

Surface Science Letters

Preparation of self-ordered molecular layers by pulse injection

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Abstract

We have used the pulse injection technique for the preparation of ordered molecular layers of Cu-TBPP molecules, avoiding any heating procedure of the molecules for their deposition. The controlled removal of the pure solvent is characterized by thermal desorption spectroscopy and is proved by the observation of large areas of clean self-ordered molecular layers by scanning tunnelling microscopy at 8 K after pulse injection and subsequent annealing. A comparison with results obtained by conventional deposition by sublimation reveals an equivalent appearance of the molecules, which is dominated by the lateral phenyl groups. The molecular structure of the Cu-TBPP layer is characterized and different domains are found which show the influence of the copper substrate on the growth orientation.

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An important issue in future nanotechnology is the use of single molecules as working units or electronic devices, where the molecules are equipped with specific functionalities [1,2]. This increasing functionality of organic molecules is accompanied by a raise in the molecular weight. As a result, the conventional deposition of molecules by sublimation from a Knudsen cell becomes difficult as the thermal energy injected into the molecule reaches the range of the intramolecular binding energies. Beyond a specific size, the molecules dissociate rather than sublime and molecular fragments are deposited instead of intact molecules. One way of avoiding this problem is the so-called pulse injection, which is a deposition method that avoids heating of the molecules. It was first used in 1997 for the adsorption of DNA molecules on Cu(111) [3] and is based on the capability of valves to open only very shortly in the ms range. In this period the molecules, which are solved in a solution, enter into the experimental chamber and adsorb

on the sample surface. As it was shown in various studies, large molecules as DNA [4], polymer chains [5,6], carbon nanotubes [7], CdSe nanocrystals [8] and functionalised C₆₀-based molecules [9] could be deposited onto metal and semiconductor substrates. It was recently shown that it is also possible to deposit much smaller molecules by pulse injection [10]. Another method, which however requires a larger experimental effort, is the “spray jet technique” where the molecules are deposited not directly from the solution but from a solution mist [11].

In order to take advantage of the non-thermal preparation method given by pulse injection, but to avoid contamination with the solvent, the sample must be annealed after deposition in a temperature range where the solvent desorbs, but the molecules remain intact. This was done for the deposition of carbon nanotubes and poly(3-hexylthiophene) molecules onto H-terminated Si(100) [12]. These molecules are rather large (with dimensions of several hundred Angstrom) compared to the solvent molecules. The annealing temperature, which leads to the desorption of the solvent, is therefore unlikely sufficient to cause desorption of the adsorbed species. However, this is still an open

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problem for small organic molecules (where the size reaches the order of the solvent molecules) where it is necessary to perform careful thermal desorption experiments to prepare a clean molecule-covered surface. In the only study done so far with rather small molecules, the STM measurements were obtained at room temperature, so that the solvent is not resolved due to its high mobility, but appears as fuzzy lines [10]. No self-ordered molecular layers, where the cleanness of the surface is of fundamental importance, have been prepared by pulse injection so far. In this paper, we report on the preparation of such layers and their characterization by scanning tunnelling microscopy (STM) at low temperatures of 8 K, where the diffusion of the solvent molecules is frozen.

The molecules we have chosen for this study are Cu-tetra-3,5-di-*tert*-butyl-phenyl porphyrin (Cu-TBPP) molecules. They consist of a central porphyrin ring and four phenyl-based lateral groups, which act as “legs” (Fig. 1a). The legs can rotate around their σ -bond, leading to several conformations on different copper surfaces [13]. It was also shown that it allows to switch them between different conformations by rotating a single leg with the STM tip [14]. When depositing larger coverages, ordered islands of Cu-TBPP molecules on different noble metal surfaces show that the intramolecular flexibility of the molecular legs to rotate leads to different conformations and appearances [15]. These islands are formed by self-ordering processes, where molecules grow according to their chemical properties relying sensitively on the interplay between molecule–substrate and molecule–molecule forces [16–18]. The cleanness of such a layer is of fundamental importance as contamination within an island would perturb the periodicity and deform the structure.

