



Self-metalation of monophosphonic acid tetraphenylporphyrin on $\text{TiO}_2(110)-(1 \times 1)$ [☆]

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ABSTRACT

Fundamental studies on the interaction of porphyrin molecules with oxide surfaces are important due to the relevance of these systems in emerging technologies. In this work, we used X-ray photoelectron spectroscopy (XPS) to study the interaction of solution-deposited monophosphonic acid tetraphenylporphyrin (MPTPP) molecules with well-defined rutile $\text{TiO}_2(110)-(1 \times 1)$ surfaces as a function of coverage and temperature. We found that molecules adsorb mainly in their free-base form with some molecules protonating on the surface at room temperature. In agreement with the behavior of carboxylic acid functionalized porphyrin molecules, raising the temperature results in porphyrin self-metalation and the temperature onset for self-metalation shifts to higher values as the coverage is increased. Furthermore, we found that self-metalation is accompanied by surface reduction, and we propose a mechanism based on the formation of oxygen vacancies driven by water desorption. Our findings contribute towards the understanding of the rich surface chemistry that porphyrin molecules have on oxide surfaces.

1. Introduction

Fundamental research on the interaction between porphyrin molecules and surfaces has been very active over the last decade as its understanding is very important for the rational design of molecular devices with applications in catalysis [1], sensing [2] and energy conversion [3]. Research has shown that porphyrin molecules have a rich surface chemistry as they can undergo a variety of chemical reactions. Free-base porphyrin molecules can interact with metal surfaces distorting their macrocycle [4,5] whereas molecules containing peripheral functional groups such as carboxylic or phosphonic acids can bind to oxide surfaces forming covalent bonds [6–9]. Furthermore, surface porphyrin molecules exhibit the insertion, exchange and loss of metal atoms from its central cavity. Co-adsorbed metal atoms can be inserted into the core of the macrocycle releasing hydrogen atoms from the aminic nitrogen atoms [10], whereas metal ions can metalate free-base porphyrins at the solid/liquid interface releasing protons [11]. Recently,

we have shown that the reverse chemical reaction also takes place at surfaces when protons demetalate adsorbed porphyrins [12]. Finally, the metal ion at the center of surface molecules can be exchanged by co-adsorbed metal atoms [13] or by metal ions from solutions [14].

In a chemical reaction known as self-metalation, a substrate metal atom is incorporated into the central cavity of the free-base porphyrin molecule. Free-base tetraphenylporphyrin (2HTPP) molecules adsorbed on Cu(111) react with Cu atoms from the substrate to form CuTPP above 400 K [15]. The rate of this reaction depends strongly on coverage as the strong interaction with the copper surface at low coverages results in a molecular conformation that self-metalates at a lower rate [16]. Furthermore, the presence of electron-withdrawing groups on the porphyrin periphery decreases the self-metalation rate [17]. On the other hand, the self-metalation rate can be increased by oxidizing the surface. For example, self-metalation of 2HTPP on Cu(001) surfaces requires temperatures of 450 K, whereas, self-metalation on the oxidized surface takes place already at 285 K [18]. Also, on metallic Co(100)

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surfaces no self-metalation takes place at room temperature but the reaction can be induced by exposure to oxygen [19]. It was shown very recently that self-metalation of tetraphenyl porphyrins can be induced at the Pd(100) surface by gas-phase oxygen already at room temperature [20]. Porphyrin self-metalation is also known to take place on oxide surfaces that have metal ions with a formal +2 oxidation state. Self-metalation of 2HTPP on MgO(100) [21–23] and CoO(111) [24] takes place at room temperature or below to form MgTPP and CoTPP, respectively. However, the behavior is different on TiO₂ surfaces where the cation inserted into the macrocycle central cavity is expected to be a titanyl group (TiO²⁺). Thus, self-metalation of 2HTPP molecules on TiO₂(110)-(1×1) surfaces to form titanyl tetraphenylporphyrin (TiotPP) takes place only above 400 K [25,26]. Finally, recent IR studies have shown that the self-metalation of 5-(4-carboxyphenyl)-10,15,20-triphenylporphyrin (MCTPP) on atomically well-defined Co₃O₄(111), CoO(111), and CoO(100) surfaces is strongly dependent on surface structure [27].

Recently we studied the self-metalation of MCTPP on TiO₂(110)-(1×1) [28]. We found that having an anchoring functional group affects self-metalation as molecules exhibit different adsorption geometries with coverage. In this work, we continue exploring the effect of the anchoring functional group by changing its chemical nature. Thus, we studied the self-metalation of monophosphonic acid tetraphenylporphyrin (MPTPP) molecules (see Fig. 1) adsorbed on TiO₂(110)-(1×1) surfaces using X-ray photoelectron spectroscopy (XPS). We followed the chemical reaction as a function of coverage and temperature. Our results shed new light into the reactions of porphyrin molecules with oxide surfaces.

