Adsorption of cobalt (II) octaethylporphyrin and 2H-octaethylporphyrin on Ag(111): new insight into the surface coordinative bond

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Abstract. The adsorption of cobalt (II) octaethylporphyrin (CoOEP) and 2H-octaethylporphyrin (2HOEP) on Ag(111) was investigated with scanning tunneling microscopy (STM) and photoelectron spectroscopy (XPS/UPS), in order to achieve a detailed mechanistic understanding of the surface chemical bond of coordinated metal ions. Previous studies of related systems, especially cobalt (II) tetraphenylporphyrin (CoTPP) on Ag(111), have revealed adsorption-induced changes of the oxidation state of the Co ion and the appearance of a new valence state. These effects were attributed to a covalent interaction of the Co ion with the silver substrate. However, recent studies show that the porphyrin ligand of adsorbed CoTPP undergoes a pronounced saddle-shape distortion, which could alter the electronic structure and thus provide an alternative explanation for the new valence state previously attributed to the formation of a surface coordinative bond. With the octaethylporphyrins investigated here, which were found to adsorb in a flat, undistorted conformation on Ag(111), the effects of geometric distortion can be separated from those of the electronic interaction with the substrate. The CoOEP monolayer gives rise to an adsorption-induced shift of the Co 2p signal (−1.9 eV relative to the multilayer), a new valence

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state at 0.6 eV below the Fermi energy, and a work-function shift of $-0.84$ eV (2HOEP: $-0.44$ eV) relative to the clean surface. Comparison with data for the distorted CoTPP confirms the existence of a covalent ion–surface interaction that is insensitive to the conformation of the ligand.

1. Introduction

In recent years, adsorbed coordination compounds have attracted considerable attention with respect to the controlled functionalization of surfaces on the nanoscale [1]. Important examples are supramolecular, two-dimensional metal-organic coordination networks (2D-MOCNs) [2] and planar metal complexes such as metalloporphyrins and metallophthalocyanines [3]–[5]. The coordination networks are generally synthesized by an in situ approach, which employs co-deposition of the metal and the ligand on the substrate surface [6]. In contrast, thin films of metalloporphyrins and metallophthalocyanines can often be prepared by ex situ metalation of the free porphyrin base and subsequent vapor deposition of the intact complexes [7, 8]. Alternatively, metalloporphyrin monolayers have been prepared by direct metalation [9] of monolayers of the free base with the stoichiometric amounts of vapor-deposited metals such as Co [10], Fe [11, 12], Zn [13] or Ce [14]. The in situ procedure, which is similar to that used for the synthesis of 2D-MOCNs, is advantageous, if unusual, and especially reactive oxidation states of the metal ions are involved. Metalation of porphyrin multilayers and phthalocyanines is also possible [15].

The metal centers of many M(II)-porphyrins and M(II)-phthalocyanines possess no axial ligands and therefore represent coordinatively unsaturated sites with potential catalytic or sensor functionality. In the adsorbed state, the underlying metal surface can occupy one of the axial sites and, as an additional ligand, influence the electronic structure of the metal center. The nature of this interaction, which is the main focus of this paper, has been studied previously, in particular on the example of the coordinated Co ion [3]. For example, Hipps and coworkers investigated films of cobalt tetraphenylporphyrin (CoTPP), along with other M(II)-tetraphenylporphyrins, on Au(111) [7, 16, 17]. Scanning tunneling spectroscopy (STS) on CoTPP submonolayer films revealed the existence of a valence state at 0.6 eV below the Fermi energy ($E_F$) [17]. This observation was followed up by Lukasczyk et al, who studied mono- and multilayers of CoTPP on Ag(111) with photoelectron spectroscopy and compared
with monolayers of the metal-free tetraphenylporphyrin (2HTPP) in order to clarify the role of the metal center in the interaction [18]. It proved that the direct contact between CoTPP in the monolayer and the Ag surface leads to changes of the valence electronic structure and the Co core-level energies. In particular, the UV photoelectron (UP) spectrum of the CoTPP monolayer shows a new signal at 0.6 eV below $E_F$, [8, 18] similar to the previous STS observations for CoTPP on Au(111) [17]. This new valence state is absent in the multilayer UP spectrum of CoTPP and the monolayer spectrum of 2HTPP on Ag(111), indicating that it is induced by the interaction between the molecule and the substrate and related to the presence of the Co ion [3, 18].

Further investigations with x-ray photoelectron spectroscopy (XPS) proved that the oxidation state of the Co ion is strongly influenced by the Ag surface. In the CoTPP multilayer, the Co 2p signal appears at the typical Co (II) position (780.0 eV), in agreement with the formal oxidation state of the ion. In the monolayer, however, the Co 2p binding energy (BE) is lowered by 1.8 eV and the signal is thus shifted to a typical Co(0) position. This shift is much larger than the corresponding shifts of the C 1s and N 1s signals (0.2–0.3 eV), indicating that the Ag surface interacts more strongly with the Co ion than with other parts of the molecule. Considering possible initial state contributions, the reduced Co 2p BE suggests an increase of electron density at the Co ion, i.e. a partial reduction. To explain these findings, it was proposed that semi-occupied or vacant Co 3d orbitals (most likely the Co 3d$_{z^2}$ that extends in the axial direction) overlap with electronic states of matching energy and symmetry of the Ag surface, resulting in the formation of new mixed states below $E_F$. These states take up electrons from the Fermi sea of the Ag(111) surface. Therefore, this model provides a consistent explanation for the occurrence of new electronic states in the valence region as well as for the transfer of electron density from the substrate to the Co ion [3, 18]. In addition, it was shown that all manifestations of the Co–Ag interaction (new valence state, core-level shifts) disappear, if a nitric oxide (NO) ligand coordinates to the remaining vacant axial site on the Co ion [19]. This effect has been interpreted as a result of the ‘surface trans effect’ [3].

