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## Self Assembly of Mixed Monolayers of Mercaptoundecylferrocene and Undecanethiol studied by STM

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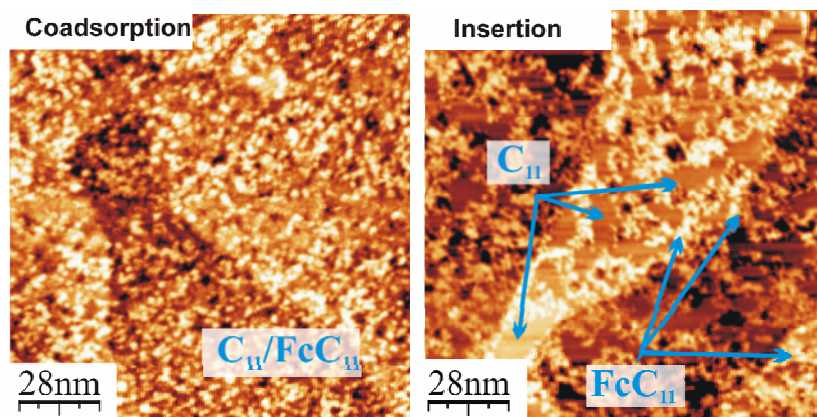
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**Abstract.** Mixed monolayers of mercaptoundecylferrocene and undecanethiol were deposited from solution by coadsorption and by a two-step insertion method, using the alkanethiol monolayer as insulating matrix. The resulting layers were characterized by UHV-STM, showing molecular resolution. For insertion-processed samples, a mesh-like surface structure of ferrocenes was observed, due to the preferential incorporation of molecules along domain boundaries and defect sites of the alkanethiol monolayer. For monolayers in the intermediate coverage regime, a crystalline phase was observed.

### 1. Introduction

The fascinating power of molecular self-assembly might be a promising tool for a possible integration of non-silicon technology into nanoelectronic devices. A particularly well characterized system of self-assembled monolayers (SAM) is the system of alkanethiols on Au (111) substrates [1]. These monolayers can be used to embed functional molecules into a mechanically stable and electrically insulating environment to study their electrical properties [2]. Especially interesting for future technological applications is the insertion of electroactive molecules like mercaptoalkylferrocenes. These monolayers can be easily oxidized and reduced in solution and are well characterized by electrochemical methods [3], although the mercaptoalkylferrocenes tend to aggregate and form multilayers [4]. Their localized electrical behavior was addressed by scanning probe methods finding a negative differential resistance effect caused by external oxygen, as well as thickness changes upon oxidation/reduction of the ferrocene moiety [5]. To further characterize the influence of the ferrocenes on the charge-transfer behavior of the molecule, it is desirable to manufacture mixed monolayers with isolated mercaptoalkylferrocenes embedded into a topographically well-defined matrix SAM of alkanethiols. Once a layer with molecularly resolved topographical properties is achieved, the well-known electrical transmission and height of the alkanethiol SAM can be used to evaluate the charge-transfer characteristics of the ferrocene moiety, using the alkanethiols as a spectroscopic reference.



**Figure 1:** Coadsorption of  $\text{FcC}_{11}$  and  $\text{C}_{11}$  at a ratio of 1:3. The brighter, crumbled surface is attributed to the ferrocene endgroups (left). Two step insertion process of  $\text{FcC}_{11}$  into  $\text{C}_{11}$  (right). Both monolayers show substrate steps and etch pits (dark depressions), indicating a chemisorbed monolayer.

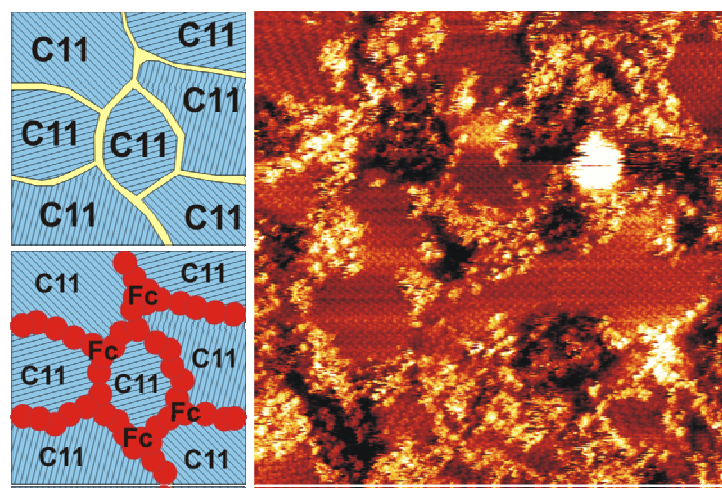
We have investigated 11-mercaptoundecyl ferrocene, constructed of an alkanethiol linker and the electro-active ferrocene moiety as endgroup. For characterization, the molecules were embedded into an alkanethiol monolayer by insertion and coadsorption. The resulting layers were characterized by ultrahigh vacuum scanning tunneling microscopy (UHV-STM).

