Self-Assembled Monolayers of Resorcin[4]arene Tetrasulfides on Gold

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Abstract: A new type of host adsorbates has been developed which possess a resorcin[4]arene headgroup with four di-*n*-decyl sulfide chains underneath. Self-assembled monolayers of these adsorbates with various functionalities at the head groups, i.e., methylene ether (the so-called *cavitand*), methyl ether, 2-fluoroethyl, hydroxyl, *N*-propylacetamide, and several carboxyl esters, on gold were characterized with polarized infrared external reflectance spectroscopy (PIERS), X-ray photoelectron spectroscopy (XPS), surface plasmon spectroscopy (SPS), and contact angle and electrochemical measurements. Highly organized monolayers are formed from 1 mM solution at 60 °C by adsorbates that have headgroups smaller or equal to the cross-sectional area occupied by the eight alkyl chains underneath (≤ 160 Å^2).

Introduction

Self-assembly of single molecules into highly ordered monolayer structures enables the production of stable films with distinct and desirable properties. This opens the route to the development of active layers for fast responding sensors by organizing receptor molecules on top of an appropriate transduction element. Self-assembled monolayers emerge by adsorption of appropriate molecules onto clean surfaces and are stable when the adsorbate has a strong interaction with the substrate and a shape that allows lateral packing.[1] Especially the self-assembly of organosulfur adsorbates on gold has attracted considerable attention. The high specificity of the sulfur-gold interaction allows the introduction of various functional groups in the monolayer, without interference in the adsorption process. The majority of the self-assembled organosulfur monolayers studied consists of adsorbates which contain an alkyl chain with a surface-active sulfur group, like alkanethiols,[2–5] di-*n*-alkyl disulfides,[6] and di-*n*-alkyl sulfides,[7,8] and possibly a terminal functional group (OH, COOH, CN, Cl, etc). The structure of these assemblies has been thoroughly studied, and their potential use in various sensor systems[9] has been investigated. Also a limited number of more complicated adsorbate structures are known, such as cyclodextrin derivatives,[10] bolaamphiphiles,[11] phosphatidylcholines,[12] glycolipids,[13] oligoimides,[14] porphyrins,[15] ferrocenes,[16] viologens,[17] 2,2′-thiobis(ethylacetoacetate),[18] poly(γ-benzylglutamate),[19] and other polymeric adsorbates.[20]

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In order to develop stable monolayers which completely passivate the gold surface and possess a highly ordered interface of densely packed receptor sites, we have investigated various self-assembling adsorbate molecules with a resorcin[4]arene headgroup and four dialkyl sulfide chains underneath. The fourfold sulfide-gold interaction of these adsorbates is well-suited for the formation of stable receptor monolayers, due to the high strength and specificity, and the length of the alkyl chains can be tuned to optimize the gold passivation. In this paper the adsorption behavior of these receptor adsorbates and the characterization of the prepared assemblies are described.[21] Recently, we have reported an example of the use of such assemblies for specific gas detection using a quartz crystal microbalance.[22]

Design of the Receptor Adsorbates

Resorcin[4]arenes[23] have a molecular structure that is well-suited for the construction of receptor adsorbates. The four resorcinol units form a conelike cavity, and underneath this cavity four points of attachment for alkyl chains are available at the methine linkages (Figure 1a). These four chains are oriented mutually parallel and perpendicular with respect to the annulus of the macrocycle. The distance between these alkyl chains at the resorcin[4]arene is ca. 5 Å, which is also the packing distance commonly found in alkanethiol monolayers.[4,24] However, only four alkyl chains do not completely fill the space underneath the resorcin[4]arene headgroup, because the sum of their cross-sectional areas (ca. 4×20 Å^2) is considerably less than the cross-sectional area of the resorcin[4]arene headgroup (140 Å^2). By attaching four dialkyl sulfide (11-thiaheneicosyl) chains to the methine linkages, eight alkyl chains can be organized underneath the cavity. When the sulfur atoms in those dialkyl sulfide adsorbates bind to the gold surface, the terminal alkyl chains are forced to loop back. The sum of cross-sectional areas of the eight alkyl chains in this conformation (ca. 160 Å^2) is slightly larger than the cross-sectional area occupied by a (unfunctionalized) resorcin[4]arene headgroup of about 140 Å^2 (Figure 1b). Therefore, the dialkyl sulfide chains underneath the headgroups are expected to be capable of forming a well-organized hydrocarbon layer, which can passivate the gold surface completely and exclude undesired interactions between the gold surface and analytes.

Several resorcin[4]arene tetrasulfides with different functionalities at the headgroup were prepared, and the adsorption behavior of these adsorbates on gold has been studied using various surface characterization techniques. The molecular structure of the resorcin[4]arene adsorbates is given in Chart 1. Adsorbates 1a,b, 2a,b, 3a—c, 4, and 5 were prepared by the acid-catalyzed condensation of resorcinol and 11-undecylenic aldehyde, followed by complete alkylation or acylation of the hydroxyl groups and subsequent addition of the decanethiol to the four terminal vinyl groups using 9-BBN as a catalyst.[21] Octa-(*N*-propylacetamide)resorcin[4]arene 6 was obtained by aminolysis of octamethyl ester 4 with *n*-propylamine in THF, and octahydroxyresorcin[4]arene tetrasulfide 7 was prepared by reductive deacetylation (Zn, MeOH/THF) of octaacetate 3a. Full
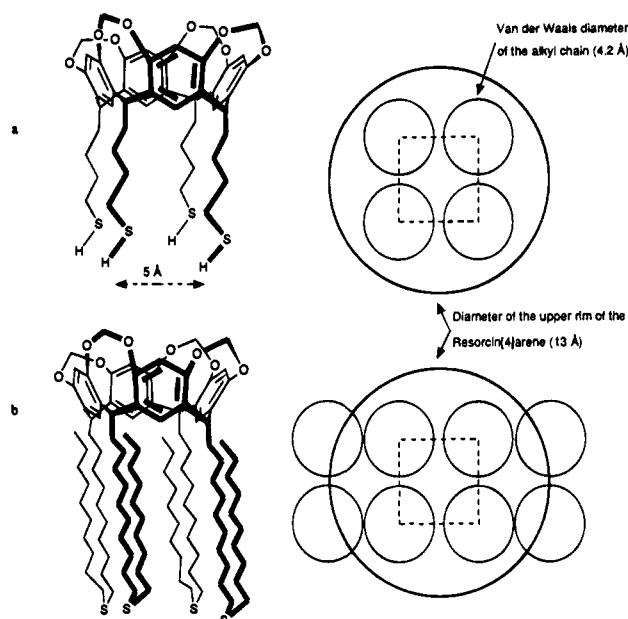

Figure 1. Cross-sectional areas of resorcin[4]arene with (a) four alkylthiol chains and with (b) four dialkyl sulfide chains. The large circles represent the area occupied by the resorcin[4]arene headgroup and the smaller circles that of the alkyl chains. The square indicates the distances of the connection points of the alkyl chains at the methine carbon of the resorcin[4]arene headgroup.

Chart 1
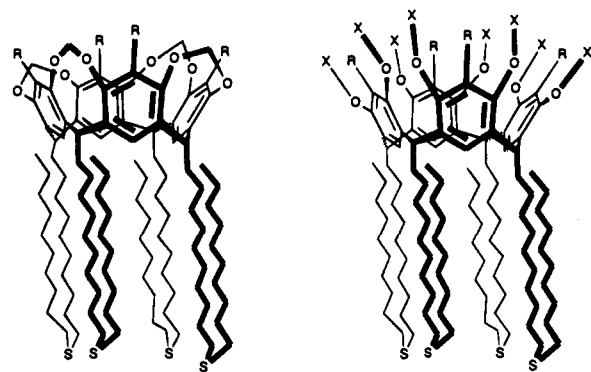
1a	R=H		2a	R=H	X=CH$_3$
1b	R=CH$_3$		2b	R=OCH$_3$	X=CH$_3$
			3a	R=H	X=C(O)CH$_3$
			3b	R=CH$_3$	X=C(O)CH$_3$
			3c	R=OC(O)CH$_3$	X=C(O)CH$_3$
			4	R=H	X=CH$_2$C(O)OCH$_3$
			5	R=H	X=CH$_2$CH$_2$F
			6	R=H	X=CH$_2$C(O)NH(CH$_2$)$_3$H
			7	R=H	X=H

experimental details of the synthesis will be published elsewhere.[25]

Monolayer Preparation. Monolayers of the resorcin[4]arene tetrasulfides 1a,b, 2a,b, 3a—c, 4, 5, and 7 were prepared from 1 mM solutions in ethanol/chloroform (7:3 v/v) and for the more polar octa(*N*-propylacetamide)tetrasulfide, 6, ethanol/chloroform (9:1 v/v) was used. Self-assembling to monolayers was achieved by keeping the adsorbate solution containing the gold substrate for 13 h at 60 °C and then slowly cooling it down to room temperature in 3 h. The substrates were subsequently rinsed with a large excess of dichloromethane to remove any physisorbed material. Remarkably, adsorption of the resorcin[4]arene tetrasulfides from solutions at room temperature yielded only submonolayers.

