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## COMMUNICATION

# Massive conformational changes during thermally induced self-metalation of 2H-Tetrakis-(3,5-di-tert-butyl)-phenylporphyrin on Cu(111)

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Accepted 00th January 2012M. Stark,<sup>a</sup> S. Ditze,<sup>a</sup> M. Lepper,<sup>a</sup> L. Zhang,<sup>a</sup> H. Schlott,<sup>a</sup> F. Buchner,<sup>a,b</sup> M. Röckert,<sup>a</sup>  
M. Chen<sup>a,c</sup>, O. Lytken,<sup>a</sup> H.-P. Steinrück,<sup>a</sup> and H. Marbach<sup>a,\*</sup>

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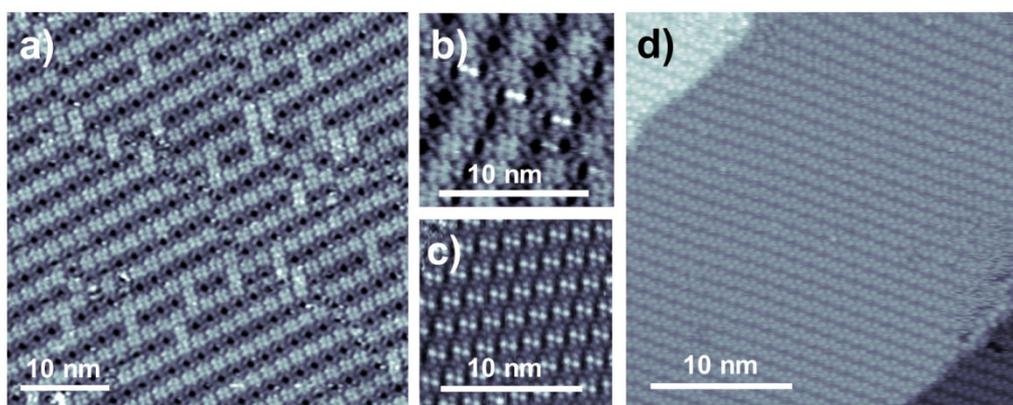
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Based on a combined scanning tunnelling microscopy and X-ray photoelectron spectroscopy study we present detailed insights into pronounced changes of long-range order and intramolecular conformation during the self-metalation of 2H-5,10,15,20-Tetrakis-(3,5-di-tert-butyl)-phenylporphyrin (2HTTBPP) to CuTTBPP on Cu(111). Upon metalation, the porphyrin literally “pops up” from the surface, due to a drastically reduced molecule-substrate interaction.

A detailed understanding of the adsorption behaviour of molecular building blocks on solid surfaces is a crucial step towards the bottom-up fabrication of functional devices<sup>1, 2</sup>. Scanning tunnelling microscopy (STM) is an especially suitable method to study the relevant elementary processes. Porphyrins are regarded as prototype functional molecular building blocks for nanotechnology applications. Recent surface science studies of porphyrins addressed their switching capabilities<sup>3-5</sup> and adsorption behaviour as well as surface-mediated metalation of free base porphyrins<sup>6</sup>. The metalation can occur with predeposited

and postdeposited metal atoms, or via the so-called self-metalation with atoms from an underlying metal substrate<sup>7-10</sup>. Thereby, the free base porphyrin picks up a substrate atom and reacts to the corresponding metalloporphyrin under the release of hydrogen. Herein, we report on the self-metalation of 2HTTBPP on Cu(111), which goes along with an massive intramolecular conformational change due to reduced molecule-substrate interactions. In a vivid image, this process can be summarized as a popping up of the molecular centre from the surface.

The investigation of free base porphyrins on single crystal Cu surfaces recently received great interest, mainly due to the very strong attractive interactions of the iminic nitrogen atoms of the porphyrin macrocycle with Cu atoms from the substrate<sup>11-15</sup>. This interactions can give rise to very peculiar adsorption behaviours like the one observed by STM for 2HTTBPP on Cu(111), see Fig 1a. The corresponding supramolecular structure exhibits a bimodal appearance, i.e. alternating bright and dark rows, which (predominantly) consist of convex and concave intramolecular conformations, respectively (see also Fig 3a-h and discussion below)<sup>4</sup>.



