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Probing the Hierarchy of Thymine–Thymine Interactions in Self-Assembled Structures by Manipulation with Scanning Tunneling Microscopy**

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Our knowledge of molecular self-assembly on solid surfaces has increased significantly over the last few years,^[1] motivated by the large number of applications based on thin and ultrathin self-assembled organic films in areas such as organic semiconductors,^[2] organic photovoltaic devices,^[3] nanomechanical biosensors,^[4] and so on. The molecular systems studied have been continuously growing in complexity, and

one area that has been studied extensively both experimentally and theoretically is self-assembled monolayers of molecules with several kinds of interacting functional groups, such as DNA bases or amino acids.^[5–8] It is generally expected that for such molecules with multifunctional groups a hierarchical self-assembly process exists. During this process directional bonds (e.g., hydrogen bonds) determine the formation of supramolecular structures in the first place (at low surface coverages), while weaker interactions (e.g., van der Waals (vdW) interactions) become more important with increasing surface coverage and then direct the subsequent self-assembly of the supramolecules formed initially. For this kind of experiment, scanning tunneling microscopy (STM) has proven to be the technique of choice since it allows a direct, real-space determination of the symmetry properties of the molecular network as well as the unit-mesh distances and angles at the atomic scale. However, to obtain further insight into the detailed molecular structures from the STM images, to address questions such as the molecular adsorption conformations and to distinguish the different interactions in self-assembled structures, comparison with advanced theoretical modeling of the STM images is required.^[6,7,9–11]

In this work we have investigated by means of high-resolution STM imaging and manipulation^[12] the spontaneous assembly and STM-induced disassembly of one of the DNA base molecules, thymine (T), deposited on the Au(111) surface under ultrahigh vacuum (UHV) conditions. The Au(111) substrate was chosen as a noble inert substrate to minimize molecule–substrate interactions, thus allowing the self-assembly process to be dominated by intermolecular interactions. Thymine is a prime example of the above-mentioned multifunctional organic molecule capable of forming strong hydrogen bonds through the carbonyl and imino groups, whereas the methyl group enables it to interact via weaker vdW interactions. The STM results reveal a two-step hierarchical self-assembly process in which, initially, hydrogen bonds steer the growth of one dimensional (1D) filaments of T molecules that subsequently (for higher coverages) self-assemble into 2D T islands via the weaker vdW interactions. This growth mode is confirmed by the state-of-the-art density functional theory (DFT) calculations, which also enable a clear identification of the 1D T filament structures. We further show that by using STM manipulation we can directly probe the hierarchy of bond strengths involved in the surface self-assembly of T molecules with highly anisotropic interactions. This is done by probing the different resistances that the bonds between the neighboring T molecules and between the supramolecular T filaments oppose to breaking under STM manipulation. Our experimental results demonstrate that STM manipulation can be used to selectively break the weaker vdW bonds, resulting in the lateral disassembly of the weakly bound 2D T islands into their constituent T filaments. These manipulation experiments support the hierarchical picture that results from a comparison between theory and STM images, and thus demonstrate the usefulness of STM manipulation to detect the “weakest link” in hierarchical self-assembled molecular structures, a

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hint that can be of the utmost relevance to identify molecular adsorption geometries from STM images.

All STM experiments were performed in a UHV chamber (base pressure 1×10^{-10} Torr) equipped with the variable-temperature, fast-scanning Aarhus STM,^[13,14] a home-built molecular evaporator, and standard facilities for sample preparation. The Au(111) substrate was prepared by several cycles of 1.5 keV Ar⁺ sputtering followed by annealing to 770 K for 15 min, resulting in a clean, flat, well-ordered herringbone reconstructed Au(111) surface.^[15] Thymine powder (Sigma–Aldrich, 99%) was loaded into a glass crucible in the molecular evaporator. After a thorough degassing of the T crucible, performed by keeping the crucible at 370 K for an extended period (≈ 24 h), T molecules were deposited onto the clean Au(111) substrate by thermal sublimation from the molecular evaporator held at 350 K for a few minutes, while the substrate was held at room temperature (RT). After deposition of T molecules the substrate was left at RT for about 10 min before being placed into the cold STM (120 K). The STM experiments were carried out at low temperature (100–150 K) to minimize the surface mobility of the T molecules and thereby stabilize the molecular structures formed on the surface. To gain further insight of the experimentally observed T structures, ab initio DFT calculations were performed using the SIESTA method.^[16,17] In each case, the full atomic relaxation was performed until the forces on atoms were lower than 0.05 eV \AA^{-1} .

