Photoactivated nano-systems: self-assembled nano-scaled systems through cyclodextrin complexation, functionalized nanoparticles and hydrogen evolution
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Self assembled systems for the photoinduced hydrogen evolution from water

Abstract

In this chapter we present a practical application of self-assembled cyclodextrin wires in aqueous solution. We show that by using a relatively simple approach we can induce “order” in systems where the efficiency is traditionally governed by diffusion. We observe increased yields due to the supramolecular effect. The catalytic center is a platinum nano-particle (Pt) stabilized with a perthiolated β-cyclodextrin (TCD). This molecule also acts as a binding port for guest molecules. We bring two photo- and electro-active units (a viologen and a cyclodextrin substituted polypyridyl complex) closer together for optimized interaction without covalent bond. Electrochemical methods show that the Pt/TCD particles are active towards hydrogen evolution from H⁺ ions in solutions with pH < 7. The relative efficiency for hydrogen evolution of the system was studied in a custom made photo-cell under continuous irradiation of the assembled species and the amount of hydrogen produced was monitored in situ with gas chromatography.

‡ Two manuscripts with the results presented here are currently in preparation
7.1. Introduction

The necessity for development of future energy sources is a very hot topic in our society nowadays. The exhaustion of fossil fuels and the more and more tangible influence of the greenhouse effect in the environment have created a tendency among citizens to switch from carbon based fuels (coal, gas, oil) to renewable energy sources with less or no impact on the environment (solar, wind, wave power, biomass, wood). Until recently nuclear power seemed the only answer to the "energy crisis" because renewable energy sources were considered not efficient enough. This has however changed and more studies are appearing with examples where application of e.g. photovoltaics can compete efficiently with nuclear energy in countries with relatively low solar irradiation. Hydrogen (H$_2$) has received increased attention because hydrogen as a fuel is high in energy yet burning hydrogen produces almost zero pollution. A variety of semiconductor metal oxides have so far been studied for water splitting as a means of producing H$_2$ from water. Most of these photocatalysts are effective only under ultraviolet (UV) light because of their wide band gap. The development of new photocatalysts for water splitting to produce H$_2$ has attracted much attention in order to make systems active over the whole visible spectrum. Molecular photocatalysts have long been explored for the hydrogen evolution using metal complexes as photosensitizers combined with hydrogen-evolution catalysts. Although sacrificial donors have so far been required for the molecular photocatalytic hydrogen evolution under visible light irradiation, it is highly desired to improve the photocatalytic efficiency for the hydrogen evolution with electron donors in water. Such molecular photocatalytic hydrogen-production systems consist of a sacrificial electron donor, a photosensitizer, an electron carrier, and a hydrogen-evolution catalyst. There is a wide range of molecules that can act as photosensitizer such as organic dyes, and inorganic systems as well as organometallic complexes. In combination with a colloidal Pt catalyst, methyl viologen (MV$^{2+}$) is frequently employed as electron carrier between the sensitizer and the catalyst. The important steps in this system are photoinduced electron transfer from a photo-excited sensitizer to MV$^{2+}$ and the subsequent electron-transport to colloidal Pt catalyst by the reduced MV$^{2+}$ (MV$^{+}$).
Catalytic systems for the hydrogen evolution from water have been studied by several groups. Perhaps those based on colloidal metal or metal oxide particles are those that attract most attention because of the higher efficiency of the catalytic center. Among metal nanoparticles, Pt is well known to be particularly attractive towards the hydrogen evolution reaction.

![Scheme 7.1](image_url)  

**Scheme 7.1.** Representation of a system for hydrogen evolution based on colloidal platinum, viologen as electron relay and Ru(bpy)$_3^{2+}$ as sensitizing dye.

Scheme 7.1 shows the general structure of systems characterized by the use of an organometallic complex as sensitizing dye. These complexes are photo and electro-active and possibly the best example is Ru(bpy)$_3^{2+}$. This compound is capable of absorbing light from the UV into to visible part of the spectrum creating a long lived excited state that is able to transfer one electron to the electron relay (viologen) in a reversible redox process. The reduced viologen is then a strong reductant which is capable of transferring electrons to the platinum particle surface where molecular hydrogen evolves. In these systems, light acts as a pump forcing the electrons in the direction of the catalytic center. Perhaps the two biggest drawbacks of these kind of catalytic cycles are the diffusion controlled efficiency of the electron transfer among the participants and the dimerization of the reduced viologen into an inactive species.

