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Molecules Coining Patterns into a Metal: The Hard Core of Soft Matter

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Using scanning tunneling microscopy (STM), we demonstrate that deposition of a monolayer of perylene ($C_{20}H_{12}$), a planar aromatic molecule, on a Cu(110) substrate leads to the formation of a periodic pattern of nanostripes. High-resolution STM data indicate that the driving force for this unexpected surface restructuring caused by such nonreactive hydrocarbons is a lock-in mechanism due to a close registry of the molecular carbon frame with respect to the underlying copper lattice which leads to an enhanced adsorption energy.

I. Introduction

At the interface between hard, inorganic materials and soft matter, structural motifs are normally transferred from the hard to the soft material which provides the basis of moulding.[1,2] On the microscopic scale, an alignment of adsorbing molecules relative to the atomic structure of the substrate surface is a prerequisite for (hetero-)epitaxial growth. For example, in the case of organic molecular beam deposition (OMBD) of aromatic molecules which are of significant interest in organic electronics, the interaction with a solid substrate can stabilize thin film phases which do not exist in the bulk material.[3−5] Especially metal substrates have been used as templates to generate two-dimensional, planar molecular networks stabilized either by metal complexation[6] or hydrogen bonding[7−9] or to planarize molecules.[10] Moreover, the confinement of adsorbates in one plane can also lead to the formation of 2D chiral surfaces.[11−13] Even complex structures can potentially be transferred from the substrate to the molecular adlayer, e.g., stripe patterns or by utilizing particular step arrangements.[14,15]

Here, we demonstrate the reverse of this transfer process: structural information from a molecular pattern is embossed into a solid substrate. Using scanning tunneling microscopy (STM), we identify the coining of a nanoscopic stripe pattern onto a Cu(110) substrate by deposition of perylene ($C_{20}H_{12}$), a planar and rigid aromatic molecule (see Figure 1a). Such a coining of a *hard*, metallic substrate by a *soft*, molecular material at first sight appears to be a contradictio in adiectio. Closer consideration, however, makes clear that the term soft used to characterize organic materials applies to the rather weak—compared to, e.g., metal−metal interactions—intermolecular interactions (i.e., van der Waals forces) rather than the strong intramolecular forces acting within molecules.[16]

In previous growth studies of perylene on Cu(110), Chen et al. reported the formation of highly ordered organic multilayers revealing a new, substrate mediated crystalline phase with a homogeneous orientation of the molecular planes parallel to the substrate.[17,18] Later studies have shown, however, that this molecular orientation is only adopted within the first monolayer and is not transferred to multilayers.[19] Instead, the subsequent multilayer growth is accompanied by a pronounced dewetting leading to the formation of 3D islands with a bulklike structure on top of the wetting layer.[20] Moreover, by combining high-resolution He-atom scattering (HAS) and scanning tunneling microscopy (STM) measurements, we have previously been able to characterize the initial stage of perylene growth on Cu(110) and identified the appearance of various submonolayer

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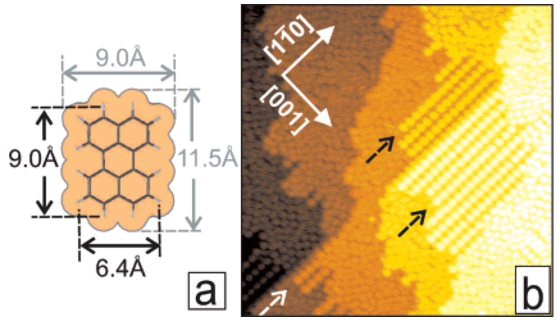

Figure 1. (a) Molecular structure of perylene ($C_{20}H_{12}$) together with the distances between the outermost hydrogen atoms (black) and the corresponding van der Waals dimensions (98% electron density, gray). (b) STM image of a saturated perylene monolayer on Cu(110) showing the closely packed regions and the incipient appearance of characteristic stripes (indicated by dashed arrows; image size 49 nm × 49 nm; tunneling parameters $U_{\mathrm{sample}} = -0.1$ V, $I_t = 1.5$ nA).

