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Nanocrystalline Electrodes Functionalized with Light Sensitized [2Fe-2S]-Iron-Sulfur Clusters for Hydrogen Production

NEFIOS-HYDRO

Schlussbericht

Ausgearbeitet durch

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Zusammenfassung

Strategies for the synthesis of new conjugates combining ruthenium(II) photoactive centres with biomimetic iron-sulfur clusters and titania semiconducting nanoparticles have been developed. Various approaches have been used for the linking of the individual species using a modular library of components. The iron-sulfur clusters have been selected to incorporate the hydrogen generation capacity found in hydrogenase. This process requires two electrons per hydrogen molecule and the ruthenium species (combined with the titania) were designed to provide the required reduction capacity through photochemistry or photoelectrochemistry.

1. Ausgangslage

The generation of dihydrogen from protons is represented by the very simple equation:

$2H^+ + 2e^- \rightarrow H_2$

The conventional method for achieving this important conversion is the direct use of electrons in electrolytic processes. This technology is well-established but has two disadvantages which make an investigation of alternative methods an attractive prospect (i) the overpotential for H_2 production is high which means that the electrolytic generation of H_2 is somewhat energetically wasteful and (ii) the electrolytic approach usually requires the generation and storgae of electrons from conventional fuel sources. The aim of our work is to take inspiration from nature where the H_2 is generated at an iron-sulfur catalytic centre in the enzyme Fe-Fe hydrogenase (Fig. 1a), with the required electrons coming from the biological storage species ATP.

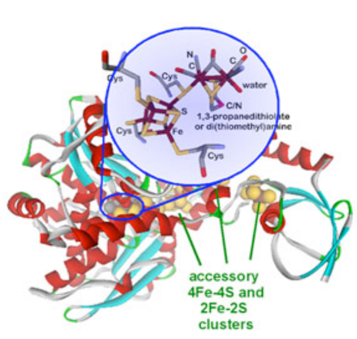	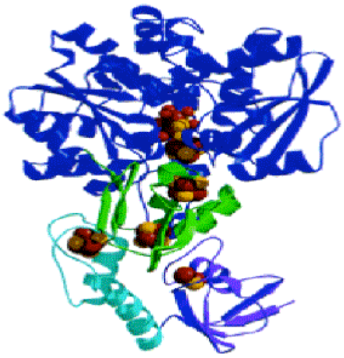
Fig. 1a Cluster centre in the Fe-hydrogenase from *Clostridium pasteurainum*	Fig. 1b Fe-hydrogenase from *Clostridium pasteurainum*

The identification and structural characterisation of the active site in Fe-Fe hydrogenase as a relatively simple iron-sulfur cluster opened the possibilty of using biomimetic analogues with ligands simpler than the protein for the chemical reduction of protons to dihydrogen using alternative electron sources.

2. Ziel der Arbeit

Our approach is to combine the proven Fe-S cluster with a more convenient source of electrons, ultimately derived from solar photons. We are developing a modular approach in which a library of photoactive components based on ruthenium(II) oligopyridine complexes and Fe-S clusters with pendant functionality. This has involved a major synthetic effort within the group to develop a suite of reproducible reactions which may be utilised. The excited state of the ruthenium complexes can provide the electrons for H_2 generation. The resultant oxidised complexes are then reduced back to the ruthenium(III) state by chemical reductants in solution (non-ideal requiring a chemical fuel) or electrons from an electrode. The latter provides the third modular component in our system – an electrochemically addressable surface. This strategy is represented in Fig. 2.

