Building 2D crystals from fivefold-symmetric molecules

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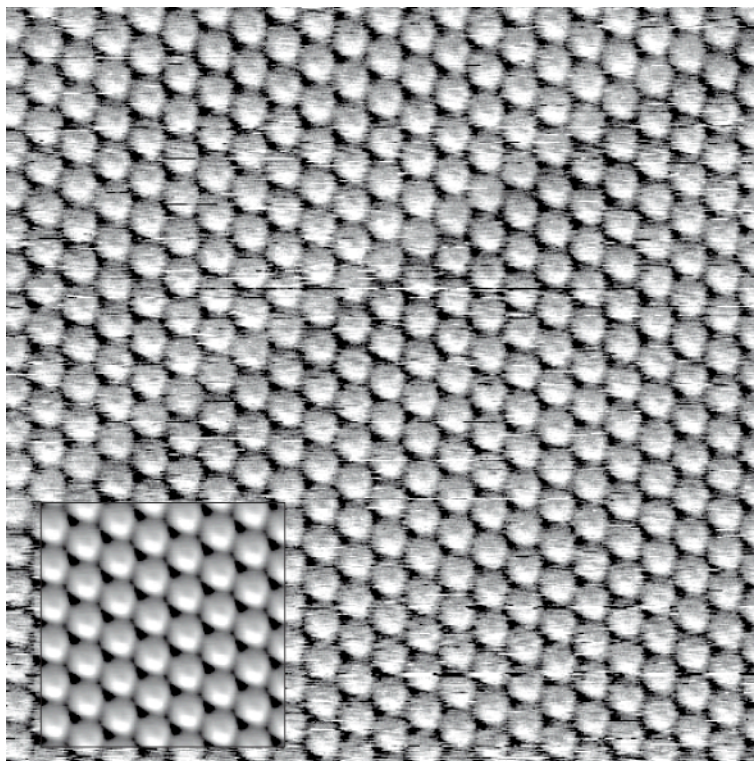*2) Organic Chemistry Institute, University of Zurich, Winterthurerstrasse 190, 8052 Zurich, Switzerland*

Figure S1. STM image (20 × 20 nm^2) of corannulene on Cu(111) (U = –0.7 V, I = 45 pA, T = 253 K). Averaging of the STM images over 191 positions (inset, see description of method below) reveals an asymmetric image for each molecule that suggests a tilt with respect to the surface.
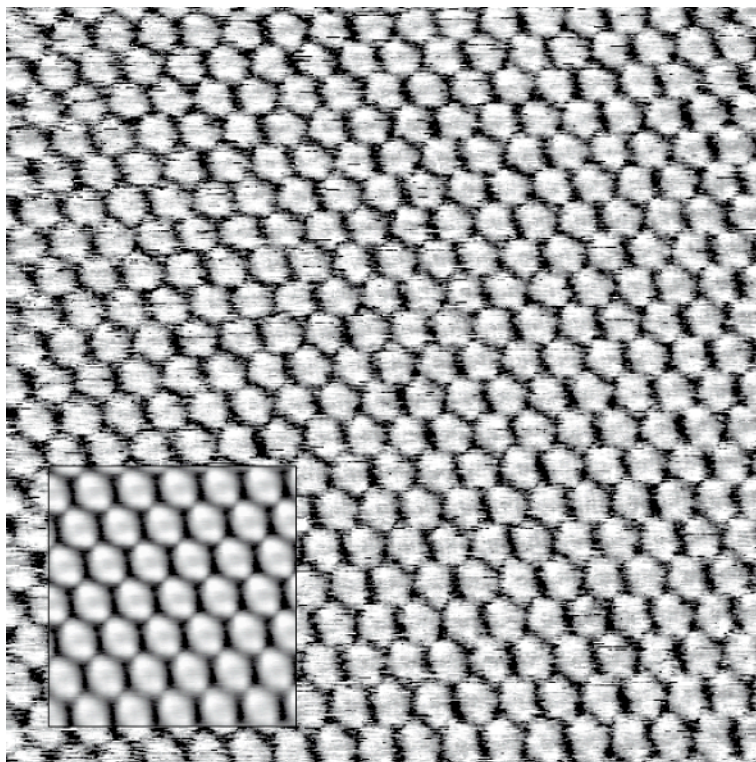
Figure S2. The medium range STM image (20 × 20 nm^2) of pentamethyl corannulene on Cu(111) (U = –0.67 V, I = 190 pA, T = 295 K) shows packing dislocations. Averaging of the STM image over 112 positions (inset) eliminates all variations in position and azimuthal orientation, but reveals the average periodicity, i.e., a (5 2, -2 3) lattice.

Experimental details:

Molecular structures
The molecular structure of **1** was obtained from crystallographic data. The structures of **2** and **3** were obtained by modifying the known structure of **1** and optimizing with MM+ using the Polak-Ribière algorithm. The drawn images of the molecules were done in HyperChem 7.

Sample preparation
All substrates were cleaned using standard Argon sputtering - annealing cycles. The molecules were evaporated from standard UHV sublimation cells in the measurement chamber and deposited onto the cleaned substrate. The substrate was held at room temperature during deposition and only cooled down in the STM for imaging if specified in the figure caption.

STM
A commercial Omicron VT-STM system with SCALA software was used for all measurements in a standard UHV chamber. The tips were made from etched Tungsten wire. All images presented in this paper were flattened or simple plane subtracted, but no other image manipulation or filtering was applied, with the exception where the averaging procedure was applied (see figure captions of Figs. S1 and S2).

STM averaging procedure
To better visualize tilting or orientation of individual molecules in the monolayer, averaged images were used as insets. By this procedure the omnipresent noise in these low current STM images can be reduced. We used a routine for the SXM-shell of the University of Basel [1,2].
A limited area of an image is selected and cross-correlated with the original image. The routine marks all the similar spots in the image and proposes them for inclusion. Manual deselecting of individual spots makes sure no faulted areas are included. The routine then averages the marked area with all included similar spots. Thorough comparison by hand of the averaged area with the original images makes sure to exclude averaging artifacts.

Packaging simulation (Fig. 3)
The images displaying packaging examples of **2** on Cu(111) are manual schematics. The molecular structures (see above) were manually placed on the copper substrate to suit the known monolayer structure and the intended azimuthal orientation. The copper substrate is drawn to scale the molecular size.

[1] Constable, E. C.; Güntherodt, H.-J.; Housecroft, C. E.; Merz, L.; Neuburger, M.; Schaffner, S.; Tao, Y. *New. J. Chem.* **2006**, *30*, 1470.
[2] Saxton, W. O.; Pitt, T. J.; Horner, M. *Ultramicroscopy* **1979**, *4*, 343.