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Communication

Diiron propanedithiolate complex bearing the pyridyl-functionalized phosphine ligand axially coordinated to a photosensitizer zinc tetraphenylporphyrin

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ABSTRACT

Treatment of the starting material (μ -PDT)Fe₂(CO)₆ (PDT = SCH₂CH₂CH₂CH₂S) with 4-diphenylphosphinoaminopyridine (PyNHPPh₂) in the presence of the decarbonylating agent Me₃NO·2H₂O afforded (μ -PDT)Fe₂(CO)₅(PyNHPPh₂) (**1**) in 56% yield. Further treatment of **1** with Zinc tetraphenylporphyrin (ZnTPP) yielded the target light-driven model compound (μ -PDT)Fe₂(CO)₅(PyNHPPh₂)(ZnTPP) (**2**) in 94% yield. The new complexes **1** and **2** were characterized by elemental analysis, NMR, IR, and X-ray crystallography. The molecular structure of **2** revealed its precursor **1** and a photosensitizer ZnTPP joined together through axial coordination. Furthermore, the fluorescence emission spectra and electrochemistry were also investigated.

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1. Introduction

In recent years, light-driven model compounds containing a catalytic diiron dithiolate moiety and a photosensitizer unit have been received considerable attention due to their unique structures and novel properties [1-6]. Besides, porphyrin and metalloporphyrin were designed as a photosensitizer in the photoinduced electron transfer system because they have high efficiency in absorbing the energy of sunlight and long lifetime of the excitedstate [7]. Some examples for the model compounds containing a [Fe₂S₂] cluster and a photosensitizer porphyrin or metalloporphyrin were shown in Chart 1. Song and co-workers reported a model for the diiron azadithiolate moiety covalently bonded to a porphyrin A [8] and afterward, its light-driven hydrogen evolution properties were studied in the presence of electron donor EtSH and proton source CF₃COOH [9]. In addition, another type of model such as **B** [10] and **C** [11] was successfully synthesized and structurally characterized. Very recently, a new model for the diiron propanedithiolate complex with the pyridyl-functionalized phosphine ligand $(\mu$ -PDT)Fe₂(CO)₅[PPh₂(4-Py)] axially coordinated to a metalloporphyrin ZnTPP D was obtained via self-assembly and its photoinduced hydrogen generation properties were investigated [12]. Based on these previous works, we carried out a study on the reaction of diiron propanedithiolate complex containing

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a pyridyl-functionalized phosphine ligand with a photosensitizer ZnTPP and have successfully prepared a new light-driven model compound. Herein, we now report our results.

2. Results and discussion

2.1. Synthesis and characterization

The synthetic methods for our target complexes based on the CO substitution reactions with monophosphine ligands [13] (Scheme 1). Treatment of (μ -PDT)Fe₂(CO)₆ with 1 equivalent of Me₃NO·2H₂O in MeCN at room temperature followed by addition of PyNHPPh₂ afforded the pyridyl-containing complex **1** in 56% yield. Further treatment of **1** with ZnTPP gave the target model compound **2** in 94% yield.

The new complexes **1** and **2** were characterized by elemental analysis and various spectroscopic techniques. The IR spectra of **1** and **2** displayed three absorption bands in the range of 2042–1948 cm⁻¹ for their terminal carbonyls and the $v_{C=0}$ values markedly shifted toward lower frequencies relative to parent complex (μ -PDT)Fe₂(CO)₆ (2072, 2033, 1993 cm⁻¹) [14] because the PyNHPPh₂ is stronger electron-donating ligand than CO [13]. Complex **2** also displayed three absorption bands at 1504, 1484, and 1437 cm⁻¹ for the pyrrole rings of ZnTPP [15]. The ¹H NMR spectra of **2** showed two singlets at δ 1.49 and 1.46 ppm for its pyridyl group and the values shifted toward high field relative to the corresponding signals of its precursor **1** due to the strong shielding effect of ZnTPP upon axial coordination [16]. The ³¹P NMR spectra of **1** and



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Scheme 1. Synthesis of complexes 1 and 2.

