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Making Hydrogen from Water Using a Homogeneous System Without Noble Metals

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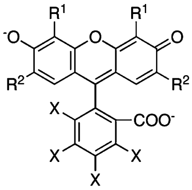
The photocatalytic production of hydrogen from aqueous protons attracts great scientific interest due to its relevance to solar energy conversion and artificial photosynthesis. Photocatalytic systems for H_2 generation typically consist of a photosensitizer, an electron relay, a sacrificial electron donor, and a heterogeneous[1−8] or homogeneous[9−11] catalyst. Although there is a plethora of systems employing noble metals in the catalyst and/or chromophore, systems based exclusively on earth-abundant elements are rare. They include semiconductor systems using CdS as a sensitizer,[12,13] systems based on the enzyme hydrogenase,[14] and a modified protein system.[15] As part of efforts to design and examine new systems based solely on earth-abundant elements, we herein describe a new homogeneous system for the photocatalytic production of H_2 from aqueous protons using highly absorbing organic dyes and a cobalt molecular catalyst.

We recently reported a homogeneous system for the photocatalytic generation of hydrogen from water consisting of a Pt^{II} chromophore, TEOA as a sacrificial reductant, and the Co-based catalyst $[Co^{III}(dmgH)_2pyCl]$ (**5**).[16] This Co catalyst was first used for the *electro*catalytic production of hydrogen.[17] In efforts to construct and examine new photocatalytic systems containing no noble metals, we replaced the Pt^{II} chromophore with the xanthene dyes Eosin Y (**1**) and Rose Bengal (**2**) that had been previously shown to catalyze the light-driven generation of H_2 from water in systems employing TiO_2/Pt[18,19] or methyl viologen/colloidal Pt[20,21] as the electron relay/catalyst components.



1, $R^1 = R^2$ = Br, X = H
2, R^1 = H, R^2 = I, X = Cl
3, R^1 = H, R^2 = Cl, X = H
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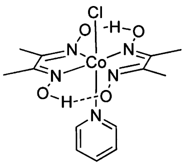

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A plot of hydrogen evolution against time upon irradiation ($\lambda >$ 450 nm) of a system containing **1**, TEOA, and **5** together with various concentrations of free $dmgH_2$ in $MeCN/H_2O$ 1:1 is shown in Figure 1. In the absence of free $dmgH_2$, the initial rate of H_2 production (~2.3 mL h^{-1}) is maintained for ~3 h before gradually reducing and finally ceasing in ~5 h after the production of ~360 turnovers of H_2. In the presence of 12 equiv of $dmgH_2$ (vs **5**), the initial rate of H_2 evolution is not significantly affected but the durability of the system greatly increases, possibly due to stabilization of an intermediate catalytic species possessing the $Co^{II}(dmgH)_2$ core.[22] Thus, the system maintains its activity for ca. 12 h producing in total ~20 mL of H_2 (~900 turnovers vs **1**). In these experiments, the termination of H_2 evolution coincides with bleaching of the photolysis solution. The systems can be revived only by the addition of both dye and catalyst indicating that both catalyst and photosensitizer decompose during photolysis and that stabilization of the catalyst by the addition of extra equivalents of $dmgH_2$ also inhibits the degradation of the dye.

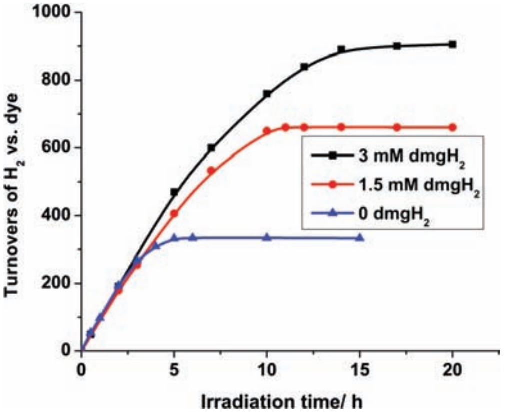

Figure 1. Hydrogen production from systems containing **1** (5×10^{-5} M), **5** (2.48×10^{-4} M), TEOA (5% v/v), and different concentrations of $dmgH_2$ in $MeCN/H_2O$ 1:1 upon irradiation ($\lambda > 450$ nm) at pH 7.

