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Observation and modeling of the conformational molecular structures driving the self-assembly of tri-adamantylbenzene on Ag(111)

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Abstract

The self-organization of tri-Adamantyl (TAB) benzene molecules has been investigated using low temperature scanning tunneling microscopy (LT-STM). The molecular structures have been also studied using molecular modeling. Particularly, these calculations have been performed on large areas (1000 nm²) from the atomic structure of the molecular building block, combining Molecular Dynamics (MD) and Monte-Carlo (MC) approaches. These investigations show that the structure of the molecule and its flexibility allow for the formation of different networks as a function of surface coverage. The calculations demonstrate that stability of the largest structures is obtained through the increase of the interfacial energy induced by rotation of the Adamantyl groups, a behavior whose consequences explain the subtle contrasts observed in the experimental STM images.

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Introduction

The organization of large molecules on solid surface is still an open field of research. Indeed, the network formation on a substrate is driven by a lot of interactions that depend on the molecular structure and on the used surface (1). On metal, a large number of molecules have been already investigated (2) (3). Their organization is often predictable either because their planar structure facilitates hydrogen bond formation (4) or because their structure favors the formations of covalent bonds (5) (6) or metal-ligand bonds in privileged directions (7) (8). The self-assemblies that result from these interactions are stable at a given temperature. As the coverage increases, evolution of these structures is closely linked to the number of layers since the second and third layers interact with the molecule sublayer and not directly with the substrate itself (see for example (9)). The relative orientation of the layer with respect to the substrate may be related to strain energy that could play a significant role as discussed in the work of McTague and Novaco (10) (11). However, these papers deal with the properties of rare gas atoms adsorbed on homogenous substrates or on graphite. The situation is more complex for molecules that may offer different conformations as a function of their surroundings. In 2006, Koudia et al reported an experimental study of monolayers of chlorine phthalocyanines in which a maturation of the molecular network was observed (12). Driven by hydrogen bonding, this evolution led to the formation of three different structures as a function of time at constant temperature. This kind of observation is relatively important since it allows the nature of the interactions to be probed with a relatively good accuracy, especially when the observations are coupled with suitable calculations (13).

In this paper, we have investigated the behavior of tri-Adamantyl benzene (TAB) molecules deposited on Ag(111) surfaces at coverage below the monolayer. These small molecules are composed of a central benzene ring coupled with three peripheral Adamantyl (ADT) groups (14). These moieties favor the decoupling of the central plateau from the metallic substrate and allow a certain mobility of the whole molecule (15). Evaporation of TAB on the surface, results in the formation of small clusters in which the molecules adopt a hexagonal network. On the largest domains, the lattice differs and the molecules are organized in a rectangular lattice. Using Molecular Dynamics and Monte-Carlo calculations, it is demonstrated that the flexibility of the peripheral groups allows their organization in head to tail structures in which the ADT have a peculiar orientation.

Experimental details and computational methods

The experiments have been conducted on a Scanning Tunneling Microscope (STM) working at liquid nitrogen temperature ($T=77$ K) (LT Omicron) with a base pressure of $3 \cdot 10^{-11}$ mbar. The substrate is a (111) oriented single Ag crystal cleaned by repeated ionic argon bombardment cycles followed by annealing at 800K for 1 hour.

The TAB molecules have been synthesized using the method defined by (16). They are first deposited on a tungsten wire out of the experimental setup. After 12 hours of turbo molecular pumping in the introduction chamber, the TAB covered wire is introduced in the preparation chamber where it is slightly heated in order to outgas the remaining solvent used to manipulate the molecules on the filament. During evaporation, the TAB flux is tuned by controlling the current flowing through the tungsten wire. The coverage of TAB on the Ag(111) surface is controlled using the pressure evolution during evaporation and duration of substrate exposition to the molecular flux.

In the present experiments, the clean Ag(111) substrate has been exposed to evaporation rates of about 0,02 monolayer per minute. These experiments are conducted while the substrate is held at room temperature allowing molecules to diffuse on the surface and form supramolecular structures. The sample is then transferred in the STM chamber where it is cooled down to liquid nitrogen temperature (77 K). The STM images and spectroscopic data are obtained when the sample is maintained at this temperature.

The experiments were combined to theoretical simulations, using both Molecular Dynamics (MD) simulations (based on the numerical solution of the Newtonian equations of motion for all atoms), and large scale Monte Carlo (MC) simulations (based on a stochastic process, which explores the space of configurations constrained to the given thermodynamic conditions). To explore dynamical and configurational effects of the Adamantyl functional groups on the resulting structure, and to study more specifically the structural features of the observed experimental structures, Molecular Dynamics calculations have been performed using the NAMD software version 2.9 running in parallel on a local cluster (17). The equations of motion were solved with a 2 fs time step. The constant temperature (300K) ensemble (NVT) was controlled using the Langevin thermostat with a relaxation constant of 1 ps^{-1} . This temperature is used because evaporation of molecules is performed at 300K and also because such a temperature significantly decreases the processing time. This is particularly important to probe large molecular domains during the MC simulations and avoid metastable states. Parameters for the molecule-substrate, and intermolecular interactions are derived from the CHARMM force field. The interactions of the surface Ag atoms with organic molecules were taken from a new improved Lennard-Jones parameterization, accurate for interfacial calculations and compatible with the CHARMM force field (18).silver

The model for the TAB molecules is based on the CHARMM force field, designed for biomolecular simulations. To our knowledge, TAB molecule has not been previously simulated entirely within the selected force field, however it has been successfully employed for simulations of Adamantane (19), (20). The intramolecular and intermolecular parameters were determined taking advantage of the automation the CHARMM General Force Field (CGenFF (21), (22), (23) in its version number of the interface 0.9.7.1 and the force field 2b8), which provides the atom typing and assignment of parameters and charges by analogy with sub-functional groups (i.e. the Adamantane). When CGenFF is guessing some parameters by analogy, penalties are addressed and were less than 20 meaning fairly analogue, and quite reliable. Input files are available upon request. The partial charges distribution based on CGenFF parameterization appears consistent and is reported in the S.I. The downloaded molecular structure was optimized by energy minimization using the conjugate gradient and line search algorithm implemented in NAMD (17).

