

PCCP

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



Journal Name

ARTICLE

Hydrogen capture by porphyrins at the TiO₂(110) surface†

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

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Metal-free porphyrin molecules adsorb on the rutile TiO₂(110) surface with their pyrrolic nitrogen atoms atop the O-bridge rows, whereas the iminic nitrogen atoms capture two additional hydrogen atoms. Hydrogenation occurs spontaneously at room temperature, irrespective of the distance of the polypyrrolic macrocycle from the surface, as varied by changing the porphyrin functionalization.

Introduction

Metal porphyrins (MPs) and phthalocyanines (MPcs) offer a large variety of electronic configurations that, when brought into contact with a substrate, can display the most diverse electronic and chemical functionalities,¹ spanning from magnetism² to catalysis.³ In this context, the metal-free molecular homologues (2H-P and 2H-Pc) display a large flexibility, as they can be suitably metalated in situ by post growth treatment, either by metal extraction from the substrate,⁴ or by incorporation of diffusing adatoms (e.g. after atomic beam deposition).⁵ Hydrogen itself can be exploited to modify the local molecular conductance by selective cleavage of one pyrrolic NH bond in 2H-P,⁶ as well as to tune the chirality by selective adsorption in MnPc.⁷

In order to generalize these functionalities, one must keep into account the nature of the substrate, which is demonstrated to affect the gas reactivity of the MP contact layer.^{3c} The interface of titania with MPs and MPcs attracts large interest because of its dual purpose applications in photocatalysis and solar cells. In particular, the rutile TiO₂(110) surface is a suitable template for the growth of poly- and hetero-aromatic molecules thanks to its large and anisotropic surface corrugation. Phthalocyanine and porphyrin films are expected to grow with the molecular macrocycles closely parallel to the substrate,^{5c,8,9} a geometry that favors

intermolecular charge transport¹⁰ and charge injection into the oxide substrate.¹¹

A number of XPS measurements of different phthalocyanines and porphyrins grown on TiO₂(110) has however put in evidence the unexpected presence of pyrrolic nitrogen in metalated species, as well as an excess of pyrrolic nitrogen with respect to the iminic one in non-metalated molecules.^{8,12-14} The nature of this component is controversial and has been alternatively attributed to chemical bonding of nitrogen to the oxygen atoms underneath,⁸ or to a local surface screening effect,^{12,14} or to hydrogen capture upon molecule de-metalation.¹³ To better address this controversial issue we focused on the simplest case of metal-free porphyrins, which contain only two types of nitrogen atoms, namely pyrrolic and iminic. We performed the experiments on three differently functionalized porphyrins: 2H-ter-butyl-tetra-phenyl-porphyrin (2H-TBTPP), 2H-tetra-phenyl-porphyrin (2H-TTP) and 2H-octa-ethyl-porphyrin (2H-OEP). These different peripheral terminations do not display specific (chemical) affinity to the substrate, and essentially change the height of the central macrocycle with respect to the surface by ~1 Å from 2H-TBTPP to 2H-OEP passing through the intermediate 2H-TTP.

Results and discussion

The ligand state of nitrogen in 2H-P can be probed by X-ray photoemission (XPS) measurements of the N 1s core level. Metal-free porphyrins are characterized by two well separate N 1s peaks of equal intensity (separation of ~2 eV), corresponding to one pair of hydrogenated (pyrrolic) nitrogen atoms and one pair of iminic (aza) nitrogen atoms.¹⁵ However, the first layer molecules always display the occurrence of a dominant component at ~400.2-400.5 eV in the N 1s photoemission spectra, as clearly shown in the bottom curves of Fig. 1 for 2H-TBTPP, 2H-TTP and 2H-OEP (from top to bottom). This binding energy corresponds to that of pyrrolic nitrogen, while the iminic component, which should display

^a CNR-IOM, Laboratorio Nazionale TASC, I-34149 Trieste, Italy. E-mail: floreano@iom.cnr.it

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

^c CNR-ENI and INSTM, via Marzolo 1, I-35131 Padova, Italy. E-mail: andrea.vittadini@unipd.it

