Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

ARTICLE TYPE: SUPPORTING INFORMATION

Hydrogen capture by porphyrins at the TiO_2(110) surface

Giacomo Lovat,[a,b] Daniel Forrer,[c] Mikel Abadia,[d] Marcos Dominguez,[a,b] Maurizio Casarin,[e] Celia Rogero,[d] Andrea Vittadini*[e] and Luca Floreano*[a]

SUPPORTING INFORMATION

1 NEXAFS C and N K-edge.

The NEXAFS spectra in TM polarization for the monolayer phase of porphyrins on TiO_2(110) are dominated by the resonances of the π-symmetry unoccupied MOs, due to the closely planar molecular orientation. This geometry is preserved also in the next few molecular layers before a 3D growth takes place. The carbon spectra in TM polarization are characterized by two main peaks (see Fig. 1). For all of the three molecules, the first resonance at ~284.1 eV corresponds to the resonance of the lowest unoccupied molecular orbital (LUMO), which is localized on the pyrrolic carbon atoms. This resonance displays a large dichroism with a residual intensity in TE polarization of ~ 10%, that can be ascribed either to a minority of second layer molecules and defects or to a small out of plane distortion of the tetra-pyrrolic macrocycle due to the hydrogen uptake. Overall, we can conclude that three porphyrin molecules display the same planar orientation of the inner macrocycle, irrespective of their different peripheral terminations.

The second resonance at ~285.2 eV is mostly contributed by the molecular orbital localized on the phenyl carbon atoms in the case of TPP and TBTPP, while it stems from the LUMO+1 of the pyrrolic rings in the case of OEP (with a much lower intensity and slightly different energy). While the latter pyrrolic LUMO+1 resonaces displays a dichroism simply following that of its LUMO counterpart, the NEXAFS resonances associated with phenyls display a smaller dichroism, indicating that they are tilted off the surface (of 25-30° and 40° for TBTPP and TPP, respectively). This tilt angle confirms that both TPP and TBTPP preserve their 3D structure, although slightly relaxed with respect to their bulk phase.

The nitrogen K-edge NEXAFS spectra, shown in Fig. 2 display a strong similarity among the different porphyrins with a char-

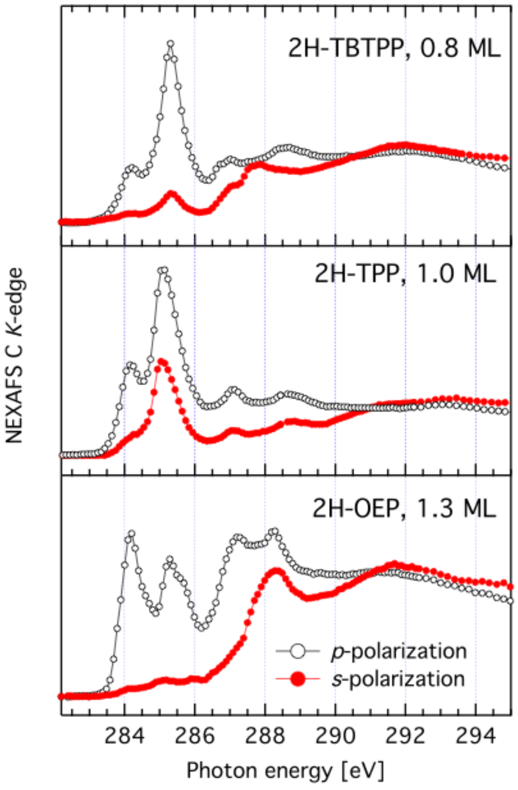


Fig. 1 Carbon K-edge NEXAFS spectra measured in TM and TE polarization (open and filled markers, respectively) for metal-free porphyrin films grown on TiO_2(110) at room temperature in the monolayer coverage range.

---

[a] CNR-IOM, Laboratorio TASC, Basovizza SS-14, Km 163.5, I-34149 Trieste, Italy.

[b] Graduate School of Nanotechnology, University of Trieste, P.za Europa 1, I-34127 Trieste, Italy.

[c] CNR-IENI and INSTM, via Marzolo 1, I-35131 Padova, Italy.

[d] Materials Physics Center MPC, Centro de FŠsica de Materiales (CSIC-UPV/EHU) and Donostia International Physics Center (DIPC), E-20018 San Sebastian, Spain.

