Effect of the Formation of Highly Ordered Platinum(II) Octaethylporphyrin adlayer on the Surface Reconstruction of Gold and Supramolecular Assembly of Fullerenes

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In general, electrochemically induced reconstruction of Au(111) is observed at potentials more negative than the potential of zero charge (pzc). Figure s1 shows a typical *in situ* STM image of a Au(111) electrode surface obtained in 0.05 M $HClO_4$. If the potential is changed to positive values such as 0.9 V vs. RHE (depending on the composition of the electrolyte solutions), the reconstructed rows disappear due to the adsorption of the anions. In other word, a phase transition from the reconstructed surface to a (1 × 1) surface takes place, by changing the potential to a positive value. The formation of a highly ordered PtOEP adlayer contributes to the stabilization of the reconstructed rows due to the strong π-electron donation from the PtOEP molecules to the Au(111) surface.

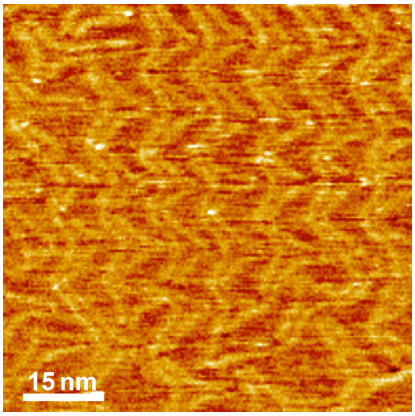

Figure s1. Typical *in situ* STM image (75 × 75 nm^2) of a reconstructed Au(111) electrode surface in 0.05 M $HClO_4$ observed at 0.10 V vs. RHE. The tip potential and tunnelling current were 0.20 V vs. RHE and 15 nA.

Figure s2 shows an STM image of C_{84} molecules assembled on a highly ordered PtOEP adlayer on a Au(111) surface, obtained at –0.10 V vs. RHE. At potentials near the hydrogen evolution potential, the adlayer was stably observed without the desorption of the PtOEP adlayer. The C_{84} molecules were aligned to sites in the gaps between the reconstructed rows.

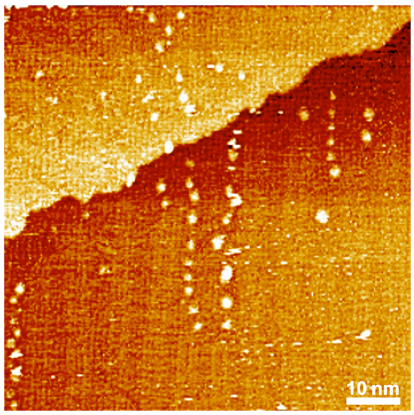

Figure s2. Typical high-resolution STM image of C_{84} layer on PtOEP adlayer observed at –0.10 V vs. RHE. The tip potential and the tunneling current were 0.42 V and 0.10 nA.

When a very different scanning condition was used, a structural change involving an exchange of the C_{60} positions occurred on the PtOEP adlayer. The structural change was caused by the scanning tip. For example, the bright spots were observed to undergo exchange reactions under a bias voltage of 0.37 V and a tunneling current of 0.30 nA, as shown in Figure s3. The regions indicated by the dotted circles in Figures s3(a) and s3(b) show the areas under discussion. The STM images were recorded with an interval of 1 min and weak bright spots were seen between the bright molecular rows. In particular, the bright spots marked with a white dotted circle in Figure s3(a) disappeared after 1 min, as seen in Figure s3(b). The black arrows shown in Figure s3(b) indicate new spots that appeared after the STM image shown in Figure s3(a) was recorded. A similar phenomenon has been reported in the literature in the case of an adlayer consisting of two C_{60}-connected nickel(II) phthalocyanine (NiPc) derivative on a highly ordered ZnOEP adlayer during a continuous scan.[S1]

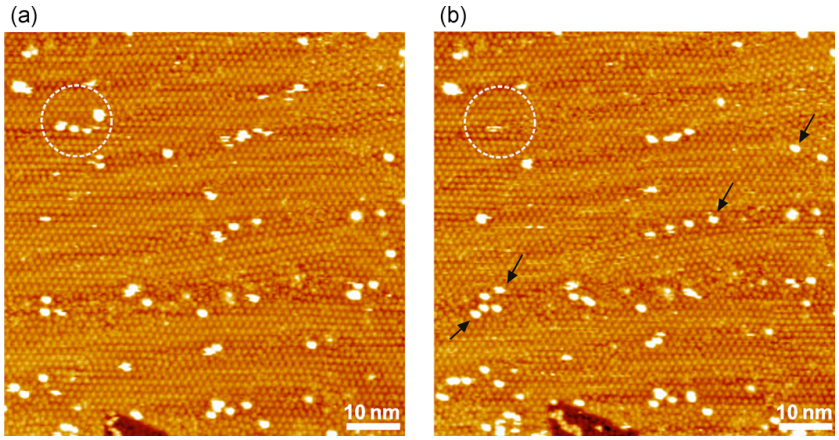

Figure s3. Time-dependent STM images of supramolecularly assembled C_{60} layer on PtOEP adlayer observed at 0.80 V vs. RHE. The tip potential and tunneling current were 0.43 V and 0.30 nA. The STM images were taken in 60 s.

Ref. S1. S. Yoshimoto, S. Masuda, T. Fukuda, N. Kobayashi, *J. Inorg. Biochem.* **2012**, *108*, 178–181.