

Incorporation and Manipulation of Coronene in an Organic Template Structure

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A two-dimensional molecular template structure of 1,3,5-benzenetricarboxylic acid (trimesic acid, TMA) was formed on a highly oriented pyrolytic graphite surface (HOPG) by self-assembly at the liquid–solid interface. Scanning tunneling microscopy (STM) investigations show high-resolution images of the porous structure on the surface. After the host structure was created, coronene molecules were inserted as guest molecules into the pores. STM results indicate that some of the guest molecules rotate inside their molecular bearing. Further investigations show that single coronene molecules can be directly kicked out of their pores by means of STM.

Introduction

Three-dimensional host–guest systems such as zeolites have been known for a long time and are used in industrial quantities as molecular sieves in separation science. In recent years, these crystals have attracted considerable interest because they have been used for the spatial fixation of compounds in single molecule experiments. Precise experiments, based on Förster transfer optical spectroscopy, have been conducted on the interaction between two single molecules, dependent on distance and mutual orientation.^{1,2}

Similar experiments in two-dimensional molecular systems have been hampered by the lack of means to provide a defined host crystal for the incorporation of single molecule guest species, yet the nondensely packed ordering of a single molecular species at a solid surface is an immediate requirement for many investigations in molecular electronics and life sciences. Furthermore, ordered arrays (in a crystallographic sense) of clusters with a precisely defined spatial distribution are needed for applications of quantum dots in optics as well as magnetic and spin systems in future storage applications. Also, the quality of the order of the self-organized semiconductor nanoclusters directly determines the performance of the two-dimensional laser.^{3,4}

To access single molecules with a scanning probe for local measurements of electronic or mechanical properties with scanning probe methods in life science experiments, the compounds should have a precise local address. In dense packed self-assembled two-dimensional monolayer crystals, the species of interest cannot be separated from their neighbors in terms of their physical environment,

rendering independent measurements impossible. In ultrahigh vacuum (UHV) and low-temperature experiments, sub-monolayer coverage can enable single molecule measurements. In UHV experiments, for example, it was already possible to demonstrate that both single C₆₀ molecules and groups of these can be confined within purely organic and metal–organic coordination networks.^{5,6} However, up to now, a nondensely packed distribution in a crystallographic sense has not yet been realized. Nanostructuring of Cu(110) surfaces using custom designed template molecules was recently impressively demonstrated.⁷ Also, vicinal surfaces usually only generate order in one dimension, with order in the second dimension being severely inhibited.^{8–10} Additionally, even though many basic single molecule measurements can be done in UHV, these conditions are often not desirable for practical applications. To create spatially ordered systems of metal clusters under ambient conditions, an approach using micelles has been used.¹¹

Here, we describe a simple ambient conditions parallel method to produce two-dimensional self-assembled molecular host systems for incorporating, in an open cavity structure, different guest compounds which become spatially precisely ordered. As an example, we show that single coronene molecules can be periodically positioned over a large area with subnanometer precision. In contrast to self-assembled close packed coronene monolayers,^{12–14} we have designed a completely new cocrystal structure

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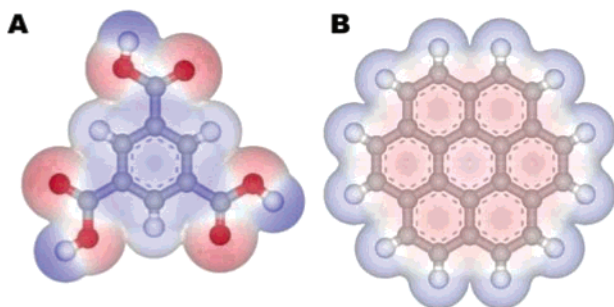


Figure 1. Chemical structure models with van der Waals radii of (A) trimesic acid ($C_9H_6O_6$) and (B) coronene ($C_{24}H_{12}$). Both molecules are planar, with TMA and coronene exhibiting a 3-fold and 6-fold symmetry axis, respectively.

with an enlarged lattice constant. Likewise, it was possible to grow a bulk crystal of trimesic acid (TMA) and coronene from solution.¹⁵ Unfortunately, structure analysis by X-ray diffraction was inhibited by disorder of the cocrystal along the *c*-axis. This structure is the basis for single molecule experiments, where we create spatially precisely defined molecular point defects. Additionally, we show that the state of movement of a single molecule dependent on the exact binding position can thus be visualized.

