# C<sub>60</sub>/Corannulene on Cu(110): A surface-supported bistable buckybowl-buckyball host-guest system

Wende Xiao, Daniele Passerone, Kamel Aït-Mansour, Pascal Ruffieux, Oliver Gröning, Erio Tosatti, Jay Siegel, and Roman Fasel

# **Supporting Information**



Quasi-free rotation of the  $C_{60}$  guests in the COR host bowls

*S I.* Close-up RT STM image showing a smooth spherical shape for  $C_{60}$  in COR bowls, and an anisotropic intramolecular structure for  $C_{60}$  molecules located at defect sites (indicated by numbers).

Manipulating C<sub>60</sub> guests out of their position within the COR host bowls



*S* 2. Manipulating  $C_{60}$  molecules away from their original positions by an abrupt reduction of the gap voltage from -1.2 V to -0.02 V during scanning. a) STM image with normal tunnelling parameters after deposition of ~1 ML  $C_{60}$  onto the COR host lattice at ET. The white arrow indicates the position where an abrupt reduction of the gap voltage is applied during the scanning. b) After an abrupt reduction of the gap voltage, some  $C_{60}$  molecules were swept away and small  $C_{60}$  vacancy islands ("B") were created. This tip created  $C_{60}$  vacancy islands ("B") has an identical apparent depth as the original one ("A") with respect to the  $C_{60}$  aggregates, suggesting that the  $C_{60}$  molecules are directly located on top of underlying COR bowls.



#### Ultraviolet photoelectron spectroscopy data

*S* 3. UPS valence band spectra from the surface-supported COR- $C_{60}$  host-guest complexes (0.5 ML  $C_{60}/1$  ML COR/Cu(110); red curve), clean Cu(110) (black), 0.5 ML  $C_{60}$  on Cu(110) (yellow), a  $C_{60}$  multilayer on Cu(110), and the empty COR host lattice on Cu(110) (green). Work functions  $\phi$  were determined from the secondary electron cut-off measured with a sample bias of -9 V.

Transformation of the low-temperature 2D  $C_{60}$  islands into strongly bound COR- $C_{60}$  host-guest complexes upon annealing to room temperature



*S* **4**. Topography after deposition of ~0.05 ML  $C_{60}$  on the COR lattice at LT and slow annealing to RT, showing random distribution of  $C_{60}$  aggregates. The inset highlights the formation of linear chains of COR- $C_{60}$  host-guest complexes.

## Gas-phase calculations for the COR-C<sub>60</sub> complex

Using the program GAMESS-(US), we performed gas-phase calculations of the COR-C60 complex at the MP2 level. We chose coordinates optimized at the Hartree-Fock level, and in order to exploit the fivefold symmetry we set the fullerene with one pentagon facing the concave face of COR. Table 1 shows the coordinates of the symmetry unique atoms at the equilibrium position.

C	2 202	0.746	2 502
C	2.303	0.740	2.392
С	2.305	1.982	1.828
С	1.178	2.802	1.828
C	1.176	0.381	3.325
С	3.031	1.745	0.593
C	2.601	2.338	-0.593
С	3.479	0.363	0.593
С	3.029	0.249	-1.828
С	1.425	1.958	-2.592
С	0.727	0.999	-3.325
С	2.600	1.575	-1.828
С	1.426	3.193	-0.593
С	0.501	1.096	-6.618
С	1.032	2.258	-6.083
С	2.429	2.167	-5.721
С	3.111	0.958	-5.721
Н	2.938	3.050	-5.342
Н	4.130	0.937	-5.342

Table 1. Coordinates (in Å) of the symmetry unique atoms at the equilibrium distance.

A first set of calculations was done at the 631-G and 631-G(d,p) level to obtain the energy curve as a function of the distance between the centers of mass of the fragments (Figure S5).



*S5.* The MP2 energy (not BSSE corrected) of the COR-C60 complex as a function of the center of mass distance at the 631-G level (red line). The same for the 631-G(dp) level (green point).

In order to compute the binding energy in a more precise way, we subtracted the energy of the single fragments from the total energy of the COR-C60 complex and we obtained 1 eV, 1.4 eV and 1.7 eV for the basis sets of 631-G, 631-G(d,p) and cc-pVdZ, respectively. After basis set superposition error (BSSE)correction, the results become 0.7 eV, 0.76 eV and 1.07 eV, respectively. We observe no significant charge transfer (<0.05 electrons both in the Mulliken and in the Lowdin representation) as is shown by the total charge density contour at a contour value of 0.04 e/Å<sup>3</sup> (Fig. S6).



*S6.* The charge density contour for the COR-C<sub>60</sub> complex, derived from the MP2 orbitals, at a contour value of 0.04 e/  $Å^3$ .

