The Effect of Boron on the Photophysical Properties of Dimetal Quadruply Bonded Complexes

DISSERTATION

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By

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Abstract

Research pertaining to renewable energy has increased considerably over the past few decades as the global energy demand rises. The need for new materials capable of efficiently converting solar energy into renewable fuel sources is critical. Additionally, as the world is further industrialized, new sensors and methods for monitoring hazardous waste must also be developed. In designing and optimizing these materials it is necessary to understand the underlying photophysical processes that occur, many of which happen on femtosecond and nanosecond timescales. The advent of femtosecond lasers has led to the development of new techniques capable of observing these ultrafast processes, the results of which will lead to more effective design of new materials.

This work focuses on synthesis, characterization, and photophysical properties of \( M_2 \) quadruply bonded compounds, where \( M_2 = \text{Mo}_2 \) or \( \text{W}_2 \). These compounds have broad and intense metal-to-ligand charge transfer (MLCT) absorption bands typically having large extinction coefficients in the range of 20,000-100,000 \( \text{M}^{-1}\text{cm}^{-1} \), which allows for a great amount of light to be absorbed. Depending on the choice of metal and the extent of \( \pi \) conjugation with the ligands, the MLCT absorption can be modulated in the range of 400-1200 nm. These compounds also have relatively long \( ^1 \text{MLCT} \) excited-states compared to other metal complexes, which typically decay to \( ^3 \text{M}_2\delta\delta^* \) states and \( ^3 \text{MLCT} \)
sates, for Mo$_2$ and W$_2$, respectively, making them uniquely suited for studies of excited-state charge distribution.

Materials containing both three- and four-coordinate boron moieties have also gained considerable attention in recent years due to their unique properties. Three-coordinate boron behaves much like a carbocation, making it strongly electron withdrawing. The empty 2$p_z$ orbital is also capable of extending the $\pi$ conjugation of organic molecules. Four-coordinate boron enhances the rigidity of organic molecules resulting in intense absorption and fluorescence features. The primary objective of this work was to fuse the interesting properties of M$_2$ compounds with those of boron.

The first chapter focuses on tuning the MLCT absorption band of M$_2$ compounds by incorporating three-coordinate boron into the ligand $\pi$ systems. The vacant $p_z$ orbital on the boron atom also permits coordination of fluoride ions which can further tune the absorption band and establish a switch for the MLCT band, resulting in a colorimetric mechanism for fluoride sensing. The following chapters investigate the influence of M$_2$ compounds and four-coordinate boron on the photoisomerization of a derivative of the avobenzone molecule, a common UVA filter used in sunscreens. Typically the tautomerization leads to degradation of the molecule, but the M$_2$ unit introduces a new energy deactivation pathway which drastically reduces decomposition. The conversion between the $^1$MLCT state to $^3$MLCT state in the W$_2$ compounds was also investigated with time-resolved infrared spectroscopy.

The ability of these compounds to absorb light in a tunable fashion makes them excellent candidates as materials in devices such as solar cells, LEDs, and sensors. The underlying
photophysical processes investigated in this work will aid in the development of future materials for solar energy conversion, photocatalysis, and sensing applications.
Dedication

To my parents
Acknowledgments

I have received an incredible amount of support from a long list of people in my life. I ask forgiveness if you are one that has been overlooked here.

I would like to first acknowledge my family. My parents, Joseph and Rebecca, for all of the sacrifices made in order to give me the opportunities I have had. I am amazingly blessed to have had you as my parents. My sister, Jamie, for teaching me how to get the most out of life. She stood firmly beside me through all of the hardest moments of my life, always knowing exactly what to do. My brothers, Tony and Stephen, for making sure that I was never bullied, and that I stuck to the right path. And my stepmother, Pam, for everything from bouncing me on her knee and entertaining me through hours of shopping to celebrating my accomplishments and loving me like a mother. Perhaps I should also thank my Aunt Mary for teaching me to read. I likely would not have gotten very far without that skill.

There are, of course, a number of people that have mentored me academically and professionally. Mr. Tom Wisard is the reason I was first inspired into the field of chemistry. His passion for the subject and selfless dedication to his students is unmatched. Dr. Aaron Hutchison was responsible for instructing more than half of my undergraduate chemistry courses and all of my undergraduate (chemistry) research
endeavors, and is the reason I decided to pursue a graduate degree in chemistry (in spite of Dr. Jenny Hutchison’s many efforts to convince me to switch to math). Aaron and Jenny have continued to serve as inspiring life mentors many years following graduation. Dr. Malcolm Chisholm is one of the greatest chemists I have ever met and it has been a privilege to be his student. He is a truly devoted educator and remarkable research scientist. I am so grateful for his encouragement and support during my time at Ohio State.

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I should also mention Dr. Evgeny Danilov, without whom much of the laser work would not have been possible. In the darkest times of failing laser systems, Evgeny would always come to restore hope (by fixing them).

I must also thank my lab brothers and sisters. They are a tremendously talented group and I am truly privileged to have had the opportunity to work alongside them. Dr. Samantha Brown-Xu is the reason that I began working with the ultrafast laser systems. She not only taught me how to use them, but was an irreplaceable companion on those
endless nights in the laser lab. For that, I am forever grateful – you will always be number one on my list…you know which one. Dr. Tom Spilker is an incredibly talented synthetic chemist and an excellent lab mentor. He let me use half of his hood space so that I could begin my work in the Chisholm group. In that time I became much better at synthesis. He is responsible for the nsTA and emission data in this work. Dr. Sharlene Lewis is another brilliant synthetic chemist who I had the pleasure of sharing a desk next to for three years. She spent many hours teaching me chemistry late into the night, and made numerous interesting compounds for me to study. Dr. Chris Durr, DBFL, was another outstanding lab mentor and friend. He made me feel welcome when I first joined the group, and helped me through all the major challenges of grad school. He also solved crystal structures for me as often as I could provide him with crystals. A special thanks to Will Kender for his help in finishing many of the projects in this work. He brought a wealth of knowledge and renewed vigor when it was needed most. Changcheng Jiang always provided great conversation during many long nights in the basement. My adopted lab brother, Dr. Bryan Albani, stood by me through some of the foulest hours of laser lab despair. I have met few people with such a positive outlook as Bryan. On behalf of the entire Chisholm group, I also thank the people at 93.3 for being the soundtrack to our labwork. That includes you Dusty and Gladys.

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1.1 A Brief History of Light

Light has long fascinated people throughout history. The first recorded theory of light and perception was conceived by the philosopher Empedocles during the fifth century B.C. in his work "On Nature". He proposed that all matter consisted of a mixture of four elements: fire, air, earth, and water. These elements are controlled by the forces of Love and Strife, and all things release tiny flowing particles which he called effluences. Perception was a result of these effluences passing from an object to a perceiver (or more specifically the perceptual organ). He believed that the human eye was lit by a flame, the fire element, to which all fire effluences could flow and the object thus be perceived.

While this model is far from modern understanding of light this line of thinking persisted for a long time. Even more than two millennia later when Isaac Newton wrote his hypothesis explaining the properties of light he believed that objects emitted “corpuscles”, which were tiny minute particles, in all directions. He also released his book around this time titled “Opticks: or, a Treatise of the Reflections, Refractions, Inflections and Colours of Light” which signaled the birth of spectroscopy – the study of light interacting with matter. Newton concluded a particle-like nature of light in his
treatise. The theory for the wave-like nature of light was being developed simultaneously by scientist Christiaan Huygens. Both Newton and Huygens believed in a luminiferous aether, thought to be the medium in which light propagated.3,4 Eventually, in 1845, Michael Faraday suggested the abolishment of the aether by stating that light was in fact related to electromagnetism (a wave) and could propagate in the absence of a medium.5 James Clerk Maxwell used classical physics to show that electromagnetic waves could self-propagate through space at a constant speed equal to the measured speed of light! He published what are now known as Maxwell’s equations in 1873 titled “A Treatise on Electricity and Magnetism.”6

Maxwell’s Equations -

Source Laws:

$$\oint_s E \cdot dS = Q/\varepsilon_0 \rightarrow \nabla \cdot E = 0$$

[Q is charge enclosed within volume of bounded surface]

Meaning: An electric field passing through a region in space can only be modified by the charge enclosed in that volume.

$$\oint_s B \cdot dS = 0 \rightarrow \nabla \cdot B = 0$$

Meaning: A volume bounded by the surface, s, can contribute nothing to the magnetic field contained within.

Circulation Laws:

$$\oint_c E \cdot dl = \oint_s \frac{\delta B}{\delta t} \cdot ds \rightarrow \nabla \times E = -\frac{\delta B}{\delta t}$$
Meaning: An electric field is generated by a time-varying magnetic field.

\[ \oint B \cdot dl = \mu \oint \left[ J + \sigma \frac{\delta E}{\delta t} \right] \cdot ds \rightarrow \nabla \times B = \mu_0 \varepsilon_0 \left( \frac{\delta E}{\delta t} \right) \]

Meaning: A magnetic field is generated by a time-varying electric field.

The conclusion is again that electromagnetic waves are self-propagating! Heinrich Hertz experimentally proved the equations shortly after.

The year 1900 marked the beginning of the development of quantum mechanics when Max Planck suggested that the exchange of energy between light and matter is quantized. This triggered an explosion of theories and experiments from scientists such as Einstein, Bohr, Heisenberg, de Broglie, Born, and Schrodinger which ultimately led to the particle-wave dual nature of light and electrons, and the modern day description of atomic and molecular structure.7

1.2 Interaction of Light with Matter

Photophysical phenomena are triggered by interactions between electromagnetic radiation and matter. In other words, transitions between eigenstates of the molecule can be induced by the presence of light. Precisely how the matter is perturbed depends on the energy of the electromagnetic radiation. The transitions of interest for the work presented here involve vibrational transitions induced by infrared radiation and optical transitions induced by ultraviolet and visible radiation. The transition between an initial state, \( S_i \), and a final state, \( S_f \), will occur if the transition dipole moment integral is nonzero, \( \int \psi_i^* \mu \psi_f \, d\tau \neq 0 \). For example, in the case of light absorption, the initial state is the ground state, \( S_0 \), and the final state is some excited electronic state, \( S_n \). This is
complicated by the presence of vibrational levels within each electronic level giving rise to the potential for multiple transitions between the same two electronic states, not just the lowest energy (0,0) transition.\textsuperscript{8} This problem is simplified by the Born-Oppenheimer Approximation, which states that electron motion is fast relative to nuclear motion and so the respective wavefunctions can be treated independently, $\Psi_{total} = \Psi_{\text{electronic}} \times \Psi_{\text{nuclear}}$. This means that the change in nuclear coordinate over the duration of an electronic transition is negligible. The Franck-Condon Principle states then that the predicted transition will thus occur where there is greatest overlap between the ground state and excited state vibrational wavefunctions and so the initial excitation may access higher vibrational levels (Figure 1.1).\textsuperscript{8}
In other words, the transition is “vertical” in the diagram since the nuclear coordinate will not change on the timescale of the electronic transition. The molecule can relax to an excited state equilibrium following the rapid excitation. A distribution of nuclear coordinates in solution can then cause the greatest overlap to be between a variety of vibrational levels resulting in a vibronic progression in the absorption spectra. The difference in energy of the absorption features informs on the spacing between vibronic levels of the excited state. The same phenomena occurs when observing the emission spectra which gives information on the vibrational levels of the ground state (Figure 1.2).
Figure 1.2. A representation of the absorption (blue) and fluorescence (green) spectra showing the approximate intensities of the transitions between vibrational levels.

While this information is useful it can be difficult to see due to the broad nature of absorption and emission spectra. It is often necessary to cool the solution with liquid nitrogen in order to sharpen the spectra. Cooling the solution reduces the vibrational energy which restricts the vibrational motion. This pushes the absorption and fluorescence spectra toward the energy of the 0-0 transition (a red-shift for absorbance and a blue-shift for fluorescence). The probability of particular transitions occurring are governed by selection rules. For electronic transitions there are three types: vibrational, orbital (Laporte), and spin rules. Those with a predicted intensity equal to zero are designated as “forbidden”, and those with a nonzero intensity are “allowed”. In some cases a transition will be fully allowed which means it meets the criteria for all selection rules. In other cases it may be only Laporte or spin allowed. The extent to which a
transition is allowed is reflected in the intensity of the absorption. The discussion above involving the Franck-Condon Principle summarizes the contribution from the vibrational selection rule. The spin selection rule states that the transition will be allowed if the initial and final states have the same multiplicity (doublet → doublet is allowed, but singlet → triplet is not). This holds mostly true for organic molecules, however, inorganic complexes often undergo singlet → triplet transitions, which will be discussed in greater detail later. The Laporte selection rule states that in order for \( \int \psi_i^* \psi_f \, \sigma t \neq 0 \) to be true, the totally symmetric irreducible representation must be contained in the cross product of the initial and final states and the dipole moment operator. This means that if the ground state is symmetric, at least one component of the dipole moment operator and the excited state must have the same symmetry. An alternative way to state the Laporte selection rule is that centrosymmetric transitions are forbidden (s→s, d→d, etc). Molecular orbitals of course involve a combination of orbitals and so are more complicated than atomic orbitals and the overall symmetry, either g or u, must be used. If the dipole moment operator is uneven to inversion then either the ground state or the excited state must also be uneven to inversion in order to result in g symmetry.

Case 1: \( u \times u \times g = g \)

Case 2: \( g \times u \times u = g \)

This means that g→u and u→g transitions are allowed, and all other cases are considered Laporte forbidden.
1.3 Photophysical Phenomena

As previously mentioned, if the initial state is the ground state, $S_0$, and the final state is some excited state, $S_n$, then the process occurring is absorption. The absorbance is typically measured by comparing the ratio of incident intensity ($I_0$) on a sample and the resulting intensity ($I$) after it passes through the sample. This is known as the %Transmittance ($%T = I/I_0$) and can be related to absorbance ($A$) by the equation $A = \log (1/T)$. Absorbance values are often more practical because they can be related directly to concentration and the path length through the sample by a proportionality constant known as the molar extinction coefficient ($\varepsilon$). This expression is known as Beer’s Law and is given by $A = \varepsilon C b$, where $C$ is the concentration and $b$ is the path length through the sample. Absorption is the preliminary process that occurs when light interacts with a molecule, however, the processes that occur following absorption are of greatest interest to this work.

There are, in general, four possible states that can be generated following excitation: one singlet state and three triplet states (Figure 1.3).

![Singlet (S=0) and Triplet (S=1) States](image)

Figure 1.3. A vector diagram depicting the four possible states that can be generated following excitation.
This gives rise to a thermodynamic threshold of 25% singlet state population and 75% triplet state population. Most organic molecules form an excited singlet state ($S_n$) after excitation with light that quickly relaxes to the lowest energy excited state ($S_1$) through a process called internal conversion (IC). According to Kasha’s rule, emission will always occur from this, lowest lying state, to return to the ground state. If this radiative process is occurring within the singlet manifold it is known as fluorescence and most often within nanoseconds though this can vary substantially. If there is significant mixing between the excited state vibrational level and the ground state then the molecule can relax nonradiatively (vibrationally). A spin change, known as intersystem crossing (ISC), can occur minimally in some cases though the rate is small relative to the rate of fluorescence in most organic molecules and so singlet emission still dominates. The change of spin is formally forbidden by the spin selection rule. The addition of a heavy atom (usually a transition metal) can substantially increase the rate of ISC by enhancing spin orbit coupling, a process by which the interaction of the electron spin with the magnetic moment of nuclear orbit is increased. This causes a blending of the eigenstates of the singlet and triplet states thus promoting the $S \rightarrow T$ transition moment. In other words, the singlet state is made less diffuse by the presence of the metal atom and so is more similar in character to the triplet state thus decreasing the angular momentum difference between the two states and enabling the otherwise forbidden transition. The rate of ISC is dependent on the identity of the metal and the character of the states involved in the transition (metal centered, ligand centered, charge transfer, etc). The amount of spin orbit coupling present can be changed by switching the identity of the metal atom.
Additionally, according to El Sayed’s rule, the rate of ISC is increased when the transition moment occurs between states of different character since the magnitude of the change in angular momentum is greater than in transitions between states of similar character. Additionally, the potential energy wells are less nested allowing better overlap of the vibrational energy levels thus facilitating the transition. The large rate of ISC therefore permits the population of the triplet manifold. Efficient ISC can result in a maximum of 75% of the total state population. The electron can relax either by phosphorescence, typically with lifetimes between nanoseconds and microseconds, or nonradiatively decay to the ground state. It is important to note that while ISC facilitates the population of the triplet state, it also plays a major role in the relaxation of the triplet state to the ground state. This can result in a shorter lifetime due to deactivation of the triplet state by spin orbit coupling. A summary of these processes is shown in Figure 1.4.
1.3.1 Types of Transitions

A summary of typical transitions for organic molecules, their approximate energies and extinction coefficients are given in Table 1.1.¹³
<table>
<thead>
<tr>
<th>Transition Type</th>
<th>Typical $\lambda_{\text{max}}$</th>
<th>Example Molecule</th>
<th>Example Molecule $\lambda_{\text{max}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma \rightarrow \sigma^*$</td>
<td>120-140 nm</td>
<td>Ethane</td>
<td>135 nm</td>
</tr>
<tr>
<td>$\eta \rightarrow \sigma^*$</td>
<td>150-250 nm</td>
<td>Methanol</td>
<td>183 nm</td>
</tr>
<tr>
<td>$\pi \rightarrow \pi^*$</td>
<td>200-700 nm</td>
<td>Benzene</td>
<td>254 nm</td>
</tr>
<tr>
<td>$\eta \rightarrow \pi^*$</td>
<td>200-700 nm</td>
<td>Acetone</td>
<td>290 nm</td>
</tr>
</tbody>
</table>

Table 1.1. The types of transitions commonly found in organic molecules, their typical energy range, and an example of each.

The $\sigma \rightarrow \sigma^*$ and $\eta \rightarrow \sigma^*$ transitions typically fall in a relatively narrow wavelength range. If the $\pi$ systems of an organic molecule is large enough, the $\pi \rightarrow \pi^*$ and $\eta \rightarrow \pi^*$ transitions can be driven into the visible region. Typically these will still be relatively high energy absorption bands.

Inorganic metal complexes further complicate things by introducing d orbitals which allow for new types of transitions such as metal centered (MC), ligand-to-metal charge transfer (LMCT), and metal-to-ligand charge transfer (MLCT) transitions. A general molecular orbital diagram of a ML$_6$ octahedral complex describing these transitions is shown in Figure 1.5.
Figure 1.5. Molecular orbital energy diagram of an ML₆ complex showing the possible electronic transitions: metal-to-ligand charge transfer (MLCT), metal-centered (MC), ligand-to-metal charge transfer (LMCT), and ligand-centered (LC).

Typical extinction coefficients of the transitions commonly observed with metal complexes are summarized in Table 1.2.\textsuperscript{14}
<table>
<thead>
<tr>
<th>Transition Type</th>
<th>Extinction Coefficient ($\epsilon$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal Centered (MC)</td>
<td></td>
</tr>
<tr>
<td>Spin/Laporte Allowed</td>
<td>100-5,000 Lmol$^{-1}$ cm$^{-1}$</td>
</tr>
<tr>
<td>Spin Allowed Only</td>
<td>5-100 Lmol$^{-1}$ cm$^{-1}$</td>
</tr>
<tr>
<td>Spin/Laporte Forbidden</td>
<td>&lt; 1 Lmol$^{-1}$ cm$^{-1}$</td>
</tr>
<tr>
<td>Ligand Centered (LC)</td>
<td>1,000-100,000 Lmol$^{-1}$ cm$^{-1}$</td>
</tr>
<tr>
<td>Ligand to Metal (LMCT)</td>
<td>1,000-50,000 Lmol$^{-1}$ cm$^{-1}$</td>
</tr>
<tr>
<td>Metal to Ligand (MLCT)</td>
<td>1,000-50,000 Lmol$^{-1}$ cm$^{-1}$</td>
</tr>
</tbody>
</table>

Table 1.2. The types of transitions commonly found in metal complexes and their approximate extinction coefficients.

1.3.2 Lifetime Considerations

The efficiencies of sensors, photocatalysts, and devices are heavily dependent on the lifetime of the excited states. Lifetimes are affected by both the amount of coupling between the organic molecule and the metal center as well as the amount of charge separation following excitation.$^{15}$ Greater coupling and smaller charge separation will lead to fast recombination, while less coupling and large charge separation will lead to longer lived charge trapped states. Some metal complexes have singlet lifetimes of less than 30 femtoseconds, while others may be as long as 30 ps. Depending on the application a long or short lifetime may be required. In any case, these processes are occurring on incredibly fast time scales and ultrafast spectroscopy is required to study them.

1.4 Ultrafast pump-probe spectroscopy: principles

The first technique used to study reactions on the microsecond-millisecond timescale was flash photolysis, developed by Norrish and Porter in 1949.$^{16,17}$ Since then, developments in electronics and laser spectroscopy have led to techniques capable of studying processes
occurring on the femtosecond timescale. There are several pump-probe techniques available now, however, two in particular are of relevance to the present work: broadband transient absorption (TA) and time-resolved infrared (TRIR). Though there are some differences between these two techniques both function off of the same fundamental principles. In each case, the femtosecond pulsed pump and probe beams are spatially and temporally overlapped in the sample. The role of the pump beam is to excite the molecules. For transient absorption the probe is a broadband white light beam, ~350 nm – 1100 nm and for time-resolve infrared a mid-IR beam is used. The probe beam then passes through to measure the absorption. The general setup is shown in Figure 1.6.

![Diagram of pump-probe experiment](image)

**Figure 1.6.** (right) A general setup of a pump-probe experiment. (left) Showing the delay between the pump and probe pulses.

The change in optical density from before and after the pump laser pulse is then displayed. Since the timescale is so short, the experiment is limited by the electronic equipment. This problem is circumvented by introducing a delay stage to control the temporal correlation between the pump and probe and allow for time resolution. Optical density snapshots can be taken by collecting data at various positions along the delay stage. When the pump beam strikes the sample, only a fraction of the molecules will be
excited resulting in a mixture of ground state and excited state molecules. The data are simplified by plotting the change in optical density (ΔOD) between the spectra with (I_{pump(on)}) and without (I_{pump(off)}) the pump beam.

\[ ΔOD = -\log \left( \frac{I_{pump(on)}}{I_{pump(off)}} \right) \]

In other words, the depletion of ground state species and the formation of transient species are more easily tracked by watching for positive and negative signals around the zero baseline. Typically these changes in absorption are relatively small and thus a large number of averages (250-300 for TA, 20,000 for TRIR) must be collected for each time delay in order to ensure good signal to noise. These scans are acquired efficiently by the use of beam choppers in the pump and probe pathways. For TA, a CCD detector is synchronized with the probe chopper and acquisition is initiated by the pump switching on. The probe chopper runs at 25 Hz and blocks 50% of the incoming pulses, which combined with the 1 kHz laser pulses results in a total of 40 pulses at 1 ms/pulse. Acquisition occurs in the first 20 ms with 20 pulses. The remaining 20 ms are used to prepare the detector for the next acquisition period. The pump beam is passed through a chopper that operates at 12.5 Hz, blocking 75% of incoming pulses, which allows for alternate collections of pump on and pump off. This is summarized in Figure 1.7.
There is often some fluctuation in the broadband continuum which can be accounted for by the use of a reference beam passing through an unpumped region of the sample. Additional noise associated with steady-state emission and electronic noise can also be subtracted. The above $\Delta OD^{19}$ equation then becomes:

$$\Delta OD = -\log \left( \frac{I_{probe(on|on)} - I_{probe(on|off)}}{I_{ref(on|on)} - I_{ref(on|off)}} \times \frac{I_{probe(off|on)} - I_{probe(off|off)}}{I_{ref(off|on)} - I_{ref(off|off)}} \right)$$
where \( I_{\text{probe}} \) and \( I_{\text{ref}} \) are the intensities of the white light of the probe and reference respectively. The \( x/y \) subscript indicates the presence or absence of the pump/probe beams. The shutter is the primary mechanism in correcting for these background processes. The total signal is collected with both the pump and probe shutters open. The steady-state emission is collected during a time period when the probe shutter is closed but the pump shutter is open. Any differences between the probe and reference beams are calculated when the pump shutter is closed and probe shutter is open. The electronic noise is collected when both pump and probe shutters are closed. These shutter positions are summarized in Figure 1.8.\(^{19}\)

---

Figure 1.8. Representation of the pump and probe conditions contributing to the overall \( \Delta \text{OD} \). (a) Total signal (on/on); (b) Fluorescence (on/off); (c) Probe spectral differences (off/on); (d) Noise (off/off).\(^{19}\)
A more complete description of the instrumental setups for both fsTA and fsTRIR can be found in the materials and methods section.

