Communication

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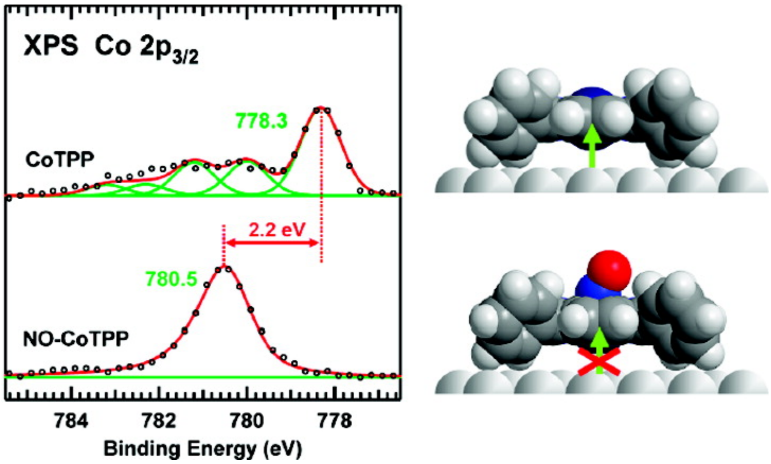

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NO-Induced Reversible Switching of the Electronic Interaction between a Porphyrin-Coordinated Cobalt Ion and a Silver Surface

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The coordination of axial ligands on metalloporphyrins is essential for the biological functionality of these complexes[1] and for their technical application as gas sensors[2,3] and catalysts.[4−6] The coordination of nitric oxide (NO) in metalloporphyrin nitrosyl complexes[7,8] is especially important, because NO plays a crucial role as a signaling molecule in biological systems.[9,10] Presumably, these nitrosyl complexes also occur as intermediates in catalytic reactions such as the reduction of NO with H_2 or CO on TiO_2-supported tetraphenylporphyrinato-cobalt(II) (CoTPP).[4] Previous studies on CoTPP/TiO_2 powder catalysts suggest that the support promotes the catalytic activity by electron transfer to the Co ion.[4] A fundamental understanding of the interaction between the metalloporphyrin and the surface, however, has not yet been established. It requires a deeper knowledge of the surface chemistry of adsorbed metal complexes—a largely unexplored field, especially with respect to catalysis. To understand how the electronic structure of a coordinated metal ion in an adsorbed complex is influenced by the surface, we recently studied the interaction of CoTPP with Ag(111).[11] Using photoelectron spectroscopy, we obtained evidence for an electron transfer from the Ag surface to the Co ion; in other words, the surface acts as an axial donor ligand. This electronic coupling between a porphyrin-coordinated Co ion and a metal surface has also been observed with scanning tunneling microscopy (STM).[12,13]

In this communication, we demonstrate that the above-mentioned Co−Ag interaction is suppressed by axial coordination of NO on the Co ion. This effect likely results from the competition between the two axial ligands (NO and Ag surface) and has important implications for catalysis on supported metal complexes and their applications in sensor technology.

In order to clarify the influence of the axial NO ligand on the electronic structure of the coordinated Co ion, we first discuss the NO-induced changes in the Co $2p_{3/2}$ signal of the X-ray photoelectron (XP) spectrum. Figure 1C displays the Co $2p_{3/2}$ signal of *multilayers* of CoTPP on Ag(111) (see the Supporting Information for the experimental details). The main peak at 780.0 eV is located at a position typical of Co in the formal oxidation state +2. The signal shows a multiplet structure, which is caused by the unpaired electron of the Co(II) ion.[11] In the CoTPP *monolayer* (Figure 1A), however, the main peak appears at 778.2 eV, that is, at a 1.8 eV lower binding energy (E_B). As previously discussed,[11] this shift is much larger than the respective peak shifts for the other elements, carbon and nitrogen (0.2−0.3 eV), and suggests operation of initial-state effects, such as the transfer of electron density from the surface to the Co ion.

