

Building 2D Crystals from 5-Fold-Symmetric Molecules

Tobias Bauert,[†] Leo Merz,[†] Davide Bandera,[‡] Manfred Parschau,[†] Jay S. Siegel,^{*,‡} and Karl-Heinz Ernst^{*,†,‡}

Empa, Swiss Federal Laboratories for Materials Testing and Research, Laboratory for Nanoscale Materials Science, Ueberlandstrasse 129, 8600 Dübendorf, Switzerland, and Organic Chemistry Institute, University of Zurich, Winterthurerstrasse 190, 8052 Zurich, Switzerland

Received December 29, 2008; E-mail: jss@oci.uzh.ch; karl-heinz.ernst@empa.ch

Periodic tessellations of the plane represent 1 of 17 discrete plane symmetry groups; none display 5-fold symmetry.¹ Geometers like Kepler, Dürer, and Penrose have proposed several clever solutions to this problem for rigid pentagons and stars,² but all result in inhomogeneous tile types, aperiodicity, or lower lattice symmetry.³ Equally true, isolated molecules with point groups displaying 5-fold symmetry must reduce their symmetry when forming crystalline monolayers.⁴ The way in which the symmetry is reduced provides insight to fundamental processes of molecular recognition in crystals.⁵ Scanning tunneling microscopy (STM) allows one to follow these complicated processes at the molecular level⁶ and has provided valuable insights into various aspects of molecular recognition among chiral molecules at surfaces.⁷

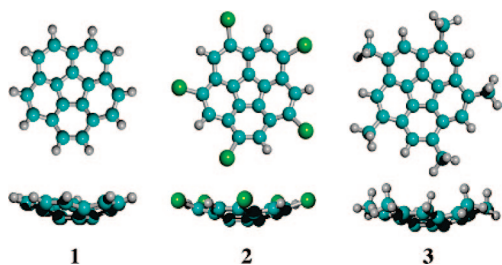


Figure 1. Top and side views on ball and stick models of corannulene (**1**) and its pentachloro (**2**) and pentamethyl (**3**) derivatives.

The C_{5v} and C_5 symmetries of corannulene (**1**) and its chiral pentasubstituted derivatives (Figure 1) offer a unique opportunity to study symmetry mismatching on surfaces. Buckybowl **1**, with a convex pentagonal form, on Cu(111) avoids C_5 symmetry by a tilt into an adsorbate geometry with one hexagonal ring oriented parallel to the surface that allows hexagonal-like closest packing.⁸ Substituents at the rim of **1**, such as seen in pentachloro- (**2**)⁹ and pentamethyl- (**3**)¹⁰ corannulene, create a slight star-like form, and these molecules maintain their C_5 axis normal to the surface. The steric constraint due to the five substituents in the close-packed monolayer blocks any proper tessellation of the plane and results in random azimuthal orientations and positional disorder.

The molecules have been deposited at room temperature under ultrahigh vacuum by evaporation from an effusion cell. Because of the perfect match of the size of aromatic hexagonal carbon rings and the substrate lattice, Cu(111) provides an ideal surface for thin films of aromatic molecules.¹¹ The strong interaction of the chloro substituents of **2** with copper created etched pits in the Cu(111) substrate; therefore gold(111) proved to be a better substrate. The so-called herringbone reconstruction in the topmost atomic layer

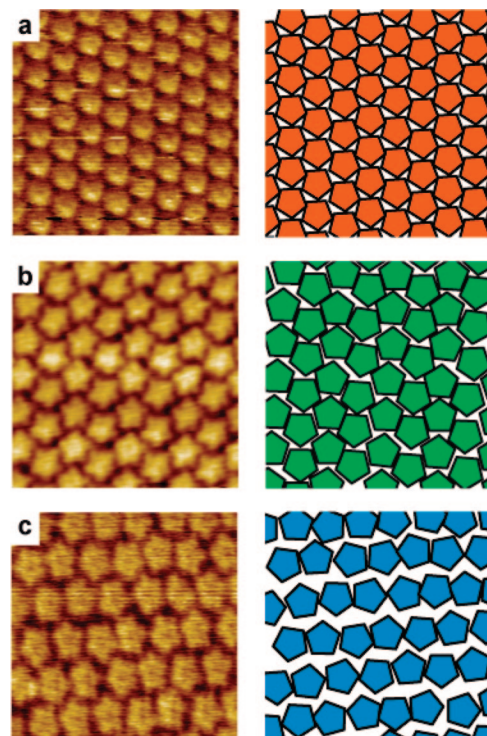


Figure 2. STM images ($8 \times 8 \text{ nm}^2$) of (a) **1** on Cu(111) ($U = -0.7 \text{ V}$, $I = 45 \text{ pA}$, $T = 253 \text{ K}$), (b) **2** on Au(11 12 12) ($U = -0.7 \text{ V}$, $I = 35 \text{ pA}$, $T = 76 \text{ K}$), and (c) **3** on Cu(111) ($U = -0.93 \text{ V}$, $I = 420 \text{ pA}$, $T = 62 \text{ K}$). The azimuthal alignments of the molecules as observed in the STM images have been transferred directly into the cartoons shown in the right column.

of this surface, however,¹² is known to influence molecular self-assembly.¹³ Hence, we used a stepped Au(11 12 12) surface, where, due to the limited widths of the (111) terraces, no extended herringbone reconstruction occurs.

