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Novel Ruthenium Phthalocyanine-Containing Model Complex for the Active Site of [FeFe]-Hydrogenases: Synthesis, Structural Characterization, and Catalytic H₂ Evolution

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Supporting Information

ABSTRACT: The first phthalocyanine (Pc) macrocyclecontaining [FeFe]-hydrogenase model complex, (*i*-BuO)₈PcRu(CO)(μ -PDT)[(Ph₂P)₂NCH₂C₅H₄N]Fe₂(CO)₄ (**6**), has been prepared by a multistep synthetic route. The treatment of 4-picolylamine with Ph₂PCl/Et₃N in CH₂Cl₂ at room temperature gave 4-picolyl-substituted azadiphosphine (Ph₂P)₂NCH₂C₅H₄N (**1**), whereas further treatment of **1** with diiron complex (μ -PDT)Fe₂(CO)₆ in refluxing *o*-xylene produced the 4-picolylazadiphosphine-chelated diiron complex (μ -PDT)[(Ph₂P)₂NCH₂C₅H₄N]Fe₂(CO)₄ (**2**). While 3,6dibudenty function that the start of the start of



dihydroxyphthalonitrile reacted with *i*-BuBr/K₂CO₃ in DMF at 80 °C to give 3,6-diisobutoxyphthalonitrile 3, further reaction of 3 with lithium wire in refluxing *i*-BuOH afforded isobutoxyphthalocyanine (*i*-BuO)₈PcH₂ (4). Furthermore, 4 reacted with Ru₃(CO)₁₂ in refluxing PhCN to give ruthenium phthalocyanine (*i*-BuO)₈PcRu(CO)₂ (5). Finally, CO substitution reaction of 5 with diiron complex 2 in the presence of Me₃NO in CH₂Cl₂ resulted in formation of the targeted model complex 6. While all the new compounds 1-6 were structurally characterized, complex 6 was found to be a catalyst for photoinduced H₂ generation.

INTRODUCTION

[FeFe]-hydrogenases (hereafter abbreviated as [FeFe]Hases) are metalloenzymes that can catalyze proton reduction to hydrogen with rapid rates in many microorganisms.¹ In recent years, [FeFe]Hases have attracted considerable attention, largely due to their unique structure and particularly their special catalytic function for the production of "clean" and renewable hydrogen fuel.² The X-ray crystallographic³⁻⁶ and FTIR spectroscopic⁷⁻⁹ studies demonstrated that the active site of [FeFe]Hases (so-called H-cluster)¹⁰ is composed of a butterfly Fe_2S_2 cluster and a cubane-like Fe_4S_4 cluster, which are linked together by a cysteine S atom. In addition, the two iron atoms in the Fe_2S_2 cluster are coordinated by a dithiolate cofactor and a given amount of CO and CN⁻ diatomic ligands (Scheme 1a). Although Szilagyi and co-workers have recently suggested the dithiolate cofactor to be most likely an oxadithiolate by using an X-ray crystallographic refinement to close to atom resolution and the DFT optimizations,¹¹ the other groups have presented experimental evidence of ¹⁴N HYSCORE,^{12a} controlled metalloenzyme activation,^{12b} and heterolytic cleavage of H₂ by an iron hydrogenase model¹³ to support that the dithiolate cofactor is most likely an azadithiolate.

Inspired by the structural information on the H-cluster described above, synthetic chemists have designed and prepared a variety of biomimetic models for the active site of [FeFe]Hases.^{14–31} Among these prepared models, the light-driven (or photoactive) models are of particular interest.^{28–31}

This is because such models might enable chemists to study the photoinduced H₂ production catalyzed by a dyad assembly that contains a photosensitizer directly or indirectly attached to the catalytic diiron subsite of a simple [FeFe]Hase model. To date, although several light-driven models have been prepared, none of them contain the well-known photosensitive phthalocyanine (Pc) macrocycles. Phthalocyanines (Pcs) are 18 π -electron conjugated aromatic systems formally made of four isoindole units connected at their 1,3-positions by aza-bridges. These two-dimensional aromatic macrocycles not only have unique structures but also have many invaluable properties.³²⁻³⁴ For example, they can present a strong absorption in the red and near-infrared region of the solar spectrum with considerably large extinction coefficients and high fluorescence quantum yields. In addition, a wide range of substituents and more than 70 different metal and nonmetal atoms can be incorporated in the Pc macrocycles by which the physicochemical and photochemical properties of the corresponding Pc derivatives could be modified and controlled.³²⁻³⁴ Therefore, to develop the synthetic methodology of [FeFe]Hase models and to prepare the first Pc macrocycle photosensitizer-containing model complex, we initiated this study. Fortunately, we have successfully synthesized such a targeted model in which the

Special Issue: Organometallics in Asia

Received: December 31, 2015

Scheme 1. (a) Basic Structure of the Active Site of [FeFe]Hases (X = CH₂, NH, or O); (b) Targeted Model Reported in This Article



pyridine N atom of a simple diiron model is coordinated to the central Ru atom of the isobutoxy-substituted phthalocyanine macrocycle (Scheme 1b). In this article, we report the synthesis and structural characterization of this novel model along with its five new precursors. In addition, the photoinduced H_2 production catalyzed by the targeted model is also described.

RESULTS AND DISCUSSION

Synthesis and Characterization of New Precursors $(Ph_2P)_2NCH_2C_5H_4N$ (1) and $(\mu$ -PDT)[$(Ph_2P)_2NCH_2C_5H_4N$]-Fe₂(CO)₄ (2). According to our designed synthetic route to the targeted light-driven model, the new precursors 1 and 2 should be first prepared. As shown in Scheme 2, treatment of 4-





picolylamine with diphenylphosphine chloride in the presence of triethylamine in CH_2Cl_2 at room temperature gave the 4picolyl-substituted azadiphosphine **1** in 65% yield. Further CO substitution reaction of the all-carbonyl diiron complex (μ -PDT)Fe₂(CO)₆ (PDT = SCH₂CH₂CH₂S) with azadiphosphine **1** in *o*-xylene at reflux afforded the simple 4picolylazadiphosphine-chelated diiron model **2** in 52% yield.

