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Preparation of Self-Assembled Monolayer of Dinuclear Iron Complex on Au Electrode and Its Reaction with Molecular Dioxygen

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Diiron(II) complex with a new dinucleating ligand containing terminal amino group, 2,6-bis[bis(6-pivalamido-2-pyridylmethyl)aminomethyl]-4-aminophenol (tppap) (1), $[Fe_2(tppap)(C_6H_5COO)_2]^+$ (2), was synthesized. The self-assembled monolayer (SAM) of 2, 2/Au, was prepared by the coupling reaction between 2 and activated ester-modified Au electrode. The redox behavior of 2/Au was observed in aqueous solution at room temperature, which suggests that 2 on Au surface has been stabilized as compared with 2 in homogeneous solution. In addition, the redox potentials of 2/Au assignable to Fe_2(II,II)/(III,III) and Fe_2(II,III/III,III) shifted to negative direction by bubbling of molecular dioxygen, which returned to the original potential by Ar bubbling. These behaviors were reversible, suggesting that 2/Au can reversibly bind/release molecular dioxygen in aqueous solution at room temperature.

Key words: diiron complex, molecular oxygen, peroxo complex, self-assembled monolayer

1. INTRODUCTION

The binding and activation of molecular oxygen (O_2) by non-heme iron proteins are key processes in biological systems. A class of proteins such as hemerythrin (Hr) and methane monooxygenase (MMO), which have similar structural motif of two carboxylate-bridged diiron sites, have received much interest in the past decade [1-5].

Hr binds O_2 as terminal peroxide by $2e^-$ reduction with diiron center, which can bind/release O_2 reversibly. On the contrary, MMO activates O_2 to convert methane to methanol under very mild condition at normal pressure and room temperature. Mechanism of O_2 activation by MMO is $4e^-$ reduction process accompanied by formation of the diiron(IV) species named compound Q, which is converted from peroxo intermediate [5].

Numerous studies on diiron model complexes have much contributed to the understanding of the structural and catalytic properties of their active sites. However, almost diiron model complexes can generate O_2 adduct only in non-aqueous solution at low temperature [6-10]. For example, we previously synthesized Fe_2 complex using dinucleating ligand [11]. This complex irreversibly reacted with O_2 to form μ-peroxo complex in acetone at –60 °C. When this peroxo complex was heated till room temperature, it was decomposed completely.

The self-assembled monolayers (SAMs) on various metal or metal oxide surfaces have recently received much attention as one of the important tools in nanotechnology and molecular engineering [12-17]. This method allows the introduction of desired functions on the surface at the molecular scale by self-assembling of specific molecular groups such as metal complexes and proteins. In addition, the molecules modified on an electrode surface generally become more stable than that in homogeneous solution. Thus, we attempted the modification of non-heme diiron model complex on the electrode surface by self-assembling method.

Herein, we report the preparation of diiron(II) complex (2) with new dinucleating ligand containing terminal amino group (1) and its self-assembled monolayer, 2/Au (Figs. 1 and 2). 2 on 2/Au was remarkably stable and bound with O_2 in aqueous solution at room temperature reversibly.

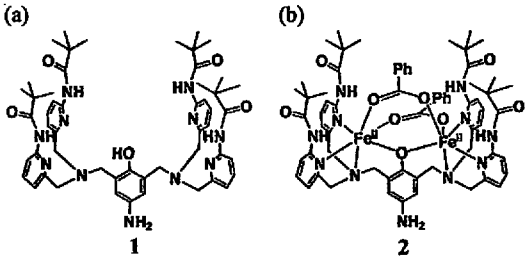

Fig. 1. Schematic views of ligand 1 (a) and complex 2 (b).

2. EXPERIMENTAL

$Fe(CF_3SO_3)_2{\cdot}4CH_3CN$ was prepared from iron powder and CF_3SO_3H [18]. All other chemicals were commercially available and used without further purification.

