Computational Studies of Face-To-Face Porphyrin Catalyzed Reduction of Dioxygen

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We are investigating the use of face-to-face porphyrin (FTF) materials as potential oxygen reduction catalysts in fuel cells. The FTF materials were popularized by Anson and Collman [1, 2], and have the interesting property that varying the spacing between the porphyrin rings changes the chemistry they catalyze from a two-electron reduction of oxygen to a four-electron reduction of oxygen. Our goal is to understand how changes in the structure of the FTF materials lead to either two-electron or four-electron reductions. This understand of the FTF catalysis is important because of the potential use of these materials as fuel cell electrocatalysts. Furthermore, the laccase family of enzymes, which has been proposed as an electrocatalytic enzyme in biofuel cell applications, also has family members that display either two-electron or four electron reduction of oxygen, and we believe that an understanding of the structure-function relationships in the FTF materials may lead to an understanding of the behavior of laccase and other enzymes. We will report the results of B3LYP [3] density functional theory [4] studies with implicit solvent models [5] of the reduction of oxygen in several members of the cobalt FTF family.

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