Supramolecular Assembly of [60] Fullerene and Highly Ordered Zinc Octaethylporphyrin Adlayer Formed on Au(111) Surface

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Supramolecular assembled layers with 1:1 composition of fullerene C_{60} and zinc octaethylporphyrin (ZnOEP) were formed on Au(111) surface by immersing Au(111) substrate successively into a benzene solution containing ZnOEP and that containing C_{60}.

Porphyrin–fullerene supramolecular assemblies have been studied extensively to generate the photocurrent in addition to their unique photophysical and photochemical properties.[1–3] Fullerenes are considered to be suitable building blocks for 3-D molecular architecture because of their strong π-electron accepting ability.[1] Especially, it is known that zinc(II) octaethylporphyrin (ZnOEP) and fullerene C_{60} form supramolecular assembly through the π–π interaction in cocrystallites.[3] Supramolecular assembly on metal surfaces has also been explored to control surface properties. For example, individual copper phthalocyanine (CuPc) molecules were observed on C_{60} array formed on Au(111) in ultrahigh vacuum (UHV).[4] Recently, we succeeded in forming 1:1 supramolecular assembly consisting of quinone-linked open-cage C_{60} derivatives and zinc octaethylporphyrin (ZnOEP) on Au(111) surface, resulting in the well-defined electrochemical response of the quinone moiety.[5] To prepare composite thin films with a high quality of supramolecular assembly by using donor–acceptor systems and to develop new functional electrodes or devices, the control of molecular assembly at the nanoscale is of importance.

In this report, we demonstrate the construction of 1:1 supramolecular assembled film of C_{60} and ZnOEP on Au(111) in 0.1 M $HClO_4$ by using scanning tunneling microscopy (STM).

C_{60} and ZnOEP purchased from Aldrich were used without further purification. Benzene was obtained from Kanto Chemical Co. (Spectroscopy Grade). Au(111) single-crystal electrodes were prepared by the Clavilier method.[6] Fullerene adlayers were formed by immersing Au(111) electrode into a 100 μM ZnOEP benzene solution for 10 s and transferred successively into ca. 10 μM C_{60} benzene solution for 10–20 s, respectively, after annealing Au(111) substrate in a hydrogen flame and quenching into ultrapure water (Milli-Q SP-TOC; ≥18.2 MΩ·cm) saturated with hydrogen.[5,6,8] Then the C_{60}/ZnOEP-adsorbed Au(111) was rinsed with ultrapure water, and it was transferred into an electrochemical STM cell filled with 0.1 M $HClO_4$ (Cica-Merck, ultrapure grade). Electrochemical STM measurements were performed in 0.1 M $HClO_4$ by using a Nanoscope E with a tungsten tip etched in 1 M KOH. To minimize residual faradaic currents, tips were coated with nail polish. The potential value was referred to reversible hydrogen electrode (RHE).

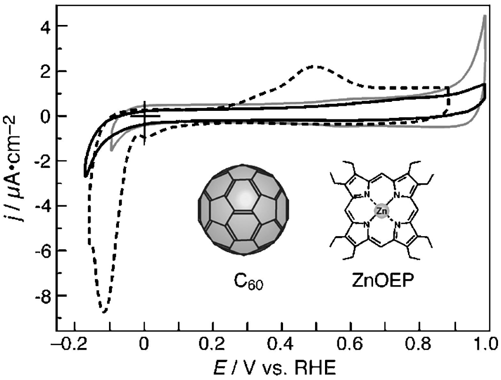

Figure 1. Cyclic voltammograms of C_{60} directly attached Au(111) (gray line) and ZnOEP-modified on Au(111) electrode in 0.1 M $HClO_4$ before (dotted line) and after (solid line) immersion into a C_{60} benzene solution. The scan rate was 50 mVs^{-1}.

Figure 1 shows typical cyclic voltammograms (CVs) of a ZnOEP-modified Au(111) (dotted line) and C_{60} on the ZnOEP-modified Au(111) electrode (solid line) in 0.1 M $HClO_4$ recorded at a scan rate of 50 mV·s^{-1}. For ZnOEP-modified Au(111) electrode, potential scan was started to negative direction from open circuit potential (around 0.75 V). During the scan to more negative direction, a reductive peak was seen around −0.1 V, whereas reoxidative peak was observed around 0.5 V, suggesting that reductive desorption and readsorption of ZnOEP molecule took place on Au(111) surface. Immersion into ca. 10 μM C_{60} benzene solution was further carried out for several time, after the ZnOEP modification onto Au(111) surface. The decrease in double-layer charging current was observed, and the peaks observed around −0.1 and 0.5 V were suppressed as indicated by solid line, whereas the increase of anodic current can be seen at 0.9 V on C_{60}-modified Au(111) electrodes because of the oxidative desorption of C_{60} molecules as indicated by gray line.[7] This result suggests that the ZnOEP adlayer on Au(111) surface prevents the oxidative desorption of C_{60} molecules.

