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ABSTRACT

Perylene tetracarboxylic diimide molecules were evaporated onto a Sn/Si(111)- $2\sqrt{3} \times 2\sqrt{3}$ surface and studied using scanning tunneling microscopy (STM) and low energy electron diffraction. At low coverages, single molecules are locked into specific adsorption geometries, which are investigated in detail using high resolution STM. The electronic structure of these individual molecules was studied using bias dependent STM images. The molecules form 1D rows that become more common with increasing coverages. Possible intermolecular O...H interactions within the rows have been identified. At around half of a monolayer (ML), the rows of molecules interact with each other and form a commensurate $4\sqrt{3} \times 2\sqrt{3}$ reconstruction. In a complete monolayer, several structures emerge as molecules fill in the space between the $4\sqrt{3} \times 2\sqrt{3}$ stripes. Possible intermolecular interactions within the 1 ML structures have been discussed. At coverages above 1 ML, the growth is characterized by island growth, where the molecules are arranged according to the canted structure within the layers.

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I. INTRODUCTION

Thin films of small molecular weight organic semiconducting molecules have gained an increasing attention since they show promising properties for use in electronic devices. The structure and quality of these thin molecular films are important for the performance of the devices. The interface between the molecules and the substrate is of particular interest since it affects both the growth mode and the electronic structure of the molecular film. The growth of the first few molecular layers that are involved in the interface depends on the intermolecular interactions as well as the substrate/molecule interaction and the size of the unit cell of the substrate. It is therefore of fundamental interest for the field of organic electronics to understand these interactions for different organic molecules on various substrates.

Previously, the organic semiconductor 3,4,9,10-perylene tetracarboxylic dianhydride (PTCDA) has been widely used as a model molecule to study the formation of thin molecular films on various substrates. On surfaces with weak to intermediate interaction strength, PTCDA molecules are mobile

and are able to form self-assembled layers. Well-ordered films of PTCDA have been grown on, for instance, Ag(111),^{1–5} Ag(110),^{4,5} Au(111),⁶ Ag/Si(111)- $\sqrt{3} \times \sqrt{3}$,^{7–9} HOPG, and MoS₂.¹⁰ Depending on parameters such as size of the unit cell of the substrates, molecule/substrate, and intermolecular interaction strengths, PTCDA has been found to form different phases. The two most common are the herringbone and square phases. In these phases, the intermolecular interaction is driven by hydrogen (H) bondings between the oxygen (O) atoms in the carboxylic endgroups and H atoms of the edges of the perylene core.

To further fundamentally understand the growth of molecular layers, an important step is to study similar molecules but with different endgroups that enable different intermolecular interactions. One such molecule, which has received less attention than PTCDA, is 3,4,9,10-perylene tetracarboxylic diimide (PTCDI), wherein the bridging O atom is replaced by a nitrogen (N) atom bound to a H atom. This substitution is important because the N-H in the imide group of PTCDI blocks the type of hydrogen bondings between the bridging O and the side H atoms of the perylene core that

is often found in layers of PTCDA. The strongest possible interaction between two PTCDI molecules is double N-H...O H-bondings mediated by the imide endgroups, but PTCDI can also interact through similar O...H H-bondings that are found for PTCDA.¹¹ So far three phases of PTCDI have been found experimentally: brick wall,^{11,12} domino,¹¹ and canted phases.^{7,10-14} These all involve the aforementioned interactions.

The Sn/Si(111)- $2\sqrt{3} \times 2\sqrt{3}$ reconstruction, henceforth called Sn- $2\sqrt{3}$, is a metal-induced reconstruction formed at a Sn coverage above 1 monolayer (ML).¹⁵⁻¹⁸ There is not yet consensus about the atomic structure of the Sn- $2\sqrt{3}$ reconstruction. Based on scanning probe microscopy and photoemission studies, models with a double layer structure involving 12-14 atoms per unit cell have been suggested. The top most layer includes two inequivalent pairs of Sn adatoms.¹⁵⁻¹⁹

