

An Atomic Force Microscopy Study of Self-Assembled Monolayers of Calix[4]resorcinarene Adsorbates on Au(111)

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The structure and orientation of calix[4]resorcinarene receptor adsorbate self-assembled monolayers (SAMs) on Au(111) were studied with atomic force microscopy (AFM). In molecularly-resolved images, two hexagonal periodicities with lattice constants of 11.6 ± 0.4 and 4.2 ± 0.2 Å, respectively, were observed. These two periodicities could be observed separately as well as simultaneously by changing the imaging force. The experimentally determined distances are assigned to different parts of the adsorbates; the 11.6 Å repeat distance is related to the lattice of the calix[4]resorcinarene recognition sites of the adsorbates, while the smaller repeat length fits well with the interchain distance of a closest packing of alkyl chains. These measurements confirm our previous assumption regarding the high degree of order of the calix[4]resorcinarene SAMs on gold.

Introduction

Self-assembled monolayers (SAMs) have attracted considerable interest, in part motivated by their potential applications. In particular, sulfur-containing compounds assembled on gold have been the subject of research in many groups,¹ following the first report of a disulfide SAM by Nuzzo and Allara.² Despite extensive investigations, a number of fundamental questions have not been fully resolved, such as the exact nature of the binding of the adsorbate molecules to the gold surface. An illustrative example is the binding of thiols and disulfides to gold; attachment of the thiol as a thiolate is generally accepted, but recently attachment as disulfide was also reported.³ Another example is the proposal of C-S bond cleavage for the binding of sulfides to gold, which is in contrast to the generally accepted binding of sulfides to gold.⁴ In spite of these basic issues, self-assembled monolayers are considered an attractive approach to surface modification and, in particular, to nanotechnology. A recent development in this field includes, e.g., the formation of micropatterns via various methods.⁵ Structures with smaller dimensions are also under investigation, as illustrated by the report of a molecular wire based on SAMs.⁶ Scanning probe microscopy (SPM) is a method with high resolution for the structural analysis of these and other structures.

In addition, SPM allows one to manipulate SAMs and even to position individual molecules in a controlled way at room temperature.⁷

A further extension of the self-assembly on gold involves surface modifications with specific molecular recognition sites as model systems for sensing devices.⁸ Several examples of biological systems⁹ and synthetic receptor adsorbates have been reported.¹⁰ Specific adsorption was studied for chlorinated hydrocarbons at self-assembled monolayers of tetrasulfide adsorbate **1** (see Chart 1) on gold.¹¹ These SAMs have previously been characterized using techniques such as infrared spectroscopy, wettability, electrochemistry, and X-ray photoelectron spectroscopy (XPS).¹² These techniques, and in particular heterogeneous electron transfer experiments, proved that highly-ordered monolayers were formed. No direct experimental evidence has been obtained so far, however, on the molecular order and packing of these adsorbates. Here we report on an AFM study of self-assembled

