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Determination of molecular orientation in ultrathin films of aminophenylthiolate on Cu(100) prepared by vapour phase deposition

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Abstract

Ultrathin layers of aminophenylthiol on Cu(100) were prepared by vapour phase deposition of 4,4'-diaminodiphenyldisulphide (DAPS). Composition and molecular orientation in the films were determined by X-ray photoelectron spectroscopy (XPS) and near edge X-ray absorption fine structure (NEXAFS) spectroscopy. DAPS molecules adsorb on Cu(100) by dissociation of the intramolecular S–S bond and the formation of aminophenylthiolate at the copper surface. NEXAFS spectra indicate the presence of well-ordered monolayers with the plane of the phenyl ring tilted by 24° with respect to the surface normal. The same tilt-angle is found in the submonolayer regime.

The fabrication of organic surfaces has recently attracted considerable interest since it has been realized that the functionalisation of *n*-alkanethiols ($CH_3(CH_2)_nSH$) can be conveniently used to achieve this goal. By choosing a particular terminating group the physical and chemical surface properties can be precisely tailored [1,2]. These new possibilities regarding the synthesis of well defined monolayers of variable composition are based on the fact that the adsorption of *n*-alkanethiols from solution onto metal surfaces (Au, Cu, Ag) leads, via spontaneous self-organisation, to well-ordered films. The structural and physical properties of these selfassembled monolayers have been characterized by a large variety of techniques (infrared spectroscopy [3,4], NEXAFS [5], X-ray diffraction [6], He atom scattering [7]). From a chemical point of view the methyl-terminated "organic surfaces" resulting from adsorption of the *n*-alkanethiols are not particularly interesting. If, however, the terminating methyl group is replaced, i.e. by a carboxyl group, the resulting surface consists of –COOH groups, is strongly hydrophillic (in contrast to the hydrophobic methyl-terminated surface [8]) and offers interesting chemical properties. For example it is conceivable to exploit the high specific reactivity of $-NH_2$, another possible endgroup, with pyromellitic dianhydride (PMDA, $C_{10}H_2O_6$), to grow a monolayer of PMDA on an amino-

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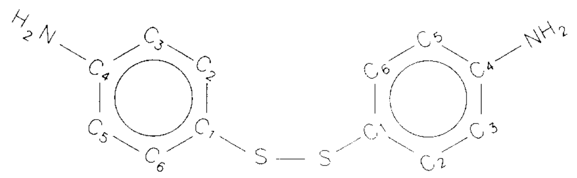

Fig. 1. The 4,4'-diaminodiphenyldisulphide (DAPS) molecule and the labelling of the carbon atoms.

terminated surface by chemical epitaxy.

In previous work [3–5] it has been shown that a certain length of the alkyl chains linking the two functions is required to obtain monolayers which are well-ordered at room temperature. The high number of gauge-conformations present in short alkanethiols can be reduced only by increasing the number of CH_2 groups to more than approximately 12–16 [5]. These long functionalized alkanethiols are, however, inappropriate for investigations in UHV, as the long alkyl chains significantly lower the vapour pressure and make a vapour phase deposition (VPD) very difficult or impossible [9].

On the other hand, investigations in UHV with well established surface sensitive techniques (XPS, NEXAFS, UPS) are necessary to analyze the monolayer film growth, to characterize the properties of the organic surface and to obtain information on the mechanism of the subsequent chemical epitaxy, the latter being also carried out by a VPD process.

In addition, an alkyl chain linking the SH and the NH_2 group is apparently not rigid enough to overcome the high surface energy of an amino-terminated surface (the amino group carries a significant dipole moment of approximately 1.2 D [10]), Si surfaces covered with aminoalkyltriethoxysilanes are generally found to be hydrophobic [11].

In this paper we report on the successful fabrication of a NH_2-terminated surface from a molecule, where another more rigid link, namely a phenyl group, is used between the anchoring thiol group and an amino endgroup. The 4,4'-diaminodiphenyldisulphide (DAPS) molecule (Fig. 1) adsorbs on metals by the cleavage of its intramolecular disulphide bond and the formation of an aminophenylthiolate species which is linked by a covalent sulphur–metal (thiolate) bond [12] to the substrate. As a result of the short "chain-length" the vapour pressure of the DAPS molecule is sufficiently high to produce ultrathin films by vapour phase deposition. Despite the short length the aminophenylthiolate is expected to exhibit sufficient stability to form well-ordered films because of the high rigidity of the phenyl group.

