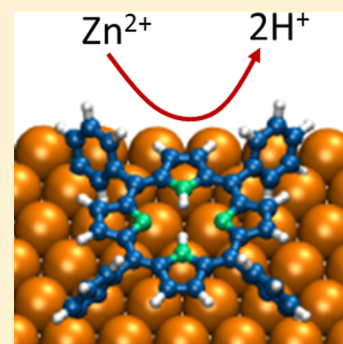


## Surface Porphyrins Metalate with Zn Ions from Solution

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## Supporting Information

**ABSTRACT:** Controlling the metalation of surface porphyrins is a critical process in porphyrin-based devices. Indeed, surface porphyrins are known to metalate in ultrahigh vacuum from codeposited metal atoms or substrate atoms; however, it is not yet known if surface porphyrins could metalate from ions in solution, that is, the most likely environment for porphyrin-based devices. Using X-ray photoelectron spectroscopy we have studied the metalation of monolayers and multilayers of a free-base tetraphenyl porphyrin adsorbed on Au(111) with ions in solution. We found that full metalation with  $Zn^{2+}$  can be achieved already at room temperature in contrast with the elevated temperatures required for metalation with codeposited metal atoms.



The investigation of porphyrins on surfaces is a research field that has attracted considerable attention over the past decade.<sup>1–8</sup> The interest in this class of molecules stems from their importance in biological processes where they are one of the key functional building blocks. For example, the iron-containing porphyrin found in hemoglobin is responsible for oxygen transport, and storage in the blood cells and the magnesium-containing porphyrin found in chlorophyll is a key component in light harvesting and photosynthesis.<sup>9</sup> Furthermore, porphyrins have been shown to be suitable for technical applications, for instance, as colorimetric gas sensors<sup>10</sup> or catalysts.<sup>11</sup> In particular, metaloporphyrins are promising because their functionality is strongly dependent on the type of metal center coordinated to the central cavity. Thus, far metaloporphyrin layers on surfaces have been prepared either by direct deposition or by metalation of a free-base porphyrin with codeposited metal atoms,<sup>12–14</sup> substrate atoms from a metal surface,<sup>15–18</sup> or lattice ions from oxide surfaces.<sup>19</sup> Metaloporphyrins are also known to exchange their metal ion with a metal substrate atom;<sup>20</sup> however, in solution, metalation occurs through the coordination of a dissolved metal ion and deprotonation of the two aminic nitrogen atoms.<sup>21</sup> Here we want to determine if it is possible to metalate free-base porphyrin adsorbed on a surface with cations from solution, that is the most likely environment for porphyrin-based devices. Thus, in this work we have studied the metalation of 5,10,15,20-tetraphenyl-21H,23H-porphyrin (2HTPP) adsorbed on Au(111) with  $Zn^{2+}$  ions in aqueous solution. We found that the two distinct N 1s X-ray photoelectron spectroscopy (XPS) features belonging to the nonprotonated iminic ( $=N-$ ) and protonated aminic ( $-NH-$ ) nitrogen atoms of the free-base porphyrin on Au(111) merge into one peak after exposure of the surface to a  $Zn^{2+}$  aqueous solution. This indicates that the

molecular layer has been fully metalated, which is further supported by the stoichiometric amount of Zn detected on the surface.

