

Self-Assembled Two-Dimensional Molecular Host-Guest Architectures From Trimesic Acid

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Abstract

The adsorption of 1,3,5-Benzenetricarboxylic (Trimesic) Acid (TMA) to a single crystal graphite surface has been studied under Ultra High Vacuum conditions. This work focuses on

inducing a particular self-assembly structure by OMBE (Organic Molecular Beam Epitaxy), characterized by periodic non-dense-packing of the molecules. Two coexisting phases could be imaged with sub-molecular resolution by STM. Induced by directed hydrogen bonding, the organic molecules built in both cases a two-dimensional grid architecture with molecular caves. This two-dimensional host structure can accept single trimesic acid guest molecules in different positions.

Introduction

Many organic molecules, especially aromatic hydrocarbons, adsorb as well ordered thin layers on crystalline metal- and semiconductor surfaces and can be imaged with STM, partly with sub-molecular resolution [1-10]. In general, the epitaxial growth of organic thin-films on inorganic surfaces strongly depends on the size and the symmetry of the molecule and the substrate, the conformity of the lattice constants, as well as the adsorbate-adsorbate and the adsorbate-substrate interactions. One of the main problems in high-resolution-imaging of such films is their mobility on the surface that depends on the chemi- or physisorption strength. Depending on the molecule and the reactivity of the surface, different approaches to overcome this problem have been made. Directed self-assembly, where the adsorbate system is stabilized via stereospecific hydrogen-bridge bonding between neighbouring molecules, is one promising route [11-16].

For some years the concept of inclusion compounds or host-guest systems has been part of the supramolecular chemistry [17]. A common strategy for the construction of such systems is to use molecules with complementary

functional groups that allow the stepwise build-up of supramolecular complexity. The resulting supramolecular arrays are governed by soft bonds, such as a), electrostatic forces, b), van der Waals interactions and c), hydrogen bonding. One goal is to build molecular "hosts" that noncovalently bind "guest" molecules using hydrogen bonding and pi-stacking forces. For this purpose, vacancies of defined size and shape are desirable. Microporous crystalline solids such as zeolites that act as robust molecular sieves to entrap organic compounds with suitable sizes or functionality are long known. However, de novo synthesis of open structures that leave space for the guest molecules has to face the following problem: since pure materials are generally close-packed, cavities are energetically unfavourable and in turn thermodynamically not stable. Therefore, the guest moieties are often co-crystallized parallel to the crystal growth, because otherwise the structure would collapse for energetic reasons. While in supra-molecular chemistry host-guest situations have mainly been investigated in solution and bulk crystals, it is not always necessary to build three-dimensional structures. For potential technical applications, such as heterogenic catalysis, molecular electronics, organic network templates for structuring metal nanoassemblies, or biomolecules in sensor devices, only the surface is of interest.

Here we present a two-dimensional host-guest architecture of trimesic acid (TMA) molecules with cavities the size of single molecules. Trimesic acid itself is shown as a possible guest in different phases of the host and in different positions.

For TMA several bulk structure polymorphs have been reported [18]. Exploiting all possibilities of hydrogen-bond formation between the carboxylic groups results in a two-dimensional network of six-molecule rings. The aim of this work has been to show, that the chemical and geometrical conditions at a solid surface can help to overcome the energetic constraint of building close-packed molecular structures and to demonstrate the possibility of preparing stable vacancies of defined size and periodic arrangement in two-dimensional molecular adsorbates.

Experimental

OMBE and Sample Preparation

The preparation and characterization of the self-assembled molecular systems have been performed in UHV at a base pressure of 2×10^{-10} mbar. Due to its superior quality indicative in clear hexagonal LEED (Low Energy Electron Diffraction) patterns, natural grown graphite was used as substrate. The sample crystal was cleaved in ambient conditions along the (0001) basal plane and then immediately transferred into the vacuum chamber. After removing surface contamination by tempering at 500°C for several hours, the quality of the

surface was checked by LEED. The organic adsorbate layers were prepared by organic molecular beam epitaxy (OMBE)[1], using a home-built Knudsen cell with a water-cooled body and three independently addressable crucibles. During evaporation the substrate was held perpendicular, at a distance of 40 mm, with respect to the aperture-plane of the Knudsen cell. The perfect orientation and position of the sample was determined using a laser beam. The crucibles of the evaporator and the temperature of the sample are adjustable using an electronic temperature controller. The evaporation temperature for the TMA molecules of 181°C was determined by a QMS (quadrupole mass spectrometer) which is mounted opposite to the Knudsen cell. The layer thickness of the adsorbate was controlled by the relative evaporation rate (determined with the QMS) and with TDS (thermal desorption spectroscopy). TMA (Merck) had a purity >98% and was further purified by heating cycles before evaporation. Tempering for 15 min at 120°C after evaporation resulted in long range (> 500 nm), highly ordered monolayers. This process was controlled in situ with the LEED optics.

