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Self-Assembled Monolayers of Discotic Liquid Crystalline Thioethers, Discoid Disulfides, and Thiols on Gold: Molecular Engineering of Ordered Surfaces

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Abstract: This paper describes a comparative study of self-assembled monolayers of different discoid molecules containing thioether, thiol, or disulfide substituents on gold. Discotic liquid crystalline hexaalkylthio-substituted triphenylenes and tricycloquinazolines, and derivatized triphenylenes with a single long ω-thioalkyl or ω-dithioalkyl substituent, are shown to self-assemble from dilute solution onto gold surfaces. Monolayers are formed owing to the known strong interaction of these functional groups with the gold. The characterization of the monolayers includes contact angle, polarized grazing incidence Fourier transform infrared spectroscopy (FTIR), quartz crystal microbalance (QCM), and atomic force microscopy (AFM) measurements. The discotic hexaalkyl thioethers assemble essentially face-on and without detectable lateral order onto the gold substrate. The alkyl chains do not lie flat on the gold but cover the aromatic cores. In contrast, the aromatic cores of the molecules in the monolayers of the discoid monosubstituted triphenylenes with a single thiol or disulfide substituent are shown to be in edge-on orientation. Furthermore, AFM reveals lateral order in these monolayers. Ordered areas, in the form of columns of edge-on oriented molecules, extend over length scales exceeding 100 nm. Domains of different orientation can be observed.

Introduction

Organic compounds have been discussed as potential candidates for application as components of electronic devices for over a decade.[1] The high degree of organization of the investigated systems, such as Langmuir−Blodgett (LB) films[2] or liquid crystals,[3] is a prerequisite for a good performance of the material. Recently, discotic liquid crystals have been discussed as new materials in photoconducting systems[4] and photovoltaic instruments.[5] In addition, quasi-one-dimensional semiconducting discotic liquid crystals have been reported.[6] In these applications the organic material is used as an active electronic component. The interface of the organic bulk material and the electrodes is therefore of crucial importance for optimized performance of the devices. However, little is known about the actual arrangement of the molecules near the interface.[7]

In order to obtain a better understanding of the behavior of discotic liquid crystalline or discoid[8] molecules at the metal−organic bulk interface, we have investigated a model system that consists of a first layer of molecules on a metal.

It is well established in the literature that thiols, disulfides, and thioethers interact strongly with gold covered substrates.[9] Highly ordered self-assembled monolayers (SAMs) are formed by spontaneous adsorption from solution. For our study we have chosen hexaalkylthio-substituted discotic liquid crystals and structurally similar hexaalkoxy-substituted discoid molecules containing one thiol or disulfide substituent (Scheme 1). Because of the high affinity of the sulfur to the gold we expect that the hexathioethers will assemble "face-on", whereas the thiol and the disulfides will assemble with "edge-on" orientation of the triphenylene cores (Figures 1 and 2).

The assembly of the compounds onto gold was monitored by quartz crystal microbalance (QCM) measurements; the final structure of the monolayers was investigated by contact angle, grazing incidence FTIR, and atomic force microscopy (AFM) measurements. Scanning probe microscopies, including scanning tunneling microscopy (STM) and AFM, are ideal tools for

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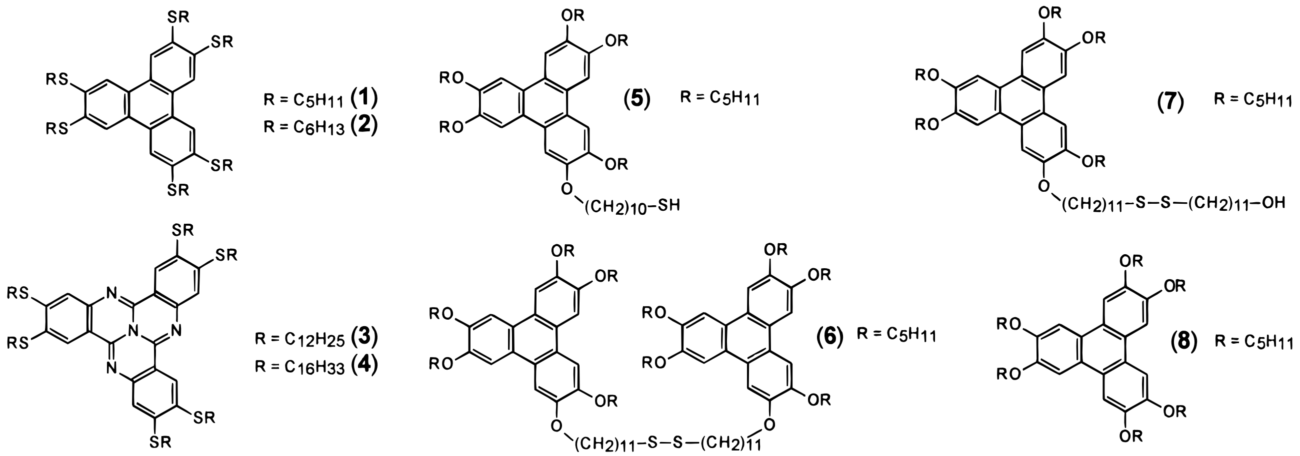
Scheme 1. Investigated Compounds with the Corresponding Numbers



