

Growth of Pentacene Molecules on Tsai-type Quasicrystals and Related Crystal Surfaces

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We present a study of the adsorption of Pentacene (Pn) molecules on the high symmetry (5-, 3- and 2-fold) surfaces of the icosahedral (*i*) Ag–In–Yb quasicrystal. We also compare the results with adsorption of Pn on a surface of a periodic crystal related to this quasicrystal, the (111) surface of the Au–Al–Tb 1/1 approximant. Scanning tunneling microscopy (STM) reveals that Pn molecules on the quasicrystal surfaces are aligned along the high symmetry directions of the substrates and selectively adsorb on Yb atoms, and thus exhibit quasicrystalline order. Pn molecules on the Au–Al–Tb approximant surface also preferably adopt Tb sites. The behaviour of selective adsorption can be understood in terms of the geometry and electronic properties of the adsorbate and substrate. The Yb–Yb (Tb–Tb) separations are comparable to the C–C or H–H distances in a Pn molecule. Pn is an electron donor, whereas the unoccupied electronic states of the substrate are dominated by the rare earth atoms, suggesting that there is an electronic transfer between **the Pn molecules and Yb (Tb) atoms.**

I. INTRODUCTION

Quasicrystals are physical systems which possess long-range order but without translational symmetry. First found in a metastable binary metallic alloy¹, quasicrystallinity has been found in a large variety of systems, including dendritic liquid crystals², ABC-star polymers³, binary nanoparticle superlattices⁴, colloids⁵, mesoporous silica⁶, and oxide thin films⁷.

When stable quasicrystals were discovered and produced in large enough samples^{8,9}, surface science studies of these materials became possible. The initial goal was to produce and characterise clean quasicrystal surfaces. Experience and know-how accumulated in the surface science community over several decades was focused on this problem, and in a short period of time the surfaces of Al-based quasicrystals were well-studied and generally understood to be unreconstructed terminations of the bulk structure¹⁰⁻¹³. Initially the most investigated surfaces were the 5-fold surfaces of icosahedral Al-Pd-Mn and Al-Cu-Fe, and the 10-fold surface of Al-Ni-Co¹³.

After the discovery of the Cd-Yb binary quasicrystal and its structural equivalent *i*-Ag-In-Yb¹⁴, the surfaces of the latter began to receive attention¹⁵⁻¹⁷. The *i*-Ag-In-Yb quasicrystal consists of a quasiperiodic arrangement of ‘Tsai’ type clusters, a hierarchical system of atomic shells with icosahedral symmetry which are joined by rhombohedral ‘glue’ units¹⁴. The quasicrystal structure can then be described in terms of these 3D clusters, or equivalently in terms of the 2D planes of atoms which are formed along the high symmetry directions of the icosahedral structure (2-fold, 3-fold, and 5-fold).

Once excellent clean surfaces of the quasicrystals described above could be prepared and characterised, the surface science focus turned to adsorption studies, and to the structure of the overlayers and thin films which resulted^{12,18,19}. A wide range of metallic and non-metallic elemental adsorbates were employed. This was in large part curiosity-driven: **would** thin films adopt the quasicrystalline order of the substrate, or order as their bulk structure? This question has been answered in part: several elements do adopt the structure of the substrate, at least in the first layer; indeed for some elements the quasicrystalline architecture persists beyond a single layer²⁰.

Interest in molecular ordering on quasicrystals surfaces was also present from an early stage. Initial efforts in our group were centred on the use of C₆₀ as an adsorbing molecule, partly because of the widespread general interest at that time in fullerenes and carbon nanotubes, but also because of the ease with which it is imaged in scanning tunnelling microscopy (STM). Indeed under favorable conditions it is possible to image the internal molecule yielding information on its bonding

orientation. Our study of C_{60} adsorption on the 5-fold surface of i -Al-Pd-Mn was published in 2001²¹; this was followed by a paper on C_{60} adsorption on the 10-fold surface of Al-Ni-Co²². Both papers indicated some local ordering of C_{60} ; however long-range ordering of C_{60} enhanced by thermal activation of the adsorbed molecules and was not achieved until later^{23,24}.

Attention also turned to adsorption of molecules with other symmetries. Five-fold symmetric corannulene ($C_{20}H_{10}$) was found to form a quasiperiodic overlayer with a decagonal **motif** on the 5-fold surfaces of i -Ag-In-Yb²⁵, and most recently 6-fold symmetric coronene ($C_{24}H_{12}$) was observed to form an ordered quasiperiodic structure on the 5-fold surface of i -Ag-In-Yb. However in this paper, we restrict our focus to a molecule with simpler symmetry: **pentacene** (Pn, $C_{22}H_{14}$).

