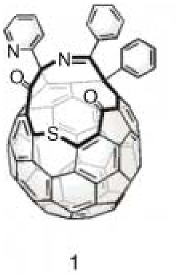
Surface Chemistry

Controlled Molecular Orientation in an Adlayer of a Supramolecular Assembly Consisting of an Open-Cage C_{60} Derivative and Zn^{II} Octaethylporphyrin on Au(111)**

*Soichiro Yoshimoto, Eishi Tsutsumi, Yosuke Honda, Yasujiro Murata, Michihisa Murata, Koichi Komatsu, Osamu Ito, and Kingo Itaya**

The supramolecular assembly of porphyrin–fullerene systems has been studied extensively because of interest in photoinduced energy- and electron-transfer processes.[1–6] Fullerenes, in particular, are considered to be suitable building blocks for the formation of three-dimensional molecular architectures because of their ability to act as strong π-electron acceptors.[1] Recently, several open-cage C_{60} derivatives were synthesized[7–9] and the unique ability of **1** to encapsulate a hydrogen molecule (H_2@**1**) was discovered.[8a] The open cavity of this molecule is responsible for its unique



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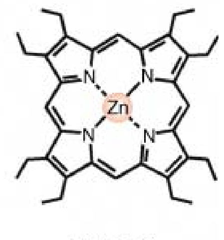

[Zn(oep)]

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[*] Dr. S. Yoshimoto, E. Tsutsumi, Y. Honda, Prof. Dr. K. Itaya+
Department of Applied Chemistry
Graduate School of Engineering
Tohoku University
Aoba-yama 04, Sendai 980-8579 (Japan)
Fax: (+81) 22-214-5380
E-mail: itaya@atom.che.tohoku.ac.jp

Prof. Dr. O. Ito
Institute of Multidisciplinary Research for Advanced Materials
Tohoku University
Katahira 2-1-1, Aoba-ku, Sendai 980-8577 (Japan)

Dr. Y. Murata, M. Murata, Prof. Dr. K. Komatsu
Institute for Chemical Research
Kyoto University
Uji, Kyoto 611-0011 (Japan)

[+] Also at CREST-JST
Kawaguchi Center Building
4-1-8 Honcho, Kawaguchi, Saitama 332-0012 (Japan)

[**] This work was supported in part by the Core Research for Evolutional Science and Technology (CREST) of the Japan Science and Technology Agency (JST) as well as by the Ministry of Education, Culture, Sports, Science, and Technology through a Grant-in-Aid for the Center of Excellence (COE) Project, Giant Molecules and Complex Systems, 2004. The authors acknowledge Dr. Y. Okinaka for his assistance in writing this manuscript and Dr. J. Inukai of Tohoku University for his useful discussion.

DOI: 10.1002/ange.200453959

functional properties. Although the π-conjugation system of **1** has been reduced by the addition of phenyl and pyridyl groups, as well as by rupture of the π system, the electronic properties of **1** are almost the same as C_{60}, as evident from electrochemical analysis.[8b] Surface modification and further design of **1** is of interest because it has an unsymmetrical shape. Supramolecular assembly on metal surfaces has also been explored to control surface properties. Several interesting studies on the self-assembled monolayers (SAMs) obtained using the fullerene–porphyrin system were reported by the research group of Imahori and Fukuzumi.[10] However, details on the orientation and arrangement of each moiety at the interface of the SAMs are still unclear. The control of molecular orientation at the nanoscale is of importance for the preparation of high-quality composite thin films through supramolecular assembly of donor–acceptor systems and for the development of new functional electrodes or devices.

Herein, we report a simple method for the construction of a 1:1 supramolecular assembled film of **1** and zinc(II) octaethylporphyrin [Zn(oep)] on an Au(111) surface and show that **1** has clear redox properties. Scanning tunneling microscopy (STM) also shows that highly ordered arrays of **1** constructed as a second layer on a well-defined [Zn(oep)] adlayer on Au(111) can be observed in 0.05 M H_2SO_4.

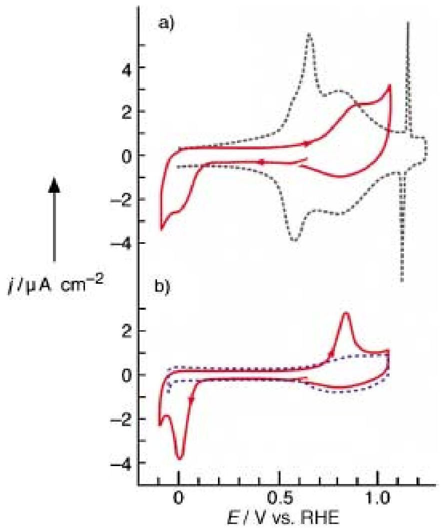

Figure 1. Typical cyclic voltammograms of a) bare Au(111) (dotted line) and **1** adsorbed onto Au(111) (solid line) and b) [Zn(oep)] (dotted line) and **1**/[Zn(oep)] adsorbed (red solid line) onto Au(111) electrodes in pure 0.05 M H_2SO_4. The scan rate was 20 mV s^{-1}.

