# Covalent Anchoring and Interfacial Reactions of Adsorbed Porphyrins on Rutile TiO$_2$(110)

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ABSTRACT: Adsorption of 5-monocarboxyphenyl-10,15,20-triphenylporphyrin (MCTPP) to rutile TiO$_2$(110) at room temperature produces molecules on the surface covalently anchored through the carboxylate group, coadsorbed with hydroxyl groups. At elevated temperatures, the free-base porphyrin molecules metalate on the surface, forming what we expect to be titanyl (Ti═O) porphyrin. The reaction is strongly coverage dependent with lower coverages metalating at lower temperatures, possibly caused by flat-lying molecules at low coverages being in closer proximity to the surface. This is in contrast to the behavior when exposed to Zn^{2+} ions in solution, where the coverage dependency is much less pronounced.
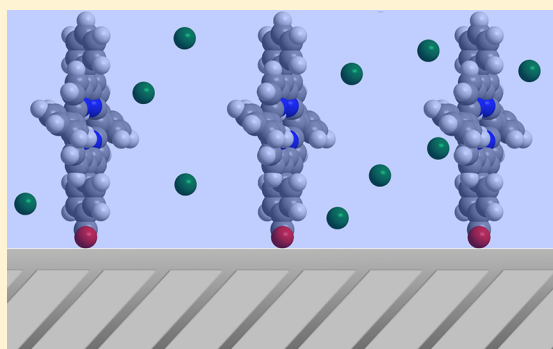
INTRODUCTION

Understanding the interaction of large organic molecules with well-defined oxide surfaces is of fundamental importance to develop new functional hybrid materials. Porphyrin molecules are among the most versatile macrocycles used to functionalize oxide surfaces producing devices such as molecular catalysts,[1] chemical sensors,[2] and photovoltaic cells.[3,4] Thus, there has been a considerable amount of recent research to understand the interaction of porphyrin molecules with oxide surfaces and to rationalize the chemical reactions that might occur after porphyrin adsorption.[5−10] Porphyrins are composed of four pyrrole rings fused via methine groups in a planar structure with a central cavity surrounded by four nitrogen atoms. Free-base porphyrins coordinate two protons at the central cavity whereas metalloporphyrin coordinate a metal ion. The electronic properties of the molecules can be tuned by changing the central metal ion or altering the macrocycle peripheral groups giving rise to a broad range of properties and applications.

The porphyrin planar molecular structure often results in a strong interaction with the oxide surface which can modify the chemical and electronic properties of the molecule. For instance, porphyrin adsorption could result in self-metalation, i.e. the insertion of metal atoms from the substrate into the macrocycle causing the formation of metalloporphyrins. Indeed, there are several studies reporting the self-metalation of free-base porphyrins with oxide substrates.[11−13] Recently, Köbl et al.[14] studied the adsorption of tetraphenylporphyrins (2HTPP) on rutile TiO$_2$(110). They found that adsorption at room temperature resulted in the formation of 4HTPP^{2+} after reaction with protons from the surface. Raising the temperature

to 400 K resulted in metalation of only the unprotonated molecules to form titanyl tetraphenylporphyrin (TiO−TPP), a further increase in temperature also metalated the protonated molecules to the titanyl form.

Recent studies on the adsorption of porphyrin molecules on well-defined oxide surfaces demonstrated the importance of the peripheral groups to bind the functionalized molecules to the surface.[15] Indeed, carboxylic acid functional groups are very commonly employed to achieve this task. Therefore, in this work we studied the adsorption of a carboxylic acid functionalized porphyrin, 5-monocarboxyphenyl-10,15,20-triphenylporphyrin (MCTPP, Figure 1 left), on rutile TiO$_2$(110) at room temperature. We used X-ray photoelectron spectroscopy (XPS) to follow the bonding of MCTPP with the rutile substrate. This reaction as well as self-metalation with the substrate were studied as a function of the initial molecular coverage and temperature. Furthermore, XPS was used to determine the degree of metalation after exposing different molecular coverages of MCTPP on TiO$_2$(110) to Zn^{2+} aqueous solutions of different pH values at room temperature.