Pentacene is a flat polycyclic aromatic hydrocarbon molecule consisting of five fused benzene rings; it is an organic semiconductor. We concentrate on the adsorption of this linear, easily-imaged molecule on three high symmetry surfaces of the Tsai-type **quasicrystal** Ag-In-Yb, and on the related Au-Al-Tb 1/1 approximant. We review previously published work on the adsorption of Pn on the 5-fold and 2-fold surfaces of i -Ag-In-Yb^{23,26}, and on the (111) surface of the related Au-Al-Tb 1/1 approximant, and present new results on Pn adsorption on the 3-fold surface of i -Ag-In-Yb. We compare and contrast the adsorption behaviour on all four of these surfaces and discuss what we have learned about the reactivity of these surfaces and their use as templates for ordered adsorption.

II. EXPERIMENTAL METHOD

All the work presented in this paper was carried out under ultra-high vacuum conditions. As mentioned in the introduction, we present results of Pn growth on four different surfaces: the 2-, 3- and 5-fold surfaces of i -Ag-In-Yb quasicrystal, and the (111) surface of Au-Al-Tb approximant. The surfaces of all four systems were prepared under repeated cycles of sputtering and annealing. The details of the surface preparation can be found in earlier publications^{15-17,27}. The Pn molecules were evaporated from homemade sources, consisting of a Pyrex tube wrapped with a Ta filament. Substrates were kept at room temperature during deposition. The surfaces were characterized by an Omicron RT-STM 1 and an Omicron VT-STM system.

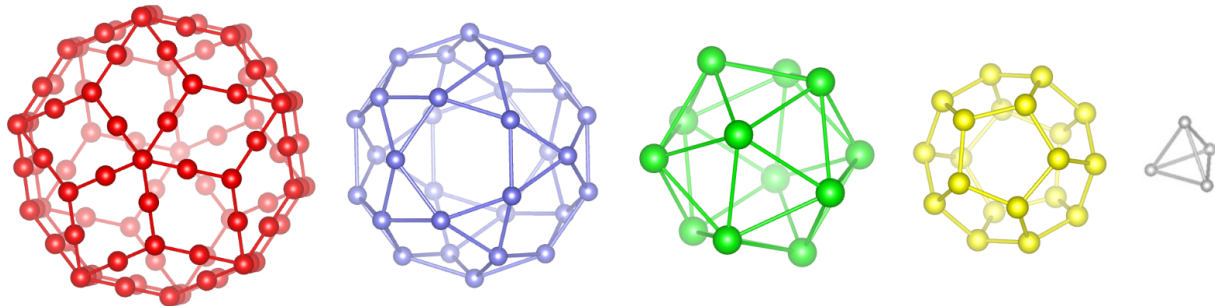


FIG. 1. Successive shells of the Tsai cluster, the building block of the i -Cd-Yb model. The third shell is formed by Yb atoms occupied at the vertices of icosahedra, other shells are formed by Cd atoms. Adapted with permission from H. Takakura, C. P. Gómez, A. Yamamoto, M. de Boissieu, and A. Tsai, "Atomic structure of the binary icosahedral yb-cd quasicrystal," *Nature Materials* 6, 58 (2007). Copyright 2007 Springer Nature.

III. RESULTS AND DISCUSSION

A. Substrate structures

The Tsai-type cluster, the aforementioned basic building block of i -Ag-In-Yb, consists of five successive shells, shown in Figure 1¹⁴. The innermost shell has Ag/In atoms forming a tetrahedron (grey). The second shell is a dodecahedron of twenty Ag/In atoms (yellow). Twelve Yb atoms in the third shell make an icosahedron (green). The fourth shell is an icosidodecahedron consisting of thirty Ag/In atoms (blue). Finally, the outermost shell is a rhombic triacontahedron with 92 Ag/In atoms located on the vertices and mid-edges (red). The Au-Al-Tb 1/1 approximant is a periodic crystal which is formed by the same Tsai clusters, located at a body centre cubic lattice with lattice parameter 1.47581 nm²⁷. Here, Yb is replaced by Tb and Ag/In by Au/Al.

The surfaces of the i -Ag-In-Yb quasicrystal can be prepared by sputtering and annealing to form atomically flat terraces. The surface structure can be explained by bulk planes terminated at the centre of the Tsai clusters. This is true for all three high symmetry surfaces: 2-, 3-, and 5-fold surfaces of i -Ag-In-Yb quasicrystal¹⁵⁻¹⁷, where each of the surface planes contain Yb atoms. The 1/1 Au-Al-Tb (111) surface also terminates at bulk planes containing Tb atoms²⁷. As we will show, the Yb and Tb atoms provide active sites for adsorption of Pn molecules.