Our choice represents an analogously constructed three components system containing a sensitizer Ru(bpy)$_3$:pyt-BCD or Ir(ppy)$_2$:pyt-BCD (organometallic complexes bearing cyclodextrins shown in chapter 4 of this thesis), and an electron relay (a symmetric bis-adamantyl viologen) that creates a charge separated state and transfers the electrons to the...
platinum catalyst, scheme 7.2. The photoinduced electron-transfer step may be improved by linking electron donor-acceptor molecules in a more strict fashion but without covalent bonds, mimicking photoinduced electron transfer processes in the natural photosynthetic reaction center.\textsuperscript{10}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{scheme72.png}
\caption{Schematic representation of how the catalytic system arranges the three components for a more efficient photoinduced electron transfer towards the platinum particle.}
\end{figure}

For $M = \text{Ir}$, $n = 3$ and $X = \text{C}$
For $M = \text{Ru}$, $n = 2$ and $X = \text{N}$

As for natural systems, in which a series of redox and photo-active molecules are closely packed and well organized in a non covalent fashion using electrostatic interactions with membranes as well as hydrophobic interactions, in our supramolecular architecture the components are held together by the latter. For our purposes, cyclodextrins can provide a joint to assemble molecules of interest in a versatile way as shown throughout this Thesis. Moreover, in the literature there are examples of the use of cyclodextrins as protection agents against dimerization of the intermediates of the catalytic cycle (i.e. the highly reactive viologen radical cation MV\textsuperscript{+} and against the in situ chemical reduction of MV\textsuperscript{+} by the evolving hydrogen.\textsuperscript{12,13} Cyclodextrins have also been used as “molding matrices” or “supports” for the platinum colloids in the groups of Shafirovich\textsuperscript{14} and Yonemitsu\textsuperscript{15} respectively, showing a great influence in overall hydrogen production probably due to the aforementioned reasons and stabilization of the platinum colloid in solution.
More than thirty years ago, separate work of Lehn and Grätzel on the now classic three component molecular photocatalytic hydrogen evolution system containing Ru(bpy)$_3^{2+}$, methylviologen and colloidal platinum was published. The renewed interest in this topic is mainly due to the current search for alternative energy sources. Since then many studies have been reported with different photosensitizers, sacrificial electron donors, differently substituted viologens or differently sized platinum colloids or particles. To our knowledge, no review of the results of this classic three-component molecular photocatalytic hydrogen evolution system is available and results are rather scattered, in terms of optimal conditions and e.g. platinum particle size.

The typical total efficiencies are around or below 0.1 %, hydrogen evolution rates range from ~1 to 9 ml/hour ( ~40 to 375 μmol/hour), typical illumination sources are 150 W Xe lamps. Whereas in photovoltaics standard conditions are clearly defined, this is not the case in the photo-catalytic community.

Our ambitious aim is to prove that the three component supramolecular system can generate hydrogen and even that the efficiency can be higher than in the diffusion controlled analogue. First an assessment of the individual components is presented.

### 7.2 Electrochemistry on the platinum nanoparticles

![Scheme 7.3. Schematic representation of the platinum nanoparticles and the stabilizing molecule. The stabilizer is a perthiolated β-cyclodextrin (TCD), the sulfur atoms are represented as grey circles.](image)

In order to understand if our design could lead to the desired goal we have to study in detail the processes and their kinetics in the separate components. We have started with the investigation of the platinum nanoparticles covered with TCD as shown in scheme
7.3. It has been established that metal nanoparticles usually exhibit size-dependent catalytic reactivity: metal nanoparticles with diameters of few nanometers (<5 nm) possess a large fraction of metal atoms on their surface, thus increasing the efficiency during catalytic processes. However, aggregation and coalescence phenomena are indeed an obstacle for practical applications. Metal nanoparticles have been stabilized in solution by partial or complete coverage with organic ligands. In any case, to retain their catalytic properties, the surface of the metal nanoparticles must remain accessible to the substrates and at the same time must avoid passivation. Kaifer and coworkers reported the synthesis of metal nanoparticles stabilized with cyclodextrin receptors and their catalytic activity towards hydrogenation of olefins. The TCD stabilized Pt nano-particles (see Chapter 2 for their synthesis and characterization) were deposited on an indium tin oxide (ITO) substrate and their catalytic activity was examined, both with cyclic voltammetry (CV). Scans from positive to negative potentials using CV allowed the deposition of monodisperse Pt nanoparticles in a simple and regular fashion as evidenced by atomic force microscopy (AFM), figure 7.1.

