Fabrication of a Carboxyl-Terminated Organic Surface with Self-Assembly of Functionalized Terphenylthiols: The Importance of Hydrogen Bond Formation

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Abstract: Self-assembled monolayers (SAMs) were prepared from different oligophenylthiol molecules (terphenylthiol, ($C_6H_5C_6H_4C_6H_4SH$, TPT), terphenylmethanethiol ($C_6H_5C_6H_4C_6H_4CH_2SH$, TPMT), and carboxy terphenylmethanethiol ($HOOCC_6H_4C_6H_4C_6H_4CH_2SH$, CTPMT)) on Au substrates. Compared to the more commonly used alkanethiols this class of organothiols has a much more rigid backbone. It is demonstrated that for organothiols with a strongly interacting function at the ω-position the larger mechanical rigidity significantly affects the molecular structure of the self-assembled films. Whereas the unsubstituted terphenylthiols, TPT and TPMT, form well-ordered monolayers with an average tilt angle of $27° \pm 5°$, immersion into ethanolic solutions of the COOH-functionalized terphenylmethanethiol CTPMT yields highly oriented *bilayers*. The second layer is linked to the first layer by hydrogen bonds. This double-layer formation has not been observed for the corresponding alkanethiols. Single layers of CTPMT on gold could, however, be prepared by adsorption from a mixture with trifluoroacetic acid (TFA) or by immersion of the bilayers into TFA. The immersion of the bilayers into potassium hydroxide solutions leads to the intercalation of potassium ions into the bilayers without removal of the second layer.

Introduction

The possibility of creating well-defined organic surfaces by self-assembly of appropriately functionalized molecules is still receiving growing interest.[1] With the help of the self-assembly technique, well-ordered two-dimensional arrays of functional groups can be fabricated which are relevant for a variety of applications, e.g., sensor devices or adhesion layers. The major part of previous work on self-assembled monolayers has concentrated on a particular class of molecules, namely ω-substituted alkanethiols.[1−3] The properties of the highly oriented molecular films prepared with this method are to a large extent dictated by the properties of the alkyl-chain backbone. Whereas the high alkyl-chain flexibility has certain advantages regarding the elastic properties of the molecular monolayers, in some cases the interaction between the functions added at the ω-position prohibits the formation of highly oriented films. In the case of SAMs obtained from nitronaphthalene-terminated alkanethiols a large amount of disorder was observed.[4] In the case of COOH-terminated alkanethiols, where the hydrogen-bonded dimers present in the ethanolic solution are not separated during the adsorption process,[5,6] the high flexibility of the alkyl chains allows for a bonding of both SH units to the surface, thus yielding highly disordered molecular films. A well-defined, COOH-terminated organic surface that is of interest for a number of applications can thus not be obtained from this class of organothiols. An obvious strategy to avoid the unwanted, high degree of molecular disorder is to replace the flexible alkyl backbone by a more rigid chain.[7,8]

Here we report on results obtained by using a terphenyl backbone. Since only a few reports in the literature have focused on SAMs made from oligophenylthiols,[9,10] we have first characterized SAMs obtained from unfunctionalized terphenylthiols (TPT) and terphenylmethanethiol (TPMT) by using photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy (NEXAFS). In the next step self-assembled films obtained from a COOH-functionalized terphenylthiol (CTMPT) were studied. In contrast to the nonfunctionalized terphenylthiols forming the expected SAMs of monolayer thickness, the formation of *bilayers* is observed for the COOH-functionalized oligophenylthiols.

Experimental Section

Synthesis of the Molecules. The synthesis of terphenylthiol was accomplished by one-pot chlorosulfonation of terphenyl with chlorosulfonic acid and phosphorus pentachloride followed by reduction with