1.4.1 fsTA data

There are four primary contributions in TA data: ground state bleaches (GSB), excited state absorptions (ESA), stimulated emission (SE), and product formation (PF). As previously mentioned, a fraction of the molecules are promoted to the excited state upon interaction with the pump pulse and so the number of molecules in the ground state is depleted. When the probe pulse passes through the sample it will detect less ground state absorption than was present prior to the pump pulse. The resulting signal will be a negative feature in the spectra, a GSB. The ESAs occur when the pump pulse generates the excited state and the probe pulse is absorbed by the sample moving the molecules to an even higher excited state. The ESAs are marked by positive features in the TA data as there is more optical density after the pump pulse than before. In some cases the probe pulse can induce the transition of an excited molecule back to the ground state which is the SE process. The feature should be similar to the steady-state fluorescence signal. The emitted photon from SE will travel along with the probe pulse causing a greater amount of optical density to be detected and a negative feature will result. The final contribution to TA spectra occurs if there is product formation (a new transient species or a long lived state) following the pump pulse. This results in a new species that has its own absorptions and will produce a positive feature in the TA spectra. Taking the ground state absorption spectra of the sample before and after TA measurements is useful in
determining if any changes occur which may indicate either decomposition of the sample or the formation of a new persistent species.20

Transient absorption can yield a great amount of information on the excited state dynamics, but there are a number of limitations. (1) The spectral features are often broad causing them to merge into one another and making their assignments much more challenging. In some cases transient features will reside in the same wavelength region as a ground state bleach resulting in a superposition of the two. This can be somewhat adjusted by “adding” the ground state spectrum into the transient absorption spectra thus restoring the depletion.21 (2) If the sample has an intense ground state absorption the probe pulse can be almost entirely absorbed by the sample leading to poor signal to noise in that region. This commonly occurs with ππ* transitions positioned in the high energy side of the visible. When using CaF2 to generate the probe, the broadband counts in the range of 350-400 nm are often low. Diluting the sample is sometimes an option if the excited state features are sufficiently intense and there is ample absorption of the pump pulse afterward. Occasionally adjusting the laser compression can change the broadband continuum in such a way that certain wavelengths are more intense which can alleviate this problem. (3) Finally, when the wavelength of the pump pulse lies in the spectral viewing region, that portion of the spectra will be lost. The wider the pulse width of the pump, the greater the gap will be. This is a common problem, especially with the wavelengths that fall in the 500-600 nm range as they are often situated directly in the middle of the spectra. For these reasons given here, fsTA has primarily been used to examine lifetimes of the species in this work. In some cases the conversion between
singlet and triplet states can be directly observed. By plotting the ΔOD versus time delay and fitting the curve exponentially the time components can be extracted.

1.4.2 fsTRIR data

The same general spectral features can be seen in TRIR spectra as well, however, the singlet emission almost always lies at higher energy than the observed wavelength range for this technique. The probe beam in this case does not pass through a chopper, but the pump beam does (500 Hz) which results in two probe pulses for every one pump pulse (Figure 1.9).

![Figure 1.9. Representation of the synchronization of the pump and probe pulses for the fsTRIR experiment (left) and the time delay between pump and probe (right).](image)

There is, however, still a reference beam and so the ΔOD is given as follows:

$$\Delta OD = -\log \left( \frac{I_{\text{probe(on/on)}}}{I_{\text{ref(on/on)}}} \times \frac{I_{\text{probe(off/on)}}}{I_{\text{ref(off/on)}}} \right)$$

The key difference between TA and TRIR, is that TRIR gives excited state structural information as well making it an incredibly powerful technique.\(^{22,23}\) The ESAs show where the electron density is residing, and how it moves throughout the duration of the experiment. This is more easily achieved by the synthetic installation of IR reporter
groups, functional groups with moderate to strong oscillator strengths and that have isolated stretching frequencies, which allow for the probing of electron density in specific regions of the molecule (metal carbonyls are a good example).\textsuperscript{22–25} Shifts from the ground state bleaches show whether there is electron density moving toward or away a particular region. For example, if an antibonding orbital is populated upon excitation with the pump, and the bond strength of a particular group is weakened as a result, the transient feature will shift to lower energy relative to the bleach. One important note here is that broad bands seen in the IR are often indicative of charge transfer character due to solvent rearrangement to accommodate the excited charge separated state. The decay or growth of these features can also be fit to confirm the lifetimes observed from the fsTA experiment.

1.5 MM Quadruply Bonded Complexes

Alfred Werner led the way in coordination chemistry by being the first to correctly assign the structure of many transition metal complexes. In 1913 he won the Nobel Prize in Chemistry for suggesting an octahedral configuration of these complexes.\textsuperscript{26} From that time until the 1960’s inorganic chemistry focused on monometallic complexes, though there was also quite a bit of work done with metal clusters. However, little regard was given to the idea of metal-metal multiple bonds. The first quadruply bonded complex, Re\textsubscript{2}Cl\textsubscript{8}\textsuperscript{2−}, was discovered by Dr. Neil Curtis. Not long after, the complete (correct) structural characterization of this compound was reported by Cotton and Harris in September 1964 and is shown in Figure 1.10.\textsuperscript{27}
The s, p, and d\textsubscript{x2-y2} orbitals are involved in the ligand binding to the rhenium centers, leaving the remaining metal orbitals to form the quadruple bond. The d\textsubscript{z2} orbitals overlap along the Re-Re axis to form a sigma bond, the d\textsubscript{xz} and d\textsubscript{yz} sets are responsible for two π bonds, and the d\textsubscript{xy} orbitals form the δ bond. The primary feature of Re\textsubscript{2}Cl\textsubscript{8}\textsuperscript{2-} that led to the assignment of the quadruple bond is the eclipsed geometry. The energy expense for this configuration is compensated by formation of the fourth bond; if the complex were twisted about the Re-Re axis the overlap of the d\textsubscript{xy} orbitals would be destroyed. The final electron configuration for d\textsuperscript{4} metals, such as those discussed in this work, is σ\textsuperscript{2}π\textsuperscript{4}δ\textsuperscript{2}. Another class of quadruply bonded complexes is that having a paddlewheel geometry, where in place of eight monodentate ligands there are four bidentate ligands. Figure 1.11 shows the molecular orbital energy level diagram for M\textsubscript{2}L\textsubscript{8} complexes and M\textsubscript{2}(O\textsubscript{2}C-R)\textsubscript{4} complexes. If the metals are d\textsuperscript{4}, the result of filling the orbitals is a quadruple bond.
Figure 1.11. Molecular orbital energy diagram for $\text{M}_2\text{L}_8$ complexes (a) and $\text{M}_2(\text{O}_2\text{C}-\text{R})_4$ complexes, where R has an extended $\pi$ system.

The linking groups for the paddlewheel complexes are most commonly carboxylate and amidinate ligands. They share the same general molecular orbital diagram as the $\text{M}_2\text{L}_8^{2-}$ when the R groups are not in conjugation with the linkers. An interesting feature in both cases is that the lowest energy allowed transition is the $^1\delta\delta^*$ transition, one involving excitation of an electron from the $\delta$ orbital to the $\delta^*$ orbital. As previously mentioned, a spin allowed and Laporte allowed d-d transition will have an extinction coefficient on the order of $\epsilon \sim 100$-5,000 M$^{-1}$cm$^{-1}$. An example of this absorption is shown in Figure 1.12, which shows a vibrational progression corresponding to the MM stretch ($\sim$350 cm$^{-1}$).
If π conjugated ligands are used then lower lying π* orbitals will be introduced between the δ and δ* orbitals (Figure 1.11, left-side, purple lines). The lowest energy transition now becomes one which involves an electron being excited from the metal d orbital to the ligand π* orbital, the 1MLCT transition. The overlap between the δ and π* orbitals is significantly improved relative to the overlap of the dxy orbitals which results in a much larger extinction coefficient of $\varepsilon \sim 10,000$-$50,000 \text{ M}^{-1}\text{cm}^{-1}$. Perhaps one of the more impressive aspects of the 1MLCT state is that it can be tuned to span the range of 350-
1,300 nm by changing the metal identity or the extent of π conjugation in the ligands (Figure 1.13).

![Absorption Spectra](image)

Figure 1.13. The absorption spectra of M₂ compounds showing the shift of the ¹MLCT to lower energy as π conjugation is increased, or when Mo₂ is substituted for W₂.

As the π conjugation in the ligands is extended, the energy of the π* orbitals is lowered leading to a lower energy ¹MLCT transition. Likewise, when the metal atom is changed from Mo to W, the δ orbitals are shifted much higher in energy making the δ orbital much closer in energy to the ligand π* orbitals. Again, the result is a lower energy ¹MLCT transition. The π* orbitals of carboxylate ligands lie at lower energy than those of amidinate ligands, which is yet another way to modulate the energy of the ¹MLCT band. This tunability gives these materials a competitive edge in any application that
requires the heavy absorption of light such as solar cells, photocatalysts, and sensing applications. Due to the large number of potential applications, recent years have focused on developing an extensive library of these compounds and then studying their photophysical properties.

1.5.1 Structures and syntheses

There are a number of subclasses of paddlewheel complexes which can be generally summarized as being one of five types: homoleptic, \textit{trans}-bis-bis, \textit{cis}-bis-bis, tris-mono, or dimers of dimers. The homleptic species has four identical ligands, the bis-bis has two sets of two different ligands which can be either trans or cis to each other, the tris-mono has two different ligand where three are identical, and the dimers of dimers have two dimetal centers bridged by a dicarboxylate ligand. These structures are summarized in Figure 1.14.
Figure 1.14. The five primary subclasses of M₂ paddlewheel complexes: homoleptic, bis-bis, tris-mono, and dimers of dimers.

The latter four types are made by way of a homoleptic starting material and so the synthesis of the homoleptic subclass will be described first.

Dimolybdenum homoleptic complexes are prepared by refluxing Mo(CO)₆ with two equivalents of the carboxylic acid in 1,2-dichlorobenzene (1,2-DCB), shown in Scheme 1.1.
Due to the volatility of Mo(CO)$_6$ it will sublime at the top of the reaction flask. It is advantageous to add about 10-20% THF, which has a much lower boiling point, to the solution in order “wash” the sublimed Mo(CO)$_6$ back down into the mixture and ensure better conversion to the homoleptic product. The same general procedure is also used to form homoleptic materials with amidinate ligands.$^{27}$

The preparation of ditungsten homoleptic complexes cannot be prepared in the same way as oxidation and degradation of the ligand occurs.$^{31}$ Instead they are most commonly prepared by the reduction of WCl$_4$ with a Na/Hg amalgam in THF. This then undergoes a salt metathesis reaction with the deprotonated acid species, shown in Scheme 1.2.


Scheme 1.2. Synthesis of homoleptic ditungsten complexes.
Typically the yield of this reaction is relatively low. One possible method for achieving higher yields is to reflux $W(CO)_6$ with neutral 2-hydroxy-6-methylpyridine in 1,2-dichlorobenzene, shown in Scheme 1.3.$^{31}$

$$2 \text{W(CO)}_6 + 4 \text{mhpH} \xrightarrow{\text{reflux}} \text{W}_2(\text{mhp})_4 + 12 \text{CO} + 2 \text{H}_2$$

Scheme 1.3. Synthesis of a ditungsten complex, $W_2(\text{mhp})_4$, directly from $W(CO)_6$, with mhpH shown below.

It is possible to start with $W_2(\text{mhp})_4$ to make other homoleptic compounds, however, this can be more challenging since the mhp ligands are less labile than carboxylate ligands. A large excess of the carboxylate ligand would need to be used, and heat applied, in order to force the mhp ligands off of the metal center. This typically leads to ligand scrambling, and only in the case of anthracene-9-carboxylic acid was the homoleptic product produced in good yield because it precipitated from solution.

The subclass of trans-bis-bis compounds are synthesized by beginning with a homoleptic starting material and substituting two of the ligands. The most common starting materials are those with pivalate (piv) or 2,4,6-triisopropylbenzoate (T$i$PB) ligands, shown in Figure 1.15.
Figure 1.15. The structures of the starting materials for homoleptic complexes: pivalic acid, pivH (left), 2,4,6-triisopropylbenzoic acid, T^PBH (middle), 2-hydroxy-6-methylpyridine, mhpH (right).

These bulky ligands help to enforce a trans geometry in the *trans*-bis-bis compounds as well as aid in solubility. Two equivalents of the carboxylate ligand of interest can be added to a solution of the homoleptic starting material and stirred for 3-5 days to yield the desired bis-bis product (Scheme 1.4).

Scheme 1.4. General synthesis of bis-bis (tetracarboxylate) complexes.

If amidinate ligands are to be used, they must first be treated with a base such as NaOCH₃. In this case the reaction will proceed more quickly (Scheme 1.5).
Scheme 1.5. General synthesis of \textit{trans}-bis(carboxylate)-bis(amidinate) complexes.

The \textit{cis}-bis-bis subclass has been done with molybdenum and can be made by beginning with a homoleptic amidinate compound and treating it with two equivalents of [(Me)₃O⁺][BF₄⁻] to remove two ligands and form a dication species, Mo₂(DAnif)₂(CH₃CN)₄²⁺. This can then be reacted with two equivalents of the desired carboxylate salt.\textsuperscript{33}

Scheme 1.6. General synthesis of \textit{cis}-bis(carboxylate)-bis(amidinate) complexes.

The work with the tris-mono subclass has been done with molybdenum and requires the preparation of Mo₂(DAniF)₃(piv), where DAniF = N,N'-di(p-anisyl)-formamidinate. This is prepared by starting with one equivalent of Mo₂(piv)₄ and three equivalents of NaDAniF. Mo₂(DAniF)₃(piv) is then stirred with the neutral desired acid to obtain the
tris-mono complex, shown in Scheme 1.7. The piv ligand can then be substituted much in the same way as the carboxylate ligands in trans-bis-bis complexes.\textsuperscript{34}

\begin{center}
\includegraphics[width=0.8\textwidth]{scheme17.png}
\end{center}

Scheme 1.7. General synthesis of tris (amidinate)-bis (carboxylate) complexes.

Finally, the dimers of dimers subclass is synthesized by reacting two equivalents of a starting homoleptic material with a single equivalent of a dicarboxylic acid, shown in Scheme 1.8.\textsuperscript{35}

\begin{center}
\includegraphics[width=0.8\textwidth]{scheme18.png}
\end{center}

Scheme 1.8. General synthesis of dimers of dimers complexes.

These materials are unique in that they allow for the investigation of electronic communication between metal centers. If the oxidation of the dimers of dimers species is a two electron process occurring at the same potential, then it indicates that there is effectively no electronic communication between the two metal centers. On the other
hand, if there are two separate oxidation potentials observed then it indicates delocalization. This was the case when oxalate was used as a bridge between two Mo₂ units. The separation between oxidation potentials was ~0.22 V.³⁶,³⁷ Presumably, a one to one mixture of the homoleptic starting material and the bridge could yield an oligomer. These tend to have low solubility and often a loop, triangle, or square is the preferred structure.

1.5.2 Photophysical properties

The molecular orbital diagrams of the M₂ paddlewheel complexes were previously introduced, however, Figure 1.16 provides a more descriptive picture of the orbitals.

![Molecular orbitals](image)

**Figure 1.16.** The frontier molecular orbitals of trans-Mo₂(O₂C-H)₂(O₂C-Th)₂.
The HOMO is the $\text{M}_2\delta$ orbital with ligand admixture. The LUMO is dependent upon the identity of the metal and the extent of conjugation in the ligands. If there is little to no conjugation the LUMO is likely to be the $\delta^*$ orbital, though it may reside close in energy to the $\pi^*$ orbitals. In this case the $^1\delta\delta^*$ transition will be the lowest energy transition. An example of a molecular orbital diagram of a compound having the $\text{Mo}_2\delta^*$ orbital below the ligand $\pi^*$ combinations can be seen in Figure 1.17 (left).

![Molecular orbital energy diagram comparing trans-$\text{Mo}_2(\text{O}_2\text{C-H})_2(\text{O}_2\text{C-Th})_2$ (red) to trans-$\text{W}_2(\text{O}_2\text{C-H})_2(\text{O}_2\text{C-Th})_2$ (green).](image)

As W character is introduced, the $\delta$ and $\delta^*$ orbitals are destabilized due to elongation of the d-d bond. Additionally, the $\pi^*$ orbitals are slightly stabilized due to better overlap with the W orbitals. The greater the amount of W character, the lower in energy the
$^1\text{MLCT}$ state will be shifted ($\text{Mo}_2 > \text{MoW} > \text{W}_2$). An example of this can be seen in Figure 1.18.

![Figure 1.18. Molecular orbital energy diagram comparing Mo$_2$(T'PB)$_4$ (red), MoW(T'PB)$_4$ (blue), and W$_2$(T'PB)$_4$ (green).](image)

If there is extended $\pi$ conjugation then the ligand $\pi^*$ orbitals will be stabilized below the $\delta^*$ orbital, and the lowest energy transition will be the $^1\text{MLCT}$ state in all cases. Again, by keeping the ligand set the same but changing the metal identity will result in a red-shift of the $^1\text{MLCT}$ state for W$_2$ compounds. An example of extending the ligand conjugation and comparing with the change between Mo$_2$ and W$_2$ is shown in Figure 1.19.
Figure 1.19. Molecular orbital energy diagram comparing trans-Mo$_2$(O$_2$C-H)$_2$(O$_2$C-2Th)$_2$ (red) to trans-W$_2$(O$_2$C-H)$_2$(O$_2$C-2Th)$_2$ (green).

For the case of trans-Mo$_2$(O$_2$C-H)$_2$(O$_2$C-Th)$_2$ the δ* orbital is lower than the Lπ* orbital by about 0.3 eV. When trans-Mo$_2$(O$_2$C-H)$_2$(O$_2$C-2Th)$_2$ is examined, the Lπ* orbital is about 0.25 eV lower in energy than the δ* orbital. In both W cases, however, the Lπ* orbital lies at lower energy than the δ* orbital.

In many cases the $^1$MLCT transition masks the presence of the much weaker $^1$δδ* transition. The splitting of the two ligand π* orbitals can also been seen. In one case the ligand π* orbitals are in-phase with each other and do not have appropriate symmetry to mix with the M$_2$δ orbital. The out-of-phase combination on the other hand is of the correct symmetry to interact with the M$_2$δ orbital resulting in the split. Since for tungsten
there is more spatial overlap with the carboxylate groups, and the metal based orbitals lie closer in energy, the amount of splitting is increased. Indeed, the extent of splitting can be an indication of the degree of electronic coupling between the ligands. This is similar to the case previously discussed when examining the oxidation potentials of the dimers of dimers compounds. In the case of a bis-bis compound the amount of communication can be determined by looking at the difference in reduction potentials. The communication is negligible if there is only one reduction potential. It can be seen that the splitting is in fact greater for \( \text{trans-} \text{W}_2(\text{O}_2\text{C-H})_2(\text{O}_2\text{C-2Th})_2 \) than for the \( \text{Mo}_2 \) counterpart.

The discussion thus far has been centered on the singlet states, however, these complexes often exhibit photoluminescence from both singlet and triplet states.\(^{40}\) The energy of the triplet state is affected by the choice of metal and ligand just as before with the singlet state. When there is no conjugation with the ligands, for either \( \text{Mo}_2 \) or \( \text{W}_2 \), the lowest energy triplet state is \( ^3\delta\delta^* \). Extending conjugation through the ligand does lower the energy of the \( ^3\text{MLCT} \) state. For \( \text{Mo}_2 \) carboxylate complexes, the \( ^3\delta\delta^* \) state lies at \(~\text{1100 nm}\) and so the lowest energy triplet state of these complexes is most often \( ^3\delta\delta^* \) regardless of the extent of \( \pi \) conjugation in the ligands. Upon cooling the complexes the emission data show a vibronic progression with \(~\text{350 cm}^{-1}\) spacing between features, attributable to the \( \text{Mo-Mo} \) bond stretch, and indicative of a metal centered triplet state (this same progression was previously shown in Figure 1.12). Since deactivation of the \( ^3\delta\delta^* \) state is primarily through the metal-metal bond stretch, the lifetime is substantially longer than the \( ^3\text{MLCT} \) state (\( \mu \text{s versus ns} \)). Additionally, if amidinate ligands are used in place of carboxylate ligands, the \( \text{Mo}_2\delta \) and \( \text{Mo}_2\delta^* \) orbitals destabilized due to the interaction with
the higher energy filled nitrogen p nonbonding orbitals, and the $^1\delta\delta^*$ and $^3\delta\delta^*$ states are destabilized similarly as a result. This causes the $^3\delta\delta^*$ emission to fall closer to 950 nm. In bis-amidinate bis-carboxylate systems, the amidinate ligands raise the energy of the $\delta\delta^*$ states and the carboxylate ligands allow for lower energy MLCT states making it possible to obtain a Mo$_2$ complex with $^3$MLCT emission. In the case of W$_2$(O$_2$CC≡CMe)$_4$, $^3\delta\delta^*$ emission was observed at ~800 nm, however, most W$_2$ complexes with $\pi$ accepting ligands typically give rise to $^3$MLCT states.$^{41}$ These $^3$MLCT states may not exhibit phosphorescence though if their energies are lowered to such an extent that the rate of nonradiative decay outcompetes the radiative process.$^{15}$ A summary of the possible state arrangements for tetracarboxylates is shown in Figure 1.20.

Figure 1.20. General Jablonski diagram comparing the order of the excited states for three scenarios: (1) M = Mo, W, L = nonconjugated; (2) M = Mo, L = conjugated; (3) M = W, L = conjugated.
The typical lifetimes and state dynamics of numerous complexes have been determined by the use of transient absorption (TA) and time-resolved infrared (TRIR) spectroscopies. In general these complexes have $^{1}$MLCT lifetimes of 1-20 ps. A few have had even longer lifetimes with the longest to date being 34 ps (see Chapter 6). Changing the identity of the metal or the type of ligand (carboxylate versus amidinate) has little effect on the $^{1}$MLCT state lifetimes. This is particularly interesting since one might expect an increase in the rate of intersystem crossing with the involvement tungsten due to the heavy atom effect. Orbital overlap and vibronic coupling between the singlet and triplet manifold must therefore play a more integral role than spin orbit coupling in these compounds. This is further supported by a series of para-halobenzoate Mo$_2$ compounds (Figure 1.21). The size of the halogen atom had little influence on the lifetime of the $^{1}$MLCT state. 

<table>
<thead>
<tr>
<th>Compound</th>
<th>$S_1$</th>
<th>$T_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>R = F</td>
<td>7.8 ps</td>
<td>66 $\mu$s</td>
</tr>
<tr>
<td>R = Cl</td>
<td>5.4 ps</td>
<td>62 $\mu$s</td>
</tr>
<tr>
<td>R = Br</td>
<td>6.7 ps</td>
<td>64 $\mu$s</td>
</tr>
<tr>
<td>R = I</td>
<td>4.1 ps</td>
<td>75 $\mu$s</td>
</tr>
</tbody>
</table>

Figure 1.21. Lifetimes of $S_1$ and $T_1$ excited states of compounds where R = F, Cl, Br, or I.
All of the $^{3}\delta\delta^{*}$ states fall within the range of 1-100 $\mu$s. Since the $^{3}\delta\delta^{*}$ state is a metal centered state, the lifetime is independent of the ligand environment. Changing from Mo$_2$ to W$_2$ does result in shorter $^{3}\delta\delta^{*}$ lifetimes though. Finally, the $^{3}$MLCT states, typical of W$_2$ compounds, are significantly shorter than the $^{3}\delta\delta^{*}$ states. A simple summary of these lifetimes is shown in Table 1.3.

<table>
<thead>
<tr>
<th>State</th>
<th>Lifetime</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{1}$Mo$_2$LCT</td>
<td>1-20 ps</td>
</tr>
<tr>
<td>$^{1}$W$_2$LCT</td>
<td>1-34 ps</td>
</tr>
<tr>
<td>$^{3}$Mo$_2\delta\delta^{*}$</td>
<td>10-100 $\mu$s</td>
</tr>
<tr>
<td>$^{3}$W$_2\delta\delta^{*}$</td>
<td>1-10 $\mu$s</td>
</tr>
<tr>
<td>$^{3}$W$_2$LCT</td>
<td>1-30 ns</td>
</tr>
</tbody>
</table>

Table 1.3. Typical lifetimes associated with M$_2$LCT states and M$_2\delta\delta^{*}$ states.

The most notable feature of these lifetimes is the exceptionally long $^{1}$MLCT lifetime. Many transition metal complexes have much faster $^{1}$MLCT lifetimes. For example, Ru(bpy)$_3^{2+}$ undergoes intersystem crossing in less than 50 fs! The S$_1$ states of these paddlewheel complexes makes them particularly well suited for studies of excited state charge distribution.

1.5.3 Excited State Mixed Valence

Photoexcitation of these M$_2$ complexes allows for studies of excited-state mixed valence. The excited electron could localize on a single ligand, or delocalize over two or more. Classification is done using the Robin-Day Classification scheme where Class I represents the case of a fully localized species, Class III represents full delocalization,
and Class II is an intermediate.\textsuperscript{44} The extent of localization or delocalization may change with time or as the singlet state converts to the triplet state. The relatively long lifetimes of the $^1$MLCT states along with fsTRIR allows for the charge distribution to be probed as the singlet state converts into the triplet manifold. Installing IR reporter groups onto the ligands can be an incredibly useful technique to probe electron density at specific locations on the ligand.\textsuperscript{34} The amount in which a particular stretch shifts from the ground state indicates how much electron density is present in the ligand $\pi^*$ orbital. A larger shift occurs when the charge is more localized in a single region.

