

Surface-Mediated *in Situ* Metalation of Porphyrins at the Solid–Vacuum Interface

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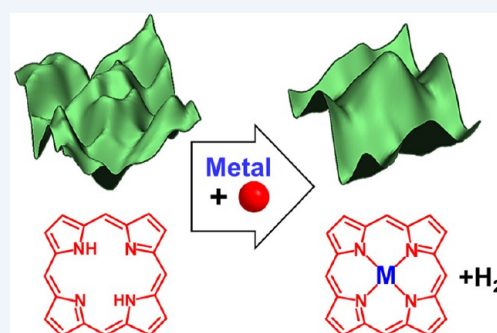
S Supporting Information

CONSPECTUS: The investigation of porphyrin derivatives at the solid–vacuum interface has become a vivid research field with the prospect to tailor functional molecular architectures and as prototype examples to study the fundamental properties of porphyrin derivatives in regard to their vital role in many natural processes. The functional properties of the porphyrin derivatives are mainly determined by the central metal atom. Thus, the recent exploration of the surface-confined *in situ* metalation of porphyrins is an important step toward the realization of molecule-based functional devices. The corresponding metalation reaction of free base porphyrin derivatives can be conveniently realized *in situ* in ultrahigh vacuum by post- or predeposition of metal atoms or directly with substrate atoms in the so-called self-metalation. Moderate heating above room temperature (RT) might be necessary either to realize the transport of the metal to the porphyrin via diffusion or to overcome an activation barrier determined by the redox reaction itself.

Surface science techniques like scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS), and temperature-programmed desorption (TPD) are powerful tools to scrutinize the reaction and give valuable insights into the metalation process. For example, the completed metalation can be reflected in an enhanced apparent height of the corresponding porphyrin in STM or can be evidenced by characteristic changes in the N 1s region in XPS. These signatures allow monitoring of the progress of the metalation, and it was found that the reaction generally proceeds with very high yield.

Surface diffusion of the coadsorbed metal atoms mediates the reaction and is crucial for the high yields of the corresponding reactions with pre- and postadsorbed metals. It was also demonstrated that the completed metalation can indeed significantly alter the adsorption behavior and the electronic properties and thus the functionality of the porphyrin molecules. These alterations can be used to monitor the kinetics of a particular porphyrin self-metalation reaction by STM and to estimate the activation barrier for that reaction based on isothermal measurements at different temperatures. Also TPD measurements of the H₂ and D₂ signals allow for the determination of corresponding activation energies for the metalation of free base porphyrins and their deuterized analogues. Gas phase DFT calculations of the metalation of the “bare” free base porphyrin macrocycle identify intermediate reaction steps with the transfer of the first hydrogen atom to the metal center being the main barrier to overcome. The values from these calculations are in fair agreement with experimentally determined ones. However, TPD based results indicate that exchanges of deuterium and hydrogen between the central nitrogen and the surface occur, which indicate an active role of the surface and challenge the findings from gas phase DFT.

The *in situ* metalation of porphyrins at the solid–vacuum interface is established as a novel and convenient route to tailor functional molecular architectures. With different surface science techniques detailed insights into the surface-mediated metalation reaction were achieved for this class of prototype functional molecules.



■ INTRODUCTION

The investigation of functional molecules on surfaces has become a vivid field in fundamental and applied sciences with the prospect to fabricate novel molecular based devices. In this regard the rational design of functional molecular architectures via surface-confined coordination chemistry was identified as a promising route to target this goal.¹ If it comes to pick a specific molecular building block, the class of porphyrins is in different

aspects a “natural choice”.^{2,3} First, the rigid porphyrin macrocycle (Figure 1a) can act as a structure forming element on surfaces, and a rich variety of peripheral ligands can be attached (Figure 1b–d), which can strongly influence the corresponding molecule–substrate and intermolecular inter-

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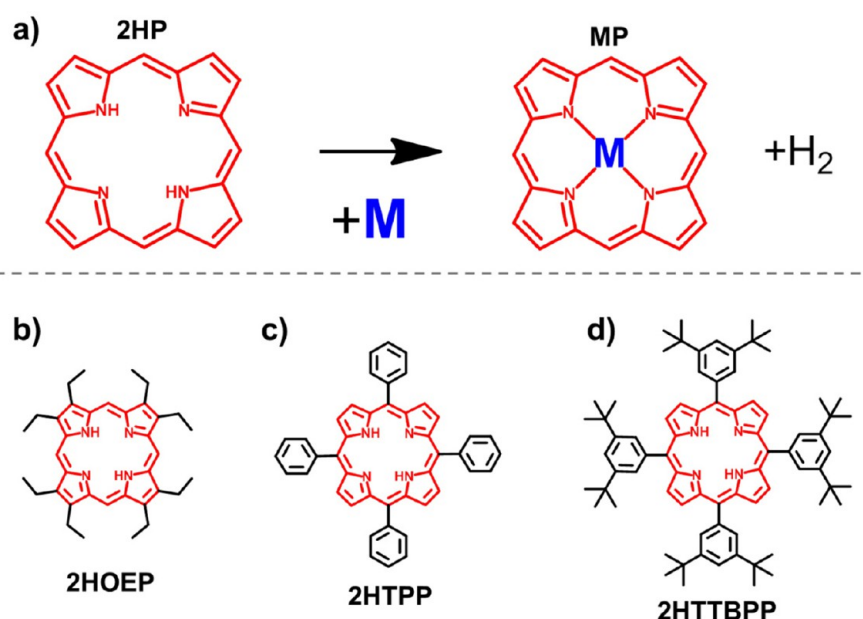


Figure 1. (a) Sketch of porphyrin metalation reaction: free base porphyrine (2HP) reacts with metal (M) to metalloporphyrin (MP) under the release of H_2 . (b–d) Selected substituted free base porphyrin derivatives: (b) 2H-octaethylporphyrin (2HOEP); (c) 2H-tetraphenylporphyrin (2HTPP); (d) 2H-tetrakis(3,5-di-*tert*-butyl)-phenylporphyrin (2HTTBPP).

