# Self-Assembled Monolayers of Non-Heme Diiron(III) Model Complexes on Au(111) Electrode: Synthesis and Proton-Coupled Redox Behavior in Water

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Self-assembled monolayers (SAMs) of non-heme diiron(III) biomimetic complexes have been prepared on Au(111) electrode surfaces to explore redox properties of diiron centers in aqueous solution in a wide pH range. The diiron(III) SAMs exhibited the proton-coupled electron-transfer reaction ($1H^+/1e^-$) in water.

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The biological role of oxo-bridged polynuclear iron systems has been a subject of considerable interest in the last decades.[1,2] Studies on various iron-oxo metalloproteins such as hemerythrin and methane monooxygenase have revealed that the active sites contain $\mu$-oxo and $\mu$-carboxylato diiron structural units. These proteins are mostly involved in transport and activation of dioxygen and the oxidation states of the iron centers can cycle from fully oxidized $Fe^{III}Fe^{III}$ to fully reduced $Fe^{II}Fe^{II}$ in the catalytic cycles with a $\mu$-hydroxo diiron species as a key intermediate. The use of non-heme diiron(III) model complexes have allowed to study redox properties of the diiron centers,[3] but the insoluble and/or unstable character of those complexes towards water have precluded their aqueous electrochemistry, which would provide significant insights into redox activities of iron–oxo proteins.

Recent advances in constructing self-assembled monolayers (SAMs) allow to form highly ordered molecular layers on atomically flat metal surfaces.[4] Variable inorganic and organometallic complexes with interesting properties have been used to modify electrode surfaces.[5] The advantage of this method includes the use of water media for electrochemistry. Here we report synthesis and electrochemical properties of SAMs of diiron(III) complexes on Au(111) electrode, which are unprecedented for gold/SAMs constructed by non-heme iron model complexes.

The synthetic approach to the diiron(III) gold/SAMs began with the preparation of discrete ($\mu$-oxo)diiron(III) complexes containing a disulfide ligand as a tether to the Au surface. Thus, tetranuclear (dimer-of-dimer) complexes **1** and **2** were prepared (Scheme 1, left). Both complexes contain a tetradentate ligand tris(2-pyridylmethyl)amine (tpa)[6] on each Fe and the ($\mu$-oxo)diiron(III) units are connected by a disulfide–dicarboxylate ligand with a different chain length; two and ten methylene linkers for **1** and **2**, respectively. Reactions of $Fe(ClO_4)_3 \cdot 10H_2O$ (0.69 mmol) with tpa (0.69 mmol) and an appropriate sodium salt of disulfide–dicarboxylate $\{-S(CH_2)_nCOONa\}_2$ ($n$ = 2 and 10, 0.17 mmol)[7] in methanol (50 cm$^3$) for 12 h at room temperature gave **1** and **2** in 58 and 20% yields, respectively.[8] They are thermally-stable crystalline solid whose spectroscopic properties[9] are similar to those of structurally analogous tpa–diiron(III) complexes, $[Fe_2(\mu\text{-}O)(\mu\text{-}RCO_2)(tpa)_2]^{3+}$ (R = $CH_3$, $C_6H_5$).[10] In 0.1 M $(n\text{-}C_4H_9)_4NPF_6/CH_3CN$, complex **1** displayed a quasi-reversible redox wave at $E_{1/2}$ = –0.04 V vs. Ag/AgCl with $\Delta E_p$ = 80 mV, assignable to $\{Fe^{III}Fe^{III}\}_2/\{Fe^{II}Fe^{III}\}_2$, at scan rates of 100–500 mV/s in the potential range between +0.4 and –0.4 V. An additional smaller irreversible peak $E_{pc}$ = –0.25 V was also found. Complex **2** showed a similar redox behavior to **1** under the same conditions ($E_{1/2}$ = –0.05 V, $\Delta E_p$ = 80–100 mV at 100–500 mV/s).

