



## Summary

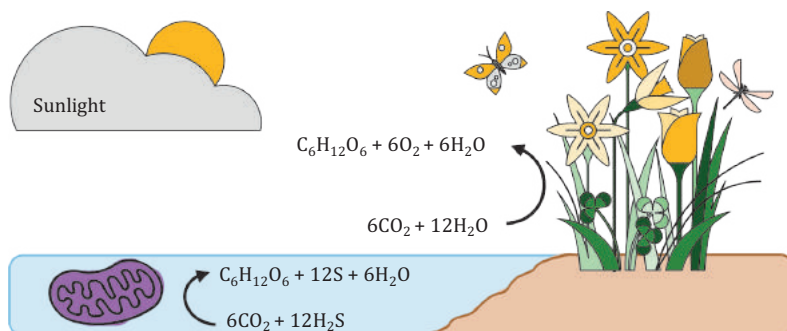
# Redox Mediation in Dye-Sensitized Photoelectrochemical Cells

Coupling Solar-Driven Oxidative Catalysis to Fuel Generation

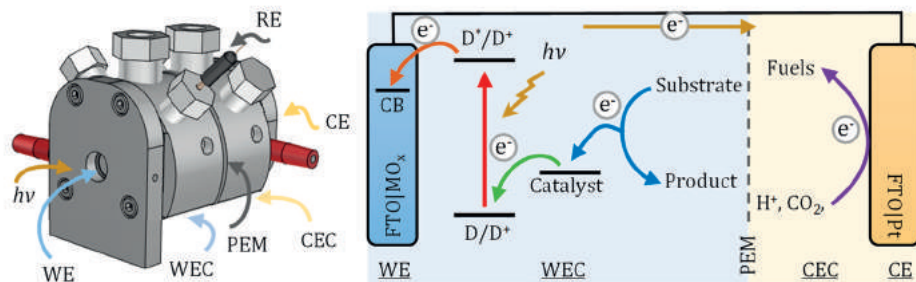
The transition from fossil fuels to sustainable energy sources is a challenging but necessary task to mitigate climate change. Several new technologies are needed to make this mission possible within our generation. A well-developed technology is capturing solar energy with photovoltaic cells (also known as PV cells) to produce electricity. The Sun is a clean energy source that never runs out, and solar power is therefore considered sustainable. Nonetheless, the Sun's night-day and winter-summer cycles significantly impact the consistency of electric power production, making it necessary to explore long-term solutions for energy storage. The sun-powered conversion of plentiful primary feedstocks such as water and CO<sub>2</sub> into combustible chemicals — solar fuels — may offer a solution.

Solar fuels can be produced indirectly by coupling PV panels to an electrolyzer, using generated electrical energy to drive electrochemical (uphill) reactions, enabling energy storage within molecular bonds. Photosynthesis, the largest natural “solar-to-chemical energy” converter, uses a direct molecular approach, combining light-harvesting pigments, electron transport chains, redox complexes, and molecular catalysts within its operating mechanism. Importantly, natural photosynthetic systems are tuned to utilize different electron donors, although water is the best known (Figure 6.1). The natural photosystem inspires scientists to develop devices that emulate photosynthetic processes by similar operation principles as natural systems. These “artificial leaves” operate using molecular components, combining light harvesting with oxidation and reduction reactions to enable chemical transformations.

Dye-sensitized photoelectrochemical cells (DSPECs) feature electrodes that employ light-absorbing dyes to absorb to power chemical transformations. The DSPEC evolved from the dye-sensitized solar cell (DSSC) featuring molecular dyes, semiconductors, and redox mediators working in harmony to absorb light and facilitate the solar-to-electric energy conversion. To create DSPECs, the redox mediators responsible for regenerating the photooxidized (or photoreduced) dye in DSSCs are replaced by redox-active catalysts to realize oxidative and reductive transformations.



**Figure 6.1.** Nature's photosynthesis with various oxidation products. Green plants perform the water-splitting reaction with oxygen gas as the oxidative product. Purple bacterial oxidize hydrogen sulfide to elemental sulfur.



**Figure 6.2.** Overview of the photoreactor and schematic representation of an operating DSPEC for substrate oxidation and reductive fuel production. WE(C) = working electrode (photoanode) (compartment), PEM = proton exchange membrane, RE = reference electrode, CE(C) = counter electrode (compartment), FTO = fluorine-doped tin oxide, D = dye  $D^+$  = oxidized dye  $D^*$  = excited dye,  $e^-$  = electrons, CB = conduction band, and  $MO_x$  = metal oxide.