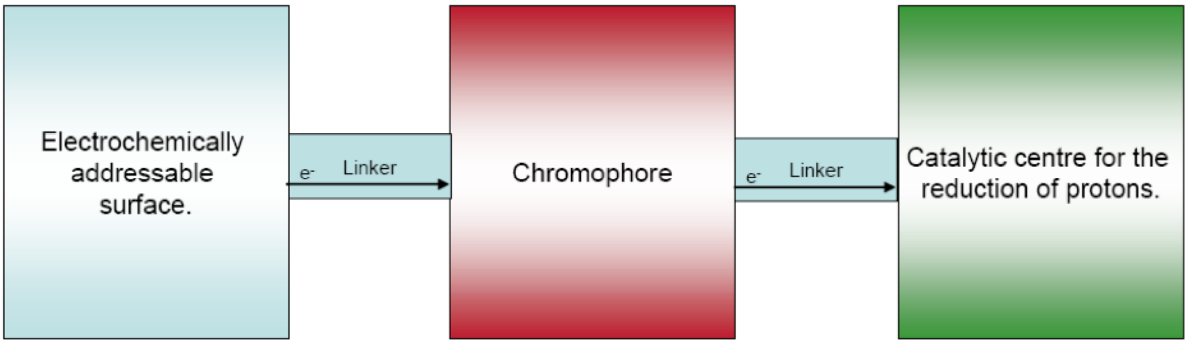

Fig. 2 Modular strategy for photoelectrochemical hydrogen production

The translation of the concept above to molecular species is realised in Fig. 3, which explicitly presents the synthetic clusters used in this project.

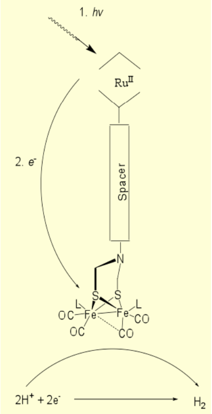

Fig. 3 The coupling of a biomimetic cluster to a photoactive ruthenium complex.

The development of conjugates of this type allows the evaluation of various synthetic staragies as well as the effectiveness of the complex-conjugate approach to hydrogen generation. As discussed in more detail in the following section, our general conclusions are that the biomimetic motifs are likely to be too fragile for any significant utilisation in "real-world" devices. However, the spin-off from this project is the identification of synthetic non-biomimetic motifs for hydrogen generation.

4. Ergebnisse

A series of prototype compounds containing chromophores for the light absorption and iron-sulfur clusters for the eventual proton reduction were prepared in the first phase of this work. The chemical structures and procedures were presented in detail in the appendix to the interim report. One issue became clear from the first attempts to prepare the chromophore-cluster conjugates – the fundamental chemistries of the ionic chropmophores and the neutral organometallic clusters were not compatible. In biology, this question is addressed by the use of proteins to provide isolated microreactor environments and the spatial separation of the various components. Much of the synthetic effort in this project addressed the challenges of preparing conjugate molecules.

Even when these compounds were prepared we found them to be extremely short lived, and in the context of this project, they had the suicidal properties of light-sensitivity, water-sensitivity and sensitivity to metal oxide surfaces.Fig. 4 presents a typical synthetic pathway to one of these conjugate species.

