Electric Conduction Properties of Self-assembled Monolayer Films of Ru Complexes with Disulfide/Phosphonate Anchors in a Au–(Molecular Ensemble)–(Au Nanoparticle) Junction

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Electric conduction properties of SAM films of Ru complexes with disulfide or phosphonate anchors have been measured by Au-nanoparticle-assisted conducting probe atomic force microscopy. The *I–V* curves of these films were nonlinear, and the resistivities depend on the headgroups and the layered structure in ways that can be explained by the contact resistance and the insulating effect of the Zn–phosphonate interlayer in metal–molecule–metal junctions. Asymmetry in these films causes a rectification effect on the *I–V* response.

Metal–(single molecule) and metal–(molecular ensemble) junctions are currently being considered as key elements in molecule-based electronic devices,[1] and their conductivity has recently been measured by using experimental setups with a mechanical break junction,[2] the nanogap at a flat electrode,[3] a crossed-wired junction,[4] or the nanogap at a mercury drop electrode.[5] Even though the break-junction and nanogap methods make it possible to probe the electrical properties of individual molecules, it is difficult to characterize their junction structure. Scanning probe microscope (SPM) measurements made with a gold-coated conducting probe, however, can be used to characterize the surface morphological structure of a single molecule or an ensemble and reproducibly measure the electric properties at the same time.[6,7]

To develop surfaces potentially useful in molecular devices, we have made self-assembled monolayer (SAM) films consisting of Ru complexes attached either to ITO by phosphonate groups or to Au by disulfide groups.[8] In the present study, we investigated the effects of metal–molecule–metal junctions by using Au-nanoparticle-assited conducting probe atomic force microscopy (CP-AFM) to measure the electric conductivity of self-assembled monolayer films bearing Ru complexes with different structures (Figure 1). Reproducibility was checked by making at least ten measurements for each sample type. As shown in Figure 2, two kinds of film structures were prepared on Au surfaces: either a single layer of symmetric or asymmetric Ru complexes (SAMs **1**–**3**) or a bilayer of asymmetric Ru complexes interconnected by Zn^{2+}–phosphonate (SAMs **4** and **5**). Samples of each kind were prepared with and without attached Au nanoparticles. SAMs **1** and **3** were prepared by immersing a precleaned Au substrate for 5 days in a 50 µM solution of the appropriate Ru complex (Figure 1) dissolved in dimethylformamide. The bilayered SAM **4** was made by immersing the SAM **3** substrate in an aqueous solution of $ZnCl_2$, rinsing it, and then immersing it in a methanol/CH_3CN (1:1 v/v) solution of the RuSP complex. The SAM **2** and **5** films, with gold nanoparticles (AuNPs), were made by incubating the SAM **1** and SAM **4** films with a toluene solution of AuNPs (Harima Kasei Co., Ltd.; 4.7 ± 0.3 nm) for 1 h at room temperature. Electric conductivity was measured under ambient conditions by CP-AFM with a conducting Pt/Ir AFM tip.

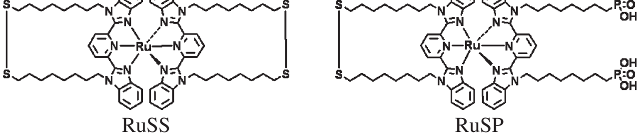
RuSS RuSP

Figure 1. Molecular structures of the Ru complexes.

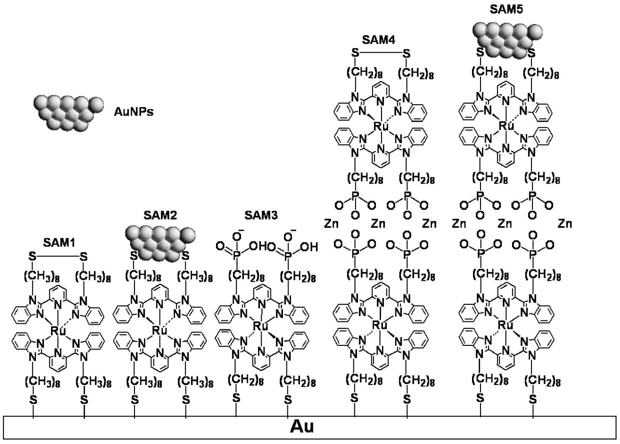

Figure 2. Schematic illustration of the metal–molecule–metal junctions on a Au substrate.

