

Synthesis, Structure, and Photoinduced Catalysis of [FeFe]-Hydrogenase Active Site Models Covalently Linked to a Porphyrin or Metalloporphyrin Moiety[†]

Li-Cheng Song,* Liang-Xing Wang, Ming-Yi Tang, Chang-Gong Li, Hai-Bin Song, and Qing-Mei Hu

Department of Chemistry, State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, People's Republic of China

Received February 22, 2009

A series of novel light-driven-type models, which contain a single diiron- ADT(azadithiolate) unit or two and four diiron-ADT units covalently bonded to a photosensitizer porphyrin or metalloporphyrin, have been synthesized and structurally characterized. Reaction of complex $[(\mu$ -SCH₂)₂NC₆H₄CHO]Fe₂(CO)₆ (A) with PhCHO, pyrrole, and CF₃CO₂H in CH₂Cl₂ followed by treatment with p-chloranil gave light-driven models 5-[(u-SCH₂)₂NFe₂(CO)₆phenyl]-10,15,20-triphenylporphyrin (1), 5,15-[(u-SCH₂)₂NFe₂(CO)₆phenyl]₂-10,20-diphenylporphyrin (2), and 5, 10-[(u-SCH₂)₂NFe₂(CO)₆phenyl]₂-15,20-diphenylporphyrin (3). While light-driven model 5,10,15, $20-[(\mu-SCH_2)_2NFe_2(CO)_6$ phenyl]₄ porphyrin (4) could be similarly prepared by reaction of complex A with pyrrole and CF_3CO_2H followed by treatment with *p*-chloranil, model 1 could also be prepared by another new method involving a final cyclization step of $(\mu$ -HOCH₂S)₂Fe₂(CO)₆ with (p-aminophenyl)triphenylporphyrin. In addition, the PPh₃-substituted model 5-[(u-SCH₂)₂NFe₂- $(CO)_5(PPh_3)$ phenyl]-10,15,20-triphenyl porphyrin (5) was prepared by reaction of 1 with PPh₃ in the presence of Me_3NO , whereas treatment of 1 with $Zn(OAc)_2$ afforded the metalloporphyrin-containing model $5-[(\mu-SCH_2)_2NFe_2(CO)_6phenyl]-10,15,20$ -triphenylporphyrinozinc (6). X-ray crystallographic studies confirmed that (i) model 3 consists of two diiron-ADT units, which are connected to the two ortho-benzene rings of the porphyrin macrocycle, and (ii) model 6 contains one molecule of MeOH, which is axially coordinated to the Zn atom of the metalloporphyrin macrocycle. Particularly noteworthy is that model 1 was found to be a photoactive catalyst for photoinduced H_2 production, and a possible pathway for such H₂ production is suggested.

Introduction

Since the high-quality crystal structures of [FeFe]-hydrogenases (hereafter referred to as [FeFe]Hases) were re-

[†]Dedicated to Professor Dietmar Seyferth on the occasion of his 80th birthday and in recognition of his outstanding contributions to organometallic chemistry.

(1) (a) Peters, J. W.; Lanzilotta, W. N.; Lemon, B. J.; Seefeldt, L. C. *Science* **1998**, *282*, 1853. (b) Nicolet, Y.; Piras, C.; Legrand, P.; Hatchikian, C. E.; Fontecilla-Camps, J. C. *Structure* **1999**, *7*, 13.

(2) For reviews, see for example: (a) Darensbourg, M. Y.; Lyon, E. J.; Smee, J. J. *Coord. Chem. Rev.* **2000**, 206–207, 533. (b) Evans, D. J.; Pickett, C. J. *Chem. Soc. Rev.* **2003**, 32, 268. (c) Song, L.-C. *Acc. Chem. Res.* **2005**, 38, 21. (d) Capon, J.-F.; Gloaguen, F.; Schollhammer, P.; Talarmin, J. *Coord. Chem. Rev.* **2005**, 249, 1664.

(3) (a) Gloaguen, F.; Lawrence, J. D.; Schmidt, M.; Wilson, S. R.; Rauchfuss, T. B. J. Am. Chem. Soc. **2001**, 123, 12518. (b) Lyon, E. J.; Georgakaki, I. P.; Reibenspies, J. H.; Darensbourg, M. Y. J. Am. Chem. Soc. **2001**, 123, 3268. (c) Razavet, M.; Davies, S. C.; Hughes, D. L.; Barclay, J. E.; Evans, D. J.; Fairhurst, S. A.; Liu, X.; Pickett, C. J. Dalton Trans. **2003**, 586. (d) Tard, C.; Liu, X.; Ibrahim, S. K.; Bruschi, M.; De Giola, L.; Davies, S. C.; Yang, X.; Wang, L.-S.; Sawers, G.; Pickett, C. J. Nature **2005**, 433, 610. (e) Thomas, C. M.; Liu, T.; Hall, M. B.; Darensbourg, M. Y. Inorg. Chem. **2008**, 47, 7009. (f) Song, L.-C.; Li, C.-G.; Gao, J.; Yin, B.-S.; Luo, X.; Zhang, X.-G.; Bao, H.-L.; Hu, Q.-M. Inorg. Chem. **2008**, 47, 4545. (g) Song, L.-C.; Li, C.-G.; Ge, J.-H.; Yang, Z.-Y.; Wang, H.-T.; Zhang, J.; Hu, Q.-M. J. Inorg. Biochem. **2008**, 102, 1973. ported,¹ a great variety of structural and functional model compounds for the active site of [FeFe]Hases, so-called H-clusters, have appeared in the literature.^{2–5} Among these model compounds, the light-driven-type models (which contain a photosensitive cationic complex [Ru(terpyridyl)₂]²⁺,^{4c} porphyrin macrocycle,^{4e} or metalloporphyrin macrocycle^{4f} attached to the catalytic diiron subsite) are of particular interest. This is because such models can allow chemists to explore if the photoexcited electron could be transferred intramolecularly from its photosensitive moiety to a diiron subsite and then could reduce a proton to give hydrogen, a

^{*}To whom correspondence should be addressed. Fax: 0086-22-23504853. E-mail: lcsong@nankai.edu.cn.