## 2. Experimental

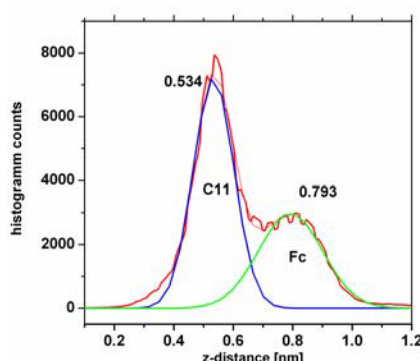
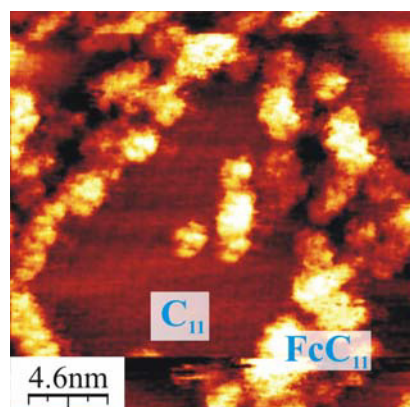
As substrates, gold-(111) thin films evaporated on mica were prepared as described previously [6]. Undecanethiol molecules (referred to as  $\text{C}_{11}$  from now on) were used as purchased (Sigma-Aldrich). 11-mercaptoundecyl ferrocene (referred to as  $\text{FcC}_{11}$  from now on) was synthesized according to Uosaki et al. [3] with modifications adapted from Kim et al. [7]. All compounds were solved in ethanol as millimolar solutions. For coadsorption experiments, the solutions were mixed in different ratios and the samples were exposed to the mixture for 24 h. For the insertion experiments, freshly prepared samples were exposed to  $\text{C}_{11}$  solution for 24 h and then transferred to a 3:1 solution of 1 mmol/l  $\text{C}_{11}$  and 1 mmol/l  $\text{FcC}_{11}$  for 10-120 minutes. During assembly, the samples and solutions were handled under controlled argon atmosphere in a glovebox. Afterwards the monolayers were thoroughly rinsed with ethanol and immediately transferred to vacuum. The samples were measured with a JEOL 4500 UHV-STM using homemade electrochemically etched tungsten tips in UHV at a base pressure of  $\sim 5 \cdot 10^{-10}$  mbar.

## 3. Results

For both processes, the sample topographies show monoatomic substrate steps as well as etch pits, resulting from the assembly process, thereby indicating a chemisorbed monolayer of homogenous thickness (Figure 1). The coadsorption experiment yields layers with isolated, elevated features, attributed to the ferrocene endgroups (Figure 1 left). The measured heights of the elevated spots agree



**Figure 2:** Meshlike insertion of  $\text{FcC}_{11}$  along domain boundaries of a  $\text{C}_{11}$  SAM. A dense alkanethiol monolayer forms a closed monolayer consisting of different domains (upper left). Along their edges preferential adsorption takes place, leading to accumulated ferrocene ribbons on the surface (lower left). On the surface of the large intact  $\text{C}_{11}$  domains, the characteristic  $c(4 \times 2)$  surface reconstruction of an alkanethiol SAM can be observed.



