High-Turnover Photochemical Hydrogen Production Catalyzed by a Model Complex of the [FeFe]-Hydrogenase Active Site

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Hydrogen has the potential to replace fossil fuels as the energy carrier of the future, particularly if it is produced in a regenerative fashion, such as by photochemical splitting of water.[1] The reductive side of this process demands the development of catalysts that promote the reduction of protons to molecular hydrogen, powered by direct excitation or by a photosensitizer. Colloidal platinum had already been presented as a heterogeneous catalyst 30 years ago,[2] and more recently, molecular platinum- and palladium-based systems have been developed.[3,4] The chemical integrity of the Pt and Pd catalysts is, however, somewhat questionable because Pd or Pt colloid formation has been detected during photochemical catalysis in some instances.[5,6] This reactivity not only precludes further improvement by synthetic manipulations, but has also led to the suggestion that the colloids rather than the molecular species are responsible for catalysis in these systems.[5,6] Moreover, neither platinum nor palladium exist in sufficient abundance to qualify any catalyst based on these metals for large-scale applications. In this regard, cobalt complexes offer a viable alternative, since they have been shown to catalyze the light-driven reduction of protons in conjunction with suitable photosensitizers.[7–9] The biomimetic approach of utilizing active-site models of the [FeFe] hydrogenases as hydrogen producing catalysts has recently received much attention because the enzymes themselves catalyze this reaction with high turnover rates close to the Nernstian potential,[10] albeit in the absence of

light.[11] Complexes of the type $[Fe_2(\mu\text{-}SCH_2XCH_2S)(CO)_4(L)_2]$ ($X = CH_2$, NR; $L = CO$, CN^-, PR_3) have been extensively studied in this context.[12,13] Unlike the cobalt complexes, however, these biomimetic Fe_2 complexes have, so far, almost exclusively been used for the electrocatalytic reduction of protons, requiring significant overpotential and often strongly acidic conditions.[14] The sparse attempts to utilize them in combination with photosensitizers for photochemical catalysis have hitherto been only moderately successful, giving less than five equivalents of H_2 per catalyst.[15,16] We hypothesize that the poor performance of this type of complex may arise from the instability of the reduced Fe_2 species as is evident from the irreversibility in the cathodic scan of their cyclic voltammograms. Unlike in electrocatalytic experiments, photocatalytic proton reduction occurs by consecutive one-electron reduction steps and the second equivalent of reducing agent may not immediately be available. It thus seems to be crucial that a catalyst for photochemical hydrogen formation must be stable in the different redox states and show strictly reversible structural changes.

Recently, $[Fe_2(\mu\text{-bdt})(CO)_6]$ (bdt = benzene-1,2-dithiolate) was presented as the first Fe_2 complex that exhibited reversible reductive electrochemistry and maintained its structural integrity to a large extent, including in the reduced state.[17] The reduction potential can be shifted to more positive values by the introduction of electron-withdrawing chloro substituents. The resulting $[Fe_2(\mu\text{-Cl}_2\text{bdt})(CO)_6]$ complex (**1**; Scheme 1, $Cl_2bdt = 3,6$-dichlorobenzene-1,2-dithiolate) was shown to catalyze the electrochemical reduction of protons at -1.2 V versus the ferrocenium/ferrocene couple ($Fc^{+/0}$).[18]

Complex **1** thus occupies an exceptional position amongst model complexes of the [FeFe]-hydrogenase active site because it combines unprecedented electrochemical reversibility in the absence of protons with catalytic activity at mild potential in their presence.