Scanning Tunnelling Microscopy

STM measurements were performed with a variable temperature UHV-STM at scan speeds from 500 to 1800 nm/s and 512x512 data points per image in constant height mode at a temperature of 25 K. The tunnelling parameters including voltages with respect to the sample are given in the figure captions. Electro-chemically etched tungsten tips, further prepared with argon sputtering (15 min@750 eV) and annealing (1 h @ 900°C), were used.

LEED

For the LEED characterization of the substrate and the adsorbate structure a commercial 4-grid-backview LEED optic was used. The images were captured with a CCD camera in combination with a frame grabber card. For high quality LEED images, the sample was cooled down in the STM and then transferred in front of the LEED optics.

Thermal Desorption Spectroscopy

For TDS the sample was brought in front of a QMS (Balzers QMG 112A, Mass 0-200 AMU; SEV). The QMS detector was surrounded by a shielding with a small aperture the size of the sample crystal. Since the base pressure in the UHV chamber is essential for the quality (signal to noise ratio) [19] the spectra were taken at a pressure below 2×10^{-10} mbar. The sample was heated by radiant heating in a linear temperature ramp of 1,7 K/s. The spectra were taken at 192,7 AMU which represents the key fragment in the mass spectrum of TMA [19].

Results and Discussion

Fig. 1 shows the planar structure of the trimesic acid molecule with threefold symmetry. It is built of a benzene ring with three carboxylic groups in the 1,3,5-positions, allowing for the spontaneous formation of a supra-molecular architecture via directed H-bonding to the neighbouring molecules. The experimental mass-spectrum of the evaporated molecules in Fig. 1 reproduces the known literature spectrum [20] and therefore demonstrates that the molecules are un-cracked. Fig. 2 shows two different network-structures found in the STM experiments. In addition to the STM images the molecular arrangements have been simulated in molecular mechanics calculations using the DREIDING II force field

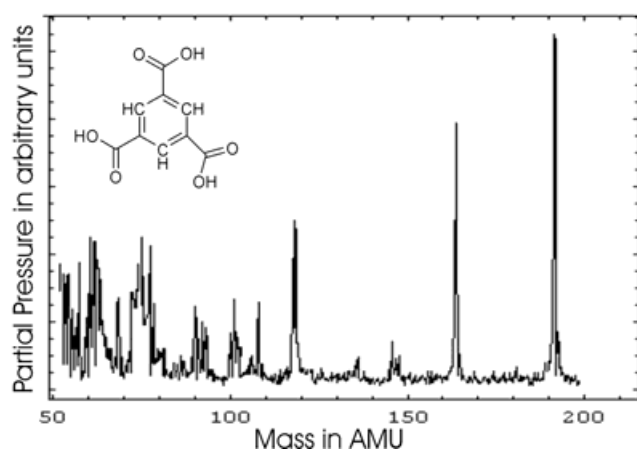


Fig. 1. Mass spectrum of Trimesic Acid with main peak at 193 AMU. The measurement reproduces quite well the spectrum found in the literature. The insert shows the chemical structure of trimesic acid (TMA).

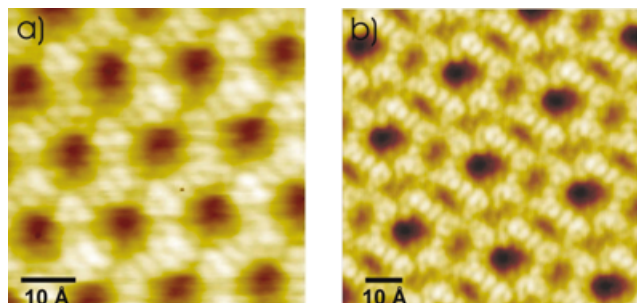


Fig. 2. STM image of TMA on graphite. a) Chicken-wire structure ($5.4 \times 5.4 \text{ nm}^2$; $U = -1.4 \text{ V}$, $I = 126 \text{ pA}$); b) flower structure ($8.2 \times 8.2 \text{ nm}^2$; $U = -1.4 \text{ V}$, $I = 126 \text{ pA}$)

within the Cerius Molecular Modelling package detailed in [21,22]. Both phases coexist on the surface in different fractions depending on the preparation conditions. In the case of best resolution (Fig. 2b and Fig. 5b), each individual TMA molecule appears as a ring with a hole inside. The position of the three bright spots at each ring matches well the position of the hydrogen atoms directly bound to the carbon atoms of the benzene ring (see structure model in Fig. 1).

