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Binding and ordering of large organic molecules on an anisotropic metal surface: PVBA on Pd(110)

Jens Weckesser [a], Johannes V. Barth [a,*], Chengzhi Cai [b], Bert Müller [c], Klaus Kern [a,d]

[a] *Institut de Physique Expérimentale, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland*
[b] *Institut für Quantenelektronik, Eidgenössische Technische Hochschule Zürich, CH-8093 Zürich, Switzerland*
[c] *ETH-BWB, CH-8952 Schlieren, Switzerland*
[d] *Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse, D-70569 Stuttgart, Germany*

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Abstract

The adsorption and ordering characteristics of 4-*trans*-2-(pyrid-4-yl-vinyl) benzoic acid (PVBA) on a Pd(110) surface were investigated by variable temperature scanning tunneling microscopy. PVBA is a rigid organic molecule ($m=225$ amu) designed for nonlinear optics. The molecules adsorb flat on the surface and bind diagonally to three neighbouring Pd-rows, which configuration is maintained at all submonolayer coverages. With the completion of the first monolayer a parquet pattern evolves, resulting from the fixed bonding geometry and space limitations. Monte Carlo simulations of the film growth confirm that the monolayer ordering is stochastic in nature, even if an extrinsic precursor mechanism is operative in the adsorption. The lateral interactions between adsorbed molecules and Pd steps or adatoms at the surface are weak. © 1999 Elsevier Science B.V. All rights reserved.

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Scanning tunneling microscopy (STM) is an excellent technique for the study of epitaxial growth phenomena on conducting substrates [1]. While most of the studies performed so far have concentrated on detailed observations in epitaxy of metal or semiconductor atoms, in more recent studies the direct observation of processes in organic molecular beam epitaxy (OMBE) has been reported [2–4]. In the present communication we present data of the PVBA [4-trans-2-(pyrid-4-yl-vinyl) benzoic acid]/Pd(110) system as an example for the ordering of a large organic molecule on an anisotropic substrate in the presence of strong adsorbate–substrate interactions. PVBA is an elongated organic molecule designed for nonlinear optics applications, with a mass of 225 amu, consisting of a benzoic acid moiety linked to a pyridyl group via a C=C bridge [5,6]. The geometry of the PVBA molecule has been simulated with the computer code AM 1 in MOPAC (Cerius 2, BIOSYM/Molecular Simulations). The molecule is almost planar and the phenylene and pyridyl rings are aligned in parallel. The structure of PVBA crystallites is stabilised mainly by hydrogen bonding [7], which is reflected in a rather high

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* Corresponding author.
E-mail address: johannes.barth@epfl.ch (J.V. Barth)

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melting point of 350°C [8]. As a consequence, substantial attractive interactions between PVBA molecules adsorbed on a surface might be expected. On the other hand, attractive lateral dipole interactions due to the inhomogenous in-plane charge distribution within the molecule might interfere. Our data, however, demonstrate that with the present system the adsorbate–substrate interactions completely determine the film growth and bonding geometry, which remains unaffected by intermolecular interactions.

The experiments were performed with a home-built variable temperature STM operational in the temperature range 40–800 K [9], incorporated in a standard ultrahigh vacuum chamber. The Pd(110) crystal was prepared by cycles of argon ion sputtering (4 μA/cm^2, 700 eV) and subsequent annealing (1000 K) resulting in large defect-free terraces of typically 1000 Å width. PVBA molecules were deposited by thermal evaporation from a Knudsen-type source at background pressures of $\approx 2 \times 10^{-10}$ mbar, the substrate temperature during evaporation ranging from 300 to 350 K. The deposition rate employed was $\approx 3 \times 10^{-5}$ ML/s as calibrated by STM data [1 monolayer (ML) corresponds to one adsorbed molecule per Pd surface atom]. The STM measurements were performed in the constant current mode at approximately 1 V and tunneling currents of about 1 nA, i.e., in the high tunneling resistance regime (≈ 1 GΩ). It was impossible to manipulate the adsorbed molecules under any tunneling conditions, which reflects the strong adsorbate–substrate interaction.