Previously phenylthiolate monolayers have been produced by vapour phase deposition of phenylthiol on two metal surfaces, Mo(110) [13–15] and Cu(111) [16]. In both cases the formation of an oriented phenylthiolate species (with a metal–S–phenyl bond) has been reported. On Mo(110) it was possible to determine the angle between surface normal and phenyl plane by NEXAFS and a value of 23° [13–15] has been found.

All experiments were carried out in ultrahigh vacuum systems with a base pressure better than 1×10^{-9} mbar. Cu(100) single crystal surfaces were prepared by repeated cycles of Ar^+ ion sputtering and subsequent annealing to 1000 K. The structural quality of the Cu(100) single crystal surfaces was controlled in regular intervals by LEED. XP spectra were recorded before each deposition in order to ensure cleanliness of the Cu substrate.

Films of different thicknesses of 4,4'-diaminodiphenyldisulphide (obtained from Riedel de Haen) were prepared by exposing the sample to the DAPS flow from a stainless steel Knudsen cell with a 100 μm aperture held at 350 K. The thickness of the deposited film could be controlled by varying the exposition times and the distance (7–20 cm) between the cell and the sample. The sample was held at room temperature during all depositions.

XPS experiments were performed with a SSI spectrometer using Al Kα radiation and a pass energy of 50 eV for the energy analyzer. A work-function decrease of 0.3 eV was observed (by a shift of the secondary electron cutoff in the UP spectra) when a clean Cu(111) surface was covered with a DAPS monolayer, in reasonable agreement with previous data for phenylthiolate on Cu(111) [16]. The work function for a monolayer of aminophenylthiolate on Cu(100) can be estimated to 4.3 eV by taking the known work function for Cu(100) of 4.6 eV [10] and assuming the same relative shift as for APT on Cu(111).

The NEXAFS experiments were carried out at HE-TGM2 monochromator at the Berlin electron synchrotron BESSY. Partial electron yield detection with a retarding voltage of −150 V was used for all measurements. The raw data was normalized to the incident photon flux by division through spectra obtained for a clean gold surface. Subsequently the substrate contribution was removed by subtracting a spectrum for the clean Cu(100) surface so that zero intensity was obtained at 280 eV. Energy calibration was performed by recording spectra of several known substances, in particular multilayers containing pyromellitic dianhydride (PMDA) with sharp resonances at 284.6 and 287.0 eV [17].

Fig. 2 shows deconvoluted S 2p XP spectra recorded after the deposition of different amounts of DAPS on Cu(100). The film thicknesses were determined from the attenuation of the Cu $2p_{3/2}$ XPS peak (E_B = 932.4 eV), using a value of 12 Å for the photoelectron mean free path. As a result of spin–orbit interaction the S 2p XPS line has a doublet structure with a splitting of 1.2 eV and an intensity ratio of 1.84 (S $2p_{3/2}$/S $2p_{1/2}$). Hence the bottom spectrum shown in Fig. 2 for a film with a thickness of 4 Å shows the presence of only one sulphur species with a binding energy of 162.2 eV for the S $2p_{3/2}$ peak. In accordance with previous work on the adsorption of phenylthiol on Mo(110) [13–15] and on Cu(111) [16] this peak is assigned to the presence of a thiolate species, where the S atoms are bond directly to the Cu substrate. With increasing deposition time a second sulphur species at higher binding energy (E_B = 163.2 eV) emerges in the XP spectra for film thicknesses of 18 and 42 Å, while the peak at lower binding energy decreases in intensity, see Fig. 2. From comparison with thick films prepared from solution the peak at higher binding energies can be assigned to S atoms in intact DAPS molecules. All S 2p spectra obtained for VPD deposition of DAPS on Cu(100) could be fitted by a combination of two doublets related to the two different S species in the thiolate (Cu–S–phenyl bond) and in the dimer (phenyl–S–S–phenyl bond). Hence, the S 2p XP signal can be used to distinguish between monolayers of aminophenylthiolate and multilayers of DAPS.