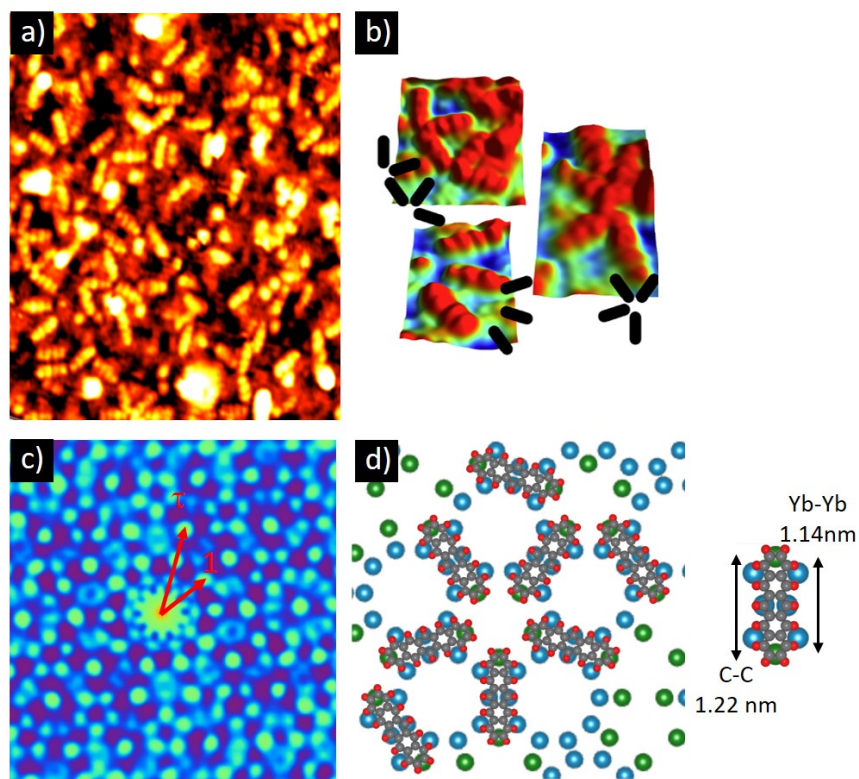


FIG. 2. (a) STM image of the 5-fold *i*-Ag-In-Yb surface after deposition of Pn at room temperature (Bias voltage = -2 V, tunneling current = 0.2 nA, 35 nm × 30 nm). (b) Magnified and 3-D view of (a). (c) Autocorrelation function of Pn molecule positions extracted from the substrate. (d) The 5-fold Ag-In-Yb surface model with Pn molecules adsorbed. Green atoms are third shell Yb and blue atoms are fourth shell Ag/In. Red and grey are H and C atoms of the Pn molecules. Adapted with permission from J. A. Smerdon, K. M. Young, M. Lowe, S. S. Hars, T. P. Yadav, D. Hesp, V. R. Dhanak, A. P. Tsai, H. R. Sharma, and R. McGrath, "Templated quasicrystalline molecular ordering," *Nano Letters* 14, 1184-1189 (2014). Copyright 2014 American Chemical Society .

B. Pentacene on the 5-fold *i*-Ag-In-Yb quasicrystal surface

Figure 2(a) shows an STM image taken from the 5-fold surface after deposition of Pn²⁸. The rod-features represent single Pn molecules. The molecules are aligned along the high-symmetry directions of the substrate, such that pentagonal arrangements of molecules are observed. The most common features seen are highlighted in Figure 2(b)²³.

The autocorrelation function (Figure 2(c)) and Fourier transform (not shown) of the distribution of Pn molecules show maxima distributed in 10-fold symmetry and located at τ -scaling distances

(where τ is the golden mean), indicating quasicrystalline order of the molecules.

To discuss the adsorption sites of the molecules, we show the model structure of the 5-fold surface in Figure 2(d). The surface is formed at bulk planes that bisect the RTH cluster such that the cross-section of the fourth shell appears as a Ag/In decagon formed at the surface (blue ring in Figure 2(d)). The Ag/In decagon is surrounded by five Yb pentagons (green atoms.) All features observed by STM can be explained if terminal benzene rings of Pn bond with two Yb atoms. The distance between the Yb atoms is 1.14 nm, which is close to the distance between outermost C-atoms along **the longer** axis of the molecule (1.22 nm).

Pn molecule consists of five benzene rings fused along C-C bonds. However, Pn molecules appear as four-lobed features (Figure 2(b)). This can be explained if there is some electronic disruption of the molecules induced by the substrate²³.

C. Pentacene on the 3-fold *i*-Ag-In-Yb quasicrystal surface

Figure 3(a) shows an STM image from the 3-fold Ag-In-Yb surface after deposition of \sim monolayer (ML) of Pn. Most of the Pn molecules are aligned along **the three** high symmetry directions of the substrate (indicated by white arrows in Figure 3(a)), which are 120° apart. A few molecules have orientations in between the high symmetry directions, 30° off from the high symmetry directions (marked by green rectangles in Figure 3(a)). A magnified image is shown in Figure 3(b). Two types of features are predominantly observed: triangles and rods. The size of the rod is ~ 1.0 – 1.4 nm, which is close to the size of a Pn molecule (H-H distance along longer axis of the molecule, 1.38 nm), indicating that the rods correspond to single Pn molecules.