Precursors 1 and 2 are air-stable solids, which have been characterized by elemental analysis and various spectroscopic techniques. For example, the ¹H NMR spectra of 1 and 2 showed one signal at ca. 4.6 ppm for their NCH₂ groups attached to their pyridine rings, whereas the ³¹P{¹H} NMR spectra of 1 and 2 displayed one singlet at 62.6 and 120.2 ppm for their two chemically equivalent P atoms. The considerably downfield shift of the ${}^{31}P{}^{1}H$ NMR signal of 2 compared to that of 1 is obviously due to the chelation of diphosphine 1 with the electron-withdrawing diiron carbonyl unit in 2. In addition, the IR spectrum of 2 exhibited three strong absorption bands in the range 1986–1908 cm⁻¹ for its terminal carbonyls, which is very close to those of the previously reported analogues.³⁵ The molecular structure of 2 was unequivocally confirmed by X-ray diffraction analysis. While Figure 1 shows its ORTEP view, Table 1 lists the selected bond lengths and angles. As shown in Figure 1, complex 2 contains a PDT ligand, which is bridged between Fe1 and Fe2 atoms to



Figure 1. ORTEP view of 2 with 30% probability level ellipsoids. Hydrogen atoms are omitted for clarity.

form two fused six-membered rings. One is the chair-shaped Fe1S1C5C6C7S2 ring, and another is the boat-shaped Fe2S1C5C6C7S2 ring. In addition, it also contains a 4-picolyl azadiphosphine, $(Ph_2P)_2NCH_2C_5H_4N$, ligand, which is chelated between Fe1 and Fe2 atoms with a symmetrically cisoid basal/basal coordination pattern to constitute a five-membered Fe1P1N1P2Fe2 ferracycle. The Fe1–Fe2 bond length (2.4998 Å) of **2** is slightly shorter than that (2.5103 Å) of its parent complex $(\mu$ -PDT)Fe₂(CO)₆³⁶ but slightly longer than those found in other azadiphosphine-chelated diiron complexes, such as $(\mu$ -PDT)Fe₂(CO)₄[(Ph₂P)₂N(*i*-Pr)] (Fe1–Fe2 = 2.4836 Å) and $(\mu$ -PDT)Fe₂(CO)₄[(Ph₂P)₂N(*n*-Bu)] (Fe1–Fe2 = 2.4837 Å).³⁵

Synthesis and Characterization of New Precursors 3,6-(*i*-BuO)₂-1,2-(NC)₂C₆H₄ (3), (*i*-BuO)₈PcH₂ (4), and (*i*-BuO)₈PcRu(CO)₂ (5). In order to synthesize the targeted lightdriven model, the other three new precursors 3-5 should also be prepared. Scheme 3 shows that (i) 3,6-diisobutoxyphthalonitrile 3 could be prepared in 96% yield by etherification reaction of 3,6-dihydroxyphthalonitrile with *i*-BuBr in the presence of K₂CO₃ at 80 °C in DMF; (ii) treatment of the isobutanol solution of 3 with lithium wire at reflux resulted in formation of octaisobutoxyphthalocyanine 4 in 14% yield; and (iii) the ruthenium dicarbonyl phthalocyanine 5 was prepared in 65% yield by reaction of free phthalocyanine 4 with Ru₃(CO)₁₂ in refluxing PhCN. It is worth noting that the formation of 5 is unexpected since reaction of free phthalocyanine *t*-Bu₄PcH₂ with Ru₃(CO)₁₂ in refluxing PhOH

0 1			
Fe(1) - C(1)	1.769(3)	P(2)-N(1)	1.723(2)
Fe(1) - P(1)	2.2043(11)	Fe(2)-P(2)	2.1996(11)
Fe(1)-S(1)	2.2510(10)	N(1)-C(20)	1.481(3)
Fe(1)-Fe(2)	2.4998(10)	Fe(2)-S(2)	2.2636(10)
P(1)-Fe(1)-S(1)	151.57(3)	Fe(1)-S(1)-Fe(2)	67.29(3)
P(1)-Fe(1)-S(2)	87.36(3)	P(1)-N(1)-P(2)	121.30(13)
P(1)-Fe(1)-Fe(2)	96.87(3)	N(1)-P(1)-Fe(1)	112.37(8)
N(1)-P(2)-Fe(2)	113.06(8)	P(2)-Fe(2)-Fe(1)	96.24(3)

Table 1. Selected Bond	l Lengths	[Å] and	Angles	[deg]	for	2
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Scheme 3. Synthetic Route to Precursors 3-5



gave rise to the corresponding ruthenium monocarbonyl phthalocyanine analogue. 37

Precursors 3-5 are also air-stable solids, which have been characterized by elemental analysis and various spectroscopic methods. The ¹H NMR spectra of **3** and **4** displayed a doublet at 3.80 and 4.71 ppm assigned respectively to their OCH₂ groups, whereas 5 showed a multiplet in the range 4.30-4.98 ppm for its OCH₂ groups. Apparently, such a considerably downfield shift of the ¹H NMR signals of 4 and 5 relative to that of 3 is similar to their analogues due to the deshielding effect of the phthalocyanine macrocycles.^{38,39} In addition, the IR and ${}^{13}C{}^{1}H$ NMR spectra of 5 are also similar to its analogues by showing one strong absorption band at 1956 cm⁻¹ for its two terminal carbonyls and one signal at 183.6 ppm for its two C atoms in its two terminal carbonyls.^{38,39} The molecular structures of the phthalocyanine derivatives 4 and 5 were unambiguously confirmed by X-ray crystallographic study. Their ORTEP views are presented in Figures 2 and 3, whereas the selected bond lengths and angles are given in Tables 2 and 3, respectively. As shown in the top view of Figure 2, compound 4 is indeed a macrocyclic molecule of 1,4,8,11,15,18,22,25-octaisobutoxyphthalocyanine. The core skeleton of this molecule deviates remarkably from planarity to form a saddle-shaped structure, which can be seen in the side view of Figure 2. Similar to its analogues,^{40,41} the two pairs of isoindoles A1A2 and B1B2 are turned aside in an opposite direction. The top view of Figure 3 shows that complex 5 contains a metal atom, Ru1, that is coordinated by the four N1/ N1A/N3/N3A nitrogen atoms and the two C1O1/C1AO1A terminal carbonyls to form an octahedral geometry. In addition,