2. Materials and methods

Studies were carried out using a rutile TiO₂(110) single crystal (CrysTec GmbH). 5-mono(4-phosphonophenyl)-10,15,20-triphenyl porphyrins (MPTPP) were obtained from PorphyChem and used as received. Absolute ethanol of analytical grade was used to prepare solutions. The TiO₂(110) sample was cleaned in ultra-high vacuum (UHV) by several sputtering and annealing cycles resulting in XP spectra showing only substrate-related peaks and the expected TiO₂(110)-(1×1)

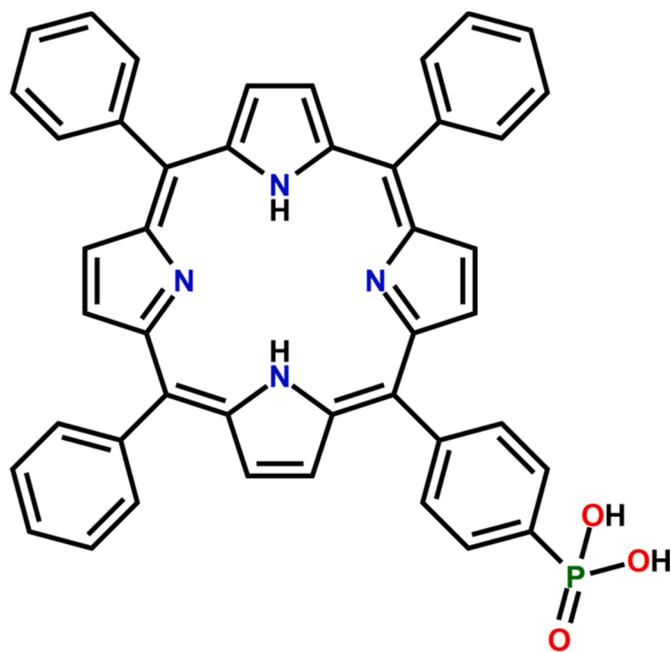


Fig. 1. Molecular structure of the monophosphonic acid functionalized porphyrin molecules (MPTPP): 5-mono(4-phosphonophenyl)-10,15,20-triphenyl porphyrin.

LEED pattern.

X-ray photoelectron spectroscopy (XPS) measurements were performed using an UHV chamber with a base pressure of 5×10^{-10} mbar equipped with a SPECS spectrometer and a monochromatic Al K α (1486.6 eV) source, at a detection angle of 20° with respect to the sample normal. No beam damage is observed when measuring XPS of MPTPP adsorbed on TiO₂(110) surfaces employing synchrotron radiation [8]. Thus, we do not expect to observe beam damage with conventional X-ray sources. Binding energies are referred to the C 1s peak of the tetraphenyl porphyrin molecules at 284.8 eV. The UHV chamber allows the sample to be transferred between UHV and a liquid reactor cell without exposure to the laboratory atmosphere. Attempts to deposit MPTPP by vacuum evaporation resulted in N 1s, O 1s, P 2p and C 1s XPS signals that do not have the expected molecular stoichiometric ratios. Hence evaporation does not result in intact molecular deposition. Therefore, MPTPP was deposited from solution by transferring the UHV-cleaned TiO₂(110) crystal into the liquid cell in an Ar atmosphere and placing it into contact with a 0.1 mM solution of MPTPP in ethanol for 1 min and subsequently rinsing in a 25 ml stream of ethanol. The ethanol left on the surface after rinsing was blown off using an Ar stream. The sample was then transferred back to the UHV analysis chamber for measurement. The XP spectra were fitted using the known line-shape parameters and peak positions from reference compounds. Details are given in the supporting information. MPTPP coverages are based on the N 1s to Ti 2p ratios, using as reference 5-(4-carboxyphenyl)-10,15,20-triphenylporphyrin (MCTPP) monolayer on TiO₂(110) created by desorbing MCTPP multilayers at 473 K. MCTPP was used as reference because, unlike MPTPP, it can be deposited by vacuum evaporation resulting in layers with a well-defined coverage. Details of the calculation are given in the supporting information.

3. Results and discussion

Recently, we studied the bonding and adsorption geometry of phenylphosphonic acid [29] and MPTPP [8] on TiO₂(110)-(1×1) surfaces. We found that adsorption results in deprotonation of some of the hydroxyl groups leading to the formation of mono- and bidentate covalent bonds with the surface. At coverages close to the monolayer molecules are adsorbed with the macrocycle standing upright. Moreover, no self-metalation was observed when 0.9 ML of MPTPP molecules were deposited on TiO₂(110)-(1×1) at room temperature. Hence, we started exploring the effect of surface coverage on self-metalation. Fig. 2 shows the N 1s XP spectra corresponding to 0.8, 0.6 and 0.3 ML of MPTPP adsorbed on TiO₂(110)-(1×1) at room temperature. The spectra can be fitted considering the known binding energy positions of the expected components corresponding to the different nitrogen chemical environments. Free-base molecules give rise to two peaks of identical intensities at 400.0 and 398.0 eV due to the aminic (-NH-) and iminic (-N=) nitrogen atoms, respectively (fitted in blue). All nitrogen atoms in the metalated molecules are equivalent and therefore result in only one peak at 398.5 eV. In the presence of protons or surface hydroxyl groups, nitrogen atoms could protonate giving rise to a peak at 400.0 eV, that is, at the same binding energy as one of the components of the free base molecules. Thus, the 400 eV N 1s component is fitted by two contributions. The blue component has equal intensity as the 398 eV peak (also blue) accounting for the aminic N atoms in the free-base molecules. The green component at 400 eV is due to protonated molecules. Furthermore, at high coverages we expect to observe shake-up satellites at ~3 eV higher binding energy. Shake-up satellites are not observed in the 0.3 ML N 1s spectrum because the signal would be too small to be observed or because a flat-lying adsorption geometry at this low surface coverage would lead to a decreased satellite intensity due to an increased interaction with the substrate. Finally, we observed a N 1s peak at ~401 eV due to nitrogen-containing unwanted species that are co-deposited from solution (fitted in gray) [30].