Experimental Section

1,3,5-Benzenetricarboxylic acid (trimesic acid, TMA) is a planar molecule with 3-fold symmetry (Figure 1A). It consists of a benzene ring with three carboxylic groups attached in the 1, 3, and 5 positions, allowing for the spontaneous formation of supramolecular architectures via directed hydrogen bonding to neighboring molecules.^{6,16} Among the various possibilities of hydrogen bonds, those between carboxylic groups can be classified as intermediate strong.¹⁷ By depositing TMA molecules on a surface, the structure demonstrated in Figure 2 can be realized, among other possibilities.¹⁸ In this case, every possible hydrogen bond is saturated under an ideal bonding angle of 180°. In the following, this TMA polymorph will be called the “chicken wire structure”. A comparable porous TMA network was also prepared by thermal evaporation on Cu(100) and by adsorption from solution on Au(111) under potential control in an electrochemical scanning tunneling microscope.²⁰

The planar coronene molecule, which is used as a guest molecule in the work presented here, consists of a total of seven interconnected benzene rings and can be considered as the smallest possible flake of a graphite sheet saturated with hydrogen atoms. On the other hand, coronene is one of the most complex molecules encountered in interstellar space and possibly plays a basic role in interstellar extinction.²¹ In Figure 1B, a coronene molecule with van der Waals radii is shown. The molecule has a diameter of ~ 1 nm.

The samples were prepared in three steps. First, a freshly cleaved highly oriented pyrolytic graphite surface (HOPG) surface was carefully characterized before a saturated solution of trimesic acid molecules in heptanoic acid was applied to the substrate. The room-temperature solubility of TMA in heptanoic acid amounts to 0.8 mmol L^{-1} . In situ scanning tunneling microscopy (STM) imaging of the self-organized monolayer of the host

structure was performed at the solution–HOPG interface before the coronene guest molecules were added in the final step. Our experiments do not allow for any conclusion on the structure of TMA in the liquid phase, but it is conceivable that TMA molecules exist therein in a precursor state, for example, hydrogen bound dimers. A liquid-crystal-like extension of the monolayer into the liquid phase above is not observed. If there were more layers floating on top of each other, presumably only the first monolayer would be conductive enough to be imaged by STM, similar to the observation in the pioneering work of Foster and Frommer.²² To accomplish the incorporation of the guests, a droplet of a saturated solution of coronene in heptanoic acid was added on top of the droplet already on the surface. Although ordered adsorption of the solvent, heptanoic acid, could, in principle, be observed on HOPGs, it did not appear in the STM images because of its comparatively lower binding energy. While molecular resolution was achieved in most experiments shortly after approaching the scanning tunneling microscope tip, it took a few minutes for the scanning tunneling microscope to stabilize and to obtain high-quality images without substantial distortions due to drift effects. Heptanoic acid is electrically nonconductive, and its vapor pressure at room temperature is low enough to allow for stable tunneling experiments in the order of 1 h. For the purpose of calibration, the HOPG lattice and the self-assembled molecular layer were imaged within the same image. This was achieved by changing the tunneling parameters during image acquisition.

STM measurements at the liquid–solid interface were carried out at room temperature with a home-built low-current scanning tunneling microscope equipped with a commercial RHK STM-1000 control system. The molecular resolution images presented were obtained in the constant current mode of the microscope, without using, for example, a voltage pulse in order to initiate the ordering process on the surface. The bias voltages were typically $\sim +800$ mV with respect to the tip, and the best results could be obtained with set point currents of ~ 150 pA.

It turned out that for tunneling with the tip immersed in organic acid solvents, mechanically cut Pt/Ir wire (90/10) tunneling tips worked better than electrochemically etched tungsten tips. We attribute that to the inertness of platinum alloys in comparison to tungsten. In addition to better image contrast, Pt/Ir tips were more stable and it was nearly always possible to recondition them by applying voltage pulses of 1.5–3.5 V to the tip.

To manipulate molecules with the scanning tunneling microscope tip, the current set point of the feedback loop was temporarily set from 150 pA to ~ 1 nA, resulting in a decreased tunneling gap and therefore increased tip–sample interaction. This was done either manually or by using the lithography feature of the controller.

