Room-Temperature Scanning Tunneling Microscopy Manipulation of Single C_{60} Molecules at the Liquid−Solid Interface: Playing Nanosoccer

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This scanning tunneling microscopy (STM) study uses a supramolecular two-dimensional architecture of trimesic acid molecules adsorbed on a graphite substrate as a host for the incorporation of C_{60} as a molecular guest. By choosing a proper solvent, it was possible to verify that self-assembly of the host−guest structure can be accomplished at the liquid solid interface. Because of the ideal steric match with the molecular bearing of the host structure, C_{60} buckminster fullerenes are feasible guests. It was possible to coadsorb C_{60} within cavities of the open TMA structure from the liquid phase, and lateral manipulation of the molecular guest by the STM tip was demonstrated at room temperature. Because of the increased tip−sample interaction as a result of lower tunneling resistance, a transfer of a C_{60} molecule from one cavity of the host structure to an adjacent one was achieved.

Introduction

Spatially controlled fixation, observation, and precise manipulation of matter down to the single molecule level is an essential requirement for nanotechnology applications, e.g., in molecular electronics, where single molecule switches comprise the ultimate limit in processor design. Most of the current knowledge is based on experiments that require both extremely low temperatures and ultrahigh vacuum (UHV) conditions. Likewise, chemical bonding of the molecules to the surface is another way to prevent thermal diffusion of the molecules on the surface. But this method results in drastic changes in the properties of the molecules, especially if they have biochemical functions.

Although apparently futuristic at the contemporary level of technical manufacturing, the single molecule manufacturing and working concept is widely realized in natural biological systems, where molecular assemblers, motors, and machines are the keys to life. In molecular storage and quantum computing, molecules or atom clusters must be arranged in a highly repetitive spatially ordered way over a huge area in comparison to the elementary building blocks. Additionally, controlled manipulation of the species must be possible. In the future, biotechnology will need nanotech concepts for biochip design, where an ordered array of molecules acting as specific binding sites or individually addressable receptors is often highly desirable. For these as well as for technical applications, ambient conditions and room temperature set a severe challenge for contemporary technological manufacturing.

Here we present a cheap and easy way to use an ambient condition method based on a two-dimensional molecular organic template acting as a host architecture for the defined fixation of guest molecules. We report on a new method for the investigation and manipulation of single molecules by STM without the need for experimentally challenging UHV techniques. The controlled manipulation of single molecules[1] becomes possible, since an organic template preadsorbed on the substrate introduces a hexagonal grid of stable adsorption sites with a next nearest neighbor distance of approximately 1.6 nm.

Previously, trimesic acid (TMA) was shown to assemble in an open, i.e., not densely packed structure on a graphite substrate.[2] A comparable supported porous TMA network was prepared by thermal evaporation on Cu(100) in UHV,[3] but the adlayer lattice constants were slightly different, and the network was somewhat distorted because of stronger interaction of TMA with the substrate. Also, a qualitatively similar TMA structure was prepared by adsorption from solution on Au(111) under potential control in an electrochemical STM.[4] For appropriate potential conditions, a reversible transition to a densely packed TMA structure was observed. The TMA host−guest system exhibits a two-dimensional periodic arrangement of cavities, appropriate for the controlled coadsorption of another species as a guest. The driving force for the self-assembly process and the dominating intermolecular interaction are the two hydrogen bonds between the two carboxylic groups of adjacent TMA molecules. The cavities have a diameter of ∼1.1 nm, making them large enough to incorporate C_{60} buckminster fullerenes, commonly referred to as buckyballs.

Buckyballs have been shown to be suitable for translational manipulation with the scanning tunneling microscope but so far only under UHV conditions.[1,5−8] It was possible to prepare a TMA host−guest system both in UHV[2,3] and at the liquid−solid interface.[4,9] In the case of TMA, a solvent-mediated polymorphism was observed for different solvents. Furthermore, it was possible to adjust one of the two polymorphs, already

