K	99.98(13)
Crystal system	triclinic
Space group	P-1
a/Å	10.7445(5)
b/Å	10.9816(6)
c/Å	12.1939(6)
α/°	87.725(5)
β/°	66.160(5)
γ/°	63.679(5)
Volume/Å ³	1162.37(12)
Z	2
ρ _{calc} /cm ³	1.579
μ/mm ⁻¹	5.985
F(000)	559.0
Crystal size/mm ³	0.307 × 0.182 × 0.092
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.044 to 154.188
Index ranges	-13 ≤ h ≤ 12, -13 ≤ k ≤ 13, -15 ≤ l ≤ 9
Reflections collected	13382
Independent reflections	4552 [R _{int} = 0.0417, R _{sigma} = 0.0423]
Data/restraints/parameters	4552/0/343
Goodness-of-fit on F ²	1.060
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0327, wR ₂ = 0.0821
Final R indexes [all data]	R ₁ = 0.0361, wR ₂ = 0.0845
Largest diff. peak/hole / e Å ⁻³	0.27/-0.40

Table S5.4: Bond lengths for **3** will be made available upon request.

Table S5.5: Bond angles for **3** will be made available upon request.

Table S5.6: Crystal data and structure refinement for **5b**.

Identification code	kn-4-102F
Empirical formula	C ₂₀ H ₂₆ B ₂ F ₈ FeN ₈ O
Formula weight	623.96
Temperature/K	100.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	9.5989(3)
b/Å	11.2659(3)
c/Å	12.6780(3)
α/°	93.176(2)
β/°	104.602(2)
γ/°	95.470(2)
Volume/Å ³	1316.18(6)
Z	2
ρ _{calc} /cm ³	1.574
μ/mm ⁻¹	5.405
F(000)	636.0
Crystal size/mm ³	0.207 × 0.081 × 0.046
Radiation	Cu Kα (λ = 1.54184)
2θ range for data collection/°	7.23 to 154.94
Index ranges	-12 ≤ h ≤ 12, -14 ≤ k ≤ 13, -16 ≤ l ≤ 14
Reflections collected	16153
Independent reflections	5298 [R _{int} = 0.0372, R _{sigma} = 0.0389]
Data/restraints/parameters	5298/24/443
Goodness-of-fit on F ²	1.051
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0549, wR ₂ = 0.1512
Final R indexes [all data]	R ₁ = 0.0600, wR ₂ = 0.1550
Largest diff. peak/hole / e Å ⁻³	0.61/-0.42

Table S5.7: Bond lengths for **5b** will be made available upon request.

Table S5.8: Bond angles for **5b** will be made available upon request.

5.7.3 NBO Calculations and NRS of **5** and similar species

NBO calculations of **1** suggest a similar bonding behavior as was described for **5** in the main text. The sd² hybrid orbitals of the metal center bind with three carbene moieties. A last carbene is left dangling. This dangling carbene acts as a donor to the Fe-C σ* bond *trans* to it and is calculated to have a large resonance stabilization energy. This lone pair does exhibit a similar compensatory donor acceptor interaction, with the carbene bonds orthogonal to it. These are however lower compared with those of **5**.

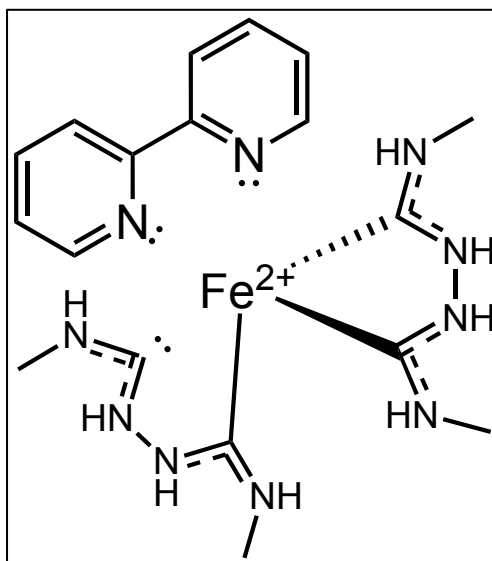


Figure S5.17: Natural resonance structure of the octahedral coordination environment of **1**.

Table S5.9: Second order perturbation theory analysis from NBO calculations of **1**.

Order	NBO	Donor Group (L)	NBO	Acceptor Group (NL)	E2(kcal/mol)	E(NL)-E(L)	F(L,NL)
1	38.	LP (1) C 20	117.	BD* (1)Fe 1- C 39	175.82	0.87	0.349
2	39.	LP (1) N 21	111.	LV (1) C 20	169.55	0.16	0.148
3	44.	LP (1) N 41	114.	LV (1) C 39	169.34	0.16	0.148
4	43.	LP (1) N 40	113.	LV (1) C 38	169.13	0.16	0.148
5	40.	LP (1) N 23	112.	LV (1) C 22	168.99	0.16	0.147
6	41.	LP (1) N 24	112.	LV (1) C 22	103.02	0.2	0.129
7	46.	LP (1) N 53	113.	LV (1) C 38	102.91	0.2	0.129
8	45.	LP (1) N 52	114.	LV (1) C 39	102.4	0.21	0.13
9	42.	LP (1) N 25	111.	LV (1) C 20	101.93	0.21	0.129
10	36.	LP (1) N 18	115.	BD* (1)Fe 1- C 22	67.6	0.96	0.228
11	37.	LP (1) N 19	116.	BD* (1)Fe 1- C 38	66.43	1.01	0.231
19	38.	LP (1) C 20	116.	BD* (1)Fe 1- C 38	40.73	0.86	0.167
27	38.	LP (1) C 20	115.	BD* (1)Fe 1- C 22	32.7	0.81	0.146

NBO calculations were performed on $\text{Fe}(\text{phen})_3^{2+}$ as a structural comparison with the heteroleptic systems discussed in this section. All the bonding in $\text{Fe}(\text{phen})_3^{2+}$ appears to be donor acceptor in nature. NRT calculations will be required to derive more understanding from this, as it is likely that the symmetry of the system makes distinguishing between resonance contributors difficult.

Table S5.10: Second order perturbation theory analysis from NBO calculations of Fe(phen)₃²⁺.

Order	NBO	Donor Group (L)	NBO	Acceptor Group (NL)	E2(kcal/mol)	E(NL)-E(L)	F(L,NL)
1	50.	LP (1) N 57	138.	LV (3)Fe 1	48.64	1.24	0.22
2	54.	LP (1) N 61	138.	LV (3)Fe 1	48.64	1.24	0.22
3	53.	LP (1) N 60	138.	LV (3)Fe 1	48.63	1.24	0.22
4	49.	LP (1) N 56	138.	LV (3)Fe 1	48.63	1.24	0.22
5	52.	LP (1) N 59	138.	LV (3)Fe 1	48.63	1.24	0.22
6	51.	LP (1) N 58	138.	LV (3)Fe 1	48.63	1.24	0.22
7	53.	LP (1) N 60	137.	LV (2)Fe 1	44.1	0.33	0.108
8	49.	LP (1) N 56	137.	LV (2)Fe 1	44.01	0.33	0.108
15	51.	LP (1) N 58	136.	LV (1)Fe 1	36.05	0.33	0.097
16	50.	LP (1) N 57	136.	LV (1)Fe 1	35.56	0.33	0.097
17	52.	LP (1) N 59	136.	LV (1)Fe 1	30.74	0.33	0.09
18	54.	LP (1) N 61	136.	LV (1)Fe 1	30.17	0.33	0.089
48	54.	LP (1) N 61	137.	LV (2)Fe 1	14.16	0.33	0.061
49	52.	LP (1) N 59	137.	LV (2)Fe 1	13.57	0.33	0.06

Even so, comparing the bonding between Fe(phen)₃²⁺ and **1** illustrates some important concepts about heteroleptics. First, the bonding is polarized. This is particularly important for Fe(II) carbene systems, which leverages the increased covalency of the Fe-C bond. This has important implications for stability, consider the resonance structure of **1** in which the entire bipyridine ligand is not bound. Finding ways to equalize and leverage the asymmetries in this bonding environment will be key to successful implementation of future design strategies.

5.7.4 Scripts for NBO Parsing

A python script utilized for the parsing of NBO calculations is included in the following sections. It includes functions for the extraction and ordering of SOPT data as well as extraction of the occupancy and hybridization information of the NBOs themselves.

Block 1: This section imports required methods and sets a filename. It then defines a function with will be utilized to open the file, search line by line for some pre-set piece of information.

```
import numpy as np
import pandas as pd
import re

filename = 'mono-carbene-Ph_energy.log'

def counter(filename):
    with open(filename, 'r') as f:
        counter = 0
        for line in f:
            counter += 1
        return counter
```

In [8]:

280

```

        searchOBJ3 = re.search(match_dict[2],line)
        PreList3 = [searchOBJ3.group()]
        d2.append(PreList3)
        #some may not match RE therefore dont show up in data frame and therefore shift data. confirm the discrepancy at # position 90 on the output
    else:
        pass
    except:
        pass

df = pd.DataFrame(d)
df2 = pd.DataFrame(d2)
#print(df2.head(50))
index = list(range(0,len(df[4])))
index2 = list(range(0,len(df2)))

#print(index)
#print(index2)
for i in index:
    if str(df[4][i]) == 'None':
        try:
            filler = str(d2[index2[0]] + d2[index2[1]])
        except:
            break
        #print(filler)
        df[4][i] = str(df[4][i])
        df[4][i] = filler
        del index2[0:2]
    else:
        pass
return df

```

The following regular expression is equivalent to the general format used in describing NBOs

which is in parenthesis:

```

‘\s+(\d+\W)\s+\W(\d+\W\d+)\W\s+(\w+\s+\W\s+\d+\W)(\w+\s+\d+|\s+\w+\s+\d+)\s+(\w+\W\d+
\W\d+\W+|\w+\W\s+\d+\W\d+\W+\w+\s+\d+\W\d+\W\s+\d+\W\d+\W+\w+\s+\d+\W\d+\W\s+\
d+\W\d+\W+|\w+\W\s+\d+\W\d+\W+\w+\s+\d+\W\d+\W\s+\d+\W\d+\W+\w+\s+\d+\W\d+\W\d
+\W\d+\W+|\w+\W\s+\d+\W\d+\W+\w+\s+\d+\W\d+\W\d+\W+|\w+\W\s+\d+\W\d+\W+\
w+\s+\d+\W\d+\W\s+\d+\W\d+\W+\w+\d+\W\d+\W\s+\d+\W\d+\W+|\w+\W\s+\d+\W\d+\W+\
w+\d+\W\d+\W\s+\d+\W\d+\W+\w+\s+\d+\W\d+\W\s+\d+\W\d+\W+)\s+’ (167. (0.69430) LV (
1) C 48      s( 0.02%)p99.99( 99.86%)d 8.38( 0.13%)

```

The program searches line by line, and when it finds information that conforms to the set of

regular expressions, it takes that line, breaks up the information and creates a data frame. A data

frame is a python/PANDAS equivalent of a spreadsheet. This can be saved as an excel spreadsheet.

Script 2: This script was utilized to parse SOPT output using pre-programmed regular expressions.

Block 1: These blocks of code allow the program to be run from any folder if the pathname to the data is provided. The directory is changed with a standard shell command. A new path is defined and allows the program to move from the directory it is currently in to another.

In [2]:

```
cd /Users/karl Nielsen/Desktop/FevsRuNBO  
  
/Users/karl Nielsen/Desktop/FevsRuNBO
```

In [3]:

```
path, dirs, files = next(os.walk("/Users/karl Nielsen/Desktop/FevsRuNBO"))  
file_count = len(files)  
starting_time_seconds = 25  
delta_t = 30
```

In [4]:

```
filename = 'Fe_energy.txt'
```

Block 2: Similar import methods were used to open the data and parse the file line by line. This function searches for keywords that indicate the start of the SOPT data and collects the information that conforms with the regular expression. It then creates a data frame which returns all the extracted data.

In [5]:

```
def second_order_parser(filename):
    start = 0
    end = 1
    d = []
    d2 = []
    with open(filename, 'r') as f:
        for line in f:
            if 'Donor (L) NBO' and 'Acceptor (NL) NBO' and 'kcal/mol' in line:
                start = 1
            if 'NATURAL BOND ORBITALS (Summary):' in line:
                end = 0
            if start == 1:
                try:
                    for line in f:
                        searchOBJ = re.search(r'\s+(\d+\W)\s+(\w+\s+|\w+\W)(\W\s+\d+\W\s+\w+\s+\d+\W\s+\w+\s+\d+|\W\s+\d+\W\s+\w+\s+\d+\W\s+\w+\s+\d+|\W\s+\d+\W\s+\w+\s+\d+\W\s+\w+\s+\d+|\W\s+\d+\W\s+\w+\s+\d+\W\s+\w+\s+\d+|\W\s+\d+\W\s+\w+\s+\d+\W\s+\w+\s+\d+|\W\s+\d+\W\s+\w+\s+\d+\W\s+\w+\s+\d+|\W\s+\d+\W\s+\w+\s+\d+\W\s+\w+\s+\d+|\W\s+\d+\W\s+\w+\s+\d+\W\s+\w+\s+\d+|\W\s+\d+\W\s+\w+\s+\d+\W\s+\w+\s+\d+|\W\s+\d+\W\s+\w+\s+\d+\W\s+\w+\s+\d+)\s+(\d+\W)\s+(\w+\s+|\w+\W)(\W\s+\d+\W\s+\w+\s+\d+\W\s+\w+\s+\d+|\W\s+\d+\W\s+\w+\s+\d+\W\s+\w+\s+\d+|\W\s+\d+\W\s+\w+\s+\d+\W\s+\w+\s+\d+|\W\s+\d+\W\s+\w+\s+\d+\W\s+\w+\s+\d+|\W\s+\d+\W\s+\w+\s+\d+\W\s+\w+\s+\d+|\W\s+\d+\W\s+\w+\s+\d+\W\s+\w+\s+\d+|\W\s+\d+\W\s+\w+\s+\d+\W\s+\w+\s+\d+)\s+(\d+\W\d+)\s+(\d+\W\d+)\s+(\d+\W\d+)',line)
                        PreList= [searchOBJ.group(1),searchOBJ.group(2),searchOBJ.group(3),searchOBJ.group(4),searchOBJ.group(5),searchOBJ.group(6),searchOBJ.group(7),searchOBJ.group(8),searchOBJ.group(9)]
                        OutArray= pd.Series(PreList).values.reshape(1,9)
                        d.append(PreList)
                except:
                    pass
            if end == 0:
                start = 0

    return pd.DataFrame(d,columns = 'Comp1 Lang1 group1 Comp2 Lang2 group2 E2(kcal/mol) E(NL)-E(L) F(L,NL)'.split(' '))
```

Block 3: This section reorganizes the data returned from the function defined above and converts the numerical values, which are received as string data, are converted to numerical form. Then the data frame is reorganized by the magnitude of the energy of the DA interaction. It creates a new filename and saves the data as a new spreadsheet. This file is saved in the folder which the NBO log file is kept.

In [6]:

```
a = second_order_parser(filename)

#organizes DF. converts str into numerical floats
a['E2(kcal/mol)'] = a['E2(kcal/mol)'].astype(float)
a['E(NL)-E(L)'] = a['E(NL)-E(L)'].astype(float)
a['F(L,NL)'] = a['F(L,NL)'].astype(float)

a.sort_values('E2(kcal/mol)', ascending=False, inplace=True)

newfile = filename.split('.')[0]+'_SOPT_analysis.xlsx'
a.to_excel(newfile)
```

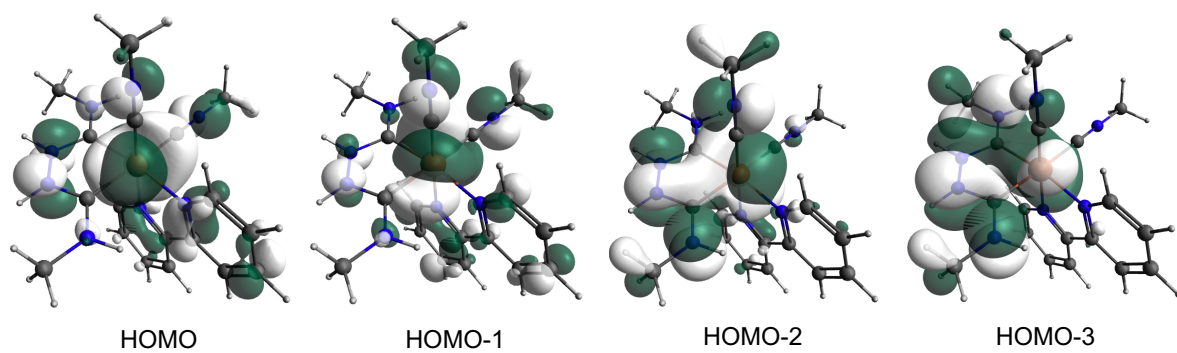


Figure S5.18: Four highest occupied molecular orbitals. The latter two exhibit bonding interactions with the carbene ligand.

**6) CHAPTER 6: MEASUREMENT OF THE REORGANIZATION
ENERGY FOR GROUND STATE RECOVERY IN A MODEL
Cu(I) PHOTOSENSITIZER**

6.1 INTRODUCTION

Much of this dissertation describes the orthogonal (x- and y-axis) strategies to improve the light harvesting capabilities in first row transition metal complexes, which were highlighted in detail in the introduction; in particular, the need to achieve charge transfer (CT) lifetimes on the order of 1 ns or greater. These strategies and their method of implementation are highly domain dependent. For example, implementing the afore mentioned y-axis strategy with isocyanide ligands in d^6 complexes must balance the charge density of the metal center and its donor ability, which are generally mutually exclusive. This likely limits the use of isocyanides for more charge dense metals. This domain dependence is exacerbated when different electronic configurations are considered. This is best illustrated by Cu(I) systems which exhibit a d^{10} electron configuration and thus do not have ligand field states to be perturbed with strong field ligands. The study of synthetic modifications Cu(I) polypyridyls has revolved around the use of kinetic effects (x-axis strategy) to control the deactivation of the MLCT manifold. This has been demonstrated to work wonderfully, indeed the $^3\text{MLCT}$ lifetime of $[\text{Cu}(\text{phen})_2^+]$ gets longer by six orders of magnitude when substituted in the imine α -position with *t*-butyl groups.^{1,2}

Recently the continuity between the size of these steric substitutions and the magnitude of their perturbations on experimental observables has been framed in the context of the ‘entatic state principle’, whereby steric groups limit the degree to which the complex loses energy to a pseudo-Jahn Teller distortion expected to occur upon the formal oxidation of Cu(I) to Cu(II) in the MLCT.^{3,4} This entatic state principle acts as a concerted strategy, whereby x- axis perturbations translate into and y- axis displacements, i.e. restricting nuclear degrees of freedom that drive the pJT increases the energy gap between the $^3\text{MLCT}$ and GS. The resulting improvements in the $^3\text{MLCT}$ lifetimes has been theorized to occur in accordance with the energy

gap law (EGL) which describes the reduced rate in non-radiative decay along with the increase in energy gap between $^3\text{MLCT}$ and the ground state, which is a result of the conversion occurring in the Marcus inverted regime.

This chapter describes the measurement of the reorganization energy of a model Cu(I) polypyridyl system to test the hypothesis that the ground state recovery process is within the Marcus inverted regime and thus described by the EGL. Because of this closed shell electronic configuration along with the large symmetry changes in the excited state, simplified term symbols are used. For example, S_0 is used to describe the ^1A ground state and T_2 describes the second triplet state. It can be inferred that the character of the states is MLCT. This formalism will be adopted here.

6.1.1 Properties of Cu(I) MLCT excited states

The unique excited state properties of Cu(I) polypyridyls are coaxed by α -substitutions on the polypyridyl ligand, a phenomenon first observed by McMillin and coworkers in 1980 and following reports.⁵⁻⁷ These papers set the trajectory of the field in a significant way, highlighting the key observations that included solvent effects and the unique temperature profile of the emission. The first observation of emission in DCM solution of $[\text{Cu}(\text{dmp})_2]^+$ was characterized as phosphorescence of a triplet charge-transfer state (T_1) due to its long lifetime. Figure 6.1a depicts the structure of this complex.⁸ These first few reports also proposed that the substitutions in the α -position limit the opening of a second or third coordination site which would facilitate formation of a solvated excited state in donor solvents like acetonitrile. This so called ‘exciplex’ model was used to explain the reduction of T_1 emission intensity in acetonitrile solution.⁷

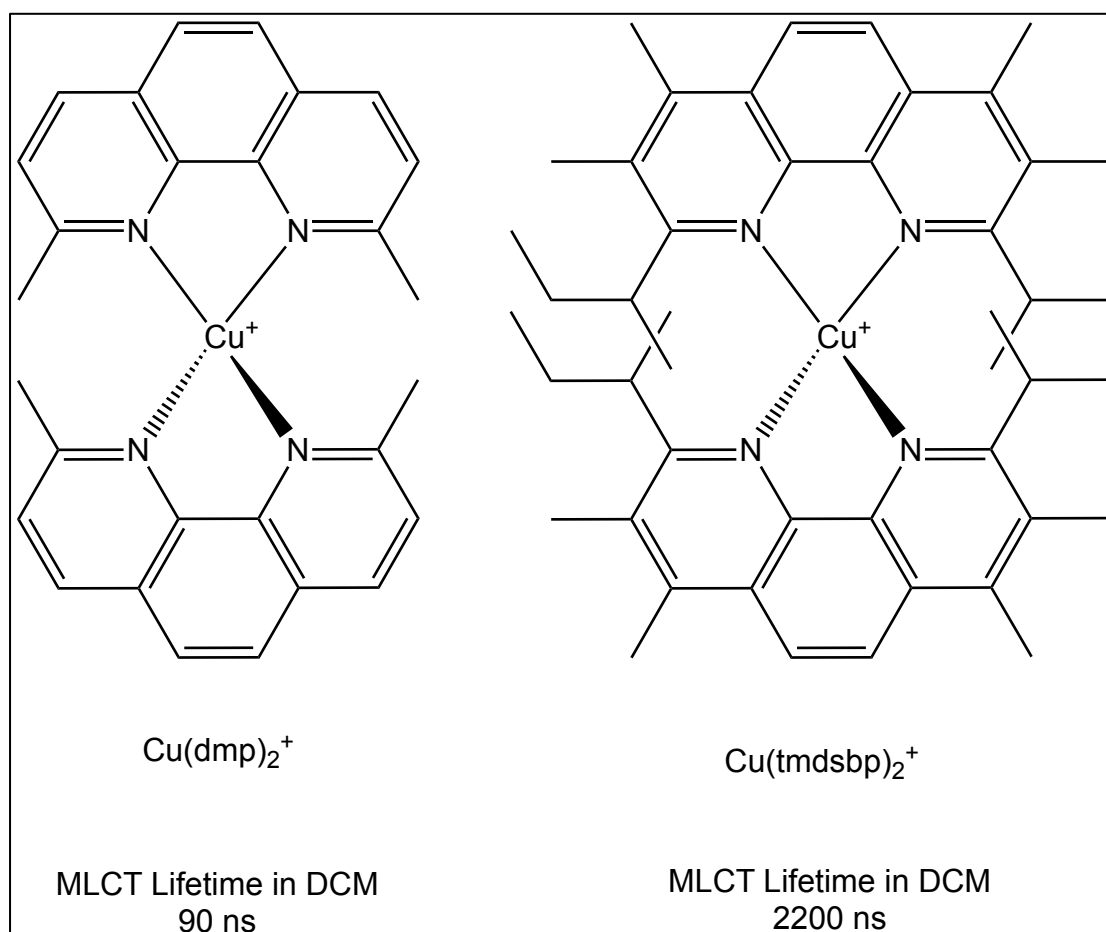


Figure 6.1: Molecular structure of two Cu(I) sensitizers in their ground state. (dmp=2,9-dimethyl-1,10-phenanthroline, tmdbp= 3,4,7,8-tetramethyl-2,9-diisobutyl-1,10-phenanthroline).

The third observation was the temperature dependence of the emission from $[\text{Cu}(\text{dmp})_2]^+$ and others. A decrease in quantum yield (Φ) with temperature was unexpected, as lower temperatures generally facilitate slower non-radiative decay (k_{nr}) and thus increase the ratio:

$$\Phi = \frac{k_r}{k_r + k_{nr}} \quad 6.1$$

Where k_r and k_{nr} are the radiative and non-radiative lifetimes of the system.^{9,10} This strange temperature dependence was consistent with what is now called thermally activated delayed fluorescence (TADF) in which a suitably small energy gap between S_1 and T_1 allows for fast back intersystem crossing (bISC).¹¹⁻¹³ The drop in quantum yield is a result of reduced k_r due to the reduced population of S_1 at lower temperatures. These phenomena, α -substitutions, exciplex

formation, and TADF are all characteristic to understanding the longer timescale photophysical phenomena and critical to understanding the how the reorganization energy in the systems can be measured.

6.1.2 State of the Art: Steric Effects on Cu(I) Excited States:

Increasing the size of the steric group is correlated with longer lifetimes and larger quantum yields. A particularly salient example of these steric effects is exhibited by the complex $[\text{Cu}(\text{tmdsbp})_2]^+$ depicted in figure 6.1. This was first synthesized by Castellano and co-workers and has a lifetime and a quantum yield several orders of magnitude larger than $[\text{Cu}(\text{dmp})_2]^+$. For this reason it has been studied a great deal since.^{14–18} Furthermore, it is even emissive in a 50% aqueous/acetonitrile solution which has made it a candidate as a photoredox catalyst. This was attributed to its rigidity as well as its impenetrability to donor solvents, although this latter observation has become recently contentious.¹⁹ This system is also thermodynamically stable, which makes it unique for sterically encumbered polypyridyls. In contrast, consider the complex $[\text{Cu}(\text{dtbp})_2]^+$ (where dtbp = 2,9-di-*tert*-butyl-1,10-phenanthroline) which is also employs a large groups in the α -position and has a 3.2 us lifetime. This bulkiness leads to instability meaning that its synthesis must be coupled to the oxidation of Cu(0) to drive its formation.^{2,20} Because of its stellar performance and stability, $[\text{Cu}(\text{tmdsbp})_2]^+$ is our choice for studying the reorganization energy of Cu(I) polypyridyls.

6.1.3 Steric Substitutions and the Pseudo Jahn-Teller Effect

As mentioned above, the structural distortion induced by the transition from a d^{10} to d^9 metal electron configuration is due to a pseudo Jahn-Teller effect occurring on the S_1 surface. Tahara and coworkers have presented the most comprehensive and convincing research into why

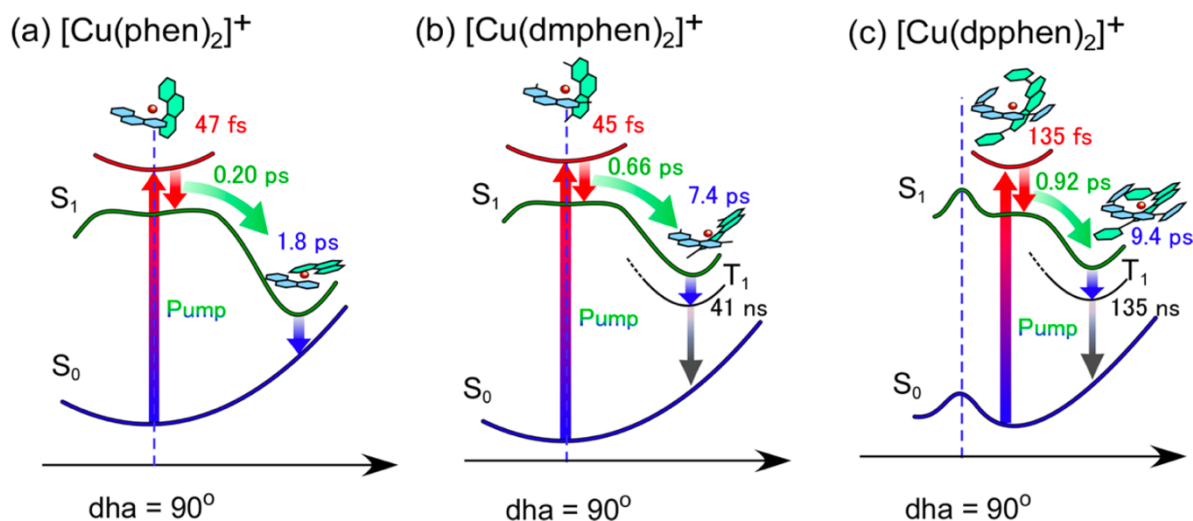


Figure 6.2: Illustration of the potential energy surfaces and their correlation to molecular structure and associated time constants. (phen=1,10-phenanthroline, dmphen=2,9-dimethyl-1,10-phenanthroline, dpphen= 2,9-diphenyl-1,10-phenanthroline). Taken from ref 3.

steric modifications improve the dynamics.^{1,21,22} One study performed, utilized femtosecond fluorescence up conversion spectroscopy to study three compounds, with different steric properties ($[\text{Cu}(\text{phen})_2]^+$, $[\text{Cu}(\text{dmp})_2]^+$, and $[\text{Cu}(\text{dpp})_2]^+$) highlighting how the specific structural changes perturb the ultrafast processes. Figure 6.2 summarizes this data and is reproduced from reference 3. This figure clearly connects surface curvature, minima/maxima, and the respective lifetimes to the magnitude of the structural distortion imparted by synthetic modification.

Notable are the differences in rate at which structural distortions occur as a function of steric substitution. In $[\text{Cu}(\text{dmp})_2]^+$ the lowest energy singlet forms within 45 fs. From which the pJT distortion occurs with a time constant of 660 fs. This is exhibited by a bathochromic shift in the emission manifold by approximately 100 nm. ISC occurs in 7.4 ps into the flattened T_1 state which lasts for 90 ns. Quantitative analysis between direct S_1 and S_2 excitation noted approximately 30% of excited S_2 population underwent ISC directly to T_1 upon which the pJT distortion occur. It is from this state that the longer timescale dynamics occur out of including ground state recovery an bISC.

This nuclear coordinate associated with deactivation was experimentally confirmed to be that of the flattening distortion by the measurement of coherent nuclear vibrations. These coherent vibrations at 125 cm^{-1} and 290 cm^{-1} were assigned using TD-DFT and determined to be related to molecular breathing and molecular “twisting” motions respectively. The latter mode in particular, is consistent with the structural mapping between Cu(I)/Cu(II) oxidation states observed crystallographically. The modes were found to have a dephasing time on the same order as the pJT distortion measured separately and taken as evidence that these vibrations were the dominant contributors to the deactivation of the Frank-Condon geometry.

This trajectory is traversed by the GSR process in reverse and thus the reorganization energy measured for GSR corresponds to the size of the distortion in the excited state. Although, kinetic measurements capture the whole reorganization energy which means that it will include other DOF that are coupled to the decay process.

6.1.4 *Thermally Activated Delay Fluorescence (TADF)*

McMillin and coworkers noted the process of delayed fluorescence and proposed models to describe the participation of the higher energy state.^{5,23} Cu(I) is unique compared to other TADF systems in that the relatively weak exchange interaction between S/T CT states, given by the low molecular weight of copper compared to its second and third row congeners, makes the energy gap ΔE_{ST} small. Furthermore, it has fast rates of ISC and bISC because of the heavy atom effect of the metal ion compared to lighter elements, making it more competitive relative to other decay pathways. Because of ‘goldilocks’ scenario, Cu(I) ions have been used ideal for high internal efficiency luminescent devices.²⁴ Castellano and co-workers described the TADF properties of $[\text{Cu}(\text{tmdsdp})_2]^+$ in the report of its synthesis. By measuring the emission at 650 nm as a function of temperature, they were able to obtain a measure of the energy gap between

singlet and triplet, that is traversed during TADF as well as observed rates for the singlet and triplet species respectively.^{14,25}

$$k_{obs} = \frac{3k_{obs,t} + k_{obs,s}e^{-\frac{\Delta E_{ST}}{k_b T}}}{3 + e^{-\frac{\Delta E_{ST}}{k_b T}}} \quad 6.2$$

Multidimensional fitting the observed rates to equation 6.2 as a function of temperature gave, $\Delta E_{ST} = 1150 \text{ cm}^{-1}$, $k_{obs,t} = 3.89 \times 10^5 \text{ s}^{-1}$, and $k_{obs,s} = 7.73 \times 10^7 \text{ s}^{-1}$. Measurement of the energy gap affords a description of the equilibrium between S and T the populations of which are described by a simple Boltzmann model.²⁶

$$\frac{[S]}{[T]} = \frac{k_{bISC}}{k_{ISC}} = \frac{1}{3} e^{-\frac{\Delta E_{ST}}{k_b T}} \quad 6.3$$

Here the steady state is maintained by the ratios of the bISC to ISC. (A way to think about these dynamics is, that Tahara's work (i.e. examination of early time processes) ends when this equilibrium distribution is established). This steady state is maintained according to this ratio for the duration of the T_1 excited state because k_{ISC} and k_{bISC} are much faster than ground state recovery process. This resulted in Castellano and coworkers fitting the long time-scale dynamics to single exponentials and showed that this is viable over a significant temperature range in ethanolic solution. This single exponential fit is not quite accurate in that it relies on the relative magnitudes of k_{isc} and k_{bisc} to be functionally independent of temperature. While we do not utilize it here, a more advanced model that is non-boltzmann in its formulation is discussed in the appendix of this chapter that could be utilized in conjunction with a global optimization procedure.

6.1.5 Exciplex formation:

McMillin proposed that the formation of an exciplex occurs upon excited state flattening, which quenches the emission of the flattened MLCT state.⁷ This is reasonable as pentacoordinate

Cu(II) complexes are well known, even when formed transiently, by oxidation for example. Chen et. al. attempted to confirm this model in the MLCT excited state of $[\text{Cu}(\text{dmp})_2^+]$ utilizing x-ray absorption near edge spectroscopy (XANES) experiment with a 5 ps temporal resolution.²⁷ The exciplex model was utilized to explain the broadening of a $1s \rightarrow 4p_z$ transition due to the accepting orbital's delocalization upon ligand binding. With this assignment established, it was proposed that pentacoordination stabilized the MLCT state, in accordance with density functional theory (DFT) calculations, thus increasing its k_{nr} relative to k_{r} in accordance with the EGL and making it radiatively silent. This assignment of pentacoordination has more recently been called into question.

The application of EXAFS and XANES with improved temporal resolution, showed the similarity of the XANES pre-edge feature in both acetonitrile and dichloromethane, the latter being non-coordinating.²⁸ The broadening of the pre-edge feature, was reassigned to an oxidation shift associated with the higher oxidation state of the metal. The solvent dependence was not neglected however and were modeled with molecular dynamics (MD) simulations. These computations suggested that solvent effects on the emission properties were due in part to a solvent stabilization which was a supplementary to the dielectric stabilization of charge-separated species, activated by the structural distortion. This concept was expanded further in a second computational report, in which calculated a radial distribution function for the solvent's closest approach ($< 3 \text{ \AA}$) to the metal complex in both the ground and excited states. The three-tier solvation shell was present for all states and all solvents. A fluxional model was proposed that precluded any formal bond between the metal center and the solvent. There was a marked difference in the path of closest approach of the solvent as a function of steric bulk, which to

some degree supports rationalizations made previously, without the need for a formal pentacoordinate excited state.

Most recently, these observations were addressed by further XAS experiments coupled with modern DFT optimizations of exciplexes and triplet excited states of $[\text{Cu}(\text{dmp})_2]^+$ and $[\text{Cu}(\text{tmdsbp})_2]^+$.¹⁹ The thermodynamics of the formal exciplexes were calculated to be above those of the relaxed triplet state by 0.24 eV, in the case of the $[\text{MeCN-Cu}(\text{dmp})_2]^+$ complex. A similar destabilized state was found to exist for a $[\text{DMF-Cu}(\text{tmdsbp})_2]^+$ complex with an energy gap of 0.73 eV and the solvent induced distortion occurs along a wagging coordinate rather than a DHA flattening mode. Utilizing XAS, no difference was observed in the coordination number between $[\text{Cu}(\text{dmp})_2]^{+/+2}$ when photoexcited. However, electrochemically generated $[\text{Cu}(\text{dmp})_2^{+2}]$ did show coordination. The solvent dependence of $[\text{Cu}(\text{dmp})_2]^+$ was explained within the exciplex model by suggesting slow formation and fast deactivation of the pentacoordinate excited state. The solvent dependence of $[\text{Cu}(\text{tmdsbp})_2]^+$ (2.9 us in DCM vs. 1.5 us in acetonitrile) was deemed to be only minor and therefore neglected. Ultimately the intuition about the exciplex model in the reports by McMillin seems to be proven correct, however the assumption that such states were lower in energy seem to be mistaken.

6.1.6 Application of Marcus Theory to the Deactivation of $[\text{Cu}(\text{tmdsbp})_2]^+$ Excited States

The application of the semi-classical Marcus theory to kinetic models of non-radiative decay are well known. Chapter 2 of this report discusses a similar application to an Fe(II) carbene system of interest. However, the methods for obtaining the non-radiative rates will be different here due to the presence of the radiative component.

The non-radiative decay rates are found by the application of the measured quantum yield to the observed rate of decay (k_{obs}):

$$\Phi k_{obs} = k_r \quad 6.4$$

The yield Φ is measured in reference to the quantum yield of emission of $[\text{Ru}(\text{bpy})_3]^{2+}$ in acetonitrile solution by usual methods.⁹ The emission decay over time can be fit to a single exponential function to find the observed rate, which in turn provides k_r . In a TADF system however, the radiative rate is a function of the temperature, owing to the Boltzmann distribution between states with different radiative rate constants illustrated by equation 6.3. For a fixed energy gap between triplet and singlets the emission intensity increases at higher temperatures due to delayed fluorescence.

$$k_{obs}\Phi = 3k_p + k_f e^{-\frac{\Delta E_{st}}{k_b T}} \quad 6.5$$

Crosby and co-workers derived a similar emission model for the quantum yield of the emission in Ru(II) systems.¹⁰ The sum of the terms on the right-hand side will be called $k_{r,eff}$ as they are dependent on the temperature. Parsing the fluorescence (k_f) and phosphorescence (k_p) rate constants will be a subject of future work.

The non-radiative rate k_{nr} can be found from the difference between the observed rate and the effective radiative rate.

$$k_{nr} = k_{obs} - k_{r,eff} \quad 6.6$$

The non-radiative rates derived from this expression will be utilized for the kinetic analyses. The Arrhenius fitting for the single process of activation energy E_a and frequency factor A is found by linearization of the standard Arrhenius model.

$$\ln(k_{nr}) = \left(\frac{E_a}{k_b T} \right) + \ln(A) \quad 6.7$$

The extension into the Marcus model is straightforward but requires a pre-emptive temperature correction of k_{nr} to account for the temperature dependence of the electronic coupling contained in the preexponential term of the Marcus equation (equation 2.6).

$$\ln\left(\frac{\hbar\sqrt{4\pi k_b T}}{2\pi} k_{nr}\right) = \left(\frac{(\lambda + \Delta G)^2}{4\pi k_b T}\right) + \ln\left(\frac{|H_{RP}|^2}{\sqrt{\lambda}}\right) \quad 6.8$$

Equation 6.8 shows the reorganization energy can be calculated with *a-priori* knowledge of the driving force given by ΔG . For this value, the emission profile can be fit to the model described by Claude and Meyer.²⁹ This expression yields the zero-point energy difference E_o between two states radiatively coupled. This approximates the driving force for the process, which is assumed to be the same as the non-radiative process. The other terms are not necessary for our purposes.

$$I(v) = \sum_{v_n=0}^n \left\{ \left(\frac{E_o - v_n \hbar \omega}{E_o} \right)^3 \left(\frac{S_n^{v_n}}{v_n!} \right) * \exp\left(-4 * \ln(2) * \left(\frac{v - E_o + v_n \hbar \omega}{\Delta v_{1/2}} \right)^2\right) \right\} \quad 6.9$$

Due to the thermal averaging of two excited states, each with its own zero-point energy, fitting the emission profile at each temperature to equation 6.9 will yield a single ΔG which is a function of the temperature, radiative rate, and zero-point energy of the states involved. To obtain proper driving forces, the spectra must be deconvolved by global target analysis. If the individual spectra of the emission profile given in the matrix **F** can be approximated if a proper coefficient matrix **P**, is found which deconvolutes the total spectrum **I** into separate spectra according to the equation.³⁰

$$\mathbf{F} = \mathbf{P}\mathbf{I}' \quad 6.10$$

The coefficient matrix is derived from the temperature dependence of the emission intensity contained in the right eigenspectrum of the single value decomposition (SVD). A tutorial on this is presented in the appendix of this chapter. The eigenspectra in $\mathbf{F}$ can be fit to the model in equation 6.9 and the E_o for each state can be found, providing unique driving forces. This will allow for finding unique reorganization energies as well.

6.2 EXPERIMENTAL

The synthesis of $\text{Cu}(\text{tmdsbp})_2\text{PF}_6$ were performed by Dr. C.E. Hauke of the Castellano Group using published literature procedures. Samples were prepared in an argon filled glovebox, where the absorption of the sample was kept between 0.1 and 0.2 OD. The temperature of all time resolved emission experiments were modulated with a Peltier cooler from Quantum Northwest. The temperatures of all steady state measurements were modulated by a cryostat from Oxford Instruments with a Lakeshore temperature controller. The laser and steady state emission setup were described previously.^{31,32} Samples were held for 15 minutes at temperature before spectral acquisition.

Lifetime measurements were fit using single exponentials using a fitting algorithm written in the MATLAB programming language. A similar program was used for the measurements of temperature dependent emission intensity by fitting a smoothed spline function and integrating. Quantum yields at room temperature were calculated relative to $[\text{Ru}(\text{bpy})_3]^{2+}$. Slit widths were maintained for each relative QY measurement, thus, to maximize the emission from the Cu(I) signal, the $[\text{Ru}(\text{bpy})_3]^{2+}$ concentration must be correspondingly low to not over saturate the detector. Then QYs at temperature with the following equation described previously²⁹:

$$\Phi_T = \Phi_{295} \frac{I_T}{I_{295}} \quad 6.11$$

Where Φ_T is the quantum yield at temperature T and I_T is the integrated intensity at T. Quantum emission parameters were obtained using the method of Claude et. al. utilizing the CocoaFit program.²⁹ Attempts were made to replicate this program in MATLAB using unconstrained non-linear fitting, however fitting errors were much larger and therefore were not used.

Radiative rate constants at each wavelength were derived by least squares fitting of the normalized emission spectrum to the radiative rate calculated from the total quantum yield and observed rate constant at 640 nm as described above. The non-radiative rates were then calculated at each observed wavelength according to equation 6.6.

A global analysis program is reported in the appendix to calculate the eigenspectra of the steady-state emission profile in accordance with equation 6.10. This can be extended to the time-dependent data as a function of wavelength and will be discussed further in future works.

6.3 RESULTS AND DISCUSSION

6.3.1 Studies of $[Cu(tmdsbp)_2]^+$ in Dichloromethane

Time-resolved emission spectroscopy provided lifetimes at discrete wavelengths, 580, 640, and 700 nm (17,240, 15,625, and 14,286 cm^{-1} respectively). The observed rates were derived from single exponential fits of the emission decay. The fit to single exponentials is consistent with the fast equilibrium model of TADF^{14,33}. The decays and respective fits are in the supplemental information for this chapter. While generally within error, there are distinct differences between the observed rates at 580 nm and the others particularly at low temperature,

suggesting differences in k_r or k_{nr} at this wavelength. The observed rates at 640 nm is given in table 6.1, the other wavelengths are reported in table S6.6 in the appendix of this chapter.

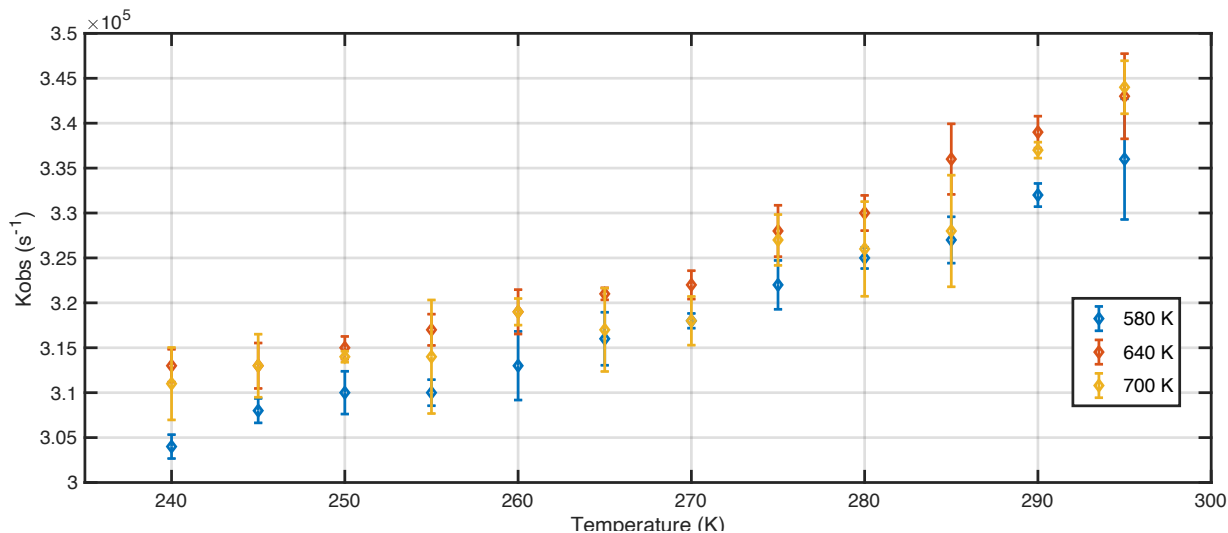


Figure 6.3: Observed rate constants from single-exponential fits of the data as a function of temperature. The slightly curved profile is consistent with literature observations.

