Buckybowls

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

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Dedicated to Professor Karl-Heinz Rieder on the occasion of his 65th birthday

Functionalization of surfaces by adsorption of aromatic organic molecules is an important approach towards new materials for photovoltaics, organic light-emitting devices (OLEDs), and molecular electronics such as organic field effect transistors (OFETs).[1] The structure of the monolayer, in turn, affects the electronic and optical properties of thin films.[2] A periodic two-dimensional (2D) supramolecular surface exhibits a restricted set of lattice symmetries, and thus not all molecular point group symmetries can be maintained exclusively in a tiling array. Self-assembled structures obtained from the interplay of lattice and molecular symmetry may therefore provide insight to fundamental processes like molecular and chiral recognition.[3] Among point group symmetries, fivefold rotational symmetry is incompatible with the translational order of a classical crystal lattice.[4] Buckminsterfullerene (C_{60}) and some of its fragment bowls possess fivefold symmetry axes; however, C_{60} also possesses subordinate two- and threefold rotational symmetries compatible with translational lattice order. The C_{5v} symmetry of buckybowls based on corannulene offers therefore a unique opportunity to study symmetry mismatching on surfaces.

The rich organometallic chemistry that has developed for bowl-shaped polynuclear aromatic hydrocarbons[5] bodes well for them forming stable monolayers on metal surfaces. Whereas in the transition-metal complexes of C_{60} the metal atom is bonded in η^2 fashion to the carbon sphere between six-membered rings,[6] buckybowls display a variety of η^1-, η^2-, and η^6-bonded complexes.[5] Here we present a study on the consequences of symmetry mismatch between the C_{5v}-symmetric corannulene (**1**, Figure 1) when it self-assembles on the C_{2v} lattice of the Cu(110) surface. Beside its twofold symmetry, this surface provides the right degree of mobility for small aromatic molecules to establish long-range order at room temperature (RT) or even below. The electronic and geometric structure has been analyzed in ultrahigh vacuum by scanning tunneling microscopy (STM), low-energy electron diffraction (LEED), angle-scanned X-ray photoelectron diffraction (XPD), ultraviolet photoelectron spectroscopy (UPS), thermal desorption spectroscopy (TDS), and density functional theory (DFT) calculations.

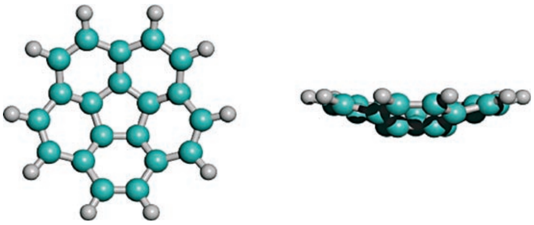

Figure 1. Ball-and-stick model of corannulene (**1**; top and side views).

Long-range STM topographies reveal the formation of ordered lattice structures (Figure 2a). Two mirror domains of a quasi-hexagonal superlattice are observed by STM and LEED (see the Supporting Information). They are tilted either clockwise or counterclockwise with respect to the [001] surface direction. Hence, adsorption induces spontaneous symmetry breaking by the formation of enantiomorphous lattice structures. Although the tendency to close packing applies equally to 2D and 3D crystals, achiral molecules tend to adopt much more often chiral symmetry in 2D adlattices where inversion symmetry is absent. The transformation matrix connecting adsorbate with substrate lattice has been determined as (3 2, −4 1) for the λ domains and (4 1, −3 2) for the ρ domains.[7]

At higher STM resolution **1** is imaged as fivefold symmetric doughnut (Figure 2b). To determine whether the

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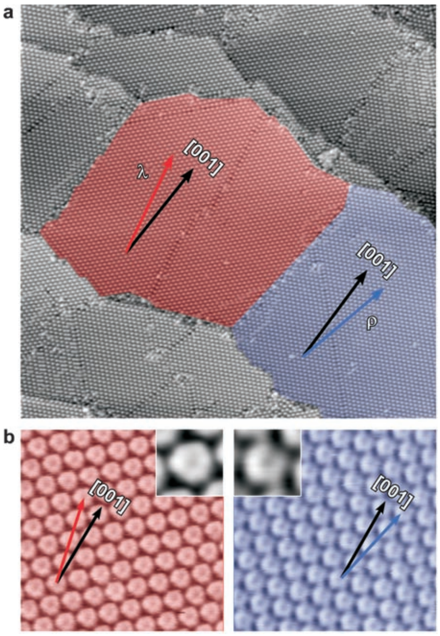

Figure 2. a) STM images of **1** reveal enantiomorphous λ (red) and ρ domains (blue); RT, 100×100 nm^2, $U=-1.6$ V; $I=37$ pA. b) At higher magnification molecules are imaged as pentagonal doughnuts; 50 K, 9.6×9.6 nm^2; $U=-0.35$ V; $I=66$ pA. Insets: 1.45×1.45 nm^2; $U=-0.51$ V; $I=56$ pA.