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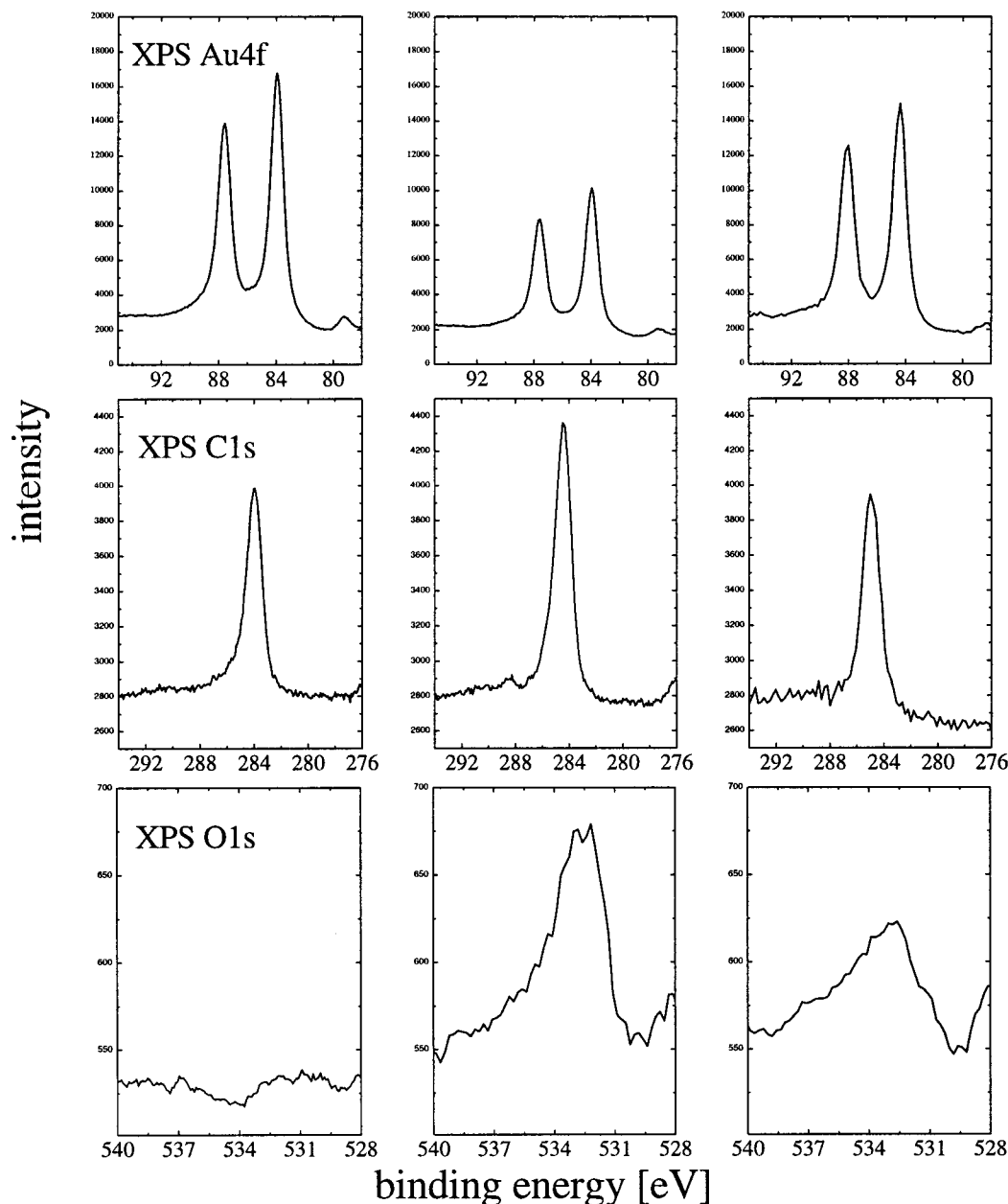
Figure 1. XP spectra for TPT (left side), CTPMT bilayers, and CTPMT monolayers on Au.

LAH. The product was purified by chromatography and crystallization.

The synthesis of terphenylmethanethiol started with the photobromination of methylterphenyl by NBS in acetone. Treatment with thioacetate in DMF followed by hydrolysis yielded the product, which was purified by crystallization.

4′-Carboxyterphenyl-4-methanethiol was prepared by Suzuki coupling of 4-tolylboronic acid (anhydride) with ethyl 4-bromobiphenyl-carboxylate, bromination by NBS, and substitution with thioacetate. Alkaline hydrolysis yielded the product, which was purified by crystallization.

Preparation of Au Substrates. The Au substrates were prepared by evaporation of 100 nm of Au onto clean, polished silicon single-crystal wafers which had been primed with a 1 nm thick Ti-adhesion layer.

Preparation of the Self-Assembled Films. For self-assembled film preparation 0.1 mM solutions of the thiols in 50 mL of dried ethanol or tetrahydrofuran were prepared. After an ultrasonic treatment the solutions were filtered. Gold samples were immersed for 24 h into the solutions.