the side view of Figure 3 shows that the two terminal carbonyls C1O1 and C1AO1A are perpendicular to the metallophthalocyanine macrocycle with angles of O1–C1–Ru1 (176.1°) and C1–Ru1–C1A (180.0°). The dihedral angle between A1 and B2 or A2 and B1(12.82°) in **5** is much smaller than that (25.06°) of its precursor **4**. To the best of our knowledge, complex **5** is the first crystallographically characterized metallophthalocyanine in which two terminal carbonyl ligands are axially coordinated to the central ruthenium atom, although some metallophthalocyanines with one axially bonded carbonyl ligand are known and crystallographically characterized.^{37–39,42}

Synthesis and Characterization of Model Complex (*i*-BuO)₈PcRu(CO)(μ -PDT)[(Ph₂P)₂NCH₂C₅H₄N]Fe₂(CO)₄ (6). On the basis of synthesis and structural characterization of new precursors 1–5, we have successfully synthesized the targeted model complex 6 via the last step in our designed synthetic route. This step involves the CO subsitution reaction of ruthenium dicarbonyl phthalocyanine 5 with 4-picolylazadi-phosphine-chelated diiron complex 2 in the presence of decarbonylating agent Me₃NO·2H₂O in CH₂Cl₂ at room temperature to give the targeted model 6 in 61% yield (Scheme 4).

Photoactive model **6** is an air-stable solid, and its structure has been fully characterized by elemental analysis, spectroscopy, and X-ray diffraction analysis. The IR spectrum of **6** showed three strong absorption bands in the region 2000-1932 cm⁻¹ for the terminal carbonyls attached to its iron and ruthenium atoms.^{38,39,43} The ¹H NMR spectrum of **6** displayed a singlet at 7.48 ppm for the eight aromatic protons attached to the four isoindole rings in its phthalocyanine macrocycle. This ¹H NMR

(a)





Figure 2. (a) Top ORTEP view and (b) side ORTEP view of 4 with 30% probability level ellipsoids. Hydrogen atoms are omitted for clarity.

signal is very close to that (7.47 ppm) displayed by its precursor 5. Consistent with its IR spectrum is that the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 6 exhibited one signal at 180.1 ppm for the one carbonyl attached to its ruthenium atom and two signals at 211.5 and 213.0 ppm for the four carbonyls attached to its iron atoms. The ${}^{31}P\{\bar{}^{1}H\}$ NMR spectrum of 6 showed a singlet at 119.1 ppm for its two chemically equivalent P atoms. This $^{31}P{^{1}H}$ NMR signal is very close to that (120.2 ppm) of its precursor 2. The molecular structure of 6 was confirmed by Xray crystallography. The ORTEP view of 6 is depicted in Figure 4, while Table 4 lists its selected bond lengths and angles. As shown in Figure 4, model complex 6 contains one molecule of diiron complex 2, whose pyridine N9 atom is coordinated to the Ru1 atom of the ruthenium monocarbonyl isobutoxyphthalocyanine moiety generated from ruthenium dicarbonyl isobutoxyphthalocynine 5 by loss of one of its two terminal CO ligands. In addition, the Ru1 atom is coordinated with the N1/ N3/N5/N7 nitrogen atoms and C95O9 terminal carbonyl ligand. The bond length Ru1-C95 (1.849 Å) is shorter than the corresponding Ru1-C1 bond length (1.967 Å) in its precursor 5, and the bond length of C95O9 (1.148 Å) is increased by 0.264 Å relative to that of C1O1 (0.884 Å) in its precursor 5. The Fe1–Fe2 bond length (2.4733 Å) is slightly shorter than that (2.4998 Å) of its precursor 2 due to the steric effect between the metallophthalocyanine macrocycle and ligand 2. It is interesting to note that complex 6 is the first



Figure 3. (a) Top ORTEP view and (b) side ORTEP view of **5** with 30% and 20% probability level ellipsoids, respectively. Hydrogen atoms are omitted for clarity.

prepared and crystallographically characterized photoactive complex with a metallophthalocyanine macrocycle that is attached to a simple [FeFe]Hase model complex.

UV-Vis Absorption Spectra and Fluorescence Emission Spectra of Light-Driven Model 6 and Related **Compounds.** To study and understand the photoinduced H₂producing behavior catalyzed by our light-driven model 6 (see bolow), we determined the UV-vis absorption spectra of 4-6and fluorescence emission spectra of 5, 6, and an equimolar mixture of 2 and 5 under the same conditions. As shown in Figure 5, the UV-vis spectrum of free phthalocyanine 4 shows one Soret band at 328 nm and three Q bands in the range 673-765 nm, whereas the ruthenium dicarbonyl phthalocyanine 5 displays one Soret band at 298 nm and two Q bands at 632 and 702 nm. It follows that the Soret and Q bands of 5 are considerably blue-shifted respectively by a maximum of 30 or 63 nm relative to the corresponding bands of its precursor free phthalocyanine 4 due to the ruthenium coordination effect.^{42,44} In addition, the UV-vis spectrum of light-driven model 6 shows one Soret band at 300 nm and two Q bands at 631 and 702 nm, which are just slightly red-shifted respectively by a maximum of 1-2 nm relative to the corresponding bands of its precursor 5. The fluorescence emission spectra of precursor 5, light-driven model 6, and the equimolar mixture of simple