The interpretation outlined here [3, 18, 19], however, has been challenged by a combined scanning tunneling microscopy (STM) and NEXAFS study of CoTPP on Cu(111), which focuses on the interplay between the molecular conformation and electronic structure. Using NEXAFS, it was shown that the CoTPP molecules undergo a surface-induced distortion and acquire a saddle-shaped conformation in the adsorbed state [20]. In this geometry, two opposing pyrrole rings of the porphyrin macrocycle are bent toward the surface by 20° relative to the surface plane, while the other two pyrrole rings are bent away from the surface. The distortion is induced by intramolecular repulsion between the peripheral phenyl groups and the porphyrin ring, which enclose a dihedral angle of only 35°. For the free CoTPP molecule, it was shown that angles below 60° lead to a deformation of the porphyrin macrocycle and that a dihedral angle of 35° causes a substantial increase of the total energy of the molecule (between 73.7 kJ mol$^{-1}$ at 40° and 136.8 kJ mol$^{-1}$ at 30°) [21]. The averaged tunneling spectrum of the thus distorted CoTPP molecule on Cu(111) shows an electronic state at 0.6 eV below $E_F$ [20], similar to the previous observations for CoTPP/Au(111) (with STS) [17] and CoTPP/Ag(111) (with UV photoelectron spectroscopy (UPS) [18] and STS [8]), where this state was attributed to the interaction between the Co ion and the metal substrate. However, visualization of the frontier orbitals of CoTPP/Cu(111) by tunneling spectroscopy mapping (dI/dV mapping) revealed that this state is not localized on the central Co ion. Instead, the maximum orbital coefficients appear at two opposing pyrrole units of the deformed porphyrin ligand [20]. These findings cast doubts...
Figure 1. (A) Ball-and-stick model of cobalt octaethylporphyrin (CoOEP). For clarity, the carbon atoms of the conjugated porphyrin cycle are shown in green, those of the ethyl groups in gray. Space-filling models of (B) CoOEP and (C) free-base octaethylporphyrin (2HOEP) in top and side view.

on the previous interpretation [18, 19] of the adsorption-induced valence signal at 0.6 eV: if this signal is related to the Co–substrate interaction, one should expect that the Co ion (rather than the pyrrole units of the ligand) appears as a bright protrusion when the bias voltage is adjusted so as to allow for tunneling from this state. Instead, the dI/dV mappings suggest an alternative explanation for the changes in the valence electronic structure: the occurrence of the state at 0.6 eV may be directly related to the deformation, which lifts the degeneracy of electronic states (occupied and unoccupied) and thereby also influences the surface chemical bond of the ligand. Accordingly, the new signal could arise from the ligand–surface interaction (for example, occupation of the former lowest unoccupied molecular orbital (LUMO) by electrons from the substrate, as has been observed for other aromatic molecules such as NTCDA and PTCDA on Ag(111) [22, 23]) rather than from the interaction between the metal center and surface. The lack of an adsorption-induced new valence state in the case of the 2HTPP monolayer could be explained with a different degree of deformation of the metal-free ligand. (Note that STM and NEXAFS studies of the structurally similar 2H-tetrapyridylporphyrin on Cu(111) suggest that the adsorbed metal-free macrocycle is more distorted than the corresponding metal complex [24, 25].)

To discriminate between the effects of molecular deformation and surface interaction on the electronic structure and to clarify the origin of the state at 0.6 eV below $E_F$, we studied cobalt (II) octaethylporphyrin (CoOEP) monolayers on Ag(111) with XPS, UPS and STM. In CoOEP (figure 1), the Co ion is exposed to the same coordination environment as in CoTPP, but the molecules adsorb in a flat, undistorted conformation, as will be shown in this paper. This is to be expected based on the molecular structure and is in line with the previous STM investigations of NiOEP on Au(111) [26]–[28], Cu(111), Ag(001), Ag(111) [29] and graphite [30, 31], and CoOEP on Au(111) [32]. Here the observed surface-induced changes in the valence electronic structure of CoOEP/Ag(111), however, are virtually identical to those reported for CoTPP, proving that they are predominately caused by the interaction between the metal center and the substrate, and not by molecular distortions.

