Spontaneous Formation of Triptycene Supramolecules on Surfaces

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In the limit of weak molecular interaction with an inorganic surface, noncovalent interactions between molecules dominate the nucleation and thin-film growth. Here, we report on the formation of three-dimensional triptycene clusters with a particularly stable structure. Once formed at the early stage of molecular adsorption, the clusters are stable for all temperatures until desorption. Furthermore, the clusters diffuse and nucleate as individual entities, therefore constituting building blocks for the later thin-film formation. High resolution scanning tunneling microscopy images indicate that the cluster is stabilized by C−H−π interactions. The formation of such molecular structures at a surface is possible because the three-dimensional structure of the triptycene molecule leads to a very weak and mobile adsorption state. These results show that it is possible to investigate complex pathways in the formation of three-dimensional supramolecules at surfaces using a scanning tunneling microscope.

Supramolecular chemistry has recently evolved as a strong field beyond molecular chemistry.[1] Supramolecules are molecular aggregates spontaneously formed and stabilized by noncovalent interactions, whose properties might differ from their constituting molecules. However, the rules to control the structure and functionality of supramolecules are complex. Noncovalent interactions are weak, long-ranged, and flexible, resulting generally in a dynamic and conformational manifold, in which the concept of the shape of a "macromolecule" cannot be defined.[2]

A promising workbench to unveil principles and rules behind noncovalent connectivity is the investigation of mechanisms governing the growth of thin films on inorganic surfaces. At the early stages of thin-film growth, noncovalent interactions between molecules tend to play an increasing role as their interaction with the supporting surface becomes weaker.[3] On metal surfaces, H-bonding van der Waals or metal−ligand interactions are operative, leading to self-ordered two-dimensional molecular phases with a structure that maximizes intermolecular bonding.[4] Several works reported the spontaneous formation of metastable clusters composed of a small number of molecules.[5−8] Since the bonding with the metal surface is still stronger than that between molecules, the clusters are bi-dimensional and exist in a limited range of temperature and coverage.

Herein, we report that molecular thin-film growth can evolve in the spontaneous formation of stable three-dimensional supramolecular structures when intermolecular noncovalent forces are stronger than the interaction with the supporting surface. To reduce the strength of the molecule−surface interaction, we focus our investigation on triptycene (Figure 1a), a molecular system with a three-dimensional structure, which avoids a planar adsorption parallel to the surface. At the surface, triptycene (TPC) exposes its concave π-moieties to the bonding with other molecules, favoring the operation of noncovalent interactions mediated by π-states. As a result of these, we find, through low temperature scanning tunneling microscopy (STM) measurements, that the growth of TPC is characterized by spontaneous formation of stable three-dimensional supramolecular clusters with a unique structure. Molecular structure and noncovalent connectivity apply here to lead to particularly stable packaging arrangements linking a fixed number of molecules, what we call here *a supramolecule*. The stability of the clusters is such that once assembled they constitute the basic building blocks for further growth of triptycene films. Our results show that working in such a weak adsorption regime is ideal to explore the rules behind supramolecular formation.

I. Experimental Methods

The experiments have been performed in a custom-made scanning tunneling microscope working in an ultrahigh vacuum ($\leq 1 \times 10^{-9}$) at 4 K. We use a gold (111) single crystal as the substrate, since it results in weak physisorption for most aromatic compounds. The Au(111) single crystal surface was cleaned in a vacuum by repeated cycles of Ne^+ sputtering and annealing to ∼750 K. Triptycene molecules (Aldrich) were sublimated from a Knudsen cell at 350 K located in the UHV chamber. During or after molecular deposition, the temperature of the sample (T_s) could be adjusted to a desired value in order to
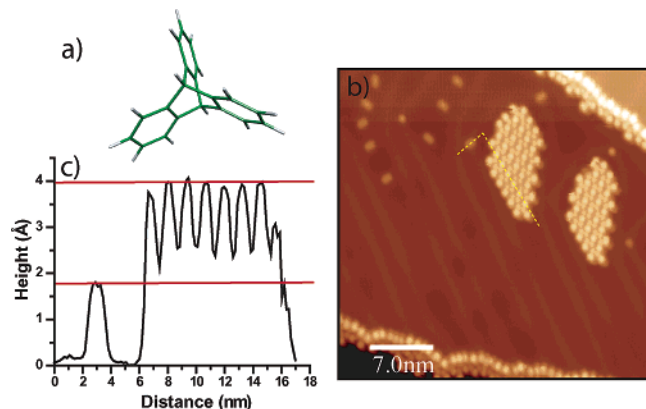
Figure 1. (a) Atomic model of triptycene ($C_{20}H_{14}$). (b) STM image of triptycene molecules on the Au(111) after sublimation onto the sample at room temperature. A dashed line indicates the location of the topography profile shown in part c. The profile (c) shows that the island height is larger than the isolated features (sample bias voltage $V_s = -1.6$ V, tunneling current $I_t = 1$ nA).

