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An Investigation into the Interactions Between Self-Assembled Adenine Molecules and a Au(111) Surface

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Two molecular phases of the DNA base adenine (A) on a Au(111) surface are observed by using STM under ultrahigh-vacuum conditions. One of these phases is reported for the first time. A systematic approach that considers all possible gas-phase two-dimensional arrangements of A molecules connected by double hydrogen bonds with each other and subsequent ab initio DFT calculations are used to characterize and identify the two phases. The influence of the gold surface on the structure of A assemblies is also discussed. DFT is found to predict a smooth corrugation potential of the gold surface that will enable A molecules to move freely across the surface at room temperature. This conclusion remains unchanged if van der Waals interaction between A and gold is also approximately taken into account. DFT calculations of the A pairs on the Au(111) surface show its negligible effect on the hydrogen bonding between the molecules. These results justify the gas-phase analysis of possible assemblies on flat metal surfaces. Nevertheless, the fact that it is not the most stable gas-phase monolayer that is actually observed on the gold surface indicates that the surface still plays a subtle role, which needs to be properly addressed.

Keywords:

- charge transfer
- DFT calculations
- hydrogen bonding
- self-assembly
- STM

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1. Introduction

The ability of molecules to self-assemble into larger nanoscale structures is an important research area owing to its potential impact on future nanotechnological devices.^[1] Many supramolecular structures can be formed by small organic molecules, including all the DNA and RNA bases.^[2–15] The self-assembly of these bases on surfaces may also have played an important role in the earliest appearance of life.^[16]

In spite of the great success that scanning probe methods have had in revealing the atomic-scale realm of matter, atomic resolution of molecular assemblies cannot be achieved in STM images in most cases involving planar organic molecules due to small corrugation of the local density of state at the Fermi level. Therefore, theoretical modeling is an essential step in interpreting such experimental scanning tunneling microscopy (STM) or atomic force microscopy (AFM) images. In most cases, modeling of such systems is difficult owing to commensurability problems arising from different periodicities of the surface potential and the gas-phase monolayer. The problem arises when one considers, within periodic boundary conditions, a monolayer of molecules and the surface explicitly, as, in general, prohibitively expensive calculations involving large supercells are needed. In self-assembled supramolecular nanostructures, intermolecular interactions are usually expected to dominate over molecule–substrate interactions. Therefore, such self-assemblies are usually modeled in the gas phase.

However, this may not always be valid because the commensurability problem as well as the surface perturbation of the electronic structure of the adsorbed molecules may render their consideration in the gas phase approximate or even invalid. For instance, DNA bases adsorbed on the Au(111)^[10,17] and adenine (A) on graphite^[18] surfaces lie flat at considerable distances from the surfaces, which demonstrates that the molecule–surface interactions are rather weak. On the other hand, A molecules are adsorbed in a strongly tilted manner on the corrugated Cu(110) surface,^[9,19] indicating much stronger molecule–surface interaction in this case. The Ag-terminated Si(111) surface^[8] is an intermediate case, as the hydrogen bonding between the A molecules is balanced by their interactions with the surface, thus leading to a flat, self-assembled structure. This is not the most favorable structure in the gas phase and only becomes energetically favorable in the presence of the surface. Notably, what is essential in this case is not the absolute strength of the molecule–surface interaction, but the lateral corrugation of the surface potential.

From an interplay between STM imaging and DFT calculations, we address the balance between the molecule–surface and molecule–molecule interactions by investigating self-assembled A structures on the Au(111) surface as a model system. Two A monolayer structures were observed by STM under ultrahigh vacuum (UHV) conditions, one of which is reported herein for the first time. To interpret the structures at the atomic level, we first show, by using state-of-the-art density functional theory (DFT) calculations, that the molecule–molecule interaction is affected very little by their interaction with the Au surface, strongly suggesting that the gas-phase analysis for most flat metal surfaces should be appropriate to

obtain all the energetically most favorable structures. These structures were obtained by using a recently developed systematic approach^[20] based on a consideration of all possible A dimer connections between molecules in two dimensions, followed by detailed DFT calculations for specific cases. A comparison of the experimentally observed and theoretically deduced structures reveals the subtle role played by the surface, even in the case of a weak molecule–surface interaction. Hence, the structures that are most stable in the gas phase become less favorable on the surface and are actually not observed. At the same time, the observed structures, although not the most favorable in the gas phase, are accurately predicted by the gas-phase calculation.

