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The Active Site Model for Iron-Only Hydrogenases Coordinatively Bonded to a Metalloporphyrin Photosensitizer

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*Summary: Treatment of the parent model [(μ-SCH$_2$)$_2$NH]Fe$_2$(CO)$_6$ (**1**) with 4-pyridinecarboxylic acid chloride or benzoyl chloride in the presence of Et$_3$N afforded the simple model compounds [(μ-SCH$_2$)$_2$NC(O)C$_5$H$_4$N]Fe$_2$(CO)$_6$ (**2**) and [(μ-SCH$_2$)$_2$NC(O)Ph]Fe$_2$(CO)$_6$ (**4**). Further treatment of **2** with the photosensitizer zinc tetraphenylporphyrin (ZnTPP) produced the target model compound [(μ-SCH$_2$)$_2$NC(O)C$_5$H$_4$N]Fe$_2$(CO)$_6$(ZnTPP) (**3**), which is the first metalloporphyrin-containing active site model for the Fe-only hydrogenases.*

The iron-only hydrogenases (FeHases) that can catalyze hydrogen evolution or uptake in microorganisms have attracted special attention.[1,2] X-ray crystallography[3] and FTIR spectroscopy[4] revealed that the active site of FeHases, the so-called H-cluster, consists of a 4Fe4S cluster linked to a diiron subsite via the sulfur atom of a cysteinyl group. At the diiron subsite the two iron atoms are coordinated by CO and cyanide ligands and additionally are bridged by a dithiolate cofactor. Recently, the bridging dithiolate was suggested to be an azadithiolate (ADT, SCH$_2$NHCH$_2$S), in which the middle N atom plays an essential role in the heterolytic cleavage or formation of H$_2$ in the enzymatic process.[5] The well-elucidated structure of the H-cluster and its unusual hydrogen-producing ability have prompted chemists to synthesize various model compounds.[6,7] We and others reported light-driven types of model compounds in which a photosensitizer such as the tetraphenylporphyrin (TPP) moiety[8] or a ruthenium terpyridine complex [Ru(terpy)$_2$]$^{2+}$ [9] is covalently bonded to a simple model for the H-cluster in an attempt to achieve H$_2$ production under the photolysis conditions. As shown in Figure 1, in the expected light-driven process, the photosensitizer in one such model will first absorb a photon. Then, the photoexcited photosensitizer is oxidatively quenched by direct means or through a spacer by the diiron site of the simple model moiety to give a reduced iron intermediate. After regeneration of the original photosensitizer by extraction of an electron from an external donor, this process is repeated to produce a doubly reduced diiron intermediate that could reduce protons to hydrogen. Herein we report the first light-driven model in which the photosensitizer metalloporphyrin MTPP (M = Zn) is coordinatively bonded to a simple biomimetic model.

The synthetic route for one such model compound, **3**, is shown in Scheme 1. Treatment of the parent ADT-type model complex [(μ-SCH$_2$)$_2$NH]Fe$_2$(CO)$_6$ (**1**)[7b] with 4-pyridinecarboxylic acid chloride in the presence of Et$_3$N afforded the simple pyridyl-containing ADT-type complex [(μ-SCH$_2$)$_2$NC(O)C$_5$H$_4$N]Fe$_2$(CO)$_6$ (**2**).[10] Further treatment of **2** with the metalloporphyrin ZnTPP resulted in formation of the target model compound [(μ-SCH$_2$)$_2$NC(O)C$_5$H$_4$N]Fe$_2$(CO)$_6$(ZnTPP) (**3**).[11]

The above-described synthetic route for **3** is convenient, and high yields are obtained. Furthermore, the metalloporphyrin ZnTPP in **3** is a good photosensitizer, since it can absorb up to 30% of the solar energy and can form the excited triplet state with a long lifetime ($\tau_T = 1200\ \mu s$) and in high quantum yield ($\phi_T = 0.88$).[12] Particularly noteworthy is that the successful synthesis of **3** can permit one to make a comparative study on

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[10] Synthesis of **2**: a solution of **1** (0.232 g, 0.60 mmol), 4-pyridinecarboxylic acid chloride (0.255 g, 1.80 mmol), and Et$_3$N (0.40 mL. 2.90 mmol) in CH$_2$Cl$_2$ (10 mL) was stirred at room temperature for 3 h. After the resulting Et$_3$NHCl precipitate was filtered, the filtrate was concentrated to ca. 1 mL under vacuum and then subjected to TLC separation using petroleum ether/acetone (5/2 v/v) as eluent. **2** (0.247 g, 84%) was obtained as a red solid from the major band. Anal. Calcd for C$_{14}$H$_8$Fe$_2$N$_2$O$_7$S$_2$: C, 34.17; H, 1.64; N, 5.69. Found: C, 34.15; H, 1.72; N, 5.64. IR (KBr disk): $\nu_{C\equiv O}$ 2074 (s), 2012 (vs), 1975 (vs), $\nu_{C=O}$1656 (s) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ 4.07, 4.30 (2 s, 4H, 2CH$_2$), 7.34 (d, J = 6.0 Hz, 2H, 2 α-H of pyridine ring), 8.77 (d, J = 6.0 Hz, 2H, 2 β-H of pyridine ring).