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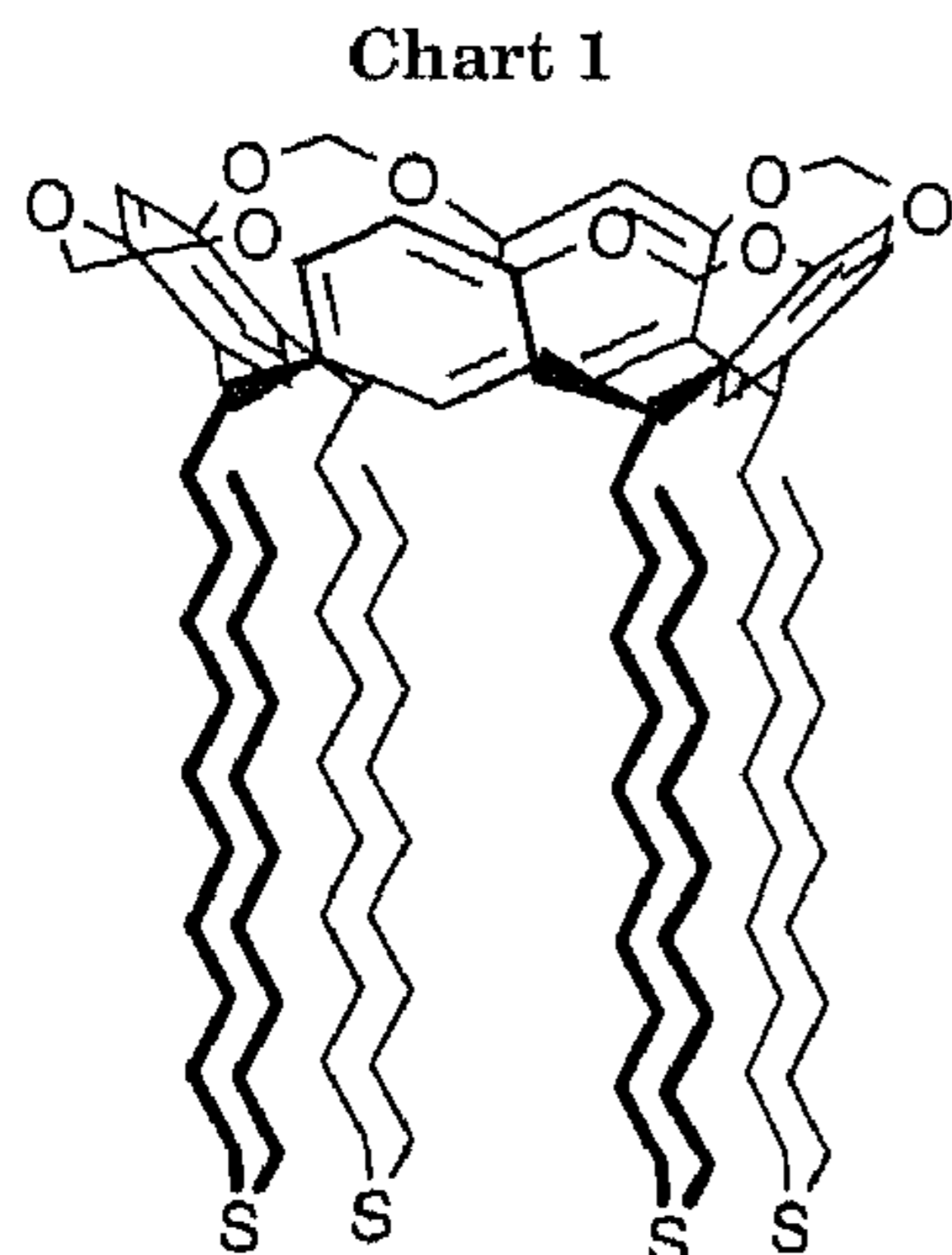
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monolayers of a receptor adsorbate on Au(111) in which these layers are imaged with molecular resolution.

Experimental Section

Substrate Preparation. Gold substrates were prepared on glass (1 in. in diameter) by evaporation of an adhesion layer of 2 nm chromium and 200 nm gold, respectively. Subsequently, the substrates were flame annealed, rinsed with ethanol (p.a.), and immersed with minimal delay into a solution containing the adsorbate. AFM investigations confirmed the formation of terraces on the gold substrates. On these terraces, the Au(111) lattice could be readily imaged.

Monolayer Preparation. Adsorbate **1** was synthesized, as reported previously.¹³ All chemicals used were of highest purity. Glassware used for monolayer adsorption was cleaned with piranha solution before use. **Warning:** piranha solution should be handled with care; it was reported that it can unexpectedly detonate.¹⁴ Next, the glassware was rinsed with large amounts of water (Millipore). Monolayers were prepared from 1 mM solutions in chloroform/ethanol (40/60, v/v) both at room temperature and at 60 °C. After 16 h, the samples were thoroughly rinsed with chloroform, ethanol, and water (Millipore), respectively. The samples prepared at elevated temperatures were allowed to cool to room temperature for 3 h before taking them out of the solution.

