Synthetic Fe Nitrogenases and Opportunities in Reductive Catalysis via PCET Pathways

Abstract: Nitrogen reduction to NH$_3$ is a requisite transformation for life. While it is widely appreciated that the Fe-rich cofactors of nitrogenase enzymes facilitate this transformation, how they do so remains poorly understood. A central element of interest has been the site(s) of dinitrogen coordination and reduction, and the atomic level mechanism of this process. Fe is the only transition metal essential to all nitrogenases, and recent biochemical and spectroscopic data implicate Fe as the most likely site of N$_2$ binding within the active site. These observations motivate the pursuit and study of synthetic nitrogenase catalysts as models for detailed study, examples of which were first discovered by our lab several years ago. In this lecture I will discuss our most recent efforts to understand how these Fe catalysts work. In particular, we have posited that proton-coupled-electron-transfer (PCET) steps may be important under certain catalytic conditions, not just for iron but also for other (e.g., Mo) catalysts that convert nitrogen to ammonia. We are undertaking extensive studies to place this idea on firm experimental footing via the study of ring-protonated metallocene intermediates featuring remarkably weak C-H bonds. We are also exploring opportunities for other reductive transformations that might be leveraged via this concept. As will be more broadly emphasized, a longer-term challenge and opportunity for the field is to discover electrochemical ammonia synthesis catalysts, and to understand how to couple such systems with solar water-splitting technologies towards solar fuels. Interfacing electrochemical PCET relays with N$_2$-fixing catalysts provides one attractive approach.

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Zoom meeting
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