Structure 1 “chicken-wire”

The first of the two structures (Fig. 2a), here called “chicken-wire” - or “honeycomb” structure, is composed of sixfold rings of trimesic acid molecules with perfect arrangement of the hydrogen bonds. A schematic model is given in Fig. 3. All hydrogen bonds have a length of $2.92 \pm 0.2 \text{ \AA}$ which is well within the range of OH-O bonds $2.7 \text{ \AA} - 3.1 \text{ \AA}$. The packing density is found to be $0.007 \text{ molecules / \AA}^2$. Every molecule is part of three neighbouring rings.

Structure 2 “flower”

In addition to the initially expected chicken-wire structure, the STM investigations showed a second possibility of a self-assembled network structure (Fig. 2b). Again sixfold rings are formed. However, in contrast to the chicken-wire structure, where each molecule is part of three neighbouring rings, the flower structure can be seen as a closed packing of the sixfold rings. Within the rings the hydrogen bonds are formed in the same way as in the chicken-wire structure. In contrast to the hydrogen bonds originating from one carboxylic group of each TMA molecule, which makes the connection to the next neighbouring ring in the chicken-wire structure, here the hydrogen bonds are formed between three molecules (see Fig. 4). In this structure all H-bonds have a length of $2.96 \pm 0.2 \text{ \AA}$ and the packing density is found to be $0.03 \text{ molecules / \AA}^2$.

Stability and Temperature Dependence

Both structures are stable from 25 K up to room temperature, as shown in LEED experiments where sharp diffraction patterns could be found. The patterns were stable for low electron energy over a period of some minutes indicating a highly stable architecture. Nevertheless, conclusive STM images could not be taken at room temperature due to the weak binding of the molecules to the substrate. This is shown in TDS experiments and molecular mechanics simulations. The TDS spectra barely show first as well as first and a half order desorption-peaks, indicative for a weak interaction between the adsorbate molecules and the substrate. More details of the LEED and TDS experiments will be published elsewhere. Molecular dynamics simulations additionally show that the molecular network is weakly bound to the graphite surface, indicative by a small corrugation barrier. Even for the case that the adsorbate is pinned through steps and defects

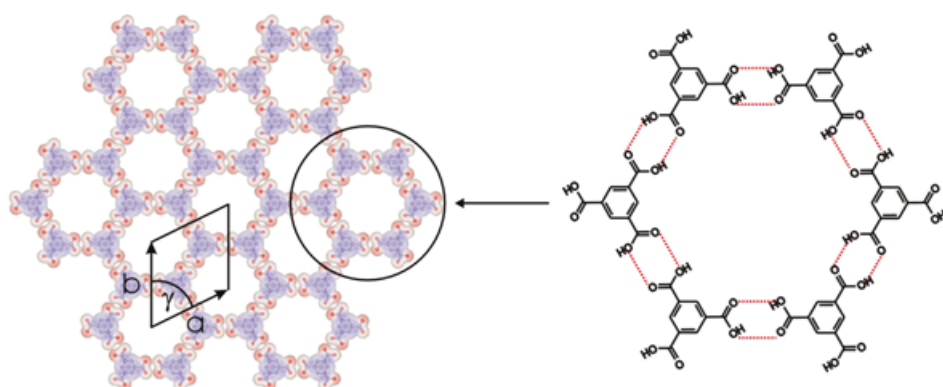


Fig. 3. Schematic picture of the chicken-wire structure ($a=b=17.2\pm 1$ Å, $\gamma=60^\circ$). In the picture on the right hand side the hydrogen bonds between the TMA molecules are indicated by dotted lines and have a length of 2.92 ± 0.2 Å.