The experiments were carried out in an ultrahigh vacuum (UHV) chamber, working at a base pressure of 10^{-10} mbar. The Cu(111) sample was cleaned by repeated cycles of Ne ion sputtering (1.3 keV) and subsequent annealing (770 K) and then transferred to the load-lock chamber where the pulse injection was done (conventional sublimation from a Knudsen cell was done in the UHV chamber) in order to keep the base pressure low. The valve used for pulse injection is a solenoid valve from Parker instrumentation with an orifice of 50 μm , equipped with a homebuilt control unit. After the preparation, the sample is transferred into the STM chamber, where it is cooled using a liquid helium cryostat. STM images were taken in constant current mode at a temperature of 8 K with a homebuilt LT-STM [19]. Bias voltages in this work are given with respect to the tip.

Even though single Cu-TBPP molecules have already been studied on Cu(111) [13], no experimental study has been done on this system at large coverages. In order to investigate the appearance of Cu-TBPP molecules in a high density, we have first deposited them conventionally by sublimation from a Knudsen cell (at a temperature of 540 K). After depositing about 1.8 ML of these molecules onto the clean Cu(111) substrate, they form layers with a

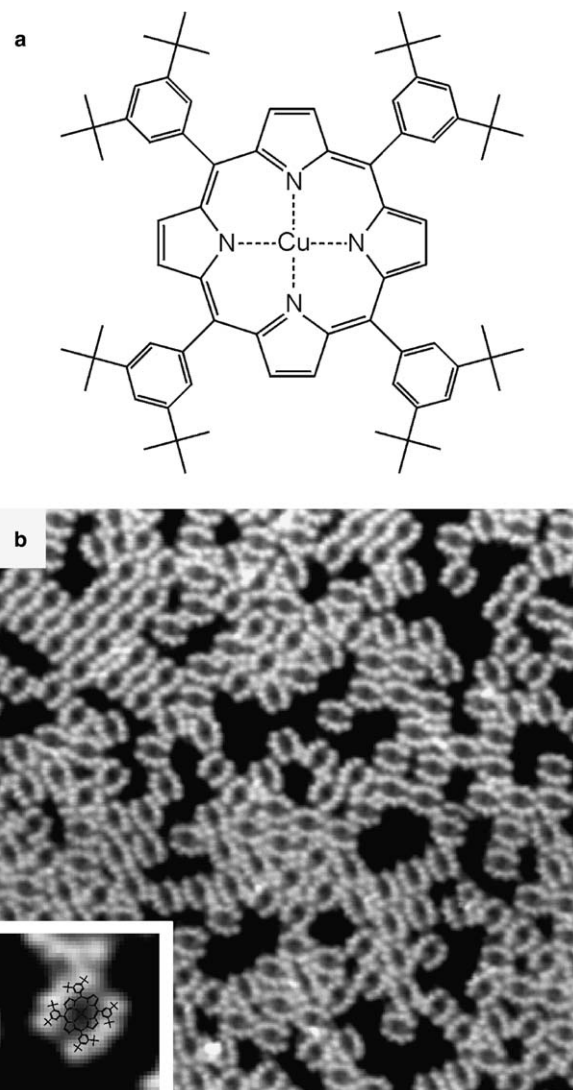


Fig. 1. (a) Chemical structure of the Cu-TBPP molecule. (b) shows an STM image of about 1.8 ML of Cu-TBPP molecules deposited onto Cu(111) by sublimation from a Knudsen cell ($330 \times 330 \text{ \AA}^2$, $U = 0.7 \text{ V}$ and $I = 150 \text{ pA}$). The inset shows one molecule enlarged: The chemical structure indicates the position of the eight *tert*-butyl groups, which are visible as lobes in the STM image.

local short-range order as presented in Fig. 1b. It can be clearly seen in the inset that the appearance of the molecules is the same as for isolated single molecules on the same surface [13]: They consist of eight lobes, which reflect the spatially extended *tert*-butyl groups (two attached to each of the four phenyl rings). The central porphyrin ring is not visible (due to the smaller height and in particular to the electronic decoupling from the surface by the legs) and appears as an elliptic “hole”. The molecules in Fig. 1b therefore lie flat on the surface, having all phenyl rings parallel to the substrate (which was deduced for single molecules from comparison with calculations [13]), when adsorbing in a complete layer.

