Part I

Local screening on π-stacked bi-molecular systems

Chapter 3

Cluster-mediated three-dimensional growth of triptycene on Au(111)

The structure of an organic thin-film is mainly determined by non-covalent recognition processes. A good understanding of the mechanisms ruling these connectivities is important in order to efficiently tailor the electronic and structural properties of molecular devices. Non-covalent connectivities entail a disperse variation of electromagnetic interactions. Fig. 3.1 presents some of the most common non-covalent interactions among organic molecules. All of these forces involve less than 1 eV of energy in the bond. Non-covalent interactions are thus individually weak forces that become strong when they are considered as a whole in the complete self-assembled system. Even though these interactions are ubiquitous in a wide variety of self-assembled organic systems [43, 44, 45, 46], the rules to control the non-covalent connections are complex and result generally in a conformation manifold in which the shape of a supramolecule can not be predicted [47].

Interaction	Range	Energy (meV)	Example
Ionic	1/r	~200-300	cation-π interaction in a Beechgaard salt crystal
Hydrogen bonding	Length of bond ~2 Å	~50-250	Stabilization of the DNA helix
π – Stacking	Length of bond ~3.8 Å	~150	Bonding between benzene molecules
Dipole-dipole	$1/r^3$	~ 50	Interaction between HCl molecules
van der Waals	$1/r^6$	< 50	Bonding between fullerene molecules

Figure 3.1: Table with the most common non-covalent interactions involved in the formation of organic self-assembled systems: ionic bonding, hydrogen bonding, π-stacking, dipole-dipole interactions and van der Waals forces. Estimations of both the range and the energy involved are given.

The addition of a surface to this scenario confines the growth of supramolecular structures to a plane. The surface can be used as a scaffold for the construction of molecular layers. The non-covalent interactions exhibited by molecules adsorbed on surfaces have a preferred directionality along the plane parallel to the surface. Examples can be found in thin-films driven by van der Waals interactions [48, 49, 50], by hydrogen-bond networks [51, 52, 53, 54, 55], or by dipole-dipole interactions [56]. In these cases the bonding with the supporting surface is stronger than the non-covalent intermolecular interactions. A flat symmetry of the molecules also forces intermolecular interactions to occur along a plane parallel to the surface. Hence, the self-assembled structures are constrained to grow in two-dimensional films that exist in a narrow range of temperature and coverage.

In this chapter we show that when intermolecular forces are stronger than molecule/ surface interactions, the molecular growth can evolve in a manner different than a layer-by-layer fashion but following a three-dimensional growth, similar to Volmer-Weber growth mechanism [57, 58].

3.1 Triptycene on Au(111)

In order to reduce the molecule-surface interaction and, thus, optimise the strength of the possible non-covalent intermolecular connections, we have chosen a low reactive metal surface, Au(111), and an organic molecule with three-dimensional shape as building block of the supramolecular system: triptycene (TPC: $C_{20}H_{14}$). It consists of a rigid body formed by two sp^3 hybridized carbon atoms bonding to three phenyl groups in a rotor shape (Fig. 3.2(a)). The adsorption on a surface is thus governed by the balance between two opposite forces: on the one hand the tendency of the phenyl rings to lie planar to the surface via π interactions, and on the other hand the rigidity of the TPC body, which do not allow the deformation of the molecule that would lead to a phenyl planar adsorption. TPC can thus expose its concave π moieties to the bonding with another molecules. In this way, the π-stacking interactions among the molecular units can be maximized as it happens in bulk (Fig. 3.2(b))[59].

Given the weak adsorption expected for TPC on Au(111), external factors like surface temperature during molecular deposition are significant in the formation of the supramolecular structures. Therefore, the growth sequence of TPC is analyzed in terms of this factor (T_s).