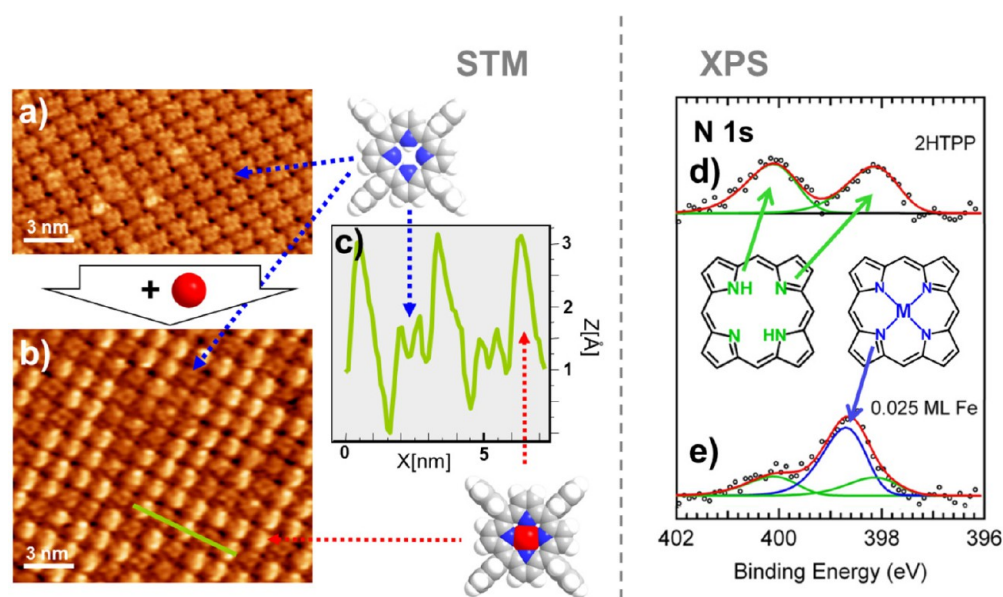


Figure 2. STM images of a monolayer of 2HTPP on Ag(111) (a) as deposited at RT and (b) after evaporation of 0.030 ML of Fe. (c) Height profile extracted along the green line in panel b. N 1s XP spectra of 2HTPP monolayer (d) on Ag(111) and (e) after deposition of 0.025 ML of Fe at RT. Adapted with permission from refs 6 and 31. Copyrights 2007 Wiley and 2008 American Chemical Society.

actions and thus have the potential to tailor the adsorption behavior.

Second, porphyrinoids are abundant in nature as main functional building blocks in important biological processes.⁴ Among these are oxygen transport in the bloodstream of mammals by iron porphyrin in heme and magnesium porphyrin in chlorophyll as a light driven proton pump. These examples not only illustrate the versatile functionalities of porphyrins in nature but also highlight the crucial role of the central metal atom. Generally, free base porphyrins can react with almost any metal to form the corresponding metalloporphyrin. Thereby

the most common oxidation state of the metal ions complexed in the porphyrin macrocycle is +II or +III.

The metalation reaction specifically at the solid–vacuum interface is sketched in the upper part of Figure 1: the free base porphyrine (2HP) reacts with a metal to metalloporphyrin (MP) under the release of H_2 . In the same way, the metalation reaction can be realized for substituted free base porphyrins as depicted in Figure 1b–d. Surface-confined metalation reactions of free base porphyrin derivatives are highly desirable to achieve *in situ* functionalization of the molecules but also to scrutinize the reaction itself with modern surface science techniques. Indeed the metalation reaction of porphyrins on surfaces in

ultrahigh vacuum was explored basically at the same time around 2007 by the group of Johannes Barth in Munich⁵ and our group in Erlangen.^{6,7} Since then more than 50 articles reporting on surface metalation of porphyrin derivatives and related tetrapyrrolic species were published. Until now, the on-surface metalation reaction was reported for a variety of different free base porphyrins with Ce,^{8,9} Co,^{3,7,10,11} Cu,^{12–26} Fe,^{5,6,27–33} Ni,^{30,34–36} Ru,³⁷ and Zn^{11,38} (a table with all surface confined metalation reactions of porphyrins reported until now is provided in the Supporting Information). Here, the main aspects of surface-confined metalation exclusively of porphyrins will be reviewed on example of our own results achieved in ultrahigh vacuum mainly around room temperature (RT). Thereby, the different protocols, the experimental identification of the completed metalation, accompanying changes in the intramolecular conformation and adsorption behavior, the role of the surface, a strategy for the local functionalization and metalation on template surfaces, and, finally, detailed insights into the metalation reaction itself will be presented and discussed.

METALATION VIA METAL EVAPORATION ONTO PORPHYRIN LAYERS

The first reported metalation experiments were conducted in the most intuitive way; this is to add metal atoms successively to a layer of predeposited free base porphyrins.^{5–7} An illustrative example is the metalation of 2HTPP on Ag(111) with Fe.^{6,31,32} Here, the *in situ* metalation with Fe is especially desirable since iron porphyrins are very sensitive toward oxidation, that is, handling under ambient conditions should be avoided. Figure 2 depicts scanning tunneling microscopy data before (Figure 2a) and after the deposition of iron onto an closed layer of 2HTPP on Ag(111) (Figure 2b,c) and corresponding XPS data acquired in a different experimental setup. In Figure 2a, a scanning tunneling (ST) micrograph of a closed monolayer, that is, 0.037 ML of 2HTPP (1 ML defined as one molecule per surface atom) on Ag(111) is depicted. The 2HTPPs adsorb flat-lying on the surface and self-assemble in a square arrangement with an intermolecular distance of ~ 1.4 nm. In STM, the free base porphyrins exhibit a central depression, which is in agreement with the topography of the molecule (“empty pocket”). Figure 2b reflects the situation after RT deposition of 0.030 ± 0.005 ML of Fe, that is, $\sim 70\%$ of the amount needed to metalate the whole monolayer. Now the majority of the molecules appear as protrusions ($\sim 60\%$), and only a minor part preserved the appearance with the central depression associated with 2HTPP. The observed protrusions are in line with an enhanced tunneling contribution through the d orbitals of FeTPP and are a strong indication for completed metalation with Fe.^{33,39} Additional evidence is provided by characteristic changes of the N 1s XPS signal after Fe deposition in Figure 2d,e. The spectrum of the 2HTPP layer in Figure 2d exhibits two pronounced N 1s peaks reflecting the two inequivalent nitrogen pairs, that is, the N 1s peaks of aminic nitrogen ($-\text{NH}-$) at 400.1 eV and iminic nitrogen ($-\text{N}=\text{C}$) at 398.2 eV. After deposition of 0.025 ML of Fe, an N 1s component evolves at 398.7 eV at expense of the aminic and iminic peaks (Figure 2e). This peak is a fingerprint of FeTPP, in which all four nitrogen atoms are equally coordinated to the metal center.