Atomic Force Microscopy. The measurements were carried out with a NanoScope II and a NanoScope III AFM (Digital Instruments, Santa Barbara, CA, USA) in the contact mode. AFM scans were performed in air and ethanol. Silicon nitride cantilevers with nominal spring constants of 0.38 and 0.12 N/m were used. The system was allowed to equilibrate prior to taking measurements. The local structure, as observed by AFM, did not change during dust-free storage of the samples at ambient conditions for at least 1 week. All images shown in this work correspond to unprocessed data obtained in the "height mode" (constant force). Digital filtering was sometimes used during the measurements in order to eliminate noise (highpass set to 4, lowpass set to 1). However, the periodicities were observed with and without filters (for an unfiltered image, see the Supporting Information).

Results

Before thermal annealing of the gold substrates, AFM¹⁵ revealed that the surface structure consisted of gold grains (diameter of 10–100 nm). Flame annealing of the gold yielded flat areas of approximately 1 μm^2 which were composed of numerous terraces. The gold lattice could be imaged readily on these terraces. The observed hexagonal lattice ($2.85 \pm 0.13 \text{ \AA}$) is consistent with the Au(111) crystal plane.¹⁶ Only substrates with similar large flat areas were used for the monolayer adsorption.

A typical AFM image of a monolayer of **1** on annealed gold showing a hexagonal lattice with a periodicity of $11.6 \pm 0.4 \text{ \AA}$ is presented in Figure 1a. A second periodicity with a lattice constant of $4.2 \pm 0.2 \text{ \AA}$ could be observed at the same position on the sample after increasing the imaging force¹⁷ from $<10 \text{ nN}$ to 20–30 nN (Figure 1b). Both lattices could be observed simultaneously in a single scan (Figure 1c) by choosing an intermediate imaging force. The two lattices have the same orientation.

For a quantitative analysis of the lattices, "up" and "down" scans were averaged in order to eliminate the influence of thermal drift. The images were analyzed by evaluating the one-dimensional fast Fourier transform (FFT) of autocorrelation filtered images in the three different symmetry directions of the observed lattices. After multiplication with the calibration factor, which takes into account the influence of sample height on measured distances,¹⁸ the observed values were plotted as histograms, and the average for each of the three directions was calculated. The hexagonal symmetry of the lattices is reflected in the identical average lattice constants for all three directions. The corresponding histograms for both periodicities are shown in Figure 2; for a typical autocorrelation image and a two-dimensional FFT, see the Supporting Information.

In different domains, periodicities were observed with different orientations relative to the fixed scan direction. Domains with different orientation of the lattices could sometimes be imaged in a single scan (Figure 3). Arrows indicate the orientation of the lattices. In general, ordered regions were larger than $50 \text{ nm} \times 50 \text{ nm}$.

Discussion

The hexagonal lattice of 11.6 \AA agrees very well with a center to center distance of 11.7 \AA between two adjacent cavitands, as was determined using computer-generated images (Figure 4).¹⁹ An interchain distance of 4.2 \AA has been found in SAMs for closely packed alkyl chains with a perpendicular orientation.²⁰

In general, different imaging forces correspond to different penetration depths of the tip into the SAM.^{18b} Thus, one can assume that the outer part of the SAM is probed when low forces are applied, and the interior is probed when higher forces are applied. This interpretation is consistent with our result that high forces allowed us to image the small periodicity and that low forces enabled us to image the large periodicity. Thus, our AFM observations strongly suggest that the larger periodicity originates from the regular packing of the cavity headgroups, whereas the smaller packing relates to densely packed alkyl chains.

If these observed lattices originate from "subsequent layers" (headgroup/alkyl chains) within the same monomolecular film, the equivalent areas per molecule of each of these layers should match. The area per molecule for the large periodicity ($\approx 117 \text{ \AA}^2$) covers 7.6 times the area of the smaller lattice ($\approx 15 \text{ \AA}^2$).²¹ This ratio of 8:1 as determined from the lattice constants corresponds very well with the molecular structure of cavitand **1** where