3.1.1 Formation of three-dimensional triptycene ordered islands

Deposition of TPC at a surface temperature of $T_s \sim 300K$ results, mainly, in the nucleation of molecules in highly ordered islands. Additionally, the Au(111) monoatomic step edges are covered by rounded molecular structures and smaller features are located at the corners of the Au(111) herringbone reconstruction (Fig. 3.3(a)). To get a hint about the composition of these structures we compare the heights of the molecular arrangements. The line profile of Fig. 3.3(b) shows that TPC distributes in two different predominant heights. The ordered islands amounts 4 Å height while some
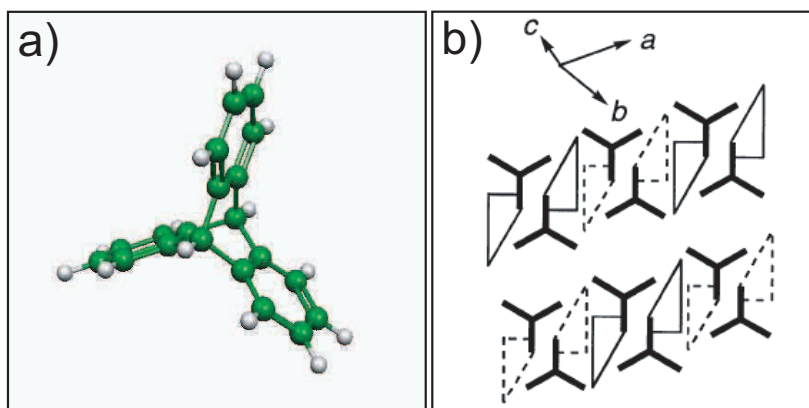
Figure 3.2: (a) Molecular model of triptycene ($C_{20}H_{14}$). Green spheres represent C atoms and white spheres account for H atoms. (b) [59] Schematic representation of the TPC crystal packing, showing the TPC-TPC alignment (bold lines) and adjacent supramolecular dimers (dashed and black lines). The molecules bond preferentially via $\pi - \pi$ interactions showing strong non-covalent connections.

round features have only 1.8 Å of height. These dimensions are much smaller than the physical size of the TPC molecules (~ 7 Å) because STM "sees" the apparent height of the molecules. Since STS measurements taken on the TPC islands reveal a molecular HOMO-LUMO gap of ~ 6 eV (Fig. 3.4), the low apparent height of TPC can be explained based on its insulating character on the surface.
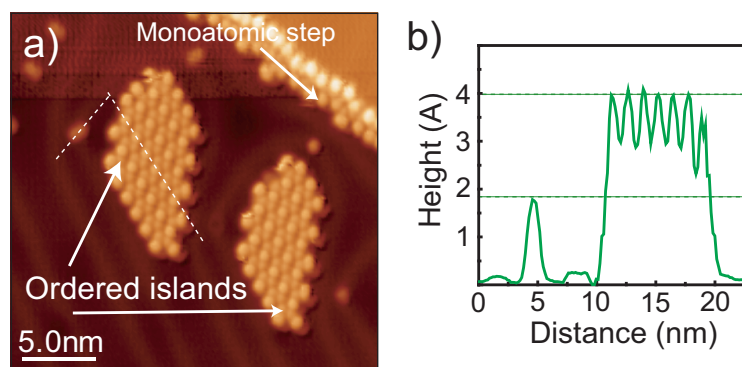
Figure 3.3: (a) STM image of TPC molecules nucleated in islands after molecular deposition at $T_s \sim 300$ K (V = -1.6 V, I = 1 nA). A dashed line indicates the topography profile presented in (b) with the two distinctive heights of 1.8 Å and 4 Å.

Regarding the height difference among the molecular structures, the ratio between them is too large for being simply addressed to different molecular orientation, adsorption sites or chemisorbed states. We believe that this difference is an indication of a three-dimensional arrangement of interconnected TPC molecules.

In order to resolve the mechanism leading to the formation of TPC structures we
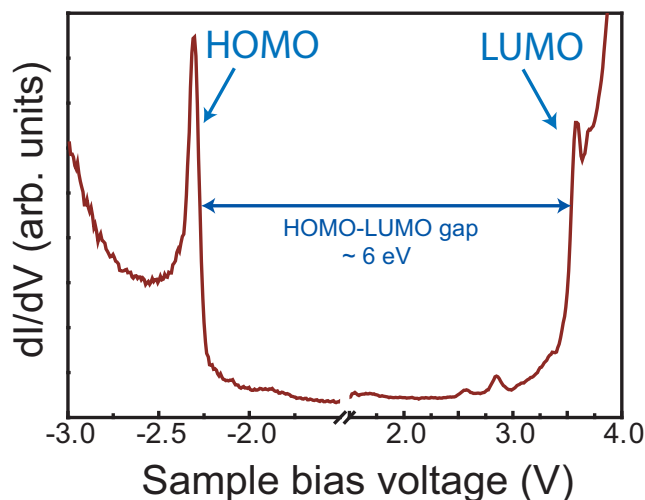
Figure 3.4: Spectroscopy performed on a TPC layer. HOMO and LUMO resonances are located at 2.4 eV and 3.5 eV below and above Fermi, respectively, revealing a molecular HOMO-LUMO gap of $\sim$ 6 eV.

