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DIPOLAR ENERGY TRANSFER IN RHENIUM(I) POLYPYRIDYL-BASED DONOR-ACCEPTOR ASSEMBLIES

By

Troy Elvin Knight

A DISSERTATION

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ABSTRACT

DIPOLAR ENERGY TRANSFER IN RHENIUM(I) POLYPYRIDYL-BASED DONOR-ACCEPTOR ASSEMBLIES

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Dipolar energy transfer is a through-space mechanism that occurs when a donor emission dipole non-radiatively couples to an absorptive dipole in the acceptor. In 1946, Theodor Förster published the theoretical framework for dipolar (Förster) energy transfer in solution. The classic $1/R^6$ distance dependence of the dipolar energy transfer rate has been widely used as a "spectroscopic ruler" to determine the distance between fluorescently labeled donor and acceptor complexes. In addition to the $1/R^6$ distance dependence, the through-space orientation (κ^2) between the donor and acceptor transition moment dipoles also affects the observed rate of energy transfer, and plays a particular role in the energy transfer efficiency in covalently attached donor-acceptor systems that are unable to sample all possible orientations in solution. The majority of the research presented in this dissertation involves understanding and quantifying the dependence of κ^2 on Förster energy transfer in covalently attached transition metal-based donor-acceptor assemblies.

The donor-acceptor systems discussed throughout this work are comprised of Re^I polypyridyl donor molecules covalently attached to various first-row transition metal complexes through an organic-based linker molecule, and are referred to as MRex (where M represents a first-row acceptor metal center and X = 2 or 3). The lowest energy excited-state of the Re^I donor moieties involves a metal-to-ligand charge transfer transition (³MLCT). This ³MLCT state is located on an isolated portion of the Re^Ibased donor moiety, which simplified the location of the donor emission dipole and in turn aided in the determination of the through-space orientation between the donor emission and acceptor absorption transition moment dipoles in the MRe_x complexes. The acceptor moieties are all $M(acac)_3$ complexes that possess charge-transfer ($M = Fe^{III}$) or ligand-field ($M = Cu^{II}$, Cr^{III}, Co^{III}, and Ni^{II}) acceptor states. Varying the nature of the acceptor transitions permitted fundamental investigations of the dependence of Förster energy transfer on through-space dipolar orientation and on the size of the transition moment dipoles involved in the energy transfer event. The synthesis and characterization, photophysical properties, and dipolar energy transfer behavior in the MRe_x complexes will be presented and discussed.

Copyright by Troy Elvin Knight 2009 Dedicated to my two grannies: Uva Nell Handley and Lillie Belle Knight. I hope I live up to the potential that both of you always saw in me.

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To begin the acknowledgements I must first give a short back story on my road to the chemistry department at Michigan State. I began my graduate work at The University of Alabama at Birmingham where my research focused on the photophysical properties of transition metal compounds, which also happens to be the focus of the McCusker group. During my third year at UAB my research advisor was unfortunately denied tenure, and I was presented with some unexpected choices, either move to another group at UAB (which I did not want to do) or transfer to another university. My former advisor always spoke very highly of Jim and his science and suggested I look into joining the McCusker group. After contacting Jim, I decided to transfer to MSU and continue my focus on inorganic spectroscopy. I have to say it was one of the best choices I have ever made and I would do it all over again if given the chance. I have learned so much from Jim and I want to sincerely thank him for teaching me how to think and act as a scientist. Achieving the high scientific aptitude that Jim possesses will be daily goals of mine as I continue my career. Thanks Jim. "SCIENCE!"

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Images in this dissertation are presented in color.

Chapter 1: Introduction of Förster Energy Transfer Theory and Transition Metal-Based Donor/Acceptor Systems.

1.1 Introduction to Förster Energy Transfer Theory

The initial descriptions of through-space energy transfer phenomena were introduced in the early 1900's by the Nobel prize winning physicist Jean Baptiste Perrin. He was the first to theorize that energy between two closely spaced molecules in solution can be transferred by the interaction of their oscillating electric dipoles, as long as a resonance condition was satisfied between the two dipoles.¹ This seminal work of Perrin ultimately led to the development of the well known fluorescence resonance energy transfer theory, or more commonly referred to as Förster theory. Ever since Theodor Förster first introduced his seminal paper in 1948,² Förster energy transfer theory has become one of the most ubiquitous photophysical processes and has been used in biology, chemistry, and physics. The $1/R^6$ distance dependence between two interacting dipoles has been widely utilized as a spectroscopic ruler³⁻⁷ to determine the distance between donor and acceptor molecules, and has been shown to correspond very closely with distances determined from structural data.⁸ Examples of various areas impacted by Förster theory include measurements of distances between

1

fluorescently labeled donor and acceptor molecules attached to proteins,⁹ determination of the conformational dynamics of RNA,¹⁰ and improving the light-harvesting capabilities of solar energy conversion devices.¹¹⁻¹⁵

In general, excited-state energy transfer processes involve the transfer of excited-state energy from a donor molecule (D) to an acceptor molecule (A), with the process beginning with the donor molecule absorbing a photon, and can be represented by equation 1-1:

$$\mathbf{D} + \mathbf{A} + h\nu \longrightarrow \mathbf{D}^* + \mathbf{A} \xrightarrow{k_{EnT}} \mathbf{D} + \mathbf{A}^*$$
(1-1)

Förster energy transfer is a through-space mechanism that occurs when a donor transition moment dipole non-radiatively couples to an acceptor transition moment dipole.^{16,17} The dipolar nature of this interaction gives rise to a R^{-6} (R = distance) dependence, allowing this mechanism to be operative over very long donor-acceptor separations. More specifically, Förster energy transfer involves the non-radiative coupling of donor emission dipoles with energetically matched acceptor absorption dipoles and is represented in Figure 1-1.



Figure 1-1. Simplified energy level diagram illustrating resonance between the donor (D) emission and the acceptor (A) absorption transition dipoles.

It can be seen from Figure 1-1 that the initially produced electronic excited states of the donor complex (D^*) non-radiatively relax to the lowest energy vibronic level of D^* , which can radiatively couple to various ground state vibrational levels of the donor (D) (blue, green, and red transitions). These emissive dipoles can then interact with energetically matched absorptive transitions of the acceptor molecule to produce acceptor excited states (A^{*}), which may be thought of as a virtual photon exchange between D^{*} and A. The transitions initiated in the acceptor molecule are equivalent to the acceptor absorbing a photon directly to generate A^{*}.

The picture of the two-state coupling shown in Figure 1-1 is a minimal model and represents the interaction of molecules in the gas phase.

Donor emission and acceptor absorption transitions in solution interact with the surrounding medium and are usually observed as broad featureless spectra. Förster's ingenious contribution to dipole-dipole energy transfer theory was his realization that coupled transitions in solution can be quantified by the spectral overlap of the donor emission spectrum with the acceptor absorption spectrum, which are both easily accessible experimental observables.¹⁸ The area of spectral overlap, which represents resonance matching of donor emission and acceptor absorption transitions, is shown qualitatively in Figure 1-2 (black lines). Förster's spectral overlap model depends on small electronic communication between the donor and acceptor molecules (the so-called "weak coupling" regime),¹⁹ which is usually experimentally observed by the linear combination of the electronic absorption spectra of separated donor and acceptor molecules corresponding to the absorption spectrum of the intact donor-acceptor assembly. Specifically, the definition of the "weak coupling" regime given by Förster relies on two characteristics: 1) equilibration of the solvent bath with D^{*} occurs on a much faster time-scale than the excited-state energy transfer dynamics, and 2) the interaction of the donor and acceptor molecules with the solvent is much greater than the electronic coupling between them.



Figure 1-2. Spectral overlap plot showing energy conservation between an arbitrary donor emission and acceptor absorption spectra.

As mentioned above, Förster theory has a direct connection to parameters that can be accessed experimentally. The energy transfer rate constant (k_{EnT}) is described by the Förster equation given in equation 1-2,²⁰

$$k_{EnT} = \frac{9000 \ln(10) \kappa^2 \Phi_D J}{128 \pi^5 \eta^4 N_A \tau_D R^6}$$
(1-2)

where κ^2 is the dipole orientation factor, Φ_D is the radiative quantum yield of the donor, η is the refractive index of the solvent, N_A is Avogadro's number, τ_D is the excited-state lifetime of the donor, R is the donor-acceptor separation, and J the spectral overlap integral. This latter term, which essentially quantifies the resonance condition necessary for dipole-dipole coupling, can be evaluated from the spectroscopic properties of the system according to equation 1-3,

$$J = \int_{0}^{\infty} \frac{\overline{F}_{D}(\overline{\nu})\overline{\varepsilon}_{A}(\overline{\nu})}{\overline{\nu}^{4}} d\overline{\nu}$$
(1-3)

where \overline{F}_{D} is the (normalized) emission spectrum of the donor and $\overline{\epsilon}_{A}$ is the absorption profile of the acceptor in units of molar absorptivity. From equation 1-2, knowledge concerning the geometric positions of the donor emission and acceptor absorption transition dipoles, which is known as the orientation factor (κ^{2}), must also be elucidated to accurately model excitedstate kinetics. The orientation factor relates the angle between the donor emission and the acceptor absorption transition dipoles relative to each other and the angle the donor and acceptor transition dipoles each create with the donor-acceptor connection line, and is given in equation 1-4:

$$\kappa^{2} = (\cos\Theta_{\rm T} - 3\cos\Theta_{\rm D}\cos\Theta_{\rm A})^{2} \qquad (1-4)$$

where Θ_T is the angle between the donor transition dipole moment (r_D) and the acceptor transition dipole moment (r_A), and Θ_D and Θ_A are the angles between the donor-acceptor connection line (R_{DA}) and the donor transition dipole moment and the acceptor transition dipole moment, respectively. The angles are defined in Figure 1-3.



Figure 1-3. Definitions of the angles used for calculating the orientation factor (κ^2) between the donor emission (r_D) and acceptor absorption (r_A) transition moment dipoles.

The values for κ^2 can range from 0 to 4 depending on the relative angles between the two transition dipoles, with $\kappa^2 = 0$ being the orthogonal interaction between the two dipoles, $\kappa^2 = 1$ being the parallel interaction, and $\kappa^2 = 4$ being the highest possible interaction with both dipoles aligned along the donor-acceptor connection line (Figure 1-4).²¹



Figure 1-4. Range of values possible for the orientation factor (κ^2) between the donor emission (blue vectors) and the acceptor absorption (red vectors) transition moment dipoles.

An isotropic value has also been determined for the dipolar orientation factor ($\kappa^2 = \frac{2}{3}$), and represents the average of all possible dipole-dipole through-space interactions between donor and acceptor species in solution.²² The isotropic value of $\frac{2}{3}$ can be thought of as the donor emission and the acceptor transition moment dipoles existing within two spherically shaped molecules in solution (Figure 1-5), with these two systems possessing unrestricted movement within all three degrees of freedom (x, y, and z). The isotropic value works well for bimolecular donor-acceptor systems in solution such as lanthanide ions,²³ or systems that behave like spheres that rapidly diffuse through all possible orientations,²⁴ but this simplification can

introduce a significant amount of error between the theoretical and observed energy transfer rate constants with covalently attached donor-acceptor systems that are unable to sample all degrees of freedom.^{25,26} Covalently attached donor-acceptor complexes, such as the Re¹-based compounds discussed throughout this dissertation, negates the possibility of freely rotating donor and acceptor molecules and thus rules out the possibility of using κ^2 values of %. Theoretically modeling and quantifying the orientation factor in covalently attached donor-acceptor systems is one of the overall themes of the work presented in this dissertation.



Figure 1-5. Illustration of spherically-shaped donor (D) and acceptor (A) complexes that possess an isotropic through-space interaction between their respective transition moment dipoles.

1.2 Transition Metal-Based Donor/Acceptor Complexes

Developing artificial energy-conversion systems is arguably the most important goal in the area of donor-acceptor photochemistry. Mother Nature has incorporated transition metal ions into various areas of the energy conversion sequences of photosynthesis,²⁷⁻³⁰ which has led many researchers to follow in her footsteps and develop transition metal-based artificial photosynthetic systems.^{31,32} Two major design lessons that can be taken from natural systems are 1) the initial light absorption step must produce a charge separation in order to generate high energy reagents that perform useful chemistry, such as excited state energy transfer or an electron transfer cascade and 2) spatial control of the excited-state energy flow must be achieved in order to deliver the useful energy to certain areas of the supramolecular array.³³ Metal-based donor-acceptor assemblies consisting of d⁶ polypyridyl complexes of Re^I, Ru^{II}, Os^{II}, and Ir^{III} have received considerable attention in this area due to possessing long-lived (nanosecond) charge-separated excited states in the form of metal-to-ligand charge transfer transitions (MLCT), relative stability of those charge transfer excited states, and well documented ground and excited-state electronic properties.³⁴⁻⁴²

The ground and excited state electronic structure of d^6 polypyridyl complexes deserves some focus in the section, due to the charge transfer excited states of Re^I polypyridyl complexes utilized as the donor electronic states throughout this entire dissertation. Figure 1-6 shows a simplified energy level diagram for 2nd and 3rd row d⁶ polypyridyl complexes.⁴³ The

absorption of a photon initially produces a ¹MLCT excited state ($t_{2g} \rightarrow \pi^*$ (polypyridyl)), which then undergoes extremely fast relaxation (~ 100 fs) through intersystem crossing and vibrational cooling dynamics to the lowest energy ³MLCT excited state.^{44,45} It is out of this thermalized ³MLCT state that all of the radiative and energy transfer dynamics occur.⁴⁶⁻⁵² The lifetime of the ³MLCT state in these complexes exist in the nanosecond to microsecond time regime,⁵³⁻⁵⁸ which is a timescale very amenable to performing useful excited-state chemistry processes and also to probe with typical photophysical instrumentation.



Nuclear coordinate (Q)



One example of the Re^{I} -based supramolecular assemblies (FeRe₃) discussed in this dissertation and possessing a charge transfer excited state in the donor moieties is shown in Figure 1-7. Förster-type energy transfer reactivity can be envisioned to occur out of the thermalized ³MLCT state of the Re^I donor complex to produce an absorptive transition in the acceptor, and in the FeRe₃ example the acceptor states are LMCT (ligand-to-metal charge transfer) transitions associated with the $Fe(acac)_3$ core (acac = acetylacetonate) (Figure 1-7). The charge transfer nature of the ³MLCT donor emission and the LMCT acceptor absorptions in the FeRe₃ complexes induce the movement of charge within the individual donor and acceptor moieties, and these electronic transitions have been modeled as the blue (donor) and red (acceptor) vectors in Figure 1-7. The assignment of a specific excited state quenching mechanism depends strongly on the redox properties of the metal and the ligands, the strength of electronic coupling mediated by the bridging ligand (ie. whether the excited electron resides on the bridging or peripheral ligands), and the energy of the lowest energy ³MLCT state of the donor.⁵⁹ The structural and electronic characteristics of the FeRe₃ assemblies (Figure 1-7), along with the other Re^I-based polynuclear assemblies reported throughout this work, are very amenable to Förster energy transfer quenching of the Re¹ donor state.


Figure 1-7. General structure of the FeRe₃ assemblies discussed in Chapter 2. The FeRe₃ donor-acceptor complex shows the thermalized ³MLCT excited state of the Re^I donor moiety utilized in all of the donor-acceptor complexes discussed in this dissertation. A single Re^I donor excited state is shown (blue vector) interacting with all three acceptor transitions (red vectors) due to a single Re^I photon absorption event per assembly.

1.3 Contents of Dissertation

The research contained in this thesis has focused on developing a more in depth understanding of energy transfer dynamics in transition metalbased donor-acceptor assemblies. Specifically, the structural and electronic properties of the metal-based donor and acceptor complexes were designed to study and quantify dipole-dipole (Förster) energy transfer processes in covalently-attached assemblies. Polypyridyl complexes of Re^I were chosen as the donor moieties due to possessing an isolated, relatively long-lived ³MLCT excited-state, which simplified the geometric location of the emission transition dipole moment of the donor and allowed for a quantitative application of Förster theory. The various sections of this thesis represent investigations into particular aspects of Förster energy transfer theory undertaken by altering the charge and spin-state of the acceptor metal centers. Specific areas of focus include quantifying through-space dipoledipole orientation (κ^2) in charge transfer-based donor-acceptor complexes, utilizing ligand-field transitions to uncover orbital specific energy transfer reactivity, and investigating the spin-state dependences of dipolar energy transfer.

The first section, Chapter 2, focuses on the synthesis, characterization, and photophysical properties of a family of chromophore-quencher

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complexes with the general formula [Fe(pyacac)₃(Re(bpy')(CO)₃)₃](OTf)₃ (where bpy' = 4,4'-5,5'-tetramethyl-2,2'-bipyridine, 2,2'-bipyridine, or 4,4'diethylester-2,2'-bipyridine). The FeRe₃ complexes contain a high-spin Fe^{III} acceptor core coordinated through three 3-(4-pyridyl)-acetylacetone ligands to three Re(bpy')(CO)₃ donor moieties. Steady-state as well as timeresolved emission and absorption measurements acquired in roomtemperature CH₂Cl₂ solutions indicate quenching of the Re^I-based ³MLCT excited state when compared to isostructural AlRe₃ model compounds. Electron transfer was found to be thermodynamically unfavorable for all three Re^I-containing systems: this fact coupled with the absence of optical signatures for the expected charge-separated photoproducts in the timeresolved differential absorption spectra and favorable spectral overlap between the donor emission and acceptor absorption profiles implicated dipolar energy transfer from the Re^I-based excited-state to the high-spin Fe^{III} core as the dominant quenching pathway in these compounds. The chargetransfer-based donor emission (³MLCT) and acceptor absorption (⁶LMCT) states were modeled as the movement of charge along particular vectors within the coordination environment [³MLCT: Re^{II}(bpy⁻) \rightarrow Re^I(bpy); ⁶LMCT: $Fe^{III}(acac) \rightarrow Fe^{II}(acac^{+})$]. Metric details obtained from singlecrystal X-ray structural data allowed for a quantitative application of Förster energy transfer theory by systematically calculating the donor-acceptor separation (R_{DA}) and spatial orientation of the charge transfer-based donor and acceptor transition moment dipoles (κ^2). The results of this analysis and agreement with experimentally derived energy transfer rate constants will be discussed.

The unambiguous assignment of Förster energy transfer as the dominant quenching pathway in the FeRe₃ assemblies, led to the design of structurally similar complexes that possess acceptor metal centers with lowintensity ligand-field absorptions that overlap with the Re^I-based donor emission spectra. The goal of the research contained in Chapter 3 was to examine if dipole-dipole energy transfer could operate in systems that possess very small transition dipole moments. Chapter 3 focuses on the synthesis, characterization, and photophysical properties of a family of donor-acceptor complexes with the general formula [Cu(pyacac)₂(Re(bpy')- $(CO)_3_2$ (Where bpy' = 4,4'-5,5'-tetramethyl-2,2'-bipyridine, 4,4'dimethyl-2,2'-bipyridine, 2,2'-bipyridine, 4,4'-dichloro-2,2'-bipyridine, or 4,4'-diethylester-2,2'-bipyridine). The CuRe₂ complexes contain a d⁹ Cu^{II} acceptor core coordinated through two 3-(4-pyridyl)-acetylacetone ligands to two Re(bpy')(CO)₃ donor moieties. Steady-state as well as time-resolved emission measurements acquired in room-temperature CH₂Cl₂ solutions

indicate quenching of the Re^I-based ³MLCT excited state when compared to isostructural BeRe₂ model compounds. Electron transfer was found to be significantly endothermic for all five CuRe₂ complexes; this fact, coupled with the ca. 10 Å donor-acceptor distance and favorable spectral overlap between the ³MLCT emission profile and ligand-field absorptions of the Cu^{II} center implicated dipolar energy transfer as the dominant quenching pathway in these compounds. Gaussian deconvolution of the ground-state absorption spectrum of $Cu(phacac)_2$ (phacac = 3-phenyl-acetylacetonate) allowed for a differential analysis of the spectral overlap between the donor emission spectra with the two observed ligand-field absorption bands of the Cu^{II} ion. The rate of energy transfer was found to increase with increasing overlap for coupling to the lower-energy ligand-field band, consistent with expectations from Förster theory. These results were supported by timedependent DFT calculations on Cu(phacac)₂, and indicated preferential coupling to a particular ligand-field transition of the Cu^{II} center. These results will be discussed in terms of an orbitally-specific energy transfer process occurring in the CuRe₂ series.

Observation of emission from an acceptor moiety provides unequivocal proof of an excited state energy transfer mechanism. Although, the structural and electrochemical properties of the FeRe₃ (Chapter 2) and CuRe₂ (Chapter 3) complexes rule out electron transfer as a viable quenching mechanism, the goal of the work contained in Chapter 4 was to introduce an acceptor metal center that emits in response to quenching the Re¹-based ³MLCT excited state. Chapter 4 focuses on the synthesis, characterization, and photophysical properties of a series of chromophorequencher complexes with the general formula [Cr(pyacac)₃(Re(bpy')- $(CO)_3)_3$ (OTf)₃ (with bpy' defined above). The CrRe₃ complexes contain a d³ Cr^{III} acceptor core coordinated through three 3-(4-pyridyl)-acetylacetone ligands to three Re(bpy')(CO)₃ donor moieties. Steady-state as well as timeresolved emission and absorption measurements acquired in roomtemperature CH₂Cl₂ solutions indicate quenching of the Re^I-based ³MLCT excited state when compared to isostructural AlRe₃ model compounds. Acquisition of the excitation spectrum of $[Cr(pyacac)_3(Re(bpy)(CO)_3)_3]$ -(OTf)₃ at λ_{max} of the Cr^{III}-based ²E \rightarrow ⁴A₂ emission in frozen EtOH/MeOH (4:1) solution reproduced it's ground-state absorption spectrum, which proves that all of the photons absorbed by [Cr(pyacac)₃(Re(bpy)- $(CO)_{3}_{3}(OTf)_{3}$ results in Cr^{III}-based emission and unequivocally proves an energy transfer mechanism. A comparison between the nature of the ligandfield acceptor states in the CrRe₃ and the CuRe₂ complexes, along with their effect on dipolar energy transfer reactivity will also discussed.

In Chapter 5, the Re^I-based compounds - [Co(pyacac)₃(Re(bpy)- $(CO)_{3}_{3}(OTf)_{3}$ and $[Ni(pyacac)_{2}(THF)_{2}(Re(bpy)(CO)_{3})_{2}](OTf)_{2}$ - were synthesized in order to investigate the spin-state dependence of dipolar energy transfer. The first section of Chapter 5 contains the synthesis, characterization, and photophysical properties of a CoRe₃ assembly that possesses a low-spin d⁶ Co^{III} metal center (${}^{1}A_{1}$, S = 0). Steady-state and time-resolved emission measurements acquired in room-temperature CH₂Cl₂ solution revealed no quenching of the Re¹-based ³MLCT excited state, with the observed excited state relaxation behavior comparable to an isostructural AlRe₃ compound. Favorable spectral overlap between the Re^I-based ³MLCT emission spectrum and the ${}^{1}A_{1} \rightarrow {}^{1}T_{1}$ ligand-field absorption profile of the Co^{III} ion was observed, suggesting dipolar energy quenching should be active in the CoRe₃ assembly. Determination of the total spin angular momentum (S_T) values possible in the CoRe₃ complex revealed that the 1A_1 \rightarrow ¹T₁ acceptor transition represents a spin-forbidden relaxation pathway for the ³MLCT donor state. This suppressed energy transfer reactivity between the ³MLCT donor and the Co^{III} core is compared with the results received in Chapter 3 on a structurally similar CrRe₃ complex the exhibits significant quenching of the Re¹-based ³MLCT state. The CrRe₃ system possesses identical overall charge and structural characteristics with the CoRe₃

complex, but simply differs in the spin-state of the acceptor metal center. The results on the CoRe₃ system highlight the ability of controlling excited state quenching reactivity by simply varying the spin-state of the reagents. The second section of Chapter 5 will focus on the synthesis, characterization, and photophysical characteristics of [Ni(pyacac)₂(THF)₂- $(\text{Re(bpy)(CO)}_3)_2$ (OTf)₂, referred to as the NiRe₂ assembly, which contains a pseudo-octahedral Ni^{II} (d⁸) acceptor metal center. Determination of the total spin angular momentum (S_T) in the NiRe₂ assembly showed the ligand-field absorption of the NiO₆ core $({}^{3}A_{2} \rightarrow {}^{3}T_{2})$ to be a spin-allowed relaxation pathway for the Re^I-based ³MLCT donor state. Comparison of the steadystate emission of [Ni(pyacac)₂(THF)₂(Re(bpy)(CO)₃)₂](OTf)₂ in THF and in CH₂Cl₂ solutions at room-temperature revealed an on/off ³MLCT quenching mechanism, with the dissociation of the axially coordinating THF molecules in CH₂Cl₂ solution generating a NiO_{6-x} (x = 1 or 2) complex and subsequent spin-forbidden energy transfer pathway.

Future directions of the research are included as a sixth chapter. Various MRe_n (n = 2 or 3) compounds that have been synthesized and characterized, proposed complexes and photophysical experiments, and the scientific questions the molecules will address comprise the content of Chapter 6.

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Chapter 2. Quantifying Förster Energy Transfer in Charge Transfer Based Donor/Acceptor Complexes: FeRe₃ Multinuclear Assemblies.

2.1 Introduction

Elucidating the mechanism of excited-state reactivity is a necessary first step for understanding and ultimately manipulating complex photoinduced chemical processes.¹⁻⁴ Accordingly, numerous fundamental studies of excited-state dynamics have been reported in the literature. Assemblies based on d⁶ polypyridyl complexes of Re¹, Ru^{II}, and Os^{II} have garnered particular attention due to relative stability of their excited states, well documented ground and excited-state electronic properties, and the ability one has to tune these properties through synthetic means. Both electron and energy transfer processes have been the subject of intense scrutiny. As a result, much has been learned about the factors that govern both of these types of excited-state reactions in transition metal-based systems.⁵⁻¹⁴

The two most widely occurring energy transfer mechanisms are electron superexchange (Dexter)¹⁵ and through-space dipole-dipole coupling (Förster).¹⁶ Dexter energy transfer is subject to a distance dependence that falls off as exp(-2R) due to its reliance on orbital overlap. As such, it is usually relegated to covalently linked systems in which the donor and

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acceptor are in close proximity (e.g., ≤ 5 Å).¹⁷⁻²² Förster transfer is a through-space mechanism that occurs when the donor emission dipole non-radiatively couples to an absorptive dipole in the acceptor.²³⁻²⁵ The dipolar nature of this interaction gives rise to a shallower R⁻⁶ dependence, allowing this mechanism to be operative over much longer distances. Förster-type reactivity is therefore usually dominant in systems that place the lowest energy excited-state on an electronically isolated portion of the donor or between metal centers that are separated over long distances.²⁶⁻²⁹

The Förster energy transfer rate constant (k_{EnT}) is described by the equation given in equation 2-1,³⁰

$$k_{EnT} = \frac{9000 \ln(10) \kappa^2 \Phi_D J}{128 \pi^5 \eta^4 N_A \tau_D R^6}$$
(2-1)

where κ^2 is the dipole orientation factor, Φ_D is the radiative quantum yield of the donor, η is the refractive index of the solvent, N_A is Avogadro's number, τ_D is the excited-state lifetime of the donor, R is the donor-acceptor separation, and J is a spectral overlap integral that essentially quantifies the resonance condition necessary for dipole-dipole coupling. This latter term can be evaluated from the spectroscopic properties of the system according to equation 2-2,

$$J = \int_{0}^{\infty} \frac{\overline{F}_{D}(\overline{\nu})\overline{\varepsilon}_{A}(\overline{\nu})}{\overline{\nu}^{4}} d\overline{\nu}$$
(2-2)

where \overline{F}_{D} is the (normalized) emission spectrum of the donor and $\overline{\mathcal{E}}_{A}$ is the absorption profile of the acceptor in units of molar absorptivity. From equation 2-1, knowledge concerning the geometric positions of the donor emission and acceptor absorption transition dipoles, which is known as the orientation factor (κ^{2}), must be elucidated to accurately model excited-state kinetics. The orientation factor relates the angle between the donor emission and the acceptor absorption transition dipoles relative to each other and the angle the donor and acceptor transition dipoles each create with the donoracceptor connection line, and is given in equation 2-3:

$$\kappa^{2} = (\cos\Theta_{\rm T} - 3\cos\Theta_{\rm D}\cos\Theta_{\rm A})^{2}$$
(2-3)

where Θ_{T} is the angle between the donor transition dipole moment and the acceptor transition dipole moment, and Θ_{D} and Θ_{A} are the angles between the donor-acceptor connection line and the donor transition dipole moment and the acceptor transition dipole moment, respectively. Although equations 2-1, 2-2, and 2-3 constitute a complete description of the rate of dipolar energy transfer, quantifying the donor-acceptor distance (R) and the orientation factor (κ^{2}) can be quite difficult in metal-based donor-acceptor

complexes, due to R typically being approximated as the metal-metal separation and κ^2 usually assigned as $\frac{2}{3}$. Taking R as the metal-metal distance is a reasonable assumption when structural data are not available. but in the point-dipole approximation of Förster theory this may or may not accurately reflect the relevant distance in systems comprised of donor and acceptor states that are charge-transfer in nature. In addition, the orientation factor of $\kappa^2 = \frac{2}{3}$ typically invoked represents an isotropic value for species sampling all possible angular distributions.⁴¹ While appropriate for bimolecular energy transfer processes, this approximation may not be reasonable given the rotational barriers that likely exist in covalently attached donor-acceptor complexes. The resulting ambiguities that can arise concerning these two variables often lead to a large variance between experiment and theory.

Moore et al. recently applied Förster theory in conjunction with molecular modeling calculations utilizing naphthalene and anthracene, which possess known directional emission and absorption transitions, covalently linked through a Zn^{II} containing macrocycle that holds the separation distance constant.^{42,43} The studies revealed that the minimized conformers, with quantitatively determined donor-acceptor distances and orientation factors, very accurately describe the observed Förster energy transfer kinetics when all of the possible conformers were taken into account. The donor-acceptor systems to be discussed in this chapter possess known donor-acceptor separations and directional electronic transitions as well, which utilize a Re^I polypyridyl based ³MLCT state as the donor and Fe^{III} tris-acetylacetonate based ⁶LMCT (ligand-to-metal charge-transfer) states as the acceptor. The current systems also have moderate spectral overlap between the donor emission and acceptor absorption profiles, which was instrumental in systematically studying and solely modeling the donor emission quenching dynamics as Förster energy transfer.

Specifically, the synthesis, structure, and photophysical properties of a series of isostructurally related molecules are reported, with the general formula [Fe(pyacac)₃(Re(tmb)(CO)₃)₃](OTf)₃ (1), [Fe(pyacac)₃(Re(bpy)-(CO)₃)₃](OTf)₃ (2), and [Fe(pyacac)₃(Re(deeb)(CO)₃)₃](OTf)₃ (3) (where pyacac = 3-(4-pyridyl)-acetylacetonate, tmb = 4,4'-5,5'-tetramethyl-2,2'-bipyridine, bpy = 2,2'-bipyridine, deeb = 4,4'-diethylester-2,2'-bipyridine, and OTf = CF₃SO₃'), and with the entire series referred to as the FeRe₃ assemblies. The Fe^{III} metal centers are covalently attached to three *fac*-Re(bpy')(CO)₃ (bpy' = tmb, bpy, and deeb) (Figure 2-1) moieties through three pyridyl-acetylacetonate bridging ligands. It was observed that the Re¹-based ³MLCT excited-states for complexes 1, 2, and 3 are significantly

quenched in the presence of the Fe^{III} metal center relative to structurally analogous AlRe₃ analogs. The AlRe₃ model systems with the general formula $[Al(pyacac)_3(Re(tmb)(CO)_3)_3](OTf)_3$ (4), $[Al(pyacac)_3(Re(bpy) (CO)_{3}_{3}(OTf)_{3}$ (5), and $[Al(pyacac)_{3}(Re(deeb)(CO)_{3})_{3}](OTf)_{3}$ (6) were synthesized in order to investigate the excited-state dynamics of the $Re(bpy')(CO)_3$ moieties in the absence of the emission quenching dynamics incurred by the Fe^{III} metal center. Varying the bpy' attached to the Re^I metal center permitted a systematic investigation of the donor-acceptor spectral overlap by modifying the energy of the ³MLCT excited-state, with the emission quenching rate constant corresponding with the amount of observed spectral overlap. In addition, the single-crystal X-ray structure data for complex 2 enabled very accurate calculations of the R_{DA} and κ^2 interactions within this system, with the same values applied to complexes 1 and 3 by assuming that variation in the polypyridyl substituents causes minor altering of the internal dimensions within this family of compounds. The rigid structure of these systems also enabled a very accurate modeling of the solution phase Förster energy transfer kinetics by assuming the R_{DA} and κ^2 values remain unchanged from those calculated from the X-ray structural data, with the theoretical rate constants accurately reproducing the experimentally observed values. Lastly, one of the major hurdles in

quantifying Förster energy transfer is accurately determining the throughspace separation and orientation factor relating donor and acceptor transition dipoles, and the work in this chapter will show that the unique structure of the FeRe₃ analogs allow for a very accurate determination of these two variables.



Figure 2-1. Polypyridyl derivatives coordinated to the Re^I metal centers.

2.2 Experimental Section

2.2.1 Synthesis and Characterization

General. All solvents used were purified and dried according to previously reported methods.⁴⁴ Spectroscopic grade CH₂Cl₂ was used for all photophysical measurements; the solvent was dried under CaH₂ reflux until

no water was detected by ¹H NMR and degassed using freeze-pump-thaw techniques. 3-(4-pyridyl)-2,4-pentanedione,⁴⁵ Al(pyacac)₃,⁴⁵ Re(tmb)(CO)₃-(OTf),⁴⁶ Re(bpy)(CO)₃(OTf),⁴⁶ Re(deeb)(CO)₃(OTf),⁴⁶ and *fac*-[Re(bpy)(CO)₃(4-Etpy)](PF₆)⁴⁷ (4-Etpy = 4-ethylpyridine) were prepared following literature procedures. 3-phenyl-2,4-pentanedione was purchased from TCI America. Elemental analyses and FT-IR data were obtained through the analytical facilities at Michigan State University. Mass spectra were obtained through the analytical facilities at The University of South Carolina.

Tris(3-(4-pyridyl)acetylacetonato)iron(III), Fe(pyacac)₃. The synthesis of this compound has been reported previously by a different method.⁴⁸ Amounts of 70.1 mg (0.432 mmol) of FeCl₃ and 230 mg (1.30 mmol) of pyacac were dissolved in 30 mL of THF and stirred for 6 hrs. Sodium *tert*-butoxide (125 mg, 1.30 mmol) was then added to the reaction flask and the solution was stirred overnight. The reaction mixture was filtered over celite to remove excess salt and the solvent removed under vacuum. The product was recrystallized from $CH_2Cl_2/hexanes$ (1:1 v/v). Yield: 131 mg (52%). Anal. Calcd for $C_{30}H_{30}N_3O_6Fe$: C, 61.65; H, 5.17; N, 7.19. Found: C, 61.49; H, 5.13; N, 7.07.

Tris(3-phenyl-acetylacetonato)iron(III), Fe(phacac)₃. The synthesis of this compound has been previously reported by a different method.⁴⁸ Amounts of 86 mg (0.53 mmol) of FeCl₃ and 277 mg (1.57 mmol) of phacac were dissolved in 30 mL of THF and stirred for 6 hrs. Sodium *tert*-butoxide (149 mg, 1.57 mmol) was then added to the reaction flask and the reaction mixture was stirred overnight. The solution was then filtered over celite to remove excess salt and the solvent removed under vacuum. The product was recrystallized from CH_2Cl_2 /hexanes (1:1 v/v). Yield: 238 mg (78%). Anal. Calcd for $C_{33}H_{33}O_6Fe: C, 68.16; H, 5.72$. Found: C, 68.11; H, 5.79.

[Fe(pyacac)₃(Re(tmb)(CO)₃)₃](OTf)₃ (1). An amount of 230 mg (0.360 mmol) of Re(tmb)(CO)₃(OTf) was dissolved in 75 mL of hot THF, after which 70 mg (0.12 mmol) of Fe(pyacac)₃ was added and the solution purged with argon for 20 min. The reaction mixture was then fit with a condenser and stirred under argon for 3 days in hot THF in the dark, after which a dark red solution formed along with an orange precipitate. The precipitate was collected and the filtrate was concentrated under vacuum to yield additional orange solid. The combined precipitates were dissolved in CH₂Cl₂, filtered through celite, and the solvent removed under vacuum. The product was recrystallized several times from CH₂Cl₂/pentane (1:1 v/v). Yield: 155 mg (52%). Anal. Calcd for C₈₄H₇₈N₉F₉O₂₄S₃FeRe₃: C, 40.70; H,

3.17; N, 5.08. Found: C, 40.36; H, 3.23; N, 4.86. IR (KBr, cm⁻¹): 2031 s, 1918 s, 1614 m, 1566 s, 1448 m, 1365 m, 1263 s, 1155 m, 1032 s, 638 m. MS: [ESI, m/z (rel. int.)]: 677.3 (70) {[Fe(pyacac)_3(Re(tmb)(CO)_3)_3]}³⁺, 1090.5 (23) {[Fe(pyacac)_3(Re(tmb)(CO)_3)_3](OTf)}²⁺, 2330.1 (1) {[Fe(pyacac)_3(Re(tmb)(CO)_3)_3](OTf)_2}¹⁺.

 $[Fe(pyacac)_3(Re(bpy)(CO)_3)_3](OTf)_3$ (2). Amounts of 70 mg (0.12) mmol) of Fe(pyacac)₃ and 210 mg (0.365 mmol) of Re(bpy)(CO)₃(OTf) were dissolved in 25 mL of THF and flushed with argon for 20 min. The reaction was stirred in the dark for 3 days at room temperature. An orange solid precipitated out of solution and was collected and washed with hexanes. The solid was then dissolved in CH₃CN, filtered through celite, and the solvent removed under vacuum. The product was recrystallized several times from acetonitrile/ether (1:1 v/v). X-ray quality crystals were obtained by slow diffusion of ether into an acetonitrile solution of the compound. Yield: 166 mg (60%). Anal. Calcd for $C_{72}H_{54}N_9F_9O_{24}S_3FeRe_3$: C, 37.37; H, 2.35; N, 5.45. Found: C, 37.00; H, 2.23; N, 5.27. IR (KBr, cm⁻ ¹): 2033 s, 1922 s, 1568 m, 1446 m, 1367 w, 1261 m, 1159 m, 1032 m, 771 638 MS: [ESI, 621 m, m. m/z (rel. int.)]: (100) $\{[Fe(pyacac)_3(Re(bpy)(CO)_3)_3]\}^{3+}$, 1006 (18) {[Fe(pyacac)₃(Re(bpy)- $(CO)_{3}_{3}(OTf)^{2^{+}}, 2161.1 (1) \{ [Fe(pyacac)_{3}(Re(bpy)(CO)_{3})_{3}](OTf)_{2} \}^{1^{+}}.$

[Fe(pyacac)₃(Re(deeb)(CO)₃)₃](OTf)₃ (3). Amounts of 29 mg (0.050 mmol) of Fe(pyacac)₃ and 108 mg (0.150 mmol) of Re(deeb)(CO)₃(OTf) were dissolved in 25 mL of THF and flushed with argon for 20 min. The reaction was stirred in the dark for 4 days at room temperature. The solution was then filtered over celite and the solvent removed under vacuum to give a The product was recrystallized several times using red solid. Yield: 65 mg (48%). Anal. Calcd for CH_2Cl_2 /pentane (1:1 v/v). C₉₀H₇₈N₉F₉O₃₆S₃FeRe₃•3CH₂Cl₂: C, 38.00; H, 2.79; N, 4.15. Found: C, 38.00; H, 2.93; N, 4.32. IR (KBr, cm⁻¹): 2036 s, 1923 s, 1732 s, 1566 s, 1462 m, 1263 s, 1153 m, 1032 s, 767 m, 638 m. MS: [ESI, m/z (rel. int.)]: 765.4 (75) { $[Fe(pyacac)_3(Re(deeb)(CO)_3)_3]$ }³⁺, 1222.6 (19) { $[Fe(pyacac)_3 (\text{Re}(\text{deeb})(\text{CO})_3)_3 |(\text{OTf})|^{2^+}, 2594.2 (1) \{ [\text{Fe}(\text{pyacac})_3(\text{Re}(\text{deeb})(\text{CO})_3)_3] - (1) \} | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) |$ $(OTf)_2\}^{1+}$.

 $[Al(pyacac)_3(Re(tmb)(CO)_3)_3](OTf)_3$ (4). An amount of 224 mg (0.360 mmol) of Re(tmb)(CO)_3(OTf) was dissolved in 75 mL of hot THF, after which 66 mg (0.120 mmol) of Al(pyacac)_3 was added and the solution purged with argon for 20 min. The reaction mixture was then fit with a condenser and stirred under argon for 3 days in hot THF in the dark, after which a dark yellow solution formed along with a yellow precipitate. The precipitate was collected and the filtrate concentrated under vacuum to yield

additional yellow solid. The combined precipitates were dissolved in CH₂Cl₂, filtered through celite, and the solvent removed under vacuum. The product was recrystallized several times from CH₂Cl₂/pentane (1:1 v/v). Yield: 185 mg (64%). Anal. Calcd for C₈₄H₇₈N₉F₉O₂₄S₃AlRe₃•CH₂Cl₂: C, 40.55; H, 3.17; N, 4.95. Found: C, 40.37; H, 3.12; N, 4.95. IR (KBr, cm⁻¹): 2031 s, 1918 s, 1612 m, 1585 s, 1452 m, 1396 m, 1263 s, 1155 m, 1032 s, 638 m. MS: [ESI, m/z (rel. int.)]: 667.7 (65) {[Al(pyacac)₃(Re(tmb)-(CO)₃)₃]}³⁺, 1076.1 (25) {[Al(pyacac)₃(Re(tmb)(CO)₃)₃](OTf)₂}¹⁺.

