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From hydrogen bonding to metal coordination and back: Porphyrin-based networks on Ag(111)

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The self-assembly of a metal-free porphyrin bearing two pyridyl coordinating sites and two pentyl chains at *trans meso* positions was investigated under ultrahigh vacuum on a Ag(111) surface by scanning tunneling microscopy (STM). The STM measurements revealed a well-ordered close-packed structure with a rhombic unit cell for coverages ≤1 monolayer with their molecular plane parallel to the surface. The growth direction of the molecular islands is aligned along the step edges, which are restructured due to molecule-substrate interactions. The shorter unit cell vector of the molecular superstructure follows the ⟨1-10⟩ direction of the Ag(111) substrate. Hydrogen bonds between pyridyl and pyrrole groups of neighboring molecules as well as weak van der Waals forces between the pentyl chains stabilize the superstructure. Deposition of cobalt atoms onto the close-packed structure at room temperature leads to the formation of a hexagonal porous network stabilized by metal-ligand bonding between the pyridyl ligands and the cobalt atoms. Thermal annealing of the Co-coordination network at temperatures >450 K results in the transformation of the hexagonal network into a second close-packed structure. Changes in the molecule-substrate interactions due to metalation of the porphyrin core with Co as well as intermolecular interactions can explain the observed structural transformations. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4908535]

I. INTRODUCTION

Porphyrins play a vital role in many processes taking place in nature. For example, proteins containing an iron(III) porphyrin center with an axial histidine ligand enable the oxygen transport in the human blood while manganese(II) porphyrins are used in the energy conversion process in chlorophyll.[1,2] Besides these illustrative examples from nature, porphyrin derivatives, owing to their thermal stability and robustness, have been widely used in material science and are believed to be candidates of choice for future organic devices.[3,4] Especially, the tunability of the porphyrin properties via the proper choice of the central metal ion opened up a wide field of possible applications such as single-molecule p-n junctions,[5] transistor based sensors,[6] as new dyes for the energy conversion in dye-sensitized solar cells,[7] as single-molecule magnets[8] or in catalysis.[9] Moreover, the possibility of appending the porphyrin backbone with peripheral interaction sites at specific positions (*meso* or β-pyrrolic) allows for implementing additional functionality. In line with the molecular tectonics approach,[10–13] porphyrin based tectons[14,15] have been largely used for the generation of a variety of 1-3D coordination networks[16,17] in the crystalline phase.

The planar nature of the porphyrin core together with its robustness and extended π-system is a valued characteristic for the use of porphyrins in molecular self-assembly on flat noble metal surfaces.[18–25] Particularly, the possibility to steer the intermolecular interactions using suitable units for hydrogen bonding, coordination bonding, or π-π interactions led to an intensive investigation of porphyrin derivatives on metal surfaces.[26–29] Among others, porphyrins appended with ligands such as pyridyl or cyano groups were studied intensively because the presence of electronegative nitrogen atoms enables different bonding motifs such as hydrogen bonding and/or metal-coordination bonding.[26,28–30] In addition to the intermolecular interactions, porphyrin-substrate interactions also play a decisive role in the self-assembly of porphyrin based molecules on surfaces. For example, deposition of metal-free porphyrins bearing phenyl moieties at the *meso* positions onto a Cu(111) substrate usually leads to mainly isolated molecules.[31,32] This is due to the strong interaction of the iminic nitrogen atoms with the copper atoms of the substrate. In contrast, deposition of the same molecule onto Ag(111) resulted in well-ordered islands. Annealing of the molecules on copper led to a self-metalation of the porphyrin core and a decrease in the molecule-substrate interaction, which manifests itself in a higher mobility of copper porphyrin complexes when compared to the metal-free porphyrin.[31] Similar metalation with a wide variety of metals such as Fe, Co, or Zn can be achieved by deposition of the metal atoms onto the surface covered with porphyrin molecules.[33–36] Generally, the metalation induces a conformational change of the adsorbed porphyrin affecting the molecule-substrate interactions.[35,37–39]

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In this study, we report on the molecular self-assembly of a (5,15-dipentyl-10,20-(4-yl-pyridine)porphyrin (DPPyP) (see Fig. 1) on Ag(111) investigated by scanning tunneling microscopy (STM). DPPyP is a porphyrin based molecule bearing two pyridyl units and two pentyl chains at *trans meso* positions. The two pyridyl units have been chosen as coordinating sites while the two pentyl chains can undergo possible van der Waals interactions with the substrate or between consecutive units. Furthermore, due to the pentyl chains, the solubility of the molecule is increased what can be exploited for potential comparative studies at the solid-liquid interface. Deposition of the DPPyP molecules onto Ag(111) at room temperature results in the formation of a close-packed rhombic network stabilized by hydrogen bonding between the pyridyl units and H atoms of the pyrrole moieties as well as by weak van der Waals interactions between the pentyl chains. Addition of cobalt atoms at room temperature leads to their coordination by the pyridyl ligands generating a hexagonal porous network. Annealing of this network at 450 K leads to a structural transformation into a second rhombic pattern, again stabilized by hydrogen bonding.