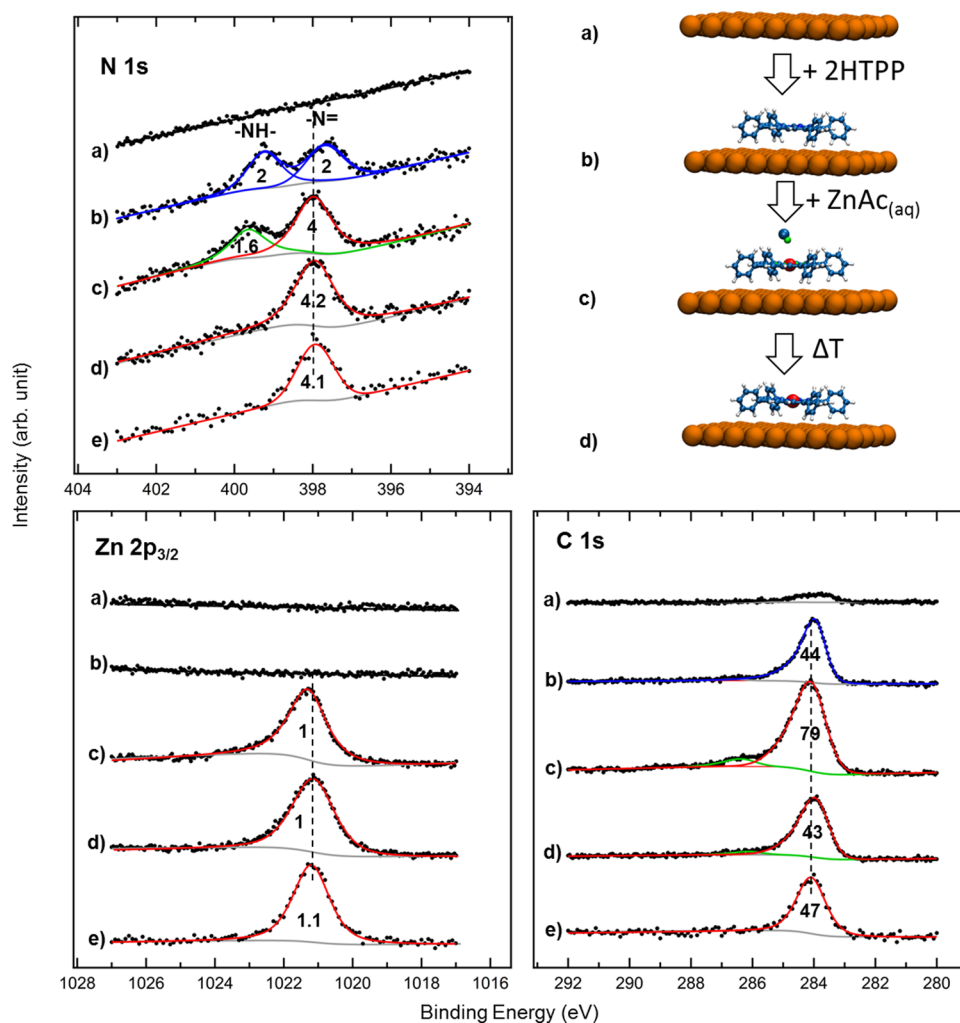
Figure 1 displays N 1s, Zn 2p, and C 1s XP spectra for: (a) the clean Au(111) surface, (b) after deposition of a 2HTPP monolayer, (c) after exposure to 0.7 M  $ZnAc_2$  (the concentration is comparable to the one employed for the metalation of porphyrins in solution), and (d) after annealing in ultrahigh vacuum (UHV) to 523 K. The monolayers of 2HTPP on Au(111) were prepared by multilayer deposition and subsequent annealing to 523 K, desorbing the multilayers and leaving a monolayer behind on the Au(111) surface. No changes are visible in XPS as monolayers of 2HTPP on Au(111) are heated to these temperatures;<sup>13</sup> however, dehydrogenation of the periphery of the molecule has been observed on Cu(111)<sup>16</sup> already at 450 K, and because dehydrogenation of the periphery of the molecule would cause very small changes in XPS, it cannot be completely excluded. The 2HTPP spectrum of the monolayer before exposure to the solution exhibits the two distinct N 1s peaks of equal area (blue fit), expected for the two aminic  $-NH-$  (399.2 eV, fwhm = 1.1 eV) and two iminic  $=N-$  (397.7 eV, fwhm = 1.1 eV) nitrogen atoms in 2HTPP.<sup>22</sup> After exposure to 0.7 M  $ZnAc_2$  for 2 h, two new features emerge: one at 398.0 eV (red fit), with the combined area of the two blue nitrogen peaks of monolayer before exposure to the solution, and another at 399.7 eV (green fit), which disappears upon annealing to 523 K. For a metalated porphyrin the two distinct N 1s peaks of the free-base molecule will merge into just one peak because all