[Al(pyacac)₃(Re(bpy)(CO)₃)₃](OTf)₃ (5). Amounts of 70 mg (0.126 mmol) of Al(pyacac)₃ and 210 mg (0.365 mmol) of Re(bpy)(CO)₃(OTf) were dissolved in 25 mL of THF and the solution flushed with argon for 20 min. The reaction was stirred in the dark for 3 days at room temperature. A yellow solid precipitated out of solution and was collected and washed with hexanes. The solid was then dissolved in CH₃CN, filtered through celite, and the solvent removed under vacuum. The product was recrystallized several times from acetonitrile/ether (1:1 v/v). X-ray quality crystals were obtained by slow diffusion of ether into an acetonitrile solution of the compound. Yield: 187 mg (65%). Anal. Calcd for C₇₂H₅₄N₉F₉O₂₄S₃AlRe₃: C, 36.90; H, 2.39; N, 5.53. Found: C, 37.51; H, 2.35; N, 5.13. IR (KBr,

cm⁻¹): 2033 s, 1920 s, 1585 s, 1446 s, 1398 s, 1263 s, 1159 s, 1029 s, 771 m, 638 s. MS: [ESI, m/z (rel. int.)]: 611.6 (100) { $[Al(pyacac)_3(Re(bpy)-(CO)_3)_3]$ }³⁺, 991.9 (30) { $[Al(pyacac)_3(Re(bpy)(CO)_3)_3](OTf)$ }²⁺, 2132.9 (1) { $[Al(pyacac)_3(Re(bpy)(CO)_3)_3](OTf)_2$ }¹⁺.

[Al(pyacac)₃(Re(deeb)(CO)₃)₃](OTf)₃ (6). Anounts of 28 mg of Al(pyacac)₃ (0.050 mmol) and 108 mg of Re(deeb)(CO)₃(OTf) (0.150 mmol) were dissolved in 25 mL of THF and flushed with argon for 20 min. The reaction was stirred in the dark for 4 days at room temperature. The solution was then filtered over celite and the solvent removed under vacuum to give an orange solid. The product was recrystallized several times from CH₂Cl₂/pentane (1:1 v/v). Yield: 60 mg (44%). Anal. Calcd for C₉₀H₇₈N₉F₉O₃₆S₃AlRe₃: C, 39.82; H, 2.90; N, 4.64. Found: C, 39.54; H, 2.85; N, 4.48. IR (KBr, cm⁻¹): 2036 s, 1930 s, 1734 s, 1585 s, 1448 s, 1273 s, 1151 m, 1032 s, 768 m, 638 m. MS: [ESI, m/z (rel. int.)]: 755.7 (42) {[Al(pyacac)₃(Re(deeb)(CO)₃)₃](OTf)²⁺, 2565.3 (1) {[Al(pyacac)₃(Re(deeb)(CO)₃)₃] $(OTf)_2$ ¹⁺.

2.2.2 Physical Measurements

X-ray Structure Determinations. Single-crystal X-ray diffraction data for complexes 2 and 5 were acquired at the X-ray facility of Michigan State University. Diffraction data were collected on a Siemens SMART diffractometer with graphite-monochromatic Mo K α radiation (λ = 0.71073Å). Data were collected at -100 °C by using an Oxford Cryosystems low temperature device. Crystallographic data are summarized in Table 1; selected bond distances and angles are listed in Table 2. Lattice parameters were obtained from least-squares analyses and data were integrated with the program SAINT.⁴⁹ The integration method employed a three dimensional profiling algorithm and all data were corrected for Lorentz and polarization factors, as well as for crystal decay effects. The absorption correction program SADABS⁵⁰ was employed to correct the data for absorption effects. The structures were solved by direct methods and expanded using Fourier techniques. All structure calculations were performed with the SHELXTL 6.12 software package.⁵¹ Anisotropic thermal parameters were refined for all non-hydrogen atoms. Hydrogen atoms were localized in their calculation positions and refined by using the riding model. Further details concerning the structure determinations may be found in Supporting Information.

Cyclic Voltammetry. Electrochemical measurements were carried out in a N₂-filled drybox (Vacuum Atmospheres) using a BAS CV-50W electrochemical analyzer. A standard three-electrode arrangement was utilized consisting of Pt working and counter electrodes and a Ag/AgNO₃ reference electrode. Measurements were carried out in either CH_2Cl_2 or CH₃CN solutions that were 0.1 M in NBu₄PF₆. The choice of solvent was dictated by the potential window required to observe a given redox couple; in cases where a compound could be examined in both solvents, differences in the observed potentials were found to be within experimental error of each other. Potentials are reported versus the ferrocene/ferrocenium couple, which was used as an internal standard, and listed in Table 3.

Electronic Absorption and Steady-State Emission Spectroscopies. Extinction coefficients for all compounds were acquired in CH_2Cl_2 solutions using a Hewlett-Packard 8452A diode array spectrophotometer. Steady-state emission spectra were acquired using a Spex Fluoromax fluorimeter and corrected for instrumental response using a NIST standard of spectral irradiance (Optronic Laboratories, Inc., OL220M tungsten quartz lamp).^{52a} Spectra were acquired on samples dissolved in thoroughly degassed CH_2Cl_2 under optically dilute conditions (o.d. ~ 0.1) and sealed under an argon atmosphere in 1 cm path length quartz cuvettes.

Radiative quantum yields (Φ_r) were determined relative to *fac*-[Re(bpy)(CO)₃(4-Etpy)](PF₆) ($\Phi_r = 0.18$ in CH₂Cl₂).⁴⁷ Quantum yields were calculated according to equation 2-4,

$$\Phi_{\text{unk}} = \Phi_{\text{std}} \frac{(I_{\text{unk}}/A_{\text{unk}})}{(I_{\text{std}}/A_{\text{std}})} \left(\frac{\eta_{\text{unk}}}{\eta_{\text{std}}}\right)^2$$
(2-4)

where Φ_{unk} and Φ_{std} are the radiative quantum yields of the sample and the standard, respectively, I_{unk} and I_{std} represent the areas of the corrected emission profiles for the sample and the standard, A_{unk} and A_{std} are the absorbance values of the sample and the standard at the excitation wavelength, and η_{unk} and η_{std} correspond to the indices of refraction of the sample and standard solutions (taken to be equal to the neat solvents). Excitation wavelengths were 355 nm for the bpy and tmb analogs and 400 nm for the deeb analogs. The corrected excitation spectrum of fac- $[Re(bpy)(CO)_3(4-Etpy)](PF_6)$ in CH_2Cl_2 overlaid well with the compound's absorption spectrum over the range of wavelengths examined (355 - 400 nm), implying that the radiative quantum yield for fac-[Re(bpy)(CO)₃(4- $E(PF_6)$ does not vary significantly over this spectral window. The reported value of $\Phi_r = 0.18$ was therefore used for determining the radiative quantum yields at both $\lambda_{ex} = 355$ nm and 400 nm.

Radiative quantum yields are not being reported for complexes 1-3 due to the presence of an emissive impurity. The source of the impurity was traced to a small amount of dissociated complex present in solution, most likely generated by water in the CH_2Cl_2 solvent. Despite our best efforts at drying the CH_2Cl_2 , there was an unacceptably large variance in repeated measurements of Φ_r . Due to the difference in time scales associated with excited-state decay between those emissive fragments and the intact assembly, the presence of these impurities does not significantly affect the kinetic analyses of these systems.

Values for the zero-point energy gap (E_{00}) of the Re¹-based ³MLCT excited states were determined by fitting the emission profiles of complexes **4-6** based on the approach described by Claude and Meyer.⁵³ Wavelength data were converted to energy units following the correction of Parker and Rees;⁵⁴ the best fit was determined by visual inspection of the results of a least-squares minimization routine.

Time-Resolved Emission Spectroscopy. Nanosecond time-resolved emission data for the AlRe₃ model complexes **4-6** were collected using a Nd:YAG-based laser spectrometer that has been described previously.^{52a} Data were acquired at room temperature in thoroughly degassed CH₂Cl₂ solutions having absorbances of ~0.1 at the excitation wavelength ($\lambda_{ex} = 355$ nm for complexes **4** and **5** and 420 nm for complex **6**). Samples were sealed under an argon atmosphere in 1 cm path length quartz cuvettes. The decay traces correspond to an average of 250 shots of the signal probed at the emission maximum of each compound.

Picosecond time-resolved emission data for the FeRe₃ complexes 1-3 were collected using a time-correlated single photon counting (TCSPC) apparatus that has been described previously.⁵⁵ Data were acquired in thoroughly degassed CH₂Cl₂ solutions having absorbances of ~0.1 at the excitation wavelength ($\lambda_{ex} = 370$ nm for complexes 1 and 2 and 430 nm for complex 3). Samples were sealed under an argon atmosphere in 1 cm path length quartz cuvettes. Each reported decay trace corresponds to a signal average of six data sets, with each data set resulting from ca. 1 hr of data acquisition time. The decay traces for all three complexes manifest a small baseline offset within the ca. nanosecond data acquisition window due to the presence of the impurity mentioned above; this was incorporated into the kinetic model. Data were fit using the OriginPro 7.5 software package.⁵⁶

Time-resolved Absorption Spectroscopy. Nanosecond timeresolved absorption measurements were collected using a Nd:YAG-based laser spectrometer that has been described previously.⁵² Data were acquired on thoroughly degassed CH_2Cl_2 solutions in 1 cm path length sealed quartz cuvettes. Sample absorbance was ~0.6 at the excitation wavelength of 355 nm. Excitation energies at the sample were ca. 2 mJ per pulse; all data were checked for linearity with respect to pump power, and steady-state absorption spectra were acquired before and after data acquisition to ensure the integrity of the sample. Differential absorption spectra were generated by plotting the amplitudes of fits of the decay kinetics acquired as a function of probe wavelength.

Sub-nanosecond time-resolved data were obtained for complex 1 using a femtosecond time-resolved absorption spectrometer that is described elsewhere.^{52b} Samples were dissolved in CH₂Cl₂ in an Ar atmosphere drybox and placed in 1 mm path length quartz cuvettes with absorbance values of ~0.6 at the excitation wavelength ($\lambda_{pump} = 370$ nm). Single-wavelength kinetics data were collected at $\lambda_{\text{probe}} = 700 \text{ nm}$ following ~100 fs excitation at 370 nm with a pump power of ca. 4 µJ. Single-photon excitation was confirmed by the linearity of the signal response with respect to pump power. Acquisition of full spectra for complex 1 was hampered by the formation of a photoproduct that precipitated over the course of several hours of data acquisition. Nevertheless, the data were sufficient to establish that identical kinetics are observed across the entire visible probe window; this will be elaborated upon in the discussion section. All data were fit using programs of local origin.

Förster Energy Transfer Rate Calculations. Calculations of energy transfer rates were carried out based on eqs 1-3. The variables of the Förster equation are presented in the Introduction section of this chapter, with the following briefly describing how the donor-acceptor separation (R_{DA}) and

the angles used to solve the orientation factor (κ^2) were defined for the FeRe3 family. Donor-acceptor distances and angles were measured using the single-crystal X-ray structure data of complex 2 with the Diamond 3.1d crystal structure and visualization software.⁵⁷ The donor-acceptor separation was ascertained by a simple through-space distance measurement between the interacting points of origin of the donor and the acceptor (donor-acceptor connection line). Θ_{T} was acquired by measuring the angle generated between the Re(bpy) donor plane versus the interacting FeO₂ acceptor plane. $\Theta_{\rm D}$ was acquired by measuring the angle the donor-acceptor connection line creates with the vector drawn from a donor origin to the Re^I metal center. Θ_A for acceptor positions D and E (Figure 2-11) were obtained by measuring the angle the donor-acceptor connection line creates with the vector drawn from an acceptor origin to the Fe^{III} metal center. Θ_A for acceptor position F (Fe^{III} center) was measured by evaluating the angle the donor-acceptor connection line creates with the vector drawn from the Fe^{III} metal center to the center of the oxygen atoms on the acac portion of the bridging ligand.

2.3 Results and Discussion

2.3.1 Synthesis and Characterization. Our interest in these systems was to investigate energy and/or electron transfer processes in structurally well-defined polynuclear charge-transfer assemblies. The choice of using Fe^{III} and Re^I was based on the well known MLCT-based reactivity of Re^I and the propensity for Fe^{III} to act as both an energy and electron acceptor.⁵⁸⁻⁶³ The utilization of the M(pyacac)₃ core (M = Fe^{III} and Al^{III}) as a ligand for Re(bpy')(CO)₃(OTf) allowed the pyridyl group to displace the weakly coordinating triflate anion and generate the tri-cationic FeRe₃ and AlRe₃ complexes. The formation of the tetranuclear assembly was facilitated by the low steric crowding afforded by the roughly 120° separation of the three pyacac ligands.

The ESI-MS data for complexes **1-6** in acetonitrile solution are consistent with the formation of the desired FeRe₃ and AlRe₃ assemblies. For example, complex **2** shows peaks corresponding to $[Fe(pyacac)_3(Re-(bpy)(CO)_3)_3]^{3+}$, $[Fe(pyacac)_3(Re(bpy)(CO)_3)_3](OTf)^{2+}$, and $[Fe(pyacac)_3-(Re(bpy)(CO)_3)_3](OTf)_2^{1+}$. X-ray quality crystals for complexes **2** and **5** were generated by diffusion of ether into an acetonitrile solution of the complexes over the course of approximately one week; this in turn provides additional evidence for the general robustness of complexes **1-6** in solution.

Nevertheless, the Fe^{III}-containing complexes 1-3 were found to be susceptible to slight decomposition in the presence of water. As mentioned in the Experimental Section, this was established via single-photon counting emission spectroscopy through the detection of a highly emissive, long-lived excited-state species. Since Fe^{III} compounds are non-emissive, this impurity is most likely a Re-bpy-containing fragment resulting from displacement of the pyacac ligand by adventitious H₂O. This decomposition pathway is not too surprising given the lability of high-spin Fe^{III} and its propensity to bind H₂O, but the extremely low intensity of the TCSPC signal corresponding to this species indicates that this represents a very minor component in solution.

The v(CO) stretching bands of the Re(bpy')(CO)₃ moieties in complexes 1-6 (Table 2-3) were assigned based on previously reported data for *fac*-[Re(4,4'-X₂-bpy)(CO)₃(4-Etpy)](PF₆) complexes.⁶⁴ The characteristic spectral profile consists of two very intense peaks. The broad band at lower energy corresponds to two overlapping transitions assigned to the A'(2) and A" modes (C_s symmetry), whereas the sharper, higher energy band is assigned as A'(1).⁶⁵ The fact that the carbonyl frequencies observed for each FeRe₃/AlRe₃ pair are virtually identical is indicative of minimal direct electronic communication between the Re^{I} and Fe^{III} metal centers in the ground states of the FeRe₃ assemblies.⁷

2.3.2 Single-Crystal X-ray Structures. X-ray quality crystals were obtained for [Fe(pyacac)₃(Re(bpy)(CO)₃)₃](OTf)₃ (2) and [Al(pyacac)₃(Re- $(bpy)(CO)_3)_3$ (OTf)₃ (5). The two complexes are isostructural and crystallize in the triclinic space group $P\overline{1}$. Crystallographic details are given in Table 2-1 with selected bond distances and angles for the two complexes listed in Table 2-2. The coordination environments about the central metal ions in both complexes (Figure 2-2) are distorted octahedra with six oxygen atoms from the acac groups comprising the coordination sphere. In the case of complex 2, the Fe–O bond distances of ca. 1.98 ± 0.02 Å are consistent with high-spin Fe^{III} and compare favorably with other structurally characterized examples of Fe^{III}-acac systems.⁴⁸ Significantly shorter metal-oxygen bonds (c.a. 0.1 Å) are observed for complex 5: such differences are to be expected given the smaller ionic radius of Al^{III}.⁴⁸ The structures of the Re(bpy)(CO)₃ moieties in both molecules are unremarkable, exhibiting the pseudo- C_{3v} coordination environment common to Re^I complexes in this class.⁶⁶⁻⁶⁹ Not surprisingly, the metric details of the Re^I fragment are insensitive to the identity of the central metal ion: bond distances, and angles associated with the primary coordination sphere as well as within the bipyridyl ligand itself
are identical within experimental error for the Fe^{III} and Al^{III} complexes. Slight differences are noted in the Re^I-core metal distances, with complex 5 being uniformly shorter by ~0.1 Å due mainly to the decrease in metaloxygen bond lengths relative to complex 2. Despite these minor differences, there is considerable structural homology between the two complexes, underscoring the appropriateness of using Al^{III} as a structurally and electronically benign replacement for Fe^{III} in this system. Efforts to obtain X-ray quality crystals for complexes 1, 3, 4, and 6 have thus far been unsuccessful, however, substituent changes on the periphery of the bipyridyl ligand will have little effect on the basic structural features in these systems.

	2	5		
formula	$C_{72}H_{54}N_9O_{24}F_9S_3FeRe_3$	C ₇₂ H ₅₄ N ₉ O ₂₄ F ₉ S ₃ AlRe ₃		
M_w	2310.87	2282.00		
cryst syst	triclinic	triclinic		
space group	P1-bar	P1-bar		
T/K	173(2)	173(2)		
a/Å	13.626(2)	13.534(2)		
b/Å	17.676(3)	17.590(3)		
c/Å	19.889(3)	19.809(3)		
α/°	89.494(3)	89.076(3)		
β/°	82.518(3)	81.890(3)		
γ/°	71.451(3)	71.053(3)		
$V/Å^3$	4500.1(11)	4413.4(12)		
Z	2	2		
$D_c/g \text{ cm}^{-1}$	1.717	1.717		
$2\theta_{\rm max}$	47	46		
reflns measured	33672	36985		
independent	12741	12190		
reflns				
observed reflns	6347	6354		
$[I > 2\sigma(I)]$				
μ (Mo K α)/cm ⁻¹	4.342	4.278		
R _{int}	0.0918	0.0899		
R1 ^a	0.0675	0.0666		
wR2 ^b	0.1373	0.1564		
GOF	1.007	1.044		

Table 2-1. Crystallographic Data for $[Fe(pyacac)_3(Re(bpy)(CO)_3)_3]$ -
(OTf)₃ (2) and $[Al(pyacac)_3(Re(bpy)(CO)_3)_3](OTf)_3$ (5).

 $\overline{{}^{a}R1 = \Sigma ||F_{o}| - |F_{c}||/\Sigma |F_{o}|}. {}^{b}wR2 = [\Sigma w (F_{o}^{2} - F_{c}^{2})^{2}/\Sigma w (F_{o}^{2})^{2}]^{1/2}, w = 1/[\sigma^{2}(F_{o}^{2}) + (aP)^{2} + bP], where P = [F_{o}^{2} + 2F_{c}^{2}]/3.$

	2		5
	Bond D	vistances (Å)	
Fe(1) - O(1)	1.992(6)	Al(1) - O(1)	1.877(10)
Fe(1) - O(2)	1.970(7)	Al(1) - O(2)	1.861(10)
Fe(1) - O(6)	1.997(6)	Al(1) - O(6)	1.871(11)
Fe(1) - O(7)	1.963(6)	Al(1) - O(7)	1.894(11)
Fe(1) - O(11)	1.981(7)	Al(1) - O(11)	1.883(12)
Fe(1) - O(12)	1.986(6)	Al(1) - O(12)	1.852(10)
Re(1) - N(1)	2.232(7)	Re(1) - N(1)	2.215(12)
Re(2) - N(4)	2.218(7)	Re(2) - N(4)	2.225(12)
Re(3) - N(7)	2.206(9)	$\operatorname{Re}(3) - \operatorname{N}(7)$	2.191(14)
Fe(1)•••Re(1)	9.88	Al(1)•••Re(1)	9.76
$Fe(1) \bullet \bullet Re(2)$	9.88	$Al(1) \bullet \bullet Re(2)$	9.74
Fe(1)•••Re(3)	9.78	Al(1)•••Re(3)	9.66
	Bond A	Angles (deg)	
O(1) - Fe(1) - O(2)) 85.4(3)	O(1) - Al(1) - O(2)	90.0(4)
C(23) - Re(1) - N(2)	1) 92.1(4)	C(23) - Re(1) - N(1)) 93.0(6)
C(21) - Re(1) - N(1)	1) 178.7(4)	C(21) - Re(1) - N(1)	ĺ) 177.9(7)
^a plane 1•••plane 2	280.1	^a plane 1•••plar	ne 2 79.0
^b plane 1•••plane 2	82.5	^b plane 1•••plan	ne 2 81.0
^c plane 1•••plane 2	68.8	^c plane 1•••plar	ne 2 69.2
^c plane 1•••plane 2	68.8	^c plane 1•••plan	ne 2 6

Table 2-2. Selected Bond Distances (Å) and Angles (deg) for [Fe(pyacac)₃(Re(bpy)(CO)₃)₃](OTf)₃ (**2**) and [Al(pyacac)₃(Re-(bpy)(CO)₃)₃](OTf)₃ (**5**).

^aPlane 1 is defined by atoms O(1), O(2), C(1), C(2), C(3), C(4), C(5); plane 2 is defined by atoms N(1), C(6), C(7), C(8), C(9), C(10). ^bPlane 1 is defined by atoms O(6), O(7), C(24), C(25), C(26), C(27), C(28); plane 2 is defined by atoms N(4), C(29), C(30), C(31), C(32), C(33). ^cPlane 1 is defined by atoms O(11), O(12), C(7), C(48), C(49), C(50), C(51); plane 2 is defined by atoms N(7), C(52), C(53), C(54), C(55), C(56).



Figure 2-2. Drawing of the cations of $[Fe(pyacac)_3(Re(bpy)(CO)_3)_3]$ -(OTf)₃ (**2**, top) and $[Al(pyacac)_3(Re(bpy)(CO)_3)_3](OTf)_3$ (**5**, bottom) obtained from single-crystal X-ray structure determinations. Atoms are represented as 50% probability thermal ellipsoids.





2.3.3 Electrochemistry. The electrochemical properties of complexes **1-6** were examined using cyclic voltammetry; the data are given in Table 2-3. The availability of the Al^{III} model complexes greatly simplifies assigning the features observed for all six complexes due to the redox-inert nature of this ion. Accordingly, the single reduction waves seen for complexes **4-6** can be immediately ascribed to the bipyridyl ligand of the Re moiety in each case.

The positive shift in potential across the series is consistent with the more electron withdrawing nature of the substituents as one progresses from the methyls of tmb (4) to the diethylester groups in complex 6. Similarly, the oxidation waves seen for all three complexes are easily assigned to the Re^I/Re^{II} couple. The influence of the bipyridyl substitutents are apparent in these data as well, with the more electron deficient ligand giving rise to the most positive oxidation potential for the Re center. The results are all consistent with what has been observed for complexes of the general form *fac*-[Re(4,4'-X₂-bpy)(CO)₃(4-Etpy)](PF₆) previously reported in the literature.⁴⁶

Given these assignments, the reductions at ca. -0.9 V observed for complexes **1-3** are clearly associated with the Fe^{III} center.⁷⁰ It can be seen that modification of the bipyridyl ligand has no discernible influence on the redox properties of the central Fe ion. In a similar vein, the ligand reduction and Re^I oxidation potentials of all three Fe-containing compounds are essentially identical to what was observed for the Al^{III} analogs. These data are indicative of (relatively) weak electronic coupling between the central metal ion and the peripheral chromophores.

	electroc	ν(CO)	$(cm^{-1})^a$		
complexes	E_{ox} (Re ^{I/II})	E_{red} (Fe ^{III/II})	E_{red} (bpy' ^{0/-})	A'(1)	A", A'(2)
FeRe ₃					
tmb(1)	$+1.47^{b.c}$	-0.91 ^{d,e}	-1.84 ^b	1918	2031
			_		
bpy (2)	$+1.41^{b}$	-0.90 ^d	-1.59 ^d	1922	2033
	L	A	a		
deeb (3)	$+1.60^{\circ}$	-0.93ª	-1.20 ^ª	1923	2036
AlRe					
tmb (4)	+1.37 ^b		-1.82 ^b	1918	2031
bpy (5)	$+1.42^{b}$		-1.57 ^{b,f}	1920	2033
deeb (6)	+1.54 ^b		-1.19 ^b	1930	2036

Table 2-3. Electrochemical and Infrared Data for Complexes 1-6.

^aMeasured as pressed KBr pellets. ^bMeasured in CH₃CN solution. ^cPotential in CH₂Cl₂ solution is +1.41 V. ^dMeasured in CH₂Cl₂ solution. ^ePotential in CH₃CN solution is -0.86 V. ^fPotential in CH₂Cl₂ solution is -1.57 V.

2.3.4 Electronic Absorption Spectroscopy. The electronic absorption spectra of the FeRe₃ (1-3) (black traces) and AlRe₃ (4-6) (blue traces) analogs have been acquired in room-temperature CH₂Cl₂ solutions and are shown in Figure 2-3. Transitions associated with these complexes were assigned based on previously reported analyses of Re¹ polypyridyl and Fe(phacac)₃ absorption spectra. Re¹ polypyridyl complexes exhibit a well known ¹MLCT ($t_{2g} \rightarrow \pi^*$ (bpy')) transition occurring from approximately 330 to 430 nm depending on the substituents of the bpy' ligand,^{71,72} with the

absorption profiles of the AlRe₃ compounds solely exhibiting these ¹MLCT based characteristics. λ_{max} for the ¹MLCT excited-state reflects the electron donating/withdrawing ability of the bpy' substituents, with λ_{max} for complexes **4**, **5**, and **6** occurring at 344 ($\varepsilon = 18,500$), 364 ($\varepsilon = 11,500$), and 394 ($\varepsilon = 14,300$) nm, respectively. As the substituents become progressively more electron donating (e.g., H for bpy and CH₃ for tmb) this feature systematically shifts to the blue and begins to overlap with the ligand-based absorptions in the ultraviolet (Figure 2-3). The AlRe₃ analogs allow for analysis of the ground-state absorption behavior of the Re¹ donor moieties without overlapping with the Fe^{III}-based charge-transfer transitions contained in the FeRe₃ analogs.

The presence of Fe^{III} in complexes 1-3 gives rise to a new, broad absorption feature on the low-energy side of the Re¹-based charge transfer band. Figure 2-4 shows the absorption spectrum of Fe(phacac)₃ which exhibits two strong transitions centered at 370 and 460 nm assigned as ${}^{6}A_{1}$ $\rightarrow {}^{6}MLCT$ ($t_{2g} \rightarrow \pi^{*}(acac)$) and ${}^{6}A_{1} \rightarrow {}^{6}LMCT$ (π (acac) $\rightarrow t_{2g}$) transitions, respectively.^{73,74} In complexes 1-3 the higher energy MLCT absorption is obscured by the more intense ${}^{1}A_{1} \rightarrow {}^{1}MLCT$ band of the Re^I chromophore, but the low energy tail of the ${}^{6}A_{1} \rightarrow {}^{6}LMCT$ transition can be seen extending out to approximately 600 nm. The linear combination of the corresponding AlRe₃ analog with Fe(phacac)₃ is also shown in Figure 2-3 (red trace), which sufficiently models the absorptive characteristics of the FeRe₃ analogs. The additive property of these constituent species reiterates the minimal groundstate electronic interaction between the Re^I and Fe^{III} metal centers observed from the infrared data.



Figure 2-3. Electronic absorption spectra of $[M(pyacac)_3(Re(bpy')-(CO)_3)_3](OTf)_3$ assemblies, where $M = Fe^{III}$ (black traces) or AI^{III} (blue traces). All spectra were acquired in room-temperature CH_2Cl_2 solution. A. $[Fe(pyacac)_3(Re(tmb)(CO)_3)_3](OTf)_3$ (1) and $[Al(pyacac)_3-(Re(tmb)(CO)_3)_3](OTf)_3$ (4). B. $[Fe(pyacac)_3(Re(bpy)(CO)_3)_3](OTf)_3$ (2) and $[Al(pyacac)_3(Re(bpy)(CO)_3)_3](OTf)_3$ (5). C. $[Fe(pyacac)_3(Re(deeb)(CO)_3)_3](OTf)_3$ (6). The dashed red lines in all three graphs correspond to linear combinations of the molar absorptivity (ϵ , (M^{-1} , cm⁻¹)) profiles of the AlRe₃ complex with that of Fe(phacac)_3.



Figure 2-4. Electronic absorption spectrum of $Fe(phacac)_3$ acquired in room-temperature CH_2Cl_2 solution.

2.3.5 Steady-State and Time-Resolved Emission. Emission spectra for the FeRe₃ and AlRe₃ complexes were obtained in room-temperature deoxygenated CH₂Cl₂. The AlRe₃ complexes represent an ideal structural model for the dynamics associated with the Re¹ based ³MLCT emission, due to the inability of engaging in quenching dynamics incurred by the Fe^{III} core in the FeRe₃ systems. The emission profiles are given in Figure 2-5, and show the emission intensity for the FeRe₃ complexes are significantly attenuated compared to the AlRe₃ model systems. The spectral profiles correspond to previously reported photophysical studies of Re^I polypyridyl systems, with the emission originating from the ³MLCT \rightarrow ¹A₁ phosphorescence.⁷⁵ The emission maximum for the tmb (526 nm), bpy (566 nm), and deeb (624 nm) derivatives reflect the electron donating and

withdrawing behavior of the polypyridyl ligands. The radiative quantum yields (Φ_r) of **4** (Φ_r = 0.51), **5** (Φ_r = 0.16), and **6** (Φ_r = 0.07) were determined relative to [(bpy)Re(CO)₃(4-Etpy)](PF₆) (Φ_r = 0.18 in CH₂Cl₂) (Table 2-4), and are comparable to the reported values for the corresponding mononuclear Re^I polypyridyl derivatives.⁴⁶

The Φ_r values for complexes 1-3 are analytically unreliable due to a small emissive impurity generated by dissociation of the complexes. The source of the dissociation was discovered to be residual amounts of water contained in the CH₂Cl₂, which generates the highly emissive *fac*-[Re(bpy')(CO)₃(pyacac)] complex. The drying and distilling procedures that were employed were exhausted until no water was detectable by ¹H NMR, but despite our best efforts small traces remained in the solvent. It should also be noted that the extent of dissociation was small over the course of the radiative quantum yield determinations, but a steady increase in the emission signal for the three systems was observed when monitored over several hours.



Figure 2-5. Corrected steady-state emission spectra for $[M(pyacac)_3-(Re(bpy')(CO)_3)_3](OTf)_3$ assemblies, where $M = AI^{III}$ (blue traces) and Fe^{III} (red traces). **A.** [Al(pyacac)_3Re(tmb)(CO)_3])_3](OTf)_3 (**4**) and [Fe(pyacac)_3(Re(tmb)(CO)_3)_3](OTf)_3 (**1**). **B.** [Al(pyacac)_3Re(bpy)-(CO)_3])_3](OTf)_3 (**5**) and [Fe(pyacac)_3(Re(bpy)(CO)_3)_3](OTf)_3 (**5**) and [Fe(pyacac)_3(Re(beb)(CO)_3)_3](OTf)_3 (**6**) and [Fe(pyacac)_3(Re(deeb)-(CO)_3)_3](OTf)_3 (**3**). The spectra were acquired in CH₂Cl₂ solutions at room temperature following excitation at 355 nm (complexes **1**, **2**, **4**, and **5**) and 400 nm (complexes **3** and **6**).

Additional details concerning the excited states of the AlRe3 and FeRe₃ complexes were obtained through nanosecond emission lifetime and time-correlated single photon counting (TCSPC) measurements. The nanosecond emission decay lifetime (τ_{obs}) in room-temperature CH₂Cl₂ solution for complexes 4, 5, and 6 are shown on the left side of Figure 2-6, and could be fit to single-exponential models with $\tau_{obs} = 2260 \pm 100$, 560 \pm 30, and 235 ± 20 ns (Table 2-4), respectively. The corresponding radiative and non-radiative decay rate constants are, $k_r = 2.3 \pm 0.1 \ x \ 10^5 \ s^{-1}$ and $k_{nr} =$ $2.2 \pm 0.1 \text{ x } 10^5 \text{ s}^{-1}$ for 4, $k_r = 2.9 \pm 0.13 \text{ x } 10^5 \text{ s}^{-1}$ and $k_{nr} = 1.5 \pm 0.07 \text{ x } 10^6 \text{ s}^{-1}$ for 5, and $k_r = 3.0 \pm 0.13 \text{ x } 10^5 \text{ s}^{-1}$ and $k_{nr} = 4.0 \pm 0.17 \text{ x } 10^6 \text{ s}^{-1}$ for 6. As with the quantum yields, the observed excited-state lifetimes and rate constants are all consistent with the assignment of ${}^{3}MLCT \rightarrow {}^{1}A_{1}$ emission reported previously for the mononuclear Re^I polypyridyl derivatives.^{46,76} The kinetics reveal that the reduction in quantum yield is due primarily to an increase in the non-radiative decay rate for ³MLCT relaxation (k_{nr}) as opposed to significant variations in radiative coupling to the ground state (Table 2-4).

The lack of emission signal observed for the FeRe₃ systems during nanosecond lifetime experiments prompted the employment of timecorrelated single photon counting (TCSPC) methods. Plots of the TCSPC data obtained in room-temperature CH₂Cl₂ solution for the FeRe₃ complexes are shown on the right side of Figure 2-6. All three decay traces could be fit with single-exponential models with $\tau_{obs} = 450 \pm 20$ ps ($k_{obs} = 2.3 \pm 0.13$ x 10^9 s⁻¹), 755 \pm 40 ps ($k_{obs} = 1.3 \pm 0.06$ x 10^9 s⁻¹), and 2.50 ± 0.1 ns ($k_{obs} = 4.0 \pm 0.09$ x 10^8 s⁻¹) for complexes **1**, **2**, and **3**, respectively (Table 2-4). The signal-to-noise ratio is relatively poor owing to a combination of virtually complete quenching of the Re^I-based ³MLCT states coupled with radiative rate constants that are on the order of 10^5 s⁻¹. The time constants of the Al^{III} model complexes are several orders of magnitude shorter than what was observed for the Fe^{III} complexes, indicating that excited-state relaxation in complexes **1-3** is dominated by reaction with the Fe^{III} core. The rate constant for the reaction can be given by equation 2-5,

$$k_{q}(FeRe_{3}) = k_{obs}(FeRe_{3}) - k_{obs}(AlRe_{3}) \quad (2-5)$$

where the values of k_r and k_{nr} for the ³MLCT excited state of a given FeRe₃ assembly are taken to be equivalent to the corresponding AlRe₃ model complex. Given the extensive quenching of the ³MLCT state as indicated by the time constant for decay in complexes 1-3, the observed lifetimes effectively correspond to the quenching time constants in all three cases.



Figure 2-6. *Left.* Nanosecond time-resolved emission data for the AIRe₃ model complexes: **4** (τ_{obs} = 2260 ± 100 ns), **5** (τ_{obs} = 560 ± 30 ns), and **6** (τ_{obs} = 235 ± 20 ns). *Right.* TCSPC data for the corresponding FeRe₃ complexes: **1** (τ_{obs} = 450 ± 30 ps), **2** (τ_{obs} = 755 ± 40 ps), and **3** (τ_{obs} = 2.5 ± 0.1 ns). All data were collected in deoxygenated CH₂Cl₂ at room temperature. The red solid lines correspond to fits to single-exponential decay models.

complexes	λ_{max}	$\frac{E_{00}}{(cm^{-1})^a}$	$\Phi_{\rm r}$	$k_{obs}(s^{-1})$	$\frac{k_r}{(\times 10^5 s^{-1})^d}$	$\frac{k_{nr}}{(\times 10^6 \text{ s}^{-1})^e}$
$\frac{FeRe_3}{tmb (1)}$	b	b	с	$2.3 \pm 0.1 \times 10^9$	f	f
bpy (2)	b	b	c	$1.3 \pm 0.1 \ge 10^9$	f	f
deeb (3)	b	b	c	$4.0 \pm 0.1 \ge 10^8$	f	f
<i>AlRe</i> 3 tmb (4)	526	19,900	0.51	$4.4 \pm 0.2 \ge 10^5$	2.3 ± 0.1	0.2 ± 0.01
bpy (5)	566	18,700	0.16	$1.8 \pm 0.1 \ge 10^6$	2.9 ± 0.1	1.5 ± 0.1
deeb (6)	624	16,800	0.07	$4.3 \pm 0.2 \ge 10^6$	3.0 ± 0.1	4.0 ± 0.2

Table 2-4. Photophysical Data of Complexes 1-6.

^aZero-point energy difference between ³MLCT excited state and ground state based on spectral fitting analysis. ^bThis value is expected to be identical to the corresponding Al^{III} complex. ^cValues are not quoted due to the presence of an emissive impurity. See text for further details. ^dk_r = $k_{obs} * \Phi_r$. ^ek_{nr} = $k_{obs} - k_r$. ^fExcited-state decay kinetics dominated by k_{obs} .

2.4 Mechanistic Considerations.

2.4.1 Electron versus Energy Transfer Quenching. Both electron and energy transfer processes can be envisioned to occur out of the Re^I-based ³MLCT excited state. Based on the presence of Fe^{III} in the ground states of these complexes, electron transfer would proceed as an oxidative quenching reaction to produce a Re^{II}/Fe^{II} charge separated species. Re^I \rightarrow Re^{II}

oxidation and $Fe^{III} \rightarrow Fe^{II}$ reduction potentials for complexes 1-3 (Table 2-3), along with the zero-point energy gaps of the ³MLCT states (E_{00}) determined from fits of the emission spectra of the corresponding AlRe₃ analogs (Table 2-4), were used to determine the thermodynamic driving force for photoinduced electron transfer.^{77,78} These calculations revealed that electron transfer is thermodynamically unfavorable for complexes 2 and 3 (~0 and +0.45 eV, respectively), and only slightly exothermic in the case of complex 1 (-0.1 eV). The magnitude of ΔG^{ET} for complex 3 is prohibitively large, particularly given the observed rate constant of nearly 10^9 s⁻¹. In the of complex 2, electron transfer at room temperature is case thermodynamically feasible; however, the fact that the quenching rate is only a factor of ~ 3 faster than what is observed for complex 3 suggests that both of these complexes are reacting via similar mechanisms, i.e., energy transfer.

The fact that electron transfer is predicted to be exothermic in the case of complex 1 prompted further study. We therefore carried out time-resolved absorption measurements on $[Fe(pyacac)_3(Re(tmb)(CO)_3)_3](OTf)_3$ (1) in an effort to identify whether a charge-separated species was being formed upon ${}^{1}A_1 \rightarrow {}^{1}MLCT$ excitation. The transient absorption spectroscopy of Re¹ polypyridyl complexes has been described by a number of workers.⁷⁹⁻⁸⁶

Their excited-state spectra typically consist of a moderately intense feature in the ultraviolet corresponding to absorptions of the polypyridyl radical anion, as well as a transient bleach due to loss of the ground-state ${}^{1}A_{1} \rightarrow$ ¹MLCT absorption. Additional absorptions can also be observed toward the red edge of the visible spectrum that are usually ascribed to bpy⁻ transitions of the excited state species. Consistent with these expectations, the differential absorption spectrum of $[Al(pyacac)_3(Re(tmb)(CO)_3)_3](OTf)_3$ (4) (Figure 2-7, top) exhibits transient absorptions at 370 nm and 760 nm that we assign to tmb⁻-based transitions. The hallmark for an excited-state electron transfer process in complex 1 would be a wavelength-dependence in the observed kinetics, namely the loss of the tmb⁻ features coupled with a persistence of the ground-state ${}^{1}A_{1} \rightarrow {}^{1}MLCT$ bleach. Instead, what we observe is complete ground-state recovery at all probe wavelengths with a time constant that is within experimental error of what was measured via time-resolved emission spectroscopy (Figure 2-7, bottom). We have recently discussed the notion that this observation does not necessarily rule out a sequential electron transfer process.⁸⁷ In the present case, however, the driving force for charge-recombination would place the back-reaction deep enough into the inverted region such that the relative rates necessary to satisfy this condition are not likely to be realized.



Figure 2-7. *Top.* Nanosecond time-resolved differential absorption spectrum of $[Al(pyacac)_3(Re(tmb)(CO)_3)_3](OTf)_3$ (4) in roomtemperature CH₂Cl₂ solution. The spectrum was constructed from the amplitudes of fits to single-exponential decay kinetics at each probe wavelength following excitation at 355 nm. *Bottom.* Time-resolved absorption data for $[Fe(pyacac)_3(Re(tmb)(CO)_3)_3](OTf)_3$ (1) in roomtemperature CH₂Cl₂ solution at $\lambda_{probe} = 700$ nm following ~100 fs excitation at $\lambda_{pump} = 400$ nm. The red solid line corresponds to a fit of the data to a single-exponential decay model with $\tau_{obs} = 400 \pm 30$ ps.

2.4.2 Dexter vs Förster Energy Transfer. In light of these observations,

the most likely explanation for ³MLCT quenching in all three of the FeRe₃

assemblies is excited-state energy transfer. As discussed in the Introduction,

the Dexter mechanism requires orbital overlap between the donor and acceptor involved in the energy transfer. The X-ray structure data for complex **2** shows a Re¹•••Fe^{III} separation of nearly 10 Å, a value that lies at the limit of what is typically considered for an exchange-based process.⁸⁷⁻⁹⁰ The lack of significant electronic coupling between the Re¹ and Fe^{III} subunits is also supported by the similarities in v(CO) frequencies of the FeRe₃ and AlRe₃ analogs, as well as the fact that the absorption spectra of the FeRe₃ assemblies can be represented in terms of a simple linear combination of its constituents (Figure 2-3). The lack of electronic communication denoted by the structural and spectroscopic data greatly attenuates the plausibility of a Dexter energy transfer mechanism for the excited-state quenching reactivity.

The applicability of the Forster mechanism is supported by the moderate degree of spectral overlap that exists between the Re^I-based ³MLCT emission and the Fe^{III}-based ⁶A₁ \rightarrow ⁶LMCT absorption for the FeRe₃ assemblies:⁹¹ this is depicted graphically in Figure 2-8. The overlap between the ³MLCT \rightarrow ¹A₁ emission of the Al^{III}-containing tmb (4) (blue trace), bpy (5) (green trace), and deeb (6) (red trace) analogs with the ⁶A₁ \rightarrow ⁶LMCT absorption of Fe(phacac)₃ is shown. In particular, the plot shows the amount of spectral overlap is greatest for the highest energy ³MLCT excited-state corresponding to the most electron donating group (tmb) and smallest for the

most electron withdrawing group (deeb). The area ascertained from the product of the normalized emission profile of an AlRe₃ analog with the extinction coefficient spectrum of the corresponding FeRe₃ complex was used to calculate the reported spectral overlap values. The magnitude of spectral overlap (J) also corresponds with the observed rate constants for energy transfer with J values of 1.0×10^{-14} (k_{ENT} = 2.3×10^9 s⁻¹), 7.6 $\times 10^{-15}$ (k_{ENT} = 1.3×10^9 s⁻¹), and 1.2×10^{-15} (k_{ENT} = 4.0×10^8 s⁻¹) M⁻¹cm³ for the tmb (1), bpy (2), and deeb (3) analogs, respectively. It is quite clear that the overlap requirement in these systems is satisfied, which strongly implicates Förster transfer as the dominant quenching mechanism in the FeRe₃ complexes.



