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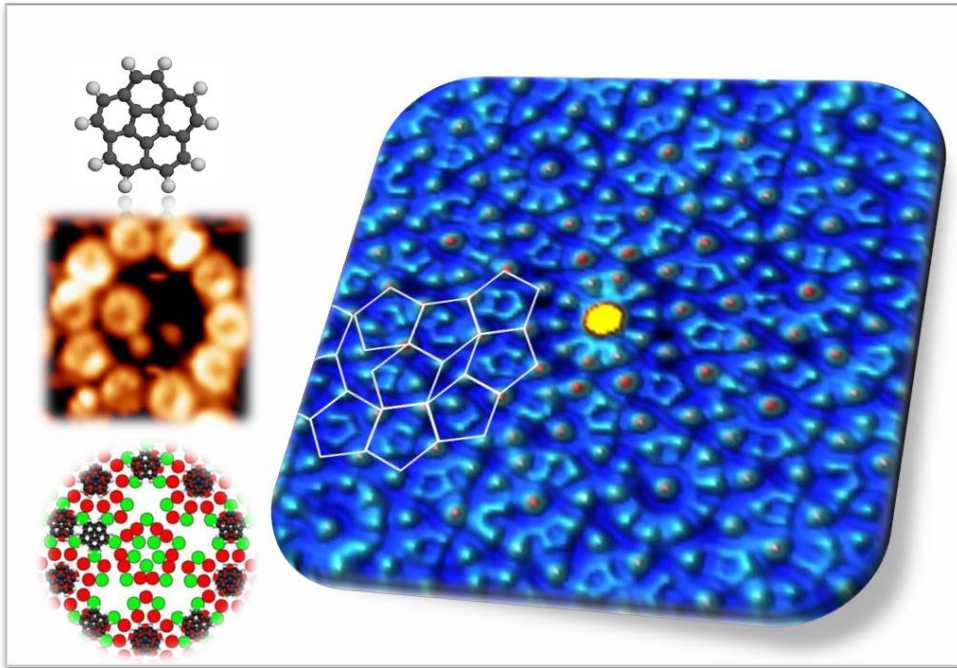
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Graphical Table of Content



A 2-dimensional quasicrystal has been grown from 5-fold symmetric corannulene molecules. It successfully uses the templating effect of the icosahedral Ag-In-Yb substrate through a rational selection of molecular moiety leading to preferential adsorption of the $C_{20}H_{10}$ molecules with its convex side down at five-fold symmetric sites, thus enforcing long-range quasiperiodic order in the film.

Building 2D quasicrystals from 5-fold symmetric corannulene molecules

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Abstract

The formation of long-range ordered aperiodic molecular films on quasicrystalline substrates provides a new challenge as well as an opportunity for further surface functionalization. A main approach to realize this aim is smart selection of molecular building blocks, which is based on symmetry matching between the underlying quasicrystal and individual molecules. From our previous study, the geometrical registry between C_{60} molecules and several 5-fold and 10-fold surfaces played a key role in the growth of quasiperiodic organic layers. However, the similar attempt to form quasiperiodic C_{60} network on *i*-Ag-In-Yb substrate has been unsuccessful, and instead resulted in disordered molecular film. Here we report on the growth of 5-fold symmetric corannulene $C_{20}H_{10}$ molecules on the 5-fold surface of the *i*-Ag-In-Yb quasicrystal. A low-energy electron diffraction (LEED) and scanning tunneling microscopy (STM) study evidenced long-range quasiperiodic order and 5-fold rotational symmetry in the self-assembled corannulene film. Decagonal molecular rings are recurrent local features resulting from the decoration of specific adsorption sites with local pentagonal symmetry, by corannulenes adsorbed with their bowl-opening pointing away from the surface. They are identified as both (Ag,In)-containing rhombic triacontahedral (RTH) cluster centers and pentagonal Yb motifs, all of which cannot be occupied simultaneously due to steric hinderance. It is proposed that symmetry matching between the molecule and specific substrate sites is the essential driving force for this organization. Compared to C_{60} deposition on the same substrate, the alteration of molecular rim by introducing CH substituents seems to increase the molecule mobility on the potential energy surface and facilitate trapping at these specific sites. This finding suggests that a rational selection of molecular moiety enables templated self-assembly of molecules leading to an ordered aperiodic corannulene layer.

Keywords

Quasicrystal ; Surface Science ; Five-fold symmetry ; Molecular self-assembly ; Corannulene.

Introduction

The discovery of quasicrystals (QCs) bestowed with forbidden symmetries such as 5-, 10- and 12-fold has been a key trigger for reconsideration of crystallography concepts as well as the whole field of condensed matter.¹ A significant interest into fundamental aspects of quasiperiodicity in mathematics, physics, and chemistry has followed, as well as intensive search for potential applications of QCs in the form of coatings or composites as alternative materials with new combinatorial properties not found in conventional alloys.² Quasiperiodic structures have been discovered in a large number of intermetallics (>100)^{3,4} but also in soft-matter systems^{5,6} and in thin oxide layers on metal surfaces⁷.

