

Supramolecular chemistry at interfaces

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Abstract: The self-assembly process of monolayers has been exploited as a tool to order and orient molecules with particular functions on flat gold surfaces in two dimensions. These functional adsorbates were derivatized with sulfide moieties for the adsorption on gold. The studied adsorbates include resorcin[4]arenes, calix[4]arenes, and carceplexes. Monolayers of these adsorbates on gold were prepared and characterized by means of a combination of various surface analytical techniques, including infrared spectroscopy, wetting, ellipsometry, X-ray Photoelectron Spectroscopy (XPS), Secondary Ion Mass Spectrometry (SIMS), electrochemistry, and Atomic Force Microscopy (AFM). The monomolecular films were studied for potential applications like sensing and switching.

INTRODUCTION

In the field of supramolecular chemistry most systems are studied in solution (1). In our group, synthetic receptors for cations, anions, and neutral molecules have been developed via a modular approach based on the combination of building blocks such as calix[4]arenes and resorcin[4]arenes (2). The host-guest interactions between these macrocyclic receptor molecules and various guests species have been studied in selective membrane transport (3) and sensors based on chemically modified field effect transistors (4). High selectivities for e.g. sodium over potassium have been obtained, which illustrates the potential of these receptors.

Self-assembled monolayers have been investigated for many purposes. In particular, monolayers of sulfur-containing compounds on gold have attracted considerable attention. The majority of the monolayer research on gold has been performed with alkanethiol- and dialkyl disulfide-derivatized adsorbates. Dialkylsulfides have been investigated less frequently. Sulfides form monolayers with a more liquid-like alkyl chain packing than alkanethiols on gold. The binding of the sulfur has in this case a coordinative character, while for alkanethiols and dialkyl disulfides the sulfur is assumed to be bound as a thiolate. In our group resorcin- and calix[4]arene adsorbates have been developed, and monolayers of these compounds have been characterized (5, 6). These adsorbates are bound to the gold surface via *four* anchoring dialkylsulfide units because only eight hydrocarbon chains will, when densely packed, completely fill the space between the gold surface and the headgroup ($\geq 140 \text{ \AA}^2$). While four parallel alkyl chains cannot form a well-packed layer underneath each macrocyclic unit, the four sulfides allow an efficient filling of the voids by looping back from the interface (as depicted in Chart 1). Thus, monolayers of adsorbates **1** and **2** and various derivatives were obtained. It was shown that these monolayers are potentially interesting for sensing applications (*vide infra* and ref. 7).

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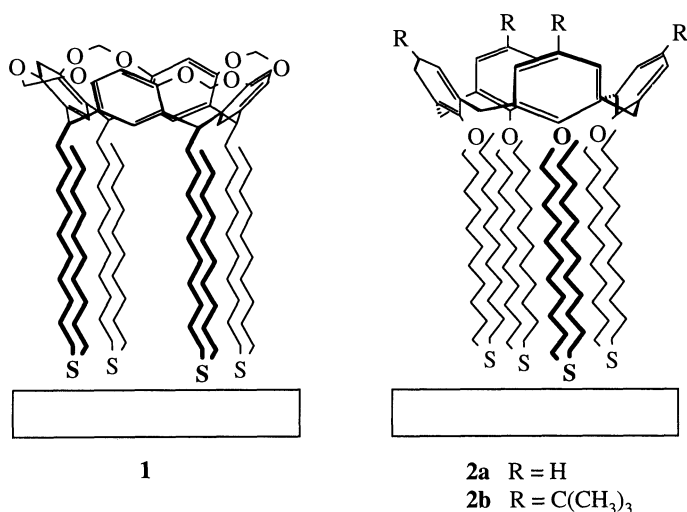


Chart 1

MONOLAYER PROPERTIES

It is generally accepted that alkanethiols and dialkyl disulfides adsorb on gold as *thiolates* (8). Dialkylsulfides have been studied far less extensively (9), but it is generally assumed that the binding to the surface occurs via coordination to gold (10). The adsorbates studied in our group are sulfide based (5). Resorcin[4]- and calix[4]arene adsorbates form stable monolayers, as was proven by the combination of various surface analytical techniques, including electrochemistry, wettability studies, XPS, ellipsometry, SPR, and SIMS (5). These techniques proved that monomolecular films were formed with a high capability of blocking heterogeneous electron transfer through the monolayer. The elemental composition was in agreement with the structure of the adsorbates.

