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

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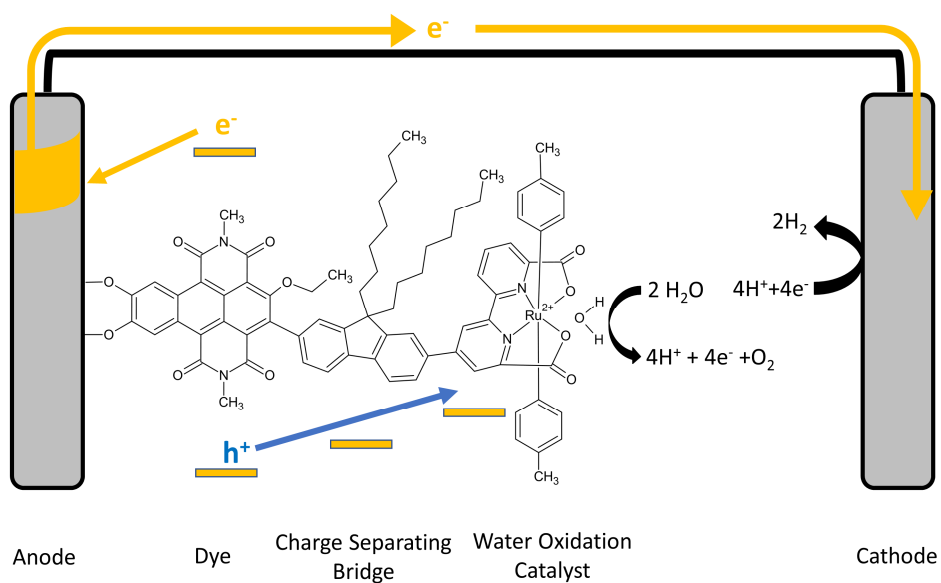
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CHAPTER 1

General Introduction



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In this introductory chapter, the general context of this thesis is presented. The disadvantages of fossil fuels and their influence on climate change is laid out, underlining the need for alternative renewable energy sources, in particular solar based fuels. Natural solar fuel production in the form of photosynthesis is discussed, and the concept of artificial photosynthesis inspired by it is introduced. Dye-Sensitized Photoelectrochemical Cells (DS-PECs) devices are discussed, underlining the parallels with the natural photosynthetic machinery. To design efficient DS-PECs, certain requirements for the properties of all the different components involved should be achieved. The aim of this work is to use computational simulations to guide the optimization of the different components in a dye-sensitized photoanode with respect to their properties and interfaces, to fulfil the requirements laid upon each respective module. Finally, an outline of this thesis is given, discussing how these problems are tackled in this work.

1.1 Solar Energy – Beyond Fossil Fuels

The industrial revolution has increased with accelerating pace global productivity, life expectancy and global population over the last 150-200 years. This massive increase has however been fueled mainly by the unsustainable exploitation of fossil energy resources and synthetic fertilizers obtained through the energy intensive Haber-Bosch process.¹⁻³ With a growing population^{4,5}, global food and energy demand are still further increasing,⁶⁻⁹ while the supply of fossil fuels remains limited.^{10,11} In addition, the CO₂ waste released in the burning of carbon based fuels has been directly linked to increasing global average temperatures and climate change.¹²⁻¹⁴ Finding renewable energy solutions is therefore one of the main challenges humanity has to tackle.

There are several candidates for renewable energy sources. Wind, hydro and tidal power can be used to generate electricity, with the first two having been used as energy supply since millennia,^{15,16} however, they are unevenly accessible around the globe. By far the largest energy source available to us is the star of our planetary system, the sun. Solar irradiation is readily accessible on most places on the globe, though unevenly distributed and time dependent.¹⁷⁻¹⁹ It is almost inexhaustible and provides a manifold of the energy needs that humanity is expected to have in the near future.^{20,21}

Renewable energy is already a rapidly increasing part of the energy mix produced and consumed around the globe.²² In the form of solar and wind farms, these sources of energy are used to generate electricity. However, there are drawbacks with converting solar and wind energy into electricity. Due to the seasonal and spatial difference in supply and demand of these power sources, storage is important to provide a reliable energy supply. Unfortunately, the conversion of electric energy to a more readily stored form is always accompanied by significant losses. One possible way of energy storage is in the form of chemical bonds. The direct synthesis of desirable chemical compounds through sun light is a powerful tool to generate clean

fuels that can be used to balance the production of renewables with their demand. A relatively simple chemical fuel that could be produced is molecular hydrogen.^{23–25}