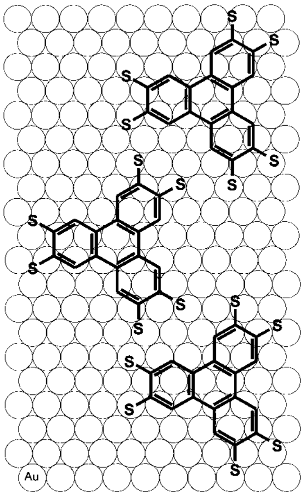


Figure 1. Three cores of hexaalkylthiotriphenylene adsorbed to a Au(111) surface in *face-on orientation*. The alkyl substituents were neglected in this schematic drawing. For the binding of the sulfur atoms, no specific positions on the gold lattice were chosen.

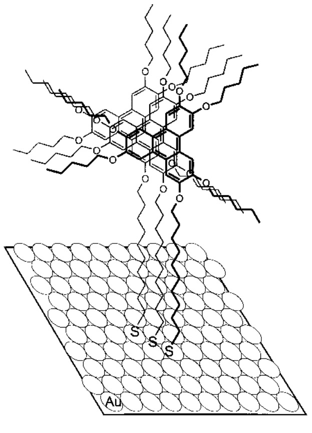


Figure 2. Three molecules of the hexaalkoxytriphenylene thiol derivative **5** adsorbed to a Au(111) surface in *edge-on orientation*. The alkyl substituents were only drawn schematically in all-trans conformation. For the binding of the sulfur atoms no specific positions on the gold lattice were chosen.

structural studies of ordered monolayers on Au(111).[10-12] SAMs have also been successfully imaged by AFM on sputtered gold.[13]

In this paper we show that the structural variations of the molecules allow us to control their orientation in the monolayers from edge-on to face-on orientation. Thus, we have a means of manipulating the surface properties of these and similar systems within a broad range. This engineering of ordered surfaces might provide a tool with which to study the influence of the interface on the desired properties in electronic devices which combine organic bulk material and metals.

Experimental Section

General Methods. The ^{1}H NMR spectra were recorded on a Bruker FT-NMR spectrometer AC 200 (200 MHz). Chemical shifts are reported in ppm (δ) downfield relative to tetramethylsilane. The field desorption (FD) mass spectrometry was done on a MAT 10 Finnegan field desorption mass spectrometer. The elemental analyses were performed by the Microanalysis Laboratories, University of Mainz.

Preparation of Substrates. For AFM measurements, gold(111), epitaxially grown on mica, was used as a substrate.[10] The surface exhibited mainly Au(111) crystal planes. In AFM scans, terraces of typically 500 nm size could be imaged. These were structured by single or multiple steps of the Au(111). In some samples these steps could be followed over length scales exceeding 2 μm. For all the other experiments, substrates were prepared by evaporation of an adhesive layer of 3 nm chromium followed by 120 nm of gold onto cleaned glass slides in a vacuum of 5×10^{-6} mbar in a Balzer evaporation machine.

Preparation of Monolayers. Monolayers were formed by immersing the gold substrates into dilute solution ($2 \text{ x } 10^{-4}$ M) of the corresponding compound in methylene chloride. After an incubation time of 15 h or longer, the samples were removed from the solution, rinsed carefully with pure solvent, and dried in a nitrogen stream. Measurements were performed immediately after the monolayer preparation.

Contact Angle Measurements. The advancing and receding contact angles θ_a and θ_r were measured with Millipore water as a probe liquid on a contact angle microscope (G-1, Krüss, Hamburg). A drop of a few microliters was placed on the monolayer. While the needle was still in contact with the drop, the volume of the drop was increased until the drop began to move.[9a] Readings were taken just before the drop moved over the surface at least three times on both sides of the drop at three different locations of the sample. These values were then

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averaged over at least three different monolayers. The hysteresis was calculated as $-\Delta \cos \theta$.

Polarized Fourier Transform Infrared Spectroscopy (FTIR) in Grazing Incidence. The IR data were obtained in measurements on a Nicolet 5DXC FTIR spectrometer which was equipped with a FT80 specular reflectance set-up (Spectratech Inc.). The chamber of the instrument was purged with dry air. The spectra were taken with a resolution of 4 cm^{-1} (2000 scans). Finally they were base-line corrected.[14] In the spectra, the absorption of CO$_2$ and sometimes water cannot be totally avoided. The observed absorbances were assigned to vibrations according to published FTIR studies on these or similar compounds.

Quartz Crystal Microbalance Measurements (QCM).[15] The QCM measurements were performed with quartz crystal substrates (9 MHz, AT-cut, $d = 8$ mm) covered with gold electrodes which were fabricated by Quartzkeramik GmbH (Stockdorf, Germany). A quartz crystal was mounted on a Teflon holder as described in ref 15b, ensuring that the front and the backside electrode were electronically independent. The crystal was driven by a home-made oscillator (15 V, 100 mA). The shape of the oscillation was controlled by an oscilloscope (HM604, Hameg GmbH, Frankfurt/M., Germany). The change in frequency was recorded by a universal counter (SC7201, Iwatsu Electronic Co. Ltd., Tokyo, Japan) which was connected to an IBM compatible computer. The QCM measurements presented here were performed at a temperature of 5 °C in a computer-controlled oven (30/40−180 DU, Weiss Umwelttechnik GmbH, Lindenstruth, Germany). After the equilibration of the quartz crystal in pure methylene chloride, the corresponding compound, dissolved in 250 μL of methylene chloride, was injected with a syringe through a Teflon tubing into the cell. The resulting concentration in the cell was always 2×10^{-4} M.

