Adsorption of Pentacene on the 2-Fold Surface of the Icosahedral Ag–In–Yb Quasicrystal

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The adsorption of pentacene molecules on the 2-fold surface of the icosahedral (i)–Ag–In–Yb quasicrystal (QC) has been studied using scanning tunnelling microscopy (STM). The STM images show that the molecules are arranged in rows, and aligned predominantly along the high-symmetry 5-fold and 2-fold axes of the surface. The row separation perpendicular to the 5-fold symmetry axes is either short $S = 0.79 \pm 0.03$ nm or long $L = 1.24 \pm 0.02$ nm. The ratio between them is close to the golden mean ($\tau = 1.618...$) and creates segments of the Fibonacci sequence. Fourier transform of the scanning tunnelling microscopy (STM) images reveal 2-fold, quasicrystalline, long-range order. A comparison of the STM features with the model structure of the substrate shows that Pn molecules adsorb at Yb sites.

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1. Introduction

Adsorption on quasicrystal surfaces has been extensively studied, with a wide range of adsorbates both elemental and molecular. Often, these studies result in the production of pseudomorphic single constituent films with geometries and symmetries dependent on chemically and structurally unique adsorption-site distributions.^{1–16} Particular success in pseudomorphic growth has been found on the high-symmetry surfaces of the i–Ag–In–Yb quasicrystal.^{17–22} Adsorption of pentacene (Pn) molecules showed the first demonstration of quasicrystalline molecular ordering on the 5-fold surface of i–Ag–In–Yb. In that study, the Pn adsorbed at Yb sites.¹⁸

The quasicrystalline phase of Ag–In–Yb is isostructural to i–Cd–Yb.^{23–25} The atomic structure of i–Cd–Yb is explained in terms of five concentric atomic shells, known collectively as a ‘Tsai-type’ cluster. The inner shell is a tetrahedron of Cd atoms, the second shell is a Cd dodecahedron, the third shell is an Yb icosahedron, the fourth shell is a Cd icosidodecahedron, and the fifth shell is a rhombic triacontahedron of Cd atoms.²⁵ In i–Ag–In–Yb, Ag/In atoms simply replace Cd so that there is some chemical disorder at the Cd shells.²⁶

The precise 3-dimensional model of the i–Cd–Yb system allows for a deep understanding of the surface structures of the high-symmetry truncations i.e., 2-fold, 3-fold, and 5-fold. In all cases, the various surface structures are explained by truncations of the model through planes with a high density of cluster-centres. As such, the structure of the 2-fold i–Ag–In–Yb surface is characterized by a row-structure formed of atomic bands which appear along one of the 2-fold axes.²⁷ Recent work showed that the Ag/In and Yb atoms produce different contrast in STM at different bias polarities.²⁸

In this paper, the growth of Pn on the 2-fold surface of the (i)–Ag–In–Yb is studied by STM. Similar to the 5-fold surface, Pn on the 2-fold surface adsorbs at Yb sites and shows quasicrystalline order.

2. Experimental Procedure

The sample surface was hand-polished with a diamond paste of 6 μm , 1 μm , and 0.25 μm grades. Once in ultra-high vacuum, the surface was prepared in cycles consisting of 30 minutes sputtering with Ar^+ ions at 2.5 keV, followed by annealing at 950 K for 2 hours. STM images were taken using an Omicron STM (VT-STM) system at room temperature. Molecules were evaporated from a homemade tube evaporator, keeping the sample at room temperature.

3. Results and Discussions

Figure 1(a) shows an STM image of Pn molecules adsorbed on the 2-fold i–Ag–In–Yb surface at a coverage of approximately 0.37 monolayer (ML). This was determined by subtracting the area of the surface covered by Pn molecules from the total area of the image.

Individual molecules are aligned in three different directions with respect to the horizontal axis (which is also one of the 2-fold axes of the substrate): $57.0^\circ \pm 0.4^\circ$, $90.2^\circ \pm 0.5^\circ$, and $122.1^\circ \pm 0.4^\circ$. These angles correspond to the directions of the 5-fold (58° and 122°) and another 2-fold (90°) high-symmetry axes of the surface, labelled in black arrows in Fig. 1(a). Figure 1(b) shows a histogram of the respective frequency of molecular orientations from Fig. 1(a), as calculated using manual measurements of each of the 496 molecules. The quantity measured in the histogram represents the orientation of molecules taken along the molecular long axes in all orientations. The high-symmetry axes are labelled, with respect to the horizontal axis of the image. The total number of molecules oriented along the 5-fold directions is higher than that of molecules arranged in the vertical 2-fold direction.

