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Epitaxial Growth of a Crystalline Organic Semiconductor: Perylene/Cu{110}

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A new, centered orthorhombic crystal, $a = 20.7$ Å, $b = 19.3$ Å, $c = 3.4$ Å, and $\beta = 90$ Å, of perylene, $C_{20}H_{12}$, has been grown epitaxially on a Cu(110) surface under UHV conditions. The crystal structure has been studied with HREELS, LEED, and STM. Vibrational spectra reveal that the molecular planes are parallel to the substrate. Electron diffraction indicates an almost square unit cell in the *ab* plane in which the *a* axis is commensurate along the ⟨110⟩ azimuth of the Cu substrate, while the *b* axis is incommensurate along the ⟨001⟩ azimuth. STM images show a large scale smooth morphology of the organic crystal indicative of layer-by-layer growth, while high-resolution images show the details of the centered orthorhombic structure of perylene and the nature of the 3D grain boundaries.

1. Introduction

The development and control of the ordering of organic semiconductor systems is of considerable current interest.[1−5] Recently, great attention has been focused on the organic molecular beam epitaxy (OMBE) of ordered organic thin films formed by macrocyclic aromatic molecules for the application in optoelectronic devices.[3,5−9] The optical and electronic properties of these crystallized organic films depend crucially on their orientation and the long range ordering,[10] which, in turn, determines their suitability for molecular electronic devices such as FETs, LEDs,[1,3,11] and so forth. It has been observed[12,13] that the improved internal ordering of the organic thin film could enhance field-effect carrier mobilities, together with increasing the electrical conductivity and reducing the activation energy for electrical conduction.

Macrocyclic aromatic molecules, such as perylene−tetracarboxylicdianhydrid (PTCDA), whose bulk structure involves planes of flat-lying molecules, appear to be the best candidates for ordered layer-by-layer growth. However, the multilayer crystallized structure achieved through the OMBE method is not necessarily the same as the single crystal structure grown from solution, particularly if the molecular interaction with the substrate is strong and can provide a new growth template. This presents an opportunity to finely tune the structure to give optimal physical, electronic, and optoelectronic properties. Recognition of the substrate structure and its symmetry elements by the growing adsorbate film determines whether the overlayer is commensurate or not. In general, a commensurate overlayer is likely to have a structure different from that of the bulk crystal, while an incommensurate overlayer is more likely to maintain its bulk crystal structure. Typically, the intermolecular potential energy surface describing planar aromatic hydrocarbons is broad and shallow; thus, the molecule−substrate interaction could play a significant role in determining the commensurability and subsequent 3D crystalline structure. In contrast, for molecules containing functional groups such as the anhydride groups in PTCDA,[14] the intermolecular interaction becomes much deeper and narrower, which in turn leads to the multilayer structure being the same as or closely similar to the thermally stable bulk structure.

In this paper, we present the observations of a novel, one-dimensionally commensurate, well ordered, large scale crystalline structure formed by perylene (I) on a Cu(110) surface. The crystal structure of the thin film is quite different from that of bulk perylene. Vibrational spectra clearly show a flat-lying molecular orientation in the multilayer. Electron diffraction and STM provide

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(1) Ozaki, H. *J. Chem. Phys.* **2000**, *113*, 6361−6375.

(2) Morozov, A. O.; Kampen, T. U.; Zahn, D. R. T. *Surf. Sci.* **2000**, *446*, 193−198.

(3) Schon, J. H.; Berg, S.; Kloc, C.; Batlogg, B. *Science* **2000**, *287*, 1022−1023.

(4) Muller, E.; Ziegler, C. *J. Mater. Chem.* **2000**, *10*, 47−53.

(5) Bohler, A.; Urbach, P.; Schobel, J.; Dirr, S.; Johannes, H. H.; Wiese, S.; Ammermann, D.; Kowalsky, W. *Physica E* **1998**, *2*, 562−572.

(6) Cho, K. J.; Shim, H. K.; Kim, Y. I. *Synth. Met.* **2001**, *117*, 153−155.

(7) Colle, M.; Tsutsui, T. *Synth. Met.* **2000**, *111*, 95−97.

(8) Feng, W.; Fujii, A.; Lee, S.; Wu, H.; Yoshino, K. *J. Appl. Phys.* **2000**, *88*, 7120−7123.

(9) Gerasimova, N. B.; Komolov, A. S.; Aliaev, Y. G.; Sidorenko, A. G. *Phys. Low-Dimens. Struct.* **2001**, *1−2*, 119−125.

(10) Toda, Y.; Yanagi, H. *Appl. Phys. Lett.* **1996**, *69*, 2315−2317.

(11) Yamaguchi, T. *J. Phys. Soc. Jpn.* **1999**, *68*, 1321−1330.

(12) Salih, A. J.; Lau, S. P.; Marshall, J. M.; Maud, J. M.; Bowen, W. R.; Hilal, N.; Lovitt, R. W.; Williams, P. M. *Appl. Phys. Lett.* **1996**, *69*, 2231−2233.

(13) Karl, N.; Marktanner, J. *Mol. Cryst. Liq. Cryst.* **2001**, *355*, 149−173.

(14) Tautz, F. S.; Sloboshanin, S.; Shklover, V.; Scholz, R.; Sokolowski, M.; Schaefer, J. A.; Umbach, E. *Appl. Surf. Sci.* **2000**, *166*, 363−369.

