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Hydrogen Production

A Nickel Thiolate Catalyst for the Long-Lived Photocatalytic Production of Hydrogen in a Noble-Metal-Free System**

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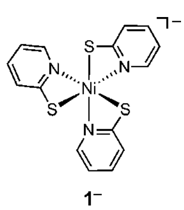
The splitting of water through artificial photosynthesis (AP) is a key transformation toward the conversion of solar energy into stored chemical potential in the form of fuel and oxidizer.[1] For water splitting, the reductive side of the reaction involves the light-driven conversion of aqueous protons into H_2. To perform this half-reaction, photocatalytic systems typically consist of a catalyst, photosensitizer (PS), and sacrificial electron donor.[2] Recent studies on noble-metal-based[3] and noble-metal-free[4] homogeneous systems for light-driven hydrogen production have shown high activity. However, significant problems in the noble-metal-free molecularly based systems include relatively low catalyst turnover numbers (TON < 500 mole H_2/mole catalyst) for hydrogen formation, and photodecomposition of the systems within a few hours. For most organic dye based systems that have recently been reported, the photochemical quenching step of the excited-state dye (PS*) is reductive, thus leading to unstable PS^- radical anions that undergo decomposition.[4b] Thus, the development of more active catalysts, specifically ones that quench PS* oxidatively, would be of great value for obtaining long-lived homogeneous AP systems. Herein, we describe a new homogenous catalyst for H_2 production that has both high activity and the ability to oxidatively quench PS*, thus leading to a much longer system lifetime.

Nickel cathodes are used in commercial electrolyzers, suggesting that nickel may be a worthwhile basis for homogeneous catalysts as well.[5] Nickel thiolate complexes have received special attention in recent years because sulfur-ligated nickel complexes mimic the [Fe-Ni]-hydrogenase active site,[6] and dimeric metal complexes based on nickel thiolate hydrides have been shown to be catalytically active for proton reduction.[7] DuBois and co-workers have also shown that mononuclear nickel(II) bis(diphosphine) complexes are effective catalysts for electrochemical hydrogen generation.[8] While photocatalytic hydrogen generation from the nickel-phosphine complexes is long-lived, the activity of the photocatalytic system with the nickel phosphine catalyst is low, with a turnover frequency (TOF) of approximately 20 equivalents of H_2 per hour.[9] Related nickel(II) complexes containing pyridine-2-thiolate ligands have been known for over two decades,[10] but their catalytic properties for proton reduction have not been reported. In the present study, the complex $[Ni(pyS)_3]^-$ ($\mathbf{1}^-$; pyS = pyridine-2-thiolate) is found to have impressive catalytic activity for the photocatalytic production of H_2 in a homogeneous system with fluorescein (Fl) as the PS and triethylamine (TEA) as the sacrificial electron donor.



$\mathbf{1}^-$

Photolysis of a solution of Fl and $\mathbf{1}^-$ in $EtOH/H_2O$ (1:1) using a green-light-emitting diode (LED) ($\lambda = 520$ nm, 0.12 W) at 15 °C results in H_2 generation which was monitored in real time by the pressure change in the reaction vessel, and quantified at the end of the photolysis by GC analysis of the headspace gases. Control experiments show that the absence of any of the three components leads to no significant H_2 production. The activity for H_2 generation was the same when approximately 1 mL of Hg was added to the vessel, thus suggesting that metal colloids are not responsible for the H_2 production.

The rate of H_2 production is highest at pH 12.0–12.4 (Figure 1). The decrease in rate at higher pH values is likely due to the lower proton concentration in solution and the fact that H_2 generation becomes more thermodynamically unfavorable with increasing pH values. In contrast, lowering the pH value from 12.0 to 9.0 leads to both a lower initial rate of H_2 production and shorter system longevity. Independent UV/vis studies show that Fl decomposes much more slowly under photolysis at pH 12.2 than at pH 10.0 (see Figure S1 in