Monolayers of CTPMT on Au were prepared by immersion of Au

samples in a solution of CTPMT in trifluoroacetic acid or by immersion of CTPMT-bilayer films on Au in trifluoroacetic acid.

The adsorption of trifluoroacetic acid was carried out in an ultrahigh vacuum chamber. The samples were cooled to 110 K before adsorption of 20 L (1 L $= 1$ s $\times$ (1×10^{-6}) mbar) of trifluoroacetic acid.

XP spectra were taken with an Al Kα-X-ray source. The NEXAFS spectra were taken at the synchrotron radiation facility BESSY in Berlin.

Visualization of the Different Behavior of COOH-Terminated Alkanethiols vs COOH-Terminated Terphenylthiols by Liquid Crystals. By employing the well-established μCP technique[11] a CTPMT pattern of parallel 50 μm wide lines with a spacing of 50 μm was generated by first stamping with HS(CH$_2$)$_{10}$COOH on a cleaned Au surface. Subsequently the surface was treated with a saturated solution of CTPMT in TFA for 1 h. A small amount of 2,4-undecadienic acid (a nematic LC) was brought onto this surface and covered by a glass slip. The pattern formed immediately.

Results

On the left side of Figure 1 we present XP spectra recorded

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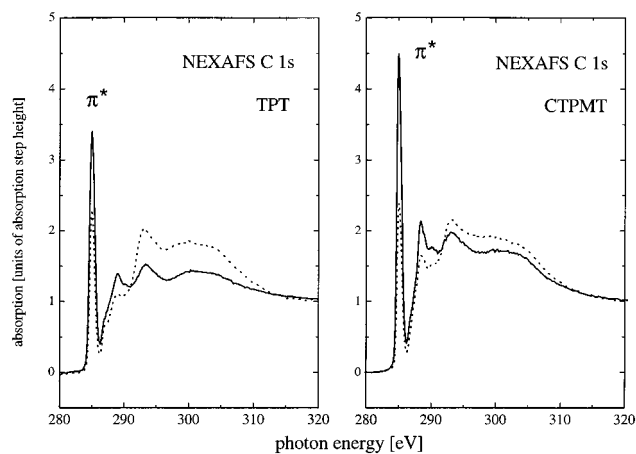
Figure 2. Left side: NEXAFS spectra of TPT on Au. Right side: NEXAFS spectra of CTPMT on Au (solid line: normal photon incidence; dashed line: grazing photon incidence).

for ultrathin organic films on Au samples, which were obtained by immersion of the substrates into solutions of terphenylthiol. Several peaks are observed, which can be assigned to carbon, sulfur, and gold; no significant contributions from other elements were found. In the middle of Figure 1 the C 1s signal, located at 284.5 eV, is shown. In the sulfur 2p spectrum (not shown) the S $2p_{1/2}$ peak is located at 162 eV. A quantitative analysis[5,6] of the relative intensities of the Au 4f and C 1s signals in the XP spectra yields a value of 16 ± 1.5 Å for the organic layer thickness. Since the length of one terphenylthiol molecule amounts to 16.2 Å and the S−Au distance to 2 Å,[12] this result indicates the presence of a densely packed, well-defined monolayer with the molecular axes slightly tilted away from the surface normal.

The XPS data obtained for the COOH-terminated CTPMT (Figure 1, middle) are qualitatively similar to the corresponding data for the TPMT film, but a closer inspection reveals a significantly higher C1s/Au4f peak ratio. A quantitative analysis yields a thickness of 34 ± 3 Å, corresponding to the presence of a *double* layer.

On the right side of Figure 1 a set of XPS data for an organic monolayer obtained by immersion of an Au substrate in a CTPMT/TFA solution is shown. No F1s signal is present, and the Au4f/C1s ratio is much larger than that for the film obtained by immersion into a CTPMT solution in ethanol. A quantitative analysis yields a thickness of 18 Å, thus indicating the presence of a single layer.