Hydrogen can be produced by electrochemical water splitting, also releasing oxygen in the process. When using a photovoltaic cell, the produced hydrogen would be carbon-neutral being synthesized using solar power.²⁶ However, a more direct process of generating hydrogen directly from sun light would be preferable.^{27,28}

Hydrogen gas is already used as an energy carrier, but most of the hydrogen is obtained from natural gas, usually with a steam reforming process that is contributing to increasing green-house gas emissions.²⁹ When producing hydrogen as a solar fuel, CO₂-neutral hydrogen could be used in a large variety of circumstances as a clean energy source. It could also decrease the carbon foot print of the Haber-Bosch process, where even a small reduction would have a huge impact due to the massive scale of this energy intensive chemical reaction that accounts for about 1-2% of the global energy consumption.³⁰

Using the solar irradiation to power chemical fuel synthesis directly without the detour of electricity generation is a promising way of producing carbon-neutral, energy rich solar fuels to feed the increasing global energy demand.

1.2 Natural and Artificial Photosynthesis

The manufacturing of energy rich chemical fuels from solar energy is a process that has been performed by plants and other photosynthetic organisms since billions of years.³¹ The earliest photosynthetic organisms obtained the electrons necessary from other reductants such as H₂S and even H₂ rather than from water.³² Oxygenic photosynthesis, where the needed electrons are gained by splitting water into oxygen, protons and electrons, has been associated with the emergence of cyanobacteria,^{33,34} but recent studies revealed a more complex picture and the origin of oxygenic photosynthesis is still an active field of ongoing research.^{35,36}

In oxygenic photosynthesis, energy rich, carbon based molecular compounds such as carbohydrates are produced from oxygen, water and carbon dioxide under the

influence of sun light.³⁷ The series of consecutive photoexcitation, charge separation and redox reactions is commonly known as Z-scheme,³⁸ due to the shape of the energetic diagram as seen in figure 1.1.

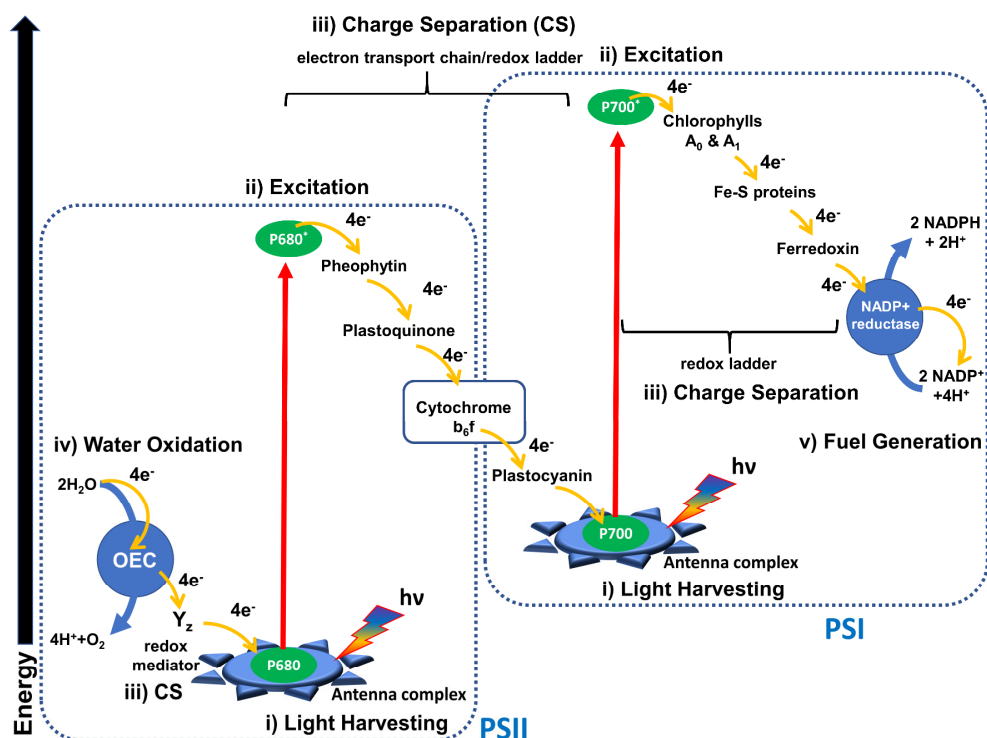
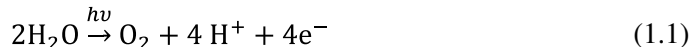


Figure 1.1. Schematic representation of the photosynthetic machinery: Light is harvested by the antenna complexes of the two Photosystems PSI and PSII. The excitation energy is collected at the chlorophyll dimers P680 and P700, where the excited electrons are transferred to the cofactors. The charge transfer state is stabilized by separating the electrons from the holes in a charge separation process (CS) via the electron transport chain and ultimately used by the NADP⁺-reductase to generate NADPH. The hole is used by the Oxygen Evolving Complex (OEC), to split water into oxygen, electrons and protons.