II. EXPERIMENTAL SECTION

A. Sample preparation and STM experiments

All experiments were carried out under ultrahigh vacuum (UHV) conditions. Two UHV systems each equipped with a preparation and an analysis chamber were used. The first system houses a commercial variable temperature STM

FIG. 1. Chemical structure of the bis-pyridyl porphyrin derivative DPPyP and intermediates used in its synthesis.

(Oxford Instruments Omicron NanoScience), which was operated at room temperature, while the second system houses a commercial low temperature STM (Oxford Instruments Omicron NanoScience), which was operated at 77 K. Mechanically cut platinum-iridium wires were used as tips and the data were processed with the WSxM software.[40] The bias voltages given in the paper refer to a grounded tip.

The Ag(111) single crystal was cleaned by repeated cycles of Ar$^+$ sputtering at an energy of 1500 eV, followed by annealing at 700 K. The molecules were deposited onto the Ag(111) surface from glass crucibles that were heated inside a home-built evaporator. Thorough degassing of the molecules was done before sample preparation. Cobalt atoms were deposited from a rod using a commercial e-beam evaporator (Oxford Applied Research). During deposition of the molecules and cobalt atoms, the substrate was kept at room temperature. The deposition rate was monitored via a quartz crystal microbalance.

B. Synthesis

DPPyP (Fig. 1) is a A$_2$B$_2$ type porphyrin. Its synthesis was achieved by a multistep procedure starting from the 5,15-dipentylporphyrin **3** (Fig. 1). This compound was prepared upon reacting dipyrromethane[41] **1** with hexanal **2** following a reported procedure.[42] The bromination of the two *meso* positions using 2 equivalent of N-Bromosuccinimide in CHCl$_3$ afforded the compound **4** in quantitative yield. The introduction of the two pyridyl groups was achieved by a Suzuki coupling reaction in the presence of Pd(PPh$_3$)$_4$ and an excess of 4-pyridinyl boronic acid **5** following a procedure described for the synthesis of similar compounds.[43] The desired porphyrin DPPyP was isolated in 50% yield (see supplementary material[44]). In addition to classical characterization methods, the structure of the final compound DPPyP was investigated by X-ray diffraction on single crystals (see supplementary material[44]). The porphyrin crystallized in the P21/c space group with no solvent molecule present in the lattice. The porphyrin core is almost planar and the dihedral angle between the porphyrin mean plane (24 atoms) and the *meso* pyridyl is close to 66°. The distance between the two opposite pyridyl nitrogen atoms, N$_{pyridyl}$–N$_{pyridyl}$ amounts to 15.4 Å (Fig. 2).
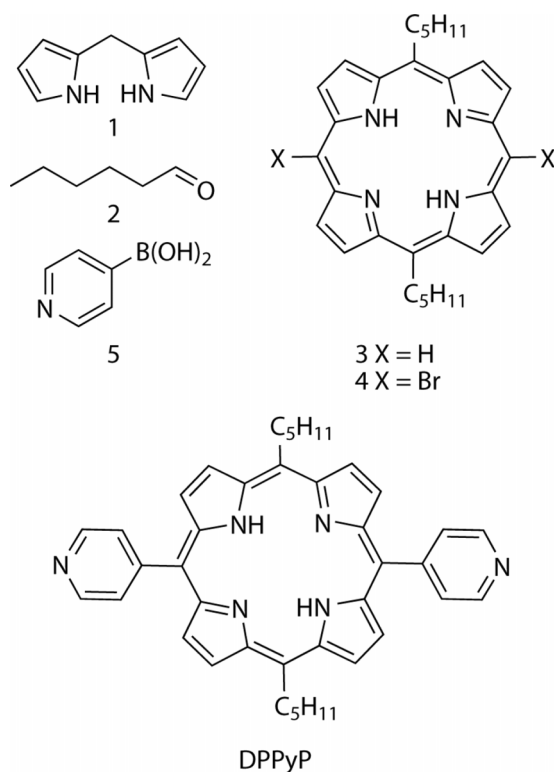
III. RESULTS