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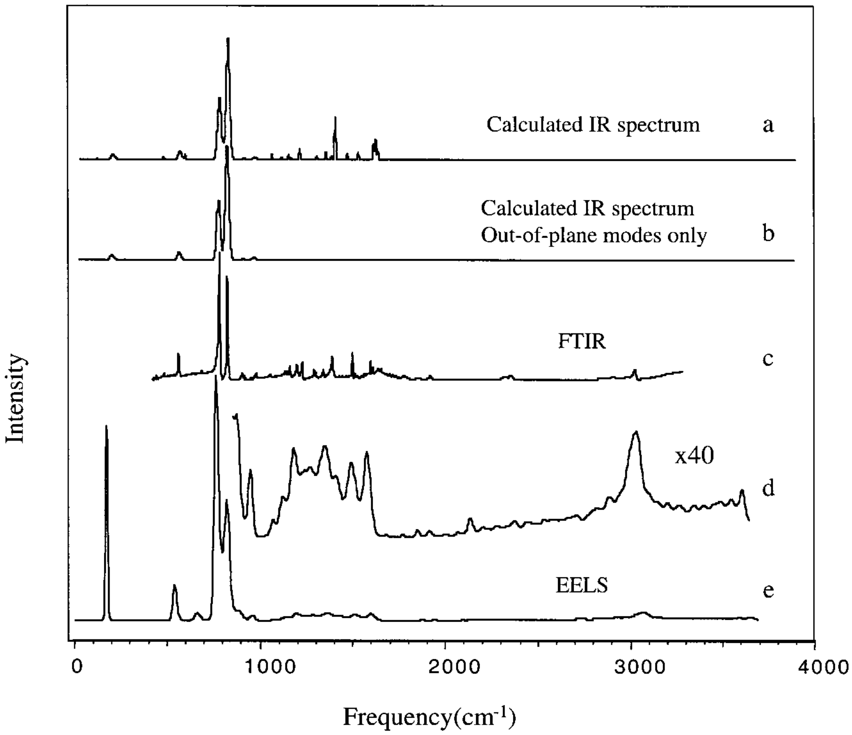
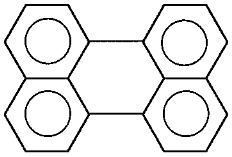


Figure 1. (a) Full, ab initio calculated IR spectrum. The calculated spectra are plotted as Gaussian shape with a width of 30 cm^{-1}. (b) Ab initio calculated IR spectrum of out-of-plane modes. (c) FTIR spectrum of a free perylene molecule. (d) Zoomed HREELS spectrum of perylene on Cu(110) between 800 and 3700 cm^{-1}. (e) HREELS spectrum of perylene on Cu(110), recorded with the primary 8 eV.

details of the unit cell dimensions and the molecular arrangement within the unit cell.



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2. Experimental Section

The experiments were carried out in two different UHV instruments equipped with low energy electron diffraction (LEED) attachments and either STM (Omicron) or high-resolution electron energy loss spectroscopy (HREELS) (VSW HIB 1000 double pass spectrometer) instruments. Both systems have a Hiden quadrupole mass spectrometer to monitor the molecular beam. The Cu(110) crystals were cut and polished mechanically, and, for STM experiments, electrochemically, to a mirror finish before insertion into UHV, where they were cleaned by standard Ar^+ bombardment (typically, 500 eV, 30 $\mu A\ cm^{-2}$) and annealing (773 K) procedures until a clean surface was obtained, characterized by sharp (1 × 1) LEED patterns and large flat terraces in STM.

Perylene is degassed for 3 h at 333 K before dosing. The chemical is used without other purification. The doser consists of a glass tube with a heating wire and a thermocouple sensor, so the dosing temperature is well controlled and the reproducibility is ensured. The same doser was used in both UHV systems. Perylene was dosed at 433 K, with the substrate at room temperature with a dosing pressure of about 1×10^{-9} mbar.

3. Results and Discussion

Focusing first on the characteristic of the film, by vibrational spectroscopy, we present a comparison of HREELS of the perylene grown epitaxially on Cu(110), the IR spectrum of the free molecule, and the results of ab initio calculations based on GAUSSIAN 98W.[15] Following this, the temperature-dependent HREELS data are presented to provide an overview of the molecular geometry on the surface. Next, the LEED pattern together with the STM results are presented and, by correlation with the spectral data, basic features in the STM images are interpreted.

After dosing for 15 min, an ordered multilayer of perylene is formed on Cu(110). Figure 1 shows the HREELS spectrum (d, e) of this surface together with the ab initio calculation results (a, b) and infrared spectrum of the free molecule (c). The EELS spectrum has been processed by background subtraction and maximum likelihood resolution enhancement.[16] The spectrum is dominated by the loss peaks at 171, 546, 767, and 825 cm^{-1}, with weaker peaks between 880 and 1600 cm^{-1}. The vibrational frequencies from the EELS spectrum of the adsorbate are in excellent agreement with the infrared absorption frequencies of the free molecule, which suggests that the molecules remain chemically intact upon adsorption. The ab initio calculations were carried out on a fully optimized free molecule with B3LYP density functional theory and the 6-31g

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[15] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98W*, Revision A.7 ed.; Gaussian, Inc.: Pittsburgh, PA, 1998.

[16] Frederick, B. G.; Nyberg, G. L.; Richardson, N. V. J. *Electron Spectrosc. Relat. Phenom.* **1993**, *64/65*, 825−834.

