Supplementary Material (ESI) for Chemical Communications

Surface-assisted bowl-in-bowl stacking of nonplanar aromatic hydrocarbons

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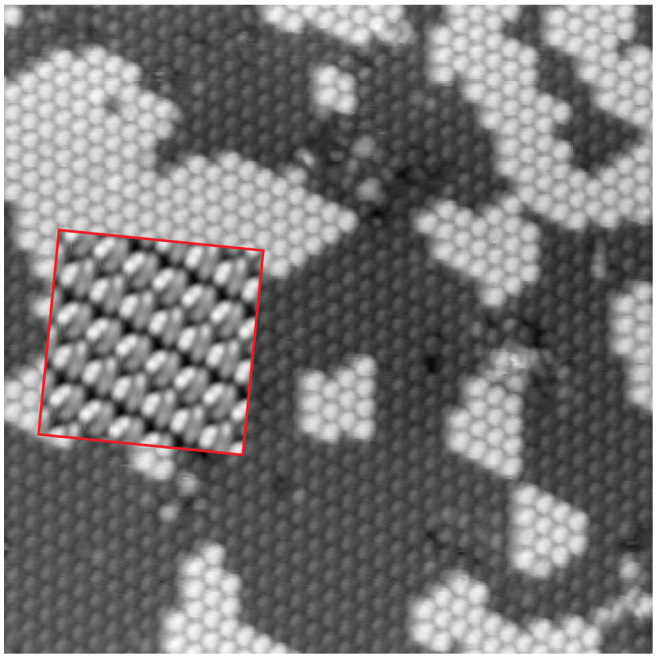

ESI-Figure 1. 28 nm × 28 nm STM image (–1.74 V, 24 pA, 50 K, identical with Fig. 1a) showing the asymmetric STM appearance in the first layer between islands of the second layer. The inset (5 nm × 5 nm; –525 mV, 100 pA, 70 K) shows the same structure from a "first-layer- only" sample, allowing better STM resolution.

Computational Methodology

All calculations have been carried out using the GAMESS[1] and GAUSSIAN[2] software packages. The B97-D density functional[3] was used together with the Def2-TZVPPD basis set[4] for determination of structure and properties. An ultrafine grid was employed for all computations. A Hessian analysis (matrix of second derivative) was calculated for all structures, to determine local minima (positive definite) or nth-order saddle points (n negative eigenvalues), vibrational modes, and thermodynamic properties. Visualization and analysis of structural and property results were obtained using QMView[7] and WEBMO.[9] Depictions of highest occupied molecular orbitals use 64000 grid points, isosurface value (MO) = 0.01, and isosurface value (ED) = 0.0030.

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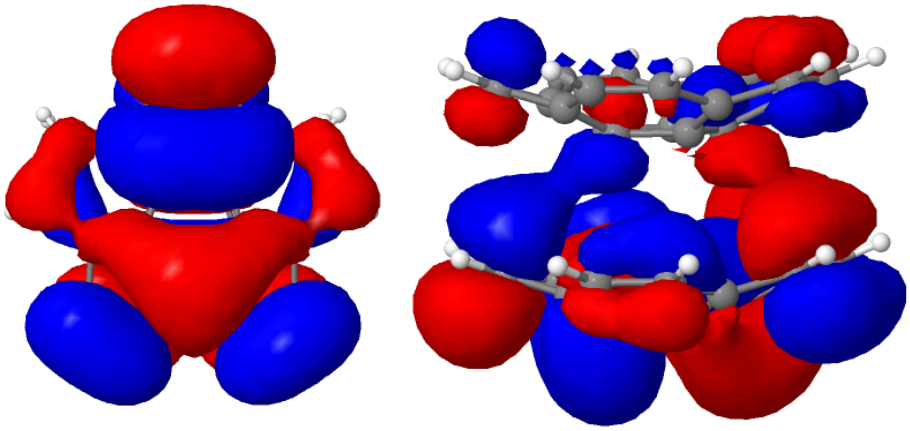
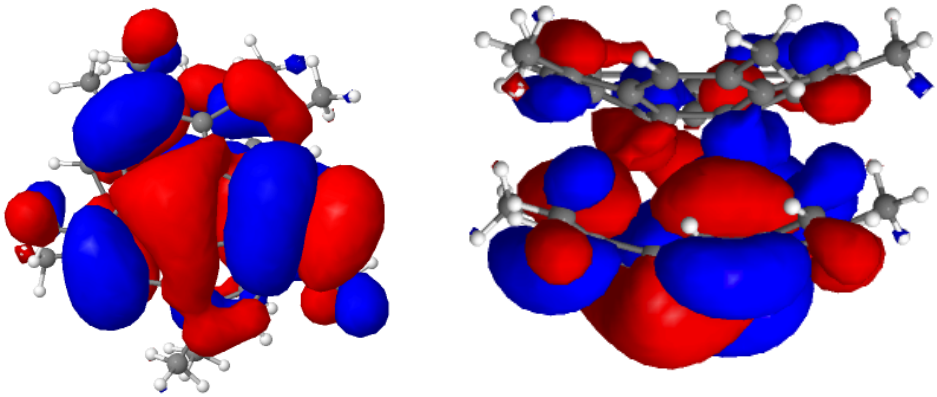
[9]WEBMO: http://www.webmo.net/index.html.



ESI-Figure 2. Top (left) and side view (right) onto the HOMO orbital phases of the corannulene stack. Opposite phases identify a π-π interaction between the geodesic fullerene fragments.



ESI-Figure 3. (a) Top (left) and side view (right) onto the HOMO orbital phases of the pentamethylcorannulene stack. Opposite phases identify a π-π interaction between the geodesic fullerene fragments.

Experimental details

Cleaning of the Cu(111) surface (MaTeK Germany) was achieved by prolonged argon ion bombardment *in vacuo*. The sputter-damaged surface was annealed at 800 K for several minutes. Thermal evaporation of **1** (383 K) and **2** (413 K) from effusion cells led to close-packed monolayers, whereby due to the contraction induced by phase transitions upon cooling, additional **1** is filled into the 1st layer at lower temperature (120 K to 200 K), before 2nd layer growth starts. All STM images were recorded with an Omicron VT STM (Scala system) in constant-current mode at bias voltages (at the sample) from ±250 to ±3000 mV and tunneling currents from 25 to 2000 pA. A strong bias dependence of the contrast was only observed for small absolute bias values.