▌**Porphyrin Metalation** |*Hot Paper*|

Zinc Porphyrin Metal-Center Exchange at the Solid–Liquid Interface

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Abstract: Demetalation of zinc 5,10,15,20-tetraphenylporphyrin (ZnTPP) under acidic conditions and ion exchange with Cu^{2+} ions at neutral pH are both rapid reactions in the liquid medium. However, for ZnTPP monolayers adsorbed on a Au(111) surface exposed to aqueous solution, we find that, although ion exchange takes place rapidly as expected, demetalation does not occur, even at pH values as low as 0. Based on this, we conclude that metal center exchange on the surface does not proceed through a free-base porphyrin as an intermediate. Furthermore, once formed, CuTPP is stable on the surface and the reverse exchange from CuTPP to ZnTPP in the presence of Zn^{2+} ions could not be achieved. The preference for copper is so strong that even an attempt to exchange adsorbed ZnTPP with Ni^{2+} ions in the presence of traces of Cu^{2+} yielded CuTPP rather than NiTPP.

Introduction

Metalloporphyrins and analogues are large organic molecules that play significant roles in vivo, for example, in light harvesting and photosynthesis (chlorophyll) and oxygen transport and storage in the blood cells of mammals (hemoglobin and myoglobin).[1–3] In recent years, porphyrins adsorbed on solid surfaces have attracted significant fundamental research interest[4–6] owing to the huge technological potential of porphyrin thin films in, for instance, dye-sensitized solar cells,[7] chemical sensors,[8] and organic light-emitting diodes.[9]

The type of metal center coordinated to the central cavity of the porphyrin macrocycle strongly determines the functionality of the molecule. Thus metalation, demetalation, and metal center exchange of the porphyrin molecule have been studied extensively in the liquid medium.[10–14] In these reactions either the two aminic protons in the central cavity of the molecule are exchanged by a metal ion from solution (metalation) or vice versa (demetalation), or the metal center of a metalloporphyrin is exchanged by another metal ion (metal center exchange). A significant number of studies also exists addressing metalation of porphyrins on surfaces under ultrahigh vacuum with codeposited metal atoms,[15,16] substrate metal atoms,[17,18]

oxide lattice ions,[19] and recently also coordination of ions from aqueous solution.[20] However, to our knowledge, the work of Doyle et al.,[21] showing the exchange of nickel metal centers with copper substrate atoms, is the only available study on metal center exchange of adsorbed porphyrins under ultrahigh vacuum.

Herein, we combine the liquid phase and surface science approach and attempt both metal center exchange and demetalation of adsorbed porphyrins at the solid–liquid interface, extending our previous work[20] on the metalation of free-base tetraphenylporphyrin (2HTPP) with ions from solution.

Results and Discussion

The ion-exchange experiments were carried out by exposing one monolayer of adsorbed ZnTPP to aqueous solutions of $CuSO_4$ at room temperature (Figure 1). Two concentrations were used: 6 μM (1 ppm) and 1 mM. After exposure to 6 μM $CuSO_4$ for one hour, the Zn $2p_{3/2}$ signal has almost completely disappeared (Figure 1b) and has been replaced by a Cu $2p_{3/2}$ peak identical in position and almost in intensity to that of the reference XP spectrum of a CuTPP monolayer on Au(111) (Figure 1e). This is consistent with ion exchange forming CuTPP, a phenomenon that is also observed in the solution chemistry of the molecule. The main N 1s peak is unaffected, except for a small shift of +0.3 eV, consistent with the reference spectrum for CuTPP. However, a small shoulder is present at 399.8 eV. This is at the binding energy position expected for organic amines, and is consistent with impurities we have previously observed after exposing an Au(111) crystal to aqueous solutions.[20] Small impurities are extremely hard to avoid in surface science experiments involving exposure to liquids or high-pressure gas, and these could either have adsorbed from the liquid during immersion or been deposited afterwards as

