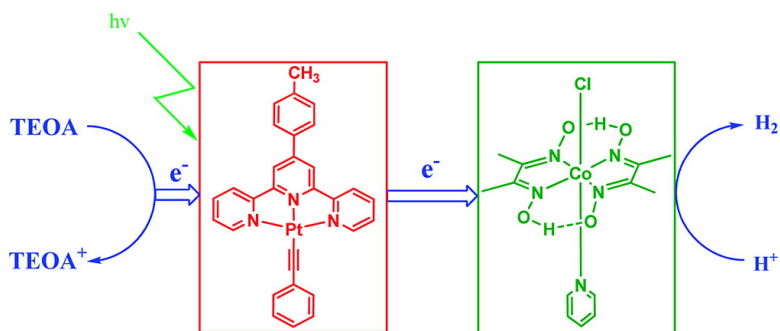## Communication

A Homogeneous System for the Photogeneration of Hydrogen from Water Based on a Platinum(II) Terpyridyl Acetylide Chromophore and a Molecular Cobalt Catalyst

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A Homogeneous System for the Photogeneration of Hydrogen from Water Based on a Platinum(II) Terpyridyl Acetylide Chromophore and a Molecular Cobalt Catalyst

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Received June 18, 2008; E-mail: eisenberg@chem.rochester.edu

The visible light driven splitting of water into its constituent elements attracts great interest relating to solar energy conversion and artificial photosynthesis. For the reductive side of water splitting — i.e., the generation of H_2 from aqueous protons and an electron source — studies have been conducted for more than three decades on heterogeneous systems having a photosensitizer (usually Ru(bpy)$_3^{2+}$ or a related d^6 chromophore), a methyl viologen (MV^{2+}) or diquat electron transfer quencher and mediator, a sacrificial electron donor, and a colloidal metal catalyst.[1−4] While a huge number of studies have been done to analyze, understand, and improve such systems, success with systems having molecular H_2 generating catalysts in place of metal colloids has been limited. The earliest efforts in this regard were described by Sutin[5] for a Ru(bpy)$_3^{2+}$−Co(bpy)$_3^{2+}$ system for hydrogen production in 1979, but no turnovers were reported. Later, Bernhard and co-workers[6] used combinatorial methods to make derivatives of [Ir(ppy)$_2$-(bpy)]$^{2+}$ in place of Ru(bpy)$_3^{2+}$ with Co(bpy)$_3^{2+}$ remaining as the electron transfer mediator and catalyst to produce hydrogen. Other reports featuring molecular or noncolloidal catalysts for light-driven H_2 generation include the use of hydrogenase enzymes and related model compounds with relatively low turnovers for the molecular catalysts.[7−9]

In efforts to develop light-driven systems having molecular catalysts for H_2 generation, prime targets are metal complexes that function as electrocatalysts for proton reduction at low overpotentials. In this regard, [Co(dmgH)$_2$pyCl]$^{3+}$ (**1**, dmgH = dimethylglyoxime, py = pyridine) has been found to produce H_2 gas at −0.90 V (vs Ag/AgCl) with ~100 turnovers,[10] while the related difluoroborylated species **2** generates H_2 at less cathodic potentials in the presence of 0.02 M strong acid.[10−13] Recently, Artero et al.[14] employed Ru(bpy)$_3^{2+}$ with **2** for photochemical H_2 generation from Et$_3$NH$^+$Cl$^−$ in MeCN, but system efficiency *decreased* dramatically in the presence of small amounts of water (0.043 M). In this communication we report for the first time the use of **1** in a photocatalytic system for H_2 generation from *aqueous* protons and an electron source in the form of a sacrificial donor. The system is found to be highly effective for the photogeneration of hydrogen.
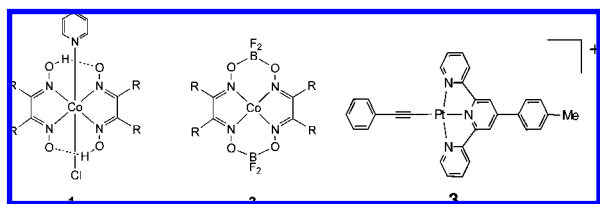
The light absorber and charge transfer component of the successful system is the previously reported Pt(II) terpyridyl phenylacetylide complex **3** that is reductively quenched by triethanolamine (TEOA) and oxidatively quenched by methyl viologen
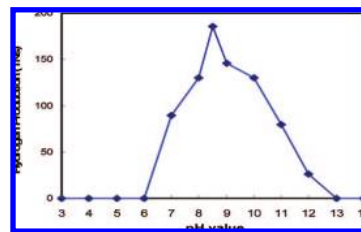

Figure 1. Effect of pH on the photogeneration of hydrogen from a system composed of **1** + **3** + TEOA after 5 h of irradiation (λ > 410 nm).

