[FeFe]-Hydrogenase active site models with relatively low reduction potentials: Diiron dithiolate complexes containing rigid bridges

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Abstract

Three diiron dithiolate complexes containing rigid and conjugated bridges, [μ-SC6H4-2-(CO)S-]Fe2(CO)6 (1), [2-μ-SC7H7N-3-(CO)-S-]Fe2(CO)6 (2), and the PPh3-monosubstituted complex [μ-SC6H4-2-(CO)S-]Fe2(CO)6(PPh3) (1-P), were prepared as biomimetic models for the [FeFe]-hydrogenase active site. The structures of complexes 1 and 2 were determined by single crystal X-ray analysis, which shows that each complex features a rigid coplanar dithiolate bridge with a 2–3° deviation from the bisect plane of the molecule. The influence of the rigid bridge on the reduction potentials of complexes 1, 2 and 1-P was investigated by electrochemistry. The cyclic voltammograms of complexes 1 and 2 display large positive shifts for the primary reduction potentials, that is, 380–480 mV in comparison to that of the pdt-bridged (pdt = propane-1,3-dithiolato) complex (μ-pdt)Fe2(CO)6 and 160–260 mV to that of the bdt-bridged (bdt = benzene-1,2-dithiolato) analogue (μ-bdt)Fe2(CO)6.

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1. Introduction

Hydrogenases are important enzymes in numerous microorganisms, which can catalyse hydrogen evolution or uptake. Among FeFe, NiFe, NiFeSe and FeS-cluster-free (Hmd) [1] hydrogenases reported so far, the [FeFe]-hydrogenases ([FeFe]Hases) are the most efficient biocatalysts for hydrogen evolution [2,3]. Crystallographic and IR spectroscopic studies on the two types of [FeFe]Hases, CpI (Clostridium pasteurianum) [4] and DdH (Desulfovibrio desulfuricans) [5], revealed that the active site of [FeFe]Hases is comprised of a 2Fe2S butterfly structure (H-cluster), which contains diatomic ligands CO and CN−, a cysteinyl-S ligand connecting to a 4Fe4S subcluster, and a three-atom linker (−CH2XCH2−, X = CH2, NH or NH2+) bridged between the two S atoms of the 2Fe2S H-cluster (Fig. 1).

The resemblance in structure between the [FeFe]Hase active site and the well-known complexes [μ-SR]2-Fe2(CO)6 draws intensive attention to the chemistry of such complexes. In recent years, a great progress has been achieved in structural and functional biomimics of the 2Fe2S subunit in the [FeFe]Hase active site. A large number of diiron dithiolate complexes, either with the alkylene bridges, e.g. pdt (propane-1,3-dithiolato) [6–23], edt (ethane-1,2-dithiolato) [24–26], and an adt (2-azopropane-1,3-dithiolato) bridge [27–32], were prepared and characterized. Some diiron dithiolate complexes were reported catalytically active for electrochemical proton reduction.
to molecular hydrogen at ca. −1.0 to −1.2 V vs. NHE in the presence of strong acids [14–16,29,33–35], which contrasts sharply with the incredibly low potential and the mild condition (−0.4 V vs. NHE at neutral pH) for the enzymatic proton reduction catalysed by the native [FeFe]Hases [36].

We are interested in building light-driven proton reduction catalytic systems, composed of a bio-inspired 2Fe2S model of the [FeFe]Hase active site and a light-harvesting component either by inter- or intramolecular combination [37]. For this purpose, the reduction property and the photo-stability of the diiron complexes are important factors and must be improved. One of our recent work is the preparation of some specially designed diiron complexes to lower the reduction potentials of the complexes and thereby to make electron transfer from a photosensitizer to a [2Fe2S] complex thermodynamically feasible.