A quantum yield of 4% was determined for H_2 photoproduction for the Eosin Y system without any added equivalents of $dmgH_2$ using a 20-nm-wide bandpass filter centered at 520 nm (see Supporting Information). While the bandpass corresponds well to the major absorption of **1** ($\lambda_{max} = 524$ nm), the rate of H_2 production was significantly decreased from that obtained with light of $\lambda >$ 450 nm. However, under these circumstances, the system also showed markedly better photostability with an unchanging solution color and a constant rate of H_2 generation over 24 h that yielded ~200 turnovers relative to **1** (Figure 2) before eventual slowdown and cessation of activity.

The iodinated analogue **2** shows similar initial catalytic activity but degrades significantly faster than **1** under the same conditions

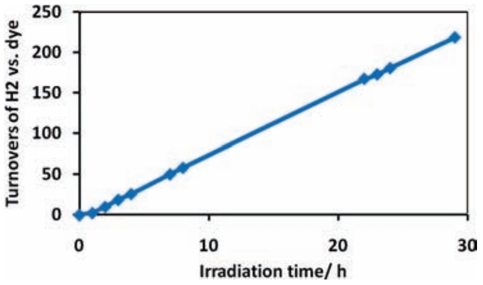

Figure 2. Turnovers of H_2 from system containing **1** (5×10^{-5} M), **5** (2.48×10^{-4} M), and TEOA (5% v/v) in $MeCN/H_2O$ 1:1 (pH 7) upon irradiation using the 20 nm wide bandpass filter centered at 520 nm.

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(Figure S1). When the chlorinated dye **3** is used as the photosensitizer, initial rates are reduced by a factor of 10 (~30 turnovers of H_2 after 5 h), while the parent fluorescein dye **4** shows *no* photocatalytic activity under the same conditions. This is in agreement with the enhanced catalytic activity previously reported for dyes **1** and **2** relative to their lighter-atom counterparts **3** and **4**.[18,19] This difference was attributed to the efficient formation of the long-lived triplet excited state for **1** and **2** following photoexcitation via intersystem crossing (ISC) facilitated by the heavy atom effect of their Br or I substituents.[18,19]

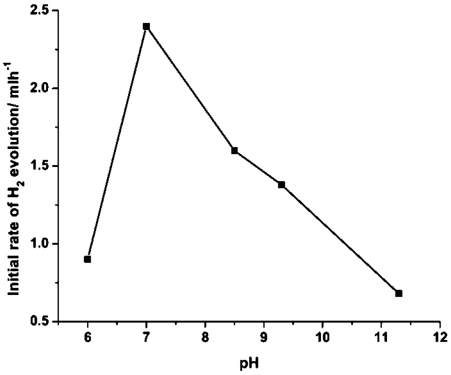


Figure 3. Effect of pH on the initial rate of photocatalytic H_2 production from a system composed of **1**, **5**, and TEOA in MeCN/H_2O 1:1.

In Figure 3, the effect of pH on the production of H_2 is shown. The initial rate of H_2 evolution maximizes at pH 7 and decreases sharply at both more acidic and more basic values. This strong dependence of the rate of H_2 evolution on pH has been observed by us in related photocatalytic systems.[16] The decrease in the rate of H_2 formation at acidic pH is likely a result of the protonation of TEOA which is thus rendered a less effective electron donor, whereas, at basic pH, the thermodynamic driving force for H_2 formation from water decreases and protonation of the reduced Co catalyst, an essential step in the postulated mechanism of H_2 formation, becomes unfavorable.

To gain a mechanistic understanding of the photogeneration of H_2 by the system composed of **1** + **5** + TEOA, absorption spectra for it were acquired at both pH 7 and 13, as well as for the non-hydrogen producing system of **4** + **5** + TEOA. Before irradiation, the absorption spectra are simply the sums of the individual components (individual spectra are shown in Figure S3). Upon irradiation ($\lambda > 450$ nm) at pH 7 under H_2 generating conditions, the formation of Co^{II} occurs within 5 min for the **1** + **5** + TEOA system as evidenced by the appearance of the characteristic absorption at ~450 nm (Figure 4a). While the non-hydrogen producing system containing fluorescein as the dye (Figure 4b) also shows evidence of Co^{II} formation, it does so more slowly and to a significantly reduced extent.

