Corannulene Derivatives

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# Self-Assembly of Fivefold-Symmetric Molecules on a Threefold-Symmetric Surface**

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Fivefold rotational point-group symmetry plays a special role because of its incompatibility with translational symmetry. This symmetry mismatch has attracted interest for a long time, going back to Dürer[1] and Kepler,[2] who demonstrated that a wealth of unusual structures could be produced by tiling the plane with regular pentagons. These ideas have been used with great success in biology to understand the structure of virus capsids made from pentamers[3,4] and in material science to clarify the nature of quasi-crystals.[5,6] Transposed into the domain of surface science, they suggest that new and interesting patterns could be formed by depositing fivefold-symmetric molecules onto a substrate.[7] An example of this approach was reported recently. The adsorption on Cu(110) of corannulene, which is a $C_{60}$ fragment bowl with a fivefold symmetry axis (Figure 1 a), was studied by scanning tunneling microscopy (STM) and other techniques.[7] The molecules form a quasi-hexagonal superlattice whose structure is dominated by the vertical molecule–substrate interaction. The molecules occupy identical adsorption sites in one domain. But the large distance between these sites leads to a rather small contribution of the fivefold molecular symmetry to the intermolecular interaction, which appears not to be strong enough for the symmetry mismatch to significantly influence the resulting structure. To observe more pronounced effects, the strength of the intermolecular interactions must be increased to reach the onset of short-range repulsive interactions, at which point the fivefold shape of the molecule is expected to contribute in a much stronger way. On crystalline surfaces, where the molecules tend to stay at or near their preferred adsorption site, this requirement can be met if the size of the molecule fits adequately with the substrate (i.e. if it is "commensurate") for neighboring molecules to approach closely or even to come in "contact".

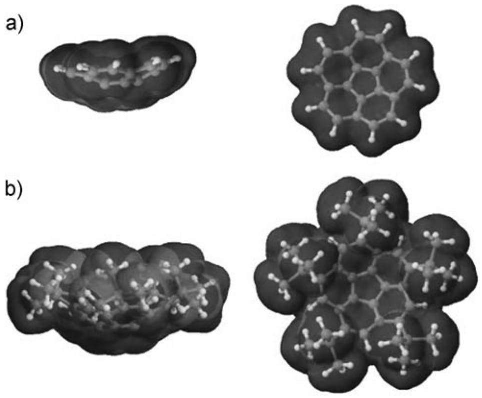

*Figure 1.* Ball-and-stick representations and van der Waals surfaces of a) corannulene and b) PTBC (top and side views). The van der Waals surfaces were produced with *Jmol*.[10]

We report herein on the adsorption of a corannulene derivative, penta-*tert*-butylcorannulene[8] (PTBC; Figure 1 b), on the high-symmetry Cu(111) surface studied by low-temperature STM (5 K) and structure calculations. Note that the synthesis of corannulene has been improved to achieve an overall yield of 32 % from 2,7-dimethylnaphthalene, compared to 13 % with standard methods (see the Supporting Information). The addition of five *tert*-butyl groups enhances the fivefold shape of the molecule relative to that of corannulene, as indicated qualitatively by the van der Waals surfaces displayed in Figure 1. Furthermore, the C–C σ bonds connecting these lateral groups to the central part of the corannulene molecule are rather flexible, giving the molecule the possibility to adapt itself to the substrate surface structure and rendering the commensurability condition mentioned above less stringent.

Note that the bowl-to-bowl inversion, which is known to happen easily at room temperature in corannulene,[9] is also likely to affect PTBC, but this process should be frozen at low temperature and for the adsorbed molecule. The PTBC molecule thus adopts two chiralities, as two equivalent sets of sites are available for the *tert*-butyl groups on the corannulene core.

Deposition of PTBC on Cu(111) at room temperature and subsequent annealing at 100 °C for one hour leads to the formation of molecular islands, (STM image in Figure 2 a), which coalesce to form a monolayer at higher coverage (see Supporting Information Figure S2). In this structure, individual molecules appear as five lobes surrounding a central depression in a fivefold-symmetric pattern (Figure 2 b). As shown below, each of the five lobes marks the position of a

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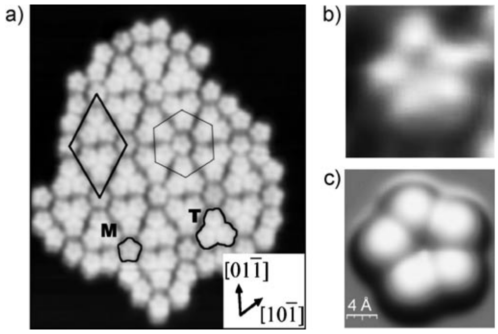

*Figure 2.* a) STM image of an island of PTBC on Cu(111). M indicates a single PTBC molecule (monomer), and T indicates an assembly of three molecules (trimer). The rhombus and the hexagon delineate a unit cell and its seven-molecule basis. $T = 5$ K, $V = -1.1$ V, $I = 174$ pA. Image size 18.1×21.4 nm. b) Enlargement of a single PTBC molecule (off-center monomer in a cavity). Image size 1.94×2.1 nm. c) Computed STM image of a single PTBC molecule.