Atomic Force Microscopy (AFM). The AFM measurements were performed on a Nanoscope III AFM (Digital Instruments, Santa Barbara, CA) utilizing the liquid cell filled with ethanol. Silicon nitride cantilevers (Olympus Tokyo, Japan; spring constant: 0.09 N/m) were used for the investigations which were done in contact mode. All the images shown represent raw data which was plane-fitted. The average distance of the observed features was calculated from cross-sectional plots which were laid perpendicular to the direction of the rows.

Synthesis. Hexapentylthiotriphenylene (**1**), hexahexylthiotriphenylene (**2**), hexadodecylthiotricycloquinazoline (**3**), and hexahexadecylthiotricycloquinazoline (**4**) were synthesized according to published procedures.[16,17] The analytical data and the phase transitions as observed by differential scanning calorimetry (DSC) indicated pure compounds.

1. Synthesis of 2-(10-Mercaptodecyloxy)-3,6,7,10,11-pentapentyloxytriphenylene (5). 1.1. 2-(10-Thiosulfatodecyloxy)-3,6,7,10,11-pentapentyloxytriphenylene (Bunte Salt). 2-(10-Bromodecyloxy)-3,6,7,10,11-pentapentyloxytriphenylene[18] (1.0 g, 1.1 mmol) was dissolved in 20 mL of ethanol. While the solution was refluxed, 0.55 g (2.2 mmol) of sodium thiosulfate pentahydrate in 4 mL of water was added through a funnel. The mixture was further refluxed for 15 h. The crude product that precipitated upon cooling was washed with water and purified by flash chromatography on silica using dichloromethane/methanol (10:1) as an eluent. Yield: 0.81 g (78%).

1.2. 2-(10-Mercaptodecyloxy)-3,6,7,10,11-pentapentyloxytriphenylene. A mixture of toluene (15 mL) and 1 M hydrochloric acid (15 mL) was degassed with nitrogene. 2-(10-Thiosulfatodecyloxy)-3,6,7,-10,11-pentapentyloxytriphenylene (0.75 g, 0.79 mmol) was added and the mixture was refluxed for 1.5 h. The aqueous phase was separated and washed with toluene. The combined phases were evaporated to dryness in vacuo. The crude product was purified by flash chromatography using petroleum ether/ethyl acetate (1:1) as an eluent: yield, 0.47 g (70%); ^{1}H NMR (CDCl$_3$, 200 MHz) δ [ppm] 0.96 (t, 15 H, **CH$_3$**), 1.2−1.7 (m, 35 H, **CH$_2$** aliphatic, **SH**), 1.8−2.0 (m, 12 H, **CH$_2$**−CH$_2$−O), 2.50 (dt, 2 H, **CH$_2$**−SH), 4.25 (t, 12 H, **CH$_2$**−O), 7.82 (s, 6 H, H aromatic); mass (FD), $m/z = 846.8$ (M$^+$). Anal. Calcd for C$_{53}$H$_{82}$O$_6$S, (847.31 g/mol): C, 75.13; H, 9.76; O, 11.33; S, 3.78. Found: C, 75.25; H, 9.92; S, 3.90.

Table 1. Results of Contact Angle Measurements[a]

monolayer of compound	advancing contact angle, θ_a, deg	receding contact angle, θ_r, deg	hysteresis $-\Delta \cos \theta$
1	93	76	0.294
2	93	77	0.277
3	102	90	0.208
4	104	94	0.172
5	97	90	0.122
6	97	88	0.157
7	78	57	0.337

[a] The measurements were done with Millipore water as a probe liquid following the dynamic method as described by Ulman.[9a]

2. Synthesis of 2-[11-(1-Hydroxyundecyl)-11′-(undecyloxy)-dithio]-3,6,7,10,11-pentapentyloxytriphenylene (Compound 7). Bis-(11,11′-undecanol)disulfide[19] [604 mg (1.48 mmol)] was reacted with 200 mg (0.297 mmol) of 2-(hydroxy)-3,6,7,10,11-pentapentyloxytriphenylene,[20] 420 mg of triphenylphosphine, and 280 mg of diethylazodicarboxylate in 25 mL of dry diethyl ether at 0 °C. After stirring for 3 days at room temperature, the solvent was evaporated, and the residue was purified by flash chromatography on silica (eluent = petroleum ether/ethyl acetate). Final purification by preparative thin layer chromatography yielded a colorless waxy solid: yield, 192 mg (61%): ^{1}H NMR (CDCl$_3$, 200 MHz) δ 0.97 (t, 15 H, **CH$_3$**), 1.5 (m, 55 H, **CH$_2$** aliphatic), 1.94 (m, 12 H, O−CH$_2$−**CH$_2$**), 2.67 (t, 4 H, S−**CH$_2$**), 3.62 (m, 2 H, **CH$_2$**−OH), 4.22 (t, 12 H, O−**CH$_2$**), 7.83 (s, 6 H, H aromatic); mass (FD), $m/z = 1063$ (M$^+$). Anal. Calcd for C$_{65}$H$_{106}$O$_7$S$_2$ (1063.70 g/mol): C, 73.40; H, 10.04; O, 10.53; S, 6.03. Found: C, 73.26; H, 10.26; S, 6.30.