Table 2. Selected Bond Lengths $[{\rm \AA}]$ and Angles [deg] for 4 and 5

	4		
O(1)-C(9)	1.446(5)	N(1)-C(4)	1.335(5)
O(2)-C(8)	1.368(5)	N(2)-C(3)	1.367(5)
O(3)-C(21)	1.366(5)	N(3)-C(3)	1.333(5)
O(4)-C(29)	1.436(5)	N(4)-C(20)	1.367(5)
C(5) - O(1) - C(9)	116.0(3)	N(1)-C(4)-N(2)	127.6(3)
C(8) - O(2) - C(13)	115.7(3)	N(3)-C(17)-N(4)	127.1(4)
C(20)-N(4)-C(17)	111.5(3)	O(1)-C(9)-C(10)	111.3(4)
C(3)-N(2)-C(4)	106.5(3)	O(2) - C(8) - C(2)	124.3(4)
	5		
Ru(1)-C(1)	1.838(6)	C(16)–N(4)	1.323(7)
Ru(1)-N(3)	2.005(5)	N(2)-C(17)	1.338(7)
Ru(1)-N(1)	2.015(4)	N(3)-C(35)	1.364(7)
O(1) - C(1)	1.2175(11)	N(2)-C(34)	1.388(7)
C(1)-Ru(1)-N(3)	91.5(3)	N(3)-Ru(1)-N(1)	89.87(18)
C(1)-Ru(1)-N(1)	89.4(2)	C(35)-N(3)-Ru(1)	124.9(4)
C(17)-N(1)-Ru(1)	125.2(4)	O(1)-C(1)-Ru(1)	174.9(7)
C(34)-N(2)-C(17)	125.5(5)	C(35)-N(3)-C(34)	109.6(5)

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Ru(1)-C(95)	1.849(3)	N(1)-C(4)	1.366(4)
Ru(1)-N(1)	2.013(2)	P(2)-N(10)	1.724(2)
Ru(1)-N(9)	2.173(2)	Fe(1)-P(1)	2.1913(9)
Fe(1)-Fe(2)	2.4733(7)	Fe(1)-S(1)	2.2494(9)
O(9) - C(95) - Ru(1)	175.5(3)	N(1)-Ru(1)-N(9)	87.91(9)
C(95)-Ru(1)-N(1)	95.44(11)	P(1)-Fe(1)-S(1)	87.65(3)
N(5)-Ru(1)-N(1)	176.20(9)	S(1)-Fe(1)-S(2)	84.33(3)
N(1)-Ru(1)-N(3)	89.64(9)	S(1)-Fe(2)-Fe(1)	56.56(2)
P(2)-Fe(2)-Fe(1)	100.38(3)	C(65)-N(9)-Ru(1)	122.35(19)

Scheme 4. Synthetic Route to Light-Driven Model 6



model 2 and precursor 5 are recorded in Figure 6. The fluorescence emission spectrum of 6 displays only one emission band at 729 nm, which is slightly blue-shifted by 2 nm relative to the corresponding band of 5 but is obviously quenched (quenching efficiency Q = 25%) compared with that of 5. Since the intensity of the fluorescence emission band of the equimolar mixture of 2 and 5 is nearly the same as that of 5, it is believed that the decreased intensity with Q = 25% of the fluorescence emission band of 6 relative to that of 5 is most likely due to the appropriate intramolecular electron transfer (ET) from the photoexcited ruthenium phthalocyanine macrocycle to the catalytic diiron subsite of simple model 2 via the coordinatively bonded 4-picolylazadiphosphine 1,^{42,44} but not by an intermolecular collision process between molecules of 6.^{28a,45}

Photoinduced H_2 Production Catalyzed by Light-Driven Model 6 with a Three-Component System.



Figure 4. ORTEP view of **6** with 30% probability level ellipsoids. Hydrogen atoms are omitted for clarity.

Generally, there are two major classes of catalytic systems used for photoinduced H_2 production. The first catalytic system consists of four separate components, namely, an electron donor, a photosensitizer, a catalyst, and a proton source.^{46–52}

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Table 4. Crystal Data and Structure Refinements Details for 2, 4, 5, and 6

	2	4	5	6
mol formula	$C_{37}H_{32}Fe_2N_2O_4P_2S_2{\cdot}1.25CH_2Cl_2$	$C_{32}H_{41}N_4O_4\cdot CHCl_3$	C ₆₆ H ₈₀ N ₈ O ₁₀ Ru	$C_{102}H_{112}Fe_2N_{10}O_{13}P_2RuS_2$
mol wt	912.56	665.06	1246.45	2024.85
cryst syst	triclinic	triclinic	triclinic	monoclinic
space group	$P\overline{1}$	$P\overline{1}$	$P\overline{1}$	P2(1)/c
a/Å	13.634(4)	7.949(4)	8.906(4)	16.5432(16)
b/Å	15.907(5)	14.096(7)	12.166(5)	32.515(3)
c/Å	20.456(7)	15.683(8)	15.992(7)	20.7429(19)
α/deg	74.973(9)	87.595(9)	106.291(5)	90
β /deg	89.387(12)	82.722(9)	105.192(5)	111.0100(10)
γ/deg	66.619(8)	77.709(8)	97.839(4)	90
$V/Å^3$	3912(2)	1703.0(15)	1563.3(12)	10415.9(17)
Ζ	4	2	1	4
$D_c/g\cdot cm^{-3}$	1.550	1.295	1.324	1.291
abs coeff/mm ⁻¹	1.144	0.311	0.315	0.552
F(000)	1866	700	656	4224
index ranges	$-17 \le h \le 17$	$-9 \le h \le 8$	$-10 \le h \le 9$	$-19 \le h \le 19$
	$-20 \le k \le 20$	$-15 \le k \le 16$	$-14 \le k \le 14$	$-38 \le k \le 32$
	$-15 \le l \le 26$	$-12 \le l \le 18$	$-19 \le l \le 19$	$-20 \le l \le 24$
no. of reflns	33 213	8440	12 379	52 145
no. of indep reflns	18 459	5944	5492	18 401
$2\theta_{\rm max}/{ m deg}$	55.78	50.02	50.04	50.04
R	0.0471	0.0696	0.0828	0.0435
R _w	0.1131	0.1899	0.2181	0.1135
GOF	1.048	1.015	1.140	1.075
largest diff peak, hole/e Å ⁻³	0.928/-0.640	0.668/-0.704	2.35/-1.24	1.682/-0.536