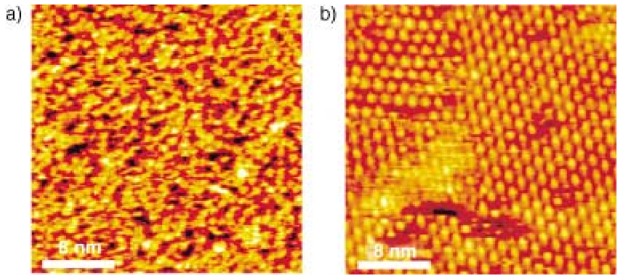

Figure 2. Typical large-scale STM images (30×30 nm^2), acquired at 0.85 V versus RHE, of the **1** adlayer a) directly formed on Au(111) and b) on [Zn(oep)]-modified Au(111) in 0.05 M H_2SO_4. The potential of the tip was 0.45 V. Tunneling currents were 0.5 nA and 0.3 nA, respectively.

Figure 1a shows typical cyclic voltammograms (CVs) recorded at a scan rate of 20 mV s^{-1} of a well-defined Au(111) (dotted line) layer and **1** directly attached to an Au(111) electrode (red solid line) in 0.05 M H_2SO_4. The voltammogram for bare Au(111) in Figure 1a in the double-layer potential region is identical to that reported previously,[11] which indicates that well-defined Au(111) is exposed to the solution. A pair of spikes observed at 1.1 V results from the order-disorder phase transition of adsorbed sulfate anions.[11a,b] For the Au(111) electrode modified with **1**, a broad reduction peak was observed between 0.1 and −0.1 V, while a re-oxidation peak appeared at 0.85 V during the anodic scan. The dotted line in Figure 1b shows the CV of a [Zn(oep)]-modified Au(111) electrode in 0.05 M H_2SO_4. No noticeable peaks were observed between 0 and 0.7 V. Subsequent immersion of the electrode into an approximately 50 μM solution of **1** in benzene for one minute resulted in a decrease in the double-layer charging current and a pair of characteristic redox peaks were clearly observed at 0 and 0.85 V during cathodic and anodic scans, respectively. This result suggests that **1** was attached on the [Zn(oep)]-modified Au(111) surface and that the carbonyl groups of **1** were oriented toward the solution phase. The CV profile drawn with a solid red line in Figure 1b is strongly associated with the electrochemical redox reaction of $>C{=}O$ to $>C^{\bullet}{-}OH$ (and $>C^{\bullet}{-}OH$ to $>C{=}O$) involving two carbonyl groups in each molecule of **1**. The amount of transferred electronic charge is estimated from the reductive peak area to be about 15.8 μC cm^{-2}. If two-electron reduction occurs on the **1**/[Zn(oep)]-modified Au(111) electrode, this value corresponds to a surface concentration of $(7.9\pm0.7)\times10^{-11}$ mol cm^{-2}. The electron-transfer process is very slow, as indicated by the CV profile shown in Figure 1b. When potential switching was carried out at potentials more negative than 0.85 V, no reduction peak at 0 V was observed. These redox peaks were not seen at C_{60}/ and C_{70}/[Zn(oep)]-modified Au(111) electrodes. Figure 2a shows a typical STM image of an adlayer of **1** formed on Au(111) in 0.05 M H_2SO_4. This STM image shows a completely disordered structure of **1** directly attached to the surface of the Au(111) layer. Individual molecules of **1** could not be distinguished under the conditions used. It is considered that **1** interacts sufficiently strongly with the Au surface to attach to the Au surface through the pyridyl and C=O groups as well as the S atom on the rim of the orifice. Such an arrangement on the modified Au(111) surface was also consistent with the CV profile shown in Figure 1a. However, highly-ordered arrays consisting of bright round spots were seen in the STM image of the [Zn(oep)]-modified Au(111) layer (Figure 2b). Some domains were clearly seen on a terrace, which suggests that the highly ordered adlayer of **1** was not formed directly on the

Au(111) layer but on the [Zn(oep)]-modified Au(111) surface.

