

Supporting information for

An Aromatic Coupling Motif for Two-Dimensional Supramolecular Architectures

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Self-assembly of HBC on Cu(111)

The preferential adsorption sites for hexa-cata-hexabenzocoronene (HBC) on Cu(111) are step edges of the underlying substrate. Only once the step edges are completely decorated with adsorbates, supramolecular structures can be found on the terraces. No individual molecules are found on the terraces. While linear structures can grow out from step edges, extended honeycomb networks are exclusively formed away from the steps on the terraces. Domain sizes vary considerably between neighboring islands (see figure S1) but can easily extend up to 10-15 honeycombs in each direction.

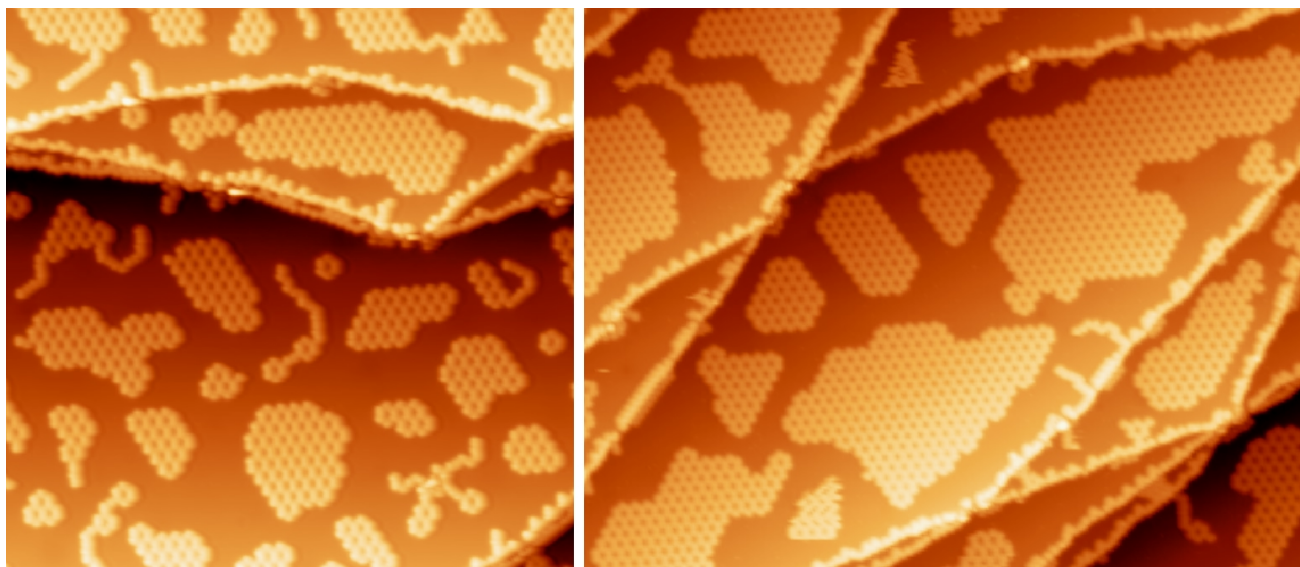


Figure S1: Overview STM images of contorted HBC on Cu(111). Parameters: 93 nm x 93 nm, -2 V, 20 pA, 5 K (left); 131 nm x 101 nm, -2 V, 10 pA, 77 K (right).

Tetrahelicene units of HBC

Hexa-cata-hexabenzocoronene can be regarded as three fused tetrahelicene units (see Fig. S2). The definition of these helical units is shown in figure S2. Starting from a given peripheral carbon ring, two mirror-symmetric tetrahelicene units can be drawn by passing around the central coronene core to the neighboring peripheral ring to the left or to the right,. Following the nomenclature for the enantiomers of heptahelicene, these units are designated as M- and P-tetrahelice. The HBC molecule can thus be regarded as consisting of either three fused M-tetrahelice or three fused P-tetrahelice units (see figure S2). Both descriptions are of course equivalent, and the HBC molecule itself is achiral. Lateral coupling of two HBCs, however, is only possible via two P- or via two M-tetrahelice units, such that upwards-/downwards-facing neighboring aromatic rings on one molecule point towards a downwards-/upwards-facing pair of rings of the neighboring molecule (see bottom of figure S2).