The experimental set-up of the pulse injection procedure is shown in Fig. 2a. The valve is mounted on the experi-

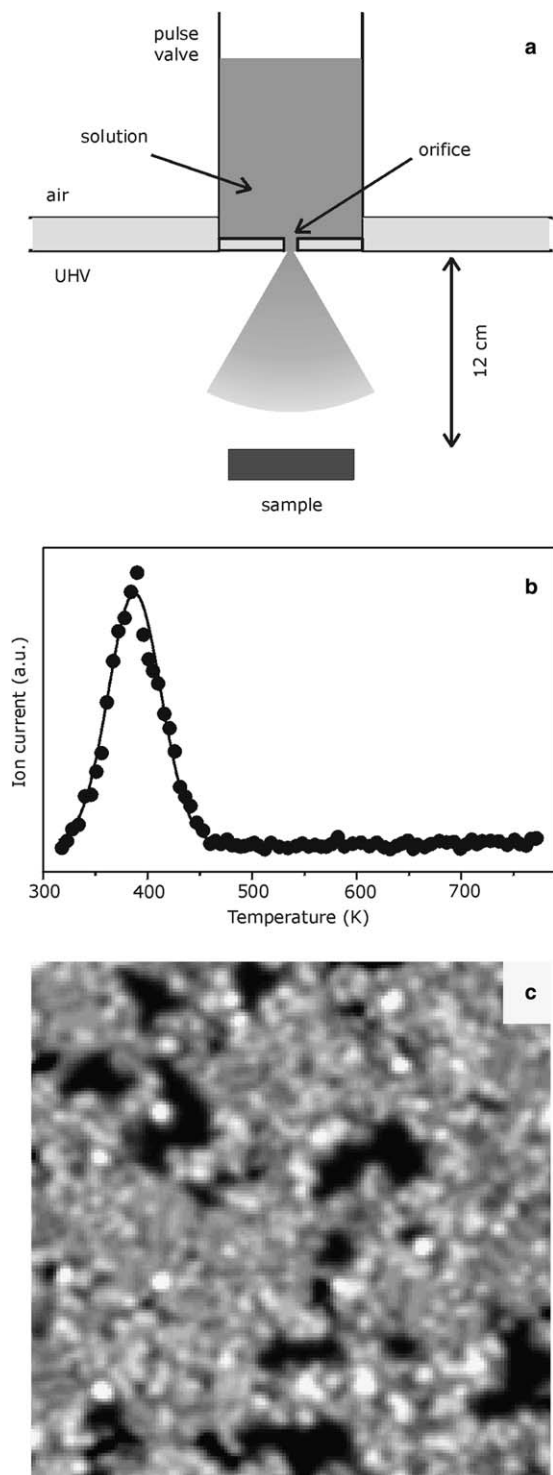


Fig. 2. (a) Scheme of the molecule injection using a pulse valve: The molecules are solved in a solution and enter the UHV chamber through the orifice with a diameter of $50\ \mu\text{m}$, which is shortly opened (ms range). The clean Cu(111) sample is positioned in front of the valve at a distance of about 12 cm. The thermal desorption spectrum (of mass 74, i.e. the molecular weight of diethyl ether) of diethyl ether is shown in (b) revealing the maximum desorption at 387 K (the solid line is drawn to guide the eye). The sample temperature during data acquisition is raised linearly by 27 K/min. (c) STM image ($430 \times 430\ \text{\AA}^2$, $U = 0.8\ \text{V}$, $I = 200\ \text{pA}$) of the Cu(111) surface directly after pulse injection.