2. Results and Discussion

STM images recorded at 150 K (Figure 1A) show that the A molecules, upon deposition onto a clean Au(111) surface at room temperature, self-assemble into 2D well-ordered, apparently nonchiral islands (phase I). This structure is consistent with the previously reported A monolayer structure observed on a Ag-terminated Si(111) surface.^[8] Surprisingly, we also observed small areas of another, also nonchiral, self-assembled monolayer structure (phase II), which coexists on the surface intermixed with phase I, usually at the elbow sites of the characteristic herringbone reconstruction of the clean Au(111) surface. After annealing to 370 K for 10 min, phase II (Figure 1B), which had not been observed previously, had grown to become the dominating structure at the expense of phase I, which vanished (Figure 1B). Both structures form honeycomb networks in which each A molecule is connected with three neighbors. However, as observed from the high-resolution STM images depicted in Figures 1C and 1D, and in particular from the gaps between the A molecules shown by ovals, we can conclude that the orientation of A molecules is different in the two structural phases. It can also be seen from Figures 1A and 1B that the adsorption of A molecules does not lift the herringbone reconstruction of the Au(111) surface, indicating that the molecule–substrate interaction is fairly weak and that the growth of the 2D self-assembled islands is mainly controlled by molecule–molecule interactions.

To gain further insight into the experimentally observed A monolayer structures at the atomic level, *ab initio* DFT calculations were performed by using the SIESTA method.^[21] In our calculations full atomic relaxation was performed until the forces on the atoms were lower than $0.05 \text{ eV } \text{Å}^{-1}$. Calculations of the stabilization energies included the basis-set super-position error (BSSE) corrections.^[22] This methodology has been extensively tested for various DNA and RNA base homopairs^[23,24] and a large selection of heteropairs^[25] by comparison with high-level quantum-chemistry (QC) calculations.^[26]

We started our theoretical analyses by considering the interaction of a single A molecule and different A–A pairs with the Au(111) surface. The Au(111) surface was modeled with a two-layer slab in which the bottom-layer atoms were fixed in the bulk positions. We used slabs of up to six

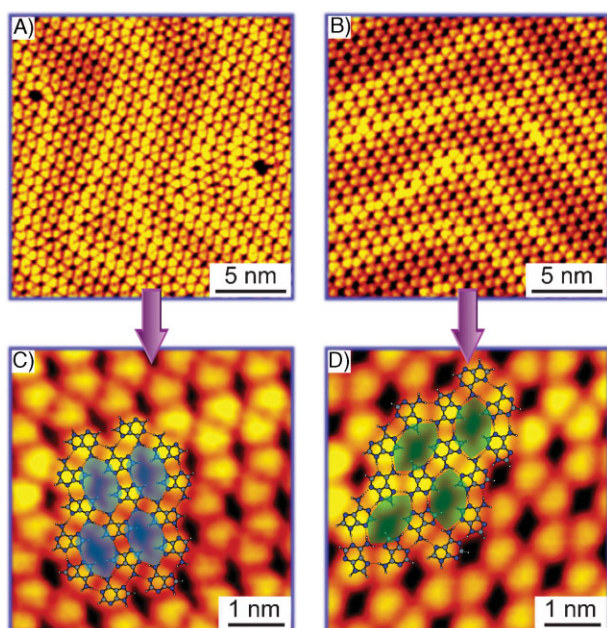


Figure 1. Experimental STM images and theoretical models for the adenine monolayers on the Au(111) surface. A and B show large areas of the two experimentally observed adenine monolayer structures, whereas C and D give close-up images with overlays of the theoretical models of A and B, respectively. Scanning conditions: $I_t = -0.5$ nA, $V_t = -1250$ mV.

layers to check that the two-layer slab was sufficient for our purposes. To position the adenine molecule on the surface, we chose a 5×5 extended supercell that had been checked to be big enough to avoid spurious interactions between the molecules across the surface. Owing to the large size of the unit cell, only a single $k=0$ point was used in our adsorption calculations.

