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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ESI-Figure 2. Top (left) and side view (right) onto the HOMO orbital phases of the corannulene stack. Opposite phases identify a $\pi$-$\pi$ 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 $\pi$-$\pi$ 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.