In recent decades, the focus of solar fuel production (both direct and indirect approaches) has been on water splitting. In this approach, water is oxidized to oxygen gas, electrons, and protons at the photoanode. The generated protons and electrons are reduced to form hydrogen gas at the (photo-) cathode, as shown in Figure 6.2. Despite many efforts, the current “water-splitting DSPECs” are still under development, as it is too early for the technology to enter the energy market. Three major efficiency-limiting factors in DSPECs are 1) electron recombination due to poor dye regeneration by the water oxidation catalyst, 2) the kinetic and thermodynamically challenging water oxidation reaction, and 3) the limited photoanode stability in aqueous environments. One way to address these issues is to replace the troublesome water oxidation reaction with organic reactions. Combining fuel generation with organic transformations yielding higher-value products could increase the relevance of the DSPEC technology.

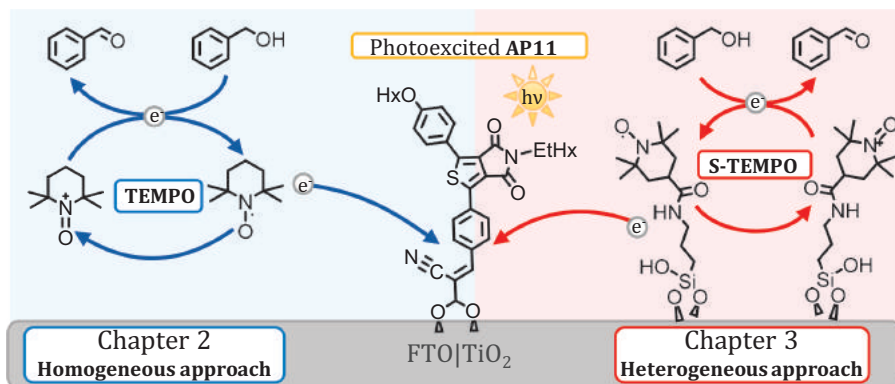
This thesis focuses on developing photoreactors that combine solar fuel production with chemical transformations. Inspired by nature’s photosynthesis, we are interested in devices that employ multiple redox steps for electron transfer between the light absorber and the oxidative (catalytic) reaction, which might lead to more efficient devices. We were curious to explore if additional redox steps in our artificial photosynthetic device architecture—by addition of redox mediators—would enhance the desired electron propagation through the system. This thesis report three different strategies to gain insight into the electron transfer mechanisms: 1) a solution-phase redox mediator approach, 2) a covalent attachment design, and 3) a redox-active matrix construct.

*Chapter 1* dives deeper into the energy problem and the current possibilities for converting solar energy into fuels. All components needed to design an artificial leaf are discussed in detail, using photosynthesis and its adaptability to different electron donors as a source of inspiration. Natural photosynthesis shows that, in addition to the pigments and catalysts, smaller redox steps to transfer electrons away from the dye play a major role in light-driven reactions. Moreover, an oxidative driving force in a chemical compound (or electrode) is crucial in driving oxidation catalysts to transfer electrons. Redox mediators within the DSSCs

play a vital role in supplying the electrons for the photooxidized dye. Within the DSSCs, this electron transfer has already been optimized. Unfortunately, this is not yet the case in DSPECs, for whom the major focus has been in endowing the catalytic process instead. If we manage to select suitable redox-active molecules, complete dye regeneration is ensured with simultaneous production of chemical oxidants. Ideally, employing redox mediators to introduce smaller redox steps should promote the desired generation of oxidative products, as removing the slow rate that precludes catalysis in electron transfer to the photooxidized dye. With this in mind, we aim to combine efficient redox mediators of DSSCs with catalytic processes.

In *Chapter 2*, we applied the concept of redox mediators in DSPECs for the light-driven oxidation of benzyl alcohol to benzaldehyde, with  $H_2$  produced as fuel at the cathode. We use 2,2,6,6-tetramethylpiperidine 1-oxyl (**TEMPO**), a well-known, efficient redox mediator in DSSCs, as a homogeneous redox shuttle (Figure 6.3, left). Additionally, the oxidized form (**TEMPO<sup>+</sup>**) within this redox couple is regularly utilized for oxidative organic transformations. Furthermore, these oxidations are routinely performed in acetonitrile, an ideal environment for dye-sensitized photoanode operation. The photoanode consists of a  $TiO_2$  film on FTO, sensitized with the thienopyrroledione-based dye **AP11**. Illuminating photoanode transforms **TEMPO** into **TEMPO<sup>+</sup>**, which further acts as a chemical oxidant for the conversion of benzyl alcohol to benzaldehyde. The DSPEC photoreactor has been carefully designed to monitor the progress of the reaction by infrared spectroscopy and gas chromatography. The **TEMPO<sup>0/+</sup>** couple is proven to mediate electron transfer efficiently from the organic substrate to the photooxidized dye. The light-driven oxidation reaction continued for 32 hours, resulting in a 100% conversion of substrate to electrons (*i.e.*, quantitative Faradaic efficiency) while maintaining excellent device stability.