Figure 2-8. Overlay of the emission spectra of $[Al(pyacac)_3(Re(tmb)-(CO)_3)_3](OTf)_3$ (**4**, blue), $[Al(pyacac)_3(Re(bpy)(CO)_3)_3](OTf)_3$ (**5**, green), and $[Al(pyacac)_3(Re(deeb)(CO)_3)_3](OTf)_3$ (**6**, red) with the electronic absorption spectrum of Fe(phacac)_3. Data were acquired in room-temperature CH_2Cl_2 solution.

2.4.3 Quantifying Förster Energy Transfer. The spectral properties of the FeRe₃ family of complexes combined with the structural rigidity of the system provides a rare opportunity to quantitatively apply Förster theory and compare calculated rates with those obtained experimentally. In addition to the overlap factor alluded to above, the rate of energy transfer is also sensitive to the relative orientation of the donor and acceptor transition dipoles (eq 2-3). An accurate determination of this quantity can be quite challenging. In one noteworthy example, Fleming and coworkers utilized TD-DFT (time-dependent density functional theory) to enable them to visualize the transition dipoles of peridinin, which in turn provided them with tremendous insights into the role geometry plays in facilitating energy transfer from the singlet excited state(s) of that system.⁹² Unfortunately, the complicated electronic structures of transition metal containing systems do not easily lend themselves to a similarly detailed analysis, so more approximate methods must usually be employed.

An excellent example of this is that of Harriman and coworkers, in which Förster energy transfer dynamics in Ru^{II} and Os^{II} polypyridine donoracceptor complexes bridged by a rigid spiro-based spacer moiety were investigated.⁹³ In their approach, energy-minimized structures were calculated for each molecule with the donor and acceptor transition dipole

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moments modeled along the six respective Ru-N and Os-N bond vectors. Using this geometric picture, calculations of donor-acceptor separations (R_{DA}) and orientation factors (κ^2) afforded a theoretical Förster rate constant that agreed very closely with the experimentally observed values. We have taken a similar approach for analyzing the FeRe₃ family of complexes, albeit with slight differences in the physical description of the system. For example, we have chosen to approximate the donor and acceptor transition dipoles as bisecting the local C₂ axes of the bpy' and acac ligands as opposed to them lying coincident with the metal-ligand bond vectors. In addition, the point of origin for the transition moment dipoles has been modeled to originate solely from the ligands involved in the donor and acceptor transitions. These choices are based largely on Density Functional Theory (DFT) calculations on $[Ru(bpy)_3]^{2+}$ by Daul⁹⁴ and Gorelsky⁹⁵ that suggest the lowest energy excited-state (³MLCT) is localized on the bpy ligands. In addition, Meyer and coworkers have shown that the majority of the amplitude of the thermalized ³MLCT wavefunction for complexes of the form fac-[Re(4,4'-X₂bpy)(CO)₃(4-Etpy)](PF₆) (X = CH₃, H, and CO₂Et) is concentrated within the π^* levels of the bpy' ligand and less so along the Re—N bond vector.⁶⁵

In light of these reported computational results, Figure 2-9 is drawn to depict the Re^I-based ³MLCT emission dipoles as blue arrows and the Fe^{III}based ⁶LMCT absorption dipoles as red arrows. The emission dipoles of the three Re^I donors (Re1, Re2, and Re3) relative to the Fe^{III} center are presented simultaneously for clarity, but only a single Re^I moiety is considered involved during an excited-state quenching event due to the low excitation photon flux used for the steady-state and time-resolved emission measurements (Figure 2-10). Figure 2-10 shows a single Re^I-based emission dipole moment spatially interacting with the three ⁶LMCT absorption dipole moments. The donor-acceptor distances $(R_1, R_2, and R_3)$ and the three angles used in the κ^2 equation (Θ_T , Θ_D , and Θ_A) are also shown, and were evaluated for each donor-acceptor dipolar interaction using the single-crystal X-ray structure data of complex 2. The Re1, Re2, and Re3 donor dipoles were examined individually relative to the three possible ⁶LMCT absorption dipoles, and an R_{DA} and κ^2 value was calculated for each case. The chargetransfer nature of the donor and acceptor transitions makes it difficult to place an exact point of origin for each, so distance and orientation factors were calculated for a range of possible loci for both the donor and acceptor (Figure 2-11). Figure 2-11 specifically illustrates the point-dipole model utilized for calculating the donor-acceptor distances and angles, with the

through-space interaction of three different donor origins at a single Re¹ emission dipole with the three ⁶LMCT absorption dipole origins located on each FeO₂ triangle of the acceptor. The points A, B, and C, were chosen to systematically vary the location of the ³MLCT wavefunction in order to investigate the origin of the donor dipole. The MLCT nature of the donor emission makes it difficult to place an exact point of origin on the bpy ligand, so donor-acceptor distances and orientation factors for the three points (A, B, and C) along each of the donor moieties (Re1, Re2, and Re3) interacting with the ⁶LMCT transition dipoles were investigated. In addition, Figure 2-11 also shows the acceptor origin was systematically varied by placing it between the oxygen atoms of each acac ligand (points D1, D2, and D3), at the center of the three FeO₂ triangles (points E1, E2, and E3), and at the Fe^{III} metal center (point F), again due to the charge-transfer nature associated in this case with the acceptor absorption dipoles. The ⁶LMCT state can be envisioned as occurring from either the non-bonding electrons of the oxygen atoms or from the delocalized π electrons of the acac ligands, and we feel these three points of origin adequately represents the charge-transfer character of the acceptor with geometric considerations of both the Fe^{III} metal center and acac ligand. This approach yielded a total of 81 donor-acceptor interactions (27 for each Re^I fluorophore), each being defined by specific R_{DA} and κ^2 values that were evaluated based on the single-crystal X-ray structure data of complex **2**. A complete list of the values of R_{DA} and κ^2 used in our analysis can be found in Tables 2-5a, 2-5b, and 2-5c.



Figure 2-9. Through-space interactions of the Re^I-based ³MLCT emission dipoles (blue arrows) with the Fe^{III}-based ⁶LMCT absorption dipoles (red arrows).



Figure 2-10. Single Re¹-based emission dipole moment spatially interacting with the three ⁶LMCT absorption dipole moments. Also shown are the donor-acceptor distances (R₁, R₂, and R₃) and the three angles used in the κ^2 equation (Θ_T , Θ_D , and Θ_A) evaluated from the single-crystal X-ray structure data of complex **2**.



Figure 2-11. Point-dipole approximation used for calculating the through-space distances (R_{DA}) and orientation factors (κ^2) needed for quantifying Förster energy transfer theory in the FeRe₃ assemblies.

Table 2-5a. R_{DA} (Å), Θ_T (°), Θ_D (°), Θ_A (°), and κ^2 values determined from the internal dimensions of complex 2 using donor/acceptor interactions A:D, B:D, and C:D.

	R(11)	R(12)	R(13)	R(22)	R(21)	R(23)	R(33)	R(31)	R(32)
A									
R _{DA}	8.46	10.73	10.41	8.40	10.65	10.41	8.38	10.89	9.70
Θ_{T}	77.81	35.87	56.34	80.28	35.52	54.45	60.72	63.14	39.82
$\Theta_{\rm D}$	84.68	91.22	86.53	86.30	92.54	87.17	87.26	86.28	95.31
Θ_{A}	154.1	46.84	61.42	158.7	49.62	59.73	147.2	28.49	82.65
κ^2	0.213	0.729	0.219	0.122	0.810	0.257	0.372	0.079	0.646
B									
$\mathbf{R}_{\mathbf{D}\mathbf{A}}$	8.64	10.75	10.53	8.55	10.63	10.51	8.31	10.82	9.44
Θ_{T}	77.81	35.87	56.34	80.28	35.52	54.45	60.72	63.14	39.82
$\Theta_{\rm D}$	77.07	85.24	80.30	78.49	86.36	81.05	82.96	83.97	92.33
Θ_{A}	147.5	51.00	60.52	150.9	53.34	58.47	142	23.37	87.5
κ^2	0.604	0.427	0.093	0.479	0.490	0.114	0.606	0.026	0.598
<u>C</u>									
R _{DA}	8.99	10.93	10.81	8.82	10.74	10.73	8.48	10.95	9.42
Θ_{T}	77.81	35.87	56.34	80.28	35.52	54.45	60.72	63.14	39.82
$\Theta_{\rm D}$	69.69	78.93	74.03	71.49	80.59	75.28	75.78	78.56	85.98
Θ_{A}	141.4	54.9	60.25	144.1	57.16	57.58	136.4	19.35	92.27
κ^2	1.050	0.230	0.021	0.884	0.300	0.03	1.050	0.012	0.603

Table 2-5b. R_{DA} (Å), Θ_T (°), Θ_D (°), Θ_A (°), and κ^2 values determined from the internal dimensions of complex 2 using donor/acceptor interactions A:E, B:E, and C:E.

	R(11)	R(12)	R(13)	R(22)	R(21)	R(23)	R(33)	R(31)	R(32)
<u>A</u>									
$\mathbf{R}_{\mathbf{D}\mathbf{A}}$	9.13	10.25	10.08	9.08	10.19	10.07	9.00	10.25	9.64
Θ_{T}	77.81	35.87	56.34	80.28	35.52	54.45	60.72	63.14	39.82
$\Theta_{\rm D}$	86.25	89.49	87.05	87.74	90.84	88.04	88.53	87.85	92.49
Θ_{A}	156.1	49.78	65.02	160.3	52.76	63.29	149.7	30.44	86.91
κ^2	0.153	0.629	0.239	0.079	0.707	0.287	0.309	0.126	0.601
<u>B</u>									
R _{DA}	9.26	10.31	10.20	9.18	10.21	10.15	8.89	10.15	9.44
Θ_{T}	77.81	35.87	56.34	80.28	35.52	54.45	60.72	63.14	39.82
$\Theta_{\rm D}$	79.17	83.21	80.63	80.52	84.4	81.63	84.84	85.15	89.41
Θ_{A}	149.9	54.12	64.06	153.1	56.63	61.94	144.9	25.01	91.87
κ^2	0.488	0.363	0.116	0.371	0.426	0.141	0.503	0.049	0.591
			///////						
<u>C</u>									
R _{DA}	9.57	10.53	10.47	9.42	10.37	10.36	9.02	10.26	9.47
Θ_{T}	77.81	35.87	56.34	80.28	35.52	54.45	60.72	63.14	39.82
$\Theta_{\rm D}$	72.16	76.71	74.16	73.95	78.42	75.65	78.13	79.33	83.06
Θ_{A}	144.1	58.12	63.69	146.7	60.56	60.95	139.6	20.71	96.63
_ κ ²	0.913	0.199	0.037	0.743	0.268	0.049	0.92	0.005	0.656

Table 2-5c. R_{DA} (Å), Θ_T (°), Θ_D (°), Θ_A (°), and κ^2 values determined from the internal dimensions of complex 2 using donor/acceptor interactions A:F, B:F, and C:F.

	R(11)	R(12)	R(13)	R(22)	R(21)	R(23)	R(33)	R(31)	R(32)
A									
R _{DA}	9.80	9.80	9.80	9.76	9.76	9.76	9.63	9.63	9.63
Θ_{T}	77.81	35.87	56.34	80.28	35.52	54.45	60.72	63.14	39.82
$\Theta_{\rm D}$	87.61	87.61	87.61	88.98	88.98	88.98	89.63	89.63	89.63
Θ_{A}	22.13	127	111.2	18.25	123.8	112.9	28.16	147.4	88.8
κ²	0.009	0.784	0.359	0.014	0.712	0.363	0.223	0.219	0.589
	_								
B									
R _{DA}	9.90	9.90	9.90	9.83	9.83	9.83	9.49	9.49	9.49
Θ_{T}	77.81	35.87	56.34	80.28	35.52	54.45	60.72	63.14	39.82
$\Theta_{\rm D}$	81.01	81.01	81.01	82.30	82.30	82.30	86.49	86.49	86.49
Θ_{A}	28.00	122.5	112.2	24.98	119.8	114.3	32.62	153.1	83.77
κ^2	0.041	1.130	0.535	0.038	1.030	0.558	0.112	0.379	0.560
<u>C</u>		<u>.</u>			<u>12</u>				
R _{DA}	10.17	10.17	10.17	10.03	10.03	10.03	9.58	9.58	9.58
Θ_{T}	77.81	35.87	56.34	80.28	35.52	54.45	60.72	63.14	39.82
$\Theta_{\rm D}$	74.35	74.35	74.35	76.11	76.11	76.11	80.21	80.21	80.21
Θ_{A}	33.5	118.4	112.7	31.09	115.8	115.4	37.6	157.8	79.08
κ²	0.215	1.430	0.750	0.200	1.270	0.793	0.007	0.853	0.451

The analysis we have carried out is predicated on two critical assumptions: (1) that the variations in substitutents on the peripheral bipyridine group do not significantly alter the metrics relevant for dipolar energy transfer (thereby allowing us to use the X-ray structure of complex 2 as the basis for analyzing all three FeRe₃ assemblies), and (2) that the geometry of each compound in solution is essentially unchanged from that

determined by solid-state X-ray crystallography. The major influence of the bipyridyl substituents will be to shift the electron density associated with the excited state according to the electron donating/withdrawing ability of the group. This assertion is supported by structure minimizations which revealed virtually identical bond distances and angles for all three complexes.⁹⁶ Given the distribution of anchoring points on the bipyridyl ring that we are evaluating, we believe this first issue is being adequately addressed. In terms of solution versus solid-state geometry, the only significant degree of freedom in these systems is rotation along the Re-N (pyridine) bond. We expect there will be some barrier to this motion, but it is unlikely to afford the same average angle in solution as found in the solid state. Even though this represents a possible difference in the structure of the compound between what we measure in the solid-state versus what exists in solution, an analysis of this motion revealed that the relative distances and orientations of the donor and acceptor transition dipoles (and therefore R_{DA} and κ^2) do not change over the entire 360° that the system can sample. Therefore, while in principal using a solid-state structure to model geometric properties in solution can be problematic, the particular structural aspects of the FeRe₃ family of complexes makes such a comparison very straightforward.

2.4.4 Rate Constant Calculations: Modeling Solution Phase Energy Transfer Dynamics. A given Re^I donor can couple to any of the three Fepyacac acceptor dipoles: the energy transfer process in these compounds can thus be described in terms of three parallel reactions. The overall rate constant for such a kinetic model is given by a linear combination of the rate constants for each reaction pathway as shown in equation 2-6,

$$k_{Re(11)} + k_{Re(12)} + k_{Re(13)} = k_{Re1}$$
 (2-6a)

$$k_{Re(21)} + k_{Re(22)} + k_{Re(23)} = k_{Re2}$$
 (2-6b)

$$k_{\text{Re}(31)} + k_{\text{Re}(32)} + k_{\text{Re}(33)} = k_{\text{Re}3}$$
 (2-6c)

where $k_{Re(ij)}$ corresponds to the rate calculated for the ith Re donor coupling to the jth Fe-pyacac acceptor; each of the $k_{Re(ij)}$ values derives from the average of the nine possible donor-acceptor vectors defined by the pointdipole origins depicted in Figure 2-11. For example, k_{Re11} represents the Re1:LMCT1 dipole-dipole interaction that is the average of the nine rate constants calculated for each of the point dipole origins along the Re1 donor and the covalently attached FeO₂ triangle (A:D1, A:E1, A:F, B:D1, B:E1, B:F, C:D1, C:E1, and C:F) (Figure 2-11). Analogous procedures were applied to the Re1:LMCT2 and Re1:LMCT3 interactions, with all three total interactions summed to yield k_{Re1} . This same analysis was applied to the Re2 and Re3 donor moieties to yield k_{Re2} and k_{Re3} , which were then averaged to give an overall theoretical rate constant ($\langle k_T \rangle$) from our model. Table 2-6 lists all nine $k_{Re(ij)}$ (Re#:LMCT#) values for complexes 1-3 along with their $\langle k_T \rangle$ values. It can be seen that there are variations in the calculated rates of energy transfer within each group of interactions owing to slight geometric differences at each Re-bpy site. Nevertheless, despite the lack of a quantitative picture of wavefunctions for the donor and acceptor charge-transfer states, the level of agreement obtained between experiment and theory – less than a factor of three across the entire series – is quite good and further supports our assignment of Förster transfer. The complete list of calculated rate constants for complexes 1-3 are given in Tables 2-7a, 2-7b, and 2-7c.

	Interaction ^a	complex 1 ^b	complex 2	complex 3 ^b
		$k_{T} (s^{-1})$	$k_{T}(s^{-1})$	$k_{T}(s^{-1})$
	Re1:LMCT1	3.6 x 10 ⁸	3.3 x 10 ⁸	5.5 x 10 ⁷
	Re1:LMCT2	2.9×10^{8}	2.7×10^{8}	$4.4 \ge 10^7$
	Re1:LMCT3	1.3×10^{8}	1.2×10^{8}	1.9×10^7
$k_{Re1} \left(s^{-1}\right)^{c}$		7.8×10^8	7.2×10^8	1.2 x 10 ⁸
	Re2:LMCT1	3.1 x 10 ⁸	2.8×10^8	4.7×10^{7}
	Re2:LMCT2	3.1×10^8	2.8×10^{8}	$4.6 \ge 10^7$
	Re2:LMCT3	$1.4 \ge 10^8$	1.3×10^{8}	2.2×10^{7}
$k_{Re2} \left(s^{-1}\right)^{c}$		7.6 x 10 ⁸	6.9 x 10 ⁸	1.2 x 10 ⁸
	Re3:LMCT1	$1.2 \ge 10^8$	1.3 x 10 ⁸	$1.8 \ge 10^7$
	Re3:LMCT2	3.9×10^8	3.6×10^8	5.9 x 10 ⁷
	Re3:LMCT3	5.3 x 10 ⁸	4.9×10^8	8.0×10^7
$k_{Re3} \left(s^{-1}\right)^{c}$		1.0 x 10 ⁹	9.8 x 10 ⁸	1.6 x 10 ⁸
$< k_{\rm T} > (s^{-1})^{\circ}$	1	8.5 x 10^8	8.0 x 10^8	1.3×10^8
$k_{obs}(s^{-1})$		2.3×10^9	1.3 x 10⁹	4.0×10^8

Table 2-6. Calculated Förster rate constants for $[Fe(pyacac)_3(Re(tmb)-(CO)_3)_3](OTf)_3$ (1), $[Fe(pyacac)_3(Re(bpy)(CO)_3)_3](OTf)_3$ (2), and $[Fe(pyacac)_3(Re(deeb)(CO)_3)_3](OTf)_3$ (3).

^aDonor-acceptor through-space interaction as defined in the text and in Figure 2-11. ^bR_{DA} and κ^2 values derived from the single-crystal X-ray data for complex 2 using the geometries outlined in Figures 2-9 and 2-10. A complete list of calculated rate constants for complexes 1-3 can be found in Tables 2-7a, 2-7b, and 2-7c. ^cRate of energy transfer calculated according to eqs 2-6. ^dOverall rate of energy transfer given by $(k_{Re1} + k_{Re2} + k_{Re3})/3$.
complex **k**_F (**Re1**) Donor **R(11) R(12) R(13)** 2.9×10^8 2.4×10^8 8.6×10^7 6.2×10^8 tmb (1) 2.7×10^{8} 2.2×10^8 8.0×10^{7} bpy (2) 5.7×10^8 Α 4.4×10^7 3.6×10^7 1.3×10^{7} 9.3 x 10⁷ deeb (3) 9.0×10^8 7.3×10^{8} 1.4×10^{8} 3.4×10^7 tmb (1) 6.7×10^8 8.3×10^8 1.3×10^{8} 3.2×10^7 B bpy (2) 1.4×10^{8} 1.1×10^{8} 2.1×10^{7} deeb (3) 5.2×10^{6} $1.0 \ge 10^9$ 6.8×10^7 6.6×10^6 1.1×10^{9} tmb (1) 9.2×10^8 6.3×10^7 6.1×10^{6} 9.9×10^8 С bpy (2) 1.5×10^{8} 1.0×10^{7} 1.0×10^{6} 1.6×10^8 deeb (3) **R(22) R(21) R(23)** k_F (Re2) 1.7×10^{8} 2.8×10^8 $1.0 \ge 10^8$ 5.5×10^8 tmb (1) 1.6×10^8 2.6×10^8 9.4×10^7 5.1×10^8 bpy (2) A 2.6×10^7 4.2×10^{7} 1.5×10^{7} 8.3 x 10⁷ deeb (3) 6.2×10^{8} 8.3×10^8 tmb (1) 1.7×10^8 4.2×10^7 5.7×10^8 1.6×10^8 3.9×10^7 7.7×10^{8} B bpy (2) 9.3 x 10⁷ 2.6×10^7 6.4×10^6 1.3×10^{8} deeb (3) 1.0×10^{9} 9.4×10^8 9.8×10^7 9.9×10^{6} tmb (1) 8.7 x 10⁸ 9.1 x 10⁷ 9.1 x 10⁶ 9.7 x 10⁸ С bpy (2) 1.4×10^{8} 1.5×10^{7} 1.5×10^{6} 1.6×10^8 deeb (3) R(33) **R(31) R(32)** k_F (Re3) 3.9×10^8 9.5×10^8 5.4×10^8 2.4×10^{7} tmb (1) 8.8×10^8 5.0×10^8 2.2×10^7 3.6×10^8 bpy (2) Α 5.9 x 10⁷ 1.4×10^{8} 8.1 x 10⁷ 3.6×10^6 deeb (3) 9.2×10^8 4.2×10^{8} 8.1×10^{6} 1.3×10^9 tmb (1) 8.5×10^8 7.5×10^{6} 3.9×10^8 1.2×10^{9} B bpy (2) 1.4×10^{8} 1.2×10^{6} 6.4×10^7 2.1×10^8 deeb (3) 1.8×10^{9} tmb (1) 1.4×10^{9} 3.5×10^{6} 4.3×10^8 1.3×10^{9} 3.2×10^{6} $4.0 \ge 10^8$ 1.7×10^{9} С bpy (2) 2.8×10^8 2.1×10^8 5.3×10^{5} 6.5×10^7 deeb (3)

Table 2-7a.Calculated Förster rate constants (s⁻¹) for complexes**1-3** at all donor-acceptor interactions occurring atA:D, B:D, and C:D.

complex Donor **R(11)** R(12) R(13) **k**_F (**Re1**) 2.7×10^8 1.3×10^{8} $1.1 \ge 10^8$ 5.1×10^8 tmb(1) 1.2×10^{8} 2.5×10^8 1.1×10^{8} 4.8×10^8 bpy (2) A 2.0×10^7 4.1×10^{7} 1.7×10^{7} 7.8×10^7 deeb (3) 5.9×10^8 3.9×10^8 1.5×10^{8} 5.2×10^7 tmb(1)bpy (2) 3.6×10^8 1.4×10^{8} 4.8×10^7 5.5×10^8 B $9.0 \ge 10^7$ 5.9×10^7 2.3×10^7 7.8×10^{6} deeb (3) $6.0 \ge 10^8$ 6.9 x 10⁸ 7.3×10^{7} 1.4×10^{7} tmb(1) 5.5×10^8 6.8×10^7 1.3×10^{7} 6.3 x 10⁸ С bpy(**2**) 1.1 x 10⁷ 9.0×10^7 2.1×10^{6} $1.0 \ge 10^8$ deeb (3) R(22) R(21) R(23) k_F (Re2) 5.3×10^8 3.2×10^8 1.4×10^{8} 7.1×10^7 tmb(1) 2.9×10^{8} bpy (2) 1.3×10^{8} 4.9×10^8 6.5×10^7 Α $1.1 \ge 10^7$ 2.1 x 10⁷ 8.0×10^{7} 4.8×10^{7} deeb (3) 1.9×10^{8} 5.7×10^8 3.1×10^8 6.5×10^7 tmb(1) 6.0×10^7 2.9×10^8 1.7×10^{8} 5.2×10^8 bpy(**2**) B 4.7×10^7 2.9×10^7 9.8×10^{6} 8.6×10^7 deeb (3) 6.6×10^8 5.3 x 10⁸ 1.1×10^{8} 2.0×10^7 tmb(1) 4.9×10^8 1.0×10^{8} 1.8×10^{7} 6.1×10^8 С bpy(**2**) 1.6×10^7 3.0×10^{6} deeb (3) 8.1 x 10⁷ 1.0×10^{8} R(32) R(33) **R(31)** k_F (Re3) 3.8×10^8 2.9×10^8 5.5×10^7 7.3×10^8 tmb(1)bpy(2) 2.7×10^8 5.0×10^7 3.5×10^8 6.7×10^8 Α $1.1 \ge 10^8$ deeb (3) 4.4×10^7 8.2 x 10⁶ 5.7×10^{7} 2.3×10^7 4.2×10^8 9.5×10^8 5.1 x 10⁸ tmb(1) 4.7×10^8 2.1×10^7 3.9×10^8 8.8×10^8 bpy(2) B 7.7×10^{7} 6.3×10^7 3.4×10^{6} 1.4×10^{8} deeb (3) 8.6×10^8 2.2×10^{6} 4.6×10^8 1.3×10^{9} tmb(1) 2.0×10^{6} 4.2×10^8 1.2×10^{9} 7.9 x 10⁸ С bpy (2) 1.3×10^{8} 3.3×10^5 6.9×10^7 2.0×10^8 deeb (3)

Table 2-7b. Calculated Förster rate constants (s⁻¹) for complexes1-3 at all donor-acceptor interactions occurring atA:E, B:E, and C:E.

Table 2-7c.Calculated Förster rate constants (s⁻¹) for complexes1-3 at all donor-acceptor interactions occurring atA:F, B:F, and C:F.

Donor	compound	R(11)	R(12)	R(13)	k _F (Re1)
	tmb(1)	5.1 x 10 ⁶	4.4 x 10 ⁸	2.0 x 10 ⁸	6.5 x 10 ⁸
Α	bpy(2)	4.7 x 10 ⁶	$4.1 \ge 10^8$	1.9 x 10 ⁸	6.0 x 10 ⁸
	deeb(3)	7.7 x 10 ⁵	6.7×10^7	3.1×10^7	9.9 x 10 ⁷
	tmb(1)	2.2×10^7	6.0×10^8	2.9×10^8	9.1 x 10 ⁸
B	bpy(2)	2.0×10^{7}	5.6 x 10 ⁸	2.6 x 10 ⁸	8.4 x 10 ⁸
	deeb(3)	3.3×10^{6}	9.1 x 10 ⁷	4.3×10^7	1.4 x 10 ⁸
	tmb(1)	9.7×10^7	6.5×10^8	3.4×10^8	1.1 x 10 ⁹
С	bpy(2)	$9.0 \ge 10^7$	6.0 x 10 ⁸	3.1 x 10 ⁸	1.0 x 10 ⁹
	deeb(3)	1.5×10^{7}	9.8 x 10 ⁷	5.1×10^{7}	1.6 x 10 ⁸
		R(22)	R(21)	R(23)	k _F (Re2)
	tmb(1)	8.1 x 10 ⁶	$4.1 \ge 10^8$	2.1×10^8	6.3×10^8
Α	bpy(2)	7.5 x 10 ⁶	3.8 x 10 ⁸	1.9 x 10 ⁸	5.8 x 10 ⁸
	deeb(3)	1.2×10^{6}	6.2×10^7	3.2×10^7	9.5×10^7
	tmb(1)	2.1×10^7	5.7 x 10 ⁸	3.1×10^8	9.0×10^8
B	bpy(2)	2.0×10^{7}	5.3 x 10 ⁸	2.9 x 10 ⁸	8.4 x 10 ⁸
	deeb(3)	3.2×10^{6}	8.6 x 10 ⁷	4.7×10^7	$1.4 \ge 10^8$
	tmb(1)	9.9×10^7	6.3×10^8	3.9×10^8	$1.1 \ge 10^9$
С	bpy(2)	9.1 x 10 ⁷	5.8 x 10 ⁸	3.6 x 10 ⁸	1.0 x 10 ⁹
	deeb(3)	1.5×10^7	9.5 x 10 ⁷	5.9 x 10 ⁷	1.7 x 10 ⁸
	_	R(33)	R(31)	R(32)	k _F (Re3)
	tmb(1)	$1.4 \ge 10^8$	$1.4 \ge 10^8$	$3.7 \ge 10^8$	6.5 x 10 ⁸
Α	bpy(2)	1.3 x 10 ⁸	1.3 x 10 ⁸	3.4×10^8	6.0 x 10 ⁸
	deeb(3)	2.1×10^7	2.1×10^{7}	5.6 x 10 ⁷	9.8 x 10 ⁷
	tmb(1)	7.7×10^7	2.6×10^8	3.8 x 10 ⁸	7.2×10^8
B	bpy(2)	7.1×10^7	2.4×10^{8}	3.6 x 10 ⁸	6.7 x 10 ⁸
	deeb(3)	1.2×10^{7}	3.9 x 10 ⁷	5.8 x 10 ⁷	1.1 x 10 ⁸
	tmb(1)	4.5×10^{6}	5.5×10^8	2.9×10^8	8.4×10^8
С	bpy(2)	4.2×10^{6}	5.1 x 10 ⁸	2.7 x 10 ⁸	7.8 x 10 ⁸
	deeb(3)	6.9×10^5	8.4 x 10 ⁷	$4.4 \ge 10^7$	1.3 x 10 ⁸

The results of this study allow us to construct a comprehensive picture of the excited-state energies and dynamics for these FeRe₃ systems (Figure The left side of Figure 2-12 is an energy level diagram for the 2-12). relevant electronic states of the Re^l-bpy' chromophore, along with kinetic pathways associated with the various excited-states. Initial population of the ¹MLCT excited-state is followed by rapid intersystem crossing (k_{isc}) to the ³MLCT excited-state.^{97,98} The thermalized triplet state can then undergo radiative (k_r) and non-radiative (k_{nr}) transitions to the ¹A₁ ground-state, or can be quenched by the Fe^{III} core via Förster energy transfer (k_{FNT}). The right side of Figure 2-12 shows the electronic structure of the $Fe(pyacac)_3$ core, which contains charge-transfer (⁶LMCT) and ligand-field electronic excited-states that are thermodynamically accessible from the ³MLCT manifold of the Re chromophore. Dipolar energy transfer results in the formation of a ⁶LMCT excited state within the Fe(pyacac)₃ core, followed by non-radiative relaxation to the ${}^{6}A_{1}$ ground-state of the Fe^{III} moiety.



Figure 2-12. Energy level diagram depicting the excited-state dynamics of the FeRe₃ assemblies. The rate constants for ${}^{1}MLCT \rightarrow {}^{3}MLCT$ intersystem crossing and vibrational cooling within the ${}^{3}MLCT$ state are based on the work of Vlček and co-workers (cf. 85), whereas the other time constants represent approximate values for complexes 1-6.

2.5 Geometry Optimization Calculation

As mentioned in the previous section, one of the more notable aspects of the FeRe₃ series are the rigid building blocks (i.e., stiff pyacac bridging ligands and coordination environments) that constitute these supramolecular complexes. These structural features allowed the crystal structure of complex **2** to be utilized in calculating the donor-acceptor distances (R_{DA}) and orientation factors (κ^2) for all three analogs based on the geometries defined in Figures 2-9, 2-10, and 2-11. The ability to directly use the singlecrystal X-ray data to model solution phase structures and by extension the solution phase energy transfer dynamics is a unique property of the FeRe₃ series (Table 2-6).

A potential drawback of this approach is the effect crystal packing forces may have on the internal structure of complex 2. From the X-ray structural data of complexes 2 and 5 (Figure 2-2), it can be seen that the pyacac bridging ligands are slightly bent away from the expected linear geometry. This structural variation represents a possible error in the donoracceptor distances (R_{DA}) and orientation factors (κ^2) calculated from the model given in Figure 2-10. In order to investigate if this possible source of error has affected the theoretical energy transfer rate constants, a gas phase geometry optimization calculation of complex 2 was performed using the Gaussian 03^{99,100} software package to determine if any differences exist between the solution phase and confined crystal structure geometries. Figure 2-13 shows the optimized geometry of complex 2, along with the observed linear connection between the Fe^{III} and Re^I metal centers via the relaxed geometry of the pyacac bridge.



Figure 2-13. Drawing of the geometry optimized structure of $[Fe(pyacac)_3(Re(bpy)(CO)_3)_3](OTf)_3$ (2).

Table 2-8 compares the $Fe^{III} \cdots Re^{I}$ distances and the dihedral angles between the FeO₂ and acac planes for the three Fe^{III}/Re^{I} donor-acceptor arms for the optimized and solid-state structures of complex **2**. From Table 2-8, the dihedral angles between the FeO₂ triangles and the corresponding acac planes are close to zero in the optimized geometry and are bent away from planarity in the solid-state, which indicates crystal packing forces are affecting the internal geometry of the FeRe₃ complexes. The bent geometry also decreases the Fe•••Re distances by 0.2 – 0.3 Å compared to the optimized geometry. The elongation of the metal-metal distances do represent a source of error in the Förster calculations that were based on the X-ray structural data of complex **2**, so an identical analysis of the donoracceptor distances (R_{DA}) and orientation factors (κ^2) for the optimized geometry of complex **2** was performed. The analyses and labeling system for the various donor and acceptor point dipoles and through-space interactions are identical to the system used for the single-crystal X-ray data outlined in section 2.4.3. The complete list of R_{DA} and κ^2 values calculated using the optimized geometry of complex **2** can be found in Tables 2-9a, 2-9b, and 2-9c.

	Optimized	single-crystal
$FeO_2/acac(1)(^{\circ})^{a}$	2.70	15.60
$FeO_2/acac(2)(^{\circ})^a$	2.80	10.75
$FeO_2/acac (3) (^{\circ})^a$	3.39	23.04
Fe•••Re1 (Å)	10.080	9.881
Fe•••Re2 (Å)	10.081	9.879
Fe•••Re3 (Å)	10.092	9.775

Table 2-8. Fe•••Re distances and FeO₂/acac dihedral angles for the optimized and single-crystal X-ray structure data for complex 2.

^aDihedral angle between the FeO₂ triangle and corresponding acac planes.

Table 2-9a. R_{DA} (Å), Θ_T (°), Θ_D (°), Θ_A (°), and κ^2 values determined from the optimized geometry of complex 2 using donor/acceptor interactions A:D, B:D, and C:D.

	R(11)	R(12)	R(13)	R(22)	R(21)	R(23)	R(33)	R(31)	<u>R(32)</u>
A									
R _{DA}	8.89	11.26	11.19	8.88	11.16	11.27	8.89	11.28	11.20
Θ_{T}	81.41	33.77	52.50	87.15	35.29	50.65	81.50	35.11	52.55
$\Theta_{\rm D}$	73.84	68.82	80.69	74.40	76.14	76.00	74.05	69.07	80.97
Θ_{A}	174.5	52.56	55.21	172.0	55.78	51.18	174.4	51.20	54.54
κ^2	0.961	0.030	0.110	0.720	0.170	0.032	0.938	0.022	0.112
B									
R _{DA}	9.28	11.73	11.42	9.26	11.49	11.60	9.27	11.75	11.43
Θ_{T}	81.41	33.77	52.50	87.15	35.29	50.65	81.50	35.11	52.55
$\Theta_{\rm D}$	67.12	63.81	75.23	67.59	70.74	70.66	67.33	64.08	75.52
Θ_{A}	167.7	47.77	60.84	164.6	56.59	51.92	167.5	46.33	60.23
κ^2	1.661	0.003	0.056	1.328	0.074	0.001	1.630	0.008	0.056
<u>C</u>									
$\mathbf{R}_{\mathbf{D}\mathbf{A}}$	9.82	12.32	11.81	9.796	11.96	12.07	9.81	12.33	11.81
Θ_{T}	81.41	33.77	52.50	87.15	35.29	50.65	81.50	35.11	52.55
$\Theta_{\rm D}$	60.42	58.52	69.30	60.84	65.02	64.99	60.62	58.79	69.59
Θ_{A}	161.6	43.87	65.87	158.4	57.65	52.98	161.4	42.35	65.33
κ^2	2.417	0.089	0.031	1.984	0.019	0.017	2.379	0.109	0.029

Table 2-9b. R_{DA} (Å), Θ_T (°), Θ_D (°), Θ_A (°), and κ^2 values determined from the optimized geometry of complex 2 using donor/acceptor interactions A:E, B:E, and C:E.

	R(11)	R(12)	R(13)	R(22)	R(21)	R(23)	R(33)	R(31)	R(32)
A									
R _{DA}	9.65	10.81	11.19	9.63	10.75	10.81	9.64	10.82	10.78
Θ_{T}	81.41	33.77	52.50	87.15	35.29	50.65	81.50	35.11	52.55
$\Theta_{\rm D}$	74.19	71.53	77.70	75.01	75.83	75.75	74.41	71.78	77.96
Θ_{A}	174.9	55.75	58.52	172.7	59.13	54.31	174.8	54.33	57.82
κ^2	0.928	0.088	0.076	0.671	0.193	0.041	0.904	0.073	0.076
B									
R _{DA}	10.02	11.23	11.07	9.99	11.09	11.15	10.01	11.24	11.07
Θ_{T}	81.41	33.77	52.50	87.15	35.29	50.65	81.50	35.11	52.55
$\Theta_{\rm D}$	68.01	66.18	72.10	68.74	70.22	70.18	68.24	66.43	72.36
Θ_{A}	168.6	50.64	64.26	165.8	59.87	54.99	168.4	49.13	63.64
κ^2	1.564	0.004	0.043	1.220	0.094	0.003	1.531	0.001	0.042
<u>C</u>									
$\mathbf{R}_{\mathbf{D}\mathbf{A}}$	10.55	11.78	11.52	10.51	11.57	11.63	10.53	11.78	11.51
Θ_{T}	81.41	33.77	52.50	87.15	35.29	50.65	81.50	35.11	52.55
$\Theta_{\rm D}$	61.70	60.56	66.13	62.36	64.33	64.32	61.92	60.81	66.39
Θ_{A}	162.9	46.42	69.32	159.9	60.83	55.93	162.7	44.84	68.77
κ^2	2.276	0.034	0.032	1.840	0.034	0.009	2.238	0.048	0.030

Table 2-9c. R_{DA} (Å), Θ_T (°), Θ_D (°), Θ_A (°), and κ^2 values determined from the optimized geometry of complex 2 using donor/acceptor interactions A:F, B:F, and C:F.

	R(11)	R(12)	R(13)	R(22)	R(21)	R(23)	R(33)	R(31)	R(32)
A									
R _{DA}	10.40	10.40	10.40	10.38	10.38	10.38	10.40	10.40	10.40
Θ_{T}	81.41	33.77	52.50	87.15	35.29	50.65	81.50	35.11	52.55
$\Theta_{\rm D}$	74.49	74.49	74.49	75.54	75.54	75.54	74.73	74.73	74.73
Θ_{A}	4.70	120.8	117.9	6.81	117.3	122.3	4.82	122.3	118.6
κ^2	0.423	1.543	0.969	0.482	1.345	1.070	0.409	1.538	0.974
B									
R _{DA}	10.77	10.77	10.77	10.73	10.73	10.73	10.75	10.75	10.75
Θ_{T}	81.41	33.77	52.50	87.15	35.29	50.65	81.50	35.11	52.55
$\Theta_{\rm D}$	68.78	68.78	68.78	69.73	69.73	69.73	69.02	69.02	69.02
Θ_{A}	10.58	126.2	112.1	13.22	116.6	121.7	10.78	127.8	112.7
κ^2	0.843	2.170	1.035	0.926	1.644	1.393	0.823	2.180	1.047
<u>C</u>									
R _{DA}	11.27	11.27	11.27	11.22	11.22	11.22	11.26	11.26	11.26
Θ_{T}	81.41	33.77	52.50	87.15	35.29	50.65	81.50	35.11	52.55
$\Theta_{\rm D}$	62.82	62.82	62.82	63.69	63.69	63.69	63.05	63.05	63.05
Θ_{A}	15.96	130.8	107.1	18.77	115.8	120.8	16.18	132.4	107.6
κ ²	1.365	2.981	1.023	1.462	1.945	1.730	1.341	3.012	1.040

Table 2-10 lists all nine $k_{Re(ij)}$ (Re#:LMCT#) values and the $\langle k_T \rangle$ value calculated for the optimized geometry of complex 2 based on the analysis outlined in section 2.4.5. The $\langle k_T \rangle$ value calculated from the single-crystal X-ray structure of 2 is also listed in Table 2-10 for comparison, with the optimized and solid-state geometries yielding $\langle k_T \rangle$ values of 9.6 x 10^8 s⁻¹ and 8.0 x 10^8 s⁻¹, respectively. The optimized geometry does give a closer energy transfer rate constant to the observed value of 1.3×10^9 s⁻¹, but only by a small factor considering the point-dipole approximations assumed in the rate calculations (R_{DA} and κ^2). These results confirm the applicability of single-crystal X-ray data to structurally well-defined donor-acceptor complexes and particularly for the donor-acceptor separations and orientation factors used in the energy transfer rate calculations in the FeRe₃ family. Due to the structural homology of the FeRe₃ complexes, geometry optimization calculations were not performed on complexes **1** (tmb) and **3** (deeb). The complete list of calculated rate constants for complex **2** are given in Table 2-11.

	Interaction ^a	complex 2 ^b
		$k_{T}(s^{-1})$
	Re1:LMCT1	6.8×10^8
	Re1:LMCT2	2.1×10^8
	Re1:LMCT3	1.1×10^{8}
$k_{Re1} (s^{-1})^{c}$		$1.0 \ge 10^9$
	Re2:LMCT1	$1.8 \ge 10^8$
	Re2:LMCT2	5.6 x 10 ⁸
	Re2:LMCT3	$1.4 \ge 10^8$
$k_{Re2} (s^{-1})^{c}$		8.8 x 10 ⁸
	Re3:LMCT1	2.2×10^8
	Re3:LMCT2	$1.1 \ge 10^8$
	Re3:LMCT3	$6.6 \ge 10^8$
$k_{Re3} (s^{-1})^{c}$		9.9 x 10 ⁸
$k_{T} (s^{-1})^{d}$		9.6×10^8
$k_{T}(s^{-1})(X-ray)$		8.0×10^8
$k_{obs}(s^{-1})$		1.3×10^{9}
、 /		

Table 2-10.Calculated Förster rate constants for $[Fe(pyacac)_3(Re-(bpy)(CO)_3)_3](OTf)_3$ (2) from geometry optimization calculations.