In general, the reported all-CO 2Fe2S structural models display the first reduction potentials in the range of −1.5 to −1.8 V vs. Fe/Ce⁺ in CH3CN [29,34,35]. Displacement of one or two CO ligands of diiron dithiolate complexes by other ligands makes the iron centers more protophilic and the reduction potentials of the complexes much more negative (−1.9 to −2.7 V vs. Fe/Ce⁺) [7,13–20,33–35]. Although much effort has focused on adjusting the redox potential, the protophilicity, and the water solubility of diiron dithiolate model complexes by CO-displacement with various ligands, such as cyanide [6–8,28], tertiary phosphines and phosphites [9–15], N-heterocyclic carbenes [16–20], isocyanides [21,22], and 1,10-phenanthroline [23], little work has been reported on tuning the reactivity and the electrochemical property of the diiron center by varying the S-to-S linker [38–43]. It was reported that the bdt-bridged (bdt = benzene-1,2-dithiolato) diiron dithiolate complex (μ-bdt)Fe2(CO)6 showed the first reduction event at −1.44 V vs. Fe/Ce⁺ with a 220 mV positive shift in comparison to the pdt-bridged complex (μ-pdt)Fe2(CO)6 [35], indicating that the reduction potential of the iron center in the diiron dithiolate complexes can be effectively tuned less negative by using the rigid and conjugated S-to-S linker. Therefore, we designed and prepared diiron complexes bearing rigid, conjugated and electron withdrawing S-to-S linkers, that is, SC6H4-2-(CO)S and 2-SC6H4N-3-(CO)S (Fig. 1). Herein, we report the preparation, the spectroscopic and crystallographic characterization, and the electrochemical properties of complexes [μ-SC6H4-2-(CO)S-μ]Fe2(CO)6 (1), [2-μ-SC6H4N-3-(CO)S-μ]Fe2(CO)6 (2), and the PPh3-mono-substituted complex [μ-SC6H4-2-(CO)S-μ]Fe2(CO)3S(PPh3) (1-P). As expected, complexes 1 and 2 display relatively low reduction potentials at −1.28 and −1.18 V vs. Fe/Ce⁺, respectively, and such low reduction potentials make light-driven electron transfer from the Ru(bpy)3₂⁺ species the first oxidation event at −1.66 V vs. Fe/Ce⁺ [44,45] to the diiron complex thermodynamically feasible.

2. Experimental

2.1. General procedure and materials

All reactions and operations related to organometallic complexes were carried out under a dry, oxygen-free dinitrogen atmosphere with standard Schlenk techniques. All solvents were dried and distilled prior to use according to the standard methods. Commercially available materials, Fe(CO)₅, 3H-1,2-benzodithiol-3-one, and 2-mercaptocetic acid, were reagent grade and used as received. Starting complex Fe₂(CO)₉ used in this study was prepared from Fe(CO)₅ in acetic acid under irradiation of an Xe lamp (500 W). 3H-1,2-Dithiolo[3,4-b]pyridin-3-one was prepared according to the literature procedure [46]. The ¹H and ³¹P NMR spectra were collected with a Bruker AVANCE II/400 spectrometer. Abbreviations used for the reported ¹H NMR spectra are as follows: s = singlet, br = singlet broad, d = doublet, t = triplet. Infrared spectra were recorded with a Jasco FT/IR 430 spectrophotometer. The intensity of reported IR signals are defined as m = medium, s = strong, vs = very strong. Elemental analyses were performed with an Elementar Vario EL III elemental analyzer.

2.2. Synthesis of [μ-SC₆H₄H₂-2-(CO)S-μ]Fe₂(CO)₆ (1)

The mixture of Fe₂(CO)₉ (0.73 g, 2 mmol) and 3H-1,2-benzodithiol-3-one (0.17 g, 1 mmol) in THF (20 mL) was stirred at room temperature for 1 h and then filtered. After removal of THF by evaporation under reduced pressure, the residue was purified by column chromatography on silica gel using petroleum ether and CH₂Cl₂ as gradient eluents. Product 1 was obtained from the second red band. Yield of 1: 0.35 g (78%). Recrystallization of 1 in the mixed solution of hexane and CH₂Cl₂ at −20 °C overnight gave single crystals suitable for X-ray diffraction analysis. Anal. Calc. for C₁₃H₆Fe₂O₅S₂ (447.98): C, 34.85; H, 0.90. Found: C, 34.99; H, 0.94%. ¹H NMR (CDCl₃): δ = 7.44 (d, J₁H₁ = 8.0 Hz, 1H), 7.33 (d, J₁H₁ = 7.6 Hz, 1H), 7.25 (d, J₁H₁ = 7.6 Hz, 1H), 7.18 (t, J₁H₁ = 7.6 Hz, 1H) ppm. IR (hexane): ν(CO) = 2082 (m), 2048 (s), 2012 (s) cm⁻¹.