As mentioned above, our fundamental studies on surface coordination chemistry have an additional, more applied background, which is related to the catalytic and sensor functionality of adsorbed metalloporphyrins and -phthalocyanines. For example, CoTPP on a TiO$_2$ support was shown to catalyze the reduction of nitrogen oxides (NO, NO$_2$) with H$_2$ or CO to
N₂, H₂O and CO₂, which is an important reaction in exhaust gas detoxification [33]–[36]. Since neither CoTPP nor TiO₂ are active alone, it has been proposed, based on EPR and UV–VIS data, that electron transfer from the TiO₂ surface to the Co ion is responsible for the activation. At the solid/liquid interface, supported Mn and Co porphyrins catalyze the epoxidation of cis-silbene and the oxidation of hydroquinone to benzoquinone, respectively [37, 38]. A binuclear Mn(II)–Mn(III) complex on silica was found to be active in various epoxidation reactions [39]. In these cases, molecular oxygen was used as the oxidation agent, which makes the catalysts especially interesting for future industrial applications. The sensor functionality of adsorbed metalloporphyrins was for example demonstrated in an electronic gas sensor, in which a Zn porphyrin monolayer was deposited on the gate electrode of a transistor [40]. Coordination of organic molecules, in particular nitrogen bases such as pyridine, causes characteristic and reversible changes in the drain current. Earlier, it had been shown that metalloporphyrins can be used in colorimetric gas sensors, which rely on characteristic color changes resulting from coordination of a molecule at the metal center [41]–[43]. Furthermore, self-assembled monolayers of metalloporphyrin oligomers on an Au surface show electronic communication along their backbone and possess the potential to control charge transfer over long distances [44]. Another field in which metalloporphyrins and phthalocyanines could play an important role in the future are dye solar cells, in which the complexes act as photosensitizers [45]–[49]. The interaction between the metal center and the solid (such as TiO₂), however, is probably of secondary importance in these systems. Although none of the above-mentioned examples have yet been used on a large industrial scale, there is a considerable potential for such applications.

2. Experimental

The experiments were performed in two separate ultra-high vacuum (UHV) systems with base pressures below 2 × 10⁻¹⁰ mbar. For XPS and UPS, a Scienova 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, overall resolution 0.3 eV) were employed. In addition to the XP spectrometer, the system comprises a differentially pumped gas discharge lamp for UPS, low-energy electron diffraction (LEED) optics (ErLEEd-1000A), two ion guns for cleaning and ion-scattering experiments, a mass spectrometer (Pfeiffer QMG 422) and several evaporators. The UP spectra were acquired with He–I radiation (21.22 eV) and a sample bias of −10 V. The overall energy resolution for UPS was < 0.1 eV. During XPS measurements, the photoelectrons were detected at an angle of 70° relative to the surface normal for increased surface sensitivity, while normal emission was used in UPS. All binding energies were referenced to the Fermi edge of the clean Ag surface (\(E_b = 0\)). The work function values reported in this work were extracted from the spectral width of the UP spectra, i.e. the distance between the Fermi edge and the secondary electron cutoff. The STM experiments were carried out using RHK UHV VT STM 300 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 [50].

The substrate was a silver single crystal (purity > 99.999%) with a polished (111) surface, which was aligned to < 0.1° with respect to the nominal orientation. 2HOEP, CoOEP, 2HTPP and CoTPP (specified purity >98%) were degassed in vacuo by heating to 413 K for 24 h.
Figure 2. (A) STM micrograph of an intermixed 2HTPP/CoTPP layer prepared by vapor deposition of a nominal 2:1 mixture of the respective species onto the Ag(111) surface. Counting over large areas results in 33% protrusions, which can be identified with CoTPP molecules. Tunneling parameters: \( I_{\text{set}} = 44 \text{ pA}, U_{\text{gap}} = -1.21 \text{ V} \). (B) Space-filling model of the saddle-shape distorted molecules in top and side view. (C, D) STM micrograph of a self-assembled CoTPP layer on Ag(111). Tunneling parameters: \( I_{\text{set}} = 58 \text{ pA}, U_{\text{gap}} = -1.18 \text{ V} \). In (D) the micrograph is superimposed by the scaled models of the distorted CoTPP molecules and the unit cell is indicated \((a = b = 1.40 \pm 0.05 \text{ nm})\).

Well-ordered monolayers of these porphyrins were prepared by vapor deposition of the respective multilayers onto the Ag(111) substrate held at 300 K and subsequent annealing at 510 K. During deposition, the temperature of the Knudsen cell was 530 K, which led to a flux of approximately 0.1 ML min\(^{-1}\). The coverage of the porphyrin monolayers on the Ag substrate, defined as the number of adsorbed molecules per surface atom, was experimentally determined with STM and corresponded to 0.035 ML.

3. Results

3.1. STM

The STM micrograph in figure 2(a) shows an intermixed monolayer of 2HTPP and CoTPP on Ag(111) and was acquired in constant-current mode with a bias voltage of \(-1.21 \text{ V}\). The layer was prepared by vapor deposition of a 2HTPP/CoTPP mixture. At the given tunneling conditions, individual CoTPP molecules are easily distinguishable from the 2HTPP molecules, since they appear as protrusions. This contrast stems from an enhanced tunneling contribution of the state at 0.6 eV below \(E_F\), which was previously assigned to the CoTPP/Ag(111) adsorption complex as discussed above. Consistently, the contrast between the species tends
Figure 3. (A) STM micrograph of an intermixed 2HOEP/CoOEP layer prepared by vapor deposition of a nominal 2:1 mixture of the respective species onto the Ag(111) surface. Counting over large areas results in 34% protrusions, which can be identified with CoOEP molecules. Tunneling parameters: $I_{\text{set}} = 31 \text{ pA}, U_{\text{gap}} = -1.17 \text{ V}$. (B, C) STM micrograph of a self-assembled intermixed 2HOEP/CoOEP layer on Ag(111). Tunneling parameters: $I_{\text{set}} = 37 \text{ pA}, U_{\text{gap}} = -0.20 \text{ V}$. In (C), the micrograph is superimposed by scaled models of the corresponding OEP molecules and the unit cell is indicated ($a = 1.55 \pm 0.10 \text{ nm}, b = 1.45 \pm 0.10 \text{ nm}$).