Further details on the internal structure, orientation, and packing arrangement of the supramolecular assembled layers of **1**/[Zn(oep)] on Au(111) are revealed in the high-resolution STM image of an area of 8×8 nm^2 (Figure 3a). Intermolecular distances between the nearest neighbor molecules of **1** were found from a cross-sectional profile to be 1.68 ± 0.07 and 1.44 ± 0.05 nm for directions along arrows I and II, respectively. These distances are greater than that for C_{60} directly adsorbed on Au(111) (ca. 1.0 nm).[12] The adlattice of **1** is superimposed as a black line in Figure 3a. The surface concentration was estimated to be 8.7×10^{-11} mol cm^{-2}, which is in good agreement with that calculated from Figure 1b. The height of the corrugation of **1** was greater than that of the [Zn(oep)] layer on Au(111). Morphological details of each molecule are clearly displayed in the height-shaded view shown in Figure 3b. Protrusions were observed in each bright spot, thus showing the presence of phenyl and pyridyl groups located on the rim of the orifice. When C_{60} molecules were used as the second layer in the modification, a round spot could be seen in each molecule without any protrusions in the high-resolution STM image.[13]

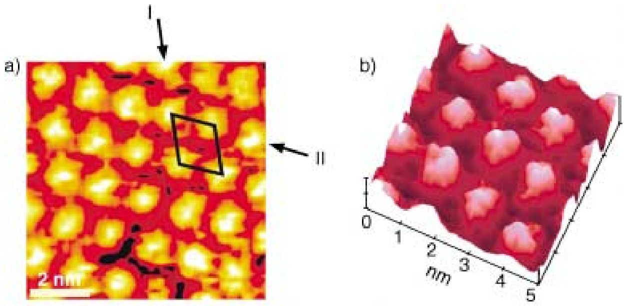

Figure 3. High-resolution STM images (8×8 nm^2) of a layer of **1**/[Zn(oep)] supramolecularly assembled on Au(111) in 0.05 M H_2SO_4; a) top view and b) height-shaded view (5×5 nm^2). The potential of the tip and the tunneling current were 0.46 V and 0.425 nA, respectively.

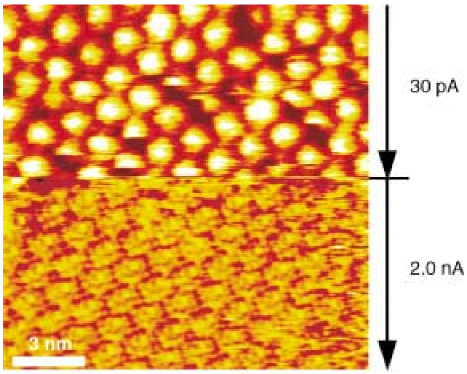

Figure 4. Composite STM image (15×15 nm^2), acquired at 0.85 V versus RHE, of a layer of the **1**/[Zn(oep)] supramolecular assembly on Au(111) in 0.05 M H_2SO_4. The potential of the tip was 0.35 V. Tunneling currents were 0.03 nA (upper part) and 2.0 nA (lower part), respectively.

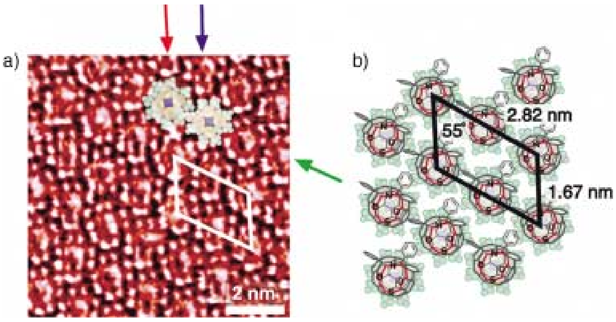

Figure 5. a) High-resolution STM image (9×9 nm^2) of the underlying [Zn(oep)] layer on Au(111) in 0.05 M H_2SO_4 and b) structural model of the supramolecularly assembled **1**/[Zn(oep)] layer on Au(111). The potential and the tunneling current were 0.46 V and 1.5 nA, respectively.