3. Synthesis of Bis(2-(11-thioundecyloxy)-3,6,7,10,11-pentapentyloxytriphenylene) (6). The compound was obtained from the reaction 2 (compound **7**) and subsequent flash-chromatography as a colorless waxy solid: yield, 54 mg (21%); ^{1}H NMR (CDCl$_3$, 200 MHz) δ 0.96 (t, 30 H, **CH$_3$**), 1.5 (m, 72 H, **CH$_2$** aliphatic), 1.94 (m, 24 H, O−CH$_2$−**CH$_2$**), 2.66 (t, 4 H, S−**CH$_2$**), 4.22 (t, 24 H, O−**CH$_2$**), 7.82 (s, 12 H, H aromatic); mass (FD), $m/z = 1720$ (M$^+$), 860 (M^{2+}). Anal. Calcd for C$_{108}$H$_{166}$O$_{12}$S$_2$ (1720.65 g/mol): C, 75.39; H, 9.72; O, 11.16; S, 3.73. Found: C, 75.25; H, 9.85; S, 3.92.

Results and Discussion

Contact Angle Measurements. We observed reproducible advancing and receding contact angles for monolayers of both discotic and discoid molecules. For monolayers of the compounds **1**−**4** a dependence of the advancing contact angle on the length of the alkyl substituents was observed (Table 1). With increasing chain length the surface became more hydrophobic and the hysteresis decreased.[9a] The alkyl chains of increasing chain length are able to shield the high energy surface of the gold more effectively than short alkyl chains.

The discoid compounds **5** and **6** formed monolayers which were less hydrophobic than the monolayers of the hexathioethers **3** and **4**. The hysteresis was reduced (Table 1). The introduction of a hydroxy-terminated moiety near the surface by assembling the mixed disulfide **7** considerably lowered the contact angles.

It is noticeable that triphenylene derivatives without any sulfur containing functional groups also adsorb onto gold. The contact angles of these layers are almost comparable to those of the

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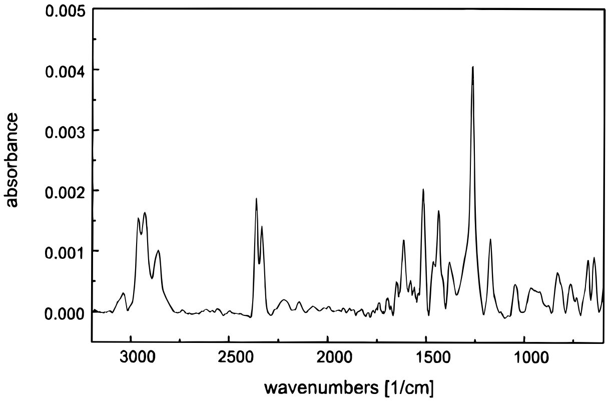

Figure 3. FTIR spectrum of a SAM of disulfide **6** on gold.

Table 2. Observed Absorptions and Corresponding Band Assignment of Vibrations in the FTIR Spectrum of SAM of Disulfide **6**[a]

$1/\lambda$ (cm^{-1})	assignment[22a]
3032	CH aromatic stretching vibration
2963	CH_3 asymmetric stretching vibration
2927	CH_2 antisymmetric stretching vibration
2866	CH_2 symmetric stretching vibration
2350	CO_2
1617	C−C aromatic stretching vibration
1520	C−C aromatic in-plane deformation
1438	C−C aromatic in-plane deformation
1387	C−H bending mode
1267	benzene-O stretching vibration
1174	C−O−C asymmetric stretching vibration
1043	C−O−C symmetric stretching vibration
831	CH aromatic out-of-plane vibration

[a] The spectrum is shown in Figure 3. SAMs of compound **5** show the same absorptions.

hexaalkylthiotriphenylenes. However, the layers of the hexaalkoxy ethers like compound **8** on gold are much weaker bound to the surface as the thioethers. This can be demonstrated in a replacement experiment with octadecanethiol (10^{-3} M solution in methylene chloride). The layer of hexaalkoxytriphenylene on gold was replaced almost completely in less than 40 min. By FTIR, the characteristic C−H stretching vibrations for octadecanethiol could be observed, indicating a crystalline packing.[9a] In addition, the contact angles are equal to those of freshly prepared monolayers of octadecanethiol on gold. In contrast, molecules in the monolayers of hexaalkylthiotriphenylenes and hexaalkylthiotricycloquinazolines were replaced more slowly under the same experimental conditions. Even after more than 24 h at room temperature no well ordered octadecanethiol monolayer could be obtained. The peak positions of the C-H stretching vibrations in the FTIR spectra indicated no crystalline order of the octadecanethiol.