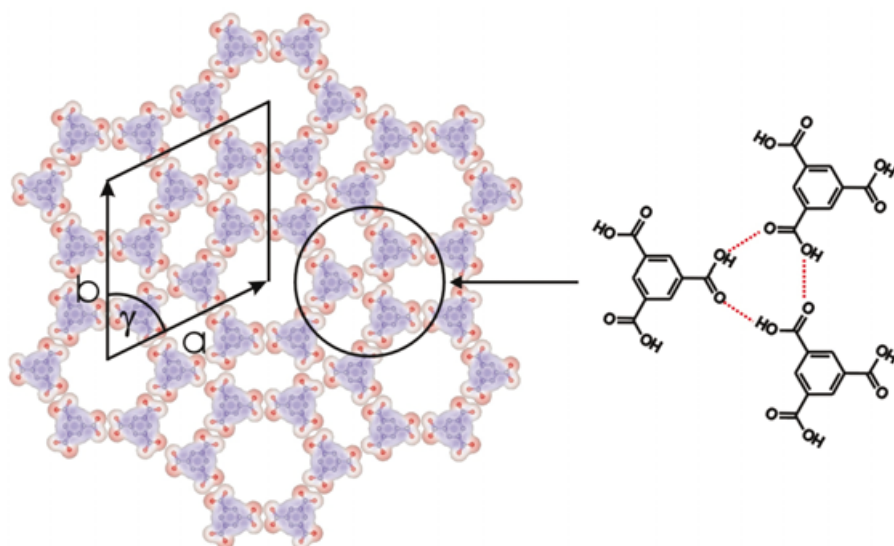


Fig. 4. Schematic picture of the flower structure ($a=27.0\pm 1$ Å, $\gamma=60^\circ$). The circle indicates the situation where the hydrogen bonds (dotted lines) are formed between three molecules. All hydrogen bonds have a length of 2.96 ± 0.2 Å.

on the substrate surface, the interaction between the STM tip and the molecules is sufficient to toggle the molecules and therefore it is difficult to obtain STM images at room temperature.

Host-Guest Situation

As mentioned above, both structures are based on sixfold rings with a hole in the center of each ring. Whereas in the chicken-wire structure the diameter of all holes is about 15 Å, there are two different types of holes in the flower structure. One in the middle of the sixfold ring, and another one inside the rectangles on each side of the hexagon, where the two neighbouring rings touch each other. The diameter of the latter is about 7.5 Å.

The whole structure can therefore act as a molecular host system with potential adsorption sites for guest molecules. After adsorption of more than one monolayer, Fig. 5 demonstrates that trimesic acid can act as a possible guest molecule in the larger cavities of both possible phases. In the case of the chicken-wire structure, the guest is always placed in an a-centric position with respect to the rings and is bound with two hydrogen bonds as shown in Fig. 7. For high tunnelling resistance ($> 10^{10}$ Ohm) the guest molecules are stable at their position. In contrast to the chicken-wire structure, where the guest molecules lie flat on the substrate, we found two possible positions for the guest molecules in the flower-structure: One lying flat inside the ring and the other one sitting in a top position some 0.05 nm above the ring or, indistinguishable by STM, standing in an upright position 0.4 nm above (see Fig. 6).