Once the molecular structure is optimized, a second minimization of the molecule adsorbed on the (111) surface is performed. The simulation box size is $23.13 \times 20.0 \text{ nm}^2$ and periodic condition boundaries are applied along the three directions. It includes a slab of 4 layers of the metal surface stacked along the $\langle 111 \rangle$ direction, which implies 25600 silver atoms. During the minimization, the Ag atoms were maintained fixed at their crystal position. The results (an optimized structure of the molecule adsorbed onto the surface) was employed to build a cluster of 79 TAB molecules, with all molecules oriented along the [1-10] surface direction. The initial arrangement of the molecules within the cluster was chosen to mimic the cluster observed in the STM images and with the same lattice spacing. The hexagonal lattice of the cluster is also rotated by 7 degrees with the [1-10] surface direction. Again, we optimized the initial configuration of the adsorbed cluster with energy minimization. After the minimization run, we performed a MD simulation thermalizing at a temperature of 298K. A 20ns run was enough to study equilibrium properties for this small cluster. During the simulation, we observed rotations of the ADT groups around the covalent bond with the benzene. Consequently, the effects of the ADT faceting and symmetry on the resulting self-assembled structure have been investigated. We have considered four conformations of TAB depending if the trivalent carbon of the ADT is pointing out to the surface, or if it is rotated of 90 degrees. The different molecular configurations have been picked up along the aforementioned MD run.

The hetero-epitaxial properties of an organic layer adsorbed on a crystalline substrate need large-scale simulations, which involves several hundreds to thousands of molecules self-assembling, meaning a colossal number of atoms. MD simulations are not feasible to study such large systems. Instead, we used the recently introduced SANO (Self-Assembly of Nano-objects has been used) methodology, specially designed to deal with the self-assembly of organic molecules onto metal surfaces (24), (25). Essentially, the method is a two-dimensional (*off-lattice*) Monte-Carlo (MC) approach coupled to an interpolation technique for fast evaluation of the interaction energies. The molecule and the substrate are assumed rigid, and the molecule-molecule and molecule-surface interactions are pre-calculated before any further simulation step. During the simulation of the self-assembly process, the potential energies are then computed as grid interpolations of the pre-computed values (26). The substantial savings in CPU time obtained with this methodology allow to perform the molecular self-assembly modeling at the required (large) length scales and unrestricted by the large number of atoms. We performed classical MC run, starting from the 2D gas-like phase of adsorbed molecules sublimed at high temperature (1500K), and progressively cooling down with an increment of 50K between each MC run until reaching room temperature. Each MC run represents 10^6 MC attempts per molecule. To improve the equilibrium time, the Rosenbluth rotational bias has been implemented, with 10 orientations considered for each MC attempt. The bi-dimensional molecular simulation box size is $28.92 \times 29.05 \text{ nm}^2$, and initial configurations consist in 400 molecules spread randomly on the bare surface. Larger scale modeling (4 times larger) has been also performed for reliability. Visualizations are made using the VMD (Visual Molecular Dynamics software (27)).

Results

The TAB molecule is composed of three adamantyl groups placed in 1st, 3rd and 5th positions of a benzene ring. The maximal distance between two opposite carbon atoms in the TAB molecule is 1.11 nm and the molecule presents a characteristic triangular shape. The peripheral groups act as three feet and create a theoretical separation of about 0.2 nm between the metallic substrate and the central carbon atoms. The π -coupling is thus reduced and the molecules are allowed to diffuse on the surface, especially when the substrate is held at room temperature.

At low coverage and when the size of the molecular domains are rather small (typically, a few nanometers in diameter) the STM reveals peculiar structures. One of them is presented in Figure 1.

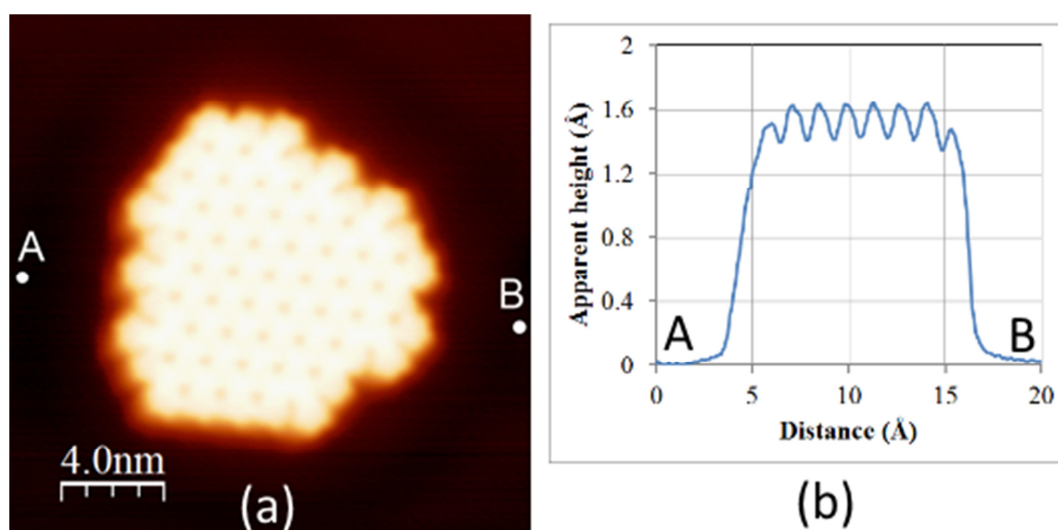


Figure 1: STM image of an island obtained with a bias voltage of -2 V ($20 \times 20 \text{ nm}^2$). The profile presented on the right shows the apparent height of the molecules along the AB direction ($T = 77 \text{ K}$).

