THE NANOSCALE SPIDER-WEB: A MOLECULAR SELF-ASSEMBLY DUE TO SUBSTRATE-MOLECULE INTERACTIONS

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One of the currently most active fields of research in Surface Science is the study of the self-assembling properties of relatively complex organic species. In solution or gas phase the geometry of the self-assembled nano-structures depends exclusively on the specific interactions between peripheral functional groups of the self-assembling molecules. On the other hand, for molecules adsorbed on a solid surface, the role of the surface cannot be neglected, and the resulting 2D molecular arrangement is the consequence of a subtle balance between molecule-substrate and molecule-molecule interactions, but very few cases (involving either vicinal [1] or chemically heterogeneous [2] surfaces) have been reported where the substrate dictates almost uniquely the 2D arrangement.

In this contribution we describe STM experiments showing how molecule-substrate interaction become the dominant force in the self-assembly of PCBM ([6,6]-phenyl C61 butyric acid methyl ester, Figure 1), a C60 derivative, on a chemically homogeneous surface, Au(111).

The 22 x √3 of the Au(111) surface has its origin in an uniaxial contraction along one close-packed [1-10] direction in which 23 atoms are distributed among 22 bulk sites, resulting in the occupation of both fcc and hcp sites. In addition, a more isotropic stress relief is obtained by the formation of stress domains in which the contraction alternates by 120º between two equivalent domains (Figure 2). It is this formation of stress domains which gives rise to the periodic network of surface lattice dislocations that make up the herringbone pattern [3].

During the first stages of deposition, PCBM adsorbs preferentially at the elbows of the reconstruction, a behavior already observed for some metals [4] and other organic molecules [5] on Au(111). But, contrary to these cases, further deposition proceeds by the formation of finger-like zigzag 1D structures (Figure 3). A close examination shows that these chains are actually formed by double rows of PCBM molecules nucleated, exclusively, within the fcc areas of the reconstruction. Upon increasing the coverage, the chains grow in length until they cover completely the fcc areas of the surface, giving rise to a highly organized network of PCBM double rows resembling a nanoscale “spiderweb” (Figure 4). Thus, the supramolecular ordering of at this stage is strictly governed by the substrate reconstruction. The origin of this preferential nucleation (a combination of both steric and electronic effects) will be discussed.

References:

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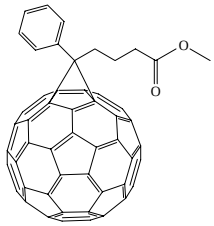

Figure 1: Chemical structure of PCBM.

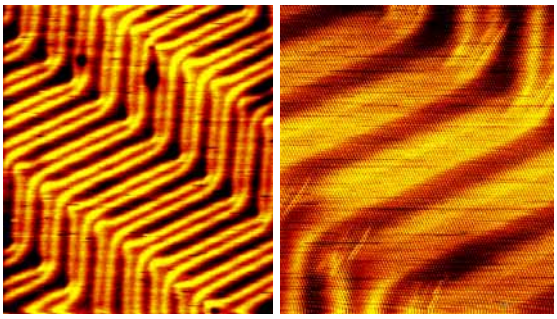

Figure 2: STM images (left: 58 nm x 66 nm, right: 23 nm x 26 nm) of the Au(111) surface showing the morphology of the "herringbone" reconstruction.

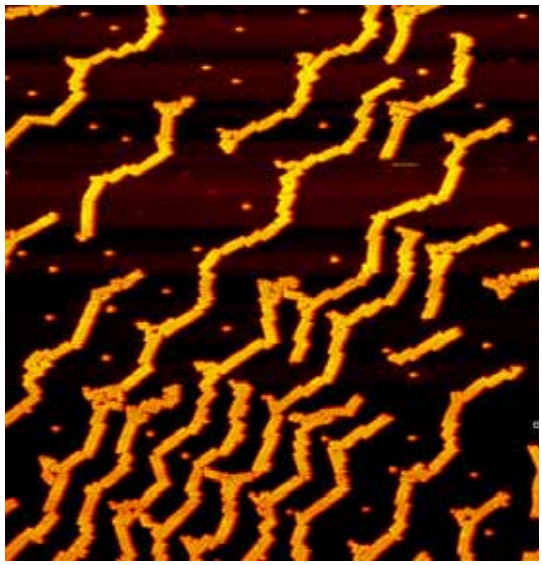

Figure 2: STM image (118 nm x 132 nm) of the Au(111) surface after depositing 0.2 ML of PCBM.

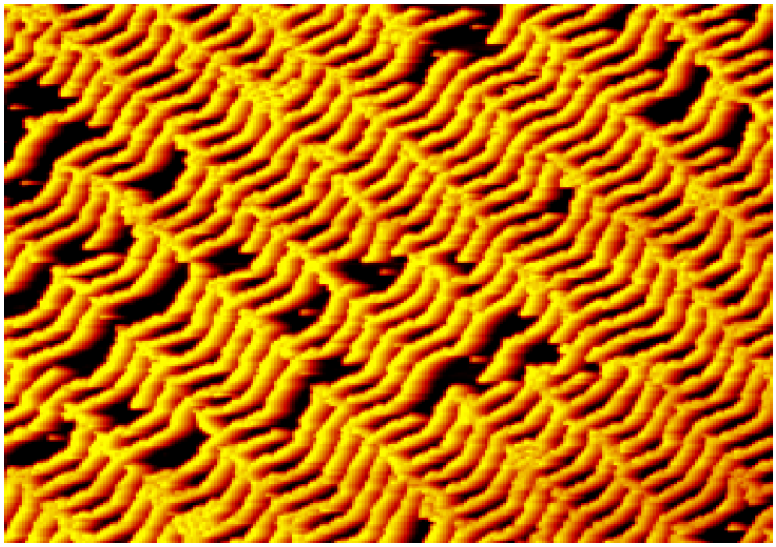

Figure 3: STM image (226 nm x 159 nm) of the Au(111) surface after depositing 0.5 ML of PCBM.