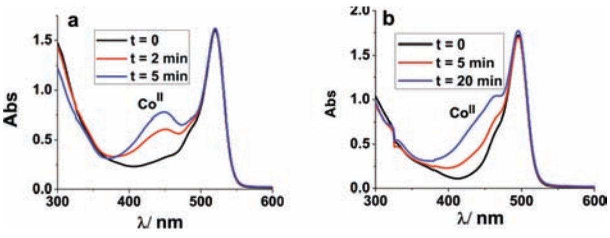


Figure 4. UV−vis absorption spectra of systems containing **5** (1.24×10^{-4} M), TEOA (2.5% v/v), and **1** (a) or **4** (b) (2.5×10^{-5} M) in MeCN/H_2O 1:1 at pH 7 before and after irradiation $\lambda > 450$ nm.

At pH 13 at which H_2 formation occurs only minimally for the Eosin Y system (**1** + **5** + TEOA), new lower energy absorptions are observed within 5 min at ca. 564 and 625 nm (Figure 5a) that are assigned to Co^I as described by Peters and co-workers.[23] For the fluorescein system (**4** + **5** + TEOA), only a weak signal in the range 550−700 nm appears after *1 h* of photolysis corresponding to slow and inefficient formation of Co^I (Figure 5b). The difference between the two systems in forming Co^I at pH 13 correlates with their relative activity in H_2 generation at pH 7. A change in the Eosin Y absorption at pH 13 is also seen, suggestive of photochemical decomposition of Eosin Y, possibly by debromination, leading to nonhalogenated dyes such as **4**.[19]

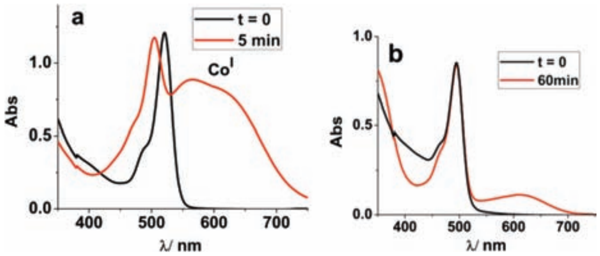


Figure 5. UV−vis absorption spectra of systems containing **5** (2.48×10^{-4} M), TEOA (1.25% v/v), and **1** (a) or **4** (b) (1.25×10^{-5} M) in MeCN/H_2O 1:1 at pH 13 before and after irradiation ($\lambda > 450$ nm).

The spectroscopic observations indicate that under H_2 generating conditions the dominant oxidation state of the catalyst is Co^{II}, while the pH 13 results indicate that the catalyst is further reduced to Co^I. It is this reduced Co species that leads to H_2 formation via initial protonation to form a generally postulated Co^{III} hydride intermediate. The light-driven steps that lead to Co^I are shown in Scheme 1 and include two possible photochemical pathways: (i) electron transfer from excited $^*EY^{2-}$ to Co^{II} (oxidative quenching of $^*EY^{2-}$) and (ii) reductive quenching of EY^{2-} by TEOA followed by electron transfer from EY^{3-} to Co^{II}. Both paths produce $TEOA^{+\bullet}$ that proceeds irreversibly by H^+ loss, electron transfer and hydrolysis to form glycolaldehyde + di(ethanol)amine along with transfer of a second H^+ and a second electron.[2,4b]

Scheme 1

Photochemical steps leading to Co^I

$$EY^{2-} \xrightarrow{h\nu} {}^{1*}EY^{2-} \xrightarrow{ISC} {}^{3*}EY^{2-}$$

Reductive quenching

$${}^{3*}EY^{2-} + TEOA \longrightarrow EY^{\bullet 3-} + TEOA^{+}$$

$$EY^{\bullet 3-} + Co^{III} \longrightarrow EY^{2-} + Co^{II}$$

Oxidative quenching

$${}^{3*}EY^{2-} + Co^{III} \longrightarrow EY^{\bullet -} + Co^{II}$$

$$EY^{\bullet -} + TEOA \longrightarrow EY^{2-} + TEOA^{+}$$

Reduction to Co^I

$${}^{3*}EY^{2-} + Co^{II} \longrightarrow Co^{I} + EY^{-}$$

$$EY^{3-} + Co^{II} \longrightarrow Co^{I} + EY^{2-}$$

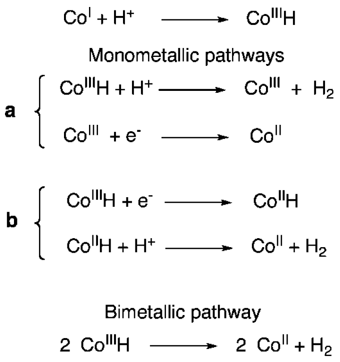
$$TEOA^{+} \longrightarrow \text{decomposition} + H^{+} + e^{-}$$