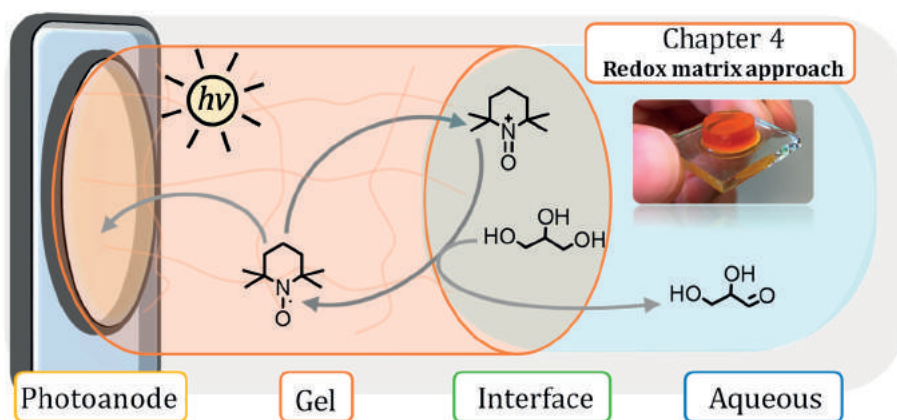
In *Chapter 3*, we discuss the influence of redox mediator placement on photoreactor function. Employing a similar photoanode in *Chapter 2*, we investigated the photoanodic stability and device efficiency of devices where redox mediating **TEMPO** is present either in a homogeneous phase (in solution) or is heterogeneous (surface mounted).



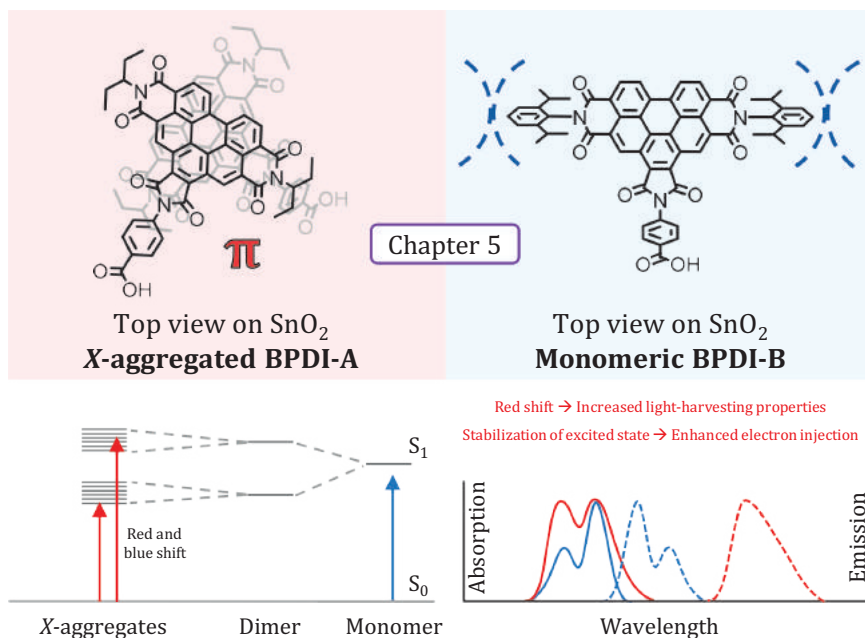
**Figure 6.3.** Schematic representation of homogeneous and heterogeneous approaches of an operating photoanode *via* **TEMPO**-mediated DSPEC system for light-driven alcohol oxidation.

heterogeneous strategy employs immobilization of a **TEMPO** analog with a silatrane anchor (**S-TEMPO**) onto the photoanode (Figure 6.3, right). Photoanodes containing the heterogeneous **S-TEMPO**<sup>+</sup> demonstrate lower photocurrent, attributed to the addition of alternative pathways for electron recombination introduced by a build-up of surface charges upon the oxidation of redox mediators. The immobilized **S-TEMPO** demonstrates an insufficient ability to mediate electron transfer between the organic substrate and photooxidized dye, resulting in device instability. When comparing the use of solution-phase redox-mediating catalysts to the covalent alternative, the homogeneous approach affords devices with a stable photocurrent and product production. This work highlighted the importance of free diffusion of the redox mediating mechanism within the device, promoting efficient dye regeneration, which assists in unhindered oxidative transformations and solar fuel production. We hope that the field of dye-sensitized devices acknowledges that unimpeded dye regeneration is one of the most important requirements to meet when designing DSPECs.