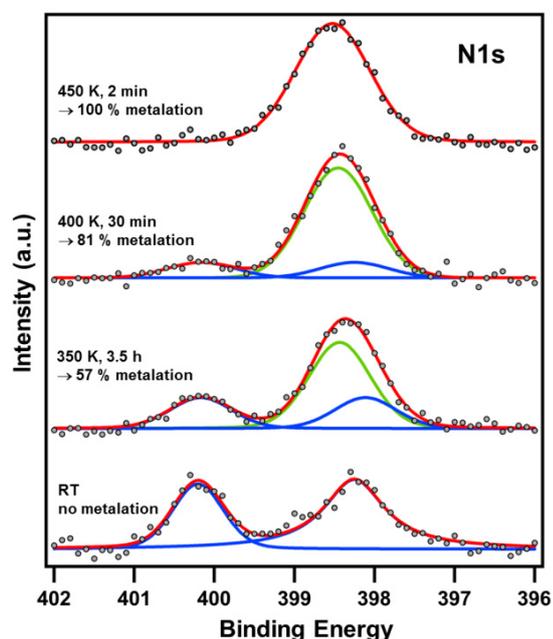
**Figure 1.** Constant current RT STM images of ordered islands of a submonolayer of 2HTTBPP on Cu(111) prepared at RT, after different heat treatments: (a) bimodal appearance observed for the as prepared layer ( $U=+1.3$  V,  $I=30$  pA); (b) transition phase from bimodal to monomodal *hex A* phase after heating for 10 minutes at 330 K ( $U=+1.3$  V,  $I=30$  pA); (c) fully developed *hex A* phase after heating for 2 minutes at 360 K ( $U=+1.8$  V,  $I=30$  pA); (d) representing monomodal *hex B* phase ( $U=-1.8$  V,  $I=30$  pA).

Phase ↓	<i>a</i> [nm]	<i>b</i> [nm]	$\alpha$ [°]	$\rho$ [molecules/nm <sup>2</sup> ]	<i>s</i> <sub>exp</sub> [nm]	<i>l</i> <sub>exp</sub> [nm]	<i>s</i> <sub>mod</sub> [nm]	<i>l</i> <sub>mod</sub> [nm]	$\theta$ [°]	$\phi$ [°]
<i>bimodal</i>	1.90±0.10	2.00±0.06	60±5	0.30	0.70±0.1	1.25±0.1	0.72	1.34	5 ±5	35 ±5
<i>hex A</i>	1.75±0.10	1.92±0.10	68±5	0.32	0.57±0.1	1.07±0.1	0.69	1.07	35/10 ±5	35 ±5
<i>hex B</i>	1.81±0.10	1.85±0.05	60±5	0.35	0.87±0.05	1.12±0.05	0.85	1.10	75 ±5	5 ±5

**Table 1.** Overview of the supramolecular and intramolecular geometrical values, as extracted from STM data; *a*, *b*: lattice parameters,  $\alpha$ : angle between lattice vectors,  $\rho$ : molecular density, *s*<sub>exp</sub> and *l*<sub>exp</sub> experimentally determined *s* and *l* values, *s*<sub>mod</sub> and *l*<sub>mod</sub> *s* and *l* values of the used models,  $\theta$ : the twist angle of the phenyl groups,  $\phi$ : the corresponding tilt angle.

Upon heating, the *bimodal* supramolecular arrangement undergoes massive transformations, as depicted in Fig 1b-d. Fig 1b represents a transient situation after 10 minutes heating at 330 K, i.e. the onset of the formation of a monomodal supramolecular structure, in the following referred to as *hex A*. The most apparent change on the molecular level is the appearance of pronounced protrusions, which occur pairwise and increase in number with increasing heating time. In Fig 1b, the *bimodal* structure is still dominating, while only very few of the peculiar protrusions are formed, preferentially at dislocations of the row structure. A fully developed *hex A* structure is depicted in Fig 1c; this structure can be achieved either by prolonged heating at 330 K or by heating for 2 minutes at 360 K. After heating the sample to 450 K for 2 minutes the molecular arrangements again changes significantly and the whole surface is now covered with the structure depicted in Fig 1d, which is referred to as *hex B*.