This molecular island, about 11 nm in diameter, exhibits different characteristics. Its apparent height above the Ag(111) surface is about 0.16 nm (Fig. 1b). In this structure, the molecules appear as small triangular objects organized in a hexagonal array with a lattice parameter of 1.5 nm. This value is larger than the molecule size and suggests that the molecules are not really stressed during self-assembly. Their density is 0.51 molecule per nm^2 . The island orientation is not related to the substrate close packed directions. For example, the base of the molecular structure presented in Fig. 1 makes an angle of about 6 degrees with the [110] type direction of Ag(111). As expected, most of the molecules present the same orientation in the layer. This is particularly highlighted in Fig. 2 obtained at a bias voltage of -0.25 V over a $7 \times 7 \text{ nm}^2$ area in the center of Fig. 1.

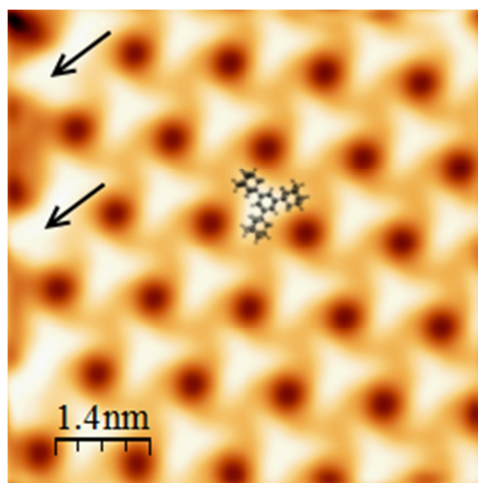


Figure 2: STM image ($7 \times 7 \text{ nm}^2$) of the top of the island showing the molecule orientation. The structure of a TAB has been superimposed ($V = -0.25 \text{ V}$, $T = 77 \text{ K}$).

The island presented includes 44 molecules organized within the same lattice. However, 20 of them are on the side of the structure and present a different orientation. This can be observed in Fig. 2 where two molecules indicated by black arrows show a different organization. Some peripheral molecules presents rotation angles with respect to the other island molecules ranging from a few degrees to about 60° depending on their position (Fig. 1). This suggests that during the island growth at ambient temperature, diffusion allows molecules to reach the structure but because of the temperature drop after the sample transfer in the STM cryostat, these molecules do not have enough time to self-organize as in the rest of the island. Furthermore, the islands formed in this way are isolated from the surrounding and do not suffer from stresses which might be induced by defects or by the other molecular domains in the case of higher coverages.

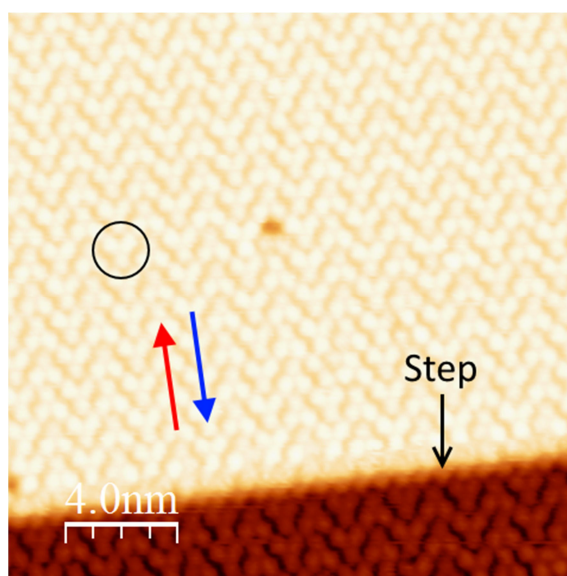


Figure 3: STM image $20 \times 20 \text{ nm}^2$ of a large self-assembly on $\text{Ag}(111)$. A single TAB molecule has been encircled ($V = 0.87 \text{ V}$, $I = 14 \text{ pA}$, $T = 77 \text{ K}$).

The molecular network changes when the island size grows. An example of this new structure is presented in Fig. 3. Each molecule exhibits a triangular shape with three bumps characteristic of the

three adamantly groups. One of them is encircled in Fig.3. The TAB molecules closest to the Ag step have the same orientation. Two adamantly groups are parallel to the step while the third is oriented at 90° (red arrow, up). In the row right off (slightly farther from the step edge), the molecules are oriented at 180° (blue arrow, down) so that in the direction parallel to the step, the molecular structure presents a chevron shape. The lattice is rectangular with $a=2.2$ nm and $b=1.2$ nm. The density is about 0.75 molecule per nm^2 which is significantly higher than for the island previously presented.

