



Complexes for Electro- and Photocatalytic Proton Reduction

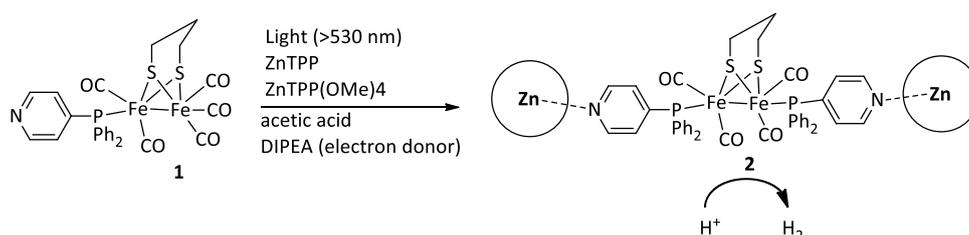
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6. Summary

Our current energy economy is largely based on the combustion of fossil fuels, such as oil and gas. However, the global oil and gas supply is rapidly depleting, and the combustion of these fossil fuels releases enormous amounts of greenhouse gasses into the Earth's atmosphere. An alternative, sustainable energy source is required. The direct conversion of sunlight into fuels is a promising strategy to satisfy mankind's demand for energy in a sustainable way. One way to do this is the light-driven water splitting reaction, which consists of two half reactions: water oxidation and proton reduction. Systems capable of performing these two half reactions photocatalytically are intensively studied. This thesis deals with the development of systems capable of photo- and/or electrocatalytic proton reduction.

6.1 Chapter 2

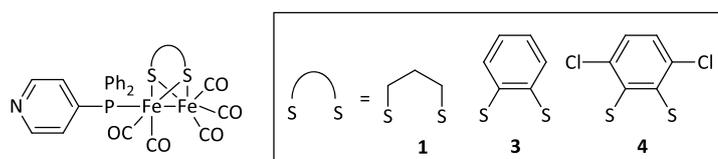
In nature, metalloenzymes called hydrogenases can catalyze the reversible oxidation of hydrogen. The elements that seem crucial for good catalytic performance in these biological systems are copied and applied in simplified synthetic hydrogenase-model complexes to obtain stable and active electrocatalysts. Research is devoted to electronically couple [FeFe] hydrogenase model complexes and photosensitizer (PS) molecules to obtain hybrid systems capable of photocatalytic proton reduction. To date, hybrid systems of this kind that are capable of reaching high turnover numbers (TON's) are scarce, especially those containing solely cheap and earth-abundant materials, but promising results have been obtained with various zinc porphyrin based PS's. Reek and coworkers reported a supramolecular assembly that consists of [FeFe] hydrogenase model system **1** and ZnTPP and ZnTPP(OMe)₄^[21]. Upon irradiation this assembly with light and in the presence of a suitable proton and electron donor, this system is capable of performing up to 5 turnovers in photocatalytic proton reduction. The active species in catalysis is believed to be complex **2**.



Scheme 11 : Upon reduction of complex **1**, complex **2** is formed, which is proposed to be active in photocatalytic proton reduction.

The turnover number (TON) is limited due to catalyst decomposition. The catalyst decomposition is believed to be caused by instability of the one-electron reduced complex,

which is an intermediate in the catalytic cycle. The aim of the work described in chapter 2 is to modify complex **1** to increase the stability of its one-electron reduced state by introducing electron withdrawing dithiolate bridgeheads. It is well-documented that electron withdrawing dithiolate bridgeheads reduce the electron density on the Fe₂ center and thereby increase the stability of the one-electron reduced complex^[2], which is believed to be key in increasing the longevity in photocatalysis^[3]. Complex **2** and **3** were synthesized and tested in electro- and photocatalysis.

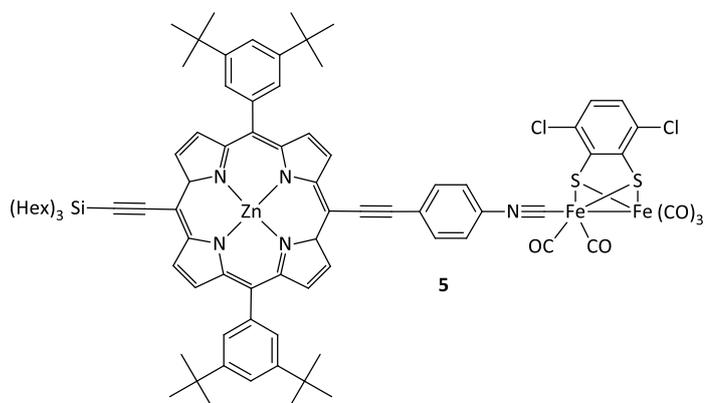


Scheme 12 : Complexes **1**, **3** and **4**.

