## SPIN AND ELECTRONIC CONTROL OF EXCITED-STATE REACTIVITY OF TRANSITION METAL-BASED CHROMOPHORES

By

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#### ABSTRACT

### SPIN AND ELECTRONIC CONTROL OF EXCITED-STATE REACTIVITY OF TRANSITION METAL-BASED CHROMOPHORES

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Spin manifests itself in a variety of ways in chemistry and physics through spectroscopy, magnetism, and chemical reactivity. Many of the common physical observables linked to spin are well documented such as UV-Vis selection rules and spin-orbit coupling. While the wellestablished field of spin chemistry has focused on how spin can affect a compound's ground-state reactivity, much less has been reported pertaining to the effects of spin effects on excited-state reactivity. To gain a fundamental understanding and to definitively establish the role of spin conservation in excited-state quenching this report will focus on characterizing the photophysical processes of dinuclear donor-acceptor systems with the form of [M(tren)(pyacac)Re(bpy')(CO)<sub>3</sub>]<sup>3+</sup> (where,  $M = Co^{III}$  or  $Cr^{III}$ . tren = tris(2-aminoethyl)amine, pyacac = 3-(4-pyridyl)-2,4pentanedione, and bpy' = 2,2'-bipyridine). The excited-state reactivity of three dinuclear CrRe compounds was characterized and quenching of the MLCT excited state by Förster energy transfer was observed via a spin-allowed S = 3/2 pathway. Three dinuclear CoRe compounds were characterized, where the low-spin Co(III) provides a way to change the spin of the system and observe the changes in excited-state quenching. Despite Förster transfer being thermodynamically favorable for the CoRe compounds, coupling to a S = 0 excited state shuts down this pathway due to spin not being conserved,  $\Delta S \neq 0$ . By using time-resolved and steady-state emission spectroscopy in conjunction with transient absorption, photo-induced electron transfer from the excited state in the CoRe compounds is observed. This demonstrates the first time spin was used to select and control the quenching mechanism of a system.

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# **KEY TO ABBREVIATIONS**

4-Etpy: 4-ethylpyridine
A: Ground-state acceptor
A*: Excited-state acceptor
acac: Acetylacetonate
AgOTf: Silver Trifluoromethanesulfonate
bpy: 2,2'-bipyridine
btfmb: 4,4'-bistrifluoromethyl-2,2'-bipyridine
CCD: Charge-coupled device
CCDC: Cambridge Crystallographic Data Centre
D: Ground-state donor
D*: Excited-state donor
DCBQ: 2,3-Dicyano-1,4-benzoquinone
DCM: Dichloromethane
DDQ: 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone
deeb: 4,4'-diethylester-2,2'-bipyridine
E <sub>00</sub> : Zero-point energy
[ES]: Excited state concentration
EtOH: Ethanol
Fc/Fc <sup>+</sup> : Ferrocene/ferrocenium couple
[GS]: Ground state concentration
H <sub>AB</sub> : Electronic coupling constant

*Istd*: Integrated emission of standard  $\bar{I}_{\lambda}^{D^*}$ : Normalized emission spectrum ILCT: Intraligand Charge Transfer *J*: Spectral overlap integral k<sub>B</sub>: Boltzmann constant k<sub>DET</sub>: Dexter rate constant K<sub>eq</sub>: Equilibrium constant k<sub>ET</sub>: Electron transfer rate constant k<sub>FRET</sub>: Förster rate constant kisc: Rate of intersystem crossing k<sub>nr</sub>: Rate of nonradiative decay k<sub>obs</sub>: Observed rate constant k<sub>q</sub>: Quenching rate constant k<sub>r</sub>: Rate of radiative decay KOH: Potassium hydroxide R: Donor-acceptor distance LMCT: Ligand-to-Metal Charge Transfer MeCN: Acetonitrile MeOH: Methanol MLCT: Metal-to-Ligand Charge Transfer *N<sub>A</sub>*: Avogadro's number OTf: Trifluoromethansulfonate o-TBBQ: 3,4,5,6-Tetrabromo-1,2-benzoquinone o-TCBQ: 3,4,5,6-Tetrachloro-1,2-benzoquinone

ppy: 2-phenylpyridine

p-TCBQ: 2,3,5,6-Tetrachloro-1,4-benzoquinone

pyacac: 3-(4-pyridyl)-2,4-pentanedione

[Q]: Quencher concentration

r: Donor-acceptor distance

r<sub>A</sub>: Acceptor transition dipole moment

r<sub>c</sub>: distance of closest approach

r<sub>D</sub>: Donor transition dipole moment

R<sub>DA</sub>: Donor-acceptor connection line

T: Temperature

TA: Transient Absorption

TBAPF<sub>6</sub>: Tetrabutylammonium hexafluorophosphate

THF: Tetrahydrofuran

tmb: 4,5,4',5'-tetramethyl-2,2'-bipyridine

tren: Tris(2-aminoethyl)amine

|S<sub>A</sub>|: Spin of ground-state acceptor

|S<sub>A\*</sub>|: Spin of excited-state acceptor

|S<sub>D</sub>|: Spin of ground-state donor

 $|S_{D^*}|$ : Spin of excited-state donor

|S<sup>P</sup>|: Spin of products

|S<sup>R</sup>|: Spin of reactants

Z: Nuclear charge

- β: Attenuation coefficient
- $\Delta G$ : Change in free energy
- $\Delta O.D.$ : Change in optical density
- $\Delta S$ : Change in spin
- $\varepsilon_A$ : Molar absorptivity
- $\eta$ : Refractive index
- $\Theta_{T}$ : Angle of transition dipole
- $\Theta_D$ : Angle between donor-acceptor and donor transition dipole
- $\Theta_A$ : Angle between donor-acceptor and acceptor transition dipole
- к: Dipole orientation factor
- $\lambda$ : Reorganization energy
- $\lambda_{ex}$ : Excitation Wavelength
- $\lambda_{max}$ : Absorption maximum
- $\lambda_{\text{probe}}$ : Probe wavelength
- τ: Lifetime
- $\tau_D$ : Lifetime of donor
- $\Phi$ : Radiative quantum yield
- $\Phi_D$ : Radiative quantum yield of donor
- $\Phi_{std}$ : Radiative quantum yield of standard
- $\Phi_x$ : Relative radiative quantum yield
- h: Reduced Planck's constant

#### **Chapter 1. Spin Angular Momentum Effects on Excited-State Reactivity**

### **1.1. Introduction**

Spin angular momentum, or spin, is an inherent property of electrons and nuclei. The classical interpretation of spin can be thought of as the angular momentum from the precession of an electron or nuclei about its own axis and was proposed by Uhlenbeck and Goudsmit in 1925<sup>1</sup> but a quantum-mechanical description of spin is more appropriate. The existence of spin was inferred from the Stern-Gerlach experiment, where silver atoms were sent through a magnetic field resulting in the atoms being deflected into two discrete points.<sup>2-4</sup> The silver atoms possess a magnetic dipole moment arising from the spin angular momentum of the unpaired electron in the 5s orbital that interacts with the magnetic field that they are passed through. This was one of the first reports that provided evidence of atoms possessing spin angular momentum. The concept of spin was incorporated into quantum mechanics in 1925 with the Pauli-exclusion principle<sup>5</sup> and later in 1928 in the derivation of relativistic quantum mechanics<sup>6,7</sup> which was the first equation to accurately predict spin. These two fundamental principles have formed the foundation for physical chemistry and quantum mechanical research.

Spin manifests itself in a variety of ways in chemistry and physics through spectroscopy, magnetism, and chemical reactivity. In UV-Vis spectroscopy spin selection rules govern the allowedness of electronic transitions; specifically, electronic transitions between states with the same spin quantum number are "spin-allowed" and have a larger extinction coefficient when compared to electronic transitions that are "spin-forbidden", or have a change in spin quantum number. Spin-orbit coupling effects can have pronounced effects in electronic absorption spectra and excited-state electronic structure, where a relativistic interaction occurs between the orbital angular momentum and the spin angular momentum. This can cause a relaxation in spin selection rules for electronic absorption as the spin of the electronic state is mixed with the orbital angular momentum. Magnetism resulting from the spin polarization of electrons and has led to diverse areas of research such as spintronics,<sup>8,9</sup> single-molecular-magnets,<sup>10,11</sup> and quantum computing.<sup>12-15</sup> Spin angular momentum is an essential component in chemistry and physics for understanding the inherent fundamental properties of chemical systems. Apart from the fundamental role spin plays in understanding these basic principles mentioned above, the effects spin has on molecular systems have been used to affect the reactivity in the ground state and more recently in the excited state.

### **1.2. Spin Effects in Chemical Reactivity**

### 1.2.1. Spin Effects in Ground-State Reactivity

Many of the common physical observables linked to spin are well documented while the well-established physical-organic field of spin chemistry focuses on the influences of applied magnetic fields on chemical and biochemical reaction dynamics.<sup>16-18</sup> Spin chemistry is based on the fundamental principle that the spin of a molecular system has a crucial role in affecting chemical reaction pathways and chemical phenomena, such as the recombination of free radicals<sup>18</sup> and magnetic isotope effects.<sup>19</sup> Magnetokinetic effects are thermodynamic or kinetic properties of a system due to the quantum mechanical limitations imposed by the intrinsic spin polarization induced by the Zeeman effect, such as radical recombination via the radical pair mechanism is shown in Figure 1.1. Each radical possesses a  $m_s$  of  $\pm \frac{1}{2}$ , however two spin-polarized intermediates are possible in the presence of a magnetic field and the formation of the reactants is only possible via the spin-conserved recombination from the singlet, S = 0, intermediate. The Zeeman interactions between the radicals and magnetic field prevents recombination of the reactants and

accelerates the reaction of the radicals due to a higher concentration of the triplet, S = 1, radical pair.



Figure 1.1. Radical recombination demonstrating the conservation of spin angular momentum.

Magnetokinetic effects not only play a role in electronic spin interactions but the nuclear spin of a system can also affect its chemical reactivity including examples such as chemically induced dynamic nuclear polarization effects (CIDNP),<sup>20</sup> and the magnetic isotope effect (MIE). In the photolysis of dibenzyl ketone the nuclear spin on the carbonyl carbon dictates the mechanism of reactivity resulting in the separation of isotopes.<sup>19</sup> Upon excitation of dibenzyl ketone the initially formed triplet excited state undergoes fragmentation to produce the acyl and benzyl radicals, shown in Figure 1.2. The radical pairs formed either undergo triplet-singlet conversion and recombine or fragment further, releasing carbon monoxide and ultimately combining to form dibenzyl. If the carbonyl carbon is <sup>13</sup>C, the rate of triplet-singlet conversion is enhanced form the hyperfine interaction and recombination to from dibenzyl is the major product.



Figure 1.2. Nuclear spin selective photolysis of dibenzyl ketone.

#### 1.2.2. Spin Effects in Excited-State Reactivity

The previous two examples demonstrate the effects spin angular momentum has on chemical reactivity in molecular systems. While the excited state of a molecule is often required to form radical pairs or initiate photolysis the effects of spin angular momentum on how the excited state reacts have not been as well understood. Excited-state reactivity can follow three possible quenching mechanisms, as shown in Figure 1.3, Dexter transfer, electron transfer, and Förster transfer. Förster transfer is a non-radiative quenching mechanism where the dipole of the excited-state donor's emission couples to the dipole of the acceptor's ground-state absorption.<sup>21</sup> This is a through space interaction and requires spectral overlap between the emission of the donor and the absorption of the acceptor. The necessity for spectral overlap also ensures that the thermodynamics of the two electronic states are energetically matched. Due to the through space nature of this quenching mechanism the rate of Förster transfer has a 1/R<sup>6</sup> distance dependence between donor



Figure 1.3. Schematic one-electron representation of excited-state quenching mechanisms.

and acceptor, making energy transfer possible up to 100 Å. The rate expression shown in equation 1.1 consists of the dipole orientation factor,  $\kappa$ , the quantum yield of the donor (in the absence of the acceptor/quencher),  $\Phi_D$ , the spectral overlap integral, *J*, the refractive index of the solvent,  $\eta$ , Avogadro's number, *N*<sub>A</sub>, the lifetime of the donor (in the absence of the acceptor/quencher),  $\tau_D$ , and the distance between the donor and acceptor, *R*.

$$k_{FRET} = \frac{9000 \ln(10)\kappa^2 \Phi_{\rm D}J}{128\pi^5 \eta^4 N_A \tau_D R^6}$$
(1.1)

The spectral overlap integral, *J*, is shown in equation 1.2 where,  $\bar{I}_{\bar{v}}^{D^*}$ , is the normalized emission spectrum of the excited-state donor with respect to wavenumbers, and  $\varepsilon_A$ , is the molar absorptivity of the acceptor as a function of wavenumbers.<sup>22</sup>

$$J^{\overline{\nu}} = \int \frac{\bar{I}_{\overline{\nu}}^{D^*} \varepsilon_A(\overline{\nu})}{\overline{\nu}^4} d\bar{\nu}$$
(1.2)

The intensity of the emission spectrum is normalized as well as its integral as shown in equation 1.3. The emission spectrum is then multiplied by the acceptors absorption spectrum and integrated to calculate *J*.

$$\int \bar{I}_{\bar{\nu}}^{D^*} d\bar{\nu} = 1 \tag{1.3}$$

The dipole orientation factor is a measure of the coupling between the donor's and acceptor's dipoles and is shown in equation 1.4.

$$\kappa^2 = (\cos\Theta_T - 3\cos\Theta_D \cos\Theta_A)^2 \tag{1.4}$$

Figure 1.4 illustrates how the orientation factor is measured where,  $\Theta_T$  is the angle between the donor transition dipole moment,  $r_D$ , and the acceptor transition dipole moment,  $r_A$ ,  $\Theta_D$  is the

angle between the donor-acceptor connection line, R<sub>DA</sub>, and the donor transition dipole moment, and  $\Theta_A$  is the angle between R<sub>DA</sub> and the acceptor transition dipole moment.<sup>23</sup> The orientation factor can range from 0-4; when the dipoles are perpendicular  $\kappa^2 = 0$ , when they are parallel  $\kappa^2 =$ 1, and when they are aligned with one another along donor-acceptor connection line, R<sub>DA</sub>,  $\kappa^2 = 4$ . The strength of coupling between dipoles is dependent on their orientation to each other and affects the rate of Förster transfer.



Figure 1.4. Definitions of the angles used for calculating the orientation factor between the dipoles of the donor's emission and acceptor's absorbance.

Dexter transfer can be thought of as a simultaneous electron exchange between an excitedstate donor and a ground-state acceptor.<sup>24</sup> This energy transfer pathway is a through-bond mechanism requiring orbital overlap between donor and acceptor. Due to this orbital overlap requirement the rate constant for Dexter transfer ( $k_{DET}$ ), shown in equation 1.5, has an exponential distance dependence, where r is the distance between donor and acceptor, r<sub>c</sub> is the distance of closest approach at molecular contact, and  $\beta$  is the attenuation coefficient.

$$k_{DET} = Ae^{(-\beta(r-r_c))} \tag{1.5}$$

Dexter transfer can occur bimolecularly if the donor and acceptor are not covalently linked and will therefore require physical contact. In contrast to Förster transfer, Dexter transfer does not require spectral overlap between the donor and acceptor but the thermodynamics of the excitedstate donor and ground-state acceptor electronic states must be favorable (i.e  $\Delta G < 0$ ). Excited-state electron transfer is another possible quenching mechanism where the excitedstate donor is either oxidized or reduced; these processes are referred to as oxidative and reductive quenching respectively. It is possible that electron transfer can result in bond breaking and/or bond formation in either the reactants or products. For the context of this dissertation the compounds studied remain intact following excited-state electron transfer.

Electron transfer can be described using semi-classical Marcus theory, where the rate constant can be determined using equation 1.6. The rate of electron transfer depends on the strength of electronic coupling, H<sub>AB</sub>, between the donor and acceptor, the driving force,  $\Delta G^{\circ}$ , and the reorganization energy,  $\lambda$ . The electronic coupling between donor and acceptor is distance and orientation dependent.<sup>25-27</sup> The reorganization energy can be thought of as the amount of energy required to transform the reactants into the products while moving along a reaction coordinate without crossing into the products potential energy surface. This energy includes components from all vibrations in the molecules, inner-sphere reorganization energy, and from the changes in polarization from the solvent environment, outer-sphere reorganization energy.<sup>26,28</sup> The driving force for excited-state electron transfer depends on the redox potentials of the donor and acceptor and also the zero-point energy of the excited state.

$$k_{ET} = \frac{2\pi}{\hbar} |H_{AB}|^2 \frac{1}{\sqrt{4\pi\lambda k_B T}} exp\left[\frac{(-\Delta G^o + \lambda)^2}{4\lambda k_B T}\right]$$
(1.6)

Previously a tetranuclear donor-acceptor system featuring three Re(I) donor moieties and an Fe(III) acceptor was studied to understand how the excited-state reactivity can be systematically changed, Figure 1.5.<sup>23</sup> In the donor-acceptor system three different polypyridyl derivatives, bpy (2,2'-bipyridine), tmb (tmb = 4,5,4',5'-tetramethyl-2,2'-bipyridine), and deeb



Figure 1.5. Re(I)-Fe(III) tetranuclear assemblies and Al(III) control molecules.

(deeb = 4,4'-diethylester-2,2'-bipyridine), were coordinated to Re(I) and these moieties act as the excited-state donor via its <sup>3</sup>MLCT state and the Fe(III) is the acceptor via its <sup>6</sup>LMCT (Ligand-to-Metal Charge Transfer) state. The donor and acceptor are covalently linked via pyacac (pyacac = (3-(4-pyridyl)-2,4-pentanedione)) which allows for the donor-acceptor distance to be experimentally measured from single crystal X-ray structure data. The X-ray data showed that the Re-Fe distance is ~10 Å, a value that lies at the limit of what is typically considered for Dexter transfer. In conjunction with the lack of significant electron coupling between metal centers that was determined from the v(CO) frequencies quenching via Dexter transfer was ruled out. The Re(I)-based <sup>3</sup>MLCT emission and the Fe(III)-based  ${}^{6}A_{1} \rightarrow {}^{6}LMCT$  absorption fulfilled the spectral overlap requirement for quenching via Förster transfer. The Al(III) analogues were used as a control due to their inability to quench the MLCT excited state. The control molecules are unable

to engage energy transfer by either mechanism or electron transfer due to their lack of absorption features in the visible (Förster), the donor-acceptor distance (Dexter), and the thermodynamics of the redox products (electron transfer).

Time-resolved emission data was used to measure the observed rate constant of the <sup>3</sup>MLCT decay for the Fe compounds studied, and when compared to the Al control molecules a three order of magnitude increase of the rate constant was observed indicative of quenching. The design motif of the donor-acceptor system inherently led to the exclusion of Dexter and electron transfer quenching mechanisms, but to further support the claim of Förster transfer being the dominant pathway the spectral overlap between donor and acceptor was systematically changed using substituents on the bpy ligand. Three polypyridyl derivatives, tmb, bpy, and deeb, were coordinated to Re(I), varying the energy of the <sup>3</sup>MLCT emission resulting in a change in spectral overlap. Electron donating substituents such as tmb were used to blue shift the MLCT emission, increasing the overlap between the donor's emission and acceptor's absorbance while deeb was used to red shift the emission resulting in the least amount of overlap. The changes in spectral overlap are in agreement with the trend of rate constants determined from time-resolved spectroscopy. The agreement between calculated and observed Förster rate constants coupled with the estimated driving force for photo-induced electron transfer being unfeasible conclude that Förster transfer is the quenching mechanism. This study provided not only a quantitative example for calculating the quenching rate constant in this tetranuclear donor-acceptor assembly, but also a platform to study the excited-state reactivity in donor-acceptor systems.

By understanding the excited-state reactivity of the Re(I)-Fe(III) system, the same design principles were used to create a series of donor-acceptor assemblies to study the effects of spin angular momentum on the excited-state reactivity. The new donor-acceptor systems had the formula  $[M(pyacac)_3(Re(bpy)(CO)_3)_3]^{3+}$  (pyacac = 3-(4-pyridyl-acetlyacetonate) in which M = Cr(III) (CrRe\_3), Co(III) (CoRe\_3), and Ga(III) (GaRe\_3), Figure 1.6.<sup>29</sup> The Ga(III) compounds served as control molecules analogous to the Al(III) compounds in the previous system. Due to the similar structural design as the Re(I)-Fe(III) compounds Förster transfer was considered to be the primary pathway for excited-state quenching. Excited-state electron transfer was endergonic for all species studied and tmb, deeb, and bpy were used to shift the spectral overlap changing the rate of Förster transfer.



Figure 1.6. Tetranuclear donor-acceptor systems featuring Cr(III) and Co(III) to study the effect of spin on excited-state reactivity.

Time-resolved emission experiments showed significant quenching in the Cr(III) species  $(\tau = 4.8 \pm 0.2 \text{ ns})$  compared to the Ga(III) control ( $\tau = 630 \pm 30 \text{ ns}$ ), both traces are shown in Figure 1.7A. This result was expected since the requirements for Förster energy transfer were met. In contrast, the <sup>3</sup>MLCT lifetime measured for the Co(III) species ( $\tau = 640 \pm 30 \text{ ns}$ ) is shown in Figure 1.7B, and was within experimental error of the <sup>3</sup>MLCT lifetime of the Ga(III) control. These results


Figure 1.7. (A) Time-resolved emission for CrRe<sub>3</sub>  $\lambda = 580$  nm after excitation at 375 nm. Inset: Nanosecond time-resolved emission data for GaRe<sub>3</sub> at  $\lambda = 580$  nm after excitation at 400 nm. (B) Time-resolved emission data for CoRe<sub>3</sub> at  $\lambda = 580$  nm after excitation at 400 nm.<sup>29</sup>

seemed to be unexpected, considering how this system was designed to undergo energy transfer via the dipolar mechanism. However, this unforeseen outcome can be justified with a simple postulation: conservation of spin angular momentum.

It was hypothesized that if the spins of the products and the reactants of the energy transfer reaction did not satisfy the conservation of spin angular momentum (vide infra) then the reaction would be forbidden and no quenching would be observed. To further illustrate this idea a generic donor acceptor interaction can be considered, shown in Figure 5. The total spin angular momentum for products and reactants can be described using Equation 1.7 in Figure 1.8, a formalism that is identical to the vector coupling of spin angular momenta used to describe magnetic exchange interactions among weakly coupled paramagnetic species.<sup>16</sup>

$$D-A \xrightarrow{hv} D^*-A \longrightarrow D-A^*$$

$$\left|S_{T}^{R}\right| = S_{D^{*}} + S_{A} = \left|S_{D^{*}} + S_{A}\right|, \dots, \left|S_{D^{*}} - S_{A}\right| \qquad \left|S_{T}^{P}\right| = S_{D} + S_{A^{*}} = \left|S_{D} + S_{A^{*}}\right|, \dots, \left|S_{D} - S_{A^{*}}\right|$$
(1.7)

Figure 1.8. Generic donor-acceptor interaction used with equation 1.7 to calculate the conservation of spin.

Here, the excited state of the donor (D\*) and ground state of the acceptor (A) are the reactants, and the ground state donor (D) and excited state acceptor (A\*) are the products of an energy transfer reaction.  $|S_D|$ ,  $|S_{D^*}|$ ,  $|S_A|$ , and  $|S_{A^*}|$  are used to represent the magnitudes of spin angular momenta of the ground and excited states of the donor and acceptor, such that  $|S^R|$  and  $|S^P|$  are the magnitudes of the total spin angular momenta for the products and reactants. In order for a reaction to be deemed spin-allowed  $\Delta S = 0$ .

The validity of using this model to explain the dynamics of this particular system hinges on the notion that the angular momentum being conserved is purely from spin angular momemntum such that spin-orbit coupling is weak enough to distinguish between spin and orbital components. Using a third-row transition metal as an excited-state donor could potentially result in a highly mixed excited state of singlet and triplet MLCT states because of the Z<sup>4</sup> dependence of nuclear charge on the spin-orbit coupling constant.<sup>30</sup> However, calculations of the excited state nature of Re(I) polypyridyls have been well documented and have described the lowest energy excited state, the excited state engaged in excited-state quenching, as 99% pure triplet in character.<sup>31,32</sup> The assumption that spin is a good quantum number in this system is confirmed based on these calculations, and the difference in reactivity being observed is purely due to spin angular momentum opposed to orbital components.



Figure 1.9. (a) Single electron representation of the spin-allowed quenching pathway for CrRe<sub>3</sub> and (b) the spin-forbidden pathway for CoRe<sub>3</sub>.

Using Equation 1.7 to predict the conservation of spin in the Cr(III) species, the total spin angular momentum of reactants is  $|S^{R}| = 5/2$ , 3/2, 1/2 (Figure 1.9a); the products of energy transfer result in  $|S^{P}| = 3/2$ . Therefore, energy transfer is spin-allowed for this system, as both have a common spin angular momentum of 3/2. When the same analysis is performed on the Co(III) species, a low-spin d<sup>6</sup> compound, the spin angular momentum of the ground-state acceptor and excited-state acceptor,  $|S_{A}|$  and  $|S_{A^*}|$ , are 0 resulting in  $|S^{R}| = 1$  and  $|S^{P}| = 0$ . Therefore, this spin conservation formalism predicts that the energy transfer reaction for the Co species is spin-forbidden; as such, quenching from the  ${}^{1}T_{1}$  state of the Co(III) acceptor should not occur. This was the first time that spin conservation could be invoked to explain the excited-state reactivity of a system. This discovery has led to new considerations that must be taken into account, not only when applying Förster theory, but when considering excited-state reactivity in general for transition-metal based systems.

Since the first report of spin angular momentum affecting excited-state reactivity there have been several examples that expand upon the role of spin effects in the excited states of molecular systems, and also support that conservation of spin angular momentum is a necessary consideration for excited-state reactivity. Recently a Re(I)bpy chromophore linked to a perylenediimide moiety was used to demonstrate that the excited-state decay dynamics for the rate of photo-induced electron transfer was dependent on the conservation of spin angular momentum resulting in a 1000-fold rate enhancement.<sup>32</sup> Similarly, the same principle was applied to control the charge-recombination at an inorganic/organic interface in quantum dots.<sup>33</sup> The previous two examples illustrate how spin conservation was leveraged to dictate excited-state decay pathways while recent examples have demonstrated how excited-state reactivity is affected in a multi-spin

system such as, selective redox chemistry in a spin-correlated radical pair (SCRP),<sup>34</sup> spin decoherence,<sup>35</sup> and magnetic exchange interactions.<sup>36</sup>

#### 1.2.3. Dimensionally Reduced Donor-Acceptor Systems

To gain a fundamental understanding and to definitively establish the role of spin conservation in excited-state quenching this research will focus on synthetically modifying the tetranuclear MRe<sub>3</sub> donor-acceptor systems previously discussed. The first goal of this dissertation is to dimensionally reduce the tetranuclear assemblies such that they consist of a single Re(I) donor and a single first-row transition-metal acceptor. This will allow for easier synthetic modifications of the donor-acceptor assembly to study multiple aspects of spin effects in excited-state reactivity. The first series of dimensionally reduced dinuclear assemblies to be prepared are shown in Figure 1.10. The essential components from the tetranuclear assembly are still present in the dimensionally reduced system: a Re(I)(bpy) donor that can be synthetically modified to change the spectral overlap, the first-row transition-metal acceptors, and the same bridging ligand between donor and acceptor. The main structural difference between the systems is the use of the tripodal capping ligand, tris(2-aminoethyl)amine (tren), to occupy the coordination positions previously used to attach multiple donors. The excited-state reactivity of the CrRe dinuclear systems is



Figure 1.10. Dimensionally reduced dinuclear assemblies.

expected to be similar to that of the tetranuclear systems due to the unchanged donor-acceptor distance, and thermodynamics of electron transfer, as well as the fact that spectral overlap still exists. In the CoRe dinuclear compounds the donor-acceptor distance is unchanged while spectral overlap between donor and acceptor are still present, but the driving force for electron transfer becomes exergonic for the Re(bpy) and Re(tmb) chromophores. The change in driving force for electron transfer is a result of increasing the Co(III) reduction potential due to the tren capping ligand changing the coordination environment from  $O_6$  to  $O_2N_4$ . In the case of the Re(btfmb) (btfmb = 4,4'-bistrifluoromethyl-2,2'-bipyridine) chromophore photo-induced electron transfer is endergonic and should resemble similar excited-state reactivity as the CoRe<sub>3</sub> compounds. The advantage in developing the dinuclear system not only allows for more simplistic synthetic modifications to further study the role of spin in excited-state reactivity but also allows the opportunity to systematically control the excited-state quenching pathway via spin conservation. While using this dinuclear design motif the limitations of the spin effects in Förster transfer at long donor-acceptor distances can be probed and the spin dependence of Dexter energy transfer can be studied for the first time in covalently linked system.

# **1.3.** Contents of Dissertation

Chapter 2 provides an overview of fundamental photophysical processes and excited state quenching mechanisms. The ground- and excited-state characterization of Re chromophores in the form of  $[\text{Re}(\text{CO})_3(\text{L})(4\text{-Etpy})]\text{OTf}$  (where L = bpy, tmb, deeb, or btfmb) (OTf = Trifluoromethanesulfonate) in the absence of quenching are analyzed in chapter 2 to serve as a basis for interpreting the results presented in future chapters. The synthesis and analysis of the photophysics for CrRe dinuclear assemblies are presented in Chapter 3. Similarly, to the tetranuclear complexes presented earlier in this chapter the dinuclear CrRe compounds exhibit

excited-state quenching of the MLCT state via Förster transfer. Substituents on the bipyridine ligand are used to alter the spectral overlap between donor and acceptor systematically changing the rate of Förster transfer. Single crystal X-ray data along with photophysical properties of the Re chromophores studied in chapter 2 are used to calculate the rate of Förster transfer for the CrRe compounds and are compared to the experimentally obtain results. Chapter 4 details the synthesis, purification, and photophysical characterization of the CoRe dinuclear assemblies. The Co(III) acceptor in this system prevents Förster transfer from occurring, due to the conservation of spin, while the coordination environment around the Co center makes excited-state electron transfer a viable pathway. By using different bipyridine ligands to modify the energy of the Re-based MLCT excited state, changing the driving force for electron transfer, the excited-state quenching mechanism can be controlled leveraging the spin restrictions put in place by the Co(III). Chapter 5 uses the fundamental principles of excited-state reactivity that were presented in Chapter 2 and applies them to studying the bimolecular quenching mechanism of an Fe(II) polypyridyl as it pertains to photoredox catalysis. Nano-second transient absorption spectroscopy is used to study the kinetics of bimolecular quenching studies between an iron(II) chromophore and benzoquinone acceptors in an effort to understand the mechanism of iron polypyridyls employed as photocatalysts in photoredox chemistry. Finally, Chapter 6 discusses the future directions created by the research presented throughout this dissertation.

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# Chapter 2. Ground-State and Excited-State Characterization of Re(I) polypyridyls: Context for Donor-Acceptor Systems

# **2.1. Introduction**

The excited-state decay dynamics of transition metal-based chromophores have been thoroughly studied and well characterized over the last 40 years.<sup>1-7</sup> The lowest-energy excited states of 2<sup>nd</sup> and 3<sup>rd</sup> row transition metal polypyridyls are Metal-to-Ligand Charge Transfer (MLCT) in nature. In a light induced MLCT state, an electron is promoted from a metal-based dorbital to a ligand-based  $\pi^*$  orbital resulting in a formally oxidized metal center and formally reduced ligand. Due to charge-separated excited states these transition metal polypyridyls, such as  $[Ru(bpy)_3]^{2+}$  (bpy = 2,2'-bipyridine),  $Ir(ppy)_3$  (ppy = 2-phenylpyridine), and  $[Re(bpy)(CO)_3(4-$ Etpy]<sup>+</sup> (4-Etpy = 4-ethylpyridine) have been used as sensitizers in solar energy conversion and photoredox catalysis.<sup>6,8-12</sup> Specifically, the photophysics of Re(I) compounds have been thoroughly studied as models to understand radiationless decay theory,<sup>13</sup> the mechanism of intramolecular electron transfer,<sup>14</sup> and for their use as catalysts for CO<sub>2</sub> reduction.<sup>15,16</sup> By understanding the photophysics and excited-state decay dynamics it is possible to make synthetic modifications to improve the function of these chromophores. For example, electron donating substituents on 2,2'-bipyridine can be used to increase the driving force of excited-state electron transfer and increase the lifetime of the MLCT state.<sup>17</sup> The ground-state and excited-state properties for this class of chromophores have been well studied<sup>18,19</sup> and are directly applicable to the donor-acceptor systems that will be studied in this dissertation.

The goal of this dissertation is to improve upon the understanding of how spin angular momentum affects excited-state reactivity of these charge-transfer chromophores. As previously mentioned at the end of Chapter 1, the McCusker group has published one of the first papers showing how spin can alter excited-state reactivity using a tetranuclear donor-acceptor system.<sup>20</sup> The tetranuclear system featured three Re(I)(bpy) excited-state donor moieties and either Co(III) or Cr(III) as the acceptor. To further expand on how spin affects excited-state reactivity, dinuclear donor-acceptors featuring one Re(I) chromophore and either Cr(III) or Co(III) will be studied. In order to understand the photophysics of the dinuclear donor-acceptors this chapter will introduce the ground-state and excited-state characterization of the individual donors, [Re(CO)<sub>3</sub>(bpy)(4-Etpy)]OTf (OTf = Trifluoromethanesulfonate), [Re(CO)<sub>3</sub>(tmb)(4-Etpy)]OTf (tmb = 4,5,4',5'-tetramethyl-2,2'-bipyridine), [Re(CO)<sub>3</sub>(btfmb)(4-Etpy)]OTf (btfmb = 4,4'-bis(trifluoromethyl)-2,2'-bipyridine), and [Re(CO)<sub>3</sub>(deeb)(4-Etpy)]OTf (deeb = 4,4'-diethylester-2,2'-bipyridine) shown in Figure 2.1.



Figure 2.1. Individual donors that will be studied in this chapter.

## 2.2. Experimental

#### 2.2.1. Synthesis

**General.** The tmb,<sup>21</sup> btfmb,<sup>22</sup> and deeb<sup>23</sup> ligands were prepared according to the literature procedures. Re(CO)<sub>3</sub>(bpy)Cl,<sup>19</sup> Re(CO)<sub>3</sub>(tmb)Cl,<sup>19</sup> Re(CO)<sub>3</sub>(deeb)Cl,<sup>18</sup> [Re(CO)<sub>3</sub>(bpy)(4-Etpy)]OTf,<sup>17</sup> and [Re(CO)<sub>3</sub>(tmb)(4-Etpy)]OTf<sup>17</sup> were prepared according to the literature procedures. Re(CO)<sub>5</sub>Cl was purchased from Sigma Aldrich and used as received. 4-Ethyl pyridine was purchased from Sigma Aldrich and distilled prior to use. Silver triflate was purchased from Sigma

Aldrich and used as received. Tetrahydrofuran was purchased from Sigma Aldrich and dried over neutral alumina under nitrogen. <sup>1</sup>H NMR were collected on an Agilent DDR2 500 MHz spectrometer at the Max T. Rogers NMR facility at Michigan State University and referenced to residual solvent shifts. Electrospray ionization mass spectra were obtained at the Michigan State University Mass Spectrometry and Metabolomics Core on a Waters G2-XS QTof mass spectrometer interfaced to a Waters Aquity UPLC.

[**Re(deeb)(CO)<sub>3</sub>(4-Etpy)](OTf).** Re(CO)<sub>3</sub>(deeb)Cl (0.3 g, 0.495 mmol) and AgOTf (0.127 g, 0.495 mmol) were combined with THF (30 mL) and refluxed under nitrogen for 6 hours. The reaction was cooled to room temperature, filtered over celite and washed with THF. The solvent was removed under reduced pressure then 4-ethylpyridine (0.424 g, 3.96 mmol) and THF (30 mL) were added, bubble degassed, and refluxed for 4 hours. The solvent was removed under reduced pressure then 4-ethylpyridine DCM and the product was precipitated with ether. The yellow residue was dissolved in DCM and the product was precipitated with ether (1:10) (0.266 g, 65%). <sup>1</sup>H NMR (500 MHz, acetonitrile-*d*<sub>3</sub>) 9.40 (d, J = 5.7 Hz, 2H), 8.91 (d, J = 1.8 Hz, 2H), 8.23 (dd, J = 5.7, 1.7 Hz, 2H), 8.07 (d, J = 5 Hz, 2H), 7.15 (d, J = 5 Hz, 2H), 4.50 (q, J = 7.1 Hz, 4H), 2.60 (q, J = 7.5 Hz, 2H), 1.45 (t, J = 7.1 Hz, 6H), 1.11 (t, J = 7.6 Hz, 3H). HRMS (ESI-TOF) m/z: [M-OTf]<sup>+</sup> calc'd for [C<sub>26</sub>H<sub>25</sub>N<sub>3</sub>O<sub>7</sub>Re] 678.13 obs. 678.125.

**Re(btfmb)**(**CO**)<sub>3</sub>**Cl.** Re(CO)<sub>5</sub>Cl (0.42 g, 1.16 mmol) and btfmb (0.34 g, 1.16 mmol) were combined with toluene (40 mL) and refluxed under nitrogen for 2 hours. The reaction was cooled to room temperature and hexanes was added, the precipitate was filtered and washed with hexanes and ether and dried overnight under vacuum (0.615 g, 88%). <sup>1</sup>H NMR (500 MHz, acetonitrile- $d_3$ ) 9.29 (d, J = 5.7 Hz, 2H), 8.87 (s, 2H), 7.96 (d, J = 5.7 Hz, 2H).

**[Re(btfmb)(CO)<sub>3</sub>(4-Etpy)](OTf).** Re(btfmb)(CO)<sub>3</sub>Cl (0.2 g, 0.33 mmol) and AgOTf (0.085 g, 0.33 mmol) were combined with THF (20 mL) and refluxed under nitrogen for 3.5 hours. The reaction was cooled to room temperature, filtered over celite and washed with THF. The solvent was removed under vacuum and 4-ethylpyridine (0.322 g, 3.0 mmol) and THF (20 mL) were added and the reaction was refluxed under nitrogen for 3 hours. The solvent was removed under vacuum and the residue under nitrogen for 3 hours. The solvent was removed under vacuum and the residue was dissolved in dichloromethane and precipitated with ether (0.164 g, 60%). X-ray quality crystals were grown from ether diffusion into 9:1 DCM/MeCN solution. <sup>1</sup>H NMR (500 MHz, acetonitrile-*d*<sub>3</sub>) 9.47 (d, J = 5.8 Hz, 2H), 8.83 (s, 2H), 8.12 (d, J = 5.5 Hz), 8.10 (d, J = 7.25 Hz, 2H), 7.18 (d, J = 6.5 Hz, 2H), 2.62 (q, J = 7.6 Hz, 2H), 1.13 (t, J = 7.6 Hz, 3H). HRMS (ESI-TOF) m/z: [M-OTf]<sup>+</sup> calc'd for [C<sub>22</sub>H<sub>15</sub>F<sub>6</sub>N<sub>3</sub>O<sub>3</sub>Re] 670.057 obs. 670.062.

# 2.2.2. Physical Characterization

**X-ray structure determination.** Single-crystal X-ray diffraction data were acquired and the structures were solved by Dr. Richard Staples at the X-ray Facility of Michigan State University.

**Ground-state absorption spectroscopy.** All spectra were collected using spectrophotometric grade acetonitrile in 1 cm quartz cuvettes and acquired using a Cary 50 spectrophotometer.

**Electrochemistry.** Electrochemical measurements were collected using a CH instruments model CHI620D electrochemical workstation in an Ar-filled dry box. A standard three-electrode setup was used to determine the redox potentials via cyclic voltammetry in acetonitrile solutions using 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) as supporting electrolyte, a Pt disc working electrode, a Ag wire pseudo-reference electrode, and a platinum wire counter electrode. Cyclic voltammetry was collected using a scan rate of 200 mV/s and Fc/Fc<sup>+</sup> was used as an internal reference. Differential pulse voltammetry was performed for [Re(btfmb)(CO)<sub>3</sub>(4-Etpy)](OTf) in

the same setup that was described for cyclic voltammetry experiments, but with an increment of 0.004 V, amplitude of 0.05 V, pulse width of 0.2 s, sampling width of 0.0167 s, and a pulse period of 0.2 s. TBAPF<sub>6</sub> was purchased from Oakwood Chemical and recrystallized from ethanol twice before use.