Figure 2 shows STM images of close-packed monolayers of **1** and **3** on Cu(111) and **2** on a (111) terrace of the gold(11 12 12) surface. In all three structures, each molecule is surrounded by six others. Considering only the molecular centroids gives the impression of hexagonal packing, consistent with the molecules adopting a closest packing arrangement. At room temperature a regular (4×4) array is observed for the saturated monolayer of **1** on Cu(111) (Figure 2a), a periodicity that has been observed for C_{60} on this surface as well.¹⁴ All molecules of a single domain appear asymmetrical by STM, indicating a substantial polar tilt of the bowl (Supporting Information, Figure S1). This conclusion agrees well with DFT calculations for **1** on a Cu(111) slab, favoring an adsorption geometry with one hexagonal ring oriented parallel to the surface over an fcc or hcp 3-fold hollow site.¹⁵ For **1** on

[†] Nanoscale Materials Science, Empa; www.empa.ch/mss.

[‡] OCI – University of Zurich.

Cu(110), a quasi-hexagonal enantiomorphous lattice with only slightly tilted molecules, appearing in STM as 5-fold-symmetric doughnuts, has been reported.¹⁶

The molecules in Figure 2b and c appear as 5-fold stars; i.e., the five chloro or methyl substituents contribute to the STM appearance. The intramolecular STM contrast does not vary as observed for **1**, indicating that there is no pronounced tilt of the bowl. Weak depressions observed in the center of the molecules imply, similar to **1** on Cu(110), that the bowl opening points away from the surface. A one-to-one reproduction of the molecules in the STM images of Figure 2 as pentagons, maintaining the azimuthal orientation, show that the lateral density decreases from **1** to **3**, while the disorder increases. On average, the structure shown in Figure 2c is characterized by a (5 2, -2 3) lattice (Supporting Information Figure S2).¹⁷ This relates to 19 surface atoms per molecule (0.935 molecules/nm²), while in the (4 × 4) lattice of **1** a surface area of 16 atoms per molecule (1.11 molecules/nm²) is occupied. The density reflected in Figure 2b for the system **2**/Au suggests an intermediate value. On Cu(110), **1** establishes a density of only 0.98 molecules/nm² because of the lower density of suitable binding sites.¹⁶

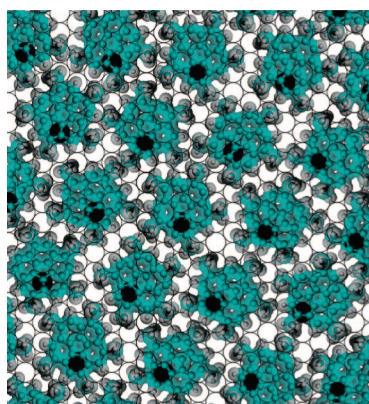


Figure 3. Example of arranging **3** on a (5 2, -2 3)/Cu(111) lattice (black atoms). Azimuthal orientation, position with respect to substrate sites, and handedness must vary to achieve this packing density.

Although **1** establishes a perfectly ordered 2D crystal on Cu(111), i.e., all molecules obey translational symmetry in a single domain (Figure 2a), the layer of **3** is disordered such that the molecules are neither azimuthally nor translationally aligned. However, their centroids are arranged on a hexagonal (5 2, -2 3) grid. The bowl of **3** is slightly shallower than that of **1**.¹⁸ Considering the bulky substituents at the rim, an alignment with the hexagonal ring parallel to the surface seems not possible. This forces the adsorbate to maintain a symmetry that is incompatible with crystal symmetry. Only when the azimuthal orientation and chirality of the adsorbate vary can the average (5 2, -2 3) structure be realized (Figure 3). The pentachloro derivative on Au reflects a different situation. The molecules are aligned in antiparallel rows, with the chloro substituents interdigitated in each single row. There are dislocations in each row after a few unit cells in this “striped lattice”. The principle of close packing¹⁹ forces the molecules into dense arrays, but due to fundamental symmetry constraints, close packing leads to disorder at different length scales. Either position and azimuthal orientation varies locally, creating a “rotator phase”, or translational symmetry is maintained only at a limited length scale with dislocations after a short distance.

Our observations at the molecular scale agree perfectly with previous modeling results for packing rigid pentagons in two dimensions. The pentagon lattices for the striped and the rotator phase, as deduced from the STM images in Figure 2b and c, have also been found via Monte Carlo simulations.²⁰ In addition, the striped phase has been created in mechanical packing experiments of styrene pentagons on a blowing air table,²¹ like the rotator phase with pentagonal aluminum discs in a vibrating-shake-table apparatus.²² Dislocations in the striped phase, a consequence of icosahedral and pentagonal packing,²³ have been observed in these studies as well. Our results thus present a reverse modeling situation, showing that molecular aggregation follows mechanical packing rules.