2 demonstrated a singlet at δ 94.68 and 95.28 ppm, respectively, for their P atom of PyNHPPh₂ coordinated to one Fe atom of the diiron subsite [17]. It follows that the ³¹P NMR value of PyNHPPh₂ (19.4 ppm in free PyNHPPh₂ [18]) will shift toward lower field upon coordination. In addition, the ¹³C NMR spectra of **1** and **2** exhibited a doublet at approximately δ 212 ppm for PFe(CO)₂ and a singlet at approximately δ 209 ppm for Fe(CO)₃ [19].

2.2. X-ray crystal structures of 1 and 2

The molecular structures of **1** and **2** have been determined by single crystal X-ray diffraction analysis. As shown in Fig. 1, complex **1** contains a butterfly $[Fe_2S_2]$ cluster with five carbonyls and one PyNHPPh₂ ligands. A diiron propanedithiolate unit has two fused six-membered rings, in which one six-membered ring C8C7S1Fe2S2C9 has a boat conformation and another six-membered ring C8C7S1Fe1S2C9 adopted a chair conformation. The pyridyl-functionalized phosphine ligand PyNHPPh₂ resides in an axial position of the square-pyramidal geometry of the Fe2 atom which is consistent with previously reported corresponding diiron dithiolate complexes with monophosphine ligands such as (μ -PDT) Fe₂(CO)₅(Ph₂PCH₂COOH) [20], (μ -PDT)Fe₂(CO)₅(Ph₂PNHCH₂CH₂ N(CH₃)₂] [21], and [(μ -SCH₂)CH(OH)]Fe₂(CO)₅(Ph₃) [22]. The Fe1-Fe2 bond length [2.5054(14) Å] is close to its parent complex (μ -PDT)Fe₂(CO)₆ [2.5103(11) Å] [14] and analogous diiron dithiolate

Fig. 1. ORTEP view of **1** with 30% probability level ellipsoids. Selected bond lengths (Å) and bond angles (°): Fe(1)−S(1) 2.2712(19); Fe(1)−S(2) 2.261(2); Fe(1)−Fe(2) 2.5054(14); Fe(2)−P(1) 2.220(2); Fe(2)−S(1) 2.270(2); Fe(2)−S(2) 2.2541(19); P(1)−N(1) 1.702(5); S(2)−Fe(1)−S(1) 84.47(8); S(2)−Fe(1)−Fe(2) 56.16(5); S(1)−Fe(1)−Fe(2) 56.48(6); P(1)−Fe(2)−Fe(1) 156.26(6); S(2)−Fe(2)−Fe(1) 56.43(6); S(1)−Fe(2)−Fe(1) 56.54(6); N(1)−P(1)−Fe(2) 116.3(2); Fe(2)−S(1)−Fe(1) 66.98(6); Fe(2)−S(2)−Fe(1) 67.40(6).

complexes (μ -PDT)Fe₂(CO)₅[Ph₂PNHCH₂CH₂N(CH₃)₂] [2.5089(8) Å] and (μ -PDT)Fe₂(CO)₅[Ph₂PNH(2-NH₂C₆H₄)] [2.5010(8) [21], but shorter than those in the structures of natural enzymes *Clostridium pasteurianum* and *Desulfovibrio desulfuricans* (2.55–2.62 Å) [23,24].

As shown in Fig. 2, light-driven model compound 2 contains its precursor **1** and a photosensitizer ZnTPP joined together through axial coordination. The Fe1–Fe2 bond length [2.545(2) Å] of 2 is longer than that of **1** [2.5054(14)Å] due to the coordination effect of metalloporphyrin [12]. It is interesting to find out that the pyridylfunctionalized phosphine ligand PyNHPPh₂ in **2** occupies a basal position of the square-pyramidal geometry of the Fe2 atom in order to reduce the steric repulsion between the porphyrin ring and the propylene group. The Zn1–N2 bond length [2.113(7) Å] is in good agreement with the corresponding length in a similar compound [10]. While the dihedral angle between the porphyrin plane and the pyridine plane is 69.5°, the twist angles between the four benzene rings and the porphyrin plane are 82.5°, 112.9°, 121.0°, and 120.1°, respectively. In addition, the porphyrin ring is slightly ruffled with 0.2822 Å out-of-plane displacement of the central zinc because of axial coordination [25].

