Thioethylpyrrole Monolayers on Gold. A Spectroscopic Study in Ultrahigh Vacuum

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The adsorption of 3-(2-thioethyl)pyrrole (3-TEP) and 1-(2-thioethyl)pyrrole (1-TEP) on gold has been studied in ultrahigh vacuum with infrared reflection absorption spectroscopy, X-ray photoelectron spectroscopy, and temperature-programmed desorption mass spectroscopy. Depositions were made from liquid phase at atmospheric pressure, from gas phase in ultrahigh vacuum, and from gas phase at atmospheric pressure. Both molecules were found to chemisorb to the gold surface regardless of the deposition method. Most of the 3-TEP, however, broke up, losing the pyrrole ring as it adsorbed on the surface. Both monolayers were sensitive to oxygen and oxidized quickly if stored in air. Deposition of 1-TEP from solution or vapor in air gave a higher desorption peak temperature than deposition from gas phase in UHV. The masses of the desorbing fragments that were detected from the heated monolayers were smaller than those seen upon introducing 1-TEP gas into the UHV system, revealing that a partial decomposition of the adsorbed molecules occurred prior to or at desorption. Some samples were electrochemically cycled to positive potentials to investigate the stability of the monolayers. A large fraction of the 1-TEP and 3-TEP stayed on the surface when cycled to 0.8 V, but some oxidation, fragmentation, and desorption were seen at higher potentials.

Introduction

Polypyrrole belongs to a class of conjugated polymeric materials that are known for their interesting electrical properties.[1−3] It is believed to be a promising new material for the design and development of electronic components, micromuscles,[4] and other devices.[5] A good adhesion between the conjugated polymer and the substrate material is essential in device applications. This paper is part of a larger study aiming at developing a molecular glue that can be used to promote the adhesion between a gold substrate and a polypyrrole film. For this purpose, bifunctional molecules that adhere strongly to gold with one group, e.g., via a thiol,[6−8] and contain another group than can copolymerize with polypyrrole are attractive candidates.[9−11] Thioethylpyrroles are molecules that could satisfy the demands for an efficient glue. The ethyl chain is expected to be short enough to allow for intrachain coupling of electrons from the pyrrole ring via the CH_2 backbone and the sulfur to the gold contact, a necessary prerequisite for electropolymerization of the polypyrrole film.

Several different aspects of the chemical and physical properties of the two compounds 1-(2-thioethyl)pyrrole (1-TEP)-and 3-(2-thioethyl)pyrrole (3-TEP) (see Figure 1a,b) and their interactions with gold surfaces previously have been studied in our laboratory. Synthesis and characterization of the monomers were treated in our first paper,[12] formation of monolayers using standard solution and vapor deposition methods was described in the second paper,[13] and the third paper focused on electrochemical characterization of these monolayers.[14] In the previous studies it was found that both TEPs chemisorb on gold. The formed layers were also found to oxidize upon prolonged
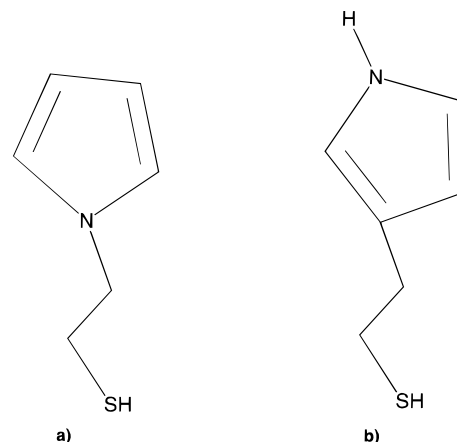

Figure 1. Chemical structures of (a) 1-(2-thioethyl)pyrrole (1-TEP), (b) 3-(2-thioethyl)pyrrole (3-TEP).

exposure to laboratory air, a result consistent with previous observations for substituted pyrroles.[15] In the experiments reported here special care has been taken to minimize exposure to oxygen. All of the infrared reflection−absorption spectroscopy (IRAS), X-ray photoelectron spectroscopy (XPS), and temperature-programmed desorption (TPD) measurements were conducted in UHV. Throughout this study, gold was chosen as the substrate metal because of its inertness and the extensive studies of the gold−thiol interface system already published.[8,16] Depositions of TEP monolayers have been done by exposing the gold surface to a low dose of TEP vapor in a UHV system. In addition to this method, we also deposited the TEP from vapor phase in air and from low-concentration solutions, usually in ethanol. These are the two deposition methods that were used in the previously described experiments.[13]

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To be regarded as an efficient and robust glue, the monolayers must withstand electrochemical cycling at potentials used to oxidize or reduce the polypyrrole film, as well as the constant potential applied for electropolymerization.[4] Samples with solution-deposited monolayers of the TEPs were treated with positive voltages, and XPS spectra were recorded to see if the monolayers themselves were affected by a treatment similar to that used for polymerization of polypyrrole.

The gold−thiol bond is known to be very strong, 1.7 eV (167 kJ/mol).[17] When heated, short chain sulfur components, such as dimethyl disulfide, are known to stay on gold up to 470 K,[7] and long chain self-assembled monolayers are known to keep their organization reversibly up to at least 390 K.[18] In the TPD experiments reported here, samples with TEP monolayers were heated and the desorbing fragments analyzed to investigate the thermal stability.

Experimental Section

Materials. Both 1-TEP and 3-TEP were synthesized in our laboratory. The synthesis of 1-TEP has been described earlier,[19] but for 3-TEP a new synthetic scheme had to be developed. The processes are described in detail elsewhere.[12] Ethanol (99.5%) was purchased from Kemetyl AB, Stockholm, and used as received.

Sample Preparation. For IRAS and TPD measurements, thermally evaporated gold films on weakly doped 20×20 mm (100)-silicon wafers were used as substrates. The silicon (obtained from Okmetic, Espoo, Finland) was cleaned for 10 min in a 5:1:1 mixture of MilliQ water, ammonia (25%), and hydrogen peroxide (30%) heated to 80 °C. After rinsing in MilliQ water and drying in nitrogen, the silicon slides were mounted in a UHV system operating at a base pressure below 10^{-9} Torr. The silicon was primed with a 25 Å thick adhesion layer of titanium before the gold (ANA Ädelmetall, Helsingborg, Sweden, 99.9%) deposition was made at 5 Å/s. A 2000 Å film was prepared with a pressure in the chamber not exceeding 10^{-7} Torr during evaporation. Immediately before use, the gold substrates were cleaned using the same method as for cleaning the silicon wafers. For XPS measurements, identically prepared but smaller (5×20 mm) substrates were used.