The possibility to grow molecular films with quasiperiodic structure is attractive, as molecules can be functionalized, enabling the study of the interplay between aperiodic order and a variety of physico-chemical properties. Recent advances in supramolecular chemistry provide a number of approaches that can lead to the formation of complex molecular patterns on metal surfaces. It includes the use of metal-directed self-assembly of linear organic linkers with four-fold, five-fold and six-fold vertices, which were found to form semiregular Archimedean periodic tiling as well as quasiperiodic square-triangle random-tiling exhibiting twelve-fold symmetry.⁸⁻¹⁰ Self-assembly of hydrogen-bonded molecules into pentameric building blocks which arrange into non-periodic domains of limited coherence length exhibiting ten-fold rotational symmetry was also reported.¹¹ Another approach is to use molecular building blocks exhibiting non-crystallographic rotational symmetry. This is the case of bowl-shaped corannulene (C₂₀H₁₀) with C_{5v} symmetry.¹² The tessellation of the surface plane using corannulene molecules or its derivatives was investigated on Cu(111) and Cu(110) surfaces.¹³⁻¹⁵ They form a large variety of 2D close-packed complex ordered supramolecular networks with long range periodicity but no quasiperiodic one. Here symmetry mismatch at the molecule-substrate interface is accommodated by a tilt of corannulene bowl with one of its hexagonal ring or C-C bond oriented parallel to the Cu(111) or Cu(110) surfaces, respectively. However, such adsorption conformation of molecules does not prevent the fabrication of 3D structures via corannulene bowl-in-bowl stacking at multilayer growth regime,¹⁶ and can even lead to the formation of quadruple anionic buckybowl films when doped with alkali metals.¹⁷

Another approach is to form quasiperiodic organic films templated on pristine QC substrates. Such substrate-mediated quasiperiodic molecular ordering was realized by adsorption of linear pentacenes consisting of five linearly-fused benzene rings deposited on the 5-fold surface of the *i*-Ag-In-Yb QC.¹⁸ No long-range order was apparent in the film structure at first sight. However, by extracting the position and orientation of individual molecules from STM images and calculating the corresponding fast-Fourier transforms and autocorrelation functions, the quasiperiodic distribution of the molecules was made apparent on a local scale and possible adsorption sites were determined. Long-range quasiperiodic order could be achieved successfully in fullerene thin films grown on various Al-based QC surfaces.¹⁹ This was demonstrated by deposition of C₆₀ on four different Al-based quasicrystalline substrates held within a specific temperature window. Here, the quasiperiodic order was mediated by preferred adsorption at 5-fold symmetric sites of the surface lattice, suggesting that the C₆₀ molecules adsorb with a C

pentagonal face down to maximize molecule-substrate interactions. This hypothesis could not be clearly evidenced experimentally but was supported by density functional theory (DFT) calculations of adsorption energies for various molecular configurations. Subsequent work devoted to C₆₀ thin films grown on the 5-fold surface of the *i*-Ag-In-Yb QC revealed the non-universal character of this approach.²⁰ No preferred adsorption sites could be evidenced experimentally in this system, resulting in a disordered molecular layer for all possible deposition temperatures. Most likely, a variety of adsorption configurations and sites may present similar adsorption energies in this system, which could not be discriminated through high deposition temperature. As it can be readily apparent from the foregoing literature description, the controlled growth of long-range quasiperiodic organic networks is still a challenge that cannot be addressed properly without adequate substrate and molecular building block selection aiming at the optimum interplay between adsorbate-substrate and intermolecular interactions.

In the current work, we present the first comparative study of adsorption of structurally related but stereochemically different C₆₀ and C₂₀H₁₀ molecules on the 5-fold surface of the icosahedral *i*-Ag-In-Yb quasicrystal. It is found that the C₆₀ adsorption did not yield any ordered molecular films on that surface as evidenced from LEED and STM studies. In contrast, the templating effect was successfully exploited in corannulene self-assembly. Analysis of STM images and associated autocorrelation pattern clearly demonstrates that corannulenes adsorb with its convex side down preferentially at five-fold symmetric sites, thus enforcing long-range quasiperiodic order in the film. Therefore, the molecule-surface interactions had to play a major role in generating principally different patterns with related C₂₀H₁₀ and C₆₀ molecules, *i.e.* either quasiperiodic or disordered networks, respectively. This finding suggests that a rational selection of molecular moiety enables templated self-assembly of molecules leading to an ordered aperiodic corannulene layer.

