Multicomponent Molecular Layers that Exhibit Electrochemical Potential Flip on Au(111) by Use of Proton-coupled Electron-transfer Reactions

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Interfacial ligand substitution of triruthenium(III) complexes confined on gold as a monolayer has proven to be useful to construct molecular heterostructures by quantitatively incorporating 4,4′-bipyridine-anchored diruthenium(III) complexes, whose multi-step redox sequence is reversibly tuned by proton-coupled electron-transfer reactions.

Precise control of chemical functions in molecules, molecular assembly, and supramolecular assembly on electrode surfaces is an important element of nanoscale science and technology for the development of molecule-based devices and switches. Redox-active transition-metal complexes and clusters, especially those showing reversible response to external stimuli such as electric field, light, coexisting electrolyte, and pH, have gathered increasing research interests recently as molecular building blocks.[1]

We have previously demonstrated a significant utility of ruthenium-based trinuclear and dinuclear complexes as stimuli-responsive molecular components which can be confined on gold electrode surfaces in the form of a self-assembled monolayer (SAM).[2–4] The SAM prepared from the trinuclear $\{Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6\}$ complexes showed reversible trap-and-release behavior towards gaseous CO and NO molecules,[2] photoinduced CO-releasing reactions,[3] and layer-by-layer film formation by conducting site-specific ligand replacement at an electrochemical interface.[4] The diruthenium $\{Ru_2(\mu\text{-}O)(\mu\text{-}CH_3COO)_2\}$ complexes are known to exhibit multi-step proton-coupled electron-transfer (PCET) reactions in aqueous organic solutions.[5] When the dinuclear complexes were confined on the organic SAM surface, precise control of electronic levels of the dinuclear complexes were successfully achieved by tuning the solution pH.[6] The ability and utility of those functional metal complexes may be significantly enhanced if interfacial synthetic procedures are available to combine, assemble, and integrate those components as a film in a desired, well-defined sequence and composition.

Here, we report our interfacial bottom-up approach to the preparation of a novel, redox-active multicomponent film that shows "electrochemical potential flip" on a Au(111) electrode, a novel concept of interfacial phenomenon in which the energy sequence of redox orbitals of two different molecular components, the "Ru_3" and "Ru_2" complexes in this case, is reversibly switched by simply changing pH of the electrolyte media.

The preparative strategy for the multicomponent film is illustrated in Figure 1. On the surface of pre-organized triruthenium complex-based SAM $\mathbf{1}^{\mathbf{aq}}$/Au,[2–4] dinuclear $[Ru_2(\mu\text{-}O)(\mu\text{-}CH_3COO)_2(2,2'\text{-bpy})_2(4,4'\text{-bpy})_2](PF_6)_2$ complex (**2**) (bpy = bipyridine)[7] is deposited through forming a Ru–N(4,4′-bpy) coordination bond. We show that the resulting surface-confined film possesses redox potential gradient within the molecular backbone and, most noticeably, the redox sequence of the individual components is reversibly altered by protonation/deprotonation at the dinuclear {Ru–O–Ru} moiety, showing electrochemical potential flip at the electrode/film/solution interface. While PCET reactions have been extensively studied in a wide variety of molecular systems,[8] this characteristics has rarely been utilized for the potential tuning of multilayer films.[9] By use of thermally robust and kinetically inert transition-metal complexes as building blocks, we report here the first example of a multicomponent molecular film on a Au(111) electrode where the potential gradient in the molecular film is precisely controlled by interfacial PCET reactions.

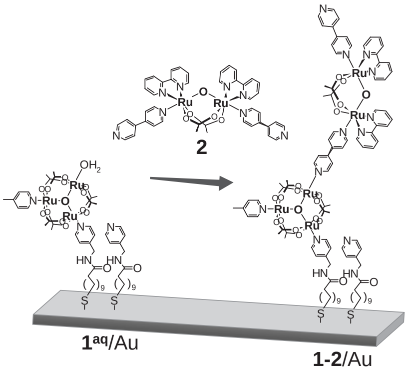

Figure 1. Schematic representation of the formation of **1**–**2**/Au film from $\mathbf{1}^{\mathbf{aq}}$/Au and **2**. For clarity, only a single molecule is shown.

A monolayer $\mathbf{1}^{\mathbf{aq}}$/Au has been prepared as reported previously.[2–4] The Ru center with an aqua ligand in $\mathbf{1}^{\mathbf{aq}}$/Au provides a binding site for **2**. Thus, immersion of the $\mathbf{1}^{\mathbf{aq}}$/Au electrode into a dichloromethane solution of **2** for 10 days at ambient temperature leads to the formation of **1**–**2**/Au, in which a $\{Ru_3\}^+$–{4,4′-bpy}–$\{Ru_2\}^{2+}$-bridged structure is involved.[10] The formation of the multicomponent film has been demonstrated by electrochemical measurements as well as spectroscopic ellipsometry, infrared reflection–absorption spectroscopy, and water contact angle measurements.[7]

Figure 2a shows cyclic voltammograms of **1**–**2**/Au recorded at pH 12 together with that of $\mathbf{1}^{\mathbf{aq}}$/Au for comparison. At this pH, two consecutive redox processes are observed for **1**–**2**/Au in the potential region between +0.2 and −0.5 V vs. Ag/AgCl. The redox couple appeared at the negative potential region {A and B} is ascribed to a two-electron/one-proton-coupled redox process, $\{Ru^{II}Ru^{II}(\mu\text{-}OH)/Ru^{III}Ru^{III}(\mu\text{-}O)\}$, occurring at the Ru_2 group. This assignment is supported by our earlier study[6] showing that the diruthenium complex monolayer with closely related structure exhibits PCET behavior at a similar