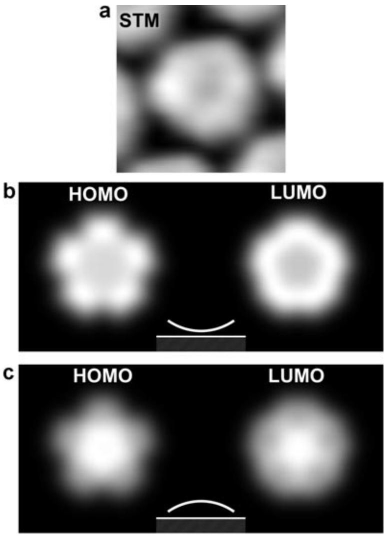

Figure 3. Comparison of a high-resolution STM image (1.45×1.45 nm^2; $U=-0.51$ V; $I=56$ pA) of a single molecule in the close-packed monolayer with simulated STM images based on extended Hückel calculations (see also the Supporting Information). The experimental appearance (a) agrees much better with the simulation for the bowl opening pointing away from the surface (b) than that with the bowl opening turned towards the surface (c).

bowl opening of **1** points towards or away from the surface, we performed STM simulations based on semiempirical extended Hückel calculations. Although this procedure[8] disregards the substrate, it proved to reproduce the topographic images of adsorbed nonplanar molecules reliably.[3c,9] A comparison of experiment and calculations is shown in Figure 3. The STM appearance of **1** agrees with a bowl lying on the Cu surface with the bowl opening pointing away from the surface. In contrast, the simulation of a bowl opening facing the surface does not show the intensity minimum at the center of the molecule.

A closer look at high-resolution STM images (Figures 2b and 3) reveals further that the pentagonal doughnut appears to be asymmetric, indicating a tilt of the bowl with respect to the surface normal. Such detail in the local adsorbate geometry is best revealed by XPD.[10] A comparison of experiment and the best-fit calculation is presented in Figure 4.[11] The best agreement was obtained without deviation from the molecular structure of the free molecule, with molecular coordinates as determined by the AM1 method. This method was shown previously to correctly reproduce the experimental X-ray data for **1**.[12] Alteration of the molecular frame led to larger reliability factors, in other words, worse agreement between experiment and single-scattering cluster (SSC) calculation. The best-fit molecular orientation is shown in Figure 4c and d. It includes a tilt along the $[\bar{1}10]$ direction of the molecular C_{5v} symmetry axis by 6° with respect to the surface normal. Assuming an isotropic surface underneath, this tilt alone breaks the C_{5v} symmetry of the adsorbate complex and causes only one carbon–carbon bond between the pentagonal and a hexagonal ring (*hub*) to be closest to the surface. Therefore, one could conclude that **1** either binds with a η^2 bond or with two η^1 bonds to the surface.[13] Since in the present case neither XPD nor STM provide information on the lateral registry of **1** and the Cu surface, we cannot favor one situation over the other. Our efforts applying DFT and force field methods to this system did not succeed. Either a strongly flattened molecule (DFT) or strongly tilted configurations (AMBER) were obtained, but both can safely be excluded from our XPD experiments. Interestingly, C_{60} and C_{70} are oriented in the same manner on the Cu(110) surface, that is, with a C–C bond shared by a pentagon and a hexagon at the bottom.[14]