**Spectroelectrochemistry.** UV-Visible spectroelectrochemical experiments were performed in a Pine Instruments electrochemical cell in an Ar-filled dry box. The 1 cm x 1 cm space at the top of the cell held the Ag reference electrode while the Pt working electrode and counter electrode were placed in the 1.7 mm x 10 mm path length window at the bottom of the cell to electrolyze the solution while the absorbance was recorded with a SI420 CCD spectrometer. Data were acquired on solutions identical to that just described for the electrochemical measurements, with the exception that solutions of each compound were adjusted to have absorbance values in the range of  $0.6 \pm 0.1$  at the maximum of the MLCT absorption peak. A ground-state absorption spectrum was taken prior to the onset of bulk electrolysis at an over potential of 0.1 V - 0.2 V relative to the redox potential of the compound.

Steady-State Emission and Time-Resolved Emission and Absorption. All samples were prepared in an argon-filled glovebox, using air-free cuvettes and spectrophotometric acetonitrile that was freeze-pump-thaw degassed prior to use. For steady-state and time-resolved emission spectroscopy the absorbance of the sample at the MLCT maximum was between 0.1 - 0.2.

Steady-state emission spectra were collected using a Horiba Fluorolog-3 fluorimeter and corrected for instrumental response using a NIST standard of spectral irradiance (Optronic Laboratories, Inc., OL220 M tungsten quartz lamp). Relative quantum yields of emission ( $\Phi_x$ ) were calculated using [Re(bpy)(CO)<sub>3</sub>(4-Etpy)](OTf) in acetonitrile as a standard ( $\Phi_{std} = 0.029$ ) which was calculated as a relative quantum yield using [Ru(bpy)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> in deaerated MeCN as a

standard ( $\Phi_{std} = 0.095$ ). The resulting emission spectra were fit with an asymmetric double sigmoidal function using IGOR pro. This function has no mathematical significance but it is able to accurately reproduce the shape of the entire emission curve and capture the small area (< 10%) that lies outside of the detector range providing a more accurate estimate of the integrated spectrum. Quantum yields were calculated using equation 2.1, where x refers to the molecule of interest and *std* to the standard;  $I_x$  and  $I_{std}$  are the integrated areas of the corrected emission spectra,  $A_x$  and  $A_{std}$  are the absorbances at the excitation wavelength, and  $\eta_x$  and  $\eta_{std}$  are the indices of refraction of the solutions.

$$\Phi_x = \Phi_{std} \left( \frac{I_x/A_x}{I_{std}/A_{std}} \right) \left( \frac{\eta_x}{\eta_{std}} \right)^2$$
(2.1)

Nanosecond time-resolved emission spectroscopy was performed using an Opotek Vibrant 355 LD Q-switched Nd:YAG laser spectrometer (described previously) that generates 5 ns laser pulses.<sup>24</sup> Excitation energies were measured between 1- 3 mJ per pulse and data was checked for linearity, and was either fit with a single exponential decay or Gaussian deconvolution for [Re(btfmb)(CO)<sub>3</sub>(4-Etpy)](OTf) to measure the observed rate constant.

Nanosecond transient absorption data were acquired using an Edinburgh Instruments LP980 spectrometer fitted with a Hamamatsu R928 photomultiplier tube and interfaced to a Tektronix TDS 3032C oscilloscope. The excitation source was an Opotek Vibrant 355 LD Q-switched Nd:YAG laser and data were collected at  $28 \pm 2$  °C.

## 2.3. Ground-State Properties

The absorption spectrum of a well-studied transition-metal-based chromophore,  $[Re(CO)_3(bpy)(4-Etpy)]OTf$  is shown in Figure 2.2 along with the other chromophores that will be studied throughout this dissertation. The spectrum features a bpy ligand-based  $\pi$ - $\pi$ \* transition



Figure 2.2. Electronic absorption spectra of Re(I) chromophores in MeCN. at 285 nm assigned from the absorption spectrum of unbound 2,2'-bipyridine.<sup>6</sup> The absorption at 370 nm has been assigned to a MLCT transition based on its structure-less absorption, solvatochromism, and sensitivity to substituents on the bpy ligand.<sup>6</sup> The MLCT transition results in Re(I) being formally oxidized to Re(II) where the ligand is formally reduced. The charge-separated nature of this excited state gives rise to its excited-state redox chemistry, Figure 2.3. As electron donating groups are substituted onto the bipyridine ligand in the case of [Re(CO)<sub>3</sub>(tmb)(4-Etpy)]<sup>+</sup>, the ligand centered  $\pi^*$  orbitals increase in energy leading to a blue shift in the MLCT absorption. When electron withdrawing groups are used the  $\pi^*$  orbitals are stabilized leading to a red shift in the MLCT absorption for [Re(CO)<sub>3</sub>(btfmb)(4-Etpy)]<sup>+</sup> and [Re(CO)<sub>3</sub>(deeb)(4-Etpy)]<sup>+</sup>.



Figure 2.3. Illustration of the charge-separated MLCT state of [Re(bpy)(4-Etpy)]<sup>+</sup> after absorption of light.

Compound	E <sub>ox</sub> (Re <sup>II/I</sup> ) (V)	$E_{red}(L^{0})$ (V)
$[\text{Re(tmb)(CO)}_3(4-\text{Et-py})]^+$	1.33	-1.81
$[\text{Re(bpy)(CO)}_3(4\text{-}\text{Et-py})]^+$	1.37	-1.56
$[\text{Re}(\text{deeb})(\text{CO})_3(4\text{-}\text{Et-py})]^+$	1.44	-1.18
$[\text{Re(btfmb)(CO)}_3(4-\text{Et-py})]^+$	1.44	-1.17

Table 2.1. Oxidation and reduction potentials for Re(I) complexes (vs. Fc/Fc<sup>+</sup>).

Due to a likely redox-active excited state being used in the donor-acceptor assemblies the oxidation and reduction potential of each chromophore was measured using cyclic voltammetry. The  $Re^{(II/I)}$  oxidation and ligand ( $L^{0/-}$ ) reduction potentials are listed in Table 2.1. As the electron donating and withdrawing ability of the substituents are changed on the bipyridine ligand the reduction potential can be altered by up to 0.64 V in the example of [Re(tmb)(CO)<sub>3</sub>(4-Et-py)]<sup>+</sup> and  $[\text{Re(btfmb)(CO)}_3(4\text{-Et-py})]^+$ . As mentioned previously this is due to stabilization of the  $\pi^*$  orbitals on the ligand, and since these orbitals are the Lowest Unoccupied Molecular Orbital (LUMO) this effect can be observed electrochemically. The change in electronics of the ligand also has an effect on the Re<sup>(II/I)</sup> oxidation potential due to the dual  $\pi$ -donor and  $\pi$ -accepting nature of bpy-based ligands.<sup>25</sup> The electron withdrawing substituents increase the accepting ability of the ligand, decreasing electron density on the Re and increasing its oxidation potential while the electron donating substituents increase the  $\pi$ -donation, destabilizing the Highest Occupied Molecular Orbitals (HOMO), the metal-based t<sub>2g</sub> orbitals. The oxidation potentials range from 1.33 to 1.44 V from  $[Re(tmb)(CO)_3(4-Et-py)]^+$  to  $[Re(btfmb)(CO)_3(4-Et-py)]^+$ , and can be assigned to the  $Re^{(II/I)}$ oxidation based on previously published reports.<sup>17</sup> Since the MLCT state can be thought of a formal oxidation of the metal center and formal reduction of the ligand, and the redox potentials measured from electrochemistry are the same orbitals involved in the MLCT state, an estimated MLCT

energy can be calculated from equation 2.2.<sup>26</sup> Solvation and electron correlation effects are not taken into account with this approximation and should only be used as qualitative comparison.

$$E(MLCT) = |E(Re^{II/I})| + |E(bpy^{0/-})|$$
(2.2)

## **2.4. Excited-State Properties**

Upon light excitation a molecule is promoted into an excited state which naturally decays back to the ground state through relaxation processes shown in Figure 2.4. These relaxation processes can be categorized into non-radiative and radiative processes. Non-radiative processes are typified by vibrational relaxation (VR), internal conversion, and intersystem crossing. Vibrational relaxation can occur within a given electronic state, usually on the picosecond timescale.<sup>27</sup> Non-radiative decay to a lower lying electronic state with the same spin multiplicity



Figure 2.4. Potential energy surface diagram depicting excited-state relaxation processes.

is referred to as internal conversion, whereas non-radiative decay to a lower lying electronic state with differing spin multiplicity is termed intersystem crossing.<sup>2</sup> In contrast to non-radiative decay, radiative decay (emission of a photon) is referred to as fluorescence when no change in spin multiplicity occurs between states and phosphorescence when the transition is spin-forbidden.<sup>2</sup>

Specifically for [Re(bpy)(CO)<sub>3</sub>(4-Et-py)]<sup>+</sup>, absorption into the <sup>1</sup>MLCT state occurs at 370 nm. The resulting non-thermalized excited state rapidly undergoes intersystem crossing into the triplet manifold with a lifetime of 130 femtoseconds. The first triplet formed is an Intraligand Charge Transfer (ILCT) state which internally converts to a lower energy <sup>3</sup>MLCT state in 870 fs.<sup>28,29</sup> The <sup>3</sup>MLCT state is the lowest-energy excited state and decays back to the ground state with a lifetime of 220 ns and an emission centered at 580 nm in acetonitrile.

The excited-state decay process of  $[\text{Re}(\text{bpy})(\text{CO})_3(4\text{-Et-py})]^+$  is illustrated in Figure 2.5, where [GS] is the concentration of the molecule in the ground state, [ES] is the concentration of the molecule in the excited state,  $k_{\text{isc}}$  is the rate constant for intersystem crossing,  $k_r$  is the rate constant for radiative decay, and  $k_{nr}$  is the rate constant for non-radiative decay.

$$[GS] \xrightarrow{hv} {}^{1}[ES] \xrightarrow{k_{isc}} {}^{3}[ES]$$
$$\xrightarrow{3}[ES] \xrightarrow{k_{r}} [GS] + hv$$
$${}^{3}[ES] \xrightarrow{k_{nr}} [GS]$$

Figure 2.5. Schematic of excited-state decay processes with appropriate rate constants.

A rate expression for the excited-state decay is shown in equation 2.3 which is first order with respect to the concentration of excited state, and  $k_{obs}$  is the observed rate constant of excited-state decay which is composed of both radiative and non-radiative rates. The solution to this differential equation is given by equation 2.4.

$$-\frac{d[ES]}{dt} = k_r[ES] + k_{nr}[ES] = (k_r + k_{nr})[ES] = k_{obs}[ES]$$
(2.3)

$$[ES] = [ES]_0 e^{-k_{obs}t}$$
(2.4)

Where [ES] is the excited-state concentration as a function of time, t,  $[E]_0$  is the initial concentration of the excited state, and  $k_{obs}$  is the observed rate constant of excited-state decay, or the inverse of the lifetime of the excited state,  $\tau_0$ . The lifetime of the excited state can be measured using spectroscopic techniques such as time-resolved emission and transient absorption. Here, [ES] is measured as a function of time and can be fit using equation 2.4, or a variation thereof, to determine the lifetime of the excited state.

The time-resolved emission spectrum of  $[\text{Re}(\text{bpy})(\text{CO})_3(4-\text{Et-py})]^+$  in acetonitrile is shown in Figure 2.6a, and was fit with a single exponential decay with a 225 ns lifetime. When electron donating groups are substituted onto the bipyridine ligand the  $\pi^*$  orbital is destabilized, resulting in a longer lifetime of 1.45 µs. The increase in lifetime relative to the bpy derivative is in accordance with the energy gap law, the destabilization of the  $\pi^*$  orbital increases the energy of the MLCT state, decreasing the vibrational overlap between the two electronic states resulting in a decreased Franck-Condon factor.<sup>17</sup> Similarly, if electron withdrawing groups are substituted onto the bpy ligand a decrease in energy of the  $\pi^*$  orbital results in a smaller MLCT- <sup>1</sup>A<sub>1</sub> energy gap, which increases the vibrational overlap (increased Franck-Condon factor) between the excited and ground state, resulting in shorter lifetimes for [Re(deeb)(CO)<sub>3</sub>(4-Et-py)]<sup>+</sup>,  $\tau = 80$  ns, and [Re(btfmb)(CO)<sub>3</sub>(4-Et-py)]<sup>+</sup>,  $\tau = 20$  ns.

The radiative and non-radiative rate constants are accessible when time-resolved emission is used in conjunction with steady-state emission spectroscopy. An emission spectrum can be used to calculate the radiative quantum yield,  $\Phi$ , as shown in equation 2.5. The quantum yield for

$$\Phi = \frac{k_r}{k_{obs}} = \frac{k_r}{k_{nr} + k_r}$$
(2.5)



Figure 2.6. Nanosecond time-resolved emission of [Re(bpy)(CO)<sub>3</sub>(4-Et-py)]OTf (a),  $\tau = 225$  ns ( $\lambda_{ex} = 370$  nm,  $\lambda_{probe} = 580$  nm), [Re(tmb)(CO)<sub>3</sub>(4-Et-py)]OTf (b)  $\tau = 1.45$  µs ( $\lambda_{ex} = 360$  nm,  $\lambda_{probe} = 540$  nm), [Re(deeb)(CO)<sub>3</sub>(4-Et-py)]OTf (c),  $\tau = 80$  ns ( $\lambda_{ex} = 410$  nm,  $\lambda_{probe} = 650$  nm), [Re(btfmb)(CO)<sub>3</sub>(4-Et-py)]OTf (d),  $\tau = 20$  ns ( $\lambda_{ex} = 410$  nm,  $\lambda_{probe} = 670$  nm).

emission is a ratio of the radiative rate constant to the observed rate constant, or a measure of the efficiency of emission from the excited state. By measuring the quantum yield and the lifetime of an excited state,  $k_r$  and  $k_{nr}$  can be calculated using equation 2.5. A quantum yield can be measured absolutely or relative to a standard. An absolute quantum yield is measured using a fluorimeter equipped with an integration sphere detector, which detects every photon that is emitted from the sample relative to the number of photons absorbed.<sup>30</sup> A relative quantum yield is calculated using

equation 2.1, mentioned previously. Throughout this dissertation quantum yields that are reported were measured as relative quantum yields, or relative to a standard with an absolute value.



Figure 2.7. Steady-state emission of  $[\text{Re}(\text{tmb})(\text{CO})_3(4\text{-Et-py})]^+$  (blue,  $\lambda_{ex} = 360$  nm),  $[\text{Re}(\text{bpy})(\text{CO})_3(4\text{-Et-py})]^+$  (green,  $\lambda_{ex} = 370$  nm),  $[\text{Re}(\text{deeb})(\text{CO})_3(4\text{-Et-py})]^+$ (orange,  $\lambda_{ex} = 400$  nm), and  $[\text{Re}(\text{btfmb})(\text{CO})_3(4\text{-Et-py})]^+$  (red,  $\lambda_{ex} = 410$  nm).

The steady-state emission spectrum of  $[\text{Re}(\text{bpy})(\text{CO})_3(4-\text{Et-py})]\text{OTf}$  in acetonitrile is shown in Figure 2.7. This compound has a quantum yield of 0.029 as reported in the literature; it is used as a standard when calculating quantum yields for new compounds in this dissertation.<sup>17</sup> The  $[\text{Re}(\text{bpy})(\text{CO})_3(4-\text{Et-py})]^+$  emission is centered at 580 nm. Due to the electronic effects of the tmb ligand, the emission maximum of  $[\text{Re}(\text{tmb})(\text{CO})_3(4-\text{Etpy})]^+$  blue shifts to 540 nm. As the energy gap between the  ${}^1\text{A}_1$  and  ${}^3\text{MLCT}$  increases, the  $k_{nr}$  decreases by 1 order of magnitude, relative to the bpy derivative (Table 2.2). Since each Re chromophore emits from the same moiety, the  ${}^3\text{MLCT}$  state, the  $k_r$  for each compound is within error of each other, and the change in quantum yield between each compound is due to the change in  $k_{nr}$ . With the electron withdrawing ligands deeb and btfmb, the  $k_{nr}$  increases, relative to bpy, and the quantum yield decreases to 0.008 and 0.0015, respectively.

Compound	kobs (s <sup>-1</sup> )	<b>k</b> r ( <b>s</b> <sup>-1</sup> )	<b>k</b> nr ( <b>s</b> <sup>-1</sup> )	Φ
$[\text{Re(tmb)(CO)}_3(4\text{-Et-py})]^+$	6.9 x 10 <sup>5</sup>	$1.0 \ge 10^5$	5.9 x 10 <sup>5</sup>	0.148±0.001
$[\text{Re(bpy)(CO)}_3(4\text{-}\text{Et-py})]^+$	$4.4 \ge 10^6$	1.3 x 10 <sup>5</sup>	4.3 x 10 <sup>6</sup>	$0.029 \pm 0.001$
$[\text{Re}(\text{deeb})(\text{CO})_3(4\text{-}\text{Et-py})]^+$	1.25 x 10 <sup>7</sup>	$1.0 \ge 10^5$	1.2 x 10 <sup>7</sup>	$0.008 \pm 0.001$
[Re(btfmb)(CO) <sub>3</sub> (4-Et-py)] <sup>+</sup>	$5.0 \ge 10^7$	$7.7 \ge 10^4$	4.99 x 10 <sup>7</sup>	$0.0015 \pm 0.0002$

Table 2.2. Observed and calculated photophysical properties for the four Re(I) complexes.

## 2.5. Excited-State Quenching

The excited state of a molecule can be characterized in detail using the techniques described above. Most applications that utilize metal polypyridyl charge-transfer excited states require quenching of the excited state either bimolecularly or intramolecularly. The radiative and non-radiative deactivation pathways shown in Figure 2.4 are purely intramolecular, but when another species is present in solution there is potential for that molecule to react with, or quench, the excited state. This can be illustrated by expanding upon equation 2.2, resulting in an additional rate constant that is dependent on the concentration of quencher, [Q], and excited state, [ES], shown in equation 2.6.<sup>26</sup>

$$-\frac{d[ES]}{dt} = k_0[ES] + k_q[ES][Q]$$
(2.6)

There are three possible excited-state quenching mechanisms that has been discussed in detail in chapter 1, Dexter transfer, electron transfer, and Förster transfer. When identifying the excitedstate quenching mechanism it is crucial to understand the fundamental differences between each

mechanism. For example, Förster transfer is a non-radiative quenching mechanism where the dipole of the excited-state donor's emission couples to the dipole of the acceptor's ground-state absorption.<sup>31</sup> This is a through space interaction, therefore the donor-acceptor distance that is used to calculate the rate of energy transfer by this mechanism must be the through-space distance, i.e. not the through-bond distance. The most unique aspect of this quenching mechanism is the requirement for spectral overlap between the emission of the donor and the absorption of the acceptor. The necessity for spectral overlap ensures that the thermodynamics of the two electronic states are energetically matched. Due to the dipolar nature of this quenching mechanism the relative orientation between the emissive and absorptive dipoles can affect the rate of energy transfer. The orientation factor,  $\kappa$ , quantifies how the dipole orientation affects the coupling between them. The rate expression for Förster transfer is shown in equation 2.7 and consists of the dipole orientation factor,  $\kappa$ , the quantum yield of the donor (in the absence of the acceptor/quencher),  $\Phi_D$ , the spectral overlap integral, J, the refractive index of the solvent,  $\eta$ , Avogadro's number,  $N_A$ , the lifetime of the donor (in the absence of the acceptor/quencher),  $\tau_D$ , and the distance between the donor and acceptor, R.

$$k_{FRET} = \frac{9000 \ln(10)\kappa^2 \Phi_{\rm D}J}{128\pi^5 \eta^4 N_A \tau_{\rm D} R^6}$$
(2.7)

The spectral overlap integral, *J*, is shown in equation 2.8 where,  $\bar{I}_{\bar{\nu}}^{D^*}$ , is the normalized emission spectrum of the excited-state donor with respect to wavenumbers, and  $\varepsilon_A$ , is the molar absorptivity of the acceptor as a function of wavenumbers.<sup>32</sup>

$$J^{\overline{\nu}} = \int \frac{\bar{l}_{\overline{\nu}}^{D^*} \varepsilon_A(\overline{\nu})}{\overline{\nu}^4} d\bar{\nu}$$
(2.8)

The integrated area of the emission spectrum is normalized as shown in equation 2.9. The emission spectrum is then multiplied by the acceptors absorption spectrum and integrated to calculate *J*.

$$\int \bar{I}_{\bar{\nu}}^{D^*} d\bar{\nu} = 1 \tag{2.9}$$

The dipole orientation factor is a measure of the coupling between the donor's and acceptor's dipoles and is shown in equation 2.10.

$$\kappa^2 = (\cos\Theta_T - 3\cos\Theta_D \cos\Theta_A)^2 \tag{2.10}$$

Figure 2.8 illustrates how the orientation factor is measured where,  $\Theta_T$  is the angle between the donor transition dipole moment,  $r_D$ , and the acceptor transition dipole moment,  $r_A$ ,  $\Theta_D$  is the angle between the donor-acceptor connection line,  $R_{DA}$ , and the donor transition dipole moment, and  $\Theta_A$  is the angle between  $R_{DA}$  and the acceptor transition dipole moment.<sup>33</sup> The orientation factor can range from 0-4; when the dipoles are perpendicular  $\kappa^2 = 0$ , when they are parallel  $\kappa^2 =$ 1, and when they are aligned with one another along donor-acceptor connection line,  $R_{DA}$ ,  $\kappa^2 = 4$ .



Figure 2.8. Definitions of the angles used for calculating the orientation factor between the dipoles of the donor's emission and acceptor's absorbance.

Dexter transfer is an energy transfer quenching mechanism, but it is unique with respect to Förster transfer as it can be thought of as a simultaneous electron exchange between an excited-state donor and a ground-state acceptor.<sup>34</sup> This energy transfer pathway is a through-bond

mechanism requiring orbital overlap between donor and acceptor, therefore when considering the viability of this mechanism the through-bond distance between donor and acceptor should be considered. Due to this orbital overlap requirement the rate constant for Dexter transfer ( $k_{DET}$ ), shown in equation 2.11, has an exponential distance dependence, where r is the distance between donor and acceptor,  $r_c$  is the distance of closest approach at molecular contact, and  $\beta$  is the attenuation coefficient.

$$k_{DET} = Ae^{(-\beta(r-r_c))}$$
(2.11)

Dexter transfer can occur bimolecularly if the donor and acceptor are not covalently linked and will therefore require physical contact. When the donor and acceptor are covalently linked at distances greater than 10 Å the rate of Dexter energy transfer is not significant and can be ruled out as a viable quenching pathway.<sup>26</sup> The most fundamental difference between Förster transfer and Dexter transfer is that Dexter transfer does not require spectral overlap between the donor and acceptor, but requires much shorter through-bond distances between donor and acceptor. However, the thermodynamics of the excited-state donor and ground-state acceptor electronic states must be favorable (i.e  $\Delta G < 0$ ).

Excited-state electron transfer is the most distinct quenching mechanism where the excitedstate donor is either oxidized or reduced, referred to oxidative and reductive quenching respectively, resulting in chemically distinct products compared to the energy transfer mechanisms. As described in chapter 1, photo-induced electron transfer can be described using semi-classical Marcus theory, where the rate constant can be determined using equation 2.12.

$$k_{ET} = \frac{2\pi}{\hbar} |H_{AB}|^2 \frac{1}{\sqrt{4\pi\lambda k_B T}} exp\left[\frac{(-\Delta G^o + \lambda)^2}{4\lambda k_B T}\right]$$
(2.12)

The rate of electron transfer depends on the strength of electronic coupling,  $H_{AB}$ , between the donor and acceptor, the driving force,  $\Delta G^{\circ}$ , and the reorganization energy,  $\lambda$ . The electronic coupling between donor and acceptor is distance and orientation dependent.<sup>35-37</sup> The reorganization energy can be thought of as the amount of energy required to transform the reactants into the products while moving along a reaction coordinate without crossing into the products potential energy surface. This energy includes components from all vibrations in the molecules, inner-sphere reorganization energy, and from the changes in polarization from the solvent environment, outer-sphere reorganization energy.<sup>36,38</sup> The driving force for electron transfer depends on the redox potentials of the donor and acceptor and also the zero-point energy of the excited state,  $E_{00}$ .

The photo-induced electron transfer reactions that will be considered throughout this dissertation involve the Re(I)bpy MLCT excited state. Because of the charge-separation of this excited state it can serve as either a reductant, due to the negative charge localized on the bipyridine, or an oxidant, due to the hole on the Re(II) metal center. In either case we will consider this MLCT state as our excited-state donor and the quencher the acceptor. The Rehm-Weller equation can be used to calculate  $\Delta G$  for an excited-state electron transfer process to predict the endothermicity of the photo-induced process, shown in equation 2.13.<sup>39</sup>

$$\Delta G_{ox} = \left(Re_{ox}^{II/I}\right) - E_{00} - \left(Q_{red}^{0/-}\right)$$
(2.13a)

$$\Delta G_{red} = (Q_{ox}^{+/0}) - \left[ \left( bpy_{red}^{0/-} \right) + E_{00} \right]$$
(2.13b)

In the case of oxidative quenching, 2.13a, where the MLCT state is oxidized and the quencher is reduced, the driving force is determined by the oxidation potential of the rhenium,  $\text{Re}_{ox}^{II/I}$ , the zero-point energy of the excited state,  $E_{00}$ , and the reduction potential of the quencher,  $Q_{red}^{+/0}$ . The

endothermicity of reductive quenching of this excited state can be calculated using equation 2.13b, where  $bpy_{red}^{0/-}$  is the reduction potential of the bipyridine ligand and,  $Q_{ox}^{+/0}$  is the oxidation potential of the quencher.

## 2.6. Probing the Mechanism of Excited-State Reactivity

The techniques mentioned above can be used to characterize the basic photophysics of the excited state when no quenching is occurring. When quenching occurs, careful design of the system being studied can potentially rule out quenching pathways making mechanistic determinations easier. If the donor and acceptor are covalently linked, altering the distance between the donor and acceptor is possible, either favoring Dexter transfer by shortening D-A distances, or eliminating the Dexter pathway by lengthening D-A distances (> 10 Å).<sup>20</sup> The emission maximum of the excited-state donor in the case of Re(I)(bpy) moieties can be modulated by substituting the bpy ligand in the 4, 4', 5, and 5' positions either blue shifting the emission in the case of electron donating groups or red shifting the maximum with electron withdrawing substituents. This strategy can be utilized to either increase or decrease the spectral overlap with the acceptor's absorbance, affecting the rate of Förster transfer or if overlap does not exist eliminating it as a viable quenching pathway.<sup>33</sup> If quenching via electron transfer is occurring the redox potentials of the donor and acceptor can be modulated by either changing the ligand environment around the metal center or using different transition metals as the donor or acceptor centers. This can either favor electron transfer by increasing the driving force or rule out this mechanism if the change in free energy is prohibitively positive ( $\Delta G > +0.3$  V).

Using spectroscopic techniques that provide experimental evidence of the components of a quenching pathway is common. As mentioned previously, the products that result from electron transfer are chemically distinct from the products of energy transfer. One valuable technique that

can identify the photo-induced oxidized or reduced products is transient absorption spectroscopy (TA). TA is a pump-probe experiment, where a molecule is excited using a pulsed laser, pump beam, and then the absorption of the transiently created excited state is measured using a white light source, the probe beam. The absorption of the excited state is measured as a function of time and can be thought of taking a UV-Vis of the excited state where the ground-state absorption spectrum is used as a blank. The data collected is then plotted as a difference of optical density ( $\Delta$  O.D.) vs. time, where if an excited-state species absorbs more than the ground state a positive feature will be observed and if the ground state absorbs more than the excited state a negative feature, or bleach, will be observed.

Transient absorption for  $[\text{Re}(\text{bpy})(\text{CO})_3(4\text{-Etpy})](\text{OTf})$  has been well characterized over the past 40 years providing a standard of the photophysics for this excited-state donor in the absence of quenching.<sup>40-42</sup> The MLCT state is characterized by its broad positive absorption feature over the visible resulting from the bpy<sup>-</sup>. This assignment can be supported using spectroelectrochemistry which can be used to distinguish between the optical features that arise from the oxidized Re(II) metal center and reduced bpy<sup>-</sup> ligand.

Spectroelectrochemistry measures the change in absorbance with respect to time as bulk electrolysis is performed at an approximate 0.1 V over potential of the oxidation or reduction of interest. The reductive and oxidative spectroelectrochemistry of  $[\text{Re(bpy)(CO)}_3(4\text{-Et-py})]OTf$  is shown in Figure 2.9. The reductive spectrum was measured by applying a potential of -1.66 V (vs. Fc/Fc<sup>+</sup>) and measuring the change in absorbance at 30 second intervals. The positive absorption features from 400-875 nm are diagnostic of  $\pi$ - $\pi$ \* transitions from the bpy radical anion.<sup>43</sup> The oxidative spectrum was measured by applying a potential of 1.47 V (vs. Fc/Fc<sup>+</sup>) and measuring the change in absorbance at 30 second intervals. The positive absorbance at 40 second intervals.



Figure 2.9. Reductive spectroelectrochemistry (left) of  $[Re(bpy)(CO)_3(4-Et-py)]OTf$  in MeCN with 0.1 M TBAPF<sub>6</sub> at -1.66 V (vs. Fc/Fc<sup>+</sup>). The absorbance spectra are acquired at 30 second intervals and progress from red to blue. Oxidative spectroelectrochemistry (right) of  $[Re(bpy)(CO)_3(4-Et-py)]OTf$  in MeCN with 0.1 M TBAPF<sub>6</sub> as supporting electrolyte at 1.47 V (vs. Fc/Fc<sup>+</sup>). The absorbance spectra are acquired at 30 second intervals and progress from red to blue.

360 nm is referred to as a bleach and results from the lack of MLCT absorption due to oxidation of the metal center. Since both oxidation of the metal center and reduction of the ligand is occuring in the MLCT state the final traces of the oxidative and reductive spectroelectrochemistry can be added together to simulate the qualitative absorption spectrum of the MLCT state.<sup>43</sup> The transient



Figure 2.10. Added spectroelectrochemistry traces (left) and transient absorption spectrum of  $[\text{Re(bpy)}(\text{CO})_3(4\text{-Etpy})](\text{OTf})$  in MeCN ( $\lambda_{ex} = 370$  nm).

absorption spectrum collected for [Re(bpy)(CO)<sub>3</sub>(4- Et-py)]OTf agrees well with what is reported in the literature<sup>40</sup> and qualitatively matches the added spectroelectrochemistry traces, Figure 2.10.

Throughout this dissertation the Re(tmb) excited-state donor moiety will be studied and excited-state electron transfer is a viable pathway in some systems. The spectroelectrochemistry and transient absorption for [Re(tmb)(CO)<sub>3</sub>(4-Etpy)](OTf) was collected to serve as a standard to help identify if quenching via electron transfer occurs in the systems studied in the future chapters.



Figure 2.11. Reductive spectroelectrochemistry (left) of  $[Re(tmb)(CO)_3(4-Et-py)]OTf$  in MeCN with 0.1 M TBAPF<sub>6</sub> at -1.91 V (vs. Fc/Fc<sup>+</sup>). The absorbance spectra are acquired at 30 second intervals and progress from red to blue. Oxidative spectroelectrochemistry (right) of  $[Re(tmb)(CO)_3(4-Et-py)]OTf$  in MeCN with 0.1 M TBAPF<sub>6</sub> as supporting electrolyte at 1.43 V (vs. Fc/Fc<sup>+</sup>). The absorbance spectra are acquired at 30 second intervals and progress from red to blue.

The reductive and oxidative spectroelectrochemistry for  $[\text{Re}(\text{tmb})(\text{CO})_3(4-\text{Etpy})](\text{OTf})$  in MeCN is shown in Figure 2.11. The reductive spectroelectrochemistry was collected by applying a -1.91 V potential (vs. Fc/Fc<sup>+</sup>) and measuring the absorption at 30 second intervals, and shows positive absorption features that are diagnostic of  $\pi$ - $\pi$ \* transitions from the tmb radical anion. The oxidative spectroelectrochemistry for  $[\text{Re}(\text{tmb})(\text{CO})_3(4-\text{Etpy})](\text{OTf})$  in MeCN shows a negative feature at 360 nm and is assigned to the MLCT bleach due to the loss of this absorption feature upon oxidation to Re(II). The positive absorption feature at 340 nm occurs from the ligand-based  $\pi$ - $\pi^*$  transition which shifts in energy due to the change in oxidation state of the Re center. The positive feature observed at 450 nm can be assigned to a LMCT transition, where an electron from the tmb ligand is promoted into the singly occupied Re-based t<sub>2g</sub> orbital due to oxidation from Re(I) to Re(II). By adding the oxidative and reductive spectroelectrochemical spectra obtained at the last time interval, Figure 2.12 (left), the absorption of the MLCT state can be simulated qualitatively and used as a guide to interpret the transient absorption spectrum.<sup>43</sup> The simulated MLCT spectrum from spectroelectrochemistry is compared to the nanosecond transient absorption spectrum obtained for [Re(tmb)(CO)<sub>3</sub>(4-Etpy)](OTf) in MeCN, shown in Figure 2.12 (right). The MLCT bleach at 370 nm that is observed in the oxidative spectroelectrochemistry is not observed in the transient absorption spectrum is also observed in the oxidative spectroelectrochemistry and is indicative of the [Re<sup>II</sup>(tmb)(CO)<sub>3</sub>(4-Etpy)](OTf) species. The simulated MLCT absorption from the transient absorption from the transient absorption from the transient absorption from the transient absorption spectrum due to the positive absorption from the tmb radical anion spanning across the entire visible spectrum. At 335 nm the sharp positive absorption observed in the transient absorption from the transient absorption from the transient absorption spectrum is also observed in the oxidative spectroelectrochemistry and is indicative of the [Re<sup>II</sup>(tmb)(CO)<sub>3</sub>(4-Etpy)](OTf) species. The simulated MLCT absorption from



Figure 2.12. Added spectroelectrochemistry traces (left) and transient absorption spectrum of  $[\text{Re(tmb)}(\text{CO})_3(4\text{-Etpy})](\text{OTf})$  in MeCN ( $\lambda_{ex} = 360$  nm).

spectroelectrochemistry qualitatively agrees with the transient absorption spectrum, where the positive features from 400-700 nm can be assigned to the tmb radical anion absorption. The positive feature in the transient absorption spectrum at 335 nm matches the positive absorption from the oxidative spectroelectrochemistry and could potentially be used as a spectral tag for  $[\text{Re}^{II}(\text{tmb})(\text{CO})_3(4-\text{Etpy})](\text{OTf})$  in the event of oxidative quenching.

Transient absorption also measures the kinetics at each wavelength studied making it possible to deduce if quenching occurs from the excited state. Figure 2.13 shows the possible products formed from electron transfer with the MLCT state of  $[\text{Re(bpy)(CO)}_3(4-\text{Etpy})](\text{OTf})$  and a quencher, Q. When oxidative quenching of  $[\text{Re(bpy)}(\text{CO})_3(4-\text{Etpy})](\text{OTf})$  occurs  $[\text{Re}^{II}(\text{bpy})(\text{CO})_3(4-\text{Etpy})](\text{OTf})$  and Q<sup>-</sup> are formed, one would expect the lifetime of the MLCT state to decrease and the lifetime when probing the wavelengths attributed to the bpy radical anion absorption to decrease. In contrast, any signals that are attributed to the oxidized Re(II) center will remain. In this specific example, based on the spectroelectrochemistry, there are no probe wavelengths that are indicative of the oxidized Re(II) in the transient absorption spectrum, making it particularly important to detect absorption features related to Q<sup>-</sup>. In the event of reductive quenching  $[\text{Re}^{I}(\text{bpy}^{-})(\text{CO})_3(4-\text{Etpy})](\text{OTf})$  is formed and the lifetime from features inherent to the



Figure 2.13. Oxidative and reductive quenching diagram of the MLCT state for [Re(bpy)(CO)<sub>3</sub>(4-Etpy)]<sup>+</sup>.

oxidized Re(II) will be lost and the absorption from the bpy radical anion will persist. Reductive quenching is not observed in any of the systems studied throughout this dissertation. The same description can be used to describe oxidative and reductive quenching for  $[Re(tmb)(CO)_3(4-Etpy)](OTf)$  with the exception that  $[Re^{II}(tmb)(CO)_3(4-Etpy)](OTf)$  formed from oxidative quenching could potentially be observed (vide supra). The single wavelength data collected for  $[Re(bpy)(CO)_3(4-Etpy)](OTf)$  and  $[Re(tmb)(CO)_3(4-Etpy)](OTf)$  in the absence of any quencher is shown in Figure 2.14.



Figure 2.14. Single wavelength transient absorption data of  $[\text{Re(bpy)(CO)}_3(4\text{-Etpy})](\text{OTf})$  in MeCN (left) ( $\tau = 190$  ns,  $\lambda_{ex} = 370$  nm,  $\lambda_{probe} = 360$  nm) and  $[\text{Re(tmb)(CO)}_3(4\text{-Etpy})](\text{OTf})$  in MeCN (right) ( $\tau = 1.25 \text{ } \mu\text{s}$ ,  $\lambda_{ex} = 370$  nm,  $\lambda_{probe} = 390$  nm).

## 2.7. Conclusion

The class of Re(I)bpy complexes have been thoroughly studied in the literature and their ground-state and excited-state properties have been well established. Throughout this chapter the ground- and excited-state properties of Re(I) chromophores have been characterized. The specific Re(I) chromophores that were studied in this chapter will be employed in Chapters 3 and 4 via donor-acceptor systems to study the effects of spin on excited-state reactivity. The experimental

techniques used to study the ground-state and excited-state properties of the four Re(I) compounds discussed serve as standards to compare to the photophysics of the dinuclear donor-acceptor systems. By using electron donating substituents on the bpy ligand the MLCT absorption shifts to 360 nm compared to 370 nm in the unsubstituted complex. The electron withdrawing substituents btfmb and deeb are used to red shift the absorption to 390 nm and 400 nm, respectively. The electronic effects from the bpy ligands can be observed from the measured redox potentials, where the ligand based reduction potentials range from -1.81 – -1.17 V (vs. Fc/Fc<sup>+</sup>). Since the <sup>3</sup>MLCT involves the bpy-based  $\pi^*$  orbitals the electronic effects observed from the absorption profile and electrochemistry manifest in the excited-state dynamics. Spectroelectrochemistry and transient absorption for [Re(tmb)(CO)<sub>3</sub>(4-Etpy)](OTf) and [Re(bpy)(CO)<sub>3</sub>(4-Etpy)](OTf) were used to determine the spectroscopic features of excited-state electron transfer products. These studies will be used as a basis for determining the quenching mechanism in the dinuclear donor-acceptor systems. Data in future chapters will discuss the mechanisms of quenching for these excited-state donors and the concepts introduced in this chapter provide a foundational basis for future analysis.
APPENDIX



Figure 2.15. <sup>1</sup>H NMR of [Re(deeb)(CO)<sub>3</sub>)(4-Etpy)](OTf) in acetonitrile-*d*<sub>3</sub>.



Figure 2.16. ESI-MS of  $[Re(deeb)(CO)_3(4-Etpy)](OTf)$  (m/z: calcd for  $[M-(4-Etpy)-OTf]^+$  571.05, obs. 571.057; calcd for  $[M-(4-Etpy)-OTf+MeCN]^+$  612.08, obs. 612.081; calcd for  $[M-OTf]^+$  678.13, obs. 678.125).



Figure 2.18. <sup>1</sup>H NMR of [Re(btfmb)(CO)<sub>3</sub>)(4-Etpy)](OTf) in acetonitrile-*d*<sub>3</sub>.



Figure 2.19. ESI-MS of [Re(btfmb)(CO)<sub>3</sub>(4-Etpy)](OTf) (m/z: calcd for [M-OTf]<sup>+</sup> 670.06, obs. 670.062).