Figure 7.1. AFM topography images (1 x 1 μm) of TCD protected platinum nanoparticles deposited a) by potential sweep and b) without, both on HOPG. The line profiles shown below the images correspond to the black line on the image. The z full grey scale corresponds to 26 and 9.5 nm respectively.
The results showed that Pt nanoparticles deposited using this procedure are active either toward hydrogen oxidation and reduction opening up interesting perspectives for catalytic applications (figure 7.2).

The arrows in figure 7.2.a) indicate the peaks that are assigned to reduction and oxidation of protons in solution to hydrogen and back. These peaks are characteristic for absorption and desorption of hydrogen in aqueous solution. It is interesting to note that the current density increases linearly with the number of cycles and time (figure 7.2.b). This fact suggests that CV may be a suitable method for depositing and to control the Pt nanoparticles density on electrode surfaces in a controlled and uniform fashion.

The electro-catalytic activity of Pt nanoparticles towards hydrogen reduction and oxidation is a well documented process. The catalyst functions as an condenser/capacitor of negative charge to provide the necessary electrochemical potential and the number of electrons for the reduction of the aqueous protons and serves as a gas evolution site. This process may occur by the following mechanism when the electron carrier is a reduced viologen.

Figure 7.2. a) CVs (100 cycles) of perthiolated-β-CD-protected Pt nanoparticles deposited on ITO electrode substrate obtained in 0.1 M KCl supporting electrolyte (scan from +1 V to -0.8 V); scan rate 0.1 V s\(^{-1}\). b) Pt nanoparticle density vs time and vs number of voltammetric scans (upper x-axis. Sealed cell, exposed area 0.4 - 0.6 cm\(^2\). pH of the solution ~ 6.

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The results show that the platinum particles are active towards the reduction of protons to hydrogen and vice versa as expected even at these relatively high pH (~6) values. Our results also show that the particle size is ideal for application in this kind of catalytic reaction, allowing the diffusion of sufficient H⁺ ions to the surface of the catalyst for the reduction process to H₂ to take place.

7.3 Selection of the sensitizer and the electron relay.

It is clear that the sensitizing dyes must have a number of characteristics to be able to use them as sensitizers for our purposes. Among others high photostability and a long excited state lifetime are a prerequisite. Also, the excited state of the photosensitizer has to be able to transfer an electron to the relay before it returns to the ground state, resulting in a charge separated state we can utilize further. Polypyridine complexes can be excited over a wide range of wavelengths along the visible spectrum, and they can be functionalized with cyclodextrins. Moreover, electron transfer from a, e.g. ruthenium polypyridine complex to viologen has been widely documented.

Not every dye is adequate for the formation of the necessary charge separated state. Assembly 7.1 is a clear example of this where the ruthenium-bis-terpyridyl complex is not able to transfer an electron to the viologen even at high excess concentrations of the acceptor molecule. This is related to the unusually short lifetime (τ < 2 ns) of the electron donor and its analogues as it is described in chapter 3A, due to the presence of the 3MC state through which the excited state decays non-radiatively to the ground state. The electron transfer process cannot compete efficiently with the deactivation process through the metal centered state that is thermally accessible at room temperature. Similar ruthenium complexes have shown the possibility of transferring electrons to quinones,
however in the case of viologens as acceptors only low temperature processes have been described.\textsuperscript{25} \textbf{Assembly 7.2} shows the use of a tris-bipyridine analogue functionalized with three \(\beta\)-cyclodextrins. In this case the lifetime is close to 1 \(\mu\)s in deaerated water and should allow enough time for the transfer to occur even at room temperature, processes that are well known from the literature.\textsuperscript{26} However in this case the dye has three cyclodextrins attached to the central metal core, which introduces a great number of synthetic difficulties especially in the purification processes. Furthermore, the compounds presents a geometry that is not totally desirable in the construction of wires since it will not necessarily favor the formation of linear wires oriented towards the catalytic center.

\begin{center}
\includegraphics[width=\textwidth]{assembly_7_1_7_2_7_3.png}
\end{center}

\textbf{Assembly 7.1} \hspace{0.5cm} \textbf{Assembly 7.2} \hspace{0.5cm} \textbf{Assembly 7.3}

