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Florian Buchner

STM Investigation of Molecular Architectures of Porphyrinoids on a Ag(111) Surface

Supramolecular Ordering,
Electronic Properties and Reactivity

Doctoral Thesis accepted by
Friedrich-Alexander-University of Erlangen-Nürnberg,
Germany

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Supervisor's Foreword

The functionalization of surfaces on the nanoscale is one of the most fascinating and at the same time challenging topics in science. It is the key to tailoring catalysts, sensors, or devices for solar energy conversion, whose functional principle is based on the interaction of an active solid surface with another (liquid or gaseous) phase. As an example, planar transition metal complexes adsorbed on solid supports are promising candidates for novel heterogeneous catalysts. An important feature of these catalysts, compared to supported metal clusters, is the fact that the active sites, i.e., the coordinated metal centers with their vacant axial coordination sites, are well defined and uniform. Metalloporphyrinoids are particularly suitable in this respect because they combine a structure forming element—the rigid molecular frame, which often induces long range order—with an active site, the coordinated metal ion. Its planar coordination environment leaves two axial coordination sites available for additional ligands. If adsorbed on a surface, one of these axial sites is occupied by the underlying substrate. The resulting electronic interaction with the surface can be used to tailor the electronic structure and thereby the reactivity of the metal center. The remaining site is free for the attachment of molecules (sensor functionality) and/or operates as a reaction center (single-site catalysis). Prototype examples are omnipresent in nature, where in particular metallo-tetrapyrrols play a decisive role in important biological processes, with the most prominent examples being iron porphyrins in heme, magnesium porphyrins in chlorophyll, and cobalt corrin in vitamin B12.

The Ph.D. thesis of Florian Buchner addresses several important and fundamental aspects of metalloporphyrinoids adsorbed on metal surfaces using a surface science approach. It was embedded in the Collaborative Research Center SFB 583, “*Redox-Active Metal Complexes: Control of Reactivity via Molecular Architecture*” at the University Erlangen-Nuremberg, which provided a perfect environment through strong cooperation partners in physics and chemistry, experimentally as well as theoretically. By applying mainly scanning tunneling microscopy with submolecular resolution Florian Buchner systematically studied supramolecular ordering and intramolecular conformation of various

porphyrinoids, their electronic interactions with the substrate, surface confined synthesis via in situ metallation, and ligand effects. He obtained outstanding results and significantly contributed to the present level of understanding in the field. Accordingly he is author and coauthor to more than ten publications on the topic in high-ranked journals, which have been extremely well received by the research community and beyond.

Florian Buchner performed his Ph.D. thesis at the Chair of Physical Chemistry II of the University Erlangen-Nuremberg, which focuses on surface and interface science. Main research interests in: (1) development of new materials with novel electronic, geometric and chemical properties, (2) investigation of elementary steps of surface reactions and (3) construction of advanced scientific apparatus. The studies aim at a fundamental physical and chemical understanding of the mechanisms and processes involved, at an atomic level. For these investigations a large variety of experimental methods are applied, including synchrotron radiation-based photoelectron spectroscopy, scanning electron and scanning tunneling microscopy, and molecular beam methods.

Erlangen, 2010

Prof. Dr. Hans-Peter Steinrück

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List of Abbreviations

CITS	Continuous Imaging Tunneling Spectroscopy
DFT	Density Functional Theory
DOS	Density of States
HOMO	Highest Occupied Molecular Orbital
HOPG	Highly Oriented Pyrolytic Graphite
LEED	Low Energy Electron Diffraction
LUMO	Lowest Unoccupied Molecular Orbital
MTPP	Metallotetraphenylporphyrin
OEP	Octaethylporphyrin
OMT	Orbital Mediated Tunneling
Pc	Phthalocyanine
QMS	Quadrupole Mass Spectrometry
STM	Scanning Tunneling Microscopy
STS	Scanning Tunneling Spectroscopy
TPD	Thermal Programmed Desorption
TPP	Tetraphenylporphyrin
TPyP	Tetrapyrrolylporphyrin
TTBPP	Tetrakis(ditertbutylphenyl)porphyrin
RT	Room Temperature
UHV	Ultra High Vacuum
UPS	Ultraviolet Photoelectron Spectroscopy
XPS	X-ray Photoelectron Spectroscopy

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- 6.6 RT constant current STM images of a monolayer of **a** 2HTPP, $U = -154$ mV, $I = 29$ pA and **b** after the evaporation deposition of Co, $\theta_{\text{Co}} = 0.012 \pm 0.002$, $U = -213$ mV, $I = 33$ pA