Similar to the assembly of alkanethiols and dialkyl disulfides the driving force for monolayer formation of dialkylsulfides is the interaction between the gold and the sulfur, despite the weaker binding of sulfides to gold. In the resorcin[4]arene and calix[4]arene adsorbates four sulfide moieties are used for the binding to gold. For the resorcin[4]arene monolayers the adsorption at elevated temperature yielded films with a considerably higher degree of order, relative to films prepared at room temperature (5). Heating would provide the mobility in the monolayer to rearrange to a thermodynamically more favorable structure with the alkyl chains predominantly in an all-trans configuration. A similar effect was observed for the calix[4]arene monolayers. To achieve a better understanding of the adsorption process, we studied the sulfur with XPS, which is a suitable technique to monitor the sulfur separately from the rest of the adsorbate. In addition to the elemental composition, information on the oxidation state of the elements can be obtained. The S_{2p_{3/2}} binding energies in alkanethiols, dialkyl disulfides or dialkylsulfides are typically between 163 and 164 eV (11). When these adsorbates are bound to gold surfaces, this binding energy shifts about 1.2 eV to lower energy. The difference between bound and unbound sulfur is therefore a good probe to study the adsorption of the resorcin[4]arene adsorbate **1** and calix[4]arene adsorbates **2** to gold. The binding of sulfur to gold has been investigated of adsorbates **1** and **2** both with films prepared at room temperature and at 60 °C. The S_{2p} region of adsorbate **1** in the XPS is shown in Fig. 1.

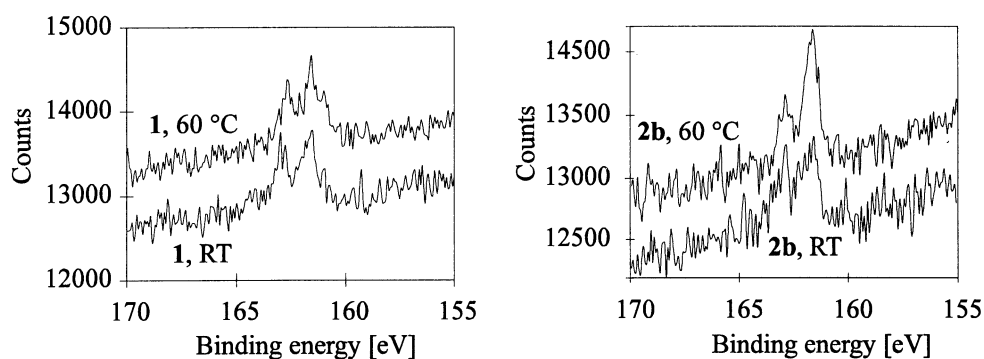


Fig. 1. S_{2p} XPS region of **1** and **2b** monolayers prepared at room temperature (bottom) and at 60 °C (top).

Due to spin-orbit coupling, the S_{2p} region consists of a doublet ($S_{2p_{1/2}}$ and $S_{2p_{3/2}}$) in which the two peaks are separated by about 1.2 eV and have a fixed intensity ratio of 2:1 (the larger peak does have the lower binding energy, ref. 12). The interpretation of the spectra is somewhat complicated due to peak overlap, which requires peak deconvolution (Fig. 2). The $S_{2p_{3/2}}$ of the unbound sulfur will overlap with the $S_{2p_{1/2}}$ of bound sulfur. When all sulfur is bound to the gold, a 2:1 ratio should result, while a smaller ratio indicates the presence of unbound sulfur.

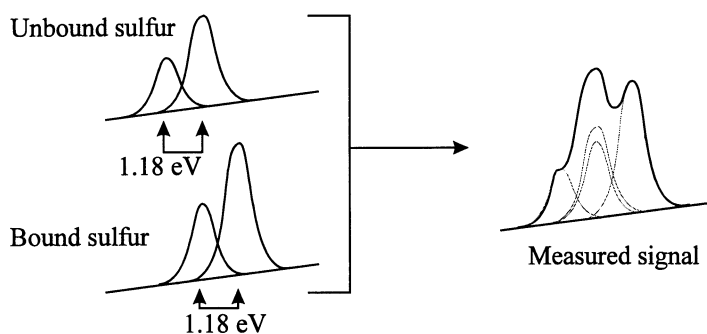


Fig. 2. Peak overlap in the S_{2p} region for bound and unbound sulfur in XPS.

