Self-assembled biomimetic [2Fe2S]-hydrogenase-based photocatalyst for molecular hydrogen evolution

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The large-scale production of clean energy is one of the major challenges society is currently facing. Molecular hydrogen is envisaged as a key green fuel for the future, but it becomes a sustainable alternative for classical fuels only if it is also produced in a clean fashion. Here, we report a supramolecular biomimetic approach to form a catalyst that produces molecular hydrogen using light as the energy source. It is composed of an assembly of chromophores to a bis(thiolate)-bridged diiron ([2Fe2S]) based hydrogenase catalyst. The supramolecular building block approach introduced in this article enabled the easy formation of a series of complexes, which are all thoroughly characterized, revealing that the photoactivity of the catalyst assembly strongly depends on its nature. The active species, formed from different complexes, appears to be the $[\text{Fe}_2(\mu\text{-pdt})(\text{CO})_4(\text{PPh}_2(4\text{-py}))_2]$ (3) with 2 different types of porphyrins (5a and 5b) coordinated to it. The modular supramolecular approach was important in this study as with a limited number of building blocks several different complexes were generated.

photocatalysis | self-assembly | supramolecular chemistry | metalloporphyrin chromophore | Stern-Volmer plot

Supramolecular chemistry, defined by Nobel Prize Laureate Jean-Marie Lehn as the “chemistry beyond the molecule,” has changed the way we look at molecules (1). Besides exploring reactivity of molecules, interaction between molecules has become of dominant importance as it provides new means of controlling properties of chemical systems. Supramolecular chemistry has rapidly evolved into a mature field, and the implementation of supramolecular strategies has resulted in breakthroughs in several disciplines (2–4). The reversible character of noncovalent chemistry gives rise to concepts such as adaptation and self-correction, creating fundamentally different system properties compared with traditional covalent strategies. The modular character associated with the building block approach in supramolecular chemistry provides an easy strategy to generate large libraries of analogous structures of nanosize dimension. Such libraries are of interest in research areas where accurate prediction of particular properties of chemical systems is inadequate or impossible. For example, means to predict the selectivity provided by transition metal catalyst are lacking, and therefore high throughput screening of libraries of catalysts is still the most powerful method to find catalyst systems with desired selectivities. Indeed, we and others have introduced supramolecular ways to make transition metal catalysts and used the building block approach to create large libraries of related catalysts, some of which show unrivaled selectivities (5–9).

Stimulated by these exciting results, we were wondering whether supramolecular strategies could also provide solutions to other challenges in catalysis. One of the greatest challenges our society is currently facing is the large-scale production of clean energy (10). Molecular hydrogen is envisaged as a key green fuel for the future, its combustion producing only water as the reaction product (11). Clearly, molecular hydrogen becomes a sustainable alternative for classical fuels only if it is also

produced in a clean fashion. Ultimately, the use of sunlight as the energy source to produce hydrogen from a proton source, ideally water, is the Holy Grail for the hydrogen economy, because the energy cycle is completely carbon free. Individual processes that constitute the Holy Grail are widely encountered in Nature, forming the center of life's existence. Sunlight is efficiently captured by the chlorophyll pigments of various light-harvesting systems, and the energy is stored in a chemical form (12). Hydrogenase enzymes in many microorganisms (reversibly) reduce protons to dihydrogen, using electrons from an external source, an intriguing reaction that is taking place usually at a dithiolate- or bis(thiolate)-bridged diiron ([2Fe2S]) active sub-site (class of Fe-only H_2 ases) (13). The elucidation of the protein structure of the [2Fe2S]hydrogenases revealed their active center (14), which has served as a huge impetus for synthetic chemists exploring properties of its structural models (15–17). It has already been demonstrated that several of these models are active electrocatalysts, producing molecular hydrogen when a certain cathodic potential is applied (18).[†] The structure of the $\text{Fe}_2(\mu\text{-S}_2)$ core appears crucial for this activity, but the remaining ligands attached to the active site, in the natural systems generally CO, CN^- , and thiolate-sulfur, can be replaced without much consequence (although the cyanide ligand can be protonated to $[\text{Fe}(\text{CNH})]$ (21). An assembly of the active components from the light-harvesting system and hydrogenases, i.e., a light-capturing device combined with the active [2Fe2S] cluster, could in principle lead to systems that use solar energy for the production of molecular hydrogen from protons (22).