EXPERIMENTAL SECTION

X-ray photoelectron spectroscopy (XPS) measurements were conducted in an ultrahigh vacuum (UHV) chamber with a base pressure below 5×10^{-10} mbar using a hemispherical SPECS electron energy analyzer and a monochromatic Al Kα X-ray
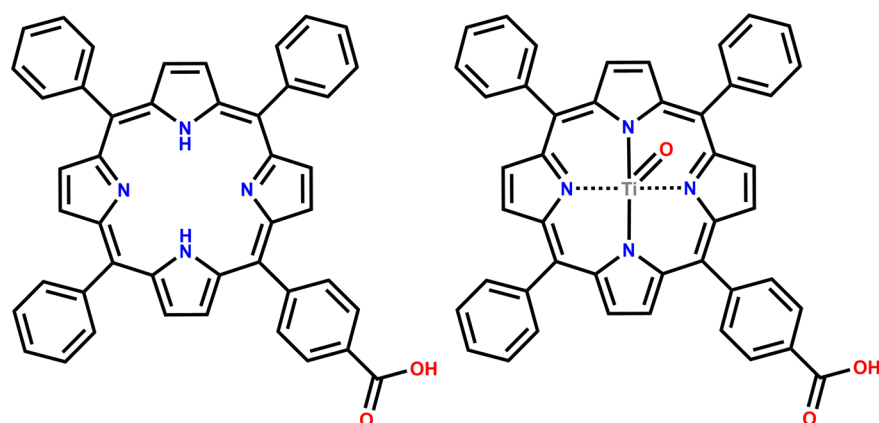
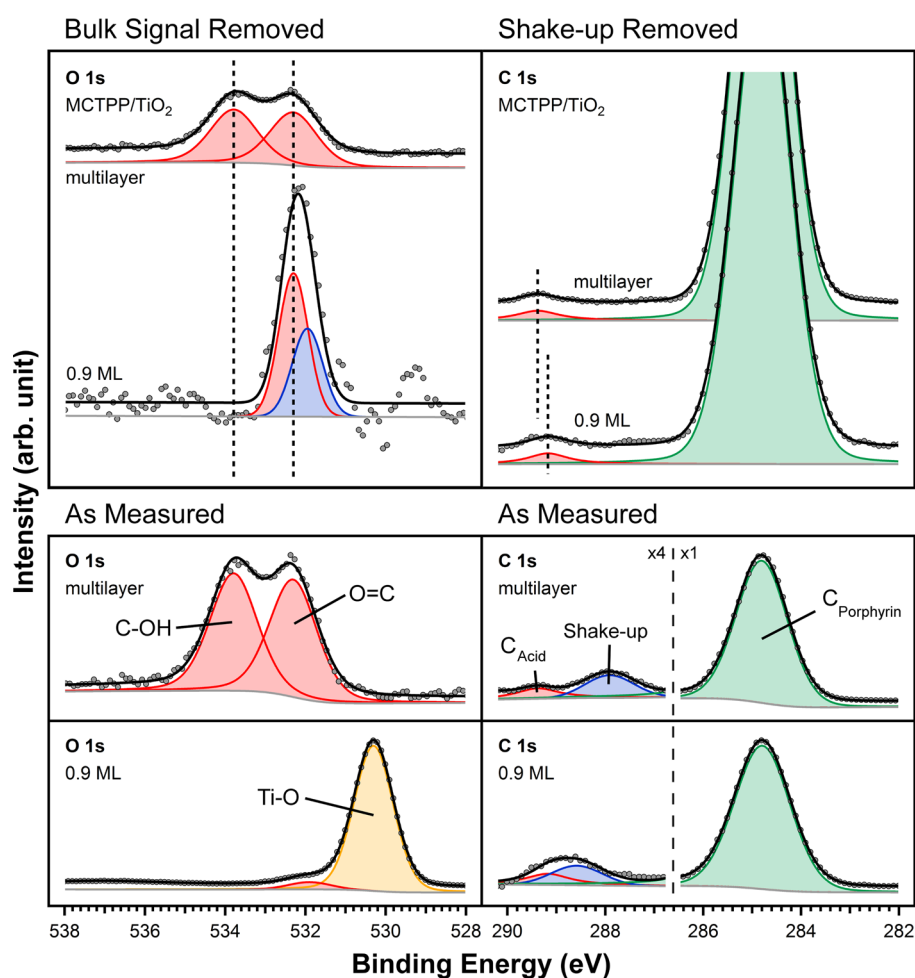**Figure 1.** MCTPP (left) and the possible self-metalation product TiO−MCTPP (right).

