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Research Report

Electrochemical Atomic Force Microscopy of a Porphin Monolayer

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(October 1994 - March 1996, Visiting Scientist)
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Abstract

High-resolution topographic information has been be achieved with an electrochemical atomic force microscope on a weakly adsorbed porphin adlayer. The substrate was an iodine-passivated Au(111) facet, and an electrolyte containing perchloric acid was used. The already well-known lateral structures were reproduced. New information about the height of different parts of the porphin complex and its adsorption forces is presented.

INTRODUCTION

In situ experiments using an electrochemical atomic force microscope (ECAFM) to obtain organic adsorbates at the electrified interface have rarely been reported in the literature. Self-assembled monolayers, for example alkane thiols, mainly on Au substrates but also on other metals, have been investigated with AFM [1] and other techniques. Other groups are working on under-potential deposition (UPD) of metals on metal electrodes using an ECAFM [2]. These reports reveal strongly adsorbed adlayers.

In this report we describe a relatively weakly adsorbed porphin on an I-passivated Au(111) facet under potential control in a solution containing perchloric acid.

EXPERIMENT

Our experiment was carried out using a commercially available ECAFM [3] combined with custom-built electrochemical setup [4]. As substrate, an I-passivated Au single-crystal bead (SCB) facet in [111] orientation was used [5]. A solution of ultrapure water [6] containing 100 mmol/kg of $HClO_4$ [7] and 0.1 mmol/kg of KI [8] was prepared. The porphin, 5,10,15,20-tetrakis-(N-methylpyridinium-4-yl)-21H,23H-porphin, tetrakis-(p-toluenesulfonate) (TMPyP) was added in a concentration of 10^{-7} mol/kg to the electrolyte. The counter-electrode was made of Pt and, as reference electrode, a Pt wire was installed. All potentials mentioned in this report are relative to reversible hydrogen evolution (RHE). The cantilevers used [9] were cleaned in ultrahigh vacuum (UHV) by heating to 450 K for about 1 h. After this step, the cantilevers were stored in an electrolyte similar to the one described above and optically checked under a microscope. The tip-apex geometry is something of an unpredictable key to high-resolution ECAFM experiments. Therefore we usually installed and tested several cantilevers on an I-passivated Au(111) facet in a non-TMPyP-containing electrolyte until atomic resolution could be obtained. Then the electrolyte was exchanged with a TMPyP-containing but otherwise identical electrolyte by overflowing the cell. This procedure was carried out under potential control and always led to large-scale ordered TMPyP adlayers like the ones described in [10,11]. The potential was fixed at the open circuit potential (OCP) of the I-passivated Au SCB, which is usually around 800 mV versus RHE.

RESULTS

Figure 1 shows a shaded height representation of a very high-resolution acquisition of TMPyP on an I-passivated Au(111) facet. The vertical resolution of 0.1 nm achieved is expected to be an absolute limit for an ECAFM in contact mode. Figure 2 shows a top view of Fig. 1, and in Fig. 3, computed TMPyP molecule structures are overlaid. Figures 1 to 3 show relatively stable central TMPyP parts with a diameter of about 0.6 nm, which is the theoretical diameter of the porphin ring structure. The calculated models in Fig. 3 have slightly axially rotated pyridinium substituents. The theoretical additional height relative to the central porphin structure could not be measured. Thus the pyridinium rings appear to lie flat on the substrate, caused by a weak adsorption force such as the Van der Waals force and others. A second possibility is the tip pressure, which obviously distorts the molecule.
Figures 1 to 3 show a hole in the central porphin ring structure for molecules that have their pyridinium substituents in scanning direction and perpendicular to the scanning direction. On the other hand the 45°-rotated molecules never show the central features. In addition Fig. 3 shows the distortion of the pyridinium substituents. The multiple representation of single