For submonolayer coverage of DPPyP on Ag(111) (Fig. 3), the molecules adsorb preferentially at the step edges and the restructuring of the step edges indicates a rather strong interaction between the molecules and the substrate. The two-dimensional (2D) islands have an anisotropic shape and grow from the step edges onto the terraces (see also supplemental material[44] Fig. S1). The growth proceeds parallel to the step edges along the ⟨1-10⟩ direction what can be seen as an indication that the intermolecular interaction along this direction is stronger in comparison to the intermolecular interaction along the "slow" growth direction. From the molecularly resolved STM images displayed in Figs. 4(a) and 4(b), the arrangement of the molecules within the close-packed structure can be deduced. For coverages ≤1 monolayer, only this type of

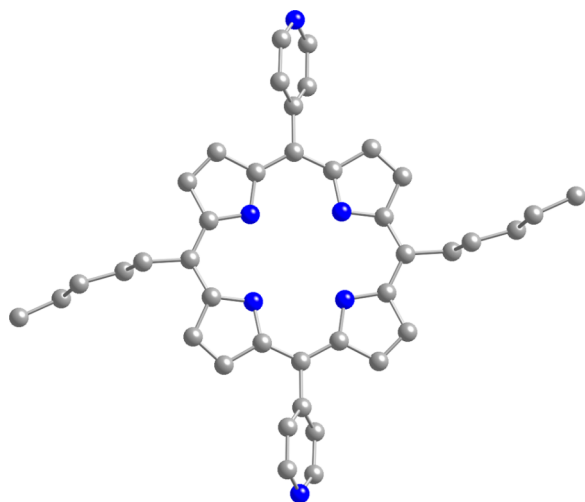FIG. 2. X-ray structure of DPPyP showing the flat nature of the porphyrin core in the crystalline phase and the *trans* disposition of the two pyridyl and pentyl units. H atoms are omitted for clarity. Bond distances and angles are described in Sec. II B.
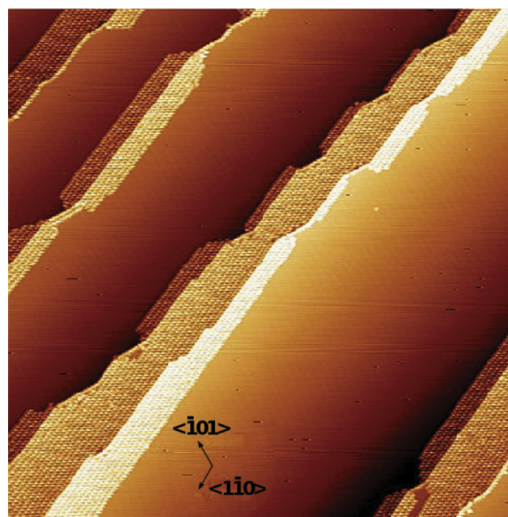

FIG. 3. Overview STM image for submonolayer coverage of DPPyP on Ag(111) (150×150 nm^2, U = −1.4 V, I = 10 pA, 77 K). The molecules align along the step edges and arrange in close-packed islands whose growth mainly takes place parallel to the step edges. The principal directions of the Ag(111) substrate are indicated by the two black arrows.

structure was found. At room temperature, we did not obtain high-resolution images (Fig. 4(a)), which we ascribe to the fact that the pentyl chains can move due to thermal agitation. In general, the movement of substituted alkyl chains limits the attainable intramolecular resolution.[45] In the high-resolution STM image in Fig. 4(b), different submolecular features can be observed. Each of the pyridyl ligands of the DPPyP molecule is imaged as one bright protrusion, while the pentyl chains can be identified as the less bright protrusions. The porphyrin core is not visible in the STM image. With this information, the orientation of the molecules with respect to one another can be deduced (see superimposed molecular structure in Fig. 4(b)). The molecules arrange in a rhombic unit cell with dimensions 1.42 nm × 1.52 nm (±0.1 nm) and internal angle of 85° (±4°). The packing density is 0.47 molecules · nm^{-2} and the short axis of the unit cell is parallel to one of the ⟨1-10⟩ directions of the Ag(111) surface. From the tentative model for the close-packed structure, displayed in Fig. 4(c), it can be seen that the pyridyl ligands interact with the pyrrole groups of neighboring DPPyP molecules via weak H-bonding between pyridyl N and pyrrole H atoms. This interaction occurs along the short unit cell axis. For tetrapyridyl porphyrins on Ag(111) similar H · · · N bonds as well as very similar intermolecular distances were reported.[23,34,46] Along the other unit cell direction, the molecules interact through their pentyl chains via weak van der Waals forces. Since the stronger intermolecular interactions occur along the short unit cell axis, which is parallel to the Ag ⟨1-10⟩ direction, the observed anisotropic island growth behavior as well as the restructuring of the step edges can now be understood.