^{(4) (}a) Lawrence, J. D.; Li, H.; Rauchfuss, T. B.; Bénard, M.; Rohmer, M.-M. Angew. Chem., Int. Ed. 2001, 40, 1768. (b) Li, H.; Rauchfuss, T. B. J. Am. Chem. Soc. 2002, 124, 726. (c) Ott, S.; Kritikos, M.; Åkermark, B.; Sun, L. Angew. Chem., Int. Ed. 2003, 42, 3285. (d) Capon, J.-F.; Ezzaher, S.; Gloaguen, F.; Pétillon, F. Y.; Schollhammer, P.; Talarmin, J. Chem.—Eur. J. 2008, 14, 1954. (e) Song, L.-C.; Tang, M.-Y.; Su, F.-H.; Hu, Q.-M. Angew. Chem., Int. Ed. 2006, 45, 1130. (f) Song, L.-C.; Tang, M.-Y.; Mei, S.-Z.; Huang, J.-H.; Hu, Q.-M. Organometallics 2007, 26, 1575. (g) Song, L.-C.; Wang, H.-T.; Ge, J.-H.; Mei, S.-Z.; Gao, J.; Wang, L.-X.; Gai, B.; Zhao, L.-Q.; Yan, J.; Wang, Y.-Z. Organometallics 2008, 27, 1409.

 ^{(5) (}a) Song, L.-C.; Yang, Z.-Y.; Bian, H.-Z.; Liu, Y.; Wang, H.-T.;
 Liu, X.-F.; Hu, Q.-M. Organometallics 2005, 24, 6126. (b) Song, L.-C.;
 Yang, Z.-Y.; Hua, Y.-J.; Wang, H.-T.; Liu, Y.; Hu, Q.-M. Organometallics 2007, 26, 2106. (c) Windhager, J.; Rudolph, M.; Bräutigam, S.;
 Görls, H.; Weigand, W. Eur. J. Inorg. Chem. 2007, 2748.

highly efficient, "clean", and renewable fuel.^{6,7} It follows that such a study is not only closely related to production of hydrogen fuel but also closely related to solar energy utilization.8,9

On the basis of our previous studies on light-driven-type models,4e,4f we continued to investigate their synthesis, structure, and properties. Now, we have synthesized a series of new light-driven models, which contain a photosensitive porphyrin or metalloporphyrin moiety covalently bonded to a single diiron-ADT(azadithiolate) unit or two and four diiron-ADT units. Why we chose porphyrin and metalloporphyrin as photosensitizers to construct such models is because they can absorb as much as ca. 45% of the energy of sunlight, and the lifetime of their excited triplet states is much longer than those of common Ru^{II}-based photosensitizers.^{10,11} In addition, we chose diiron-ADT unit to construct this type of models because the ADT bridge was recently suggested to play a key role in H_2 production catalyzed by natural enzymes.^{12,13} In this paper we report the synthetic and structural studies regarding such new lightdriven models. In addition, the photoinduced H₂ production catalyzed by one of such models is also described.

Results and Discussion

Synthesis of Porphyrin-Functionalized Light-Driven Models 1-4 by the Lindsey Method and Their Structural Characterizations. When *p*-benzaldehyde-substituted diiron-ADT complex A reacted with benzaldehvde, pvrrole, and CF_3CO_2H in CH_2Cl_2 at room temperature followed by treatment of the resulting mixture with *p*-chloranil at reflux in a molar ratio of 1:1:2:2:1.5 between the five starting materials, we isolated four products of tetraphenylporphyrin (H₂TPP) and the porphyrin-functionalized light-driven model compounds 1-3 in 14%, 18%, 8%, and 17% yields, respectively (Scheme 1). However, in contrast to this, as described in our communication,4e with treatment of complex A with benzaldehyde, pyrrole, and CF₃CO₂H in CH₂Cl₂ at room temperature followed by treatment with p-chloranil at reflux in a molar ratio of 1:3:4:4:3 between the five starting materials, only two compounds, namely, H₂TPP and 1, could be obtained, in 19% and 23% yields, without obtaining any appreciable amounts of 2 and 3. Such observations imply that both types and yields of the porphyrin-containing model compounds produced from the Lindsey method¹⁴ are substantially influenced by the utilized molar ratio of the five starting materials.

According to the reported mechanistic study of the Lindsey method,¹⁴ the above-mentioned formation of H₂TPP and the porphyrin-functionalized model compounds 1-3 is believed to involve cocyclization of complex A with PhCHO and pyrrole in the presence of catalyst CF₃CO₂H followed by oxidation of the resulting porphyrinogens with *p*-chloranil. In principle, this synthetic method due to inclusion of the two different aldehydes of A and PhCHO should produce not only H_2 TPP and compounds 1-3 with a single diiron-ADT unit and two diiron-ADT units but also another two compounds with three and four diiron-ADT units. However, in this case although H_2 TPP and 1-3 were obtained, the latter two compounds were not able to be isolated due to their too small amounts. Fortunately, one of the latter two, namely, compound 4, with four diiron-ADT units, was successfully prepared by using the Lindsey method involving only one kind of aldehyde. Thus, treatment of A with pyrrole and CF₃CO₂H in CH₂Cl₂ at room temperature followed by oxidation of the intermediate porphyrinogen at reflux with p-chloranil in a molar ratio of A:pyrrole:CF₃CO₂H:p-chloranil = 1:1:1:0.75 resulted in formation of model 4 in 14%vield (Scheme 2).