The STM image changed dramatically when the tunneling current was increased from 30 pA to 2.0 nA in the middle of the scan (Figure 4). The adlayer of **1** immediately disappeared and the underlying [Zn(oep)] layer on Au(111) was visible, thus indicating that a layer of molecules of **1** formed on the highly ordered [Zn(oep)] adlayer to form an exactly 1:1 supramolecular assembly. In fact, the top layer of **1** was easily removed with either tunneling currents higher than 0.5 nA or by using low bias conditions, and the underlying [Zn(oep)] layer was clearly visible with a tunneling current of 1.5 nA (Figure 5a). Careful inspection of Figure 5a allows two different orientations of [Zn(oep)] molecules to be distinguished in the molecular rows. Each [Zn(oep)] molecule can be recognized as a square with eight additional spots at the corners, which correspond to the eight ethyl groups. It is seen that the [Zn(oep)] molecules in the row marked by a red arrow have a different molecular orientation from those in the row marked by a blue arrow. The adlayer structure of [Zn(oep)] on Au(111) was identical to that of [Co(oep)][14a] and [Fe(oep)][14b] on Au(111). Only one difference was found in the STM image between [Zn(oep)] and [Co(oep)] (or [Fe(oep)]), that is, the center of each [Zn(oep)] unit appeared as a dark spot, whereas that of [Co(oep)] (or [Fe(oep)]) was the brightest spot. This difference can be explained in terms of a difference in the d_{z^2} orbitals.[15] Intermolecular spacings between the molecules in the rows marked by red and green arrows in Figure 5a were determined to be 1.67 ± 0.07 and 1.42 ± 0.05 nm, which are in good agreement with the values observed in Figure 3a. The adlattice is superimposed in Figure 5a. The adlattice includes two [Zn(oep)] molecules with an included angle of $55 \pm 3°$, which arises because neighboring [Zn(oep)] molecules alternately possess two different orientations for alignment in the direction indicated by the green arrow. In this system, the adlattice for the top layer of **1** is different from that of the underlying layer of [Zn(oep)], while the surface concentration of the top layer is the same as that of the underlying layer. A proposed structural model is shown in Figure 5b. The intermolecular distances between molecules of **1** are nearly equal to the distance between [Zn(oep)] molecules, a fact which indicates that a molecule of **1** is located directly above the center of each [Zn(oep)] molecule. This structure was consistently observed between 1.0 and 0 V. Structural change of the layer of **1** through the redox reaction could not be identified by STM, even at 0 V. When a polycrystalline Au electrode such as a disk or a wire was used as the substrate, the redox reaction was barely seen, even with the **1**/[Zn(oep)] system. This result shows that the formation of a highly ordered [Zn(oep)] layer is a key factor in controlling the molecular orientation of **1**. Adlayers of C_{60} and C_{70} on [Zn(oep)]-modified Au(111) also behaved similarly as that of **1** when the adlayers were prepared in the same manner.[13] The clearly enhanced redox peaks in the CV profile at the **1**/[Zn(oep)]-modified Au(111) layer and the high-resolution STM image strongly support the conclusion that the orientation of **1** is controlled by the [Zn(oep)] layer. Thus, the redox reaction shown in Figure 1b is assigned to a two-electron and two-proton reaction.

In conclusion, immersing an Au(111) substrate successively into solutions of [Zn(oep)] and **1** in benzene results in a well-defined electrochemical response of **1** as a consequence of the formation of a supramolecular assembly of **1** and [Zn(oep)]. This system has a wide peak separation, which may enable its application in electrochemical switching devices.

Experimental Section

Open-cage C_{60} derivative **1** was synthesized by using the procedure described previously.[8a] [Zn(oep)] was purchased from Aldrich and used without further purification. Benzene was obtained from Kanto Chemical Co. (spectroscopy grade). Au(111) single-crystal electrodes were prepared by the Clavilier method.[16] Adlayers of **1**/[Zn(oep)] were formed by immersing an Au(111) electrode successively into a solution of [Zn(oep)] (ca. 100 μM) in benzene for 10 s and into a solution of **1** (50 μM) in benzene for 30–60 s, after annealing the Au(111) surface in a hydrogen flame and quenching it in ultrapure water (Milli-Q SP-TOC = 18.2 M cm) saturated with hydrogen.[14] The **1**/[Zn(oep)]-modified Au(111) layer was rinsed with ultrapure water and then transferred into an electrochemical STM cell and filled with 0.05 M H_2SO_4 (Cica-Merck, ultrapure grade). Cyclic voltammetry was carried out at 20 °C using a potentiostat (HOKUTO HAB-151, Tokyo) and the hanging meniscus method in a three-compartment electrochemical cell in a N_2 atmosphere. Electrochemical STM measurements were performed in 0.05 M H_2SO_4 by using a Nanoscope E with a tungsten tip etched in 1 M KOH. Tips were coated with nail polish to minimize residual faradic currents. STM images were recorded in the constant-current mode with a high-resolution scanner (HD-0.5I). All potential values are referenced to the reversible hydrogen electrode (RHE).

Received: February 6, 2004 [Z53959]

Keywords: fullerenes · porphyrinoids · scanning probe microscopy · supramolecular chemistry · surface chemistry

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