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Temperature-Dependent Chemical and Structural Transformations from 2H-tetraphenylporphyrin to Copper(II)-Tetraphenylporphyrin on Cu(111)

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Ⓢ Supporting Information

ABSTRACT: Temperature-dependent chemical and structural changes of a submono-layer of 2H-tetraphenylporphyrin (2HTPP) on Cu(111) were studied with photoelectron spectroscopy (XPS/UPS) and scanning tunneling microscopy (STM). 2HTPP reacts with Cu atoms from the substrate to form copper(II)-tetraphenylporphyrin (CuTPP). This metalation reaction starts at about 400 K and was investigated at various temperatures up to 500 K. At room temperature, adsorbed 2HTPP adopts an orientation with the molecular plane parallel to the substrate; the same holds for its reaction product CuTPP after annealing to 400 K. In contrast, annealing at 450 K yields a tilted orientation of CuTPP, as indicated by STM and supported by C 1s XPS shifts and changes in the Cu(111) surface state. Subsequent annealing at 500 K restores a flat-lying orientation; however, the appearance of the complex in STM images differs from the original appearance of CuTPP. In summary, 2HTPP undergoes three irreversible transformations upon annealing on Cu(111), a metalation reaction to CuTPP followed by two intramolecular structural changes.
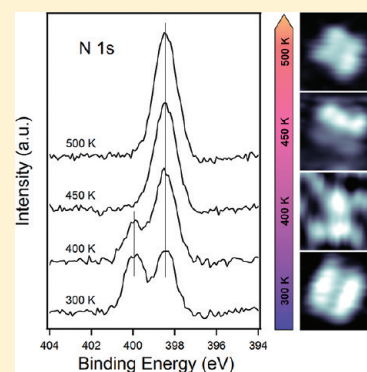
1. INTRODUCTION

The investigation of large organic molecules on surfaces has become an actively explored field with the prospect of engineering functional molecular architectures. Porphyrins appear to be particularly suitable as molecular building blocks, because they combine a rigid planar framework as a structure-forming element with the ligand functionality of the molecular center, which can coordinate metal atoms and ions. This intrinsic functionality has been employed for the direct metalation of adsorbed metal-free porphyrin and phthalocyanine molecules with coadsorbed metal atoms on solid surfaces. Examples include the reactions of 2H-tetraphenylporphyrin (2HTPP) and 2H-phthalocyanine (2HPc) with Fe, Co, Ni, Cu, Zn, and Ce.[1−13] The mechanism of the metalation reaction has been the subject of intensive research.[5,14] Furthermore, it was found that the order of deposition is not important; that is, adsorbed 2HTPP or 2HPc react with metal atoms irrespective of which reactant is deposited first.[7,14,15] Based on this observation, it has been proposed that adsorbed metal atoms and molecules diffuse toward each other before the molecular centers coordinate and subsequently react with metal atoms.[8] Because of activation barriers, the actual metalation reaction, during which the metal is oxidized to its dication, requires elevated temperatures for some metals.[5,7,11,14] The fact that porphyrins and phthalocyanines react, for example, with Fe, Cu, or Zn atoms predeposited on Ag(111) or Au(111) implies that

these molecules "pick up" metal atoms from these surfaces,[7,14,15] as no metalation with the corresponding substrate atoms (Ag, Au) occurs. Initially, it was unclear whether reaction with Au and Ag does not occur because Au(II) or Ag(II) are energetically not favorable or whether the molecules are generally unable to pick up metal atoms that are embedded in the substrate surface. However, recent investigations on Cu surfaces show a reaction with substrate Cu atoms: The metalation of protoporphyrin IX on Cu(110) and Cu(100) proceeds already at room temperature,[16] whereas for 2H-porphyrin and 2H-diphenylporphyrin on Cu(110) the reaction starts between 360 and 410 K.[11] Very recently, the "self-metalation" of 2HTPP on Cu(111) at 420 K was reported in a detailed X-ray spectroscopy study,[17] in which it was also shown that the molecules undergo adsorption-induced deformation and are oriented with the porphyrin plane parallel to the surface after annealing to 420 and 490 K. These studies demonstrate that substrate atoms can indeed be incorporated into the porphyrin macrocycle, probably through an intermediate state as isolated adatoms on the substrate. Consequently, the absence of this reaction on Ag and Au surfaces is due to the noble character of these metals. On Cu(110), dehydrogenation of the

two porphyrins at higher temperatures due to C—H bond scission has been reported.[11] In particular, the dehydrogenation of diphenylporphyrin starting at 420 K is relevant for this work.