2.3. Synthesis of [2-μ-SC₆H₄N-3-(CO)S-μ]Fe₂(CO)₆ (2)

The mixture of Fe₂(CO)₉ (0.73 g, 2 mmol) and 3H-1,2-dithiolo[3,4-b]pyridin-3-one (0.17 g, 1 mmol) in THF

![Fig. 1. The active site of [FeFe]Hases (left) and synthetic models of the present work (right).]
(20 mL) was stirred at room temperature for 2 h and then filtered. The working up procedure is similar as that for I. Yield of 2: 0.08 g (18%). Single crystals suitable for X-ray diffraction analysis were obtained by evaporation of the hexane and CH$_2$Cl$_2$ mixed solution of 2 at room temperature. Anal. Calc. for C$_{12}$H$_3$Fe$_2$NO$_7$S$_2$ (448.97): C, 32.10; H, 0.67; N, 3.12. Found: C, 32.48; H, 0.69; N, 3.16%. 1H NMR (CDCl$_3$): 8.32 (s br, 1H), 7.73 (d, $J_{HH} = 7.6$ Hz, 1H), 7.22 (t, $J_{HH} = 5.2$ Hz, 1H) ppm. IR (hexane): $\nu$CO 2084 (m), 2050 (s), 2014 (s) cm$^{-1}$.

2.4. Synthesis of [$\mu$-SC$_6$H$_4$-2-(CO)S-Fe$_2$ (CO)$_5$ (PPh$_3$) (I-P)]

Compound PPh$_3$ (0.26 g, 1 mmol) was added to a toluene solution (20 mL) of I (0.45 g, 1 mmol) in one portion at room temperature. The mixture was stirred for 0.5 h, and then the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with petroleum ether and CH$_2$Cl$_2$ (1/1, v/v) as eluent. The main band was collected and the analytically pure product 1-P was obtained by cooling the concentrated solution to $-20^\circ$C overnight. Yield of 1-P: 0.56 g (82%). Anal. Calc. for C$_{36}$H$_{19}$Fe$_2$O$_6$PS$_2$ (682.26): C, 52.81; H, 2.81. Found: C, 52.48; H, 2.86%. 1H NMR (CDCl$_3$): 8.32 (s br, 1H), 7.73 (d, $J_{HH} = 7.6$ Hz, 1H), 7.22 (t, $J_{HH} = 5.2$ Hz, 1H) ppm. IR (hexane): $\nu$CO 2084 (m), 2050 (s), 2014 (s) cm$^{-1}$.

2.5. X-ray crystal structure determination

The single-crystal X-ray diffraction data were collected with a Bruker SMART Apex II diffractometer at 298(2) K using Mo K$_{\alpha}$ radiation ($\lambda = 0.71073$ Å). Data processing were accomplished with the SAINT processing program. Absorption corrections were applied using SADABS. The structures were solved using direct method and refined by the full-matrix least-squares procedure with SHELXTL. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed geometrically and refined in a riding model. Crystal data and structure refinement details for complexes 1 and 2 were summarized in Table 1.

2.6. Electrochemistry

Cyclic voltammograms were recorded on a BAS-100B electrochemical potentiostat using a three electrode cell at a scan rate of 100 mV s$^{-1}$ under argon atmosphere. The working electrode was a glass carbon disk (0.071 cm$^2$) polished with 3 and 1 μm diamond pastes and sonicated in ion-free water for 10 min prior to use. The reference electrode was a non-aqueous Ag/Ag$^+$ (0.01 M AgNO$_3$) in CH$_3$CN and the auxiliary electrode was a platinum wire. The acetonitrile (Aldrich, spectroscopy grade) used for electrochemical measurements was freshly distilled from CaH$_2$ under nitrogen. A solution of 0.05 M nBu$_4$NPF$_6$ (Fluka, electrochemical grade) in CH$_3$CN was used as electrolyte. All potentials reported here are versus FeC/Fe$^+$ couple.

2.7. Laser flash photolysis

Nanosecond transient absorption measurements were performed on a LP-920 pump–probe spectroscopic setup (Edinburgh). The excitation source was the unfocused third harmonic (532 nm, 7 ns fwhm) output of a Nd:YAG laser (Continuum surelite II); the probe light source was a pulse-xenon lamp. The signals were detected by Edinburgh analytical instruments (LP900) and recorded on a Tektronix TDS 3012B oscilloscope and computer. All samples in flash photolysis experiments were deaerated with argon for ca. 20 min.