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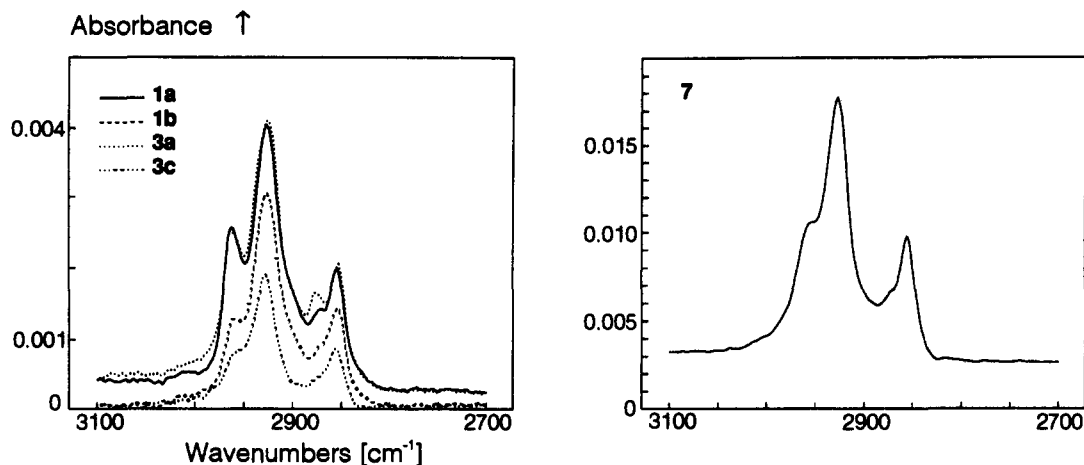
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Figure 2. The carbon—hydrogen stretch region of the PIERS spectra of the films prepared from resorcin[4]arene tetrasulfides on gold.

For comparison, self-assembled monolayers of 1-alkanethiols were prepared by immersing gold substrates in 1 mM solutions of the adsorbates in methanol for 16 h at room temperature. Likewise, self-assembled monolayers of di-*n*-decyl sulfide were prepared from 1 mM solutions in ethanol.

Monolayer Characterization

Polarized Infrared External Reflectance Spectroscopy.
Polarized infrared external reflection spectra (PIERS) of the films on top of the gold surface were recorded to obtain information about the orientation of the resorcin[4]arene tetrasulfides with respect to the surface. Band assignments of the carbon—hydrogen stretch vibrations have been based on previous studies on 1-alkanethiol monolayers on gold.[2]

All prepared films show strong carbon-hydrogen stretch vibrations. The asymmetric methylene stretch was found at $2925-2927$ cm^{-1}, $2-7$ cm^{-1} higher than in the reference KBr pellet spectra. Also the symmetric methylene stretch vibration was shifted from $2850-2853$ cm^{-1} (KBr pellet) to $2852-2856$ cm^{-1} on gold (Figure 2). These peak values are in excellent agreement with those reported for a di-*n*-dodecyl sulfide monolayer on gold.[7] For crystalline polyethylene, the $\nu_a(CH_2)$ mode is assigned at 2920 and the $\nu_s(CH_2)$ mode at 2850 cm^{-1}, and in the liquid state these peak values shift to 2928 and 2856 cm^{-1}, respectively.[26] Compared to these values, it is indicative that the prepared assemblies possess some gauche conformations in the alkyl chains. These gauche defects arise from the back-looping of the chains near the gold surface and the mismatch between the molecular structure of the resorcin[4]arene and the structure of the gold surface.

The weaker methyl stretch vibrations are difficult to observe for most of the monolayers, because these are overshadowed by the methylene stretching modes. Generally, the $\nu_a(ip)$ can be seen separately at $2958-2964$ cm^{-1}, and the $\nu_s(FR)$ at $2871-2877$ cm^{-1} appears as a small shoulder peak, but the $\nu_s(FR)$ occurring in the range $2935-2940$ cm^{-1} cannot be distinguised. As expected, the octaacetate **3a** monolayer shows much more intensive methyl stretching modes. However, these are not observed for the methyl-cavitand **1b** monolayer, because the asymmetric aromatic methyl stretch vibration overlaps with the $\nu_a(CH_2)$ mode.

The absorbance intensity of the $\nu_a(CH_2)$ mode is almost equal for the assemblies prepared from cavitand **1a**, methyl-cavitand **1b**, and octaacetate **3a**. The film prepared with the dodeca-
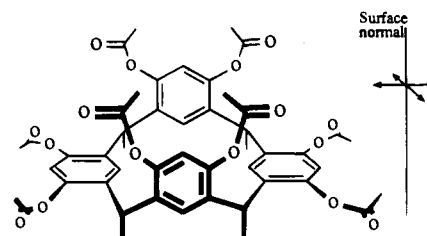

Figure 3. The possible structure of the headgroup of octaacetate **3a** as suggested by the absence of the carbonyl stretch vibration in the PIERS spectrum.

acetate tetrasulfide **3c**, however, shows intensities for all carbon—hydrogen stretch vibrations that are only half as strong as for the others. This indicates that the density of adsorbate molecules in this film is lower compared to the other films. The film prepared from the octol tetrasulfide **7** shows the opposite behavior. All carbon—hydrogen stretches are about four times more intensive than those of most of the other tetrasulfides, indicating that this octol adsorbate forms a multi-layered structure. Whether this structure is a bilayer or a multi-layer cannot be concluded from the infrared spectra alone, since the higher intensity can also be explained as partially originating from a less perpendicular orientation of the alkyl chains.

In the lower wavenumber region of the PIERS spectra ($2000-700$ cm^{-1}) several absorptions are observed which were also apparent in the KBr pellet reference spectra, such as the CH_2 scissors mode at 1460 cm^{-1} and carbon oxygen stretches, like the acetal stretch vibration of **1b** at 978 cm^{-1}. Films prepared from dodecaacetate tetrasulfide **3c** show the expected carbonyl stretching mode at 1790 cm^{-1}, which can be attributed to the four acetate groups at the 5, 11, 17, and 23 positions of the resorcin[4]arene. However, the carbonyl stretching mode which is visible near 1760 cm^{-1} in the KBr pellet spectrum, and which can be attributed to the eight acetate groups on the 4, 6, 10, 12, 16, 18, 22, and 24 positions, is absent in the PIERS spectrum of the monolayer. Also in the PIERS spectrum of the film of the octaacetate **3a** this carbonyl stretching mode is absent. An explanation for this observation may be that the transition dipole moments of the corresponding carbonyl stretch vibration are oriented parallel to the gold surface, as is depicted in Figure 3 for **3a**. This orientation of the octaacetate headgroups is in reasonable agreement with the orientation found in the solid state X-ray diffraction structure of a similar compound.[27]

X-ray Photoelectron Spectroscopy. X-ray photoelectron spectra of the films were recorded to determine the elemental

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Table 1. Elemental Composition of the Films, Measured at an Angle of 20° with Respect to the Surface Normal, Using Nonmonochromatic Mg Kα Radiation

adsorbate	%C	%O	%S	%Au	%rest
1a	48.4	4.3	2.9	44.5	
1b	53.9	9.9	1.5	34.7	Si
2a	51.2	4.4	2.3	42.1	Si
2b	50.7	7.9	1.6	39.7	Si
3a	44.3	5.2	2.2	48.3	
3b	45.7	6.1	1.9	46.3	Si
3c	52.4	7.7	2.6	37.2	
4	36.9	1.6	2.8	58.7	
6	47.9	6.0	2.9	40.8	N 2.4
7	45.3	6.6	2.8	58.7	

