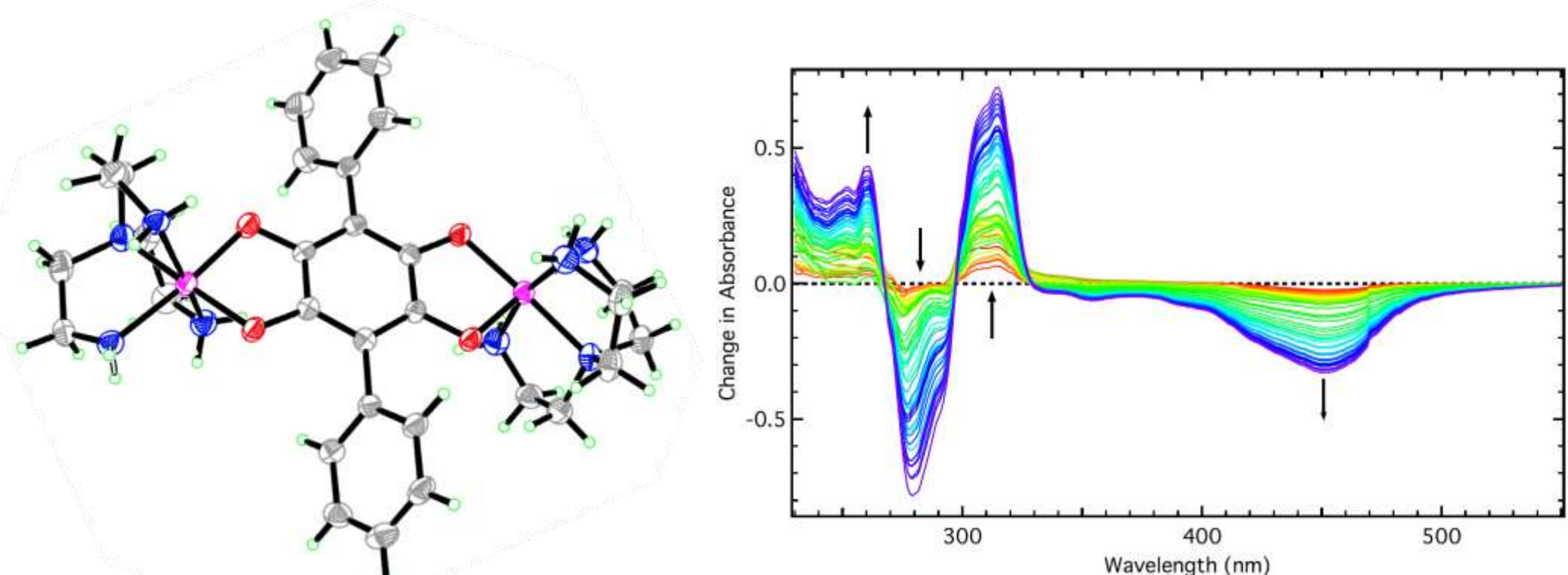


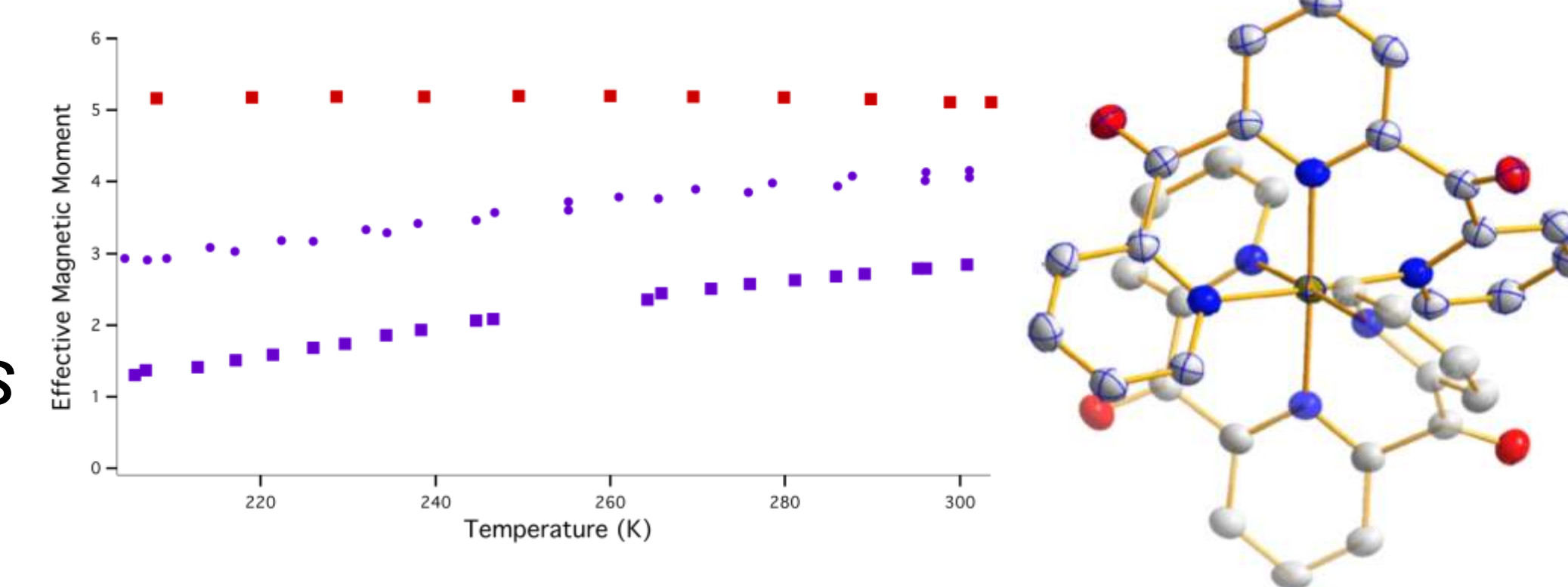
Physical and Photophysical Properties of Transition Metal Complexes