Deposition of 1-TEP in UHV. Deposition of 1-TEP, IRAS measurements on the formed layers, and thermal desorption took place in a vacuum system designed for this kind of measurement. This system is described in detail elsewhere.[20] A few drops of 1-TEP were placed in a glass test tube which was attached to the UHV system through a leak valve and pumped with a turbomolecular pump until a pressure of approximately 10^{-3} Torr was reached. The valve was slowly opened allowing 1-TEP vapor to enter the UHV chamber (base pressure 10^{-9} Torr). In the chamber a Hiden HAL2/301 quadropole mass spectrometer residual gas analyzer was utilized to monitor the composition of gas molecules. During deposition both the test tube and the sample were held at room temperature, and the maximum pressure in the UHV chamber was 3×10^{-7} Torr. This deposition method could not be used for the highly unstable 3-TEP molecules[12] since they decomposed during the pump-down and deposition processes, which took several hours.

Deposition of TEP Monolayers from Ethanol Solutions. Monolayers of TEPs were also prepared by immersing gold substrates in a 10 mM ethanol solution of TEP. Immersion times from a few seconds to several hours were used. After immersion the samples were rinsed in ethanol, ultrasonicated in ethanol for at least 3 min, and rinsed again before being blown dry in nitrogen or argon gas. For the unstable 3-TEP compound,

special care had to be taken to minimize exposure to air and the time the compound was at room temperature.

Deposition of TEP Monolayers from Vapor at Atmospheric Pressure. Yet another method for preparation of TEP monolayers was to place a gold substrate, prepared and cleaned as described above, and a drop of TEP next to each other in a covered glass container. The 1-TEP was partly vaporized and some molecules from the 1-TEP gas adhered to the surface. After 20 min of vapor exposure the sample was taken from the container and analyzed without further treatment.

Infrared Spectroscopy of Bulk Materials. IR absorption spectra of bulk 1-TEP and 3-TEP were recorded on a Bruker IFS48 Fourier transform infrared spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector. A drop of the TEP was placed between two potassium bromide windows, and 100 interferograms were averaged at 4 cm^{-1} resolution. As a reference, a spectrum was recorded of the two KBr windows without TEP.

Infrared Reflection−Absorption Spectroscopy. IRAS spectra of thin layers were recorded using a Bruker IFS113 spectrometer with an external beam connected to the UHV system. A mercury cadmium telluride (MCT) detector was used which limited the spectral range to wavenumbers above 750 cm^{-1}. During a typical measurement 1000−2000 interferograms were averaged with 2 cm^{-1} resolution. The angle of incidence was 82°, and the radiation was polarized parallel to the plane of incidence.

X-ray Photoelectron Spectroscopy. The XPS experiments were performed with a SCIENTA ESCA 300 spectrometer using focused, monochromatic Al Kα radiation (1487 eV).[21] All XPS measurements were performed with a pass energy of 300 eV and an analyzer entrance slit width of 0.8 mm. The power of the X-ray electron gun was kept constant at 8 kW. Each measurement was performed on a new spot by moving the sample, thus minimizing the amount of damage caused by the X-ray irradiation. The regions recorded were Au 4f, S 2p, C 1s, N 1s, and O 1s. The pressure in the analysis chamber was approximately 2×10^{-10} Torr and the temperature of each sample was 28 °C when recording the spectra. The electron takeoff angle was 90° with respect to the surface for all measurements reported here.

Temperature-Programmed Desorption. The TPD measurements took place in the same measurement chamber as the IRAS measurements (base pressure $<2 \times 10^{-10}$ Torr). The copper sample holder could be resistively heated, and the temperature was monitored with a Pt100 resistance element. A temperature regulator allowed stable temperature control as well as linear ramping of the temperature. The TPD traces were recorded using a heating ramp of 15 K/min while desorbing molecules with masses in the range 2−130 were counted. In this chamber, a more sensitive Hiden HAL 3F/301 PIC pulse-counting mass spectrometer was used. The maximum pressure reached during desorption was 7×10^{-8} Torr.

Electrochemical Cycling of Monolayers. The electrochemical cycling was done using an Autolab pgstat10 from Eco-Chemie, computer-controlled by their General Purpose Electrochemical System software. Electrochemistry was performed in single-compartment, three-neck glass electrochemical cells. A thick gold wire was normally used as the counter electrode. A Ag/AgCl reference electrode (BAS) was usually employed: the Ag/AgCl wire was in a 3 M NaCl solution separated from the electrolyte in the electrochemical cell by a Vycor plug. Scans were performed in propylene carbonate with lithium perchlorate as the supporting electrolyte, PC/LiClO$_4$ (0.1 M), at 10 or 20

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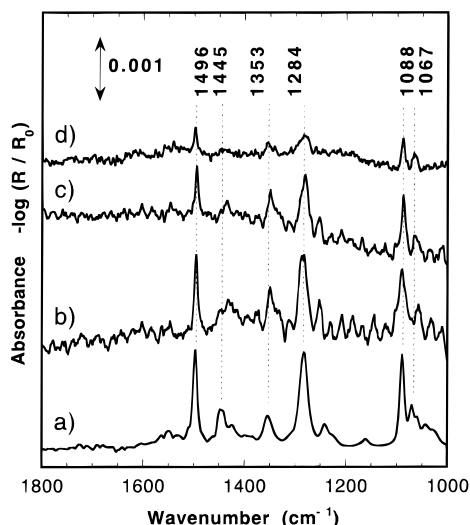*J. Phys. Chem. B, Vol. 102, No. 34, 1998* **6531**

Figure 2. Infrared spectra of (a) 1-TEP bulk material (transmission measurement), (b) 1-TEP deposited from ethanol solution on Au, (c) 1-TEP thin film in b after heating to 370 K, (d) 1-TEP film deposited in UHV. The fringes in b and c are due to an artifact in the beam splitter of the FT-IR interferometer.

Figure 3. Infrared spectra of (a) 3-TEP bulk material (transmission measurement), (b) 3-TEP deposited from vapor on Au in air.

mV/s between −0.2 or 0 V and +2.0 V (vs Ag/AgCl). For further information about the procedure see Smela et al.[14] Water and oxygen were not excluded. After applying the positive voltages the potential was restored to 0 V, and the samples were taken out of the electrolyte, rinsed, and dried before measurements with IRAS and XPS.