All the manipulations for preparation of the ligand and the diiron(II) complex were carried out under argon atmosphere. Ligand 1 and complex 2 were prepared by modification of the previous method [11, 19]. The detailed synthetic methods of 1 and 2 are described below:

Ligand **1**.

2,6-Bis[bis(6-pivalamido-2-pyridylmethyl)aminomethyl]4-nitrophenol (0.5 mmol) was dissolved in a small amount of dry MeOH, and thereto 10% Pd-C (catalytic amount) and anhydrous ammonium formate (2.4 mmol) were added. After the reaction solution (slightly exothermic) was stirred at room temperature for about 4 hours, a white powder was deposited. The powder and catalyst were collected by filtration and washed with methanol. After only the powder was dissolved in chloroform, the residue was removed by filtration through a celite pad. The chloroform solution was evaporated under a reduced pressure to give white powder, which was dried *in vacuo*. Yield 68.9%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.31 (36H, s, *t*-Bu), 3.71 (4H, s, CH), 3.75 (8H, s, CH), 6.66 (2H, s, Ar), 7.16 (4H, d, py, J = 7.5 Hz), 7.60 (4H, t, py, J = 7.8 Hz), 8.07 (4H, d, py, J = 8.1 Hz), 8.08 (4H, br, NH). MS m/z 928.5 $[M + H]^+$.

Complex **2**.

A 2 mL of MeOH solution of $Fe(CF_3SO_3)_2{\cdot}4CH_3CN$ (0.2 mmol) was added to 2 mL of CH_2Cl_2 solution of TPPAP (0.1 mmol). To the resultant solution was added 2 mL of MeOH containing C_6H_5COONa (0.2 mmol) and Et_3N (0.1 mmol). The resultant yellow solution was allowed to stand for several days to give yellow crystals, which was collected by filtration, washed with methanol and ether, and dried in reduced pressure. Yield 34%. Found: C, 55.97; H, 5.21; N, 10.57%. Calcd. for $2(CF_3SO_3){\cdot}$MeOH: C, 55.86; H, 5.65; N, 10.54%.

Preparation of **2**/Au.

The Au electrode was prepared by the evaporation of Au (99.999%) on mica with 1,000-Å thickness. The monolayer of 3,3'-dithiobis(succinimidylpropionate) (DTSP) was prepared by immersing of the annealed Au electrode in acetone solution of DTSP (4 mM) for 1 min. After rinsing with acetone and MeOH, the resultant SAM was dipped into MeOH solution of **2** (1 mM) for one day (Fig. 2).

Measurements.

UV-vis absorption spectra were taken on a Jasco V-570 spectrophotometer with a UNISOKU temperature controller. ^{1}H NMR spectra were measured with a Gemini 300 MHz NMR spectrometer in $CDCl_3$ with TMS as an internal reference standard. Cyclic voltammograms were recorded by ALS600A electrochemical analyzer with a custom-made three-electrode configuration electrochemical cell. Each voltammogram was measured in an aqueous solution containing 0.1 M of $NaCF_3SO_3$ with Ag/AgCl reference electrode or 0.1 M of $TBAClO_4$ in CH_3CN was 0.01 M $Ag/AgNO_3$ in 0.1 M $TBAClO_4$ (0.6 V *vs.* Fc/Fc^+). The counter electrode was a coiled platinum wire. The working electrode was a glassy carbon for measurement of **2** in solution and a vapor-evaporated Au for **2**/Au. ESI-MS spectra were measured on a Micromass LCT API-TOF MS with a nanoelectrospray source. All spectra were obtained by spraying a MeOH solution.

3. RESULTS AND DISCUSSION

3.1 Oxygenation reaction of **2** in solution

Fig. 3 indicates the UV-vis spectral change of reaction of **2** with dioxygen in acetone at –60 °C, in which the solution color turned from yellow to violet. After the reaction with O_2, a broad peak at λ_{max} = 585 nm (ε = 3,200 $M^{-1}cm^{-1}$) appeared (Fig. 3b), which was assigned to LMCT band of the peroxo to Fe(III) ion based on comparison with the behaviors in similar peroxo diiron complexes [9]. This peak disappeared with increase in temperature (Fig. 3c), suggesting that the peroxo complex is stable only at low temperature.