phases until a saturated (4.25 × 5) monolayer is formed.[21] This study revealed further that with time or upon gently annealing the saturated monolayer transforms into a slightly less densely packed but thermally rather stable (5 × 5) structure. The appearance of this phase is accompanied by an enhanced step density at the surface which had been attributed mistakenly to steps between molecular planes of perylene multilayers by Chen et al.[17]

Here, we report a detailed STM study of the microstructure of this perylene/copper interface with a particular emphasis on the origin of the step formation and its effect on the resulting film morphology. On the basis of high-resolution STM data, we demonstrate that the (5 × 5) phase is in fact a perylene driven restructuring (*coining*) of the copper surface which constitutes a starting point for further surface modifications involving a ripple formation and finally a facetting.

II. Experimental

The present experiments were carried out using an ultrahigh vacuum STM (JEOL JSPM-4500S). Typically, we use tunneling voltages in the range of $U_{\mathrm{sample}} = 1-2$ V and currents of $I_t = 0.8 - 2$ nA. Most of the STM data were acquired at room temperature; for some experiments, the sample was cooled to $T \approx 110$ K using liquid nitrogen to reduce diffusion and possible image distortions due to mobile admolecules.

Prior to each perylene deposition, the Cu(110) substrate was cleaned in situ by Ar^+-sputtering (800 eV) and subsequent annealing (up to 950 K). Initially, these cleaning cycles were repeated until a sharp (1 × 1) electron diffraction (LEED) pattern with a low diffuse background signal was observed and the STM measurements revealed no traces of contaminations. In subsequent experiments, 2−3 cleaning cycles proved sufficient to establish a clean surface.

Perylene (Fluka, purity ≥ 99%) was deposited from a glass crucible mounted inside a resistively heated Knudsen cell. To maintain a constant flux upon deposition which was monitored by a quartz microbalance (Leybold Inficon XTC2), the temperature of the perylene containing glass crucible was stabilized within ±1 K at typical operation temperatures of 400−440 K. Before deposition, the Knudsen cell was carefully outgassed.

III. Results and Discussion

In a previous study, we have demonstrated that a well-defined saturated monolayer of perylene on Cu(110) can be prepared by first depositing a thin multilayer film at room temperature followed by short-time annealing at 380−420 K or by saturating the surface at this elevated temperatures.[21] This procedure is based on the rather different chemical environment experienced by molecules at the interface and within the organic multilayers. Because of the rather weak essentially van-der-Waals interaction in multilayer films, perylene starts to sublimate already at temperatures of about 360 K (under vacuum conditions) whereas the chemisorbed monolayer remains stable on the copper surface to at least 550 K. Guided by the previous results, a saturated perylene monolayer has been prepared in this study by exposing the Cu(110) surface to an amount of perylene equivalent to several monolayers at a substrate temperature of ≈390 K during deposition and for several minutes afterward. To consider also the possibility of perylene readsorption from the residual gas after thermal desorption of the multilayers, some of the samples had been reheated additionally after perylene deposition and cooling.

Figure 1b displays a typical STM micrograph of a saturated monolayer of perylene on Cu(110) prepared by the procedure described above. In addition to closely packed regions, molecular rows oriented along the [1$\bar{1}$0] direction (indicated by dashed arrows in Figure 1b) can be seen and resemble previous STM data that have been obtained for the same system.[17,18,21] The molecular rows seem to nucleate at steps of the copper surface and subsequently extend onto the terraces as shown in Figure 1b. In fact, a propagation of such rows has been observed occasionally in consecutive STM images recorded at room temperature and hence indicate some growth dynamics.