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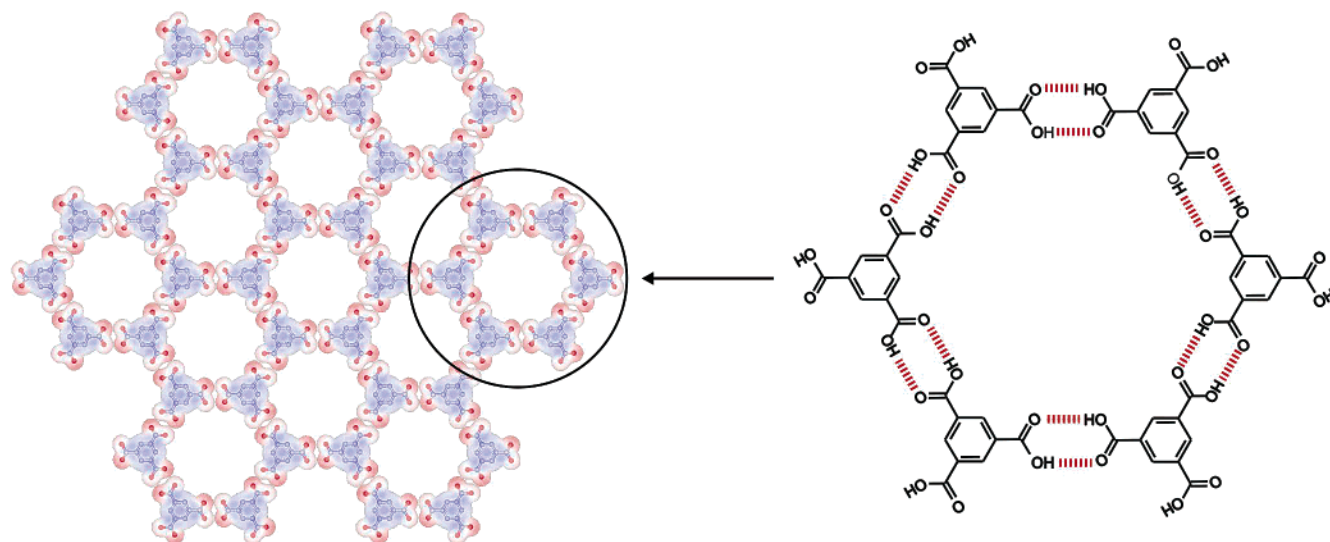
Figure 1. Model of the TMA chickenwire structure. TMA molecules are depicted with the van der Waals surfaces of the atoms. This model visualizes that each single molecule is bound to the three adjacent molecules via hydrogen bonding of the carboxylic functionalities. The hydrogen-bonding scheme is indicated on the enlarged single cavity depicted on the right-hand side of the sketch.

revealed in previous UHV experiments,[2] by choosing the suitable solvent.[9] Furthermore, it has been shown that the synthesis of molecules with an alkane spacer between the benzene core and terminating carboxylic groups leads to the formation of larger cavities.[10] These open host−guest systems confirm the tendency of adsorbate layers to dense packing. Hence the maximization of the interaction energy with the substrate is not always decisive for the structure of tailored molecules. Moreover, the coadsorption of TMA with different metal atoms leads to the formation of relatively stable organometallic complexes.[3,11−13] In UHV experiments with host−guest systems, for example, it was already possible to demonstrate that both single C_{60} molecules and groups of these can be confined within purely organic and metal−organic coordination networks.[14,15] Furthermore, it was shown, that additional functional groups of the host molecules, which protrude into the cavity, can be exploited to tune the interaction with the guest.[14]

Experimental Section

All experiments were conducted under ambient conditions with a home-built pocket-size scanning tunneling microscope, controlled by commercial STM-1000 electronics made by RHK. Mechanically cut PtIr (90/10) tips were used. In situ treatment by short voltage pulses improved their stability and capability of submolecular resolution. The organic TMA template layer was prepared by applying a small droplet of a saturated solution, with heptanoic acid as a solvent, on a freshly cleaved graphite surface at room temperature. Heptanoic acid is, at least for the tunneling voltage range suitable for STM investigations, an electrically nonconductive liquid, thus enabling simple experiments with noninsulated tips. Its vapor pressure at room temperature is low enough to allow stable tunneling experiments in the order of 1 h. By choosing a solvent with the same functional group as the solute, the TMA solubility apparently becomes sufficiently large to provide enough molecules for the self-assembly of closed monolayers. Experiments with typical solvents, which were successfully used in investigations of alkane derivatives, e.g., phenyloctane or dodecane, failed. After the self-assembly of the TMA network was confirmed by STM, a droplet of a C_{60} solution in heptanoic acid was added to the liquid phase above the substrate. All STM topographs were

recorded in the constant current operation mode with tunneling currents of around 70 pA and voltages between +800 mV and +1500 mV with respect to the tip.

Results and Discussion

In an initial step, the TMA template structure was prepared on a graphite surface. The honeycomb-like structure, referred to as chickenwire structure in the following, exhibits a periodic arrangement of cavities 1.1 nm in diameter with a nearest-neighbor distance of 1.6 nm. TMA consists of a benzene core with three carboxylic groups symmetrically attached in the 1, 3, and 5 positions, therefore making it a suitable building block for supramolecular architectures. These functional groups connect the molecules via hydrogen bonding like lego building bricks.