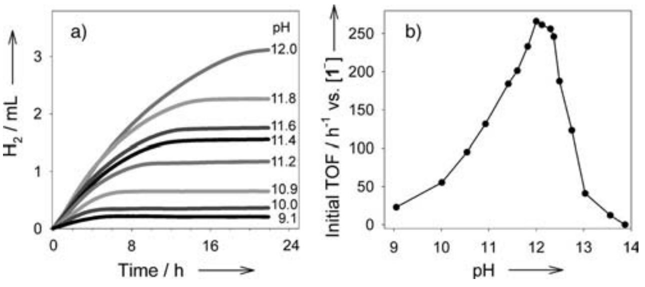


Figure 1. a) Hydrogen production from systems containing $\mathbf{1}^-$ (1.0×10^{-5} M), Fl (1.0 mM), and TEA (5% v/v) in $EtOH/H_2O$ (1:1; 5.0 mL). The system was irradiated using $\lambda = 520$ nm LED at different pH values. b) Effect of the pH value on the initial rate of hydrogen production. The turnover frequencies are given as a ratio of moles of H_2 per moles of $\mathbf{1}^-$.

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the Supporting Information), which is in agreement with the literature.[11] Previous reports of AP systems using triethylamine as the sacrificial electron donor have suggested that TEA performs as a better electron donor at higher pH.[3d,4c] At lower pH, protonation of TEA diminishes its ability to function as an electron donor, and TEA^+ decomposition (which begins with deprotonation)[2b,12] becomes less facile.

In the system with Fl and TEA at fixed concentrations, the initial rate of H_2 generation has a first-order dependence on $[\mathbf{1}^-]$ (Figure 2). At 4.0 μM $[\mathbf{1}^-]$ this system exhibits unprecedented activity for a noble-metal-free system, achieving a turnover number of 5500 moles H_2 per mole of catalyst after 40 hours and an initial TOF of 250 moles of H_2 per mole catalyst per hour. At higher catalyst concentrations, even though a larger amount of H_2 is evolved, the TON does not scale linearly with catalyst concentration because of the limited lifetime of the system (see Figure S2 in the Supporting Information).

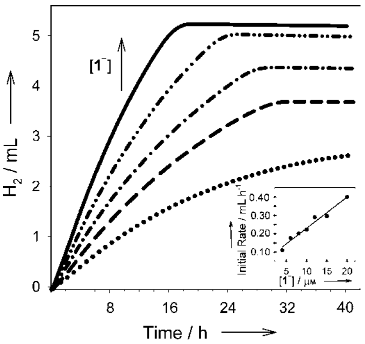


Figure 2. Hydrogen production from systems containing Fl (2.0 mM) and TEA (5% v/v) in $EtOH/H_2O$ (1:1; 5.0 mL) at pH 12.2 upon irradiation with $\lambda = 520$ nm LED when $[\mathbf{1}^-]$ was 4.0×10^{-6} M, 8.0×10^{-6} M, 1.0×10^{-5} M, 1.2×10^{-5} M, or 2.0×10^{-5} M. Inset: the initial rate of hydrogen production.

When [Fl] is varied, the TOF reaches a maximum at 1.0 mM [Fl], which indicates that at this value of [Fl] the system becomes limited by the concentration of the catalyst $[\mathbf{1}^-]$ (Figure 3). However, the system has a longer lifetime at higher [Fl], thus suggesting that Fl decomposes during photolysis. This hypothesis is supported by UV/vis studies that show the disappearance of the characteristic Fl absorption during the course of H_2 evolution (see Figure S3 in the Supporting Information). In these studies, the rate for H_2 production stays roughly constant until [Fl] becomes lower than 1 mM and decreases drastically when [Fl] is below 0.2 mM. This phenomenon leads to the abrupt cessation of H_2 production visible in Figure 2 and Figure 3.