Si: small signals of oxidized silicon observed

Table 2. Measured Resonance Angles and Calculated Thickness of Uncovered Gold and Resorcin[4]arene Tetrasulfide Assemblies

adsorbate	external angle of resonance (deg), (±0.01)	thickness (Å), (±2)
uncovered gold	−25.47 (±0.05)	
1a	−25.06	20
1b	−24.91	28
2a	−25.03	22
2b	−24.98	24
3a	−25.07	20
3b	−25.10	18
3c	−25.04	21
7	−24.87	30

Table 3. Contact Angles of the Assemblies on Gold with Water (H$_2$O) and Hexadecane (HD) Droplets, Using the Captive Drop Method[a]
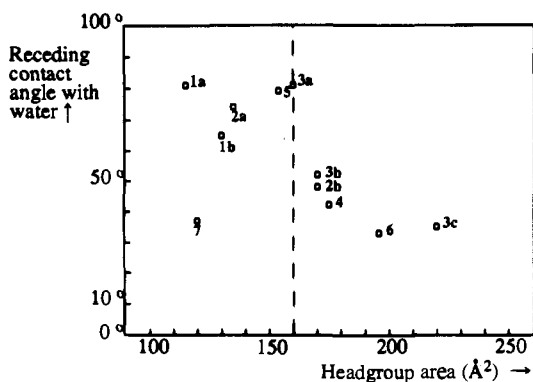
adsorbate	$\theta_a^{H_2O}$ (deg)	$\theta_r^{H_2O}$ (deg)	θ_a^{HD} (deg)	θ_r^{HD} (deg)
decanethiol	108 ± 2	91 ± 1	40 ± 2	19 ± 2
di-n-decyl sulfide	103 ± 2	85 ± 2	34 ± 2	<10
1a	105 ± 4	81 ± 2	26 ± 2	<10
1b	94 ± 2	59 ± 2	<10	<10
2a	102 ± 2	74 ± 2	25 ± 2	<10
2b	89 ± 2	46 ± 2	<10	<10
3a	99 ± 2	81 ± 3	12 ± 2	<10
3b	104 ± 2	51 ± 2	20 ± 2	<10
3c	83 ± 2	35 ± 2	<10	<10
4	95 ± 2	62 ± 2		
5	104 ± 2	79 ± 4		
6	84 ± 2	42 ± 3		
7	90 ± 2	37 ± 1	<10	<10
1a(8)	91 ± 2	54 ± 2		
1a(12)	92 ± 3	60 ± 2		
2a(8)	91 ± 2	64 ± 2		
2a(9)	89 ± 2	57 ± 4		
2a(11)	97 ± 3	66 ± 2		
2a(12)	88 ± 2	47 ± 2		

[a] The values are an average of at least four different measurements.

composition and to identify the species present in the assemblies. Reference spectra of an octadecanethiol and a di-n-decyl sulfide monolayer on gold were in good agreement with reported[3,7] spectra. The XPS spectra of the assemblies prepared from most resorcin[4]arene tetrasulfides (**1a,b**, **2a,b**, **3a−c**, **4**, and **7**) are very similar to the spectra of the reference monolayers, except that also the expected O1s signal at 532 eV was observed (Table 1). Furthermore, no other elements, like N, P, Cl, etc., were detected, indicating that the monolayers were not polluted and that chloroform[28] was not incorporated in the monolayer structure. The XPS spectrum of the film prepared from the dodecaacetate tetrasulfide **3c** has a C1s signal that shows a small shoulder at higher binding energy values (289 eV), originating from the carboxyl carbon atoms.[29]

The XPS spectrum of the film prepared from the octa(N-propylacetamide) **6** showed besides the gold, carbon, oxygen, and sulfur signals, also the N1s signal at 399 eV. The appearance of the nitrogen signal in this film and its absence in the assemblies prepared from the other adsorbates strongly support that the obtained signals originate from the resorcin[4]arene tetrasulfides. Therefore, the XPS spectra show that the prepared films consist of the resorcin[4]arene tetrasulfide adsorbates and do not comprise adventitiously adsorbed impurities.

Surface Plasmon Spectroscopy. Surface plasmon spectra were recorded to measure the thickness of the prepared films and thus to determine whether monolayers, submonolayers, or multilayers have been formed.

When a clean gold slide is covered with a 1-decanethiol monolayer, the external angle of resonance shifted 0.29 (±0.01)°. This corresponds to a calculated thickness for the 1-decanethiol monolayer of 14 Å, assuming a refractive index of the monolayer of 1.45. The error in this calculation is estimated to be 2 Å and is mainly due to the relative uncertainty of the refractive index of the assemblies and the exact angle of resonance for a clean gold slide. The measured thickness of 14 (±2) Å is in good agreement with earlier reported ellipsometrically determined thicknesses of 17 (±2) Å,[2] 12 (±3) Å,[3] and 15.6 (±1) Å.[4] For a di-n-decyl sulfide monolayer an angular shift of 0.25° was recorded, which corresponds to a thickness of 12 (±2) Å. This is in good agreement with the ellipsometrically determined value of 12 (±2) Å.[7] For most resorcin[4]arene tetrasulfides (**1a**, **2a,b**, and **3a−c**) angular shifts of 0.41−0.49° were found, corresponding to layer thicknesses of about 18−24 (±2) Å (see Table 2). These values are in good agreement with the expected thickness of 19−21 Å based

on CPK-models of a densely packed monolayer in which the alkyl chains are oriented perpendicular to the surface. These results point to the formation of highly organized monolayers of these tetrasulfides on top of the gold surface.

Remarkably, the angular shifts of the methyl-cavitand **1b** and the octol **7** point to significantly thicker films (ca. 29 Å). Since the headgroup of **7** contains eight hydroxyl groups, it is not unlikely that this adsorbate forms a bilayered structure by hydrogen-bonded head-to-head interactions. These interactions cannot occur with the methyl-cavitand **1b**, but this adsorbate has the largest rigid cavity in the series, and it is conceivable that the relatively large angular shift is due to the presence of a guest molecule which is complexed in the cavity under the measuring conditions. When, for instance, ethanol or acetone molecules are present in the cavities on top of the formed assembly, the high dielectric constant of these solvents will induce a large extra angular shift resulting in an apparent extra thickness of the monolayers.

Contact Angle Measurements. Information about the polarity and organization of the functionalities exposed by the assembly can be obtained from the wetting behavior of the monolayer films. All monolayers showed high advancing contact angles with water (83−105°), indicating that the outer interfaces are hydrophobic in nature (Table 3). Also the adsorbates having relatively polar methoxy, acetoxy, and hydroxy functionalities at the resorcin[4]arene headgroup (**2a,b**, **3a−c**, **4**, and **7**) exhibit hydrophobic outer interfaces. In order to create this water-repelling interface, the methoxy or acetoxy functionalities have to be oriented with their methyl groups toward the interface. The high advancing contact angle with

(28) Since the XPS spectra of the assemblies are studied in UHV, no signals from solvent molecules were expected. Chloroform can still be present in the assemblies at ambient pressure.

(29) The assemblies prepared from the other carboxyl containing tetrasulfides (**3a,b**, **4**, and **6**) did not show this shoulder signal because these assemblies contain relatively less carboxyl carbon atoms.

No.	R	X
1a	H	-CH$_2$-
1b	CH$_3$	-CH$_2$-
2a	H	CH$_3$
2b	OCH$_3$	CH$_3$
3a	H	Ac
3b	CH$_3$	Ac
3c	OAc	Ac
4	H	CH$_2$C(O)OCH$_3$
5	H	CH$_2$CH$_2$F
6	H	CH$_2$C(O)NH(CH$_2$)$_3$H
7	H	H

Figure 4. Dependency of the contact angle of water droplets on the headgroup-size of the resorcin[4]arene tetrasulfides.

water (90°) of the octol adsorbate **7** reveals that the hydroxyl groups in this film are not located near the interface, which is in accordance with the PIERS and SPS measurements.