Results and Discussion

IRAS on 1-TEP Deposited from Solution. The 1-TEP molecule has several characteristic IR absorption bands, most of them originating from the pyrrole ring. Figure 2a shows the transmission spectrum of a drop of liquid 1-TEP between two KBr windows. The IRAS spectrum of 1-TEP deposited on gold from ethanol solution is shown in Figure 2b. The IRAS spectrum was recorded in UHV with a sputter-cleaned gold sample as reference. All the strong characteristic pyrrole bands,[12,22] e.g., the pyrrole ring in-plane vibrations at 1067, 1088, 1284, and 1496 cm^{-1} in the transmission spectrum, are also seen in the IRAS spectrum with essentially the same relative intensities, indicating that a stable and isotropic layer of the molecule is formed. Furthermore, spectral simulations of peak intensities were used to estimate the thickness of the 1-TEP layer.[23] The observed intensities (close to 0.001 −log R/R_0 units for the most prominent peaks) suggest that slightly less than a full monolayer of 1-TEP molecules (≈0.5 nm) is formed on the gold surface. The small shifts in wavenumbers seen for some bands are due to optical effects that are caused by the IRAS experimental geometry.[24]

In a recent study,[13] we found that 1-TEP is slowly oxidized at room temperature in laboratory atmosphere to form some sort of carbonyl compounds,[15] which give rise to a strong IR vibration at around 1720 cm^{-1}. This peak increases in intensity upon prolonged exposure to air. The bulk material does not oxidize in the same manner, even after 3 h in air at room temperature,[12] revealing that the molecule is more sensitive to chemical oxidation in the adsorbed state. The carbonyl band is not seen in the spectrum recorded in UHV, Figure 2b. A spectrum from the same sample as in 2b after heating to 370 K in UHV is shown in Figure 2c. The relative intensity ratios and band positions do not change, but a small overall intensity
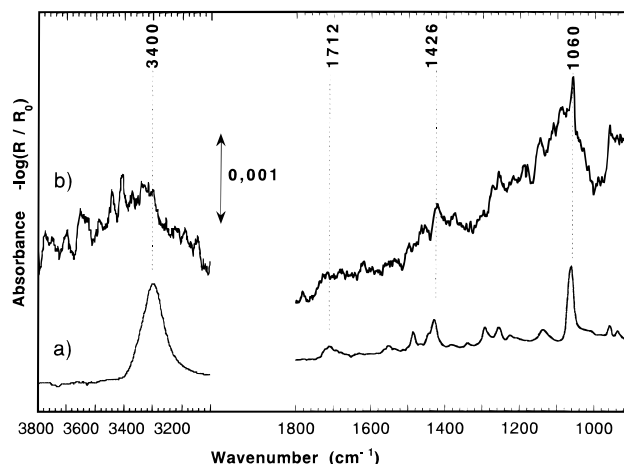
reduction is seen at 370 K. This suggests that a fraction of the layer, most likely consisting of more weakly bound 1-TEP molecules, has desorbed at 370 K, leaving a strongly bound layer. Moreover, only small variations in relative intensities are observed, implying that the structure and orientation of the adsorbed 1-TEP molecules do not change upon heating the sample. In the other deposition method examined, a drop of 1-TEP and a gold substrate were placed together in a sealed glass beaker for 20 min. This method gave IRAS spectra indistinguishable from those obtained by solution deposition.

1-TEP Deposited in UHV. A film of 1-TEP could also be deposited on the gold substrate, without any exposure to air, by introducing 1-TEP vapor at low pressure into the UHV system where a sputter-cleaned gold sample was mounted. The dose used was approximately 20 langmuirs of 1-TEP at a maximum pressure of 3 × 10^{-7} Torr. The IRAS spectrum of the gold sample exposed to this gas is shown in Figure 2d. This layer is less dense than those formed by solution and atmospheric gas-phase deposition. Again the relative intensities of the pyrrole bands are almost the same as in the transmission spectrum, Figure 2a. This shows that the 1-TEP molecules in this layer, as well as those prepared from solution and atmospheric gas-phase deposition, form an isotropic layer on gold. The lateral interactions are obviously too weak to form a well-oriented self-assembled monolayer, cf. SAMs of long chain alkanethiols on gold.[6]

IRAS Spectra of 3-TEP. For 3-TEP the interpretation of the data becomes more complicated. The compound itself is not stable at room temperature and oxidizes quickly if exposed to air. The compound was therefore stored under nitrogen at −80 °C, and special care was always taken to minimize the time of exposure to heat and air. The IR spectrum from a drop of 3-TEP between two KBr windows is shown in Figure 3a. A representative spectrum of a thin layer of 3-TEP on gold is presented in Figure 3b. This spectrum is from a layer prepared by gas-phase deposition in air, but no correlation was found between deposition method (gas or solution) and the spectral features exhibited. The N−H band at 3400 cm^{-1} appears broadened and slightly shifted in the monolayer spectrum compared to the bulk spectrum, indicating that new forms of intermolecular hydrogen bonding are present in the adsorbed state. Hydrogen bonding may occur between neighboring pyrrole units or between a pyrrole unit and polar groups (decomposition products) on the surface.[13] The sharp bands seen in the region 3200−3800 cm^{-1} originate from residual

water vapor in the FTIR spectrometer. The main peaks seen in the low-frequency region at 1060 and 1426 cm^{-1} in the bulk spectrum, Figure 3a, are reproduced in the surface spectrum, Figure 3b. However, some of the characteristic pyrrole ring bands disappear, which we assign to a structural rearrangement or a chemical decomposition of the adsorbed 3-TEP molecules. Unfortunately, we have not been able to deduce the chemical structure of the species formed upon adsorption. UV−vis spectroscopy[13] indicates, however, that some 3-TEP molecules still remain intact on the surface of an air-exposed sample.

3-TEP samples exposed to air have been found to exhibit a strong carbonyl band at around 1715 cm^{-1} and several broad bands in the 1300−1000 cm^{-1} region.[13] Interestingly, the overall appearance of the IRAS spectrum of the air-exposed 3-TEP sample agrees very well with the spectrum of 3-mer-captopropionic acid adsorbed on gold,[25] an observation which leads us to propose that short chain carboxylic acid species are formed as oxidation products. The COOH related bands are almost absent in the spectrum recorded in UHV, Figure 3b, which means that our efforts to minimize air exposure resulted in a 3-TEP overlayer nearly free from oxidation products such as COOH species.