[11] Synthesis of **3**: a solution of **2** (0.019 g, 0.04 mmol) and zinc tetraphenylporphyrin (0.027 g, 0.04 mmol) in CH$_2$Cl$_2$ (1.0 mL) was allowed to stand at room temperature for 4 h, and then the resulting solution was layered with hexane (5.0 mL) for 3 days to give 0.041 g (88%) of **3** as a purple solid. Anal. Calcd for C$_{58}$H$_{36}$Fe$_2$N$_6$O$_7$S$_2$Zn: C, 59.53; H, 3.10; N, 7.18. Found: C, 59.54; H, 3.21; N, 7.12. IR (KBr disk): $\nu_{C\equiv O}$ 2078 (s), 2039 (vs), 2002 (vs), $\nu_{C=O}$ 1664 (s), $\nu_{\text{pyrrole ring}}$1523 (m), 1486 (m), 1439 (m) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ 3.27(d, 2H, 2 α-H of pyridine ring), 3.87, 4.07 (2 s, 4H, 2CH$_2$), 5.95 (d, 2H, 2 β-H of pyridine ring), 7.73 (s, 12H, 8 m-H and 4 p-H of C$_6$H$_5$), 8.20 (s, 8H, 8 o-H of C$_6$H$_5$), 8.89 (s, 8H, pyrrole rings).

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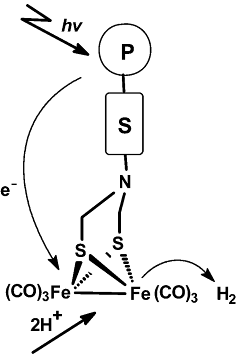
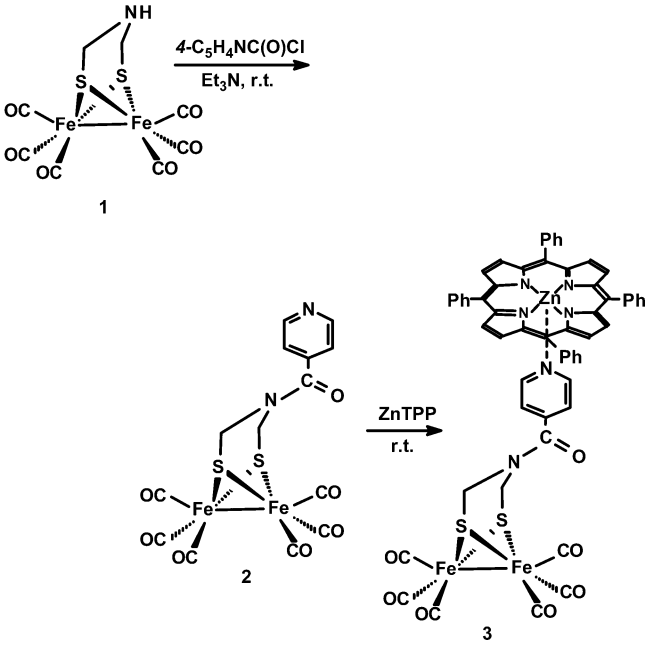


Figure 1. Simple illustration for the photoinduced proton reduction to hydrogen: (P) photosensitizer; (S) spacer.

Scheme 1



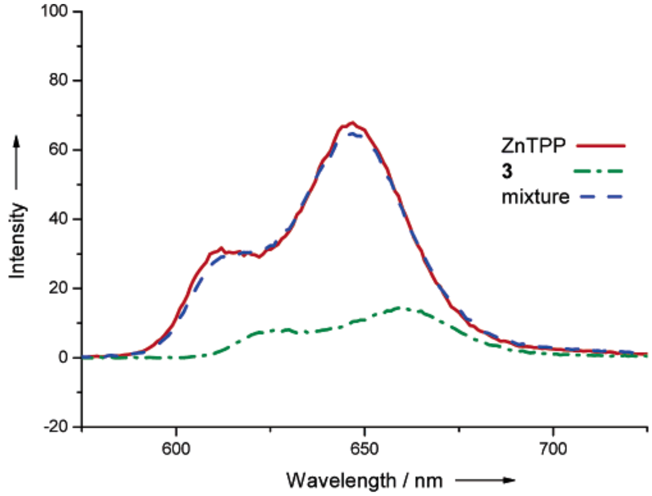


Figure 2. Fluorescence emission spectra ($\lambda_{ex} = 440$ nm) of **3**, ZnTPP, and an equimolar mixture of ZnTPP and **4** in CH_2Cl_2 (1×10^{-3} M).