mental chamber in order to deposit the solution from air atmosphere onto the sample kept under UHV conditions ($p = 6 \times 10^{-9}$ mbar). The molecules are solved in diethyl ether until saturation. The solution is not exposed to any heating procedure, because gentle heating of the valve (together with the bake-out of the load-lock chamber) is done before filling. After opening of the valve for 116 ms, the saturated solution enters through the orifice ($50\ \mu\text{m}$ diameter) into the chamber, where the pressure rises quickly above 10^{-3} mbar (i.e. the limit of the manometer range). This procedure is done six times for a molecular coverage sufficient for the growth of molecular layers. The sample (kept at room temperature during preparation) is positioned about 12 cm in front of the orifice.

Large areas of clean and ordered molecular layers can only be prepared by removing the solvent from the surface after the deposition. Thermal desorption spectroscopy (TDS) measurements are done by positioning the sample in front of a quadrupole mass spectrometer after depositing only the diethyl ether solvent by pulse injection onto the clean Cu(111) sample. The sample is then slowly heated up to 770 K and the ion current is plotted as a function of temperature. The resulting spectrum in Fig. 2b shows one single peak at 387 K and no additional contributions at higher temperatures. This means that all molecules are desorbed after annealing at about 490 K. Diethyl ether therefore appears to be a very suitable solvent for the preparation of ordered Cu-TBPP layers, because its desorption temperature lies in the same range (about 420 K to 520 K), in which the formation of self-ordered layers of Cu-TBPP on Au(110) occurs [15].

Directly after the pulse injection, only disordered structures are visible by STM on the surface (Fig. 2c) and no Cu-TBPP molecules can be resolved (note that presumably much more solvent than Cu-TBPP molecules are present in the solution). In order to remove the solvent after pulse injection, the sample was annealed at 493 K for 5 min. The subsequently taken STM images are shown in Fig. 3, where a highly ordered structure is visible, which completely covers the surface. This result shows that the annealing temperature, determined by TDS, is sufficient for the desorption of the solvent. The structure in Fig. 3 consists of rows of parallel molecules where the molecules in adjacent rows are rotated by 90° to each other. It was not observed directly after deposition from a Knudsen cell (Fig. 1b) and is facilitated by the annealing procedure of the surface, which has been found for many other types of molecular layers [15]. The molecular density in this layer is higher than in the local ordered regions in Fig. 1b, therefore the lobes of the ter-butyl groups of different molecules smear out (Fig. 3b) and do not show distinct lobes as in Fig. 1b. As shown in the model (Fig. 3c), the elliptic regions of low contrast (“holes”) in the structure correspond to the central porphyrin ring of the molecules, while the bright regions reflect the ter-butyl groups. The molecular legs are therefore flat on the surface, even though a few lobes appear brighter in Fig. 3b. This is probably due to small