After relaxation, a very small stabilization energy of approximately -0.1 eV was found for a single adenine molecule on the Au(111) surface, which is in excellent agreement with recent plane-wave DFT calculations (-0.1 eV).^[17] The molecule was then displaced and rotated by different random amounts and subsequently allowed to relax again, with very similar results. This result means that the potential-energy surface is very smooth laterally, in agreement with similar calculations for guanine on Au(111).^[10]

In all cases, the A molecule was found to lie flat at a distance of about 3.5 Å from the surface, in good agreement with other observations for weakly bound π^* systems lying flat on fcc (111) metal surfaces.^[4,10,13] An experimental study of adenine adsorption on Au(111)^[27] also suggests planar geometry. The planar adsorption geometry is facilitated by a partial charge transfer from the surface to the π^* system of the heteroaromatic molecule. The calculated charge-difference density of the molecule on the surface (i.e. the electron density of the whole system minus the individual densities of all parts in the geometry of the whole system) also reveals a small charge redistribution between the molecule and the surface (Figure 2). The most notable charge redistribution is for the amino group, for which planarity is broken in favor of a

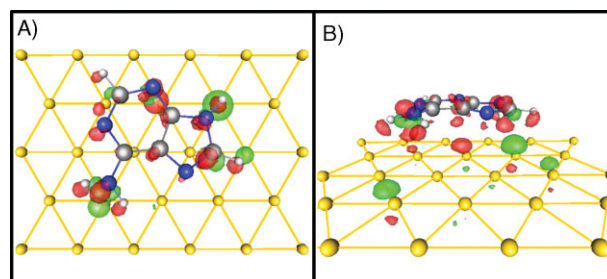


Figure 2. Top (A) and side (B) views of the density difference of the adenine on the Au(111) surface. Green contours correspond to positive electron-density difference of 0.004 electrons \AA^{-3} (i.e. charge-excess regions), whereas the red contours correspond to the negative electron-density difference of -0.004 electrons \AA^{-3} (charge-depletion regions).

pyrimidal formation, indicating sp^3 hybridization, in agreement with plane-wave DFT calculations.^[13]

To investigate the influence of the gold surface on the ability of the molecules to form dimers and self-assembled monolayers, DFT calculations of the six most stable (in the gas phase) A pairs on the surface were performed by using a 6×6 extended Au(111) supercell slab with two Au layers. All A dimers participating in the monolayer structures responsible for the two observed phases (see below) were modeled on the Au(111) surface. The relaxed geometries (some of which are shown in Figure 3 and Figure 4) for all dimers and their flipped counterparts (B corresponds to the flipped A) were found to be planar and extremely similar to those in the gas phase. If the amino groups of the molecules do not participate in the

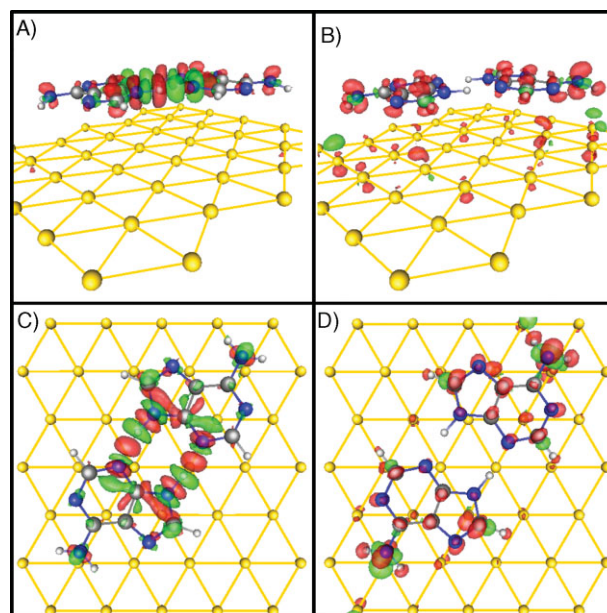


Figure 3. Side (A and B) and top (C and D) views of the difference density of the most-stable adenine pair $A_5A_5(1)$ on the Au(111) surface. A and C correspond to the total density difference (between all three species) at the level of 0.01 electrons \AA^{-3} , whereas B and D show the partial density difference between the pair and the surface at 0.004 electrons \AA^{-3} . The color scheme is the same as in Figure 2.