The receding contact angles with water of the resorcin[4]-arene tetrasulfide films were lower (33−81°) than those of the reference adsorbates 1-decanethiol and di-*n*-decyl sulfide. Figure 4 shows that the receding contact angle for adsorbates with relatively small headgroups (**1a,b**, **2a**, **3a**, and **5**) is significantly higher than for adsorbates with large headgroups. Apparently, adsorbates with headgroups larger than the cross-sectional area of the eight alkyl chains underneath (160 Å^2) form less organized monolayers. This relation between headgroup size and monolayer quality is also apparent from capacitance measurements (*vide infra*).[30]

A clear exception is found for octol tetrasulfide **7**, which shows a low contact angle (37°), while the headgroup is only 140 Å^2. However, PIERS and SPS measurements already indicated that this adsorbate forms a disordered bilayer.

The octamethylate **2a** monolayer has a significant lower receding contact angle than monolayers of **1a** and **3a**. Since all three monolayers are well organized, the lower contact angle of **2a** is probably due to the larger flexibility of the headgroup of **2a**. Adsorbate **1a** has a rigid cavitand headgroup, and the octaacetate headgroup of **3a** is known to pseudo-rotate very slowly in solution, whereas octamethylate **2a** pseudo-rotates very fast in solution. Hence, the receding contact angles probably also reflect the mobility of the resorcin[4]arene headgroups of the monolayers.

The advancing contact angles with hexadecane of the films prepared with the resorcin[4]arenes were much lower (<10−26°) than those of the reference films. Apparently the hexadecane droplet has a much stronger interaction with the surface of the resorcin[4]arene tetrasulfide monolayers than with the

well-packed methyl interface of the reference films. This is not unlikely since at the outer interface of the resorcin[4]arene monolayers the aromatic headgroups are located.

The effect of the length of the terminal alkyl chains on the alkyl chain packing of the monolayers has been investigated using modifications of adsorbates **1a** and **2a** with terminal alkyl chains other than decyl. The terminal chain length of these adsorbates is given in parentheses, for example, **1a(8)** means the cavitand adsorbate with a terminal octyl chain. Figure 5 shows that all films prepared from these adsorbates have lower contact angles than those with the decyl chains. This implies that the best ordered monolayer structures are formed by adsorbates with intermediate and terminal alkyl chains of equal length. Electrochemical measurements confirm this conclusion (*vide infra*).

Electrochemical Measurements. Capacitance. The integrity of the monolayers toward electrolyte intrusion was determined from capacitive currents in indifferent electrolyte solution (0.1 M K$_2$SO$_4$) between −100 and +100 mV$_{MSE}$ at 100 mV·s^{-1}. The measured capacitance for a 1-decanethiolate monolayer (1.24 (±0.02) μF·cm^{-2}) agreed reasonably well with earlier reported values of 1.55,[2] 1.68,[4] and 1.95[31,32] μF·cm^{-2}. Monolayers of di-*n*-decyl sulfide were found to have a slightly larger capacitance (1.5 (±0.1) μF·cm^{-2}), indicating that ionic species permeate somewhat deeper into this monolayer. The resorcin[4]arene tetrasulfide assemblies **1a,b**, **2a**, **3a**, and **5** show a smaller capacitance (0.99 to 1.20 (±0.05) μF·cm^{-2}), indicating that these adsorbates form better insulating films (Table 4). This is not unexpected since these assemblies not only consist of a highly organized alkyl chain layer but also have an extended layer of resorcin[4]arene headgroups. Assemblies prepared from the other resorcin[4]arene tetrasulfides (**2b**, **3b,c**, **4**, **5**, and **7**) have significantly larger capacitances of 1.5−3.2 μF·cm^{-2}, indicating that these adsorbates form disordered monolayers (Table 4).

The part of the monolayer in which ionic species cannot permeate (effective thickness) was calculated from the measured capacitance and the relative permittivity of the monolayer.[2,33] Since relative permittivities of organized monolayers are unknown, these values are usually assumed to be in between 2.0 and 2.6.[2,33,34] Taking a value of 2.3, an effective thickness of 17−20 (±2) Å can be calculated for the resorcin[4]arene tetrasulfides (**1a,b**, **2a**, **3a**, and **5**) with a relatively small headgroup (cross-sectional area ≤ 160 Å^2) (Table 4 and Figure 6). This again indicates that these tetrasulfides form highly organized assemblies, in which the alkyl chains are more or less perpendicularly oriented to the surface. The tetrasulfides with larger resorcin[4]arene headgroups show significantly lower effective thicknesses of 7−14 (±2) Å, indicating that the electrolyte solution can permeate deeply into these layers. Apparently these adsorbates form disordered assemblies. This dependency of the quality of the monolayer on the size of the resorcin[4]arene headgroup is in agreement with the results obtained from the wettability experiments.

The effective thicknesses of monolayers of cavitand tetrasulfides with either terminal octyl **1a(8)** or dodecyl **1a(12)** chains

(30) In addition to the degree of organization, also the nature of the functionalities at the interface determines the contact angles and capacitance of the monolayers. Therefore headgroup size is not the only variable. The striking result is, however, that the adsorbates with the small headgroups form monolayers which show to be well organized, although their headgroup polarities vary significantly (*cf.* **2a** with **3a**), whereas increase of the headgroup without a large change of polarity appears to result in less ordered monolayers (cf. **2a** with **2b** and **3a** with **3b**).
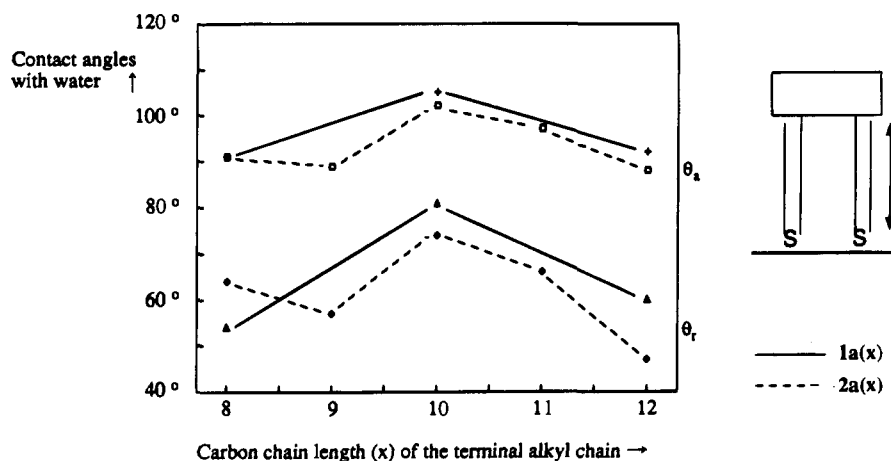
(31) Widrig, C. A.; Chung, C.; Porter, M. D. *J. Electroanal. Chem.* **1991**, *310*, 335−359.

(32) The measured capacitances are slightly smaller than those reported in literature, because massive disk gold electrodes are employed that have a significantly lower roughness than evaporated gold electrodes, which are used in the literature reports, see: Creager, S. E.; Hockett, L. A.; Rowe, G. K. *Langmuir* **1992**, *8*, 854−861.

(33) Miller, C.; Cuendet, P.; Grätzel, M. *J. Phys. Chem.* **1991**, *95*, 877−886.

(34) Sondag-Huethorst, J. A. M.; Fokkink, L. G. *J. Langmuir* **1992**, *8*, 2560−2566.

Figure 5. Dependency of the contact angle of water droplets on the terminal chain length of the resorcin[4]arene tetrasulfides **1a**(x) and **2a**(x). The number (x) denotes the number of carbon atoms in the terminal chain length.