In this contribution, we show that the supramolecular building-block approach offers a powerful means to bring chlorophyll-type pigments and an active diiron cluster together to form active assemblies capable of generation of molecular hydrogen by using visible light as the energy source. Because diiron complexes with diverse electron-donating phosphine ligands have been prepared that form active electrocatalysts, we considered the preparation of [2Fe2S] complexes based on versatile pyridyl-functionalized phosphine ligands. These complexes have supramolecular handles to form chromophore-associated superstructures, by using

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Data deposition: The atomic coordinates have been deposited in the Protein Data Bank, www.pdb.org (PDB ID codes CCDC 693432 for compound 1, 693433 for compound 3, 693434 for compound 4, 693435 for compound 1-5a, and 693436 for 4-(6)3).

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[†]It is noteworthy that some of the biomimetic complexes in the reduced form capture and reduce protons at fairly low voltages that are very close to those of the natural hydrogenases (approximately -1 V vs. ferrocene/ferrocenium couple). See refs. 19 and 20.

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strategies previously developed by us to encapsulate transition metal catalysts (23). In this approach, the pyridyl-functionalized phosphine ligands coordinate with phosphorus to the active metal center, whereas the nitrogen donor coordinates selectively to chromophores such as zinc(II)porphyrins (**5**) and zinc(II)salphen (**6**) macrocycles. The supramolecular building block approach in this design facilitates the easy preparation of several analogous assemblies in which the number of chromophores as well as the average location of these units with respect to the active site can be varied in a subtle way.[‡]

Results and Discussion

Various diiron complexes were prepared with different numbers of pyridyl functionalities ($n = 0-3$) for the assembly of various zinc(II)porphyrin and zinc(II)salphen chromophores (see Scheme 1). In addition, the application of tris(3-pyridyl)phosphine ligands result in encapsulation of the diiron core, which may lead to favorable site-isolation effects, preventing the formation of inactive dimeric [FeFe]₂ species often encountered in [2Fe2S]-redox chemistry (25). We envisioned that the encapsulation of the [2Fe2S] complex would result in a better biomimetic model because such deactivation pathways are unknown

[‡]While this work was in progress, an independent report by Li *et al.* (24) appeared showing an alternative supramolecular approach toward an active photoactive hydrogen-generating system based on zinc(II)porphyrin and a biomimetic [2Fe2S] complex tethered to a pyridyl function on the dithiolate bridge.

Fig. 1. Solid-state molecular structures of the diiron complexes **1** (A) and **3** (B) as determined by single crystal X-ray diffraction. Hydrogen atoms have been omitted for clarity. The structure of **4** is shown in Fig. S19 of the *SI Appendix*.

for the actual hydrogenase enzyme, probably because the active site is completely embedded in the protein structure.

The (4-pyridyl)diphenylphosphine complex [Fe₂(μ-pdt)(CO)₅{PPh₂(4-py)}] (**1**) (pdt = propylene-1,3-dithiolate), the triphenylphosphine complex [Fe₂(μ-pdt)(CO)₅(PPh₃)] (**2**), and the tris(3-pyridyl)phosphine complex [Fe₂(μ-pdt)(CO)₅{P(3-py)₃}] (**4**) were synthesized by decarbonylation of parent [Fe₂(μ-pdt)(CO)₆] with the aid of Me₃NO. The bis{(4-pyridyl)diphenylphosphine} complex [Fe₂(μ-pdt)(CO)₄{PPh₂(4-py)}₂] (**3**) was formed after reduction of **1** by using 1 eq of [Co(η⁵-C₅Me₅)₂] as a 1-electron reducing agent. All new complexes were characterized by X-ray structure determination (Fig. 1), NMR, IR and mass spectroscopies, and elemental analyses [see Figs. S1–S21 in *supporting information (SI) Appendix*]. X-ray analyses show that the central [2Fe2S] units of the 4 complexes have butterfly conformations, the coordination environment of each iron atom being approximately square-pyramidal. As expected, the CO-ligand substitution with a phosphine appears only at the apical position *trans* to the Fe–Fe bond and has only a small effect on the Fe–Fe distances [2.5217(5) Å in **1**, 2.5247(6) Å in **2**, 2.5209(5) Å in **3** and 2.5225(3) Å in **4**] (26).