In the following, we address the origin of this thermally induced transformation from the bimodal structure into the *hex A* and *hex B* arrangements. In previous studies of different free base porphyrins on Cu surfaces, the so called self-metalation reaction was observed<sup>7-10</sup>. For example, on Cu(111) 2H-Tetraphenylporphyrin (2HTPP) reacts with Cu surface atoms to CuTPP, at temperatures as low as ~390 K<sup>8</sup>. Therefore, one can anticipate that a similar reaction occurs for the here investigated 2HTTBPP. To find out, whether such a reaction occurs, we performed X-ray photoelectron spectroscopy (XPS). The corresponding N 1s spectra in Fig 2 indeed evidence that

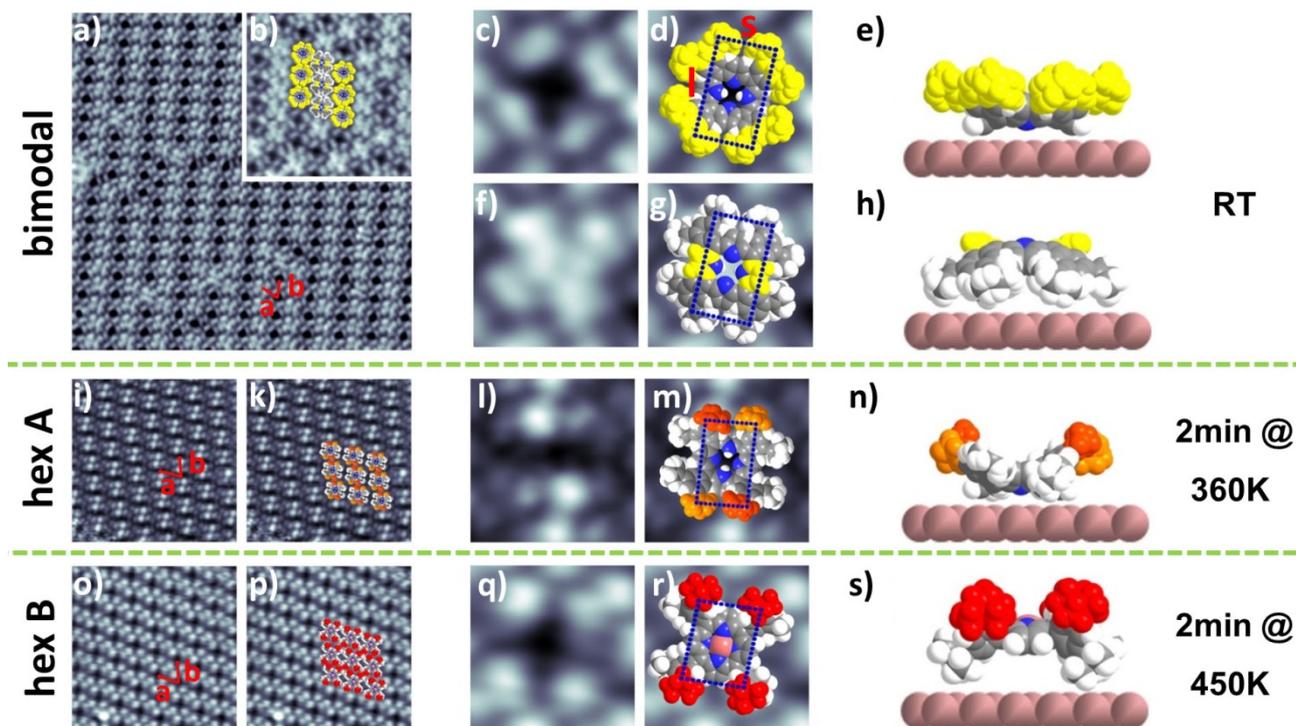


**Figure 2.** N 1s XP spectra of 2HTTBPP on Cu(111), for the as prepared layer (bottom) and after the indicated heat treatments; the topmost spectrum corresponds to fully metalated CuTTBPP.

the 2HTTBPP reacts to CuTTBPP: 2HTTBPP has two non-equivalent nitrogen atoms (iminic and aminic), yielding two clearly distinguishable N 1s peaks, as is evident from Fig 2 (bottom). After heating the sample to 450 K for 2 minutes, the spectrum shows only one peak (top spectrum), which is characteristic for the metalized porphyrin, CuTTBPP, in which all four nitrogen atoms are equally coordinated to a central Cu atom. In addition, we show two spectra after heating to lower temperatures (350 K for 210 min, and 400 K for 30 min). In these spectra, contributions from both, 2HTTBPP and CuTTBPP, are seen, and from the relative intensities the corresponding degrees of metalation can be determined, by using a fitting procedure. Comparison of the XPS data with the STM data yields the conclusion that the *hex B* structure consists of CuTTBPP. For the preparation conditions of the partially metalated situations shown in Fig 2, we always observe coexisting domains in STM, in which the surface ratio covered with *hex B* molecules roughly resembles the degree of metalation determined in XPS.