Keeping the monolayer film at slightly elevated temperature (≈350 K) for several hours or briefly annealing at about 450 K causes an almost complete change of the surface morphology which is characterized by a regular pattern of parallel rows oriented along the [1$\bar{1}$0]-substrate azimuthal axis. The bright stripes appearing in the STM micrograph (Figure 2a and b) are 9−10 Å wide with a stripe-to-stripe distance of about 18 Å, thus revealing a distinctly different structure than the clean copper surface which exhibits ordered terraces of about 80 nm separated by atomic steps (see the inset of Figure 2a). Only occasionally small regions exhibiting a densely packed phase still coexist. In high-resolution STM images recorded at low-temperature, it is possible to identify individual perylene molecules as shown in Figure 2b. When using a positive sample bias, the molecules exhibit a dumbbell shape with a characteristic waist in the centerline. This waist can be attributed to the pinches between the two naphthalene units of perylene and thus enables us to determine the azimuthal molecular orientation. All visible molecules reveal the same shape and orientation and hence indicate a uniform alignment of the long molecular axis along the [1$\bar{1}$0] direction yielding a (5 × 5) superstructure which had been identified before by HAS measurements.[21]

At first glance, such images seem to indicate a partial desorption of perylene molecules from the saturated mono-

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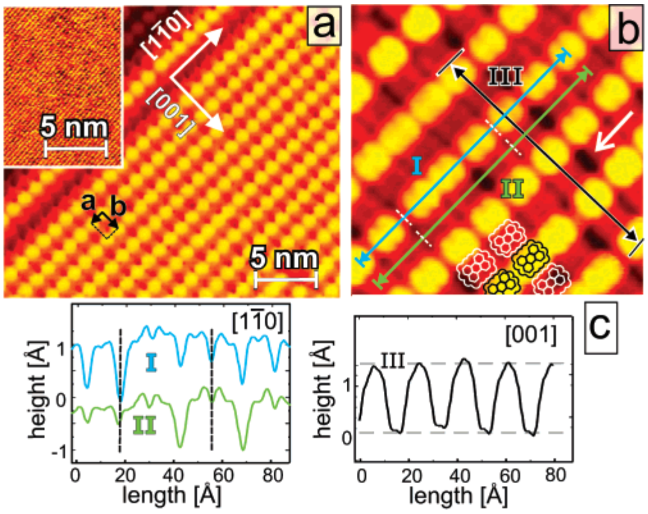

Figure 2. STM micrographs of the (5 × 5) perylene structure imaged at $T \approx 110$ K ($U = 1.5$V, $I_t = 0.8$ nA) (a and b) together with corresponding line profiles along the rim (I) and the bottom (II) of the troughs and perpendicular to the rows (III) (c). The inset in a reveals the clean Cu(110) surface.

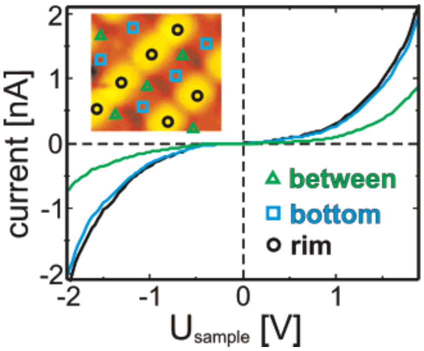

Figure 3. STS spectra recorded for the (5 × 5) perylene adlayer together with the topographic STM image (inset) obtained during spectroscopic CITS measurement. The symbols indicate the positions where single spectra have been evaluated to yield the averaged $I(V)$ spectra: (black circles and blue squares) center of molecules at the rim and the bottom and (green triangles) in between the molecules.