The N 1s spectra corresponding to 0.8, 0.6 and 0.3 ML show that

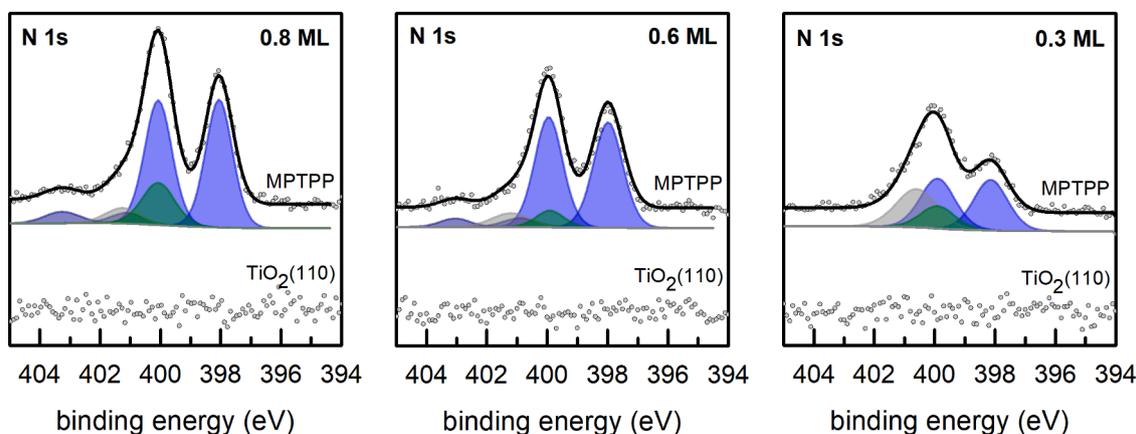


Fig. 2. N 1s XP spectra corresponding to the bare $\text{TiO}_2(110)-(1 \times 1)$ surface and after the deposition of 0.8, 0.6 and 0.3 ML of MPTPP at room temperature. Free-base molecule components are fitted in blue, components due to protonated molecules are fitted in green and the components due to impurities co-deposited from solution are fitted in gray. The small components at high binding energies are due to N 1s shake-up satellites.

MPTPP molecules are mainly in the free-base form, with 17%, 6% and 18% of molecules in the protonated form, respectively. Since the MPTPP molecules were deposited from solution, followed by rinsing the substrate with ethanol, the number of protonated surface molecules might be controlled by the proton transfer reactions that take place at the solid/liquid interface during rinsing. At 0.3 ML, we observe a significant increase in the peak related to N-containing surface impurities. This is reasonable as the rutile surface is very reactive and adsorbs species from solution very rapidly [31]. Thus, at low MPTPP coverages, where the fraction of uncovered surface is greater, we expect to observe more adsorption of impurities from solution. Finally, the spectra in Fig. 2 show that for all coverages, no self-metalation takes place at room temperature. This situation changes when the temperature is increased

as discussed below.

Fig. 3 shows the effect of heating on the N 1s spectra corresponding to 0.8, 0.6 and 0.3 ML of MPTPP on $\text{TiO}_2(110)-(1 \times 1)$. Firstly, we notice that at 400 K the peak related with N-containing impurities (gray) has decreased substantially in the spectra corresponding to 0.3 ML and vanished for 0.6 and 0.8 ML. Raising the temperature further results in the appearance of a new contribution at 398.5 eV (fitted in red), which corresponds to a metalated porphyrin molecule and we assigned to TiOMPTPP [25]. Interestingly, the minimum temperature required to observe self-metalation increases with coverage. This is clearly shown in Fig. 4a where the fraction of metalated molecules is plotted versus temperature. Here we should note that the expected Ti $2p_{3/2}$ binding energy position for titanyl porphyrin [32] (around 458.1 eV) as well as