The second catalytic system is composed of three separate components, namely, an electron donor, a proton source, and a complicated photoactive catalyst in which a photosensitizer is attached to a simple catalyst.^{28–31,53–57} In order to test whether our model **6** could be used as a photoactive catalyst to realize expected H₂ production, we carried out a study on photo-induced H₂ production using a three-component catalytic system that contains light-driven model **6**, electron donor Et₃N, and proton source H₂O. It was found that H₂ was indeed generated when a THF solution of the three-component system was irradiated by a 50 W Xe lamp with a UV cutoff filter ($\lambda > 400$ nm). However, when the same experiment was carried out in the absence of any one of the three components or without light irradiation, no H₂ evolution was observed. It follows that the presence of electron donor Et₃N, proton source



Figure 6. Fluorescence emission spectra ($\lambda_{ex} = 630$ nm) of **5**, **6**, and an equimolar mixture of **2** and **5** in THF (1×10^{-5} M).

H₂O, light-driven model **6**, and light irradiation is essential for such photoinduced H₂ production. In addition, as shown in Figure 7, the H₂ production increased linearly during 140 min irradiation and then became very slow. A total of 180 min irradiation produced 0.13×10^{-3} mmol of H₂. Such a low catalytic efficiency is mainly due to serious decomposition of model **6** evidenced by a color change of the dark green solution to blue. It is interesting to note that **6** is the first phthalocyanine-macrocycle-containing [FeFe]Hase model that has been found to be a catalyst for photoinduced H₂ production, although the catalytic efficiency is low.

To compare the photoinduced catalytic efficiency of the light-driven model 6-containing three-component system with the simple model 2-containing four-component system, we further carried out a control experiment for the photoinduced



Figure 7. Time dependence of photoinduced H_2 production from a THF (4 mL) solution of Et_3N (1.44 M) and H_2O (4 mL) catalyzed by light-driven model 6 (0.10 mM).

 H_2 production using the four-component system consisting of simple model **2**, electron donor Et_3N , photosensitizer Ru phthalocyanine **5**, and proton source H_2O . The experiment was conducted under the same conditions as those using the threecomponent system involving light-driven model **5**. As a result, no H_2 evolution was observed during 120 min light irradiation. It follows that the intermolecular ET from the photoexcited photosensitizer **5** to the catalytic diiron subsite of simple model **2** could not occur. This is consistent with the aforementioned spectral study that the fluorescence emission spectrum of the equimolar mixture of **2** and **5** is almost the same as that of **5**.

According to the above-mentioned fluorescence spectral study and photoinduced H_2 production study as well as the previously reported mechanisms for photoinduced H_2 production catalyzed by other light-driven models (such as the photosensitizer porphyrin or C_{60} -containing models),^{58,59} we might suggest a pathway to account for the photoinduced H_2 production catalyzed by light-driven model **6**. As shown in Figure 8, when model **6** is irradiated, the electron of the Pc



Figure 8. Suggested pathway for photoinduced H_2 production catalyzed by model **6**.

moiety in 6 can be excited to give 6^* . Then, the excited electron can be transferred intramolecularly to the diiron-PDT unit to give the charge-separated species 6^\pm . After 6^\pm reduces protons to give H₂, it becomes 6^+ with a positive charge on the Pc moiety of 6. Furthermore, when 6^+ gets one electron from the sacrificial electron donor **D**, the photocatalyst 6 is regenerated and the catalytic cycle is completed. Finally, it should be noted that although this suggested pathway appears to be reasonable, some details regarding this pathway still need to be further investigated.

CONCLUSIONS

We have synthesized the first Pc-macrocycle-containing lightdriven model complex 6 via the following six separated reaction steps: (i) amination reaction of Ph₂PCl with 4-picolylamine with the aid of Et₃N to give azadiphosphine 1; (ii) CO substitution reaction of diiron complex $(\mu$ -PDT)Fe₂(CO)₆ with 1 in o-xylene to produce azadiphosphine-chelated diiron complex 2; (iii) etherification reaction of 3,6-dihydroxyphthalonitrile with *i*-BuBr/K₂CO₃ to afford 3,6-diisobutoxyphthalonitrile 3; (iv) cyclization reaction of 3 with i-BuOH/Li to afford phthalocyanine macrocycle 4; (v) coordination reaction of 4 with $Ru_3(CO)_{12}$ to yield ruthenium dicarbonyl phthalocyanine 5; and finally (vi) CO substitution reaction of 5 with diiron complex 2 to yield the targeted model 6. The Xray crystallographic study on metallophthalocyanine 5 confirms that it is a ruthenium dicarbonyl phthalocynine molecule, in which its Ru(II) center is coordinated to four N atoms of the Pc macrocycle and its two terminal CO ligands are perpendicular to the Pc macrocycle plane. Interestingly, 5 is the first crystallographically characterized metallophthalocyanine in which two terminal CO ligands are axially coordinated to the central metal atom. In addition, the X-ray crystallographic study on model 6 confirms that it is indeed a dyad assembly that contains one molecule of the 4-picolylazadiphosphine-chelated diiron complex 2 and the pyridine N atom of complex 2 is coordinated to the Ru(II) center of the ruthenium isobutoxyphthalocyanine macrocycle. Particularly worth noting is that the three-component system consisting of model 6, electron donor Et₃N, and proton source H₂O has been found to be a catalytic system for photoinduced H₂ production, although the production efficiency is low due to the weak intramolecular ET from the excited RuPc macrocycle to the catalytic diiron subsite of simple model 2 as well as serious decomposition of light-driven model 6 under such photocatalytic conditions.