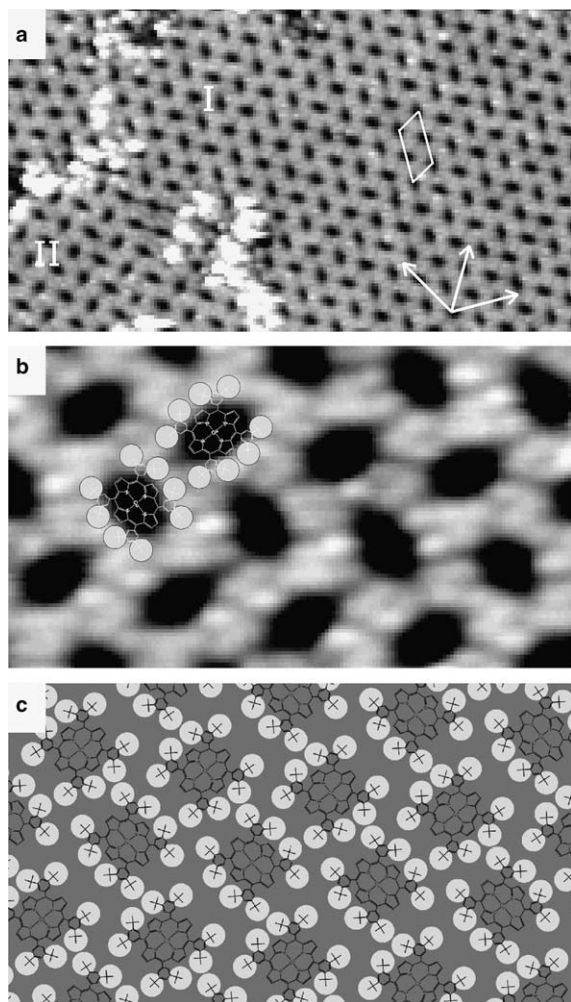


Fig. 3. (a) STM image ($430 \times 243 \text{ \AA}^2$, $U = 0.8 \text{ V}$, $I = 80 \text{ pA}$) of the Cu(111) surface covered with Cu-TBPP molecules after heating at 493 K for 5 min. The unit cell of the ordered layer is marked by a rhombus ($20 \times 35 \text{ \AA}^2$). Different domains of the structure are named I and II. The symmetry directions of the Cu(111) substrate are indicated by arrows. (b) shows an enlarged view of the same structure ($89 \times 51 \text{ \AA}^2$, $U = 0.8 \text{ V}$, $I = 80 \text{ pA}$) where the dark regions correspond to the central porphyrin rings of the molecules and only the ter-butyl legs contribute to the contrast. The corresponding model of this self-ordered layer is shown in (c). The chemical structures of two molecules are superimposed in the STM image (b).

variations in the ter-butyl-phenyl orientation, because the intermolecular distance is rather small.

The unit cell of the structure, indicated in Fig. 3a, is rhombic with an angle of 60° between the base vectors. Two molecules are found in each unit cell, which has a size of $20 \times 35 \text{ \AA}$. The base vectors of the unit cell are rotated by 30° to the symmetry directions $\langle -110 \rangle$ of the Cu(111) substrate, which are known from atomic resolution images of the bare substrate. At the lower left corner of Fig. 3a, another domain of this molecular structure is visible, named II. It is rotated by 60° to domain I, while the high-resolution image in Fig. 3b shows the third domain which was found of this structure, rotated by another 60° . The self-ordered layer thus appears in three different orientational domains, which reflects the six-fold symmetry

of the substrate, similar to other systems [15,17]. Although the molecular layers reveal a very high order and perfect cleanness, small amounts of contaminants (or rest solvent molecules) are found at the boundary between different ordered domains (as in Fig. 3a). These boundaries offer energetically preferred adsorption sites to contaminants (or rest solvent molecules), as they accumulate in these regions or at step edges. Note that no solvent molecules are visible on the ordered layer, although their diffusion is suppressed at the low temperature of 8 K of the present measurements (in contrast to previous work at room temperature [10] where they appear as fuzzy lines in the images). This demonstrates the cleanness of the molecular structure over large areas of several hundred \AA , limited by domain boundaries or step edges.

In conclusion, we have shown that it is possible to prepare self-ordered layers of Cu-TBPP molecules on Cu(111) by pulse injection. The choice of diethyl ether as solvent turned out to be very useful as thermal desorption spectroscopy showed that it can be removed from the surface by annealing at about 490 K. At this temperature, the Cu-TBPP molecules remain intact on the surface and form self-ordered layers. The structure of these layers could be resolved by STM, showing the high density of the molecules compared to deposition without annealing. Different domains were identified on the surface, separated by boundaries which are typically slightly contaminated, while the molecular layers are very clean over large distances. No solvent molecules were found on the ordered layers, although the low temperature during STM measurements would allow their imaging. The present results demonstrate the capability of shortly opening valves with a small orifice (in the μm range) to be used for the growth of clean molecular layers by pulse injection.

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