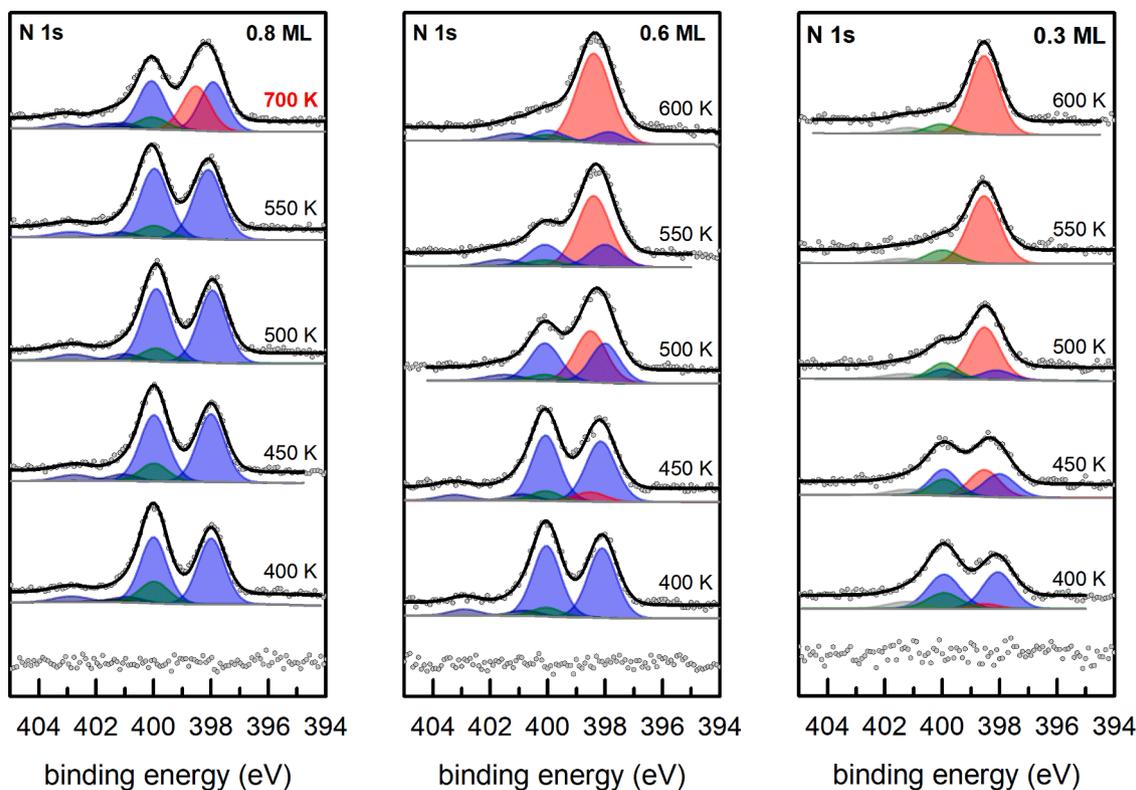


Fig. 3. N 1s XP spectra as a function of temperature measured after the adsorption of 0.8, 0.6 and 0.3 ML of MPTPP molecules on $\text{TiO}_2(110)-(1 \times 1)$. Blue curves correspond to free-base porphyrin molecules, red curves to metalated molecules, green curves to protonated molecules and gray curves to impurities co-deposited from solution.

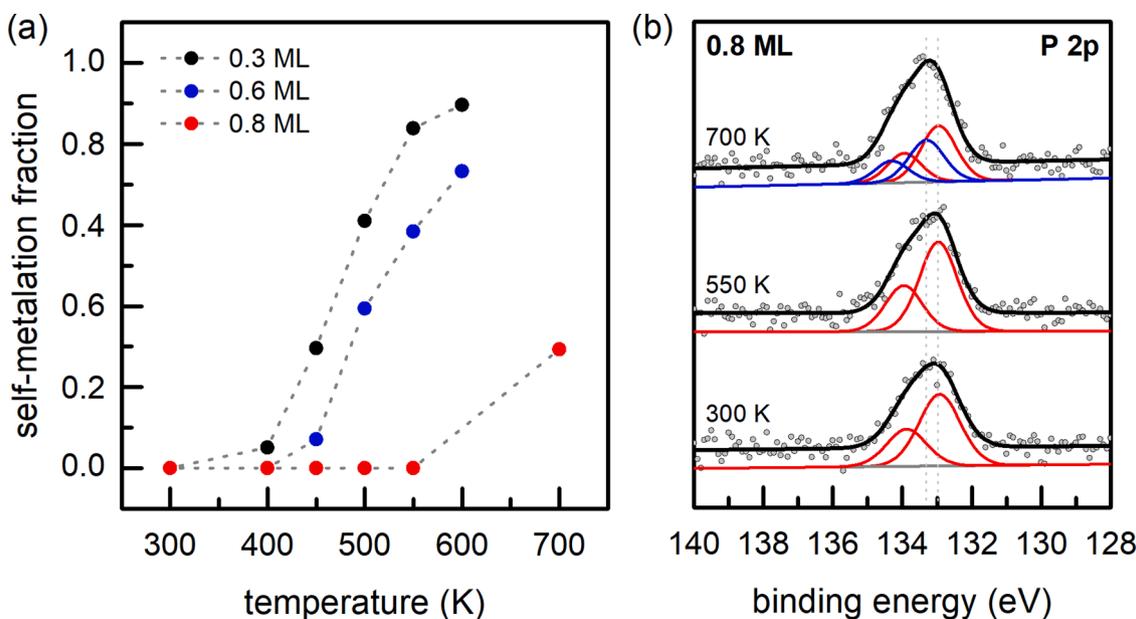


Fig. 4. (a) Fraction of self-metalated molecules as a function of temperature for 0.8, 0.6 and 0.3 ML of MPTPP adsorbed on $\text{TiO}_2(110)-(1 \times 1)$. (b) P 2p XP spectra of 0.8 MPTPP ML at different temperatures.

reference XPS measurements of titanyl porphyrin adsorbed on $\text{TiO}_2(110)-(1 \times 1)$ [25] indicate that the Ti 2p XPS component of the titanyl cation in the molecule is too small to be distinguished from the dominating Ti 2p component of the substrate atoms.

The temperature behavior observed in Fig. 4a resembles that observed when MCTPP molecules (same molecule with a carboxylic acid functional group instead of the phosphonic acid group) are heated on $\text{TiO}_2(110)-(1 \times 1)$ surfaces [28]. Increasing coverages require higher temperatures to start the self-metalation reaction. We attribute this behavior to a change in the adsorption geometry with coverage as increasing coverages could result in more molecules with the macrocycle tilted away from the surface hindering the self-metalation reaction. In the present case, we do not have direct evidence in this regard. However, the P 2p XPS signal shown in Fig. 4b could provide useful information. The P 2p XPS peaks are essentially invariant with coverage and temperature showing a $2p_{3/2}/2p_{1/2}$ doublet with peaks at 133.0 and 134.0 eV. However, we note that at 700 K the P 2p XPS signal corresponding to 0.8 ML broadens at high binding energy and could be fitted adding an extra doublet with peaks at 133.3 and 134.3 eV. This might indicate a change in the binding configuration that could facilitate self-metalation at high coverages.