The Sn- $2\sqrt{3}$ surface is an interesting substrate for growing perylene derivatives. First, the size of its unit cell ($13.3 \times 13.3 \text{ \AA}^2$) is of comparative size to PTCDA ($14.1 \times 9.2 \text{ \AA}^2$) and PTCDI ($14.2 \times 9.2 \text{ \AA}^2$) molecules, which could allow for interesting single molecule adsorption within a unit cell. Second, growth of PTCDA on this substrate shows that the interaction strength is such that it allows for individual molecules to be locked on the surface and imaged by scanning tunneling microscopy (STM) at room temperature (RT), and also allows for the formation of 1D rows, stabilized by intermolecular interactions.^{20,21} It is therefore of fundamental interest to study a different perylene derivative, with different endgroups on the Sn- $2\sqrt{3}$ substrate. In this paper, the growth of PTCDI molecules on the Sn- $2\sqrt{3}$ surface has been studied using scanning tunneling microscopy (STM) and low energy electron diffraction (LEED). PTCDI was evaporated onto the Sn- $2\sqrt{3}$ surface in steps from the submonolayer up to an average coverage of 5 ML.

II. EXPERIMENTAL DETAILS

The experiment was conducted using an ultra-high vacuum system with separate preparation and analysis chambers. The analysis chamber was equipped with an Omicron Variable Temperature STM using an electrochemically etched W tip and an Omicron SPECTALEED. The base pressures in the analysis- and preparation chambers were 3×10^{-11} and 2×10^{-11} mbar, respectively. The sample used was a Shiraki-etched²² Si(111), B-doped to a resistivity of 0.7-1.5 $\Omega \text{ cm}$. The oxide on the Si(111) sample was removed by stepwise direct current heating up to 940 °C. The Sn/Si(111)- $2\sqrt{3} \times 2\sqrt{3}$ reconstruction was created by evaporating 1.4 ML Sn onto the Si(111) surface and subsequently annealing at 560 °C for 2 min. This resulted in a sharp $2\sqrt{3} \times 2\sqrt{3}$ LEED pattern, and the surface quality was also verified with STM. PTCDI was evaporated in several steps from submonolayer coverages up to 5 ML using a Knudsen cell held at 275 °C with an evaporation rate of 0.05 ML/min, while the sample was kept at room temperature. The surface was studied by LEED and STM after each evaporation step. All measurements were

performed with the sample at room temperature, and all tunneling bias voltages in the paper are sample-biased.

III. RESULTS

A. LEED

A LEED image recorded of the clean Sn- $2\sqrt{3}$ substrate is presented in Fig. 1(a). The image shows a nice $2\sqrt{3} \times 2\sqrt{3}$ pattern with low background, meaning the surface structure is of good ordering. When 0.5 ML PTCDI was evaporated onto the surface, a new set of spots appear, as shown in Fig. 1(b). The new spots are faint and make a $4\sqrt{3} \times 2\sqrt{3}$ pattern. As more PTCDI molecules were evaporated onto the surface, the intensity of the extra spots is reduced until they are completely gone at a coverage of around 1 ML PTCDI, leaving only a slightly weaker $2\sqrt{3} \times 2\sqrt{3}$ pattern.

B. Submonolayer coverage

In order to study the electronic interaction upon the single molecule deposition, a set of STM images have been recorded at different biases at a low PTCDI coverage of about 0.12 ML, as presented in Figs. 2(a)-2(f). In all images, a white rectangle is used to mark a row of five molecules which can be used as a reference when comparing the images. The molecules appear as bright protrusions at tunneling biases larger than ± 1.0 V. For low biases, however, the results are quite different. In the ± 0.5 V images shown in Figs. 2(c) and 2(d), the positions where the molecules reside appear as darker areas in both filled- and empty-state STM images. Thus it is quite striking that single molecules do not have an occupied state, nor an unoccupied state near the Fermi level. Instead of imaging the molecules, the substrate beneath them is imaged with lowered intensity. Furthermore, the contrast of the bare Sn- $2\sqrt{3}$ areas near the molecules is opposite when looking closely into Figs. 2(c) and 2(d). This means there is a clear fluctuation in the local density of states from the substrate itself near the Fermi level.

A filled-state STM image recorded at about 0.25 ML coverage is presented in Fig. 3(a). In this image, the upper

FIG. 1. LEED images recorded using 25 eV electron energy on (a) a clean substrate and (b) 0.5 ML PTCDI coverage. The arrows in (b) point to two $4\sqrt{3} \times 2\sqrt{3}$ spots.

