**Photoinduced processes in dye-sensitized photoanodes under the spotlight: a multiscale in silico investigation**
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# Summary

Since the advent of the industrial revolution, the rate of technological development, increasing productivity, and population growth has started to reach unprecedented heights. This however has been achieved by exploitation of exhaustible fossil resources, carbon based fuels emitting $CO_2$ that has been captured through natural photosynthesis hundreds of millions of years ago. Not only are these resources limited, but the increase in $CO_2$ levels has also been closely linked to climate change, with detrimental effects to the planet's ecosystem and our habitat. Exchanging fossil resources by renewables is crucial for reducing carbon emissions and to mitigate climate change.

**Chapter 1** of this work discusses these problems and shines light on how solar energy can be used for carbon-neutral manufacturing of synthetic fuels: natural and artificial photosynthesis are introduced, drawing parallels between them and underlying the common fundamental processes involved. Dye-Sensitized Photoelectrochemical Cells are promising artificial photosynthesis devices for carbon neutral solar fuels production, however, the efficiency of these devices remains too low for upscaling and industrial production at affordable cost. This work is focused on understanding photoinduced processes in DS-PECs and proposing potential components with improved properties through computational investigation.

Due to the different time, spatial and materials dimensions in these complex devices, a wide array of computational tools is used to bridge these multi scale processes. In **Chapter 2** an overview is provided of the theory behind the different computational methods employed, starting from the Born Oppenheimer Approximation. DFT as well as semi-empirical methods are described, with which large scale simulations of DS-PEC components become viable. Furthermore, non-adiabatic molecular dynamics are discussed, including the mean field Ehrenfest dynamics and semi-classical AO-MO propagation, that allow for real time simulations of photoinduced electron transfer processes.

## *Summary*

Improving the design of DS-PECs can only be achieved if important fundamental processes are understood. One crucial step in natural as well as artificial photosynthesis is the initial, photoinduced charge transfer step. In nature, there is growing evidence that this ultrafast process involves resonances at the frequencies of specific nuclear vibrations to establish the coherent superposition of excitonic and charge transfer electronic states in the form of vibronic coupling. To understand and disentangle these effects, the coherent charge transfer in a pseudo base model system is investigated in **chapter 3**. It is found that the N-H stretching couples to the electronic motion, driving population transfer from the excitonic to the charge transfer state. Isotope exchange of H by D to shift the frequencies of this mode does not suppress coherent charge transfer, as it leads to a shift in electronic oscillations, allowing different nuclear modes to fulfill resonance condition and couple to the charge transfer process. Furthermore, dynamical symmetry breaking proves crucial for coherent charge transfer. Concerted electronic and nuclear angular motion in the coherent charge transfer process suggests exchange of angular momentum.

In **chapter 4**, the photoinduced electron injection from an NDI based dye into a TiO$_2$ electrode is simulated including full explicit solvation. To be able to simulate these massive extended systems, a quantum-classical, semi-empirical method is used that combines nuclear trajectory generation by DFTB with an AO-MO quantum propagation of photoexcited electron and hole based on an extended Hückel Hamiltonian. The effects of nuclear motion, conformational and trajectory averaging, as well as explicit solvation are disentangled: the results suggest that nuclear motion and trajectory averaging are absolutely crucial to describe the injection process satisfactorily, while explicit solvation is important for correct sampling of conformational space. Using these findings, NDI based dyes with three different anchoring moieties are evaluated with regards to their electron injection properties, with the NDI attached via a catechol anchor showing the greatest promise.

**Chapter 5** deals with the oxidation of water to molecular oxygen and protons through a Ru-based molecular water oxidation catalyst. A thorough computational study on the catalytic cycle, including Gibbs free energies and preferred reaction mechanism, was performed using a variety of functionals and the semi empirical GFN-xTB. While all methods predict the experimentally observed reaction mechanism correctly, the Gibbs free energies remain highly dependent on the employed method. Although B3LYP proved the most reliable, the large computational cost involved limits its applicability. Therefore, an efficient work flow to evaluate Gibbs free energies of the catalytic steps in a water oxidation cycle by combining geometries and frequencies obtained by GFN-xTB with electronic energies by the hybrid functional B3LYP is proposed and validated. This combination shows good agreement with full B3LYP and experimental oxidation potentials, with a decrease of computational time by 2 orders of magnitude. With this speed up, computational screening of oxidation potentials or extended molecular dynamics equilibrations including full explicit solvation become viable.

C**hapter 6** discusses the problem of back transfer of separated electron and hole, increasing the likelihood of recombination and therefore lowering the overall efficiency. To tackle this problem, a series of charge separating dyes of the structure D-$\pi$-A with a polyphenyl amine as donor, fluorenes as bridging $\pi$-systems and a PMI as acceptor, are investigated for an efficient, spatial charge separation that reduces back transfer. It is found that TPA donors lead to larger spatial separation between hole and electron than DPA donors. Increasing the bridge length by introducing one additional fluorene leads to a better charge separation efficiency in comparison with dyes including only one fluorene, while additional fluorenes do not increase the efficiency any further. Furthermore, decoupling of the different components through breaking the conjugation via introduction of methyl groups also results in better hole transfer away from the acceptor in comparison to the planar dye. This is most efficient when decoupling all three components through methyl groups on the fluorene. Finally, the insights from these investigations are used to design *in silico*

an optimized charge separating dye that shows an impressively increased hole transfer in comparison to all other investigated dyes.

Concluding this thesis, **Chapter 7** gives an additional outlook that combines findings and methods from the different chapters to demonstrate that simulating the photoinduced processes *in silico* in an extended photoanode system including electrode, dye and water oxidation catalyst might well be in reach. In conclusion, valuable insight into fundamental photoinduced processes can be gained by computational simulation. *In silico* investigations allow for screening of a large number of potential molecular components and optimization of their properties and interfaces in a DS-PEC, potentially guiding experimental research before tedious synthetic realization.