Several other possible electron donors were tried, but TEOA proved to be the most effective at hydrogen production under the same reaction conditions. Some hydrogen production was also observed when using triethylamine and EDTA (but with a more than 20-fold decrease in activity). Other potential electron donors such as $Na_2S_2O_4$, NaI, and Na_2S resulted in no hydrogen evolution. It is worth noting that when no H_2 was produced, the solutions maintained the pink color characteristic of EY^{2-}, even after 24 h of irradiation by light with a 450 nm cutoff filter.

Previously reported transient absorption studies have shown that reductive and oxidative electron transfers from xanthene dyes such as **1** and **2** occur via their lowest-lying triplet excited states.[25,26] In support of this, no quenching of the singlet fluorescence of dyes **1**−**4** is observed upon addition of either TEOA or **5** indicating that the singlet excited state does not take part in electron transfer. This evidence reinforces the view that the reduction of catalyst **5** occurs via the intermediacy of the dye-based triplet excited state, $^{3*}EY^{2-}$, that is produced after intersystem crossing (ISC) of the initially formed singlet excited state, $^{1*}EY^{2-}$. The specific role of $^{3*}EY^{2-}$ in the conversion of Co^{II} to Co^{I} is either by direct electron transfer between the two species or by reductive quenching of $^{3*}EY^{2-}$ by TEOA followed by electron transfer between EY^{3-} and Co^{II}. This interpretation is consistent with the observation that only the heavy atom-containing dyes **1** and **2** effectively induce the $Co^{II/I}$ transition. Scheme 1 outlines the steps leading to Co^{I}.

The formation of H_2 proceeding from Co^{I} and protons has been investigated in different ways, beginning with the kinetics of chromous ion reduction of Co glyoximate complexes and going to electrocatalytic investigations of H_2 formation by these and related cobaloxime systems.[17,23,24] It is postulated in all of these studies that the initial step toward making H_2 is protonation of Co^{I} to form a Co^{III} hydride. This step relates to the basicity of the specific Co^{I} species and the system pH. From this point, both monometallic and bimetallic mechanisms have been postulated (Scheme 2). One monometallic pathway (**a**) envisions H_2 generation by protonation of the Co^{III} hydride, H_2 elimination, and reduction of Co^{III} to Co^{II}, while another (**b**) involves reduction of Co^{III} hydride to Co^{II} hydride followed by protonation to give $H_2 + Co^{II}$. A bimetallic mechanism proposes a reaction between two Co^{III} hydrides to form $H_2 + 2\ Co^{II}$. Electrochemical studies have yielded different results that have led to both monometallic and bimetallic pathways being supported.

Scheme 2



In the photochemical generation of H_2 using **5** as the catalyst and a Pt(terpyridyl)(acetylide)$^{+}$ complex as the sensitizer, variation of the rate of H_2 evolution as a function of catalyst concentration was found to be linear, supporting a monometallic mechanism.[27] Analogous measurements in the present study with Eosin Y as the sensitizer and **5** as the catalyst also show a linear correlation with the H_2 generation rate (Figure S4), again supporting a monometallic pathway. While the particular monometallic mechanism is not established from this study, we favor mechanism **b** in which the Co^{III} hydride is first reduced to Co^{II} hydride followed by reaction with H^{+} to give $H_2 + Co^{II}$ based on the need to control catalyst redox potentials through protonation and charge management, as suggested for water oxidation.[28]

In conclusion, a homogeneous photocatalytic hydrogen evolving system has been constructed form earth abundant and inexpensive components. Further studies on improving the performance, efficiency, and durability of the system are in progress.

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Supporting Information Available: Experimental details, UV−vis spectra and electrochemical study. This material is available free of charge via the Internet at http://pubs.acs.org.

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