

Spin-based Control of Excited-state Reactivity

Matthew D. Woodhouse, Bekah E. Bowers, and James K. McCusker*

Department of Chemistry, Michigan State University, East Lansing, Michigan, USA

jkm@chemistry.msu.edu

Electron spin is a fundamental property of Nature. Although many of the more common physical observables linked to spin are well documented, the degree to which spin helps to define the chemistry of molecular systems is not as clear. This question constitutes the conceptual underpinning of our research effort. Specifically, we are interested in the design of donor-acceptor molecular assemblies that will allow us to probe the extent to which spin and spin-polarization manifests in their physical and photophysical properties. Previous work from our lab demonstrated that the concept of conservation of angular momentum is a necessary consideration for dipolar energy transfer [1]. We have now extended this concept to demonstrate that one can leverage this idea to differentiate between competing energy and electron transfer reaction pathways following photoexcitation of a donor-acceptor assembly [2]. This presentation will describe the synthesis and characterization of new compositional platform that we have developed based on a dimensional reduction of our previously published work that allows for the creation of systems amenable to both electron and energy transfer from an initially formed MLCT excited state (Figure 1). Time-resolved emission and absorption data will be described that reveal selectivity for excited-state electron transfer to Co(III) despite favorable conditions for dipolar energy transfer due to the introduction of a spin restriction for energy transfer. The possibility of generalizing this approach to more complex systems will also be discussed.

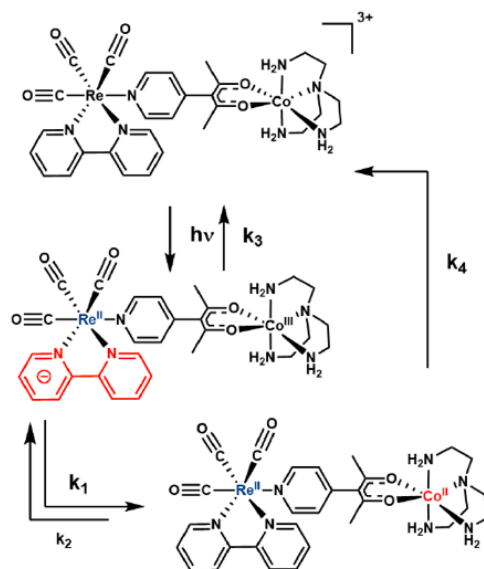


Figure 1. Proposed mechanism of photo-induced electron transfer in a spin-tailored donor-acceptor system.

[1]. D. Guo *et al.* *Science* **334**, 1684-1687 (2011)

[2]. M.D.Woodhouse *et al.*, manuscript in preparation.