Figure 2(a) shows a Fast Fourier Transform (FFT) of the Pn from Fig. 1(a), calculated after filtering out the substrate contribution. The high-symmetry directions of the surface are indicated by white arrows. High intensity spots are marked by coloured circles, where white and green circles indicate spots aligned along the 2-fold and 5-fold axes of the

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Fig. 1 (a) An STM image ($V_b = -2$ V, $I_t = 0.106$ nA) of Pn on the 2-fold (*i*)–Ag–In–Yb surface ($76\text{ nm} \times 76\text{ nm}$). (b) Histogram of the orientations of Pn, taken from (a). The high-symmetry axes of the surface are labelled.

Fig. 2 (a) The FFT of Fig. 1(a), taking the Pn contribution only. (b) A section of Fig. 1(a) where molecular rows formed along one 2-fold axis are highlighted by black dots and dashed lines ($32\text{ nm} \times 32\text{ nm}$). (c), (d) Fibonacci sequences formed from rows of molecules are aligned and orientated along both of the 5-fold axes ($20\text{ nm} \times 20\text{ nm}$).

surface, respectively. The spots are in turn linked by two rectangles; the smallest rectangle edge is marked as unity. The remaining edges of both rectangles are therefore related to each other by the golden mean, $\tau = 1.618\dots$, as indicated by the dashed yellow lines and labels. The high-intensity, τ -scaled spots confirm the quasicrystalline nature of the Pn thin film.

The real-space separations between the pairs of white circles in Fig. 2(a) along the horizontal and vertical 2-fold

axes are $1.31 \pm 0.02\text{ nm}$, and $2.13 \pm 0.03\text{ nm}$, respectively. These separations correspond to the row-like structure of Pn molecules: Fig. 2(b) shows an enlarged section of Fig. 1(a), where the centres or ends of Pn molecules are marked by black circles. Joining these circles are dashed lines which represent the horizontal 2-fold direction of the surface. The average perpendicular separation of these rows is $2.18 \pm 0.07\text{ nm}$. This matches closely with the value calculated from the vertical white spots in Fig. 2(a). In similar fashion,

common separations between the centres of Pn molecules along the rows are 1.22 ± 0.04 nm and 0.82 ± 0.02 nm; the former value matches the real-space distance measured from the horizontal green spots in Fig. 2(a). The spots which correspond to the smaller distance are presumably too weak to be observed in the FFT.

The real-space separation between the pairs of green-circled, τ -scaled spots along each of the 5-fold symmetry axes of Fig. 2(a) are 0.71 ± 0.03 nm and 1.16 ± 0.02 nm. These values correspond to the perpendicular separation of rows formed by molecules oriented along one of the 5-fold directions of the surface. Figures 2(c), (d) show an enlarged section of Fig. 1(a), where molecules which are oriented along one of the 5-fold directions are highlighted with a motif of a Pn molecule (122° in (c), 58° in (d)). Overlaying lines on top of these molecules and directions show the row structure inferred by the spots in the FFT. The separations between adjacent rows are either short, $S = 0.79 \pm 0.03$ nm or long, $L = 1.24 \pm 0.02$ nm as marked. As expected from the quasicrystalline nature of the FFT, it is possible for these rows to follow sections of the Fibonacci sequence, as highlighted in Figs. 2(c), (d).

Locally, the alignment of molecules along the high-symmetry directions results in common motifs. These motifs are highlighted and numbered in Fig. 3(a), and are enlarged in Figs. 3(b), (c). Motif 1 (highlighted by white squares) is formed by four molecules orientated along the 5-fold axes, as indicated by the measured angles of $\alpha = 114^\circ \pm 3^\circ$ and $\beta = 67^\circ \pm 1^\circ$. These angles correspond to those between the two 5-fold directions. The separations between the centre of the molecules in the horizontal and vertical directions

are 1.41 ± 0.06 nm, 1.90 ± 0.07 nm. Motif 2 (highlighted by white triangles) is formed by three molecules with orientations along the 5-fold and 2-fold axes, and appears either in an 'up' or 'down' configuration as indicated by the direction of the triangle. The internal angle of the triangle where the two 5-fold molecules meet is $57^\circ \pm 5^\circ$. This is expected given the high-symmetry surface directions. The distance between the centres of the two molecules on the two 5-fold axes is 1.18 ± 0.03 nm and the corresponding value of the molecules along the 5-fold and 2-fold axes is 1.25 ± 0.07 nm. These distances are related to the model structure of the substrate, which we will discuss later.

After further deposition of Pn (total coverage approximately 0.6 ML), a set of diamond-like features were observed. Figure 3(d) shows one such arrangement; highlighted by four solid black diamonds. The diagonals of individual diamonds are measured as 3.09 ± 0.04 nm and 1.91 ± 0.05 nm. The ratio of these lengths is 1.62 ± 0.05 .