Figure 2.20 X-ray crystal structure of [Re(btfmb)(CO)<sub>3</sub>(4-Etpy)](OTf).



Figure 2.21. Cyclic voltammogram of  $[\text{Re(bpy)(CO)}_3(4\text{-Et-py})](\text{OTf})$  in MeCN with 0.1 M TBAPF<sub>6</sub> as supporting electrolyte, a scan rate or 200 mV/s, and internally referenced to Fc/Fc<sup>+</sup> (peak at 0 V). The peak at 1.37 V is assigned to the Re<sup>II/I</sup> oxidation, the peak at -1.56 V is assigned to the by<sup>0/-</sup> reduction.



Figure 2.22. Cyclic voltammogram of  $[Re(tmb)(CO)_3(4-Et-py)](OTf)$  in MeCN with 0.1 M TBAPF<sub>6</sub> as supporting electrolyte, a scan rate or 200 mV/s, and internally referenced to Fc/Fc<sup>+</sup> (peak at 0 V). The peak at 1.33 V is assigned to the Re<sup>II/I</sup> oxidation, the peak at -1.81 V is assigned to the bpy<sup>0/-</sup> reduction.



Figure 2.23. Cyclic voltammogram of  $[\text{Re}(\text{btfmb})(\text{CO})_3(4\text{-Et-py})](\text{OTf})$  in MeCN with 0.1 M TBAPF<sub>6</sub> as supporting electrolyte, a scan rate or 200 mV/s, and internally referenced to Fc/Fc<sup>+</sup> (peak at 0 V). The peak at 1.40 V is assigned to the Re<sup>II/I</sup> oxidation, the peak at -1.17 V is assigned to the bpy<sup>0/-</sup> reduction.



Figure 2.24. Differential pulse voltammogram of  $[\text{Re}(\text{btfmb})(\text{CO})_3(4-\text{Et-py})](\text{OTf})$  in MeCN with with 0.1 M TBAPF<sub>6</sub> as supporting electrolyte and internally referenced to Fc/Fc<sup>+</sup>. The peak at 1.44 V is assigned to the Re<sup>II/I</sup> oxidation and a second peak observed at 1.52 V is due to the irreversibility of the Re<sup>II/I</sup> oxidation.



Figure 2.25. Cyclic voltammogram of  $[\text{Re}(\text{deeb})(\text{CO})_3(4\text{-Et-py})](\text{OTf})$  in MeCN with 0.1 M TBAPF<sub>6</sub> as supporting electrolyte, a scan rate or 200 mV/s, and internally referenced to Fc/Fc<sup>+</sup> (peak at 0 V). The peak at 1.44 V is assigned to the Re<sup>II/I</sup> oxidation, the peak at -1.18 V is assigned to the bpy<sup>0/-</sup> reduction.

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# Chapter 3. Design and Synthesis of Re(I)-Cr(III) Dinuclear Donor-Acceptor Systems 3.1. Introduction

The effects of spin angular momentum that are linked to physical observables such as magnetism, UV-vis selection rules, and spin-orbit coupling are well documented. The field of spin chemistry has demonstrated that the reactivity of molecular systems can be largely affected by its spin.<sup>1-3</sup> While these spin effects pertaining to the ground-state reactivity have been investigated the effects that spin has on the excited-state reactivity is much less understood. The goal of this dissertation is to understand the role spin plays in affecting the excited-state quenching pathway with particular interest in how it can be leveraged to control the quenching mechanism.

Donor-acceptor systems containing a Re(I) donor and first-row transition metal acceptors have been used in the McCusker group to study excited-state energy transfer processes and provide a platform for further understanding how spin affects these processes.<sup>4-6</sup> Excited-state energy transfer can occur through either electron superexchange (Dexter)<sup>7</sup> or via through-space dipoledipole coupling (Förster).<sup>8</sup> Dexter transfer is a through-bond interaction requiring orbital overlap and the rate of energy transfer has an exponential distance dependence between donor and acceptor. Due to the short distance dependence of this mechanism it is a dominant pathway when the donor and acceptor are in close proximity (e.g. <10 Å). Förster transfer occurs when the dipole of the excited-state donor's emission couples to the dipole of the acceptor's ground-state absorption. This through space interaction requires spectral overlap between the emission of the donor and absorption of the acceptor ensuring the resonance condition necessary for dipole-dipole coupling and that the thermodynamics of the two electronic states are energetically matched. Unlike Dexter transfer, the rate of Förster transfer has a 1/R<sup>6</sup> distance dependence between donor and acceptor, making energy transfer possible up to 100 Å.<sup>9,10</sup>

$$k_{FRET} = \frac{9000 \ln(10)\kappa^2 \Phi_{\rm D}J}{128\pi^5 \eta^4 N_A \tau_D R^6}$$
(3.1)

The rate constant for Förster transfer can be calculated using equation 3.1 and consists of the dipole orientation factor,  $\kappa^2$ , the quantum yield of the donor (in the absence of the acceptor/quencher),  $\Phi_D$ , the refractive index of the solvent,  $\eta$ , Avogadro's number,  $N_A$ , the lifetime of the donor (in the absence of the acceptor/quencher),  $\tau_D$ , the distance between the donor and acceptor, R, and the spectral overlap integral, J. The overlap integral can be calculated using equation 3.2, where ,  $\bar{I}_{\bar{\nu}}^{D^*}$ , is the normalized emission spectrum of the excited-state donor with respect to wavenumbers, and  $\varepsilon_A$ , is the molar absorptivity of the acceptor as a function of wavenumbers.

$$J^{\overline{\nu}} = \int \frac{\bar{I}_{\overline{\nu}}^{D^*} \varepsilon_A(\overline{\nu})}{\bar{\nu}^4} d\bar{\nu}$$
(3.2)

The dipole orientation factor is a measure of the coupling between the donor's and acceptor's dipoles and is shown in equation 3.3.

$$\kappa^2 = (\cos\Theta_T - 3\cos\Theta_D \cos\Theta_A)^2 \tag{3.3}$$

The orientation factor can range from 0-4; when the dipoles are perpendicular  $\kappa^2 = 0$ , when they are parallel  $\kappa^2 = 1$ , and when they are aligned with one another along donor-acceptor connection line, R<sub>DA</sub>,  $\kappa^2 = 4$ . The strength of coupling between dipoles is dependent on their orientation to each other and affects the rate of Förster transfer.

The tetranuclear  $\text{Re}_3\text{Fe}$  systems introduced in Chapter 1 established how the rate of Förster transfer can be quantitatively calculated in a covalently linked transition metal-based system.<sup>4</sup> The donor-acceptor system features three Re(I)(bpy) (bpy = 2,2'-bipyridine) moieties as the excited-state

donor, via the <sup>3</sup>MLCT state, and an Fe(III) first-row transition metal acceptor shown in Figure 3.1, complexes 1-3. The donor and acceptor are covalently linked via the bridging ligand, pyacac (pyacac = (3-(4-pyridyl)-2,4-pentanedione)), which allows for the donor-acceptor distance to be experimentally measured from single crystal X-ray structure data. Based on the X-ray data, the through-bond distance between Re and Fe center is too large for Dexter transfer to be the operative quenching mechanism. The experimentally measured donor-acceptor distance and the lack of significant electron coupling between metal centers, determined from the v(CO) frequencies, ruled out Dexter transfer as the quenching mechanism. The Re(I)-based <sup>3</sup>MLCT emission and the Fe(III)-based <sup>6</sup>A<sub>1</sub> $\rightarrow$ <sup>6</sup>LMCT absorption fulfilled the spectral overlap requirement necessary for Förster transfer. Due to the donor and acceptor being covalently linked, the orientation of the donor's emissive dipole and the acceptor's absorptive dipole are fixed in space relative to one another. This allowed for  $\kappa^2$  to be accurately calculated providing a scenario where Förster theory could be used quantitatively to calculate the rate of energy transfer via this mechanism.



Figure 3.1. Tetranuclear donor-acceptor systems used to study excited-state quenching mechanisms.

Three different polypyridyl derivatives, bpy, tmb (tmb = 4,5,4',5'-tetramethyl-2,2'bipyridine), and deeb (deeb = 4,4'-diethylester-2,2'-bipyridine), were coordinated to Re(I) and the energy of the <sup>3</sup>MLCT emission is changed resulting in a change in spectral overlap. The changes in spectral overlap are in agreement with the trend of rate constants determined from time-resolved spectroscopy. The agreement between calculated and observed Förster rate constants coupled with the estimated driving force for photo-induced electron transfer conclude that Förster transfer is the quenching mechanism.

The Re<sub>3</sub>Fe complexes provided a covalently linked donor-acceptor system where its design favored the Förster mechanism and allows for other variables to be studied within the same structural motif. A second series of tetranuclear compounds were studied using Cr(III) and Co(III) as acceptors to study how spin affects excited-state quenching using the same design principles and structural motifs as the previous system, Figure 3.1 complexes  $4-9.^{6}$  The Re<sub>3</sub>M (M = Cr(III) or Co(III)) complexes featured the same Re(I)bpy excited-state donor and the same bridging ligand to maintain a similar Re-M distance. The design of this system allows for Förster transfer to be the dominant quenching mechanism as long as spectral overlap persists. In the Re<sub>3</sub>Cr compounds the  ${}^{4}A_{2} \rightarrow {}^{4}T_{2}$  absorption from the Cr(III)(acac) (acac = acetylacetonate) core satisfies the spectral overlap condition required for the dipolar mechanism. This absorption is not charge-transfer in nature, unlike the Fe(III) LMCT in the previous system, and the dipole for the acceptor resides on the Cr(III) center. This results in a minor change in the donor-acceptor distance but is still outside the limits of Dexter transfer. The unfavorable thermodynamics for photo-induced electron transfer along with the trend in the spectral overlap corresponding to the change in quenching rate constant established Förster transfer as the quenching mechanism. The Re<sub>3</sub>Co compounds studied were also expected to engage in the dipolar quenching mechanism due to the  ${}^{1}A_{1} \rightarrow {}^{1}T_{1}$  absorption providing spectral overlap between donor and acceptor. Due to the change in spin between Co(III) (S = 0) and Cr(III) (S = 3/2) quenching of the <sup>3</sup>MLCT state was not observed in the Co compounds. This observation was the first report of spin dependence in excited-state reactivity and was explained through the spin conservation model introduced in Chapter 1.

To provide a fundamental understanding of the effects of spin conservation on excitedstate reactivity this chapter focuses on the design, synthesis, and characterization of dinuclear ReCr compounds shown in Figure 3.2. The dimensional reduction of the tetranuclear system to a dinuclear system allows for easier synthetic modifications in the future to expand upon the spin dependence on excited-state quenching. The same essential components from the tetranuclear systems are still present in the dimensionally reduced system: a Re(I)(bpy) donor, the same firstrow transition-metal acceptors, and the same bridging ligand between donor and acceptor. A tripodal capping ligand, tris(2-aminoethyl)amine (tren), will be used to only allow one Re(I)(bpy) moiety to be linked to the acceptor. Provided that the coordination environment around the Cr(III) does not remove the spectral overlap and does not make excited-state electron transfer exergonic the ReCr dinuclear compounds should follow the exact same quenching pathway as the tetranuclear analogues. Three ReCr complexes will be characterized and the bpy derivatives used will alter the spectral overlap and should result in a change in the Förster rate constant. The first



Figure 3.2. Dimensionally reduced CrRe donor-acceptor complexes CrRe(bpy) (1), CrRe(deeb) (2), and CrRe(tmb) (3).

goal of this project and the focus of this chapter will be to determine if the dinuclear compounds follow the same spin conservation effects as the tetranuclear complexes.

## **3.2. Experimental**

#### 3.2.1. Synthesis

**General.** The tmb,<sup>11</sup> deeb,<sup>12</sup> and pyacac (3-(4-pyridyl)-2,4-pentanedione)<sup>13</sup> ligands were prepared according to the literature procedures. Re(CO)<sub>3</sub>(bpy)Cl,<sup>14</sup> Re(CO)<sub>3</sub>(tmb)Cl,<sup>14</sup> Re(CO)<sub>3</sub>(deeb)Cl,<sup>15</sup> [Re(CO)<sub>3</sub>(bpy)(pyacac)]OTf,<sup>6</sup> [Re(CO)<sub>3</sub>(tmb)(pyacac)]OTf,<sup>6</sup> and [Re(CO)<sub>3</sub>(deeb)(pyacac)]OTf<sup>6</sup> were prepared according to the literature procedures.  $Cr(tren)Cl_3^{16}$  and  $Na(acac)^{17}$  (acac = acetlyacetonate) were prepared from literature procedures. Re(CO)<sub>5</sub>Cl was purchased from Sigma Aldrich and bpy was purchased from Oakwood Chemicals and used as received. 4-Methyl pyridine was purchased from Sigma Aldrich and distilled over CaH2 under vacuum prior to use. Tris(2aminoethyl)amine (tren) was distilled under reduced pressure over KOH and activated carbon twice prior to use. Acetyl Chloride was purchased from Sigma Aldrich and distilled prior to use. Silver triflate was purchased from Oakwood Chemical and stored in a nitrogen glovebox. Tetrahydrofuran and Methanol were purchased from Sigma Aldrich and dried over neutral alumina under nitrogen. Triethylamine was distilled over KOH and activated carbon prior to use. Sizeexclusion chromatography was performed with SorbaDex lipophilic hydrophilic gel filtration matric (Sorbtech). <sup>1</sup>H NMR were collected on an Agilent DDR2 500 MHz spectrometer at the Max T. Rogers NMR facility at Michigan State University and referenced to residual solvent shifts. Electrospray ionization mass spectra were obtained at the Michigan State University Mass Spectrometry and Metabolomics Core on a Water G2-XS QTof mass spectrometer interfaced to a Waters Aquity UPLC. Elemental analyses were obtained through the analytical facilities at Michigan State University on samples that had been dried under vacuum overnight and ground in a vial in an Ar glovebox prior to analysis.

[Cr(tren)(acac)](OTf)<sub>2</sub>. A suspension of Cr(tren)Cl<sub>3</sub> (0.25 g, 0.824 mmol) and AgOTf (0.630 g, 2.47 mmol) in 20 mL of MeOH was stirred at room temperature in the dark overnight under nitrogen. The white precipitate was filtered over celite and washed with MeOH. Na(acac) (0.100 g, 0.824 mmol) was added to the pink solution and stirred at room temperature under nitrogen for 24 hours. The solvent was removed under reduced pressure and purified using neutral alumina chromatography (3:1 MeCN:H<sub>2</sub>O), the product was collected in the first red band. The product was further recrystallized from methanol and ether yielding a red solid (30%, 0.150 g). HRMS (ESI-TOF) m/z: [M-(OTf)]<sup>+</sup> calcd for [C<sub>12</sub>H<sub>25</sub>N<sub>4</sub>O<sub>5</sub>F<sub>3</sub>SCr] 446.090, obs. 446.093. Elemental analysis: Anal. calcd (Found) for C<sub>13</sub>H<sub>25</sub>N<sub>4</sub>O<sub>8</sub>S<sub>2</sub>F<sub>6</sub>Cr: C 26.22 (26.11) H 4.23 (4.34) N 9.41 (9.32).

[**Re(bpy)(CO)**<sub>3</sub>(**pyacac)Cr(tren)**](**OTf)**<sub>3</sub>. A suspension of Cr(tren)Cl<sub>3</sub> (0.20 g, 0.66 mmol) and AgOTf (0.512 g, 1.99 mmol) in MeOH (20 mL) was stirred at room temperature in the dark overnight under nitrogen. The purple solution was filtered over celite and washed with MeOH. [Re(bpy)(CO)<sub>3</sub>(pyacac)]OTf (0.50 g, 0.66 mmol) was dissolved in MeOH (10 mL) and NEt<sub>3</sub> (0.067 g, 0.66 mmol) was added resulting in a dark orange/brown solution. The [Re(bpy)(CO)<sub>3</sub>(pyacac)] solution was added dropwise to a stirring solution of Cr(tren)(OTf)<sub>3</sub> and heated to 50 °C for one hour. The solution was cooled to room temperature and the volume was reduced to 10 mL under reduced pressure and filtered using cotton. The product was purified using size-exclusion chromatography in MeOH and the product was collected in the orange band and recrystallized from MeCN/ether (0.132 g, 16%). HRMS (ESI-TOF) m/z: [M-(OTf)]<sup>+</sup> calcd for [C<sub>31</sub>H<sub>36</sub>N<sub>7</sub>O<sub>11</sub>S<sub>2</sub>F<sub>6</sub>CrRe] 1099.08, obs. 1099.073; Elemental analysis: Anal. calcd (Found) for C<sub>32</sub>H<sub>36</sub>N<sub>7</sub>O<sub>14</sub>S<sub>3</sub>F<sub>9</sub>CrRe: C 30.80 (30.65) H 2.91 (3.16) N 7.86 (7.82).

[**Re(tmb)(CO)<sub>3</sub>(pyacac)Cr(tren)](OTf)<sub>3</sub>.** A suspension of Cr(tren)Cl<sub>3</sub> (0.081 g, 0.265 mmol) and AgOTf (0.204 g, 0.797 mmol) in acetone (10 mL) was stirred at room temperature in the dark overnight under nitrogen. The purple solution was filtered over celite and washed with acetone. [Re(tmb)(CO)<sub>3</sub>(pyacac)]OTf (0.215 g, 0.265 mmol) was dissolved in MeOH (10 mL) and NEt<sub>3</sub> (0.027 g, 0.265 mmol) was added. The [Re(tmb)(CO)<sub>3</sub>(pyacac)] solution was added dropwise to a stirring solution of Cr(tren)(OTf)<sub>3</sub> and refluxed for 2 hours. The solution was cooled to room temperature and the solvent was removed under reduced pressure, dissolved in MeCN and filtered using cotton. The product was purified using size-exclusion chromatography in MeOH and the product was collected in the red band and recrystallized from MeCN/ether (0.093 g, 27%). HRMS (ESI-TOF) m/z: [M-(OTf)]<sup>+</sup> calcd for [C<sub>35</sub>H<sub>44</sub>N<sub>7</sub>O<sub>11</sub>S<sub>2</sub>F<sub>6</sub>CrRe] 1155.14, obs. 1155.133; Elemental analysis: Anal. calcd (Found) for C<sub>36</sub>H<sub>44</sub>N<sub>7</sub>O<sub>14</sub>S<sub>3</sub>F<sub>9</sub>CrRe: C 33.16 (33.02) H 3.40 (3.53) N 7.52 (7.57).

[Re(deeb)(CO)<sub>3</sub>(pyacac)Cr(tren)](OTf)<sub>3</sub>. A suspension of Cr(tren)Cl<sub>3</sub> (0.123 g, 0.405 mmol) and AgOTf (0.312 g, 1.21 mmol) in acetone (10 mL) was stirred at room temperature in the dark overnight under nitrogen. The purple solution was filtered over celite and washed with acetone. [Re(deeb)(CO)<sub>3</sub>(pyacac)]OTf (0.364 g, 0.405 mmol) was dissolved in MeOH (10 mL) and NEt<sub>3</sub> (0.041 g, 0.405 mmol) was added. The [Re(deeb)(CO)<sub>3</sub>(pyacac)] solution was added dropwise to a stirring solution of Cr(tren)(OTf)<sub>3</sub> and refluxed for 2 hours. The solution was cooled to room temperature and the solvent was removed under reduced pressure, dissolved in MeCN and filtered using cotton. The product was purified using size-exclusion chromatography in MeOH and the product was collected in the orange band and recrystallized from MeCN/ether (0.184 g, 33%). HRMS (ESI-TOF) m/z: [M-(OTf)]<sup>+</sup> calcd for [C<sub>37</sub>H<sub>44</sub>N<sub>7</sub>O<sub>15</sub>S<sub>2</sub>F<sub>6</sub>CrRe] 1243.12, obs. 1243.116;

Elemental analysis: Anal. calcd (Found) for C<sub>38</sub>H<sub>44</sub>N<sub>7</sub>O<sub>18</sub>S<sub>3</sub>F<sub>9</sub>CrRe: C 32.78 (32.61) H 3.19 (3.32) N 7.04 (7.01).

#### 3.2.2. Physical Characterization

**X-ray structure determination.** Single-crystal X-ray diffraction data were acquired and the structures were solved by Dr. Richard Staples at the X-ray Facility of Michigan State University. The crystal structures have been submitted to the CCDC database and can be accessed by their CCDC accession numbers:  $[Re(deeb)(CO)_3(pyacac)Cr(tren)](OTf)_3$  (1946955) and  $[Cr(tren)(acac)](OTf)_2$  (1862969).

**Ground-state absorption spectroscopy.** All spectra were collected using spectrophotometric grade acetonitrile in 1 cm quartz cuvettes and acquired using a Cary 50 spectrophotometer.

**Electrochemistry.** Electrochemical measurements were collected using a CH instruments model CHI620D electrochemical workstation in an Ar-filled dry box. A standard three-electrode setup was used to determine the redox potentials via cyclic voltammetry in acetonitrile solutions using 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) as supporting electrolyte, a Pt disc working electrode, a Ag wire pseudo-reference electrode, and a platinum wire counter electrode. Cyclic voltammetrey was performed with a scan rate of 200 mV/s and Fc/Fc<sup>+</sup> was used as an internal reference. TBAPF<sub>6</sub> was purchased from Oakwood Chemical and recrystallized from ethanol twice before use.

**Spectroelectrochemistry.** UV-Visible spectroelectrochemical experiments were performed in a Pine Instruments electrochemical cell in an Ar-filled dry box. The 1 cm x 1 cm space at the top of the cell held the Ag reference electrode while the Pt working electrode and counter electrode were placed in the 1.7 mm x 10 mm path length window at the bottom of the cell to electrolyze the

solution while the absorbance was recorded with SI420 CCD spectrometer. Data were acquired on solutions identical to that just described for the electrochemical measurements, with the exception that solutions of each compound were adjusted to have absorbance values in the range of  $0.6 \pm 0.1$  at the maximum of the MLCT absorption peak. A ground-state absorption spectrum was taken prior to the onset of bulk electrolysis at an over potential of 0.1 V - 0.2 V relative to the redox potential of the compound.

Steady-State Emission and Time-Resolved Emission and Absorption. All samples were prepared in an argon-filled glovebox, using air-free cuvettes and solvents were freeze-pump-thaw degassed prior to use. For steady-state and time-resolved emission spectroscopy the absorbance of the sample at the MLCT maximum was between 0.1 - 0.2.

Steady-state emission spectra were collected using a Horiba Fluorolog-3 fluorimeter and corrected for instrumental response using a NIST standard of spectral irradiance (Optronic Laboratories, Inc., OL220 M tungsten quartz lamp). The resulting emission spectra were fit with an asymmetric double sigmoidal function using IGOR pro. This function has no mathematical significance but it is able to accurately reproduce the shape of the entire emission curve and capture the small area (< 10%) that lies outside of the detector range providing a more accurate estimate of the integrated spectrum. Relative quantum yields of emission ( $\Phi_x$ ) were calculated using [Re(bpy)(CO)<sub>3</sub>(4-Etpy)](OTf) in acetonitrile as a standard ( $\Phi_{std} = 0.029$ ) which was calculated as a relative quantum yield using [Ru(bpy)<sub>3</sub>](PF<sub>6</sub>) in deaerated MeCN as a standard. Quantum yields were calculated using equation 3.4, where x refers to the molecule of interest and *std* to the standard; *I<sub>x</sub>* and *I<sub>std</sub>* are the integrated areas of the corrected emission spectra, *A<sub>x</sub>* and *A<sub>std</sub>* are the absorbances at the excitation wavelength, and  $\eta_x$  and  $\eta_{std}$  are the indices of refraction of the solutions.

$$\Phi_{\chi} = \Phi_{std} \left( \frac{I_{\chi}/A_{\chi}}{I_{std}/A_{std}} \right) \left( \frac{\eta_{\chi}}{\eta_{std}} \right)^2$$
(3.4)

The zero-point energy gap ( $E_{00}$ ) was estimated by a single mode fit of the steady-state emission spectrum as described by Claude and Meyer.<sup>18</sup> The spectrum was corrected according to Parker and Reese when converting from wavelength to energy units.<sup>19</sup>

Picosecond time-resolved emission data for the CrRe complexes were collected by Professor Gary Blanchard using time-correlated single photon counting (TCSPC) with an apparatus that has been described previously.<sup>20</sup>

**Low-temperature steady-state emission spectroscopy.** Steady-state emission at 77 K were collected on samples prepared in an Ar glovebox in spectroscopic grade 1:4 MeOH/EtOH in sealed quartz test tubes with a round cross section and an absorbance at the excitation wavelength of 0.3. Data were collected on Hamamatsu Photonic Quantaurus absolute PL QY spectrometer (C11347) using the liquid nitrogen accessory.

**Förster Energy Transfer Rate Calculations.** Calculations of energy transfer rates were carried out based on equations 3.1-3. The donor-acceptor distances were measured using the single-crystal X-ray structure data of [Re(deeb)(CO)<sub>3</sub>(pyacac)Cr(tren)](OTf)<sub>3</sub> using the centroid of the bpy ligand as the point dipole for the donor and the Cr atom as the point dipole for the acceptor. The crystals of [Re(deeb)(CO)<sub>3</sub>(pyacac)Cr(tren)](OTf)<sub>3</sub> were twined and two independent molecules crystallized in the asymmetric unit. The donor-acceptor distance was measured at 9.9016(33) Å and 10.0151(29) Å. The standard deviation reflects the error in the calculation of the centroid - Cr distance while the difference in distance between the two crystals further reflects the error in D-A distance. Obtaining X-ray quality crystals for complexes **1** and **3** were unsuccessful, however, substituent changes on the periphery of the bipyridyl ligand will have little effect on the structural

features affecting the donor-acceptor distance. The averaged centroid – Cr distance, 9.9583 Å, was used to calculate the rate constants for complexes **1** - **3**. Since the nature of the ligand field state acting as the excited-state acceptor lacks one specific direction for the point dipole the orientation factor,  $\kappa^2$ , was approximated to be 2/3.  $\Phi_D$  and  $\tau_D$  values used are reported in Chapter 2. A more in depth explanation of calculating Förster rate constants can be found in these references.<sup>21,22</sup>

# **3.3. Results and Discussion**

## 3.3.1. Synthesis

There are two general synthetic routes that can be employed for the dimensionally reduced systems. The pyacac bridging ligand can either be bound to the Re first via the pyridyl ring or the Cr via the acac. The synthesis of  $[Re(bpy)(CO)_3(pyacac)]^+$  type molecules have been reported previously and was used for the synthesis of the tetranuclear compounds. The synthesis of Cr(tren)Cl<sub>3</sub> has also been reported in the literature providing a strong precedent for following the synthetic route depicted in Figure 3.3 (top). The displacement of the chloride ligands on the Cr(III) would then afford the desired compounds, due to the lability, or lack thereof, of Cr(III) a silver salt can be used to displace the chloride ions with a less coordinating ion. The ideal silver salt is silver



Figure 3.3. Synthetic route for dinuclear compounds using previously published starting materials (top) and an alternate route (bottom).

triflate (AgOTf) because the [Re(bpy)(CO)<sub>3</sub>(pyacac)]<sup>+</sup> precursors are isolated as triflate salts preventing mixed salts of the dinuclear complex from forming, and triflate is a weaker ligand than chloride making the ligand substitution easier. However, the formation of fluoride adducts when high-valent metals have open/weak coordination sites has been observed. The purity of the compounds studied is extremely important so the correct interpretation of the photophysical data is reported. Due to the paramagnetic Cr(III) center in the compounds <sup>1</sup>H NMR was not useful for the characterization of these compounds and HRMS was used to identify the products. The [M-(OTf)]<sup>+</sup> ion was detected by HRMS for each compound along with mono- and bis-fluoride adducts, but the desired compounds were isolated using size-exclusion chromatography in MeOH. Fragments of the dinuclear compounds containing only Cr and Re were also observed in HRMS, but performing HRMS-MS on the [M-(OTf)]<sup>+</sup> ion confirmed that these fragments result from fragmentation in the mass spectrometer and are not impurities.

# 3.3.2. Ground-State Characterization of CrRe Compounds

The individual acceptor,  $[Cr(tren)(acac)](OTf)_2$ , and individual donors, introduced and characterized in Chapter 2, were characterized to understand the ground-state and excited-state characteristics of the CrRe complexes. The UV-vis spectra of  $[Cr(tren)(acac)](OTf)_2$  and the three CrRe compounds are shown in Figure 3.4 where the LMCT absorption in  $[Cr(tren)(acac)](OTf)_2$  is centered at 30,000 cm<sup>-1</sup> and overlaps with the MLCT absorption of the donor-acceptor compounds. As the MLCT absorption is shifted to lower energy with electron-withdrawing substituents on the bpy ligand the overlap with the LMCT decreases but now overlaps with the <sup>4</sup>A<sub>2</sub>  $\rightarrow$  <sup>4</sup>T<sub>2</sub> Cr ligand field absorption (Figure 3.4 inset). The molar absorptivity for the <sup>4</sup>T<sub>2</sub> absorption centered at 19,500 cm<sup>-1</sup> for  $[Cr(tren)(acac)]^{2+}$ ,  $[Re(bpy)(CO)_3(pyacac)Cr(tren)]^{3+}$ , and  $[Re(tmb)(CO)_3(pyacac)Cr(tren)]^{3+}$  is 125 M<sup>-1</sup>cm<sup>-1</sup> and are measured within experimental error of



Figure 3.4. Ground-state absorption spectrum of **1** (green), **2** (red), **3** (blue), and  $Cr(tren)(acac)](OTf)_2$  (black) in MeCN. Inset: ground-state absorption of the  ${}^{4}A_{2} \rightarrow {}^{4}T_{2}$ . each other. The MLCT absorption for [Re(deeb)(CO)<sub>3</sub>(pyacac)Cr(tren)]<sup>3+</sup> overlaps with the ligand field absorption obscuring the  $\lambda_{max}$ , but the shoulder at 18,000 cm<sup>-1</sup> agrees well with the other compounds.

The IR spectrum for  $[\text{Re(bpy)(CO)}_3(\text{pyacac})\text{Cr(tren)}]^{3+}$  is shown in Figure 3.19 and the v(CO) stretching bands were assigned based on the previously reported data for *fac*- $[\text{Re(bpy)(CO)}_3(4\text{-Etpy})](\text{PF}_6)$  complexes.<sup>23</sup> The two v(CO) bands are observed at 2030 cm<sup>-1</sup> and 1905 cm<sup>-1</sup> where the lower energy band consists of the overlapping transitions assigned to the A'(2) and A'' modes in C<sub>s</sub> symmetry and the higher energy band is assigned to the A'(1) mode.<sup>24</sup> The energy ordering of these bands are A'(1) > A'(2) > A''. These carbonyl stretching frequencies match the reported literature values indicating there is minimal electronic coupling between the Re(I) and Cr(III) metal centers.<sup>25</sup>

#### 3.3.3. Excited-State Characterization

To determine the validity of using the dimensionally reduced dinuclear complexes as a platform to study spin conservation effects in excited-state reactivity time-resolved and steady-state emission experiments were used to characterize the photophysics of the excited states in compounds 1-3. Time-resolved experiments are used to determine if there is a change in lifetime between the donor-acceptor compounds and the individual donors studied in Chapter 2 to assess if quenching is occurring. Steady-state emission is used to compare the quantum yields and calculate the radiative and non-radiative rate constants to determine the rate of quenching and compare it the calculated rate of Förster transfer.

Time-correlated single photon counting (TCSPC) data was collected by Professor Gary Blanchard to measure the lifetime of the <sup>3</sup>MLCT state and is shown in Figure 3.5. The excitation wavelength used for compounds **1**– **3** were  $\lambda_{ex} = 380$  nm,  $\lambda_{ex} = 400$  nm, and  $\lambda_{ex} = 370$  nm, respectively. The kinetics of the <sup>3</sup>MLCT state were probed at the emission maximum for each compound which were determined from the steady-state emission spectra (vide infra),  $\lambda_{probe} = 580$ nm,  $\lambda_{probe} = 650$  nm, and  $\lambda_{probe} = 535$  nm for compounds **1**– **3**, respectively. All three decay traces could be fit with single-exponential decays which resulted in lifetimes of  $\tau = 12.5$  ns ( $k_{obs} = 8.0$  x  $10^7$  s<sup>-1</sup>),  $\tau = 4.2$  ns ( $k_{obs} = 2.5 \times 10^8$  s<sup>-1</sup>), and  $\tau = 13.0$  ns ( $k_{obs} = 7.7 \times 10^7$  s<sup>-1</sup>) for complexes **1**, **2**, and **3**, respectively (Table 3.1). The lifetimes of the individual Re donors are shown in the inset of Figure 3.5 and were fit with single-exponential decays resulting in lifetimes of  $\tau = 225$  ns ( $k_{obs} =$  $4.4 \times 10^6$  s<sup>-1</sup>),  $\tau = 80$  ns ( $k_{obs} = 1.25 \times 10^7$  s<sup>-1</sup>), and  $\tau = 1.45$  µs ( $k_{obs} = 6.9 \times 10^5$  s<sup>-1</sup>) for [Re(bpy)(CO)<sub>3</sub>(4-Etpy)]OTf, [Re(deeb)(CO)<sub>3</sub>(4-Etpy)]OTf, and [Re(tmb)(CO)<sub>3</sub>(4-Etpy)]OTf, respectively. The observed rate constants for the CrRe dinuclear compounds are increased by 1

$$k_q(CrRe) = k_{obs}(CrRe) - k_{obs}Re$$
(3.5)



Figure 3.5. (a) TCSPC data for [Re(bpy)(CO)<sub>3</sub>(pyacac)Cr(tren)](OTf)<sub>3</sub> ( $\lambda_{ex} = 380$  nm,  $\tau = 12.5$  ns). Inset: Time-resolved emission of [Re(bpy)(CO)<sub>3</sub>(4-Etpy)](OTf) ( $\lambda_{ex} = 370$  nm,  $\tau = 225$  ns). (b) TCSPC data for [Re(tmb)(CO)<sub>3</sub>(pyacac)Cr(tren)](OTf)<sub>3</sub> ( $\lambda_{ex} = 370$  nm,  $\tau = 13.0$  ns). Inset: Time-resolved emission of [Re(tmb)(CO)<sub>3</sub>(4-Etpy)](OTf) ( $\lambda_{ex} = 370$  nm,  $\tau = 1.45$  µs). (c) TCSPC data for [Re(deeb)(CO)<sub>3</sub>(pyacac)Cr(tren)](OTf)<sub>3</sub> ( $\lambda_{ex} = 400$  nm,  $\tau = 4.2$  ns). Inset: Time-resolved emission of [Re(deeb)(CO)<sub>3</sub>(4-Etpy)](OTf) ( $\lambda_{ex} = 410$  nm,  $\tau = 80$  ns). All data were collected in MeCN and fit to a single-exponential decay (red line). (d) Structures of the CrRe dinuclear compounds 1–3.

order of magnitude in the case of compounds **1** and **2** and two orders of magnitude for compound **3**. The decreased lifetimes in the donor-acceptor systems is indicative of quenching to the Cr(III) acceptor and the rate constant,  $k_q$ , can be calculated using equation 3.5, where the  $k_r$  and  $k_{nr}$  for the <sup>3</sup>MLCT state of a given CrRe compound are assumed to be equivalent to the corresponding individual Re donor (Table 3.1).

The steady-state emission spectra for compounds 1 - 3 are shown in Figure 3.6 and were collected in MeCN at room temperature. The emission profiles observed are in agreement with the  ${}^{3}MLCT \rightarrow {}^{1}A_{1}$  phosphorescence that has previously been reported for Re(I) polypyridyls.<sup>26</sup> The gradual shifting of the emission maxima for the tmb (535 nm), bpy (580 nm), and deeb (650 nm)



Figure 3.6. Steady-state emission spectra for CrRe(bpy) (green trace,  $\lambda_{ex} = 370$  nm), CrRe(deeb) (red trace,  $\lambda_{ex} = 410$  nm), and CrRe(tmb) (blue trace,  $\lambda_{ex} = 360$  nm) in MeCN and were fit to an asymmetric double sigmoidal function (dotted lines). The UV-vis of [Cr(tren)(acac)](OTf)<sub>2</sub> (black trace) in MeCN demonstrates the spectral overlap between <sup>3</sup>MLCT emission and <sup>4</sup>A<sub>2</sub>  $\rightarrow$  <sup>4</sup>T<sub>2</sub> absorption.

complexes are a consequence of the electron donating ability of the tmb ligand and withdrawing ability of deeb.

The quantum yields were calculated using equation 3.4 and using  $[\text{Re}(\text{bpy})(\text{CO})_3(4-\text{Etpy})]\text{OTf}$  as a standard (Table 3.1). The quantum yield of **1** ( $\Phi = 0.0024$ ) decreases by an order of magnitude, where the quantum yield of **3** ( $\Phi = 0.0020$ ) decreases by 3 orders of magnitude, and **2** ( $\Phi = 0.0013$ ) decreases 8-fold when compared to their respective Re standards. The radiative, k<sub>r</sub>, and non-radiative, k<sub>nr</sub>, rate constants are calculated for compounds **1** – **3** and the k<sub>r</sub> for each compound are within error of each other indicating that the change in the observed rate constant is due to an increase in the k<sub>nr</sub>, consistent with <sup>3</sup>MLCT quenching via the Cr<sup>III</sup> acceptor (Table 3.1).

## 3.3.4. Mechanistic Considerations

From the time-resolved and steady-state emission data there is a significant increase in  $k_{nr}$  for compounds 1 - 3 relative to their respective Re donors indicating that quenching of the Rebased <sup>3</sup>MLCT is occurring. As detailed in Chapter 2 there are three possible mechanisms for excited-state quenching, energy transfer by either the Förster or Dexter mechanism or electron

Compound	τ (kobs s <sup>-1</sup> )	Φ	<b>k</b> nr ( <b>s</b> <sup>-1</sup> )	$\mathbf{k}_{\mathbf{r}}\left(\mathbf{s}^{\mathbf{-1}}\right)$	<b>k</b> q ( <b>s</b> <sup>-1</sup> )
CrRe(bpy) (1)	12.5  ns	0.0024±0.0002	7.9 x 10 <sup>7</sup>	$2.0 \ge 10^5$	$7.56 \ge 10^7$
[Re(bpy)(CO) <sub>3</sub> (4-Etpy)] <sup>+</sup>	$(8.0 \times 10^7)$ 225 ns	0.0287±0.0001	4.3 x 10 <sup>6</sup>	1.3 x 10 <sup>5</sup>	-
CrRe(deeb) (2)	$(4.4 \text{ x } 10^6)$ 4.0 ns	0.0013±0.0002	2.49 x 10 <sup>8</sup>	$3.2 \times 10^5$	$2.38 \times 10^8$
	$(2.5 \times 10^8)$				
[Re(deeb)(CO) <sub>3</sub> (4- Etpy)] <sup>+</sup>	80  ns (1.25 x 10 <sup>7</sup> )	0.0080±0.0001	1.2 x 10'	$1.0 \times 10^{3}$	-
CrRe(tmb) (3)	13.0 ns	0.0020±0.0002	7.68 x 10 <sup>7</sup>	1.6 x 10 <sup>5</sup>	7.36 x 10 <sup>7</sup>
[Re(tmb)(CO) <sub>3</sub> (4-Etpy)] <sup>+</sup>	$(7.7 \times 10^7)$ 1.45 µs	0.148±0.001	5.9 x 10 <sup>5</sup>	1.0 x 10 <sup>5</sup>	-
	(6.9 X 10°)				

Table 3.1. Photophysical properties of complexes 1 - 3.

transfer. The design of this donor-acceptor system has eliminated the possibility of two quenching mechanisms allowing for a straightforward interpretation of the data. Dexter transfer is a throughbond process and the rate of energy transfer is exponentially dependent upon the donor acceptor distance via a bond connectivity pathway. The X-ray structure for **2** was used to determine the through-bond distance between the donor and acceptor and is much longer than the operative limit of Dexter transfer (<10 Å). The thermodynamics for photo-induced electron transfer was calculated using the Rehm-Weller equation, equation 3.6, where  $\Delta G_{ox}$  is the change in free energy,  $Re_{ox}^{II/I}$  is the oxidation potential of the Re,  $E_{00}$ , is the zero-point energy of the excited state, and  $Cr_{red}^{II/II}$  is the reduction potential of the Cr.<sup>27</sup>

$$\Delta G_{ox} = \left( R e_{ox}^{II/I} \right) - E_{00} - \left( C r_{red}^{III/II} \right)$$
(3.6)

The oxidation potentials were determined from cyclic voltammetry, the  $E_{00}$  were determined from spectral fitting of the steady-state emission spectra<sup>18,19</sup> and the  $\Delta G_{ox}$  calculated for each compound is reported in Table 3.2. The Cr<sup>III/II</sup> reduction was not observed in the solvent window for any dinuclear compounds and is estimated to be < -2.0 V. The  $\Delta G_{ox}$  for oxidative electron transfer is prohibitively large and is not a viable quenching mechanism for this system. Reductive quenching can also be ruled out since the formation of Cr(IV) results in this pathway

energies u	used to cal	culate A	ΔG.	I I I I	_	, <b>I</b>

Compound	E <sub>ox</sub> (Re <sup>II/I</sup> ) (V)	$E_{red}(L^{0/-})(V)$	E <sub>00</sub> (eV)	ΔG (eV)
CrRe(bpy) (1)	1.46	-1.65	2.17	>1.81
CrRe(deeb) (2)	>1.8*	-1.19	1.94	>1.86
CrRe(tmb) (3)	1.34	-1.89	2.36	>0.98

\*The oxidation wave was obscured by the solvent oxidation



Figure 3.7. Low-temperature steady-state emission of CrRe(bpy) (green trace,  $\lambda_{ex} = 370$  nm), CrRe(deeb) (red trace,  $\lambda_{ex} = 400$  nm), and CrRe(tmb) (blue trace,  $\lambda_{ex} = 360$  nm) in 1:4 MeOH:EtOH at 77 K. The emission maxima observed from 500–600 nm are from the <sup>3</sup>MLCT and the emission at 740 nm is from the Cr-based <sup>2</sup>E emission.

being thermodynamically unfeasible.