Results and Discussion

As mentioned above, the samples were prepared in three steps. After cleavage and characterization of the HOPG substrate, the host structure, formed by self-assembly of TMA molecules at the liquid–solid interface, was preadsorbed on the surface. The resulting STM pattern can be seen in Figure 3. As proposed, the structure consists of hexagons with a TMA molecule on every corner. Careful analysis of the submolecular structure of single TMA molecules reveals that the little depression in the center of each molecule can be interpreted as the “hole” in the middle of the benzene ring.

Each of the three carboxylic groups per molecule forms two hydrogen bonds with its neighbors (see the dashed lines on the right-hand side of Figure 2). This results in a total of six O–HO hydrogen bonds per TMA molecule, which offers great in-plane stability of the network. Due to the limited resolution and delocalization effects, these six single bonds cannot be resolved separately, but in the STM picture, three double bonds per molecule can be identified as a feature between the molecules. Since the

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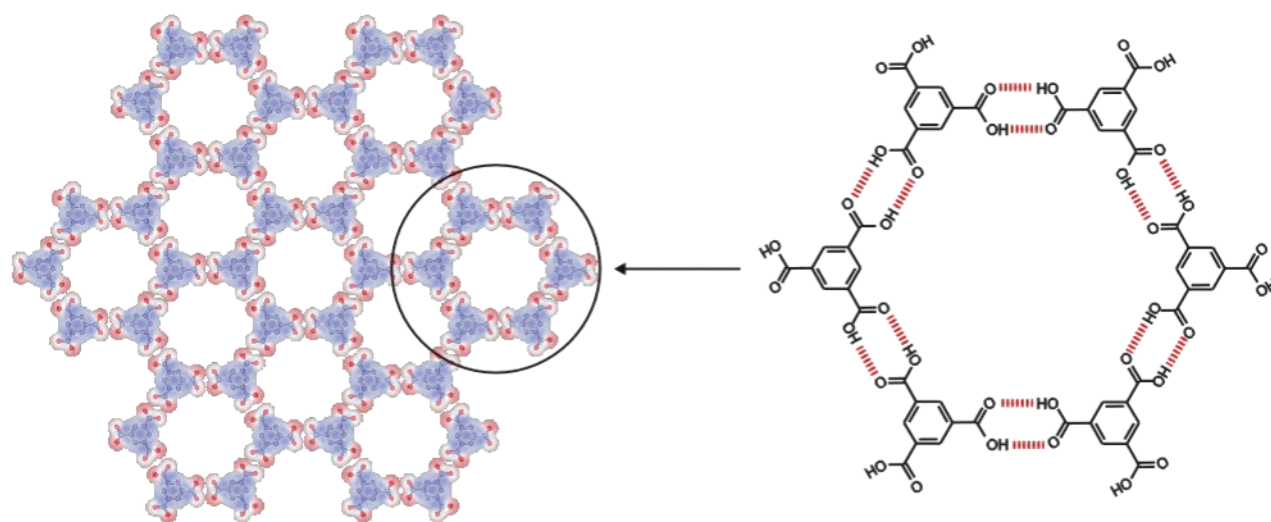


Figure 2. Schematic picture of the chicken wire structure. This model demonstrates that each single molecule is bound to the three adjacent molecules via hydrogen bonding of the carboxylic functionalities. The diameter of the cavities is ~ 1 nm, and their nearest neighbor distance comes to ~ 1.6 nm. On the right-hand side of the figure, the hydrogen bonds between the TMA molecules are indicated by dashed lines.

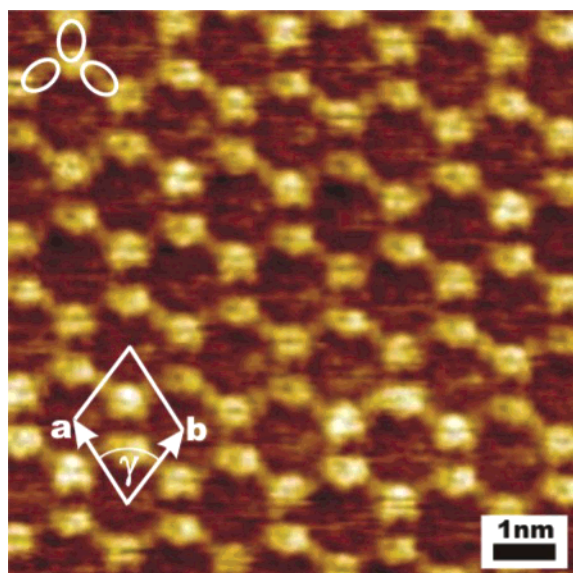


Figure 3. STM topography image of a monolayer of TMA physisorbed on the interface between an organic solution of TMA in heptanoic acid and the HOPG ($a = 1.6 \pm 0.1$ nm, $b = 1.6 \pm 0.1$ nm, $\gamma = 59 \pm 1^\circ$). The TMA structure is tilted $\sim 5^\circ$ with respect to the HOPG lattice. The tilt angle is known from measurements where in half of the topograph the adlayer was imaged and in the other half the graphite substrate was atomically resolved by the application of the appropriate tunneling parameters.

