Condensation of Fivefold-Symmetric Molecules in Two Dimensions

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Abstract: We report the formation of a two-dimensional glass by solidification of a two-dimensional gas of five-fold-symmetric molecules on a copper surface upon cooling. Direct observation with scanning tunneling micros-copy allows a detailed insight into the implications of a symmetry mismatch between molecular geometry and crystal lattice.

Keywords: Fivefold-symmetry · Phase transition · Polymorphism · STM · Two-dimensional glass

1. Introduction

Fivefold-symmetry is regularly observed in nature and chemistry (Fig. 1), but is in-compatible with the translational order of a classical crystal lattice.[1] There are strong indications that supercooled liquids and metallic glasses possess icosahedral short-range order,[2] and this geometry might be equally important for the glass transi-tion and the structure of liquids during the melting process.[3] But how does a liquid freeze if the geometry of its molecules pre-vent close packing into a regular crystal? Or how do such molecules arrange them-selves on a surface when they adsorb from a solution or the gas phase? In order to realize a perfect tiling in a plane, fivefold-symmetric shapes must be combined with other shapes.[4] This can be observed in the beautiful tessellations in Islamic architec-ture,[5] and the theoretical considerations by Dürer, Kepler and Penrose.[6] However, exclusive C_{5v} symmetry cannot be main-tained in a periodic tiling in two-dimen-sional (2D) supramolecular structures.[7]
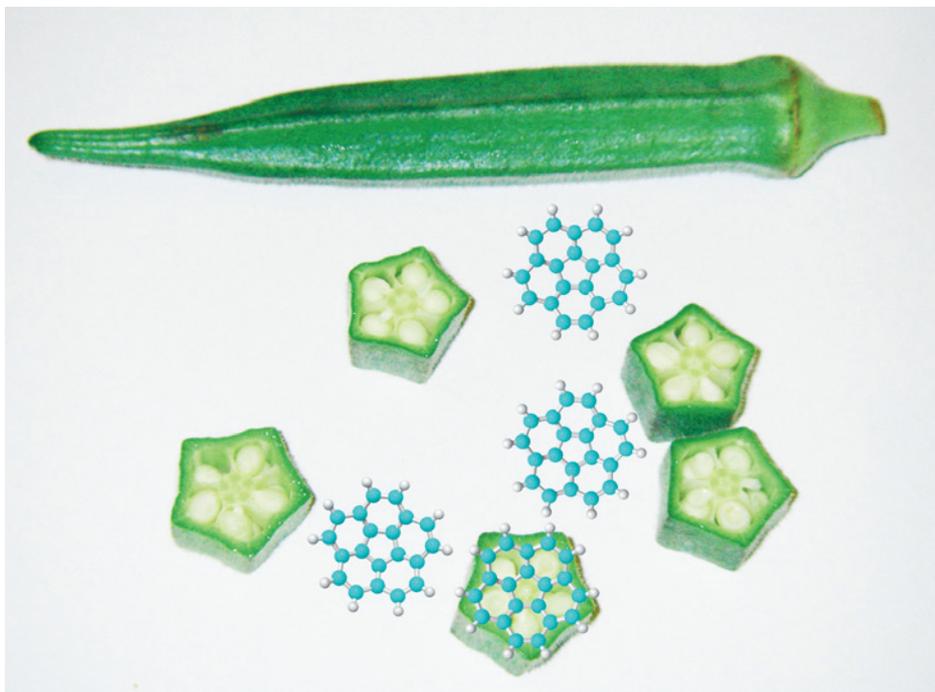

Fig. 1. Examples of fivefold-symmetry in nature and chemistry. Slices of okra and the buckybowl molecule corannulene exhibit C_{5v} symmetry.

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A rich chemistry has been developed for bowl-shaped polynuclear aromatic hy-drocarbons.[8] The buckybowl corannulene (Fig. 1) has C_{5v} symmetry and offers the op-portunity to study symmetry-mismatching on surfaces that stems from the interplay of lattice and molecular symmetry. It has been shown previously, that 2D self-assembled structures, studied with the scanning tun-neling microscope (STM), are well-de-fined model systems to provide insight into fundamental processes like molecular and chiral recognition.[9] Recently, we reported a spontaneous symmetry breaking process for corannulene on the rectangular Cu(110) surface and formation of enantiomorphous mirror domains.[10] Here we present an STM study on the consequences of sym-metry mismatch between corannulene and the hexagonal Cu(111) surface. The inter-action between the copper and the aromatic molecule is moderately weak and therefore allows a balance with the intermolecular interactions. Because of the perfect match of the size of aromatic hexagonal C6 rings and the substrate lattice, Cu(111) provides an ideal surface for thin films of aromatic molecules.[11]