Experimental

All experimental data were recorded in a commercial ultra-high vacuum (UHV) system equipped with standard facilities for sample preparation, LEED, variable-temperature STM and X-ray photoelectron spectroscopy (XPS) techniques.

The studied single grain *i*-Ag-In-Yb quasicrystalline sample was grown by the Bridgman method at the Institute of Multidisciplinary Research for Advanced Materials (IMRAM-Japan)²⁷. It has a composition of Ag₄₂In₄₂Yb₁₆ (in at.%). A sample was extracted to present a surface oriented perpendicular to one of its five-fold axis identified by Laue backscattering. Prior to loading into the UHV chamber (base pressure 10⁻¹⁰ mbar), the surface was polished using diamond paste down to 0.25 μm. Afterwards the surface of *i*-Ag-In-Yb quasicrystal was cleaned by several sputtering (Ar⁺, 2 keV, 20 min) and annealing (~ 690 K, 90 min) cycles under UHV conditions. The substrate temperature was controlled by a pyrometer with an emissivity set to 0.35. The latter treatment led to a terrace and step surface morphology where terraces

have been identified as a subset of dense Yb-rich planes of the bulk structure intersecting RTH building blocks in their equatorial planes.

The molecular films were grown reproducibly on the *i*-Ag-In-Yb surface held either at room (300 K) or at moderate (420–520 K) temperatures by deposition of corannulene (white powder, >97%, TCI) from a Ta crucible resistively heated to 359–367 K. Prior to the sublimation experiment, the molecular powder was thoroughly degassed, while the cleanliness as well as the composition of the *i*-Ag-In-Yb surface was checked with XPS. Monitoring of the C 1s core level spectrum by XPS has also been used to confirm that the corannulene molecules do not undergo modification and fragmentation upon adsorption on hot intermetallic surface. The overall quality of molecular layers was investigated by LEED and STM mainly operating at room temperature (RT, ~ 300 K). The STM experimental data were also acquired at low temperature (LT, ~ 60 K).

Results and Discussion

Atomic structure of the fivefold i-Ag-In-Yb substrate

A characteristic LEED pattern of the pristine surface is shown in Fig. 1(a). It consists of rings of ten diffraction spots whose diameters present τ -scaling relationships, where $\tau \sim 1.618$ is the golden mean. Moreover, each ring comprises two inequivalent sets of 5 diffraction spots indicating five-fold rotational symmetry, consistent with previous reports by Sharma *et al.*²¹ Large scale STM images show a stepped-terrace surface morphology with essentially two basic step heights $S=0.28$ nm and $L=0.85$ nm. Other larger step heights observed are linear combination of these two basic steps. Representative STM images of the surface structure are shown in Fig. 2 with unprecedented resolution. The STM contrast is strongly bias dependent.

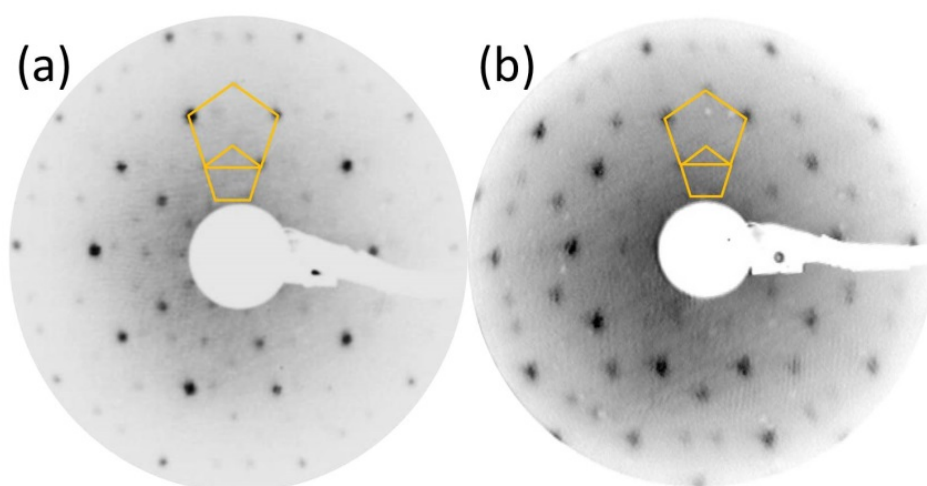


Fig. 1 LEED patterns (primary beam energy equal to 14 eV) of the pristine icosahedral Ag-In-Yb quasicrystalline surface (a) and of the thin organic film deposited at 423 K (b). Both patterns show a

similar quasiperiodic distribution spots located on rings presenting τ -scaling relationships (see yellow pentagons). Note that the diffraction spots appear more intense after molecular deposition.