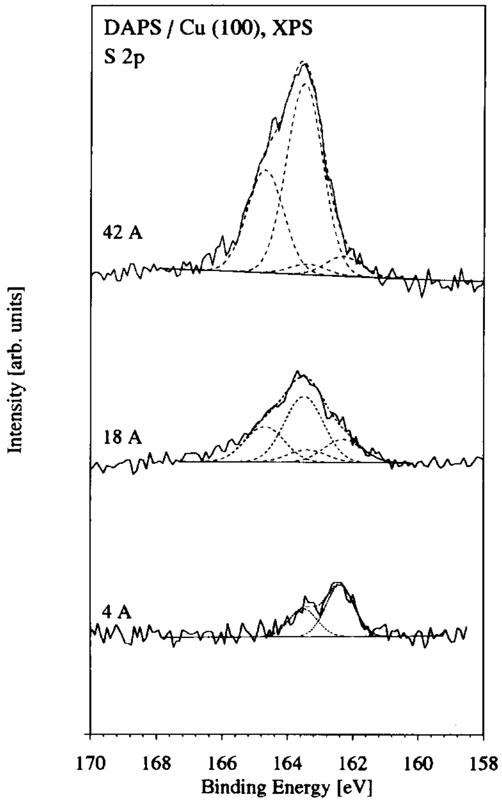

Fig. 2. S 2p X-ray photoelectron spectra of aminophenylthiolate films on Cu(100) prepared by vapour phase deposition of DAPS molecules. Film thicknesses were determined by the attenuation of the Cu 2p XPS peak.

C 1s and N 1s XP spectra (not shown) show only subtle changes for different film thicknesses ($\Delta E_B \leq 0.2$ eV for N 1s) between mono- and multilayers, which can be explained by relaxation effects. A direct interaction between the amino- or phenylmoieties and the substrate can be ruled out on the basis of this data.

On the basis of the XPS data we therefore conclude that in the first layer DAPS molecules dissociate by bond scission of the intramolecular S–S bond and aminophenylthiolate (APT) is formed which bonds to the Cu(100) surface atoms through the sulphur atoms, in agreement with previous work [13–16]. After completion of the APT monolayer DAPS molecules adsorb intact and form multilayers.

To determine the growth mode of the monolayer the C 1s, N 1s and S 2p XPS intensities were measured as a function of deposition time. At long (20 cm) distances between the Knudsen cell and the sample the XP signal intensity increase was consistent with a sticking coefficient close to unity. It is noteworthy that by dosing at this distance, even for very long deposition times, no multilayer signal was observed in the S 2p XP spectra. For the formation of DAPS multilayers a short (7 cm) sample–cell distance, i.e. a high partial pressure of DAPS, is necessary.

Heating of the monolayer to 400 K resulted in major changes in the XPS data. The S 2p peaks were shifted approximately 1.0 eV towards lower binding energies. The C 1s signal was observed to decrease in intensity and the N 1s peaks disappeared completely. These observations are consistent with a thermally activated dissociation of the aminophenylthiolate at 400 K, involving a cleavage of the C–S bond and the desorption of NH containing species. Only atomic sulphur and carbon fragments are left on the Cu(100) surface. A similar behaviour was observed for phenylthiolate/Mo(110) [13,18], but in that case the onset of thermal C–S bond scission occurred below room temperature. On Cu(100) no indication of thermal decomposition of aminophenylthiolate was observed for temperatures below 400 K.

Fig. 3 shows two C 1s NEXAFS spectra of a DAPS monolayer on Cu(100) acquired at glancing (20°) and normal (90°) photon incidence, respectively. The strong variation of the different spectral features with photon angle of incidence directly reveals a high degree of molecular orientation. From the amount of angular variation of the different resonance intensities the molecular orientation can be determined quantitatively [19]. In order to do this, however, the spectrum has to be deconvoluted to obtain the different resonance intensities. This in turn requires precise knowledge about the position of these resonances and their assignment.

