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A stable molecular nickel catalyst for the homogeneous photogeneration of hydrogen in aqueous solution†

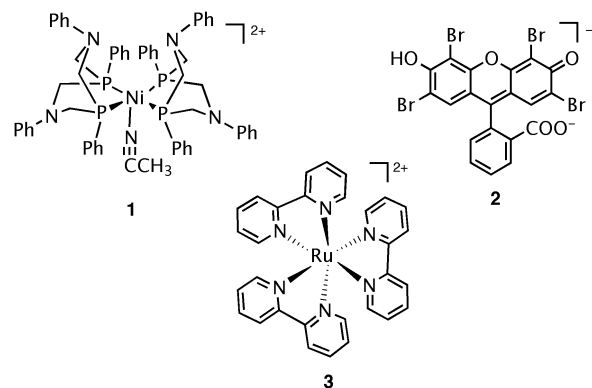Matthew P. McLaughlin, Theresa M. McCormick, Richard Eisenberg* and Patrick L. Holland*

Light-driven H_2 production is catalyzed by $[Ni(P_2^{Ph}N_2^{Ph})_2](BF_4)_2$ when irradiated with visible light in water/acetonitrile mixed solvent in the presence of a photosensitizer (PS) and ascorbate. The catalyst gives over 2700 turnovers over 150 h, and does not degrade despite photodecomposition of the PS.

Hydrogen gas (H_2) is currently produced from natural gas, and thus is not yet the clean fuel that is often envisioned. If water reduction using solar energy were used on a large scale to generate H_2, however, then H_2 could become the environmentally-friendly fuel of the future. For this reason, systems for photocatalytic H_2 production from aqueous solutions have attracted considerable attention in recent years.[1–3] Photocatalytic H_2 production systems at a minimum require an electron donor, a photosensitizer (PS), and a proton reducing catalyst.[1] Although there are a number of systems for photocatalytic H_2 production under visible light, most contain rare and expensive metal components, the most common being colloidal Pt as the catalyst.[1] Recently, chemists have developed systems based on earth-abundant elements but catalyst instabilities remain a major problem.[4–16] As part of our efforts to construct and examine systems containing earth-abundant components, we describe herein a homogenous system for photocatalytic H_2 production that uses a nickel molecular catalyst in combination with a PS and the sacrificial electron donor ascorbate. The catalyst is stable to decomposition over the system lifetime, and yields the highest number of catalyst turnovers yet obtained in photocatalytic systems with an earth abundant catalyst.

DuBois and coworkers described the nickel(II) complex $[Ni(P_2^{Ph}N_2^{Ph})_2](BF_4)_2$ (**1**, Scheme 1), which functions as an efficient and stable electrocatalyst for the production of H_2 from acidic nonaqueous solutions with low overpotentials (TOF > 350 s^{-1}, 0.30 V).[17–19] In the present study, complex **1** is employed in conjunction with eosin Y (**2**, Scheme 1), an organic dye that has been shown to act as a PS in a light-driven system for the generation of H_2 from water.[13] The system

functions in 1:1 H_2O:CH_3CN with a pH range of 1–5 and maximum activity at pH 2.25 (see Table S9 in ESI for [H^+] calculation in mixed solvents†).[20] Eosin Y is only moderately stable under photocatalytic conditions when using light with $\lambda > 410$ nm, and decomposes between 8 and 48 h depending on the catalyst concentration and irradiation power. The catalyst may also be paired with $[Ru(bpy)_3]Cl_2$ (**3**) as the PS, to evaluate the long-term stability of **1** as the catalyst. The system is inactive in the absence of any of the three components (catalyst, PS, or sacrificial donor).

The initial rate of H_2 production is invariant (maximum TOF by catalyst = 20 h^{-1}, Fig. 1) using various concentrations of either **2** or **3** as the PS. However, the rate decreases after longer irradiation times (>1 h) indicating the degradation of at least one system component. Following total bleaching of the PS, the system's activity is *completely* restored by the addition of either **2** or **3** as the PS. The reconstitution of the system activity in this way indicates that the catalyst component is stable during irradiation, and that the system's photoinstability is due to PS decomposition. The stability of the catalyst is evident from $^{31}P\{^1H\}$ and ^1H NMR data; after photodegradation in a reaction mixture with deuterated solvents, the peaks in the NMR spectra associated with the catalyst are identical to those in the starting material. Through the addition of ascorbic acid and **3** during the course of photolysis, it is possible to obtain 2700 turnovers relative to catalyst (Fig. 2). To our knowledge, this is the highest TON (based on catalyst) yet reported for a

