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Large-scale use of fossil fuels allowed for impressive developments of our society, providing a cheap and abundant energy supply. Nevertheless, it is now clear that the intense exploitation of these natural resources came with the high price of releasing huge amounts of carbon dioxide in the atmosphere; a potent greenhouse gas responsible for the climate changes that we are recently observing. Thus, the dependency of our current society on fossil fuels is not sustainable, and the need of for a different energy source to sustain our massive energy demand is of prime importance. Ideally, the energy source of our future should be sustainable and carbon-neutral. Looking at the resources available within our planet, the most abundant energy source is by far solar radiation. Photovoltaics, the technology to convert sunlight into usable electricity is already available and widely distributed. However, it solely provides electricity, which only accounts for 20% of our current energy demand. Furthermore it is intrinsically dependent on solar radiation intermittency i.e. photovoltaics are powerless in the dark and as a consequence solutions for energy storage are required.

A complementary approach would be required to convert sunlight into compounds (chemical bonds) that can be stored and used when needed at later stages. As it turns out, such a process has been operative on our planet for billions of years. Performed by plants and certain microorganisms, it is known as photosynthesis, and it is able to utilize solar energy to extract reducing equivalents from water that are then used to fix carbon dioxide into carbohydrates (chemical bonds). Looking at the complex machinery evolved by Nature, clear blueprints can be obtained to reproduce the light-induced water oxidation reaction, which is the core reaction of the process. Although fixation of carbon dioxide into carbohydrates might not be the best approach to pursue for our current energy issue, Nature has also evolved dedicated machineries able to discard excess reducing equivalents in the form of hydrogen. This process is operated by enzymes called hydrogenases, which are present in various types of bacteria. This also provides us with detailed blueprints for the conversion of reducing equivalents, gathered from the light-induced water oxidation reaction, into dihydrogen, which is considered as a promising energy carrier for the future.

The aim for mankind is therefore to develop 'artificial photosynthesis' devices that are able to combine and perform both reactions as described: light-driven water oxidation and (light-driven) proton reduction. Many different approaches are already present in literature, classified depending on the components employed for the construction of the device. Among them, devices based on molecular components are of great interest, as they can benefit from the rational design of the components. In this respect, great attention is devoted to the development of suitable catalysts to efficiently perform the two reactions of interest.

The focus of this thesis is the development of molecular catalysts for the proton reduction reaction. As the hydrogenase enzymes excel at producing dihydrogen, outperforming even

the best synthetic catalysts based on precious metals, yet are found to contain organometallic clusters based exclusively on earth-abundant elements such as iron, nickel and sulfur; they are of great interest also in view of possible applications. Not surprisingly, the molecular architecture of many proton reduction catalysts is thus inspired by the design evolved by Nature for the hydrogenase enzymes. In particular, the focus has been directed to synthetic models of the iron-iron hydrogenase enzyme (H-cluster), as this is undoubtedly the fastest hydrogen evolving catalyst. Several years of combined research efforts on the natural di-iron system led to identification of the key features responsible for the high activity and efficiency observed, namely:

- a di-iron organometallic core
- a proton-relay (azadithiolate bridge)
- an electron reservoir (Fe_4S_4 -cluster)
- second coordination sphere around the H-cluster (protein matrix)

Synthetic models are readily available but most often the only feature is the di-iron core. Several reports deal with the incorporation of a proton relay, which proved to be of great importance for the activity of the catalysts. Only a handful of complexes combine the first three features described, but even then the activity and efficiency of such complexes are nowhere near those of the natural enzyme. This suggests that the second coordination sphere around synthetic models, typically an ignored feature, might also be of great importance to approach the enzymatic rates and efficiency.

This thesis focuses on synthetic models of the iron-iron hydrogenases, specifically on benzenedithiolate bridged complexes. In chapter 2 we present synthetic di-iron model complexes where either one or two carbonyl ligands have been substituted for more electron-rich ligands that carry proton-relay moieties. The presence of the proton-relays has been shown to confer interesting advantages to the complexes. As such, protonation of the proton-relays allows for dissolution of the complexes in acidic aqueous media where proton reduction takes place at the first reduction event of the complexes. Furthermore, this protonation offers a useful handle to effectively counterbalance the increased electron density of the di-iron core, originating from ligand substitution. We note that proton-coupled electron transfer steps (PCET) are important to lower the first reduction potential of the complexes, thereby effectively lowering the catalytic overpotential. This work demonstrates that the presence of proton-relays alone allows for catalytic rates far beyond those of the natural system, although the driving force required (overpotential) is still relatively high.