The chemical structure formula of PVBA is represented in Fig. 1a. A high resolution STM image with a small amount ($\theta = 0.018$ ML) of PVBA evaporated on the Pd(110) surface is depicted in Fig. 1b. The image reveals the random distribution and the adsorption geometry of PVBA molecules. The individual molecules lie flat on the surface and are imaged as 1.25 Å high protrusions with a length of approximately 11 Å, quite independent from the tunneling conditions. The apparent size of the molecules in the STM images is in accordance with the calculated molecular length of 12.3 Å in the unrelaxed configuration of a free molecule [10]. The 'dog-bone' shape of the molecule, which is associated with the two coupled phenylene and pyridyl rings within PVBA, is clearly discernible. In the STM image reproduced in Fig. 1b the close-packed Pd atomic rows are resolved and the corresponding $[1\bar{1}0]$ direction is

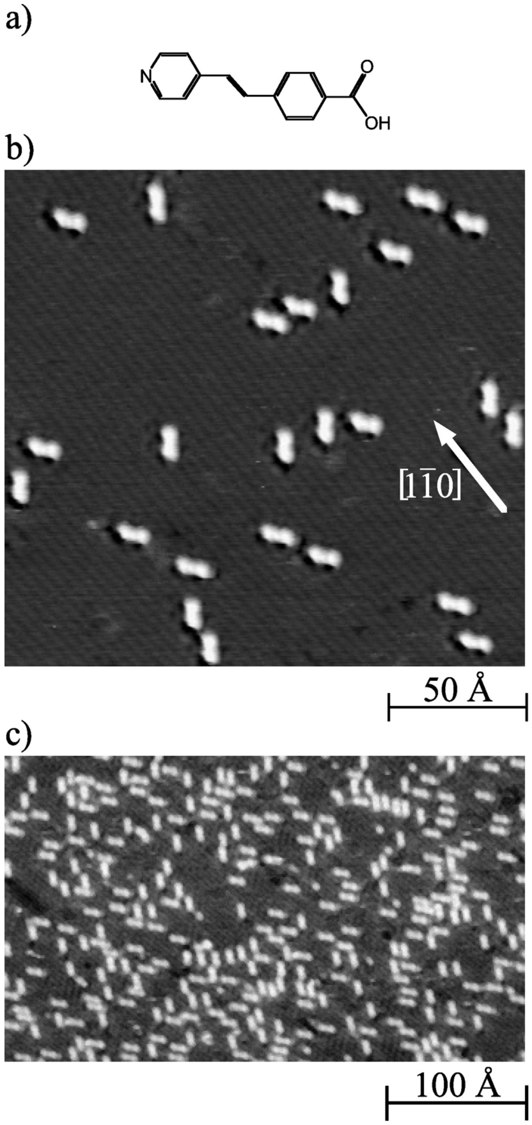

Fig. 1. (a) Chemical structure formula of 4-trans-2-(pyrid-4-yl-vinyl) benzoic acid (PVBA); (b) high resolution STM image with a small coverage ($\theta = 0.018$ ML) ($U_t = 1.0$ V; $I_t = 1.0$ nA); and (c) medium coverage ($\theta = 0.037$ ML) of PVBA on Pd(110). All data obtained at a substrate temperature of 325 K with a deposition flux of 3×10^{-5} ML/s.

marked by an arrow. The angle between the molecular axis and the $[1\bar{1}0]$ Pd rows is determined to ±35°. The molecular axis is thus oriented along the $[1\bar{1}1]$ or $[1\bar{1}\bar{1}]$ lattice direction, respectively. Consequently the molecules are bound to three neighbouring Pd atomic rows, as illustrated by the ball model in Fig. 2. In view of the substrate symmetry and the molecular asymmetry, four equivalent configurations for adsorption are possible. In the STM images, however, only the two different orientations corresponding to the right- and left-hand species of the molecule can be distinguished. The molecules are resolved symmetrically in the STM imaging process and thus it is impossible to distinguish between head (pyridyl group) and tail (carboxylic group). Dissociative adsorption with desorption of CO_2 cannot be entirely ruled out, but seems unlikely since there are no indications for the disruption of a carboxylic acid by Pd in the literature (possibly deprotonation occurs). In addition, very similar imaging characteristics were acquired for weakly bound PVBA on the noble metal Ag(111) surface [11]. Hence it is believed that the symmetric shape results from the transparency of the carboxylic group not contributing to the tunneling current. Similar observations have been reported for fatty acids, where only the hydrocarbon backbones are imaged by STM and the carboxylic groups are nonconducting parts of the molecules [12] and for other large planar π-conjugated molecules adsorbed in a flat lying position on a metal surface, where the π-orbitals dominating the bonding to the metal states are imaged by STM [4]. The position of the molecule in $[1\bar{1}0]$ could not be determined exactly, since atomic resolution of the substrate in this direction could not be achieved in the presence of the molecules. Presumably the two aromatic rings are located in the fourfold hollow sites of the substrate as was found in STM investigations of benzene on Pd(110) [13] or Ni(110) [14]. This PVBA adsorption geometry guarantees optimal coordination of the molecular subunits to the palladium surface atoms without strong distortions of intramolecular or substrate structure (cf. Fig. 2). These results suggest that such organic molecules interact predominantly via the π-electrons of the carbon ring system with the Pd-substrate in accordance with NEXAFS results for related systems [15,16]. It is interesting to note that a molecule aligned in one orientational configuration cannot be transformed into the mirror configuration by a simple rotation. Rather it would have to be flipped additionally about its own axis. Such a process is associated with a high activation barrier, which is the reason why molecular rotations have never been observed with the present system. By contrast, the thermal migration of individual molecules could be directly monitored. A detailed analysis of STM data obtained in the temperature range 330–370 K reveals a strictly one-dimensional diffusion along the close-packed Pd-rows with an activation barrier of (0.83 ± 0.03) eV and an attempt frequency of $10^{(10.3 \pm 0.4)}\,s^{-1}$ [17]. No

