Session: Photocatalysis, Solar Fuels and and Solar Cells

Photophysical investigation of a macromolecular pentad for water oxidation

Jens Föhlinger[1], Masanori Yamamoto[2], Jonas Petersson[1], Hiroshi Imahori[2,3], and Leif Hammarström[1]

[1] *Uppsala university, Department of Chemistry - Ångström Laboratory, Box 523, 751 20 Uppsala, Sweden*

[2] *Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan*

[3] *Institute for Integrated Cell-Material Sciences (WPI-iCeMS), Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan*

E-mail: jens.fohlinger@kemi.uu.se

Artificial photosynthesis using sun light as energy source and water as an abundant electron source to produce fuels such as hydrogen is a promising concept to meet future energy demands. In this study, we investigate an electron acceptor - sensitizer - water oxidation catalyst system combining the photosynthetic functions light harvesting, charge separation and water oxidation.[1]

The dynamics of the first photo-induced charge separation was followed by time resolved transient UV/VIS absorption spectroscopy from the femto second to micro second time scale. The accumulative charge separation was tested by oxygen evolution in the presence of an electron relay (benzyl viologen) and a sacrificial oxidant (sodium persulfate).

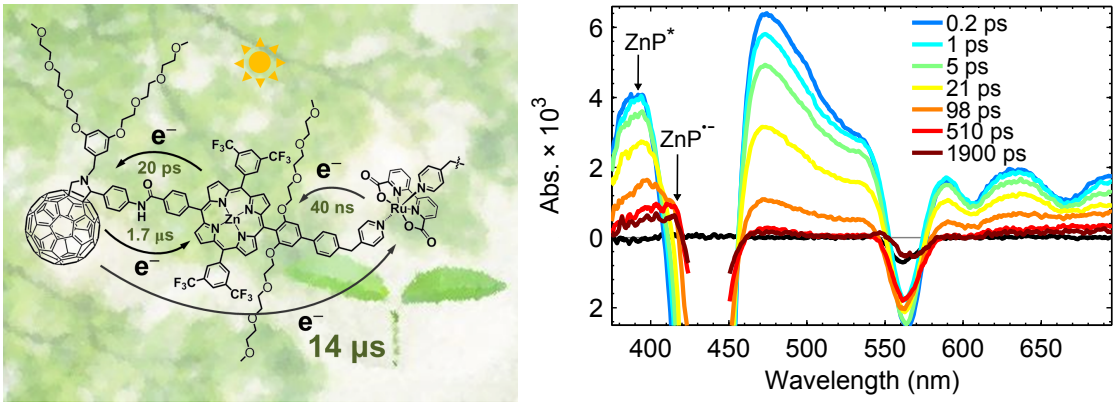

Figure 1: Left: overview of the photophysical and photochemical processes after excitation of the C_{60}-ZnP-Ru-ZnP-C_{60} pentad. The second arm of the pentad is omitted for clarity. Right: time resolved transient absorption spectra at different time delays.

The transient absorption data show a charge separation between the ZnP and the C_{60} moieties with a time constant of tens of picoseconds. The following charge shift of the hole from the ZnP moiety to the Ru catalyst with a 40 nanosecond time constant is out-competing the recombination which takes place with a 1.7 µs time constant, see figure 1. In the presence of benzyl viologen (BV^{2+}) as a redox mediator and sodium persulfate ($Na_2S_2O_8$) as a sacrificial oxidant, C_{60}-ZnP-Ru-ZnP-C_{60} showed a photocatalytic ability for water oxidation with a turnover number of 7 and an initial turnover frequency of 0.1 min^{-1} under visible-light-illumination.

To the best of our knowledge, this is the first example of WOCsensitizeracceptor-linked photosynthetic model system where light harvesting, charge separation and water oxidation are integrated into a single molecule.

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References:

[1] M. Yamamoto, J. Föhlinger, J. Petersson, L. Hammarström, H. Imahori, *Angew. Chem. Int. Ed.* **2017**, 3329.