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Direct Synthesis of a Metalloporphyrin Complex on a Surface

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Metalloporphyrins control the decisive steps in various natural and technological processes, which often involve the reversible attachment of a molecular ligand to the central metal ion.[1] A convenient way to study this key step on model compounds in a solvent-free environment is to investigate ordered monolayers of metalloporphyrins adsorbed on an inert metal surface.[2,3] With these model systems, the formation of a complex bond between the porphyrin center and an *additional* molecular ligand can be studied with a wide range of surface-science techniques. For example, changes in the valence level electronic structure of the complex and in the oxidation state of the metal center can be monitored with photoelectron spectroscopy. In addition, adsorbed metalloporphyrins are excellent model systems to study the interaction of a (complexated) metal ion with a surface in a well-defined distance. The bond length and, thereby, the strength of this interaction can be tuned by spacer substituents on the periphery of the porphyrin unit.[4]

The preparation of the metalloporphyrin monolayers by evaporation deposition requires a high thermal stability and a sufficiently low reactivity of the complex to allow preparation in solution and subsequent isolation. An example for a very reactive metalloporphyrin is Fe(II)-tetraphenylporphyin, which is particularly interesting with respect to oxygen adsorption but also extremely sensitive toward oxidation and therefore difficult to handle and to obtain as a pure compound.[1] Therefore, it is also difficult to prepare clean monolayer films of those metalloporphyrins. A possible way out is the in situ synthesis of the complex on the surface, and a recent STM study on the interaction of tetrapyridylporphyrin with Fe atoms[5] indeed encourages a further pursuit of this approach. Here, we provide the first direct spectroscopic evidence that metalloporphyrins can easily be obtained in an ultraclean, ultrahigh vacuum (UHV) environment by evaporation deposition of the respective metal onto monolayers of the metal-free porphyin ligand (free base). For our study, we chose cobalt as the metal center, because monolayers of Co(II)-tetraphenylporphyrin (Co(II)-TPP) can easily be produced by evaporation deposition of the metalloporphyrin and have previously been studied.[2,4,6,7] Thus, reliable reference data are available.

Figure 1 shows N 1s X-ray photoelectron (XP) spectra taken in the course of the metalation process. Graph 1A displays a spectrum of a monolayer of the metal-free ligand, tetraphenylporphyrin (2H-TPP), on the Ag(111) surface. In the monolayer, the molecules adsorb with the porphyrin plane being parallel to the surface, as confirmed by LEED and STM investigations.[4] The two N 1s peaks represent the two different sorts of N atoms, *pyrrolic* (−*N*H−) and *iminic* (−C═*N*−) nitrogen. Pyrrolic N usually leads to higher N 1s binding energies than iminic N.[8] Therefore, the signal at 400.1 eV can be assigned to pyrrolic N, the other one at 398.1 eV to iminic N. Evaporation deposition of small amounts of Co, 0.022 ML with respect to the surface Ag atoms of the substrate, onto the 2H-TPP monolayer leads to substantial changes in the spectrum: the two 2H-TPP-related peaks lose intensity, while a new peak, which is attributed to N with a complex bond to Co, appears at 398.8 eV (Graph 1B). Further Co deposition, in total 0.047 ML, leads eventually to the N 1s spectrum displayed in Graph 1D that is almost identical to the reference spectrum in Graph 1E, obtained from a monolayer of pure Co(II)-TPP on Ag(111). This Co(II)-TPP monolayer was prepared by evaporation deposition of commercial Co(II)-TPP and contains 0.043 porphyrin molecules per surface Ag atom.[4] Therefore, the amount of 0.047 ML Co only slightly exceeds the stoichiometric amount of Co needed for the metalation of all 2H-TPP centers in the monolayer. The fact that the metalation is almost complete with 0.047 ML Co proves that the reaction proceeds with a high yield. From the spectra in Figure 1 it is obvious that the four N atoms in the porphyrin become chemically identical as a result of the metal deposition. This is only possible if the two H atoms are removed. In addition, the strong resemblance of the spectra of the in situ metalated porphyrin and the directly deposited Co(II)-TPP strongly suggests that the H atoms have been replaced by the metal atom.

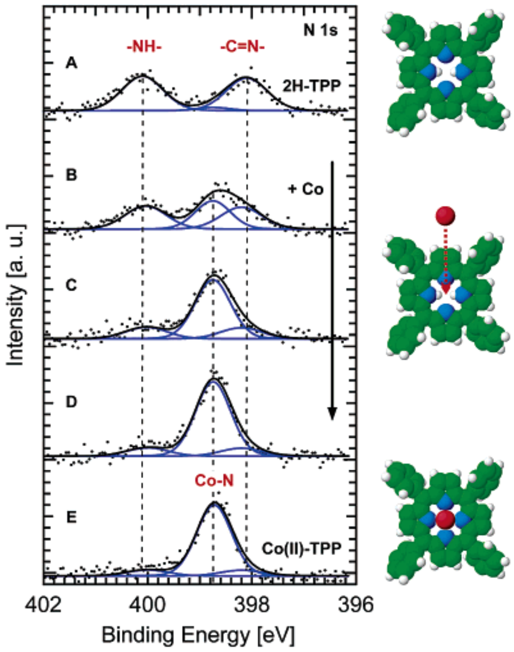

Figure 1. N 1s XP spectra of (A) a monolayer of tetraphenylporphyrin (2H-TPP) on Ag(111) and after deposition of (B) 0.022 ML Co, (C) 0.036 ML Co, and (D) 0.047 ML Co on the 2H-TPP monolayer at 300 K. (E) N 1s XP spectrum of a monolayer of Co(II)-TPP on Ag(111) for comparison.