In the literature, related homogenous AP systems[4a] show good activity for H_2 generation, albeit with short system lifetimes, using halogenated derivatives of Fl such as Eosin Y as the PS, but no activity when using Fl in that role. The explanation for this is that the halogenated dyes generate predominantly the long-lived $^3\pi\pi^*$ state that is needed to make bimolecular quenching competitive with radiative and nonradiative decay pathways for PS*. However, in the present study, we find that Fl is about twice as active as Eosin Y in terms of the rate and the amount of H_2 produced (see Figure S4 in the Supporting Information). Additionally, sulfur- and selenium-derivatized rhodamine photosensitizers, which are active in systems with a $[CoCl(pyr)(dmgH)_2]$ catalyst for H_2 generation,[4b] are not active with $\mathbf{1}^-$. In fact, rapid bleaching of these rhodamine photosensitizers is seen in systems containing TEA (at similar rates with or without $\mathbf{1}^-$) under irradiation with 520 nm light, thus indicating that while reductive quenching to form PS^- does occur, PS^- is not able to reduce $\mathbf{1}^-$ for possible hydrogen formation. Rapid decomposition of these chalcogenated rhodamine analogues upon reduction to form PS^- has been reported previously.[4a,b]

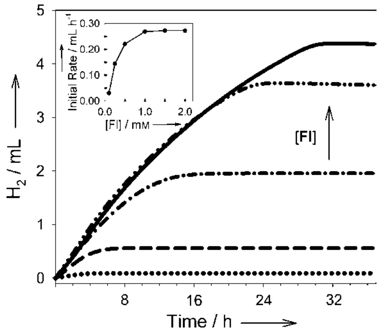


Figure 3. Hydrogen production from systems containing $\mathbf{1}^-$ (8.0×10^{-6} M) and TEA (5% v/v) in $EtOH/H_2O$ (1:1; 5.0 mL) at pH 12.2 upon irradiation with $\lambda = 520$ nm LED when [Fl] was 1.0×10^{-4} M, 2.5×10^{-4} M, 5.0×10^{-4} M, 1.0×10^{-3} M, or 2.0×10^{-3} M. Inset: the initial rate of hydrogen production.

To examine the decomposition of the Fl/$\mathbf{1}^-$/TEA system in more detail, UV/vis absorption spectra were measured during photolysis. In the presence of only sacrificial donor, Fl bleaches very rapidly under 520 nm light (Figure 4b) as a result of the instability of Fl^- formed upon reductive quenching, but Fl decomposition becomes much slower in the presence of $\mathbf{1}^-$ (Figure 4a). Some decomposition of $\mathbf{1}^-$ is also seen in this experiment, but at a slower rate than that for Fl. A control experiment shows that $\mathbf{1}^-$ is stable with TEA in $EtOH/H_2O$ (1:1) under irradiation ($\lambda > 450$ nm) over three days. Thus the decomposition of $\mathbf{1}^-$ is coupled to the

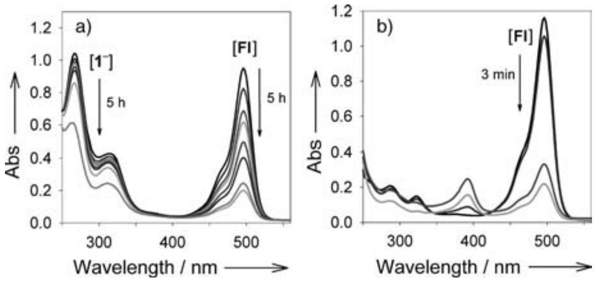
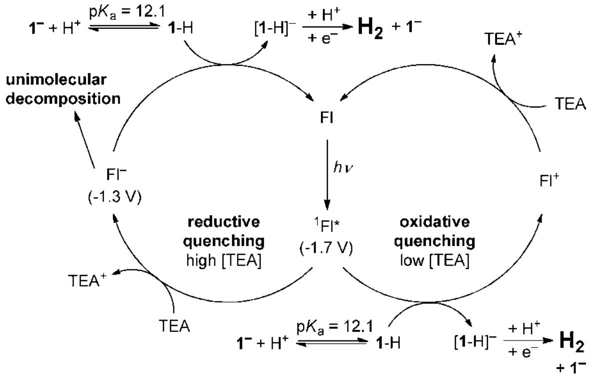


Figure 4. Absorption spectra of systems containing Fl (1.0×10^{-5} M) and TEA (5% v/v) in $EtOH/H_2O$ (1:1) at pH 12.2 upon irradiation ($\lambda > 450$ nm), with $\mathbf{1}^-$ (2.0×10^{-5} M) (a) and without $\mathbf{1}^-$ (b).

decomposition of Fl under reductive quenching conditions using TEA. To restart the system after cessation of H_2 generation, both **1**$^-$ and Fl must be added. Similar behavior was observed for a system in which Eosin Y was used as the PS (see Figure S5 in the Supporting Information).