From the result of X-ray crystallography, it has been clarified that **2** has two Fe centers bridged by two benzoate and one phenoxo groups, and the charge of the complex has been determined to be +2 from the existence of one counter anion ($CF_3SO_3^-$) [11]. The hydrogen bond is formed between N-H site of pivalamido group and O atom of bridging benzoate. This hydrogen bond induces the electron delocalization of the carboxyl group of the bridged benzoate, resulting that the bridging benzoate group is easy to leave. From these findings, we suggested that the oxygenation of **2** proceed *via* a five-coordinated species: one of two benzoate groups has been kept by the effect of hydrogen bonds. Similar diiron complex without pivalamido groups did not generate peroxo adduct [20]. Thus, **2** would react with O_2 to generate μ-peroxo complex.

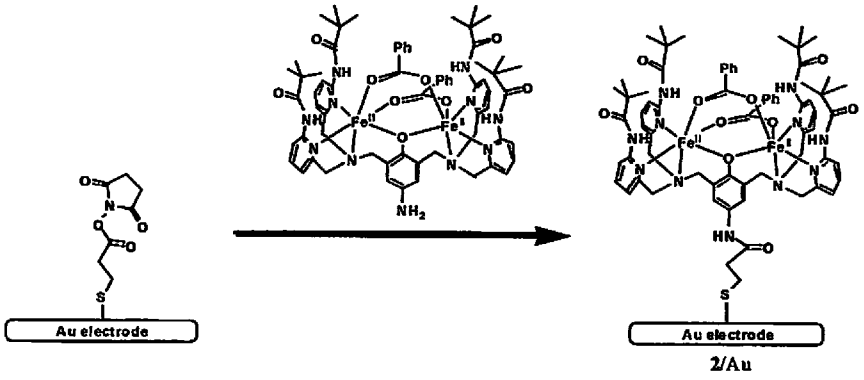

Fig. 2. Preparation of **2**/Au.

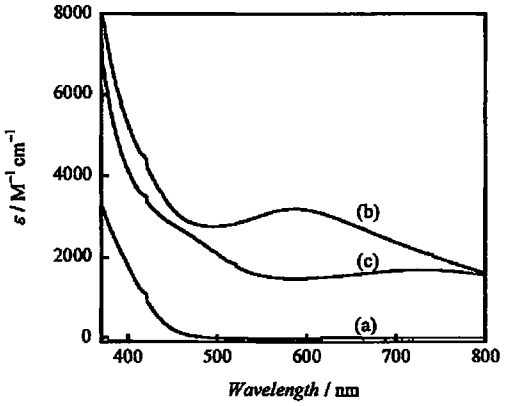

Fig. 3. UV-vis spectral change of **2** in acetone under Ar (a), O_2 (b) at −60 °C, and under O_2 with rising up to room temperature (c), respectively.

3.2 Redox behavior of **2** in solution and on Au electrode

Fig. 4 shows the cyclic voltammogram of **2** in CH_2Cl_2. One anodic wave ($2e^-$ process) and two cathodic waves (two $1e^-$ processes) were observed at E_{pa} = 0.92 V and E_{pc} = 0.67, 0.40 V *vs.* Ag/Ag^+, assignable to Fe_2(II,II/III,III), Fe_2(II,II/II,III), and Fe_2(II,III/III,III) couples, respectively, which corresponded well to those of the Fe_2 complexes with similar structures previously reported. Each redox process was not reversible, suggesting that **2** in CH_2Cl_2 is not so stable. This instability is probably explained in terms of the hydrogen bond between $N\text{-}H_{pivalamido}$ and $O_{benzoate}$. The bridging benzoate can easily release from one O site that is not restricted by hydrogen bond, so **2** may form several structures in solution.