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Our group is interested in the physical and photophysical properties of transition metal complexes. Our approach relies on a confluence of synthetic chemistry, a cornucopia of physical techniques ranging from magnetism to time-resolved spectroscopy, and high-level theory. The simultaneous examination of chemical problems on all three of these fronts places us in a unique position to explore the physical chemistry of inorganic compounds.

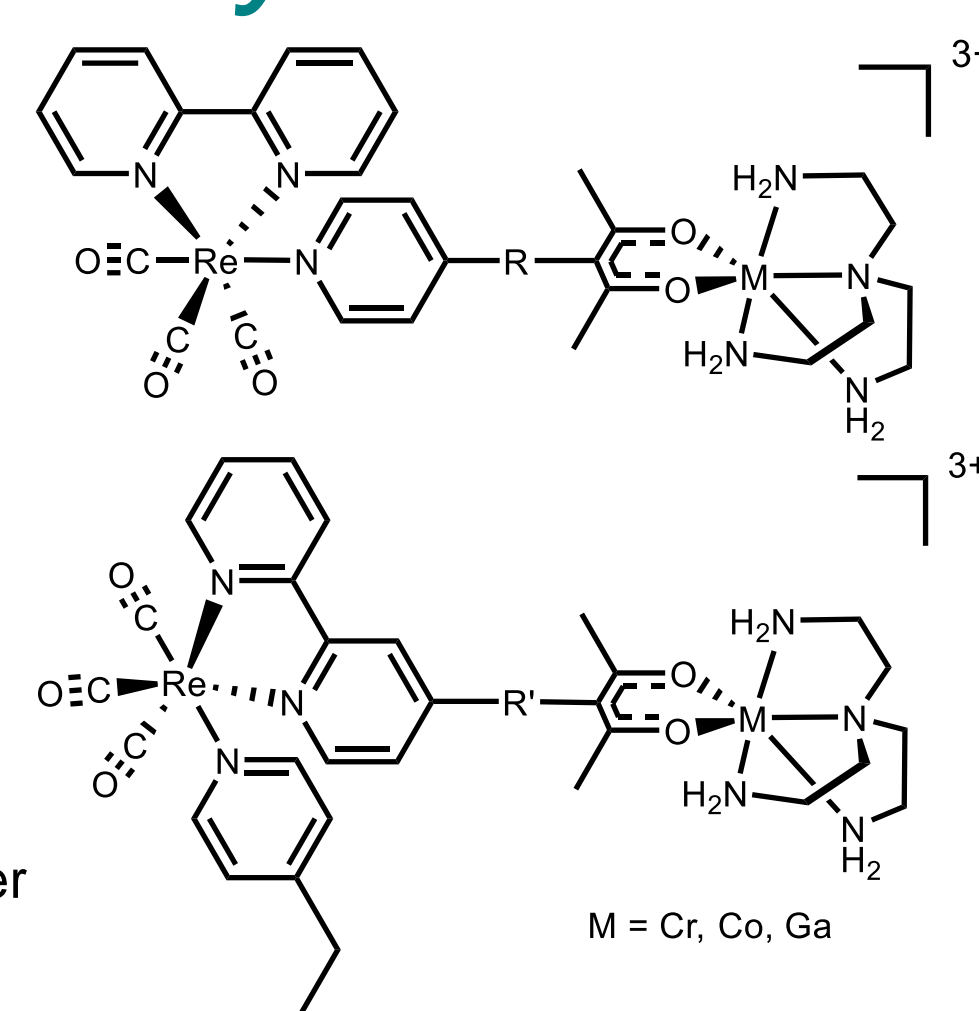
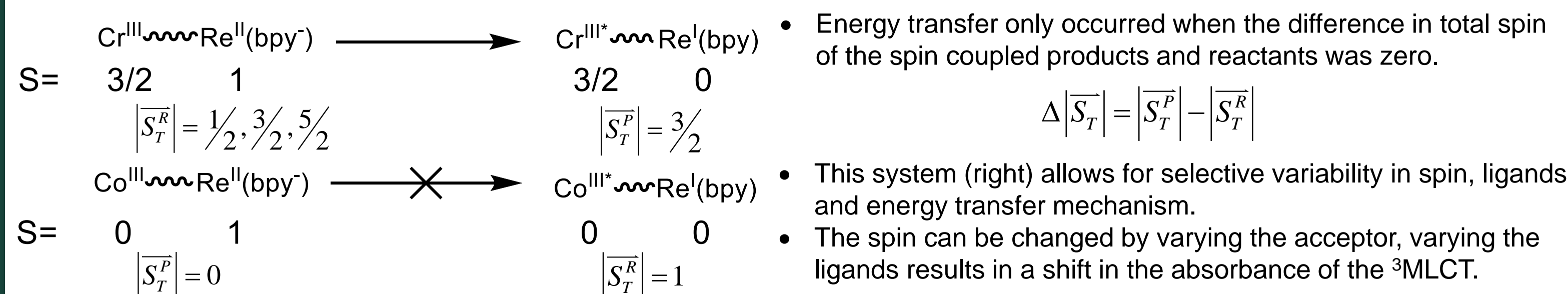