Deposition of cobalt atoms onto the close-packed network leads to a structural transformation: the close-packed structure is transformed into a Co-coordinated hexagonal porous network (Fig. 5). The individual network domains were found to be up to several hundred nanometers in size and a porphyrin molecule was infrequently trapped inside a pore (Fig. 5(a)). The rhombic unit cell measures 3.3 nm × 3.3 nm (±0.2 nm) with an internal angle of 60° (±3°). The network vertices are made up from Co atoms to which three DPPyP molecules coordinate with the N atoms of their pyridyl ligands. The individual Co atoms can be identified in the STM image shown in Fig. 5(b). The pentyl chains of DPPyP, which point towards the center of the pores, lead to a fuzzy appearance as well as to streaks inside the pores, which is a consequence of their mobility at room temperature (see supplementary material,[44] Fig. S2). Fig. 5(c) displays the suggested structure model of the porous network. The formation of a similar porous network on Au(111) from the combination of Fe atoms and a dipyridyl porphyrin derivative having phenyl instead of pentyl ligands has recently been reported.[19] Its sizes fit well with our observations and support the formation of Co · · · N coordination bonds. Only very recently, a fourfold coordination motif formed between Co atoms and dipyridyl porphyrin derivatives on HOPG has been suggested.[47] The difference in the number of coordinated ligands can be rationalized by the fact that the metal substrate (in our case Ag) plays the role of the fourth ligand[48] and thus, a threefold coordination motif is observed whereas HOPG obviously does not fulfil this role. In the STM image in Fig. 5(a) on the left side, a small patch of uncoordinated DPPyP molecules can be seen. This is most probably a kinetically trapped structure since the amount of deposited Co atoms should be sufficient (clusters of Co atoms are visible in Fig. 5(a)) to obtain only the porous network.

Annealing the sample at 450 K leads again to a structural transformation: the hexagonal porous network is converted into a second close-packed rhombic structure (Fig. 6). The molecules are arranged in elongated anisotropically shaped islands whose length can be ~100 nm while the width can be as small as only four molecular rows (Fig. 6(a)). This behavior is very similar to what was observed for as-deposited DPPyP on Ag(111) (*vide supra*), except that the islands point away from the step edges instead of aligning parallel to the step edges, and can be interpreted in the following way. Since the intermolecular interactions through H-bonding between
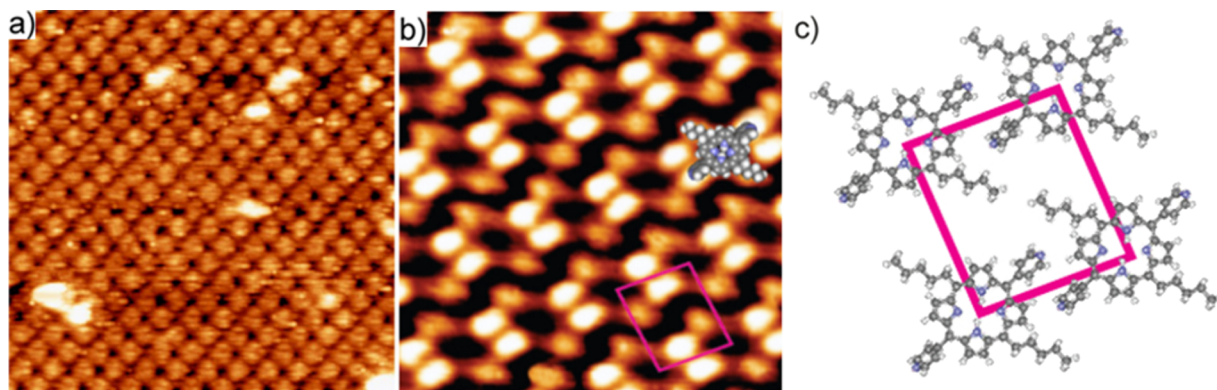
FIG. 4. Close-packed rhombic network of DPPyP on Ag(111). (a) Molecularly resolved STM image (25×25 nm², U = −2.5 V, I = 22 pA, RT) displaying the arrangement of the molecules within the close-packed structure. (b) High-resolution STM image (7×7 nm², U = −2.5 V I = 10 pA, 77 K) where the pyridyl as well as the alkyl ligands can be discerned. A molecule is superimposed to denote the molecular orientation. The unit cell is indicated in pink. (c) Tentative model for the close-packed structure which is stabilized by a combination of H-bonding between the pyridyl ligands and hydrogen atoms of a pyrrole group of neighboring molecules and van der Waals forces between the alkyl chains of neighboring molecules.

