

The Effects of Spin Polarization on Chemical Reactivity

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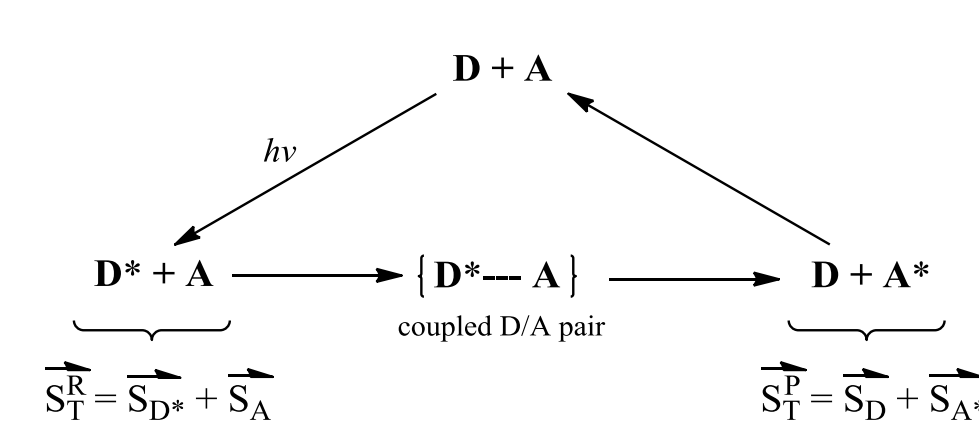
MICHIGAN STATE UNIVERSITY



Research Goals

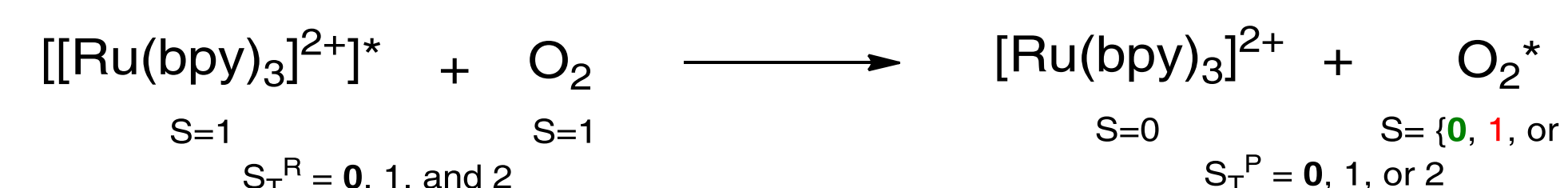
Our chemical systems are tailored to study the physical and photophysical properties of spin polarized molecules. These molecules exhibit magnetic properties that allow us to study reactivity based on spin. In addition to experiment, theoretical models can be adapted utilizing Heisenberg spin exchange. Heisenberg spin exchange is a magnetic phenomenon in which a bridge for communication exists between unpaired electron spins within a molecule and/or between molecules. Contained within this poster, spin polarization manifests itself in studies of spin conservation in energy transfer processes, spin distribution effects on energy transfer, synthetic modulation of spin distribution and creating spin-allowed transitions based on the Heisenberg spin exchange model.

Conservation of Spin in Energy Transfer

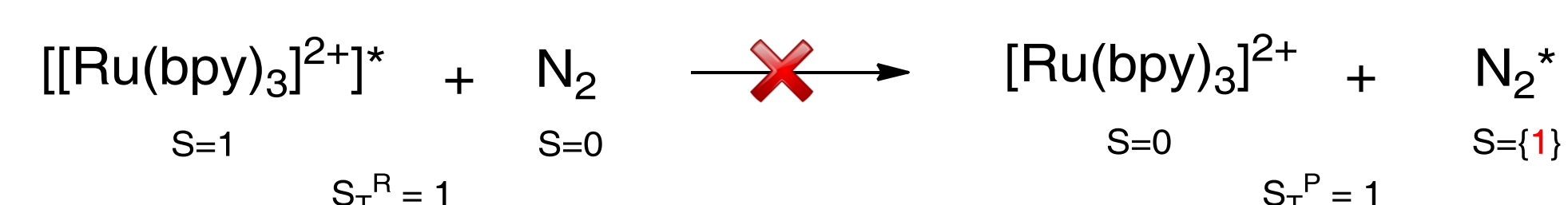


In systems where electronic spin is a good quantum number, reactions will occur when thermodynamically favorable and when the total spin angular momentum space of the reactants has overlap with the spin angular momentum space of the products.

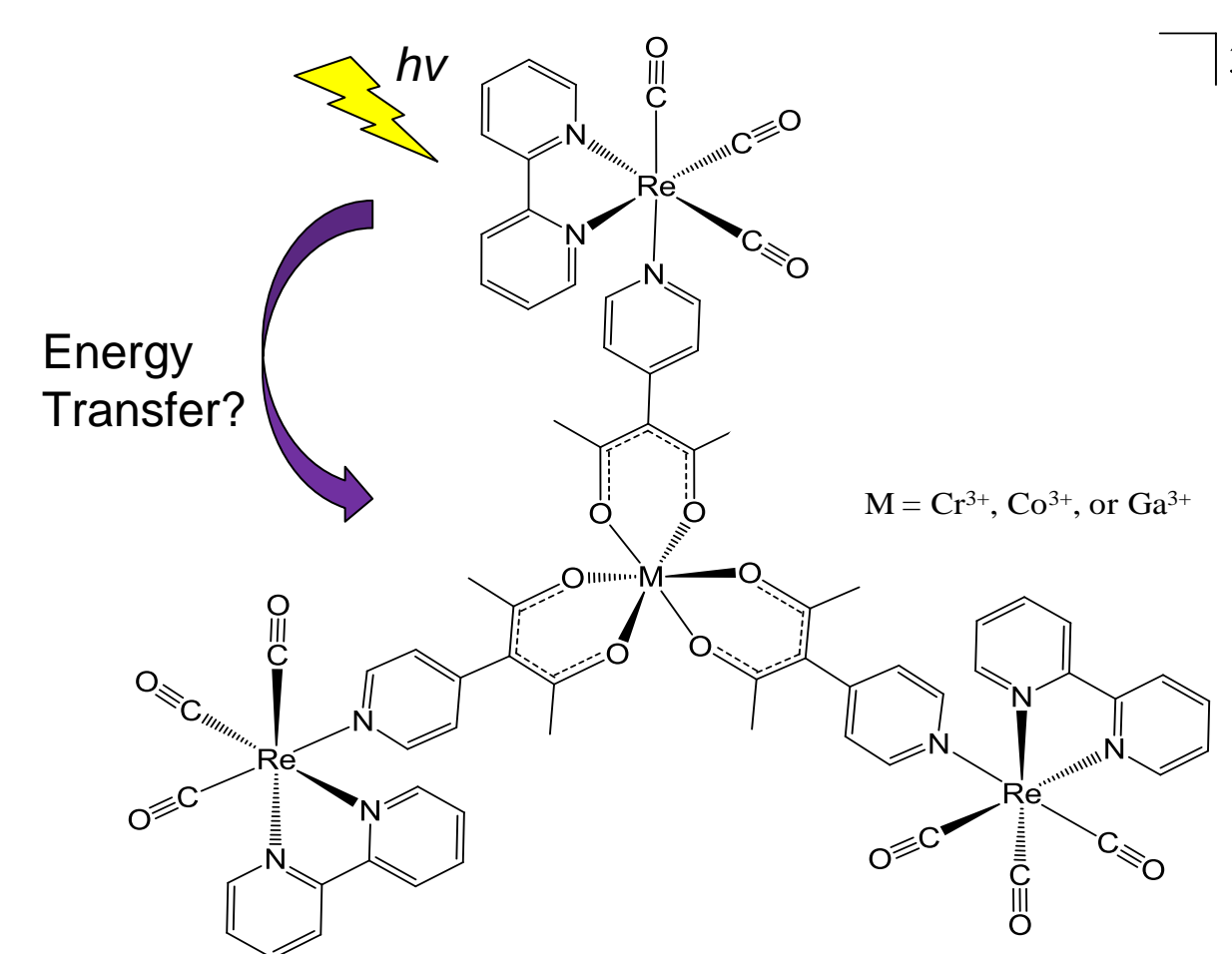
The photoexcited ³MLCT excited state of Ru(bpy)₃²⁺ is able to be quenched by O₂ via energy transfer because out of the range of possible spin allowed O₂ excited states, the lowest singlet excited state of O₂ is lower in energy than the ³MLCT energy donor state.