Spin and Spin Polarization Effects on Chemical Systems

Scientists have studied spin and magnetism in different chemical systems for decades; areas of intense research include single-molecule magnets, bioinorganic chemistry, materials science, and more recently, quantum computing and spintronics. The spin of a system is also key to interpret their optical spectra: a well-known example is the difference in the timescales of fluorescence (a spin-allowed process, where the spins of the initial and final states are the same) and phosphorescence (a spin-forbidden process). We are interested in the effects that spin and spin polarization have on the physical properties of a system, as well as on its reactivity (with emphasis on electron and energy transfer). To this end, we design and synthesize specific molecules to help answer our questions, and then investigate their properties with a wide range of techniques.

Conservation of Spin in Excited State Reactivity

Conservation of spin angular momentum was observed for dipolar energy transfer from the ³MLCT of a Re(I) donor to a first row transition metal acceptor; the reaction was allowed or forbidden based on the spin coupling of reactants and products.



By changing where the 1st row transition metal is linked to the Re(I) Forster or Dexter Energy Transfer will predominate. A short linker will favor Dexter Transfer and as the distance is increased Forster transfer will be favored.

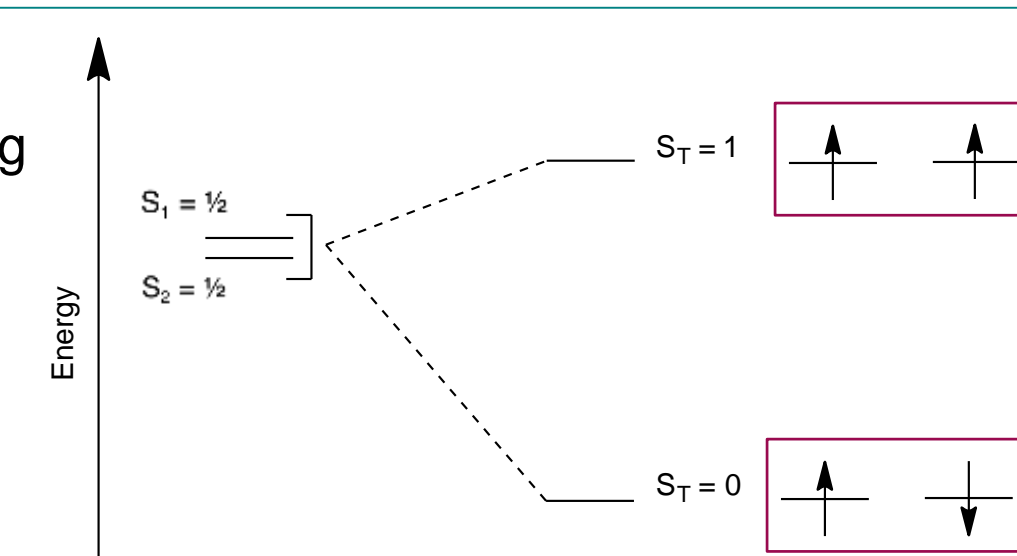
Heisenberg Spin Exchange

When two (or more) paramagnetic centers in a system are spin-coupled, their relative orientations have different energies depending on the nature of their interaction. The strength of the coupling is expressed by the coupling constant, *J*.

Mathematically, spin coupling is treated as the interaction of magnetic dipoles, using the Heisenberg-Dirac-Van Vleck Hamiltonian:

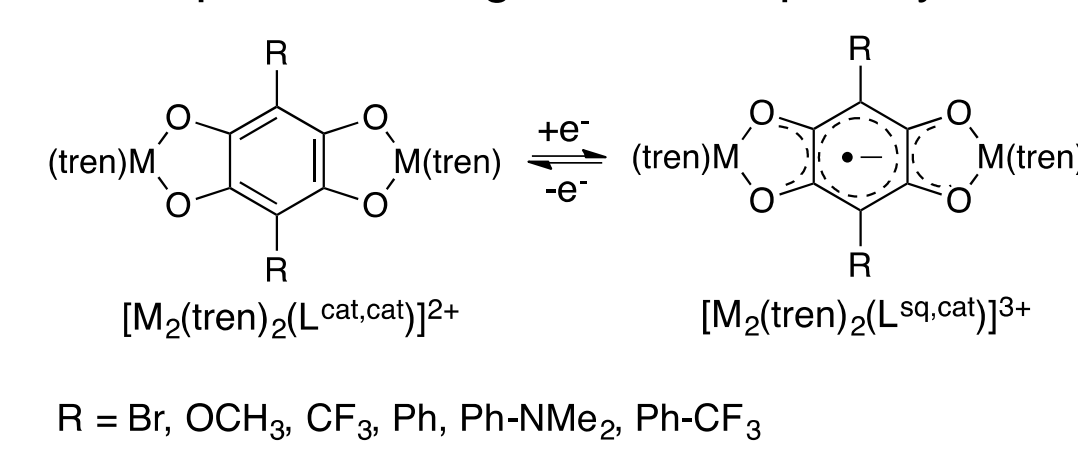
$$\hat{H} = -2JS_1S_2$$

Depending on the magnitude of *J* and the temperature, different spin states can be populated.