to vanish for bias voltages significantly larger than $-0.6 \text{ eV}$, e.g. $> -0.2 \text{ V}$ [8]. The self-assembled layer exhibits a square order with a lattice constant of $1.40 \pm 0.05 \text{ nm}$, which is the typical arrangement for various tetraphenylporphyrins on different substrates ([3] and references therein). In figure 2(c), a submolecularly resolved constant-current STM image of CoTPP on Ag (111) is depicted. Individual CoTPP molecules appear with the aforementioned cigar- or saddle-shape in which the ‘ends’ of the cigar correspond to two opposing pyrrole groups as indicated by the superimposed scaled models in figure 2(d). As discussed above, the origin of the observed shape is interpreted as due to a conformational adaptation upon adsorption, e.g. for CoTPP on Ag(111) [3] and Cu(111) [20], a considerable rotation of the phenyl substituents is proposed, as shown in figure 2(b). As a consequence of the resulting intramolecular repulsion, the central porphyrin macrocycle is deformed, such that two opposing pyrrole groups are tilted upwards (marked yellow in figure 2(b)) and the other two downwards. The appearance in STM is then dominated by the topography of the distorted molecule resulting in the cigar shape.

In figure 3, a molecularly resolved STM image of an intermixed 2HOEP and CoOEP monolayer is depicted. The preparation of this layer was realized analogous to the one
Figure 4. Co 2p$_{3/2}$ XP spectra of CoOEP on Ag(111). (A) CoOEP multilayer (∼10 ML), (B) CoOEP monolayer.

described above for the 2HTPP/CoTPP layer, i.e. by vapor deposition of a mixture of the corresponding (OEP) species. The CoOEP molecules can again be identified by their appearance as protrusions in the constant-current STM image acquired at a bias voltage of −1.17 V. It should be mentioned that this contrast also tends to fade for bias voltages close to the Fermi energy, i.e. > −0.2 V (not shown here). Considering the interpretation for the discrimination of CoTPP above [8], this finding consequently indicates an electronic state of the CoOEP/Ag(111) adsorbate complex between −1.17 and −0.2 eV, which is indeed evidenced by UPS at −0.6 eV as presented in figure 5 and discussed in detail below. In contrast to the quadratic arrangement of the 2HTPP/CoTPP monolayer, the intermixed 2HOEP/CoOEP monolayer exhibits an oblique (but almost hexagonal) arrangement with lattice constants of $a = 1.55 \pm 0.10$ nm and $b = 1.45 \pm 0.10$ nm and an enclosed angle $\alpha = 60^\circ \pm 3^\circ$. A closer inspection of the intramolecular conformation of the OEP molecules is possible on the basis of the submolecularly resolved STM image shown in figure 3(b). The individual molecules appear either with a central depression (2HOEP) or with an elevated center (CoOEP), surrounded by eight protrusions. We identify these features with the eight ethyl groups pointing away from the surface (compare figure 1), in line with previous STM studies of similar systems (for example NiOEP/Au(111) [26] and CoOEP/Au on mica [51] at the solid/vacuum interface; CoOEP/Au(111) [32] and NiOEP/HOPG [30] at the solid/liquid interface). The superimposed and scaled models in figure 3(c) are in perfect agreement with our interpretations. We also found that the symmetry of the individual OEP molecules in STM as observed in figure 3(b) persists at least over a bias voltage range from −1.2 to −0.1 V, i.e. there is no indication for a reduced symmetry due to deformation, as was found for the conformationally adapted CoTPP and discussed in detail above. Consequently, we conclude that the OEP molecules, in particular CoOEP, adsorb on Ag(111) such that the porphyrin macrocycle remains in a flat, undistorted conformation.

3.2. XPS

Figure 4 shows the Co 2p$_{3/2}$ XP spectra of CoOEP multilayer and monolayer on the Ag(111) surface. The main peak for the CoOEP multilayer is located at 780.6 eV, which is a typical
Table 1. XPS core-level shifts (in eV) between multilayer and monolayer coverages of various porphyrins on Ag(111). All signals shift toward lower BE in the monolayer. Data for CoTPP taken from [18].

|        | CoOEP | 2HOEP | CoTPP | 2HTPP |
|--------|-------|-------|-------|-------|
| Co 2p  | 1.9   | –     | 1.8   | –     |
| C 1s   | 0.6   | 0.2   | 0.2   | 0.3   |
| N 1s   | 0     | 0.3   | 0.3   | 0.1   |

position for cobalt (II) compounds [52, 53] and, thus, in agreement with the formal oxidation state of the cobalt ion in CoOEP. The signal shows a complex multiplet structure, which results most likely from the open-shell character of the Co ion (d⁷) and is in agreement with previous measurements on CoTPP and cobalt (II) tetakis-(3,5-bis-(tert-butylphenyl) porphyrin (CoTTBPP) [16, 18]. In the XP spectrum of the CoOEP monolayer, the main peak appears at a much lower BE of 778.9 eV, which is typical of Co(0). Again, the signal shows a satellite structure that is attributed to the paramagnetic character of the Co center. Direction and magnitude of the surface-induced chemical shift of the Co 2p signal are very similar to the shifts observed previously for CoTPP and CoTTBPP on Ag(111) [18].