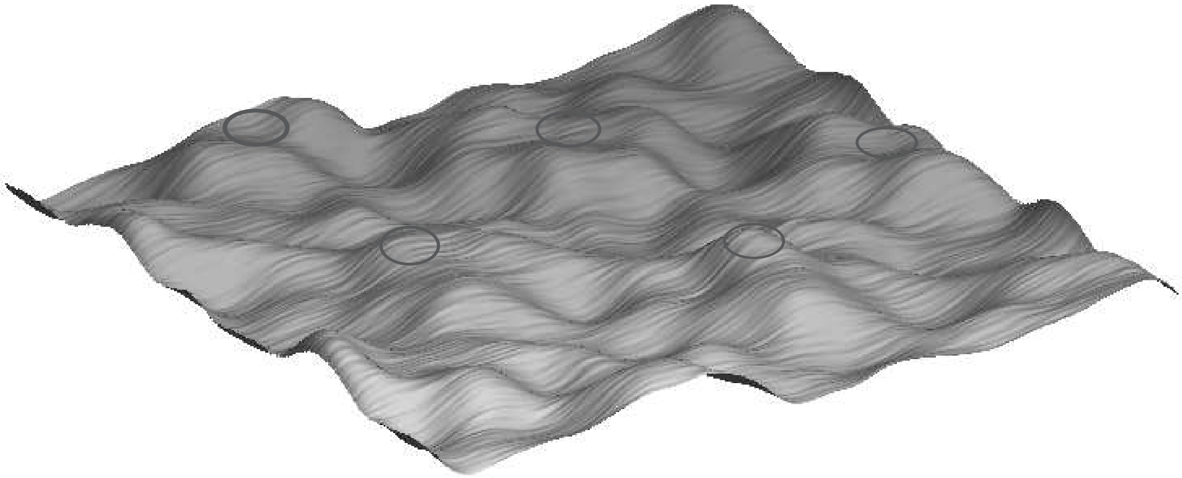

FIG. 1. A very high-resolution topographic image of porphin molecules at an I-passivated Au(111) facet. Ellipses mark the centers of the individual porphin molecules. The image size is 4×4 nm^2 and the represented height is 0.1 nm. It was acquired as 512 lines by 512 points and afterwards low-pass filtered. The applied tip force was 120 pN in contact mode. The electrolyte used contained 100 mmol/kg of $HClO_4$, 0.1 mmol/kg of KI, and 10^{-7} mol/kg of TMPyP, and the potential was held at 800 mV versus RHE.

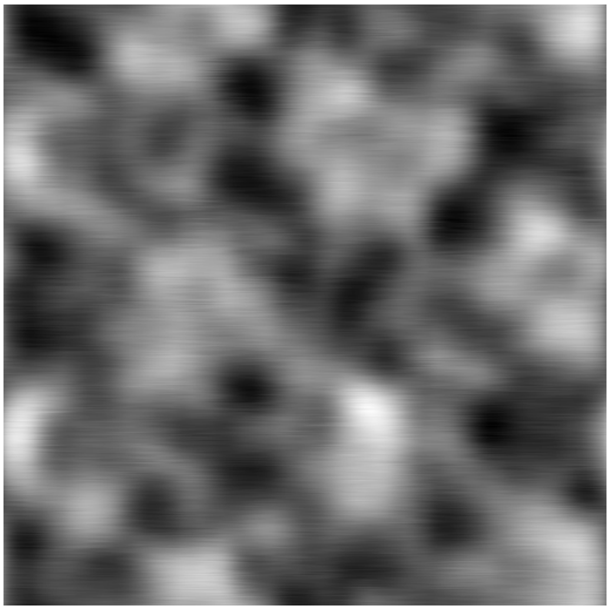

FIG. 2. Top view of the image presented in Fig. 1. The bright central spots are about 0.1 nm high, whereas the darker parts of the pyridinium substituents are about 0.07 nm high.

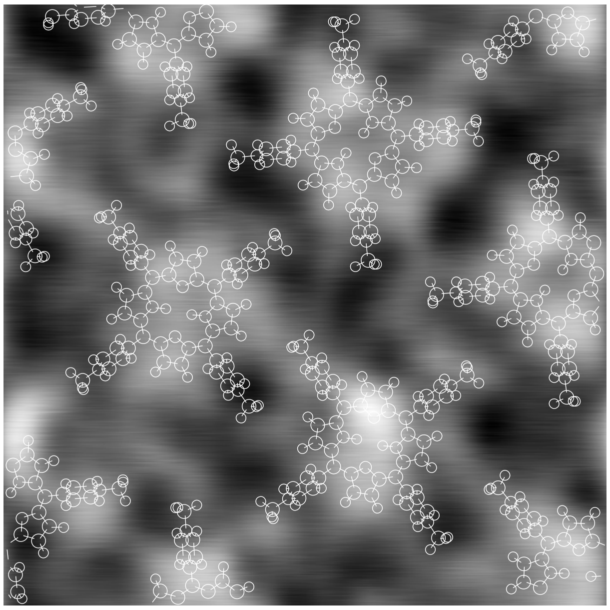

FIG. 3. Same data as in figures 1 and 2 The computed and overlaid TMPyP molecules show the low distortion in the central part of the molecule. The pyridinium substituents are sometimes bent. They show a tendency to stabilize in the depressions of the underlying I layer.