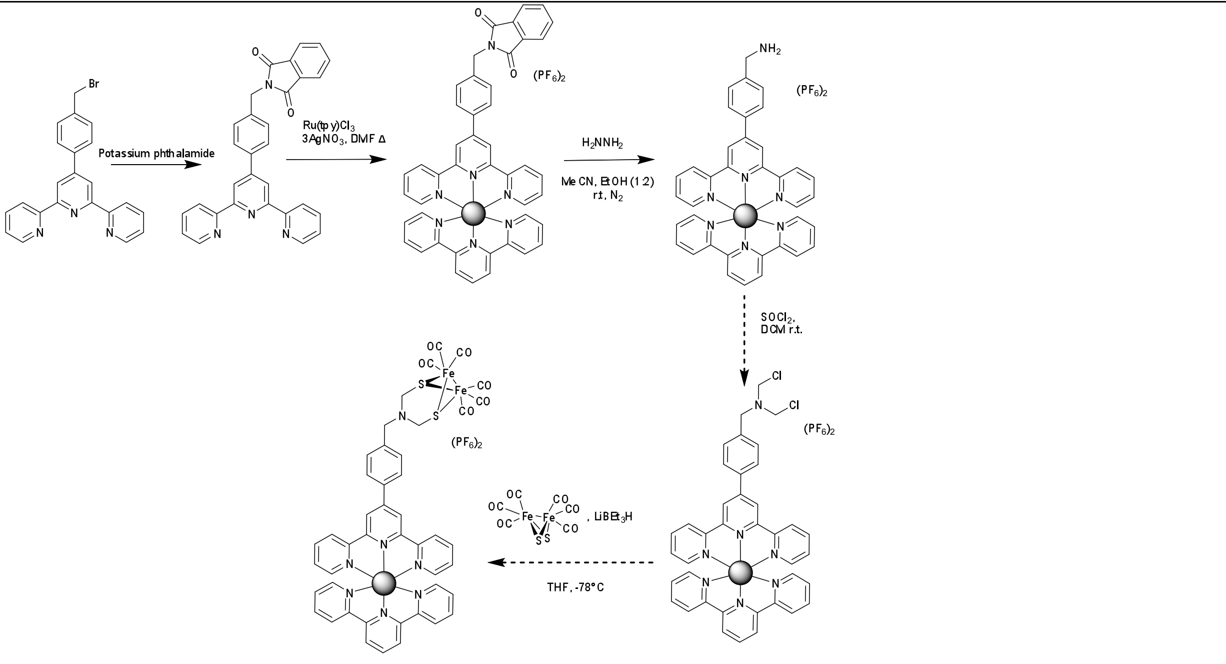

Fig. 4 Initial approaches to photoactive biomimetic conjugates

The emhasis is on the development of a functional system incorporating chromophores and catalytic hydrogen production centres rather than optimising of elegant synthetic routes to conjugates that would be unstable under proposed working conditions. The initial results with the conjugates were disappointing and we decided to take full advantage of the modular approach and evaluate systems in which the two components were not covalently linked but rather electronically coupled at the substrate surface.

Initial attempts to functionalise the iron-sulfur clusters with silyl substituents prior to subsequent attachment to substrate surface were also unsuccessful, again as a result of the fundamental incompatibility of the chemistries of the organometallic fragments and the required chemistry.

We therefore decided to develop a new method for surface functionalisation which did not involve covalent modification of the surface or the adsorbate. A standard glass-titania surface was functionalised with Nafion® perfluoronated ion-exchange resin and subsequently derivatised by treatment with a cationic ruthenium(II) complex (Figure 5a). The Ru III/II couple observed adsorbed on the glass substrate shows that the electronic transport through the Nafion® membrane is sluggish due to the large difference in the anodic and cathodic wave potentials (Figure 5b). We are currently investigating the ability of these conjugates to facilitate proton reduction.

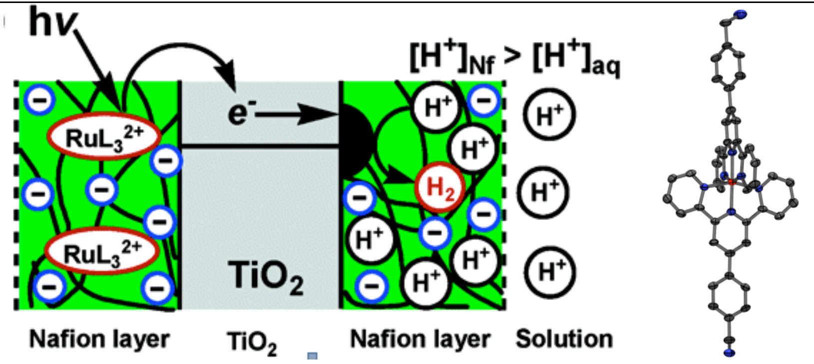

Fig. 3a The cation exchange-functionalised surface of the Nafion® membrane conjugate

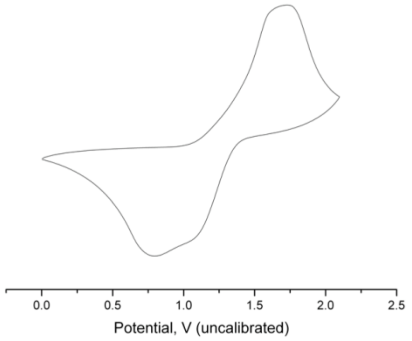

Fig. 3b The electrochemical response of the Nafion®-ruthenium(II) surface

We decided that the easiest method to monitor H_2 production would be using a two electrode system in which one working electrode is modified with Nafion® and ruthenium(II) complex**.** The electrochemical setup is shown in Fig. 6. A small cylindrical trough was used with a hole large enough to close with the macro-electrode. A second, micro-working electrode was situated directly above the macro-electrode (400 µm). A platinum wire was employed as a counter-electrode and an Ag/AgCl reference electrode included in the system. An important parameter to consider and investigate for this experiment is the best potential to apply for both working electrodes. It is important that minimal H_2 production is observed during the experiment as H_2 bubbles can mechanically block the electrode surfaces. This experiment works under the principle of a change in current. The greater the current, the greater the H_2 turnover.