Using cyclic voltammetry (CV) and infrared spectroscopy coupled to CV (IR coupled CV) we demonstrated that the stability of the one-electron reduced complex is increased with increasing electron withdrawing character of the dithiolate bridgeheads, which results in an increased reversibility of the [Fe^IFe^I]/[Fe^IFe⁰] redox couple. For complex **1** this reduction is irreversible, whereas for complex **2** this reduction is 55% reversible and for complex **3** it is 65% reversible. Supramolecular assemblies of various zinc porphyrin PS's with complexes **3** or **4** were studied in photocatalysis, including PS's that absorb light of long wavelengths ($\lambda > 600$ nm) to avoid light-induced catalyst decomposition. However, catalyst decomposition occurs after photo-induced electron transfer (PET) from the PS to the proton reduction catalyst (PRC). No photocatalytic activity is observed, which we believe to be due to catalyst decomposition.

6.2 Chapter 3

In chapter 2 we demonstrated that photocatalytic proton reduction is hampered by the instability of the one-electron reduced complex. The stability is increased when the electron density on the Fe₂ center is decreased. Therefore we sought to replace the strongly electron donating phosphine ligand with a weaker donating isocyanide ligand. We developed complex **5**, in which a zinc porphyrin PS is connected to a [FeFe] hydrogenase model system through an isocyanide ligand, which is a less electron donating ligand than the phosphine used in chapter 2.



Scheme 13 : Complex 5

Using CV and IR coupled CV we demonstrated that the $[\text{Fe}^{\text{I}}\text{Fe}^{\text{I}}]/[\text{Fe}^{\text{I}}\text{Fe}^{\text{0}}]$ redox couple of complex **5** is fully reversible and occurs at a mild potential (-1.42 V vs. Fc/Fc+). However, the potential at which catalysis takes place is too negative to be light-driven with the currently used PS's. In addition, even though we calculated the free Gibbs energy change for PET from the PS to the PRC to be negative, PET is not observed.

6.3 Chapter 4

The second part of this thesis deals with the development of electrodes for electrocatalytic (chapter 4) and photocatalytic (chapter 5) proton reduction that can be directly implemented in a device for photocatalytic water splitting. In order to create such a device, the water oxidation reaction and the proton reduction reaction must be electronically coupled, and the electronic levels of all individual components must be properly aligned to create enough driving force for all consecutive electron transfer steps to take place. In the first device design (scheme **A** in figure **1**) the potential required for the water splitting reaction is created by absorption of light at the water oxidation side, and the proton reduction is electrocatalytically driven.

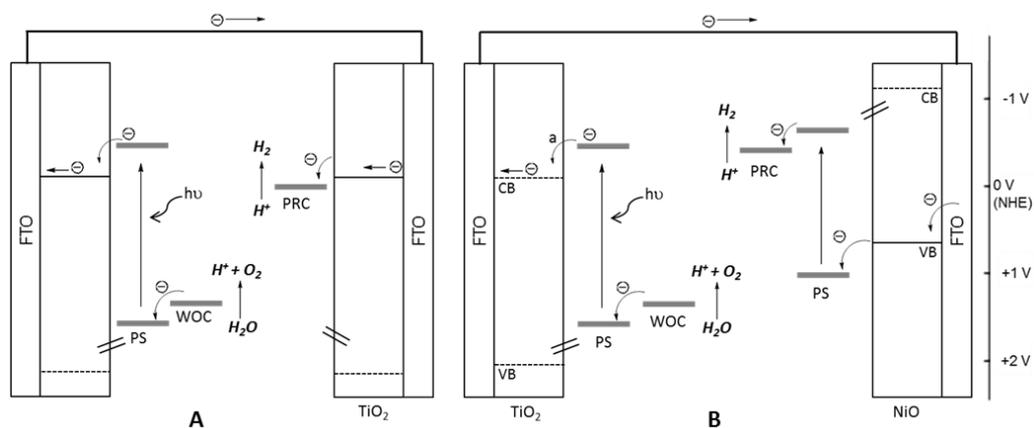
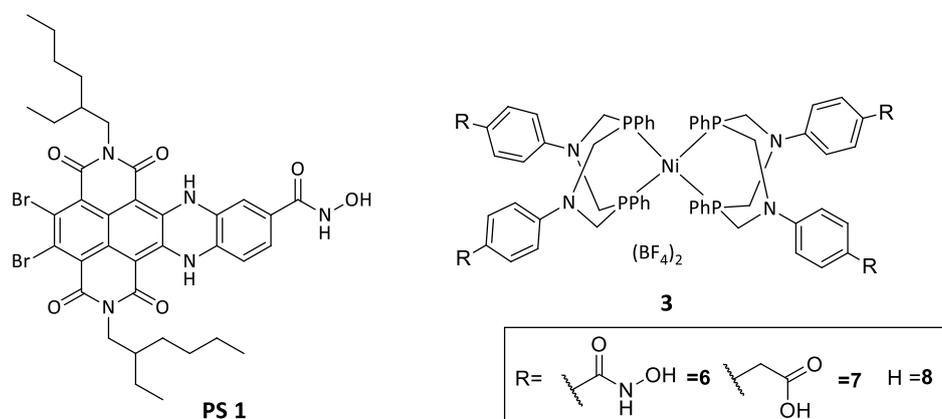