2.3. Fluorescence emission spectra

The fluorescence emission spectra of ZnTPP without and with complex **1** were studied under the same conditions. As shown in Fig. 3, ZnTPP shows two fluorescence emission bands at 598 and 645 nm. After addition of 20 equiv. of complex **1**, the fluorescence emission bands are red-shifted by 15–16 nm with respect to the corresponding bands of ZnTPP and the intensities are quenched with an efficiency of 75%. This is because the assembly of ZnTPP and complex **1** exists via axial coordination between the pyridine nitrogen atom and zinc atom in ZnTPP [11]. The decreased intensities of the bands of ZnTPP with complex **1** relative to free ZnTPP may be due to the electron transfer from photoexcited ZnTPP to the diiron subsite [10].

2.4. Electrochemistry of complex 1

The electrochemical properties of complex **1** were studied by cyclic voltammetry. As shown in Fig. 4, complex **1** displayed one



 $\begin{array}{l} \label{eq:Fig. 2. ORTEP view of 2 with 30\% probability level ellipsoids. Selected bond lengths (Å) and bond angles (°): Zn(1)–N(2) 2.113(7); Fe(1)–S(1) 2.250(3); Fe(1)–S(2) 2.245(3); Fe(1)–Fe(2) 2.545(2); Fe(2)–P(1) 2.213(3); Fe(2)–S(1) 2.245(3); Fe(2)–S(2) 2.250(3); P(1)–N(1) 1.708(7); S(2)–Fe(1)–S(1) 84.89(10); S(2)–Fe(1)–Fe(2) 55.59(8); S(1)–Fe(1)–Fe(2) 55.43(8); P(1)–Fe(2)–Fe(1) 105.77(9); S(1)–Fe(2)–Fe(1) 55.43(8); N(1)–P(1)–Fe(2) 112.2(3); Fe(2)–S(1)–Fe(1) 68.97(9); Fe(1)–S(2)–Fe(2) 68.98(9). \end{array}$



Fig. 3. Fluorescence emission spectra ($\lambda_{ex} = 545$ nm) of ZnTPP (5 × 10⁻⁵ M) in CH₂Cl₂ without (solid line) and with complex 1 (1 × 10⁻³ M, dotted line).



Fig. 4. Cyclic voltammogram of complex 1 (1 mM) in 0.1 M n-Bu₄NPF₆/MeCN with HOAc (0–10 mM) at a scan rate of 100 mV S⁻¹.

irreversible reduction at -1.89 V and one quasi-reversible reduction at -2.21 V, attributed to the Fe^IFe⁰ and Fe⁰Fe⁰ state, respectively [26]. After addition of 2 mM acetic acid, the current intensity at -1.89 V was increased, but did not increase any more with sequential addition of acetic acid. However, the second reduction peak at -2.21 V markedly increases with sequential addition of acetic acid. The sharp increase in its current intensity is typical of an electrochemical catalytic process [27].

3. Conclusions

In summary, we have successfully synthesized a light-driven model compound from a photosensitizer ZnTPP axially coordinated to a diiron propanedithiolate complex bearing the pyridylfunctionalized phosphine ligand. The new complexes **1** and **2** were structurally characterized by various spectroscopic techniques as well as by X-ray crystallography. Further studies of their catalytic properties are in progress in our laboratory.

4. Experimental

4.1. Materials and methods

All reactions were performed using standard Schlenk and vacuum-line techniques under N₂ atmosphere. Acetonitrile was distilled over CaH₂ under N₂. Me₃NO·2H₂O and other materials were available commercially and used as received. (μ -PDT)Fe₂(CO)₆ [14], PyNHPPh₂ [18] and ZnTPP [28] were prepared according to literature procedures. IR spectra were recorded on a Nicolet MAGNA 560 FTIR spectrometer. ¹H (³¹P, ¹³C) NMR spectra were obtained on a Bruker Avance 500 MHz spectrometer. Elemental analysis was performed by a Perkin–Elmer 240C analyzer. Fluorescence emission spectra were determined on a Hitachi F-4600 fluorescence spectrometer.