N₂ is unable to quench the ³MLCT because only triplet excited states of N₂ are allowed if spin angular momentum is to be conserved and the lowest energy triplet excited state of N₂ is higher in energy than the donating excited state and thus the reaction is not thermodynamically favored.



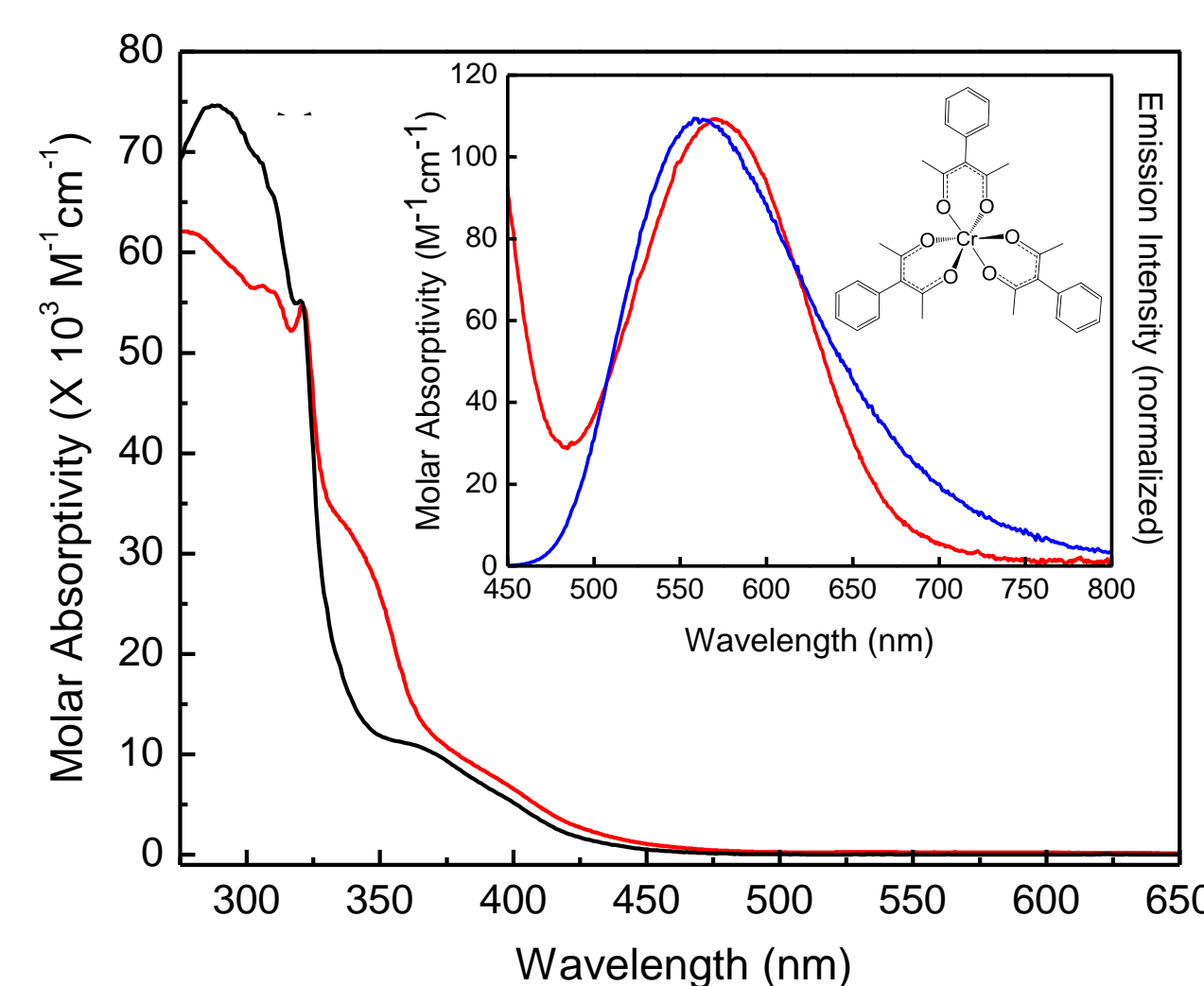
[M(pyacac)₃{Re(bpy)(CO)₃}₃]³⁺



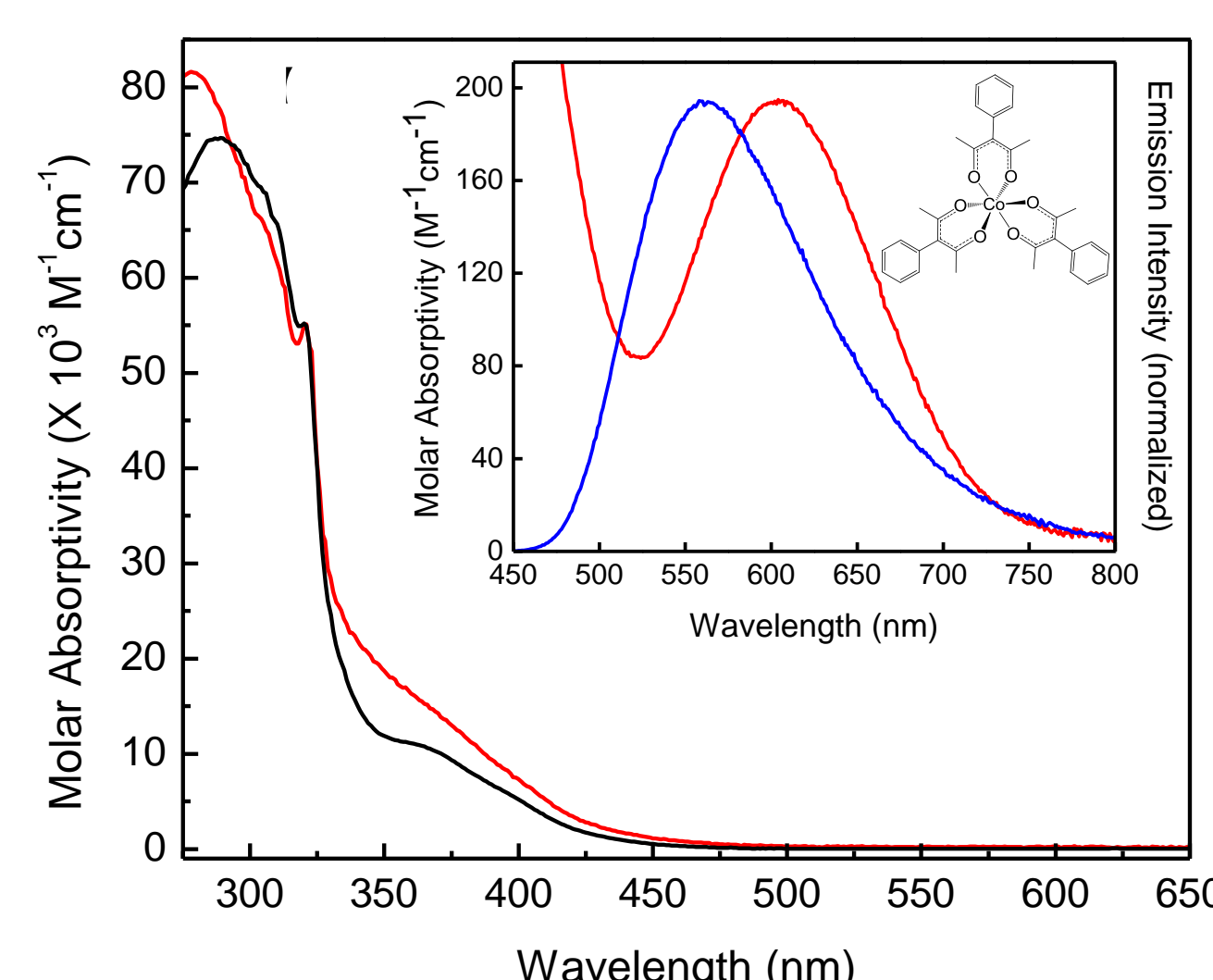
- Designed Re^I-polypyridyl-transition metal assemblies for testing the validity of spin selection rules in energy transfer reactions.
- Cr³⁺, Co³⁺ and Ga³⁺ ions have similar charge-to-radius ratios.
- Low spin Co^{III} (d⁶) and Cr^{III} (d³) have different spin states but similar energies in their ligand field transitions.