Density functional theory (DFT) calculations have proven invaluable in assigning the character of vibrational shifts and aiding in the determination of the charge distribution in these complexes. The $^1$MLCT state can be approximated by calculations on the anion species $[M_2L_2L'_2]^\cdot$. DFT calculations will always predict a delocalized case, however, if the shift of the IR reporter group is substantially greater in the experimental it is indicative of a localized case. Studies of the compounds $M_2(O_2C-T'/PB)_2(O_2C-Ph-C≡N)_2$ and $M_2(O_2C-CH_3)_2((Pr'N)_2C-C≡C-Ph)_2$, where $M_2 = Mo_2$ and $W_2$, are examples of both delocalized and localized cases, respectively, and will be presented subsequently.\textsuperscript{45}

The delocalized case involves the cyanobenzoate complexes. The TRIR spectra for both compounds in the range of the \nu(C≡N) stretch can be seen in Figure 1.22.
Figure 1.22. The fsTRIR spectra for $\text{Mo}_2(\text{O}_2\text{C-T'PB})_2(\text{O}_2\text{C-Ph-C≡N})_2$ and $\text{W}_2(\text{O}_2\text{C-T'PB})_2(\text{O}_2\text{C-Ph-C≡N})_2$.\textsuperscript{45}
The ground state bleach in both cases falls around 2230 cm$^{-1}$, and a single transient band is present at 2160 cm$^{-1}$. The total shift is approximately -70 cm$^{-1}$ to lower energy. This shift is consistent with the population of the ligand π* orbital leading to a decrease in bond strength. In both cases the shift closely matches that predicted by DFT calculations which led to the assignment of a delocalized case. The primary difference between Mo and W is that the transient feature decays entirely over the time of the experiment as it undergoes ISC to the $^3\delta\delta^*$ state. For W, the $^3$MLCT state is formed and so electron density is still residing on the ligand at longer times resulting in the persistence of the transient feature. The $^3$MLCT state appears to also be delocalized as the magnitude of the ν(C≡N) shift does not appreciably change throughout the experiment.

The localized case involves the bis amidinate compounds. The TRIR spectra for the compounds are shown in Figure 1.23.
Figure 1.23. The fsTRIR spectra for Mo$_2$(O$_2$C-CH$_3$)$_2$((Pr$^i$N)$_2$C≡C-Ph)$_2$ and W$_2$(O$_2$C-CH$_3$)$_2$((Pr$^i$N)$_2$C-C≡C-Ph)$_2$.\textsuperscript{45}
Here the DFT calculations on the anion predict a shift of \(~-130 \text{ cm}^{-1}\) for \(\nu(\text{C≡C})\), but two shifts of differing magnitudes are seen. The first, \(-240 \text{ cm}^{-1}\) for Mo and \(-190 \text{ cm}^{-1}\) for W, are substantially larger than the predicted shift. The second, \(-45 \text{ cm}^{-1}\) for Mo and \(-30 \text{ cm}^{-1}\) for W, are quite a bit smaller. The large shift is indicative of the charge localizing on a single amidinate ligand. The minor shift is caused by a small amount of electron density “spill-over” to the second ligand. Again, the transient features decay entirely for the molybdenum compound. For the tungsten compound, the two transient bands shift even further to lower energy as time progresses. This indicates that the charge is still distributed unevenly in the triplet state, and that the electron density is contracting toward the metal center and weakening the C≡C bond by further populating the antibonding orbital.

The photophysical properties of these M₂ complexes allow for numerous applications such as solar energy conversion and material conductivity. Due to its versatility there is great interest in precisely tuning the properties of these complexes. One route in achieving this is by incorporating boron atoms into the ligands.

1.6 Properties of Boron

The development of organic light emitting diodes (OLEDs), bulk heterojunction solar cells (BHSCs), dye sensitized solar cells (DSSCs), and nonlinear optics has led to a push for inexpensive materials that are easy to synthesize and process and that have strong optical properties. Traditional inorganic materials in many instances are being replaced
by fully organic or metal-organic hybrids. Both three and four coordinate boron have gained significant attention in these applications in recent years. The ability of boron to switch between three and four coordinate geometries, and the vast tunability of fluorophores containing boron has led to a multitude of sensing applications as well.

1.6.1 Three-coordinate boron

The primary research focus up until recently has been to create n-type materials by using electron rich atoms such as nitrogen, sulfur, and selenium. Since a three coordinate nitrogen atom is isoelectronic with a carbanion, replacing a carbon atom with a nitrogen atom is a relatively easy way to install an electron rich site into a molecule. Presumably then a three coordinate boron atom would function in the opposite way to create an electron deficient site, isoelectronic with a carbocation. The initial development of materials containing three coordinate boron moieties was hampered, however, by instability brought on by the vacant p$_z$ orbital being susceptible to attack by moisture, oxygen, and photodegradation. It was Williams et al. working at Kodak in the 1970’s that discovered that using bulky protecting groups such as mesityls could substantially enhance stability. Trimesitylborane was photochemically inert in all solvents. Two mesityl groups were adequate to provide the same level of stability. Even a single mesityl group shows marked improvement, though to a much lesser extent than two. The reason for this is that the methyl groups on the mesityl serve to cage the vacant p$_z$ orbital on the boron atom, shielding it from attack (Figure 1.24).
Indeed, it is sufficient to protect the atom from all but F⁻ and CN⁻ anions. This unique aspect of shielding has led to these types of molecules being used as selective sensors for F⁻ and CN⁻. Additionally, the pₓ orbital can be oriented in such a way as to allow for extended conjugation with neighboring π systems. Tris(9-anthryl)borane was prepared by Tamao et al. They found that the π conjugation extended through the boron pₓ orbital giving rise to an additional band at lower energy (in the visible region) than the π-π* bands (UV region) in the UV-vis spectrum. Upon anion complexation, the low energy band disappeared leaving only the high energy bands and resulting in a change from highly colored to colorless. It was this particular line of thinking that led to the F⁻ titrations in Chapter 3. Shirota et al showed that three-coordinate boron substituted thiophene, bithiophene, and terthiophene molecules formed amorphous glasses and had excellent electron transporting properties. A computational database of these types of derivatives bound to Mo₂ and W₂ are given in Chapter 4.
1.6.2 Synthesis of 3-coordinate boron compounds

The three-coordinate boron compounds can be prepared using a relatively straightforward synthetic procedure. The general process typically involves lithiation of an aromatic organic compound followed by the addition of dimesitylboron fluoride. An example of this is shown in Scheme 1.9 using thiophene as the starting material.\textsuperscript{55}

![Scheme 1.9. Synthesis of a -B(mes)_2 monosubstituted thiophene ring.](image)

As the number of thiophene rings increases the communication between the two ends is dampened and scrambling can occur resulting in a mixture of starting material, as well as mono and disubstituted boron species (Scheme 1.10).\textsuperscript{56}

![Scheme 1.10. General synthesis of mono and disubstituted –B(mes)_2 compounds containing thiophene rings using nBuLi.](image)
Control over the temperature and the number of equivalents of n-butyl lithium used can help increase the yield of the desired product, however, it is more common to begin with a halogen substituted starting material. For more aromatic systems such as phenyl rings it is necessary to begin with a halogen substituted species. Starting with a monohalide and using one equivalent of n-butyl lithium and dimesitylboron fluoride will yield the singly substituted boron species in good yield (Scheme 1.11).

Scheme 1.11. Synthesis of a –B(mes)₂ monosubstituted phenyl ring.

Treating an aryl dihalide starting material with one equivalent of nBuLi and dimesitylboron fluoride allows for the synthesis of asymmetric monosubstituted boron species while using two equivalents gives the symmetric disubstituted boron compound (Scheme 1.12).

Scheme 1.12. General synthesis of mono and disubstituted –B(mes)₂ compounds containing phenyl rings using nBuLi.

A mixed halogen species such as 1,4-bromoiodobenzene can be used to selectively replace the iodine with dimesitylboron fluoride, leaving the bromine available for a subsequent reaction. There are two reactions in particular that are of interest to this work. The first reaction involves a second addition of nBuLi, followed by bubbling in CO$_2$ (g) in order to carboxylate the boron species (Scheme 1.13).

Scheme 1.13. General carboxylation procedure using nBuLi.

The second reaction is a Sonagashira coupling reaction in order to install a triple bond which could then be monitored by time-resolved infrared spectroscopy (Scheme 1.14).^59

Scheme 1.14. Example Sonagashira coupling reaction used to add a triple bond.

1.6.3 Four-coordinate boron

The continued search for light emitting materials has led to an extensive library of four-coordinate boron compounds. Of these compounds there is one class that stands at the forefront - 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene, or BODIPY. ^60 These have found use in many sensing applications due to their rigid planar structures caused by chelation to ligands with rich $\pi$ systems through means of the vacant p orbital, which give rise to
sharp and intense absorption and fluorescence features, large extinction coefficients and photostability.\textsuperscript{61,62}

Figure 1.25. General structures for BODIPY (left) and fluorescein (right).

These dyes also allow for easy postsynthetic modification. The core can be functionalized in a number of positions to effect changes in the solubility or photophysical properties of the dye. The absorption and emission wavelengths can be conveniently tuned by extending the conjugation through double bonds to $\pi$ systems. The absorption and emission spectra of a typical BODIPY core are shown in Figure 1.26.\textsuperscript{63}
An additional advantage to BODIPY based sensors is that they show little dependence on pH = 2-11. Many sensors traditionally invoke fluorescein as the fluorescent core, however, this molecule has limited synthetic versatility and depends heavily on pH (it shows intense fluorescence at pH = 7 which is almost entirely quenched at pH = 5). This limits the number of applications in both environmental and biological sensing. Since BODIPY does not suffer from these restrictions, there has been a surge in the development of new sensors involving the BODIPY core. One example of this is in sensing Hg$^{2+}$ ions using a chelation enhanced fluorescence mechanism to produce a “turn-on” switch. In this case, the unbound sensor has a lone pair of electrons at appropriate energy which resides higher than the HOMO of the fluorophore. The lone pair is able to donate an electron following photoexcitation of the sensor and the
fluorescence is then quenched by a photoinduced electron transfer (PET) process (Figure 1.27). In other words, the PET results in filling of the hole on the fluorophore HOMO making it impossible for the excited electron to fluoresce back to the ground state.

Figure 1.27. Fluorescence quenching by PET followed by back electron transfer.

When the mercury ion interacts with the lone pair on the sensor the orbital is stabilized and drops below the HOMO of the fluorophore. This prevents the PET process from taking place and fluorescence is restored (Figure 1.28).

Figure 1.28. PET is deactivated by the metal and fluorescence is restored.

Two examples of sensors that employ a PET mechanism are shown in Figure 1.29.
Figure 1.29. Sensors that use the PET mechanism.

A number of other ions can be sensed by simply changing the functionality on the phenyl ring. This demonstrates the versatility of these fluorophores.

The characteristics of four-coordinate boron that are most relevant to this work are the intense absorption and fluorescence properties brought on by the $\text{-BF}_2$ unit binding to a $\pi$ system. In Chapters 5 and 6 this is achieved by binding a $\text{-BF}_2$ unit to a diketone moiety.

1.6.4 Synthesis of 4-coordinate boron compounds

The general procedure for a basic BODIPY involves a one pot synthesis. Benzaldehyde is initially mixed with 2,4-dimethylpyrrole and trifluoroacetic acid in dichloromethane. The condensation product is treated with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (or $p$-chloranil) to oxidize it and finally triethylamine and boron trifluoride etherate are added to yield the final BODIPY product (Scheme 1.15).\textsuperscript{68,69}
A substituted aldehyde can be used in place of benzaldehyde in order to make compounds with different solubility or electronic properties. In the case of this work, 4-formylbenzoic acid was used so that the resulting product could be attached to a Mo$_2$ center. Generally, the methylated pyrrole is also used in order to achieve a higher yield by preventing any scrambling during the condensation step. Unsubstituted pyrrole can be used at a yield reduction which allows for the phenyl ring to not be as restricted. It is also important to note that the -BF$_2$ unit can be added to a diketone in the same way it is added to the dipyrrin above.

**1.7 Statement of Purpose**

The broad goal of this thesis is to advance the understanding of the photophysical properties of M$_2$ paddlewheel complexes with π conjugated ligands using ultrafast time-resolved spectroscopy. These complexes are ideal systems to study the excited state charge dynamics and how the charge distribution transforms with time. As previously mentioned, they have numerous potential applications, and this work has sought to expand those applications by fusing the interesting properties of M$_2$ complexes with those of boron in order to develop sensors, invoke changes in ligand conformation, and perturb excited state decay pathways.
In Chapter 3, new bis-bis M₂ complexes were synthesized with diarylboron substituents incorporated into the carboxylate ligands in order to modulate the metal-to-ligand charge transfer transition. This resulted in an approximate 100 nm red shift (~4600 cm⁻¹) in the absorption band. Fluoride titrations were performed in order to “switch” the effect of the boron moiety off which established a mechanism for a colorimetric fluoride sensor; the color would change as the boron sites became saturated. Though there was little effect on the excited state ¹MLCT lifetimes, this was the first case where stimulated emission was observed in the fsTA spectra, indicating that the emission was enhanced relative to previous M₂ complexes.

Chapter 4 is a computational study that extends the work done in Chapter 3. The ligand systems consist of thiophene rings as opposed to phenyl rings in order to study the effect of stringing multiple rings together in order to extend to the conjugation. The monothiophene, bithiophene, and terthiophene carboxylate derivatives with and without the −B(mes)₂ moiety incorporated, as well as with the addition of F⁻ ions, for Mo₂ and W₂ were investigated. Additionally, calculations were performed on ligands that incorporated both −B(mes)₂ and triple bonds as a platform for synthesizing compounds with IR reporter groups.

Chapter 5 involves a series of ligands that are derivatives of the molecule avobenzone. Avobenzone is one of the most common UVA filters found in sunscreens, and is known to undergo a photoinduced tautomerization which ultimately can lead to the degradation of the molecule resulting in harmful products. Here the derivatives were attached to Mo₂ quadruple bonds to observe the effect on the isomerization. The result was a suppression
of the photoisomerization by introduction of a $^1$MLCT state at lower energy than the $^1\pi\pi^*$ state. Rapid internal conversion deactivated the $^1\pi\pi^*$ state resulting in a significant reduction of degradation. Additionally, a –BF$_2$ unit was incorporated into the “acac” binding mode of the β-diketone in order to study the change in photophysical properties. The result was a large red shift in the absorption band, and a 100 fold increase in excited state absorption intensity.

Chapter 6 was an investigation of the same ligand series as in Chapter 5 but bound to W$_2$ quadruple bonds. In this case both the singlet and triplet states of the W$_2$ compounds were MLCT in character which allowed for observation of the transformation from the $^1$MLCT state to the $^3$MLCT state using time-resolved infrared. This made it possible to track changes in the charge distribution as a function of time. Also there is again evidence that the photoisomerization is deactivated. Incorporation of the –BF$_2$ unit in this case did not have the same effect as before.
CHAPTER 2 : MATERIALS AND METHODS

2.1 General Considerations

Preparation and handling of air-sensitive materials was performed in an inert (argon or nitrogen) atmosphere using glove box manipulations or Schlenk techniques. Any solvents used throughout synthesis, purification, and analysis of the air-sensitive compounds were dried, distilled, and degassed by standard methods. The solvents were stored in Kontes top flasks over 4 Å molecular sieves. All other chemicals were used as received. A 400 MHz Bruker DPX Advance 400 spectrometer was used for all $^1$H NMR spectra. The spectra were recorded relative to the solvent protio impurity in THF-d$_8$ (1.73 ppm), DMSO-d$_6$ (2.50 ppm), or CDCl$_3$ (7.24 ppm) and chemical shifts are given relative to that value.

2.2 Mass spectrometry

Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry was performed on all Mo$_2$ and W$_2$ compounds. For the compounds reported in Chapter 3, a Bruker Reflex III mass spectrometer operated in a reflective, positive ion mode with an N$_2$ laser was used. For all other chapters a Bruker ultrafleXtreme mass spectrometer was used, in positive ion mode. The compounds were dispersed in a matrix of dithranol in THF solution. The data was standardized with 9
peptides that had molecular weights ranging from ~ 750 g/mol to 3,100 g/mol, supported in a matrix of α-cyano-4-hydroxycinnamic acid (HCCA).

2.3 Electrochemical studies

Cyclic voltammograms were collected at a scan rate of 100 mV/s using a Pine Research Instrumentation Wavenow potentiostat-galvanostat. The measurements were performed under a nitrogen atmosphere in a 0.1 M solution of t-Bu₄NPF₆ in THF using platinum working and platinum auxiliary electrodes patterned on ceramic, with a silver wire pseudo-reference electrode (Pine Research Instrumentation). The potentials for all complexes are internally referenced to the Cp₂Fe/Cp₂Fe⁺ couple.

2.4 Single Crystal X-Ray Diffraction

Single crystals were handled under a pool of fluorinated oil. Examination of the diffraction pattern was done on a Nonius Kappa CCD diffractometer with Mo Kα radiation. All work was done at 150 K using an Oxford Cryosystems Cryostream Cooler. Data integration was done with Denzo, and scaling and merging of the data was done with Scalepack. The structures were solved by the direct methods program in SHELXS-13. Full-matrix least-squares refinements based on F² were performed in SHELXL-13, as incorporated in the WinGX package. For each methyl group, the hydrogen atoms were added at calculated positions using a riding model with U(H) = 1.5Ueq (bonded carbon atom). The rest of the hydrogen atoms were included in the model at calculated positions using a riding model with U(H) = 1.2Ueq (bonded atom). Neutral atom scattering factors were used and include terms for anomalous dispersion. Mo₂(T²PB)₂(Bz)₂ was largely disordered, particularly in the T²PB moiety which was
modeled in two locations and restrained using the SAME, EXYZ and EADP commands. The same procedure was invoked in the disordered solvent THF which was coordinated axially along the Mo₂ bond. Furthermore it was necessary for the anisotropic U values of this disordered solvent to be restrained using the SIMU command. Mo₂(T'PB)₂(Bzald)₂ also had several different areas of disorder. Two of the isopropyl groups on the T'PB moiety were disordered over two locations as was the axially coordinated THF molecule. In each case, two orientations of the disorder were allowed to refine on a free variable and similarity restraints along with ridged bond restraints were used to ensure a stable refinement. The structure also contained highly disordered solvent in the lattice. Modeling of this residual electron density was not straight forward and despite several attempts at refinement the solvent molecules remained unstable. The residual density was removed from the model using the SQUEEZE\textsuperscript{74} protocol in PLATON\textsuperscript{75}, which ultimately removed 84 electrons from a solvent accessible void of 201 Å\textsuperscript{3} and corresponds to hexanes, a solvent used in crystallization.

Selected crystallographic information for the compounds are provided in the Appendices. The crystallographic data are registered with the Cambridge Crystallographic Data Center under the file numbers CCDC 943288 [Mo₂(T'PB)₂(Bz)₂] and CCDC 1030789 [Mo₂(T'PB)₂(Bzald)₂] and can be accessed free of charge via www.ccdc.cam.ac.uk/data_request/cif.
2.5 Steady-state spectroscopy

2.5.1 Electronic absorption

A Perkin-Elmer Lambda 900 spectrometer was used to record UV-Vis-NIR electronic spectra at room temperature with 1 cm x 1 cm quartz cuvettes sealed by Kontes tops. The same instrument was used to measure the low temperature UV-Vis-NIR electronic spectra using a sealed Specac advanced liquid transmission cell with NaCl windows at 108 K. The solvent used to form the glass was 2-methyltetrahydrofuran. The cell was placed inside a Specac variable temperature cell holder with a Specac variable temperature cell controller to monitor the temperature. Molar absorptivities, $M^{-1}\text{cm}^{-1}$, were determined using samples of known concentrations and calculated using Beer’s Law, $A = \varepsilon c l$.

2.5.2 Steady State Emission Spectra

The data collected in the range of 350-800 nm were acquired using a SPEX Fluoromax-2 spectrofluorometer. THF was used for the spectra obtained at room temperature, and 2-MeTHF was used for 77 K. The steady-state near-IR emission spectra were collected using a home-built instrument with a germanium detector. The samples were prepared with an absorbance of ~0.3 in a J. Young NMR tube using 2-MeTHF for both room temperature and 77 K measurements. Samples were excited into the $^1\text{MLCT}$ band whenever possible.

2.5.3 Ground-state FT-IR Spectra

Ground state infrared spectra were recorded with a Perkin-Elmer Spectrum GX FT-IR spectrometer. Solution samples were sealed in a Perkin-Elmer semidemountable cell
with a 4.0 mm CaF$_2$ front and back window separated by a 0.1 mm Teflon spacer. The solvent was subtracted from the spectra, baseline corrected, and then plotted as % transmittance.

### 2.6 Time-Resolved Measurements

#### 2.6.1 Nanosecond Transient Absorption Spectra (nsTA)

The nsTA experiments were performed using a home-built instrument. The pump beam is generated from the frequency doubled (532 nm) or tripled (355 nm) output of a Spectra-Physics GCR-150 Nd:YAG laser (5 mJ/pulse, 8 ns fwhm). The pump excitation power at the sample was 100 mW. For the probe, a 150 W Xe arc lamp pulsed with home-built electronics was used. The probe passes through the sample perpendicular to the pump and then through a monochromator. A Hamamatsu R928 photomultiplier tube (PMT) detects the signal which is then digitalized with a Tektronics 400 mHz oscilloscope. The samples were prepared with an absorbance of ~ 0.1-0.3 in a 1 cm quartz cuvette with Kontes top. Samples were excited into the $^1$MLCT band when possible. Kinetics for the time-resolved data were fit to a sum of exponentials, $S(t) = \sum_i A_i \exp(-t/\tau_i) + C$, where $A_i$ is the amplitude, $\tau_i$ is the lifetime, and $C$ is an offset, in SigmaPlot 12.0. Standard errors of the exponential fits are given as the error bars of the lifetimes.

#### 2.6.2 Femtosecond Transient Absorption Spectra (fsTA)

A fundamental, 795 nm beam with ~50 fs laser pulses and repetition rate of 1 KHz is produced from a Coherent mode-locked titanium-sapphire (Ti:Sapphire) oscillator pumped with a Nd:YAG diode laser at 532 nm and Legend USP regenerative amplifier.
The pulses are amplified by an Evolution 30 using a Ti:Sapphire laser cavity pumped with a 520 nm Nd:YLF diode laser. The fundamental beam is split to eventually form the pump and probe beams. The pump beam is generated in an optical parametric amplifier (OPA) equipped with sum frequency generation (SFG) and UV-vis harmonics optics boxes, which allows for tunability spanning from the UV to near infrared region of the continuum.\textsuperscript{77} The output of the laser pulse from the OPA is broadened to approximately 150 fs. This beam then moves through a chopper, shutter, focusing lens, then finally into the sample. The other part of the fundamental beam (~2 μJ) passes through a chopper and shutter as well before moving along the delay stage. The broadband continuum (~350-1100 nm) reference beam is generated by focusing the beam through a calcium fluoride crystal which is then vertically split (~5 mm) into the probe and reference beams.\textsuperscript{78} The probe is spatially and temporally overlapped with the pump in the sample before passing into the CCD array (Symphony Jobin Yvon, 2048 x 512 pixels). The pump passes through the sample at a 30° angle with respect to the probe in order to minimize scattering of the pimp beam in the detector. This instrumental setup can be found in greater detail in the work by Burdzinski, et al.\textsuperscript{21} Figure 2.1 shows the full laser diagram of the fsTA experiment.
The samples were prepared with an absorption of 0.3-0.8 (with the exception of \( \text{Mo}_2(\text{TiPB})_2(\text{AvoBF}_2)_2 \), which was diluted to an absorbance of \(~0.1\) in THF or toluene in a quartz cuvette with a 1.0 mm path length and a Kontes top. The power of the excitation pulses was set to be between 1 and 2 \( \mu \text{J} \). Wavelength calibrations and group velocity dispersion (GVD) corrections were applied to all spectra. The resulting kinetics data for the fsTA experiment were fit to a sum of exponentials, \( S(t) = \sum A_i \exp(-1/\tau_i) + C \), where \( A_i \) is the amplitude, \( \tau_i \) is the lifetime, and \( C \) is an offset, in Igor Pro 6.0. Standard errors of the exponential fits are given as the error bars of the lifetimes.