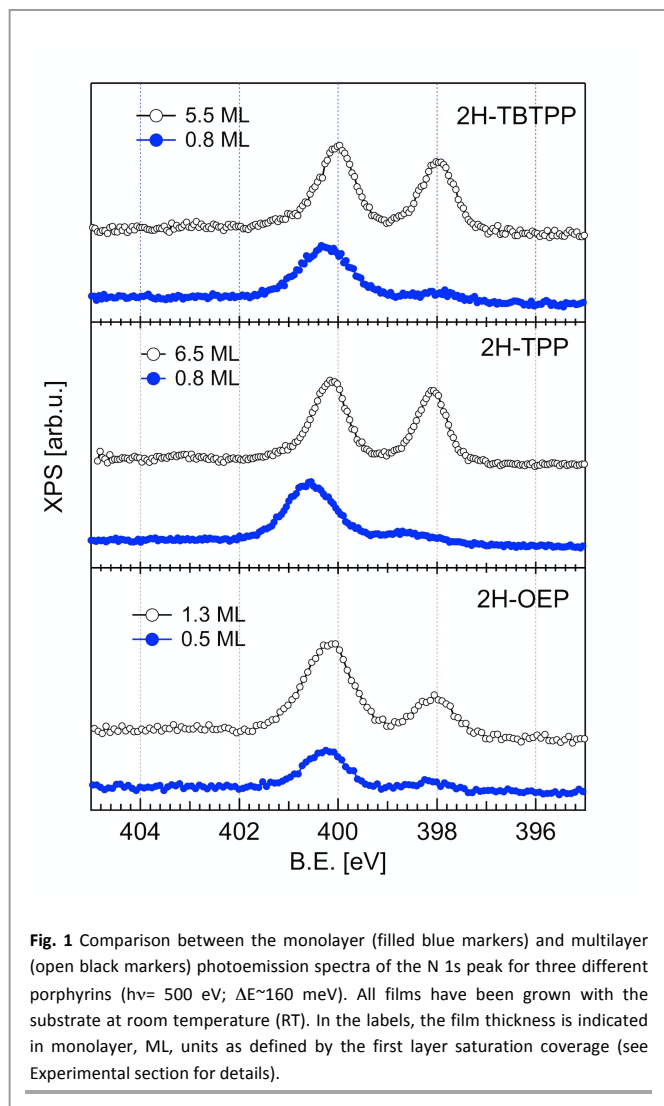
^d Materials Physics Center MPC, Centro de Física de Materiales (CSIC-UPV/EHU) and Donostia International Physics Center (DIPC), E-20018 San Sebastian, Spain.

^e Dipartimento di Scienze Chimiche, Università di Padova, via Marzolo 1, I-35131 Padova, Italy.

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

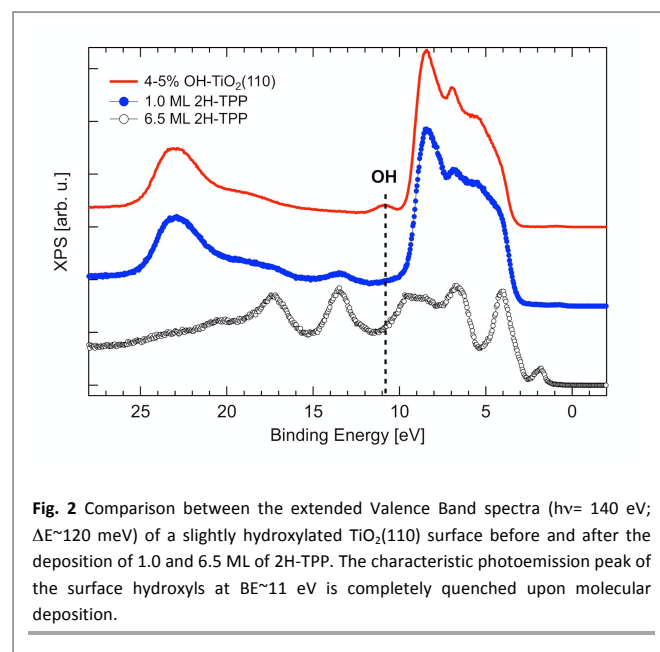
† Electronic Supplementary Information (ESI) available: original NEXAFS data at the K-edge ionization threshold of C and N, XPS fitting analysis of N 1s, computational details. See DOI: 10.1039/x0xx00000x

the same intensity of the pyrrolic one in presence of regular porphyrins, is residual and is observed to increase only upon condensation of sequent layer molecules at ~ 398 eV binding energy (see top curves of Fig. 1). We recall that also in metalated species, the four central nitrogen atoms become equivalent, but they yield a binding energy (BE) close to that of the iminic nitrogen atom ($\Delta BE \sim +0.3$ eV), without significant differences among different metal elements.



Concerning the molecular orientation, the polarization dependent near-edge x-ray absorption spectroscopy (NEXAFS) at the K-edge of nitrogen and carbon always displays a large dichroism of the resonances associated with the pyrrolic rings (see Supplementary Figs. 1 and 2), which indicates that the three molecules are equivalently oriented with the central macrocycle almost parallel to the substrate. The main difference among the adsorption geometries of the molecules is thus the height of the macrocycle above the substrate (2H-TBTPP is ~ 0.5 Å higher than 2H-TPP, which is ~ 0.5 Å higher than 2H-OEP, from simple steric arguments and neglecting minor relaxation effects). This excludes that the absence of the iminic component in the N 1s spectra might be due a strong core level shift (~ 2 - 2.5 eV) of aza-nitrogen, as originated either