On the left side of Figure 2 the NEXAFS spectra recorded for TPT monolayers with two different angles of photon incidence are displayed. For details on the data-acquisition and normalization procedure see ref 6. Both spectra reveal a sharp resonance located at 285.0 eV assigned to excitations into the empty π*-orbital of the phenyl units.[13] The phenyl π*-resonance at 285 eV is most intense in the spectrum obtained for normal photon incidence (90°, solid line), thus revealing that the phenyl-ring planes are oriented preferentially normal to the surface plane. A quantitative analysis of this dichroism[13] yields an average angle of 27° ± 5° between the phenyl units and the surface normal. The NEXAFS spectra recorded for the TPMT monolayers exhibit a pronounced similarity to those obtained for terphenylthiol.

Also the data obtained for films made from the CTPMT (Figure 2, right side) are qualitatively similar to the NEXAFS
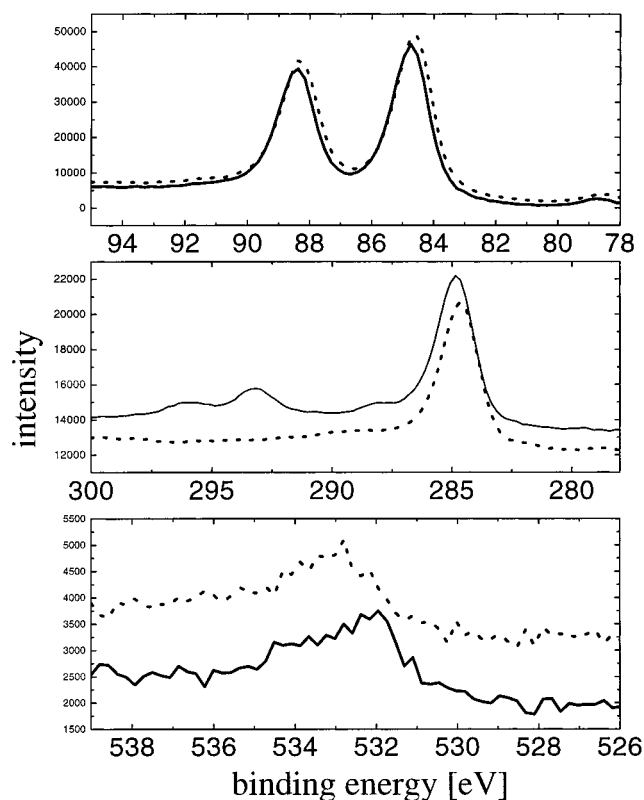

Figure 3. XPS Au 4t, C1s, and O1s (from top to bottom) data of CTPMT bilayers before (dashed lines) and after immersion into a KOH solution.

data shown above; a detailed analysis reveals that the signal below the first NEXAFS resonance at 285 eV exhibits a significantly smaller background, thus indicating the presence of a thicker layer.[14] As before, the π*-resonance at 285.0 eV exhibits a rather strong dichroism, corresponding to an average tilt angle for the terphenyl molecular axis of 21° ± 5° away from the surface normal.

The NEXAFS data for the CTPMT monolayer prepared from a CTPMT/TFA mixture (not shown) are similar to the CTPMT double-layer data; a quantitative analysis of the π*-resonance dichroism yielded a tilt angle of 17° ± 5° between the terphenyl molecular axis and the surface normal.

Figure 3 shows XP spectra obtained after immersion of the CTPMT-bilayer films in ethanolic KOH solutions. The main difference is the presence of the K2p photoelectron lines; a quantitative analysis yields an elemental K/O ratio of 0.52.

Force Field Simulations. To investigate the possible molecular arrangements within SAMs obtained by adsorption of TPT on Au substrates we have carried out molecular dynamics simulations employing periodic boundary conditions using a commercial software package.[15] Nine thiolate molecules with the S-atom carrying a formal charge of −0.3 e were placed at the positions of a $\sqrt{3}*\sqrt{3}$ superstructure on a three-layer Au substrate with 36 surface atoms (total of 108 Au atoms) in the periodic box. A positive charge was added to the substrate to obtain a total charge of 0. In previous work it was found that the Au−S−C angle potential does not show a strong variation.[12,16,17] Therefore the only constraint imposed on the

