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Synthetic and structural study on some new porphyrin or metalloporphyrin macrocycle-containing model complexes for the active site of [FeFe]-hydrogenases

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ABSTRACT

To mimick the natural enzymes [FeFe]-hydrogenases, some new porphyrin and metalloporphyrin moiety-containing model complexes, namely $5\text{-}[p\text{-}Fe_2(CO)_6(\mu\text{-}SCH_2)_2CHO_2CC_6H_4]$,10,15,20-triphenylporphyrin (**2**), $5\text{-}[p\text{-}Fe_2(CO)_6(\mu\text{-}SCH_2)_2CHO_2CC_6H_4]$,10,15,20-triphenylporphyrinozinc (**3**), $5\text{-}[p\text{-}Fe_2(CO)_6(\mu\text{-}SCH_2)_2NC_2H_4SC_6H_4]$,10,15,20-triphenylporphyrin (**7**), and $5\text{-}[p\text{-}Fe_2(CO)_5(\mu\text{-}SCH_2)_2NC_2H_4SC_6H]$,10,15,20-triphenylporphyrin (**8**), have been successfully prepared by our designed synthetic routes involving the corresponding precursor compounds $[(\mu\text{-}SCH_2)_2CHO_2CC_6H_4CHO\text{-}p]Fe_2(CO)_6$ (**1**), $p\text{-Boc-}NHC_2H_4SC_6H_4CHO$ (**4**), $5\text{-}(p\text{-Boc-}NHC_2H_4SC_6H_4)$,10,15,20-triphenylporphyrin (**5**), and $5\text{-}(p\text{-}NH_2C_2H_4\ SC_6H_4)$,10,15,20-triphenylporphyrin (**6**). All these new compounds **1**–**8** have been characterized by elemental analysis and various spectroscopic methods, and particularly for **1**–**3** and **7** by X-ray crystallography. In addition, the density functional theory computations on **8** were performed to assist its structural characterization.

1. Introduction

Hydrogenases are natural enzymes that catalyze the reversible redox reaction between proton and hydrogen in various microorganisms [1]. According to the metal content in the active site, hydrogenases are primarily classified as [FeFe]-hydrogenases ([FeFe]Hases), [NiFe]-hydrogenases ([NiFe]Hases), and [Fe]-hydrogenases (Hmd) [2–8]. While [FeFe]Hases are mainly used for proton reduction to hydrogen, [NiFe]Hases are employed for hydrogen oxidation to protons [9–11], Hmd is utilized to activate hydrogen for use in catabolic processes of microorganisms [7,8]. Currently, [FeFe]Hases are receiving more attention over [NiFe]Hases and Hmd, because of their unusual structures and particularly their extremely rapid rates for production of “clean” and highly efficient H_2 fuel [12,13]. Recent X-ray crystallography [14–16] and FTIR spectroscopy [17–19] revealed that the active site of [FeFe]Hases, so-called H-cluster [9], consists of a cubane-like $[Fe_4S_4]$ cluster that is linked to a butterfly $[Fe_2S_2]$ cluster via the cysteinyl S atom. In addition, the two iron atoms of the $[Fe_2S_2]$ cluster are bridged by a propanedithiolate (PDT), azadithiolate (ADT), or oxadithiolate (ODT) ligand and are coordinated by a given amount of CO and CN^- ligands (Fig. 1).

Encouraged by the structural studies on H-cluster, the synthetic chemists have designed and synthesized a variety of structural and functional models for the active site of [FeFe]Hases [20–38]. Among these models, the porphyrin or metalloporphyrin-containing models are of particular interest, since they belong to the dyads light-driven type models in which the photosensitizer porphyrin or metalloporphyrin is covalently or coordinatively attached to a simple diiron model complex. To date, although several such model complexes have been prepared [34–38], none of them contains the photosensitizer porphyrinylester or metalloporphyrinylester moiety that is covalently attached to a simple diiron model (such as **2** and **3** in Fig. 2) or includes a porphyrinylthioether moiety that is covalently or coordinatively bound to a simple diiron model (such as **7** and **8** in Fig. 2). To develop the synthetic methodology for such new types of porphyrin or metalloporphyrin-containing H-cluster model complexes, we initiated this study. Herein we report the results of this study.

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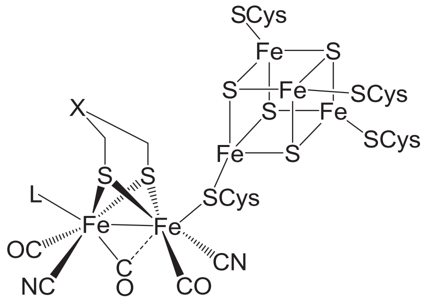

Fig. 1. The simplified structure of H-cluster in different functional states (L = H_2O, CO, H, or H_2; X = CH_2, NH, or O).

