

Molecules deposition on highly reactive surfaces: The case study of porphyrins on Fe(001)

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Summary. — The choice of low-interacting substrates to support a molecular layer is extremely relevant for the realization of working devices, especially when molecules with an open structure, such as metal tetraphenylporphyrins (MTPP), are used. Conversely, in the present work, I employ a prototypical highly reactive substrate (such as Fe(001)) to weight its influence on the structural and electronic properties of deposited molecules. To this goal, I have exploited photoemission spectroscopy (XPS and UPS, porphyrin core and valence states properties), Near-Edge X-ray Absorption Fine Structure spectroscopy (NEXAFS, molecule orientation with respect to the buried substrate) and scanning tunneling microscopy (STM, MTPP assembling properties) on three different MTPP molecules (namely, ZnTPP, CoTPP and VOTPP). While Zn- and CoTPP shows basically a planar configuration, VOTPP has the oxygen atom placed outside the main tetra-pyrrole ring, which can influence the molecules assembling on clean substrates.

1. – Introduction

In the last decades, a lot of effort has been devoted to the comprehension of the phenomena occurring when molecules are deposited on top of substrates [1]. These compounds have found interesting applications in microelectronics, sensing, photovoltaics, coating and spintronics [2, 3], due to the fine tuning of the molecular properties offered by the advances in the chemical synthesis. The ultimate goal of this research is to exploit molecules as single working units [4]. For this purpose, the molecules should be decoupled from the substrate underneath in order to arrange regularly and maintain their electronic and magnetic properties [5, 6]. I have joined this field of research by proposing a prototypical system where flat molecules, such as metal tetraphenylporphyrins (MTPP), are deposited on a highly reactive Fe(001) substrate, previously passivated by an ultra-thin

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oxygen layer (Fe(001)- $p(1 \times 1)\text{O}$) [7]. On the one hand, the open structure of MTPPs can directly test a possible interaction between the molecule and Fe(001)- $p(1 \times 1)\text{O}$, where they lie flat in an ordered (5×5) superstructure. On the other hand, I proved that a single layer of oxygen atom is able to preserve the main electronic characteristics of the porphyrins [7, 8]. In this work, I present the dramatic role of the unscreened Fe(001) substrate on both the assembling and electronic properties of three different MTPPs: Zn-, Co- and VOTPP. While the former show an almost flat configuration, the latter are characterized by an oxygen atom placed outside of the main tetra-pyrrole ring, which could affect the growth of VOTPP on clean metal surfaces. The system is studied by photoemission spectroscopy (XPS and UPS), Near-Edge X-ray Absorption Fine Structure spectroscopy (NEXAFS) and scanning tunneling microscopy (STM).

2. – Materials and methods

The preparation and analysis of the samples were performed in ultra-high vacuum conditions (pressure $\leq 10^{-10}$ mbar). The substrate was a thick (≈ 500 nm) Fe film grown on MgO(001), whose surface was cleaned by cycles of sputtering and annealing at 400 °C. Porphyrins were evaporated by means of Knudsen cells (deposition rate below 1 Å/min), with the sample kept at room temperature (RT). UPS was performed with a non-monochromatic HeI photons ($h\nu = 21.2$ eV). The emitted electrons were collected by a 150 mm hemispherical electron analyzer from SPECS GmbH. The energy resolution for UPS measurements was 50 meV. STM measurements were obtained at RT in constant-current mode using a commercial Omicron system. XPS and NEXAFS spectra were acquired at the ALOISA beamline at the Elettra synchrotron radiation facility (Trieste, Italy). The M 2*p* photoemission spectra were acquired at normal emission and grazing incidence ($\sim 4^\circ$). NEXAFS spectra were acquired according to the methodology described in [9]. To investigate the sample dichroism, spectra have been collected with the surface oriented either parallel to the electric field (*s*-polarization) or closely normal to it (*p*-polarization). The photon energy resolution was set to 0.08 eV.

3. – Results and discussion

3.1. Morphology and orientation. – The morphology and the crystallinity of the system have been analyzed through STM and LEED. The results are reported in fig. 1. The as-prepared Fe(001) surface shows flat terraces (panel (a)) and the expected LEED (1×1) symmetry (panel (b)) [10, 11]. When, *e.g.*, the ZnTPP molecules are deposited on this surface, STM does not reveal any molecular order (fig. 1(c)). Similarly, the LEED panel does not display any clear diffraction pattern (fig. 1(d)). No differences are observed with other MTPP molecules when deposited on clean Fe (data not reported). However, a different situation could be expected for VOTPP molecules at least regarding the orientation of the main tetra-pyrrole ring: the oxygen atom could be interposed between the molecule and the substrate, favoring a parallel orientation between these two. For the VOTPP orientation on Fe(001), I have acquired NEXAFS spectra of both a single and thicker layers (fig. 1(e)). The 1 ML sample produces the same dichroism of the thick VOTPP film, where a parallel orientation of the molecule with respect to the substrate is not expected. I have to conclude that the unprotected Fe(001) precludes the growth of well-packed, oriented porphyrin films, irrespective of their planar or 3D structure.

