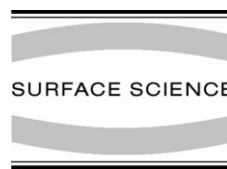




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# STM and STS investigation of ultrathin tin phthalocyanine layers adsorbed on HOPG(0001) and Au(111)

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## Abstract

The initial adsorption of tin phthalocyanine (SnPc) on graphite and gold surfaces was studied by low-temperature UHV-STM. At submonolayer coverages on highly oriented pyrolytic graphite (HOPG), SnPc forms substrate-defined molecular chains, while SnPc monolayers reveal dense packed structures with the molecules symmetry. A comparative study with CuPc on HOPG reveals similar chains in the submonolayer regime. No chains were found upon SnPc adsorption onto Au(111). At ordered SnPc/HOPG films with thickness around one monolayer, local  $I(V)$  curves were collected with high reproducibility. Their wide energy gap shows the semiconductive properties of the SnPc monolayers. A strongly increased differential conductivity was observed at distinct energy values. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Scanning tunneling microscopy; Scanning tunneling spectroscopies; Epitaxy; Physical adsorption; Self-assembly; Graphite

## 1. Introduction

Metal phthalocyanines have attracted the interest of research already for some time because of their bulk semiconductivity and in some cases one-dimensional ohmic conductivity. One reason for research in this field is that there is hope that phthalocyanines may play an important role in new electronic devices based on organic molecules [1]. Furthermore, thin films of metal phthalocya-

nines can be used as highly specific gas sensors [2–4]. Therefore, the knowledge of their structural and electronic behaviour both as bulk crystals and as molecular adsorbates on well-defined substrates is essential. In recent time, the structure of several phthalocyanine adsorbates on crystalline substrates has been investigated mainly by scanning tunneling microscopy (STM) [5–10] and low energy electron diffraction (LEED) [11,12]. Their electronic structure has been measured by ultra-violet photoelectron spectroscopy [13,14], X-ray photoelectron spectroscopy [14], inelastic electron tunneling spectroscopy [15] and scanning tunneling spectroscopy (STS) [16–18]. Theoretical work has considered both the structural [19,20] and the energetic [21] configuration of phthalocyanines adsorbed on a substrate.

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In this work, we have studied the adsorption behaviour of SnPc at submonolayer and monolayer coverages. All metal phthalocyanines are similar in their general molecular structure. A more or less flat phthalocyanine skeleton surrounds the central metal atom, as shown in Fig. 1. Since the ionic radii of the two metals are different, their special molecular structure differs slightly: CuPc is perfectly flat, whereas SnPc has a protruding tin atom because of the big ion radius of Sn, which is bigger than the cavity in the phthalocyanine backbone. For the free SnPc molecule, Day et al. have proved this by density functional theory calculations [20]. This protruding central atom makes the molecule interesting for a possible application in a single-molecular storage device: Either the tin atom is located on one side of the ring, or on the other. Both sites are not equivalent, as Day et al. have shown [20]. Also, the phthalocyanine skeleton of SnPc is not really flat: two opposite phthalodinitrile parts remain flat. In the relaxed state the others bend away to the side opposite of the tin atom. We will show, that the geometry of the SnPc molecule has a considerable influence on the STM image of the molecule. Using this, we may get information

about the three-dimensional orientation of the individual SnPc molecule on the substrate surface.

Until now, no adsorption data of SnPc are known at all. The same applies to STS data, which are of special interest for possible applications of the molecule. In contrast to this, STM data of CuPc multi and monolayers are readily available [7–9,22], but only few data exist about CuPc submonolayer films [6]. Therefore, some experiments with CuPc were added to round out the knowledge about the submonolayer growth of CuPc, and to have more reference data for SnPc.

## 2. Experimental

The whole work was carried out in a UHV system, consisting of a preparation and an analysis chamber, with a base pressure below  $2 \times 10^{-10}$  mbar. All preparations were done in the preparation chamber under control of a mass spectrometer, whereas the STM measurements were performed in the analysis chamber at a slightly lower base pressure. We have used a variable temperature STM (Omicron VT-STM) equipped with a liquid helium flow cryostat. The minimum sample temperature in this STM is 25 K, which is low enough to immobilize the molecules under investigation.

For all measurements electrochemically etched tungsten tips were used. To keep the thickness of the native tungsten oxide low, the tips were inserted into UHV immediately after preparation. Once in vacuum, they were annealed for several hours at 430 K to desorb water and other contaminants from the etch process. Higher annealing temperatures were not possible, since the tip carriers contained a ferromagnet. The substrates consisted of highly oriented pyrolytic graphite (HOPG), which was freshly cleaved immediately before insertion into UHV, and afterwards also annealed for some hours at 450 K in UHV.