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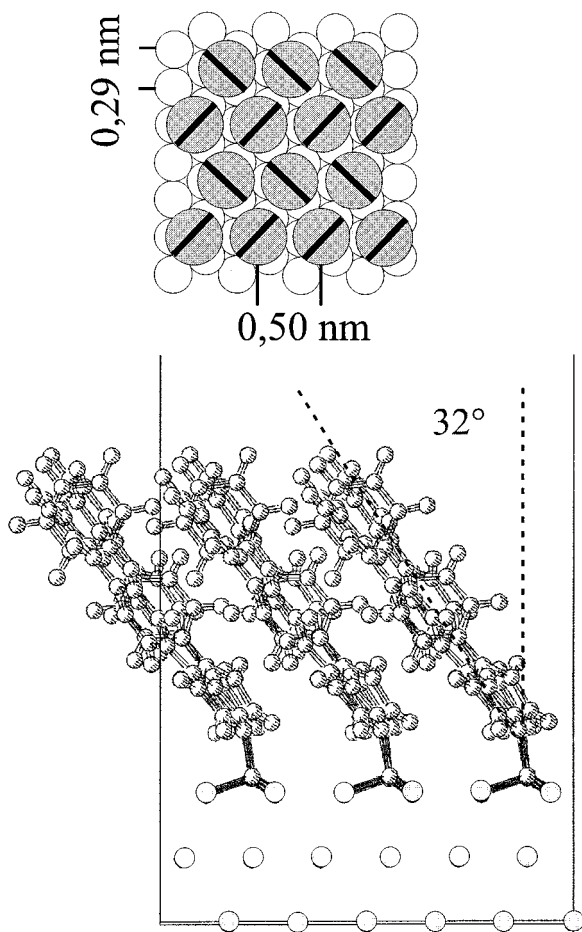
Figure 4. Molecular arrangement of the terphenylthiolate monolayer on Au(111) obtained by consistent valence force-field simulations.

molecular dynamics simulations was to fix the Au–S distance at 0.25 nm; all other interactions were taken from ref 16. The calculations were started with the thiolate molecules exhibiting the most stable conformation of the free molecule (phenyl rings rotated with respect to each other by 20°) and the molecular axis oriented perpendicular to the surface. After several minimization and annealing cycles, in which the monolayer was slowly heated to 300 K and then cooled back down to 100 K, the molecular structure converged to the one shown in Figure 4. This stable structure is characterized by a tilt angle of 32° between the terphenyl molecular axis and the surface normal. The angle between the phenyl rings was found to decrease from 20°, the value for the free molecule, to 0°, in excellent agreement with the molecular structure found in bulk terphenyl single crystals.[18] Note that the tilt-angle found here is significantly larger than reported in a previous analysis.[9] Since in this earlier work not all degrees of freedom could be treated, we consider the present results obtained from a full minimization more accurate.

Discussion

For the TPT monolayer the XPS data reveal film thicknesses of 16 ± 1.5 Å, in agreement with previous results obtained with ellipsometry.[9] The total length of the molecule amounts to 16.2 Å and the S–Au distance to 2 Å.[12] The thickness obtained by XPS is thus consistent with a tilt angle of 27° as obtained from

a detailed analysis of the π^*-resonance dichroism in the corresponding NEXAFS data. The force-field calculations demonstrate that a packing of TPT with the S atoms arranged on a $\sqrt{3} \times \sqrt{3}$ overlayer yields a tilt angle of 32°. We thus conclude that adsorption of TPT on Au substrates yields highly oriented molecular films with an average tilt angle of 27° ± 5°.

In case of the TPMT monolayers a film thickness of 16 ± 1.5 Å was obtained from an analysis of the XPS data. The dichroism of the π^*-resonance in the XAS spectra reveals an average tilt angle of 28.5° of the phenyl ring plane relative to the surface normal. These values are within experimental error identical to those reported above for the TPT monolayer and demonstrate that the introduction of a methylene unit between the oligophenylene unit and the mercapto group does not significantly affect the molecular orientation within the film. Since the difference of the Au–S–C angle (153° and 137.5° for TPT and TPMT, respectively) amounts to 15.5°, this observation is consistent with the weak dependence of the Au–S–C potential on the bond angle (see above).