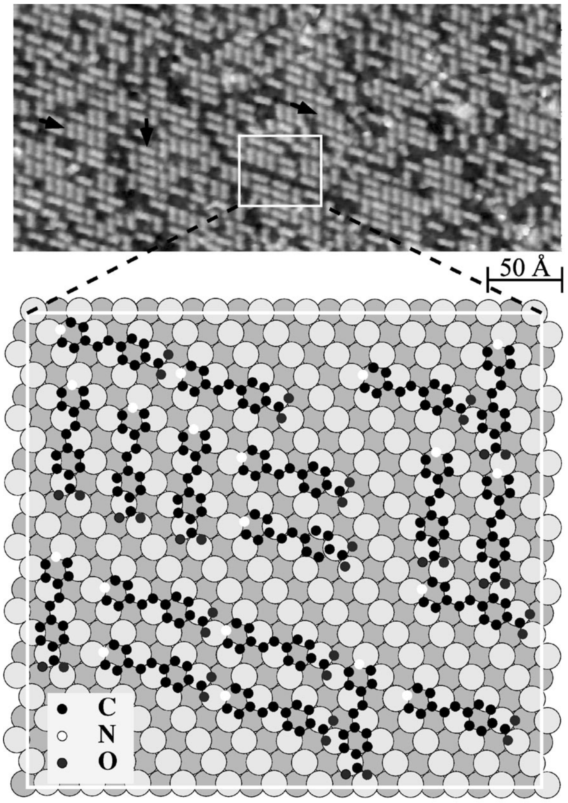

Fig. 2. Top: STM image of a nearly completed monolayer of PVBA on Pd(110) ($\theta = 0.076$ ML $\cong 0.60\Theta_{id}$) ($U_t = -1.0$ V; $I_t = 0.8$ nA). Arrows mark clusters of three or more side by side parallel molecules. Bottom: ball model of the molecular ordering of PVBA on Pd(110) for the area marked in the STM image.

effects of lateral interactions became apparent in the molecular surface migration. The rather high migration barrier indicates a PVBA–Pd(110) binding energy of several eV, which is in line with the strong interaction of aromatic vinyl compounds and palladium atoms documented in organometallic chemistry [18].

With medium coverage little change occurs in the PVBA film structure. This is illustrated by the STM image in Fig. 1c, where a medium coverage of PVBA on Pd(110) is reproduced. Again, the two different rotational geometries prevail. The molecules also remain randomly distributed on the surface, and even after annealing or deposition at 450 K, where the molecules are highly mobile, there are no indications of island formation. These findings demonstrate that the expected attractive interactions between the molecules are very weak or even absent and merely the short-range repulsions exist, which are always present. Presumably the fixed adsorption geometry lowers the possible energy gain from hydrogen bond formation. This forces the angle between the molecular axis and the close-packed Pd-rows to $\pm 35^\circ$ for optimal coordination of the molecular subunits with the Pd surface atoms. As a consequence the angle between two PVBA molecules corresponds to 110° instead of the ideal angle of 180° for hydrogen bonding [7]. Dipole interactions must be similarly weak. It is believed that the molecular dipoles are efficiently shielded by the electron gas of the metal surface. On less corrugated substrates with weaker adsorbate–substrate interactions, e.g., a fcc(111) noble metal surface, where the molecules are free to rotate, the hydrogen bonding and dipole interactions should play a major role in the ordering and molecular chains or clusters should be formed. Such a behaviour was indeed observed for PVBA on Ag(111) and Cu(111) surfaces [11].