The phthalocyanines, supplied by Aldrich, had a purity of 97%. No further purification was carried out outside the UHV. However, the material was outgassed for more than 100 h slightly below the sublimation temperature inside the UHV to evaporate volatile contaminants. Afterwards, the

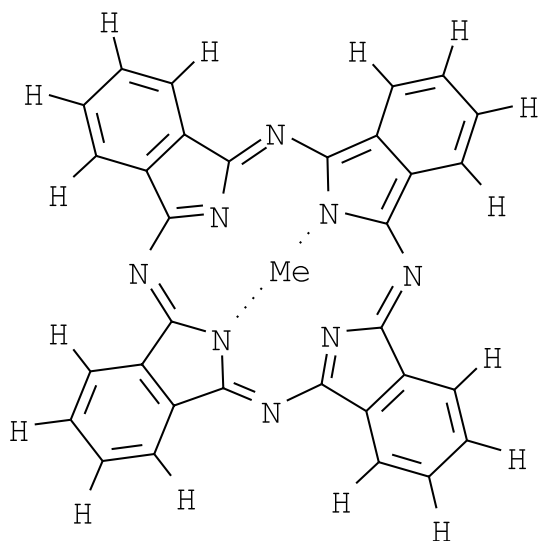


Fig. 1. Molecular structure of the metal phthalocyanines used in this work (Me = Sn, Cu).

evaporated material was checked by a quadrupole mass spectrometer for cleanliness. The sample preparation was started only when the mass spectrum did not contain any water peak.

Evaporation occurred from a home-made thermal evaporator with quartz crucible and chromel–alumel thermocouple, controlled by a Eurotherm temperature controller. If not mentioned else, the substrates were held at room temperature during evaporation. The thickness of the evaporated layer was determined by a quartz microbalance. The thickness measurement was done as follows: a low, constant flux was adjusted and measured until several nanometers of SnPc were grown. By downscaling the evaporation time at constant settings, films with thickness between 0.5 and 1 monolayers (ML) could be produced.

Special care was taken of the spectroscopic measurements. The tunnel contact was checked by  $I(z)$  curves for real tunneling, followed by image collection. Spectra were taken only on surface areas showing well-resolved and reproducible images.  $I(V)$  curves were collected at selected points, keeping the tunnel distance constant by shortly switching off the feedback loop. Only in cases of at least three similar successive spectra the data were evaluated to avoid influence of unstable tips or sample areas onto the STS data.

### 3. Results and discussion

#### 3.1. Sub-monolayer of CuPc on HOPG

Several groups have already studied the physisorption of CuPc monolayers on atomically flat surfaces, both by STM [7–9] and LEED [11,12], as stated already in the introduction. All of them have found well-ordered structures, with the molecules lying flat at the substrate surfaces. Depending on the substrate, these structures were mostly close-packed with fourfold symmetry of the adsorbate pattern caused by the symmetry of the phthalocyanine molecules. We have concentrated on the investigation of the very initial growth process of the CuPc/HOPG system. Therefore, a CuPc submonolayer was deposited onto a cooled substrate ( $\sim 220$  K), transferred to the STM, im-

mediately cooled with liquid He, and imaged at 62 K to freeze the molecular movement. The molecules appear as slightly distorted squares with a side length of 13 Å and a height of 3 Å. These values meet the expected size of CuPc very well. The reason for the slightly rhombic shape of the molecules is a scanner drift of the STM. A typical image of the overall molecular arrangement is shown in Fig. 2. It is obvious that the molecules are not uncorrelated distributed over the surface. Instead, they form short linear chains of mostly three to six in a line. Also the directions of the chains are not arbitrary: An analysis shows three main directions of the chains, which are connected to the three symmetry directions of the underlying graphite substrate. The fact that in Fig. 2 these directions are not exactly under 60° angles is again due to scanner drift. Furthermore, also within the chains the molecules are not rotated freely. Instead, they arrange in the same orientation with respect to the substrate. We suppose that this effect is due to intermolecular interactions. On the other hand, such well-ordered chains of molecules can also be considered as an initial stage in the formation of a close-packed two-dimensional molecular arrangement with fourfold symmetry, as