- 6.7 **a–d** Series of STM images after the successive evaporation deposition of equal amounts of Co. **a** $U = -1.21$ V, $I = 42$ pA; **b** $U = -1.25$ V, $I = 40$ pA; **c** $U = -1.19$ V, $I = 48$ pA; **d** $U = -1.21$ V, $I = 41$ pA
- 6.8 STM image after the evaporation deposition of **a** $\theta_{\text{Co}} \sim 0.12$ ML ($U = -1.23$ V, $I = 41$ pA) and **b** $\theta_{\text{Co}} \sim 0.3$ ML ($U = -1.23$ V, $I = 41$ pA). **c** High-resolution micrograph extracted from **b**, highlighting explicitly oriented features. **d** Corresponding space-filling models were superimposed; the *drawn in arrows* point out the possible diffusion path below the porphyrins
- 6.9 Schematic energy profile for Co atom insertion into 2H-porphyrin, reprinted from the publication of Shubina et al. [6]
- 7.1 TPD spectrum of 2HTTBPP on Ag(111). The applied heating rate was 1 K/s
- 7.2 **a** Constant current image of 2HTTBPP in the multilayer regime. Tip-induced peninsulas in vertical direction were observed ($U = +2.08$ V; $I = 58$ pA). **b** Micrograph recorded with the tip scanning in horizontal direction, inducing horizontal oriented peninsulas. On top of these, the molecules are arranged oblique ($U = +2.08$ V; $I = 33$ pA). **c** Monolayer of 2HTTBPP, which was acquired after heating the multilayer 45 s at 550 K. An oblique structure was observed ($U = +1.65$ V; $I = 20$ pA). **d** Sharp 2D-Fourier peaks evidence the periodicity of the structure
- 7.3 **a** Constant current image of a monolayer of 2HTTBPP ($U = -967$ mV, $I = 46$ pA). The unit cell consists of two molecules; the central molecule has a different azimuthal orientation, as indicated by the *drawn in rectangles*. The *dash-dotted lines* depict molecular rows 1 and 2, differing by the azimuthal orientation and apparent height. **b** The unit cell consists of two molecules; the central molecule has a different azimuthal orientation, as shown in **a**. **c** and **d** Enlarged STM of a monolayer of 2HTTBPP and CoTTBPP
- 7.4 **a** Constant current image showing a monolayer of 2HTTBPP molecules superimposed with corresponding hard-sphere models (+1.12 V and 22 pA). The size of the STM images (**b**)–(**e**) is (3×3) nm². **b** 2HTTBPP extracted from “row 1”; the four protrusions are attributed to the upper *tert*-butyl groups. **c** Figure 7.5b is superimposed with the corresponding hard-sphere models. **d** and **e** show a single 2HTTBPP molecule extracted from “row 2”
- 7.5 Space filling models of 2HTTBPP on Ag(111): **a** Top view illustrating the proposed conformation of 2HTTBPP in “row 1”; **b** conformation of molecules located in “row 2”; **c** side view on (**a**); **d** side view on (**b**); a height difference of the space-filling models with different intra-molecular conformations is clearly visible
- 7.6 **a** and **b** Inverse height modulation of the depicted 2HTTBPP rows (label 1 and 2). The respective rows contain molecules, which exhibit a specific type of deformation (indicated by rectangles, which are drawn with full or dotted line). Remarkably, the molecules in the apparently elevated rows “2” in (**a**) appear lowered in (**b**), even if the corresponding type of deformation of 2HTTBPP is assumed. (**a**) +1.12 V and 22 pA; (**b**) +1.20 V and 23 pA