Förster transfer is the last potential quenching mechanism and the requirement for spectral overlap between the donor's emission and acceptor's absorbance is fulfilled. Figure 3.6 shows how the  ${}^{4}A_{2} \rightarrow {}^{4}T_{2}$  absorption in [Cr(tren)(acac)](OTf) overlaps with the <sup>3</sup>MLCT emission of each dinuclear compound. Experimental evidence of Förster transfer is shown in Figure 3.7 with the low-temperature steady-state emission of compounds 1 - 3 after direct excitation into the Re-based MLCT. Excitation at 370 nm, 400 nm, and 360 nm for compounds 1, 2, and 3, respectively, at 77 K resulted in emission from the <sup>3</sup>MLCT state from 400-700 nm and an additional emission at 740 nm. The <sup>3</sup>MLCT emission red shifts as EWG are substituted onto the bpy ligand, and vibronic structure is only observed for compound **3**. The vibronic structure observed for CrRe(tmb) is due

to a ligand localized  $\pi$ - $\pi$ \* phosphorescent state. The energy of MLCT states are much more sensitive to changes in temperature compared to ligand localized states. At 77 K the solvent forms a glass preventing the solvent's dipoles from stabilizing the MLCT excited state, this effect is known as the rigidochromic effect and has been well documented.<sup>28,29</sup> The rigidochromic effect only affects the energies of the MLCT states, opposed to ligand localized states, due to the dipole associated with the charge-separated nature of the excited state. This results in the MLCT states increasing in energy where the ligand localized  $\pi$ - $\pi$ \* states are unaffected. The electron donating substituents on the tmb ligand results in the MLCT state being higher in energy relative to the bpy and deeb derivatives such that the <sup>3</sup>MLCT state is now close in energy to the ligand localized state where dual emission occurs and the vibronic structure results from the ligand localized emission. This observation has been well-documented for Re(I) polypyridyls which possess MLCT states at comparable energies to <sup>3</sup> $\pi$ - $\pi$ \* states.<sup>30-33</sup>



Figure 3.8. Low-temperature steady-state emission of  $[Cr(tren)(acac)](OTf)_2$  in 1:4 MeOH:EtOH at 77 K ( $\lambda_{ex} = 520$  nm).

The emission at 740 nm for the three dinuclear CrRe compounds matches the emission maximum and the spectral shape that was observed for the low-temperature emission of [Cr(tren)(acac)](OTf)<sub>2</sub>. Low-temperature steady-state emission of [Cr(tren)(acac)](OTf) at 77 K in 1:4 MeOH:EtOH glass is shown in Figure 3.8. Excitation at 520 nm into the <sup>4</sup>T<sub>2</sub> results in phosphorescence at 740 nm from the <sup>2</sup>E which is in agreement with similarly related Cr<sup>III</sup> compounds.<sup>34</sup> The phosphorescence of the <sup>2</sup>E state after excitation into the <sup>4</sup>T<sub>2</sub> ligand field state for  $[Cr(tren)(acac)]^{2+}$  suggests that if the  ${}^{4}T_{2}$  state is formed in the CrRe dinuclear compounds from Förster transfer emission of the <sup>2</sup>E should be observed. The emission at 740 nm is observed for the three dinuclear CrRe compounds that match the emission maximum and spectral profile of the  ${}^{2}E$ emission in [Cr(tren)(acac)]<sup>2+</sup>. It is important to note that the low-temperature steady-state emission for the dinuclear compounds were collected after selective excitation into the Re-based MLCT manifold, and since emission from the Cr-based <sup>2</sup>E state is being observed this provides experimental evidence that energy transfer via the Förster mechanism produces the  ${}^{4}T_{2}$  state which intersystem crosses to the emissive <sup>2</sup>E state. The excitation wavelength for each dinuclear compound was varied while still selectively exciting into the Re-based MLCT manifold and the emission maxima assigned to the <sup>2</sup>E state at 740 nm was unchanged proving that the low intensity emission is not an instrumental artifact (Figure 3.25). The low-temperature steady-state emission data for the three CrRe dinuclear complexes provided experimental evidence that energy transfer to the Cr(III) is occurring, and based on the design of this donor-acceptor system the quenching proceeds via Förster energy transfer. Therefore, upon excitation into the MLCT state, Förster transfer to the  ${}^{4}T_{2}$  state occurs which undergoes intersystem crossings into the phosphorescent  ${}^{2}E$ state.35,36

### 3.3.5. Förster Rate Calculations

Based on the steady-state and time-resolved emission experiments a reduction in the quantum yields and an order of magnitude increase in the observed rate constant for the CrRe complexes indicates that dynamic quenching of the <sup>3</sup>MLCT state is occurring. The distance between the donor and acceptor is > 10 Å eliminating Dexter transfer as a possible quenching mechanism. By using the Rehm-Weller equation from the spectral fitting and the redox potentials measured via electrochemistry, it can be determined that oxidative or reductive quenching cannot occur ( $\Delta G > 0$ ). By the inherent design of the system this leads to Förster transfer being the only possible quenching mechanism as long as the spectral overlap between the <sup>4</sup>T<sub>2</sub> absorption and <sup>3</sup>MLCT emission is met. The UV-Vis and emission spectra of the three CrRe compounds show that the resonance condition for Förster transfer is met. Experimental evidence of energy transfer was observed for the CrRe compounds using low-temperature steady-state emission. Following excitation into the Re-based MLCT state emission at 740 nm is observed from the phosphorescent transfer.

To further verify Förster transfer is the quenching mechanism for this system the rate constant can be calculated using equation 3.1 and compared to the experimentally determined quenching rate constant,  $k_q$ , from the time-resolved data. The spectral overlap between the <sup>3</sup>MLCT emission and <sup>4</sup>T<sub>2</sub> for each compound is shown in Figure 3.6, where CrRe(tmb) has the largest overlap and as the emission red shifts with EWG the overlap is decreased. Based on this trend it should be expected that the CrRe(tmb) compound has the largest quenching rate constant followed by CrRe(bpy) and then CrRe(deeb). To quantitatively determine the Förster rate constant equations 3.1–3.3 were used. The donor-acceptor distances were measured using the single-crystal X-ray
structure data of [Re(deeb)(CO)<sub>3</sub>(pyacac)Cr(tren)](OTf)<sub>3</sub> using the centroid of the bpy ligand as the point dipole for the donor and the Cr atom as the point dipole for the acceptor. The averaged centroid – Cr distance, 9.9583 Å, was used to calculate the rate constants for complexes **1** - **3**. Obtaining X-ray quality crystals for complexes **1** and **3** were unsuccessful, however, substituent changes on the periphery of the bipyridyl ligand will have little effect on the structural features affecting the donor-acceptor distance. Since the nature of the ligand field state acting as the excited-state acceptor lacks one specific direction for the point dipole the orientation factor,  $\kappa^2$ , was approximated to be 2/3.  $\Phi_D$  and  $\tau_D$  values used are reported in Chapter 2.

The spectral overlap values and the calculated Förster rate constants for compounds 1-3 are shown in Table 3.3. It should be noted that because the rate constant of Förster transfer is being compared between the three dinuclear compounds, and the rate of Förster transfer will change based on the change in the spectral overlap integral, it is necessary to calculate the spectral overlap integral in wavenumbers due to wavelength not scaling linearly with energy. By calculating the spectral overlap integral in energy units the comparison between the calculated Förster rate constant between the three dinuclear compounds will be representative to the experimentally observed results. These calculated values show the appropriate trend for what is expected from the UV-Vis and emission spectra, where the CrRe(tmb) compound possess the most spectral overlap and as the emission red shifts the spectral overlap decreases for the CrRe(bpy) and CrRe(deeb) complexes, Table 3.3. The quenching rate constants for each compound are calculated using equation 3.5 and are in agreement for the calculated Förster rate constants for CrRe(tmb) and CrRe(bpy). The change in  $k_{FRET}$  between these two compounds and the change in  $k_q$  is relatively small however the calculated rate constant for Förster transfer is on the same order of magnitude as the observed quenching rate constant. The observed quenching rate constant for CrRe(deeb) is

larger than the calculated Förster rate constant, this is a result of the poor signal/noise ratio from the TCSPC data due to very low quantum yield. As described in detail in Chapters 1 and 2, Förster energy transfer is a nonradiative process, therefore to compare the relative amount of quenching due to Förster transfer among the three dinuclear compounds the  $k_q/k_{nr}$  ratio can be calculated. This ratio describes the relative amount of quenching compared to the inherent nonradiative processes of the MLCT decay. The k<sub>q</sub>/k<sub>nr</sub> values for each dinuclear compound are shown in Table 3.3 and ratio of quenching to nonradiative decay increases as the calculated spectral overlap and rate of Förster transfer increases. The k<sub>q</sub>/k<sub>nr</sub> value for CrRe(tmb) indicates that 99% of the nonradiative rate constant is due to quenching and this amount decreases as the spectral overlap decreases. In the case of CrRe(bpy),  $k_q/k_{nr}$  decreases compared to CrRe(tmb) indicating that 96% of the nonradiative decay in this compound can be attributed to quenching, it is important to note that the calculated spectral overlap also decreases when compared to CrRe(tmb). Among the three dinuclear compounds the smallest ratio of k<sub>q</sub>/k<sub>nr</sub> is calculated for CrRe(deeb), which also is calculated to have the smallest spectral overlap integral. Despite the poor signal/noise observed in the time-resolved experiment for CrRe(deeb), the amount of quenching relative to each compounds  $k_{nr}$  matches the trend in  $k_{FRET}$ . The trend observed between the ratio of quenching and nonradiative decay to the spectral overlap integral and the calculated Förster rate constant using Förster theory provides even further evidence that Förster energy transfer is the dominant quenching mechanism.

Not only has the Cr-based emission been experimentally observed, the product of Förster energy transfer, but Förster theory can also be used to demonstrate that the rate of quenching increases as the spectral overlap between the donor's emission and acceptor's absorbance is increased. While the quenching mechanism for these three dinuclear CrRe compounds have been established, the excited-state reactivity observed for dinuclear compounds is identical to the tetranuclear CrRe<sub>3</sub> compounds that have been previously studied. In both dinuclear and tetranuclear systems, photo-induced electron transfer and Dexter transfer cannot occur, and Förster energy transfer is the quenching mechanism via a spin-allowed S = 3/2 pathway. This proves that the use of the tripodal capping ligand, tren, can be used to change the structural motif of this donor-acceptor system and still allow for the effects of spin on excited-state reactivity to be studied.

Table 3.3. Spectral Overlap, Calculated Förster Rate Constant, and Observed Quenching Rate Constants for Complexes 1 - 3.

Compound	$J (\mathrm{M}^{-1}\mathrm{cm}^3)$	<i>k</i> fret (s <sup>-1</sup> )	$k_{\mathrm{q}}(\mathrm{s}^{-1})$	$k_{ m q}/k_{nr}$
CrRe(tmb) (3)	1.00 x 10 <sup>-15</sup>	2.19 x 10 <sup>7</sup>	$7.63 \ge 10^7$	0.99
CrRe(bpy) (1)	6.54 x 10 <sup>-16</sup>	1.75 x 10 <sup>7</sup>	$7.56 \ge 10^7$	0.96
CrRe(deeb) (2)	1.50 x 10 <sup>-16</sup>	$4.4 \ge 10^6$	2.38 x 10 <sup>8</sup>	0.95

# **3.4.** Conclusion

Previously a tetranuclear FeRe<sub>3</sub> donor acceptor system was designed and the Förster rate constant was calculated quantitatively. This initial system provided a platform to further study excited-state reactivity mechanisms. The next generation of tetranuclear donor acceptor systems featured Cr and Co as the first-row transition metal acceptor to study the effects of spin on excited-state reactivity. Quenching of the Re-based <sup>3</sup>MLCT was observed for the Cr compounds, via Förster transfer, while no quenching occurred in the Co compounds due to a lack of spin conservation. To further understand the role of spin in excited-state reactivity, a dinuclear donor-acceptor system was developed which features all of the essential components from the tetranuclear system. A tripodal capping ligand, tren, was used to only link 1 Re donor to the first-row transition metal acceptor. In this chapter three CrRe dinuclear compounds were synthesized

and their photophysical properties were studied. By changing the ligand environment around the Cr center the redox potentials and the  ${}^{4}T_{2}$  absorption were changed relative to the Cr(acac)<sub>3</sub> core in the tetranuclear systems. However, quenching via electron transfer was still thermodynamically unfavorable and spectral overlap between the ligand field absorption and <sup>3</sup>MLCT emission fulfilled the resonance condition needed for Förster transfer. Steady-state and time-resolved emission of the three CrRe compounds showed dynamic quenching of the <sup>3</sup>MLCT state. Given the donor-acceptor distance is too large for Dexter transfer to occur and the Rehm-Weller equation predicts the driving force for oxidative and reductive quenching to be thermodynamically unfavorable it is expected that Förster is the quenching mechanism. Low-temperature steady-state emission experiments resulted in the observation of a Cr-based <sup>2</sup>E phosphorescence following selective MLCT excitation, indicative of energy transfer to  ${}^{4}T_{2}$  state. This experimental evidence coupled with the agreement between experimentally observed rate constants and calculated Förster rate constants proves that Förster transfer is the quenching mechanism in the dinuclear CrRe compounds. The dinuclear compounds possess the same essential components of the tetranuclear system and observed similar excited-state reactivity, demonstrating that this new dinuclear motif can be used to further study the effects of spin on excited-state reactivity.

APPENDIX



Figure 3.9. Crystal structure of [Cr(tren)(acac)](OTf)<sub>2</sub>.



Figure 3.10. HRMS of  $[Cr(tren)(acac)](OTf)_2$  in MeOH (m/z: calcd for  $[M-2(OTf)-1H]^+$  296.130, obs. 296.136; calcd for  $[M-OTf]^+$  446.090, obs. 446.093).



Figure 3.11. Crystal structure of [Re(deeb)(CO)<sub>3</sub>(pyacac)Cr(tren)](OTf)<sub>3</sub>.



Figure 3.12. HRMS of  $[Re(bpy)(CO)_3(pyacac)Cr(tren)](OTf)_3$  in MeOH (m/z: calcd for  $[M-OTf]^+$  1099.080, obs. 1099.073; calcd for  $[M-Re(bpy)(CO)_3-2(OTf)]^+$  523.120, obs. 523.117; calcd for  $[M-Cr(tren)(pyacac)-3(OTf)]^+$  427.010, obs. 427.011; calcd for  $[M-Re(bpy)(CO)_3-3(OTf)-1H]^+$  373.160, obs. 373.157; calcd for  $[M-Re(bpy)(CO)_3-3(OTf)]^{2+}$  187.080, obs. 187.083.



Figure 3.13. HRMS-MS for  $[Re(bpy)(CO)_3(pyacac)Cr(tren)](OTf)_3$  in MeOH of the  $[M-OTf]^+$  ion (m/z 1099.073). The peaks with only Cr and Re in the HRMS are from fragmentation in the mass spectrometer and not from impurities (m/z: calcd for  $[M-Re(bpy)(CO)_3-2(OTf)]^+$  523.120, obs. 523.116; calcd for  $[M-Cr(tren)(pyacac)-3(OTf)]^+$  427.010, obs. 427.010; calcd for  $[M-Re(bpy)(CO)_3-3(OTf)-1H]^+$  373.160, obs. 373.158.



Figure 3.14. HRMS of  $[Re(tmb)(CO)_3(pyacac)Cr(tren)](OTf)_3$  in MeOH (m/z: calcd for  $[M-OTf]^+$  1155.140, obs. 1155.133; calc'd for  $[M-Cr(tren)(pyacac)+MeCN]^+$  524.100, obs. 524.105; calcd for  $[M-Re(bpy)(CO)_3-2(OTf)]^+$  523.120, obs. 523.115; calcd for  $[M-Re(bpy)(CO)_3-3(OTf)-1H]^+$  373.160, obs. 373.156; calcd for  $[M-Re(bpy)(CO)_3-3(OTf)]^{2+}$  187.080, obs. 187.084.



Figure 3.15. HRMS-MS for  $[Re(tmb)(CO)_3(pyacac)Cr(tren)](OTf)_3$  in MeOH of the  $[M-OTf]^+$  ion (m/z 1155.133). The peaks with only Cr and Re in the HRMS are from fragmentation in the mass spectrometer and not from impurities (m/z: calcd for  $[M-Re(bpy)(CO)_3-2(OTf)]^+$  523.120, obs. 523.118; calcd for  $[M-Re(bpy)(CO)_3-3(OTf)-1H]^+$  373.160, obs. 373.157).



Figure 3.16. HRMS of  $[\text{Re}(\text{deeb})(\text{CO})_3(\text{pyacac})\text{Cr}(\text{tren})](\text{OTf})_3$  in MeOH (m/z: calcd for  $[\text{M-OTf}]^+$  1243.120, obs. 1243.116; calcd for  $[\text{M-Cr}(\text{tren})(\text{pyacac})-3(\text{OTf})+\text{MeCN}]^+$  612.080, obs. 612.078; calcd for  $[\text{M-Cr}(\text{tren})(\text{pyacac})-3(\text{OTf})]^+$  571.050, obs. 571.050; calcd for  $[\text{M-Re}(\text{bpy})(\text{CO})_3-2(\text{OTf})]^+$  523.120, obs. 523.117; calcd for  $[\text{M-Re}(\text{bpy})(\text{CO})_3-3(\text{OTf})-1\text{H}]^+$  373.160, obs. 373.156).



Figure 3.17. HRMS-MS of  $[Re(deeb)(CO)_3(pyacac)Cr(tren)](OTf)_3$  in MeOH of the  $[M-OTf]^+$  ion (m/z 1243.116). The peaks with only Cr and Re in the HRMS are from fragmentation in the mass spectrometer and not from impurities (m/z: calcd for  $[M-Cr(tren)(pyacac)-3(OTf)]^+$  571.050, obs. 571.051; calcd for  $[M-Re(bpy)(CO)_3-2(OTf)]^+$  523.120, obs. 523.117; calcd for  $[M-Re(bpy)(CO)_3-3(OTf)-1H]^+$  373.160, obs. 373.157).



Figure 3.18. HRMS of [Re(tmb)(CO)<sub>3</sub>(pyacac)Cr(tren)](OTf)<sub>3</sub> in MeOH indicating the presence of mono- and bis-fluoride adducts formed in the synthesis (m/z: calcd for [M-OTf+HF]<sup>+</sup> 1175.150, obs. 1175.160; calcd for [M-OTf+2(HF)] 1195.150, obs. 1195.170).



Figure 3.19. IR spectrum of  $[Re(bpy)(CO)_3(pyacac)Cr(tren)](OTf)_3$ , v(CO) bands are observed at 2030 cm<sup>-1</sup> and 1905 cm<sup>-1</sup>.



Figure 3.20. Cyclic voltammogram of  $[\text{Re}(\text{bpy})(\text{CO})_3(\text{pyacac})\text{Cr}(\text{tren})(\text{acac})](\text{OTf})_3$  at positive potentials in MeCN with 0.1 M TBAPF<sub>6</sub> as supporting electrolyte. Data was collected with a scan rate of 200 mV/s and internally referenced to Fc/Fc<sup>+</sup>. The peak at 1.46 V is assigned to the Re<sup>II/I</sup> oxidation.



Figure 3.21. Cyclic voltammogram of  $[\text{Re(bpy)(CO)}_3(\text{pyacac})\text{Cr(tren)(acac)}](\text{OTf})_3$  in MeCN with 0.1 M TBAPF<sub>6</sub> as supporting electrolyte at negative potentials. Data was collected with a scan rate of 200 mV/s and internally referenced to Fc/Fc<sup>+</sup>. The peak at -1.65 V is assigned to the bpy<sup>0/-</sup> reduction.



Figure 3.22. Cyclic voltammogram of  $[\text{Re}(\text{deeb})(\text{CO})_3(\text{pyacac})\text{Cr}(\text{tren})(\text{acac})](\text{OTf})_3$  in MeCN with 0.1 M TBAPF<sub>6</sub> as supporting electrolyte. Data was collected with a scan rate of 200 mV/s and internally referenced to Fc/Fc<sup>+</sup>. The first reduction potential at -1.19 V is attributed to the reduction of the bipyridyl ligand and the reduction at -1.58 V is attributed to the reduction of the seter.



Figure 3.23. Cyclic voltammogram of  $[Re(tmb)(CO)_3(pyacac)Cr(tren)(acac)](OTf)_3$  in MeCN with 0.1 M TBAPF<sub>6</sub> as supporting electrolyte at positive potentials. Data was collected with a scan rate of 200 mV/s and internally referenced to Fc/Fc<sup>+</sup>. The peak at 1.34 V is assigned to the Re<sup>II/I</sup> oxidation.



Figure 3.24. Cyclic voltammogram of  $[Re(tmb)(CO)_3(pyacac)Cr(tren)(acac)](OTf)_3$  in MeCN with 0.1 M TBAPF<sub>6</sub> as supporting electrolyte at negative potentials. Data was collected with a scan rate of 200 mV/s and internally referenced to Fc/Fc<sup>+</sup>. The peak at -1.89 V is assigned to the tmb<sup>0/-</sup> reduction.



Figure 3.25. Low-temperature steady-state emission of CrRe(bpy) (green trace,  $\lambda_{ex} = 360$  nm), CrRe(deeb) (red trace,  $\lambda_{ex} = 385$  nm), and CrRe(tmb) (blue trace,  $\lambda_{ex} = 370$  nm) in 1:4 MeOH:EtOH at 77 K. The emission maxima observed from 500–600 nm are from the <sup>3</sup>MLCT and the emission at 740 nm is from the Cr-based <sup>2</sup>E emission. The excitation wavelengths for each compound are shifted by 10 nm relative to the excitation wavelengths used in Figure 3.7, and because the emission maximum for all peaks are unaffected the emission at 740 nm is not due to an instrument artifact.

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# Chapter 4. Using Spin to Control the Excited-State Quenching Mechanism in Re(I)-Co(III) Donor-Acceptor Systems

### **4.1. Introduction**

The effects of spin in ground-state reactivity of molecular systems has been well documented by the field of spin chemistry. Much less is known about how spin affects the excited-state reactivity. In 2011, the McCusker group reported the first case of spin directly affecting the excited-state reactivity.<sup>1</sup> The spin effects were studied using covalently linked donor-acceptor systems shown in Figure 4.1. This system features a Re(I) polypyridyl chromophore as the donor with three ligands of different donating ability, bpy (2,2'-bipyridine), tmb (tmb = 4,5,4',5'-tetramethyl-2,2'-bipyridine), and deeb (deeb = 4,4'-diethylester-2,2'-bipyridine), to alter the energetics of the excited state. The Re(I) polypyridyl is covalently linked to a first-row transition



Figure 4.1. Tetranuclear donor-acceptor systems used to study the role of spin conservation in excited-state reactivity.

metal as the acceptor, Cr(III), Co(III), and Ga(III), using the bridging ligand pyacac (pyacac = 3-(4-pyridyl)-2,4-pentanedione). The Cr(III) acceptor possess a paramagnetic  $d^3$  electron configuration, S = 3/2, in the ground state while the Co(III) ground state is diamagnetic with a low-spin  $d^6$  electron configuration, S = 0. By changing the spin between the Cr and Co acceptors, the excited-state dynamics of the Re bpy-based excited state changed in accordance.

There are three possible mechanisms that an excited state can react through, these are Förster transfer,<sup>2</sup> Dexter transfer,<sup>3</sup> and electron transfer and were introduced in Chapter 1. The inherent design of this system was used to favor specific quenching mechanisms while preventing others. The donor and acceptor are covalently linked and the distance was experimentally determined to be ~10 Å using single crystal X-ray data. This donor-acceptor distance rules out energy transfer via the exchange mechanism due its exponential dependence on distance. Application of the Rehm-Weller equation in conjunction with spectral fitting of the emission spectra rules out quenching via electron transfer due to the thermodynamics of the redox products. Thus, if quenching occurs it will be through the Förster mechanism. For Förster transfer to occur the donor's emission must overlap with the acceptor's absorbance and the process must be thermodynamically favorable,  $\Delta G < 0$ .

The electronic absorption spectra for  $[Cr(pyacac)_3 \{Re(bpy)(CO)_3\}_3](OTf)_3$  (CrRe<sub>3</sub>),  $[Ga(pyacac)_3 \{Re(bpy)(CO)_3\}_3](OTf)_3$  (GaRe<sub>3</sub>), and  $[Co(pyacac)_3 \{Re(bpy)(CO)_3\}_3](OTf)_3$ (CoRe<sub>3</sub>) are shown in Figure 4.2 and the  ${}^{1}A_{1} \rightarrow {}^{1}MLCT$  transition is observed in the nearultraviolet. The inset in Figure 4.2a and Figure 4.2b shows the spectral overlap between the  ${}^{3}MLCT$ emission of GaRe<sub>3</sub> and the  ${}^{4}A_2 \rightarrow {}^{4}T_2$  absorption of Cr(phacac)<sub>3</sub>, and the  ${}^{1}A_1 \rightarrow {}^{1}T_1$  absorption of Co(phacac)<sub>3</sub>, respectively (phacac = tris(3-phenyl-acetlyacetonato)). The M(phacac)<sub>3</sub> (M = Co, Cr) compounds were used as a surragote to replicate the metal-centered absorption in the



Figure 4.2. (A) Electronic absorption spectra of  $[Cr(pyacac)_3 \{Re(bpy)(CO)_3\}_3](OTf)_3$  (CrRe<sub>3</sub>, red trace) and  $[Ga(pyacac)_3 \{Re(bpy)(CO)_3\}_3](OTf)_3$  (GaRe<sub>3</sub>, black trace). Inset: Emission spectrum of GaRe<sub>3</sub> (blue trace) and electronic absorption spectrum of Cr(phacac)\_3 (red trace). (B) Electronic absorption spectra of  $[Co(pyacac)_3 \{Re(bpy)(CO)_3\}_3](OTf)_3$  (CoRe<sub>3</sub>, red trace) and GaRe<sub>3</sub> (black trace). Inset: Emission spectrum of GaRe<sub>3</sub> (blue trace). All data collected at room temperature in CH<sub>2</sub>Cl<sub>2</sub>.<sup>1</sup>

M(pyacac)<sub>3</sub> core. These spectra suggest sufficient spectral overlap exists between the ligand field absorption for both the CrRe<sub>3</sub> and CoRe<sub>3</sub> compounds and the emission of the <sup>3</sup>MLCT fulfilling the resonance condition necessary for Förster transfer. The GaRe<sub>3</sub> compound is used as a control molecule because Ga(III) has a d<sup>10</sup> electron configuration and does not possess an absorption in the visible to satisfy the spectral overlap required for Förster transfer.

Excitation of the CrRe<sub>3</sub> assembly at 375 nm results in an emission characteristic of the Rebased <sup>3</sup>MLCT, shown in Figure 4.3a. The factor of 100 decrease in the observed lifetime and the weak emission of the <sup>3</sup>MLCT state relative to the GaRe<sub>3</sub> control molecule establishes dynamic quenching is occurring. This observation alone does not provide any mechanistic evidence towards to the nature of the reaction between the <sup>3</sup>MLCT state and the Cr(pyacac)<sub>3</sub> core, but the distance between these moieties and the thermodynamics of electron transfer rules out these mechanisms. The Förster transfer mechanism was definitively established as the quenching mechanism from



Figure 4.3. (A) Time-correlated single-photon counting data for CrRe<sub>3</sub> at  $\lambda = 580$  nm after excitation at 375 nm,  $\tau = 4.8 \pm 0.2$  ns. Inset: Nanosecond time-resolved emission data for GaRe<sub>3</sub> at  $\lambda = 580$  nm,  $\tau = 630 \pm 30$  ns. (B) Nanosecond time-resolved emission data for CoRe<sub>3</sub> at  $\lambda = 580$  nm,  $\tau = 640 \pm 30$  ns. Inset: Steady-state emission spectra for CoRe<sub>3</sub> (red trace) and GaRe<sub>3</sub> (black trace). All data collected at room temperature in CH<sub>2</sub>Cl<sub>2</sub>.<sup>1</sup>

observing the  ${}^{2}E \rightarrow {}^{4}A_{2}$  phosphorescence of the Cr(III) at low temperature resulting from energy transfer to the  ${}^{4}T_{2}$  ligand field state.

The photophysics of the CoRe<sub>3</sub> compound following 400 nm excitation is drastically different comparatively. Figure 4.3b shows the insensitivity of the lifetime of CoRe<sub>3</sub> compared to the Ga control,  $640 \pm 30$  ns compared to  $630 \pm 30$  ns, and the inset shows the steady-state emission and quantum yields of each compound are nearly identical,  $0.16 \pm 0.02$  and  $0.17 \pm 0.02$ , indicating that quenching of the <sup>3</sup>MCLT state is not occurring in the CoRe<sub>3</sub> compound. The same mechanism restrictions are in place from the Cr(III) compounds, where electron transfer is thermodynamically uphill and Dexter transfer cannot occur. For the case of Förster transfer the spectral overlap integral is twice as large for CoRe<sub>3</sub>,  $16.6 \times 10^{-16} \text{ M}^{-1} \text{ cm}^{3}$ , compared to CrRe<sub>3</sub>,  $8.07 \times 10^{-16} \text{ M}^{-1} \text{ cm}^{3}$ , this is a consequence of the increased extinction coefficient for the <sup>1</sup>A<sub>1</sub>  $\rightarrow$  <sup>1</sup>T<sub>1</sub> absorption compared to the <sup>4</sup>A<sub>2</sub>  $\rightarrow$  <sup>4</sup>T<sub>2</sub> absorption. Despite the increased spectral overlap, which should result in a larger rate

constant for Förster transfer relative to the Cr analog, no reactivity of the <sup>3</sup>MLCT state with the Co(III) core is observed.

The difference in excited-state reactivity can be explained through an analysis of the spincoupled pathways that differ due to the difference in spin between Cr(III), S = 3/2, and Co(III), S = 0, Figure 4.4. In both compounds the excited-state donor, <sup>3</sup>MLCT state, has a spin multiplicity of  $|S_{D^*}| = 1$  and upon energy transfer from this state to the M(pyacac)<sub>3</sub> (M = Co(III) or Cr(III)) results in the spin of the donor  $|S_D| = 0$ . For the CrRe<sub>3</sub> compound the <sup>4</sup>A<sub>2</sub> ground state of the Cr center results in the spin of the reactants from  $|S_R| = 1/2$ , 3/2, and 5/2. The formalism of creating this spin manifold is identical to vector coupling of spin angular momenta used to describe magnetic exchange interactions among weakly coupled paramagnetic species.<sup>4</sup> The product of energy transfer from the <sup>3</sup>MLCT state to the Cr(III) would result in formation of the <sup>4</sup>T<sub>2</sub> ligand field state, S = 3/2, and the total spin of the products,  $|S_P| = 3/2$ . Energy transfer through the S = 3/2 pathway conserves spin angular momentum and Förster transfer is spin allowed resulting in dynamic quenching the MLCT state.

In the case of the CoRe<sub>3</sub> compound the low-spin d<sup>6</sup> configuration of the Co center directly affects the conservation of spin. The ground state of the Co(III) results in the total spin of the reactants  $|S_R| = 1$ . For Förster transfer to occur the <sup>3</sup>MLCT emission requires coupling to a Co(III)



Figure 4.4. (a) Single electron representation of the spin-allowed quenching pathway for CrRe<sub>3</sub> and (b) the spin-forbidden pathway for CoRe<sub>3</sub>.

excited state with  $|S_{A^*}| = 1$ , however, the  ${}^1T_1$  absorption results in  $|S_{A^*}| = 0$  state and therefore the total spin of the products does not conserve spin angular momentum,  $|S_P| = 0$ . Förster transfer is spin forbidden and does not occur which results in the kinetics being indistinguishable from the GaRe<sub>3</sub> control molecule. This was the first report that used spin to affect the outcome of excited-state quenching.



Figure 4.5. CoRe dinuclear compounds  $[Co(tren)(pyacac)Re(bpy)(CO)_3](OTf)_3$  (CoRebpy, 1),  $[Co(tren)(pyacac)Re(btfmb)(CO)_3](OTf)_3$  (CoRebtfmb, 2), and  $[Co(tren)(pyacac)Re(tmb)(CO)_3](OTf)_3$  (CoRetmb, 3).

In Chapter 3 the design of dinuclear donor-acceptor systems were introduced in an effort to further understand how spin plays a role in excited-state reactivity. In this chapter, the same general motif of the CrRe compounds will be used to study three dinuclear CoRe compounds shown in Figure 4.5. Three bipyridine ligands, bpy, tmb, and btfmb (4,4'-bis(trifluoromethyl)-2,2'-bipyridine), are coordinated to the Re modulating the energetics of the MLCT excited state. These compounds possess all of the fundamental aspects that were present in the tetranuclear systems. The same excited-state donor and bridging ligand is used which keeps the donor-acceptor distance virtually unchanged at ~ 10 Å. The one difference between the two systems are the use of the tripodal capping ligand tren (tris(2-aminoethyl)amine) thus maintaining one donor and acceptor. While it is expected that the same spin conservation will be in effect with only 1 Re chromophore the change in coordination environment around the first-row metal can change the spectral overlap of the  ${}^{1}T_{1}$  absorption and the Co<sup>III/II</sup> reduction potential.

Using the previous tetranuclear system it was discovered that the conservation of spin angular momentum is necessary for an excited-state quenching pathway to be operative. This chapter will focus on how the change in coordination environment around the Co(III) makes oxidative quenching a thermodynamically feasible pathway and how spin can be used dictate the mechanism of excited-state quenching.

## 4.2. Experimental

## 4.2.1. Synthesis

**General.** The tmb,<sup>5</sup> deeb,<sup>6</sup> btfmb,<sup>7</sup> and pyacac<sup>8</sup> (3-(4-pyridyl)-2,4-pentanedione) ligands were prepared according to the literature procedures. Re(CO)<sub>3</sub>(bpy)Cl,<sup>9</sup> Re(CO)<sub>3</sub>(tmb)Cl,<sup>9</sup> Re(CO)<sub>3</sub>(deeb)Cl,<sup>10</sup> [Re(CO)<sub>3</sub>(bpy)(pyacac)]OTf,<sup>1</sup> [Re(CO)<sub>3</sub>(tmb)(pyacac)]OTf,<sup>1</sup> and  $[Re(CO)_3(deeb)(pyacac)]OTf^1$  were prepared according to the literature procedures. Co(tren)Cl<sub>3</sub><sup>11</sup> and  $Na(acac)^{12}$  (acac = acetylacetonate) were prepared from literature procedures. Re(CO)<sub>5</sub>Cl was purchased from Sigma Aldrich and bpy was purchased from Oakwood Chemicals and used as received. 4-Methyl pyridine was purchased from Sigma Aldrich and distilled over CaH<sub>2</sub> under vacuum prior to use. Tris(2-aminoethyl)amine (tren) was distilled under reduced pressure over KOH and activated carbon twice prior to use. Acetyl Chloride was purchased from Sigma Aldrich and distilled prior to use. Silver triflate was purchased from Oakwood Chemical and stored in a nitrogen glovebox. Tetrahydrofuran and Methanol were purchased from Sigma Aldrich and dried over neutral alumina under nitrogen. Triethylamine was distilled over KOH and activated carbon prior to use. Size-exclusion chromatography was performed with SorbaDex lipophilic hydrophilic gel filtration matric (Sorbtech). <sup>1</sup>H NMR were collected on an Agilent DDR2 500 MHz spectrometer at the Max T. Rogers NMR facility at Michigan State University and referenced to residual solvent shifts. Electrospray ionization mass spectra were obtained at the Michigan State

University Mass Spectrometry and Metabolomics Core on a Waters G2-XS QToF mass spectrometer interfaced to a Waters Aquity UPLC. Elemental analyses were obtained through the analytical facilities at Michigan State University on samples that had been dried under vacuum overnight and ground in a vial in an Ar glovebox prior to analysis.

[Co(tren)(acac)](OTf)<sub>2</sub>. A suspension of [Co(tren)Cl<sub>2</sub>]Cl (0.500g, 1.60 mmol), silver triflate (1.23 g 4.80 mmol) and 30 mL H<sub>2</sub>O was stirred in the dark overnight under nitrogen. The precipitate was filtered over celite and washed with 30 mL H<sub>2</sub>O. To the filtrate was added Na(acac) (0.195 g, 1.60 mmol) under nitrogen and bubble degassed for 30 minutes. The solution was stirred at room temperature for 24 hours. The solvent was removed under reduced pressure and the crude product was purified by neutral alumina chromatography (3:1 MeCN/H<sub>2</sub>O) and the product was collected in the first red band. The desired fractions were combined, the volume was reduced under pressure, and recrystallized from methanol and ether yielding a red solid. (Yield 56%, 0.545 g). <sup>1</sup>H NMR (500 MHz, Deuterium Oxide)  $\delta$  5.73 (s, 1H), 3.60 (td, *J* = 13.1, 5.9 Hz, 2H), 3.40 (td, *J* = 13.9, 5.0 Hz, 2H), 3.25 (t, *J* = 7.1 Hz, 2H), 3.08 (dd, *J* = 14.1, 5.8 Hz, 2H), 2.91 (t, *J* = 7.1 Hz, 2H), 2.75 (dd, *J* = 12.5, 4.9 Hz, 2H), 2.18 (s, 3H), 2.10 (s, 3H). <sup>13</sup>C NMR (126 MHz, Deuterium Oxide)  $\delta$  192.45, 190.65, 98.51, 60.82, 60.33, 44.45, 42.92, 26.36, 25.93. HRMS (ESI-TOF) m/z: [M-(OTf)]<sup>+</sup> calcd for [C<sub>12</sub>H<sub>25</sub>N<sub>4</sub>O<sub>5</sub>F<sub>3</sub>SCo] 453.080, obs. 453.083.

**Re(btfmb)**(**CO**)<sub>3</sub>**Cl.** Re(CO)<sub>5</sub>Cl (0.42 g, 1.16 mmol) and btfmb (0.34 g, 1.16 mmol) were combined with toluene (40 mL) and refluxed under nitrogen for 2 hours. The reaction was cooled to room temperature and hexanes was added, the precipitate was filtered and washed with hexanes and ether and dried overnight under vacuum (0.615 g, 88%). <sup>1</sup>H NMR (500 MHz, acetonitrile-*d*<sub>3</sub>) 9.29 (d, J = 5.7 Hz, 2H), 8.87 (s, 2H), 7.96 (d, J = 5.7 Hz, 2H).