Fig. 5a, b and c show the Ti 2p XP spectra corresponding to 0.3, 0.6 and 0.8 MPTPP ML as a function of temperature, respectively. At low temperatures, the Ti 2p spectrum is composed of a doublet due to TiO_2 with Ti $2p_{3/2}$ and $2p_{1/2}$ components at 459.0 and 464.7 eV, respectively. As the temperature increases, a new low binding energy Ti $2p_{3/2}$ peak appears at 457.3 eV, which is attributed to Ti^{3+} and which indicates reduction of the surface. For 0.3 and 0.6 ML the Ti^{3+} peak appears above 450 K, whereas for larger MPTPP coverages heating to 700 K is required. This is clearly seen in the temperature evolution of the normalized Ti^{3+} intensity (Fig. 5d). It is well known that heating the bare $\text{TiO}_2(110)-(1 \times 1)$ surface results in self-reduction due to desorption of oxygen from the protruding rows of bridging two-fold coordinated O atoms [33]. However, controlled experiments, where we heated the bare $\text{TiO}_2(110)-(1 \times 1)$ surface in UHV up to 800 K do not show surface Ti^{3+} sites. This observation is in line with recent measurements that show self-reduction only after heating in UHV above 1300 K [34]. Thus, the observed variations in surface Ti^{3+} are not due to processes that take place on clean $\text{TiO}_2(110)-(1 \times 1)$ surfaces. Furthermore, we observed that the same surface reduction phenomenon occurs in the same temperature

range after heating sub-monolayers of phenylphosphonic acid on $\text{TiO}_2(110)$. Thus, we can rule out self-metalation as the cause of surface reduction. Indeed, self-metalation involves insertion of a TiO_2^{2+} group into the macrocycle, which should create surface defects without reducing the surface. Instead, we propose a model based on the recombination of surface hydroxyl groups to form water and bridging oxygen vacancies. Here we should note that MPTPP adsorption at the solid/liquid interface followed by rinsing should result in hydroxylated surfaces. It is well-known that surface hydroxyl groups react and desorb as water molecules at around 500 K, leaving behind bridging oxygen vacancies [35]. Creation of oxygen vacancies alone should not reduce the surface as in this case it does not involve an electron transfer reaction. However, oxygen vacancies can act as traps of electrons which are donated by Ti interstitials resulting in reduction of formally Ti^{4+} sites to Ti^{3+} [36]. Note that migration of Ti interstitials from deeper layers to interstitial sites in the layers nearer the surface can take place above 400 K [37]. Our finding is in line with recent measurements showing that annealing H^+ -implanted- $\text{TiO}_2(110)$ crystals resulted in a Ti^{3+} XPS signal increase in the 450–590 K temperature range [38] as observed here for 0.3 and 0.6 ML. In the case of 0.8 ML Ti^{3+} is only observed after annealing to 700 K. This is in line with the behavior of 1.0 ML of phenylphosphonic acid on $\text{TiO}_2(110)$, where no surface reduction is observed after heating to 780 K [29]. We suggest that this behavior is due to the stabilization of the hydroxyl groups via the interaction with the phosphonic acid anchoring groups pushing hydroxyl recombination and formation of water to higher temperatures.

4. Conclusions

Adsorption of monophosphonic acid tetraphenylporphyrin (MPTPP) molecules from solution on $\text{TiO}_2(110)-(1 \times 1)$ surfaces leads to the formation of free-base and protonated molecules with no self-metalation observed at room temperature. Raising the temperature results in the presence of metalated molecules on the surface, which are formed after the insertion of a titanyl group into the macrocycle. Higher MPTPP coverages require increasing temperatures for the self-metalation reaction to take place. Interestingly, self-metalation is accompanied by formation of Ti^{3+} surface defects; however, the two reactions are not linked. Instead, surface reduction is explained in terms of the formation of O vacancies due to the desorption of water after the recombination of