The investigation of metal-free porphyrin derivatives on Cu surfaces has also gained considerable attention because of the interaction of the iminic nitrogen atoms with the Cu substrate. This interaction is so strong that it dominates the adsorption behavior of 2HTPP on Cu(111), for example, where it prevents the formation of supramolecular long-range ordered structures.[18–21] The adsorbate–substrate complex between 2HTPP and Cu(111) was proposed to be a precursor state for metalation,[20–23] similarly to the initial complex between a neutral Zn atom and a 2HTPP molecule found in earlier work[5] and in analogy with the "sitting-atop complex" observed during metalation of porphyrins in solution.[24–26]

In this work, we investigate temperature-dependent chemical reactions, in particular metalation with substrate atoms, and structural changes of 2HTPP on Cu(111). Notably, we found that the molecule exhibits a tilted orientation after annealing at 450 K, whereas annealing at higher temperatures leads to an orientation in which the molecular plane is parallel to the surface.

2. EXPERIMENTAL SECTION

The experiments were performed in two separate ultra-high-vacuum (UHV) systems with base pressures below 2×10^{-10} mbar. For X-ray and UV photoelectron spectroscopies (XPS and UPS, respectively), a Scienta ESCA-200 spectrometer equipped with an Al Kα X-ray source (1486.6 eV), an X-ray monochromator, and a hemispherical energy analyzer (SES-200) was employed. The UV photoelectron (UP) spectra were acquired with He—I radiation (21.2 eV), and photoelectrons were collected along the normal to the sample surface. The overall energy resolution for UPS was <0.1 eV. For XPS, the photoelectrons were detected at an angle of 70° relative to the surface normal for increased surface sensitivity. All binding energies were referenced to the Fermi edge of the clean Cu(111) surface ($E_b \equiv 0$). The STM experiments were carried out using an RHK UHV VT STM 300 instrument with RHK SPM 100 electronics and cut Pt/Ir tips as probes. All voltages refer to the sample, and the images were recorded in constant-current mode. Moderate low-pass filtering was applied for noise reduction. The STM data were processed with the software WSxM (http://www.nanotec.es); a description of the program can be found in ref 27.

The substrate was a copper single crystal (purity >99.999%) with a polished (111) surface, which was aligned to <0.1° with respect to the nominal orientation. The substrate was Ar$^+$ sputtered and subsequently annealed for several cycles. The cleanliness and long-range order of the surface were checked with XPS and LEED, respectively. 2HTPP with a specified purity of >98% was degassed in vacuo by heating to 450 K for 4 h.

For XPS/UPS and STM, 2HTPP submonolayers with a coverage of approximately 0.014 ML were prepared by vapor deposition onto the Cu(111) substrate held at 300 K. Note that the quantitative measure of the molecular coverage is given by the unit 1 ML, which is defined as one molecule per surface atom of the substrate. During deposition, the temperature of the Knudsen cell was 640 K, which led to a flux of approximately 0.0023 ML/min. The coverage was experimentally determined by analyzing the attenuation of the substrate signals by low-energy ion scattering (LEIS) spectroscopy and

XPS in the ESCA (electron spectroscopy for chemical analysis) chamber. LEIS spectroscopy is highly surface sensitive and can accurately determine the coverage of adsorbed porphyrins, and its data were supported by Cu 2p XPS data. In STM, the coverage can be directly determined from the microscopic data. In addition, in both chambers, a quartz microbalance was used to estimate the evaporated amount of porphyrin material. Overall, the error of the reported coverages is in the range of ±10%. Annealing of the sample was always done for 2 min at the indicated temperatures, namely, 400, 450, and 500 K. All photoemission spectra and some of the STM images were obtained at room temperature, whereas other STM images were acquired at 200 K as indicated.

3. RESULTS AND DISCUSSION

First, we address the metalation reaction. As shown in previous work, a straightforward way to monitor the progress of the metalation of 2HTPP by XPS is to follow the changes in the N 1s signal: As the reaction proceeds, the two separate peaks of 2HTPP[28] gradually evolve into a single peak for the metalated porphyrin, because, in the final metalloporphyrin complex, the four nitrogen atoms are chemically equivalent.[2,5,8,15,16] As shown in Figure 1, the N 1s XP spectrum of a 2HTPP
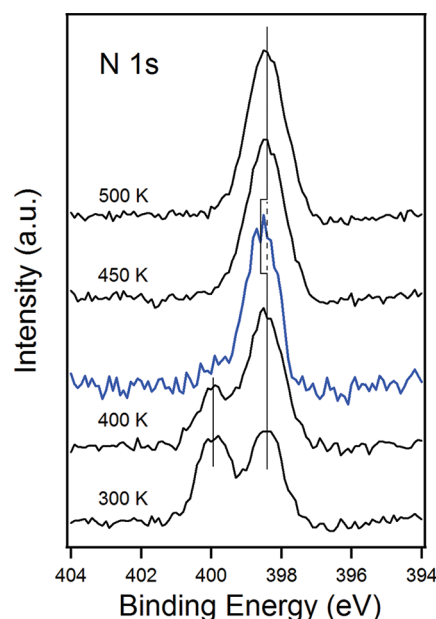