The strong shift of the Co 2p signal (−1.9 eV, see also table 1), suggests a direct electronic interaction of the Co ion with the underlying Ag surface. If initial state effects are taken into account, the direction of the shift can be interpreted as a partial reduction of the Co ion by electrons from the silver surface, as has been proposed for CoTPP on Ag(111) [18]. In addition, final state effects such as charge-transfer screening, which would also indicate a substantial electronic interaction between the Co ion and the Ag surface, could contribute to the shift.

In contrast to the substantial shift of the Co 2p3/2 signal, the C 1s signals of CoOEP multilayer and monolayer differ by only 0.6 eV, while no significant shift is observed for the N 1s signal (see table 1 and the XPS data in the supporting information). The shift of the C 1s signal toward lower BE can be attributed to final state effects, especially a more effective screening of the final core hole by the metal surface as compared with the weaker dielectric screening in the multilayer. The larger shift of the C 1s signal of CoOEP as compared with that of CoTPP (see table 1) most likely reflects the shorter average distance of the C atoms to the substrate for CoOEP and the resulting more efficient screening. The negligibly small shift of the N 1s signal suggests that the relaxation shift is compensated by a concomitant chemical shift to higher binding energies. This shift possibly results from a chemical bond between the N atoms and the Ag surface, which leads to a transfer of electron density to the substrate. Interactions of the porphyrin nitrogen atoms and the substrate have previously been reported for FeOEP on a Co film [54]. The bonding mechanism of CoOEP on Ag(111) can thus be described by a bonding–backbonding synergism, in which electron density is transferred from the substrate to the Co ion and partially returned to the substrate via the nitrogen atoms.

3.3. UPS and work function changes

Figure 5 shows UV photoelectron spectra of (a) CoOEP multilayer, (b) CoOEP monolayer, (c) 2HOEP monolayer and (d) clean Ag(111). The multilayer spectrum (figure 5(a)) features an intense signal centered at 1.9 eV below EF. This signal is attributed to the highest occupied
Figure 5. He–I UP spectra of (a) CoOEP multilayer (∼5ML), (b) CoOEP monolayer, (c) 2HOEP monolayer, and (d) the clean Ag(111) surface. The full-range spectra can be found in the supporting information, figure S3, available from stacks.iop.org/NJP/11/125004/mmedia.

molecular orbital of the complex, possibly a singly occupied orbital (SOMO). In the monolayer spectrum (figure 5(b)), this peak is shifted to 1.7 eV, most likely due to the more efficient screening by the metal surface (relaxation shift). Apart from this signal, the monolayer spectrum shows an additional peak at 0.6 eV, which is absent in the multilayer spectrum and therefore related to the interaction of the CoOEP molecule with the Ag(111) surface. In order to clarify the role of the cobalt ion in this interaction, comparison with a monolayer of the metal-free ligand 2HOEP was made. In the respective UP spectrum (figure 5(c)), the additional peak is absent, indicating that the cobalt ion is indeed involved in the interaction. In fact, the 2HOEP monolayer spectrum completely lacks adsorbate-induced contributions in the energy range (or they have very low intensity). Thus, the SOMO-related signal that appears in the CoOEP spectra is probably also related to the presence of the Co ion and most likely corresponds to orbitals with predominant Co 3d character. Comparison with the UP spectra of CoTPP on Ag(111) [18] show that the SOMO-related signal appears at 2.3 eV in the multilayer spectrum and at 1.8 eV in the monolayer, i.e., at slightly higher binding energies than in the case of CoOEP. The interaction-induced signal at 0.6 eV, however, has the same position for CoTPP and CoOEP.

Additional information about the nature of the molecule–substrate interaction was obtained from the adsorbate-induced work function changes (or vacuum level shifts), which were extracted from the UP spectra as described in section 2. As shown in table 1, CoOEP and 2HTPP monolayers lower the work function of the Ag(111) surface by 0.84 and 0.44 eV, respectively. Reductions of the work function by organic molecules have frequently been observed and have been attributed to the Pauli repulsion between the electrons of the molecule and those of the metal. This ‘cushion effect’ leads to a depletion of charge between the molecule and the metal and is thus responsible for the formation of the adsorption-induced dipole layer, which causes the work function change [55]. The difference in $\Delta \Phi$ between the monolayers of CoOEP and
2HOEP may be attributed to the presence of the Co ion and its electronic interaction with the Ag surface. In table 2, the work function changes caused by CoOEP and 2HOEP are compared with the respective data for CoTPP and 2HTPP on Ag(111), as were reported in [18]. CoOEP induces a larger work function change than CoTPP, whereas 2HOEP has less influence on the work function than 2HTPP. Note that the work function change induced by 2HTPP is especially large and even exceeds the value for CoTPP. This could be interpreted as the result of a distortion-induced large dipole moment of the 2HTPP molecules. CoTPP acquires a smaller dipole moment, because the Co ion counteracts the vertical displacement of the electronegative N atoms. The table also shows the positions of the highest occupied molecular levels; these values equal the barrier heights for hole injection at the organic/metal interface [56]. All data in table 2 refer to monolayer coverage. The energy of the highest occupied level for 2HOEP could not be determined with certainty, because the intensity of the levels close to the Fermi energy is obviously too low. The first clearly visible signal at 4.1 eV below \( E_F \) is probably not derived from the HOMO state.

