Immobilization of a Binuclear Ruthenium(III) Complex on a Gold (111) Surface: Observations of Proton-coupled Electron Transfer and Electrochemical Durability in Aqueous Media

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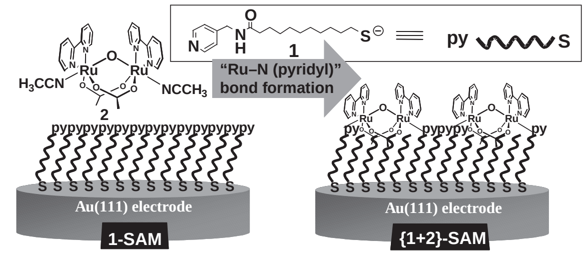
An oxo-bridged diruthenium(III) complex was immobilized on a Au(111) electrode through the coordination by terminal pyridyl groups of self-assembled monolayer of alkyl chains, and the immobilized complex underwent proton-coupled electron-transfer reactions in a very wide pH range (2–12) with remarkable monolayer durability for multiple potential cycles.

Proton-coupled electron transfer (PCET) plays a crucial role in energy transduction in a wide range of biological and chemical processes.[1] The synthesis and assembly of molecular components capable of displaying the PCET reactions thus offer promising molecular systems which are potentially useful for proton-responsive molecular devices. In this context, a considerable interest has been placed on the assembly of proton-responsive molecules on a solid surface.[2]

Previously, we have reported the preparation of a self-assembled monolayer (SAM) of non-heme diiron(III) complexes with the $\{Fe^{III}–(\mu\text{-O})–Fe^{III}\}$ core on a Au(111) electrode, as the first example of SAM with biomimetic model complexes and showed that the surface-immobilized complex displayed a single step of PCET reaction, $\{Fe^{III}–(\mu\text{-O})–Fe^{III}\}/\{Fe^{II}–(\mu\text{-OH})–Fe^{III}\}$, in a pH range of 2–12.[3] The ruthenium(III) analog $[Ru_2(\mu\text{-O})(\mu\text{-}CH_3COO)_2(2,2'\text{-bipyridine})_2(\text{pyridine})_2]^{2+}$ and its derivatives[4] are known to undergo two consecutive redox reactions, $Ru^{III}Ru^{III}/Ru^{II}Ru^{III}$ and $Ru^{II}Ru^{III}/Ru^{II}Ru^{II}$, that are proton-coupled in solution,[5] and will thus provide a new coordination motif where the *multiple* numbers of electron-transfer processes are controlled by proton on the electrode surface. Here, we report successful immobilization of the diruthenium (Ru_2) complex on a Au(111) electrode and the PCET characteristics at an aqueous solution/monolayer interface. The Ru_2 complex is immobilized on the electrode surface easily through ligand substitution, and the surface-immobilized complex shows well-defined PCET characteristics in a very wide pH region (2–12). This study offers a prominent, new candidate for molecular components useful for proton-responsive molecular devices that work at an electrochemical interface.

Fabrication procedures are illustrated in Scheme 1. Self-assembled monolayer, **1**-SAM, which offers 4-pyridyl terminal groups at the solution/solid interface, has been prepared. For the surface attachment of the Ru_2 complex, a new derivative, $[Ru_2(\mu\text{-O})(\mu\text{-}CH_3COO)_2(2,2'\text{-bipyridine})_2(CH_3CN)_2](PF_6)_2$ (**2(CH$_3$CN)$_2$**), has been designed and synthesized.[6] This molecule has two CH_3CN ligands at the oxo-trans positions and offers binding sites to surface-immobilized 4-pyridyl groups on Au(111). Thus, immobilization of **2(CH$_3$CN)$_2$** was carried out by immersing the **1**-SAM-modified Au(111) electrode[7] into a CH_3CN/H_2O (1:9, v/v) solution of **2(CH$_3$CN)$_2$** for 4 days at 25 °C, resulting in the formation of $\{\mathbf{1}+\mathbf{2}\}$-SAM. This immersion time is long enough for the attachment of **2** since the corresponding ligand substitution of the derivatives completes within several minuets in solution.[8] Infrared spectrum of $\{\mathbf{1}+\mathbf{2}\}$-SAM reveals the presence of the Ru_2 components on the electrode surface, showing a strong absorption at 1439 cm^{-1} due to bridging acetates within the diruthenium(III) core. Water contact angle changed significantly upon immobilization from 33.0(±2.0)° for **1**-SAM to 24.6(±3.2)° for $\{\mathbf{1}+\mathbf{2}\}$-SAM. An electrochemical reductive desorption experiment displayed a broad but single wave (−1.0 V vs. Ag/AgCl) for $\{\mathbf{1}+\mathbf{2}\}$-SAM in a 0.5 mol dm^{-3} KOH (aq) suggesting the homogeneous placement of the Ru_2 centers on the electrode surface.