Upon further increasing the coverage a parquet-like pattern of flat lying molecules evolves, as demonstrated by the STM image reproduced in Fig. 2. With this monolayer structure the PVBA film on Pd(110) is completed at room temperature. Multilayer growth could not be observed. In the lower part of Fig. 2 a ball model for the rectangular area marked in the STM image is shown. Since it is impossible to distinguish between molecular head or tail groups, only the two different rotational geometries are drawn and all molecules of one orientation are identically aligned. From the ball model the nearest neighbour distance of adsorbed PVBA is determined to be $\sqrt{4a_1^2+a_2^2}=6.74$ Å, where a_1 and a_2 are the lattice constants of the Pd surface in $[1\bar{1}0]$ and [001], respectively. Locally, ordered clusters where molecules are oriented parallel at next-neighbour positions are found, as marked by the arrows in the STM image in Fig. 2. Overall, however, the film structure is not ideal and a substantial fraction of the bare surface remains that cannot be filled up with molecules. Packing with higher density is obviously prevented by the strictly one-dimensional motion along the $[1\bar{1}0]$-direction in connection with the simultaneous bonding of the molecule to three neighbouring Pd-rows. Even deposition or annealing up to 450 K does not result in an improved ordering, whereas upon annealing to higher temperatures of approximately 600 K STM data show that the surface is littered with undefinable material. This is associated with the decomposition of the chemisorbed molecules and fragment desorption. Thus a more densely packed monolayer could not be fabricated. The relative coverage of the monolayer in Fig. 2 corresponds to approximately 60% of a perfectly ordered defect-free layer where the surface unit-cell contains eight Pd atoms (corresponding to an ideal monolayer coverage of $\Theta_{\mathrm{id}}=1/8$ ML).

During the course of the experiments we noted that the PVBA sticking coefficient does not fall rapidly as expected (with the formation of a well-ordered overlayer a $(\Theta_{\mathrm{id}}-\Theta)^8$ power law should hold [19]). Rather, it remained nearly constant up to a coverage of at least $0.25\Theta_{\mathrm{id}}$. As a consequence, an extrinsic precursor mechanism [20–22] must be operative in the PVBA film formation. This implies that adsorbing molecules hitting on top of an already occupied surface area are weakly bound and able to migrate to free sites on the Pd(110) surface. Now, it is conceivable that this process may influence the ordering of the PVBA film, since the precursor molecules are presumably free to rotate and their final accommodation may be influenced by the already adsorbed molecules or the interactions of the precursors with the latter. In order to get more insight in the mechanism of PVBA ordering, we performed Monte Carlo simulations of the adsorption process. The MC-simulations have been performed on a 100×100 large rectangular lattice with periodic boundary conditions. Each molecule is determined by the two coordinates (x and y) of the phenylene-ring plus a variable being 0 or 1 for the left- or right-hand molecular species. At the surface one adsorbed molecule inhibits adsorption at 18 neighbouring positions (cf. Fig. 2). Molecules are adsorbed only when the surface site chosen by the random number generator is free, otherwise they are rejected. A random configuration of the film is obtained within the immobile adsorption model [19] excluding the PVBA surface migration. A typical result from such a Monte Carlo simulation is reproduced in Fig. 3a, whose inspection clearly reveals that the cluster formation of molecules can be rationalized simply within this model. For a quantitative analysis several runs of the MC-simulation with different seed-values have been performed and the distribution of cluster sizes was determined. The statistics shown in Fig. 3b compare the results of the MC-simulation with the experimental findings. Experimental and simulation statistics are each based on a total number of approximately 3000 molecules and clusters. The agreement between experiment and simulation is very satisfying and shows that the film ordering can be fully understood on the basis of a 'hit and stick model'. The extrinsic precursor mechanism does not lead to a film ordering which is superior to that from statistical, immobile adsorption with the present system. In addition, monolayer completion with the maximum coverage of about $0.65\Theta_{\mathrm{id}}$ obtained by the MC-simulations agrees well with the experimental results. Nevertheless, it is suggested that precursor-mediated molecular ordering is feasible with other systems.

Finally, we address the anisotropic nature of the PVBA–Pd interactions. In Fig. 4 an STM image of PVBA evaporated on the clean Pd(110) surface is shown. Subsequently a (1×2) missing row reconstruction was induced on the surface by dosing hydrogen [23]. The black stripes in the image are missing Pd rows, whereas the white stripes are added Pd rows formed of the released Pd atoms. Even if there is a substantial number of highly mobile Pd atoms on the surface, they do not bind laterally to the adsorbed PVBA molecules. There is also no preferential adsorption of PVBA at the atomic step (left side of the image). This means that even though the adsorbate–substrate interaction is rather strong, the lateral interactions of adsorbed PVBA with released Pd atoms and Pd steps are small. The strong direction-dependence of the interaction signals again that binding from the PVBA molecules to the Pd substrate is mainly due to the π-electrons [15,16].