FIG. 2. STM images of a 40 nm $\times$ 40 nm recorded at 0.12 ML PTCDI coverage, using $I = 0.3$ nA and tunneling biases (a) $U = 1.5$ V, (b) $U = 1.0$ V, (c) $U = 0.5$ V, (d) $U = -0.5$ V, (e) $U = -1.0$ V, (f) $U = -1.5$ V. The same row of five molecules is marked with white rectangles as reference points that are enlarged in the insets in each image.

Sn-pairs are clearly dominant in contrast to the weaker lower Sn-pairs. In order to reveal the molecular adsorption sites, the two inequivalent Sn-pairs involved in the Sn- $2\sqrt{3}$ reconstruction are marked with red and black circles inside the white circle labeled C in Fig. 3(a). For the clean surface, the

FIG. 3. Features involved in submonolayer coverage. (a) Filled-state STM image recorded at 0.25 ML PTCDI coverage, 15 nm $\times$ 15 nm, $U = -1.0$ V, $I = 0.8$ nA. Two different adsorption sites are marked with A and B, the two Sn-pairs are presented in the white ring labeled C, and two different growth directions are marked with a and b. (b) The two different adsorption sites A and B and their relation to the substrate. (c) Difference in the electronic configuration of the two different adsorption sites. (d) Possible interactions between molecules in the two growth directions a and b.

Sn-pairs can be aligned in three different directions, resulting in three possible domains.²¹ In the domain imaged in Fig. 3(a), the Sn atoms within a pair are aligned along the $[10\bar{1}]$ direction. With the submolecular resolution in Fig. 3(a), it is interesting to investigate individual molecules and their relation to the substrate. It is easy to find single molecules inside a $2\sqrt{3} \times 2\sqrt{3}$ unit cell at low coverages although the majority of them nucleate next to other molecules and have a tendency to form rows. Inspecting the highly resolved molecules in Fig. 3(a) makes it possible to identify two different adsorption sites. They are marked with circles in the image and are named as A and B. In Fig. 3(b), a schematic representation of the PTCDI molecules in the two different adsorption sites A and B, on a model of the Sn- $2\sqrt{3}$ surface, is presented. Again, the pairs are aligned along the $[10\bar{1}]$ direction, and the center axes of the molecules are oriented $\pm 10^\circ$ with respect to this direction. In both adsorption geometries, the molecule is situated so that the core of the molecules sits between the top Sn atoms and the various H and O atoms are above the Sn atoms. In addition, carboxylic carbon (C) atoms are also close to one of the Sn atoms.

Looking closely, the general shapes of the molecular orbitals involve 10 lobes, 3 pairs along the molecular center axis and 4 lobes around the 4 pairs of H atoms at the edges of the molecule. Studying the well resolved molecules in Fig. 3(a) further, differences in the shapes of the orbitals between the molecules on the two adsorption sites are observed. As a result, the configurations of the two molecules A and B circled in Fig. 3(a) have been reproduced in Fig. 3(c) with the 10 lobes found in STM. Each lobe has been drawn with a blue ellipse. In both configurations A and B, one of the lobes in the center of the molecule is more intense than the other. Checking carefully each molecule also has two brighter lobes at the edges, but they are tilting in different directions for A and B. Comparing the intensity of the lobes in Fig. 3(c) with the positions of the molecules in Fig. 3(b), it can be determined

that these brighter lobes are the ones closest to the upper Sn-pairs.

Several molecules are found to group together and form 1D rows, as shown in Fig. 3(a). Two different configurations of rows are identified and have been marked as *a* and *b*. Models of the PTCDI molecule have been placed on the molecules in these rows in the figure to further illustrate the different configurations. Interestingly, the formation of the rows does not change the position of each molecule with respect to the substrate, i.e., the molecules in the rows have the same adsorption sites as the single molecules. More specifically, the molecules in row *a* are of type A, while the molecules in row *b* are type B. Since the growth of the 1D rows is so closely related to the adsorption geometries of the individual molecules, the directions of the 1D rows also follow the symmetry lines of the substrate. In the case of rows *a* and *b*, they follow the substrate directions $[2\bar{1}1]$ and $[\bar{1}12]$, respectively. To understand the formation of these rows, it is interesting to investigate the relation between the molecules within a row. Two molecules from rows *a* and *b* have been schematically reproduced in Fig. 3(d), where it is possible to identify possible intermolecular interactions in the form of double $O \cdots H$ H-bondings between neighboring molecules within the row.

