O₂ and H₂: Activation and Reduction using Bio-inspired Small Molecules

Abstract

Axial ligands play a dominating role in determining the electronic structure and reactivity of iron porphyrin active sites and synthetic models. The entire thesis work had three major objectives. First major objective was to derive the ground state electronic structure of iron porphyrin complexes with an axial thiolate, phenolate and imidazole ligands that bind heme in nature, using a combination of spectroscopy and theoretical calculations. The oxygen reduction catalyzed by these iron porphyrin complexes help to elucidate the varying push effects of the three different axial ligands. The spectroscopic data and the differences in kinetics help to develop a quantitative understanding of the "push effect" and, in particular, the electrostatic and covalent contributions to it.

Then this π-anisotropic anionic ligands (thiolate and phenolate) tune the reduction potential (E⁰) by 600 mV due to changing of the solvent and H-bonding to the axially bound ligands. The most important perspective in this thesis is that the thiolate bound iron porphyrin complexes exhibit valence tautomerism between ferric thiolate and ferrous thyl radical states in organic solvents, at room temperature. The ferric thiolate state is favored by greater enthalpy and the ferrous thyl state is favored by entropy which is prevalent at RT. The ferrous thyl form react with O₂ leading to degradation of these ferric complexes in air; a property unique to ferric thiolate complexes. We established that hydrogen bonding to the ferric thiolate form is preferred over the ferrous thyl form in aqueous THF, akin to the one observed in the active site of P450, lead to stabilization of the ferric thiolate state, imparting stability to these compounds against degradation in the presence of O₂.

In the last perspective, we are interested in the focus of understanding of the factors that led to lowering of overpotential in hydrogen evolution reaction (HER) by bio-inspired synthetic models of [FeFe]-H₂ases. The hydrogen is produced using H₂ase models with much lower over potential by understanding the importance of aryl substitution on the bridging nitrogen of an azadithiolate ligand.

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