Figure 1. N 1s XP spectra recorded after deposition of 0.014 ML of 2HTPP onto Cu(111) at 300 K and after annealing for 2 min to the indicated temperatures (blue curve: 400 K, 2 h). All spectra were recorded at 300 K.

submonolayer on Cu(111) consists of two well-resolved peaks, which are assigned to aminic nitrogen (—NH—, 400.0 eV) and iminic nitrogen (—N=, 398.4 eV), in agreement with previous XPS literature.[28–30] The signal of aminic N decreased when the sample was heated to 400 K, indicating that a fraction of the 2HTPP molecules had undergone the metalation reaction to CuTPP. Keeping the sample at this temperature for 2 h led to almost complete metalation (blue curve in Figure 1). After the sample had been annealed to 450 and 500 K for 2 min, the aminic signal vanished completely. From 450 to 500 K, the N signal no longer changed, indicating that the metalation process was complete at 450 K. The N 1s
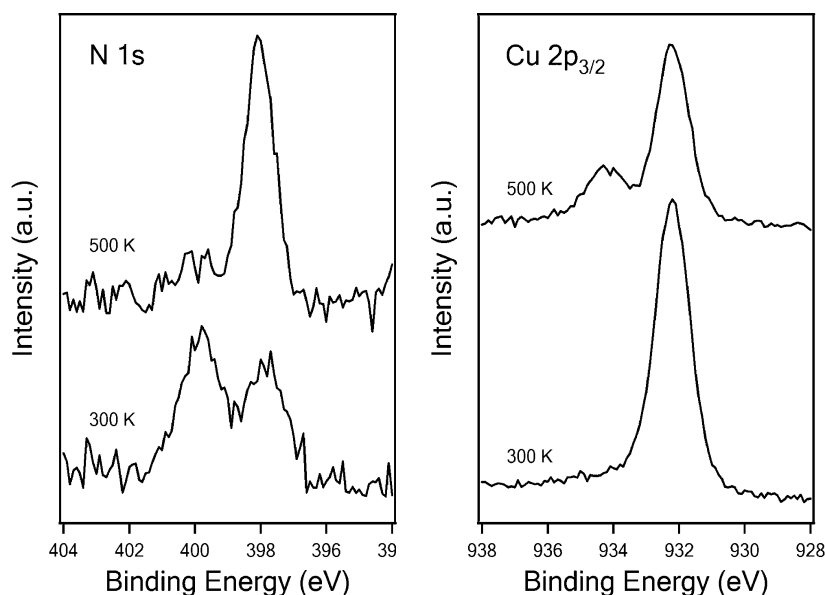
Figure 2. N 1s and Cu $2p_{3/2}$ XP spectra of 2HTPP (0.018 ML, 50% of a monolayer) coadsorbed with 0.1 ML of Cu atoms on Au(111) at 300 K and after annealing to 500 K for 2 min. Two N 1s peaks (aminic N at 398.4 eV and iminic N at 400.0 eV) at 300 K evolve into one peak whose position is close to that of iminic N in 2HTPP. Correspondingly, a Cu(II)-related Cu $2p_{3/2}$ peak appears at 934.3 eV upon annealing to 500 K. The decrease of the peak related to Cu(0) (932.2 eV) between 300 and 500 K is attributed to the diffusion of Cu atoms into the Au substrate.

binding energy of CuTPP apparently coincides with that of the iminic N of 2HTPP. These findings are in agreement with a very recent report by Diller et al. on the metalation of 2HTPP on Cu(111).[17] The small differences in the peak positions (~0.2 eV) are most likely due to different binding energy references, in combination with differences in the approaches used to determine the exact binding energy.

Because the metal is oxidized to its dication in the course of the metalation reaction, the observation of Cu(II)-related XPS signals would provide complementary evidence for the formation of CuTPP. However, the small Cu(II)-related signals from CuTPP (<1% of the total Cu 2p signal) is concealed here by the tail of the much larger Cu(0)-related substrate signals. To acquire the corresponding information, Au(111) was used as the substrate, and the metalation of 2HTPP was conducted with codeposited Cu; the resulting N 1s and Cu $2p_{3/2}$ XP spectra are shown in Figure 2. In agreement with the interpretation of the N 1s XPS data above, complete metalation of 2HTPP with Cu was found to occur at 500 K, as indicated by a single N 1s peak and a well-resolved Cu(II)-related Cu $2p_{3/2}$ peak at 934.3 eV. The Cu(0)-related peak at 932.2 eV decreased upon sample heating because of the diffusion of Cu atoms into the Au substrate bulk. Despite the fact that it was not possible to observe a Cu $2p_{3/2}$ peak of oxidized Cu for 2HTPP on Cu(111), the results in Figure 2, in combination with the N 1s data in Figure 1, provide compelling evidence that 2HTPP can pick up Cu atoms from the Cu(111) substrate and oxidize them at elevated temperatures.