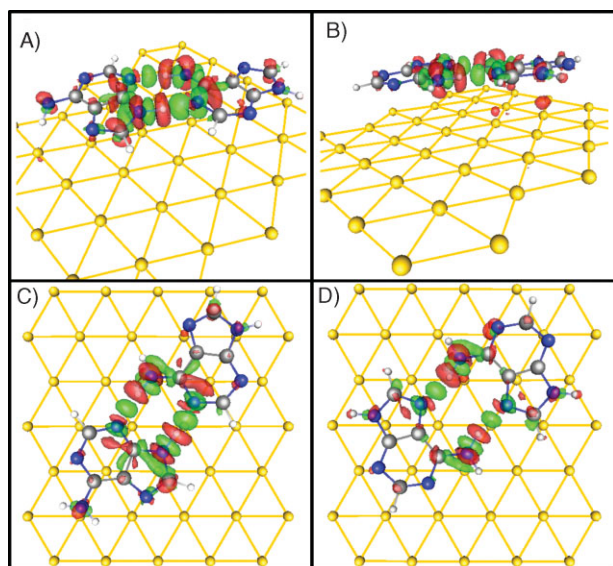


Figure 4. Side (A and B) and top (C and D) views of the total difference density (at the level of 0.01 electrons \AA^{-3}) of two adenine pairs $A_2B_5(2)$ (left panels) and $A_1A_1(6)$ (right panels) on the Au (111) surface, in which amino group atoms are involved in the bonding. The color scheme is the same as in Figure 2.

hydrogen bonding, as is the case for the most-favorable pair shown in Figure 3, they remain in an sp^3 -hybridized state with pyramidal geometry. Notably, the hydrogen atoms point downwards towards the surface and the nitrogen atom upwards.

To study the energy profile of the adsorption systems, we considered a number of energies given in Table 1: $E_{\text{def}}(D) = E(A_1) + E(A_2) - 2E(A_0)$ and $E_{\text{def}}(\text{Au}) = E(\text{Au}) - E(\text{Au}_0)$ are the A–A dimer (D) and surface-deformation energies (positive); $E_{\text{ads}} = E(D + \text{Au}) - E(D) - E(\text{Au})$ is the dimer-adsorption energy, and the stabilization energy of the dimer adsorbed on the surface is $E_{\text{Hb}}(D) = E(D) - E(A_1) - E(A_2)$ (negative). The sum of these energies makes up the total

stabilization energy of the whole system, $E_{\text{stab}} = E(D + \text{Au}) - E(\text{Au}_0) - 2E(A_0)$. In these equations, D, A_1 , A_2 , and Au refer to the geometries of each part of the system in the configuration on the surface, and zero subscript refers to the geometries of isolated species. For comparison purposes, the BSSE correction^[22] was included in all our calculated energies. Consequently, the energies $E_{\text{def}}(D)$, $E_{\text{def}}(\text{Au})$, $E_{\text{Hb}}(D)$, and E_{ads} do not add up to E_{stab} because the various BSSE corrections are non-additive.

From a detailed analysis of the results in Table 1, we find that: 1) The deformation energies of the surface are negligible, whereas those for the A dimers amount to less than 20% of their stabilization energies; 2) The adsorption energies of the A dimers are all very small, similar for different pairs, and in all cases almost exactly equal to twice the adsorption energy of a monomer reported above; 3) The energy profile of A dimers and their flipped counterparts are practically identical and very close to that in the gas phase; and, finally, 4) The total stabilization energies of all systems follow the same order as in the gas phase. A small stability increase can be observed in Table 1 for all A pairs in which the amino group is involved in hydrogen bonding; however, this effect, albeit systematic, is within the precision of our calculations.

The obtained evidence of the weak effect of the surface on the ability of A molecules to form dimers through double hydrogen bonds is further corroborated by the charge-density differences shown in Figures 3A, 3C, and 4 for selected pairs on the Au(111) surface. We find the characteristic “kebab” structure showing regions of excess (green) and depleted (red) electron density along the donor–acceptor line for each hydrogen bond. Well-developed structures of these alternating regions along each bond, clearly seen in the figures, correspond to their high stability. If we compare these density differences with those obtained in the corresponding gas-phase calculations,^[23] we find that they are practically identical.

In spite of these similarities to the gas-phase situation, the charge-density difference shown in Figures 3 and 4 suggests that a certain density redistribution does happen owing to

Table 1. Energy profile of adenine pairs on the Au(111) surface.