Table 1. Amount of sulfur bound to gold depending on the adsorption temperature for adsorbates **1** and **2**, and binding energy for $S_{2p_{3/2}}$.

Adsorbate	$S_{2p_{3/2}} / S_{2p_{1/2}}$ (± 0.3)	Bound Sulfur [%]	Binding Energy $S_{2p_{3/2}}$ [eV]
didecylsulfide	2.0	100	161.9
1 , RT	1.5	86	161.7
1 , 60 °C	2.0	100	161.5
2a , RT	1.0	66	161.7
2a , 60 °C	1.8	96	161.7
2b , RT	0.8	56	161.6
2b , 60 °C	1.7	93	161.7

The intensity ratio between the peak at 161.7 eV ($S_{2p_{3/2}}$ for bound sulfur), and the peak at 162.9 eV ($S_{2p_{1/2}}$ for bound, and $S_{2p_{3/2}}$ for unbound sulfur) are shown in Table 1 for adsorbates **1** and **2** prepared at room

temperature and at 60 °C. The amount of bound sulfur, calculated based on the intensity ratio, is included in Table 1 as well. For all monolayers the amount of bound sulfur increases significantly when the films are prepared at 60 °C. All sulfur is bound to the surface when monolayers of cavitand **1** were prepared at elevated temperature. The data suggest that in the calix[4]arene **2** monolayers still some unbound sulfur is present.

These observations are in good agreement with the previous results regarding the degree of order in the monolayers of resorcin[4]arene **1** and calix[4]arenes **2**. For monolayers with a higher degree of order an increased amount of sulfur bound to the surface was found. These results confirm our hypothesis that monolayer rearrangement occurs at elevated temperatures (5). In monolayers prepared at room temperature the alkyl chains adopt a loose packing, while not all sulfur is bound to the surface. Heating of the monolayer increases the mobility in the system and allows rearrangement to the thermodynamically most favorable structure. The increase of the number of sulfur atoms bound to the gold forms the driving force for the monolayer rearrangement, together with the rearrangement of the aliphatic chains to the predominantly all-trans conformation.

In none of our studies we found an indication that one of the C-S bonds was cleaved upon adsorption on gold. Conflicting with these results, Zhong and Porter suggested that sulfides adsorb on gold as thiolates (13). We and others have refuted this suggestion by proving that the sulfide moiety remains intact after adsorption to the gold surface (14). Direct evidence appeared from Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) experiments, in which the molecular peak M^+ and $(M + Au)^+$ were distinctly present in the spectra of sulfide monolayers.

The high degree of order in the resorcin[4]arene **1** monolayers could be confirmed recently by the elucidation of the molecular packing of these monolayers. AFM images obtained from a monolayer of **1** showed two hexagonal lattices. One lattice had a periodicity of $11.6 \pm 0.4 \text{ \AA}$ (Fig. 3a), and a second periodicity was observed with a lattice constant of $4.2 \pm 0.2 \text{ \AA}$ (Fig. 3b). The small periodicity could be observed at the same position on the sample after increasing the imaging force from $< 10 \text{ nN}$ to $20\text{--}30 \text{ nN}$ (15). By choosing an intermediate imaging force, both lattices could be observed simultaneously in a single scan.