Steady state emission spectra were collected over the same temperature range as the time-resolved data. The raw data was fit to a skewed gaussian function, with low error. The high and low temperature steady state spectral fits are included in the appendix to this chapter. There is some disagreement with the model particularly at blue wavelengths, however the skewed model allowed for good extrapolation into wavelength region past 800 nm which is unmeasured due to detector sensitivity. This error in the fitting is systematic and thus does not likely contribute to issues with quantum yield calculation. The skewed- gaussian fits were integrated and the areas were utilized in a relative quantum yield calculation against $[\text{Ru}(\text{bpy})_3]^{2+}$ in aerated acetonitrile. The quantum yields as a function of temperature reported in table 6.1. The drop in quantum yield is a sign of thermally activated delayed fluorescence. The quantum yield would usually increase in $[\text{Ru}(\text{bpy})_3]^{2+}$ for example because of the reduction in the non-radiative rate for the ground state recovery process. With a smaller singlet contribution at lower temperature, the emission intensity drops and thus decreases the quantum yield. The reduction in the effective radiative rate

is shown in table 6.1 and represents a drop of almost exactly 33%. Compare this to the drop in the quantum yield of only 22%. The larger drop-in radiative rate is consistent with a larger ratio of k_f/k_p than in the corresponding ratio of non-radiative rates, assuming a similar change in population ratios.

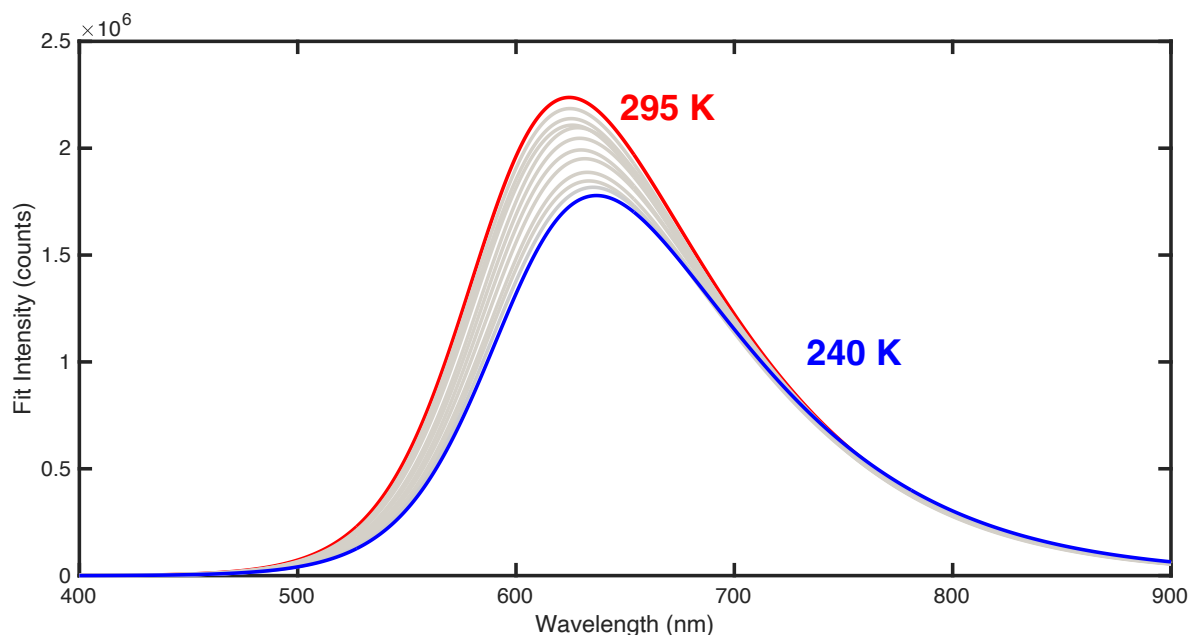


Figure 6.4: Variable temperature steady state emission spectra of $[\text{Cu}(\text{tmdsbp})_2]^+$ in DCM solution. The corrected emission intensities were fit skewed gaussian functions. Data past 800 nm were extrapolated from the fit.

Table 6.1: Quantum yields (Φ), observed decay rates (k_{obs}^{640}), effective radiative rates ($k_{\text{r,eff}}^{640}$), and non-radiative rates ($k_{\text{nr,eff}}^{640}$) at the 640 nm probe region.

Temperature (K)	Φ	$k_{\text{obs}}^{640} (\times 10^5 \text{ s}^{-1})$	$k_{\text{r,eff}}^{640} (\times 10^4 \text{ s}^{-1})$	$k_{\text{nr,eff}}^{640} (\times 10^5 \text{ s}^{-1})$
295	7.1 (0.1)	3.43	2.44	3.18
290	6.9 (0.1)	3.39	2.34	3.15
285	6.8 (0.1)	3.36	2.28	3.12
280	6.7 (0.1)	3.30	2.21	3.08
275	6.6 (0.1)	3.28	2.16	3.06
270	6.4 (0.1)	3.22	2.06	3.01
265	6.4 (0.1)	3.21	2.05	3.00
260	6.2 (0.1)	3.19	1.98	2.99
255	6.0 (0.1)	3.17	1.90	2.98
250	5.9 (0.2)	3.15	1.86	2.96
245	5.9 (0.3)	3.13	1.85	2.94

Table 6.1 (cont'd)

240	5.8 (0.2)	3.13	1.82	2.94
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The temperature dependence of $k_{nr,eff}$ depends both upon the temperature dependence of the individual non-radiative rate constants $k_{nr,t}$ and $k_{nr,s}$ but also the population ratios between them. This could be possible to decouple these non-radiative rates, however this is not done here, and the effective non-radiative rates were used for the analysis.

6.3.2 Derivation of Emission Eigenspectra

A global target analysis was performed on the steady state spectra as a function of temperature to yield the emission spectra of both the singlet and triplet states. This was performed in a homebuilt MATLAB program for the simultaneous analysis of steady-state and time-resolved emission data. Only the module for the steady-state emission spectra was utilized here. Decomposition of the data by the SVD was performed and simulated spectra were generated in accordance with the methods described in Hofrichter in temperature rather than time.³⁰ The temperature dependence of the eigenspectra were found to be linear functions in temperature based on the right eigenvectors and the corresponding amplitude matrix was utilized to generate the eigenspectra in a manner similar to equation 6.10. These spectra are shown in the figure 6.5 where the fluorescence spectrum is scaled by 50x upon normalization of its intensity. These were fit to the quantum emission model using CocoaFit, by equation 6.9. The triplet spectrum gave $E_0 = 16,200$ (18) cm^{-1} . The full spectrum without deconvolution was found to have $E_0 = 16,440$ (8) cm^{-1} which represents a thermal convolution of the two states. The two states were measured previously to be 1100 cm^{-1} apart, however with population weighting the 240 cm^{-1} difference in E_0 is reasonable.

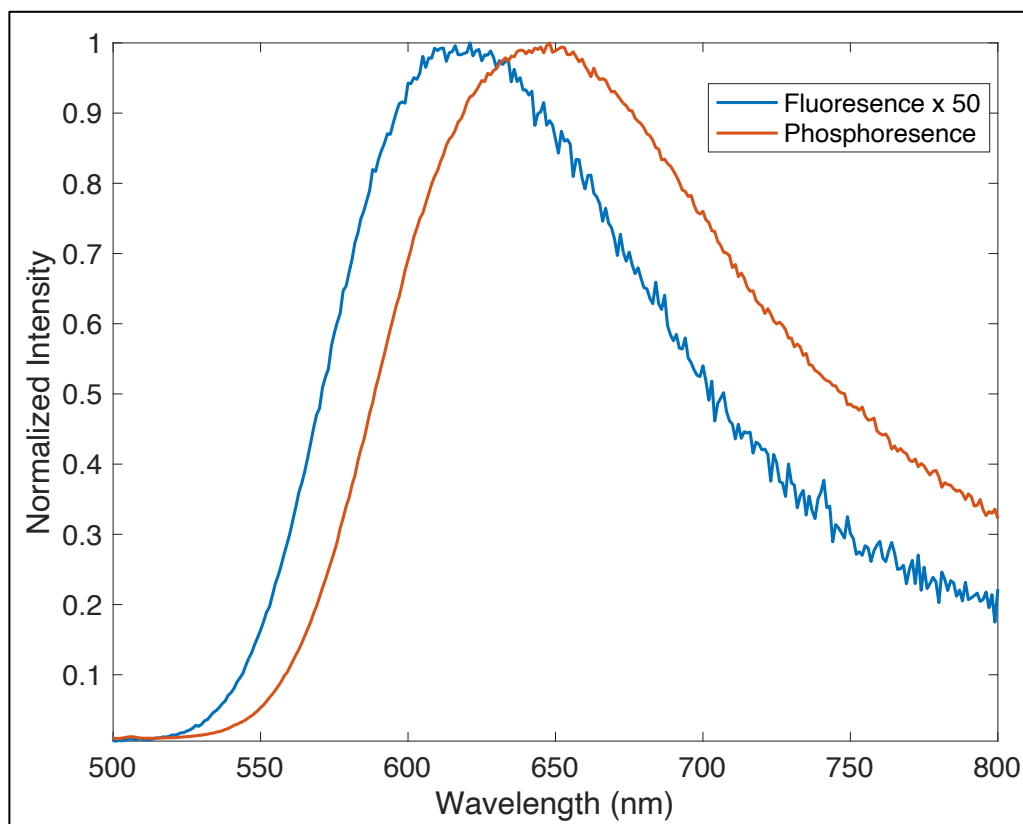


Figure 6.5: Eigenspectra derived from global fit of the steady state emission data. Fitting to the quantum emission model gave $E_0 = 16,200$ (18) cm^{-1} for the phosphorescence spectrum.

6.3.3 Marcus Analysis

The non-radiative rates were utilized in an Arrhenius and Marcus analysis according to equations 6.7 and 6.8. Two temperature regimes were observed in the data, which are distinguished in figure 6.6 as red and blue regions. The wavelength regions were fit separately and given in figure 6.6. The fits of each domain at each wavelength are included in the appendix. It is important to not the necessity of a global analysis for fitting of this data in the future.

The two domains were posited to be related to the multiple kinetic. Extracting out the separate k_{nr} processes from the variable temperature data is a goal of future work. The Arrhenius parameters reflect the differences in barriers, shown in table 6.3, where a larger activation barrier is observed for the higher temperature regime along with a larger frequency factor indicating more efficient surface hopping, a product of increased singlet character. A Marcus analysis was

performed on both temperature regions separately, using the different driving forces obtained from the QM fit of the triplet eigen spectrum in figure 6.5 for the low temperature domain, and the full spectrum at 295 K for the high temperature domain. These parameters are reported in Table 6.3 where the E_o from the fit is labeled as ΔG .

Table 6.2: Non-radiative rate constants for each wavelength region. Obtained from $k_{obs}=k_r-k_{nr}$.

Temperature (K)	$k_{nr}^{580} (x10^5 s^{-1})$	$k_{nr}^{640} (x10^5 s^{-1})$	$k_{nr}^{700} (x10^5 s^{-1})$
295	3.24	3.18	3.28
290	3.20	3.15	3.22
285	3.16	3.12	3.13
280	3.14	3.08	3.11
275	3.12	3.06	3.13
270	3.09	3.01	3.03
265	3.07	3.00	3.03
260	3.05	2.99	3.05
255	3.03	2.98	3.00
250	3.04	2.96	3.01
245	3.02	2.94	2.99
240	2.99	2.94	2.97

Table 6.3: Arrhenius and Marcus parameters for high and low temperature regions.

Wavelength (nm)	High Temperature			Low Temperature		
	580	640	700	580	640	700
$E_a (cm^{-1})$	200 (10)	213 (7)	248 (29)	130 (7)	126 (5)	125 (12)
$A (x10^6 s^{-1})$	6.95 (0.35)	7.29 (0.24)	8.84 (1.3)	4.78 (0.19)	4.55 (0.13)	4.59 (0.31)
$\Delta G (cm^{-1})$	16440 (8)			16200 (18)		
$\lambda (cm^{-1})$	13190 (15)	13100 (12)	12870 (31)	13530 (20)	13580 (19)	13590 (23)
$H_{ab} (cm^{-1})$	0.07 (0.01)	0.07 (0.01)	0.07 (0.01)	0.05 (0.01)	0.05 (0.01)	0.05 (0.01)

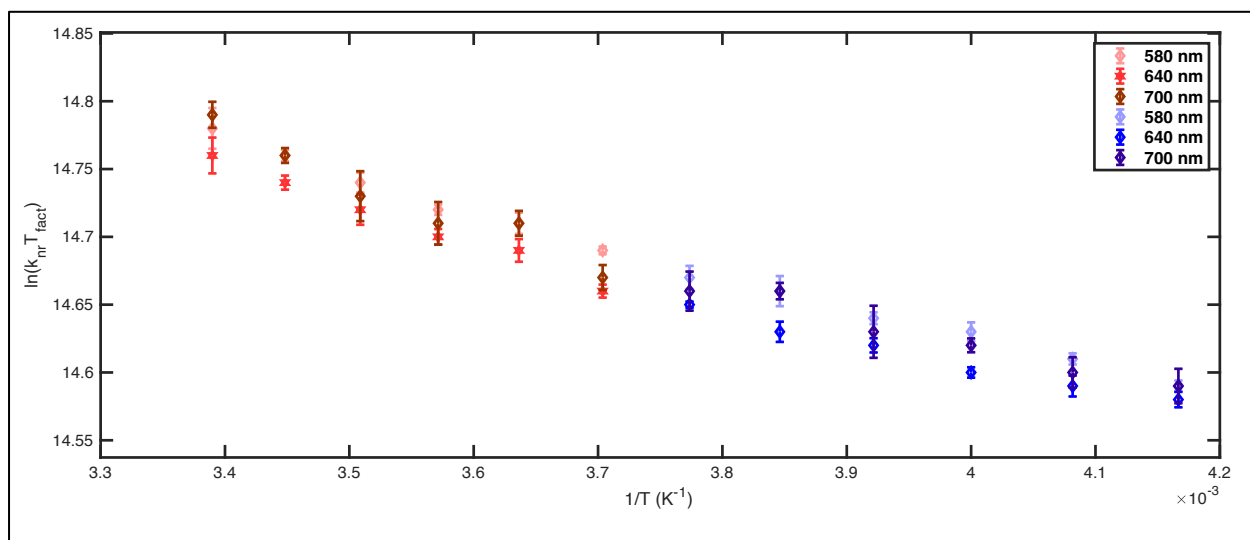


Figure 6.6: Arrhenius plots for the high temperature (red, 295-270 K) and low temperature (blue, 265-240 K) regimes. The individual fits are included in the appendix to this chapter. No optimization for selection of the temperature domains were performed.

Comparing the reorganization energies to the driving forces, it is now possible to confirm that the dynamics of $[\text{Cu}(\text{tdmsbp})_2]^+$ are in fact located in the Marcus inverted region. From this observation, we can rationalize the larger barrier for recovery in the high temperature domain, which includes a contribution from a higher energy singlet state, bringing the average barrier height to a larger value. This behavior consistent with the inverted regime and the energy gap law to which the dynamics can be now ascribed to. These observations also manifest in the driving forces, in which the higher energy regime should have a higher average energy as it includes more intensity at bluer wavelengths. Likewise, it is not surprising then that the low temperature domain has an overall lower zero-point energy as it describes less of this state. The trends in reorganization energy lower energy domain are shifted further along a particular nuclear coordinate by approximately 480 cm^{-1} at the probe wavelength of 640 nm. Again, this reflects the thermally weighed averages of the processes, and thus doesn't necessarily imply there is a 480 cm^{-1} translation along a particular coordinate. It does suggest that the singlet and triplet states are not precisely nested which is commonly assumed. This structural difference

could be a result of the different molecular orbital contributions to the excited state wavefunction called for by El-Sayed's rules for intersystem crossing.³⁴ Finally, electronic coupling for the ground state recovery process is very weak and further suggest that the marginal increase in the high temperature domain is primarily due to the singlet character of that state while confirming the EGL model is valid consistent with the requirements for weakly coupled systems. The weak coupling illustrates the necessity of prolonging MLCT excited states in chromophore design.

The relatively large reorganization energy may suggest an alternative coordinate is necessary to describe the ground state recovery process. The DHA geometry of the relaxed state for the complex is negligibly different, from the FC geometry. This minor distortion in DHA likely couples to other degrees of freedom, which may contribute in a small way individually but as a whole is quite large.³³ As noted by Tahara and Coworkers, rotation about the methyl group in the α -position of phenanthroline, must be coupled to evolution along the DHA coordinate.²² In the case described here, there are several more rotational degrees of freedom in the *sec*-butyl group which could contribute. It is likely that these are coupled to each other as well. These extra degrees of freedom, while sacrificing some excited state energy, likely isolate the excited population far away from avoided crossings relevant for the ground state recovery process, which is consistent with the low electronic coupling. This analysis must be taken with a grain of salt, as the non-radiative rates are composites of two thermally interacting states which should have different degrees of electronic coupling.

6.3.4 Studies of $[Cu(tmdsbp)_2]^+$ in Acetonitrile

The reorganization energy is in part dependent on outer sphere degrees of freedom. Changing the dielectric environment can aid in establishing trends this outer-sphere effect.

Therefore, other solvents were pursued to gain a qualitative understanding of how λ changes with dielectric perturbation.

The methods described above were applied to $[\text{Cu}(\text{tmdsbp})_2]^+$ in acetonitrile solution. The emission decay data was fit to a single-exponential functions and show a similar trend in temperature with DCM. A drop in the excited state lifetime is observed consistent with literature observations. The nature of this drop in lifetime is the subject of considerable debate *vide supra*.

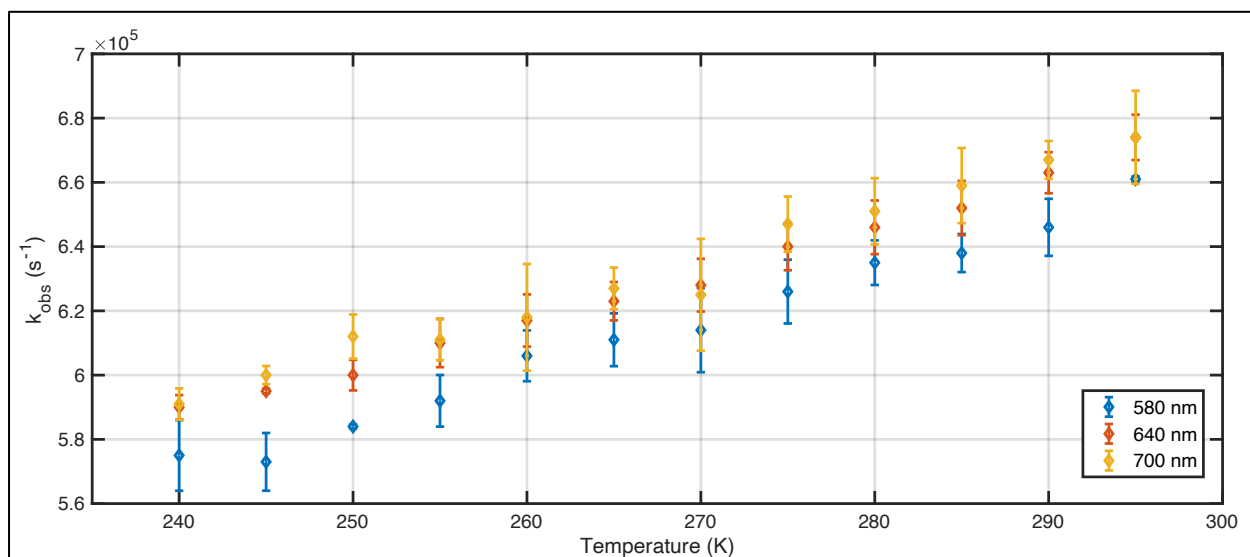


Figure 6.7: Observed rate constants for the emission in acetonitrile obtained from single exponential fits of the kinetic profiles.

Table 6.4: Experimental observables in acetonitrile solution. Quantum yields (Φ), observed decay rates (k_{obs}^{640}), effective radiative rates ($k_{\text{r,eff}}^{640}$), and non-radiative rates ($k_{\text{nr,eff}}^{640}$) at the 640 nm probe region.

Temperature (K)	Φ	$k_{\text{obs}}^{640} (\times 10^5 \text{ s}^{-1})$	$k_{\text{r,eff}}^{640} (\times 10^4 \text{ s}^{-1})$	$k_{\text{nr,eff}}^{640} (\times 10^5 \text{ s}^{-1})$
295	2.9 (0.1)	6.74	1.96	6.54
290	3.1 (0.1)	6.63	2.06	6.42
285	3.3 (0.1)	6.52	2.16	6.3
280	3.5 (0.3)	6.46	2.26	6.23
275	3.8 (0.2)	6.4	2.41	6.16
270	3.8 (0.3)	6.28	2.42	6.04
265	3.9 (0.2)	6.23	2.43	5.99
260	3.8 (0.3)	6.17	2.37	5.93

Table 6.4 (cont'd)

255	2.9 (0.2)	6.1	2.29	5.87
250	3.7 (0.3)	6	2.2	5.78
245	3.6 (0.3)	5.95	2.12	5.74
240	3.5 (0.3)	5.9	2.08	5.69

The variable temperature steady state emission spectra, show a marked deviation from those collected in dichloromethane and other solvents like ethanol/methanol. At low temperature, the emission intensity increases, until around 270 K whereupon it begins to drop, reflected in figure 6.8 and quantum yields presented in Table 6.4. Several quantum yields measured in various solvents are plotted in figure S6.15. The emission in butyronitrile exhibits a similar trend to that in acetonitrile, suggesting that it is related to the cyano functionality. It is interesting that such a temperature dependence is observed in the steady state spectra but are not observed in the time dependent data. This would seem to suggest some form of static quenching process which is facilitated by thermal activation, where solvent penetration is unfavorable at lower temperatures. Interestingly however, the quantum yields at room temperature agree with those reported previously. This in theory could be a ground state effect but would need to be verified by temperature dependent steady state absorption. Other explanations such as dynamic quenching by oxygenic impurity for example are not viable as k_{obs} has not been affected. This is only expressed in the radiative rates, which also suggest that the non-radiative rates are unaffected by whatever solvent dependent process is occurring.

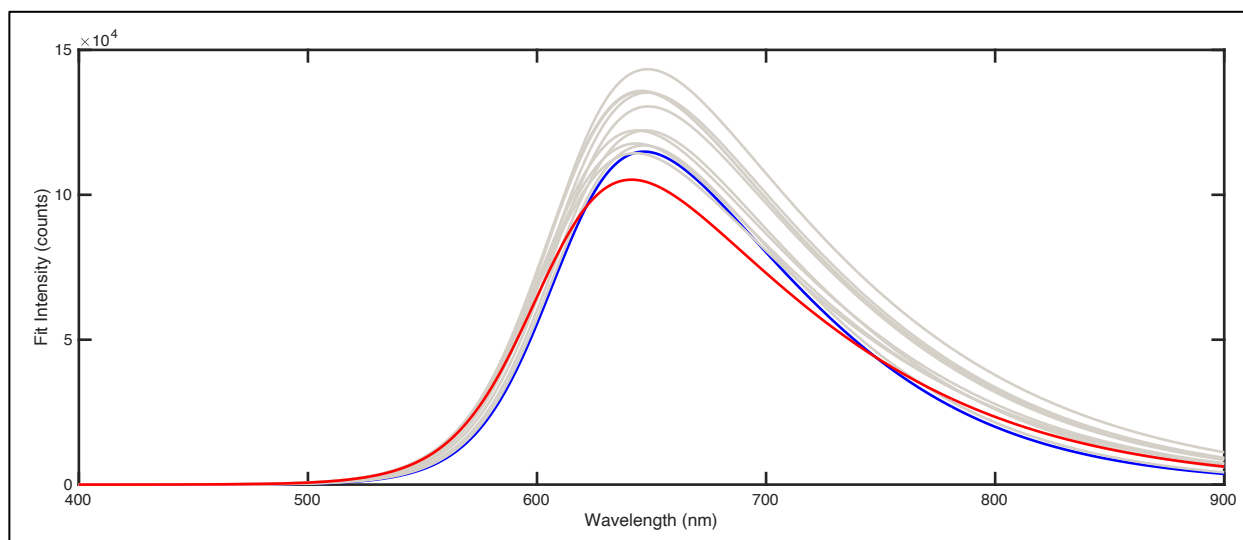


Figure 6.8: Fits of the steady state emission spectra over the 295 K to 240 K temperature range. The red and blue traces correspond to the maximum and minimum temperatures respectively. The spectrum peaks in intensity around 270 K and begins to decrease as the temperature is increased further. The data after 800 nm are simulated from the fits.

6.3.5 Eigen-spectra Fitting Marcus Analysis

The steady-state spectra were decomposed with global target analysis in a manner like that of the DCM data and the eigen-spectra were fit with the quantum mechanical emission model. The residuals for the fit were $\sim 20\%$ compared with the 1% error of the DCM data. This is in part due to the incompleteness of the model for the acetonitrile data which doesn't include the approximately parabolic temperature dependence of the main component. The non-radiative components were calculated, and an Arrhenius and Marcus analysis was performed yielding data of a similar order of magnitude compared to dichloromethane. The parameters derived for the two temperature regimes show similarities with those from the DCM data. For example, the activation energies and frequency factors are larger for the high temperature regime *vide supra*. On average, the reorganization energy is larger at low temperature, although the margin which this is true is much more significant in the acetonitrile data. The coupling constants are less different in this case as a few are within the margin of error which is unsurprising as the

electronic wavefunctions describing the states involved are not going to be perturbed to a significant degree by standard dielectric effects (this does not include solvent coordination etc).

There are differences between the parameters measured in each solvent. We know on average that the lifetime is shorter for acetonitrile, which is directly translate to on average, lower barriers, and increased frequency factors for the acetonitrile case. It is very interesting to note the lack of significant difference in the reorganization energies between solvents. While, none are within error, several wavelengths, have smaller values for λ in acetonitrile. This is interesting as common, wisdom would have it that easily polarized dielectrics, like acetonitrile, have larger outer-sphere reorganization energies. This relative similarity would be consistent with the coupling of rotational degrees of freedom in the aliphatic side chain with those of the DHA change, which is expected to be relatively unaffected by solvent. Thus, bulk of the reorganization energy is due to internal degrees of freedom.

Table 6.5: Arrhenius and Marcus parameters for $[\text{Cu}(\text{tmdsbp})_2]^+$ in acetonitrile solution.

Wavelength (nm)	High Temperature			Low Temperature		
	580	640	700	580	640	700
E_a (cm^{-1})	148 (14)	171 (9)	177 (19)	117 (16)	92 (6)	92 (11)
A ($\times 10^6 \text{ s}^{-1}$)	10.9 (0.8)	12.2 (0.6)	12.7 (1.2)	9.20 (0.88)	7.96 (0.27)	8.05 (0.50)
ΔG (cm^{-1})	16023(4)			15990 (10)		
λ (cm^{-1})	13220 (15)	13030 (12)	12990 (22)	13480 (22)	13740 (13)	13740 (17)
H_{ab} (cm^{-1})	0.08 (0.01)	0.09 (0.01)	0.09 (0.01)	0.08 (0.01)	0.07 (0.01)	0.07 (0.01)

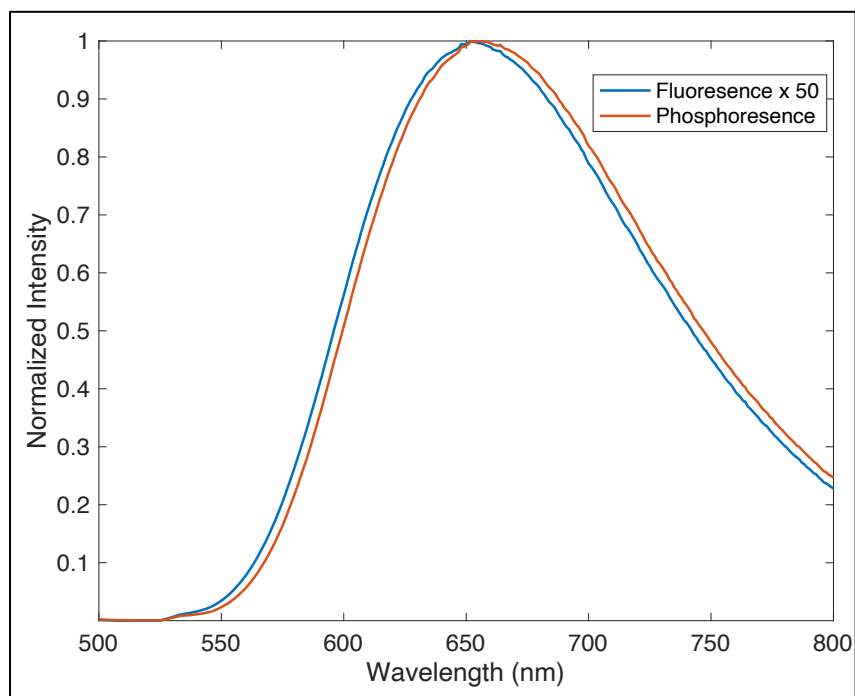


Figure 6.9: Eigenspectra derived from global fit of the temperature dependent steady state emission data in acetonitrile. Fitting to the quantum emission model gave $E_o = 15,990 (18) \text{ cm}^{-1}$ for the phosphorescence spectrum. The ridge near 525 nm is an artefact of baseline correction.

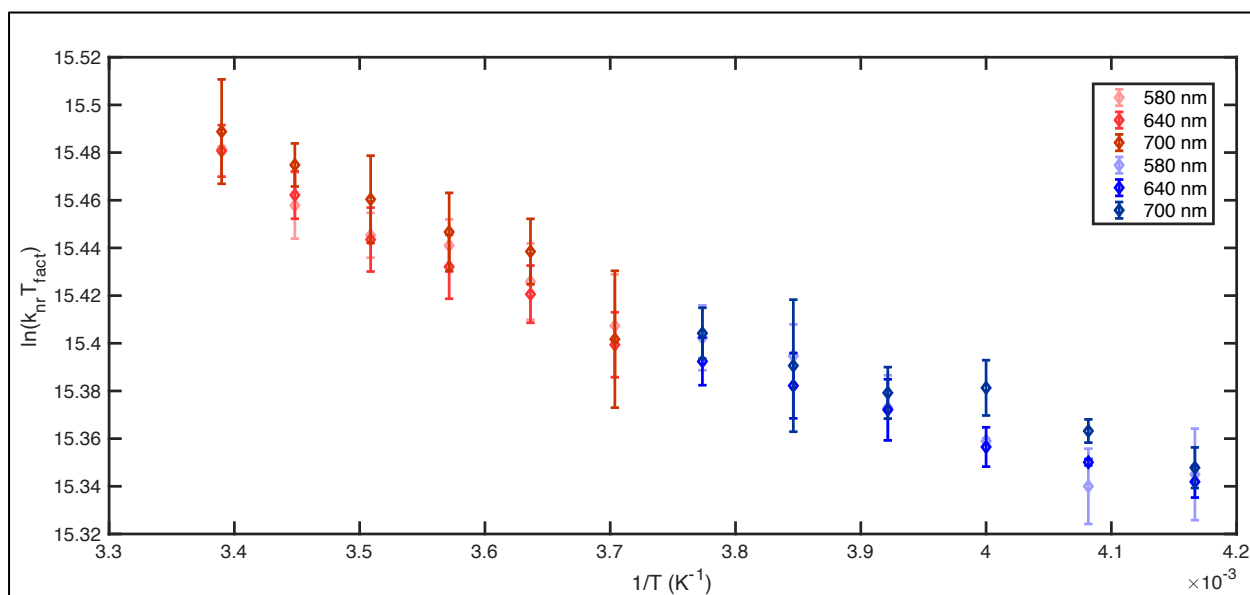


Figure 6.10: Arrhenius/Marcus plot for the non-radiative decay rate acetonitrile solution. The fits of each temperature and wavelength regime are depicted in the appendix of this chapter.

6.4 CONCLUSIONS AND FUTURE WORKS

Here we have calculated the reorganization energy for the ground state recovery processes of the excited ensemble of $[\text{Cu}(\text{tmdsbp})_2]^+$. We note that the ratio of driving force and reorganization energy put the observed dynamics of the system into the Marcus Inverted region, confirming hypotheses for such in the literature. It is therefore likely that the entatic design principle is valid. We note the likelihood of the GSR process being coupled to rotational degrees of freedom of the *sec*-butyl groups and their interactions with the rest of the molecule. We have established a method for the extraction of singlet/triplet spectra from temperature dependent steady state emission data by leveraging the single-value decomposition to obtain equilibrium constants associated with the several excited state equilibria. We have observed a thermally active solvent dependence associated with the cyano- functional group leading to a drop in emission intensity at higher temperatures. The reasons for this are unclear. This study has taken a thermal approach to dissecting the complicated long-timescale dynamics of the excited state evolution of Cu(I) chromophores.

This method will benefit significantly from the application of a global analysis on more than just the steady state spectra. This will serve two significant roles. The first would be to generate global observed rate constants, which are independent of the probe region. This will provide a wavelength independent account of the decay of the equilibrated system and as such, the radiative and non-radiative parameters will not require different sets of components from which to. The second would be to yield the two different components to non-radiative decay which can be described by equation 6.12. This presumes an Arrhenius behavior into the two competing processes. This could easily be extended to the Marcus analysis in a similar way.

$$k_{nr} = \frac{3k_{nrt} + k_{nrs}e^{-\frac{\Delta E_{st}}{k_bT}}}{3 + e^{-\frac{\Delta E_{st}}{k_bT}}} = \frac{\left(3A_1e^{-\frac{E_a}{k_bT}} + A_2e^{-\frac{E_b+\Delta E_{ST}}{k_bT}}\right)}{3 + e^{-\frac{\Delta E_{ST}}{k_bT}}} \quad 6.12$$

Such a program will require the analysis of both time-resolved and steady-state data in a single program. This has been performed in MATLAB and the global analysis module for the eigenspectra of the steady-state spectra has been performed and reported in the sections above. The program will create synthetic versions of spectra, quantum yields, and rate constants which will need to be resolved with direct measurements of these parameters. The program in its current form lacks a robust statistical module. This will be key before it is used for the types of analysis this work requires.

The methodology discussed here could in theory be extended to other Cu(I) emitters, which undergo TADF emission. The reorganization energy can thus be measured from rate data and be used in the correlative process of the entatic strategy.

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APPENDIX

6.6.1 Time Resolved Emission Data

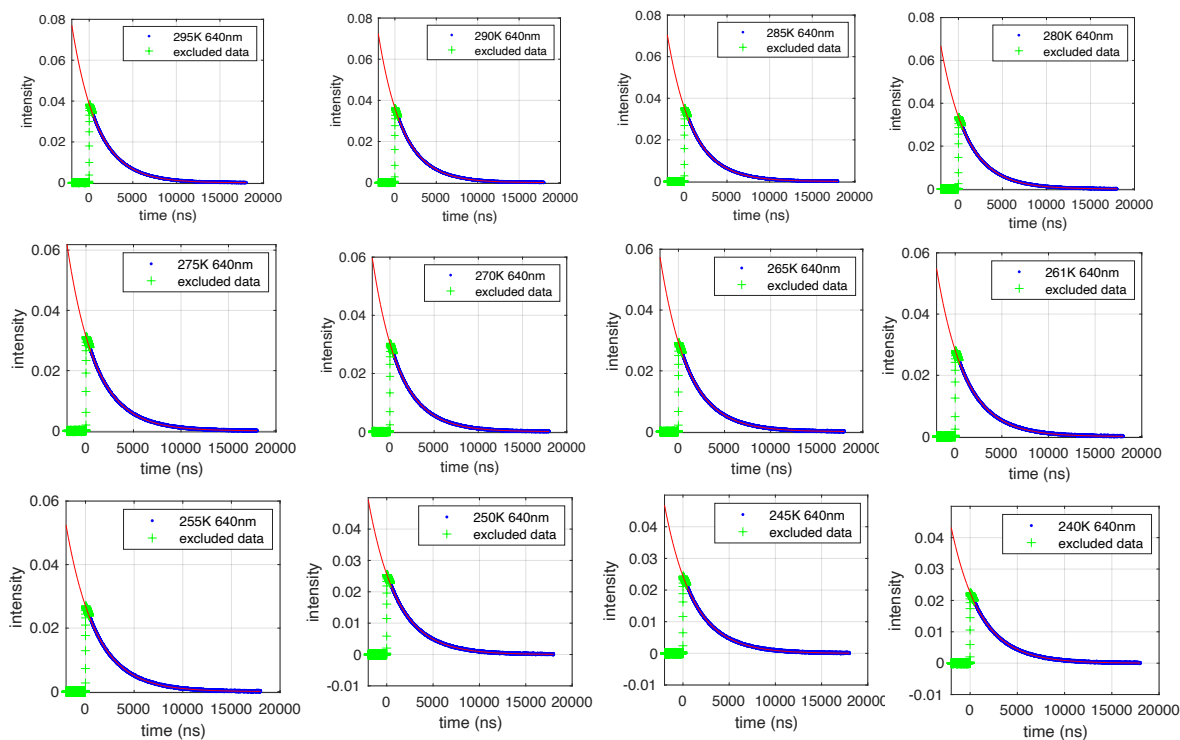


Figure S6.11: Kinetic traces of the decay of 640 nm emission. All data were fit to single exponentials. The time constants for all wavelength regions are reported in the table below.

Table S6.6: Observed rates for the data in DCM and the corresponding lifetimes.

Temperature (K)	k_{obs} 580 (s^{-1})	k_{obs} 640 (s^{-1})	k_{obs} 700 (s^{-1})	τ 580 (ns)	τ 640 (ns)	τ 700 (ns)
295	3.37E+05	3.43E+05	3.44E+05	2964	2912	2907
290	3.32E+05	3.39E+05	3.37E+05	3016	2950	2964
285	3.27E+05	3.36E+05	3.28E+05	3056	2977	3044
280	3.25E+05	3.30E+05	3.26E+05	3082	3026	3069
275	3.22E+05	3.28E+05	3.27E+05	3107	3045	3055
270	3.18E+05	3.22E+05	3.18E+05	3148	3101	3145
265	3.16E+05	3.21E+05	3.17E+05	3166	3111	3152
260	3.13E+05	3.19E+05	3.19E+05	3193	3135	3130
255	3.10E+05	3.17E+05	3.14E+05	3226	3155	3189
250	3.10E+05	3.15E+05	3.14E+05	3223	3176	3181
245	3.08E+05	3.13E+05	3.13E+05	3246	3194	3196
240	3.04E+05	3.13E+05	3.11E+05	3285	3199	3218

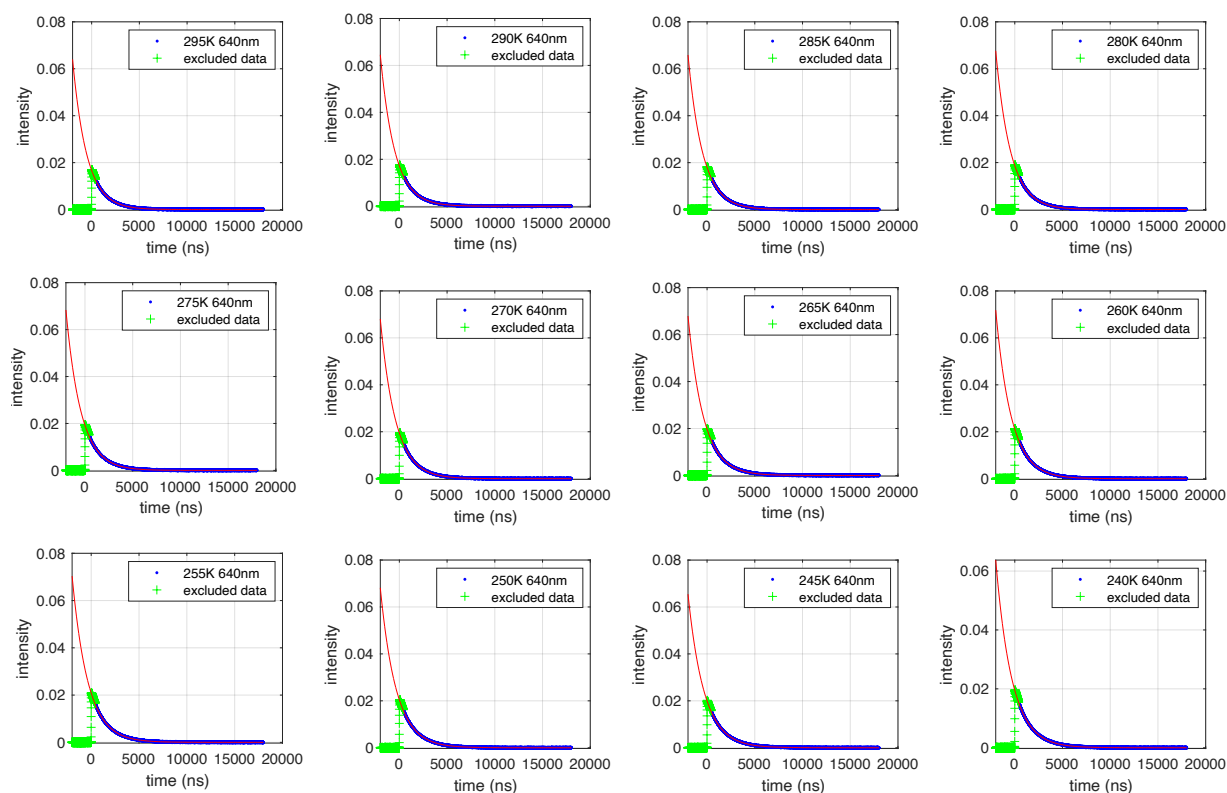


Figure S6.12: Kinetic traces of the decay of 640 nm emission in acetonitrile solution. All data were fit to single exponentials. The time constants for all wavelength regions are reported in the table below.

Table S6.7: Observed rates of emission decay and the corresponding lifetimes in acetonitrile solution.

Temperature (K)	k_{obs} 580 (s^{-1})	k_{obs} 640 (s^{-1})	k_{obs} 700 (s^{-1})	τ 580 (ns)	τ 640 (ns)	τ 700 (ns)
295	6.61E+05	6.74E+05	6.74E+05	1513	1485	1483
290	6.46E+05	6.63E+05	6.67E+05	1548	1508	1500
285	6.38E+05	6.52E+05	6.59E+05	1567	1533	1519
280	6.35E+05	6.46E+05	6.51E+05	1574	1547	1536
275	6.26E+05	6.40E+05	6.47E+05	1597	1561	1545
270	6.14E+05	6.28E+05	6.25E+05	1628	1593	1600
265	6.11E+05	6.23E+05	6.27E+05	1637	1604	1596
260	6.06E+05	6.17E+05	6.18E+05	1651	1622	1618
255	5.92E+05	6.10E+05	6.11E+05	1688	1639	1636
250	5.84E+05	6.00E+05	6.12E+05	1713	1667	1635
245	5.73E+05	5.95E+05	6.00E+05	1746	1680	1665
240	5.75E+05	5.90E+05	5.91E+05	1738	1694	1691

6.6.2 Steady State Emission Data

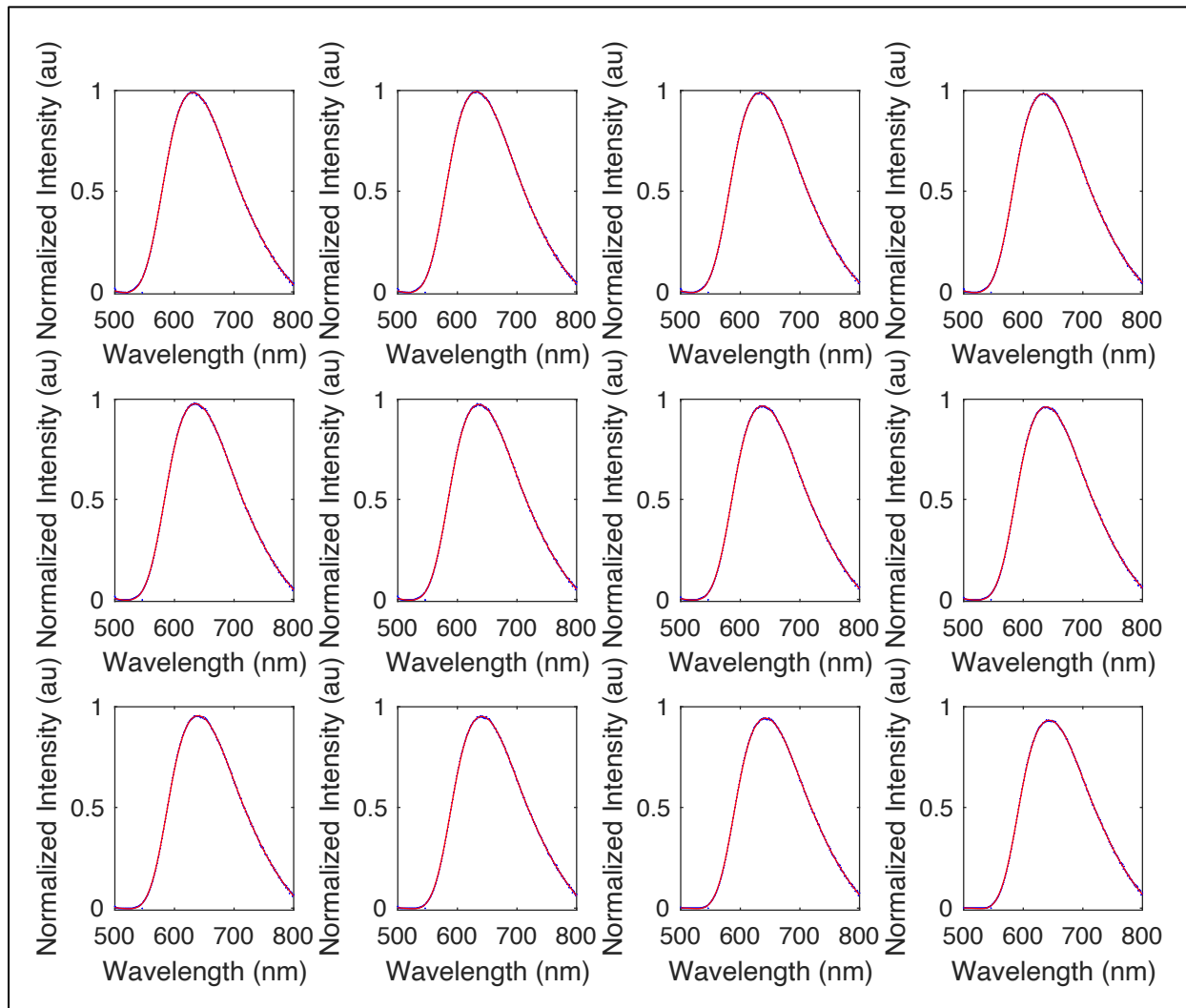


Figure S6.13: DCM steady state emission data (blue) and the associated fits (red line). Temperature decreases from left to right, top to bottom where the top left is 295 K and the bottom right is 240K. The fit was then integrated to obtain the quantum yields presented in the document.