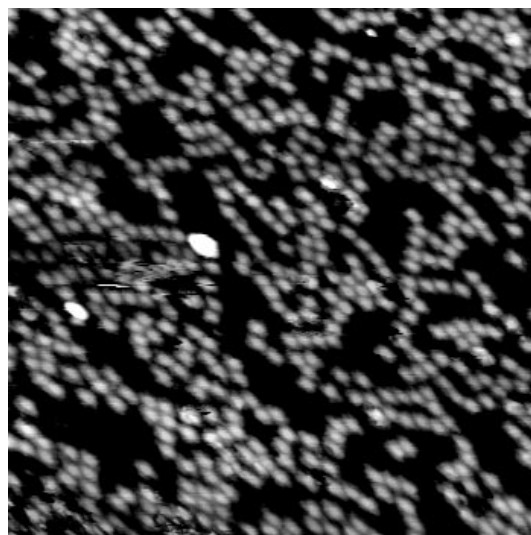


Fig. 2. 0.6 ML of CuPc on HOPG. Scan area  $44 \times 44$  nm<sup>2</sup>,  $U_T = 2.5$  V,  $I_T = 25$  pA, constant current mode. Temperature during measurement 62 K. Individual molecules can be observed clearly. The two bright particles are contaminations.

it has been found for the monolayer CuPc/HOPG adsorbate system e.g. in the work of Ludwig et al. [7].

### 3.2. STM investigation of SnPc submonolayers on HOPG

As CuPc, SnPc submonolayers on graphite (0001) also may not be observed by STM at room temperature because of the high mobility of the SnPc molecules on the graphite surface. In general the same preparation and cooling procedure as for CuPc was applied in the experiments with this material. Fig. 3 shows a sample, which has been coated with a nominally 0.5 ML film of SnPc on graphite. In contrast to the CuPc samples, it has been deposited onto the substrate at an elevated temperature of about 400 K. Therefore one should expect an increased order of the adsorbate structure compared to Fig. 2 (e.g. not only linear chains, but two-dimensional ordered domains), since the molecules should be able to find a stable position on the substrate's surface, as long as the sample remains at elevated temperatures. However, in the STM images we find no big domains, but again a clear formation of linear chains of

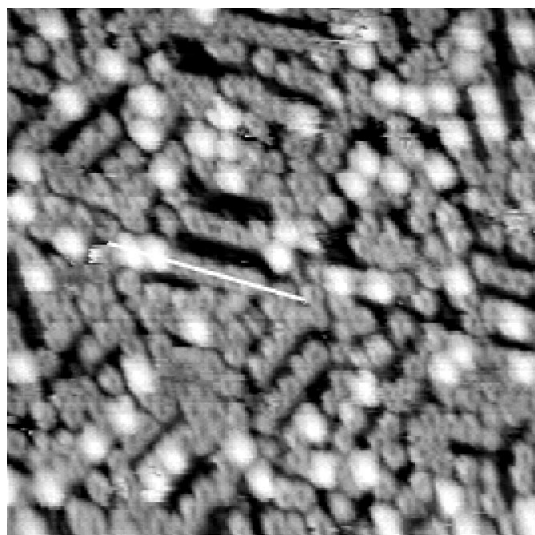


Fig. 3. SnPc on graphite, thickness 0.5 ML. Scan size  $34 \times 34$  nm<sup>2</sup>,  $T = 35$  K,  $V_T = 2.1$  V,  $I_T = 42$  pA. The white line indicates the location of the cross-section shown in Fig. 4.

molecules. These chains consist of typically three to six molecules as they do for CuPc. It is conspicuous, that the molecular chains are aligned along three dominant directions, which are defined by the surface unit cell vectors of the substrate. Until now, however, we have no knowledge about the real orientation of these directions relative to the unit cell vectors of the underlying graphite lattice.

A cross-sectional view along eight molecules within one line is shown in Fig. 4. Such cross-sections through constant current mode images reveal that the very bright areas are just twice as high as the other bumps. Therefore we assume that these parts of the image correspond to molecules forming a second layer of flat-lying molecules. It is interesting that the growth of a second molecular layer starts already long before the first layer is completed. This growth behaviour can also be found in Fig. 5, which shows a similar case as Fig. 3 at a higher molecular surface coverage.

