Adsorption-Induced Self-Organization of Calix[4]arene on Au(111) Surfaces

Takemitu Sakai, Akihiro Ohira, Masayo Sakata, Chuichi Hirayama, and Masashi Kunitake*
Department of Applied Chemistry and Biochemistry, Faculty of Engineering, Kumamoto University, 2-39-1 Kurokami, Kumamoto 860-8555

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The construction and sub-molecular visualization of a self-organized adlayer of calix[4]arene on a Au(111) surface were achieved by potential-controlled adsorption and in situ STM. In situ STM images revealed that the self-organized molecular array consisted of a calix[4]arene dimer. The two molecules in a cone conformation with a sideways orientation were connected in a "head to head" orientation between the hydroxy groups.

Recently, the high-resolution observation of supramolecular structures using scanning probe microscopes such as STM and AFM have become important tools for supramolecular chemistry.[1] In general, the preparation of a highly-ordered molecular layer on an atomically well-defined surface is critical for the successful STM observation of molecules at submolecular resolution level.[2–4] Self-assembly techniques have become popular as a simple method to form ordered adlayers on metal surfaces.[2] As a novel technique, Itaya and one of authors have proposed an adsorption-induced self-organization method, which is not based on strong chemisorption with the S–Au bond, for the formation of highly-ordered molecular arrays of various organic molecules.[3] Using this concept, we have investigated the construction and visualization of 2D supramolecular arrangements of host molecules, such as cyclodextrins, on the metal surfaces.[4] The construction and sub-molecular scale visualization of highly-ordered host molecules are interesting as a visible supramolecular structure. The structure of the self-organized adlayers should reflect the intermolecular interactions. This means that the observation of self-organized adlayers of molecules will give us visual information on the local intermolecular interactions, which are difficult to obtain by spectroscopic methods.

The key to the adsorption-induced self-organization technique is to control the adsorption by choosing suitable substrates and electrode potentials. Controlled conditions, i.e., a relatively weak adsorption, can induce the packing arrangement by an acceleration of molecular mobility on the surface or a shift in the adsorption/desorption equilibrium of the molecules. As an example of host molecules, the self-organization of cyclodextrins (CyD) into a "nanotube" structure, was found to be induced by potential controlled adsorption onto a Au(111) surface in sodium perchlorate solution.[4] Here, we report the potential-induced self-organization and the successful in situ imaging of a two-dimensionally ordered array of the aromatic, cyclic and neutral molecule calix[4]arene,[5] which is well-known as a host molecule.

The modification of the calix[4]arene on the Au(111) surface was conducted as follows. Just after annealing and quenching in pure water, a well-defined bare Au(111) substrate was immersed in a near-saturated aqueous solution ($< 10^{-6}$ M) of calix[4]arene. The modified sample was set into an STM cell filled with a pure perchloric acid solution. The in situ STM experiments were conducted under potential control, and the STM images were obtained in constant current mode.

After immersion into the calix[4]arene solution, the terraces of the Au(111) surface were completely covered by sub-nanometer spots, and thus the calix[4]arene molecules would have adsorbed randomly without any potential control, which corresponds to approximately +0.80 V vs RHE. In contrast, when the potential is moved towards the negative region beyond +0.40 V, an intact "reconstructed" Au(111) lattice can be observed (data not shown). This indicates that the calix[4]arene molecules desorb from the Au(111) surface at a negative potential. In general, the coverage of neutral molecules is the highest at a potential of zero charge (PZC), and the negative polarized electrode surface shows a tendency to prevent the adsorption of neutral molecules.[6] With no control of the electrode potential, the molecule–substrate interactions between the molecules and the substrates would be stronger than the intermolecular interactions, thus resulting in disordered adlayers. Furthermore, the negatively polarized electrode surface would tend to prevent the adsorption of neutral molecules.[4]

The most suitable adsorption conditions to induce self-organization can be expected to be somewhere between the desorption and disordered states. Calix[4]arene molecules have been found to form a self-organized array on an unreconstructed Au(111) surface at a middle potential range. In order to observe the self-organized adlayers of calix[4]arene, the potential of the calix[4]arene-premodified Au(111) surface was moved gradually towards a negative potential from the open circuit potential (approximately +0.80 V). The adsorbate–substrate interactions then gradually weaken, and the adsorbates start to become self-ordered at approximately +0.60 V. As a result, the random protrusions started to disappear at approximately +0.55 V, and the surface became flat momentarily and small islands of self-organized calix[4]arene started to appear as shown in Figure 1. These arrays had a rod-like structure, with a triangular arrangement. The triangular arrangements of rod-like structure were due to the long-distance lattice match between the molecular adlayers and the Au lattices. The number of rod-like structures increased, and the adlayers expanded onto the terraces with time. However, the surface was not completely covered by the arrays. This could be due to loose materials on the substrate surface, or a lack of calix[4]arene in the solution. After the array had been constructed at this potential, the same structure was observed consistently in the potential range between +0.45 and +0.55 V.