Scheme 1. Chemical structures of the compounds and monolayer fabrication procedures.

The PCET reactions of the Au(111) electrode covered with $\{\mathbf{1}+\mathbf{2}\}$-SAM were studied under argon atmosphere, and the pH-dependent cyclic voltammograms (CVs) are shown in Figure 1. Sodium perchlorate (0.1 mol dm^{-3}) was used as a supporting electrolyte, and a Britton–Robinson buffer was used to adjust the solution pH.

At pH 2.0 (Figure 1a, top), the CV reveals sequential two redox waves at $E^{0\prime} = +0.21$ and -0.05 V vs. Ag/AgCl. Since

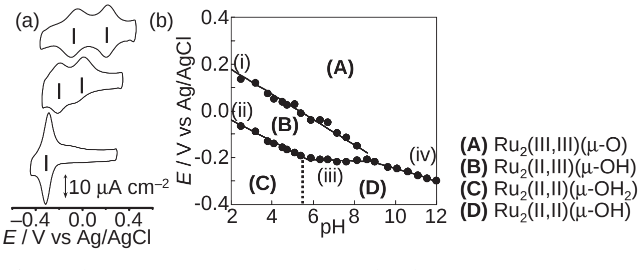


Figure 1. pH-Dependence of CVs of $\{\mathbf{1}+\mathbf{2}\}$-SAM prepared on the Au(111) working electrode in contact with 0.1 mol dm^{-3} $NaClO_4$ aqueous media containing Britton–Robinson buffer. (a) top: pH 2.2; middle: pH 5.9; bottom: pH 12.0. A counter electrode is a Pt coil and a reference electrode is an Ag/AgCl. Scan rate = 500 mV s^{-1}. (b) A potential–pH diagram. The surface pK_a of the $\{Ru^{II}–(\mu\text{-}OH_2)–Ru^{II}\}$ core (C) is estimated to be 5.8 (a dotted line).

1-SAM, prior to the adsorption of **2**, shows no redox response in the same potential region, they are ascribed to the redox activity of the Ru_2 complex. On the basis of solution studies,[4] both are one-proton/one-electron processes, ascribable to $\{Ru^{III}–(\mu\text{-O})–Ru^{III}\}/\{Ru^{II}–(\mu\text{-OH})–Ru^{III}\}$ (+0.21 V) and $\{Ru^{II}–(\mu\text{-OH})–Ru^{III}\}/\{Ru^{II}–(\mu\text{-OH}_2)–Ru^{II}\}$ (−0.05 V). As expected for the surface-attached redox centers, peak current intensities were increased linearly with increasing scan rates (Supporting Information). By integrating charge under the CV waves, the surface coverage of **2** is calculated to be $2.9(\pm0.3) \times 10^{-11}\ \text{mol cm}^{-2}$. According to our preliminary modeling study, this value is reasonable if the dicationic complex ion and two $PF_6{}^-$ counter ions are close packed in the 1:2 ratio on the two-dimensional plane. Influence of geometrical orientation of the 4-pyridyl groups in **1**-SAM may also be significant for coordination to the metal centers.

On increasing solution pH, the two waves are shifted to the negative direction (Figure 1a, middle), and they eventually merge into a single wave with the $E^{0\prime}$ being shifted further negatively (Figure 1a, bottom). The potential–pH diagram (e.g., Pourbaix diagram) is presented in Figure 1b. In the potential and pH ranges examined, there are four redox processes, labeled as (i) to (iv), and, therefore, four redox states of the Ru_2 compound, (A) to (D), are generated on the electrode surface. The least-square fitting provides slopes of −0.054, −0.046, −0.003, and −0.027 V per pH unit for processes (i), (ii), (iii), and (iv), respectively. These slopes are qualitatively consistent with the expected values for proton-coupled electron-transfer mechanisms: $\{1H^+/1e^-\}$ process for (i) and (ii), proton-independent $1e^-$ process for (iii), and $\{1H^+/2e^-\}$ process for (iv).[9] We emphasize that the Pourbaix diagram of the diruthenium complex of this type is firstly reported here,[10] and reversible switching of the multiple redox states of the immobilized complex is successfully demonstrated on the electrode surface by use of PCET characteristics in aqueous media.