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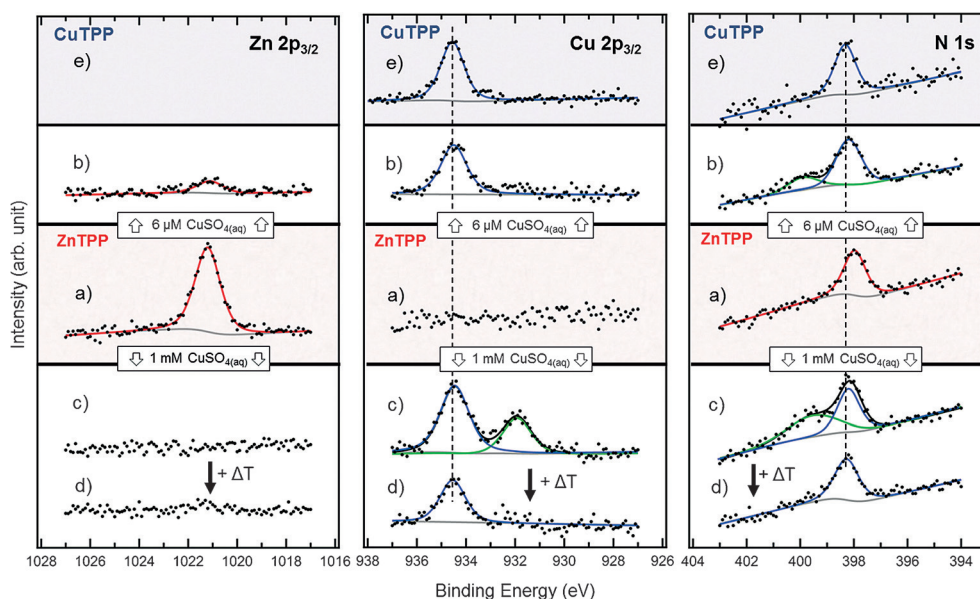
Figure 1. XP spectra of the Zn 2p$_{3/2}$, Cu 2p$_{3/2}$, and N 1s regions of one monolayer ZnTPP as deposited on Au(111) (a) and after exposure to an aqueous solution of either b) 6 μM or c) 1 mM CuSO$_4$ at room temperature for one hour. Included is also the spectrum after annealing the sample exposed to the 1 mM solution to 523 K for 5 min (d), and, as a reference, the spectra of one monolayer of CuTPP as deposited on Au(111) (e).

the crystal was transferred back into UHV and the thin film of clean water used for rinsing the crystal evaporates from the surface.

For higher concentrations of CuSO$_4$ (1 mM), all Zn^{2+} ions are exchanged completely with Cu^{2+} from solution, as evident by the absence of any signal in the Zn 2p$_{3/2}$ region after exposure (Figure 1c). However, the main Cu 2p$_{3/2}$ peak is now larger than expected for complete metalation, and a second peak has appeared at 931.9 eV, indicative of both Cu^{2+} (ca. 934 eV) and Cu$^{(0)[22]}$ (ca. 932 eV) impurities adsorbed on the surface. The presence of Cu$^{(0)}$ could be due to underpotential deposition of copper.[23] The Cu^{2+} impurity could be from traces of CuSO$_4$ that have not been completely rinsed away. This is furthermore accompanied by a significantly larger N 1s impurity peak at 399.8 eV (Figure 1c). However, annealing to 523 K for 5 min in vacuum (Figure 1d) completely removes the coadsorbed impurities, in agreement with previous observations,[20] and the resulting XP spectra are almost identical to the reference spectra for a CuTPP monolayer (Figure 1e). To test if the ion exchange is reversible we exposed one monolayer of CuTPP adsorbed on Au(111) to a 10 mM aqueous solution of zinc acetate for an hour at room temperature, but no exchange was visible in XPS (results not shown).

From these results, we conclude that the adsorbed tetraphenylporphyrin molecule has a much higher affinity for Cu^{2+} than Zn^{2+}, in agreement with stability trends reported for demetalation of metalloporphyrins in solution,[24] where CuTPP is more stable than ZnTPP.