Pair	E_{stab} [eV]	E_{ads} [eV]	E_{Hb} [eV]	$E_{\text{Hb}}^{\text{gas}}$ [eV] ^[a]	$E_{\text{def}}(D)$ [eV]	$E_{\text{def}}(\text{Au})$ [eV]
$A_5A_5(1)$	−1.01	−0.15	−0.85	−0.86	0.17	0.01
$B_5B_5(1)$	−1.02	−0.16	−0.85	−0.86	0.18	0.01
$A_2B_5(2)$	−0.88	−0.17	−0.70	−0.70	0.17	0.01
$B_2A_5(2)$	−0.88	−0.18	−0.70	−0.70	0.17	0.00
$A_1B_5(3)$	−0.85	−0.19	−0.66	−0.66	0.15	0.00
$B_1A_5(3)$	−0.87	−0.21	−0.66	−0.66	0.17	0.00
$A_2A_2(4)$	−0.78	−0.19	−0.58	−0.58	0.12	0.01
$B_2B_2(4)$	−0.77	−0.18	−0.56	−0.58	0.12	0.01
$B_2A_1(5)$	−0.76	−0.21	−0.55	−0.54	0.12	0.01
$A_2B_1(5)$	−0.78	−0.23	−0.55	−0.54	0.12	0.01
$A_1A_1(6)$	−0.64	−0.16	−0.44	−0.47	0.11	0.01
$B_1B_1(6)$	−0.64	−0.16	−0.44	−0.47	0.11	0.01

[a] E_{stab} is the total energy gained by the system. E_{ads} is the energy of adsorption for the pair on the surface. E_{Hb} is the strength of the hydrogen bonds on the surface. The corresponding gas-phase hydrogen bonding is given as $E_{\text{Hb}}^{\text{gas}}$. All energies include the essential BSSE corrections. Additionally, the deformation energies $E_{\text{def}}(D)$ and $E_{\text{def}}(\text{Au})$, which characterize the sum of energy losses due to the deformation of each species, are given for the dimer and the Au(111) surface, respectively. B corresponds to flipped A.

interaction with the surface. In particular, there is some polarization of the amino groups, clearly visible (see especially Figures 3B and 3D, where only the effect of the surface is shown). These results suggest that care still needs to be exercised when suggesting particular models for the two experimentally observed self-assembled A monolayer structures, as there is, indeed, a small influence of the surface.

Therefore, we used the following approach to determine the appropriate atomistic models for the two A phases observed in the STM images: 1) Systematic generation of all possible gas-phase A monolayer structures by considering all possible A dimer connections leading to an hexagonal network; 2) Preselection of those that have suitable lattice vectors (within some error), are of the correct space symmetry, and have high stabilities; 3) Full-scale SIESTA calculations of these structures; and 4) final selection. This approach is a slightly modified version of a previously developed method.^[28]

By means of this approach two monolayer structures were identified to explain the observed assemblies and these are shown as overlays in Figures 1C and 1D. The two structures have different orientation of the A molecules: In phase I, A molecules are of the same chirality, whereas in phase II, A molecules of both chiralities are present in equal amounts in the structure. The structure I is chiral; this, however, may not be distinguishable in the STM image; the structure II is nonchiral, in agreement with the observed chirality of this phase.

The two structures were found to have very similar gas-phase stabilities of -0.88 and -0.91 eV per molecule for phases I (Figure 1C) and II (Figure 1D), respectively. In fact, the existence of the thermodynamically more stable (in the gas phase) structure II is rather surprising and unexpected, because, in contrast to structure I, it does not contain the most-stable A pair, $A_5A_5(1)$.^[23] Thus, if one were to rely only on the most-stable A pairs to construct all monolayer possibilities,^[29] one would inevitably fail to identify these particular monolayer structures.

The transition between the two self-assembled monolayer structures can be explained as follows. Initially, the molecules that are deposited on the surface aggregate into the strongest base unit, namely the centrosymmetric dimer $A_5A_5(1)$. These dimers are free to join one another to form the monolayer phase I with homochiral domains. However, as the temperature is increased, a larger phase space is available to the molecules, which facilitates the formation of phase II. Our SIESTA molecular dynamics (MD) simulations indicate that an individual molecule on a surface may flip at relatively low temperatures (400 K). Hence, several processes may contribute to the formation of the heterochiral phase II: 1) Mixing of molecules from neighboring homochiral islands of opposite chirality: the molecules detach from the islands edges and then diffuse across the surface; 2) Detached molecules flip and then attach again, and 3) Detached molecules may desorb, with subsequent adsorption of molecules of either chirality.

Actually, the two A monolayers that are observed and modeled here are not the most stable ones in the gas phase. Interestingly, the most-stable gas-phase monolayer was used to explain the observed assemblies on the Cu(111), graphite, and MoS_2 surfaces.^[4-7] The calculation of the monolayers with

the gold surface is too expensive to perform, even for a single monolayer, as was explained above, and we can only speculate here on the role of the Au(111) surface in picking up the particular structures. The observed effect of the surface is especially puzzling, as we have carefully proven by comparing geometry, energy profiles, and electron densities of the A dimers in the gas phase and on the surface that the effect of the surface on the A–A dimers must be very small.