^aDonor-acceptor through-space interaction as defined in the text and in Figure 2-11. ${}^{b}R_{DA}$ and κ^{2} values derived from the minimized gas phase structure using the geometries outlined in Figures 2-9 and 2-10. A complete list of the calculated rate constants for complex 2 can be found in Table 2-10. ^cRate of energy transfer calculated according to eqs 2-6a, 2-6b, and 2-6c. ^dOverall rate of energy transfer given by $(k_{Re1} + k_{Re2} + k_{Re3})/3$.

Table 2-11. Calculated Förster rate constants (s⁻¹) for the
optimized structure of complex 2 at all donor-
acceptor interactions.

Interaction	R(11)	R(12)	R(13)	k _F (Re1)
A-D	9.0 x 10 ⁸	6.8×10^6	2.6×10^7	9.3×10^8
B-D	1.2 x 10 ⁹	6.1 x 10 ⁵	1.2×10^{7}	1.2 x 10 ⁹
C-D	1.3 x 10 ⁹	1.2×10^{7}	5.3 x 10 ⁶	1.3 x 10 ⁹
A-E	5.3×10^8	2.6×10^7	2.2×10^7	5.8 x 10 ⁸
B-E	7.2×10^8	9.1 x 10 ⁵	1.1 x 10 ⁷	7.3 x 10 ⁸
C-E	7.7 x 10 ⁸	5.9 x 10 ⁶	6.4 x 10 ⁶	7.8×10^8
A-F	$1.6 \ge 10^8$	5.6×10^8	3.6×10^8	1.1 x 10 ⁹
B-F	2.5×10^8	6.5 x 10 ⁸	3.1 x 10 ⁸	1.2 x 10 ⁹
C-F	3.1 x 10 ⁸	6.7 x 10 ⁸	2.3×10^{8}	1.2 x 10 ⁹
	R(22)	R(21)	R(23)	k _F (Re2)
A-D	6.8 x 10 ⁸	4.1×10^7	7.3 x 10 ⁶	7.3×10^8
B-D	9.8 x 10 ⁸	$1.5 \ge 10^7$	$8.7 \ge 10^4$	$1.0 \ge 10^8$
C-D	1.0 x 10 ⁹	3.0×10^{6}	2.5×10^{6}	1.0 x 10 ⁹
A-E	3.9×10^8	5.8×10^7	1.2×10^{7}	4.6×10^8
B-E	5.7 x 10 ⁸	2.3×10^{7}	6.2×10^5	5.9 x 10 ⁸
C-E	6.4×10^8	6.5×10^6	1.7 x 10 ⁶	6.5×10^8
A-F	$1.8 \ge 10^8$	5.0×10^8	4.0×10^8	1.1 x 10 ⁹
B-F	2.8×10^8	$5.0 \ge 10^8$	$4.2 \ge 10^8$	1.2 x 10 ⁹
C-F	3.4×10^8	4.5×10^8	$4.0 \ge 10^8$	1.2 x 10 ⁹
	R(33)	R(31)	R(32)	$k_F(Re3)$
A-D	8.8×10^8	4.8×10^6	2.6×10^7	9.1×10^8
B-D	1.2 x 10 ⁹	1.4 x 10 ⁶	1.2×10^{7}	1.2 x 10 ⁹
C-D	1.2 x 10 ⁹	1.4 x 10 ⁷	5.0 x 10 ⁶	1.2 x 10 ⁹
A-E	5.2×10^8	2.1×10^7	2.2×10^{7}	5.6×10^8
B-E	7.1 x 10 ⁸	2.5 x 10 ⁵	1.1 x 10 ⁷	7.2 x 10 ⁸
С-Е	7.6 x 10 ⁸	8.3 x 10 ⁶	6.0 x 10 ⁶	7.7 x 10 ⁸
A-F	1.5×10^8	5.7×10^8	3.6×10^8	1.1 x 10 ⁹
B-F	2.5 x 10 ⁸	6.5 x 10 ⁸	3.1 x 10 ⁸	1.2 x 10 ⁹
C-F	3.1 x 10 ⁸	6.9 x 10 ⁸	2.4×10^8	1.2 x 10 ⁹

2.6 Conclusions

The synthesis, structures, and photophysical properties of a series of donor-acceptor complexes based on Re¹-bipyridine donors and Fe^{III}-acac acceptors have been described. Steady-state and time-resolved emission spectroscopies indicated that the strongly emissive Re¹-based ³MLCT excited-state was significantly quenched when compared to model complexes in which the Fe^{III} center had been replaced by Al^{III}. The favorable overlap between the donor emission and acceptor absorption profiles coupled with a ca. 10 Å donor-acceptor separation, unfavorable driving forces for electron transfer, and the absence of features characteristic of charge separation in the transient absorption spectra allowed for an assignment of Förster (dipolar) energy transfer as the dominant excited-state reaction mechanism. The well-defined structural aspects of this system permitted a quantitative geometric analysis of the dipole-dipole coupling giving rise to the observed dynamics. The calculated energy transfer rate constants differed from the experimental values by less than a factor of three, a level of agreement that is significantly better than what is typically encountered. In addition to providing quantitative support for Förster transfer in this system, this study also demonstrates the degree of accuracy

that can be achieved if the metric details concerning dipole-dipole interactions can be explicitly described.

2.7 References and Notes

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Chapter 3. Orbital-Specific Energy Transfer: CuRe₂ Complexes

3.1 Introduction

The development of molecular assemblies that can serve as photoactive components of optical systems¹⁻⁹ requires exquisite control of their photophysical properties. This level of control, in turn, can only be achieved if the nature of the ground and excited states of the constituents can be elucidated.¹⁰⁻¹² Polypyridyl complexes of Re^I, Ru^{II}, Os^{II}, and Ir^{III} have received considerable attention in this regard due to their synthetic accessibility as well as the structure-function correlations that have emerged from several decades of research on their photo-induced properties.¹³⁻²⁴ As a result, compounds within this class have been utilized in a variety of settings ranging from fundamental studies of electron donor/acceptor interactions²⁵⁻³² to artificial photosynthetic systems³³⁻³⁶ and, most recently, as catalysts for water splitting reactions.³⁷⁻⁴⁰

Recent work from our own group focused on energy transfer dynamics in a tetranuclear assembly consisting of three Re^I polypyridyl donors surrounding an Fe^{III}(acac)₃ moiety.⁴¹ Emission from the Re^I-based ³MLCT excited state was efficiently quenched by the Fe^{III} core; dipolar coupling between the Re^I fluorophore and absorptions associated with the Fe^{III} center was quantitatively established through a detailed metrical analysis of the relative orientations of the donor/acceptor transition dipoles. Energy transfer rate constants on the order of 10^9 s⁻¹ were observed in this system, driven in part by the charge-transfer nature of the optical transitions involved. It occurred to us that this basic compositional motif could provide a convenient platform for examining additional fundamental aspects of dipolar energy transfer. The notion of coupling to weakly absorbing acceptors was of particular interest in light of other work we have carried out on energy transfer involving spin-coupled di-iron(III) complexes.^{42,43} Ligand-field states are intriguing candidates in this regard, due to their low oscillator strengths ($\varepsilon \sim 10 - 100 \text{ M}^{-1}\text{cm}^{-1}$) while at the same time representing nearly ideal manifestations of the point-dipole approximation central to Förster theory.

Low energy ligand-field states of first-row transition metal complexes have been implicated as energy acceptors in a number of studies involving multinuclear assemblies.⁴⁴⁻⁵⁸ Recently, Ford and coworkers have shown that ligand-field states of Cr^{III} in *trans*- $Cr(cyclam)X_2^+$ (X = CI^- or ONO^-) complexes quench the photoluminescence of CdSe/ZnS core/shell quantum dots (QDs) via a Förster energy transfer mechanism.^{59,60} The investigation showed that highly absorbing QDs act as antennae which in turn photosensitize the weakly absorbing Cr^{III} -based ${}^{4}A \rightarrow {}^{4}T$ ligand-field states of an attached $Cr(cyclam)(ONO)_2^+$ complex to trigger the release of NO; potential applications of this water soluble system include the delivery of bioactive agents to specific physiological targets. Other recent examples of metal-centered acceptor states come from the work of Ward and coworkers, who have demonstrated significant quenching of MLCT type emission by f-f acceptor states in Ln(III)-containing donor/acceptor systems.⁶¹⁻⁶⁵ The shielding of the 4f electron shell of the Ln(III) ions by the outer core 5s and 5d electrons allow lanthanide coordination complexes to retain atomic-like absorption and emission profiles,⁶⁶ resulting in line-like spectra that allow for straightforward assignments of acceptor states that energetically overlap with the ³MLCT emission profiles. These studies constitute excellent examples of metal-centered transitions involved in excited-state energy transfer, albeit with some ambiguity as to the mechanism of energy transfer The clear-cut assignment of a dipolar operative in these systems. mechanism in the FeRe₃ series mentioned above led us to design structurally analogous complexes that contain ligand-field states possessing favorable spectral overlap with the Re¹-based ³MLCT emission spectra. The current study thus replaces the ⁶LMCT acceptor states of the FeRe₃ series⁴¹ with ligand-field (d-d) states in an effort to quantitatively explore energy transfer

using an acceptor that represents a nearly ideal manifestation of the pointdipole approximation central to Förster theory.

The synthesis, structure, and photophysical properties of a new family of trinuclear CuRe₂ chromophore-quencher complexes having the general form $[Cu(pyacac)_2(Re(bpy')(CO)_3)_2](OTf)_2$ (where pyacac = 3-(4-pyridyl)acetylacetonate and bpy' = 4,4'-5,5'-tetramethyl-2,2'-bipyridine (tmb, 1), 4,4'-dimethyl-2,2'-bipyridine (dmb, 2), 2,2'-bipyridine (bpy, 3), 4,4'dichloro-2,2'-bipyridine (dclb, 4), and 4,4'-diethylester-2,2'-bipyridine (deeb, 5), and $OTf = CF_3SO_3$) are reported. The Cu^{II} metal centers are covalently attached to two fac-Re(bpy')(CO)₃ (bpy' = tmb, dmb, bpy, dclb, and deeb) moieties through two pyridyl-acetylacetonate bridging ligands (Figure 3-1). Variations in the substituents on the bipyridyl groups allowed for systematic energetic tuning of the emission profile of the Re¹-based ³MLCT state relative to the absorption profile of the Cu^{II} center. Emission from the Re^I fluorophores in complexes 1, 2, 3, 4, and 5 was found to be significantly guenched in the presence of the Cu^{II} metal center relative to structurally analogous BeRe₂ analogs. The BeRe₂ model systems (Figure 3-1) with the general formula $[Be(pyacac)_2(Re(tmb)(CO)_3)_2](OTf)_2$ (6), $[Be(pyacac)_2(Re(dmb)(CO)_3)_2](OTf)_2 \quad (7), \quad [Be(pyacac)_2(Re(bpy)(CO)_3)_2] - (7)_2(Re(bpy)(CO)_3)_2] - (7)_2(Re(bpy)(CO)_3)_2 - (7)_2(Re(bp$ $(OTf)_2$ (8), $[Be(pyacac)_2(Re(dclb)(CO)_3)_2](OTf)_2$ (9), and $[Be(pyacac)_2(Re-$ $(deeb)(CO)_3)_2$ (OTf)₂ (10) were synthesized in order to investigate the excited-state relaxation kinetics of the Re(bpy')(CO)₃ moieties in the absence of the emission quenching dynamics incurred by the Cu^{II} metal center. The confluence of data acquired on the CuRe₂ systems (donoracceptor separation, redox properties, and spectral overlap analyses) unequivocally establishes dipolar energy transfer as the dominant quenching Time-dependent density functional theory (TD-DFT) mechanism. calculations on the Cu^{II} core - $Cu(phacac)_2$ (phacac = 3-phenylacetylacetonate) - in a dichloromethane solvent bath revealed the orbital composition and transition energy of the Cu^{II} ligand-field acceptor states. The unique electronic properties of the Cu^{II} acceptor coupled with the computational work have allowed identification of an orbitally-specific pathway for energy transfer, a result that illustrates the role of relative transition dipole orientation operating at the atomic-orbital level.





1 (Cu) and 6 (Be): $R_1 = R_2 = CH_3$ 2 (Cu) and 7 (Be): $R_1 = CH_3$, $R_2 = H$ 3 (Cu) and 8 (Be): $R_1 = R_2 = H$ 4 (Cu) and 9 (Be): $R_1 = CI$, $R_2 = H$ 5 (Cu) and 10 (Be): $R_1 = CO_2Et$, $R_2 = H$

Figure 3-1. Structures of the $CuRe_2$ and $BeRe_2$ multinuclear assemblies.

3.2 Experimental Section

3.2.1 Synthesis and Characterization

General. All solvents used were purified and dried according to previously reported methods.⁶⁷ Spectroscopic grade CH₂Cl₂ was used for all photophysical measurements and was dried under CaH₂ reflux until no water was detected by ¹H NMR. Solvents for both steady-state and time-resolved emission measurements were thoroughly degassed using freeze-pump-thaw techniques. 3-(4-pyridyl)-2,4-pentanedione,⁶⁸ Cu(pyacac)₂,⁶⁹ Cu(phacac)₂,⁷⁰ Be(pyacac)₂,⁷¹ Re(tmb)(CO)₃(OTf),⁷² Re(dmb)(CO)₃(OTf),⁷² Re(bpy)(CO)₃- $\operatorname{Re(dclb)(CO)_3(OTf)}^{72}$ $\operatorname{Re(deeb)(CO)_3(OTf)}^{72}$ $(OTf).^{72}$ and fac- $[\text{Re(bpy)(CO)}_3(4-\text{Etpy})](\text{PF}_6)^{73}$ (4-Etpy = 4-ethylpyridine) were prepared according to literature procedures. 3-phenyl-2,4-pentanedione was purchased from TCI America. Elemental analyses and FT-IR data were obtained through the analytical facilities at Michigan State University; mass spectra were obtained through the analytical facilities at The University of South Carolina.

 $[Cu(pyacac)_2(Re(tmb)(CO)_3)_2](OTf)_2$ (1). An amount of 99 mg (0.24 mmol) of Cu(pyacac)_2 was dissolved in 40 mL of hot THF, after which 300 mg (0.475 mmol) of Re(tmb)(CO)_3(OTf) was added and the solution was purged with argon for 20 min. The reaction mixture was then fit with a condenser and stirred under argon for 24 hours in hot THF in the dark, after which time a blue-green solid formed. The precipitate was collected, washed with dry THF, and recrystallized from acetonitrile/ether. Yield: 129 mg (32%). Anal Calcd for $C_{56}H_{52}N_6F_6O_{16}S_2CuRe_2$: C, 40.06; H, 3.12; N, 5.00. Found: C, 40.19; H, 3.30; N, 4.79. IR (KBr, cm⁻¹): 2030 s, 1925 s, 1902 s, 1614 m, 1575 s, 1417 m, 1261 m, 1157 m, 1032 s, 639 m. MS: [ESI⁺, m/z (rel. int.)]: 690.5 (62) {[Cu(pyacac)_2(Re(tmb)(CO)_3)_2]}²⁺, 1530.1 (2) {[Cu(pyacac)_2(Re(tmb)(CO)_3)_2](OTf)}¹⁺.

[Cu(pyacac)₂(Re(dmb)(CO)₃)₂](OTf)₂ (2). An amount of 77 mg (0.19 mmol) of Cu(pyacac)₂ was dissolved in 40 mL of hot THF, after which 219 mg (0.369 mmol) of Re(dmb)(CO)₃(OTf) was added and the solution was purged with argon for 20 min. The reaction mixture was then fit with a condenser and stirred under argon in hot THF for 24 hours in the dark, after which a light green solid formed. The mixture was allowed to cool to room temperature and hexanes were slowly added to precipitate additional green solid. The solid was collected, washed with dry THF, and recrystallized from acetonitrile/ether. Yield: 132 mg (44%). Anal Calcd for $C_{52}H_{44}N_6F_6O_{16}S_2CuRe_2$: C, 38.48; H, 2.73; N, 5.18. Found: C, 38.22; H, 2.75; N, 5.27. IR (KBr, cm⁻¹): 2030 s, 1927 s, 1915 s, 1619 m, 1573 s, 1419 m, 1259 m, 1159 m, 1031 m, 638 m. MS: [ESI⁺, m/z (rel. int.)]: 662.4 (60)

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 $\{[Cu(pyacac)_2(Re(dmb)(CO)_3)_2]\}^{2+}, 1474 (4) \{[Cu(pyacac)_2(Re(dmb)-(CO)_3)_2](OTf)\}^{1+}.$

 $[Cu(pyacac)_2(Re(bpy)(CO)_3)_2](OTf)_2$ (3). An amount of 80 mg (0.19 mmol) of Cu(pyacac)₂ was dissolved in 40 mL of hot THF, after which 220 mg (0.382 mmol) of Re(bpy)(CO)₃(OTf) was added and the solution was purged with argon for 20 min. The reaction mixture was then fit with a condenser and stirred under argon in hot THF for 24 hours in the dark, after which time a light green solid formed. The precipitate was collected, washed with dry THF, and recrystallized from acetonitrile/ether. X-ray quality crystals were obtained from slow diffusion of ether into an acetonitrile solution of the compound. Yield: 255 mg (65%). Anal Calcd for C₄₈H₃₆N₆F₆O₁₆S₂CuRe₂: C, 36.79; H, 2.32; N, 5.36. Found: C, 36.94; H, 2.43; N, 5.25. IR (KBr, cm⁻¹): 2033 s, 1913 s, 1604 w, 1575 s, 1419 m, 1259 m, 1160 m, 1031 m, 772 m, 638 m. MS: $[ESI^+, m/z \text{ (rel. int.)}]$: 634.4 (100) ${[Cu(pyacac)_2(Re(bpy)(CO)_3)_2]}^{2+}, 1417.8 (5) {[Cu(pyacac)_2(Re(bpy) (CO)_{3}_{2}(OTf)^{1+}$.

 $[Cu(pyacac)_2(Re(dclb)(CO)_3)_2](OTf)_2$ (4). An amount of 73 mg (0.18 mmol) of Cu(pyacac)_2 was dissolved in 40 mL of hot THF, after which 227 mg (0.352 mmol) of Re(dclb)(CO)_3(OTf) was added and the solution was purged with argon for 20 min. The reaction mixture was then fit with a condenser and stirred under argon in hot THF for 24 hours in the dark, after which a dark green solid formed. The mixture was allowed to cool to room temperature and hexanes were slowly added to precipitate additional dark green solid. The precipitate was collected, washed with dry THF, and recrystallized from acetonitrile/ether. Yield: 195 mg (65%). Anal Calcd for $C_{48}H_{32}N_6Cl_4F_6O_{16}S_2CuRe_2$: C, 33.82; H, 1.89; N, 4.93. Found: C, 33.69; H, 1.99; N, 4.61. IR (KBr, cm⁻¹): 2033 s, 1933 s, 1574 s, 1468 m, 1257 m, 1156 m, 1031 m, 840 w, 638 m. MS: [ESI⁺, m/z (rel. int.)]: 703.3 (30) {[Cu(pyacac)_2(Re(dclb)(CO)_3)_2]}²⁺, 1555.6 (1) {[Cu(pyacac)_2(Re(dclb)-(CO)_3)_2](OTf)}¹⁺.

[Cu(pyacac)₂(Re(deeb)(CO)₃)₂](OTf)₂ (5). An amount of 74 mg (0.18 mmol) of Cu(pyacac)₂ was dissolved in 40 mL of hot THF, after which 255 mg (0.354 mmol) of Re(deeb)(CO)₃(OTf) was added and the solution was purged with argon for 20 min. The reaction mixture was then fit with a condenser and stirred under argon in hot THF for 24 hours in the dark, after which time a light green solid formed. The precipitate was collected, washed with dry THF, and recrystallized usng CH₂Cl₂/hexanes. Yield: 200 mg (61%). Anal Calcd for C₆₀H₅₂N₆F₆O₂₄S₂CuRe₂•CH₂Cl₂: C, 38.15; H, 2.79; N, 4.30. Found: C, 37.90; H, 2.62; N, 4.66. IR (KBr, cm⁻¹): 2035 s, 1926 s, 1732 m, 1573 m, 1408 m, 1323 m, 1263 s, 1154 m, 1031 m, 767 m, 638 m. MS: [ESI⁺, m/z (rel. int.)]: 778.5 (100) {[Cu(pyacac)₂(Re(deeb)-(CO)₃)₂]}²⁺, 1706.1 (3) {[Cu(pyacac)₂(Re(deeb)(CO)₃)₂](OTf)}¹⁺.

$[Be(pyacac)_2(Re(tmb)(CO)_3)_2](OTf)_2$ (6). An amount of 67 mg (0.19 mmol) of Be(pyacac)₂ was dissolved in 40 mL of hot THF, after which 233 mg (0.369 mmol) of Re(tmb)(CO)₃(OTf) was added and the solution was purged with argon for 20 min. The reaction mixture was then fit with a condenser and stirred under argon in hot THF for 24 hours in the dark. The volume of the mixture was reduced to ~ 10 mL, and hexanes were slowly added to precipitate a yellow solid. The yellow solid was collected, washed with dry THF, and recrystallized from acetonitrile/ether. X-ray quality crystals were obtained from slow diffusion of ether into an acetonitrile solution of the compound. Yield: 135 mg (45%). Anal Calcd for C₅₆H₅₂N₆F₆O₁₆S₂BeRe₂: C, 41.40; H, 3.23; N, 5.17. Found: C, 41.53; H, 3.44; N, 5.00. IR (KBr, cm⁻¹): 2031 s, 1916 s, 1613 m, 1575 m, 1417 m, 1261 m, 1155 m, 1031 m, 847 m, 638 m. MS: [ESI⁺, m/z (rel. int.)]: 663.2 (86) { $[Be(pyacac)_2(Re(tmb)(CO)_3)_2]$ }²⁺, 1475.5 (2) { $[Be(pyacac)_2(Re(tmb)-$

 $(CO)_{3}_{2}](OTf)\}^{1+}$.

 $[Be(pyacac)_2(Re(dmb)(CO)_3)_2](OTf)_2$ (7). An amount of 69 mg (0.19 mmol) of Be(pyacac)_2 was dissolved in 40 mL of hot THF, after which 227 mg (0.382 mmol) of Re(dmb)(CO)_3(OTf) was added and the solution was purged with argon for 20 min. The reaction mixture was then fit with a condenser and stirred under argon in hot THF for 24 hours in the dark. The volume of the mixture was reduced to ~10 mL, and hexanes were slowly added to precipitate a yellow solid. The yellow solid was collected, washed with dry THF, and recrystallized from acetonitrile/ether. Yield: 123 mg (41%). Anal Calcd for $C_{52}H_{44}N_6F_6O_{16}S_2BeRe_2$: C, 39.82; H, 2.83; N, 5.36. Found: C, 40.00; H, 2.94; N, 5.47. IR (KBr, cm⁻¹): 2031 s, 1915 s, 1620 m, 1576 s, 1418 m, 1260 m, 1159 m, 1031 s, 847 m, 638 m. MS: [ESI⁺, m/z (rel. int.)]: 635.2 (100) {[Be(pyacac)₂(Re(dmb)(CO)₃)₂]}²⁺, 1419.4 (2) {[Be(pyacac)₂(Re(dmb)(CO)₃)₂](OTf)}¹⁺.

[Be(pyacac)₂(Re(bpy)(CO)₃)₂](OTf)₂ (8). An amount of 72 mg (0.20 mmol) of Be(pyacac)₂ was dissolved in 40 mL of hot THF, after which 228 mg (0.396 mmol) of Re(bpy)(CO)₃(OTf) was added and the solution was purged with argon for 20 min. The reaction mixture was then fit with a condenser and stirred under argon in hot THF for 24 hours in the dark, after which time a crystalline yellow solid formed in the yellow reaction solution. The mixture was allowed to cool to room temperature and the yellow precipitate and yellow solution were separated by filtration. The precipitate was collected, washed with dry THF, and recrystallized from acetonitrile/ether. ESI-MS and single crystal X-ray analysis of the yellow
crystalline material revealed the formation of a Be₃Re₃ hexamer that contains a previously reported Be₃O₃ core⁷⁴⁻⁷⁶ that will be discussed in section **3.3.1**. The volume of the yellow reaction solution was reduced to ~10 mL, and hexanes were added to produce additional yellow solid. The solid was collected, washed with dry THF, and recrystallized from acetonitrile/ether. Yield: 31 mg (10%). Anal Calcd for C₄₈H₃₆N₆F₆O₁₆S₂-BeRe₂: C, 38.12; H, 2.40; N, 5.56. Found: C, 38.25; H, 2.61; N, 5.39. IR (KBr, cm⁻¹): 2033 s, 1919 s, 1604 m, 1576 s, 1419 m, 1261 m, 1161 m, 1031 m, 849 m, 771 m, 636 m. MS: [ESI⁺, m/z (rel. int.)]: 607.1 (83) {[Be(pyacac)₂(Re(bpy)(CO)₃)₂]}²⁺

[Be(pyacac)₂(Re(dclb)(CO)₃)₂](OTf)₂ (9). An amount of 66 mg (0.18 mmol) of Be(pyacac)₂ was dissolved in 40 mL of hot THF, after which 234 mg (0.363 mmol) of Re(dclb)(CO)₃(OTf) was added and the solution was purged with argon for 20 min. The reaction mixture was then fit with a condenser and stirred under argon in hot THF for 24 hours in the dark, after which time a dark yellow solid formed. The mixture was allowed to cool to room temperature and hexanes were slowly added to precipitate additional solid. The dark yellow solid was collected, washed with dry THF, and recrystallized from acetonitrile/ ether. Yield: 199 mg (66%). Anal Calcd for $C_{48}H_{32}N_6Cl_4F_6O_{16}S_2BeRe_2$: C, 34.94; H, 1.95; N, 5.09. Found: C, 35.06; H, 2.22; N, 4.81. IR (KBr, cm⁻¹): 2035 s, 1919 s, 1575 s, 1467 m, 1258 s, 1158 m, 1030 m, 846 m, 755 w, 638 m. MS: $[ESI^+, m/z \text{ (rel. int.)}]$: 676.0 (100) $\{[Be(pyacac)_2(Re(dclb)(CO)_3)_2]\}^{2+}$, 1501.1 (1) $\{[Be(pyacac)_2(Re(dclb)-(CO)_3)_2](OTf)\}^{1+}$.

 $[Be(pyacac)_2(Re(deeb)(CO)_3)_2](OTf)_2$ (10). An amount of 60 mg (0.17 mmol) of Be(pyacac)₂ was dissolved in 40 mL of hot THF, after which 240 mg (0.334 mmol) of Re(deeb)(CO)₃(OTf) was added and the solution was purged with argon for 20 min. The reaction mixture was then fit with a condenser and heated under argon for 24 hours in darkness. The volume of the mixture was reduced to ~ 10 mL, and hexanes were slowly added to precipitate an orange solid. The orange solid was collected, washed with dry THF, and recrystallized using acetonitrile/ether. Yield: 136 mg (45%). Anal Calcd for C₆₀H₅₂N₆F₆O₂₄S₂BeRe₂: C, 40.02; H, 2.91; N, 4.67. Found: C, 39.63; H, 2.92; N, 4.45. IR (KBr, cm-1): 2035 s, 1925 s, 1732 m, 1576 m, 1464 m, 1323 m, 1263 s, 1155 m, 1031 m, 849 m, 767 m, 638 m. MS: $[ESI^{+}, m/z \text{ (rel. int.)}]: 751.3 (79) \{ [Be(pyacac)_2(Re(deeb)(CO)_3)_2] \}^{2+}, 1651.6 \}$ (2) { $[Be(pyacac)_2(Re(deeb)(CO)_3)_2](OTf)$ }¹⁺.

3.2.2 Physical Measurements

X-ray Structure Determinations. Single-crystal X-ray diffraction data for complexes 3 and 6 were acquired at the X-ray facility of Michigan State University. Diffraction data were collected on a Siemens SMART diffractometer with graphite-monochromatic Mo K α radiation (λ = 0.71073Å). Data were collected at -100 °C by using an Oxford Cryosystems low temperature device. Crystallographic data are summarized in Table 1; selected bond distances and angles are listed in Table 2. Lattice parameters were obtained from least-squares analyses and data were integrated with the program SAINT.⁷⁷ The integration method employed a three dimensional profiling algorithm and all data were corrected for Lorentz and polarization factors, as well as for crystal decay effects. The absorption correction program SADABS⁷⁸ was employed to correct the data for absorption effects. The structures were solved by direct methods and expanded using Fourier techniques. All structure calculations were performed with the SHELXTL 6.12 software package.⁷⁹ Anisotropic thermal parameters were refined for all non-hydrogen atoms. Hydrogen atoms were localized in their calculation positions and refined by using the riding model. Further details concerning the structure determinations may be found in Supporting Information.

Cyclic Voltammetry. Electrochemical measurements were carried out in a N_2 -filled drybox (Vacuum Atmospheres) using a BAS CV-50W electrochemical analyzer. A standard three-electrode arrangement was utilized consisting of a Pt working electrode, graphite counter electrode, and a Ag/AgNO₃ reference electrode. Measurements were carried out in CH_3CN solution that was 0.1 M in NBu_4PF_6 . Potentials are reported versus the ferrocene/ferrocenium couple, which was used as an internal standard.

Electronic Absorption and Steady-State Emission Spectroscopies. Extinction coefficients for all compounds were acquired in roomtemperature CH_2Cl_2 solution using a Varian Cary 50 UV-Visible spectrophotometer. Steady-state emission spectra were acquired using a Spex Fluoromax fluorimeter and corrected for instrumental response using a NIST standard of spectral irradiance (Optronic Laboratories, Inc., OL220M tungsten quartz lamp).⁸⁰ Spectra were acquired on samples dissolved in thoroughly degassed CH_2Cl_2 under optically dilute conditions (o.d. ~ 0.1) and sealed under an argon atmosphere in 1 cm path length quartz cuvettes.

Radiative quantum yields (Φ_r) were determined relative to *fac*-[Re(bpy)(CO)₃(4-Etpy)](PF₆) ($\Phi_r = 0.18$ in CH₂Cl₂).⁷³ Quantum yields were calculated according to equation 5-1,

$$\Phi_{\rm unk} = \Phi_{\rm std} \, \frac{(I_{\rm unk}/A_{\rm unk})}{(I_{\rm std}/A_{\rm std})} \left(\frac{\eta_{\rm unk}}{\eta_{\rm std}}\right)^2 \tag{5-1}$$

where Φ_{unk} and Φ_{std} are the radiative quantum yields of the sample and the standard, respectively, I_{unk} and I_{std} represent the areas of the corrected emission profiles for the sample and the standard, A_{unk} and A_{std} are the

absorbance values of the sample and the standard at the excitation wavelength, and η_{unk} and η_{std} correspond to the indices of refraction of the sample and standard solutions (taken to be equal to the neat solvents). Excitation wavelengths were 355 nm for the tmb, dmb, and bpy analogues, 375 nm for the dclb analogues, and 400 nm for the deeb analogues. The corrected excitation spectrum of fac-[Re(bpy)(CO)₃(4-Etpy)](PF₆) in CH₂Cl₂ compared favorably with the compound's absorption spectrum over the range of wavelengths examined (355 - 400 nm), implying that the radiative quantum yield for fac-[Re(bpy)(CO)₃(4-Etpy)](PF₆) does not vary significantly over this spectral window; the reported value of $\Phi_r = 0.18$ was therefore used for determining the radiative quantum yields at $\lambda_{ex} = 355$ nm, 375 nm, and 400 nm. Values for the zero-point energy gap (E_{00}) of the Re¹based ³MLCT excited states were determined by fitting emission profiles based on the approach described by Claude and Meyer.⁸¹ Wavelength data were converted to energy units employing the correction of Parker and Rees:⁸² the best fit was determined by visual inspection of the results of a least-squares minimization routine.

Time-Resolved Emission Spectroscopy. Nanosecond time-resolved emission data for the BeRe₂ model complexes 6-10 were collected using a Nd:YAG-based laser spectrometer that has been described previously.⁸⁰ Data were acquired at room temperature in thoroughly degassed CH_2Cl_2 solutions having absorbances of ~0.1 at the excitation wavelengths. Samples were sealed under an argon atmosphere in 1 cm path length quartz cuvettes. The decay traces correspond to an average of 250 shots of the signal probed at the emission maximum of each compound.

Picosecond time-resolved emission data for the CuRe₂ complexes 1-5 were collected using a time-correlated single photon counting (TCSPC) apparatus that has been described previously.⁸³ Data were acquired in thoroughly degassed CH_2Cl_2 solutions having absorbances of ~0.1 at the excitation wavelength. Samples were sealed under an argon atmosphere in 1 cm path length quartz cuvettes. Each reported decay trace corresponds to a signal average of six data sets, with each data set resulting from ca. 30 minutes of data acquisition time. The decay traces for all five complexes manifest a small baseline offset within the ca. nanosecond data acquisition window due to the presence of a small amount of an emissive impurity identified as fac-[Re(bpy')(CO)₃(pyacac)] based on their similarities to the long-lived kinetics observed for the corresponding BeRe₂ model complexes. Decay traces for all five Cu-containing complexes were therefore fit with biexponential kinetic models by fixing the long-lived component to the

lifetime of the corresponding BeRe₂ complex. Data were fit using the OriginPro 7.5 software package.⁸⁴

DFT Calculations. The Gaussian 03^{85} software package was used for all calculations. The nuclear coordinates used for Cu(phacac)₂ in the calculations were based on the single-crystal X-ray structure reported by Carmichael et al.⁷⁰ The geometry optimization was performed with the UB3LYP functional and LANL2DZ basis set. The effect of CH₂Cl₂ solvent on the optimization was modeled using the polarizable continuum model (PCM);⁸⁶⁻⁸⁹ no symmetry restrictions were imposed. Time-dependent density functional theory (TD-DFT) calculations were performed with the UB3LYP functional and the 6-311G** basis set, also incorporating CH₂Cl₂ using the PCM model. All calculations used tight convergence criteria,⁹⁰ and assumed a molecular charge of 0 and a ground-state spin of S = ¹/₂. The molecular orbitals were generated using GaussView.⁹¹

3.3 Results and Discussion

3.3.1 Synthesis and Structural Characterization. Our interest in developing these systems was to investigate dipole-dipole energy transfer processes in structurally well-defined assemblies that possess weakly absorbing acceptors. The choice of using Re^I and Cu^{II} was based on the well

known MLCT-based reactivity of Re¹ and the low oscillator strength absorptions associated with Cu^{II} ligand-field states. The utilization of the $M(pyacac)_2$ core (M = Cu^{II} and Be^{II}) as a ligand for Re(bpy')(CO)₃(OTf) allowed the pyridyl group to displace the weakly coordinating triflate anion and generate the di-cationic CuRe₂ and BeRe₂ complexes. The formation of the binuclear assembly was facilitated by the low steric crowding afforded by the 180° separation of the two pyacac ligands, along with the propensity of both metal ions to form 4-coordinate complexes.

The ESI-MS data for complexes **1-10** in acetonitrile solution are consistent with the formation of the CuRe₂ and BeRe₂ assemblies. For example, complex **3** shows peaks corresponding to $[Cu(pyacac)_2(Re(bpy)-(CO)_3)_2]^{2+}$ and $[Cu(pyacac)_2(Re(bpy)(CO)_3)_2](OTf)^{1+}$. X-ray quality crystals for complexes **3** and **6** were generated by diffusion of ether into an acetonitrile solution of the complexes over the course of approximately one week; this in turn provides additional evidence for the general robustness of complexes **1-10** in solution.

As mentioned in the synthetic procedure of $[Be(pyacac)_2(Re(bpy)-(CO)_3)_2](OTf)_2$ (8) (section 3.2.1), a crystalline byproduct consisting of a Be_3Re_3 hexamer was formed during the course of the reaction. The Be_3Re_3 complex was confirmed by elemental analysis, ESI-MS, and single-crystal

X-ray structural analysis. Yield: 39 mg (15%). Anal Calcd for C₇₂H₅₇N₉F₉-O₂₇S₃Be₃Re₃: C, 37.06; H, 2.46; N, 5.40. Found: C, 36.67; H, 2.79; N, 5.21. MS: $[ESI^+, m/z \text{ (rel. int.)}]$: 628.6 (100) $[(Be_3(OH)_3(pyacac)_3)((Re(bpy) (CO)_{3}_{3}_{3}_{3}_{3}^{3+}$, 1017.5 (20) $[(Be_{3}(OH)_{3}(pyacac)_{3})((Re(bpy)(CO)_{3})_{3})](OTf)^{2+}$. The structure of the complex is given in Figure 3-2, and shows the core of the complex consisting of three Be^{II} ions bridged by three hydroxo groups that form the Be₃O₃ core of the molecule, along with the Be₃O₃ core connected through three pyacac ligands to three Re(bpy)(CO)₃ moieties that contain pseudo- C_{3v} symmetry commonly observed in ReN₃C₃ coordination environments. Synthesis procedures and single-crystal X-ray structural data for derivatives of the Be₃O₃ core - Be₃(OH)₃L₃ (L = bis-chelate complex) complexes have been reported in the literature.⁷⁴ The geometry of the Be_3O_3 core and the Be-O bond distances of [(Be₃(OH)₃(pyacac)₃)((Re(bpy)- $(CO)_{3}_{3}(OTf)_{3}$ are very similar to these reported systems. The first steps in the synthesis of the Be(pyacac)₂ starting material needed to synthesize complex 8 is to make an aqueous solution of pyacac and pyridine and then add $Be(SO_4)_2$ to the alkaline mixture, which could possibly generate both $Be(pyacac)_2$ and the $Be_3(OH)_3(pyacac)_3$ complex needed to form the $[Be_3Re_3](OTf)_3$ system. Direct probe MS measurements on solid $Be(pyacac)_2$ and in THF solution exhibited only m/z = 361.4 expected for

 $Be(pyacac)_2$, and not m/z = 606.6 expected for the $Be_3(OH)_3(pyacac)_3$ complex, which rules out the possibility of Be₃(OH)₃(pyacac)₃ being formed during the synthesis of $Be(pyacac)_2$. In addition, the formation of the crystalline Be₃Re₃ hexamer was only observed during the synthesis of complex 8 and not for the four other $BeRe_2$ compounds (6, 7, 9, and 10). This behavior suggests the most likely reason for the formation of the [(Be₃(OH)₃(pyacac)₃)((Re(bpy)(CO)₃)₃)](OTf)₃ cystalline material is due to the THF solubility differences between this complex and the four other possible Be₃Re₃ derivative comprised of tmb, dmb, dclb, or deeb. The four other Be₃Re₃ complexes were not observed in the ESI-MS analysis, which suggests that either they were never formed in the reaction solutions of complexes 6, 7, 9, and 10 or were removed during the purification (recrystallization) processes.



Figure 3-2. Drawing of the cation $[(Be_3(OH)_3(pyacac)_3)]((CO)_3)_3)](OTf)_3$ obtained from single-crystal X-ray structure determinations.

3.3.2 Single-Crystal X-ray Structures. X-ray quality crystals of $[Cu(pyacac)_2(Re(bpy)(CO)_3)_2](OTf)_2$ (**3**) and $[Be(pyacac)_2(Re(tmb)(CO)_3)_2]-(OTf)_2$ (**6**) were obtained following diffusion of ether into acetonitrile solutions of the complexes. The complexes both crystallize in the monoclinic space group P2(1)/c. Crystallographic details are given in Table 3-1 with selected bond distances and angles for the two complexes listed in Table 3-2. The coordination environment about the central metal ion in complex **3** (Figure 3-3, *Top*) is formed from the four oxygen atoms of the

acac ligands. The Cu–O bond distances of ca. 1.917 ± 0.002 Å and a 0.0 Å deviation of the Cu^{II} ion from the O₄ mean-plane are both consistent with pseudo- D_{2h} square-planar Cu^{II} and compare favorably with other structurally characterized examples of Cu^{II}-acac systems.^{69,70,92,93} The structure of complex 3 also shows Cu---O distances of 2.702 and 2.545 Å corresponding to axial interactions of the $CF_3SO_3^-$ counter ions with the Cu^{II} core. The axial Cu---O distances are notably longer than typically observed for tetratragonally distorted CuO₆ complexes such as $[Cu(H_2O)_6]^{2+,94-96}$ suggesting that the two Cu---O associations are at best weakly covalent metal-ligand interactions; spectroscopic evidence indicates that these interactions are not retained in solution (vida infra). As expected, significantly shorter metal-oxygen bonds (c.a. 0.3 Å) are observed for the tetrahedral coordination environment of complex 6 (Figure 3-3, Bottom) due to the smaller ionic radius of Be^{II.71} The internal geometries of the $Re(bpy)(CO)_3$ and $Re(tmb)(CO)_3$ moieties in complexes 3 and 6 exhibit the **pseudo-** C_{3v} coordination environment common to Re¹ complexes in this class⁹⁷⁻¹⁰⁰ and are also insensitive to changes in the substituents of the **Polypyridyl** ligand. Differences are noted in the Re^I•••M^{II} distances, with **complex 6** being uniformly shorter by ~ 0.3 Å, which is again due to the smaller Be^{II} ion and the concomitant decrease in metal-oxygen bond lengths relative to complex 3. Despite these minor differences there is considerable structural homology between the two complexes, underscoring the appropriateness of using Be^{II} as a structurally and electronically benign replacement for Cu^{II} in these systems.

	3	6		
formula	$C_{48}H_{36}N_6F_6O_{16}S_2CuRe_2$	$C_{56}H_{52}N_6F_6O_{16}S_2BeRe_2$		
M _w	1566.9	1624.6		
cryst syst	Monoclinic	Monoclinic		
space group	P2(1)/c	P2(1)/c		
T/K	173(2)	173(2)		
a/Å	10.3213(12)	18.7639(3)		
b/Å	24.532(3)	16.9382(3)		
c/Å	12.1608(14)	21.0542(4)		
$\alpha/^{\circ}$	90	90		
β/°	104.027(2)	106.241(1)		
$\gamma^{\prime \circ}$	90	90		
$V/Å^3$	2987.3(6)	6424.5(2)		
Ζ	2	4		
$D_c/g \text{ cm}^{-1}$	1.833	1.696		
$2\theta_{max}$	50	136.4		
reflns measured	29110	72385		
independent reflns	5253	11601		
observed reflns	4827	10856		
$M(Mo K\alpha)/cm^{-1}$	4.556	8.63		
R _{int}	0.026	0.041		
R1 ^a	0.019	0.048		
wR2 ^b	0.0443	0.132		
GOF	1.005	1.050		

Table 3-1.	Crystallographic	Data	for	$[Cu(pyacac)_2(Re(bpy)(CO)_3)_2](OTf)_2$
	(3) and [Be(pyaca	$ac)_2(Rotation)$	e(tm	$b)(CO)_3)_2](OTf)_2$ (6).

