

Kyoto Graduate student seminars, Leif Hammarström

1. Electron Transfer, Photoinduced Electron Transfer and Marcus Theory.

In the seminar I will present the basic physical/chemical models behind Marcus theory for electron transfer (ET), with an experimentalists approach. I will discuss the essential parameters that determine the ET rate constant, and how these parameters can be evaluated and controlled. I will further discuss Photoinduced ET and the problem of photochemical charge separation, with examples from the literature.

Literature:

J. R. Bolton and M. Archer, "Basic Electron Transfer Theory", *Advances in Chemistry*, Vol. 228, ACS 1992.

R.A. Marcus, *Angew.Chem. IEE.* **1993**, *32*, 1111 -1121

V. Balzani et al., *ChemSusChem*, **2008**, *1*, 26 –58.

2. Accumulative charge separation and coupling to multi-electron catalysis.

Catalytic redox reactions generally involve multiple electron transfer, and solar fuels production is an excellent example of that. Photoinduced charge separation on the other hand typically separates only one electron and hole per absorbed photon. Therefore, solar fuels production requires accumulation of electrons and holes from several cycles of light absorption-charge separation. This results in new challenges that do not arise on the single electron-hole level, but that needs to be met to create a successful artificial photosynthetic system. I will discuss these challenges and possible solution strategies. I will also discuss the different roles of sacrificial agents versus genuine charge separation.

Literature:

N. S. Lewis & D. G. Nocera *PNAS*, **2006**, *103*, 15729 –15735.

L. Hammarström, *Acc. Chem. Res.* **2015**, *48*, 840-850.

3. Proton-coupled electron transfer (PCET) and its role in solar fuels catalysis.

I will present the basic features of PCET and models to describe these reactions. The coupling of electron and proton will be described, as well as the different possible PCET mechanisms. Furthermore, I will describe how PCET influences solar fuels catalysis and can be used to optimize these reactions.

Literature:

S. Reece and D. G. Nocera, *Annu. Rev. Biochem.* **2009**, *78*, 673-699

S. Hammes-Schiffer *J. Am. Chem. Soc.* **2015**, *137*, 8860–8871

Hammarström and Styring *Energy Environm. Sci.* **2011**, *4*, 2379-2388

4. Photoinduced electron transfer in molecule-semiconductor systems – towards molecular devices.

The combination of molecular and semiconductor components has led to interesting concepts for solar energy devices. The most well-known is the dye-sensitized solar cell, which offers a cheap, low-tech alternative to costly silicon photovoltaics. Thanks to efficient interfacial ET from the excited dye, and a slow charge recombination, very efficient devices can be made in spite of a highly defective, meso-porous material. This strategy has recently been extended to dye-sensitized solar fuel devices, in which molecular catalysts are added. Instead of

generating a photovoltage, these devices use the free energy of charge separation to split water into O₂ and H₂ (or reduced CO₂ products). I will discuss the function, mechanisms and challenges of such devices.

Literature:

A. Hagfeldt *et al.* *Chem. Rev.* **2010**, *110*, 6595–6663 or B. E. Hardin *et al.*, *Nature Photonics*, **2012**, *6*, 162. (DSSCs)

F. Odobel *et al.*, *Coord. Chem. Rev.* **2012**, *256*, 2414-2423; (p-type DSSCs)

Ashford *et al.*, *Chem. Rev.* **2015**, *115*, 13006–13049 (DSSFs or DS-PEC cells)

L. J. Antila *et al.* *ACS Energy Lett.* **2016**, *1*, 1106-1111.