2.6.3 Femtosecond Time-Resolved Infrared Spectra (fsTRIR)

A fundamental, 795 nm beam with \(~50\) fs laser pulses and repetition rate of 1 KHz is produced from a Coherent mode-locked titanium-sapphire (Ti:Sapphire) oscillator.
pumped with a Nd:YAG diode laser at 532 nm and Legend USP regenerative amplifier. The pulses are amplified by an Evolution 30 using a Ti:Sapphire laser cavity pumped with a 520 nm Nd:YLF diode laser. The pump beam is generated in a similar way as in the fsTA experiment with an optical parametric amplifier (OPA) equipped with sum frequency generation (SFG) and UV-vis harmonics optics boxes, though the fundamental is split evenly. The remaining 50% is used to generate the probe beam with a second OPA equipped with a difference frequency generation (DFG) optics box. This produces a mid-IR with wavelengths between 4000-900 cm\(^{-1}\) and a bandwidth of 200-80 cm\(^{-1}\). This beam is split into the probe and reference beams (~5 mm vertically separated) which ultimately are detected by a liquid N\(_2\) cooled HgCdTe detector (Triax 320, 32 x 2 pixels). A more detailed description of the laser system and instrumental setup can be found in the work by Burdzinski, et al.\(^ {21}\) A diagram of the fsTRIR setup is shown in Figure 2.2.

![Diagram of the fsTRIR setup](image)

Figure 2.2. The laser system and experimental setup used for the fsTRIR experiment.
The samples were prepared with an absorbance of ~ 1 at $\lambda_{\text{max}}$ in THF (with the exception of Mo$_2$(TPB)$_2$(AvoBF$_2$)$_2$ which was diluted to an absorbance of ~0.2). Solutions were sealed in a PerkinElmer semi-dismountable cell with a 0.1 mm Teflon spaced between 4 mm CaF$_2$ windows. The excitation power at the sample was set between 1 and 2 $\mu$J. The resulting kinetics data for the time-resolved experiments were fit to a sum of exponentials, $S(t) = \sum_i A_i \exp(-1/\tau_i) + C$, where $A_i$ is the amplitude, $\tau_i$ is the lifetime, and $C$ is an offset, in Igor Pro 6.0. Standard errors of the exponential fits are given as the error bars of the lifetimes.

### 2.7 Electronic Structure Calculations

Gaussian09 was used in conjunction with density functional theory (DFT) to optimize the model complexes for each compound in the gas phase. For the molybdenum and tungsten atoms, the Stuttgart/Dresden (SDD) energy consistent pseudopotentials and the SDD energy consistent basis set were used with the B3LYP functional. For the lighter H, C, B, F, and O atoms, the 6-31G* basis set was used with the same functional. In order to ensure the convergence of second derivatives, a force constant analysis was performed on the optimized gas-phase structures. Vibrational frequency analysis was then performed to confirm that these structures were global minima on the potential energy surface. A correction factor of 0.96 (B3LYP, 6-31g*) was applied to all
calculated vibrations. GaussView 5.0.8 isosurface contour plots are presented in the molecular orbital diagrams with an isovalue of 0.02. The functional and basis sets used for the DFT calculations were used again for the time dependent DFT (TD-DFT) which allowed for the simulation of electronic absorption spectra. A standard GaussView σ value of 0.4 eV was used in generating the simulated UV-vis.

2.8 Synthesis

Synthetic procedures for the compounds described in this work are organized by chapter. The ligands benzoic acid (BzH) and 4-Formylbenzoic acid (HBzald) were purchased from Sigma Aldrich and used without further purification. Homoleptic starting materials Mo$_2$(T$i$PB)$_4$ and W$_2$(T$i$PB)$_4$ were synthesized according to published procedures.

2.8.1 Chapter 3

Synthesis of 4-(dimesitylboranyl)benzoic acid, HBMP. Synthesis modified from reference. Dibromobenzene (0.472 g, 2.00 mmol) was dried for 2h under vacuum on a Schlenk line, dissolved in 15 mL THF and cooled to -78 °C followed by a dropwise addition of n-butyl lithium (2.3 M, 0.87 mL, 2.00 mmol) in hexanes. Solution turned yellow after being allowed to stir for 30 min then a solution of dimesityl boron fluoride (0.536 g, 2.00 mmol) in 20 mL Et$_2$O was added slowly to the reaction flask. The flask was kept at -78 °C for 2h then allowed to reach room temperature overnight. The solvent was removed under vacuum and 4-(bromophenyl)dimesitylborane was obtained as a white powder by column chromatography with hexanes as elutant. Yield: 0.567 g (70
4-(bromophenyl)dimesitylborane (0.500 g, 1.23 mmol) was dried for 2h under vacuum on a Schlenk line, dissolved in 20 mL THF and cooled to -78 °C followed by a dropwise addition of n-butyl lithium (2.5 M, 0.49 mL, 1.23 mmol) in hexanes. Solution turned red after being allowed to stir for 30 min, then carbon dioxide was passed through a drying tube filled with anhydrous calcium sulfate and bubbled through the reaction solution for 2h. After which time the reaction turned cloudy white. The flask was opened to air and the product was extracted with dichloromethane after acid workup followed by a recrystallization with hexanes to give a white powder. Yield: 0.310 g (67%).  ¹H NMR (CDCl₃): δH (250 MHz) 8.05 (d, 2H, JHH = 8Hz), 7.59 (d, 2H, JHH = 8Hz), 6.83 (s, 4H), 2.32 (s, 6H), 1.98 (s, 12H) ppm.

Synthesis of Mo₂(TiPB)₂(BMP)₂, I. HBMP (0.070 g, 0.189 mmol) and Mo₂(TiPB)₄ (0.112 g, 0.095 mmol) were dissolved in toluene and allowed to stir for 3 days yielding a red solution. The solvent was removed in vacuo and the resulting orange solid was washed 3 times with 20 mL of hexanes and dried. ¹H NMR (THF – d₈): δH (400 MHz) 8.36 (d, 4H, JHH = 8Hz), 7.68 (d, 4H, JHH = 8Hz), 7.00 (s, 4H), 6.86 (s, 8H), 3.03 (m, 2H), 2.88 (m, 4H), 2.30 (s, 12H), 2.08 (s, 24H), 1.24 (d, 12H, JHH = 7Hz), 1.04 (d, 24H, JHH = 7Hz) ppm. UV-Vis: (in THF at 293K) 521 nm, 322 nm; (in toluene at 293K) 488 nm, 323 nm; (in pyridine at 293K) 541 nm, 440 nm. MALDI-TOF: Molecular formula: Mo₂C₈₂B₂H₉₈O₈. Calculated: 1432.6. Found: 1432.3 (M⁺).
Synthesis of $\text{W}_2(\text{T}^\text{3PB})_2(\text{BMP})_2$, II. HBMP (0.080 g, 0.216 mmol) and $\text{Mo}_2(\text{T}^\text{3PB})_4$ (0.147 g, 0.108 mmol) were dissolved in toluene and allowed to stir for 3 days yielding a blue solution. The solvent was removed in vacuo and the resulting blue solid was washed 3 times with 20 mL of hexanes and dried. $^1\text{H}$ NMR (THF – $d_8$): $\delta_H$ (400 MHz) 8.13 (d, 4H, $J_{HH} = 8$Hz), 7.66 (d, 4H, $J_{HH} = 8$Hz), 6.99 (s, 4H), 6.86 (s, 8H), 3.01 (m, 2H), 2.83 (m, 4H), 2.30 (s, 12H), 2.07 (s, 24H), 1.23 (d, 12H, $J_{HH} = 7$Hz), 0.99 (d, 24H, $J_{HH} = 7$Hz) ppm. UV-Vis: (in THF at 293K) 754 nm, 402 nm, 322 nm. MALDI-TOF: Molecular formula: $\text{W}_2\text{C}_82\text{B}_2\text{H}_98\text{O}_8$. Calculated: 1604.7. Found: 1604.0 (M$^+$).

Synthesis of $\text{Mo}_2(\text{T}^\text{3PB})_2(\text{Bz})_2$. HBz (0.041 g, 0.339 mmol) and $\text{Mo}_2(\text{T}^\text{3PB})_4$ (0.208 g, 0.177 mmol) were dissolved in toluene and allowed to stir for 3 days yielding an yellow solution. The solvent was removed in vacuo and the resulting yellow solid was washed 3 times with 20 mL of hexanes and dried. $^1\text{H}$ NMR (THF – $d_8$): $\delta_H$ (400 MHz) 8.38 (d, 4H, $J_{HH} = 6$Hz), 7.56 (d, 4H, $J_{HH} = 6$Hz), 6.99 (s, 4H), 3.03 (m, 2H), 2.87 (m, 4H), 1.23 (d, 12H, $J_{HH} = 7$Hz), 1.02 (d, 24H, $J_{HH} = 7$Hz) ppm. UV-Vis: (in THF at 293K) 429 nm, 339 nm. MALDI-TOF: Molecular Formula: $\text{Mo}_2\text{C}_{46}\text{H}_{56}\text{O}_8$. Calculated: 932.2. Found: 932.7 (M$^+$).

Synthesis of $\text{W}_2(\text{T}^\text{3PB})_2(\text{Bz})_2$. HBz (0.041 g, 0.399 mmol) and $\text{Mo}_2(\text{T}^\text{3PB})_4$ (0.230 g, 0.169 mmol) were dissolved in toluene and allowed to stir for 3 days yielding a red solution. The solvent was removed in vacuo and the resulting red solid was washed 3 times with 20 mL of hexanes and dried. $^1\text{H}$ NMR (THF – $d_8$): $\delta_H$ (400 MHz) 8.16 (d, 4H, $J_{HH} = 8$Hz), 7.71 (d, 4H, $J_{HH} = 8$Hz), 6.98 (s, 4H), 3.01 (m, 2H), 2.84 (m, 4H), 1.22 (d, 12H, $J_{HH} = 7$Hz), 0.96 (d, 24H, $J_{HH} = 7$Hz) ppm. UV-Vis: (in THF at 293K) 593 nm, 557
nm, 405 nm. MALDI-TOF: Molecular Formula: W$_2$C$_{46}$H$_{56}$O$_8$. Calculated: 1108.3. Found: 1107.8 (M$^+$).

2.8.2 Chapter 5

Synthesis of 4-(3-oxo-3-phenylpropanoyl)benzoic acid (HAvO). Dimethylterephthalate (DMT, 5.2 g, 26.8 mmol) was dried under vacuum for 2 h prior to use. The flask was then filled with argon, and acetophenone (4.00 g, 3.54 mL, 33.3 mmol) was added by syringe followed by ~30 mL of dry THF and left to stir for 30 min. NaH (60% oil suspension, 1.56 g, 39 mmol) was weighed into a separate flask and dried for 30 min under vacuum and then filled with argon. Dry THF (~ 50mL) was added to the NaH flask and stirred for 15 min to form a suspension, which was then added dropwise to the reaction flask containing DMT and acetophenone. A reflux apparatus was assembled and an oil bath was used to bring the temperature to ~95 °C. The solution turned bright yellow while refluxing for 6 h. The THF solution was concentrated under a dynamic vacuum, and the flask was then cooled in an ice bath and quenched with ~3 mL of cold, concentrated HCl. The resulting residue was dissolved in DCM and washed with water. DCM layer was collected, dried over MgSO$_4$, and filtered. DCM was removed under vacuum and the resulting solid was recrystallized from methanol to give a pale yellow product methyl 4-(3-oxo-3-phenylpropanoyl)benzoate, MeAvo.

Methyl 4-(3-oxo-3-phenylpropanoyl)benzoate (MeAvo, 1.6 g, 5.66 mmol) was weighed and added to a flask containing anhydrous LiOH powder (1.6 g, 66.8 mmol). A 50 mL mixture of 1:1 THF:H$_2$O was added to the flask and was allowed to stir overnight. The resulting yellow solution was washed twice with 40 mL of dichloromethane. The
water fraction was then chilled in an ice bath and acidified with 3M HCl until the yellow color had completely vanished. The white solid was filtered and washed with 100 mL of H₂O. This was then dissolved in minimal Et₂O and filtered through cotton. The solvent was removed via dynamic vacuum to afford a pale yellow solid HAvo. Yield: 26%. ¹H NMR (DMSO-d₆ 400 MHz): 17.03 (s, 1H), 13.32 (s, 1H), 8.27 (d, 2H), 8.20 (d, 2H) 8.09 (d, 2H), 7.68 (t, 1H), 7.59 (t, 2H), 7.43 (s, 1H).

**Synthesis of 4-(2,2-difluoro-6-phenyl-2H-1λ³,3,2λ⁴-dioxaborinin-4-yl)benzoic acid (HAvoBF₂).** HAvo (0.230 g, 0.857 mmol) was dried for ~1 h under vacuum, then ~30 mL dry DCM was added to the reaction flask. Triethylamine (1.0 mL, 7.21 mmol) and boron trifluoride etherate (1.0 mL, 11.55 mmol) were syringed into the flask. The solution turned bright yellow immediately upon injection of triethylamine. The reaction was then left to stir overnight. The next day DCM was removed under vacuum and ~100 mL of water was added. The solid did not dissolve in water, and was collected by vacuum filtration. The filtrate was directly neutralized into a solution of sodium bicarbonate. The solid was then recrystallized from toluene, collected by centrifugation, and dried under vacuum. Yield: 50%. ¹H NMR (DMSO-d₆ 400 MHz): 13.46 (s, 1H), 8.50 (d, 2H), 8.43 (d, 2H) 8.17 (d, 2H), 8.06 (s, 1H), 7.87 (t, 1H), 7.70 (t, 2H).

**Synthesis of Mo₂(T²PB)₂(Bzald)₂, I.** Toluene (ca. 25 mL) was added to mixture of Mo₂(T²PB)₄ (0.268 g, 0.227 mmol) and 4 formylbenzoic acid (H-Bzald, 0.070 g, 0.466 mmol) resulting instantly in a red solution. This was left to stir for 3 days at room temperature. The solution was concentrated by removing toluene under vacuum, then washed with a minimum of toluene, methanol (2 x 5 mL), and hexanes (4 x 20 mL). The
compound was dried under vacuum to yield a pink-red powder. Yield: 70%. $^1$H NMR (DMSO-$d_6$ 400 MHz): 8.45 (d, 4H), 8.21 (d, 4H) 7.01 (s, 4H), 2.90 (m, 6H), 1.19 (d, 12H), 0.95 (d, 24H). MALDI-TOF: Molecular Formula: Mo$_2$C$_{48}$H$_{56}$O$_{10}$. Calculated: 985.20 Found: 985.51. UV-Vis (THF): 521 nm ($\varepsilon = 12,400$ M$^{-1}$cm$^{-1}$).

**Synthesis of Mo$_2$(T$^6$PB)$_2$(Avo)$_2$, II.** Toluene (ca. 25 mL) was added to a mixture of Mo$_2$(T$^6$PB)$_4$ (0.224 g, 0.190 mmol) and 4-(3-oxo-3-phenylpropanoyl)benzoic acid (HAvo, 0.110 g, 0.410 mmol) resulting in the immediate formation of a red solution. This was left to stir for 3 days at room temperature. The solution was concentrated by removing toluene under vacuum and subsequently washed with a minimum of toluene, 2×5 mL of methanol, 1×20 mL of ether, and 4×20 mL of hexanes. The compound was dried under vacuum to give a red powder. Yield: 65%. $^1$H NMR (THF-$d_8$ 400 MHz): 17.19 (s, 2H), 8.50 (d, 4H) 8.34 (d, 4H), 8.16 (d, 4H), 7.60 (t, 2H), 7.53 (t, 4H), 7.28 (s, 2H), 7.01 (s, 4H), 3.05 (m, 4H), 2.87 (m, 2H) 1.23 (d, 12H) 1.05 (d, 24H). MALDI-TOF: Molecular Formula: Mo$_2$C$_{64}$H$_{68}$O$_{12}$. Calculated: 1221.28 Found: 1221.76. UV-Vis (THF): 528 nm ($\varepsilon = 10,900$ M$^{-1}$cm$^{-1}$), 345 nm.

**Synthesis of Mo$_2$(T$^6$PB)$_2$(AvoBF)$_2$, III.** Toluene (ca. 25 mL) was added to mixture of Mo$_2$(T$^6$PB)$_4$ (0.215 g, 0.182 mmol) and 4-(2,2-difluoro-6-phenyl-2H-1λ$_3$,3,2λ^4-dioxaborinin-4-yl)benzoic acid (HAvoBF$_2$, 0.102 g, 0.323 mmol) resulting in the immediate formation of a blue solution. This was left to stir for 3 days at room temperature. The solution was concentrated by removing toluene under vacuum and then washed with a minimum of toluene, 2×5 mL methanol, and 4×20 mL hexanes (ca. 5 mL). The solid was dried under vacuum to yield a blue powder. Yield: 60%. $^1$H NMR (THF-
\(d_8\) 400 MHz): 8.56 (s, 8H), 8.36 (d, 4H), 7.77 (m, 6H), 7.64 (t, 4H), 7.02 (s, 4H), 3.05 (m, 4H), 2.87 (m, 2H), 1.22 (d, 12H), 1.05 (d, 24H). MALDI-TOF: Molecular Formula: Mo\(\text{C}_{64}\text{B}_2\text{F}_4\text{H}_{66}\text{O}_{12}\). Calculated: 1317.28 Found: 1317.48.

UV-Vis (THF): 643 nm (\(\varepsilon = 15,700 \text{ M}^{-1}\text{cm}^{-1}\)), 370 nm.

2.8.3 Chapter 6

Synthesis of 4-(3-oxo-3-phenylpropanoyl)benzoic acid (HAvo) and 4-(2,2-difluoro-6-phenyl-2H-1\(\lambda^3\),3,2\(\lambda^4\)-dioxaborinin-4-yl)benzoic acid (HAvoBF\(_2\)) was shown above under Chapter 5 synthesis.

Synthesis of W\(_2\)(T\(^\text{ii}\)PB\(_2\))(Bzald)\(_2\), I. Toluene (ca. 25 mL) was added to a mixture of W\(_2\)(T\(^\text{ii}\)PB\(_4\)) (0.180 g, 0.132 mmol) and 4-formylbenzoic acid (HBzald, 0.040 g, 0.266 mmol) resulting instantly in a yellow solution. This was left to stir for 3 days at room temperature in an inert atmosphere box. At the end of three days the solution had turned blue. The solution was concentrated by removing toluene under vacuum which was then filtered to capture the solid on a glass frit. The solid was washed with a minimum of toluene, methanol (2 x 10 mL), and hexanes (3 x 20 mL). The compound was dried under vacuum to yield a dark blue powder. \(^1\)H NMR (THF-\(d_8\) 400 MHz): 10.05 (s, 2H), 8.28 (d, 4H), 8.08 (d, 4H), 6.99 (s, 2H), 2.83 (m, 6H), 1.21 (d, 12H), 0.97 (d, 24H). MALDI-TOF: Calculated: Molecular Formula: W\(_2\text{C}_{48}\text{H}_{56}\text{O}_{10}\). 1160.29 Found: 1160.37. UV-Vis (THF): 748 nm (\(\varepsilon = 19,000 \text{ M}^{-1}\text{cm}^{-1}\)).

Synthesis of W\(_2\)(T\(^\text{ii}\)PB\(_2\))(Avo)\(_2\), II. Toluene (ca. 25 mL) was added to a mixture of W\(_2\)(T\(^\text{ii}\)PB\(_4\)) (0.188 g, 0.134 mmol) and 4-(3-oxo-3-phenylpropanoyl)benzoic acid (HAvo, 0.875 g, 0.326 mmol) resulting in the immediate formation of a dark yellow solution.
This was left to stir for 3 days at room temperature in an inert atmosphere box which resulted in a deep blue solution. The solution was concentrated by removing toluene under vacuum. The solid was subsequently removed from the solvent by filtering over a glass frit. The solid was then washed with a 10 mL of toluene, 5x 20 mL methanol, 4x 30 mL of hexanes. The compound was dried under vacuum to give a blue powder. \( ^1H \) NMR (THF-\( d_8 \) 400 MHz): 17.24 (s, 2H), 8.33 (d, 4H) 8.25 (d, 4H), 8.14 (d, 4H), 7.54 (m, 6H), 7.23 (s, 2H), 6.99 (s, 4H), 3.84 (m, 6H), 1.21 (d, 12H) 0.99 (d, 24H). MALDI-TOF: Molecular Formula: \( \text{W}_2\text{C}_{64}\text{B}_{2}\text{F}_{4}\text{H}_{68}\text{O}_{12} \). Calculated: 1396.37 Found: 1396.42. UV-Vis (THF): 355, 796 nm \((\varepsilon = 31,000 \text{ M}^{-1}\text{cm}^{-1})\).

**Synthesis of \( \text{W}_2(\text{T}^\text{iPB})_2(\text{AvoBF}_2)_2 \), III.** Toluene (ca. 15 mL) was added to mixture of \( \text{W}_2(\text{T}^\text{iPB})_4 \) (0.236 g, 0.175 mmol) and 4-(2,2-difluoro-6-phenyl-2H-1\( \lambda^3\),3,2\( \lambda^4\)-dioxaborinin-4-yl)benzoic acid (HAvoBF\(_2\), 0.110 g, 0.348 mmol) resulting in the eventual formation of a dark green solution. This was left to stir for 3 days at room temperature. The solution was concentrated by removing toluene under vacuum. The solid was removed from the solution by filtering over a glass frit. The solid was then washed with 3 x 25 mL methanol, 3 x 25 mL of toluene, and 5 x 20 mL hexanes. The solid was dried under vacuum to yield a dark green powder. \( ^1H \) NMR (THF-\( d_8 \) 400 MHz): 8.50 (d, 4H), 8.30 (t, 8H), 7.70 (m, 4H), 7.63 (t, 4H), 7.00 (s, 4H), 2.84 (m, 6H), 1.21 (d, 12H), 1.00 (d, 24H). MALDI-TOF: Molecular Formula: \( \text{W}_2\text{C}_{64}\text{B}_{2}\text{F}_{4}\text{H}_{68}\text{O}_{12} \). Calculated: 1492.37 Found: 1492.49. UV-Vis (THF): 371, 1017 nm \((\varepsilon = 39,000 \text{ M}^{-1}\text{cm}^{-1})\).
CHAPTER 3: MODULATING THE M$_2$δ-TO-LIGAND CHARGE TRANSFER TRANSITION BY THE USE OF DIARYLBORON SUBSTITUENTS

(Adapted from a 2013 paper published in Dalton Transactions)

3.1 Introduction

Arylboron compounds have attracted considerable attention due to their photophysical properties.$^{46}$ Three-coordinate boron geometries are isoelectronic with carbocations. This establishes a convenient way to install electron withdrawing groups into organic molecules. The boron atoms possess a vacant p$_z$ orbital which can be used to extend ligand conjugation. The notably strong emission spectra associated with arylboranes can then be quenched upon the addition of ions such as F$^-$ and CN$^-$ that are capable of binding to the Lewis acidic center of the boron.$^{50,86}$ This feature makes them attractive materials for implementation as sensors.

Recent work in the Chisholm lab has focused on the photophysical properties of carboxylate ligands attached to M$_2$ quadruple bonded centers of the form trans-M$_2$(T$^+$PB)$_2$L$_2$, where L is a π acceptor ligand such as cyanobenzoate,$^{45}$ cyanoacrylate,$^{87}$ α,α’-thienylcarboxylate,$^{88}$ or 2,6-azulenecarboxylate.$^{89}$ The trans geometry of these compounds is thermodynamically favored due to the extended planar structure which
results from extensive Lπ-M2δ-Lπ conjugation. An example structure is shown in Figure 3.1.

Figure 3.1. Molecular structure of W₂(TiPB₂)(Azu-2)₂ [Azu-2 = 6-carboethoxy-2-azulenecarboxylate] with the anisotropic displacement parameters drawn at the 50% probability level.⁸⁹

A general frontier molecular orbital diagram is shown in Figure 3.2 which illustrates how the M₂δ orbital interacts with only the out-of-phase π* combination of the trans ligands.
Figure 3.2. $M_2 \delta$ orbital interaction with the in-phase and out-of-phase ligand $\pi^*$ orbital combinations.\textsuperscript{89}

This causes a splitting of the in- and out-of-phase $L\pi^*$ combinations. In $D_{2h}$ symmetry the $M_2 \delta$ to in-phase $L\pi^*$ combination, typically the HOMO $\rightarrow$ LUMO transition, is a fully allowed $^1$MLCT transition which occurs in the visible and near infrared region of the spectrum. This transition has recently been of particular interest, and in this work we investigate the influence of introducing a -BAr\textsubscript{2} group to a simple $\pi$-acceptor ligand, benzoate. Result of this inquiry are presented henceforth.

3.2 Results and Discussion

3.2.1 Synthesis

The synthesis of the boron containing carboxylic acid, 4-(dimesitylboranyl)benzoic acid (BMPH), and its reaction to form the new compounds, $trans$-$M_2(T^{i}PB)_2$(BMP)$_2$, where $M$ = Mo for compound I, and $M$ = W for compound II, are shown in Scheme 3.1.
Scheme 3.1. The synthesis of bis-bis compounds \( \text{trans-}M_2(T'PB)_2(\text{BMP})_2 \).