Figure 2a shows a typical STM image of an adlayer of C_{60} formed on Au(111) in 0.1 M $HClO_4$. A well-defined adlayer of C_{60} molecules was clearly seen on the Au(111) terrace. Individual molecules of C_{60} could be discriminated as a round spot. The intermolecular distance between C_{60} molecules was measured to be 1.0 nm. Each molecular row rotated by 30° with respect to the atomic step line. The adlayer structure of C_{60} was assigned to be the so-called $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$ structure. As reported in several papers, the epitaxial thin film of C_{60} on Au(111) was found to take two different close-packed structures, $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$ and the so-called "in-phase" (38 × 38), not only in UHV[8] but also in solution.[7,9] On the contrary, highly-ordered C_{60} arrays consisting of bright round spots were found on the ZnOEP-modified Au(111) in the high-resolution STM image of an area of

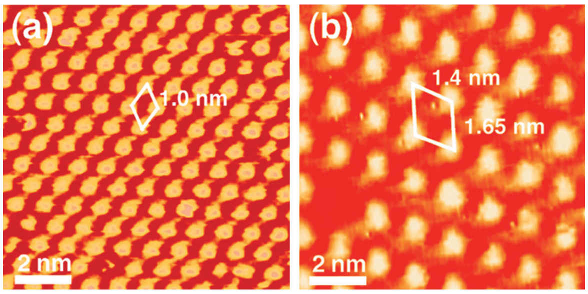

Figure 2. Typical STM images (10 × 10 nm^2) of C_{60} array on (a) clean Au(111) and (b) the ZnOEP-modified on Au(111) surface acquired at 0.85 V vs RHE in 0.1 M $HClO_4$. Tip potentials and tunneling current were (a) 0.35 V and 1.5 nA and (b) 0.46 V and 0.55 nA, respectively.

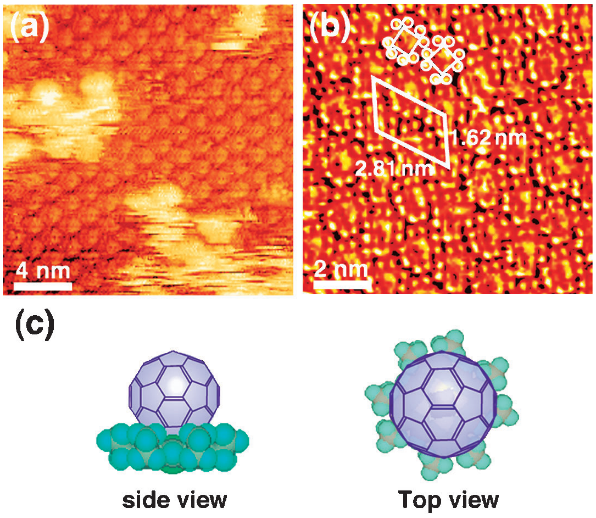

Figure 3. Typical STM images of C_{60} on the ZnOEP-modified on Au(111) electrode acquired at 0.8 V vs RHE in 0.1 M $HClO_4$. Tip potentials and tunneling current were 0.46 V and (a) 1.0 nA and (b) 1.5 nA, respectively. (c) Proposed model of supramolecular assembled layer of C_{60} and ZnOEP molecule.

10 × 10 nm^2 as shown in Figure 2b. The size of each spot on the ZnOEP-modified Au(111) was larger than that directly attached on Au(111), suggesting that the underlying ZnOEP layer affects electronic structure of C_{60} molecule. On the basis of cross-sectional profiles, intermolecular distances between the nearest neighbor C_{60} molecules were found to be either 1.65 ± 0.07 or 1.40 ± 0.05 nm for directions along each molecular row. The corrugation height of C_{60} was clearly greater than that of the ZnOEP layer on Au(111).

The underlying ZnOEP layer on Au(111) was clearly visible at an increased tunneling current and/or when the bias potential was changed. Actually, the top layer of C_{60} was easily removed with the operation of scanning at tunneling currents higher than 0.5 nA. Figure 3a shows typical STM image obtained by using tunneling current of 1 nA. C_{60} molecules of top layer were aggregated as clusters, and the underlying ZnOEP first layer was clearly observed under this experimental condition. The result indicates that the interaction between C_{60} and ZnOEP adlayer is so weak. Close-up view of underlying ZnOEP layer is shown in Figure 3b. Careful inspection of Figure 3b allows to distinguish between two different orientations of ZnOEP molecules in the molecular rows. Each ZnOEP molecule can be recognized as a square with eight additional spots at the corners corresponding to eight ethyl groups. The adlayer structure of ZnOEP on Au(111) was identical to that of CoOEP and FeOEP on Au(111) reported in our previous papers.[10,11] Note that the ZnOEP adlayer was the same as that before C_{60} adsorption. Although the unit cell is superimposed in Figure 3b as the parallelogram with the length of 1.62 and 2.81 nm because of two different orientations of ZnOEP molecules, intermolecular spacings between the molecules in the rows in Figure 3b were measured to be 1.65 ± 0.07 and 1.40 ± 0.05 nm. As described in our recent paper, the formation of open-cage C_{60} derivative and the highly ordered ZnOEP adlayer with 1:1 supramolecular assembly was confirmed by stepping the tunneling current from 30 pA to 2.0 nA in the middle of scanning the STM image.[5] In the case of C_{60}, 1:1 supramolecular assembled layer of C_{60} and ZnOEP could be also formed on Au(111) surface. A structural model is proposed in Figure 3c. The fact that the intermolecular distances between C_{60} molecules are nearly equal to the distance between ZnOEP molecules, indicates that each C_{60} is located on the center above each ZnOEP molecule. This adlayer structure was consistently observed in the potential range between 0.95 and 0 V.

In conclusion, by immersing an Au(111) substrate successively into a benzene solution containing ZnOEP and that containing C_{60}, unique molecular assembly of C_{60} was obtained as a result of the formation of supramolecular assembly of C_{60} molecule and ZnOEP adlayer.

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