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JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

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A Cobalt−Dithiolene Complex for the Photocatalytic and Electrocatalytic Reduction of Protons

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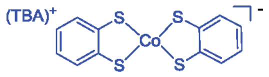
S *Supporting Information*

ABSTRACT: The complex $[Co(bdt)_2]^-$ (where bdt = 1,2-benzenedithiolate) is an active catalyst for the visible light driven reduction of protons from water when employed with $Ru(bpy)_3^{2+}$ as the photosensitizer and ascorbic acid as the sacrificial electron donor. At pH 4.0, the system exhibits very high activity, achieving >2700 turnovers *with respect to catalyst* and an initial turnover rate of 880 mol H_2/mol catalyst/h. The same complex is also an active electrocatalyst for proton reduction in 1:1 CH_3CN/H_2O in the presence of weak acids, with the onset of a catalytic wave at the reversible redox couple of −1.01 V vs Fc^+/Fc. The cobalt−dithiolene complex $[Co(bdt)_2]^-$ thus represents a highly active catalyst for both the electrocatalytic and photocatalytic reduction of protons in aqueous solutions.

Conversion of solar energy into stored chemical potential via artificial photosynthesis (AP) represents a promising approach to providing carbon-free energy needed for sustainable development.[1−4] In general, systems for AP are designed to split water photochemically into its constituent elements, water oxidation to O_2 and aqueous proton reduction to H_2. Despite extensive study of the components and dynamics of these systems, an active and robust system for using the energy from sunlight to drive molecular hydrogen production in water remains a continuing challenge in AP.[5] One facet of this challenge is the development of new active catalysts composed of abundant, inexpensive metals.

During the past decade, efforts toward new catalyst development have focused on electrocatalysts for proton reduction.[6−16] In this regard, some cobaloxime catalysts derived from dimethylglyoxime operate at particularly low overpotentials,[9,17,18] while the related $Co(dmgH)_2(pyr)Cl$ catalysts function in photochemical as well as electrochemical systems.[6,10,19] In recently reported photochemical H_2 generation, cobaloxime catalysts $Co(dmgH)_2(4\text{-pyr-R})Cl$ have shown good activity[20−24] with turnover numbers (TONs) as high as 9000 with respect to chromophore.[24−26] The TONs, however, are modest based on catalyst (<300, with TOF (turnover frequency) < 100/h). Here we report that $(Bu_4N)[Co(bdt)_2]$ (**1**, where bdt = 1,2-benzenedithiolate) exhibits striking activity (>2700 TONs with respect to catalyst and an initial turnover frequency of >800/h) when paired with $Ru(bpy)_3^{2+}$ as the chromophore and ascorbic acid as the sacrificial electron donor in aqueous mixtures under moderately acidic conditions. $Co(bdt)_2^-$ has also been found to be active for electrocatalytic proton reduction upon the addition of either toluenesulfonic acid or trifluoroacetic acid in aqueous acetonitrile solutions (1:1 CH_3CN/H_2O).



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Dithiolene complexes have been an active subject of study since the 1960s, and are found in biological cofactors[27] as well as interesting synthetically useful systems.[28−31] They are well-known to undergo reversible electron transfers, and their ligands are more resistant to hydrogenation than other common ligands, including the diglyoximates used in previous cobalt-based proton reduction systems. The reversible redox behavior makes these systems of potential interest for multielectron chemistry in H_2 reduction.[32]

To this end, the cobalt catalyst **1** was found to generate H_2 in a system with $Ru(bpy)_3^{2+}$ as the chromophore and ascorbic acid as the sacrificial donor upon irradiation with visible light. In these studies, hydrogen evolution was observed after irradiation with 520 nm LEDs (0.15 W, 0.1 M ascorbic acid in 1:1 CH_3CN/H_2O) at 15 °C. The production of hydrogen was monitored in real time by the pressure change in the reaction vessel and confirmed by GC analysis with a TCD detector. The optimal pH for this system is 4.0,[34] with a decrease in activity at both lower and higher pH values (Figure S11, Supporting Information). Initially, the catalyst is very active, evolving 0.53 mL H_2/h using 4.8×10^{-6} M **1** (Figure 1), corresponding to a TOF of 880 h^{-1} with respect to catalyst.