The adsorption sites which lead to the observed Pn structure were examined by comparing the STM data with the *i*-Ag-In-Yb model. Figure 4(a) shows a slab of the 2-fold surface. Here, the fifth shell Ag/In and third shell Yb atoms are represented by red and green circles, respectively. The first, second and fourth shell as well as cluster centers were omitted from the model. First, the potential adsorption sites were considered in terms of geometry: to grow a quasicrystalline layer, the adsorption sites must have a distinct arrangement. In this arrangement, the distribution of Yb atoms among the surface plane is, trivially, sparser than that of Ag/In. Likewise, there are Yb-Yb separations which are similar to the distances between the internal benzene rings

Fig. 3 (a) An STM image ($V_b = -2$ V, $I_t = 0.106$ nA) highlighting repeating local motifs of Pn (60 nm $\times$ 60 nm). The white boxes and triangle mark the positions of motifs 1 and 2. (d) A high coverage STM image of molecules, where a set of diamonds is highlighted in black (8.4 nm $\times$ 8.4 nm).

Fig. 4 (a) Atomic structure of a plane intersecting the cluster centres in the (*i*)-Cd-Yb structure model, green: third shell Yb and red: fifth shell Ag/In. (b) Pentacene adsorption sites superimposed on the *i*-Cd-Yb model. (c) Fibonacci separation of rows along 5-fold axis $L = 1.34$ nm, $S = 0.83$ nm.

which make up the Pn molecule, and the total length of a Pn molecule (~ 1.4 nm). From a chemical standpoint, Pn is an electron donor,²⁹⁾ and it has been shown that the unoccupied states of the 2-fold surface are dominated by Yb atoms.²⁸⁾ It is likely, therefore, that there is a strong interaction between molecule and substrate at the Yb sites. Indeed, this was shown on the 5-fold surface.¹⁸⁾

The Yb-Yb separation with the best match to the length of a Pn molecule was observed along the 5-fold symmetry axes marked on Fig. 4(a) by a black molecule motif. The separation between these two atoms is 1.27 nm; the outer rings of a Pn molecule could reside directly on top of each atom, with some small offset. Two examples of this have been highlighted by overlaying model Pn molecules on the substrate model in Fig. 4(a). Likewise, an Yb pair separation along the vertical 2-fold direction was 0.97 nm, as marked on Fig. 4(a) with a vertical black molecule motif, provides a similar adsorption site, albeit with a slightly larger offset for the rings' centres. Finally, a horizontal Yb-Yb separation of 0.6 nm matches with the distance between the next two-neighbouring benzene rings (~ 0.4 nm), such that the centre of the Pn molecule could sit between the Yb pair. A horizontal Pn molecule is overlaid in Fig. 4(a) to highlight this separation.

The increased density of the 5-fold orientated molecules compared to the 2-fold can be explained by the local environment of the respective adsorption sites. Along the 5-fold Yb-Yb separation, there are three 5th shell atoms, as marked, forming a linear chain of 5 atoms. This arrangement is less complex than some of the arrangements of Ag/In atoms between two Yb sites along the 2-fold axes.

As Fig. 4(b) illustrates, pairs of Yb atoms can be decorated with Pn molecules in this analysis. In Fig. 4(b), Pn molecules are highlighted by different colours representing their directions: black molecules are oriented along the 5-fold axes and dark blue molecules are oriented along the 2-fold axes. This decoration enables an explanation of the observed Pn structure. First, the motifs highlighted in Fig. 3 are considered. Marked on Fig. 4(b) are groups of molecules which form both motifs 1 and 2. The angles between pairs of Pn molecules which form motif 1 are marked as α and β , giving 116.5° and 63.3° matching with those measured experimentally. Likewise, the distance between the centre of the molecules is 2.05 nm, and 1.26 nm along the vertical and

horizontal directions, respectively, as highlighted by a black rectangle in Fig. 4(a), a good fit to the experimental values. These also match the real-space separations of the horizontal and vertical rows taken from the FFT in Fig. 2(a). The same results were observed for both motifs 2 and 3.

As shown in Fig. 4(c), a consequence of selecting the Yb pairs as adsorption sites is the formation of rows along the 5-fold direction. The perpendicular separation of these rows is either $S = 0.83$ nm or $L = 1.33$ nm. These row-separations follow sections of the Fibonacci sequence, as marked. This is consistent with the experimental observation of 5-fold orientated Pn molecules forming rows separated by a Fibonacci sequence, as in Figs. 2(c), (d).

4. Conclusion

We have demonstrated that Pn molecules adsorbed on the 2-fold *i*-Ag-In-Yb surface are arranged in a quasicrystalline manner, with a structure which is dependent on the Yb distribution of the surface. Individual molecules are adsorbed at pairs of Yb atoms, either along the 5-fold or 2-fold symmetric axes of the surface. Consequently, molecular motifs are formed, and molecular rows along the 5-fold directions of the surface produce Fibonacci chains.

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