A model of the TMA chickenwire structure and a STM topograph thereof are depicted in Figures 1 and 2, respectively. The 6-fold symmetry of the network is evident, and small circular bright protrusions correspond to single TMA molecules. As pointed out previously, within the chickenwire structure all possibilities for carboxylic hydrogen bonding are saturated.[2] Although the TMA molecule is rather small, and hence the interaction with the van der Waals substrate comparatively weak, the strong intermolecular interaction within the layer stabilizes the host−guest system, enabling STM investigations at room temperature.

Adding the dissolved buckyballs to the liquid phase above the surface demonstrates that they adsorb preferentially into the open pores of the template structure, thus making C_{60} a feasible molecular guest within the TMA chickenwire structure.

The fact that only a relatively low density of occupied cavities can be observed is explained by the solution behavior of C_{60} in heptanoic acid. Buckyballs are not physically dissolved in the fatty acid but remain colloidal. After dissolving C_{60} in heptanoic acid, the solution is black, whereas the color changes to violet when typical organic solvents such as benzene are used. Because of the stability of the C_{60} colloidal crystals, the incorporation of single guest molecules is a rather rare event and only few occupied cavities can be observed. On the other hand, it was possible to demonstrate an almost complete occupation of the TMA cavities when inserting coronene as a guest.[16]
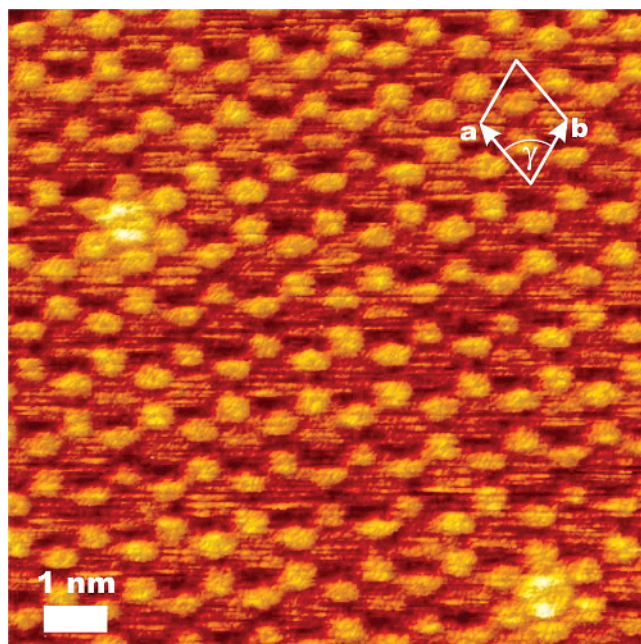
Figure 2. STM constant current topograph of the TMA host−guest network (10 × 10 nm²); circular cavities surrounded by six TMA molecules are clearly evident. The diameter of the pores is 1.1 nm, and the lattice constant of the hexagonal cavity lattice is $a = b = (1.6\pm0.1)$ nm and $\gamma = (60\pm1)°$ as depicted in the upper right corner. The incorporation of two C_{60} molecules inside the cavities of the TMA host network appear as bright protrusions.

Figure 2 gives an example where, in addition to the host structure, two C_{60} molecules are adsorbed in the centers of the cavities of the TMA chickenwire structure. Apparently, the TMA template stabilizes the adsorption of single C_{60} molecules on the graphite surface, since no adsorption can be observed when the liquid phase is comprised of C_{60}/heptanoic acid solution only. A similar stabilization might possibly be achieved in a densely packed C_{60} monolayer. We attribute the absence of a close-packed C_{60} monolayer at the liquid−solid interface to the low concentration of single C_{60} molecules in heptanoic acid as discussed above. Furthermore, the host−guest network introduces a grid of stable adsorption sites for the buckminster fullerene. All STM pictures show the C_{60} only resting inside the cavity and never in an intermediate state atop the host structure. Also, intuitively, the stable adsorption site can be deduced to be inside the cavity, obviously maximizing the interaction between both host−guest and guest−substrate. Certainly, the perfect steric match between guest and host structure is favorable for a high stabilization energy of C_{60} within the TMA bearing.

To estimate the stabilization energy of C_{60} within the host structure, molecular mechanics simulations using a Dreiding II force field[17] were performed. The binding energy is calculated as the difference between the total energies of a situation representing the energy minimum of the guest molecule within the cavity and far away. The calculated value accounts to 31 kcal/mol. In this, the influence of the liquid phase on the total binding energy was not taken into account. Apparently the total stabilization energy is altered due to the solvation of C_{60}.