Cyclic voltammetric studies show that complexes **1** and **2** undergo a typical irreversible reduction at −2.10 and −2.05 V (versus Fc/Fc⁺) respectively, attributed to the initial generation of the reactive mixed-valence Fe⁰Fe^I state. In the presence of acetic acid (HOAc) both complexes are efficient electrocatalysts for the reduction of protons to molecular hydrogen (acetonitrile, glassy carbon cathode, *SI Appendix*), in line with previous observations (18). The electrocatalytic proton reduction potentials coincide with the Fe⁰Fe^I reduction of complexes **1** and **2**, being shifted 500 mV less negatively than the proton reduction under identical conditions (Fig. 2). It is known that small changes in the parent complex can result in markedly different redox-reaction pathways (25), but the presence of the pendant 4-pyridyl

Fig. 2. Cyclic voltammogram of 1.0 mM $[\text{Fe}_2(\mu\text{-pdt})(\text{CO})_5(\text{PPh}_2(4\text{-py}))]$ (**1**) (Left) and 1.0 mM $[\text{Fe}_2(\mu\text{-pdt})(\text{CO})_5(\text{PPh}_3)]$ (**2**) (Right) with 0–52 mM and 0–35 mM HOAc, respectively, in MeCN. Glassy carbon microdisc working electrode, scan rate 200 mV s^{-1} .

group in complex **1** does not significantly alter the redox behavior and electrocatalytic properties of $[\text{2Fe2S}]$ -phosphine complexes.

The supramolecular assemblies of the macrocycle chromophore and the pyridylphosphine-substituted diiron catalysts are readily formed in the solution. The addition of Zn(II)TPP (**5a**) to complex **1** in CDCl_3 caused a typical coordination-induced shift in the ^1H NMR ($\Delta\delta = 6.0 \text{ ppm}$) for the ortho-protons of the pyridine moiety, indicative of selective binding of the chromophore to the nitrogen-donor atom of complex **1** (27). Titration experiments monitored by UV-vis spectral changes

[decreasing steady-state fluorescence intensity and red-shifted absorption band pattern of Zn(II)TPP , see Figs. S24–S28 in *SI Appendix*] revealed the association constant $K_{\text{ass}} = 1.1 \cdot 10^3 \text{ M}^{-1}$ for the assembly **1·5a** in toluene, which is typical for this type of dynamic system. The binding of **5a** to **1** is only slightly weaker than determined for free $\text{PPh}_2(4\text{-py})$ ($K_{\text{ass}} = 6.3 \cdot 10^3 \text{ M}^{-1}$) (24), and there is no significant difference between association to **5a** or **5b** ($K_{\text{ass}} \text{ 1·5b} = 1.0 \cdot 10^3 \text{ M}^{-1}$). Similar assemblies of **5a** were formed with complexes **3** and **4**, albeit with a different stoichiometry of the chromophores and the $[\text{2Fe2S}]$ active site. As expected, no spectral changes were observed for Zn(II)TPP in the presence of complex **2** lacking the pyridyl functionalities.

The formation of the supramolecular complex **1·5a** was confirmed by X-ray structure determination (Fig. 3). The coordination of the Zn(II)TPP to the pyridyl nitrogen has only a minor effect on the geometry of the diiron cluster. The Fe–Fe distance is only slightly shorter [2.4878(11) to 2.4918(12) Å for the 3 independent molecules in the asymmetric unit] than in **1** (2.5216 Å). Importantly, in the assembly Zn(II)TPP is positioned above the propane-1,3-dithiolate bridge of the cluster at a distance of merely 4.2 Å. The average distance of the Zn(II)TPP macrocycle to the diiron core is only 7.2 Å, which is well within the range for an electron-hopping process (28). The X-ray structure of **4·(6)**₃ showed unambiguously that Zn(II)salphen chromophores are coordinated to all 3 pyridyl groups of P(3-py)_3 at the diiron core. Interestingly, the diiron cluster is partly encapsulated by the hemi-

Fig. 3. Solid-state molecular structures of assemblies **1·(5a)** and **4·(6)**₃ as determined by X-ray crystallography. Hydrogen atoms and solvent molecules have been omitted for clarity. For more information on the structures, see Fig. S22 and Fig. S23 and Table S5 and Table S6 in the *SI Appendix*.