XPS Measurements on 1-TEP Monolayers. The XPS spectra for a solution-prepared 1-TEP monolayer recorded in the S, N, and C regions, Figure 4, show that the relative amounts of these elements are almost the same as they theoretically should be for bulk 1-TEP, Table 1. A probable explanation for the peak seen in the O 1s region (Table 1, right column) is atmospheric oxygen that might interact with the TEP monolayer during transfer, forming some kind of carbonyl compound (see discussion below). Spectra from different but identically prepared samples showed variable amounts of oxygen, but the S/N ratio was always close to 1:1. A thin physisorbed water film on top of the surface is another reasonable explanation for the presence of oxygen in the XPS spectra.

Self-assembled monolayers of long chain alkane thiols are well-ordered structures easily prepared without oxidation of either the sulfur atom or any of the carbons in the chain. In Figure 4a,b, lower traces, an XPS spectrum for such a layer is shown for comparison. The narrow peaks and an S 2p$_{3/2}$/S 2p$_{1/2}$ intensity ratio close to 2:1 undoubtedly reveal that only one type of carbon and one type of sulfur are present.

Figure 4a, middle trace, shows the C 1s spectrum of a solution-deposited 1-TEP film. The main peak at 284.5 eV represents the carbons in the 1-TEP molecule, except for the carbon atoms that are bound to nitrogen or sulfur atoms, which instead give the shoulder at 285.7 eV. A low binding energy shoulder is also seen near 283.8 eV. We attribute this shoulder to carbon atoms very close to the metal surface, suggesting that some of the rings are lying flat on the metal.[26] An electron released close to a metal surface is repelled by the imaginary negative mirror charge induced inside the metal by the positive core ion.[27] This gives the electron a higher kinetic energy and thereby an apparently lower binding energy, Figure 4. This interpretation is in agreement with the findings in a recent study on the adsorption of terthiophenes on gold,[26] where the authors used angle-dependent XPS to identify the depth distribution of the thiophene rings along the terthiophene chain. The ring closest to the gold surface exhibited, in that case, a C 1s peak near 283.9 eV.

In some deliberately air exposed samples a small fraction of the carbon is oxidized to a carbonyl species, giving the small peak at 289.5 eV, as indicated in Figure 4a, upper trace. The intensity of this peak is strongly correlated with the time the
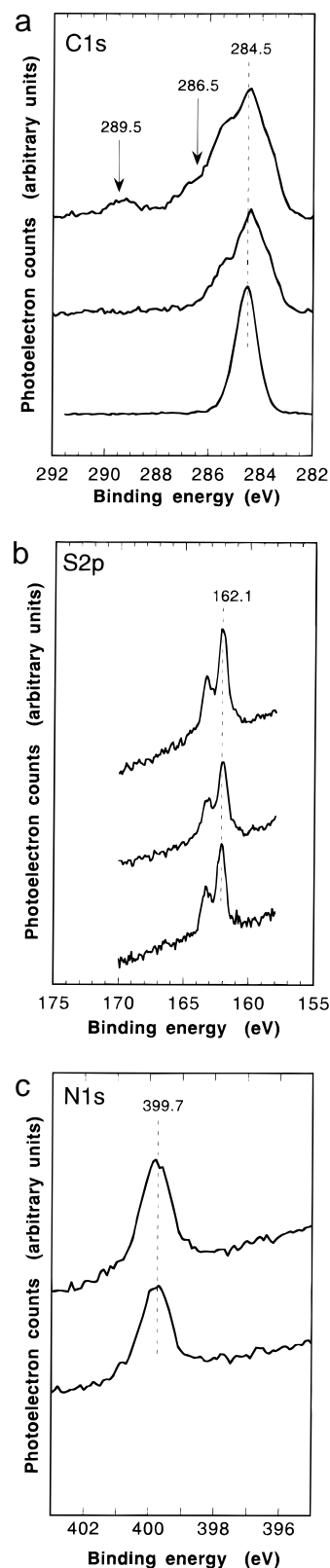

Figure 4. XPS spectra of (a) C 1s, (b) S 2p, (c) N 1s; (upper trace) 1-TEP on gold, exposed to air; (middle trace) 1-TEP on gold, minimum air exposure; (lower trace) HS(CH$_2$)$_{17}$CH$_3$ alkane thiol on gold (N 1s not shown).

samples were subjected to air. Also in IRAS, a band from C=O vibrations is often seen at 1720 cm^{-1} on samples that have been exposed to atmosphere during preparation and mounting.[13] Oxygen is always seen in the XPS spectra; hence some of it might originate from such C=O groups. A small shoulder at

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TABLE 1: Element Ratios Obtained by XPS Measurements on 1-TEP and 3-TEP Layers with Different Adsorption Times

	S rel int	N/S	C/S	O/S
theoretical		1	6	0
1-TEP		0.92	5.90	0.52
3-TEP				
1 min	1	0.25	3.27	0.61
10 min	1.26	0.22	2.66	0.38
20 h	1.61	0.26	2.76	0.46

286.5 eV also appears with increasing air exposure, suggesting that C−O groups are formed as well, also indicated in Figure 4a.

The S 2p XPS spectrum (Figure 4b) resembles the spectrum of the well-ordered *n*-alkanethiol self-assembled monolayer (lower trace). Compared to atomic sulfur at 164.1 eV,[28] this S2p peak is shifted toward lower binding energy, 162.1 eV, consistent with thiolate binding to the gold surface.[29] The splitting of 1.19 eV in the S 2p peak is due to spin−orbit coupling. The relative intensities of the S $2p_{3/2}$/S $2p_{1/2}$ peaks are also close to 2:1, confirming that only one type of sulfur is present. The narrowness of the N 1s peak (Figure 4c) at 399.7 eV also indicates that only one type of nitrogen is present, just as expected for 1-TEP.

No difference is seen between two subsequent 1-TEP XPS spectra, indicating that exposure to X-rays did not damage the surface. According to Wirde et al.,[29] an alkanethiol monolayer can be damaged by prolonged X-ray exposure. However, at the used X-ray flux, no significant changes in the XPS spectrum were observed until after almost 1 h of exposure.