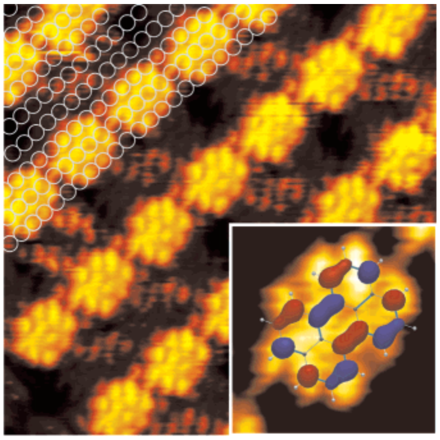

Figure 4. High-resolution STM image of the (5 × 5) superstructure showing a submolecular contrast together with a superimposed model of the outermost atoms of the (unreconstructed) Cu(110) surface. The inset shows a magnified image of a single molecule with enhanced contrast and the superimposed lowest unoccupied molecular orbital (LUMO) of perylene. The tunneling parameters are as follows: $U_{sample} = -0.01$ V, $I_t = 7$ nA. The image size is 7 nm × 7 nm.

layer, leaving behind periodic stripes of molecules, as has been seen previously for pentacene adsorbed onto this same Cu(110) substrate.[22] Closer inspection of high-resolution STM data, however, reveals that also the bottoms of the troughs between the rows are covered by perylene molecules. This becomes even more obvious in line scans which were taken along the [1$\bar{1}$0] azimuth at the rim and the bottom of the troughs (profiles I and II in Figure 2c) and reveal rather similar size, shape, and spacing of the molecules. From line scans perpendicular to these rows (profile III in Figure 2c), a height difference between the upper and lower molecules of 1.3 ± 0.1 Å was derived which corresponds within the experimental error to the step height between neighbored Cu(110) planes ($d_{(110)} = 1.28$ Å).

Moreover, we have carried out spatially resolved scanning tunneling spectroscopy (STS) measurements for this phase. In order to reduce the variations between subsequent $I(V)$ curves, we employed current imaging tunneling spectroscopy (CITS) where along with each pixel of a topographic image an $I(V)$ spectrum is measured. Typically this yields STM topographs of 128 × 128 pixels with corresponding $I(V)$ curves of more than 100 points for each pixel, hence allowing an exact correlation between features in the $I(V)$ curves and the topography of the sample surfaces. In Figure 3, we present typical $I(V)$ curves which were obtained by averaging about 20 individual spectra recorded at equivalent positions within the molecular film as indicated in the inset. Virtually indistinguishable spectra were obtained when the STM tip was positioned at the center of molecules adsorbed either on the rim of the rows or at the bottom of the troughs (black and blue curves in Figure 3), thus demonstrating that the two molecular species are electronically identical. In contrast, a deviant curve was obtained when the tip was positioned between the molecules (green curve). Since also the presence of molecular multilayers can be safely ruled out on the basis of their thermal stability,[21] the present STM data clearly indicate a restructuring of the Cu(110) surface with the observed steps originating in the copper substrate itself.

Occasionally, high-resolution STM images with submolecular contrast could also be obtained for very low bias voltages (see Figure 4). However, this high resolution could not be achieved in a routine fashion and thus is attribute to a special tip state, e.g., an extremely sharp tip or a tip that has picked up a perylene molecule. Similar observations have been reported in the literature.[23,24] In previous works, frequently, a submolecular contrast of adsorbed molecules has been attributed to the spatial distribution of frontier molecular orbitals.[24−26] To allow such a comparison, a magnified STM image of a single molecule is shown in the inset of Figure 4 together with a superimposed lowest unoccupied molecular orbital (LUMO) calculated for an individual perylene molecule.[27] We note, however, that due

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to the electronic coupling of the molecular states with metal substrates the molecular orbitals can be strongly distorted as compared to the free molecules. Only in the case of a rather weak substrate interaction, for example, on insulators, does this simple assignment remain valid.[24] In fact, the observed absence of characteristic thresholds in the corresponding *I*(*V*) curves (see Figure 3) which would indicate an onset of resonant tunneling through the highest occupied molecular orbital (HOMO) or LUMO thus corroborates a rather strong electronic coupling of the chemisorbed perylene on the copper surface. Moreover, when considering the HOMO−LUMO energy gap of about 3 eV for a free or van-der-Waals-bound perylene molecule, it seems impossible that for bias voltages within this gap molecular orbitals can be imaged. Therefore, it is more likely that under such tunneling conditions the molecules appear to be rather transparent,[28,29] and instead, the electronic structure of the substrate surface is modified through the adsorbed molecules, i.e., *interface states* are imaged.