- 7.7 STM images of 2HTTBPP acquired at different bias voltages. **a** Constant current image recorded at +1.20 V and 23 pA. Four corner molecules and a central one participate to the unit cell, which is drawn in the images. **b–c** Micrographs acquired at ± 284 mV ($I = 23$ pA)
- 7.8 **a** STM image of a monolayer of 2HTTBPP on Ag(111) ($U = +1.87$ V, $I = 18$ pA). **(b)** Mixed monolayer of 2H- and Fe-TTBPP after deposition of 0.02 ML of Fe ($U = -401$ mV, $I = 22$ pA). The layer now exhibits a bimodal appearance, showing 60% of protrusions, which can be attributed to FeTTBPP
- 8.1 TPD spectrum of 2HPc on Ag(111)
- 8.2 Constant current STM image **a** of a complete monolayer of 2HPc and **b** after the deposition of iron ($\theta_{\text{Fe}} = 0.012$ ML) onto the 2HPc monolayer. In **b** some molecules exhibit a central *bright spot*, suggesting the formation of FePc. **c** Height profile extracted along the *greenline* in **(b)**. Space-filling models of 2HPc and FePc are shown above and below the height profile, respectively. The *arrows* indicate the positions of the molecules in the images and the profile. The tunneling parameters of the STM micrographs were: **a** -0.67 V, 39 pA; **b** -1.45 V, 33 pA
- 8.3 **a** Constant current STM image of a monolayer of 2HPc exhibiting two topographically different 2HPc species. **b, d** Clockwise arranged sequence of STM images after the incremental deposition of Fe ($\theta_{\text{Fe}} = 0.012$ ML in each step). The *bar graphs* of each figure show the percentages of the two 2HPc species with different apparent heights and of phthalocyanines with coordinated Fe atoms (=FePc). The tunneling parameters of the STM micrographs were: **a** -0.26 V, 22 pA; **b** -1.44 V, 34 pA; **c** -1.42 V, 22 pA; **d** -0.99 V, 0.33 pA
- 8.4 Constant current STM images of **a** a mixed monolayer of 2HPc (95%) and FePc (5%), generated by direct deposition of a 2HPc/FePc mixture; **b** after vapor-deposition of Fe ($\theta_{\text{Fe}} = 0.012 \pm 0.003$ ML) on this mixed monolayer; **c** a larger area of the layer of image 3b. The following tunneling parameters were applied: **a** -0.88 V, 25 pA; **b** and **c** -1.22 V, 34 pA
- 9.1 Constant current STM images of a monolayer of CoTPP on Ag(111). All STM micrographs were acquired with a current of $I_{\text{set}} = 0.3$ nA and the indicated bias voltages at RT. In **(a–c)** the appearance of depressions, denoted as “pits”, is evident for bias voltages of -1.2 and -0.6 V. **a** and **d** are acquired at the identical surface region, but at different bias voltages; in both images the same specific molecule
- 9.2 Correlation of UP spectra of homogenous monolayers of 2HTPP (*green line*) and CoTPP (*blue line*) with a bias series (-1.2 V to -100 mV in 100 mV steps) of constant current STM images acquired at a current of 0.3 nA. The corresponding bias voltages are marked with the *red arrows*, referring to the energy scale of the UP spectrum (relative to $E_{\text{F}} \equiv 0$)
- 9.3 Constant current STM images of a monolayer of CoTPP **a** and **b** and a 1:2 ex situ mixture of 2HTPP/CoTPP **d** and **e** on Ag(111). Enlarged images **c** and **f** of **b** and **e**, respectively. The tunneling parameters are: **a** $I_{\text{set}} = 0.3$ nA,