The IRAS and XPS results obtained so far clearly show that intact 1-TEP layers are formed on gold regardless of preparation method provided that the layers are protected from air exposure. Deliberately air exposed 1-TEP samples exhibit C=O and C−O species in the C 1s spectrum, Figure 4a (upper trace), which is consistent with chemical attack of oxygen at the α-carbons in the pyrrole ring.[12,15]

XPS Measurements on 3-TEP Monolayers. XPS measurements taken on a 3-TEP layer deposited from solution and mounted into the UHV system immediately after ultrasonication and rinsing are presented in Table 1 and Figure 5. To slow the spontaneous decomposition and oxidation of 3-TEP, the solution was held at 0 °C during the adsorption process, which varied in time from 1 min to 20 h. In the spectrum obtained after 1 min of exposure to the 3-TEP solution, the main C 1s peak is asymmetric with a high binding energy tail extending up to 287 eV, as seen in Figure 5a. The shoulder is not as pronounced as in the corresponding spectrum of 1-TEP (Figure 4a, middle spectrum), decreases further with increasing exposure time, and is hardly observed in the 10 min spectrum. As seen in Figure 5a, no sign of C=O compounds near 289 eV is detected. Whereas the relative ratio N:S for 1-TEP is 1:1, as expected for a layer of monomers, it is around 1:4 for 3-TEP, Table 1. We, therefore, conclude that many of the 3-TEP molecules have decomposed and estimate that about three-fourths of the pyrrole rings have left the surface, or never adhered to it as intact entities. NMR measurements on 3-TEP have been used to show that 3-TEP molecules in solution do not decompose in this manner.[13]

XPS spectra of 3-TEP layers deposited from ethanol solutions with deposition times ranging from 1 min to 20 h all show roughly the same N:S ratio (see Table 1 and Figure 5), indicating that the loss of nitrogen is not a slow equilibrium process occurring on the surface, but happens upon adsorption. In fact,
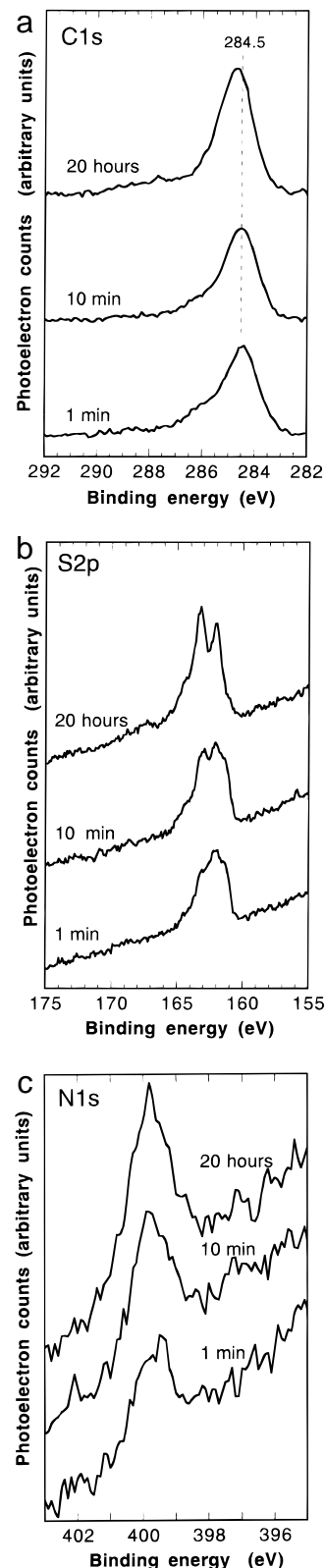

Figure 5. XPS spectra of 3-TEP on Au prepared from ethanol solutions using different adsorption times: (a) C 1s, (b) S 2p, (c) N 1s.

the total amount of adsorbed material increases slightly with longer adsorption time. Furthermore, the thiolate oxidizes slowly to a disulfide with increasing adsorption time, as indicated by the shift in the S 2p peak toward higher binding energy,[29] Figure 5b.

The main carbon C 1s peak moves to higher binding energy with longer absorption times, but the shift is less than 0.5 eV.

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TABLE 2: Relative Mass Spectrometer Intensities of Some Selected Fragments of TEP Molecules[a]

Mass m/e	Relative intensity	Tentative assignment	
128 127	12 46	**1**	
93	36	**2 = 1 - SH**	
80	100	**3a = 2 - CH₂** --> **3b**	
69, 68, 67	8, 58, 59	**4 = 3a - C, CH**	
66, 65, 64	21, 20, 23	**5a = 3a - CH₂** --> **5b** --> **5c**	
53, 52	51, 22	**6 = 3b - HCN**	

[a] Values were obtained by introduction of 1-TEP gas into the UHV system. Tentative assignments of the fragments are also given.

A plausible explanation of this observation could be that some molecules are lying flat on the surface at low and intermediate coverages, whereas they erect themselves and possess a perpendicular orientation at higher coverages. This would allow more 3-TEP molecules to adsorb, which is consistent with the increase in intensity for the C 1s, N 1s, and S 2p peaks with increasing adsorption time, as seen in Figure 5. A reorientation would also result in a decrease in the number of pyrrole rings that are attached to or appear close to the metal. Thus, the 283.9 eV peak disappears,[26] leading to an overall upward shift of the main C 1s peak.

A minor decrease is observed for both the C/S and the O/S ratios with increasing absorption times. This might be caused by a slow thermodynamic process in which carbon and oxygen contaminations are replaced by more strongly bound thiolates. The total number of adsorbed sulfur atoms measured with XPS is estimated to be 50% higher for 3-TEP than for 1-TEP. Ellipsometry measurements also indicate more material on the 3-TEP surfaces than on the 1-TEP ones.[13] This is not a surprising observation if most pyrrole rings are lost, leaving only short alkanethiol chains that can be more densely packed than the 3-TEP molecules bearing the bulky pyrrole ring. The high packing of short chain thiols would not occur if the 3-TEP molecules lost their bulky pyrrole group after the samples had been taken out of the solution, another indication that our assumption of a quick decomposition at adsorption is correct.

The advancing contact angles with water are $\theta_a = 51°$ for 3-TEP and $\theta_a = 72°$ for 1-TEP.[13] Interestingly, the value of the contact angle hysteresis, $\Delta = \theta_a - \theta_r$ (where θ_r is the receding contact angle) which is a measure of the chemical heterogeneity of a surface,[30] varies for the two layers. In the case of 3-TEP the hysteresis is high, $\Delta = 23°$ as compared to 8° for 1-TEP, indicating a more heterogeneous surface for 3-TEP. The surface most likely consists of intact 3-TEP molecules ($\approx$25%) mixed with some short alkanethiol chains, which are very reactive and immediately become oxidized into COOH species upon air exposure.[13] Thus, we conclude that 3-TEP is a far more sensitive molecule that undergoes decomposition at adsorption followed by oxidation, which leads to a complex and heterogeneous overlayer structure.