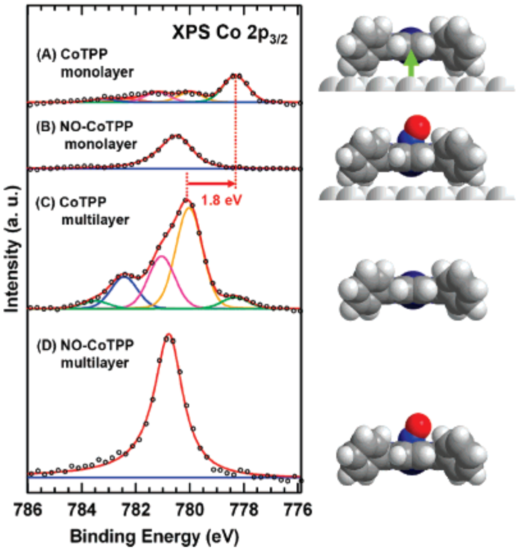

Figure 1. Co $2p_{3/2}$ XP spectra of CoTPP and NO−CoTPP on Ag(111). (A) CoTPP monolayer, (B) NO−CoTPP monolayer, (C) CoTPP multilayer (ca. four layers), and (D) NO−CoTPP multilayer (ca. four layers). The shoulder at 778 eV in (C) originates from the CoTPP monolayer. The other curves in the signal deconvolution of (A) and (C) are displayed for illustrative purposes; they do not necessarily represent the full complexity of these signals.

Subsequently, we dosed NO onto the CoTPP monolayer at 140 K to produce the complex (nitrosyl)(tetraphenylporphyrinato)cobalt(II) (NO−CoTPP) by axial coordination of NO to the Co ion. The formation of the NO−Co bond causes two major changes in the Co $2p_{3/2}$ signal (Figure 1B). First, the multiplet structure has vanished; the signal now consists of a single peak. This change reflects the fact that NO, like CoTPP, has an unpaired electron. Upon formation of the NO−Co bond, these electrons form an electron pair, and the nitrosyl complex now has closed-shell character. The second NO-induced change is the shift of the Co $2p_{3/2}$ signal by 2.2 eV toward higher binding energy; the new position is close to that of the CoTPP multilayer signal (Figure 1C). As we will discuss below, this shift indicates that the NO ligand suppresses the Co−Ag interaction.

To study the NO−CoTPP complex in a state in which it is *not* interacting with the surface, we performed the analogous measurements on NO−CoTPP *multilayers*; Figure 1D shows the respective Co $2p_{3/2}$ signal. Similar to the monolayer of this complex, formation of the NO−Co bond leads to a single peak without multiplet structure. The position of this peak, 780.8 eV, differs by only 0.4 eV from the peak position of the NO−CoTPP *monolayer*. This difference is much smaller than the respective value for CoTPP, 1.8 eV, and only slightly exceeds the differences for carbon (0.2 eV) and nitrogen (0.3 eV). These small shifts toward lower binding energy between multilayer and monolayer are most likely dominated by final-state effects (e.g., relaxation shift).

The fact that the difference in the Co $2p_{3/2}$ binding energy between the multilayer and the monolayer is much larger for CoTPP than for NO−CoTPP suggests that the influence of the surface on the coordinated Co ion is strongly reduced by the axial NO ligand.

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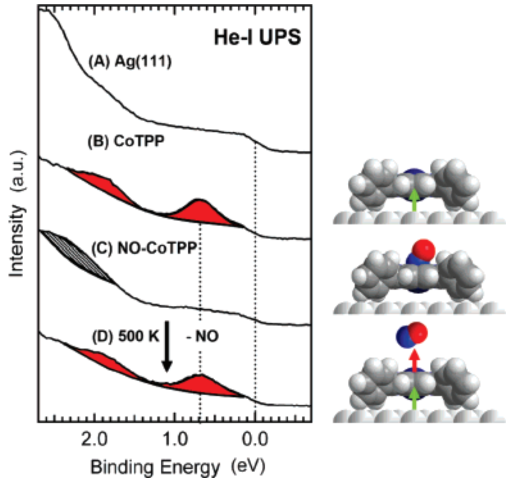

Figure 2. He−I UP spectra ($h\nu = 21.22$ eV) of (A) clean Ag(111) surface, (B) CoTPP monolayer, (C) NO−CoTPP monolayer, and (D) after heating the NO−CoTPP monolayer to 500 K for removal of the NO ligand.