In view of the structural characterization of 1 being described in our communication,^{4e} we now report the structural characterizations of new compounds 2-4. Compounds 2-4 are air-stable solids. For example, the IR spectra of 2-4displayed three absorption bands in the range 2075-1992 cm⁻¹ for their terminal carbonyls¹⁵ and one absorption band in the region 3314-3365 cm⁻¹ for N-H vibrations of their pyrrole rings.¹⁶ The ¹H NMR spectra of **2–4** each exhibited one singlet in the region 4.43-4.63 ppm for CH₂ groups in their diiron-ADT units and another singlet in the upfield range from -2.71 to -2.81 ppm for NH groups in their pyrrole rings due to strong shielding effects of the porphyrin macrocycle.¹⁷ The mass spectrum of **4** showed a molecular ion M^+ + H peak at m/z 2154.4961. All observed peaks are isotopically resolved and in good agreement with their corresponding theoretical distributions (see Supporting Information). Actually, compound 3 is the isomer of 2, whose structure was confirmed by X-ray diffraction analysis. While the molecular structure of 3 is shown in Figure 1, Table 1 lists its selected bond lengths and angles. As can be seen in Figure 1, compound 3 contains two diiron-ADT units, which are covalently connected through the bridgehead N1 and N2 atoms to C15 and C56 of the two ortho-benzene rings. In addition, the two diiron-ADT units each have a chair and a boat six-membered ring, whose common N1 and N2 atoms are bound to C15 or C56 by an axial type of bond. The bond lengths of Fe1-Fe2 (2.5013 Å) and Fe3-Fe4 (2.5049 Å) in 3 are almost the same as that of Fe1-Fe2 (2.5000 Å) in 1 and very close to those found in similar diiron carbonyl complexes.¹⁸ The C–N bond lengths (1.356-1.377 Å) in the porphyrin macrocycle of 3 are nearly the same as the corresponding ones (1.364-1.378 Å) of 1, lying between

⁽⁶⁾ Lubitz, W.; Tumas, W. Chem. Rev. 2007, 107, 3900.

⁽⁷⁾ Alper, J. Science 2003, 299, 1686.

⁽⁸⁾ For reviews, see for example: (a) Graetzel, M. Acc. Chem. Res. (a) 161 (161) (16

 ⁽b) Eisenberg, R.; Nocera, D. G. Inorg. Chem. 2005, 44, 6799.
 (c) Armaroli, N.; Balzani, V. Angew. Chem., Int. Ed. 2007, 46, 52.

⁽d) Baykara, S. Z. Int. J. Hydrogen Energy 2005, 30, 545.

⁽¹⁰⁾ Darwent, J. R.; Douglas, P.; Harriman, A.; Porter, G.; Richoux, M.-C. Coord. Chem. Rev. 1982, 44, 83.

⁽¹¹⁾ Okura, I. Coord. Chem. Rev. 1985, 68, 53.

⁽¹²⁾ Nicolet, Y.; de Lacey, A. L.; Vernède, X.; Fernandez, V. M.; Hatchikian, E. C.; Fontecilla-Camps, J. C. J. Am. Chem. Soc. 2001, 123,

⁽¹³⁾ Fan, H.-J.; Hall, M. B. J. Am. Chem. Soc. 2001, 123, 3828.

⁽¹⁴⁾ Lindsey, J. S.; Schreiman, I. C.; Hsu, H. C.; Kearney, P. C.; Marguerettaz, A. M. J. Org. Chem. 1987, 52, 827.

⁽¹⁵⁾ Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. Principles and Applications of Organotransition Metal Chemistry, 2nd ed.; California University Science Books: Mill Valley, 1987.

^{(16) (}a) Thomas, D. W.; Martell, A. E. J. Am. Chem. Soc. 1959, 81, 5111. (b) Limnach, H.-H.; Hennig, J.; Stulz, J. J. Chem. Phys. 1983, 78, 5432

^{(17) (}a) Kruper, W. J.; Chamberlin, T. A.; Kochanny, M. J. Org. Chem. 1989, 54, 2753. (b) Bookser, B. C.; Bruice, T. C. J. Am. Chem. Soc. 1991, 113, 4208.

^{(18) (}a) Stanley, J. L.; Rauchfuss, T. B.; Wilson, S. R. Organometallics 2007, 26, 1907. (b) Lyon, E. J.; Georgakaki, I. P.; Reibenspies, J. H.; Darensbourg, M. Y. Angew. Chem., Int. Ed. 1999, 38, 3178. (c) Song, L.-C.; Ge, J.-H.; Zhang, X.-G.; Liu, Y.; Hu, Q.-M. Eur. J. Inorg. Chem. 2006, 3204.

Scheme 1





the normal single and double C–N bond lengths.¹⁹ The four benzene rings are twisted with respect to the planar porphyrin macrocycle in order to minimize the steric repulsions between the two ortho-hydrogen atoms in each of the four phenyl groups with the two proximal pyrrole rings. The dihedral angles between the porphyrin plane and the benzene rings involving C18 and C53 are 71.9° and 87.7°, respectively. It follows that the spectroscopic data of 2-4 and the crystallographic data of 3 are very similar to the corresponding data of 1^{4e} and coincide very well with their structures shown in Schemes 1 and 2.

Synthesis of Light-Driven Model 1 by a New Method and Its Reactions with PPh₃ and Zn(OAc)₂ to Give Porphyrin- and Metalloporphyrin-Functionalized Light-Driven Models 5 and 6. Model 1 could be prepared by another synthetic method in a much higher yield (43%). This method involves a "one-pot" reaction of the bridging thiol complex (μ -HS)₂Fe₂(CO)₆ (prepared by reaction of (μ -S₂)Fe₂(CO)₆ with Et₃BHLi followed by treatment of (μ -LiS)₂Fe₂(CO)₆ with CF₃CO₂H)²⁰ with

^{(19) (}a) Silvers, S. J.; Tulinsky, A. J. Am. Chem. Soc. 1967, 89, 3331.
(b) Sessler, J. L.; Johnson, M. R.; Creager, S. E.; Fettinger, J. C.; Ibers, J. A. J. Am. Chem. Soc. 1990, 112, 9310.

⁽²⁰⁾ Seyferth, D.; Henderson, R. S.; Song, L.-C. J. Organomet. Chem. 1980, 192, C1.



Figure 1. Molecular structure of 3 with 30% probability level ellipsoids.

37% aqueous formaldehyde in THF from -78 °C to room temperature and subsequent treatment of the resulting complex $(\mu$ -HOCH₂S)₂Fe₂(CO)₆²¹ with (*p*-aminophenyl)triphenylporphyrin (Scheme 3).