Let us now discuss the individual molecules of Figs. 3 and 5. The molecules in the first layer have got a dark core, whereas the molecules of the second layer have a bright one. The question is now, if this observation is due to a mainly electronic or a mainly geometric effect. It is clear, that the tin atom protruding out of the molecular plane may cause such a behaviour geometrically: its centre rises out of the plane of the phthalocyanine skeleton by 1.1 Å, as is known from X-ray diffraction [23] (XRD) and ab initio calculations of the molecular structure [20] of SnPc. It is quite amazing that the molecules arrange with such a well-defined orientation in the first and second layers. Normally, one would expect an arbitrary distribution of molecules with bright and dark

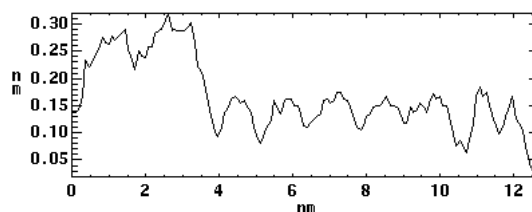


Fig. 4. Cross-section through a chain of molecules from Fig. 3. The two high hills correspond to two molecules of the upper layer, and the others represent molecules of the lower layer.

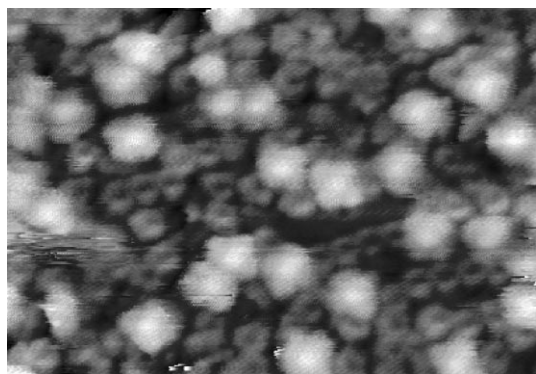


Fig. 5. First and second layers of SnPc on graphite, at another, slightly thicker film than shown in Fig. 3 (0.8 ML). In the second layer, the four-leafed structure of the SnPc molecules and their bright core is clearly visible, whereas the molecules of the first layer have got a dark core. Scan size  $22 \times 15 \text{ nm}^2$ ,  $V_T = 2.1 \text{ V}$ ,  $I_T = 41 \text{ pA}$ ,  $T = 35 \text{ K}$ .

centre in each layer. Such a geometrical interpretation is, of course, not the only one, which is possible. Since the STM images a local density of states profile, the spatial and energetic electron distribution in the molecules of the first and the second layer could be indicated to be different.

Let us discuss the electronic effect first: It is known from other experiments [24] that the central atom may play a significant role in how a metal phthalocyanine appears in the STM image. In most of the works planar phthalocyanines with dark core were found, as e.g. CuPc [5–8,25,28],  $\text{H}_2\text{Pc}$  [26], NiPc [24], independently on the underlying substrate and the tip bias. Sautet et al. [27] also found a dark core in their theoretical predictions for CuPc on Cu(100). Some of the MePc's, (as CoPc [28] and FePc [24]), however, appear with a bright core atom in the STM images, for all tip biases. After several studies with different metal phthalocyanines Lu et al. conclude [24] that the different occupation of electronic d levels of the core atom is the reason for the different appearance in the STM images. In case of half-filled  $d_{zz}$  orbitals a strong electronic coupling to the substrate occurs, resulting in an increased tunnel current and a bright appearance in the STM image. This is the case for CoPc and FePc, both having half filled  $d_{zz}$  orbitals. Our case, however, is different: Tin is not a transition metal, and there

are no partially filled d orbitals. The only other group-IV phthalocyanine used in STM investigations until now is lead phthalocyanine (PbPc). Therefore, we want to use this molecule as the reference substance for our further discussion. Several attempts have been made to investigate PbPc by STM, because PbPc has a similar pyramidal shape as SnPc and since there were ideas to use this shape in a single-molecular storage device. Only one work could show molecularly resolved STM images of PbPc. In this study, Strohmaier and co-workers observed a PbPc monolayer adsorbed on  $\text{MoS}_2$  [29]. They found, that in the case of PbPc two different intramolecular patterns could be found, one showing a bright core, and the other showing a dark one. Immediately after the sample preparation, both cases occurred with the same probability, and mixed layers were observed. Therefore, not a different electronic coupling to the substrate, but a geometric effect due to the pyramidal shape of the molecules was concluded. Simply spoken, half of the molecules pointed upwards, the other half downwards. After one or more days, however, only molecules with a dark core could be found, indicating a kind of molecular reordering. Since a rotation of the whole molecule is unlikely, they assumed a tunneling of the central atom to the other side of the Pc skeleton. Strohmaier et al. describe this process as a kind of relaxation.