Figure 69 : Devices for photocatalytic water splitting.

In chapter 4 we describe the synthesis and immobilization of PRC **6** (scheme 4) on TiO₂ nanoparticles that are coated on fluorine doped tin oxide (FTO). We demonstrate that this system is capable of electrocatalytic proton reduction in aqueous solutions (pH 2.1) at moderate overpotentials (280 mV). Unfortunately, the TON is limited (~35) due to catalyst decomposition and/or leaching of the catalyst from the electrode.



Scheme 14 : PS **1** and PRC's **6** and **7**.

6.4 Chapter 5

In the second device design (scheme **B** in figure **1**) both the water oxidation and the proton reduction reaction are light-driven. In chapter 5 we describe the co-immobilization of PS **1** with both PRC **6** and PRC **7** on NiO nanoparticles coated on FTO electrodes for the development of an electrode capable of photocatalytic proton reduction. Using cyclic voltammetry and amperometry, photocurrent is observed when irradiating the FTO/PS **1**

working electrode with light of wavelengths (> 470 nm) in 0.1 M phosphate buffer (pH 2.1), or with PRC **8** in acetonitrile. This means that electrons are transferred from the FTO electrode, through the NiO, to PS **1**. Similar photocurrents were observed when PRC **6** (or PRC **7**) is co-immobilized on the NiO. The photocatalytic activity of the NiO/PS **1**/complex **6** (or **7**) was tested by irradiating the electrodes in acidic solutions (0.1M phosphate buffer pH 2.1, 0.1M TFA buffer pH 2.1 or DMFH.OTf in MeCN) while applying a bias voltage of -0.1 V vs. Ag/AgCl. Unfortunately, no photocatalytic production of hydrogen was observed, probably because the (double) reduction of the catalyst, which is required for catalysis, does not take place.

6.5 Conclusion

In conclusion, we have demonstrated that lowering the electron density on the Fe₂ center of the studied [FeFe] hydrogenase model complexes results in an increased stability of the one-electron reduced complex, which results in an increased reversibility of the [Fe^IFe^I]/[Fe^IFe⁰] redox couple. In chapter 1 we demonstrate that catalyst decomposition occurs after PET from the PS to the catalyst. To circumvent this, we developed a PS/PRC hybrid system in which the [Fe^IFe^I]/[Fe^IFe⁰] redox couple is fully reversible. However, due to the relatively low electron density on the Fe₂ center, this complex is not prone to protonation in its neutral form, and therefore, catalysis occurs at a relatively negative potential and cannot be light-driven by the PS. To tackle this problem an internal base can be incorporated into the catalyst, to make the catalyst prone to protonation, and thereby shifting the catalytic potential to less negative potentials.

Furthermore, in chapter 4 we report a strategy for constructing an electrode capable of electrocatalytic proton reduction at a moderately low overpotential, that consists solely of earth-abundant materials. Although the system must be further developed to improve its stability, with this strategy a high PRC loading is achieved. As described in chapter 5, PS **1** was co-immobilized to drive catalysis with light. Although electron transfer through the electrode surface to PS **1** was demonstrated, no photocatalytic activity was observed. Possibly, the electron transfer between PS and PRC can be optimized by optimizing the orientation of the PRC with respect to the catalyst, for instance by placing them in series rather than random co-immobilization.

6.6 References

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