Herein, we report, for the first time, the use of complex **1** in a photocatalytic hydrogen production scheme that results

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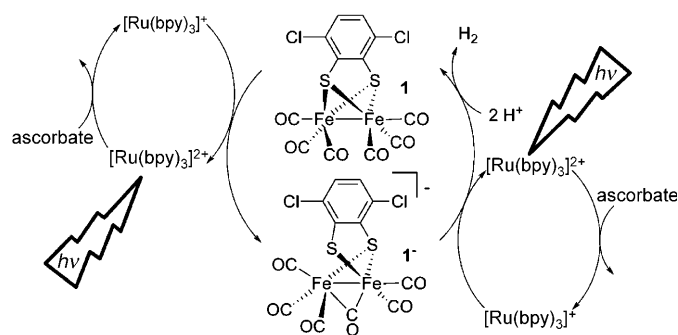
Scheme 1. Proposed catalytic cycle for the photochemical reduction of protons catalyzed by [Fe$_2$(μ-Cl$_2$bdt)(CO)$_6$] (Cl$_2$bdt = 3,6-dichlorobenzene-1,2-dithiolate) in 1:1 H$_2$O/DMF. The structure of **1**$^-$ is analogous to that in ref. [17].

in remarkably high turnover rates and numbers. [Ru-(bpy)$_3$]$^{2+}$ (bpy = bipyridine) serves as a photosensitizer and ascorbic acid serves as a proton and sacrificial electron donor for homogeneous photochemical proton reduction. To ensure the solubility of all components, a solvent mixture of DMF/H$_2$O was used in all experiments. In such a system the reaction free energy for electron transfer from photogenerated [Ru(bpy)$_3$]$^+$ to **1** can be estimated from the electrochemically determined $E_{1/2}$ to be $\Delta G^0 = -0.44$ eV.

Photochemical hydrogen evolution experiments were performed with a [Ru(bpy)$_3$]$^{2+}$/**1** ratio of 10:1 at the almost neutral pH of 5.5. The hydrogen formed was identified and quantified by gas chromatography. As shown in Figure 1, more than 200 equivalents of hydrogen per complex **1** are produced in 2.5 h with a maximum turnover frequency of 2.7 H$_2$ per catalyst per minute. Under these conditions, the quantum yield for hydrogen formation was calculated from the absorbed photons (93.1 nmol photons per second) and
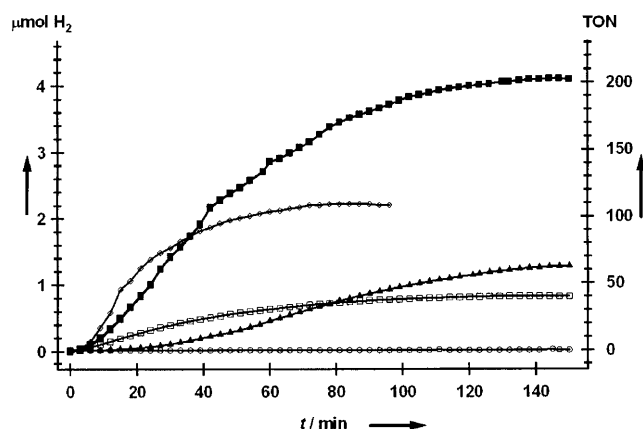
the maximum hydrogen production rate (0.93 nmol s^{-1}) to be 1% (see Figure S1 in the Supporting Information). The quantum yield and turnover frequency can reach even higher levels of 1.4% and 3.7 turnovers per minute, respectively, at pH 6.4. At this pH, however, catalysis stops earlier, yielding only 100 turnovers. Due to this decrease in overall turnovers, H$_2$ evolution at even higher pH was not further investigated. Lowering the pH to 3.5, under otherwise identical conditions, also resulted in a drop of activity to 40 turnovers of H$_2$ per catalyst over 2.5 h. It thus seems that the catalyst operates optimally at around pH 5.5 at which point the highest level of hydrogen production is obtained. Maintaining this pH, but lowering the ratio of [Ru(bpy)$_3$]$^{2+}$/**1** to 1:1 also proved to be counterproductive and turnover numbers dropped to 65.