The cyclic voltammogram of **2**/Au in aqueous solution showed one anodic wave ($2e^-$ process) and two cathodic waves (two $1e^-$ processes) at E_{pa} = −0.32 V and E_{pc} = −0.38, −0.55 V *vs.* Ag/AgCl (Fig. 5a). The linear relationship between peak currents and scan rates indicates that this redox process is originated from the species immobilized on the surface. Thus, it has been demonstrated that **2** is modified on the Au surface. Compared to the above result in solution, these waves were assigned to Fe_2(II,II)/(III,III), Fe_2(II,II)/(II,III), and Fe_2(II,III)/(III,III) couples, respectively. Each redox potential of **2**/Au widely shifted to the negative direction compared to **2** in solution. This shift has probably been caused by the effect of negatively charged surface by linking of DTSP. Similar negative shift of the redox potential of complexes immobilized on the surface have been reported [17].

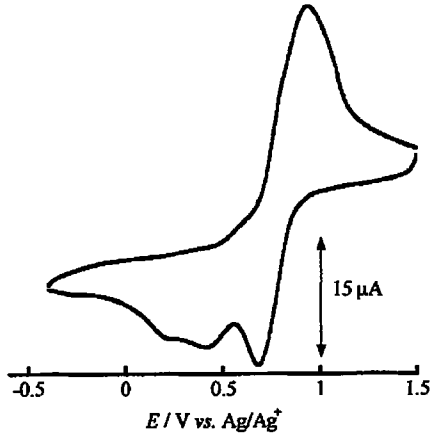

Fig. 4. Cyclic voltammogram of **2** in CH_2Cl_2 containing 0.1 M $TBAClO_4$. Scan rate is 0.1 V s^{-1}.

3.3 Oxygenation reaction of **2**/Au

The redox potential of **2**/Au in aqueous solution dramatically changed by bubbling of O_2 gas. The waves assigned to Fe_2(II,II/III,III), and Fe_2(II,III/II,III) shifted to negative direction (*ca.* 0.08 V) in comparison with those before the bubbling (Fig. 5b). In addition, these two redox potentials shifted to positive direction by Ar bubbling and finally returned to the original potentials. This change was repeated reversibly. Thus, the waves of Fig. 5b were assigned to the waves of μ-1,2-peroxo complex, $Fe_2(O_2)$(II,II/III,III) and $Fe_2(O_2)$(II,III/III,III), respectively. This finding indicates that the reversible O_2 adsorption/desorption has occurred on **2**/Au in aqueous solution at room temperature. That is, the peroxo complex of **2** became extremely stable by modifying on Au surface. Here we can state that complex **2** on **2**/Au has behaved like the solid state to prevent the degradation of **2**; the peroxo adduct of **2** has been stabilized in aqueous solution at room temperature.

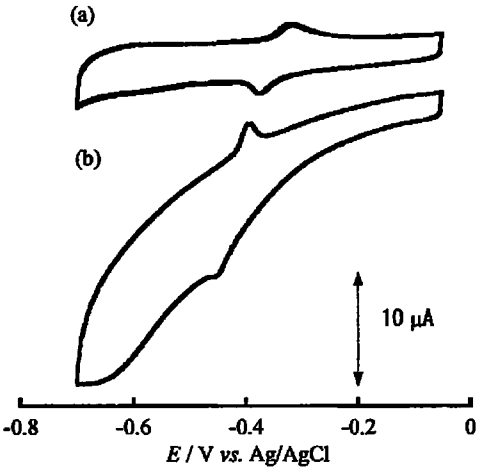

Fig. 5. Cyclic voltammograms of **2**/Au in 0.1 M $NaCF_3SO_3$ aqueous solution (a) under Ar and (b) after bubbling of O_2. Scan rate is 0.05 V s^{-1}.

