

**SELF-ORGANIZED CALIX[4]ARENES ON Au(110):
FULLY RESOLVED STRUCTURE BY A COMBINED STM, LEED,
AND GIXRD STUDY**

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Large organic molecules doted of complex architectures have demonstrated long range self-organization when deposited on surfaces¹. In order to understand the mechanism of 2D self-arrangement, we have carried out a study in ultra high vacuum (UHV) on calix[4]arenes combining structural information provided by Scanning Tunneling Microscopy (STM), Low Energy Electrons Diffraction (LEED) and Grazing Incidence X-Ray Diffraction (GIXRD) using synchrotron light.

A (1x2) reconstructed missing-row Au(110) has been used as substrate because the missing row reconstruction of this surface might be used as guide to arrange the molecules with a good matching between the metal lattice and the molecular dimensions. The molecule consists of four phenols linked by -CH₂- group in *ortho*-position (fig.1). This architecture offers a high flexibility and, as consequence, various conformational shapes exist for the same entity². At room temperature, perfect self-organized overlayers are observed by STM (fig.2). Each molecular unit can be unambiguously identified by STM as well as the conformer and the relative position of each molecule with respect to the others. From the LEED pattern analysis and STM profiles, it was concluded that every other row of molecules is shifted with respect to the neighboring rows. In addition, in the shifted rows, the molecules are in a mirror position with respect to the surface plane. This 2D arrangement is probably steered by the hydrogen bonding interactions, which form a network between the alcohol groups of neighboring molecules. Clearly, in this system, the intermolecular interactions govern the orientation, conformation and the two-dimensional (2D) organization of these molecules at the metal surface while the gold rows of the underlying substrate acting as guide in the direction [1 $\bar{1}$ 0]. On the other hand, as revealed by GIRXD, the missing row reconstruction undergoes a (1x2) to (1x3) phase transition (fig. 3). This change implies a collective motion of a large amount of gold atoms as observed by XRD. Other works^{3,4} on induced Au(110)-(1x3) reconstruction report a charge transfer occurring between the metal and the adsorbate, especially when the metal surface is negatively charged. These results are of importance for interfacial supramolecular assemblies since such a charge transfer could either promote or forbid further interaction with other organic or inorganic species.



Figure 1: The crown shape conformer of calix[4]arene.

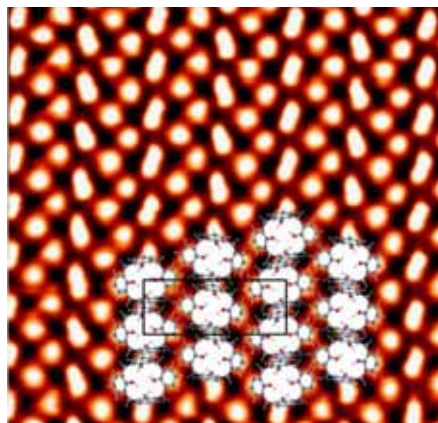


Figure 2: STM images of the fully covered surface. Each molecule can be perfectly identified as well as the unit cell of the molecular net which is (3.16×6) times larger than the Au(110)-(1x1) cell.

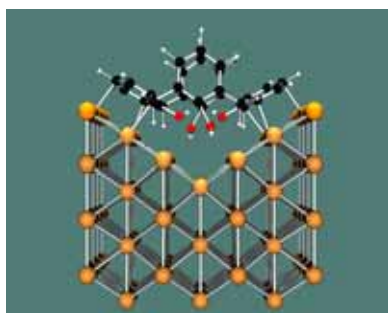


Figure 3: Fully resolved structure of the molecular overlayer and the underneath substrate from GIXRD measurements showing an expanded view of the Au(110)-(1x3) structure along the $[1\bar{1}0]$ direction in order to accommodate the calixarene molecule on top of the substrate.

References:

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