- Ga^{III} is spectroscopically silent due to its d¹⁰ electronic configuration, which allows us to differentiate the photo-physical properties of Re^I-polypyridyls in the absence of energy transfer.

Knight, T. E.; Guo, D.; Claude, J. P.; McCusker, J. K. *Inorg. Chem.* **2008**, *47*, 7249.

Steady-State Absorption Spectra of MRe₃³⁺

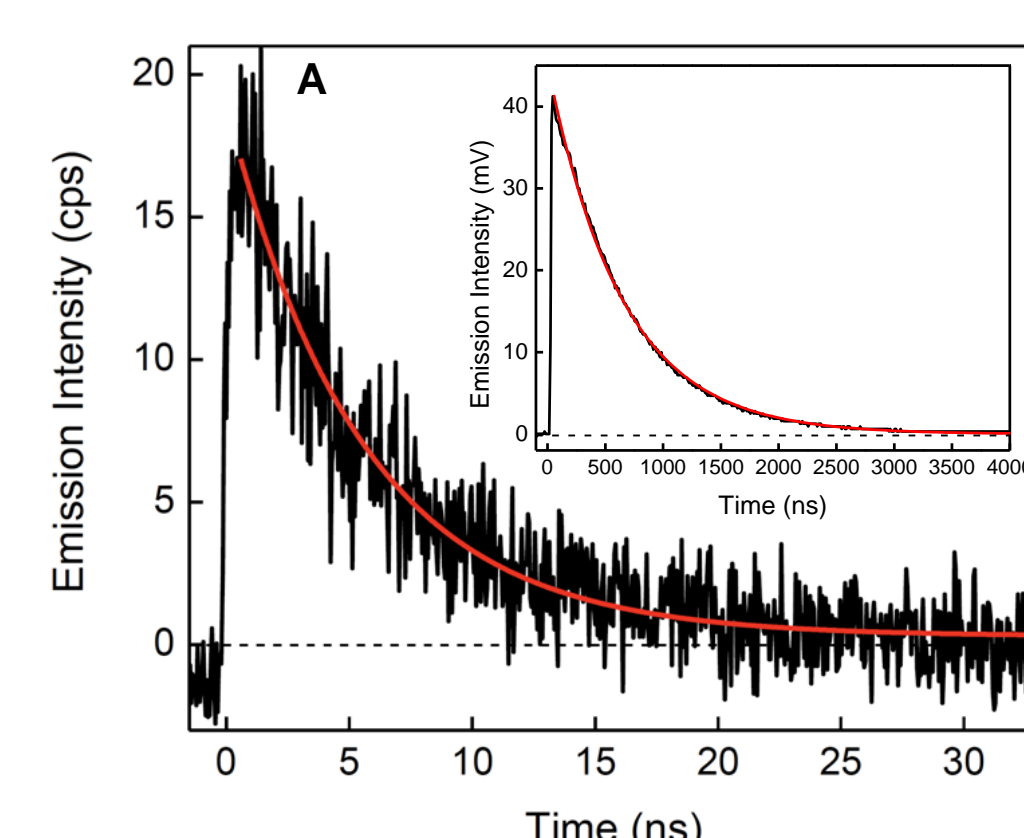


Plots of the electronic absorption spectra of [Cr(pyacac)₃(Re(bpy)(CO)₃)₃](OTf)₃ (CrRe₃, red trace) and [Ga(pyacac)₃(Re(bpy)(CO)₃)₃](OTf)₃ (GaRe₃, black trace). *Inset*: Overlay of the emission spectrum of GaRe₃ (purple trace) with the electronic absorption spectrum of Cr(pyacac)₃ (red trace); the latter was used as a surrogate for the Cr(pyacac)₃ core. Spectra were acquired in CH₂Cl₂ solutions at room temperature.