On the basis of the improved synthesis of model 1, we further studied its chemical reactivities, leading to the preparation of its PPh₃ and porphyrinozinc derivatives. Thus, treatment of 1 with 1 equiv of decarbonylating agent Me₃NO in mixed solvent CH₂Cl₂/MeCN at room temperature followed by treatment with 1 equiv of PPh₃ resulted in formation of the PPh₃-monosubstituted derivative 5 in 46% yield, whereas 1 was treated with excess $Zn(OAc)_2$ in MeOH at room temperature to afford the photosensitizer ZnTPPcontaining model compound 6 in 91% yield (Scheme 4).

Compounds 5 and 6 are air-stable solids, which were characterized by elemental analysis and IR and ¹H NMR spectroscopy, as well as for 6 by X-ray crystallography. The IR spectra of 5 and 6 showed three absorption bands in the region 2043-1933 or 2073-1998 cm⁻¹ for their terminal carbonyls, respectively. The former three bands for 5 are considerably red-shifted relative to those corresponding to 1-4 and 6, obviously due to one of their carbonyls being replaced by the stronger electron donor PPh₃.¹⁵ The ¹H NMR spectrum of 5 displayed one singlet at -2.76 ppm for the two protons attached to N atoms in its pyrrole rings,¹⁷ but in that of 6 this type of singlet disappeared, consistent with the two protons of 1 being replaced by metal cation Zn^{2+} . The ³¹P NMR spectrum of **5** exhibited one singlet at 65.66 ppm for the P atom in its PPh₃ ligand. The molecular structure of 6 was unambiguously confirmed by X-ray crystallography. Figure 2 shows its ORTEP plot, whereas Table 2 lists its selected bond lengths and angles. As shown in Figure 2, compound 6 comprises one diiron-ADT unit and one metalloporphyrin moiety, which are covalently bonded together through N5 and C42 atoms by an axial type of bond. The Fe1–Fe2 bond length of 6 (2.500 Å) is very close

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 3

	8	.,	8,
Fe(1) - S(1)	2.266(2)	N(1)-C(15)	1.413(7)
Fe(1)-S(2)	2.269(2)	Fe(1)-Fe(2)	2.5013(17)
Fe(2)-S(2)	2.259(2)	Fe(3)-Fe(4)	2.5049(7)
Fe(2)-S(1)	2.279(3)	N(3) - C(22)	1.367(7)
S(1) - Fe(1) - S(2)	84.72(7)	S(2) - Fe(2) - Fe(1)	56.67(6)
S(1)-Fe(1)-Fe(2)	56.85(7)	N(3)-C(22)-C(21)	126.4(5)
S(2)-Fe(1)-Fe(2)	56.27(5)	C(13) - N(1) - C(14)	114.1(5)
S(2) - Fe(2) - S(1)	84.67(8)	C(22) - N(3) - C(25)	111.1(4)

to the corresponding one (2.55 Å) in the reduced form of the natural enzymes.¹² In addition, as can be seen in Figure 3, there is one molecule of MeOH axially coordinated to the Zn1 atom with a Zn1–O8 bond length of 2.179 Å. The coordinated MeOH apparently originated from the mixed solvent CHCl₃/MeOH used in the single-crystal growing process. The sum of bond angles around N5 is 356.7°, a value very close to 360°, implying that the p-orbital of the N5 atom is well conjugated with the π -system of the disubstituted benzene ring. In addition, the four benzene rings around the metalloporphyrin moiety are twisted relative to the porphyrin plane with a dihedral angle from 61.2° to 68.1° in order to reduce the steric repulsions between the proximal hydrogen atoms of the benzene and pyrrole rings in the metalloporphyrin macrocycle.

Photoinduced Hydrogen Evolution Catalyzed by Light-Driven Model 1. The photoinduced catalytic systems for H₂ production usually consist of four separate components: an electron donor, a photosensitizer, a catalyst, and a proton source.²²⁻²⁶ However, recently a three-component system was used for study of the photoinduced H_2 production.²⁷ This system is composed of an electron donor, a proton source, and a light-driven model that contains a photosensitizer ZnTPP coordinatively bonded to a simple H-cluster model. It is worth pointing out that this coordinatively assembled model (in fact, it was not isolated and fully characterized; for the isolated and fully characterized one, see ref 4f) is different from our covalently assembled lightdriven models 1-6. In order to examine if such covalently assembled models could act as photoactive catalysts to achieve the expected H_2 production, we chose model 1 to constitute a three-component system with electron donor and proton source, which was utilized to carry out the expected H₂ production experiments.

Interestingly, it was found that H₂ indeed was produced when a 500 W Hg lamp with a UV cutoff filter ($\lambda > 400 \text{ nm}$) irradiated a CH₂Cl₂ solution consisting of model 1, electron donor EtSH, and proton source CF₃CO₂H (TFA) (entry 1, Table 3). However, when the same experiment was carried out in the absence of EtSH or TFA, only a trace amount of H_2 could be detected (entries 2/3, Table 3). Furthermore, no H₂ was delected when the experiment was run without light irradiation or in the absence of model 1, or in the case in which model 1 was replaced by an equimolar mixture of photosensitizer H₂TPP and simple model

(27) Li, X.; Wang, M.; Zhang, S.; Pan, J.; Na, Y.; Liu, J.; Åkermark, B.; Sun, L. J. Phys. Chem. B 2008, 112, 8198.

⁽²²⁾ Ozawa; Haga, M.; Sakai, K. J. Am. Chem. Soc. 2006, 128, 4926.

⁽²³⁾ Rau, S.; Walther, D.; Vos, J. G. Dalton Trans. 2007, 915.

⁽²⁴⁾ Fihri, A.; Artero, V.; Razavet, M.; Baffert, C.; Leibl, W.; Fontecave, M. Angew. Chem., Int. Ed. 2008, 47, 564.

⁽²⁵⁾ Rosenthal, J.; Bachman, J.; Dempsey, J. L.; Esswein, A. J.; Gray, T. G.; Hodgkiss, J. M.; Manke, D. R.; Luckett, T. D.; Pistorio, B. J.;

Veige, A. S.; Nocera, D. G. Coord. Chem. Rev. 2005, 249, 1316.