[e] Dipartimento di Scienze Chimiche, Universitá di Padova, via Marzolo 1, I-35131 Padova, Italy.

* Corresponding authors: andrea.vittadini@unipd.it, floreano@iom.cnr.it

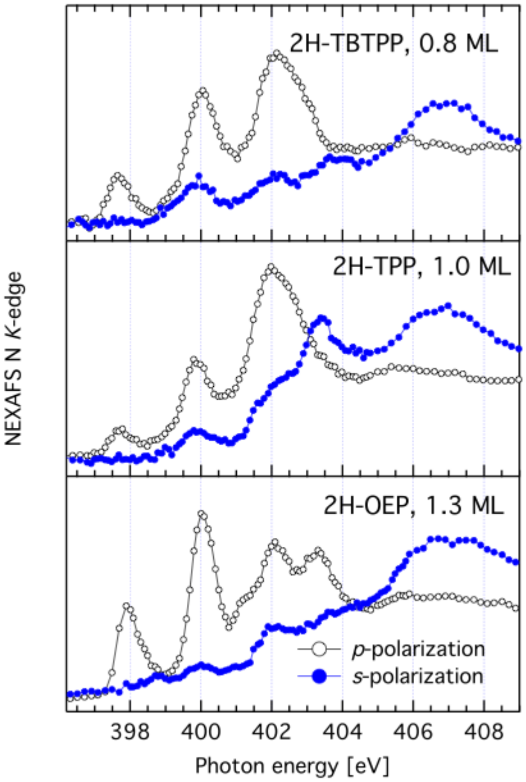


Fig. 2 Nitrogen K-edge NEXAFS spectra measured in TM and TE polarization (open and filled markers, respectively) on the same films of previous Figure.

acteristic sequence of resonances at ∼398, 400 and 402 eV. The first two peaks correspond to the π-symmetry unoccupied MOs localized on the iminic (LUMO at 397.7-398.0 eV) and pyrrolic nitrogen (LUMO+1 at ∼400 eV). For all the three molecules, the residual intensity recorded at the iminic LUMO resonance can be associated with the residual iminic intensity observed in the corresponding photoemission spectra (see Fig. 1 in the article and following XPS analysis). It is worth recalling that, at variance with XPS, the intensity of the NEXAFS resonances is not simply reflecting the compound stoichiometry. The residual iminic component (corresponding to the minority phase of unreacted molecules) displays a dichroism larger than that of the LUMO+1 resonance (corresponding to the majority phase of hydrogen-reacted molecules), indicating that the rings associated with the pyrrolic nitrogen are tilted off the surface by an angle larger than that of the rings associated with iminic nitrogen. This observation is in qualitative agreement with DFT calculations showing an increase of the average tilt angle of the macrocycle rings upon hydrogen uptake.

2 N 1s core level photoemission

2.1 Coverage dependence

In Fig. 3, we show that the spectroscopic footprint of a fully hydrogenated macrocycle is observed from the early stage of deposition in the submonolayer range (spectrum taken at 0.4 ML).