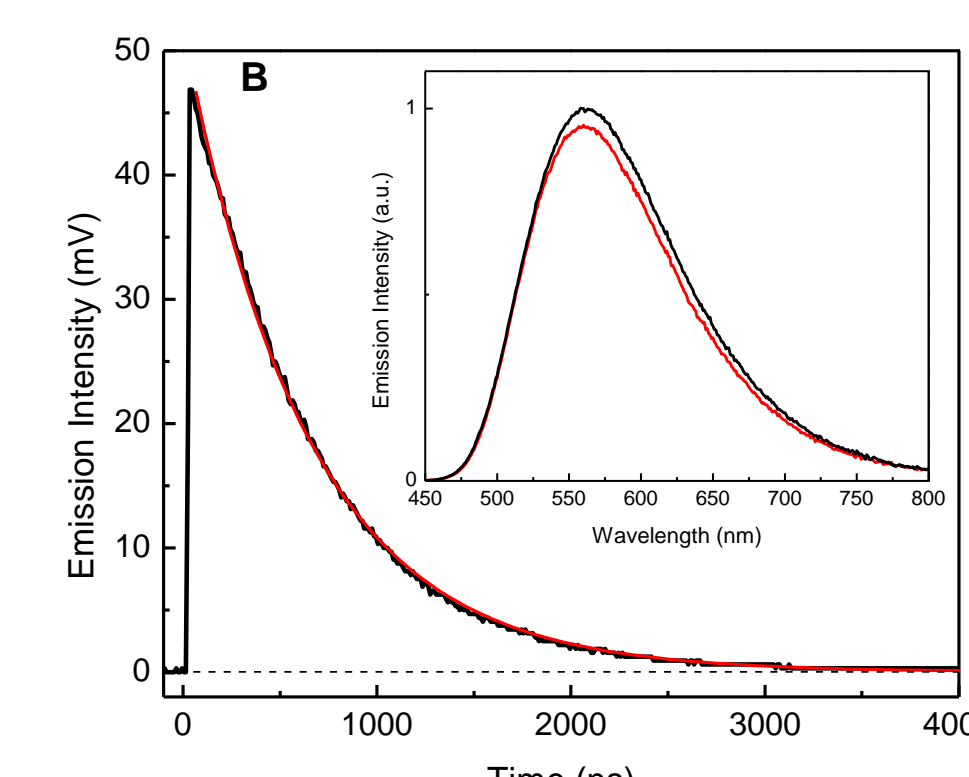


Plots of the electronic absorption spectra of [Co(pyacac)₃(Re(bpy)(CO)₃)₃](OTf)₃ (CoRe₃, red trace) and GaRe₃ (black trace). *Inset*: Overlay of the emission spectrum of GaRe₃ (purple trace) with the electronic absorption spectrum of Co(pyacac)₃ (red trace); the latter was used as a surrogate for the Co(pyacac)₃ core. All spectra were acquired in CH₂Cl₂ solutions at room temperature.

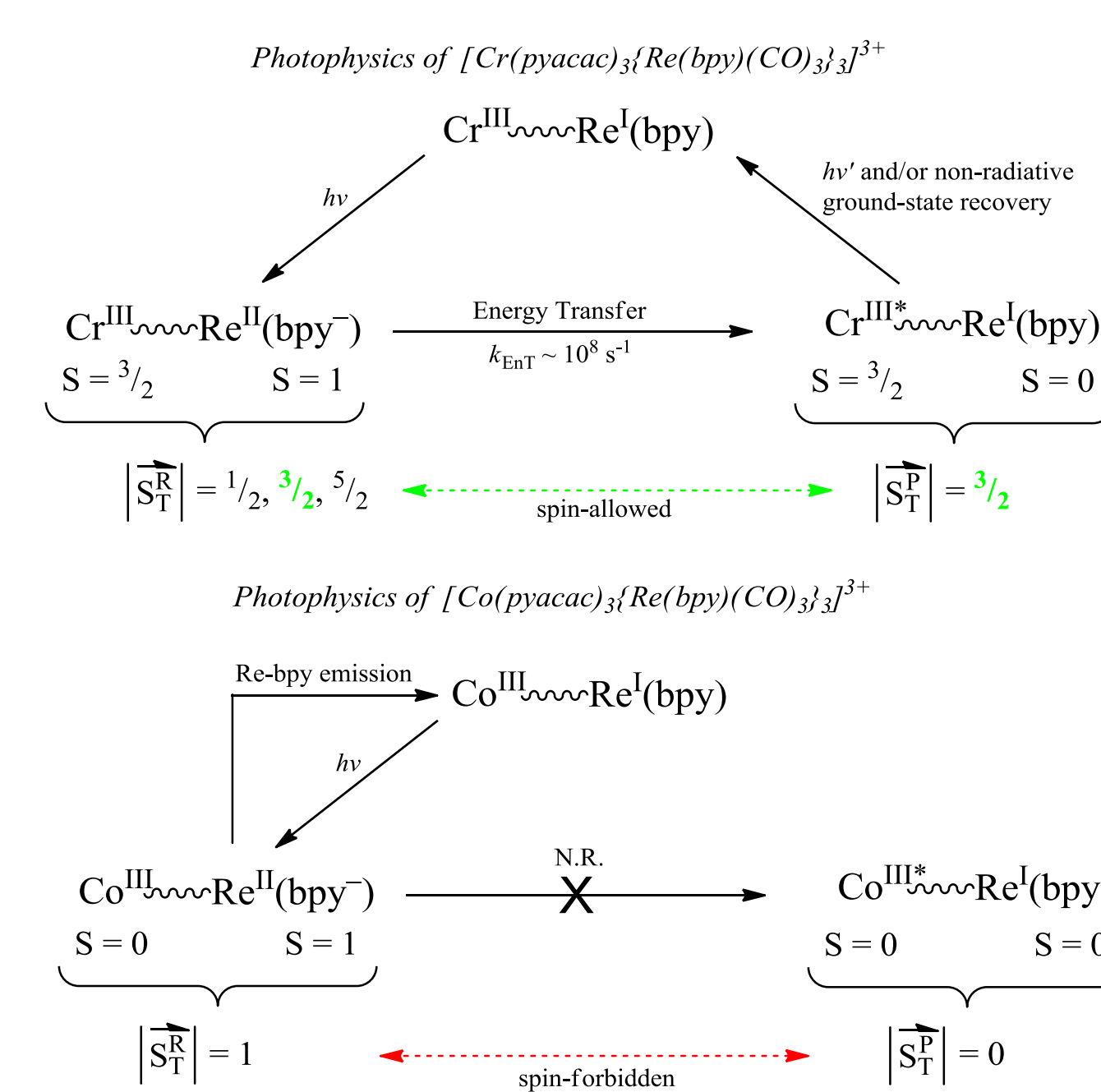
Photophysics of [M(pyacac)₃{Re(bpy)(CO)₃}₃]³⁺