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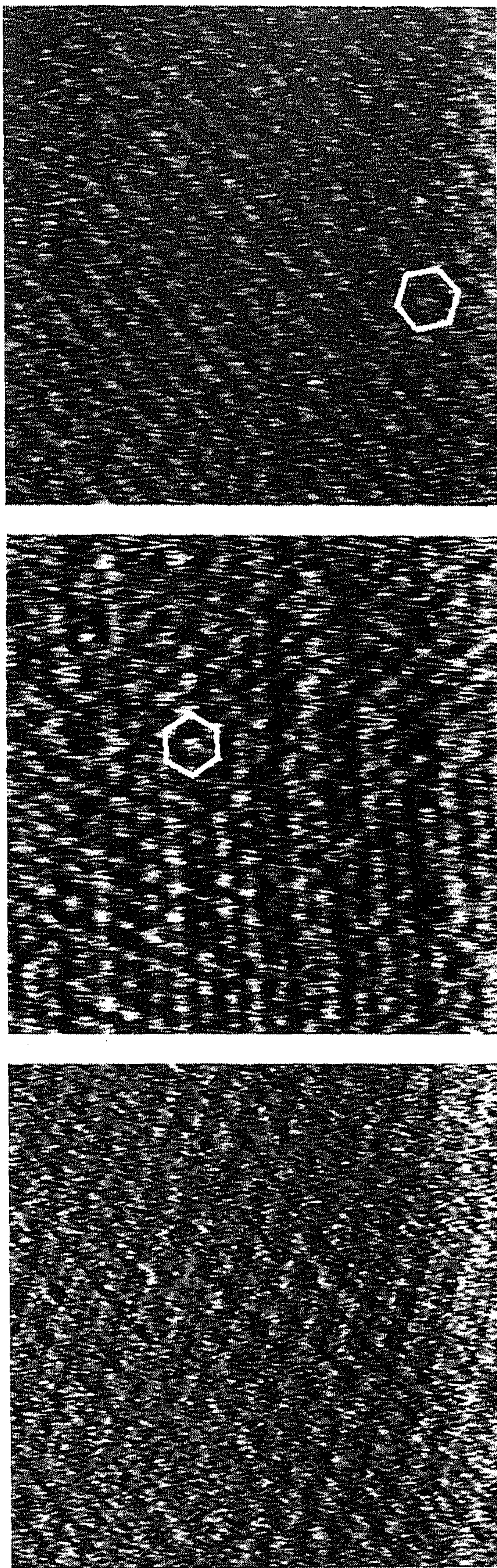


Figure 1. AFM images of calixand 1 monolayers (the symmetry and the nearest neighbor distance of the lattice are indicated with a white hexagon). (a, top) Periodicity of 11.6 Å observed with a force of ca. 5 nN (image size 17.8 nm × 17.8 nm); (b, middle) Periodicity of 4.2 Å observed with a force of ca. 25 nN (image size 6.4 nm × 6.4 nm). (c, bottom) Both periodicities observed with a force of ca. 12 nN (image size 14.4 nm × 14.4 nm).