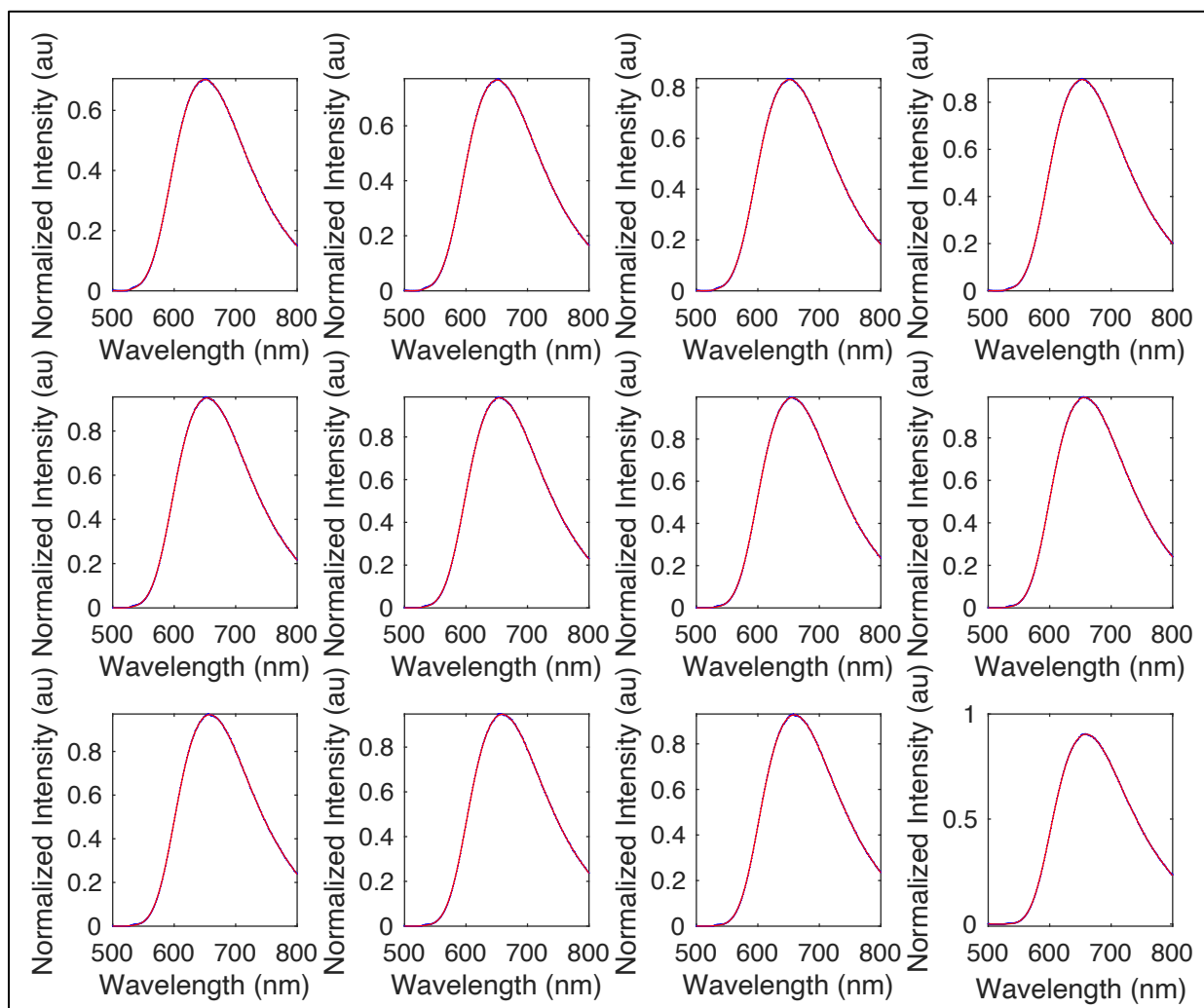


Figure S6.14: Acetonitrile steady state emission data (blue) and the associated fits (red) at high and low temperature. Temperature decreases from left to right, top to bottom where the top left is 295 K and the bottom right is 240K. The fit was then integrated to obtain the quantum yields presented in the document.

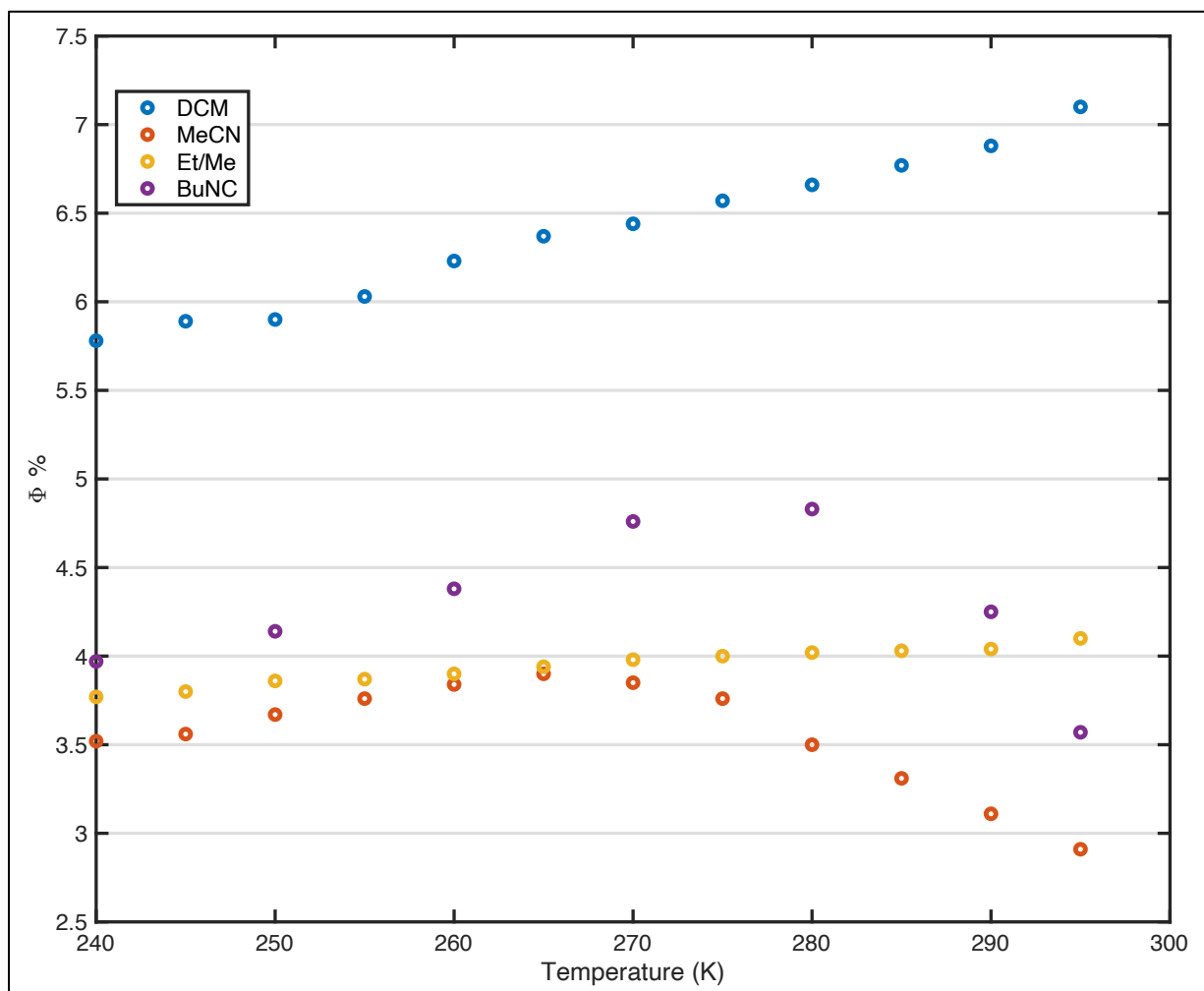
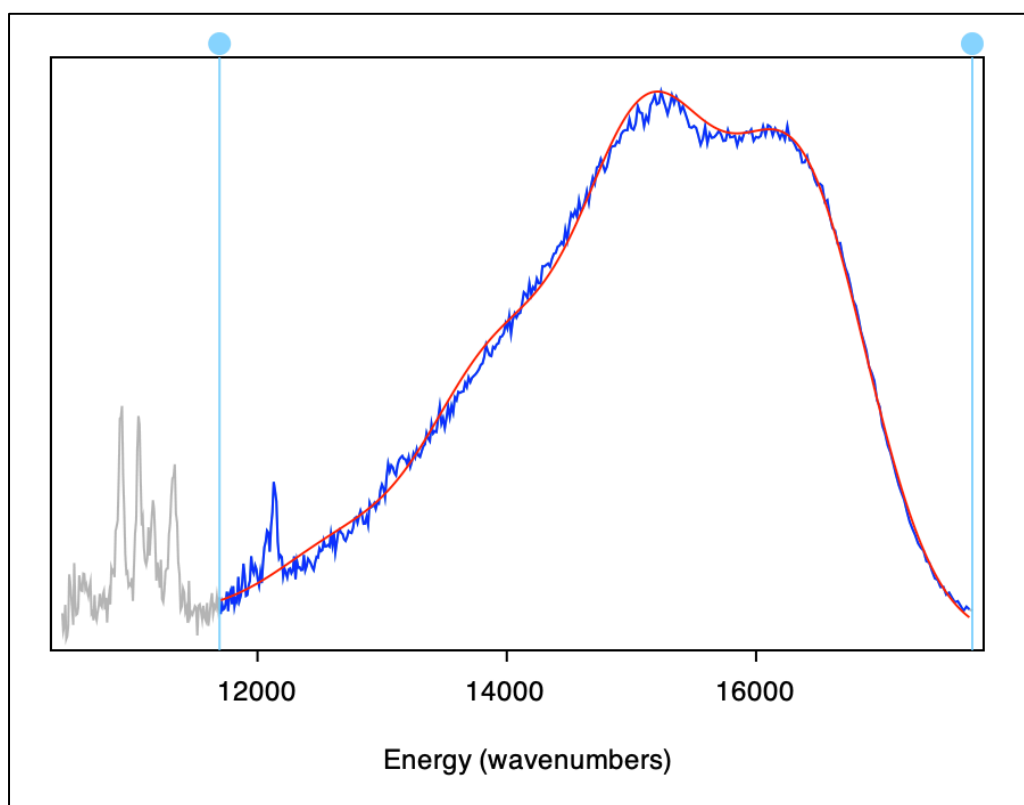


Figure S6.15: Quantum yields measured in various solvents. The nitrile solvents likely participate in some thermally activated static quenching which perturbs the radiative rates to some degree but does not provide pathways for significantly faster non-radiative decay.



Parameter	From Fit
E_0 (cm ⁻¹)	$16,345 \pm 6$
$\hbar\omega_M$ (cm ⁻¹)	1224 ± 4
S_M	1.36 ± 0.01
$\Delta\tilde{\nu}_{0,1/2}$ (cm ⁻¹)	1304 ± 7
λ (cm ⁻¹)	1660 ± 13

Figure S6.16: (top) Emission of $[\text{Cu}(\text{tmdsbp})_2]^+$ at 77 K. The fit was obtained with the CocoaFit program from Claude and Meyer. The table below describes the parameters obtained for the fitting. The reorganization energy is calculated from the Huang-Rhys factor by $\hbar\omega_M * S_M$. (bottom) associated parameters from the fitting.

6.6.3 Creating Visual Intuition of the Singular Value Decomposition (SVD):

The singular value decomposition is a data analysis method. For our purposes it can be understood more precisely as an analytical tool to decompose data that has two independent

variables, into orthogonal contributions of these independent variables. The data with two independent variables, can be set up in a matrix, which is populated by the dependent variables. In our case, the independent variables are temperature and wavelength. Other domains, like time and wavelength can be useful (See B.C. Paulus Thesis).

A 2D matrix (given by I) which contains an emission spectrum in frequency as a function of temperature is decomposed into three separate matrices according to the equation:

$$I = U * S * V' \quad 6.13$$

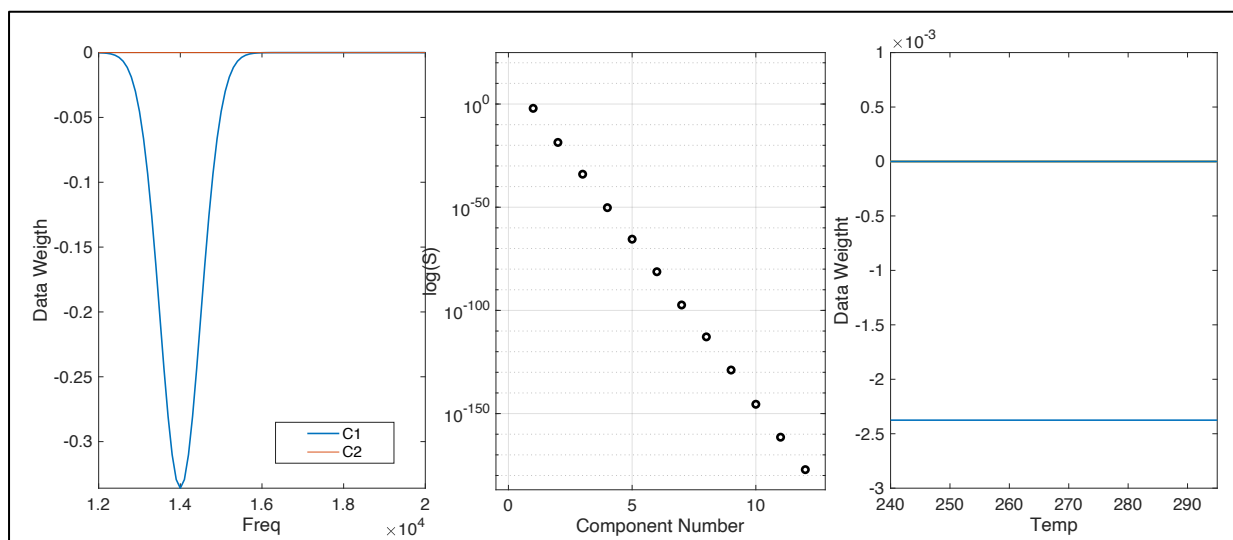


Figure S6.17: Trivial Case of SVD with no change in spectral profile with temperature.

The emission band is gaussian centered at $14,000 \text{ cm}^{-1}$ and is unchanging with temperature. This is not strictly reasonable but the unchanging gaussian represents a trivial case. The eigen spectrum of this theoretical species is illustrated on the left-hand side. The actual spectrum is a gaussian with positive amplitude having a mean centered at $14,000 \text{ cm}^{-1}$ and a bandwidth of 500 cm^{-1} . The eigen spectrum has a negative intensity. The singular values, while there are, by definition, as many components as there are temperature points, only have one that is relevant. Furthermore, there is no temperature dependence in the right eigenvector, which is

also negative. To recreate the spectrum, we must multiply with the equation above. Notice that the amplitude of the recreated spectrum will be positive, as both the left and right eigenvectors contain only negative values. The only component relevant is the first, as given by its significance of 1 in the middle panel.

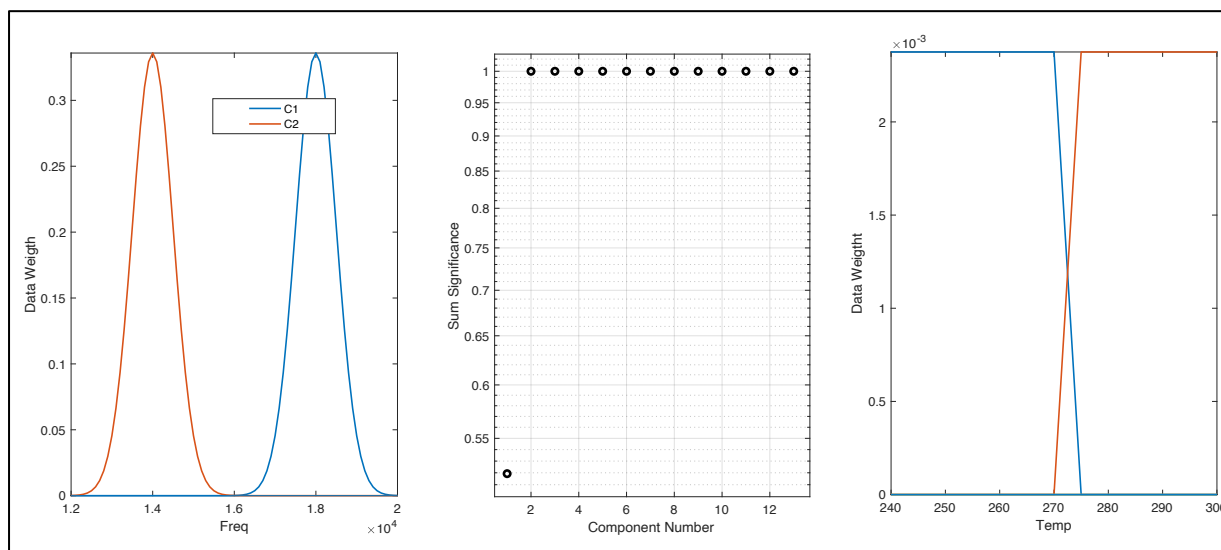


Figure S6.18: Two band SVD. Notice that in their respective temperature domains, each band is a trivial case, like that described above.

Let us consider a different case in which the emission from two states are examined. These are both represented by gaussians centered at 14,000 and 18,000 cm^{-1} . The emission from each is turned on or off by a step function at a middling temperature. Again, this is not physically reasonable but illustrates how the SVD changes with equally contributing components. The eigenspectra of an emission band at 14,000 cm^{-1} and 18,000 cm^{-1} . These pop on or off based on the values of the right eigenvectors (right panel), at high temperature there is exclusive emission from C_2 and at low temperatures there is only emission from C_1 . The sum of the singular values illustrates this in that the sum of first and second components equal 1, and they each describe $\sim 50\%$ of the data set. Component 1 is slightly larger in its contribution due to the asymmetry of the temperature region. This is important to note because the values derived are all self-contained

and depend highly on the input conditions, i.e. the symmetry of the temperature and frequency domain.

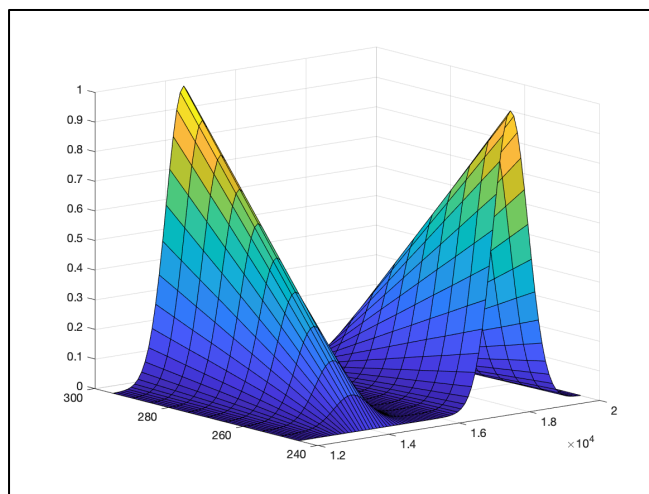


Figure S6.19: Non-trivial, Two State emission with a linear temperature dependence.

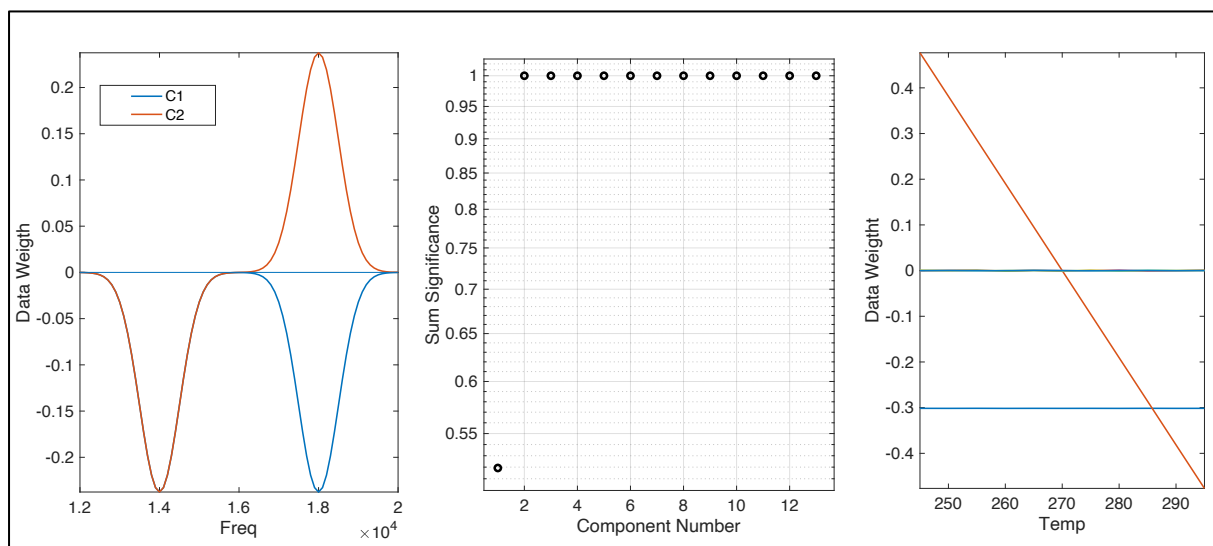


Figure S6.20: SVD of the non-trivial emission case. Note that the significance of each band is still approximately 50:50. The eigenvectors however are different in how they describe the temperature dependence of each state.

Finally let us consider a more realistic case, in which the two gaussians lose and gain intensity gradually over the entire temperature range with some function. This case is illustrated by the surfaces above. This can be decomposed with SVD. Consider first the similarities with above, namely the cumulative significance plot in the center. This still includes the first two

components each with ~50% of the variance in the data and their sum is equal to 1. This is the same as the on/off case above, the right and left eigenvectors are however different. Consider the ingredients to make the spectrum at high temperature. It is easiest to illustrate this mathematically in the equation below where the significance is given by 0.5.

$$I_{295} = U1 * 0.5 * V1(1) + U2 * 0.5 * V2(1) \quad 6.14$$

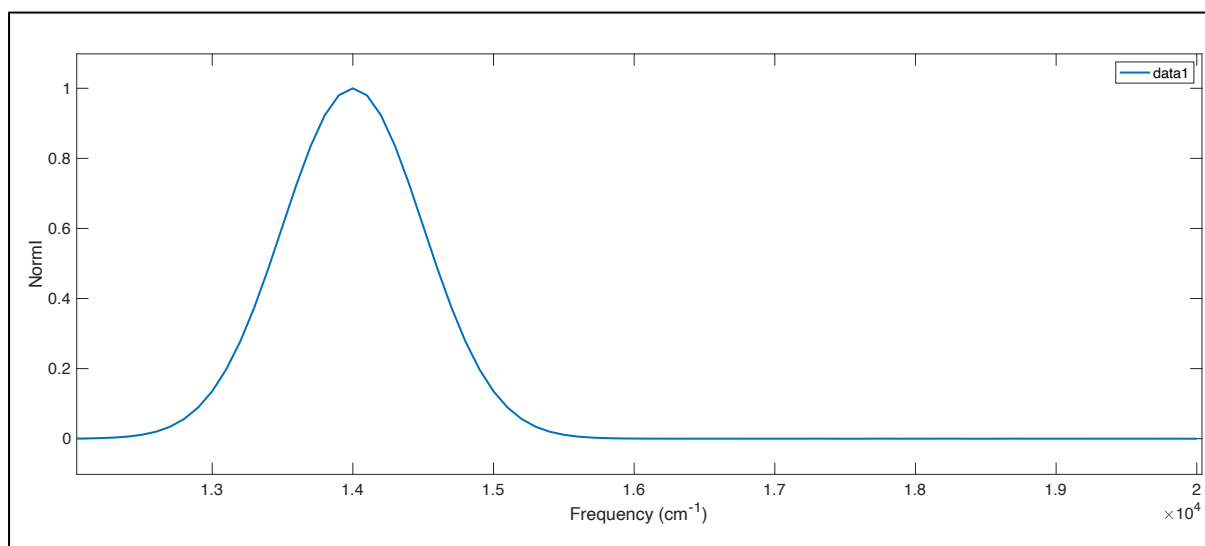


Figure S6.21: Reconstructed band at 295K from the SVD. Note how the bands of each component cancel around 18,000 cm⁻¹.

This spectrum at 295 will include U1, which is completely negative over the whole spectrum, which is multiplied by a negative value term 1 in the equation positive. U2 is an odd function. At 295 the term V2 is negative, meaning that the U2 function inverts, and its positive lobe, as depicted, becomes negative and its negative lobe becomes positive. The sum of terms 1 and 2 with their differing signs, yield a positive spectrum centered at 14,000 cm⁻¹ the place where the two lobes that were added with the same sign. This is depicted below for 295 K.

6.6.4 Single Value Decomposition of VT emission spectra.

The primer above should prepare one to understand the SVD data presented for the complex studied in various solvents. The SVD was performed and then the data was analyzed with the following MATLAB script. This script includes the decomposition process as well as the later fittings to the linearized Boltzmann model and then the generation of k_r matrix. The code is given in portions but runs at once in a single script. It is broken up when presented for relevance.

```
%Reads 2D excel file into a table called A_table
A_table=xlsread('2D_data_mat_useme.xlsx');

section extracts wavelength and temperature information from A_table
wavelength is converted to wavenumbers
it then removes that information from A_table
wavelength = A_table(:,1);
wavelength(1) = [];
wavenumber = (1./wavelength)*1E7;
A_table(:,1) = [];
temperature = A_table(1,:);
A_table(1,:) = [];

%this makes a copy of A_table and then normalizes A_table
%comment out the normalization if you do not want the SVD normalized
A_table_unnorm = A_table;
A_table = max(A_table./max(A_table),0);

%this performs the SVD and assigns the components to matrices U,S and V.
%U is a 301x12 matrix (wavelength x temperature)
%S is a 12x12 matrix that holds the significance of the vectors in U
%V is a 12x12 matrix that describes weighting factors for items in U
[U,S,V] = svd(A_table,'econ');

%this section plots relevant significance information. The first plot is
%the Skree plot, giving the log of the significance of each component
%the second plot is the cumulative significance which can be thought of as
%the percentage of the variance of the data that is described by each
%component
figure Name 'Significance'
subplot(1,2,1)
```

```

semilogy(diag(S), 'ko', 'LineWidth', 2.5)
set(gca, 'FontSize', 12), axis tight
xlabel 'Component Number'
ylabel 'log(S)'
grid on
subplot(1,2,2)
semilogy(cumsum(diag(S))./sum(diag(S)), 'ko', 'LineWidth', 2.5)
set(gca, 'FontSize', 12), axis tight
xlabel 'Component Number'
ylabel 'Sum Significance'
grid on
set(gcf, 'Position', [1400 100 900 750]);

%This section looks at the U and V vectors as well as their reconvolution
%and comparison with the raw data. It plots them to a figure with three
%subplots that describe each
%the first figure plots the first two eigenspectra
figure Name 'Components'
subplot(1,3,1)
set(gca, 'FontSize', 12), axis tight
xlabel 'Wavelength (nm)'
ylabel 'Data Weigth'
box on
hold on
plot(wavelength, U(:,1), wavelength, U(:,2), wavelength, U(:,3), 'LineWidth', 1.5)
)
refline(0,0)
legend('C1', 'C2')
legend('Position', [0.25552, 0.12794, 0.1963, 0.075309])

%this plots the first two right eigenvectors
subplot(1,3,2)
set(gca, 'FontSize', 12), axis tight
xlabel 'Temperature (K)'
ylabel 'Data Weigtht'
box on
hold on
plot(temp, V(:,1), 'd', temp, V(:,2), 'd', temp, V(:,3), 'd', 'LineWidth', 1.5)
refline(0,0)

%This section reconstructs the data from the first 'r' components
%it then plots them in the third subplot
r = 3;
I295 = A_table(:,1);
Arec = U(:,1:r)*S(1:r,1:r)*V(:,1:r)';
I295_rec = Arec(:,1);

```

```
subplot(1,3,3)
set(gca,'FontSize',12), axis tight
xlabel 'Wavelength (nm)'
ylabel 'Data Weightht'
box on
hold on
plot(wavelength,I295,'g', wavelength,I295_rec,'bx','LineWidth',1.5)
legend('Raw','Rec')
legend('Position',[0.58953,0.12603,0.1963,0.075309])
hold off
```

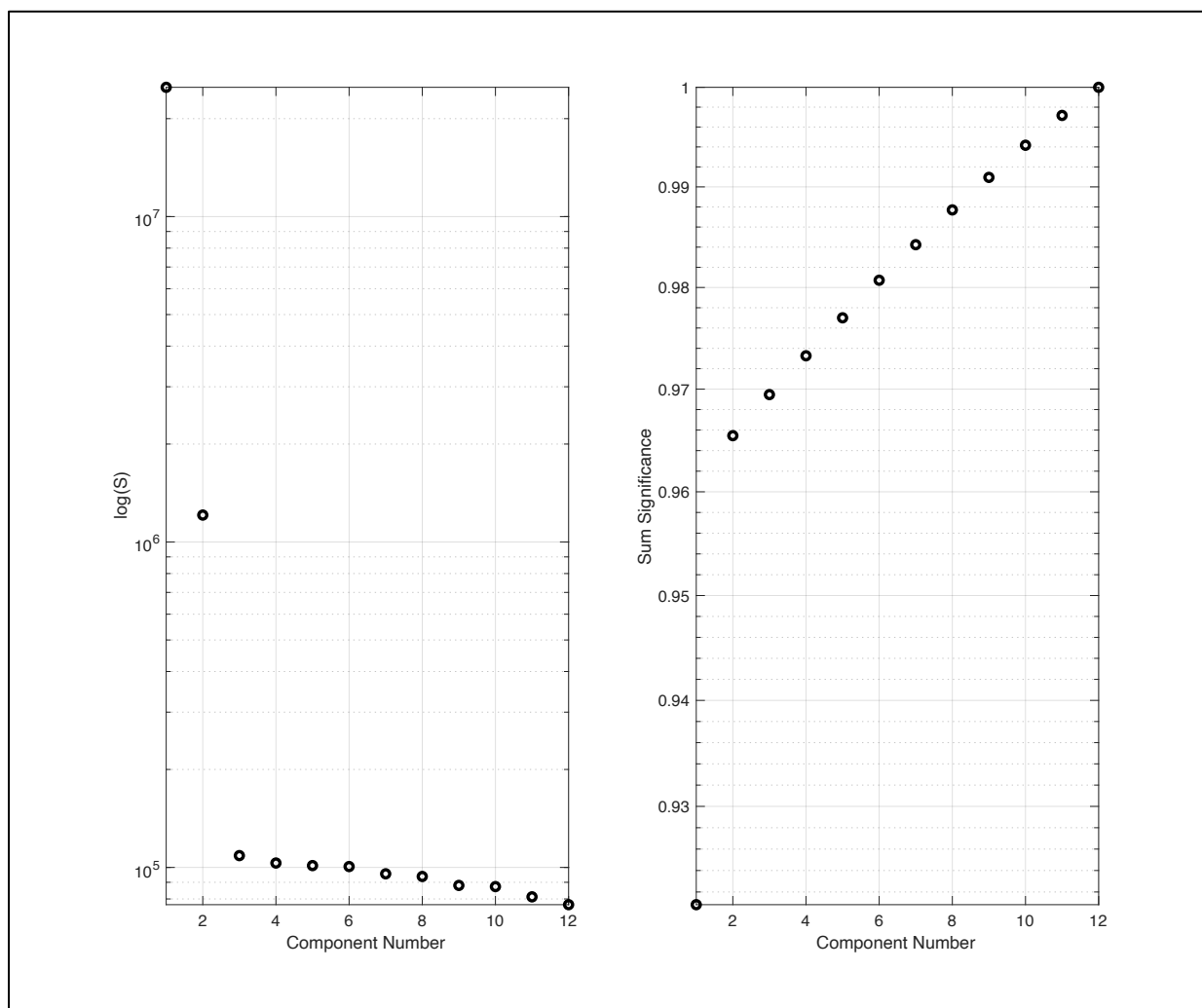



Figure S6.22: Skree plot (left) and cumulative sum of significance (right) for DCM data.

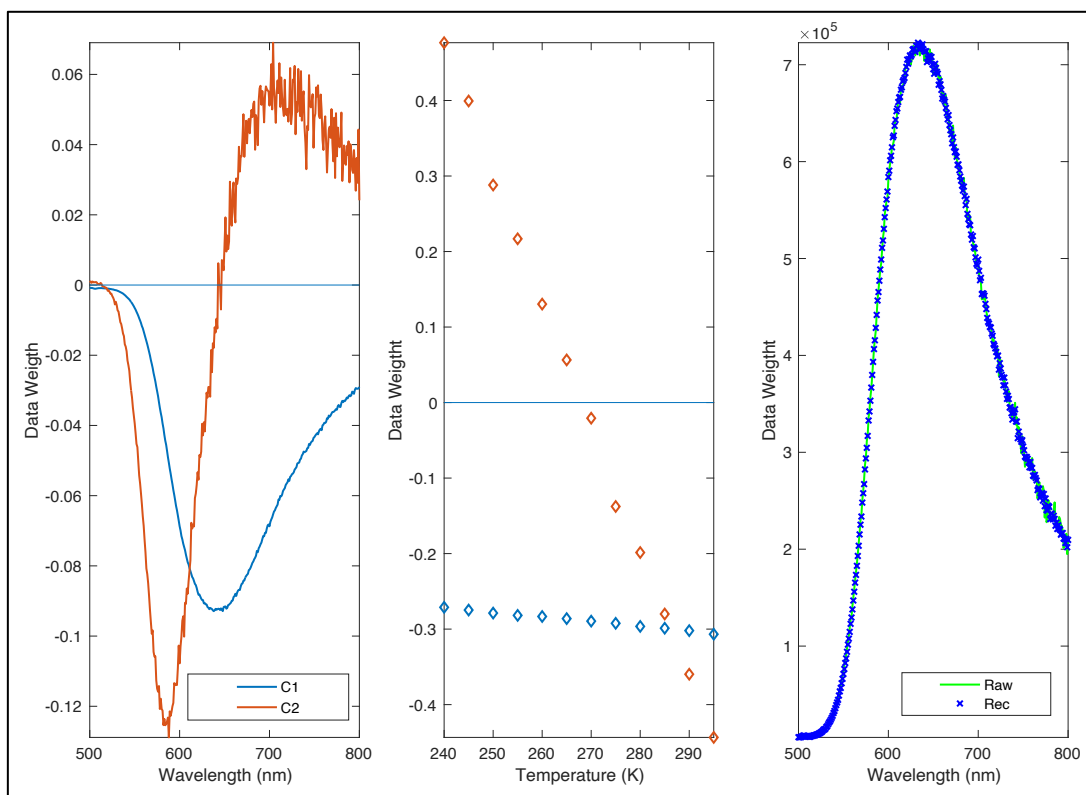


Figure S6.23: SVD data for DCM. Left panel: first two eigen-spectra. Middle panel: first two right eigen vectors. Right panel: reconstruction of the spectra from the first two components at 295 K. (bottom) third component right and left eigenvectors.

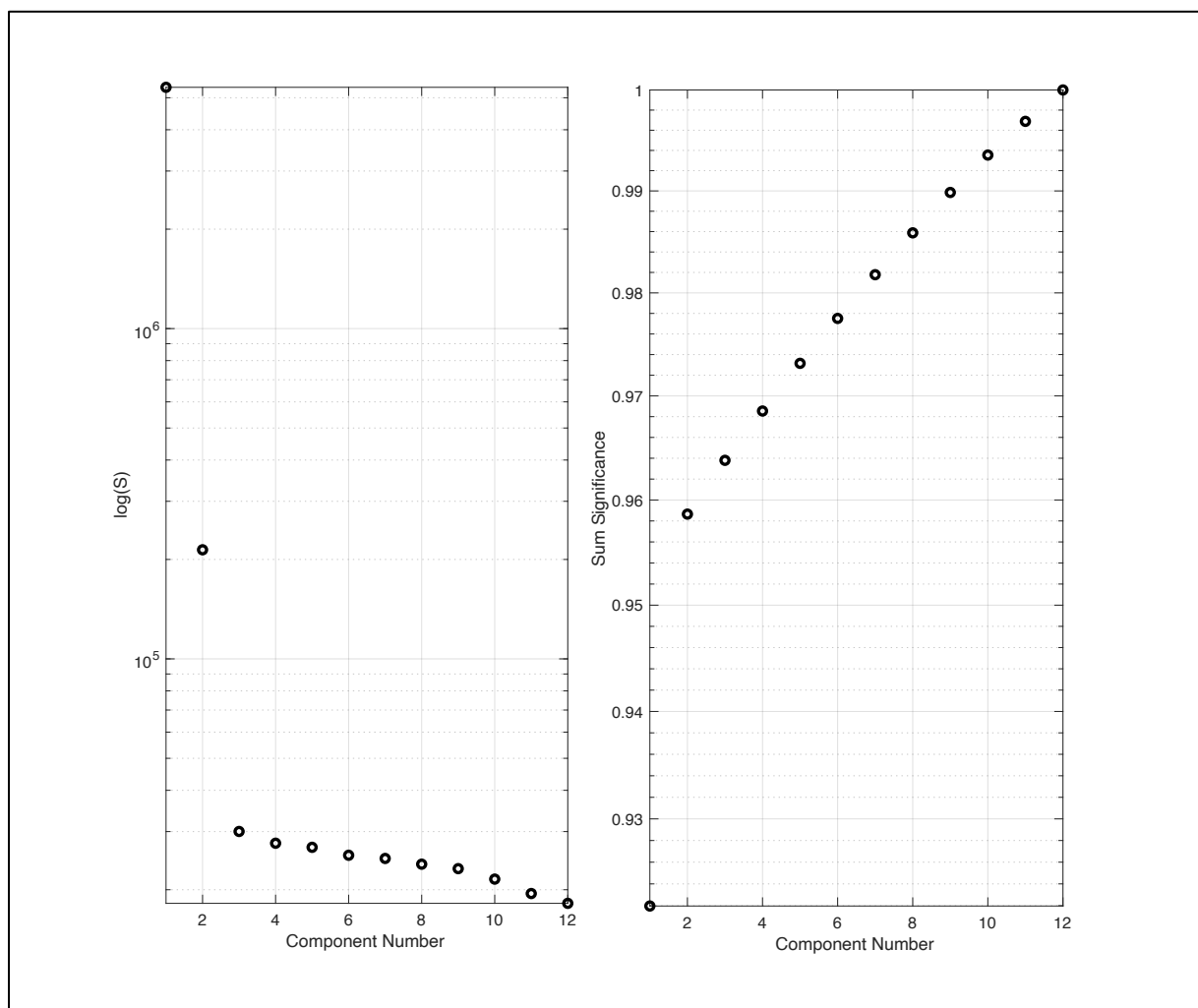


Figure S6.24: Skree plot (left) and cumulative sum of significance (right) for acetonitrile data.

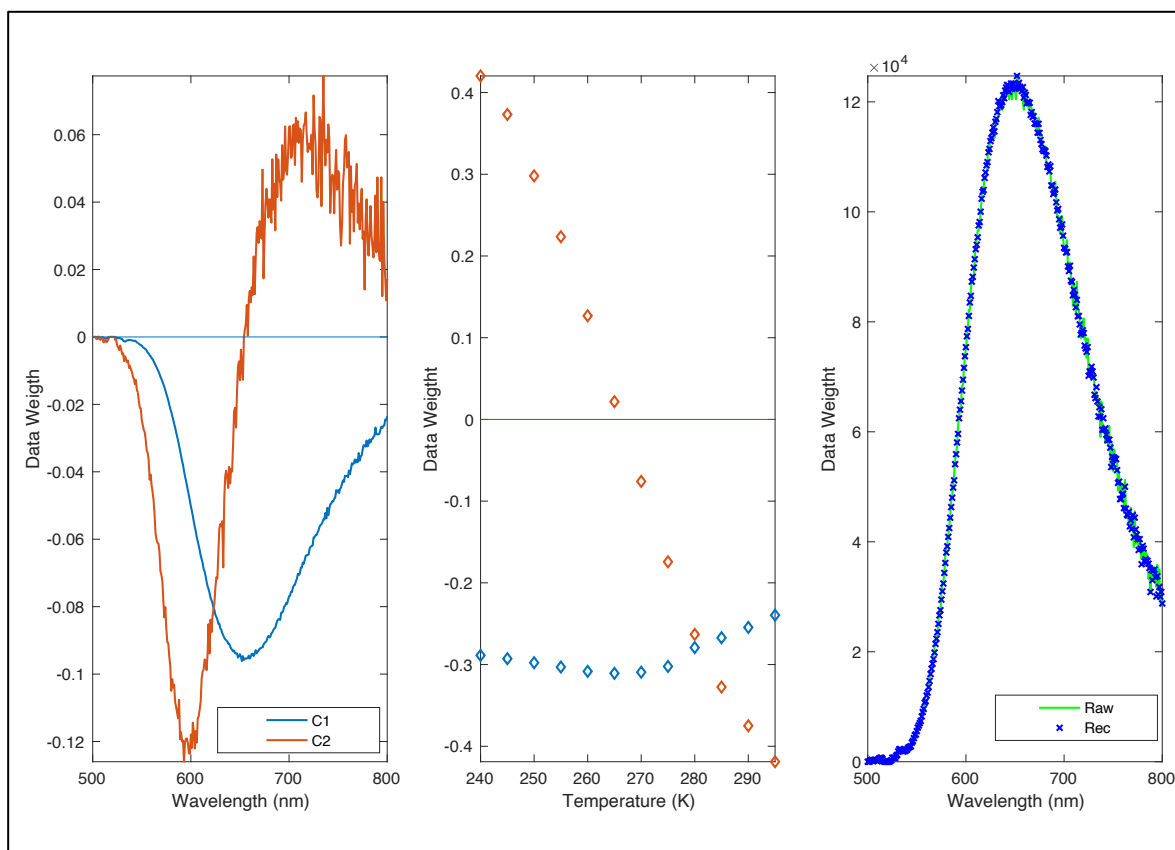


Figure S6.25: SVD data for acetonitrile. Spectra from two components was reconstructed at 295K on the right panel.

6.6.5 MATLAB script for integrated global analysis and residual output

The following code describes the shell script for the multi-objective optimization procedure. Within this are several other written functions that are called from separate files. These functions are boldened and can be referenced to the scripts following the shell.

The input is a .txt file called 'FILENAME_README.txt' which includes the names of the individual files which contain the data to be read and processed. The steady-state data is opened in a similar manner but is reported in a separate file. The outputs in its current format are visualizations of the global analysis step for the steady-state data.

% This section of code imports the time-resolved spectra can be made into a separate module in future

```
% This section of code imports the time-resolved spectra
pwd
fid = fopen('FILENAME_README.txt');
by_temp_cell={};
trace_580 = [];
trace_640 = [];
trace_700 = [];

while ~feof(fid)
    for n=1:12
        textline = fgetl(fid);
        T = readtable(textline);
        time = table2array(T(:, 'Labels')); % * sets time zero subtract
from this*

        %convert time into nanoseconds
        time = time./1E9;
        time(1:999,:) = [];

        %arrays based on the full spectral width measured during
experiment
        A = table2array(T(:, 2:4));

        %baseline correct the data
        A = baseline_correction(A);

        %normalize the data
        A = A./max(max(A));
```

```

    %remove negative time
    A(1:999,:) = [];

    %append to a cell by temperature
    by_temp_cell{n} = [A];

    %separate by wavelength
    trace_580 = [trace_580,A(:,1)];
    trace_640 = [trace_640,A(:,2)];
    trace_700 = [trace_700,A(:,3)];
end
end

by_wavelength_cell = {trace_580,trace_640,trace_700};

data_inputs = data_inputs_actonitrile;

[output] = multi_obj_optimization(data_inputs,time,wavelength);

temp = 295:-5:240;

plot(temp,output{1,1})
plot(temp,output{1,2})
plot(time,output1-output2)

mesh(temp,wavelength,output{1,1})
mesh(temp,wavelength,output{1,2})
mesh(temp,wavelength,output{1,1}-output{1,2})

```

The main optimization function in this iteration includes separate modules. The title of this script is misleading in its current iteration as this is not truly a multi-objective optimization however the structure could be (and will likely need to be) adapted to such an optimization procedure (such as a genetic algorithm or similar).