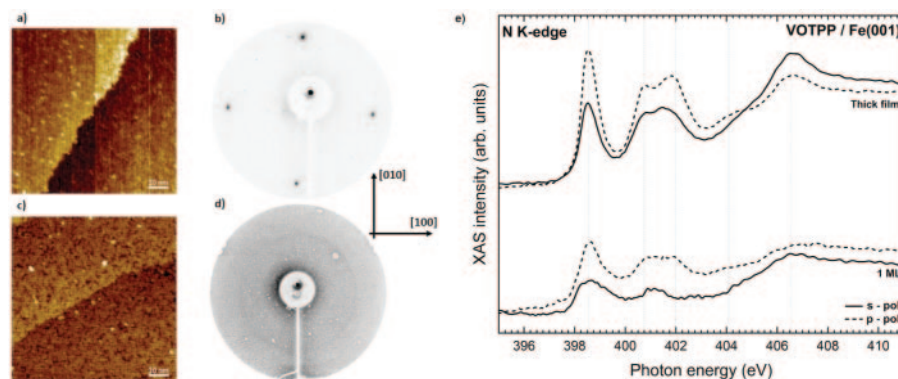


Fig. 1. – $80 \times 80 \text{ nm}^2$ STM image acquired on (a) the bare Fe(001) and (c) the 1 ML ZnTPP/Fe(001) sample ($V_{\text{bias}} = 0.3 \text{ V}$, $I_{\text{tunnel}} = 1 \text{ nA}$). LEED pattern acquired with a beam energy of 55 eV on (b) the bare Fe(001) surface and (d) 1 ML ZnTPP/Fe(001). (e) NEXAFS spectra acquired at the N K-edge with *s*- (full line) and *p*- (dashed line) polarized light for the system 1 ML (bottom) and a thick film (top) of VOTPP on Fe(001).

3.2. Chemical and electronic stability. – When I studied the growth of VOTPP on Fe(001)-*p*(1×1)O, the porphyrin stoichiometry was preserved [12]. Conversely, a XPS investigation of the V $2p$ signal reveals a metal ion reduction when VOTPP are placed on Fe(001) (see fig. 2(a)). The energy position of the V^{4+} and V^{2+} peaks are compatible with results on similar systems involving VOTPP and VTPP [13]. As a consequence, I hypothesize a possible removal of the oxygen atom from the main tetra-pyrrole ring, for a significant, but still minority portion of the molecular film. This directly proves the strong interaction between the molecules and the substrate. At larger coverages, the interaction with the substrate is screened by the first deposited molecular layers and the chemical stability of the macrocycle is preserved.

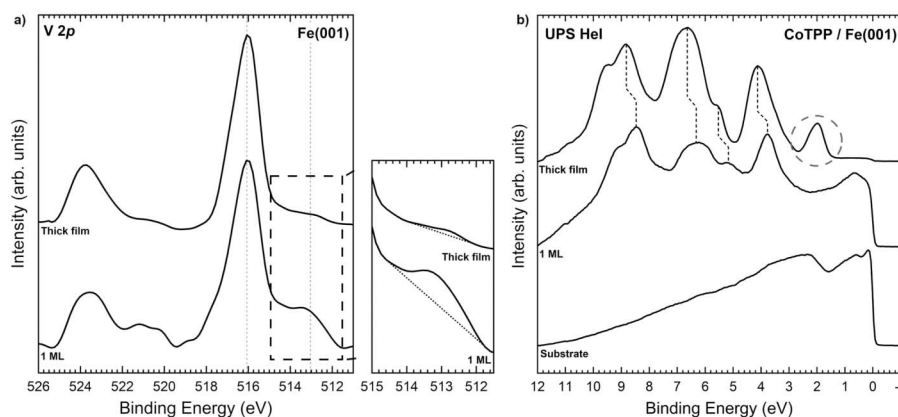


Fig. 2. – (a) XPS spectra acquired on 1 ML (bottom) and a thick VOTPP film (top) on Fe(001). Vertical dotted lines in the V $2p_{3/2}$ energy region mark the photoemission features from V^{4+} and V^{2+} species, the latter further magnified in the inset. (b) UPS spectra acquired at different coverages of CoTPP on Fe(001). The dashed circle highlights the photoemission feature from the HOMO level.

The electronic stability of porphyrins on Fe(001) can be investigated by UPS (fig. 2(b)). Here, I show the noticeable effect observed on the CoTPP HOMO level. The spectroscopic feature related to the macrocycle HOMO level is clearly detected on the multilayer sample (fig. 2(b), highlighted in red). This feature becomes completely quenched on the single layer. I have proven that the HOMO peak is instead well visible on UPS data acquired on the CoTPP/Fe(001)- $p(1 \times 1)$ O system [9,14], proving that the CoTPP properties (and this also applies to all the other MTPPs) are preserved only if at least a single layer of oxygen atom is interposed between them and the iron substrate.

In conclusion, these results offer a short survey of the effects produced by an interacting substrate to the particular and precious characteristic of porphyrin molecules.

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