Electron-Transfer Processes

Synthesis and Structure of a Biomimetic Model of the Iron Hydrogenase Active Site Covalently Linked to a Ruthenium Photosensitizer**

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Although known for more than 75 years,[1] sulfur-containing binuclear complexes of iron have recently experienced a renaissance as interesting synthetic targets as they closely resemble the active site of iron hydrogenases (FeH), a naturally occurring class of enzymes which regulate the production and consumption of hydrogen in microorganisms.[2–5] Crystallographic studies revealed the active site of the natural system to consist of two iron(I) cations which are linked by an unusual bridging dithiolate ligand.[6,7] It has been

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suggested that this ligand contains a nitrogen heteroatom and possesses the structure SCH_2NHCH_2S.[8,9] The remaining primary coordination sphere around the dinuclear iron active site is occupied by the diatomic ligands CO and CN^-, as well as by a thiol-linked tetranuclear Fe cluster.[6,7,10–12] In the natural system one coordination site remains vacant to allow for hydride or hydrogen coordination.[10]

Recently, Rauchfuss and co-workers have shown that a biomimetic model of FeH can serve as a catalyst for electrochemical hydrogen production.[13] In the context of our interest in photochemical fuel production[14] we became intrigued by the possibility of covalently linking a biomimetic model of the iron hydrogenase active site to a ruthenium photosensitizer in an attempt to afford hydrogen production by the action of light. The projected process is illustrated in Figure 1. It commences with the absorption of a photon by the ruthenium photosensitizer (step 1, Figure 1). The photoexcited ruthenium complex is oxidatively quenched by the dinuclear iron site, which gives rise to a reduced iron species (step 2, Figure 1). After regeneration of the photosensitizer (by an external electron donor), this process is repeated to afford a doubly reduced diiron species which could then drive the reduction of protons. The possibility of introducing ligands different from CO on to the iron portion of the system is of great importance as the redox properties of the structure can thereby be altered significantly to suit the electronic requirements of this process.

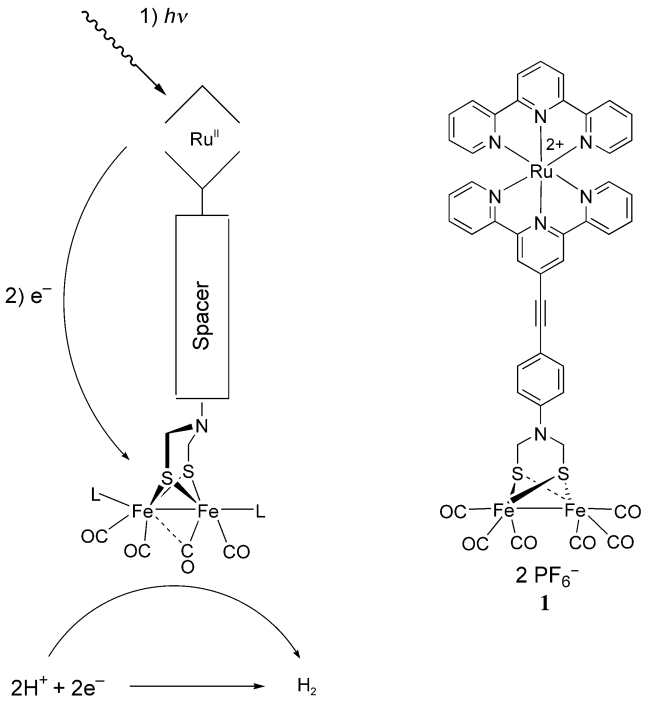
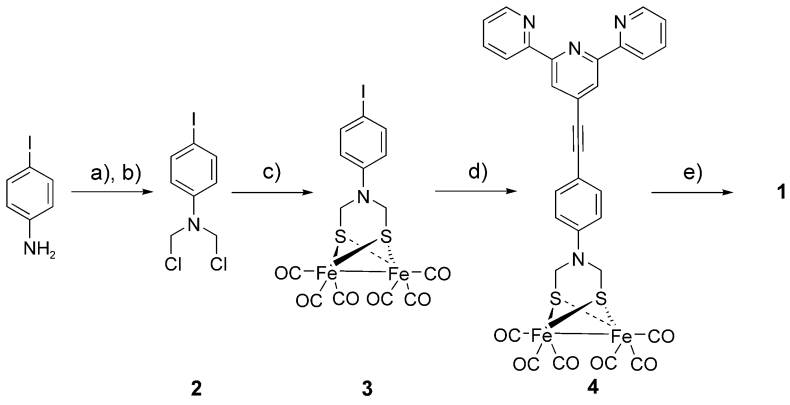


Figure 1. Schematic representation for the projected photoinduced reduction of protons. L = CO, CN^-, PX_3, or thiolates.