To obtain further evidence for this assumption, we collected information about the chemical state of the Co ion by recording the cobalt-related photoemission signals, which are displayed in Figure 2. The Co $2p_{3/2}$ spectra in the Graphs 2A−2C were taken

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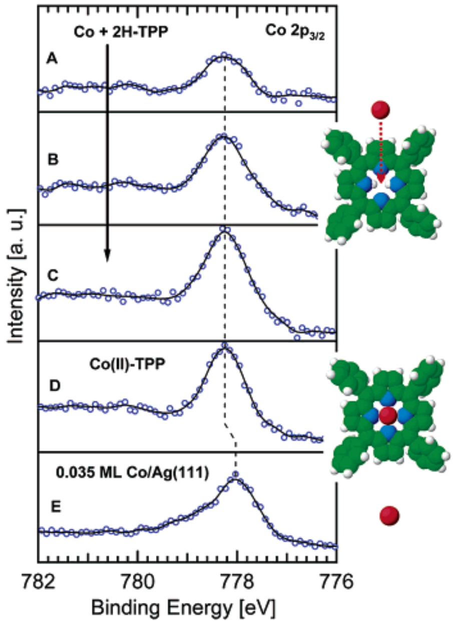

Figure 2. Co $2p_{3/2}$ XP spectra of a monolayer of tetraphenylporphyrin (2H-TPP) on Ag(111) after deposition of (A) 0.022 ML Co, (B) 0.036 ML Co, and (C) 0.047 ML Co. Co $2p_{3/2}$ XP spectra of (D) a monolayer of Co(II)-TPP on Ag(111) and (E) 0.035 ML Co on Ag(111) for comparison. The solid curves are lines to guide the eye.

after deposition of the same incremental amounts of Co onto a 2H-TPP monolayer as in Figure 1. These spectra increasingly resemble the reference spectrum of a directly deposited monolayer of Co(II)-TPP in Graph 2D. Moreover, the signal position in Graphs 2A−2D differs significantly from the signal position for Co directly deposited on the Ag surface (Graph 2E), confirming that Co is not deposited directly onto the Ag surface. The combined data in Figures 1 and 2 provide strong evidence that the deposited Co atoms are indeed complexated by the porphyrin molecules.

Interestingly, the Co $2p_{3/2}$ signal position for the complexated Co ion, 778.1 eV, is closer to the position of a Co(0) species than to that of Co(II), although the nominal oxidation state of the Co ion in Co(II)-TPP is two. Comparison with XP spectra of Co(II)-TPP multilayers, in which the main peak is located at a typical Co(II) position of 780 eV (Figure S1), suggests that this shift to lower binding energies is related to an electronic interaction of the complexated Co ion with the Ag surface. This observation will be addressed in a forthcoming publication.[4] Briefly, the phenyl spacer groups on the periphery of the molecule are apparently not sufficient to completely suppress the interaction between the Co ion and the Ag surface. For example, the UV photoelectron spectra in Figure S2 show additional intensity around 0.6 eV below E_F in the case of Co(II)-TPP monolayers. This signal, which is absent for Co(II)-TPP multilayers, 2H-TPP monolayers, and submonolayer coverages of Co on Ag, has previously been observed by tunneling spectroscopy on Co(II)-TPP monolayers.[6] Previous STM studies on various adsorbed metallotetraphenylporphyrins[7] and metallophthalocyanines[9] have also provided evidence for an electronic interaction, mediated by the d_{z^2} orbital on the ion, with the surface. We conclude that the shift of the Co signal to lower binding energies is probably due to a surface-to-ion electron transfer that reduces the effective oxidation state of the ion. Additionally, final state effects could play a role as will be discussed elsewhere.[4] We would like to emphasize that this Co−Ag interaction does not lead to a decomposition of the adsorbed metalloporphyrin below 600 K.[4]

The mechanism of the metalation reaction is presently unclear. Formally, the replacement of the two pyrrolic hydrogen atoms by the metal atom is a redox reaction involving the oxidation of Co(0) to Co(II) and the reduction of hydrogen. An intermediate participation of the metal surface in the course of the reaction is likely, considering the above-mentioned electronic interaction between metal ion and surface in the adsorbed metalloporphyrins. The insertion of the Co atom into the porphyrin is possibly accompanied by a transfer of the pyrrolic H atoms to the metal atom. Subsequent oxidation of the metal, recombination of the two H atoms to H_2, and desorption of the H_2 molecule would complete the reaction. Although the two systems may be too different to be compared, the desorption energy of H_2 from Co *surfaces* (62−80 kJ/mol)[10] seems to be sufficiently low to also permit H_2 desorption from the *complexated Co ion* at room temperature. Thus far, we have not been able to observe the released H_2, mainly because the amounts are small compared to the H_2 background pressure, especially during metal evaporation. However, investigations with deuterated 2D-TPP are presently performed in our lab. It should be possible to detect the D_2 released during the metalation.

In summary, we have demonstrated that adsorbed porphyrin monolayers can be efficiently metalated in situ under clean UHV conditions by evaporation deposition of metal atoms. This establishes the possibility to study metalloporphyrins—in particular with surface science techniques—that are too reactive to be synthesized in solution or thermally not stable enough for evaporation deposition. It should also be possible to perform the described process at low sample temperatures ($\ll$300 K) and thus to stabilize porphyrin complexes that decompose already below room temperature.

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Supporting Information Available: Experimental details, XP spectra of Co(II)-TPP, UP spectra of 2H-TPP, Co(II)-TPP, and Co on Ag(111), definitions of the units *ML* and *monolayer*. This material is available free of charge via the Internet at http://pubs.acs.org.

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