2. Results and discussion

*2.1. Synthesis and spectroscopic characterization of simple model complex [(μ-SCH_2)$_2$$CHO_2CC_6H_4CHO$-p]$Fe_2(CO)_6$] (**1**) and the porphyrin or metalloporphyrin-containing model complexes 5-[p-$Fe_2(CO)_6$(μ-SCH_2)$_2$$CHO_2CC_6H_4$],10,15,20-triphenylporphyrin (**2**) and 5-[p-$Fe_2(CO)_6$(μ-SCH_2)$_2$$CHO_2CC_6H_4$],10,15,20-triphenylporphyrinozinc (**3**)*

According to our designed synthetic route for preparation of the porphyrinylester or metalloporphyrinylester moiety-containing model complexes **2** and **3**, we should first prepare the simple *p*-formylbenzoate functionalized model complex **1**. The treatment of the C-hydroxy functionalized complex [(μ-SCH_2)$_2$CH(OH)]$Fe_2(CO)_6$ with *p*-formylbenzoyl chloride (prepared in situ by reaction of *p*-formylbenzoic acid with $SOCl_2$) [39] in CH_2Cl_2 in the presence of Et_3N gave the simple model complex **1** in 62% yield. Further treatment of **1** with benzaldehyde and pyrrole in 1:3:4 M ratio in the presence of $BF_3 \cdot OEt_2$, followed by treatment with oxidant *p*-chloranil afforded model complex **2** in 21% yield along with tetraphenylporphyrin (TPP) in 18% yield. Finally, the metalloporphyrinylester moiety-containing model complex **3** was produced by reaction of **2** in $CHCl_3$ with $Zn(OAc)_2$ in MeOH at room temperature in 88% yield (Scheme 1).

Complexes **1**–**3** are air-stable red solids, which have been characterized by elemental analysis and spectroscopy. For instance, the IR spectra of **1**–**3** displayed three to four absorption bands in the region 2075–1992 cm^{-1} for their terminal carbonyls and one absorption band in the range 1706–1722 cm^{-1} for their organic carbonyls, respectively. In addition, **2** and **3** showed three absorption bands in the region 1558–1339 cm^{-1} assigned to the skeleton vibrations of pyrrole rings in their porphyrin and porphyrinozinc macrocycles, respectively [40]. The ^{1}H NMR spectra of **1**–**3** showed a broad singlet or a multiplet at about 4.6 ppm for their bridgehead C-attached axial hydrogen atoms, whereas **2** exhibited a singlet at −2.80 ppm for the two protons attached to N atoms in its pyrrole rings [41]. The UV–vis spectra of **2** and **3** were determined in CH_2Cl_2, which showed one Soret band at 412 and 414 nm in the near-UV region, respectively. In addition, **2** displayed four Q bands in the range 514–645 nm, whereas **3** exhibited two Q bands at 548 and 586 nm in the visible region. Apparently, the different Q bands displayed by **2** and **3** are caused by the different photosensitizer moieties [34,35], namely the porphyrinylester moiety for **2** and the metalloporphyrinylester moiety for **3**.

*2.2. Crystal structures of **1**–**3***

The molecular structures of **1**–**3** were unambiguously confirmed by X-ray diffraction techniques (Fig. 3–5, Table 1–3). As can be seen intuitively from Fig. 3, complex **1** contains a diiron PDT moiety in which the six-membered ring Fe1S1C7C8C9S2 has a chair conformation and the other six-membered ring Fe2S1C7C8C9S2 a boat conformation. The *p*-formylbenzoate group is attached to the common C8 atom of the two six-membered rings by an equatorial bond and a hydrogen atom is attached to C8 by an axial bond. Both Fe1 and Fe2 atoms adopt the expected square-pyramidal geometry and the Fe1–Fe2 bond length (2.5007 Å) is very close to the corresponding those of its parent complex [(μ-SCH_2)$_2$CH(OH)]$Fe_2(CO)_6$ and similar diiron complexes [26,42–44].

Fig. 4 shows that complex **2** has the same diiron PDT moiety as **1**, but the equatorial *p*-formylbenzoate group in **1** has been replaced by an equatorial porphyrinylester moiety. In the porphyrin cycle the C–N bond lengths in pyrrole rings are nearly the same (1.366–1.380 Å), which lie between those of normal single and double C–N bonds [45]. It is worth pointing out that the four benzene rings attached to porphyrin cycle is planar and twisted relative to the porphyrin plane in order to reduce the steric interactions between the phenyl hydrogen atoms proximal to the porphyrin cycle and the pyrrole rings.

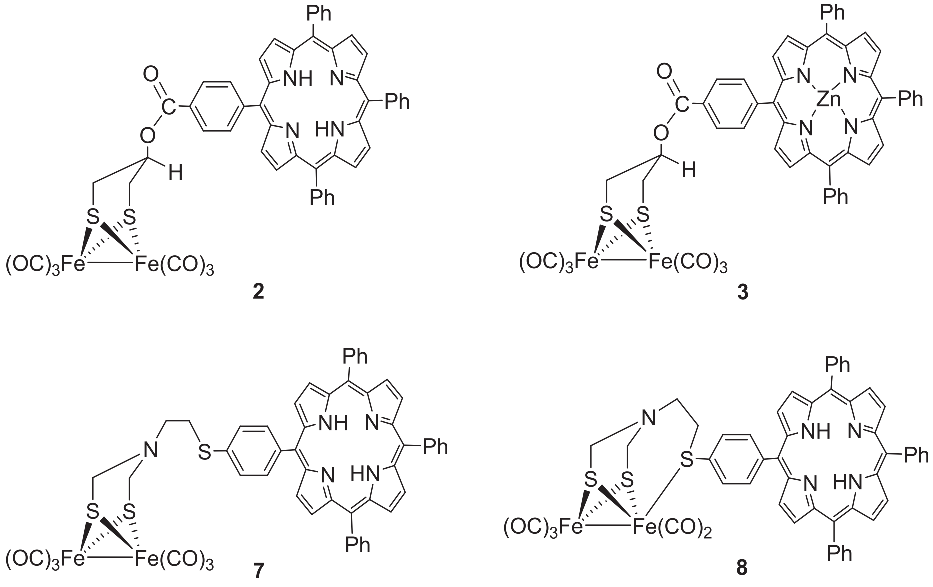

Fig. 2. The target light-driven models **2**, **3**, **7**, and **8** reported in this article.