

Direct Observation of Redox Reaction of Self-Assembled Trinuclear Ruthenium Complexes on a Au(111) Surface

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Introduction

Self-assembled monolayers (SAMs) have been the focus of much research effort over the past decades. The ability to deliberately manipulate and control the chemical and electronic properties of a surface directs to wide ranging applications in fields such as biology, electronics, and catalysis. Variable inorganic and organometallic complexes with interesting properties have been used to modify electrode surface. Among them, we are interested in novel SAMs based on transition-metal multinuclear complexes with well-defined multistep redox and reactivity properties.

Recently, scanning tunneling microscopy (STM), with its ability to provide electronic and structural information with subangstrom resolution, has been one of the most powerful and promising techniques for elucidating the nature of electrode-solution interfaces, and revealed interfacial structures of atoms and molecules on substrates in solution [1].

In the present study, by using STM, we observed directly interfacial redox reactions occurring in monolayers of an oxo-centered triruthenium complex $[\{Ru_3(O)(CH_3COO)_6(mpy)(CO)\}_2(C_{10}PY)]$, where $mpy = 4\text{-methylpyridine}$ and $C_{10}PY = \{(NC_5H_4)CH_2NHC(O)-(CH_2)_{10}S^-\}_2$.

Experimental

The (111) surface used was a facet on a single-crystal Au bead prepared by melting an Au wire. The surface was cleaned before each experiment by flame annealing followed by quenching into H₂-saturated water. The monolayer was formed by immersing the clean Au(111) electrode into a freshly prepared 0.1 mM ethanol solution of the self-assembling molecules. *In-situ* STM observations were carried out with a Nanoscope E (Digital Instrument), and electrochemically-etched tungsten tip was used with coating of transparent nail polish to minimize the faradic current. All the electrode potentials are reported with respect to a saturated calomel electrode (SCE) in 0.1 M HClO₄.

Results and Discussion

Figure 1 shows a structure of triruthenium complex and a schematic representation of redox reaction of self-assembled triruthenium complex monolayers on a Au(111) in 0.1 M HClO₄. As reported previously, the SAMs of triruthenium complexes show a well-defined reversible redox wave, Ru₃(III,III,III)/(II,III,III), in an aqueous solution containing 0.1 M HClO₄ at 0.6 V vs. SCE [2].

Figure 2 shows an *in-situ* STM image of self-assembled triruthenium complex monolayers on a Au(111) in 0.1 M HClO₄ acquired at 0.4 V and 0.8 V. When the potential was stepped from 0.4 V to 0.8 V (the position marked by an arrow), a large number of bright spots appeared on the surface (lower part of the image). The bright spots caused by the redox reaction are believed to correspond to the Ru₃(III,III,III) form of individual molecules of the triruthenium complex. We note that this

behavior was reversible.

Figure 3 shows a typical high-resolution *in-situ* STM image of self-assembled triruthenium complex monolayers on a Au(111) in 0.1 M HClO₄. In this image, each triruthenium complex can be recognized as a circle consisting of several bright spots.

Detailed analyses of the STM image will also be presented.

References

- [1] K. Itaya, *Prog. Surf. Sci.*, **58**(3), 121-248 (1998).
- [2] A. Sato, M. Abe, T. Inomata, T. Kondo, S. Ye, K. Uosaki and Y. Sasaki, *Phys. Chem. Chem. Phys.*, **3**, 3420-3426 (2001).

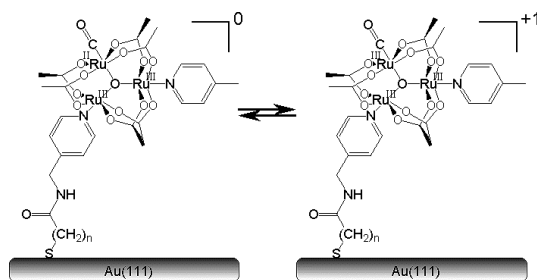


Figure 1 A schematic representation of redox reaction of self-assembled triruthenium complex monolayers on a Au(111).

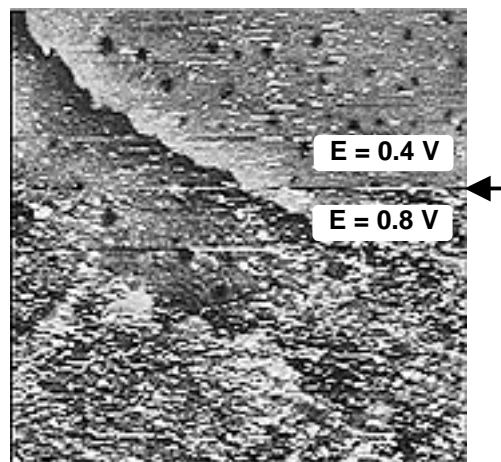


Figure 2 *In-situ* STM image (100 x 100 nm²) of self-assembled triruthenium complex monolayers on a Au(111) in 0.1 M HClO₄ acquired upon stepping the potential from 0.4 V to 0.8 V (from upper to lower part of the image). The potential was stepped at the position marked by an arrow.

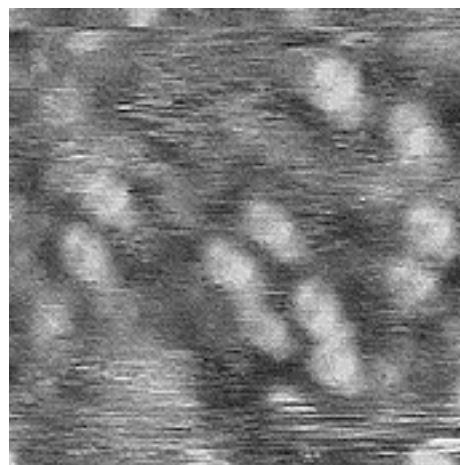


Figure 3 Typical high-resolution *in-situ* STM image (10 x 10 nm²) of self-assembled triruthenium complex monolayers on a Au(111) in 0.1 M HClO₄ at 0.8 V vs. SCE.