At positive bias (i.e. probing the unoccupied electronic states of the surface, Fig. 2a), the structure can be described by decagonal rings of diameter 1.9 ± 0.1 nm located at the node of a Penrose P1 tiling made of pentagons, boats and rhombus. The edge length of the P1 tiling is 2.5 ± 0.1 nm. The internal decoration of the pentagonal tile consists of pentagonal motifs pointing either up or down, the smallest ones having an edge length of 0.57 ± 0.05 nm and being centered by a dark spot. These small pentagons decorate the vertices of τ^2 -scaled pentagon (edge-length equal to 1.54 nm) and pointing in the opposite direction, etc... The central part of the P1 pentagonal tiles is not uniform and varies from tile to tile.

At negative bias (i.e. probing the occupied electronic states of the surface, Fig. 2b), larger decagonal rings appear at the node of the P1 tiling. They have a diameter equal to the edge length of the P1 tiling. A triangular like motif is located inside these rings. The decoration of the pentagonal tiles vary from tile to tile, but five bright spots usually decorate the vertices of a pentagon with edge length equal 1.54 nm and pointing in the opposite direction compared to the P1 pentagonal tile. These bright spots belong to five different decagonal rings. Consistently with the previous interpretation by Sharma *et al.*,²¹ all these motifs observed by STM can be well explained by planes intercepting RTH cluster centres derived from the model of the isostructural *i*-Cd-Yb phase proposed by Takakura *et al.*²² (Fig. 2c). At positive bias, mainly the Yb atoms are imaged. The smallest pentagonal motifs with a dark centre correspond to Yb pentagons with edge length 0.57 nm. The decagonal rings with diameter 1.9 nm are made of ten Yb atoms surrounding the Ag/In rings decorating the node of the P1 tiling (highlighted by green circles in Fig. 2c). These Yb atoms belong to different RTH cluster units. At negative bias, the motifs inside the rings at the node of the P1 tiling should correspond to the Ag/In decagonal rings (red rings surrounding RTH cluster centers in Fig. 2c). The fact that they appear with a distorted form may be due to a non-uniform distribution of Ag and In atoms on the icosidodecahedral shells of the RTH units.

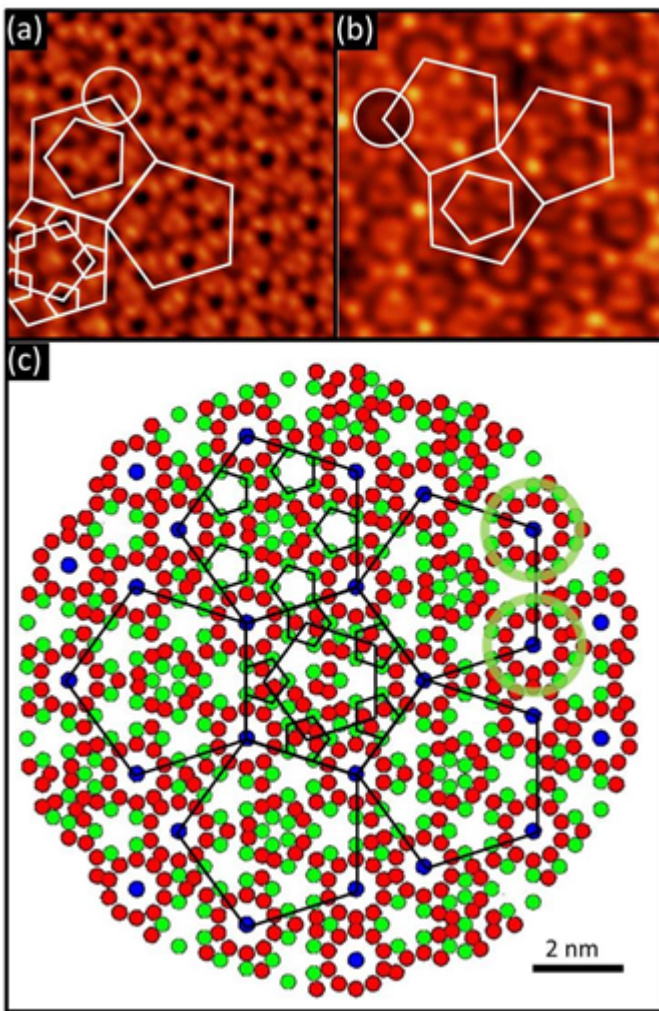


Fig. 2 (a,b) Atomic structure of the five-fold *i*-Ag-In-Yb surface imaged by STM at positive and negative bias. (a) $10 \times 10 \text{ nm}^2$, $V_B = +1.8 \text{ V}$; (b) $10 \times 10 \text{ nm}^2$, $V_B = -0.5 \text{ V}$. The most frequent local motifs are highlighted in white. The largest pentagonal tiles are P1 tiles with edge length equal to 2.54 nm. (Note that images (a) and (b) do not correspond to the exact same location on the terrace). (c) Atomic structure of a representative bulk plane intercepting RTH cluster centers from the *i*-Cd-Yb model by Takakura *et al.*²² Green dots represent Yb atoms, red dots represent Cd(Ag/In) atoms, blue dots represent RTH cluster centers. The P1 tiling connects RTH cluster centers. Smaller pentagonal motifs formed by the Yb sublattice are also shown in black.