3. Results and discussion

3.1. Preparation and spectroscopic characterization of 1, 2 and 1-P

The diiron complexes containing ethylene- and benzene-1,2-dicarboxyl S-to-S linkers were reported previously without electrochemical investigation [47,48], while the diiron dithiolate complexes with the SC$_6$H$_4$-2-(CO)S and 2-SC$_6$H$_3$N-3-(CO)S linkers have not been found in literature. It was reported that the reaction of 1,2-benzodithiol-3-one or 3 with 2 equiv. of Fe$_2$(CO)$_9$ in THF afforded a [4Fe3SC] cluster [49]. In contrast, treatment of 3 with 2 equiv. of Fe$_2$(CO)$_9$ in THF gave diiron dithiolate complexes 1 and 2 containing rigid bridges, respectively (Scheme 1). Complex 1 with an SC$_6$H$_4$-2-(CO)S

<table>
<thead>
<tr>
<th>Complex</th>
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<th>2</th>
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<tr>
<td>Formula</td>
<td>C$_1$H$_3$Fe$_2$O$_7$S$_2$</td>
<td>C$_1$H$_4$Fe$_2$NO$_7$S$_2$</td>
</tr>
<tr>
<td>$M_w$</td>
<td>447.98</td>
<td>448.97</td>
</tr>
<tr>
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<td>Orthorhombic</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>Space group</td>
<td>P$\overline{2}_1$$\overline{2}_1$$\overline{2}_1$</td>
<td>P$\overline{2}_1$$\overline{2}_1$$\overline{2}_1$</td>
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<tr>
<td>$a$ (Å)</td>
<td>8.2714(11)</td>
<td>8.2581(3)</td>
</tr>
<tr>
<td>$b$ (Å)</td>
<td>11.9718(17)</td>
<td>11.8094(4)</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>16.314(2)</td>
<td>16.2662(6)</td>
</tr>
<tr>
<td>$V$ (Å$^3$)</td>
<td>1615.5(4)</td>
<td>1586.33(10)</td>
</tr>
<tr>
<td>$Z$</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>$\mu$ (mm$^{-1}$)</td>
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<td>2.126</td>
</tr>
<tr>
<td>Crystal size (mm)</td>
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<td>0.08 $\times$ 0.20 $\times$ 0.26</td>
</tr>
<tr>
<td>$\theta_{\text{min/max}}$ (°)</td>
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<td>2.77–27.50</td>
</tr>
<tr>
<td>Reflections collected</td>
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<td>6234</td>
</tr>
<tr>
<td>Unique data/parameters</td>
<td>3486/217</td>
<td>3532/217</td>
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<tr>
<td>Residual electron density (e Å$^{-3}$)</td>
<td>0.264, –0.240</td>
<td>0.335, –0.217</td>
</tr>
</tbody>
</table>

Table 1 Crystal data and structure refinements for 1 and 2

In contrast, treatment of 3 with 2 equiv. of Fe$_2$(CO)$_9$ in THF afforded a [4Fe3SC] cluster [49]. In contrast, treatment of 3 with 2 equiv. of Fe$_2$(CO)$_9$ in THF gave diiron dithiolate complexes 1 and 2 containing rigid bridges, respectively (Scheme 1). Complex 1 with an SC$_6$H$_4$-2-(CO)S...
linker was obtained in a good yield, while the yield of complex 2 was relatively low when the benzene ring in the rigid bridge was changed to a pyridine ring, although the complete consume of 3H-1,2-dithiolo[3,4-b]pyridin-3-one was observed by TLC. In addition to complex 2 the reaction of Fe₂(CO)₉ and 3H-1,2-dithiolo[3,4-b]pyridin-3-one generated a fair amount of precipitate, which is a mixture. The structure of the precipitate is still unknown. The PPh₃-monosubstituted complex 1-P was synthesized in high yield by CO-displacement of 1 in toluene at room temperature.

Complexes 1, 2 and 1-P were characterized by IR, NMR and elemental analysis. The results of elemental analyses for the three complexes are in good agreement with the supposed compositions. The IR data for 1, 2 and 1-P are summarized in Table 2 together with the data for the analogous bdt- and pdt-bridged diiron complexes for a ready comparison.

The shifts of the νₐ CO bands can reflect the variation of electron density on the iron center. The average values of the ν₀ CO bands for complexes 1 and 2 shift by 13 and 15 cm⁻¹ to higher frequency in comparison to that of (μ-pdt)Fe₂(CO)₆, and the ν₀ CO absorption bands of 1 and 2 show 4–6 cm⁻¹ blue-shifts compared to the three ν₀ CO bands for (μ-bdt)Fe₂(CO)₆ with a rigid phenylene bridge. The displacement of a CO ligand by a better donor, a PPh₃ ligand, results in large red-shifts of the ν₀ CO bands for 1-P in comparison to those for its parent complex 1. The red-shift value (Δν₀ COav = 44 cm⁻¹) for 1 to 1-P is comparable with that (Δν₀ COav = 49 cm⁻¹) for the PPh₃-monso-substituted diiron complex reported previously [13]. Complex 1-P displays a 19 cm⁻¹ blue-shift for the ν₀ COav in comparison to that of the analogous complex (μ-pdt)Fe₂(CO)₆(PPh₃).

