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Unsensitized Photochemical Hydrogen Production Catalyzed by Diiron Hydrides

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Supporting Information

ABSTRACT: The diiron hydride $[(\mu\text{-H})Fe_2(pdt)(CO)_4(dppv)]^+$ ($[H\mathbf{2}]^+$, dppv = *cis*-1,2-$C_2H_2(PPh_2)_2$) is shown to be an effective photocatalyst for the H_2 evolution reaction (HER). These experiments establish the role of hydrides in photocatalysis by biomimetic diiron complexes. Trends in redox potentials suggests that other unsymmetrically substituted diiron hydrides are promising catalysts. Unlike previous catalysts for photo-HER, $[H\mathbf{2}]^+$ functions without sensitizers: irradiation of $[H\mathbf{2}]^+$ in the presence of triflic acid (HOTf) efficiently affords H_2. Instead of sacrificial electron donors, ferrocenes can be used as recyclable electron donors for the photocatalyzed HER, resulting in 4 turnovers.

Reflecting interest in renewable energy,[1] the hydrogen evolution reaction (HER) is receiving considerable attention.[2] Thermal HER typically involves heterogeneous platinum- and nickel-based catalysts,[3] but homogeneous catalysts now operate at enzyme-like rates.[4] Photochemical routes to hydrogen originally focused on processes catalyzed by platinum colloids in the presence of sensitizers such as $[Ru(bipy)_3]^{2+}$.[5,6] In recent years, this theme has been reinvented using bioinspired catalysts, guided by the idea that these earth-abundant catalysts might replace Pt.[7] Significant progress has been made, although many catalysts still suffer limitations related to robustness and efficiency. In this report, we describe concepts and preliminary results that address some of these limitations and point to new strategies.

The most studied bioinspired photochemical HER catalysts are diiron dithiolato complexes exemplified by $Fe_2(pdt)(CO)_6$ (**1**, pdt = 1,3-propanedithiolate) and analogues.[8] Such compounds are highly simplified mimics of the active site of the [FeFe]-hydrogenase,[9] nature's fastest catalysts for HER (Figure 1). Although the hydrogenases have no direct photochemical function in nature, simple bioinspired models have attracted attention since the initial work of Ott, Kritikos, Åkermark, and Sun.[10] The active sites of the [FeFe]-hydrogenases do not feature six carbonyls, but are more substituted systems of the formula $Fe_2(dithiolate)(CO)_3L_3$. Many studies demonstrate that **1** and its analogues catalyze the HER in the presence of appropriate sensitizer, as well as proton and sacrificial electron donors. At wavelengths >400 nm, yields of 0.33−4 equiv of H_2 are typically realized[11] in the presence of acids such as ascorbic and trifluoroacetic acid as well as sacrificial electron donors such as ascorbate, thiols, and triethylamine. Recently, high TONs (200−700) have been achieved using iridium-based sensitizers or novel electron-accepting dithiolates in combination with ruthenium sensitizers.[12]

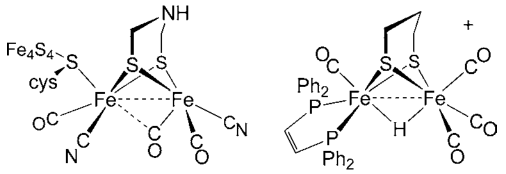

Figure 1. Structures of active site of [FeFe]-hydrogenase and the catalyst $[HFe_2(pdt)(CO)_4(dppv)]^+$ ($[H\mathbf{2}]^+$, one of two isomers).

Hexacarbonyl-based catalysts like **1** function because of their mild reduction potentials. The $\mathbf{1}^{0/-}$ couple at $E_{1/2} = -1.60$ V[13] is less negative than that of $[Ru(bipy)_3]^{2+/+}$ ($E_{1/2} = -1.69$ V, all couples referenced to $Fc^{+/0}$ in MeCN solution), which is photogenerated from reductive quenching of photoexcited $[Ru(bipy)_3]^{2+}$ by ascorbate.[12] The prevailing mechanism for this photocatalyzed HER invokes the transient formation of an anionic Fe(0)−Fe(I) complex $[\mathbf{1}]^-$, which is protonated to give a hydride. Although hydrides have never been detected in such systems (Figure 2), the overall mechanistic scenario is similar to thermal HER catalyzed by **1** and related species.[14] One design flaw with **1** and related bioinspired systems is the photolability

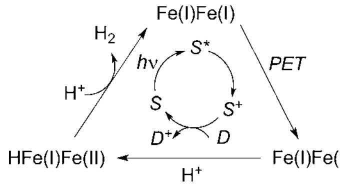

Figure 2. Mechanism for photosensitized hydrogen evolution catalyzed by typical diiron dithiolato carbonyls. *S* = sensitizer, *PET* = photon-driven electron-transer, *D* = donor. In this report, ferrocenes are used as donors and we do not use sensitizers.