Fig. 4. The steady-state fluorescence quenching of the singlet excited state of the associated Zn(II)TPP in **1·5a**. (A) Fluorescence spectral changes observed during the titration of Zn(II)TPP in toluene with complex **1**. Concentration of stock solution $[\text{Zn(II)TPP}] = 7.31 \cdot 10^{-6} \text{ mol dm}^{-3}$ (with optical density of 0.106 at 560 nm) and **1** varied between 0 and $1.9 \cdot 10^{-4} \text{ mol dm}^{-3}$. Excitation at 560 nm, the isosbestic point of the Q-bands of Zn(II)TPP . The corresponding Stern-Volmer plot (B) in which $F(0)/F$ (ratio of unquenched fluorescence intensity and quenched fluorescence) versus concentration quencher (**1**) is plotted (fitting: $y = 1.35 \times 10^3 x + 1.00$).

Table 1. Photogeneration experiments of molecular hydrogen with various self-assembled catalysts

Entry	[Fe2S] cluster	Zn(II)TPP (5a), mM	Zn(II)TPP(OMe) ₄ (5b), mM	Substrate, mM	λ_{exc} , nm	Dihydrogen gas, ml
1	4	4 [†]	—	10	>390	0.22 [‡]
2	4	—	4	10	>530	—
3	4	4	—	10	>530	—
4	1	4	—	10	>530	—
5	1	—	4	10	>530	—
6	3	2	2	10	>530	0.22 (30%) ^{§¶}
7	1	2	2	10	>530	0.22 (30%) ^{§¶}
8	2	2	2	10	>530	—

Reactions were performed by using a deaerated toluene solutions (5 mL) containing 1 mM [2Fe2S] complex, 2 mM Zn(II)TPP, 2 mM Zn(II)TPP(OMe)₄, and 10 mM [NPr₂EtH][OAc] under continuous irradiation by a 180-W Xe high-pressure lamp. Irradiation time was 80 min. Infrared radiation of the lamp was removed by absorption in a water flow cell. Wavelength range was selected by using a cut-off filter. The reaction temperature was 293 K.

[†]Zn(salphen) used as chromophore [salphen = *N,N'*-phenylene-bis(3,5-di-*tert*-butylsalicylideneimine)]. In the presence of 4 eq of **5a**, the formation of molecular hydrogen was not observed; instead, the complex disproportionates.

[‡]Decomposition was observed under reaction conditions.

[§]A 30% yield with respect to the proton donor. Assuming hydrogen saturation of the toluene solution, 100% yield is reached.

[¶]In the absence of porphyrin **5a** and **5b**, the complexes did not produce hydrogen upon irradiation.

sphere defined by the 3 chromophores, in analogy to a rhodium catalyst previously used for unusually selective reactions (29).

Because complexes **1**, **3**, and **4** are electrocatalytically active toward the proton reduction and capable of forming supramolecular assemblies with macrocycle photosensitizers, the photo-physic of the assemblies was studied. The steady-state fluorescence measurements on **1·5a** revealed significant quenching of the singlet excited state of associated Zn(II)TPP compared with free Zn(II)TPP (Fig. 4A). Analysis of the linear Stern–Volmer plot in terms of dynamic quenching leads to a quenching rate constant of $k_q = 7.0 \cdot 10^{11} \text{ s}^{-1} \text{ M}^{-1}$, which is much higher than the diffusion-limited rate. On the other hand, if only static quenching is assumed, an association constant $K_{\text{ass}} = 1.3 \cdot 10^3 \text{ M}^{-1}$ is found that compares well with the association constant independently determined for **1·5a** by the UV-vis titration. These results indicate that the ground-state assembly formation promotes efficient static nonradiative quenching of the Zn(II)TPP singlet excited state. This quenching is attributed to electron transfer from the excited macrocycle sensitizer to the [2Fe2S] core (see below). Accordingly, the fluorescence lifetime of Zn(II)TPP was found to be decreased from 1.96 ns for the free porphyrin to 0.3 ns in the assembly with **1** and concomitantly, the yield of the triplet state decreased, whereas the triplet lifetime of ³ZnTPP* ($\tau = 30.5 \text{ } \mu\text{s}$, see Fig. S32 in *SI Appendix*) remains unaffected by the assembly formation.