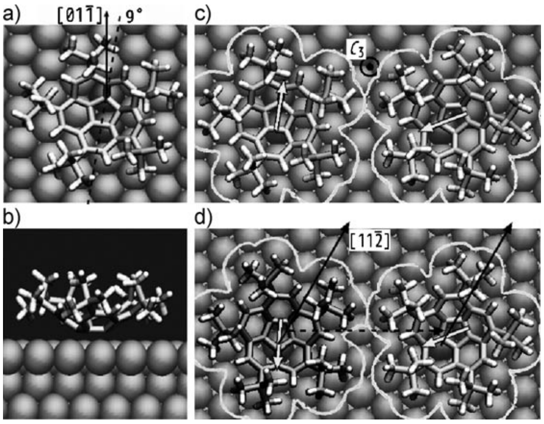

*Figure 3.* Calculated adsorption configuration of a, b) the PTBC monomer on Cu(111), c) the homochiral dimer and d) the heterochiral dimer. The white lines in (c) and (d) correspond to the van der Waals surfaces of the molecules, and the arrows show the symmetry operations in the dimers.

*tert*-butyl group, as previously observed with Lander molecules.[11,12]

This supramolecular structure can be described as a tiling of the plane involving two types of units: single PTBC molecules (monomers) and assemblies of three molecules (trimers). The trimers appear as compact, apparently threefold-symmetric objects, with a shape similar to a tip-truncated triangle. Because they are not perfect triangles, they cannot fill the plane, and some space is necessarily not covered. This "lost" space is used to generate hexagonal cavities, which can accommodate one monomer (Figure 2a). This particular arrangement results in a nearly perfect filling of the plane.

A careful examination of Figure 2a (see Supporting Information Figure S3) shows that the monomer can be imaged in two different ways in the cavities: In the first one, the molecule is off-center in the cavities, with two *tert*-butyl groups closer to adjacent trimers. In the second, the monomer appears with six lobes. The reasons for this latter phenomenon are unclear, and a definitive interpretation cannot be provided at this stage.

The lattice in Figure 2a is hexagonal, with a unit cell given in matrix notation by $\left(\begin{smallmatrix} 11 & 7 \\ -7 & 18 \end{smallmatrix}\right)$ (relative to the ([10$\bar{1}$], [01$\bar{1}$]) basis set), comprising 247 copper atoms and a sixfold-symmetric basis of seven molecules, as indicated in Figure 2a. On average, one molecule occupies an area of more than 35 substrate atoms. Two domains of this structure exist, which are related by a mirror symmetry element of the substrate (see Supporting Information Figures S4 and S5).

The adsorption calculations for a single molecule were carried out with an extended semiempirical atom superposition and electron delocalization approach (ASED+;[13] see the Supporting Information). The molecule is found to sit with the bowl opening pointing outwards from the surface. The shape of the bowl is close to that in the free molecule, but its depth has increased by 0.5 Å (see the Supporting Information). The pentagonal hub is positioned parallel to the surface on a bridged site with one of the spoke bonds making an angle of approximately 9° with a [01$\bar{1}$] row of the substrate (Figure 3a, b).

As can be inferred from Figure 3b, the *tert*-butyl groups do not play a major role in the adsorption of a single PTBC molecule. They are too far from the surface to contribute except by their van der Waals interaction with the substrate. The adsorption configuration of a single PTBC molecule should then be comparable to that of corannulene. Indeed, the adsorption configuration of PTBC is close to that determined for corannulene in a monolayer domain on Cu(110),[7] except that the molecular axis is tilted by 6° relative to the surface normal on Cu(110).

The STM image of a PTBC monomer on a bridge site was computationally reproduced with the elastic quantum chemistry scattering technique (ESQC;[14] Figure 2c), which takes into account the complete atomic structure of the tip and the surface (see the Supporting Information). A good qualitative correspondence with the experimental STM images is found (Figure 2b), with the five lobes corresponding to the five *tert*-butyl groups.