3.2. Molecular structures of complexes 1 and 2

The molecular structures of complexes 1 and 2 were determined by X-ray crystal diffraction. The ORTEP drawings are shown in Figs. 2 and 3. Selected bond lengths and angles are listed in Table 3. Crystallographic studies show the structural resemblance of the framework of 1 and 2 to previously reported 2Fe2S models [6–14]. The central structure of the 2Fe2S core is in a butterfly conformation and each Fe atom is coordinated with a pseudo-square-
pyramidal geometry. The deviations of the iron atoms from the 2S2C-formed basal plane are 0.38 Å for Fe(1) and 0.37 Å for Fe(2). Similar crystal structures and geometry parameters were found for the two complexes except for the difference in the atoms of C(13) in $1$ and the N(1) in $2$. The Fe–Fe distances, 2.5212(6) Å for $1$ and 2.5152(7) Å for $2$, are in good agreement with those (2.48–2.52 Å) found for other all-CO diiron complexes [6,27–32]. The average distance of the Fe–S(1) bonds is 0.011–0.017 Å longer than that of the Fe–S(2) bonds due to weaker electron donating capability of the S(1) attached to the carbonyl group than that of the S(2) bonded to a phenyl group.

The rigid dithiolate bridge is the special feature for complexes $1$ and $2$ compared to reported pdt- and adt-bridged diiron complexes. The calculated plane of the SRS bridge is nearly a bisect plane of the molecular structure. Except for two Fe(CO)$_3$ units all atoms are in the plane with the average deviation of 0.0289 Å for $1$ and 0.0159 Å for $2$. The drawing of complex $2$ along the direction of S(1) to S(2) is shown in Fig. 3 (bottom). The angle between the calculated plane of the rigid bridge and the Fe–Fe bond deviates from 90° by 2.7° for $1$ and 3.2° for $2$, resulting in the asymmetric molecular structures. Complexes $1$ and $2$ are both crystallized in a chiral space group, orthorhombic $P_{2_1}2_12_1$.

### 3.3. Electrochemistry of complexes $1$, $2$ and $1$-P

Cyclic voltammograms (CV) were recorded in cathodic direction as shown in Fig. 4, to evaluate the effect of the rigid bridges on the redox property of the iron centers in the diiron complexes. The first reduction event of complex $1$ takes place at $-1.28$ V vs. Fc/Fc$^+$. Complex $2$ shows the reduction event at $-1.18$ V with 100 mV anodic shift relative to that for complex $1$. The primary reduction potentials of $1$ and $2$ are 380–480 mV less negative than that for the propanedithiolate complex ($l$-pdt)Fe$_2$(CO)$_6$ ($-1.66$ V vs. Fc/Fc$^+$) [35]. Insertion of a carbonyl group between one of the S atoms and the phenylene unit results in 160 mV anodic shift as compared to that for ($l$-bdt)Fe$_2$(CO)$_6$ ($-1.44$ V vs. Fc/Fc$^+$) [35]. It is noticeable that both complexes $1$ and $2$ display completely irreversible...