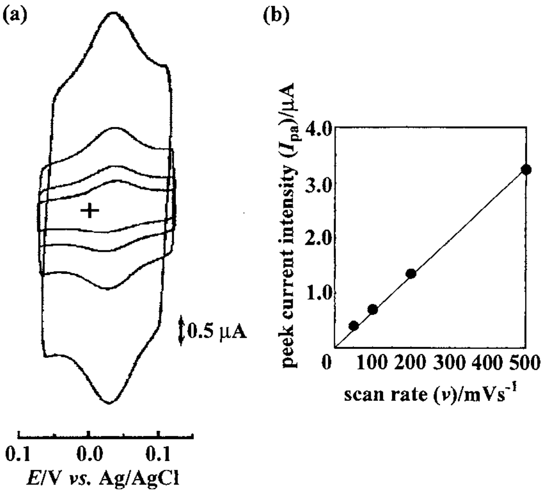
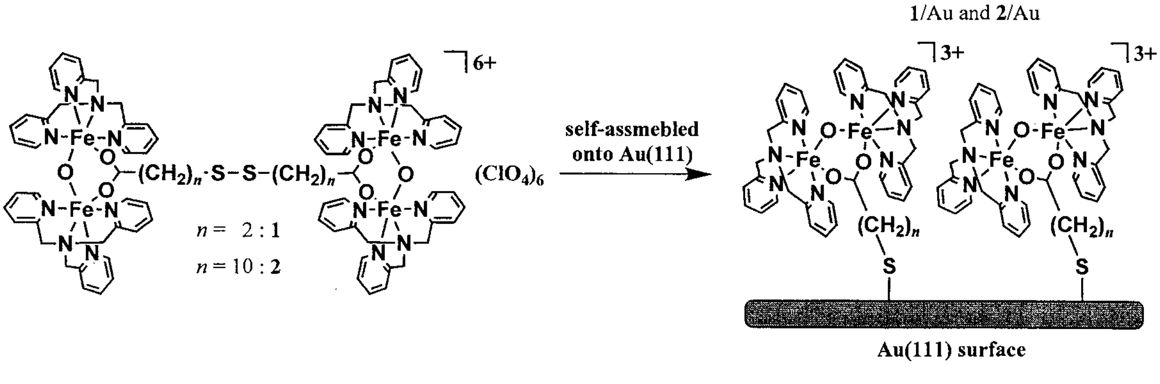


**Figure 1.** (a) Cyclic voltammograms of self-assembled monolayers of diiron(III) complex **2**/Au in aqueous solution containing 0.1 M $NaClO_4$ at 25 °C (pH 8.0; scan rates 50, 100, 200 and 500 mV/sec respectively). (b) Linear relationship between anodic peak current intensities ($I_{pa}$) and scan rates ($\nu$) for one-electron redox process of **2**/Au.

**Scheme 1.**



Self-assembled monolayers of **1** and **2**, denoted as **1**/Au and **2**/Au, respectively, were prepared by immersing a freshly prepared Au(111) electrode[11] into an acetonitrile solution containing **1** or **2** (1 mM) for 12–15 h at 25 °C (Scheme 1).

Surface cyclic voltammetry was performed using aqueous solution (milli-Q water, phosphate buffer) containing 0.1 M $NaClO_4$ with a three-electrode cell consisting of the gold/SAMs (**1**/Au or **2**/Au) as the working electrode, a platinum wire as the counter electrode, and an Ag/AgCl as the reference electrode. The cyclic voltammograms for **2**/Au are presented in Figure 1a, exhibiting a well-defined reversible one-electron redox process, $Fe^{III}Fe^{III}/Fe^{II}Fe^{III}$, at $E_{1/2}$ = +0.065 V vs. Ag/AgCl with the full-width at half-maxima ($W_{1/2}$) of 140 mV at scan rates of 50–500 mV/s (pH 8). As shown in Figure 1b, the peak current linearly increased with scan rates. This along with the fast electron-transfer event exemplified in very small $\Delta E_p$ values (10 mV) indicates that the redox waves are associated with surface-attached diiron(III) molecules. No appreciable decrease of the current intensity was observed for **1**/Au upon repeated scans at pH 7–8 as far as the potential is maintained between –0.1 and +0.1 V, while in the case of **2**/Au the peak intensity became smaller for the same experiment.

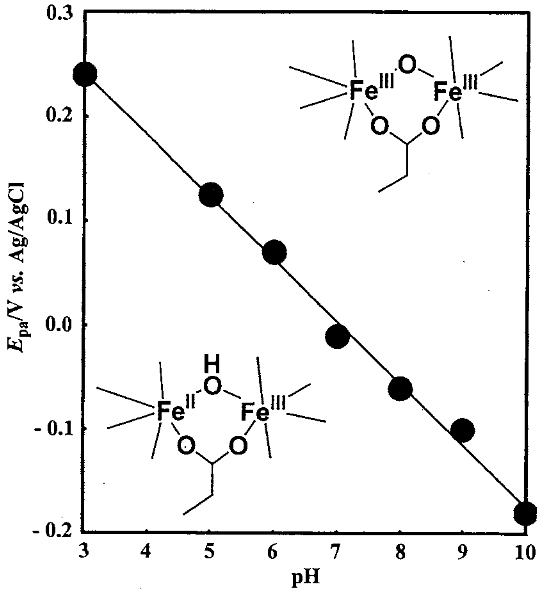


**Figure 2.** The plot of the anodic peak potentials ($E_{pa}$) with pH of the solution (0.1 M $NaClO_4$ with a phosphate buffer), obtained for **1**/Au at a scan rate of 100 mV/s.