The inputs for this section are the 2D data matrices of the time resolved data grouped separately by wavelength and by temperature as well as the set of steady state emission spectra with temperature.

```

function [output_cell] =
multi_obj_optimization(data_inputs,time,wavelength)

    output_cell = {};

```

```

%generation of the SVD data as well as the objective function targets
[SVD_SS_norm,I_SS_full] = singular_value(data_inputs{5});

TR_grouped_by_wavelength = data_inputs{1,4};

[SVD_TR_trace_580,I_TR_full_580] =
singular_value(TR_grouped_by_wavelength(1));
[SVD_TR_trace_640,I_TR_full_640] =
singular_value(TR_grouped_by_wavelength(2));
[SVD_TR_trace_700,I_TR_full_700] =
singular_value(TR_grouped_by_wavelength(3));

%objective function targets
QY_real = [0.0710000000000000 0.0690000000000000
0.0680000000000000 0.0670000000000000 0.0660000000000000
0.0640000000000000 0.0640000000000000 0.0620000000000000
0.0600000000000000 0.0590000000000000 0.0590000000000000
0.0580000000000000];
I_SS_full;
I_TR_full_580;
I_TR_full_640;
I_TR_full_700;
VT = SVD_TR_trace_640{1};

[synthetic_full_spectrum,SS_params] =
SS_em_optimization(SVD_SS_norm,I_SS_full);
[output_TR,Raw_TR_out,TR_params] =
TR_kobs_optimization(TR_grouped_by_wavelength,SS_params(1:3),time);

output_cell{1} = synthetic_full_spectrum;
output_cell{2} = I_SS_full;
output_cell{3} = SS_params;
output_cell{4} = output_TR;
output_cell{5} = Raw_TR_out;
output_cell{6} = TR_params;

SS_spectra_plotter(SVD_SS_norm,wavelength,SS_params);

End

function BLC_corr = baseline_correction(A)
BLC_corr = [];
for n = 1:3
    int = A(:,n);
    first4hund = int(1:200);
    BLCfact = mean(first4hund);
    BLCint = int-BLCfact;

```

```

        BLC_corr = [BLC_corr,BLCint];
    end
end

function [] = SS_spectra_plotter(SVD_SS_norm,wavelength,parameters)

    %call SVD params
    U = SVD_SS_norm{1};
    S = SVD_SS_norm{3};

    %select and reshape amplitude parameters
    P = [parameters(5),parameters(6);parameters(7),parameters(8)];

    %generate spectra
    F = U(:,1:2)*S(1:2,1:2)*P;

    %plot spectra
    fig = figure('Name','Flouresence and Phosphoresence Spectra');
    set(gca,'FontName','Arial','FontSize',14), axis tight
    xlabel 'Wavelength (nm)'
    ylabel 'Normalized Intensity'
    box on
    hold on
    plot(wavelength,F(:,1)./max(F(:,1)),wavelength,-F(:,2)./max(-
F(:,2)),'LineWidth',1.5)
    legend('Fluoresence x 50','Phosphoresence')
    legend('Position',[0.68,0.80,0.19,0.075309]) %x,y,xdim,ydim
    hold off

    %save a pdf of the spectrum
    figname = 'acetonitrile';
    saveas(fig,strcat(figname,'_eigenspectra.pdf'));
end

```

This code performs the global analysis of the steady state emission data. The inputs are the decomposed steady state spectra utilizing a function like that described in the previous section of the appendix. The outputs include the minimized composite spectrum as well as the parameters that were generated based on the model. The amplitude parameters in matrix are used to create eigenspectra.

```

function [output,parameters] = SS_em_optimization(SVD_SS_norm,I_SS_full)

    %initial guesses
    I0 = [1,2,1,1,-.0609,2.2,-.32,-1.84];

    %for fmin unc, constraints are placed in the actual QM model fucntion
    options = optimoptions('fmincon','StepTolerance',1e-
7,'Algorithm','sqp','SpecifyObjectiveGradient',true);

```



```

%bounds
ub = [.01,3,-.0005,100,100,100,100,100];
lb = [.001,0,-.01,-100,-100,-100,-100,-100];

yst =@(I) composite_SS(SVD_SS_norm,I); %creates the calculated data
subset based on quantfitFunction.m this is a nested function

objective = @(I) sum((I_SS_full - (yst(I))).^2,'all'); %this is the
objectvie function for the optimization

[x,fval,exitflag,output,grad,hessian] =
fmincon(objective,I0,[],[],[],[],lb,ub);

output = composite_SS(SVD_SS_norm,x);

parameters = [x(1),x(2),x(3),x(4),x(5),x(6),x(7),x(8)];

end

function [composite] = composite_SS(SVD_SS_norm,I)

%fixed inputs
T = 295:-5:240; %in kelvin
kb = 0.695; %in wavenumber
U = SVD_SS_norm{1};
S = SVD_SS_norm{3};
kisc = 8E12;
T0 = 1;

%dependencies
m1 = I(1);
b1 = I(2);
m2 = I(3);
b2 = I(4);
P = [I(5),I(6);I(7),I(8)];

%calculate population based on model
y1 = -m1*T+b1; %describes how kobs changes with temperature
y2 = -m2*T; %describes how ? changes with temperature

C = [y1;y2]';

%create synthetic V vectors based on the equilibrium constants at each T
Vstar = C*P;

composite = U*S*Vstar';
%s2 = size(composite)
end

```

This section takes in the time resolved emission data at each wavelength and finds a global fit of the data at each temperature. The output of this program is the observed rates for each

temperature for the thermally equilibrated system as well as the composite data which can be passed to the figure generator to save eigenspectra.

```
function [output1,Raw_TR_out,parameters] =
TR_kobs_optimization(numeric_cells,line_params,time)

%create independent variable matraces
temp = 295:-5:240;

%create empty vectors for concatenation
SVD_out_cell = {};
Raw_TR_out = [];
output1 = [];
parameters = [];

%set variables for amplitudes
m1 = line_params(1);
b1 = line_params(2);
m2 = line_params(3);

for n = 1:12

    %calculate amplitudes
    A1 = m1*temp(n)+b1;
    A2 = m2*temp(n);

    SVD_input = numeric_cells{n};

    [SVD_output,I_TR_full] = singular_value(SVD_input');

    SVD_out_cell{n} = SVD_output;
    Raw_TR_out = [Raw_TR_out; I_TR_full];

    %initial guesses
    I0 = [1E5,1E6,1,1,1,1];

    %for fmin unc, constraints are placed in the actual QM model fuction
    options = optimoptions('fmincon','StepTolerance',1e-
7,'Algorithm','sqp','SpecifyObjectiveGradient',true);

    %bounds
    ub = [1E7,1E14,100,100,100,100];
    lb = [0,0,-100,-100,-100,-100];

    yst =@(I) composite_TR(SVD_output,A1,A2,time,I); %creates the
calculated data subset based on quantfitFunction.m this is a nested fuction

    objective = @(I) sum((I_TR_full - (yst(I))).^2,'all'); %this is the
objectvie fuction for the optimization

    [x,fval,exitflag,output,grad,hessian] =
fmincon(objective,I0,[],[],[],[],lb,ub);

    output1 = [output1; composite_TR(SVD_output,A1,A2,time,x)];
```

```

        parameters = [parameters;[x(1),x(2),x(3),x(4),x(5),x(6)]];
    end
end

function composite = composite_TR(SVD_output,A1,A2,time,I)

    %fixed inputs
    U = SVD_output{1};
    S = SVD_output{3};
    t = time;

    %dependencies
    kobs1 = I(1);
    kobs2 = I(2);
    P = [I(3),I(4);I(5),I(6)];

    %calculate time resolved populations as a function of temperature
    y1 = A2*exp(-kobs1.*t);
    y2 = A1*exp(-kobs2.*t);

    %create a concentration profile
    C = [y1,y2];

    %create synthetic V vectors based on the time constnats of each decay
    Vstar = C*P;

    composite = U*S*Vstar';
end

```

The script still needs a function which performs a global fit as a function of temperature on the time resolved data. Another required module would perform the Arrhenius/Marcus analysis on the globally analyzed data. Doing this over several data sets will require some front end modifications as well, and a function which performs a statistical analysis on the parameters derived over several data sets.

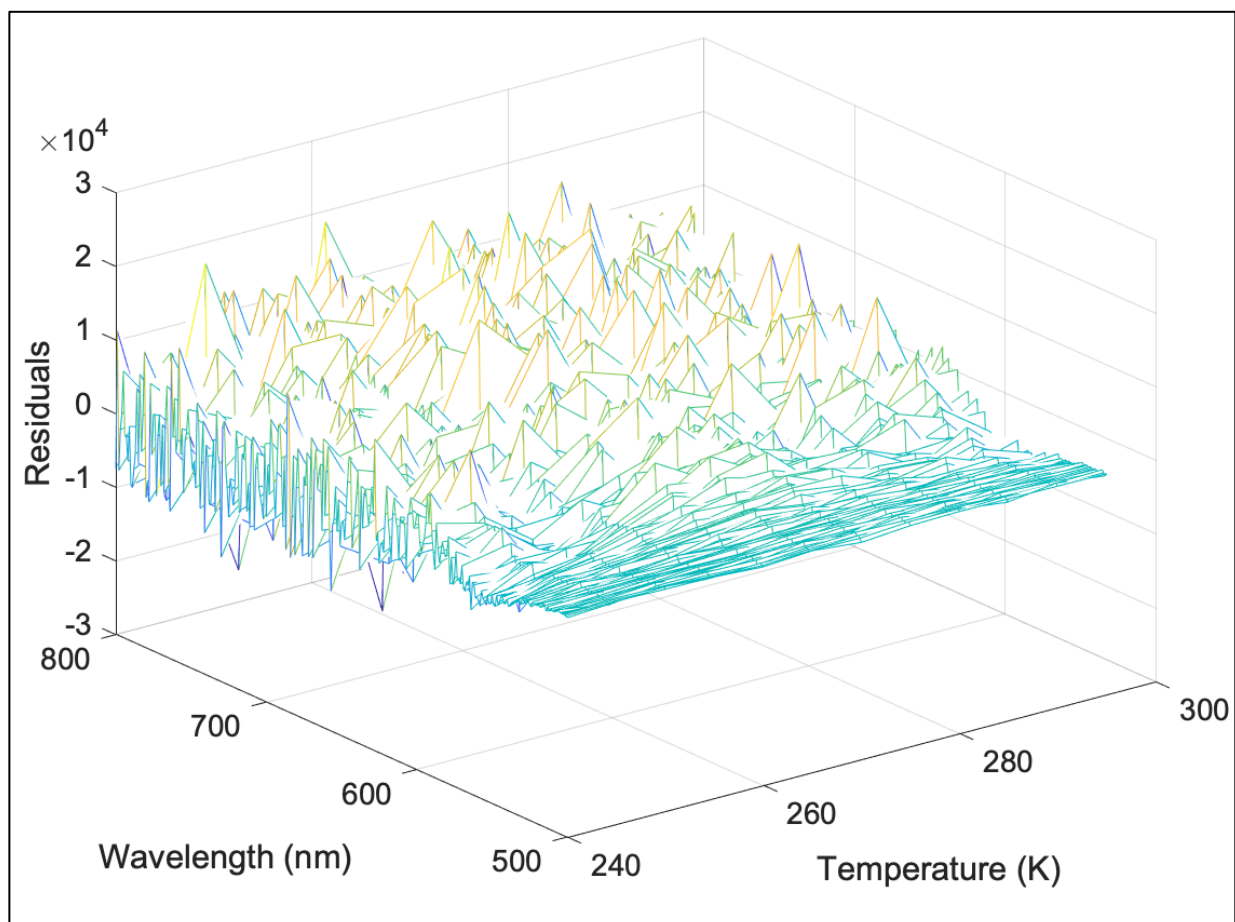


Figure S6.26 Residuals of intensity for a single iteration of the global analysis program of the steady-state emission data in DCM solvent. Note the measured intensities for this dataset are on the order of 1×10^5 .

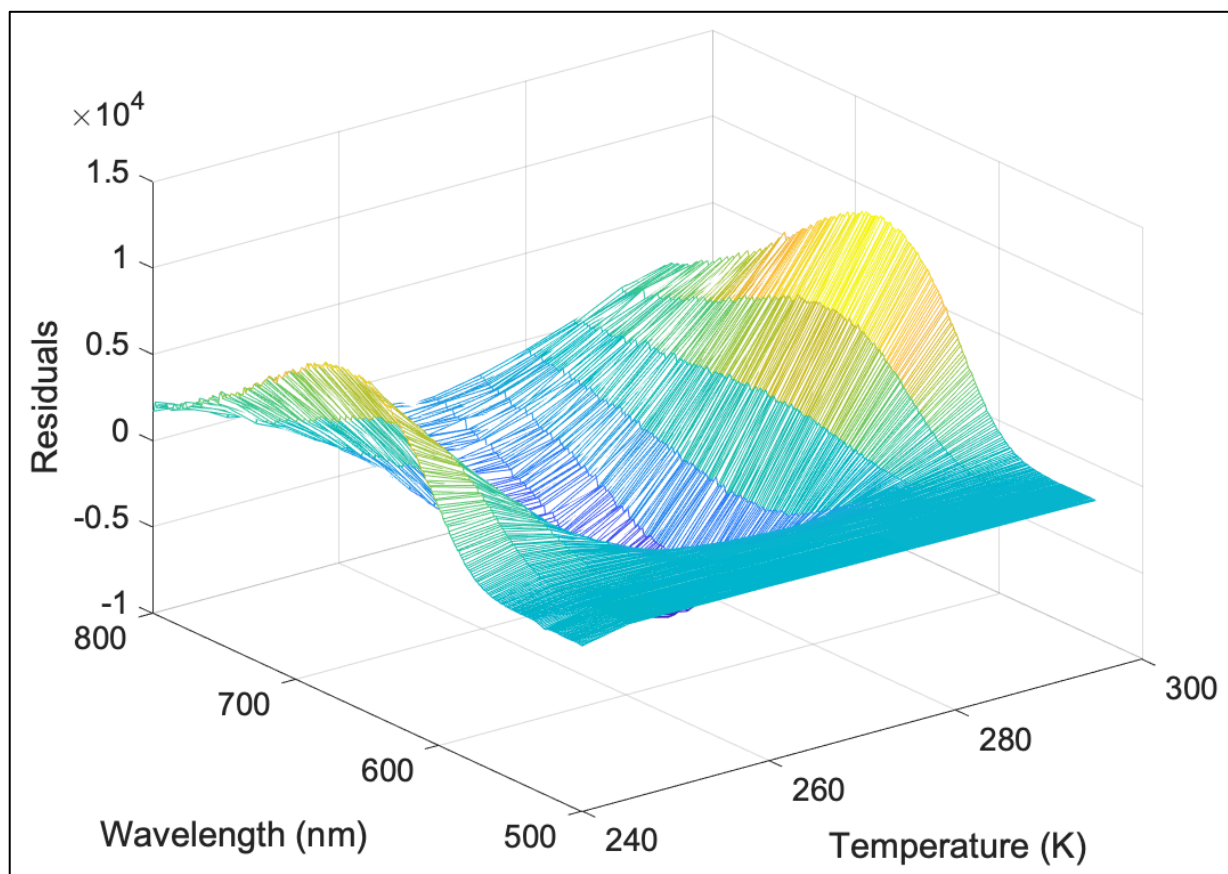


Figure S6.27: Residuals for a single iteration of the global analysis program of the steady-state emission data in acetonitrile solvent. The function which generates the temperature dependent populations is incomplete and as such, the model does not describe the parabolic temperature dependence on the emission quantum yields.

6.6.6 Arrhenius and Marcus Analysis

The preexponential factors were corrected for their temperature dependence by collection of terms. For the given Marcus equation below:

$$k_{nr} = \frac{2\pi}{\hbar} |H_{RP}|^2 \frac{1}{\sqrt{4\pi\lambda k_b T}} e^{\left(\frac{(\lambda + \Delta G)^2}{4\pi k_b T}\right)} \quad 6.15$$

All constants and the temperature in the preexponential are brought to the left-hand side to give the following:

$$\frac{\hbar\sqrt{4\pi k_b T}}{2\pi} k_{nr} = \frac{|H_{RP}|^2}{\sqrt{\lambda}} e^{\left(\frac{(\lambda+\Delta G)^2}{4\pi k_b T}\right)} \quad 6.16$$

We call these terms T_{factor} , as its magnitude depends on temperature.

$$T_{factor} k_{nr} = \frac{|H_{RP}|^2}{\sqrt{\lambda}} e^{\left(\frac{(\lambda+\Delta G)^2}{4\pi k_b T}\right)} \quad 6.17$$

The linearized version of this gives:

$$\ln(T_{factor} k_{nr}) = \left(\frac{(\lambda + \Delta G)^2}{4\pi k_b T}\right) + \ln\left(\frac{|H_{RP}|^2}{\sqrt{\lambda}}\right) \quad 6.18$$

Note that fitting a single line in the data below gives errors in the high and low regions of the plot and thus two lines were used to fit two different temperature domains. This gives two sets of parameters which are given in the main document.

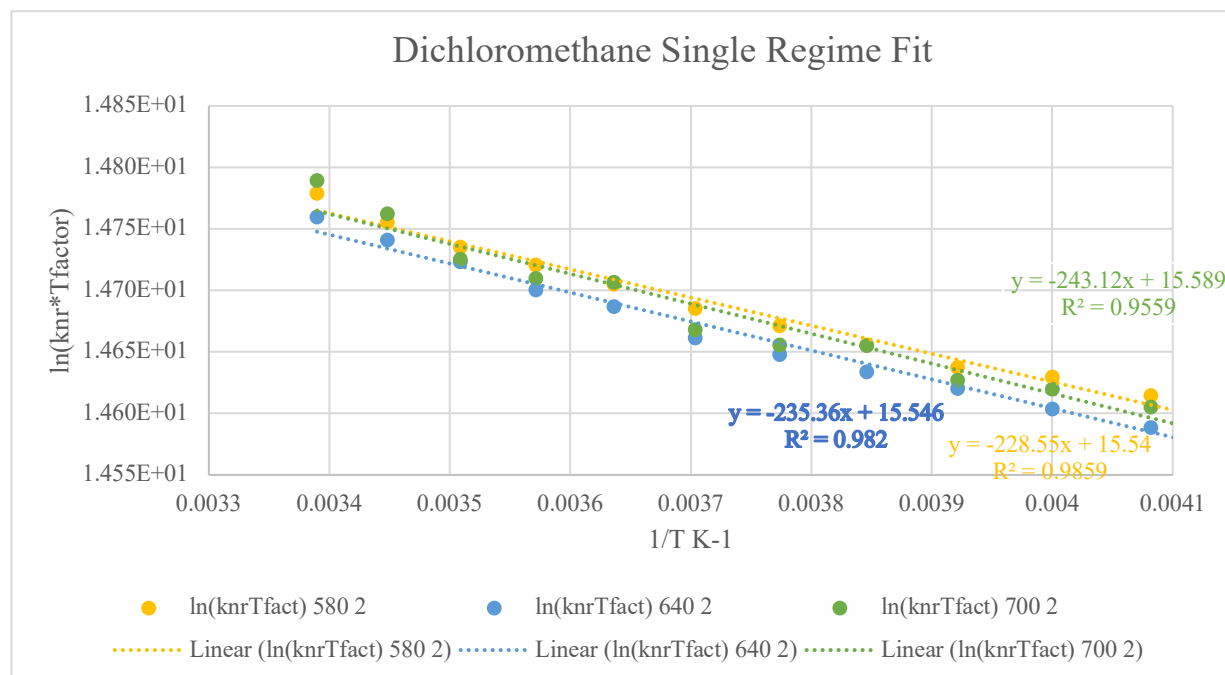


Figure S6.28: Arrhenius fit to a single line for DCM.

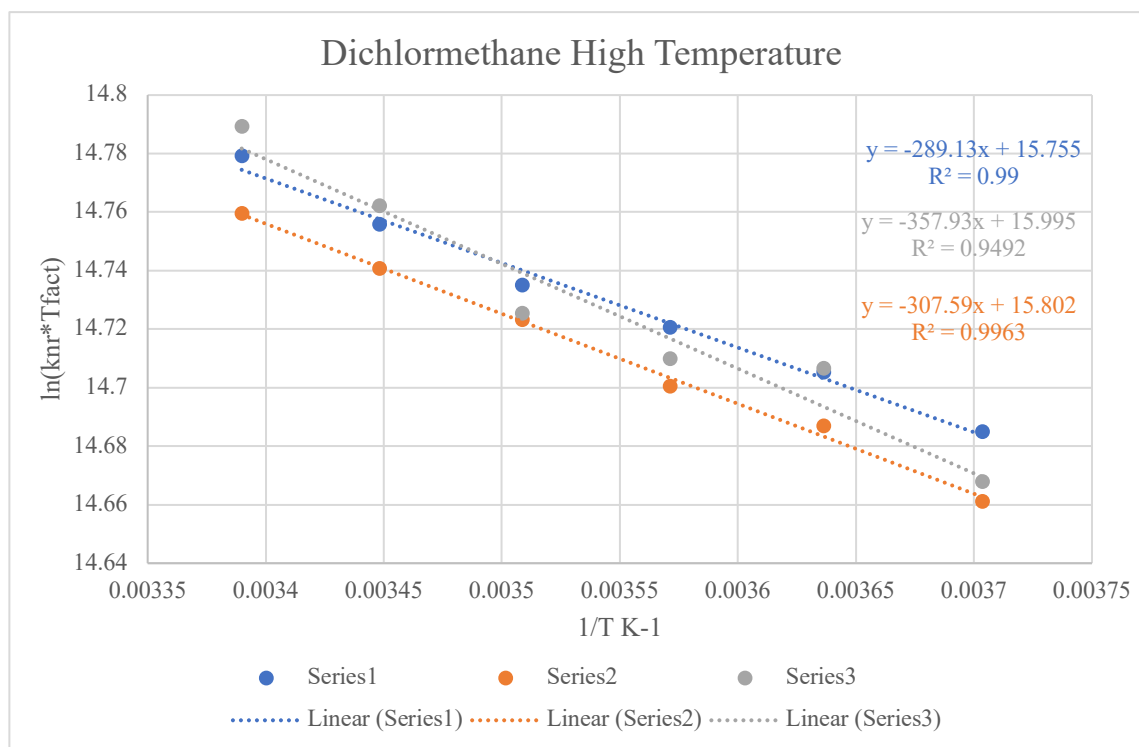


Figure S6.29: Arrhenius plots of high temp regime in DCM. Blue 580nm, Orange 640 nm, Grey 700 nm.

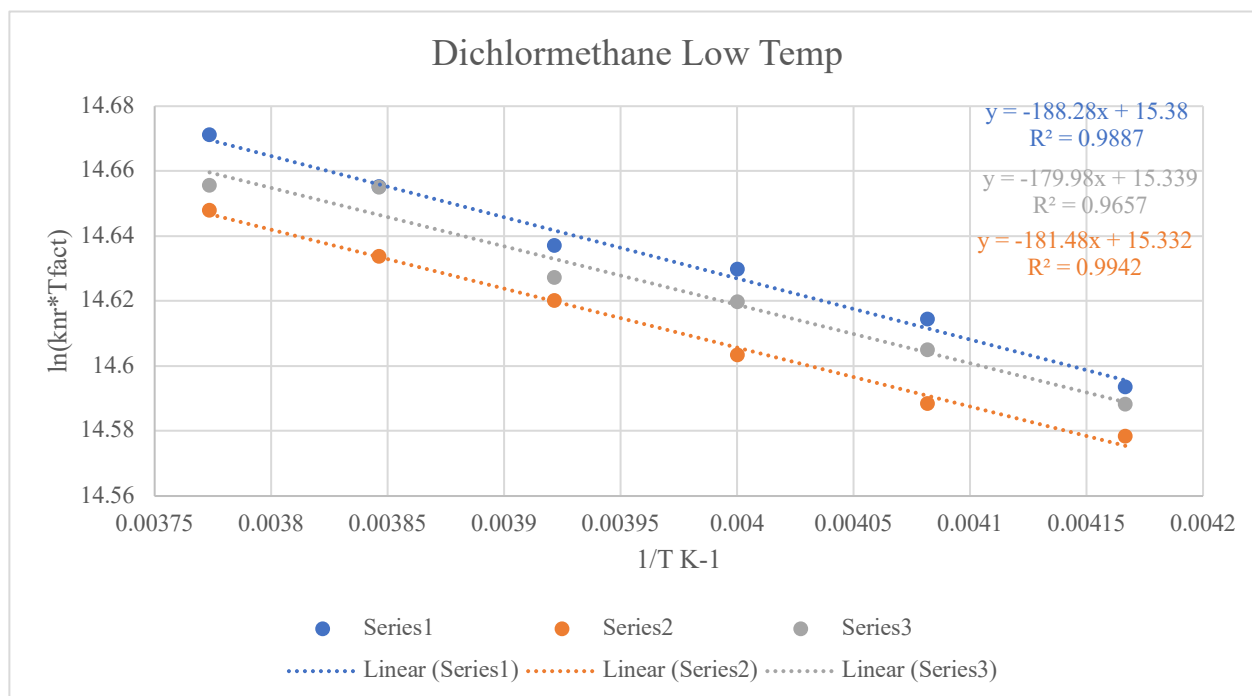


Figure S6.30: Arrhenius plots of low temp regime in DCM. Blue 580nm, Orange 640 nm, Grey 700 nm.

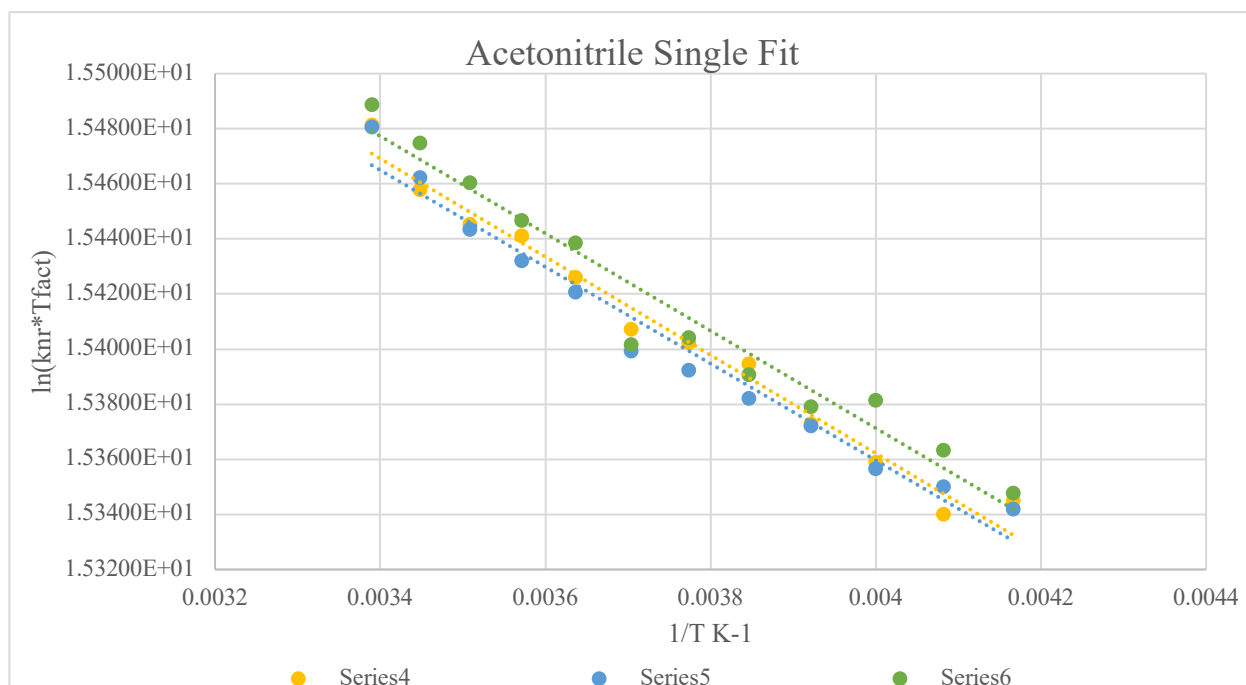


Figure S6.31: Acetonitrile Arrhenius plot fit to single temperature region.

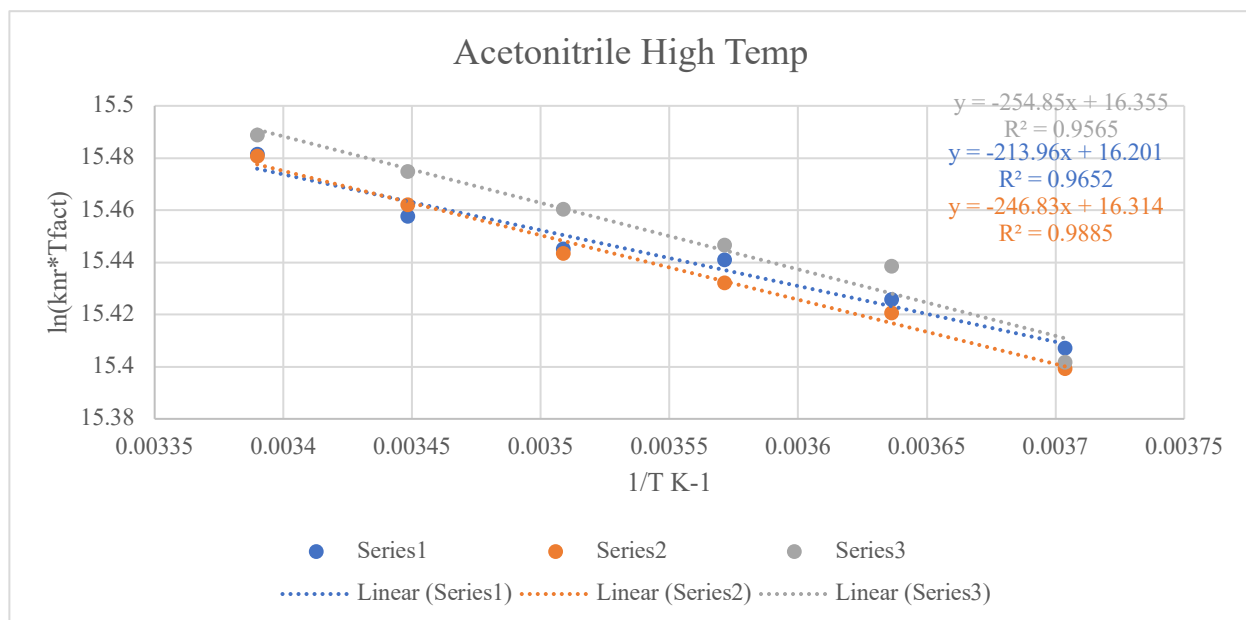


Figure S6.32: Arrhenius plots of high temp regime in MeCN. Blue 580nm, Orange 640 nm, Grey 700 nm.

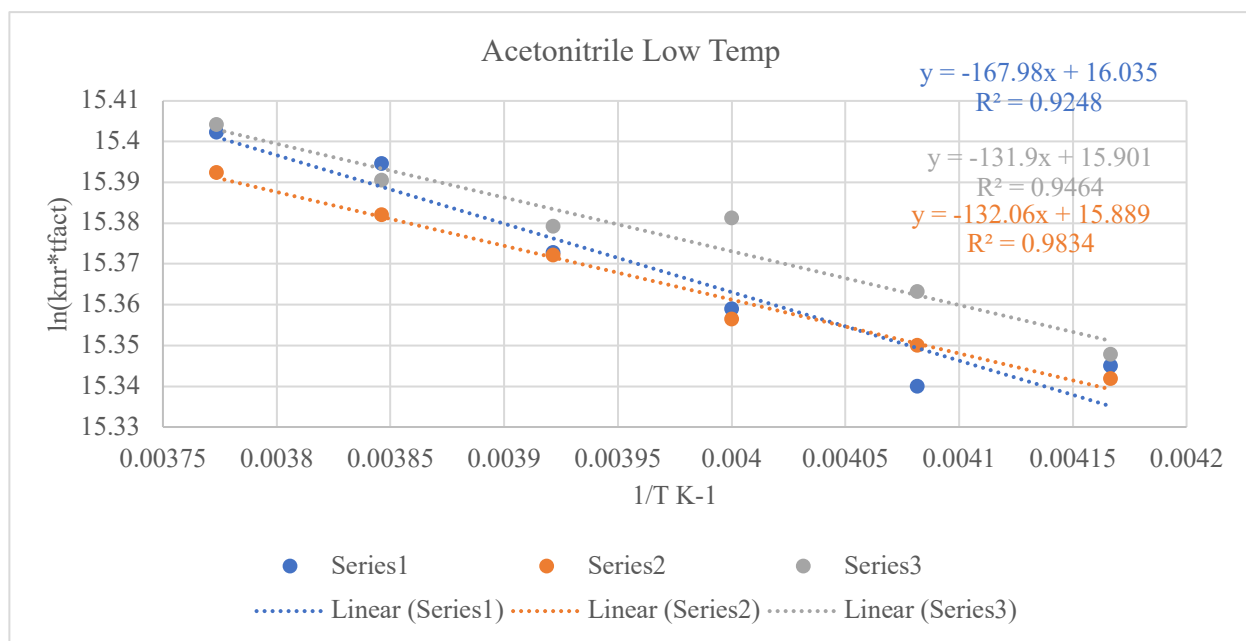


Figure S6.33: Arrhenius plots of low temp regime in MeCN. Blue 580nm, Orange 640 nm, Grey 700 nm.

6.6.7 Non-Boltzmann modeling of TADF

The model for TADF is dependent on the assumption of a fast equilibrium between states. The state populations are given as a ratio of intersystem and back intersystem crossing rate constants. This neglects the temperature dependence of these rate constants, which are dependent on the Franck-Condon weighted density of states in a Golden-Rule expression is temperature dependent.^{13,26}

Recently, a model has been proposed that describes the dynamics but does not describe the thermal properties.³⁵ The system is described by the two sets of differential equations, where the fleck indicates a differential in time.

$$S' = I - (k_{isc} + k_f + k_{nrs})S + k_{bisc}T \quad 6.19$$

$$T' = -(k_{bisc} + k_p + k_{nrt})T + k_{isc}S \quad 6.20$$

The term I is the generation rate of the singlet. Given the rate of the JT distortion process that creates it, it can be assumed to be unity.²⁵ If integrated over an extended period of time, the steady state populations can be derived giving the following. The steady state singlet population is equivalent to the expression previously derived.

$$S = \frac{I\phi_l}{(k_f + k_{nrs})\phi_l + k_{nrt} + k_p} \quad 6.21$$

$$T = \frac{I\phi_l^2}{(k_f + k_{nrs})\phi_l + k_{nrt} + k_p} \quad 6.22$$

$$\phi_l = \phi_g^{-1} = (k_{bisc} + k_{nrt} + k_p)/k_{isc} \quad 6.23$$

The term ϕ_l represents the triplet loss ratio. Its inverse represents the gain ratio. The ratio of the steady state populations yields the triplet gain ratio ϕ_g . Thus, the ratio of the steady state populations are a function of three non-radiative processes and one radiative one and independent of the rates of processes preceding the formation of the initial singlet population.

If these rate constants are modeled by an Arrhenius model in temperature, the expression for the triplet gain ratio is given by a sum of two exponential functions in temperature neglecting the rate of phosphorescence.

$$\phi_g = \frac{A_1}{A_2} e^{\frac{\Delta E_1}{k_b T}} + \frac{A_1}{A_3} e^{\frac{\Delta E_2}{k_b T}} \quad 6.24$$

$$\Delta E_1 = E_{a,2} - E_{a,1} \quad 6.25$$

$$\Delta E_2 = E_{a,3} - E_{a,1} \quad 6.26$$

The first process corresponds to $S_1 \rightarrow T_1$ by ISC, the second $T_1 \rightarrow S_1$ by bISC, and the third is $T_1 \rightarrow S_0$ process. The energy difference corresponds to the relative energy difference in the activation energies between each process. Note that this expression describes the steady state distributions as a function of temperature. This can be incorporated into the expression for the observed rate constants in place of the Boltzmann model.

$$k_{obs} = \frac{3k_{obs,t} + k_{obs,s} \left[\frac{A_1}{A_2} e^{\frac{\Delta E_1}{k_b T}} + \frac{A_1}{A_3} e^{\frac{\Delta E_2}{k_b T}} \right]}{3 + \left[\frac{A_1}{A_2} e^{\frac{\Delta E_1}{k_b T}} + \frac{A_1}{A_3} e^{\frac{\Delta E_2}{k_b T}} \right]} \quad 6.27$$

**7) CHAPTER 7: A DATA SCIENCE APPROACH TO
VIBRATIONAL ANALYSIS IN LOW-ORDER SYMMETRY
SYSTEMS**

7.1 INTRODUCTION

7.1.1 Tracking Multi-dimensional Perturbations of Synthetic Modification

In synthetic design, and chemistry more broadly, structure property relationships are key for understanding.¹⁻⁵ A structural modification A has leads to an x% increase in property B. This is generally sufficient if a particular modification leads to low dimensionality perturbations with linear responses. Consider the y-axis strategy for increasing ligand field strength using carbene ligands. Higher donor-strength leads to a better stabilization of bonding orbitals and a proportional increase in the energy of anti-bonding orbitals which increases the energy of excited states who have significant orbital contribution of these orbitals called ligand field (LF) states. This is a unidimensional problem where the ligand field strength (LFS) and excited state lifetimes are nearly 1:1 mappings.

This does not mean that the inputs of this strategy are not complex, proper ligand design is quite difficult and must consider many diverse factors. This has been used to great effect in systems like iron carbenes. The outputs of the y-axis strategy are simple, however. The problem becomes much more difficult cases in which multidimensional or non-linear outputs may result from a modification.^{6,7} This would seem to be the case with the x-axis strategy, in which there is no reason a particular synthetic modification should result in a linear response or a perturbation to a single reaction coordinate. Consider the case of the $[\text{Fe}(\text{dcpp})_2]^{2+}$ a system with increased symmetry of the ligand field, led to stronger vibronic coupling and shorter overall lifetimes.^{8,9} Anyone who has tried to catch a poplar seed knows the difficulty of reaching for the seed and unintentionally sending it on a different path, making it difficult to catch. Synthetic modifications with the intention disrupting vibronic motion along a particular axis is a similar

problem. A framework that can describes these kinetic effects of synthetic modification in a digestible, predictable, and useful way is thus necessary.

In studying the effects of synthetic modification on the kinetics of excited state deactivation, experimental data is validated with computational output.^{2,10–13} Visualizations of vibrations serve as a model from which a modification can be devised to dampen modes that would otherwise bring an excited population in the proximity of intersections on relevant potential energy surfaces, the regions in which electronic coupling is highest and the B.O. approximation breaks down. This is probably best illustrated when one considers the vibronic coupling to the flattening distortion in Cu(I) polypyridyls. The flattening distortion leads to an increased rate of non-radiative decay in accordance with the energy gap law. However, this has been shown to be particularly effective for Cu(I) systems as there are few other modes which will drive the deactivation. This statement is a result of experimental observation and could not have been made *a priori*. It also cannot be extrapolated to other systems, for example Fe(II) pseudo-octahedral complexes, where there may be multiple coordinates which lead to excited state deactivation.^{2,14} This requires a lot of experimentation to find out what frequencies are relevant. A comprehensive example from the McCusker group was the design of an Fe(II) cage complex which was synthetically tailored to disrupt nuclear degrees of freedom which were found to be relevant by coherence measurements.² These coherent measurements found relevant degrees of freedom in conjunction with computational modeling and were gauged as the appropriate modes to synthetically tailor by their agreement with experiment.

The term “good agreement” is dependent on several factors including a vibration’s relative isolation from other modes. This is the reason that -CN functionalities are used as vibrational tags for probing excited state populations due to their resonances being isolated.^{15,16}

Figure 7.1 illustrate a complex in which this concept was applied to track rates of intervibrational relaxation in the charge transfer excited states of Ru(II) compounds. Other vibrations, in portions of the spectrum with a relatively large density of states, the determination of being in “good agreement” becomes difficult. In this case type 2 errors abound, where visualizations of vibrational modes, that are not represented by measured vibrations, could be utilized in molecular design. Fortunately, coherence measurements allow for a narrowed set of modes highlighted by their measured frequencies.

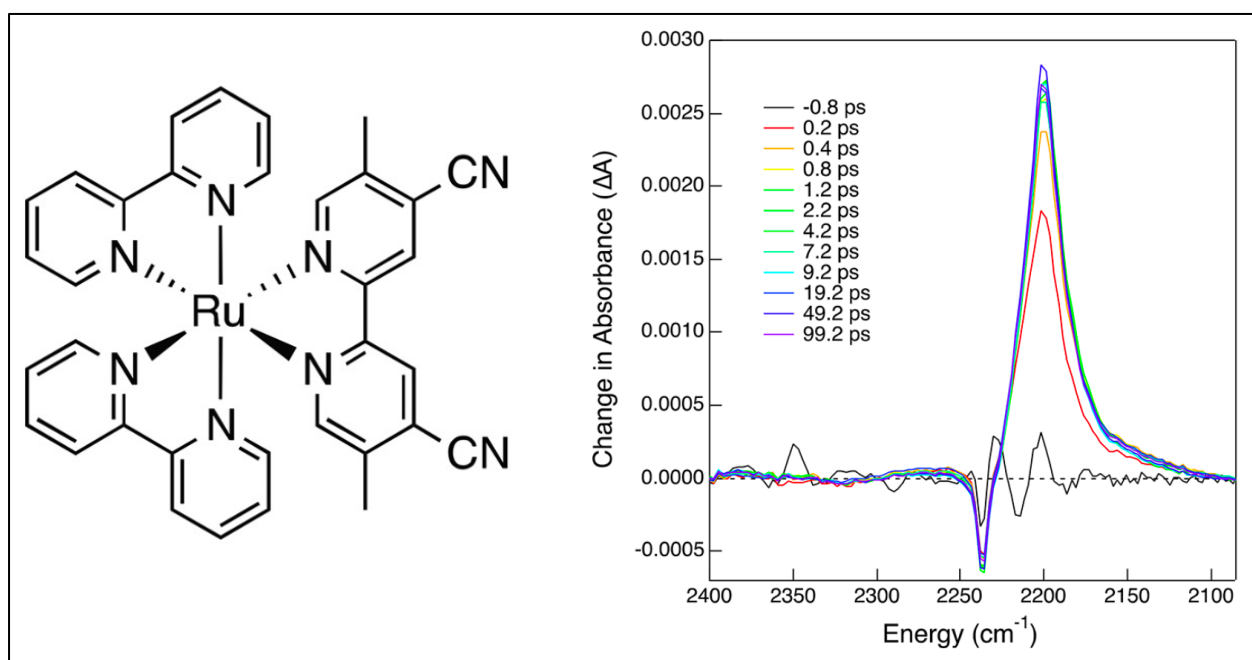
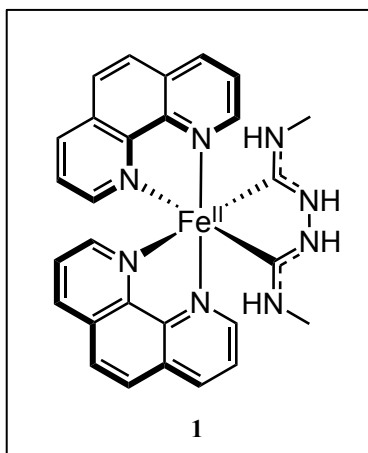


Figure 7.1: Structure of a Ru(II) complex which leverages the change in energy of the the cyano stretching frequency upon reduction of the ligand in the MLCT. Taken from reference 11.

Importantly, synthetic modifications are not neutral. Structural modification causes frequencies to change within a certain range based on steric and electronic effects. In a homologous series these perturbations may only slightly change the frequency. The change in frequency, coupled with the large density of vibrational states means it is difficult to track vibrations across modifications or even electronic states. An example of electronic perturbation can be given by the case of the $[\text{Fe}(\text{phen})_2(\text{C}_4\text{H}_{10}\text{N}_4)]^{2+}$ complex (**1**) studied in the first chapter. It

is important to note the 106 cm^{-1} mode for coupling the Jahn-Teller (JT) distortion in the triplet state was highlighted. The reorganization energy of the $^3\text{MC} \rightarrow ^1\text{MC}$ process is large, suggesting displaced potentials. It stands to reason that this mode contributes significantly to the ground state recovery process. What happens to this mode in other states, for example $^3\text{MLCT}$, ^5MC , and ^1MC , if these do not exhibit the same electronic deformation as the ^3MC ? As all these states have the same number of normal modes of vibration ($3N-6$), something approximating the 106 cm^{-1} mode should be present in each state, which would act as a vibrational acceptor as a matter of conservation of momentum. As the JT distorted state has a unique electronic structure and therefore a different vibrational force constant, it is not likely that these states will exhibit a similar frequency. What we are concerned about is the nuclear trajectories and not the frequencies. Upon looking at the vibrational frequencies, it is not immediately obvious which vibrations map onto one another.



Drawing 7.1: The complex 1 used in this chapter to develop the method.

While this uncertainty is most clear in the case of the JT distorted triplet state, this is still true across the set of all vibrations to some degree or another and may be more interesting. Consider the 71 cm^{-1} mode in the ^3MC state. If we were to match frequencies with ^5MC we would find the best agreement with this frequency is 75 cm^{-1} . Clearly these vibrations are distinct

when visualized as done in figure 7.2. We find by inspection that the 84 cm^{-1} mode in ^5MC is better suited as a match. Rather than using the frequency to find the mode, we can find the mode first and then draw chemical conclusions based on the change in frequency. For example, the increased frequency (71 to 84 cm^{-1}) of this carbene bending mode suggests increased rigidity. This rigidity is likely due to increased Fe-C bond length and the ability for Fe to donate to the empty p-orbital of the carbene is reduced. This electronic deficiency of the carbene carbons is compensated for by increased nitrogen lone pair donation, increasing double bond character and thus rigidity which should increase the force constant for such a vibration. The ability to map between modes allows for a rich discussion about structural and electronic perturbation.