Now we return to the STM images shown in Figs. 3 and 5. We find only molecules with a dark core in the first layer. As for PbPc, one should expect a mixed layer of molecules with a bright core or a dark core, due to the similar geometric and electronic structure of PbPc and SnPc. A comparison of the intramolecular appearance of SnPc with that of the transition metal Pc's, however, is much more problematic because of the much more different electronic structure of the core atom. Whilst the outer electronic structures of tin and lead are rather similar, their ionic radii differ significantly. This helps us to explain the effect, why only molecules with a dark core were found in our STM images: If we consider the central atom traversing through the plane of the phthalocyanine backbone, this may occur with a much higher probability for tin than for lead

because of its significantly smaller ion radius. Thus, a faster rearrangement for tin than for lead (where the switching time was about one day) should be expected, which is really the case: Our measurements were carried out between 30 min and several hours after preparation of the film. Also the fact, that we have evaporated the SnPc to a warm substrate, should lead to a faster relaxation. Therefore, we observe only relaxed molecules in our STM images. Still, we have no idea about the driving force for this effect. It should be electronically caused, but only molecular electronic calculations of the molecule and its substrate, which should include also the f electrons, can solve the problem.

Next, the contrast of the central atom in the second molecular layer is interesting: All the molecules seem to have a bright core; no exceptions were found (see Fig. 5). We suppose that these molecules are geometrically ordered, as they do for the first layer, but this time with the central atom directed upwards. On the other hand, an electronic imaging effect cannot really be excluded for the explanation, since the conduction mechanism through such molecules is not yet clear.<sup>2</sup>

Let us now regard the outer shape of the molecules. In the upper layer they clearly show their fourfold symmetry and the bright tin atom. On the other hand, the SnPc molecules of the first layer are imaged as more or less bowl shaped and not as a four-leafed clover. On the first glance this is amazing, however it may be explained by the intramolecular bending of the phthalodinitrile parts of the molecule, which form a slightly bowl-shaped molecular framework: Day et al. [20] have shown by density functional based calculations for the free SnPc molecule that two opposite lying phthalodinitrile groups bend away from the tin atom's side, whereas the other two remain nearly flat. As mentioned before, they found that the Sn atom protrudes the molecular plane by 1.1 Å. This

is also known from XRD measurements [23] for the molecules in the bulk crystal. Therefore, the molecule cannot be deposited “flat” on the substrate, if the tin atom is located on the substrate's side. This is the reason, why we observe the molecules of the first layer not with fourfold symmetry. Besides this, we find in Fig. 5, that molecules of the upper layer appear bigger than molecules in the lower one. We explain this by a geometric tip effect due to the rather blunt tungsten tip relative to the dimensions of a single molecule.

### 3.3. SnPc monolayers on HOPG

Next, we consider SnPc layers with thickness close to one monolayer. Fig. 6 shows such a case, where slightly less than one monolayer SnPc was sublimed onto the substrate. The substrate was kept at room temperature during deposition. As indicated in the image, three main tendencies were found. First, the molecules form well-ordered domains of flat lying molecules, which arrange in a close-packed pattern corresponding to the fourfold symmetry of the SnPc molecule. The domain shown in Fig. 6 has a side length of more than 160 nm. Second, disordered areas are found, where the molecules show no long-range order. This case is

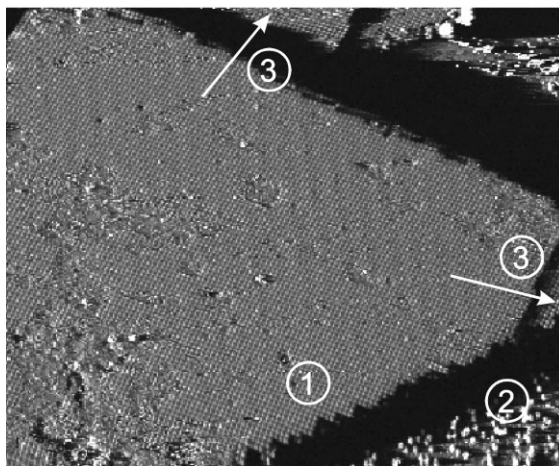


Fig. 6. Ordered domain (1) and disordered areas (2) of SnPc on HOPG. Image size  $145 \times 180 \text{ nm}^2$ , nominal thickness approximately 1 ML. Areas marked with (3) show the stacking of the layer. Tunnel conditions:  $V_T = 2.3 \text{ V}$ ,  $I_T = 10 \text{ pA}$ ,  $T = 50 \text{ K}$ .