Figure 2. O 1s and C 1s spectra of MCTPP adsorbed on TiO$_2$(110). For clarity, the spectra are shown both as measured (bottom) and with the dominating substrate contribution in the O 1s region and the shakeup-satellite contribution in the C 1s region removed (top).

source. All spectra were aligned to the Ti 2p peak of 459.0 eV (the shifts required were less than 0.3 eV).

Prior to each experiment, the TiO$_2$(110) crystal was cleaned by several cycles of sputtering and annealing. The cleanliness was checked with XPS. Besides small traces of carbon (below 1% of a monolayer, see Figure 3), no impurities were found. MCTPP was deposited by evaporation in UHV from a Knudsen cell, while the clean TiO$_2$(110) single-crystal sample was kept at room temperature. This procedure was already used

before by Werner et al.[15] To ensure the deposited molecules were indeed intact 5-monocarboxyphenyl-10,15,20-triphenyl-porphyrin, we confirmed the carbon-to-nitrogen-to-oxygen ratios of deposited multilayers. For coverage calculation, a porphyrin monolayer reference was created by desorbing multilayers at 473 K for 30 min (further annealing at higher temperatures caused no additional loss of carbon). The carbon intensity is around three times higher than for a flat-lying monolayer of the unfunctionalized 2HTPP on TiO$_2$(110)[14] and
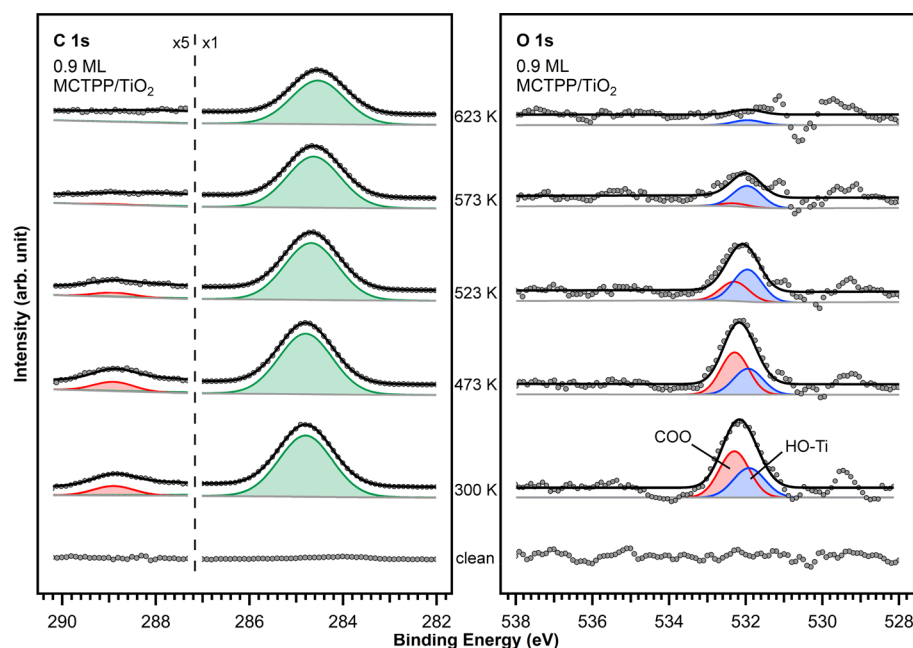
Figure 3. C 1s and O 1s spectra of 0.9 ML MCTPP on TiO$_2$(110) at room temperature and annealed to the indicated temperatures for 10 min. The carbon shakeup satellite and substrate oxygen peak have been removed for better clarity (see Figure 2). At elevated temperature, first the carboxylate groups and then the hydroxyl groups decompose.

on Cu(111).[16] This would indicate an upright-standing layer. More details on porphyrin multilayer desorption can be found elsewhere.[14]

Exposure to aqueous solutions was carried out in an argon-filled Teflon liquid cell attached to the UHV chamber.[17] To minimize the amount of impurities, no additional buffers or chemicals were used, unless otherwise specified. After exposure, the single crystal was retracted from the solution, resulting in a drop of solution adhering to the surface of the crystal. To prevent deposition of unwanted species on the crystal surface after evaporation of the drop, the surface was rinsed with 20 mL of Milli-Q water, and the resulting drop of water blown away with an argon jet used to dry the sample before it was transferred back into UHV. At no point during transfer or exposure to solution the crystal was exposed to air.