STM measurements provide complementary evidence for the metalation of 2HTPP. The strong localized adsorbate–substrate interaction through the iminic N atoms leads to slow diffusion at room temperature[20] and thus makes it possible to image individual 2HTPP molecules on Cu(111) (Figure 3a). Another consequence of the site-specific interaction is the absence of supramolecular ordering of the metal-free porphyrins. In contrast, formation of long-range ordered

domains is usually observed for metallotetraphenylporphyrins (MTPPs) on Cu(111).[21]

Figure 3b shows an STM image acquired at room temperature after the sample had been annealed to 400 K for 2 min. At this temperature, we observed isolated 2HTPP molecules along with noisy streaks oriented parallel to the fast scanning direction (horizontal). These streaky features are typical for molecules diffusing much faster than the scan speed of the microscope, that is, for molecules that are not directly visible as individual molecules in the microscope under the imaging conditions and can thus be considered as a two-dimensional gas phase.[31] In line with the corresponding XPS data in Figure 1, these "fast" molecules are assigned to CuTPP. In CuTPP, all nitrogen atoms are coordinated to the Cu metal center, and therefore, the domination of the site-specific molecule–substrate interactions, as found for 2HTPP, is switched off, which leads to a higher mobility of the CuTPP molecules. This behavior was previously observed for a mixture of 2HTPP and CoTPP on Cu(111), where STM showed individual 2HTPP molecules not forming an ordered supramolecular structure, in contrast to ordered CoTPP islands coexisting with a two-dimensional gas phase of CoTPP.[21] To obtain further evidence for the presence of CuTPP, we analyzed the density of the 2HTPP molecules before and after sample annealing to 400 K and found a decrease of about 10% after the heating step, which is equivalent to a metalation degree of about 10%. Prolonged heating at 400 K further increased the metalation degree, indicating that the metalation reaction at this temperature is too slow to metalate all 2HTPP molecules in the given 2 min annealing time.

After sample annealing to 450 and 500 K, no individual molecules could be imaged by STM at room temperature, but the images obtained were noisy and showed streaky features typical for a mobile two-dimensional gas phase (see Figure S1 in the Supporting Information). This indicates that all of the 2HTPP molecules have reacted to form highly mobile CuTPP, again in agreement with the corresponding N 1s XP spectra in
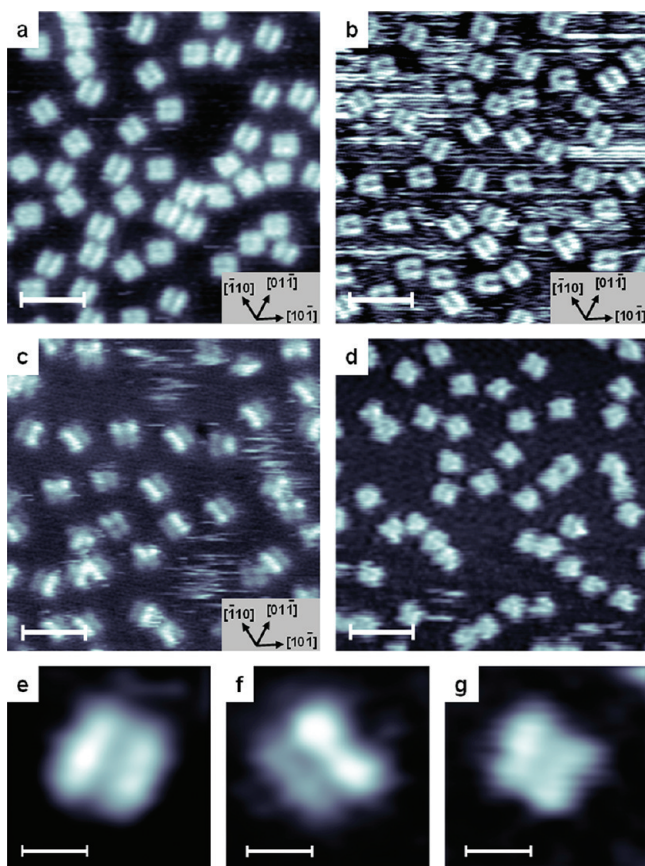
Figure 3. STM images of 0.014 ML of 2HTPP on Cu(111): (a) after deposition and after sample annealing for 2 min to (b) 400, (c) 450, and (d) 500 K. (e−g) STM images of single molecules: (e) after deposition and after sample annealing to (f) 450 and (g) 500 K. Images a, b, and e were recorded at room temperature, and images c, d, f, and g were recorded at 200 K. Tunneling parameters: (a,e) $U = -0.87$ V, $I = 17$ pA; (b) $U = -0.50$ V, $I = 12$ pA; (c,f) $U = -1.43$ V, $I = 21$ pA; (d,g) $U = -0.89$ V, $I = 24$ pA. Scale bars = (a−d) 4 and (e−g) 1 nm.