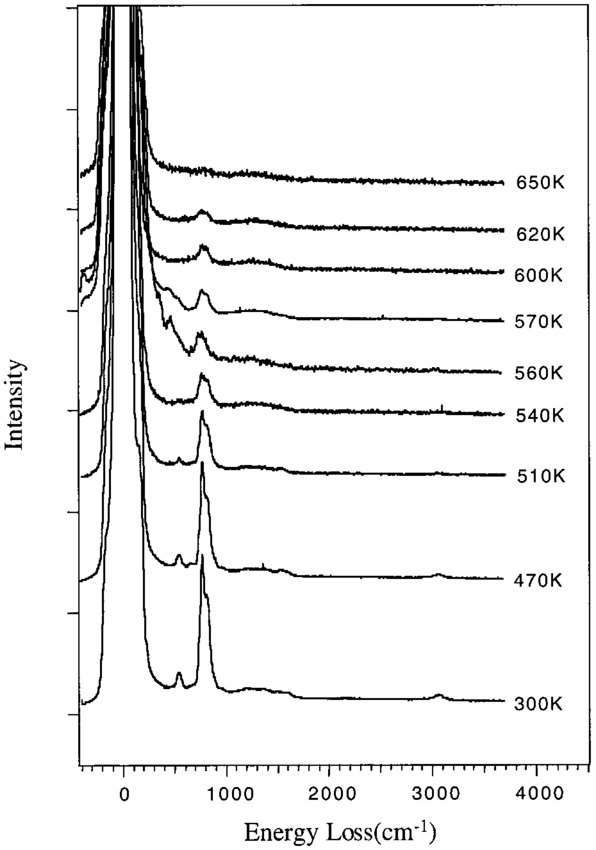

Figure 2. HREEL measurement as a function of annealing temperature. All spectra were recorded at room temperature. The intensities have been normalized against the elastic peak. Each spectrum has been shifted up for display.

basis set using GAUSSIAN 98W.[15] Spectrum b shows only the out-of-plane modes with calculated IR intensities, while spectrum a includes all the dipole active modes. It is clear that only the out-of-plane modes in EELS have strong loss intensities while the in-plane modes are relatively weak. For perylene, both ab initio calculations and the IR spectrum of the free molecule indicate that the in-plane modes are inherently weaker than the out-of-planes modes. However, in EELS, the out-of-plane modes are about 40 times stronger than the in-plane modes. Even allowing for the bias in EELS toward low frequency modes, such a high intensity ratio in EELS can be attributed only to the fact that most of the molecules are in a flat-lying geometry relative to the substrate with excitation of in-plane modes forbidden by the surface selection rule.

The flat-lying geometry is further confirmed by the temperature dependent EELS measurement. EELS spectra in Figure 2 show the decrease of the loss intensities as a function of annealing temperature. All spectra were measured at room temperature after annealing for 1 min at the stated temperature. Only the out-of-plane modes decrease in intensity while the in-plane modes maintain their intensities even at 650 K. Therefore, it is most probable that the intensity of the in-plane modes is contributed from the adsorption of the molecules at surface defects (step edges, kinks, etc.), while the crystalline overlayers are formed by the flat-lying molecules.

It is also found that the loss intensities have a stepped dependence on annealing temperature which can be separated into several regimes, as shown in Figure 3, which shows the measured loss intensity at 767 cm^{-1} as a function of the annealing temperature. It is clear that, between room temperature (300 K) and 465 K, the loss intensity shows little decrease, while, between 465 and 540 K, the loss intensity decreases dramatically. Above 540 K, the loss intensity slowly decreases until 600 K followed by complete disappearance of the loss intensity. Therefore, it can be concluded that the epitaxial crystal is thermally stable in UHV up to 465 K and is completely evaporated by 540 K. Between 540 and 600 K, a monolayer of perylene is stable but desorbs above 600 K. Thus, the interaction between perylene and the Cu substrate is stronger than the intermolecular interactions.

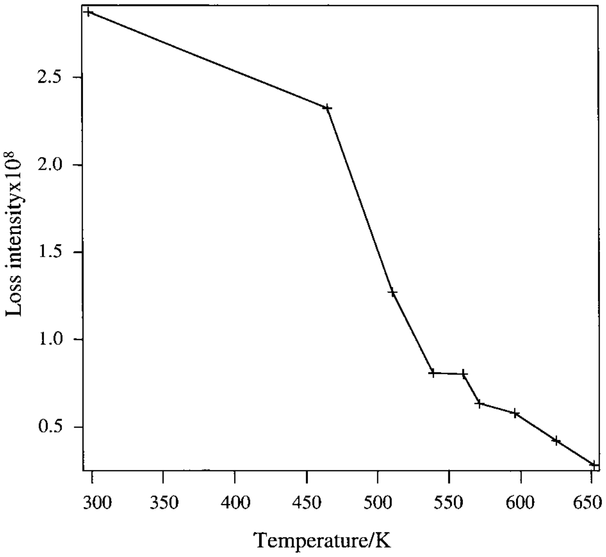

Figure 3. Loss intensity at 767 cm^{-1} as a function of annealing temperature. The intensity has been normalized against the elastic peak.