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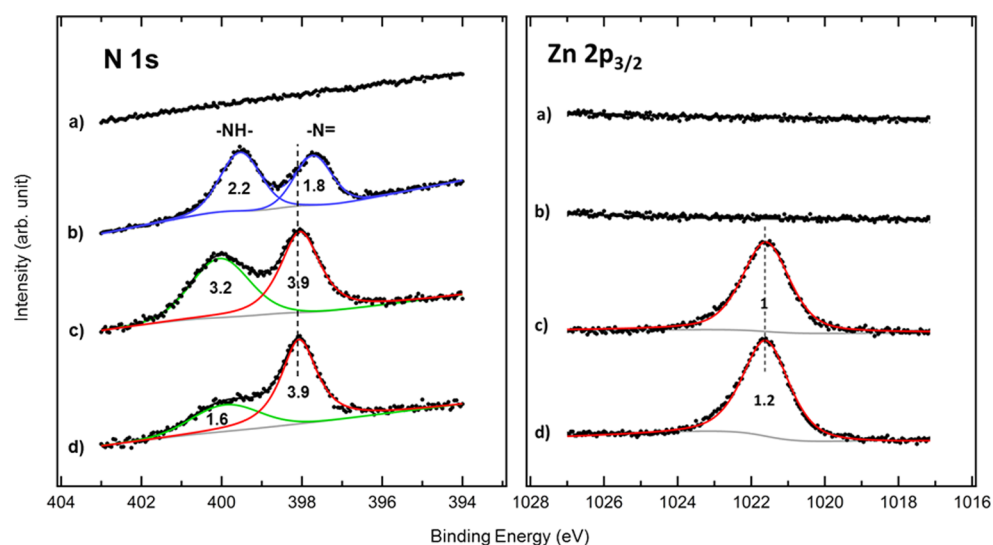
**Figure 1.** XP spectra of the N 1s, Zn 2p, and C 1s region displaying the changes that occur in different stages of the experiment: (a) clean Au(111) surface, (b) after 1 monolayer preparation of 2HTPP, (c) after exposing the 2HTPP monolayer with 0.7 M ZnAc<sub>2</sub> solution for 2 h, (d) after subsequent -annealing to 523 K for 5 min, and (e) 1 monolayer ZnTPP on Au(111) reference spectra. Blue fits represent 2HTPP molecules, red fits represent ZnTPP, and green curves represent coadsorbed organics. Gray lines show the Shirley-background and black numbers indicate relative areas. (top right) Schematic sketch displaying the suggested surface species that correspond to the XP spectra.

four nitrogen atoms of a metalated porphyrin are equivalent. The position of the red feature at 398.0 eV is at the position for ZnTPP on Au(111) (see reference spectrum in Figure 1) and is therefore in agreement with a complete metalation of all 2HTPP molecules on the surface. The change is accompanied by a Zn 2p<sub>3/2</sub> signal at 1021.3 eV with a nitrogen-to-zinc ratio of 4.2:1 (when corrected for sensitivity factors), very close to the expected ratio of 4:1 for ZnTPP. Figure 1e shows that the 1 monolayer ZnTPP deposited on Au(111) reference spectra we measured agrees with the spectra obtained after metalation from solution. We therefore conclude that Zn<sup>2+</sup> ions from solution have metalated the 2HTPP molecules, forming ZnTPP. We suggest that the aminic protons of the 2HTPP molecules are exchanged with the Zn<sup>2+</sup> ions, forming acetic acid.

We attribute the green N 1s feature at 399.7 eV, which disappears after annealing to 523 K, to an unwanted nitrogen impurity adsorbed from the solution onto the surface; due to the binding energy position, we suspect organic amines. Here we should note that the ultrapure Milli-Q water employed in the experiments has a total organic carbon level below 60 ppb and is the source of the observed N containing impurities (see

Supporting Information). The adsorption of the nitrogen-containing impurity is accompanied by an increase in the amount of carbon on the surface, which disappears together with the nitrogen impurity when annealed to 523 K, as expected. The amount of Zn remains unchanged during annealing to 523 K, but a small binding energy shift of 0.2 eV toward lower binding energies is visible in the Zn 2p region. We suspect this to be caused by the coadsorption of the impurity, visible in the N 1s and C 1s regions, either due to a change in the local work function, slightly shifting all binding energies of the mostly physisorbed molecules,<sup>23</sup> or due to direct adsorption of the N-containing molecule on the Zn metal center of the ZnTPP molecule.<sup>24</sup>