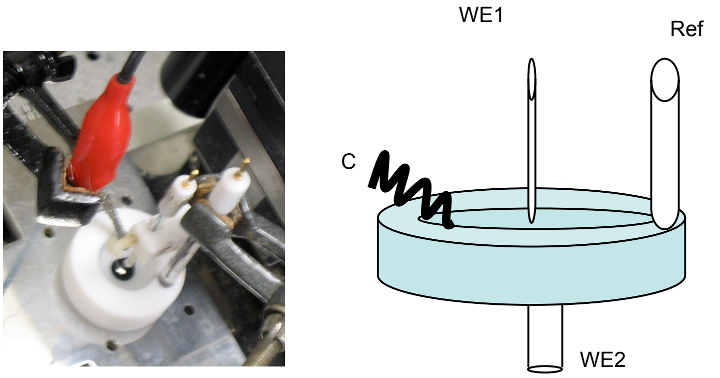

Fig. 6a Electrochemical set-up for monitoring H_2 production

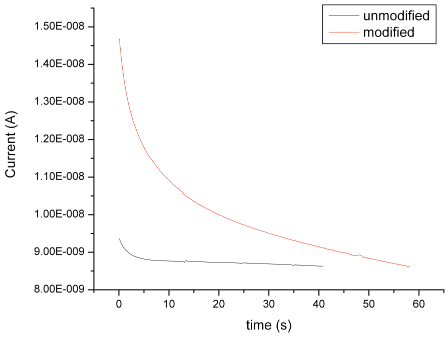

Fig. 6b Current at the µ-electrode with a modified and unmodified macro-electrode

One of the main problems with the electrode preparation was the uneven coverage of the Ru(II) complex due to an uneven Nafion® layer. Initial experiments using 0.5 M H_2SO_4 were promising and showed differences in the current depending on whether the macro-electrode was modified or left unmodified.

In the final year of the project, a new Post-doctoral co-worker (Dr Swarna Latha Kokatam) was recruited who had significant previous expertise with both Fe-S clusters and with electrochemical characterisation of photoactive compounds. She has managed to overcome the difficulties associated with the preparation compounds incorporating both thienyl bridges (to lower the band gap) and alkynyl linkers (to optimise electron transfer). Two parallel routes have been developed in which the metallation step is early or late in the procedure (Figs. 7a and 7b). The key intermediates have been structurally characterised (Fig. 7c)

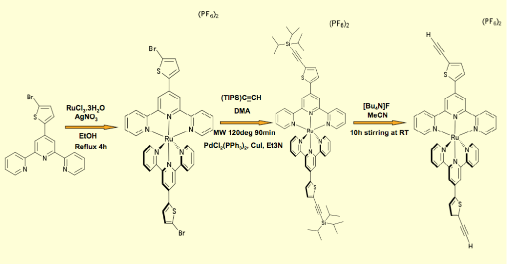

Fig. 7a Functionalisation of a metal complex to give terminal alkyne linkers

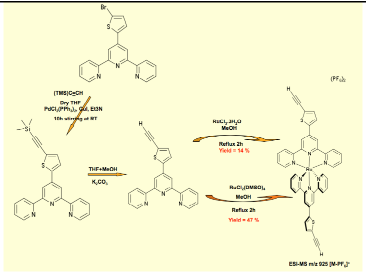

Fig. 7b Prefunctionalisation of a ligand with alkyne linker

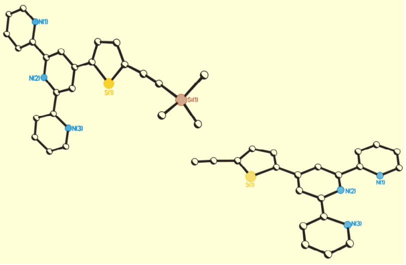

Fig. 7c Solid state structures of key intermediates

The biomimetic component and the alkyne are then linked using the Sonogashira methodology as indicated in Fig. 8. After a long period of optimisation, we have found that these reactions require stoichiometric amounts of the copper(I) "catalyst"!