the pyridyl and pyrrolic H atoms of neighboring molecules are stronger in comparison to the van der Waals interactions between the pentyl chains, the molecules prefer to build up 1D rows through H-bonding. Two such 1D arrangements interact via the pentyl fragments of DPPyP leading to the formation of a 2D island (the pentyl chains can be imagined working like the teeth of a zipper). Because the pentyl chains of neighboring 1D rows can be either located on the left or on the right side with respect to adjacent rows, the appearance of dislocation lines is expected. This is indeed the case as it can be seen in Fig. 6(b) (indicated by the bent blue line).

The rhombic unit cell has the following parameters: a = 1.42 (±0.1) nm, b = 1.54 (±0.1) nm, Θ = 70° (±4°), and the packing density amounts to 0.49 molecules · nm⁻². The suggested structural model is displayed in Fig. 6(c). Compared to the unit cell for as-deposited DPPyP, the internal angle is smaller and the packing density is slightly higher. However, we assume that this slightly higher packing density is not the driving force for the different arrangement of the molecules within this second close-packed structure. Instead, this is a hint that the molecule-substrate interaction is changed. Further support for this assumption comes from the fact that (i) the step edges are not restructured, (ii) the molecular rows are generally

not parallel to the step edges, and (iii) the island growth does not necessarily start at the step edges (see supplementary material,[44] Fig. S3). It is well-known that the porphyrin core can be spontaneously metalated upon deposition of Co atoms onto metal-free porphyrin or phthalocyanine layers at room temperature.[31,33,36,39] The incorporation of the cobalt atom into the porphyrin core accompanied by a deprotonation of the imine nitrogen atoms results in a different interaction of the porphyrin with the Ag substrate.[39] This information can be related to our case. The DPPyP molecules become Co-metalated complexes: this results in a different molecule-substrate interaction finally leading to a changed unit cell for the close-packed structure. The structural transformation upon annealing at 450 K can be explained by the breakage of the Co-pyridyl coordination bond in what is most likely a consequence of the optimization of the free surface energy.[28,45] A similar structural change was reported for tetrapyridyl porphyrins coordinated to Cu atoms on Au(111).[30] Upon annealing at 570 K, the Cu-coordinated square network was transformed into a H-bonded close-packed structure. The higher annealing temperature for the structural transformation (570 K vs. 450 K in our case) can be explained by the fact that four metal-ligand bonds per molecule need to be broken in the case of the tetrapyridyl porphyrins with four
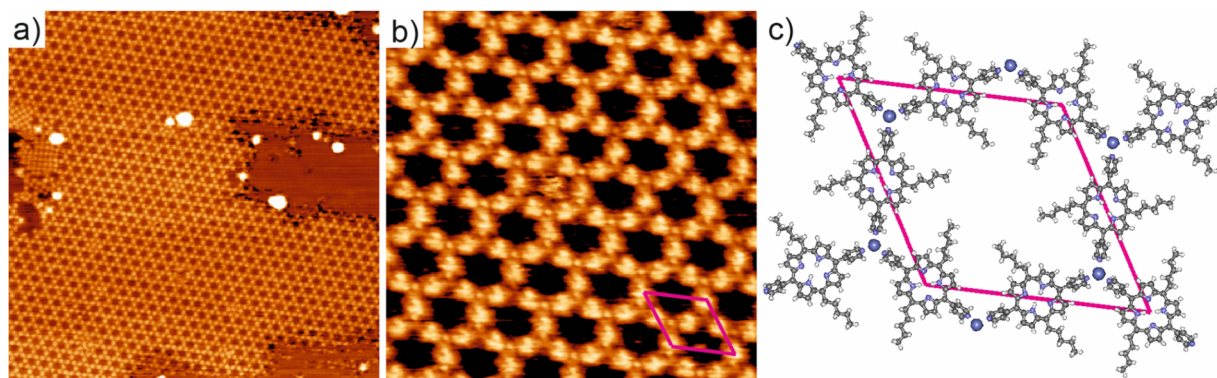