Table 4. Measured Capacitances and Calculated Effective Thicknesses Using a Relative Permittivity of 2.3[a]

adsorbate	capacitance (μF·cm^{-2})	effective thickness (Å)
1a	1.14 ± 0.05	18 ± 2
1b	0.99 ± 0.05	20 ± 2
2a	1.13 ± 0.05	18 ± 2
2b	1.70 ± 0.05	12 ± 1.4
3a	1.17 ± 0.05	18 ± 2
3b	3.16 ± 0.05	7 ± 1
3c	2.25 ± 0.05	9 ± 1.1
4	1.5 ± 0.1	14 ± 4
5	1.2 ± 0.08	17 ± 3
6	2.9 ± 0.1	7 ± 4
7	2.00 ± 0.05	10 ± 1.2
1a(8)	1.35 ± 0.05	15 ± 2
1a(12)	1.50 ± 0.05	14 ± 2
2a(8)	1.36 ± 0.05	15 ± 2
2a(9)	1.02 ± 0.05	20 ± 2
2a(11)	1.08 ± 0.05	19 ± 2
2a(12)	1.02 ± 0.05	20 ± 2
octanethiol	1.55 ± 0.05	13 ± 1.5
decanethiol	1.24 ± 0.05	16 ± 2
dodecanethiol	1.21 ± 0.05	17 ± 2
octadecanethiol	0.80 ± 0.05	25 ± 2
di-n-decyl sulfide	1.5 ± 0.1	14 ± 4

[a] See ref 2.

is clearly smaller (15 and 14 Å, respectively) than that of the cavitand tetrasulfide with terminal decyl chains **1a** (18 Å). This again points to a decrease of monolayer organization when the length of the terminal chain is different from the intermediate chain. For the octamethylate tetrasulfide the sensitivity for variation of the terminal alkyl chain is lower; only the tetrasulfide **2a**(8) with terminal octyl chains shows a smaller effective thickness than the parent compound **2a**.

Heterogeneous Electron Transfer. By measuring the electrical current density between the gold electrode covered with a monolayer and redox active species in solution, the presence of defects in the monolayer structure can be detected.[35]

Cyclic voltammograms were recorded in 1 mM K$_3$Fe(CN)$_6$, 0.1 M K$_2$SO$_4$ electrolyte solutions. The voltammogram of a freshly cleaned gold electrode is depicted in Figure 7. Voltammograms recorded with gold electrodes covered with a monolayer of 1-octanethiol, 1-decanethiol, and 1-dodecanethiol were
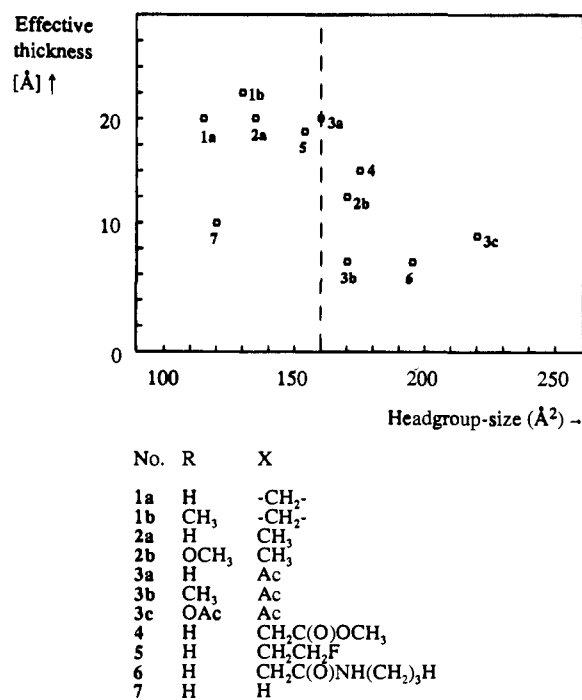
(35) (a) Rubinstein, I.; Sabatini, E.; Maoz, R.; Sagiv, J. *Proc. Electrochem. Soc.* **1986**, *86*, 175−180. (b) Sabatini, E.; Rubinstein, I.; Maoz, R.; Sagiv, J. *J. Electroanal. Chem.* **1987**, *219*, 365−371. (c) Sabatini, E.; Rubinstein, I. *J. Phys. Chem.* **1987**, *91*, 6663−6669. (d) Chailapakul, O.; Crooks, R. M. *Langmuir* **1993**, *9*, 884−888.
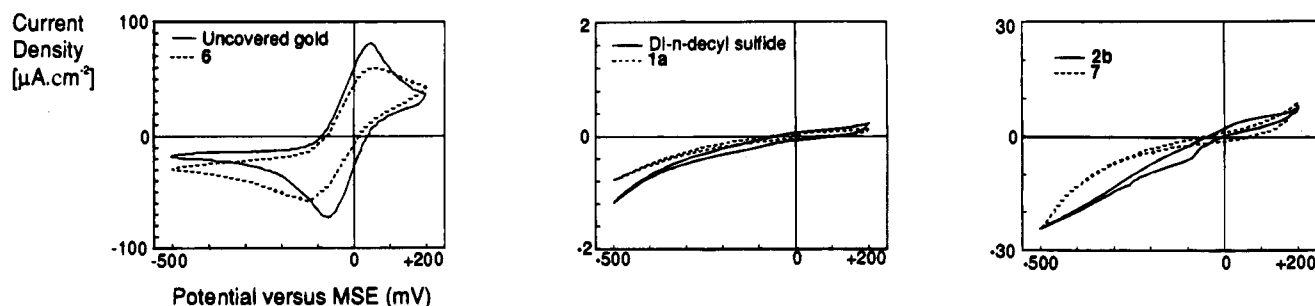

No.	R	X
1a	H	-CH$_2$-
1b	CH$_3$	-CH$_2$-
2a	H	CH$_3$
2b	OCH$_3$	CH$_3$
3a	H	Ac
3b	CH$_3$	Ac
3c	OAc	Ac
4	H	CH$_2$C(O)OCH$_3$
5	H	CH$_2$CH$_2$F
6	H	CH$_2$C(O)NH(CH$_2$)$_3$H
7	H	H

Figure 6. Calculated effective thicknesses of the tetrasulfide assemblies as a function of the cross-sectional area of the resorcin[4]arene headgroup of the tetrasulfide.

in good agreement with those reported in the literature.[2,4] The redox-waves of K$_3$Fe(CN)$_6$ near the formal potential were almost completely reduced; only at high overpotential some faradaic current was observed. At larger scanning windows than −500 to +200 mV$_{MSE}$ the current density increased with every cycle measured, indicating that the monolayers were destroyed. Therefore, all measurements were made within the potential limits given above.

The voltammograms recorded for monolayers of di-n-decyl sulfide, and the resorcin[4]arene tetrasulfide adsorbates **1a,b**, **2a**, **3a**, **3c**, and **5** were quite similar (Figure 7). Very low maximal cathodic current densities of 2−3 μA·cm^{-2} at −550 V$_{MSE}$ were observed. Clearly, these adsorbates form monolayers that possess as few defects as the 1-alkanethiols. However, resorcin[4]arenes **2b**, **3b**, **6**, and **7** block the heterogeneous electron transfer less well (Figure 8). The voltammogram of the octol **7** shows large current densities at large overpotential, pointing to shallow defects in the film structure. The resorcin[4]arene tetrasulfides **2b**, **3b**, and **6** also show the redox waves

Figure 7. Heterogeneous electron transfer between a 1 mM $K_3Fe(CN)_6$, 0.1 M K_2SO_4 electrolyte solution and a gold electrode, through monolayer assemblies of di-n-decylsulfide, **1a**, **2b**, **6**, and **4**. Note the difference in coordinate scale. The voltammograms of **1b**, **2a**, **3a**, **3c**, and **5** are quite similar to that of **1a**. The voltammogram of **3b** has a similar shape as that of **2b**.
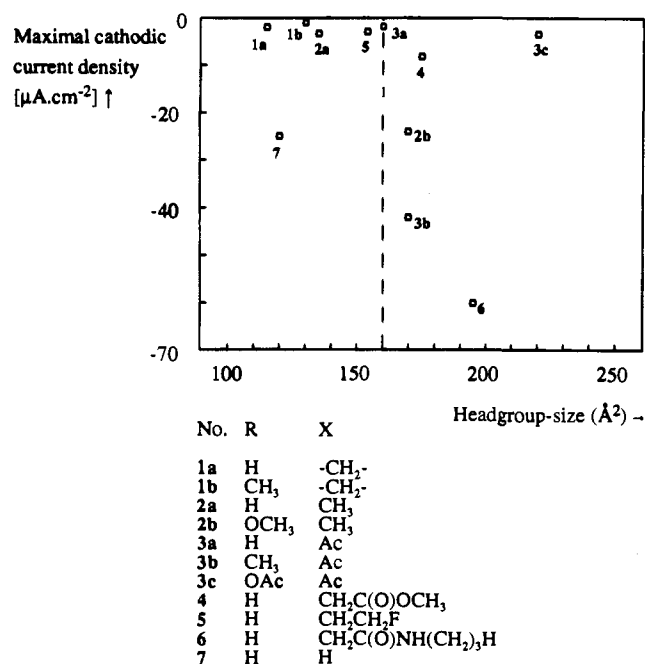