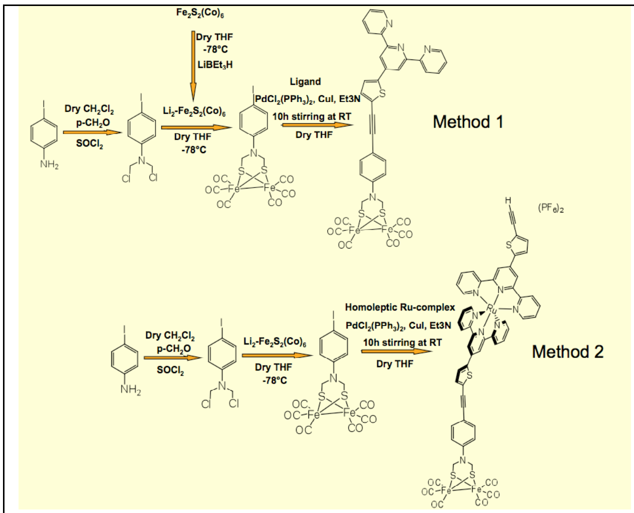

Fig. 8a Coupling methodology for the preparation of the conjugates

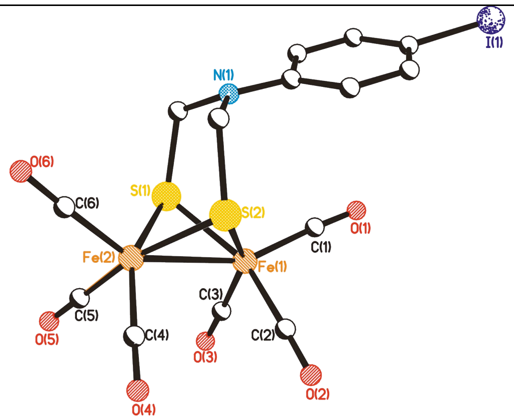

Fig. 8b The solid state structure of the key intermediate

The final piece of synthetic work was the synthesis of the conjugate containing the attachment group for linking to the titania (Fig. 9)

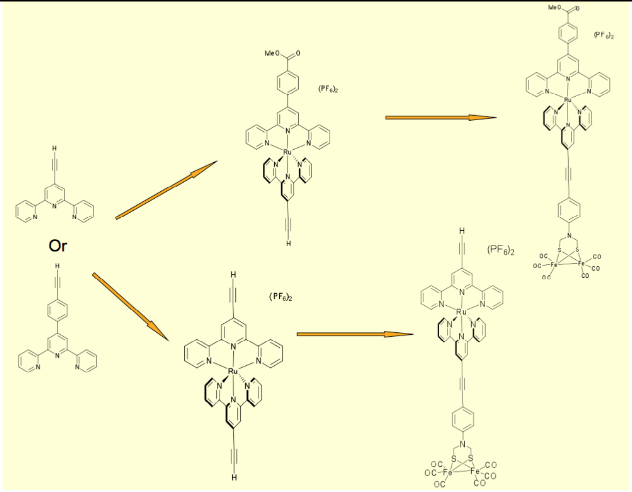

Fig. 9 Conjugate containing all of the functional components and the linker for attachment to titania

5. Diskussion

This project has developed biomimetic conjugates for dihydrogen production from protons using iron-sulfur clusters. The first period of the project was concerned with initial synthetic approaches to conjugates of this type and evaluation of prototype systems. Synthetic problems associated with the prototype systems led to an evaluation of alternative strategies. In the second year of the project a new co-worker with extensive experience of compounds of this type was employed and most of the synthetic problems overcome.

The general conclusion is that these conjugate species are too unstable for utilisation in hydrogen generation systems outside laboratory conditions.

6. Schlussfolgerungen

This project has acted as the basis for a number of successful daugher projects involving the use of nanoparticles for the chemical, electrochemical or photoelectrochemical production of water or water-splitting reactions. Project ANWASP is funded by the KTI and concerns the preparation and surface functionalisation of mixed iron-titania nanoparticles for use in water splitting. A project funded through the Danish Science Ministry concerns the combination of biomimetic manganese clusters with photoactive components and nanoparticles to generate synthetic analogues of the oxygen evolving centre in photosynthesis. A BfE project with EMPA and UNIBAS has been funded for the investigation of iron oxide nanoparticles in water splitting and hydrogen chemistry. A project involving the use of manganese oxide nanoparticles for oxidation has been funded by Nano-Argovia. An NCCR in sustainable energy has been proposed with Basel as one of the key partners.

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