The results of the wetting studies indicate that the alkyl chains of the discotic thioethers are located at or near the monolayer surface. Furthermore, owing to the shorter alkyl substituents thiol **5** and disulfide **6** form less hydrophobic SAMs than the thioethers **3** and **4**.[21]

Polarized Grazing Incidence FTIR Spectroscopy. In Figure 3 the FTIR spectrum of a SAM of the disulfide **6** is shown. Almost all the vibrations that could be detected in the isotropic samples were detected in the SAMs. The observed absorptions are listed in Table 2. The absorbances were assigned to vibrations according to published FTIR studies of these or similar compounds.[22] Owing to the selection rules for grazing incidence spectroscopy on metal surfaces, only vibrations with a component of the dipole transition moment perpendicular to the surface can be detected. Thus, FTIR allows one to study the composition and the orientation of molecules in self-assembled monolayers and thin films on metals.[9a,23]

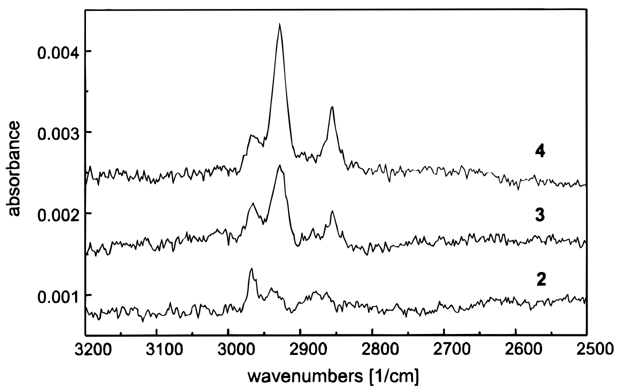

Figure 4. Section of the FTIR spectra of SAMs of compounds **2**, **3**, and **4** on gold showing the C−H stretching vibrations. The absorption of the methyl groups is almost constant, whereas the absorptions of the C−H stretching vibrations of the methylene groups increase with increasing chain length of the alkyl substituents.

Table 3. Observed IR Absorptions and Corresponding Band Assignment of Vibrations of SAMs of Thioethers **2**−**4**[a]

assignment	FTIR of **2**, $1/\lambda$ (cm^{-1})	FTIR of **3**, $1/\lambda$ (cm^{-1})	FTIR of **4**, $1/\lambda$ (cm^{-1})
CH_3 asymmetric stretching vibration	2968	2965	2968
CH_2 asymmetric stretching vibration	2934	2928	2927
CH_3 symmetric stretching vibration	2880	2882	2883
CH_2 symmetric stretching vibration	2859	2855	2855

[a] The FTIR spectra are shown in Figure 4.

Monolayers of thiol **5** and the corresponding disulfide **6** have identical spectra. This indicates that the aromatic triphenylene cores of the molecules in SAMs of **5** and **6** are oriented identically. In the spectra of the mixed disulfide **7**, we also found evidence for a comparable orientation.

For the SAMs of the discotic thioethers **1**−**4** only the C−H stretching vibrations could be detected (Figure 4). From the position of the maxima of absorption of the C−H stretching vibrations, any order of the alkyl substituents comparable to *n*-alkylthiol monolayers on gold can be excluded (see Table 3). The intensity of the absorbance of the C−H stretching vibrations of the methylene groups obviously scales with the length of the alkyl chain. This is in accordance with the trend of increasing hydrophobicity in the contact angle measurements. Hence, the alkyl chains are located near the monolayer−air interface in a disordered way. Other peaks that are very pronounced in the KBr spectra are not observed. The overall intensity is also quite low compared to the spectra of the ω-thioalkyl-substituted triphenylenes.

These observations indicate a totally different orientation of the thioethers compared to the discoid molecules. As the vibrations observed in the isotropic samples all have a major component along the plane of the aromatic core, our FTIR data

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Table 4. Idealized Estimation of the Expected Mass Changes in the QCM Measurements for the Adsorption of Monolayers of **2**, **3**, and **5** Based on the *Measured* Frequency Change of **5**[a]

compound, orientation	intercolumnar spacing (in hexagonal mesophase), Å	surface requirement A, Å^2	molecular mass M, g/mol	M/A [g/(mol Å^2)]	expected frequency change,[b] Hz
2, face-on	21.74 (ref 27)	371	926	2.5	−7
2, edge-on	21.74 (ref 27)	78	926	11.9	−32
3, face-on	29 (ref 17)	660	1523	2.3	−6
3, edge-on	29 (ref 17)	104	1523	14.6	−39
5, face-on	21 (AFM data)	371	847	2.3	−6
5, edge-on	21 (AFM data)	76	847	11.1	−30 (*measured*)

[a] The surface requirements were estimated from the reported intercolumnar distances and intracolumnar spacings of the materials in their hexagonal liquid crystalline mesophases. For face-on orientation a circle was assumed, and for edge-on orientation a rectangle respectively. [b] The expected frequency change was calculated based on the *measured* frequency change of **5**. In SAMs of **5** the aromatic cores are proven to be oriented edge-on by our FTIR and AFM results.