<sup>2</sup> Also, downward oriented central atoms in the second layer's molecules could lead to an increased local conductivity, by forming “atomic wires”, appearing as a bright spot. This would also mean that first layer molecules with a dark central spot in case of upwards directed central atoms could be “electrically insulated” from the substrate.

similar to what we have found at lower coverages. The third phenomenon is the development of a second ordered layer. Evidence for it is shown in Fig. 6 at the places labelled with (3). The image shown in Fig. 6 was taken at 50 K and shows a stable adsorbate pattern. Images taken at similar temperature, but with lower molecular coverage were much less stable and a change of the domain structure could be observed from one picture to the next. One example for such a structure is shown in Fig. 7. The occurrence of several structural defects may be seen very well. Although the molecules are rather densely packed too, at this sample a very high molecular mobility could be observed, even at temperatures as low as 38 K. The reason for this increased mobility is seen in the molecular density of the adsorbate in comparison to that shown in Fig. 6. Indeed, if we analyse the lattice parameters of the two different adsorbates, we find the following data: The unit cell vectors of the closer packed phase (shown in Fig. 6) are  $a = 15 \text{ \AA}$ ,  $b = 13\text{--}15 \text{ \AA}$  ( $\pm 1.5 \text{ \AA}$  each), with an angle  $\alpha$  between the base vectors of  $74 \pm 2^\circ$ . The length of  $b$  is changing from sample to sample. In case of the less densely packed phase (which corresponds with Fig. 7) we find stable lattice pa-

rameters of  $a = 17 \text{ \AA}$ ,  $b = 19 \text{ \AA}$  ( $\pm 1.5 \text{ \AA}$  each),  $\alpha = 74 \pm 2^\circ$ , which is approximately one substrate lattice parameter wider. As a result, both phases have got the same angles in their unit cells, but different lattice parameters. Fig. 6 shows a close-packed film, which is stable during all investigations, whereas the film shown in Fig. 7 contains molecules with an intermolecular distance of approximately one substrate unit cell. This loosely packed structure is much less stable, because almost no intermolecular stabilisation is possible. It is interesting, that Strohmaier et al. found such differently dense packed phases in the case of lead phthalocyanine on  $\text{MoS}_2$ , too [29]. In contrast to our findings, they saw a structure of molecules, which was close-packed in one direction and one substrate unit cell apart in the other direction. Such a structure can be regarded as a transition structure to the loosely packed one, which we have observed here.

### 3.4. STS at SnPc/HOPG

At monolayers of SnPc on HOPG local  $I(V)$  curves were recorded. Only such spectra were evaluated, which fulfilled the following criteria: Before and after the spectrum collection molecular resolution of the STM image was required. No differences between the images before and after the voltage sweep were allowed. This ensured that only spectra were collected, where the voltage sweep did not influence the molecular ordering of the adsorbate. This is important, since under the influence of the changing high electric field of the tip molecular rearrangements are easily possible.

Fig. 8 shows such spectra. The dotted lines represent the individual measurements, while the solid line is their numerical average. No data selection was carried out between the  $I(V)$  measurements. Molecular films of SnPc show much more stable  $I(V)$  curves than we did observe on other organic adsorbates. Clearly to be seen is a semiconductive behaviour with an area of at least 2.5 eV without detectable current. If we calculate the electric conductivity as the derivative  $dI/dV$ , then we find a curve as shown in Fig. 9. At  $-2.0$  and  $+1.4 \text{ V}$  we find strongly increased local conductivities and some less pronounced maxima of

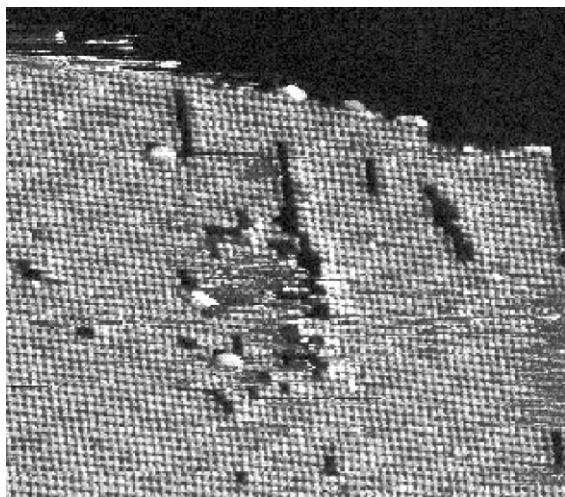


Fig. 7. Domain of SnPc on HOPG. Defects in form of missing molecules, missing chains or badly ordered areas are clearly to observe. Nominal layer thickness: 0.8 ML. Image size  $85 \times 95 \text{ nm}^2$ ,  $T = 38 \text{ K}$ ,  $V_T = 2.5 \text{ V}$ ,  $I_T = 10 \text{ pA}$ .