Mass Spectroscopy of 1-TEP Vapor in UHV. 1-TEP vapor was introduced into the UHV chamber with the mass spectrometer running. The m/e values from the strongest peaks registered are shown in Table 2 together with tentative assign-

ments. The molecule exhibits a specific cracking pattern. The mass of 1-TEP is 127 u, a mass at which a peak is observed, even though it is not the strongest one due to the cracking of molecules in the mass spectrometer. On the basis of references on the cracking pattern of other pyrrole components[15,22] we have given tentative assignments for all strong mass peaks registered;[12] see Table 2. Fragments with m/e value within ± 1 from the assigned value are often observed in organic molecules due to loss or capturing of a hydrogen atom. The smaller masses, such as 52 and 53, seen in Table 2 may also in part originate from contaminating hydrocarbon molecules in the UHV chamber, which limits the usefulness of studying these masses. The high-mass fragments that are specific for the investigated molecule and give strong signals, such as 80 and 93, are more suitable to use in the analysis. Introduction of gaseous 3-TEP into the chamber was not possible, but from the structural similarities of the two molecules we do expect a similar cracking pattern.

Thermal Stability of Solution-Deposited 1-TEP Layers. As stated above, IRAS spectra taken in UHV on 1-TEP monolayers deposited from solution show that a large fraction of the molecules stay on the surface without any structural change after heating to 370 K, Figure 2c, but that they are gone at 540 K. To investigate what happens between these temperatures and how the molecules leave the surface, temperature-programmed desorption (TPD) measurements were employed. Such measurements, done by heating the sample 15 K/min, on a solution-deposited 1-TEP layer exhibit a desorption peak at around 455 K, Figure 6a. As seen, the peaks for all the analyzed masses occur at the same temperature, indicating that the molecules do not decompose prior to desorption. The desorption temperature is comparable with those of other small organosulfur molecules on gold surfaces, such as the dimethyl disulfide studied by Nuzzo,[7] which desorbs at 473 K. Redhead[31] has proposed a method of calculating the activation energy of desorption from a TPD trace. Employing this method, assuming first-order desorption with the preexponential factor ν_0 set to 10^{13} s^{-1}, on the 1-TEP system we get an activation energy of desorption of 1.31 eV/molecule (127 kJ/mol). Moreover, the desorbing masses, Figure 7, give a different pattern than the pure 1-TEP gas. The smaller masses dominate, indicating that a significant fraction of the molecules break up into fragments before they reach the mass spectrometer. This fragmentation of 1-TEP most likely occurs at the desorption near 450 K and is therefore considered to be the main cause for the desorption of the molecule. Thus, the desorption of the 1-TEP is assigned to a thermally activated decomposition process of the intact molecules rather than to a specific cleavage of Au−S or C−S bonds.

Thermal Stability of UHV-Deposited 1-TEP Layers. Heating the sample exposed to 1-TEP in UHV yields the TPD traces shown in Figure 6b. The desorption is less distinct than in Figure 6a. This is a common phenomenon observed in TPD analysis of gas-phase deposited layers in UHV. Although we are dosing via a capillary ending a few centimeters in front of the sample, it is not possible to completely avoid that a fraction of gas molecules stick to the sample holder. These molecules will also desorb during the heating ramp and contribute to the background pressure. Thus they may interfere with those from the sample, leading to a broader and less distinct TDP trace. This problem does not occur for solution deposition since preparation is performed outside the UHV system, leaving the sample holder free from interfering molecules. It is seen that the maximum rate of desorption for UHV-deposited 1-TEP on
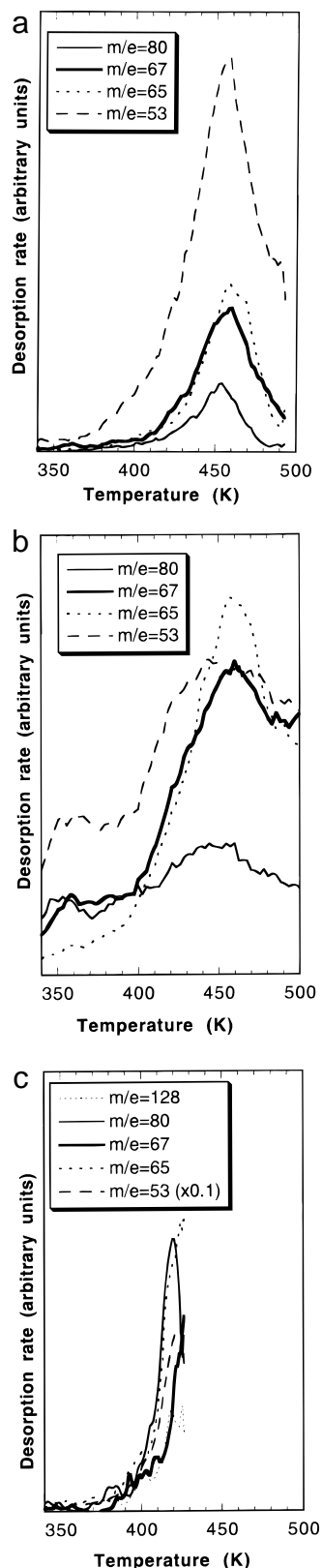
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Figure 6. Temperature-programmed desorption traces (heating rate 20 K/min) of (a) 1-TEP film deposited on Au from ethanol solution, (b) 1-TEP film deposited in UHV on Au, (c) 3-TEP film deposited on Au from vapor in air.

gold occurs at roughly the same temperature as for the solution-deposited layer. It can also be noted that the cracking patterns, Figure 7, display a similar trend; that is, the small masses seem to increase in intensity. Thus, both the gas-phase and solution-deposited layers of 1-TEP seem to decompose at desorption.
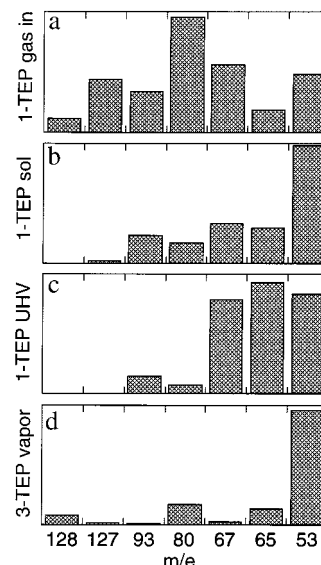

Figure 7. Relative intensities of detected mass fragments upon (a) introduction of gaseous 1-TEP into the UHV system, (b) TPD of solution-deposited 1-TEP, (c) TPD of UHV-deposited 1-TEP, (d) TPD of vapor-deposited 3-TEP.