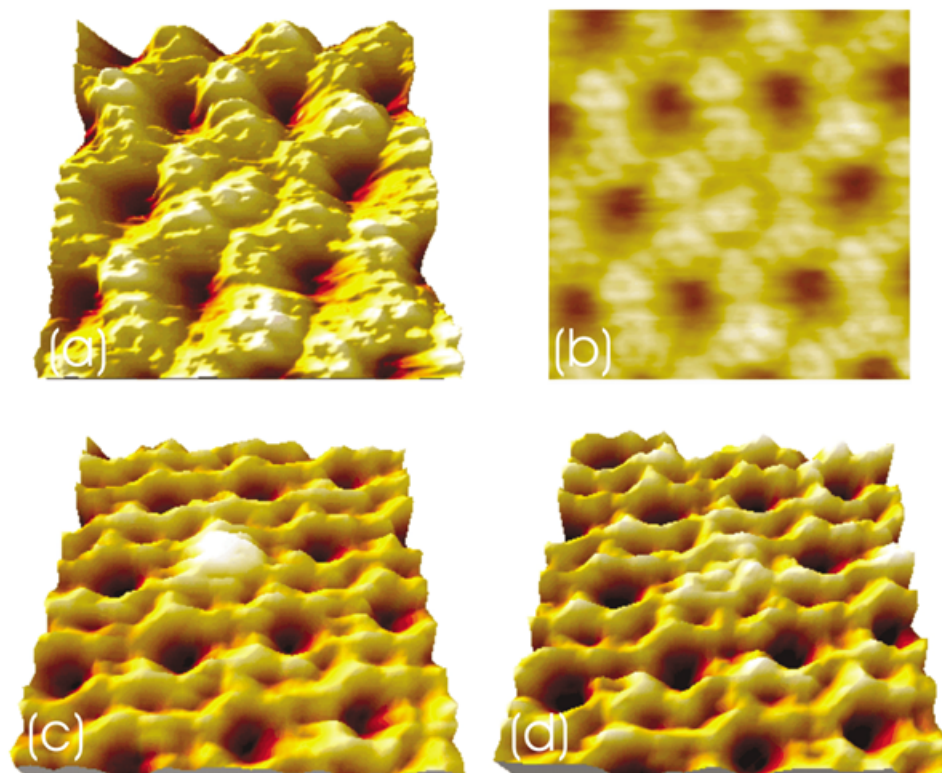


Fig. 5. Guest molecules in the two different phases. (a) and (b) show a guest molecule (TMA) in the chicken-wire structure. The guest is always found in "low" position. (c) shows the guest molecule in the flower structure in "high" position while (d) shows the guest molecule in the flower structure in "low" position.

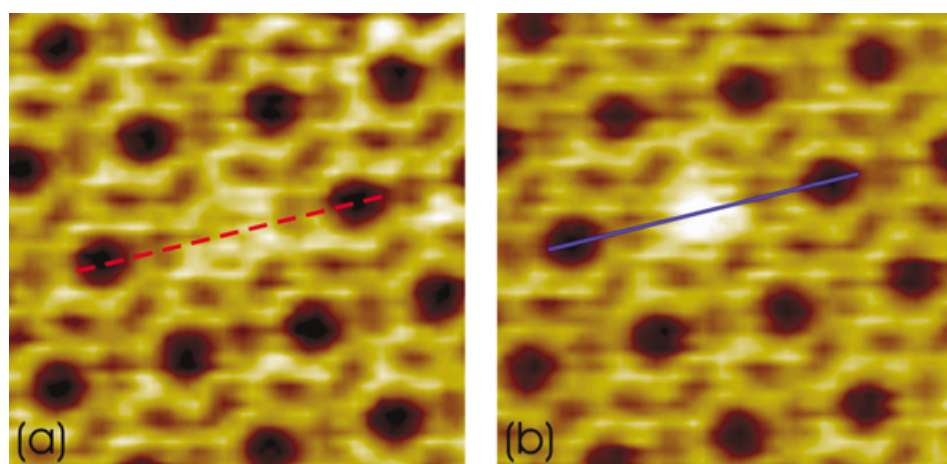


Fig. 6. Guest molecules in the flower structure. (a) Guest molecule in "low" position; (b) Guest molecule in "high" position; (c) linescans at positions marked in pictures (a) and (b)

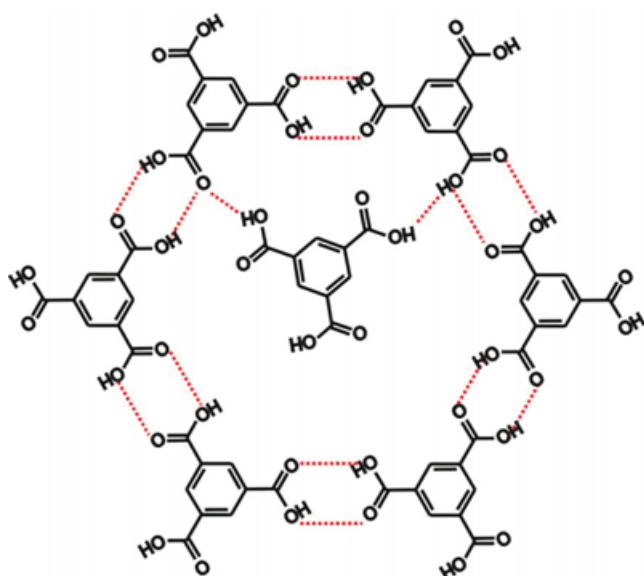


Fig. 7. Model of the TMA molecule as guest inside a sixfold TMA-ring. The guest is bound with two hydrogen bonds in an acentric position. Due to the symmetry there are six equivalent places for such a guest.

Summary and Outlook

The first STM investigations of trimesic acid molecules adsorbed on natural grown graphite showed the coexistence of two different phases: the chicken wire and the flower structure. For both phases a structure model with hydrogen bonds is given and proven by sub-molecular resolution STM images. Both phases are open structures with cavities, which allow guest molecules to be placed at predefined positions within the host structure. As one possible guest trimesic acid molecules could be imaged in different positions. These guests are stable in their positions at room temperature. Further investigations on metal atom guests and on the influence of the scanning process on the host-guest situation are under way. Generally, an improved understanding of the interactions in relatively simple complexes of such synthetic host molecules will lead to a better understanding of the concepts of preorganization and template-directed synthesis and the much more complex biological systems in which, most prominently, the host molecules are either proteins or nucleic acids.

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