Aggregation of C$_{70}$-Fragment Buckybowls on Surfaces: π−H and π−π Bonding in Bowl Up-Side-Down Ensembles

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ⓢ *Supporting Information*

ABSTRACT: The self-assembly of the C$_{38}$H$_{14}$-buckybowl, a fragment bowl of the C$_{70}$ fullerene, has been studied with scanning tunneling microscopy on the Cu(111) surface. Isolated molecules adsorb bowl opening-up with the center C6 ring parallel to the surface. In extended 2D islands, however, 1/3 of the molecules are oriented such that the bowl opening points down. From a detailed analysis of relative orientation of the molecules, the nature of intermolecular lateral interactions is identified. In densely packed islands, π−π bonding between convex sides of the bowls dominate, while π−H bonding between rim and convex sides plays the important role in small molecular 2D clusters.

Figure 1. Top and side views onto ball-and-stick molecular models of corannulene (a) and the C$_{2v}$-symmetric C$_{70}$ fragment buckybowl C$_{38}$H$_{14}$ (b, **1**).

A common misconception in molecular crystallography is that short distances between functional groups of two molecules are taken as attractive intermolecular bonding, instead realizing that short distances rather emerge from packing constrains of all molecules in the vicinity.[1] In frozen dimers or small ensembles, however, conclusions on directional attractive binding motifs should be valid. Understanding noncovalent interactions in carbon-based materials is also of fundamental importance for future nanotechnologies.[2] For various reasons, atomically flat noble metal surfaces in ultrahigh vacuum are perfect templates for studying intermolecular interactions under well-defined conditions. First, they provide high 2D diffusivity for organic molecules so that they can freely interact and aggregate upon cooling. Moreover, they enable the use of scanning tunneling microscopy (STM), a proximal method that provides submolecular resolution and information on the relative alignment of molecules and, as we demonstrate here, allows conclusions on the nature of the intermolecular interaction.

Fragments of fullerenes, so-called buckybowls, have attracted much interest recently due to their rich metal coordination chemistry.[3] Because of their special electronic properties based on the pronounced difference of chemical activity between their concave and convex sides, these bowl-shaped, polynuclear hydrocarbons are particularly promising for organic electronics, such as organic light emitting devices (OLEDs) or organic field effect transistors (OFETs). Corannulene (C$_{20}$H$_{10}$, Figure 1a), for example, shows an intense blue-light electroluminescence.[4] Because of its ability to form very stable tetra-anions, it is an excellent electron acceptor and induces substantial interface
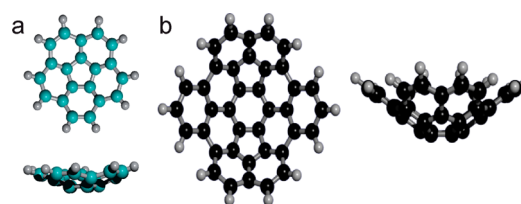
dipoles when adsorbed on metal surfaces.[5−7] Modification of surfaces with buckybowls has also been motivated by better understanding crystallization phenomena at surfaces, like reversible phase transitions,[8,9] and by stereochemical issues, such as bowl-in-bowl complexation[10,11] and pentagonal molecular tiling in the plane.[12−15]

The hydrogen termination at the rim of buckybowls usually permits only weak adsorptive interactions with a surface, whereas the substantial higher electron density at the convex side causes strong electrostatic interactions with metallic surfaces. Hence, buckybowls preferentially adsorb in a bowl-opening-up configuration on metal surfaces.[6,8,13−15] However, it is anticipated that stronger lateral interactions between larger bowls in a 2D lattice should favor bowl opening-down configurations in order to maximize the π−π interactions between convex sides. Here we show via STM that the 2D aggregation of the C$_{70}$-fragment bowl C$_{38}$H$_{14}$ (**1**, Figure 1) on a Cu(111) surface leads indeed to such stereochemical arrangement. At submonolayer coverages, that is, under conditions of 2D self-assembly at which attraction among the molecules dominates in lateral interactions, one-third of the molecules in a 2D long-range ordered structure are aligned with their bowl opening pointing down. Due to an exact analysis of the relative alignment of the buckybowls, binding motifs such as π⋯H−C bonding between bowl rim and convex bowl-surfaces as well as π−π interaction between convex bowl-surfaces are revealed.