RESULTS AND DISCUSSION

Covalent Anchoring. Figure 2 bottom panel shows the O 1s and C 1s XPS spectra obtained after depositing 0.9 ML and multilayers of MCTPP on TiO$_2$(110) at room temperature. The O 1s XPS spectrum of the multilayer shows a two-peak structure, resulting from intact molecules with the expected 1:1 ratio due to the C−OH (533.8 eV) and C═O (532.3 eV) peaks of the carboxylic acid group. For 0.9 ML of MCTPP, the 1:1 two-peak structure in the O 1s spectrum is replaced by a single feature appearing as a small shoulder at the high-binding-energy side of the dominating substrate O 1s peak; see Figure 2 bottom left. To better visualize this small feature, we fitted and subtracted the substrate contribution assuming the shape of the substrate O 1s peak to be identical to that of a reference spectrum of the clean surface. The resulting spectrum with the substrate contribution subtracted is visible in Figure 2 upper left. The area of the remaining O 1s spectrum corresponding to 0.9 ML is larger than expected from the carbon-to-oxygen ratio of the intact molecule. We therefore fitted the feature as the sum of covalently anchored carboxylate groups (red) and

coadsorbed hydroxyl groups (blue) created by the deprotonation of the acid group. The positions of both species agree with those expected for carboxylate[18] and hydroxyl groups[19,20] (532.3 and 531.9 eV, respectively). Overall, the O 1s data indicate that the carboxylic acid group has deprotonated and bound covalently to the oxide surface.

The C 1s spectra corresponding to multilayers and 0.9 ML of MCTPP on TiO$_2$(110) show the same peak structure: a big peak at 284.8 eV, assigned to the 44 carbon atoms of the porphyrin macrocycle and the phenyl rings, which cannot be separated, and two smaller features at higher binding energies, which are attributed to the shakeup satellite of the main peak (287.9 eV) and the single carbon atom of the acid group (289.4 eV). In comparison to the multilayer spectrum, the position of the acidic carbon atom in the 0.9 ML spectrum is shifted toward lower binding energies by 0.2 eV. This is an indication for deprotonation of the acid group.[21] The top panel in Figure 2 shows the two spectra with subtracted shakeup satellite feature for a better view on the acid peak position.