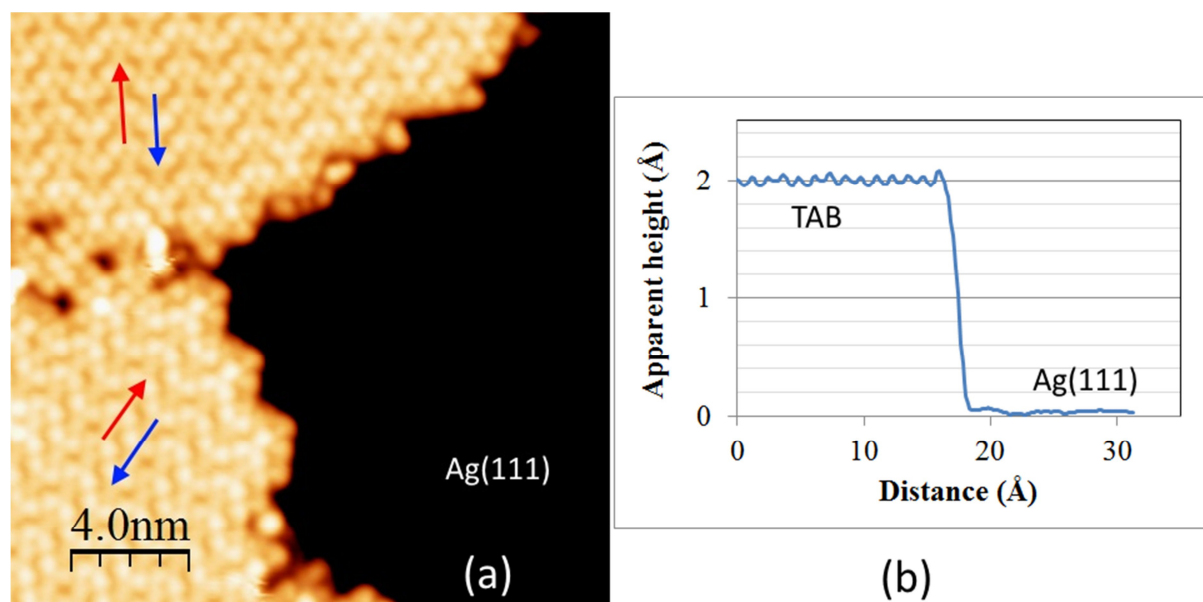


Figure 4: (a) STM image of a grain boundary between two molecular structures ($V=1V$, $I=15$ pA, $T=77K$). (b) Cross section between the molecular layer and the silver substrate showing an apparent height of 0.2 nm.

The molecules are self-assembled without any correlation with the substrate crystallographic directions and molecular domains of different orientation on the surface exhibit boundaries as the one presented in Fig. 4(a). In this example, the angle between the two domain orientations is equal to 40° . The apparent height above the metallic substrate is 0.2 nm (Fig. 4(b)). This value is slightly greater than for the island structure whatever the used bias voltage. The cross section also shows the periodic corrugation observed over the molecular layer: its maximum value is about 65 pm. However, the contrast of TAB is not homogenous over the whole molecule as observed on the small island (Fig. 2). To show this effect, an image performed on the structure at a smaller scale and a bias voltage of 1V is presented in Fig. 5. A single molecule has been encircled and the two molecular orientations in the layer (up and down) are indicated by the colored arrows.

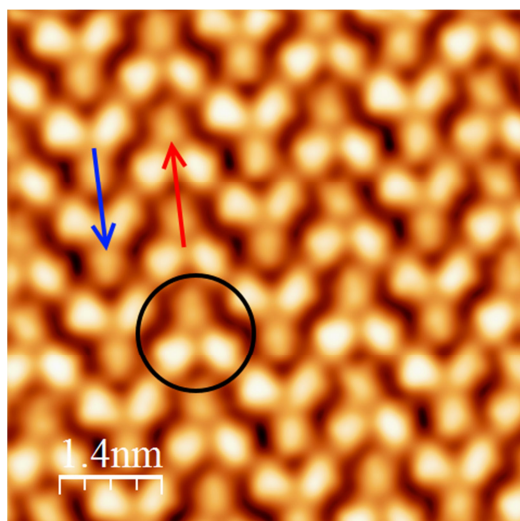


Figure 5: STM image ($7 \times 7 \text{ nm}^2$) of a self-assembly ($V = 1\text{V}$). The colored arrows give the orientation of TAB in the layer and the circle surrounds a single molecule. ($T = 77\text{K}$)

At 1V , the three adamantyl groups appear as small bumps but do not exhibit the same apparent height. Two of them show a larger corrugation with respect to the third. The corrugation difference between the highest and the lowest lobe is about 20 pm . This contrast enhances the chevron appearance of the structure. This observation does not result from a tip effect since in the up and down orientations, these subtle contrasts appear exactly the same way after a rotation of π of the whole molecule. This suggests that the conformation of each molecule in the layer depends on its surrounding and that one adamantane is “oriented” differently from the two others with respect to the surface.

To support interpretation of the experimental observations, large scale modeling of the molecular self-assembly has been conducted as described in the methods section. We first describe the results of the simulations performed for the cluster of 79 TAB molecules adsorbed onto the $\text{Ag}(111)$ surface. We observe that the ADT groups tend to rotate axially from 45 to 90° around the covalent bond formed with the benzene ring. This rotation leads to different conformations of the molecule with respect to the surface, and therefore, leads to different symmetries. Four of these configurations are represented in Fig. 6. The highest symmetry of the molecule with respect to the surface is when the three ADT are pointing out to the substrate (the case denoted TAB 3.0 in Fig. 6). We also observed either three rotated ADTs (TAB 0.3), which leads to a conformational asymmetric (*chiral*) molecule, which is less probable. Then, it is often observed that two ADTs are rotated (TAB 1.2), while one remains standing up leading to a mirror symmetry of the molecule (red dashed line). Therefore, two possibilities are considered: ADTs rotated either down, or laterally.