pyridinium substituents is the result of oversampling. If a pyridinium substituent happens to be perpendicular to the scanning direction, its image will be composed of 55 scan lines. If the scanning resolution is lower, then the scanning direction-dependent distortion of the central porphin ring and its pyridinium substituents cause a cross-like shape for molecules rotated 45° from the scanning direction and a torus-like shape for the other molecules. Figure 4 shows this behavior in its aligned rows running from bottom right to the top left. Figure 5 shows the result of probing the TMPyP adlayer rigidness. The top part of the image was the starting point. The ECAFM force was set to 240 pN. This led to the removal of the TMPyP adlayer by the frictional forces, which are several times higher than the normal force, but difficult to quantify. The I adlayer is visible, but of course with some noise caused by the TMPyP, which always tends to reassemble. After scanning downwards 1 nm, the force was reduced to 120 pN. The TMPyP adlayer recovered completely in only 20 s.

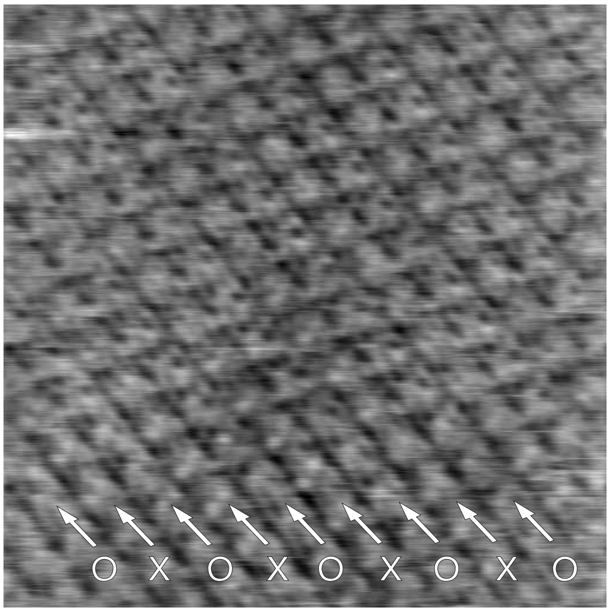

FIG. 4. Typical large-scale image of 20×20 nm^2 on a single grain. The experimental conditions were the same as those for Fig. 1. The typical behavior of alternating cross-like ($\times$) and torus-like ($\bigcirc$) rows is clearly visible.

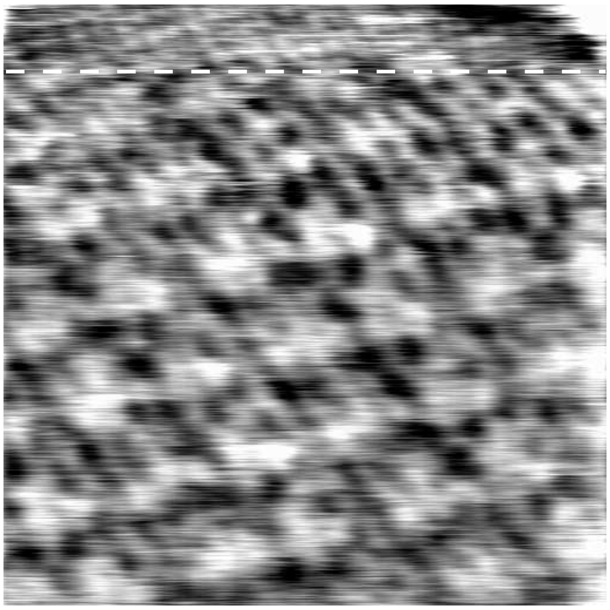

FIG. 5. On top of the 10×10 nm^2-sized image, iodine can be observed. This is caused by the high tip force of about 240 pN. When the tip force is reduced to 120 pN (dashed line), the TMPyP adlayer immediately starts to reassemble. At first, the molecules are squeezed into the depressions of the iodine adlayer. After some seconds, the adlayer has totally recovered to the well-known lattice structure, shown in the bottom part of the image.