by a local screening or by a chemical bonding of nitrogen to the oxygen rows underneath. Rather, the local relaxation (tilting) of the phenyl rings in 2H-TPP might be responsible of the slightly larger binding energy (0.2-0.3 eV) with respect to 2H-OEP and 2H-TBTPP molecules, which terminations are likely less leaning to fit the substrate corrugation. We are then left with the hypothesis of hydrogen uptake, either molecular (from the vacuum residual gas) or atomic (from the substrate). In fact, a large and consolidated body of literature indicates that a significant amount of hydrogen is diluted in the TiO_2 bulk, as favored by thermal treatment, metal (acceptor) contaminants, and electron irradiation.¹⁶ XPS is not a suitable probe of low concentration bulk-diluted species due to its intrinsic surface sensitivity (escape depth of 5-10 Å), however a few percent concentration of surface confined hydrogen species can be obtained by water dissociation at a slightly reduced $\text{TiO}_2(110)$ surface.¹⁷ These hydroxyl species can be easily monitored by photoemission of the valence band, where they give rise to a characteristic satellite of the O 2p band at ~ 11 eV.¹⁸



In Fig. 2 we compare the valence band spectra of a clean, albeit slightly hydroxylated $\text{TiO}_2(110)$ surface (estimated OH concentration of 4-5 %) before and after the deposition of a layer of 2H-TPP, which is the intermediate height molecule. The hydroxyl peak is fully quenched upon molecular deposition in agreement with the hypothesis of hydrogen uptake. We remark that i) full hydrogenation of nitrogen in the first porphyrin layer cannot be fulfilled only by the surface hydroxyls and ii) the nitrogen hydrogenation is observed also in absence of surface hydroxyls without any difference of the corresponding pyrrolic N 1s peak. This implies that either hydrogen is captured and dissociated from the residual gas pressure or that the porphyrin macrocycle locally lowers the kinetic barriers, which otherwise keep H interstitials in the subsurface region.

In order to further check the hypothesis of nitrogen hydrogenation, we performed ab initio calculations within the frame of gradient-corrected density functional theory (GGA-DFT) for the intermediate case of 2H-TPP (see Computational details). Calculations predict that the gas-phase hydrogenation of 2H-TPP is slightly exothermic at 0 K (see Table 1), whereas, by assuming an ideal gas behavior for H₂, we can estimate that $\Delta G \approx +0.3$ eV at 298 K. This agrees with the fact that 2H-TPP, and not 4H-TPP, is the species stable at RT in the gas phase. At the same time, it strengthens the possibility that the TiO₂ substrate, which can provide dissociated hydrogen on the surface, favors the stabilization of the 4H-TPP species.

Table 1. Hydrogenation reaction energies

Reaction	ΔG [eV]
2H-TPP(gas) + H ₂ (gas) → 4H-TPP(g)	-0.10*
2H-TPP(ads) + 2H(ads) → 4H-TPP(ads)	-1.40**

*Zero-point energy corrections have been applied.

** To avoid a lengthy study of the (weak) interactions among the adsorbed species, we assumed as initial state two identical and separate slabs, one containing 2H-TPP(ads) and the other one containing two H atoms adsorbed at two (far) oxygen-bridge, O_{br}, atoms. As a final state, we instead considered two slabs representing 4H-TPP(ads) and a bare surface, respectively. See text for details about the structural configuration.

We then examined the case of adsorbed 2H-TPP, using periodically repeated slab models with PBE-D theoretical lattice constants of the substrate.¹⁹ In order to refine the configuration model of the adsorbed molecule, we performed scanning tunnelling microscopy (STM) measurements of a submonolayer coverage of 2H-TPP, where the N 1s spectra display the same CLS as the monolayer one (see Supplementary Fig. 3) and the uncovered substrate lattice can be easily recognized to determine unambiguously the 2H-TPP adsorption site.

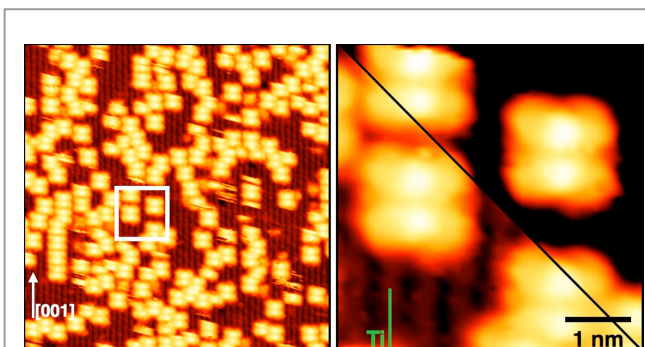


Fig. 3 Left: STM image (27.5x27.5 nm²) of ~1/3 ML of 2H-TPP deposited on the sample at room temperature ($V_s = -1.5$ V; $I = 60$ pA). The substrate Ti^{5f} (O_{br}) rows along the [001] direction appear as bright (dark) stripes. Right: zoom in of the area indicated by the white square, as displayed with different contrast in order to highlight the molecular adsorption atop the dark O_{br} rows (bottom) and to enhance the intramolecular structure (top).