[**Re(btfmb)(CO)<sub>3</sub>(pyacac)](OTf).** Re(btfmb)(CO)<sub>3</sub>Cl (0.20 g, 0.33 mmol) and AgOTf (0.085 g, 0.33 mmol) were combined with THF (20 mL) and refluxed under nitrogen for 3.5 hours. The reaction was cooled to room temperature, filtered over celite and washed with THF. The solvent was removed under vacuum and pyacac (0.178 g, 1.00 mmol) and THF (20 mL) were added and the reaction was refluxed under nitrogen for 12 hours. The solvent was removed under vacuum and the residue was dissolved in dichloromethane and precipitated with ether and filtered (0.15 g, 50%). <sup>1</sup>H NMR (500 MHz, acetonitrile-*d*<sub>3</sub>) 16.96 (s, 1H), 9.47 (d, J = 5.5 Hz, 2H), 8.83 (s, 2H), 8.20 (d, J = 6.65 Hz), 8.10 (t, J = 6.00 Hz, 2H), 7.20 (d, J = 6.65 Hz, 2H), 1.77 (s, 6H).

[Co(tren)(pyacac)Re(bpy)(CO)<sub>3</sub>](OTf)<sub>3</sub>. A suspension of [Co(tren)Cl<sub>2</sub>]Cl (0.058g, 0.19 mmol) and silver triflate (0.143 g, 0.558 mmol) in acetone (10 mL) was stirred at room temperature in the dark for 2 hours under nitrogen. The solution was filtered over celite, washed with acetone (30 mL) and the solvent was removed under reduced pressure. The pink residue was dissolved in MeOH (5 mL) and a solution of Na(BPh<sub>4</sub>) (0.191 g, 0.558 mmol) in 5 mL of MeOH was added. Upon addition a white precipitate formed and the solution was cooled in an ice bath for 30 minutes and then filtered over cotton. In a separate flask [Re(bpy)(CO)<sub>3</sub>(pyacac)](OTf) (0.140 g, 0.186 mmol) was dissolved in 5 mL of MeCN and triethylamine (26 µL, 0.186 mmol) was added resulting in a dark orange solution. This solution was cooled in an ice bath for 30 minutes and the white precipitate was filtered over cotton. The solvent was removed under reduced pressure and then dissolved in 5 mL of MeOH. This solution was added dropwise to the Co(tren)(BPh<sub>4</sub>)<sub>3</sub> solution and stirred at 50°C for one hour. After cooling to room temperature the solvent was removed under reduced pressure and  $H_2O(20 \text{ mL})$  was added and the solid was filtered and washed with H<sub>2</sub>O (2x 15 mL). The crude product was dissolved in MeCN and purified using size-exclusion chromatography in MeCN and the first dark brown band was collected. The product was

metathesized to the chloride salt by eluting a 2% HCl/MeCN solution through a clean sizeexclusion column directly followed by the crude product. Methanol was used to elute the orange band and the solvent was removed under reduced pressure. The orange solid was dissolved in MeOH (5 mL) in a nitrogen filled drybox and a solution of sodium triflate (0.030 g, 0.17 mmol) in 5 mL MeOH was added. The white precipitate was filtered over celite and washed with MeOH (20 mL). The product was further purified using size-exclusion chromatography in MeOH (0.011 g, 5%). HRMS (ESI-TOF) m/z: [M-(OTf)]<sup>+</sup> calcd for [C<sub>31</sub>H<sub>36</sub>N<sub>7</sub>O<sub>11</sub>S<sub>2</sub>F<sub>6</sub>CoRe] 1106.07, obs. 1106.071. <sup>1</sup>H NMR (500 MHz, methanol- $d_4$ ) 9.36 (d, J = 5.55 Hz, 2H), 8.61 (d, 8.2 Hz, 2H), 8.44 (dd, J = 6.65 Hz, 2 Hz, 2H), 8.36 (td, J = 7.85 Hz, 1.55 Hz, 2H), 7.88 (td, J = 5.50 Hz, 1.15 Hz, 2H), 7.38 (dd, 6.65 Hz, 3.8 Hz, 2H), 3.57 (td, 13.1 Hz, 5.65 Hz, 2H), 3.45 (td, 13.75 Hz, 4.7 Hz, 2H), 3.26 (t, 7.15 Hz, 2H), 3.14 (dd, 13.8 Hz, 5.5, 2H), 2.89 (t, 7.1 Hz, 2H), 2.78 (dd, 12.25 Hz, 4.5 Hz, 2H), 1.86 (s, 3H), 1.79 (s, 3H).

[Co(tren)(pyacac)Re(tmb)(CO)<sub>3</sub>](OTf)<sub>3</sub>. A suspension of [Co(tren)Cl<sub>2</sub>]Cl (0.038g, 0.12 mmol) and silver triflate (0.095 g, 0.37 mmol) in acetone (10 mL) was stirred at room temperature in the dark for 2 hours under nitrogen. The solution was filtered over celite, washed with acetone (30 mL) and the solvent was removed under reduced pressure. The pink residue was dissolved in MeOH (5 mL) and a solution of Na(BPh<sub>4</sub>) (0.126 g, 0.37 mmol) in 5 mL of MeOH was added. Upon addition a white precipitate formed and the solution was cooled in an ice bath for 30 minutes and then filtered over cotton. In a separate flask [Re(tmb)(CO)<sub>3</sub>(pyacac)](OTf) (0.10 g, 0.12 mmol) was dissolved in 5 mL of MeCN and triethylamine (17  $\mu$ L, 0.12 mmol) was added resulting in a dark orange solution. This solution was cooled in an ice bath for 30 minutes and the white precipitate over cotton. The solvent was removed under reduced pressure and then dissolved in 5 mL of MeOH, this solution was added dropwise to the Co(tren)(BPh<sub>4</sub>)<sub>3</sub> solution and

stirred at 50°C for one hour. After cooling to room temperature the solvent was removed under reduced pressure and H<sub>2</sub>O (20 mL) was added and the solid was filtered and washed with H<sub>2</sub>O (2x 15 mL). The crude product was dissolved in MeCN and purified using size-exclusion chromatography in MeCN and the first dark brown band was collected. The product was metathesized to the chloride salt by eluting a 2% HCl/MeCN solution through a clean sizeexclusion column directly followed by the crude product. Methanol was used to elute the orange band and the solvent was removed under reduced pressure. The orange solid was dissolved in MeOH (5 mL) in a nitrogen filled drybox and a solution of sodium triflate (0.021 g, 0.12 mmol) in 5 mL MeOH was added. The white precipitate was filtered over celite and washed with MeOH (20 mL). The product was further purified using size-exclusion chromatography in MeOH (0.010 g, 6%). HRMS (ESI-TOF) m/z: [M-(OTf)]<sup>+</sup> calcd for [C<sub>35</sub>H<sub>44</sub>N<sub>7</sub>O<sub>11</sub>S<sub>2</sub>F<sub>6</sub>CoRe] 1162.13, obs. 1162.13. <sup>1</sup>H NMR (500 MHz, methanol-d<sub>4</sub>) 8.97 (s, 2H), 8.46 (d, 6.6 Hz, 2H), 8.37 (s, 2 H), 7.43 (d, J = 6.60 Hz, 2H), 3.57 (td, 13.1 Hz, 5.65 Hz, 2H), 3.48 (td, 13.75 Hz, 4.7 Hz, 2H), 3.27 (t, 7.15 Hz, 2H), 3.14 (dd, 13.8 Hz, 5.5, 2H), 2.91 (t, 7.1 Hz, 2H), 2.78 (dd, 12.25 Hz, 4.5 Hz, 2H), 1.89 (s, 3H), 1.80 (s, 3H).

[Co(tren)(pyacac)Re(btfmb)(CO)<sub>3</sub>](OTf)<sub>3</sub>. A suspension of [Co(tren)Cl<sub>2</sub>]Cl (0.044g, 0.14 mmol) and silver triflate (0.108 g, 0.42 mmol) in acetone (10 mL) was stirred at room temperature in the dark for 2 hours under nitrogen. The solution was filtered over celite, washed with acetone (30 mL) and the solvent was removed under reduced pressure. The pink residue was dissolved in MeOH (5 mL) and a solution of Na(BPh<sub>4</sub>) (0.144 g, 0.42 mmol) in 5 mL of MeOH was added. Upon addition a white precipitate formed and the solution was cooled in an ice bath for 30 minutes and then filtered over cotton. In a separate flask [Re(btfmb)(CO)<sub>3</sub>(pyacac)](OTf) (0.125 g, 0.140 mmol) was dissolved in 5 mL of MeCN and triethylamine (20  $\mu$ L, 0.14 mmol) was added resulting

in a dark orange solution. This solution was cooled in an ice bath for 30 minutes and the white precipitate was filtered over cotton. The solvent was removed under reduced pressure and then dissolved in 5 mL of MeOH, this solution was added dropwise to the Co(tren)(BPh<sub>4</sub>)<sub>3</sub> solution and stirred at 50°C for one hour. After cooling to room temperature the solvent was removed under reduced pressure and H<sub>2</sub>O (20 mL) was added and the solid was filtered and washed with H<sub>2</sub>O (2x 15 mL). The crude product was dissolved in MeCN and purified using size-exclusion chromatography in MeCN and the first dark brown band was collected. The product was metathesized to the chloride salt by eluting a 2% HCl/MeCN solution through a clean sizeexclusion column directly followed by the crude product. Methanol was used to elute the orange band and the solvent was removed under reduced pressure. The orange solid was dissolved in MeOH (5 mL) in a nitrogen filled drybox and a solution of sodium triflate (0.024 g, 0.14 mmol) in 5 mL MeOH was added. The white precipitate was filtered over celite and washed with MeOH (20 mL). The product was further purified using size-exclusion chromatography in MeOH (0.006 g, 3%). HRMS (ESI-TOF) m/z:  $[M-(OTf)]^+$  calcd for  $[C_{33}H_{34}N_7O_{11}S_2F_{12}CoRe]$  1242.05, obs. 1242.05. <sup>1</sup>H NMR (500 MHz, methanol- $d_4$ ) 9.62 (d, J = 5.55 Hz, 2H), 9.25 (s, 2H), 8.49 (d, J = 5.40 Hz, 2 H), 8.23 (d, J = 5.9 Hz, 2H), 7.40 (d, J = 5.85 Hz, 2H), 3.57 (td, 13.1 Hz, 5.65 Hz, 2H), 3.45 (td, 13.75 Hz, 4.7 Hz, 2H), 3.26 (t, 7.15 Hz, 2H), 3.13 (dd, 13.8 Hz, 5.5, 2H), 2.89 (t, 7.1 Hz, 2H), 2.78 (dd, 12.25 Hz, 4.5 Hz, 2H), 1.89 (s, 3H), 1.83 (s, 3H).

[Co(tren)(pyacac)Re(deeb)(CO)<sub>3</sub>](OTf)<sub>3</sub>. A suspension of [Co(tren)Cl<sub>2</sub>]Cl (0.040 g, 0.20 mmol) and silver triflate (0.15 g, 0.59 mmol) in acetone (10 mL) was stirred at room temperature in the dark for 2 hours under nitrogen. The solution was filtered over celite, washed with acetone (30 mL) and the solvent was removed under reduced pressure. The pink residue was dissolved in MeOH (5 mL) and a solution of Na(BPh<sub>4</sub>) (0.20 g, 0.59 mmol) in 5 mL of MeOH was added.

Upon addition a white precipitate formed and the solution was cooled in an ice bath for 30 minutes and then filtered over cotton. In a separate flask [Re(deeb)(CO)<sub>3</sub>(pyacac)](OTf) (0.175 g, 0.20 mmol) was dissolved in 5 mL of MeCN and triethylamine (27  $\mu$ L, 0.20 mmol) was added resulting in a dark orange solution. This solution was cooled in an ice bath for 30 minutes and the white precipitate was filtered over cotton. The solvent was removed under reduced pressure and then dissolved in 5 mL of MeOH, this solution was added dropwise to the Co(tren)(BPh4)<sub>3</sub> solution and stirred at 50°C for one hour. After cooling to room temperature the solvent was removed under reduced pressure and H<sub>2</sub>O (20 mL) was added and the solid was filtered and washed with H<sub>2</sub>O (2x 15 mL). The crude product was dissolved in MeCN and purified using size-exclusion chromatography in MeCN and the first dark brown band was collected. The product was metathesized to the chloride salt by eluting a 2% HCl/MeCN solution through a clean sizeexclusion column directly followed by the crude product. Methanol was used to elute the orange band and the solvent was removed under reduced pressure. The orange solid was dissolved in MeOH (5 mL) in a nitrogen filled drybox and a solution of sodium triflate (0.034 g, 0.20 mmol) in 5 mL MeOH was added. The white precipitate was filtered over celite and washed with MeOH (20 mL). Further attempts to purify using size-exclusion chromatography in MeOH were unsuccessful and lead to hydrolysis of the ester.

#### 4.2.2. Physical Characterization

**X-ray structure determination.** Single-crystal X-ray diffraction data were acquired and the structures were solved by Dr. Richard Staples at the X-ray Facility of Michigan State University. The crystal structure for  $[Co(tren)(acac)](OTf)_2$  has been submitted to the CCDC database and can be accessed by the CCDC accession number (1824686).

**Ground-state absorption spectroscopy.** All spectra were collected using spectrophotometric grade acetonitrile in 1 cm quartz cuvettes and acquired using a Cary 50 spectrophotometer.

Electrochemistry. Electrochemical measurements were collected using a CH instruments model CHI620D electrochemical workstation in an Ar-filled dry box. A standard three-electrode setup was used to determine the redox potentials via cyclic voltammetry in acetonitrile solutions using 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) as supporting electrolyte, a Pt disc working electrode, a Ag wire pseudo-reference electrode, and a platinum wire counter electrode. Cyclic voltammetrey was collected using a 200 mV/s scan rate and Fc/Fc<sup>+</sup> was used as an internal reference. Differential pulse voltammetrey performed for was [Co(tren)(pyacac)Re(tmb)(CO)<sub>3</sub>](OTf)<sub>3</sub> and [Co(tren)(pyacac)Re(btfmb)(CO)<sub>3</sub>](OTf)<sub>3</sub> in the same setup that was described for cyclic voltammetry experiments, but with an increment of 0.004 V, amplitude of 0.05 V, pulse width of 0.2 s, sampling width of 0.0167 s, and a pulse period of 0.2 s. TBAPF<sub>6</sub> was purchased from Oakwood Chemical and recrystallized from ethanol twice before use.

**Spectroelectrochemistry.** UV-Visible spectroelectrochemical experiments were performed in a Pine Instruments electrochemical cell in an Ar-filled dry box. The 1 cm x 1 cm space at the top of the cell held the Ag reference electrode while the Pt working electrode and counter electrode were placed in the 1.7 mm x 10 mm path length window at the bottom of the cell to electrolyze the solution while the absorbance was recorded with SI420 CCD spectrometer. Data were acquired on solutions identical to that just described for the electrochemical measurements, with the exception that solutions of each compound were adjusted to have absorbance values in the range of  $0.6 \pm 0.1$  at the maximum of the MLCT absorption peak. A ground-state absorption spectrum was taken

prior to the onset of bulk electrolysis at an over potential of 0.1 V - 0.2 V relative to the redox potential of the compound.

Steady-State Emission and Time-Resolved Emission and Absorption. All samples were prepared in an argon-filled glovebox, using air-free cuvettes and solvents were freeze-pump-thaw degassed prior to use. For steady-state and time-resolved emission spectroscopy the absorbance of the sample at the MLCT maximum was between 0.1 - 0.2.

Steady-state emission spectra were collected using a Horiba Fluorolog-3 fluorimeter and corrected for instrumental response using a NIST standard of spectral irradiance (Optronic Laboratories, Inc., OL220 M tungsten quartz lamp). The resulting emission spectra were fit with an asymmetric double sigmoidal function using IGOR pro. This function has no mathematical significance but it is able to accurately reproduce the shape of the entire emission curve and capture the small area (< 10%) that lies outside of the detector range providing a more accurate estimate of the integrated spectrum. Relative quantum yields of emission ( $\Phi_x$ ) were calculated using [Re(bpy)(CO)<sub>3</sub>(4-Etpy)](OTf) in acetonitrile as a standard ( $\Phi_{std} = 0.029$ ) which was calculated by using [Ru(bpy)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> in deaerated MeCN as a standard. Quantum yields were calculated using equation 3.4, where x refers to the molecule of interest and *std* to the standard; *I<sub>x</sub>* and *I<sub>std</sub>* are the integrated areas of the corrected emission spectra, *A<sub>x</sub>* and *A<sub>std</sub>* are the absorbances at the excitation wavelength, and  $\eta_{std}$  are the indices of refraction of the solutions.

$$\Phi_x = \Phi_{std} \left( \frac{l_x/A_x}{l_{std}/A_{std}} \right) \left( \frac{\eta_x}{\eta_{std}} \right)^2$$
(3.4)

The zero-point energy gap ( $E_{00}$ ) was estimated by a single mode fit of the steady-state emission spectrum as described by Claude and Meyer.<sup>13</sup> The spectrum was corrected according to Parker and Reese when converting from wavelength to energy units.<sup>14</sup>

Picosecond time-resolved emission data for the [Co(tren)(pyacac)Re(bpy)(CO)<sub>3</sub>](OTf)<sub>3</sub> complexes were collected by Professor Gary Blanchard using time-correlated single photon counting (TCSPC) with an apparatus that has been described previously.<sup>15</sup>

## 4.3. Results and Discussion

#### 4.3.1. Synthesis and Characterization

The synthesis of  $[Co(tren)(acac)](OTf)_2$  was pursued to provide a general procedure that could be used for the CoRe complexes as well as ground-state characterization of the individual acceptor moiety in the new  $N_4O_2$  coordination environment. The previously reported [Co(tren)(Cl)<sub>2</sub>]Cl was used as the starting material and silver triflate was used to displace the chlorides making the substitution of the acac facile. This general approach was applied to the synthesis of compounds 1-3 using the appropriate [Re(bpy)(CO)<sub>3</sub>(pyacac)]OTf. Despite multiple attempts and purification techniques the substitution of the  $[Re(bpy)(CO)_3(pyacac)]OTf$  with Co(tren)(OTf)<sub>3</sub> resulted in impurities in the <sup>1</sup>H NMR. These impurities are from different species of Re(bpy) and Co(tren) based on their chemical shift and multiplicity. Based on the observations for the synthesis of the CrRe complexes discussed in Chapter 3, HRMS was used to identify the presence of fluoride adducts that form from heating Co(tren)(OTf)<sub>3</sub>. In the case for the CrRe complexes the removal of the fluoride adducts can be achieved through size-exclusion chromatography, but for the synthesis of the CoRe complexes this was not possible. To prevent fluoride adducts from forming the starting materials containing triflate were metathesized. The Co(tren)(OTf)<sub>3</sub> was metathesized to the BPh<sub>4</sub> salt and the Re(pyacac) starting materials were deprotonated with NEt<sub>3</sub> and the HNEt<sub>3</sub>OTf was filtered removing the presence of all fluorides

before heating the reaction. Using this procedure, the CoRe complexes could be purified using size-exclusion chromatography.

# 4.3.2. Photophysical Properties of CoRe Complexes

The electronic absorption spectra of  $[Co(tren)(acac)](OTf)_3$  and the three CoRe complexes are shown in Figure 4.6. For  $[Co(tren)(acac)]^{2+}$  the LMCT absorption is centered at 330 nm and the ligand field transition for the  ${}^{1}A_{1} \rightarrow {}^{1}T_{1}$  absorption is observed at 510 nm. When compared to the ligand field absorption of Co(phacac), used to identify the spectral overlap in the tetranuclear systems, this absorption is blue shifted by ~ 100 nm indicating a larger ligand field strength for  $[Co(tren)(acac)]^{2+}$ .



Figure 4.6. Ground-state absorption spectra of CoRe(bpy) (green trace), CoRe(tmb) (blue trace), CoRe(btfmb) (red trace), and [Co(tren)(acac)](OTf)<sub>2</sub> (black trace). Inset: Absorption of the  ${}^{1}A_{1} \rightarrow {}^{1}T_{1}$  transition in the CoRe complexes and [Co(tren)(acac)](OTf)<sub>2</sub>.
The absorption spectra for the CoRe complexes show vibronic structure in the bipyridinebased  $\pi \rightarrow \pi^*$  transition at 325 nm. For CoRe(tmb), CoRe(bpy), and CoRe(btfmb) the  ${}^1A_1 \rightarrow$  ${}^1MLCT$  absorption is observed at 365 nm, 375 nm, and 385 nm, respectively, and this absorption feature red shifts as electron withdrawing substituents on the bipyridine ligand are used. The absorption maximum is obscured in the cases of CoRe(tmb) and CoRe(bpy) due overlapping with higher energy absorption features and only the red shoulder of MLCT is observed. The CF<sub>3</sub> substituents on the bipyridine ligand, for the CoRe(btfmb) compound, red shift the MLCT absorption to the degree that its maximum no longer overlaps with higher energy absorptions. The inset of Figure 4.6 shows the  ${}^1T_1$  absorption for each compound, and the red edge of the MLCT for CoRe(btfmb) overlaps with this ligand field absorption. The Co-based ligand field absorption for CoRe(btpy) and CoRe(tmb) have the same absorption maximum as  $[Co(tren)(acac)]^{2+}$ suggesting weak electronic coupling.

The use of the tripodal tren ligand changes the ligand field strength around the Co center which resulted in a change in the  ${}^{1}T_{1}$  absorption compared to the Co(acac)<sub>3</sub> core. Electrochemistry was used to measure the Re<sup>II/1</sup> oxidation potential and the Co<sup>III/II</sup> reduction potential for complexes 1 - 3 and [Co(tren)(acac)]<sup>2+</sup>, Table 4.1. The Co<sup>III/II</sup> reduction potential for all of the complexes studied are irreversible, the potential for [Co(tren)(acac)]<sup>2+</sup> is measured at -0.85 V (vs. Fc/Fc<sup>+</sup>) in MeCN and is in agreement with what is reported in the literature.<sup>16</sup> The reduction potential for this compound is 0.81 V more positive than the Co<sup>III/II</sup> reduction for Co(phacac)<sub>3</sub>, -1.66 V (vs. Fc/Fc<sup>+</sup>). This significant change in reduction potential can be attributed to the change in coordination environment between the two compounds. [Co(tren)(acac)]<sup>2+</sup> possess a +2 overall charge with only one anionic acac ligand bound making it easier to reduce than the neutral Co(phacac)<sub>3</sub> where three anionic acac ligands are bound. When the [Co(tren)(acac)]<sup>2+</sup> moiety is appended to Re(byy)(CO)<sub>3</sub>

Compound	Eox(Re <sup>II/I</sup> ) (V)	$E_{red}(L^{0})(V)$	Ered(Co <sup>III/II</sup> ) (V) <sup>a</sup>	E00 (eV)	ΔG (eV)
[Co(tren)(acac)] <sup>2+</sup>	-	-	-0.85	-	-
CoRe(bpy) (1)	1.41	-1.47	-0.72	2.17	-0.04
CoRe(btfmb) (2)	$1.52^{b,c}$	-1.15	-0.71	1.90	+0.33
CoRe(tmb) (3)	1.37 <sup>c</sup>	-1.83	-0.76 <sup>c</sup>	2.31	-0.18

Table 4.1. Oxidation and reduction potentials for  $[Co(tren)(acac)]^{2+}$  and complexes 1-3.

<sup>*a*</sup> The Co<sup>III/II</sup> reduction is irreversible in all compounds and the peak cathode current is used to estimate the reduction potential. <sup>*b*</sup> The Re<sup>II/I</sup> oxidation is irreversible in the cyclic voltammogram. <sup>*c*</sup> Potentials were measured using DPV. All potentials are internally referenced to Fc/Fc<sup>+</sup>.

via pyacac, i.e. complexes 1 - 3, the overall charge of the molecule is now 3+ and the Co<sup>III/II</sup> reduction potential for CoRe(bpy) increases by 0.13 V to -0.72 V (vs. Fc/Fc<sup>+</sup>). This same effect is observed for the Re<sup>II/I</sup> oxidation potential for CoRe(bpy), as the charge of the molecule increases the oxidation of the Re becomes more difficult and increases by 40 mV compared to  $[\text{Re(bpy)(CO)}_3(4-\text{Etpy})]^+$ , and similarly the bpy reduction increases by 0.09 V for CoRe(bpy). The Re<sup>II/I</sup> oxidation potential of CoRe(btfmb) is irreversible when performing cyclic voltammetry and the potential was measured at 1.52 V (vs. Fc/Fc<sup>+</sup>) using differential pulse voltammetry. The oxidation potential for CoRe(btfmb) increases by 0.08 V, to 1.52 V, from 1.44 V in  $[\text{Re(btfmb)(CO)}_3(4-\text{Etpy})]^+$  and is explained from the change in overall charge of the compound. The increase in oxidation potential of CoRe(btfmb) relative to CoRe(bpy) is a direct consequence of the electron withdrawing substituents on the bipyridyl ligand removing electron density from the Re center making it harder to oxidize. These substituents also lower the bpy-based  $\pi^*$  orbitals resulting in a more positive ligand-based reduction potential, however, the Co<sup>III/II</sup> reduction potential is not significantly affected in all three dinuclear compounds. Likewise, the Co<sup>III/II</sup> reduction potential for CoRe(tmb) increases by 0.09 V relative to  $[Co(tren)(acac)]^{2+}$ , but is comparable to the potentials measured for CoRe(bpy) and CoRe(btfmb). Most importantly the

change in the coordination environment around the Co by using the tren capping ligand compared to the  $Co(III)(acac)_3$  core in the tetranuclear compounds increases the  $Co^{III/II}$  reduction and results in a change in the thermodynamics for oxidative quenching of the <sup>3</sup>MLCT state.

The steady-state emission for the CoRe complexes are shown in Figure 4.7 and the broad profile of the emission is characteristic of the Re polypyridyl-based <sup>3</sup>MLCT phosphorescence. For CoRe(bpy) (green trace) the compound is excited at 370 nm and the emission maximum is observed at 580 nm. Each emission profile is fit with an asymmetric double sigmoidal function (dotted lines) this function has no mathematical significance but it is able to accurately reproduce



Figure 4.7. Steady-state emission of CoRe(bpy) (green trace,  $\lambda_{ex} = 370$  nm), CoRe(btfmb) (red trace,  $\lambda_{ex} = 410$  nm), and CoRe(tmb) (blue trace,  $\lambda_{ex} = 360$  nm) in MeCN. The emission spectra were fit to an asymmetric double sigmoidal function (dotted lines). The UV-vis of [Co(tren)(acac)](OTf)<sub>2</sub> (black trace) in MeCN demonstrates the spectral overlap between <sup>3</sup>MLCT emission and <sup>1</sup>A<sub>1</sub>  $\rightarrow$  <sup>1</sup>T<sub>1</sub> absorption.

the shape of the entire emission curve. This fit provides a more accurate band shape due to the excitation artifact observed at  $2^*\lambda_{ex}$  for CoRe(bpy) and CoRe(tmb). For CoRe(tmb) (blue trace) the compound is excited at 360 nm with an emission maximum at 535 nm, and for CoRe(btfmb) (red trace) the compound is excited at 410 nm and has an emission maximum at 665 nm. CoRe(btfmb) is fit to an asymmetric double sigmoidal function to capture the small area (< 10%) that lies outside of the detector range (> 800 nm) providing a more accurate estimate of the integrated spectrum. The red shift of the emission maximum as substituents on the bpy ligand change from electron donating groups (EDG) to electron withdrawing groups (EWG) is a result of the detabilization and stabilization of the  $\pi^*$  orbitals, respectively.

Spectral fitting of each emission spectra was performed to determine the  $E_{00}$  of each  $^{3}MLCT$  state and the values are shown in Table 4.1. The  $E_{00}$  of each emission along with the redox potentials can be used in the Rehm-Weller equation, equation 4.2, to determine the  $\Delta G$  of excited-state electron transfer.<sup>17</sup>

$$\Delta G_{ox} = \left(Re_{ox}^{II/I}\right) - E_{00} - \left(Q_{red}^{0/-}\right)$$
(4.2a)

$$\Delta G_{red} = (Q_{ox}^{+/0}) - \left[ \left( bp y_{red}^{0/-} \right) + E_{00} \right]$$
(4.2b)

Equation 4.2a describes the thermodynamics for oxidative quenching of the MLCT state, for the CoRe compounds these products are Re(II) and Co(II). Reductive quenching is described in equation 4.2b and results in the formation of the bpy radical anion and Co(IV). The Co<sup>IV/III</sup> oxidation potential for all the compounds studied is not observed (> +2.0 V) and the  $\Delta G_{red}$  for reductive quenching is prohibitively large. The  $\Delta G_{ox}$  can be calculated from the Re oxidation potentials, the Co reduction potentials, and the E<sub>00</sub> determined from spectral fitting of the emission profiles and these values are shown in Table 4.1. Based on the  $\Delta G_{ox}$  calculated for compounds **1** – **3** oxidative quenching for CoRe(bpy) and CoRe(tmb) is thermodynamically possible, -0.04 eV and -0.18 eV respectively, but not possible for the CoRe(btfmb), +0.33 eV. In the previous CoRe<sub>3</sub> tetranuclear assemblies the change in free energy for photo-induced electron transfer was prohibitively positive. The change in coordination environment around the Co(III) center in the CoRe dinuclear compounds directly shifts the Co(III) reduction to a more positive potential resulting in the driving force for photo-induced electron transfer being a thermodynamically viable pathway for the CoRe(bpy) and CoRe(tmb) compounds. Based on the results from the tetranuclear CoRe<sub>3</sub> compounds, quenching via Förster transfer did not occur due to it being a spin-forbidden process and no attenuation in the MLCT lifetime was observed. Therefore, because the driving force for electron transfer for the CoRe(btfmb) compound is prohibitively positive and Förster transfer is spin forbidden process quenching of the MLCT excited state should not be observed.

The quantum yields for compounds 1-3 are compared to the individual Re donors in Table 4.2. It is apparent from the quantum yields that quenching is occurring for the CoRe(bpy) compound due to the order of magnitude decrease and quantum yield. The quantum yield for CoRe(tmb) decreases by 2 order of magnitude relative to [Re(tmb)(CO)<sub>3</sub>(4-Etpy)]<sup>+</sup> suggesting a larger degree of quenching is occurring. The quantum yield for CoRe(btfmb) is lower when

Compound	Φ
CoRe(bpy) (1)	0.0038±0.002
$[\text{Re(bpy)(CO)}_3(4\text{-Et-py})]^+$	0.029±0.001
CoRe(btfmb) (2)	0.00069±0.0001
$[\text{Re(btfmb)(CO)}_3(4\text{-Et-py})]^+$	0.0015±0.0002
CoRe(tmb) (3)	$0.0039 \pm 0.0001$
[Re(tmb)(CO) <sub>3</sub> (4-Et-py)] <sup>+</sup>	0.148±0.001

Table 4.2. Quantum yields for three dinuclear CoRe compounds 1 - 3.

compared to  $[\text{Re(btfmb)(CO)}_3(4\text{-Etpy})]^+$  but only by a factor of 2 which is a much smaller change compared to the order of magnitudes of difference between the other CoRe compounds and their respective standards.

Nanosecond time-resolved emission for CoRe(bpy) is shown in Figure 4.8 in MeCN. Upon excitation at 370 nm and probing the kinetics at 580 nm, the emission maximum of the MLCT state, biexponential kinetics are observed,  $\tau_1 = 225$  ns and  $\tau_2 = 15$  ns. The 15 ns component is indicative of dynamic quenching of the <sup>3</sup>MLCT state supported by the decrease in quantum yield from steady-state emission. However, the biphasic kinetics revealing a 225 ns component that is the same time constant observed for [Re(bpy)(CO)<sub>3</sub>(4-Etpy)]<sup>+</sup> is intriguing. To be able to understand the photophysical processes that are occurring for this compound it is imperative to establish that the biphasic kinetics that are observed are inherent to this compound and do not arise



Figure 4.8. Time-resolved emission of  $[Co(tren)(pyacac)Re(bpy)(CO)_3](OTf)_3$  in MeCN ( $\lambda_{ex} = 370$  nm,  $\lambda_{probe} = 580$  nm). Amplitude of  $\tau_1 = 0.029$  and amplitude of  $\tau_2 = 0.86$ .

from instrumental artifacts, photodecomposition, or impurities. For time-resolved emission the amplitude of a given time component is directly related to the concentration of that emissive excited state. Therefore, due to the weak driving force that is predicted for electron transfer,  $\Delta G$ =-0.04 eV, and the spin restriction of Förster transfer, one possible expectation for the kinetics of this system is that no quenching occurs. Under this hypothesis that would indicate that the 15 ns component, that accounts for 95% of the total amplitude, is from an impurity and the 225 ns component is from the unquenched CoRe(bpy) compound. An impurity resulting in 95% of a Re polypyridyl emissive signal can be ruled out based on the  ${}^{1}H$  NMR. In another scenario where the oxidative quenching is occurring, the 15 ns component is attributed to quenching of the <sup>3</sup>MLCT of CoRe(bpy), and the 5% amplitude of the 225 ns component would then arise from an independent Re(bpy)-based impurity. The presence of a Re(bpy)-based impurity can be ruled out based on the purity of the <sup>1</sup>H NMR. The possibility for photodecomposition resulting in biphasic kinetics can also be ruled out from the indifference of the absorption spectra and <sup>1</sup>H NMR before and after spectroscopy. The chloride salt, [Co(tren)(pyacac)Re(bpy)(CO)<sub>3</sub>](Cl)<sub>3</sub>, was isolated before metathesis to the triflate salt and photodecomposition is apparent based on the <sup>1</sup>H NMR collected after time-resolved and steady-state emission, Figure 4.9a. By observing photodecomposition of the chloride salt by <sup>1</sup>H NMR suggests that <sup>1</sup>H NMR is an appropriate technique to detect photodecomposition in conjunction with monitoring the UV-Vis before and after the experiments. The <sup>1</sup>H NMR of the triflate salt, [Co(tren)(pyacac)Re(bpy)(CO)<sub>3</sub>](OTf)<sub>3</sub>, after steady-state and time-resolved experiments is shown in Figure 4.9b, and is identical to the  ${}^{1}$ H NMR measured before the spectroscopy experiments, Figures 4.32 and 4.33. Based on the purity of the sample, the amplitudes of each time component, and ruling out photodecomposition, this suggests that the biphasic kinetics observed for CoRe(bpy) are inherent to this compound.



Figure 4.9. (a) <sup>1</sup>H NMR of  $[\text{Re}(\text{bpy})(\text{CO})_3(\text{pyacac})\text{Co}(\text{tren})](\text{Cl})_3$  in methanol- $d_4$  taken after spectroscopy. The presence of new peaks indicates photodecomposition. (b) <sup>1</sup>H NMR of  $[\text{Re}(\text{bpy})(\text{CO})_3(\text{pyacac})\text{Co}(\text{tren})](\text{Cl})_3$  in methanol- $d_4$  taken after spectroscopy.

Due to the short time constant measured for CoRe(bpy) being close to the instrument response function (IRF), 7 ns, time correlated single photon counting (TCSPC) was performed to provide an accurate time constant where the IRF is 25 ps at full width half maximum.<sup>15</sup> To ensure that the 15 ns component measured in the nanosecond time-resolved experiments is not from laser scatter performing TCSPC with a much shorter IRF can fully resolve the 15 ns time constant from the IRF. TCSPC for CoRe(bpy) was collected in MeCN by Professor Gary Blanchard and is shown in Figure 4.10. The kinetics of the MLCT state are measured at 580 nm following 370 nm excitation and the data was fit to a biexponential decay using the 225 ns time constant from the nanosecond experiment and measured the fast component to be 10 ns. The increased temporal

resolution of TCSPC unequivocally established that the 10 ns component is not an artifact from laser scatter in the nanosecond experiments.



Figure 4.10. TCSPC of [Co(tren)(pyacac)Re(bpy)(CO)<sub>3</sub>](OTf)<sub>3</sub> in MeCN ( $\lambda_{ex} = 370$  nm,  $\lambda_{probe} = 580$  nm).

Based on the donor-acceptor distance Dexter transfer cannot occur in these compounds, this then leaves either Förster transfer or oxidative quenching to be responsible for the dynamic quenching observed based on the steady-state and time-resolved experiments. As stated previously Förster transfer did not occur in the tetranuclear assemblies due to the lack of coupling to the  $|S_{A^*}|$ = 1 state resulting in this quenching pathway being spin forbidden. The same spin conservation effect is present in the CoRe(bpy) compound removing Förster transfer as a possible pathway for quenching. The  $\Delta G_{ox}$  estimated for oxidative quenching using the Rehm-Weller equation makes electron transfer a thermodynamically feasible pathway and Figure 4.11 demonstrates that this process conserves spin angular momentum and is spin allowed. Formation of the low-spin Co(II) is used to assess the spin of the products because electron transfer will initially occur to this state and then reorganization to the high-spin Co(II) will occur because nuclear motion occurs on a slower time-scale than electronic changes. Therefore, using the low-spin Co(II) state to determine the spin conservation for this process is appropriate. This shows that oxidative quenching is thermodynamically possible and conserves spin angular momentum but this does not account for the biphasic kinetics observed in the time-resolved experiments.



Figure 4.11. Single electron representation of the spin-allowed oxidative quenching pathway for CoRe complexes.

Oxidative quenching of the <sup>3</sup>MLCT state to produce Re(II) and Co(II) is consistent with the decreased quantum yield and the short time constant,  $\tau_2 = 10$  ns, for CoRe(bpy), however the 225 ns component is not accounted for. Based on the driving force for electron transfer being only 40 meV exergonic we propose that a rapid electron transfer equilibrium is occurring in this system. Before the equilibrium is established equation 4.3 shows the rate law for the <sup>3</sup>MLCT state. Where  $k_1$  is the rate constant for oxidative quenching,  $k_{-1}$  is the rate constant for back electron transfer, and  $k_3$  is the rate constant for <sup>3</sup>MLCT  $\rightarrow$  <sup>1</sup>A<sub>1</sub> decay, depicted in Figure 4.12.

$$\frac{d[Re^{II}(bpy^{-})Co^{III}]}{dt} = -(k_1 + k_2)[Re^{II}(bpy^{-})Co^{III}] + k_{-1}[Re^{II}(bpy)Co^{II}]$$
(4.3)

Before the equilibrium is established between the <sup>3</sup>MLCT and Re(II)-Co(II) two rate constants affect the concentration of the <sup>3</sup>MLCT state, k<sub>1</sub>, the rate of forward electron transfer, and k<sub>2</sub>, decay to the ground state. Two rate constants are observed in the time-resolved experiments from the biexponential kinetics, the 10 ns component attributed to the electron transfer process and the 225 ns component indicative to decay to the ground state. The 225 ns component can be attributed to the <sup>3</sup>MLCT  $\rightarrow$  <sup>1</sup>A<sub>1</sub> decay because this is the same lifetime measured for the <sup>3</sup>MLCT state of [Re(bpy)(CO)<sub>3</sub>(4-Etpy)]<sup>+</sup> discussed in Chapter 2. Once the equilibrium has established the ratio of k<sub>1</sub>/k<sub>2</sub> is equal the concentration of the electron transfer product to <sup>3</sup>MLCT, equation 4.4, and the expression in equation 4.5 can be substituted into equation 4.3 resulting in the rate law after equilibrium has been established, equation 4.6.

$$K_{eq} = \frac{k_1}{k_{-1}} = \frac{[Re^{II}(bpy)Co^{II}]}{[Re^{II}(bpy^{-})Co^{III}]}$$
(4.4)

$$k_{1}[Re^{II}(bpy^{-})Co^{III}] = k_{-1}[Re^{II}(bpy)Co^{II}]$$
(4.5)

$$\frac{d[Re^{II}(bpy^{-})Co^{III}]}{dt} = -k_2[Re^{II}(bpy^{-})Co^{III}]$$
(4.6)

After the equilibrium is established the concentration of the <sup>3</sup>MLCT state is only dependent on one rate constant, and because biexponential kinetics are observed from the time-resolved experiments it can be concluded that this system is in a pre-equilibrated state. Based on this kinetic model electron transfer before the equilibrium is established results in quenching of the <sup>3</sup>MLCT state where a shorter lifetime is observed, i.e. 10 ns component, in addition to the decay from the <sup>3</sup>MLCT to the ground state occurs with a rate constant typical for Re polypyridyl excited states, i.e. 225 ns component.