The photocatalytic activities of the different [2Fe2S] complexes **1–4** and their assemblies with the photosensitizers **5(a, b)** and **6** toward evolution of molecular hydrogen were evaluated in deaerated toluene at room temperature in the presence of NPr₂EtH·OAc as the proton source and sacrificial electron donor. The thermostated solutions were continuously irradiated with light from a 180-W high-pressure Xe lamp, by using proper cut-off filters and a water filter to absorb heat. Initially, we started with complex **4** and assembly **4·(6)**₃ because the encapsulation of the diiron cluster would prevent the detrimental formation of dimeric [FeFe]₂ species and was expected to lead to extra stabilization. During the irradiation experiment ($\lambda_{\text{exc}} \geq 390 \text{ nm}$) dihydrogen was indeed formed, but the complex decomposed rapidly into a precipitate, probably because of nonselective visible light excitation of chromophore **6** in a spectral region where also the diiron component absorbs (Table 1, entry 1). All further experiments were therefore performed with assemblies containing porphyrins (**5**) as the photosensitizers that were selectively excited at $\lambda_{\text{exc}} \geq 530 \text{ nm}$ (i.e., into the porphyrin S₀ → S₁ transition). In contrast to the previous

experiment, irradiation experiments with in situ-generated assembly **4·(5a)**₃ or **4·(5b)**₃ did not lead to any H₂ gas evolution (Table 1, entries 2,3). IR monitoring of the experiment revealed disproportionation of complex **4** into the all-CO cluster [Fe₂(μ-pdt)(CO)₆] that is unable to associate ZnTPP chromophores. This result indirectly proves photoreduction of the cluster core, followed by dissociation of the strongly nucleophilic ligand P(3-py)₃. Also the irradiation experiments with assemblies **1·5a**, **1·5b**, **3·(5a)**₂, and **3·(5b)**₂, i.e., assemblies with a single chromophore present, did not show any photocatalytic activity.

Most importantly and rather unexpectedly, catalyst **3** photogenerated significant (5 eq with respect to the cluster concentration) amounts of H₂ gas[§] in the presence of 2 molar eq of both **5a** and **5b** (Table 1, entry 6). Under these conditions, mixed assemblies with 2 different chromophores are likely formed. This observation suggests that the photoactive assembly surprisingly requires the presence of the 2 different chromophores. Control experiments using catalyst **1**, which has only 1 pyridyl functional group for the chromophore attachment, also showed photocatalytic activity under identical experimental conditions as for **3·(5a)(5b)** (Table 1, entry 7). However, in-depth IR study indicates that the active species is identical because during photoirradiation in the presence of **5a** and **5b** and the proton donor, complex **1** disproportionates to complex **3**, which can form **3·(5a)(5b)** (Scheme 2 and *SI Appendix*). In the absence of the chromophores and proton source, complex **1** decomposes to unidentified compounds upon irradiation ($\lambda_{\text{exc}} > 530 \text{ nm}$).

This reduction-induced rearrangement appears to be a general reactivity of compound **1** because **3** can be directly synthesized by the chemical reduction of **1** with 1-electron donor [Co(η⁵-C₅Me₅)₂], and **3** is formed upon photoreduction ($\lambda_{\text{exc}} > 530 \text{ nm}$) using the ZnTPP/Pr₂EtN mixture. Because control experiments showed that hydrogen evolution was only observed when the assembly **3·5a·5b** could be formed, we propose that the latter is the active species. Recent theoretical studies have suggested that the asymmetry of the diiron center may be a desirable feature of biomimetic models explaining the need for 2 different chromophores (30). Although the corresponding detailed mecha-

[§]The total amount of gas collected reached 0.22 mL (8.9 μmol); however, taking into consideration the amount of hydrogen gas dissolved in the toluene, this amount of gas is only a lower limit. Assuming H₂-saturation of the toluene solution after the reaction ceased, the upper-limit of hydrogen production can be estimated to be as high as 0.6 mL (nearly 100% conversion).