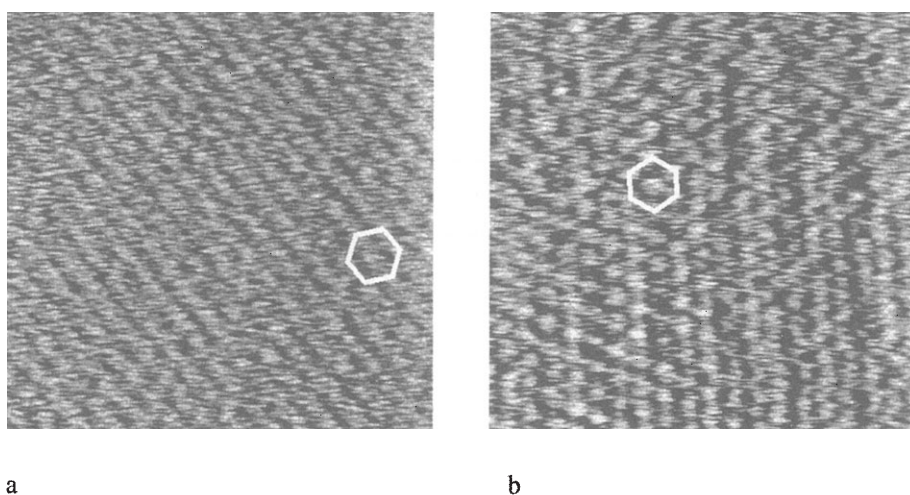


Fig. 3. AFM images of resorcin[4]arene **1** monolayers (the symmetry and the nearest neighbor distance of the lattice is indicated with a white hexagon). (a) Periodicity of 11.6 \AA observed with a force of ca. 5 nN (image size $17.8 \times 17.8 \text{ nm}^2$); (b) Periodicity of 4.2 \AA observed with a force of ca. 25 nN (image size $6.4 \times 6.4 \text{ nm}^2$).

Domains were observed in resorcin[4]arene monolayers with different orientations of the periodicities relative to the scan direction. Sometimes, domains with different orientation of the lattices could be imaged in a single scan. In general, the ordered regions in these monolayers were larger than approximately $50 \times 50 \text{ nm}^2$ (16).

The hexagonal lattice of 11.6 \AA in the resorcin[4]arene monolayers agrees very well with a center to center distance of 11.7 \AA between two adjacent molecules, as was determined using a computer generated hexagonal packing of the receptor moieties at Van der Waals distance (Fig. 4). The smaller periodicity of 4.2 \AA relates to the alkyl chain packing, which is very similar to closely packed alkyl chains with a perpendicular orientation (17).

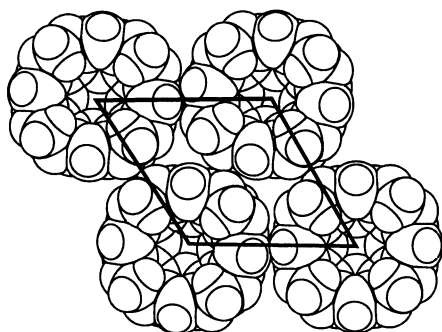


Fig. 4. Computer generated image of hexagonal packing of the resorcin[4]arene moieties of adsorbate **1** at Van der Waals contact from which a center to center distance of 11.7 \AA was determined. The parallelogram represents the unit cell.

In general, different imaging forces correspond to different penetration depths of the tip into the SAM (18). Thus, one can assume that the outer part of the SAM is probed when low forces are applied, and that the interior is probed when high forces are applied. This interpretation is consistent with the result that low forces reveal the large periodicity and high forces reveal the small periodicity. Thus, these 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. The distance of 4.2 \AA indicates that the alkyl chains adopt a perpendicular orientation for the resorcin[4]arene monolayer.

Another indication that the two observed lattices in monolayers of adsorbate **1** originate from “subsequent layers” (headgroup / alkyl chains) within the same monomolecular film, arises from the match between the equivalent areas of these layers. The area per molecule for the large periodicity ($\cong 117 \text{ \AA}^2$) covers 7.6 times the area of the smaller lattice ($\cong 15 \text{ \AA}^2$). This ratio of *ca.* 8:1 as determined from the lattice constants corresponds very well with the molecular structure of resorcin[4]arene **1** where eight alkyl chains fill the space underneath the resorcin[4]arene.

MONOLAYERS FOR SENSING APPLICATIONS

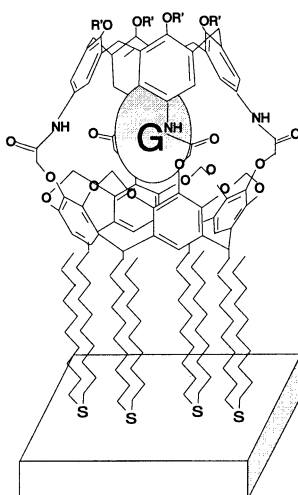
The high degree of order in these films make them attractive for sensing applications, as non-specific interactions are thus minimized. These non-specific interactions have been observed in Langmuir-Blodgett films of calix[*n*]arenes during (selective) permeation experiments, *i.e.* permeation across these films is governed by diffusion between neighboring molecules and not through the molecular pores of the calix[*n*]arenes (19).