Cyclic voltammetry (CV) revealed a reversible electrochemical response for the $Ru^{II/III}$ couple at $E_{1/2} = 811\,mV$ for SAM **1**, 810.5 mV for SAM **3**, and 800.5 mV vs. Ag/AgCl for SAM **4**. The peak current for SAM **4** was almost twice that for SAM **1**. The surface coverages of SAMs **1**, **3**, and **4** were respectively 7.6×10^{-11}, 1.8×10^{-10}, and $1.2 \times 10^{-10}\,mol/cm^2$, which were close to the fully covered value calculated from molecular modeling ($9.8 \times 10^{-11}\,mol/cm^2$).

The current–voltage (*I–V*) curves of SAMs **2**, **3**, **4**, and **5** are shown in Figure 3. The *I–V* curve of SAM **1** (Figure S4[15]) was similar to those of SAMs **2** and **5**, both of which showed nonlinear characteristics at tip bias voltage V between -1 and $+1$ V, but the current of SAM **1** was smaller than those of SAMs **2** and **5**. However, ohmic behavior was found at low bias ($-200\,mV < V < 200\,mV$), and resistivity of each SAM was obtained from the slope in this linear region (Figure S5[15]). The resistivities obtained for SAM **2** and SAM **5** were respectively 1.97 and 300 GΩ, so the insertion of a Zn–phosphonate layer

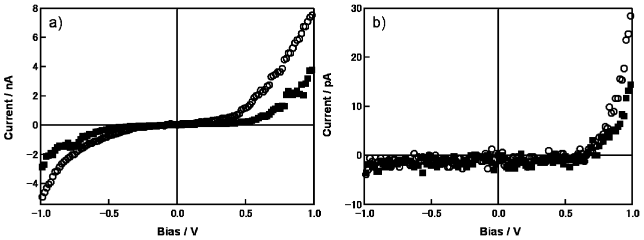

Figure 3. a) Current–voltage curve of SAM **2** (○) and SAM **5** (■) and b) of SAM **3** (○) and SAM **4** (■).

seems to increase the resistance by acting as an insulating barrier. The present resistivities are comparable to those for other dithiolated molecules in contact with Au nanoparticles: carotenedithiol (4 GΩ),[9] phenyleneethynyldithiol (1.7 GΩ),[10] and peptidedithiol (225 GΩ).[11] Comparing the *I*–*V* curve of SAM **3** with that of SAM **1**, the current for SAM **3** decreased 100-fold, suggesting that the large contact potential barrier exists at the –PO_3H–Pt/Ir tip interface. Furthermore, as shown in Figure 3b, SAMs **3** and **4** rectify current in the forward direction relative to that in the reverse one, which is in contrast to the results for SAMs **1**, **2**, and **5**. At 1 V the ratio of the forward to the reverse bias current is 7.2 for SAM **3** and 4.0 for SAM **4**. Not only the contact barrier between tip and the headgroup but also the asymmetry on two Au–Pt/Ir tip electrodes may affect the rectification effect.[12]

The resistivity of the SAM **5** film, in which the disulfide groups at the top of SAM **4** were derivatized with Au nanoparticles, was about 200 times less than that of SAM **4**. The contact resistance thus appears to be decreased by the strong binding between the disulfide headgroups and Au nanoparticles. The effects of molecule–metal (or electrode) contact on the conductance of single molecules with various anchoring groups (–SH, –NH_2, –COOH, and PMe_2) have been studied recently by single-molecule conductance measurements, in which the contact resistance arising from the surface anchoring groups and metal work function[13] plays a key role in the electron-transport properties of the metal–(molecule)–metal junction.

In conclusion, we have presented the electric conduction properties of SAM films of Ru complexes measured using the CP-AFM method. The *I*–*V* curves of these films can be explained by the contact resistance and the effect of the Zn–phosphonate interlayer in the bilayered structure.[14] Furthermore, asymmetry (as in SAM **3**) leads to a rectification effect in the *I*–*V* response.

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