increase or reduce the thermal motion of the adsorbates. All STM data presented here were acquired after cooling the sample down to a temperature of 5 K, regardless of the deposition or annealing temperature. Analysis of the data has been done using the WSxM program.[9]

II. Results and Discussion

In a first step, the TPC molecules were deposited onto a gold (111) surface at $T_s \sim 300$ K. The most prominent resulting structures are islands of extremely high order (Figure 1b). Additionally, smaller features are located at the corners of the Au(111)(22 × √3) reconstruction. To get a hint about the composition of the molecular islands, we note that the apparent island height is ∼4 Å, a factor of 2 larger than the isolated dimers (∼1.8 Å)[10] (Figure 1c). This large difference of height cannot be simply understood on the basis of different molecular orientations and/or chemisorption states. Instead, we presume that this difference is an indication that TPC islands are formed by a complex three-dimensional arrangement of interconnected TPC molecules.

To resolve the nature and the formation of such complex arrangements of TPC molecules, we investigate the morphology of TPC islands as a function of the substrate temperature during molecular adsorption. At lower temperatures, the molecular mobility is reduced and different transient stages occurring during the island formation can be *frozen*, allowing their observation with the scanning tunneling microscope. Figure 2a–d shows a sequence of STM images obtained after deposition at low temperature (Figure 2a,b) and subsequent annealing to higher temperatures (Figure 2c,d). Figure 2e–h zooms on the characteristic molecular features observed at every temperature. The corresponding height profiles are plotted in Figure 2i.

After molecular deposition at $T_s = 70$ K, no ordered structure is observed. Instead, the Au(111) surface is covered by an inhomogeneous distribution of groups of molecules with various conformations but with an apparent height equivalent to the monomolecular height (1.8 Å). The most common ones have a trigonal shape which we attribute to the nucleation of three TPC molecules (Figure 2f). A few isolated molecules can be identified (Figure 2e), supporting the fact that, after sublimation, TPC molecules arrive at the surface as individual species. Thus, the weak interaction with the gold surface causes already at
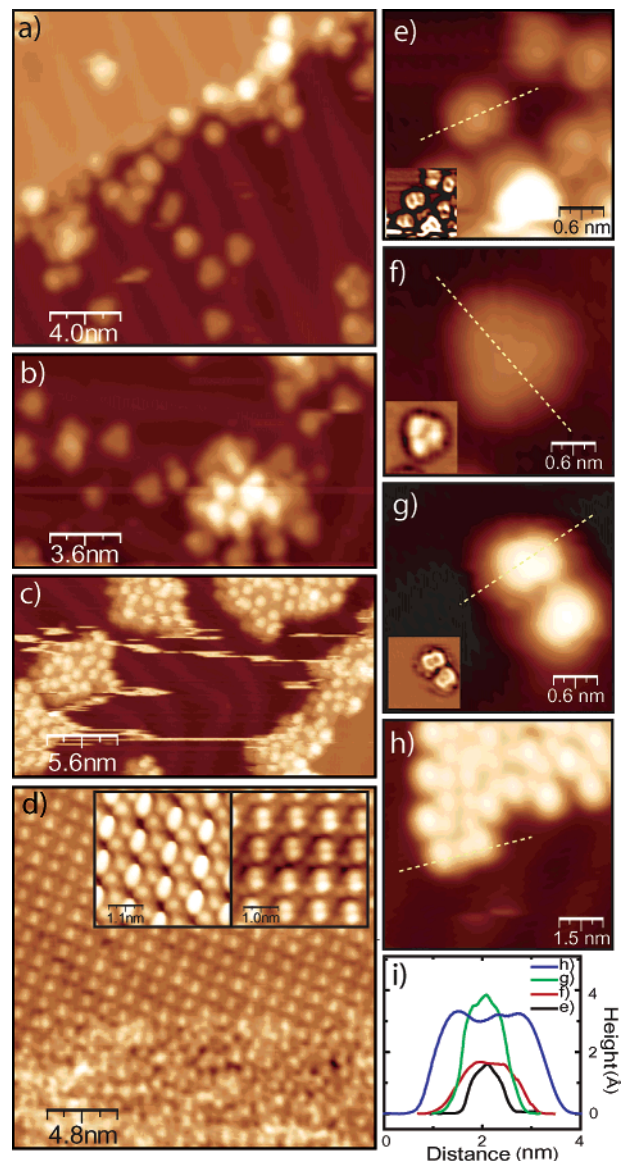