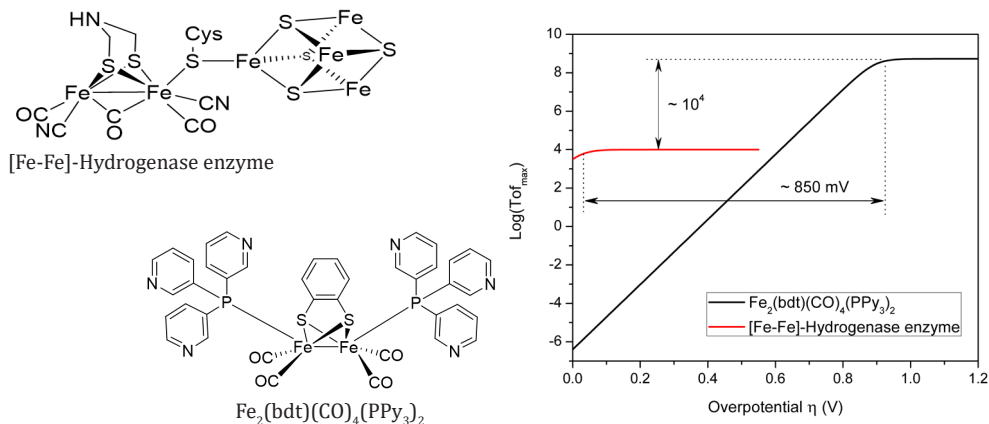


Figure 1. Left molecular structure of the active site of the natural enzyme (H-cluster) and synthetic model $\text{Fe}_2(\text{bdt})(\text{CO})_4(\text{PPy}_3)_2$. Right: comparative Tafel plot for the two catalysts depicted, showing that the synthetic model is a far more active catalyst than the natural one but it also requires a higher driving force.

The first step towards the development of devices based on molecular components is typically the preparation of conductive electrodes decorated with molecular catalysts. In chapter 3 we describe the immobilization and study of a benzenedithiolate di-iron complex onto conductive (nano)FTO electrodes. The electrodes are shown to be competent for the hydrogen evolution reaction from acidic aqueous media at relatively low driving force (overpotential). Comparison of the immobilized catalyst to the freely diffusing species in organic solvents shows that the same catalyst can operate at lower overpotentials, yet with similar rates, when immobilized onto the electrode surface.

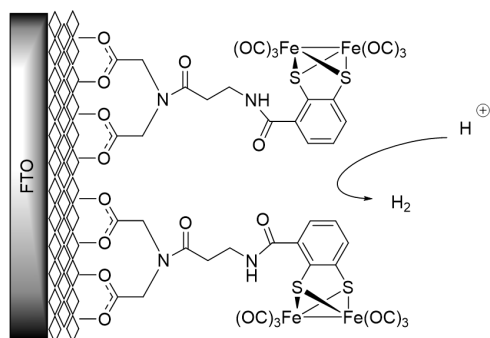


Figure 2. Schematic representation of the modified high surface area, catalyst decorated electrodes prepared. The electrodes display $\sim 1.6 \text{ mAcm}^{-2}$ current density at 500 mV overpotential in 0.05 M NaHSO_4 buffer solution at pH 3.5.

Part of this thesis is dedicated to mimicking the protein environment around the H-cluster. We envisioned that supramolecular cage assemblies could be a suitable platform for such a study. In particular, $M_{12}L_{24}$ cages have been the focus of this investigation, as they feature a relatively large cavity, and synthetic modification of the cage building blocks provides a straightforward way to tune and customize the nano-confined space defined by their structure. As literature provides little information regarding the electron transfer kinetics of redox-active species encapsulated into large supramolecular assemblies, chapter 4 revolves around the preparation of $M_{12}L_{24}$ nano-spheres containing redox-active probes. Throughout the chapter we have demonstrated the feasibility of electron transfer to the encapsulated redox probes, paving the way for the encapsulation of electro-active systems and electrocatalytic applications of such supramolecular assemblies.

Chapter 5 extends on some of the findings described in chapter 4. In particular, in chapter 4 we have prepared $M_{12}L_{24}$ cages that co-encapsulate several redox-active probes. Electrochemical measurements indicate that those moieties are electronically independent as they feature a single redox event, thereby generating cages featuring several charges at their cavity. Nevertheless we suspected that the electrolyte used during the measurements plays a major role at neutralizing the net accumulation of charges within the cavity of the spheres as it can freely diffuse across the cage rim. Furthermore, considering the Faraday principle, applicable to macroscopic conductive objects featuring a hollow cavity, extra charges added to those objects redistributes to their outer shell as to minimize the repulsive forces created. As the $M_{12}L_{24}$ cages are based on fully conjugated building blocks that are held together by metallic ions, thus extending the conjugation throughout the entire supramolecular structure, such nanometer-sized objects would resemble macroscopic Faraday cages. We therefore prepared an exceptionally large size electrolyte to be used during the electrochemical measurement. As the electrolyte cannot enter the cage windows due to its steric hindrance charge accumulation within the cavity of the spheres is thereby, in principle allowed. Our preliminary results indicate that the void of $M_{12}L_{24}$ does have some similarities with macroscopic Faraday cages, as the data suggest that charging of the redox-active species encapsulated at their cavity generates electrostatic repulsive interactions among the charged redox probes. Physical redistribution of those charges toward the outer shell of the cage is suggested by a loss in their electrochemical reversibility at slow scan rates, which also suggests a follow-up reactivity of the redox probes.