NiTPP should be even more stable than CuTPP,[24] which led us to perform an additional experiment where we exposed a ZnTPP monolayer to a 100 mM aqueous solution of NiSO$_4$ in the presence of Cu^{2+} (1 ppm) for an hour at room temperature (Figure 2). Curiously, although the zinc was successfully ex-
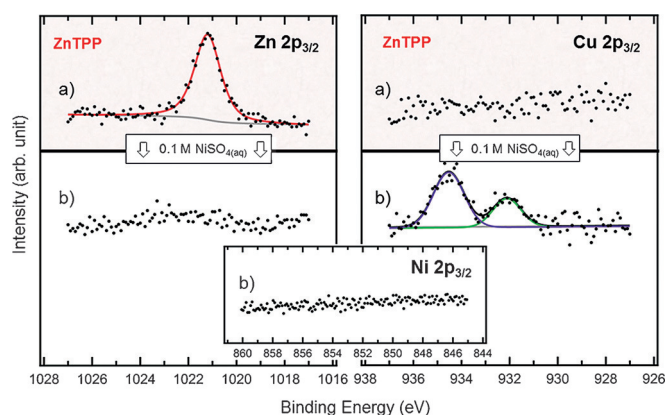

Figure 2. XP spectra of one monolayer ZnTPP a) before and b) after exposure to 100 mM aqueous NiSO$_4$ solution with 1 ppm copper ions for one hour at room temperature.

changed, as evident by the absence of a Zn 2p$_{3/2}$ signal after exposure to NiSO$_4$, the expected Ni 2p$_{3/2}$ signal for NiTPP did not appear. A closer look at the Cu 2p$_{3/2}$ region reveals a spectrum almost identical to that after exposure to 1 mM CuSO$_4$. Thus rather than exchanging with Ni^{2+} ions, the Zn^{2+} ions were exchanged with copper ions which were present in a much lower concentration. It would seem that although in solution NiTPP is more stable than CuTPP, the opposite is true for adsorbed molecules. The deposition of the Cu$^{(0)}$ impurity (932 eV) on the surface (Figure 2) at this low concentration of Cu^{2+} might be due to the higher concentration of sulfate rather than the presence of Ni^{2+}. Underpotential deposition of copper involves the coadsorption of copper and the anion and will therefore depend strongly on the anion concentration.[23] Hence, if the anion concentration is increased enough underpotential deposition might occur even for low Cu^{2+} concentra-

tions. An additional experiment (not shown) exposing an adsorbed monolayer of CuTPP to an aqueous solution of 10 mм $NiSO_4$ confirmed that CuTPP, once formed on the surface, is stable and does not exchange with Ni^{2+} ions from solution.

As we shall see below, our results indicate that the surface-mediated ion exchange mechanism does not proceed through a free-base intermediate. Thus we propose a reaction pathway similar to the one proposed in the liquid phase,[10] which is depicted for comparison in Figure 3. Throughout this pathway,
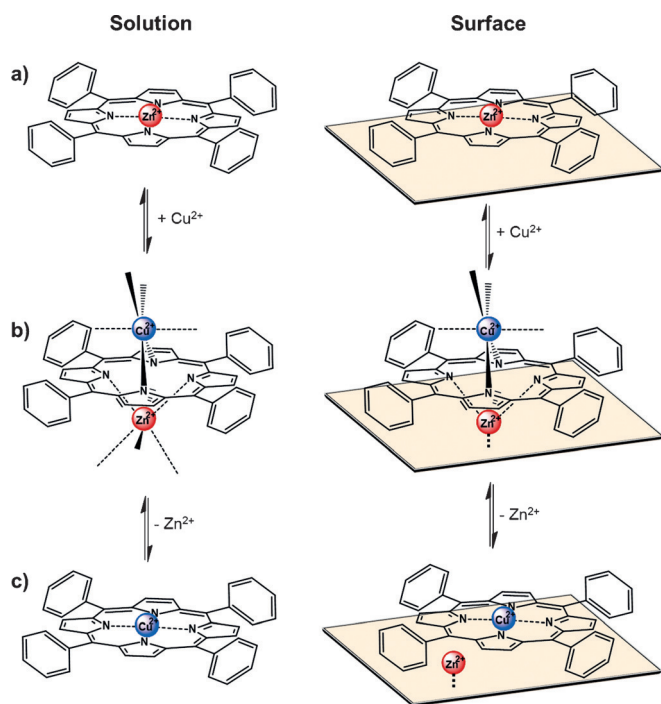

Figure 3. A possible reaction pathway for the surface-mediated metalation reaction with the surface acting as a ligand for the outgoing metal ion compared with the known reaction pathway from solution.

an intermediate (b) is formed in which the porphyrin ligand coordinates both the ingoing and outgoing metal ion. At the solid–liquid interface, the surface could act as a ligand for the outgoing metal ion, as illustrated in Figure 3.