As deposited at RT, all the molecules display a preferential adsorption configuration with a common azimuthal orientation. From the analysis of the STM images shown in Fig. 3, we can see that all molecules adsorb atop the oxygen rows with the squared molecular edge parallel to the substrate [001] direction. The individual molecules display a characteristic saddle-shape, which was reported also for 2H-TPP adsorbed on noble metals, and is originated by the opposite upward/downward tilt off the macrocycle plane of adjacent pyrrolic units. The corresponding nodal plane is oriented transverse to the oxygen rows and three distinct lobes can be distinguished on each side.

Because of i) the observed parallel to the surface orientation of the macrocycle (from NEXAFS dichroism) and ii) the D_{2h} symmetric appearance of the molecules, we could limit our tests to two azimuthal orientations: with two opposite nitrogen atoms (N-N axis) oriented either along the substrate [001] direction or at 45° from it (see Fig. 4). We considered adsorption on both Ti 5-fold coordinated (Ti^{5c}) and oxygen-bridge 2-fold coordinated (O_{br} or O^{2c}) rows in both on-top and on-bridge sites (see Computational details). The most favored adsorption site for both 2H-TPP and its hydrogenated homologue 4H-TPP is found to be the bridge position between two adjacent O_{br} atoms along [001], with the N-N axis also parallel to the [001] direction. The resulting adsorption energies for the case of 4H-TPP are shown in Fig. 4, as computed for 3-layer slabs and large-core pseudopotentials.

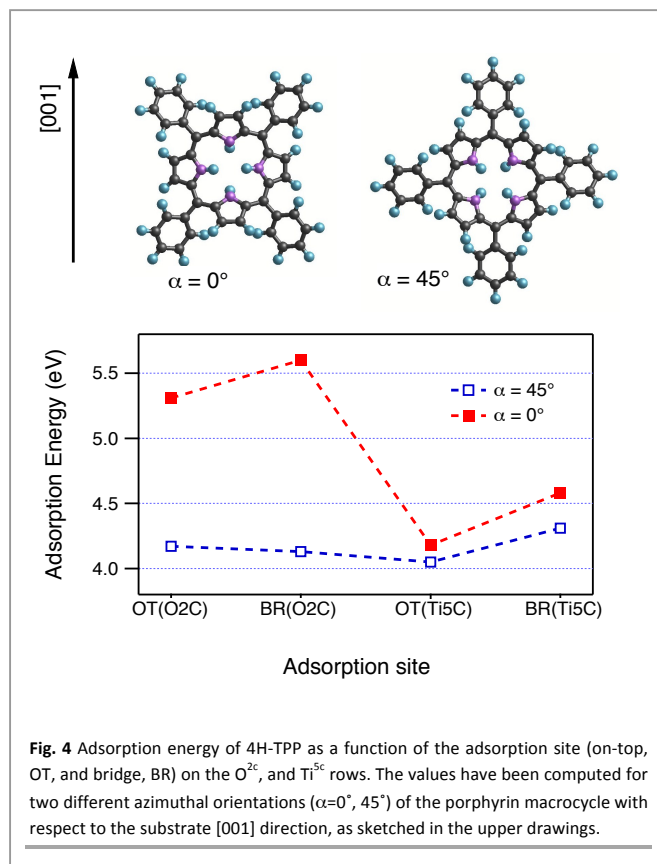
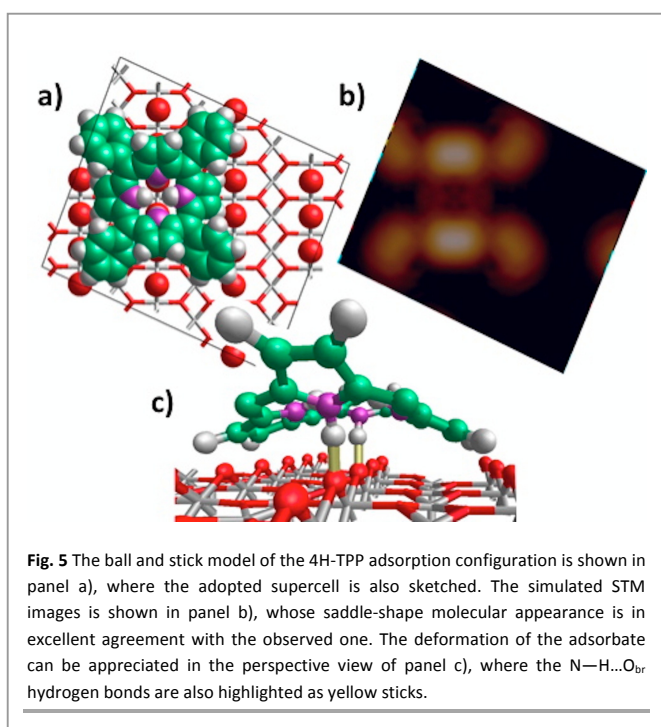


Fig. 4 Adsorption energy of 4H-TPP as a function of the adsorption site (on-top, OT, and bridge, BR) on the O^{2c}, and Ti^{5c} rows. The values have been computed for two different azimuthal orientations ($\alpha=0^\circ$, 45°) of the porphyrin macrocycle with respect to the substrate [001] direction, as sketched in the upper drawings.