⁽²⁶⁾ Amao, Y.; Tomonou, Y.; Ishikawa, Y.; Okura, I. Int. J. Hydrogen Energy 2002, 27, 621.





 $[(\mu$ -SCH₂)₂NH]Fe₂(CO)₆ (HADT) (entries 4–6, Table 3). It follows that electron donor EtSH, proton source TFA, lightdriven model 1, and the light irradiation are essential for such photoinduced H₂ production. In addition, the experiments (entries 1/5, Table 3) proved that the separated photosensitive and catalytic moieties cannot replace the corresponding light-driven model 1 to achieve such photoinduced H₂ production. In fact, this is consistent with our previous comparative study^{4e} on the fluorescence emission spectrum of model 1 with those of H₂TPP and an equimolar mixture of H₂TPP and HADT, which revealed that an efficient intramolecular electron transfer occurs from the photoexcited porphyrin moiety to the covalently linked diiron-ADT unit, but not the intermolecular electron transfer between the two separate components H₂TPP and HADT. Figure 3 shows the time dependence of photoinduced H₂ production by using EtSH and p-HSC₆H₄CO₂H as electron donors. As can be seen in Figure 3, during 1 h irradiation the turnover number (TON, calculated based on the catalytic diiron subsite) in the EtSH case reaches 0.31, whereas that in the p-HSC₆H₄CO₂H case is equal to 0.14. This means that EtSH is a better electron donor than p-HSC₆H₄CO₂H. Although the TON

(0.31) found by using the covalently assembled complex **1** is considerably low relative to those obtained by using the other types of covalently assembled photocatalysts,^{22,24} it is the first example to realize such H_2 producion by using the covalently assembled H-cluster model as a photoactive catalyst.

According to our above-mentioned observations and some reported mechanisms for similar cases, ^{11,28} we suggest a pathway to accout for the photoinduced H₂ production catalyzed by light-driven model 1 (Figure 4). That is, when model 1 is irradiated, the electron of the porphyrin moiety of 1 can be excited to give 1*. Then, the photoexcited electron can be transferred intramolecularly to the diiron-ADT unit to give the charge-separated species 1[±]. After 1[±] reduces a proton to give H₂, it becomes 1⁺ with a positive charge on the porphyrin moiety of 1. Furthermore, when 1⁺ gets one electron from the sacrificial electron donor **D**, the photocatalyst 1 is regenerated and the catalytic cycle is completed. Finally, it should be noted that this proposed pathway is mainly speculative and some of its suggested intermediates still need to be further identified.

Concluding Remarks

We have synthesized six novel light-driven models, 1-6, by the Lindsey method with some modifications, as well as by Me₃NO-assisted CO substitution of 1 with PPh₃ and by porphyrin N coordination of 1 with metal cation Zn^{2+} . In addition, we have also prepared model 1 in a much higher yield by another method involving a final cyclization step between (µ-HOCH₂S)₂Fe₂(CO)₆ and (p-aminophenyl)triphenylporphyrin. The structural characterization of 1-6revealed that (i) model 1 contains a photosensitive tetraphenylporphyrin moiety covalently bonded to the N atom of a single diiron-ADT unit, (ii) models 2-4 consist of a tetraphenylporphyrin moiety covalently bonded to each N atom of the two and four diiron-ADT units, and (iii) models 5 and 6 contain a porphyrin moiety or a metalloporphyrin moiety, which is covalently bonded to the N atom of either the all-CO diiron-ADT unit or the PPh3-substituted diiron-ADT unit.

^{(28) (}a) Okura, I.; Kinumi, Y. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 2922.
(b) Miller, D.; McLendon, G. *Inorg. Chem.* **1981**, *20*, 950. (c) Amao, Y.; Tomonou, Y.; Okura, I. *Sol. Energy Mater. Sol. Cells* **2003**, *79*, 103.



Figure 2. Molecular structure of 6. MeOH with 30% probability level ellipsoids.

				0					
TILL	C 1 1	D	r				(1)	6	
I anie Z	Selected	Rond	Lengths (A 1	and A	ngles i	degi	TOP 6	
	DUICUUU	DOING 1			unu 1		uve i		

	-		
Fe(1) - S(1)	2.283(3)	N(5) - C(42)	1.419(9)
Fe(1) - S(2)	2.275(3)	Fe(1)-Fe(2)	2.500(2)
Fe(2) - S(2)	2.268(3)	N(1)-C(1)	1.375(8)
Fe(2)-S(1)	2.285(3)	N(1)-Zn(1)	2.069(6)
S(1) - Fe(1) - S(2)	85.08(9)	Fe(1) - S(1) - Fe(2)	66.37(8)
S(1) - Fe(1) - Fe(2)	56.86(6)	C(46) - N(5) - C(45)	113.6(6)
S(2) - Fe(1) - Fe(2)	56.48(8)	C(1) - N(1) - Zn(1)	126.0(4)
S(2) - Fe(2) - S(1)	85.18(8)	N(1)-Zn(1)-N(3)	166.8(2)

Interestingly, the covalently assembled light-driven model 1 was found to be a catalyst for H₂ production in the presence of a suitable electron donor and the proton source TFA under light irradiation. A possible pathway for such photoinduced H₂ production is suggested, which involves an intramolecular electron transfer process from the photosensitive porphyrin moiety to the catalytic diiron-ADT unit. Further studies are in progress to see if the more diiron-ADT-units-containing models 2-4 and the metalloporphyrin-containing model 6 could have higher photocatalytic activity than model 1. In addition, further structural modifications of models 1-4 to improve their photocatalytic capability will also be carried out by means of the facile substitution of their Fe-attached terminal carbonyls with other ligands^{2c} and the potential coordination capability of their porphyrin macrocycles with other metal cations.^{10,11}

Experimental Section

General Comments. All reactions were carried out under an atmosphere of highly purified nitrogen by using standard Schlenk and vacuum-line techniques. Dichloromethane was distilled from CaH₂ under N₂, methanol from Mg powders, and tetrahydrofuran from Na/benzophenone ketyl. Acetonitrile was distilled once from P₂O₅ and then from CaH₂ under N₂. $(\mu$ -S)₂Fe₂(CO)₆, ²⁹ [(μ -SCH₂)₂NC₆H₄CHO]Fe₂(CO)₆ (A), ^{4e} and (*p*-aminophenyl)triphenylporphyrin^{17a} were prepared according to literature procedures. Et₃BHLi, Zn(OAc)₂, aqueous





Figure 3. Time dependence of photoinduced H_2 production from CH_2Cl_2 solutions (10 mL) consisting of EtSH (\blacksquare , 10 mM) or *p*-HSC₆H₄CO₂H (\triangle , 10 mM) and TFA (10 mM) catalyzed by model **1** (0.1 mM).