As seen in Figure 1a, the STM images recorded at 120 K show that at low surface coverage (less than 0.1 ML) the T molecules, upon deposition onto a clean Au(111) surface at room temperature, self-assemble into 1D filaments. It is seen from Figure 1a that the filaments grow along random directions on the surface and the adsorption of T molecules does not lift the characteristic herringbone reconstruction of the clean Au(111) surface. These two findings suggest that the molecule–substrate interaction is fairly weak, and that growth of the 1D filaments is mainly con-

trolled by molecule–molecule interactions. The weakness of the interaction between a T molecule and the gold surface was also confirmed by our DFT calculations (adsorption energy near 0.05 eV) as discussed below. Interestingly, upon a gradual increase in the coverage of the deposited T molecules up to 0.1–0.2 ML, a local ordering sets in and some of the T filaments start to attach to each other side by side and grow into small patches of T islands. However, all these structures can still be considered as consisting of mainly T filaments (Figure 1b). As the coverage is increased even further (up to 0.3–0.4 ML), well-ordered 2D T islands nucleate and grow as the overall dominating structure on the surface. A few filaments can still be observed at the upper boundaries of the 2D islands (Figure 1c). If, instead of depositing the T molecules sequentially, we deposit the same coverage of T molecules continuously, we observe similar well-ordered 2D T islands. This growth mode is different from the growth mode of another DNA base molecule (cytosine), which initially also forms 1D filaments along random growth directions at low surface coverage but we never observed the cytosine filaments to merge into 2D ordered structures even at a saturation surface coverage.^[18]

To gain further insight into the atomistic structure of the observed T filaments, we carried out ab initio DFT calculations for a variety of different filament structures. To systematically construct all possible filament structures, it is convenient to first assume that linear T chains (see inset in Figure 2e) are constructed by repeating just two molecules (thymine pairs^[19]) periodically. Following this method, we find 9 possible chain structures that were all fully relaxed using the DFT method. The two energetically most favorable chain structures (referred to as A and B in the following) with similar binding energies of 0.77 eV per molecule are shown in Figure 2a. They consist of two rows of T molecules linked to each other by hydrogen bonds. The model B filament can be obtained from model A by flipping the molecules of one of the rows. The two lowest-energy chain structures are found to have the same lattice vector of 6.8 \AA , which fits the experimentally observed linear T filament structures of $6.5 \pm 0.5 \text{ \AA}$ quite well. Figure 2e shows a comparison of the two most stable calculated linear filament structures (marked A and B) with the filaments observed in the STM images at low coverage. An excellent agreement is found for both of them, since the T molecules have a symmetrical, featureless appearance in the STM images and hence we cannot distinguish between the two chain models A and B of T filaments in the STM images from symmetry considerations. Fur-