Figure 1. Cooling the sample to 200 K suppressed the lateral movement sufficiently, rendering the molecules directly visible in the STM image. Parts c and f of Figure 3 show individual molecules at 200 K after sample annealing to 450 K. The observation that most of these molecules appear with brighter and darker sides suggests that they adopted a tilted orientation relative to the substrate surface. After the sample had been annealed to 500 K, the two sides of the molecules clearly appeared with the same brightness in the images obtained at 200 K, indicating that the porphyrin ring was again oriented parallel to the substrate (Figure 3d,g).

Based on the STM data discussed above, one can discriminate four different appearances that can be attributed to different adsorption behaviors:

(i) After adsorption at room temperature, 2HTPP on Cu(111) appears as individual molecules by STM and does not form supramolecular aggregates, that is, the adsorption behavior is dominated by the strong molecule−substrate interaction (mainly through iminic N binding to surface Cu atoms).

(ii) Upon annealing to 400 K for 2 min, a small fraction of the adsorbed 2HTPP is metalated to CuTPP, which has an increased mobility and thus appears as noisy streaks in

STM images. These mobile CuTPP molecules also form islands with a square order at lower temperature or at higher coverage even at room temperature, as depicted in Figure 4a. The appearance of the molecules in the supramolecular array indicates an adsorption geometry with the porphyrin core parallel to the surface.
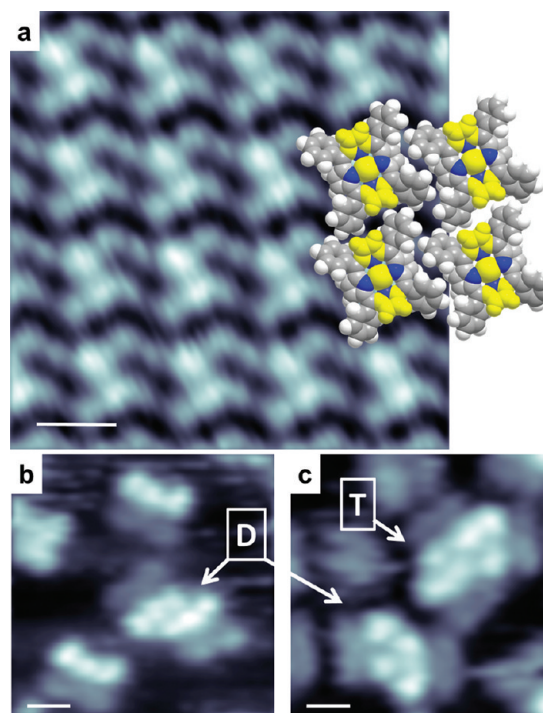

Figure 4. (a) STM image acquired at room temperature of a square array of CuTPP formed after annealing 0.023 ML of 2HTPP to 400 K. The individual molecules exhibit a rather symmetric appearance; that is, they are not tilted. Scaled models of CuTPP are overlaid. (b,c) Constant-current STM images of CuTPP on Cu(111) recorded at 200 K after annealing to 450 K. The topography of the molecules in this case appears with brighter and darker sides, indicating that the porphyrin plane is tilted. Interestingly, these tilted molecules form dimers and trimers indicated by D and T, respectively, in the images. Tunneling parameters: (a) $U = +1.26$ V, $I = 31$ pA; (b) $U = -1.21$ V, $I = 30$ pA; (c) $U = -1.15$ V, $I = 34$ pA. Scale bar =1 nm.

(iii) Upon annealing to 450 K for 2 min, all 2HTPP is metalated to form the corresponding CuTPP, which cannot be imaged at room temperature because of its high mobility. However, it can be imaged at 200 K as individual molecules, which appear with brighter and darker sides, indicating that the porphyrin plane is tilted. Interestingly, the formation of dimers, trimers, and tetramers can be observed, particularly at higher coverages. In these aggregates, the molecules always interact through their brighter sides (Figure 4b,c).