\textbf{Scheme 7.4.} \textit{Comparison of ruthenium polypyridyl complexes studied as possible sensitizing dyes in this study. The host compounds in assemblies 1 and 2 are related to the complexes described in chapters 3A and 3B of this thesis respectively; the host in assembly 3 comes from the family of complexes studied in chapter 4.}
For **assembly 7.3**, derived from the family of compounds studied in chapter 4 of this Thesis, we found that synthesis and purification are greatly simplified when compared to the other two examples given, even in the presence of the cyclodextrin binding site. The lifetime of this ruthenium compound is significantly reduced compared to Ru(bpy)$_3^{2+}$ (ca. 25 ns) however it is long enough to allow an efficient competition between a radiative/non-radiative decay to the ground state and the electron transfer process. The study of the electron transfer process is very complicated in these compounds because of the amphiphilic nature of the electron acceptor. The very hydrophobic adamantane attached to the positively charged viologen in ada-MV tends to form aggregates (possibly micelles) in solution. These aggregates have a strong effect on the photophysical properties of the metal complexes. In fact the emission quantum yields increase with increasing viologen concentration as well as the excited state lifetimes, figure 7.3.

![Figure 7.3](image.png)

**Figure 7.3.** Steady state titration (left) of ruthenium complex Ru(bpy)$_3$(pytl-Me) with ada-MV, similar results were observed for Ru(bpy)$_3$(pytl-βCD). From the spectra it is clear that the luminescence of the ruthenium complexes does not decrease when the concentration of quencher increases, however a band at 525 nm corresponding to the scattering increases with increase of the amphiphile concentration. In the time resolved measurements (right), strong scattering due to micellation/aggregation could be observed even at low concentrations of quencher.

The confirmation of the electron transfer process comes from time resolved electronic spectra in the nanosecond time range where the signals corresponding to the reduced viologen can be clearly seen. These signals are characteristic for the viologen radical
cation and have been reported before. Figure 7.4 shows such a transient spectrum in which the reduced viologen can be seen as a strong absorption peak at 390 nm and a weaker and broad signal centered around 600 nm. The process occurs within the first frames of decay of the complex \( \text{Ir(ppy)}_2(\text{pytl-CD}) \) (see scheme 4.1 and 4.2 for the chemical structures) and is difficult to quantize because of the strong overlap of signals. Similar experiments were carried out for \( \text{Ru(bpy)}_2(\text{pytl-CD}) \).

By comparison with the transient absorption spectra of the iridium complex alone we can assign the bands in the mixture of the iridium with the viologen as follows: i) the low energy absorption is due to the formation of the reduced viologen and a second band at 390 nm is also related to the radical monocation of the viologen; ii) the bands at 350 and 450 are clearly due to the iridium excited state and decay almost completely within the 900 ns time window of the measurement (for lifetime see chapter 4).

**Figure 7.4.** Nanosecond transient absorption spectra of \( \text{Ir(ppy)}_2(\text{pytl-CD}) \) in absence (left) and presence (right) of viologen quencher showing photoinduced electron transfer from \( \text{Ir(ppy)}_2(\text{pytl-CD}) \) to ada-MV in aqueous solution. The signals for the viologen radical cation are clearly seen at 400 and 600 nm.

The radical monocation of the reduced viologen is extremely long lived (> 5.5 μs). In fact using the redox potential of the \( \text{Ir(ppy)}_2(\text{pytl-CD}) \) (\( E_{\text{ox}} = 0.880 \text{V} \)) and viologen (\( E_{\text{red}} V^{2+/V^+} = -0.95 \text{V} \)) we can estimate a driving force for the forward electron transfer using the equation:

\[
\Delta G = E_{\text{ox}} - E_{\text{red}} - E_0
\]

\( E_0 \) is calculated to be 2.65 eV from the 77K luminescence spectra of the iridium complex (chapter 4). For the forward electron transfer we obtain a \( \Delta G_{\text{red}} = -0.82 \text{ eV} \). The back
electron transfer has a driving force calculated to be $\Delta G_{\text{back}} = -1.83$ eV, a very exergonic process. We attribute the slow back reaction to the high exoergonicity of the process.

For the case of the Ru(bpy)$_2$(pytl-$\beta$CD) we estimate an oxidation potential of $E_{\text{ox}} = 0.93$ V$^{30}$ and the $E_{\text{re}}$ is measured to be 2.2 eV. These data give a forward driving force for the electron transfer of $\Delta G_{\text{fwd}} = -0.32$ eV and a back electron transfer that is again very exergonic with a driving force of $\Delta G_{\text{back}} = -1.88$ eV. The lifetime of the reduced viologen was also measured to be in the microsecond range. The driving forces for the forward and back electron transfers are schematically represented in scheme 7.5.