The complementary XPS data allow us to explicitly identify the protrusions in STM (Figure 1b,c) with FeTPP. With this, the yield of the metalation reaction can be determined simply

by counting the protrusions (metalated porphyrins) in the STM image. An example is shown in Figure 3a–d in which iron

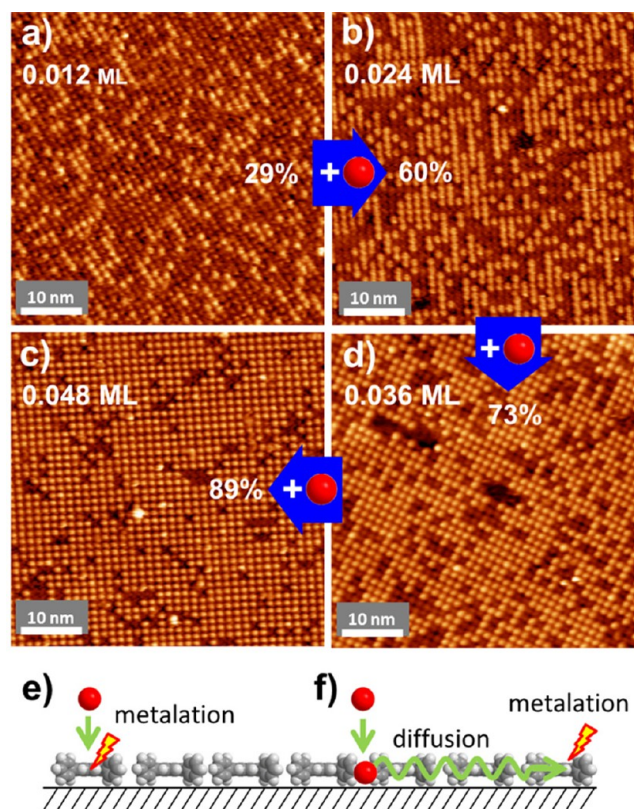


Figure 3. (a–d) Series of STM images after the successive deposition of equal amounts of Fe. The deposited Fe amounts are indicated along with the metalation degrees. Sketches of (e) the direct metalation and (f) metalation after diffusion. Adapted with permission from ref 6. Copyright 2007 Wiley.

was successively deposited in increments of 0.012 ± 0.002 ML, that is, one-third of the stoichiometric amount needed to completely metalate a monolayer of 2HTPP on Ag(111). The agglomerated amounts of iron along with the corresponding metalation degrees are indicated. Comparing the numbers, it becomes evident that for the first two deposition increments the efficiency of the metalation reaction is 100% percent within the margin of error (Figure 2a, 29% vs 33% for 0.012 ML; Figure 2b, 60% vs 66% for 0.024 ML). Since the evaporation of the iron atoms onto the surface is a statistical process, the probability that all Fe atoms directly “hit” the center of a 2HTPP molecule, as sketched in Figure 3e, is zero. Therefore, at least some of the iron atoms first have to diffuse to the corresponding site as illustrated in Figure 3f. The high mobility of the iron atoms on the 2HTPP/Ag(111) was also demonstrated by the deposition of excess Fe, which leads to the formation of Fe islands (not shown here). Therefore, one concludes that the metalation process is at least partially surface-mediated in the presented case. The findings for the system Fe/2HTPP/Ag(111) are not singular, since basically identical observations were made for Co/2HTPP/Ag(111),^{3,7,10,11} Fe/2H-tetrapyrrolylporphyrin (2HTPPyP)/Ag(111),⁵ Fe/2H-octaethylporphyrin (2HOEP)/Ag(111),³⁴ and Ni/2HOEP/Cu(111).³⁵ Examples for systems in which additional heating was required or the yield of the metalation reaction appeared reduced were Zn/2HTPP/Ag(111),^{3,11,38}

Ce/2HTPP/Ag(111),^{8,9} and Fe/2*H-meso*-tetramesitylporphyrin (2HTMP)/Cu(001).²⁹ In addition, the metalation reaction is not restricted to a porphyrin monolayer but also proved to be efficient for the metalation of ~20 layers of 2HTPP on Ag(111) with Fe.³¹ These examples underline that the metalation reaction on surfaces is rather the rule than an exception and thus appears to be of general nature.

■ METALATION OF PORPHYRINS WITH PREADSORBED METAL ATOMS

A next logical step was to explore the metalation by changing the sequence of the deposited materials, that is, to first deposit the metal and then the porphyrins. The feasibility of this approach was first shown by Kretschmann et al. who demonstrated by XPS that predeposited Zn on Ag(111) can be “picked up” and metalate post-deposited 2HTPP after moderate heating to 550 K.³⁸ In Figure 4 STM data of an experiment with predeposited iron is depicted as illustrative example. Figure 4a shows the Ag(111) surface after deposition of 0.025 ML iron, which forms small clusters directly at the step edges (Volmer–Weber growth mode).^{31,32} Figure 4b depicts the situation after subsequent deposition of 0.037 ML of 2HTPP.

The high resolution ST micrograph in Figure 4e along with corresponding XP spectra (not shown here) prove the coexistence of 2HTPP with the iron clusters, and thus no metalation occurred. Just after heating to 550 K, a stoichiometric amount of the porphyrins appear as protrusions in Figure 4c, or with the typical so-called “saddle shape” conformation in the high resolution ST micrograph in Figure 4f, while the iron clusters are dissolved. Complementary evidence for the metalation was provided by XPS (not shown here).³¹ From these findings, it can be concluded that heating to 550 K is needed to dissolve the iron clusters and make the individual iron atoms available for metalation via diffusion to a 2HTPP molecule (Figure 4d). In this picture, the metalation reaction is kinetically hindered, and thus heating is needed to overcome this kinetic hindrance.