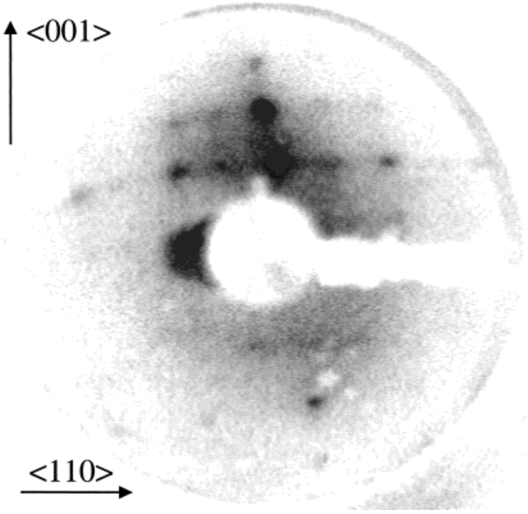

Figure 4. LEED pattern of the multilayer perylene on Cu(110), recorded at 19 eV. The electron beam has an incident angle of 10° off the surface normal in the ⟨001⟩ azimuth.

We now consider the crystallinity of the overlayer as indicated by low-energy electron diffraction (LEED) and scanning tunneling microscopy (STM). Figure 4 shows the LEED pattern of the multilayer, recorded at 19 eV. The diffraction pattern shown in Figure 4 corresponds to a real space periodicity which gives a rectangular (almost square) unit cell of 20.7 ± 0.5 Å × 19.3 ± 0.5 Å, with the vectors aligned along the two high-symmetry axes of the substrate. Along the ⟨110⟩ azimuth, the periodicity is commensurate with the substrate unit cell with 8-fold periodicity, corresponding to a unit cell vector of 20.4 Å. However, the perpendicular unit cell vector, although azimuthally aligned along ⟨001⟩ , has a length of 19.3 Å, which does not bear a simple relationship to the corresponding substrate vector, 3.60 Å. Conventionally, an adsorbate/substrate system is commensurate in a given direction if the size of the adsorbate and substrate unit cells, along the relevant direction, can be expressed as a rational number. Of course, within experimental error, in reality this is almost always possible. So, if the ratio cannot be expressed by relatively small integers, particularly in the substrate term, it is usual to refer, as here, to an incommensurate structure. For perylene on Cu(110), the system is commensurate along ⟨110⟩ and incommensurate along ⟨001⟩ , indicating that there is an azimuthal dependence to the adsorbate−substrate and adsorbate−adsorbate interactions. It is meaningful, therefore, to refer to organic molecular beam epitaxy (OMBE), since the substrate exerts marked epitaxial influences in the growing film, in contrast to organic molecular beam deposition (OMBD), where crystallinity, if present at all, is dominated by the bulk interaction with little or no influence from the substrate. Obviously, the balance between different interactions will determine the influence of the substrate as a template for the epitaxy of the organic structure. While HREELS can give information on molecular orientation and the LEED pattern presents the size and shape of the unit cell, STM images normally can indicate the number of molecules within the unit cell and, frequently, even finer structural details, depending on the image resolution.

In Figure 5a, we show a large area STM image (2 μm × 2 μm) of a typical epitaxial multilayer of perylene on Cu(110). The surface of the film appears to be extremely flat. The line profile A (Figure 5b) remarkably shows a significant height variation of only 6 Å in a length of 2 μm. Even the clean Cu(110) surface gives a height variation of 15 Å on this length scale, corresponding to 11 atomic steps. Also, the terrace edge of the multilayer structure is very different from that of the clean Cu-{110}, which has rather well defined straight terrace edges. These effects suggest that the multilayer crystallinity structure is not limited by the terrace size of the clean surface. The line profile B also gives some indication of the depth of hole defects. There are two types of point defect on the multilayer. One is relatively large and deep with a width of 40 nm and a depth of ∼3 nm. Variations in depth correspond to only a few monolayer thicknesses and can be interpreted as holes completely through the multilayer structure either to the substrate or perhaps to the first monolayer. Furthermore, since the size of a perylene monolayer step can be measured as 1.7 Å (vide infra), this suggests a film thickness of ∼18 ± 3 monolayers. The second type of defect is smaller and shallower with a width of 10 nm and a depth of only 0.6 nm. We suggest that this type of point defects corresponds to shallow defects developed several layers into the multilayer structure.