The experiments were performed in an ultrahigh vacuum chamber ($p = 5 \times 10^{-10}$ mbar). The molecules were deposited *in vacuo* from an effusion-cell evaporator ($T = 583$ K) onto the substrate surface at room temperature. STM images were acquired with a variable-temperature STM (Omicron Nano-

technology GmbH, SCALA PRO 4.1 software) after cooling the sample to 60 K in constant-current mode with bias voltages ranging from −3.08 to +2.57 V and tunneling currents in the range between 37 pA and 1.23 A. The Cu(111) single crystal (MaTecK, Jülich) was cleaned by cycles of argon ion bombardment and subsequent annealing to 900 K for 2 min. $C_{38}H_{14}$ was synthesized as described in detail previously.[16] All images were processed using SXM-Shell (Univ. Basel, Switzerland) and/or SPIP 3.0 (Image Metrology, Denmark). In part, inverse-Fourier-Transformation and low-pass filtering was applied for image noise reduction. Evaluation of unit cell dimensions was performed through inverse Fourier Transformation in the SPIP program with a statistical evaluation of the extracted lengths and angles. Modeling of molecular structure and the relative molecular alignment was performed with HyperChem for Windows. The Cu(111) surface was mimicked by a fixed single Cu atom layer with bulk distances. For periodic boundary conditions, a surface cell containing 374 Cu atoms in a single layer (size $17a \times 11\sqrt{3}a$; $a = 2.5533$ and 50 Å into the vacuum) was chosen. For the geometry optimization, a conjugate Polak-Ribiere gradient was used with a termination gradient smaller than 10^{-4} kcal·Å^{-1}·mol^{-1}.

Figure 2a shows an STM image of large self-assembled structures as well as individual molecules of 1 on Cu(111) at 60 K and a coverage of about a half of a closed-packed monolayer. Isolated molecules (Figure 2b) exhibit an elliptical shape with a dark protrusion in the center. Such appearance is explained by a bowl opening pointing up orientation of the adsorbate. Consequently, the rim dominates the STM-contrast of the buckybowl, as confirmed by Extended Hückel calculations for the expected STM appearance (Figure S1). At a tunneling polarity that probes unoccupied electronic states, the two rim-naphthalene and the two rim-benzene groups are clearly resolved (Figure 2b). The essentially equal brightness of all these parts of the rim for the isolated molecule (Figure 2b) suggests a parallel surface alignment of the center C6 ring, which is, as lowest part of the bowl, then the adsorption site at the molecule. One of the five C6 rings of corannulene adsorbed on Cu(111) has previously been identified as binding site,[8] with a binding energy of 64 kcal/mol.

The self-assembly within the large islands is characterized by a complex pattern and different alignments of molecules. The edges of such islands are decorated with molecules that show an identical tilt of the bowls (Figure 2c). Such tilt is already observed for a molecule in a dimer (Figure 2d). The top-most part is a benzene ring of the rim, hence, dominating the STM contrast. In such tilted configuration, it seems that the opposite end-benzene ring is now the molecular binding site to the surface. The cause for the tilt, however, seems to be $\pi\cdots H$ bonding between the top benzene ring and rim hydrogen atoms of the not-tilted adjacent bowl (Figure 2d). For the row of tilted molecules at the island edge (Figure 2c), a similar bonding scenario is assumed. Although buckybowls can substantially restructure metal surfaces,[17] any role of copper atoms in the intermolecular binding can be safely excluded here.

Within the islands, the molecules are congealed into a rather complex motif. Ignoring a few alignment defects, the long-range order is best described by a (27×27) unit cell (Figure 3).[18] The STM appearance suggests three different modes of alignment. One-third of the 27 molecules in the unit cell show a contrast that is clearly different to the above-described rim-dominated STM contrast. They show only a bright
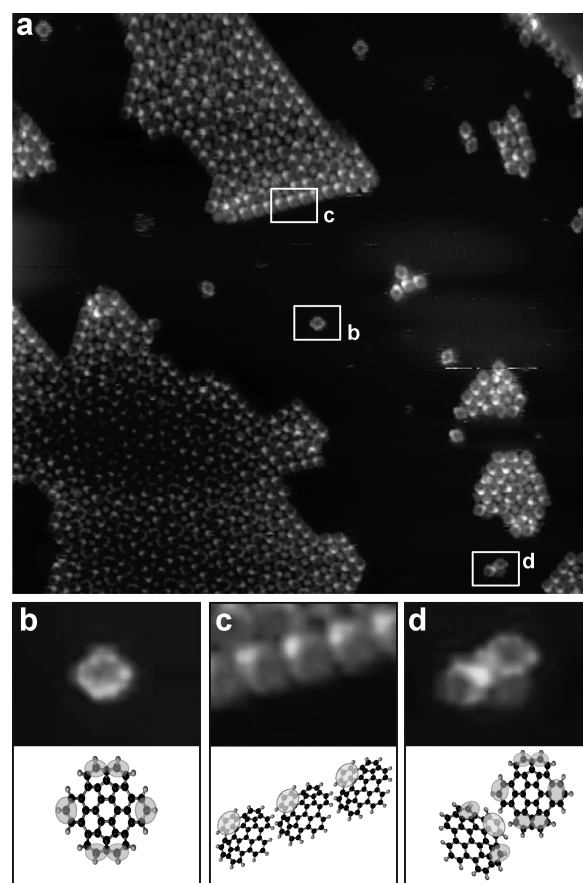