■ THE “SELF-METALATION” OF PORPHYRINS WITH SUBSTRATE ATOMS

The possibility to metalate porphyrin derivatives with preadsorbed metal atoms triggers the question whether the corresponding reaction could also be realized with atoms directly from a metal substrate. The feasibility of this approach was first demonstrated in 2011 with various free base porphyrins on different copper surfaces by González-Moreno et al.²² and later in the same year by Doyle et al.²⁶ Shortly after that, the term “self-metalation” was introduced for these type of reactions with substrate atoms by Diller et al.¹⁹ Up to now, the vast majority of successful self-metalation reactions with porphyrins were reported on Cu substrates,^{2,12–14,16,18–26,40} but also on Fe³⁰ and Ni,^{30,35} the corresponding reaction was observed. Obviously self-metalation occurs on substrates that are considered as reactive, while there are no indications that the reaction proceeds on rather inert substrates like Ag and Au. The self-metalation of 2HTPP on Cu(111) as the most intensively investigated system is chosen as a first illustrative example.^{12–16,19,20} In Figure 5a, the bottom XPS N 1s signal of 2HTPP on Cu(111) held at RT exhibits two dominant peaks (see Figure 2), one stemming from the aminic (–NH–, 400.0 eV) and the other from iminic nitrogen (–N=, 398.4 eV).

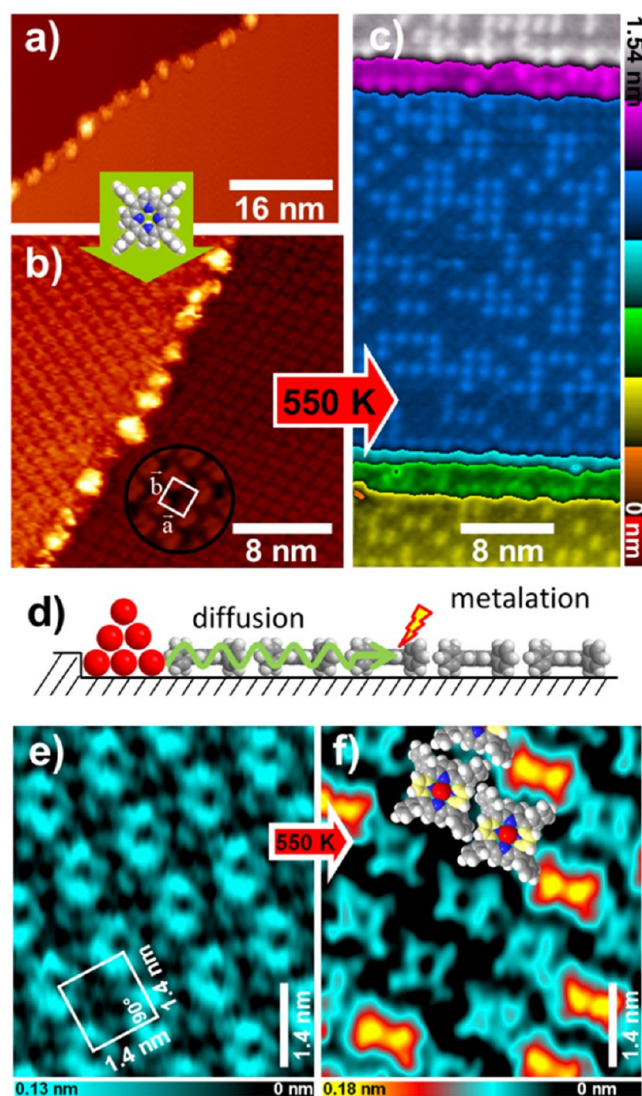


Figure 4. STM images of the Ag(111) surface (a) after deposition of 0.025 ML of Fe deposited at RT and (b) after subsequent deposition of 0.037 ML of 2HTPP. (c) Situation after heating to 550 K. (d) Simplified scheme of metalation process involving diffusion of iron to 2HTPP. (e) Self-assembled 2HTPP layer on Ag(111). (f) High resolution micrograph of situation in panel c. As indicated by the superimposed structure models, two opposing pyrrol rings per FeTPP molecule (marked yellow) are clearly visible and indicate the metalated FeTPP. Adapted with permission from ref 31. Copyright 2008 American Chemical Society.

After heating to 400 K for 2 min, the shape of the corresponding signal in Figure 5a changes such that the signal of the aminic N decreases, indicating that a fraction of the 2HTPPs are metalated. This trend is even more pronounced for elongated periods of heating at 400 K (here 2 h) or after 2 min heating to 450 K. In both cases, the aminic signal basically vanished, indicative of complete metalation of the porphyrin layer. Interestingly the adsorption behavior of 2HTPP on Cu(111) is very different from the one on Ag(111). As illustrated in Figure 5b, a strong attractive interaction mainly between the iminic nitrogen atoms in the 2HTPP and the Cu substrate literally pulls the molecule toward the surface resulting in a “flat” intramolecular conformation.

This could be derived from near edge X-ray adsorption fine structure (NEXAFS) measurements by Diller et al.¹⁹ and is also