- $U_{\text{bias}} = -0.6 \text{ V}$; **b-c** $I_{\text{set}} = 0.3 \text{ nA}$, $U_{\text{bias}} = -1.0 \text{ V}$; **d** $I_{\text{set}} = 41 \text{ pA}$, $U_{\text{bias}} = -1.0 \text{ V}$; **e-f** $I_{\text{set}} = 30 \text{ pA}$, $U_{\text{bias}} = -1.4 \text{ V}$
- 9.4 **a** and **b** Constant current STM images (both with $I_{\text{set}} = 0.27 \text{ nA}$) of a monolayer CoTPP on Ag(111) at negative bias voltage -1 V (**a**) and the same surface area at positive bias voltage $+1 \text{ V}$ (**b**). The apparent contrast inversion is visualized in (**c**), which represents an overlay of the processed STM images in (**a**) and (**b**) as described in the text. The profiles of the apparent height along the colored lines in (**a**) and (**b**) are shown in (**d**)
- 9.5 Local ST spectra reflecting the LDOS of CoTPP (*blue line*) and 2HTPP (*red line*) are plotted. The ST spectra were extracted from CITS data of a mixed layer of CoTPP and 2HTPP
- 9.6 Schemes and STM images illustrating the preparation route to generate the intermixed porphyrin layer consisting of the three different species: 2HTPP, CoTPP and FeTPP. **a** Scheme showing the evaporation of a mixture of 2HTPP and CoTPP onto the Ag(111) substrate. **b, c** Medium-resolution STM images of mixed 2HTPP/CoTPP layers generated from mixtures with different ratios of the two porphyrin species as indicated. Both images were acquired at negative bias voltages around -1 V where the metalloporphyrin (CoTPP) appears as a protrusion. The ratio of the molecules appearing as protrusions is in excellent agreement with the CoTPP portion in the original mixture. **d** Scheme of the in situ evaporation of Fe onto a mixed 2HTPP/CoTPP layer. Fe will metalate available 2HTPP under the release of H_2 with almost 100% yield. By evaporating a defined amount of Fe the fraction of the resulting FeTPP within the intermixed layer can be controlled. Thus the whole process enables the generation of an intermixed 2HTPP, CoTPP and FeTPP layer with defined ratios of the corresponding species
- 9.7 STM images of the same surface area of an intermixed 2H-, Co- and FeTPP at different bias voltages. Obviously at the higher bias voltage as shown in (**a**) and (**b**) a bimodal appearance of the three porphyrin species is observed ($U_{\text{Gap}} = -810 \text{ mV}$ and $I_{\text{Set}} = 30 \text{ pA}$). The 2HTPP appears with a central depression, whereas the two metalloporphyrin species, namely CoTPP and FeTPP appear both with the typical saddle-shape, which means that they are undistinguishable at the actual tunneling condition. In (**c**) and (**d**) the same surface areas as in (**a**) respective (**b**) are imaged at reduced bias voltage ($U_{\text{Gap}} = -240 \text{ mV}$ and $I_{\text{Set}} = 35 \text{ pA}$). It is apparent that at this tunneling condition three different appearances of individual molecules can be observed. Whereas the 2HTPP images remain essentially the same, a fraction of the saddle-shaped molecules now appear with a central protrusion. These molecules can be identified as CoTPP, which means that (in contrast to 2HTPP and FeTPP) CoTPP exhibits a strong bias-dependent appearance in STM. Thus the discrimination of the three species becomes possible at reduced bias voltages
- 9.8 STM micrograph demonstrating an altered appearance of CoTPP upon a changing bias voltage from -1.0 V to -0.3 V ($I = 35 \text{ pA}$) in one image.

In the *upper part* a longish shape of CoTPP is apparent, whereat in the *lower part* of the image a central dot presents the main feature

- 9.9 Experimental (**a, b**) and calculated (**c–j**) STM images of a single CoTPP molecule on Ag(111) at low negative (*top row*) and high negative bias voltages (*bottom row*). As indicated in the images the calculations were performed for the porphyrin adsorbed on Ag(111) and for the porphyrin in the gas phase as well as for different intramolecular geometries ($\Theta = 60^\circ$ and $\Theta = 90^\circ$). The experimental observation of the central protrusion at low bias voltages in (**a**) could only be reproduced in the simulations in (**c**), (**e**) and (**g**), where the CoTPP is adsorbed on Ag(111), i.e., this characteristic feature could not be reproduced for the gas phase calculations as shown in (**i**) even though the same molecular geometry has been used. The experimentally observed saddle-shape in the high bias regime in (**b**) was reproduced assuming $\Theta = 60^\circ$ in (**d**), (**f**) and (**j**). Thus a good agreement for both bias regimes could only be achieved considering both the molecule surface interaction as well as the dihedral angle $\Theta = 60^\circ$. In the calculations an indefinitely sharp tip is assumed, which results in unrealistic details in the calculated STM images. To exemplarily address this problem a gaussian smooth was applied to the images (**e**) and (**d**), the results are shown in (**c**) respective (**d**)
- 9.10 Comparison of calculated (**a, b**) and experimental (**c, d**) constant current STM images and the corresponding scaled molecular models (**e**). The calculations were performed individually for the single molecules with the porphyrins adsorbed on Ag(111) and with a phenyl-ring twist angle of $\Theta = 60^\circ$ (saddle-shape of porphyrin core). The resulting calculated data was then merged in the shown molecule sequence and after that a Gaussian smooth was applied (compare Fig. 9.9c and d)
- 9.11 Density-functional single-particle energy levels of CoTPP (*left column*), FeTPP (*right column*), Ag(111) (*center, black*) and the corresponding adsorbate systems MTPP/Ag(111) (*second and fourth column*). The energy levels have been shifted for each column such that the Fermi energy (E_F) is zero; spin label β corresponds to minority spin channel; energy levels of orbitals which significantly contribute to the STM image (cf. Fig. 4) are color-coded in *red*; *black arrows* indicate the contribution of MTPP and Ag(111) orbitals to the corresponding level in the adsorbate system; contour images of salient orbital densities of MTPP have been generated based on a density contour value of $2.5 \times 10^{-3} \text{ e}/\text{\AA}^3$
- 9.12 Side-view of the orbital density of the highest-occupied orbital (labeled 941β in Fig. 6) in the CoTPP/Ag(111) adsorbate systems at three different density contour values, showing that the d_{z2} orbital on the cobalt center of CoTPP has a constructive overlap with the silver 5s band; *left* $17.5 \times 10^{-4} \text{ e}/\text{\AA}^3$, *center* $1.5 \times 10^{-4} \text{ e}/\text{\AA}^3$, *right* $0.5 \times 10^{-4} \text{ e}/\text{\AA}^3$
- 9.13 **a–c** LDOS maps of CoTPP, respectively 300, 400 and 600 meV below the Fermi level, which were directly calculated out of experimentally acquired current–voltage curves. **d** and **e** Enlarged LDOS maps with corresponding