A schematic energy diagram of the CoOEP/Ag(111) interface at monolayer coverage is presented in figure 6. It was derived from UPS data within the approximation of Koopmans’ theorem [57] and is in line with the work of Seki and co-workers [56, 58] about porphyrin/metal interfaces, in which the energy levels of the porphyrins are fixed to the vacuum level of the metal with a finite energy shift at the interface (work function or vacuum level shift).

### Table 2. Work function changes, \( \Delta \Phi \), and energies of the highest occupied molecular levels with respect to \( E_F \) (in eV). Data for CoTPP and 2HTPP from [18].

|         | CoOEP | 2HOEP | CoTPP | 2HTPP |
|---------|-------|-------|-------|-------|
| \( \Delta \Phi \) | \(-0.84\) | \(-0.44\) | \(-0.72\) | \(-0.84\) |
| \( E_F^\gamma \) | \(-0.6\) | \((-4.1)\) | \(-0.62\) | \(-2.4\) |

4. Discussion

As outlined above, the UV photoelectron spectrum of a CoTPP monolayer on Ag(111) shows a new electronic state at 0.6 eV below \( E_F \), which was previously attributed to the electronic interaction between the Co ion and the Ag surface [18]. Since then, it has been shown that CoTPP undergoes substantial saddle-shape distortion on Cu(111) [20] and Ag(111) (this paper). In addition, visualization of the frontier orbitals of CoTPP/Cu(111) by spatial \( dI/dV \) mapping reveals a state at 0.6 eV below \( E_F \) that is localized on the porphyrin ring rather than on the Co ion [20]. These findings raise the question of whether the adsorption-induced changes in the valence electronic structure, in particular the state at 0.6 eV below \( E_F \), result from the geometric deformation of the molecule rather than from a direct interaction of the metal center with the surface. To decide this question, we studied monolayers of CoOEP, in which the porphyrin ring remains undistorted upon adsorption on Ag(111), as was shown in section 3.1. The most likely reason for this difference to CoTPP is the fact that the eight peripheral ethyl groups can point to one side of the macrocycle. In this conformation, the porphyrin ring and the eight aliphatic C atoms of the \( \text{CH}_2 \) groups directly connected to the ring lie in one plane while the terminal methyl groups point upwards, that is, toward the vacuum. The molecule can thus adsorb on a flat surface without significant out-of-plane deformation of the porphyrin ring.
Figure 6. Schematic diagram of the electronic levels at the CoOEP/Ag(111) interface at monolayer coverage. $\Phi$ is the work function of clean Ag(111) and $\Delta \Phi$ the adsorbate-induced work function shift or shift of the vacuum level. IP denotes the ionization potential of the adsorbed CoOEP. $\varepsilon_V^F$ is the position of the highest occupied molecular level with respect to $E_F$ and equals the barrier height for the hole injection at the organic/metal interface. H is the highest adsorbate-related level, induced by the interaction between the Co ion and the substrate. H-1 is the former highest occupied level of the CoOEP molecule.

Despite the undistorted conformation of the adsorbed molecule, the monolayer UP spectrum of CoOEP shows the same signal at 0.6 eV and the same enhanced tunneling contribution in this energy range as was found for the distorted CoTPP molecule. This is clear proof that the 0.6 eV state is directly related to the interaction of the Co porphyrin with the surface and not caused by molecular distortion. The fact that the state is not found in the monolayer spectrum of the metal-free 2HOEP indicates that the Co ion plays the decisive role in this interaction.

Based on the above-mentioned study of CoTPP/Cu(111) [20] one may suspect that the Co ion does not directly bind to the metal surface, but that the interaction occurs through the porphyrin ligand. However, the large surface-induced shift of the Co 2p signal, $-1.9$ eV for CoOEP/Ag(111), and the much smaller shifts of the C 1s and N 1s signals make this interpretation seem unlikely. In addition, the coordinatively unsaturated, open-shell Co ion with its relatively low-lying unoccupied d levels is more likely to engage in additional chemical bonds than the N or C atoms of the porphyrin ligand. Interestingly, the $dI/dV$ mappings for CoTPP/Cu(111) [20] at a bias voltage of $-0.4$ eV show a state to which both the metal center and the porphyrin ring contribute. Considering the different surface electronic structures of
Cu(111) and Ag(111), the question arises whether the states at −0.6 eV on CoTPP/Cu(111) and CoTPP/Ag(111) are indeed comparable or whether for example the state at −0.4 eV accounts for the Co–substrate interaction in the case of Cu(111). In this context, it is interesting to note that no interaction-induced signal at −0.6 eV was observed for CoTPP and CoOEP monolayers on Au(111) in our preliminary UPS experiments [59], contrary to the earlier STS study by Hipps and co-workers [17].

Another interesting question is related to the distance dependence of the interaction. In the previous work, Barlow et al compared tunneling spectra of cobalt phthalocyanine (CoPc) and CoTPP on Au(111) and found that the former shows increased tunneling through the metal center [17]. This was explained with the smaller Co–surface distance for CoPc. Similarly, for the flat-lying, planar CoOEP, one would expect a shorter distance between the Co ion and the surface than for CoTPP. In the latter, the porphyrin ring rests on its four phenyl substituents, which are not in plane with the ring and should therefore, despite the distortion, lead to a larger ion–surface distance compared with CoOEP. It is therefore rather remarkable that the UP and Co 2p XP spectra of CoOEP and CoTPP on Ag(111) are nearly identical and show very similar changes between the multilayer and monolayer. Precise measurements of the distances between the metal ion and the surface, for example by x-ray standing waves, should provide the additional information necessary for a further discussion and understanding of the distance dependence of the Co–substrate interaction. The differences between CoOEP and CoTPP monolayers with respect to the work function changes (section 3.3) and the C 1s and N 1s core-level shifts (section 3.2) indicate that there are indeed distance-dependent effects in the bonding mechanisms of the different Co porphyrins.