Scheme 2. Formation of the active species 3-(5a)(5b) under photoreductive conditions. The tertiary amine $N\text{Pr}_2\text{Et}$ is the sacrificial electron donor supplying the 2 electrons necessary for the molecular hydrogen production.

nism of the dihydrogen evolution is not unraveled at this point, the single pyridyl group at each iron center is most likely essential for the docking of 2 different types of zinc(II)porphyrins and forming the active supramolecular assembly.

Conclusions

We report a self-assembled catalyst system that is able to use light as primary energy source to generate molecular hydrogen. The primary biomimetic $[2\text{Fe}2\text{S}]$ hydrogenase catalyst is used with supramolecular handles to assemble the light-capturing chromophore in close proximity of the active diiron center to facilitate the photoinduced electron transfer. Importantly, closely related $[2\text{Fe}2\text{S}]$ complexes with very similar electrocatalytic properties show a distinctively different behavior upon (photo)reduction. For this reason, the supramolecular approach has been important because it enables the easy modular variation of complexes; in addition, we found an active catalyst that is difficult to prepare by traditional strategies and that we did not predict beforehand. Detailed studies show that in both experiments with complexes 1 and 3, the assembly 3-(5a)(5b) is the active species formed, either directly or via light-induced disproportionation. Remarkably, the hydrogen-producing system requires 2 different chromophores (5a and 5b) present in solution. This study reconfirms the observation that small changes in the parent $[2\text{Fe}2\text{S}]$ complex can result in different and unpredictable reaction pathways upon reduction. The supramolecular strategy is highly promising for further development in this important area, because the building-block approach also facilitates rapid optimization.

Methods

General Procedures. Unless stated otherwise, reactions were carried out under an atmosphere of argon by using standard Schlenk techniques. THF and hexane were distilled from sodium benzophenone ketyl, toluene was distilled

from sodium under nitrogen, and dichloromethane was distilled from CaH_2 under nitrogen. NMR spectra (^1H , $^{31}\text{P}\{^1\text{H}\}$, and $^{13}\text{C}\{^1\text{H}\}$) were measured on Varian Mercury 300 MHz or Varian INOVA 500-MHz spectrometers. High-resolution fast atom bombardment mass spectrometry (HRMS FAB) measurements were carried out on a JEOL JMS SX/SX 102A spectrometer. Starting materials $[\text{Fe}_2(\mu\text{-pdt})(\text{CO})_6]$, diphenyl(4-pyridyl)phosphine, tris(3-pyridyl)phosphine, $[\text{Fe}_2(\mu\text{-pdt})(\text{CO})_5(\text{PPh}_3)]$ (2), ZnTPP (5a), and ZnTPP(OMe) $_4$ (5b) were synthesized by literature methods (see [SI Appendix](#))

General Synthesis of $[\text{Fe}_2(\mu\text{-pdt})(\text{CO})_5(\text{PR}_3)]$. $[\text{Fe}_2(\mu\text{-pdt})(\text{CO})_6]$ (0.192 g, 0.50 mmol) and the appropriate phosphine (0.125 g, 0.50 mmol) was dissolved in toluene (10 mL). Trimethylamine *N*-oxide dihydrate (0.037 g, 0.50 mmol) was added, and the solution was stirred for 20 min. The IR spectra showed no starting material after 15 min. The solvent was removed under reduced pressure, and the crude product was purified by chromatography on silica with dichloromethane/pentane = 2:1 as eluent. See [SI Appendix](#) for NMR data and X-ray analyses details.

Synthesis of $[\text{Fe}_2(\mu\text{-pdt})(\text{CO})_4(\text{PPh}_2(4\text{-py}))_2]$ (3). $[\text{Fe}_2(\mu\text{-pdt})(\text{CO})_5(\text{PPh}_2(4\text{-py}))]$ (0.0784 g, 0.125 mmol) and decamethylcobaltocene (0.0413 g, 0.125 mmol) were dissolved in 5 mL of THF. The reaction mixture was stirred for 1 h at room temperature. The solvent was evaporated, and the crude product was washed with diethyl ether (2×10 mL). The yield was 0.0435 g (41%). See [SI Appendix](#) for NMR data and X-ray analyses details.