(iv) Upon annealing to 500 K for 2 min, the CuTPP molecules are still too mobile at room temperature to be imaged in our STM instrument, but they are again visible as individual molecules at 200 K. Their apparent height and appearance by STM are now similar to those of 2HTPP; that is, the appearance indicates that the porphyrin plane is again oriented parallel to the substrate surface. Another similarity to the adsorption behavior of 2HTPP is that no two-dimensional aggregates are formed.
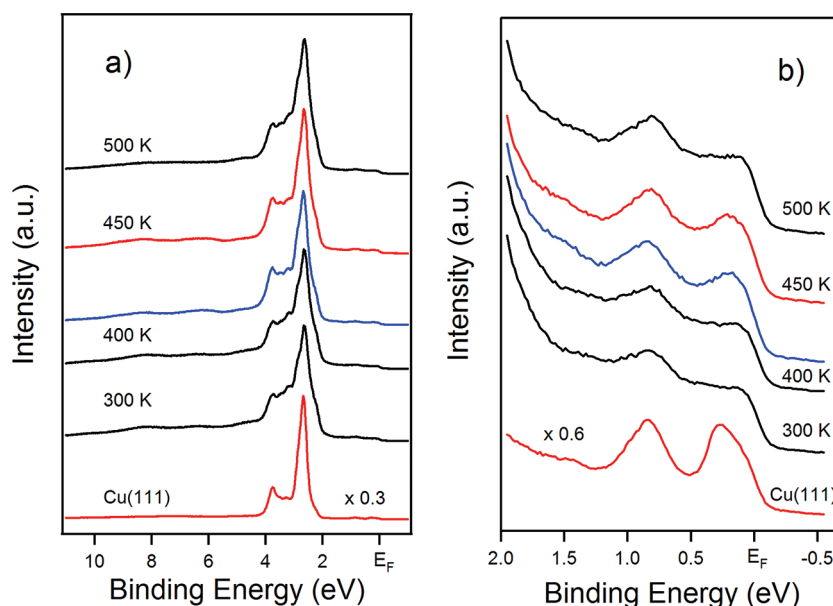
Figure 5. UV photoelectron spectra of clean Cu(111), after deposition of 0.014 ML of 2HTPP and after sample annealing to the indicated temperatures for 2 min (blue curves: annealing for 2 h at 400 K). The spectra were recorded at room temperature in normal emission geometry using He–I radiation. (a) Extended binding energy region and (b) region close to the Fermi energy (E_F). In panel b, the peak centered at 0.3 eV is the Shockley surface state from the clean Cu(111) surface, and the peak at 0.9 eV is the satellite of the Cu 3d band due to parasitic He–I$_\beta$ at 23.1 eV.

Based on the observations described above and results from the literature[11,17,34,35] the data can be interpreted further. Brede et al.[34] reported that, at low temperatures (∼25 K), CuTPP molecules on Cu(111) appear as four identically bright lobes and two longish protrusions close to a central depression under tunneling conditions ($U = -1$ V, $I = 50$ pA) very similar to those used here. This temperature is obviously low enough to image individual CuTPP molecules. The structures observed here after annealing to 450 and 500 K show different appearances than 2HTPP and CuTPP at 400 K, which we attribute to "secondary" reactions after metalation, leading first to a tilted and then again to a flat configuration. Comparing the apparent heights of CuTPP by STM after the three annealing steps, we found that, after heating to 400 K, CuTPP either in the square arrangement (cf. Figure 4a) or as two-dimensional gas exhibits basically the same apparent height as the brighter part of the tilted molecules annealed to 450 K, whereas the darker side of the latter have an apparent height similar to that of the individual molecules after heating to 500 K. This means that, after heating to 450 K, one side of the CuTPP molecule is brought closer to the surface, and after annealing to 500 K, the whole molecule appears with a reduced height, presumably realized by a lowering of the other side of the molecule. A reduced height (i.e., a closer proximity to the surface) can also be associated with an increased molecule–substrate interaction. This is in line with the higher mobility of the undistorted CuTPP at 200 K compared to the porphyrins annealed to 450 and 500 K, which can be imaged as isolated individual molecules. The distance between the porphyrin plane of tetraphenylporphyrins and the substrate is mainly determined by the orientation of the peripheral phenyl substituents, especially by the dihedral angle between the phenyl and the porphyrin plane. An angle of 90° results in the maximal distance, while 0° means that the phenyl rings are oriented parallel to the substrate surface and thus lead to a minimal distance. It is well established that the most frequently observed supramolecular square order of adsorbed tetraphenylporphyrins