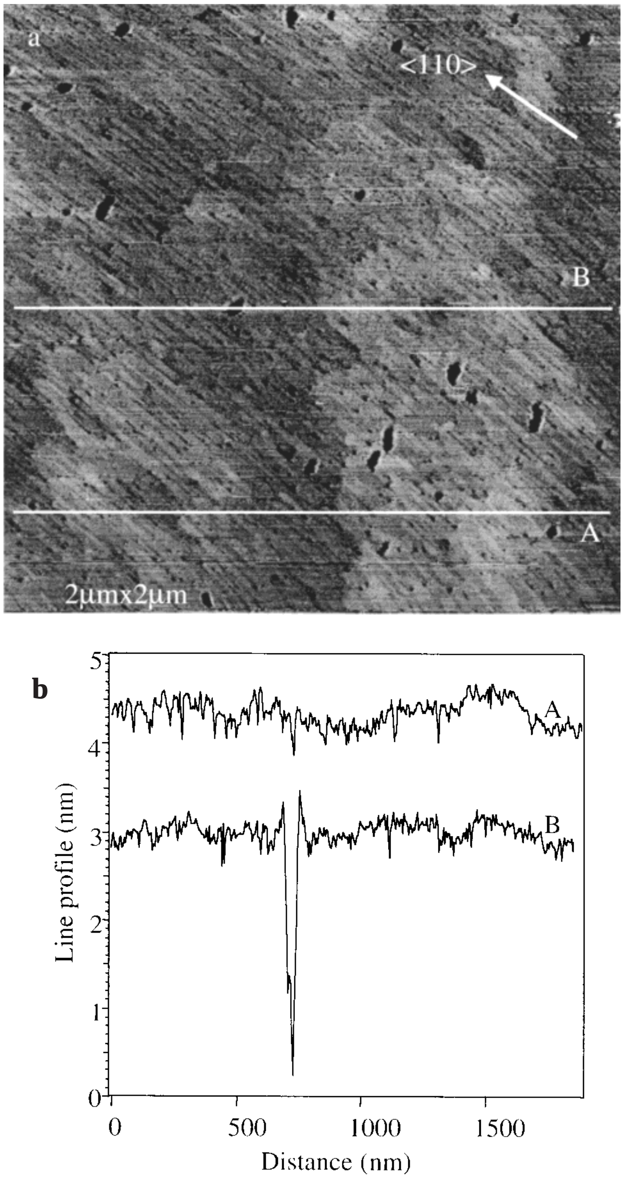

Figure 5. (a) Large scale, STM image (2 μm × 2 μm, sample bias = 0.01 V, tunneling current = 0.47 nA) showing the morphology of the multilayer structure. (b) Line profiles along lines A and B.

An STM image (270 nm × 270 nm) with a higher resolution (Figure 6) shows, indeed, that individual terraces are defined by the overlayer structure rather than the terraces of the clean Cu surface. In this image, the multilayer structure can be well resolved, confirming a layer-by-layer growth mechanism. The finger-like features are narrow molecular chains formed from one or two rows of molecules. All the "fingers" point along the ⟨110⟩ direction; that is, most of the terrace edges are aligned along the ⟨110⟩ azimuth of the Cu(110) substrate, while, along the ⟨001⟩ azimuth, the steps are very heavily kinked. This indicates a much stronger adsorbate−adsorbate and adsorbate−substrate interaction along the ⟨110⟩ azimuth than along the ⟨001⟩ azimuth. The preferential ordering along the ⟨110⟩ azimuth has also been confirmed on the monolayer structure of perylene on Cu(111).[17] Meanwhile, most of

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[17] Wang, D.; Wan, L. J.; Xu, Q. M.; Wang, C.; Bai, C. L. *Surf. Sci.* **2001**, *478*, L320−L326.

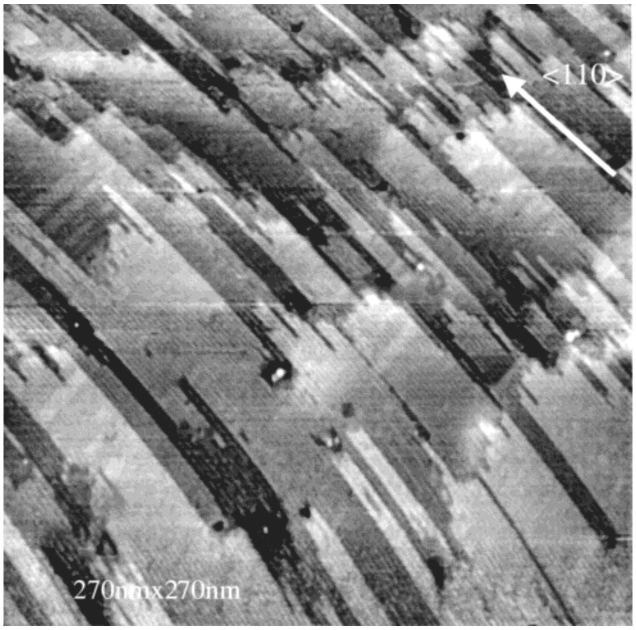

Figure 6. STM image (270 nm × 270 nm) obtained at a sample bias = 0.01 V and a tunneling current = 0.47 nA.

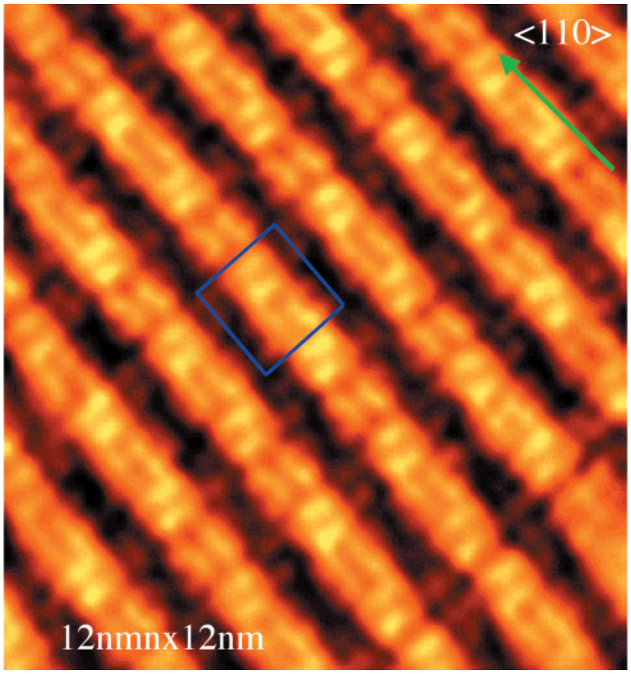

Figure 7. High-resolution STM image (12 nm × 12 nm, same tunneling conditions as in Figure 5) showing the unit cell.

the point defects are localized on the domain boundaries and inhibit the 2D epitaxy of the ordered overlayer.