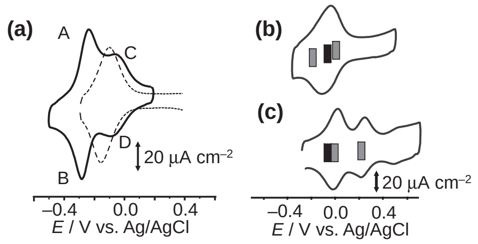

Figure 2. Cyclic voltammograms showing the formation of multicomponent film on Au(111). (a) **1**–**2**/Au (a solid line) at pH 12 and $\mathbf{1}^{\mathbf{aq}}$/Au (a broken line) at pH 2. Scan rate = 0.5 V s^{-1}. (b) **1**–**2**/Au at pH 6 and (c) **1**–**2**/Au at pH 2. Bars indicate the assignment of the redox waves; black and gray bars correspond to redox processes due to the Ru_3 and Ru_2 components, respectively. See text for details.

potential (−0.30 V). The other redox couple {C and D} with a smaller peak intensity is thus ascribed to a Ru_3-based one-electron process, $\{Ru^{II}Ru^{III}Ru^{III}/Ru^{III}Ru^{III}Ru^{III}\}$, which is also evident from comparison with the reference CV data (a broken line). Peak currents linearly vary with the scan rate up to 1.0 V s^{-1}, indicating the surface confinement of the two redox-active components.[7] Integration of anodic charge under the two waves (including three electrons) was estimated to be 26 μC cm^{-2}. This value indicates the presence of redox-active components of 2.0×10^{-10} mol cm^{-2} on the surface (2 electrons for $\{Ru_2\}$ and 1 electron for $\{Ru_3\}$), which suggests a nearly stoichiometric linking of **2** to $\mathbf{1}^{\mathbf{aq}}$/Au by assuming the $\{Ru_3\}$ base layer coverage of 1.2×10^{-10} mol cm^{-2} from a broken line in Figure 2a.

The observed stoichiometric layering also suggests the preference of monodentate coordination of **2** with a single 4,4′-bpy ligand for the attachment to the Ru_3 base layer, thus forming a linearly stretched molecular wire on the electrode surface as shown in Figure 1. Spectroscopic ellipsometry reveals the film thickness of **1**–**2**/Au as 4.4 ± 0.2 nm, which is reasonably consistent with a geometric distance of the proposed structure of **1**–**2**, ca. 4.6 nm. For comparison, another binding mode of **2** offering two 4,4′-bpy ligands as bridges to the Ru_3 monolayer may give rise to a smaller thickness as much as 3.0 nm.[7]

By varying the solution pH, electronic levels of the molecular wire are tuned as a result of PCET reactions expected for the Ru_2 moiety. Figures 2b and 2c show CVs recorded at different pH of the electrolyte solution. The Ru_2-based, two-electron/one-proton-coupled redox wave at pH 12, as already shown in Figure 2a, begins to shift to the positive direction as the solution pH is gradually lowered to pH 6. Owing to the insensitive nature of the Ru_3-based wave toward pH, the Ru_2-based wave merges into the Ru_3-based one-electron redox wave, resulting in the appearance of a rather broadened wave at −0.09 V (Figure 2b). Total anodic charge was 22 μC cm^{-2}. When the solution pH is further lowered, stepwise two redox waves appear (Figure 2c). This two-step behavior is ascribed to two consecutive one-electron/one-proton-coupled redox processes due to the Ru_2 moiety: i.e., $\{Ru^{II}Ru^{II}(\mu\text{-}OH_2)/Ru^{II}Ru^{III}(\mu\text{-}OH)\}$ (−0.02 V) and $\{Ru^{II}Ru^{III}(\mu\text{-}OH)/Ru^{III}Ru^{III}(\mu\text{-}O)\}$ (+0.21 V),[5,6] and also due to occurrence of the Ru_3-based redox expected at ca. −0.05 V. Observed integrated charge in 2:1 ratio (total charge of 25 μC cm^{-2}) also supports this assignment. The pH-triggered change in redox potential sequence is achieved in a reversible manner as long as the multicomponent film remains on the electrode surface.[11] Protonation at a terminal bpy group seems to have a minor contribution to the overall CV behavior. Importantly, at any pH region studied, the Ru_3 group efficiently mediates electron transfer between the Ru_2 center and the electrode surface at a distance close to 4 nm.

In conclusion, by employing interfacial ligand substitution we have successfully achieved the synthesis of multicomponent multinuclear complex-based films whose redox potential sequence is reversibly flipped by solution pH with use of PCET reactions of the Ru_2 complex. The potential tuning is achievable under aqueous electrochemical conditions in an extremely wide pH region (2–12). The coordination-based bottom-up approach described in this paper thus provides useful molecular systems that should be of substantial interest in fabricating novel switching materials and their applications.

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10 We have found that the choice of immersing solvent is an important factor for the efficient formation of the layer-by-layer film: the stoichiometric layering is observed only when anhydrous dichloromethane is used as a solvent. Coordinating solvents, such as acetonitrile, lead to a smaller amount of deposition (normally less than 25%) even after immersion of 10 days.

11 Slow degradation of the film is observed when multiple potential cycles are conducted (ca. 50% loss of the Ru_2 moiety after 60 redox cycling of the $\{Ru^{II}Ru^{II}(\mu\text{-}OH_2)/Ru^{II}Ru^{III}(\mu\text{-}OH)\}$ process.