Temperature Stability and Self-Metalation. Figure 3 shows the C 1s and O 1s XPS spectra with the C 1s shakeup and the O 1s bulk signal removed corresponding to 0.9 ML of MCTPP on TiO$_2$(110) as a function of temperature. Upon heating, the carboxylate group is stable up to 473 K, but has vanished in both the C 1s and O 1s regions at 573 K, as indicated by the behavior of the acidic carbon and carboxylate oxygen contributions. The dominant C 1s peak of the porphyrin macrocycle at 284.8 eV, however, exhibits only a slight decrease in intensity, indicating a decomposition of the carboxylate group, rather than a recombination with coadsorbed protons and desorption of intact porphyrin molecules. The moderate loss of carbon observed between 523 and 623 K (11%) could be the result of dewetting or desorption of some porphyrin molecules, presumably as tetraphenylporphyrin, caused by the decomposition of the carboxylate covalent anchor group.
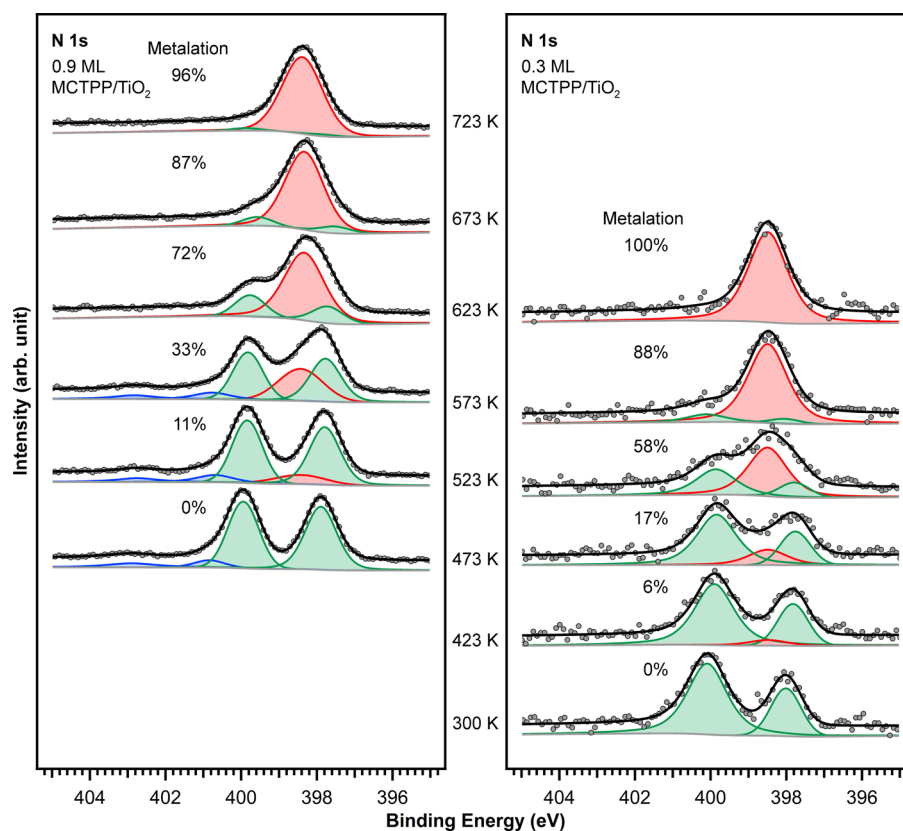
Figure 4. N 1s spectra of 0.9 and 0.3 ML MCTPP adsorbed on TiO$_2$(110) from 300 to 723 K. During annealing, the green peaks assigned to the free-base porphyrin are decreasing, while a new peak is rising. This feature is assigned to the self-metalation product, which we think is TiO-MCTPP. The 0.3 ML sample metalates at lower temperatures. We suggest this is due to a change in geometry, going from flat-lying to tilted adsorption structure with increasing coverage.
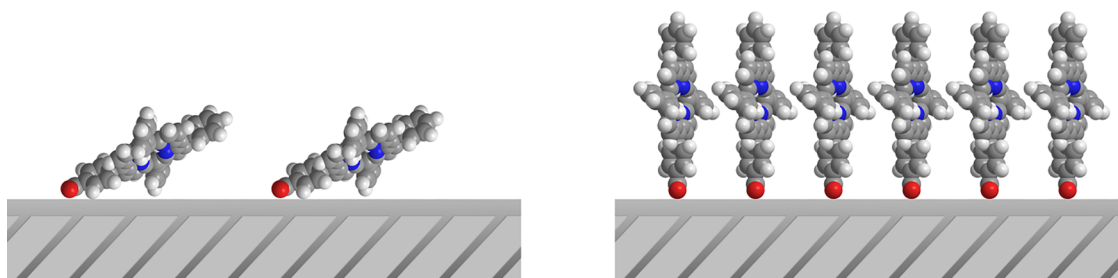

Figure 5. Qualitative scheme showing the expected change in adsorption geometry from flat lying to upright standing with increasing coverage.

The hydroxyl groups (531.9 eV) are stable to slightly higher temperatures than the carboxylate groups. We also expect more hydroxyl groups to form as the molecules begin to metalate. Nevertheless, in agreement with Du et al.[22] we find that the hydroxyl groups disappeared by 623 K.

Decomposition of the carboxylate anchor groups is not the only reaction at elevated temperatures: We also observe a coverage-dependent self-metalation reaction. Figure 4 shows the N 1s spectra corresponding to 0.9 and 0.3 ML of MCTPP on TiO$_2$(110) as a function of temperature. At low temperatures, we find the expected two-peak structure in the N 1s region, corresponding to the aminic (−NH−, 399.9 eV) and iminic (−N═ , 397.9 eV) nitrogen atoms of the free-base porphyrin molecule. At elevated temperature, the two peaks combine into one, indicating that all four nitrogen atoms have become chemically equivalent, a distinctive sign of metalation. XPS cannot unequivocally identify the metalation product,

which could be due to commonly observed impurities in TiO$_2$ single crystals[23] such as Ca^{2+} and Mg^{2+}. However, high resolution XPS measurements rule out the presence of such ions in our crystals and thus we suggest that the self-metalation product would be titanyl (Ti═O) porphyrin, see Figure 1.