FIG. 5. Cobalt-coordinated porous network of DPPyP on Ag(111). (a) Overview STM image (100×100 nm², U = −1.2 V, I = 105 pA, RT). On the left, a small area of the close-packed structure is visible which was not transformed into the porous network. (b) STM image (20×20 nm², U = −1.0 V, I = 130 pA, RT) in which both the DPPyP molecules and the coordinated Co atoms can be discerned. The unit cell is indicated in pink. (c) Tentative structure model for the cobalt coordinated porous DPPyP network. One cobalt atom (blue sphere) coordinates to three pyridyl ligands. The unit cell is indicated in pink.
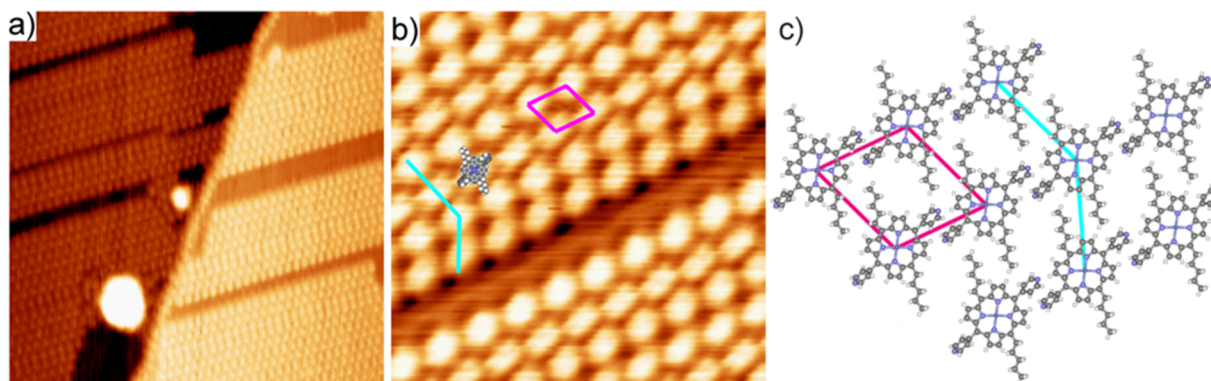
FIG. 6. Second close-packed rhombic network after annealing the hexagonal network at 450 K. (a) Overview STM image (50×50 nm², U = −1.5 V, I = 80 pA, RT) showing elongated islands growing away from the step edges. (b) Close-up view (15×15 nm², U = −2.6 V, I = 25 pA, RT) of the new rhombic pattern. A molecular model is superimposed to illustrate the orientation of the molecules within the islands. The appearance of dislocation lines is indicated by the bent blue line. The unit cell is indicated in pink. (c) Tentative model of the close-packed structure which is stabilized via H-bonding between the pyridyl ligands and the pyrrolic hydrogen atoms as well as van der Waals forces between the pentyl chains. The unit cell is indicated in pink.

pyridyl ligands per molecule while in our case, only two metal-ligand bonds per molecule need to be disrupted.

IV. CONCLUSIONS

We investigated the effect of Co deposition as well as annealing on the 2D structure formation of the bis-pyridyl porphyrin derivative DPPyP on Ag(111) for coverages ≤1 monolayer. For as-deposited DPPyP on Ag(111) at room temperature, the molecules form a close-packed structure with a rhombic unit cell which is stabilized by a combination of H-bonding between pyridyl and pyrrolic NH moieties and van der Waals interactions between appended pentyl chains. Due to the different strengths of the two intermolecular interactions, the islands display an anisotropic shape. The strong molecule-substrate interactions are reflected in the restructuring of the Ag step edges. Upon deposition of Co atoms onto the close-packed structure, the formation of a hexagonal porous network is induced through Co coordination by the N atoms of the pyridyl units. By annealing at 450 K, the organization was transformed into a second close-packed structure, whose unit cell is similar to the first close-packed structure mentioned above. The intermolecular interactions are similar for both close-packed structures while the molecule-substrate interaction is changed due to the metalation of the porphyrin core by Co atoms. This study shows that by the careful selection of the molecular building block, the substituents, and the adatom material, control over the molecular arrangement can be achieved, which will open new paths towards the fabrication of specific self-assembled patterns on surfaces.

ACKNOWLEDGMENTS

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