With increasing PTCDI coverages, the 1D rows of molecules become more common. A filled-state STM image recorded at a PTCDI coverage of 0.5 ML is presented in Fig. 4(a). This image is recorded on a domain where the

Sn-pairs are oriented differently compared to the one in Fig. 3(a). In Fig. 4(a), the Sn atoms within a pair are aligned along the $[0\bar{1}1]$ direction. In this STM image, there are several different rows and three of these have been named as *a*–*c* and PTCDI models have been drawn on them. The rows of types *a* and *b* involve molecules that have adsorption geometries of A and B, respectively. Rows *a* and *b* in this domain therefore correspond to rows *a* and *b* in Fig. 3(a). Interestingly, a third type of row is also found and is denoted as *c* in Fig. 4(a). This additional row follows the $[2\bar{1}\bar{1}]$ direction, which is perpendicular to the direction of the Sn-pairs. Looking closely, the adsorption geometry of the molecules in row *c* is type B and the molecules are positioned almost side to side so that their H atoms at the edges are facing each other. This growth direction is not as frequent as the other two. In general, the other two growth directions dominate the surface and they can form long chains as presented in the larger area STM image in Fig. 4(b). In both Figs. 4(a) and 4(b), the rows show an interesting growth pattern: a certain distance between parallel rows is observed. This distance follows from that the positions of the molecules are so closely related to certain adsorption sites at the substrate surface. In Fig. 4(a), two unit cells have been drawn: a white diamond for the $\text{Sn-}2\sqrt{3}$ unit cell and a larger unit cell for four molecules in neighboring rows. The larger unit cell, which has a periodicity of $4\sqrt{3} \times 2\sqrt{3}$, is twice the size of the unit cell of the $\text{Sn-}2\sqrt{3}$ substrate.

C. Monolayer coverage

As the PTCDI coverage increases up toward a complete ML, the morphology of the molecular layer becomes more complicated. An STM image of a PTCDI coverage just below 1 ML is presented in Fig. 5(a). The main feature of the molecular layer originates from the same 1D rows that were found at lower coverages. To make a comparison, some of these rows have been marked with white rectangles in the figure. At coverages close to 1 ML, not all molecules can fit into the previously described adsorption sites. As a consequence, formation of 2D structures is observed as the molecules reside at different sites. One of these 2D structures has been marked as *d* in Fig. 5(a). The structure *d* is formed by molecules filling in between two of the 1D rows. Another common structure has been marked with dashed circles in Fig. 5(a) and is denoted as *e*. This structure is basically a ring of six molecules placed around a seventh center molecule. It should be noted that the orientation of each individual molecule in these circular shapes is not well-defined and differs from structure to structure. This is easily seen by comparing the structures encircled in Fig. 5(a).

As previously mentioned, these new structures involve molecules that do not correspond to the previous adsorption sites A and B. It is thus difficult to figure out the precise adsorption geometry of these molecules as the substrate is almost completely covered by molecules. It is, however, still possible to map the relative orientation and position of each molecule in these structures. This has been performed in Fig. 5(b), where models of structures *d* and *e* are presented. It should be noted that for structure *e*, the model is just one

FIG. 4. Filled-state STM images recorded at 0.5 ML PTCDI coverage using $U = -1.5$ V and $I = 0.3$ nA. (a) A $20\text{ nm} \times 13\text{ nm}$ image: three different growth directions are marked *a*, *b*, and *c*. The $2\sqrt{3} \times 2\sqrt{3}$ unit cell of the substrate and the $4\sqrt{3} \times 2\sqrt{3}$ unit cell of the superstructure are both marked using white parallelograms. (b) Larger area $40\text{ nm} \times 25\text{ nm}$ image.

FIG. 5. (a) Filled-state STM image recorded at 1 ML PTCDI coverage using $U = -1.5$ V and $I = 0.3$ nA. (a) A $30\text{ nm} \times 15\text{ nm}$ image. Some molecular rows have been marked with white rectangles, and their respective type of adsorption geometry has been labeled (A or B). Two types of 2D structures found at 1 ML have been marked with parallelograms and dashed circles; they have also been denoted *d* and *e*, respectively. (b) Molecular models of the structures marked *d* and *e* in (a).

example, as there are several versions of this structure with different individual molecular orientations. The model presented for structure *e* corresponds to the circle marked with *e* in Fig. 5(a). It should also be noted that there is no tendency for the molecules to grow a second layer before the first layer is completed as no second layer was found in STM images recorded at around 1 ML coverage.