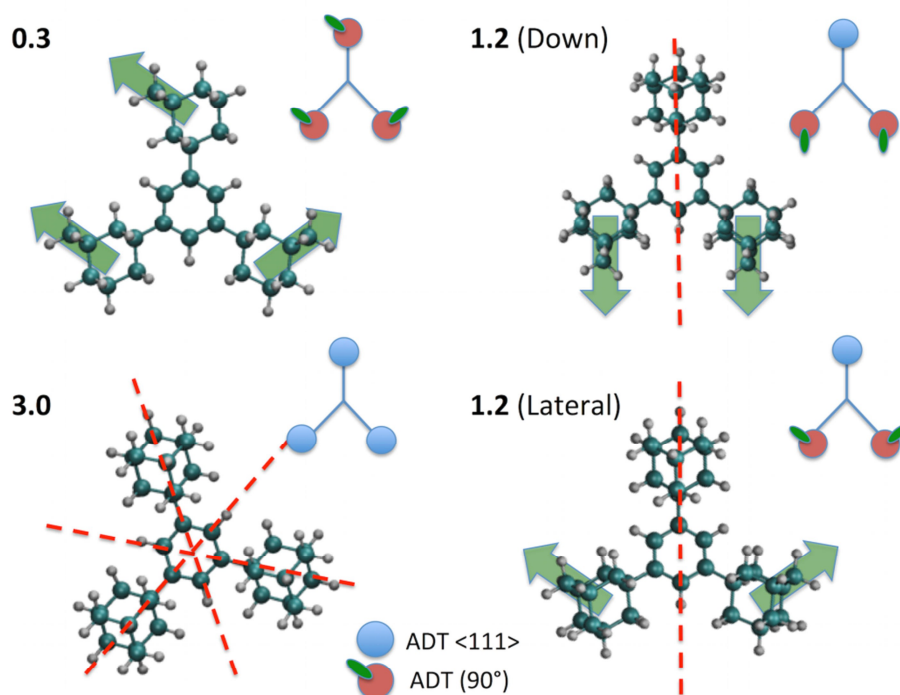


Figure 6: TAB molecular conformations extracted from simulations. The TAB molecule is shown in ball and sticks representation. For better understanding, small cartoons illustrate the ADTs orientations (red circles: tilted; blue circles: pointing at the <111> direction). We assigned a label TABX.Y to each configuration: X indicates the number of ADT groups following the <111> orientation (blue balls) and Y the number of tilted groups (red balls).

Large-scale MC calculations following the SANO method have been performed for each conformation of the molecules TAB3.0 and TAB0.3 (the calculations are then conducted with a frozen molecular conformation). The molecular self-assembly is simulated starting at high temperature and cooling down the system gradually up to room temperature. No head to tail configuration could be observed. Instead, hexagonal close compact structures for the TAB3.0, and disoriented hexagonal packing in the case of the TAB0.3 molecules were obtained. Interestingly, because of the highest symmetry of TAB3.0, a compact structure arises (Fig. 7). The arrangement is following the dense [1-10] type directions of the surface.

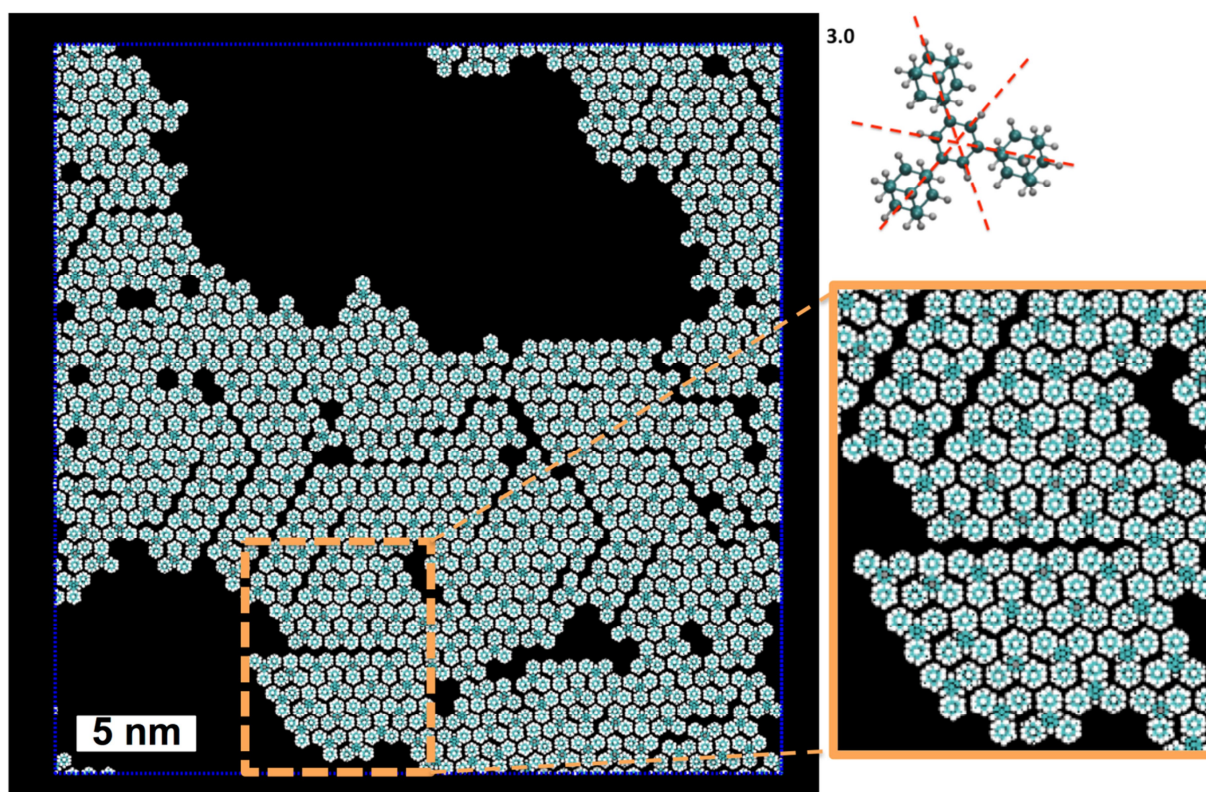


Figure 7: Snapshot of a configuration obtained after modeling the self-assembly of 400 molecules of TAB3.0 model. For clarity, the surface is not represented.