No.	R	X
1a	H	-CH$_2$-
1b	CH$_3$	-CH$_2$-
2a	H	CH$_3$
2b	OCH$_3$	CH$_3$
3a	H	Ac
3b	CH$_3$	Ac
3c	OAc	Ac
4	H	CH$_2$C(O)OCH$_3$
5	H	CH$_2$CH$_2$F
6	H	CH$_2$C(O)NH(CH$_2$)$_3$H
7	H	H

Figure 8. Measured maximal cathodic current densities of the tetrasulfide assemblies (-500 to $+200$ mV$_{MSE}$, 100 mV·s^{-1}) as a function of the cross-sectional area of the resorcin[4]arene headgroup of the tetrasulfide.
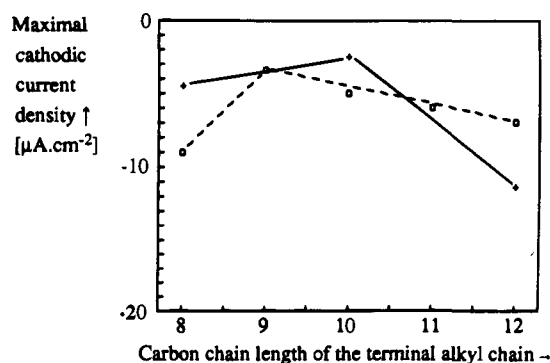

Figure 9. Effect of the variation of the terminal chain length of the tetrasulfides on the maximal cathodic current density. The straight line represents the monolayers of the **1a**(x) adsorbates and the dashed line those of the **2a**(x).

of $K_3Fe(CN)_6$ near the formal potential of $K_3Fe(CN)_6$, indicating that these assemblies also contain pinhole defects.

Variation of the terminal alkyl chain affects the blocking capability of the monolayers, as is shown in Figure 9. For the rigid cavitand, elongation of the terminal chain to dodecyl, **1a**-(**12**), significantly increases the maximum cathodic current

density. In contrast, for a monolayer of the octamethylate adsorbate, having a more flexible headgroup, shortening of the alkyl chain to octyl, **2a**(**8**), has the most deteriorating effect.

Temperature Dependency of Monolayer Formation. The adsorption behavior of the resorcin[4]arene tetrasulfides on gold surfaces was found to be complicated. The quality of the assemblies formed is strongly dependent on the temperature and the solvent used during the adsorption process. At room temperature, submonolayers are formed that block the heterogeneous electron transfer only moderately. For cavitand **1a** the cathodic current density was 10 μA·cm^{-2} at -500 mV$_{MSE}$ and SPS measurements indicated that the thickness of these layers was only $12-14$ (± 2) Å. Moreover, no sufficiently intense signals in the PIERS and XPS spectra could be obtained from these submonolayers, apparently because these submonolayers were not stable in the vacuum applied during these measurements.

However, the monolayer quality was considerably improved when the resorcin[4]arene tetrasulfides were adsorbed from a hot solution. The highest quality monolayer films were formed from 1 mM solutions of the adsorbates in ethanol/chloroform (7:3 v/v) for 13 h at $60-70$ °C and then cooling down during 3 h to room temperature. Monolayers of **1a** prepared by this procedure showed a maximum cathodic current density of only 2 μA·cm^{-2} at -500 mV$_{MSE}$. Adsorption from less polar solvents, like THF or chloroform, resulted in thinner monolayers with more defects, whereas solvents of higher polarity were not applicable because of the limited solubility of the resorcin[4]-arene tetrasulfides.

Thermal Stability. The stability of the monolayers was studied by exposing them to hot solvents for certain periods of time and evaluating the monolayer quality electrochemically. Monolayers of 1-decanethiol, di-n-decyl sulfide, and methyl-cavitand tetrasulfide **1b** which were exposed to boiling water retained their effective thickness in capacitance measurements. However, their ability to block the heterogeneous electron transfer was slightly decreased, indicating the formation of a small amount of pin-hole defects. In boiling methanol the effective thickness of all three films decreased only slightly, but the blocking ability of the layers dropped faster, indicating the formation of several defects. In tetrachloroethylene at 75 °C a fast decrease of the effective thickness to about half of the original value was found in the first 5 min of exposure of all three monolayers. After 40 min of exposure, the amount of adsorbate left on the surface was somewhat higher for **1b** (effective thickness 6 Å) than for the di-n-decyl sulfide (effective thickness 4 Å), whereas almost no 1-decanethiol was left.

Discussion

Assembly Structure. The resorcin[4]arene tetrasulfide adsorbates form self-assembled films on clean gold surfaces, as

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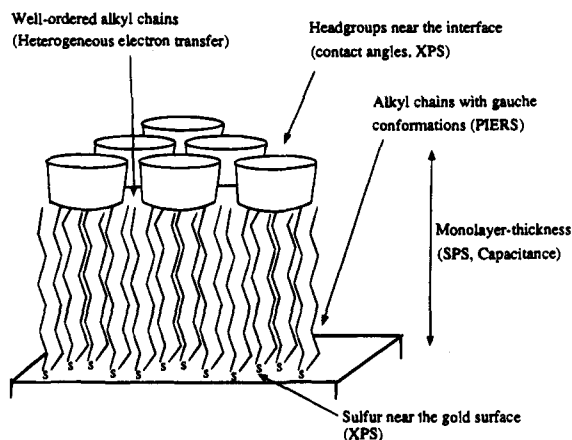
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Figure 10. Monolayer structure formed by the tetrasulfides with a small resorcin[4]arene headgroup.

was confirmed by PIERS and XPS measurements. The SPS and capacitance thickness measurements showed that these films are monolayers, and the contact angle measurements confirmed that the resorcin[4]arene headgroups are located near the outer interface of the monolayer. Only the octol tetrasulfide **7** forms a disordered bilayer. The results of the monolayer characterization are summarized in Figure 10. Three aspects of the monolayer structure will be discussed subsequently: the influence of the headgroup on the monolayer structure, the influence of the terminal chain length on the monolayer structure, and the alkyl chain organization and orientation in the monolayer.

Influence of the Resorcin[4]arene Headgroup. The quality of the monolayer depends to a large extent on the shape and size of the headgroup. Contact angle and electrochemical measurements showed that well-organized monolayers were obtained from adsorbates **1a,b**, **2a**, **3a**, and **5**. These adsorbates have a resorcin[4]arene headgroup with a cross-sectional area smaller than the total area occupied by the eight underlying alkyl chains ($8 \times 20 = 160$ Å^2). In this case the eight alkyl chains underneath the headgroup are allowed to form a densely packed structure. When the cross-sectional area of the headgroup exceeds the 160 Å^2 limit, as is the case of **2b**, **3b**, **4**, and **6**, the underlying alkyl chains cannot condense to a closely packed structure. Although this relation between headgroup size and monolayer organization is quite striking in this series of adsorbates, there are, of course, also other parameters, like polarity and hydrogen-bonding properties which influence the monolayer structure.[30] This is shown for the octol tetrasulfide **7**, which forms a disordered bilayer structure. Also the disordered structure found for the octa(N-propylacetamide) tetrasulfide **6** is probably not only caused by the large size of the headgroup but also by intermolecular hydrogen bond formation.

Dodecaacetate tetrasulfide **3c** has the largest headgroup and is thus expected to form the lowest quality monolayer. This is confirmed by the contact angle, capacitance, PIERS, and SPS measurements. However, an unpredicted blocking efficiency in the heterogeneous electron transfer to $Fe(CN)_6^{3-}$ is observed for this adsorbate. Although the structure of this assembly is not resolved, a possible explanation for this observation is that the acetate headgroups shield the surface by forming an ordered network of gearwheels above a disordered layer of alkyl chains.