In conclusion, we have shown that C_{5v} symmetry of corannulene can be circumvented by a substantial tilt in the adsorbate. If this is not possible, e.g., due to bulky substituents at the rim of the buckybowl, hexagonal lattices with dislocations or azimuthal disorder at a local length scale are observed. Our work shows that STM is very valuable to investigate crystal structures and phenomena that need insight beyond an averaging method like X-ray diffraction and that computational hard-object-modeling to mimic lattice structures can be a valid approach.

Acknowledgment. Financial support by the Swiss National Science Foundation (SNF) is gratefully acknowledged.

Supporting Information Available: Experimental details and (averaged) STM images. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Cracknell, A. P. *Thin Solid Films* **1974**, *21*, 107.
- (2) Lück, R. *Mater. Sci. Eng., A* **2000**, *294–296*, 263, and references therein.
- (3) Hargittai, I., Ed. *Fivefold Symmetry*; World Scientific: Singapore, 1992.
- (4) Plass, K. A.; Grzesiak, A. L.; Matzger, A. J. *Acc. Chem. Res.* **2007**, *40*, 287.
- (5) Barth, J. V. *Annu. Rev. Phys. Chem.* **2007**, *58*, 375.
- (6) De Feyter, S.; De Schryver, F. C. *Chem. Soc. Rev.* **2003**, *32*, 139.
- (7) Ernst, K.-H. *Top. Curr. Chem.* **2006**, *265*, 209.
- (8) Hexagonal-like stands for *parallelogramatic*; i.e. the centroids of the elementary molecules in the lattice form a scalene triangle. The plane group is p_1 .
- (9) Grube, G.; Elliott, E.; Stephens, R.; Siegel, J. S. *Org. Lett.* **2003**, *5*, 713.
- (10) Seiders, T. J.; Baldrige, K. K.; Elliott, E.; Grube, G.; Siegel, J. S. *J. Am. Chem. Soc.* **1999**, *121*, 7439.
- (11) (a) Fasel, R.; Parschau, M.; Ernst, K.-H. *Angew. Chem., Int. Ed.* **2003**, *42*, 5177. (b) Parschau, M.; Fasel, R.; Ernst, K.-H. *Cryst. Growth Des.* **2008**, *8*, 1890. (c) Fasel, R.; Cossy, A.; Ernst, K.-H.; Baumberger, F.; Greber, T.; Osterwalder, J. *J. Chem. Phys.* **2001**, *115*, 1020.
- (12) Barth, J. V.; Brune, H.; Ertl, G.; Behm, R. J. *Phys. Rev. B* **1990**, *42*, 9307.
- (13) (a) Clair, S.; Pons, S.; Brune, H.; Kern, K.; Barth, J. V. *Angew. Chem., Int. Ed.* **2005**, *44*, 7294. (b) Chambliss, D. D.; Wilson, R. J.; Chiang, S. *Phys. Rev. Lett.* **1991**, *66*, 1721. (c) Böhringer, M.; Morgenstern, K.; Schneider, W.-D.; Berndt, R. *Angew. Chem., Int. Ed.* **1999**, *38*, 821.
- (14) (a) Hashizume, T.; Motai, K.; Wang, X. D.; Shinohara, H.; Saito, Y.; Maruyama, Y.; Ohno, K.; Kawazoe, Y.; Nishina, Y.; Pickering, H. W.; Kuk, Y.; Sakurai, T. *Phys. Rev. Lett.* **1993**, *71*, 2959. (b) Larsson, J. A.; Elliott, S. D.; Greer, J. C.; Repp, J.; Meyer, G.; Allenspach, R. *Phys. Rev. B* **2008**, *77*, 115434.
- (15) Pervarati, R.; Baldrige, K. K. *J. Chem. Theory Comput.* **2008**, *4*, 2030.
- (16) Parschau, M.; Fasel, R.; Ernst, K.-H.; Gröning, O.; Brandenberger, L.; Schillinger, R.; Greber, T.; Seitonen, A.; Wu, Y.-T.; Siegel, J. S. *Angew. Chem., Int. Ed.* **2007**, *46*, 8258.
- (17) The transformation matrix (m_{11} m_{12} , m_{21} m_{22}) links the adsorbate lattice vectors (b_1 , b_2) to the substrate lattice vectors (a_1 , a_2) via $a_1 = m_{11}a_1 + m_{12}a_2$ and $b_2 = m_{21}a_1 + m_{22}a_2$.
- (18) Wu, Y.-T.; Siegel, J. S. *Chem. Rev.* **2006**, *106*, 4843.
- (19) Kitajgorodskij, A. I. *Acta Crystallogr.* **1965**, *18*, 585.
- (20) Schilling, T.; Pronk, S.; Mulder, B.; Frenkel, D. *Phys. Rev. E* **2005**, *71*, 036138.
- (21) Limon Duparemeur, Y.; Gervois, A.; Troadec, J. P. *J. Phys.: Condens. Matter* **1995**, *7*, 3421.
- (22) Sachdev, S.; Nelson, D. R. *Phys. Rev. B* **1985**, *32*, 1480.
- (23) Nelson, D. R. *Phys. Rev. B* **1983**, *28*, 5515.

JA8101083