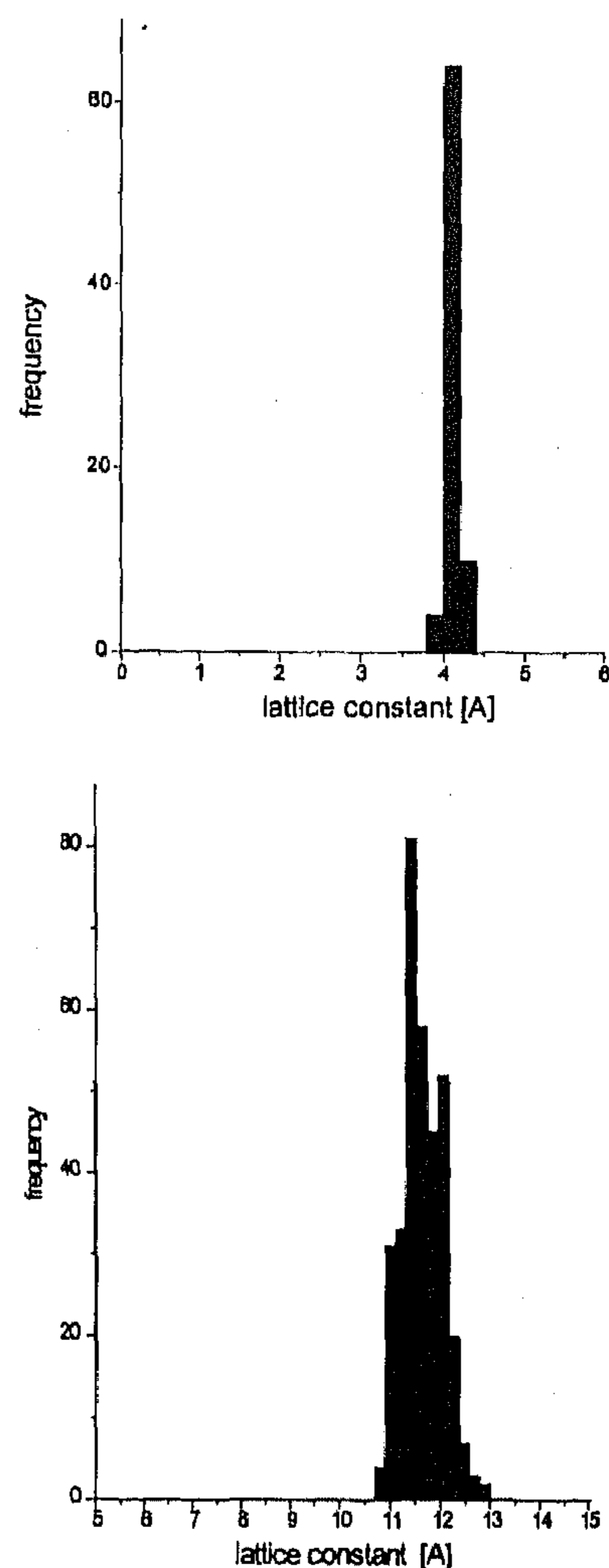


Figure 2. Analyses of the one-dimensional fast Fourier transform in three symmetry directions for the two observed periodicities.