have studied the growth of the molecular layer as a function of the surface temperature during the TPC deposition. When molecules are sublimated onto a cold surface, the island formation can be hindered and precursor stages can be frozen, allowing the observation with the STM. Four different intermediate temperatures, which reflect appreciable changes in the supramolecular structures have been studied, i.e. $\sim$ 70 K, 85 K, 100 K and 170 K. Fig. 3.5 (a)-(i) describes these transitional stages of growth. All the measurements here presented are performed after cooling down the sample to the base temperature of 4.8 K.

After deposition at $T_s \sim$ 70 K, there is no ordered arrangement of TPC molecules (Fig. 3.5(a)). The Au(111) surface is covered by an inhomogeneous distribution of molecular features. The height distribution associated to these structures is also inhomogeneous, but the most characteristic value is 1.8 Å (graph of Fig. 3.5(f)). We identify this dimension with individual-height molecules. Most of the features observed are thus attributed to small groups of molecules, with different shape but with the common characteristic of 1.8 Å height. The most common structure has a trigonal shape like the one depicted in the inset of Fig. 3.5(b) and (c) (Laplacian filter). We assign this structure to the nucleation of three TPC molecules. The presence of these features indicates that, upon sublimation, the molecules arrive as individual items to the surface. Already at this low temperature, the interaction between TPC and the Au(111) surface is weak enough to allow some mobility of the adsorbates.

At moderately higher temperatures, $T_s \sim$ 85 K, TPC nucleates in clusters which exhibit a characteristic height of 4 Å (Fig. 3.5(d)). The TPC thus packs preferentially in three-dimensional structures rather than following a two-dimensional growth, result that reinforces the idea of a intermolecular connectivity stronger than the molecule-surface interaction.
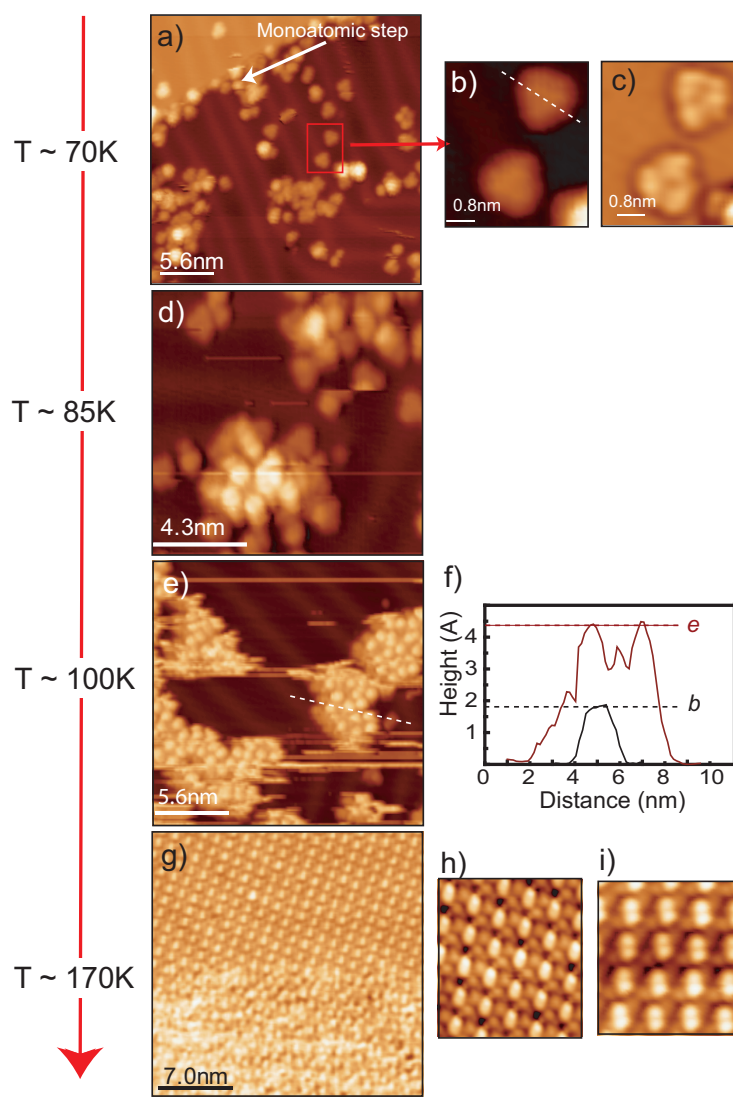
Figure 3.5: Growth of TPC at different surface temperatures. (a) Molecular deposition at $T_s \sim 70$ K results in the formation of structures with individual molecule height (V = -3 V, I = 0.3 nA). (b) is a zoom of (a) and (c) its laplacian filter revealing the internal structure. The dashed line in (b) indicates a line profile shown in (f). (d) STM image at $T_s \sim 85$ K (V = -3 V, I = 0.6 nA). At this temperature TPC starts the nucleation in clusters. (e) Further annealing at $T_s \sim 100$K induces a precursor state of island formation (V = -2.4 V, I = 0.3 nA). (f) Linescans along the dashed white lines of (b) (single-molecule height) and (d) (multilayer height). (g) At $T_s \sim 170$ K, starts the nucleation of the ordered structure (upper part of the image) (V = 1 V, I = 0.1 nA). (h) (V = 0.5 V, I = 0.3 nA) and (i) (V = -2.5 V, I = 0.2 nA) show the ordered structure exhibited by the islands.