The benzoate compounds \( \text{trans-}M_2(T'PB)_2(\text{Bz})_2 \) \([\text{Bz} = \text{O}_2\text{C-Ph}]\) were similarly prepared from the reactions between \( M_2(T'PB)_4 \) and two equivalents of benzoic acid stirred in toluene. The new compounds have been characterized by MALDI-TOF mass spectrometry and \(^1\text{H}\) NMR spectroscopy as well as several other spectroscopic techniques described subsequently. Although no single crystal x-ray determination has been carried out in this study for compounds I and II, there is ample precedent for their structures. Furthermore, the structure of \( \text{Mo}_2(T'PB)_2(\text{Bz})_2 \), which can be viewed as the parent
compound to I is reported below. A planar central phenyl-CO₂-M₂-O₂C-phenyl unit is anticipated for all compounds in their ground-state. The orientation of the –B(mesityl)₂ group will also be such that the B 2p₂ orbital will be perpendicular to the plane in order to allow for extended π conjugation. The mesityl units will undoubtedly be twisted out of conjugation with the vacant B 2p₂ orbital due to steric interactions of the methyl groups.

3.2.2 Crystal and Molecular Structure of Mo₂(T⁺PB)₂(Bz)₂

The benzoate compound, Mo₂(T⁺PB)₂(Bz)₂, crystallized on a center of inversion located in the middle of the Mo₂ bond. The dihedral angle associated with the CO₂ and the T⁺PB moiety is ~96° which effectively removes the ring from conjugation with the metal center. The dihedral angle associated with the CO₂ and the phenyl ring of the benzoate moiety, however, is less than 9° which allows for considerable conjugation with the metal center. The solvent used in crystallization was THF and is coordinated axially along the Mo₂ bond. The remainder of the structure is similar to previously reported Mo₂ tetracarboxylates.⁴⁵,⁸⁷–⁸⁹ The structure was significantly disordered and was modeled accordingly. Further refinement details can be found in Appendix A and in the Crystallographic Information File (CIF).
Figure 3.3. ORTEP representation of Mo₂(T'PB)₂(Bz)₂ (sea green = molybdenum, scarlet = oxygen, gray = carbon) drawn at 50% probability. Hydrogens, solvent, and disorder excluded for clarity.

3.2.3 Electronic Structure Calculations

Density functional theory (DFT) and time-dependent density functional theory (TDDFT) calculations were performed using Gaussian09\textsuperscript{79} in order to assist in the interpretation of the photophysical properties of the new compounds. Model compounds were used where the bulky T'PB ligands were substituted with formate in order to simplify the calculations. This is a reasonable approximation since \textit{trans}-M₂(T'PB)₂L₂ structures tend
to contain T\(^{1}\)PB ligands that are twisted close to 90° with respect to the carboxylate linkers, effectively removing them from conjugation with the metal center. The mesityl groups in the boron containing model compounds have also been replaced with hydrogen atoms for a similar purpose. This assumption was investigated by calculating the simulated UV-vis spectrum of the molybdenum compound using mesityl groups and comparing with the compound having hydrogen atoms. The MLCT absorption band differed by only 3 nm which makes this a reasonable approximation. This simplification is discussed in greater detail in Chapter 4. Similar calculations were performed on the benzoate model compounds, \textit{trans-M}_2(O_2CH)_2(Bz)_2.

The calculated frontier molecular orbital energy level diagram for the molybdenum model compound \(\textbf{I'}\) is shown in Figure 3.4 along with a comparison to the benzoate compound.
Figure 3.4. Frontier molecular orbital energy level diagram of model compound I’ (right) and the parent benzoate compound Mo$_2$(TPB)$_2$(Bz)$_2$ (left), along with Gaussview 5.0.8 plots of I’ (isovalue = 0.02).

A similar diagram for the tungsten compound II’ and its benzoate parent compound are shown in Figure 3.5.
Figure 3.5. Frontier molecular orbital energy level diagram of model compound II’ (right) and the parent benzoate compound \( W_2(T'PB)_2(Bz)_2 \) (left) \([Bz = O_2C-Ph]\), along with Gaussview 5.0.8 plots of II’ (isovalue = 0.02).

The calculations reveal two interesting points: 1) The introduction of boron (-BH\(_2\)) in the para position of the ring stabilizes the HOMO, the M\(_2\)\(\delta\) orbital, by \( \approx 0.35 \) eV with respect to the parent benzoate compounds. 2) The introduction of the –BH\(_2\) group greatly lowers the energy of the two ligand based \(\pi^*\) orbitals. For \( \text{Mo}_2(T'PB)_2(Bz)_2 \), the LUMO is the \(\text{Mo}_2\delta^*\) orbital, but addition of the –BH\(_2\) moiety in I’ stabilizes both the \(\text{L}\pi^*\) orbitals to lower energy than that of the \(\text{Mo}_2\delta^*\) orbital resulting in the in-phase ligand \(\pi^*\)
combination as the new LUMO. For tungsten the $W_2\delta^*$ orbital lies at higher energy than in $Mo_2$ and so the in-phase $L\pi^*$ combination is the LUMO for both $II'$ and the parent compound. The HOMO-LUMO gap is substantially smaller, however, in $II'$. Since the HOMO→LUMO transition is a fully allowed metal-to-ligand charge transfer (MLCT) electronic transition, the band will be shifted to lowest energy in the case of $II'$, and both $I'$ and $II'$ will be red-shifted with respect to their parent compounds. The ease of electrochemical oxidation will follow in the order $II > I$.

3.2.4 Electronic Absorption and Steady-State Emission Spectra

The electronic absorption spectra of $I$ and $II$ collected in THF are shown in Figure 3.6 along with their respective benzoates.

![Figure 3.6. Electronic absorption spectra of compounds $I$ and $II$ with their corresponding parent benzoate compounds in THF.](image-url)
As predicted by the electronic structure calculations, the MLCT transitions for both compounds are significantly red-shifted with respect to their benzoate counterparts. The intense broad absorption bands of compound I, $\lambda_{\text{max}} = 521$ nm, and of compound II, $\lambda_{\text{max}} = 755$ nm, are consistent with their purple-red and green solutions, respectively. The two tungsten compounds exhibit an additional electronic transition at 400 nm which is assignable to the W$_2$$\delta$ to -CO$_2$ $\pi^*$ transition associated with the TiP$_2$ ligands. At higher energy, $\sim 330$ nm, for both compounds I and II, is the band arising from the ligand based $\pi\pi^*$ transitions.

The breadth of the $^1$MLCT transition is in part due to thermal energy which can overcome the thermodynamically favored planar structure and result in the presence of an ensemble of rotamers in solution involving numerous dihedral angles between the O$_2$C-phenyl-B2p$\pi$ units. Photoexcitation to the $^1$MLCT state is likely to be accompanied by a dipole change since the motion of the two trans ligands are not correlated, leading to a significant solvent dependence. The absorption spectra in toluene compared to THF can be found in Appendix A. The steady-state emission spectra show less of a solvent dependence though compound I is only weakly emissive from the S$_1$ state in toluene. The singlet emission for compound II falls too close to the limits of our instrumentation for a reliable comparison.

Both compounds I and II have triplet states (as determined by the time-resolved spectroscopy presented below) but only I shows phosphorescence which appears at 1080 nm. This is typical of Mo$_2$$^{4+}$ carboxylate compounds and is assignable to the $^3$Mo$_2$$\delta$$\delta^*$
state (see Appendix). Furthermore the lifetime of the T\textsubscript{1} emission is 66 μs, which is notably longer than the typical lifetimes of \textsuperscript{3}MLCT states. No phosphorescence is observed for compound \textbf{II} which likely has a lower energy \textsuperscript{3}MLCT that presumably relaxes through a nonradiative decay pathway, according to the energy gap law.

3.2.5 Electrochemical Studies

Both compounds \textbf{I} and \textbf{II} in THF show a reversible (or quasi-reversible) oxidation wave in their cyclic voltamograms (see Appendix), which are shifted to higher potential relative to the benzoate compounds. The oxidation potential of the tungsten compound is significantly lower than that of the molybdenum which is consistent with the Mo\textsubscript{2}\textdelta orbital lying at lower energy than the W\textsubscript{2}\textdelta orbital as predicted by the calculations.

Compounds \textbf{I} and \textbf{II} also show reduction waves corresponding to placing an electron in the LUMO which is the in-phase ligand π* combination of the BMP ligands. The HOMO-LUMO gap can be estimated from the electrochemical data. This is compared with that calculated from the UV-vis spectra in Table 3.1.

<table>
<thead>
<tr>
<th>Compound</th>
<th>(E_{1/2}(OX)) (V)\textsuperscript{a}</th>
<th>(E_{1/2}(RED)) (V)\textsuperscript{a}</th>
<th>(E_{\text{gap}}) (V)\textsuperscript{a}</th>
<th>UV-Vis (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>\textbf{I}</td>
<td>0.58</td>
<td>-1.86</td>
<td>2.44</td>
<td>2.35</td>
</tr>
<tr>
<td>\textbf{II}</td>
<td>-0.48</td>
<td>-2.24</td>
<td>1.76</td>
<td>1.63</td>
</tr>
</tbody>
</table>

\textsuperscript{a} E\textsubscript{1/2} values are referenced to the Cp\textsubscript{2}Fe\textsuperscript{2+/0} couple

Table 3.1. The HOMO-LUMO energy gap obtained from the electrochemical experiments and UV-vis spectra of compounds \textbf{I} and \textbf{II} are compared.
3.2.6 Time-resolved Spectroscopic Studies

The excited state of compounds I and II have been examined by femtosecond transient absorption spectroscopy (fsTA), which has allowed for the determination of singlet state lifetimes. For molybdenum the S₁ state was found to have a lifetime of 12 and 13 ps in THF and toluene, respectively. There is a feature at 615 nm in toluene and 650 nm in THF that corresponds to the stimulated emission. The position of these bands and the observed red shift in going from toluene to THF supports the solvent dependence previously described and is consistent with the steady-state emission data shown in the appendices. The position of the transient corresponding to the singlet excited state is solvent independent. The ground-state bleach persists at long times indicating the formation of a triplet state. The lifetime of this state was determined to be 66 μs by nanosecond transient absorption spectroscopy (nsTA). The fsTA spectra of I is shown in Figure 3.7 and the nsTA of I can be found in the appendices.
For compound II, transient features for both the singlet state and triplet state are observed. These features lie close to each other. The peak at 565 nm is attributable to the singlet excited state and has a lifetime of 12 ps. The isosbestic point at 435 nm indicates a transformation of the singlet state to the triplet state. The triplet state was found to have a lifetime of 75 ns. The significantly shorter lifetime of the T\(_1\) state for II compared with that of I is consistent with the assignment of \(^3\)MLCT. The fsTA spectra of II is shown in Figure 3.8 and the nsTA spectra are given in the appendices.
3.2.7 The Influence of Fluoride Ions

As previously noted, arylboron compounds have been extensively used in the detection of \( \text{F}^- \) (and \( \text{CN}^- \)) which has a high affinity for coordination to the 3-coordinate boron center due to the vacant p orbital. In the present case, a THF solution of the molybdenum compound \( \text{I} \) was titrated with a THF solution of [Bu₄N][F⁻]. As shown in Figure 3.9, the intense MLCT absorption at 521 nm is completely quenched as the B \( 2p_\pi \) acceptor unit is saturated to become the \( -\text{Ph-B(mes)}_2\text{F}^- \) anion. The weak absorption at 400 nm corresponds to the new \( \text{Mo}_2\delta \) to \( -\text{O}_2\text{C-Ph}^- \) transition.

Figure 3.8. fsTA spectra of \( \text{II} \) in THF at RT with \( \lambda_{\text{ex}} = 800 \) nm.
Upon the addition of water, the F\textsuperscript{-} anion becomes solvated and the MLCT band at 521 nm is restored. This process is shown in Figure 3.10. The full intensity of the transition is not restored due to dilution of the solution by the additions.
Figure 3.10. The absorption spectrum of I in THF where the MLCT at 521 nm is first quenched by the addition of fluoride and then regenerated by the addition of water.

The influence of fluoride on the MLCT of the tungsten compound II is similar to that of I and is shown in Figure 3.11.
The compound decomposes upon the addition of water and could not be regenerated. Instead, the compound appears to decompose in water over time.

3.3 Conclusions

The new compounds I and II show intense MLCT bands in the visible region which are notably red-shifted with respect to the parent compounds, \textit{trans-}M_{2}(T\textsuperscript{3}PB)_{2}(Bz)_{2} due to the incorporation of the B 2p\textsubscript{π} acceptor orbital to the \pi system of the benzoate ligand. The influence of the vacant p orbital is also seen in the calculations of the model
compounds which substantially lowers the energy of the ligand π* orbital combinations. The introduction of fluoride ions through titration allows for coordination to the −B(mes)$_2$ moiety which effectively switches the influence off and causes a quenching of the original MLCT band. For compound I this process can be reversed by the addition of water to restore the band by solvating the F$^-$ ions. Compound II cannot be restored in the same fashion as it decomposes upon contact with water.
CHAPTER 4 : A COMPUTATIONAL STUDY ON THE INFLUENCE OF DIARYLBORON SUBSTITUENTS AND EXTENDING CONJUGATION ON THE METAL-TO-LIGAND CHARGE TRANSFER BAND OF DIMOLYBDENUM AND DITUNGSTEN PADDLEWHEEL COMPOUNDS

4.1 Introduction

Previous work on the influence of incorporating diarylboron substituents into dimetal paddlewheel compounds, as discussed in the previous chapter, focused on modulating a single phenyl ring. The addition of the boron moiety has a profound effect on the photophysical properties of the compound, shifting the metal-to-ligand charge transfer (MLCT) band ~ 4600 cm\(^{-1}\) to lower energy.\(^9\) There remains an interest in further tuning this band through the extension of \(\pi\) conjugation in the ligands by adding additional aromatic rings. In the case of biphenyl, the rings adapt an equilibrium geometry in which they are twisted almost 45° with respect to each other. This results in diminished overlap and hinders the degree of electronic communication between the rings. Another aromatic ring, thiophene, more readily lends itself to extended conjugation through multiple rings. The torsion angle for a bithiophene molecule is < 20°, which is significantly less than the biphenyl case (Figure 4.1).
Thiophene oligomers have gained considerable attention in the field of optoelectronics because of their potential use as hole transport materials. This particular property led to a study of thiophene, bithiophene, and terthiophene carboxylate ligands attached to Mo₂ quadruple bonds. This chapter seeks to extend the investigation to ditungsten compounds and also incorporate diarylboron substituents into these ligands. Further modulation can be achieved through the coordination of fluorine atoms to the boron sites. Additionally, alkynyl groups are used to extend the conjugation in the phenyl based ligands in order to install IR reporter groups and create candidates for excited-state charge distribution studies using time-resolved infrared.

4.2 Results and Discussion

4.2.1 Molecular Structure

All model compounds investigated in this work are of the trans-bis-bis type. Typically, bulky ligands such as T'PB are used to facilitate the trans geometry which is the thermodynamically favored structure due to extensive Lπ-M₂δ-Lπ conjugation. A crystal structure of Mo₂(T'PB)₂(O₂C-2Th)₂ is shown in Figure 4.2.
Figure 4.2. Crystal structure of trans-Mo$_2$(T'PB)$_2$(2Th)$_2$. A disordered solvent molecule of THF, and thiophene disorder is omitted for clarity.\textsuperscript{88}

In this case, the T'PB ligands are twisted \( \sim 80^\circ \) with respect to the carboxylate plane resulting in a substantial loss of conjugation with the metal center. The \textit{trans}-2Th ligands on the other hand are nearly planar with respect to their corresponding carboxylate plane allowing for conjugation with the metal center. This structure is similar to a multitude of
other compounds of the type \( \text{trans-M}_2(\text{TIPB})_2\text{L}_2 \) and thus the model compounds used in this computational study will follow the same general geometry.

4.2.2 Abbreviations

Due to the large number of model compounds discussed in this chapter, an abbreviation system will be used. All ligands containing a diarylboron substituent will begin with a “B”. Those ligands also having a coordinated fluoride ion will terminate in “F”. The most common convention for representing bithiophene and terthiophene is to abbreviate thiophene as “Th” and place either a “B” or “T” in front to designate the number of rings. In order to simplify this further and keep from confusing between “boron” or “bi” a slightly different system will be used. Instead, “1”, “2”, or “3” will be used to designate the number of thiophene rings. For example, if the ligand contains boron and has two thiophene rings it will be designated as “B2Th”. Additionally, “CC” is used to designate a triple bond, and “Ph” to designate a phenyl ring. A table of the ligand structures and their abbreviations used in this chapter are shown in Table 4.1 below.
<table>
<thead>
<tr>
<th>Structure</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Structure 1" /></td>
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</tr>
<tr>
<td><img src="image2.png" alt="Structure 2" /></td>
<td>B1Th</td>
</tr>
<tr>
<td><img src="image3.png" alt="Structure 3" /></td>
<td>B1ThF</td>
</tr>
<tr>
<td><img src="image4.png" alt="Structure 4" /></td>
<td>2Th</td>
</tr>
<tr>
<td><img src="image5.png" alt="Structure 5" /></td>
<td>B2Th</td>
</tr>
</tbody>
</table>

(Continued on next page)

Table 4.1. The ChemDraw structures and corresponding abbreviations for the ligands discussed in Chapter 4.
### Table 4.1 (continued)

<table>
<thead>
<tr>
<th>Chemical Structure</th>
<th>Identification</th>
</tr>
</thead>
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<td>B2ThF</td>
</tr>
<tr>
<td><img src="image" alt="3Th" /></td>
<td>3Th</td>
</tr>
<tr>
<td><img src="image" alt="B3Th" /></td>
<td>B3Th</td>
</tr>
<tr>
<td><img src="image" alt="B3ThF" /></td>
<td>B3ThF</td>
</tr>
</tbody>
</table>

(Continued on next page)
(Table 4.1 continued)

<table>
<thead>
<tr>
<th>Structure</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Structure 1" /></td>
<td>BPhCC</td>
</tr>
<tr>
<td><img src="image2.png" alt="Structure 2" /></td>
<td>BPhCCPh</td>
</tr>
</tbody>
</table>

A select few representations of Mo₂ model compounds along with their abbreviations are given in Table 4.2.
<table>
<thead>
<tr>
<th>Structure</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Structure 1" /></td>
<td>MoBPhCC</td>
</tr>
<tr>
<td><img src="image2.png" alt="Structure 2" /></td>
<td>MoBPhCCPh</td>
</tr>
<tr>
<td><img src="image3.png" alt="Structure 3" /></td>
<td>MoB2Th</td>
</tr>
</tbody>
</table>

Table 4.2. The GaussView 5.0.8 structures and corresponding abbreviations for select model compounds of Mo₂.

### 4.2.3 Computational Methods

All calculations were performed using Gaussian09 with Becke’s three parameter hybrid exchange and Lee-Yang-Parr correlation functionals (B3LYP).\(^{79,82,83}\) The 6-31G* basis set was used for H, C, O, B, F, and S. The Stuttgart/Dresden (SDD) energy-consistent pseudopotentials for Mo and W were also used.\(^{80}\) The structures were optimized in C₁.
symmetry and the force constants were calculated to ensure each stationary point was a minimum. A frequency analysis was done to obtain vibrational data and confirm that each structure was a minimum. Time-dependent DFT calculations using the same basis set and level of theory were then performed to obtain simulated UV-vis spectra using a standard GaussView $\sigma$ value of 0.4 eV. For more details on the line broadening function see the work by Stephens and Harada. A correction value of 0.96 was applied to the calculated vibrational frequencies.

In order to save on computational time and resources, a few simplifications were made. First, the bulky T'iPB ligands were substituted with formate groups. This is a reasonable approximation since the T'iPB moiety is twisted to nearly 90° out of conjugation in most trans-$M_2(T'iPB)_2L_2$ cases. Second, the bulky mesityl groups bound to the boron atom were substituted with hydrogen atoms with similar reasoning. The quality of this approximation was investigated by performing calculations on both MoB1Th where the hydrogen atoms were used in place of mesityls, and on MoBMes1Th where mesityls were used. A GaussView representation of MoBMes1Thmes is shown in Figure 4.3.
Figure 4.3. GaussView 5.0.8 representation of MoBMes1Th. Hydrogens omitted for clarity.

The simulated UV-vis spectra of MoB1Th and MoBMes1Th are compared in Figure 4.4.
As can be seen in Figure 4.4 the $\lambda_{\text{max}}$ of the low energy band, which is assignable to the $^1\text{MLCT}$ transition, differs by only a few nanometers. There is a band for MoBMes1Th at $\sim 380$ nm which is assignable to mesityl $\rightarrow$ benzoate transitions. Since the primary feature of importance in this study is the $^1\text{MLCT}$ transition, it would appear that using hydrogen atoms in place of mesityl groups is a good approximation.

4.2.4 Electronic Structure of Thiophene Derivatives

A frontier molecular orbital energy level diagram comparing model compound Mo1Th and MoB1Th are shown in Figure 4.5.
The HOMO in both cases is the Mo$_2$δ orbital with an admixture from the ligands and for Mo1Th the LUMO is the Mo$_2$δ* orbital. The in- and out-of-phase ligand π* combinations lie at higher energy and are assignable to the LUMO+1 and LUMO+2 orbitals. The introduction of the –BH$_2$ group to the thiophene ring has two effects: the first is the Mo$_2$δ orbital is stabilized by 0.4 eV and the second is the Lπ* orbitals are stabilized to an even greater extent causing them to substantially drop in energy by over 1 eV. The net result is the HOMO-LUMO gap is reduced from 3.14 eV to 2.61 eV, which in MoB1Th corresponds to a fully allowed metal-to-ligand charge transfer transition. This transition is thus expected to be red-shifted for MoB1Th relative to Mo1Th. These
results are consistent with the previously studied trans-Mo2(TPB)2(BMP)2 compound discussed in Chapter 3.

The frontier molecular orbital energy level diagrams of the W2 analogues are compared in Figure 4.6.

![Frontier molecular orbital energy level diagram](image)

**Figure 4.6.** Frontier molecular orbital energy level diagram of W1Th (left) and WB1Th (right) along with Gaussview 5.0.8 plots (isovalue = 0.02).

In the case of tungsten, the metal based orbitals are raised in energy by ~ 0.5 eV relative to molybdenum, which results in the W2δ* orbital being shifted above the Lπ* combinations in W1Th. The HOMO is the W2δ orbital with some ligand mixing for both W1Th and WB1Th. Addition of the –BH2 group results again in the stabilization of the W2δ orbital and Lπ* combinations. The greater stabilization of the Lπ* combinations
relative to the W₂δ orbital results in the reduction of the HOMO-LUMO gap from 2.72 eV to 2.14 eV. The ¹MLCT transitions in these two compounds are thus anticipated to be red-shifted relative to their molybdenum counterparts, with WB₁Th having the lowest energy ¹MLCT transition of the four compounds.

A frontier molecular orbital diagram comparing Mo₁Th, Mo₂Th, and Mo₃Th is shown in Figure 4.7, and is consistent with previously results.⁸⁸

Figure 4.7. Frontier molecular orbital energy level diagram comparing Mo₁Th, Mo₂Th, and Mo₃Th.
A similar diagram comparing MoB1Th, MoB2Th, and MoB3Th is shown in Figure 4.8 to allow for comparison. Diagrams for the W$_2$ analogues can be found in the appendix.

Figure 4.8. Frontier molecular orbital energy level diagram comparing MoB1Th, MoB2Th, and MoB3Th.
For all compounds, each additional thiophene ring has a diminished influence. In other words, a greater stabilization is seen with the first additional thiophene ring and that effect tails off as more rings are added. The effect of the \(-\text{BH}_2\) is also reduced accordingly, and the \(L\pi^*\) orbitals are stabilized less as the number of rings increases. The \(M_2\delta\) orbital is also destabilized due to more mixing with the ligands. Seemingly, the \(L\pi^*\) orbitals end up lying close to \(-2.75\) eV in all cases, regardless of position of the \(L\pi^*\) orbitals in the parent compounds. The difference in the HOMO-LUMO gap is thus primarily determined by the extent of destabilization of the \(M_2\delta\) orbital which leads to MoB3Th having the smallest HOMO-LUMO gap of 2.35 eV. A similar trend is seen with the \(W_2\) series, though each thiophene ring addition seems to have an even lesser effect with the exception of \(W1\text{Th}\) to \(W2\text{Th}\). The difference between \(W\text{B2Th}\) and \(W\text{B3Th}\) is only 0.04 eV indicating a smaller amount of ligand mixing and that two thiophene rings may be the limit for modulating the HOMO-LUMO transition in this case. The \(W\text{B3Th}\) compound has the smallest HOMO-LUMO gap of just 1.93 eV.

4.2.5 Fluoride Considerations of Thiophene Derivatives

Due to the Lewis acidity of the boron atom and potential application in sensing, it is of interest to study the effect of coordinating a fluoride ion to the boron center. The addition of a fluoride ion in all cases causes the entire system to shift to higher energy. In particular the \(L\pi^*\) orbitals are significantly destabilized, thus raising the energy of the \(^1\text{MLCT}\) transition. The fluoride ion effectively introduces a negative charge to the trans ligands making them more difficult to reduce. As the number of thiophene rings increases, the negative charge can be dispersed over a larger area, and the \(L\pi^*\) orbitals
are considerably stabilized. The energies of the frontier molecular orbitals and HOMO-LUMO gaps for these compounds, as well as all of the previously discussed compounds can be found in the appendix.