This model and the analysis of the rate laws before and after the equilibrium can be used



Figure 4.12. Kinetic model for electron transfer equilibrium in CoRe(bpy).

to explain the biphasic kinetics for CoRe(bpy). Equation 4.7 relates the equilibrium constant,  $K_{eq}$ , to the change in free energy,  $\Delta G$ . The  $\Delta G$  can be calculated independently from the Rehm-Weller equation and  $k_1$  is measured from the time-resolved data, therefore by using equation 4.4  $k_{-1}$  can be calculated to be 50 ns.

$$\Delta G_{ox} = -RT ln(K_{eq}) \tag{4.7}$$

To further support the validity of this kinetic model for this system a solution to the differential equation 4.3 was solved for using MATLAB by Dr. Bryan Paulus allowing for k<sub>-1</sub> to be included in the fit. Equation 4.8 is the solution to the differential equation solving for [Re<sup>II</sup>(bpy<sup>-</sup>)Co<sup>III</sup>] as a function of time. In equation 4.8 the rate for back electron transfer is described as k<sub>2</sub> and the MLCT  $\rightarrow$  <sup>1</sup>A<sub>1</sub> decay is described as k<sub>3</sub>. This allows for the biexponential kinetics to be modeled with three rate constants. This is significant because the three rate constants used in equation 4.8 account for the electron transfer equilibrium.



Equation 4.8 was fit to the TCSPC data for CoRe(bpy), Figure 4.10, and three lifetimes were measured,  $\tau_1 = 14.6$  ns,  $\tau_2 = 79$  ns, and  $\tau_3 = 225$  ns. The time constants are labeled to

correspond with the processes described in Figure 4.12. This fitting analysis allows for  $k_2$  to be fit directly to the data without using the Rehm-Weller equation. This also allows for  $\Delta G$  to be calculated independently of the Rehm-Weller equation using equation 4.7 and the experimentally determined  $k_1$  and  $k_2$  rate constants.

[Co(tren)(pyacac)	Re(bpy)(CO)	$_{3}]^{3+}$ .		-
	Parameter	<b>Biexponential Fit</b>	Solution to Differential	

Table 4.3. Comparison of time constants and  $\Delta G$  via different fitting methods for

Parameter	Blexponential Fit	Solution to Differential		
		<b>Equation Fit</b>		
$\tau_1$	10 ns	14.6 ns		
$\tau_2$	50 ns	79 ns		
$\tau_3$	225 ns	225 ns		
$\Delta G_{ox}$	-0.04 eV	-0.043 eV		
$\mathbf{K}_{\mathrm{eq}}$	5	5.4		

Table 4.3 shows the comparison between the time constants and  $\Delta G$  calculated between using the two different methods. The  $\tau_1$  values measured from each fit are in good agreement within each other and differ by less than 5 ns. The  $\tau_2$  value calculated from the biexponential fit via equation 4.7 is within 30 ns of the time constant fit using equation 4.8. The  $\Delta G$  calculated from using  $\tau_1$  and  $\tau_2$  from the differential solutions fit is nearly identical to the  $\Delta G$  calculated using the Rehm-Weller equation. The consistency between these two approaches to explain the photophysics of this compound further supports the proposed kinetic model for CoRe(bpy).

Despite the spectral overlap between the <sup>3</sup>MLCT emission and <sup>1</sup>T<sub>1</sub> absorption and the relatively small driving force for excited-state electron transfer, the inherent design of the CoRe(bpy) compound should favor quenching via Förster transfer. However, because Förster transfer does not conserve spin angular momentum this thermodynamically favored quenching pathway is shut down and oxidative quenching becomes the primary pathway. In the tetranuclear

systems spin was used to completely eliminate Förster transfer for the CoRe<sub>3</sub> compounds. Where the dinuclear donor-acceptor motif is one of the first examples where spin is used to select the quenching mechanism.

The CoRe(tmb) complex was studied and the use of the tmb ligand increases the energy the <sup>3</sup>MLCT state such that the driving force for oxidative quenching increases relative to CoRe(bpy), -0.18 eV. The nanosecond time-resolved emission spectroscopy in MeCN for CoRe(tmb) is shown in Figure 4.13. The kinetics of the MLCT state are measured at 535 nm following 370 nm excitation, the data is fit to a biexponential decay with measured time constants of  $\tau_1 = 1.45 \,\mu\text{s}$  and  $\tau_2 = 17 \,\text{ns}$ . The 1.45  $\mu\text{s}$  time constant is the same observed rate constant for the <sup>3</sup>MLCT lifetime of [Re(tmb)(CO)<sub>3</sub>(4-Etpy)]<sup>+</sup>, discussed in Chapter 2, while the 17 ns component indicates dynamic quenching. Similar to the CoRe(bpy) compound, due to the amplitudes of each component and the absence of impurities from the <sup>1</sup>H NMR the biphasic kinetics are inherent to



Figure 4.13. Time-resolved emission of  $[Co(tren)(pyacac)Re(tmb)(CO)_3](OTf)_3$  in MeCN ( $\lambda_{ex} = 370 \text{ nm}$ ,  $\lambda_{probe} = 535 \text{ nm}$ ). Amplitude for  $\tau_1 = 0.035$  and amplitude for  $\tau_2 = 0.77$ .

the CoRe(tmb) compound. Due to the increased driving force for oxidative quenching and Förster transfer being spin-restricted, the same kinetic model, Figure 4.12, is used to explain the observed kinetics.

To obtain an accurate value for the short time constant the time-resolved emission spectrum for CoRe(tmb) was only collected up to 450 ns, this allows for measuring more data points per time interval. Similar to the analysis of the CoRe(bpy) kinetics, the time-resolved emission data for CoRe(tmb) was fit to a biexponential decay resulting in lifetimes of  $\tau_1 = 17$  ns and  $\tau_2 = 1.45$ µs, Table 4.4. The Rehm-Weller equation was used to estimate a driving force of -0.18 eV for oxidative electron transfer and using equations 4.4 and 4.7  $\tau_2$  was calculated to be 20 µs. These results can be compared to the data shown in Figure 4.14 when fit using equation 4.8, the 1.45 µs component that was measured from the longer timescale experiment, Figure 4.13, was held



Figure 4.14. Time-resolved emission of  $[Co(tren)(pyacac)Re(tmb)(CO)_3](OTf)_3$  in MeCN ( $\lambda_{ex} = 370 \text{ nm}$ ,  $\lambda_{probe} = 535 \text{ nm}$ ). The data is fit to a solution of differential equations to fit the kinetic model of rapid equilibrium for electron transfer.

Parameter	<b>Biexponential Fit</b>	Solution to Differential		
		<b>Equation Fit</b>		
$\tau_1$	17 ns	20 ns		
$\tau_2$	20 µs	800 ns		
$\tau_3$	1.45 µs	1.45 μs		
$\Delta G_{ox}$	-0.18 eV	-0.10 eV		
K <sub>eq</sub>	1200	41		

Table 4.4. Comparison of time constants and  $\Delta G$  via different fitting methods for  $[Co(tren)(pyacac)Re(tmb)(CO)_3]^{3+}$ .

constant. When the data is fit using equation 4.8 three time constants are measured,  $\tau_1 = 20$  ns,  $\tau_2 = 800$  ns, and  $\tau_3 = 1.45$  µs. These values were used to the calculate  $\Delta G$  independently of the Rehm-Weller equation and are compared in Table 4.4. The calculated  $\Delta G$  between the two methods differ by 0.08 eV, and this difference manifests itself when calculating  $\tau_2$  and K<sub>eq</sub>. While the difference between the two methods for  $\Delta G$  is larger when compared to CoRe(bpy), this kinetic model still accurately accounts for the biphasic kinetics observed and the overall increase in driving force for electron transfer. The  $\tau_1$  values measured from each method are in good agreement with each other and differ by 3 ns.

Even though the average calculated  $\Delta G_{ox}$  for CoRe(tmb) using both fitting methods is -0.14 eV it is still possible that an equilibrium for electron transfer is still operative despite an increased driving force.<sup>18-22</sup> As shown in Figure 4.11 the initial product for electron transfer results in low-spin Co(II), while conversion to the high-spin Co(II) requires reorganization energy and imposes a kinetic barrier for this conversion. This allows the low-spin Co(II) to participate in the rapid photo-induced electron transfer equilibrium. The photophysics of the CoRe(bpy) and CoRe(tmb) compounds can be accurately described using the rapid electron transfer equilibrium model that has been proposed. By modulating the substituents on the bpy ligand, the electronics of the <sup>3</sup>MLCT state can be altered to



Figure 4.15. Time-resolved emission of  $[Co(tren)(pyacac)Re(btfmb)(CO)_3](OTf)_3$ (left) ( $\tau = 15$  ns,  $\lambda_{ex} = 410$  nm,  $\lambda_{probe} = 665$  nm) and  $[Re(btfmb)(CO)_3(4-Etpy)](OTf)$ (right) ( $\tau = 20$  ns,  $\lambda_{ex} = 410$  nm,  $\lambda_{probe} = 665$  nm) in MeCN.

affect the change in free energy of electron transfer. In this regard the photophysics of the dinuclear CoRe(btfmb) compound was studied. The driving force for oxidative quenching for CoRe(btfmb) was determined using the Rehm-Weller equation and is prohibitively large,  $\Delta G_{ox} = +0.33$  eV. Therefore, quenching via electron transfer should not occur. The time-resolved emission for CoRe(btfmb) is shown in Figure 4.15 (left) after excitation at 410 nm and measuring the kinetics of the MLCT state at 665 nm. Monoexponential kinetics are observed with a time constant of  $\tau = 15$  ns. Due to the observed time constant being relatively close to the measured IRF of the instrument (7 ns) Gaussian deconvolution was used to fit the kinetics. The lifetime of CoRe(btfmb) is compared to the individual Re standard, [Re(btfmb)(CO)<sub>3</sub>(4-Etpy)]<sup>+</sup>, in Figure 4.15 (right) following 410 nm excitation and measuring the kinetics at 665 nm. Gaussian deconvolution of the time-resolved data measures a lifetime of  $\tau = 20$  ns. At first glance the 5 ns difference, 25% change

in lifetime, between these two compounds potentially indicates that the quenching is occurring in CoRe(btfmb). However, the change in lifetime can be explained due to ion pairing effects because the overall charge of CoRe(btfmb) has an overall charge of +3 compared to an overall charge of +1 for  $[\text{Re(btfmb)(CO)}_3(4-\text{Etpy})]^+$ .<sup>23</sup> The observation of monoexponential kinetics, with a positive  $\Delta G$  for electron transfer, along with with the potential for ion pairing effects to alter the lifetime when the overall charge of the molecule is increased suggests that quenching of the <sup>3</sup>MLCT state in CoRe(btfmb) does not occur. While the data suggests that CoRe(btfmb) does not exhibit any quenching, this would then indicate that Förster transfer is not occurring and it is still a spinforbidden process in the dinuclear compounds. If Förster energy transfer does not occur in the CoRe(btfmb) complex, then it can be concluded that it does not occur in the CoRe(bpy) and CoRe(tmb) complexes. This demonstrates the first time spin has been used to control the excitedstate quenching mechanism. By studying the three dinuclear CoRe compounds, the substituents on the bpy ligand can be used to change the  $E_{00}$ , affecting the  $\Delta G$  for electron transfer, and the spin of the Co(III) can be used to "shutdown" the Förster transfer pathway. Electronic control of the E<sub>00</sub> makes electron transfer possible for the CoRe(bpy) and CoRe(tmb), but not for CoRe(btfmb) and the spin of Co(III) prevents Förster transfer from occurring in all three compounds.

While the change in lifetime between the CoRe(btfmb) and the  $[Re(btfmb)(CO)_3(4-Etpy)]^+$ standard could be explained by the difference in overall charges, this discrepancy can be eliminated by studying a gallium control molecule, Figure 4.16. The dinuclear GaRe(btfmb) compound can be synthesized and characterized to provide a better suited control molecule rather than the  $[Re(btfmb)(CO)_3(4-Etpy)]^+$  that was studied. Gallium(III) is able to act as a control because of its  $d^{10}$  electronic configuration, redox properties, and the donor-acceptor distance. Metals with a  $d^{10}$ electronic configuration do not possess any ligand field absorptions, therefore Förster energy



Figure 4.16.  $[Ga(tren)(pyacac)Re(btfmb)(CO)_3]^{3+}$ , GaRe(btfmb), used as a control molecule for the CoRe dinuclear systems.

transfer cannot occur due to the lack of absorption of the Ga(III). The redox properties of Ga(III), the reduction to Ga(II) or the oxidation to Ga(IV), are expected to eliminate the electron transfer as a quenching mechanism. By replacing the Co(III) with Ga(III) the through-bond distance between the donor and acceptor is expected to be essentially unchanged, therefore, Dexter transfer cannot occur. The dinuclear GaRe(btfmb) should not be able to engage in quenching and the overall charge of the compound is the same as the CoRe(btfmb) compound. This allows for the comparison of the <sup>3</sup>MLCT lifetimes between the CoRe(btfmb) and GaRe(btfmb) compounds and eliminates ion pairing effects that could cause differences in the photophysical properties.

The photophysical properties for compounds 1 - 3 are summarized in Table 4.5. The time constant pertaining to the rate of electron transfer in CoRe(bpy) and CoRe(tmb) is used to calculate the k<sub>nr</sub> and k<sub>r</sub>. The quenching rate constant, k<sub>q</sub>, is calculated for these compounds using the observed rate constant for the individual Re compounds and then compared to k<sub>nr</sub>. The k<sub>q</sub>/k<sub>nr</sub> ratio for CoRe(bpy) and CoRe(tmb) illustrates the increase in quenching for CoRe(tmb) relative to the nonradiative rate constants intrinsic to these compounds. The increased quenching for CoRe(tmb) compared to CoRe(bpy) is consistent with an increased driving force for oxidative quenching. Based on the observed trend between with the rate of quenching and driving force the data discussed so far supports the kinetic model for a photo-induced electron transfer equilibrium.

Compound	τ (kobs s <sup>-1</sup> )	Φ	knr (s <sup>-1</sup> )	kr (s <sup>-1</sup> )	kq	$k_q^{Co}/k_{nr}^{Co}$
					$(k_{obs}^{Co} - k_{obs}^{std})$	
[Re(bpy)(CO) <sub>3</sub> (4-Etpy)] <sup>+</sup>	225 ns	0.029±0.001	4.3 x10 <sup>6</sup>	1.3 x10 <sup>5</sup>	-	-
[C D (1 )] <sup>3+</sup>	$(4.4 \text{ x}10^{\circ})$	0.0020.0002	6.6 107	2 < 105	C 4 10 <sup>7</sup>	0.02
[CoRe(bpy)] <sup>34</sup>	$(6.9 \text{ x} 10^7)$	0.0038±0.002	6.6 x10'	$2.6 \times 10^{3}$	6.4 x10 <sup>7</sup>	0.93
$[\text{Re(tmb)(CO)}_3(4\text{-Etpy})]^+$	1450 ns $(6.0 \times 10^5)$	$0.148 \pm 0.001$	5.9 x10 <sup>5</sup>	$1.0 \text{ x} 10^5$	-	-
[CoRe(tmb)] <sup>3+</sup>	20 ns	0.0039±0.0001	5.0 x10 <sup>7</sup>	1.9 x10 <sup>5</sup>	4.9 x10 <sup>7</sup>	0.98
	$(5.1 \text{ x} 10^7)$					
[Re(btfmb)(CO) <sub>3</sub> (4-	20 ns	$0.0015 \pm 0.0002$	$4.9 \text{ x} 10^7$	$7.7 \text{ x} 10^4$	-	-
Etpy)] <sup>+</sup>	$(5.0 \text{ x} 10^7)$					
[CoRe(btfmb)] <sup>3+</sup>	15 ns	$0.00069 \pm 0.0001$	$6.6 \text{ x} 10^7$	$4.6 \text{ x} 10^4$	-	-
	$(6.7 \text{ x} 10^7)$					

Table 4.5. Photophysical properties of CoRe compounds.

To further support this model and to provide conclusive experimental evidence of the electron transfer products nanosecond transient absorption spectroscopy for CoRe(bpy) and CoRe(tmb) was performed. Probing the single-wavelength kinetics at 390 nm for CoRe(bpy) following MLCT excitation at 370 nm is shown in Figure 4.17. The data is fit to a biexponential Gaussian deconvolution with measured time constants of  $\tau_1 = 15$  ns and  $\tau_2 = 190$  ns. The positive



Figure 4.17. Transient absorption of CoRebpy in MeCN ( $\lambda_{ex} = 370 \text{ nm}, \lambda_{probe} = 390 \text{ nm}$ ).

transient absorption at 390 nm is typical for <sup>3</sup>MLCT states of Re polypyridyls<sup>24-26</sup> and can be further explained from the spectroelectrochemistry, Figure 4.18. The oxidative spectrum for CoRe(bpy) is shown in Figure 4.18 (left) and consists of a bleach from 370 nm – 400 nm while in the reductive spectrum the bpy radical anion shows an intense absorption from 350 - 450 nm. The positive feature observed in the transient absorption data is a result from a bpy radical anion absorption in the <sup>3</sup>MLCT state.

The biphasic kinetics observed in Figure 4.17 further supports the proposed kinetic model. The 190 ns lifetime observed is slightly shorter compared to the time-resolved emission data due to local heating in the sample compartment, however this observed lifetime is in agreement with the transient absorption kinetics of the <sup>3</sup>MLCT decay for  $[\text{Re(bpy)(CO)}_3(4-\text{Etpy})]^+$ ,  $\tau = 190$  ns. Transient absorption spectroscopy is inherently less sensitive compared to time-resolved emission and observing biphasic kinetics in both techniques supports that the kinetics arise from the <sup>3</sup>MLCT



Figure 4.18. Oxidative spectroelectrochemistry (left) of  $[Co(tren)(pyacac)Re(bpy)(CO)_3](OTf)_3$  in MeCN with 0.1 M TBAPF<sub>6</sub> at 1.51 V (vs. Fc/Fc<sup>+</sup>). The absorbance spectra are acquired at 30 second intervals and progress from red to blue. Reductive spectroelectrochemistry (right) of  $[Co(tren)(pyacac)Re(bpy)(CO)_3](OTf)_3$  in MeCN with 0.1 M TBAPF<sub>6</sub> at -1.57 V (vs. Fc/Fc<sup>+</sup>). The absorbance spectra are acquired at 30 second intervals and progress from red to blue. Direction of arrows indicate the change in absorbance as a function of time.

state of CoRe(bpy) and not from an impurity.

Similar biphasic kinetics are also observed for CoRe(tmb) when probing at 390 nm following 370 nm excitation, Figure 4.19. The data is fit to a biexponetial Gaussian deconvolution measuring time constants of  $\tau_1 = 15$  ns and  $\tau_2 = 1250$  ns. The 1250 ns component is the same time constant observed for the <sup>3</sup>MLCT decay of [Re(tmb)(CO)<sub>3</sub>(4-Etpy)]<sup>+</sup>,  $\tau = 1250$  ns, and is slightly shorter when compared to the time-resolved emission data due to the variation in temperature in the sample compartment (i.e. not thermostatted) as discussed above. The spectroelectrochemical spectra of CoRe(tmb) can be used as a guide to interpret the absorption features in the transient absorption data. The oxidative spectroelectrochemistry spectrum features a bleach from 350 nm – 390 nm and an absorption from 400 nm – 500 nm, Figure 4.20 (left). The bleach is observed due



Figure 4.19. Single-wavelength kinetic trace of CoRe(tmb) in MeCN ( $\lambda_{ex} = 370$  nm,  $\lambda_{probe} = 390$  nm). Inset: Single-wavelength kinetic trace of CoRe(tmb) showing the  $\tau_2 = 1250$  ns.

to the loss in absorbance of the MLCT state upon oxidation to Re(II), and the positive absorption occurs from a LMCT transition. The reductive spectrum is shown in Figure 4.20 (right) and features a positive absorption from 350 nm - 440 nm and a bleach at 500 nm. The positive feature is assigned to absorptions of the tmb radical anion and the negative feature at 500 nm is due to the loss of absorbance from the Co(III) upon reduction to Co(II). This is not observed in the reductive spectroelectrochemical spectrum for CoRe(bpy) due to the bpy radical anion absorption features from 450 nm to 550 nm.

Multiple probe wavelengths were used to study the kinetics of both CoRe(bpy) and CoRe(tmb) and the full spectrum for CoRe(tmb) is shown in Figure 4.21, while the single-wavelength traces are presented in the appendix. The full transient absorption spectrum of CoRe(tmb) at two different time delays are shown in Figure 4.21, t = 0 ns is shown in blue, and the time delay at 200 ns is shown in green. Positive absorption features are observed from 380 nm



Figure 4.20. Oxidative spectroelectrochemistry (left) of  $[Co(tren)(pyacac)Re(tmb)(CO)_3](OTf)_3$  in MeCN with 0.1 M TBAPF<sub>6</sub> at 1.47 V (vs. Fc/Fc<sup>+</sup>). The absorbance spectra are acquired at 30 second intervals and progress from red to blue. Reductive spectroelectrochemistry (right) of  $[Co(tren)(pyacac)Re(tmb)(CO)_3](OTf)_3$  in MeCN with 0.1 M TBAPF<sub>6</sub> at -1.93 V (vs. Fc/Fc<sup>+</sup>). The absorbance spectra are acquired at 30 second intervals and progress from red to blue. Direction of arrows indicate the change in absorbance as a function of time.

– 490 nm and biphasic kinetics are observed from 380 nm – 440 nm where monoexponential kinetics are observed from 450 nm – 490 nm. From 450 – 490 nm only the  $\tau_1 = 15$  ns component is observed. The transient absorption decreases towards red wavelengths and since the amplitude of the 1.25 µs component has a relatively weak signal compared to the 15 ns component the 1.25 µs component is not observed from 450 – 490 nm. The transient absorption spectra of <sup>3</sup>MLCT states of Re(I) polypyridyls characteristically possess positive features associated with the bpy radical anion absorption and bleaching of the MLCT absorption is not observed.<sup>24-26</sup> Monitoring the kinetics from the signal arising from the MLCT bleach would provide diagnostics of the kinetics associated with Re(II)-based species. This would be the ideal method for observing the kinetics associated with the electron transfer products, specifically the Re(II)-Co(II) species. Unfortunately, the MLCT bleach is not observed for this system. While there is a positive feature observed from 450 nm – 490 nm in the oxidative spectroelectrochemistry this absorption is relatively weak when compared to the reductive spectroelectrochemistry which also possess an



Figure 4.21. Transient absorption spectrum of CoRe(tmb) in MeCN at specified time delays (blue = 0 ns, green = 200 ns,  $\lambda_{ex}$  = 370 nm).

absorption feature in this same wavelength range. Even by using the oxidative spectroelectrochemical spectrum as a guide to identify absorptions inherent to the Re(II) species both the tmb radical anion and Re(II) absorptions overlap, convoluting the kinetic analysis. Furthermore, detection of absorptions from the Co(II) are not indistinguishable from absorptions from the tmb radical anion in the reductive spectroelectrochemistry and ligand field absorptions of Co(II) will result in relatively weak signal and were not be observed.

Absorption features distinct to the electron transfer product, the Re<sup>II</sup>Co<sup>II</sup> species, were not observed. However, the kinetics observed from the transient absorption experiments can be assigned to the <sup>3</sup>MLCT state for CoRe(bpy) and CoRe(tmb) from the positive absorption features of the bipyridine radical anion absorptions that are typical for these class of chromophores. The biphasic kinetics observed in the transient absorption data for both CoRe(bpy) and CoRe(tmb) support the observations from the time-resolved emission experiments verifying that both time constants are innate to the molecules studied and are not the result of photodecomposition or an impurity. The rapid electron transfer equilibrium for CoRe(tmb) and CoRe(bpy) can be supported by the quantum yields, time-resolved emission, time-resolved absorption, and a comparison of the quenching rate constants. This leads to the first report of using spin to control the excited-state quenching mechanism.

## 4.4. Conclusion

To further understand the effects of spin on the excited-state reactivity of molecules three dinuclear donor-acceptor complexes were synthesized and characterized, CoRe(bpy), CoRe(tmb), and CoRe(btfmb). The use of a capping ligand, tren, changes in coordination environment around the Co metal-center allowing one Rebpy donor to bind. The dimensional reduction also affects its reduction potential and its ligand field absorptions. While these compounds met the spectral

overlap requirements for Förster transfer between the <sup>1</sup>T<sub>1</sub> absorption and the <sup>3</sup>MLCT emission the Co<sup>III/II</sup> reduction potential is shifted positive such that oxidative quenching of the excited state is thermodynamically accessible for the CoRe(bpy) and CoRe(tmb) compounds. The driving force for electron transfer is estimated to be -0.04 eV for CoRe(bpy) and -0.18 eV for CoRe(tmb). The steady-state emission data showed quenching with reduced quantum yields and biphasic kinetics in the time-resolved emission experiments for the bpy and tmb compounds. By using spectroelectrochemistry to interpret the nanosecond transient absorption data the biphasic kinetics observed could be explained using a kinetic model featuring a rapid electron transfer equilibrium. The time-resolved data was fit using two different methods and the results were in agreement with each other, supporting the proposed kinetic model. The spin angular momentum for quenching via Förster transfer is not conserved and is not observed, however the oxidative quenching of the <sup>3</sup>MLCT state resulting in the formation of Co(II) conserves spin angular momentum between the reactant and products. The spin restriction for Förster transfer blocks this quenching pathway leading to oxidative quenching occurring. While the tetranuclear systems were the first report of spin affecting the excited-state reactivity, the data presented in this chapter provides the first report of using spin to dictate the quenching pathway.

APPENDIX

The <sup>1</sup>H NMR assignment for [Co(tren)(acac)](OTf)<sub>2</sub> is in agreement with what has been previously reported for [Co(tren)(acac)](Cl)<sub>2</sub>,<sup>16</sup> however the complex splitting pattern has not been assigned. To properly characterize the dinuclear CoRe compounds the <sup>1</sup>H NMR of [Co(tren)(acac)](OTf)<sub>2</sub> was assigned using gHSQC and gCOSY. The <sup>1</sup>H NMR along with the structure of [Co(tren)(acac)]<sup>2+</sup> is shown in Figure 4.22. Proton **a** is easily assigned to the central carbon of the acac ligand, protons **h** and **i** are each singlets and integrate to 3 H and are assigned to the methyl groups on the acac ligand. Protons **b** – **g** integrates to 2 H each and are from the tren ligand, the specific assignments can be concluded from 2D experiments.



Figure 4.22. <sup>1</sup>H NMR of [Co(tren)(acac)](OTf)<sub>2</sub> in deuterium oxide.

gHSQC is used to assign each proton peak to a carbon atom, Figure 4.23. Protons **b** and **g** are on the same carbon, **2**, proton **d** is on carbon **3**, protons **c** and **e** are both on carbon **4**, and proton **f** is on carbon **5**. Due to the chemical shift of the carbon peaks **2** and **3** are assigned to the carbons

closest to the tertiary amine while **4** and **5** are assigned to the carbons closest to the primary amine. The simplest assignment for the tren ligand is that each peak corresponds to a  $CH_2$  and each proton on a methylene bridge is equivalent, however this cannot be possible based on the coupling observed from the gCOSY in Figure 4.24.



Figure 4.23. gHSQC NMR of [Co(tren)(acac)](OTf)<sub>2</sub> in deuterium oxide.

Proton **b** is coupled to protons **c**, **e**, and **g**, under the assignment of each peak in the <sup>1</sup>H NMR corresponding to a CH<sub>2</sub> this would require 5 bond coupling to either **c** or **e** with a 5.9 Hz coupling constant. This suggests that the rigid geometry of the tren ligand and the diastereotopic nature of the protons creates a unique chemical environment for each proton of a CH<sub>2</sub>. The proton assignments are shown in Figure 4.25 and the coupling constants for each peak can be explained through gCOSY.





Proton **b** is vicinally coupled to protons **e** and **c** (J= 13.1 Hz) and geminally coupled to proton **g** (J=5.9 Hz) explaining the triplet of doublet splitting pattern. The coupling of proton **c** to protons **b**, **e**, and **g** with coupling constants of 13.9 Hz and 5.0 Hz explain vicinal coupling to protons **b** and **g** and germinal coupling to **e**. Protons **e** are vicinally coupled to **b** and geminally coupled **c** (J=14.1 Hz, 5.8 Hz), but not coupled to proton **g**. Given the assignment of protons shown in Figure 4.25 the dihedral angle between proton **e** and **g** was calculated to be 107° from a structure minimzation using ChemDraw 3D, this is the angle that will give the lowest vicinal coupling by the Karplus equation. The <sup>1</sup>H-NMR can be explicitly assigned by using gHSQC, gCOSY, and the Karplus equation.



Figure 4.25. <sup>1</sup>H assignment for [Co(tren)(acac)]<sup>2+</sup>.



Figure 4.26. Crystal structure of [Co(tren)(acac)](OTf)<sub>2</sub>.



Figure 4.27. HRMS  $[Co(tren)(acac)](OTf)_2$  in MeOH (m/z: calcd for  $[M-2(OTf)-1H]^+$  303.120, obs. 303.123; calcd for  $[M-OTf]^+$  453.08, obs. 453.083).



Figure 4.28. <sup>13</sup>C NMR of [Co(tren)(acac)](OTf)<sub>2</sub> in deuterium oxide.



Figure 4.29. <sup>1</sup>H NMR of Re(btfmb)(CO)<sub>3</sub>)Cl in acetonitrile- $d_3$ .



Figure 4.30. <sup>1</sup>H NMR of [Re(btfmb)(CO)<sub>3</sub>)(pyacac)]OTf in acetonitrile-*d*<sub>3</sub>.



Figure 4.31. HRMS of  $[Re(bpy)(CO)_3(pyacac)Co(tren)](OTf)_3$  in MeOH (m/z: calcd for  $[M-OTf]^+$  1106.07, obs. 1106.071; calcd for [M-3(OTf)-Co(tren)] 603.08, obs. 603.083; calcd for  $[M-Cr(tren)(pyacac)-3(OTf)+MeCN]^+$  468.04 obs. 468.037; calcd for  $[M-Cr(tren)(pyacac)-3(OTf)]^+$  427.010 obs. 427.011; calcd for  $[M-Re(bpy)(pyacac)(CO)_3-2(OTf)]^+$  354.04, obs. 354.039.



Figure 4.32. HRMS-MS of the  $[M-OTf]^+$  (m/z 1106.071) for  $[Re(bpy)(CO)_3(pyacac)Co(tren)](OTf)_3$  in MeOH. The peaks with only Co and Re in the HRMS are from fragmentation in the mass spectrometer and from impurities (m/z: calcd for [M-3(OTf)-Co(tren)] 603.08, obs. 603.083; calcd for  $[M-Cr(tren)(pyacac)-3(OTf)]^+$  427.010 obs. 427.011; calcd for  $[M-Re(bpy)(pyacac)(CO)_3-2(OTf)]^+$  354.04, obs. 354.039.



Figure 4.33. <sup>1</sup>H NMR of [Re(bpy)(CO)<sub>3</sub>(pyacac)Co(tren)](OTf)<sub>3</sub> in methanol-*d*<sub>4</sub>, 1.5–10.0 ppm.



Figure 4.34. <sup>1</sup>H NMR of [Re(bpy)(CO)<sub>3</sub>(pyacac)Co(tren)](OTf)<sub>3</sub> in methanol-*d*<sub>4</sub>, 7.2–9.5 ppm.



Figure 4.35. <sup>1</sup>H NMR of [Re(bpy)(CO)<sub>3</sub>(pyacac)Co(tren)](OTf)<sub>3</sub> in methanol-*d*<sub>4</sub>, 1.7–3.8 ppm.


Figure 4.36. HRMS of  $[Re(tmb)(CO)_3(pyacac)Co(tren)](OTf)_3$  in MeOH (m/z: calcd for  $[M-OTf]^+$  1162.130, obs. 1162.130).



Figure 4.37. <sup>1</sup>H NMR of [Re(tmb)(CO)<sub>3</sub>(pyacac)Co(tren)](OTf)<sub>3</sub> in methanol-*d*<sub>4</sub>, 1.0–9.5 ppm.



Figure 4.38. <sup>1</sup>H NMR of [Re(tmb)(CO)<sub>3</sub>(pyacac)Co(tren)](OTf)<sub>3</sub> in methanol-*d*<sub>4</sub>, 7.3–9.2 ppm.



Figure 4.39. <sup>1</sup>H NMR of [Re(tmb)(CO)<sub>3</sub>(pyacac)Co(tren)](OTf)<sub>3</sub> in methanol-*d*<sub>4</sub>, 1.75–3.7 ppm.



Figure 4.40. <sup>1</sup>H NMR of  $[Re(tmb)(CO)_3(pyacac)Co(tren)](Cl)_3$  in methanol- $d_4$ . The NMR was taken after spectroscopy and the presence of new peaks (starred) indicates photodecomposition.



Figure 4.41. HRMS of  $[\text{Re}(\text{btfmb})(\text{CO})_3(\text{pyacac})\text{Co}(\text{tren})](\text{OTf})_3$  in MeOH (m/z: calcd for  $[\text{M-OTf}]^+$  1242.05, obs. 1242.05; calcd for [M-3(OTf)-Co(tren)+H] 740.06, obs. 740.06; calcd for  $[\text{M-Cr}(\text{tren})(\text{pyacac})-3(\text{OTf})]^+$  562.98 obs. 562.98; calcd for  $[\text{M-Re}(\text{bpy})(\text{pyacac})(\text{CO})_3-2(\text{OTf})]^+$  354.04, obs. 354.039.



Figure 4.42. <sup>1</sup>H NMR of [Re(btfmb)(CO)<sub>3</sub>(pyacac)Co(tren)](OTf)<sub>3</sub> in methanol-*d*<sub>4</sub>, 1.5–10 ppm.



Figure 4.43. <sup>1</sup>H NMR of [Re(btfmb)(CO)<sub>3</sub>(pyacac)Co(tren)](OTf)<sub>3</sub> in methanol-*d*<sub>4</sub>, 7–10 ppm.



Figure 4.44. <sup>1</sup>H NMR of [Re(btfmb)(CO)<sub>3</sub>(pyacac)Co(tren)](OTf)<sub>3</sub> in methanol-*d*<sub>4</sub>, 1.8–3.9 ppm.



Figure 4.45. <sup>1</sup>H NMR of [Re(deeb)(CO)<sub>3</sub>(pyacac)Co(tren)](OTf)<sub>3</sub> in methanol-*d*<sub>4</sub>. After multiple attempts of purification, the peaks associated with the ethyl ester were no longer observed and impurities in the aromatic region persisted.



Figure 4.46. Cyclic voltammogram of  $[Co(tren)(acac)](OTf)_2$  in MeCN with 0.1 M TBAPF<sub>6</sub> as supporting electrolyte and internally referenced to Fc<sup>+</sup>/Fc. The cathodic peak at -0.85 V is assigned to the irreversible Co<sup>III/II</sup> reduction potential.



Figure 4.47. Cyclic voltammogram of  $[\text{Re}(\text{bpy})(\text{CO})_3(\text{pyacac})\text{Co}(\text{tren})](\text{OTf})_3$  in MeCN with 0.1 M TBAPF<sub>6</sub> as supporting electrolyte and internally referenced to Fc<sup>+</sup>/Fc. The irreversible peak at -0.72 V is assigned to the Co<sup>III/II</sup> reduction and the peak at -1.47 V is assigned to the bpy reduction.



Figure 4.48. Cyclic voltammogram of  $[Re(bpy)(CO)_3(pyacac)Co(tren)](OTf)_3$  in MeCN with 0.1 M TBAPF<sub>6</sub> as supporting electrolyte and internally referenced to Fc<sup>+</sup>/Fc. The peak at 0 V is from the internally referenced Fc<sup>+</sup>/Fc and the peak at 1.41 V is assigned to the Re<sup>II/I</sup> oxidation.



Figure 4.49. Cyclic voltammogram of  $[\text{Re(btfmb)(CO)}_3(\text{pyacac})\text{Co(tren)}](\text{OTf})_3$  in MeCN with 0.1 M TBAPF<sub>6</sub> as supporting electrolyte and internally referenced to Fc<sup>+</sup>/Fc. The irreversible peak at -0.71 V is assigned to the Co<sup>III/II</sup> reduction and the peak at -1.15 V is assigned to the btfmb reduction.



Figure 4.50. Cyclic voltammogram of  $[\text{Re}(\text{btfmb})(\text{CO})_3(\text{pyacac})\text{Co}(\text{tren})](\text{OTf})_3$  in MeCN with 0.1 M TBAPF<sub>6</sub> as supporting electrolyte and internally referenced to Fc<sup>+</sup>/Fc. The irreversible peak at 2.5 V was the first peak observed when scanning to positive potentials is most likely due to oxidation of the ligand.



Figure 4.51. Differential pulse voltammogram of  $[\text{Re}(\text{btfmb})(\text{CO})_3(\text{pyacac})\text{Co}(\text{tren})](\text{OTf})_3$  in MeCN with 0.1 M TBAPF<sub>6</sub> as supporting electrolyte and internally referenced to Fc<sup>+</sup>/Fc. The peak at 1.52 V is assigned to the Re<sup>II/I</sup> oxidation potential and the increase in current after the peak is due to the onset of oxidation of the solvent which can be seen by the increase in current in the cyclic voltammogram above.



Figure 4.52. Cyclic voltammogram of  $[\text{Re}(\text{tmb})(\text{CO})_3(\text{pyacac})\text{Co}(\text{tren})](\text{OTf})_3$  in MeCN with 0.1 M TBAPF<sub>6</sub> as supporting electrolyte and internally referenced to Fc<sup>+</sup>/Fc. The irreversible peak at -0.89 V is observed from the Co<sup>III/II</sup> reduction and the peak at -1.83 V is assigned to reduction of the tmb. Due to the irreversible nature of the Co<sup>III/II</sup> reduction the peak cathodic current varied with multiple cycles and DPV was performed to determine an accurate Co<sup>III/II</sup> potential.



Figure 4.53. Cyclic voltammogram of  $[Re(tmb)(CO)_3(pyacac)Co(tren)](OTf)_3$  in MeCN with 0.1 M TBAPF<sub>6</sub> as supporting electrolyte and internally referenced to Fc<sup>+</sup>/Fc. The peak at 1.20 V is assigned to the Re<sup>II/I</sup> oxidation, multiple cycles shifted to potential and DPV was performed to determine an accurate Re<sup>II/I</sup> potential.



Figure 4.54. Differential pulse voltammetry of  $[Co(tren)(pyacac)Re(tmb)(CO)_3](OTf)_3$  in MeCN with 0.1 M TBAPF<sub>6</sub> as supporting electrolyte and internally referenced to Fc<sup>+</sup>/Fc. The peak at - 0.76 V is assigned to the Co<sup>III/II</sup> reduction.



Figure 4.55. Differential pulse voltammetry of  $[Co(tren)(pyacac)Re(tmb)(CO)_3](OTf)_3$  in MeCN with 0.1 M TBAPF<sub>6</sub> as supporting electrolyte and internally referenced to Fc<sup>+</sup>/Fc. The peak at 1.37 V is assigned to the Re<sup>II/I</sup> oxidation.



Figure 4.56. Single-wavelength kinetic traces for CoRe(bpy) in MeCN following excitation at 370 nm and fit with a biexponential Gaussian deconvolution. (a)  $\lambda_{probe} = 350$  nm,  $\tau_1 = 15$  ns,  $\tau_2 = 190$  ns. (b)  $\lambda_{probe} = 420$  nm,  $\tau_1 = 15$  ns,  $\tau_2 = 190$  ns. (c)  $\lambda_{probe} = 440$  nm,  $\tau_1 = 15$  ns.



