INORGANIC CHEMISTRY SEMINAR

POSTPONED

Prof. Shiyu Zhang

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“Modeling Enzymatic Reactivity with Copper Coordination Complexes”

Abstract: Synthetic models of enzyme intermediates play an important role in evaluating mechanistic hypotheses put forth for critical biochemical reactions. In the first part of my talk, I will discuss how synthetic dicopper complexes can be used as models to understand the reactivity of NO and NO_2^- at copper enzymes. We discovered that dicopper complex could activate NO or nitrite to generate a unique dicopper (II,III) oxo nitrosyl species $[Cu_2(mu\text{-}O)(mu\text{-}NO)]^{2+}$, which exhibits oxidative and nitrosative reactivity. This new mode of reactivity has important implications in how Nature employs NO and nitrite as electron acceptors for hydrocarbon oxidation. In the second part of my talk, I will present our work on developing synthetic models of multicopper oxidase (MCO), a copper protein that utilizes a trinuclear copper cluster to catalyze four-electron reduction of O_2 to H_2O. Despite the abundant literature on synthetic tricopper clusters, no synthetic models thus far can reproduce the reductive regeneration process from $Cu^{II}Cu^{II}Cu^{II}$ to $Cu^{I}Cu^{I}Cu^{I}$ state. We found that an enzyme-like macrocyclic ligand can provide the rigid coordination environment required to support multiple electron transfers at tricopper clusters. With this tricopper model system, we demonstrate the three-electron two-proton PCET from $Cu^{II}Cu^{II}Cu^{II}(mu_3\text{-}O)$ to $Cu^{I}Cu^{I}Cu^{I}(mu_2\text{-}OH_2)$ within a narrow potential range of 170 mV, exemplifying the redox potential leveling effect of secondary proton relays during the accumulation of multiple redox equivalents at metal clusters..

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4:00 p.m. | Mol Sci 3440

UCLA College | Physical Sciences Chemistry & Biochemistry

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