To further shed light on the nature of the observed supramolecular structures, high resolution STM micrographs of individual porphyrins were acquired and analysed. In Fig 3, the molecular arrangements are depicted (left), along with micrographs of corresponding individual porphyrins within the arrangements with sub-molecular resolution (center), and the extracted intramolecular conformations (right). The conformational flexibility of TTBPP species on different substrates is well known and was reported before<sup>16-20</sup>. From the inspection of Fig 3, it becomes immediately apparent that the different supramolecular arrangements go along with different intramolecular conformations. It is well established that the appearance of the individual molecules in STM is dominated by the four upper tert-butyl groups<sup>16-19</sup>, which form a rectangle as indicated in Fig 3d, 3g, 3m and 3r. From the lengths of the two sides *s* and *l* of these rectangles, the intramolecular conformations can be extracted using the perimeter and aspect ratio of the latter, according to a procedure described elsewhere<sup>4, 16</sup> (A sketch visualizing this procedure and additional information is provided in the SI). In a simplified model, the conformation of a molecule is described by twisting and/or tilting the phenyl rings with respect to the porphyrin plane; the corresponding twist angle is denoted as  $\theta$  and the tilt angle as  $\phi$ <sup>16</sup>. The full set of parameters for the supramolecular arrangements is given in Table 1. In addition the two intramolecular conformations in the *bimodal* phase were confirmed by STM simulations based on DFT calculations of the electronic structure<sup>4</sup>.

The *bimodal* structure in Fig 3a was recently investigated in great detail by Ditze et al.: The intramolecular conformation with  $\theta = 5 \pm 5^\circ$  and  $\phi = 35 \pm 5^\circ$  resembles the shape of a bowl, which can either occur standing “upright” on the surface (Fig 3c-e, concave conformation) or upside down (Fig 3f-h, convex conformation). The supramolecular order is formed by alternating rows of molecules in the concave and convex conformations. While the concave conformation is in line with a strong attractive interaction of the iminic nitrogen atoms with the Cu substrate, the convex conformation is stabilized by entropic effects. This was derived from studying the thermally induced reversible conformational switching of 2HTTBPP in the *bimodal* structure<sup>4</sup>. Upon moderate heating, the



**Figure 3.** Overview of the observed supramolecular porphyrin phases and the derived molecular models on Cu(111): (a-h) **bimodal** phase of 2HTTBPP as prepared at room temperature. (i-n) **hex A** phase of 2HTTBPP after heating to 360 K for 2 minutes. (o-s) representing **hex B** phase of CuTTBPP after thermally induced metalation reaction. The scanning parameters are: (a)  $U=+1.3$  V,  $I=30$  pA; (b-g)  $U=+1.8$  V,  $I=25$  pA; (i-r),  $U=+1.8$  V,  $I=30$  pA; (a)  $35.0 \times 35.0$  nm<sup>2</sup>; (b, i, k, o, p)  $13.5 \times 13.5$  nm<sup>2</sup>; (c, d, f, g, l, m, q, r)  $2.5 \times 2.5$  nm<sup>2</sup>.