Thermal Desorption of 3-TEP Layers Deposited from Vapor in Air. For a 3-TEP monolayer heated in UHV, the mass detector registers material leaving the surface at 420 K, which indicates that the 3-TEP molecules, or their decomposition products, are less strongly bound to the gold than 1-TEP (Figure 6c). For 3-TEP the activation energy of desorption is 1.21 eV/molecule (117 kJ/mol). The spread in desorption temperature for the different masses is larger than for 1-TEP, and some of them appear to desorb above 420 K, which is consistent with the assumption that the layer is composed of several different species desorbing at slightly different temperatures. The heating unfortunately had to be aborted at 430 K due to a too high background pressure in the chamber. As seen in Figure 7, the smaller, pure hydrocarbon, masses dominate the cracking pattern, even though some intact molecules are still detected, masses 128 and 127. This observation, together with the XPS data, which show more S atoms but fewer N atoms in the 3-TEP than in the 1-TEP layers, further confirms the conclusion that the 3-TEP molecules have, to a large extent, lost their pyrrole rings at adsorption, whereas the 1-TEP molecules adsorb as intact entities. This conclusion seems at first glance to contradict the cracking patterns in the high-mass region in Figure 7, which show that a larger fraction of intact molecules are desorbing from the 3-TEP layer (cf. mass 128 in 3-TEP and 1-TEP patterns). A possible explanation of this phenomenon is that 1-TEP, which desorbs at a slightly higher temperature than 3-TEP, decomposes at desorption, while the intact 3-TEP molecules ($\approx$25% of the molecules in the complex layer) in the 3-TEP layer desorb as intact entities. The high fraction of low masses in the desorption from 3-TEP may very well reflect the composition on the surface; that is, it originates presumably from decomposed 3-TEP molecules on the surface.

Electrochemical Cycling of 1-TEP Monolayers. The cyclic voltammogram for 3-TEP shows three anodic current peaks at +0.56, +0.60, and +0.75 V.[14]

After the 1-TEP monolayer was electrochemically cycled to +0.85 V, beyond the three peaks, its XPS spectrum changed (Figure 8). The total amount of sulfur dropped by 22%, suggesting a partial desorption. Furthermore, the shape of the S 2p peak changed from a typical thiolate form to a mixture of
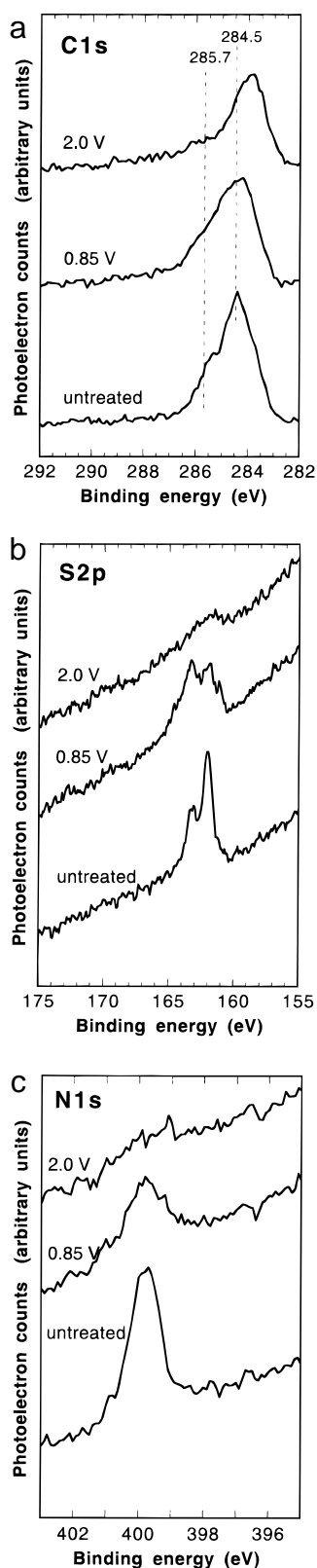
Figure 8. XPS spectra of 1-TEP on Au (a) C 1s, (b) S 2p, (c) N 1s electrochemically cycled to different voltages (vs Ag/AgCl).

thiolate and disulfide.[29] The amount of carbon also decreased, especially the high-binding-energy carbon, and the main peak moved toward lower binding energies. The high-binding-energy part of the peak originates from carbon atoms bound to electronegative atoms, such as nitrogen and sulfur, implying that some intact 1-TEP molecules had left the surface. The

N/S ratio decreased from 0.9 in uncycled 1-TEP to 0.6 in the cycled sample, which furthermore suggests that some molecules decomposed, losing the pyrrole ring, or parts of it, upon cycling.

Cycling to +2 V (Figure 8, upper trace) causes desorption of most of the 1-TEP layer, leaving some trace carbon shifted toward lower binding energies. Only a very small amount of sulfur and nitrogen can be detected; see Figure 8. The carbon atoms that are left seem to have a binding energy as low as 283.8 eV, which is consistent with carbon atoms close to the surface.

Electrochemical Cycling of 3-TEP Monolayers. The electrochemical behavior of solution-deposited 3-TEP is far more complex than for 1-TEP. Figure 9 shows C 1s, S 2p, and N 1s spectra taken at different potentials: 0.4, 0.8, and 1.4 V as well as the spectrum of an untreated sample (the same spectrum as in Figure 5). The cyclic voltammogram for 3-TEP shows only one anodic current peak at +0.56 V.[14]

The S 2p region of all the electrochemically treated samples displays a mixture of thiolate and disulfide at 161−164 eV and a peak at 168.2 eV, which indicates that some kind of SO_x compound is formed.[32−34] It is interesting to note that the 168.2 eV peak appears already at 0.4 V, a potential well below the oxidation peak in the cyclic voltammogram. Thus, at 0.4 V no current has been flowing through the system.[14] The C 1s spectrum is also changed upon cycling to 0.4 V. The main peak is shifted upward 0.5 eV, and a broad new feature extends up to 290 eV. The exact mechanism causing these high binding energy peaks in both carbon and sulfur spectra to appear is unclear. A significant part of it may originate from atmospheric oxidation that occurred during transportation between the two different labs, 5 h in N_2 at room temperature. Note also that a small feature at 168 eV also is seen for the 3-TEP layer that has been kept in the 3-TEP solution for 20 h, Figure 5b. The uncycled sample (Figure 9, lower trace), on the other hand, was prepared by 10 min solution deposition followed by rinsing, drying, and rapid introduction into the UHV. Another possible explanation for the existence of highly oxidized carbon could be that traces of propylene carbonate electrolyte, used in the cycling experiments, still remain on the surface. This hypothesis is, however, ruled out as the C 1s peak of organic carbonates is expected to appear at even higher binding energies. Polycarbonate, for example, exhibits a strongly shifted C 1s peak at 290.4 eV.[35] Propylene carbonate also gives a strong and characteristic IR band at 1790 cm^{-1}, which is not seen in the IRAS spectra of cycled monolayers. Cycled monolayers display a C=O peak near 1720 cm^{-1} (data not shown). The N 1s peak, however, appears to be unaffected by cycling to 0.4 V.

