

ON-SURFACE SYNTHESIS OF METALLO-PORPHYRIN NANO-TUBES BY VACUUM SUBLIMATION ONTO NOBLE METALS SUBSTRATES

Marta Trelka¹, Christian Urban¹, David Écija¹, Paula de Mendoza², José María Gallego³, Roberto Otero¹, Antonio M. Echavarren², Rodolfo Miranda¹

¹ Dpto. de Física de la Materia Condensada, Universidad Autónoma de Madrid
Cantoblanco, 28049 – Madrid, Spain

² Institut Català d'Investigació Química, 43007 – Tarragona, Spain

³ Instituto de Ciencia de Materiales de Madrid - CSIC, Cantoblanco, 28049 – Madrid, Spain

josemaria.gallego@uam.es

Molecular electronics is a promising alternative for the continuing miniaturization of electronic devices. The capability of synthesizing and depositing molecular wires on solid surfaces is a key step within this context. The majority of the most promising current candidates to molecular wires, such as carbon nanotubes, DNA strands or individual polymer molecules [1], are too large and fragile for depositing them on solid surfaces by in-vacuum sublimation. Other kinds of wet deposition methods, such as drop-casting, are not so well controlled, which, in turn, hinders the understanding and design of their conductivity.

Since the molecular mass of the chemical species well-suited for deposition on solid surfaces by in-vacuum sublimation is limited, one could envisage a mechanism to grow the polymeric molecular wires by depositing smaller subunits that would subsequently assemble into the polymer after they have been adsorbed on the surface. This approach has successfully been used to steer the assembly of organic molecules into 1D structures [2], although the electrical conductivity of such “supramolecular” wires is still to be addressed. The 1D molecular wires so created are mostly like “ribbons”, due to the fact that the molecules tend to lie flat on the surface to maximize substrate-adsorbate interaction. The on-surface synthesis of molecular wires with more complex geometrical shapes, such as tubular or cylindrical, has only been described for the case of carbon nanotubes, and only on surfaces covered with catalytic nanoparticles [3] or on silicon carbide surfaces, where the constituent carbon for the nanotube growth arises from bulk segregation [4]. The aforementioned ideal situation in which molecular subunits assemble into 1D structures with cylindrical symmetry has not been described so far in the literature.

In this work we describe the growth of 1D tube or cylinder-looking structures obtained after deposition of the organic compound Zn *meso*-tetramesitylporphyrin (Zn-TMP, see Figure 1) on the noble-metal surfaces Au(111) and Cu(100) by vacuum sublimation (See Figure 2) with the substrate held at room temperature (RT). Our experiments indicate that the “nanotubes” are only a meta-stable structure, since they disassemble into flat-lying Zn-TMP monomers upon annealing to 500 K (see Figure 3). The disassembled Zn-TMP adsorbates are tightly bound to the surface, as evidenced by the fact that they can be easily imaged by Scanning Tunnelling Microscopy even at room temperature, and the difficulty to manipulate them even under the harsher tunnelling conditions. Two mechanisms for such a phenomenon will be discussed.

References:

- [1] N. Robertson, C. A. McGowan, *Chem. Soc. Rev.*, **32** (2003) 96.
 [2] J. Weckesser, A. De Vita, J.V. Barth, C. Cai, K. Kern, *Phys. Rev. Lett.*, **87** (2001) 096101;
 R. Otero, Y. Naitoh, F. Rosei, P. Jiang, P. Thstrup, A. Gourdon, E. Laegsgaard, I. Stensgaard, C. Joachim, F. Besenbacher, *Angew. Chem. Intl. Ed.* **43** (2004) 2091; T. Yokoyama, S. Yokoyama, T. Kamikado, Y. Okuno, S. Mashiko, *Nature* **413** (2001) 619.
 [3] J. Liu, A. G. Rinzler, H. Dai, J. H. Hafner, R. K. Bradley, P. J. Boul, A. Lu, T. Iverson, K. Shelimov, C. B. Huffman, F. Rodriguez-Macias, Y.-S. Shon, T. R. Lee, D. T. Colbert, R. E. Smalley, *Science* **280** (1998) 1253.
 [4] V. Derycke, R. Martel, M. Radosavljevic, F. M. Ross, Ph. Avouris, *Nano Lett.* **2** (2002) 1043

Figures:

Figure 1. Stick-and-ball model of the Zn porphyrin used in this study.

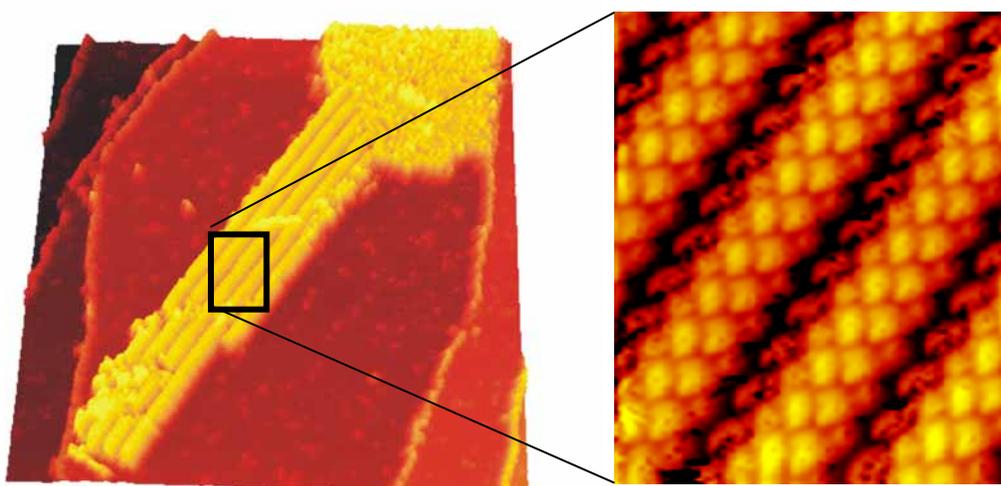
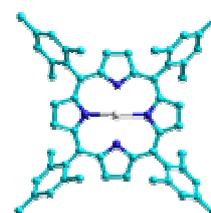


Figure 2. $98.4 \times 98.4 \text{ nm}^2$ STM image of long tubes coexisting with disorder after depositing ZnTMP on Cu(100) and a zoom-in showing the spiral shape of the tubes

Figure 3. $21 \times 25 \text{ nm}^2$ STM image showing individual flat lying ZnTMP molecules on Cu(100) after annealing the tubes to 500 K.