Structure of fullerene films grown on the quasicrystalline surface

A first attempt to self-assemble fullerene molecules (C_{60} , Fig. S1a) on the *i*-Ag-In-Yb substrate held at room temperature revealed the formation of a non-periodic disordered thin organic film as evidenced by the vanishing of the LEED pattern. This is consistent with previous report by Nugent *et al.*²⁰ showing a random distribution of C_{60} on this surface observed in STM images. Adsorption followed a hit and stick model, probably due a strong bonding of the C_{60} on the quasicrystalline surface resulting in kinetic hindrance. In addition, the molecules appeared with different heights in STM suggesting a variety of adsorption configuration on this surface. These are compelling evidences that no preferential adsorption sites can be selected for fullerenes on *i*-Ag-In-Yb surface.

Similar disordered C_{60} layers are formed at RT on Al-based quasicrystals.^{23,24} However ordered aperiodic films can be obtained by using the hot substrate deposition method, within a specific temperature window (between 623 and 673 K).¹⁹ Hot substrate deposition is required to ease molecular diffusion allowing the full potential energy surface to be explored. As mentioned earlier, this procedure facilitates molecular trapping at sites presenting the lowest adsorption energies. These sites are quasiperiodically distributed, resulting in a quasiperiodic molecular film. The same approach was attempted for C_{60} deposited on *i*-Ag-In-Yb but was unsuccessful - even at the highest temperature compatible with the maximum substrate annealing temperature. The reason might be that the adsorption energy differences between various possible adsorption configurations/sites are smaller for C_{60} on Ag-In-Yb compared to Al-based quasicrystal, making it impossible to discriminate specific adsorption configuration/sites populated according to a Boltzmann distribution.

Structure of corannulene films grown on the quasicrystalline surface

In the following, we select corannulene $C_{20}H_{10}$ as an alternative to C_{60} . Corannulene (Fig. S1b) is a non-planar polycyclic aromatic hydrocarbon molecule with C_{5v} symmetry.¹² It consists of a C pentagonal ring surrounded by five benzene rings and it has a bowl-like stereo structure. It can be viewed as a fragment of buckminsterfullerene and is frequently termed buckybowl. It is expected that the reduced symmetry of corannulene compared to C_{60} and the presence of hydrogen at its rim might modify the adsorbate-substrate potential energy surface as well as the adsorbate mobility. The aim is to enhance the trapping probability of molecules at five-fold symmetric quasilattice sites and induce quasiperiodicity in the film.

The corannulene molecules were deposited on the quasicrystalline substrate held at various temperatures between 300 and 520 K, i.e. a moderate temperature range compared to C_{60} . The global structure was probed by LEED. A representative diffraction pattern of the saturated monolayer is shown in Fig. 1b. It displays a quasiperiodic distribution of sharp spots similar to that of the clean substrate. In this case, the film was grown with the substrate held at 423 K and annealed for 5 min at this temperature after the deposition. The spots look more intense after deposition compared to the clean substrate and more diffraction spots are visible. Such LEED pattern demonstrates that the molecular film adopts a long range quasiperiodic order. The pattern looks slightly more 10-fold than 5-fold compared to that of the clean surface at 14 eV beam energy. However, for some other electron beam energies, the decagonal rings of spots appear as two sets of five spots with different intensities. It suggests that the molecular film has 5-fold rotational symmetry like the substrate. A non-centrosymmetric LEED pattern may also indicate that the substrate still contribute in part to the diffracted intensity. A diffraction pattern with similar characteristic is obtained already after room temperature deposition. In this case the background is higher indicating a more defective structure. The fact that the corannulene film is already ordered at RT differs from previous report on the growth of C_{60} films on several quasicrystalline surfaces. As stated earlier, a thermal treatment is required to facilitate the molecular diffusion and trapping at the most energetically favoured adsorption sites. According to the current LEED study, corannulene deposited on *i*-Ag-In-Yb substrate kept at RT might conceivably possess sufficient surface mobility to form quasiperiodic supramolecular structure even without subsequent surface annealing.