A small increase of the temperature, $T_s \sim 100$ K, induces the nucleation of the clusters previously formed at the precedent stage in disordered islands with 4 Å height (Fig. 3.5(e) and (f)). These islands are weakly bonded to the surface as they are easily dragged by the STM tip. The horizontal lines of the scan represent the drag of a molecular structure when moved by the action of the STM tip during the scanning of the image. Interestingly, the height is the same as the cluster islands, meaning that, instead of dragging single molecules, the STM tip moves full TPC clusters. This demonstrates that, once formed, the TPC clusters are a very stable structure and behave as a single unit. It represents, thus, a clear example of a homomolecular building block formed upon non-covalent interactions among its constituents. Furthermore, the size of the clusters is quite homogeneous, entailing the existence of a "magic number" of TPC molecules that gives stability to the cluster and may explain the spontaneous formation of the supramolecules.

At a surface temperature of $T_s \sim 170$ K we find the transition between the disordered cluster arrangement and the highly ordered TPC island (Fig. 3.5(g)). Both ordered and disordered domains have the same height, meaning that the clusters previously formed are not decomposed upon organization of the three-dimensional island. Several ordered structures are found (3.5(h) and (i)). All of them have approximately the same unit cell dimensions and molecular shape; the difference among them lie on the unit cell orientation.

The experimental findings show that TPC self-assemble on a Au(111) surface following a Volmer-Weber growth [57, 58] (they nucleate in three-dimensional islands before having filled the first monolayer). This type of growth has been reported in the case of inorganic thin film growth. Here, it is reported for the first time with organic molecules, emphasizing the important role of the intermolecular interactions. The stable and three-dimensional TPC building blocks created upon non-covalent interactions on the Au(111) surface at a temperature of $T_s \sim 85$ K - 100 K, diffuse for $T_s \geq 170$ K and rearrange forming the ordered islands.

3.1.2 Structure of the supramolecular cluster

Unfortunately, the interesting three-dimensionality of the islands is a handicap for the structure analysis by means of STM. Tunneling microscopy is only sensitive to the topmost layer of the molecular structure. In order to resolve the molecular arrangement and, hence, the nature of the intermolecular interactions responsible for the cluster formation, we have performed combined ab-initio and semiempirical calculations.

We can propose an initial model about the structure of the molecular cluster based on the STM images. The unit cell of the ordered island is defined by two specific structures: (i) a two-fold central maximum and (ii) two lower triangles located at both sides of (i). The two-fold feature can be identified as a TPC molecule facing its two arene rings towards the STM tip, while the lower two triangular shapes would correspond to TPC molecules with their three-fold axis oriented perpendicular to the surface. The relative orientation of features (i) and (ii) comprises an angle between 70° and 90° depending on the unit cell (Fig. 3.6(a) and (b)). The stabilization of the three TPC molecules of the top-most layer can not be due to $\pi - \pi$ non-covalent interactions, since they would involve an angle larger than 120° (Fig. 3.6(c)). A relative orientation