Figure 2. (a) STM-image (60×60 nm^2, $U = 0.7$ V, $I = 168$ pA, $T = 60$ K) of various self-assembled motifs of 1 on Cu(111). Large islands, in which the molecules show different modes of relative alignment, are observed. (b) Single molecules appear as elliptic shapes. The entire rim is imaged with equal brightness, indicating an adsorbate with the bowl-opening pointing away from the surface. (c) The edges of the islands are decorated with molecules that show an identical distinct tilt of the bowl. (d) A lateral interaction leading to a tilt of one molecule is already observed for dimers. The correlation of the STM contrast with the corresponding parts of the molecules is indicated as gray ellipses below the cut-outs (b−d, all 5.2×4.0 nm^2).

protrusion in the center of the molecule, suggesting a bowl opening-down orientation. The opening-down species are decorated with molecules in two different ways: either by six tilted bowls with a benzene ring pointing up (Figure 3b) or by three benzene ring-up and three naphthalene groups-up bowls (Figure 3c). Consequently, the unit cell contains 9 bowl opening-down, 12 benzene-up, and 6 naphthalene-up molecules. In this structure, the bowl opening-down species actually forms a (9×9) sublattice on the Cu(111) surface (indicated by the smaller cell in Figure 3a).

The models for the two bowl opening-down motifs are shown in Figure 3d,e. Only three of the six molecules decorating the opening-down bowl have their convex sides pointing toward the center bowl. The convex bowl sides of the other three molecules point away from the center bowl, because they have established $\pi-\pi$ interactions with the convex sides of adjacent opening-down bowls. Figure 4 highlights this feature by means of a virtual line scan through three molecules in the STM image (Figure 3c) and the corresponding structure model (Figure 3e). The molecule close to point B interacts through its convex side with the opening-down bowl in the middle. The
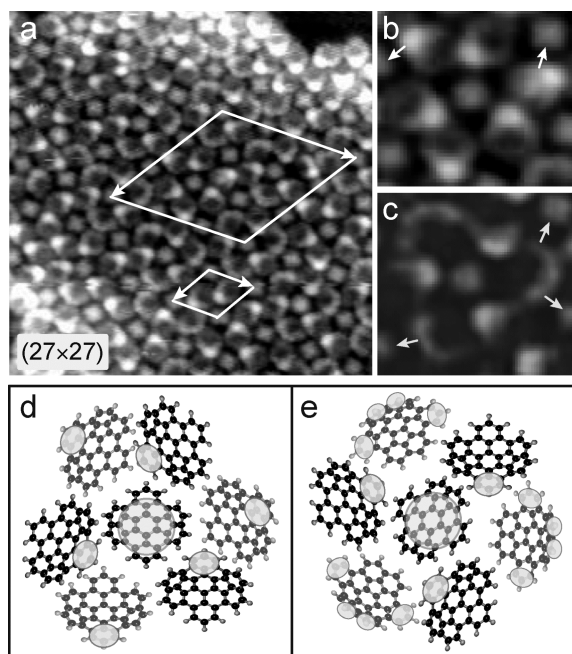
Figure 3. (a) STM image (17 × 17 nm², U = 699 mV, I = 168 pA, T = 60 K) of the long-range ordered island phase. The (27 × 27) unit cell and a smaller (9 × 9) cell are indicated. One-third of the molecules show a contrast explained by a bowl opening pointing down alignment. (b and c) Details (4 × 4 nm²) of the island structure shown in (a). An opening-down bowl is surrounded by six benzene ring-up bowls (b) or by three benzene ring-up and three naphthalene group-up bowls. The arrows point at adjacent opening-down bowls from molecules that face them with their convex side. (d and e) Molecular model of the motifs shown in (b) and (c).
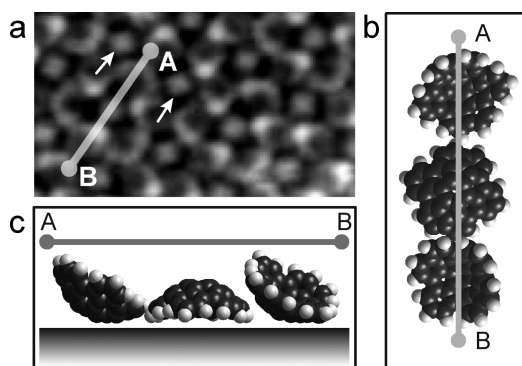

Figure 4. Alignment of three molecules of a structure motif including the three different observed orientations, benzene and naphthalene up, as well as opening-down. The molecules lie on one line (a). The naphthalene group-up bowl interacts with its two benzene rings with two opening-down bowls (marked by arrows in (a)).

naphthalene group-up molecule on the other side of the opening-down bowl actually interacts with two opening-down bowls located near point A (arrows in Figure 4).