Spin Exchange Effects in Tetraoxolene-Bridged Bimetallic Complexes

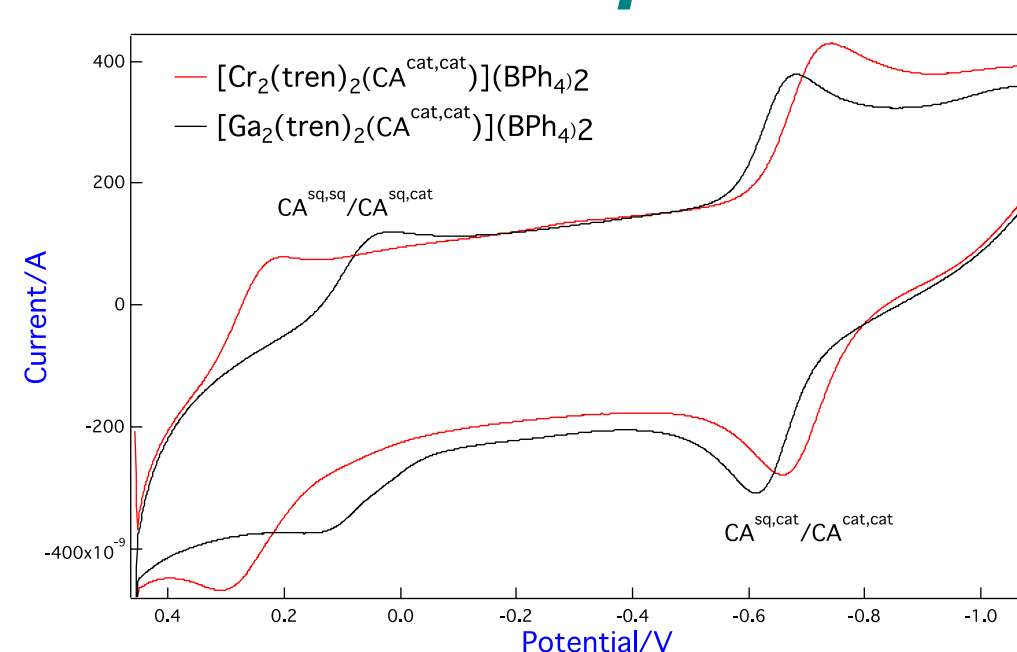
The net thermodynamic stabilization of the system (ΔE_{ex}) can be quantified from the spin coupling constant, *J*, by variable-temperature magnetic susceptibility measurements.



However, spin exchange does not exhibit the R⁶ distance dependence expected for a dipole-dipole coupling phenomenon.

An experimental demonstration may be able to help understand the reason behind the successful prediction of the Heisenberg spin model.

[M₂(tren)₂(L)]^{2+/3+} represents a series of proposed systems, within which spin exchange can be turned on/off by incorporating redox-active L^{ox}/L^{cat} and relatively redox-inert Cr^{III} or Ga^{III}.



Some studies show redox potentials of spin-coupled active sites are shifted upon the introduction of spin exchange coupling.

The shifting of redox potentials is also observed in one of the spin-exchange coupling systems, Cr₂(tren)₂(CA^{cat})₂²⁺, successfully synthesized by our group.

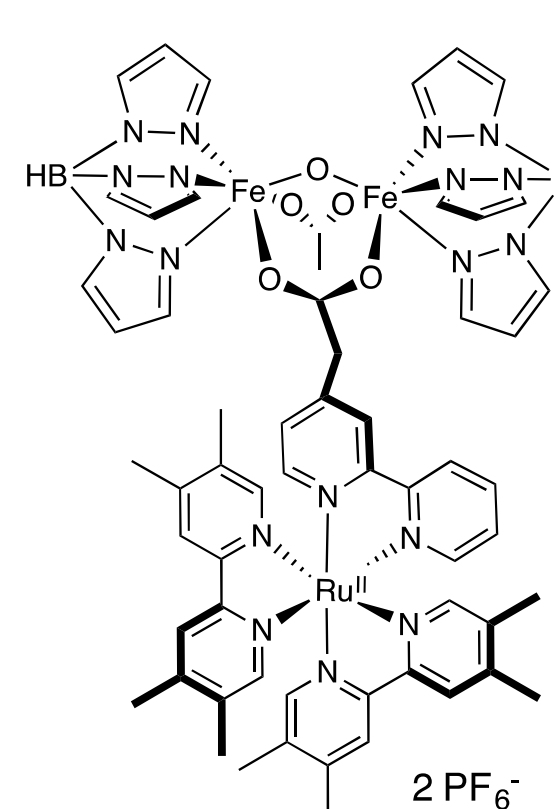
The comparison of the free energy, *K_C*, of stabilization revealed from electrochemistry and *J* can be our first avenue to understanding the thermodynamic consequences of spin exchange.