contrast in STM topographs is generally scan angle dependent,²³ this cloud is clearly visible if scanned with a flat angle with respect to the cloud (fast scan direction horizontal). For clarity, the features representing the double hydrogen bonds between adjacent carboxylic groups for one molecule are marked in the upper left corner of Figure 3.

The large, almost circular cavities within the chicken wire structure have a diameter of ~ 1 nm and will serve as a molecular bearing for guest molecules, as will be demonstrated in this paper. Within the cavities, additional streaky features appear. A possible explanation is offered

by transient adsorption of either solvent or solute molecules. Since either this adsorption site is obviously not stable on a STM time scale or the cavities are emptied out by interaction with the scanning tunneling microscope tip, no whole molecules can be imaged. This claim is supported by the absence of similar features inside the pores when the TMA structure is prepared and investigated in a UHV environment.¹⁸

In a third preparation step, dissolved coronene molecules (saturated solution in heptanoic acid) were added onto the surface already containing the host structure. The outcome of the self-assembly process of coronene into the cavities of the TMA host structure was observed in situ by STM. After all the cavities were filled, the STM picture in Figure 4 was taken, where the perfect arrangement of the guest molecules within the TMA bearings is demonstrated. Occasionally occurring point defects, namely, single coronene vacancy sites, were observed. Although interactions with the scanning tunneling microscope tip cannot be excluded, thermal excitations due to the system's finite temperature are likely to be the cause of these vacancies. These vacancies prove unambiguously that the protrusions in the center of the cavities are really due to coronene occupation. Otherwise, the observed STM contrast could be attributed to an imaging anomaly, as was observed with some tips not sharp enough to probe the bottom of the cavities. Coronene itself appears as a big disklike molecule with a diameter of ~ 1 nm in the STM picture. The size and shape of the coronene molecules is consistent with an adsorption with the molecular plane parallel to the substrate. Obviously, this adsorption geometry maximizes the interaction with the substrate and was also found in previous STM studies.^{13,14} Every coronene molecule is surrounded by six TMA molecules of the apparently undisturbed chicken wire structure, which can be clearly identified in the STM measurement. It was possible to routinely reproduce this coadsorption experiment.

It is noteworthy that investigations at the liquid–solid interface of coronene in heptanoic acid without the TMA host structure did not show ordered structures. This is indicative of the fact that the TMA network serves as a molecular bearing which stabilizes and enables the coronene adsorption from solution.

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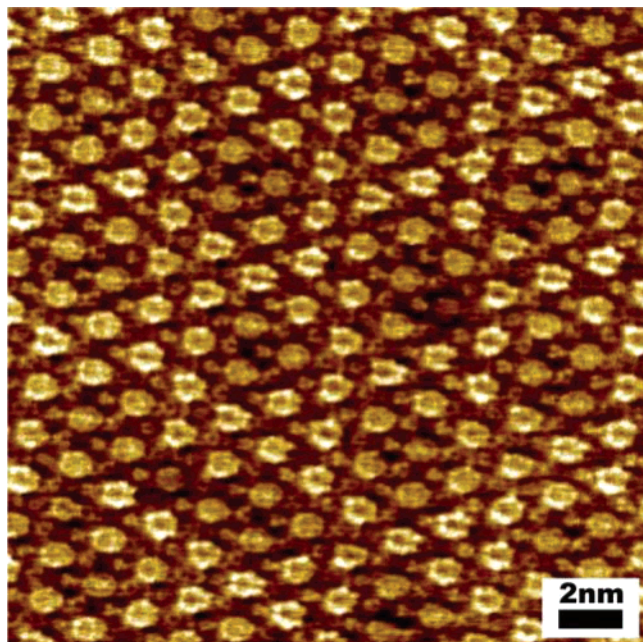


Figure 4. STM image of coronene molecules inserted into the TMA host structure. The coronene molecules appear as features with a diameter of ~ 1 nm and are surrounded by six hydrogen bonded TMA molecules. A substrate mediated superstructure in the molecular appearance with a unit cell of ~ 6 nm can be recognized.