After having identified this unusual adsorbate phase, it remains to unravel the underlying mechanism. Adsorbate induced modifications of metal surfaces including also the presently studied Cu(110) surface have been observed for oxygen, sulfur, or organic molecules containing electronegative units (e.g., benzoic acid, carboxylic, or anhydride groups).[30−35] While all these molecular species have reactive units which can strongly interact with the underlying metal, the driving force for the presently observed severe changes of the substrate morphology after adsorption of a nonreactive, pure hydrocarbon is unclear. The absence of any heteroatoms or functional units in these aromatic adsorbates actually points toward the presence of a different, new mechanism.

The key to understand this new mechanism is a precise determination of the relative positions of adsorbate and substrate Cu atoms. Unfortunately, this is difficult to achieve solely on the basis of STM data, because a precise analysis is limited by the nonlinear behavior of the piezo scanners, thermal drift, and piezo creep. However, high-resolution He-atom scattering data provided accurate information about the lateral structure of the stripe phase which was identified previously as a commensurate (5 × 5) superstructure.[21] By using the size of that unit cell ($|\vec{a}| = 12.8$ Å, $|\vec{b}| = 18.1$ Å) for a precise absolute cross-calibration, the STM data allowed a detailed deduction of the geometrical arrangement of the perylene molecules on the copper substrate which is summarized in Figure 5. The saturated monolayer formed at room temperature (RT) corresponds to the densest 2D packing of planar perylene molecules compatible with their van-der-Waals dimensions on a flat, ideal Cu(110) surface yielding a herring bone motif with two differently oriented molecules per (4.5 × 5) unit cell. In contrast, in the high-temperature (HT) stripe phase, the copper substrate restructures which yields a periodic array of narrow terraces consisting of three rows of atoms which are separated by troughs of (nearly) the same width *w*. Perylene molecules cover both the terraces and the bottom of the troughs of this (5 × 5) phase.

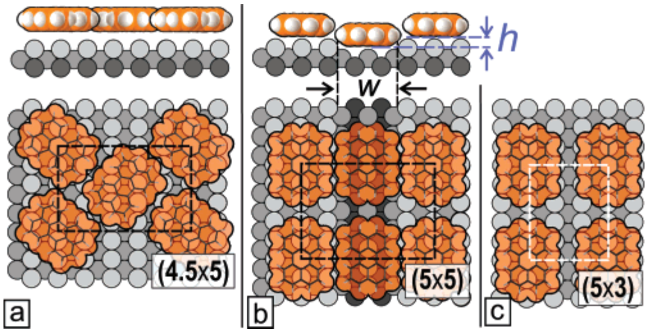

Figure 5. Structure models of (a) the saturated perylene monolayer (RT phase) and (b) the (5 × 5) stripe phase (HT phase) formed on the reconstructed Cu(110) substrate. For comparison, also a stripe phase on an unreconstructed copper surface is shown in c.

Since the molecular coverage in the HT phase is 10% lower than in the RT phase, the total gain in perylene adsorption energy must be caused by the orientation of the perylene molecules relative to the substrate. For the RT phase, the long axis of the molecules is rotated with respect to the high symmetry directions of the copper substrate, whereas, for the HT phase, all molecules are uniformly aligned along the characteristic rows of the Cu(110) surface. Of course also on the nonrestructured Cu(110) surface, perylene molecules can adopt a uniform alignment. The corresponding molecular packing density in such a hypothetical (5 × 3) phase, however, is about 17% lower than that on the striped surface (see Figure 5c). Therefore, we propose that the driving force for the formation of this HT phase is a significant gain in adsorption energy for such aligned molecules which leads to a close registry of the molecular frame and the underlying copper lattice.