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Scheme 1 Complexes in the photocatalytic system: (**1**) $[Ni(P_2^{Ph}N_2^{Ph})_2]^{2+}$, (**2**) Eosin Y, (**3**) $[Ru(bpy)_3]^{2+}$.
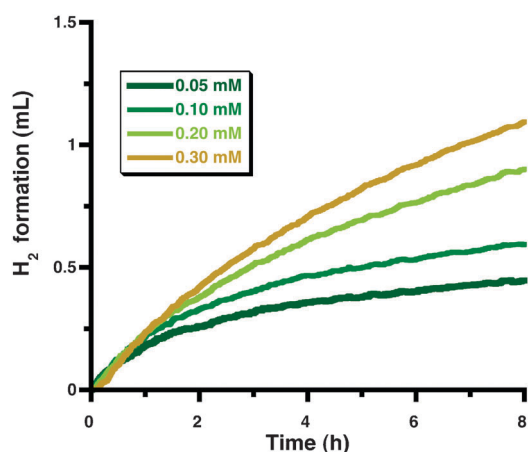
Fig. 1 H$_2$ generation from 0.14 mM catalyst **1**, 100 mM ascorbic acid (pH = 2.25), with varying concentrations of PS **2** in 1:1 H$_2$O:CH$_3$CN, irradiated with 520 nm LEDs.

photocatalytic system employing a molecular catalyst consisting of earth abundant elements.[4–16]

The photodecomposition of **2** is shown in Fig. 3. While the photochemical properties and decomposition of Ru(bpy)$_3$$^{2+}$ (**3**) in light-driven H$_2$-generating systems has been studied extensively,[1,21,22] fewer reports describe photocatalytic systems based on eosin (**2**).[4,13,23–25] In the absence of catalyst, a solution of **2** in H$_2$O:CH$_3$CN (1:1) is stable upon irradiation (λ > 410 nm), but in the presence of ascorbic acid the solution bleaches within 10 min. The photostability of **2** is enhanced dramatically by the addition of catalyst **1**. The ability of the catalyst to inhibit eosin decomposition is reminiscent of a H$_2$ generating system in which the PS is a Se-derivatized rhodamine dye and the catalyst is Co(dmgH)$_2$(Cl)(py) where dmgH = dimethylglyoxime.[12] In that system, PS* is quenched by the sacrificial electron donor to give PS$^-$ which in turn transfers an electron to the catalyst. In the absence of active catalyst, PS$^-$ decomposes rapidly by a presumed unimolecular path. It is likely that PS$^-$ in the present system similarly partitions between electron transfer to the catalyst and photodecomposition.
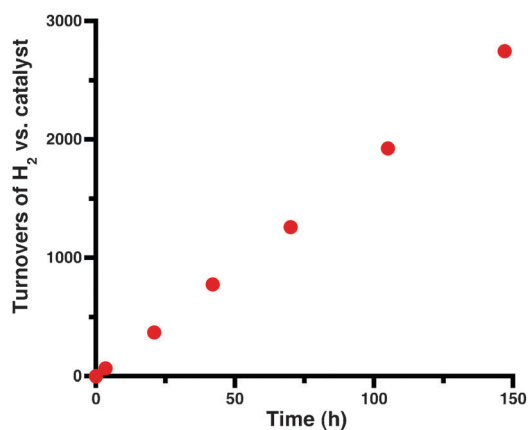

Fig. 2 Turnovers of H$_2$ generation from a system composed of 0.14 mM catalyst **1**, 500 mM ascorbic acid (pH = 2.25), and 0.40 mM PS **3** in 1:1 H$_2$O:CH$_3$CN irradiated with a 410 nm cutoff filter. Aliquots of the PS (400 μmol) and ascorbic acid (320 nmol) were added after each measurement to restore activity.
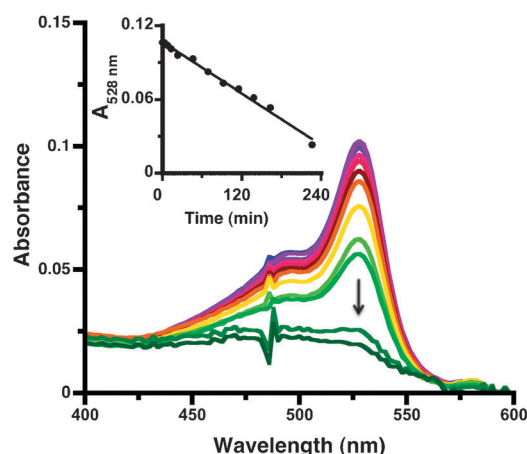

Fig. 3 UV-Vis absorption spectra during 240 min of photolysis. Sample contains 0.14 mM catalyst **1**, 0.10 mM PS **2**, and 100 mM ascorbic acid (pH = 2.25) in 1:1 H$_2$O:CH$_3$CN, irradiated with a 410 nm cutoff filter. **Inset**: Absorbance at 528 nm from **2** over time.