We recently prepared a ruthenium(tris)bipyridine type of photosensitizer linked to a diiron complex, in which the iron atoms are connected by a dithiol bridge.[15] Herein we present the synthesis of a novel system in which a 2-aza-1,3-dithiol-bridged dinuclear iron complex is covalently linked to a ruthenium photosensitizer. The system was designed to fulfil various aspects: $[Ru(terpy)_2]^{2+}$ (terpy = 2,2′:6′,2″-terpyridine) was chosen as the photosensitizer because of its geometric advantages over other Ru complexes with didentate ligands.[16] An acetylenic linker between the redox-active termini was selected not only to gain precise control over their spatial separation, but also to prolong the lifetime of the excited state of $[Ru(terpy)_2]^{2+}$[17] so that electron transfer to the iron portion can occur. Finally, the dithiolate bridge in the diiron site was chosen to contain a nitrogen heteroatom, as this arrangement may play an essential role in the production of hydrogen in the natural system.[8,9] With this reasoning, **1** was selected as the target complex.



Scheme 1. a) *p*-CH_2O, CH_2Cl_2, RT, 3 h; b) $SOCl_2$, RT, 30 min; c) $Li_2(SFe(CO)_3)_2$, THF, −78 °C, 5 min, 76%; d) 4′-ethynyl-2,2′:6′,2″-terpyridine, $[PdCl_2(PPh)_2]$, CuI, Et_3N, toluene, 40 °C, 3 h, 57%; e) $[RuCl_2(terpy)]$·DMSO, MeOH, reflux, 4 h, 29%.

The diiron portion was established by applying a recently published procedure for the preparation of some related complexes.[18] Thus, the lithium salt of diironhexacarbonyldisulfide[19] was treated with *N,N*-di(chloromethyl)-4-iodoaniline (**2**), which in turn was synthesized from *p*-iodoaniline in two steps (Scheme 1).[18] Structural analysis of **3** by single-crystal X-ray diffraction[20] (Figure 2) revealed the familiar distorted square-pyramidal arrangement around the iron nuclei. The Fe–Fe bond length of 2.499(1) Å is in good agreement with other crystal structure data of this type of complex.[18,21] The arene substituent resides in an axial position directly above one carbonyl ligand. The π conjugation between the phenyl ring and the nitrogen p orbital is somewhat interrupted in the solid state, as evident from a deviation of the nitrogen atom by 0.164(3) Å from the plane defined by the C7, C8, and C9 atoms. The sum of the C-N-C angles around N1 is 356°. The azadithiolate-bridged diiron species **3** represents the first complex of this kind where the nitrogen atom is linked to an aromatic system.

The iodo functionality in the iron complex **3** could be utilized for further elaboration by reaction of the former complex with 4′-ethynyl-2,2′:6′,2″-terpyridine[22,23] under the cross-coupling conditions used by Sonogashira et al.[24] to