FIG. 6. Filled-state $60\text{ nm} \times 60\text{ nm}$ STM image recorded at multilayer PTCDI coverage using $U = -1.5$ V and $I = 0.3$ nA.

D. Multilayer coverage

A filled-state STM image recorded at 4 ML PTCDI coverage is presented in Fig. 6. After the first monolayer is complete, the growth is mainly characterized by island growth. The molecules prefer to bind to sites where the local coverages are more than two monolayers or thicker, as a consequence it is almost impossible to find 2 ML islands even at PTCDI coverages just above 1 ML. For the same reason, areas with a thickness of only one monolayer were also found for average coverages well above 5 ML. All in all, this results in a rough topography at multilayer coverages. The structure within each layer, on the other hand, is highly ordered in islands with thicknesses above 2 ML. The molecules are arranged in the canted structure, where the molecules in each layer grow in rows and the molecules in every other row are oriented with slightly different angles.

IV. DISCUSSION

The set of STM images recorded at different biases shown in Fig. 2 provide interesting information about the electronic structure of PTCDI on the $\text{Sn-}2\sqrt{3}$ surface. At biases larger than ± 1.0 V, the molecules are imaged as bright protrusions in both filled- and empty-states. At lower tunneling biases however, the molecules appear as dark areas in the STM images. This indicates that there are no states in the molecules within these lower biases. The highest occupied molecular orbital (HOMO) should therefore be positioned around -1 eV and the lowest unoccupied molecular orbital (LUMO) around 1 eV, resulting in a gap of around 2 eV. Thus the electronic structure of PTCDI is modified by the interaction with the substrate, as the HOMO and LUMO of bulk PTCDI are positioned with respect to the Fermi level at -2.3 eV and 1.4 eV, respectively.²³ The interaction with the substrate has a different nature compared to that on $\text{Ag/Si(111)-}\sqrt{3} \times \sqrt{3}$, where the molecules were found at tunneling biases of ± 0.5 V.²⁴ On the other hand, in the case of PTCDA on $\text{Sn-}2\sqrt{3}$, scanning tunneling spectroscopy data recorded at a PTCDA coverage of 0.6 ML, when the entire surface is covered by the $4\sqrt{3} \times 2\sqrt{3}$ reconstruction, show the HOMO and LUMO positions with respect to the Fermi level at -1.0 eV and 1.1 eV, respectively.²⁰ The electronic modification of PTCDA on $\text{Sn-}2\sqrt{3}$ compares well to the STM images in Fig. 2, which suggests a very similar interaction for both PTCDI and PTCDA on $\text{Sn-}2\sqrt{3}$.

The PTCDI molecules are not mobile on the $\text{Sn-}2\sqrt{3}$ substrate, as individual molecules are readily found at low coverages. This is very different to the more common behavior of PTCDI being mobile and forms well defined 2D structures through self-assembly on substrates such as $\text{Ag/Si(111)-}\sqrt{3} \times \sqrt{3}$,^{7,14} graphene,¹⁰ MoS_2 ,¹⁰ and Au(111) .^{11,13,25} On $\text{Ag/Si(111)-}\sqrt{3} \times \sqrt{3}$, PTCDI are highly mobile and move until they encounter either a step edge or a defect in the substrate, which acts as nucleation sites for the molecules. In that system, at extremely low coverages (<0.02 ML), it is possible to find single molecules and 1D rows next to these nucleation sites,⁷ but for coverages higher than this, the molecules grow well-ordered 2D islands in which the

molecules arrange themselves in the canted structure.^{7,14} The behavior is in stark contrast to what is found here for PTCDI on Sn-2 $\sqrt{3}$. On this substrate, the molecules do not move to defects or step edges but instead are found at specific sites on defect free and flat Sn-2 $\sqrt{3}$ areas. The interaction between the molecules and these sites is also strong such that they sit in not only well defined adsorption positions on the surface, but also well defined adsorption geometries with respect to the high symmetry directions of the sample. More specifically the molecule/substrate interaction results in the two adsorption geometries A and B described in Fig. 3(b). This indicates that the interaction between the molecules and the substrate is comparatively strong. The interaction found here between these sites on the Sn-2 $\sqrt{3}$ substrate is quite universal since more or less the same adsorption geometries were found for PTCDA on this substrate.^{20,21}