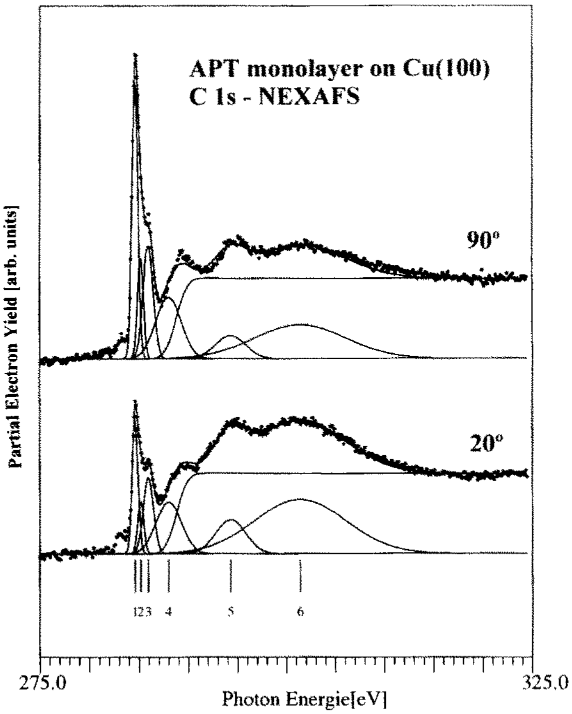

Fig. 3. C 1s NEXAFS spectra of a monolayer of aminophenylthiolate (APT) on Cu(100). The spectra were acquired at glancing (20°) and normal (90°) photon incidence, respectively.

The assignment of the various resonances observed in our C 1s NEXAFS spectra shown in Table 1 is based on previous work for phenylthiolate on Mo(110) [13–15] and aniline on Ag(110) [20], on our data for DAPS multilayers (see below) and on results of selfconsistent quantum chemistry calculations (SCF-AM1 [21,22]). The molecular orbital energies resulting from these calculation for the lowest unoccupied MOs cannot be directly related to the experimental data since the presence of the core hole created in the photoionisation process lowers the MO energies by several eV. In order to account for this relaxation (which also depends on the location of the core hole) the equivalent core approximation [19] has been employed.

The most prominent features in the NEXAFS spectrum of the aminophenylthiolate monolayer are two intense, sharp peaks with maxima at

Table 1
Curve fit parameters for NEXAFS spectra recorded for a thin film (4 Å) aminophenylthiolate on Cu(100) (fit parameters for a diaminodiphenyldisulphid multilayer are shown in parentheses; an error-function was used to model the step-edge as described in Ref. [15])

	E (eV)	FWHM (eV)	Assignment
Edge	288.8	3.0	
1	284.62	0.7 (0.59)	π_1^* $C_{2,3,5,6}$
2	285.18 (285.07)	0.7 (0.59)	π_2^* C_4
3	285.95	1.2 (0.94)	π_2^* C_1
4	288.00 (287.24)	3.0 (3.4)	π_3^*, σ^* (C–S)
5	294.30	3.6	σ^* (C–C)
6	301.4	11.0	σ^* (C–C)

284.6 and 286.0 eV. As shown in Table 1 the first peak is related to a superposition of the excitation from the 1s level of C_2 and C_3 into a π^* orbital which is derived form the lowest unoccupied π_1^* orbital (LUMO) of ground-state aminophenylthiol and the excitation from the 1s level of C_1 into another orbital which is derived from the second lowest π_2^* orbital. The sharp second peak in the NEXAFS spectra at 286.0 eV is assigned to a transition of the C_4 1s electron into an unoccupied orbital derived from the second lowest π_2^* orbital in aminophenylthiol (resonance 3 in Fig. 3). This is in agreement not only with our calculations but also with the fact that the energy difference to the main π_1^* resonance is the same as observed for aniline [20].

As in the case of aniline and phenol [20], the energy difference between the resonances 1, 2 and 3 is not only due to different molecular orbital energies (final state effects) but also to chemical shifts of the C 1s levels (initial state effect) as seen in XP spectra. Whereas the C 1s XPS energy for $C_{2,3,5,6}$ amounts to 284.2 eV, the core-levels of C_1 and C_4 are shifted by 0.5 and 1.3 eV to larger binding energies due to the interaction with the thiol and the amino group, respectively. Note that in benzene the corresponding π_1^* and π_2^* orbitals are degenerate, in aminophenylthiolate the degeneracy is lifted due to the presence of the amino and thiol groups. Because of final state symmetry excitation from the 1s states of C_1 and C_4 into π_1^* is not possible. In addition to this selection rule our SCF calculations show that the π_2^* orbital has only small electron density at $C_{2,3,5,6}$ and a high density at C_1 and C_4, thus corroborating the above assignment of resonance 1 to the transition from the 1s levels of $C_{2,3,5,6}$ into the π_1^* orbital and of resonances 2 and 3 to transitions from C_1 and C_4, respectively, into the π_2^* orbital.