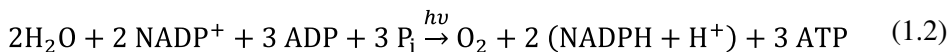
The photosynthetic machinery contains two photoactive, dye-protein complexes, known as photosystems (PS) I and II, respectively. These protein assemblies contain antenna complexes that are responsible for capturing and collecting incoming photons through molecular chromophores, such as chlorophyll and carotenoids.^{39,40}

The excitation energies of these chromophores are tuned by the protein environment, so that the energy of the absorbed photon is transferred coherently in the form of excitons towards the central part of the photosystem, the reaction center.⁴¹ This coherent exciton migration is also found in the simplest light harvesting systems, chlorosomes.^{42–44} Finally, at the reaction center of the PS, the exciton energy is used to photoexcite an electron in a chlorophyll *a* molecular dimer that, depending on its excitation wave length, is called P680 in PSII and P700 in PSI. The photoexcited electron is then transferred to a neighboring cofactor leading to a charge separated state, in a process that is facilitated and stabilized by specific nuclear motions.^{45,46} Experimental and theoretical evidence suggest that resonances between nuclear and electronic motion play an important role in the photoinduced electron transfer in the reaction center as well.^{47–53}

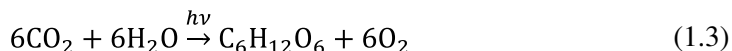
The hole left in the P680 at the reaction center of PSII is filled by an electron donated from the OEC⁵⁴ and obtained by splitting water into oxygen, protons and electrons as given in equation 1.1.



The photoexcited electron is further separated from the hole and the PSII through a series of consecutive electron transfer steps involving redox mediators embedded in the thylakoid membrane, regenerating the ground state of PSII.⁵⁵ (see Figure 1.1) This fast electron transfer is needed to spatially separate hole and electron and thus to prevent charge recombination during the relatively slow hole transfer and water splitting reaction steps. Electronic energy is thereby sacrificed to stabilize the charge separated state.⁵⁶ The electron then fills a hole generated by the photoexcitation of PSI. The photoexcited electron is then donated, through a smaller electron transfer chain, to the NADP⁺ reductase, which reduces NADP⁺ and protons to NADPH. NADPH and ATP, that is gained through the chemical potential gradient of H⁺ between lumen and stroma as well the released energy by the electron transport chain, are then used in the dark reaction as reductant and energy supplier respectively. Equation 1.1 should therefore rather be described by



where P_i corresponds to a phosphate equivalent (PO_4^{3-}). This is also called the light reaction. As mentioned before, NADPH and ATP are then used in the dark reaction to reduce CO_2 into energy rich carbohydrates. For the example of glucose, the total chemical equation of oxygenic photosynthesis then becomes⁵⁷



For each oxygen molecule generated, at least 8 photons have to be absorbed to transfer the needed 4 electrons from water to NADP^+ .⁵⁸

Even though the evolutionary history of oxygenic photosynthesis has not been completely revealed, it is clear that its emergence has led to an incredible change of the terrestrial environment and ecosystem. The waste product oxygen that was released by the photosynthetic organisms into the oceans was first subdued by coprecipitation with iron ions to form oxides in the shape of banded iron formations.⁵⁹ However, after saturation of this buffering system, the released oxygen lead to a huge spike in first solvated and then atmospheric oxygen that lead to a mass extinction event called the Great Oxygen Catastrophe.^{60,61}

We live on a planet that has been deeply shaped by the changes due to this event: It led to the high oxygen atmosphere and the emergence of new organisms that use oxygen for respiration.^{62–65} The importance of oxygenic photosynthesis can therefore not be overstated. All of the fossil fuel we use now, has its origin in oxygenic photosynthesis performed hundreds of millions of years ago, removing CO_2 from the atmosphere.⁶⁶ If we want to generate carbon neutral chemical fuels, we need to find efficient ways of copying this process and use solar energy to directly generate the desired compounds in the form of artificial photosynthesis. To produce artificial solar fuels, two general pathways can be taken: (i) in an indirect approach, a photovoltaic cell can be coupled to an electrolyzer to use the generated electricity to split water in oxygen and the fuel hydrogen; or (ii) a direct, integrative approach can

be used where without the detour of electricity production, the photoexcited electron can be used for reduction of *e.g.* protons to hydrogen or carbon dioxide or carbon monoxide to methanol or even hydrocarbons, while the hole is used for water oxidation.