The 3-fold surface is comparatively rough compared to the other high symmetry surfaces, characterized by a low atomic density at the surface plane²⁹. As such, isolating adsorbate and substrate contributions can be difficult. However, we conclude that the triangular features are formed by Pn molecules due to the following reasons: the triangular features have identical sizes and orientations; the orientation of the triangles is the same as the isolated Pn molecules; the edge length of the triangles is 1.2–1.3 nm, and the triangles are observed at ~ 0.35 nm height from the substrate (darker area of STM image). Triangles of this height, size, and singular orientation were not observed on the clean surface¹⁶. Likewise, the edge length of the triangles is close to the size of Pn molecules.

Figures 3(c) and (d) show the autocorrelation function and fast Fourier transform of Pn

molecule positions extracted from the substrate. The maxima in both appear at τ -scaling distances, confirming quasicrystalline ordering of the molecules.

Both the triangular and rod features can be explained if the two terminal benzene rings of Pn adsorb between Yb atoms, similar to the 5-fold surface. The distance between the two Yb atoms is 0.97 nm, which is close to the centre-to-centre distance of the two terminal benzene rings, 0.98 nm. Figure 3(e) shows a model schematic of the adsorption scheme. This model produces the triangular features of identical size and orientation as observed by STM. The distance between adjacent triangles in the model is 2.53 nm, which is also consistent with the value observed by STM (2.52 ± 0.02 nm). Furthermore, we occasionally observe two parallel molecules separated by 0.96 ± 0.04 nm, which is also reproduced in the model with a separation of 0.84 nm apart (features marked by circles in Figure 3(a, b, e)).

The Pn molecules aligned in-between the high symmetry directions of the substrate can be modelled considering different adsorption sites. In this case, a Pn molecule is pinned between a Yb-triangle; a terminal benzene ring is adsorbed on top of an atom of the Yb-triangle, and two hydrogen atoms are attached to the other two Yb atoms of the triangle (see magnified view in Figure 3(f)). The Yb-Yb distance is 0.60 nm, which is close to the H-H distance, 0.47 nm.

D. Pentacene on the 2-fold *i*-Ag-In-Yb quasicrystal surface

The 2-fold surface of Ag-In-Yb is atypical with respect to the other high symmetry surfaces, in that each shell of the bisected Tsai clusters at the surface ‘donate’ atoms to the surface structure: at the 3- and 5-fold surfaces, only the third and fourth shells contribute. As a consequence, the 2-fold surface structure is comparatively dense and therefore chemically more complex, as each Ag/In shell has a certain amount of chemical disorder. However, as we will show, this additional complexity does not prevent the formation of a well-ordered, quasiperiodic Pn film²⁶.

Figure 4(a) shows an STM image taken of the 2-fold surface after deposition of approximately 0.37 ML of Pn. The high-symmetry directions of the surface are shown at the bottom right. Individual molecules are found to align their length along 3 directions with respect to the horizontal axis (which is the shorter of the two 2-fold axes of the surface): $57.0 \pm 0.4^\circ$, $122.1 \pm 0.4^\circ$, and $90.2 \pm 0.5^\circ$, corresponding to the two 5-fold and remaining 2-fold direction, respectively. The majority of molecules are aligned along either of the 5-fold directions (Figure 1(b) of ref.²⁶).

Analysis in Fourier space confirms the long-range order of the Pn molecules: Figure 4(b) shows