A structural model for the two enantiomorphous domains based on experimental results for local and long-range adsorbate ordering is presented in Figure 4e. Each unit cell contains one molecule of **1** with nearest-neighbor distances of 10.5, 10.8, and 11.1 Å. Not considering the molecular unit, the adlattice belongs to the *p*2 plane group of the 17 plane groups that fill 2D space,[15] in other words, it possesses a twofold rotational symmetry. Analogous to inversion symmetry in 3D crystals, twofold rotations provide close packing in the plane, and there is indeed a propensity for this plane group in 2D crystals.[16] Although the glide plane perpendicular to the surface is possible,[17] this rarely gives close packing.[16] The fivefold symmetry of **1**, however, is not compatible with a twofold symmetric 2D crystal lattice. Hence, only translational symmetry is conserved, and this C_{5v}-symmetric molecule crystallizes into an adlattice that belongs to the *p*1 plane group. The best-fit model also shows a 6° azimuthal rotation of a molecular mirror plane away from the $[\bar{1}10]$ direction (Figure 4c). Hence, the single adsorbate complex would be chiral, but this result is within the experimental error for this parameter. Chirality is expressed here on the supramolecular level,[3d] that is, by opposite alignment of the molecules with

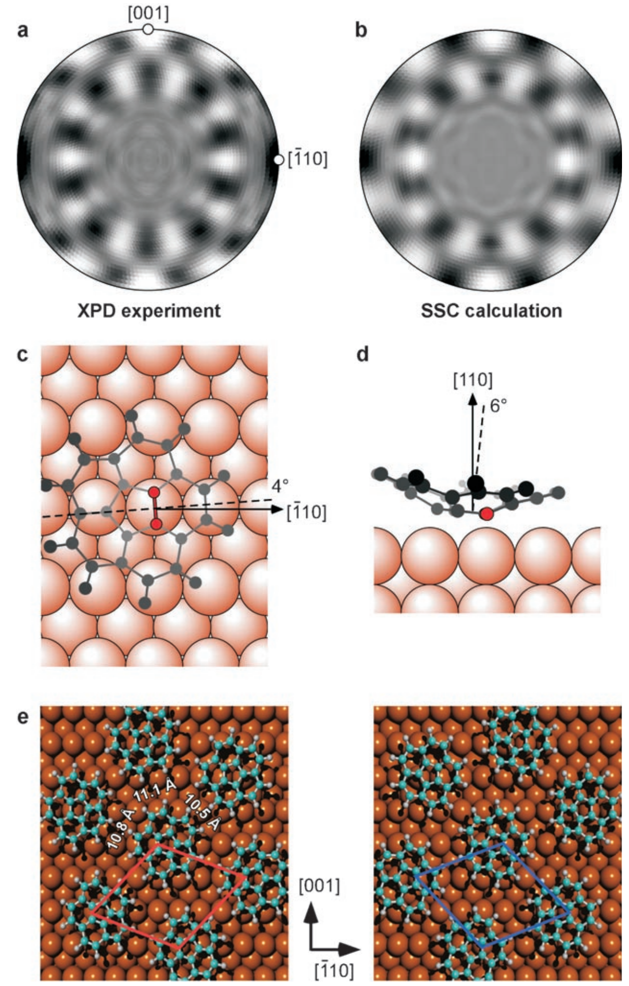

Figure 4. Molecular orientation of **1** on Cu(110). a) Experimentally observed C 1s XPD pattern. b) XPD pattern of the best-fit SSC calculation. c,d) Illustrations (side and top views) of the molecular orientation resulting from the best-fit SSC calculation. A tilt of the C_5 symmetry axis by 6° is observed, causing a C–C bond between a C6 and the C5 ring (highlighted in red) to be closest to the surface (on-top site was arbitrarily chosen). e) Lattice models for the two enantiomorphous λ and ρ domains. Closer packing would only be available with unequal adsorption sites.

respect to the adsorbate lattice vectors. To observe this organizational chirality,[3e] a chiral adsorbate is not required.

For insight into the nature of the chemical bond between **1** and the Cu(110) surface, we have investigated this surface by means of UPS. Adsorption of **1** leads to a significant decrease of the electronic work function of 1.1 eV: from 4.7 eV for clean Cu(110) to 3.6 eV for the close-packed monolayer of **1**. When the Helmholtz formula[18] is applied with the molecular dipole moment of 2.1 Debye and the corresponding dipole density of $9.87\times10^{17}\ \mathrm{m^{-2}}$, a decrease in the work function of 0.78 eV for the bowl opening pointing away from the surface and an increase of 0.78 eV for a surface-oriented bowl opening is expected. The sign of the work-function shift corresponds to the structure proposed by STM. Its magnitude, however, is larger—an indication for substantial polarization, as also known for C_{60} on copper.[19]