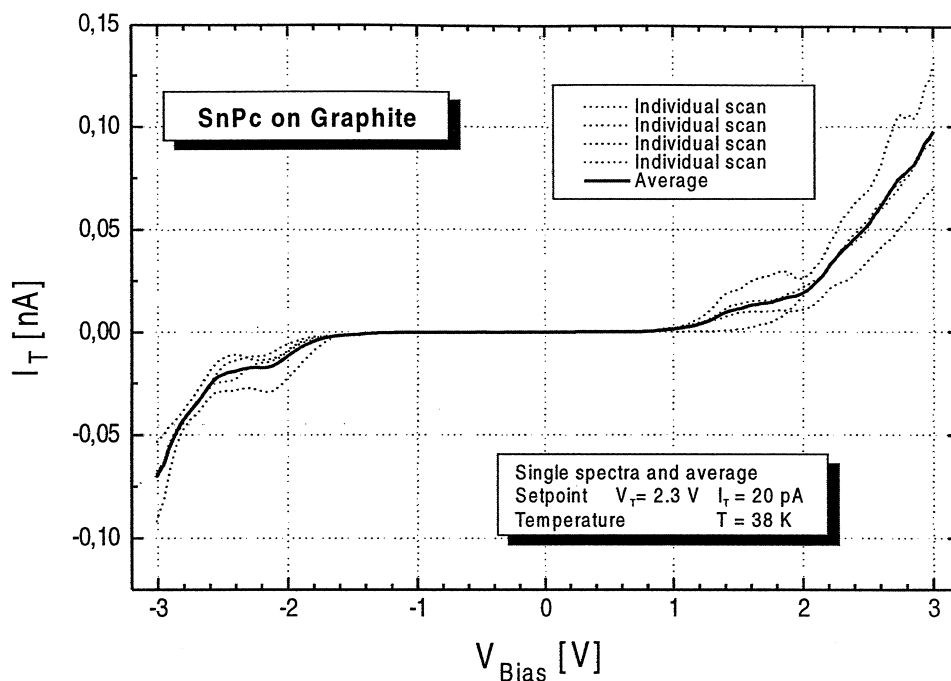


Fig. 8. Single  $I(V)$  spectra and their average collected on a SnPc monolayer. No data smoothing has been applied.

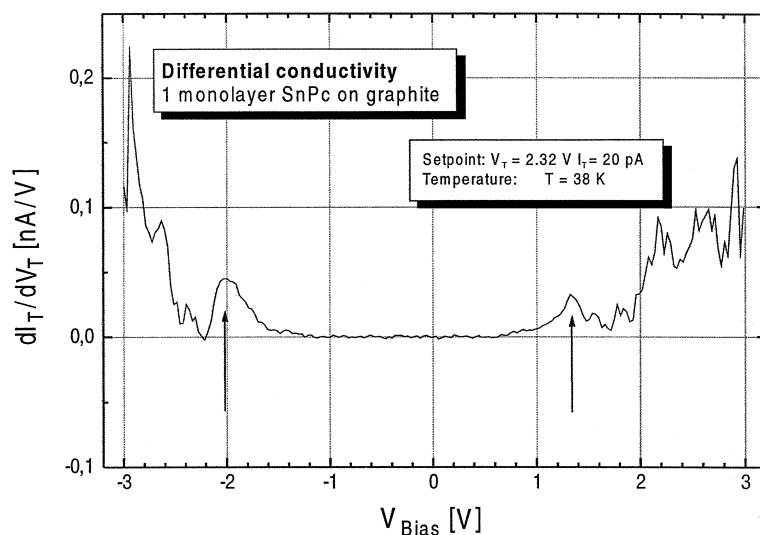


Fig. 9. Same data basis as Fig. 8., gradient of the average value.

conductivity can be observed at  $-2.6$ ,  $+2.2$  and  $+2.6$  V. If we consider the first maxima to be caused by resonant tunneling through the molecule's LUMO and HOMO, respectively, then the

gap width would have a value of  $3.4$  eV. This value seems reasonable, since for other phthalocyanines values of  $2.0$  eV ( $H_2Pc$ ) and higher (transition metal  $Pc$ 's) have been found [30]. A small con-



ductivity within this gap may be caused by electronic states of contaminations or influence of the substrate. For the molecule SnPc itself, however, until now neither photoelectron spectroscopy data nor molecular orbital calculations are available for comparison.

### 3.5. STM measurements at SnPc/Au(111) sub-monolayers

In addition to the adsorption experiments on graphite we have carried out some work on Au(111) substrates to study the substrate's influence on the adsorbate pattern. The substrates were thin gold-on-glass films, which were flame-annealed in air, immediately before UHV deposition of a submonolayer SnPc was done. Again, the behaviour of the individual molecules was studied.