In following previous NEXAFS studies of phenylthiolate on Mo [13,14] we attribute peak 4 to the π_3^* resonance and the broad peaks centred at 294 and 301 eV (5,6) to σ^* (C–C) resonances.

The deconvolution of the NEXAFS spectra for APT monolayers shown in Fig. 3 is based on the above peak assignment, assuming an energy of 288.8 eV for the absorption step-edge. This energy is obtained by adding the mean value of the C 1s XPS energies and the work function of the APT-covered Cu(100) surface (see above). No clear evidence was found for the σ^* (C–S) resonance as reported in a previous analysis of NEXAFS data for phenylthiolate on Mo(110) [13–15]. The identification of this resonce should be straightforward as its intensity should show the opposite variation of intensity with photon angle of incidence than the π^* peaks and thus be strongest at grazing incidence. By comparison with the multilayer data (see below) a tiny feature at 288.5 eV observed at grazing incidence in Fig. 3 can possibly be related to this resonance.

The variation of the intensity I_m of a given NEXAFS resonance corresponding to an excitation of a C 1s electron into a molecular orbital m with angle of incidence of the photons θ obtained from the deconvolution of the NEXAFS spectra can now be used to determine the molecular orientation. This analysis is based on the angular variation of the excitation probability

$$I(\theta) = |\langle \boldsymbol{E}, \boldsymbol{T}_m \rangle|^2,$$

where the transition dipole moment $\boldsymbol{T}_m$ is given by the matrix element [19]

$$\boldsymbol{T}_m = \langle \psi_{\mathrm{C\,1s}} | \boldsymbol{r} | \psi_m \rangle,$$

where $\psi_{\mathrm{C\,1s}}$ and ψ_m are the molecular orbitals for a C 1s and the (relaxed) empty molecular orbital m, respectively. $\boldsymbol{r}$ denotes the distance operator. As $\psi_{\mathrm{C\,1s}}$ is strongly localized at the respective C atom, $\boldsymbol{T}_m$ is oriented parallel to the vector $(\psi^m_{p_x}, \psi^m_{p_y}, \psi^m_{p_z})$, where the components correspond of the contribution of the three 2p atomic orbitals to the molecular orbital m. The latter information can be obtained directly from our calculations and shows that for the π^* resonances $\boldsymbol{T}_m$ is oriented perpendicular to the phenyl ring, as expected by the simple "building-block" scheme [19].

The parameters used in the deconvolution process are shown in Table 1. In principle the angular variation of any resonance in the NEXAFS spectra can be used to determine the average molecular tilt-angle, but the resonances suited best for this procedure are those which are clearly separated from the rest of the spectrum. From Table 1 it is obvious that resonance 1 (corresponding to excitations into the π^*_1 resonance of the phenyl ring) fulfils these requirements best. From the intensity ratio $R_1 = I_1(90°)/I_1(20°)$ of 2.05 and using a value of 95% for the degree of polarisation of the incident photons this yields an angle of 23.8° between the plane of the phenyl ring and the surface normal [19]. The intensity ratios of the other resonances are somewhat smaller, which is explained by the nonvanishing overlap between different resonances. For the π^*_2 resonance 2 an intensity ratio of $R_2 = 1.93$ is obtained, which would yield a tilt-angle of $\alpha = 24.6°$. This difference of about 1° has about the same size as other sources of experimental error (e.g. precise value of degree of polarisation). The largest error in a determination of a tilt-angle arises from the normalisation of NEXAFS intensities to the step-edge height, which was determined from the NEXAFS intensity at 325 eV. EXAFS oscillations which are possibly present at this energy [19] may have different amplitudes for grazing and perpendicular photon incidence and can in principle lead to an error in peak intensities. In our data, however, EXAFS oscillations above 310 eV appear to be smaller than the noise in the data. Altogether we estimate the error in peak intensities from this normalisation procedure to be smaller than 5%, which corresponds to an error of about 1° in the tilt-angle determination. An error bar of 3° thus provides an upper limit to the experimental uncertainties and we conclude that the average tilt-angle of APT on Cu(100) amounts to 24° ± 3°.

In order to investigate the orientation for aminophenylthiolate on Cu(100) for smaller coverages NEXAFS spectra were also recorded in the submonolayer-regime starting at ~ 30% of a monolayer. The intensity ratio of the π^*_1 resonance for perpendicular and glancing incidence did not show any significant dependence on coverage in the submonolayer regime. The absence of a coverage dependent reorientation seems thus to indicate that the Cu–S–phenyl bond-angle is rather well defined and effectively determines the molecular orientation also for small coverages.

