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Dynamic force microscopy study of 3,4,9,10-perylenetetracarboxylic dianhydride on KBr(001)

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A scanning force microscope operated in the dynamic force mode has been used to analyze the arrangement of 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) molecules on a KBr(001) surface. The molecules do not form a close-packed layer but crystallites with the shape of truncated pyramids. Even after depositing only 0.3 molecular layers of PTCDA, these crystallites have a height of 20–30 molecular layers. We have been able to resolve individual molecules of the top layer and on some of the crystallites facets. The results agree with the known "herringbone" structure of the bulk. A comparison of the experimentally observed contrast to a simple force field calculation based on semiempirical interaction potentials is given.

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The growth of organic molecules on inorganic surfaces has been the subject of many investigations. The application of scanning tunneling microscopy (STM) has been remarkably successful to reveal the complex structural interplay of ordered domains of the organic molecules with a well-ordered substrate. However, STM requires a conducting substrate. Insulating inorganic surfaces have recently become accessible to studies with true atomic resolution by the development of "noncontact" atomic force microscopy (NC-AFM).[1–3] This technique allows to substantially reduce the interaction between the probe and the sample using stiff cantilevers. Thus tip damage by a possible snap to contact can be avoided. This technique has now been used to obtain molecular resolution of thin layers of organic molecules,[3] mainly on conducting and semiconducting surfaces.[4–9] In view of potential applications for molecular electronics, insulating substrates are important[10] since they permit to build individual devices which may be contacted by localized electrodes. So far little work has been performed on purely insulating substrates by NC-AFM.[11,12] Nony *et al.*[13] observed individual molecules confined in rectangular pits on KBr. Burke *et al.* succeeded in resolving the arrangement of C_{60} molecules on KBr.[14]

Among various organic molecules considered for molecular electronics, PTCDA is a prototype which has been investigated intensively on a vast number of substrates e.g., on graphite,[15,16] InAs(001),[17] Au(111),[18] Ag(110),[19,20] Au(100).[21] At monolayer coverage several different superstructures have been found for different metallic substrates. On metallic surfaces like gold, silver, or copper PTCDA exhibits Stranski-Krastanov growth leading to the formation of large crystallites at higher coverage. The structure of bulk crystals has been determined by electron and x-ray diffraction.[22–26] While the shape of crystallites may be analyzed in real space by electron microscopy or conventional atomic force microscopy, e.g., on GaAs(001) (Refs. 27 and 28) or on Ag(111) (Refs. 29 and 30) the corresponding molecular arrangement has been observed for the first time in real space by low current scanning tunneling microscopy.[31] In the present paper we report on the investigation of 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) crystallites on KBr by non contact atomic force microscopy. The crystallites are formed by molecular layers parallel to the surfaces of the substrate. For the top layer, as well as for some of the facets, individual molecules could be resolved.

The experiments have been performed in an ultra high vacuum system providing an analysis chamber that contains the AFM and a preparation chamber that allows to sputter and heat samples and tips. A load lock allows a quick exchange of cantilevers and samples. For the investigation of KBr a cleavage stage has been added that permits the preparation *in situ*. The images were obtained by a commercial UHV-AFM (Omicron). The data acquisition (GXSM) (Ref. 32) and some of the electronics have been modified. The oscillation of the cantilever has been controlled by a separate unit (Easy-PLL, Nanosurf).

Cantilevers with a spring constant of approximately $k=30$ N/m and an unperturbed resonance frequency of $f_0=270$ kHz have been used (μ-Mesh and Nanoworld). The amplitude of the oscillation was kept constant at about $A=25$ nm by changing the excitation amplitude accordingly while the driving frequency was varied such that the cantilever was always driven at resonance. The distance between the cantilever and the sample surface has been adjusted by maintaining a constant frequency shift of −3 to −23 Hz. The bias voltage was once set to −1.4 V at the tip leading to a minimal electrostatic tip-sample interaction prior to the acquisition of images.