At TEA concentrations below 0.36 M the Fl systems have lower activity (see Figure S6 in the Supporting Information), but system lifetime is prolonged significantly (Figure S7). Previous studies on organic-dye-containing homogeneous AP systems have shown that hydrogen formation proceeds through electron transfer from PS$^-$ formed by reductive quenching in the photochemical step,[4] but this step competes with decomposition of PS$^-$ by a unimolecular pathway (Scheme 1). When active catalyst is present, electron transfer from PS$^-$ can compete favorably with its unimolecular decomposition, and if not, PS$^-$ decomposes. A control experiment consisting of the photolysis of Fl and TEA with 520 nm irradiation and no **1**$^-$ gives complete bleaching of Fl within 3 hours. So, the presence of **1**$^-$ stabilizes the system by reducing the lifetime of unstable PS$^-$ in solution.



Scheme 1. Reaction scheme for H_2 photogeneration; **1**-H is the protonated form of **1**$^-$. The reduction potentials for ^{1}Fl* and Fl$^-$ are given versus SCE, and drawn from Ref. [4a].

To explore this hypothesis further, photochemically driven electron-transfer steps were studied individually through ^{1}Fl* quenching in CH_3CN/H_2O mixtures (for higher solubility of **1**$^-$ than in $EtOH/H_2O$ mixtures) that were also effective solvent environments for H_2 production. In 1:1 or 9:1 CH_3CN/H_2O solvent mixture at pH 12.2, the fluorescence of Fl (excited at 460 nm) is quenched by TEA following linear Stern–Volmer behavior with a rate constant of $k_q = 5.5 \times 10^7\,M^{-1}s^{-1}$ (see Figures S8–9 in the Supporting Information). Interestingly, catalyst **1**$^-$ also quenches the fluorescence of Fl with a rate constant k_q that is more than two orders of magnitude faster than that for TEA. The rate constant of $9.6 \times 10^9\,M^{-1}s^{-1}$ is at the diffusion-controlled limit (Figure S10). Similar emission quenching rate constants are obtained with Eosin Y using **1**$^-$ and TEA as respective oxidative and reductive quencher (Figure S12–13).

Even though k_q for oxidative quenching is 175 times larger than k_q for reductive quenching, the reductive quenching of ^{1}Fl* dominates because of the much higher concentration of TEA (0.36 M) relative to **1**$^-$ (ca. 10^{-5} M). When the initial concentration of TEA is lowered to 7.0 mM, oxidative quenching by **1**$^-$ becomes more competitive (Scheme 1), thus reducing the amount of unstable PS$^-$ generated and increasing the system lifetime greatly. Thus, we find that the system longevity in this system is substantially increased with a lower concentration of TEA, and H_2 production slows only when TEA is consumed. The addition of additional TEA causes H_2 generation to resume with a similar rate. The process can be repeated to give a system lifetime that is prolonged to more than 60 hours, as shown in Figure 5. UV/vis spectra taken during the longer photolysis (Figure 5, insert) show negligible decomposition of Fl in the first 24 hours and only 25 % of the Fl decomposed in 60 hours. The long-lived activity is a substantial improvement over previous noble-metal-free systems, which lose all activity within 12 hours.