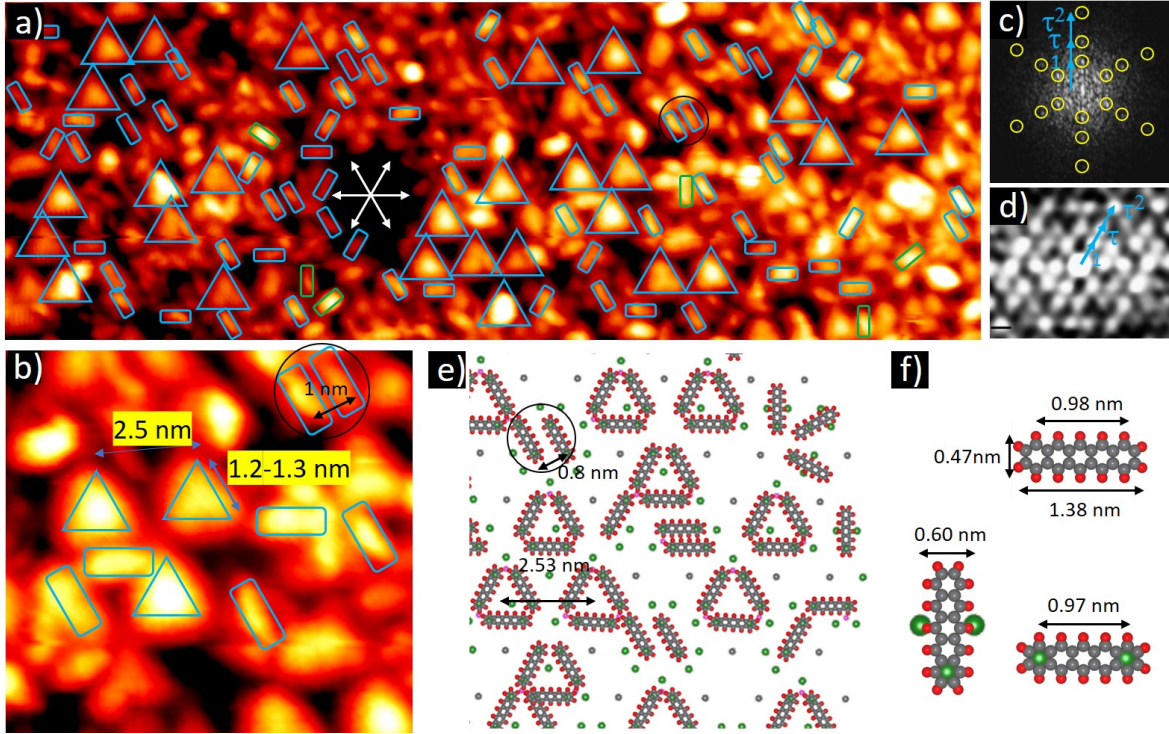


FIG. 3. (a) STM image of the 3-fold *i*-Ag-In-Yb surface after deposition of Pn at room temperature (Coverage = 0.8 ML, bias voltage = -1.8 V, tunneling current = 0.12 nA, 17 nm × 50 nm). High symmetry directions of the substrate are indicated by white arrows. (b) Magnified view of STM image highlighting **triangular** and rod features. (c, d) FFT (c) and autocorrelation function (d) of STM image after removal of the substrate. (e) The 3-fold Ag-In-Yb surface model with Pn molecules adsorbed. For simplicity, only Yb atoms (green) are shown, and fourth shell Ag/In atoms are omitted. (f) Magnified view of the model showing adsorption sites (Red H atom, grey C atom, and green Yb atom).

an FFT taken after isolating the molecular signal from Figure 4(a) via a flooding algorithm³⁰. High intensity spots are highlighted by white or green circles, which are aligned along the 2-fold and 5-fold directions of Fourier space respectively, as indicated by the axes in the bottom left of the figure. The separation of the white spots from the origin along the horizontal and vertical directions, calculated in real-space, are 1.31 ± 0.02 nm and 2.13 ± 0.03 nm, respectively. These values correspond to a rectangular row-like structure which is indicative of the underlying substrate^{17,31}. Likewise, the real-space separation of the green dots along each of the 5-fold symmetric axes in Figure 4(b) are 0.71 ± 0.03 nm and 1.16 ± 0.02 nm. These values correspond to the perpendicular separations of molecular rows aligned along the 5-fold axes of the surface,

with an example indicated in Figure 4(c). Here, blue schematics of Pn molecules highlight rows which are aligned along the 5-fold axis, marked by black lines. The perpendicular separations of the lines measured from the green spots of the FFT are shown as S and L where $L/S = \tau$. These rows follow sections of the Fibonacci sequence as expected from the quasicrystalline nature of the FFT and underlying substrate.

The potential adsorption sites of the Pn molecules were considered in terms of geometry and chemistry, with a similar conclusion to the 3-fold and 5-fold surfaces: that Yb atoms are responsible for the Pn structure. Geometrically, to grow a quasicrystalline layer, the adsorption sites must have a distinct arrangement. Considering this, it is trivial to state that the distribution of Yb atoms among the surface plane is sparser than the Ag/In atoms. Furthermore, there are Yb–Yb separations in the model which are similar to the distances between the internal benzene rings of the Pn molecule. Chemically, Pn is an electron donor³² and, it has been shown that the unoccupied states of the 2-fold surface are dominated by Yb atoms³¹.

Figure 4(d) shows a model schematic of the proposed adsorption scheme. Green circles indicate Yb atoms, red circles indicate fifth shell atoms. The Yb–Yb atom separation closest to the length of a Pn molecule (~ 1 nm) along the 5-fold direction is 1.27 nm, with an example highlighted along one of the 5-fold axes, so that the outer ends of the molecule sit directly on top each atom, with some small offset. Indeed, the separation of the rectangular row-like structure of the Pn molecules along the 2-fold axes can be replicated considering the central position between pairs of these atoms (i.e., where the centre of the molecule resides) – as shown by the black rectangle marked in Figure 4(d). These separations, 1.26 nm and 2.05 nm are good matches to the experimental data.