Same calculations have been performed for TAB1.2 (down and lateral) at same conditions (Fig 8). In all cases, the experimentally observed surface structures are reproduced with a precision of the lattice parameters of 0.2 \AA . The behavior is enhanced when considering the two lateral and down mirror symmetries of the molecule. The molecular network in a head to tail configuration follows different orientations and are not anymore following the dense directions of the substrate atoms. Note that we could not stabilize only one broad domain in our simulations. Probably, the presence of edges or defects on the surface would lead to a better stacking of the molecules, or something more subtle occurs during the self-assembly dynamically. Though, more than 65% of the molecules are involved in a head to tail arrangement, in diverse coexisting small clusters which is very satisfactory for a self-assembly including only rigid molecules.

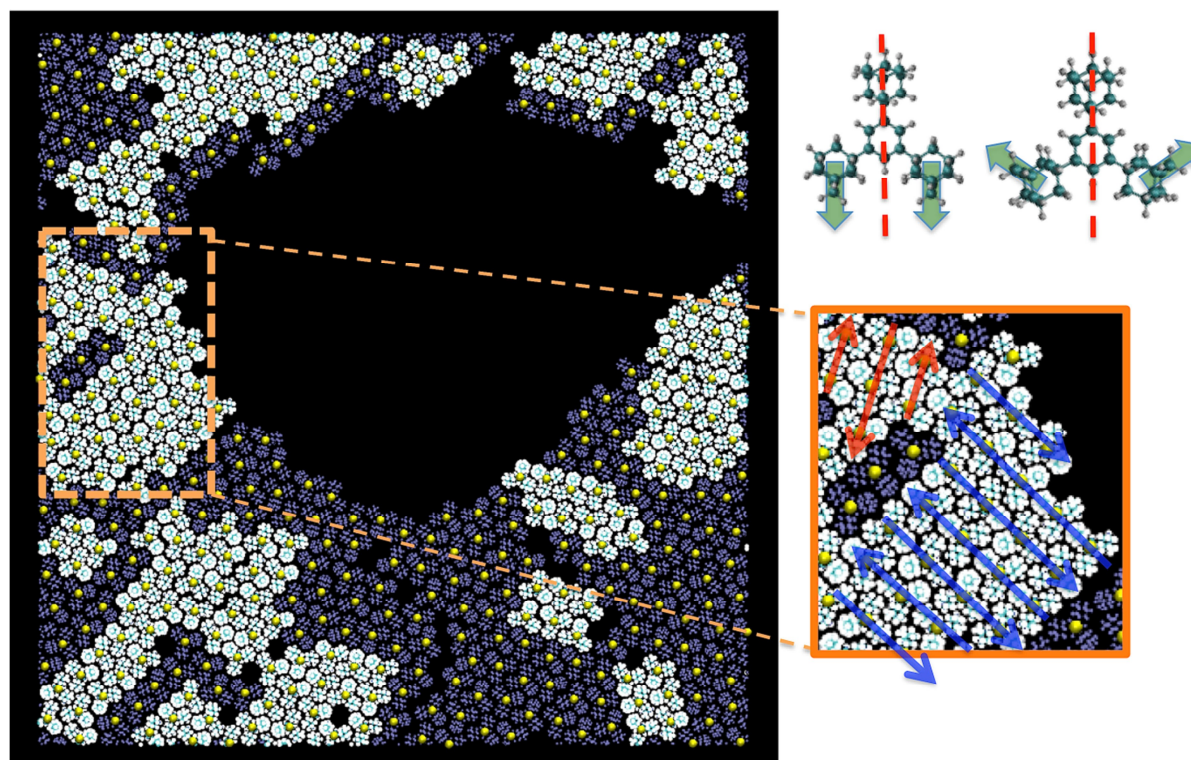


Figure 8: Snapshot of a configuration obtained after modeling the self-assembly of 400 molecules of TAB1.2 model. For clarity, the surface is not represented, and head to tail arrangements are emphasized with bright colors. Inset represents a zoom of the dashed region. Arrows indicate the head to tail stacking (same scale than Fig.7).

The pair correlation functions calculated for both TAB3.0 and TAB1.2 self-assembled structures are reported in the Supplementary Information. The first correlation peaks are respectively at 1.07 nm and 1.1 nm, corresponding to the closest compact molecular configurations shown in Figs. 7 and 8 (also in good agreement with the intermolecular distances found experimentally on the largest domains Fig. 3). Interestingly, both present the same second correlation peak at a distance of 1.25, which actually covers a range of 1.2 to 1.3 nm at 280K, meaning that both structures are identical for this distance. The fact that we could not obtain a broad extended domain in the MC calculation has led to both compact and head to tail local structures. It is worth to point out that both structures present the same amount of molecules at the distance of 1.25 nm (same amplitude and coverage), meaning that these configurations are very close structurally.