The measurement results show that several functionalities can be introduced at the resorcin[4]arene headgroup without affecting the structure of the monolayer, provided the cross-sectional area of the headgroup does not exceed the limit imposed by the eight alkyl chains (160 Å^2). Exceptions are hydrogen-bonding functionalities, which cause the formation of disordered

bilayer structures in the case of octol **7**, and disordered mono- or multilayers in the case of octa(N-propylacetamide) **6**. Some precedents are known of organosulfur adsorbates with terminal hydrogen-bonding functionalities which form disordered assemblies. For example, Troughton et al.[7] reported that 12-thiatricosanoic acid forms a highly disordered monolayer, and Evans et al.[36] reported that a monolayer of 11-hydroxyundecane-1-thiol monolayer reorganized to a disordered monolayer. These assemblies buried their terminal functionalities deeply into the film in order to interact with each other.

Influence of the Terminal Chain Length. The quality of the monolayers is also influenced by the length of the alkyl chains of the tetrasulfides. Adsorbates with terminal chains smaller or larger than 10 carbon atoms form monolayers which are more wetted by water, more permeable for electrolyte solution, and have less blocking capability. Clearly adsorbates with both alkyl chains of the same length give the best ordered monolayers, although differences can be small for adsorbates having terminal alkyl chains of only one carbon atom less or more. Contact angle measurements were found to be more sensitive to detect these differences than the electrochemical measurements (Figures 5 and 9).

Electrochemical measurements indicate that adsorbate **2a**-**(12)** with the flexible octamethylate headgroup forms somewhat better monolayers than adsorbate **1a(12)**, having a rigid headgroup. In both assemblies the ends of the terminal alkyl chains have to compete with the headgroups for the available space, and it is not surprising to find that the flexible headgroup is better able to adopt to this requirement.

Alkyl Chain Organization and Orientation. Both SPS and capacitance thickness measurements indicate that in the well-organized monolayers the alkyl chains are oriented almost perpendicular to the surface. However, this is not the exclusive orientation, because intensive methylene stretch vibrations can be observed in the PIERS spectra. Furthermore, these spectra indicate that the alkyl chains have many gauche conformations. Since the alkyl chains in the resorcin[4]arene tetrasulfide monolayers cannot be regarded as completely all-trans rigid chains, calculation of a tilt angle would be meaningless. Based on the thickness measurements we may assume that the chains are generally perpendicularly oriented, but a large distribution of orientation angles is possible. These arise from three structural features, (i) the back-looping of the alkyl chains near the gold surface, (ii) the relatively short alkyl chain length, and (iii) the mismatch between the molecular structure of the four dialkyl sulfide chains and the overlayer structure of the sulfide atoms chemisorbed onto the gold surface.

Two examples of looped chain monolayers are known: 1,-32-dotriacontanedioic acid on silver[37] and di-n-dodecyl sulfide on gold.[7] According to the PIERS spectra the long chains of the former monolayer are mostly well-organized, whereas the shorter chains of the latter monolayer are disordered. Hence, the even shorter decyl chains in the tetrasulfide monolayers are probably too short to acquire a crystalline-like alkyl chain packing. The structural mismatch between the gold surface and the tetrasulfide structure adds extra strain to the alkyl chains. The resorcin[4]arene orients the four alkyl chains in a 5 Å square, whereas the sulfide atoms probably bind in the hollow sites formed by three gold atoms, which have a hexagonal symmetry. Despite this strain, the alkyl chain packing is very efficient in stabilizing the assembly and shielding the gold surface from the surroundings, as can be inferred from the

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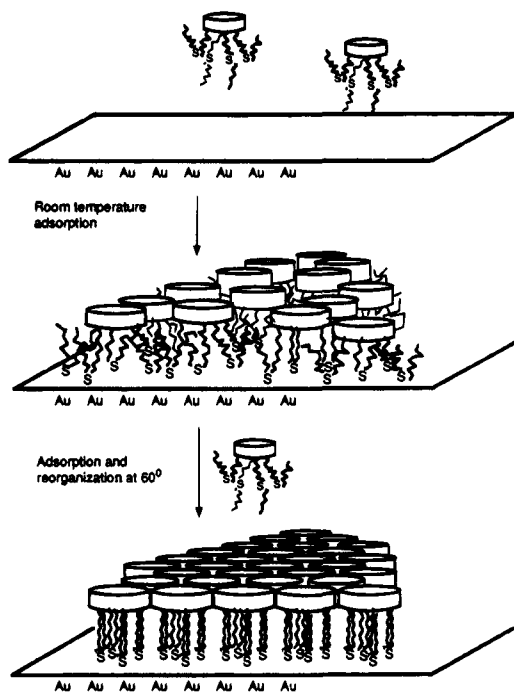(37) Allara, D. L.; Atre, S. V.; Elliger, C. A.; Snyder, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 1852–1854.

Monolayers of Resorcin[4]arene Tetrasulfides on Au

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Figure 11. Adsorption at room temperature yields a disordered submonolayer, whereas adsorption at 60 °C, followed by slow cooling, forms well-organized monolayers.

electrochemical measurements. Furthermore, the high degree of alkyl chain ordering is also displayed by the destructive effect caused by small structural changes in the adsorbate structure (i.e., the effect of size of the resorcin[4]arene headgroup and length of the terminal alkyl chain).

Adsorption Behavior of the Tetrasulfide Adsorbates. The resorcin[4]arene tetrasulfides adsorb spontaneously onto clean gold surfaces. At room temperature disordered submonolayers are formed. However, when the adsorption solution is heated, monolayers of much better quality are obtained. Furthermore, when the adsorption solution is chosen as polar as is permitted by the solubility of the adsorbates, monolayers are obtained in which the alkyl chains are well organized. Evidently, there is a thermal activation barrier in the self-organization process, which can be attributed to the strong sulfide-gold interaction. When the tetrasulfide adsorbs onto the surface, it will not necessarily bind with all alkyl chains in the most densely packed parallel orientation. At room temperature the loose packing of the four sulfur legs of the adsorbate will be largely fixed by the strong sulfide-gold interaction, and kinetically controlled disordered layers are formed. At higher temperatures, however, the sulfide–gold binding is reversible which allows the formation of the thermodynamically most favorable monolayer structure with all alkyl chains oriented in a parallel fashion (Figure 11). The heating of the gold substrate in the solution will also increase the desorption rate of adsorbed impurities and will enhance the mobility of the gold atoms on the surface.[38] Undoubtedly also these processes can contribute to the improvement of the quality of the monolayer.

Stability. The resorcin[4]arene tetrasulfide monolayers do not undergo any noticeable change when stored at ambient temperature in air, water, or polar organic solvents, in analogy with 1-alkanethiol monolayers. However, they are etched by aggressive chemicals, such as acid chlorides. The monolayers are stable in vacuum, as could be inferred from PIERS and XPS measurements, but repetitive vacuum-atmospheric pressure

changes deteriorate the monolayers. In solution, the resorcin-[4]arene tetrasulfides desorb from the surface at temperatures above 60 °C, which process is faster in apolar solvents than in polar solvents. The resorcin[4]arene tetrasulfide monolayers are stable in the same electrical potential region (-500 to $+200$ mV_{MSE}) as monolayers of di-*n*-decyl sulfide and 1-alkanethiols with relatively short carbon chain lengths (8–12); beyond these potential limits they desorb, unlike the longer 1-alkanethiols.

Conclusions

Resorcin[4]arene tetrasulfides assemble from dilute solutions at 60 °C on gold surfaces to monolayers. Tetrasulfide adsorbates with relatively small resorcin[4]arene headgroups (cross-sectional area ≤ 160 Å^2) form well-organized monolayers. These monolayers expose their headgroups to the outer interface and have a densely packed alkyl chain layer underneath these headgroups which completely passivates the gold surface. Many functionalities can be introduced to the headgroups of the adsorbates, but hydrogen-bonding and reactive functionalities are not compatible in the self-assembling process of the monolayer.

Experimental Section

Chemicals. The resorcin[4]arene adsorbates were synthesized according to the synthetic routes given schematically in the preliminary communication of this work.[21] Full experimental details have been submitted for publication elsewhere.[25] In all experiments, reagents and solvents of high purity (p.a.) were used. Organic solvents and potassium ferrocyanide were from Merck, and potassium sulfate and potassium ferricyanide were obtained from Janssen. High purity water was produced locally and stored in large glass barrels through which nitrogen was continuously bubbled.