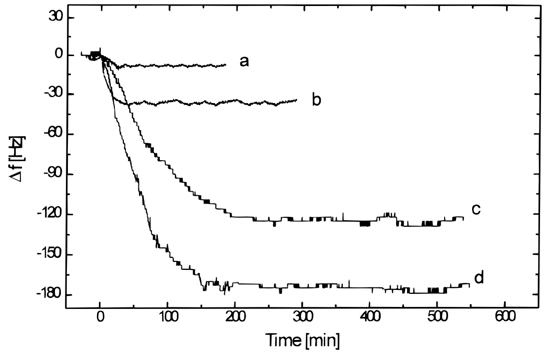

Figure 5. Response of the QCM (a) after injection of compound **8**, (b) the thiol **5**, (c) the hexaalkylthiotriphenylene **2**, and (d) the hexaalkylthiotricycloquinazoline **3**.

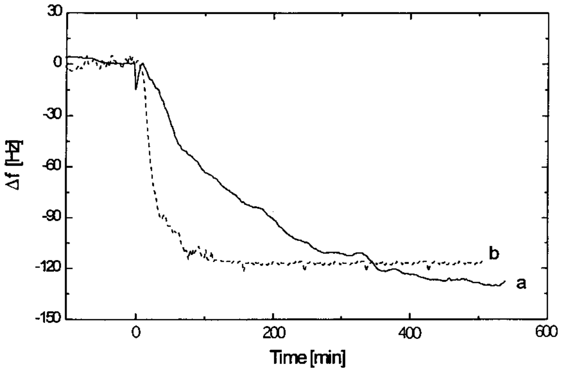

Figure 6. The exposure of the gold-covered QCM quartz crystal to thioether **2** results in trace (a). After careful rinsing of the substrate it was placed in pure solvent and equilibrated. The subsequent injection of compound **2** results in trace (b). A change in frequency difference as well as a different profile of the response were observed.

indicate an edge-on orientation of the ω-thioalkyl-substituted triphenylenes **5**−**7** and a face-on orientation of the thioethers **1**−**4**.

Quartz Crystal Microbalance (QCM) Measurements. We used the QCM in a semiquantitative way to monitor the assembly of the investigated compounds onto gold. In general, the QCM measurements are suitable for monitoring the kinetics of adsorption as well as for calculating the adsorbed mass on a gold covered quartz. The adsorbed mass can be calculated from the change of the resonance frequency of the quartz.[24] QCM data on the self-assembly of organosulfur compounds to gold have been reported in the literature before.[25] In addition, fullerenes were shown to self-assemble onto amine modified gold electrodes by Caldwell et al.[26] We estimated the expected mass changes for the adsorption of monolayers of **2** and **3** (and **5)** for the two limiting orientations based on the measured frequency change of **5**. The frequency change for **5** was measured to be 30 Hz. The results obtained from the other techniques employed in this study (FTIR and AFM) indicate an edge-on orientation of **5**. The surface requirements were estimated based on the reported intercolumnar and intracolumnar distances of the materials in their hexagonal liquid crystalline mesophases.[17,27] The results of this idealized estimation can be found in Table 4. We would expect only small changes for the adsorption of SAMs of **2** and **3** in face-on orientation.

In Figure 5 the changes of the resonance frequency of the quartz after injection of the corresponding compound (plotted as a function of time), are summarized. The hexaalkoxytriphenylene **8** was chosen as a blank in order to reveal the effect of changes of the density and viscosity of the solution upon addition of a structurally similar compound. For compound **8** a small decrease of the resonance frequency is observed.

In contrast, the addition of the thiol **5** leads to a rather fast response of the quartz, but only a small change of the resonance frequency. The net mass transfer to the gold covered electrode is complete after less than 1 h.

The response to the addition of the thioethers **2** and **3** is slower, and it takes longer until the equilibrium is reached. The changes of resonance frequency are large compared to the thiol **5**. They are also far too large for an adsorption of a monolayer in (a hypothetical) edge-on orientation.

Thermal drift or other artifacts of the instrument can be excluded because all compounds reach an equilibrium. The rather big frequency changes for compounds **2** and **3** indicate that much more mass is adsorbed than one would expect for a monolayer. An initial multilayer formation has been reported in literature for the self-assembly of long-chain *n*-alkyl thiols onto gold from solutions in acetonitrile.[25] The interaction of the alkyl chains of a first layer of molecules with further molecules has also been described in ref 7.

The formation of multiple physisorbed layers in QCM experiments can be demonstrated by adsorbing further material on a carefully rinsed quartz which is only covered with a monolayer of **2**. Figure 6 shows the corresponding plot of frequency versus time. Not only is the observed frequency change smaller for the carefully rinsed sample, but also the profile of the curve is different. This can be explained by the different surface of the gold electrode. The untreated gold surface is essentially clean, whereas the sample which is rinsed after the first assembly is covered by a SAM of molecules of

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(24) See, e.g.: Buttry, D. A. In *Electroanalytical Chemistry. A Series of Advances*; Bard, A. J., Ed.; Marcel-Dekker: New York, 1991; Vol. 17, pp 1−85.

(25) Schneider, T. W.; Buttry, D. A. *J. Am. Chem. Soc.* **1993**, *115*, 12391−12397.