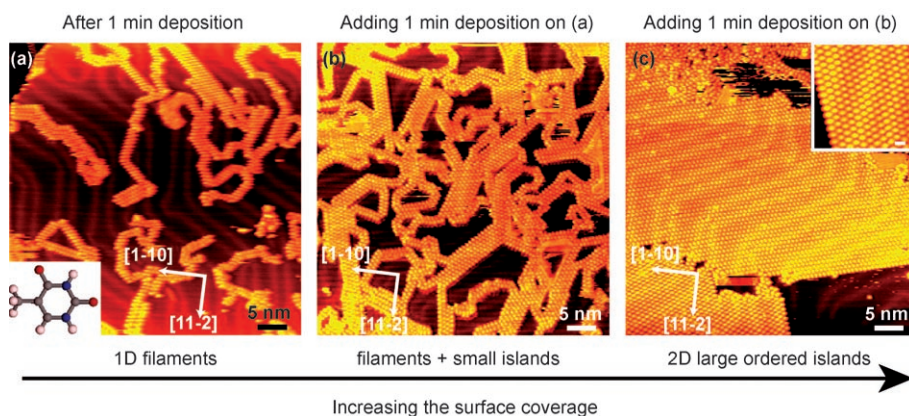


Figure 1. a) STM image of several self-assembled 1D T filaments with random growth directions on the Au(111) surface at low surface coverage. The lower inset shows the chemical structure of a thymine molecule (tunneling conditions: $I_t = -0.23 \text{ nA}$, $V_t = -1051 \text{ mV}$). b) STM image containing 1D T filaments and small islands corresponds to an increased surface coverage ($I_t = -0.61 \text{ nA}$, $V_t = -1486 \text{ mV}$). c) STM image of extended 2D ordered T islands observed when the surface coverage is increased even further to $\approx 0.3\text{--}0.4 \text{ ML}$ ($I_t = -0.65 \text{ nA}$, $V_t = -2102 \text{ mV}$). The inset shows a zoomed STM image of the 2D T island structure with high molecular resolution.

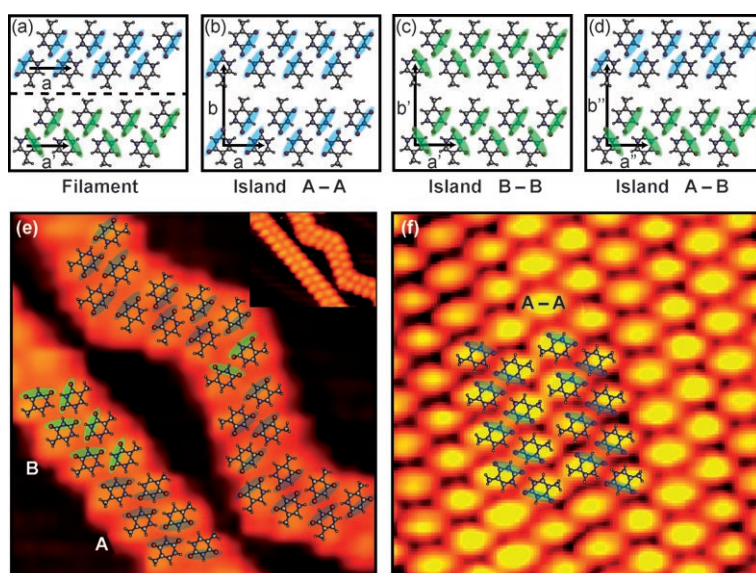


Figure 2. a) DFT calculations of the most stable filament structures A and B with very similar lattice vectors \mathbf{a} and \mathbf{a}' . The color coding is used to distinguish two different hydrogen bonded filament structures. (b), (c), and (d) show three possible models for the observed 2D islands as shown in (f). All three have very similar lattice vectors as shown in the figures. e) Overlay of two calculated most stable filament structures A and B (as shown in (a)) on the STM image of a linear filament, and a theoretically proposed structure for a bent filament. The upper inset shows a zoomed STM image of the T filaments with molecular resolution. f) Comparison of the periodic A–A structure of 2D T island shown in Figure 2 b with the STM image.

thermore, the two most stable filaments may also link to one another end-to-end (note that end-to-side connections as in the case of cytosine^[18] are not possible in this case since they are sterically hindered by the methyl groups). These connections can be systematically constructed by considering all possible ends of finite filaments and their stability estimated by the binding energies of the corresponding T dimers involved in the link. Some links result in bent T filaments, while others keep the linearity of the filament structures (see the overlay in Figure 2 e).

From the different possibilities for which T molecules^[19] bind into the chain structures discussed above and from the coverage-dependent phase transition from the 1D filaments to the 2D islands, we suggest that the 2D T islands are hierarchically made up by the most stable T filaments attached parallel to each other and bound together by vdW interactions between their methyl groups.^[20,21] Since the two filament models (A and B) are very similar and filaments may mix in a linear structure, many 2D island structures exist. Examples of A–A, B–B, and A–B structures are shown in Figure 2 b–d, respectively. The

binding energies of all these structures are expected to be very similar. As an example, we show in Figure 2 f that a good agreement exists between the model A–A of T islands and the observed STM image. Such a self-assembled monolayer of thymine molecules at the solid–liquid interface has also been proposed previously.^[22] Therefore, we suggest that the 2D islands present on the surface are actually disordered in the sense that they contain various mixtures of T filaments joining end-to-end as well as side-by-side. The latter connections are stabilized by the vdW interactions between the methyl groups of T molecules in neighboring T filaments.