Unfortunately, precise electronic structure calculations are not available for this system and, moreover, the standard method for theoretical calculations of molecules bound to metal surfaces, density functional theory (DFT), cannot be applied in a direct way to primarily van-der-Waals-bound molecules.[36,37] However, a reliable estimate of the change in cohesion energy accompanying the creation of copper steps can be obtained by employing effective medium theory which yields an energy of about 0.1 eV per adsorbed perylene molecule (see the Supporting Information). This value is rather small as compared to the adsorption energy of about 1.85 eV obtained by thermal desorption experiments.[21]

The proposed lock-in mechanism of adsorbed molecules with regard to the copper lattice can be further corroborated by studying their relative positions. Perylene has a C_2 symmetry, and therefore, the adsorption position with the lowest energy is expected to reveal at least that symmetry.

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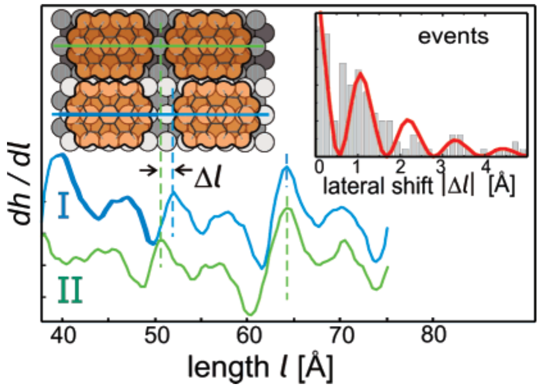

Figure 6. Derivative of line scans along neighboring closely packed molecular rows (recorded at the rim and the bottom of the troughs, I and II in Figure 2b and c) revealing the presence of distinct shifts of Δl between adjacent perylene molecules. The inset displays the statistical distribution of such lateral shifts together with a fit to a correlation function.

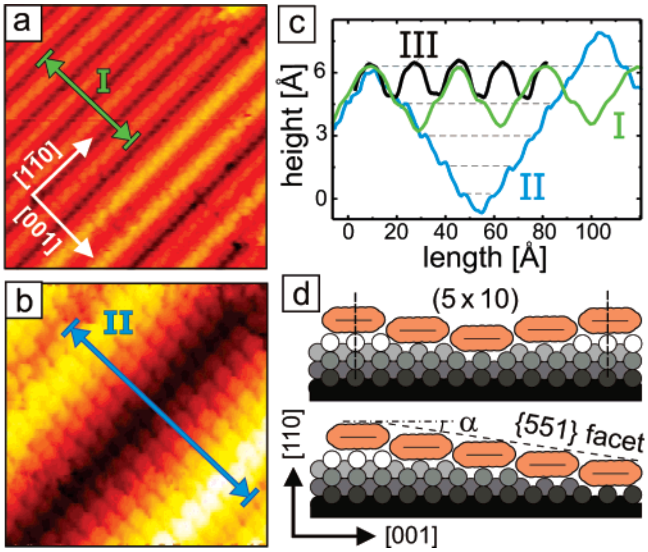

Figure 7. Summary of STM images showing other *row* structures formed upon adsorption of perylene on Cu(110), (a) (5 × 10) superstructure and (b) {551} facets (tunneling parameters: $U_{\mathrm{sample}} = -2.0$ V, $I_t = 0.8$ nA) together with corresponding height profiles (c) and structure models of the more complex row structures (d). Profile III was taken from Figure 2c.