The force curve shown in Fig. 6 is in good agreement with the prior result. The small force peaks for jumping into contact (approach) and tip pulloff (retract) are indications of the rigid TMPyP adlayer, which can be broken through locally by the tip, but the surrounding molecules damp any further tip–substrate interactions. The characteristics shown in Fig. 7 are in contrast to those in Fig. 6. During approach, an attractive phase can be obtained. This originates from the double layer and/or the diffuse region of potential drop on the silicon nitride tip and the I-passivated Au(111) surface. After contact, the behavior is as usual. The huge pulloff force shows the unstable surface. The tip interacts strongly with the surface and

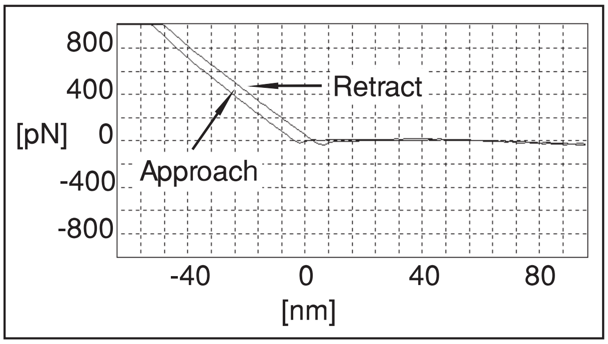

FIG. 6. ECAFM force curve plot of a TMPyP-I-Au(111) surface in an electrolyte containing 100 mmol/kg of $HClO_4$, 0.1 mmol/kg of KI, and 10^{-7} mol/kg of TMPyP at a potential of 800 mV versus RHE.

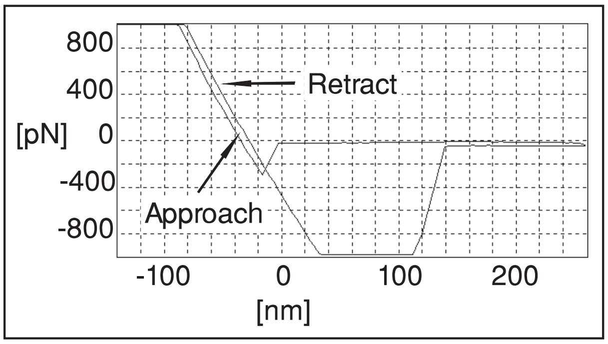

FIG. 7. ECAFM force curve plot of an I-Au(111) surface in an electrolyte containing 100 mmol/kg of $HClO_4$ and 0.1 mmol/kg of KI at a potential of 800 mV versus RHE.

requires a very unpredictable force to release.

The force curves presented in Figs. 6 and 7 are captured under equivalent conditions, but the experiment presented in Fig. 6 contains TMPyP and that presented in Fig. 7 contains no TMPyP. Subtracting the attractive part of the jump into contact force (approach) of Fig. 6 from that of Fig. 7 results in a difference of about 240 pN. Because the TMPyP adlayer acts as a force compensator, it can be concluded that the measured 240 pN is the sum of all adsorption forces between the TMPyP adlayer and its I-passivated Au(111) substrate. As mentioned above, this result confirms the experiment presented in Fig. 5.

The real height of a TMPyP adlayer on an I-passivated Au(111) substrate was measured to be 0.1 nm. Furthermore the tribological behavior of scanning probes onto the TMPyP adlayer was explained and the acting sum of adsorption forces of about 240 pN between the TMPyP adlayer and the I-passivated Au(111) substrate was investigated.

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[2] C. Chen *et al.*, J. Am. Chem. Soc. 114, 451 (1992).

[3] The contact-mode ECAFM was a Nanoscope III of Digital Instruments, Santa Barbara, CA, USA.

[4] P. Müller and K. Itaya, IBM Research Report, Electrochemical Atomic Force Microscopy on Single-Crystal Bead Facets, RZ 3005 (March 30, 1998).

[5] P. Müller and K. Itaya, IBM Research Report, Single Crystals with Clean Atomically Flat, Low-Index Facets, RZ 3008 (March 30, 1998).
[6] Millipore Milli-Q, ($R > 18$ Ωcm).
[7] $HClO_4$, perchloric acid, Cica Merck, ultrapure grade.
[8] KI, potassium iodide, Kanto Chemicals, ACS grade.
[9] Cantilevers from Olympus, Japan, made of silicon nitride with a sharpened pyramid tip, a length of 200 μm and a spring constant of 0.022 N/m. The backside is coated with gold to reflect the detection beam.
[10] M. Kunitake *et al.*, Langmuir 11, 2337 (1995).
[11] M. Kunitake *et al.*, Langmuir 13, 1607 (1997).