4.2. Synthesis of complex $(\mu$ -PDT)Fe₂(CO)₅(PyNHPPh₂) (1)

To a solution of $(\mu$ -PDT)Fe₂(CO)₆ (0.386 g, 1 mmol) in CH₃CN (20 mL) was added a solution of Me₃NO·2H₂O (0.111 g, 1 mmol) in CH₃CN (15 mL). The mixture was stirred at room temperature for 15 min and then (4-C₅H₄N)NH(PPh₂) (0.278 g, 1 mmol) was added. The new mixture was stirred overnight to give a red solution. The solvent was reduced *in vacuo* and the residue was subjected to TLC separation using ethyl acetate/petroleum ether (v/v = 1:1) as eluent. The main red band collection afforded complex **1** as a red



Chart 1. Examples for the model compounds containing a [Fe₂S₂] cluster and a photosensitizer porphyrin or metalloporphyrin.

solid (yield: 0.356 g, 56%). Anal. Calcd for C₂₅H₂₁Fe₂N₂O₅PS₂: C, 47.20; H, 3.33; N, 4.40%. Found: C, 47.51; H, 3.52; N, 4.16%. IR (KBr disk): $\nu_{C=0}$ 2041 (vs), 1984 (vs), 1948 (vs) cm⁻¹. ¹H NMR (500 MHz, CDCl₃): δ 8.24 (br, 2H, Py-H), 7.77–7.45 (m, 10H, Ar–H), 6.45 (s, 2H, Py-H), 5.78 (d, *J*_{P–H} = 18.0 Hz, 1H, NH), 2.04–2.00 (m, 2H, SCH₂CH₂CH₂S), 1.72–1.62 (m, 4H, 2SCH₂) ppm. ³¹P NMR (200 MHz, CDCl₃, 85% H₃PO₄): δ 94.68 (s) ppm. ¹³C NMR (125 MHz, CDCl₃): δ 212.58 (d, *J* = 13.0 Hz, PFeCO), 209.50 (FeCO), 150.23, 148.96, 148.87, 130.88, 134.64, 134.27, 130.97, 130.69, 130.68, 128.88, 128.80 (Ar–C), 30.23, 22.48 (CH₂) ppm.

4.3. Synthesis of complex (µ-PDT)Fe₂(CO)₅(PyNHPPh₂)(ZnTPP) (2)

A mixture of 1 (0.064 g, 0.1 mmol) and zinc tetraphenylporphyrin (0.068 g, 0.1 mmol) was dissolved in CH₂Cl₂ (3 mL) and then the solution was layed with hexane (5 mL). After 2 days, a purple solid of 2 (0.124 g, 94%) was obtained from filtration and washing with hexane. Anal. Calcd for C₆₉H₄₉Fe₂N₆O₅PS₂Zn: C, 63.05; H, 3.76; N, 6.39%. Found: C, 62.77; H, 3.99; N, 6.53%. IR (KBr disk): $v_{C=0}$ 2042 (vs), 1985 (vs), 1949 (vs); v_{pyrrole ring} 1504 (m), 1484 (m), 1437 (m) cm⁻¹. ¹H NMR (500 MHz, CDCl₃): δ 8.84 (s, 8H, pyrrole-H), 8.16 (s, 8H, Py and Ar-H), 7.77-7.72 (m, 12H, Ar-H), 7.43-7.33 (m, 10H, Ar-H), 5.53 (br, 1H, NH), 1.93-1.89 (m, 4H, 2SCH₂), 1.59, 1.49, 1.46 (3s, 6H, Py-H and CH₂) ppm. ³¹P NMR (200 MHz, CDCl₃, 85% H₃PO₄): δ 95.28 (s) ppm. ¹³C NMR (125 MHz, CDCl₃): δ 212.36 (d, I = 13.2 Hz, PFeCO), 209.33 (FeCO), 149.95, 148.68, 148.59, 146.74, 143.63, 134.52, 134.19, 133.82, 131.48, 130.68, 130.59, 128.75, 128.67, 127.12, 126.22, 120.47, 112.09 (pyrrole-C and Ar-C), 31.60, 30.07 (CH₂) ppm.