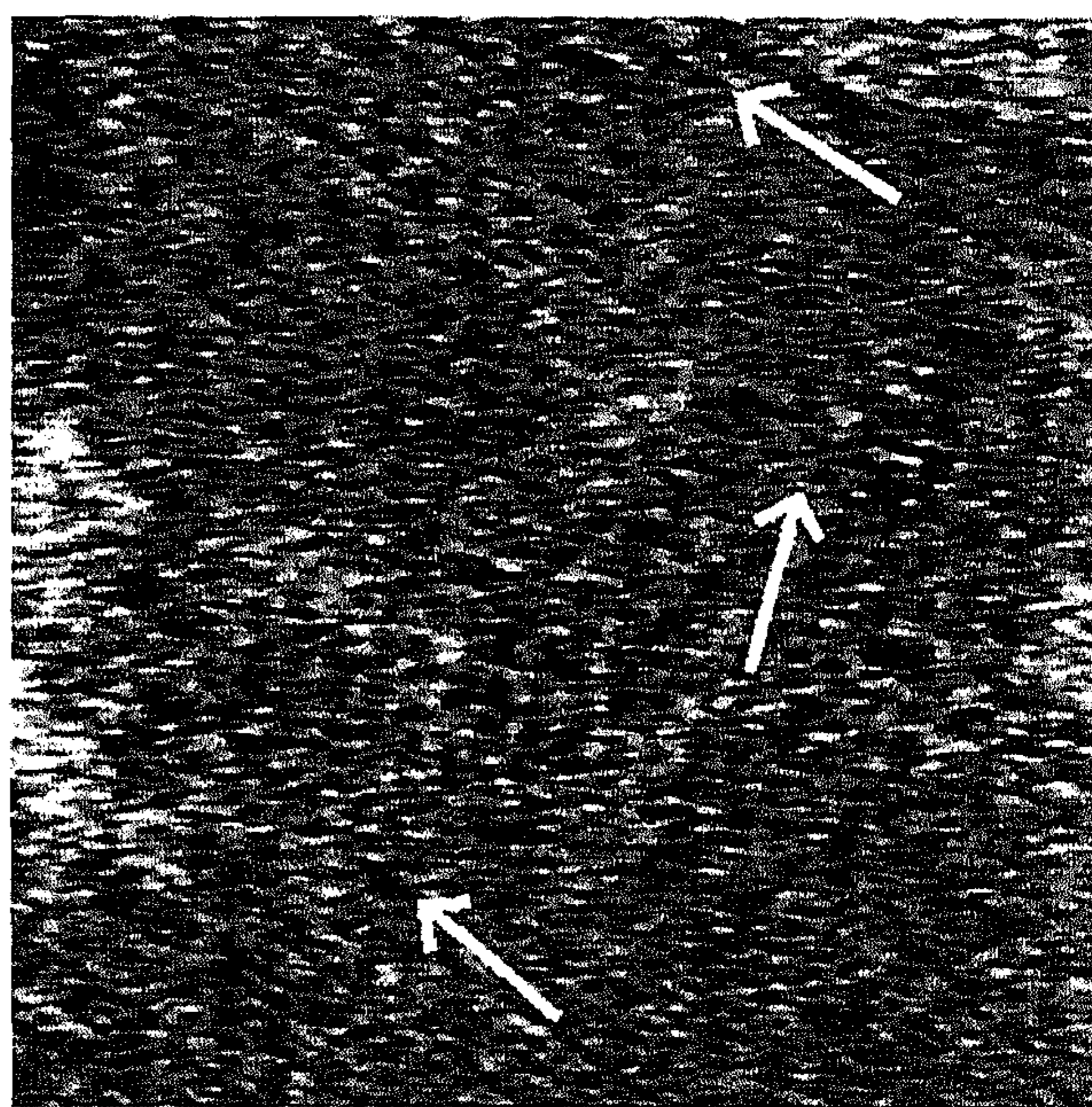


Figure 3. AFM image in which domains with different orientations of the hexagonal packing are observed (imaging force ca. 12 nN). The direction of the different domains is indicated with white arrows (image size 21.0 nm × 21.0 nm).

eight alkyl chains fill the space underneath the calixand. This observation further supports the conclusions of our previous work,¹² that filling the void space is a prerequisite to obtain well-ordered layers. In addition, the 8:1 ratio