It is important to restate that we are describing the system in terms of trajectories first and not frequencies. These matched frequencies allow us to utilize new language to describe how a synthetic modification could act in a homologous series. For example, changing a methyl group to an ethyl group and calculating the excited state configurations, we can compare effect on the set of matched vibrations which is comprised of modes 71 cm^{-1} and 84 cm^{-1} in the triplet and quintet respectively, which should have counterparts in the substituted compound.

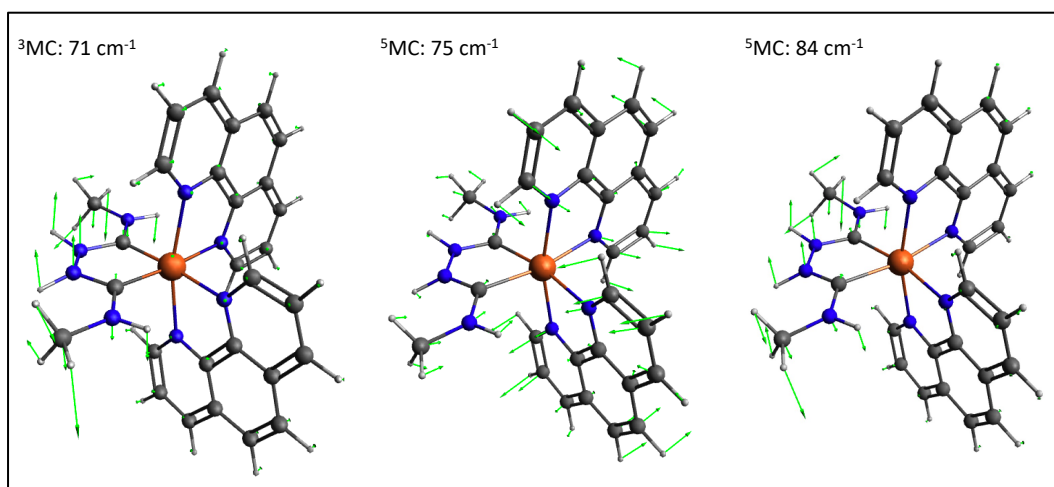


Figure 7.2: Manually matched vibrations between the triplet and the quintet states of **1**.

7.1.2 *Methods of Vibrational Analysis*

While the discussion above was facilitated by a trivial examination of the vibrations in a small frequency range, a robust and high throughput method for creating these sets of vibrations across spin-states, modifications or even density functionals would be very useful. This concept of a matched set is not new, however. It is the basis for functional group analysis. For example, one could consider the entire set of C=O stretching normal modes in all small molecule ketones. This is relatively straightforward to do as the vibration is somewhat isolated and sharp. Functional group analysis becomes difficult in regions of the IR spectrum with a large density of states, best illustrated by the ‘fingerprint’ region that occurs at low frequency.

This fingerprint region can be analyzed if a certain degree of symmetry is present in the molecule. Utilizing group theory, linear transformations that are defined in a molecule’s point group are applied to a set of cartesian basis vectors. The resultant change in the basis vectors, or the lack thereof, determine how a molecule transforms by a given symmetry element. Vibrations that transform in the same way are grouped by symmetry labels. See chapter 3 of *Molecular Symmetry and Group Theory* by Carter for a robust discussion on the topic.²⁶ The number of groupings possible for this type of analysis is proportional to the number of symmetry elements in each system. In asymmetric systems this type of analysis becomes somewhat useless as there are no linear transformations to apply to basis vectors which could allow for categorization. Symmetry, while useful is limiting in that it has a limited number of labels.

Thus, we would like another method in which the number of vibrations scales with the number of vibrations. The Singular Value Decomposition (SVD) is a type of linear transform which is defined for every 2D matrix.¹⁷ Its application to a set of displacement vectors is thus symmetry independent and can work for any system. As discussed in earlier chapters, it is

commonly used in spectroscopy to decompose multidimensional data into eigenspectra which can be fit globally to propose kinetic models of excited state processes. See the appendix for chapter 6 for a discussion of the SVD to build intuition on this topic. In symmetry analysis, the number of categories a vibration can belong to depend on the number of symmetry elements in its point group. The number of categories a vibration could belong to in the SVD by contrast is dependent on the number inputs, in effect the number of atoms. This provides a more fine-grained method for categorization. The next section builds intuition around the SVD and how it could be utilized in vibrational analysis.

7.1.3 Image Recognition and its Potential Application for Vibrational Analysis

Application of the SVD to vibrations has significant parallels with image recognition. We therefore take this section to provide intuition of image recognition and its similarities with vibrational analysis. It should be noted that much of this discussion comes from Data Driven Science and Engineering by Steve Brunton and Nathan Kutz.¹⁷ Dr. Brunton also has excellent YouTube resources on these topics and more.

Image recognition utilizes data reduction to break down an image into a linear combination of vectors that describe ‘features’ of the object. In facial recognition for example, these are the general features are highlighted in figure 7.3. The vectors, that make up a face and look like shadowy outlines of a head, noses, brows, and other features. These are the eigenvectors of the transform applied. Because they are face-like they are called ‘eigenfaces’ to distinguish them from their linear combinations which are what we would identify as a real face. Figure 7.3 which is open access, shows former President George Bush and the coefficients of the various components that make up the image, which are obtained by decomposition (SVD is one such decomposition algorithm). Changing the coefficients in the linear combination of

components would yield a different face. This makes the sequence of coefficients a unique description of the image. Sets of these coefficients are called encodings.

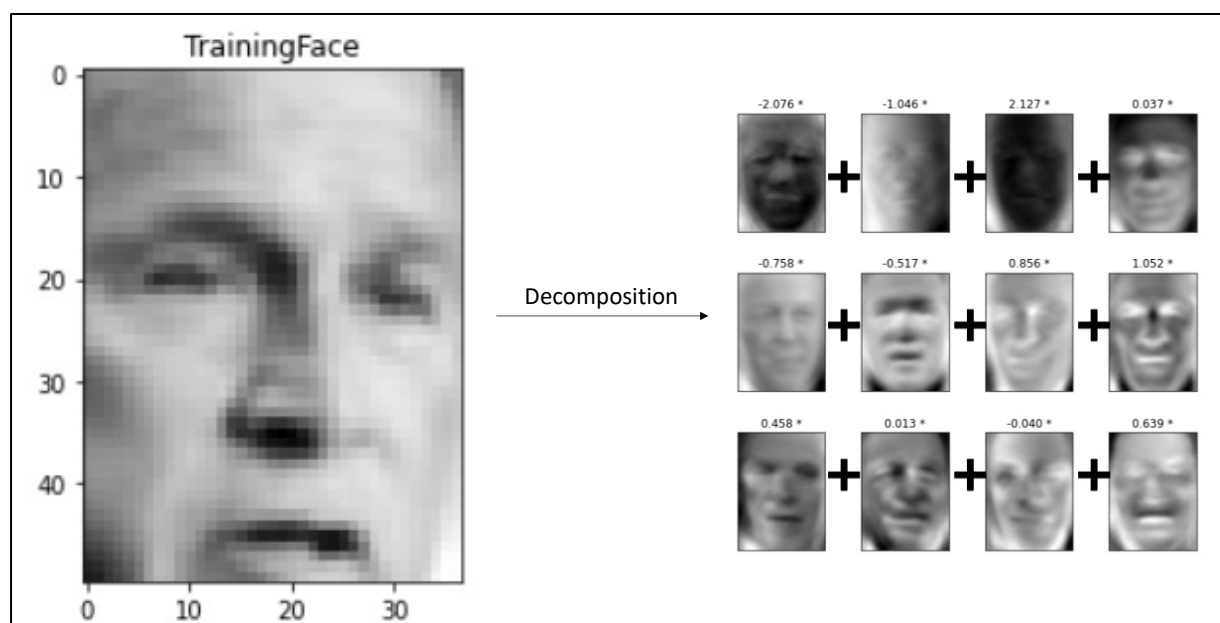


Figure 7.3: Decomposition of an image into eigenfaces. The linear combination of eigenfaces is what defines the image. Different weighting factors will yield different faces.

The encodings of the image allow it to be compared with other images which have their own encodings. Similar images have similar encodings, similar, coefficients of their eigenfaces. This allows for measurement of similarity between images. Facial recognition software to a first approximation, involves input of a new face, which is decomposed to its encodings and compared with a database of previously generated encodings, from which a match is or is not found. This is a simplification as modern image recognition utilizes machine learning and neural networks that are more complex than just the comparison of the eigenface coefficients. For our purposes however, this approximation is sufficient.

To understand how this applies to a molecular vibration, we need to consider what an image is to a computer. A greyscale image is a matrix, the dimensions of which are the number of pixels in that image. Each pixel has a specific index, which if changed, changes the image.

Each numerical entry in that matrix has some magnitude between 0 and 255. The value determines the brightness of that pixel. True black is 0 and true white is 255. A 100x100 pixel image can represent anything by changing the values of the pixel at a defined index. This 100x100 pixel image can be reshaped into a 10,000x1 vector. What is an image then? It is an index and a brightness vector at that index. A color image is similar, but instead of a single index and vector for a pixel, each pixel has three channels which describe the RGB coloration, and again the magnitude of these vectors determines the brightness of each color in each channel.

We discussed in the previous section of the utility of considering the displacement vectors of a vibration over their frequency. A normal mode's displacement vectors can be treated in the same way as a digital image, where an atom has a defined index position (pixel) which has a particular displacement vector (brightness) associated with it. Thus, a particular molecule, is analogous to 10,000x1 but instead of 10,000 indices there is the number of atoms in the molecule. Each vibration is different set of brightness vectors on this index. This can actually be demonstrated by considering figure 7.4 which depicts the 71 cm^{-1} mode of the triplet state of **1** and its corresponding .bmp image.

What is pictured is a 19x2 pixel image magnified severalfold. Where 19 is the number of atoms taken from the structure. These atoms were the 18 atoms closest to and including the metal center in a through bond fashion. The red and green pixels represent the positive and negative directions respectively. The second dimension is a mirror image of the first, to eliminate the absolute orientation of vector direction. The first 6 pixels on the left-hand side correspond to the carbene ligand. The first two are very dark as they correspond with the carbene carbons. The latter four represent the nitrogens of the backbone which show significant magnitude of their displacement vectors and thus are very bright. The dark pixels in the middle correspond to the

coordinating and adjacent atoms of the phenanthroline ligands, which have very small displacement vectors in this mode and thus have a very low brightness.

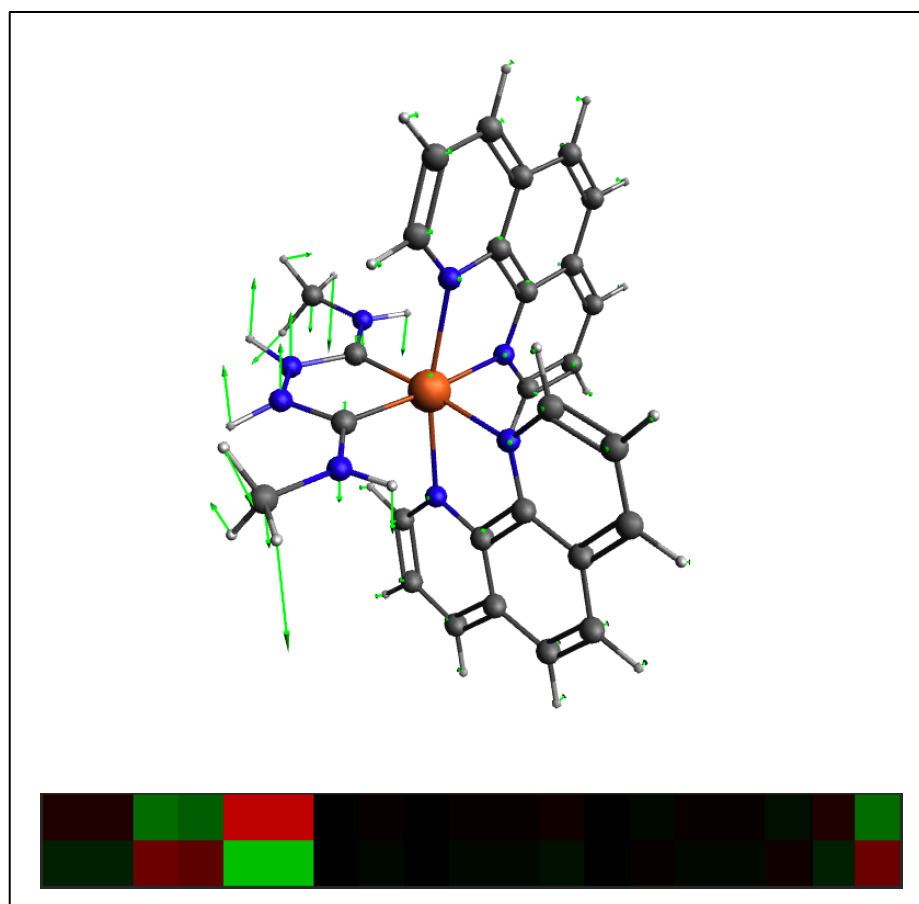


Figure 7.4: Structural representation of a vibration. (bottom) a .bmp image representation of the same vibration with the 19 inner atoms.

The transform of the vibrational displacement vectors into images is not necessary, if the displacement vectors themselves, are ordered by atomic position, they can be utilized without conversion to the image. This concept can be applied across synthetic modifications and spin states, from which vibrations can be compared. The only requirement is that each atomic position (pixel) stays consistent throughout the analysis. For example, atomic position 19 should represent the motion of the Fe atom in every molecule. This ordering is what will be called the ordered basis.

What information is chosen for the ordered basis is key. The SVD is highly dependent on what is included from the start (again see Ch. 6 appendix). When developing the encodings of facial images, extra information is removed. Removal of noise, i.e. things in the background, from an image is key for the encodings to be specific to what the image is trying to represent, which is a face. You have likely participated in the process of removing noise from images, as it is commonly used in ReCAPTCHA verifications, an online confirmation mechanism to demonstrate you are in fact not a robot. A portion of an image is selected by the human user given a prompt. For example, selecting the portion of an image that contains a fire hydrant, is then used to classify a fire hydrant from other objects that may also be present in similar environments like sidewalks, lamp posts etc.

With molecular homologues, which may have a different number of atoms, it is therefore crucial to set what atomic basis is used, equivalent to cropping out portions of an image which are irrelevant and may provide misclassification. For example, modified $[\text{Fe}(\text{bpy})_3]^{2+}$ species, may have different numbers of atoms due to the substituents in the 4,4' position. However, they still contain a common core of atoms, particularly near the metal center. The vibrational motion of this central core of atoms may be analyzed in the manner described above and used to benchmark the effects of synthetic modifications on the displacement vectors of the atoms.

7.1.4 Principle-Component Analysis and its Applications for Normal-Mode Analysis

Once decomposed and encoded, a molecular vibration can be compared with other vibrations which have undergone a similar procedure. Principle Component Analysis (PCA) is a decomposition algorithm that leverages the SVD for decomposition that can be used to represent the data. This has been used before for a normal mode analysis in protein systems. For example, it has been used to capture the long period normal modes of vibration present in molecular-

mechanics simulations of protein motion.¹⁸ Here, PCA allowed the authors to take generalized information (i.e. a random walk atomic motions) to find temporally long range structure in that protein motion, which are its normal modes. In this chapter we intend to do something similar however, this concept is intended to be run in the opposite direction, taking structured information, like a well-defined normal mode of vibration and generalizing, not over time but over structure.

The remainder of this chapter attempts to treat molecular vibrations in the manner described in this introduction. Computed displacement vectors will be decomposed by the SVD and their applications to structural understanding will be discussed as the methodology is developed throughout. Then the modes across spin states will be compared utilizing the method, structural intuition, and PCA. Different structural modifications will be examined. As the methodology was developed primarily on the spin-states of **1**, the form the discussion takes, does depend on this system to some degree. Compound specific assumptions will be made clear where applicable. The method will later be applied Cr(III) systems studied by our group as a case study at the end of this chapter.

7.2 EXPERIMENTAL

7.2.1 General

The computational modeling for the Fe(II) carbene systems were covered in chapters 1 and 3 of this dissertation. The computational modeling of the Cr(acac)₃ systems was performed by Dr. Bryan Paulus and the procedures for which are outlined in his dissertation and other documents.²⁷ The coherence measurements for all species in this dissertation were measured by him also and the procedures for which are outlined in his dissertation and other documents.

7.2.2 Algorithms and Data Processing

Visualization of molecular vibrations were done in Avogadro from Gaussian 16 .log output files. Programmatic acquisition of computational data like the frequencies and displacement vectors, were performed in a Jupyter Notebook, running python 3.0 with the cclib open-source computational chemistry library of functions (found at: cclib.github.io). All algorithms utilizing this library to extract and organize data were written by the author. Copies of all utilized code is printed in the appendix to this chapter. All subsequent data processing was performed in MATLAB unless specified otherwise, using code written by the author.

7.3 RESULTS AND DISCUSSION

7.3.1 Establishing the Atomic Basis

First a basis must be chosen for our system. As we are concerned with correlations across chemical structures, this imposed structure must be general enough to be applicable to all systems studied but not too general as to lose information. Utilizing the exact structure would limit the generalizability. For example, consider the figure below which highlights the structurally equivalent atoms between **1** and **2** (this was studied in chapter 3). The structure of **1** could almost described the entire structure of **2**, while the reverse cannot be said as the former contains a larger set of atoms. It is true that as the number of normal modes of vibration is dependent on the number of atoms, which means that there will be modes which cannot match. This however is not detrimental and in fact can be useful information.

In choosing the basis, the type of atom and its local symmetry must also be considered too. In the **1** and DMP case again, each has a carbon atom attached to the periphery of the carbene. In the former case, it is a sp^3 hybridized carbon and a sp^2 hybridized carbon in the latter. These are carbons in the same position; however, they are not equivalent. We could evoke a

symmetry argument highlight their inequivalence by suggesting their local vibrational environment should be different due to connectivity and electronic considerations.

From chemical intuition, the atoms highlighted in the figure below will represent our ordered array of atoms. This does not include the hydrogen atoms or peripheral phen atoms. This 19-atom basis was chosen to simplify the discussion but still allow for the maximum amount of information to be included for all dimensions of the system. This will be true for all the discussion with the carbene systems unless otherwise specified. For example, atom 1 will always be a carbene carbon and motion associated with atom 1 will always be associated with the carbene carbon.

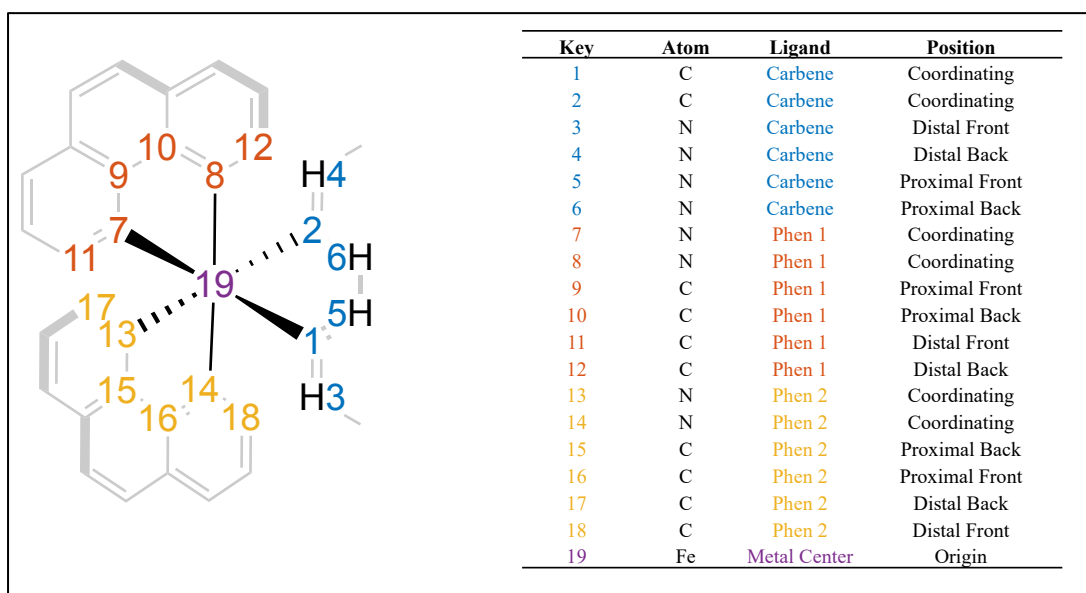


Figure 7.5: Atomic basis selection of **1**. The number of atoms included were minimized to maximize the generality. The accompanying table includes descriptions of each atom as well as being color coded to correspond to the ligand environment.

In machine learning for image recognition, the algorithm determines the best basis from which to describe the system, i.e. the system learns what information is useful and what is not. Assuming the analogy between images and vibrations hold, this could be possible for establishing our basis and may be preferable in future iterations in that it is unbiased. From this

perspective, the method presented here is mathematically non-rigorous, however in practice, chemical intuition seems to do an adequate job of picking relevant atoms as will be shown.

A method for quickly selecting a basis however in a fast and accurate way, the workflow of which is shown in figure 7.6. This involves the modification of the Z matrix, which contains the atoms cartesian coordinates. Atoms are excluded from the basis in Avogadro by deletion and generation of the remaining atoms' cartesian coordinates giving a matrix Z' . These coordinates are then compared with the native Z matrix. Indices are generated to create Boolean vector with size $n \times 1$, where n is number of atoms in the selected basis. The displacement vectors are in a $(3N-6) \times n \times 3$ matrix. The Boolean vector is applied to the set of basis vectors for each vibration to yield a matrix of size $(3N-6) \times n \times 3$.

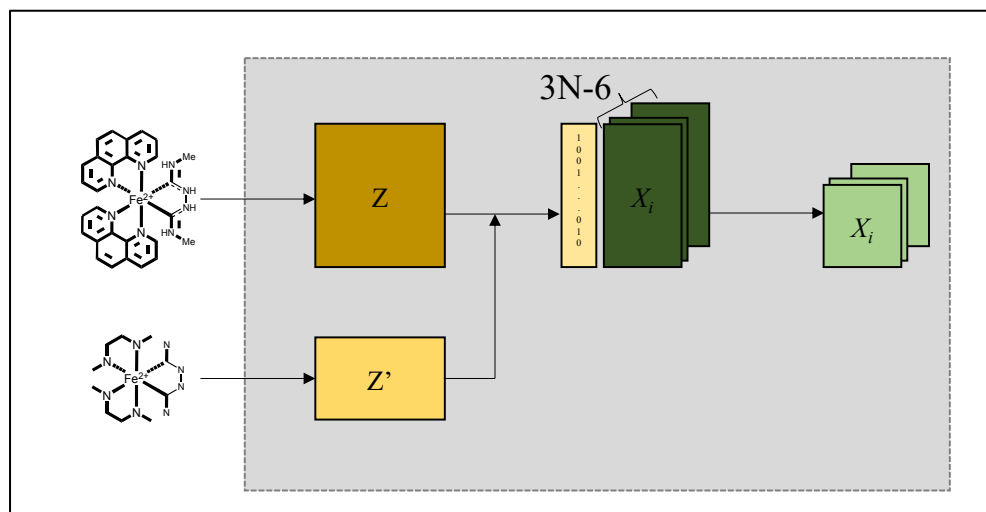


Figure 7.6: pictorial representation of the basis selection algorithm. A set of coordinates are selected in Avagadro to make a matrix Z' . This is utilized along with the full Z matrix to create a binary vector which contains the information of what should be included. This is then applied to the cartesian descriptions of each vibration and creating a lower dimension X matrix.

7.3.2 Establishing the Vector Basis

For the three ligand field states of **1**, we obtain our displacement vectors from the sum of the three cartesian values associated with each atom of the atomic basis. This matrix we will call X and has dimensions 183×19 . Here 183 is the number of normal modes of vibration and 19 is

the basis n . It is important to distinguish between the atomic basis and the vector basis here. It is entirely possible to skip the summation step in which case $\mathbf{X}$ would be of size 183×57 , where each atom has three vectors associated with it one for each of the cartesian directions. This likely to be the best route for achieving our goals in mapping vibrational frequencies, as the sum of the individual vectors reduces the information present, which could be utilized to distinguish between vibrations. It will become obvious in latter discussions however that having the vector basis and the atom basis equal is advantageous for interpretability as it localizes results in the molecular structure and not in the cartesian space.

7.3.3 Decomposing $\mathbf{X}$

The matrix $\mathbf{X}$ can be decomposed by SVD. This gives the data in three orthogonal matrices described by the equation below. Each of which contains simplified forms of the information present in $\mathbf{X}$ that is inaccessible by mere inspection.

$$\mathbf{X} = \sum_{i=1}^{19} U_i * S_i * V_i' \quad 7.1$$

The right eigenvector, $\mathbf{V}$, a 19×19 matrix, describes the weight of each atom's contribution to a particular singular vector. If the three-space vector basis were used, this would balloon into a much larger and more complicated matrix. To illustrate its utility, the heatmap of the values in $\mathbf{V}$ in figure 7.7 shows the contribution of each atom in the basis by the singular values which are on the x-axis. These 19 vectors distributed on the x-axis are equivalent to the eigenfaces discussed in the introduction. Therefore, these will be called eigenmodes. Notice it is possible to group the eigenmodes based on their ligand character, which suggests that eigenmodes contains structural information. The labels on the x-axis are the magnitudes of the singular values that weight each eigenmode.

Singular values in the $\mathbf{S}$ matrix, describe the weighting factors of each component to the whole displacement space. The larger the value, the larger its contribution to the displacement space. In facial recognition, facial features which are common to a set of faces, have large singular values. The chemical meaning of the magnitude of these singular values can be illustrated by considering the lowest significance singular value (0.47) in the lower right-hand corner of figure 7.7. Significant intensity is found for atom 19, which corresponds to Fe. Due to its mass and the relationship between momentum and displacement, it's not surprising that the atom associated with the lowest singular value is the Fe atom.

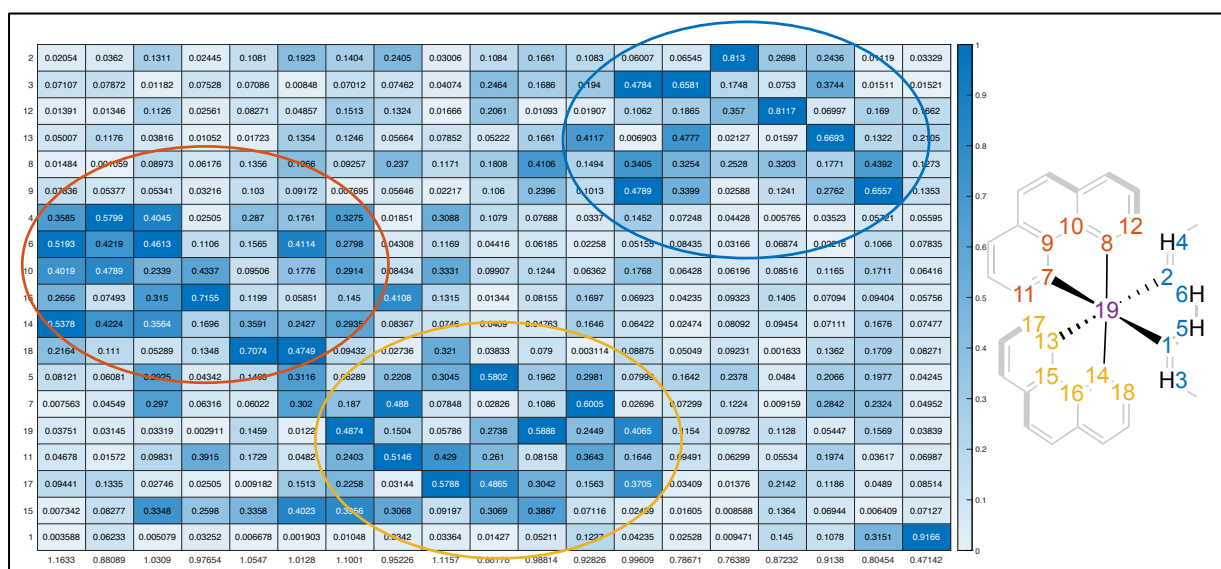


Figure 7.7: Heatmap representation of the $\mathbf{V}$ vectors from the decomposed displacement matrix for the triplet state of **1** organized by their ligand origin. The color of each oval corresponds to the ligand origin.

While its significance is relatively low, it does not mean that it is unimportant. In fact, the singular values are evenly distributed between all components, with the largest component representing less than 10% of the spread in the data as shown in the cumulative significance plot in figure 7.8. This is not surprising as normal modes of vibrations are orthonormal with respect to one another. Thus, not any 2D matrix could be used as described in the introduction but rather an evenly distributed matrix of atomic displacements must be used to derive useful information.

The U matrix describes the coefficients for linear combination of eigenmodes that make up a specific calculated normal mode. This 183x19, matrix is equivalent to the set of coefficients of the eigenfaces in figure 7.3. This allows a similarity comparison with other modes that have similar coefficients in the U vectors.

Figure 7.7 shows that the eigenmodes contains vibrational information that is structurally dependent, thus linear combinations of this vibrational information also contains structural information. The next section establishes this further.

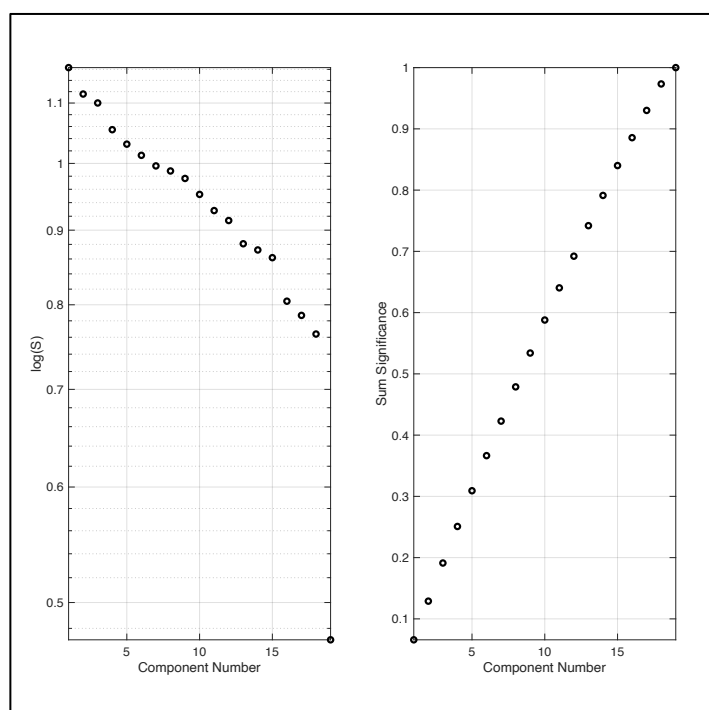


Figure 7.8: Singular values from the decomposition of the displacement matrix for the triplet state of **1**. Note that no component is a viable description of the data by itself.

7.3.4 Further Exploring the Right Singular Vectors

The right singular vectors (RSV) give the atom-by-atom description of the data called eigenmodes. They are equivalent to the shadowy face like images (eigenfaces) in figure 3. They contain features of the vibrations. Intuition can be gained by exploring these further. The following figures take the V vectors for ^5MC , ^3MC , and ^1MC states of **1** and display them as stem

diagrams. They are ordered by their respective singular values. Where the largest is at the top left and the smallest is at the bottom. The amplitudes of the stems are correlated with how relevant a particular atom is in that vector. The sign of the amplitude is not of absolute importance but is important in a relative sense as it allows for distinguishing between atomic motion of similar amplitudes. For example, panel 1 in the figure 7.9 and figure 7.10 shows a similar oscillating profile in orange for the quintet and triplet states respectively. This suggests an anti-symmetric bending adjacent atom in the phenanthroline ligand in both species. The last panel shows significant amplitude of atom 19 which is Fe. This is described by the lowest singular value for the reasons described above.

As mentioned in the introduction, the face an image depicts is determined by the coefficients of the eigenfaces in a linear combination, changing these coefficients change the face. If we wished to describe a vibration in which there was perforation of the phenanthroline ligand and significant iron movement, the coefficients in the U would be 0.5 for eigenmode 1 and 0.5 eigenmode 19, where it would be zero for all other eigenmodes.

The data visualized in this way can lend a bit of chemical intuition as well. For example, large amplitude motions which occur on the carbene are generally not accompanied with large amplitude motion elsewhere. If the largest amplitude is located on the carbene then we can expect lower than average amplitudes on the other two ligands. While this statement is non-rigorous as it was found by inspection, this type of statement could be quantified, aided by the methods laid out here.

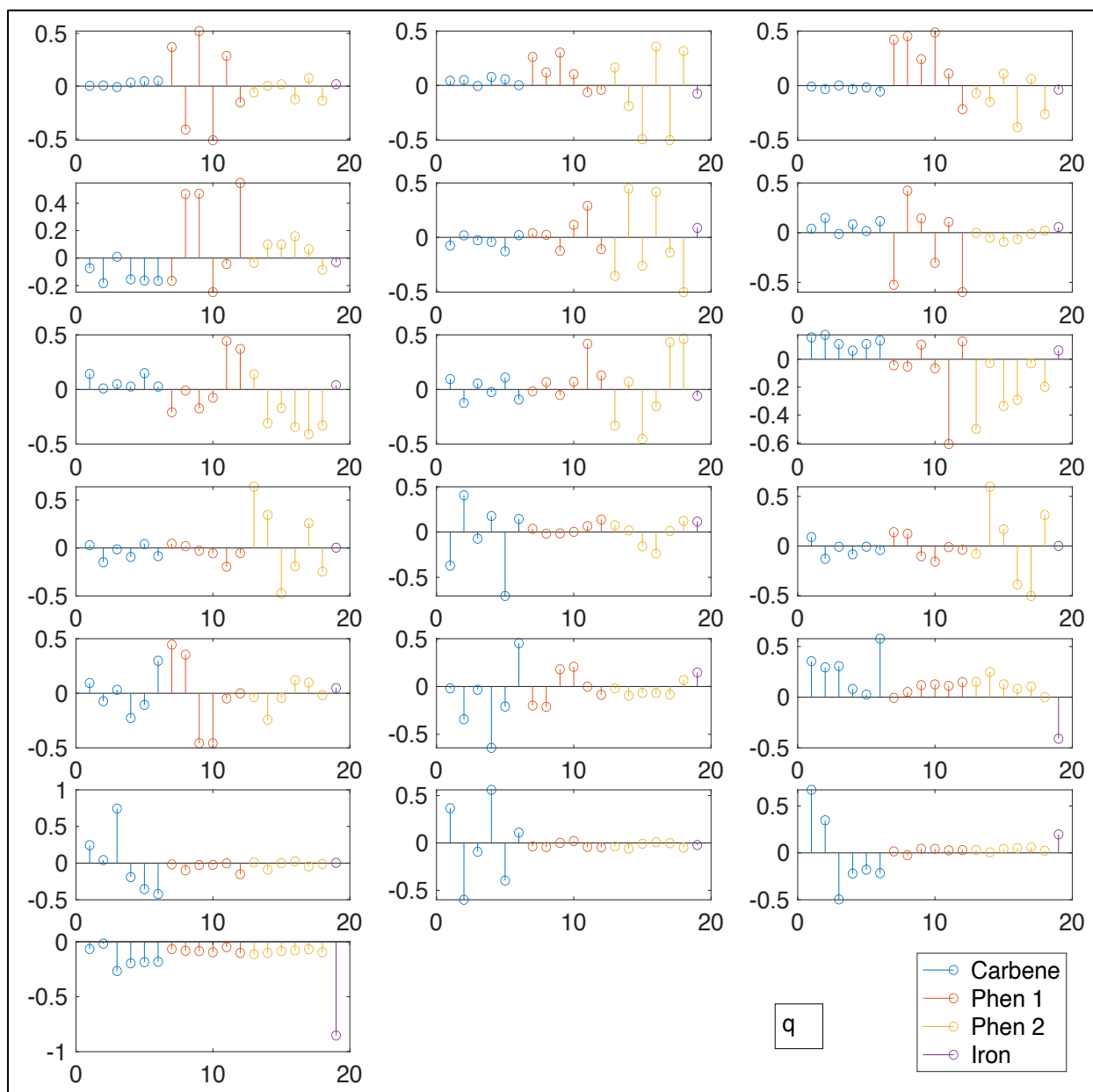


Figure 7.9: Stem diagrams of the eigenmodes of the quintet state. The largest contributing eigenmode is in the top left corner. The amplitude of the coefficient is proportional to the amount each atom contributes to the eigenmode. The x-axis corresponds to the atom index given in figure 7.5.

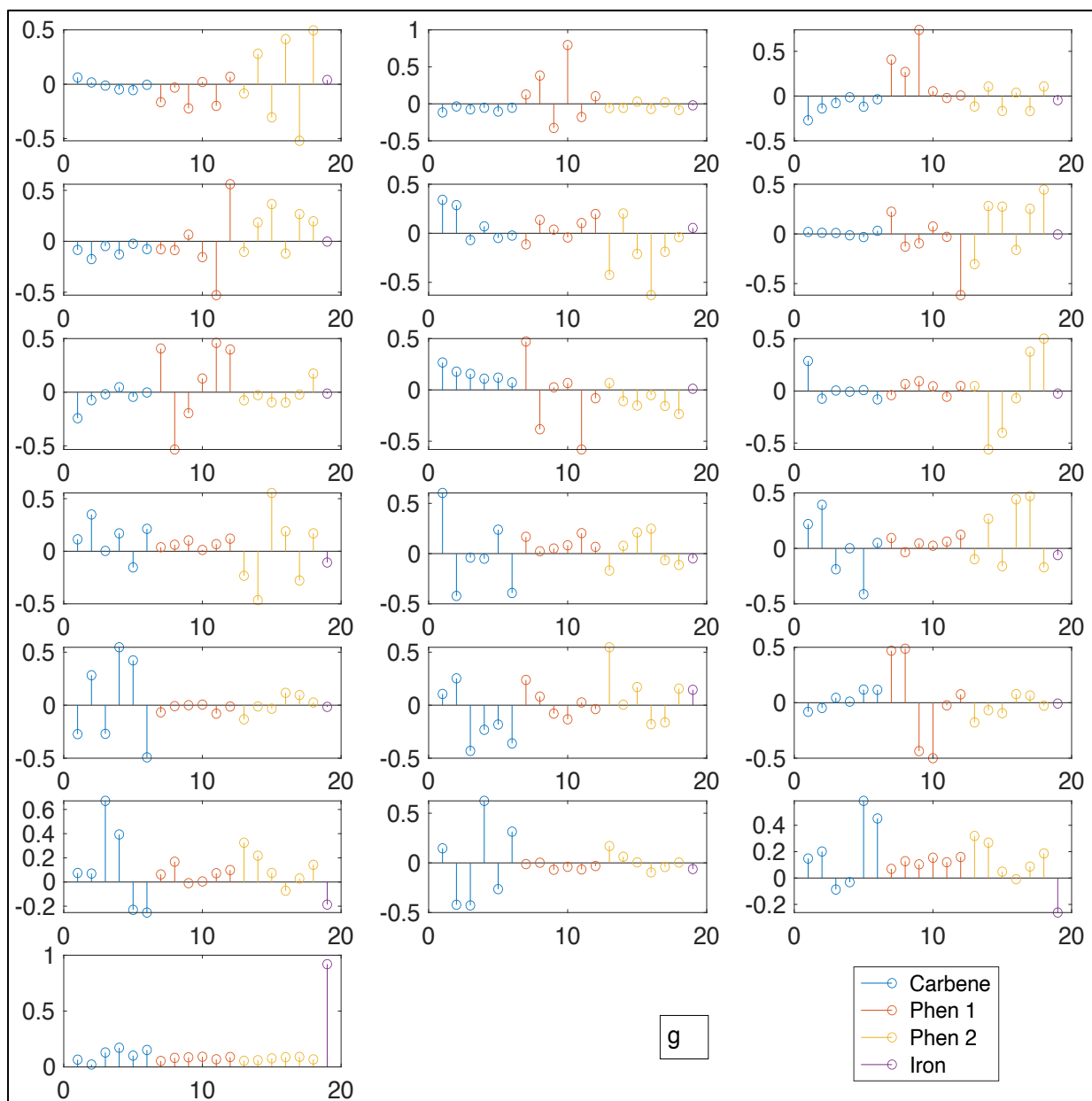


Figure 7.10: Stem diagrams of the eigenmodes of the ground state. See figure 7.9 for a general description.

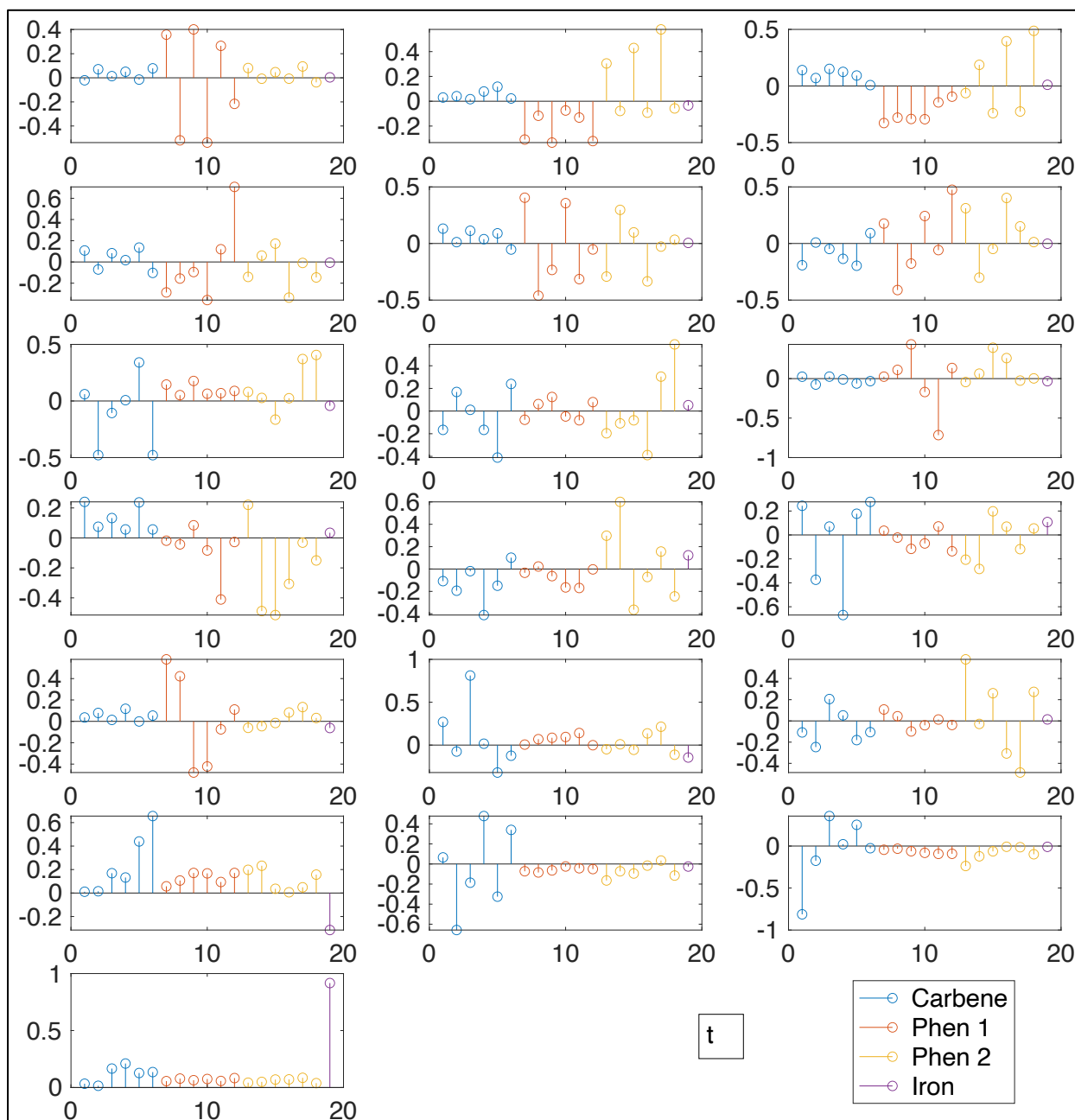


Figure 7.11: Stem diagrams of the eigenmodes of the triplet state. See figure 7.9 for a general description.s

By symmetry, the two phen ligands should be indistinguishable. This is, however, not the case and is a product of the summation process in forming our vector basis. For example, a displacement vector of $-0.1 \text{ \AA}$ is inequivalent to a displacement vector of $0.1 \text{ \AA}$, even though they might describe the same type of motion if a 180° rotation was performed mid vibration.

If we consider the eigenmodes across spin-states, we can note some similarities. For example, the first mode of the ^5MC and ^3MC are the same, describing a type of anti-parallel bending of the phen ligand. The ground state in contrast, shows a similar perforation-like pattern but extends across both phen ligands. Consideration must also be taken for the 19th eigenmodes, which in some cases show motion which could be described as unidirectional and thus may represent a type of translation. However, it must be noted that a positive amplitude in an eigenmode does not specify which positive direction a particular atom is moving, just that it is positive.

We can find modes that are similar across states with search algorithm utilizing linear regression between modes. This program, printed in the supplemental information, deems modes similar when an $R^2 = 0.7$ is found between the magnitudes of their eigenmode vectors. The correlated modes are given in the table below. We note the similarity between the displacement vectors of the triplet and quintet states, in that they have more eigenmodes in common than does either of the other combinations.