2. Methods and Materials

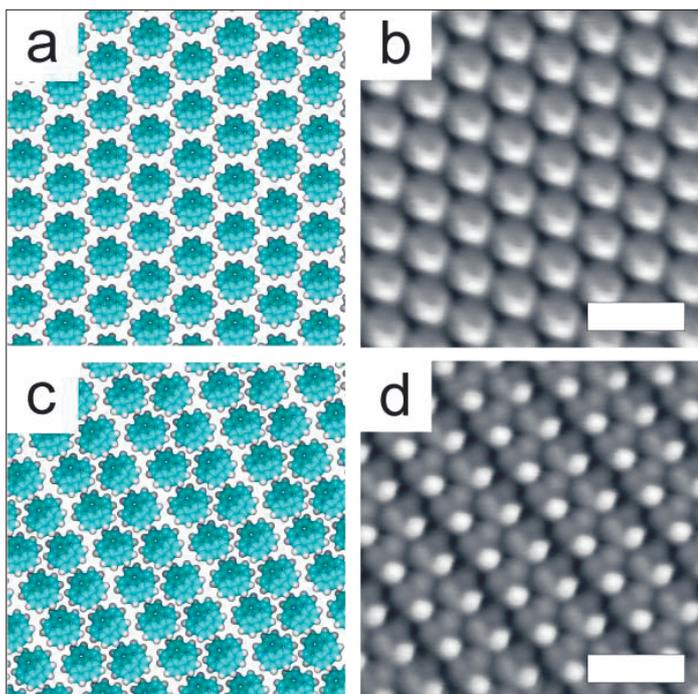The adsorbate system has been inves-tigated under ultra-high vacuum (UHV)

Fig. 2. Models and averaged STM images of the room temperature phase of corannulene on Cu(111) (a,b) and of the low-temperature phase (c,d). The molecules are tilted and reduce therefore the symmetry. Scale bars are 2 nm. STM parameters: (b) –710 mV, 50 pA, 558 nm/s, 253 K, averaged over 127 positions. (d) –1800 mV, 80 pA, 326 nm/s, 72 K, averaged over 25 positions.
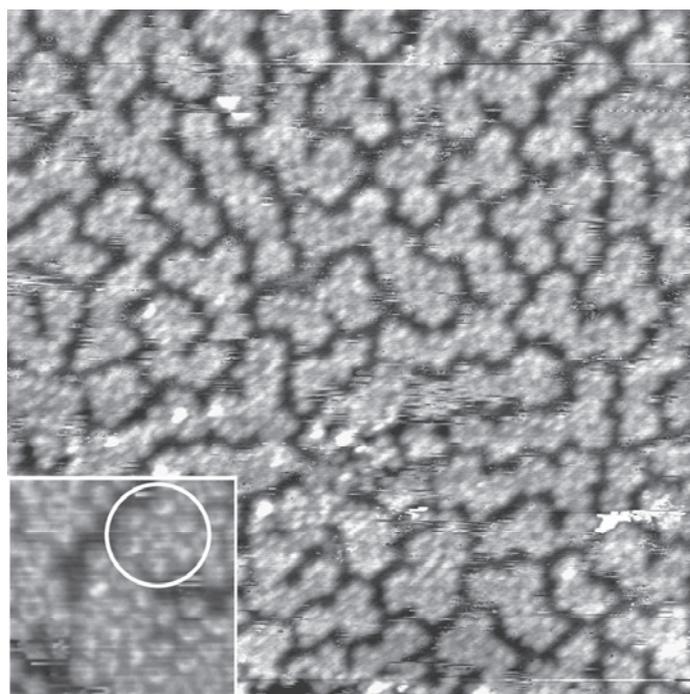

Fig. 3. STM image (50 nm × 50 nm) at 74 K of a 2D glass. A non-periodic phase is formed when the 2D gas congeals. The eight-nm inset shows the local ordering: several molecules, surrounded by tilted molecules, rest upright on the central five-membered ring, thus appearing as pentagonal doughnuts. This results in molecular 'worms', typically 3–5 molecules wide and bare copper areas (black). STM parameters: –1800 mV, 30 pA, 407 nm/s, 74 K, (inset) –1800 mV, 140 pA, 1627 nm/s, 69 K.

