Metalorganic Nanostructures with a pure coordination bond

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Metalorganic networks and nanostructures have become an interesting research subject (see for example the reviews [1-5]), due to the potential applications as nano-templates for adsorbates with catalytical properties or for the study of their low dimensional properties. Among these systems, many have been named as the result of a non-covalent coordination interaction [4-5], where a dehydrogenation of the organic molecules takes place [6].

Here we present our work in the formation of metalorganic nanostructures based on the iron and PTCDA coordination on a gold surface. By means of scanning tunnelling microscopy/spectroscopy (STM-STS) [7], X-ray photoemission spectroscopy (XPS), and abinitio theoretical calculations, we complete a view of this pure coordination system.

STM images show different metalorganic nanostructures depending on the preparation procedure (coverage, ratio and temperature): from 0D nanodots obtained at low coverages, to 1D chains after 360-380K annealing, and 2D coverage when the 1:1 ratio is observed. XPS spectras for the C1s and O1s peaks show how the coordination between the iron and the molecule induce a redistribution of the charge in the organic molecule, stronger at the carboxylic group. At the same time the Fe peak shows no significant change for the metalorganic structures, with the iron atoms keeping their metallic state Fe⁰, as expected for a pure coordination bond.

Finally the theoretical calculations show the stability of the proposed models and how the HOMO – LUMO orbitals at the 2D nanostructures are located at different molecules (in figure b). This last is the reason for the strong difference observed at these structures in the STM images measured at both polarities.

References:

- [1] J.V. Barth, G. Costantini, and K. Kern, "Engineering atomic and molecular nanostructures at surfaces.," Nature, vol. 437, 2005, pp. 671-9.
- [2] T. Kudernac, S. Lei, J.a. Elemans, and S. De Feyter, "Two-dimensional supramolecular self-assembly: nanoporous networks on surfaces.," Chemical Society reviews, vol. 38, 2009, pp. 402-21.
- [3] H. Liang, Y. He, Y. Ye, X. Xu, F. Cheng, W. Sun, X. Shao, Y. Wang, J. Li, and K. Wu, "Two-dimensional molecular porous networks constructed by surface assembling," Coordination Chemistry Reviews, vol. 253, 2009, pp. 2959-2979.
- [4] J.V. Barth, "Molecular architectonic on metal surfaces.," Annual review of physical chemistry, vol. 58, 2007, pp. 375-407.
- [5] J.V. Barth, "Fresh perspectives for surface coordination chemistry," Surface Science, vol. 603, 2009, pp. 1533-1541.
- [6] S.L. Tait, Y. Wang, G. Costantini, N. Lin, A. Baraldi, F. Esch, L. Petaccia, S. Lizzit, and K. Kern, "Metal-organic coordination interactions in Fe-terephthalic acid networks on Cu(100).," *Journal of the American Chemical Society*, vol. 130, 2008, pp. 2108-13.

[7] J. Méndez, R. Caillard, G. Otero, N. Nicoara, and J. Martín-Gago, "Nanostructured Organic Material: From Molecular Chains to Organic Nanodots," Advanced Materials, vol. 18, 2006, pp. 2048-2052.

Figures:

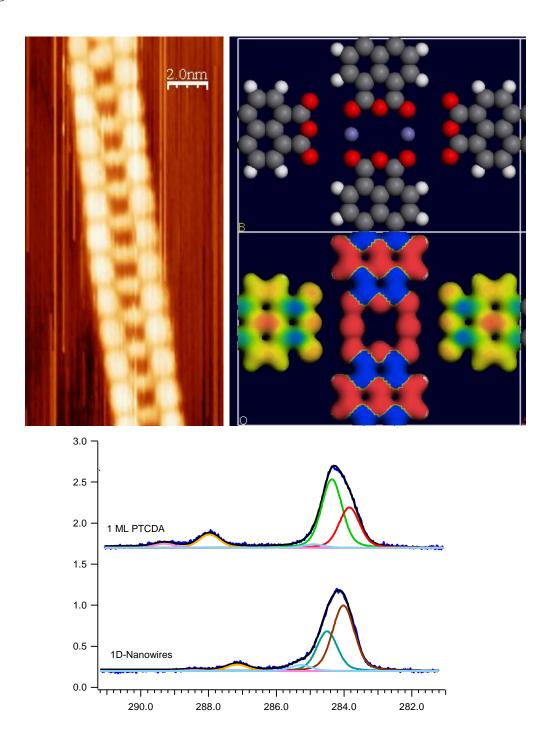


Figure. a) STM image of a "ladder-like" structure made of PTCDA molecules and iron atoms. **b)** Relaxed model of a periodic metalorganic network and the calculated HOMO – LUMO orbitals. **c)** C1s photoemission spectra for a PTCDA monolayer on gold and for a gold substrate covered with 1D metalorganic chains.