Control experiments in which either complex **1**, [Ru(bpy)$_3$]$^{2+}$, or ascorbic acid are separately omitted do not show significant hydrogen production (Figure 1). Catalysis stops after approximately 150 min under all of the experimental conditions described above. Since there are no substantial changes in the sample pH or in the UV/Vis absorption spectrum of the photosensitizer during the experiment, catalyst inactivation is the most likely cause for this observation. Indeed, when a solution of **1** in neat DMF is exposed to irradiation that approximates the conditions of the hydrogen evolution experiments (see the Supporting Information for details), substantial changes can be observed in the CO region of the IR spectrum. These changes occur gradually on a timescale comparable to termination of catalysis (Figure S2 in the Supporting Information). The sample becomes virtually depleted of complex **1** and signals of photoproducts dominate the IR spectrum in the CO region. Unfortunately, the spectrum obtained is complex and does not allow for a straightforward assignment of one or several product species. Potential instability of the photoproducts and their formation in low quantities may further impede a more detailed analysis.

Reductive quenching of *[Ru(bpy)$_3$]$^{2+}$ by ascorbic acid and the subsequent reoxidation of [Ru(bpy)$_3$]$^+$ by **1** as elementary reactions of the proposed catalytic cycle were verified and studied in more detail by transient absorption and emission spectroscopy (Figure 2 and Figures S3–S5 in the Supporting Information). As apparent from the corresponding transient absorption spectra, no other species contribute, to a considerable extent, at any of the observed wavelengths (Figures S3 and S4 in the Supporting Information).

The emission decay traces show that the *[Ru(bpy)$_3$]$^{2+}$ excited state ($\tau_0 = 810$ ns) is quenched with an efficiency of about 96% ($\tau = 30$ ns) by 100 mM ascorbic acid in 1:1 DMF/H$_2$O at pH 5.5 (Figure S5 and Table S1 in the Supporting Information). The quenching is unaffected by the presence of **1**, showing that the primary reaction occurs between the excited state and the electron donor. Quenching produces [Ru(bpy)$_3$]$^+$ in almost quantitative yield, as monitored by its transient absorption at 510 nm and the disappearance of the 455 nm bleach due to *[Ru(bpy)$_3$]$^{2+}$ (Figure 2, inset; Table S1 in the Supporting Information). A decrease of the

Figure 1. Light-driven hydrogen production by **1** (14 μM, 21 nmol) in the presence of [Ru(bpy)$_3$]$^{2+}$ and ascorbic acid (100 mM) in deoxygenated 1:1 DMF/H$_2$O at 20°C. All samples were irradiated with light in the wavelength range 455–850 nm. H$_2$ was detected by in situ gas chromatography. ■ = 140 μM [Ru(bpy)$_3$]$^{2+}$, pH 5.5; ◇ = 135 μM [Ru(bpy)$_3$]$^{2+}$, pH 6.4; ▲ = 17 μM [Ru(bpy)$_3$]$^{2+}$, pH 5.5; □ = 140 μM [Ru(bpy)$_3$]$^{2+}$, pH 3.6; ○ = no catalyst 140 μM [Ru(bpy)$_3$]$^{2+}$, pH 5.5.
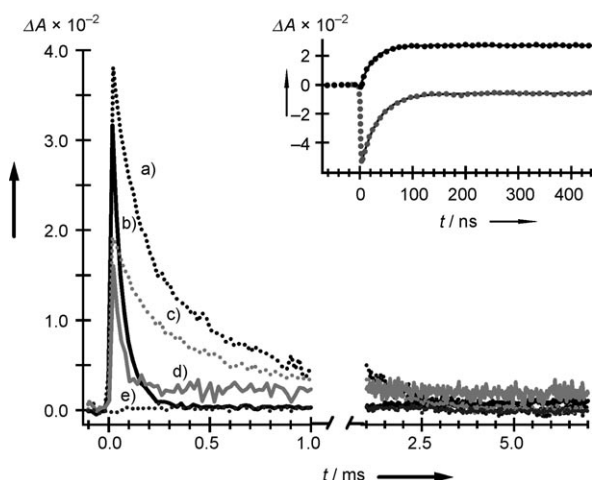
Figure 2. Effects of pH and the presence of catalyst **1** on the 510 nm transient absorption signal of $[Ru(bpy)_3]^+$. Conditions: 14 μM $[Ru(bpy)_3]^{2+}$, 0.1 M ascorbic acid in deoxygenated 1:1 DMF/H$_2$O at room temperature. Excitation wavelength: 470 nm. a) no catalyst, pH 5.5; b) 14 μM catalyst, pH 5.5; c) no catalyst, pH 3.5; d) 14 mm catalyst, pH 3.5, e) no catalyst, no ascorbic acid, pH 3.1. The inset shows 510 (•••••) and 455 nm (••••••) transient absorption traces at pH 5.5 on shorter timescales, with rise times of approximately 30 ns.