Figure 2. STM images after deposition of TPC molecules at (a) $T_s = 70$ K, at (b) $T_s = 85$ K, and after further annealing to (c) $T_s = 100$ K and (d) $T_s = 170$ K. The inset in part d shows the two typical domain unit cells found. (e–h) Zoom images on characteristic features found after the preparation temperatures indicated in parts a–c (see text). The insets show the corresponding Laplacian-filtered images to enhance intramolecular corrugation.[9] (i) Height profile of features in parts e–h comparing their different apparent heights ((a,b) $V_s = -3.0$ V; (c) -2.4 V; (d) 1.0 V (insets 0.5 and -2.5 V); (e) 2.7 V; (f) -3.0 V; (g) 1.9 V; (h) 1.2 V).

this low temperature some degree of transient mobility, steering the formation of metastable molecular groups.

At slightly higher temperatures, that is, at $T_s = 85$ K, TPC molecules nucleate into higher structures, which already show the characteristic height of ∼4 Å (Figure 2b). Such three-dimensional arrangements can be observed even in isolated clusters, with the same apparent height (Figure 2g). This confirms the tendency of TPC molecules to pack in three-dimensional arrangements instead of two-dimensional islands. Furthermore, the cluster height is similar to the height of islands formed at higher temperatures (Figure 1), thus independent of the coverage, which tentatively we associate with the existence of a particularly stable molecular packing arrangement.

For temperatures higher than $T_s = 100$ K, TPC clusters nucleate in partially disordered islands (Figure 2c,h), still
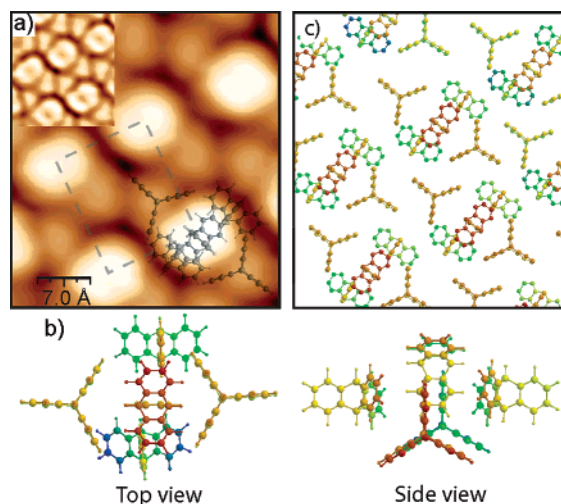
Figure 3. (a) STM image of an ordered island with a rectangular unit cell with dimensions of 1.5×1.3 nm^2 ($I_t = 1.3$ nA, $V_s = -2.1$ V). The inset shows the STM image processed with a Laplacian filter[9] to emphasize the intramolecular structure. (b) Top view and side view of the proposed cluster structure based on the STM image (a) and on force-field molecular dynamics (MM3) calculations. The blue-to-red color code is associated with the further-to-closer distance from the observer.

exhibiting high mobility as an indication of very weak interaction with the metal surface. It is common to observe horizontal lines and features (Figure 2c) indicative of the lateral dragging of molecular structures by the scanning motion of the tip. Interestingly, the height of these lines is also ~4 Å, the characteristic height of the islands and molecular clusters. They thus indicate that the STM tip drags full clusters away from the island and/or back to it, instead of single molecules. Therefore, TPC clusters once formed behave as a stable unit, representing a clear example of a molecular building block stabilized by noncovalent interactions, that is, a supramolecule.

Although the cluster islands show some local order, they remain fairly disordered on a larger scale up to temperatures around $T_s = 170$ K, above which a transition to an ordered phase occurs (Figure 2d). Several ordered structures are then found, all having a similar shape (inset of Figure 2d). Finally, upon reaching annealing temperatures above $T_s = 340$ K, TPC completely desorbs from the Au(111) surface. It is interesting to note that this temperature is of the order of the sublimation temperature from the TPC powder ($T_s = 350$ K), thus confirming once more that the interaction of TPC with the Au(111) surface is very weak.

