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Supporting Information

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Buckybowls on Metal Surfaces: Symmetry Mismatch and Enantiomorphism of Corannulene on Cu(110)

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(a) Synthesis of corannulene

A modification of the method of Rabiedau et al.[1] was used for the preparation of corannulene. 1,2,5,6-Tetrabromo-corannulene was treated with zinc and potassium iodide in DMF, instead of hydrochloric acid and ethanol, and the reaction mixture was heated at 160 ºC for ~24-36 hours (TLC control). After removal of solvents, the residue was diluted with CH_2Cl_2 and filtered through a 3 cm thick layer of celite. The solvent of the filtrate was removed and the pale-yellow solid was subjected to chromatography on silica gel. Elution with hexane/CH_2Cl_2 (10/1) afforded corannulene (65-70%) as a light yellow solid. Crystallization from ether at ~20 ºC gave the title compound as light yellow crystals.
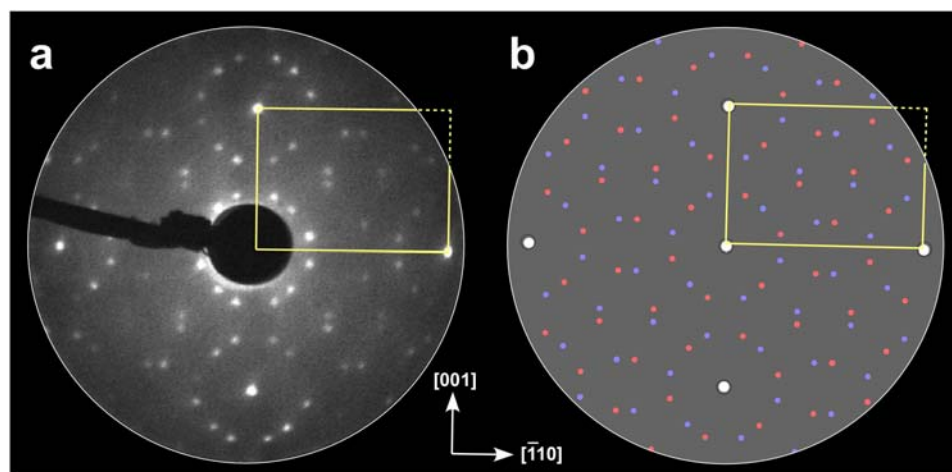
(b) LEED results

Figure S1. a) The LEED image (E_P = 51 eV) for the saturated monolayer shows a 'split-spot' pattern, indicating the presence of mirror domains. b) A computer simulation reveals that this pattern is a superposition of (3 2, –4 1) and (4 1, –3 2) domains, with unit cell vectors of 10.5 and 10.8 Å, and a short diagonal length of 11.1 Å.The reciprocal Cu(110) unit cell is indicated by rectangles. The simulation was performed using the LEEDPat2 program (available at http://w3.rz-berlin.mpg.de/~hermann/LEEDpat/) written by K. Hermann and M. A. Van Hove.