The (001) surface of the KBr crystal has been prepared by cleaving *in situ*. To remove contaminations the crystal has been heated to 200 °C for 1 h prior to cleavage and it has been heated afterwards again to 160 °C to reduce the number of trapped charges. PTCDA has been thermally evaporated by a home-built crucible. In order to remove more volatile contaminants the crucible was kept for 12 h at a temperature of 250 °C, slightly below the sublimation temperature of 300 °C. The flux of molecules has been controlled by a quadrupole mass spectrometer. The equivalent of about 0.3 monolayers has been deposited on the freshly prepared KBr surface at ambient temperature. No thermal an-

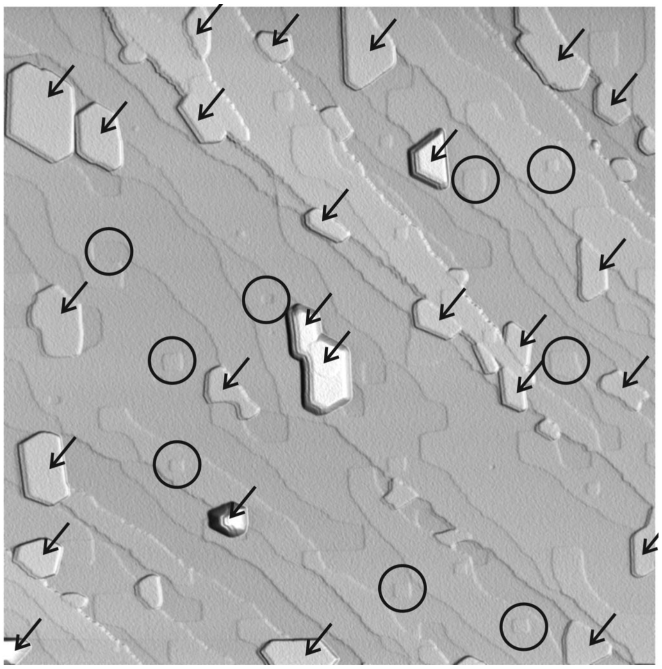

FIG. 1. Overview of a large area ($2\ \mu\text{m}\times 2\ \mu\text{m}$) of the KBr(001) surface covered with 0.3 molecular layers of PTCDA. PTCDA islands are marked by arrows. The circles highlight rectangular pits and protrusions of the bare KBr. The image has been acquired using $\Delta f=-3$ Hz or $\gamma=kA^{3/2}\Delta f/f_0=-1.3\ \text{fNm}^{1/2}$, the height range is about 10 nm.

nealing of the molecular layer has been applied.

An overview over a large area is given in Fig. 1. For most of the area, the substrate is flat with a typical distance of 50–100 nm between atomic steps. Some rectangular pits or protrusions marked by circles confirm the (100) orientation of the surface. A typical wedge-shaped structure created by cleavage is observed running from the upper left to the lower right side. On top of this surface one clearly recognizes crystallites of PTCDA marked by black arrows. They form truncated pyramids with elongated hexagonal bases. The areas between the crystallites appear as the bare KBr surface. Between different crystallites no atomic or molecular resolution has been obtained, similar to observations reported by Nony *et al.*[6] The authors proposed that this might be due to mobile molecules diffusing on the surface at room temperature. Our findings are consistent with this explanation. A considerable fraction of the crystallites are located on the lower terrace of a step edge. Due to the higher coordination at the lower side of a step edge the concentration of molecules is increased leading to a preferential growth of crystallites at these sites. For some crystallites, one of the facets is aligned with the [100] or [010] direction of the KBr substrate, while for others, the orientation of the facets appears to be influenced, e.g., by an adjacent step. For the coverage of 0.3 molecular layers chosen in this experiment, the height of the crystallites varies between a few and up to 30 layers. From previous work[33] on other substrates, it is known that crystallites of PTCDA on surfaces are usually formed layer by layer with the (102) plane of the bulk structure parallel to the surface of the substrate. The interaction between these layers is only given by van der Waals forces. It is found in general that the slopes to the substrate are given by six facets: two of them are parallel to the short side of the rectangular unit cell of the bulk of PTCDA, while the four other are parallel to the two diagonals. Facets parallel to the long axis are not observed. In consequence, a hexagonal shape of the crystallites results.