5. Conclusions

CoOEP and 2HOEP on Ag(111) self-assemble in an oblique structure. Contrary to CoTPP, which acquires a distorted saddle-shaped conformation in the adsorbed state, CoOEP and 2HOEP exhibit no indications for a distorted porphyrin ring and thus adsorb planar on Ag(111). The XPS data show that the substrate strongly influences the Co 2p core-level signal, which shifts by −1.9 eV relative to the multilayer, indicating direct electronic interaction between the Co ion and the Ag surface and partial reduction of the Co ion. The UP spectrum of the CoOEP monolayer shows an adsorption-induced signal at 0.6 eV, which is related to the presence of the Co ion and is interpreted as a mixed electronic state formed by Co 3d levels and matching levels of the substrate. The N 1s signal of CoOEP suggests that the N atoms are involved in a bonding–backbonding mechanism, which includes electron transfer from the Ag surface to the Co ion and reverse electron transfer from the N atoms to the substrate. The fact that the valence signal at 0.6 eV and the shift of the Co 2p level are observed for both CoOEP (undistorted) and CoTPP (distorted) indicates that both effects are not related to the adsorption-induced conformational changes of the porphyrin but, rather, to the direct electronic interaction of the Co ion and the substrate.

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References

[1] Barth J V 2007 Annu. Rev. Phys. Chem. 58 375
[2] Lin N, Stepanow S, Ruben M and Barth J V 2008 Top. Curr. Chem. 128 150
[3] Gottfried J M and Marbach H 2009 Z. Phys. Chem 223 53
[4] Auwärter W, Schifferin A, Weber-Bargioni A, Pennec Y, Riemann A and Barth J V 2008 Int. J. Nanotechnol. 5 1171
[5] Yoshimoto S and Itaya K 2007 J. Porphyrs Phthalocyan. 11 313
[6] Lin N, Stepanow S, Vidal F, Kern K, Alam M S, Strömsdörfer S, Dremov V, Müller P, Landa A and Ruben M 2006 Dalton Trans 2794
[7] Scudiero L, Barlow D E, Mazur U and Hipps K W 2001 J. Am. Chem. Soc. 123 4073
[8] Comanici K, Buchner F, Flechtner K, Lukasczyk T, Gottfried J M, Steinruck H-P and Marbach H 2008 Langmuir 24 1897
[9] Shubina T E, Marbach H, Flechtner K, Kretschmann A, Jux N, Buchner F, Steinruck H-P, Clark T and Gottfried J M 2007 J. Am. Chem. Soc. 129 9476
[10] Gottfried J M, Flechtner K, Kretschmann A, Lukasczyk T and Steinrück H-P 2006 J. Am. Chem. Soc. 128 5644
[11] Auwärter W, Weber-Bargioni A, Brink S, Riemann A, Schifferin A, Ruben M and Barth J V 2007 ChemPhysChem 8 250
[12] Buchner F, Schwald V, Comanici K, Steinrück H-P and Marbach H 2007 ChemPhysChem 8 241
[13] Kretschmann A, Walz M-M, Flechtner K, Steinrück H-P and Gottfried J M 2007 Chem. Commun. 568–70
[14] Weber-Bargioni A, Reichert J, Seitsonen A P, Auwärter W, Schifferin A and Barth J V 2008 J. Phys. Chem. C 112 3453
[15] Buchner F, Flechtner K, Bai Y, Zillner E, Kellner I, Steinrück H-P, Marbach H and Gottfried J M 2008 J. Phys. Chem. C 112 15458
[16] Scudiero L, Barlow D E and Hipps K W 2000 J. Phys. Chem. B 104 11899
[17] Barlow D E, Scudiero L and Hipps K W 2004 Langmuir 20 4413
[18] Lukasczyk T, Flechtner K, Merte L R, Jux N, Maier F, Gottfried J M and Steinrück H-P 2007 J. Phys. Chem. C 111 3090
[19] Flechtner K, Kretschmann A, Steinrück H-P and Gottfried J M 2007 J. Am. Chem. Soc. 129 12110
[20] Weber-Bargioni A, Auwärter W, Klappenberger F, Reichert J, Lefrancois S, Strunskus T, Wöll C, Schifferin A, Pennec Y and Barth J V 2008 ChemPhysChem 9 89
[21] Wöllfe T, Görfling A and Hieringer W 2008 Phys. Chem. Chem. Phys. 10 5739
[22] Schöll A, Zou Y, Kiliän L, Schmidt T, Fink R and Umbach E 2006 Surf. Sci. 600 1240
[23] Bendounan A, Forster F, Schöll A, Batchelor D, Ziof F, Umbach E and Reiner F 2007 Surf. Sci. 601 4013
[24] Auwärter W, Klappenberger F, Weber-Bargioni A, Schifferin A, Strunskus T, Wöll C, Pennec Y, Riemann A and Barth J V 2007 J. Am. Chem. Soc. 129 11279–85
[25] Klappenberger F, Weber-Bargioni A, Auwärter W, Marschall M, Schifferin A and Barth J V 2008 J. Chem. Phys. 129 214702
[26] Scudiero L, Barlow D E and Hipps K W 2002 J. Phys. Chem. B 106 996
[27] Yoshimoto S, Sugawara S and Itaya K 2006 Electrochemistry 74 175–8
[28] Pan G B, Yan H J and Wan L J 2006 Nano 1 95
[29] Ramoino L, von Arx M, Schintke S, Baratoff A, Guntherodt H J and Jung T A 2006 Chem. Phys. Lett. 417 22–7
[30] Ogunrinde A, Hipps K W and Scudiero L 2006 Langmuir 22 5697–701
[31] Scudiero L and Hipps K W 2007 J. Phys. Chem. C 111 17516
[32] Yoshimoto S, Inukai J, Tada A, Abe T, Morimoto T, Osuka A, Furuta H and Itaya K 2004 J. Phys. Chem. B 108 1948–54