Only a few functionalized self-assembled monolayers have been reported with the objective to achieve selectivity. Selectivity can be accomplished with relatively simple systems, as was shown for monolayers containing carboxylic acid endgroups. These monolayers showed selectivity for organophosphonates in the presence of copper ions (20). Another relatively simple system consists of mixed monolayers of alkanethiols and isophthalamide adsorbates which bind barbiturate (21). A more advanced monolayer was a resorcin[4]arene-based assembly described by Stirling *c.s.*, in which binding of vitamin C to the monolayer was observed (22). Kaifer *c.s.* reported mixed monolayers of β -cyclodextrin and pentanethiol, and they showed with cyclic voltammetry that ferrocene can be complexed in the cavity (23).

Interactions of various vapors with monolayers of receptor adsorbate **1** (Chart 1) were performed with a Quartz Crystal Microbalance (QCM). A high sensitivity was observed for tetrachloroethylene compared to other chlorinated hydrocarbons such as chloroform and dichloromethane (24). The specificity of the reported molecular recognition has been questioned (25). Low polarity polymers, such as poly(isobutylene) and poly(vinyltetradecanal), would show an identical sensitivity pattern as the resorcin[4]arene monolayer, which would indicate that the cavities are not primarily responsible for the selectivity. In order to establish a better understanding of the adsorption behavior we have further investigated this monolayer system with Surface Plasmon Resonance (SPR) with which a higher stability could be accomplished (7). This study showed that the receptor monolayer induces a significantly different selectivity pattern when compared to an alkanethiol monolayer. In general, the receptor monolayer shows a two times higher sensitivity for the vapors relative to the octadecanethiol monolayer. For tetrachloroethylene, however, a twelve times higher sensitivity is observed. This strongly indicates a specific interaction between the guest and the host system.

DEVELOPMENT OF SWITCHING MONOLAYER

The self-assembly process is a means to order and orient molecules. Previously, our group has developed a non-symmetrical carceplex that exhibited a novel type of stereoisomerism based on the orientation of the guest in the carcerand (26). Surface confinement of such a carceplex would orient the carcerand while the guest remains free to adopt two orientations. As appeared from the systematic study of guests described before, different energy barriers between the two states could be obtained, depending on the size of the cavity and of the incarcerated guest. Analogous to the calix[4]arene and resorcin[4]arene adsorbates, a non-symmetrical carceplex adsorbate (**3**) was synthesized. Self-assembled monolayers of carceplex **3** were



3-DMF

Chart 2

prepared on gold, and were characterized with a number of surface sensitive techniques (like FTIR, ellipsometry, contact angle measurement, XPS, and SIMS), showing that well-ordered monolayers were obtained.

The monolayer infrared spectrum provides clear information about the order and orientation of the carceplex **3·DMF** on the monolayer (Chart 2, Table 2). The methylene C-H stretches have the same absorption maxima in the monolayer as in the bulk, which indicates a high degree of order. The amides in the carceplex appear in the bulk infrared spectrum as amide I (predominantly C=O stretch) and amide II (predominantly N-CO stretch). In the monolayer spectrum, however, only amide II appears at 1537 cm⁻¹ as a clear absorption, while amide I is very weak or absent. The orientation of the transition dipole of amide I is in the proposed monolayer structure parallel to the gold, and therefore is not absorbed by the (*p*-polarized) infrared beam. This confirms that the orientation of the carceplex **3·DMF** is 'upright', similar to the previously reported adsorbates.

Table 2. Selected infrared peak positions for carceplex **3·DMF** in the bulk and the monolayer.

Vibration	bulk [cm ⁻¹]	monolayer [cm ⁻¹]
-CH ₂ -, symmetrical	2853	2853
-CH ₂ -, asymmetrical	2924	2926
Amide I	1696	not observed
Amide II	1526	1537

The successful confinement of carceplex **3·DMF** is the first step toward a new switching device. For such a device it is necessary to be able to determine the orientation of the guest and to switch between the two possible orientations. Efforts have been made to orient the guest under influence of an external electrical field, and to detect the change of the average orientation with a SQUID (Super Conducting Interference Device) or by means of Maxwell displacement currents. Further investigations are required for the development of this new switching device.

SUMMARY

Self-assembled monolayers are an elegant tool to control molecular orientation. Thus calix- and resorcin[4]arene monolayers were formed, for which sensing applications based on molecular recognition were shown. The calix[4]arene-based carceplex was confined in space by means of self-assembly to gold. This approach is a step toward a new type of molecular switch.

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