Similarly, molecules aligned along the 2-fold axes adsorb atop two Yb atoms: the vertical molecules have two benzene rings sitting directly on top of two Yb atoms separated by 0.97 nm, while the horizontal molecules have two inner benzene rings sitting on Yb atoms separated by 0.6 nm. The increased density of 5-fold aligned molecules is attributed to the local environment of the described adsorption sites: along the 5-fold Yb–Yb separation, there are three fifth shell atoms, as marked, which forms a linear chain of 5 atoms. This chain is much less complex than some of the possible arrangements along the 2-fold axes. The assignment of these adsorption sites is given further weight by additional Pn coverage. At 0.6 ML, we see the construction of several molecular motifs which replicate certain Yb motifs in the surface model, including square-like, diamond, and triangular designs (Figures 3, 4(b) of ref.²⁶). An example of the triangle motif is shown in Figure 4(d) by the three Pn molecules.

E. Pentacene on the (111) Au–Al–Tb surface

Periodic Tsai-type approximant systems share the same basic Tsai cluster building block as their quasicrystalline cousins. While 2/1 approximants also exhibit the ‘glue’ units of the Cd–Yb model, the 1/1 structure simply consists of a body-centred packing of the Tsai cluster unit¹⁴. Despite the structural similarities, approximants are indeed separate systems and therefore exhibit individualistic behaviour.

We have recently shown that the (111) surface of the Au–Al–Tb 1/1 approximant crystal (analogous to the 3-fold surface of *i*–Ag–In–Yb) forms a partial reconstruction, the first reported surface reconstruction of a Tsai-type material²⁷. Here, the Au/Al atoms create rows while the Tb atoms follow the expected bulk structure: the result is a surface which is a combination of 2-fold (Au/Al) and 3-fold (Tb) symmetry. Figure 5(a) shows a model of the surface structure, where atoms are colour-coded according to their shell: the first is grey, the second is yellow, the third is green, the fourth is blue, the fifth is red. The row structure of the Au/Al atoms is evident, while Tb triangles are highlighted and enclosed by red, blue, and yellow triangles. The Tb atoms of the yellow triangles occupy the sub-surface layer. Each of the Tb triangles can be considered as a basis decorating three, large, triangular sub-lattices. Likewise, a dashed rhombus indicates a smaller quasi-cell which can link each of the triangles together across the surface, with a nominal ‘lattice’ parameter of $a = b = 1.04$ nm. The juxtaposition of these two chemical symmetries makes for potentially intriguing adsorption studies, especially when considering any similarities or differences compared to other Tsai-type systems. Indeed, our deposition of Pn on the (111) surface shows adsorption behaviour which is both commensurate with the studies discussed, and, dependent on the unique landscape afforded by the reconstruction³³.

Figure 5(b) shows an STM image of the surface after depositing ~ 0.3 ML of Pn with the substrate held at room temperature. Inset shows the autocorrelation function calculated after extracting the centres of the molecular positions. According to the autocorrelation function, the Pn molecules adsorb at positions which form a rhombohedral lattice, with parameters $a = 1.26 \pm 0.08$ nm, $b = 1.28 \pm 0.05$ nm. This is a match to the distribution of the Tb triangles across the surface, so that the Pn molecules appear to adsorb at Tb atomic sites – similar to Pn adsorption on *i*–Ag–In–Yb surfaces which show a strong rare-earth atom/molecule bond. Close analysis of the sites and orientations of the molecules indicate that there are a range of viable adsorption sites (Figure 3 of ref.³³). However, each site has at least one benzene ring sitting directly on top of

a Tb atom, or, at least one ring pinned between two Tb atoms (or both). Critically, certain sites and orientations appear more favourable than others. Molecules aligned along the [011] direction i.e., perpendicular to the Au/Al row direction, are observed more frequently: several examples are highlighted with black circles in Figure 5(b). These vertical molecules were found to only occupy positions at either the red or blue Tb triangles in Figure 5(a).

Higher Pn coverage (~ 0.7 ML) data at room temperature leads to a saturation of the viable adsorption sites, creating a film which exhibits structural order, yet rotational or orientational disorder (Figure 5(a) of ref.³³). Figure 5(c) shows the effect of post-annealing this film to 600 K. The majority of the Pn molecules are now oriented either vertically or horizontally i.e., perpendicular or parallel to the Au/Al row direction. The molecules are marked with coloured arrows or bars to indicate their adsorption site: eight possible sites were identified. The majority of the molecules occupy red or blue ‘down’ sites, which correspond to the vertical sites observed in Figure 5(b). The remaining arrow or bar sites in Figures 5(c, d) correspond to adsorption positions not previously observed, indicating that the post-deposition annealing promotes new adsorption sites. The adsorption scheme for each site is shown schematically with respect to the underlying substrate in Figure 5(d), where green circles are Tb, and grey circles are Au/Al.