EXPERIMENTAL SECTION

General Comments. All reactions were performed by using standard Schlenk and vacuum-line techniques under highly prepurified N2. Solvents were distilled under nitrogen by using standard procedures. $(\mu$ -PDT)Fe₂(CO)₆⁶⁰ was prepared according to the published method. Other chemicals such as 4-picolylamine, 3,6dihydroxyphthalonitrile, Ph2PCl, Me3NO·2H2O, Ru3(CO)12, and Ru(bpy)₃Cl₂·6H₂O were purchased from commercial suppliers and used without further purification. Preparative TLC was carried out on glass plates ($26 \times 20 \times 0.25$ cm) coated with silica gel H ($10-40 \mu$ m). IR spectra were recorded on a Bruker Tensor 27 infrared spectrophotometer. ¹H, ¹³C{¹H}, and ³¹P{¹H} NMR spectra were taken on a Bruker Avance 400 NMR spectrometer. Elemental analyses were performed with an Elementar Vario EL analyzer. UV-vis spectra and fluorescence emission spectra were recorded using a Hitachi U-3900 spectrophotometer and a Hitachi F-4600 spectrophotometer, respectively. Melting points were determined on an X-4 microscopic melting point apparatus and were uncorrected.

Preparation of $(Ph_2P)_2NCH_2C_5H_4N$ (1). A 100 mL three-necked flask equipped with a dropping funnel, a mechanical agitator, and a serum cap was charged with 4-picolylamine (0.56 g, 5.0 mmol), triethylamine (1.02 g, 10.0 mmol), and 20 mL of CH_2Cl_2. After the mixture was cooled to 0 °C, a solution of diphenylphosphine chloride (2.21 g, 10.0 mmol) in 10 mL of CH_2Cl_2 was dropwise added, and then the new mixture was stirred at room temperature for 4 h. After removal of the volatiles at reduced pressure, the residue was washed thoroughly with water (3 × 10 mL) and ethyl alcohol (3 × 5 mL) and finally dried under vacuum to give 1 as a white solid (1.55 g, 65%), mp 136–138 °C. Anal. Calcd for C₃₀H₂₆N₂P₂: C, 75.62; H, 5.50; N, 5.88.

Found: C, 75.54; H, 5.46; N, 5.81. IR (KBr disk): ν_{C-H} 3069 (s), 3052 (s), $\nu_{C=N}$ 1599 (s), $\nu_{C=C}$ 1478 (s), 1433 (vs), ν_{C-N} 1265 (s), ν_{C-P} 1091 (vs), ν_{N-P} 1057 (s) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): 4.52 (t, ³J_{P-H} = 10.8 Hz, 2H, NCH₂), 6.64 (d, *J* = 5.2 Hz, 2H, *m*-H of NC₅H₄), 7.28–7.38 (m, 20H, 4C₆H₅), 8.26 (d, *J* = 5.2 Hz, 2H, *o*-H of NC₅H₄) ppm. ¹³C{¹H} NMR (100 MHz, CDCl₃): 55.5 (NCH₂), 123.4, 128.4, 129.2, 132.8, 133.1, 138.9, 149.2 (C₆H₅, NC₅H₄) ppm. ³¹P{¹H} NMR (162 MHz, CDCl₃, 85% H₃PO₄): 62.6 (s) ppm.

Preparation of $(\mu$ -PDT)[(Ph₂P)₂NCH₂C₅H₄N]Fe₂(CO)₄ (2). A 100 mL three-necked flask equipped with a reflux condenser, a magnetic stir-bar, and a serum cap was charged with 1 (0.476 g, 1.0 mmol), (µ-PDT)Fe2(CO)6 (0.386 g, 1.0 mmol), and 50 mL of oxylene. After the stirred mixture was refluxed for 1 h, solvent was removed at reduced pressure, and then the residue was subjected to TLC separation with CH_2Cl_2 /ethyl acetate (v/v = 30:1) as eluent. From the major red band, 2 was obtained as a red solid (0.419 g, 52%), mp 240-241 °C. Anal. Calcd for C₂₇H₂₂Fe₂N₂O₄P₂S₂: C, 55.11; H, 4.00; N, 3.47. Found: C, 55.07; H, 4.06; N, 3.19. IR (KBr disk): $\nu_{C\equiv 0}$ 1986 (s), 1955 (vs), 1908 (s) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): 2.10 (br s, 2H, CH₂CH₂CH₂), 2.24, 2.48 (2br s, 4H, 2SCH₂), 4.66 (br s, 2H, NCH₂), 6.99-7.77 (m, 24H, 4C₆H₅, NC₅H₄) ppm. ¹³C{¹H} NMR (100 MHz, CDCl₃): 25.3 (CH₂CH₂CH₂), 31.3 (SCH₂), 52.4 (NCH₂), 127.5, 128.2, 128.3, 128.4, 130.2, 131.5, 132.2, 132.8, 132.9, 135.1, 139.2 (C_6H_5 , NC_5H_4), 212.6, 214.4 ($C\equiv$ O) ppm. ³¹P{¹H} NMR (162 MHz, CDCl₃, 85% H₃PO₄): 120.2 (s) ppm.