On a TOF basis, the catalyst is most active at low concentrations, and hydrogen evolution is observed using [**1**] as low as 8.0×10^{-7} M. Figure 1 shows the effect of varying catalyst concentration on the rate and overall yield of hydrogen evolution. Increasing the catalyst concentration increases the overall rate of hydrogen evolution and the total amount of hydrogen evolved for the system. The initial rates for hydrogen evolution are obtained from the linear portion of each curve during the first hour of illumination and indicate a first order dependence on catalyst concentration for this system (Figure 1). However, at higher catalyst concentrations (>0.1 mM), while more hydrogen is evolved, the rate of H_2 production does not increase linearly with catalyst concentration. When the catalyst concentration is fixed at 4.8×10^{-6} M and the chromophore concentration is varied (Figure 2), system activity increases with increasing concentrations of chromophore. The initial rate of hydrogen

Received: August 19, 2011
Published: August 24, 2011

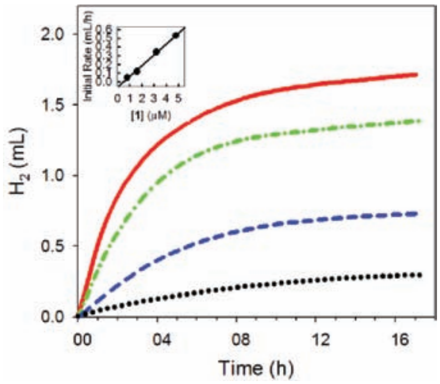

Figure 1. Hydrogen evolved with 5×10^{-4} M [$Ru(bpy)_3{}^{2+}$] and 0.1 M ascorbic acid in 1:1 CH_3CN/:H_2O at pH 4.0 with [**1**] = 4.8×10^{-6} M (red), 3.2×10^{-6} M (green), 1.6×10^{-6} M (blue), and 8.0×10^{-7} M (black). (Inset) Initial rate of H_2 evolution vs [**1**].

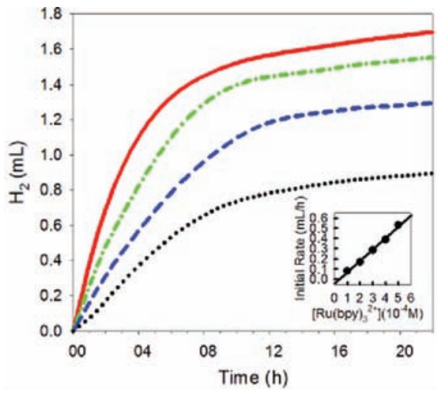

Figure 2. Hydrogen evolved with [**1**] = 4.8×10^{-6} M and [ascorbic acid] = 0.1 M at pH 4.0 in 1:1 CH_3CN/H_2O when [$Ru(bpy)_3$]$^{2+}$ was 4.0×10^{-4} M (red), 3.0×10^{-4} M (green), 2.0×10^{-4} M (blue), and 1.0×10^{-4} M (black). (Inset) Initial rate of H_2 evolution vs [$Ru(bpy)_3{}^{2+}$].

production has a first-order dependence on the chromophore concentration (Figure 2). The same trend is also observed when the catalyst is present in higher concentrations (1.0×10^{-5} M). The relatively high chromophore concentrations and the first-order dependence on [$Ru(bpy)_3$]$^{2+}$ suggest that the activity is limited by the concentration of chromophore.

Figures 1 and 2 show that after 8 h of irradiation, the rate of hydrogen evolution decreases dramatically, indicating decomposition of at least one system component. For comparison, cobaloxime catalysts decompose after only 3 h of irradiation.[24] To probe the mechanism of decomposition, a mixture of $Co(bdt)_2{}^-$, $Ru(bpy)_3{}^{2+}$, and ascorbic acid in 1:1 CH_3CN/H_2O at pH 4.0 was monitored using UV−vis spectroscopy after irradiation with visible light (Figure S14, Supporting Information). After 12 h of illumination, the absorbances attributed to both the catalyst and chromophore decreased dramatically. This suggests that decomposition of both catalyst and chromophore occur as hydrogen evolution slows after 8 h.

