

## Isotropic orientation of surface confined proteins for investigations of solvent exposed active sites - the case study of photosystem 2

Self-assembled monolayers of redox enzymes on electrodes are a valuable tool for the investigation of catalytic properties and mechanisms. The current response provides direct information on the kinetics of the electron transfer and catalysis without any reporter molecules in solution that may otherwise affect the enzymatic reaction. Control of protein orientation on the surface enables the solvent exposure of active site of the enzyme. Hence, change in catalytic activity with respect to changes in solvent properties can be monitored in real time.

Photosystem 2 (PS2), which was invented first by cyanobacteria 3.5 billion years ago, is the only enzyme that catalyzes the light-driven oxidation of water. This process is inevitable, linked to the generation of reactive oxygen species (ROS) at different sites of the complex. ROS leads to inactivation of the catalytic center, a unique tetramanganese-pentaoxygen calcium ( $Mn_4O_5Ca$ ) complex, and to damage of the protein environment. In the living cell, the central D1 subunit, that coordinates mainly the catalytic metal cluster, is constantly replaced every 20 min by a highly complex repair machinery, but the molecular mechanisms of PS2 photoinhibition are poorly understood. Recent observations point at a possible role of the solvent access to the active site in inducing or controlling the release of ROS. We will assemble photosystem 2 monolayers on electrode surface to investigate the role of solvent on PS2 inactivation by monitoring catalytic currents for water splitting under illumination. Half-life extracted from photocurrent measurements will be compared for different solvent conditions.