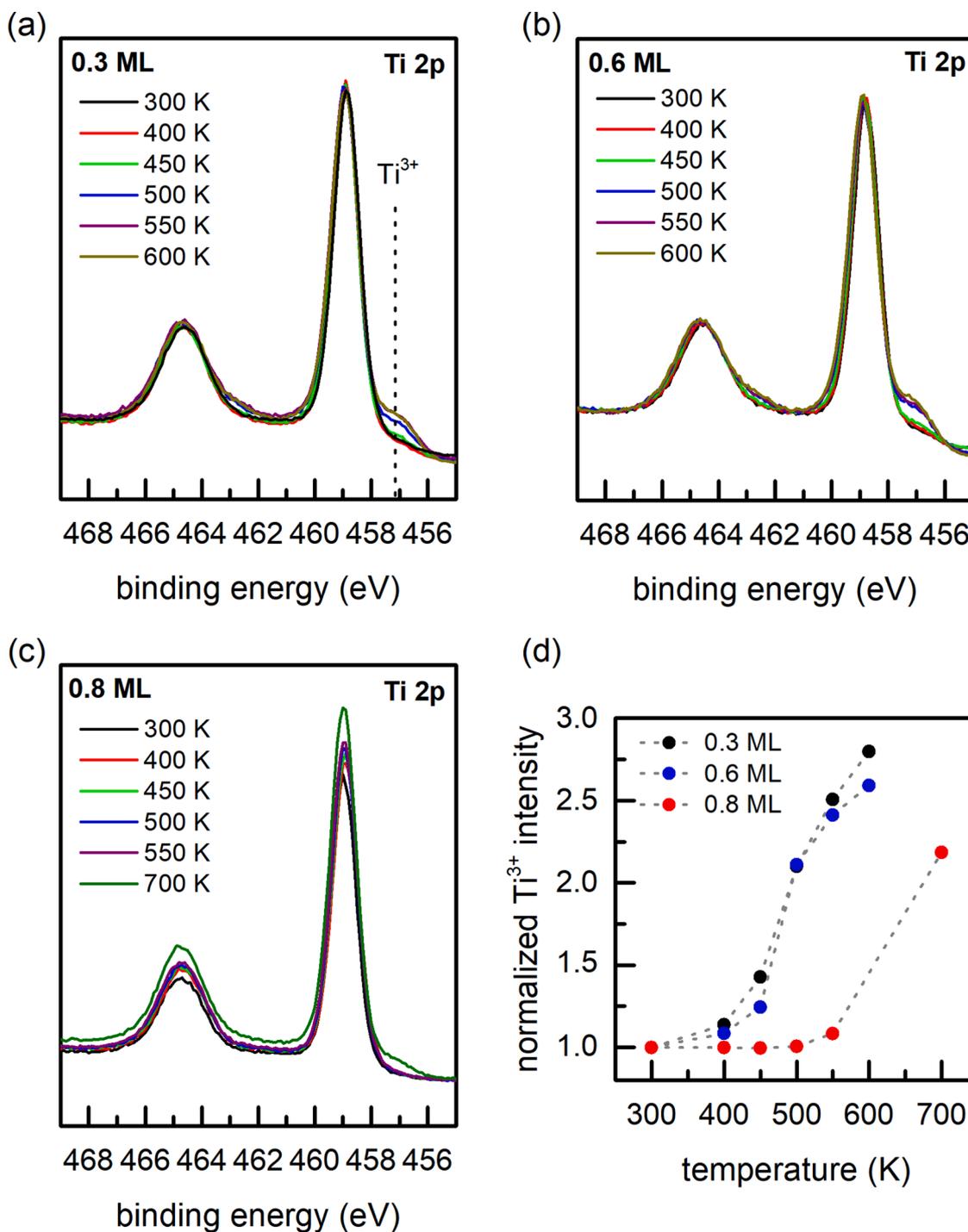


Fig. 5. Ti 2p XP spectra of (a) 0.3, (b) 0.6 and (c) 0.8 MPTPP ML on TiO₂(110)-(1×1) as a function of temperature, and (d) the normalized Ti³⁺ integrated intensity as a function of temperature.

surface hydroxyl groups. Our findings provide new insights into the rich surface chemistry of porphyrin molecules adsorbed on oxide surfaces.

CRediT authorship contribution statement

Cynthia C. Fernández: Conceptualization, Methodology, Writing – review & editing, Investigation, Visualization, Formal analysis. **Daniel Wechsler:** Conceptualization, Methodology, Writing – review & editing, Investigation. **Ole Lytken:** Conceptualization, Methodology, Writing – review & editing. **Hans-Peter Steinrück:** Conceptualization, Methodology, Writing – review & editing, Supervision, Funding acquisition.

Federico J. Williams: Conceptualization, Methodology, Writing – original draft, Writing – review & editing, Supervision, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:[10.1016/j.susc.2021.122005](https://doi.org/10.1016/j.susc.2021.122005).