The configurations parallel to the [001] direction (azimuth $\alpha = 0^\circ$) and placed on O_{br} row sites are largely favored (~1 eV)

with respect to the other ones, the oxygen-bridge site being favored over the on-top one by ~ 0.3 eV because of the stronger H-bond interaction. For 2H-TPP this difference is reduced to 0.2 eV because H-bonds are in general weaker. Our best estimates for adsorption energies, computed with 4-ML slabs and small-core pseudopotentials, are 5.31 eV and 3.41 eV for 4H-TPP and 2H-TPP, respectively.

We emphasize that in the most favored configuration two equivalent $\text{N}-\text{H}\cdots\text{O}_{\text{br}}$ hydrogen bonds are formed, as depicted in Fig. 5c; this configuration favors the downward tilt of the corresponding pyrrolic rings (Fig. 5a), whose peripheral carbon atoms protrude above the macrocycle plane and yield an enhanced intensity in the topographic images, as shown in the simulation of Fig. 5b. The other two central rings display a tilt in the opposite direction yielding a dimmed contrast in the direction transverse to the O_{br} rows.



The topographic images calculated for 2H-TPP are very similar to those of 4H-TPP, where the main structural difference is found to be the average tilt angle of the pyrrolic rings that increases by 6° upon hydrogen uptake. This difference cannot be appreciated in our STM images (room temperature), but is consistent with the observed dichroism of the residual iminic component in the N *K*-edge NEXAFS, as compared to the pyrrolic one (see Supplementary Fig. 2). In this equilibrium configuration, the energy reaction of hydrogen uptake from the surface is much more exothermic (-1.40 eV) with respect to the gas-phase case (Table 1). It is worth noticing that, while the mechanism of hydrogen incorporation into bulk TiO_2 is controversial,^{17,20} there is a general consensus about the interlayer H diffusion barrier calculated to be ~ 1 eV for the $\text{TiO}_2(110)$ planes,²¹ which opens the way also to a possible mechanism of bulk hydrogen uptake.

DFT simulations of the N1s photoemission peaks were performed using clusters extracted from the previously optimized slab models. These include the adsorbed species as well the relevant part of the first TiO_2 layer, and a convenient number of saturating hydrogen atoms. Results (reported in Table 2) reproduce quite well the observed core level shift (CLS) between the iminic and pyrrolic nitrogen of 2H-TPP. The uptake of two hydrogen atoms is expected to yield a small shift of ~ 0.3 eV towards higher binding energy, BE, with respect to the pristine pyrrolic pair (which are coordinated to the oxygen atoms underneath). Such a small CLS is not resolved in our XPS measurements, nonetheless it is fully consistent with the broadening ($\Delta\text{FWHM} = +0.4$ eV) of the main nitrogen component observed in the monolayer range with respect to the multilayer one (see peak analysis in Supplementary Fig. 4).

Table 2. N 1s binding energy and core level shift with respect to pyrrolic N

Molecule	Pyrrolic B.E. [eV]	Iminic CLS [eV]	Iminic+2H CLS [eV]
2H-TPP multiLayer	400.15 <i>exp</i>	-2.06 <i>exp</i>	-
2H-TPP ML	400.55 <i>exp</i>	-1.95* <i>exp</i>	-
2H-TPP gas	393.30 <i>calc</i>	-1.95 <i>calc</i>	-
2H-TPP ads	392.78 <i>calc</i>	-1.83 <i>calc</i>	-
4H-TPP ads	392.73 <i>calc</i>	-	+0.32 <i>calc</i>

* From the minority component of unreacted molecules.

Experimental and theoretical Methods

Experimental details

We performed Synchrotron radiation spectroscopy measurements at the ALOISA beamline^{22a} of the Elettra Synchrotron (Trieste, Italy). We imaged the molecules with an Aarhus microscope (provided by SPECS) at the Centro de Fisica de Materiales (CSIC-UPV, San Sebastian, Spain), whose experimental chamber is also equipped with an XPS analyzer for checking the preparation of the molecular films.^{4c}

All XPS measurements have been performed in transverse magnetic polarization (TM, i.e. close to p-polarization) and normal emission geometry, with the sample kept a grazing angle of 4° . Spectra have been collected with a hemispherical electron spectrometer (mean radius 66 mm) equipped with a 2D delay-line detector. We measured the VB spectra at a photon energy of 140 eV with an overall energy resolution of ~ 120 meV. We measured core level photoemission spectra of O 1s, Ti 2p, N 1s and C 1s with photon energy of 650 and 500 eV at corresponding overall resolution of 280 and 160 meV, respectively. We calibrated the photoemission spectra to the binding energy of Ti 2p_{3/2} = 459.1 eV and Ti 3p = 37.6 \pm 0.05 eV.