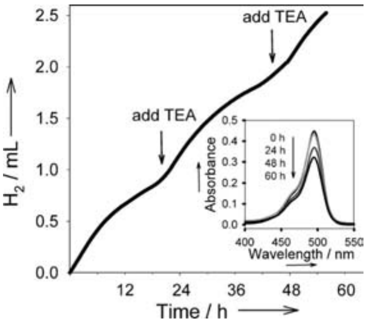
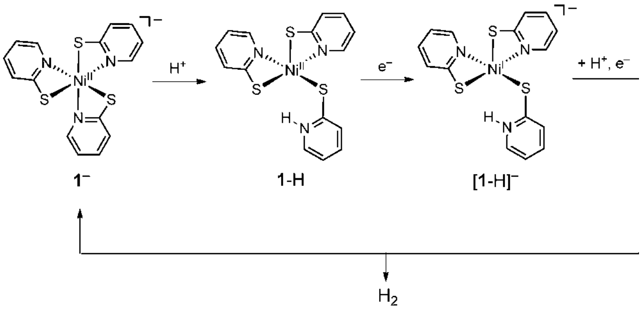


Figure 5. Hydrogen production from systems containing **1**$^-$ (4.0×10^{-5} M), Fl (5.0×10^{-4} M), TEA (7 mM) in $EtOH/H_2O$ (1:1) (5.0 mL) at pH 12.2 upon irradiation with 520 nm LED. 0.1 % v/v of TEA was added at the indicated times, when all TEA was consumed during the experiment. Inset: UV/vis absorption spectra of aliquots taken during the course of the photolysis after dilution by a factor of 100.

Electrochemical studies were used for insight into the catalytic mechanism. Interestingly, cyclic voltammograms (CVs) of **1**$^-$ in dry *N,N'*-dimethylformamide (DMF) containing 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) showed no reduction wave from −0.4 to −2 V vs. SCE in the absence of available protons, thus indicating that **1**$^-$ itself cannot accept an electron from ^{1}Fl* (−1.7 V) or Fl$^-$ (−1.3 V). Thus, we conclude that a protonated form of **1**$^-$ (which we term **1**-H) is the electron acceptor. Indeed, the UV/vis spectrum of **1**$^-$ undergoes a significant pH-dependent change in $EtOH/H_2O$ (1:1), from two strong absorption bands at $\lambda = 313$ and 268 nm (at pH > 13) to bands at $\lambda = 350$ and 275 nm at pH < 10 (see Figure S14 in the Supporting Information). A standard titration curve gave a pK_a value of 12.1 for **1**-H (Figure S15), which suggests that much of the catalyst is in its protonated form during our photolysis studies. Protonated **1**-H is expected to be a competent oxidant of ^{1}Fl*, based on a new cathodic feature at −1.4 V vs. SCE that appears when 1 equivalent of trifluoroacetic acid (TFA) is added to a solution of **1**$^-$ in DMF (Figure S16). Higher concentrations of TFA give an electrocatalytic wave that grows from this reduction feature (Figure S17). These data suggest that the protonated form of $\mathbf{1}^-$ is the active catalyst for proton reduction. Though further studies are needed to describe the mechanism in full detail, our combined studies are consistent with the proposal in Scheme 1. Computational studies suggest that **1**-H is most likely protonated at a pyridine nitrogen atom, accompanied by dechelation.[13] Reduction of such an intermediate could give an electron-rich nickel(I) intermediate [**1**-H]$^-$ (Scheme 2) as an intermediate toward H_2 formation. Protonation of a pendant nitrogen base would be reminiscent of the accepted mechanism for iron-only hydrogenase[14] and nickel bis(diphosphine) catalysts for H_2 production.[8]



Scheme 2. Possible structures of nickel species involved in H_2 formation.

In conclusion, we report a biomimetic pyridine thiolate nickel complex that is a robust molecular catalyst for hydrogen production from aqueous solvent mixture in a noble-metal-free system. The catalyst achieves the highest activity for a homogeneous AP system, with over 5500 turnovers (relative to $\mathbf{1}^-$) after 40 hours of illumination and a TOF of greater than 250 moles H_2 per mole $\mathbf{1}^-$ per hour. An oxidative quenching pathway in the photochemically driven step is important in obtaining a stable AP system for hydrogen production, and the mechanism may use the pyridine as a hemilabile ligand that is protonated on the way to H−H bond formation.

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