Preparation of 3,6-(*i***-BuO)₂-1,2-(NC)₂C₆H₄ (3). A 250 mL threenecked flask equipped as that for the preparation of 2 was charged with 3,6-dihydroxyphthalonitrile (8.0 g, 50 mmol),** *i***-BuBr (16.3 mL, 150 mmol), K₂CO₃ (41.4 g, 200 mmol), and 150 mL of DMF. The reaction mixture was stirred at 80 °C for 16 h. After the mixture was cooled to room temperature, it was poured into 800 mL of ice water. The resulting white solid was filtered and washed thoroughly with water and dried in air. 3 was obtained as a white solid (13.0 g, 96%), mp 194–196 °C. Anal. Calcd For C₁₆H₂₀N₂O₂: C, 70.56; H, 7.40; N, 10.29. Found: C, 70.41; H, 7.23; N, 10.18. IR (KBr disk): \nu_{C=H} 2975 (s), 2932 (m), 2904 (m), 2874 (m), \nu_{C=N} 2223 (s), \nu_{C-O} 1287 (vs), 1269 (s) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): 1.05 (d,** *J* **= 6.4 Hz, 12H, 4CH₃), 2.09–2.20 (m, 2H, 2CH), 3.80 (d,** *J* **= 6.4 Hz, 4H, 20CH₂), 7.14 (s, 2H, C₆H₂) ppm. ¹³C{¹H} NMR (100 MHz, CDCl₃): 19.1 (CH₃), 28.3 (CH), 76.4 (OCH₂), 105.2, 113.2, 118.7, 155.4 (CN, C₆H₂) ppm.**

Preparation of (i-BuO)₈PcH₂ (4). The same equipped flask as that for the preparation of 2 was charged with 3 (2.72 g, 10.0 mmol) and 60 mL of isobutanol. While stirring, the mixture was heated to 80 °C, and then lithium wire (2.10 g, 300 mmol) was added in portions. The resulting mixture was refluxed for 3 h. After the mixture was cooled to room temperature, it was poured into 250 mL of ice water. The mixture was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic phase was washed with brine and dried with anhydrous MgSO₄. After removal of the drying agent and volatiles, the residue was subjected to neutral Al₂O₃ column chromatography with toluene/ THF (v/v = 60:1) as eluent. From the major green band, 4 was obtained as a green solid (0.382 g, 14%), mp >300 °C. Anal. Calcd for C₆₄H₈₂N₈O₈: C, 70.43; H, 7.57; N, 10.27. Found: C, 70.26; H, 7.37; N, 10.10. IR (KBr disk): $\nu_{\rm N-H}$ 3305 (m), $\nu_{\rm C-H}$ 2956 (s), 2910 (m), 2871 (m), $\nu_{C=N}$ 1598 (s), $\nu_{C=C}$ 1499 (vs), 1468 (s), ν_{C-O} 1271 (vs), 1237 (vs), ν_{C-N} 1035 (vs) cm⁻¹. ¹H NMR (400 MHz, d_6 -C₆D₆): 1.26 $(d, J = 6.8 \text{ Hz}, 48\text{H}, 16 \text{ CH}_3), 2.64-2.74 \text{ (m, 8H, 8CH)}, 4.71 \text{ (d, } J =$ 6.8 Hz, 16H, 8OCH2), 7.52 (s, 8H, 4NC8H2 of Pc ring) ppm. $^{13}\text{C}\{^{1}\text{H}\}$ NMR (100 MHz, d₆-C₆D₆): 19.6 (CH₃), 28.6 (CH), 79.1 (OCH₂), 119.2, 126.9, 149.1, 151.9 (NC₈H₂ of Pc ring) ppm. UV-vis (THF, 1 × 10⁻⁵ M): λ_{max} (log ε) = 328 (4.79), 673 (4.56), 748 (5.09), 765 (5.13) nm.

Preparation of (i-BuO)₈PcRu(CO)₂ (5). A 25 mL three-necked flask equipped as that for the preparation of 2 was charged with 4 (0.109 g, 0.1 mmol), Ru₃(CO)₁₂ (0.128 g, 0.2 mmol), and 5 mL of benzonitrile. The reaction mixture was refluxed at 190 °C for 1 h and then cooled to room temperature. After the solvent was removed at reduced pressure, the residue was subjected to silica gel column

chromatography with toluene/THF (v/v = 30:1) as eluent. From the major dark green band, **5** was obtained as a dark green solid (0.065 g, 52%), mp 175–177 °C. Anal. Calcd for $C_{66}H_{80}N_8O_{10}Ru: C, 63.60; H, 6.47; N, 8.99. Found: C, 63.35; H, 6.37; N, 9.01. IR (KBr disk): <math>\nu_{C-H}$ 2957 (s), 2927 (s), 2871 (s), $\nu_{C=0}$ 1956 (vs), $\nu_{C=N}$ 1595 (s), $\nu_{C=C}$ 1499 (vs), 1469 (s), ν_{C-0} 1237 (s), 1209 (vs), ν_{C-N} 1058 (vs) cm⁻¹. ¹H NMR (400 MHz, d_6 - C_6D_6): 1.00–1.32 (m, 48H, 16CH₃), 2.36–2.68 (m, 8H, 8CH), 4.30–4.98 (m, 16H, 8OCH₂), 7.47 (s, 8H, 4NC₈H₂ of Pc ring) ppm. ¹³C{¹H} NMR (100 MHz, d_6 - C_6D_6) 19.7, 19.8 (CH₃), 28.7 (CH), 79.6 (OCH₂), 119.6, 130.1, 143.8, 151.3 (NC₈H₂ of Pc ring), 183.6 (C=O) ppm. UV-vis (THF, 1 × 10⁻⁵ M): λ_{max} (log ε) = 298 (4.82), 632 (4.61), 702 (5.24) nm.