In contrast to cobaloxime systems where the addition of free dimethylglyoxime (dmgH) ligand somewhat increases the longevity of the system,[21] the addition of excess bdt ligand significantly decreases the overall activity (Figure S12, Supporting Information). When a mixture of $Co(bdt)_2{}^-$, $Ru(bpy)_3{}^{2+}$, and 5 equivalents of 1,2-benzenedithiol in a 0.1 M solution of ascorbic acid is irradiated with visible light (>410 nm), the formation of a broad absorbance band at 390 nm occurs in the UV−vis spectra that is not characteristic of the original catalyst or chromophore (Figure S15, Supporting Information). In the absence of excess ligand, this absorbance is not observed. This result, in addition to the lower hydrogen-evolving activity observed when additional equivalents of ligand are present, suggests that excess bdt promotes the formation of an inactive complex by coordination, rather than serving to replenish decomposed ligand as in the case of $Co(dmgH)_2$(4-pyr-R)Cl.[21]

While ascorbic acid (AA) is used as a sacrificial electron donor in the H_2 generating system reported here, the overall net conversion of ascorbic acid to H_2 + dehydroascorbic acid is in fact thermodynamically uphill (ΔG = 79.1 kJ, $\Delta E = -0.41$ V[35]), and therefore energy storing. However the most important use of a sacrificial electron donor in these systems is to permit investigation of component effectiveness and reaction mechanism in the reductive half of water splitting. Previously reported systems using $Ru(bpy)_3{}^{2+}$ and ascorbic acid are known to proceed through a reductive quenching pathway, with photoexcitation of the chromophore to give $^*Ru(bpy)_3{}^{2+}$ followed by reductive quenching by ascorbic acid to produce $Ru(bpy)_3{}^+$ which then reduces the catalyst.[36,37] Consistent with these previous reports, we find that in 1:1 CH_3CN:H_2O at pH 4.0, ascorbic acid quenches $^*Ru(bpy)_3{}^{2+}$ following Stern−Volmer behavior (Figure S16, Supporting Information) with $k_q = 1.3 \times 10^8$ $M^{-1}s^{-1}$. The $Co(bdt)_2{}^-$ catalyst is also found to quench $^*Ru(bpy)_3{}^{2+}$ following Stern−Volmer behavior with a significantly greater rate constant of $k_q = 3.9 \times 10^{10}$ near the diffusion-controlled limit (Figure S17, Supporting Information).

While the catalyst quenches the chromophore with a rate constant that is 2 orders of magnitude larger than that for ascorbic acid, reductive quenching by ascorbic acid dominates in our system because of the much larger concentration of AA (0.1 M) relative to that of $Co(bdt)_2{}^-$ (5×10^{-6} M). Therefore, the initial photochemical steps are the formation of $Ru(bpy)_3{}^+$ from AA, followed by protonation which, depending on the electronic structure of $Co(bdt)_2{}^{2-}$ may occur at Co or the bdt ligand.

It was of also of interest to explore the electron requirements for the catalyst by performing the reaction electrocatalytically. Most of the well studied electrocatalysts operate in nonaqueous media, whereas efforts on the reductive side of water splitting would ideally incorporate proton reduction electrocatalysts that operate in largely aqueous environments.[38,39] Since $Co(bdt)_2{}^-$ displays a reversible redox couple (1.01 V vs Fc^+/Fc) that is less negative relative to $Co(dmgH)_2$(pyr)Cl and has proven to be active for photocatalytic H^+ reduction in 1:1 CH_3CN:H_2O, it was of interest to see if **1** also functions as an active electrocatalyst in aqueous media. A related bis(dithiolene) complex was reported in 2010 by Sarkar and coworkers to act as an electrocatalyst for H_2 generation when deposited on a glassy carbon electrode, but we were unable to reproduce that work.[33]

Figure 3 shows the cyclic voltammograms (CVs) of **1** in a 1:1 CH_3CN/H_2O solution containing 0.1 M KNO_3. In the absence of acid, a reversible redox couple is observed at −1.01 V vs Fc^+/Fc, that is attributed to the $Co(bdt)_2{}^-/Co(bdt)_2{}^{2-}$ couple. The addition of trifluoroacetic acid (TFA) triggers the appearance of a catalytic wave that grows from the reversible redox couple. Controlled potential coulometry experiments at −1.01 V