The surface coverages of the diiron units (estimated from the integration of the reversible wave for the initial scan) are ca. $10^{13}$ and $10^{12}$ $cm^{-2}$ for **1**/Au and **2**/Au, respectively, the former value indicating the formation of densely-packed monolayers. Reductive desorption waves of **1**/Au and **2**/Au were observed at –0.55 and –0.68 V, respectively, in 0.5 M KOH aq. (20 mV/s), but their broadened shape implicates less ordered monolayer structure. We speculate that substitutionally labile character of $Fe^{III}/Fe^{II}$ centers along with sterically bulky and highly-charged (+3) diiron headgroups would significantly affect the stability and the morphology of the resulting SAMs.

The pH-dependent redox property of **1**/Au was examined in the region 3 < pH < 10. As shown in Figure 2, the anodic peak potential ($E_{pa}$) of the diiron-based redox wave ($W_{1/2}$ = 170 mV) is linearly related to pH with a slope of –59 mV/pH which exactly matches the $1H^+/1e^-$ proton-coupled electron-transfer reaction (eq. 1).

$$\{Fe^{III}\text{–}(\mu\text{-O})\text{–}Fe^{III}\}^{4+} \underset{-1e^-,\,-1H^+}{\overset{+1e^-,\,+1H^+}{\rightleftharpoons}} \{Fe^{II}\text{–}(\mu\text{-OH})\text{–}Fe^{III}\}^{4+} \qquad \text{eq. 1}$$

This is the first exclusive experimental evidence for the proton-coupled redox reactions of the Fe–O–Fe moieties in water obtained in a wide pH range. In spite of the inaccessibility of the present SAMs to measurements under highly basic (pH > 10) and acidic (pH < 2) conditions due to the monolayer decompositions, the upper and lower limits of the $pK_a$ values can be set from the plot for two different oxidation levels: $pK_a > 10$ for $\{Fe^{II}\text{–O–}Fe^{III}\}$ and < 3 for $\{Fe^{III}\text{–O–}Fe^{III}\}$. We note that these values are well consistent with those reported for structurally analogous diruthenium(III) complex $[Ru_2(\mu\text{-O})(\mu\text{-}CH_3CO_2)_2(bpy)_2(mim)_2]^{2+}$ (bpy = 2,2'-bipyridine; mim = 1-methyl-imidazole), where $pK_a$ values of the bridging oxo group are ca. 14 and 2 for the $\{Ru^{II}\text{–O–}Ru^{III}\}$ and $\{Ru^{III}\text{–O–}Ru^{III}\}$, respectively.[12] Our successful reproduction of the pH-dependent redox behavior of diruthenium(III) complex SAMs[13] further supports that the pH-dependent character observed for the present diiron SAMs truely reflects the proton-coupled redox behavior of the Fe–O–Fe moiety.

In summary, this work provides the first example of self-assembled monolayers of biomimetic non-heme diiron(III) centers, which present proton-coupled redox reactions in water. We are hoping that the synthetic methodology described here will further develop novel SAMs presenting interesting redox and catalytic activities based upon surface-ordered metal complex assemblies.

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7 The synthetic procedures of the ligand will be reported elsewhere.
8 Anal. **1**: Found: C, 40.82; H, 3.89; N, 9.53; S, 3.01; Cl, 9.34%. Calcd for **1**•$6H_2O$: C, 40.21; H, 3.98; N, 9.62; S, 2.75; Cl, 9.13%; **2**: Found: C, 45.66; H, 4.75; N, 8.94; S, 2.65; Cl, 8.60%. Calcd for **2**•$H_2O$: C, 45.82; H, 4.66; N, 9.09; S, 2.60; Cl, 8.63%.
9 UV-vis (acetonitrile) $\lambda_{max}$ / nm ($\varepsilon$ / $M^{-1}$ $cm^{-1}$), **1**: 697 (300), 491 (2300), 458 (2400), 331 (22 000); **2**: 698 (290), 489 (2000), 459 (2400), 331 (22 500). Selected IR data ($cm^{-1}$, KBr pellet), **1**: 1608 ($\nu_{asym}(COO^-)$), 1446 ($\nu_{sym}(COO^-)$), 1096 ($\nu(ClO_4^-)$); **2**: 1610 ($\nu_{asym}(COO^-)$), 1446 ($\nu_{sym}(COO^-)$), 1088 ($\nu(ClO_4^-)$).
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