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of the metal carbonyl.[15] For example, upon irradiation with a medium-pressure Hg lamp with a 400 nm cutoff filter, CH_2Cl_2 solutions of **1** exhibit substantial photodegradation to insoluble, CO-free products, which do not catalyze HER and which cannot be regenerated with CO.

To address the photolability of diiron carbonyl catalysts, we investigated the use of derivatives substituted with phosphine ligands. The approach is potentially powerful because many substituted derivatives of the type $Fe_2(pdt)(CO)_{6-x}(PR_3)_x$ are known from the extensive efforts to model the active site of the hydrogenase enzyme.[16] Most commonly, substituted derivatives contain two phosphine ligands, and this broad class of complexes was examined in this work. As reflected by their ν_{CO} values, the disubstituted derivatives exhibit stronger Fe−CO bonds: $\nu_{CO(avg)}$ = 2050 cm^{-1} for **1** versus 1950 cm^{-1} for both $Fe_2(pdt)(CO)_4(dppv)$ (**2**) and $Fe_2(pdt)(CO)_4(PMe_3)_2$ (**3**). These phosphine-substituted complexes are more basic, forming cationic hydrides with pK_a^{MeCN} estimated to be 15.[17] The overarching problem with photochemical applications of these substituted iron(I) carbonyls is their reduction potentials,[18] which are too negative relative to typical sensitizers. For example, the couples $[\mathbf{2}]^{0/-}$ and $[\mathbf{3}]^{0/-}$ are −2.12 and −2.3 V, almost 600 mV more negative than the $[\mathbf{1}]^{0/-}$ couple. Photon energies required for their photoreduction would be in the hard UV, which excludes most of the solar spectrum. A useful finding, however, is that the *diiron(II) hydrides exhibit substantially lower reduction potentials*. Thus, $[HFe_2(pdt)(CO)_4(dppv)]BF_4$ ($[H\mathbf{2}]BF_4$) and $[HFe_2(pdt)(CO)_4(PMe_3)_2]BF_4$ ($[H\mathbf{3}]BF_4$) have reduction potentials in CH_2Cl_2 solution of −1.33 and −1.4 V (Figure 3). The reduction potentials for these hydride cations is milder than many sensitizers[19] as well as **1**.

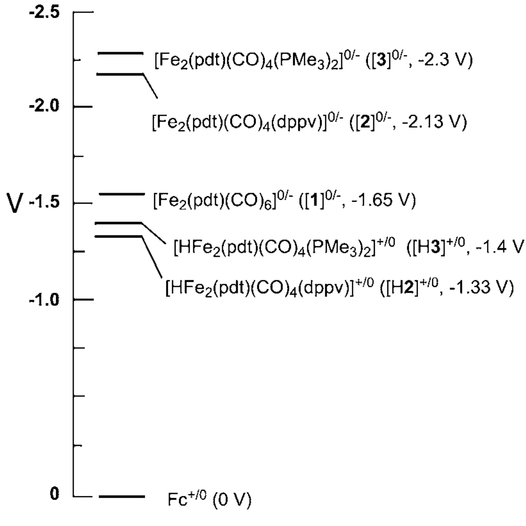


Figure 3. Redox potentials of diiron dithiolato carbonyls and their hydrides.

One clear advantage to the use of substituted metal carbonyls is the increased photostability of their hydrides. ^{31}P NMR analysis indicates 8% and 16% degradation for CH_2Cl_2 solutions of $[H\mathbf{2}]BF_4$ and $[H\mathbf{3}]BF_4$, respectivly, over the course of 2 h ($\lambda > 400$ nm).