conditions (p ≈ 10^{-8} Pa). Corannulene was evaporated from an effusion cell *in vacuo* onto the copper crystal at room temperature. The polished Cu crystal surface (MaTecK) was cleaned *via* standard sputtering and annealing cycles as described in detail before.[12] Cleanliness and quality of the surfaces and the surface coverage of the adsorbate systems have been determined with STM. Corannulene of high purity was prepared by literature methods.[13] The crude pale-yellow solid of corannulene first obtained was subjected to chromatography on silica gel. Elution with hexane/CH_2Cl_2 (10/1) afforded corannulene (65–70%) as a light yellow solid. Crystallization from ether at ~20 ºC gave corannulene as light yellow crystals.

3. Results and Discussion

3.1 *Reduction of Symmetry*

Depending on temperature and adsorbate density, corannulene shows many different polymorphs on Cu(111). Recently, we reported reversible phase transitions in a corannulene monolayer controlled by temperature.[14] Fig. 2 shows two of these phases, a (4 × 4) structure at room temperature (Fig. 2a,b) and a 'striped' structure at low temperature (Fig. 2c,d). The molecules are adsorbed in a tilted geometry that reduces the C_{5v} to a simple mirror symmetry,

allowing the molecules to be packed in a quasi-hexagonal lattice.[15] Moreover, the hexagonal C_6 ring is placed parallel above threefold-coordinated hollow sites.[14,16] At low temperatures a denser packing is achieved by different azimuthal alignments of the molecules (Fig. 2c,d). The lattice is also built from tilted molecules with the same single adsorbate structure.

3.2 *2D Glass*

Upon cooling of a room-temperature monolayer, the much denser striped phase (Fig. 2b) is formed. As a consequence, bare copper surface must be revealed in other areas. Single molecules, too mobile to be imaged in STM, form a 2D gas in these areas. Further cooling leads to 2D solidification. Fig. 3 shows an STM image of the result. No long-range order is observed and a 2D glass of low density has been formed. A common motif contains molecules with their bowl opening pointing up, thus appearing as pentagonal doughnuts in STM, and surrounded by six other tilted molecules (Fig. 3, inset). Computational and mechanical modeling of hard pentagonal disks in a plane identified a hexagonal grid, either with orientational disorder of the pentagons or dislocations in the lattice as closest packing at higher densities.[17] At lower density, however, a fluid phase of pentagons has been reported in Monte Carlo simulations.[17a] which looks similar

to the structure observed here in the areas of the frozen gas. The remaining difference stems from the fact that the pentagonal corannulene bowls still tend to tilt away from C_5 symmetry, which was not allowed in the modeling with hard pentagons. We assume that molecules can only be aligned with their central C_5 carbon ring parallel to the surface when stabilized by adjacent, tilted bowls 'leaning' at the rim. Hence, at this local scale of the glass, we see a six-fold coordination. Recently we achieved upstanding bowls by attaching five chlorine atoms or methyl groups to the rim, not allowing a hexagonal carbon ring to be aligned parallel to the surface plane due to steric constraint.[18]