Figure 4 shows that metalation starts taking place at approximately 423 K at low coverage whereas 523 K are required at higher coverage. We expect the 100 K difference in metalation temperature between 0.3 and 0.9 ML to be caused by a change in adsorption geometry, from flat-lying to upright standing shown in Figure 5, which has been observed previously for MCTPP on Co$_3$O$_4$(111).[15] Furthermore, for Zn-MCTPP on TiO$_2$(110), Zajac et al.[24] reported a flat-lying adsorption geometry at low coverages, while Olszowski et al.[25] found a tilted adsorption geometry for higher coverages. An upright-standing adsorption geometry is also in agreement with the carbon intensity being around 3 times higher than for the
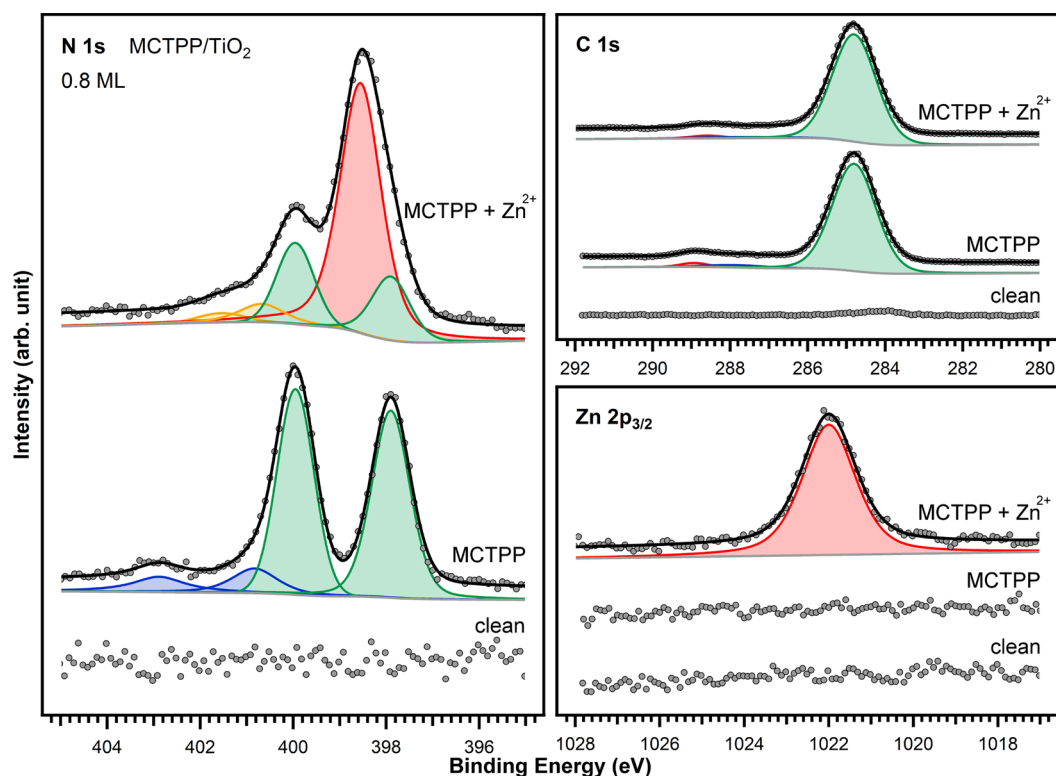
Figure 6. N 1s, C 1s, and Zn $2p_{3/2}$ spectra of 0.8 ML MCTPP on $TiO_2(110)$ before and after exposure to a 0.001 M aqueous solution of zinc acetate at pH 6 for 2 h.

flat-lying unfunctionalized 2HTPP on $TiO_2(110)$[14] and Cu(111).[16]

A change from flat-lying to upright-standing molecules would move the central pocket of the molecule away from the surface and thereby inhibit the metalation reaction, which involves a transfer of a titanyl (Ti═O) unit from the surface to the molecule. It is worth noticing that the metalation at high coverage (0.9 ML) does not take place until after the carboxylate anchor group has decomposed, see Figure 3. We therefore suggest that the metalation at high coverage is caused by the decomposition of the carboxylate anchor groups, allowing the molecules to easier bend down and metalate. If we have a closer look at the 0.9 ML N 1s spectra we could see that the shakeup peaks (fitted in blue) appear to have gone away at 623 K. This could be a slight indication of the flat-lying to upright standing proposed adsorption geometry transition as we do not expect to see the shakeup features in flat-lying molecules due to substrate screening. We should also note that the loss of the shakeup peaks in the N 1s spectra takes place at the temperatures where the carboxylic function is lost. This behavior is in agreement with the proposed conversion from upright-standing molecules to flat lying needed to achieve self-metalation.