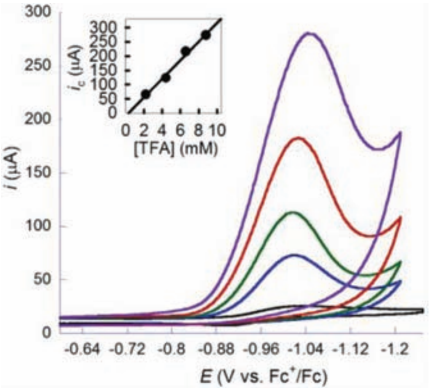

Figure 3. Cyclic voltammograms of 0.5 mM **1** in a 0.1 M solution of KNO_3 in 1:1 CH_3CN/H_2O (black) upon addition of 2.2 mM TFA (blue), 4.4 mM TFA (green), 6.6 mM TFA (red), and 8.8 mM TFA (purple). Scan Rate: 100 mV/s with a glassy carbon working electrode. (Inset) i_c vs [TFA].

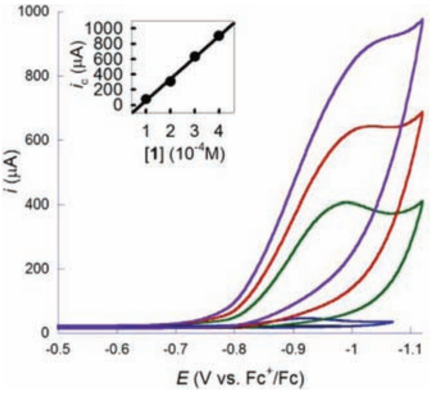

Figure 4. Cyclic Voltammograms of 65 mM tosic acid in 0.1 M KNO_3 in 1:1 CH_3CN/H_2O with concentrations of **1** of 0.1 mM (blue), 0.2 mM (green), 0.3 mM (red), and 0.4 mM (purple). Scan rate: 100 mV/s with a glassy carbon working electrode.

vs Fc$^+$/Fc confirm that the observed current enhancements correspond to the formation of hydrogen, exhibiting a faradaic yield of >99% when the potential is held at −1.0 V vs SCE (see Supporting Information). The linear correlation between i_c/i_p and [TFA] (Figure S3−S7, Supporting Information) indicates a second order process with respect to TFA.[40] The trend is consistent at different scan rates, as well as when using toluenesulfonic acid as the proton source (see Supporting Information). Smaller current enhancements are observed in dry organic solvents (CH_3CN, or dimethylformamide). This may explain why the efficiency of the photocatalytic system decreases substantially in solvent ratios containing more CH_3CN than water.

To probe this system further, aliquots of catalyst were added to an excess (65 mM) of toluenesulfonic acid in 1:1 CH_3CN/H_2O (Figure 4) and examined by CV. The onset of a catalytic wave occurs at catalyst concentrations as low as 0.1 mM. The cathodic peak current has a linear dependence on catalyst concentration (Figure S8−S9, Supporting Information). This suggests that the rate is first order with respect to catalyst concentration.[38,40] This is consistent with the trend observed for the photocatalytic system.

The electrochemical data give insight into the mechanism. As demonstrated by the catalytic wave at the potential of the $Co(bdt)_2^-/Co(bdt)_2^{2-}$ couple, reduction to the dianion occurs which is likely followed by protonation. While the metal oxidation state of the dianion can be assigned formally as Co(II), the noninnocent nature of the dithiolene ligand raises the possibility that protonation can take place at *either* the metal or sulfur.[41,42] This differs from the cobalt glyoxime systems that are thought to proceed through the protonation of a Co(I) center to give a Co(III)H intermediate.

In summary, we report a cobalt−dithiolene complex (**1**) that is active for the photocatalytic reduction of protons when paired with $Ru(bpy)_3^{2+}$ as photosensitizer and ascorbic acid as the sacrificial donor. The catalyst achieves unprecedented activity, achieving >2700 TONs with respect to [**1**] (with an initial TOF of 880 mol H_2/mol **1**/h) after 12 h of illumination. Additionally, the complex functions as an active electrocatalyst for proton reduction in solvent media that contain 50% water. Thus, cobalt−dithiolene complexes are a promising new direction for catalysts that achieve both the photocatalytic and electrocatalytic generation of H_2.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Detailed experimental procedures, X-ray crystallographic data (including CIF), synthetic procedures, additional photochemical and electrochemical data. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

W.M. thanks Matthew McLaughlin, Theresa McCormick, and Min-Sik Eum for helpful discussions. We acknowledge the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, U.S. Department of Energy, Grant DE-FG02-09ER16121 for funding.

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