Looking at the ensemble of guest molecules in Figure 4, their submolecular contrast appears periodically modulated, forming a superstructure. This modulation is expressed in a slightly different contrast and shape of individual coronene molecules, and a hexagonal symmetry is evident for this superstructure.

For the unit cell of the superstructure, a lattice constant of ~ 6 nm can be deduced, with the lattice vector slightly skewed (by $\sim 5^\circ$) with respect to the TMA–coronene structure. Because the bare TMA structure was also found to be tilted by $\sim 5^\circ$ with respect to the substrate, an alignment of the superstructure to the underlying atomic lattice of the graphite substrate can be stated within the experimental error.

Since the STM contrast depends to a great extent on the spatial overlap and the mixing of the electronic states of the adsorbate and the substrate, molecules adsorbed on different sites can be expected to exhibit disparities in contrast in the STM images. Moreover, in the case presented here, the molecules not only exhibit a variation in contrast but also show quite different shapes. In Figure 5, two examples of molecules with different shapes are marked by arrows 1 and 2, respectively.

Molecule 1 appears as six bright lobes arranged around a central depression of the molecule. Each of the lobes can be assigned to one of the six outer benzene rings of the coronene molecules. A comparable contrast was observed for the adsorption of coronene directly on a HOPG,¹³ for example, Ag(111)¹⁴ and Au(111)^{24–26} surfaces. On the other hand, molecule 2 appears as two concentric rings resembling the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of an isolated coronene molecule as calculated from first principles.¹²

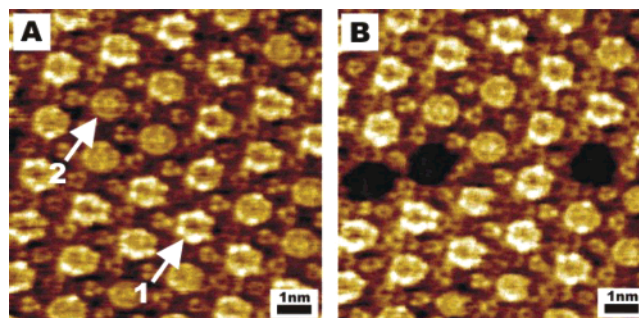


Figure 5. (A) Subset of a STM image of coronene in the TMA host structure showing two different types of molecules; molecule 1 represents a still-standing coronene molecule, while molecule 2 is proposed to be rotating. (B) The same subset from part A after the removal of some guest molecules. ($U_T = 0.8$ V; $I_T = 147$ pA)

Apart from the molecules of type 1 or 2, intermediate states can also be found in the STM topograph.

An explanation for the different submolecular features of the coronene guests is offered by a periodical modulation of the adsorbate–substrate interaction within the cavities. The Moiré-like superstructure arises from a superposition of the two lattices, the graphite substrate and the TMA host network. Because these two lattices are incommensurate, the adsorption sites for coronene within the cavities and thus the interaction strength are modulated in a periodic manner. This, consequently, leads to a variation in the distance between the planar coronene molecule and the substrate. Pure coronene monolayers grow commensurate on HOPGs, thus confirming that the molecules “snap in” in a stable adsorption site.

Assuming that the molecule–substrate distance of a type 1 molecule is smaller, its greater apparent height and submolecular features when compared to molecule 2 in the STM topographs can be attributed to an electronic effect mediated by a better coupling to the substrate. Probably for the same reason, only three out of six surrounding TMA molecules are clearly visible in this case. A higher binding energy of type 1 molecules is also supported by the fact that features resulting from a single benzo group of the molecules can be resolved in great detail, therefore confirming the fixation of this species.

The contrast of molecule 2 is better resembled by the electronic structure of unperturbed, isolated molecules, indicating an increased adsorbate–substrate distance. However, in the experimental results, type 2 molecules appear with a more or less rotational symmetry, whereas the molecular orbitals¹² have a 6-fold symmetry. A model which suggests alternating backward and forward rotational movement (i.e., wiggling) of these more weakly bound molecules could explain this discrepancy.