Another difference between high and low coverages is the ratio between the aminic (−NH−) and iminic (−N═) N 1s species for the free-base molecule at room temperature. At high coverage, the ratio is the expected 1:1, but at lower coverage the aminic peak increases in intensity, indicating partial protonation of the iminic nitrogen atoms of the porphyrin molecule. This behavior has been observed before on $TiO_2(110)$ by Lovat et al.[9,26] and Köbl et al.[14] for tetraphenyl porphyrin. However, where Lovat and Köbl find complete protonation for tetraphenyl porphyrin, we only find a small degree of

protonation for MCTPP at low coverage and none at high coverage. We expect this to be another consequence of the transition from flat-lying to upright-standing molecules, bringing the center of the molecules further away from the surface and the protons on the surface. Because of the transfer of protons from the carboxylic acid anchor group to the surface, a higher degree of protonation of the macrocycle might be expected, but we do not observe this.

Metalation in a Zn^{2+} Aqueous Solution. Figure 6 shows the N 1s, C 1s, and Zn $2p_{3/2}$ XPS spectra of 0.8 ML MCTPP on $TiO_2(110)$ before and after exposing the sample to a Zn^{2+} aqueous solution at room temperature. After removal from solution, the two-peak structure of the free-base molecule in the N 1s region is partially replaced by the single peak of the metalated Zn-MCTPP molecule. Furthermore, there are no significant changes in the C 1s spectrum and only a slight (7%) increase in the overall N 1s peak area, which we have previously identified as small amounts of nitrogen-containing impurities from the solution adsorbed on the surface.[27,28] As expected, the metalation reaction is accompanied by presence of a stoichiometric quantity of Zn at the surface. On the basis of the area of the metalated N 1s peak, the degree of metalation in Figure 6, directly after exposure to solution, can be calculated to be 69%. This agrees very well with the value of 71% calculated from the zinc to carbon ratio. Our results imply that metalation of MCTPP on $TiO_2(110)$ with Zn^{2+} ions from solution takes place at room temperature, in contrast with the self-metalation reaction discussed above which requires elevated temperatures.

Figure 7 shows normalized N 1s XPS spectra corresponding to MCTPP on $TiO_2(110)$ after exposure to a Zn^{2+} containing aqueous solution as a function of molecular coverage. We observe around 15% increase in the degree of metalation as the coverage decreases below 0.4 ML. Just as for self-metalation in
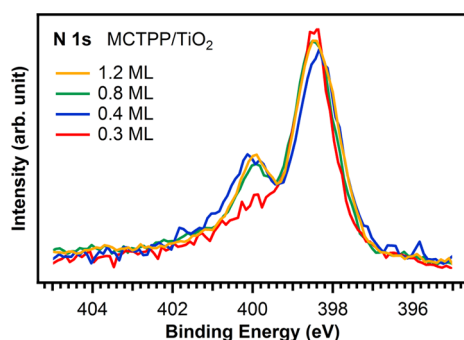
Figure 7. Normalized N 1s spectra of MCTPP on TiO2(110) after exposure to an aqueous solution of 0.001 M zinc acetate at pH 6 for 2 h, indicating a coverage dependency for coverages below 0.4 ML.

vacuum, higher degree of metalation is achieved in solution for lower coverages, but the effect is not as pronounced as in vacuum. Presumably higher coverages would present more MCTPP lateral interactions which could result in less metalation.

pH-Dependency. Figure 8 shows the N 1s spectra corresponding to low coverage and high coverage MCTPP on TiO$_2$(110) exposed to Zn^{2+} ions in solutions of different pH. Metalation involves the abstraction of two protons and is therefore favored under neutral and alkaline conditions, whereas demetalation, which involves the insertion of two protons, is favored under acidic conditions.[29,30] Thus, we observe the highest degree of metalation at pH 6 and a lower degree at pH 3. Figure 8 clearly shows that at pH 14 we observe the lowest degree of metalation. We should recall here that at this pH the prominent zinc species in solution is Zn-(OH)$_4^{2-}$,[31,32] which in order to be inserted into the pocket of the porphyrin molecule would need to lose 4 OH$^-$, a very unfavorable process under this conditions. Also, at pH 14 we

expect the TiO$_2$ surface to be negatively charged (IPE below 7). Thus, metalation at pH 14 is not simple to realize.