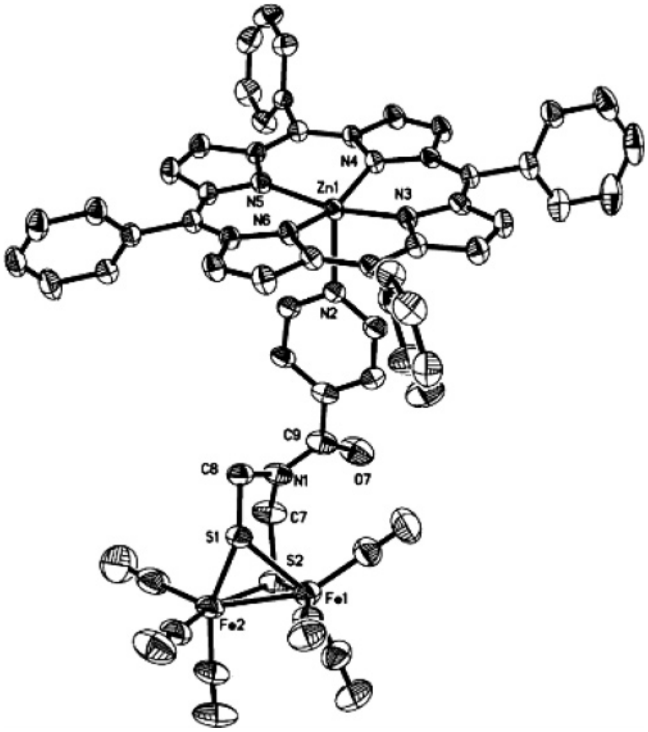


Figure 3. Molecular structure of **3** (30% probability displacement ellipsoids). Selected bond lengths (Å) and angles (deg): Fe1−Fe2 = 2.5147(15), Fe1−S1 = 2.2449(19), N1−C8 = 1.429(7), Zn1−N2 = 2.200(4), Zn1−N3 = 2.043(4); S1−Fe1−S2 = 84.95(7), Fe2−S1−Fe1 = 68.18(6), C8−N1−C7 = 116.0(5), N3−Zn1−N4 = 89.67(15), N3−Zn1−N2 = 96.58(16).

the influence of the bond type between the photosensitizer and the simple model upon electron transfer and H_2 production under the photolysis conditions.

The model compound **3** and its precursor **2** have been fully characterized by elemental analysis and various spectroscopic methods.[10,11] The IR spectrum of **3** displays three absorption bands at 1523, 1486, and 1439 cm^{-1} for the skeleton vibrations of the pyrrole rings in its metalloporphyrin ZnTPP;[13] it also displays three absorption bands at 2078, 2039, and 2002 cm^{-1} due to its terminal carbonyls and one absorption band at 1664 cm^{-1} for its pyridyl group attached carbonyl in the coordinated **2**. The ^1H NMR spectrum of **3** exhibits all of the proton signals for the corresponding organic groups in the metalloporphyrin moiety,[14] as well as two doublets at δ 3.27 and 5.95 for the protons of the pyridyl group and two singlets at δ 3.88 and 4.08 for those of the methylene groups in the coordinated **2**. The remarkably high field shift for the protons of the pyridyl group in coordinated **2** compared to those (δ 7−9) in free ligand **2** obviously is due to the strong shielding effect of the metalloporphyrin macrocycle upon the axially coordinated **2**.[15] The UV/vis spectrum of **3** displays one Soret band at 427 nm and two Q bands at 559 and 600 nm, which are very close to those reported for free ZnTPP.[14]

The fluorescence emission spectra of **3**, ZnTPP, and an equimolar mixture of ZnTPP and $[(\mu\text{-}SCH_2)_2NC(O)Ph]Fe_2(CO)_6$ (**4**) determined under the same conditions are shown in Figure 2. Actually, **4** is an analogue of the simple model **2** without the

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pyridyl N atom, which was prepared and fully characterized (see the Supporting Information) in order to compare the fluorescence spectral properties between model **3** and the mixture of **4** with ZnTPP. As shown in Figure 2, **3** shows two fluorescence emission bands at 626 and 659 nm, which are red-shifted by 13−14 nm relative to the corresponding bands of free ZnTPP.[16] Importantly, these bands are strongly quenched in complex **3**, with a quenching efficiency of 78%. It is believed that the markedly decreased intensities of the two fluorescence bands of **3** relative to those of free ZnTPP are mainly due to the strong intramolecular electron transfer from the photoexcited ZnTPP moiety to the coordinatively bonded **2**, but not by an intermolecular collision process between molecules of **3**.[17] This is because the intensities of the two fluorescence bands of the equimolar mixture of ZnTPP and **4** are nearly the same as those of the corresponding bands of free ZnTPP. Apparently, such a strong intramolecular electron transfer is important for the photoinduced proton reduction to H_2 catalyzed by the light-driven types of models.[8,9]