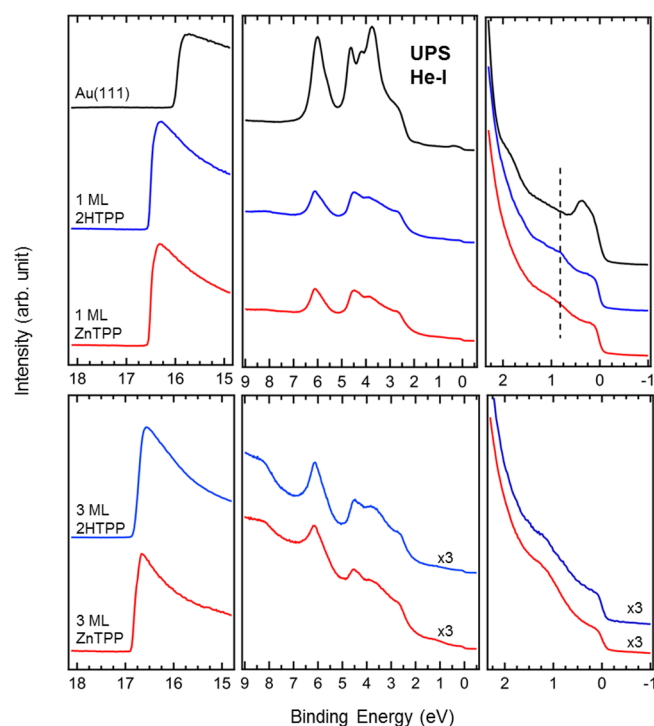
Previous studies have shown that metalation with codeposited metal atoms, or self-metalation with surface atoms, is possible not just for monolayers but also for multilayers, albeit with lower yields or higher temperatures required.<sup>6,16</sup> Figure 2 shows the N 1s XPS spectra of 2HTPP multilayers (~3 monolayers) on Au(111) before and after exposure to ZnAc<sub>2</sub> solution. The multilayer spectra can be fitted in an almost identical manner to that used for the monolayer spectra; however, the ratio between the two nitrogen signals in the



**Figure 2.** XPS N 1s overview of a multilayer ( $\sim 3$  monolayers) metalation experiment on Au(111). (a) Clean Au(111) surface, (b) after multilayer evaporation of 2HTPP, (c) after exposure of the sample to 0.7 M ZnAc<sub>2</sub> solution for 2 h, and (d) after subsequent UHV-annealing to 523 K for 5 min. The color codes correspond to these used in Figure 1.

2HTPP multilayer is not exactly 2:2, which is due to loss features appearing at higher coverages.<sup>15</sup> After exposure to the 0.7 M ZnAc<sub>2</sub> solution, the two distinct N 1s peaks of the 2HTPP molecule (blue fit) merge into the one peak corresponding to the metalated ZnTPP molecule (red fit), which coexists with another peak at the position of the nitrogen impurity (green fit). After a short annealing time, the area of the green impurity peak decreases significantly, but unlike the monolayer experiment it does not completely disappear. Longer annealing times led not only to the disappearance of the green feature but also to desorption of the ZnTPP multilayers into the gas phase. We expect metalation of porphyrin multilayers with codeposited metal atoms (or self-metalation with the surface) to occur at the surface followed by diffusion of metalated molecules from the surface into the multilayers.<sup>1</sup> On the contrary, we could assume that metalation of porphyrin multilayers with cations in solution occurs at the interface between the multilayer and the solution, probably followed by diffusion of the cations into the multilayer metalating porphyrin molecules.