The C_{60} molecule inside a cavity appears as a ∼1 nm wide bright protrusion surrounded by six smaller features originating from the otherwise unperturbed TMA network. In the intramolecular structure of the C_{60} molecule, no distinct signature originating from the inhomogeneous spatial distribution of the frontier orbitals can be reproducibly found. Apart from an insufficient resolution of the STM experiment, a reasonable

explanation is offered by thermally induced rotation of the C_{60} molecule at room temperature, well-known from adsorbate layers[18] and bulk crystals.[19] Indeed, submolecularly resolved STM experiments revealing an internal structure of C_{60} molecules are only reported for low temperatures or strongly interacting substrates in an UHV environment.[20,21]

When imaging with an adequately low tunneling current ($I_T \approx 70$ pA), the guest molecules remain stable in their position during the experiment. This is unambiguously proven by a series of consecutive images showing two or more C_{60} fullerenes with their relative position unchanged.

The chosen system enabled the demonstration that a controlled room-temperature manipulation of single molecules with the scanning tunneling microscope tip is possible at the liquid−solid interface. Similar to the meanwhile established technique for manipulating atoms and molecules,[22−24] a reduction of the tunneling gap in the vicinity of the molecule induces its lateral movement. By application of a temporarily higher reference current ($I_T \approx 150$ pA) with the feedback loop active, it was possible to transfer buckyballs from one template cell to an adjacent one. The series of consecutive images, depicted in Figure 3, illustrates the manipulation of a single C_{60} molecule into the neighboring cavity. Figure 3a shows the starting situation with a single fullerene coadsorbed within the TMA template. Figure 3b, scanned from top to bottom, demonstrates the manipulation step. After half of the guest molecule appeared in the image, the tunneling parameters were changed from imaging to manipulation conditions for a few lines. The horizontal line in the model of Figure 3d indicates the position where the reference current was increased temporarily. During the manipulation, the feedback remained active and constant current was maintained. After the molecule jumped into the next stable adsorption site in the center of the neighboring cell, the tunneling parameters were switched back to imaging conditions. Because of the presence of "half-filled" template cells before and after the manipulation process in Figure 3b, it is obvious that the molecule really changed its position. Finally, after manipulation, the molecule appears as a whole in the neighboring cell and the successful lateral manipulation is demonstrated in Figure 3c. Because of its comparatively high binding energy and stability respectively, the TMA host network remains unaffected by the manipulation process. Up to now, it has only been possible to transfer C_{60} molecules into an adjacent cell, and no step widths greater than one unit cell of the template were accomplished in a single manipulation step. In contrast to many of the reported manipulation experiments where the tunneling resistance differs by about 3 orders of magnitude between imaging and manipulation mode,[6,25,26] here an increase of the tunneling current by a factor of 2 is already sufficient. For this reason, a rather low energetic barrier between the stable adsorption sites of adjacent TMA cells can be assumed. However, the barrier is large enough that thermally induced hopping was not observed. For lateral manipulation of rather large organic molecules[4,20,22] and C_{60},[4,5] pushing of the molecule by the STM tip is reported. Therefore, pushing seems to be the most likely mechanism. In contrast to previously reported STM manipulation experiments, the stable adsorption sites are not determined by the underlying atomic lattice of the substrate. Because of the TMA template, the distance between stable adsorption sites for the C_{60} guest molecule is greatly enlarged.