Figure 4.57. Single-wavelength kinetic traces for CoRe(tmb) in MeCN following excitation at 370 nm and fit with a biexponential Gaussian deconvolution. (a)  $\lambda_{probe} = 380 \text{ nm}$ ,  $\tau_1 = 16 \text{ ns}$ ,  $\tau_2 = 1250 \text{ ns}$ . (b)  $\lambda_{probe} = 400 \text{ nm}$ ,  $\tau_1 = 16 \text{ ns}$ ,  $\tau_2 = 1250 \text{ ns}$ . (c)  $\lambda_{probe} = 410 \text{ nm}$ ,  $\tau_1 = 16 \text{ ns}$ ,  $\tau_2 = 1250 \text{ ns}$ . (d)  $\lambda_{probe} = 420 \text{ nm}$ ,  $\tau_1 = 16 \text{ ns}$ ,  $\tau_2 = 1250 \text{ ns}$ .



Figure 4.58. Single-wavelength kinetic traces for CoRe(tmb) in MeCN following excitation at 370 nm and fit with a biexponential Gaussian deconvolution. (a)  $\lambda_{probe} = 430 \text{ nm}$ ,  $\tau_1 = 16 \text{ ns}$ ,  $\tau_2 = 1250 \text{ ns}$ . (b)  $\lambda_{probe} = 440 \text{ nm}$ ,  $\tau_1 = 16 \text{ ns}$ ,  $\tau_2 = 1250 \text{ ns}$ . (c)  $\lambda_{probe} = 450 \text{ nm}$ ,  $\tau_1 = 16 \text{ ns}$ . (d)  $\lambda_{probe} = 460 \text{ nm}$ ,  $\tau_1 = 16 \text{ ns}$ .



Figure 4.59. Single-wavelength kinetic traces for CoRe(tmb) in MeCN following excitation at 370 nm and fit with a biexponential Gaussian deconvolution. (a)  $\lambda_{probe} = 470$  nm,  $\tau_1 = 16$  ns. (b)  $\lambda_{probe} = 480$  nm,  $\tau_1 = 17$  ns. (c)  $\lambda_{probe} = 490$  nm,  $\tau_1 = 15$  ns.

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# Chapter 5. Mechanistic Origin of Photoredox Catalysis Involving Iron(II) Polypyridyl Chromophores

## **5.1. Introduction**

Photoredox catalysis is one of the most rapidly growing fields in chemistry<sup>1-3</sup> and driven by its interest in developing new approaches to known chemistry as well as the discovery of previously unknown reactions the transformational impact on both academic and industrial research is undeniable.<sup>4-7</sup> The use of transition metal-based compounds possessing excited states capable of engaging in electron and energy transfer reactions with organic substrates is central to this effort. Photoredox catalysis enables reactions to be driven from the energy captured by light, proceed via alternate kinetic pathways, and through milder reaction conditions. Recent work has extended this excited-state reactivity motif to include organic chromophores<sup>8,9</sup> while photoredox catalysis has leveraged the well-documented photophysics endemic to the charge-transfer excited states of 2<sup>nd</sup>- and 3<sup>rd</sup>-row transition metal polypyridyl complexes such as tris(2.2'bipyridine)ruthenium(II) ( $[Ru(bpy)_3]^{2+}$ ) and (*fac*-tris(2-phenylpyridine)iridium(III) (*fac*-Ir(ppy)<sub>3</sub>).<sup>10-14</sup> The metal-to-ligand charge-transfer (MLCT) states accessed upon visible light excitation of these types of chromophores possess lifetimes on the order of microseconds and are capable of storing roughly 2 V of energy.<sup>15-17</sup> The nature of the lowest-energy excited state in these compounds is charge separated in nature localizing a negative charge on the periphery ligand and positive charge on the metal center. These characteristics allow them to engage in a wide range of chemical reactions reliant on electron and/or energy transfer with a given substrate.

Ruthenium and iridium polypyridyls have been utilized so regularly as photoredox catalysts because of their advantageous characteristics. An ideal photocatalyst possesses a strong absorption feature over a distinct spectral region, an excited state lifetime on the order of

nanoseconds to microseconds, photo-stability, and reversible redox chemistry. These chromophores possess visible MLCT absorptions with an extinction coefficient on the order of 10.000 M<sup>-1</sup> cm<sup>-1</sup> that have microsecond lifetimes, and photodecomposition and irreversible redox chemistry does not occur. Despite all of the advantages of ruthenium- and iridium-based chromophores in photoredox catalysts these metals are among the rarest in the earth's crust raising issues with cost and scalability of applications utilizing these compounds.<sup>18</sup> Given these issues as well as the possibility of discovering new chemical reactions an initiative for utilizing chromophores with earth-abundant transition metals has started in the last decade.<sup>19-22</sup> Multiple reports of copper,<sup>23-26</sup> molybdenum,<sup>27-29</sup> and chromium<sup>30-34</sup> photocatalysts have been employed to sensitize photoredox reactions. Not only have the photophysics of these earth-abundant chromophores have been well documented but the excited-state quenching mechanism of these photocatalysts have been explored as well. In recent years iron(II) polypyridyls have been used as photocatalysts but unlike the other earth-abundant transition metal catalysts, the mechanism of these reactions pertaining to the excited-state quenching of the chromophores have not been clear.<sup>35-37</sup> Utilizing iron(II) polypyridyls as photocatalysts present an interesting case because they are isoelectronic with ruthenium(II) and iridium(III) congeners, commonly leading to the misconception that their nature of excited-state quenching will be identical to the second- and third-row metals.

The photophysics of iron(II) polypyridyls have been well studied and although they are isoelectronic to ruthenium(II) and iridium (III) these compounds exhibit very different photophysical properties.<sup>38</sup> The stark difference in their MLCT lifetimes directly translates to their difference in excited-state reactivity as photocatalysts. For iron(II) tris(2,2'-bipyridine) ([Fe(bpy)<sub>3</sub>]<sup>2+</sup>) absorption in the visible excites the low-spin <sup>1</sup>A<sub>1</sub> ground state to a <sup>1</sup>MLCT state

which intersystem crosses to the <sup>3</sup>MLCT state in ~20 fs.<sup>39-41</sup> Deactivation from the MLCT manifold occurs in ~200 fs, which is a consequence of low lying ligand field states providing a pathway for ultra-fast non-radiative decay.<sup>42-45</sup> The lowest-energy excited state, <sup>5</sup>T<sub>2</sub>, for  $[Fe(bpy)_3]^{2+}$  is formed within 200 fs and ground-state recovery occurs in 1.02 ns in MeCN.<sup>46,47</sup> These ligand field states lie lower in energy relative to the MLCT states in iron due to the primogenic affect, which decreases the radial extension of the 3d orbitals resulting in a weaker ligand field.<sup>38</sup> An important consequence of implementing iron as a photocatalyst is that the nature of the lowest-energy excited state is metal-centered and is formed orders of magnitude faster than diffusion. Despite this excited state not being charge separated, like the MLCT states in Ru and Ir complexes, the lifetimes of iron polypyridyls are sufficiently long enough with respect to the time scale of molecular diffusion making the catalytically relevant excited state the <sup>5</sup>T<sub>2</sub> state.

While the discovery of a new chemical reaction can represent the desired end point of some studies, understanding the mechanism of photoredox reactions utilizing iron(II) polypyridyls can lead to improvements in catalytic efficiency as well as widening the substrate scope. If the quenching mechanism of the catalytically relevant excited state is known synthetic modifications to the photocatalyst can be used to improve their performance. If electron transfer is the operative quenching mechanism specific ligands and/or metals can be chosen to increase the driving force. Substituents on polypyridyl ligands can be used to increase the MLCT energy, increasing the driving force. Reactions that proceed via oxidative quenching may benefit from using *fac*-Ir(ppy)<sub>3</sub> opposed to [Ru(bpy)<sub>3</sub>]<sup>2+</sup> as the latter has a much higher oxidation potential, while using [Ru(bpy)<sub>3</sub>]<sup>2+</sup> has a larger excited-state reduction potential.<sup>15</sup> If energy transfer occurs modifications pertaining to altering the redox potentials may not be beneficial and instead substituting the ligands to increase the spectral overlap between the chromophore and substrate

(Förster transfer) could lead to more efficient quenching. These previous examples are, with no question, applicable to MLCT-based excited states and making modifications to metal-centered excited states should also be considered. The ligand environment and use of strong- or weak-field ligands can drastically change the energy levels of the ligand field states affecting the zero-point energy ( $E_{00}$ ) of the excited state much more dramatically than electron donating and withdrawing substituents on a polypyridyl ligand. It should also be noted that ligand environment not only will affect the  $E_{00}$  but will also affect its redox potential, both pertinent variables for effecting the driving force for electron transfer. With insight into the mode of reactivity of the excited state a particular photocatalyst can be chosen to perform the desired reactions optimally and efficiently.

While understanding the mechanism of a photocatalyst is a fundamental step in implementing photoredox reactions in organic synthesis characterizing the excited-state redox potentials is paramount for understanding the substrate scope. The excited-state oxidation potential,  $E(M^{+/*})$ , can be calculated using equation 5.1, where  $E(M^{+/0})$  is the ground-state oxidation potential and  $E_{00}$  is the zero-point energy of the relevant excited state. The excited-state reduction potential,  $E(L^{*/-})$ , can be calculated using equation 5.2, where  $E(L^{0/-})$  is the ground-state reduction potential.

$$E(M^{+/*}) = E(M^{+/o}) - E_{00}$$
5.1

$$E(L^{*/-}) = E(L^{o/-}) + E_{00}$$
5.2

For  $[Ru(bpy)_3]^{2+}$  and *fac*-Ir(ppy)<sub>3</sub>, or any photocatalyst where its lowest-energy excited state is emissive, the excited-state redox potentials can be experimentally determined from cyclic voltammetry and spectral fitting of the steady-state emission.<sup>48,49</sup> Once the excited-state redox potential is known the driving force for photo-induced electron transfer can be determined using the Rehm-Weller equations, shown in equations 5.3, where  $(Q_{red}^{0/-})$  is the reduction potential of the quencher in the case of oxidative quenching and  $(Q_{ox}^{+/0})$  is the oxidation potential of the quencher in the case of reductive quenching.<sup>50</sup>

$$\Delta G_{ox} = E(M^{+/0}) - E_{00} - (Q_{red}^{0/-})$$
(5.3a)

$$\Delta G_{red} = (Q_{ox}^{+/0}) - \left[ \left( bp y_{red}^{0/-} \right) + E_{00} \right]$$
(5.3b)

Calculating the excited redox potentials and using the Rehm-Weller formalism to determine the driving force for photo-induced electron transfer is applicable to iron(II) polypyridyls. However, due to the non-emissive nature of the catalytically relevant metal-centered excited state, the  ${}^{5}T_{2}$  state, spectral fitting to determine the  $E_{00}$  from steady-state emission is not possible.

The  $E_{00}$  for the metal-centered excited states for iron(II) polypyridyls have not been reported along with the mechanism of these chromophores in photoredox catalysis. In an effort to understand the quenching mechanism of these photocatalysts bimolecular quenching studies using nanosecond transient absorption (ns-TA) spectroscopy were performed. [Fe(tren(py)<sub>3</sub>)]<sup>2+</sup> (where tren(py)<sub>3</sub> = tris(2-pyridyl-methylimino-ethyl)amine) was used as the iron(II)-based photosensitizer and a series of benzoquinones were used as acceptors, Figure 5.1. The photophysics of [Fe(tren(py)<sub>3</sub>)]<sup>2+</sup> have been thoroughly studied in detail and the ground-state recovery of the <sup>5</sup>T<sub>2</sub> state is 55 ns in MeCN making it possible to facilitate these studies using nanosecond time-scale experiments.<sup>42-45</sup> It should be noted that the electronic structures and dynamics of [Fe(tren(py)<sub>3</sub>)]<sup>2+</sup> and compounds such as [Fe(bpy)<sub>3</sub>]<sup>2+</sup> and [Fe(phen)<sub>3</sub>]<sup>2+</sup> (where phen = 1,10-phenanthroline) (the latter two have been used as photoredox catalysts by several researchers) are identical with



Figure 5.1. Iron(II)-based chromophore ( $[Fe(tren(py)_3]^{2^+})$  and the benzoquinones used for ns-TA bimolecular quenching experiments. DDQ = 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone, DCBQ = 2,3-Dicyano-1,4-benzoquinone, *o*-TCBQ = 3,4,5,6-Tetrachloro-1,2-benzoquinone, *o*-TBBQ = 3,4,5,6-Tetrachloro-1,2-benzoquinone. regard to the ultrafast MLCT-state deactivation (~100 fs), the identity of the ligand-field excited states that lie below the initially formed MLCT state, and their relative energies. The significant difference is the weaker ligand-field strength of the tren(py)\_3 ligand, which lowers the energies of the ligand-field excited states. This results in the  ${}^5T_2$  state being lower in energy and will be reflected in the excited-state redox potential and therefore affect the types of reactions the photocatalyst can be used in, but the excited-state quenching mechanism will be the same. The benzoquinone acceptors were chosen due to their wide range of reduction potentials making it possible to study reactions with a large range of driving force.

## 5.2. Experimental

### 5.2.1. Synthesis

**General.** 2,3-dichloro-5,6-dicyano-*para*-benzoquinone (DDQ) and 2,3-dicyano-*para*hydroquinone were purchased from Oakwood Chemical and used without further purification. 3,4,5,6-tetrachloro-*ortho*-benzoquinone (*o*-TCBQ) was purchased from Sigma-Aldrich and

recrystallized from dilute acetic acid. 2,3,5,6-tetrachloro-para-benzoquinone (p-TCBQ) and 1,2dihydroxybenzene were purchased from Sigma-Aldrich and used without further purification. (*o*-TBBO)<sup>51,52</sup> and  $[Fe(tren(pv)_3)](PF_6)_2^{53}$ 3,4,5,6-tetrabromo-ortho-benzoquinone were synthesized according to previously reported procedures. Spectrophotometric grade acetonitrile (MeCN) was purchased from Alfa Aesar and spectrograde acetone was purchased from Jade Scientific. Both were degassed by freeze-pump-thawing before being stored in an Ar-filled drybox. 2,3-dicyano-1,4-benzoquinone (DCBQ). 2,3-dicyano-para-hydroquinone (1.0 g, 6.2 mmol) was dissolved in glacial acetic acid (12 mL) by heating. In a separate flask, red fuming nitric acid (6 mL) was chilled in an ice bath to which glacial acetic acid (6 mL) was added slowly. The solution of 2,3-dicyano-*para*-hydroquinone was cooled for 5 minutes in an ice bath and the red fuming nitric acid/glacial acetic acid solution was added and immediately stirred in an ice bath for 30 minutes. The resulting solution was extracted with dichloromethane (3 x 100 mL), dried with sodium sulfate, and the solvent was removed under reduced pressure. Chloroform (30 mL) was added to the resulting brown residue, refluxed for 30 minutes, and cooled overnight in a freezer. The solid was collected by filtration and washed with cold chloroform and dried overnight in a desiccator. Yield: 65%. The <sup>1</sup>H-NMR spectrum matches that reported in the literature (500 MHz, CDCl<sub>3</sub>, 2H, s, 7.09 ppm).<sup>54 13</sup>C-NMR, 150 MHz, CDCl<sub>3</sub>, 177.7 ppm, 137.4 ppm, 128.1 ppm, 109.9 ppm. Elemental Analysis Calcd for C<sub>8</sub>H<sub>2</sub>N<sub>2</sub>O<sub>2</sub>: C, 60.77; H, 1.28; N, 17.72. Found: C, 60.25; H, 1.28; N, 17.48.

## 5.2.2. Physical Characterization

**Electrochemistry.** Electrochemical measurements were collected using a CH instruments model CHI620D electrochemical workstation in an Ar-filled dry box. A standard three-electrode setup was used to determine the reduction potentials of the benzoquinones and the Fe(II/III) oxidation

potential for  $[Fe(tren(py)_3)](PF_6)_2$  via cyclic voltammetry in acetonitrile and acetone solutions using 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) as supporting electrolyte, a Pt disc working electrode, a Ag wire pseudo-reference electrode, and a platinum wire counter electrode. TBAPF<sub>6</sub> was purchased from Oakwood Chemical and recrystallized from ethanol twice before use. *o*-TCBQ, *o*-TBBQ, and *p*-TCBQ are referenced internally to the Fc<sup>+</sup>/Fc couple, whereas DDQ and DCBQ potentials are referenced internally to the decamethylferrocene /decamethylferrocenium (Fc(cp<sup>\*</sup>)<sub>2</sub>/Fc(cp<sup>\*</sup>)<sub>2</sub><sup>+</sup>) couple, which itself was internally referenced to the ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) couple in both MeCN and acetone.

**Spectroelectrochemistry.** UV-Visible spectroelectrochemical experiments were performed in a Pine Instruments electrochemical cell in an Ar-filled dry box. The 1 cm x 1 cm space at the top of the cell held the Ag reference electrode while the Pt working electrode and counter electrode were placed in the 1.7 mm x 10 mm path length window at the bottom of the cell to electrolyze the solution while the absorbance was recorded with SI420 CCD spectrometer. Data were acquired on solutions identical to that just described for the electrochemical measurements, with the exception that solutions of each compound were adjusted to have absorbance values in the range of  $0.6 \pm 0.1$  at the maximum of the lowest-energy mid-visible absorption peak. A ground-state absorption spectrum was taken prior to the onset of bulk electrolysis at an over potential of 0.10 V - 0.20 V relative to the reduction potential of the compound.

**Ground-state and Nanosecond Time-resolved Absorption Spectroscopy.** Ground-state electronic absorption spectra were acquired using a Varian 50 UV-Vis electronic absorption instrument. Nanosecond time-resolved absorption data (ns-TA) were acquired using an Edinburgh Instruments LP980 spectrometer fitted with a Hamamatsu R928 photomultiplier tube and interfaced to a Tektronix TDS 3032C oscilloscope. The excitation source was an Opotek Vibrant

355 LD Q-switched Nd:YAG laser. Data were collected at  $26 \pm 2$  °C (not thermostatted). Samples for Stern-Volmer quenching experiments using [(Fe(tren(py)<sub>3</sub>)](PF<sub>6</sub>)<sub>2</sub> as the sensitizer and the various benzoquinones as quenchers were prepared in an Ar-filled dry-box. A stock solution of [(Fe(tren(py)<sub>3</sub>)](PF<sub>6</sub>)<sub>2</sub> (~ 0.5 mM) and tetrabutylammonium hexafluorophosphate (~0.1 M) was prepared from dry, degassed MeCN or acetone. Varying amounts of quenchers were weighed in 5 ml volumetric flask and 1 mL of the stock solution was added and diluted to give a final Fe(II) MLCT absorption between 0.7–0.8. Due to slight variations in temperature in the sample compartment, the lifetime of [(Fe(tren(py)<sub>3</sub>)]<sup>2+</sup> was measured after each sample to ensure an accurate k<sub>obs</sub>/k<sub>0</sub> value for the Stern-Volmer plot.

## **5.3. Results and Discussion**

# 5.3.1. Characterization of $[Fe(tren(py)_3)]^{2+}$ and Electrochemistry of Benzoquinones

The ground-state absorption spectrum of  $[Fe(tren(py)_3]^{2+}$  is shown in Figure 5.2, it possesses a low-spin d<sup>6</sup> ground-state electron configuration with a  ${}^{1}A_{1} \rightarrow {}^{1}MLCT$  absorption maximum at 560 nm. Excitation in the visible produces the  ${}^{1}MLCT$  state that converts to the lowest-energy excited state, the high-spin  ${}^{5}T_{2}$  state, in ~200 fs that then decays to the ground state in 55 ns. The presence of this state is indicated by a loss of absorbance across the entire visible spectrum due to the Fe – N bond elongation from population of the eg\* orbitals which decreases the overlap between orbitals involved in the absorption decreasing the oscillator strength.<sup>42</sup> The ns-TA spectrum of  $[Fe(tren(py)_3)]^{2+}$  is shown in Figure 5.3 featuring a bleach across the entire spectrum consistent with what has been previously reported for this compound.<sup>42</sup> The well-known photophysics of  $[Fe(tren(py)_3)]^{2+}$  makes determining the kinetics related to the  ${}^{5}T_{2}$  state in the bimolecular quenching studies straightforward.



Figure 5.2. Ground-state absorption spectrum of  $[Fe(tren(py)_3)]^{2+}$  in MeCN.

To accurately determine the driving force for photo-induced electron transfer cyclic voltammetry was used to measure the redox potentials of  $[Fe(tren(py)_3)]^{2+}$  and the benzoquinone acceptors. The oxidation potential for  $[Fe(tren(py)_3)]^{2+}$  is shown in Figure 5.4 in MeCN (left) and acetone (right). The iron(II) oxidation potential was measured at +0.51 V in acetone and +0.55 V in MeCN, a minor change in the oxidation potential due to solvent is expected for a metal-based oxidation. Two reduction potentials were observed at -1.51 V and -1.95 V in MeCN and are ligand based in agreement with what has been previously reported.<sup>42</sup> Table 5.1 shows the measured reduction potentials for the five benzoquinones used as electron acceptors spanning 0.5 V. DDQ benzoquinone has the most positive reduction potential and should possess the largest driving force for electron transfer among all of the acceptors while *p*-TCBQ has the most negative reduction potential making it the hardest to reduce. The difference in reduction potentials between MeCN and acetone exemplifies how solvent can affect the driving force for electron transfer.



Figure 5.3. Transient absorption spectrum of  $[Fe(tren(py)_3)]^{2+}$  in MeCN following 580 nm excitation.



Figure 5.4. Cyclic voltammetry of [Fe(tren(py)<sub>3</sub>)]<sup>2+</sup> in MeCN (left) and acetone (right).

	Ered (V) vs. Fc/Fc <sup>+</sup>	
Compound	MeCN	Acetone
DDQ	0.14	0.07
DCBQ	-0.09	-0.15
o-TCBQ	-0.26	-0.33
o-TBBQ	-0.28	-0.35
p-TCBQ	-0.37	-0.42

Table 5.1. Summary of reduction potentials of benzoquinones used as electron acceptors.

#### 5.3.2. Bimolecular Quenching Experiments

Bimolecular quenching studies using  $[Fe(tren(py)_3)]^{2+}$  and the series of benzoquinones shown in Figure 5.1 were carried out using time-resolved absorption spectroscopy to probe the kinetics of the reaction shown in equation 5.1.

$$[Fe(tren(py)_3)]^{2+*} + A \to [Fe(tren(py)_3)]^{3+} + A^{-}$$
(5.1)

Data acquired in acetone and acetonitrile using DDQ as an acceptor under pseudo-firstorder conditions are shown in Figure 5.5. The samples were excited at 580 nm into the MLCT absorption and the single-wavelength kinetics were recorded using 560 nm as the probe wavelength. The negative  $\Delta$ O.D. observed at each concentration of DDQ is consistent with the



Figure 5.5. Single-wavelength kinetics of transient absorption quenching experiments between  $[Fe(tren(py)_3)]^{2+}$  and DDQ in acetone (left) and acetonitrile (right) with 0.1 M TBAPF<sub>6</sub> as supporting electrolyte ( $\lambda_{ex} = 580$  nm,  $\lambda_{probe} = 560$  nm).



Figure 5.6. Single-wavelength kinetics of transient absorption quenching experiments between  $[Fe(tren(py)_3)]^{2+}$  and *p*-TCBQ in acetone (left) and acetonitrile (right) with 0.1 M TBAPF<sub>6</sub> as supporting electrolyte ( $\lambda_{ex} = 580$  nm,  $\lambda_{probe} = 560$  nm).

negative feature associated with the  ${}^{5}T_{2}$  based on the full TA spectrum of  $[Fe(tren(py)_{3})]^{2+}$ . The measured lifetime associated with the  ${}^{5}T_{2}$  state systematically decreases with increasing concentration of DDQ indicating dynamic quenching of the ligand-field excited state in both solvents.

Analogous experiments using *p*-TCBQ as the acceptor in acetone and acetonitrile are shown in Figure 5.6. *p*-TCBQ has a significantly more negative reduction potential and an insensitivity of the  ${}^{5}T_{2}$  lifetime to the concentration of quinone is observed. The difference in lifetimes between the *p*-TCBQ data collected in acetone and acetonitrile is due to slight variations in temperature in the sample compartment, as mentioned above. This suggests that there is no reaction taking place between the  ${}^{5}T_{2}$  state and *p*-TCBQ.

The three other benzoquinones were studied to understand if the excited-state reactivity of the metal-centered excited state was correlated to the reduction potentials of the acceptors. The overlay of the normalized single-wavelength kinetics between  $[Fe(tren(py)_3)]^{2+}$  and DCBQ in acetone is shown in Figure 5.7. Similar to the kinetics observed for quenching experiments with



Figure 5.7. Single-wavelength kinetics of transient absorption quenching experiments between  $[Fe(tren(py)_3)]^{2+}$  and DCBQ in acetone with 0.1 M TBAPF<sub>6</sub> as supporting electrolyte ( $\lambda_{ex} = 580$  nm,  $\lambda_{probe} = 560$  nm).

DDQ, the  ${}^{5}T_{2}$  lifetime systematically decreases with the increased concentration of DCBQ. The reduction potential for DCBQ is slightly more negative than DDQ but dynamic quenching of the photosensitizer shows that the ligand field excited state is reacting with the quencher. Quenching studies of DCBQ in acetonitrile were attempted but this benzoquinone was not soluble at sufficient concentrations and the turbidity of the sample led to unsatisfactory ratio of laser scatter to signal.

Replacing the DCBQ with the *o*-TCBQ quencher lowers the reduction potential but quenching of the  ${}^{5}T_{2}$  state is still observed in acetonitrile and acetone based on the measured lifetimes. The normalized single-wavelength kinetics in acetonitrile are shown in Figure 5.8 following 580 nm excitation and probing 560 nm. Variations in temperature in the sample compartment was observed during these experiments and to ensure accurate  $k_{obs}/k_0$  values at each concentration of quencher the lifetime of  $[Fe(tren(py)_3)]^{2+}$  was measured before each sample. The sample of  $[Fe(tren(py)_3)]^{2+}$  with 15 mM *o*-TCBQ has a shorter measured  ${}^{5}T_2$  lifetime relative to



Figure 5.8. Single-wavelength kinetics of transient absorption quenching experiments between  $[Fe(tren(py)_3)]^{2+}$  and *o*-TCBQ in MeCN with 0.1 M TBAPF<sub>6</sub> as supporting electrolyte ( $\lambda_{ex} = 580$  nm,  $\lambda_{probe} = 560$  nm)(a = the shorter lifetime at lower quencher concentration is a result of measuring a 50 ns lifetime for  $[Fe(tren(py)_3)]^{2+}$  at the time of the experiment, as mentioned above). the sample with 21 mM *o*-TCBQ despite having a lower quencher concentration due to measuring a 55 ns lifetime for iron(II) chromophore in the absence of quencher.

Quenching studies of *o*-TCBQ carried out in acetone following 580 nm excitation and probing the kinetics at 560 nm are shown in Figure 5.9. The systematic decrease in lifetime of the  ${}^{5}T_{2}$  state is indicative of dynamic quenching. As the concentration of *o*-TCBQ increases the presence of a positive feature is observed at 200 ns and increases with quencher concentration. Figure 5.10 shows single-wavelength kinetics observed at 560 nm fit with tri-exponential Gaussian deconvolutions due to signal contributions from laser scatter, the quenched  ${}^{5}T_{2}$  state, and the positive feature. The positive feature observed at long times is attributed to *o*-TCBQ. To determine the exact species giving rise to the positive absorption the single-wavelength kinetics were monitored at 610 nm, shown in Figure 5.11.

At 10 mM and 15 mM concentrations of o-TCBQ there is a small negative feature at time



Figure 5.9. Single-wavelength kinetics of transient absorption quenching experiments between  $[Fe(tren(py)_3)]^{2+}$  and *o*-TCBQ in acetone with 0.1 M TBAPF<sub>6</sub> as supporting electrolyte ( $\lambda_{ex} = 580$  nm,  $\lambda_{probe} = 560$  nm).

zero followed by an excited-state absorbance. The excited-state absorbance observed at all concentrations were fit with a single exponential decay,  $\tau = 290$  ns. The bleach at low concentrations is assigned to the  ${}^{5}T_{2}$  state but due to the relatively small signal from the ligand field state at this probe wavelength as the concentration of quencher increases, increasing the excited-state absorption feature, the bleach signal is obscured. The excited-state absorption feature could either result from the *o*-TCBQ radical anion formed from oxidative quenching or an excited state that is formed upon direct excitation. The ground-state absorption and reductive spectroelectrochemical spectra for *o*-TCBQ are shown in Figure 5.12. The dominant absorption feature in the visible is a  $n \rightarrow \pi^{*}$  transition centered at 440 nm with a 3000 M<sup>-1</sup>cm<sup>-1</sup> extinction coefficient. There is a small shoulder at 560 nm with an extinction coefficient of 240 M<sup>-1</sup>cm<sup>-1</sup>, at 25 mM this would result in an absorbance of 6 at 560 nm. Due to the large absorbance of the benzoquinone at the excitation wavelength used for the quenching experiments direct excitation of *o*-TCBQ is highly likely. The spectroelectrochemistry spectrum shows that upon reduction of



Figure 5.10. Quenching studies in acetone solution using  $[Fe(tren(py)_3)]^{2+}$  following MLCT excitation at 580 nm and probing at 560 nm. (a) 15 mM *o*-TCBQ, fit with a tri-exponential Gaussian deconvolution due to contribution from laser scatter and a positive feature ( $\tau_1 = 7 \text{ ns}, \tau_2 = 43 \text{ ns}, \tau_3 = 285 \text{ ns}$ ) ( $k_0/k_{obs} = 51 \text{ ns}/43 \text{ ns} = 1.18$ ). (b) 20 mM *o*-TCBQ, fit with tri-exponential Gaussian deconvolution due to contribution from laser scatter and a positive feature ( $\tau_1 = 7 \text{ ns}, \tau_2 = 40 \text{ ns}, \tau_3 = 290 \text{ ns}$ ), ( $k_0/k_{obs} = 49 \text{ ns}/40 \text{ ns} = 1.23$ ). (c) 25 mM *o*-TCBQ, fit with a tri-exponential Gaussian deconvolution due to signal contribution from laser scatter and a positive feature ( $\tau_1 = 7 \text{ ns}, \tau_2 = 40 \text{ ns}, \tau_3 = 290 \text{ ns}$ ). (d) 35 mM *o*-TCBQ, fit with a tri-exponential Gaussian deconvolution from laser scatter and a positive feature ( $\tau_1 = 7 \text{ ns}, \tau_2 = 30 \text{ ns}, \tau_3 = 275 \text{ ns}$ ). (d) 35 mM *o*-TCBQ, fit with a tri-exponential Gaussian deconvolution from laser scatter and a positive feature ( $\tau_1 = 7 \text{ ns}, \tau_2 = 30 \text{ ns}, \tau_3 = 275 \text{ ns}$ ). (d) 35 mM *o*-TCBQ, fit with a tri-exponential Gaussian deconvolution from laser scatter and a positive feature ( $\tau_1 = 7 \text{ ns}, \tau_2 = 12 \text{ ns}, \tau_3 = 270 \text{ ns}$ ).



Figure 5.11. Single-wavelength nanosecond time-resolved absorption data from quenching studies between  $[Fe(tren(py)_3)]^{2+}$  and *o*-TCBQ in acetone solution with 0.1M TBAPF<sub>6</sub>. The data were acquired at  $\lambda_{probe} = 610$  nm, which is selective for the excited state produced upon direct excitation of the quinone.

*o*-TCBQ a bleach is observed at 440 nm with a broad absorption feature from 525 nm to 950 nm which could also give rise to the positive feature observed in the quenching studies. Transient absorption data of *o*-TCBQ in MeCN in the absence of  $[Fe(tren(py)_3)]^{2+}$  is shown in Figure 5.13 (a). Direct excitation into the  $n \rightarrow \pi^*$  transition at 475 nm and probing at 605 nm resulted in an excited-state absorption with a 270 ns lifetime. Given the high degree of correlation of fitting parameters for the lifetime of the excited-state absorption feature in the quenching experiments to the independently measured lifetime of *o*-TCBQ, the 290 ns component in Figure 5.10 and 5.11 and the 225 ns positive feature in Figure 5.13 (b) is due to directly excited *o*-TCBQ from spectral overlap at this excitation wavelength. The invariance of this time constant of this feature across the entire range of conditions for which a reduction in the <sup>5</sup>T<sub>2</sub> lifetime is evident confirms the benign nature of this excited-state species with regard to the kinetics being probed.


Figure 5.12. (a) Ground-state absorption spectrum of *o*-TCBQ in MeCN. (b) Reductive spectroelectrochemical spectrum of *o*-TCBQ in MeCN with 0.1 M TBAPF<sub>6</sub>.



Figure 5.13. (a) Transient absorption data acquired on a MeCN solution of *o*-TCBQ in the absence of  $[(\text{Fe}(\text{tren}(\text{py})_3)]^{2+}$  ( $\lambda_{\text{ex}} = 475 \text{ nm}$ ,  $\lambda_{\text{probe}} = 605 \text{ nm}$ ). The measured lifetime is  $\tau = 270 \text{ ns}$  and corresponds to an excited state of *o*-TCBQ that is produced upon direct excitation of the quinone. (b) Corresponding data collected on a solution 10 mM in *o*-TCBQ in the presence of  $[(\text{Fe}(\text{tren}(\text{py})_3)]^{2+}(\lambda_{\text{ex}} = 580 \text{ nm}, \lambda_{\text{probe}} = 600 \text{ nm})$ . The data were fit to a tri-exponential function (including Gaussian deconvolution) with time constants of  $\tau_1 = 7 \text{ ns}$  (laser scatter),  $\tau_2 = 50 \text{ ns}$  (slightly quenched  ${}^5\text{T}_2$  excited state of [Fe(tren(py)\_3)]^{2+}), and  $\tau_3 = 225 \text{ ns}$ . Given the high degree of correlation among the fitting parameters under these conditions, we believe that the 225 ns component is associated with the same species giving rise to the kinetics shown in (a), i.e. *o*-TCBQ that has been directly excited due to spectral overlap at this excitation wavelength.

Similar spectral overlap complications arise with the use of *o*-TBBQ as a quencher. *o*-TBBQ has a reduction potential of -0.28 V in MeCN and -0.35 V in acetone, these values are 0.02 V more negative than *o*-TCBQ. The normalized single-wavelength traces in acetone are shown in Figure 5.14 featuring a bleach from the  ${}^{5}T_{2}$  state and a positive feature at large *o*-TBBQ concentrations. At all concentrations the  ${}^{5}T_{2}$  and the positive feature are fit with biexponential Gaussian deconvolutions resulting in a 50 ns and 7 ns lifetime for each respective component. In this case there is no reduction in the measured lifetime of the  ${}^{5}T_{2}$  state of  $[Fe(tren(py)_{3})]^{2+}$ . This is an indication that this metal-centered excited state is not sufficiently reducing to react with *o*-TBBQ and therefore provides a lower limit on the excited-state oxidation potential of this species. Similar results are obtained from the quenching studies in MeCN, shown in Figure 5.15.

The single-wavelength traces in Figure 5.15a are normalized to the bleach maximum to clearly show the indifference in the  ${}^{5}T_{2}$  lifetime and the traces in 5.15b are normalized to most



Figure 5.14. Normalized overlay of single-wavelength kinetics acquired for bimolecular quenching studies with  $[Fe(tren(py)_3)]^{2+}$  and *o*-TBBQ in acetone with 0.1M TBAPF<sub>6</sub> ( $\lambda_{ex} = 580$  nm,  $\lambda_{probe} = 560$  nm).



Figure 5.15. Normalized overlay of single-wavelength kinetics acquired for bimolecular quenching studies with  $[Fe(tren(py)_3)]^{2+}$  and *o*-TBBQ in acetonitrile with 0.1M TBAPF<sub>6</sub> ( $\lambda_{ex} = 580$  nm,  $\lambda_{probe} = 560$  nm). (a) Normalized to the bleach maximum to clearly show the indifference in the excited state lifetime. (b) Normalized to the most positive or negative peak maximum.

negative or positive peak maximum. The positive feature observed in both acetone and acetonitrile decays on the timescale of the instrument response function (IRF) of the instrument (7 ns). The excited-state absorption is due to directly exciting the *o*-TBBQ due to the spectral overlap of the quenchers absorption with the excitation wavelength used in the quenching experiments. Figure 5.16 shows the absorption feature of *o*-TBBQ (red trace) and the absorption profile of  $[Fe(tren(py)_3)]^{2+}$  at the concentration used for the quenching experiments. The absorbance of  $[Fe(tren(py)_3)]^{2+}$  in 8.5 mM *o*-TBBQ (purple trace), the identical concentration of components used for the single-wavelength trace in Figure 5.15, shows that the *o*-TBBQ has significant ground-state absorption at 580 nm.

From the bimolecular quenching studies dynamic quenching and a reduction of the measured lifetime of the  ${}^{5}T_{2}$  state occurred with DDQ, DCBQ, and *o*-TCBQ while *o*-TBBQ and *p*-TCBQ had no effect on the ground-state recovery of  $[Fe(tren(py)_{3})]^{2+}$ . Stern-Volmer plots summarizing the  $k_{obs}/k_{o}$  values obtained at each concentration of quencher in acetone and acetonitrile is shown in Figure 5.17, and each set of data is fit to a line of best fit for each benzoqui-



Figure 5.16. Electronic absorption spectra of  $[(Fe(tren(py)_3)](PF_6)_2 (black), o-TBBQ (red) and a solution containing both <math>[(Fe(tren(py)_3)](PF_6)_2 \text{ and } o-TBBQ \text{ at a concentration of 8.5 mM (purple), all in MeCN solution.}$ 

none. Using the Stern-Volmer equation, equation 5.2, the quenching rate constant,  $k_q$ , can be calculated where  $k_{obs}$  is the observed rate constant of a sample with quencher,  $k_o$  is the observed rate constant of the chromophore in the absence of quencher, and [Q] is the concentration of quencher.

$$\frac{k_{obs}}{k_o} = 1 + \frac{k_q[Q]}{k_o}$$
(5.2)

The  $k_q$  for each quencher in acetone and acetonitrile are shown in Table 5.2. In both solvents quenching with DDQ resulted in the largest quenching rate constant while quenching with *o*-TCBQ resulted in the smallest rate of quenching. It is important to note that the data obtained from the Stern-Volmer plot does not unequivocally distinguish the quenching mechanism. A Stern-Volmer plot from dynamic quenching via electron transfer or energy transfer, either Förster or Dexter, yields experimentally indistinguishable plots. The application of additional experiments and analysis must be used to identify the nature of the reaction responsible for quenching the <sup>5</sup>T<sub>2</sub> state of [Fe(tren(py)<sub>3</sub>)]<sup>2+</sup>.



Figure 5.17. Stern-Volmer plot of transient absorption data of quenching studies carried out between  $[Fe(tren(py)_3)]^{2+}$  and the quinone acceptors indicated in acetone (a) and acetonitrile (b).

Table 5.2. Quenching rate constants for quenchers in acetone and acetonitrile with 0.1 M TBAPF<sub>6</sub>.

	$k_q (M^{-1} s^{-1})$				
Quencher	Acetone	Acetonitrile			
DDQ	$2.7 \times 10^5$	$2.6 \ge 10^5$			
DCBQ	$2.6 \ge 10^5$	а			
o-TCBQ	$2.1 \ge 10^5$	$2.1 \ge 10^5$			

a = DCBQ was not soluble in MeCN at the desired concentrations.

#### 5.3.3. Mechanistic Considerations

The data presented so far has clearly established dynamic quenching and a reduction of the measured lifetime of the  ${}^{5}T_{2}$  state. However, understanding the mechanism of quenching provides valuable information with respect to the application of iron(II) polypyridyls in photoredox catalysis. Three possible excited-state quenching pathways exist; energy transfer either through the Förster or Dexter mechanism or electron transfer. Quenching of the ligand field excited state via Förster transfer can be immediately ruled out because energy transfer by this mechanism is necessitated by non-radiative coupling of the chromophore's emission dipole.<sup>55</sup>  $[Fe(tren(pv)_3)]^{2+}$ . and other iron(II) polypyridyls, are non-emissive from the <sup>5</sup>T<sub>2</sub> state due to  $\Delta S = 2$  change in spin between the excited state and ground state. Dexter energy transfer does not require radiative coupling of an emissive state and the close proximity between chromophore and acceptor, a requirement for orbital overlap, can be achieved in this system due to it being a bimolecular system.<sup>56</sup> However, quenching of the excited state to either a singlet or triplet excited state of a quinone acceptor would not conserve the angular momentum for the overall process and is therefore forbidden.<sup>57</sup> This is further illustrated in Figure 5.18 where the excited state of  $[Fe(tren(py)_3)]^{2+}$  is a quintet (i.e., S = 2) and since the ground state of the quinone and the iron chromophore are both diamagnetic (S = 0), only an excited state of the quinone having a spin of 2 (S = 2) could engage in energy transfer to conserve the total spin angular momentum.