On the local-scale the supramolecular structures formed on atomically clean quasiperiodic surface were studied by STM as a function of coverage. Typical STM images of organic layers grown on the fivefold *i*-Ag-In-Yb substrate kept at 473 K are shown in Figs. S2a and 3a for submonolayer coverage and almost complete monolayer respectively. The coverages are defined as the fraction of the surface covered by the molecules estimated from STM image analysis. They reveal the presence of single round-shaped protrusions of ~ 0.9 – 1.0 nm in diameter and their agglomerates into different motifs that are equally dispersed across the terraces (see clusters, lines and arcs in Fig. S2). The dimension of isolated molecules corresponds well to the size of the free corannulene, while a weak depression clearly distinguished in its center implies that the molecular bowl opening points outwards from the surface as discussed elsewhere (see reference 13). In other words, the corannulene adsorbs with its convex side (e.g., five-member carbon ring) facing towards the intermetallic substrate beneath. A subsequent careful inspection of organic layer has also enabled to detect the formation of molecular rings composed of ten corannulenes (see Fig. 3c). Thus, these bowl-shaped molecules can locally assemble into 10-fold symmetric motif on 5-fold *i*-Ag-In-Yb surface as indicated by green arrows in Fig. 3c. It may also explain the more 10-fold appearance of the organic film in the LEED pattern shown in Fig. 1b. Such corannulene ring with radius of 2.12 nm can be alternatively viewed as two 36° -rotated pentagons with edge length of ~ 2.5 nm (see Fig. S2c). The latter value is in excellent agreement with the edge dimension of pentagonal tile connecting RTH cluster centers of the pristine icosahedral quasicrystalline substrate below (Fig. 2c). The nearest-neighbour distance in the molecular ring is measured at 1.3 ± 0.1 nm, and is identical to the smallest molecules separation found in the film. This value is significantly higher than those of 1 ± 0.1 nm measured in close-packed corannulene structures formed on Cu(111) experiments.¹⁵

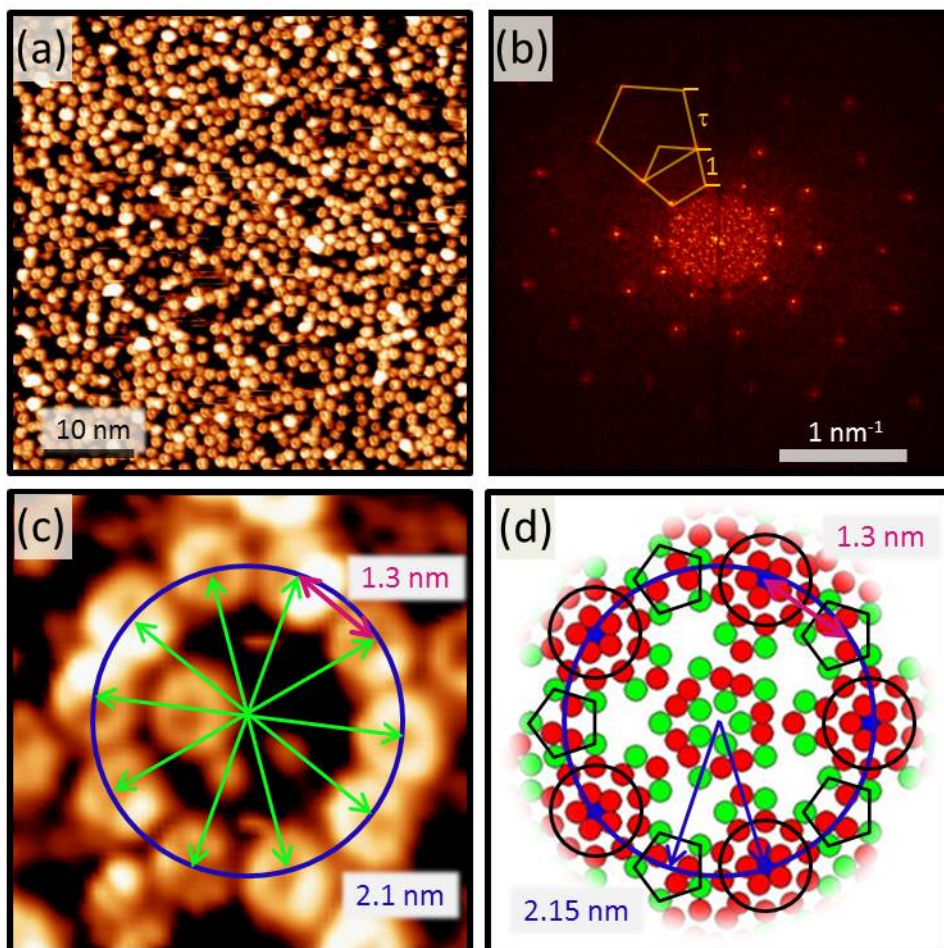


Fig. 3 (a) STM image of the almost complete corannulene monolayer (0.85 ML) grown on the fivefold *i*-Ag-In-Yb surface maintained at 473K and (b) its corresponding FFT pattern. The aperiodic nature of the organic layer is confirmed by rings of ten spots having diameters presenting τ -scaling relationships (see inflated yellow pentagonal motifs). (c) Close up STM image of a molecular ring composed of 10 corannulenes and corresponding (d) tentative model illustrating the preferential corannulene adsorption on Yb- and (Ag,In)-based sites highlighted by alternating small pentagons and circles, respectively. Ten green arrows in (c) indicate the 10-fold symmetry of corannulene motif.