CH₂O, pyrrole, benzaldehyde, CF₃CO₂H, tetrachlorobenzoquinone (*p*-chloranil), Me₃NO·2H₂O, PPh₃, EtSH, and *p*-HSC₆H₄CO₂H were available commercially and used as received. Preparative TLC was carried out on glass plates ($25 \times 15 \times 0.25$) coated with silica gel G ($10-40 \mu$ m). IR spectra were recorded on a Bio-Rad FTS 135 infrared spectrophotometer. ¹H and ³¹P NMR spectra were taken on a Bruker Avance 300 and a Varian Mercury Plus 400 NMR spectrometer, respectively. Elemental analyses were performed with an Elementar Vario EL analyzer, while ESI-MS data were obtained on a Bruker APEX IV FT-MS instrument operated in ESI positive mode. Melting points were determined on a Yanaco MP-500 apparatus and were uncorrected.

Preparation of $5-[(\mu-SCH_2)_2NFe_2(CO)_6phenyl]-10,15,20-tri$ $phenylporphyrin (1), <math>5,15-[(\mu-SCH_2)_2NFe_2(CO)_6phenyl]_2-10,20$ diphenylporphyrin (2), and $5,10-[(\mu-SCH_2)_2NFe_2(CO)_6phenyl]_2-$ 15,20-diphenylporphyrin (3) by the Lindsey Method Involving PhCHO and Substituted Benzaldehyde A. The mixture of substituted benzaldehyde A (0.295 g, 0.60 mmol), PhCHO (0.06 mL, 0.60 mmol), pyrrole (0.08 mL, 1.2 mmol), and CF₃CO₂H (0.09 mL, 1.2 mmol) in CH₂Cl₂ (240 mL) was stirred at room

Table 3. Photocatalytic H₂ Production Experiments in CH₂Cl₂ Solutions by Using EtSH as the Sacrificial Electron Donor^{*a*}

entry	photocatalyst	electron donor	proton source	irradiation time	TON
1	model 1	EtSH	TFA	1 h	0.31
2	model 1		TFA	1 h	< 0.01
3	model 1	EtSH		1 h	< 0.01
4	model 1	EtSH	TFA		0
5	H ₂ TPP/HADT	EtSH	TFA	1 h	0
6	,	EtSH	TFA	1 h	0

^a TONs are calculated based on model 1.

temperature in the dark for 15 h to give a purple-red solution. To this solution was added *p*-chloranil (0.221 g, 0.90 mmol), and the new mixture was refluxed for 1 h to give a brown-green solution. Solvent was removed at reduced pressure, and the residue was subjected to flash column chromatography (Al₂O₃, CH₂Cl₂). The eluate was evaporated at reduced pressure to a volume suitable for TLC separation using CH₂Cl₂/petroleum ether (v/v = 1:1) as eluent. From the first band, H₂TPP (0.013 g, 14%) was obtained as a purple solid, which was identified by comparison of its IR and ¹H NMR spectra with those of the authentic sample.^{17,18}

From the second band, model compound 1 (0.036 g, 18%) was obtained as a purple-red solid, which was also identified by comparison of its IR and ¹H NMR spectra with those previously reported.¹⁴ From the third band, compound 2 (0.032 g, 8%) was obtained as a purple-red solid, mp 220 °C (dec). Anal. Calcd for C₆₀H₃₆Fe₄N₆O₁₂S₄: C, 52.05; H, 2.62; N, 6.07. Found: C, 52.24; H, 2.69; N, 5.87. IR (KBr disk): *v*_{NH} 3325 (m); *v*_{C≡O} 2075 (s), 2034 (vs), 1992 (vs) cm⁻¹. ¹H NMR (300 MHz, CDCl₃): -2.81 (s, 2H, 2NH), 4.43 (s, 8H, 4CH₂), 6.92, 6.94 (2s, 4H, 4 m-H of C₆H₄), 7.66, 7.68 (2s, 6H, 4 *m*-H of C₆H₅, 2 *p*-H of C₆H₅), 8.00, 8.03 (2s, 4H, 4 o-H of C₆H₄), 8.13, 8.15 (2s, 4H, 4 o-H of C₆H₅), 8.77 (s, 8H, pyrrole rings) ppm. From the fourth band, 3 (0.070 g, 17%) was obtained as a purple-red solid, mp 214 °C (dec). Anal. Calcd for C₆₀H₃₆Fe₄N₆O₁₂S₄: C, 52.05; H, 2.62; N, 6.07. Found: C, 51.97; H, 2.87; N, 5.93. IR (KBr disk): v_{NH} 3314 (m); $\nu_{C=0}$ 2073 (vs), 2034 (vs), 1997 (vs) cm⁻¹. ¹H NMR (300 MHz, CDCl₃): -2.74 (s, 2H, 2NH), 4.57 (s, 8H, 4CH₂), 7.06, 7.09 (2s, 4H, 4m-H of C₆H₄), 7.75, 7.77 (2s, 6H, 4m-H of C₆H₅, 2p-H of C₆H₅), 8.12, 8.15 (2s, 4H, 4 *o*-H of C₆H₄), 8.21, 8.24 (2s, 4H, 4 o-H of C₆H₅), 8.86 (s, 8H, pyrrole rings) ppm.