In Chapter 4, we aim to increase the relevance of DSPEC technology by extending it to challenging organic transformations that typically require aqueous alkaline conditions. For this reason, we examined the role of the aqueous phase compared to organic electrolytes on photoanode stability. We used glycerol as a model molecule for biomass oxidation as its oxidation with **TEMPO**<sup>+</sup> is only possible in aqueous environments at high pH (8.5). This specific reaction creates a challenge to ensure photoanode protection from unforgiving aqueous reaction conditions, thereby extending the utility of the device. We have created a biphasic system employing an acetonitrile-based gel layer that embeds **TEMPO** at the photoanode, protecting it from the alkaline aqueous layer with the glycerol substrate (Figure 6.4). The **TEMPO** gel serves as a redox matrix, acting as both redox mediator and catalyst. The redox-gel works similarly to the homogeneous system, where **TEMPO** oxidizes to **TEMPO**<sup>+</sup> at the photoanode by the photoexcited dye. **TEMPO**<sup>+</sup> can freely shuttle through the gel to the acetonitrile-aqueous interface, where it acts as the oxidizing agent for the selective



**Figure 6.4.** Schematic representation of an aqueous (blue) biphasic DSPEC with a **TEMPO** containing redox-gel layer (orange) for glycerol oxidation.



**Figure 6.5.** Proposed chemisorption and aggregation of **BPDI-A** and **BPDI-B** on  $\text{FTO}|\text{SnO}_2$ , simplified scheme of exciton theory for different absorption behaviors of X-aggregates and its translation to optical measurements.

conversion of glycerol to glyceraldehyde. Our redox-gel protected system demonstrated a 10-fold increase in glycerol conversion compared to the all-aqueous system. At the same time, we produce  $\text{H}_2$  at the cathode with a 90% Faradaic efficiency. Finally, devices with redox-gel protection exhibited high stability, with the photoanode unchanged after 48 hours of use. The addition of protective redox-active matrices to DSPECs combines efficient dye regeneration and catalytic properties thanks to a freely diffusing mediator while facilitating the requirement for easy product retrieval. The protection of the photoanode by the redox-active matrix makes DSPECs compatible with alkaline reaction conditions needed for covalorization of biobased compounds. Thus, we anticipate that the addition of redox-active matrices in future DSPEC design can remove most of the photoanodic limitations experienced upon selecting a specific photoreforming reaction.

In *Chapter 5*, we use the DSPEC to generate  $\text{Br}_2$ , a chemical oxidant used to drive water oxidation catalysts. We use a rational dye design to optimize the performance and stability of photoanode. The nature of imide-chain substituents in high oxidation potential benzoperylenediimide (**BPDI**) dyes was investigated to reveal their influence on aggregation phenomena upon metal oxide sensitization. Alkyl (**BPDI-A**, 2-ethylpropyl) and aryl (**BPDI-B**, 2,6-diisopropylphenyl) imide substituted **BPDIs** were synthesized and demonstrated to have similar optoelectronic properties in solution (*i.e.*, monomeric form). In contrast, upon chemisorption onto mesoporous  $\text{SnO}_2$  photoanodes, the increased ability of **BPDI-A** to form

aggregates by  $\pi$ -stacking leads to very different properties (Figure 6.5). The self-assembly of the **BPDI-A** enhanced short-circuit photocurrent in DSSCs by a 5-fold, compared to **BPDI-B** with only a doubling of the dye loading. Aggregation of **BDPI-A** shows both *J*- and *H*-aggregation (known as *X*-aggregation) phenomena leading to enlarge visible light absorbance and stabilization of the excited state, effects that are partly responsible for the improved photovoltaic performance. Thanks to the hydrophobic nature of the **BPDI** aggregates, the photoanodes show good stability in harsh aqueous environments. We achieved quantitative Faradaic efficiency for the light-driven production of the strong oxidant  $\text{Br}_2$  coupled with concomitant generation of the solar fuel  $\text{H}_2$  as the sole reduction product at the counter electrode. In contrast to popular belief, we conclude that self-assembly by  $\pi$ -stacking is a powerful tool for developing dye-sensitized devices by tuning the light-harvesting and charge separating characteristics.

In this thesis, we have shown that the implementation of redox-active molecules has a beneficial effect on the multi-electron transfer steps between the oxidative reaction and the photoanode. We managed to enhance cell efficiencies by making an organic photosynthetic cell, which elegantly combines the generation of chemical oxidants with organic redox catalysis in a one-pot manner. There are endless combinations of different redox mediators, dyes, substrates, and reaction conditions. We imagine that coupling and carefully placing the right components and integrating them in the proper choice of photoanodic environments would lead to the most efficient DSPEC systems. Solar fuels can be produced together with the formation of photoreformed products that are selected according to society's wishes. Our aspiration is that this thesis will influence scientists to think out of the box and move the combination of solar products and solar fuel closer to market readiness.