CREATING A NANO-SCALE POROUS NETWORK OF PORPHYRIN MOLECULES

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Molecular self-assembly is a very promising alternative for designing and fabricating new nano-scale materials in the so-called "bottom-up" approach [1,2,3]. In addition, the possibility of creating patterns of molecular networks with predefined, well-controlled geometries that could be used as a sort of nanoporous molecular material is opening new ways to fields as different as catalysis, electronics, or information storage. In particular, porphyrin molecules are of special interest due to the main role the play in a wide variety of biological, and chemical processes, and also photovoltaic devices.

In this work we report on the self-assembly of meso-tetrakis (2-4-6-trimetil) fenil porphyrin (TMsP, Fig. 1) when vapour-deposited in UHV conditions on Cu(100). For low coverages, the porphyrins can be found isolated or forming small clusters on the surface (Fig. 2). Intramolecular resolution allows to determine their conformation and orientation, which come dictated by the substrate, the porphyrin main axis being parallel to the Cu[110] directions. Upon increasing the coverage, the TMsP molecules self-assemble to form a square lattice with a $\begin{pmatrix} 6 & 2 \\ 2 & 6 \end{pmatrix}$ structure (Fig. 3). Interestingly, our calculation reveal that the intermolecular distance and relative orientation are almost independent of the substrate, indicating that the assembly process comes mainly dictated by the intermolecular forces.

An open, nano-porous, square network of TMsP can also be fabricated by depositing the molecules on Cu(100) c(2 x 2) / N. This surface, formed after adsorbing < 0.5 ML of N on Cu(100) and annealing to 600 K, is composed of square N islands, ~ 5 nm wide, separated by thin Cu lines [4], and has been used as a template to create arrays of metallic nanostructures [5]. When the TMsP molecules are deposited on this surface, they nucleate almost exclusively on the Cu lines, leaving empty the N islands (Fig. 4). In this way, by carefully controlling the width of the Cu lines and the molecule coverage, a film with 5 nm wide square pores of variable density that could be use as template for the growth of other nanoparticles can be created.

References:

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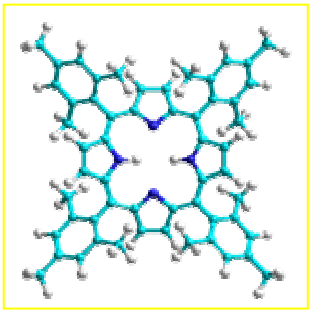

Figure 1: Chemical structure of TMsP.

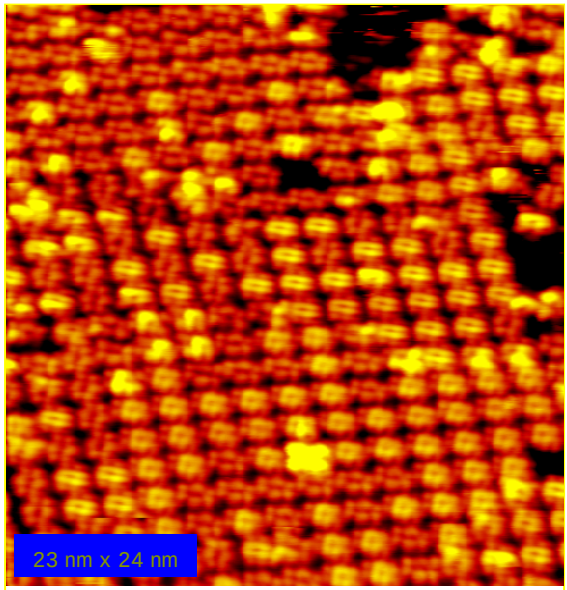

Figure 3: STM image of the Cu(100) surface almost completely covered by 1 ML of TMsP.

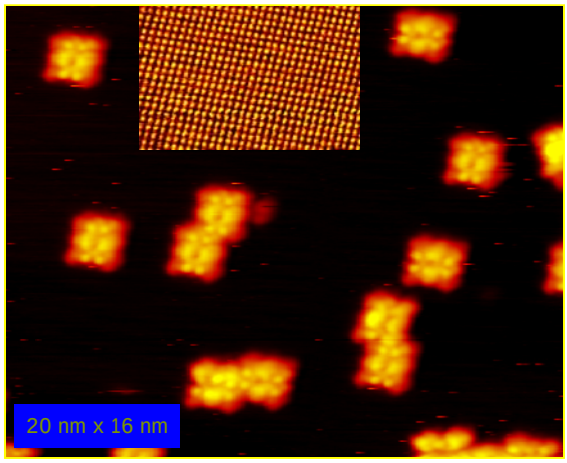

Figure 2: STM images of the Cu(100) surface after depositing ~ 0.1 MLS of TMsP. The inset shows an image of the Cu surface with atomic resolution

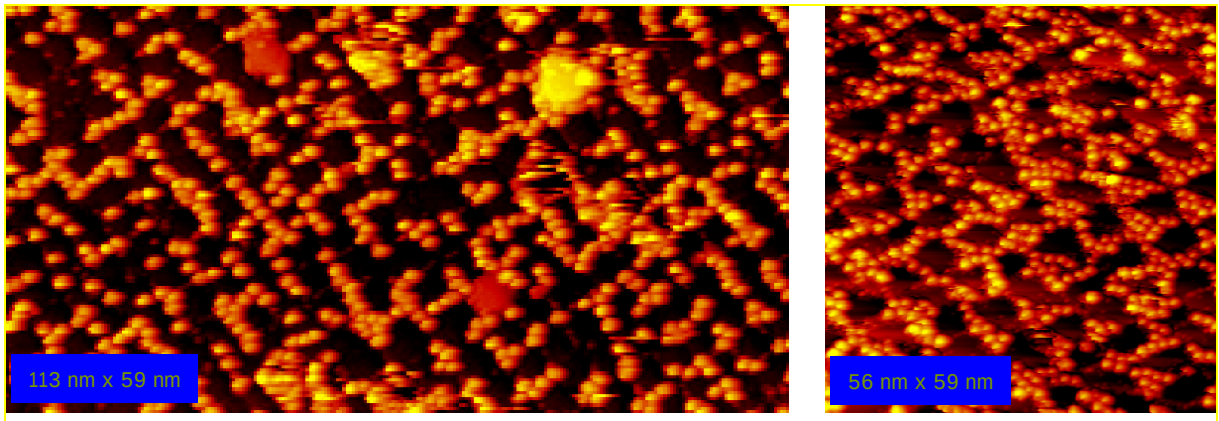

Figure 3: STM images of the Cu(100) c(2 x 2) / N surface after depositing increasing amounts of TMsP: a) 0.2 ML; b) 0.5 ML.