Breaking Scaling Relationships in Molecular Electrocatalysts for the CO_2 Reduction Reaction

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For molecular electrocatalysts, beneficial decreases in effective overpotential are typically correlated with detrimental decrease in catalytic activity. This *scaling relationship* arises when both effective overpotential and kinetic reactivity scale with metal site nucleophilicity. Our research strategy is to break typical molecular scaling relationships by designing molecular electrocatalysts with redox-active ligands where the catalytic reaction is initiated by redox activation of the ligand. These systems decouple metal site nucleophilicity from effective overpotential, thus allowing us to break the correlation between catalyst reactivity and effective overpotential.

In this talk, we will discuss how incorporating electronic substituents onto the redox-active ligand structure of Co(pyridyldiimine) complexes facilitates ligand reduction and leads to an inverse molecular scaling relationship for electrocatalytic CO_2 reduction. We will explore the strategy of incorporating cationic charges into the complex as a means of breaking and inverting scaling relationships both through the incorporation of charged substituents into the ligand scaffold and through construction of homo- and heterobimetallic Co-Co and Co-Zn complexes. We will also discuss whether the activity enhancement from these cationic substituents is best described as through-space electrostatic stabilization of reactive intermediates, or through-bond inductive effects related to the stabilization of the catalytic intermediates. Finally, we will explore how these complexes operate for CO_2 reduction and other electrocatalytic reductions when incorporated into larger coordination polymers and macromolecular scaffolds.