Preparation of (i-BuO)₈PcRu(CO)(µ-PDT)[(Ph₂P)₂NCH₂C₅H₄N]- $Fe_2(CO)_4$ (6). A 100 mL three-necked flask equipped with a magnetic stir-bar and two serum caps was charged with 5 (0.062 g, 0.05 mmol), Me₃NO·2H₂O (0.011 g, 0.1 mmol), and 20 mL of CH₂Cl₂. The mixture was stirred at room temperature for 1 h, and then 2 (0.081 g, 0.1 mmol) was added. The resulting mixture was stirred for another 2 h at room temperature. After removal of the solvent at reduced pressure, the residue was subjected to silica gel column chromatography with toluene/THF (v/v = 90:1) as eluent. From the black-green band, 6 was obtained as a black solid (0.062 g, 61%), mp 216-218 °C. Anal. Calcd for C₁₀₂H₁₁₂Fe₂N₁₀O₁₃P₂RuS₂: C, 60.50; H, 5.58; N, 6.92. Found: C, 60.25; H, 5.42; N, 7.15. IR (KBr disk): ν_{C-H} 2956 (s), 2930 (m), 2871 (m), $\nu_{C=0}$ 2000 (s), 1968 (vs), 1932 (s), $\nu_{C=N}$ 1596 (m), $\nu_{\rm C=C}$ 1498 (s), 1469 (m), 1434 (m), $\nu_{\rm C-O}$ 1265 (m), 1238 (m), 1208 (vs), $\nu_{\rm C-N}$ 1110 (m), 1058 (s) cm⁻¹. ¹H NMR (400 MHz, *d*_6-C_6D_6): 1.27 (d, J = 2.8 Hz, 48H, 16CH₃), 1.41 (br s, 2H, CH₂CH₂CH₂), 1.57, 1.67 (2br s, 4H, 2SCH₂), 1.94 (br s, 2H, NCH₂), 2.71–2.81 (m, 8H, 8CH), 3.28, 3.29 (2s, 4H, NC5H4), 4.64-4.70, 5.02-5.07 (2m, 16H, 80CH₂), 5.78, 6.63, 6.83, 7.39 (4br s, 20H, $4C_6H_5$), 7.48 (s, 8H, $4NC_8H_2$ of Pc ring) ppm. $^{13}C\{^{1}H\}$ NMR (100 MHz, $d_6-C_6D_6$): 18.5, 18.7 (CH₃), 23.6 (CH₂CH₂CH₂), 27.9 (CH), 29.9 (SCH₂), 48.6 (NCH₂), 79.0 (OCH₂), 116.4, 118.5, 125.2, 128.4, 129.4, 129.6, 130.0, 131.4, 131.6, 131.8, 133.1, 137.6, 137.9, 138.1, 139.8, 142.1, 144.9, 151.1 (C_6H_5 , NC_5H_4 , NC_8H_2 of Pc ring), 180.1 (RuC \equiv O), 211.5, 213.0 (FeC \equiv O) ppm. ³¹P{¹H} NMR (162 MHz, d_6 -C₆D₆, 85% H₃PO₄): 119.1 (s) ppm. UV-vis (THF, 1×10^{-5} M): λ_{max} (log ε) = 300 (4.83), 631 (4.56), 702 (5.21) nm.

Photoinduced H₂ Production Catalyzed by Light-Driven Model 6. A 30 mL Schlenk flask fitted with a N₂ inlet tube, a serum cap, a magnetic stir-bar, and a water-cooling jacket was charged with model 6 (2.03 mg, 0.001 mmol), Et₃N (2 mL, 14.4 mmol), H₂O (4 mL), and THF (4 mL). The resulting solution was stirred and irradiated for 120 min at about 25 °C (controlled by the cooling jacket) through a UV cutoff filter ($\lambda > 400$ nm) by using a 50 W Xe lamp. During the photoinduced catalytic reaction, the evolved H₂ was withdrawn periodically using a gastight syringe and analyzed by gas chromatography with a Shimadazu GC-2014 instrument equipped with a thermal conductivity detector and a carbon molecular sieves column (3 mm × 2.0 m) and with N₂ as the carrier gas. The total amount of H₂ produced during 120 min of irradiation was 0.13 × 10⁻³ mmol.

X-ray Structure Determinations of 2, 4, 5, and 6. Single crystals of 2 suitable for X-ray diffraction analysis were grown by slow diffusion of hexane into its CH₂Cl₂ solution at about -5 °C, whereas single crystals of 4, 5, and 6 suitable for X-ray diffraction analyses were grown by slow diffusion of methanol into their CHCl₃ solutions at about -5 °C. A single crystal of 2 or 5 was mounted on a Rigaku MM-007 (rotating anode) diffractometer equipped with a Saturn 724 CCD. Data were collected at 113 K by using a confocal monochromator with Mo Kα radiation ($\lambda = 0.71073$ Å) in the ω - θ scanning mode. Data collection, reduction, and absorption correction were performed with the CRYSTALCLEAR program.⁶¹ A single crystal of 4 or 6 was mounted on a Bruker APEX-II CCD diffractometer. Data were collected at 173 K using a graphite monochromator with Mo K radiation (0.71073 Å) in the ω - θ scanning mode. Absorption correction was performed by the SADABS program.⁶² All structures were solved by direct methods using the SHELXS-97 program⁶³ and refined by full-matrix least-squares techniques (SHELXL-97)⁶⁴ on *F*².

Organometallics

Hydrogen atoms were located by using the geometric method. Details of crystal data, data collections, and structure refinements are summarized in Table 4.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.5b01040.

Full tables of crystal data, atomic coordinates and thermal parameters, and bond lengths and angles for 2, 4, 5, and 6 (CIF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We are grateful to the Ministry of Science and Technology of China (973 Programs 2014CB845604 and 2011CB935902) and the National Natural Science Foundation of China (21132001, 21272122, and 21472095) for financial support.

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