- semitransparent space-filling models. **f** Superimposition of **d** and **e** illustrating the relative location of the energy-disperse features to each other. **f** Local STS curves extracted at distinct positions of the LDOS maps
- 9.14 **a** LDOS map of FeTPP 130 meV below the Fermi level, which was calculated out of experimentally acquired current–voltage curves. **b** Enlarged LDOS map superimposed with a semitransparent space-filling mode. **c** Local ST curves extracted from FeTPP and 2HTPP
- 9.15 **a** Constant current image recorded at $U = 202$ mV and $I = 36$ pA. **b** Enlarged version of (**a**) with the individual molecules marked by numbers and space-filling models nearby. **c** Corresponding LDOS map of the same area 150 meV below the Fermi level. **d** and **e** Enlarged LDOS maps respectively 200 and 800 meV below E_F . **f** Superimposed version of (**d**) and (**e**) illustrating the relative position of the energy-dispersive features
- 10.1 STM images acquired after successive deposition of iron onto Ag(111). The coverage θ_{Fe} is indicated in the corresponding STM images. The size/scale of all shown micrographs is identical (100×100) nm². The corresponding tunneling parameters are: **a** $I = 166$ pA, $U = -930$ mV; **b** $I = 50$ pA, $U = -263$ mV; **c** $I = 100$ pA, $U = -287$ mV; **d** $I = 50$ pA, $U = -212$ mV; **e** $I = 58$ pA, $U = -289$ mV; **f** $I = 61$ pA, $U = -305$ mV; **g** $I = 44$ pA, $U = -199$ mV; **h** $I = 68$ pA, $U = -302$ mV; **i** $I = 68$ pA, $U = -313$ mV
- 10.2 **a–d** Space filling models of flat lying 2HPc and FeTPP on Ag(111): **a** *top view* of 2HPc, **b** *top view* of FeTPP, **c** *side view* of 2HPc, **d** *side view* of FeTPP; for the latter, the terminal phenyl rings determine that the porphyrin macrocycle is lifted off from the surface. **e** STM image ($I = 32$ pA, $U = -1.49$ V) showing a square arrangement of FePc molecules on Ag(111). The central dot per molecule can be attributed to the iron ion. Corresponding space filling models in the image illustrate the arrangement. **f** STM image ($I = 61$ pA, $U = -10$ mV) showing a square arrangement of FeTPP molecules on Ag(111). Each of the molecules exhibits three dots, which correspond with the position of two opposing pyrrol rings and the central iron ion, emphasized by the superimposed models
- 10.3 STM images obtained **a** after deposition of $\theta_{Fe} = 0.3$ ML onto a monolayer of 2HTPP ($I = 34$ pA, $U = -197$ mV) and **b** the corresponding blow-up of the area marked with a *white square* in **a** highlighting the two dimensional iron islands. The small *bright spots* (~ 1 nm diameter) correspond to a complete monolayer of FeTPP due to metalation of 2HTPP with Fe. **c** STM image obtained after deposition of $\theta_{Fe} = 0.2$ ML onto a monolayer of 2HPc ($I = 23$ pA, $U = -1.88$ V) and **d** the corresponding blow-up of the area marked with *white square* in **c** highlighting two different types of Fe islands. The small *bright spots*