A further enlarged image (Figure 7, 12 nm × 12 nm) shows the molecular details of the ordered structure. The image has been recorded with very low sample bias (0.01 V, 0.47 nA), which is typical of that required for aromatic molecules with their π-orbital parallel to the surface. The multilayer structure of perylene, as confirmed with EELS measurement, is indeed formed by layers of flat-lying molecules. In STM, the tunneling junction is achieved with molecular orbitals that match both the substrate and tip in energy, space, and symmetry. Since the π-orbitals of aromatic molecules are very close to the Fermi level of metals, zero bias is suitable for forming stable tunneling conditions to resolve the molecular features. The marked rectangular shaped unit cell has a vector of 20.7 Å along the ⟨110⟩ azimuth and 19.3 Å along the ⟨001⟩ azimuth, in excellent agreement with the LEED results.

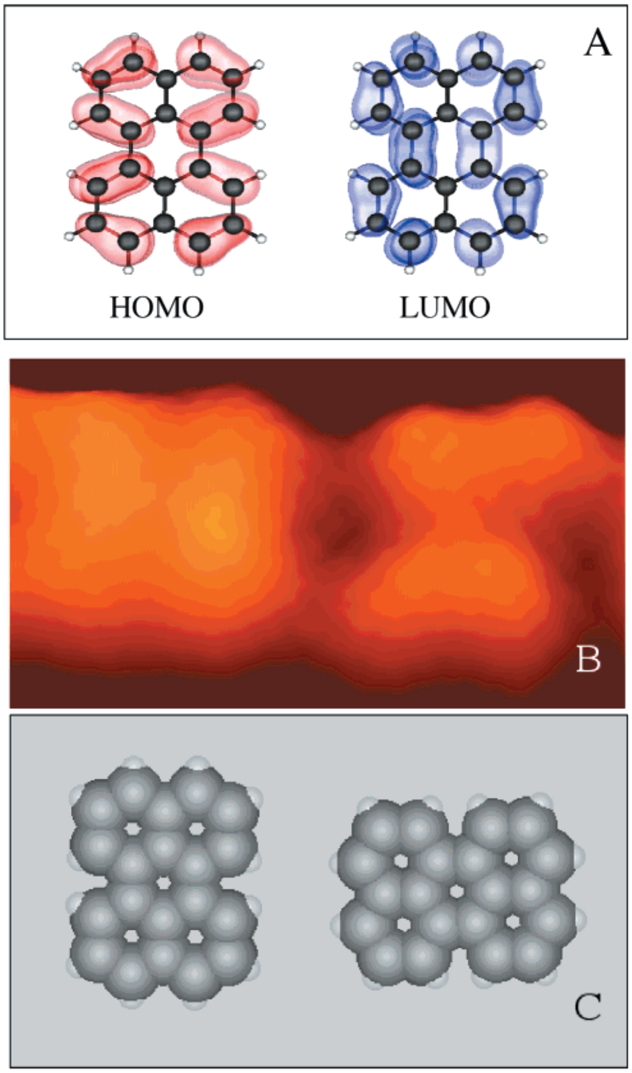

Figure 8. (A) Frontier molecular orbitals of perylene from ab initio calculations. (B) Enlarged STM image of a small area containing two molecules. (C) Model of the arrangement of the molecules within the unit cell.

There are two distinct molecular sized features within the unit cell. Each consists of two parallel bars 4.2 Å apart. In one feature, the bars are aligned along the ⟨110⟩ azimuth, while in the other they are aligned along the ⟨001⟩ azimuth. The flat-lying perylene molecule formed by two naphthalene units has a rectangular shape with a width of 8.7 Å and a length of 11.3 Å. To determine the molecular azimuth orientation in each feature, the frontier orbitals of the free molecule have been identified using ab initio Gaussian 98W calculations. Figure 8 shows the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), which we considered relevant to the low bias STM image. Most significantly, both orbitals have a nodal plane bisecting each of the two naphthalenes in the molecule. The separation into the two bars for each molecule in the image is related to this node in the frontier orbitals. We, therefore, suggest that the flat-lying molecules are aligned with their longer axis parallel to the bar. Figure 8B shows the image of two neighboring molecules, with the relative orientation of the two corresponding molecules within the unit cell shown in Figure 8C. The van der Waals' dimensions of the molecular rectangle are 11.3 and 8.7 Å, so close packing of molecules with alternating orientation should lead to a unit cell of 20 Å (11.3 + 8.7 Å), close to the observed 8-fold periodicity of the substrate (20.7 Å). On the other hand, along the ⟨001⟩ azimuth, the molecular rows are in-phase in terms of their relative orientation and have a separation of 19.3 Å. Here, we emphasize that the layered periodic structure of perylene on Cu(110) presented here, with the planes of all molecules parallel to each other and the substrate surface, does not represent any plane of the bulk crystal.[18,19] The unit cell of bulk perylene is formed by four molecules in two pairs. Within each pair, the molecules are staggered with their molecular planes parallel to each other at a separation of 3.4 Å, while adjacent pairs have their molecular planes perpendicular to each other. The structure is favored by the interaction of molecular quadrupoles. Although all the molecular planes are perpendicular to the (001) bulk crystal plane, there is no crystal plane in which all the molecular planes are parallel, as found for the film on the Cu(110) surface. This demonstrates that the templating effects of the substrate are strong enough to initiate and maintain the novel molecular arrangement. In turn, this gives the possibility of manipulating and designing the overlayer structure to optimize film properties.

