

INORGANIC SEMINAR

The Photophysics and Photochemistry of First-row Transition Metal Complexes: Quantum Coherence, the Marcus Inverted Region, and Applications in Excited-state Chemistry

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There has been considerable renewed interest in the photophysical properties of first-row transition metal complexes, driven in part by a long-standing desire to shift to earth-abundant materials for a variety of photolytic applications. A significant challenge to achieving this goal is the fundamental difference in the excited-state properties of first-row metal complexes as compared to their second- and third-row congeners subsequent to light absorption.¹ Our group has been working on understanding the origins of this difference in an effort to develop design principles that will assist in overcoming these intrinsic challenges and develop new paradigms for the creation of photo-active first-row chromophores for applications in solar energy conversion strategies as well as photoredox catalysis.

This presentation will provide a brief survey of the work we have been engaged in over the past several years employing a combination of synthetic chemistry and ultrafast spectroscopy. Our primary focus has been on compounds involving metals with a d^6 valence electronic configuration.² In the case of Fe(II), leveraging information from vibronic coherence was found to provide what amounts to a roadmap for effective synthetic design to lengthen the lifetime of MLCT excited states,³ whereas the excited-state redox activity of Co(III)-based ligand-field excited states⁴ coupled with dynamics occurring in the Marcus inverted region (Figure 1) enabled previously unforeseen applications in photoredox catalysis.⁵ Future directions of our research efforts in each of these areas will also be discussed.

References

1. McCusker, J.K. *Science* **2019**, *363*, 484-488.
2. For a recent review focused on $d6$ metals in particular, see: Sinha, N.; Wenger, O. *J. Am. Chem. Soc.* **2023**, *145*, 4503-4520.
3. Paulus, B.C.; Adelman, S.L.; Jamula, L.L.; McCusker, J.K. *Nature* **2020**, *582*, 214-218.
4. Alowakennu, M.M.; Ghosh, A.; McCusker, J.K. *J. Am. Chem. Soc.* **2023**, *145*, 20786-20791.
5. Chan, A.Y.; Ghosh, A.; Yarranton, J.T.; Twilton, J.; Jin, J.; Arias-Rotondo, D.M.; Sakai, H.A.; McCusker, J.K.; MacMillan, D.W.C. *Science* **2023**, *382*, 191-197.

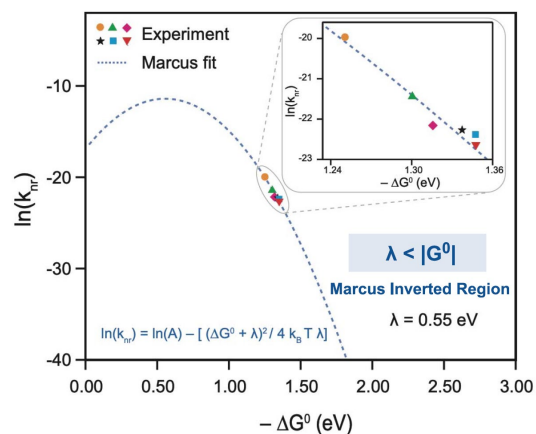


Figure 1. Photophysical data on a series of Co(III) polypyridyl complexes. The data reveal that the excited-state relaxation dynamics of this class of compounds occur in the Marcus inverted region, which allowed for their application in photoredox-catalyzed C-N bond formation chemistry. From ref. 5.



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