When cycling to 0.8 V, past the current peak in the cyclic voltammogram,[14] no dramatic change is seen in the XPS spectra (Figure 9), apart from a small thiolate/disulfide conversion. Increasing the voltage to 1.4 V (Figure 9, upper trace) reveals an overall reduction of the C, N, and S peaks. The S 2p peak at 168 eV increases in intensity, indicating that even more thiolate has been oxidized to SO_x species, but a substantial amount of material still is left on the surface.

A somewhat surprising observation in the XPS spectra of 3-TEP is that strongly oxidized carbon and sulfur species are present already at 0.4 V, a potential well below the current peak in the cyclic voltammogram. Moreover, the XPS spectra of 3-TEP do not change upon increasing the potential to a value above the first current peak (0.8 V), whereas 1-TEP starts to decompose and desorb at this potential. It is reasonable to assume that the changes seen already at 0.4 V are chemical rather than electrochemical by nature. Thus, the 3-TEP
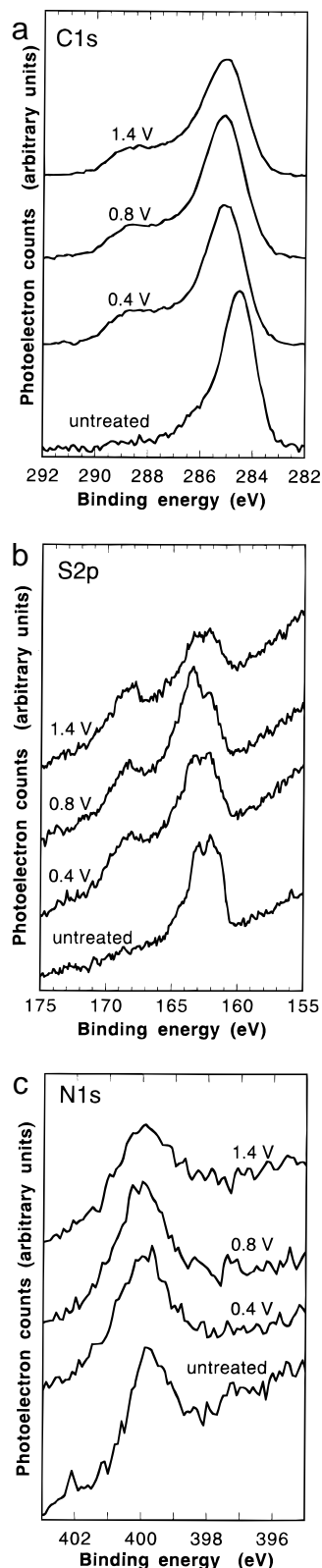
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Figure 9. XPS spectra of 3-TEP on Au (a) C 1s, (b) S 2p, (c) N 1s electrochemically cycled to different voltages (vs Ag/AgCl).

molecules have most likely oxidized during sample handling and transportation (5 h in N_2) into electrochemically more stable species which desorb at significantly higher voltages ($\approx$1.4 V). It is, however, mysterious that highly oxidized sulfurs (SO_x) can remain stable on the gold surface up to 1.4 V, as alkyl-sulfonates are easily rinsed off with water.[36] Further electrochemical work would be necessary to clarify this observation.

Conclusions

This paper follows up a number of previously published studies of the same molecules. We concentrate in this study on measurements in ultrahigh vacuum and report, for the first time, IRAS spectra without interfering with oxygen of 1-TEP and 3-TEP monolayers on gold. In addition to this, XPS and TPD measurements have been used to address the complex decomposition of these molecules at adsorption on gold, as well as during desorption. XPS has also been used to investigate the electrochemical stability of the TEPs.

Although the TEPs are structurally analogous, their oxidation, electrochemical, and stability properties in the adsorbed state vary substantially. The 1-TEP molecule adsorbs strongly and in an intact form on gold regardless of deposition method. The molecules do not thermally desorb until 455 K, corresponding to an energy of desorption of 127 kJ/mol. Oxygen exposure of the 1-TEP layer leads to chemical attack at the pyrrole ring and formation of C=O (C−O) species, in full agreement with the oxidation behavior of N-substituted pyrroles. Electrochemical cycling of 1-TEP causes thiolate−disulfide conversion followed by desorption of the oxidized molecule. Thus, 1-TEP on gold appears to be a well-behaved model system which displays properties similar to analogous short chain thiols on gold.

The 3-TEP/Au system is more complicated and displays many unexpected properties, which we believe is due to the inherent reactivity of the molecule. First of all, it decomposes immediately upon adsorption, forming a heterogeneous mixture of intact 3-TEP molecules ($\approx$25%) in a sea of decomposed short chain thiols of still unknown identity. However, it is known from previous studies that these decomposition products oxidize quickly if exposed to air to form carboxylic acid groups. The electrochemical properties of the 3-TEP layers are even more complicated. It seems that cycling to 0.4 V, a potential well below the current peak in the cyclic voltammogram, causes a substantial oxidation of the carbon and sulfur atoms. We find it difficult to assign this oxidation to a specific electrochemical process since almost no current has flowed through the electrochemical cell at this potential. Changes of the potential to a value above the first current peak did not influence the state of oxidation, suggesting that the effects seen in the XPS spectra are chemical by nature. Perhaps the 3-TEP molecules have oxidized into more stable species before cycling, a phenomenon which we think is due to the inherent oxygen sensitivity of 3-TEP. The electrochemical properties of 1- and 3-TEP with and without pyrrole in the supporting electrolyte and the suitability of using the TEPs as a glue to improve the adhesion with polypyrrole are discussed elsewhere.[14,37]

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