Electron and Energy Transfer to an Exchange-Coupled Acceptor

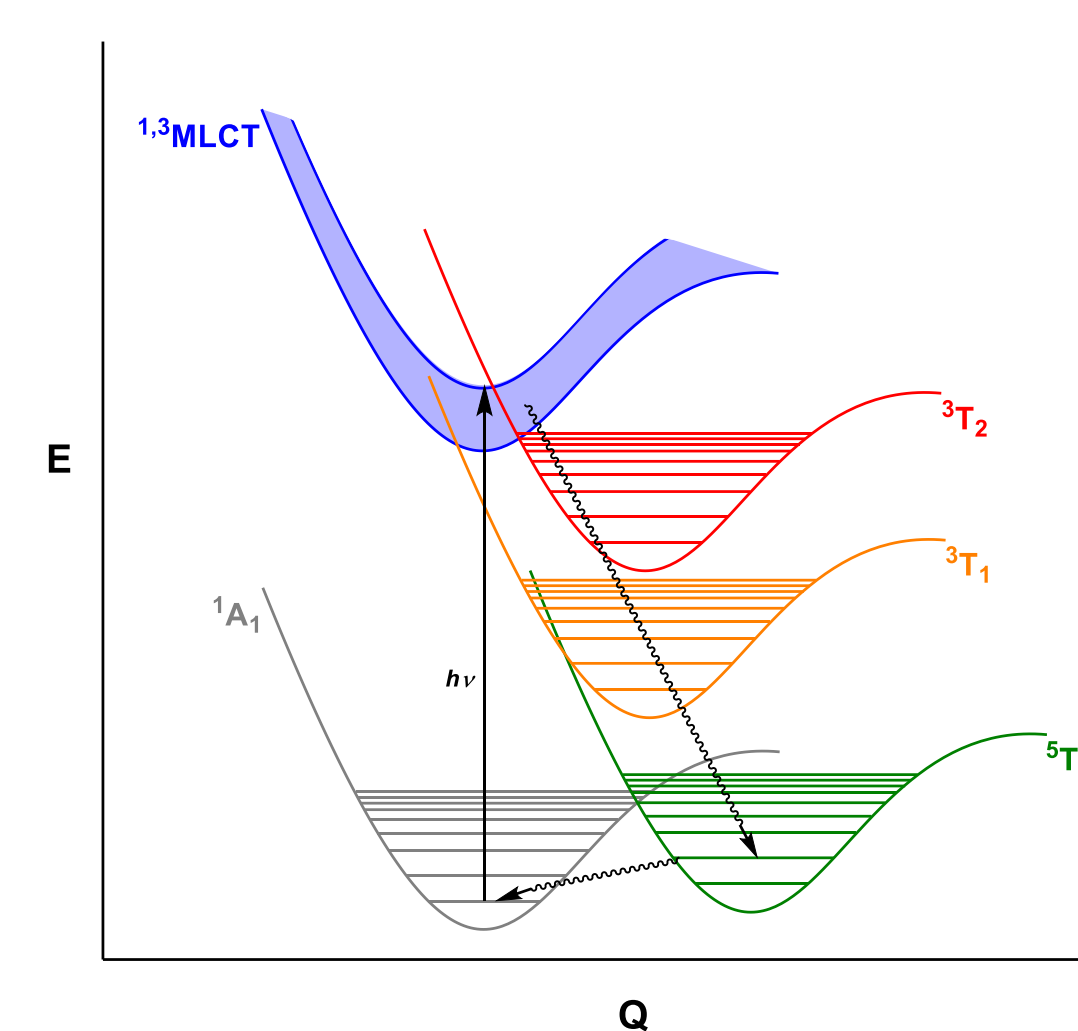
In this project, Heisenberg Spin Exchange allows us to change the spin state of a system while keeping the changes in its composition/structure to a minimum. We use [Ru(bpy)₃]²⁺ compounds as donors and (Tp)₂Fe₂(μ-O)(μ-O₂CR)₂ or [(Tp)₂Fe₂(μ-OH)(μ-O₂CR)₂]⁺ as acceptors (Tp is tris(1-pyrazolyl)borate). These diiron(III) compounds are antiferromagnetically coupled, with *J*_{oxo} ~ 100 cm⁻¹ and *J*_{hydroxo} ~ 10 cm⁻¹.

Previous work in our group suggests that the magnitude of spin coupling (and therefore, the spin levels that are populated at a given temperature) has an effect on the reactivity of the acceptor. However, the quenching in the case of the OH-bridged dimers was diffusion-limited, which made a quantitative analysis impossible. To overcome this we have designed intramolecular assemblies.