References

- [1] C. Costentin, H. Dridi, J.M. Savéant, Molecular catalysis of O_2 reduction by iron porphyrins in water: heterogeneous versus homogeneous pathways, *J. Am. Chem. Soc.* 137 (2015) 13535–13544, <https://doi.org/10.1021/jacs.5b06834>.
- [2] Y. Ding, W.H. Zhu, Y. Xie, Development of Ion chemosensors based on porphyrin analogues, *Chem. Rev.* 117 (2017) 2203–2256, <https://doi.org/10.1021/acs.chemrev.6b00021>.
- [3] J.M. Gottfried, Surface chemistry of porphyrins and phthalocyanines, *Surf. Sci. Rep.* 70 (2015) 259–379, <https://doi.org/10.1016/j.surfrep.2015.04.001>.
- [4] K. Diller, F. Klappenberger, M. Marschall, K. Hermann, A. Nefedov, C. Wöll, J. V. Barth, Self-metalation of 2H-tetraphenylporphyrin on Cu(111): an x-ray spectroscopy study, *J. Chem. Phys.* 136 (2012), 014705, <https://doi.org/10.1063/1.3674165>.
- [5] W. Auwärter, A. Weber-Bargioni, A. Riemann, A. Schiffrin, O. Gröning, R. Fasel, J. V. Barth, Self-assembly and conformation of tetrapyrrolyl-porphyrin molecules on Ag(111), *J. Chem. Phys.* 124 (2006), 194708, <https://doi.org/10.1063/1.2194541>.
- [6] D. Wechsler, C.C. Fernández, H.-P. Steinrück, O. Lytken, F.J. Williams, Covalent anchoring and interfacial reactions of adsorbed porphyrins on rutile $TiO_2(110)$, *J. Phys. Chem. C* 122 (2018) 4480–4487, <https://doi.org/10.1021/acs.jpcc.7b12717>.
- [7] C.C. Fernández, D. Wechsler, T.C.R. Rocha, H.-P. Steinrück, O. Lytken, F. J. Williams, Adsorption geometry of carboxylic acid functionalized porphyrin molecules on $TiO_2(110)$, *Surf. Sci.* 689 (2019), 121462, <https://doi.org/10.1016/j.susc.2019.121462>.
- [8] C.C. Fernández, D. Wechsler, T.C.R.R. Rocha, H.P. Steinrück, O. Lytken, F. J. Williams, Adsorption of phosphonic-acid-functionalized porphyrin molecules on $TiO_2(110)$, *J. Phys. Chem. C* 123 (2019) 10974–10980, <https://doi.org/10.1021/acs.jpcc.9b01019>.
- [9] A. Rienzo, L.C. Mayor, G. Magnano, C.J. Satterley, E. Ataman, J. Schnadt, K. Schulte, J.N. O'Shea, X-ray absorption and photoemission spectroscopy of zinc protoporphyrin adsorbed on rutile $TiO_2(110)$ prepared by in situ electrospray deposition, *J. Chem. Phys.* 132 (2010), 084703, <https://doi.org/10.1063/1.3336747>.
- [10] G. Di Santo, C. Castellarin-Cudia, M. Fanetti, B. Taleatu, P. Borghetti, L. Sangaletti, L. Floreano, E. Magnano, F. Bondino, A. Goldoni, Conformational adaptation and electronic structure of 2H-tetraphenylporphyrin on Ag(111) during Fe metalation, *J. Phys. Chem. C* 115 (2011) 4155–4162, <https://doi.org/10.1021/jp111151n>.
- [11] M. Franke, F. Marchini, H.-P. Steinrück, O. Lytken, F.J. Williams, Surface porphyrin metalate with Zn ions from solution, *J. Phys. Chem. Lett.* 6 (2015) 4845–4849, <https://doi.org/10.1021/acs.jpcc.5b02218>.
- [12] C.C. Fernández, M. Franke, H.-P. Steinrück, O. Lytken, F.J. Williams, Demetalation of surface porphyrins at the solid–liquid interface, *Langmuir* 37 (2021) 852–857, <https://doi.org/10.1021/acs.langmuir.0c03197>.
- [13] C.M. Doyle, J.P. Cunniffe, S.A. Krasnikov, A.B. Preobrajenski, Z. Li, N.N. Sergeeva, M.O. Senge, A.A. Cafolla, Ni–Cu ion exchange observed for Ni(II)–porphyrins on Cu(111), *Chem. Commun.* 50 (2014) 3447, <https://doi.org/10.1039/c3cc48913b>.
- [14] M. Franke, F. Marchini, N. Jux, H.P. Steinrück, O. Lytken, F.J. Williams, Zinc porphyrin metal-center exchange at the solid–liquid interface, *Chem. A Eur. J.* 22 (2016) 8520–8524, <https://doi.org/10.1002/chem.201600634>.
- [15] J. Xiao, S. Ditze, M. Chen, F. Buchner, M. Stark, M. Drost, H.-P. Steinrück, J. M. Gottfried, H. Marbach, Temperature-dependent chemical and structural transformations from 2h-tetraphenylporphyrin to copper(II)-tetraphenylporphyrin on Cu(111), *J. Phys. Chem. C* 116 (2012) 12275–12282, <https://doi.org/10.1021/jp301757h>.
- [16] M. Röckert, S. Ditze, M. Stark, J. Xiao, H.-P. Steinrück, H. Marbach, O. Lytken, Abrupt coverage-induced enhancement of the self-metalation of tetraphenylporphyrin with Cu(111), *J. Phys. Chem. C* 118 (2014) 1661–1667, <https://doi.org/10.1021/jp412121b>.
- [17] M. Lepper, J. Köbl, L. Zhang, M. Meusel, H. Hölzel, D. Lungerich, N. Jux, A. de Siervo, B. Meyer, H.P. Steinrück, H. Marbach, Controlling the self-metalation rate of tetraphenylporphyrins on Cu(111) via cyano functionalization, *Angew. Chem. Int. Ed.* 57 (2018) 10074–10079, <https://doi.org/10.1002/anie.201803601>.
- [18] J. Nowakowski, C. Wäckerlin, J. Girovsky, D. Siewert, T.A. Jung, N. Ballav, Porphyrin metalation providing an example of a redox reaction facilitated by a surface reconstruction, *Chem. Commun.* 49 (2013) 2347, <https://doi.org/10.1039/c3cc39134e>.
- [19] C. Wang, R. Wang, J. Hauns, T. Fauster, Self-metalation of porphyrins by cobalt oxide: photoemission spectroscopic investigation, *J. Phys. Chem. C* 124 (2020) 14167–14175, <https://doi.org/10.1021/acs.jpcc.0c01722>.
- [20] F. Armillotta, E. D'Incecco, M. Corva, M. Stredansky, J. Gallet, F. Bournel, A. Goldoni, A. Morgante, E. Vesselli, A. Verdini, Self-Metalation of Porphyrins at the solid–gas interface, *Angew. Chem Int. Ed.* (2021), <https://doi.org/10.1002/anie.202111932>.