While there is a compelling case for ruling out the possibility of quenching via energy transfer, leaving electron transfer as the only remaining option, having direct experimental evidence supporting the mechanism is the gold standard. The photo-induced electron transfer mechanism is best established via spectroscopic identification of either the oxidized donor and/or the reduced acceptor. In order to identify the photoproducts of photo-induced electron transfer in



 $[Fe(tren(py)_3)]^{2+}$  and a benzoquinone acceptor is spin forbidden. the bimolecular quenching studies spectroelectrochemistry can be used to obtain the absorption profile of the reduced or oxidized species. The reductive spectroelectrochemical spectra for the benzoquinones acceptors that exhibit quenching, DDQ, DCBQ, and o-TCBQ, and are displayed in Figure 5.19. Each spectra is obtained in a 0.1 M TBAPF<sub>6</sub> MeCN solution while bulk electrolysis is occuring at a -0.1 V over potential for the first reduction of the benzoquinone. Therefore the spectra in Figure 5.19 are representitive of the UV-Vis absorption features of the reduced benzoquinones formed from photo-induced electron transfer from the  $[Fe(tren(py)_3)]^{2+}$  ligand field excited state. The reduced DDQ and DCBQ possess multiple absorption bands in the visible from 400 - 600 nm while the spectrum of the reduced *o*-TCBQ also has a absorption from 500 - 950nm. The oxidative spectroelectrochemical spectrum of  $[Fe(tren(py)_3)]^{2+}$  has been reported in the literature and features a negative absorbance across the entire spectrum, 350 - 600 nm.<sup>42</sup> The oxidized iron compound is characterized by a loss of absorbance that is identical to the bleach that arises from formation of the  ${}^{5}T_{2}$  complicating the detection of the oxidized chromophore in the quenching experiments. The oxidized iron chromophore is not detected in the transient absorption quenching studies and any detection of photo-induced electron transfer products relies in detection of the reduced benzoquinone acceptor. However, the bleach from the  ${}^{5}T_{2}$  state and the absorption



Figure 5.19. Spectroelectrochemical spectra of DDQ (a), *o*-TCBQ (b), and DCBQ (c) acquired using 0.1 M TBAPF<sub>6</sub> in MeCN. feature from the benzoquinone radical anion overlap over the same spectral region. This results in

the negative  $\Delta O.D.$  signal from the iron chromophore overshadowing any excited-state absorptions that would occur from the reduced benzoquinone acceptors.

Despite not being able to observe the products of photo-induced electron transfer there is a clear correlation between the quenching dynamics and the reduction potential of the quinones used in this study. Table 5.3 shows the trend in the quenching rate constant with the reduction potential of the benzoquinones in acetonitrile and acetone. The quencher with the highest reduction potential, DDQ, has the largest quenching rate constant in both acetonitrile and acetone and as the reduction potential decreases and the benzoquinone acceptors become more difficult reduce and consequently the quenching rate constant decreases. Based on this direct observation that the rate of dynamic quenching correlates with the reduction potential of quenchers indicates that electron transfer is the mechanism of reactivity for  $[Fe(tren(py)_3)]^{2+}$ . The quenching rate constants for DDQ and DCBQ are identical within error of each other despite a 0.22 V difference in reduction potential and can be explained from a kinetic barrier resulting from the reorganization energy required upon oxidation of the iron(II) excited state to iron(III). Initially a spin = 3/2 ligand field state is formed upon oxidative quenching, the high-spin iron(III) ligand field state, S = 5/2, is much more stable and requires reorganization energy to accommodate this change. Despite the larger driving force for DDQ the kinetic barrier for reorganization energy limits the quenching rate constant.

Table 5.3. Reduction potentials and quenching rate constants for quenchers in acetone and acetonitrile with 0.1 M TBAPF<sub>6</sub>.

	Acetone			MeCN		
Quencher	$E_{red} (V)^a$	$k_q (M^{-1} s^{-1})$	$\Delta G(V)$	$E_{red} (V)^a$	$k_q (M^{-1} s^{-1})$	$\Delta G(V)$
DDQ	0.07	2.7 x 10 <sup>5</sup>	-0.41	0.14	2.6 x 10 <sup>5</sup>	-0.44
DCBQ	-0.15	2.6 x 10 <sup>5</sup>	-0.19	-0.09	b	-0.18
o-TCBQ	-0.33	2.1 x 10 <sup>5</sup>	-0.01	-0.26	2.1 x 10 <sup>5</sup>	-0.01
o-TBBQ	-0.35	-	0.01	-0.28	-	0.01
p-TCBO	-0.42	-	0.08	-0.37	-	0.10

 $a = vs. Fc/Fc^+$ . b = DCBQ was not soluble in MeCN at the desired concentrations.

Figure 5.20 depicts the electron transfer reaction from the quintet excited state, S = 2, to the diagmagnetic ground state of the benzoquinone acceptor, S = 0, which produces a quartet iron(III) complex, S = 3/2, and the doublet benzoquinone radical anion, S = 1/2, where  $\Delta S = 0$  for the reaction conserving spin angular momentum. The S = 3/2 state of the iron(III) complex is the initially formed product and the state that should be considered when determining if angular momentum for the reaction is conserved. After electron transfer occurs through the spin-allowed S = 2 pathway the S = 3/2 state can then undergo reorginization to the more stable high-spin, S = 5/2, iron(III) compound.



Figure 5.20. Reaction scheme depicting that oxidative quenching of the  ${}^{5}T_{2}$  state by the benzoquinones conserves angular momentum.

Given the compelling case for electron transfer occurring from the metal-centered excited state of the iron chromophore the zero-point energy of this excited state can be alluded to from the thermodynamic properties of the benzoquinone acceptors. Specifically, the cutoff potential for reactivity can be used to estimate the effective redox potential assuming this break in reactivity corresponds to a transition from an exergonic to an endergonic reaction. The effective excited-state oxidation potential of the  ${}^{5}T_{2}$  state of  $[Fe(tren(py)_{3})]^{2+}$  can be estimated to be ~ -0.35 ± 0.05 V versus the ferrocene/ferrocenium couple in acetone and ~ -0.25 ± 0.05 V in acetonitrile. The 0.1 V shift in the effective driving force for the reaction in response to the change in solvent is yet another indication that electron transfer is the operative reaction mechanism, as energy transfer processes are far less sensitive to variations in solvent dielectric.<sup>58</sup>

## **5.4.** Conclusions

Photoredox catalysis has utilized 2<sup>nd</sup>- and 3<sup>rd</sup>-row transition metal-based chromophores such as  $[Ru(bpy)_3]^{2+}$  and fac-Ir(ppy)\_3. Their advantageous lowest-energy excited state is a MLCT state with lifetimes on the order of nanoseconds to microseconds. These chromophores also possess a strong absorption feature over a distinct spectral region, photo-stability, and reversible redox chemistry. Despite all of the advantages of ruthenium- and iridium-based chromophores in photoredox catalysts these metals are among the rarest in the earth's crust leading to initiative for utilizing chromophores with earth-abundant transition metals. In recent years iron(II) polypyridyls have been used as photocatalysts but unlike the other earth-abundant transition metal catalysts the mechanism of these reactions pertaining to the excited-state quenching of the chromophores have not been clear. When iron(II) polypyridyls have been used as photocatalysts there has been a common misconception that their nature of excited-state quenching will be identical to the secondand third-row metals. The stark difference in the photophysics between Ru and Ir polypyridyls and the Fe congeners directly translates to their difference in excited-state reactivity as photocatalysts. For iron(II) polypyridyls visible excitation leads to formation of the <sup>1</sup>MLCT state which intersystem crosses to the <sup>3</sup>MLCT state and deactivation forming the lowest-energy ligand field excited state,  ${}^{5}T_{2}$ , occurs in ~200 fs. An important consequence of implementing iron as a photocatalyst is that the nature of the lowest-energy excited state is metal-centered and is formed orders of magnitude faster than diffusion. Despite this excited state not being charge separated, like the MLCT states in Ru and Ir complexes, the ground-state recovery time of  $[Fe(tren(py)_3)]^{2+}$ is 55 ns which is sufficiently long enough with respect to the time scale of molecular diffusion making the catalytically relevant excited state the  ${}^{5}T_{2}$  state. If the quenching mechanism of the catalytically relevant excited state is known synthetic modifications to the photocatalyst can be used to improve their performance.

In an effort to understand the quenching mechanism of iron(II) polypyridyls as photocatalysts bimolecular quenching studies using ns-TA spectroscopy were performed with a series of benzoquinone acceptors. Dynamic quenching of the  ${}^{5}T_{2}$  state was observed and electrochemistry was used to measure the redox potentials. The quenching rate constant observed correlated with the reduction potential of the benzoquinone, and coupled with energy transfer, dipolar and exchange, not being a possible pathway it was concluded that electron transfer from the  ${}^{5}T_{2}$  state to the DDQ, DCBQ, and *o*-TCBQ acceptors is the mechanism of excited-state reactivity. The cut-off potential of reactivity was used to measure the effective excited-state oxidation potential for the electron transfer process, ~ -0.35 ± 0.05 V in acetone and ~ -0.25 ± 0.05 V in acetone and ~ -0.25 ± 0.05 V in acetone and ~ -0.25 ± 0.05 V in acetone the transfer were not identified in the transient absorption experiments the 0.1 V shift in excited-state oxidation potential due to solvent as well as the rate of quenching correlating to the benzoquinone reduction potential is supportive of photo-induced electron transfer from metal-centered excited state. This work provides the first evidence of the mechanism of iron(II) polypyridyls in photoredox catalysis.

APPENDIX



Figure 5.21. <sup>13</sup>C-NMR of DCBQ in CDCl<sub>3</sub> (177.7 ppm, 137.4 ppm, 128.1 ppm, 109.9 ppm).



Figure 5.22. Cyclic voltammographs of DDQ (green), ferrocene (black), and DCBQ (red) in acetone.



Figure 5.23. Cyclic voltammographs of *o*-TCBQ (black), *o*-TBBQ (red), and *p*-TCBQ (green) in acetone.



Figure 5.24. Cyclic voltammographs of DDQ (red) and ferrocene (black) in MeCN.



Figure 5.25. Cyclic voltammograph of DCBQ in MeCN.



Figure 5.26. Cyclic voltammographs of *o*-TCBQ (black), *o*-TBBQ (red), and *p*-TCBQ (green) in MeCN.



Figure 5.27. Quenching studies in acetone solution using  $[Fe(tren(py)_3)]^{2+}$  following MLCT excitation at 580 nm and probing at 560 nm. (a) 8 mM DDQ, fit with a single exponential ( $\tau_1 = 49$  ns) ( $k_0/k_{obs} = 55$  ns/49 ns = 1.12). (b) 14 mM DDQ, fit with bi-exponential Gaussian deconvolution due to contribution from laser scatter ( $\tau_1 = 7$  ns,  $\tau_2 = 46$  ns), ( $k_0/k_{obs} = 55$  ns/46 ns = 1.2). (c) 23 mM DDQ, fit with bi-exponential Gaussian deconvolution from laser scatter ( $\tau_1 = 7$  ns,  $\tau_2 = 41$  ns), ( $k_0/k_{obs} = 55$  ns/41 ns = 1.34). (d) 27 mM DDQ, fit with bi-exponential Gaussian deconvolution from laser scatter ( $\tau_1 = 7$  ns,  $\tau_2 = 37$  ns), ( $k_0/k_{obs} = 55$  ns/37 ns = 1.48).



Figure 5.28. Quenching studies in acetone solution using  $[Fe(tren(py)_3)]^{2+}$  following MLCT excitation at 580 nm and probing at 560 nm. (a) 10 mM DCBQ, fit with bi-exponential Gaussian deconvolution due to contribution from laser scatter ( $\tau_1 = 7$  ns,  $\tau_2 = 45$  ns), ( $k_0/k_{obs} = 51$  ns/45 ns = 1.13). (b) 20 mM DCBQ, fit with bi-exponential Gaussian deconvolution due to contribution from laser scatter ( $\tau_1 = 7$  ns,  $\tau_2 = 45$  ns), ( $k_0/k_{obs} = 51$  ns/45 ns = 1.13). (b) 20 mM DCBQ, fit with bi-exponential Gaussian deconvolution due to contribution from laser scatter ( $\tau_1 = 7$  ns,  $\tau_2 = 39$  ns), ( $k_0/k_{obs} = 51$  ns/39 ns = 1.3). (c) 25 mM DCBQ, fit with bi-exponential Gaussian deconvolution from laser scatter ( $\tau_1 = 7$  ns,  $\tau_2 = 36$  ns), ( $k_0/k_{obs} = 50$  ns/36 ns = 1.38).



Figure 5.29. Quenching studies in acetone solution using  $[Fe(tren(py)_3)]^{2+}$  following MLCT excitation at 580 nm and probing at 560 nm. (a) 10 mM *o*-TCBQ (top left), fit with bi-exponential

Figure 5.29. (cont'd) Gaussian deconvolution due to contribution from laser scatter ( $\tau_1 = 7 \text{ ns}$ ,  $\tau_2 = 48 \text{ ns}$ ) ( $k_0/k_{obs} = 51 \text{ ns}/48 \text{ ns} = 1.1$ ). (b) 15 mM *o*-TCBQ, fit with a tri-exponential Gaussian deconvolution due to contribution from laser scatter and a positive feature ( $\tau_1 = 7 \text{ ns}$ ,  $\tau_2 = 43 \text{ ns}$ ,  $\tau_3 = 285 \text{ ns}$ ) ( $k_0/k_{obs} = 51 \text{ ns}/43 \text{ ns} = 1.18$ ). (c) 20 mM *o*-TCBQ, fit with tri-exponential Gaussian deconvolution due to contribution from laser scatter and a positive feature ( $\tau_1 = 7 \text{ ns}$ ,  $\tau_2 = 40 \text{ ns}$ ,  $\tau_3 = 290 \text{ ns}$ ), ( $k_0/k_{obs} = 49 \text{ ns}/40 \text{ ns} = 1.23$ ). (d) 25 mM *o*-TCBQ, fit with a tri-exponential Gaussian deconvolution due to signal contribution from laser scatter and a positive feature ( $\tau_1 = 7 \text{ ns}$ ,  $\tau_2 = 30 \text{ ns}$ ,  $\tau_3 = 275 \text{ ns}$ ). (e) 35 mM *o*-TCBQ, fit with a tri-exponential Gaussian deconvolution due to signal contribution from laser scatter and a positive feature ( $\tau_1 = 7 \text{ ns}$ ,  $\tau_2 = 30 \text{ ns}$ ,  $\tau_3 = 275 \text{ ns}$ ). (e) 35 mM *o*-TCBQ, fit with a tri-exponential Gaussian deconvolution due to signal contribution from laser scatter and a positive feature ( $\tau_1 = 7 \text{ ns}$ ,  $\tau_2 = 30 \text{ ns}$ ,  $\tau_3 = 275 \text{ ns}$ ). (e) 35 mM *o*-TCBQ, fit with a tri-exponential Gaussian deconvolution due to signal contribution from laser scatter and a positive feature ( $\tau_1 = 7 \text{ ns}$ ,  $\tau_2 = 30 \text{ ns}$ ,  $\tau_3 = 275 \text{ ns}$ ). (e) 35 mM *o*-TCBQ, fit with a tri-exponential Gaussian deconvolution due to signal contribution from laser scatter and a positive feature ( $\tau_1 = 7 \text{ ns}$ ,  $\tau_2 = 12 \text{ ns}$ ,  $\tau_3 = 270 \text{ ns}$ ).



Figure 5.30. Quenching studies in acetone solution using  $[Fe(tren(py)_3)]^{2+}$  following MLCT excitation at 580 nm and probing at 560 nm. (a)10 mM *o*-TBBQ, fit with a single exponential ( $\tau_1 = 50$  ns).(b) 20 mM *o*-TBBQ, fit with bi-exponential Gaussian deconvolution due to significant signal from the positive feature due to partial excitation of *o*-TBBQ ( $\tau_1 = 7$  ns,  $\tau_2 = 50$  ns). (c) 30 mM *o*-TBBQ, fit with bi-exponential Gaussian deconvolution due to significant signal from the positive feature due to partial excitation of *o*-TBBQ ( $\tau_1 = 7$  ns,  $\tau_2 = 50$  ns). (d) 42 mM *o*-TBBQ, fit with bi-exponential Gaussian deconvolution due to significant signal from the positive feature due to partial excitation of *o*-TBBQ ( $\tau_1 = 7$  ns,  $\tau_2 = 50$  ns). (d) 42 mM *o*-TBBQ, fit with bi-exponential Gaussian deconvolution due to significant signal from the positive feature due to partial excitation of *o*-TBBQ ( $\tau_1 = 7$  ns,  $\tau_2 = 50$  ns). (d) 42 mM *o*-TBBQ, fit with bi-exponential Gaussian deconvolution due to significant signal from the positive feature due to partial excitation of *o*-TBBQ ( $\tau_1 = 7$  ns,  $\tau_2 = 50$  ns). (d) 42 mM *o*-TBBQ, fit with bi-exponential Gaussian deconvolution due to significant signal from the positive feature due to partial excitation of *o*-TBBQ ( $\tau_1 = 7$  ns,  $\tau_2 = 50$  ns).



Figure 5.31. Quenching studies in acetone solution using  $[Fe(tren(py)_3)]^{2+}$  following MLCT excitation at 580 nm and probing at 560 nm. (a) 10 mM *p*-TCBQ, fit with a single exponential ( $\tau_1 = 50$  ns). (b) 20 mM *p*-TCBQ, fit with a single exponential ( $\tau_1 = 50$  ns). (c) 30 mM *p*-TCBQ, fit with a single exponential ( $\tau_1 = 50$  ns). (c) 30 mM *p*-TCBQ, fit with a single exponential ( $\tau_1 = 50$  ns). (d) 40 mM *p*-TCBQ, fit with a single exponential ( $\tau_1 = 50$  ns).



Figure 5.32. Quenching studies in acetonitrile solution using  $[Fe(tren(py)_3)]^{2+}$  following MLCT excitation at 580 nm and probing at 560 nm. (a) 10 mM DDQ, fit with bi-exponential Gaussian deconvolution due to contributions from laser scatter ( $\tau_1 = 5$  ns,  $\tau_2 = 50$  ns), ( $k_0/k_{obs} = 55$  ns/50 ns = 1.1). (b) 15 mM DDQ, fit with bi-exponential Gaussian deconvolution due to contributions from laser scatter ( $\tau_1 = 6$  ns,  $\tau_2 = 45$  ns), ( $k_0/k_{obs} = 55$  ns/45 ns = 1.22). (c) 30 mM DDQ, fit with bi-exponential Gaussian deconvolution due to contributions from laser scatter ( $\tau_1 = 8$  ns,  $\tau_2 = 34$  ns), ( $k_0/k_{obs} = 49$  ns/34 ns = 1.44).



Figure 5.33. Quenching studies in acetonitrile solution using  $[Fe(tren(py)_3)]^{2+}$  following MLCT excitation at 580 nm and probing at 560 nm. (a) 10 mM *o*-TCBQ, fit with a single exponential ( $\tau_1 = 50$  ns), ( $k_0/k_{obs} = 55$  ns/50 ns = 1.1). (b) 15 mM *o*-TCBQ, fit with bi-exponential Gaussian deconvolution due to contributions from laser scatter ( $\tau_1 = 7$  ns,  $\tau_2 = 42$  ns), ( $k_0/k_{obs} = 50$  ns/42 ns = 1.19). (c) 21 mM *o*-TCBQ, fit with bi-exponential Gaussian deconvolution due to significant signal contribution from laser scatter ( $\tau_1 = 7$  ns,  $\tau_2 = 44$  ns), ( $k_0/k_{obs} = 55$  ns/44 ns = 1.25).



Figure 5.34. Quenching studies in acetonitrile solution using  $[Fe(tren(py)_3)]^{2+}$  following MLCT excitation at 580 nm and probing at 560 nm. (a) 8.5 mM *o*-TBBQ, fit with bi-exponential Gaussian deconvolution due to signal from the positive feature resulting from direct excitation of *o*-TBBQ ( $\tau_1 = 7 \text{ ns}, \tau_2 = 55 \text{ ns}$ ). (b) 17 mM *o*-TBBQ, fit with bi-exponential Gaussian deconvolution due to signal from the positive feature resulting from direct excitation of *o*-TBBQ ( $\tau_1 = 7 \text{ ns}, \tau_2 = 55 \text{ ns}$ ). (b) 17 mM *o*-TBBQ, fit with bi-exponential Gaussian deconvolution due to signal from the positive feature resulting from direct excitation of *o*-TBBQ ( $\tau_1 = 7 \text{ ns}, \tau_2 = 55 \text{ ns}$ ). (c) 25 mM *o*-TBBQ, fit with bi-exponential Gaussian deconvolution due to signal from the positive feature resulting from direct excitation of *o*-TBBQ ( $\tau_1 = 7 \text{ ns}, \tau_2 = 55 \text{ ns}$ ). (d) 34 mM *o*-TBBQ, fit with bi-exponential Gaussian deconvolution due to signal from the positive feature resulting from direct excitation of *o*-TBBQ ( $\tau_1 = 7 \text{ ns}, \tau_2 = 55 \text{ ns}$ ). (d) 34 mM *o*-TBBQ, fit with bi-exponential Gaussian deconvolution due to signal from the positive feature resulting from direct excitation of *o*-TBBQ ( $\tau_1 = 7 \text{ ns}, \tau_2 = 55 \text{ ns}$ ). (d) 34 mM *o*-TBBQ, fit with bi-exponential Gaussian deconvolution due to signal from the positive feature resulting from direct excitation of *o*-TBBQ ( $\tau_1 = 7 \text{ ns}, \tau_2 = 55 \text{ ns}$ ).



Figure 5.35. Quenching studies in acetonitrile solution using  $[Fe(tren(py)_3)]^{2+}$  following MLCT excitation at 580 nm and probing at 560 nm. (a) 11 mM *p*-TCBQ, fit with a single exponential ( $\tau_1 = 55$  ns). (b) 21 mM *p*-TCBQ, fit with a single exponential ( $\tau_1 = 55$  ns). (c) 31 mM *p*-TCBQ, fit with a single exponential ( $\tau_1 = 55$  ns). (d) 42 mM *p*-TCBQ, fit with a single exponential ( $\tau_1 = 55$  ns).

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## **Chapter 6. Future Directions**

## **6.1. Introduction**

The research presented thus far has demonstrated how the effects of spin angular momentum manifest in the excited-state reactivity of molecular systems. While Chapter 2 focused on characterizing the photophysical properties of the four Re polypyridyl moieties used in the donor-acceptor systems, Chapter 3 and 4 showed how the newly designed dinuclear system can be used to study the role of spin in excited-state reactivity. In the case of the CoRe compounds discussed in Chapter 4, the spin restriction for Förster transfer prevents energy transfer and oxidative quenching occurs. This is the first report of using spin to control the excited-state reactivity pathway. Chapter 5 examined the excited state quenching mechanism of an iron(II) polypyridyl as it pertains to photoredox catalysis. The information regarding how spin affects excited-state quenching mechanisms was used in conjunction with experimental evidence to show these iron(II) chromophores engage in oxidative quenching from their <sup>5</sup>T<sub>2</sub> ligand field states. This chapter will focus on experiments to further strengthen the conclusion made in Chapter 4 and outline future directions for this project to further understand spin effects in excited state reactivity.

# 6.2. Dinuclear GaRe Control Molecules

The results discussed in Chapter 4 pertaining to the dinuclear CoRe complexes lead to the conclusion of oxidative quenching of the <sup>3</sup>MLCT via a rapid equilibrium. The steady-state emission, time-resolved emission, and transient absorption data in conjunction with fitting the data by two different methods are in support of this model. Despite the large degree of agreement between the data and the model, this hypothesis can be further supported by using time-resolved infrared (TRIR) spectroscopy. The carbonyl stretching frequencies in these compounds are

observed in a distinct spectral region,  $1900 \text{ cm}^{-1} - 2050 \text{ cm}^{-1}$ , and the v(CO) bands have been well characterized in the ground state and <sup>3</sup>MLCT state.<sup>1,2</sup> In the IR spectrum for [Re(bpy)(CO)<sub>3</sub>(4-Etpy]<sup>+</sup> (bpy = 2,2'-bipyridine and 4-Etpy = 4-Ethylpyridine) the C<sub>s</sub> symmetry results in three v(CO) bands, two A' modes and one A'' mode, while two v(CO) bands are observed at 1927 cm<sup>-1</sup>, overlapping A' and A", and 2035 cm<sup>-1</sup>, A'. Upon excitation the <sup>3</sup>MLCT state results in a hole on the Re center, this decreases the  $\pi$  back-bonding to the carbonyls and all three v(CO) are resolved and shifted to higher energy, 1971 cm<sup>-1</sup> (A"), 2010 cm<sup>-1</sup> (A'), and 2074 cm<sup>-1</sup> (A'). Using TRIR spectroscopy the kinetics of the MLCT state of the dinuclear CoRe(bpy) compound can be studied using the v(CO) as a probe. In the proposed kinetic model oxidative electron transfer results in formation of a Re(II)-Co(II) species, and the v(CO) of these species may be shifted relative to that of the <sup>3</sup>MLCT state. The change in v(CO) between the electron transfer products and the <sup>3</sup>MLCT state can be used to identify the kinetics of the electron transfer products. Based on the kinetic model for this system shown in Figure 6.1, this should not only allow for the kinetics related to the electron transfer process in the <sup>3</sup>MLCT state to be observed but also the kinetics pertaining to charge recombination,  $k_3$ . The biexponential kinetics observed in time-resolved emission and transient absorption should also be present while probing the v(CO),  $k_1$  and  $k_2$ , with the addition of observing k<sub>3</sub>. The observation of charge recombination would provide experimental evidence of the products for oxidative quenching.



Figure 6.1. Kinetic model for electron transfer equilibrium in CoRe(bpy).

The steady-state and time-resolved emission data collected for  $[Co(tren)(pyacac)Re(btfmb)(CO)_3]^{3+}$  (tren = Tris(2-aminoethyl)amine, pyacac = (3-(4-pyridyl)-2,4-pentanedione), and btfmb = 4,4'-bis(trifluoromethyl)-2,2'-bipyridine) suggested that quenching of the <sup>3</sup>MLCT state does not occur. When the data for CoRe(btmfb) is compared to  $[\text{Re(btfmb)(CO)}_3(4-\text{Etpy})]^+$ , the lifetime decreases by 5 ns and the quantum yield is reduced by a factor of 2. While the difference in lifetime and quantum yield can be explained through solvation and ion pairing effects,<sup>3</sup> a result of increasing the overall charge of the molecule to +3, a more appropriate control molecule can be used. The gallium compound shown in Figure 6.2 can be used as a control molecule due to its inability to engage in quenching, similar atomic radius compared to Co and Cr, and oxidation state. Ga(III) does not possess any absorption features in the visible due to its d<sup>10</sup> configuration, this eliminates the possibility for Förster transfer to occur, and the thermodynamics for electron transfer are not favorable. The synthesis and characterization of a gallium control molecule will definitively eliminate the discrepancy between the photophysics of CoRe(btfmb) and  $[Re(btfmb)(CO)_3(4-Etpy)]^+$ . The +3 oxidation state for Ga and its similar atomic radius to Co and Cr removes ionic pairing and solvent effects in the excited-state decay dynamics.



Figure 6.2.  $[Ga(tren)(pyacac)Re(btfmb)(CO)_3]^{3+}$ , GaRe(btfmb), used as a control molecule for the CoRe dinuclear systems.

While the evidence to support the rapid electron transfer equilibrium for the CoRe systems is self-consistent, using TRIR and characterizing the photophysics of the GaRe(btfmb) control

molecule will provide irrefutable evidence that spin can be used to dictate and control the excitedstate quenching pathway. TRIR takes advantage of the well characterized and spectrally distinct region of the carbonyl stretching frequencies in the <sup>3</sup>MLCT state, providing an additional handle to observe all kinetic processes of this system. The CoRe(btfmb) compound does not exhibit any discernable quenching but the very minor difference in the photophysics when compared to [Re(btfmb)(CO)<sub>3</sub>(4-Etpy)]<sup>+</sup> requires the use of a more accurate control molecule. The GaRe(btfmb) compound cannot engage in any quenching mechanism and has an identical structural motif, atomic radius and oxidation state to the CoRe analog, this will eliminate any doubt of the <sup>3</sup>MLCT of CoRe(btfmb) reacting with the Co(III) center.

The previous proposed experiments focus on the short term future works for the research discussed throughout this dissertation and the ideas presented for the remainder of this chapter will focus on new donor-acceptor systems to expand upon the results and conclusions reported in this thesis.

#### 6.3. Probing Spin Effects at Increased Donor-Acceptor Distances and in Dexter Transfer

## 6.3.1. Increasing the Donor-Acceptor Distance

The research presented in Chapters 3 and 4 have developed and characterized a dinuclear donor-acceptor system to study the spin effects in excited-state reactivity. The tetranuclear and dinuclear systems demonstrate that zero-field spin effects should be considered in Förster theory. The general structural motif of the dinuclear system can be expanded upon by modifying the bridging ligand between the donor and acceptor. By introducing phenyl spacers between the pyridine and acetylacetonate in the bridging ligand the donor-acceptor distance can be systematically increased, Figure 6.3. While the Förster transfer pathway was shut off due to the
spin restrictions in the dinuclear CoRe compounds, the proposed compounds in Figure 6.3 will allow the spin restrictions of Förster theory to be analyzed at larger donor-acceptor distances. Förster transfer can be operative up to 100 Å but whether the spin restrictions that were observed in the previous systems will persist has not been studied. The through-space donor-acceptor distance of the dinuclear system with no phenyl spacer is ~ 10 Å, when six phenyl groups are substituted between the pyridine and acetylacetonate the donor-acceptor distance is ~ 40 Å.



Figure 6.3. Proposed compounds to study the spin affects at increased donor-acceptor distances.

## 6.3.2. Transition Between Dexter and Förster Transfer

Both the original tetranuclear assembly and the dimensionally reduced dinuclear system were designed to rule out quenching via Dexter transfer on the basis of the distance between donor and acceptor. The fact that the <sup>3</sup>MLCT excited state is associated with the bipyridyl ligand creates a situation where the through-bond pathway to the acceptor is in excess of 10 Å, the upper limit for through-bond energy transfer. Eliminating this quenching pathway provided straight forward analysis in the previous systems, but the role of spin in exchange energy transfer cannot be studied because the separation is already too large for this mechanism. A new series of compounds shown in Figure 6.4 are proposed with a slight, but significant, modification. Modifying the bipyridyl ligand with an acetylacetonate group decreases the donor-acceptor distance since the MLCT is localized on the bipyridine. This results in decreasing the through-bond pathway between the

<sup>3</sup>MLCT and the first-row transition metal acceptor resulting in Dexter transfer being the dominant quenching pathway. The CoRe complexes exhibit photo-induced electron transfer for the bpy and tmb (tmb = 4,5,4',5'-tetramethyl-2,2'-bipyridine) but not for btfmb due to the lowered energy of the excited state. By modifying the pyridyl ring that is not connected to the acceptor with an electron withdrawing group, such as CF<sub>3</sub>, the energy of the excited will decrease such that excited state electron transfer will not occur in these proposed systems.



Figure 6.4. Proposed complexes to decrease the donor-acceptor distance.

While Dexter transfer is the dominant quenching pathway the requirement for coupling to an absorptive feature of the acceptor is no longer needed. The  ${}^{1}T_{1}$  ligand field state for Co(III) was the only possible excited-state acceptor for Förster transfer, but under this regime the lower energy  ${}^{3}T_{2}$  and  ${}^{3}T_{1}$  states can act as potential acceptors. Figure 6.5 shows a proposed route for the synthesis of the modified bpy-linker.<sup>4-16</sup> Based on the design of this system and from what was learned from the previous dinuclear compounds, the Cr(III) and Co(III) compounds will quench the Re-based  ${}^{3}MLCT$  excited state.

The design of this new system not only allows for the spin effects of Dexter transfer to be studied but the competition between these two energy transfer mechanisms can be studied as well.



Figure 6.5. Proposed synthetic route for the modified bpy-acac system.

Based on the spin conservation model, Co(III) is predicted to quench via Dexter transfer but not Förster transfer. By installing various linkers between the bpy-acac ligand the donor-acceptor distance can gradually increase, shifting the predominant mechanism from Dexter to Förster transfer. Therefore, the degree of quenching in the Co compounds will vary based on the donoracceptor distance. It is predicted that at short distances the Co will quench but at longer distances, where Förster transfer is the operative mechanism, no quenching will be observed. Since Cr is able to quench via Dexter or Förster transfer, the sensitivity as a function of donor-acceptor distance will be much less. These experiments will not only validate the spin conservation model but will offer insight into how spin plays a role in the competition of rate constants for these two energy transfer mechanisms.

## 6.4. Systematic Increase of Driving Force for Electron Transfer for Iron(II) Photocatalysts

The results presented in Chapter 5 is the first time the excited-state quenching mechanism for an iron(II) polypyridyl has been studied. By using nanosecond time-resolved absorption spectroscopy bimolecular quenching studies with benzoquinone acceptors provided evidence of oxidative quenching from the  ${}^{5}T_{2}$  ligand field state. The electron transfer mechanism was confirmed from the correlation between the quenching rate constant,  $k_{q}$ , and the reduction potential of the benzoquinone acceptors and the change in the excited-state oxidation potential with solvent. Since the excited-state quenching mechanism for iron(II) polypyridyls have been established synthetic modifications to the ligands can be performed to optimize the photocatalyst.

The nature of the lowest-energy excited states for iron(II) polypyridyls are metal-centered in nature. Since electron transfer occurs from these metal-centered states, as in the case for  $[Fe(tren(py)_3)]^{2+}$  (where tren(py)<sub>3</sub> = tris(2-pyridyl-methylimino-ethyl)amine), increasing the ligand field strength increases the energy of the <sup>5</sup>T<sub>2</sub> state and results in an increased driving force for oxidative quenching. By studying the excited-state quenching mechanisms for the compounds shown in Figure 6.6, the systematic change in ligand field strength will demonstrate the importance of understanding the excited-state mechanism for optimizing photocatalysts.





Figure 6.6. Proposed iron(II) polypyridyls to systematically change the driving force for photoinduced electron transfer.

Relative to  $[Fe(tren(py)_3)]^{2+}$ ,  $[Fe(2-OMe-phen)_3]^{2+}$  (2-OMe-phen = 2-methoxy-1,10phenanthroline) displays a much weaker ligand field due to the steric bulk of the methoxy substituent. The steric bulk on the ligand results in this iron polypyridyl being spin crossover (SCO) where the high-spin  ${}^{5}T_2$  state is thermally accessible from the low-spin  ${}^{1}A_1$  state, which remains the lowest-energy state. Since the  ${}^{5}T_2$  state is significantly lower in energy compared to  $[Fe(tren(py)_3)]^{2+}$ , the E<sub>00</sub> (zero-point energy) is lower and consequently the driving force for

electron transfer is lowered. By using the same benzoquinone acceptors presented in Chapter 5  $[Fe(2-OMe-phen)_3]^{2+}$  will display a much lower cutoff potential for reactivity, and no quenching will be observed. The synthesis and physical properties linked to its SCO nature have been previously reported and the ground-state recovery for [Fe(2-OMe-phen)<sub>3</sub>]<sup>2+</sup> is 15 ns at room temperature.<sup>17</sup> Since the lifetime is within a factor of 2 to the instrument response function (IRF) of the nanosecond transient absorption system it may be necessary to use ultrafast transient absorption to measure the quenching rate constants. The ligand field strength and the driving force can be increased relative to  $[Fe(tren(py)_3)]^{2+}$  by studying  $[Fe(bpy)_3]^{2+}$ . It is expected that the stronger field ligand should possess a higher cutoff potential for reactivity and react with benzoquinones with a more negative reduction potential compared to  $[Fe(tren(py)_3)]^{2+}$ . The ligand field strength can be increased even further by substituting a bpy ligand with two cyano ligands in the case of  $[Fe(bpy)_2(CN)_2]$ . This should increase the E<sub>00</sub> of the <sup>5</sup>T<sub>2</sub> state even more than  $[Fe(bpy)_3]^{2+}$  and result in the largest cutoff potential for this series of compounds. The cyano ligands also provide another spectroscopic handle to observe the quenching kinetics via timeresolved infrared spectroscopy. The ground-state recovery times for  $[Fe(bpy)_3]^{2+}$  and [Fe(bpy)<sub>2</sub>(CN)<sub>2</sub>] are 1 ns and sub-1 ns, in MeCN respectively, and will require ultrafast spectroscopy to observe the quenching kinetics.<sup>18</sup> Studying the kinetics of excited-state reactivity between the compounds in Figure 6.5 and the benzoquinone acceptors used in Chapter 5 will demonstrate the importance of ligand and photocatalyst design by systematically changing the driving force for oxidative quenching.

To further demonstrate the importance of the photophysics of the photocatalyst and its design, excited-state quenching of the compounds shown in Figure 6.7 with benzoquinone acceptors can be studied. The lowest-energy ligand field state for  $[Fe(bpy)_3]^{2+}$  is metal-centered in

nature and requires the quencher to react with the metal center. To understand the consequences that these metal-centered excited states impart on the kinetics of bimolecular quenching, bulky *tert*-butyl groups can be used to inhibit access to the metal center in the case of  $[Fe(dtbbpy)_3]^{2+}$ (dtbbpy = 4,4'-di-tert-butyl-2,2'-bipyridine). Despite [Fe(dtbbpy)<sub>3</sub>]<sup>2+</sup> possessing a similar lifetime, 1 ns,<sup>19</sup> and  $E_{00}$  relative to  $[Fe(bpy)_3]^{2+}$  the bulky substituents on the periphery of the molecule could result in a slower rate of quenching. To demonstrate the kinetic impact of the nature of the excited state,  $[Fe(btz)_3]^{2+}$  (btz = 3,3'-dimethyl1,1'-bis(p-tolyl)-4,4'-bis(1,2,3-triazol-5-ylidene)) utilizes the strongly electron  $\sigma$ -donating N-heterocyclic carbene (NHC) ligands to increase the energy of the ligand field manifold such that the lifetime of the <sup>3</sup>MLCT is increased to 528 ps,<sup>20</sup> compared to ~ 200 fs for a typical iron(II) polypyridyl. For  $[Fe(btz)_3]^{2+}$  it is expected that excitedstate reactivity will occur from the <sup>3</sup>MLCT state and the nature of this excited state is fundamentally different from other iron(II) polypyridyls. The <sup>3</sup>MLCT localizes negative charge on the periphery of the molecule where biomolecular reactivity is kinetically facile for oxidative quenching compared to accessing the metal center of  $[Fe(dtbbpy)_3]^{2+}$ . Due to the MLCT nature of the  $[Fe(btz)_3]^{2+}$  excited state, oxidative and reductive quenching are potential reaction pathways. Typical iron(II) polypyridyls with a  ${}^{5}T_{2}$  lowest-energy excited state are incapable of engaging in



Figure 6.7. Iron(II) chromophores used to study how the nature of the excited state affects the kinetics of quenching.

reductive quenching due to the thermodynamics associated with creating Fe(I). The Fe(III) hole in the MLCT state of  $[Fe(btz)_3]^{2+}$  allows for iron- based photocatalysts to engage in reductive quenching mechanisms. Based on the nature of the excited state involved in excited-state reactivity, the kinetics associated with quenching can be determined by studying the bimolecular reactivity of the compounds shown in Figure 6.7 with benzoquinone acceptors. REFERENCES

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