 $\overline{{}^{a}R1} = \sum ||F_{o}| - |F_{c}|| / \sum |F_{o}|. \ ^{b}wR2 = [\sum w(F_{o}^{2} - F_{c}^{2})^{2} / \sum w(F_{o}^{2})^{2}]^{1/2}, \ w = 1 / [\sigma^{2}(F_{o}^{2}) + (aP)^{2} + bP], \text{ where } P = [F_{o}^{2} + 2F_{c}^{2}] / 3.$

3		6			
Bond Distances (Å)					
Cu(1) - O(1)	1.920(2)	Be(1) - O(1)	1.618(9)		
Cu(1) - O(2)	1.914(2)	Be(1) - O(2)	1.590(9)		
Cu(1) - O(1A)	1.920(2)	Be(1) - O(6)	1.601(9)		
Cu(1) - O(2A)	1.914(2)	$Be(1) \rightarrow O(7)$	1.610(10)		
Re(1) - N(1)	2.168(2)	Re(1) - N(1)	2.220(5)		
Re(1) - N(2)	2.170(2)	Re(1) - N(2)	2.156(6)		
Re(1) - N(3)	2.214(2)	Re(1) - N(3) = 2.161(5)			
Re(1)-C(22)	1.918(4)	Re(1) - C(25) = 1.921(7)			
Re(1)-C(23)	1.927(4)	Re(1)-C(26)	1.922(7)		
Re(1)-C(24)	1.915(4)	Re(1)—C(27) 1.913(7)			
Cu(1) O(8)	2.702				
Cu(1) O(8A)	2.545				
$Cu(1) \bullet \bullet \bullet Re(1)$	9.707	Be(1)•••Re(1)	9.466		
Cu(1)····Re(1A)	9.707	$Be(1) \bullet \bullet Re(2)$	9.416		
Bond Angles (deg)					
O(1)-Cu(1)-O(2)	92.0(8)	O(1)-Be(1)-O(2)	105.6(5)		
O(1)-Cu(1)-O(1A)	180.0(13)	O(1) - Be(1) - O(6)	108.8(6)		
N(1) - Re(1) - N(2)	75.02(9)	N(2) - Re(1) - N(3)	75.3(2)		
C(22)-Re(1)-N(3)	95.22(11)	C(26)-Re(1)-N(1)	92.0(2)		
C(23)-Re(1)-N(3)	175.8(5)	C(25)-Re(1)-N(1)	176.9(3)		
^a plane 1•••plane 2	87.414	^c plane 1•••plane 2	60 448		
^b plane 1•••plane 2	87.414	^d plane 1•••plane 2	75.75		

Table 3-2. Selected Bond Distances (Å) and Angles (deg) for [Cu(pyacac)₂. (Re(bpy)(CO)₃)₂](OTf)₂ (**3**) and [Be(pyacac)₂(Re(tmb)(CO)₃)₂]-(OTf)₂ (**6**).

^aPlane 1 is defined by atoms O(1), O(2), C(1), C(2), C(3), C(4), C(5); plane 2 is defined by atoms N(3), C(6), C(7), C(8), C(9), C(10). ^bGiven by the atoms that define the two planes in the adjacent pyacac ligand. ^cPlane 1 is defined by atoms O(1), O(2), C(1), C(2), C(3), C(4), C(5); plane 2 is defined by atoms N(1), C(6), C(7), C(8), C(9), C(10). ^dGiven by the atoms that define the two planes in the adjacent pyacac ligand.



Figure 3-3. Drawings of $[Cu(pyacac)_2(Re(bpy)(CO)_3)_2](OTf)_2$ (**3**, *Top*) and $[Be(pyacac)_2(Re(tmb)(CO)_3)_2](OTf)_2$ (**6**, *Bottom*) obtained from single-crystal X-ray structure determinations. Atoms are represented as 50% probability thermal ellipsoids.

3.3.3 Electronic Absorption Spectroscopy. The electronic absorption spectra of complexes 1-10 were acquired in room-temperature CH₂Cl₂ solution and are given in Figure 3-4. Re¹ polypyridyl complexes exhibit a ${}^{1}A_{1} \rightarrow {}^{1}MLCT (t_{2g} \rightarrow \pi^{*} (bpy'))$ transition in the range of 330 to 430 nm depending on the substituents of the bpy' ligand,^{101,102} with electron donating and withdrawing groups shifting λ_{max} for this feature to the blue and red, respectively. In the present series, the absorption maximum systematically shifts from ca. 350 nm for the tmb-containing complexes (1 and 6) to ca. 400 nm in the Re¹-deeb analogues (5 and 10). The presence of charge transfer transitions associated with the Cu^{II} core in the ultraviolet (Figure 3-5, *Left*) gives rise to differences in this region between these adducts and their corresponding Be^{II} analogues. Nevertheless, the general similarities among these spectra, particularly with regard to the ${}^{1}A_{1} \rightarrow {}^{1}MLCT$ absorption of the Re¹-bpy' chromophores, is suggestive of minimal electronic coupling between these groups and the Cu^{II} center in complexes 1-5.

In addition to the Re^I-based charge-transfer transitions, the CuRe₂ complexes also possess ligand-field transitions associated with the squareplanar CuO₄ core. The low-energy tails of the charge-transfer transitions associated with the Re^I chromophores largely obscures these absorptions in compounds 1-10, however, the electronic absorption spectrum of Cu(phacac)₂ allows for an examination of these mid-visible d-d bands (Figure 3-5, *Right*). The two peaks at 530 nm ($\varepsilon = 47 \text{ M}^{-1}\text{cm}^{-1}$) and 652 nm ($\varepsilon = 50 \text{ M}^{-1}\text{cm}^{-1}$) arise from four spin-allowed ligand-field transitions corresponding to $d_{xz} \rightarrow d_{xy}$, $d_{yz} \rightarrow d_{xy}$, $d_{z^2} \rightarrow d_{xy}$ and $d_{x^2} - y^2 \rightarrow d_{xy}$ based on the polarized crystal spectrum of Cu(phacac)₂¹⁰³ and the coordinate system shown in Figure 3-5 (*Right*). This absorption spectrum, which accurately reflects the optical properties of the Cu^{II}O₄ core of complexes 1-5, will therefore provide the basis for the spectral overlap analysis to be described later.

It should be noted that the structure of complex **3** shown in Figure 3-3 reveals two $CF_3SO_3^-$ counter ions interacting with the Cu^{II} core that could in principle yield 5- or 6-coordinate Cu^{II} metal centers for the five $CuRe_2$ complexes (**1-5**) in solution. These interactions would be expected to alter the absorption profile of the Cu^{II} core,¹⁰⁴ thereby negating the utility of the $Cu(phacac)_2$ spectrum as a surrogate for the acceptor in the $CuRe_2$ series. Systematic titration of a CH_2Cl_2 solution of $Cu(phacac)_2$ with $(NEt_4)(CF_3SO_3)$ (2 - 40 eq.) did not cause any discernable change in the absorption spectrum of $Cu(phacac)_2$ (Figure 3-6). This result indicates that the triflate group is not associating with the Cu^{II} center in solution, thereby

validating the use of the $Cu(phacac)_2$ ground-state absorption spectrum in spectral overlap analyses of the $CuRe_2$ assemblies.



Figure 3-4. Electronic absorption spectra of $[M(pyacac)_2(Re(bpy')-(CO)_3)_2](OTf)_2$ where, $M = Cu^{II}$ (red traces) and Be^{II} (blue traces). All spectra were acquired in CH_2Cl_2 solution at room temperature. A. $[Cu(pyacac)_2(Re(tmb)(CO)_3)_2](OTf)_2$ (1) and $[Be(pyacac)_2(Re(tmb)-(CO)_3)_2](OTf)_2$ (6). B. $[Cu(pyacac)_2(Re(dmb)(CO)_3)_2](OTf)_2$ (2) and $[Be(pyacac)_2(Re(dmb)(CO)_3)_2](OTf)_2$ (7). C. $[Cu(pyacac)_2(Re(bpy)-(CO)_3)_2](OTf)_2$ (3) and $[Be(pyacac)_2(Re(bpy)(CO)_3)_2](OTf)_2$ (8). D. $[Cu(pyacac)_2(Re(dclb)(CO)_3)_2](OTf)_2$ (4) and $[Be(pyacac)_2(Re(dclb)-(CO)_3)_2](OTf)_2$ (5) and $[Be(pyacac)_2(Re(deeb)(CO)_3)_2](OTf)_2$ (10).



Figure 3-4 (Cont'd).



Figure 3-5. Left. Electronic absorption spectrum of $Cu(phacac)_2$ showing the higher energy charge transfer and organic-based transitions. *Right*. Electronic absorption spectrum of a concentrated solution of $Cu(phacac)_2$ showing the two mid-visible ligand-field bands. Both spectra were acquired in room-temperature CH_2Cl_2 solution.



Figure 3-6. Systematic titration of a CH_2Cl_2 solution of $Cu(phacac)_2$ with (NEt₄)(CF₃SO₃) (2 - 40 eq.)

3.3.4 Steady-State and Time-Resolved Emission. Emission spectra for the $CuRe_2$ and $BeRe_2$ complexes were obtained in room-temperature deoxygenated CH_2Cl_2 solutions and are shown in Figure 3-7. The spectral

profiles for all of the compounds correspond well to previously reported photophysical studies of Re¹ polypyridyl systems, with the emission originating from the ³MLCT \rightarrow ¹A₁ transition.¹⁰⁵ Emission maxima for the tmb (524 nm), dmb (550 nm), bpy (568 nm), dclb (600 nm), and deeb (620 nm) derivatives reflect the expected trend in zero-point energy of the ³MLCT state based on the electron donating and withdrawing behavior of the substituents on the polypyridyl ligands. Likewise, the radiative quantum yields (Φ_r) for complexes 6-10 (Table 3-3) are all comparable to the reported values for the corresponding mononuclear Re¹ polypyridyl derivatives.⁷²

The data on complexes 1-5 reveal that the emission intensities for the Cu^{II} -containing compounds are significantly attenuated compared to the BeRe₂ model complexes. Unfortunately, radiative quantum yields for complexes 1-5 were found to be analytically unreliable due to a small amount of an emissive impurity present in solutions of these compounds. $Cu(phacac)_2$ was determined to be non-emissive in room-temperature CH_2Cl_2 solution: the impurity is therefore likely due to the presence of *fac*- $[Re(bpy')(CO)_3(pyacac)]$ generated by displacement of the pyacac ligand by residual amounts of H₂O contained in the CH_2Cl_2 . The drying and distilling procedures that were employed were exhausted until no water was detectable by ¹H NMR, but the low concentration of the CuRe₂ compound

used for the emission measurements means that even trace amounts of H_2O could be sufficient to generate a small amount of dissociated species. A similar problem was encountered in our previous study of FeRe₃ assemblies;⁴¹ as in that system, the presence of this emissive component proves to be inconsequential for the ensuing analysis.¹⁰⁶



Figure 3-7. Corrected steady-state emission spectra for [M(pyacac)2- $(\text{Re(bpy')(CO)}_3)_2](\text{OTf})_2$ where, $M = Cu^{II}$ (red traces) and Be^{II} (blue traces). All spectra were acquired in room-temperature deoxygenated CH₂Cl₂ solution. A. [Cu(pyacac)₂(Re(tmb)(CO)₃)₂](OTf)₂ (1) and [Be- $(pyacac)_2(Re(tmb)(CO)_3)_2](OTf)_2$ (6). В. [Cu(pyacac)2(Re(dmb)- $(CO)_{3}_{2}(OTf)_{2}$ (2) and $[Be(pvacac)_{2}(Re(dmb)(CO)_{3})_{2}](OTf)_{2}$ (7). C. [Cu(pyacac)₂(Re(bpy)(CO)₃)₂](OTf)₂ (3) and [Be(pyacac)₂(Re(bpy)- $(CO)_{3}_{2}(OTf)_{2}$ (8). **D**. $[Cu(pvacac)_{2}(Re(dclb)(CO)_{3})_{2}(OTf)_{2}$ (4) and $[Be(pyacac)_2(Re(dclb)(CO)_3)_2](OTf)_2$ (9). E. $[Cu(pyacac)_2(Re(deeb) (CO)_{3}_{2}[OTf)_{2}(5)$ and $[Be(pyacac)_{2}(Re(deeb)(CO)_{3})_{2}](OTf)_{2}(10)$. The spectra were acquired following excitation at 355 nm (complexes 1, 2, 3, 6, 7, and 8), 375 nm (complexes 4 and 9), and 400 nm (complexes 5 and 10). For each plot, the emission profiles have been normalized with respect to the absorbance of each sample at its excitation wavelength. The relative magnitudes of the signals are therefore accurate representations of their relative intensities. The emission corresponding to the CuRe₂ analogues are due largely to the presence of Re(bpy')(CO)₃(pyacac) in solution. See main text for further details.





Quantitative information concerning emission quenching by the Cu^{II} center in complexes 1-5 was obtained via time-resolved emission spectroscopy. Data for the BeRe₂ model complexes could be fit to single-exponential decay kinetic models; emission traces and values for the observed decay

rates for all five BeRe₂ complexes are given on the left side of Figure 3-8 and Table 3-3, respectively. As with the quantum yields, the observed excited-state lifetimes are consistent with an assignment of ${}^{3}MLCT \rightarrow {}^{1}A_{1}$ emission.^{72,107} The kinetics reveal that the reduction in quantum yield across the series is due primarily to an increase in the non-radiative decay rate for ³MLCT relaxation (k_{nr}) as opposed to significant variations in radiative coupling to the ground state. The only deviation from this trend is the smaller value of k_{nr} for complex 10. This is most likely due to the additional conjugation present in the π system of the deeb ligand, which allows for increased delocalization of the excited electron relative to other members of the series. This increased delocalization is expected to give rise to a smaller net displacement of the ground- and excited-state potential energy surfaces, which in turn leads to a decrease in the rate of non-radiative decay.^{73,80,81,108}

Analogous measurements on the nanosecond time-scale for the CuRe₂ complexes failed to reveal any signal beyond that of the trace impurity mentioned above. Consequently, time-correlated single-photon counting (TCSPC) was employed to measure the excited-state lifetime of the Cu^{II}- containing complexes (1-5). A plot of the TCSPC data obtained for complexes 1-5 in deoxygenated CH_2Cl_2 solution is shown on the right side of Figure 3-8; data for all five CuRe₂ complexes (1-5) are listed in Table 3-3.

The observed time constants for excited-state decay for complexes 1-5 are all significantly larger than the corresponding BeRe₂ model complexes, ranging from a factor of ca. 20 in the case of complex 4 to more than two orders of magnitude for complex 1. The signal-to-noise ratio for the TCSPC data is relatively poor owing to a combination of significant quenching of the Re¹-based ³MLCT states coupled with radiative rate constants for emission on the order of 10^5 s⁻¹. Nevertheless, these observations clearly indicate the presence of a very efficient quenching process stemming from a reaction between the Re¹-based ³MLCT excited state and the Cu¹¹ core of the CuRe₂ assemblies.



Figure 3-8. Left. Nanosecond time-resolved emission data for the BeRe2 model complexes in room-temperature deoxygenated CH2Cl2 solutions: 6 ($\tau_{obs} = 1990 \pm 100 \text{ ns}$), 7 ($\tau_{obs} = 645 \pm 30 \text{ ns}$), 8 ($\tau_{obs} = 540 \pm 100 \text{ ns}$) 30 ns), 9 ($\tau_{obs} = 110 \pm 10$ ns), and 10 ($\tau_{obs} = 250 \pm 20$ ns). The solid red lines correspond to fits to single-exponential decay models. The data were acquired by monitoring at the emission maximum of each compound. Right. Time correlated single-photon counting (TCSPC) emission data for the CuRe₂ complexes in room-temperature deoxygenated CH₂Cl₂ solutions: 1 ($\tau_1 = 14.9 \pm 0.7$), 2 ($\tau_1 = 8.1 \pm 0.4$), 3 $(\tau_1 = 8.2 \pm 0.4)$, 4 $(\tau_1 = 5.6 \pm 0.3)$, and 5 $(\tau_1 = 5.0 \pm 0.3)$. The data were acquired by monitoring at the emission maximum of each compound. The solid red lines correspond to fits to bi-exponential decay models; in each case the second component (τ_2) corresponds to emission from trace amounts of Re(bpy')(CO)₃(pyacac) present in solution. τ_2 was taken to be the emission lifetime of the corresponding BeRe₂ model complex.



		E ₀₀			k _r ^c	k _{nr} ^{d,e}
complex	λ(nm)	$(cm^{-1})^{a}$	$\Phi_{\rm r}$	$k_{obs}(s^{-1})^{b}$	$(\times 10^5 \text{ s}^{-1})$	$(\times 10^6 \text{s}^{-1})$
tmb (1)	f	f	f	$6.7\pm0.3\times10^7$	f	67 ± 4
tmb (6)	524	19,900	0.63	$5.0\pm0.3\times10^5$	3.2 ± 0.2	$0.19 \pm .01$
dmb (2)	f	f	f	$1.2\pm0.1\times10^8$	f	120 ± 6
dmb (7)	550	19,200	0.25	$1.6 \pm 0.1 \times 10^{6}$	4.0 ± 0.2	1.2 ± 0.1
bpy (3)	f	f	f	$1.2\pm0.1\times10^{8}$	f	120 ± 6
bpy (8)	568	18,750	0.18	$1.9\pm0.1\times10^{6}$	3.4 ± 0.2	1.6 ± 0.1
dclb (4)	f	f	f	$1.8 \pm 0.1 \times 10^{8}$	f	180 ± 10
dclb (9)	600	17,650	0.03	$8.8\pm0.5\times10^6$	2.6 ± 0.1	8.5 ± 0.4
				0		
deeb (5)	f	f	f	$2.0\pm0.1\times10^{8}$	f	200 ± 10
(10)	620	16,900	0.07	$4.0\pm0.2\times10^{6}$	2.8 ± 0.2	3.7 ± 0.2

Table 3-3. Photophysical Data for [M(pyacac)₂(Re(bpy')(CO)₃)₂](OTf)₂ (complexes 1-10).

^aZero-point energy difference between ³MLCT excited state and ground state derived from a spectral fitting analysis. ^bError bars on k_{obs} represent the standard deviation (2 σ) of five independent measurements. ^c $k_r = k_{obs} * \Phi_r$. ^d $k_{nr}(CuRe_2) = k_{obs}(CuRe_2) - k_r(BeRe_2)$. ^e $k_{nr}(BeRe_2) = k_{obs}(BeRe_2) - k_r(BeRe_2)$. ^fThis value is not quoted due to the presence of an emissive impurity, but is expected to be identical to the corresponding Be^{II} complex. See text for details.

3.4 Mechanistic Considerations

3.4.1 Electron versus Energy Transfer Quenching. Time-resolved emission data, while clearly revealing the presence of an excited-state reaction, provides no information as to the mechanistic origin of that Indeed, both electron and energy transfer processes can be reaction. envisioned to occur out of the Re¹-based ³MLCT excited state. Based on the presence of Cu^{II} in the ground states of these CuRe₂ complexes, electron transfer (k_{ET}) could in principle proceed either by oxidative or reductive quenching to produce Cu^I or Cu^{III} as photo-products (Figure 3-9). In order to determine if electron transfer is thermodynamically viable in our system, the electrochemical properties for the CuRe₂ as well as the BeRe₂ analogues were measured. Cyclic and differential pulse voltammograms for complexes 1-10 were recorded in CH₃CN solution; the data are listed in Table 3-4.¹⁰⁹ The availability of the Be^{II} model complexes considerably simplifies assigning many of the electrochemical properties of all ten complexes due to the redox-inert nature of this ion. Accordingly, the single reduction waves seen for complexes 6-10 can be immediately ascribed to the bipyridyl ligand of the Re moiety in each case. The positive shift in potential across the series is consistent with the more electron withdrawing nature of the substituents as one progresses from the methyls of tmb (6) to the diethylester groups in complex 10. Similarly, the oxidation waves seen for complexes 6-10 are easily assigned to the Re^I/Re^{II} couple. The influence of the bipyridyl substitutents are apparent in these data as well, with the more electron deficient ligand giving rise to the most positive oxidation potential for the Re center. The results are all consistent with what has been observed for complexes of the general form *fac*-[Re(4,4'-X₂-bpy)(CO)₃(4-Etpy)](PF₆) previously reported in the literature.⁷²

In addition to the Re^I-based features, complexes 1-5 should also exhibit redox chemistry associated with the central Cu^{II} ion, which prompted the investigation of the electrochemical properties of Cu(phacac)₂. The electrochemical properties of Cu(acac)₂ and related complexes in CH₃CN solution have been previously reported,^{110,111} with the Cu^{II} metal center observed to undergo highly irreversible reductive (Cu^{II} \rightarrow Cu^I) and oxidative (Cu^{II} \rightarrow Cu^{III}) processes. Cu(phacac)₂ exhibits a wave at -1.48 V in CH₃CN solution which can be assigned to the Cu^{II} \rightarrow Cu^{II} reduction; this potential shifts to and at -1.73 V in CH₂Cl₂. The Cu^{II} \rightarrow Cu^{III} oxidation occurs at +1.31 V in CH₃CN and lies outside the solvent window of CH₂Cl₂ (i.e., > 1.5 V). Although the Cu^{II} potentials are masked in certain cases by the Re^Iand polypyridyl-based processes, the assignments reported in Table 3-4 for the CuRe₂ series are validated by their close correspondence to the data acquired on the BeRe₂ systems.

The Re^I \rightarrow Re^{II} oxidation potentials for complexes 1-5, Cu^{II} \rightarrow Cu^{II} reduction and $Cu^{II} \rightarrow Cu^{III}$ oxidation potentials of Cu(phacac)₂, along with the zero-point energy gaps of the ${}^{3}MLCT$ states (E₀₀) determined from fits of the emission spectra of the corresponding BeRe₂ analogs (Table 3-3) were used to determine the thermodynamic driving force for photoinduced electron transfer.^{112,113} The values of ΔG^{ET} listed in Table 3-4 reveal that electron transfer is significantly uphill for both oxidative and reductive quenching processes in all five CuRe₂ complexes. Significantly, these reactions become more endothermic in CH₂Cl₂ (the solvent used for the photophysical measurements) due to the shifts in the Cu^{II}-based redox processes indicated above. These electrochemical data therefore effectively rule out electron transfer as a viable quenching mechanism for the CuRe₂ series.

$$(bpy')Re^{I} \sim Cu^{II} \longrightarrow (bpy')Re^{II} \sim Cu^{II} \longrightarrow (bpy')Re^{II} \sim Cu^{II} \longrightarrow (bpy')Re^{II} \sim Cu^{II} \longrightarrow (bpy')Re^{I} \rightarrow Cu^{II} \rightarrow C$$

Figure 3-9. Illustration of oxidative (k_{ET1}) and reductive (k_{ET2}) electron transfer quenching processes out of the Re^I-based ³MLCT excited-state to produce Cu^I or Cu^{III} as photo-products, respectively.

			ГТ	TT.
			$\Delta G^{E_{ox}}$	$\Delta G^{E_1}_{red}$
	electrochemi	cal potential (V)	$(eV)^{a}$	$(eV)^{o}$
complex	$E_{ox} (Re^{I/II})^{c}$	$E_{red} (bpy'^{0/-})^{c}$		
tmb (1)	+1.30	-1.83	+0.56	+0.67
tmb (6)	+1.28	-1.81		
dmb (2)	+1.31	-1.71	+0.66	+0.64
dmb (7)	+1.31	-1.68		
bpy (3)	+1.36	-1.61	+0.77	+0.60
bpy (8)	+1.34	-1.57		
dclb (4)	+1.41	-1.38	+0.95	+0.50
dclb (9)	+1.44	-1.34		
1 1 (#)	. 1 . 6 1	1.00		
deeb (5)	+1.51	-1.23	+1.14	+0.44
deeb (10)	+1.50	-1.19		
	Ε (C u ^{II/III}) ^c	$\mathbf{F} \cdot (\mathbf{C} \mathbf{u}^{\mathbf{I} \mathbf{I} \mathbf{I}})$		
$O_{\rm ex}(ab a a b)$		$1.72d(1.40)^{\circ}$		
$Cu(pnacac)_2$	+1.51	-1./3 (-1.48)		

Table 3-4. Electrochemical Data and Calculated Electron Transfer Driving
Forces (ΔG^{ET}) for Complexes 1-10.

^aCalculated using the ΔG^{ET}_{ox} equation given in Ref. 113 and using the Cu^{II} \rightarrow Cu^I reduction in Cu(phacac)₂ in CH₂Cl₂ as the reduction potential of the acceptor. ^bCalculated with the ΔG^{ET}_{red} equation given in Ref. 113 and using the Cu^{II} \rightarrow Cu^{III} oxidation in Cu(phacac)₂ in CH₃CN as the oxidation potential of the acceptor. ^cMeasured in CH₃CN solution. ^dMeasured in CH₂Cl₂ solution.

Based on the analysis presented above, the most likely explanation for ³MLCT quenching in all five of the CuRe₂ assemblies is excited-state energy transfer. The two most important mechanisms are electron superexchange

(Dexter)¹¹⁴ and dipole-dipole coupling (Förster).¹¹⁵ Dexter energy transfer is subject to a distance dependence that falls off as e^{-2R} due to its reliance on orbital overlap. As such, it is usually relegated to covalently linked systems in which the donor and acceptor lie in close proximity and are electronically coupled. Förster transfer is a through-space mechanism that occurs when the donor emission non-radiatively couples to an absorptive feature of the acceptor. The dipolar nature of this interaction gives rise to a shallower R^{-6} distance dependence, allowing this mechanism to be operative over much longer distances.¹¹⁶ The X-ray structure data for complex 3 shows a Re^I•••Cu^{II} separation of nearly 10 Å, a value that lies at the limit of what is typically considered for an exchange-based process.^{46,117-119} The similarity in the charge-transfer region between the absorption spectra of complexes 1-5 and their respective BeRe₂ analogues, as well as their electrochemical properties, suggests minimal electronic exists coupling between the Re^I and Cu^{II} subunits. This point is amplified by the computational results of Meyer and coworkers which reveal that the majority of the amplitude associated with the thermalized ³MLCT wavefunction for complexes of the form *fac*- $[Re(4,4'-X_2bpy)(CO)_3(4-Etpy)](PF_6)$ (X = CH₃, H, and CO₂Et) is concentrated within the π^* levels of the 4,4'-X₂bpy derivatives and less so on the 4-Etpy ligand.¹²⁰ This situation decreases the possibility of the pyacac

bridging ligands in the CuRe₂ series imparting significant electronic coupling between the Re^I and Cu^{II} metal centers. This combination of the structural and electronic characteristics of the CuRe₂ series make it unlikely that Dexter-type exchange is playing a dominant role in the energy transfer dynamics of these systems.

3.4.2 Spectral Overlap Analysis: State-Selective Energy Transfer. The classic equation describing the Förster energy transfer rate constant (k_{EnTr}) is given in equation 3-3,¹²¹

$$k_{EnTr} = \frac{9000\ln(10)\kappa^2 k_r J}{128\pi^5 \eta^4 N_A R^6}$$
(3-3)

where κ^2 is the dipole orientation factor, k_r is the radiative rate constant of the donor, J is the spectral overlap integral, η is the refractive index of the solvent, N_A is Avogadro's number, and R is the donor-acceptor separation. The spectral overlap integral (J), which essentially quantifies the resonance condition for energy transfer, can be evaluated from the spectroscopic properties of the system and is given in equation 3-4,

$$J = \int_{0}^{\infty} \frac{\overline{F}_{D}(\overline{v})\overline{\varepsilon}_{A}(\overline{v})}{\overline{v}^{-4}} d(\overline{v})$$
(3-4)

where \overline{F}_D is the normalized emission spectrum of the donor and $\overline{\varepsilon}_A$ is the absorption profile of the acceptor in units of molar absorptivity. A plot of the
emission spectra of complexes **6** through **10** along with the visible absorption spectrum of $Cu(phacac)_2$ is shown in Figure 3-10. It can be seen that the systematic shift in the emission maximum across the series results in a modulation of the overlap between the donor and the acceptor. As mentioned previously, the absorption spectrum of the Cu^{II} acceptor consists of a ligand-to-metal charge transfer feature in the blue/near-ultraviolet region, as well as ligand-field transitions in the mid-visible; the substituent changes on the bpy ligands serve to tune the resonance between the ³MLCT emission of the Re^I-bpy' fluorophore and these various acceptor state(s).



Figure 3-10. Overlay of the emission spectra of $[Be(pyacac)_2(Re(tmb)-(CO)_3)_2](OTf)_2$ (**6**, purple), $[Be(pyacac)_2(Re(dmb)(CO)_3)_2](OTf)_2$ (**7**, blue), $[Be(pyacac)_2(Re(bp))(CO)_3)_2](OTf)_2$ (**8**, green), $[Be(pyacac)_2-(Re(dcb)(CO)_3)_2](OTf)_2$ (**9**, orange), and $[Be(pyacac)_2(Re(deeb)-(CO)_3)_2](OTf)_2$ (**10**, red) with the electronic absorption spectrum of Cu(phacac)_2 (black trace).

The Förster model defines a proportionality between the spectral overlap integral and the rate of energy transfer subject to variations in the donor-acceptor distance, the intrinsic radiative lifetime of the donor, as well as the relative orientation of the coupled transition dipoles (κ^2). In viewing the series of complexes 1 through 5 as a whole, several of these variables can be accounted for explicitly as a means of examining trends in the rate of energy transfer. The availability of the BeRe₂ model complexes affords values of k_r for each compound in the series. We can therefore write an expression for the rate of energy transfer normalized for the rate of radiative decay as equation 5a:

$$\frac{k_{EnTr}}{k_r} = C \cdot \kappa^2 \cdot J \tag{3-5a}$$

where C represents the collection of constants from the Förster equation (including the R⁻⁶ donor-acceptor distance term). Our previous study on Fe^{III}-containing assemblies⁴¹ demonstrated that one could use metrical data afforded from single-crystal X-ray structures in conjunction with reasonable estimates for the positions of the relevant transition dipole vectors to calculate κ^2 explicitly. In the present case, the metal-localized nature of the d-d states on the Cu^{II} center makes this approach more difficult (vide infra), however, we can invert this process and calculate values for κ^2 based on our

experimental data. Values for k_{EnTr}/k_r , the overlap integral (J_{total}), as well as κ^2 for compounds 1-5 are listed in Table 3-5. These numbers reveal the surprising result that the value of κ^2 is not constant across the series. Using a donor-acceptor distance of 10.37 Å (a value corresponding to the distance between the Cu^{II} center and the midpoint of a vector that bisects the N-Re-N bond angle⁴¹), κ^2 for compound 1 is found to be 2.8 whereas for compound 5 the corresponding value is 5.7; this latter result exceeds the maximum value of $\kappa^2 = 4$ calculated for head-to-tail parallel transition dipoles.¹¹⁵

The underlying reason for the apparent disconnect between the predictions of eq 3-5a and the results obtained for compounds 1 through 5 can be understood by examining the normalized rates of energy transfer across the series in a slightly different manner. For any two members of the series i and j, we can write equation 3-5b for the relative change in the rate of energy transfer as a function of spectral overlap:

$$\begin{bmatrix} k_{EnTr} \\ k_r \end{bmatrix}_j = \frac{C_j \cdot \kappa_j^2 \cdot J_j}{C_i \cdot \kappa_i^2 \cdot J_i}$$
(3-5b)

The isostructural nature of compounds 1 through 5 implies that, to a reasonable degree of precision, the donor-acceptor distance is essentially

constant across the series.¹²² Cancellation of these terms affords equation 3-5c:

$$\frac{\begin{bmatrix} k_{EnTr} \\ k_r \end{bmatrix}_j}{\begin{bmatrix} k_{EnTr} \\ k_r \end{bmatrix}_i} = \frac{\kappa_j^2}{\kappa_i^2} \cdot \frac{J_j}{J_i}$$
(3-5c)

This expression indicates that the relative rates of (k_r-normalized) energy transfer should correlate with the ratio of their spectral overlap integrals weighted by a proportionality constant equal to the relative magnitudes of their orientation factors: dipolar coupling involving the same two states (i.e., the ³MLCT state of the Re-bpy' moieties and the Cu^{II} acceptor) should therefore yield a slope of 1 since their orientation factors will cancel. Using the data for compound 1 as our ith reference state we find that $\kappa_{i}^{2}/\kappa_{1}^{2}$ increases from 1.18 for compound 2 to 2.03 for compound 5. These data confirm the trend suggested by the individual κ^2 values listed in Table 3-5, namely that the orientation factor associated with energy transfer in this system is different in one region of the spectrum versus another. Specifically, our analysis reveals a net increase in the rate of energy transfer as the donor emission comes into resonance with the low-energy portion of the Cu^{II} absorption profile.

complex	J _{total} ^a	J_{G1}^{a}	J_{G2}^{a}	J_{G3}^{a}	$k_{EnT} (\times 10^8 \text{ s}^{-1})^{b}$	k_{EnT}/k_r^c	κ^{2d}
tmb (1)	4.29	0.127	2.26	1.90	0.67	208	2.8
dmb (2)	5.14	0.046	2.07	3.03	1.18	295	3.3
bpy (3)	5.52	0.027	1.92	3.57	1.18	347	3.7
dclb (4)	6.68	0.0045	1.29	5.39	1.71	658	5.7
deeb (5)	7.09	0.0014	0.97	6.12	1.96	700	5.7

Table 3-5. Calculated Spectral Overlap Integrals and Energy Transfer RateConstants for Complexes 1-5.

^aReported in units of 10^{-16} M⁻¹cm³. ^bk_{EnT} = k_{obs}(CuRe₂) – k_{obs}(BeRe₂) (Table 3-3). ^cValues for k_r were taken from the corresponding BeRe₂ complex (Table 3-3). ^dCalculated based on eq. 3-5 for R = 10.37 Å.

In order to determine whether there are, in fact, differential contributions from the excited-state manifold of Cu^{II} to the energy transfer dynamics of this system, we deconvolved the absorption profile of $Cu(phacac)_2$ into a sum of Gaussians as a means of examining each portion of the compound's excited-state structure individually (Figure 3-11A). As expected, the spectrum is well-described by three bands corresponding to the high-energy charge-transfer feature (G1) and two, lower-intensity bands assigned to ligand-field transitions (G2 and G3).¹⁰³ Using this fitted spectrum, the total spectral overlap integral (J_{total}) can be apportioned according to its various components (where $J_{total} = J_{G1} + J_{G2} + J_{G3}$) (Figure 3-11B and Figure 3-11C). The data in Table 3-5 reveals that the charge-transfer state contributes minimally to the overall spectral overlap, with

contributions ranging from a high of ca. 3% in the case of compound 1 to less than 0.02% in compound 5. This is a clear, quantitative indication that the ligand-field terms are the dominant acceptor states in this system. As the emission spectrum is tuned toward the red the total spectral overlap increases, however, the contribution from the higher energy ligand-field transition(s) decreases from 53% in compound 1 to 14% in compound 5. At the same time, fractional overlap with the G3 component increases from 44% to 86% of the total. Since the value of κ_j^2/κ_1^2 from eq 3-5c is observed to increase across the series, we can infer from this analysis that the rate of energy transfer from the ³MLCT state of the Re-bpy' moiety is intrinsically faster when coupling to the G3-component of the Cu^{II} absorption profile as compared to G2. This conclusion is further supported by noting that the ratio of orientation factors as defined by eq 3-5c yields the same value of 2.03 for compounds 4 and 5, implying that $\kappa^2 \kappa^2_4 = 1$. Inspection of the data in Table 5 reveals an increase in J_{total} for compound 5 versus compound 4 but comparatively little change in the relative contributions of G2 and G3. In this context, the variation in κ^2 across the entire series can be interpreted in terms of differences in the orientation of the transition dipoles associated with G2 and G3: once changes in spectral overlap are isolated to G3 (i.e., compounds 4 and 5), the proportionality factor in eq 3-5c collapses to unity.



Figure 3-11. A. The ground state absorption spectrum of $Cu(phacac)_2$ in CH_2Cl_2 (black) fit with a series of three Gaussians (G1 (solid trace), G2 (dotted trace), and G3 (dashed trace)). **B** and **C**. Overlay of the emission spectra of $[Be(pyacac)_2(Re(tmb)(CO)_3)_2](OTf)_2$ (6, purple), $[Be(pyacac)_2(Re(dmb)(CO)_3)_2](OTf)_2$ (7, blue), $[Be(pyacac)_2(Re(bp))-(CO)_3)_2](OTf)_2$ (8, green), $[Be(pyacac)_2(Re(dclb)(CO)_3)_2](OTf)_2$ (9, orange), and $[Be(pyacac)_2(Re(deeb)(CO)_3)_2](OTf)_2$ (10, red) with G2 and G3, respectively.

Figure 3-11 (cont'd)



The analysis presented above clearly points to a substantive difference in the nature of the excited states associated with the two observed absorption features of the Cu^{II} core in terms of their ability to engage in energy transfer from the Re-bpy' fluorophore. We therefore carried out a time-dependent DFT calculation on Cu(phacac)₂ in CH₂Cl₂ solution in order to obtain a more detailed theoretical description of these states. The transition energies, oscillator strengths, and orbital compositions of the four lowest energy excited states that are predicted from this calculation are listed in Table 3-6. The low oscillator strengths ($f_{calc} = 0.0000$) calculated for all four transitions are consistent with the Laporte-forbidden nature of d-d absorptions. The calculated transition energies along with the absorption spectrum of Cu(phacac), acquired in CH₂Cl₂ solution are plotted in Figure 3-12. The results of the calculation are in reasonably good agreement with experiment, which we take as an indication of the general validity of the

wavefunctions comprising these four absorptive features.

Table 3-6. Calculated Orbital Composition of the Lowest-Energy Spin Allowed Absorptions of Cu(phacac)₂ in CH₂Cl₂ solution.

	$E(cm^{-1})$	f_{calc}^{a}	orbital transitions $(c_i)^b$
Excited State 1 ^c	18,831	0.0000	$\begin{array}{c} 86\beta \to 108\beta \ (0.17) \\ 87\beta \to 108\beta \ (0.12) \\ 90\beta \to 108\beta \ (0.23) \\ 96\beta \to 108\beta \ (0.94) \\ 100\beta \to 108\beta \ (0.11) \end{array}$
Excited State 2 ^c	18,703	0.0000	$86\beta → 108\beta (0.23)$ $87\beta → 108\beta (0.31)$ $97\beta → 108\beta (0.92)$
Excited State 3 ^d	16,280	0.0000	86β → 108β (0.42) 87β → 108β (0.33) 90β → 108β (0.23) 100β → 108β (0.85)
Excited State 4 ^d	14,778	0.0000	$84\beta → 108\beta (0.17)$ $95\beta → 108\beta (0.62)$ $107\beta → 108\beta (0.75)$

^aCalculated oscillator strength. ^bc_i corresponds to the coefficient for the specific orbital transition in the calculated absorption feature. The contribution of each component to the total wavefunction is given by c_i . ^cExcited states 1 and 2 comprise the G2 transition of the deconvolved spectrum in Figure 3-11A. ^dExcited states 3 and 4 comprise the G3 transition of the deconvolved spectrum in Figure 3-11A.



Figure 3-12. The four lowest energy transitions of $Cu(phacac)_2$ determined from a TD-DFT calculation plotted against the ground state absorption spectrum of $Cu(phacac)_2$ in CH_2Cl_2 (black). The green and red dotted lines represent the G2- and G3-based transitions, respectively. The calculated oscillator strengths for all four transitions are zero (Table 3-6); the intensities of the calculated absorptions have therefore been arbitrarily scaled to facilitate comparison with the experimental spectrum.

GaussView renderings of the orbitals involved in the four calculated excited states are shown in Figure 3-13. Excited States 1 (18,831 cm⁻¹), 2 (18,703 cm⁻¹), and 4 (14,778 cm⁻¹) are dominated by $d_z^2 \rightarrow d_{xy}$ (96 $\beta \rightarrow$ 108 β), $d_{yz} \rightarrow d_{xy}$ (97 $\beta \rightarrow$ 108 β), and $d_{xz} \rightarrow d_{xy}$ (107 $\beta \rightarrow$ 108 β) ligandfield transitions, respectively. Excited State 3 (16,280 nm) has a small contribution from the 90 $\beta \rightarrow$ 108 β ($d_{x^2-y^2} \rightarrow d_{xy}$) transition, but is dominated by the 100 $\beta \rightarrow$ 108 β (73%) component that contains contributions from both charge-transfer and metal-centered excited states. A closer look at 100 β reveals a large metal-ligand bonding component to the wavefunction, along with density located solely on the Cu^{II} metal center buried within this bonding contribution. The metal-centered density suggests a significant fraction of d-d character exists in the $100\beta \rightarrow 108\beta$ transition, which would explain the lack of oscillator strength associated with Excited State 3. TD-DFT calculations were also performed on Cu(phacac)₂ in frozen D_{2h} symmetry in a CH₂Cl₂ environment in order to compare with the results from the minimized solution phase geometry. Results of the two TD-DFT analyses exhibited close correspondence in both energy ordering and orbital compositions for the four low-energy transitions, suggesting that the structure of Cu(phacac)₂ doesn't vary significantly between the solution phase and idealized geometries.



Excited State 4

Figure 3-13. Drawings of the orbitals involved in the lowest-energy spin allowed transitions of $Cu(phacac)_2$ based on a TD-DFT calculation. The coordinate system used is that shown in Figure 3-5 with the CuO_4 coordination environment drawn in the xy plane. See Table 3-6 for further details.

