

**SCANNING TUNNELLING MICROSCOPY AND SPECTROSCOPY
INVESTIGATIONS OF ORGANIC PTCDA MOLECULES GROWN ON FE/AU(111)
SUBSTRATE**

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Abstract:

Nowadays, there is a huge research activity in the field of ordered organic molecules deposited on metal/semiconductor substrates mainly motivated by the promising physical-chemical properties of this as-grown materials [1,2]. Among the techniques used to performed physical characterizations, scanning probe, in particular, scanning tunnelling microscopy (STM) and spectroscopy (STS) can be employed to combine structural characterization while probing the electronic “signature” of the organic molecule at the atomic scale [3,4].

We focus our investigation on 3,4,9,10 perylene tetracarboxilic dianhydride (PTCDA) molecules grown on Fe/Au(111) arrays. STM topographic images show different PTCDA arrangements (see figure), never observed on the clean gold substrate. Typically, PTCDA form ordered layers with “herring-bone” or “square” structure [3,5] on clean Au(111). On this substrate, the molecule-molecule interaction predominates over the weak PTCDA-gold interaction. By the contrary, the presence of iron atoms and clusters confers a new electronic scenario [6]. The electronic structure of the system is modified and the molecule interaction is altered. As a result, new molecular dispositions are observed: chains of molecules, ladders, donuts and blocks of molecules.

Examination of the topographic images indicates that some of the molecules at new dispositions appear brighter with the STM. Spectroscopic images performed by Current Image Tunnelling Spectroscopy (CITS) show a strong contrast in the density of states of the different molecules depending on the geometrical disposition and/or the presence of iron atoms close to the PTCDA.

In this work, we investigate the different molecular arrangements and the role of the iron atoms and clusters. By means of STM and STS, we also examine changes in the electronic structure of the systems due to charge transfer between the PTCDA and the iron.

References:

- [1] T. Yokoyama, S. Yokoyama, T. Kamikado, Y. Okuno, and S. Mashiko, "Selective assembly on a surface of supramolecular aggregates with controlled size and shape", *Nature* **413** (2001) 619.
- [2] S. Forest, "Ultra thin Organic Films Grown by Organic Molecular Beam Deposition and Related Techniques", *Chem. Rev.* **97**, 1793 (1997).
- [3] T. Schmitz-Hübsch, T. Fritz, R. Sellam, R. Staub, and K. Leo, "Epitaxial growth of PTCDA on Au(111)", *Phys. Rev B* **55**, 7972 (1997).
- [4] M. Toerker, T. Fritz, H. Proehl, F. Sellam and K. Leo "Tunnelling spectroscopy study of 3,4,9,10-perylenetetracarboxylic dianhydride on Au(1 0 0)", *Surface Science* **491**, 1-2, 255-264 (2001).
- [5] N. Nicoara, E. Roman, J.M. Gómez-Rodríguez, J.A. Martín-Gago and J. Méndez, "Electronic properties of organic/metal interfaces: PTCDA on gold" *Organic Electronics* (submitted)
- [6] J. Méndez, R. Caillard, G. Otero, N. Nicoara, J.A. Martín-Gago, "Nanostructuring organic materials: from molecular chains to organic nanodots" *Advanced Materials* (accepted)

Figure: Scanning Tunnelling imaging at 300 K of molecular aggregations. At small coverage, individual groups of molecules or clusters are preferentially positioned at the elbows of the reconstruction patterns of Au(111) surface. Moreover, one can see that Fe islands allow to fix molecules and create wires and others different forms on the Fe/Au(111) surface.