Discussion

From these observations, it can be concluded that the structure of the layer depends on the number of molecules involved in the assembly and of their conformation. In the experimental observations as well as in the calculated structures, there is no evidence of any sliding of the organic islands on the silver substrate. At low coverage, the molecules are self-assembled in a hexagonal lattice. In the largest domains, they are organized head to tail and form a rectangular network. The compactness of the self-assembly grows from 0.51 to 0.75 molecules per nm². In the case of the small islands, the molecules rotate to form the network but the MC calculations show that the ADT groups also rotate

during the layer growth. The molecular organization in the broad domain is well reproduced in the MC calculations including several hundreds of molecules. It is assumed that this peculiar organization takes place as soon as the first molecules form an aggregate. To illustrate this point, molecular mechanics (MM) calculations have been conducted at the single molecule level. These calculations have been performed using the universal force field with parameters identical to those proposed in (28). The substrate is composed of three planes of Ag atoms. As expected a single molecule is lying flat of the surface. The smallest calculated distance between the top Ag atoms and the H atoms of TAB is about 0.2 nm, a result in good agreement with the value usually obtained for physisorption of molecules on a metal (the calculated adsorption energy is 0.42 eV per molecule). The molecule is then relatively far from the metallic substrate which allows certain mobility. In a second step, the structure of two molecules deposited on the silver surface has been investigated using the same technique. For this, two TAB molecules have been deposited on the Ag(111) and the most stable configurations have been calculated using the force field. The lowest energy state is given for two molecules in an “up” and “down” position (Fig. 9a).

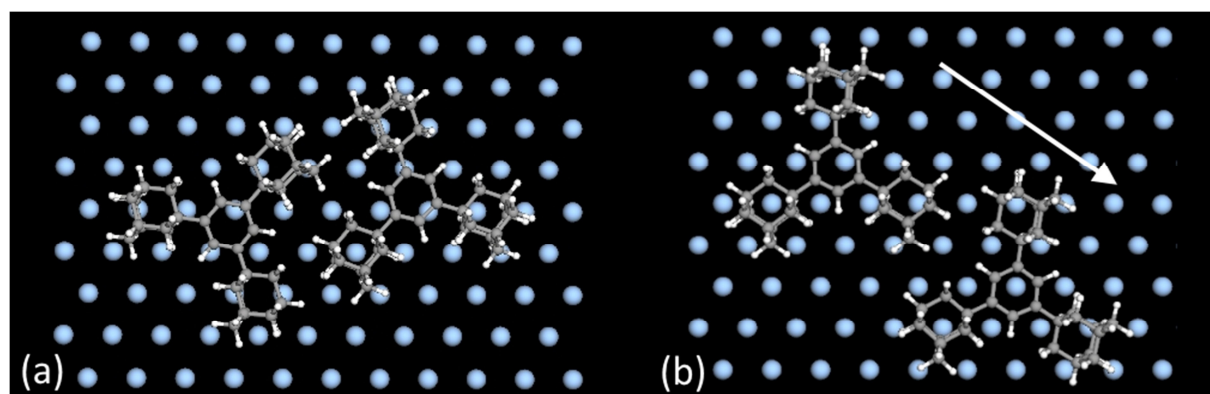


Figure 9: calculated conformations of two TAB on Ag(111).

The second conformation (Fig. 9b) is obtained for the two molecules in a head to tail position and with a small rotation of the two TAB with respect to the row direction (indicated by the white arrow). The energy difference between the two conformations is very small (0.19 eV that is 95 meV per molecule). The direction of these structures is also independent of the [110] type direction of the substrate, a property already observed in the experimental images. The calculated intermolecular distance is in good agreement with the experimental value: 1.05 nm in Fig. 9a and 1.30 nm in Fig. 9b while the measurements performed in the rectangular network give 1.2 nm for the first neighbor distance. Then, the calculations show that the two organizations (up and down and head to tail along a row) are already obtained when only two molecules are adsorbed on the substrate which easily explains the structure of the networks observed experimentally.

Energy calculations performed from the MC investigations bring another insight on this system and are reported in table 1.

	TAB 3.0	TAB 2.1	TAB 1.2 (Lateral)	TAB 1.2 (down)	TAB 1.2 (Mixed)
E total	-801.45	-799.44	-795.12	-791.99	-794.55
E intermolecular	-45.72	-42.92	-45.10	-39.90	-43.08
E interfacial	-755.73	-756.52	-750.02	-752.09	-751.47

Table 1: Total balance energy extracted from the MC production runs (kJ/mol of molecule) for different conformations of the TAB molecule in the self-assembled structures. The numerical labels for the different TAB conformations are defined in Figure 6.

As for the two adsorbed molecules studied above, it can be observed that all the configurations are also very close energetically, since the difference energies (intermolecular or interfacial) is of the order of 2 kJ/mol per molecule (21 meV) thus in the range of the thermal energy. Among the three possible conformations, the TAB3.0 molecule appears, in absolute, the most stable but it does not reproduce the rectangular network observed in the STM images (Fig. 3). The most likely model is obtained with TAB1.2 (mixed of down and lateral) which appears to be the less stable but which gives the correct assembly after MC modeling (Figs. 7 and 8). The interfacial energy for TAB3.0 and TAB2.1 (meaning respectively that 3 and 2 ADTs have rotated pointing out to the $\langle 111 \rangle$ direction) tells that the molecules will more likely adopt finally one of these conformations. Interestingly, the TAB2.1 presents the deepest interfacial energy, meaning that for a broad domain, the ADT might adopt this conformation.

Using the optimized conformations found after the MD calculations, ESQC-STM images (29) have been calculated in order to interpret the contrasts observed in Fig. 5. Among the different possibilities, only the TAB2.1 geometry matches with the experimental observations and the results are presented in Fig. 10. The two TAB pointing to the $\langle 111 \rangle$ direction are located at the bottom. As experimentally observed, the molecule exhibits three lobes with a maximum apparent height of 0.3 nm but this apparent height is different for the three groups. The two $\langle 111 \rangle$ ADT present the most important corrugation, the third exhibiting a lower contrast. These results are in good agreement with the experimental STM images of the self-assembly (Fig. 5) in which the molecules present an asymmetric contrast along the up and down rows and a quasi-mirror symmetry perpendicularly to the rows (chevron structure).