Another difference between the three pH values is the amount of nitrogen-containing impurities on the surface after exposure to the solutions. The smallest amount of impurities, yellow-shaded areas in Figure 8, is observed at pH 6. This has the simple explanation that pH 6 was the measured pH value of the pure 0.001 M zinc acetate solution, without additional chemicals added. In order to adjust the pH value for the two other experiments acetic acid and potassium hydroxide were used which introduced additional impurities to the solutions.

Under acidic conditions, reprotonation and detachment of MCTPP molecules from the surface could become feasible, but the observed decrease in carbon coverage after exposure was less than 10%. However, this stability of the anchored molecules under acidic conditions might be caused by the low solubility of MCTPP in water, rather than the stability of the carboxylate−TiO$_2$ bond. The TiO$_2$ surface itself is stable in neutral and alkaline solutions, but at pH 0 it will dissolve slowly with a rate of approximately 2 nm/day.[33]

■ CONCLUSIONS

Adsorption of 5-monocarboxyphenyl-10,15,20-triphenylporphyrin (MCTPP) on rutile TiO$_2$(110) at room temperature results in deprotonation of the acid group resulting in the formation of a covalent carboxylate bond to the surface. As deposited, no metalation with the substrate and only little protonation of the iminic nitrogen atoms is visible. Increasing the temperature results in decomposition of the carboxylate anchor groups and in self-metalation with the TiO$_2$ surface to form what we expect to be titanyl MCTPP. The self-metalation reaction proceeds at a 100 K lower temperature for low molecular coverages. Thus, our data suggests that the molecules undergo a flat-lying to upright-standing adsorption geometry transition as the surface coverage is increased. We propose that in order to self-metalate higher molecular coverages, loss of the
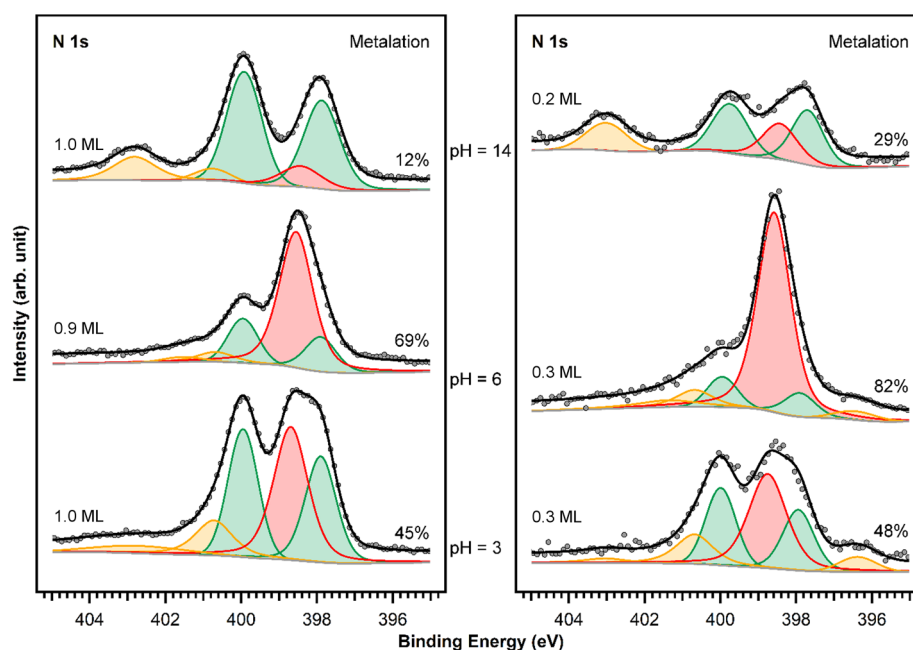

Figure 8. N 1s spectra of high- and low-coverage MCTPP on TiO2(110) after exposure to an aqueous solution of 0.001 M zinc acetate at three pH values for 2 h. The pH values were controlled with acetic acid (pH 3) and potassium hydroxide (pH 14), and the highest degree of metalation is obtained at a pH of 6.

carboxylate anchor group and a configurational change to a flat-lying geometry need to take place. Exposing the MCTPP on TiO$_2$(110) to Zn^{2+} aqueous solutions results in spontaneous metalation already at room temperature. The degree of metalation depends on the molecular coverage and solution pH with the lower coverages at pH 6 resulting in the highest degree of metalation observed.

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Notes

The authors declare no competing financial interest.

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