The molecular structures of the target model compound **3** (Figure 3) and the simple model **2** (Figure 4) have been confirmed by X-ray diffraction techniques.[18] As shown in Figure 3, model **3** contains a diiron−ADT moiety in which a boat six-membered ring (Fe1−S1−C8−N1−C7−S2) is fused together with a chair six-membered ring (Fe2−S1−C8−N1−C7−S2) and the pyridylcarbonyl group is attached to the N1 atom by an axial type of bond.[7c,8] Both iron atoms adopt a square-pyramidal geometry with an Fe−Fe distance of 2.5147(15) Å, close to those reported for the oxidized form (2.62 and 2.60 Å)[3] and the reduced form (2.55 Å)[5a] of the natural enzyme active sites.

X-ray crystallography also revealed that the metalloporphyrin moiety of **3** is indeed coordinatively bonded to the N2 atom of the pyridyl group via its central Zn1 atom. The Zn1−N2 bond length is equal to 2.200(4) Å. In addition, the dihedral angle between the pyridine ring and the porphyrin plane is about 82°, whereas the four benzene rings are twisted relative to the porphyrin plane with a twist angle from 67.0 to 82.5°. Apparently, such a benzene ring arrangement occurs in order to reduce the steric repulsions between the benzene ring hydrogen atoms close to the porphyrin moiety and those of the pyrrole rings.

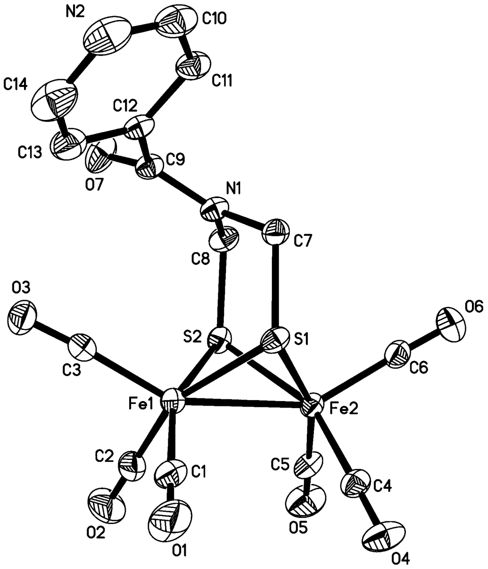

Figure 4. Molecular structure of **2** (30% probability displacement ellipsoids). Selected bond lengths (Å) and angles (deg): Fe1−Fe2 = 2.5114(14), Fe1−S1 = 2.2650(18), N1−C7 = 1.443(6), N1−C9 = 1.354(7); S1−Fe1−Fe2 = 55.82(4), Fe2−S1−Fe1 = 67.65-(5), S1−Fe1−S2 = 84.62(6), C8−N1−C7 = 115.1(4).

In conclusion, we have synthesized and fully characterized the first light-driven model compound (**3**), which contains a photosensitizer coordinatively bonded to a simple model (**2**). Since the synthetic method of **3** is based on coordination of the central metal atom in the metalloporphyrin ZnTPP with the pyridyl N atom of **2**, it can be expected that a great variety of such coordination types of models could be similarly prepared by reactions of the other metalloporphyrins[19] with **2** or the other simple pyridyl-containing models. Further syntheses of such light-driven models and studies of their catalytic ability for proton reduction to hydrogen are in progress in our laboratory.

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Supporting Information Available: CIF files giving X-ray crystallographic data for **2**−**4** and text and figures giving details of the synthesis and characterization of **2**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[18] X-ray data for **3**: $C_{58}H_{36}Fe_2N_6O_7S_2Zn{\cdot}2o\text{-}Cl_2C_6H_4$, triclinic, space group $P\bar{1}$, $a = 11.076(3)$ Å, $b = 11.521(3)$ Å, $c = 27.595(7)$ Å, $\alpha = 94.493(4)°$, $\beta = 98.338(4)°$, $\gamma = 107.800(4)°$, $F(000) = 1488$, GOF = 1.009. X-ray data for **2**: $C_{14}H_8Fe_2N_2O_7S_2$, monoclinic, space group $C2/c$, $a = 25.027(10)$ Å, $b = 9.658(4)$ Å, $c = 14.988(7)$ Å, $\beta = 92.606(8)°$, $F(000) = 1968$, GOF = 1.123.

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