An important support of our peak assignment is provided by investigating multilayers of diaminodiphenyldisulphid. A typical NEXAFS spectrum for a $d \geq 60$ Å film is shown in Fig. 4, together with a deconvolution using the parameters given in Table 1. The spectrum is qualitatively similar to the spectra for the aminophenylthiolate monolayers (Fig. 3), but in this case no strong variation of resonance intensities with photon angle of incidence is observed, indicating a more random arrangement of DAPS molecules in the multilayer. Note that the slope of the absorption step used in the deconvolution is much larger than for the APT monolayer. This difference is due to the fact that in the monolayer case the primary electrons generated in the photoionisation process are backscattered by Cu substrate atoms instead of C atoms in the multilayer case. Cu atoms have a strongly different variation of backscattering amplitude with electron energy and as a result the EXAFS contributions decrease considerably slower with energy in the monolayer case [19].

The deconvolution of the multilayer data reveals only minor changes with respect to the data for the aminophenyl monolayer, see Table 1. The halfwidth of the two π^* resonances is slightly

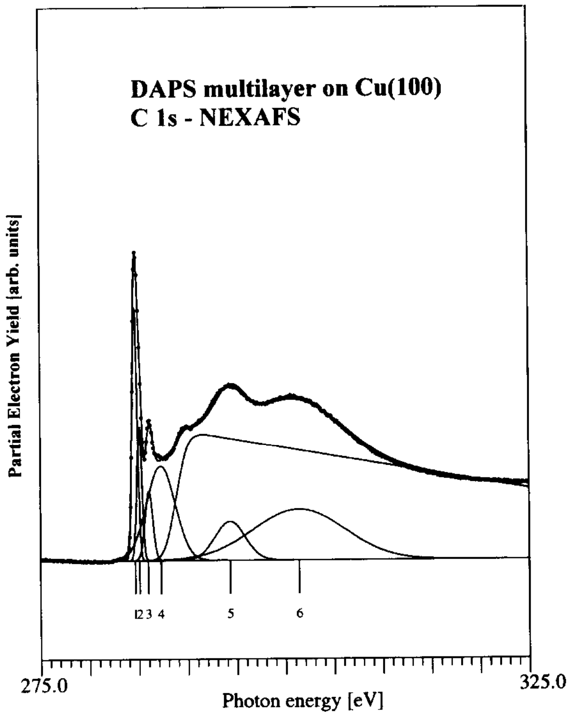

Fig. 4. C 1s NEXAFS spectra of multilayers $d \geq 60$ Å of diaminodiphenyldisulphid (DAPS) on Cu(100). No variation of resonance intensities for different angles of photon incidence was observed.

smaller than for the monolayer (0.6 eV compared to 0.7 eV), and the π_2^* resonance is found to shift by ~ 0.1 eV to smaller values, while the position of the π_1^* is found to remain unchanged. This small shift is probably insignificant and may be due to the fact that the deconvolution was carried out using Gaussian lineshapes, while the peaks are known to be slightly asymmetric [19]. The resonance (4) which is assigned to π_3^* and σ^* (C–S) occurs at slightly lower energies in the DAPS multilayer. This can be attributed to a change in the energy of the σ^* (C–S) resonance because of the presence of a C–S–S–C bond instead of a metal–S–C bond.

In conclusion, we have demonstrated that oriented monolayers of aminophenylthiolate can be grown on Cu(100) by vapour phase deposition of diaminodiphenyldisulphid. The resulting amino-terminated organic surfaces have been successfully used to grow oriented films of pyromellitic dianhydride by chemical epitaxie [22]. The APT binds to the substrate via the sulphur atom and its phenyl ring exhibits an average tilt-angle of 24° ± 3° between surface normal and phenyl ring plane. The same orientation is observed in the submonolayer-regime. After completion of the APT monolayer further deposition of DAPS leads to a weakly bonded multilayer of randomly oriented DAPS molecules. The fact that the orientation angle observed in our word is the same as observed for phenylthiolate adsorbed on Mo(110) [13,19] indicates that the orientation of the APT group is mainly given by the metal–phenylthiolate bond-angle and only to a lesser extent by intermolecular interactions within the phenylthiolate or aminophenylthiolate monolayer.

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