According to molecular mechanics simulations, the barrier for a rotational movement of coronene within the TMA bearing is in the order of 50 meV, which is on one hand certainly well below the accuracy of this type of simulation but on the other hand indicative for the possibility of a rotational movement of the guest molecules. This way, the observed differences of the submolecular features of type 1 and 2 molecules could be explained by wiggling of guests with a larger molecule–substrate distance. Furthermore, the stronger interaction of type 1 molecules with the substrate prevents this type of rotation within the observation time.

Although there were slight differences in the appearance of coronene on various substrates, a ringlike structure, like the one given here, has so far not been reported. This is yet one more hint that the contrast here cannot be

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explained purely by a modulation of the electronic structure of the coronene due to different adsorption sites but instead supports the suggestion of wiggling molecules.

Also, lateral vibration of type 2 molecules can be excluded as the origin of the smeared out appearance. If the molecules were vibrating laterally instead of rotating, they would appear larger than the fixed molecules. Since this is not the case, the STM contrast of the guest molecules cannot be attributed to lateral vibrations.

Gimzewski et al. made very similar observations which they have interpreted as rotating and still-standing HBDC (hexa-*tert*-butyl decacyclene) molecules on a Cu(100) surface,²⁷ depending on the adsorption site of the molecule on the copper surface.

Their given model suggests switching the rotation of HBDC on and off by a small lateral manipulation.

Besides incorporating guest molecules, a molecular bearing implies the possibility to remove or manipulate the guest molecules. For a defined manipulation of the guest molecules, the stability of the host system is an important aspect. The outstanding stability of the TMA network is demonstrated in Figure 5. After the image in part A was taken, some molecules in the middle of the image were removed from the host structure by a temporarily increased reference current under constant current conditions. The result of the manipulation process is given in Figure 5B. Obviously, the host network remains unaffected by the manipulation process, therefore enabling a selective removal of the coronene molecules. The reason for the high stability of the host network is the six hydrogen bonds every TMA molecule forms with its neighbors. Because the adsorbate–substrate interaction is quite weak for such small molecules on the HOPG, this plays a minor role for the stability of the TMA structure. On the other hand, in manipulation experiments with C₆₀ molecules as a guest in the chicken wire structure, the transfer from one cavity to an adjacent one was demonstrated.²⁸ The main difference is the density of the guest species. Whereas for the C₆₀ guests only single molecules were stabilized in the network, here almost every cell is filled. Consequently, the coronenes are removed by the interaction with the tip rather than transferred to another cell, as a double occupancy is not stable.

In the system presented here, the TMA–coronene structure on the HOPG is in equilibrium with the solution above. By removing molecules from the structure, this equilibrium is perturbed. Thus, it was possible to observe a self-healing process within minutes. All cavities were

reoccupied with coronene molecules from the liquid phase. To permanently vacate the cavities without this healing effect, either the molecule reservoir above the surface has to be removed or this experiment has to be performed in UHV, thus controllably adsorbing just a monolayer or less of guest molecules onto the surface. The UHV realization of the host structure has already been demonstrated.¹⁸

To get an estimate for the stabilization energy of the coronene within the host structure, molecular mechanics simulations using a Dreiding II force field²⁹ were performed. The binding energy of coronene in the molecular bearing is calculated as the difference between the total energies of a situation representing the energy minimum of the guest molecule within the cavity and the coronene molecule far away. The calculated value comes to 54 kcal/mol. In this value, 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 coronene.

Conclusions

We have shown that trimesic acid self-assembled via hydrogen bonding at the liquid–solid interface serves as an organic template for the ordering of coronene molecules in a new two-dimensional crystal structure. The STM contrast of the guest molecules exhibits a periodic modulation affecting the shape, internal structure, and apparent height of the molecules. This contrast modulation is explained by varying the interaction with the substrate, rotation of the coronene guests, or a combination thereof. Furthermore, it was demonstrated that an increased interaction with the scanning tunneling microscope tip can temporarily vacate the cavities of the host network. Reoccupation from the liquid phase above was observed, therefore confirming a self-healing effect of the system. Due to their spatial confinement, single molecule experiments on isolated molecules and metal or semiconductor clusters or magnetic particles should be possible. The intentional molecular manipulation demonstrated here may serve as a means for studying single molecular dynamics such as the change of functional location, even enabling an exchange of different molecules in the future. The investigation of the rotational movement at different temperatures shall provide insight into the phenomenon of single molecule rotation in a molecular bearing.

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