We have investigated the monolayer durability for multiple applied potential cycles. Figure 2 shows CVs recorded at various pHs and in different applied potential ranges. Remarkably, at pH 2.2, CV shows fully constant response over 100 times as far as the potential was cycled between +0.40 and 0.06 V, indicating that the monolayer is highly stable for the $\{1H^+/1e^-\}$ reaction involving the $\{Ru^{III}–(\mu\text{-O})–Ru^{III}\}$ and $\{Ru^{II}–(\mu\text{-OH})–Ru^{III}\}$ states. Similarly, a negligible change in CV was observed for the $\{1H^+/2e^-\}$ reaction at pH 11.5 (Figure 2b). CV change was observed, however, when the negative potential scan limit was extended to −0.2 V at pH 2.2 (Figure 2c) so that the highly reduced and doubly protonated form, $\{Ru^{II}–(\mu\text{-OH}_2)–Ru^{II}\}$, was generated. From charge under the CV wave, ca. 70% of the surface-attached Ru_2 moieties was lost after 100 potential cycles. We attribute the decreased redox activity to dissociation of the Ru_2 moiety from the pyridyl groups in the organic monolayer rather than dissociation of the whole molecule from the electrode surface. The maintenance of the organic monolayer is supported by infrared spectroscopy. Furthermore, in the reductive desorption experiments, the surface coverage observed after the potential cycles appeared to be fully consistent with that observed for $\{\mathbf{1}+\mathbf{2}\}$-SAM ($1.1 \times 10^{-9}\ \text{mol cm}^{-2}$ in $0.5\ \text{mol dm}^{-3}$ KOH aq).

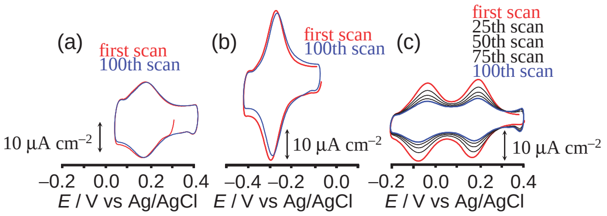


Figure 2. Selected CVs during consecutive 100 potential cycles at different solution pHs and in different applied potential region, demonstrating the electrochemical durability of $\{\mathbf{1}+\mathbf{2}\}$-SAM in contact with aqueous electrolyte media. (a) pH 2.2, +0.40 to +0.06 V. (b) pH 11.5, −0.10 to −0.45 V. (c) pH 2.2, +0.40 to −0.20 V. Scan rate = $500\ \text{mV s}^{-1}$.

In summary, the CV measurements reveal successful immobilization of the dirutheмium(III) complex on the densely packed organic SAM surface via ligand exchange and show well-defined PCET behavior in a very wide pH range. The system shows remarkably high sustainability to multiple redox cycling in both highly acidic and basic media as far as the applied potential range is controlled. Our "interfacial coordination strategy" to assemble and confine metal complexes on surface is quite simple and free from long-term synthetic work. Also, in the present case, the compound is easy to remove from the surface, when necessary, by just controlling the redox state of the molecule. These features may provide a significant appeal for a new molecular device application.

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6 This complex has also been prepared by A. Nagasawa and his co-workers: H. Sawamoto, Master Thesis, Saitama University, **2000**. A detailed synthetic work-up and characterization data of the complex will be described in a separate full paper.

7 **1**-SAM was prepared by immersing a flame-annealed Au(111) electrode ($S = 0.16\ \text{cm}^2$; roughness factor, 1.1) into a ethanolic solution of $\{(4\text{-py})CH_2NHC(O)(CH_2)_{10}S\}_2$ (50 µM) for 12 h at 25 °C. The surface coverage was $1.1 \times 10^{-9}\ \text{mol cm}^{-2}$ on the basis of reductive desorption experiment (the reduction peak potential, −1.1 V vs. Ag/AgCl in $0.5\ \text{mol dm}^{-3}$ KOH (aq).

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9 The deviation of the slopes from those expected for ideal Nernstian reactions (0.059 and 0.029 V per pH unit for $\{1H^+/1e^-\}$ and $\{1H^+/2e^-\}$, respectively) requires further examination, since, in some reported cases, the pH dependency is influenced by, for example, the interfacial proton concentration and the distance between the redox center and the electrode surface.

10 Details of the PCET reactions in homogeneous solutions will be reported separately: A. Kikuchi, T. Fukumoto, K. Umakoshi, Y. Sasaki, A. Ichimura, to be submitted.