We measured the NEXAFS spectra at the carbon and nitrogen *K*-edge by partial electron yield, with a channeltron

equipped with a repeller grid kept at a negative bias in order to let the Auger electron of the corresponding ionization edge pass through. The photon energy resolution was set to ~ 100 meV for both ionization thresholds. The orientation of the surface with respect to the photon beam polarization (linear) was changed from TM to transverse electric (TE, i.e. s-polarization) by rotation of the surface around the photon beam axis while keeping a constant grazing angle of 6° . Absolute calibration of the photon energy scale is performed a posteriori by using as a reference the carbon and nitrogen absorption features detected in the drain current recorded on the gold coating of the last beamline optics (synchronized acquisition). The scattering geometry of the ALOISA endstation, as well as the absolute calibration procedure are described in more detail in Ref. [22b].

We employed a number of different samples purchased from Mateck that were also exchanged between the ALOISA Synchrotron beamline and the STM apparatus. We followed the same preparation protocol for cleaning the surface: sputtering with Ar^+ at 800 eV followed by short annealing up to 1000 ± 50 K (1 min at maximum temperature), which yields dark blue samples. All the STM images were acquired at room temperature with a tungsten electrochemically etched tip. In both experimental apparatuses, we deposited molecules from boron nitride Knudsen cells at typical temperature of 460 ± 10 K for 2H-OEP and 570 ± 10 K for both 2H-TPP and 2H-TBTPP. The corresponding deposition rate is found to be in the range of 0.1-0.5 $\text{\AA}/\text{min}$, as monitored by room temperature quartz microbalances. In the ALOISA apparatus, the monolayer coverage has been defined by recording the XPS intensity after thermal desorption of a multilayer. All of the porphyrins have been shown the saturation of the monolayer at an equivalent coverage of ~ 2.5 \AA .

Computational details

Adsorption of 2H-TPP on the $\text{TiO}_2(110)$ surface was studied with DFT calculations using the Quantum ESPRESSO package.^{23a} The PBE functional^{23b} in conjunction with Grimme dispersion corrections^{23c,d} was used. Ion cores were described by Vanderbilt ultrasoft pseudopotentials (PPs), which included C, N, and O 1s orbitals. Ti ions were described either by "large core" PPs including 1s--3p electrons, or with "small cores", including 1s--2p electrons (see below). The kinetic energy cutoff of the planewave expansion was 25 Ry (200 Ry for the Vanderbilt augmentation charge).

To simulate low-coverage conditions, we adopted an oblique $\left(\frac{3}{6} \frac{3}{1}\right)$ supercell including 21 unit cells. The theoretical PBE-D lattice constants of TiO_2 were used.¹⁹ Because of the large size and conformational flexibility of the adsorbate, which requires both large memory usage and long run times, the energetics of the 2H-TPP/4H-TPP species with the TiO_2 surface was first explored on thin (three TiO_2 layers) slab models using "large core" PPs. The structure and the stability of the most favorable configurations were eventually recomputed more accurately using "small core"

pseudopotentials and four TiO_2 layers. The two bottom layers of the slabs were frozen in the bulk structure. Because of the large size of the supercells, only the Γ point of the Brillouin zone was sampled.

We estimated the the N 1s CLSs of the isolated 2H-TPP and the adsorbed 2H-TPP and 4H-TPP molecules by means of hybrid-DFT calculations, employing the PBE0 functional.²⁴ Calculations were carried out with the ADF code.²⁵ Wavefunctions were expanded over a TZP basis set of Slater-type orbitals. Inner electrons of Ti, O, and C up to the 3p, 1s and 1s levels respectively, were treated as frozen cores, whereas all electrons pertaining to N atoms were allowed to relax. The scalar Zero Order Regular Approximation (ZORA) to the relativistic Hamiltonian was applied.²⁶ Molecular clusters cut out from the optimized slab and properly saturated with H atoms were used as models for adsorbed molecules. In both the 2H-TPP and the 4H-TPP cases, the surface was represented as a $\text{Ti}_{31}\text{O}_{92}\text{H}_{60}$ cluster.