In aqueous solution, at pH values below 4, zinc porphyrins demetalate,[10] and the central zinc ion is replaced by four protons from solution, forming a porphyrin diacid ($4HTPP^{2+}$). Figure 4 shows our attempt to demetalate one monolayer of ZnTPP (Figure 4a) adsorbed on Au(111) by exposure to an aqueous solution of 0.1 м CF_3COOH (pH 1). Since we rinse our sample with neutral water after the exposure to the trifluoroacetic acid solution and before transferring the sample back into UHV for analysis, we do not expect to see the porphyrin diacid on the surface, but rather the free-base (2HTPP) molecule, which is the stable form at pH 7. In XPS, the free-base molecule 2HTPP (Figure 4c) is easily distinguished from a metalated molecule, because of the two inequivalent nitrogen species, aminic (—NH—) and iminic (=N—), in the free-base molecule giving rise to two distinct N 1s peaks in a 1:1 ratio.[4] A reference spectrum of one-monolayer 2HTPP on Au(111) is shown
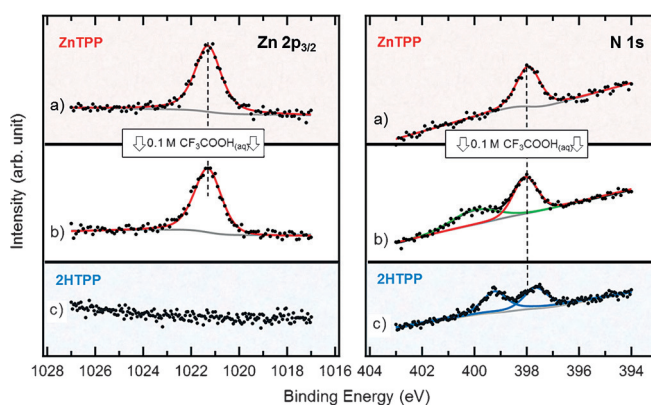

Figure 4. XP spectra of one monolayer of ZnTPP on Au(111) a) before and b) after exposure to an aqueous solution of 0.1 м CF_3COOH for one hour at room temperature. The signal intensities after exposure were corrected for the attenuation caused by coadsorbed organics, using the attenuation of the Au 4f signal. Spectrum (c) is a reference spectrum of one-monolayer 2HTPP on Au(111).

for comparison in Figure 4c. However, apart from the usual adsorption of a small amount of nitrogen impurities as visible in the N 1s region, no demetalation is evident in Figure 4b, and both Zn $2p_{3/2}$ and N 1s regions remain essentially unchanged. Decreasing the pH value further to 0 by increasing the trifluoroacetic acid concentration to 1 м (not shown) had no effect other than producing more adsorbed impurities on the surface; the adsorbed ZnTPP molecules did not show any signs of demetalation. Demetalation in the trifluoroacetic acid solution (pH 1) and remetalation during the rinsing process (pH 7) can be excluded, since the sample is removed from the solution before rinsing. Hence, only the small fraction of dissolved Zn^{2+} ions present in the droplet adhering to the Au(111) surface, as it is pulled out of the solution, would be available for remetalation and most of those ions will be rinsed away by the water.

The finding that adsorbed ZnTPP does not demetalate implies that the ion exchange reaction on the surface does not proceed through a free-base porphyrin as an intermediate, in agreement with most but not all studies[25] of the ion exchange reaction in solution.

The metalation/demetalation reaction mechanism in solution has been a debated topic for decades.[25] Fleischer and Wang first proposed an intermediate to occur during the reaction, the so-called sitting-atop (SAT) complex.[27] In the SAT-complex (Figure 5b left), the metal atom is located out of the porphyrin plane, coordinating four water ligands and two of the four nitrogen atoms of the porphyrin, while the other two nitrogen atoms are coordinating two protons pointing in the opposite direction. Later, the SAT complex was observed spectroscopically by NMR, UV/Vis, FTIR, and other methods,[25, 28] but an X-ray crystal structure analysis is still missing.