Preparation of 5-[(µ-SCH₂)₂NFe₂(CO)₆phenyl]-10,15,20-triphenylporphyrin (1) by a New Method. A red solution of $(\mu$ -S)₂Fe₂(CO)₆ (0.172 g, 0.50 mmol) in THF (10 mL) was cooled to -78 °C and then treated dropwise with Et₃BHLi (1.0 mL, 1.0 mmol) to give a green solution containing $(\mu$ -LiS)₂Fe₂(CO)₆. After stirring for 15 min, CF₃CO₂H (0.16 mL, 2.0 mmol) was added to cause an immediate color change from green to red, indicating the complete conversion of (µ-LiS)₂Fe₂(CO)₆ to $(\mu$ -HS)₂Fe₂(CO)₆. After the mixture was stirred for an additional 10 min at -78 °C, 37% aqueous formaldehyde (0.085 mL, 1.0 mmol) was added. The new mixture was allowed to warm to room temperature and stirred at this temperature for 1 h to give $(\mu$ -HOCH₂S)₂Fe₂(CO)₆. After (*p*-aminophenyl)triphenylporphyrin (0.30 g, 0.50 mmol) was added, the new mixture was stirred at room temperature for 1.5 h. Solvent was removed in vacuo, and the residue was subjected to TLC using $CH_2Cl_2/$ petroleum ether (v/v = 2:1) as eluent. From the purple band, 1 (0.215 g, 43%) was obtained as a purple-red solid.

Preparation of 5,10,15,20-[(μ -SCH₂)₂NFe₂(CO)₆phenyl]₄porphyrin (4) by the Lindsey Method Involving Only the Substituted Benzaldehyde A without PhCHO. A solution of A (0.147 g, 0.30 mmol), pyrrole (0.021 mL, 0.30 mmol), and CF₃CO₂H (0.023 mL, 0.30 mmol) in CH₂Cl₂ (30 mL) was stirred at room temperature in the dark for 24 h to give a purple-red solution. To this solution was added *p*-chloranil (0.055 g, 0.225 mmol), and the new mixture was refluxed for 1 h to give a brown-green



Figure 4. Proposed photocatalytic pathway for H_2 production catalyzed by model 1.

solution. Solvent was removed at reduced pressure, and the residue was subjected to flash column chromatography (Al₂O₃, CH₂Cl₂). The eluate was evaporated in vacuo to a suitable volume for TLC separation using CH₂Cl₂/acetone (v/v = 1:1) as eluent. From the first band, **4** (0.092 g, 57%) was obtained as a purple solid, mp 156 °C (dec). Anal. Calcd for C₇₆H₄₂Fe₈-N₈O₂₄S₈: C, 42.37; H, 1.96; N, 5.20. Found: C, 42.11; H, 1.95; N, 5.29. IR (KBr disk): v_{NH} 3365 (m); $v_{C=0}$ 2075 (vs), 2033 (vs), 1998 (vs) cm⁻¹. ¹H NMR (300 MHz, CDCl₃): -2.71 (s, 2H, 2NH), 4.63 (s, 16H, 8CH₂), 7.13, 7.16 (2s, 8H, 8 *m*-H of C₆H₄), 8.17, 8.19 (2s, 8H, 8 *o*-H of C₆H₄), 8.88 (s, 8H, pyrrole rings) ppm. ESI-MS: *m/z* 2154.4961 [M⁺ + H].

Preparation of 5-[(µ-SCH₂)₂NFe₂(CO)₅(PPh₃)phenyl]-10,15,20triphenylporphyrin (5) by CO Substitution of 1 with PPh₃. A solution of Me₃NO·2H₂O (0.004 g, 0.034 mmol) in MeCN (5 mL) was added gradually to a stirred solution of model 1 (0.034 g, 0.034 mmol) in CH₂Cl₂ (10 mL) at room temperature. After the mixture was stirred at this temperature for 20 min, PPh₃ (0.010 g, 0.034 mmol) was added and the new mixture was stirred at room temperature for 1 h. Volatiles were removed under vacuum, and the residue was subjected to TLC using CH_2Cl_2 /petroleum ether (v/v = 1:1) as eluent. From the main band, compound 5 (0.018 g, 46%) was obtained as a purple-red solid, mp 195 °C (dec). Anal. Calcd for $C_{69}H_{48}Fe_2N_5O_5PS_2{\rm :}$ C, 67.16; H, 3.92; N, 5.68. Found: C, 67.13; H, 3.91; N, 5.75. IR (KBr disk): $\nu_{\rm NH}$ 3317 (m); $\nu_{\rm C=0}$ 2043 (vs), 1985 (vs), 1933 (s) cm⁻ ¹H NMR (300 MHz, CDCl₃): -2.76 (s, 2H, 2NH), 3.21, 4.41, 4.44 (3s, 4H, 2CH₂), 6.97, 6.99 (2s, 2H, 2m-H of C₆H₄), 7.51 (s, 9H, 3 p-H and 6 m-H of P(C₆H₅)₃), 7.75 (s, 9H, 3 p-H and 6 m-H of C₆H₅), 7.85 (s, 6H, 6 o-H of P(C₆H₅)₃), 8.05, 8.07 (2s, 2H, 2 *o*-H of C₆H₄), 8.21, 8.23 (2s, 6H, 6 *o*-H of C₆H₅), 8.84 (s, 8H, pyrrole rings) ppm. ³¹P NMR (121 MHz, CDCl₃, 85% H₃PO₄): 65.66 (s) ppm.