Table 7.1: Similar eigenmodes across spin-states of **1**. The label start and finish are only necessary from the way these were searched, in which the eigenmodes of finishing state were found from the starting states. It has not kinetic or chemical implication.

Start T	Finish Q	Start T	Finish G	Start Q	Finish G
1	1	13	15	10	10
13	13	17	17	13	15
14	16	19	19	19	19
17	17	-	-	-	-
18	18	-	-	-	-
19	19	-	-	-	-

To summarize, the set of displacement vectors can be decomposed into three separate matrices by the SVD. The U matrix gives the coefficients for a linear combination of eigenmodes contained in the matrix V which contains atom specific information that is structurally specific. Some of these eigenmodes are similar across the outputs given by different spin-states, their similarity is found independently.

7.3.5 Mode Recreation and Internal Correlations

It is common for vibrational modes in a single molecule to be classified by symmetry labels, where they are grouped with all other modes that undergo a similar transformation after the application symmetry operations. The symmetry operation is applied to an $3N \times 3N$ square diagonal matrix.²⁶ A symmetry operation is applied by a similarly large matrix that describes what each unit vector should do. The unit vectors that are retained in their original positions, i.e. on the diagonal, are the eigenvectors of the transformation. It is the trace of the matrix, represents the number of eigenvectors of a transform which is utilized to generate reducible representations.

The SVD method applies various linear transformations to the matrix X , two rotations and multiplication by a scalar. These operations are defined in terms of their right and left eigenvectors and only require a single set of transformations rather than application of several in accordance with symmetry rules. This gives the opportunity to classify vibrations by more than just the number of linear transformations given in a point group. The number of classifications scales with n , the number of atoms in the vector basis. This means there must be some degeneracy in describing the set of normal modes.

In the case of **1**, where the vector and atomic bases are equal, there are 19 discrete ways to describe 183 modes. It is exactly this degeneracy that could allow for correlations between

vibrations in the whole set of 183 vibrational modes for a given system. The modes which show significant character of a given eigenmode can be isolated. Consider the first eigenmode of the triplet state of **1** which will be called V_I and is illustrated in the first panel of figure 11.

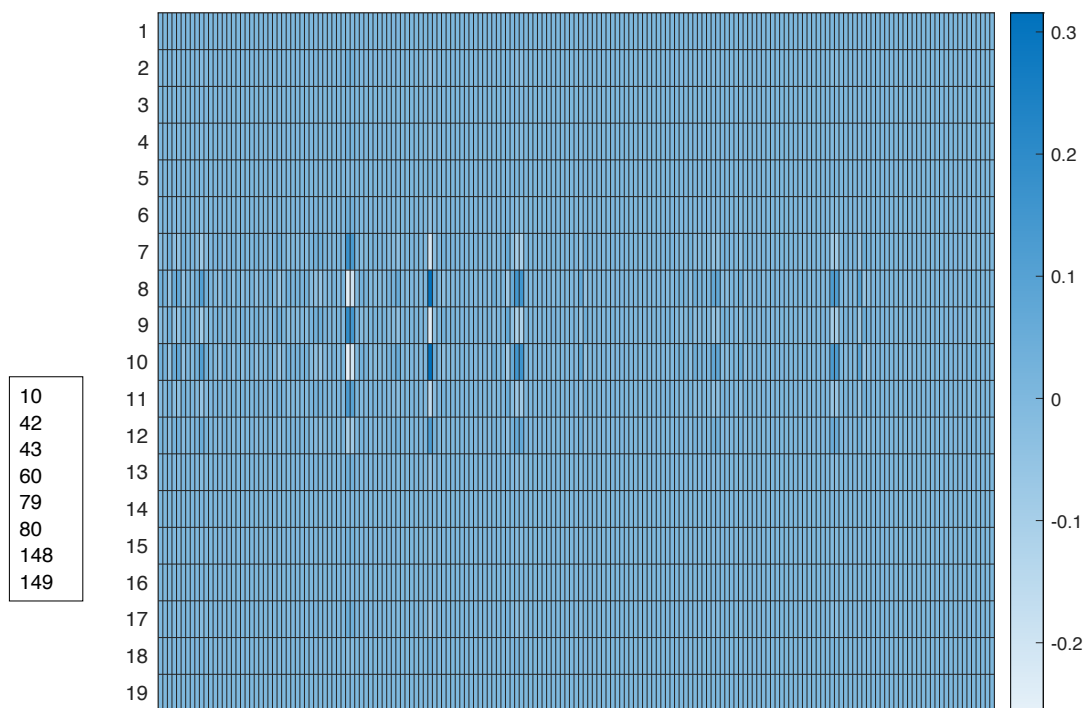


Figure 7.12: Heatmap of the reconstructed displacement matrix, utilizing the singular value and right eigenvector associated with component 1. The horizontal axis represents each vibrational mode, and the vertical axis represents each atom in the basis. The magnitude of these displacements highlights the relevance of that component in each vibration. Indices of modes with sufficient magnitude are represented in the box on the left-hand side.

Recreating the set of real displacements from eigenmode 1 is given by X_I as described by:

$$X_1 = U * S_1 * V_1' \quad 7.2$$

This recreated matrix of size 183x19 is depicted as a heatmap in figure 7.12, where the x-axis represents an index position for each normal mode, ascending left to right. It does not fully describe the displacement of the normal mode's vibrational motion. It does describe the features of that mode that are captured by V_I as well as all other modes which have a significant

contribution from this feature. This figure shows the same anti-parallel phen bending of the same atoms as is seen in the first panel of figure 7.9. As is common for symmetry analysis to say a particular vibration transforms as a particular irreducible representation, it is possible to say in an equivalent sense that these modes belong to V_I . Some modes belong more than others. Some modes do not belong at all. The amount a mode belongs to V_I depends on the portion of the displacement this eigenmode captures, thus larger recreated displacements suggest greater belonging.

The real displacements in X_I were analyzed, and outstanding vibrations belonging to the various eigenmodes were found for each. A vibration was defined outstanding by an absolute value of its real displacements as either greater than 0.1 or less than. We call this cutoff δ above which a vibration is said to belong to a particular eigenmode. The modes which were found to be outstanding are indexed in a box. This is seen on the left-hand side of the figure 13 for V_I in the triplet state. Plots like figure 13 for all eigenmodes of the triplet state are presented in the appendix of this chapter.

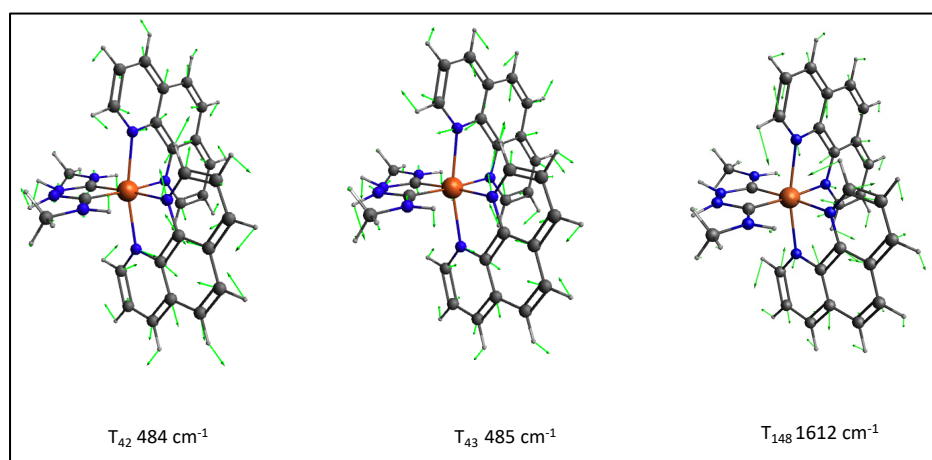


Figure 7.13: Visualizations of vibrations selected from the outstanding modes given in figure 7.12. All show the perforation pattern associated with component 1.

Consider modes 42 and 43 of the triplet, which show a large contribution from V_I . These modes are visualized below. The nuclear trajectories of the atoms where the adjacent imine

nitrogen atoms have opposite directions and a similar magnitude. This is also true for the proximal and distal carbon atoms of the phenanthroline as well. The utility of this method is further illustrated by considering mode 148 at 1612 cm^{-1} which shows a similar behavior to the lower energy modes. Correlations like this can be made in lower order systems easily, however in more complex systems like this one, the dimensionality reduction and removal of extraneous information, allows this to be simplified as well as automated, this correlation along with the other 8 vibrational modes that show a large contribution from eigen mode 1. All modes that have real displacements greater than the cutoff of 0.1 are listed in the tables below for all three systems studied. This method was applied to the triplet, quintet, and ground states for all eigenmodes. The eigenmodes by which each mode belongs is given as table in the appendix to this chapter.

7.3.6 Issues with Filtering for Classification

While this method is illustrative, the δ cutoff yields a significant amount of unclassified information. Only 83 modes yield a real-displacement greater than δ for all 19 eigenmodes. This number could be increased by decreasing δ , however the number of connections increases too making classification more difficult. To explain this, we can consider the linear combination:

$$\mathbf{x}_n = \sum_{i=1}^{19} a_i V_i \quad 7.3$$

Where $\mathbf{x}_n$ corresponds to the set of real displacements on each atom of a specific vibration n . Here a_i is a normalized coefficient describing how much of each eigenvector describes $\mathbf{x}_n$ (i.e. the coefficients in U). Consider an extreme case, where a_i could equal 1, in which case the eigenvector perfectly describes the real displacement vector. By necessity, the remaining coefficients must equal zero. From this filtering method, this mode n would likely be selected as

belonging to eigenmode i . This does depend on the singular values too however, which means that heavy atoms or atoms which do not move much, are not classified, which should be captured by the method. In another extreme a_i could equal 0.05, corresponding to the motion being divided approximately evenly between the 19 eigen modes. This mode will not be classified by our method, even though it must have some defined shape, because no single eigenmode rises above δ . A special case of this second extreme includes the high energy C-H vibrations which show near 0 amplitude on the atoms of our basis. Reducing the magnitude of δ , may lead to more modes being classified, but will lead to more noise, in the form of false positives. This difficulty means that only large amplitude motions can be classified, something that will not track when considering the application to synthetic modifications, particularly when steric modifications are used to dampen (stop movement) of some atoms. Thus, another approach must be taken.

7.3.7 Principal Component Analysis and K-nearest Neighbor's Search

The drawbacks of the classification scheme above can be avoided by classification independent of amplitude. Principle component analysis (PCA) is a covariance matrix-based reduction by the SVD. Like singular vectors, principal components are ordered by importance, where the first principal component (PC) describes the direction of largest variance of a dataset. The second PC describes direction of the second largest variance uncorrelated (orthogonal) to the first and so-on.^{19,20}

Highlighting terminology may be important. In PCA, the columns of the 2D matrix are called observables. In general, this can be some experimental observable, for example the presence of a gene, humidity among other variables as a function of time etc. The rows are observations or instances of the set of observables. For example, a specific moment in time in

which a system was observed or an animal specimen treated with drug x. For work here, an observation is given by the normal mode and the observables are the displacement vectors located on each atom. The components are the eigenmodes described previously. Components, PCs, and eigenmodes will be used interchangeably.

Because they were defined separately, the formal equations describing the SVD and PCA are slightly different.¹⁷ The principal component $\mathbf{Z}$ is a weighted sum of each atoms A_i contributions to a particular vibration, where n is the total number of atoms in the chosen basis. The loadings ϕ_i tell how much a particular atom contributes to the PC. It is ϕ_i describes the amplitudes of the eigenmodes.

$$\mathbf{Z} = \sum_{i=1}^n \phi_i A_i \quad 7.4$$

$$\mathbf{X}_j = \sum_{i=1}^n \Phi_j \mathbf{Z}_{ij} \quad 7.5$$

A given normal mode's set of displacement vectors, $\mathbf{X}_j$, is a weighted average of each principal component. These scores are represented by Φ_{ij} . It is possible to represent each normal mode as an ordered pair in a 2D PC space. These ordered pairs can be displayed in a biplot, which includes how each feature, in this case the atoms, correlate with each PC.

Consider the 1st and 16th eigenmodes of the triplet state. The stem diagrams for each are reproduced in figure 7.14. These two eigenmodes represent the PC space where values along the x-axis are positively correlated with the first eigenmode (PC1 or component 1) and the 16th eigenmode (PC2 or component 2). The biplot shows the loadings (ϕ_i) of each atom and the scores (Φ_j) of each normal mode in the PC space. Atoms 8 and 10 are indicated with data tips in the biplot. Both show a correlation with PC1. Considering the stem diagrams of the eigenmodes,

atoms 8 and 10 both have large amplitudes and point in the same direction. Vibrational modes that strongly described by PC1 are visualized as structures that include normal mode 79 and 60. The similarity in the phen motion is clear, although one is of higher frequency and localized on a single ligand rather than distributed between both. Mode 7, which lies nearly on the PC 2 axis is visualized also. There is effectively no phen motion, but a significant amount of carbene displacement. The dominance of the carbene motion is shown in the stem diagram for the 16th eigenmode.

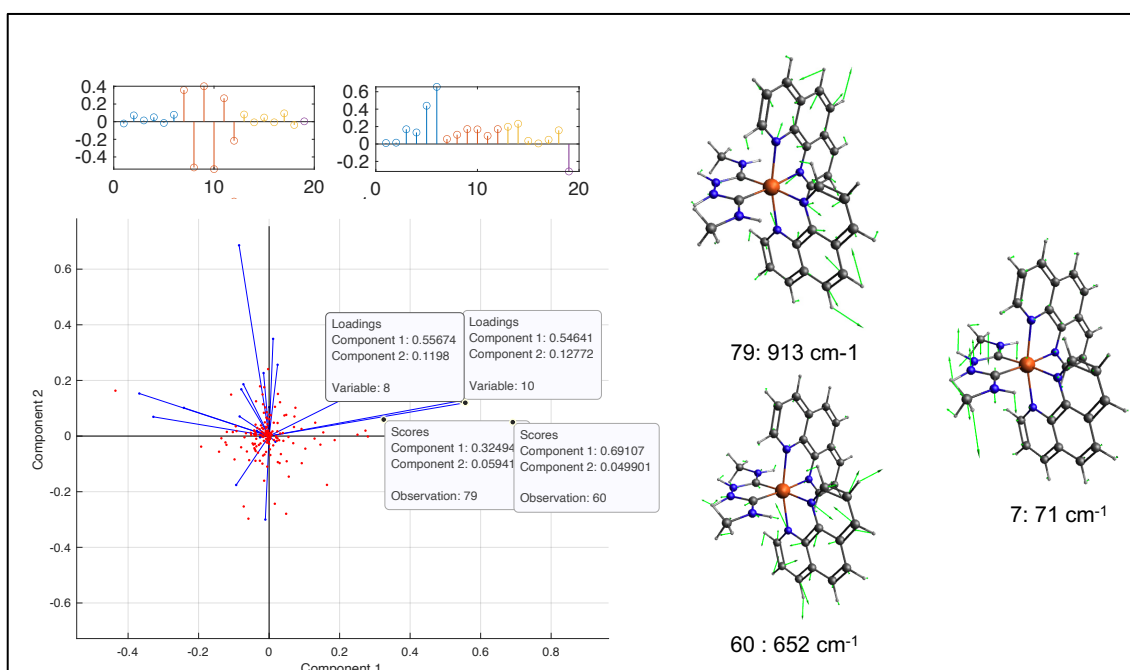


Figure 7.14: (top left) depictions of the stem plots of the eigenmodes represented as component 1 and component 2 in the biplot. (Bottom left) The cartesian axes that these eigenvectors make up is called the PC space and it is depicted in the plot (or biplot). The red dots represent the ordered pair of each normal mode in the PC space. The blue vectors show the atomic contribution to each principal component. For example, atoms 8 and 10 are both positively correlated to PC1 but are low amplitude in PC2. (right) Structures of selected vibrations. Note that mode 79 and 60 look similar and are in a similar region of the PC space. Mode 7 is not related and is highly correlated with PC2.

What is clear is that the modes that are similar in shape are close to one another in the biplot. The distance between them highlights their similarity. We note a significant clustering of data points around the origin of this plot, these points are not well described by these two PCs.

This representation has a distinct advantage from the filtering method described previously. Defining a δ does not consider the similarity between the modes which are not well described by a given set of eigenmodes. Thus, the information of the data clustered around the origin is lost. Their proximity to one another, even in cases where a mode is not well described by the set of PCs is useful information for categorization.

The distance measurement in the PC domain can be measured by the K-Nearest Neighbors method, which is a measure of Euclidian distance between a point and its K (some integer number) of nearest points.¹⁹ This is common for classification algorithms. For example, if one was to classify an image by being an apple or a mountain lion, the image would be decomposed into descriptors, placed in a cartesian space where its position depends on these descriptors, and classified by the class label of the K number of observations closest to it. Examining normal modes with the KNN algorithm, gives a quantitative measure of similarity between modes.

This process while it allows for measurement of similarity, can also accommodate some difference. By considering the number of times a given mode is within the K -nearest set, two modes that do not have to share the same set of PCs or encodings can be matched if the number of similar PCs in common is more than the rest of the $3N-6$ possible modes. The similarity between the modes is given by the Euclidean distance between the mods giving a numerical measure of similarity given in the equation below for two-space. The qualitative measure, the number of PCs in common and the quantitative measure, the Euclidian distance, allow for a flexible algorithm for classification.

$$d(\Phi^1_{ij}, \Phi^2_{ij}) = \sqrt{(\Phi^1_i - \Phi^2_i)^2 + (\Phi^1_j - \Phi^2_j)^2} \quad 7.6$$

A MATLAB program for this PCA and KNN search algorithm printed in the appendix of this chapter and is illustrated graphically in figure 7.15. The key concept is the use of the binning of PC-spaces and then searching all PCs. As shown with SVD, neglecting a single eigenmode will lead to a significant loss of information. Thus, 3D principal component spaces are created starting with the first three (PCs one, two, and three). This process we will call binning. The KNN search is run in that 3D space and the 11 closest modes are recorded along with their Euclidian distance values. The binning parameters are shifted by one unit, where the first PC is removed and replaced with the fourth PC. The 3D space is generated from these new binning parameters. The KNN search is then run again. This process is repeated until all PCs have been included in three binning events. It is possible to measure the n -dimensional Euclidian distance, where binning events were neglected. However, this did not lead to successful mode matching.

The output of this program is a table of similarity scores (S) which is the number of PCs that were found to be in common over all binning events. The histogram in figure 7.15 illustrates the similarity as a function of normal mode position where two modes were found to have a large significance. Also, the total Euclidean distance for two modes is given by the sum of the individual distances. This divided by S gives the average distance, the smaller of which generally denotes increased similarity. This algorithm was applied in several contexts in the following sections.

7.3.8 Correlations Between Internal Degrees of Freedom

Finding modes which are of similar character in each molecule is a useful exercise. It is in part the goal of grouping vibrational modes by symmetry. The algorithm described above was used for this purpose. For mode 9 (86 cm^{-1}) in ^3MC state are presented in table 7.2. The total distance is the sum of each of the most prevalent PCs. A similar vibrational motif is observed in

all three: the asymmetric bend along the C_2 axis of the phenanthroline ligand. In some cases, this is difficult to see, as these are qualitatively different modes in many respects. The large amplitude of the Fe atom in the 333 cm^{-1} mode for example may bias one to not qualify these modes as similar visually, it is only upon the decomposition that this becomes possible. The modes described in the table are not the only relevant modes but are selected for having the highest S value.

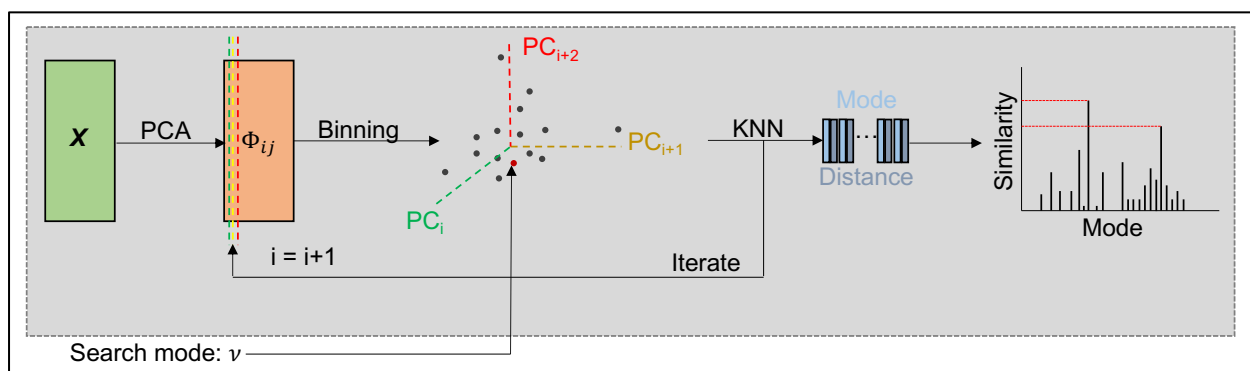


Figure 7.15: Graphical representation of the PCA decomposition and the KNN search methodology. Real displacement vectors are decomposed by PCA. The set of scores for this decomposition are binned into a 3D cartesian space. A search mode is input and the closest 10 neighbors are found using the KNN search function and each discovered mode is tallied. The 3D cartesian space is iterated through all PCs whereupon the final similarity scores are determined by the final counts.

Table 7.2: Top 3 matches of internal modes for mode 9 in the triplet state of **1**.

Mode Number	Frequency (cm^{-1})	S	Total distance	Average distance
16	153.3	6	0.26	0.04
23	232.7	6	0.37	0.06
32	333.1	6	0.46	0.08

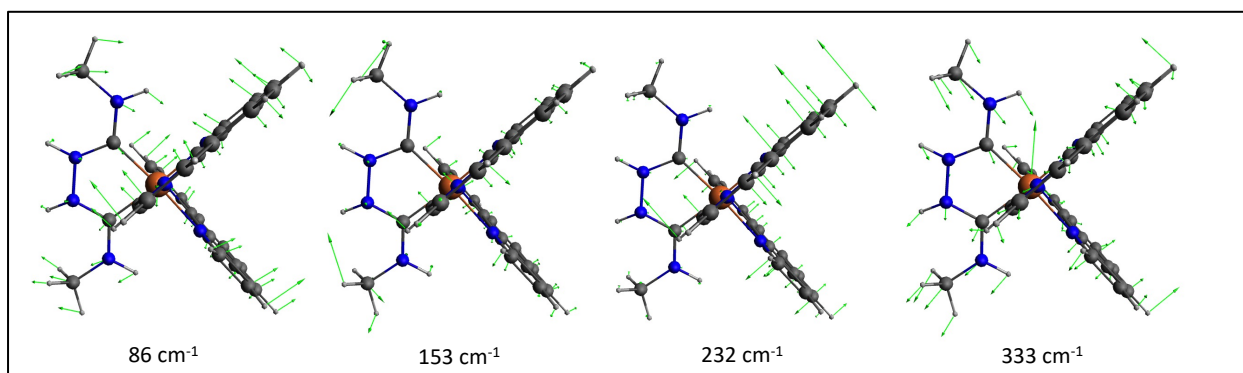


Figure 7.16: Visualizations of the modes that were found to match with mode 9 (86 cm^{-1}).

Consider the higher energy mode of 619 cm^{-1} . This is described primarily by its perforation of the carbene atoms in opposite directions from the line that bisects them, illustrated in the figure 7.17. We can see this in both modes 150 and 58 as well, where this occurs in the carbene plane, which contrasts with mode 56 which is almost perpendicular to this ligand plane. This highlights an important feature of the vector basis which neglects the cartesian vectors on each atom in favor of their summation. This loss of information, upon the summation, leads to this correlation but may fall short if discretion between in-plan and out-of-plane motion is needed. Mode number 19 (not pictured) is visually distinct and describes a unidirectional trajectory for the atoms in the carbene. This is an example of a failed classification.

Table 7.3: Top 5 matches of internal modes for mode 56 in the triplet state of **1**.

Mode Number	Frequency (cm-1)	<i>S</i>	Total distance	Average Distance
126	1401.0	14	1.30	0.09
150	1617.3	12	1.82	0.15
58	627.1	11	1.18	0.11
147	1561.6	11	1.52	0.14
19	170.0	10	0.51	0.05

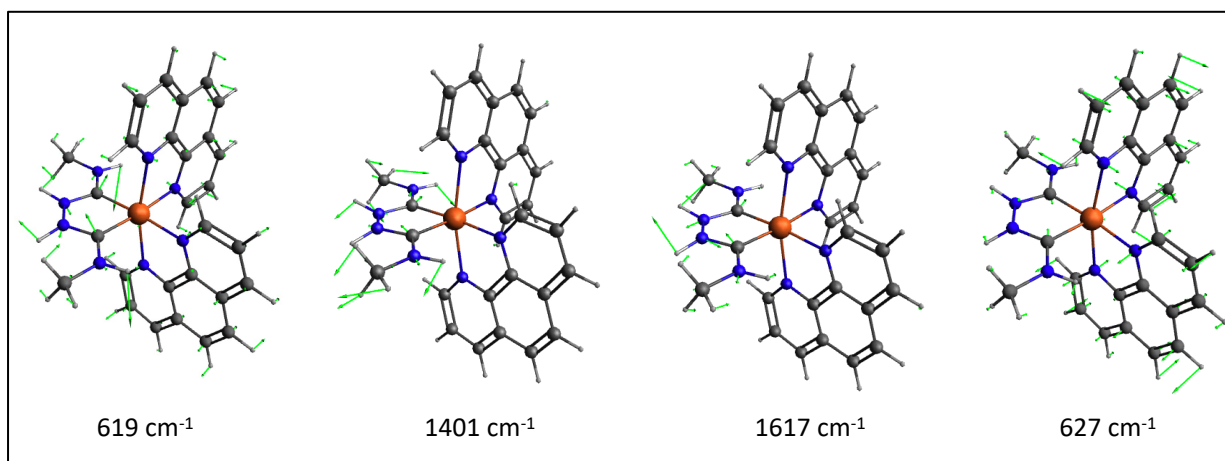


Figure 7.17: Visualizations of the modes that were found to match with mode 56 (619 cm⁻¹).

Calling this a failed classification is subjective because it did return some matches. To solve this, increasing the complexity by choosing the whole cartesian vector basis rather than just their sums there would likely have distinguished between the in-plane carbene motion of the first two and the out-plane carbene motion of the last. This suggests the necessity of a combined symmetry and displacement analysis.

7.3.9 Internal Correlations and Coherent Vibrations

Internal correlations can be used to index vibrational data obtained by experiment. This is particularly useful in for measured coherences. Coherent oscillations, superimposed on transient absorption decays, arise because of multiple vibrational levels being excited by the spectrally broadened but temporally narrow pulse as dictated by the uncertainty principle:

$$\Delta t \Delta \nu \geq \frac{h}{4\pi} \quad 7.7$$

Where Δt and $\Delta \nu$ represent the uncertainty in the measurements of time and frequency respectively. A given temporal bandwidth, which must be finitely small, determines a finitely large spectral bandwidth. Modes with vibrational spacing's larger than this spectral bandwidth will not be excited and thus unmeasurable by this method.

Table 7.4: Measured coherences of **1** and their computationally derived frequencies. Coherence measurements performed by Dr. Bryan Paulus.²¹

Measured (cm ⁻¹)	Calculated (cm ⁻¹)	Index
66	71	7
103	106	10
115	113	11
159	160	17
163	164	18
225	232	23
408	421	34

Using the algorithm described above, coherent modes can be examined in the context of their eigenmode contributions and compared with modes of higher frequency, which would not be observed for the reasons described above. Table 7.4 gives the several coherences measured for **1**. In an earlier chapter, we established that the dynamics of the whole ~7 ps lifetime involve the triplet state, we will consider these motions primarily. Each index in table 7.4 was input into the algorithm and relevant matches were found. The index of the matched modes, their frequencies, and matching parameters are reported in table 7.5.

At the outset none of the searched modes belong to similar set of PCs. This suggests a higher order orthogonality of the coherent modes, in that the set of PCs that describe each measured coherence do not overlap significantly between measured coherences. This is further illustrated by the lack of any significance in any common modes. Mode 28 does appear as a match in three cases, for 11,17, and 18 however this is the only one to show up in multiple channels. This makes sense intuitively if one considers the partitioning of vibrational energy after laser excitation. These results would seem to suggest that the population is evenly sorted into separate coherent channels, each with a different set of PCs and thus reaction coordinates, all of which light up upon laser excitation.

We can consider the counterfactual in support of the claim above. If each measured mode was matched with many other modes having a similar set of PCs or have a significant overlap

between the matched population, it would be possible to suggest that such a clustering would imply similar reaction coordinates. This is not observed. This picture is consistent with an excitation of several coherent modes acting across orthogonal channels. This discussion is lurching into the realm of speculation and thus will not be continued here.

Table 7.5: Matched Modes of the frequencies reported in table 7.4.

7	70	806.4	7	0.75	0.11
	75	862.3	6	0.08	0.01
	2	25.4	5	0.79	0.16
	16	153.3	5	0.82	0.16
	108	1165.5	5	0.4	0.08
10	46	517.9	7	1.63	0.23
	71	813.4	5	0.13	0.03
	74	850.8	5	0.49	0.1
	132	1453.3	5	0.13	0.03
	137	1483.6	5	0.14	0.03
11	12	136.5	10	0.57	0.06
	28	279.8	7	0.42	0.06
	87	995.3	7	0.55	0.08
	15	148.8	5	0.42	0.08
	31	330.1	5	0.42	0.08
17	152	1624.3	6	0.61	0.1
	8	83.2	5	0.52	0.1
	14	146.1	5	0.31	0.06
	28	279.8	5	0.39	0.08
	46	517.9	5	0.47	0.09
18	28	279.8	13	1.01	0.08
	3	31.1	9	0.67	0.07
	26	269	6	0.33	0.06
	11	113.9	5	0.47	0.09
	31	330.1	5	0.77	0.15

Table 7.5 (cont'd)

23	88	1011	6	0.13	0.02
	40	459.9	5	0.48	0.1
	75	862.3	5	0.11	0.02
	106	1161.7	5	0.14	0.03
	9	86.2	4	0.36	0.09
34	26	269	7	0.31	0.04
	38	433.1	7	0.27	0.04
	112	1228.4	6	0.41	0.07
	91	1014.5	5	0.17	0.03
	133	1454	5	0.21	0.04

7.3.10 Correlations Between Excited States

The method above was applied to the various spin-states of the Galileo cation. Displacement vectors for each of the 19 atoms in each state 183 mode were put into a matrix with dimensions 549x19. In the PC, this treats the 19 atoms as variables and each mode as a separate observation. Similar modes will be considered similar observations. The first 183 modes are those of the ground, the second set of 183 modes are of the triplet, and the third set of 183 are the quintet.

Running the search for the 88 cm⁻¹ mode in the ground state gave matches of the 86 cm⁻¹ and 81 cm⁻¹ modes in the triplet and quintet respectively. The distance values of which are reported in table 7.6. These modes are also visualized. These describe a bending of the phenanthroline backbone with a less discernable behavior in the carbene ligands. The stem diagram highlights differences in the real displacements of the basis. Much of the displacement occurs on the phenanthrolines particularly around atoms 17 and 18. This is true for all three states; however, it is much more pronounced in the quintet state. It is likely due to the weakened interaction with the metal center due to the increase in bond length. Such a weakened interaction should lead to larger amplitude motion which is observed. This information can be used

synthetically by considering this large amplitude motion as a degree of freedom which could be synthetically modified such that the amplitude aligns more with the ground state. It is perhaps tenuous to suggest that such a reduction in amplitude leads to more nested potentials, however in aggregate this would be the case.

Table 7.6: Top two matched modes for search mode 9 in the ground state.

Mode Number	Frequency (cm ⁻¹)	<i>S</i>	Total Distance	Average Distance
192	86.2	11	0.31	0.03
374	80.9	7	0.36	0.05

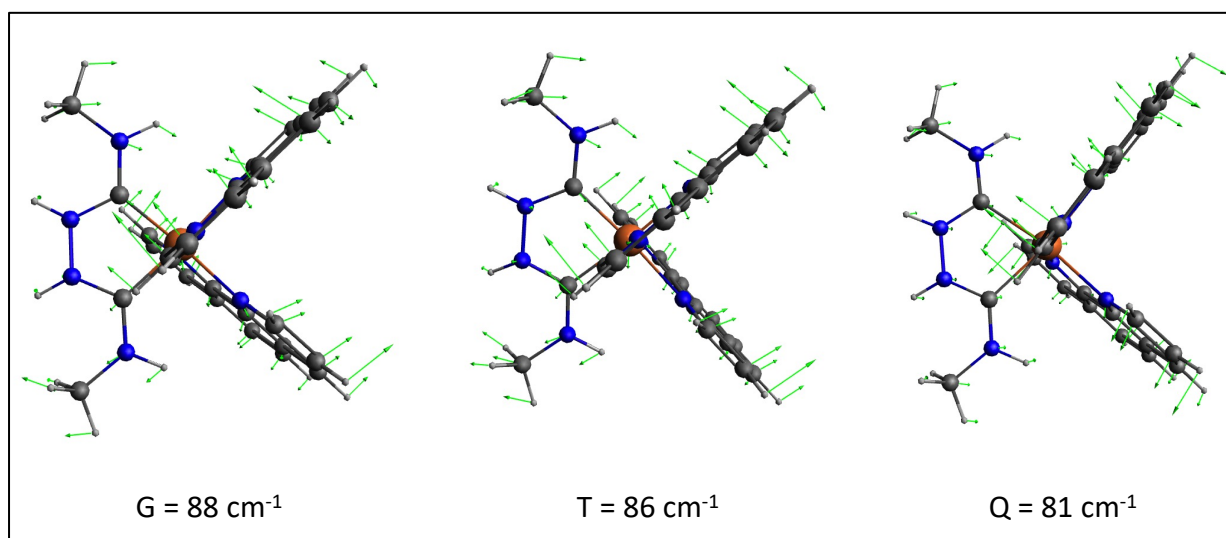


Figure 7.18: Visualized displacements of vibrations resulting from the searched mode 9 in the ground state of **1**.

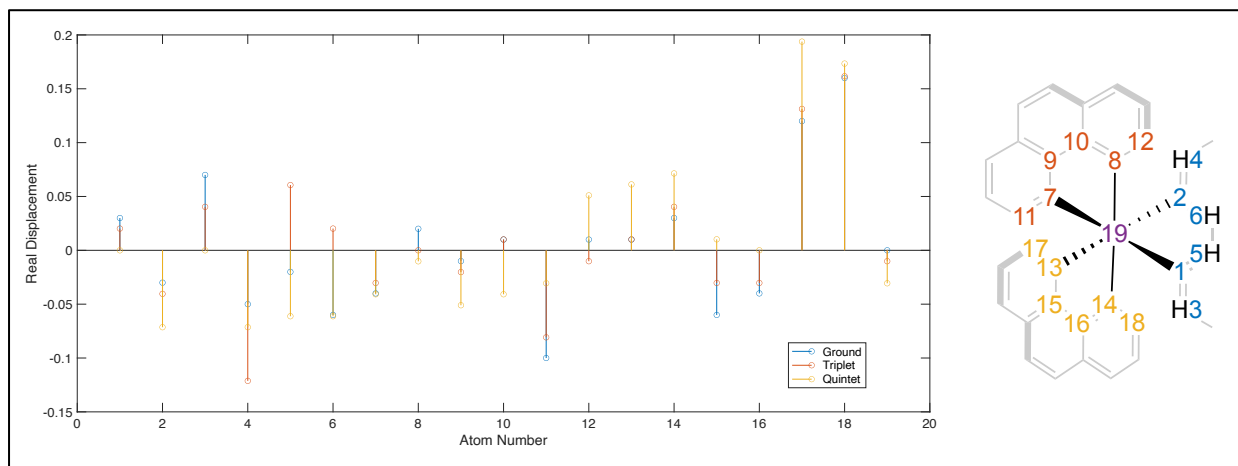


Figure 7.19: Stem plot for the real displacements of the atomic basis in vibrations found in table 7.6.

Consider the search for the 233 cm^{-1} in the ground state. This gave matches for the 81 cm^{-1} and 232 cm^{-1} in the quintet and the triplet respectively. Note that we had matched the 81 cm^{-1} mode in the previous example, and it is likely a false positive. However, if they are visualized then we can see this is a reasonable mistake as they both involve a similar type of behavior on the phen backbone. If we consult the figures, we note that the 237 cm^{-1} which describes a similar lengthwise folding to the modes mapped for S and T, however it is localized on a single phen ligand. Thus, the reason for the false positive is that the mode is distributed across both phen ligands and thus conforming better to the chosen mode. If the internal correlation is run for the 81 cm^{-1} mode, the 237 cm^{-1} is in the top three matches. This false positive could be attributed to the limited basis, which is used here, as much of the displacement in the higher frequency mode has shifted to the outer atoms, which are not included in our basis, which may be solved by expanding the basis.

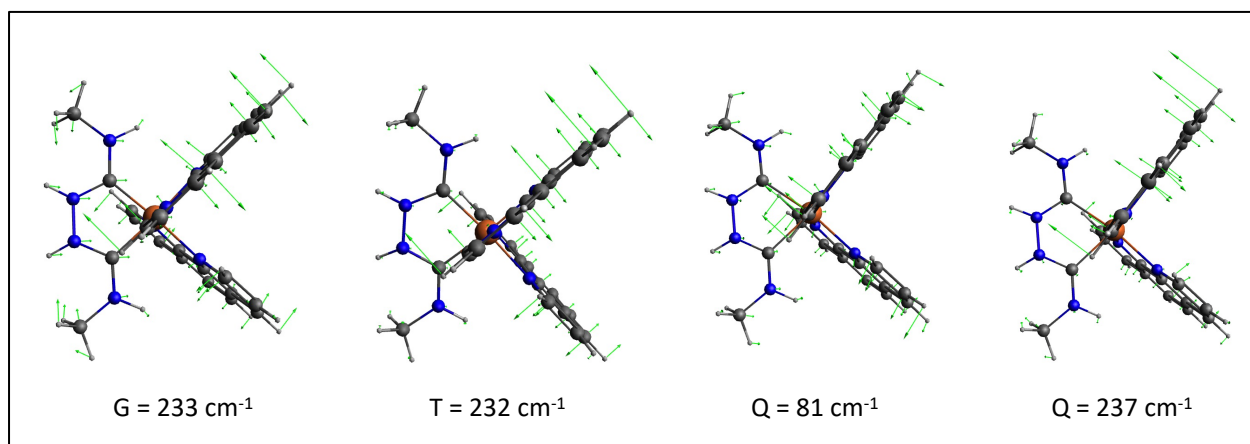


Figure 7.20: Visualized displacements of results for the search mode 23 in the ground state of **1**. Note the better match in the quintet was not found by the program.

Table 7.7: Top two matched modes for search mode 23 in the ground state.

Mode Number	Frequency (cm^{-1})	<i>S</i>	Total Distance	Average Distance
374	80.9	9	0.39	0.04
206	232.7	6	0.27	0.05

A final example can be shown for mode 1227 cm^{-1} (110) in the ground, which describes in plane motions of the phenanthroline ligands. This maps 1115 cm^{-1} and 1225 cm^{-1} in the triplet and 1223 cm^{-1} in the quintet, which are visualized below. While some orientations of the vectors in the 1115 cm^{-1} of the triplet are different, they clearly represent a similar type of vibration. The third most significant match, likely the true match given the similarity in frequency, was also included and is qualitative like the 1115 cm^{-1} mode and the others. While this is not technically a matched mode, it is useful, as we could expect these modes to behave in a correlated way upon synthetic modification. The program found the corresponding match in the quintet state, confirmed by visualization.

Table 7.8: Top three matched modes for search mode 110 in the ground state.

Mode Number	Frequency (cm^{-1})	<i>S</i>	Total Distance	Average Distance
283	1115.7	9	0.19	0.02
476	1223.3	9	0.22	0.02
293	1224.6	8	0.13	0.02

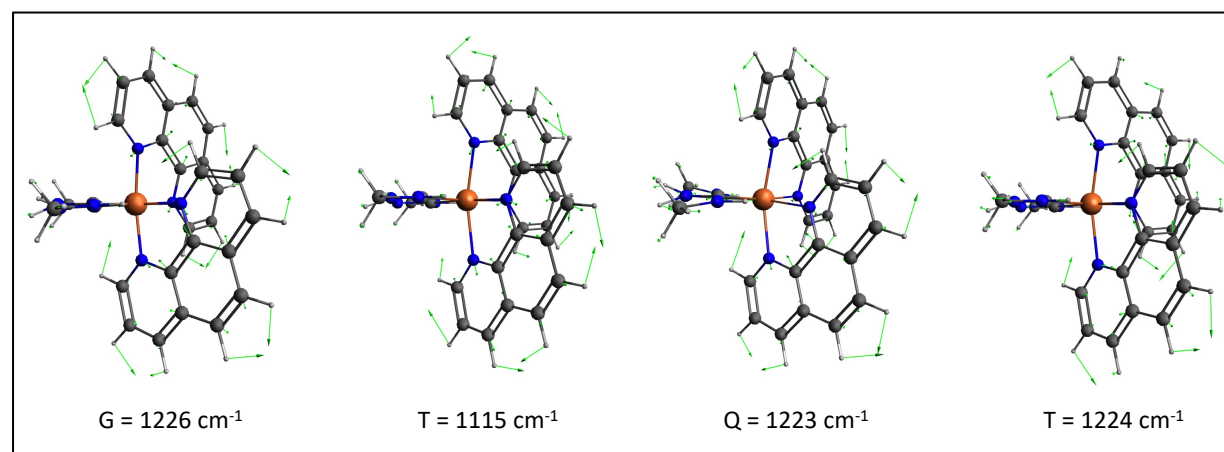


Figure 7.21: Visualized displacements of results for the search mode 110 in the ground state of **1**. Note the better match in the triplet was not found by the program.

These few examples were utilized to illustrate the applicability of the program across the spectrum of possible frequencies. It also illustrates the margin of error and gives a sense of what the magnitudes of the similarity parameters, and what they mean.

7.3.11 Mapping of Jahn-Teller Distortion

In a previous chapter, the significance of the 106 cm⁻¹ mode to the reorganization energy in the ground state recovery process from a ³MC state was noted. This mode is relevant in its correlation with the Jahn-Teller distortion expected for the triplet electron configuration and occupation of the lowest energy triplet MC states. This electronic feature is not present in the other two states. The examination of this mode with respect to other states may test the limits of this correlation or provide a map for where that JT mode goes in the other states.

Mapping mode 106 cm⁻¹ in the triplet state, yields two modes of relatively distinct frequency and a large average displacement. These modes are 434 and 115 cm⁻¹ in the ground and quintet states respectively. If we visualize the modes, we note there is significant ‘chomping’ character in each. However, it is important to note the differences, particularly around the equatorial phenanthroline bonds. In the ground state, this chomping motion is accompanied by a bond elongation of the Fe-N_{eq} bonds. The phase is important here as the axial nitrogen atoms move towards the metal center so do the equatorial bonds. In contrast, the quintet state, the shortening of the axial bond is coupled to an elongation of the Fe-N_{eq}. These are both in contrast to the triplet in which the Fe-N_{eq} atoms are better described as rocking, rather than stretching.

Table 7.9: Top two matched modes for search mode 192 in the triplet state.

Mode Number	Frequency (cm ⁻¹)	<i>S</i>	Total Distance	Average Distance
34	434.4	7	1.21	0.17
377	115.1	6	1.47	0.25

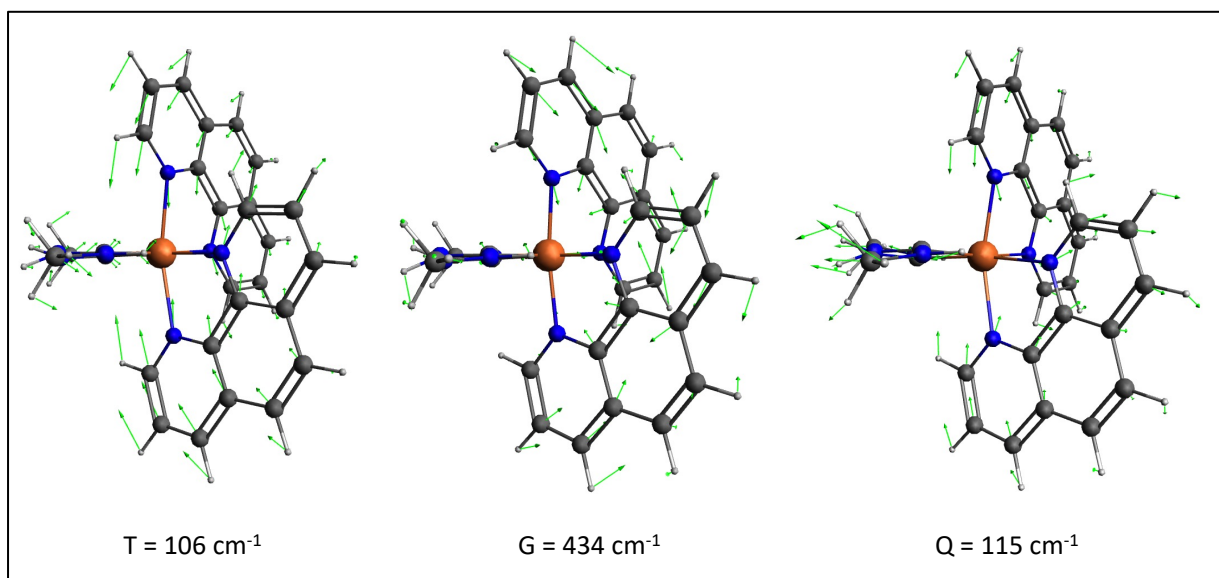


Figure 7.22: Visualized displacements of results for the search mode 192 in the triplet state of **1** which was found to contribute primarily to the reorganization energy using the linear reaction pathway. Notice the chomping motion of the phenanthroline ligands along the axial Fe-N bonds. The modes in the ground and quintets states show this chomping motion, although to a lesser degree.