For adsorbed ZnTPP, it is possible that a coordination of the out-of-plane Zn^{2+} ion of the SAT complex to the Au(111) surface (Figure 5b right) is energetically much more favorable than the solution-equivalent coordination to four water molecules. This could significantly stabilize the SAT complex relative
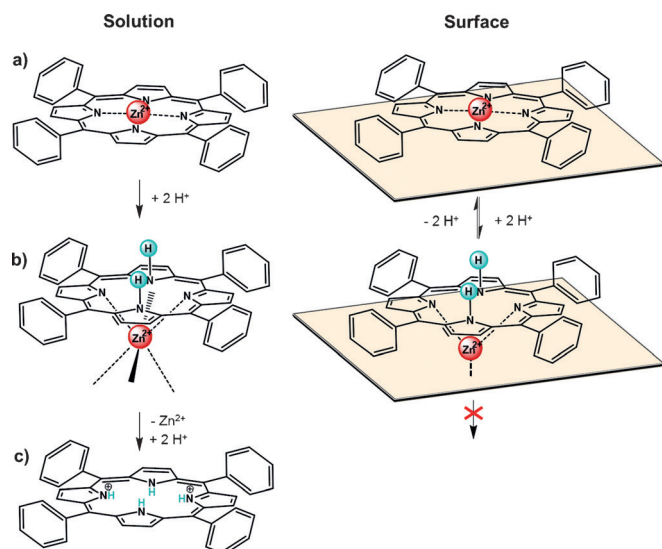
Figure 5. The demetalation mechanism of porphyrins in solution (left), proceeding through the sitting-atop (SAT) complex first proposed by Fleischer and Wang,[26, 27] forming a protonated porphyrin diacid, and our suggested model for the surface reaction (right), stopping at the SAT complex.

to the demetalated porphyrin diacid, to the point where the SAT complex is the stable form of the adsorbed porphyrin in acidic solution. Once rinsed with water, the SAT complex will deprotonate to ZnTPP, which is why we observe ZnTPP and not the SAT complex after exposure to acidic solutions.

Conclusion

In agreement with the solution chemistry of porphyrins, adsorbed ZnTPP on Au(111) exchanges metal ions with Cu^{2+} ions from a $CuSO_4$ solution, forming CuTPP. This reaction was not reversible as it was not possible to ion exchange the adsorbed CuTPP back to ZnTPP in a solution of zinc acetate. However, unlike the solution chemistry of porphyrins it was not possible to ion exchange adsorbed CuTPP with Ni^{2+} ions, suggesting that the surface plays an active role in the stability of the metal center. Finally, it was not possible to demetalate adsorbed ZnTPP in acidic solution, which could be explained by the coordination of Zn^{2+} to the surface and thereby strong stabilization of the reaction intermediate. This finding also implies that the ion exchange reaction on the surface does not proceed through a free-base porphyrin intermediate.

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 source. Binding energies reported in this work are referenced to the Fermi edge of Au(111) at $E_B = 0$.

Zinc 5,10,15,20-tetraphenylporphyrin (ZnTPP) and copper 5,10,15,20-tetraphenylporphyrin (CuTPP) were deposited by evaporation in UHV from a Knudsen cell evaporator kept at 463 K, while

the clean Au(111) single-crystal sample was kept at room temperature. The resulting multilayers were annealed to 523 K for 5 min, desorbing the multilayers and leaving one monolayer behind. This is a quick and easy way to prepare monolayers; however, although heating to 523 K does not change the XP spectrum of the monolayer,[16] dehydrogenation of the periphery of the molecule, as has been observed on both Ag(111)[24] and Cu(111),[18] can never be fully excluded since it would cause only very small changes to the XP spectra.

Exposure to aqueous solutions was carried out in an argon-filled liquid cell attached to the UHV chamber. After exposure, the drop of solution still adhering to the surface of the crystal was rinsed away with 50 mL of clean water. This results in a water droplet now adhering to the surface which was blown away with an argon jet, leaving a thin film of water on the surface to evaporate as the sample is transferred back into UHV. At no point during transfer or exposure to solution was the crystal exposed to air. Details of the applied procedure are described elsewhere.[29] The Milli-Q water used for the experiments was further purified from organics by exposing it to UV light for one hour under argon atmosphere prior to solution preparation. Upon irradiation, OH radicals are formed which oxidize organic species present in solution. The total organic content of the purified Milli-Q water was determined to be lower than 60 ppb by measuring the chemical oxygen demand required for oxidation. To avoid additional potential contaminants, buffered solutions to keep the pH stable were deliberately not used.

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