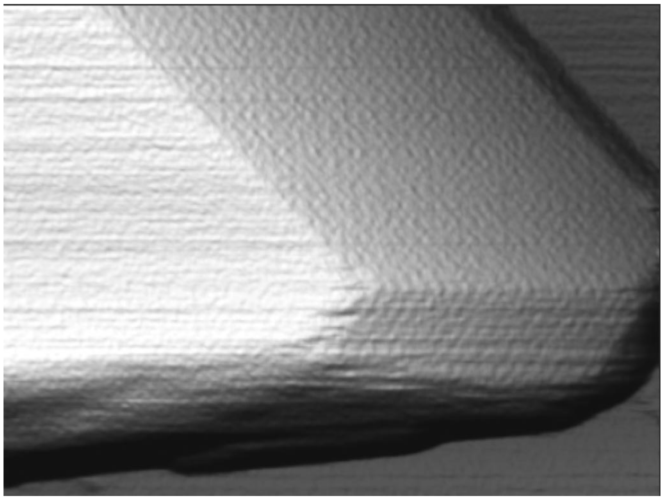

FIG. 2. Part of an individual PTCDA crystallite showing molecular resolution on the flat top as well as on two of the three observed facets. The image of $80\ \text{nm}\times 60\ \text{nm}$ has been acquired using $\Delta f=-3$ Hz ($\gamma=-1.3\ \text{fNm}^{1/2}$).

A more detailed image of a crystallite is shown in Fig. 2. One recognizes the flat top layer and three facets, one of which appears very steep ($\alpha \geqslant 35°$). This steep slope to the lower side of the image is not molecularly resolved probably due to the convolution with the tip shape. Its steep shape indicates the sharpness of the tip. Molecular resolution is obtained on the top of the truncated pyramid as well as on two of the facets ($\alpha \approx 11°$). Assuming that the adjacent surface is given by the bare substrate, the number of layers forming the crystallite is determined to 27 by counting the layers. The regular pattern on the facets indicates the faultless stacking of the subsequent layers. Hence a perfectly crystalline structure is observed. As shown in a previous paper[31] the stacking of subsequent layers of the crystallites may be determined from the analysis of several images of the facets with molecular resolution.

Figure 3(a) displays the dynamic force mode image of an area of approximately $10\times 10\ \text{nm}^2$ of the top layer of a crystallite. The frequency shift has been kept constant at $\Delta f=-10$ Hz corresponding to a normalized value[34] of $\gamma=kA^{3/2}\Delta f/f_0=-4.4\times 10^{-15}\ \text{Nm}^{1/2}$. The image has not been corrected for thermal drift leading to a distortion of the otherwise rectangular unit cell. The corrugation amounts to about 0.05 nm. The upper left corner shows the Fourier transformation.

To evaluate the validity of the intuitive identification of the brighter objects with individual PTCDA molecules, simple force field calculations have been performed. The tip of the cantilever has been modeled by a cluster of 17 silicon atoms with a tetramer pointing towards the surface. It has been assumed to be rigid with a bond length of 0.233 nm,