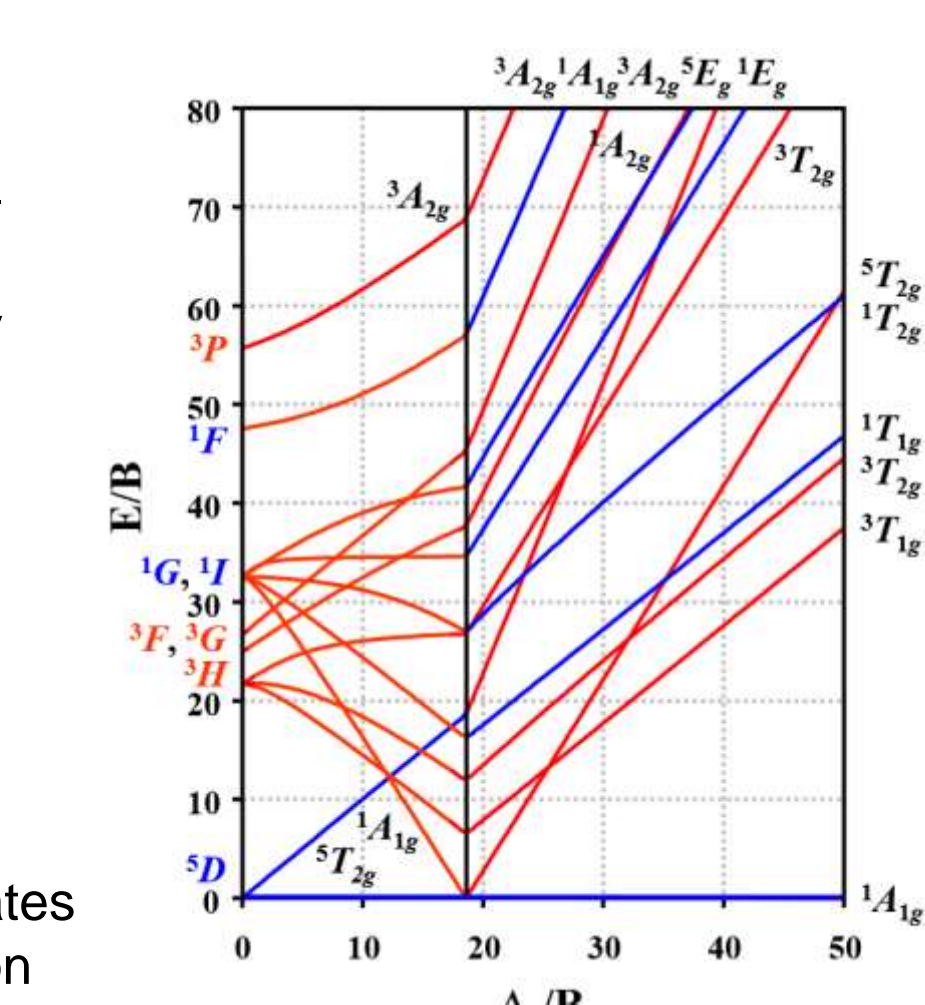
The first generation of D-A systems (shown on the right) exhibits strong quenching of the Ru(II) emission, but are very unstable in solution, even under inert atmosphere. The synthesis and characterization of the second generation (using both carboxylate bridges to attach the Ru(II) donor) and third generation (using the Tp ligand to append the Ru(II) moiety) of D-A assemblies are in progress.



Excited State Studies of Fe^{II} Polypyridyl Systems

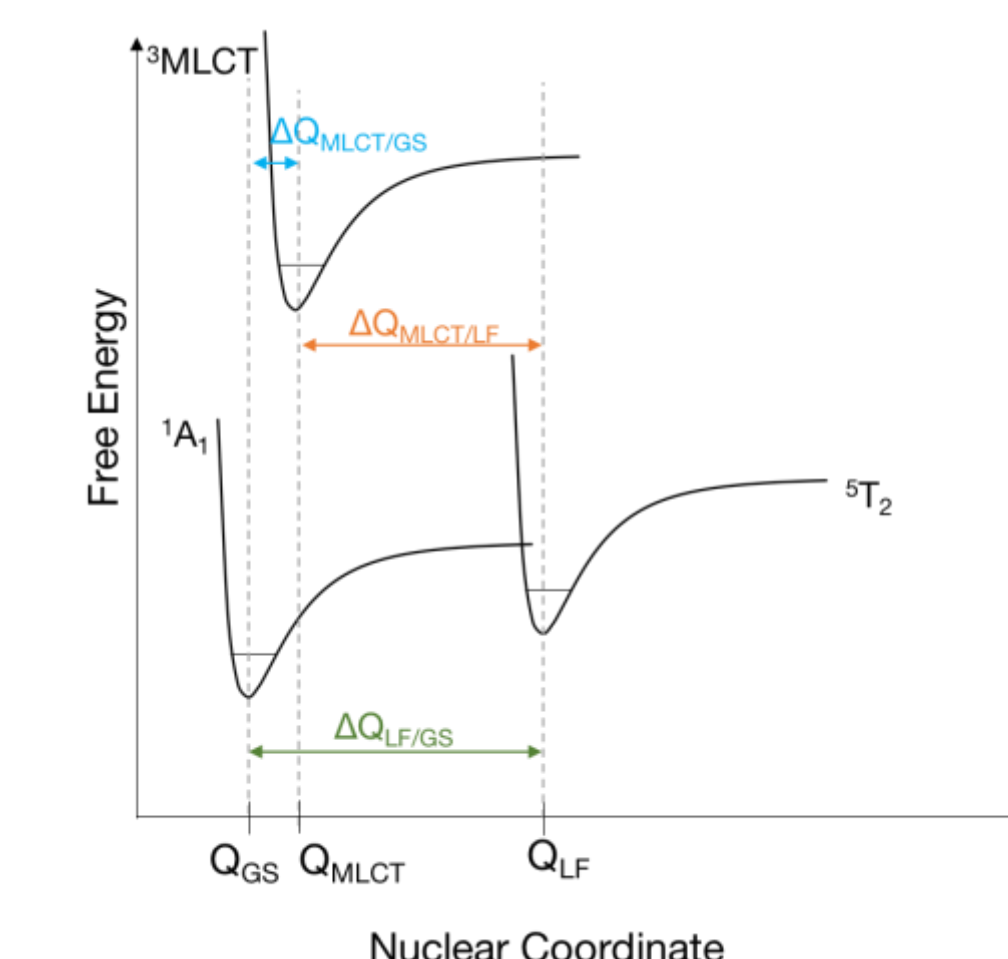
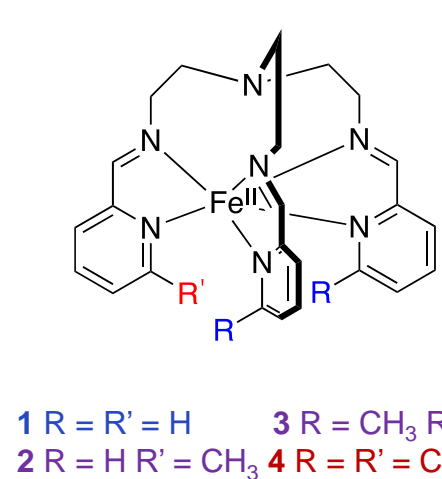


