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| | Experiment title: X Ray diffraction study of self-organized calix[4]arenes film deposited on Au(110)-(2x1) | Experiment number: SI 1050 |
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Report:

Large organic molecules doted of complex architectures have demonstrated long range self-ordering when deposited on surfaces¹. In order to understand the mechanism of 2D self-organization, 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 together with Molecular Mechanics calculations.

A (1x2) missing-row reconstructed Au(110) was used as substrate since the ridges-valleys structure of this surface might provide guides 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 (fig.1).

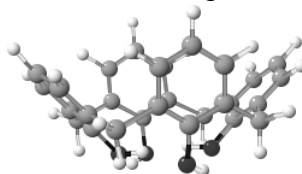
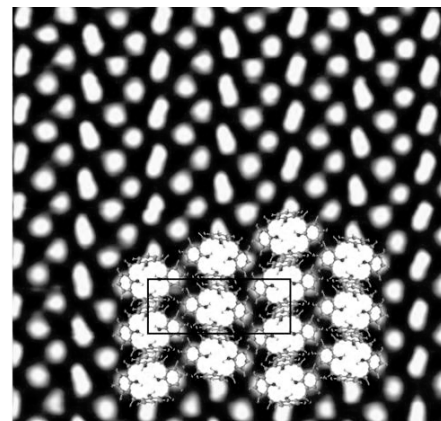


Fig. 1: The crown shape conformer of calix[4]arene

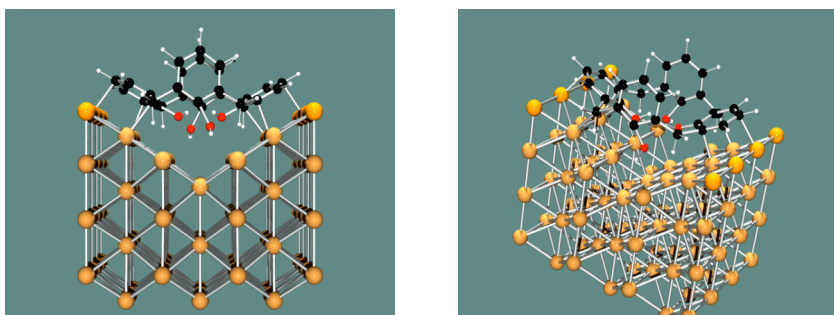
This architecture offers a high flexibility and, as consequence, various conformational shapes exist for the same entity². At room temperature, perfect self-organized overlayers were observed by STM (fig.2). Each molecular unit can be unambiguously identified by STM as well as the conformer and the relative 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 its neighbours. In addition, in the shifted rows, the molecules are in a mirror position with respect to the surface plane. Molecular mechanics calculations indicate rather weak intermolecular interactions in this system while molecule-substrate interactions are comparatively much stronger.

Fig. 2: STM images of a fully covered surface. Each molecule can be perfectly identified as well as the unit cell of the molecular net which is (3.16x6) times larger than the Au(110)-(1x1) cell.



On the other hand, as revealed by GIXRD, the missing row reconstruction undergoes a (1x2) to (1x3) phase transition (fig. 3). Other works^{3,4} on induced Au(110)-(1x3) reconstruction report a charge transfer occurring between the metal and the adsorbates, 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.

Fig. 3: Fully resolved structure of the molecular overlayer and the underneath substrate from GIXRD measurements.



The calixarene superstructure is found to be incommensurate in the [1-10] direction and commensurate in the [001] direction, giving rise to a (3.16 x 6) supercell⁵. The structure was fully resolved by GIXRD. Eight gold layers and two calixarene molecules located at (0, 0) and (0.5, 0.5) in the unit cell of the molecular net were considered in the simulation of the structure factors ($\chi^2=2.9$). Molecules adsorb in the troughs of the (1x3) MR valleys. The compact stacking of fig. 2 is allowed by a tilt of two opposite phenols (those in the [1-10] direction) that end up in almost upright position. Meanwhile, as shown on the front view of fig. 3, the other two facing phenol cycles tilt down to lay parallel to the (111) facets with a Au-C distance close to 2.3 Å indicative of very strong substrate-molecules interactions, interactions at the origin of the phase transition of the substrate.

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