Cyclic Voltammetry. Cyclic voltammograms of $\approx 10^{-4}$ M parent compounds in 10^{-1} M Bu_4NPF_6 electrolyte solution (MeCN) were recorded in a gas-tight single-compartment 3-electrode cell equipped with platinum working electrode (apparent surface of 0.42 mm^2), coiled platinum wire auxiliary, and silver wire pseudoreference electrodes. The cell was connected to a computer-controlled PAR Model 283 potentiostat. All redox potentials are reported against the ferrocene/ferrocenium (Fc/Fc^+) redox couple used as internal standard. Electrocatalysis studies were performed by the addition of different amounts of acetic acid.

Hydrogen Evolution. In the photochemical hydrogen-evolution experiment, the diiron complex (1-4, 5×10^{-6} mol), the chromophore (5a, 5b, 6, total amount 2×10^{-5} mol) were dissolved under nitrogen in toluene (5 mL) in a Schlenk vessel equipped with a magnetic stirrer. After 5 min of stirring in the dark, the solution was transferred to a clean Schlenk tube, and ionic liquid $[\text{NPr}_2\text{EtH}][\text{OAc}]$ (4 μL , 5×10^{-5} mol) was added. The solution was purged for 3 min with dry argon. The Schlenk vessel was connected to a gas burette, and the solution was subjected to continuous irradiation by an 180-W Xe high-pressure Xe lamp (Oriol). Infrared radiation of the lamp was removed by absorption in a water flow cell. Wavelength was selected by using a cut-off filter (>390 nm and >530 nm). The reaction temperature was 293 K. GC analyses was performed on an Interscience CompactGC, separating H_2 , CO, CH_4 , O_2 , and N_2 on a 5-Å molsieve column, by using argon as carrier gas and a TCD detector.

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- Lehn J-M (2002) Toward self-organization and complex matter. *Science* 295:2400–2403.
- Cordier P, Tournilhac F, Soulie-Ziakovic C, Leibler L (2008) Self-healing and thermoreversible rubber from supramolecular assembly. *Nature* 451:977–980.
- Knowles TP, et al. (2007) Role of intermolecular forces in defining material properties of protein nanofibrils. *Science* 318:1900–1903.
- Pluth MD, Bergman RG, Raymond KN (2007) Acid catalysis in basic solution: A supramolecular host promotes orthoformate hydrolysis. *Science* 316:85–88.
- Reetz MT (2001) Combinatorial and evolution-based methods in the creation of enantioselective catalysts. *Angew Chem Int Ed* 40:284–310.
- Slagter VF, Roeder M, Kamer PCJ, Van Leeuwen PVNM, Reek JNH (2004) Supraphos: A supramolecular strategy to prepare bidentate ligands. *J Am Chem Soc* 126:4056–4057.
- Breit B, Seiche W (2003) Hydrogen bonding as a construction element for bidentate donor ligands in homogeneous catalysis: Regioselective hydroformylation of terminal alkenes. *J Am Chem Soc* 125:6608–6609.
- Sandee AJ, Reek JNH (2006) Bidentate ligands by supramolecular chemistry—The future for catalysis? *Dalton Trans* 3385–3391.
- Jiang X-B, et al. (2006) Screening of a supramolecular catalyst library in the search for selective catalysts for the asymmetric hydrogenation of a difficult enamide substrate. *Angew Chem Int Ed* 45:1223–1227.
- Lewis NS, Nocera DG (2006) Powering the planet: Chemical challenges in solar energy utilization. *Proc Natl Acad Sci USA* 103:15729–15735.
- Kerr RA, Service RF (2005) What can replace cheap oil—and when? *Science* 309:101.
- Voet D, Voet JG (1995) *Biochemistry* (Wiley, New York), 2nd Ed.
- Peters JW, Lanzilotta WN, Lemon BJ, Seefeldt LC (1998) X-ray crystal structure of the Fe-only hydrogenase (Cpl) from *Clostridium pasteurianum* to 1.8 angstrom resolution. *Science* 282:1853–1858.
- Nicolet Y, Piras C, Legrand P, Hatchikian CE, Fontecilla-Camps JC (1999) *Desulfovibrio desulfuricans* iron hydrogenase: The structure shows unusual coordination to an active site Fe binuclear center. *Structure (London)* 7:13–23.
- Darensbourg MY, Lyon EJ, Zhao X, Georgakaki IP (2003) The organometallic active site of $[\text{Fe}]$ hydrogenase: Models and entatic states. *Proc Natl Acad Sci USA* 100:3683–3688.
- Mealli C, Rauchfuss TB (2007) Models for the hydrogenases put the focus where it should be—Hydrogen. *Angew Chem Int Ed* 46:8942–8944.
- Darensbourg MY, Lyon EJ, Smeets JJ (2000) The bio-organometallic chemistry of active site iron in hydrogenases. *Coord Chem Rev* 206–207:533–561.
- Capon J-F, Gloaguen F, Schollhammer P, Talarmin J (2005) Catalysis of the electrochemical H_2 evolution by di-iron sub-site models. *Coord Chem Rev* 249:1664–1676.
- Yu Z, et al. (2008) Diiron dithiolate complexes containing intraligand $\text{NH}\dots\text{S}$ hydrogen bonds: $[\text{FeFe}]$ hydrogenase active site models for the electrochemical proton reduction of HOAc with low overpotential. *Dalton Trans* 2400–2406.
- Jiang S, et al. (2007) Fe-S complexes containing 5-membered heterocycles: Novel models for the active site of hydrogenases with unusual low reduction potential. *Dalton Trans* 896–902.