The analysis of the energy transfer dynamics of compounds 1 through 5 indicated a significant difference in the rate of energy transfer for coupling to the two absorption bands of the Cu^{II} absorption profile, a difference that appears to be linked to the dipole orientation factor κ^2 . At first glance this would seem to be an unlikely scenario given the metal-centered nature of ligand-field absorptions; as mentioned in the Introduction, d-d acceptor represent a nearly ideal manifestation of the point-dipole states approximation inherent to Förster theory. Fleming and co-workers have demonstrated how one can use density matrix formulations to obtain detailed representations of transition dipoles for energy transfer processes involving carotenoids.¹²³ The transition metal-based nature of the excited states involved in the present study makes an analogous approach difficult, however, visual inspection of the ground- and excited-state orbital configurations reveals two interesting features. A comparison of the calculated transition energies from TD-DFT with the Cu(phacac)₂ ground state absorption spectrum shows the higher energy G2 band is dominated by the 96 $\beta \rightarrow 108\beta$ (d_{z²} \rightarrow d_{xy}) and 97 $\beta \rightarrow 108\beta$ (d_{yz} \rightarrow d_{xy}) transitions, whereas the lower energy G3 band is comprised mainly of the $100\beta \rightarrow 108\beta$ and the $107\beta \rightarrow 108\beta$ (d_{xz} \rightarrow d_{xy}) transitions. One striking difference between these transitions is the lack of an x-axis component in the

wavefunctions corresponding to the occupied orbitals of the two highestenergy excited states. Ligand-field transitions – at least those arising from either d¹ or d⁹ configurations where a one-electron orbital picture can be invoked – can be thought of in terms of a transfer of charge between the different planes defined by the orbital's azithumal quantum number (m_l). In this regard, the transitions contributing to the G2 feature (d_{z²} \rightarrow d_{xy} and d_{yz} \rightarrow d_{xy}) will be distinct in a geometric sense from the d_{xz} \rightarrow d_{xy} transition that characterizes the lowest-energy feature in G3. Absent more detailed information it's difficult to quantify whether this should give rise to an increase or decrease in dipolar coupling to the Re¹-based excited state, but it seems reasonable to expect a difference.

A second distinction between the G2 and G3 bands that could be playing a role in the observed dynamics is the nature of Excited State 3. Despite its low oscillator strength and all indications from experimental data of its ligand-field nature,¹⁰³ Figure 3-13 illustrates that the $100\beta \rightarrow 108\beta$ transition is qualitatively different from the other three excited states comprising the visible absorption spectrum of Cu(phacac)₂. Based on the spatial distribution of orbital 100β there appears to be some charge-transfer character to this transition, although clearly not sufficient to impact the oscillator strength for the absorption. Nevertheless, the larger change in charge distribution associated with Excited State 3 could be having a subtle influence on the magnitude of the transition dipole, which in turn would enhance the rate of energy transfer when coupling to this state. It is interesting to note the fact that the G3 feature is composed of distinct excited states explains at least qualitatively why the value of κ^2 calculated from eq. 3-5a for compounds 4 and 5 was found to exceed the theoretical maximum of 4 (Table 3-5). Given the above analysis, each of these excited states should be viewed as an independent acceptor: coupling to both of these states as part of the overlap factor for G3 would therefore lead to an "effective" value of κ^2 (e.g., a sum of contributions) as opposed to the value one would calculate assuming a single donor-acceptor interaction. A more detailed theoretical treatment of this system would clearly be required in order to explore these ideas further.

3.5 Conclusions

The synthesis, structures, and photophysical properties of a series of covalently linked assemblies containing Re^I-bipyridyl donors and a Cu^{II}-acac acceptor have been described. Steady-state and time-resolved emission spectroscopies indicated that the strongly emissive Re^I-based ³MLCT excited-state was significantly quenched in the presence of the Cu^{II} center

relative to electronically benign Be^{ll} analogues. Favorable overlap between the donor emission and the visible absorption spectrum of the acceptor, coupled with a ca. 10 Å donor-acceptor separation and unfavorable driving forces for electron transfer, allowed for an assignment of Förster energy transfer as the dominant mechanism for excited-state reactivity in this system. A detailed examination of the rates of energy transfer across the series revealed that the degree of dipolar coupling between the donor and acceptor was not constant across the absorption envelope of the Cu^{II} acceptor, but instead exhibited preferential coupling to the lower-energy portion of the ligand-field manifold. Fitting the absorption spectrum of the Cu^{II} chromophore with a series of Gaussians allowed for a differential analysis of the spectral overlap that quantified differences in the dipole orientation factor κ^2 as the emission profile was tuned across the absorption spectrum of the acceptor. A TD-DFT analysis of the central Cu^{II} species revealed the composition of the Cu^{II}-based ligand-field acceptor states and permitted the identification of the specific molecular orbitals responsible for the dipolar energy transfer quenching as well as the likely origins of their distinct roles in energy transfer. This study, in addition to providing a unique example of orbitally-specific energy transfer, also illustrates the importance of considering the substructure of absorption bands in terms of its potential impact on dipolar energy transfer dynamics.

3.6 References and Notes

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Chapter 4. Confirming Förster Energy Transfer Involving Ligand-Field Acceptor States: CrRe₃ Complexes.

4.1 Introduction

The theoretical formalism of dipole-dipole energy transfer is described by the well-known Förster equation (equation 4-1), that elegantly relates experimental observables to the rate constant for energy transfer (k_{EnT}) :^{1,2}

$$k_{EnT} = C \frac{\kappa^2 k_r J}{R^6}$$
(4-1)

where C is a collection of constants, and κ^2 , k_r , J, and R are as defined previously (eq. 1-1). The spectral overlap integral (J) describes the resonance condition for energy transfer and is by far the most essential variable in the Förster equation, and is given in equation 4-2.

$$J = \int_{0}^{\infty} \frac{\overline{F}_{D}(\overline{\nu})\overline{\varepsilon}_{A}(\overline{\nu})}{\overline{\nu}^{4}} d(\overline{\nu})$$
(4-2)

The spectral overlap integral (J) quantifies the energetic correspondence between the donor emission and the acceptor absorption transition moment dipoles, and is described in detail in Chapter 1. The degree of spectral overlap is directly proportional to the magnitude of the Förster rate constant (k_{EnT}) , and must be non-zero in order for dipole-dipole energy transfer to be considered as a possible excited-state quenching pathway.

Results from the CuRe₂ assemblies presented in Chapter 3 showed that ligand-field acceptor states of $Cu(pyacac)_2$ (pyacac = 3-(4-pyridyl)-2,4pentanedione) can quench the ³MLCT (metal-to-ligand charge transfer) excited states of Re^I-polypyridyl donor complexes. The spectral overlap values between the Re^I donor emission spectra with the ligand-field absorption profile of Cu^{II} did not manifest a direct correlation with the magnitude of the energy transfer rate constants within the structurally homologous series. The ground state absorption spectrum of the d⁹ Cu^{II} core exhibits two broad absorption bands that are attributed to four spin-allowed ligand-field transitions,³ which did not allow for the spectral overlap integrals of each individual d-d transition with the Re¹ emission to be determined. The ground state absorption profile of $Cu(phacac)_2$ (phacac = 3-phenyl-2,4-pentanedione) was fit with a series of Gaussians in order to evaluate the spectral overlap of the individual Cu^{II}-based ligand-field acceptor states with the emission spectra of the Re¹-polypyridyl donor moieties. The trend in spectral overlap values with each of the Gaussians, along with computational efforts on Cu(phacac)₂ revealed that the throughspace orientation (κ^2) of the 3d orbitals relative to the ³MLCT donor

emission dipoles also play a role in the Förster energy transfer dynamics. In contrast to the four distinct orbital based transitions corresponding to the ligand-field bands of Cu^{II}, the ${}^{4}A_{2} \rightarrow {}^{4}T_{2}$ ligand-field absorption of Cr^{III} is characterized by a multielectronic wavefunction deriving from a single configuration (Figure 4-1).⁴



Figure 4-1. One electron-orbital description of the ${}^{4}A_{2} \rightarrow {}^{4}T_{2}$ electronic transition in Cr^{III}. This diagram depicts the electronic configurations from which the multielectronic wavefunction corresponding to the ${}^{4}A_{2}$ and ${}^{4}T_{2}$ are derived.

The focus of the work contained in this chapter is two fold, 1) utilize the nature of the Cr^{III} ligand-field transition to examine if the rate of ³MLCT emission quenching can directly correlate with the spectral overlap between ligand-field-type transitions and Re^I-based emission spectra and 2) utilize the emissive properties of Cr^{III} ligand-field excited states to provide unequivocal proof that the Re^I-based donor complexes undergo energy transfer dynamics with ligand-field acceptor states.

The synthesis, structure, and photophysical properties of a series of isostructurally related molecules, with the general formula

 $[Cr(pyacac)_3(Re(tmb)(CO)_3)_3](OTf)_3$ (1), $[Cr(pyacac)_3(Re(bpy)(CO)_3)_3]$ - $(OTf)_3$ (2), and $[Cr(pyacac)_3(Re(deeb)(CO)_3)_3](OTf)_3$ (3) (where pyacac = 3-(4-pyridyl)-acetylacetonate, tmb = 4,4'-5,5'-tetramethyl-2,2'-bipyridine, bpy = 2.2'-bipyridine, deeb = 4.4'-diethylester-2.2'-bipyridine, and OTf = CF_3SO_3) are described. The Cr^{III} metal centers are covalently attached to three fac-Re(bpy')(CO)₃ (bpy' = tmb, bpy, and deeb) moieties through three pyridyl-acetylacetonate bridging ligands (Figure 4-2). It was observed that the Re¹-based ³MLCT excited-states for complexes 1, 2, and 3 are significantly quenched in the presence of the Cr^{III} metal center relative to structurally analogous AlRe₃ analogues (complexes 4, 5, and 6 from Chapter 2). Varying the bpy' attached to the Re^I metal center permitted a systematic spectral overlap analysis with the Cr^{III} ligand-field absorption profile. Emission and excitation spectra for complex 2 and $Cr(phacac)_3$ were also acquired in frozen 4:1 EtOH/MeOH, the results of which serve to confirm quenching of the Re¹-based ³MLCT excited state by an energy transfer mechanism.



Figure 4-2. Structure of the $[M(pyacac)_3(Re(bpy')(CO)_3)_3](OTf)_3$ assemblies (where $M = Cr^{III}$ or Al^{III} and bpy' = tmb, bpy, or deeb).

4.2 Experimental Section

4.2.1 Synthesis and Characterization

General. All solvents used were purified and dried according to previously reported methods.⁵ Spectroscopic grade CH_2Cl_2 was used for all photophysical measurements; the solvent was dried under CaH_2 reflux until no water was detected by ¹H NMR and degassed using freeze-pump-thaw

techniques. 3-(4-pyridyl)-2,4-pentanedione,⁶ $Cr[N(SiMe_3)_2]_2(THF)_2$,⁷ Al(pyacac)₃,⁶ Re(tmb)(CO)₃(OTf),⁸ Re(bpy)(CO)₃(OTf),⁸ Re(deeb)(CO)₃-(OTf),⁸ and *fac*-[Re(bpy)(CO)₃(4-Etpy)](PF₆) (4-Etpy = 4-ethylpyridine)⁹ were prepared following literature procedures. The synthetic procedures for [Al(pyacac)₃(Re(tmb)(CO)₃)₃](OTf)₃ (4), [Al(pyacac)₃(Re(bpy)(CO)₃)₃]-(OTf)₃ (5), and [Al(pyacac)₃(Re(deeb)(CO)₃)₃](OTf)₃ (6) are reported in Chapter 2. 3-phenyl-2,4-pentanedione was purchased from TCI America. Elemental analyses and FT-IR data were obtained through the analytical facilities at Michigan State University. Mass spectra were obtained through the analytical facilities at The University of South Carolina.

 $[Cr(pyacac)_3(Re(tmb)(CO)_3)_3](OTf)_3$ (1). Preparation of $[Re(tmb)-(CO)_3(pyacac)](OTf)$ precursor was prepared as follows: 193 mg (0.306 mmol) of Re(tmb)(CO)_3(OTf) and 185 mg (1.04 mmol) of pyacac were dissolved in 40 mL of THF. The reaction solution was flushed with argon for 20 min and then refluxed for 6 hrs under argon. The volume of the reaction mixture was then reduced to 10 mL and hexanes were added to precipitate a yellow solid. The solid was then washed with ~ 100 mL of diethyl ether to remove excess pyacac, dried under vacuum overnight, and then used as is for the synthesis of compound 1. The synthesis of compound 1 is given as follows: 78 mg (0.151 mmol) of $Cr[N(SiMe_3)_2]_2(THF)_2$ was

dissolved in 5 mL of THF and cooled to -78° C in a N₂-filled drybox. 368 mg (0.455 mmol) of [Re(tmb)(CO)₃(pyacac)](OTf) in 20 mL of THF was added dropwise to the cold solution over 5 min. A light green precipitate was observed immediately upon addition, and the mixture was allowed to stir for 20 min. The reaction mixture was removed from the drybox and additional green solid was precipitated by addition of hexanes. The green precipitate was dissolved in ACN, filtered through celite, and the solvent removed under vacuum. The product was recrystallized several times from acetonitrile/ether (1:1 v/v). Yield: 166 mg (44%). Anal. Calcd for C₈₄H₇₈N₉F₉O₂₄S₃CrRe₃•2H₂O: C, 40.17; H, 3.29; N, 5.02. Found: C, 39.99; H, 3.56; N, 5.02. IR (KBr, v(CO) (cm⁻¹)): 2030 s, 1912 s, 1565 s, 1031 s, 638 m. MS: [ESI, m/z (rel. int.)]: 676 (100) {[Cr(pyacac)₃(Re(tmb)- $(CO)_{3}_{3}^{3+}, 1088.6 (33) \{ [Cr(pyacac)_{3}(Re(tmb)(CO)_{3})_{3}](OTf) \}^{2+}, 2326.3 (1) \}$ $\{ [Cr(pyacac)_3(Re(tmb)(CO)_3)_3](OTf)_2 \}^{1+}.$

 $[Cr(pyacac)_3(Re(bpy)(CO)_3)_3](OTf)_3$ (2). Preparation of the [Re-(bpy)(CO)_3(pyacac)](OTf) precursor was prepared as follows: 365 mg (0.634 mmol) of Re(bpy)(CO)_3(OTf) and 372 mg (2.10 mmol) of pyacac were dissolved in 40 mL of THF. The reaction solution was flushed with argon for 20 min and then refluxed for 4 hrs under argon. The volume of the reaction mixture was then reduced to 10 mL and hexanes were added to precipitate a yellow solid. The solid was then washed with $\sim 100 \text{ mL}$ of diethyl ether to remove excess pyacac, dried under vacuum overnight, and then used as is for the synthesis of compound 2. The synthesis of compound 2 is given as follows: 67 mg (0.130 mmol) of $Cr[N(SiMe_3)_2]_2(THF)_2$ was dissolved in 5 mL of THF and cooled to -78° C in a N₂-filled drybox. 294 mg (0.390 mmol) of [Re(bpy)(CO)₃(pyacac)](OTf) in 10 mL of THF was added dropwise to the cold solution over 5 min. A light green precipitate was observed immediately upon addition, and the reaction mixture was allowed to stir for 20 min. The mixture was removed from the drybox and additional green solid was precipitated by addition of hexanes. The green precipitate was dissolved in ACN, filtered through celite, and the solvent removed under vacuum. The product was recrystallized several times from acetonitrile/ether (1:1 v/v). Yield: 36 mg (12%). Anal. Calcd for C₇₂H₅₄N₉-F₉O₂₄S₃CrRe₃: C, 37.49; H, 2.36; N, 5.46. Found: C, 37.41; H, 2.50; N, 5.45. IR (KBr, v(CO) (cm⁻¹)): 2032 s, 1916 s, 1568 m, 1031 m, 638 m. MS: [ESI, m/z (rel. int.)]: 619.9 (63) {[Cr(pyacac)₃(Re(bpy)(CO)₃)₃]}³⁺, 1004.4 (14) $\{[Cr(pyacac)_3(Re(bpy)(CO)_3)_3](OTf)\}^{2+}, 2158 (1) \{[Cr(pyacac)_3(Re(bpy) (CO)_{3}_{3}(OTf)_{2}^{1+}$

[Cr(pyacac)₃(Re(deeb)(CO)₃)₃](OTf)₃ (3). Preparation of the [Re-(deeb)(CO)₃(pyacac)](OTf) precursor was prepared as follows: 165 mg

(0.230 mmol) of Re(deeb)(CO)₃(OTf) and 51 mg (0.288 mmol) of pyacac were dissolved in 40 mL of THF. The reaction solution was flushed with argon for 20 min and then refluxed for 12 hrs under argon. The volume of the reaction mixture was then reduced to 10 mL and hexanes were added to precipitate a yellow solid. The solid was then washed with $\sim 100 \text{ mL}$ of diethyl ether to remove excess pyacac, dried under vacuum overnight, and then used as is for the synthesis of compound 3. The synthesis of compound 3 is given as follows: 48 mg (0.092 mmol) of $Cr[N(SiMe_3)_2]_2(THF)_2$ was dissolved in 5 mL of THF and cooled to -78° C in a N₂-filled drybox. 248 mg (0.276 mmol) of [Re(deeb)(CO)₃(pyacac)](OTf) in 10 mL of THF was added dropwise to the cold solution over 5 min. A light green precipitate was observed immediately upon addition, and the reaction mixture was allowed to stir for 20 min. The mixture was removed from the drybox and additional green solid was precipitated by addition of hexanes. The green precipitate was dissolved in ACN, filtered through celite, and the solvent removed under vacuum. The product was recrystallized several times from acetonitrile/ether (1:1 v/v). Yield: 76 mg (30%). Anal. Calcd for $C_{90}H_{78}N_9F_9O_{36}S_3CrRe_{3} \cdot 1.5H_2OC$, 39.08; H, 2.95; N, 4.56. Found: C, 38.69; H, 3.18; N, 4.86. IR (KBr, v(CO) (cm⁻¹)): 2036 s, 1925 s, 1577 m, 1031m, MS: [ESI, m/z (rel. int.)]: 764.1 (16) {[Cr(pyacac)₃(Re(deeb)-638 m.
$(CO)_{3}_{3}]^{3+}$, 1220.6 (2) { $[Cr(pyacac)_{3}(Re(deeb)(CO)_{3})_{3}](OTf)\}^{2+}$, 2590.3 (0.5) { $[Cr(pyacac)_{3}(Re(deeb)(CO)_{3})_{3}](OTf)_{2}\}^{1+}$.

Tris(3-phenyl-acetylacetonato)chromium(III), Cr(phacac)₃. This compound has been previously synthesized by a different method.¹⁰ 269 mg (0.519 mmol) of Cr[N(SiMe₃)₂]₂(THF)₂ was dissolved in 15 mL of THF and cooled to -78°C in a N₂-filled drybox. 275 mg (1.56 mmol) of pyacac 10 mL of THF was added dropwise to the cold solution over 5 min. A deep green colored solution was observed immediately upon addition, which was allowed to stir for 20 min. The reaction mixture was removed from the drybox and a dark blue solid was precipitated by addition of hexanes. The blue precipitate was dissolved in CH₂Cl₂, filtered through celite, and the solvent removed under vacuum. The product was recrystallized from CH₂Cl₂/hexanes (1:1 v/v) and yielded purple crystals. Yield: 150 mg (50%). Anal. Calcd for C₃₃H₃₃O₆Cr: C, 68.62; H, 5.76. Found: C, 68.41; H, 5.71.

4.2.2 Physical Measurements

Electronic Absorption and Steady-State Emission Spectroscopies. Extinction coefficients for all compounds were acquired using a Varian Cary 50 UV-Visible spectrophotometer. All spectra were acquired in roomtemperature CH_2Cl_2 solution. Steady-state emission spectra were acquired using a Spex Fluoromax fluorimeter and corrected for instrumental response using a NIST standard of spectral irradiance (Optronic Laboratories, Inc., OL220M tungsten quartz lamp).¹¹ Spectra were acquired on samples dissolved in thoroughly degassed CH_2Cl_2 under optically dilute conditions (o.d. ~ 0.1) and sealed under an argon atmosphere in 1 cm path length quartz cuvettes.

Radiative quantum yields (Φ_r) were determined relative to *fac*-[Re(bpy)(CO)₃(4-Etpy)](PF₆) ($\Phi_r = 0.18$ in CH₂Cl₂).⁹ Quantum yields were calculated according to equation 4-2,

$$\Phi_{\rm unk} = \Phi_{\rm std} \, \frac{(I_{\rm unk}/A_{\rm unk})}{(I_{\rm std}/A_{\rm std})} \left(\frac{\eta_{\rm unk}}{\eta_{\rm std}}\right)^2 \tag{4-3}$$

where Φ_{unk} and Φ_{std} are the radiative quantum yields of the sample and the standard, respectively, I_{unk} and I_{std} represent the areas of the corrected emission profiles for the sample and the standard, A_{unk} and A_{std} are the absorbance values of the sample and the standard at the excitation wavelength, and η_{unk} and η_{std} correspond to the indices of refraction of the sample and standard solutions (taken to be equal to the neat solvents). Excitation wavelengths were 355 nm for the bpy and tmb analogs and 400 nm for the deeb analogs. The corrected excitation spectrum of *fac*-[Re(bpy)(CO)₃(4-Etpy)](PF₆) in CH₂Cl₂ compared favorably with the compound's absorption spectrum over the range of wavelengths examined

(355 - 400 nm), implying that the radiative quantum yield for *fac*-[Re(bpy)(CO)₃(4-Etpy)](PF₆) does not vary significantly over this spectral window. The reported value of $\Phi_r = 0.18$ was therefore used for determining the radiative quantum yields at both $\lambda_{ex} = 355$ nm and 400 nm.

Values for the zero-point energy gap (E_{00}) of the Re^I-based ³MLCT excited states were determined by fitting the emission profiles of complexes **4-6** based on the approach described by Claude and Meyer.¹² Wavelength data were converted to energy units following the correction of Parker and Rees;¹³ the best fit was determined by visual inspection of the results of a least-squares minimization routine.

Time-Resolved Emission Spectroscopy. Nanosecond time-resolved emission data for the AlRe₃ model complexes **4-6** were collected using a Nd:YAG-based laser spectrometer that has been described previously.¹¹ Data were acquired at room temperature in thoroughly degassed CH_2Cl_2 solutions having absorbances of ~0.1 at the excitation wavelengths. Samples were sealed under an argon atmosphere in 1 cm path length quartz cuvettes. The decay traces correspond to an average of 250 shots of the signal probed at the emission maximum of each compound.

Picosecond time-resolved emission data for the CrRe₃ complexes 1-3 were collected using a time-correlated single photon counting (TCSPC) apparatus that has been described previously.¹⁴ Data were acquired in thoroughly degassed CH_2Cl_2 solutions having absorbances of ~0.1 at the excitation wavelength. Samples were sealed under an argon atmosphere in 1 cm path length quartz cuvettes. Each reported decay trace corresponds to a signal average of three data sets, with each data set resulting from ca. 30 minutes of data acquisition time. Data were fit using the OriginPro 7.5 software package.¹⁵

Low-Temperature Spectroscopy. Low-temperature steady-state spectroscopic data were acquired using a Janis SVT-100 optical dewar. The experimental protocols that were employed have been described elsewhere.¹⁶

4.3 Results and Discussion

4.3.1 Synthesis and Characterization. Although the structural and redox properties of the Re¹-based multinuclear assemblies presented in this document strongly support energy transfer, the arguments have been based on exclusion of other possibilities as opposed to direct evidence. Observation of emission from an acceptor moiety involved in excited-state quenching dynamics is fairly bulletproof evidence of an operative energy transfer mechanism. None of the acceptor metal centers discussed thus far (Fe^{III} and Cu^{II}) exhibit emission characteristics, and therefore no

photophysical signatures have been observed to unequivocally prove energy transfer. Cr(acac)₃-type complexes show emission out of the ²E ligand-field excited state at low-temperature,⁴ which inspired the incorporation of Cr^{III} as an acceptor metal center in the Re^I-based donor-acceptor structural motifs.

The formation of the tetranuclear CrRe₃ assemblies, as with the FeRe₃ complexes reported in Chapter 2, was facilitated by the low steric crowding afforded by the 120° separation of the three pyacac ligands attached to the Cr^{III} center. ESI-MS data for complexes **1-3** in acetonitrile solution are consistent with the formation of the desired CrRe₃ assemblies. For example, complex **2** shows peaks corresponding to $[Cr(pyacac)_3(Re(bpy)(CO)_3)_3]^{3+}$, $[Cr(pyacac)_3(Re(bpy)(CO)_3)_3](OTf)^{2+}$, and $[Cr(pyacac)_3(Re(bpy)(CO)_3)_3]$. (OTf)₂¹⁺. The general robustness of the CrRe₃ complexes is also evidenced by the relative invariance of the steady-state emission intensity of complex **2** in CH₂Cl₂ solution over the course of several hours (vida infra), in stark contrast to what was observed for the FeRe₃ complexes described in Chapter **2**.

The v(CO) stretching bands of the Re(bpy')(CO)₃ moieties reported in the Synthesis and Characterization section (4.2.1) were assigned based on previously reported data for *fac*-[Re(4,4'-X₂-bpy)(CO)₃(4-Etpy)](PF₆) complexes.¹⁷ The characteristic spectral profile consists of two very intense peaks. The broad band at lower energy corresponds to two overlapping transitions assigned to the A'(2) and A" modes (C_s symmetry), whereas the sharper, higher energy band is assigned as A'(1).¹⁸ The similarity of the carbonyl frequencies observed for each CrRe₃/AlRe₃ pair is indicative of minimal direct electronic communication between the Re^I and Cr^{III} metal centers in the ground states of the CrRe₃ assemblies.¹⁹

4.3.2 Electronic Absorption Spectroscopy. The electronic absorption spectra of complexes 1-6 were acquired in room-temperature CH₂Cl₂ solutions; spectra for all 6 complexes are shown in Figure 4-3. The observed features were assigned based on previously reported analyses of Re^{I} polypyridyl absorption spectra. Re^{I} polypyridyl complexes exhibit a $^{1}A_{1}$ \rightarrow ¹MLCT (t_{2g} $\rightarrow \pi^{*}$ (bpy')) transition occurring from approximately 330 to 430 nm depending on the substituents of the bpy' ligand.^{20,21} The absorption profiles of the AlRe₃ compounds permitted analysis of the donor-based ¹MLCT transitions without overlapping transitions associated with the Cr^{III}containing systems (1-3). The absorption maximum for the ¹MLCT excitedstate reflects the electron donating/withdrawing ability of the bpy' substituents, with λ_{max} for complexes 4, 5, and 6 at occurring at 344 ($\epsilon =$ 18,500 M⁻¹cm⁻¹), 364 ($\epsilon = 11,500$ M⁻¹cm⁻¹), and 394 ($\epsilon = 14,300$ M⁻¹cm⁻¹) nm, respectively. As the substituents become progressively more electron donating (e.g., H for bpy and $(CH_3)_4$ for tmb) this feature systematically shifts to the blue and begins to overlap with the ligand-based absorptions in the ultraviolet (Figure 4-3).



Figure 4-3. Electronic absorption spectra of $[M(pyacac)_3(Re(bpy')-(CO)_3)_3](OTf)_3$ assemblies, where $M = Cr^{III}$ (red traces) and Al^{III} (blue traces). All spectra were acquired in room-temperature CH_2Cl_2 solution. A. $[Cr(pyacac)_3(Re(tmb)(CO)_3)_3](OTf)_3$ (1) and $[Al(pyacac)_3-(Re(tmb)(CO)_3)_3](OTf)_3$ (4). B. $[Cr(pyacac)_3(Re(bpy)(CO)_3)_3](OTf)_3$ (2) and $[Al(pyacac)_3(Re(bpy)(CO)_3)_3](OTf)_3$ (5). C. $[Cr(pyacac)_3(Re-(deeb)(CO)_3)_3](OTf)_3$ (3) and $[Al(pyacac)_3(Re(deeb)(CO)_3)_3](OTf)_3$ (6).

The presence of Cr^{III} in complexes 1-3 gives rise to a new, broad absorption feature on the high-energy side of the Re¹-based charge-transfer band. Figure 4-4 shows the absorption spectrum of Cr(phacac)₃ in roomtemperature CH₂Cl₂ which exhibits a strong transition centered at 390 nm assigned to a ${}^{4}A_{2} \rightarrow {}^{4}LMCT$ (π (acac) \rightarrow t_{2g}) transition. The ${}^{4}A_{2} \rightarrow {}^{4}LMCT$ absorption in complexes 1-3 is somewhat obscured by the ${}^{1}A_{1} \rightarrow {}^{1}MLCT$ band of the Re¹ chromophore, but a small shoulder is apparent in the three CrRe₃ absorption spectra (Figure 4-3). Figure 4-4 also shows a broad peak at 570 nm ($\epsilon = 113 \text{ M}^{-1}\text{ cm}^{-1}$) which is assigned to the ${}^{4}A_{2} \rightarrow {}^{4}T_{2}$ ligand-field transition of the Cr^{III} metal center. These assignments are based on the wellknown ground state absorption properties of Cr(acac)₃ derivatives.²²⁻²⁴



Figure 4-4. Electronic absorption spectrum of $Cr(phacac)_3$ acquired in room-temperature CH_2Cl_2 solution.

4.3.3 Steady-State and Time-Resolved Emission. Emission spectra for the CrRe₃ and AlRe₃ assemblies were obtained in room-temperature deoxygenated CH₂Cl₂ solution. As discussed in Chapter 2, the AlRe₃ complexes represent an ideal structural model for the dynamics associated with the Re^I based ³MLCT emission due to the inability of the Al^{III} ion to engage in either electron or energy transfer quenching. The emission profiles for the CrRe₃ and AlRe₃ complexes are given in Figure 4-5. The spectral profiles for both the Cr^{III}- and Al^{III}-containing complexes correspond to previously reported photophysical studies of Re¹ polypyridyl systems, with the emission originating from the ${}^{3}MLCT \rightarrow {}^{1}A_{1}$ phosphorescence.²⁵ The emission maximum for the tmb (526 nm), bpy (566 nm), and deeb (624 nm) derivatives reflect the electron donating and withdrawing behavior of the polypyridyl ligands. The radiative quantum yields (Φ_r) for complexes 1-6 were determined relative to $[(bpy)Re(CO)_3(4-$ Etpy)](PF₆) ($\Phi_r = 0.18$ in CH₂Cl₂) and are given in Table 4-1. The Φ_r values for the AlRe₃ model complexes, which were originally reported and discussed in Chapter 2, are comparable to the reported values for the corresponding mononuclear Re^I polypyridyl derivatives.⁸ As can be seen in Figure 4-5, the emission intensity for all three CrRe₃ complexes are significantly attenuated compared to the AlRe₃ model systems indicating extensive quenching of the Re^I-based ³MLCT excited-state. In addition, smaller radiative quantum yields (Φ_r) calculated for the CrRe₃ complexes (1-3) compared to the Al^{III} model complexes (Table 4-1) indicated significant quenching ³MLCT excited-state as well.

It should also be noted that Φ_r values for previously reported chromophore-quencher complexes of FeRe₃ (Chapter 2) and CuRe₂ (Chapter 3) were analytically unreliable due to small amounts of H₂O contained in the CH₂Cl₂ that caused slight dissociation of the complexes over time, which produced Re(bpy')(CO)₃(pyacac) species as emissive impurities. The emission intensity of complex 2 remained constant when monitored over the course of 4 hrs in CH₂Cl₂ solution (Figure 4-6), which attests to the robustness of the CrRe₃ complexes. Therefore, quantitative radiative quantum yield values for complexes 1-3 could be reported (Table 4-1).



Figure 4-5. Corrected steady-state emission spectra for $[M(pyacac)_3$. $(Re(bpy')(CO)_3)_3](OTf)_3$ assemblies, where $M = A1^{III}$ (blue traces) and Cr^{III} (red traces). **A.** $[A1(pyacac)_3Re(tmb)(CO)_3]_3](OTf)_3$ (**4**) and $[Cr(pyacac)_3(Re(tmb)(CO)_3)_3](OTf)_3$ (**1**). **B.** $[A1(pyacac)_3Re(bpy)-(CO)_3)_3](OTf)_3$ (**5**) and $[Cr(pyacac)_3(Re(deb)(CO)_3)_3](OTf)_3$ (**6**) and $[Cr(pyacac)_3(Re(deeb)(CO)_3)_3](OTf)_3$ (**6**) and $[Cr(pyacac)_3(Re(deeb)-(CO)_3)_3](OTf)_3$ (**3**). All six spectra were acquired in deoxygenated room-temperature CH_2Cl_2 solutions following excitation at 355 nm (complexes **1**, **2**, **4**, and **5**) and 400 nm (complexes **3** and **6**). For each plot, the emission profiles have been normalized with respect to the absorbance of each sample at its excitation wavelength. The relative magnitudes of the signals are therefore accurate representations of their relative intensities.



Figure 4-6. Corrected steady-state emission spectra for $[Cr(pyacac)_3-(Re(bpy)(CO)_3)_3](OTf)_3$ (2) monitored over the course of 4 hrs in room-temperature CH_2Cl_2 solution. The various emission traces are represented as follows: the initial spectrum (black trace), after 1 hr (red trace), after 2 hrs (blue trace), after 3 hrs (green trace), and after 4 hrs (orange trace).

Additional details concerning the excited states of the AlRe₃ and CrRe₃ complexes were obtained through nanosecond emission lifetime and time-correlated single photon counting (TCSPC) measurements. The nanosecond emission lifetime data in room-temperature CH₂Cl₂ solution for complexes **4**, **5**, and **6** were initially reported in Chapter 2, with $\tau_{obs} = 2260 \pm 100$, 560 \pm 30, and 235 \pm 20 ns, respectively. The corresponding radiative and non-radiative decay rate constants for **4**, **5**, and **6** are given in Table 4-1. As with the quantum yields, the observed excited-state lifetimes and rate constants are all consistent with Re¹-based ³MLCT \rightarrow ¹A₁ emission,^{8.26} which were discussed in Chapter 2.

The lack of discernable signal observed for the CrRe₃ systems during nanosecond lifetime experiments prompted the employment of timecorrelated single photon counting (TCSPC) methods. Plots of the TCSPC data obtained in room-temperature CH₂Cl₂ solution for the CrRe₃ complexes are shown in Figure 4-7. Complexes 1 and 2 could be fit with singleexponential models with $\tau_{obs} = 6.8 \pm 0.1$ ns and 4.8 ± 0.1 ns, respectively (Table 4-1). Complex 3 exhibited bi-exponential kinetics with lifetimes of $\tau_1 = 7.0 \pm 0.3$ ns and $\tau_2 = 190 \pm 15$ ns (Table 4-1). Due to the similar values of τ_2 and the AlRe₃ model complex (deeb, 6), the slower component is assigned to residual amounts of [Re(deeb)(CO)₃(pyacac)](OTf) starting material remaining after purification of complex 3. The signal-to-noise ratio for the three TCSPC data sets (1-3) are relatively poor owing to a combination of virtually complete quenching of the Re^I-based ³MLCT states coupled with radiative rate constants that are on the order of 10^5 s⁻¹. As can be seen from the ³MLCT lifetimes in the AlRe₃ and CrRe₃ compounds mentioned above, τ_{obs} for the three Al^{III} assemblies are significantly longer than what was observed for the Cr^{III} complexes, indicating that ³MLCT relaxation in complexes 1-3 is dominated by reaction with the Cr^{III} core.



Figure 4-7. Time correlated single-photon counting (TCSPC) data for the CrRe₃ complexes: **1** ($\tau_{obs} = 6.8 \pm 0.1$ ns), **2** ($\tau_{obs} = 4.8 \pm 0.2$ ns), and **3** ($\tau^{1} = 7.0 \pm 0.3$ ns) and $\tau^{2} = 190 \pm 15$ ns). All data were collected in deoxygenated room-temperature CH₂Cl₂ solution. The red solid lines correspond to fits to single-exponential decay models for **1** and **2**, and a bi-exponential decay model for **3** due to the presence of [Re(deeb)-(CO)₃(pyacac)](OTf) as an emissive impurity. See text for further details.

		E ₀₀		$k_{obs}(s^{-1})$	k _r	k _{nr}
complexes	λ_{max}	$(cm^{-1})^{a}$	Φ_{r}	$(\times 10^8 {\rm s}^{-1})$	$(\times 10^{6} \text{s}^{-1})^{b}$	$(\times 10^{6} \text{ s}^{-1})^{c}$
$CrRe_3$						
tmb (1)	526	19,700	0.024	1.5 ± 0.1	3.6 ± 0.2	150 ± 10
bpy(2)	566	18.600	0.009	2.1 ± 0.1	1.9 ± 0.1	210 ± 10
-FJ (-)						
deeb (3)	624	17 000	0.003	1.4 ± 0.1^{d}	0.48 ± 0.02	140 + 10
ucco (5)	024	17,000	0.005	1.7 ± 0.1	0.40 ± 0.02	140 ± 10
AIRes						
$tmh(4)^e$	526	10 000	0.51	0.0044	0.23 ± 0.01	0.22 ± 0.01
uno (4)	520	19,900	0.51	0.0044	0.23 ± 0.01	0.22 ± 0.01
	5//	10 700	0.16	0.010	0.00 + 0.01	15101
bpy (5)*	200	18,700	0.10	0.018	0.29 ± 0.01	1.5 ± 0.1
deeb $(6)^{\circ}$	624	16,800	0.07	0.043	0.30 ± 0.01	4.0 ± 0.2

Table 4-1. Photophysical Data of Complexes 1-6.

^aZero-point energy difference between ³MLCT excited state and ground state based on spectral fitting analysis. ^b $k_r = k_{obs} * \Phi_r$. ^c $k_{nr} = k_{obs} - k_r$. ^dValue reported is the faster component (τ_1) of the bi-exponential behavior observed in the TCSPC data for complex 3. See text for further details. ^cThese data were reproduced from Chapter 2 for comparison purposes.

4.4 Mechanistic Considerations

4.4.1 Electron versus Energy Transfer Quenching. Both electron and energy transfer processes can be envisioned to occur out of the Re^I-based ³MLCT excited state. Based on the presence of Cr^{III} in the ground states of the CrRe₃ complexes, electron transfer would proceed as either an oxidative quenching reaction to produce (bpy')Re^{II}—Cr^{II} or a reductive quenching

reaction to produce (bpy')Re^{II}-Cr^{IV}. Based on previously reported electrochemical data by Murray and Hiller on Cr(acac)₃,²⁷ a Cr^{IV} redoxproduct that would be produced in the reductive quenching mechanism would be highly unlikely and will not be discussed further. In order to determine if the oxidative quenching process is a thermodynamically viable mechanism in the $CrRe_3$ systems, the $Cr^{III} \rightarrow Cr^{II}$ reduction potential of $Cr(acac)_{3}^{27}$ the Re^I \rightarrow Re^{II} oxidation potentials for the AlRe₃ model complexes (4-6), and the zero-point energy gaps of the ${}^{3}MLCT$ states (E₀₀) determined from fits of the emission spectra of the corresponding CrRe₃ analogues (Table 4-1), were used to calculate the thermodynamic driving force for photoinduced electron transfer (ΔG^{ET}) in complexes 1-3.^{28,29} The calculated ΔG^{ET} values are all significantly uphill with values of +1.18 V (tmb, 1), +1.56 V (bpy, 2), and +1.87 V (deeb, 3). The large endothermic ΔG^{ET} values effectively rule out electron transfer as a viable ³MLCT quenching mechanism in the CrRe₃ series. It should also be noted that cyclic voltammetry on Cr(phacac)₃ in CH₂Cl₂ solution was performed with neither the $Cr^{III} \rightarrow Cr^{IV}$ oxidation or $Cr^{III} \rightarrow Cr^{II}$ reduction peaks observed in the solvent window, agreeing with the very large ΔG^{ET} values calculated from the $Cr(acac)_3$ literature values.

Direct experimental evidence for energy transfer in the CrRe₃ series was obtained from low-temperature emission spectroscopy. The lowest energy excited state of Cr(acac)₃-type complexes (the ²E ligand-field state) does not emit at room-temperature but exhibits a sharp emission spectrum with λ_{max} from approximately 750 to 850 nm in frozen solution.^{22} The narrowness of the band, which is assigned as the ${}^{2}E \rightarrow {}^{4}A_{2}$ emission, results minimal nuclear displacement associated from the with the intraconfigurational nature of the excited state.³⁰⁻³³ Figure 4-8 shows the emission spectrum of Cr(phacac)₃ in 4:1 EtOH/MeOH at 82 K that exhibits the sharp ${}^{2}E \rightarrow {}^{4}A_{2}$ emission. It should also be noted that this lowtemperature ${}^{2}E \rightarrow {}^{4}A_{2}$ emission of Cr(phacac)₃ represents the expected result of Förster energy transfer quenching of the ³MLCT donor state by the Cr^{III}based ${}^{4}A_{2} \rightarrow {}^{4}T_{2}$ ligand-field transition in the CrRe₃ series, and not by the ${}^{4}A_{2} \rightarrow {}^{2}E$ state. The extremely small spectral overlap calculation between Re^I-based emission and the spin-forbidden ${}^{4}A_{2} \rightarrow {}^{2}E$ transition negates the possibility of dipolar energy transfer coupling between the two states.



Figure 4-8. Steady-state emission spectrum of $Cr(phacac)_3$ in 4:1 EtOH/MeOH at 82 K following excitation at 375 nm.

As discussed above, observation of ${}^{2}E \rightarrow {}^{4}A_{2}$ emission from the Cr^{III} core (Figure 4-8) in the CrRe₃ assemblies would be direct experimental evidence for energy transfer quenching. Steady-state emission data for complex 2 in 4:1 EtOH/MeOH at 82 K is given in Figure 4-9. Based on the $Cr(phacac)_3$ emission spectrum shown in Figure 4-8, the resulting emission characteristics for complex 2 have been assigned to the Cr^{III} -based $^{2}E \rightarrow {}^{4}A_{2}$ transition. In order to distinguish between direct excitation of the Cr^{III}-based ${}^{4}A_{2} \rightarrow {}^{4}T_{2}$ absorption giving rise to the observed ${}^{2}E \rightarrow {}^{4}A_{2}$ emission, and ${}^{2}E_{-}$ based emission signal resulting from energy transfer dynamics in complex 2, the extinction coefficient values at $\lambda_{pump} = 375$ nm in CH₂Cl₂ were compared between complex 2 and Cr(phacac)₃. The comparison showed that $\sim 9\%$ of the 375 nm photons absorbed by complex 2 directly excite the $Cr(acac)_3$ core, while the rest are absorbed by the ${}^{1}A_{1} \rightarrow {}^{1}MLCT$ transition of the Re¹

donor. The red trace in Figure 4-9 represents the emission spectrum of complex 2 if only absorption by the Cr^{III} acceptor (9% contribution) was responsible for producing the ${}^{2}E \rightarrow {}^{4}A_{2}$ emissive photons (i.e. no energy transfer). The emission spectrum of complex 2 (black trace) clearly shows a much larger intensity than would be expected from simple Cr(acac)₃ excitation, which implicates energy transfer from the Re^I-based {}^{3}MLCT excited state into the Cr^{III} core as being responsible for the increase in ${}^{2}E \rightarrow {}^{4}A_{2}$ emission intensity.



