

Structure of self-assembled iron-phthalocyanines on the Au(110) surface through STM imaging and DFT calculations

S. Fortuna,^{1,2*} P. Gargiani,⁴ M. G. Betti,⁴ C. Mariani,⁴ A. Calzolari,³ S. Fabris^{1,2}

¹CNR-IOM DEMOCRITOS, Theory@Elettra group, S.S. 14, km 163.5, I-34149 Trieste, Italy

²SISSA, Via Bonomea 265, I-34136, Trieste, Italy

³CNR-Nano Istituto di Nanoscienze, Centro S3, I-41125 Modena, Italy

⁴Dipartimento di Fisica, Università di Roma La Sapienza, Roma, Italy

Corresponding author: S. Fortuna

E-mail: sara.fortuna@uniud.it

*now at the Department of Medical and Biological Sciences, University of Udine, Italy

Key words: phthalocyanine, Au(110), self-assembly.

Introduction

STM imaging is a powerful tool to unravel the pattern formed by surface-adsorbed molecules, generally controlled by the interplay between intermolecular and molecule-substrate interactions. For instance metal-supported metal-phthalocyanines, large conjugated cross-shaped molecules capable to coordinate most of the transition metals, can self-assemble on flat metallic surfaces into ordered aggregates whose ordering details depend on the symmetry and periodicity of the substrate. For instance square and hexagonal lattices have been observed on (111) surfaces, while Kagome lattices are observed on graphene.

Highly anisotropic surfaces can act as templates for the self-assembly, as in the case of (110) surfaces of fcc metals, where organic molecules have been observed to align along the [110] direction. A special case is that of the Au(110) surface where also the propensity of the surface toward reconstruction comes into play. Indeed the metal-surface interaction between aromatic molecules and Au(110) induces the rearrangement of the naturally reconstructed 1×2 -Au(110) surface into surfaces of different periodicities. Density functional theory calculations can reveal the energetic origins of the molecule-driven substrate reconstruction, as exemplified in our recent work on the FePC/Au(110) (full paper in Ref.[1-2]).

Results and Conclusions

The molecule-driven surface reconstruction of the FePC on Au(110) allows to understand whether and up to which extent the molecule-substrate interplay can induce a self-templating effect of the metal surface that can guide the linear self-assembly of a planar molecular system. By STM imaging (Figure 1, center), we have observed $\times 5$ reconstructions of the clean Au(110)- 1×2 surface in correspondence to FePC molecular chains with a regular patterning of the surface with FePC chains aligned along the reconstructed channels with each chain separated by a row of Au atoms. The diffraction patterns (Figure 1, left) confirm the 1D ordering along the channels and a $\times 5$ periodicity along the [001] direction.

DFT calculations (Figure 1, right) predict that the periodicity along the 1D assembly is driven by intermolecular interactions. The calculated energetics show that the $\times 5$ reconstruction formed by alternating $\times 2 \times 3$ valleys is expected to be a common surface defect due to its surface energy comparable to that of the naturally occurring $\times 2$ reconstruction.

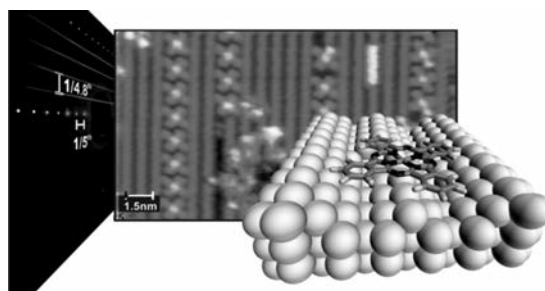


Figure 1. [left] LEED image relative to the FePC $\times 5$ single layer with a superposition of the expected pattern obtained from STM and a theoretical surface model. The $\times 5$ spots in the [001] direction indicate the long-range ordering of the molecular chains along this direction. The stripes stacked along the perpendicular [1100] direction are due to the absence of a definite phase among the adjacent molecular rows. [center] STM topography collected at -0.77 V and 0.4 nA in constant current mode at $T = 60$ K on a FePC/Au(110) at a coverage of about 0.1 SL of FePC. [right] Model of molecular adsorption and surface reconstruction resulting from the calculated energetics for the FePC/Au(110) system. The reconstruction underneath the molecule is formally obtained by the removal of two rows of Au atoms from the clean surface.

Adsorption of a FePc molecule on these $\times 2 \times 3$ line defects yields a significant binding energy, although the calculated energetics predicts that a larger molecular binding is achieved by first reorganizing the metal surface underneath the molecule in a symmetric structure.

The energy cost to reconstruct the surfaces into a more suitable template is largely compensated by the larger adsorption energy on this optimized substrate. We call this effect “self-templating”. The self-templating molecule-substrate interaction process also induces a rehybridization of the electronic states localized on the central metal atom with the surface acting as a fifth ligand on the FePc metallorganic states [2].

As the electronic properties of supported organic overlayers strongly depend on the structural properties of the interface, the synergetic study of molecular-driven surface reconstructions is a key aspect in the design of novel nanodevices.

Acknowledgments

We thank the synchrotron radiation national facility ELETTRA - Sincrotrone Trieste and the Università di Roma “La Sapienza”. We acknowledge the CINECA Award N. HP10CABDLS, 2011, for the availability of high performance computing resources and support. This work was supported by the MIUR project “PRIN/COFIN” contract N. 2008525SC7 and 20087NX9Y7. In addition, the research leading to these results has received specific funding under the “Young SISSA Scientists’ Research Projects” scheme 2011-2012, promoted by the International School for Advanced Studies (SISSA), Trieste, Italy.

References

1. S. Fortuna, et al. *J Phys Chem C*. 2012;116:6251
2. M.G.Betti, et al. *J Phys Chem C*. 2012;116:8657