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**Table 3**

Selected bond lengths (Å) and angles (deg) for $1$ and $2$

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<tr>
<th>Bond lengths</th>
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<tr>
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<td>2.5152(7)</td>
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<td>2.2551(9)</td>
<td>2.2511(11)</td>
</tr>
<tr>
<td>Fe(1)–S(2)</td>
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<td>2.2407(10)</td>
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<td>2.2502(8)</td>
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<tr>
<th>Bond angles</th>
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<td>Fe(1)–S(1)–Fe(2)</td>
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<td>67.75(3)</td>
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<td>85.80(3)</td>
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<td>148.36(15)</td>
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<td>99.5(2)</td>
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<td>98.34(18)</td>
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<td>146.85(13)</td>
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<td>99.21(16)</td>
<td>99.80(18)</td>
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<td>C(4)–Fe(2)–C(5)</td>
<td>91.35(18)</td>
<td>91.72(19)</td>
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Fig. 3. (top) ORTEP drawing of $2$ with thermal ellipsoids at the 30% probability level, (bottom) ORTEP drawing of $2$ along the direction of S(1) to S(2).
reduction events, while the reduction of the phenylene-bridged analogue appears chemically reversible. It shows that not only the FeⅠFeⅠ complexes 1 and 2 but also their reduced species are less stable than the phenylene-bridged diiron complex. Replacement of a CO ligand in 1 by PPh₃ leads to a 190 mV negative shift of the reduction event to /C₀ 1.47 V. The current height in the CVs of complexes 1, 2 and 1-P is compared with that in the CV of [(l-pdt)Fe₂(CO)₆] with identical concentration and under the same measuring condition. The approximately equal current height in the CVs of complexes 1, 2 and 1-P and [(l-pdt)Fe₂(CO)₆] suggests that the primary reduction of complexes 1 and 2 is a one-electron process (FeⅠFeⅠ/FeⅠFeⅠ). The electrochemical results indicate that in addition to introduction of non-CO ligands to the iron center, variation of the S-to-S bridge can also effectively tune the reduction potentials of diiron model complexes.

3.4. Laser flash photolysis

Light-driven electron transfer from the Ru(bpy)₃⁺ species, generated by reductive quenching of the excited state of Ru(bpy)₂⁺³, to the 2Fe2S complexes 1 and 2 was detected in CH₃CN/H₂O (3/1, v/v) using ascorbic acid (H₂A) as electron donor. Laser excitation (532 nm, pulse width 7 ns) of the deoxygenated solution of Ru(bpy)₂⁺³ and H₂A resulted in the instant formation of Ru(bpy)₃⁺, which is a long-lived species (τ = 16.9 μs) [37]. The lifetime of Ru(bpy)₃⁺ was shortened to 1.7 μs in the presence of complex 1 (1 × 10⁻⁴ M, Fig. 6). The kinetic constant for electron transfer from Ru(bpy)₃⁺ to 1 was determined to be
6.0 × 10^9 M^{-1} S^{-1} by varying the concentration of 1 from 0.025 to 0.15 mM in the triad system, which is somewhat faster than the previously reported rate constants for electron transfer from Ru(bpy)_3^2+ to the well-known diiron model complexes ([Fe_3(CO)]_6 (3.9 × 10^9 M^{-1} S^{-1}) and [(μ-SCH_2)_3NCH_2CH_3]Fe_2(CO)_6] (3.5 × 10^9 M^{-1} S^{-1}) [37]. The concomitant kinetics for the decay of Ru(bpy)_3^2+ and the buildup of the Fe_3Fe_0 species further supports the conclusion that one-electron transfers from Ru(bpy)_3^2+ to 1. No good transient absorption spectrum was obtained for complex 2 due to its poor photo-stability under irradiation. An apparent color change of the solution was observed after irradiation of 2 in CH_3CN/H_2O for 1 min and a precipitate appeared immediately, while the solution of complex 1 remained clear and the color of the solution did not display observable change during the flash photolysis measurement. The result indicates that complex 1 is more photo-stable than complex 2.

4. Conclusion

The rigid and conjugated bridges can be readily introduced to the diiron dithiolate complexes, which show relatively low reduction potentials for the Fe_3Fe_1 to Fe_3Fe_0 process. The results indicate that the S-to-S bridge can apparently influence the redox property of the diiron dithiolate model complexes, providing another approach, besides CO-displacement, to tune the reduction potentials of candidate catalysts for electro- and photo-chemical proton reduction to molecular hydrogen. The driving force for light-induced electron transfer from photosensitizer to diiron complex is enhanced by lowering the reduction potential of the diiron complex, resulting in a somewhat faster electron transfer rate for complex 1 in comparison to that for well-known pdt- and adt-bridged all-CO diiron complexes.

5. Abbreviations

pdt propane-1,3-dithiolato
bdt benzene-1,2-dithiolato
edt ethane-1,2-dithiolato
adt 2-azopropane-1,3-dithiolato
THF tetrahydrofuran
bpy bipyridyl
CV cyclic voltammogram
NHE normal hydrogen electrode
Hmd H_2-forming methylenetrihydrodemethanoperin dehydrogenase
Fc/Fc^+ ferrocene/ferrocnium
Hases hydrogenases

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Appendix A. Supplementary material

CCDC 652825 (1) and 652826 (2) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jinorgbio.2007.12.018.

References