BEYOND THE LOWEST EXCITED STATE: HIGHER EXCITED-STATE REACTIVITY IN IRON(II) VIA PYRIDINIUM–CARBENE COORDINATION

Björn Pfund, Bekah E. Bowers, Atanu Ghosh, and James K. McCusker

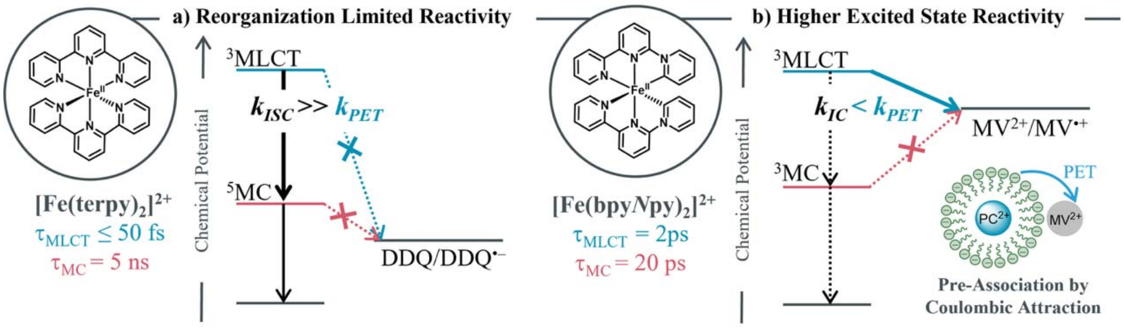
Department of Chemistry, Michigan State University, Michigan, United States

Fe(II)-based photocatalysts are attractive earth-abundant alternatives to isoelectronic Ru(II) systems. Yet their initially formed metal-to-ligand charge-transfer (MLCT) states decay within (sub)picoseconds, traditionally precluding diffusion-controlled photoredox catalysis. Rapid relaxation to longer-lived metal-centered quintet states (^{5}MC) has therefore been considered the only viable reactive pathway.

We systematically evaluated this pathway using strong-field ligand environments designed to promote photoinduced electron transfer from the ^{5}MC state. Despite favorable lifetimes and thermodynamic driving forces, no productive reactivity was observed. Detailed kinetic analysis reveals that electron transfer from ^{5}MC states is fundamentally limited by spin conservation constraints and large reorganization energies. These factors outweigh the modest excited-state energy stored in ^{5}MC, rendering this pathway intrinsically unproductive.[1]

These findings require a conceptual shift in Fe(II) photocatalysis. Rather than attempting to tune the ^{5}MC states, we design a pyridinium–carbene Fe(II) complex that retains and deploys excited-state energy prior to relaxation. By carefully balancing electronic structure, reorganization energy, and substrate pre-association, this system enables picosecond electron transfer directly from the higher-lying MLCT state, a regime long considered inaccessible for Fe(II) complexes. Combined Eyring and Marcus analyses establish quantitative relationships between excited-state energetics, reorganization energy, and reaction rate, providing predictive guidelines for retaining and deploying excited-state energy before dissipation.[2]

By demonstrating productive reactivity from higher excited states in Fe(II) complexes, this work overturns the long-standing paradigm that the lowest excited state defines photoredox chemistry. It establishes energy retention prior to relaxation as a guiding design principle for earth-abundant photocatalysis.



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[1] B. Pfund†, B. B. Bowers†, H. F. Beissel, A. Ghosh, J. K. McCusker. *J. Am. Chem. Soc.* **2025**, 147, 39898–39911.

[2] B. Pfund†, A. Ghosh†, J. T. Yarranton, X-.J. Lien, J. K. McCusker: **2026**, *under review*.