Preparation of 5-[(µ-SCH₂)₂NFe₂(CO)₆phenyl]-10,15,20-triphenylporphyrinozinc (6) by Coordination Reaction of 1 with Zn-(OAc)₂. To a saturated MeOH solution (2 mL) of Zn(OAc)₂ was added model 1 (0.100 g, 0.100 mmol), and then the mixture was stirred at room temperature for 10 h. The resulting mixture was filtered, and the filtrate was sequentially washed using an aqueous solution saturated with NaHCO3 or NaCl. The separated organic layer was dried with anhydrous MgSO₄. After removal of MgSO₄, volatiles were evaporated under vacuum and the residue was subjected to TLC using CH₂Cl₂/petroleum ether (v/v = 2:1) as eluent. From the main band, compound 6 (0.097 g, 91%) was obtained as a purple-red solid, mp 220 °C (dec). Anal. Calcd for C₅₂H₃₁Fe₂N₅O₆S₂Zn: C, 58.75; H, 2.94; N, 6.59. Found: C, 58.51; H, 3.10; N, 6.47. IR (KBr disk): *v*_{C≡O} $2073 (s), 2034 (vs), 1998 (vs) cm^{-1}$. ¹H NMR (400 MHz, CDCl₃): 4.38 (s, 4H, 2CH₂), 6.99, 7.01 (2s, 2H, 2 m-H of C₆H₄), 7.75 7.77 (m, 9H, 3 p-H and 6 m-H of C₆H₅), 8.14, 8.16 (2s, 2H, 2 o-H

Table 4. Crystal Data and Structure Refinement Details for 3 and 6

	3	6
mol formula	$C_{60}H_{36}Fe_4N_6O_{12}$ $S_4 \cdot C_6H_4Cl_2$	$\begin{array}{c} C_{52}H_{31}Fe_2N_5O_6\\ S_2Zn\cdot 2MeOH \end{array}$
mol wt	1531.58	1127.09
cryst syst	triclinic	triclinic
space group	$P\overline{1}$	$P\overline{1}$
a/Å	12.306(8)	17.693(15)
$b/\text{\AA}$	16.377(10)	17.919(15)
$c/\text{\AA}$	18.815(11)	19.180(17)
α/deg	106.470(5)	109.077(8)
β/deg	100.242(9)	110.158(13)
γ/deg	105.804(9)	102.100(2)
$V/Å^3$	3363(4)	5026(7)
Z	2	4
$D_{\rm c}/{\rm g~cm^{-3}}$	1.513	1.489
abs $coeff/mm^{-1}$	1.114	1.186
F(000)	1552	2304
index ranges	$-14 \le h \le 14$	$-20 \le h \le 21$
-	$-19 \le k \le 19$	$-21 \le k \le 21$
	$-22 \le l \le 22$	$-21 \le l \le 22$
$2\theta_{\rm max}/{\rm deg}$	50	50.02
no. of rflns	30 324	37 545
no. of indep rflns	11775	17 379
goodness of fit	1.093	1.112
R	0.0753	0.0865
R _w	0.1872	0.1826
largest diff peak and hole/e $Å^{-3}$	0.577 and -0.625	0.746 and -0.681

of C₆H₄), 8.22, 8.24 (2s, 6H, 6 *o*-H of C₆H₅), 8.96, 8.98 (2s, 8H, pyrrole rings) ppm.

Photoinduced H₂ Evolution Catalyzed by Light-Driven Model 1. A 30 mL Schlenk flask equipped with a N₂ inlet tube, a serum cap, a magnetic stir-bar, and a water-cooling jacket was charged with model **1** (1 mg, 0.001 mmol), EtSH (7 μ L, 0.1 mmol) or *p*-HSC₆H₄CO₂H (15 mg, 0.1 mmol), CF₃CO₂H (7 μ L, 0.1 mmol), and CH₂Cl₂ (10 mL). While stirring, the resulting solution was thoroughly deoxygenated by bubbling with nitrogen and then was irradiated through a Pyrex-glass filter ($\lambda > 400$ nm) using a 500 W Hg lamp at about 25 °C (controlled by the cooling jacket) for 1 h. The purpose of using such a UV cutoff filter is to obtain visible light and to avoid decomposition of EtSH and *p*-HSC₆H₄CO₂H.³⁰ During the photoinduced cata-

(30) Weiss, J.; Fishgold, H. Nature 1936, 137, 71.

lysis, the evolved H₂ was withdrawn periodically using a gastight syringe, which was analyzed by gas chromatography on a Shimadazu GC-2014 instrument with a thermal conductivity detector and a carbon molecular sieve column (3 mm × 2.0 m) and N₂ as the carrier gas. The total amount of H₂ produced during 1 h irradiation is 0.31×10^{-3} mmol when using EtSH, whereas the corresponding amount of H₂ is 0.14×10^{-3} mmol when EtSH was replaced by *p*-HSC₆H₄CO₂H.

X-ray Structure Determination of 3 and 6. Single crystals of 3 suitable for X-ray diffraction analysis were grown by slow evaporation of its o-Cl₂C₆H₄/hexane solution at room temperature, whereas those of 6 were obtained by slow diffusion of MeOH into its CHCl₃ solution at room temperature. A single crystal of 3 or 6 was mounted on a Rigaku MM-007 (rotating anode) diffractometer equipped with a Saturn 70CCD. Data were collected at room temperature, using a confocal monochromator with Mo K α radiation ($\lambda = 0.71070$ A) in the $\omega - \phi$ scanning mode. Data collection, reduction, and absorption correction were performed by the CRYSTALCLEAR program.³¹ The structures were solved by direct methods using the SHELXS-97 program³² and refined by full-matrix leastsquares techniques $(SHELXL-97)^{33}$ on F^2 . Hydrogen atoms were located by using the geometric method. Details of crystal data, data collections, and structure refinements are summarized in Table 4.

Acknowledgment. We are grateful to the National Natural Science Foundation of China and the Research Fund for the Doctoral Program of Higher Education of China for financial support.

Supporting Information Available: Full tables of crystal data, atomic coordinates, and thermal parameters and bond lengths and angles for **3** and **6** as CIF files. The ESI-MS spectrum of **4**. These materials are available free of charge via the Internet at http://pubs.acs.org.

(33) Sheldrick, G. M. SHELXL97, A Program for Crystal Structure Refinement; University of Göttingen: Germany, 1997.

⁽³¹⁾ Sheldrick, G. M. SADABS, A Program for Empirical Absorption Correction of Area Detector Data; University of Göttingen: Germany, 1996.

⁽³²⁾ Sheldrick, G. M. SHELXS97, A Program for Crystal Structure Solution; University of Göttingen: Germany, 1997.