To characterize the ordered multilayer structure in further detail and, in particular, the registration between adjacent layers, Figure 9 shows an STM image covering several terraces. The line profile (Figure 9b) across the layers shows three layers, labeled A, B, and C, with an interlayer space of 1.7 Å. When the molecular orientation within a layer and those in different layers are compared, it is found that the molecules on the same line along the ⟨001⟩ azimuth have the same molecular orientation, even in different layers. Furthermore, the molecular rows along the ⟨110⟩ azimuth within one layer are out-of-phase with the rows in the adjacent layers along the surface normal. Thus, the orientation and position of the upper layer molecules are determined by the lower layers. This strict registry between different layers suggests a strong interlayer interaction and accounts for the stability of this novel structure. Compared with the monoclinic bulk crystal, the 3D crystalline structure epitaxially grown on the Cu(110) surface can be described as a centered orthorhombic crystal (shown in Figure 10), with $a = 20.7$ Å, $b = 19.3$ Å, and $c = 3.4$ Å. The bc plane is a centered structure.

Several line defects can be found on the image shown in Figure 9. All are aligned along the ⟨001⟩ azimuth and appear as minima in the line profile along ⟨110⟩ shown in Figure 9c. There are two types of line defects; one is relatively deep, labeled as X, and the other is more shallow, labeled as Y. At X type line defects, on either side of the line, the adjacent molecules are both aligned with their longer axes along the ⟨001⟩ azimuth rather than alternating. As a consequence, these molecules are spaced at a greater intermolecular distance (~10 Å) than that required by the van der Waals' diameter (~9 Å), which gives rise to a space between these two

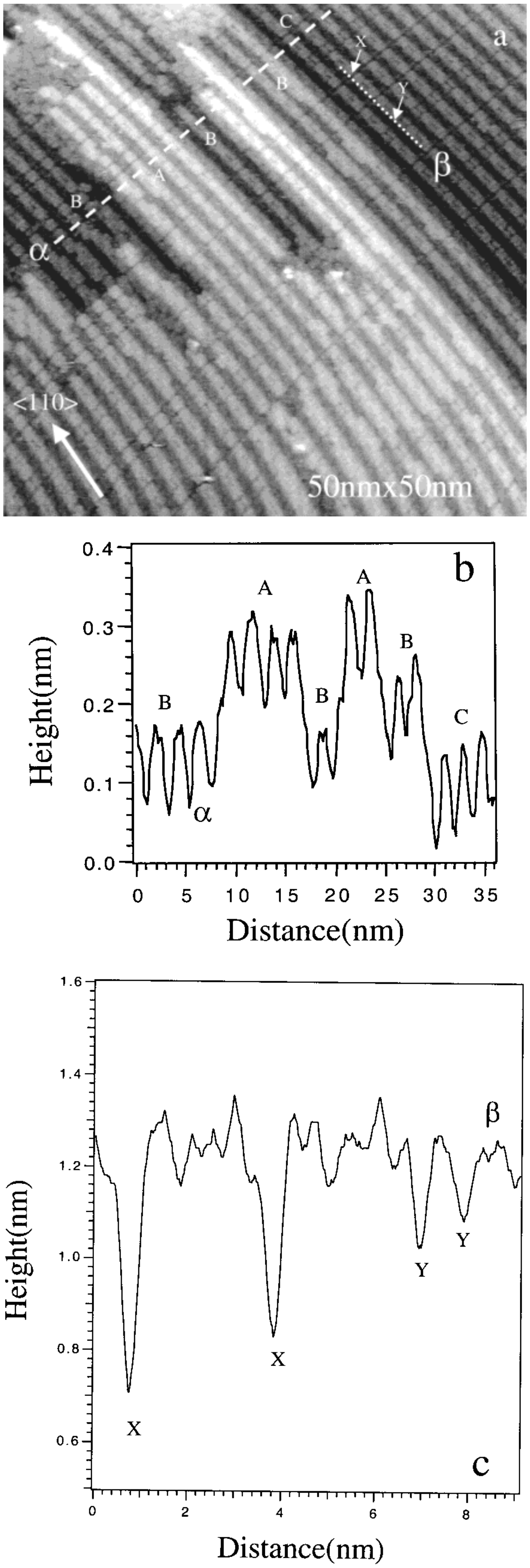

Figure 9. (a) STM image (50 nm × 50 nm) showing the molecular arrangement between different layers. (b) Line profile (α) showing a three layered structure. (c) Line profile (*β*) showing two types of line defects.

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[18] Camerman, A.; Trotter, J. *Proc. R. Soc. A* **1964**, *279*, 129−146.

[19] Donaldson, D. M.; Robertson, J. M.; White, J. G. *Proc. R. Soc. A* **1953**, *220*, 311−321.