We analyzed the Pn adsorption not only from a geometric standpoint, but from an electronic one. The STM signal observed for each molecule showed a double-lobe structure consistent with relatively poor molecular resolution of Pn on metal surfaces^{34–36}. At a local level, the Pn molecules often exhibited a difference in contrast between the two lobes (Figure 4 of ref.³³). The occurrence of brighter lobes of the Pn molecules appears linked to the underlying Tb atom concentration, suggesting a higher flow of electrons at these locations.

IV. SUMMARY

We have presented the adsorption behaviour of Pn molecules on four different surfaces: 5-, 3- and 2-fold surfaces of *i*-Ag-In-Yb quasicrystal and the (111) surface of the Au-Al-Tb 1/1 approximant. We find that Pn molecules preferentially adsorb on Yb (Tb) sites, reflecting the symmetry of the substrates. Autocorrelation and Fourier transform analysis of STM images confirm quasicrystalline order of the Pn molecules on the *i*-Ag-In-Yb surfaces.

We conclude that adsorption of Pn on selective sites is due to both geometrical and electronic factors. The Yb-Yb (Tb-Tb) distances on the substrate are comparable to the C-C or H-H sep-

arations in Pn. Likewise, as Pn is an electron donor and the unoccupied electronic states of the substrate are dominated by the rare earth atoms, Pn is most likely to bond to Yb (Tb). Adsorption of molecules on selective species of the alloy substrate is not uncommon. C₆₀ molecules on the Al-based quasicrystal surfaces are found to adsorb preferably on Mn or Fe atoms, where electrons transfer from the adatom to C₆₀^{23,24}.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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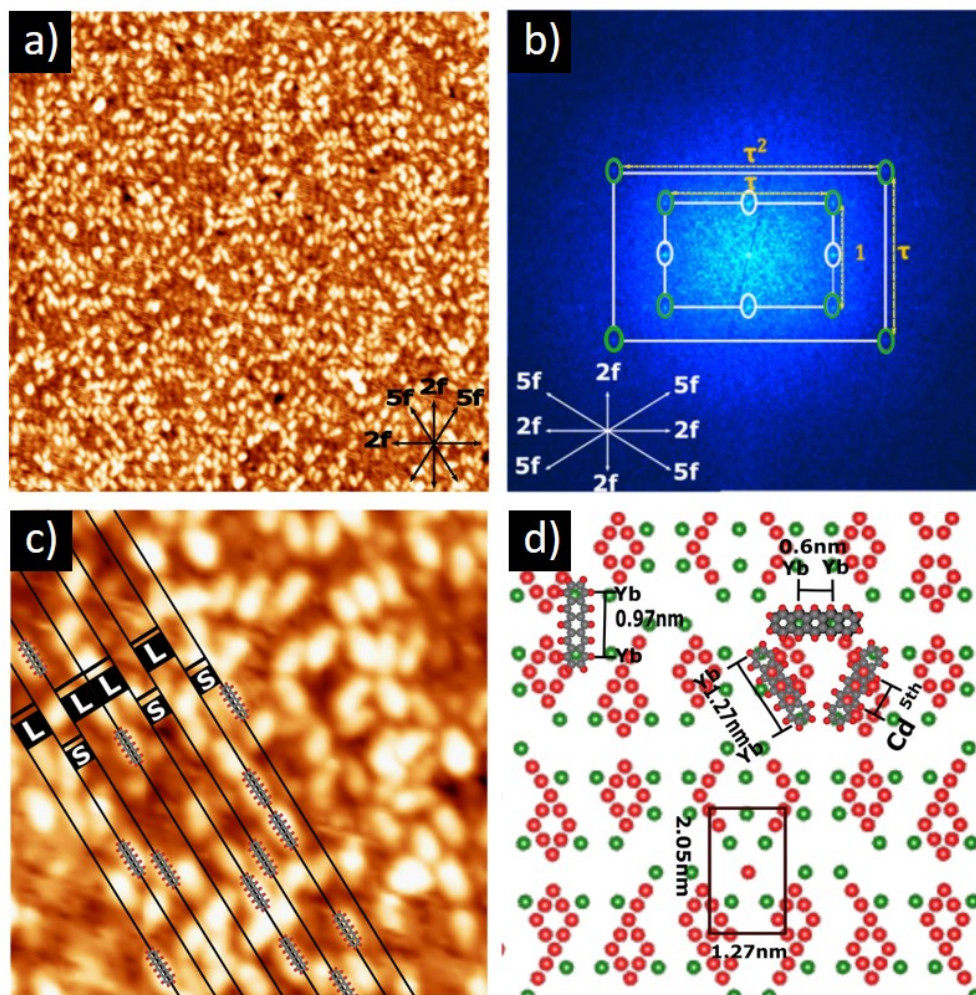