ascorbate (pK_a=4.1) fraction by lowering the pH to 3.5 decreases the reductive quenching efficiency and only 53% (τ=390 ns) of *$[Ru(bpy)_3]^{2+}$ is converted to $[Ru(bpy)_3]^+$. This finding may at least partly explain the five-fold drop in activity that is observed in the catalysis experiment. A control experiment showed that no $[Ru(bpy)_3]^+$ is produced in the absence of ascorbic acid (Figure 2). The half-life of photogenerated $[Ru(bpy)_3]^+$ is reduced from 200 to 50 μs (Figure 2) in the presence of **1** (14 μM), irrespective of pH, which implies that the primary reaction step of the catalytic sequence is the reduction of complex **1** to **1**$^-$ by $[Ru(bpy)_3]^+$.

Radical anion **1**$^-$ is only attainable photochemically, since its electrochemical reduction potential is more positive than that of neutral complex **1**. DFT calculations indicate that the inverted potential is a result of the scission of one Fe$-$S bond in **1**$^-$.[17] Due to the electrochemical inaccessibility of **1**$^-$, the subsequent steps in the catalytic cycle could not be studied so far. Protonation, disproportionation, or a second reduction are all plausible fates for **1**$^-$. The experiments described above show that pH 6.4 is still sufficiently acidic to protonate the reduced states of the catalyst (**1**$^-$, **1**$^{2-}$) to form a hydride intermediate, and to protonate this hydride to form hydrogen. None of the catalyst protonation steps seem to be rate limiting, since the highest turnover rates are obtained at higher pH. At lower pH, on the other hand, reductive quenching is less efficient and catalysis also becomes slower. Disproportionation or bimolecular catalysis appear to be insignificant, since the same turnover frequencies and numbers are obtained at 10 times lower absolute concentrations if the ratio of $[Ru(bpy)_3]^{2+}$/**1** is kept at 10:1 (data not shown). We therefore suggest that catalysis occurs intramo-

lecularly and the rate is limited by the transfer of the second electron to the catalyst.

Our results show that a synthetic model complex of the [FeFe]-hydrogenase active site can be an efficient catalyst for the photochemical production of hydrogen. Complex **1** operates in aqueous solution at almost neutral pH and achieves high turnover numbers that are competitive with those obtained from current state-of-the-art cobalt-based systems. Since synthetic model complexes may achieve the same high turnover numbers and frequencies that are reported for the enzymes themselves, [FeFe]-hydrogenase active-site mimics may well prove to be superior to other homogeneous catalysts in the future.

Experimental Section

See the Supporting Information for detailed information on materials, hydrogen evolution, quantum yield determination (Figure S1), catalyst stability under irradiation (Figure S2), and flash photolysis experimental procedures, as well as more flash photolysis data (Figures S3–5) and the calculation of reductive quenching efficiencies (Table S1).

Acknowledgements

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