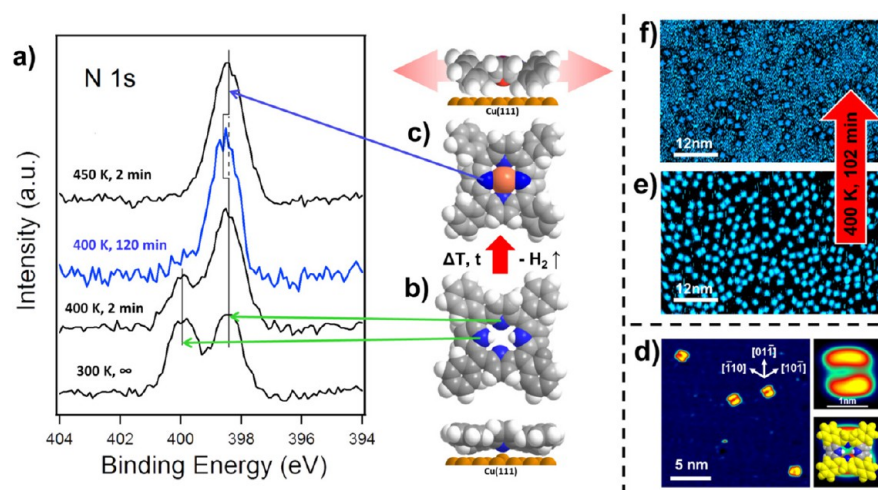


Figure 5. (a) N 1s XPS spectra recorded at RT after deposition of 0.014 ML of 2HTPP onto Cu(111) at 300 K and after annealing to the indicated temperatures for the denoted times. (b) Strong attractive molecule–substrate interaction causes a flat conformation of 2HTPP, which is rather immobile at RT. (c) CuTPP exhibits reduced interaction and is very mobile at RT. (d–f) STM images of (d) 2HTPP as prepared on Cu(111), (e) 2HTPP as prepared on Cu(111) (coverage = 0.135 molecules/nm²), and (f) after annealing to 400 K for 102 min. Adapted with permission from refs 12, 16, and 41 Copyrights 2012 Wiley, 2012 American Chemical Society, and 2011 American Chemical Society.

manifested in the smaller energy separation (1.6 vs 1.9 eV) of the 2HTPP N 1s peaks on Cu(111) compared with Ag(111). For CuTPP, this attractive interaction is significantly reduced since in CuTPP all four nitrogens are equally coordinated to the metal center. As a result 2HTPP adsorbs as isolated molecules oriented along one of the three main crystallographic directions of the Cu(111) and “slowly” diffuses along the latter at RT (Figure 5d), while the mobility of CuTPP is too high to image isolated molecules with STM at RT. This peculiar adsorption behavior can be used to quantitatively follow the reaction process by simply counting the remaining stationary 2HTPP molecules in Figure 5e,f.¹² It becomes apparent that after heating to 400 K for 120 min (Figure 5f) only a minor fraction of the stationary molecules remains (Figure 5e); instead noisy features are visible due to fast diffusing CuTPPs. The drastically reduced interaction of the metalated species can be also observed for the self-metalation of 2HTTBPP (Figure 1d) on Cu(111) in which considerable changes of the supramolecular order and intramolecular conformation occur during and after metalation, such that the molecules literally “pop-up” from the surface.²⁵

The majority of self-metalation reactions reported so far require heating above RT.^{12–16,18–21,23,25,26,40} However, for protoporphyrin IX (2HPPIX) on Cu(100) and Cu(110),^{22,24} 2HTPP on Fe(110), Ni(111),³⁰ and oxygen reconstructed Cu(001),²³ and 2HOEP on Ni islands on Cu(111),³⁵ the self-metalation proceeds already below RT. In addition, it was reported that X-ray exposure is suitable to trigger the self-metalation of 2HTPP on Cu(111) at low temperature.²⁰

Another important aspect of the self-metalation protocol is the possibility to use structured composite surfaces as templates for the localized metalation and thus functionalization of porphyrins. The principle could be proved on a Cu(111) surface with Ni islands as shown in the STM image and the corresponding sketch in Figure 6a. The general idea to achieve local functionalization by the adsorption of suitable molecules on a template surface is illustrated in Figure 6b. After evaporation of 2HOEP onto the composite surface at RT, the STM images in Figure 6c document immobilized molecules on the Ni islands, which exhibit a pronounced protrusion in the

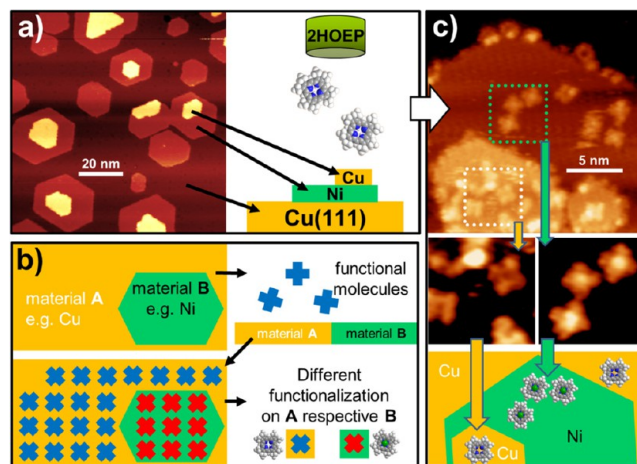


Figure 6. (a) Cu(111) surface with Ni islands as the realization of a templated substrate. (b) Scheme of the general concept. (c) STM image of adsorbed OEP molecules on the Ni/Cu(111) model template at RT; porphyrins on the Ni island exhibit a central protrusion indicating the metalation to NiOEP; porphyrins on the 2nd story copper layer exhibit a central cavity, which is indicative of 2HOEP. Adapted with permission from ref 35. Copyright 2013 IOP.

center of the molecule, indicative of the self-metalation to NiTPP. The reaction proceeds selectively on the Ni islands but not on the pristine Cu(111) surface or the Cu islands on top of the Ni islands, which form during the preparation of the latter.

INSIGHTS INTO THE ENERGETICS AND PROCESS OF THE SURFACE-CONFINED METALATION REACTION

As discussed above, the metalation reaction with coadsorbed metals is surface-mediated in the sense that the transport of the metal to the macrocycle is realized through diffusion. Therefore, sufficient diffusivity of the metal is needed and might require thermal activation as in the case of 2HTPP/Ag(111) with preadsorbed Fe (see Figure 4). However, from the trend that the metalation with Co, Fe, and Ni proceeds at RT while that with Cu and Zn needs additional heating, one