4.4. X-ray structure determination

Single crystals of 1 and 2 suitable for X-ray diffraction analysis were grown by slow evaporation of the CH_2Cl_2 /hexane solution at

Table 1

Crystal Data and Structure Refinements Details for 1 and 2.

Complex	1	$2 \cdot CH_2Cl_2$
Empirical formula	C ₂₅ H ₂₁ Fe ₂ N ₂ O ₅ PS ₂	$C_{70}H_{51}Cl_2Fe_2N_6O_5PS_2Zn$
Formula weight	636.23	1399.23
Temperature (K)	113 (2)	113 (2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	P2(1)/c	P-1
a (Å)	13.435 (3)	10.972 (2)
b (Å)	17.600 (4)	12.994 (3)
c (Å)	11.101 (2)	23.187 (5)
α (°)	90	85.06 (3)
β (°)	90.07 (3)	85.30 (3)
γ (°)	90	76.17 (3)
$V(Å^3)$	2624.9 (9)	3191.7 (11)
Ζ	4	2
$D_{\text{calc}} (g \cdot \text{cm}^{-3})$	1.610	1.455
$\mu (\mathrm{mm}^{-1})$	1.365	1.052
F(000)	1296	1430
Crystal size (mm ³)	$0.20 \times 0.18 \times 0.12$	$0.20\times0.18\times0.10$
$\theta_{\min}, \theta_{\max}$ (°)	1.52, 25.02	1.62, 25.02
Reflections collected/unique	20324/4613	23384/11060
R _{int}	0.0893	0.1258
hkl range	$-15 \le h \le 15$	$-13 \le h \le 13$
	$-20 \le k \le 20$	$-15 \le k \le 15$
	$-13 \le l \le 12$	$-27 \leq l \leq 18$
Completeness to θ_{max} (%)	99.6	98.0
Data/restraints/parameters	4613/98/362	11060/0/803
Goodness of fit on F ²	1.083	1.053
$R1/wR2 \ (I > 2\sigma(I))$	0.0553/0.1383	0.0966/0.1765
R1/wR2 (all data)	0.0916/0.2009	0.1602/0.2068
Largest diff neak and hole/e $Å^{-3}$	0.831/_0.782	1 699/_1 031

4 °C. A single crystal of **1** or **2** was mounted on a Rigaku MM-007 CCD diffractometer. Data were collected at 113 K by using a graphite monochromator with Mo K α radiation ($\lambda = 0.71073$ Å) in the $\omega - \varphi$ scanning mode. Data collection, reduction and absorption correction were performed by *CRYSTALCLEAR* program [29]. The structure was solved by direct methods using the SHELXS-97 program [30] and refined by full-matrix least-squares techniques (SHELXL-97) [31] on F^2 . Hydrogen atoms were located using the geometric method. Details of crystal data, data collections, and structure refinement are summarized in Table 1.

4.5. Electrochemistry

Acetonitrile (HPLC grade) was used for electrochemistry assays. A solution of 0.1 M *n*-Bu₄NPF₆ in MeCN was used as electrolyte in all cyclic voltammetric experiments. Electrochemical measurements were made using a BAS Epsilon potentiostat. All voltammograms were obtained in a three-electrode cell with a 3 mm diameter glassy carbon working electrode, a platinum counter electrode, and an Ag/Ag⁺ (0.01 M AgNO₃/0.1 M *n*-Bu₄NPF₆ in MeCN) reference electrode. The working electrode was polished with 0.05 μ m alumina paste and sonicated in water for 10 min prior to use. All potentials are quoted against the ferrocene/ferrocenium (Fc/Fc⁺) potential.

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Appendix A. Supplementary material

CCDC 806953 (1) and 806952 (2) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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