[e.g., on Ag(111)] is caused by attractive interactions of the phenyl substituents of neighboring molecules, such that these phenyl groups establish a T-type interaction in which the planes of the two phenyl rings are perpendicular to each other.[34,35] In other words, a prerequisite to establish the T-type interaction is a sufficiently large dihedral angle between the porphyrin core and the phenyl substituents.[21,35] Generally, the angles of the phenyl groups are the result of a delicate balance of the attractive interactions between the porphyrin core and the substrate on one hand and the steric repulsion resulting from the proximity of parts of the phenyl rings to the porphyrin core on the other. As a result, the porphyrin core is forced into a saddle shape conformation, in which two opposing pyrrol groups are pointing toward and two are pointing away from the substrate.[4,17,35−38] For 2HTPP on Cu(111), the attractive interactions between the iminic nitrogens and specific Cu surface sites are so high that the porphyrin macrocycle is pulled very close to the substrate; as a result, the phenyl rings are almost parallel to the surface, and thus, no attractive T-type interactions between 2HTPP molecules can exist.[21] In addition, Rojas et al. suggest that a considerable charge transfer between 2HTPP and the Cu(111) surface causes repulsive electrostatic interactions between the free base porphyrins. This repulsion can also effectively prevent the formation of supramolecular arrangements.[18,19] Upon annealing to 400 K, the formation of CuTPP starts, according to the N 1s XPS and STM results. The enhanced mobility of this complex indicates that metalation reduces the interaction between the porphyrin core and the substrate; as a result, the dihedral angle is increased, and T-type interactions become possible, which is in line with the observation of CuTPP domains with square order. This interpretation is supported by a recent X-ray spectroscopy (XPS/NEXAFS) study of 2HTPP and CuTPP on Cu(111). For 2HTPP, an angle of only 20° between the surface plane and the phenyl ring was measured, in contrast to 40−50° for CuTPP; that is, the 2HTPP exhibits a "flat" conformation with the porphyrin core closer to the substrate surface.[17]

The proposed temperature-induced changes of the molecular geometry, particularly the molecule-surface distance, are in agreement with the valence band spectra shown in Figure 5. The spectrum of the clean Cu(111) surface (Figure 5b, bottom) shows a well-defined Shockley surface state centered at 0.3 eV. Upon adsorption of 0.014 ML of 2HTPP, this peak is largely suppressed (Figure 5b, second spectrum from bottom); this behavior is typical for surface states, which are known to be sensitive to any surface modification, including adsorption.[32] The intensity of the Cu 3d bulk signals around 2−4 and 0.9 eV (satellite due to nonmonochromatized He−I radiation) is also reduced by the 2HTPP adsorbate, but to a lesser degree (Figure 5a); this reduction is mainly caused by adlayer-induced signal damping. The signals related to the Cu(111) substrate are similar for all temperatures, with small changes due to modifications in damping for the different adsorption geometries. The only exception is the surface state: It increases in intensity after annealing to 400 K for 2 min and even more so when annealing is extended to 2 h (blue curves in Figure 5). Because this treatment results in almost complete metalation, according to our STM and XPS measurements (cf. Figures 1 and 3), the reappearance of the surface state can be attributed to the increased distance between molecule and surface and the thereby reduced interaction. Annealing at 450 K, which leads to the formation of tilted molecules, leaves the spectrum in the vicinity of E_F almost unchanged. One might expect that the tilting should reduce the intensity of the surface state, because one side of the molecules engages in an increased interaction. However, other factors such as the reduced "footprint" of the tilted molecules may play a role here and lead to a less pronounced occurrence of the expected behavior. Annealing at 500 K again suppresses the Cu(111) surface state strongly, which is attributed to the increased interaction of the flat molecule with the substrate.

It should be noted that the observed effects are not related to partial thermal desorption of the molecules: The constant N 1s and C 1s intensities (see Figures 1 and 6) indicate that the total coverage does not change significantly during annealing. In addition, the changes of the intensity of the surface state in Figure 5 are in line with the results from coverage-dependent surface-state band-structure mapping for a very similar molecular system in ref 33.

The tilting of the molecules and the other changes of the molecule−surface distance derived from STM are also reflected in the temperature-dependent C 1s XP spectra (Figure 6). Annealing to 400 K for 2 h (blue curve) shifts the C 1s signal to higher binding energies by 0.4 eV; a smaller shift (∼0.1 eV) occurs already after annealing for 2 min at this temperature. This shift is attributed to a reduced final state screening, which occurs when the distance between the surface and the molecule increases as a result of metalation. As expected on the basis of this interpretation, the C 1s peak shifts back toward lower binding energies when the molecule−surface distance decreases as a result of annealing at 450 and 500 K. After annealing at 500 K, the C 1s peak has the same position as that of 2HTPP at 300 K.