*bimodal* structure transforms into the monomodal *hex A* structure (Fig 3i), i.e. all molecules exhibit the same intramolecular conformation (Fig 3l-n), and appear static, i.e. they do not show any thermally induced switching. For this conformation the position of the macrocycle is very similar to the concave conformation. The main difference between these two conformations is that the four phenyl rings are significantly twisted out of the porphyrin plane ( $\theta = 35 \pm 5^\circ$ ) for *hex A*. From the close proximity of the porphyrin macrocycle to the Cu substrate (Fig 3n) and the information from XPS that the porphyrin is not yet metalated in *hex A*, we conclude that the strong attractive interaction of the iminic nitrogen atoms of the free base porphyrin causes this conformation. In addition, the upper tert-butyl groups from the phenyl rings with the larger twist angle ( $\theta = 35 \pm 5^\circ$ , indicated in red in Fig 3k, m, n) are arranged such, that they are in close proximity to their likes of molecules in the neighboring rows (Fig 3i-l). As a consequence, the corresponding protrusions from two neighboring molecules appear with a dumbbell shape. This close proximity, together with the increased molecular density (*bimodal*:  $\rho = 0.30$  molecules/nm<sup>2</sup>, *hex A*:  $\rho = 0.32$  molecules/nm<sup>2</sup>), indicate an additional stabilizing contribution from the attractive interaction between the corresponding side groups. This interpretation is confirmed by the observations of the onset of the *hex A* formation (Fig 1b), which is the formation of the pairwise protrusions between neighboring concave molecules at dislocations in the *bimodal* structure, already after 10 minutes at 330 K. Taking the irreversibility of the conformational change from *bimodal* to *hex A* into account, it appears that the *hex A* structure is energetically favorable over the *bimodal* arrangement, but has to overcome some activation barrier in order to be formed.

Upon further heating, the *hex A* structure transforms into the *hex B* structure, as shown in Fig 1d and Fig 3o, p. From the XPS data, it is evident that the free base porphyrin is transformed to CuTTBPP in the *hex B* arrangement. The intramolecular conformation drastically changes to a situation where the center of the porphyrin with the coordinated Cu atom is now significantly lifted above the Cu(111) surface. This interpretation is also supported by a shift of the C 1s peaks in XPS to higher binding energies, in agreement with a reduced final state screening as the molecule moves away from the surface (see Figure S3 in supplementary information). Consequently, the twist angle  $\theta = 75 \pm 5^\circ$  changed such that the phenyl rings are almost perpendicular to the porphyrin macrocycle. At the same time, the tilt angle is also significantly reduced to  $\phi = 5 \pm 5^\circ$ . This modified molecular conformation obviously allows for attractive interactions between the side groups of neighboring CuTTBPPs, as judged by the close proximity of the corresponding protrusions (Fig. 3o, p) and the again increased molecular density of  $\rho = 0.35$  molecules/nm<sup>2</sup>. Overall, the intramolecular conformation in *hex B* is very similar to the one expected for the isolated molecule in the gas phase ( $\theta = 70^\circ$ ;  $\phi = 0^\circ$ )<sup>20</sup>. Obviously, the strong attractive interaction of 2HTTBPP with the substrate is almost completely switched off by the insertion of the Cu atom. As a consequence, the central part of the molecule literally pops up from the surface, resulting in a very different intramolecular conformation. In a vivid picture, the 2HTTBPP in the *hex A* phase behaves almost like a loaded spring which is hold by the strong attractive interactions of the iminic nitrogens with the Cu substrate and is released upon metalation.

In summary, we gained detailed insights into the thermally induced morphological and chemical transformations of 2HTTBPP on Cu(111). Starting at  $\sim 330$  K, the initially *bimodal* supramolecular structure changes to the monomodal *hex A* arrangement with reduced

intramolecular symmetry. At higher temperatures and/or prolonged heating times, 2HTTBPP undergoes a metalation reaction with Cu substrate atoms to form CuTTBPP in the *hex B* phase. The observed massive structural change can be conclusively explained by reduced molecule-substrate interactions after metalation.

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## Notes and references

<sup>a</sup> Lehrstuhl für Physikalische Chemie II, Egerlandstrasse 3 and Interdisciplinary Center for Molecular Materials (ICMM), Universität Erlangen-Nürnberg, D-91058 Erlangen, Germany.

<sup>b</sup> Present address: Helmholtz Institut Ulm and Institut für Oberflächenchemie und Katalyse, Universität Ulm, Albert-Einstein Allee 11, D-89081 Ulm, Germany.

<sup>c</sup> Present address: Fachbereich Chemie, Physikalische Chemie, Philipps-Universität Marburg, Hans-Meerwein-Straße 6, D-35032 Marburg, Germany.

E-Mail: hubertus.marbach@fau.de

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**TOC:**

2HTTBPP on Cu(111) phase behaves almost like a loaded spring which is hold by the strong attractive interactions of the iminic nitrogens with the Cu substrate and is released upon metalation.