4.2.6 Electronic Structure of Benzoate Derivatives

Calculations on compounds with the BPhCC and BPhCCPh ligands were performed in order to investigate the electronic structure of analogues of the previously discussed BMP ligand (BMP = 'O₂C-phenyl-B(mes)₂) that have IR reporter groups. A frontier molecular orbital diagram comparing MoBMP, MoBPhCC, and MoBPhCCPh is shown in Figure 4.9.
Both new compounds are expected to have lower energy $^1$MLCT transitions than the MoBMP compound. The BPhCC ligand seems to have the same effect on the Mo$_2$δ orbital as the BMP ligand, but stabilizes the Lπ* orbitals to a greater extent resulting in a HOMO-LUMO gap decrease of about 0.2 eV. Interestingly, the energy of the $^1$MLCT transition for MoBPhCCPh falls between those of MoBMP and MoBPhCCPh. The –BH$_2$
unit has a greater influence on the Lπ* system of these compounds than it does on the Mo2δ orbital. When the additional ring is added, this influence is diminished but proportionally affects the LUMO more. The result is a slightly wider HOMO-LUMO gap. Similar results were seen with the W2 analogues, and the frontier molecular orbital diagram is given in the appendix.

Frequency calculations on the ground-state and anion geometries of these compounds were also performed in order to acquire a predicted shift in the vibrational frequency of the IR reporter group. These values are shown in Table 4.3.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Calculation Type</th>
<th>v(C≡C) / cm⁻¹ Uncorrected</th>
<th>v(C≡C) / cm⁻¹ Corrected</th>
<th>Shift / cm⁻¹</th>
</tr>
</thead>
<tbody>
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<td>2220</td>
<td>107</td>
</tr>
<tr>
<td>MoBPhCCPh</td>
<td>Anion</td>
<td>2201</td>
<td>2113</td>
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<td></td>
<td>Anion</td>
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<td>WBPhCCPh</td>
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<td></td>
<td>Ground-state</td>
<td>2303</td>
<td>2211</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Anion</td>
<td>2231</td>
<td>2142</td>
<td>69</td>
</tr>
</tbody>
</table>

Table 4.3. Calculated v(C≡C) vibrational frequencies for the ground-state and anion geometries of MoBPhCC, MoBPhCCPh, WBPhCC, and WBPhCCPh.

All compounds have an isolated v(C≡C) vibrational frequency which shifts 70-110 cm⁻¹ to lower energy in moving from the ground-state to anion calculation. The extent of electronic delocalization upon photoexcitation of the 1MLCT band can now be determined by comparing these values to those obtained using time-resolved infrared. The DFT calculations reflect a predicted delocalized scenario. If the experimental shift is
considerably more red-shifted, a localized case would be indicated. If the shift matches that predicted by the calculations, a delocalized case is identified.

4.3 Conclusions

All model compounds in this computational study are expected to exhibit broad $^1$MLCT transitions in the visible region. The –BH$_2$ unit is a good approximation for the -B(mesityl)$_2$ unit for studying these types of compounds. The introduction of the boron 2p$_\pi$ orbital notably extends the conjugation of the ligands resulting in a significant red-shift in the $^1$MLCT band compared to the parent compounds. Further modulation of the $^1$MLCT band can be accomplished by changing the metal center, extending the ligand conjugation by adding more aryl rings, or the addition of fluoride ions. The extent in which the band can be tuned by adding additional rings, however, is limited. In all cases there is a decrease in the HOMO-LUMO gap as number of rings is increased, but the effect can be as small as 0.04 eV as was the case with compound WB3Th. The addition of alkynyl groups have two primary benefits: 1) they themselves extend conjugation to further tune the $^1$MLCT band and 2) they are IR reporter groups which permit these compounds to be studied by time-resolved infrared spectroscopy.
CHAPTER 5: ELECTRONIC AND SPECTROSCOPIC PROPERTIES OF AVOBENZONE DERIVATIVES ATTACHED TO Mo$_2$ QUADRUPLE BONDS:
SUPPRESSION OF THE PHOTOCHEMICAL ENOL TO KETO TRANSFORMATION

(Adapted from a 2015 paper published in the Journal of the American Chemical Society)

5.1 Introduction

UVA radiation (315-400 nm) and UVB radiation (280-315 nm) exposure pose a risk to human health. The Earth’s ozone layer is capable of absorbing a large part of UVB radiation. The goal of most sunscreens then is to absorb UV radiation that is not blocked by ozone layer. Avobenzone is a UVA filter commonly employed in sunscreens that has been extensively studied due to its unique ground state enol-keto tautomerization.$^{95,96}$ The enol form predominates in this equilibrium, but it can be shifted in favor of the keto form by exciting the molecule with UV light.$^{97-100}$ This photoinduced conformation change is of interest due to its potential as a photoswitch, as well as the effect it has on the excited state dynamics. Additionally, this tautomerization is relevant to the use of avobenzone in sunscreen. Avobenzone has been shown to decompose into potentially toxic byproducts via a complicated light activated process.$^{101}$ A summary of this process is shown in Scheme 5.1.
Scheme 5.1. A summary of the processes occurring with the avobenzone molecule upon photoexcitation.

The understanding of this process is essential for determining a way to prevent the decomposition from occurring. One possible method for this is through incorporation of the molecule onto transition metal centers. With the inclusion of a carboxylic acid moiety, avobenzone derivatives can be attached to transition metal complexes without changing the molecular structure. This allows for the study of the analogues in a new electronic environment. It is of interest to note that photoisomerization of organic molecules, and changes in the excited state dynamics upon coordination to metal carbonyl complexes, has been investigated using ultrafast time-resolved infrared (TRIR). These studies focused primarily on the sensitization of isomerization by means of the metal complexes, whereas this study introduces an avenue to deactivation. Mo$_2$
centers are an ideal platform to investigate a series of derivatives due to facile coordination by way of a carboxylate linker.

As previously discussed, the influence of 3-coordinate arylboron moieties on the photophysical properties of dimetal paddlewheel complexes were investigated. In this work, the effect of coordinating a $\text{BF}_2$ unit to the $\beta$-diketone functionality of the avobenzone derivative to form a 4-coordinate arylboron species was studied. The resultant ligand was inspired by the sharp and intense spectral features of the BODIPY fluorophore. The primary difference is that the coordination involves oxygen atoms as opposed to nitrogen atoms in the BODIPY unit.

![BODIPY and Avobenzone](image)

Figure 5.1. Structures of BODIPY (left) and avobenzone (right).

The effect of both the enol-keto tautomerization and the incorporation of a $\text{BF}_2$ unit into a Mo$_2$ paddlewheel system is hereafter reported.
5.2 Results and Discussion

5.2.1 Synthesis

The series of carboxylic acids used in the preparation of the new Mo₂ compounds are shown in Table 5.1 along with their formal names and abbreviations used in this chapter.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Abbreviation</th>
<th>Formal Name</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Structure" /></td>
<td>HBzald</td>
<td>4-formylbenzoic acid</td>
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<td><img src="image2" alt="Structure" /></td>
<td>HAvo</td>
<td>4-(3-oxo-3-phenylpropanoyl)benzoic acid</td>
</tr>
<tr>
<td><img src="image3" alt="Structure" /></td>
<td>HAvoBF₂</td>
<td>4-(2,2-difluoro-6-phenyl-2H-1,3,2,3,2-dioxaborinin-4-yl)benzoic acid</td>
</tr>
</tbody>
</table>

Table 5.1. Structure, formal name, and abbreviations of avobenzone carboxylic acid derivatives.

Only the HBzald was commercially available and so the syntheses of the other two ligands are shown in Scheme 5.2.
The molybdenum compounds were made from the reactions between Mo$_2$(T$^i$PB)$_4$ and two equivalents of the appropriate carboxylic acid in toluene. The new compounds were isolated by removing the toluene under a dynamic vacuum and washing the resultant powders first with a trace amount of toluene to remove any potentially unreacted Mo$_2$(T$^i$PB)$_4$ and then with methanol and hexanes to remove the liberated HT$^i$PB. Compound II was additionally washed with ether. The new compounds I (L = Bzald), II (L = Avo), and III (L = AvoBF$_2$) are also sparingly soluble in toluene but not significantly soluble in methanol or hexane. All three compounds are appreciably soluble in THF which has been commonly used in their spectroscopic characterization. The compounds are air and moisture sensitive. As such, they have been handled under inert atmosphere (N$_2$ or Ar) along with rigorously dried and deoxygenated solvents.
All three new compounds gave molecular ions by MALDI-TOF mass spectrometry and were further characterized with $^1$H NMR. Additional details pertaining to synthesis and characterization can be found in Appendix C and Chapter 2.

5.2.2 Single Crystal X-Ray Structure of I

An ORTEP drawing of the molecular structure of I can be seen in Figure 5.1 and a table of selected crystallographic data can be found in Appendix C.

![Molecular structure of I](image)

Figure 5.2. Molecular structure of I drawn at 50% probability, where blue = molybdenum, scarlet = oxygen, and gray = carbon. Hydrogens, solvent, and disorder are omitted for clarity.
The phenyl ring of the T'PB moiety has a torsion angle of 81.4° with respect to the –CO₂ unit, removing it from conjugation with the metal center. The benzaldehyde ligand on the other hand is nearly coplanar having only a 5.5° torsion angle with respect to the –CO₂ unit. A full description of the structural solution and refinement of I can be found in the appendix. No molecular structure determination was carried out for compounds II or III, however, it is anticipated that they too conform to the trans-Mo₂(T'PB)₂L₂ geometry as previously seen in numerous compounds. In all cases the T'PB ligands are twisted close to 90° from the –CO₂ plane, while the –L ligands lie in the plane with their respective –CO₂ units thus facilitating the extended Lπ-Mo₂δ-Lπ conjugation.

5.2.3 Electronic Structure Calculations

Density functional theory (DFT) and time-dependent density functional theory (TDDFT) were used in order to assist in the interpretation of spectroscopic data. The same simplification was made as before where the bulky T'PB ligands were replaced with formate groups since the T'PB ligands are twisted out of conjugation with the metal. The model compounds with Bzald, Avo, and AvoBF₂ ligands are designated as I’, II’, and III’ respectively. Since the Avo ligand can exist in two forms, enol or keto, calculations were performed for both. The major form present in solution (>97%) is the enol form, which will be further discussed below.

It is anticipated that the keto form of II’ will be most similar to I’ since the methylene unit separating the two ketonic groups in II’ removes the potential for extended conjugation. In other words, both have an isolated ketone in their structures as opposed to the enol form which contains a hydrogen bridge between the two ketonic groups. A
comparison of the frontier molecular orbitals of I’ and II’ (keto) can be found in Figure 5.3.

![Diagram of frontier molecular orbitals](image)

Figure 5.3. Frontier molecular orbital energy level diagram of model compound I’ (left) and the keto form of II’ (right) along with Gaussview 5.0.8 plots of the keto form of II’ (isovalue = 0.02).

The HOMO for both compounds is the Mo₂δ orbital with some small admixture from the ligands. The LUMO and LUMO+1 are the in-phase and out-of-phase π* trans-ligands combinations. The ordering of the orbitals and their relative energies for both I’ and II’ (keto) are similar because π conjugation does not extend past the β-keto group in II’ (keto) making it effectively a benzaldehyde moiety. The HOMO-LUMO gap is also
similar for both complexes and the time-dependent DFT calculations predict that the lowest energy electronic transition involves the metal-to-ligand charge transfer between these two orbitals. The Mo$_2\delta^*$ orbital is the LUMO+2 and although this is an allowed electronic transition, its oscillator strength is small. It will likely not be visible since it can be masked by the more intense $^1$MLCT transition that is in close proximity.

Planarity is forced in compound II' (enol) by the bridging hydrogen and in III' by coordination of the –BF$_2$ unit. Thus it is appropriate to compare the frontier molecular orbital diagrams which are shown in Figure 5.4.

Figure 5.4. Frontier molecular orbital energy level diagram of the enol form of model compound II' (left) and III' (right) along with Gaussview 5.0.8 plots of III' (isovalue = 0.02).
In each case the conjugation is extended much further through the ligands. The HOMO in both compounds is primarily the Mo$_2$δ orbital and the LUMO and LUMO+1 are the in- and out-of-phase ligand π* orbital combinations. The incorporation of the –BF$_2$ unit in III\textsuperscript{'} greatly stabilizes the Lπ* combinations resulting in a decrease of the HOMO-LUMO gap by approximately 0.4 eV. The time-dependent DFT calculations predict this will be the lowest energy transition making it $^1$MLCT in character. The Mo$_2$δ* orbital lies at higher energy than the Lπ* combinations (LUMO+2) by ~ 0.70 eV. The Mo$_2$δ to Mo$_2$δ* transition is expected to be masked once again by the more intense $^1$MLCT transition.

It is interesting to note that the predicted difference between the HOMO-LUMO gap of II\textsuperscript{' (keto)} and that of II\textsuperscript{' (enol)} is only 0.15 eV. The time-dependent DFT calculations show that the energy of the $^1$MLCT transitions will differ by only 15 nm. The primary difference between the two forms lies in the position of the ligand based ππ* transitions. For II\textsuperscript{' (enol)}, the ππ* transition occurs at 350 nm and for II\textsuperscript{' (keto)} this band is shifted close to 290 nm. This difference has also been seen in avobenzone derivatives not bound to a metal center and will be a distinguishing feature in the assignment of the form.\cite{99} A comparison of the frontier molecular orbital diagrams for II\textsuperscript{' (enol)} and II\textsuperscript{' (keto)} are shown in the appendix.

Frequency analysis calculations pertaining to the predicted infrared active bands will be discussed below with the time-resolved infrared studies.
5.2.4 $^1$H NMR Studies

The $^1$H NMR spectra were collected in THF-d$_8$ and are given in the appendix. The major point of emphasis is that compound II appears to exist solely in the enol form (> 97%) as evidenced by the proton resonance at 17.2 ppm (hydroxyl) and 7.3 ppm (CH). There is no signal in the region where the shift for the keto protons is expected, 4.7-5.0 ppm. Furthermore, the integration of the shift for the CH proton at 7.3 ppm is in accordance with the integration values for the aromatic protons. This supports the conclusion that the equilibrium state lies almost entirely in favor of the enol form.

The free HAvo ligand was also investigated using $^1$H NMR in THF-d$_8$. In this case, a peak at 4.75 ppm evidenced an approximate 3% of the keto form. Coordination of this ligand to a Mo$_2$ center thus shifts the equilibrium further in favor of the enol form.

5.2.5 UV-vis Spectroscopy

Photostability of compound II and the free ligand, HAvo, was studied using UV-vis spectroscopy by photoexciting the molecules with 365 nm light for a period of 25 h. Results are shown in Figure 5.5.
In each case the samples were prepared to have the same intensity of absorption at 350 nm, and placed in UV-vis cuvettes sealed with Kontes tops using degassed THF at room temperature. Throughout the experiment with HAvo, the band at 350 nm (typical of the enol form) decreases as a new band at 245 nm forms. The new band remains after 24 h without UV irradiation (see Appendix C). In similar studies, the evolution of the band at 245 nm can be indicative of keto formation or decomposition products. The keto form
will convert back to the enol form when left in the dark, however, which suggests that we observe photodecomposition of the HAvo ligand.

When compound II was irradiated, the absorbance decrease was significantly reduced and occurred at a much slower rate than the free HAvo ligand. There is a slight blue-shift in the $^1$MLCT band that is observed as well. The decrease in absorbance appears to happen both under irradiation and when left in the dark. This suggests decomposition of the Mo$_2$ quadruple bond, which is known to occur to a small extent through slow oxygen leaking of the cuvette over time.

The photolysis experiment was repeated using a higher energy excitation of 254 nm over a 4 h time period (see appendix). For HAvo, the decrease in absorbance occurred more rapidly and did not recover after 16.5 h in the dark. No band at 245 nm formed either, which may be indicative of further decomposition under the higher energy conditions. Compound II was again found to be more robust than the free HAvo ligand, exhibiting only a minor decrease in absorbance during the 4 h time period. The blue-shift of the $^1$MLCT band occurs to a greater extent, with the $\lambda_{\text{max}}$ shifting from 540 nm to 517 nm. When left in the dark for 16.5 h, the same minor decrease in absorbance as before is observed, however, the $\lambda_{\text{max}}$ of the $^1$MLCT band red-shifts by $\sim$ 5 nm. The blue-shift is thus assigned to the light activated tautomerization from the enol to the keto form of the Avo ligands on the Mo$_2$ center, and the red-shift is the thermal recovery of the enol form. The extent of tautomerization under 254 nm illumination is small, and occurs to an even lesser extent, or perhaps not at all, with 365 nm illumination. Under all conditions of the photolysis experiments, compound II was found to undergo significantly less
decomposition than the free HAvO ligand. Since the goal of sunscreen is to absorb the UVA wavelengths of light, the results pertaining to the lower energy excitation of 365 nm are of greatest relevance.

The UV-vis spectra of I and II in THF at room temperature along with their steady-state emission spectra are shown in Figure 5.6.

![UV-vis spectra](image)

Figure 5.6. Electronic absorption and emission spectra ($\lambda_{ex} = 520$ nm) of compounds I and II in THF at room temperature.

Both compounds have a similar energy $^1$MLCT absorption, however, the prominent absorption at 350 nm in II which corresponds to the enol form contrasts markedly with that of I. In comparing the absorption and emission spectra, it can be seen that compound II exhibits a $\sim$1100 cm$^{-1}$ larger Stokes shift than compound I (4400 cm$^{-1}$ vs. 5500 cm$^{-1}$).
for I and II, respectively). This implies greater structural rearrangement in the excited state of compound II with respect to I.

The absorption spectra for III at room temperature and 108 K are shown in Figure 5.7.

![Figure 5.7. Electronic absorption spectra of compound III in THF at 298 K (green) and 108 K (black).](image)

Compound III in THF has a broad electronic transition centered at 650 nm, which is notably red-shifted relative to compound II. As expected, this band sharpens and shifts to lower energy when the sample is cooled. The ligand based ππ* transition is more intense and also red-shifted. There is weak fluorescence at ~ 850 nm, though this regrettably falls between the ranges of our visible and near infrared detectors.

All three compounds exhibit phosphorescence in the near-IR at ~1060 nm, which is characteristic of emission from the $^3\text{Mo}_2\delta\delta^*$ state (see appendix).
5.2.6 Transient Absorption Spectroscopy

Compounds I, II, and III were studied by fs and ns transient absorption spectroscopy, and the results of these experiments are displayed in Table 5.2.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$S_1$ lifetime (ps)</th>
<th>$S_1$ Assignment</th>
<th>$T_1$ Lifetime (μs)</th>
<th>$T_1$ Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>5</td>
<td>$^1$MLCT</td>
<td>64</td>
<td>$^3\delta\delta^*$</td>
</tr>
<tr>
<td>II</td>
<td>13</td>
<td>$^1$MLCT</td>
<td>63</td>
<td>$^3\delta\delta^*$</td>
</tr>
<tr>
<td>III</td>
<td>15</td>
<td>$^1$MLCT</td>
<td>7</td>
<td>$^3\delta\delta^*$</td>
</tr>
</tbody>
</table>

Table 5.2. Summary of the lifetimes and state assignments for compounds I, II, and III.

The fs TA spectra for I, $\lambda_{ex} = 568$ nm, are shown in Figure 5.8.
Figure 5.8. fsTA spectra of I in THF at RT, $\lambda_{ex} = 568$ nm, with kinetic trace taken at 490 nm shown in the inset.

The transient at 380 nm decays within 5 ps, corresponding to the $S_1$ lifetime of the compound. The ground-state bleach at 520 nm persists at long times as the $T_1$, $^3\text{Mo}_2\delta\delta^*$ state is formed, which, based on the nsTA data, has a lifetime of 64 μs. The nsTA data for all three compounds along with kinetic traces is given in the appendix.

Compound II was investigated with excitation into the $^1\text{MLCT}$ band and into the higher energy, ligand based $\pi\pi^*$ band. The resulting spectra are qualitatively the same. Those obtained with $\lambda_{ex} = 350$ nm are shown in the appendix and those with $\lambda_{ex} = 568$ nm are shown in Figure 5.9.
Figure 5.9. fsTA spectra of II in THF at RT, $\lambda_{\text{ex}} = 568$ nm, with kinetic trace taken at 540 nm shown in the inset.

At early times there is a transient at 520 nm which shifts slightly to higher energy as time progresses and the ground-state bleach decays. There is a second, higher energy transient at 380 nm which only partly decays leaving a residual absorption at 370 nm at long times. The lifetime of the $S_1$, $^1$MLCT state is determined to be 13 ps and that of the $T_1$, $^3$Mo$_2\delta\delta^*$ state is 63 μs from fsTA and nsTA, respectively.

The fsTA spectra for III are shown in Figure 5.10.
Figure 5.10. fsTA spectra of III in THF at RT, \( \lambda_{ex} = 650 \) nm, with kinetic trace taken at 500 nm shown in the inset.

The most notable feature is the transient at 475 nm which is two orders of magnitude more intense than the spectra of compounds I and II, supporting the idea that a \(-BF_2\) unit could be used to enhance the excited state properties of these compounds. Two ground-state bleaches can also be seen at \(~375\) nm and at the lower energy edge of the spectra corresponding to the \( ^1\pi\pi^* \) and \(^1\)MLCT states, respectively. The lifetime of the \(^1\)MLCT state is 15 ps and that of the \(^3\)Mo2\(\delta\delta^*\) state is 7 \(\mu\)s.
5.2.7 Time-Resolved Infrared Spectroscopy

Computational methods were used to aid in the assignment of the features associated with the fsTRIR data. In particular, frequency analysis calculations on the anions $\text{I}^-$, $\text{II}^-$ (enol), $\text{II}^-$ (keto) and $\text{III}^-$ were used for the assignment of the singlet features. This approximation works to simulate an additional electron residing on the carboxylate ligands after photoexcitation. The fsTRIR spectra for compound $\text{I}$, $\lambda_{\text{ex}} = 568$ nm, are shown in Figure 5.11 for the region 1750-1450 cm$^{-1}$. The ground state spectrum is depicted by the black dotted line.

\[
\begin{align*}
\Delta \text{OD} & \quad 0.0000 \quad 0.0005 \quad 0.0010 \quad 0.0015 \quad 0.0020 \\
\text{Wavelength / cm}^{-1} & \quad 1750 \quad 1700 \quad 1650 \quad 1600 \quad 1550 \quad 1500
\end{align*}
\]

Figure 5.11. fsTRIR spectra of $\text{I}$ in THF at RT, $\lambda_{\text{ex}} = 568$ nm, with kinetic trace taken at 1588 cm$^{-1}$ shown in the inset.
Upon excitation we observe the bleach of \( \nu(C=O) \) at 1705 cm\(^{-1} \) corresponding to the depletion of the \( \nu(C=O) \), and the appearance of two transient bands at 1690 and 1655 cm\(^{-1} \) which may be assigned to \( \nu(C=C)_{\text{ring}} \) stretches in the photoexcited state. The frequency analysis of I* shows the highest energy stretch in the region 1750-1450 cm\(^{-1} \) is associated with \( \nu(C=O) \). At lower energy we also see the bleach of \( \nu_{\text{as}}(CO_2) \) at 1505 cm\(^{-1} \) and the appearance of a band at \( \sim 1495 \) cm\(^{-1} \) assignable to \( \nu_{\text{as}}(CO_2) \). These features are fairly typical of \(^1\)MLCT states in metal carboxylates. The decay of these bands occurs within \( \sim 5 \) ps, consistent with fsTA measurements, to give rise to transient bands assignable to the \(^3\)Mo\( _2\delta\delta^* \) state. Of particular note is the appearance of the 1540 cm\(^{-1} \) band which is assignable to \( \nu_{\text{as}}(CO_2) \) and arises from an electron being removed from the Mo\( _2\delta \) orbital involved with backbonding to the ligand causing the stretch to shift to higher energy. There is also a band at \( \sim 1580 \) cm\(^{-1} \), most likely a C-C vibration of the ring, that represents some electron density still residing on the ligand at times >2 ns.

The fsTRIR spectra for compound II, \( \lambda_{\text{ex}} = 568 \), are shown in Figure 5.12 in the region 1750-1350 cm\(^{-1} \).
Again the ground state absorptions are depicted by the dotted black line. At high energy, the most notable feature in the transient IR spectrum is the absence of a band at ~1710 cm\(^{-1}\). Ground state frequency analysis calculations indicate that the highest energy vibration in this region is one involving the hydrogen-bonded C=O moiety and the C-C of the ring for the enol form of \(\text{II}\). Related calculations on the anions, \(\text{II}^-\text{(enol)}\) and \(\text{II}^-\text{(keto)}\), show that only the enol form lacks a stretching mode in this region while the keto form exhibits a strong vibration at ~1700 cm\(^{-1}\) associated with \(\nu(C=O)\). The early transient IR bands at ~1620 and 1580 cm\(^{-1}\) are most likely due to C-O and C-C coupled modes and the band at 1490 cm\(^{-1}\) is assignable to \(\nu_{as}(CO_2)\). Bleaches at 1385 cm\(^{-1}\) and 1520 cm\(^{-1}\) are also observed and are due to the ground state depletion of \(\nu_{s}(CO_2)\) and
$\nu_{as}(CO_2)$, respectively. At longer time in the $T_1$ state we again see the bleaches of these CO$_2$ stretches and the appearance of $\nu_{as}(CO_2)$ at ~1540 cm$^{-1}$ indicative of the $^3$Mo$_2\delta\delta^*$ state.$^{15}$ Additionally, the long lived bands around 1400 cm$^{-1}$ are likely due to $\nu_{as}(CO_2)$ stretches.