Adsorption simulations were extended to systems of first two, then three PTBC molecules in close proximity. The energetically most favored configuration was calculated for both homochiral (Figure 3c) and heterochiral dimers (Figure 3d). In both cases, the molecules adopt approximately the same adsorption site as the isolated molecule. They are located on the same type of bridge sites with the same orientation (within ±0.2 Å for the position and ±2° for the orientation). In Figure 3c, the two adsorbed molecules are approximately symmetry related by a 120° rotation along a $C_3$ axis of the substrate, which does not change the chirality. In Figure 3d, they are related by a substrate mirror symmetry plane intersecting the surface along the [11$\bar{2}$] direction, which changes the chirality of the molecule. The two molecules constituting the dimer cannot align their edges as in a Dürer–Kepler pentagon tiling because of the molecular orientation imposed by the substrate. The center-to-center intermolecular distance is 14.3 Å. As shown in Figure 3c, d, the van der Waals surfaces of the two PTBC molecules are in contact for this distance, suggesting that this structure is the most compact configuration achievable for a dimer on this substrate.

The optimized structure for the homochiral trimer is presented in Figure 4a. The molecules occupy approximately equivalent bridge sites: the positions of two of the molecules are nearly identical to the dimer positions, while the third PBTC molecule (in the lower left-hand corner) is shifted by 0.6 Å away from the bridge site and towards a hollow site. The molecules in the trimer are approximately symmetry related by 120° rotations along a $C_3$ axis of the substrate, giving the trimer an approximate threefold symmetry. Calculations were also performed for a trimer consisting of two PTBC molecules of one chirality and a third PTBC molecule of the opposite enantiomer. The resulting structure (Figure 4b) is not significantly different, and the three molecules are even closer to their optimal adsorption site.

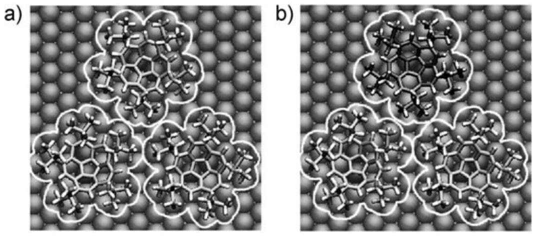

*Figure 4.* Optimized adsorption configuration of a) a homochiral and b) a heterochiral PTBC trimer.

Remarkably, the positions of the *tert*-butyl groups are nearly identical for both trimers. These two configurations are then expected to be indistinguishable in the STM image. There are three points of contact between the three PTBC molecules constituting the trimer, as indicated by the van der Waals surfaces drawn in Figure 4. This observation suggests that the compactness of the structure is limited by the short-range repulsive interactions, which are determined by the complex details of the conformation of the three *tert*-butyl groups involved in the intermolecular contact. Comparison of the two structures indicates that the interaction of the corannulene with the surface plays a less important role, as the adsorption configuration of the individual molecules is slightly different in the two structures. This observation is supported by energy calculations, which give a decrease of the isolated-molecule adsorption energy of 0.04 eV from the bridge site to the hollow site (0.13 eV to the top site), while the van der Waals energy of a trimer is 0.15 eV.

The information extracted from the STM data and the calculations are combined in the model presented in Figure 5. It was built from trimers with the optimized adsorption structure in Figure 4a. Note that it could have been done equally well with the structure in Figure 4b, since the van der Waals surfaces are nearly identical in both cases. It is seen that a good agreement with the experimental data can be reached. There is only one point of contact between adjacent trimers, as indicated by the van der Waals surfaces drawn in Figure 5.

These observations show that the complex structure adopted by the PTBC monolayer on Cu(111) results from the contribution of three distinct interactions: Attractive van der Waals interactions, which tend to maximize the compactness of the structure, short-range repulsive interactions, which contribute in the contact regions between the molecules, and interaction of the corannulene core with the substrate, which tries to maintain the molecule in the optimal site of the isolated molecule. The structure is highly compact: each PTBC molecule is in contact with at least two neighbors, except for the PTBC molecule centered in the cavity, as discussed previously. This arrangement is due to the fulfillment of the commensurability condition discussed above: the molecules can be very nearly in contact while adsorbed on their optimal site.

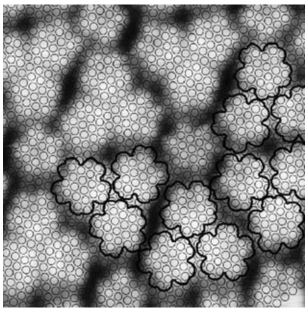

*Figure 5.* The van der Waals contours of molecular trimers superimposed on an STM image ($T = 5$ K, $7.7 \times 7.7$ nm$^2$, $V = -0.7$ V, $I = 124$ pA). Surface atoms are indicated by gray circles.

In conclusion, we have found an original structure of self-assembled molecules in which they form trimers interacting with each other and giving rise to a cavity hosting a single molecule. The presence of the trimers can be seen as a way to generate structures with symmetry compatible with that of the substrate. The symmetry mismatch between the fivefold symmetry of the molecules and the threefold symmetry of the substrate is resolved in this way.

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