Figure 4-9. The black trace is the corrected steady-state emission spectra of $[Cr(pyacac)_3(Re(bpy)(CO)_3)_3](OTf)_3$ (2) in 4:1 EtOH/MeOH at 82 K following excitation at 375 nm. The red trace corresponds to the intensity of the emission spectrum scaled by the relative absorbances of the Re^I-bpy and Cr^{III}(pyacac)_3 chromophores. See text for further details.

Additional evidence for excited state energy transfer was obtained by measuring the excitation spectrum of complex 2 at an energy corresponding to emission solely from the Cr^{III} fluorophores. Figure 4-10 shows the

absorption spectrum of complex 2 at 298 K along with the excitation spectrum of complex 2 at 82 K resulting from monitoring the Cr^{III}-based ²E \rightarrow ⁴A₂ emission maximum ($\lambda_{max} = 795$ nm). As can be seen in Figure 4-10, the overall shape of the absorption and excitation spectra are conserved, which demonstrates that emission produced from the ²E \rightarrow ⁴A₂ transition of the Cr^{III} center originates from both the Re^I-based ¹MLCT and Cr^{III}-based absorptions. These spectra provide additional evidence that the ²E \rightarrow ⁴A₂ emission results from energy transfer quenching of the Re^I-based ³MLCT excited state. A noticeable deviation in the two spectra are noted in the near UV region of Figure 4-10, and results from poor photon-to-current efficiency for the photo-diode employed to adjust for lamp fluctuations in excitation spectrum.



Figure 4-10. Ground-state absorption spectrum of $[Cr(pyacac)_3(Re-(bpy)(CO)_3)_3](OTf)_3$ (2) in 4:1 EtOH/MeOH solution at 298 K (black trace), and the excitation spectrum of 2 in 4:1 EtOH/MeOH at 82 K monitoring at $\lambda_{em} = 795$ nm (red trace).

4.4.2 Dexter vs Förster Energy Transfer. In light of the prohibitively large electron transfer driving forces and the low-temperature emission and excitation spectra for complex 2, the ³MLCT quenching in all three of the CrRe₃ assemblies has been assigned as excited-state energy transfer. The two most important mechanisms for energy transfer are electron superexchange (Dexter)³⁴ and through-space dipole-dipole coupling (Förster).³⁵ Dexter energy transfer is subject to a distance dependence that falls off as e^{-2R} due to its reliance on orbital overlap. As such, it is usually relegated to covalently linked systems in which the donor and acceptor are in close proximity (\leq 5 Å).^{36,37} Due to the structural and electronic similarities between the CrRe₃ series and the FeRe₃ assemblies (Chapter 2), Dexter energy transfer has been ruled out as a possible quenching mechanism in the CrRe₃ complexes. See the detailed comparison between the two energy transfer mechanisms given in Chapter 2 (2.4.2) for further details.

In addition to the similarities between the CrRe₃ and FeRe₃ assemblies mentioned above, the applicability of the Förster mechanism in the CrRe₃ series is supported by the moderate degree of spectral overlap that exists between the Re^I-based ³MLCT emission and the Cr^{III}-based ⁴A₂ \rightarrow ⁴T₂ absorption: this is depicted graphically in Figure 4-11. The overlap between the ${}^{3}MLCT \rightarrow {}^{1}A_{1}$ emission of the Al^{III}-containing tmb (4) (blue trace), bpy (5) (green trace), and deeb (6) (red trace) analogues with the ${}^{4}A_{2} \rightarrow {}^{4}T_{2}$ absorption of Cr(phacac)₃ (black trace) is shown, with the bpy derivative possessing the greatest amount of spectral overlap. The area ascertained from the product of the normalized emission profile of an AlRe₃ analogue with the extinction coefficient spectrum of Cr(phacac)₃ was used to calculate the reported spectral overlap values. Förster theory predicts that as the spectral overlap (J) increases across a structurally homologous series, the observed rate constant for energy transfer should increase by that same factor. The magnitude of spectral overlap (J) shows excellent agreement with the trend in k_{obs} values of the CrRe₃, with J values of 6.92 x 10⁻¹⁶ (k_{obs} = 1.5 x 10⁸ s⁻¹), 8.07 x 10⁻¹⁶ ($k_{obs} = 2.1 \times 10^8 \text{ s}^{-1}$), and 6.28 x 10⁻¹⁶ ($k_{obs} = 1.4 \times 10^8 \text{ s}^{-1}$) 10^8 s^{-1}) M⁻¹cm³ for the tmb (1), bpy (2), and deeb (3) analogs, respectively. It is quite clear that the overlap requirement in these systems is satisfied, which strongly implicates Förster transfer as the dominant quenching mechanism in the CrRe₃ complexes.



Figure 4-11. Overlay of the emission spectra of $[Al(pyacac)_3(Re(tmb)-(CO)_3)_3](OTf)_3$ (**4**, blue), $[Al(pyacac)_3(Re(bpy)(CO)_3)_3](OTf)_3$ (**5**, green), and $[Al(pyacac)_3(Re(deeb)(CO)_3)_3](OTf)_3$ (**6**, red) with the electronic absorption spectrum of Cr(phacac)_3. Data were acquired in room-temperature CH₂Cl₂ solution.

4.4.3 Comparison with the CuRe₂ Assemblies. A plot of the spectral overlap between the Re^I-based ³MLCT emission and the Cu^{II}-based ligand-field absorptions for the CuRe₂ assemblies was reported and discussed in Chapter 3 (Figure 3-10). The ground state absorption spectrum of Cu(phacac)₂ in CH₂Cl₂ solution shows a two-band structure, with these bands representing four discrete d-d transitions. Table 4-2 gives the spectral overlap integrals, energy transfer rate constants (k_{EnT}), and k_{EnT}/k_r values for the CuRe₂ and the CrRe₃ families. As discussed in Chapter 3, k_{EnT}/k_r values are used as the energy transfer rate constants due to variations in k_r for the Re^I donor moieties. Dividing k_{EnT} by k_r essentially normalizes out the variation in the radiative component and allows for sole evaluation of the

energy transfer coupling. As can be seen from Table 4-2, the differences in spectral overlap (J) among the CrRe₃ series directly corresponds to the observed trend in the k_{EnT}/k_r values, but an analogous correlation for the CuRe₂ series is not observed. In addition to spectral overlap considerations in the CuRe₂ series, variations in through-space coupling (κ^2) of the ³MLCT transition moment dipoles with the four separate ligand-field absorption dipoles of the Cu^{II} acceptor had to be taken into account to interpret the dipolar energy transfer dynamics (Chapter 3). It was found that the two CuRe₂ complexes possessing the lowest energy ³MLCT excited states (dclb and deeb) possess very favorable energetic (J) and through-space interactions (κ^2) with the lowest energy Cu^{II} d-d transition, which in turn yielded the fastest observed energy transfer rate constants for the two derivatives (Table 4-2). The direct dependence of the trend in k_{EnT}/k_r with the amount of spectral overlap seen for the CrRe₃ complexes essentially validates the analysis of the Cu^{II}-containing complexes presented in Chapter This validation comes from the fact that the ${}^{4}A_{2} \rightarrow {}^{4}T_{2}$ ligand-field 3. acceptor transition derives from a single configuration of the Cr^{III} ion, which results in identical through-space interactions with the three ³MLCT emission dipoles within the series and produces a direct spectral overlap dependence of the energy transfer rate constants.

		k _{EnT}	
compound	J ^a	$(\times 10^8 {\rm s}^{-1})^{\rm b}$	k_{EnT}/k_r
$[Cr(pyacac)_3(Re(tmb)(CO)_3)_3](OTf)_3 (1)$	6.92	1.50	650
[Cr(pyacac) ₃ (Re(bpy)(CO) ₃) ₃](OTf) ₃ (2)	8.07	1.70	718
[Cr(pyacac) ₃ (Re(deeb)(CO) ₃) ₃](OTf) ₃ (3)	6.28	1.40	452
$[Cu(pyacac)_2(Re(tmb)(CO)_3)_2](OTf)_2^{c}$	4.29	0.67	208
$[Cu(pyacac)_2(Re(dmb)(CO)_3)_2](OTf)_2^{c}$	5.14	1.18	295
$[Cu(pyacac)_2(Re(bpy)(CO)_3)_2](OTf)_2^{c}$	5.52	1.18	347
$[Cu(pyacac)_2(Re(dclb)(CO)_3)_2](OTf)_2^c$	6.68	1.71	658
$[Cu(pyacac)_2(Re(deeb)(CO)_3)_2](OTf)_2^{c}$	7.09	1.96	700

Table 4-2. Calculated Overlap Integral Values (J) and Energy TransferRate Constants for the CrRe3 and CuRe2 Complexes.

^aReported in units of 10^{-16} M⁻¹cm³. ^bk_{EnT} = k_{obs}(CrRe₃) - k_{obs} (AlRe₃). ^cThese data were reproduced from Chapter 3 for comparison purposes.

4.5 Conclusions

The synthesis and photophysical properties of a series of donoracceptor complexes based on Re^I-bpyridine donors and Cr^{III}-acac acceptors have been described. Steady-state and time-resolved emission spectroscopies indicated that the strongly emissive Re^I-based ³MLCT excited state was significantly attenuated when compared to model complexes in which the Cr^{III} center had been replaced by Al^{III}. Observation of enhanced ²E \rightarrow ⁴A₂ emission of the Cr^{III} acceptor in complex **2** in frozen 4:1 EtOH/MeOH unequivocally identified energy transfer as the ³MLCT quenching mechanism. The favorable overlap between the ³MLCT donor emission and the ${}^{4}A_{2} \rightarrow {}^{4}T_{2}$ acceptor absorption profile, coupled with a ca. 10 Å donor-acceptor separation, allowed for an assignment of Förster (dipolar) energy transfer as the dominant excited-state reaction mechanism. Lastly, enhancement of the Cr^{III} acceptor emission observed in complex **2** gives direct evidence for energy transfer as the ³MLCT excited state quenching mechanism assigned in all of the Re^I-based polynuclear donoracceptor assemblies discussed throughout this dissertation.

4.6 References and Notes

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Chapter 5. Spin Dependent Energy Transfer: CoRe₃ and NiRe₂ Complexes.

5.1 Introduction

The area of focus contained in this chapter is on understanding the role of electronic spin in determining the rate of excited-state energy transfer in polynuclear transition metal-based donor-acceptor complexes. In addition to possessing favorable thermodynamics, excited-state energy transfer reactions, just as in simple bimolecular reactions, must conserve the total spin angular momentum of the reactants and products throughout the course of the reaction. From vector physics, the possible total spin angular momentum $(|S_T|)$ values for a combination of two complexes with spins $|\overrightarrow{S_1}|_{\text{and}} |\overrightarrow{S_2}|_{\text{are}} |\overrightarrow{S_1} + \overrightarrow{S_2}|_{,} |\overrightarrow{S_1} + \overrightarrow{S_2} - 1|_{,...,} |\overrightarrow{S_1} - \overrightarrow{S_2}|_{.}$ For example, if $|\overline{S_1}| = 2$ and $|\overline{S_2}| = 1$ then the $|\overline{S_T}|$ values are 3, 2, and 1. A generic representation of an excited-state energy transfer reaction between an excited donor with $|\overline{S_D^*}|$ and a ground state acceptor with $|\overline{S_A}|$ is given in equation 5-1:

$$\left|\overrightarrow{\mathbf{S}_{\mathrm{D}}^{*}}\right| + \left|\overrightarrow{S_{A}}\right| \xrightarrow{k_{EnT}} \left|\overrightarrow{\mathbf{S}_{\mathrm{D}}}\right| + \left|\overrightarrow{S_{A}^{*}}\right|$$
(5-1)

In addition to favorable thermodynamics, the reaction defined by equation 5-

1 must possess a common $|\mathbf{S}_T|$ between the reactants and products. A classic example of spin conservation involved in energy transfer reactions is the quenching of ³MLCT (metal-to-ligand charge transfer) excited-states of low-spin d⁶ polypyridyl complexes.¹ Figure 5-1 illustrates total spin angular momentum conservation in an excited-state energy transfer reaction between

a d⁶ polypyridyl-based ³MLCT state ($|\overline{\mathbf{S}_{D}^{*}}| = 1$), which describes the excited state properties of the Re^I donors utilized throughout this dissertation, and an

 O_2 molecule that possesses a triplet ground state $(|\vec{S}_A| = 1)$. A $|\vec{S}_T|$ value of 1 is conserved between the reactant complexes and product complexes involved in the energy transfer process, indicated by the connecting arrow, and therefore the excited state reaction is spin-allowed. Investigating this fundamental property of excited-state reactivity utilizing transition metalbased donor-acceptor systems, will be the focus of this chapter.



Figure 5-1. Illustration of total spin angular momentum conservation in the energy transfer quenching of a ${}^{3}MLCT$ excited-state by O₂.

The first section of this chapter will focus on the synthesis and photophysical properties of a tetranuclear complex with the general formula $[Co(pyacac)_3(Re(bpy)(CO)_3)_3](OTf)_3$. The Co^{III} metal center is covalently attached to three fac-Re(bpy)(CO)₃ moieties through three pyridylacetylacetonate bridging ligands (Figure 5-2). It was observed that the relaxation dynamics of the Re¹-based ³MLCT excited-state in the CoRe₃ assembly is similar to a structurally analogous AlRe₃ model complex. Based on spectral overlap determinations, the ${}^{1}A_{1} \rightarrow {}^{1}T_{1}$ ligand-field state of the Co^{III} acceptor shows very favorable energetic matching with the Re^I-based ³MLCT donor emission, which indicates the Co^{III} ligand-field state should serve as an efficient quenching pathway out of the Re^I excited-state. These results contrast with the excited-state dynamics described in the previous chapter for the isostructural CrRe₃ complex - $[Cr(pyacac)_3(Re(bpy)(CO)_3)_3]$ -

(OTf)₃. The difference in reactivity can be explained by considering the role of spin conservation in the energy transfer reaction: whereas the ${}^{4}A_{2} \rightarrow {}^{4}T_{2}$ ligand-field transition of the Cr^{III} center in the CrRe₃ assembly yields a spinallowed energy transfer pathway out of the Re^I-based ³MLCT excited-state.

Evaluation of $|S_T|$ for excited-state energy transfer in the CoRe₃ system shows that coupling to the Co^{III}-based ${}^{1}A_{1} \rightarrow {}^{1}T_{1}$ ligand-field transition represents a *spin-forbidden* relaxation pathway. This represents the first example of an energy transfer reaction in which spin polarization is dictating reactivity.

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Figure 5-2. Structure of the CoRe₃ assembly.

The second section of this chapter will focus on the structural and photophysical properties of a chromophore-quencher molecule with the general formula $[Ni(pyacac)_2(THF)_2(Re(bpy)(CO)_3)_2](OTf)_2$ (where pyacac = 3-(4-pyridyl)-acetylacetonate, THF = tetrahydrofuran, bpy = 2,2'-bipyridine, and OTf = CF₃SO₃⁻). The Ni^{II} metal center is covalently attached to two *fac*-Re(bpy)(CO)₃ moleties through two pyridyl-acetylacetonate bridging ligands (Figure 5-3). The X-ray structural data for the NiRe₂ system shows two THF solvent molecules axially coordinated to the Ni^{II}
metal center that produces a pseudo-octahedral NiO₆ core (${}^{3}A_{2}$). It was observed that the Re^I-based ${}^{3}MLCT$ excited-state for the NiRe₂ assembly is significantly quenched when compared to an electronically benign BeRe₂ model complex. Based on spectral overlap considerations, the ${}^{3}A_{2} \rightarrow {}^{3}T_{2}$ ligand-field state of Ni^{II} was assigned as the thermodynamically viable quenching pathway for the Re^I-based ${}^{3}MLCT$ excited state. Measuring the ${}^{3}MLCT$ emission properties of the NiRe₂ compound in CH₂Cl₂ and in THF solutions revealed an axial ligand dissociation mechanism. The NiRe₂ assembly, and particularly chemistry associated with the Ni^{II} ion, represents an excellent example of the utility of basic coordination chemistry in controlling excited-state reactivity.



Figure 5-3. Structure of the NiRe₂ assembly.

5.2 Experimental Section

5.2.1 Synthesis and Characterization

General. All solvents used were purified and dried according to previously reported methods.² Spectroscopic grade CH₂Cl₂ was used for all photophysical measurements; the solvent was dried under CaH₂ reflux until no water was detected by ¹H NMR and the solvents used in the emission experiments were degassed using freeze-pump-thaw techniques. 3-(4pyridyl)-2,4-pentanedione,³ Ni(phacac)₂,⁴ and fac-[Re(bpy)(CO)₃(4-Etpy](PF₆)⁵ (4-Etpy = 4-ethylpyridine) were prepared following literature procedures. The synthetic procedure for [Re(bpy)(CO)₃(pyacac)](OTf) is presented in Chapter 4. The synthetic procedure for [Al(pyacac)₃(Re(bpy)- $(CO)_{3}_{3}(OTf)_{3}$ is presented in Chapter 2 and the synthetic procedure for $[Be(pyacac)_2(Re(bpy)(CO)_3)_2](OTf)_2$ is presented in Chapter 3. 3-phenyl-2,4-pentanedione was purchased from TCI America and Ni(1,5cyclooctadiene)₂ was purchased from Sigma-Aldrich. Elemental analyses and FT-IR data were obtained through the analytical facilities at Michigan State University. Mass spectra were obtained through the analytical facilities at The University of South Carolina.

 $[Co(pyacac)_3(Re(bpy)(CO)_3)_3](OTf)_3$. Amounts of 11 mg (0.04 mmol) of Co(acetate)_2•4H₂O and 98 mg (0.13 mmol) of $[Re(bpy)(CO)_3-$

(pyacac)](OTf) were dissolved in 10 mL of ethanol and heated at 100°C for 20 min in air. The reaction solution turned a dark green color and a yellowish precipitate formed in the solution. The green filtrate was collected, the solvent removed under vacuum, and the resulting green solid placed under vacuum overnight. The product was recrystallized several times from acetonitrile/ether (1:1 v/v). Yield: 25 mg (25%). Anal. Calcd for C₇₂H₅₄N₉F₉O₂₄S₃CoRe₃•2H₂O: C, 36.80; H, 2.49; N, 5.36. Found: C, 36.40; H. 2.47; N, 4.98. MS: [ESI, m/z (rel. int.)]: 622.3 (5) $\{[Co(pyacac)_3(Re(bpy)(CO)_3)_3]\}^{3+}, 1007.9 (2) \{[Co(pyacac)_3(Re(bpy) (CO)_{3}_{3}(OTf)^{2+}$

[Ni(pyacac)₂(Re(bpy)(CO)₃)₂](OTf)₂. In 30 mL of THF were dissolved 285 mg (0.379 mmol) of [Re(bpy)(CO)₃(pyacac)](OTf) in a N₂filled drybox. 52 mg (0.189 mmol) of Ni(1,5-cyclooctadiene)₂ were then added and the solution turned a deep red color, along with the formation of a green precipitate. The reaction mixture was allowed to stir for 24 hrs in the drybox, after which time the reaction mixture was removed from the drybox and the green precipitate collected. The green solid was washed with THF, placed under vacuum overnight, and then recrystallized several times from acetontrile/ether (1:1 v/v) to yield the product. X-ray quality crystals were obtained by slow diffusion of THF into an acetonitrile solution of the compound. Yield: 41 mg (14%). Anal. Calcd for $C_{48}H_{36}N_6F_6O_{16}S_2NiRe_2$: C, 36.91; H, 2.32; N, 5.38. Found: C, 35.86; H, 2.61; N, 4.99. IR (KBr, v(CO) cm⁻¹): 2033 s, 1922 s. MS: [ESI, m/z (rel. int.)]: 632.0 (35) {[Ni(pyacac)_2(Re(bpy)(CO)_3)_2]}²⁺, 1413.0 (1) {[Ni(pyacac)_2(Re(bpy)-(CO)_3)_2]}¹⁺.

Tris(3-phenyl-acetylacetonato)cobalt(III), Co(phacac)₃. The synthesis of this compound has been previously reported by a different method.⁶ Amounts of 85 mg (0.534 mmol) of $Co(acetate)_2 \cdot 4H_2O$ and 205 mg (1.16 mmol) of phacac were dissolved in 10 mL of H₂O and heated at 100°C for 20 min in air. A dark green precipitate that formed in the reaction solution was collected, washed with water, and recrystallized from hot ethanol. Yield: 100 mg (50%). Anal. Calcd for C₃₃H₃₃O₆Co•0.3EtOH: C, 67.45; H, 5.86. Found: C, 67.05; H, 5.45.

5.2.2 Physical Measurements

X-ray Structure Determinations. Single-crystal X-ray diffraction data for [Ni(pyacac)₂(THF)₂(Re(bpy)(CO)₃)₂](OTf)₂ were acquired at the Xray facility of Michigan State University. Diffraction data were collected on a Siemens SMART diffractometer with graphite-monochromatic Mo K α radiation ($\lambda = 0.71073$ Å). Data were collected at -100 °C by using an Oxford Cryosystems low temperature device. Crystallographic data are summarized

in Table 5-1; selected bond distances and angles are listed in Table 5-2. Lattice parameters were obtained from least-squares analyses and data were integrated with the program SAINT.⁷ The integration method employed a three dimensional profiling algorithm and all data were corrected for Lorentz and polarization factors, as well as for crystal decay effects. The absorption correction program SADABS⁸ was employed to correct the data for absorption effects. The structures were solved by direct methods and expanded using Fourier techniques. All structure calculations were performed with the SHELXTL 6.12 software package.⁹ Anisotropic thermal parameters were refined for all non-hydrogen atoms. Hydrogen atoms were localized in their calculation positions and refined by using the riding model. Further details concerning the structure determinations may be found in Supporting Information.

Electronic Absorption and Steady-State Emission Spectroscopies. Extinction coefficients for all compounds were acquired in CH_2Cl_2 solutions using a Varian Cary 50 UV-Visible spectrophotometer. Steady-state emission spectra were acquired using a Spex Fluoromax fluorimeter and corrected for instrumental response using a NIST standard of spectral irradiance (Optronic Laboratories, Inc., OL220M tungsten quartz lamp).¹⁰ Spectra were acquired on samples dissolved in thoroughly degassed CH_2Cl_2 under optically dilute conditions (o.d. ~ 0.1) and sealed under an argon atmosphere in 1 cm path length quartz cuvettes.

Radiative quantum yields (Φ_r) were determined relative to *fac*-[Re(bpy)(CO)₃(4-Etpy)](PF₆) ($\Phi_r = 0.18$ in CH₂Cl₂).⁵ Quantum yields were calculated according to equation 5-2,

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

where Φ_{unk} and Φ_{std} are the radiative quantum yields of the sample and the standard, respectively, I_{unk} and I_{std} represent the areas of the corrected emission profiles for the sample and the standard, A_{unk} and A_{std} are the absorbance values of the sample and the standard at the excitation wavelength, and η_{unk} and η_{std} correspond to the indices of refraction of the sample and standard solutions (taken to be equal to the neat solvents). An excitation wavelength of 355 nm was used for all the compounds studied in this chapter.

Time-Resolved Emission Spectroscopy. Nanosecond time-resolved emission data for $[Co(pyacac)_3(Re(bpy)(CO)_3)_3](OTf)_3$, $[Al(pyacac)_3(Re-(bpy)(CO)_3)_3](OTf)_3$, and $[Be(pyacac)_2(Re(bpy)(CO)_3)_2](OTf)_2$ were collected using a Nd:YAG-based laser spectrometer that has been described previously.¹⁰ Data were acquired at room temperature in thoroughly degassed CH₂Cl₂ solutions having absorbances of ~0.1 at $\lambda_{ex} = 355$ nm. Samples were sealed under an argon atmosphere in 1 cm path length quartz cuvettes. The decay traces correspond to an average of 250 shots of the signal probed at the emission maximum of each compound.

Picosecond time-resolved emission data for $[Ni(pyacac)_2(THF)_2(Re-(bpy)(CO)_3)_2](OTf)_2$ were collected using a time-correlated single photon counting (TCSPC) apparatus that has been described previously.¹¹ Data were acquired in thoroughly degassed CH₂Cl₂ solutions having absorbances of ~0.1 at $\lambda_{ex} = 370$ nm. The sample was sealed under an argon atmosphere in 1 cm path length quartz cuvette. The reported decay trace corresponds to a signal average of three data sets, with each data set resulting from ca. 30 minutes of data acquisition time. Data were fit using the OriginPro 7.5 software package.¹²

5.3 Results and Discussion for [Co(pyacac)₃(Re(bpy)(CO)₃)₃](OTf)₃

5.3.1 Synthesis and Characterization. The interest in the CoRe₃ system was to synthesize a donor-acceptor complex with similar overall charge and structural characteristics to the CrRe₃ compounds presented in Chapter 4. The ${}^{4}A_{2} \rightarrow {}^{4}T_{2}$ ligand-field acceptor state of Cr^{III}(acac)₃ is replaced by a ${}^{1}A_{1} \rightarrow {}^{1}T_{1}$ transition in the case of the CoRe₃ system, allowing the comparison

of energy transfer rates simply on the differences in spin-state associated with the acceptor.

As with the FeRe₃ (Chapter 2) and CrRe₃ (Chapter 4) complexes, the formation of the tetranuclear CoRe₃ assembly was facilitated by the low steric crowding afforded by the 120° separation of the three pyacac ligands attached to the Co^{III} center. ESI-MS data for $[Co(pyacac)_3(Re(bpy)-(CO)_3)_3](OTf)_3$ in acetonitrile solution are consistent with the formation of the desired complex, with m/z peaks observed for $[Co(pyacac)_3(Re(bpy)-(CO)_3)_3]^{3+}$ and $[Co(pyacac)_3(Re(bpy)(CO)_3)_3]^{2+}$.

5.3.2 Electronic Absorption Spectroscopy. The electronic absorption spectra of $[Co(pyacac)_3(Re(bpy)(CO)_3)_3](OTf)_3$ and $[Al(pyacac)_3(Re(bpy)-(CO)_3)_3](OTf)_3$ were acquired in room-temperature CH_2Cl_2 solutions and are shown in Figure 5-4. Transitions associated with the Al^{III} complex were assigned in Chapter 2, with the shoulder centered at 360 nm assigned to the Re^{I} -based ${}^{I}A_{I} \rightarrow {}^{I}MLCT$ ($t_{2g} \rightarrow \pi^{*}$ (bpy')) transition (Figure 5-4). The AlRe₃ complex allows for analysis of the ground-state absorption behavior of the Re^{I} donor moieties without overlapping with the Co^{III} -based charge-transfer transitions associated with the CoRe₃ assembly.



Figure 5-4. Electronic absorption spectra of $[Co(pyacac)_3(Re(bpy)-(CO)_3)_3](OTf)_3$ (red trace) and $[Al(pyacac)_3(Re(bpy)(CO)_3)_3](OTf)_3$ (blue trace) acquired in room-temperature CH_2Cl_2 solution.

The presence of Co^{III} in the CoRe₃ complex gives rise to a new, broad absorption feature occurring at approximately 340 nm and overlapping with the Re^I-based charge transfer band (Figure 5-4). Figure 5-5 (*Top*) shows the absorption spectrum of Co(phacac)₃ that exhibits the 340 nm transition which is assigned to a ${}^{1}A_{1} \rightarrow {}^{1}LMCT$ (π (acac) \rightarrow e^{*}_g) transition. Co(phacac)₃ also possesses a transition at $\lambda_{max} = 605$ nm (Figure 5-5, *Bottom*) with a measured extinction coefficient of 193 M⁻¹cm⁻¹. This band is easily assigned to the ${}^{1}A_{1} \rightarrow {}^{1}T_{1}$ transition, the lowest-energy spin-allowed d-d band of a pseudo-octahedral Co^{III} species.^{6,13} It should also be noted that the ${}^{1}A_{1} \rightarrow {}^{1}T_{1}$ transition occurs at approximately the same energy as the ${}^{4}A_{2}$ $\rightarrow {}^{4}T_{2}$ transition of Cr(phacac)₃ reported in Chapter 4, and should have similar spectral overlap with ³MLCT emission of the Re^I-bpy fluorophore.

Comparing the effect on the rate of ${}^{3}MLCT$ relaxation incurred by the Co^{III} and Cr^{III} ligand-field acceptor states will be the focus of the discussion section.



Figure 5-5. Top. Electronic absorption spectrum of Co(phacac)₃ showing the higher energy charge transfer and organic-based transitions. *Bottom.* Electronic absorption spectrum of a concentrated solution of Co(phacac)₃ showing the mid-visible ${}^{1}A_{1} \rightarrow {}^{1}T_{1}$ ligand-field transition. Both spectra were acquired in room-temperature CH₂Cl₂ solution.

Figure 5-5 (cont'd)



5.3.3 Time-Resolved Emission. Insight into the Re^I-based ³MLCT excited state relaxation behavior of the CoRe₃ and AlRe₃ complexes were obtained through nanosecond emission lifetime measurements. Nanosecond timeemission data in room-temperature CH₂Cl₂ solution for resolved $[Al(pyacac)_3(Re(bpy)(CO)_3)_3](OTf)_3$ and $[Co(pyacac)_3(Re(bpy)(CO)_3)_3]$ -(OTf)₃ are given in Figure 5-6. As discussed in Chapter 2, emission from the AlRe₃ complex could be fit to a single-exponential model with $\tau_{obs} = 530$ \pm 20 ns, with corresponding radiative (k_r) and non-radiative (k_{nr}) decay rate constants of $3.0 \pm 0.1 \times 10^5 \text{ s}^{-1}$ and $1.6 \pm 0.1 \times 10^6 \text{ s}^{-1}$, respectively, corresponding to ground-state recovery for the Re¹-based ³MLCT excited state. The time-resolved emission data for $[Co(pyacac)_3(Re(bpy)(CO)_3)_3]$ -(OTf)₃ could likewise be fit to a single-exponential model with τ_{obs} = 595 ± The ³MLCT emission lifetime in the CoRe₃ assembly is ~ 60 ns 20 ns.

longer than the electronically benign AlRe₃ model compound. The slightly longer observed time constant is not completely understood, but the data do illustrate the absence of ³MLCT quenching in the CoRe₃ system. Additional CoRe₃ material needs to be synthesized and the time constants re-measured before the longer emission lifetime in the CoRe₃ complex can be scrutinized.



Figure 5-6. *Left.* Nanosecond time-resolved emission data for [Al-(pyacac)₃(Re(bpy)(CO)₃)₃](OTf)₃ ($\tau_{obs} = 530 \pm 20$ ns). The data were originally presented in Chapter 2 and are reproduced here for comparison purposes. *Right.* Nanosecond time-resolved emission data for [Co(pyacac)₃(Re(bpy)(CO)₃)₃](OTf)₃ ($\tau_{obs} = 595 \pm 20$ ns). Both traces (Al and Co) were acquired in deoxygenated room-temperature CH₂Cl₂ solution monitoring at the emission maximum (565 nm). The solid red lines correspond to fits to mono-exponential decay models for both complexes.

5.3.4 Spin-Dependent Dipolar Energy Transfer. As mentioned in the Introduction, in addition to possessing a downhill thermodynamic driving force (i.e. spectral overlap), the total spin angular momentum must be conserved during an energy transfer event. In Chapter 4, significant

quenching of the Re^I-based ³MLCT excited state was observed for a

structurally similar CrRe₃ complex ($\tau_{obs}^{^{3}MLCT} = 4.8 \pm 0.1$ ns) that possesses a similar ligand-field absorption profile and maximum as the CoRe₃ assembly, and therefore should produce similar spectral overlap with the ³MLCT emission profile and manifest corresponding rates of ³MLCT relaxation. The similarity in emission lifetimes between the CoRe₃ and AlRe₃ complexes indicates that the Co^{III} center is **not** engaging in excitedstate reactivity with the Re¹-based ³MLCT state, even though Förster energy transfer quenching is thermodynamically favorable due to a significant amount of spectral overlap observed between the ${}^{1}A_{1} \rightarrow {}^{1}T_{1}$ ligand-field transition of Co(phacac)₃ and the Re^I-based ³MLCT donor emission spectrum (Figure 5-7). The only differing characteristic that could be giving rise to the large variance observed for the ³MLCT relaxation kinetics between the CoRe₃ and CrRe₃ assemblies is the spin-state of the Co^{III} $({}^{1}A_{1})$ and $Cr^{III}({}^{4}A_{2})$ metal centers.



Figure 5-7. Overlay of the emission spectrum of [Al(pyacac)₃(Re(bpy)-(CO)₃)₃](OTf)₃ (blue trace) with the electronic absorption spectrum of Co(phacac)₃ (red trace).

Figure 5-8 shows spin conservation diagrams between the Re^I-based ³MLCT excited state with the Cr^{III} (*Top*) and Co^{III} (*Bottom*) acceptor cores in the CrRe₃ and CoRe₃, respectively. The Cr^{III} ground state in the CrRe₃ complex is ⁴A₂ ($|\vec{S}_A| = 3/2$), and when coupled with the ³MLCT excited state of the Re^I donor ($|\vec{S}_D^{+}| = 1$) generates total spin angular momentum ($|\vec{S}_T|$) values of 5/2, 3/2, and 1/2. As an energy transfer (EnT) reaction occurs out of the Re^I-based ³MLCT excited state to produce the Cr^{III}-based ⁴A₂ \rightarrow ⁴T₂ ligand-field transition, an $|\vec{S}_T| = 3/2$ is generated on the products side of the diagram from the coupling of the resulting Re^I ground state

 $(|\mathbf{S}_D| = 0)$ with the Cr^{III}-based ${}^{4}T_2$ excited state $(|\mathbf{S}_A^{*}| = 3/2)$. As can been seen in Figure 5-8, an $|\mathbf{S}_T|$ value of 3/2 between the reagents and the products is conserved, which provides the spin-allowed energy transfer pathway.

Conversely, Figure 5-8 (Bottom) shows the corresponding process for the CoRe₃ assembly. The Co^{III} ground state in the CoRe₃ complex is ${}^{1}A_{1}$ $(|S_A| = 0)$, and when coupled with the ³MLCT excited state of the Re¹ donor $(|\mathbf{S}_{D}^{*}| = 1)$ generates a total spin angular momentum $(|\mathbf{S}_{T}|)$ value of 1 on the reagents side. The acceptor state of the Co^{III} ion is the ${}^{1}A_{1} \rightarrow {}^{1}T_{1}$ ligand-field state ($|S_A^*| = 0$), and when coupled with the Re^I ground state $(|\mathbf{S}_D| = 0)$ an $|\mathbf{S}_T| = 0$ is produced on the products side. As can be seen in Figure 5-8 (*Bottom*), a mutual $|\overline{\mathbf{S}_T}|$ value between the reagents $(|\overline{\mathbf{S}_T}| = 1)$ and the products $(|S_T| = 0)$ is not conserved, therefore the energy transfer reaction is spin-forbidden. The spin statistics outlined in Figure 5-8 illustrates the theoretical framework behind the shorter ³MLCT emission

lifetime observed in the CrRe₃ complex compared to the CoRe₃ assembly. The results discussed throughout this section highlight the control one can have on excited-state reactivity by simply changing the spin state of a single reagent.

$$EnT$$
 (bpy)Re^I Cr^{III}
 EnT
 (bpy)Re^I (Cr^{III})*

 $S_D = 1$
 $S_A = 3/2$
 $S_D = 0$
 $S_A = 3/2$
 $S_T = 5/2, 3/2, 1/2$
 $S_T = 3/2$

$$(bpy)Re^{II} \sim Co^{III} \qquad \xrightarrow{EnT} \qquad (bpy)Re^{I} \sim (Co^{III})^*$$

$$S_D = 1 \qquad S_A = 0 \qquad S_D = 0 \qquad S_A = 0$$

$$S_T = 1 \qquad S_T = 0$$

Figure 5-8. *Top.* Spin conservation diagram illustrating the spinallowed energy transfer pathway between the ³MLCT excited-state of the Re¹ donor and the Cr¹¹¹ acceptor. *Bottom.* Spin conservation diagram illustrating the spin-forbidden pathway between the ³MLCT excitedstate of the Re¹ donor and the Co¹¹¹ acceptor.

5.4 Results and Discussion for [Ni(pyacac)₂(THF)₂(Re(bpy)(CO)₃)₂]-(OTf)₂

5.4.1 Synthesis and Characterization. The interest in the NiRe₂ complex was to explore the effect solvent coordination can play on Förster energy transfer dynamics in covalently attached donor-acceptor complexes, and whether the rate of energy transfer can be controlled by simply varying the coordination strength of the solvent. Unlike the square-planar Cu^{II}(acac)₂ center utilized in the CuRe₂ series (Chapter 3), square-planar Ni^{II}(acac)₂ possesses a large propensity to bind molecules in the axial positions.¹⁴⁻¹⁷ These solvent interactions change the ligand-field environment from 4- to 6- coordinate, and more importantly to the work in this chapter, the spin-state of the Ni^{II} center.¹⁸

The formation of the trinuclear NiRe₂ assembly was facilitated by the low steric crowding afforded by the 180° separation of the two pyacac ligands attached to the Ni^{II} center. ESI-MS data for [Ni(pyacac)₂(THF)₂(Re-(bpy)(CO)₃)₂](OTf)₂ in acetonitrile solution are consistent with the formation of the desired complex, with m/z peaks observed for [Ni(pyacac)₂(Re-(bpy)(CO)₃)₂]²⁺ and [Ni(pyacac)₂(Re(bpy)(CO)₃)₂](OTf)¹⁺, corresponding to the loss of the two axial THF ligands during the course of the measurement. X-ray quality crystals were generated by diffusion of THF into an

acetonitrile solution of the compound over the course of approximately one week, which provides evidence for the general robustness of the complex in solution. In addition, the steady-state emission intensity of the NiRe₂ system in THF solution remained constant when monitored over the course of 5 hrs, which proves the compound remains intact during the duration of the various photophysical measurements that will be presented.

The v(CO) stretching bands of the Re(bpy)(CO)₃ moiety reported in Section **5.2.1** were assigned based on previously reported data for the *fac*-[Re(bpy)(CO)₃(4-Etpy)](PF₆) complex.¹⁹ The characteristic spectral profile consists of two very intense peaks. The broad band at lower energy corresponds to two overlapping transitions assigned to the A'(2) and A" modes (C_s symmetry), whereas the sharper, higher energy band is assigned as A'(1).²⁰ The similarity of the carbonyl frequencies observed in the NiRe₂/BeRe₂ pair is indicative of minimal direct electronic communication between the Re¹ and Ni¹¹ metal centers in the ground states of the NiRe₂ assemblies.²¹

5.4.2 Single-Crystal X-ray Structures. X-ray quality crystals were obtained for $[Ni(pyacac)_2(THF)_2(Re(bpy)(CO)_3)_2](OTf)_2$. The NiRe₂ assembly crystallizes in the triclinic space group P-1. Crystallographic details are given in Table 5-1 with selected bond distances and angles for the

two complexes listed in Table 5-2. A square-planar coordination environment about the central metal ion (Figure 5-9) is formed from the four oxygen atoms of the acac ligands lying in the equatorial plane. The Ni-O bond distances of 1.971 ± 0.005 and 1.981 ± 0.005 Å and a 0.0 Å meanplane deviation of the Ni^{II} ion from the O₄ plane are both consistent with square-planar Ni^{II} and compare favorably with other structurally characterized examples of Ni^{II}-acac systems.^{4,22} The structure of the NiRe₂ assembly also shows Ni-O (THF) distances of 2.155 ± 0.006 Å corresponding to axial bonding of THF molecules to the Ni^{II} core. The axial Ni–O distances are similar to Ni(acac)₂(H₂O)₂,²³ which indicates the two axial interactions represent true covalent metal-ligand interactions. The internal geometries of the Re(bpy)(CO)₃ moieties exhibit the classic pseudo- C_{3v} coordination environment common to Re^I complexes in this class.²⁴⁻²⁶ Lastly, the Re^I•••Ni^{II} distances (9.868 Å) are similar to the Re^I•••M distances reported for the FeRe₃ (Chapter 2) and CuRe₂ (Chapter 3) complexes, which will manifest similar through-space donor-acceptor interactions in the NiRe₂ assembly as has been discussed for the previous MRe_x (x = 2 or 3) complexes.

formula	$C_{56}H_{52}N_6F_6O_{18}S_2NiRe_2$
M _w	1706.26
cryst syst	triclinic
space group	P-1
T/K	173(2)
a/Å	11.220(2)
b/Å	11.819(2)
c/Å	15.737(2)
a/°	80.188(9)
β/°	72.111(9)
· γ/°	68.904(8)
V/Å ³	1848.7(5)
Ζ	1
$D_c/g \text{ cm}^{-1}$	1.800
$2\theta_{max}$	57
reflns measured	9762
independent reflns	6125
observed reflns $[I > 2\sigma(I)]$	4075
μ (Mo K α)/cm ⁻¹	3.738
R _{int}	0.0775
R1 ^a	0.0509
wR2 ^b	0.1351
GOF	0.995

Table 5-1. Crystallographic Data for [Ni(pyacac)₂(THF)₂(Re(bpy)-(CO)₃)₂](OTf)₂.

 $\overline{{}^{a}R1 = \Sigma ||F_{o}| - |F_{c}||/\Sigma |F_{o}|} \cdot {}^{b}wR2 = [\Sigma w (F_{o}^{2} - F_{c}^{2})^{2}/\Sigma w (F_{o}^{2})^{2}]^{1/2}, w$ = 1/[$\sigma^{2}(F_{o}^{2}) + (aP)^{2} + bP$], where P = [$F_{o}^{2} + 2F_{c}^{2}$]/3.

Table 5-2. Selected	Bond	Distances	(Å)	and	Angles	(deg)	for
[Ni(pyaca	ac) ₂ (TH	F) ₂ (Re(bpy)($(CO)_3$	2](OT	$f)_2$.		