- Upon photoexcitation into metal-to-ligand charge transfer (MLCT) bands, many Ru^{II} polypyridyl systems eventually populate a ³MLCT state which renders a charge separated excited state with lifetimes on the order of nanoseconds to milliseconds—making it attractive for photoredox and solar energy processes.
- Isoelectronic systems based on relatively more earth-abundant Fe^{II} are considerably shorter-lived (< 200 fs) due to depopulation of MLCT states via energetically lower ligand field (LF) states.
- The goal of the Fe^{II} Photophysics Projects in the McCusker Group is to rationally design Fe^{II} polypyridyl systems in such ways as to better understand and control the excited state electronic structure which may allow these chromophores to be more efficient in photoredox processes.
- Our efforts to achieve this are through the following approaches:
 - Kinetic Control:** Understanding vibrational modes in MLCT deactivation
 - Thermodynamic Control:** Perturbing the energetics of MLCT and LF excited states
 - Device Property Control:** Modulating Fe^{II} dye design to alter competitive electron transfer rates



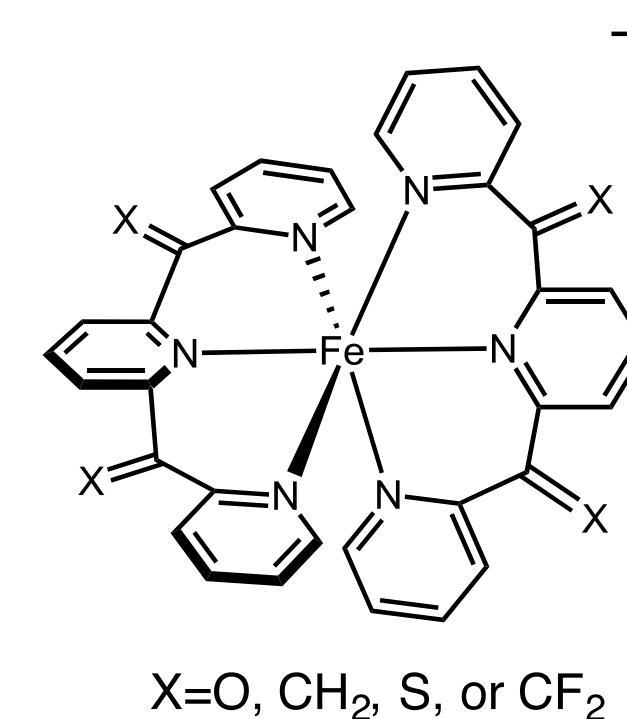
Defining the Nuclear Coordinate of MLCT Deactivation

- Excited state transitions can be associated with changes in geometry (i.e. vibrational modes) along a nuclear coordinate
- Once identified, the vibrational modes that compose the nuclear coordinate for the decay of the MLCT states into the ⁵T₂ LF state can be targeted with synthetic modification to hinder their progression, thereby prolonging the lifetime of the MLCT states.
- <200 fs deactivation of the MLCT states in Fe^{II} rules out direct observation of the vibrational modes associated with its decay, so another approach must be taken.
 - The MLCT → ⁵T₂ nuclear coordinate ($\Delta Q_{MLCT/LF}$) may be considered as ($\Delta Q_{MLCTGS} - \Delta Q_{LF/FGS}$).
 - The first aim of this project is to find $\Delta Q_{LF/FGS}$.
- Iron(II) spin crossover (SCO) complexes **2** and **3** have a thermal equilibrium between ¹A₁ and ⁵T₂, allowing for ΔG_0 to be experimentally determined with magnetic susceptibility measurements, which can then be related to $\Delta Q_{LF/FGS}$.
- Previous attempts to prepare the series to the right resulted in products containing all four complexes, making the accurate determination of ΔG_0 impossible.
- Developing a route to prepare pure SCO complexes is the synthetic challenge of this project.