Conclusions

In conclusion, our systematic study of metal-free porphyrins with different functional ends confirms that the $\text{TiO}_2(110)$ substrate strongly favors the capture of surface hydrogen by tetrapyrrolic macrocycles, independently of the functional terminations. The energy gain associated with this chemical reaction is found to be larger than the barrier for hydrogen interlayer diffusion, which makes conceivable a hydrogen extraction path from the titania bulk. When comparing our systems with the case of phthalocyanines, one should consider the competitive reaction channel offered by the four additional meso-nitrogen atoms. In fact, upon hydrogen exposure, first layer MnPc molecules on Au(111) have been shown to dissociate and link two hydrogen atoms at opposite meso sites.⁷ This reaction path might be enhanced at the $\text{TiO}_2(110)$ surface, as observed for the porphyrin case, thus explaining the excess of pyrrolic nitrogen reported also for metalated species like FePc¹² and ZnPc.¹⁴

Acknowledgements

We acknowledge support from the MIUR of Italy through PRIN project DESCARTES (n. 2010BNZ3F2), and by CINECA (ISCRA-B project E-TROPPO), from the Spanish Government (Grant MAT2013-46593-C6-4-P) and from the Basque Department of Education (Grant IT-621-13). M.A. also thanks the financial support of DIPC.

Notes and references

- 1 W. Auwärter, D. Ecija, F. Klappenberger and J.V. Barth, *Nat. Chem.* 2015, **7**, 105.
- 2 (a) J. Miguel, C.F. Hermanns, M. Bernien, A. Krüger and W. Kuch, *J. Phys. Chem. Lett.* 2011, **2**, 1455; (b) C. Krull, R. Robles, A. Mugarza and P. Gambardella, *Nat. Mater.* 2013, **12**, 337; (c) S. Vijayaraghavan, W. Auwärter, D. Ecija, K. Seufert, S. Rusponi, T.