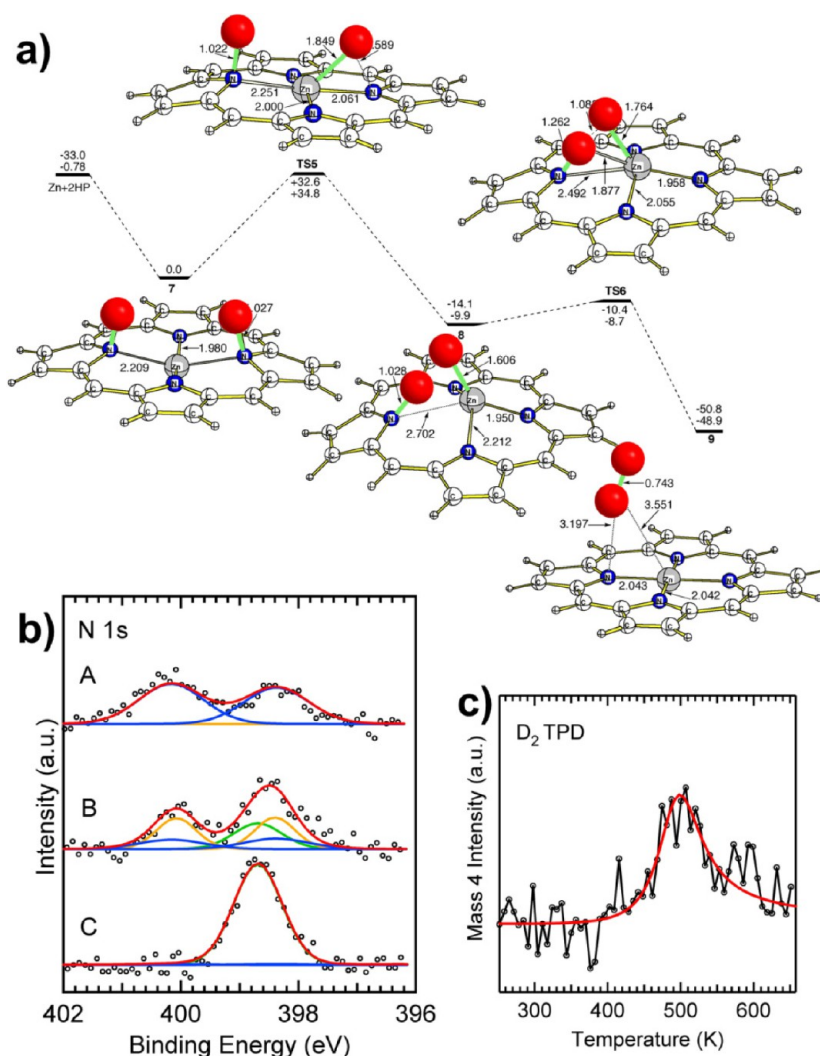


Figure 7. (a) Schematic energy profile for Zn atom insertion into 2HP in kcal mol⁻¹ at B3LYP/6-31G(d) (first entry) and B3LYP/6-31G(d,p)+LANL2DZ (second entry). Bond lengths are in Å. (b) N 1s XP spectra of (A) a monolayer of 2HTPP on Ag(111) after vapor deposition of Zn on the 2HTPP monolayer at 115 K ($\theta_{\text{Zn}} = 0.037$ ML), (B) after subsequent warming of the Zn/2HTPP coadsorbate to 300 K, and (C) after heating to 550 K. (c) Temperature-programmed reaction curve (detected mass $m/z = 4$) of the reaction between 2DTPP and Zn on a Ag(111) surface. The heating rate was 5.0 K/s. Adapted with permission from ref 11. Copyright 2007 American Chemical Society.

might conclude that the corresponding activation energies are higher in the latter cases.

Indeed gas phase DFT calculations for the “bare” free base macrocycle reveal the lowest activation energy for the metalation with Fe followed by Co and Ni, all with an activation energy below ~ 25 meV, while the reactions with Cu and Zn exhibit substantially higher barriers.¹¹ Generally, the metalation of a free base porphyrin at the solid–vacuum interface is a redox reaction in which the metal center is coordinated and oxidized and finally substitutes the two hydrogens, which are released as H₂. The corresponding substeps, including conformational intermediates and hydrogen transfers, were identified in the calculations, as depicted for Zn in Figure 7a. As rate limiting step, the transfer of the first hydrogen from the aminic nitrogen to the already coordinated metal center could be identified, and the corresponding activation barrier ΔE^\ddagger was 1.41 or 1.51 eV depending on the applied functional.¹¹ These values can be compared with the experimental metalation with Zn investigated by TPD experiments with deuterium substituted 2DTPP on Ag(111). The corresponding QMS signal of D₂ is depicted in Figure 7c and

was used to determine ΔE^\ddagger as 1.34 eV, that is, in good agreement with the calculated values. Overall these findings indicate the existence of an intermediate state similar to the “sitting-atop” complex (SAT, metal ion already coordinated while hydrogens atoms are still in place) proposed for the metalation reaction in solution. Indeed for a few porphyrin–metal systems, the experimental proof of an intermediate state was reported.^{25,26}

Further detailed insights into the metalation reaction could be achieved for the self-metalation of 2HTPP on Cu(111). Here ΔE^\ddagger could be determined by simply counting the remaining immobile 2HTPP molecules as a function of time and temperature (see Figure 5e,f). The corresponding self-metalation for a 2HTPP starting coverage of 0.135 molecules/nm² could be identified as a pseudo-first-order reaction, and the corresponding Arrhenius analysis yielded $\Delta E^\ddagger = 1.48$ eV with the prefactor $A = 10^{15}$ s⁻¹,¹² that is, in between the theoretical predicted gas phase values of 1.03 and 1.60 eV depending on the functional and basis sets.¹¹ However, a strong coverage dependency of the latter metalation reaction, as evidenced by STM, XPS,¹³ and TPD,¹⁴ immediately clarifies that the

theoretical approach with the “bare” 2HTP in the gas phase is not sufficient to describe the system. In particular, an abrupt enhancement of the self-metalation is associated with the onset of the so-called checkerboard structure, that is, a transition from isolated 2HTPP molecules to a supramolecular ordered phase, starting at coverages of ~ 0.36 molecules/nm². In the ordered structure, every second 2HTPP molecule is slightly elevated from the Cu(111) surface and exhibits a “relaxed” intramolecular conformation similar to the one of CuTPP illustrated in Figure 5c. Starting with a low 2HTPP coverage (0.14 molecules/nm²) in Figure 8a, the situation after heating to 400 K for 10 min in Figure 8b remains practically unchanged, that is, only very few 2HTPPs are metalated. In Figure 8c, the checkerboard phase is visible in STM at a coverage of 0.49 molecules/nm². After heating to 400 K for 10 min, the majority of the molecules is organized in square ordered supramolecular domains of CuTPP, that is, less than 15% did not metalate.