Scheme 7.5. Driving forces calculated for the forward and back electron transfer processes.

One of the problems related to the necessary high concentration of the electron accepting component is its tendency to aggregate. The possible solution for this observation could be the attachment of the cyclodextrin on the viologen and the adamantane on the ruthenium center. A similar procedure was recently described by Forster and co-workers$^{31}$ where no aggregation or micellation was reported by the authors. This agrees also with the data published by Park et al in reference to the dimerization of reduced viologens$^{32}$. This viologen having a beta cyclodextrin attached to one nitrogen and a methyl group attached to the other nitrogen, show a protective role of the cyclodextrin towards dimerization and, thus, a role of preventing two reduced viologens from encountering in solution. A similar approach was used in the following experiments on
the assembled system, where micellation is reduced significantly due to the substitution of the viologen symmetrically with two adamantanes.

### 7.4 Hydrogen evolution experiments.

In the previous sections we have shown that the Pt nanoparticles are catalytically active and that the pyridine-triazole complexes together with viologen systems are good active components. The following scheme shows the chemical structures of the selected complexes used as photosensitizers, the viologen compound that acts as electron relay and the platinum catalyst where the catalytic reaction takes place assembled in one of the possible supramolecular architectures which will be investigated for the \( H_2 \) production.

### Scheme 7.6. Chemical structures of the compounds studied in the hydrogen evolution process. Iridium and ruthenium complexes used as sensitizing dye, symmetrical viologen used as electron relay and schematic representation of the platinum nano-particle where the actual reduction process occurs. In the assembled system when \( M = Ir, n = 3 \) and \( X = C \); when \( M = Ru, n = 2 \) and \( X = N \). The sacrificial donors tested were methanol, EDTA or TEA.
By mixing the components in aqueous solution we obtain the self assembled system represented at the bottom of scheme 7.6 as well as several combinations which are possible by combining the building blocks: the assembly is purely statistic. We are aware that only the first and perhaps the second (“dimer” of sensitizing dye) assemblies in scheme 7.7 are able to produce H₂. Nevertheless, we believed that the approach should represent an improvement vs the pure diffusionally controlled redox process.

Scheme 7.7. Possible assemblies formed in solution by the building blocks present in the experiments. When $M = Ir, n = 3$ and $X = C$; for $M = Ru, n = 2$ and $X = N$.

As electron donors mainly three candidates were tested. Methanol because of its availability from biomass, triethanolamine (TEOA) because of its good electron donating properties and EDTA, a classical electron donor example.
TEOA was soon discarded because of the formation of insoluble decomposition products that turned the reaction mixtures heavily turbid. Experiments were carried out under constant irradiation. The system was studied in a home made cell constructed in the Radboud University of Nijmegen. A picture of this cell is shown in figure 7.5.

In a typical experiment an aqueous solution was prepared with the sensitizing dye \((\text{Ru(bpy)}_2(pytl-\beta\text{CD}) \text{ or Ir(ppy)}_2(pytl-\beta\text{CD}))\) with concentration in the millimolar range (0.1 mM) with 10 times excess of viologen relay ada-MV-ada (scheme 7.4) and 1 mg of platinum nanoparticles stabilized with TCD. To this solution a sacrificial electron donor was added in 100 times excess towards the sensitizing dye. Finally to assure the presence of enough \(H^+\) ions the concentration of HCl was set to ca 200 equivalents. The solution was then carefully degassed. The total volume of the aqueous solution was always kept to 10 ml in a cell with capacity for 36 ml.

![Figure 7.5](image)

**Figure 7.5.** Picture of the reaction vessel employed in the hydrogen evolution experiments. The photograph shows the actual cell with a total volume 50 ml in the center of the image. The cell was covered with a quartz glass lid that was hold air tight with three metal screws. The Xenon lamp of 150 W of power continuously irradiated the cell from above. The cell has one inlet for vacuum/nitrogen connected to a Schlenk line and another inlet to take the samples of gas with a microsyringe. The whole system was thermostatted with a water cooling system.
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Solutions were monitored for molecular hydrogen evolution by directly measuring the amount of molecular hydrogen contained in the gas phase inside the reaction cell ($V_{cell}=36$ ml) through GC analysis. In order to convert the chromatographic peak areas into moles of hydrogen gas, a calibration curve was constructed by preparing different mixtures of $N_2$ and $H_2$ of known ratios and measuring their $H_2$ peak integrations. The gas mixing and injecting processes, as well as the illumination experiment itself, were performed at $T=20^\circ$C (where $R=24.055$), meaning that 1 mol of gas occupies 24.055 L. It is important to notice that all the $H_2$ amounts mentioned from now on are determined by analyzing only the gas phase. The $H_2$ which remains dissolved in the solution - or even entrapped inside bubbles on the solution surface - cannot be measured.