Gold Substrates. Four different types of gold substrates were used. For the PIERS measurements gold was resistively evaporated (200 nm, 0.3 nm·s^{-1}, 10^{-6} mbar, room temperature) onto an oxygen-plasma cleaned glass slide (7.5 × 2.5 × 0.2 cm). The gold substrates used for the SPS measurements were also prepared by evaporation at room temperature on glass (2.6 × 2.0 × 0.05 cm). The thickness of the prepared gold layers was 46 ± 1 nm.[39] The gold substrates used for XPS and contact angle measurements were prepared by e-beam evaporation of 200 nm gold onto freshly cleaved mica (2.5 cm diameter discs that were cut with a laser-gun) in UHV ($<10^{-6}$ mbar) at a rate of 0.2 nm·s^{-1}. During the evaporation the substrates were heated to 225 °C[40] to give the gold atoms sufficient mobility to produce a reasonably flat surface, with large Au(111) terraces. The substrates were cooled down below 70 °C before the clock was back-filled with pure nitrogen. The substrates were taken from the holders and immediately immersed into the adsorbate solutions. Massive gold electrodes were prepared by pressing a grain of gold using a KBr pellet press to form a massive gold disk (diameter 1 cm, thickness 0.3 cm). One side of the disk was polished with several diamond powder suspensions, until an optically smooth surface was obtained. This electrode was boiled in sulfuric acid two times and rinsed three times with boiling high purity water. The electrodes were transferred to the electrochemical set-up with minimal delay. The cell was filled with 0.1 M perchloric acid, and nitrogen was bubbled through for 3 min. Cyclic voltammograms were recorded between -350 and $+1350$ mV_{MSE} until only the oxidation of the surface gold atoms and the reduction of this gold oxide film was observed.[41] Usually 2–4 h were required. Subsequently, the electrode was taken from the cell, rinsed with high purity water, shaken to loose the water film, and immersed with minimal delay into the adsorbate solution. In some cases, a water film persisted on the electrode surface, and a few minutes of ultrasonication in the immersion solution were

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(41) Dalbera, J. P.; Hinnen, C.; Rousseau, A. *J. Physique Colloq.* **1977**, *38*, C5-185.

very effective to remove this water film. Used electrodes were cleaned by repeating the cleaning procedure with boiling sulfuric acid, etc.

Monolayer Preparation. All glassware used to prepare monolayers was immersed in *piraña* at 70 °C for 1 h. Subsequently, the glassware was rinsed with large amounts of high purity water. The freshly prepared and cleaned gold substrates were immersed with minimal delay into 1 mM adsorbate solution. Octadecanethiol and di-*n*-decyl sulfide were dissolved in ethanol. The resorcin[4]arene tetrasulfides were dissolved in 10 mL of ethanol/chloroform (7:3 v/v), except for the more polar adsorbate **6**, which was dissolved in ethanol/chloroform (9:1 v/v). The adsorbate solution with the immersed gold electrode was heated in a 50 mL round bottom flask equipped with a balloon filled with argon at 60−65 °C for 13 h. Subsequently, the solutions were allowed to cool to room temperature in 3 h. The electrode was carefully taken from the solution and submerged into 10 mL of pure dichloromethane to remove any physisorbed material. Subsequently, the electrodes were rinsed with pure ethanol and water. Most electrodes were water-repelling and were obtained dry after rinsing. Others were gently dried with a slow stream of pure nitrogen.

Instrumentation. The PIERS spectra were recorded by Walter Scholdei at the Max-Planck-Institut für Polymerforschung in Mainz (F.R.G.) with a Nicolet 60SX FT-IR spectrometer equipped with a liquid-nitrogen-cooled MCT detector. The resolution was 4 cm^{-1}. The angle of incidence was 80° with respect to the surface normal. Monolayers were prepared on the outer side (2.0 × 2.5 cm) of the rectangular gold slide (7.5 × 2.5 cm) by immersing the substrate 2 cm in the solution. Subsequently, the part covered with the monolayer was masked and a fresh layer of 100 nm gold was resistively evaporated onto the uncovered gold part. A self-made translation stage was used to position the IR-beam alternatively on the uncovered and the covered parts of the gold substrate. The measurement cell was purged with a stream of argon for 3 min before the measurement started.

The XPS spectra were recorded by Marcel Simons at Akzo-Nobel Central Research, Dept CRL in Arnhem (NL) with a VG Escalab MkII spectrometer. Nonmonochromatic Mg Kα radiation was used. The take-off angle (relative to the surface normal) was 20°.

The surface plasmon spectra were recorded on a home-made optical set-up with a Kretschmann configuration, using a He-Ne laser (2 mW) and a quartz prism. The coefficient for the applied SPS set-up and gold substrates was calculated[42] to be 49.4 ± 0.2 Å/deg for a thin, homogeneous organic film with a refractive index of 1.45. The refractive index of 1.45 was chosen as an approximated value for the films,[3] because it is about the mean value of liquid and solid alkylthiols (hexadecanethiol (liquid) = 1.435, octadecanethiol (solid) = 1.465). The uncertainties given in the thicknesses are mainly due to the uncertainty in the refractive index; an increment of 0.05 in refractive index gives a decrease in layer thickness of ca. 1 Å.

The contact angle measurements were measured at Philips Research Laboratories Eindhoven with a home-made video-system which records the growth and shrinkage of solvent-droplets (1−2 μL) via a small syringe. At the moments of expansion and contraction a photograph was made, and the contact angle was determined from the photograph.[34]

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(42) Kooyman, R. P. H.; Kolkman, H.; van Gent, J.; Greve, J. *Anal. Chim. Acta* **1988**, *213*, 35.

All electrochemical measurement were performed in a selfmade electrochemical cell (volume 100 mL), which was equipped with a platinum counter electrode (area about 6 cm^2), a side tube to accommodate a mercury sulfate reference electrode (+0.61 V$_{SHE}$, Radiometer K601), and a screw cap to position a gold working electrode (geometrical area 0.44 cm^2). The applied potentiostat was a PAR 173, the clock frequency generator a Philips PM 5190 LF synthesizer, and the electrometer a PAR 178, and a Kipp BD 91 plotter was used. The electrochemical cell was cleaned with boiling sulfuric acid and subsequently rinsed with high purity water before use.

Capacitance Measurements. The coated electrodes were carefully placed in the electrochemical cell. Subsequently, the cell was filled with 50 mL of a 0.1 M K$_2$SO$_4$ electrolyte solution. Nitrogen was bubbled through the cell for 3 min. Cyclic voltammograms were measured at 0 V$_{MSE}$, between −100 and +100 mV, with a scan rate of 100 mV·s^{-1}. The measurement was started at 0 V$_{MSE}$ with a potential decrease. In most cases stable voltammograms were obtained; in these cases only the tenth cycle was measured. The capacitance values are not corrected for surface roughness of the gold electrodes. However, AFM measurements showed that the polished and cleaned surfaces had an extremely small roughness factor of 1.01.

Heterogeneous Electron Transfer Measurements. The electrolyte solution in the electrochemical cell was replaced by a 1 mM K$_3$Fe-(CN)$_6$, 0.1 M K$_2$SO$_4$ solution. Cyclic voltammograms were recorded between −500 and +200 mV$_{MSE}$, with a scan rate of 100 mV·s^{-1}, starting at 0 V$_{MSE}$ with a potential decrease. In the cases where a stable voltammogram was obtained, only the tenth cycle was measured.

Reproducibility. Every electrochemical and contact angle measurement was repeated three to five times. In every group of measurements, one or two measurements were not successful. In these cases much too low contact angles or much too large capacitances and maximal cathodic current densities were recorded. These measurements were rejected. This low reproduciblity is probably caused by the critical conditions for the monolayer preparation and the electrochemical cleaning of the gold surface. Measured contact angles, capacitances, and maximal cathodic current densities were averaged. The error in the contact angle was 1−4°, and the error in the capacitance was 0.02−0.1 μF·cm^{-2}. Because of possible differences in roughness between electrodes, the error which is minimally given was chosen to be 0.05 μF·cm^{-2}. The maximal cathodic current densities were more difficult to reproduce; errors of 0.5−8 μA·cm^{-2} were observed.