The rate of H$_2$ production was monitored under a variety of conditions. At both pH 2.25 and 2.65, the initial rate of H$_2$ production (over the first 40 min) has a first order dependence on [**1**] and is independent of [**2**] or [**3**]. The rate is independent of the choice of PS, despite the difference in reducing power of **2**$^-$ (−1.11 V) vs. **3**$^-$ (−1.26 V).[1,2] Variation of the pH independently of the other system components shows that above a pH of 2.5 the initial rate of H$_2$ production has a first order rate dependence on proton concentration. The combined data fit to an apparent rate law of the form

$$\text{rate} = k_1[\text{catalyst}][\text{H}^+] \qquad (1)$$

with $k_1 \approx 3.7 \times 10^5$ M^{-1}s^{-1}. This is a phenomenological rate constant, and not necessarily specific to any particular catalytic step. Solutions with pH < 2.25 exhibit lower rates of H$_2$ production using either [**2**] or [**3**] as the PS. It is likely that at pH < 2.25, protonation of ascorbate (pK_a = 4.2) results in reduced efficiency of the sacrificial electron donor.[15] Unlike the previously reported eosin-Co(dmgH)$_2$(Cl(py) and Se-derivatized rhodamine dye-Co(dmgH)$_2$(Cl(py) systems, where the initial H$_2$ evolution rates were limited by [PS] and steps involving the PS,[12,13] the initial rate of the present system appears to be limited by the catalyst concentration.

Dubois and coworkers have reported the use of **1** as an electrocatalyst for H$_2$ production, with much higher maximum rates (TOF > 350 s^{-1}) than observed here.[19] However, those experiments in acetonitrile used extremely strong acids (e.g. protonated dimethyl formamide (DMFH$^+$)), whereas the photocatalytic experiments described here used 1:1 water:acetonitrile mixtures with pH > 2.25. We evaluated whether the large concentration of water affected the redox behavior of **1** through a series of cyclic voltammetry experiments. The cyclic voltammogram of **1** in 1:1 H$_2$O:CH$_3$CN features a reversible one-electron reduction wave at −0.74 mV (ΔE$_p$ = 0.094 V at a scan rate of 0.100 V s^{-1}) versus the ferrocene/ferrocenium couple (Fc/Fc$^+$). This reduction wave has a similar potential as the analogous nickel(II/I) couple in water-free CH$_3$CN (E$_{1/2}$ = −0.84 mV vs. Fc/Fc$^+$).[19] In both cases, the addition of DMFH$^+$ results in a substantial current
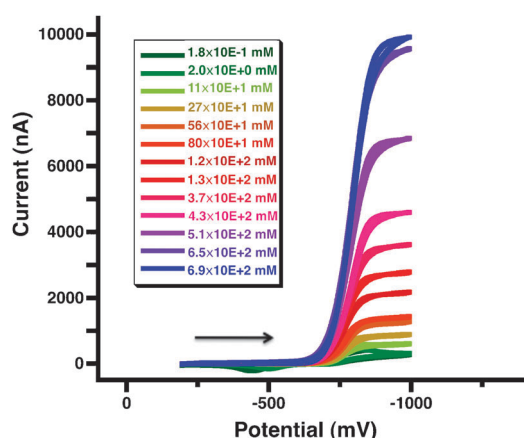
Fig. 4 Current enhancements for successive cyclic voltammograms of 0.10 mM catalyst **1**, with 0.10 M NBu$_4$BF$_4$ and increasing concentrations of protonated dimethyl formamide (DMFH$^+$) in 1 : 1 H$_2$O : CH$_3$CN. Scan rate of 0.025 V s^{-1} with a glassy carbon working electrode. Potentials are referenced to Fc$^+$/Fc.

enhancement, eventually reaching a maximum $i_c/i_p = 52$ (Fig. 4), which is similar to the current enhancement in pure CH$_3$CN and with smaller amounts of water ($i_c/i_p = 60$).[26] Additionally, as seen at lower concentrations of water,[26] the electrocatalytic H$_2$ production maintains a second-order rate dependence on acid.[19] So, the redox potential and electrocatalytic ability of **1** are similar despite the change in solvent.

The observed rate law for electrocatalysis with catalyst **1** is second-order in [H$^+$] for [H$^+$] > 2.0 mM,[27] in contrast to the first-order dependence seen in our photocatalytic experiments. Both rate laws fit to the literature mechanism,[27] if at the lower [H$^+$] in our experiments the rate limiting step changes from H$_2$ loss (which occurs after two protonations) to the initial protonation step. It is reasonable that the protonation of pendant amines (p$K_a \approx 6$ in CH$_3$CN) would be inefficient at a more moderate pH.[27–29] Cyclic voltammetry of **1** in 1 : 1 H$_2$O : CH$_3$CN after the addition of 100 mM ascorbic acid (pH = 2.25) shows a small current enhancement, $i_c/i_p \approx 1.4$, for the nickel(II/I) couple. Further mechanistic details are under investigation, but the available evidence suggests that the rate limiting step changes as a function of pH, which leads to the difference in rate law.

In summary, [Ni(P$_2^{Ph}$N$_2^{Ph}$)$_2$](BF$_4$)$_2$ (**1**) has been shown to operate as a stable H$_2$ production catalyst when irradiated with visible light in aqueous mixtures in the presence of a PS and ascorbate as the sacrificial electron donor at modestly acidic pH. Our results are consistent with the proposed mechanistic framework for H$_2$ generation by **1**, with a change in the rate determining step resulting from a change in pH.[27] The remarkable stability of catalyst **1** in this photocatalytic system, and in multicomponent electrocatalytic systems,[30] suggests great promise for its incorporation into other multicomponent photocatalytic systems.

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