These observations lead to the conclusion that corannulenes should indeed be in registry with the underlying *i*-Ag-In-Yb surface and exhibit stronger adsorbate-substrate interactions at several anchoring sites as will be discussed later. Finally, it is possible to distinguish from one to three corannulenes trapped in the pore of the molecular ring illustrated in Figs. 3c. The presence of complete corannulene rings on the surface is actually limited. Most of the time, the rings are incomplete and instead one observes more frequently intersecting arcs, wavy lines and rarely small pentagonal motifs (see Fig. S2). Moreover, the rims of some molecules are non-homogeneously visualized which might indicate non-planar adsorption geometry of their pentagonal carbon rings with respect to the surface.

The long-range quasiperiodic order is obvious in calculated FFT of STM images of the molecular film. As can be seen in Fig. 3b, the FFT reveals sharp spots distributed on a number of 10-fold symmetric rings with different radii exhibiting τ -scaling relationships. These characteristics correspond well to the

Fig. 4 Autocorrelation pattern from the STM image shown in Fig. 3a of the corannulene layer grown on *i*-Ag-In-Yb substrate. The bright protrusions are aligned along quasiperiodically spaced lines defining a pentagrid, with $s \sim 1.6 \pm 0.1$ nm and $l = \tau \cdot s \sim 2.5 \pm 0.1$ nm. The brightest dots are located at the nodes of a quasiperiodic P1 tiling with edge length equal to 2.5 nm. A patch of this tiling is superimposed on the ACF pattern (white lines). A pentagonal P1 is highlighted in blue, with its irregular decoration in yellow.

Tentative model based on experimental results

To determine a tentative model of corannulene self-assembly on *i*-Ag-In-Yb surface, all structural information deduced from real and reciprocal space has to be combined. First, the LEED patterns of the substrate and film show similar spatial distribution of spots, indicating that the film structure is pseudomorphic with that of the substrate, meaning that the molecules must be preferentially adsorbed on a specific subset of quasilattice sites. The STM imaging of individual molecules indicates that they are usually adsorbed with their bowl opening pointing up, therefore contacting the surface plane with its pentagonal carbon ring. In some cases, an inhomogeneous contrast is observed at the rim of some molecules suggesting that their C_5 symmetry axis may be slightly tilted with respect to the surface normal. The most conspicuous features in STM images are the decagonal rings of corannulenes which can be described as two 36° -rotated pentagons with edge length of 2.5 nm as depicted in Fig. 5a. From the analysis of the autocorrelation of STM images, it was found that the molecules preferentially adsorb on a pattern reproducing the P1 tiling with edge length 2.5 nm (the ubiquitous pentagonal tile is depicted in Fig. 5b). From perfect correlation of this pentagonal tiling with the P1 tiling connecting RTH cluster centers of the underlying QC substrate, a preferential adsorption of corannulene at RTH sites can reasonably be inferred (see black circles in Fig. 3d). These adsorption sites have local five-fold symmetry. According to the work by Nozawa *et al.*²⁶, they are decorated mainly by In atoms. The surface planes intercepting RTH cluster centers contain other five-fold symmetric sites made of Yb pentagons with edge length of 0.57 nm as shown in Fig. 2c and 3d. Two such Yb pentagons are located symmetrically from the mid-edge positions between two RTH cluster centers. The molecular decoration of both Yb pentagons and RTH sites – as shown by alternating black pentagons and circles in Fig. 3d respectively – perfectly reproduces the decagonal rings observed experimentally. In this case the nearest-neighbor (NN) distance would correspond to separation of corannulenes located at RTH cluster center and Yb pentagon, matching the intermolecular distance measured at 1.3 nm (see Fig. 3d). In turn, the consideration of Yb pentagons as alternative adsorption site for the molecules in addition to RTH cluster centers can also explain the presence of a large amount of incomplete or even slightly distorted molecular rings in acquired STM images (see Fig. S2d). Indeed, the distance between the centers of two adjacent Yb pentagons located symmetrically from the mid-edge positions between two RTH cluster centers is 0.84 nm. Therefore these two sites cannot be occupied simultaneously due to steric hindrance between the molecules.