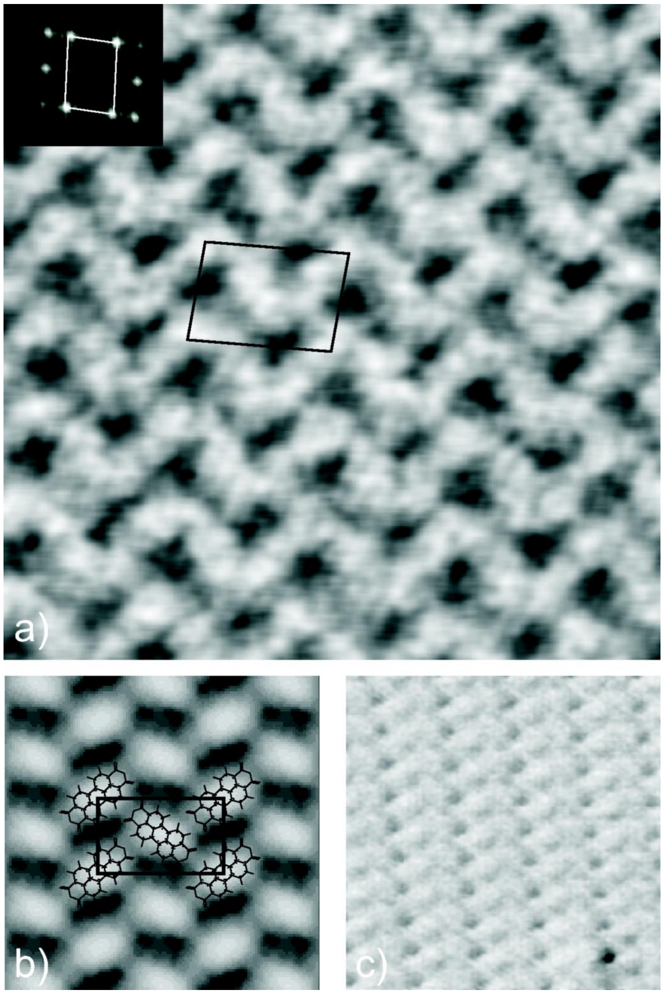

FIG. 3. (a) Molecular resolution of PTCDA obtained on the top of a crystallite. The set point for the frequency shift has been increased to $\Delta f = -10$ Hz ($\gamma = -4.4$ fNm$^{1/2}$) compared to Figs. 1 and 2. The displayed area is approximately 10 nm × 10 nm. The upper left corner shows the Fourier transform of the image. Neither the topographic image nor the Fourier transform have been corrected for thermal drift. In both images the primitive unit cell of the structures is shown. (b) Simulated hypersurface for $\gamma = -5$ fNm$^{1/2}$ based on a simple force field calculation. The displayed area amounts to 5×5 nm^2. The height varies between 0.49 and 0.54 nm referring to the distance between the center of the outermost atom of the tip and the center plane of the molecules. To indicate the position of the molecules, they have been sketched for one unit cell. (c) Molecular resolution image on the top layer of a different PTCDA crystallite on KBr showing a localized defect in the lower right corner. The scan area is approximately 10×10 nm^2. This image has been acquired using $\Delta f = -11.8$ Hz ($\gamma = -5.2$ fNm$^{1/2}$).

which corresponds to the bulk value. We suppose that PTCDA grows on KBr in the α phase with the (102) plane parallel to the surface as it was observed on other ionic crystals.[23] From the experimental data we cannot distinguish between the α and the β phase. A rectangular unit cell with the lattice parameters $a = 1.196$ nm and $b = 1.991$ nm (Ref. 24) has been used to model the surface. The rigidity of this structure has been assumed. The van der Waals interaction with the surface is described by a summation of Lennard-Jones pair potentials that have been taken from a standard database (Hyperchem), using the AMBER molecular force field parameters.[35] Long-range forces and covalent bonds have been neglected. The frequency shift was obtained from the force field using the large amplitude approximation $\gamma \approx (2\pi)^{-1/2} F \sqrt{U/F}$, where F is the force and U is the potential energy taken at the turning point.[36]

Figure 3(b) displays the calculated surface of the constant frequency shift for $\gamma = -5 \times 10^{-15}$ Nm$^{1/2}$. It exhibits a corrugation of 0.05 nm. Both the spatial arrangement of the protrusions as well as the corrugation are in good agreement with the experimental observations. For one unit cell, the location of the molecules is schematically drawn. In agreement with the naive assumption discussed above, molecules appear as protrusions. The good agreement between the observation and the simulation confirms that the molecular arrangement corresponds indeed to the assumed herringbone structure and that the top layer corresponds to the [102] plane of this structure. This structure is also found on various other substrates such as Au, Ag, or Cu.

As mentioned above, the calculation has been performed for an uncharged silicon tip. In order to evaluate the contributions of different types of forces, and to obtain information about the chemical nature of the tip used in the experiment, calculations using a charged tip have been performed. If a positive or negative elementary charge at the tip is assumed, additional electrostatic contributions to the force arise; however, they do not significantly alter the calculated contrast.

While most images obtained for the top layer of a crystallite of PTCDA show a perfect periodicity, sometimes local defects are observed. An example is displayed in Fig. 3(c). In the lower right corner a localized hole appears that does not alter the periodicity of the surrounding molecular arrangement. To maintain the constant frequency shift the tip has to approach closer to the surface by about 0.05 nm compared to the unperturbed surface. The physical origin is not yet understood. Note that more details of the molecular arrangement are observed in this image compared to Fig. 3(a) due to the closer tip-sample distance.

Our findings for PTCDA on KBr reveal the potential of non-contact atomic force microscopy for the investigation of organic molecules on insulating substrates. In view of potential application in molecular electronics or optoelectronics, it is important that the structure of organic layers can be equally well investigated on conducting, semiconducting and insulating substrates. In contrast to the observation of C_{60} on KBr by Burke *et al.*[14] where islands with a height of one layer have been analyzed, the present paper focuses on the analysis of molecular crystallites with up to 30 layers. Images with molecular resolution obtained for the top layer reveal that the molecules arrange in the so-called herringbone structure, in agreement with the bulk structure determined by electron and x-ray diffraction. The identification of this structure is strongly supported by a simple approximate calculation for the surface of constant frequency shift based on empirical force fields.

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