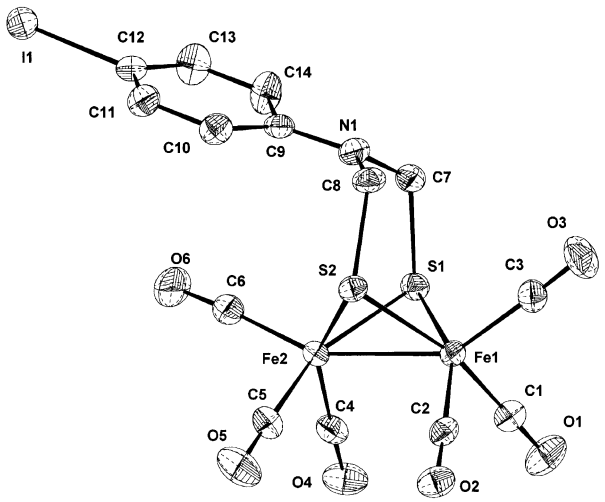


Figure 2. ORTEP (ellipsoids at 30% probability level) view of **3**[20] Selected bond lengths [Å]: Fe1-Fe2 2.4988(8), Fe1-S1 2.2537(10), Fe1-S2 2.2630(10), Fe2-S1 2.2573(10), Fe2-S2 2.2682(10), Fe1-C1 1.798(4), Fe1-C2 1.799(3), Fe1-C3 1.795(4), Fe2-C4 1.778(4), Fe2-C5 1.792(4), Fe2-C6 1.812(4), S1-C7 1.847(4), S2-C8 1.861(4), N1-C7 1.431(5) N1-C8 1.413(5), N1-C9 1.404(5).

afford the terpyridine-coupled dinuclear iron complex **4**. In the solid state, the iron carbonyl portion of **4** is stable towards ligand substitution by the polypyridine unit as unambiguously demonstrated by single-crystal X-ray diffraction studies[20] (Figure 3). Apart from the ethynylterpyridine fragment, the crystal structure of **4** closely resembles that of **3**. The rigidity of the system enables the distance from the nitrogen atom (N2) of the central pyridine ring to the Fe cations to be calculated as 11.892(3) and 13.996(3) Å. The electronic similarities between complexes **3** and **4** are further corroborated by their respective IR spectra, which are alike and

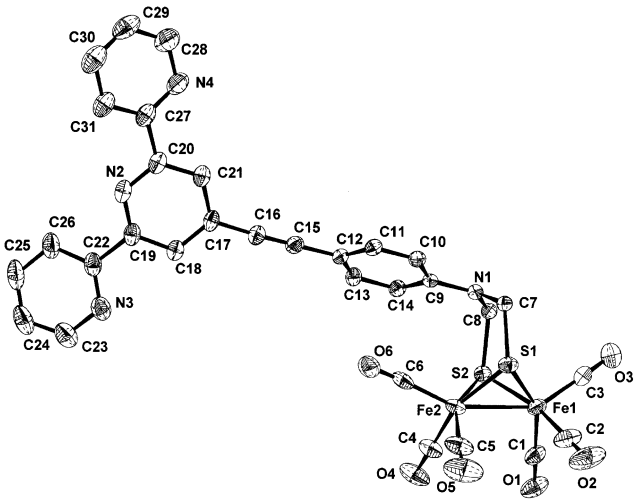


Figure 3. ORTEP (ellipsoids at 30% probability level) view of **4**[20] Selected bond lengths [Å]: Fe1-Fe2 2.5056(7), Fe1-S1 2.2625(9), Fe1-S2 2.2631(9), Fe2-S1 2.2559(9), Fe2-S2 2.2576(8), Fe1-C1 1.778(4), Fe1-C2 1.789(4), Fe1-C3 1.778(4), Fe2-C4 1.784(4), Fe2-C5 1.785(4), Fe2-C6 1.801(4), S1-C7 1.850(3), S2-C8 1.852(3), N1-C7 1.432(4) N1-C8 1.424(4), N1-C9 1.402(4).

exhibit three major bands in the CO region at 2076, 2038, and 2001 cm^{-1}. This resemblance indicates that the iron carbonyl portion is insensitive to the presence of an acetylenic substituent on the aniline as well as to the terpyridine. Solutions of **4** in organic solvents are unstable at room temperature and decompose within minutes upon exposure to light, presumably as a result of light-induced decarbonylation followed by intermolecular terpyridine complexation. However, as a freshly prepared solution in methanol which is kept in the dark, ligand **4** coordinates readily to the {Ru(terpy)} fragment,[25] which gives rise to the desired trinuclear complex **1**. The IR spectrum of a solution of **1** in CH_2Cl_2 shows a pattern in the CO region that is identical to that found for complexes **3** and **4**. This observation indicates there is negligible electronic communication between the redox-active ruthenium center and the iron termini. In contrast to **4**, solutions of **1** are stable and can be stored under ambient conditions for extended periods of time.