At the reconstructed copper surface presented above, this is achieved by placing the central ring of the perylene molecule either at a *top* position or at a *bridge* position of the centermost of the three substrate rows. If molecules are in perfect registry with substrate atoms on the terraces and on the bottom of the troughs, then their positions must reflect the relative shift of the substrate corrugation between subsequent (110) layers which amounts to $g_{\mathrm{Cu}}/\sqrt{8} = 1.28$ Å for copper. In fact, a detailed inspection of Figure 2b reveals that in contrast to the very regular spacing between closely packed rows, the distances between the molecules along such rows are more irregular. This leads to an appearance of deeper and broader gaps between neighboring molecules which are clearly visible in the respective profiles. As a consequence, also the registry between the molecules in the upper and the lower rows is not perfect; frequently, small lateral shifts along the direction of the rows are visible as dark gaps (indicated by the white arrow in Figure 2b).

In order to quantify this behavior, the positions of the molecules inside the rows have been determined precisely by using the derivative of the corresponding line scans. In such curves which are shown in Figure 6 for the two profiles displayed in Figure 2c, distinct extrema can be seen which are assigned to the inflection points of the line scans across the molecules. By using the position of the maxima as a measure of the border of molecules, lateral shifts Δl between neighboring molecules in the upper and the lower rows were determined. We note that such an analysis was essentially made possible by the above-mentioned absolute cross-calibration of our STM images which compensates for possible image distortions. The resulting distribution of shifts based on the analysis of more than 100 neighbored molecules is shown in the inset of Figure 6. It is clearly visible that this distribution is not a smoothly varying curve but instead exhibits in addition to a main peak at $\Delta l = 0$ Å (i.e., perfect registration) several distinct side maxima. The data have been further analyzed by fitting a damped correlation function $\propto \cos^2(\omega\Delta l)$ which yielded a periodicity of 1.16 ± 0.03 Å. According to our model, the position of such side maxima can be related to molecules shifted by half of the copper nearest neighbor distance, i.e., $\Delta l = a_{\mathrm{nn}}/2 = 1.28$ Å to adopt identical adsorption sites at the terrace and the bottom of the troughs as indicated in Figure 6 which is in close agreement with the observed value. We note, further, that in images taken in spectroscopic CITS mode molecular jumps between discrete positions with $\Delta l \approx 1.3$ Å have been observed occasionally in consecutive images. This behavior is most probably tip-induced as in CITS mode rather large voltages (up to ±3V) are employed. Nevertheless, before and after manipulation, the molecule resides in (closely spaced) minima of the unperturbed energy surface of the substrate interaction potential. Although the statistics of the distribution of the analyzed shifts is too poor to precisely determine a potential energy surface seen by the adsorbed molecules (as performed in ref 38), it can be clearly related to the atomic corrugation of the substrate surface. We attribute the surprising markedness of this effect to the rather close match of the ring size of perylene and the nearest neighbor distance at the copper surface.

In addition to the (5 × 5) phase with its characteristic alternating step-up/step-down pattern, more complex row structures with a distinctly larger corrugation have been observed if the surface had been annealed over longer periods of time. A first indication for the appearance of additional row structures is already visible in Figure 2a where isolated rows with a deeper trough can be seen. This structure which was not observed for the bare Cu(110) surface appears occasionally also on a larger scale as displayed in Figure 7a and thus cannot be due to a preexisting morphology of the copper substrate but is induced by the adsorption of perylene. The corresponding line scans indicate that the separation of the rim and the depth of the central trough are about twice as large as for the (5 × 5) phase (see Figure 7c) while similar distances between the molecules were found along the rows. On the basis of these dimensions, we therefore identify this structure as a (5 × 10) phase a model of which is shown in Figure 7d.

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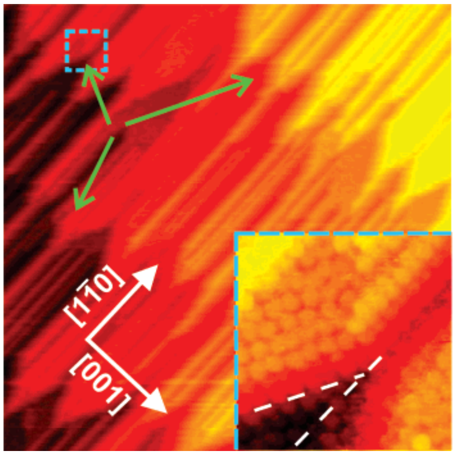

Figure 8. Typical large-scale STM images showing the appearance of various perylene induced row structures on the Cu(110) surface upon extended annealing. The image sizes are as follows: 135 nm × 135 nm.