Submolecular high resolution STM imaging revealed more details, and clearly showed that the array consisted of calix[4]arene molecules. Figure 2 shows a typical example of a high-resolution STM image of the calix[4]arene array. Each calix[4]arene molecule can be recognized in the image as a trapezoid spot aligned alternately into the rod, although the

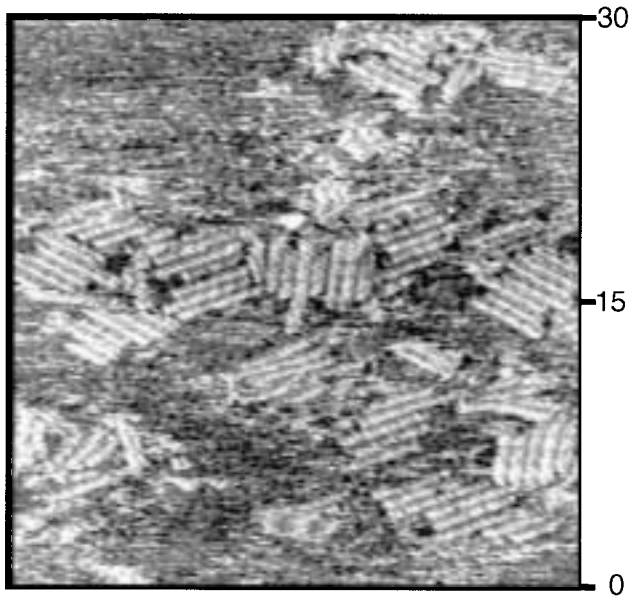

Figure 1. In situ STM image of the calix[4]arene arrays on a Au(111) surface in 0.1 M perchloric acid.
The image was obtained at Es = +0.55 V, Et = +0.37 V and It = 0.95 nA.

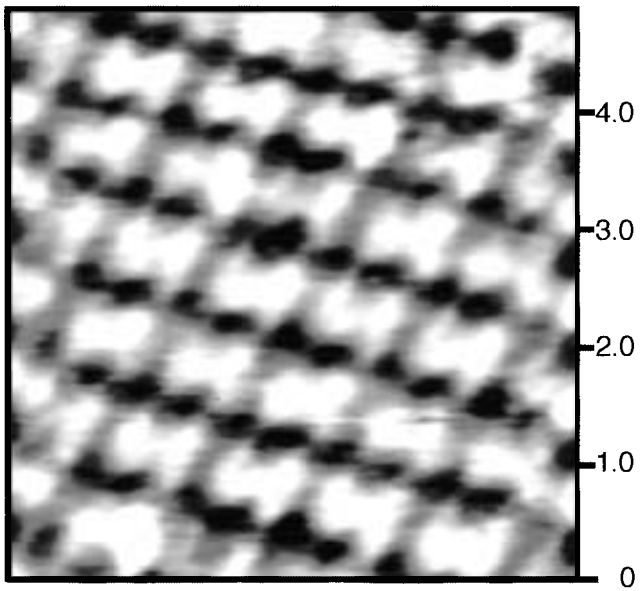

Figure 2. High resolution STM image of the calix[4]arene arrays on a Au(111) surface in 0.1 M perchloric acid observed at +0.5 V. The image was obtained at Et = +0.4 V and It = 3.1 nA.

image lacks the resolution for the visualization of the inner features of calix[4]arene. Interestingly, the orientation of calix[4]arene adopted on alternate arrangement with a sideways orientation. The cavities of the adsorbed calix[4]arene molecules would face sideways but not upwards and the calix[4]arene molecules would attach to the adjacent molecules in a regular "head to head, tail to tail" orientation. The periodicities of trapezoid spots along the rods and the rods were approximately 0.6 ± 0.1 and 1.1 ± 0.1 nm, respectively. These features and sizes suggest that the calix[4]arene molecules

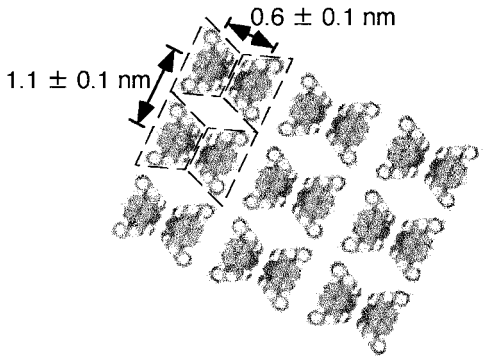

Figure 3. Schematic representation of the model of calix[4]arene array on the Au(111) surface.

formed a cone conformation with sideways orientation.[5] The structure of the array of calix[4]arene is illustrated schematically in Figure 3. The dominant driving force for the formation of the rod-like structures of calix[4]arene dimers in the array would be intermolecular van der Waals interactions. The similar alternating molecular arrangement of CyDs was observed in 2D-molecular arrays prepared by the adsorption-induced self-organization technique[4] and for polyrotaxane, in which the CyD rings are threaded by poly(ethylene glycol).[7]

In conclusion, the alternating arrangement of calix[4]arene with a sideways orientation and a triangular arrangement of rods in the array indicate strong intermolecular interactions and epitaxial interactions from the underlying substrate, respectively. The details and mechanisms of these self-organization behaviors, including those of calix[6]arene and calix[8]arene, are now in progress.

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