Whereas the vast majority of reports in the past have concentrated on ligand-exchange reactions on the Fe-Fe portion,[2–5] this work represents one of the few examples in the literature[26] where chemistry is performed on the organic bridge of an assembled dinuclear iron complex and ultimately leads to a covalent connection to a ruthenium photosensitizer. The preparation of **4** with its free terpyridine metal-binding pocket will enable the incorporation of many different metals, thus offering an insight into electron-transfer processes in a biomimetic model of the active site of FeH. The design of **1** allows the exchange of ligands on the iron portion to facilitate electron transfer from the photoexcited ruthenium complex. Such a modified molecular assembly could promote the light-driven reduction of protons. Experimental efforts in these directions together with in-depth photophysical studies of the system are currently in progress.

Experimental Section

4: $[PdCl_2(PPh_3)_2]$ (18 mg, 0.025 mmol) and CuI (2 mg, 0.01 mmol) were added successively to a degassed solution of iodoarene **3** (150 mg, 0.25 mmol) and 4′-ethynyl-2,2′:6′,2″-terpyridine (73 mg, 0.28 mmol) in triethylamine and toluene (1:1, 20 mL) at 40 °C. After the mixture had been stirred in the dark for 3 h at this temperature, it was concentrated in vacuo and the black residue was subjected to column chromatography, conducted in the dark (Al_2O_3, CH_2Cl_2), to give **4** as a red solid (102 mg, 0.14 mmol, 57%). Elemental analysis (%) calcd for $C_{31}H_{18}Fe_2N_4O_6S_2$: C 51.83, H 2.52, N 7.80; found: C 51.70, H 2.62, N 7.67; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.71$ (m, 2H), 8.59 (m, 2H), 8.54 (s, 2H), 7.85 (m, 2H), 7.50 (d, $J = 8.7$ Hz, 2H), 7.34 (m, 2H), 6.70 (d, $J = 8.7$ Hz, 2H), 4.30 ppm (s, 4H, NCH_2S); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 206.8$, 155.7, 155.4, 149.1, 144.7, 136.9, 133.8, 133.7, 123.9, 122.6, 121.2, 115.3, 113.6, 94.1, 87.0, 49.4 ppm; IR (CH_2Cl_2): $\tilde{\nu} = 2214$ (C≡C), 2076, 2038, 2001 cm^{-1} (C=O).

1: $[RuCl_2(terpy)(DMSO)]$ (67 mg, 0.14 mmol) was added to a degassed solution of **4** (100 mg, 0.14 mmol) in methanol (30 mL). The mixture was refluxed in the dark for 4 h, before the solvent was removed in vacuo. The remaining brown solid was purified by flash chromatography on silica gel (solvent: CH_3CN:H_2O:sat. aq KNO_3 = 90:9:1). After removal of the solvent in vacuo and anion exchange with NH_4PF_6, the red solid was recrystallized from CH_2Cl_2/Et_2O (55 mg, 0.04 mmol, 29%). Elemental analysis (%) calcd for $C_{46}H_{29}F_{12}Fe_2N_7O_6P_2RuS_2$: C 41.21, H 2.18, N 7.31; found: C 41.50, H 2.15, N 7.56; ^{1}H NMR (300 MHz, CD_3CN): $\delta = 8.82$ (s, 2H), 8.75 (d,

$J = 8.3$ Hz, 2H), 8.49 (m, 4H), 8.42 (t, $J = 8.3$ Hz, 1H), 7.93 (m, 4H), 7.70 (d, $J = 9.0$ Hz, 2H), 7.39 (m, 2H), 7.34 (m, 2H), 7.17 (m, 4H), 6.98 (d, $J = 9.0$ Hz, 2H), 4.50 ppm (s, 4H, NCH_2S); ^{13}C NMR (75 MHz, CD_3CN): $\delta = 209.0$, 159.6, 159.3, 156.9 (2C), 154.2 (2C), 147.6, 139.8 (2C), 137.7, 135.6, 132.3, 129.3, 128.1, 126.5, 126.1 (2C), 125.4, 117.4, 113.0, 99.7, 87.4, 50.8 ppm; IR (CH_2Cl_2): $\tilde{\nu} = 2192$ (C≡C), 2077, 2038, 2001 cm^{-1} (C=O); ESI-MS: Ru-isotopic pattern centered at $m/z = 1197.9$ (100%) $[M-PF_6^-]^+$, calcd for $[M-PF_6^-]^+$: $m/z = 1197.9$.

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