MOLECULAR CONFORMATION, ORGANIZATIONAL CHIRALITY, AND Fe METALLATION OF MESO-TETRAMESITYLPORPHYRINS ON Cu(100)

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The controlled study of biomimetic systems is of paramount importance in order to understand the fundamental processes that govern biological systems. In this sense, ordered layers of organic compounds on solid surfaces can be used as model systems to study chemical reactivity or energy transfer mechanisms. Specifically, porphyrins and metalloporphyrins are key components in many biological processes, and Fe porphyrins in particular are of special interest as they are at the core of haemoglobin, the protein in the red blood cells responsible for the transport of oxygen. Morever, porphyrin derivatives have been used in chemical sensors, molecular wires, information storage memory devices, catalysts, solar cells, etc. The behaviour of different metalloporphyrin systems may be significantly altered by adsorption on metal surfaces. Therefore the observation of their surface structures is of fundamental importance to fully understand the effect of structural and conformational changes on their reactivity.

In this work we report on the self-assembly of meso-tetramesitylporphyrin (TMP, Fig. 1) when vapour-deposited in UHV conditions on Cu(100). Although at room temperature the molecules are very mobile, for low coverages they remain isolated or forming small clusters on the surface (Fig. 2a), indicating a rather low intermolecular interaction. Intramolecular resolution (Fig. 3), in combination with photoemission experiments and theoretical calculations, allows to determine their conformation and thus the effect of the copper surface. The molecular orientation comes dictated by the substrate, with the porphyrin main axis parallel to the Cu[110] directions.

Only for higher coverages do the porphyrins nucleate into islands (Fig. 2b) forming a square lattice with a $\begin{pmatrix} 6 & 2 \\ 2 & 6 \end{pmatrix}$ structure. 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. The STM images show the existence of two types of molecules within the islands, probably corresponding to two different conformations (Fig. 4). In addition, the porphyrins can be Fe metallated by sublimation of Fe at room temperature on a porphyrin overlayer deposited on the Cu surface (Fig. 5), which opens the way to the study of the reactivity of Fe-TMP.

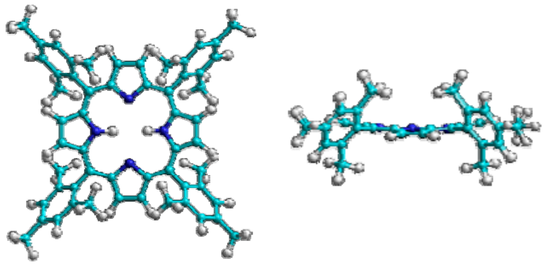

Figure 1: Top and lateral view of the minimum-energy gas-phase conformation of meso-tetramesitylporphyrin (TMP).

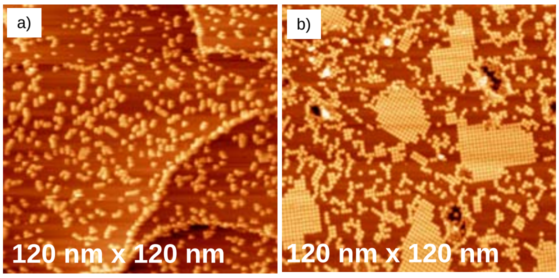

Figure 2: Large scale STM images after depositing a) 0.2 ML, and b) 0.45 ML ML of TMP on the Cu(100) surface.

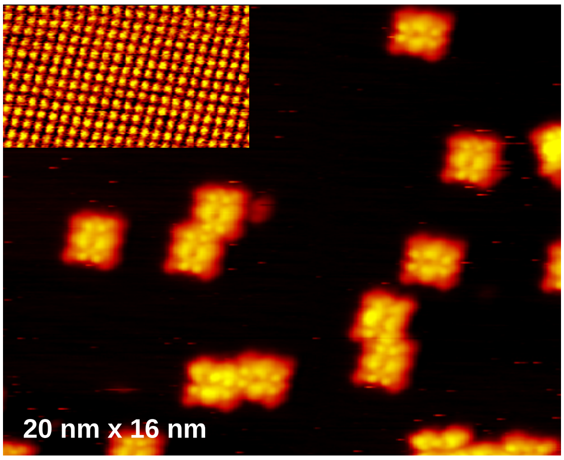

Figure 3: STM images of the Cu(100) surface after depositing ~ 0.2 ML of TMP. The inset shows the atomic lattice of the Cu substrate.

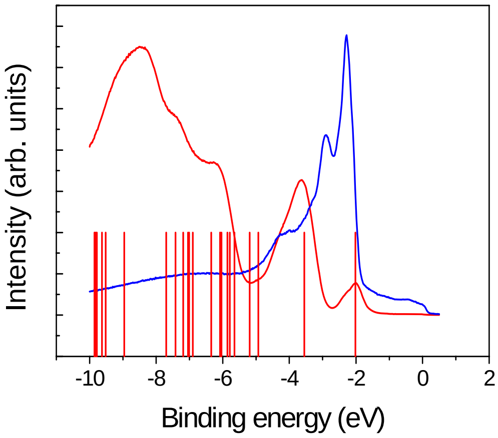

Figure 4: UPS spectra of the clean Cu(100) surface (blue), and after TMP deposition (red).

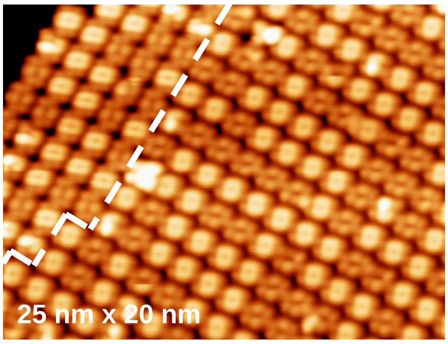

Figure 5: STM image of a porphyrin island showing two types (dark and bright) of molecules,

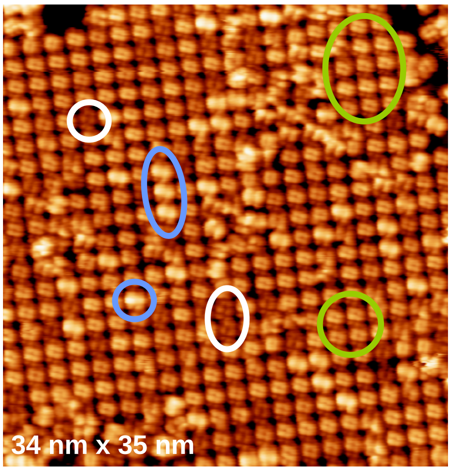

Figure 6: STM image of a porphyrin island after depositing a small amount of Fe.

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