From the real-displacement overlay's it was observed that the triplet amplitudes are much larger in almost every displacement vector in the phen ligands. This fact is consistent with the lower frequency (106 cm^{-1}) compared with the other two modes, which appear more constrained indicated by their amplitudes. Significant differences in the carbene backbone are observed between the quintet and others, which can be thought of as a counterbalance to the Fe-N_{eq} elongation. This mapping is fascinating and could provide a relational definition of the JT distortion, namely a mode prone to JT distortion should be the lowest frequency amongst the set of modes that share similar PCs.

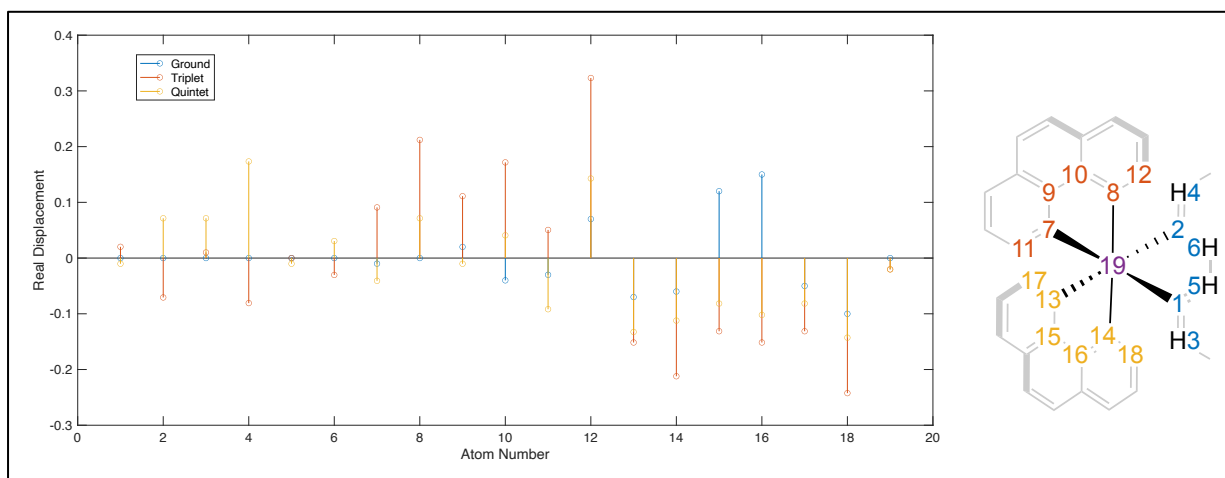
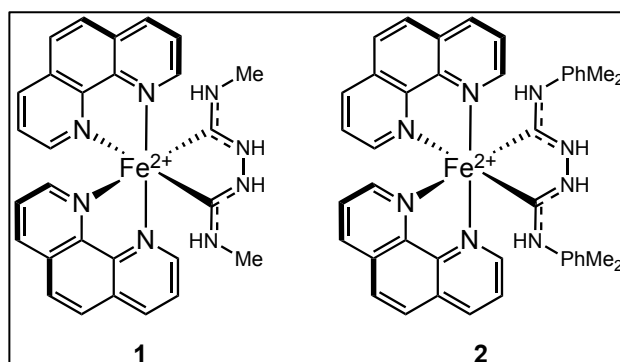


Figure 7.23: Stem plot for the real displacements for the vibrations found by searching mode 192 in the triplet state. Note the large displacements of the atoms 12 and 18 in the triplet state which corresponds to the axial α -carbons on the phenanthroline moieties. Large amplitude motion of these, as well as the other atoms of the phenanthroline suggest the chomping motion.

The breadth of the frequency range (106 cm^{-1} to 434 cm^{-1}) validates the goals of this exercise. Not only are correlated modes across large frequency ranges found but are also correlated with modes in very narrow frequency ranges. Utilizing this method will be particularly useful in considering modes contained in the fingerprint region of the spectrum.

7.3.12 Correlations Between Synthetically Modified Carbene Structures



Drawing 7.2: Structural comparison of complexes studied in this section.

Mapping modes between different structures is a key point of this work. As such the mapping between **1** and **2** was carried out. Due to the magnitude of the structural difference between species the vector basis was expanded to include the unit vectors on each atom, giving a

57-element vector basis on a 19-element atom basis. This was done to provide the maximum amount of information to work with. It does mean that there will be differences in the analysis, however the main points have been illustrated above.

One difference is the reduced interpretability of results. The eigenmodes for example are no longer representative of atomic contributions but are unit vectors associated with each atom. We will therefore avoid the use of these plots to illustrate correlations but will attempt to map the results determined from the cartesian vector basis inputs to atomic contributions. The selection of basis was performed in MATLAB. Further, there are 261 normal modes in **2** which means that it is impossible to correlate every mode between species. However, it will still be possible to find similarities. The phenanthroline ligands remain the same for example and internal modes are consistent. This assumption neglects electronic effects. The 310 cm^{-1} vibration in both species, representing modes 29 and 40 in **1** and **2** respectively, are illustrated in figure 7.24. Their similarity in frequency and displacement suggests that our neglect in electronic effects is reasonable. These modes would be a good calibration of the method.

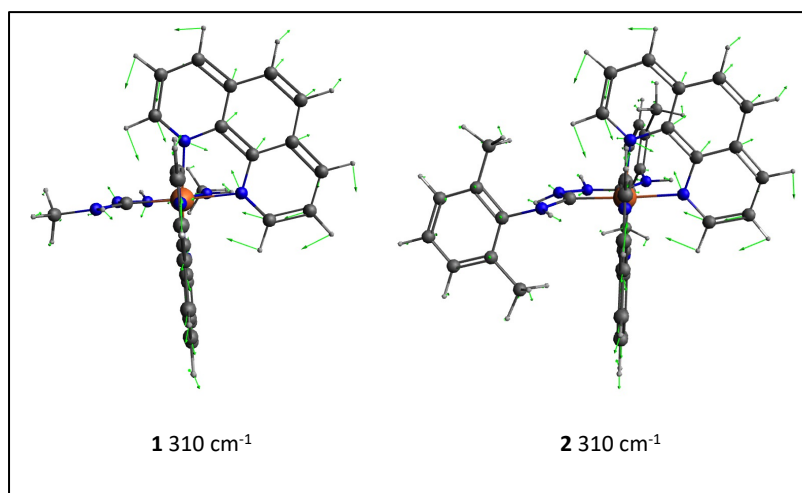


Figure 7.24: Visualized displacements of the control vibrations of **1** and **2**. The similarity in frequency is due to the localization of the displacements on the phenanthroline ligand.

The algorithm was applied to mode 29 in **1** and the top five modes of significance are reported in the table 10. The top match is illustrated in figure 7.25. There is significant difference

in the shape of the orientation of the displacement vectors. Displacement vectors are perpendicular to the plane of the phenanthroline in contrast to the in-plane motion of the displacement vectors. They are in fact rotated by 90 degrees. If the control vibration (i.e. mode 223 at 310 cm⁻¹) in the **2** complex is searched, the most significant is found to be mode 78 in **1** the pictorial representation of which is included in the figure. These vectors are rotated in the phenanthroline plane. This rotational relationship between vectors suggests that the vector bases are themselves rotated in space.

Table 7.10: Top 5 matches for the search modes in **1** and **2** respectively. Note the lack of similarity any correlation between the two control modes.

Search	Match	Frequency (cm ⁻¹)	<i>S</i>	Total Distance	Average Distance
29	263	631.2	12	0.40	0.03
	152	1621.4	10	0.73	0.07
	234	443.0	10	0.62	0.06
	287	846.3	10	0.68	0.07
	355	1334.3	10	0.46	0.05
223	78	887.0	12	0.84	0.07
	157	1661.9	12	0.66	0.06
	27	289.2	11	0.59	0.05
	131	1450.4	9	0.53	0.06
	230	406.8	8	0.53	0.07

The rotational relationship between the systems was examined further. Below are figures of the atomic and vector bases which illustrate this relationship. The figure below shows the raw geometric inputs of the atoms. The atomic bases are rotated relative to one another as they do not overlap in space.

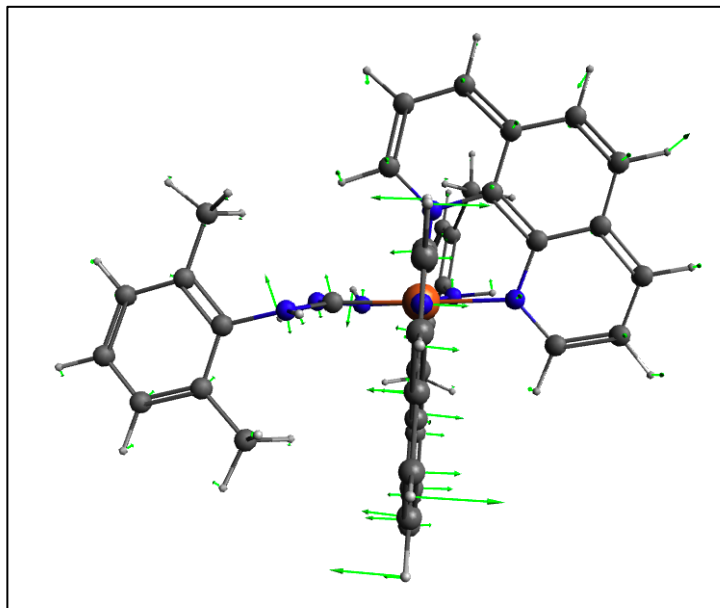


Figure 7.25: Dominant match in **2** from search mode 29 in complex **1**. Displacement vectors are orthogonal to those in figure 7.24.

Treating atom coordinates as vectors centered at the origin, a programmatic rotation was applied, using the method of Möller et. al.²² This treats the atom positions as vectors from the origin. These vectors of **1** are considered fixed and the vectors of **2** are treated as variable. A program in MATLAB was used to apply a transformation to the **2** atom coordinates such that they overlap with the atom coordinates of **1**. The product of this rotation is observed in figure 7.26, which have the atomic bases superimposed. Vectors of a similar magnitude are in some cases rotate by 180° or 90° to one another.

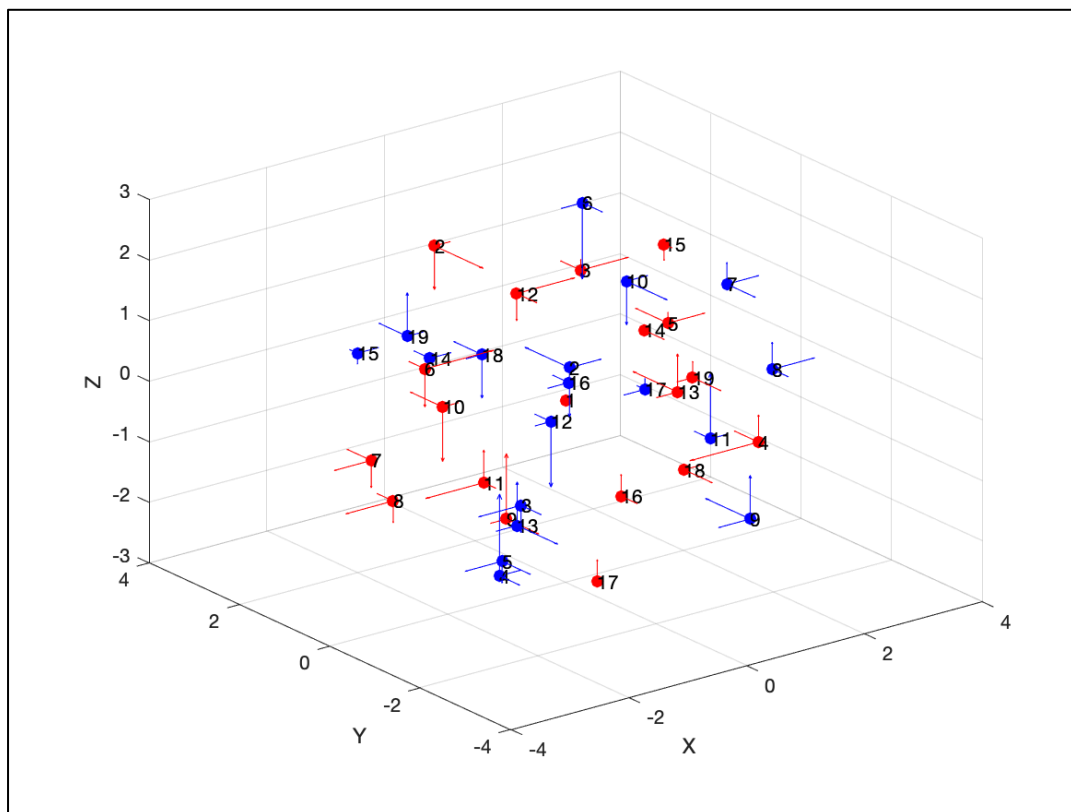


Figure 7.26: Visualization of the Z-matrices of **1** and **2** in blue and red respectively. The unit vectors are superimposed on each position. Clearly, the two matrices are rotamers of one another. This can also be seen in computational visualization software like Avogadro or Gauss-View.

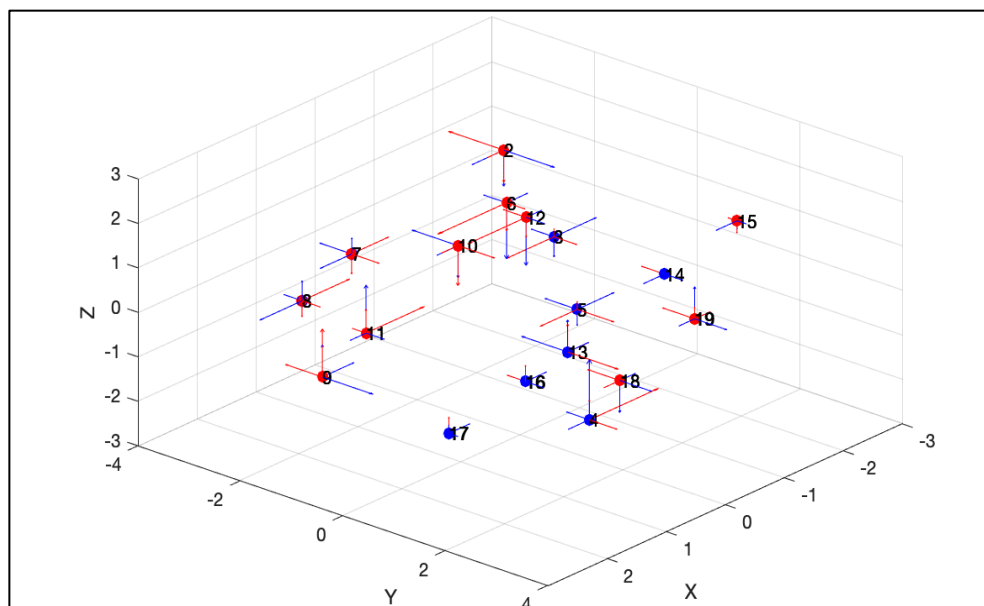


Figure 7.27: Visualization of the Z-matrices of **1** and **2** in blue and red respectively after the application of the rotation.

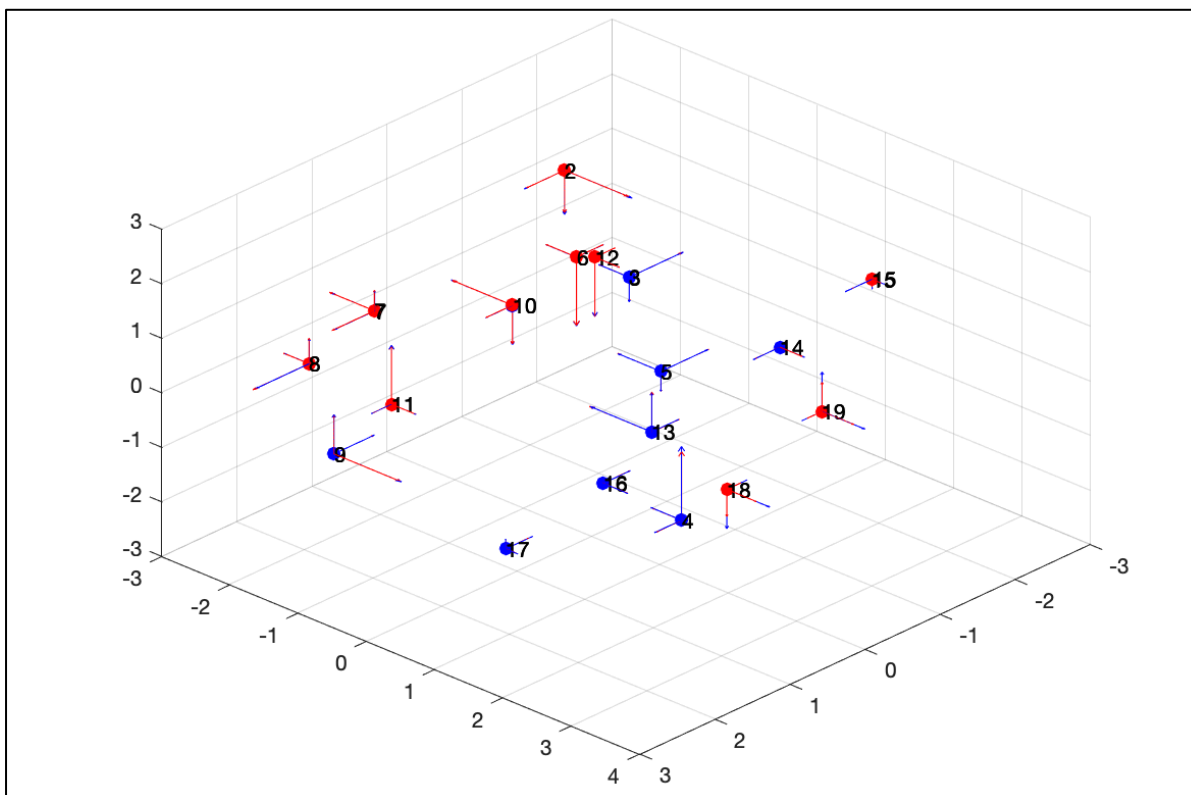


Figure 7.28: Visualization of the Z-matrices of **1** and **2** after the rotation of the unit vectors in their corresponding plane.

Applying the method to each basis vector in the basis vectors of **2** were rotated onto the corresponding vectors in **1**. These vectors when added together would yield a set of displacement vectors which could in theory be correlated. Attempts to do this on a large scale have not been successful. This was not a problem in the spin-state studies, as the orientation of vectors due to each structure being derived from the same set of coordinates. Generating a program for converting the Z-matrices and vector bases into similar domains will be necessary if this method is to be scalable as comparison between structures computed with different absolute geometries will be necessary. This could be done with relatively straight forward linear algebra but is not pursued here as this would broaden the scope of this thesis.

7.4 CASE STUDY: Cr(III) ACETYLACETONE DERIVATIVES

Recent work by our group has examined the vibronic coherences in a set of structurally similar Cr(III) complexes which were substituted in the α -position of the acac (acac = acetalacetone) ligand.^{21,23–25} Coherence dephasing times were utilized to establish the depopulation of 4T_2 to 2E state by internal conversion, where the coherently active modes are dephased on a longer timescale than internal conversion also disproving vibrational relaxation in an earlier assignment. The coherent modes above were measured for the substituted series by Dr. Bryan Paulus and reported in his thesis and the computations were performed by him as well. We will examine these modes utilizing the methods described above.

Table 7.11: Measured coherences of $[\text{Cr}(\text{acac})_3]$ derivatives. Reported from reference 20.

Compound	frequency, cm^{-1} (damping time, fs)			
Cr-(3-Clac) ₃	93 (5450)	149 (1100)		449 (581)
Cr-(3-Brac) ₃		123 (2500)		
Cr-(3-Iac) ₃	55 (2060)	101 (2400)	181 (200)	204 (1420)

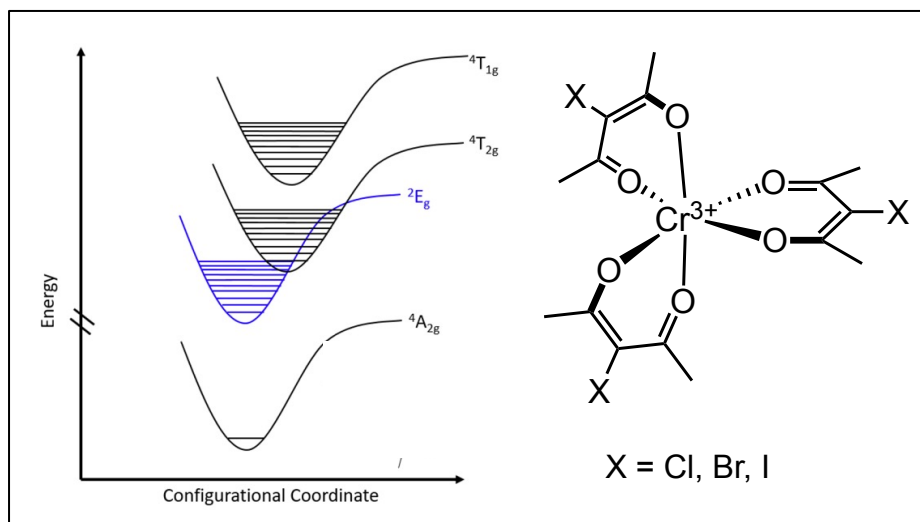


Figure 7.29: (left) Potential energy surface diagram of the ligand field states of $\text{Cr}(\text{acac})_3$ species. The geometry of the 2E_g excited state and $^4A_{2g}$ ground state are nested making the ground state a reasonable approximation for the vibrational structure of the 2E_g . (right) Structure of the substituted complexes examined in this section. Taken from reference 20.

7.4.1 Basis Selection:

In the $\text{Cr}(\text{acac})_3$ systems, the atomic basis is not limited; this has advantages for indexing by increasing the amount of information present. The basis is not limited by structural dissimilarity between species. There are 123 normal modes and 43 total atoms in each basis. The following table lists the atoms and their corresponding positions which match with the labeled structure. This key is not organized by ligand but could be done in a later analysis. We are assuming the discussion in the previous sections should limit the need to illustrate the structural bases here. The absolute index between species is kept consistent which is an algorithmic requirement.

Table 7.12: Atomic basis description for atoms in each member of the $\text{Cr}(\text{acac})_3$ series. X corresponds to the halides.

Abs. No	Atom	Atom No.	Description	Abs. No.	Atom	Atom No.	Description
1	Cr	-	-	23	H	1	-
2	C	1	carbonyl	24	H	2	-
3	C	2	alpha	25	H	3	-
4	C	3	methyl	26	H	4	-
5	C	4	methyl	27	H	5	-
6	C	5	carbonyl	28	H	6	-
7	C	6	carbonyl	29	H	7	-
8	C	7	alpha	30	H	8	-
9	C	8	methyl	31	H	9	-
10	C	9	methyl	32	H	10	-
11	C	10	carbonyl	33	H	11	-
12	C	11	carbonyl	34	H	12	-
13	C	12	alpha	35	H	13	-
14	C	13	methyl	36	H	14	-
15	C	14	methyl	37	H	15	-
16	C	15	carbonyl	38	H	16	-
17	O	1	-	39	H	17	-
18	O	2	-	40	H	18	-
19	O	3	-	41	X	1	-
20	O	4	-	42	X	2	-
21	O	5	-	43	X	3	-
22	O	6	-				

This indistinguishability of some atoms comes from the fact the calculations were performed in the ground state where no symmetry breaking is expected. The ground state is used by the approximation for the geometry of the 2E_g state. This is viable because the potentials between the 2E_g and the $^4T_{2g}$.

7.4.2 Method Validation

The model was validated using these complexes which are structurally similar, and we expect less variation between species. All modes in $\text{Cr}-(3\text{-Clac})_3$ were passed and the quality of matches with $\text{Cr}-(3\text{-Brac})_3$ and $\text{Cr}-(3\text{-Iac})_3$ were gauged. A validation algorithm was written to run a global search on the first 123 vibrations (i.e. all modes present in $\text{Cr}-(3\text{-Clac})_3$ were mapped to the other complexes). The two modes with the highest significance are indexed. Several parameters were derived from these indexed vibrations.

The first will be called the speciation which assumes that the vibrations with a given character in each species map 1:1 onto a vibration of the other species. This is given by a score of 1 or 0. A score of 1 is given if both top two modes are from different species finding a set of matches between $\text{Cr}-(3\text{-Clac})_3$, $\text{Cr}-(3\text{-Brac})_3$ and $\text{Cr}-(3\text{-Iac})_3$. A score of zero is given if no such set is found, even if the matches represent a match. The average speciation is taken as a gauge of the accuracy in the trajectory of the displacement vectors in each species. Speciation does not consider the magnitude of the displacement vectors. The speciation however does not imply a direct match and may still be 1 even if the matches represent different normal modes.

$$\Delta v_1 = |v_{\text{search}} - v_{\text{match1}}| \quad 7.8$$

$$\Delta v_2 = |v_{\text{search}} - v_{\text{match2}}| \quad 7.9$$

$$\Delta v_3 = |v_{\text{match1}} - v_{\text{match2}}| \quad 7.10$$

An important part of this work is to avoid indexing vibrations by their frequencies, however that does not mean that frequencies are irrelevant in indexing, particularly when only monotonic modifications are made which is the case in this series. A second measure of accuracy is the frequency error Δv defined in the equations above. Here Δv_1 , Δv_2 , and Δv_3 represent the first, second, and third frequency errors respectively, which represent the frequency differences between the search mode and matched modes, as well as differences in the matched modes. v_{search} is the frequency of the searched mode. v_{match1} and v_{match2} represent the frequencies of the first and second most significant matches. A value of $\Delta v > 100 \text{ cm}^{-1}$ is deemed to mean a match is in error although this is not a hard cutoff. The relative magnitudes of the differences can be considered too which may aid in validating the cutoff. The table below highlights such a logic.

Table 7.13: Matrix for understanding the frequency errors.

Result	Δv_1	Δv_2	Δv_3	Equality
Match	< 100	< 100	< 100	$\Delta v_1 \approx \Delta v_2 \approx \Delta v_3$
Partial match 1	< 100	> 100	> 100	$\Delta v_1 < \Delta v_2 \approx \Delta v_3$
Partial match 2	> 100	< 100	> 100	$\Delta v_1 \approx \Delta v_3 > \Delta v_2$
No match	> 100	> 100	> 100	N/A

In the matched case, frequency errors are small, and all are approximately equal. In the case of a partial match with the most significant mode, the frequency error 1 is less than 100 suggesting a similarity, while the frequency error 2 is larger than 100 suggesting a large difference between the search mode and second most significant mode frequencies. If this is the case, then the difference between the two matched modes must be large and approximately equal to frequency error 2. A partial match will predominate the types of errors observed.

The validation scheme was applied to the Cr(acac)₃ systems. It was found that the average speciation was 0.56, which suggests that around 56% of the top 2 matches included the bromo and iodo species giving a cross species set. Matches that returned with high error, include a speciation of 0, frequency differences greater than 100 cm⁻¹. The following table lists the averaged parameters for all 123 normal modes searched for. The complete table of matches as well as the table of non-averaged parameters are given in the appendix of this chapter. This also includes the validation by hand, where the top two matches are given a score of 1 or 0 to suggest a visual match was obtained or not.

Table 7.14: Validation parameters for the method.

Speciation	Avg S.	Freq Error 1 (cm ⁻¹)	Freq Error 2 (cm ⁻¹)	Freq Error 3 (cm ⁻¹)	Total Avg. Dist.	Manual verified (%)
0.56	20.78	94	235	270	0.065	48

The relatively low speciation ~56% and the manually verified match percentage of 48% suggests the potential for improvement of the method. While sufficiently greater than random chance, this is still underwhelming in its performance, but it provides a benchmark from which the method can be improved upon.

7.4.3 Application of Mode Matching

The method was applied to the coherent modes in table 11. Starting with the ~150 cm⁻¹ modes present in each species. The algorithm captures the similarity observed manually. If the 153 cm⁻¹ mode in Cr-(3-Clac)₃, two modes with a large similarity are observed. Note the captured frequencies are very close to the measured modes described in table C1. The fourth closest match, the 73 cm⁻¹ mode in Cr-(3-Iac)₃, which is not very closely matched.

Table 7.15: Top 3 matches for the 153 cm⁻¹ mode in Cr-(3-Clac)₃.

Mode Number	Frequency cm ⁻¹	<i>S</i>	Total Distance	Average Distance
133	122	30	1.63	0.05
256	101	25	1.71	0.07
254	73	7	0.42	0.06

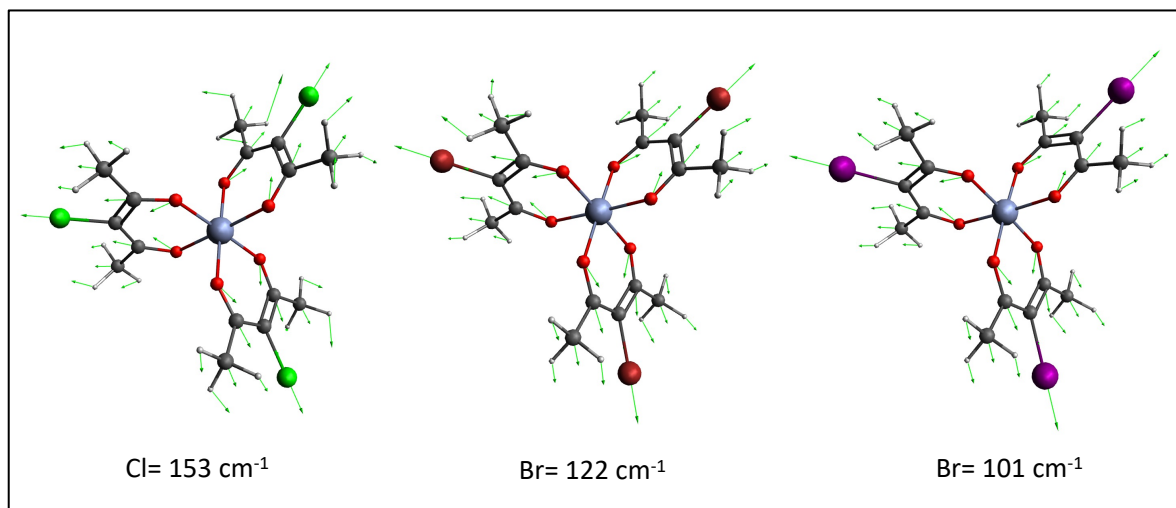


Figure 7.30: Visualized displacements for the 153 cm⁻¹ mode in Cr-(3-Clac)₃. These are in very good agreement and suggest a benchmark for standardization of matches.

The 204 cm⁻¹ measured frequency in Cr-(3-Iac)₃ was considered by searching for calculated mode 202 cm⁻¹. It was found to not have any significant matches a majority of which were found in the Cr-(3-Brac)₃ species. The best match was 212 cm⁻¹ in Cr-(3-Brac)₃ which is shown in the figures below. General trajectories are consistent, for example all atoms on the methyl groups move in a similar way, but the angle at which they occur are somewhat different between structures. There is not a mode in the Cr-(3-Clac)₃ that is deemed relevant. An associative search was performed by searching for the mode 212 cm⁻¹ in Cr-(3-Brac)₃. This yields better match for the Cr-(3-Iac)₃ 202 cm⁻¹. The returned match of 230 cm⁻¹ for the Cr-(3-Clac)₃ species is slightly different. It is difficult to gauge this as a match, even when the vibrations are visualized. The conservative position is that it is not a match. The data for this

associative search is included in the table below. The trend 201 cm^{-1} and 212 cm^{-1} is a similar pattern observed in the $\sim 150\text{ cm}^{-1}$ set's frequencies with the decrease in the size of the halide.

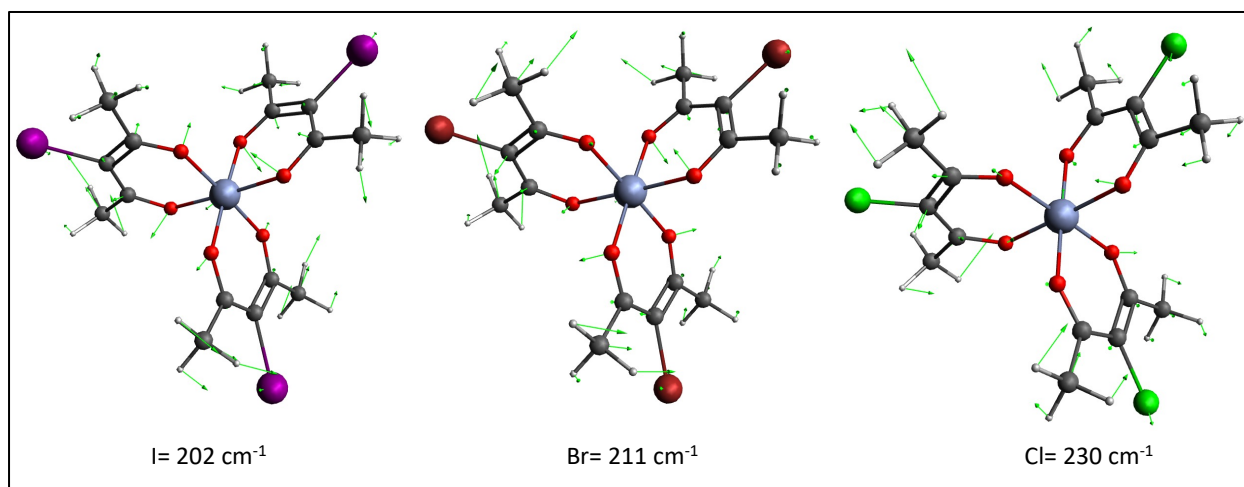


Figure 7.31: Visualized displacements for the modes matched from mode 269 in $\text{Cr}(\text{-3-Iac})_3$. The 230 cm^{-1} mode in the Cl-derivative was found by associative search of the bromo species. This does not represent a match.

Table 7.16: Matches and associative search results for the 269 mode in $\text{Cr}(\text{-3-Iac})_3$.

Search	Match	Frequency (cm^{-1})	S	Total Distance	Average Distance
269	146	212	8	0.57	0.07
	343	1488	8	0.62	0.08
	276	255	6	0.24	0.04
	291	456	6	0.69	0.12
	6	53	5	0.19	0.04
146	269	202	17	1.9	0.1
	23	230	16	1.5	0.1
	143	185	7	0.84	0.12

The measured $\text{Cr}(\text{-3-Clac})_3$ 449 cm^{-1} was considered. A significant match was found in $\text{Cr}(\text{-3-Brac})_3$ 441 cm^{-1} . $\text{Cr}(\text{-3-Iac})_3$ 431 cm^{-1} was included too however lacked the magnitude of significance compared with the former. An associative search of $\text{Cr}(\text{-3-Brac})_3$ 441 cm^{-1} did yield $\text{Cr}(\text{-3-Iac})_3$ 431 cm^{-1} as a top match, however with little significance. This proximity to degeneracy or near degeneracy, could be a driving factor as to why there is no high energy coherences in $\text{Cr}(\text{-3-Brac})_3$ or $\text{Cr}(\text{-3-Iac})_3$, as vibrational energy is easily distributed between

several possible nuclear degrees of freedom, leading to decoherence. A definitive statement like this is somewhat begging the question, however it illustrates a testable hypothesis that was only made possible by the algorithmic methodology applied.

Table 7.17: Matches and associative search results of the calculated 449 cm^{-1} mode in $\text{Cr}-(3\text{-Iac})_3$.

Search	Match	Frequency cm^{-1}	S	Total Distance	Average Distance
39	165	440.9	34	1.07	0.03
	37	445.3	7	0.60	0.09
	286	431.0	6	0.78	0.13
	49	613.4	5	0.35	0.07
165	39	449.9	35	1.08	0.03
	37	445.3	8	0.93	0.12
	286	431.0	8	1.17	0.15
	40	451.3	7	0.82	0.12
	38	445.4	6	0.24	0.04

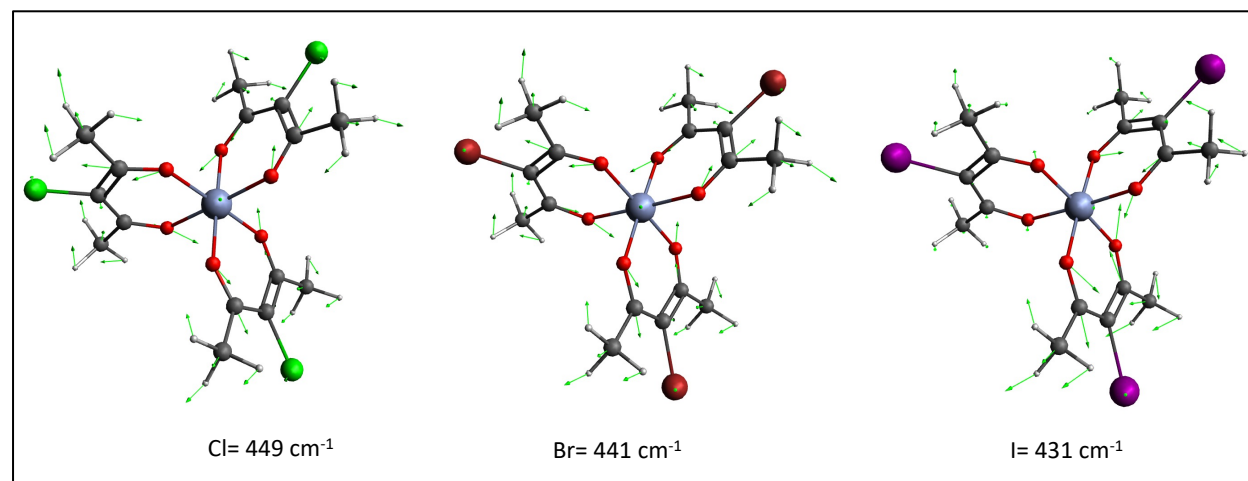


Figure 7.32: Visualized displacements for the modes matched from mode 239 in $\text{Cr}-(3\text{-Clac})_3$. The 431 cm^{-1} mode in the I-derivative was found by associative search of the 165 modes in the Br-derivative.

The measured $\text{Cr}-(3\text{-Clac})_3$ 93 cm^{-1} was examined. This gave two modes with large significance, $\text{Cr}-(3\text{-Brac})_3$ 83 cm^{-1} and $\text{Cr}-(3\text{-Iac})_3$ 78 cm^{-1} . This highlights the distinction between the measured $\text{Cr}-(3\text{-Iac})_3$ 55 cm^{-1} mode and the $\text{Cr}-(3\text{-Clac})_3$ 93 cm^{-1} . Suggesting the similar column in table C1 is inappropriate.

Examination of calculated Cr-(3-Iac)₃ 47 cm⁻¹, a similar frequency to the measured 55 cm⁻¹ was performed. The author notes the likelihood of error in this assumption. It can be noted from the table that this automatic search was a failure. A manual search gives the images below which suggests that the reason for the failure is that the displacement vectors in the Cr-(3-Iac)₃ species are near perfect opposites to the Cr-(3-Clac)₃ and Cr-(3-Brac)₃, which when searched for map onto each other extremely well. This type of mirror image relationship was noted in the validation section. This failure suggests opportunities to improve the algorithm, by considering the perfect opposites of each mode as well. The trajectory has physical meaning, the displacement vector describes the force along that trajectory. The vectors on the Cr-(3-Clac)₃ and bromo species should describe the resorting force of the vibration in the Cr-(3-Iac)₃ species.

From the analysis above, the table C1 can be filled in with the modes uncovered in this section. The frequencies in green were found by direct automatic search and the frequency in red was found through associative searching. As the algorithm failed for the Cr-(3-Iac)₃ 55 cm⁻¹ search, we leave the remaining spaces blank. The 181 cm⁻¹ mode was not considered as there are no similar calculated frequencies.

Table 7.18: Measured coherent frequencies with the frequencies of modes mapped in this section in green.

Compound		frequency, cm ⁻¹ (damping time, fs)				
Set	1	2	3	4	5	6
Cr-(3-Clac) ₃		93 (5450)	149 (1100)			449 (581)
Cr-(3-Brac) ₃		83	123 (2500)		212	441
Cr-(3-Iac) ₃	55 (2060)	78	101 (2400)	181 (200)	204 (1420)	431

7.5 CONCLUSIONS AND FUTURE WORKS

This chapter established the use of image decomposition to correlate vibrational modes internally, across spin-states, and across synthetic modifications. Prerequisite data processing includes a consistent atomic basis between atoms in similar positions. The indistinguishability of

atoms may make this method unusable in cases of very high symmetry. Thus, this method, is best suited for molecular structures which lack symmetry elements. It was found that the use of PCA on the set of displacement vectors followed by K-nearest-neighbors search was the best method for finding similarities in a manner that can tolerate differences across modification. This has an advantage to recreation of displacement vectors as the latter is limited in that its dependent on the amplitude of a vibration. This allows us to think of vibrational modes as classes across series, independent of their frequency or symmetry.

Finding these associations across systems may allow for the apportioning of reorganization energies, calculated, or measured, into atomic or group contributions to the total reorganization energy. For example, the contribution to the ethylene in 1,10-phenanthroline could be given a reorganization energy in comparison to a similar 2,2'-bipyridine complexes by considering the magnitude of the displacements of atoms in relevant vibrations found by the matching algorithm.

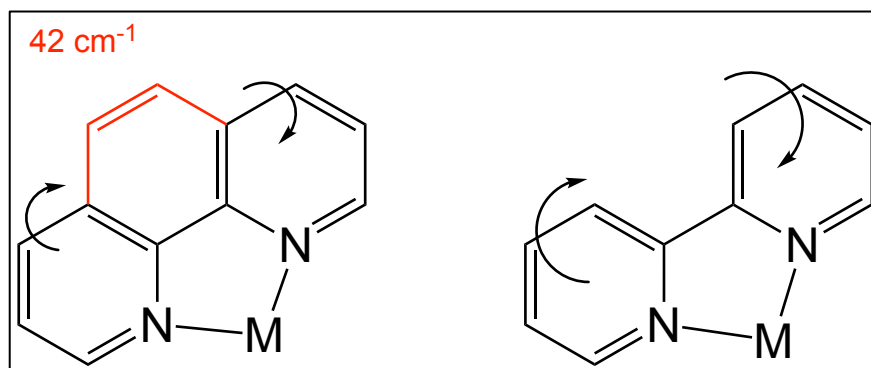


Figure 7.33: The matching algorithm could be utilized to find group contributions to the total reorganization energy by comparing the modes of similar vibrations and their magnitude of the corresponding displacement vectors. The value given for the reorganzaition energy is just for demonstration purposes.

The methodology is not perfect and is still prone to errors. In the case study, the method was validated on a series of Cr(III) species that had only minor modifications to their structure. The present form of the algorithm gave 48% of matches verified as accurate by visual inspection.

One primary reason for this is the highly literal nature of the method. This is shown by the tendency for the program to score perfect mirror images poorly. For example, displacement vectors in one species are colinear with the resorting force vector in another species and thus are not considered a match, even though they represent the same shape of a vibration. Another example of this literality was shown by the rotational relationship between **1** and **2**, where two normal modes, with the same frequencies and approximately the same set of displacement vectors were not found as matches. These could be achieved with minor cosmetic changes to the method which could be achieved in a few functions added on to the methods reported in the appendix.

With these minor changes accounted for, there are a few large changes that should be addressed. The most notable is the method chosen for binning PCs, which compares PCs adjacent to one another and thus limits the search region to these PCs. For example, the cartesian vector space in the current program could examine nearest neighbors of vibration i in PC_1 , PC_2 , and PC_3 but would not be able to include the cartesian vector space of PC_1 , PC_5 , and PC_{14} as these are not adjacent to one another. For an atom basis of 19 elements, the current binning method only includes 19 out of the ~969 configurations of PCs. There is clearly a lot of information being excluded. This type of analysis could be facilitated by a random integer search, where the PCs considered are randomly chosen, with the constraint that every PC is included at least 3x in different configurations. A ratio of significance could be utilized as an objective function, where the program will run until the ratio of the most significant mode to the average significance of the other modes is greater than some shelf value. This will add computational time and cost; however, it will likely allow for an improved search.



Figure 7.34: The class label ‘Apple’ and ‘Mountain Lion’ would be applied to sets of similar images where the encodings of each image will become associated with each class label.

This chapter has established a data science approach for examining vibrations and molecular structure. The analogy to image recognition is a great example of this. As with digital images, it would be possible to utilize machine learning (ML) algorithms to learn the relationships between compounds. A significant domain of ML, called supervised image recognition, which utilizes labeled images to train an algorithm. For example, the images in figure 34 would be given the class labels {‘Apple’, ‘Mountain Lion’}. Many similar images with similar class labels will be fed through the supervised algorithm, which decomposes the image into its encodings, and learn the features of that class label by trial and error until it can map a new image, without a class label, into one of the classes with a high degree accuracy. The algorithm developed in this chapter, which does not ‘learn’ in the ML sense could be utilized to generate labeled training data for such a supervised learning algorithm. Without this, the process of determining whether a given mode is a match or is not would be nearly impossible as it would have to be done by hand. Furthermore, it would be highly subjective as a person would tend to fixate on dominant vectors in each vibration rather than the vibration.