Considering the reported dehydrogenation of a porphyrin on Cu(110) starting at 420 K,[11] the tilting of the CuTPP after annealing to 450 K can be interpreted as the result of a partial dehydrogenation reaction of β- and/or ortho-hydrogen atoms at the porphyrin macrocycle and the phenyl groups.[11,13] Because of the reduced steric hindrance, the two neighboring phenyl rings exhibit smaller dihedral angles, that is, orientation
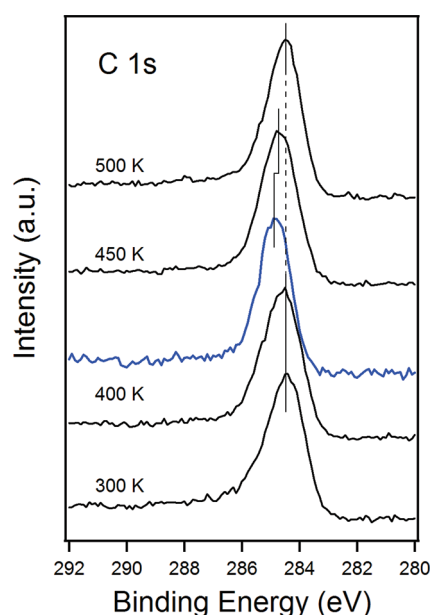

Figure 6. C 1s XP spectra recorded after deposition of 0.014 ML of 2HTPP onto Cu(111) at 300 K and after annealing to the indicated temperatures for 2 min (black curves) and for 2 h (blue curve). All spectra were recorded at 300 K with a photoelectron collection angle of 70° with respect to the surface normal for increased surface sensitivity.

parallel to the substrate (the reduced apparent height appears darker in STM images). The other two phenyl rings on the opposite side (brighter apparent height in STM images) still exhibit larger dihedral angles, and consequently, on this side, T-type interactions of the corresponding phenyl rings from neighboring molecules can still be established, leading to the observed dimers, trimers, and tetramers as depicted in Figure 4b,c. After annealing to 500 K, dehydrogenation also occurs for the remaining two phenyl groups; as a result, the whole molecule is lowered, and all phenyl rings are almost parallel to the substrate surface. The observed absence of attractive interactions between the individual molecules is in line with this interpretation. The tilting after annealing to 450 K thus represents an intermediate state of the dehydrogenation process, in which only one side of the molecular periphery lost hydrogen atoms. In this scenario, annealing to 500 K completes the dehydrogenation on the other side of the molecule, a process that again leads to flat-lying molecules. The unsaturated C atoms can form C−C bonds between neighboring C atoms of the phenyl groups and the porphyrin core, which would require the respective positions also to be dehydrogenated. This reaction has recently been proposed to explain the flattening of 2HTPP on Ag(111) after annealing to 525 K. It was shown by theoretical calculations that the resulting flat porphyrin structures are possible but less stable than the original molecule by at least 1.8 eV.[39] In contrast, the formation of σ bonds to the substrate appears unlikely, because this would result in a reduced mobility of the porphyrin.

4. CONCLUSIONS

Tetraphenylporphyrin (2HTPP) adsorbed on Cu(111) undergoes complex temperature-driven chemical and structural changes. One major chemical change is a redox reaction of the porphyrin center with Cu atoms from the substrate, resulting in the formation of copper(II)-tetraphenylporphyrin

(CuTPP). This reaction was found to start around 400 K and can easily be monitored by XPS, which shows characteristic changes of the porphyrin-related N 1s signal. STM reveals the following changes of the adsorption geometry as function of temperature: (1) site-specific adsorption of 2HTPP at room temperature; (2) partial reaction of 2HTPP to CuTPP at 400 K, with CuTPP again adsorbed parallel but at a larger distance to the surface than 2HTPP; (3) CuTPP molecules display one brighter and one darker side after annealing at 450 K, because of a tilted configuration relative to the substrate; and (4) finally, restoration of the orientation of the porphyrin plane parallel to the surface after annealing to 500 K, but now with a smaller distance to the surface, similar to that of 2HTPP. The latter two changes are attributed to successive dehydrogenation reactions of CuTPP. For CuTPP after heating to 500 K and generally for 2HTPP, the formation of long-range order is suppressed even at low temperature, because of a nearly parallel orientation of the phenyl groups relative to the surface, which prevents intermolecular attractive T-type interactions. The UP spectra show that the Cu(111) surface state is largely suppressed by the adsorption of 2HTPP but partly recovers after annealing to 400 K for 2 h or 450 K for 2 min. This partial recovering at 450 K can be understood as a decrease of the effective coverage of atoms in close contact to the substrate by molecular tilting. After annealing to 500 K, the surface state is again suppressed by the now flat-lying molecules. The reported results indicate that both the functionality of the porphyrin core and the structure of the whole metal complex can be influenced by successive surface-assisted and temperature-driven reactions. In this respect, our findings support the prospect of novel pathways for tailoring the properties of tetraphenylporphyrins on Cu(111) and potentially other metal surfaces.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Large-scale STM image of 2HTPP on Cu(111) after annealing to 450 K. This material is available free of charge via the Internet at http://pubs.acs.org..

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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dx.doi.org/10.1021/jp301757h | *J. Phys. Chem. C* 2012, 116, 12275−12282