Although virtually all photo-HER catalysts require sensitizers (usually based on platinum metals), we discovered that these phosphine-substituted diiron hydrides do not. Thus, irradiation of $[H\mathbf{2}]BF_4$ and $[H\mathbf{3}]BF_4$ (1.11 mM CH_2Cl_2 solutions) in the presence of one equiv of ether-HBF_4 yielded >0.95 equiv of H_2 (based on HBF_4) over the course of 1 h as verified by gas chromatography (see Supporting Information). A series of experiments focused on $[H\mathbf{2}]BF_4$. When the concentration of $[H\mathbf{2}]BF_4$ was increased 5-fold, the rate of hydrogen production increased by a factor of 5.7. Similar H_2 yields and evolution rates were obtained with $[H(OEt_2)]BF_4$ (pK_a^{MeCN} = 0.1) or HOTf (pK_a^{MeCN} = 2.6). The strength of the acid is important since hydrogen evolution using $[H(PPh_3)]BF_4$ in place of $[H(OEt_2)]BF_4$ proceeds more slowly (by a factor of 0.42). With 10 equiv HOTf, the rate of H_2 evolution increased only by a factor of 1.65. After the evolution of H_2 from $[H\mathbf{2}]BF_4$ and $[H\mathbf{3}]BF_4$, the colorless reaction solution is devoid of metal carbonyls, and a white precipitate is evident. The generality of the photo-HER is strengthened in the finding that $[HFe_2(edt)(CO)_4(diars)]BF_4$ produces H_2 at about twice the rate as did $[H\mathbf{2}]BF_4$ (edt = 1,2-ethanedithiolate, diars = 1,2-$C_6H_4(AsMe_2)_2$).

The photodriven hydrogen evolution from $[H\mathbf{2}]BF_4$ and $[H\mathbf{3}]BF_4$ proceeds in the *absence of a photosensitizer*. This finding implicates a role for one or more excited states wherein the hydride ligand is more hydridic than in the ground state. It is known that $[H\mathbf{3}]^+$ undergoes substitution and H−D (with D_2) exchange upon irradiation with sunlight.[20] This substitution and exchange reactivity is inhibited by CO, unlike the photo-HER by $[H\mathbf{2}]BF_4$. Optical spectra of **2** and $[H\mathbf{2}]^+$ are presented in Figure 4. In an effort to understand the possible origin of the photoinduced elimination of H_2, we examined the low lying excited states of $[HFe_2(pdt)(CO)_4(\mathit{cis}\text{-}(PH_2)_2C_2H_4)]^+$, a simplified analogue of $[H\mathbf{2}]^+$. Calculations based on time-dependent density functional theory (TD-DFT) and DFT suggest that the Fe−H−Fe center becomes more unsymmetrical in the relevant excited states, but dramatic changes in the Fe−H bonding were not observed computationally.

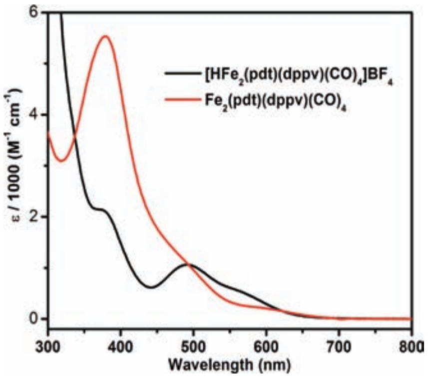


Figure 4. UV−vis spectra of $Fe_2(pdt)(CO)_4(dppv)$ (**2**) and $[HFe_2(pdt)(CO)_4(dppv)]BF_4$, $[H\mathbf{2}]BF_4$ in CH_2Cl_2 solution at room temperature.

Having established that $[H\mathbf{2}]BF_4$ efficiently produces H_2 upon irradiation in the presence of acids, we addressed the low TON. As a working hypothesis, we suggest that H_2 evolution follows the stoichiometry in eq 1.

$$[HFe_2(pdt)(dppv)(CO)_4]^+ + H^+ \xrightarrow{h\nu} [Fe_2(pdt)(CO)_4(dppv)]^{2+} + H_2 \quad (1)$$

The resulting dicationic iron complex, with a 32 e^- configuration, is predicted to rapidly degrade via CO dissociation (related 33 e^- diiron complexes are known[21] but are photolabile). The redox couple $[\mathbf{2}]^{+/2+}$ would be positive of the couple $[\mathbf{2}]^{0/+}$, determined in this work to be −190 mV (i_{pa}/i_{pc} = 1.2, 0.1 M NBu_4PF_6 in CH_2Cl_2, 100 mV/s). We also verified that $[\mathbf{2}]^+$ is thermally labile. This analysis of redox couples suggests that the oxidized derivatives $[\mathbf{2}]^{n+}$ and $[\mathbf{3}]^{n+}$ could be reduced by relatively mild electron donors. The selection of electron donors is constrained by $E([\mathbf{2}]^{0/+})$ and the requirement that the donor be unreactive toward the acid substrate for the HER. Several ferrocenes satisfy this requirement, and for this study we focused on *sym*-octamethylferrocene ($Fc^\#$), which we verified reversibly oxidizes at −512 mV in CH_2Cl_2 solution versus $Fc^{+/0}$.[22]