The XPS data recorded for organic films obtained by immersing Au substrates into ethanolic solutions of COOH-terminated CTPMT reveal a thickness of 34 ± 3 Å, substantially larger than the corresponding value for the unfunctionalized terphenylthiol (TPMT). The most straightforward explanation for this observation is the formation of a double layer, where a second layer of COOH-terminated CTPMT is bound to the first layer by hydrogen bonds. This observation can be rationalized by considering that the strength of a –COOH··HOOC– bond amounts to 63 kJ/mol.[19] This rather large binding energy implies that dimers are present in the ethanolic solution. Since the carboxylic acid bond is highly directional and because the TPMT backbone is rather rigid it is highly plausible that the dimers are preserved in the adsorption process. The fact that the same high dichroism as for the unsubstituted TPMT is observed in the NEXAFS data for the COOH-functionalized TPMT further corroborates the presence of a double layer. Maoz et al. have investigated the bilayer formation on Si substrates using COOH-terminated silanes,[20] but in this case the layers stick together via hydrogen bonds between the OH groups located at the Si atoms of the second layer and the carboxyl endgroups of the first layer. Additionally, the bilayer was formed in two subsequent adsorption steps. Here, the self-assembly process directly leads to the formation of highly oriented bilayers with strong interlayer COOH··HOOC– hydrogen bonding.

Although the formation of double layers in SAMs made from CTPMP appears to be a consistent interpretation of the experimental data, there seems to be a fundamental inconsistency with the results reported previously for monolayers obtained from COOH-functionalized alkanethiols. Several groups have reported the formation of *single* layers in this case.[5,6,21,22] We propose that these differences are due to the large flexibility of the alkyl backbone. In the adsorption process the two alkyl chains present in the hydrogen-bonded dimer (see above) are sufficiently flexible to allow both mercapto (–SH) units to form bonds with the surface. Of course such an adsorption will not

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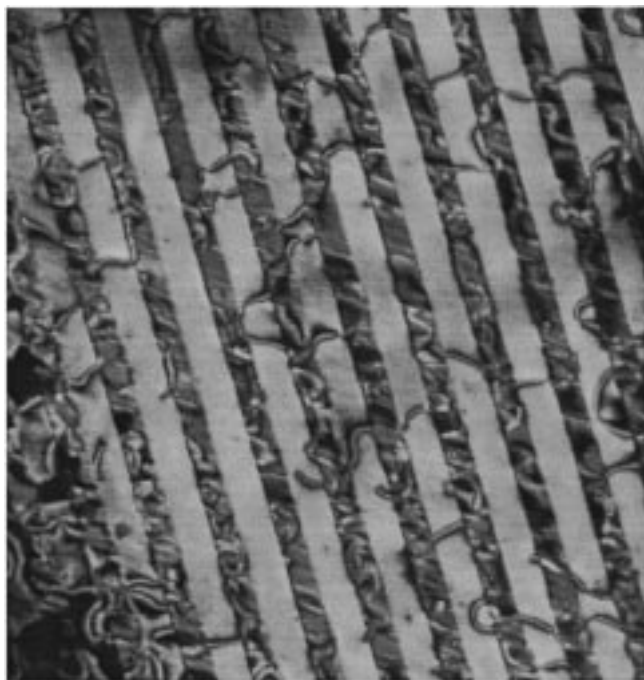
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Figure 5. Image recorded with an optical microscope by using the cross-polarization method of the nematic LC 2,4-undecadienic acid on a stamped pattern of COOH-terminated alkanethiolate and oligo-phenylthiolate monolayers with equal chain length ($HS(CH_2)_{10}COOH$ and $HSCH_2(C_6H_4)_3COOH$). Each strip in the image has a width of 50 μm; in the bright regions the Au substrate is covered with the COOH-terminated alkanethiol.

result in the formation of highly oriented molecular films and indeed it has been found that these films are highly disordered.[5,6] For the CTPMT molecules, on the other hand, the rigidity of the terphenyl backbone inhibits a binding of both mercapto groups to the surface, and double layers are formed instead of a disordered single layer.

That the density of COOH functions is indeed very different in films made from CTPMP and an COOH-terminated alkanethiol ($HS(CH_2)_{10}COOH$) of the same length is also demonstrated by the optical microscope image shown in Figure 5. The LC molecules exhibit drastic changes in their optical properties depending on their molecular arrangement, which for thin films will strongly depend on the interaction of the molecules with the substrate. The strong contrast seen in Figure 5 thus reveals pronounced differences in the coupling between the undecadienic acid (which will form hydrogen bonds with the surface free acid groups) and the two different −COOH-terminated organic surfaces. Although these results only allow for qualitative statements about the density of free COOH functions at the organic surface, the present conclusions are fully consistent with previous experiments on the interaction of alkane acids with COOH-terminated alkanethiolate monolayers as reported by Sun et al.[22] They found that less than a monolayer of alkane acid is bonded to the COOH-terminated SAM. In view of the present results this observation can be readily explained by a smaller concentration of COOH units in the surface region.

