Biomimetic Approaches to Artificial Photosynthesis

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In Photosystem II, light-induced water oxidation is catalyzed by a manganese cluster. Using ruthenium(II)-polypyridine complexes as light-absorbing pigments we made the first Ru-Mn and Ru-Mn_2 complexes and demonstrated light-induced manganese oxidation. The coupling of single-electron light reactions to accumulation of redox equivalents on a potentially catalytic complex is very rarely mimicked, but an obvious necessity for a light-driven water-splitting system. Thus, we have achieved at least three light-driven oxidation steps of a manganese dimer, a process accompanied by ligand exchange reactions that compensated for the accumulated charge and made continued oxidation possible. These reactions were investigated in some detail by EPR, FTIR-spectroelectrochemistry and on-line ESI-MS/electrochemistry techniques.

In the first Mn_2-Ru-acceptor triad we have recently demonstrated a surprisingly long-lived, light-induced charge separation. The half-life of c.a. 200 us is more than two orders of magnitude better than for previously reported Ru-based triads. In a 140 K fluid solvent, this half-life was dramatically increased to c.a. 0.5 s, which is comparable to the long-lived states observed in natural reaction centers. The particular properties of the manganese complex, which led to these interesting results, will be discussed.

A tyrosine residue, Tyr_Z, close to the manganese cluster in Photosystem II is a site for proton-coupled electron transfer. Detailed mechanistic studies of Ru-Tyr and Ru-Trp complexes revealed that the corresponding reaction is in most cases concerted, but can be switched the between concerted and step-wise. Within a new mechanistic model we proposed, we obtained quantitative data for the parameters that govern the competition between these mechanisms.

We have recently made mimics for the Fe-hydrogenase active sites, which catalyze hydrogen production from protons. We demonstrated electrocatalytic hydrogen production and suggested a new catalytic mechanism that may be relevant also for the natural system. Recent studies have been aimed at identifying important intermediates in these reactions.

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References: L. Hammarström *Curr. Opinion. Chem. Biol.* **2003**, *7*, 666; L. Sun et al. *Chem. Soc. Rev.* **2001**, *30*, 36.