Additional Yb pentagonal sites are also found inside the P1 tiles, which can lead to additional corannulenes trapped inside the decagonal ring (a maximum of 3 or 4 can be anticipated based on steric hindrance, consistent with observations). This hypothesis is also supported by autocorrelation data featuring irregular pentagons embedded in P1 tiles as indicated by small yellow contour in Figs. 4 and

5b. Additional inflated motifs in the autocorrelation function as the one shown in Fig. 5c can also be found in the proposed model (Fig. 5d). Therefore the most salient observations can be reproduced by assuming preferred adsorption of corannulenes at five-fold symmetric sites. This subset of sites consists of both RTH cluster centres located at the node of a P1 tiling and Yb pentagonal motifs decorating the P1 tiles. Decorating these sites with molecules while respecting steric hindrance rules allow to reproduce the main structural features observed in real space as well the corresponding FFT.

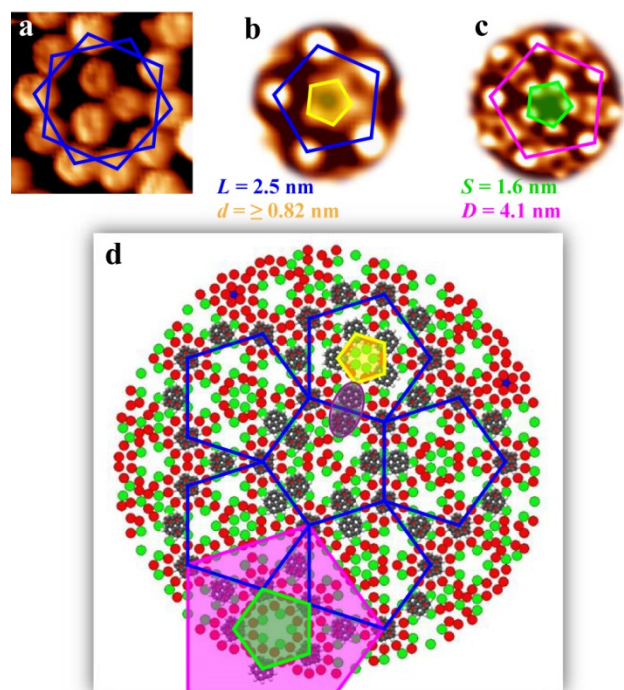


Fig. 5 Tentative model of corannulene self-assembly on *i*-Ag-In-Yb substrate (d) based on the most prominent features of both STM image (a) and its autocorrelation patterns (b,c).

Conclusions

In summary, we have presented the first comparative study of adsorption of structurally related but stereochemically different C_{60} and $C_{20}H_{10}$ molecules on the 5-fold surface of the icosahedral *i*-Ag-In-Yb quasicrystal. Both molecules have similar lateral dimensions and have the same pentagonal carbon ring surrounded by five phenyls. However, while C_{60} molecules have 2-, 3- and 5-fold rotational symmetries, $C_{20}H_{10}$ only have C_{5v} symmetry. Therefore both organic moieties can match the underlying surface symmetry, but the C_{60} have more degrees of freedom regarding its adsorption geometry on such complex substrate compared to $C_{20}H_{10}$. As a result, it is found that the C_{60} adsorption on 5-fold symmetry *i*-Ag-In-Yb surface did not yield any ordered molecular films as evidenced from LEED and STM studies. In contrast, the templating effect was successfully exploited in corannulene self-assembly, even at moderate deposition temperatures. Analysis of STM images and associated autocorrelation pattern clearly demonstrates that corannulenes adsorb with its convex side down preferentially at five-fold symmetric sites (RTH cluster centers and Yb pentagons), thus enforcing long-range quasiperiodic order in the film. Since corannulene can be viewed as a fragment of C_{60} with only C_{5v} symmetry, it can be hypothesized that these molecules probably enhance the dominant role of molecule-substrate

symmetry matching. As the NN distance of 1.3 nm on *i*-Ag-In-Yb substrate is rather large, it suggests sufficiently weak intermolecular interaction in the organic film. Therefore, the molecule-surface interactions had to play a major role in generating principally different patterns with related C₂₀H₁₀ and C₆₀ molecules, i.e. either quasiperiodic or disordered networks, respectively. The role of the symmetry matching should be investigated further, possibly through density functional calculations of the molecular adsorption energies for example.

Finally, there are many bowl-shaped corannulene derivatives with C₅ rotational axis with various functionalities.¹² They represent a class of molecules which can potentially self-assemble into quasiperiodic patterns on quasicrystalline templates using the same mechanism used in the present work with corannulene. Also the saturated quasiperiodic monolayer could potentially be extended in the third dimension, by further piling of corannulenes with a bowl-in-bowl geometry. This has already been demonstrated for periodic molecular pattern and could be extended to form the equivalent of a decagonal molecular quasicrystal.

Acknowledgements

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