(MV^{2+}) at nearly diffusion-controlled rates (respective k_q's of 1.43 × 10^9 and 3.25 × 10^9 M$^{−1}$ s$^{−1}$).[15,16] In earlier reports of the use of this chromophore for the photogeneration of H_2, **3** was employed with an electron relay such as MV^{2+} or a related diquat (DQ^{2+}), TEOA as a sacrificial electron donor, and colloidal Pt as the catalyst.

When **1** was substituted for colloidal Pt in the four-component system (**3** + MV^{2+} + TEOA + **1** in MeCN/H$_2$O), no H_2 was produced after 10 h of irradiation with a 410 nm cutoff filter, and when DQ^{2+} was used in the system with **1**, only trace amounts of H_2 were generated. Despite the negative results regarding H_2 generation, the four-component systems containing **1** exhibited the color of the corresponding radical cation of the electron relay (dark blue for $MV^{+\bullet}$ and pink for $DQ^{+\bullet}$) indicating that oxidative quenching of **3** by the electron relay had occurred.

The absence of further reaction to generate H_2 suggested that the radical cations of the electron relays were insufficient to reduce complex **1** for proton reduction and H_2 generation. Accordingly, the systems were revised by removal of the electron relay and employment of a different quencher for **3**. Toward this end, it was found that the Co(III) complex **1** functions as an oxidative quencher for **3**, following good Stern−Volmer behavior (see Figure S1) consistent with dynamic quenching and a rate constant k_q of 1.27 × 10^9 M$^{−1}$ s$^{−1}$. In light of the large value of k_q, the system for the photogeneration of H_2 was simplified to **3** + **1** + TEOA with the omission of the viologen or diquat electron relay. This three-component system does produce hydrogen upon visible light irradiation with λ > 410 nm. Identification and quantification of the H_2 produced in the photolysis were conducted by GC analysis using a 5 Å molecular sieve column, TCD detector, and nitrogen carrier gas. The amount of hydrogen generated was determined using CH$_4$ as an internal calibrant as reported previously.[14] Control experiments indicated that all three components of the system were essential for H_2 generation; the absence of any of them led to no appreciable amounts of hydrogen.

As shown in Figure 1, initial system pH has a marked effect on hydrogen production. The amount of H_2 generated in a 5 h photolysis maximizes at pH 8.5 and decreases to negligible levels below pH 7 and above pH 12. For these photolyses, component concentrations were 1.11 × 10$^{−5}$ M photosensitizer **3**, 1.99 × 10$^{−4}$
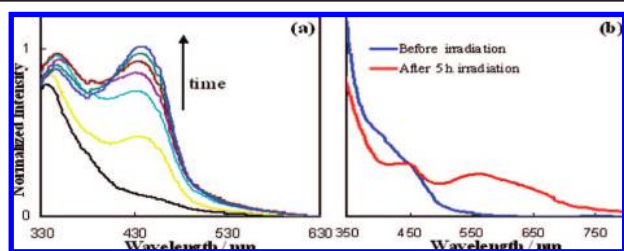
Figure 2. Time-dependent UV−vis spectra of solutions initially containing 1.61×10^{-2} M TEOA, 1.11×10^{-5} M **3**, and 1.99×10^{-4} M catalyst **1** in a mixture of MeCN/water (3:2 v/v) at pH = (a) 8.5 and (b) 12.

M Co complex **1**, and 1.61×10^{-2} M TEOA in MeCN/water (3:2 v/v) solvent. The pH value of each run was adjusted by addition of 0.1 M HCl or 0.1 M NaOH. The absence of H_2 formation when the pH is below 7 likely results from either protonation of TEOA or inhibition of proton loss from TEOA$^+$, both of which render TEOA an ineffective sacrificial donor. When the pH is >12, the driving force for H_2 production is greatly reduced and protonation of the Co catalyst, an essential step postulated in forming H_2 (vide infra), may become very unfavorable. The dependence on pH in H_2 photogeneration is commonly seen in many hydrogen production systems. At pH 8.5, maximum turnovers were achieved numbering ~400 based on the Pt chromophore after 10 h of irradiation $\lambda >$ 410 nm. When TEOA concentration was increased to 0.27 M, ~1000 turnovers were obtained after 10 h of irradiation.