If we look at the photosynthetic machinery in a modular way, we can split it in several different components responsible for the following processes:

- i) Light harvesting – antenna complexes around or associated with PSI and PSII
- ii) Photoinduced excitation - $P680 \rightarrow P680^*$ and $P700 \rightarrow P700^*$ dyes
- iii) Charge separation – electron transport chain/redox ladders/redox mediator
- iv) Water oxidation – Oxygen Evolving Complex (OEC)
- v) Fuel generation – $NADP^+$ -reductase

In figure 1.1, the different processes and their respective modules are marked.

For an effective artificial photosynthesis device, it is of advantage to keep this modular approach and design components specialized in a specific function and as efficient as possible while also optimizing the interfaces between them. Each of these components can then be adapted towards the needs of the artificial photosynthesis device, dependent on reactants, products and materials involved.

1.3 Dye-Sensitized Photoelectrochemical Cells

One possible artificial photosynthesis device that has attracted much interest in recent years are Dye-Sensitized Photoelectrochemical Cells (DS-PECs).^{67,68,27,69–71} A schematic of a tandem DS-PEC can be seen in figure 1.2. In DS-PECs, a semiconductor electrode, such as anatase TiO_2 , is sensitized with a molecular chromophore able to absorb energy in the visible light range. The photoexcited dye at the photoanode then injects the excited electron into the Conduction Band (CB) of the semi-conductor.^{72–75} The electron is transferred through an external circuit to the cathode. The hole left at the dye is then transferred to a suitable water oxidation

catalyst (WOC), which extracts electrons from water through water oxidation, regenerating the dye's ground state.^{69,76–78} The released protons diffuse through a Proton Exchange Membrane (PEM) towards the cathode, where, together with the electron, fuel generation takes place via reduction of the protons through a Hydrogen Evolution Catalyst (HEC).²⁷ In tandem DS-PECs, this is coupled to another photoexcitation of a dye on the cathode side.^{28,79}

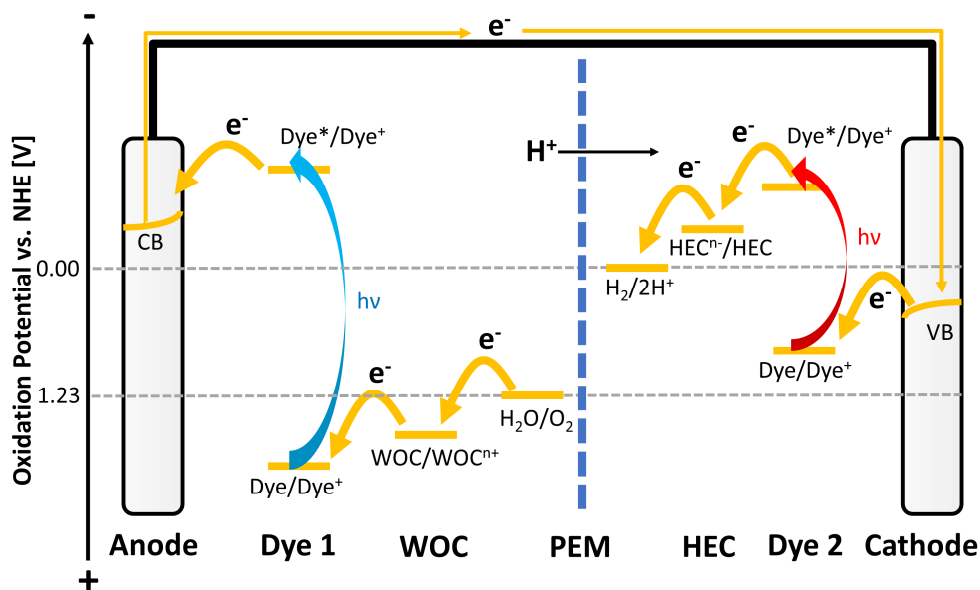


Figure 1.2. Schematic representation of a Dye-Sensitized Photo Electrochemical Cell (DS-PEC). The Photoexcited dye at the anode injects an electron into the conduction band of the electrode, which is used on the cathode side for hydrogen evolution. The hole is used by a molecular Water Oxidation Catalyst (WOC) to oxidize water, under release of oxygen and protons. The protons diffuse via a Proton Exchange Membrane (PEM) towards the cathode to be used for hydrogen evolution.