Time correlated single-photon counting (TCSPC) data for CrRe₃ at λ = 580 nm following excitation at 375 nm. The red solid line corresponds to a fit to a single-exponential decay model with T_{obs} = 4.8 ± 0.2 ns. *Inset*: Nanosecond time-resolved emission data for GaRe₃ at λ = 580 nm following excitation at 400 nm. The solid red line corresponds to a fit to a single-exponential decay model with T_{obs} = 630 ± 30 ns. All data were collected at room temperature in deoxygenated CH₂Cl₂ solutions.

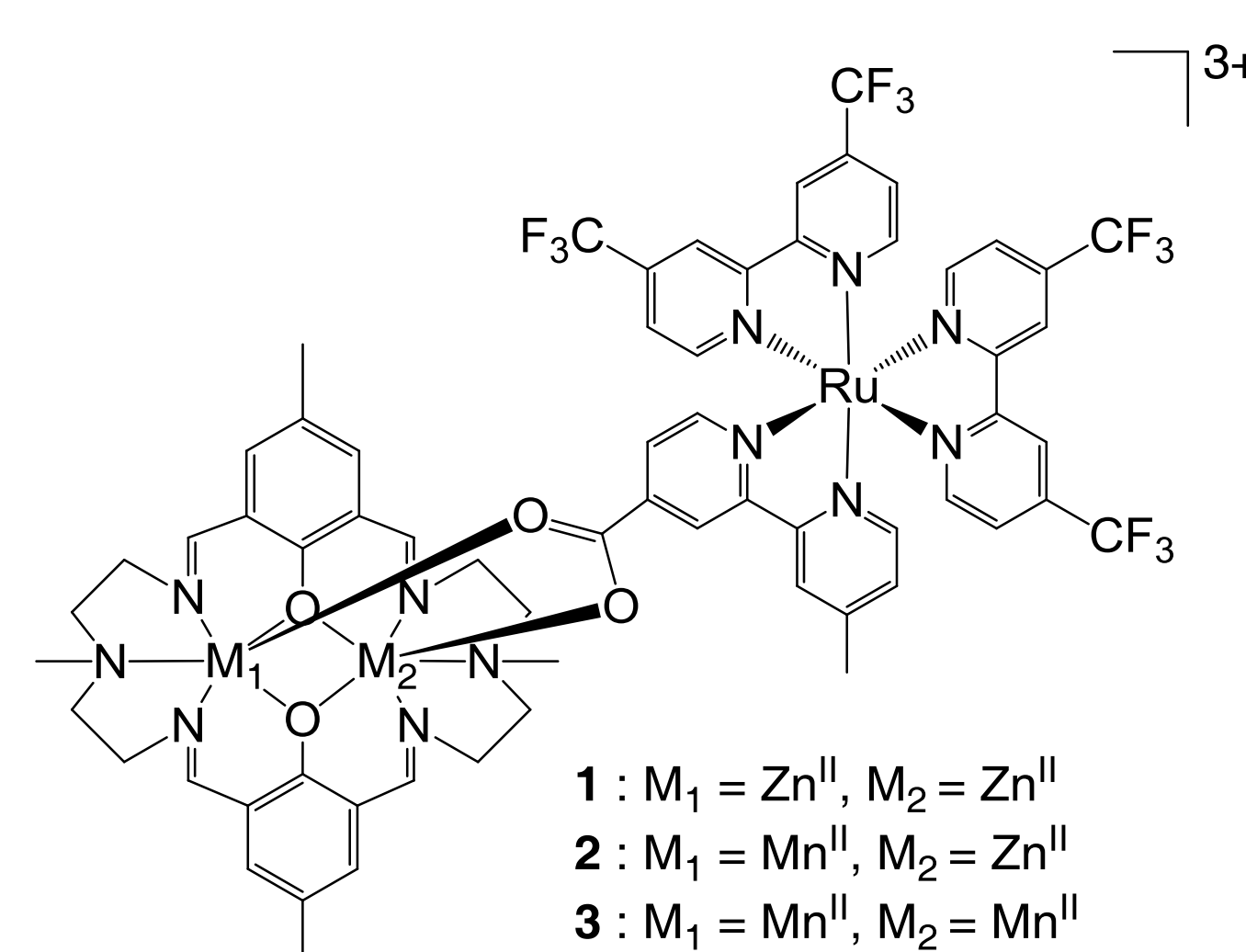


Nanosecond time-resolved emission data for CoRe₃ at λ = 580 nm following excitation at 400 nm. The solid red line corresponds to a fit to a single-exponential decay model with T_{obs} = 640 ± 30 ns. *Inset*: Steady-state emission spectra for CoRe₃ (red trace) and GaRe₃ (black trace). The emission profile for the CoRe₃ complex has been corrected for the differential absorption of Co^{III} versus the Re-bpy moiety. All data were acquired at room temperature in deoxygenated CH₂Cl₂ solutions.