The most efficient combination examined was $\text{Ir(ppy)$_2$(pytL-CD)}$/MV/Pt-CD/EDTA and it will be shown here as example for the response of the systems to the variations introduced by us in the chemical structure of the components. During the first 15 minutes, 4.6 μmoles of $H_2$ were produced and the gas evolution was apparent by small bubble formation on the surface of the solution, figure 7.6. After 3 hours of constant irradiation, the EDTA electron source was depleted and the reaction stopped as a consequence of the lack of regeneration of the oxidized photosensitizer. The total amount of $H_2$ produced was 137 μmoles.

Figure 7.6. Hydrogen evolution measurements using EDTA as sacrificial electron donor and iridium as sensitizing dye.
During the experiment were ada-MV-ada was employed as electron relay instead of the simpler MV, we observed blue coloration of the reaction mixture. This coloration must come from the [ada-MV-ada]$^+$ for it is generally known that the reduced form of viologen gives a strong blue color to solutions. Apparently, the ada-MV-ada compound associates in solution in its reduced form interrupting the directional flow of electrons towards the catalytic center partially if not completely, this accounts for the very low hydrogen produced as shown in figure 7.6.

In the case of the iridium complexes studied as sensitizing dyes (chapter 4), our data also indicate that the efficiency of the system is directly related to the quantum yield of the photosensitizer. This is again given as an example in figure 7.6 where an experiment is shown with Ir(ppy)$_2$(pytl-Me) as sensitizing dye. As just explained the compound with the significantly lower quantum yield (shorter lifetime), translated this to a lower efficiency in hydrogen production.

In order to have complete selectivity or a preference in the binding we would need an asymmetrically substituted electron relay with stronger affinity towards one of the cyclodextrin binding sites. A viologen substituted with a cholesterol derivative seems to be the most promising candidate and work is currently being developed in this direction. Non-symmetrically substituted viologens and various conveniently functionalized cyclodextrins systems (with two sizes of cyclodextrins) would open up new opportunities for future developments.

### 7.5 Conclusions

The nanoparticles synthesized with cyclodextrins as stabilizers are highly active towards catalytic reactions of different kinds. The activity of the metal surface is not passivated by the attachment of the stabilizer. Electrochemistry is a promising technique to deposit this type of water soluble nanoparticles onto electrodes in a homogeneous fashion, giving highly active surfaces of monodispersed reactive sites.

In the hydrogen evolution experiments, we can state that our platinum colloids in combination with metallocyclodextrins work best with methyl-viologen as electron relay.
The substitution of the viologen with cyclodextrin binders leads to detrimental micellation and viologen radical cation stabilization effects. The cyclodextrin substituted Iridium complex is the most efficient photosensitizer for our purposes. Hydrogen evolution rates obtained with this system are (0.75 ml/hour; 32 μmol/hour), and an absolute lower limit of the turn-over number is 275, as 1 μmole of metal complex can generate 137 μmoles H₂ gas (~3.3 ml). As such, the envisaged supramolecular organization works different from what we anticipated. It appears that the long lifetime (and correlated high quantum yield) of emission and the high energy of the Iridium complex are beneficial factors. It has to be realized that binding events with this complex are not straightforward (see Chapter 4).

**Experimental**

Cyclic voltammograms and chronoamperometry characteristics were recorded using an electrochemical analyzer (CH Instruments, model CHI730A). A conventional three-electrode configuration was used, where the working electrode was an ITO glass plate on which a Pt-CD were deposited, a platinum coil was used as a counter electrode and either an Ag/AgCl or a KCl-saturated calomel electrode (SCE) were used as reference electrodes. The area of the working (typically between 0.2-0.3 cm²) electrode was kept constant during all measurements.

**Acknowledgements**

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7.6 References

[1] Nussbaumer, T. *Energy Fuels* 2003, 17, 6, 1510-1521


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[20] The voltammetry peaks seen at -0.2 volts correspond to the stripping off of platinum oxide, peaks at -0.8 V for the reduction of sulfides of the cyclodextrin.