21. Rocchini E, *et al.* (2000) Synthesis and properties of iron-group hydrido-cyano complexes $\text{trans-[MH(CN)(L)}_2\text{]}$, M = Fe, Ru or Os, L = diphosphine, and their hydrogen, trifluoroboron and triphenylboron isocyanide derivatives of the type $\text{trans-[MH(CNH)(L)}_2\text{O}_3\text{SCF}_3$, $\text{trans-[MH(CNBX}_3\text{)(L)}_2\text{]}$, X = F or Ph, and $\text{trans-[M(H}_2\text{)(CNBF}_3\text{)(dppp)}_2\text{]BF}_4$ [dppp = $\text{Ph}_2\text{P(CH}_2\text{)}_3\text{PPh}_2$]. *J Chem Soc Dalton Trans* 3591–3602.
22. Sun L, Åkermærk B, Ott S (2005) Iron hydrogenase active site mimics in supramolecular systems aiming for light-driven hydrogen production. *Coord Chem Rev* 249:1653–1663.
23. Kleij AW, Reek JNH (2006) Ligand-template directed assembly: An efficient approach for the supramolecular encapsulation of transition-metal catalysts. *Chem Eur J* 12:4218–4227.
24. Li X, *et al.* (2008) Noncovalent assembly of a metalloporphyrin and an iron hydrogenase active-site model: Photo-induced electron transfer and hydrogen generation. *J Phys Chem B* 112:8198–8202.
25. Borg SJ, Tye JW, Hall MB, Best SP (2007) Assignment of molecular structures to the electrochemical reduction products of diiron compounds related to [Fe-Fe] hydrogenase: A combined experimental and density functional theory study. *Inorg Chem* 46:384–394.
26. Li P, *et al.* (2005) Influence of tertiary phosphanes on the coordination configurations and electrochemical properties of iron hydrogenase model complexes: Crystal structures of $[(\mu\text{-S}_2\text{C}_3\text{H}_6)\text{Fe}_2(\text{CO})_6\text{-nL}_n]$ (L = PMe_2Ph , n = 1, 2; PPh_3 , P(OEt)_3 , n = 1). *Eur J Inorg Chem*, 10.1002/ejic.200400947.
27. Slagt VF, Kamer PCJ, Van Leeuwen PWNM, Reek JNH (2004) Encapsulation of transition metal catalysts by ligand-template directed assembly. *J Am Chem Soc* 126:1526–1536.
28. Closs GL, Miller JR (1988) Intramolecular long-distance electron transfer in organic molecules. *Science* 240:440–447.
29. Kuil M, Soltner T, Van Leeuwen PWNM, Reek JNH (2006) High-precision catalysts: Regioselective hydroformylation of internal alkenes by encapsulated rhodium complexes. *J Am Chem Soc* 128:11344–11345.
30. Tye JW, Darensbourg MY, Hall MB (2006) De novo design of synthetic di-iron(I) complexes as structural models of the reduced form of iron-iron hydrogenase. *Inorg Chem* 45:1552–1559.