(26) Caldwell, W. B.; Chen, K.; Mirkin, C. A.; Babinec, S. J. *Langmuir* **1993**, *9*, 1945−1947.

(27) Idziak, S. H. J.; Heiney, P. A.; McCauley, J. P., Jr.; Carroll, P.; Smith, A. B., III *Mol. Cryst. Liq. Cryst.* **1993**, *237*, 271−275 and references therein.

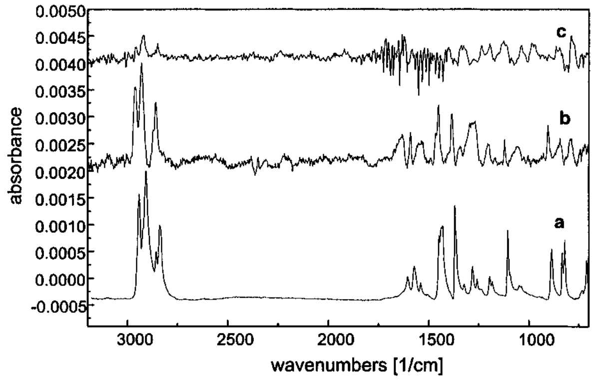

Figure 7. (a) Transmission FTIR spectrum (KBr) of compound **2**, (b) polarized grazing incidence FTIR spectra of nonrinsed sample of **2** on gold, and (c) polarized grazing incidence FTIR spectra of subsequently rinsed sample of **2** on gold. The spectra of the thin films on gold (b, c) are shown in the scale which is shown on the ordinate, the transmission FTIR (a) was reduced in size. For details see the Discussion in the text.

compound **2**. The observed difference in the frequency change corresponds roughly to the adsorbed mass of the monolayer. The order of magnitude matches quite well with the expected frequency change for a face-on orientation of the molecules (Table 4).

By means of FTIR we can also prove that the formation of disordered multiple physisorbed layers is characteristic of the adsorption process of these thioethers under these experimental conditions (*in situ*, no rinsing). On carefully rinsed substrates only a tightly bound layer remains chemisorbed. In Figure 7 the FTIR spectra for KBr pellet (isotropic sample), nonrinsed, and subsequently rinsed samples are plotted. It should be mentioned that immediate rinsing is necessary in order to obtain monolayers that are free of residual physisorbed material. However, most of the peaks shrink or disappear upon rinsing.

Thus, in solution, disordered multiple physisorbed layers are adsorbed loosely to the tightly bound initial monolayer of the liquid crystal. The additional material can be removed by immediately carefully rinsing the sample. The kinetics of the adsorption of the first layer cannot be detected directly by QCM owing to the in situ formation of these multiple layers.

Atomic Force Microscopy (AFM). For AFM measurements on SAMs, the imaging in a liquid is necessary in order to reduce the forces between tip and sample, and thus to avoid tip-induced structural changes in the SAMs. The AFM experiments in this study were performed in ethanol on monolayers of compounds **2** and **5** assembled onto Au(111). The applied force had to be kept low, typically 0.1 nN.

Monolayers of compound **2** did not show any detectable order on the molecular scale by means of AFM. We also carried out STM measurements with SAMs of the discotic liquid crystals **2**−**4** on Au(111). Again no ordered structures could be imaged.[28] Based on structural considerations, it is very unlikely that the cores of the molecules form a laterally highly ordered layer because the main driving force in SAMs, like those of octadecanethiol, is the crystallization of the alkyl chains. Furthermore, the six sulfur atoms of the thioether bonds of each molecule are fixed to the aromatic core. Assuming that all six sulfur atoms bind to the gold, it becomes impossible to generate a closely packed lattice of the cores when a preferred binding site for each sulfur is chosen on the Au(111) lattice. In addition, the long, disordered alkyl chains, especially for the tricycloquinazolines, might prevent the imaging of small ordered aggregates of a few molecules.

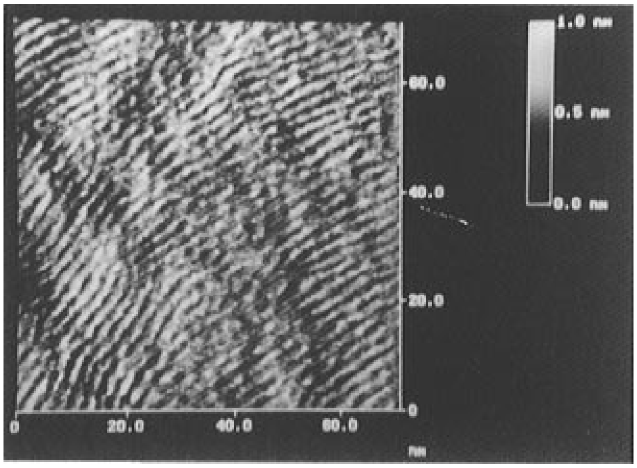

Figure 8. AFM image of a SAM of thiol **5** imaged on Au(111) in ethanol.

