Conformational Control for Biomimetic Energy Transduction

Reactions catalyzed by metalloenzymes underpin global geo- and biochemical cycles, bioenergy conversion processes, cellular transport, and biosynthetic processes that are of fundamental import to human and global health. The vast majority of these metalloenzymes exhibit rate-determining conformational changes that gate active site chemistry. This mechanistic pattern suggests that such conformational gating may be important in maintaining fidelity, control, and energy efficiency during thermodynamically and kinetically challenging transformations. To test this hypothesis, my lab is preparing and interrogating synthetic and artificial systems that serve as simplified models for conformationally gated control over metal ion reactivity. Using light to drive changes in coordinate ligand conformation, we exert control over the kinetics of electron transfer in synthetic copper complexes. Using allosteric binding events to drive changes in protein macrostructure, we exert control over a metallocofactor microenvironment in artificial metalloproteins. Finally, driving proton-coupled electron transfer, we examine the kinetics of carboxylate shift rearrangements in biomimetic dinuclear cobalt complexes. All of these works are unified by the goals of (a) quantitating the kinetic and thermodynamic impacts of conformational control, and (b) leveraging this impact in applications ranging from solar energy conversion, to biomedical imaging, and catalyst design.