Figs. 10 and 11 show consecutive images of such a sample at a temperature of 50 K. Even at this temperature, the molecules are still very mobile. This can be seen both in the low resolution of the images and in the rearrangement of the molecules between two scans. Three prominent areas of such a rearrangement are pointed out in the im-

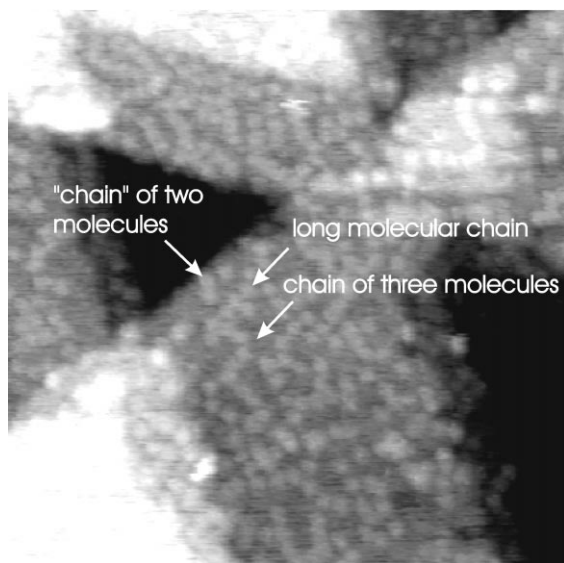


Fig. 10. Topography image of 0.5 ML SnPc/Au(111), image size  $56 \times 56 \text{ nm}^2$ ,  $V_T = 2.5 \text{ V}$ ,  $I_T = 44 \text{ pA}$ ,  $T = 50 \text{ K}$ . The molecules are arbitrarily distributed over the surface, no favoured direction can be observed.

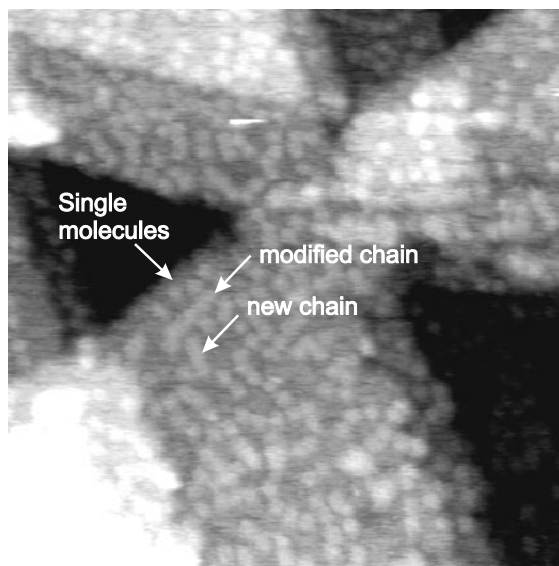


Fig. 11. The same area, identical parameters, one scan later: Careful examination reveals a molecular rearrangement, however neither a clear formation nor a destruction of ordered structures take place.

ages. In contrast to SnPc on HOPG no preferred orientations of the adsorbate are found, although both Au(111) and HOPG(0001) have got a six-fold symmetry. Also, no chain formation could be seen. The molecules behave more like a two-dimensional liquid. In our opinion, the reason for the much smaller tendency of chain formation than on graphite is the high mobility of the molecules itself. Counteracting to this movement the inter-molecular binding forces are too small to form stable molecular chains.

## 4. Conclusions

We have shown molecularly and submolecularly resolved STM images of the slightly non-planar molecule tin phthalocyanine on graphite. In the case of deposition of slightly less than one monolayer, we observed the formation of domains with two different molecular densities. The observation of layers in the 0.5 ML range showed the formation of molecular chains with a well-defined orientation of the molecule's central atoms towards the substrate. This orientation corresponds

well with literature data of relaxed lead phthalocyanine molecules on MoS<sub>2</sub>. The non-planar structure of the molecule strongly influences the STM images. Both the out-of-plane located tin atom, and the slightly bowl-shaped molecular framework are found in the STM images. Comparative measurements with the molecule copper phthalocyanine on HOPG show a similar chain formation as we have observed for SnPc. In contrast to the adsorption on graphite, SnPc on Au(1 1 1) tends to arrange more or less arbitrarily without the formation of chains. Local  $I(V)$  measurements on closed layers of SnPc on HOPG showed the semiconductive properties of the molecular layer, with a clear band gap of 3.4 eV.

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