The fsTRIR spectra for compound III are shown in Figure 5.13.

Figure 5.13. fsTRIR spectra of III in THF at RT, $\lambda_{ex} = 650$ nm, with kinetic trace taken at 1582 cm$^{-1}$ shown in the inset.

In comparison to I and II the vibrational modes of III are notably more intense in the $^1$MLCT state. The absorptions at 1620 and 1580 cm$^{-1}$ are similar to those seen for compound II and may similarly be assigned to C-O and C-C ring stretches. The strong bleach at 1544 cm$^{-1}$ is associated with the C-O and C-C stretches in the ring containing the -BF$_2$. This intense ground state absorption at 1544 cm$^{-1}$ is not present in either I or II.
The vibrations in the region of 1400 cm\(^{-1}\) are most likely symmetric C-C ring vibrations based on predictions of the calculated vibrational modes for III\(^*\). It appears that the introduction of the -BF\(_2\) unit enforces the planarity and greatly enhances the intensity of the ring vibrational modes at the expense of the carboxylate stretching vibrations. For example, in the T\(_1\) state the anticipated \(\nu_{as}(\text{CO}_2)\) intensity at \(\sim 1540\) cm\(^{-1}\) is significantly smaller relative to the ring vibration intensities. The presence of this band at long times still implies formation of the \(^3\)Mo\(_2\)δδ\(^*\) state.

5.3 Conclusions

As shown in the fsTRIR data, compound I has a transient feature associated with the \(\nu(\text{C}=\text{O})\) while this stretch is absent in compound II. This demonstrates that when \(\lambda_{ex} = 568\) nm, II is in the enol form in the excited state and no evidence of the keto form is present. The \(^1\)H NMR data similarly shows that the ground-state equilibrium of compound II is > 97% enol form. The photolysis experiments indicate an enol to keto tautomerization after 4 h of 254 nm irradiation, though this occurs to a substantially lesser extent with 365 nm irradiation. In all photolysis experiments, compound II was found to be more robust than the free HAvo ligand against degradation caused by UV light.

Previous studies aimed at the deactivation of the avobenzone tautomerization involved investigation of substituent effects, and this method has been unsuccessful in eliminating the isomerization and decomposition of the molecule when exposed to UVA light. In this work, it has been shown that the introduction of a metal which has a lower energy \(^1\)MLCT state with respect to the ligand centered \(^1\)ππ\(^*\) state will result in rapid internal
conversion to the \(^1\)MLCT state after excitation to the \(^1\)\(\pi\pi^*\) state. The lower energy \(^1\)MLCT state then converts to the \(^3\)Mo\(_2\)\(\delta\delta^*\) state within 60 ps. This is in contrast with the avobenzone molecule which has an excited state lifetime of \(~ 500\) ns which leads to both the isomerization and decomposition.\(^{103}\) While compound II is air sensitive and thus could not be incorporated into sunscreens, we propose that attaching avobenzone to a metal with a lower \(^1\)MLCT state could prevent decomposition by providing an alternative decay pathway.

All compounds in this study have \(S_1\) lifetimes of 5-20 ps and \(T_1\) lifetimes of 7-64 \(\mu\)s. Compound III is unique in that it exhibits excited state absorptions, in both the fsTA and fsTRIR spectra, \(~ 100\) fold more intense than typical due to the enforced planarity of the ligand by the \(–BF_2\) unit.
6.1 Introduction

In the previous chapter, the photoisomerization of the molecule, avobenzone, was discussed. This process is again summarized in Scheme 6.1 for convenience.

Scheme 6.1. A summary of the processes occurring with the avobenzone molecule upon photoexcitation.
The primary objective focused on the deactivation of the tautomerization pathway through the attachment of avobenzone carboxylate derivatives to a Mo$_2$ quadruple bond as well as coordination of a –BF$_2$ unit. The avobenzone derivatives, formal names, and abbreviations are shown in Table 6.1.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Abbreviation</th>
<th>Formal Name</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Structure 1" /></td>
<td>HBzald</td>
<td>4-formylbenzoic acid</td>
</tr>
<tr>
<td><img src="image2.png" alt="Structure 2" /></td>
<td>HAvO</td>
<td>4-(3-oxo-3-phenylpropanoyl)benzoic acid</td>
</tr>
<tr>
<td><img src="image3.png" alt="Structure 3" /></td>
<td>HAvoBF$_2$</td>
<td>4-(2,2-difluoro-6-phenyl-2H-1,3,2-dioxaborinin-4-yl)benzoic acid</td>
</tr>
</tbody>
</table>

Table 6.1. Structure, formal name, and abbreviations of avobenzone carboxylic acid derivatives.
This chapter is a continuation of that work, where the same derivatives are attached to a \( W_2 \) quadruple bond to synthesize compounds of the form \( \text{trans-} W_2(T'PB)_2L_2 \). A key difference, however, is that while these compounds also have low energy \( ^1\text{MLCT} \) states, the triplet states are uniquely \( ^3\text{MLCT} \) in character as opposed to \( ^3{}M_2\delta\delta^* \), as was seen with the Mo\(_2\) compounds. Since both the \( S_1 \) and \( T_1 \) states extend over the ligand, the properties of charge distribution can be compared as the excited states evolve with time using time-resolved infrared spectroscopy.

### 6.2 Results and Discussion

**6.2.1 Syntheses**

The new compounds, \( \text{I, II, and III} \) were synthesized according to the reaction given in the equation below.

\[
\text{eq 1. } \quad W_2(T'PB)_4 + 2\text{LH} \xrightarrow{\text{toluene, RT, 3 days}} \text{trans-} W_2(T'PB)_2L_2 + 2T'PBH
\]

The products formed as powders within 3 days. The volume of the solution was reduced with a dynamic vacuum which gave a greater yield of solid. The solution was then filtered to collect the solid, which was washed with methanol and toluene to remove unreacted starting materials, and hexanes to remove \( T'PBH \). Compounds \( \text{I and II} \) are deep blue and compound \( \text{III} \) is green. All three compounds are soluble in THF, though to a lesser extent than the Mo\(_2\) analogues.

The compounds were characterized by \( ^1\text{H} \) NMR which are shown in the appendix. The ground-state IR spectra were recorded and are noted as traces in the time-resolved
infrared spectra. The high resolution MALDI-TOF-MS spectra gave discrete molecular ions. The data for III⁺ is shown in Figure 6.1 and that for I⁺ and II⁺ are shown in the appendix.

Figure 6.1. The III⁺ ion from the MALDI-TOF-MS, showing the fragmentation products (III-F)⁺ at 1473.49 and (III-BF₂)+H⁺ at 1444.52.

The result for III⁺ is interesting in that the spectrum is notably weaker and in addition to the molecular ion peak, III⁺, two loss products are also seen. The first is attributable to the formation of (III-F)⁺ and the second is (III-BF₂)+H⁺. These peaks arise from the fragmentation of the oxygen-boron bonds and proton absorption by the matrix. It should be noted that there is no evidence for these fragmentation products by ¹H NMR prior to analysis by MALDI-TOF MS, which indicates they are formed during the experiment.
6.2.2 Electronic Structure Calculations

Density functional theory, DFT, and time-dependent density functional theory calculations, TDDFT, were performed on model compounds I’, II’, and III’ in order to better interpret the spectral data. The same simplifications were used for these compounds as before, replacing the T’PB ligands with formate groups. Calculations on the anions [I’]−, [II’]−, and [III’]−, where the negative charge extends across the ligands as [L-W₂-L]−, were used to simulate the ¹MLCT excited state and assist in the assignment of the vibronic features obtained by time-resolved infrared spectra. These will be discussed more below when the ultrafast data are presented.

The frontier molecular orbital energy level diagram comparing compounds I’ and II’ (enol) is shown in Figure 6.2.
Figure 6.2. Frontier molecular orbital energy level diagram of model compound I’ (right) and the enol form of II’ (left) along with Gaussview 5.0.8 plots of the enol form of II’ (isovalue = 0.02).

For compound I’, the W₂δ orbital at 0.5 eV is the HOMO, and the LUMO and LUMO+1 are the in- and out-of-phase ligand π* combinations with a separation of 0.3 eV. The LUMO orbital consists of only ligand character, while the LUMO+1 is an admixture of out-of-phase ligand combination and the W₂δ orbital in an antibonding fashion. The W₂π orbitals lie at lower energy than the HOMO.
For compound II’, the W₂δ orbital is again the HOMO, and the LUMO and LUMO+1 are in- and out-of-phase ligand π* combinations which also have a separation of ~ 0.3 eV. In this case there is an additional set of essentially identical ligand π* orbital combinations associated with the outermost ring of the ligand at higher energy (LUMO+2 and LUMO+3). The W₂π orbitals lie below the HOMO and further down in energy are a pair of ligand-based orbitals having oxygen lone pairs character.

The LUMO+2 for compound I’ and the LUMO+4 for compound II’ corresponds to the W₂δ* orbital. Additionally, the fully allowed HOMO → LUMO transition in each case is a metal-to-ligand charge transfer (MLCT) transition with an associated energy of approximately 2.3 eV and 2.4 eV for I’ and II’, respectively.

A frontier molecular orbital energy level diagram for compound III’ compared to II’ (enol) is shown in Figure 6.3.
Figure 6.3. Frontier molecular orbital energy level diagram of the enol form of model compound II' (left) and III' (right) along with Gaussview 5.0.8 plots of III' (isovalue = 0.02).

Here, the HOMO is the $W_2\delta$ orbital and the LUMO and LUMO+1 are the L$\pi^*$ combinations, separated by 0.2 eV, which is slightly less than in compounds I' and II'. The smaller separation occurs due to a greater amount of mixing between the $W_2\delta$ orbital and the extended $\pi$ system of the ligands. There is also an additional set of L$\pi^*$ orbitals at higher energy, the LUMO+3 and LUMO+4 orbitals. In compound III' the introduction of the -BF$_2$ unit causes all of the L$\pi^*$ orbitals to be considerably stabilized. This also results in a reordering of the molecular orbitals when compared with II'; in
compound II', the W₂δ* orbital was the LUMO+3, but in compound III' it is the LUMO+4.

There are two low energy transitions involving the HOMO → LUMO and the HOMO → LUMO+2, based on the time-dependent DFT calculations. The HOMO → LUMO and the HOMO → LUMO+2 transitions are predicted to occur at 714 nm (predicted oscillator strength, f ~ 1.1) and 434 nm (f ~ 0.3), respectively. There is a predicted band at higher energy, 353 nm (f ~ 1.0), which is a combination of the HOMO → LUMO+2, and HOMO-3 → LUMO+1 and HOMO-4 → LUMO (n → π*) transitions. Thus the lowest energy transition for this compound is the HOMO → LUMO transition at 714 nm which is 1MLCT in character.

6.2.3 Electronic Absorption and Steady-State Emission Studies

Compounds I and II are intensely colored blue, and compound III is a pale green color in THF. The UV-vis spectra are shown in Figure 6.4.
Compounds I and II have similar absorption bands at 748 nm and 796 nm, respectively, which correspond to the HOMO → LUMO, $^1$MLCT transition. This $^1$MLCT transition for compound III is centered at 1017 nm, which is notably red-shifted relative to those for compounds I and II. The time-dependent DFT calculations predicted a HOMO-LUMO gap of 1.98 eV (628 nm), though this method typically overestimates the energy of this band due to spin orbit coupling and partly because they are gas phase calculations. The $W_2\delta \rightarrow CO_2\pi^*$ of the TPB ligands occurs at 400 nm, and is most easily identified in the trace for compound I. This band in compounds II and III is obscured by both a ligand centered $\pi\pi^*$ transition and a higher energy $^1$MLCT transition ($W_2\delta$ to higher energy $L\pi^*$ combination).
The low temperature absorption and emission spectra of these compounds was also recorded. The spectra for compound I is shown in Figure 6.5.

Figure 6.5. Electronic absorption (at RT and 108 K) and emission spectra ($\lambda_{ex} = 658$ nm, at RT and 77 K) of compound I in 2-methyltetrahydrofuran.

A vibronic feature associated with the $^1$MLCT band can be seen at low temperature. The absorption band red-shifts, and the emission band blue-shifts toward the 0-0 transition. At room temperature, the emission band is further red-shifted relative to the low temperature spectrum due to variable temperature rotations of the CO$_2$-aryl plane which favors a more planar position as the temperature is lowered. Again, the band at 400 nm corresponds to the $\text{W}_2\delta \rightarrow \text{CO}_2\pi^*$ transition. The band at 532 nm also becomes more
prevalent at low temperature and is most likely associated with the $W_2\delta \rightarrow W_2\delta^*$ transition.

The spectra for compounds II and III are similar to those of compound I with respect to temperature effect and are shown in the appendix. Compound III is notable in that the $^1$MLCT band red-shifts, to even lower energy, from 1017 nm to 1110 nm upon cooling. Additionally, it exhibits weak fluorescence at 1290 nm.

### 6.2.4 Transient Absorption Studies

All three compounds were examined by nanosecond and femtosecond transient absorption spectroscopy in order to obtain lifetimes. The spectra for compound I, $\lambda_{ex} = 700$ nm, are shown in Figure 6.6.

![fsTA spectra of I in THF at RT, $\lambda_{ex} = 700$ nm with kinetic trace taken at 590 nm shown in the inset.](image)

Figure 6.6. fsTA spectra of I in THF at RT, $\lambda_{ex} = 700$ nm with kinetic trace taken at 590 nm shown in the inset.
Two ground-state bleaches are present: the feature at 400 nm corresponds to the bleach of the $W_2\delta$ to $T'\Pi PB CO_2\pi^*$ absorption and the feature at 700 nm is the bleach of the $W_2\delta$ to $L\pi^*$ absorption. These are somewhat initially obscured by transient absorptions at 400 nm and 600 nm. As these transient features decay, the bleaches grow in to give the spectrum of the longer lived triplet state. The decay of these features occurs in 15 ps, which is the lifetime associated with the $^1$MLCT state. Additionally, a fairly intense absorption band at 475 nm appears, which increases in intensity as time evolves ultimately leading to the triplet state absorption band at 485 nm. The triplet lifetime is between 3-10 ns, as determined by nsTA, which is typical of a $^3$MLCT state for these $W_2$ tetracarboxylate complexes.$^{30}$

The spectra for compound II with, excitation at 700 nm, are shown in Figure 6.7.
Figure 6.7. fsTA spectra of II in THF at RT, $\lambda_{ex} = 700$ nm with kinetic trace taken at 500 nm shown in the inset.

Here there is a bleach at 350 nm due to the ground-state $\pi\pi^*$ transition, and a transient absorption at 490 nm associated with the $^1$MLCT state. This band decays with time to give a persistent triplet state feature at 470 nm. The lifetime of the decay is 34 ps, which represents the longest lifetime of a $^1$MLCT state in these M$_2$ quadruply bonded complexes. The length of this lifetime presumably arises because of poor mixing of the $S_1$ and $T_n$ states, which are not close in energy. The triplet lifetime again falls between 3-10 ns.

The spectra for compound III, $\lambda_{ex} = 350$ nm, are shown in Figure 6.8.
At early times, there is a ground-state bleach of the ligand centered $^1\pi\pi^*$ band at 350 nm, and an intense absorption at 425 nm. This absorption quickly undergoes internal conversion from the $^1\pi\pi^*$ state to the $^1$MLCT state ($\sim 0.1$ ps). The $^1$MLCT absorption decays rapidly to give a triplet state absorption at 440 nm. The lifetime of the $^1$MLCT state is notably shorter, $\sim 3$ ps, which is approximately one tenth of that seen for compound II. Also, at lower energy and longer times, there is a slight rise of a weak transient absorption centered at 540 nm.
6.2.5 Time-resolved Infrared Studies

The \(^1\)MLCT and \(^3\)MLCT nature of these complexes is uniquely suited to study the progression of the electronic distribution as one state converts to the other by use of time-resolved infrared spectroscopy. The computational methods described earlier for the ground state, anion, and triplet state frequency analysis have been used to aid in the assignment of the vibrational modes. It is assumed here that the anion calculation represents the case of the \(^1\)MLCT state where the complex has been reduced and the charge is delocalized over both ligands. The energy of the bands associated with the anion, however, are anticipated to be somewhat shifted since the calculation neglects the presence of a positive charge on the W\(_2\) center. A correction factor of 0.96 has been applied to all calculated values discussed in this section (B3LYP, 6-31g*). These methods are best employed in identifying principal vibrations, which in addition to the previously published Mo\(_2\) series lead us to the described assignments.\(^{104}\)

Compound I in the region 1800-1350 cm\(^{-1}\) was investigated, with \(\lambda_{ex} = 700\) nm, shown in Figure 6.9. The ground state spectrum is depicted by the black dotted line.
Figure 6.9. fsTRIR spectra of I in THF at RT, $\lambda_{ex} = 700$ nm with kinetic trace taken at 1526 cm$^{-1}$ shown in the inset.

There are bleaches at 1700 cm$^{-1}$, 1590 cm$^{-1}$, and 1570 cm$^{-1}$ which are due to the ground state stretches, $\nu$(C=O), $\nu_{as}$(C=C$_{ring}$), and $\nu_{as}$(CO$_2$), respectively. Upon excitation a ligand based $\delta^*$ orbital is populated which in general reduces the bond strength and effectively weakens the stretching frequencies associated with the partially reduced ligands. The frequency analysis of I$^\circ$ predicts a coupling between the aldehyde and ring stretches leading to multiple mixed modes in both the singlet and triplet states. For the singlet state, $^1$MLCT, the transient band at 1680 cm$^{-1}$ therefore is assigned to a $\nu$(C=C$_{ring}$-C=O) mode that has a substantial amount of aldehyde character. The band at 1640 cm$^{-1}$ corresponds to a more isolated $\nu$(C=C$_{ring}$-C=O) stretch. At lower energy, 1550 cm$^{-1}$, we
see the appearance of another, yet lower in energy $\nu(C=\text{ring}-C=O)$ for the $S_1$ state and the band at 1490 cm$^{-1}$ is assigned as the $\nu_{\text{as}}(\text{CO}_2)$ for the TiPB carboxylates. Additionally, the bands around 1420 cm$^{-1}$ are assignable to symmetric $\nu(C=\text{ring})$ modes. The decay of the early bands occurs within 20 ps, which is consistent with the fsTA kinetics data. At longer times the bands associated with the triplet, $^3\text{MLCT}$ state can be seen. There are bands at 1605 cm$^{-1}$, 1580 cm$^{-1}$, and 1415 cm$^{-1}$ which correspond to $\nu(C=\text{ring})$ modes. The vibration at 1490 cm$^{-1}$ is likely the $\nu(\text{CO}_2)$ mode of the TiPB ligands. The presence of these long lived ligand based stretches supports the assignment of a $^3\text{MLCT}$ state. Notably, there is no intense peak which corresponds to the $\nu(C=O)$. This implies that at long times there is little electron density which resides on the aldehyde unit. These vibrational modes are noted in Appendix D with comparisons for the neutral compounds, the anions, and the triplet states.

Compound II recorded in THF, with $\lambda_{\text{ex}} = 700$ nm, is shown in Figure 6.10. Again, the ground state spectrum is shown with the black dotted trace.
Figure 6.10. fsTRIR spectra of II in THF at RT, $\lambda_{ex} = 700$ nm with kinetic trace taken at 1640 cm$^{-1}$ shown in the inset.

Here there is no bleach of the $\nu$(C=O) at ~1720 cm$^{-1}$. The lack of a strong bleach with the presence of broad bands on top suggests that the excited state of this molecule is in the enol form. A strong and sharp bleach with a related sharp positive feature are expected around this wavelength for the keto form of the ligand. There are no such features which is in agreement with the previously reported Mo$_2$ compound where there was also no keto form present (in either the ground or excited states). A comparison of the TRIR spectra of the free ligand HAvO and II with $\lambda_{ex} = 325$ nm in the region of 1760-1660 cm$^{-1}$ can be found in the appendix. Additionally, there is a bleach at 1600 cm$^{-1}$ which can be assigned to the $\nu$(C=C$_{ring}$) of the enol form of the ligands. The excited state spectra in the region of
1580-1480 cm\(^{-1}\) could contain subsequent bleaches though the resolution makes them challenging to assign.

The excited state vibrational modes of II are most easily described as pertaining to the ring formed by three main areas of the ligand: vinyl and hydroxyl groups of the enol form, the outer aromatic ring C=C stretches, the inner aromatic ring C=C stretches. The outer ring refers to the phenyl group furthest from the Mo\(_2\) center while the inner refers to the ring which is closest. Some modes contain stretching combinations where all three are active. In general the stretches dominated by the vinyl moiety appear highest in energy followed by the outer ring, inner ring, and lastly the combinations. All modes have a significant amount of C-H wagging associated with them. The highest energy band in the \(^1\)MLCT state occurs at \(~1650\) cm\(^{-1}\) and is attributed to \(\nu(\text{vinyl/OH})\). At \(1590\) cm\(^{-1}\) is the \(\nu(\text{C=C}_{\text{ring}})\) of the outer aromatic ring and at \(~1580\) cm\(^{-1}\) is the \(\nu(\text{C=C}_{\text{ring}})\) of the inner ring. The various combinations then follow to lower energy. The vibrations at \(1435\) cm\(^{-1}\) and \(1405\) cm\(^{-1}\) relate to modes having some CO\(_2\)Avo character in combination with all of the rings. All of these \(^1\)MLCT bands decay within 30 ps, which is in good accordance with the fs TA data. There is also a broad transition at \(~1800\) cm\(^{-1}\) which may result from a LUMO to LUMO+1 electronic transition that is formally allowed by the LaPorte selection rule, \(u \rightarrow g\). The estimated energy of this transition is \(~2000\) cm\(^{-1}\) based off the TD-DFT calculations.

There are only two absorptions, at \(1490\) cm\(^{-1}\) and a broad band at \(1400\) cm\(^{-1}\), that remain at long times and are associated with the triplet state. These appear to be related to the \(\nu(\text{CO}_2)\) mode of the T\(^+\)PB ligand and the \(\nu(\text{vinyl-CO}_2\text{Avo})\) mode, respectively. The latter
band also shifts slightly to lower energy as conversion from the $^1$MLCT state to the $^3$MLCT state occurs implying more electron density on the CO$_2$AvO moiety. Additionally, the bands associated with the outer ring are absent in the triplet state. This suggests that the electron density is moving toward the vinyl and carboxylate of the AvO ligand and contracting toward the W$_2$ center in the triplet state. The principal vibrational modes for both the enol and keto forms of II are noted in Appendix D.

The spectra for compound III are shown in Figure 6.11.

![Figure 6.11. fsTRIR spectra of III in THF at RT, $\lambda_{ex}$ = 350 nm with kinetic trace taken at 1635 cm$^{-1}$ shown in the inset.](image)

Again, the vibrational modes can be described as being primarily outer ring, inner ring, middle ring (associated with the -BF$_2$ group), or a combination of the three. There are two intense bleaches at 1535 and 1485 cm$^{-1}$ assignable to the $\nu$(C=C$_{ring}$) of the inner
aromatic ring and a $\nu(C=C_{\text{ring}})$ of all three rings combined. Interestingly, these initially grow in with time, $\approx 1$ ps, corresponding to the alignment of the two aryl ligands with time as they assume a planar position. A similar process is observed with the intense transient band at 1630 cm$^{-1}$ which grows in to 1650 cm$^{-1}$ and decays back to zero within two nanoseconds. This is likely a combination of $\nu(C=C_{\text{ring}})$ modes and again the growth of this peak and its movement to higher energy corresponds to the ligand planarization.

The absorption at 1570 cm$^{-1}$ is due to a $\nu(C=C)$ mode of the outer ring. Additionally between 1520 and 1490 cm$^{-1}$ we observe two more $\nu(C=C_{\text{ring}})$ bands followed by the THF solvent window at 1470 cm$^{-1}$. Finally at lower energy (1450-1400 cm$^{-1}$) there are several $\nu(C=C_{\text{ring}})$ modes associated with combinations of the rings with contributions of the $-\text{CO}_2$ groups of the AvoBF$_2$ ligands.