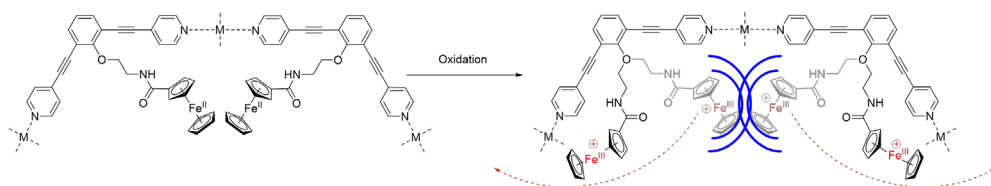


Figure 3. Schematic representation of the envisioned charge reorganization within the cavity of the $M_{12}L_{24}$ sphere, upon electrochemical oxidation of the redox-active probes.

After having established the feasibility of electron transfer to redox-active probes encapsulated into $M_{12}L_{24}$ nano-cages, in chapter 6 we developed two general strategies to encapsulate di-iron complexes into specific nano-environments. Encapsulation provides the catalyst with a second coordination sphere that is fine-tuned to provide preorganization of proton substrates around the catalyst. Proton preorganization proved to be important, as it allows for faster catalytic rates compared to cages that do not have proton preorganization but most strikingly we showed for the first time that changing the local environment around the catalyst drastically decreases its catalytic overpotential, demonstrating the importance of the second coordination sphere around synthetic hydrogenase models. In principle, our strategy allows for closely mimicking the essential amino acid residues found around the natural H-cluster; we believe this is a key factor that will give access to synthetic catalysts that will finally approach enzymatic rates and overpotentials.

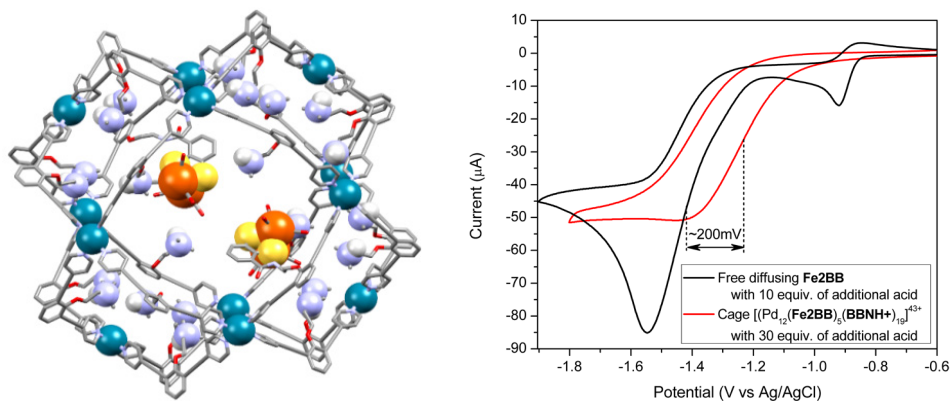


Figure 4. Left: Spartan model of $M_{12}L_{24}$ cage featuring two encapsulated di-iron hydrogenase synthetic models (shown in orange and yellow CPK-style). Each of the remaining 22 building blocks possesses an acidic ammonium functional group (shown in light blue and white CPK-style) effectively achieving proton preorganization around the hydrogenases models. Right: voltammograms indicating that the caged catalyst shows 200 mV lower overpotential for the proton reduction reaction (red line) as compared to the free diffusing catalyst functionalized building block (black line).

The research described in this thesis shows that the second coordination sphere plays a very important role in proton reduction catalysis. Proton substrate preorganization around synthetic models drastically increases the activity of the catalysts while the overpotential can be reduced by switching the working solvent to aqueous media or by installing electron-withdrawing groups on the synthetic models. Nevertheless, the design of more sophisticated second-coordination sphere architectures is essential to achieve the enzymatic efficiency e.g. catalysis at negligible overpotential and sufficient rates. In this work we have shown a valid strategy for the encapsulation of model compounds into specific customized environments by using large supramolecular cages. This approach can be further extended to develop smart matrices that preorganize proton substrates, allow for PCET and force the di-iron model to adopt the rotated structure, allowing for terminal hydrides catalytic pathways. We believe that mimicking the protein environment is the way to decrease the catalytic overpotential of hydrogenase model complexes.