Bond Distances (Å)

Ni(1) - O(1)	1.971(5)
Ni(1) - O(2)	1.981(5)
Ni(1) - O(1A)	1.971(5)
Ni(1) - O(2A)	1.981(5)
Re(1) - N(1)	2.238(5)
Re(1) - N(2)	2.152(6)
Re(1) - N(3)	2.112(10)
Re(1) - C(12)	1.903(12)
Re(1) - C(13)	1.901(10)
Re(1) - C(14)	1.912(9)
Ni(1) O(6)	2.155(6)
Ni(1) O(6A)	2.155(6)
Ni(1)•••Re(1)	9.868
Ni(1)•••Re(1A)	9.868

Bond Angles (deg)

O(1)-Ni(1)-O(2)	89.6(2)
O(1)-Ni(1)-O(1A)	179.999(2)
N(1)-Re(1)-N(2)	88.0(2)
C(12)-Re(1)-N(1)	92.1(4)
C(14)-Re(1)-N(1)	178.2(4)
^a plane 1•••plane 2	87.539
^b plane 1•••plane 2	87.539

^aPlane 1 is defined by atoms O(1), O(2), C(7), C(8), C(8), C(10), C(11); plane 2 is defined by atoms N(1), C(2), C(3), C(4), C(5), C(6). ^bGiven by the atoms that define the two planes in the adjacent pyacac ligand.



Figure 5-9. Drawing of the cation $[Ni(pyacac)_2(THF)_2(Re(bpy)-(CO)_3)_2](OTf)_2$ obtained from single-crystal X-ray structure determination. Atoms are represented as 50% probability thermal ellipsoids.

5.4.3 Electronic Absorption Spectroscopy. The electronic absorption spectra of [Ni(pyacac)₂(THF)₂(Re(bpy)(CO)₃)₂](OTf)₂ and [Be(pyacac)₂(Re-(bpy)(CO)₃)₂](OTf)₂ were acquired in room-temperature CH₃CN solutions and are shown in Figure 5-10. Transitions associated with these complexes were assigned based on previously reported analyses of Re¹ polypyridyl absorption spectra and^{27,28} the ground state absorption data for the structurally similar CuRe₂ complexes previously discussed (Chapter 3). The lowest energy absorption feature for BeRe₂ is centered at 360 nm ($\varepsilon = 6,800$ M⁻¹cm⁻¹) and is assigned as the Re¹(bpy)-based ¹A₁ \rightarrow ¹MLCT (t_{2g} $\rightarrow \pi^*$ (bpy¹)) transition. The BeRe₂ complex allows for analysis of the ground-state absorption behavior of the Re¹ donor moieties without overlapping with

the Ni^{II}-based charge-transfer absorptions associated with the NiRe₂ analogue. These charge transfer transitions are very apparent in the NiRe₂ absorption spectrum due to the sizable increase in the molar absorptivity values observed in the \sim 340 to 400 nm range.



Figure 5-10. Electronic absorption spectra of $[Ni(pyacac)_2(THF)_2(Re-(bpy)(CO)_3)_2](OTf)_2$ (red trace) and $[Be(pyacac)_2(Re(bpy)(CO)_3)_2]-(OTf)_2$ (blue trace) acquired in room-temperature CH₃CN solution.

In addition to the Re^I-based charge transfer transition, the NiRe₂ complex also possesses ligand-field transitions associated with the Ni^{II} core. The electronic absorption spectrum of Ni(phacac)₂ in CH₂Cl₂ solution, which serves as a model for the ligand-field transitions associated with the Ni^{II} center of the NiRe₂ assembly is shown in Figure 5-11. The shape of these low energy Ni^{II}-based transitions with $\lambda_{max} = 640$ nm, as well as the observed $\varepsilon_{max} = 17$ M⁻¹cm⁻¹ has been observed previously by Fackler and Cotton.²⁹



Figure 5-11. Electronic absorption spectra of $Ni(phacac)_2$ acquired in room-temperature CH_2Cl_2 solution.

5.4.4 Steady-State and Time-Resolved Emission. Emission spectra for $[Ni(pyacac)_2(THF)_2(Re(bpy)(CO)_3)_2](OTf)_2$ and [Be(pyacac)₂(Re(bpy)- $(CO)_{3}_{2}(OTf)_{2}$ were obtained in deoxygenated room-temperature $CH_{2}Cl_{2}$ solution. The BeRe₂ analogue represents an ideal structural model for the dynamics associated with the Re^I based ³MLCT emission, due to the inability of engaging in quenching dynamics incurred by the Ni^{II} core in the NiRe₂ system. The emission profiles are given in Figure 5-12, and show the emission intensity for the NiRe₂ is significantly quenched relative to the Be^{II}-containing system. The spectral profile for the BeRe2 compound was first observed in Chapter 3, with the emission originating from the ³MLCT \rightarrow ¹A₁ phosphorescence.³⁰ The emission maximum for both the Ni^{II}- and Be^{II}-containing derivatives is 565 nm suggesting similar emission characteristics for the NiRe₂ complex. A radiative quantum yield (Φ_r) of

0.18 was calculated for the BeRe₂ derivative (Chapter 3) when determined relative to [(bpy)Re(CO)₃(4-Etpy)](PF₆) ($\Phi_r = 0.18$ in CH₂Cl₂). The Φ_r value exactly corresponds with the reported value of the mononuclear Re¹(bpy) standard indicating the ³MLCT relaxation in the BeRe₂ model complex can be solely assigned to the Re^I donor moiety. A Φ_r value for the NiRe₂ complex is analytically unreliable due to dissociation of the pseudooctahedral NiO₆ coordination environment in CH₂Cl₂ solution. Figure 5-13A shows the emission spectrum of NiRe₂ in CH₂Cl₂ solution over a period of 27 hours, which shows a steady increase in the ${}^{3}MLCT \rightarrow {}^{1}A_{1}$ emission intensity occurring as the NiRe₂ complex remains in the CH₂Cl₂ solution over the course of the experiment. The increase in intensity is attributed not to dissociation of the Re(bpy)(CO)₃(pyacac) donor moiety from the Ni^{II} metal center, as was seen for the FeRe₃ (Chapter 2) and $CuRe_2$ complexes (Chapter 3) due to residual amounts of H₂O contained in the CH₂Cl₂, but loss of the axial THF ligands attached to the Ni^{II} center to generate a NiO_{6-x} (x = 1 or 2) environment. This is confirmed by Figure 5-13B, which shows the emission intensity of the NiRe₂ complex in THF solution remains constant when monitored over the course of 5 hours. If the NiRe₂ complex was dissociating to generate Re(bpy)(CO)₃(pyacac) species in solution, the dissociation process would be occurring to varying degrees regardless of

solvent. The possible NiO_{6-x} structures formed in solution are discussed in the next section.



Figure 5-12. Corrected steady-state emission spectra for $[Ni(pyacac)_2-(THF)_2(Re(bpy)(CO)_3)_2](OTf)_2$ (red trace) and $[Be(pyacac)_2(Re(bpy)-(CO)_3)_2](OTf)_2$ (blue trace). Acquired in deoxygenated room-temperature CH₂Cl₂ solution following excitation at 355 nm. The emission profiles have been normalized with respect to the absorbance at 355 nm, and therefore the relative magnitudes of the signals are accurate representations of their relative intensities.



Figure 5-13. A. Corrected emission spectra of $[Ni(pyacac)_2(THF)_2(Re-(bpy)(CO)_3)_2](OTf)_2$ in CH₂Cl₂ solution over a period of 27 hours ($\lambda_{ex} = 355$ nm) exhibiting a steady increase in emission intensity. See text for further details. **B.** Corrected emission spectra of $[Ni(pyacac)_2(THF)_2-(Re(bpy)(CO)_3)_2](OTf)_2$ in THF solution over a 5 hour time period ($\lambda_{ex} = 355$ nm) showing a constant emission intensity over the course of data collection.

Additional details concerning the excited-state states of the BeRe₂ and NiRe₂ complexes were obtained through nanosecond emission lifetime and time-correlated single photon counting (TCSPC) measurements. The nanosecond emission decay lifetime (τ_{obs}) in room-temperature CH₂Cl₂

solution for [Be(pyacac)₂(Re(bpy)(CO)₃)₂](OTf)₂, which was originally reported and analyzed in Chapter 3, is shown on the left side of Figure 5-14 and could be fit to a single-exponential model with $\tau_{obs} = 530 \pm 30$ ns. The corresponding radiative (k_r) and non-radiative (k_{nr}) decay rate constants are $3.4 \pm 0.2 \times 10^5 \text{ s}^{-1}$ and $1.6 \pm 0.1 \times 10^6 \text{ s}^{-1}$, respectively, which were all consistent with the assignment of ${}^{3}MLCT \rightarrow {}^{1}A_{1}$ emission given in Chapter 3. A plot of the TCSPC data obtained in room-temperature CH₂Cl₂ solution for $[Ni(pyacac)_2(THF)_2(Re(bpy)(CO)_3)_2](OTf)_2$ is shown on the right side of Figure 5-14. The decay trace could be fit with a bi-exponential model with $\tau_1 = 5.0 \pm 0.4$ ns and $\tau_2 = 25 \pm 4$ ns, with the source for the bi-exponential behavior observed in the NiRe₂ system proposed in the next section. Regardless of the bi-exponential behavior, the observed time constants for excited-state decay in the Ni^{II}-containing system are significantly larger than the corresponding BeRe₂ model complex, indicating the presence of a very efficient quenching process stemming from a reaction between the Re¹-based ³MLCT excited state and the Ni^{II} core.



Figure 5-14. Left. Nanosecond time-resolved emission data for $[Be(pyacac)_2(Re(bpy)(CO)_3)_2](OTf)_2$ ($\tau_{obs} = 530 \pm 30$ ns). Right. TCSPC data for $[Ni(pyacac)_2(THF)_2(Re(bpy)(CO)_3)_2](OTf)_2$ ($\tau_1 = 5.0 \pm 0.4$ ns and $\tau_2 = 25 \pm 3$ ns). Both traces (Be and Ni) were acquired in deoxygenated room-temperature CH₂Cl₂ solution monitoring at the emission maximum (565 nm). The solid red lines correspond to fitting to a mono-exponential decay model for BeRe₂ and to a bi-exponential decay model for NiRe₂.

5.4.5 Mechanistic Considerations: Dexter vs Förster Energy Transfer.

Dexter energy transfer,³¹ which is described as a simultaneous doubleelectron exchange mechanism, requires orbital overlap between the donor and acceptor involved in the energy transfer.³² The X-ray structure data for [Ni(pyacac)₂(THF)₂(Re(bpy)(CO)₃)₂](OTf)₂ (Figure 5-9) shows a Re¹···Ni^{II} separation of nearly 10 Å, a value that lies at the maximum of what is typically considered for an exchange-based process due to the exponential dependence (e^{-2R}) (R = donor-acceptor separation) of orbital overlap.³³ The 10 Å metal-metal distance, coupled with observed similarities in the v(CO) frequencies of the NiRe₂ and BeRe₂ complexes (Section **5.2.1**), largely negate the possibility of significant electronic coupling between the Re¹ and Ni¹¹ subunits. This point is amplified by the computational results of Meyer and coworkers on similar Re¹ mononuclear complexes that show the ³MLCT wavefunction would not exist on the bridging pyacac ligand,²⁰ which drastically negates the possibility of the pyacac bridging ligands imparting significant electronic coupling between the Re¹ and Ni¹¹ metal centers. This combination of the structural and electronic characteristics of the NiRe₂ complex makes it unlikely that Dexter-type exchange is playing a dominant role in the energy transfer dynamics of these systems.

Work discussed in Chapter 3 on the structurally similar $[Cu(pyacac)_{2^{-}}(Re(bpy)(CO)_{3})_{2}](OTf)_{2}$ assembly found Förster energy transfer to be the dominant excited-state quenching mechanism. The CuRe₂ compound contains the same Re¹ donor species (ie. equivalent redox potentials and emission characteristics), pyacac bridging ligand, and similar donor-acceptor separations as the NiRe₂ system. Although the results of the CuRe₂ derivative can't unequivocally assign the quenching mechanism for the NiRe₂ complex, the findings do point to analogous excited-state reactivity out of the ³MLCT state of the Re¹ donor. In addition, the spectral overlap between the Re¹-based ³MLCT emission with the Ni¹¹ ligand-field states also

implicates Förster-type reactivity as the dominant excited-state quenching mechanism in the NiRe₂ system. A qualitative picture of the spectral overlap of the Re(bpy) donor moiety with the Ni^{II} ligand-field manifold of Ni(phacac)₂ is shown in Figure 5-15, which corresponds to a calculated spectral overlap value of $J = 2.14 \times 10^{-16} \text{ M}^{-1} \text{ cm}^{-3}$. The spectral overlap value $(J = 5.52 \times 10^{-16} \text{ M}^{-1} \text{ cm}^{-3})$ between the Re^I-based ³MLCT emission and the Cu^{II} ligand-field states in the CuRe₂ complex (Chapter 3) is similar to the [Ni(pyacac)₂(THF)₂(Re(bpy)(CO)₃)₂](OTf)₂, which manifests as similar I CuRe₂

observed kinetics between the two complexes ($k_{obs}^{CuRe_2} = 1.2 \pm 0.1 \times 10^8$

and $k_{obs}^{NiRe_2} = 2.0 \pm 0.2 \times 10^8$). The similar spectral overlap and energy transfer quenching dynamics observed between the CuRe₂ and NiRe₂ complexes provides additional proof of Förster-type reactivity occurring in [Ni(pyacac)₂(THF)₂(Re(bpy)(CO)₃)₂](OTf)₂.



Figure 5-15. Overlay of the emission spectrum of $[Be(pyacac)_2(Re-(bpy)(CO)_3)_2](OTf)_2$ (blue trace) with the electronic absorption spectrum of Ni(phacac)_2 (red trace).

5.4.6 Spin Dependent Dipolar Energy Transfer. As mentioned in the Introduction, in addition to possessing a downhill thermodynamic driving force, the total spin angular momentum - an abiding property of reactants and products - must be conserved during the course of a chemical reaction. Conservation of total spin angular momentum during an excited state energy transfer event must also be retained. From the structure of the NiRe₂ complex given in Figure 5-9, two THF solvent molecules are coordinated in the axial positions of the Ni^{II} metal center to generate a Ni(acac)₂(THF)₂ complex (i.e. NiO₆ coordination sphere) in the core of the donor-acceptor assembly. The single-crystal X-ray structure data of the NiRe₂ assembly (Table 5-2) shows the Ni—O (THF) distances are ~ 0.2 Å longer than the Ni—O (acac) distances, suggesting a weaker metal-ligand covalent

interaction between Ni^{II} and the oxygens of the THF ligands. The dissociation of both THF ligands from NiRe₂ in solution would yield a ratio of donor-acceptor complexes with a pseudo-octahedral NiO₆ and pseudo-D_{2h} NiO₄ cores in solution depending on the propensity for NiRe₂ to lose THF ligands. Figure 5-16 shows spin conservation diagrams between the Re¹-based ³MLCT excited state with a pseudo-octahedral NiO₆ (*Top*) and pseudo-D_{2h} NiO₄ (*Bottom*) acceptor cores. The Ni^{II} ground state in the NiO₆ core is ³A₂ ($|\vec{S}_A| = 1$), and when coupled with the ³MLCT excited state of

the Re^I donor $(|\vec{S}_D^*| = 1)$ generates total spin angular momentum $(|\vec{S}_T|)$ values of 2, 1, and 0. Based on the overlap integral plot given in Figure 5-15, the acceptor state of the NiO₆ core is the ${}^{3}A_{2} \rightarrow {}^{3}T_{2}$ ligand-field transition. As energy transfer (EnT) quenching occurs out of the ${}^{3}MLCT$

excited state to produce the Ni^{II}-based ${}^{3}A_{2} \rightarrow {}^{3}T_{2}$ transition, an $|\vec{S}_{T}|$ of 1 is generated on the products side of the diagram from the coupling of the resulting Re^I ground state $(|\vec{S}_{D}| = 0)$ with the Ni^{II}-based ${}^{3}T_{2}$ excited state $(|\vec{S}_{A}^{*}| = 1)$. As can been seen in Figure 5-16, an $|\vec{S}_{T}| = 1$ between the reagents and the products is conserved, which provides the spin-allowed energy transfer pathway.

Conversely, Figure 5-16 (*Bottom*) shows coupling between the Re¹ excited state and the ligand-field states of the NiO₄ core. The Ni^{II} ground state in NiO₄ is ¹A₁ ($|\vec{S}_A| = 0$), and when coupled with the ³MLCT excited state of the Re¹ donor ($|\vec{S}_D| = 1$) generates a total spin angular momentum $(|\vec{S}_T|)$ value of 1 on the reagents side. On the products side, the acceptor states of the NiO₄ core are S = 0 \rightarrow S = 0 ligand-field transitions ($|\vec{S}_A| = 0$) and the ground state of the Re¹ produced after the energy event is $|\vec{S}_D| = 0$ A mutual S_T value between the reagents ($|\vec{S}_T| = 1$) and the products ($|\vec{S}_T| = 0$) is not conserved, therefore energy transfer is spin-forbidden.
$$(bpy^{-})Re^{II} \sim NiO_{6} \xrightarrow{EnT} (bpy)Re^{I} \sim (NiO_{6})^{*}$$

$$S_{D} = 1 \qquad S_{A} = 1 \qquad S_{D} = 0 \qquad S_{A} = 1$$

$$S_{T} = 2,1,0 \qquad S_{T} = 1$$

$$\begin{array}{cccc} & & & & & & \\ (bpy^{-})Re^{II} & & NiO_4 & & & \\ S_D = 1 & S_A = 0 & & & \\ & & & & \\ S_T = 1 & & & & \\ & & & & \\ & &$$

Figure 5-16. *Top.* Spin conservation diagram illustrating the spinallowed energy transfer pathway between the ³MLCT excited-state of the Re¹ donor and the pseudo-octahedral NiO₆ acceptor. *Bottom.* Spin conservation diagram illustrating the spin-forbidden pathway between the ³MLCT excited-state of the Re¹ donor and the pseudo-D_{2h} NiO₄ acceptor.

It is proposed that the differences in total spin angular momentum ($|S_T|$) conservation in the energy transfer reaction between the Re¹-based ³MLCT state and the ligand-field states of NiO₆ and NiO₄ cores, illustrated in Figure 5-16 (*Top*), give rise to the different behavior observed in the steady-state emission spectra of Ni(pyacac)₂(THF)₂(Re(bpy)(CO)₃)₂](OTf)₂ in CH₂Cl₂ and THF solutions (Figure 5-13). This proposed axial ligand dissociation mechanism is manifested in the steady-state emission spectrum of the NiRe₂ assembly in CH₂Cl₂ solution (Figure 5-13A), in which the emission signal is seen to steadily increase over the course of many hours in solution indicating

lesser quenching of the ³MLCT excited states over time. The THF dissociation mechanism has been attributed to a simple ligand exchange process between the NiRe₂ complex and the very large concentration of CH₂Cl₂ solvent molecules. This projected route is confirmed by the steadystate emission data for the NiRe₂ complex in THF solution (Figure 5-13B), in which no change in the emission intensity was observed over the course of 5 hrs. The unvarying emission intensity of the NiRe₂ system in THF solution is assigned to suppression of the axial ligand dissociation mechanism occurring in the presence of a large excess of THF molecules. The results of the steady-state emission data for the NiRe₂ assembly in the two solvent systems reveal that dipolar energy transfer dynamics can be manipulated by simply varying the spin of the acceptor metal center, and furthermore, can be controlled by simply varying the coordination environment around a single metal center.

Due to the above discussion on the steady-state emission data for Ni(pyacac)₂(THF)₂(Re(bpy)(CO)₃)₂](OTf)₂ in CH₂Cl₂, the time-correlated single photon counting (TCSPC) data for the NiRe₂ assembly (Figure 5-14, *Right*) requires further discussion. The two relaxation processes (τ_1 = 5.0 ns and τ_2 = 25 ns) observed are both significantly faster than the τ_{obs} = 530 ns measured for the BeRe₂ model complex (Figure 5-14, *Left*), which suggests

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there are two competing quenching processes out the Re¹-based ³MLCT excited state. If the NiO_6 and NiO_4 acceptor cores (discussed above) were the only two Ni^{II} coordination environments produced in the CH₂Cl₂ solution, a time-constant resulting from the spin-allowed pathway ($\tau_1 = 5.0$ ns) and a baseline offset representing the spin-forbidden coupling $(\tau_{obs}^{NiO_4} \approx \tau_{obs}^{BeRe_2})$ would be the only observed kinetic processes within the time frame shown in the TCSPC data (Figure 5-14, Left). Another possible coordination environment for the Ni^{II} core in the NiRe₂ complex is NiO₅, which would result from dissociation of a single THF solvent molecule to form Ni(acac)₂(THF). Based on the work of Raymond and coworkers in the 1960's, the NiO₅ structure could exist either in square-pyramidal or trigonal bipyramidal geometries due to the soft potential that exists between the two geometries.³⁴ Existence of either the square-pyramidal (pseudo- C_{4v}) or trigonal bipyramidal (pseudo- D_{3h}) NiO₅ structures in solution could be responsible for the τ_2 = 25 ns observed in the TCSPC data for the NiRe_2 assembly (Figure 5-14). Further work, including photophysical and solution phase magnetic susceptibility data on the NiRe₂ and Ni(acac)₂(THF)_x complexes, will need to be performed to unmask the 25 ns component.

5.5 Conclusions

1

The synthesis, structures, and photophysical properties of a series of donor-acceptor complexes based on Re¹-bipyridine donors with a Co^{III}-acac acceptor (CoRe₃; Section 5.3) and a Ni^{II}-acac acceptor (NiRe₂; Section 5.4) have been described. Steady-state and time-resolved emission spectroscopies indicated that the Re¹-based ³MLCT excited state relaxation kinetics is significantly affected by the spin-state of the acceptor metal center. In the CoRe₃ complex, the Co^{III}-based ligand-field transition (${}^{1}A_{1} \rightarrow$ $^{1}T_{1}$) represents a thermodynamically viable relaxation pathway out the ³MLCT donor state, but the similarity in ³MLCT emission lifetimes between the CoRe₃ assembly and an AlRe₃ model complex ruled out the Co^{III} ligandfield state as a possible reaction pathway. The reason for the similar kinetics between the complexes was shown to derive from lack of total spin angular momentum conservation in the excited-state energy transfer reaction of CoRe₃. In the NiRe₂ system, the Ni^{II}-based ligand-field transition (${}^{3}A_{2} \rightarrow$ ${}^{3}T_{2}$) provided a spin-allowed quenching pathway out of the Re^I-based ³MLCT excited-state when compared to a Be^{II}-containing model complex, and a much faster ³MLCT relaxation was observed in the NiRe₂ assembly. Favorable spectral overlap between the ³MLCT donor emission and acceptor ligand-field states coupled with a ca. 10 Å donor-acceptor distance, allowed

for an assignment of Förster (dipolar) energy transfer as the dominant excited-state quenching mechanism in the Ni^{II}-containing complexes. These complexes represent excellent examples of the ability to manipulate excited-state reactivity by simply varying the spin-state of a single reagent involved.

5.5 References

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Chapter 6. Future Work

6.1 Overall Goals

Chapter 6 focuses on continuing the fundamental investigation of Förster energy transfer dynamics in Re¹-based donor-acceptor assemblies discussed throughout this dissertation. The majority of the discussion in this chapter will center on proposing various spectroscopic tools and additional donor-acceptor complexes that will be needed to address two remaining goals of the research effort: 1) the complete characterization of the dynamical behavior (i.e. vibrational) of the Re(bpy')(CO)₃ donor moieties undergoing ³MLCT energy transfer quenching processes and 2) the synthesis of additional CoRe₃ derivatives to further understand the spin-dependent energy transfer processes proposed for the CoRe₃ and CrRe₃ complexes outlined in Chapter 5.

6.2 Goal 1: Monitoring ³MLCT Relaxation in the Re(bpy')(CO)₃ Donors 6.2.1 Background. The ³MLCT excited state of the Re^I fluorophores can be thought of as Re^{II}(bpy⁻)(CO)₃, in which the Re^I metal has been formally oxidized and the polypyridyl ligand formally reduced to generate $Re(t_{2g}^{5})$ —bpy(π^{*-}). A brief description of the electronic structure and photophysical properties of d^6 polypyridyl complexes is given in the Introduction. As one can imagine, the ground state vibrational properties of the $Re(bpy)(CO)_3$ moiety will be significantly perturbed in the charge The ground-state vibrational signatures for the transfer excited state. polypyridyl-based C-C and C-N stretching modes and the CO stretching frequencies are the two particular areas of the Re(bpy)(CO)₃ donor moiety that will be significant altered in the excited-state. The bond order of the C-C and the C-N bonds of the bpy will be decreased due to population of a bpy-based π^* orbital, and the bond order of the CO ligands will be increased due to less backbonding contribution from the oxidized Re metal center.¹ Time-resolved infrared spectroscopy (TRIR) has been shown to be an excellent technique for probing the relaxation dynamics associated with transition metal-based excited states.^{2,3} Due to the high oscillator strengths and backbonding interactions associated with the CO ligands, TRIR has been used to monitor the excited-state CO stretching frequencies to characterize the ³MLCT excited state relaxation in [Re(X₂-bpy)(CO)₃(4-Etpy)](PF₆) (where $X = CH_3$, H, or CO₂Et and 4-Etpy = 4-ethylpyridine).^{4,5} The v(CO) bands associated with $[Re(X_2-bpy)(CO)_3(4-Etpy)](PF_6)$ were observed to shift to higher energy in response to an increase in the triplebond character of the CO ligands due to less Re-CO backbonding. In

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addition, the technique has been shown to monitor and assign the mechanism of excited-state reactivity out of the ³MLCT excited state of Re^Ibased donor-acceptor assemblies by monitoring the extent to which the v(CO) bands shift in energy.⁶⁻⁸

Based on the TRIR data reported for the mono- and poly-nuclear Re¹based complexes discussed above, application of TRIR spectroscopy to the MRe_x (x = 2 or 3) assemblies presented throughout in dissertation would be a nice compliment to the steady-state and time-resolved emission data. All of the MRe_x complexes possess Re(bpy')(CO)₃ donor moieties that possess v(CO) bands that could serve as spectroscopic tags to monitor relaxation out of the ³MLCT excited state. Additionally, even though the donor-acceptor distances, electrochemical properties, and spectral overlap considerations in the MRe_x complexes prove dipolar energy transfer as the dominant ³MLCT quenching process, the energies for the v(CO) bands in the ³MLCT excited state derived from TRIR would be different depending on whether energy or electron transfer quenching was operative (vida infra).

6.2.2 Dicyano Derivatives of CuRe₂ and BeRe₂. With an eye toward developing a system that could be used for assigning the excited-state quenching mechanisms in the MRe_x complexes via TRIR, I have synthesized and characterized $[Cu(pyacac)_2(Re(dcnb)(CO)_3)_2](OTf)_2$ and $[Be(pyacac)_2-$

 $(\text{Re}(\text{dcnb})(\text{CO})_3)_2](\text{OTf})_2$ (where dcnb = 4,4'-dicyano-2.2'-bipyridine). Just as with the complexes reported in Chapter 3, the Cu^{II} and Be^{II} metal centers are covalently attached to two *fac*-Re(bpy')(CO)₃ moieties through two pyridyl-acetylacetonate bridging ligands (Figure 6-1). The BeRe₂ complex was synthesized to investigate the v(CO) bands associated with the ³MLCT excited state of the Re(dcnb)(CO)₃ moiety in the absence of emission quenching reactivity in the CuRe₂ assembly.





Figure 6-1. Structures of $[Cu(pyacac)_2(Re(dcnb)(CO)_3)_2](OTf)_2$ and $[Be(pyacac)_2(Re(dcnb)(CO)_3)_2](OTf)_2$

6.2.3 Synthesis and Characterization

The synthesis procedure for $[Cu(pyacac)_2(Re(dcnb)(CO)_3)_2](OTf)_2$ is same as reported for the CuRe₂ series in Chapter 3. Amounts of 75 mg (0.18 mmol) of Cu(pyacac)₂ and 225 mg (0.360 mmol) of Re(dcnb)(CO)₃(OTf) were used in the preparation of the CuRe₂ compound. Yield: 83 mg (28%). Anal Calcd for C₅₂H₃₂N₁₀F₆O₁₆S₂CuRe₂ •4H₂O: C, 35.92; H, 2.32; N, 8.05. Found: C, 35.74; H, 2.10; N, 7.84. MS: $[ESI^+, m/z \text{ (rel. int.)}]$: 684.4 (35) $\{[Cu(pyacac)_2(Re(dcnb)(CO)_3)_2]\}^{2+}$, 1517.9 (1) $\{[Cu(pyacac)_2(Re(dcnb)-(CO)_3)_2](OTf)\}^{1+}$.

The synthesis procedure for $[Be(pyacac)_2(Re(dcnb)(CO)_3)_2](OTf)_2$ is same as reported for the BeRe₂ series in Chapter 3. Amounts of 67 mg (0.19 mmol) of Be(pyacac)₂ and 233 mg (0.372 mmol) of Re(dcnb)(CO)₃(OTf) were used in the preparation of the BeRe₂ compound. Yield: 141 mg (47%). Anal Calcd for C₅₂H₃₂N₁₀F₆O₁₆S₂BeRe₂ •4H₂O: C, 37.08; H, 2.39; N, 8.31. Found: C, 37.22; H, 2.18; N, 8.04. MS: $[ESI^+, m/z \text{ (rel. int.)}]$: 657.1 (41) $\{[Be(pyacac)_2(Re(dcnb)(CO)_3)_2]\}^{2+}$, 1463.3 (1) $\{[Be(pyacac)_2(Re(dcnb)-(CO)_3)_2](OTf)\}^{1+}$.

6.2.4. Electronic Absorption Spectroscopy. The electronic absorption spectra of $[Cu(pyacac)_2(Re(dcnb)(CO)_3)_2](OTf)_2$ and $[Be(pyacac)_2(Re-(dcnb)(CO)_3)_2](OTf)_2$ were acquired in room-temperature CH₃CN solutions and are shown in Figure 6-2. Transitions associated with these complexes were assigned based on previously reported analyses of CuRe₂/BeRe₂ complexes reported in Chapter 3. The Re^I-based ${}^{1}A_{1} \rightarrow {}^{1}MLCT$ ($t_{2g} \rightarrow \pi^{*}$ (bpy')) transition occurs at $\lambda_{max} = 395$ nm for both complexes, with the absorption profile of [Be(pyacac)₂(Re(dcnb)(CO)₃)₂](OTf)₂ solely exhibiting these ${}^{1}MLCT$ based characteristics. The BeRe₂ complex allows for analysis of the ground-state absorption behavior of the Re^I donor moieties without overlapping with the Cu^{II}-based charge-transfer transitions associated with the CuRe₂ assembly. In addition, the similarity in the shape and energy of the ${}^{1}MLCT$ absorption bands in the two complexes indicates minimal electronic communication between the Re^I and Cu^{II} metal centers in the ground state.



Figure 6-2. Electronic absorption spectra of $[Cu(pyacac)_2(Re(dcnb)-(CO)_3)_2](OTf)_2$ (red trace) and $[Be(pyacac)_2(Re(dcnb)(CO)_3)_2](OTf)_2$ (blue trace) acquired in room-temperature CH₃CN solution.

6.2.5 Time-Resolved Emission. Quantitative information concerning emission quenching by the Cu^{II} center was obtained via time-resolved emission spectroscopy. Data for the BeRe₂ model complex could be fit to a single-exponential decay kinetic model ($\tau_{obs} = 110 \pm 10$ ns); emission trace for the observed decay rate in the BeRe₂ complex is given on the left side of Figure 6-3. Due to a lack of signal observed with the nanosecond emission apparatus for the CuRe₂ complex, time-correlated single-photon counting (TCSPC) was employed to measure the excited-state lifetime of the Cu^{ll}containing complexes. A plot of the TCSPC data obtained for the CuRe₂ complex in deoxygenated CH₂Cl₂ solution is shown on the right side of Figure 6-3; the observed time constant $(4.1 \pm 0.4 \text{ ns})$ for excited-state decay in the CuRe₂ complex is significantly shorter than the BeRe₂ model complex, and shows the Re^I-based ³MLCT excited state is significantly quenched in the presence of Cu^{II} relative to Be^{II}. The analysis of the timeresolved emission data for $[Cu(pyacac)_2(Re(dcnb)(CO)_3)_2](OTf)_2$ and $[Be(pyacac)_2(Re-(dcnb)(CO)_3)_2](OTf)_2$ were performed analogous to the CuRe₂ complexes reported in Chapter 3 and the reader is directed there for further discussion.



Figure 6-3. *Left.* Nanosecond time-resolved emission data for $[Be(pyacac)_2(Re(dcnb)(CO)_3)_2](OTf)_2$ ($\tau_{obs} = 110 \pm 10$ ns) acquired in room-temperature deoxygenated CH₂Cl₂ solution ($\lambda_{pump} = 400$ nm; $\lambda_{probe} = 625$ nm). *Right.* Time correlated single-photon counting (TCSPC) emission data for $[Cu(pyacac)_2(Re(dcnb)(CO)_3)_2](OTf)_2$ acquired in room-temperature deoxygenated CH₂Cl₂ solution ($\lambda_{pump} = 400$ nm; $\lambda_{probe} = 625$ nm). The solid red line corresponds to a fit to a bi-exponential decay model with $\tau_1 = 4.1 \pm 0.4$ ns and $\tau_2 = 110$ ns (fixed); the latter corresponds to emission from Re(dcnb)(CO)₃(pyacac) present in solution as a trace impurity.

6.2.6 Proposed TRIR Experiments. The Re(dcnb)(CO)₃ donor moieties of

 $[Cu(pyacac)_2(Re(dcnb)(CO)_3)_2](OTf)_2$ and $[Be(pyacac)_2(Re(dcnb)(CO)_3)_2]$ -(OTf)_2 represent ideal candidates for probing quenching dynamics of charge transfer-based excited states using TRIR. In addition to monitoring the dynamical shift in the CO ligands that occur in response to the Re^{II} (d⁵) metal center in the ³MLCT excited state, the high oscillator strength of the CN substituents on the bipyridyl ligand should serve as ideal spectroscopic tags for measuring the excited state relaxation associated with the reduced polypyridyl ligand. Measuring the energies of the v(CO) and v(CN) bands associated with the ³MLCT excited state in the BeRe₂ complexes will be critical to the mechanistic analysis in the CuRe₂ analogue. If excited-state energy transfer is the dominant mechanism in the CuRe₂ complex, then the shifts (v(GS) to v(ES)) observed for the v(CO) and v(CN) bands in the Be^{II} and Cu^{II}-containing systems will correspond. Due to the shorter excitedstate lifetime measured for the CuRe₂ complex (Figure 6-3), the only difference between the two experiments will be the shorter time window that will be needed to collect the CuRe₂ data. The energy transfer process in the CuRe₂ system is in essence, a faster pathway for the ³MLCT state to relax and therefore will exhibit similar v(CO) and v(CN) bands as seen for the charge transfer excited state in the BeRe₂ complex. If electron transfer is the dominant quenching process in the CuRe₂ assembly, the shifts in the v(CO)bands of the Be^{II}- and Cu^{II}-containing systems will not correlate due to the "complete" oxidation of the Re^I metal center that would occur during an electron transfer event in CuRe₂, compared with partial oxidation (~70%) occurring during a charge transfer excitation. In addition, the v(CN) observed in the BeRe₂ complex should disappear due to electron transfer quenching removing the excited electron from the π^* level of the dcnb ligand.

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6.3 Goal 2: Additional Derivatives for the CoRe₃ Series

6.3.1 Background. In Chapter 5, a CoRe₃ donor-acceptor complex - $[Co(pyacac)_3(Re(bpy)(CO)_3)_3](OTf)_3$ - was synthesized in order to explore the spin-state dependence of excited state energy transfer reactions. Based on the observation of significant spectral overlap between the ³MLCT emission profile of the Re(bpy) donor moiety and the ${}^{1}A_{1} \rightarrow {}^{1}T_{1}$ ligand-field absorption band in the Co^{III} acceptor, dipolar energy transfer quenching of the ³MLCT state is thermodynamically favorable and predicted to occur. Nanosecond emission lifetime measurements on the CoRe₃ complex in CH₂Cl₂ solution exhibited similar ³MLCT relaxation kinetics as an electronically benign AlRe₃ model system. Determination of the total spin orbital angular momentum (S_T) for the energy transfer quenching reaction in CoRe₃ revealed a spin-forbidden coupling mechanism between the photoinduced reagents and the energy transfer products. Furthermore, comparison of the ³MLCT emission lifetimes of CoRe₃ and a structurally identical CrRe₃ complex that possesses similar spectral overlap characteristics and a spinallowed coupling mechanism between the reagents and products showed a ca. 100 fold decrease in the lifetime of CrRe₃, and confirmed that dipolar energy transfer can be turned on or off depending on the spin-state of a single ion.

The trend in observed energy transfer rate constants for the series of $CrRe_3$ complexes presented in Chapter 4 showed a direct dependence on the magnitude of spectral overlap between the Re^I-based ³MLCT emission spectra and the Cr^{III}-based ⁴A₂ \rightarrow ⁴T₂ ligand-field acceptor transition. Figure 6-4 reproduces the spectral overlap plot for the CrRe₃ series originally reported in Chapter 4, with the bpy derivative (green trace) exhibiting the highest spectral overlap value and the largest energy transfer rate constant. To adequately compare the CrRe₃ (spin-allowed) and the CoRe₃ (spin-forbidden) ³MLCT relaxation processes, additional Re(bpy') derivatives of the CoRe₃ complex will need to be prepared to generate an analogous spectral overlap plot for the CoRe₃ series.



Figure 6-4. Overlay of the emission spectra of $[Al(pyacac)_3(Re(tmb)-(CO)_3)_3](OTf)_3$ (blue), $[Al(pyacac)_3(Re(bpy)(CO)_3)_3](OTf)_3$ (green), and $[Al(pyacac)_3(Re(deeb)(CO)_3)_3](OTf)_3$ (red) with the electronic absorption spectrum of Cr(phacac)_3. Plot is reproduced from Figure 4-12 (Chapter 4). The largest calculated spectral overlap (bpy; green) resulted in the fastest energy transfer rate constant within the series.

6.3.2 Proposed CoRe₃ Derivatives. Based on the spectral overlap plot between the $[Al(pyacac)_3(Re(bpy)(CO)_3)_3](OTf)_3$ emission profile ($\lambda_{max} =$ 565 nm) and the Co(phacac)₃ ${}^1A_1 \rightarrow {}^1T_1$ ligand-field manifold ($\lambda_{max} = 605$ nm) reported in Chapter 5, additional CoRe₃ derivatives possessing lower energy Re(bpy') emitters need to be synthesized (preferably one with an emission maximum of ~ 600 nm) to generate an analogous spectral overlap plot created for the CrRe₃ series. One obvious choice is to synthesize the deeb derivative (deeb = 4,4'-diethylester-2,2'-bipyridine), due mainly to already possessing [Al(pyacac)_3(Re(deeb)(CO)_3)_3](OTf)_3 as a structural model and secondly that the λ_{max} for emission is 625 nm which lies just on the low energy side of the Co(phacac)_3 ${}^1A_1 \rightarrow {}^1T_1$ ligand-field band but still retains descent spectral overlap.

Based on literature reports that show an emission maximum of ~ 600 nm in CH₂Cl₂ solution, the next CoRe₃ analogue proposed is the dclb derivative (dclb = 4,4'-dichloro-2,2'-bipyridine). The synthesis and photophysical characterization of the [Al(pyacac)₃(Re(dclb)(CO)₃)₃](OTf)₃ structural model have already been performed based on experimental protocols used for similar AlRe₃ complexes reported in Chapter 2. The steady-state and nanosecond time-resolved emission data for [Al(pyacac)₃-(Re(dclb)(CO)₃)₃](OTf)₃ is shown in Figure 6-5. The photophysical properties of $[Al(pyacac)_3(Re(dclb)(CO)_3)_3](OTf)_3$ correspond with the other AlRe₃ derivatives reported in Chapter 2, and the observed emission properties are assigned to the Re¹-based ³MLCT \rightarrow ¹A₁ transition.



Figure 6-5. Left. Steady-state emission spectrum of $[Al(pyacac)_3(Re(-dclb)(CO)_3)_3](OTf)_3$ in room-temperature CH_2Cl_2 solution ($\lambda_{pump} = 375$ nm); $\lambda_{max} = 595$ nm for ³MLCT $\rightarrow {}^1A_1$ emission. Right. Nanosecond time-resolved emission data for $[Al(pyacac)_3(Re(dclb)(CO)_3)_3](OTf)_3$ ($\tau_{obs} = 120 \pm 10$ ns) acquired in deoxygenated room-temperature CH_2Cl_2 solution ($\lambda_{pump} = 415$ nm; $\lambda_{probe} = 595$ nm).

Figure 6-6 shows the spectral overlap plot between the Al^{III}containing bpy, dclb, and deeb ³MLCT emission profiles with the ¹A₁ \rightarrow ¹T₁ ligand-field absorption band of Co(phacac)₃. As can be seen from Figure 6-6, ideal spectral overlap between the Re(dclb) moiety (green trace) and the Co^{III 1}A₁ \rightarrow ¹T₁ absorption band (black trace) is observed, and most importantly a spectral overlap plot analogous to the one in the CrRe₃ series has been generated. In other words, a *spin-allowed* spectral overlap plot and a *spin-forbidden* spectral overlap plot have now been generated to compare two structurally identical donor-acceptor complexes that differ simply by the acceptor spin-state.



Figure 6-6. Overlay of the emission spectra of $[Al(pyacac)_3(Re(bpy)-(CO)_3)_3](OTf)_3$ (blue), $[Al(pyacac)_3(Re(dclb)(CO)_3)_3](OTf)_3$ (green), and $[Al(pyacac)_3(Re(deeb)(CO)_3)_3](OTf)_3$ (red) with the electronic absorption spectrum of $Co(phacac)_3$.

In closing, the final two compounds required to complete the CoRe₃ series - $[Co(pyacac)_3(Re(dclb)(CO)_3)_3](OTf)_3$ and $[Co(pyacac)_3(Re(deeb)-(CO)_3)_3](OTf)_3$ - need to be synthesized and characterized. The synthesis procedure for these two remaining complexes should follow the same procedure used for $[Co(pyacac)_3(Re(bpy)(CO)_3)_3](OTf)_3$ reported in Chapter 5.

6.4 References

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