Figure 5 shows a comparison of the valence band spectra of the clean Cu(110) surface, the **1**/Cu(110) monolayer, the gas-phase spectrum of **1**,[20,21] and a DFT calculation of the free molecule (see the Supporting Information). Whereas the lower-lying molecular states can clearly be identified in the monolayer spectrum, a broad band is observed in the region of the HOMO to HOMO-3 states. Their energies overlap with the Cu valence band, which suggests that the broad features observed between 2 and 5 eV below the Fermi energy derive from hybridization of the orbitals of **1** with the Cu 3d and Cu 4sp bands. This strong interaction is also reflected in the fact that **1** is not thermally desorbed from the surface but undergoes decomposition above 500 K followed by desorption of hydrogen gas and formation of a carbon layer. Significant charge transfer from the metal surface to the **1** molecule is not observed in the UPS spectra, which is consistent with the relatively low electron affinity of **1** (about 0.5 eV).[22]

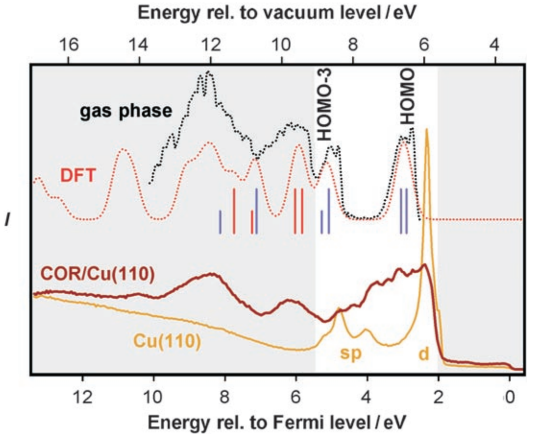

Figure 5. UPS data for the monolayer of **1** (red), clean Cu(110) (yellow), **1** in the gas phase (dotted black line; adapted from Ref. [20]), and a spectrum calculated for the free molecule (dotted red line). A strong hybridization between Cu 3d and Cu 4sp bands and the HOMO to HOMO-3 states of **1** is observed between 2 and 5 eV below the Fermi energy.

In conclusion, the fivefold symmetric corannulene forms spontaneously enantiomorphous 2D lattice structures on the rectangular Cu(110) surface. The symmetry mismatch between substrate and molecule results in the lowest crystal plane group available for 2D lattices. A pronounced charge redistribution between the metal and the molecule leads to an adsorbate complex geometry in which the buckybowl is tilted such that a single *hub* bond becomes closest to the surface. With the bowl opening pointing away from the surface, the **1**/Cu(110) surface could therefore be used as a template for noncovalent binding of other bowl- or ball-shaped molecules such as C_{60}. However, it would be intriguing to force **1** into an upside-down configuration by introducing appropriate functional groups to the rim. Then the five-membered ring may then be utilized for further directed surface chemistry. If additionally the metal substrate is catalytically active for adding more carbon to the bowl **1** at the rim, the directed and controlled growth of carbon nanotubes on a metal substrate might become feasible.

Experimental Section

The synthesis of **1**[23] is described in the Supporting Information. The molecules were evaporated in ultrahigh vacuum from a Knudsen-cell type evaporator held at 364 K during deposition; the clean Cu sample was kept at 400 K throughout the deposition. The Cu(110) crystal surface (MaTecK, Jülich) was cleaned by cycles of argon bombardment and subsequent annealing to 800 K for 10 min. STM images were acquired in constant-current mode with the substrate either kept at room temperature or at 50 K, and occupied states were probed. STM simulations were based on semiempirical extended Hückel calculations for free molecules as described in the Supporting Information. DFT calculations were performed employing the hybrid exchange-correlation function PBE0[24] as the exchange-correlation functional in the Kohn–Sham equations. The wave functions were expanded in the basis set TZVP consisting of Gaussian functions, and the calculations were done with the code TurboMole.[25] All the ionic degrees of freedom were relaxed. XPD experiments[10,11] were performed for the C1s line with X-ray energies of 920 eV. XPD simulations were performed using a modified single-scattering cluster (SSC) calculation scheme as implemented by Friedman and Fadley,[10,26] including spherical wave corrections.

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