Experiments confirm that $Fc^\#$ largely inhibits decomposition of the diiron catalyst during HER. Thus, irradiation of a CH_2Cl_2 solution of 1:1:2 mixture of $[H\mathbf{2}]BF_4$, HOTf, and $Fc^\#$ resulted in good yields of both H_2 and **2**[23]/$[H\mathbf{2}]^+$ as verified by ^{31}P NMR and IR spectroscopic analysis of the reaction solution. The resulting blue-green solution was shown by UV−vis spectroscopy to contain $[Fc^\#]^+$ (λ_{max} = 750 nm). Ferrocenium derivatives were *not* produced when these experiments were conducted with weaker electron donors Fc (E = 0 V) and 1,1′-dimethylferrocene (E = −120 mV). Although $Fc^\#$ is useful for recycling **2**, it is not useful for the PMe_3 complex $[H\mathbf{3}]^+$ (Supporting Information).

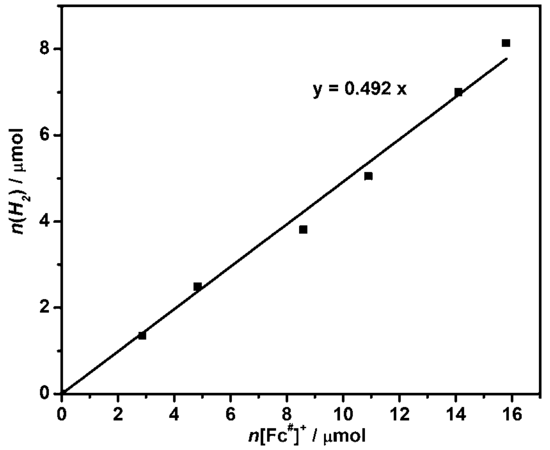
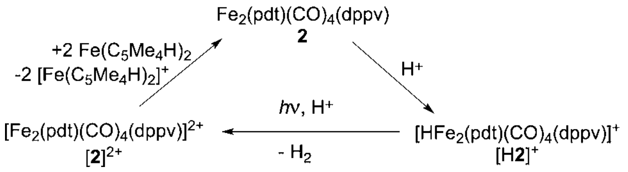


Figure 5. Plot of yield of hydrogen ($n(H_2)$) vs ferrocenium ($n[Fc^\#]^+$) by photolysis of $[H\mathbf{2}]BF_4$ (2 μmol), HOTf (20 μmol), and $Fc^\#$ (40 μmol) at various times (see the Supporting Information).

Photocatalytic hydrogen production was conducted using CH_2Cl_2 solutions of the hydride $[H\mathbf{2}]BF_4$. Irradiation of a CH_2Cl_2 solution of $[H\mathbf{2}]BF_4$, HOTf, and $Fc^\#$ in a 1:10:20 ratio was monitored by UV−vis spectroscopy and gas chromatography. As shown in Figure 5, the evolution of H_2 correlates linearly with the formation of the ferrocenium salts in the expected 1:2 ratio. After 3 h photolysis, the yields of H_2 and $[Fc^\#]^+$ were 8.1 and 15.8 μmol, respectively. Control experiments verified that under the conditions of the photoreaction, the reaction between HOTf and $Fc^\#$ is negligible. In effect, $[H\mathbf{2}]^+$ functions as a photocatalyst for the cycle in Scheme 1.

In summary, this paper discloses novel perspectives on the use of bioinspired catalysts for hydrogen evolution. First, we showed that diiron hydrides have redox potentials suitable as catalysts for H_2 evolution. This insight portends a broadened role for metal hydrides in photocatalysis, sensitized and otherwise. In general, the photochemistry of metal hydrides has been lightly investigated,[6,24] and most published work emphasizes short wavelengths.[25] Second, a simplifying discovery is that the bioinspired diiron dithiolato hydrides operate without use of sensitizers, which are both expensive and, in some cases, complicating as their degradation could lead to nanoparticulate HER catalysts. The mechanism of this photo-HER remains a subject of further investigation. Finally, we have demonstrated that photo-HER can be coupled to the reversible oxidation of ferrocenes, a family of inexpensive, robust, and recyclable donors. This last aspect addresses the well-recognized problem of using sacrificial electron donors in previous photochemical H_2 evolution systems. Future reports will expand, with both computational and experimental experiments, on the preliminary results disclosed above.

Scheme 1. Proposed Catalytic Cycle for Hydrogen Evolution Catalyzed by $[H\mathbf{2}]^+$



■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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