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CHEMISTRY &
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DATE	TIME	LOCATION
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CHEMISTRY & BIOCHEMISTRY SEMINAR SERIES: Metal-chalcogenide clusters as modules in photosynthetic assemblies

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Abstract:

Discrete, well-defined metal-chalcogenide clusters are ubiquitous in Nature and accomplish many of the chemical transformations critical to sustaining life on earth. These include the Mn_4CaO_5 oxygen-evolving complex of Photosystem II that oxidizes water to generate molecular oxygen, the Fe-Mo active site of nitrogenase that reduces atmospheric N_2 to ammonia, and Fe-S clusters that are essential electron transfer relays in photosynthetic reaction center proteins. This talk will describe our group's efforts to develop a comprehensive understanding of the electro- and photochemical activity of discrete metal-chalcogenide clusters, specifically Cu- and Co-based clusters, with an eye toward integrating them as modules in artificial photosynthetic assemblies. Cu_6(pyrimidine-thiol)$_6$ clusters possess excited state lifetimes in the 1 – 10 microsecond range, with slight variation depending on solvent polarity and ligand protonation state. These long-lived excited states facilitate photoinduced charge separation to model electron acceptors, confirmed by time-resolved optical and EPR spectroscopies, as well as driving H_2 evolution using a molecular HER catalyst. To investigate clusters as reservoirs and shuttles in photoinduced electron transfer pathways, we have constructed a Hammett-type series of "Chevrel-type" $Co_6Se_8(P(C_6H_4R)_3)_6$ clusters with R = Cl, F, H, CH_3, and OCH_3 via a stepwise synthetic approach. Despite consistent electronic and structural properties across the series, cyclic voltammetry indicates that the electron transfer energetics are strongly influenced by ligand substitution, with the $E_{1/2}$ of a given redox event spanning ~0.5 V. These results provide an early look at our efforts to incorporate metal-chalcogenide clusters in molecular architectures designed to stabilize photoinduced charge transfer, charge accumulation, and multi-electron redox catalysis.

About the Speaker:

Karen Mulfort is a Chemist and Group Leader of the Solar Energy Conversion Group at Argonne National Laboratory. Her research program focuses on the design and discovery of molecular architectures for artificial photosynthesis, and understanding the physical, chemical, and electronic factors that contribute to effective conversion of light energy to chemical energy. Her work is focused largely on utilizing earth-abundant elements and she is particularly interested in discovering the impact of outer coordination sphere and microenvironment on molecular photochemistry and photocatalysis. Karen was a Director's Postdoctoral Fellow at Argonne with David Tiede, after earning her Ph.D. in Materials Chemistry from Northwestern University with Joseph Hupp in 2008.

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