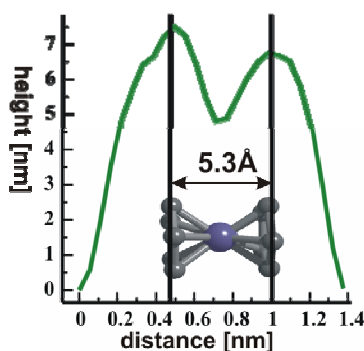
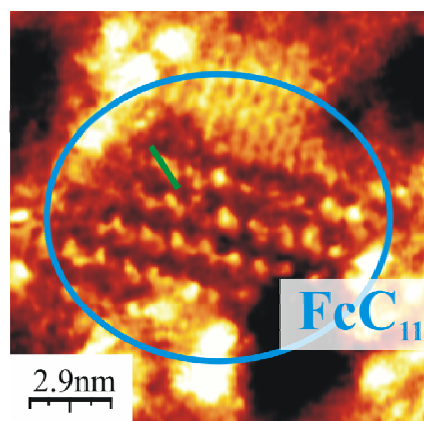
**Figure 3:** Topography of Fc- $C_{11}$  inserted into  $C_{11}$ . In the center, an ordered  $C_{11}$  domain is visible, surrounded by a ferrocene surface ribbon. On the height distribution, histogram two distinct peaks are visible. Fitting two Gaussian peaks to the graph results in an average height difference of  $\sim 2.7$  Å.

with the expected height of embedded ferrocenes from earlier measurements. However, even for diluted ratios, no molecular resolution of the matrix monolayer could be achieved and a decreased ordering or impairing of the imaging process due to the entangled ferrocene/alkanethiol structure was assumed.

The surface of the insertion-processed sample shows a mesh-like structure of ferrocene ribbons running along the alkanethiol domain boundaries (Figure 1 right). During the insertion step, a combination of desorption of chemisorbed molecules and insertion of new molecules from solution occurs, which takes place preferentially at defect sites. Thus, the existing alkanethiol domains remain highly ordered, whereas the inserted ferrocenes accumulate along domain boundaries and edges of steps and etch pits (Figure 2). The quality and order of the monolayer with inserted  $FcC_{11}$  molecules can be increased by careful tempering in solution at around 50 °C. However, at elevated temperatures slow desorption of the alkanethiols takes place, which was avoided by using a 3:1 mixture of 1 mmol/l  $C_{11}$  and  $FcC_{11}$  during the insertion step. The mixed monolayers, produced by this insertion method, show uniformly ordered alkanethiol domains, which exhibit the characteristic surface reconstruction of a closely packed, standing-up alkanethiol monolayer (Figure 2, 3).

The height difference between  $FcC_{11}$  and  $C_{11}$  was determined from a topography histogram (Figure 3). The extracted height difference at a tunneling setpoint of 1.65 V/ 350 pA is roughly 2.7 Å, compared to an expected physical length difference of roughly 3.7 Å between the two molecules, taken from single crystal X-ray measurements. Considering that a longer molecule appears shortened, compared to a shorter one of a roughly similar current decay constant and taking into account a slightly tilted arrangement, these numbers agree quite well. This height difference indicates the presence of single ferrocene endgroups on the SAM surface eliminating the formation of aggregated clusters of multiple molecules on the surface.

Upon stronger temperature treatment in solution, up to 65 °C and for longer heating times,  $C_{11}$



**Figure 4:** Topography of an ordered  $FcC_{11}$  domain for an intermediate coverage, mixed monolayer. The profile of the marked ferrocene shows two separated peaks, indicating both cyclopentadiene rings oriented perpendicular to the surface.



desorbs from the surface and a mixed layer with lying-down alkanethiols is formed. In this intermediate coverage regime, an ordered phase was observed for  $\text{FcC}_{11}$  (Figure 4). The ordered phase consists of periodic, slightly barbell shaped elements, which were attributed to the ferrocene endgroups, lying on the surface. A profile of one element shows two distinct peaks at a distance of 5.3 Å, which is in close agreement with the distance between both cyclopentadien rings of the ferrocene moiety, suggesting an upright, perpendicular placement of the endgroup on the surface. A very similar structure was observed for slightly modified  $\text{FcC}_{11}$ , as described previously [8].

#### 4. Conclusion

Mixed monolayers of  $\text{FcC}_{11}$  and  $\text{C}_{11}$  molecules were prepared by coadsorption and by a two-step insertion process. The coadsorption process results in a dense, mixed monolayer with an entangled structure of ferrocenes and alkanethiols. This process was examined no further, due to difficulties at high-resolution imaging. The two-step insertion process yields a monolayer with crystalline alkanethiol domains, separated by mesh-like ferrocene ribbons formed along the domain walls. The height of the ferrocenes at the boundaries points towards separated ferrocene endgroups and no or little agglomeration of multiple molecules on the surface of the SAM. These monolayers are suitable for future spectroscopic measurements. After strong temperature treatment, an intermediate surface coverage of molecules was achieved. In this regime, domains of a regular ferrocene structures were observed on the surface.

#### 5. Acknowledgements

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