

1D ZnO Chains as the Spinal Cord of Adsorbed Metalloporphyrin Nanotubes Linked by Water Ligands

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Zinc oxide is a technologically attractive material due to its unique piezoelectric and optoelectronic properties. In recent years a very intense activity has been directed towards the fabrication of ZnO nanowires for applications such as room-temperature, ultra-violet lasing, field-effect transistors, chemical and biochemical sensors, etc. The growth of such nanowires is usually carried out by vapour-liquid-solid method, in which liquid droplets of surfactant direct the growth of the ZnO nanowire. The width of the resulting nanowire is thus determined by the size of the surfactant droplets, usually no smaller than 50 nm [1].

On the other hand, it is well known that 1D structures made out of face-to-face stacked metallomacrocycles can be stabilized by ligand coordination between the metal centres. For example, Ru and Os porphyrins can form long 1D, conductive polymers in which pyrazine ligands bridge the metal centres in neighbouring porphyrins. The resulting structure can thus be regarded as a nanotube in which an organic outer scaffolding protects an inner, strictly 1D metal-ligand spinal cord [2].

In this work we describe the formation of long 1D ZnO chains as spinal cords of self-assembled Zn-porphyrin nanotubes created by deposition of aquo(tetramesitylporphyrinato)zinc(II) (H₂O-ZnTMP) on noble-metal surfaces. Our low-temperature Scanning Tunnelling Microscopy (STM) experiments reveal that the deposition of H₂O-ZnTMP on Au(111) and Cu(100) leads to the formation of long 1D tube-like structures, which are not found upon deposition of the metal-free H₂TMP. Moreover, the nanotubes are also disrupted upon annealing to temperatures in which the H₂O ligands detach from the Zn atoms, as monitored by X-Ray Photoemission Spectroscopy (XPS). Density Functional Theory (DFT) calculations also support this view, yielding binding energies of about 0.7 eV per monomer due to the presence of the water links, whereas in the absence of water ligands the attractive interaction energy between the ZnTMP units is negligible.

This work demonstrates that coordination bonds can be preserved upon sublimation and surface adsorption, opening new ways to steer the coordinative co-polymerization of adsorbed species by deposition of supramolecular units that already contain some of the coordination bonds to be found in the desired final product. We have shown that this method can be used to grow 1D metalloporphyrin coordination copolymers with a ZnO spinal cord with potential applications in molecular optoelectronic devices such as optoelectronic gates.

References:

- [1] Z. L- Wang, J. Phys.: Condens. Matter, **16** (2004) R829.
 [1] J. P. Collman, J. T. McDevitt, G. T. Yee, et al., Proc. Natl. Acad. Sci. USA, **83** (1986) 4581.

Figures:

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

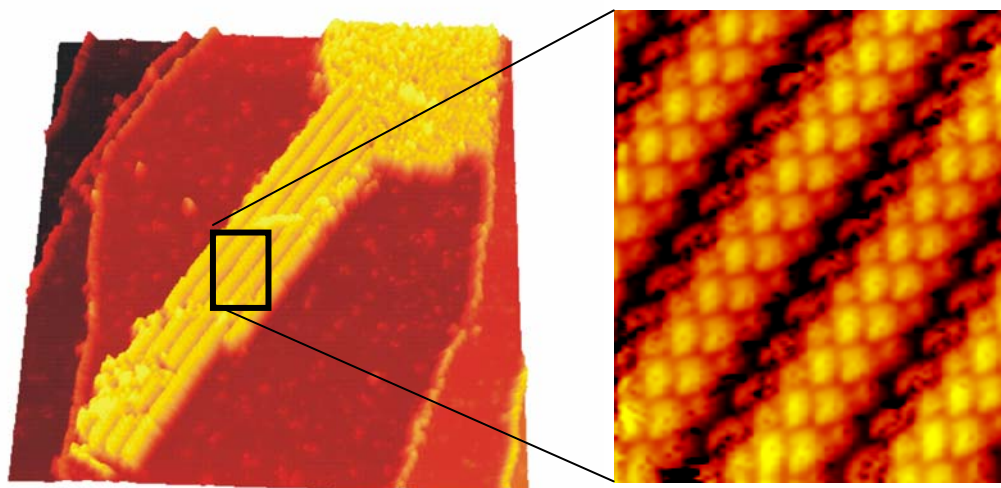
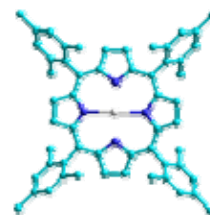


Figure 2. 98.4×98.4 nm² STM image of long tubes coexisting with disorder after depositing ZnTMP on Cu(100) and a zoom-in showing the spiral shape of the tubes

Figure 3. 21×25 nm² STM image showing individual flat lying ZnTMP molecules on Cu(100) after annealing the tubes to 500 K.