- (~ 1 nm diameter) correspond to a complete monolayer of FePc due to metalation of 2HPc with Fe
- 10.4 STM images obtained after deposition of **a** $\theta_{\text{Fe}} = 0.8$ ML onto a 2HTPP monolayer ($I = 36$ pA, $U = -1.21$ V), **b** $\theta_{\text{Fe}} = 0.6$ ML onto a 2HPc monolayer ($I = 41$ nA, $U = -1.50$ V)
- 10.5 STM images obtained after deposition of roughly 2 ML of iron onto **a** Ag(111) ($I = 61$ pA, $U = -305$ mV), **b** 2HPc on Ag(111) ($I = 32$ pA, $U = -1.20$ V) and **c** 2HTPP on Ag(111) ($I = 47$ pA, $U = -1.10$ V)
- 11.1 STM image series of a CoTPP layer on Ag(111) during exposure to NO at RT. The corresponding NO dosages are inserted in the micrographs. The rearrangement with increasing NO dose starting from the undisturbed square order in (**a**), to an almost hexagonal arrangement in (**e**), to an oblique structure in (**f**) is obvious and clearly develops towards larger unit cells. The unit cell areas as extracted from the experimental data are: **a** 1.91 nm² and **f** 2.74 nm². All images have a size of (47×47) nm² and were acquired at $U_{\text{BIAS}} = -0.23$ V and $I_{\text{SET}} = 300$ pA
- 11.2 **a–o** STM images of ordered phases of CoTPP on Ag(111) before (**a–c**) and after (**d–o**) NO exposure. The corresponding values for NO exposure, the lattice vectors and angle and the density of the molecules per unit area are inserted in column 1. The respective area of the unit cell and the tunneling parameters are as follows: **a** $U = -1.18$ V, $I = 58$ pA/A = 1.96 nm²; **d** $U = -1.9$ V, $I = 45$ pA/A = 2.22 nm²; **g** $U = -1.90$ V, $I = 45$ pA/A = 2.38 nm²; **j** $U = -1.90$ V, $I = 48$ pA/A = 2.56 nm²; **m** $U = -0.94$ V, $I = 70$ pA/A = 3.13 nm²
- 11.3 XP spectra of the N 1s region of a CoTPP layer on Ag(111) after exposure to 5000 L NO. The corresponding fitted peaks are identified with different nitrogen species as indicated (the XPS data are extracted from [12])
- 11.4 **a** Constant current image of the *straight square* phase ($U = -1.90$ V, $I = 45$ pA). A fraction of molecules appears modified (marked with *circles*). **b** Micrograph of the *hex I* phase exhibiting three molecules which appear modified ($U = -1.9$ V, $I = 45$ pA), **c** enhanced image of (**a**)
- 11.5 **a** He-I UP spectra ($h\nu = 21.22$ eV) of (A) clean Ag(111) surface, (B) CoTPP monolayer, (C) NO-CoTPP monolayer, and (D) after heating the NO-CoTPP monolayer to 500 K for removal of the NO ligand [2]. **b** Local ST spectra recorded at opposing pyrrol rings and the central cobalt. **c** Enlarged STM image of CoTPP (label 2), including a modified version of the porphyrin (label 1), which is probably induced by attachment of NO ($U = -1.9$ V, $I_{\text{T}} = 45$ pA)
- 12.1 **a** *Top* and **b** *side view* on space filling models of 2HOEP on Ag(111). The upwardly directed conformation of the ethyl groups was chosen based on high-resolution STM images from literature [2]. **c** *Top* and **d** *sideview* on a MTPP model, emphasizing the distance of the porphyrin macrocycle to the surface
- 12.2 Simultaneously acquired TPD spectra of 2HOEP and CoOEP on Ag(111). The applied heating rate was 1 K/s

- 12.3 **a** Long-range ordered intermixed 2HOEP/CoOEP monolayer with a nominal amount of 2:1 ($U = -1.17$ V, $I = 31$ pA). **b** High-resolution constant current image ($U = -200$ mV, $I = 37$ pA). **c** The micrograph in **b** was superimposed with corresponding space filling models. The unit cell is drawn in, exhibiting lattice vectors of $a = 1.55 \pm 0.10$; $b = 1.55 \pm 0.10$; $\alpha = 60 \pm 3^\circ$
- 12.4 Series of STM images of a 2HOEP/CoOEP layer acquired at different bias voltages; **a** $U = -200$ mV ($I = 37$ pA), **b** $U = -400$ mV ($I = 39$ pA), **c** $U = -600$ mV ($I = 36$ pA) and **d** $U = -1.00$ V ($I = 34$ pA)
- 12.5 **a** and **b** Enlarged STM image of an intermixed 2HOEP/CoOEP layer acquired at -200 mV and -1.00 V respectively. **c** and **d** Extracted height profiles over the side groups of CoOEP and 2HOEP at the indicated positions (**a** $I = 37$ pA, **b** $I = 34$ pA)