FIG. 4. (a) STM image of the 2-fold *i*-Ag-In-Yb surface after deposition of Pn at room temperature (Coverage = 0.4 ML, Bias voltage = - 2 V, tunneling current = 0.1 nA, 76 nm × 76 nm). High symmetry directions of the substrate are indicated by arrows. (b) FFT of Figure (a), considering contribution from Pn only. (c) A section of Figure (a) highlighting the alignment of molecules along one of 5-fold axes. The separations of molecules ($S = 0.79 \pm 0.03$ nm, $L = 1.24 \pm 0.02$ nm) form a Fibonacci sequence. (d) The 2-fold Ag-In-Yb surface model with Pn molecules adsorbed (green Yb atoms, red fifth shell Ag/In atoms). Adapted with permission from A. Alofi, D. Burnie, S. Coates, R. McGrath, and H. R. Sharma, "Adsorption of pentacene on the 2-fold surface of the icosahedral Ag-In-Yb quasicrystal," *Materials Transactions* 62, 312-316 (2021). Copyright 2021 The Japan Institute of Metals and Materials.

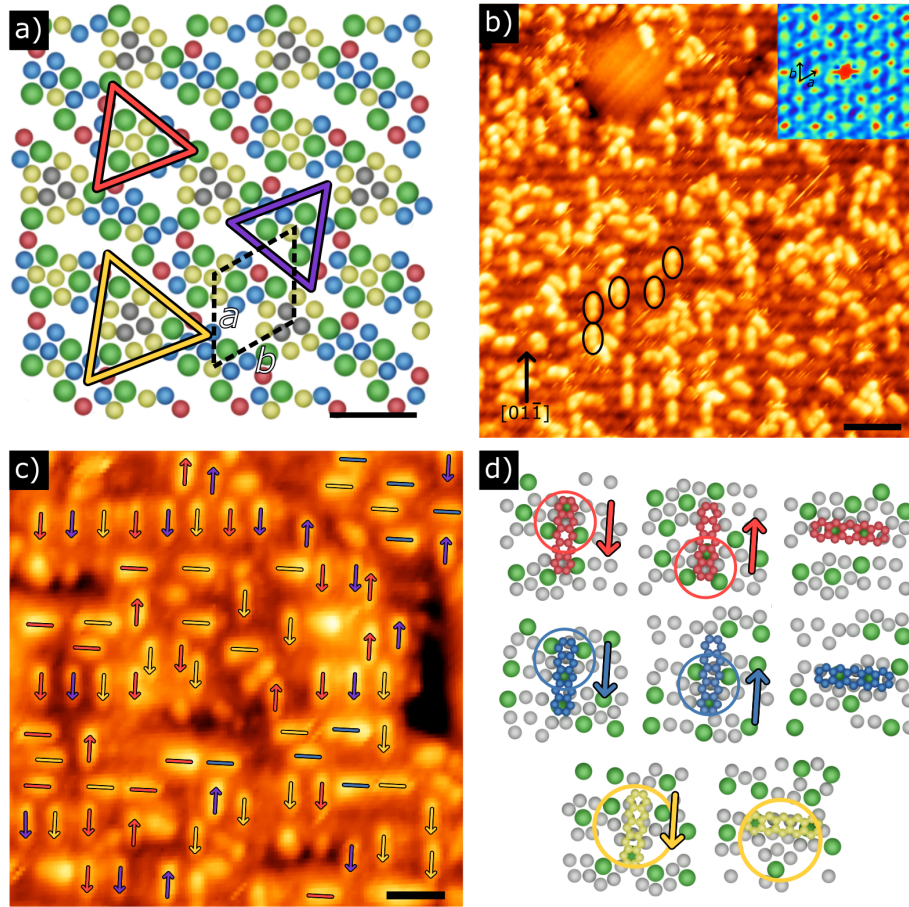


FIG. 5. (a) Model structure of the (111) surface of the 1/1 Au–Al–Tb approximant. Green Tb atoms, the remaining colours are a stoichiometric mix of Au/Al. Colour scheme of atoms is adopted from Figure 1. Triangular features important for adsorption sites are marked. (b) STM image of the Au–Al–Tb(111) surface after deposition Pn (coverage = 0.3 ML, bias voltage = -1.9 V, tunneling current = 0.3 nA, 40 nm × 40 nm). Inset is an autocorrelation function of the molecule centres, with unit cell vectors marked. (c) STM image from the same surface after deposition of Pn of 0.7 ML coverage at room temperature and subsequently annealed at 600 K (bias voltage = -1.8 V, tunneling current = 0.3 nA, 12 nm × 12 nm). Molecules are marked with coloured arrows or bars indicate their adsorption site. A total of eight possible sites were identified. (d) Model structure of the substrate showing Pn adsorption sites. Adapted with permission from S. Coates, R. McGrath, H. R. Sharma, and R. Tamura, Pentacene growth on the (111) surface of the 1/1 au-al-tb approximant: Influence of surface geometry on adsorption," *Phys. Rev. Mat.* 5, 076002 (2021). Copyright 2021 American Physical Society.