Figure 3 top panel shows ultraviolet photoelectron spectra (UPS) acquired on the pristine Au(111) surface, 1 monolayer 2HTPP on Au(111), and 1 monolayer ZnTPP (metalated from solution and annealed to 523 K) on Au(111). The bottom panel of Figure 3 shows the equivalent spectra obtained for 3 monolayers of 2HTPP on Au(111) and 3 monolayers of ZnTPP (metalated from solution and annealed to 523 K) on Au(111). The left box shows the corresponding secondary electron cutoff of UP spectra acquired at  $-8$  V sample bias. From the binding energy position of the cutoff, we can determine the work function of the surface by  $\Phi = h\nu - E_{\text{cutoff}}$  yielding  $\Phi = 5.27$  eV for pristine Au(111), 4.72 eV for each 1 monolayer 2HTPP and ZnTPP on Au(111), and 4.33 eV for 3 monolayers of 2HTPP and ZnTPP on Au(111). This means that the porphyrin overlayer lowers the work function of the substrate by  $-0.55$  eV in the monolayer case and by  $-0.94$  eV in the multilayer case, no matter if the macrocycle is coordinated to a Zn<sup>2+</sup> ion or not. This indicates that the 3 monolayers porphyrin film has a larger surface dipole than the 1 monolayer film, giving rise to a larger work function change.



**Figure 3.** Top panel: UP spectra of the clean Au(111) surface (black), 1 monolayer 2HTPP on Au(111) (blue), and ZnTPP on Au(111) (red) synthesized through exposure to ZnAc<sub>2</sub> solution. Bottom panel: UP spectra of 3 monolayers 2HTPP on Au(111) (blue) and 3 ML of ZnTPP on Au(111) (red) synthesized through exposure to ZnAc<sub>2</sub> solution. The spectra in the left box showing the secondary electron cutoff were acquired with  $-8$  V sample bias.

Furthermore, it also indicates that the interaction between the Zn<sup>2+</sup> ion in ZnTPP and the Au(111) surface does not influence the surface dipole significantly. In accordance with that, previous XPS and UPS results showed that there is no or very little interaction between the Zn center of ZnTPP and a Ag(111) surface,<sup>25</sup> and we expect the same to be true on the even less reactive Au(111) substrate.

In the region close to the Fermi edge (right box Figure 3), the Au(111) spectrum shows a significant feature below the Fermi edge, which was identified as a Shockley surface state and can be detected only in normal emission.<sup>26</sup> Upon adsorption of tetrapyrroles on Au(111), the Shockley state is depopulated, as shown in Figure 3. A detailed description of the relevant effects can be found elsewhere.<sup>27</sup> The region close to the Fermi edge is similar for 1 monolayer of 2HTPP and ZnTPP, as displayed in Figure 3 top panel. A minor difference is the intensity of the surface state at ~0.9 eV, which is higher for 2HTPP. Because it is known that free base porphyrins interact with metal substrates via bond formation between their iminic nitrogen atoms and the surface,<sup>6</sup> we suggest this feature to be due to this localized interaction. A possible explanation for the depletion of this state when the molecule is metalated would be a weakening of the nitrogen-surface bond as the nitrogen-zinc bond is formed. This minor difference is not observed between 2HTPP and ZnTPP in the multilayer spectra; however, in this case, we observe new features at around 1.25 and 8.5 eV below the Fermi edge due to molecular orbitals in the porphyrins,<sup>28</sup> features that cannot be observed in the monolayer due to their lower intensity.

In summary, we have shown that it is possible to metalate tetraphenyl porphyrins adsorbed on Au(111) by exposing the surface to Zn<sup>2+</sup> ions in an aqueous solution. The synthesis works for monolayers as well as multilayers and at lower temperature than that required for metalation with coadsorbed metal atoms.

## EXPERIMENTAL METHODS

Photoelectron spectroscopy measurements were performed in an UHV chamber using a SPECS electron energy analyzer, a monochromatic X-ray source, and a He I UV source. The porphyrin layers were prepared by thermal evaporation on a clean Au(111) surface. Exposure to Zn<sup>2+</sup> aqueous solution was carried out using a liquid cell attached to the UHV chamber without exposing the crystal to the laboratory atmosphere following the procedure discussed elsewhere.<sup>29</sup>

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcllett.5b02218.

Photoelectron spectroscopic data demonstrate that the N-containing impurities observed after placing the 2HTPP/Au(111) system in contact with the Zn<sup>2+</sup> solutions are picked up from milli-Q water employed in the experiments. (PDF)

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### Notes

The authors declare no competing financial interest.

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