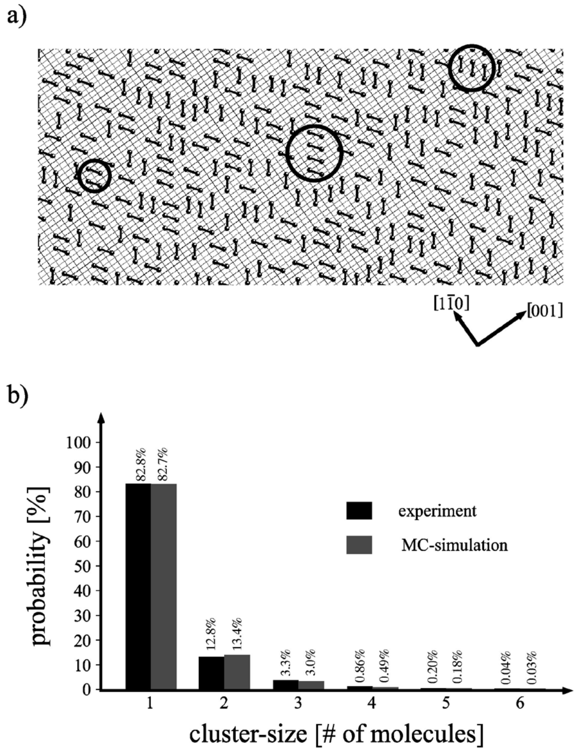

Fig. 3. (a) Monte Carlo simulation for PVBA on Pd(110) film growth with site-blocking and immobile adsorption. Circles mark molecular clusters which are similarly found in the STM images in Fig. 2, where an extrinsic precursor mechanism is operative. (b) Comparison of cluster size distribution obtained from STM images and Monte Carlo simulations. There is no significant difference in the ordering, indicating that the extrinsic precursor mechanism with the molecules' adsorption does not improve the film ordering for the present system.

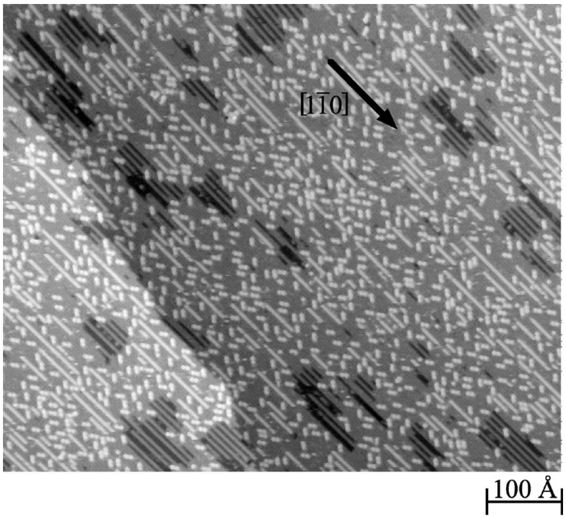

Fig. 4. STM image of the Pd(110) surface covered with 0.018 ML PVBA (U_t = 1.4 V; I_t = 1.1 nA) and subsequent local H-induced missing-row reconstruction. The added Pd rows are formed of the released Pd atoms. The measurements demonstrate the small lateral interactions of adsorbed PVBA and palladium at 300 K.

Accordingly, we found strong lateral interactions of Pd with C_{60} molecules adsorbed on Pd(110). In this case the ball shape of the molecular geometry provides the additional possibility of lateral π-bonding [24].

In conclusion, we have demonstrated that the adsorption and growth of PVBA on the Pd(110) surface is dominated by strong adsorbate–substrate interactions. Our STM data demonstrate that the PVBA molecules adsorb in two rotational configurations giving optimal coordination of the molecular subunits with the Pd surface atoms. This adsorption geometry is maintained over the entire submonolayer range. In contrast to expectations, no effects of lateral molecular interactions are revealed, which is attributed to strong adsorbate–substrate interactions. They result in a fixed adsorption geometry, which is maintained under all conditions. With the completion of the first monolayer thus a parquet pattern evolves due to space limitations. Corresponding Monte Carlo simulations of the PVBA growth reveal the stochastic nature of the parquet pattern.

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