New Journal of Physics 11 (2009) 125004 (http://www.njp.org/)
[33] Mochida I, Tsuji K, Suetugu K, Fujitsu H and Takeshita K 1980 *J. Phys. Chem.* 84 3159
[34] Mochida I, Suetugu K, Fujitsu H and Takeshita K 1982 *J. Catal.* 77 519
[35] Mochida I, Suetugu K, Fujitsu H and Takeshita K 1982 *J. Chem. Soc., Chem. Commun.* 166–71
[36] Mochida I, Suetugu K, Fujitsu H and Takeshita K 1983 *J. Phys. Chem.* 87 1524
[37] Hulsken B, Van Hameren R, Gerritsen J W, Khoury T, Thordarson P, Crossley M J, Rowan A E, Nolte R J M, Elemans J A A W and Speller S 2007 *Nat. Nanotechnol.* 2 285
[38] Berner S, Biela S, Ledung G, Gogoll A, Backvall J E, Puglia C and Oscarsson S 2006 *J. Catal.* 244 86
[39] Castaman S T, Nakagaki S, Ribeiro R R, Ciuffi K J and Drechsel S M 2009 *J. Mol. Catal. A: Chem.* 300 89–97
[40] Takulapalli B R, Laws G M, Liddell P A, Andreasson J, Erno Z, Gust D and Thornton T J 2008 *J. Am. Chem. Soc.* 130 2226–33
[41] Vaughan A A, Baron M G and Narayanaswamy R 1996 *Anal. Commun.* 33 393
[42] Rakow N A and Suslick K S 2000 *Nature* 406 710
[43] Filippini D, Alimelli A, Di Natale C, Paolesse R, D’Amico A and Lundstrom I 2006 *Angew. Chem., Int. Ed. Engl.* 45 3800
[44] Van Ryswyk H, Moore E E, Joshi N S, Zeni R J, Eberspacher T A and Collman J R 2004 *Angew. Chem., Int. Ed. Engl.* 43 5827–30
[45] Yum J H, Jang S R, Humphry-Baker R, Gratzel M, Cid J J, Torres T and Nazeeruddin M K 2008 *Langmuir* 24 5636–40
[46] Cid J J, Yum J H, Jang S R, Nazeeruddin M K, Ferrero E M, Palomares E, Ko J, Gratzel M and Torres T 2007 *Angew. Chem., Int. Ed. Engl.* 46 8358–62
[47] Campbell W M, Jolley K W, Wagner P, Wagner K, Walsh P J, Gordon K C, Schmidt-Mende L, Nazeeruddin M K, Wang Q, Gratzel M and Officer D L 2007 *J. Phys. Chem. C* 111 11760–62
[48] Wang Q, Campbell W M, Bonfantani E E, Jolley K W, Officer D L, Walsh P J, Gordon K, Humphry-Baker R, Nazeeruddin M K and Gratzel M 2005 *J. Phys. Chem. B* 109 15397–409
[49] Schmidt-Mende L, Campbell W M, Wang Q, Jolley K W, Officer D L, Nazeeruddin M K and Grätzel M 2005 *ChemPhysChem* 6 1253–8
[50] Horcas I, Fernandez R, Gomez-Rodriguez J M, Colchero J, Gomez-Herrero J and Baro A M 2007 *Rev. Sci. Instrum.* 78 013705
[51] Zhang Y, Tao X, Gao H Y, Dong Z C and Hou J G 2009 *Phys. Rev. B* 79 075406
[52] Wagner C D, Riggs W M, Davis L E, Moulder J F and Muilenberg G E 1979 *Handbook of X-Ray Photoelectron Spectroscopy* (Eden Prairie, MN: Perkin-Elmer Corporation, Physical Electronics Division)
[53] Kim K S 1975 *Phys. Rev. B* 11 2177–85
[54] Wende H et al 2007 *Nat. Mater.* 6 516
[55] Witte G, Lukas S, Bagus P S and Wöll C 2005 *Appl. Phys. Lett.* 87 263502
[56] Ishii H, Sugiymama K, Ita E and Seki K 1999 *Adv. Mater.* 11 605
[57] Koopmans T 1934 *Physica* 1 104
[58] Yoshimura D, Ishii H, Narioka S, Sei M, Miyazaki T, Ouchi Y, Hasegawa S, Harima Y, Yamashita K and Seki K 1996 *J. Electron Spectrosc. Relat. Phenom.* 78 359
[59] Bai Y, Schmid M, Sekita M, Steinrück H-P and Gottfried J M 2009 to be published