# *Special Seminar in Physical Chemistry*

at the University of Pennsylvania

# Molecular Mechanisms of Artificial Photosynthesis


*Abstract*

In photosynthesis each absorbed photon leads to charge separation on a single-electron level only, while catalytic water splitting and hydrogen production are multi-electron, multi-proton processes. Artificial molecular systems have therefore typically shown light-driven water oxidation and fuel production as half reactions only, using sacrificial agents to accumulate redox equivalents on only one side. In order instead use the energy of reversibly photogenerated charge separated states, it is important to learn to control *accumulative electron transfer* on molecular components. Moreover, water splitting and proton reduction at the catalysts requires management of proton release and/or uptake, which control the electron transfer processes by *proton-coupled electron transfer* (PCET). The understanding and control of PCET can guide design of greatly improved molecular catalysts.

Molecular catalysts for solar fuels processes offer far greater tunability of properties compared to solid materials. This means a greater challenge in design but also a greater potential, if the design principles are understood. Rational design and comparative studies rely, however, on detailed information about the mechanism of catalysis that in most cases is not available. In contrast, turnover frequencies are often reported for overall product formation under conditions where the actual catalytic steps are not rate-limiting and no information on the critical reaction steps is obtained. Experimental studies under conditions where the mechanism can be determined and/or intermediate steps be followed are clearly desirable in order to allow for rational design and evaluation of new catalysts.

In my presentation I will present and discuss the above topics, with examples from our work within the Swedish Consortium for Artificial Photosynthesis.


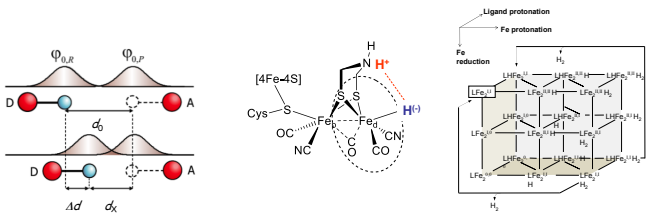


*Figure 1. Schematic figures related to the mechanisms of proton reduction catalysed by FeFe-complexes.*


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