At all submonolayer coverages, the molecules readily form 1D rows, which become increasingly more common as the coverages approach half a ML. The formation of these rows is mainly governed by the interaction between the substrate and the molecules. This is because the adsorption geometries of the molecules in the 1D rows and the single molecules on the surface are the same. Considering the intermolecular interactions rather as a stabilizing force, it is therefore understandable why the two different adsorption geometries only allow for growth in specific directions: Starting from a specific adsorption geometry (A or B), it is only possible to grow rows along specific directions and simultaneously allowing for the O...H H-bondings, as shown in Fig. 3(d). Three different growth directions were illustrated in Fig. 4(a), and they are denoted as *a*–*c*. The growth directions *a* and *b* are described above, but the intermolecular interaction for growth direction *c* is identified to be different. The growth direction *c* does not involve the O...H H-bondings; instead, the molecules are oriented so that their long axis is perpendicular to the row direction, and hence they expose the H-atoms along their sides to each other. A similar growth pattern has been found for di-indenoperylene (DIP) on the Cu(100) surface.²⁶ In that case, the DIP molecules formed well structured layers where the molecules lay next to each other, exposing their H atoms on the sides of the perylene core to each other. It is therefore plausible that also the row type *c* could lower the energy of the molecules and provide a stabilizing effect. The rows of types *a* and *b* have also been found for PTCDA on Sn-2 $\sqrt{3}$,^{20,21} and thus they were stabilized by the same intermolecular interaction described here for PTCDI. The third type *c* on the other hand was not found for PTCDA on this substrate.

In the images recorded at a coverage of about half a ML, as shown in Figs. 4(a) and 4(b), parallel rows are aligned next to each other and form patches of a commensurate 4 $\sqrt{3} \times 2\sqrt{3}$ reconstruction. At the same PTCDI coverage, the LEED image in Fig. 1(b) shows extra spots that hence originate from the patches of this reconstruction. Comparing the results from half a ML coverage of PTCDI further with those from PTCDA on Sn-2 $\sqrt{3}$, one can also note that the overall morphology is much more homogeneous for PTCDA. It was found that

PTCDA formed large areas of rows following the 4 $\sqrt{3} \times 2\sqrt{3}$ reconstruction.^{20,21} For PTCDI, the reconstruction is generally found as smaller areas and the 1D rows are more often interrupted by molecules sitting in a different type of adsorption site or a molecule sitting one adsorption site off. One could also argue that another reason why the regions of nice 4 $\sqrt{3} \times 2\sqrt{3}$ reconstruction is smaller for PTCDI compared to PTCDA is the presence of the row type denoted *c* in Fig. 4(a). These rows, even though they are less common and generally shorter, could break off the growth of the other types of rows.

At a PTCDI coverage of around 1 ML, there are several structures in small patches; however, there is no long range ordering. This is why only the 2 $\sqrt{3} \times 2\sqrt{3}$ pattern from the substrate is found in LEED at coverages around 1 ML and higher. As mentioned before and shown in Fig. 5, the 1 ML film contains several structures, where the two most common are denoted *d* and *e*. In structure *d*, the molecules are nicely fitted between two previous rows of the 4 $\sqrt{3} \times 2\sqrt{3}$ reconstruction. This structure provides enhanced stability as it allows the N–H part of the endgroups of many molecules to interact with an O atom of a neighboring molecule while at the same time it also allows the rest of the O atoms to interact with the H atoms at the sides of other neighboring molecules. The structure *d* is very similar to a three row structure that was found for PTCDA on Sn-2 $\sqrt{3}$.²⁰ In fact, at 0.9 ML PTCDA coverage, the surface is dominated by structures of two and three rows involving molecules, which are oriented themselves similarly as what is described in Fig. 5(b) for the structure *d*.

The other type of structure, denoted *e* in Fig. 5(a), is formed by a ring of six molecules centered around a seventh. This type of structure includes all the ring structures with six molecules around a center molecule independent of their orientation. The example of ring structure marked *e* in Fig. 5(a), which is modelled in Fig. 5(b), provides interesting features. As can be seen in the model, this instance of the structure has three molecules with the same orientation sitting on a row with four other molecules around the center molecule. The four surrounding molecules can be determined to have the adsorption geometry B. The three molecules along the central line have an apparent different adsorption geometry compared to the two previously described adsorption sites A or B. The molecules in this row are positioned and oriented in a way which allows them to interact with each other through double N–H...O H-bondings. These rows where molecules are interacting through these double N–H...O H-bondings are generally short, and they are often found with the ring shaped structures.