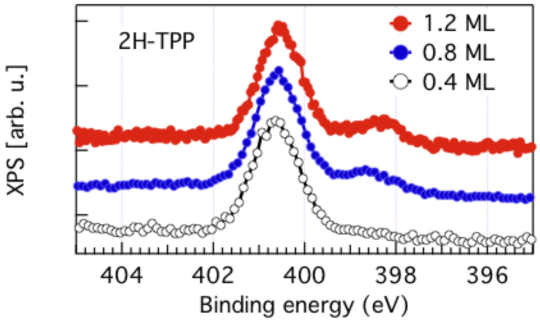
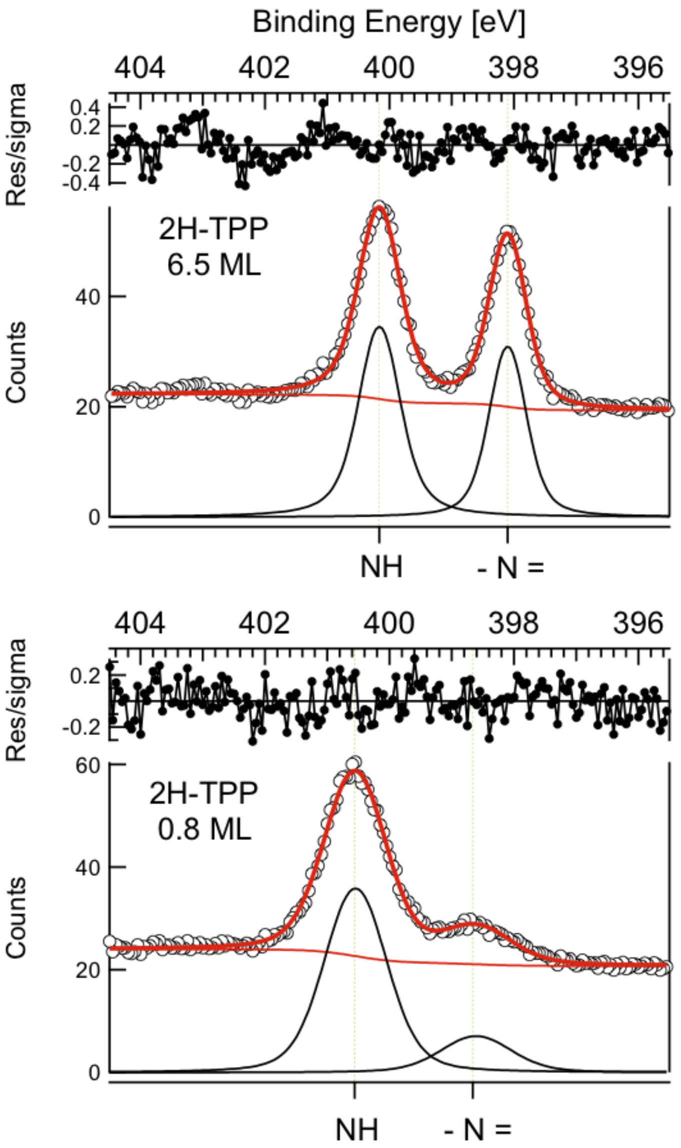


Fig. 3 Photoemission spectra of 2H-TPP measured at 0.4, 0.8 and 1.2 ML coverage with a photon energy hν = 500 eV. Molecules have been deposited at room temperature on a clean TiO_2(110) surface.

A contribution from a minority of unreacted molecules starts to appear close to the completion of the first layer (spectrum taken at 0.8 ML), as witnessed by the appearance of the iminic peak at 398.5 eV. The whole spectrum starts to shift to lower binding energy, when the coverage exceeds the first monolayer (see spectrum at 1.2 ML) due to the increasing weight of second layer molecules. The same behavior is observed also for 2H-OEP and 2H-TBTPP.

2.2 XPS analysis

The N 1s photoemission peaks have been fitted to true Voigt function with a Shirley background. The fitting analysis is shown in Fig. 4 for the case of 2H-TPP molecules at the coverage of 5.5 and 0.8 ML. The overall FWHM of the pyrrolic peak is found to be 0.69 and 1.05 eV at 5.5 and 0.8 ML, respectively.



Pyrrolic nitrogen (NH)
BE = 400.16 eV
FWHM(l) = 0.39 eV
FWHM(g) = 0.57 eV
Area = 36.1
Shirley bkg = 0.047

Iminic nitrogen (-N=)
BE = 398.1 eV
FWHM(l) = 0.27 eV
FWHM(g) = peak NH
Area = 27.5
Shirley bkg= peak NH

Pyrrolic nitrogen (NH)
BE = 400.55 eV
FWHM(l) = 0.29 eV
FWHM(g) = 1.02 eV
Area = 50.2
Shirley bkg = 0.055

Iminic nitrogen (-N=)
BE = 398.61 eV
FWHM(l) = 0.39 eV
FWHM(g) = peak NH ±0.1 eV
Area = 11.5
Shirley bkg = off

Fig. 4 Photoemission spectra of 2H-TPP at 6.5 (top) and 0.8 ML (bottom). The experimental data (open markers) are taken from Fig. 1 of the article (measured at hν = 500 eV with ΔE$\sim$160 meV). Fitting curves are shown as full lines and resolved in single peaks. The corresponding fitting analysis is reported on the right side.