3.3 *Order in the Chaos*

Upon solidification of the 2D gas, we also observe density fluctuations, and locally, a mid-range ordering at higher density. Fig. 4 shows such an ordered phase embedded in the glassy area. This perfect periodic structure contains different types of molecular orientations. Completely upright molecular bowls are arranged into trimers (C_3 symmetry) that are, in turn, lined-up in rows. These rows are decorated with tilted molecules at the gaps between the trimers. In addition, located between these rows are zigzag rows of tilted molecules. Overall, there are seven molecules in this large unit cell.
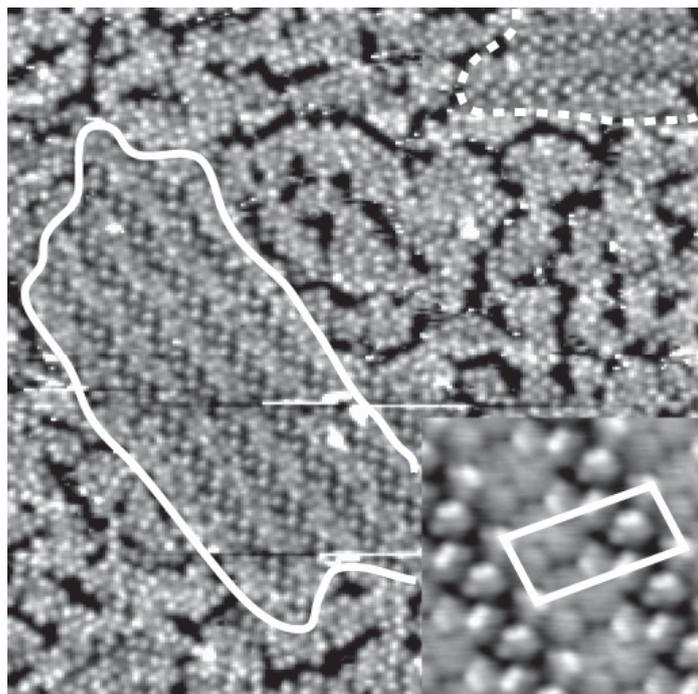
Fig. 4. STM image (50 nm × 50 nm) of an area showing an ordered structure within the glass. Two rotational domains (marked white and dashed white) are shown. The inset shows an averaged seven-nm-image. The unit cell is comprised of three upright molecules (medium gray) and four tilted molecules. STM parameters: –2000 mV, 200 pA, 1149 nm/s, 72 K, (inset) is averaged over 17 positions.
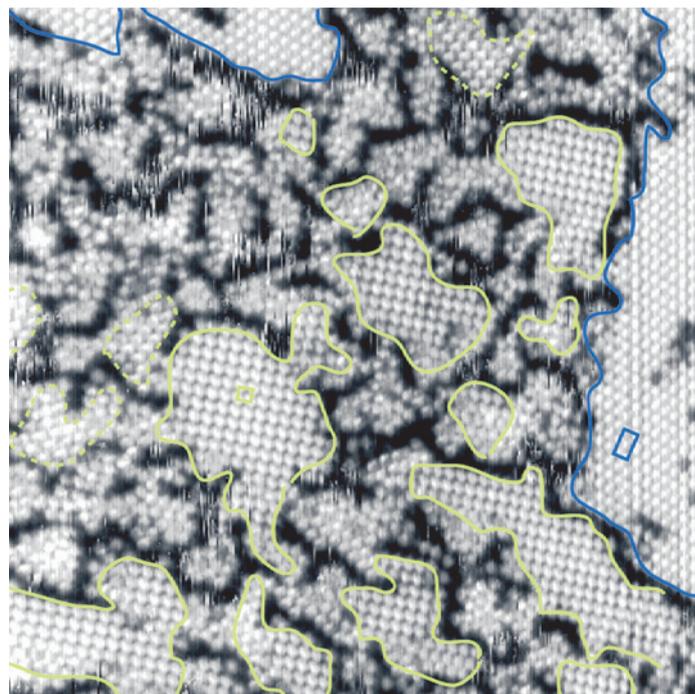

Fig. 5. STM image (50 nm × 50 nm) of a rectangular structure with medium density. Domains of this structure are marked yellow. The analysis shows a (3 4, –3 1) matrix and hence a local coverage of 1/15 molecules per Cu atom. Rotational domains are marked dashed yellow. The blue lines mark the much denser stripe-domain (Fig. 1b). STM parameters: –1800 mV, 50 pA, 781 nm/s, 66 K.

In areas with even higher density in the glass phase, structures with all molecules tilted into the same direction are observed again. Fig. 5 shows an STM image of such ordered structure. Quite surprising, the lattice is almost quadratic, which is compatible with the underlying hexagonal metal substrate with a (4 3, –1 3) lattice. This shows that at low temperature (74 K) the locally self-assembled lattice due to solidification is slightly denser (equivalent to 15 Cu atoms) than the (4 × 4) lattice (16 Cu atoms), which is observed at room temperature for the saturated monolayer.

4. Summary

As previous modeling results on pentagonal disks packed in two dimensions suggest, lattice order for fivefold-symmetric molecules is only achieved at high packing densities. Solidification of a low-density 2D gas leads to a glass with non-periodic repetition of packing motives at nearest-neighbor length scale. Medium density – achieved by fluctuations during freezing – leads to small areas of ordered structures. Only at tight packing, long-range structures are observed. The observed strategy to avoid the C_{5v} symmetry in dense corannulene monolayers is a tilt of the molecules away from C_5 symmetry. In an intermediate-density structure trimer formation, stabilized by decoration with tilted molecules, has been identified as symmetry-lowering strategy. Our study shows that STM allows insight into partially ordered systems, where space-averaging methods like X-ray or electron diffraction will not reveal local ordering effects.

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