In both compounds, the ³MLCT excited state has a spin multiplicity of |S_D| = 1, which upon undergoing energy transfer to the M(pyacac)₃ core results in reformation of the singlet ground state of the Re-bpy moiety. In the case of M = Cr^{III}, the ⁴A₂ ground state creates a spin manifold in the reactant angular momentum space spanning |S_R| = 1/2, 3/2, and 5/2, which requires coupling to an excited state of the acceptor having |S_A| = 1/2, 3/2, or 5/2 in order to realize a spin-allowed pathway. Angular momentum conservation is clearly satisfied with the ⁴T₂ excited state of the Cr^{III} core (|S_A| = 3/2), as are thermodynamic considerations. Thus, dipolar energy transfer can proceed through the commonality of S = 3/2 states in both the reactants and products, and excited-state quenching of the ³MLCT emission is observed. Upon replacement of Cr^{III} by Co^{III}, the thermodynamics of energy transfer are comparable; however, the low-spin d⁶ configuration of the Co(pyacac)₃ core fundamentally alters the momentum conservation condition. Specifically, the ³MLCT → ¹A₁ emission requires coupling to an excited state of the Co^{III} having |S_A| = 1, not |S_A| = 0 which defines the ¹A₁ → ¹T₁ absorption. Dipolar energy transfer is therefore spin-forbidden for the CoRe₃ assembly, thus giving rise to emission from the Re-bpy luminophore that is indistinguishable from the Ga^{III} model complex.

Spin Distribution Studies of M^{II}M^{II} Energy Transfer Complexes



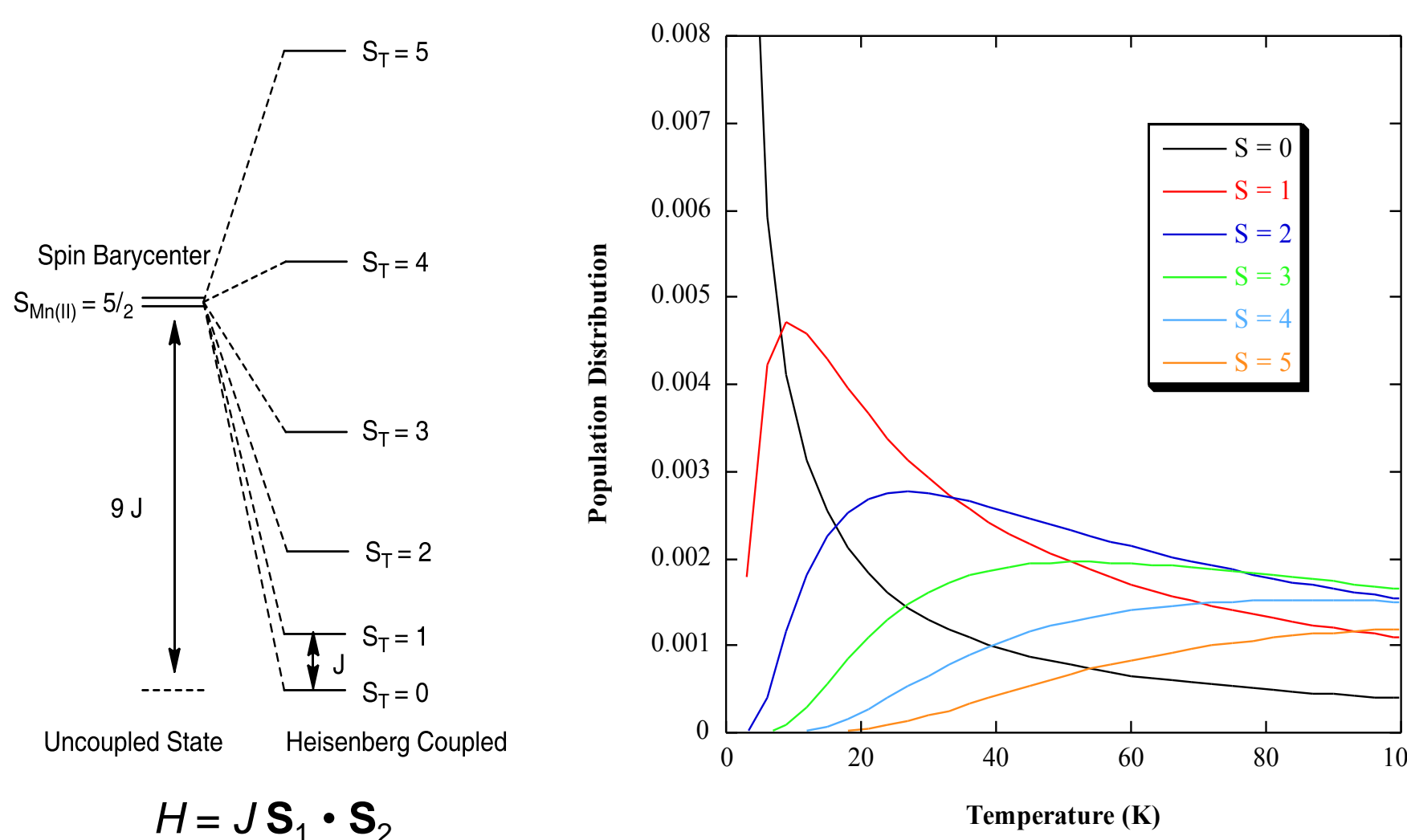
This class of covalently attached donor-acceptor systems allows us to study how different spin states in the same molecule modulate energy transfer reactivity by accessing different spin-allowed reaction paths.

To correctly interpret the rates of energy transfer, the following complexes were studied:

- The ZnZn complex serves as our structural model to understand the dynamics of the ruthenium ³MLCT excited state donor in the absence of any energy transfer quenching due to Mn^{II} in the bimetallic acceptor.
- The MnZn complex allows us to investigate the intrinsic temperature dependence of quenching via energy transfer to the Mn^{II} ion in the absence of additional spin allowed pathways provided by Heisenberg exchange.
- The MnMn complex allows us to observe the effects of the multiple spin-allowed pathways made available via the Heisenberg spin exchange between the ligand field states of both manganese centers in the acceptor.

Soler, M.; McCusker, J. *J. Am. Chem. Soc.* **2008**, *130*, p.4708.