of features i) and ii) is compatible with a structure built upon π interactions in a face-to-edge fashion, energetically equivalent to the $\pi - \pi$ orientation [60, 61].
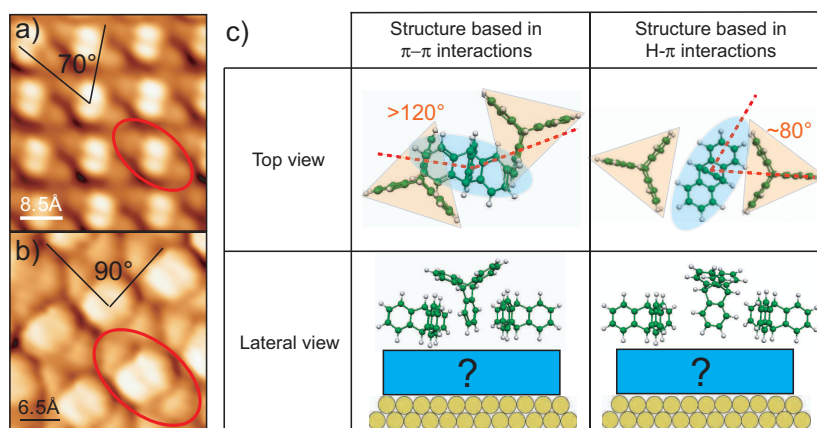
Figure 3.6: (a) and (b) STM topography images of the orderd TPC islands. The structure of the top-most layer can be associated with molecules having a two-fold (higher) and three-fold (lower) orientations with respect to the surface. The red ellipse marks the molecular motif of the unit cell. (c) Table with possible structures of the top-most layer based on the STM topography images, maximizing either the $\pi - \pi$ in plane (left) or the H-π edge-to-face (right) interactions. The shadows represent the characteristic features of the cluster. According to the angles defined by the directions of the 2-fold feature and the lower triangles, only the H-π interaction is possible. In the lateral view, the blue rectangle remarks the fact that this model focuses only on the top most layer configuration and not in the molecules that lie in deeper layers.

Since the height of the clusters is larger than the single-molecular features, it should exist another layer which can not be observed by STM. Its function is to act as anchoring point for the three TPC observed in the top-most structure. In order to maximize the interaction with the underlying Au(111) surface, the TPC molecules belonging to the anchoring layer are expected to orient their phenyl moieties towards the substrate (bottom molecules in Fig. 3.7(a)). Taking into account the size of the molecular unit cell, only two "anchoring" molecules can be included in the cluster, interacting with the top layer also in a face-to-edge fashion. The resulting guessed-structure is shown in Fig. 3.7 (a)(lateral view) and (b)(top view).

In order to validate our guess and check the stability of this molecular configuration, the atomic positions of the TPC cluster shown in Fig. 3.7 have been fully relaxed using calculations based on the MM3 force-field [62, 63, 64]. This method has been specifically parameterized to account for π-interactions in both $\pi - \pi$ and H-π fashions [64]. The proposed structure of Fig. 3.7 turns out to be a very stable configuration, with 41.7 kcal/mol cohesion energy, larger than the energy obtained for clusters formed by 3, 4 and 5 TPC molecules favoring the π-π stacking interactions. The top molecule in this 5-TPC cluster slightly rotates from the 3-TPC cluster conformation favoring the H-π stacking with the anchoring TPC molecules. It is thus oriented 90° with respect to the axis defined by the two horizontal TPC.
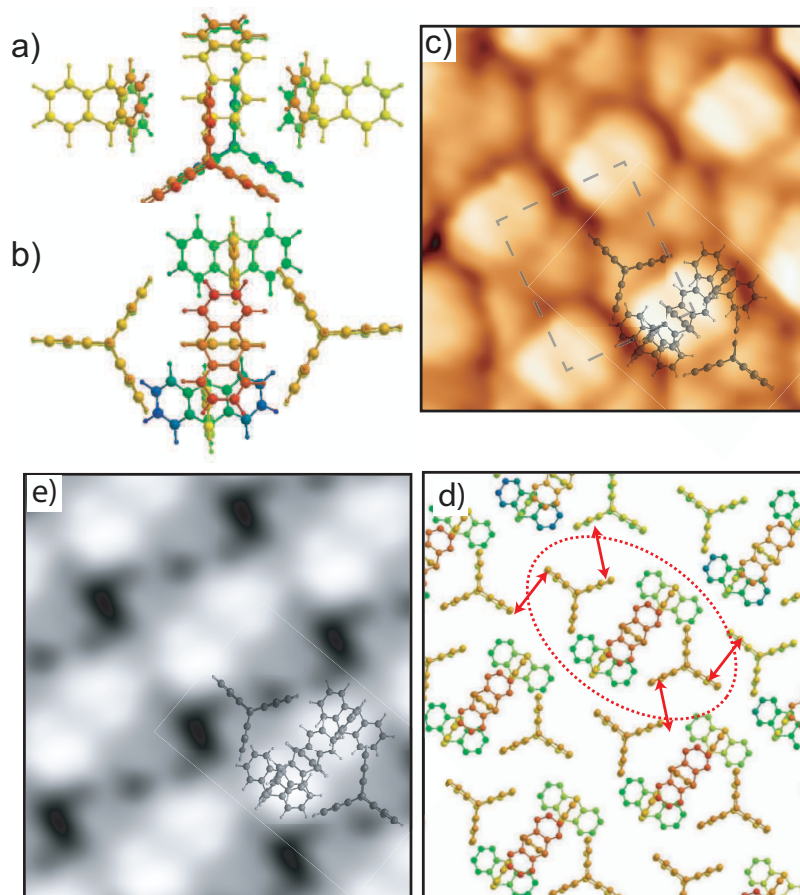
Figure 3.7: (a) Lateral view and (b) top view of the proposed cluster (5-TPC molecules) structure based on the STM images. The cluster structure has been minimized using force-field molecular dynamics (MM3). The blue-to-red color code is associated with the further-to-closer distance from the observer. (c) STM image of a TPC ordered island with a rectangular unit cell. (d) Model of the cluster arrangement corresponding to the STM image (c). The red arrows mark the $\pi - \pi$ interactions that bring the clusters together. (e) Theoretical simulation of an STM image for the ordered island (a). The simulation has been done on the cluster arrangement shown in (d) using the SIESTA code.