Since the T filaments are linked together by the fairly weak vdW interactions resulting in the formation of

the 2D T islands, one could speculate that the islands might somehow be more easily disassembled into randomly distributed filaments than into monomeric T molecules or any other supramolecular portion of the ordered islands. This hypothesis can indeed be confirmed experimentally since we have succeeded in reversing the growth process and forming 1D filaments from 2D islands by perturbing the 2D island structures by the STM tip, as shown in Figure 3 a–c, where the scanning temperature is kept at 100–120 K. During the scanning of the T islands we applied a voltage pulse, ramping the voltage from 1 V to 10 V in a few milli-

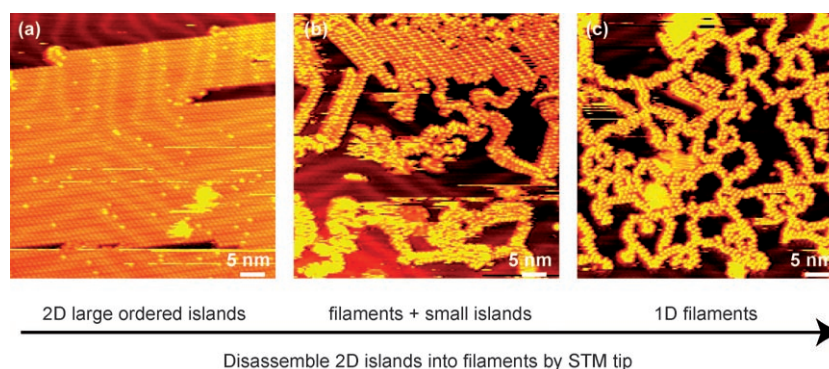


Figure 3. In situ STM images (a–c) show that the 2D T islands can be decomposed into 1D T filaments by STM-tip-related manipulation. After pulsing on the bottom-right corner of Figure 3 a, a localized disturbed part (lower part) and unperturbed area (upper part) are found, as shown in Figure 3 b. After giving several pulses on Figure 3 b, a homogeneous area of filamentary structure is found, as shown in Figure 3 c. It indicates that weak vdW interactions between parallel T filaments can easily be overcome. However, the stronger H-bonding that binds the filaments is not affected so much. Imaging conditions are the same for all images: $I_t = -0.6$ nA, $V_t = -2102$ mV.

seconds. Note that after STM manipulation (i.e., blowing apart the 2D islands), we only observed 1D filaments rather than random T fragments with different shapes and sizes. This observation implies that there are different interactions between T molecules that can be split into two types: i) Strong H-bonding, which binds the molecules in filaments, and ii) much weaker vdW interactions (at least one order of magnitude weaker than H-bonding), which bind filaments together. Although at the moment the detailed mechanism causing the transition from the 2D islands into the 1D filaments is not clear, it might be caused by field-assisted manipulation^[23] or by inelastic tunneling.^[24] At the same time, it might also be that some T molecules desorb from the surface due to the voltage pulse,^[25] leading to a slightly lower coverage after the manipulation. However, regardless of the detailed mechanism actually in play, we demonstrated that this manipulation process is capable of breaking the 2D islands into separate filaments by targeting the fragile vdW interactions without disturbing the stronger hydrogen bonds that hold the filaments together.

In this study, the adsorption of T molecules on the Au(111) surface has been investigated at various coverages using STM imaging and manipulation. We have shown that the multiple functionalities with which thymine molecules are endowed allow them to interact through both strong multiple hydrogen bonds and weak vdW interactions. This leads to a kinetically hierarchical self-assembly in which 1D T filaments stabilized by hydrogen bonds are formed initially at low coverages, after which the filaments, steered by the vdW interactions, self-assemble laterally into 2D T islands. We have shown that a high-voltage pulse applied during scanning leads to a disassembly of the ordered 2D islands into the same 1D filaments as obtained by depositing T molecules at low coverages. Notice that the assignment of the different interactions leading to 1D filaments and 2D islands is done on the basis of high-level theoretical calculations and predictions. However, similar conclusions could be obtained exclusively on the basis of the selectivity in the intermolecular bond-breaking mechanism. Thus, this technique of selective disassembly of hierarchical self-organized molecular structures into their higher-level supramolecular constituents might offer valuable new insights into the nature of the intermolecular interactions, and thus, in assigning orientations of molecules in the observed STM images.

Keywords:

hydrogen bonding • manipulation •
scanning tunneling microscopy • self-assembly

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