- [21] J. Schneider, M. Franke, M. Gurrath, M. Röckert, T. Berger, J. Bernardi, B. Meyer, H.P. Steinrück, O. Lytken, O. Diwald, Porphyrin metalation at MgO surfaces: a spectroscopic and quantum mechanical study on complementary model systems, *Chem. A Eur. J.* 22 (2016) 1744–1749, <https://doi.org/10.1002/chem.201503661>.
- [22] G. Di Filippo, A. Classen, R. Pöschel, T. Fauster, Interaction of free-base tetraphenylporphyrin with magnesium oxide: influence of MgO morphology on metalation, *J. Chem. Phys.* (2017) 146, <https://doi.org/10.1063/1.4975229>.
- [23] L. Egger, M. Hollerer, C.S. Kern, H. Herrmann, P. Hurdax, A. Haags, X. Yang, A. Gottwald, M. Richter, S. Soubatch, F.S. Tautz, G. Koller, P. Puschnig, M. G. Ramsey, M. Sterrer, Charge-promoted self-metalation of porphyrins on an oxide surface, *Angew. Chem. Int. Ed.* 60 (2021) 5078–5082, <https://doi.org/10.1002/anie.202015187>.
- [24] D. Wechsler, C.C. Fernández, Q. Tariq, N. Tsud, K.C. Prince, F.J. Williams, H. Steinrück, O. Lytken, Interfacial reactions of tetraphenylporphyrin with cobalt-oxide thin films, *Chem. A Eur. J.* 25 (2019) 13197–13201, <https://doi.org/10.1002/chem.201902680>.
- [25] J. Köbl, T. Wang, C. Wang, M. Drost, F. Tu, Q. Xu, H. Ju, D. Wechsler, M. Franke, H. Pan, H. Marbach, H.P. Steinrück, J. Zhu, O. Lytken, Hungry porphyrins: protonation and self-metalation of tetraphenylporphyrin on $TiO_2(110)$ - 1 × 1, *ChemistrySelect* 1 (2016) 6103–6105, <https://doi.org/10.1002/slct.201601398>.
- [26] G. Lovat, D. Forrer, M. Abadia, M. Dominguez, M. Casarin, C. Rogero, A. Vittadini, L. Floreano, Very high temperature tiling of tetraphenylporphyrin on rutile $TiO_2(110)$, *Nanoscale* 9 (2017) 11694–11704, <https://doi.org/10.1039/C7NR04093H>.
- [27] T. Wähler, R. Schuster, J. Libuda, Surface structure controls self-metalation: *in-situ* IR studies of anchored porphyrins on atomically-defined cobalt oxide surfaces, *J. Phys. Chem. C* 124 (2020) 21538–21548, <https://doi.org/10.1021/acs.jpcc.0c06248>.
- [28] D. Wechsler, P. Vensaus, N. Tsud, H.P. Steinrück, O. Lytken, F.J. Williams, Surface reactions and electronic structure of carboxylic acid porphyrins adsorbed on $TiO_2(110)$, *J. Phys. Chem. C* 125 (2021) 6708–6715, <https://doi.org/10.1021/acs.jpcc.1c01133>.
- [29] J. Köbl, D. Wechsler, E.Y. Kataev, F.J. Williams, N. Tsud, S. Franchi, H.P. Steinrück, O. Lytken, Adsorption of phenylphosphonic acid on rutile $TiO_2(110)$, *Surf. Sci.* 698 (2020), 121612, <https://doi.org/10.1016/j.susc.2020.121612>.
- [30] D. Wechsler, C.C. Fernández, J. Köbl, L.M. Augustin, C. Stumm, N. Jux, H. P. Steinrück, F.J. Williams, O. Lytken, Wet-chemically prepared porphyrin layers on rutile $TiO_2(110)$, *Molecules* 26 (2021) 2871, <https://doi.org/10.3390/molecules26102871>.
- [31] J. Balajka, M.A. Hines, W.J.I. DeBenedetti, M. Komora, J. Pavelec, M. Schmid, U. Diebold, High-affinity adsorption leads to molecularly ordered interfaces on TiO_2 in air and solution, *Science* 361 (2018) 786–789, <https://doi.org/10.1126/science.aat6752>.
- [32] P. Palmgren, T. Claesson, A. Önsten, B. Agnarsson, M. Månsson, O. Tjernberg, M. Göthelid, Band bending and structure dependent HOMO energy at the ZnO (0001)-titanyl phthalocyanine interface, *Surf. Sci.* 601 (2007) 4222–4226, <https://doi.org/10.1016/j.susc.2007.04.113>.
- [33] U. Diebold, The surface science of titanium dioxide, *Surf. Sci. Rep.* 48 (2003) 53–229, [https://doi.org/10.1016/S0167-5729\(02\)00100-0](https://doi.org/10.1016/S0167-5729(02)00100-0).
- [34] M. Rogala, G. Bihlmayer, P. Dabrowski, S. Rodenbücher, D. Wrana, F. Krok, Z. Klusek, K. Szot, Self-reduction of the native $TiO_2(110)$ surface during cooling after thermal annealing – in-operando investigations, *Sci. Rep.* 9 (2019) 12563, <https://doi.org/10.1038/s41598-019-48837-3>.
- [35] Y. Du, N.G. Petrik, N.A. Deskins, Z. Wang, M.A. Henderson, G.A. Kimmel, I. Lyubintsky, Hydrogen reactivity on highly-hydroxylated $TiO_2(110)$ surfaces prepared via carboxylic acid adsorption and photolysis, *Phys. Chem. Chem. Phys.* 14 (2012) 3066–3074, <https://doi.org/10.1039/C1CP22515D>.
- [36] A.C. Papageorgiou, N.S. Beglitis, C.L. Pang, G. Teobaldi, G. Cabailh, Q. Chen, A. J. Fisher, W.A. Hofer, G. Thornton, Electron traps and their effect on the surface chemistry of $TiO_2(110)$, *Proc. Natl. Acad. Sci.* 107 (2010) 2391–2396, <https://doi.org/10.1073/pnas.0911349107>.
- [37] S. Wendt, P.T. Sprunger, E. Lira, G.K.H. Madsen, Z. Li, J.O. Hansen, J. Matthiesen, A. Blekinge-Rasmussen, E. Laegsgaard, B. Hammer, F. Besenbacher, The role of interstitial sites in the Ti 3D defect state in the band gap of titania, *Science* 320 (2008) 1755–1759, <https://doi.org/10.1126/science.1159846>.
- [38] M.I. Nandasiri, V. Shuthanandan, S. Manandhar, A.M. Schwarz, L. Oxenford, J. V. Kennedy, S. Thevuthasan, M.A. Henderson, Instability of hydrogenated TiO_2 , *J. Phys. Chem. Lett.* 6 (2015) 4627–4632, <https://doi.org/10.1021/acs.jpcc.5b02219>.