We tentatively suggest that the following factors may be at play: 1) Although interaction of a single A molecule and even of an A dimer with the Au surface is small, this may not be the case for large islands of A molecules observed in STM images (the accumulated strain due to mismatch may render some of the monolayers less preferable than the others); 2) We have not taken into account the van der Waals interactions between the molecules and the surface.

It is well known that DFT calculations do not account for van der Waals interactions. As our DFT adsorption energies are small, one may expect the van der Waals energies to be small as well. On the other hand, this is not always the case. It is known, for example, that for adenine adsorbed on graphite,^[18] the van der Waals interactions are significant. Cluster quantum-chemistry (QC) calculations of single A molecules with small Au clusters predict noticeable energies.^[17] Although cluster calculations may not be representative in this case, as only small cluster sizes were considered in Reference [17] and hence the polarization effects they accounted for may be quite different from those of a real (infinite) metal (for instance, it is known that the reactivity of Au clusters changes significantly with size),^[30] it is quite possible that van der Waals interactions are important in our system. In this respect, we note that although the first-principles calculations of the van der Waals contribution to the binding energy are not straightforward,^[31] we do expect that it may increase the binding energy of A on the Au(111) surface. However, because of the nature of the van der Waals interaction, we believe that there will be no effect on its corrugation across the surface; that is, there will be no strong dependence of the energy of A on the lateral position of the molecule on the gold surface. Indeed, we found in our preliminary calculations with the force field developed in Reference [17] on the basis of QC calculations of A interacting with small Au clusters, that the adsorption energy of A on the Au(111) surface should be close to -1.0 eV, mainly due to the van der Waals interactions. However, the effect of the van der Waals interactions on the corrugation of the surface potential is still very small, with the calculated diffusion barriers amounting to no more than 10% of the binding energy (no more than 0.1 eV). This is in agreement with what was found for adenine on a graphite surface.^[18] Therefore, even inclusion of the van der Waals interactions does not change our conclusion that A molecules may freely diffuse across the surface at room temperature.

3. Conclusions

In summary, two adenine self-assembled monolayer structures, one of which is reported for the first time herein,

were experimentally observed by STM to coexist on the Au(111) surface. Extensive calculations of adenine and its pairs with the Au(111) surface show that the interaction of one or two molecules with the flat metal surface, such as Au(111), is very weak. Moreover, the effect of the surface on the hydrogen bonding between molecules is also very small. However, the small redistribution of the electron density between the adenine molecules and the Au surface that we observed indicates that there might be some lateral registry with the underlying surface. This interaction perturbs the much stronger intermolecular interactions binding the molecules together in the monolayer. The peculiar effect of this is that the most-stable gas-phase monolayer^[2,11,28,29] seems to be distorted so much on the surface that to relieve the strain another gas-phase monolayer, which has a different periodic pattern, becomes more energetically favorable, especially for islands larger than a certain size. Hence, although the gas-phase analysis of possible monolayer structures should still be considered as an essential step in the modeling of supra-molecular assemblies on flat metal surfaces, care should be exercised in choosing possible configurations as models for the observed structures: one cannot rely on the order of stability of different gas-phase structures as these may be modified by the cumulative effect of the surface.

Surfaces such as Au(111), which have weak interactions with small molecules as well as weak registry requirements and little or no influence on the hydrogen bonding within nanostructures, should be ideal templates for molecular self-assembly, which may reveal many phases. In fact, multiple phases of similar small molecules, such as the DNA base guanine,^[10] cyanuric acid, and melamine^[32] have already been observed on the Au(111) surface. In addition, gas-phase modeling techniques for the nanostructures are seen to be accurate in such cases if conducted with due care.

4. Experimental Section

All STM experiments were performed in a UHV chamber (base pressure 1×10^{-10} Torr) equipped with a variable-temperature, fast-scanning Aarhus STM,^[33] 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.^[34] Adenine powder (Sigma-Aldrich, 99%) was loaded into a glass crucible in the molecular evaporator. After thorough degassing of the adenine crucible by keeping the crucible at 370 K for an extended period (≈ 24 h), adenine molecules were deposited on the clean Au(111) substrate by thermal sublimation from the molecular evaporator held at 370 K, while the substrate was held at room temperature. The STM experiments were carried out at low temperatures (100–150 K) to minimize the surface mobility of the adenine molecules and thereby stabilize the molecular structures formed on the surface.

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