(c) Density functional theory calculation results

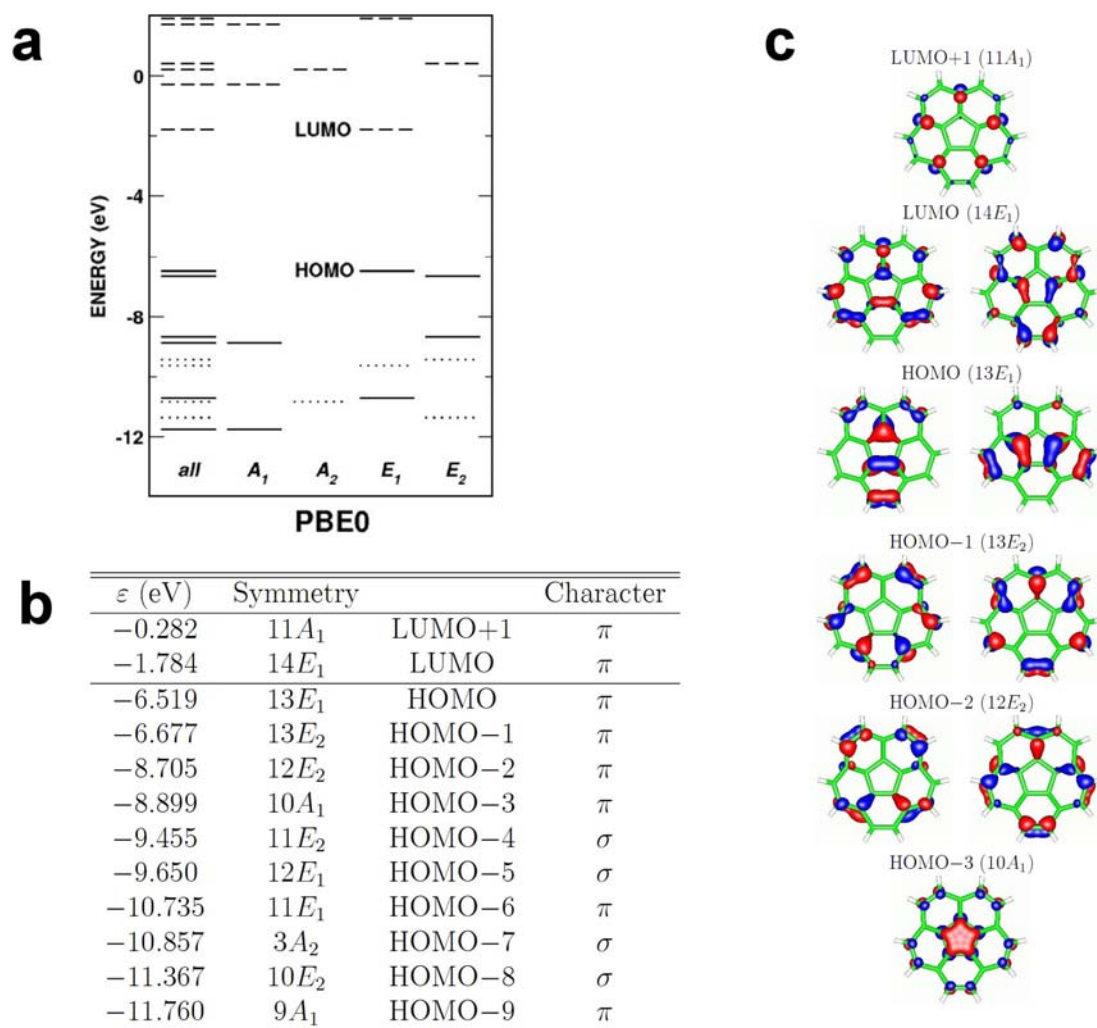| ε (eV)	Symmetry		Character
−0.282	$11A_1$	LUMO+1	π
−1.784	$14E_1$	LUMO	π
−6.519	$13E_1$	HOMO	π
−6.677	$13E_2$	HOMO−1	π
−8.705	$12E_2$	HOMO−2	π
−8.899	$10A_1$	HOMO−3	π
−9.455	$11E_2$	HOMO−4	σ
−9.650	$12E_1$	HOMO−5	σ
−10.735	$11E_1$	HOMO−6	π
−10.857	$3A_2$	HOMO−7	σ
−11.367	$10E_2$	HOMO−8	σ
−11.760	$9A_1$	HOMO−9	π

Figure S2. a) Molecular orbital diagram of corannulene calculated from the Kohn-Sham orbitals. b) Orbital eigenvalues ε (with respect to the vacuum level) within DFT using the PBE0 functional. The frontier molecular orbitals (the highest occupied and lowest unoccupied orbitals) are shown in (c), and the symmetries are listed in the format nS, where n is the running number of the current symmetry operation S; E_1 and E_2 representations are doubly degenerate. The character in the table (b) refers to π_z-type orbitals with respect to the curved surface of the molecule; the occupied orbitals with σ character (i.e. with local s and $p_{x,y}$ character) are shown with dotted lines in the level diagram.