To examine the system in more detail, UV−vis absorption spectra of photolysis solutions were measured. Prior to irradiation, Co complex **1** exhibits two strong absorption bands at 223 and 249 nm, assignable to $\pi-\pi^*$ transitions of the dmgH ligand, and no significant absorption in the visible region (see Figure S2). Changes observed during the photolyses are shown in Figure 2. Before irradiation, there is only an absorption tail extending into the visible region that is experimentally discernible from the summed spectra of Pt chromophore **3** and Co(III) catalyst **1**. After 10 min of photolysis, an absorption band centered at 440 nm is seen (Figure 2a), consistent with the formation of Co(II) as reported for the related complex **2**.[12,17] This new band increases in intensity with irradiation time and reaches a plateau after 50 min. When the system is monitored spectroscopically at pH 12, at which the rate of H_2 generation is greatly decreased, two overlapping bands at ca. 550 and 650 nm are seen after 5 h in addition to the one at 440 nm (see Figure 2b). The two lower energy bands are nearly identical to ones previously reported in the reduction of **2**[12] and are assigned to Co(I).

It is noteworthy that a system composed of chromophore **3**, Co complex **2**, and TEOA in MeCN/H_2O at pH 8.5 does not produce H_2 upon irradiation in contrast with what is found for the corresponding system with **1**, but the former system does generate the blue color characteristic of Co(I). Relevant to this observation are the Co(II)/Co(I) potentials for **1** and **2** which in MeCN are −0.88 and −0.30 V adjusted to NHE, respectively (see Supporting Information). Another important observation in analyzing and understanding the system we are describing here is the fact that substitution of Pt chromophore **3** by Ru(bpy)$_3{}^{2+}$ does *not* lead to H_2 generation, most likely because the excited state has an insufficient driving force (Ru(bpy)$_3{}^{3+}$/Ru(bpy)$_3{}^{*2+}$ = −0.86 V vs NHE) to reduce Co(II) which forms from **1**.

Based on all of the results described above, a mechanism for the photogeneration of H_2 can be put forth as in Scheme 1. The first three steps are photochemical and suggest both oxidative quenching of **3*** by **1** and reductive quenching of **3*** by TEOA, consistent with their measured k_q values. The decomposition of TEOA$^+$ proceeds via a well-known sequence to glycolaldehyde + di(ethanol)amine with transfer of a second reducing electron and

Scheme 1
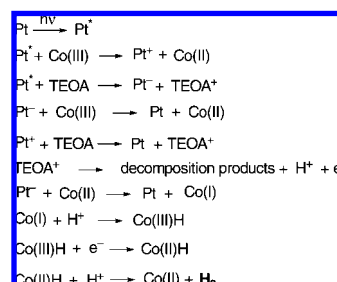
is pH sensitive.[2,4] Oxidation of TEOA may also be initiated by thermal electron transfer of the amine with oxidized chromophore **3**$^+$. Initial reduction of **1** commences with the conversion of Co(III) to Co(II) followed by further electron transfer to Co(I) for proton reduction.[10] The basicity of Co(I) to form Co(III) hydride correlates with the Co(II)/Co(I) reduction potential, explaining why **1** is effective at pH 8.5 whereas **2** is not. Subsequent reduction of the Co(III) hydride species followed by protonation leads to H_2 evolution and regeneration of Co(II) which is the dominant Co species in the system during photolysis. An alternative H_2-forming sequence involves a bimolecular reaction of two Co(III) hydrides to yield H_2 + 2 Co(II).[12,18] Further studies are needed to establish which path is operative in the present system.

In conclusion, a homogeneous system containing the Pt(II) terpyridyl acetylide chromophore, a Co(III) bis(dimethylglyoximate) complex, and a sacrificial electron donor have been developed to generate H_2 from water photochemically. Further studies are in progress to optimize the reaction conditions for efficient hydrogen production by variation of the electronic properties of Co(III) catalyst.

Supporting Information Available: Experimental details for hydrogen production, quenching study. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA804650G