So far, an opening-down adsorption geometry has only been reported for sumanene on Ag(111).[19] This orientation has been explained by an inversion of the molecule during the process of adsorption in order to orient the three sumanene C6 rings parallel to C6 rings of adjacent opening-up molecules. The inversion barrier of 19.6 kcal/mol for sumanene in solution is considerably lower than that for **1**,[20] which amounts to 79.8 kcal/mol.[16] It is therefore more likely that the $C_{38}H_{14}$ bowl

turns during nucleation of the islands assembly such that it shows the best π−π overlap with convex sides of adjacent molecules.

The here reported complex island structure, covering 27 Cu surface atoms per molecule, is only observed for submonolayer coverages and low temperatures, when nucleation and growth is governed by attractive interactions. Such interactions are also identified for dimers and smaller aggregates (Figure 2). At full monolayer coverage, a different, slightly denser structure (one molecule per 25 Cu surface atoms) is observed (Figure S2).

The intermolecular interactions concluded from the STM investigation are confirmed by molecular mechanics modeling, using the Amber force field approach (Figure 5). The dimer
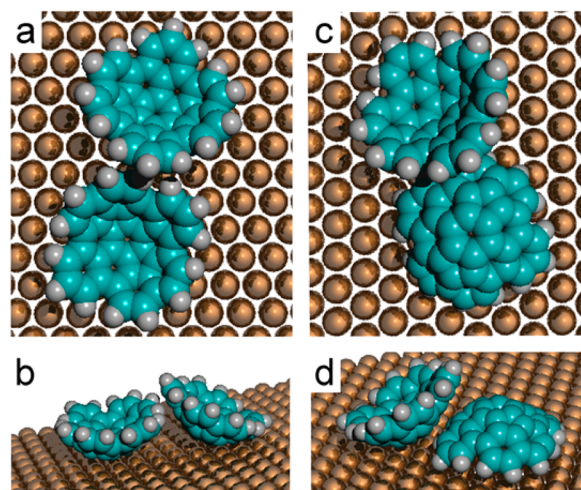

Figure 5. Top and side views on alignments of bowl-dimers as obtained from molecular modeling calculations. (a and b) Interaction of two bowl opening-up molecules. (c and d) Interaction of opening-up bowl with an opening-down bowl. These final configurations agree well with the models derived from STM.

motif (Figures 2d, 5a,b) was modeled by keeping the six carbon atoms of the center bottom ring fixed, while all other carbon atoms, including those of the second bowl, were allowed to relax. The difference of the energy for interacting and noninteracting molecules leads to an interbowl binding energy of 4.3 kcal/mol, which lies in the typical range for C−H···π bonds.[21,22] The initial placement of the second bowl had only a small influence on the final results, which were all within a difference of 0.04 kcal/mol in energy. A configuration that is only slightly higher in energy, but almost identical in structure, and hence not distinguishable with STM, is shown in Figure S3.

The bowl opening-down interaction observed in the 27-molecule unit cell was modeled by placing one bowl opening down and the other opening up without keeping any molecular part in the initial configuration fixed. The final lowest energy configuration has a binding energy of 8.0 kcal/mol (Figure 5c,d). This result is in good agreement with calculated values obtained for benzene−carbon nanotube interactions,[22] substantially larger than π−π interactions in benzene dimers,[23] and much smaller than corannulene bowl-in-bowl interactions, for example.[10] As observed in the complex island structure, the dimer configuration shows a small azimuthal tilt of the opening-up bowl such that the benzene ring is not parallel to the opening-down bowl (Figure 5c). The closest distance is rather established by two C6 rings in naphthalene groups, one at the rim of the opening-down bowl and one more toward the

center, located below the upper benzene ring in the opening-up bowl (Figure 5d). Such alignment is probably supported by a favored surface-binding of the low-lying benzene ring of the opening-up bowl (Figure 5a,c). An example with the naphthalene group of the opening-up bowl interacting with the opening-down bowl results in higher energy (Figure S4). As for the dimer, modeling more bowls within a (9 × 9) bowl opening-down unit cell delivers exclusively benzene ring-top motifs of the opening-up bowl, but indicates that in addition C−H···π bonds might be present as well (Figure S5).

In conclusion, we have studied the 2D self-assembly of a larger buckybowl with STM at submolecular resolution. By exact analysis of the relative alignments of the bowls in different motifs, the nature of the intermolecular bonding, namely C−H···π and π−π bonds, is identified. Relative alignments of molecules obtained from molecular modeling calculations support this assignment.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b02412.

> STM appearance modeling, STM image of complete monolayer and more molecular mechanics modeling examples (PDF)

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Notes

The authors declare no competing financial interest.

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