In a second stage, we have aligned the TPC clusters to simulate the structure of a quasi-rectangular island like in Fig. 3.7(c). The relaxed structure is shown in Fig. 3.7(d) and (e). The two TPC molecules oriented with the 3-fold axis perpendicular to the surface act as "molecular glue" among the TPC clusters, bringing them together via $\pi - \pi$ interactions (Fig. 3.7(d)) and giving stability to the ordered structure observed experimentally for molecular depositions at $T_s \geq 170$ K.

Although the structure of the supramolecule which we have proposed seems adequate to account for the main features of the STM image, we can also correlate our experimental STM data with the simulations through accurate electronic structure calculations that can be used to simulate LDOS surfaces. In a frame of a collaboration with Prof. Nicolás Lorente[1] and Dr. Riccardo Rurali[2] at the University Paul Sabatier, Toulouse, we have used density functional theory (DFT) under the SIESTA code [65, 66] with the GGA approximation to calculate the one-electron local density of states (LDOS) of the structure minimized with molecular mechanics. This approach allows us to obtain the most reliable structure of the cluster coupled with first-principles electronic structure. A simulation of an STM image can be then built up using the Tersoff-Hamann approach [16]. The results (Fig. 3.7(e)) show a general agreement with the experimental STM images of the ordered islands. The higher TPC molecules appear with a characteristic double-lobed structure attributed to the two phenyl rings pointing towards the STM tip. Middle TPC molecules are imaged in the simulation as lower and featureless trigonal structures. Lower TPC molecules produce no apparent feature in the experimental topography. Due to the high number of atoms that would be involved, we have neglected the metallic substrate in the simulation. This is a reasonable approximation taking into account the reported weak interaction between clusters and the metal surface.

3.2   Conclusions

The supramolecular growth of triptycene (TPC) on Au(111) has been reported in this chapter. This system is characterized by a weak adsorption of the molecules on the supporting surface, such that non-covalent interactions between the molecules are favored during the growth. The ordered molecular structures do not grow in a Frank-van der Merve (layer-by-layer) fashion but through self-assembling of supramolecular clusters of TPC molecules. These basic building blocks consist of an arrangement of 5 individual molecules stabilized by edge-to-face π interactions. In a second step, TPC clusters nucleate in disordered islands with multilayer height at temperatures of 100 K. Above 170 K the building blocks form the highly ordered domains whose structure has been determined by means of semiempirical and ab-initio DFT calculations.

Such molecular growth is analog to the so called Volmer-Weber mechanism of thin film growth. Here, TPC clusters present, in addition, a very stable packing arrangement, which maximizes their cohesion energy through C-H-π interactions. These results show that the rules behind supramolecular chemistry at inorganic surfaces can be explored by working in weak physisorption regimes.

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