Furthermore, even deeper troughs extending over several tens of nanometers along the $[1\bar{1}0]$ direction were sometimes observed. Figure 7b displays a typical high-resolution STM image of such a structure which reveals the presence of up to six separate terrace levels. A comparison of the height profiles measured across the troughs for the various row structures (see Figure 7c) indicates that the deeper troughs can be described by the same structural motif established for the (5 × 10) phase. Considering further the atomic packing in the copper crystal, this leads to a staircase of short terraces and yields the presence of local {551} facets on the substrate surface. Such facets form an angle of $\alpha = 8°$ with respect to the macroscopic (110) plane as depicted schematically in Figure 7d and appear in alternating inclination to maintain the macroscopic orientation of the surface. This value is in close agreement with an angle of about $10° \pm 3°$ determined from the slope of the profile (curve II in Figure 7c).

In connection with the development of the (5 × 5) structure (cf. Figure 1b), it was already mentioned that this phase initially starts by forming short rows which nucleate at steps of the substrate. In fact, the analysis of many (large-scale) STM images reveals that all reconstructed regions nucleate at [001]-oriented substrate steps while with progressing restructuring the characteristic rows continue to extend along the $[1\bar{1}0]$ direction and form a variety of row structures displayed in Figure 8. This can be explained by the rather high diffusivity of copper atoms particularly at steps.[39] A closer inspection of Figure 8 reveals further that the mesoscopic ripples formed by the {551}-oriented facets are terminated by characteristic *spearheadlike* structures (indicated by green arrows). The sides of these triangles form an angle of 32° with the $[1\bar{1}0]$ direction (see inset in Figure 8) and are inclined by about 6° relative to the macroscopic (110) surface, suggesting the presence of modified {551} facets with kinks along the closely packed steps. We note that the observed unidirectional growth of the various surface structures involves a substantial mass transport of substrate atoms which can be understood by the rather anisotropic diffusion of adatoms present on the Cu(110) surface.[40]

IV. Conclusions

The present results demonstrate that perylene molecules, which form quite soft bulk crystals with a relatively low sublimation temperature are able to coin stripe patterns in a metallic substrate. These patterns which are obtained upon adsorption of perylene on Cu(110) and subsequent annealing at 390−450 K are not a structural motif of the perylene crystal structure (which is determined by weak van-der-Waals-type intermolecular interactions) but of the size and the shape of the single molecule. The stripe structure with the smallest periodicity is identified as a (5 × 5) phase which consists of substrate stripes reflecting the width of the perylene molecule, 9 Å. Evolving from this building pattern, also the appearance of stripes of doubled width and depth and finally the formation of small {551} facets is observed.

We wish to emphasize that in part rather similar structures have been observed previously by Chen et al.[17] and were attributed to crystalline perylene films. The present analysis, however, unambiguously demonstrates that these structures are not related to organic multilayers but reflect a complex restructuring of the perylene/Cu(110) interface itself which is caused by a lock-in mechanism of the carbon frame relative to the copper surface lattice. In that case, the rigid backbone of the polycyclic hydrocarbon appears to be harder than the more flexible metal surface and acts as an embossing die. This coining effect may open the possibility of producing more complicated surface structures on metal substrates by using planar organic molecules with different shapes. It will be of interest to explore whether introducing additional heteroatoms like N or O into the aromatic rings can further increase the interaction with the surface and the transfer of structural information to the metal substrate.

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Supporting Information Available: Theoretical estimate of the cohesion energy of step formation. This material is available free of charge via the Internet at http://pubs.acs.org.

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