Since the original aim of the present study was the fabrication of a well-defined organic surface terminated by −COOH functions, further experiments were carried out to obtain a CTPMT *mono*layer. Au substrates were immersed into solutions of CTPMP in TFA. Since the acetic acid (AA)−trifluoroacetic
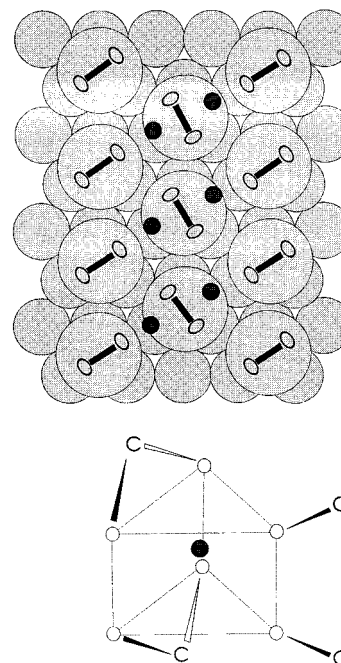

Figure 6. Model of the K^+ intercalation into the CTPMT-bilayer film (dark circles: K^+ ions) showing the orientation of the carboxyl groups and the position of the K^+ ions. Each K^+ ion is coordinated by 6 O atoms.

acid (TFA) binding energy (67 kJ/mol[23]) is slightly larger than that for the TFA−TFA bond (58 kJ/mol[23]) virtually all CTPMT molecules within this solutions will form CTPMT:TFA dimers. SAMs prepared by immersing Au substrates into these solutions consist of single layers of CTMPT, as evidenced by XPS. The absence of a significant F1s signal in the XPS data indicates that the TFA layer on top of the COOH−TPMT desorbs after vacuum transfer. This conclusion is fully consistent with the TDS data (see Supporting Information) where all TFA desorption peaks are located below 250 K.

The fact that a second layer of CTPMT is stable on top of the CTPMT monolayer after removal from the solution whereas the TFA quickly desorbs (see above) can be attributed to the intermolecular interactions being larger for the CTPMT than for the TFA monolayer. In a CTPMT monolayer on a COOH-terminated surface the intermolecular interactions are equal to or even larger than the binding energy of the hydrogen bonds to the substrate, thus resulting in thermally much more stable films. The same explanation can be used to account for the fact that the formation of double layers has not been observed in previous work, e.g., for 4-carboxylthiophenol.[24,25] For this molecule the backbone is too short to stabilize the second layer via intermolecular interactions and the carboxyl thiophenol bilayer evaporates upon removal from the solution.

While immersion of the CTPMT bilayers in TFA leads to the removal of the second CTPMT layer and the formation of highly oriented single layers, an immersion into KOH solution leads to the intercalation of K^+ in the bilayer film without removal of CTPMT molecules. In Figure 7 a possible structural model of the K-atom arrangement in the bilayer film is shown. Each K^+ ion is coordinated by 6 O atoms (3 O atoms from each layer).[26] The K:O ratio of 0.52 as obtained from a