Coverage dependent XPS measurements are in line with the STM findings, and the combined data is depicted in Figure 8f, along with STM images of different starting coverages in Figure 8e. It is evident that the yield of the metalation reaction (decrease of 2HTPPs) after heating to 400 K for 10 min increases drastically with the onset of the checkerboard phase (orange region). Corresponding XPS data evidence a constant high yield of the reaction for high coverages in the blue region in Figure 8f and extends the investigation to the multilayer regime. In particular the high yield for coverages larger than two monolayers indicates that the reaction proceeds via molecule exchange from the higher layers with the ones in contact with the surface or less intuitively by a very effective transport of substrate metal atoms into higher layers. However, recent results by Chen et al. demonstrate that molecular exchange in the self-metalation of multilayers of the similar phthalocyanine (2HPc) on Cu(111) indeed occurs.⁴² Therefore, it is proposed that this molecule exchange process actually at least dominates the corresponding metalation reaction. A similar mechanism might account for the high yield metalation of 2HTPP with postdeposited Fe on Ag(111) discussed above. Complementary H₂-TPD signals depicted in Figure 9a also evidence the abrupt increase of the metalation yield at higher coverages. Therein the first desorption peaks coincide with the release of H₂ after the completed metalation (red arrows). The shift of this signal to lower temperatures with increasing coverage is in line with the findings depicted in Figure 8f. The Redhead analysis (with prefactor $A = 10^{15} \text{ s}^{-1}$ from ref 12) yielded an activation energy of 1.36 eV¹⁴ for the metalation of the fully developed checkerboard structure (red signal), that is, indeed lower than the 1.46 eV estimated by STM for lower coverage.¹² Overall the self-metalation rate enhancement is mainly attributed to a smaller activation barrier for the elevated molecules, which have an internal conformation similar to that of CuTPP, whereas the less reactive molecules in direct contact with the surface are strongly distorted.¹³ At higher temperatures, additional peaks arise in TPD due to successive dehydrogenation reactions, as illustrated in Figure 9a, which partially overlap with the metalation peak at lower coverages.

Therefore, corresponding TPD experiments were conducted with 2DTPP. However, these experiments revealed that D and H exchange processes occur at the nitrogen atoms and the periphery of the porphyrin molecule. This is for example manifested in the positions of the D₂, DH, and H₂ signals in Figure 9b in which the D₂ signal occurs at the lowest temperature. It is proposed that the exchange proceeds through

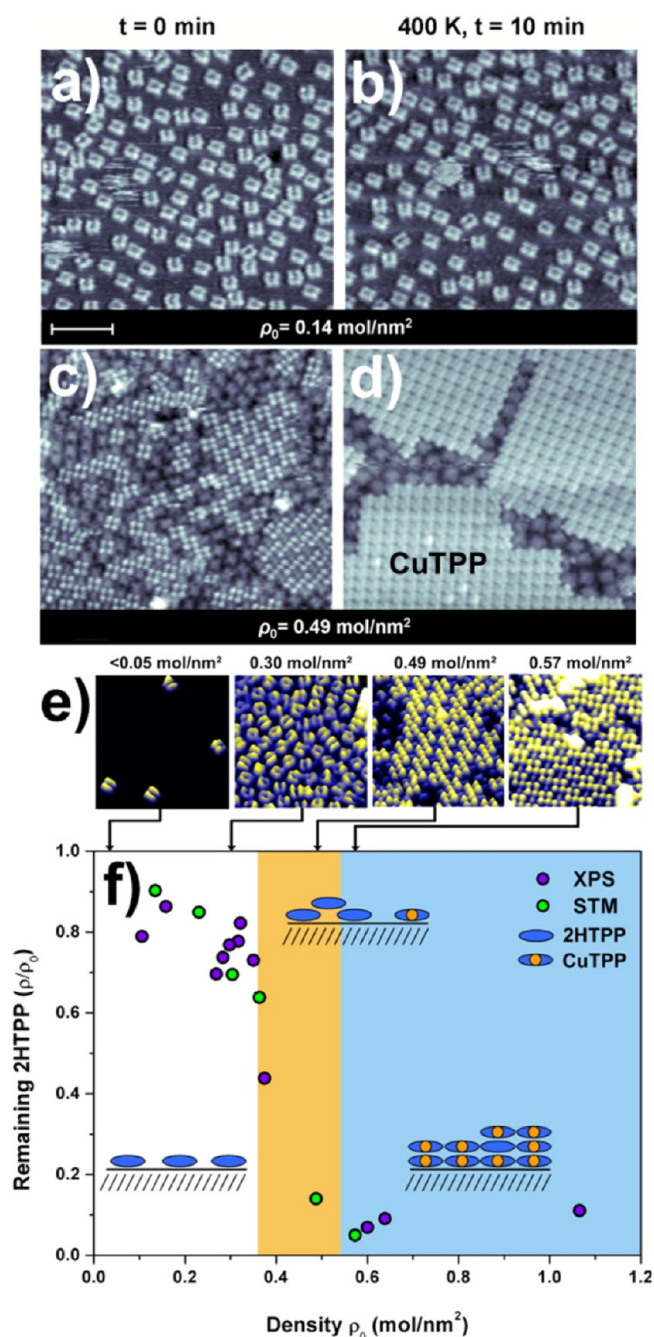


Figure 8. (a–d) STM of two different 2HTPP coverages as prepared at RT (a, c) and after heating to 400 K for 10 min (b, d). (e) STM of indicated 2HTPP coverages on Cu(111) illustrating the onset of the checkerboard structure. (f) Coverage-dependent metalation of 2HTPP on Cu(111) for 10 min at 400 K measured by XPS (purple dots) and STM (green dots). Adapted with permission from ref 13. Copyright 2013 American Chemical Society.

intermediate adsorption of D and H, respectively, on the Cu surface as sketched in Figure 9c. As a consequence one anticipates that the surface plays a vital role in the reaction beyond diffusive processes and questions the proposal of the SAT complex as intermediate state.