For the triplet state there is no band at $\approx 1650$ cm$^{-1}$, but rather two bands at 1605 and 1590 cm$^{-1}$. These appear to be the highest energy bands in this region and are associated with the $\nu(C=C_{\text{ring}})$ of the inner ring and the $\nu(C=C_{\text{ring}})$ of an inner/middle ring combination, respectively. At 1500 cm$^{-1}$ there is a band associated with the vinyl C-H mode, and at lower energy, 1430-1390 cm$^{-1}$, are further vibrations associated with the inner and middle rings having $-\text{CO}_2$ character. The band at 1430 cm$^{-1}$ that is most likely associated with the inner ring appears to shift slightly to lower energy, indicating an increase in electron density. The new distribution of charge in the triplet state appears to only affect the inner and middle rings. The stretching frequencies of the outer ring observed in the $^1\text{MLCT}$ state decay rapidly and in the $^3\text{MLCT}$ state there is no evidence of stretching frequencies associated with the outer ring. Indeed, in comparing the vibrations associated with the
1MLCT and 3MLCT states, a contraction of the charge density toward the central W₂ unit with time is once again observed. These principal modes are compared in Appendix D.

6.3 Conclusions

The quadruple bonded complexes show much lower energy electronic transitions relative to their Mo₂ analogues due to the higher energy of the W₂δ orbital. The addition of a -BF₂ unit to the Avo ligand caused the 1MLCT absorption band of compound III to shift well into the near infrared to 1017 nm. All three compounds show weak singlet emission in the NIR but no emission from the 3MLCT state, which has a lifetime between 3-10 ns. These states are much shorter than the 3W₂δδ* states that have lifetimes on the order of microseconds and exhibit phosphorescence at 800 nm. As expected, the time-resolved spectra show no evidence of an enol-keto transformation in II when excited into the 1MLCT or enol ππ* bands. The unique nature of these W₂ compounds allows for the direct observation of the 1MLCT to 3MLCT conversion by time-resolved infrared spectroscopy, since the decay of the 1MLCT state occurs at earlier times and electron density resides on the ligands throughout the rest of the experiment. The electron density on the ligands was found to contract as the molecule converts from the 1MLCT state to the 3MLCT state.
CHAPTER 7 : PERSPECTIVES AND FUTURE DIRECTIONS

Major strides have been made in the past ten years to better understand the photophysical properties of M$_2$ paddlewheel compounds with π conjugated ligands. The relatively long lifetime of the $^1$MLCT state makes them uniquely suitable for study by time-resolved spectroscopic techniques, which can be used to observe the excited state charge dynamics and monitor how the charge distribution evolves with time. These processes are directly tied to a wide range of applications in solar energy conversion and photocatalysis. A comprehensive understanding of the excited states, and precise tunability, is required to optimize device efficiencies. This thesis has expanded the understanding of these photophysical properties and broadened the application of M$_2$ compounds to sensors and ligand conformation control.

Chapter 3 showed that the incorporation of diarylboron substituents into the π systems of M$_2$ compounds could have a substantial impact on the orbital energies giving rise to major red-shifts in the $^1$MLCT absorption bands; functionalizing a simple benzoate ligand with 3-coordinate boron led to a 4600 cm$^{-1}$ red-shift in absorption. The fluorescence was also significantly enhanced such that stimulated emission could be observed in the fsTA spectra. The boron atom, caged by mesityl groups, additionally allows for the selective coordination of fluoride anions, which permits further tunability and establishes a switching mechanism for the $^1$MLCT absorption band. The diarylboron
functionality is therefore another tool in the precise modulation of the photophysical properties of these M$_2$ compounds.

The findings of Chapter 4 expanded on the incorporation of 3-coordinate boron substituents by investigating its influence as the $\pi$ conjugation of the ligand was extended. While increased conjugation does give rise to further tunability, a limit is reached in which the effect of the boron substituent is diminished and additional aryl rings result in only a minimal change. An alkynyl group is also able to extend the $\pi$ conjugation but has the added benefit of being an IR reporter group. The $\nu$(C≡C) vibrational mode is isolated from the other vibrations of the molecule, and so the shift that occurs as the molecule is photoexcited can be monitored by time-resolved infrared spectroscopy. The addition of the boron atom tends to drive the energy of the in-phase and out-of-phase L$\pi^*$ orbital combinations closer in energy. The degree of separation between these orbitals is often an indication of the extent of coupling. If the coupling is reduced, the communication between the two is decreased and the electron is more likely to localize on a single ligand. Future work thus involves investigating the extent of charge delocalization in these M$_2$ compounds having incorporated 3-coordinate boron substituents.

Chapter 5 began the studies involving ligand conformation control and the effect of 4-coordinate boron on the properties of these compounds. Derivatives of the avobenzone molecule, one of the most common UVA filters found in sunscreens, were attached to Mo$_2$ quadruple bonds. The first goal, of suppressing the tautomerization, was achieved through the introduction of a lower energy $^1$MLCT state relative to the ligand based $^1\pi\pi^*$
state. This allowed for rapid internal conversion from the $^1\pi\pi^*$ to the $^1$MLCT state which could then convert to the even lower energy $^3\text{Mo}_2\delta\delta^*$ state. The extent of molecular degradation was substantially reduced when attached to the Mo$_2$ center. Since Mo$_2$ compounds are air-sensitive, this primarily demonstrated that the same principle could be applied to sunscreens using a different metal with a lower energy $^1$MLCT state in order to reduce photodegradation of avobenzone. The addition of the –BF$_2$ unit to the β-diketone moiety also had a considerable effect on the photophysical properties. The absorption band was red-shifted more than $3100$ cm$^{-1}$ and there was a 100 fold increase in the intensity of the excited state absorption features.

The work in Chapter 5 was extended to W$_2$ quadruple bonds in Chapter 6. The introduction of the low energy $^1$MLCT state again led to the deactivation of the photoisomerization of the avobenzone derivative. The incorporation of the –BF$_2$ unit also caused the $^1$MLCT absorption band to red-shift from 798 nm to 1017 nm, well into the near infrared. This means that the $^1$MLCT bands for the compounds reported in this dissertation alone span the range of 400-1020 nm. The $^1$MLCT and $^3$MLCT states of the W$_2$ compounds reported in Chapter 6 allowed for the observation of the charge density by time-resolved infrared spectroscopy as the singlet state transformed to the triplet state, then decayed back to the ground-state. This showed that in all cases the electron density contracted toward the metal center as time progressed.

The 4-coordinate boron ligands in Chapters 5 and 6 were inspired by the BODIPY fluorophore, though they involve the coordination of the –BF$_2$ unit to the ligand through boron-oxygen bonds. The next step is to investigate a formal BODIPY based ligand with
the –BF$_2$ unit coordinated through boron-nitrogen bonds. Alkynyl groups could also be added in order to more readily probe the excited state electron distribution of M$_2$ compounds having 4-coordinate boron ligands.

The combinations of the interesting properties of M$_2$ paddlewheel compounds and those of boron create truly fascinating and versatile systems which have a broad range of potential applications. More precise modulation of the orbital energy levels in M$_2$ compounds is now possible through boron incorporation, which has further progressed efforts toward a comprehensive understanding of the excited state behavior of these compounds. The fundamental principles involved here may be the solution to many of the world’s major problems.
Figure A.1. The electronic absorption and steady-state emission spectra of I in toluene and THF.
Figure A.2. The phosphorescence spectra of I at RT and 77 K, $\lambda_{\text{ex}} = 405$ nm.

Figure A.3. Cyclic voltammogram of compounds I and II in THF.
Figure A.4. fsTA spectra of I in toluene at RT, $\lambda_{ex} = 568$ nm.

Figure A.5. Kinetic trace from fsTA spectra of I in THF taken at 390 nm (left) and kinetic trace from fsTA spectra of I in toluene taken at 419 nm (right).
Figure A.6. Kinetic trace from fsTA spectra of II in THF taken at 620 nm.

Figure A.7. nsTA spectra of I in THF at RT, $\lambda_{ex} = 532$ nm (left) with kinetic trace taken at 520 nm (right).

Figure A.8. Figure A.8. nsTA spectra of II in THF at RT, $\lambda_{ex} = 355$ nm (left) with kinetic trace taken at 520 nm (right).
Figure A.9. The color changes associated with Mo$_2$(T'PB)$_2$(BMP)$_2$ as fluoride is titrated into the solution. The top-left image is before any addition of fluoride, the top-middle image is when 1 equivalent of fluoride has been added, and the top-right image is for saturated fluoride. The bottom-left image is an “action shot” of water being added, and the bottom-right image is after the fluoride has been completely solubilized by the addition of water.
Figure A.10. The color changes associated with $\text{W}_2(\text{T'PB})_2(\text{BMP})_2$ as fluoride is titrated into the solution. The top-left image is before any addition of fluoride, and the bottom-right image is for saturated fluoride. The images in between show the remarkable variation of color throughout the titration.
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<thead>
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<th>Compound</th>
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</tr>
</thead>
<tbody>
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</tr>
<tr>
<td>Formula weight</td>
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</tr>
<tr>
<td>Temperature (K)</td>
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<tr>
<td>Space group</td>
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<td>10.2136(2)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>10.3526(2)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>12.6092(2)</td>
</tr>
<tr>
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<tr>
<td>β (°)</td>
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<tr>
<td>γ (°)</td>
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<td>V (Å³)</td>
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</tr>
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<td>Dcalc (Mg/m³)</td>
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</tr>
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<tr>
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<td>F(000)</td>
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</tr>
<tr>
<td>Reflections collected</td>
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<tr>
<td>Unique reflections</td>
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<tr>
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<tr>
<td>Data/restraints/parameters</td>
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<tr>
<td>R1a (%) (all data)</td>
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</tr>
<tr>
<td>wR2b(%) (all data)</td>
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</tr>
<tr>
<td>Goodness-of-fit on F²</td>
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</tr>
<tr>
<td>Largest diff. peak and hole (e Å⁻³)</td>
<td>0.647 and -1.192</td>
</tr>
</tbody>
</table>

\[ aR1 = \frac{\sum ||F_o|-|F_c||}{\sum |F_o|} \times 100 \]
\[ bwR2 = \left\{ \frac{\sum w(F_o^2-F_c^2)^2}{\sum w(F_o^2)} \right\}^{1/2} \times 100 \]
Figure B.1. Frontier molecular orbital energy level diagram comparing W1Th, W2Th, and W3Th.
Figure B.2. Frontier molecular orbital energy level diagram comparing WB1Th, WB2Th, and WB3Th.
Figure B.3. Frontier molecular orbital energy level diagram comparing WBMP, WBPhCC, and WBPhCCPh.
Table B.1. The energies of the frontier molecular orbitals for Mo\(_2\) compounds with thiophene based ligands.

<table>
<thead>
<tr>
<th></th>
<th>Mo1Th E (eV)</th>
<th>Mo2Th E (eV)</th>
<th>Mo3Th E (eV)</th>
</tr>
</thead>
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<td>LUMO+5</td>
<td>-0.74</td>
<td>-0.71</td>
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</tr>
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<td>LUMO+4</td>
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</tr>
<tr>
<td>LUMO+3</td>
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<td>-0.91</td>
<td>-1.15</td>
</tr>
<tr>
<td>LUMO+2</td>
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<td>-1.83</td>
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<td>-2.27</td>
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<td>-4.86</td>
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<tr>
<td>HOMO-1</td>
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<tr>
<td>HOMO-2</td>
<td>-6.82</td>
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<td>HOMO-3</td>
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<td>HOMO-5</td>
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\textbf{Gap} \quad 3.14 \quad 2.81 \quad 2.59

Table B.2. The energies of the frontier molecular orbitals for Mo\(_2\) compounds with thiophene based ligands functionalized with boron substituents.

<table>
<thead>
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<th>MoB1ThH E (eV)</th>
<th>MoB1ThPh E (eV)</th>
<th>MoB1Thmes E (eV)</th>
<th>MoB2Th E (eV)</th>
<th>MoB3Th E (eV)</th>
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<td>-1.41</td>
<td>-1.78</td>
</tr>
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<td>-1.56</td>
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</tr>
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<td>LUMO+2</td>
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\textbf{Gap} \quad 2.61 \quad 2.68 \quad 2.69 \quad 2.43 \quad 2.35
Table B.3. The energies of the frontier molecular orbitals for Mo\(_2\) compounds with thiophene based ligands functionalized with \(-\text{BH}_2\text{F}\).

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<thead>
<tr>
<th></th>
<th>MoB1ThF E (eV)</th>
<th>MoB2ThF E (eV)</th>
<th>MoB3ThF E (eV)</th>
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Table B.4. The energies of the frontier molecular orbitals for W\(_2\) compounds with thiophene based ligands.

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<tr>
<th></th>
<th>W1Th E (eV)</th>
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<td>LUMO+3</td>
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Table B.5. The energies of the frontier molecular orbitals for W$_2$ compounds with thiophene based ligands functionalized with –BH$_2$.

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Table B.6. The energies of the frontier molecular orbitals for W$_2$ compounds with thiophene based ligands functionalized with –BH$_2$F.
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<th>MoBCCPh E (eV)</th>
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Table B.7. The energies of the frontier molecular orbitals for Mo\textsubscript{2} compounds with phenyl based ligands.

Table B.8. The energies of the frontier molecular orbitals for W\textsubscript{2} compounds with phenyl based ligands.
APPENDIX C : SUPPORTING INFORMATION FOR CHAPTER 5

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</tr>
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</tr>
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</tr>
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<td>Space Group</td>
<td>Triclinic, P-1</td>
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<td>$c$ (Å)</td>
<td>15.5398(2)</td>
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<tr>
<td>$\alpha$ (°)</td>
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</tr>
<tr>
<td>$\beta$ (°)</td>
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</tr>
<tr>
<td>$\gamma$ (°)</td>
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</tr>
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<tr>
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</tr>
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<tr>
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</tr>
<tr>
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<td>Goodness-of-fit on F$^2$</td>
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</tr>
<tr>
<td>Largest diff. peak and hole (e Å$^{-3}$)</td>
<td>0.714 and -0.662</td>
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$^a$R1 = $\Sigma$ |$|F_o|-$ |$|F_c|$| / $\Sigma$ |$|F_o|$| x 100

$^b$wR2 = $\Sigma$ w ($F_o^2$-$F_c^2$)$^2$ / $\Sigma$ (w |$F_o|^2$)$^{1/2}$ x 100
Figure C.1. The $\text{I}^+$ ion from MALDI-TOF-MS.

Figure C.2. The $\text{II}^+$ ion from MALDI-TOF-MS.
Figure C.3. The $\text{III}^+$ ion from MALDI-TOF-MS.
Mo$_2$(AVB)$_2$(TPB)$_2$

$^1$H NMR, 400 MHz, d$_8$-THF

Figure C.4. $^1$H NMR spectrum of II in THF-d$_8$ at room temperature.
Figure C. 5. Frontier molecular orbital energy level diagram of the enol form of compound II’ (left) and the keto form of II’ (right) along with GaussView 5.0.8 plots of the enol form of II’ (isovalue = 0.02).
Figure C.6. UV-vis spectra of HAvo in THF following irradiation, $\lambda_{ex} = 365$ nm, taken in the dark over 24 h.

Figure C.7. UV-vis spectra of II in THF following irradiation, $\lambda_{ex} = 365$ nm, taken in the dark over 24 h.
Figure C.8. UV-vis spectra of HAvo in THF under irradiation, $\lambda_{ex} = 254$ nm, taken at different time intervals.

Figure C.9. UV-vis spectra of HAvo in THF following irradiation, $\lambda_{ex} = 254$ nm, taken in the dark over time.
Figure C.10. UV-vis spectra of II in THF under irradiation, $\lambda_{ex} = 254$ nm, taken at different time intervals.

Figure C.11. UV-vis spectra of II in THF following irradiation, $\lambda_{ex} = 254$ nm, taken in the dark over time.
Figure C. 12. Near-IR emission spectra of I (red, $\lambda_{ex} = 405$ nm), II (blue, $\lambda_{ex} = 405$ nm), and III (green, $\lambda_{ex} = 648$ nm) in 2-MeTHF at 77 K.

Figure C. 13. nsTA spectra of I in THF at RT, $\lambda_{ex} = 532$ nm (left) along with the kinetic trace taken at 520 nm (right).
Figure C.14. fsTA spectra of II in THF at RT, $\lambda_{ex} = 350$ nm, with kinetic trace taken at 600 nm shown in the inset.

Figure C.15. nsTA spectra of II in THF at RT, $\lambda_{ex} = 532$ (left) along with the kinetic trace taken at 510 nm (right).
Figure C.16. nsTA spectra of III in THF at RT, $\lambda_{ex} = 600$ nm (left) along with the kinetic trace taken at 600 nm (right).
Figure D.1. $^1H$ NMR spectrum of I taken in THF-d$_8$. 

$W_2(Bzald)_2(TiPB)_2$

$^1H$ NMR, 400 MHz, d$_8$-THF
Figure D.2. $^1$H NMR spectrum of II taken in THF-$d_8$.

Figure D.3. $^1$H NMR spectrum of III taken in THF-$d_8$. 
Figure D.4. The I$^+$ ion from MALDI-TOF-MS.

Figure D.5. The II$^+$ ion from MALDI-TOF-MS.
Figure D.6. Frontier molecular orbital energy level diagram of the enol form of model compound II’ (left) and the keto form of II’ (right) shown alongside Gaussview 5.0.8 plots of the enol form of II’ (isovalue = 0.02).
Figure D.7. Electronic absorption (at room temperature and 108 K) and emission spectra ($\lambda_{ex} = 658$ nm, at room temperature and 77 K) of compound II in 2-MeTHF.

Figure D.8. Electronic absorption (at room temperature and 108 K) and emission spectra ($\lambda_{ex} = 405$ nm, at room temperature and 77 K) of compound III in 2-MeTHF.
Figure D.9. fsTRIR spectra of HAvo in THF at RT, $\lambda_{ex} = 325$ nm.

Figure D.10. fsTRIR spectra of II in THF at RT, $\lambda_{ex} = 325$ nm.
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<td>1727.04</td>
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<td>2</td>
<td>1590.72</td>
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<td>3</td>
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Table D.1. Principal vibrational modes from frequency analysis calculations of the ground state (GS), anion, and triplet state of I’.

![GaussView representations of the vibrational modes of I’](image)

Table D.2. Selected GaussView representations of the vibrational modes of I’ from previous table.
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<table>
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<table>
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Table D.3. Principal vibrational modes from frequency analysis calculations of the ground state (GS), anion, and triplet state of II'(enol).

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Table D.4. Selected GaussView representations of the vibrational modes of II'(enol) from previous table.
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<th>GS</th>
<th>Frequency / cm(^{-1})</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1710.72</td>
<td>C=O</td>
</tr>
<tr>
<td>2</td>
<td>1696.32</td>
<td>C=O</td>
</tr>
<tr>
<td>3</td>
<td>1590.72</td>
<td>C=(\text{ring(inner)})</td>
</tr>
<tr>
<td>4</td>
<td>1488.96</td>
<td>CO(_2)(TPB)</td>
</tr>
<tr>
<td>5</td>
<td>1424.64</td>
<td>C=(\text{ring-CO}_2)(Avo)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Anion</th>
<th>Frequency / cm(^{-1})</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1706.88</td>
<td>C=O</td>
</tr>
<tr>
<td>2</td>
<td>1615.68</td>
<td>C=(\text{ring(inner)})-C=O</td>
</tr>
<tr>
<td>3</td>
<td>1549.44</td>
<td>C=(\text{ring(inner)})-C=O</td>
</tr>
<tr>
<td>4</td>
<td>1491.84</td>
<td>C=(\text{ring(inner)})-C=O</td>
</tr>
<tr>
<td>5</td>
<td>1421.76</td>
<td>C=(\text{ring-CO}_2)(Avo)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Triplet</th>
<th>Frequency / cm(^{-1})</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1712.64</td>
<td>C=O</td>
</tr>
<tr>
<td>2</td>
<td>1593.6</td>
<td>C=(\text{ring(outer)})</td>
</tr>
<tr>
<td>3</td>
<td>1560</td>
<td>C=(\text{ring(inner)})-CO(_2)</td>
</tr>
<tr>
<td>4</td>
<td>1536</td>
<td>CO(_2)(TPB)-C=(\text{ring})</td>
</tr>
<tr>
<td>5</td>
<td>1486.08</td>
<td>C=(\text{ring(inner)})-CO(_2)(Avo)</td>
</tr>
</tbody>
</table>

Table D.5. Principal vibrational modes from frequency analysis calculations of the ground state (GS), anion, and triplet state of II\(^{\prime}\)(keto).

<table>
<thead>
<tr>
<th>GS2</th>
<th>GS3</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="GS2.png" alt="Image" /></td>
<td><img src="GS3.png" alt="Image" /></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Anion2</th>
<th>Anion3</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="Anion2.png" alt="Image" /></td>
<td><img src="Anion3.png" alt="Image" /></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Triplet4</th>
<th>Triplet5</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="Triplet4.png" alt="Image" /></td>
<td><img src="Triplet5.png" alt="Image" /></td>
</tr>
</tbody>
</table>

Table D.6. Selected GaussView representations of the vibrational modes of II\(^{\prime}\)(keto) from previous table.
<table>
<thead>
<tr>
<th></th>
<th>Frequency / cm(^{-1})</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1592.64</td>
<td>C=C(_\text{ring}) (inner)</td>
</tr>
<tr>
<td>2</td>
<td>1579.2</td>
<td>C=C(_\text{ring}) (outer)-C=O</td>
</tr>
<tr>
<td>3</td>
<td>1526.4</td>
<td>C=C(_\text{ring}) (comb)</td>
</tr>
<tr>
<td>4</td>
<td>1512.96</td>
<td>C=C(_\text{ring}) (middle)</td>
</tr>
<tr>
<td>5</td>
<td>1487.04</td>
<td>CO(_2) (TPB)</td>
</tr>
<tr>
<td>6</td>
<td>1477.44</td>
<td>C=C(_\text{ring}) (comb)</td>
</tr>
<tr>
<td>Anion</td>
<td>Frequency / cm(^{-1})</td>
<td>Description</td>
</tr>
<tr>
<td>1</td>
<td>1589.76</td>
<td>C=C(_\text{ring}) (outer)</td>
</tr>
<tr>
<td>2</td>
<td>1583.04</td>
<td>C=C(_\text{ring}) (inner)</td>
</tr>
<tr>
<td>3</td>
<td>1569.6</td>
<td>C=C(_\text{ring}) (outer)</td>
</tr>
<tr>
<td>4</td>
<td>1522.56</td>
<td>C=C(_\text{ring}) (inner)-CO(_2) (AvoBF(_2))</td>
</tr>
<tr>
<td>5</td>
<td>1496.64</td>
<td>C=C(_\text{ring}) (comb)-CO(_2) (TPB)</td>
</tr>
<tr>
<td>6</td>
<td>1488.96</td>
<td>C=C(_\text{ring}) (comb)-CO(_2) (AvoBF(_2))</td>
</tr>
<tr>
<td>7</td>
<td>1475.52</td>
<td>C=C(_\text{ring}) (outer) CO(_2) (AvoBF(_2))</td>
</tr>
<tr>
<td>8</td>
<td>1431.36</td>
<td>C=C(_\text{ring}) (comb) CO(_2) (AvoBF(_2))</td>
</tr>
<tr>
<td>9</td>
<td>1412.16</td>
<td>C=C(_\text{ring}) (comb) CO(_2) (AvoBF(_2))</td>
</tr>
<tr>
<td>10</td>
<td>1377.6</td>
<td>C=C(_\text{ring}) (inner/middle)</td>
</tr>
<tr>
<td>Triplet</td>
<td>Frequency / cm(^{-1})</td>
<td>Description</td>
</tr>
<tr>
<td>1</td>
<td>1594.56</td>
<td>C=C(_\text{ring}) (comb)</td>
</tr>
<tr>
<td>2</td>
<td>1531.2</td>
<td>C=C(_\text{ring}) (middle)-CO(_2) (TPB)</td>
</tr>
<tr>
<td>3</td>
<td>1526.4</td>
<td>C=C(_\text{ring}) (inner/middle)</td>
</tr>
<tr>
<td>4</td>
<td>1509.12</td>
<td>C=C(_\text{ring}) (middle)</td>
</tr>
<tr>
<td>5</td>
<td>1478.4</td>
<td>C=C(_\text{ring}) (outer)</td>
</tr>
<tr>
<td>6</td>
<td>1455.36</td>
<td>C=C(_\text{ring}) (inner)-CO(_2) (AvoBF(_2))</td>
</tr>
<tr>
<td>7</td>
<td>1402.56</td>
<td>C=C(_\text{ring}) (middle)-CO(_2) (AvoBF(_2))</td>
</tr>
</tbody>
</table>

Table D.7. Principal vibrational modes from frequency analysis calculations of the ground state (GS), anion, and triplet state of III'.

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<table>
<thead>
<tr>
<th>GS3</th>
<th>GS4</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Diagram" /></td>
<td><img src="image2.png" alt="Diagram" /></td>
</tr>
<tr>
<td><img src="image3.png" alt="Diagram" /></td>
<td><img src="image4.png" alt="Diagram" /></td>
</tr>
<tr>
<td><img src="image5.png" alt="Diagram" /></td>
<td><img src="image6.png" alt="Diagram" /></td>
</tr>
<tr>
<td><img src="image7.png" alt="Diagram" /></td>
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</tr>
</tbody>
</table>

Table D.8. Selected GaussView representations of the vibrational modes of III' from previous table.
REFERENCES