The comparison of PTCDI and PTCDA on the Sn-2 $\sqrt{3}$ surface is interesting, as it permits direct comparison of similar molecules interacting with a well-defined substrate. PTCDI generally forms 2D structure on more weakly interacting surfaces through N–H...O H-bondings between the endgroups of molecules. For PTCDA, this type of arrangement is impossible as the end of each molecule has three O atoms. In the case of PTCDA, the interaction is in general between the endgroup

of one molecule and the H atoms along the side of the perylene core of another. On the $\text{Sn-}2\sqrt{3}$ substrate where the interactions are more strongly governed by the interaction with the substrate, the molecules sit at the same adsorption geometries. Photoelectron spectroscopy experiments measured for PTCDA on $\text{Sn-}2\sqrt{3}$ seem to support this.²⁷

It was found that the O 1s core-level spectra remained unchanged from low coverages to high coverages of PTCDA, and this was interpreted as the O atoms in the carboxylic anhydride group are not being involved in the interaction with the substrate. The main change was found in C 1s core-level spectra where the peak related to the C in the carboxylic group were partially shifted strongly toward lower binding energy at low coverages. This would indicate that the carboxylic C atoms are involved in the interaction with the substrate. In the case of PTCDI, there are imide groups instead of the carboxylic ones in PTCDA, but both types of endgroups are connected to the perylene core through two C atoms. Considering the similarities in adsorption sites on the $\text{Sn-}2\sqrt{3}$ substrate for both molecules, it is plausible that the C atoms in the imide groups of PTCDI are the most active part of the molecule in the interaction with the substrate. Returning to the difference in morphology quality between PTCDA and PTCDI on $\text{Sn-}2\sqrt{3}$, one could also explain it from the general preferred interactions among molecules for these two, rows *a*, *b*, and *c*, together with a fixed adsorption geometry. The interactions that are involved in the formation of the rows and the structure *a* discussed in Fig. 5 all involve $\text{O}\cdots\text{H}$ H-bondings between O in the endgroups and H at the edges of the perylene cores. Again, these interactions are the same ones involved when PTCDA form 2D structures on other substrates. For PTCDI, this type of interaction is generally secondary because the main interaction is through double $\text{N-H}\cdots\text{O}$ H-bondings on other substrates. This in itself could explain why PTCDA form larger regions of high quality $4\sqrt{3} \times 2\sqrt{3}$ reconstruction compared to PTCDI on $\text{Sn-}2\sqrt{3}$.

The possible difference in interaction strength between PTCDA and PTCDI with the $\text{Sn-}2\sqrt{3}$ substrate may account for the difference in long-range ordering. The fact that PTCDA forms large areas of $4\sqrt{3} \times 2\sqrt{3}$ reconstruction could be because the PTCDA molecules are slightly more mobile on the surface, which enables them to line up with neighboring molecules via intermolecular interactions and thereby create long-range ordering. The PTCDI films show less long-range ordering than PTCDA, which may be due to a slightly stronger interaction with the substrate. This would make the PTCDI molecules more locked into their initial adsorption sites and hence less prone to arrange with neighboring molecules via intermolecular interactions. However, this needs further investigation.

V. CONCLUSIONS

The growth of PTCDI on the $\text{Sn/Si(111)-}2\sqrt{3} \times 2\sqrt{3}$ surface has been studied from the submonolayer up to 5 ML PTCDI coverages. The morphology and electronic structure

of the molecules have been investigated using STM and LEED. At low coverages, individual molecules are found to be locked in specific adsorption geometries. Bias dependent STM images show that the molecules do not have any electronic states close to the Fermi level. With increasing coverages, the molecules preferably form 1D rows. Three types of rows are identified, and $\text{O}\cdots\text{H}$, H-bondings are important for the formation of the most common of these rows. At coverages around half a monolayer, the rows form patches of $4\sqrt{3} \times 2\sqrt{3}$ reconstruction. At coverages close to a full ML, the molecular morphology involves several structures. The interactions in these structures are found to be stabilized through $\text{O}\cdots\text{H}$ and $\text{O}\cdots\text{H-N}$, H-bondings. The growth above one ML coverages is characterized as island growth, and the molecules in these islands grow according to the canted structure.

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