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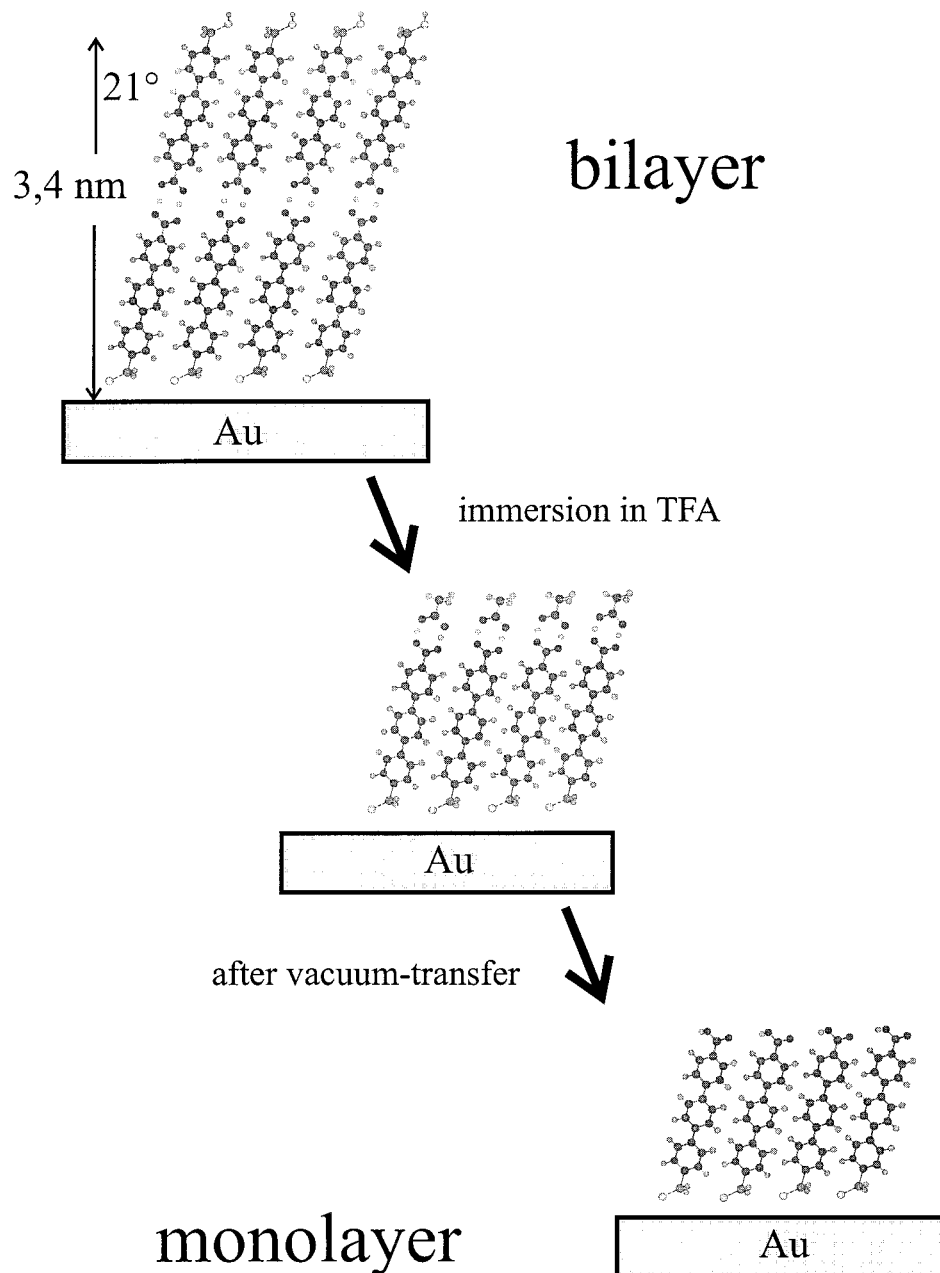
Figure 7. Scheme for the transformation of the bilayer of CTPMT into a monolayer with trifluoroacetic acid (TFA).

quantitative analysis of the XPS data is consistent with such a model.

Conclusions

By carrying out a detailed analysis of different oligophenylthiols we find that the presence of a rigid backbone in organothiols significantly affects the self-assembled adsorption on Au substrates. In the case of the COOH-terminated carboxy terphenylmethanethiol ($HOOCC_6H_4C_6H_4C_6H_4CH_2SH$, CTPMT) the formation of double layers is observed. Similar results are expected for other rigid organothiols with strongly interacting functionalities ($-OH$, $-NH_2$, ...) at the ω-position. We were, however, able to fabricate CTPMT monolayers, thus yielding highly oriented, COOH-terminated organic surfaces by immersing Au substrates in a solution of CTPMT and trifluoroacetic

acid, TFA, or by treatment of a preformed CTPMP bilayer with TFA, as depicted in Figure 7. Our results indicate that the organic surfaces of the CTPMT monolayers exhibit a significantly higher density of $-COOH$ functions than corresponding films made from COOH-terminated alkanethiols, thus demonstrating the importance of rigid backbones when creating chemically active organic surfaces with strongly interacting functions using the self-assembly method.

Supporting Information Available: Synthesis details of the thiols used and a thermal desorption spectrum of TFA (5 pages, print/PDF). See any current masthead for ordering information and Web access instructions.

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