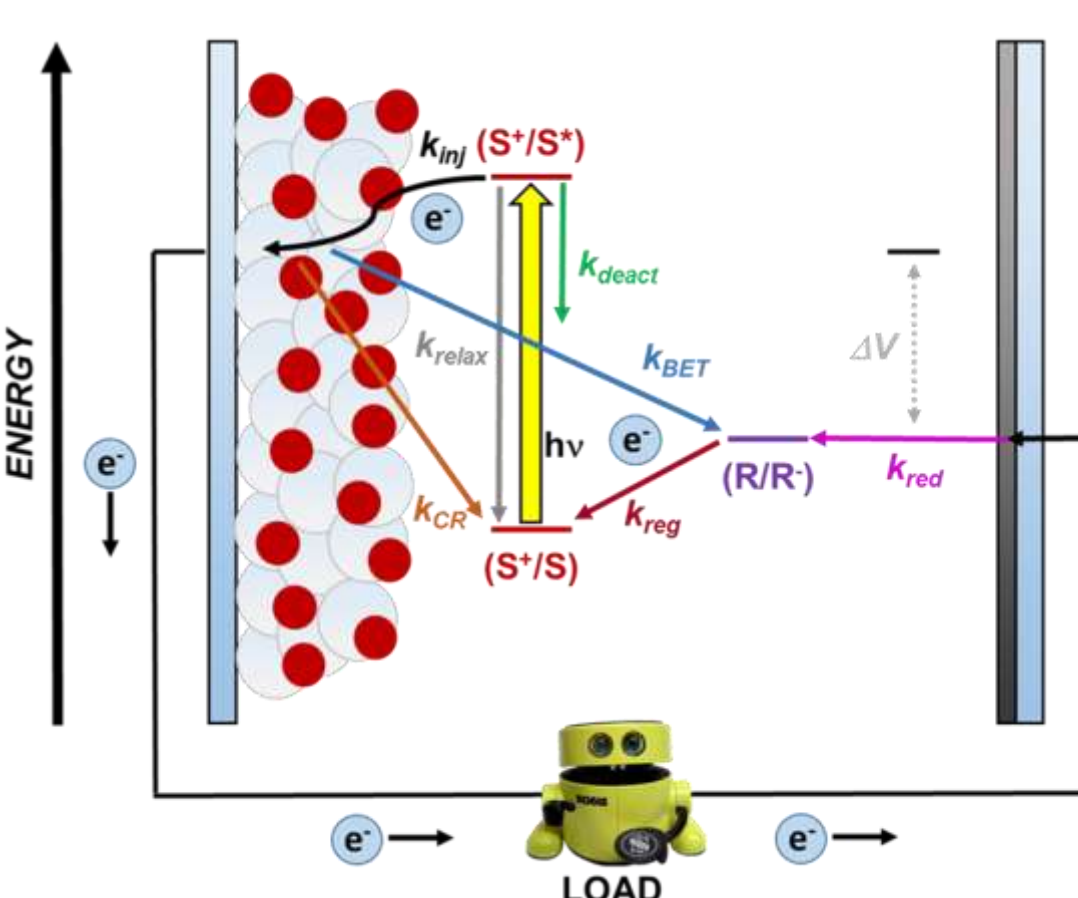


Manipulating Excited State Electronic Structure

- In an attempt to extend the MLCT lifetime of low spin /s-Fe^{II} polypyridyls, a complex with near perfect octahedral symmetry around the Fe^{II} center was synthesized, [Fe(dcpp)₂]²⁺, shown to the left, where X = O.
- Originally, increasing the symmetry of an Fe^{II} polypyridyl complex was meant to increase its ligand field strength and therefore "decongest" the excited state relaxation pathways, prolonging the MLCT lifetime.
- However, [Fe(dcpp)₂]²⁺ shows no extension of the MLCT lifetime (280 ps) and a 4-fold shorter ground state recovery in comparison to the well-studied model compound, [Fe(bpy)₃]²⁺ (100 ps).
- When X = CH₂, the Fe^{II} complex possesses similar excited state dynamics and electrochemical behavior.
 - This unexpected behavior has prompted the investigation of what sets [Fe(dcpp)₂]²⁺ apart from its X = CH₂ analogue.
- We hypothesize that there are two different aspects associated with the X = O complex that lead to its unique properties. We have set out to make synthetic modifications to the ligand that will allow for their study:
 - To determine the effect of the dipole in the C=O bond, a X = CF₂ derivative should remove lone pair electron clouds while maintaining a large induced dipole in the C=X bond.
 - To examine the consequences of the polarizability of the electron cloud around the oxygen atom, a derivative with X = S would maintain the polarizability of the electron cloud while removing the aforementioned induced dipole.
- Comparing all four complexes will parse out the effects of the bridging group on the excited state dynamics of the complexes allowing for the synthetic control of the MLCT lifetime.



Interfacial Electron Transfer Studies of Fe^{II} Sensitizers



- It was initially shown in 1998 by Ferrere and Gregg that solar cells containing Fe^{II} polypyridyl dyes are orders of magnitude less efficient than those with ruthenium-containing congeners.
- This has been predominately attributed to MLCT → LF deactivation (*k_{detr}*) which hinders MLCT → TiO₂ conduction band (CB) interfacial electron transfer (*k_{inj}*). Recent computational studies on Fe^{II}(bpy)₂(CN)₂ dyes suggest that different anchoring groups have a variety of binding modes to TiO₂, and some of these may have *k_{inj}* rates similar or better than *k_{detr}* (~100 fs).
- To test molecular design aspects of anchoring group and/or ligand substitution pattern on solar cell performance, we are synthesizing a host of [Fe^{II}(bpy)_n(CN)_{6-2n}] complexes with **carboxylate**, **hydroxamate**, **catechol** and **acetylacetonate** linker substituents to use in our solar cells.
- We personally fabricate our solar cells and conduct photoelectrochemical studies.
- Our steady-state measurements are compared to time-resolved spectroscopic results performed by our spectroscopy subgroup to glean insight into the full picture of electron transfer dynamics in these Fe^{II}-based solar cells.