DISCUSSION AND OUTLOOK

The metalation of free base porphyrins at the solid–vacuum interface has been established as a useful and convenient tool to

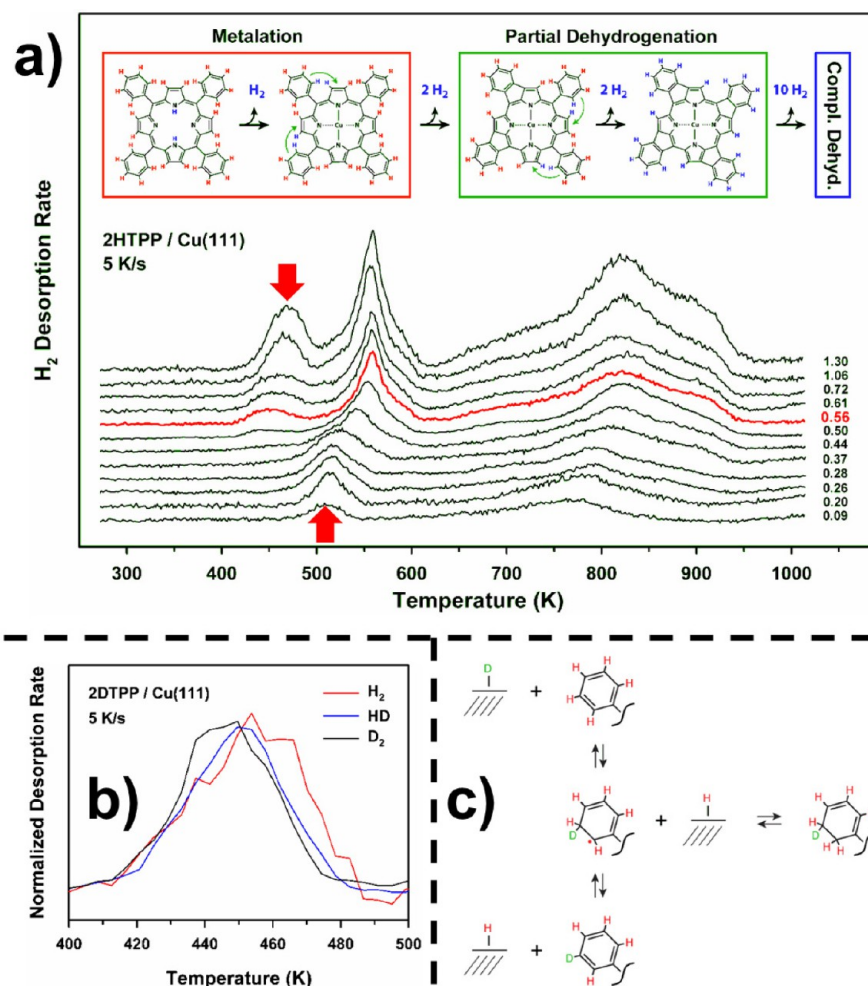


Figure 9. (a) Scheme of dehydrogenation processes and hydrogen desorption signals from the self-metalation reaction of 2HTPP on Cu(111) as a function of coverage and temperature. (b) Normalized TPD spectra of H_2 , HD, and D_2 released during self-metalation of 0.54 2DTPP molecules/ nm^2 on Cu(111) (heating rate 5 K/s). (c) H and D detachment and attachment processes, which are expected to also occur at the pyrrole rings. Adapted with permission from ref 15. Copyright 2014 American Chemical Society.

modify the properties of these surface-confined functional molecules. On correspondingly patterned surfaces, even the locally confined metalation and functionalization of porphyrins could be achieved by self-metalation.³⁵ Overall, the metalated state is energetically favored^{11,30} and might need moderate heating to overcome the activation barriers for surface diffusion of the metal atoms³¹ or the reaction itself.^{9,11,19,25,38} The metalation is accompanied by changes in the electronic interaction with the substrate^{5,33,40} and can trigger significant changes of the intramolecular conformation,^{8,9,19,25} as well as the supramolecular arrangement.^{13,14,25} In the case of self-metalation of 2HTPP on Cu(111), these changes can be used to trace the progress of the reaction with STM and thus to evaluate the activation energy of the surface-mediated reaction.⁴³ In addition, it was found that this particular self-metalation exhibits a boost in yield with increasing coverage, accompanied by a particular supramolecular phase in which every second molecule exhibits a different intramolecular conformation compared with the low coverage situation. It is proposed that the specific intramolecular conformation indeed effectively lowers the activation energy for the metalation. While DFT gas phase calculations for the metalation of 2HP are suitable to explain the observations in specific systems, this approach must fail for the discussed coverage/conformational

dependence. Therefore, future theoretical efforts should consider intramolecular conformations, molecule–molecule interactions, and probably more importantly molecule–substrate interactions. A first step to account for molecule–substrate interactions was reported by Goldoni et al., who performed DFT calculations to estimate the energies for 2HTPP and NiTPP adsorbed on Ni(111), that is, the porphyrin before and after self-metalation.³⁰ These calculations result in an overall energy gain of 0.89 eV.³⁰ However, corresponding gas phase calculations with the bare porphyrin macrocycle yielded values ranging from 5.0 to 8.6 eV.¹¹ This generally indicates the need for sophisticated theoretical approaches fully including the surface, which is especially evident since recent TPD based metalation experiments with deuterated free base porphyrin (2DTPP) delivered new insights into the metalation reaction, that is, evidence that deuterium or hydrogen can be transferred from the nitrogen in the porphyrin macrocycle to the substrate surface (and back).¹⁵ This result underlines the importance of the substrate beyond surface diffusion and corroborates that the metalation of porphyrins at the solid–vacuum interface is a surface-mediated process.

Future experimental efforts concerning the establishment of novel metalation protocols might target the further exploration of the local self-metalation on templated surfaces or the

expansion of the recently reported metalation of 2HTPP on Ag(111) with Ru from the gaseous precursor $\text{Ru}_3(\text{CO})_{12}$ as reported by Papageorgiou et al.³⁷ to other compounds like Fe or Co carbonyls.

In summary, various effective protocols were successfully explored to use *in situ* metalation reactions to tailor-make molecular architectures. Surface science methods are well suited to scrutinize the reaction itself and allowed for novel detailed insights into surface-mediated reactions of a prototype functional molecule.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.accounts.5b00243.

Overview of surface confined porphyrin metalation reactions explored until now (PDF)

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