- Houwaart, P. Sautet, M.-L. Bocquet, P. Thakur, S. Stepanow, U. Schlickum, M. Etzkorn, H. Brune and J.V. Barth, *ACS Nano* 2015, **9**, 3605.
- 3 (a) F. Sedona, M. Di Marion, D. Forrer, A. Vittadini, M. Casarin, A. Cossaro, L. Floreano, A. Verdini and M. Sambì, *Nat. Mater.* 2012, **11**, 970; (b) B.E. Murphy, S.A. Krasnikov, N.N. Sergeeva, A.A. Cafolla, A.B. Preobrajenski, A.N. Chaika, O. Lübben and I.V. Shvets, *ACS Nano*, 2014, **8**, 5190; (c) D.A. Duncan, P.S. Deimel, A. Wiengarten, R. Han, R.G. Acres, W. Auwärter, P. Feulner, A.C. Papageorgiou, F. Allegretti and J.V. Barth, *Chem. Commun.* 2015, **51**, 9483.
- 4 (a) R. Gonzalez-Moreno, C. Sanchez-Sanchez, M. Trelka, R. Otero, A. Cossaro, A. Verdini, L. Floreano, M. Ruiz-Bermejo, A. Garcia-Lekue, J.A. Martin-Gago and C. Rogero, *J. Phys. Chem. C* 2011, **115**, 6849; (b) A. Goldoni, C.A. Pignedoli, G. Di Santo, C. Castellarin-Cudia, E. Magnano, F. Bondino, A. Verdini and D. Passerone, *ACS Nano* 2012, **12**, 10800; (c) M. Abadia, R. Gonzalez-Moreno, A. Sarasola, G. Otero-Irureta, A. Verdini, L. Floreano, A. Garcia-Lekue and C. Rogero, *J. Phys. Chem. C* 2014, **118**, 29704; (d) M. Stark, S. Ditze, M. Lepper, L. Zhang, H. Schlott, F. Buchner, M. Röckert, M. Chen, O. Lytken, H.-P. Steinhilber and H. Marbach, *Chem. Commun.* 2014, **50**, 10225; (e) J. Mielke, F. Hanke, M.V. Peters, S. Hecht, M. Persson and L. Grill, *J. Am. Chem. Soc.* 2015, **137**, 1844.
- 5 (a) W. Auwärter, A. Weber-Bargioni, S. Brink, A. Riemann, A. Schiffrin, M. Ruben and J.V. Barth, *Chem. Phys. Chem.* 2007, **8**, 250; (b) G. Di Santo, C. Castellarin-Cudia, M. Fanetti, B. Taleatu, P. Borghetti, L. Sangaletti, L. Floreano, E. Magnano, F. Bondino and A. Goldoni, *J. Phys. Chem. C* 2011, **115**, 4155; (c) C. Wang, Q. Fan, S. Hu, H. Ju, X. Feng, Y. Han, H. Pan, J. Zhu and J.M. Gottfried, *Chem. Commun.* 2014, **50**, 8291.
- 6 W. Auwärter, K. Seufert, F. Bischoff, D. Eciya, S. Vijayaraghavan, S. Joshi, F. Klappenberger, N. Samudrala and J.V. Barth, *Nat. Nanotech.* 2012, **7**, 41.
- 7 K. Yang, L. Liu, L. Zhang, W. Xiao, X. Fei, H. Chen, S. Du, K.-H. Ernst, and H.-J. Gao, *ACS Nano* 2014, **8**, 2246.
- 8 P. Palmgren, B.R. Priya, N.P.P. Niraj and M. Göthelid, *M. Sol. Energy Mater. Sol. Cells* 2006, **90**, 3602.
- 9 N. Ishida and D.J. Fujita, *Phys. Chem. C* 2012, **116**, 20300.
- 10 S. Verma and H.N. Ghosh, *J. Phys. Chem. Lett.* **2012**, **3**, 1877.
- 11 G. Mattioli, F. Filippone, P. Giannozzi, R. Caminiti and A.A. Bonapasta, *Chem. Mater.* 2009, **21**, 4555.
- 12 P. Palmgren, K. Nilson, S. Yu, F. Hennies, T. Angot, C.I. Nlebedim, J.-M. Layet, G. Le Lay and M. Göthelid, *J. Phys. Chem. C* 2008, **112**, 5972.
- 13 A. Rienzo, L.C. Mayor, G. Magnano, C.J. Satterley, E. Ataman, J. Schnadt, K. Schulte and J.N. O'Shea, *J. Chem. Phys.* 2010, **132**, 084703.
- 14 S. Yu, S. Ahmadi, C. Sun, P.T.Z. Adibi, W. Chow, A. Pietzsch and M. Göthelid, *J. Chem. Phys.* 2012, **136**, 154703.
- 15 P. Borghetti, G. Di Santo, C. Castellarin-Cudia, M. Fanetti, L. Sangaletti, E. Magnano, F. Bondino and A. Goldoni, *J. Chem. Phys.* 2013, **138**, 1444702.
- 16 (a) O.W. Johnson, J. DeFord, and J.W. Shaner, *J. Appl. Phys.* 1973, **44**, 3008; (b) O.W. Johnson, S.-H. Paek and J. DeFord, *J. Appl. Phys.* 1975, **46**, 1026; (c) Y. Chen, R. Gonzalez and K.L. Tsang, *Phys. Rev. Lett.* 1984, **53**, 1077; (d) P.M. Kowalski, B. Meyer and D. Marx, *Phys. Rev. B* 2009, **79**, 115410.
- 17 X.-L. Yin, M. Calatayud, H. Qiu, Y. Wang, A. Birkner, C. Minot and Ch. Wöll, *Chem. Phys. Chem.* 2008, **9**, 253.
- 18 L.E. Walle, A. Borg, P. Uvdal and A. Sandell, *Phys. Rev. B* 2009, **80**, 235436.
- 19 D. Forrer and A. Vittadini, *Chem. Phys. Lett.* 2011, **516**, 72.
- 20 (a) M. Calatayud, X.-L. Yin, H. Qiu, Y. Wang, A. Birkner, C. Minot and Ch. Wöll, *Phys. Rev. Lett.* 2010, **104**, 119603; (b) G.H. Enevoldsen, H.P. Pinto, A.S. Foster, M.C.R. Jensen, W.A. Hofer, B. Hammer, J.V. Lauritsen and F. Besenbacher, *Phys. Rev. Lett.* 2010, **104**, 119604.
- 21 Y. Du, N.G. Petrik, N.A. Deskins, Z. Wang, M.A. Henderon, G.A. Kimmel and I. Lyubinetsky, *Phys. Chem. Chem. Phys.* 2012, **14**, 3066.
- 22 (a) L. Floreano, G. Naletto, D. Cvetko, R. Gotter, M. Malvezzi, L. Marassi, A. Morgante, A. Santaniello, A. Verdini, F. Tommasini and G. Tondello, *Rev. Sci. Instrum.* 1999, **70**, 3855; (b) L. Floreano, A. Cossaro, R. Gotter, A. Verdini, G. Bavdek, F. Evangelista, A. Ruocco, A. Morgante and D. Cvetko, *J. Phys. Chem. C* 2008, **112**, 10794.
- 23 (a) P. Giannozzi et al., *J. Phys. Condens. Matter* 2009, **21**, 395502; (b) J. Perdew, K. Burke and M. Enzerhof, *Phys. Rev. Lett.* 1996, **77**, 3865; (c) S. Grimme, *J. Comput. Chem.* 2006, **27**, 1787; (d) V. Barone, M. Casarin, D. Forrer, M. Pavone, M. Sambì and A. Vittadini, *J. Comput. Chem.* 2009, **30**, 934.
- 24 C. Adamo and V. Barone, *J. Chem. Phys.* 1999, **110**, 6158.
- 25 Amsterdam Density Functional v. 2014 <http://www.scm.com/ADF>
- 26 (a) E. van Lenthe, E.J. Baerends and J.G. Snijders, *J. Chem. Phys.* 1993, **99**, 4597; (b) E. van Lenthe, E.J. Baerends and J.G. Snijders, *J. Chem. Phys.* 1994, **101**, 9783.