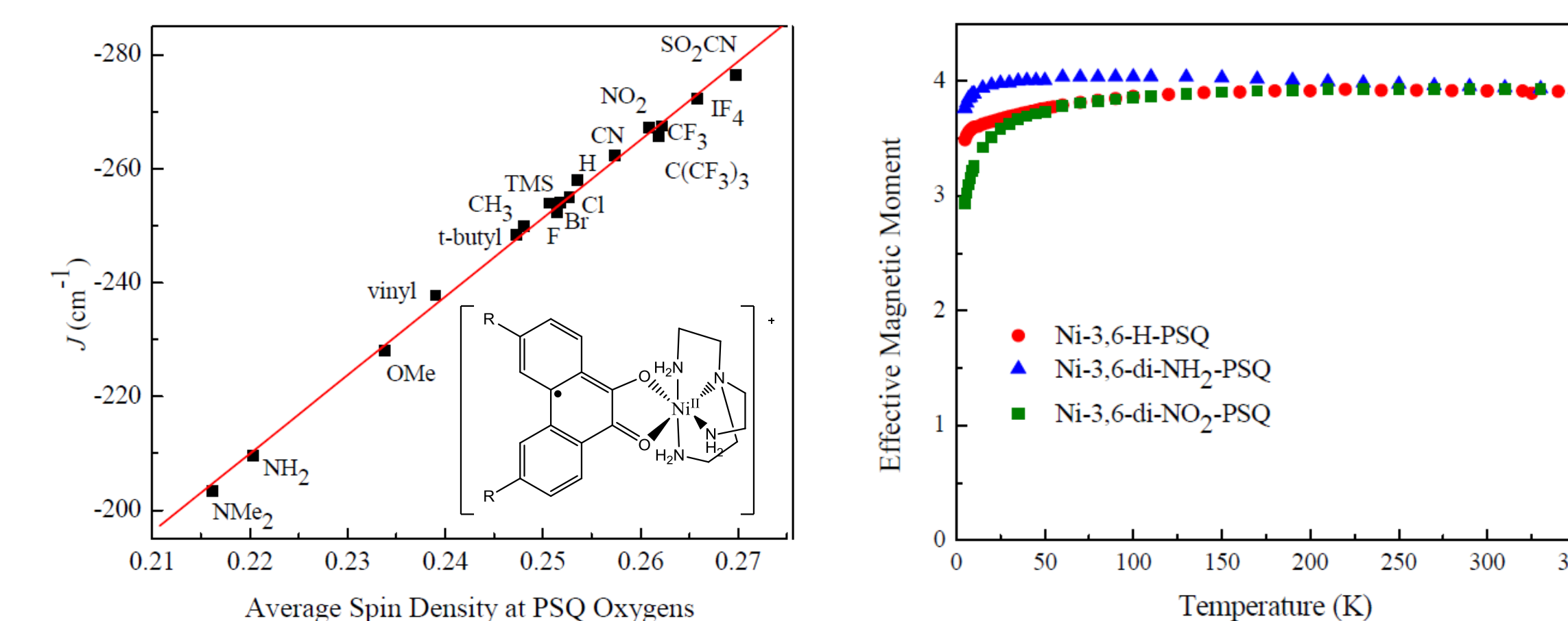
Spin Distribution in M^{II}-M^{II} Complexes



- The spin exchange interaction can be modeled by a Heisenberg Hamiltonian.
- The MnMn complex exhibits small antiferromagnetic coupling (J = 3 cm⁻¹) which results in the two S = 5/2 Mn^{II} centers interacting to form an energetic ladder of spin states ranging from S_T = 0 to S_T = 5.
- The entire spin ladder is energetically accessible below 100 K, allowing all spin dependent dynamics to be probed in an optical glass.
- Population of the thermally accessible higher spin states is controlled via temperature.

Soler, M.; McCusker, J. *J. Am. Chem. Soc.* **2008**, *130*, p.4708.

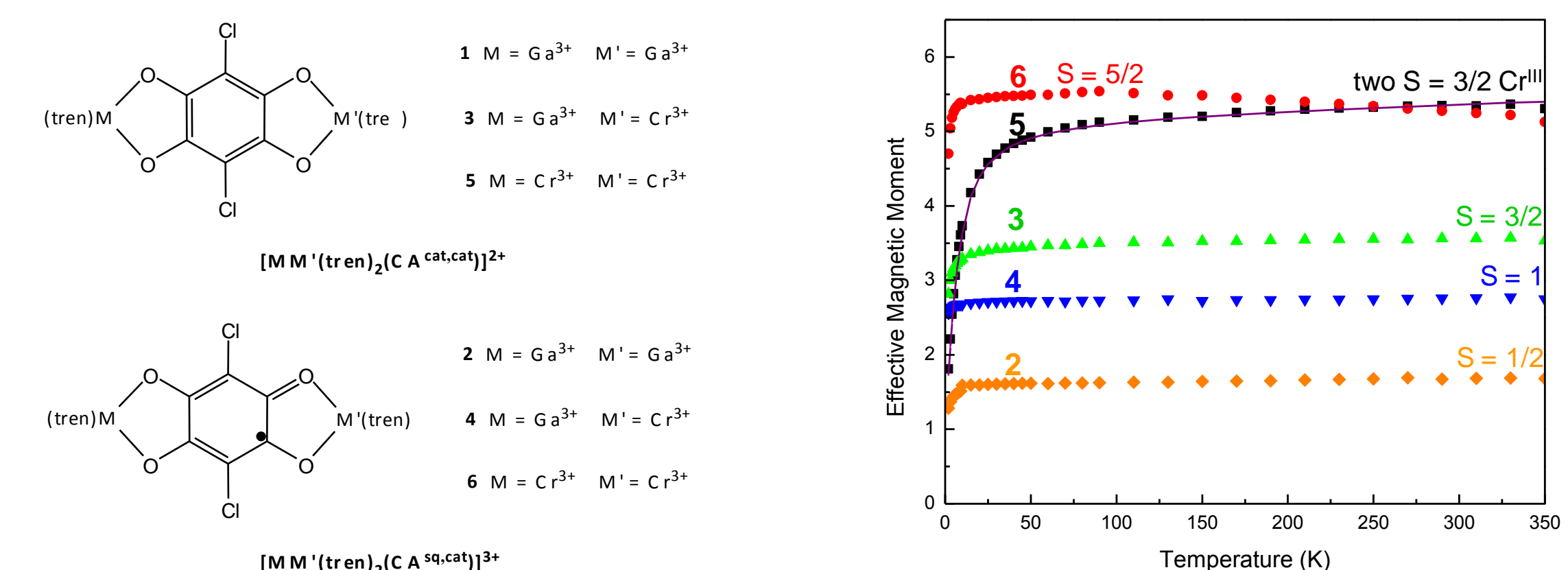
Synthetic Control of Spin Distribution in Spin Exchange Complexes



Correlation between the UB3LYP/6-311g** calculated average α-spin density (NPA) at the phenanthrosemiquinone (PSQ) oxygen atoms and the J value in [Ni(tren)(3,6-di-R-PSQ)]⁺ complexes.