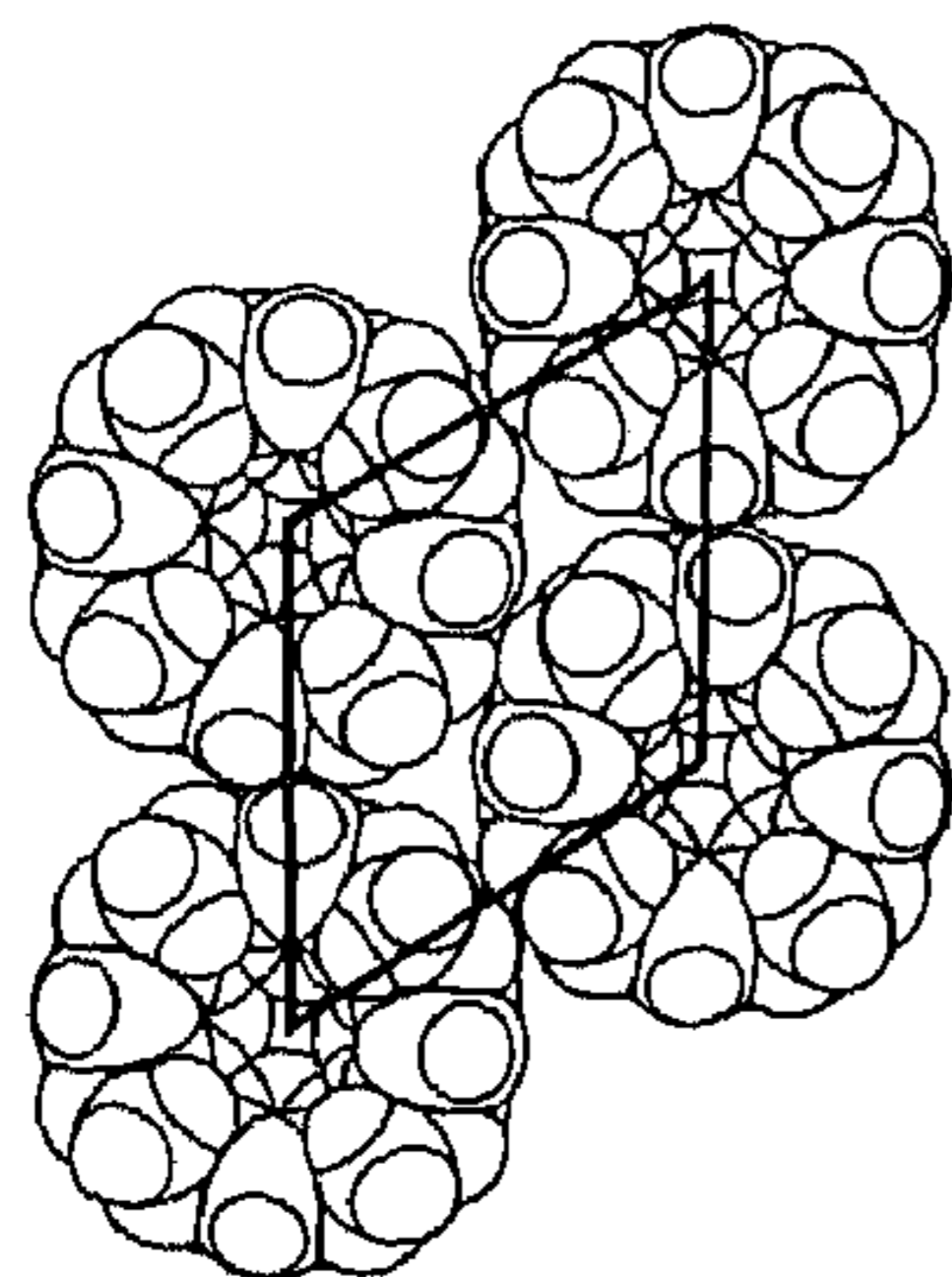


Figure 4. Computer-generated image of hexagonal packing of the calix[4]resorcinarene moieties of adsorbate **1** at van der Waals contact from which a center to center distance of 11.7 Å was determined.

shows once more that no carbon–sulfur bond cleavage occurs in these systems, as has been suggested by Porter.⁴

An identical molecular packing was found by AFM for layers prepared at room temperature and at elevated temperatures. Previously, a significant improvement of the blocking ability of the monolayers was observed with heterogeneous electron transfer when monolayers were adsorbed from solutions at elevated temperatures compared to adsorption at room temperature. The elevated temperature enables rearrangement of the molecules in the monolayer to form a more densely packed layer.^{12,22}

(22) Electrochemical measurements were performed on polycrystalline gold beads, while Au(111) was used for the AFM measurements. The molecular packing on these two substrates is not necessarily the same.

This AFM study clearly shows that the preparation of the SAMs at different temperatures does not alter the molecular packing in the ordered regions of the film. The rearrangement during the thermal annealing of the monolayers decreases the size of the disordered regions, which improves the blocking ability of the monolayer during heterogeneous electron transfer measurements.

Conclusion

The structure and orientation of calix[4]resorcinarene receptor adsorbate self-assembled monolayers on Au(111) were studied with atomic force microscopy. In molecularly-resolved images, two hexagonal periodicities with lattice constants of 11.6 ± 0.4 and 4.2 ± 0.2 Å, respectively, were observed. These two periodicities could be observed separately as well as simultaneously by changing the imaging force. The experimentally determined distances are assigned to different parts of the adsorbates, suggesting that the 11.6 Å repeat distance is related to the lattice of the calix[4]resorcinarene part of the adsorbates, while the smaller repeat distance fits well with a closest packing of alkyl chains. These measurements confirm our previous assumption on the high degree of order of these monolayers of calix[4]resorcinarene SAMs on gold.

Supporting Information Available: An unfiltered image in which both periodicities can be observed, a two-dimensional fast Fourier transform for the small periodicity, and an autocorrelation image for the large periodicity (3 pages) are available. Ordering information is given on any current masthead.

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