

## Formation Process of Self-Assembled Monolayer of Porphyrin Molecule with 4 Thiol Groups on Au(111)

Nana Aoki, Bing Zhang, Tomoko Arisaka, and Toshihiro Kondo

Ochanomizu University

2-1-1, Ohtsuka, Bunkyo-ku, Tokyo 112-8610, Japan

E-mail: g1140627@edu.cc.ocha.ac.jp

### Introduction.

Porphyrin derivatives are well-known to have unique optical, electrochemical, and catalytic properties and then have extensively used as a building block in construction of molecular devices. In order to construct effective molecular photodevices using porphyrin's optical properties, ordered porphyrin layer with a flatly adsorbed configuration on a solid surface should be required because a transition moment of porphyrin is parallel to a porphyrin ring. In order to construct molecular catalysts, on the other hand, flatly adsorbed porphyrin layer also should be required because substrate binds along the direction perpendicular to the porphyrin ring. Moreover, ordered multilayers of porphyrins can be constructed by alternating construction of ligand and porphyrin layers if the flatly adsorbed porphyrin monolayer is formed on the solid surface as a first layer.

Thiol derivatives are chemisorbed with ordered structures on the metal surfaces as self-assembled monolayers (SAMs) and the alkylthiol SAMs on gold have been extensively investigated because of their high stability, high packing density, and high orientation. SAMs of porphyrin derivatives have been already reported, however, porphyrins were not flatly adsorbed on the gold surface in all of them [1].

In this report, a porphyrin derivative with 4 thiol groups as surface binding groups, 5,10,15,20-tetrakis(*m*-mercapto-*p*-methoxy-phenyl) porphyrin (TMMPP) (Fig. 1) was synthesized and the TMMPP SAM was constructed on the Au(111) surface. In this molecule, 4 methoxy groups were also introduced to the para-position of the phenyl group of the porphyrin ring to two-dimensionally arrange in order on a gold surface. We discussed the self-assembly process of TMMPP SAM based on the results of electrochemical and scanning tunneling microscopy (STM) measurements.

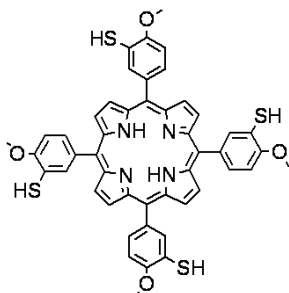


Figure 1. TMMPP.

### Experimentals.

TMMPP was synthesized and TMMPP SAM on Au(111) was prepared by dipping the Au(111) substrate into benzene solution containing 50  $\mu\text{M}$  TMMPP for certain periods. Linear sweep voltammograms (LSVs) of the Au(111) electrodes modified with TMMPP SAM were measured from 0 V (vs. Ag/AgCl) to -1.4 V in 0.1 M KOH solution with a scan rate of 20  $\text{mV s}^{-1}$ .

*Ex situ* STM measurement was performed in ultrapure water at room temperature.

### Results and Discussion.

Figure 2 shows STM images and a cross-sectional profile of the TMMPP SAM on the Au(111) surface, which was prepared by a dipping of the substrate into the TMMPP solution for 20 h, which is a relatively long dipping period. For this dipping period, adsorbed amount of TMMPP on the Au(111) surface was saturated to be ca.  $5.5 \times 10^{13}$  molecules  $\text{cm}^{-2}$ , leading to ca.  $1.9 \text{ nm}^2$  molecule $^{-1}$ , based on the results of the electrochemical reductive desorption measurement. A line due to the molecular ordering was clearly observed with intervals of ca. 2.0 nm, 3.7 nm, or 5.0 nm. Moreover, the direction of this molecular array intersected with the step line of the substrate by  $60^\circ$ . From the molecular model of TMMPP, each bright spot seems to consist of 1, 4, or 9 TMMPP molecules. These results indicated that the flatly adsorbed TMMPP was arranged in order on the atomic arrangement of the underlying Au(111) surface at the final stage of the TMMPP self-assembly.

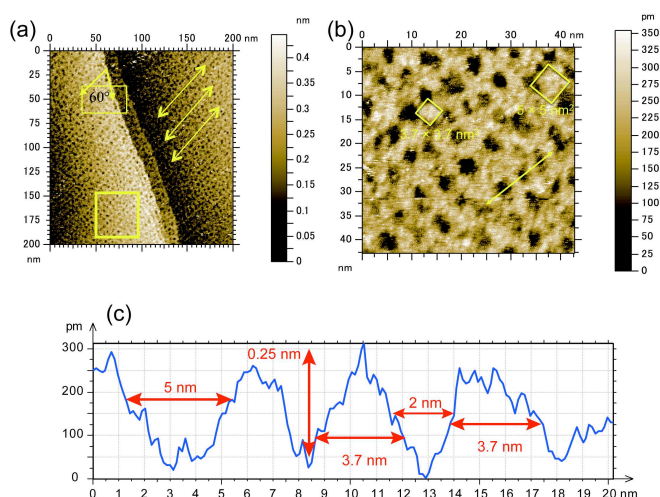


Figure 2. (a) and (b) STM images of the TMMPP SAM on Au(111), which was prepared for 20 h dipping. (a)  $200 \times 200 \text{ nm}^2$  and (b)  $45 \times 45 \text{ nm}^2$ , which was magnified from the yellow square in (a). (c) Cross sectional profile of the yellow arrow in (b).

### References

- [1] T. Kondo et al., *J. Am. Chem. Soc.*, 119 (1997) 8367; *Bull. Chem. Soc. Jpn.*, 71 (1998) 2555; *Z. Phys. Chem.*, 212 (1999) 23; *Chem. Lett.*, (2000) 964.