Summarizing the experimental growth sequence, TPC molecules on a gold surface spontaneously nucleate in stable 3D supramolecular structures. The fact that all the clusters have the same size suggests that they are composed by a well determined number of TPC molecules arranged in a particularly very stable 3D structure. It is thus important to question about the nature of the interactions stabilizing the cluster and about the structure of such a particularly stable molecular arrangement.

STM can provide a view of the topmost part of the cluster structure within the islands. The image in Figure 3a shows that the unit cell is composed of molecules with two different orientations: a higher molecule with a two-lobed shape is packed between the other two, oriented with a threefold structure. On the basis of these data, a precise model of the arrangement of these three molecules can be constructed (Figure 3b (top view)). The model shows that the relative molecular arrangement in the domain unit cell is such that they interact in

a face-to-edge fashion,[11] characteristic of C−H−π intermolecular interactions.

The threefold structures appear in the STM images slightly lower than the twofold ones, with a height of ~3.5 Å. This is however larger that that the corresponding height of single molecules and small clusters found after the low temperature clusters. The larger apparent height of both structures indicates that they are probably supported by additional molecules underneath, whose arrangement is obviously hidden from the STM tip. In Figure 3b, we propose a tentative structure for the cluster unit determined using the arrangement of the topmost molecules resolved in Figure 3a and the periodicity of the islands. Essentially, only two additional TPC molecules can be included in the lower layer without increasing the size of the unit cell. The stability of the cluster structure proposed in Figure 3b has been checked by computer modeling the cluster arrangement. Noncovalent bonding, and specially π-stacking interactions, are hardly taken into account precisely using semiempirical or ab initio methods. Instead, we have used empirical energy minimization simulations based on the MM3 force field.[12] This method has been specifically parametrized to account for π-interactions between molecules.[13] MM3 implemented in the Tinker package[17] has thus been applied to find minimum energy configurations of various TPC cluster model arrangements.

In consistency with our experimental observations, the simulations find that the cluster stability is increased by maximizing the number of π−π and C−H−π intermolecular interactions. For the case of isolated clusters, various packing arrangements of three, four, or five TPC molecules are found to be stable. The cluster with the structure shown in Figure 3b has the largest cohesion energy per molecule, namely, 35.2 kJ/mol. This value amounts to only 20.1 kJ/mol for a three-molecule cluster with the arrangement of the three topmost molecules observed by the scanning tunneling microscope in Figure 3a. Larger clusters do not account for the experimental lattice dimension and are thus not considered. Figure 3d shows a proposed model of the resulting quasi-rectangular arrangement of clusters agreeing with the experimental STM image in Figure 3a. The model accounts for the interaction between clusters in the island to be driven by π−π stacking forces between two neighbor threefold oriented TPC molecules.

III. Conclusion

Our results demonstrate that in the limit of weak molecular interaction with an inorganic surface noncovalent bonds between molecules dominate. We find a hierarchical two-step growth mode of TPC molecules: the spontaneous formation of stable three-dimensional supramolecules, which then become basic building blocks for further molecular thin-film growth.

The formation of three-dimensional structures is favored due to the dominant role of noncovalent interactions among TPC molecules, which here are therefore presumed to be stronger than those between TPC and the Au(111) surface. This process is analogous to the so-called Volmer−Weber mechanism of growth[14,15] or to the formation of metal clusters on oxide surfaces.[16] Applied to molecular thin-film growth, our results indicate that stable packing arrangements between molecules may additionally result in the formation of three-dimensional clusters. Triptycene clusters spontaneously formed on a Au-(111) surface exhibit a characteristic "magic" (i.e., energetically favorable) size and structure, resulting in a complete monodisperse size distribution of molecular clusters. Through high resolution STM images, combined with computer modeling of

stable cluster structures, we find that such stability is an expression of both the molecular three-dimensional structure and the predominant role of C−H−π intermolecular forces. In bulk, TPC shows a similar face-to-edge packing in three dimensions, but the packing fashion differs,[18] probably because the complex crystal unit cell, involving four molecules in different orientations, is not stable at the gold surface. Thus, in the playground of our experiment, we envisage that control of the structure of supramolecular clusters should be possible to address by adjusting molecular functionalization and structure, surface symmetry, and temperature. These strategies would allow one to design the structure of molecular thin films and, hence, their functionality.

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