The NO-induced changes of the valence states, which were probed with UV photoelectron spectroscopy (UPS) (Figure 2), support this conclusion.

Curves A and B of Figure 2 show the UP spectra of the clean Ag(111) surface and of the CoTPP monolayer on this substrate, respectively. As previously shown, the signal at 0.7 eV in Figure 2B results from the electronic interaction of the coordinated Co ion with the Ag surface.[11] Briefly, the half-occupied Co $3d_{z^2}$ orbital interacts with matching states of the surface, resulting in two new levels below the Fermi level (E_F), which are accessible for electrons from the Fermi sea. This model predicts transfer of electron density from the surface to the Co ion and is thus consistent with the shift of the Co $2p_{3/2}$ signal toward lower binding energy in the monolayer XP spectrum. Figure 2C shows a UP spectrum of the NO−CoTPP monolayer. Apparently, the NO ligand suppresses the interaction-induced peak at 0.7 eV. If the NO ligand is removed by heating to 500 K, the interaction signal reappears (Figure 2D). The same heating step also restores the Co $2p_{3/2}$ signal of the CoTPP monolayer (see Figure S1 of the Supporting Information).

Therefore, the UPS results are consistent with the initial conclusions from the discussion of the XP spectra in Figure 1. Both data sets show that the Co ion in adsorbed NO−CoTPP is much less influenced by the surface than in adsorbed CoTPP. In other words, the NO ligand weakens the interaction between Co ion and substrate. This process is reversible because, after thermal desorption of the NO ligand, the complex resumes its state before NO coordination and the Co−Ag interaction is restored.

Why does NO influence the interaction between the metal ion and the surface? A possible answer is based on the concept of the *trans effect*. This concept postulates a competition between two ligands in trans position and, for example, explains how ligands control the exchange of other ligands in square-planar complexes:[14] if a ligand (L^1) is in a trans position with respect to another ligand (L^2), which is the stronger σ-donor or π-acceptor, then the substitution of L^1 is accelerated. This trans influence is attributed to the fact that the two ligands compete for the same metal d orbitals. NO is considered to be a ligand that exerts a strong trans effect.[14] As a result, the bond to the ligand in trans position to the NO ligand, here the Ag surface, is weakened.

Previous density functional theory (DFT) studies[15] support this interpretation. They show that the highest occupied orbital of NO−CoTPP arises from the interaction between the singly occupied molecular orbitals of both molecules, that is, from a combination of d_{z^2}(Co)−π^*(NO) σ and π interactions. In other words, NO binds to the same Co d orbital that presumably interacts with the Ag surface.[11] As a result, the Co−Ag interaction is replaced by a stronger interaction between the NO and the Co ion. This interaction leads to a larger separation of the interaction-induced energy levels, and as a result, the unoccupied antibonding level is then located above E_F. This level cannot be filled with electrons from the Fermi sea, and thus, the electron transfer from the Ag surface to the Co ion is suppressed (Figure S2, Supporting Information).

In conclusion, the electronic interaction between a porphyrin-coordinated metal ion and a surface is reversibly switched by an NO ligand on the metal ion. To explain this observation, we have applied concepts of chemical bonding in transition metal complexes to surface-confined coordination compounds, in which the metal surface acts, from the point of view of the coordinated metal ion, as an additional ligand. Our findings have important implications for catalysis on supported metalloporphyrins. The functional principle of these systems is based on the control of the reactivity of the metal center by the interaction with the underlying surface. This principle can be applied to tailor catalysts consisting of supported planar metal complexes, in which the influence of the surface is adjusted by the type of the surface and by varying its distance to the reactive metal center. To some extent, this approach mimics enzymatic systems such as the heme thiolate proteins, in which an axial thiolate ligand controls the reactivity of the Fe center.[16] The fact that a ligand modifies the interaction of the metal center with the surface, as has been demonstrated in this work, implies that the reverse process is also possible: to influence an axial ligand and its reactivity by a strongly interacting surface in trans position.

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Supporting Information Available: Experimental details, Co 2p and N 1s XP spectra, molecular orbital diagram, and additional references. This material is available free of charge via the Internet at http://pubs.acs.org.

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