Modern image recognition is performed by convolutional neural networks (CNN) which utilize filters to reduce the dimension of input data. While the details of these filters are beyond

the scope of this work, a pictorial representation of such an algorithm is given in figure 35, which examines handwriting. In this case, a filter is applied that recognizes portions of the of the black and white numeral. If the image is scanned left-to-right, a portion of an image will be given a score for its congruence with said filter. For example, a filter that looks for the pattern black-black-white-white will identify edges of the numeral on the right-hand side, and the pixels in that portion of the image is given a high score. Another filter could be applied that looks for the left-hand side of the image, looking for the pattern, white-white-black-black. The data is reduced by considering the scores in the first step.

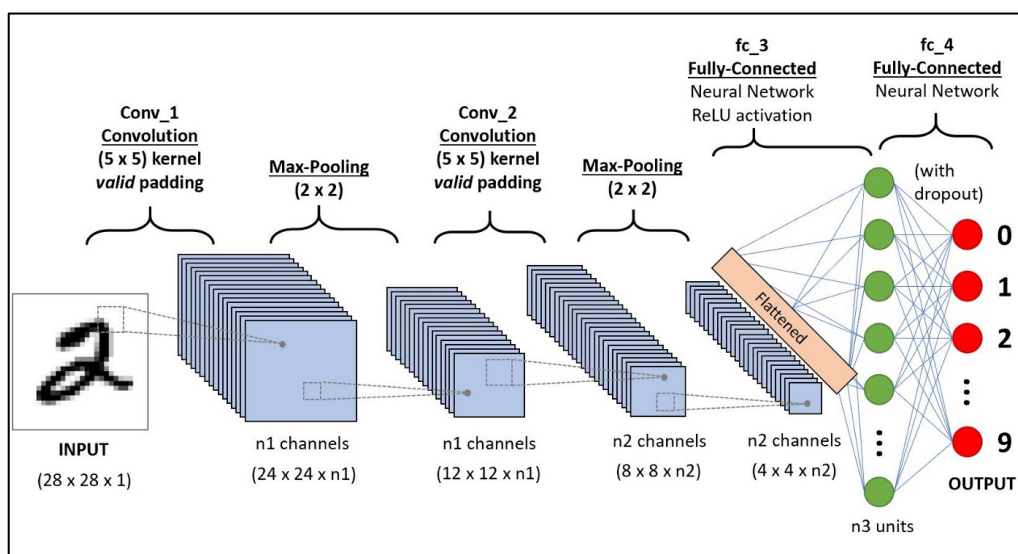


Figure 7.35: Graphical representation of a handwriting recognition algorithm. The first steps are the convolutional steps where filters are applied to the images and are decomposed by their structural elements. Taken from reference 27.

In the examination of molecular vibrations, filters could be used to find structural elements consistent in a set of molecules. For example, a filter associated with specific vibrational symmetry could be applied to local moieties to isolate different vibrational elements, which could be done on a large scale.

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APPENDIX

7.8.1 Importation of displacement vectors from Gaussian .log files

The following script was written in python, utilizing the Jupyter notebook work environment, which is a cell-based coding platform. Each block will be presented, and comments will be made below. Copies of the notebook will be made available upon request.

```
cd/Users/karlNielsen/Desktop/Bryan_CrAcAc_freq
```

```
In [19]:
```

```
import cclib

parser = cclib.io.ccpopen('Cr3Brac3_freq_UB3LYP_6311gdp_tight_cpcmToluene.log')
data = parser.parse()

#these keys are just for testing if everything has worked prints general information about cclib import
print("There are %i atoms and %i MOs" % (data.natom, data.nmo))
print('There are %i modes'% (3*data.natom-6))
atom_ID = list(range(0,data.natom))
```

```
There are 43 atoms and 664 MOs
```

```
There are 123 modes
```

Block 1: Directory is selected with standard shell commands. Select the directory where the file you want to examine is located. This section imports the python package cclib which can be obtained by the ‘pip install cclib’ key in the command window or terminal. This opens the .log

file, and assigns the data to a data object. This object can be called using the keywords found here (<https://cclib.github.io>). Useful data is printed to confirm everything has worked.

In [20]:

```
import pandas as pd
import numpy as np
import math
```

Block 2: Standard python imports required for functionality.

In [21]:

```
class atom():
    '''
        this object is an atom which has its specific coordinates from the final step of the optimization.
        this class also can convert the atom IDs to internal coordinates which can then become attributes of the class
        it also includes the atomic symbol associated with the atom
    '''
    def __init__(self, atom_ID):

        coords = data.atomcoords
        coord_dims = np.shape(coords)
        final_coords = coords[coord_dims[0]-1]

        self.atom_number = data.atomnos[atom_ID]
        self.xcoord = final_coords[atom_ID][0]
        self.ycoord = final_coords[atom_ID][1]
        self.zcoord = final_coords[atom_ID][2]

        #this method off of this class is called by inputting the atom_ID full vector into the method. ex atom.internalator(atom_ID)
    def internalator(self):
        internal_coords = []
        for positions in atom_ID:
            internal_coords.append([atom(0).xcoord - atom(positions).xcoord, atom(0).ycoord - atom(positions).ycoord, atom(0).zcoord - atom(positions).zcoord])
        return internal_coords
```

Block 3: This block creates an object for the z-matrix called atom. Each instance of this object has x,y, and z coordinates. The ‘internalator’ method for this object takes the absolute cartesian coordinates. This is a vestigial method but included for completeness.

In [6]:

```
all_disps = pd.DataFrame()  
for elem in list(range(0,data.vibdisps.shape[0])):  
    transfer = pd.DataFrame(data.vibdisps[elem])  
    transfer.to_excel('Cr3Brac3_disp_mode_' + str(elem+1)+'.xlsx')
```

Block 4: Uses the atom object to parse through the cartesian displacement vectors for each atom in each vibration and creates and saves an excel file. After this is run, there will be 3N-6 excel files, one for each vibration, so ensure this is in a clean folder.

7.8.2 Selection of vector and atomic basis

This section describes the process highlighted in figure 6 of the main text. The following sections are in MATLAB and describe the process of taking the desired atomic basis, creating a binary vector which is then used as a multiplier to reduce the large matrices X to a set of smaller matrices X' which are then reshaped and concatenated into the matrix $\mathbf{X}$ that will be decomposed in a later section. This program does not add up the cartesian displacement vectors and so the vector basis is 3x the atomic basis (57 vectors on 19 atoms).

%This block is the shell make the desired atomic basis at the functions %are at the end. The inputs: desired basis (Zprime) & complete basis (Z)

```
norm_disps = zeros(261,57);  
  
[desired,complete] = internalizer(dmp_desired_basis,dmp_complete_basis);  
  
for i = 1:261  
    filename = sprintf(['DMP_ground_disp_mode_%d'],i);  
    disps = xlsread(filename);  
    disps(:,1) = []; disps(1,:) = [];  
  
    basis = basis_maker(desired,complete);  
  
    disps = basis_selector(disps,basis);  
  
    rotated_disps = [disps(1,:)];
```



```

norm_disps = [norm_disps disp(:,1) disp(:,2) disp(:,3)];

disp_vect = reshape(disp',57,1);
for j=1:3:57
    norm_disps(i,j:j+2) = disp_vect(j:j+2);
end
end
%norm_disps = norm_disps';

```

```

function include = basis_maker(desired,complete)
    ordering = [1 9    8 6    7    4    5    3    2    13    12    11
               10   16   17   14   15   19   18]';
    size_complete = size(complete);
    size_desired = size(desired);

    multiplier = zeros(size_complete(1),1);

    for n = 1:size_desired(1)
        for m = 1:size_complete(1)
            search1 = desired(n,:);
            search2 = complete(m,:);

            score = sum(search1) - sum(search2);

            if score == 0
                multiplier(m) = 1;
            end
        end
    end

    include = complete.*multiplier;

    include( all(~include,2), : ) = [];

    include = [[0 , 0 ,0];include];

    if isequal(desired,include) == 1
        return_multiplier = multiplier;
    else
        error('The geometries cannot converge.')
    end
end

```

```

function condensed_disps = basis_selector(disps,basis)

    size_disps = size(disps);

    condensed_disps = [];

    check = [basis, disps];

    for n = 1:size_disps(1)
        if check(n,1) == 1
            condensed_disps = [condensed_disps; check(n,2:4)];
        end
    end
end

function Rft = rotator(DMP,gal)
    %This function is based on the work of Möller et. al. 1999.

    f = (DMP/norm(DMP))';
    t = (gal/norm(gal))';

    scaling = f'./DMP;

    v = cross(f,t);
    c = dot(f,t);

    h = (1-c)/(dot(v,v));

    v1 = v(1)^2;
    v2 = v(2)^2;
    v3 = v(3)^2;

    Rft1 = [c+h*v1 h*v(1)*v(2)-v(3) h*v(1)*v(3)+v(2)];
    Rft2 = [h*v(1)*v(2)+v(3) c+h*v2 h*v(2)*v(3)-v(1)];
    Rft3 = [h*v(1)*v(3)-v(2) h*v(2)*v(3)+v(1) c+h*v3];

    Rft = [Rft1;Rft2;Rft3];

    dmp_rot = Rft*f;
    dmp_rot*norm(DMP);

    dot(dmp_rot,t)

    dmp_rot = (dmp_rot*norm(DMP))';
    gal;
end

```

```

function [desire_internal,complete_internal] =
internalizer(desired,complete)

    desire_internal = [];
    complete_internal = [];

    root1 = desired(1,:);
    root2 = complete(1,:);

    size_desire = size(desired);
    size_complete = size(complete);

    for n = 1:size_desire(1)
        shift = desired(n,:) - root1;
        desire_internal = [desire_internal; shift];
    end

    for n = 1:size_complete(1)
        shift = complete(n,:) - root2;
        complete_internal = [complete_internal; shift];
    end
end

```

7.8.3 Single Value Decomposition

The SVD was performed using a script analogous to the one reported in the appendix of chapter 6 of this dissertation. Here we report the significance statistics of decomposition of the **X** matrix of the quintet and ground states of **1**.

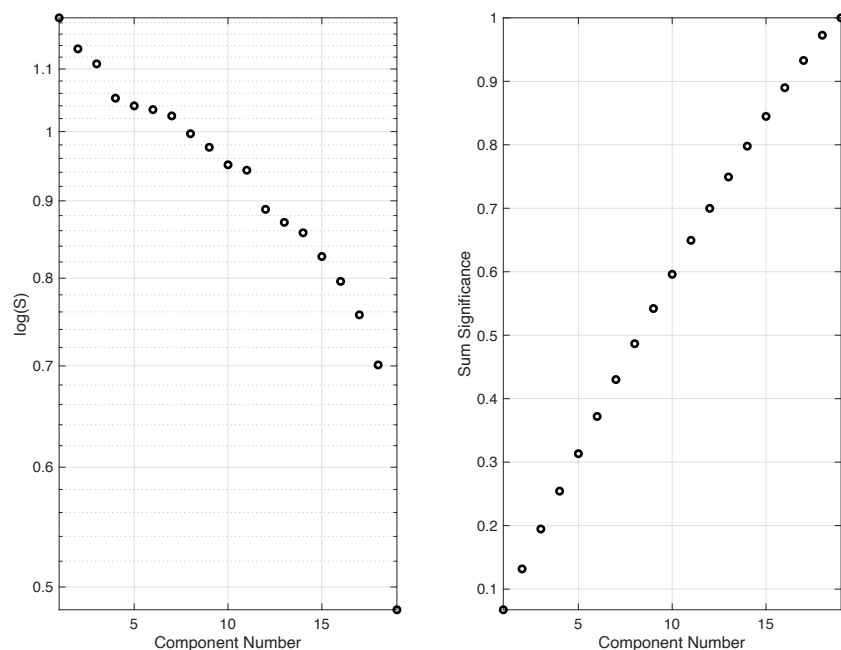


Figure S7.36: (left) Scree plot for the 19-vector basis of the quintet state of **1**. (right) cumulative significance of the singular values for the same state.

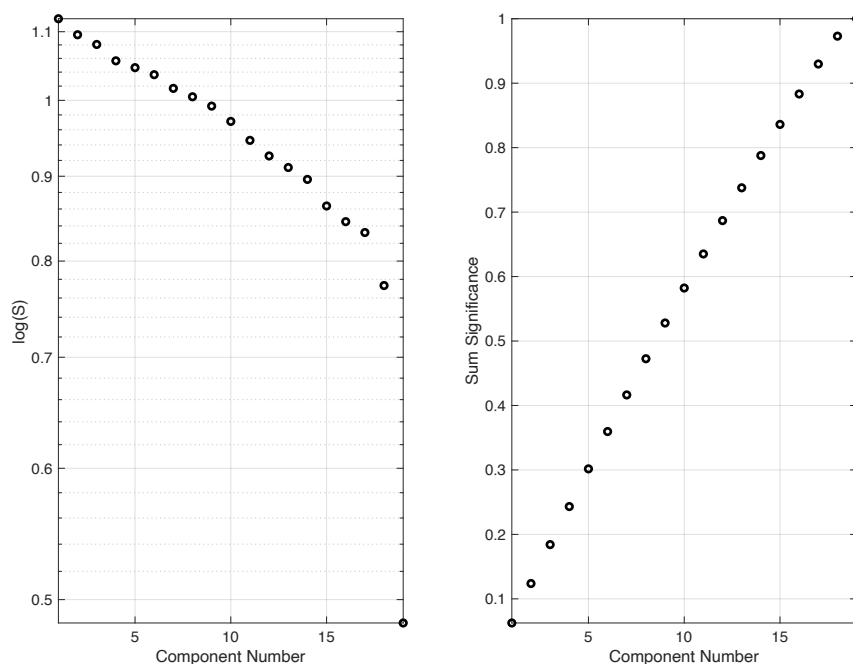


Figure S7.37: (left) Scree plot for the 19-vector basis of the ground state of **1**. (right) cumulative significance of the singular values for the same state.

A question that should be addressed regarding the optimal basis from which to represent the data, i.e. how many components to include. This can be gauged by the linearity of the sum of

significance plot over the whole domain. The further away from linearity the more skewed the data is toward one atom or another. Consider decompositions of low component spectra which show a nearly 90-degree bend near the first two components.

7.8.4 Filtering Procedure for the Displacements Reconstructed from Singular Vectors

This script generates the vibrational heatmaps with the important modes appended. Modes are determined to be important if they have a reconstructed amplitude of greater than 0.1. This is determined in the function called discriminator. This output is made into a new cell called 'important_vibrations'. This cell is presented in the tables below.

```
%This script takes the individually reconstructed real displacements from
%a cell structure called SVD_reconst which in this case is a 183x19x19
%structure. It selects important modes based on their amplitudes and saves
%a pdf of the figure with the important modes appended.
```

```
for n = 1:19
    p = SVD_reconst{n};

    transfer = discriminator(p);
    important_vibrations{n} = transfer;

    figure
    h = heatmap(p, "ColorMethod", "median");
    Ax = gca;
    Ax.XDisplayLabels = nan(size(Ax.XDisplayData));

    figname = strcat('Ground Heatmap ', string(n));
    annotation('textbox', [0 0 .5
.5], 'String', string(transfer), 'FitBoxToText', 'on');

    saveas(h, strcat(figname, '.pdf'));
end
```

```
function [out_array] = discriminator(p)
```

```

scorecard = [];
for n = 1:183 %change based on number of vibrations
    for m = 1:19
        if abs(p(n,m)) > 0.1
            score_card(n) = n;
        end
    end
end
out_array = nonzeros(score_card);
end

```

Table S7.19 Important vibrations for each of the eigenmodes of the triplet state of **1** determined by the script in this section. The column headers correspond the eigenmodes visualized in figure 10 of the main text. The numbers underneath are the normal mode indexes. Normal modes can be described by multiple eigenvectors.

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
10	5	10	10	60	74	26	23	45	21	31	3	62	3	57	5	48	47	1
42	10	19	22	73	93	31	31	63	52	59	7	65	6	124	7	54	49	19
43	17	22	29	123	148	55	44	77	62	67	11	100	7	153	22	55	54	22
60	19	30	30	149		59	55	80	78	123	18	101	15		32	97	56	32
79	29	53	45	154			122	93	79	145	26	110	18		33	109	57	
80	32	62	52				149	94	94		28	120	19		62	114	61	
148	42	65	73					95			31	128	20			151	92	
149	52	73	74					98			32	129	22				126	
	63	78	77					121			87	145	31				150	
	64		78					122			92	146	33				151	
	65		93					123				152	61					
			94										70					
			95										87					
			96										108					
			122										119					
			123															
			128															
			145															
			149															
			157															

Table S7.19 (cont'd) Important vibrations for each of the eigenmodes of the quintet state of **1** determined by the script in this section. The column headers correspond the eigenmodes visualized in figure 9 of the main text.

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
42	4	10	6	32	10	53	52	11	40	1	37	145	10	22	5	33	35	2
60	30	14	10	61	60	78	77	12	41	5	124		20	25	6	34	48	21
79	32	31	60	73	79		93	21	61	19	135		33	30	9	54	56	22
80	38	39	65	74	80			46	66	25	146		85	32	13	55	59	25
122	43	62	93	122	93			53	67	27	153		88	33	18	114	97	62
149	52	63	122		94			62	94	28			97	54	19	148	109	
150	53	65	123		122			78	99	29					20			
	65	73	154		149			80	123	30					59			
	73	77			150			94	145	32					70			
	74	78			154				149	33					119			
	77				155					34								
										54								
										119								

Table S7.20: Important vibrations for each of the eigenmodes of the ground state of **1** determined by the script in this section. The column headers correspond the eigenmodes visualized in figure 11 of the main text.

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
17	7	13	17	13	14	52	16	56	33	18	61	18	17	67	6	3	6	16
27	14	14	45	14	29	58	17	74	58	24		30	31	110	19	18	33	19
29	29	16	63	17	58	59	58	78	61	25		56	33	121	25	20	60	28
32	33	19	93	21	93	77	59	120	93	30		87	61	131	31	55	65	31
34	35	29	94	31	94	78	61	150	94	55		92		145	60	56		32
52	42	35	122	32	96	79	77	151	145	56					65	116		33
53	43	58	150	42	123	80	79			57					70	149		
59	58	65		44	146	96	80			61					87			
73	59	67		53	154	123	93											
74	65	77		59		150	94											
78	67	78		61			96											
93	77	122		74			151											
157	78	123		157			155											
	79	150																
	80	151																

Table S7.20 (cont'd)

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
	122	154																
	123	155																
	150																	
	151																	
	154																	
	155																	

The heatmap diagrams which were generated from the script in this section will be made available upon request.

7.8.5 Principal Component Analysis and K-Nearest Neighbors Search

The primary and final methodology is based on the PCA and KNN search algorithms.

The graphical representation of this is presented in figure 15 of the main document.

```
%this script takes the input matrix called 'mixed' which is the composite
%data of the real-displacement matrices of the compounds that are being
%considered. For example the 183x19 displacements for the ground, triplet
%and quintet states of 1 are joined to a 549x19 matrix. The program outputs
%a table called 'scored_modes' which are presented as the data tables in
%the section of the main document.
```

```
%this section performs the PCA and defines the search mode
```

```
[coeff,score,latent,tsquared,explained] = pca(mixed,"Algorithm","svd");
All_modes_mapped = {};
dims = size(mixed);
```

```
***user input search mode and search width***
```

```
search_mode = 11;
search_span = 11;
```

```
K_cells = {};
dists = {};
```

```
for n = 1:dims(2)
    if n <= (dims(2)-2)
        search = score(search_mode,n:n+2);
        [Idx D] = knnsearch(score(:,n:n+2),search,'K',search_span);
```



```

        Idx(1) = [];
        K_cells{n} = [Idx];
        D(1) = [];
        dists{n} = [D];
    elseif n == (dims(2)-1)
        search = score(search_mode,[n,n+1,1]);
        [Idx D] = knnsearch(score(:,[n,n+1,1]),search,'K',search_span);
        Idx(1) = [];
        K_cells{n} = [Idx];
        D(1) = [];
        dists{n} = [D];
    elseif n == dims(2)
        search = score(search_mode,[n,1,2]);
        [Idx D] = knnsearch(score(:,[n,1,2]),search,'K',search_span);
        Idx(1) = [];
        K_cells{n} = [Idx];
        D(1) = [];
        dists{n} = [D];
    end
end

scored_modes = KNN_dist_normalize(D_compiled_actual,K_cells,dists);

%this section generates a graph of the search mode and the corresponding
%scores that were found by KNN

G = graph(1,dims(1),'omitselfloops');
G = rmedge(G,1,dims(1));

for n = 1:dims(2)
    search = K_cells{n};

    G = addedge(G,search_mode,search(1,:));
    G = rmedge(G,search_mode,search_mode);
end

e = table2array(G.Edges);

%this section makes a histogram of the data
figure
hist(e(:,2),dims(1))
plot(G,'layout','force','NodeLabel',1:dims(1),'NodeFontSize',10,'EdgeColor',
',[0.65,0.65,0.65],'Nodecolor',[0.00,0.00,0.00],'MarkerSize',3)

```

```

function [out_table] = KNN_dist_normalize(D_compiled,K_cells,dists)

    %this function takes the discovered modes and puts them into a nice
    %table.

    K_cells = cell2mat(K_cells);
    dists = cell2mat(dists);

    dims3 = size(K_cells);
    standard_values = unique(K_cells);
    dims2 = size(standard_values);
    out_array = zeros(dims2(2),5);

    K_cells = reshape(K_cells, [1 dims3(1)*dims3(2)]);
    dists = reshape(dists,[1 dims3(1)*dims3(2)]);

    value_bool = zeros(size(dists));

    for p = 1:dims2(2)
        search_value = standard_values(p);
        for m = 1:dims3(2)
            if K_cells(m) == search_value
                value_bool(m) = 1;
            else
                value_bool(m) = 0;
            end
        end
        bool_dist = dists.*value_bool;

        total_number = sum(value_bool);
        total_dist = sum(bool_dist);

        out_array(p,:) = [search_value D_compiled(search_value)
total_number total_dist [total_dist/total_number]];

    end
    out_table = array2table(out_array);
end

function mixed2 = reflector(mixed,search_mode,speciation)

    mixed1 = mixed(1:search_mode(size(search_mode,1)),:);
    mixed1 = mixed1.*speciation;

    speciation2 = speciation+1;

```

```

for n=1:size(speciation,1)
    if speciation2(n) == 2;
        speciation2(n) = 0;
    end
end

mixed2 = mixed(1:search_mode(size(search_mode,1)),:);
mixed2 = (mixed2.*speciation2)*-1;

mixed3 = mixed1+mixed2;

mixed_mod
end

```

The KNN search algorithm is very simple conceptually; it projects a circle around a specific element in the search space. This continues until K elements have been counted. Each element has a distance element associated with it which can be thought of as either the radius of the circle which intersects it or Euclidean distance. Euclidian distance is used when considering higher dimensions. The figure below illustrates this process graphically for a searched element.

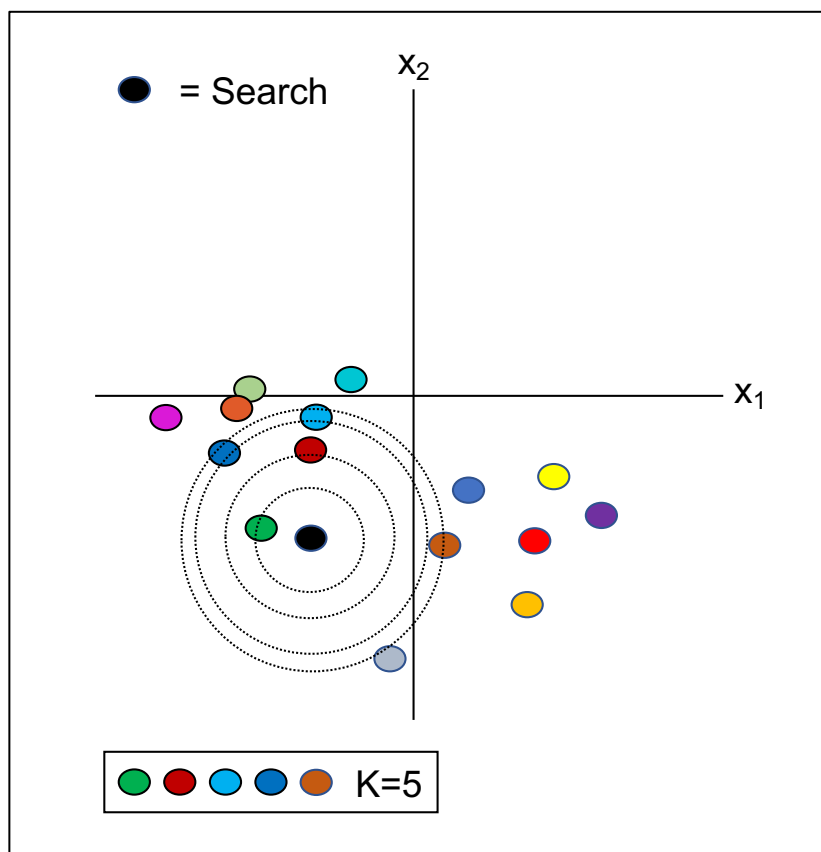


Figure S7.38: Graphical representation of the KNN search algorithm for an element of the Cartesian space of x_1 and x_2 . The concentric circles are intended to represent the search space around the black dot. The algorithm stops when five elements are found.

7.8.6 Validation

The methodology was validated with control script which iteratively runs the PCA/KNN algorithm takes the results and calculates the parameters which were discussed in the introduction. The validation was only performed on the Cr(III) complexes. For this validation process, the modes associated with the Cl-species are taken as search modes: however, all modes were considered as potential matches, which means other modes in the Cl-species could be found as matches. The table of all validation results are included after the script.

```
%this program takes input called 'mixed'. A a search mode is selected
%between 1-123 (3N-6 in acac species) and searches for each mode. It runs
the KNN/PCA
```

```

% for each search mode. It calculates the validation parameters in the
% function called paramters. The program returns an array called
avg_specs.

validation_array = [];
validation_cell = {};
avg_specs = [];

mixed = mixed_real;
for g = 13
    for p = 1:(size(mixed,1)/3)
        search_mode = p;
        search_span = g;
        PCA_KNN_correlator

        B = sortrows(scored_modes,"out_array3",'descend');
        B = table2array(head(B,2));

        validation_array = [validation_array; B];
        validation_cell{p} = B;

    end

    [summary,speciation,freq_error1,freq_error2,freq_error3,Tavg_distance]
= parameters(validation_cell,validation_array,freqsCl);

    avg_specs = [avg_specs summary(1)];
end

spec_multi = [ones(123,1); speciation; speciation];

mixed_mod = spec_multi.*mixed;

mixed = mixed_mod;
for g = 13
    for p = 1:(size(mixed_mod,1)/3)
        search_mode = p;
        search_span = g;
        PCA_KNN_correlator

        B = sortrows(scored_modes,"out_array3",'descend');
        B = table2array(head(B,2));

        validation_array = [validation_array; B];
        validation_cell{p} = B;

    end
end

```

```

    [summary,speciation,freq_error1,freq_error2,freq_error3,Tavg_distance]
= parameters(validation_cell,validation_array,freqsCl);

    avg_specs = [avg_specs summary(1)];
end

```

```

function
[summary,speciation,freq_error1,freq_error2,freq_error3,Tavg_distance] =
parameters(validation_cell,validation_array,freqsCl)
    speciation = [];
    freq_error1 = [];
    freq_error2 = [];
    freq_error3 = [];

    br1 = 124;
    br2 = 246;
    br3 = 369;

    %need species distribution
    for n = 1:size(freqsCl,1)
        examine = validation_cell{n};

        %need species distribution
        ex1 = examine(:,1);

        if br1<=ex1(1) & ex1(1)<=br2 & br2+1<=ex1(2) & ex1(2)<=br3
            speciation = [speciation; 1];

        elseif br1<=ex1(2) & ex1(2)<=br2 & br2+1<=ex1(1) & ex1(1)<=br3
            speciation = [speciation; 1];

        else
            speciation = [speciation; -1];
        end

        %need average similarity
        avg_similar =
(sum(validation_array(:,3))/size(validation_array,1));

        %need total average distance
        Tavg_distance =
(sum(validation_array(:,5))/size(validation_array,1));

        %need average frequency difference
        ex2 = examine(:,2);

        freq_error1 = [freq_error1; abs(freqsCl(n) - ex2(1))];
        freq_error2 = [freq_error2; abs(freqsCl(n) - ex2(2))];
    end
end

```

```

        freq_error3 = [freq_error3; abs(ex2(1) - ex2(2))];
    end

    summary =
    [sum(speciation/123), avg_similar, mean(freq_error1), mean(freq_error2), mean(
    freq_error3), Tavg_distance];

end

```

Table S7.21: Raw validation output. Only the top two modes were considered. Table continues uninterrupted until page 439.

Search Mode	Matched Modes	Mode frequency	<i>S</i>	Total Distance	Average Distance	Manual Match
1	146	211.86	10	1.23	0.123	0
	148	227.53	10	1.32	0.132	
2	125	12.22	35	2.35	0.067	1
	248	8.51	17	1.34	0.079	
3	126	16.29	25	1.96	0.079	1
	249	11.10	16	1.55	0.097	
4	127	43.58	43	1.32	0.031	1
	250	39.37	36	1.85	0.052	
5	128	45.32	35	0.98	0.028	1
	251	41.41	19	0.64	0.033	
6	129	50.89	43	1.06	0.025	0
	86	1401.54	7	0.20	0.029	
7	130	78.18	41	1.64	0.040	1
	253	72.21	34	1.54	0.045	
8	254	72.78	29	1.14	0.039	1
	131	79.04	23	1.50	0.065	
9	132	83.18	42	1.76	0.042	1
	255	77.98	28	1.74	0.062	
10	134	126.47	36	0.80	0.022	1
	257	137.39	32	1.34	0.042	
11	135	132.71	39	1.03	0.026	1
	258	144.24	32	2.26	0.071	
12	136	138.02	31	0.98	0.031	0
	94	1462.99	13	0.50	0.039	
13	137	141.96	31	0.67	0.021	0
	139	154.42	12	0.45	0.038	
14	138	145.31	31	0.94	0.030	1
	261	156.83	14	1.99	0.142	

Table S7.21 (cont'd)

15	133	122.08	30	1.63	0.054	1
	256	101.55	25	1.71	0.068	
16	139	154.42	34	0.43	0.013	0
	137	141.96	9	0.36	0.040	
17	140	165.96	10	0.75	0.075	0
	266	166.25	10	1.06	0.106	
18	141	166.11	16	2.34	0.146	1
	263	159.15	11	1.49	0.135	
19	266	166.25	17	1.71	0.101	0
	22	228.95	12	0.90	0.075	
20	143	185.40	23	2.01	0.087	0
	124	8.58	9	1.40	0.155	
21	141	166.11	14	1.69	0.121	1
	263	159.15	8	0.67	0.084	
22	272	221.93	17	2.18	0.128	0
	19	182.33	15	1.18	0.078	
23	146	211.86	17	1.84	0.108	0
	3	22.08	8	1.20	0.150	
24	143	185.40	10	1.33	0.133	0
	260	154.07	8	1.30	0.162	
25	267	166.64	11	0.79	0.072	0
	184	990.60	10	0.82	0.082	
26	31	277.03	9	0.82	0.091	0
	279	274.48	9	0.86	0.096	
27	149	228.56	15	1.70	0.113	0
	15	153.31	8	0.63	0.078	
28	152	260.36	25	1.93	0.077	0
	25	260.46	12	2.19	0.182	
29	355	3060.18	11	0.36	0.033	0
	23	230.41	8	0.91	0.113	
30	274	252.37	25	1.69	0.068	0
	33	286.68	9	1.20	0.133	
31	277	266.59	22	0.96	0.043	0
	268	200.59	8	0.73	0.092	
32	278	272.73	25	1.47	0.059	1
	154	271.40	17	1.83	0.108	

Table S7.21 (cont'd)

33	279	274.48	24	1.53	0.064	1
	156	273.17	23	1.84	0.080	
34	158	345.73	22	1.40	0.064	1
	284	383.57	14	0.97	0.069	
35	192	1043.08	8	0.30	0.037	0
	285	385.01	8	0.95	0.119	
36	159	359.15	38	1.27	0.033	1
	283	352.04	27	1.53	0.057	
37	41	451.54	8	0.69	0.086	0
	165	440.88	7	0.34	0.048	
38	291	455.72	14	0.66	0.047	0
	168	459.44	10	0.69	0.069	
39	165	440.88	34	1.07	0.031	0
	37	445.30	7	0.60	0.085	
40	166	454.21	9	1.28	0.142	0
	167	458.88	8	0.40	0.050	
41	37	445.30	10	0.82	0.082	0
	285	385.01	8	0.48	0.060	
42	289	450.43	29	0.85	0.029	0
	43	477.07	11	1.29	0.117	
43	160	388.99	30	2.35	0.078	1
	282	349.48	10	0.68	0.068	
44	43	477.07	7	0.63	0.089	0
	161	403.83	7	0.62	0.088	
45	166	454.21	7	0.55	0.078	0
	289	450.43	7	0.36	0.052	
46	169	556.27	31	1.19	0.038	0
	294	560.47	9	0.46	0.051	
47	293	559.19	20	2.15	0.107	0
	320	1069.40	11	0.58	0.053	
48	171	558.35	39	1.65	0.042	1
	294	560.47	29	1.67	0.058	
49	172	613.94	40	0.82	0.021	1
	295	600.77	31	1.80	0.058	
50	173	614.88	34	1.17	0.034	1
	296	601.27	16	0.80	0.050	
51	174	630.01	36	0.70	0.019	1
	297	615.15	26	0.92	0.036	

Table S7.21 (cont'd)

52	175	652.73	17	1.26	0.074	0
	53	658.18	10	0.45	0.045	
53	175	652.73	13	1.15	0.089	0
	52	658.09	10	0.45	0.045	
54	177	653.49	34	1.12	0.033	1
	300	666.60	13	1.13	0.087	
55	42	454.62	9	0.80	0.088	0
	26	261.09	8	0.53	0.066	
56	181	927.44	10	1.05	0.105	0
	60	929.09	8	0.56	0.070	
57	180	706.41	35	0.86	0.024	1
	303	693.76	23	1.35	0.059	
58	181	927.44	36	1.66	0.046	1
	304	930.11	29	1.79	0.062	
59	306	932.52	29	1.08	0.037	0
	287	431.36	8	0.31	0.039	
60	305	932.35	29	1.33	0.046	1
	183	928.84	12	0.72	0.060	
61	184	990.60	32	1.13	0.035	1
	307	976.54	11	1.02	0.092	
62	185	991.65	33	1.51	0.046	0
	92	1456.41	8	1.36	0.170	
63	186	994.23	28	1.25	0.045	0
	214	1454.73	13	1.16	0.089	
64	311	1040.60	11	1.16	0.105	1
	188	1033.76	10	1.62	0.162	
65	188	1033.76	23	1.96	0.085	0
	186	994.23	11	1.50	0.136	
66	190	1042.65	24	0.88	0.037	1
	317	1064.76	19	0.76	0.040	
67	191	1042.73	21	0.80	0.038	0
	192	1043.08	11	0.17	0.015	
68	192	1043.08	11	1.14	0.104	0
	177	653.49	9	1.10	0.122	
69	320	1069.40	13	1.35	0.104	0
	346	1489.62	11	1.03	0.094	
70	189	1037.31	11	0.69	0.063	0
	182	928.71	8	0.39	0.048	

Table S7.21 (cont'd)

71	170	556.82	10	1.50	0.150	0
	358	3137.35	9	0.70	0.078	
72	170	556.82	10	0.98	0.098	0
	224	1484.71	8	0.67	0.083	
73	313	1057.12	26	0.84	0.032	1
	195	1046.03	13	0.42	0.033	
74	197	1046.78	39	1.02	0.026	1
	314	1057.85	37	1.62	0.044	
75	198	1047.51	27	1.13	0.042	1
	315	1058.19	15	0.52	0.035	
76	199	1308.08	36	1.07	0.030	1
	322	1321.78	13	1.08	0.083	
77	200	1308.61	41	1.24	0.030	1
	323	1322.24	16	1.40	0.087	
78	162	403.97	10	1.16	0.116	0
	74	1047.48	6	0.50	0.083	
79	313	1057.12	11	0.48	0.044	0
	129	50.89	9	0.88	0.098	
80	202	1380.67	12	1.02	0.085	0
	82	1394.32	10	0.84	0.084	
81	207	1397.68	14	1.17	0.083	0
	84	1395.87	11	1.14	0.104	
82	330	1426.16	12	0.82	0.068	0
	339	1464.51	11	0.95	0.087	
83	206	1396.58	33	1.66	0.050	1
	331	1426.26	10	0.91	0.091	
84	355	3060.18	16	1.26	0.079	0
	81	1377.20	10	0.90	0.090	
85	304	930.11	10	1.26	0.126	0
	79	1374.72	9	1.57	0.174	
86	209	1400.75	35	1.32	0.038	1
	322	1321.78	8	0.60	0.074	
87	210	1401.56	38	0.80	0.021	1
	305	932.35	8	0.90	0.113	
88	211	1450.50	16	0.48	0.030	0
	213	1453.43	9	0.97	0.108	
89	212	1450.95	23	0.74	0.032	1
	338	1455.37	9	0.70	0.078	

Table S7.21 (cont'd)

90	339	1464.51	21	0.68	0.032	0
	105	1617.85	8	1.15	0.144	
91	100	1485.26	7	0.50	0.072	0
	139	154.42	7	0.38	0.054	
92	216	1455.61	22	0.94	0.043	0
	70	1045.46	7	0.56	0.080	
93	214	1454.73	18	1.15	0.064	0
	215	1454.97	13	1.06	0.081	
94	217	1466.26	30	0.69	0.023	0
	134	126.47	19	0.64	0.034	
95	218	1466.56	42	0.98	0.023	1
	344	1488.54	29	1.78	0.062	
96	345	1488.92	43	0.66	0.015	1
	219	1467.40	42	0.85	0.020	
97	220	1468.24	23	0.79	0.034	1
	360	3138.19	21	0.65	0.031	
98	221	1468.42	37	1.32	0.036	0
	129	50.89	10	0.40	0.040	
99	222	1469.22	37	0.88	0.024	1
	347	1490.37	20	0.86	0.043	
100	223	1484.26	25	0.72	0.029	0
	229	3045.39	14	1.09	0.078	
101	224	1484.71	8	0.50	0.062	0
	225	1484.98	8	0.69	0.086	
102	224	1484.71	17	1.15	0.068	0
	65	1039.76	10	1.48	0.148	
103	350	1527.78	29	2.04	0.071	0
	122	3149.55	8	0.49	0.062	
104	227	1584.75	34	1.31	0.039	1
	337	1455.28	9	1.33	0.148	
105	228	1616.24	39	0.96	0.024	1
	351	1548.36	15	1.62	0.108	
106	365	3184.48	17	1.57	0.092	0
	138	145.31	15	0.93	0.062	
107	231	3045.49	42	0.69	0.016	1
	352	3059.42	42	0.34	0.008	
108	230	3045.47	39	0.77	0.020	1
	367	3184.87	17	1.29	0.076	

Table S7.21 (cont'd)

109	354	3060.04	43	0.72	0.017	1
	234	3046.11	30	0.97	0.032	
110	356	3060.42	34	1.08	0.032	1
	232	3045.96	30	2.12	0.071	
111	233	3046.08	21	1.19	0.057	0
	115	3102.65	9	0.30	0.033	
112	235	3102.66	37	0.99	0.027	1
	360	3138.19	15	0.21	0.014	
113	359	3137.65	42	1.36	0.032	1
	236	3102.84	39	1.88	0.048	
114	358	3137.35	43	0.54	0.013	1
	237	3103.00	42	0.51	0.012	
115	238	3103.86	30	0.93	0.031	1
	363	3139.64	30	1.12	0.037	
116	361	3138.88	42	0.31	0.007	1
	240	3104.27	40	0.42	0.011	
117	362	3139.31	40	1.49	0.037	1
	239	3104.07	38	1.85	0.049	
118	366	3184.54	39	2.32	0.059	1
	242	3147.80	35	3.01	0.086	
119	365	3184.48	43	0.61	0.014	1
	241	3147.62	41	0.73	0.018	
120	243	3147.88	36	1.12	0.031	1
	357	3060.77	15	0.33	0.022	
121	245	3148.28	41	0.78	0.019	1
	369	3184.99	41	0.60	0.015	
122	222	1469.22	16	0.49	0.030	0
	99	1465.39	14	0.36	0.026	
123	246	3148.35	42	0.95	0.023	1
	367	3184.87	10	0.28	0.028	
					total verified	59
					verified percentage	0.47

Table S7.22: Validation parameters from the data presented in table 4. The averages of these data are given in the main document. Table continues uninterrupted until page 442.

Search Mode	Speciation	Freq Error 1 (cm ⁻¹)	Freq Error 2 (cm ⁻¹)	Freq Error 3 (cm ⁻¹)
1	0	199.0	214.7	15.7
2	1	4.7	8.4	3.7
3	1	5.8	11.0	5.2
4	1	4.2	8.4	4.2
5	1	3.8	7.7	3.9
6	0	2.4	1348.2	1350.6
7	1	8.9	14.8	6.0
8	1	15.0	8.7	6.3
9	1	8.3	13.5	5.2
10	1	8.8	2.1	10.9
11	1	6.5	5.0	11.5
12	0	5.4	1319.6	1325.0
13	0	3.6	8.9	12.5
14	1	3.0	8.5	11.5
15	1	31.2	51.8	20.5
16	0	0.6	13.1	12.5
17	1	7.4	7.1	0.3
18	1	8.5	15.5	7.0
19	0	16.1	46.6	62.7
20	0	22.3	199.1	176.8
21	1	41.9	48.8	7.0
22	0	7.0	46.6	39.6
23	0	18.6	208.3	189.8
24	1	52.2	83.6	31.3
25	1	93.8	730.1	824.0
26	0	15.9	13.4	2.6
27	0	32.9	108.1	75.3
28	0	8.7	8.6	0.1
29	0	2790.9	38.8	2829.8
30	0	20.5	13.8	34.3
31	0	10.4	76.4	66.0
32	1	13.2	14.5	1.3
33	1	12.2	13.5	1.3
34	1	7.6	30.3	37.8
35	1	689.2	31.2	658.1

Table S7.22 (cont'd)

36	1	1.4	5.7	7.1
37	0	6.2	4.4	10.7
38	1	10.3	14.0	3.7
39	0	9.1	4.6	4.4
40	0	2.9	7.6	4.7
41	0	6.2	66.5	60.3
42	0	4.2	22.5	26.6
43	1	88.1	127.6	39.5
44	0	8.8	82.0	73.2
45	1	32.5	36.3	3.8
46	1	0.8	5.0	4.2
47	0	3.1	513.3	510.2
48	1	1.0	3.1	2.1
49	1	0.5	12.7	13.2
50	1	0.4	13.2	13.6
51	1	0.7	14.2	14.9
52	0	5.4	0.1	5.5
53	0	5.5	0.1	5.4
54	1	5.1	8.0	13.1
55	0	252.5	446.0	193.5
56	0	220.2	221.8	1.7
57	1	4.1	16.7	12.6
58	1	0.1	2.8	2.7
59	0	3.8	497.4	501.2
60	1	3.3	0.3	3.5
61	1	17.2	31.3	14.1
62	0	16.6	448.2	464.8
63	0	14.8	445.7	460.5
64	1	1.0	5.9	6.8
65	0	6.0	45.5	39.5
66	1	0.3	21.8	22.1
67	0	0.5	0.2	0.4
68	0	0.4	390.0	389.6
69	0	24.0	444.3	420.2
70	0	8.1	116.8	108.6
71	1	488.8	2091.7	2580.5
72	0	489.1	438.8	927.9
73	1	10.2	0.9	11.1

Table S7.22 (cont'd)

74	1	0.7	10.4	11.1
75	1	0.6	10.0	10.7
76	1	5.0	8.7	13.7
77	1	5.0	8.7	13.6
78	0	914.0	270.5	643.5
79	1	317.6	1323.8	1006.2
80	0	4.0	17.7	13.7
81	0	20.5	18.7	1.8
82	0	31.8	70.2	38.3
83	1	1.9	31.6	29.7
84	0	1664.3	18.7	1683.0
85	0	467.9	23.3	444.6
86	1	0.8	79.8	79.0
87	1	0.9	470.1	469.2
88	0	2.9	5.9	2.9
89	1	3.0	7.4	4.4
90	0	14.0	167.4	153.3
91	0	29.1	1301.8	1330.8
92	0	0.8	411.0	410.2
93	0	1.8	1.5	0.2
94	0	3.3	1336.5	1339.8
95	1	3.4	25.4	22.0
96	1	25.3	3.7	21.5
97	1	3.5	1673.4	1669.9
98	0	3.6	1414.0	1417.5
99	1	3.8	25.0	21.2
100	0	1.0	1560.1	1561.1
101	0	0.9	0.6	0.3
102	0	1.0	446.0	444.9
103	0	59.4	1562.4	1621.8
104	1	2.6	132.1	129.5
105	1	1.6	69.5	67.9
106	1	139.6	2899.6	3039.2
107	1	0.5	14.5	13.9
108	1	0.4	139.8	139.4
109	1	14.5	0.6	13.9
110	1	14.8	0.3	14.5
111	0	0.4	57.0	56.6

Table S7.22 (cont'd)

112	1	1.0	36.6	35.5
113	1	35.9	1.1	34.8
114	1	35.4	1.1	34.4
115	1	1.2	37.0	35.8
116	1	36.0	1.4	34.6
117	1	36.3	1.1	35.2
118	1	35.5	1.2	36.7
119	1	35.4	1.5	36.9
120	1	1.5	88.7	87.1
121	1	1.2	35.5	36.7
122	0	1680.3	1684.2	3.8
123	1	1.5	35.0	36.5