## Frenkel-Kontorova-type model calculations

The experimental observation of a bistable behavior for small fullerene islands on a COR substrate suggests an analogy with the well-known Frenkel-Kontorova model [1]. When this model is applied to infinite overlayers with different natural lattice parameter with respect to the substrate, the system must find a compromise between lateral interactions and substrate pinning. This interplay can generate commensurate regions, dislocations, and solitons.

In our case, the overlayer is a finite island of fullerenes on a COR substrate, which has a different set of lattice parameters. A single fullerene always prefers to sit in the minimum of the substrate potential, but an island of a few molecules can profit of the lateral cohesive energy. If, however, the equilibrium lateral distance within the island is different from the substrate periodicity, the  $C_{60}$  molecules must pay a price to the substrate potential. This 'price' is lower if the island is lifted from the substrate by a certain amount. The question is whether this behaviour could give rise to distinct stable or metastable states for the adsorbed island.

In order to verify this possibility, we generated a simple one-dimensional (1D) model for concurrent lateral and substrate potential interactions. The lateral interaction between two  $C_{60}$  at a distance *r* was taken as the Girifalco potential with the following form:

$$V(r) = -2\alpha \left[ \frac{1}{s(s-1)^3} - \frac{1}{s(s+1)^3} \right] + 2\beta \left[ \frac{1}{s(s-1)^9} - \frac{1}{s(s+1)^9} \right]$$

where s=r/2a, *a* is the C<sub>60</sub> radius and  $\alpha,\beta$  are suitably chosen constants. The equilibrium position of this potential is at r = 10.05 Å. The substrate potential was modelled as

$$Vs(x,z) = 5\exp\left(\frac{-z^2}{0.4}\right) \left(1 - \cos\left(\frac{2\pi x}{p}\right) - \frac{1}{4} \left[1 - \cos\left(\frac{2\pi x}{p}\right)\right]^2\right) - \exp\left(\frac{-z^2}{1.36}\right)$$

for z>0, whereas for z<0 we completed the potential with a steep wall. We chose p = 11 Å corresponding to the COR experimental lattice spacing. Figure S7 shows the profile of the potential at different heights. At (0,0) the potential has a minimum corresponding to the RT state of C<sub>60</sub>, just above the COR bowl.



Using the above two potentials, the energy of an island made of N  $C_{60}$  molecules was minimized as a function of the position of the individual molecules. The positions (in *x* and *z*) of the individual  $C_{60}$  balls were used as degrees of freedom, and a conjugate gradient algorithm with several different sets of initial conditions was adopted.

For a size of the  $C_{60}$  island larger or equal than N=6 there appears a bistability: two distinct minima of the potential energy are found. The absolute minimum corresponds to all fullerenes sitting at a height *z*=0 (the RT state deep in the COR bowl), and the secondary minimum to an island floating further above the surface. Different kinds of solutions

for the secondary minimum are found, depending on initial conditions and on the island size. For N=6, the two frontal molecules are at z=0, the most central ones at z=1 Å, and the remaining two balls at z=0.6 Å. For N=7, only 4 out of 7 balls were at z=1 Å, whereas the other three balls (more external) were found at z=0. This is due to the lack of coordination of the frontier balls in the 1D-chain. For N=8 and N=10, N-2 central balls were found at an average height of around 1 Å, with the two lateral balls sitting at z=0. In the N=12 case, only 8 central balls were stabilized at a higher elevation.

Once the two minima were found, we used a two-point band optimization method to estimate the barrier between the two states [2]: the one with all balls at z=0 and the one with the majority of balls at a higher altitude. We show the corresponding results in Figure S8. We observe that for N=12 there is a barrier between the two states, that is lowered as the size of the chain is reduced (N=10 and N=8). Eventually, for N<6, we could not find "high" solutions anymore.

A further step towards a more realistic description was to project the model corrugation previously described on a two-dimensional (2D) lattice with the experimental unit vectors, giving distances between the "COR-like" substrate molecules of 10.5 and 11 Å, respectively. An additional degree of freedom (namely the *y*-coordinate) was added for each fullerene molecule. In this 2D model, a "floating" solution is found in the case of an island of N=7 balls (a central ball with 6 neighbors), with all balls at a height of about 1 Å with respect to the lower height solution. The elastic band algorithm leads to a very small barrier (~0.1 eV) toward the adsorption of all balls in the deepest minimum.





 (a) Kontorova T.; Frenkel, Y. I.; Zh, *Eksp. Teor. Fiz.* **1938**, 8; (b) Hamilton, J. C.; Stumpf, R.; Bromann, K.; Giovannini, M.; Kern, K.; Brune, H. *Phys. Rev. Lett.* **1999**, 82, 4488.

[2] Czerminski, R.; Elber, R. Int. J. Quantum Chem. 1990, Suppl. 24, 167.