Conclusion

In this work, the successful incorporation of molecular guests in a hydrogen-bound two-dimensional host network of trimesic
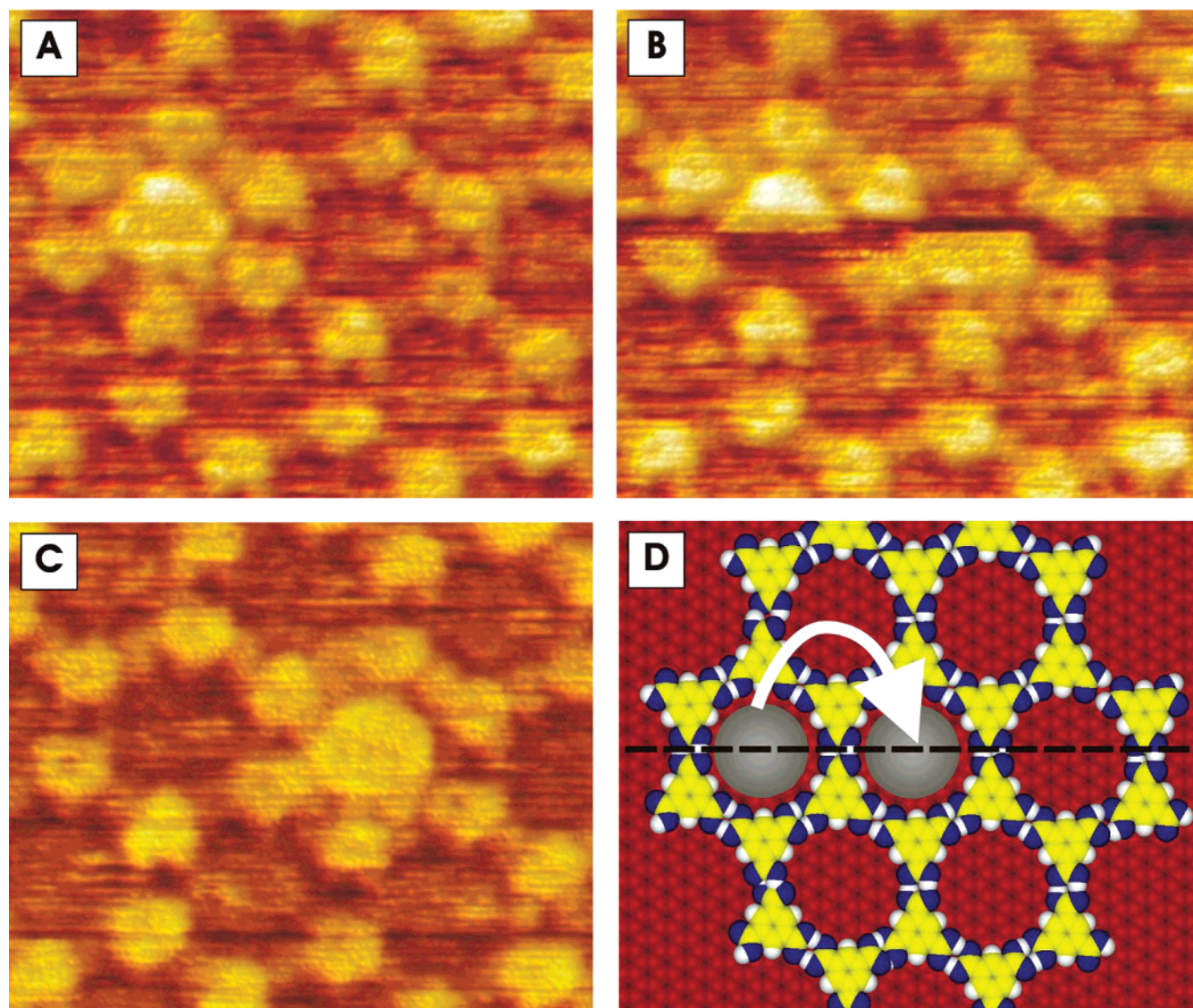
Figure 3. (a) STM topograph of the starting situation with a single C_{60} guest molecule inside the TMA host network ($a - c = 4.6 \times 4.6$ nm^2). (b) Manipulation step: after half the molecule was scanned, the tunneling current was switched from imaging ($I_T \approx 70$ pA) to manipulation ($I_T \approx 150$ pA) conditions; after the molecule was transferred to the adjacent cavity the imaging conditions were restored. (c) Final result of the lateral manipulation with the whole molecule imaged in the target cavity. (d) Illustration of the TMA network and the manipulation process; the horizontal line indicates the lines which were scanned with an increased reference current.

acid at the liquid−solid interface was demonstrated. The size, shape, and nature of C_{60} buckminster fullerenes makes them suitable guests for the circular, 1.1 nm wide periodically arranged cavities of the TMA template. Coadsorption from the liquid phase was observed. C_{60} adsorbs in the center of the TMA cavities. Obviously, this adsorption site is the most stable, since it was not possible to observe any intermediate adsorption states. When the tunneling parameters were altered toward a lower tunneling resistance, the defined lateral manipulation of single C_{60} molecules was demonstrated at the liquid solid interface at room temperature, thereby considerably reducing the experimental effort for manipulation experiments of matter on the ultimate dimensional limit.

Because of the high mobility of molecules at the liquid−solid interface, this template-based method is expected to be particularly useful to stabilize single molecules for tunneling spectroscopy investigations. It is conceivable to extend the host−guest approach presented here to other molecular guests. This could be achieved by adapting the cavity size or the chemical nature of the host system.

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