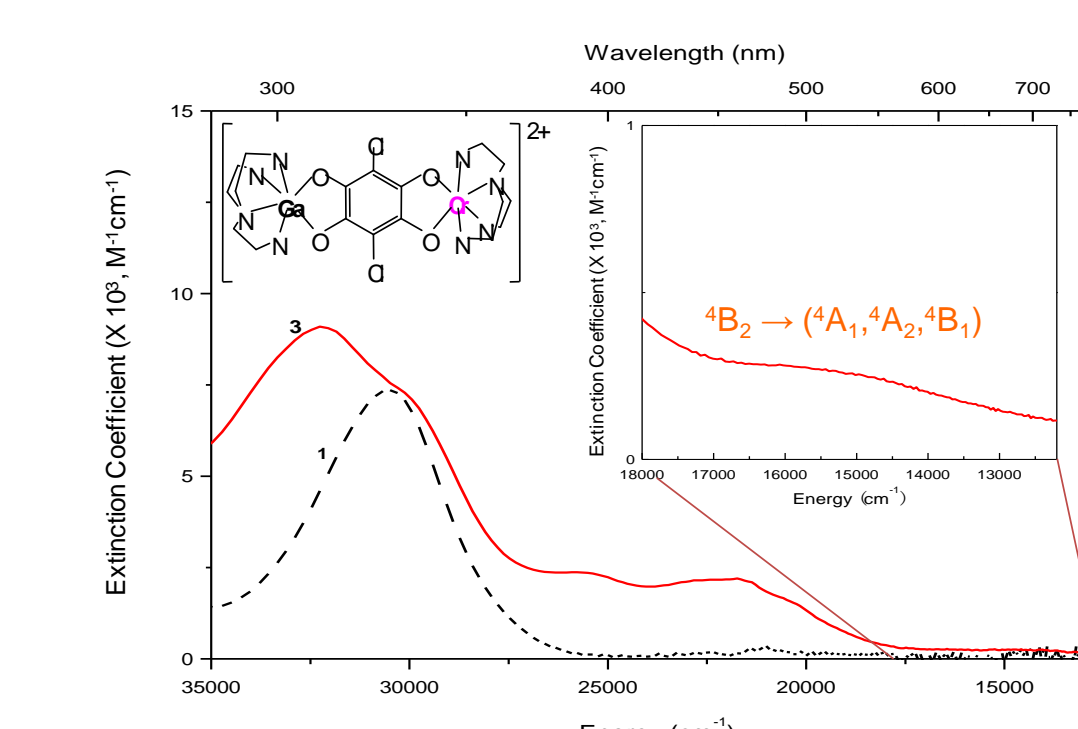
The effective magnetic moment vs. temperature for 3,6-di-H-, -NH₂- and -NO₂ derivatives of [Ni(tren)(3,6-di-R-PSQ)]⁺. J was established for the -NH₂ derivative to be -119 cm⁻¹.

Spin Exchange Effects in Tetraoxolene-Bridged Bimetallic Complexes



Turn on/off spin exchange by incorporating CA^{90,cat}/CA^{cat,cat}. Use (relatively) redox-inert metal ions, leading to well-defined oxidation states of the ligand. Incorporate Ga^{III} to help differentiate physical properties due to spin exchange.

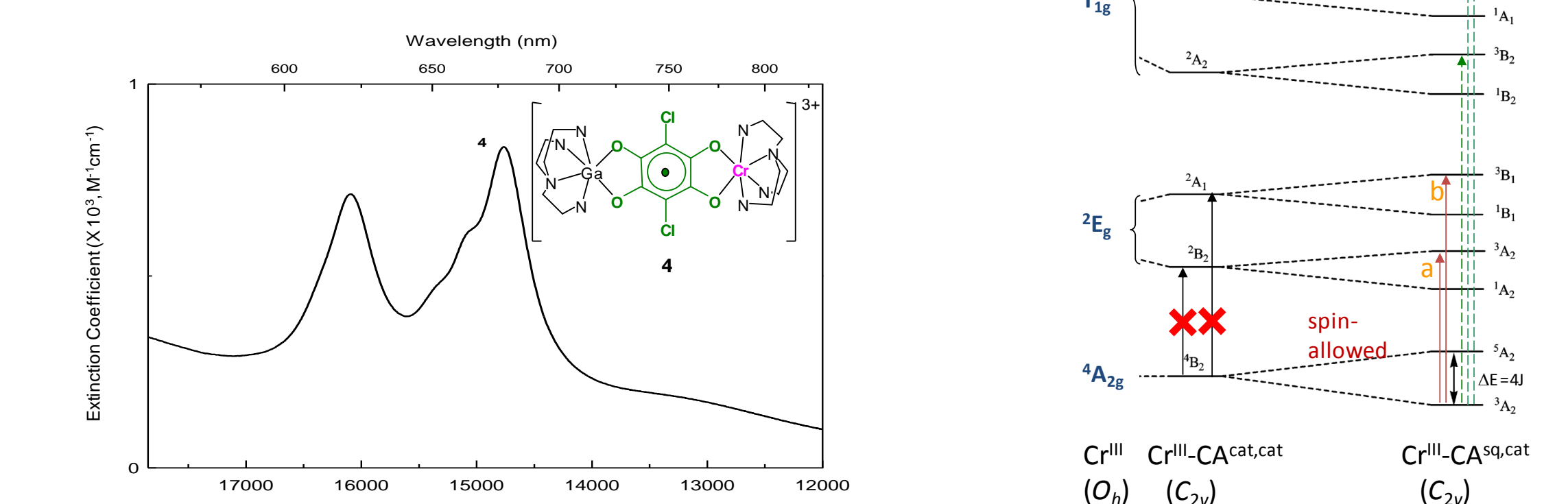
Complexes 2 and 3 show temperature-independent behaviors, indicating no spin exchange in these molecules. The result of 5 reveals weak intra-molecular antiferromagnetic coupling between two Cr^{III} centers, whereas the data of complexes 4 and 6 indicate strong spin exchange coupling between Cr^{III} and the radical bridge.



When one Ga^{III} ion was replaced by Cr^{III} in the CA^{cat,cat} bridged dimer, several new absorptions appeared. Besides CA^{cat,cat} localized transition, the bands in mid-visible are assigned as charge-transfer bands, whereas the lowest energy feature is assigned as spin-allowed d-d transitions of Cr^{III}.

Guo, D.; McCusker, J. *Inorg. Chem.* **2007**, *46*, 3257-74.

New Spin-Allowed Transitions



When Cr^{III} is coupled with a semiquinone, the ligand-field states of Cr^{III} are split and spin-allowed transitions are created. The intensity of the bands associated with ligand-field states is enhanced. We assign these two intense features as ²E_g derived state transitions (a and b), but further study by single-crystal polarized absorption spectroscopy is needed.