The efficiency of DS-PECs are closely linked to the optimal choice of components, their energetic alignment and their arrangement, which should favor charge separation and hinder recombination.^{80,81} This holds especially true due to the large time mismatch between electron injection and water oxidation.⁷³ To optimize the overall process, it is of advantage to separate the DS-PEC into different modules

specialized in performing specific processes, using the same modular separation as present in natural photosynthesis (see figures 1.1 and 1.3).

A molecular dye/photosensitizer is used to absorb photons, getting photoexcited in the process.

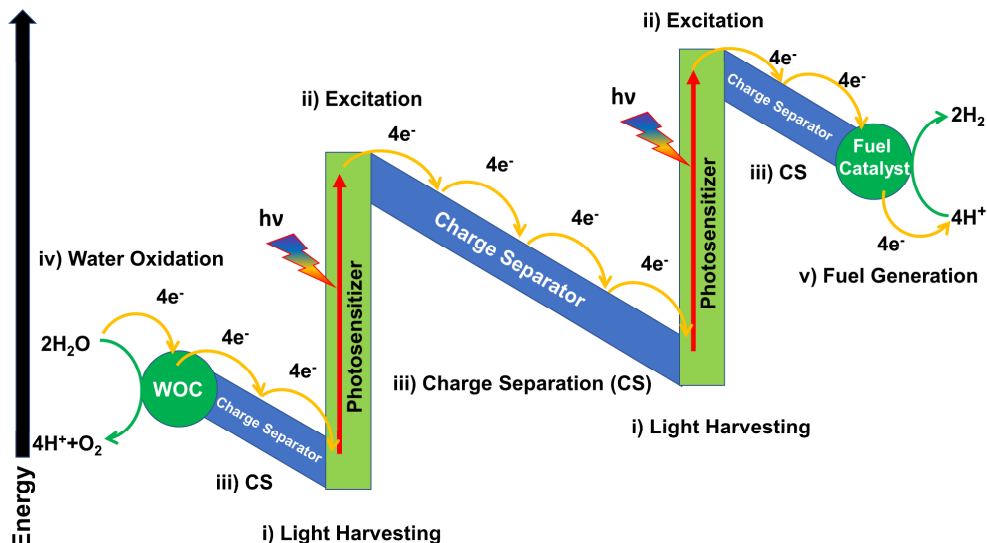


Figure 1.3. Schematic diagram of a tandem DS-PEC, showing the parallels to the z-scheme in natural photosynthesis: Light is harvested by the two photosensitizers/dyes (i), resulting in photoexcitation of the dyes (ii). The excited electrons are separated from the holes via charge separators (iii). The holes are used by a molecular WOC to oxidize water (iv), the electrons are ultimately used to reduce protons to hydrogen (v).

Since there is no commonly used additional module for light harvesting in DS-PECs, a dye needs to be an efficient light absorber in the visible light range. Large spatial charge separation can be achieved via different approaches. In the simplest DS-PECs, the separation is performed by the semiconductor electrodes, as the photoinjected electron relaxes from the band state it was injected in, to the conduction band edge, which is generally a bulk state away from the surface due to band bending. The electron is further removed by transfer to the other half-cell, the (photo)cathode. Adding further charge separators between different modules can

decrease the recombination rate: This can be done *e.g.* via molecular or redox shuttle approaches, using redox partners in the electrolyte to remove the hole from the dye, such as iodide, ferrocene, $\text{Fe}(\text{ClO}_4)_2$ or 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO).^{82–85} In a redox shuttle, however, this separation is typically non-directional, even though approaches for launching the shuttle away from the electrode exist, and back transfer still plays a large role due to the bottle neck of diffusion.⁸⁶ Several different molecular approaches can be taken:

i) implementing an energetic gradient by using either a chain of dye molecules with tuned Highest Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) energies to favor a separation of electron and hole or a push-pull dye, *ii*) inclusion of an effective barrier for either the electron or hole, by using molecular moieties with either significantly lower HOMO or higher LUMO energies or a molecular rectifier.^{87–90}

Water oxidation takes place in a molecular, homogeneous transition metal-based water oxidation catalyst (WOC). This catalyst can either be bound covalently to the dye or semiconductor interface, or in solution with redox shuttles carrying the charges between photooxidized dye and WOC.

