

Proton-Coupled Electron Transfer in Bio-inspired Molecular Catalysts

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Perhaps owed to the efficiency of biological systems, nature often serves as a seminal source of inspiration for the design of catalysts in artificial photosynthesis and energy conversion processes toward the development of alternative renewable energy. Often proton-coupled electron transfer (PCET) is involved in the interconversion of energy. Understanding the role of PCET in the mechanism of bio-inspired catalysts can aid in the design of next generation catalysts and the elucidation of guiding design principles. In nature, hydrogenases are the most active catalysts for hydrogen production, with rates and overpotentials comparable to synthetic Pt catalysts while utilizing earth abundant metal centers in their binuclear active sites. Our collective studies on hydrogenase-based models over the years have revealed two emerging themes: (1) one metal center is acid-base active while the adjacent metal center is redox active, and (2) the importance of thermodynamically less stable but active intermediates.

Nature also often relies on mediators to couple electrons and protons between various cycles in catalysis, a prime example being photosynthesis, where the slow water splitting reaction and the fast redox of a reaction center is mediated by a Tyr-His redox pair in Photosystem II. Understanding the PCET processes in Tyr-His models is helpful for fuel cell design, where the splitting of water provides protons and electrons for hydrogen production. To understand the kinetics of this reaction, we have applied our vibronically nonadiabatic PCET rate theory to predict and interpret kinetic isotope effects for Tyr-His model systems. Importantly, we predicted new models capable of two or more proton transfers coupled to an electron transfer—and these predictions were later validated experimentally. Quinones also play a role in the mediation of electrons and protons across membranes during photosynthesis. Our analysis of fundamental redox behaviors of over one hundred quinones using linear scaling relationships, such as Hammett correlations, revealed key deviations resulting from hydrogen-bonding, halogenated, charged, and sterically-bulky substituents, which are now being used to further develop quinone-based catalysts and devices.