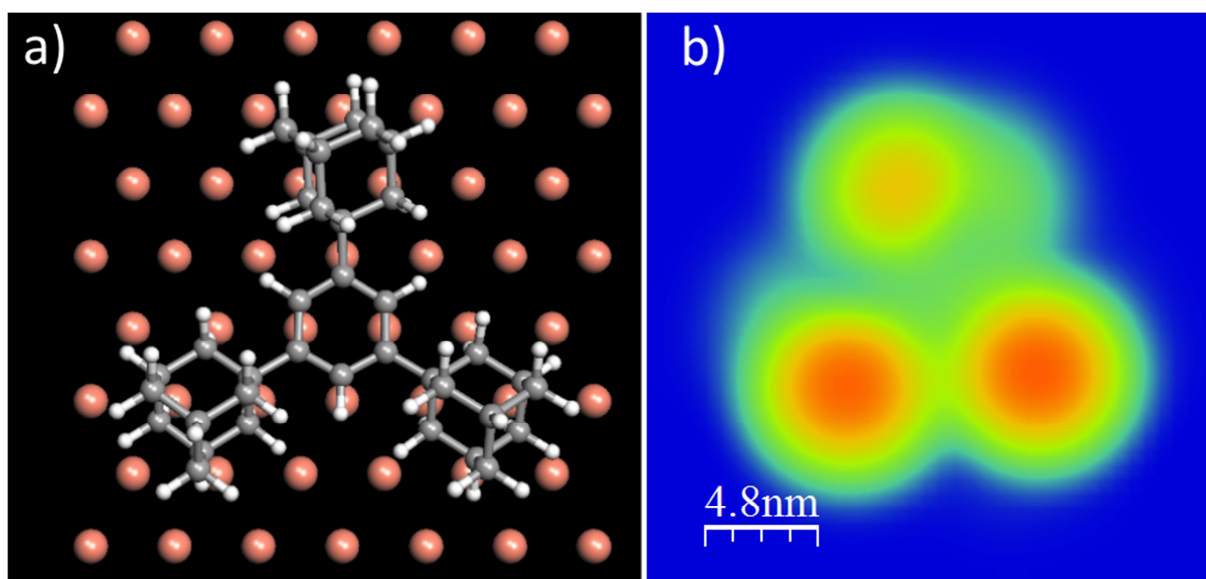


Figure 10: (a) Calculated structure of TAB on Ag(111) in the TAB2.1 conformation (for clarity, a single layer of Ag is shown). (b) ESQC-STM image calculated using the LUMO orbital.

Thus, one scenario can be outlined for the largest domains. During the self-assembly process, the molecules are entropically mixed with rotated ADTs and with quasi mirror symmetry, leading to the head to tail extended domain. Then, during the temperature lowering, the ADTs optimize their interfacial energy in alternately rotating two ADTs, leading to the observed contrast. In this case, the TAB2.1 model appears to be the more suitable. The gain in energy produced by this new orientation is certainly small but sufficient to favor the complete organization of the layer.

The last point to be discussed concerns the shape of TAB in the STM images. This latter depends on the structure of the molecular layer. In the small islands with a hexagonal organization, each TAB appears as a small triangle. The presence of the ADT group is only noticed on a few molecules at the edges of the island. In this case these molecules are disoriented with respect to the rest of the structure. On the broad domains, each TAB is characterized by three bumps whatever the bias voltage, each originating from an ADT peripheral group. MD and MC calculations clearly indicate that the ADT orientation with respect to the Ag(111) surface ($\langle 111 \rangle$ or 90°) generates different structures. Thus, TAB0.3 favors the formation of disoriented hexagonal packings while TAB3.0 and TAB2.1 lead to extended hexagonal domains. The head to tail structures are obtained with TAB1.2 molecules, which, once the supramolecular assembly is organized, can still turn their ADTs to improve the interfacial energy. Since the STM images of the different structures have been performed using the same tips, this suggests that the ADT orientation of the molecule and the coupling between neighboring molecules induces subtle modifications in its electronic structure which affects the STM topography.

Conclusion

The self-assembly of tri-Adamantyl benzene molecules has been investigated using scanning tunneling microscopy and calculations using Monte Carlo and Molecular Dynamics approaches. These investigations demonstrate that the molecules self-assemble in two different structures (hexagonal and rectangular) as a function of the number of involved molecules. On the most extended domains, the calculations indicate that the rotation of the ADT groups allows the molecules to increase their interfacial energy and to gain stability. ESQC-STM images calculated using this last conformation, explain with a great accuracy the subtle contrast observed in the experimental STM images. More generally, this approach combining experimental investigations and molecular modeling demonstrates that it is possible to obtain relevant information on the molecular conformations and the intermolecular and molecule-substrate interactions in self-assembled domains.

Acknowledgements

TR & JF acknowledge the CESGA Supercomputing Center (Finisterrae Supercomputer) for computer time and technical assistance.

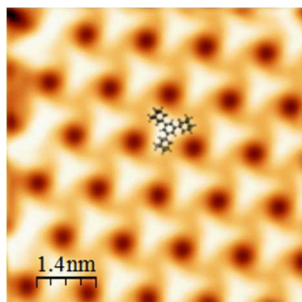
T.R. was supported by a JAEdoc contract co-funded by CSIC and the European Union funds, and is thankful to the Spanish Ministry of Employment and Social Security and Baobab Company for their support.

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STM image of the hexagonal network of tri-Adamantyl benzene molecules on Ag(111)