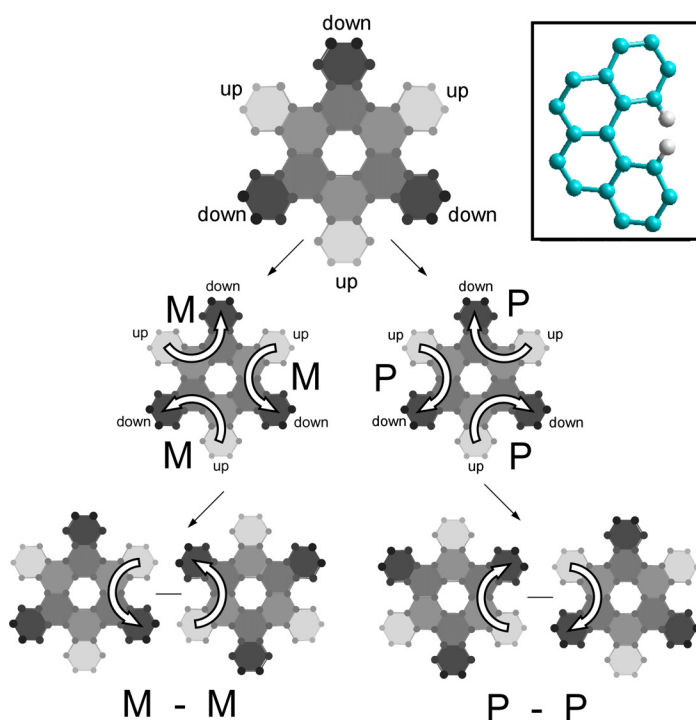


Figure S2: Definition of the helical subunits of HBC. Two helical tetrahelicene units of opposite chirality can be defined starting from every peripheral 6-membered ring. The grayscale coloring of the carbon atoms and the benzene rings visualizes the relative heights with dark units pointing "down". Lateral aromatic coupling is only possible via P-P or M-M tetrahelicene units.

Inset: Schematic representation of a tetrahelicene unit. Only the hydrogen atoms responsible nonplanarity (due to steric hindrance) are shown for visibility.

Stability of the interdigitated helical aromatic units coupling motif

Depending on the tunneling parameters and the state of the tip apex, a displacement of molecular units comprising several molecules can be induced by scanning repeatedly over a given supramolecular structure. An example of such a tip-induced movement of an intact polymolecular structure is shown in figure S3 where the three terminal molecules of an initially linear structure have been displaced between consecutive STM images. The intramolecular coupling is hence strong enough for entities comprising several molecules to be moved intactly.

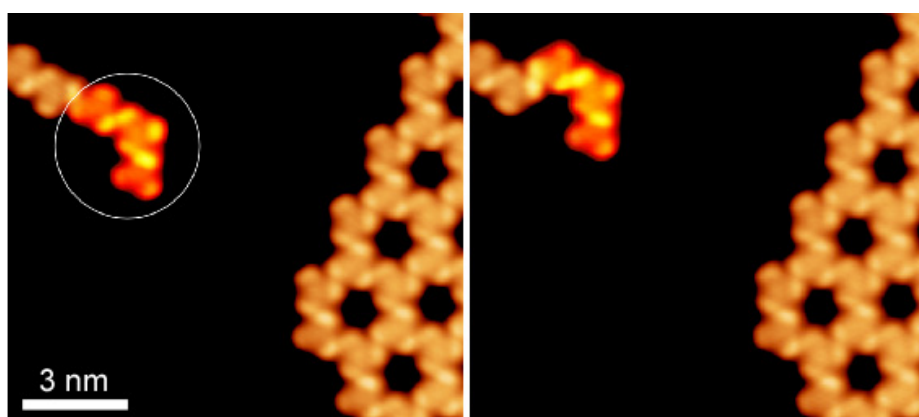


Figure S3: Consecutive STM images (-1.8V, 50pA) of the same region showing the intact displacement of a supramolecular unit (circle; highlighted in yellow-red).