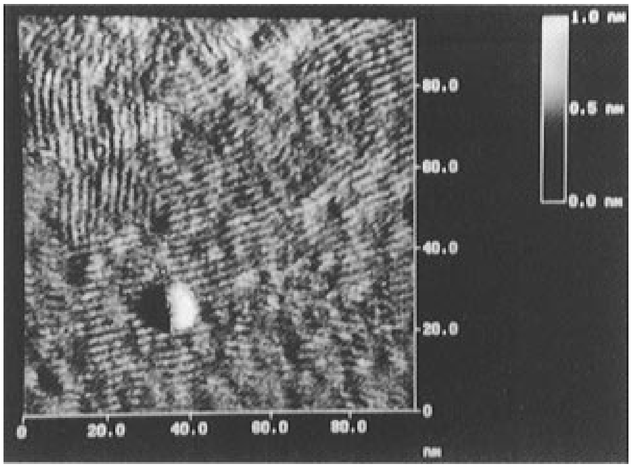

Figure 9. AFM image of a SAM of thiol **5** imaged on Au(111) in ethanol. Different domains of orientational order of the columnar superstructure can be recognized.

For monolayers of **5**, AFM revealed the superstructure of the triphenylene cores. In Figure 8 an array of parallel stripes or rows can be recognized. These structures typically extended over tens to several hundreds of nanometers. Another AFM image of a SAM of **5** is shown in Figure 9. Here one can clearly distinguish domains of different orientation. Thus, an influence of the tip scanning over the monolayer surface on the monolayer structure can be excluded. The superstructure has long-range order and even crosses defects in the gold. We interpret these stripes as columns of the discoid part of the molecules which are oriented with the columnar axis approximately parallel to the substrate. The images prove the edge-on orientation of the aromatic triphenylene core. Similar order has been visualized before in LB films of amphiphilic triphenylenes and monolayers of discotic liquid crystalline donor−acceptor twin compounds adsorbed onto silicon.[29] For SAMs of compound **5** on Au(111) we measured a distance between the stripes of 20−22 Å. This

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[28] Monolayers of hexaalkyloxytriphenylenes on graphite are laterally highly organized and can be imaged with STM. The driving force for the ordering is in this case the adsorption of the alkyl chains onto the graphite. See, e.g.: Askadskaya, L.; Boeffel, C.; Rabe, J. P. *Ber. Bunsenges. Phys. Chem.* **1993**, *97*, 517−521.

[29] (a) Josefowicz, J. Y.; Maliszewskyj, N. C.; Idziak, S. H. J.; Heiney, P. A.; McCauley, J. P.; Smith, A. B., III *Science* **1993**, *260*, 323−326. (b) Tsukruk, V. V.; Reneker, D. H.; Bengs, H.; Ringsdorf, H. *Langmuir* **1993**, *9*, 2141−2144.

corresponds to the intercolumnar spacing in the hexagonal mesophase of the liquid crystalline material. Idziak et al.[27] measured an intercolumnar distance of 21.74 Å by X-ray diffraction.

Unfortunately, we were not able to image the intracolumnar spacing. When small scan sizes were chosen, the resolution decreased and was finally lost. This apparent mechanical instability of the ordered superstructure is not surprising. It can be attributed to the insufficient filling of the empty space below the discoid cores by the alkyl chains. For SAMs of thioether derivatives of calix[4]arenes and carceplexes on gold, it has been shown by van Velzen et al.[30] and Huisman et al.[31] that it is necessary to fill the entire space below big receptor molecules in order to obtain a closely packed, defect-free SAM that exhibits good electrochemical barrier properties.

The orientation of the molecules in SAMs of **6** and **7** is identical with the orientation of the molecules of **5,** as proven by FTIR spectroscopy above. Therefore, we suggest that they also form SAMs with the same columnar superstructure. In the recent reports on the photoconductivity of triphenylenes,[4] it was shown that the photocurrent is mediated by hole conduction through the columns in the hexagonal mesophase. A hopping mechanism could be excluded. Therefore compound **5** forms SAMs that, in theory, should be photoconducting in a plane parallel to the gold plane.

Conclusions

Discotic liquid crystalline hexaalkylthio-substituted triphenylenes and tricycloquinazolines, and derivatized triphenylenes with a single long ω-thioalkyl or ω-dithioalkyl substituent were shown to self-assemble from dilute solution onto gold surfaces. By variation of the molecular structure, the two limiting orientations of face-on and edge-on orientation of similar molecules could be achieved on the same substrate. The discotic liquid crystalline hexaalkylthiotriphenylenes and the hexaalkylthiotricycloquinazolines form laterally nonstructured monolayers on gold with essentially face-on oriented molecules. The alkyl chains do not lie flat on the gold, but cover the aromatic cores. The process of assembly was proven to result in loosely bound disordered multiple layers which are removed by careful rinsing of the substrate, leaving a tightly bound monolayer behind. In contrast, the aromatic cores of the monothioalkyl and dithioalkyl triphenylene derivatives are oriented edge-on. They assemble in superstructures in the form of parallel columns on the gold. AFM was successfully used to image the highly ordered surface. The surface of these compounds is remarkably well ordered over hundreds of nanometers.

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(30) Thoden van Velzen, E. U.; Engbersen, J. F. J.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1994**, *116*, 3597−3598.

(31) Huisman, B.-H.; Rudkevich, D. M.; van Veggel, F. C. J. M.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1996**, *118*, 3523−3524.