The last step, the fuel generation, takes place at the cathode. It can involve proton reduction as in figure 1.2, or *e.g.* CO_2 reduction.^{71,91} This can either be driven purely electrochemically using the electrons obtained from the photoanode and their potential or can include a second photoactivation in a so-called tandem cell, mirroring the Z-scheme in natural photosynthesis. In this project we focus mainly on the processes occurring at the photoanode of a DS-PEC device.

Successful integration of the respective modules also involves the minimization of overpotential. To achieve this, three key requirements need to be fulfilled: *i*) to prevent back transfer and/or fluorescence, the charge separated states in the process need to be stabilized, *ii*) for the catalysis to proceed, overpotential for both the WOC as well as the fuel generating catalyst need to be supplied to drive their respective

chemical reactions, iii) due to the release of oxygen and hydrogen, free energy needs to be supplied for the device to run at the thermoneutral voltage.^{92,93}

As mentioned above, requirement i) is often achieved by a chain of electron transfer events, where free energy is sacrificed to spatially separate hole and electron. Requirement ii) depends on the choice of catalyst, while requirement iii) corresponds to an additional 0.25 V (1.48 V vs. 1.23 V) at standard conditions.⁹³ Keeping losses low and still meeting these requirements demands optimal energetic alignment between the different components, while supplying enough excess energy through the excitation of the dyes with light still in the visible range. Fulfilling these demands to increase device efficiency is a challenging task of finding and integrating suitable molecular modules.

1.4 Aim of the Thesis and Outline

The production of chemical fuels from solar energy is a non-trivial task and stands or falls on both the efficiency of the single modules, but also on the optimal combination and integration of the different modules to one another. Computational simulations can be a powerful tool to design and optimize different components *in silico* to help finding promising candidates and combinations before tedious and expensive trial and error synthesis. This remains the main goal of this thesis.

However, the large variety of the involved processes demands for a wide range of computational methods. In this thesis, several diverse computational methods are employed to tackle this wide variety of chemical and physical challenges. Therefore, in chapter 2 these methods and their theoretical background are laid out and explained.

The 3rd chapter deals with the fundamental process of photoinduced charge transfer in a donor-acceptor supramolecular complex. The role of non-adiabatic coupling between nuclear and electronic motion and coherence effects is investigated. We have been able to reveal in detail how vibrational-electronic resonances facilitate the photoinduced electron transfer. Investigations of isotope

effects on the charge transfer process show how appropriate nuclear modes are selected, while dynamic symmetry breaking proves crucial for the coherent interconversion between excitonic and charge transfer state. Our simulations further emphasize the convergence of time scales between nuclear and electronic motion and angular momentum transfer between electronic and nuclear degrees of freedom.

In chapter 4, real time simulations of photoexcited electron and hole in a dye-sensitized photoanode reveal the process of electron injection into the semiconductor electrode. Both, a core extended naphthalene diimide (NDI) based dye with three different anchoring moieties as well as the three anchoring molecules themselves are tested regarding their electron injection properties. Using a quantum-classical semi-empirical approach, our simulations of photoinduced electron injection within these large extended systems with full explicit solvation reveal that nuclear dynamics and trajectory averaging prove crucial in a realistic simulation of the electron injection process. Furthermore, the effect of an explicit description of the electrolyte on the electron transfer dynamics is revealed.

Chapter 5 deals with the water oxidation and introduces a computationally efficient method to investigate the catalytic cycle in a water oxidation catalyst. We introduce a novel workflow that combines Density Functional Theory (DFT) and the tight binding approach GFN-xTB to obtain reliable free-energy differences at a highly reduced computational cost.

In chapter 6, focus is laid on the spatial separation of photoexcited electron and hole via charge separating push-pull dyes and how to optimize them. It includes a study on the effect of electron donating and withdrawing properties of the push system in these interesting organic molecules. Furthermore, a systematic theoretical investigation dissects the influence of bridge length, additional phenyl groups and decoupling through sterically challenging ligands on the charge separation capabilities. These results were applied in an *in silico* optimization of such a charge separating dye, improving the charge separation efficiency significantly.

CHAPTER 1

In chapter 7, an outlook is given on a system combining the components to form a full dye-sensitized Photoanode in a DS-PEC with the inclusion of the light harvesting and charge transfer component (an NDI based dye) and hole transfer to a covalently bound water oxidation catalyst.

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