(d) Extended Hückel Theory simulations of STM images

To interpret the STM images we performed simulations based on semi-empirical extended Hückel calculations in the framework of the Hyperchem package.[2] The molecular electron density of the molecule, without taking the surface into account, is given by a three-dimensional reconstruction of the Slater orbitals on the basis of the eigenvectors calculated by Hyperchem. A constant electron density contour is obtained by integrating over the molecular orbitals into which tunneling occurs under the given experimental conditions. A constant current STM image is mimicked by displaying the vertical position of the contour in a color-coded image.[3] Variation of the density level for which the contour is plotted results in STM images representing different tip-sample distances and tunneling currents. The finite size of the tip apex is considered by convolution of the simulated constant current STM image with a Gaussian of 2 Å FWHM. This simple approach neglects the influence of the substrate surface, and tacitly assumes that the metal substrate mainly modifies the alignment of frontier orbital energies and broadens

discrete molecular levels into resonances, but does not significantly alter the symmetry and overall appearance of the electron density distribution. Similar methods relating calculated charge density maps of molecular orbitals to experimental STM data have successfully been used in previous studies.[4]
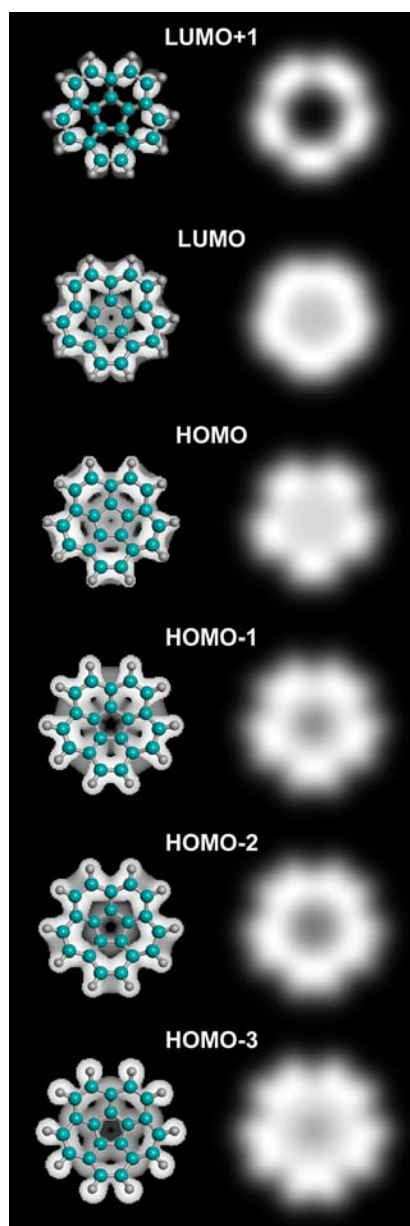

Figure S3. Left: Topographies of constant current electron density contours for the corannulene frontier molecular orbitals as calculated from extended Hückel theory. The position of the molecular frame, with its bowl opening pointing out of the plane of the figure, is indicated. Right: Constant-current STM images mimicked by convolution of the constant electron density topographies shown in the left column with a Gaussian of 2 Å FWHM, reflecting the finite size of the tip apex. Although the STM images simulated for the different orbitals differ in their details, a characteristic doughnut shape with a depression at the center of the molecule is always observed for corannulene facing with its bowl opening towards the STM tip. The opposite overall appearance, namely a single broad protrusion, is obtained from simulations of the opposite molecular orientation with the bowl opening pointing away from the STM tip.

References

[1] A. Sygula, G. Xu, Z. Marcinow, P.W. Rabideau, *Tetrahedron* **2001**, *57*, 3637.

[2] HYPERCHEM™, Hypercube, Inc., 1115 NW 4th Street, Gainesville, Florida 32601; www.hyper.com.

[3] O. Gröning, R. Fasel, STM generator software, Empa, Swiss Federal Laboratories for Materials Testing and Research, Switzerland, 2004.

[4] a) P. H. Lippel, R. J. Wilson, M. D. Miller, Ch. Wöll, S. Chiang, *Phys. Rev. Lett.* **1989,** *62,* 171; b) V. M. Hallmark, S. Chiang, K.-P. Meinhardt, K. Hafner, *Phys. Rev. Lett.* **1993**, *70*, 3740; c) P. Sautet, *Chem. Rev.* **1997**, *97*, 1097; d) R. Fasel, M. Parschau, and K.-H. Ernst, *Nature* **2006,** *439*, 449; e) W. Auwärter, A. Weber-Bargioni, A. Riemann, A. Schiffrin, O. Gröning, R. Fasel, J.V. Barth, *J. Chem. Phys.* **2006**, *124*, 194708.