4. CONCLUSION

In summary, we prepared self-assembled monolayer of diiron(II) complex, **2**/Au, and observed the interesting redox behavior by captured molecular oxygen in aqueous solution at room temperature. We also succeeded in observation of its reversible oxygen adsorption/ desorption. The immobilization of **2** onto Au electrode surface makes it stabilize extremely. This is the rare example that the reversible adsorption/desorption of dioxygen has been observed by the immobilization of the non-heme functional model complex on the electrode.

Acknowledgments

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References

[1] P. C. Wilkins, R. G. Wilkins, *Coord. Chem. Rev.*, **79**, 195-214 (1987).
[2] R. E. Stenkamp, *Chem. Rev.*, **94**, 715-26 (1994).
[3] M. -H. Baik, M. Newcomb, R. A. Friesner, S. J. Lippard, *Chem. Rev.*, **103**, 2385-420 (2003).
[4] B. J. Wallar, J. D. Lipscomb, *Chem. Rev.*, **96**, 2625-58 (1996).
[5] L. J. Shu, J. C. Nesheim, K. Kauffmann, E. Munck, J. D. Lipscomb, L. Que, Jr., *Science*, 275, **515** (1997).
[6] N. Kitajima, N. Tamura, H. Amagai, H. Fukui, Y. Moro-oka, Y. Mizutani, T. Kitagawa, R. Mathur, K. Heerwegh, C. A. Reed, C. R. Randall, L. Que, Jr., K. Tasumi, *J. Am. Chem. Soc.*, **116**, 9071-85 (1994).
[7] Y. Hayashi, T. Kayatani, H. Sugimoto, M. Suzuki, K. Inomata, A. Uehara, Y. Mizutani, T. Kitagawa, Y. Maeda, *J. Am. Chem. Soc.*, **117**, 11220-9 (1995).
[8] T. Ookubo, H. Sugimoto, T. Nagayama, H. Masuda, T. Sato, K. Tanaka, Y. Maeda, H. Okawa, Y. Hayashi, A. Uehara, M. Suzuki, *J. Am. Chem. Soc.*, **118**, 701-2 (1996).
[9] M. Suzuki, H. Furutachi, H. Okawa, *Coord. Chem. Rev.*, **200-202**, 105-29 (2000).
[10] H. Zheng, S. J. Yoo, E. Munck, L. Que, Jr., *J. Am. Chem. Soc.*, **122**, 3789-90 (2000).
[11] Unpublished results.
[12] H. Yamada, H. Imahori, Y. Nishimura, I. Yamazaki, S. Fukuzumi, *Chem. Commun.*, 1921-22 (2000).
[13] T. Inomata, M. Abe, T. Kondo, K. Umakoshi, K. Uosaki, Y. Sasaki, *Chem. Lett.*, 1097-98 (1999).
[14] Jerzy Zak, Hongping Yuan, Mankit Ho, L. Keith Woo, Marc D. Porter, *Langmuir*, **9**, 2772-4 (1993).
[15] K. Fujita, N. Nakamura, N. Ohno, B. S. Leigh, K. Niki, H. B. Gray, J. H. Richards, *J. Am. Chem. Soc.*, **126**, 13954-61 (2004).
[16] K. Nakano, K. Doi, K. Tamura, Y. Katsumi, M. Tazaki, *Chem. Commun.*, 1544-5 (2003).
[17] H. Wackerbarth, F. B. Larsen, A. G. Hansen, C. J. Mckenzie, J. Ulstrup, *Dalton Trans.*, 3438-44 (2006).
[18] K. S. Hangen, *Inorg. Chem.*, **39**, 5867-9 (2000).
[19] M. Suzuki, H. Kanatomi, I. Murase, *Chem. Lett.*, 1745-8 (1981).
[20] M. Suzuki, A. Uehara, H. Oshio, K. Endo, M. Yanaga, S. Kida, K. Saito, *Bull. Chem. Soc. Jpn.*, **60**, 3547-55 (1987).

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