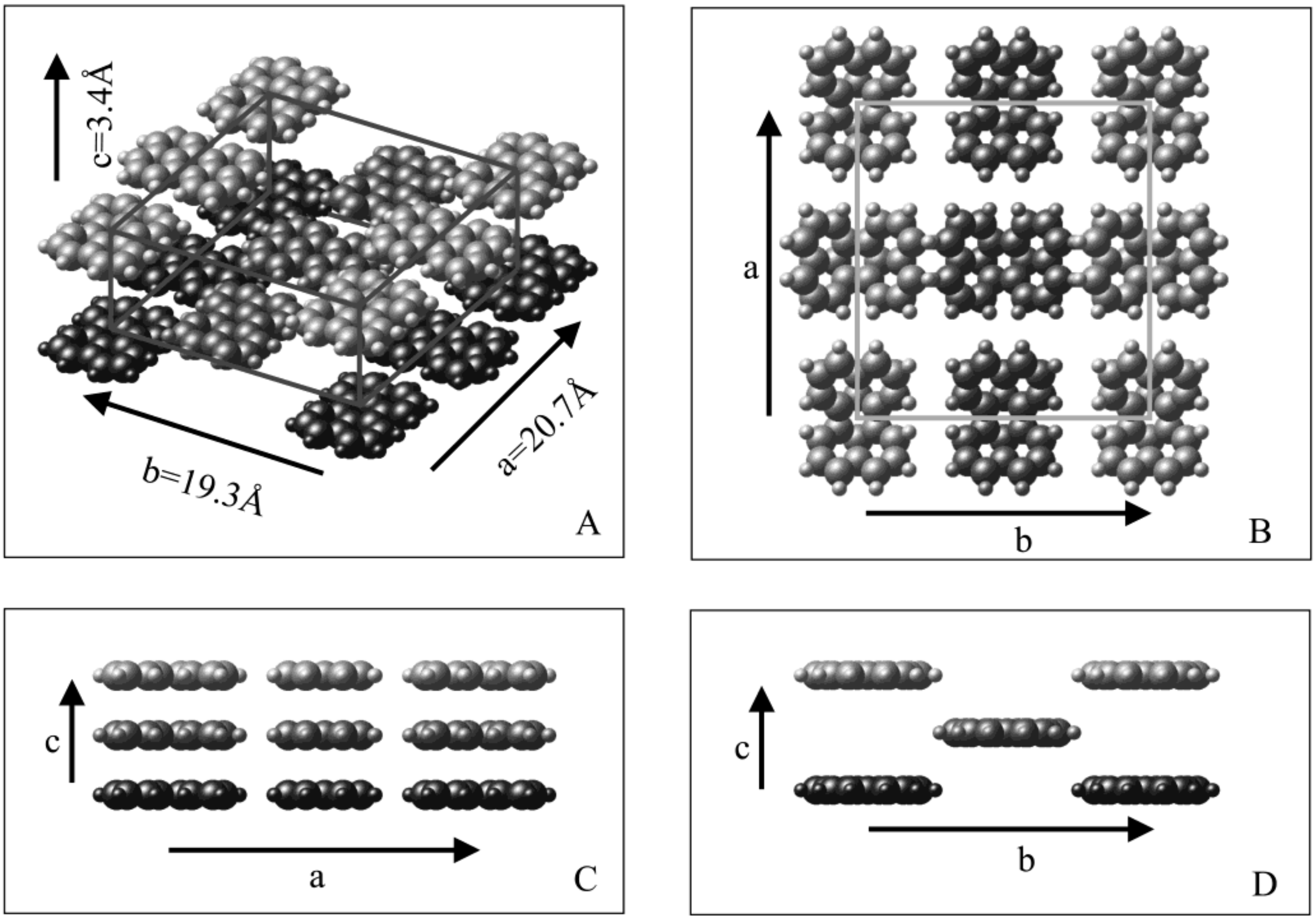

Figure 10. (A) 3D model of the centered orthorhombic perylene overlayer structure with dimensions $a = 20.7$ Å, $b = 19.3$ Å, $c = 2.4$ Å, and $\beta = 90°$. The gray scale indicates the depth of the molecule. (B) Projection of the *ab* plane. (C) Projection of the *ac* plane. (D) projection of *bc* plane, which shows the centered structure.

parallel molecules and the occurrence of an antiphase domain boundary. Such boundaries persist up to at least 1 μm in the ⟨001⟩ direction with no kinks and through many layers, thus being a true 3D antiphase grain boundary. Such antiphase boundaries are never found between neighboring molecules with their long access along the row, in the ⟨110⟩ direction, which would give rise to strong repulsive interactions between the two molecules. The separation between such neighboring X type line defects can only be an odd number of molecular units (3 in the case of Figure 9c). The Y type line defects appears to be normal in terms of the molecular arrangement of the top layer. We assume that this shallow line defect has an X type line defect underneath, subsequently covered by normal periodicity; that is, a grain boundary occurs parallel to the crystal surface.

Summary

A novel long range periodic multilayer structure of perylene has been grown on Cu(110). Vibrational spectra show that all the molecules in the growing film have their molecular plane parallel to the substrate. LEED *of the multilayer* shows an almost square unit cell which is commensurate (8-fold periodicity) in the ⟨110⟩ azimuth but incommensurate in the ⟨001⟩ direction. STM indicates a very flat multilayer structure. High-resolution images reveal the detailed molecular arrangement within the unit cell, which indicates a novel, centered orthorhombic crystal structure formed on the Cu(110) substrate. The quality of the crystal can be determined from the appearance of antiphase domains in the STM images.

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