

Ammonia Coordination Introducing a Magnetic Moment in an On-Surface Low-Spin Porphyrin**

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The controlled manipulation of spin states in atoms/molecules is of profound interest towards the design of future spin-based devices.^[1,2] A prominent example of how spin states are modified ($S = 2 \leftrightarrow S = 0$) can be found in nature's Fe^{II} porphyrin moiety within hemoglobin and its coordination with the O₂ ligand.^[3] Recently, we have implemented this concept in a synthetic on-surface arrangement using metallo-porphyrins adsorbed on ferromagnetic surfaces. By axial coordination with an external NO ligand the induced magnetic moment in the ($S = 1/2$) Co^{II} porphyrin has been switched-off.^[4] These experiments depend on a characteristic property of paramagnetic metallo-porphyrins as well as phthalocyanines: their interfacial chemical interaction with the ferromagnetic surface ligand induces a magnetic moment stable up to room temperature.^[4,5] Axial coordination can also be used to control the magnetic anisotropy^[6] as well as the strength and sign of the exchange interaction.^[4b]

Controlling on-surface/interface spin systems^[4,5j,k,6,7] is a prerequisite for applications in organic spintronics^[1] which makes this research field increasingly popular. Recently, we combined chemically directed self-assembly and coordination chemistry to obtain selectively switchable, highly ordered supramolecular 2D spin arrays.^[5j] Concerning chemical control of the magnetic moment, only off-switching^[4,5j] and spin-tuning,^[4b,5k] that is, switching spin-on $\rightarrow$ spin-off and spin-on $\rightarrow$ spin-on' (a modified spin state) have been established. So far this set of on-surface chemical spin operations was incomplete since the spin-off $\rightarrow$ spin-on case was missing. Generally,

switching the spin in organometallic complexes by external ligands to the on-state is more difficult to achieve than switching to the off-state, since chemical bonding has to overcome the spin-pairing energy. An additional complication arises from the possibility that the surface can modify the spin states before as well as after the axial ligation.^[4b] This can also lead to spin-quenching on the surface.^[4b,8] Here we report on the first demonstration of an on-surface chemical spin on-switch, for Ni^{II} porphyrins ($S = 0$) adsorbed on a ferromagnetic (FM) Co substrate, by the diamagnetic ($S = 0$) external NH₃ ligand. A schematic representation of this spin on-switch ($S = 0 \leftrightarrow S = 1$) is shown in Figure 1 a.

To study this effect, Ni^{II} tetraphenylporphyrin (NiTPP; see Figure 1 a) molecules were thermally sublimed in ultra-high vacuum onto clean Co thin films on Cu(001) single crystals.^[4,5e,f,j] For a description of the methods see the Supporting Information.

In scanning tunneling microscopy (STM) experiments (Figure 1 b), we consistently find the molecules adsorbed in a random fashion on Co and Ni substrates,^[4,5f] in contrast to self-assembly of NiTPP on Au and Ag substrates.^[9a] Most of the NiTPP molecules on the Co surface can be recognized as rectangular shapes—the so-called saddle-shape conformation^[9b] (Figure 1 c), whereas a minority of the molecules is observed as four-leaf clovers,^[5f] that is, in the flat, square-planar conformation of the free molecule. The adsorption-induced saddle-shape conformation is characterized by a tetrahedrally distorted macrocycle^[9b,c] and its coexistence with

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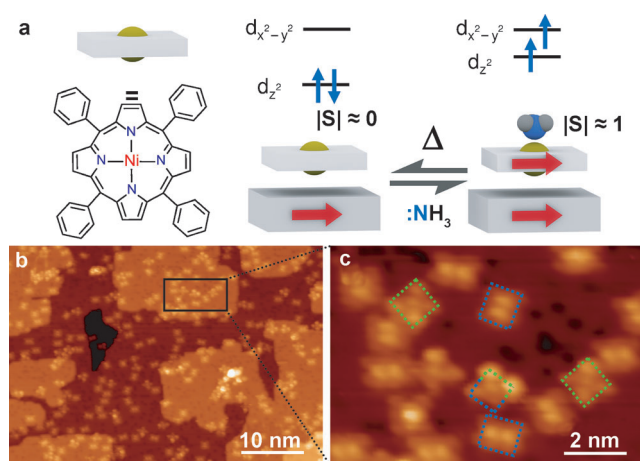


Figure 1. a) NiTPP and the reversible spin on-switch ($S=0 \leftrightarrow S=1$). The molecular orbital diagram shows that the NH_3 ligand increases the energy of the $3d_{z^2}$ orbital and thus allows a $S=1$ high-spin state. b) Constant current STM image of NiTPP on Co(001) without NH_3 (tunneling parameters: 20 pA, 650 mV, W-tip). The considerable molecule-surface interaction leads to irregular arrangement of the ad-molecules. c) The zoom-in STM image shows that the NiTPP molecules are found in either one of two conformations: saddle-shape (blue rectangles) and flat (green squares).

the flat conformation has been observed in our previous studies.^[4] Note, that an intermediate conformation (half flat, half saddle-shape) is also observed (Figure 1c, marked half

green, half blue). STM data obtained after exposure to NH_3 at 78 K depict bright blurry protrusions which partly have a streak-like appearance^[5,10] (see the Supporting Information). This suggests considerable degrees of freedom of the NH_3 ligand or partial removal of NH_3 during the scanning process.^[5,10]

The electronic and magnetic properties of both ad-molecules (NiTPP) and substrate (Co(001) thin films), as well as the magnetochemical effect induced by the NH_3 ligand were investigated by element-specific X-ray absorption spectroscopy (XAS) and X-ray magnetic circular dichroism (XMCD)^[11a] measurements (Figure 2) at the Surface/Interface: Microscopy (SIM) beamline of the Swiss Light Source (SLS).^[11b] For 3d transition metals, the absorption cross-section at the $L_{3,2}$ edges ($2p \rightarrow 3d$ electronic transitions) provides element-specific information on the magnetization of the surface adsorbed transition-metal complexes (here NiTPP) and the substrate (here Co) separately.

Figure 2 shows the Ni and Co $L_{2,3}$ edge XAS/XMCD signals sequentially obtained at about 70 K with the substrate kept in its remanent magnetization on the native NiTPP/Co system (a), after exposure to NH_3 gas (b), after thermal desorption of NH_3 (c) and, finally, after re-exposure to NH_3 gas (d). Note that the Ni $L_{3,2}$ edge XAS is affected by far-edge oscillations, originating from the Co thin-film substrate, giving rise to a slowly varying background in XAS/XMCD signals. In the main panels we show the spectra upon subtraction of the background measured on a reference substrate.

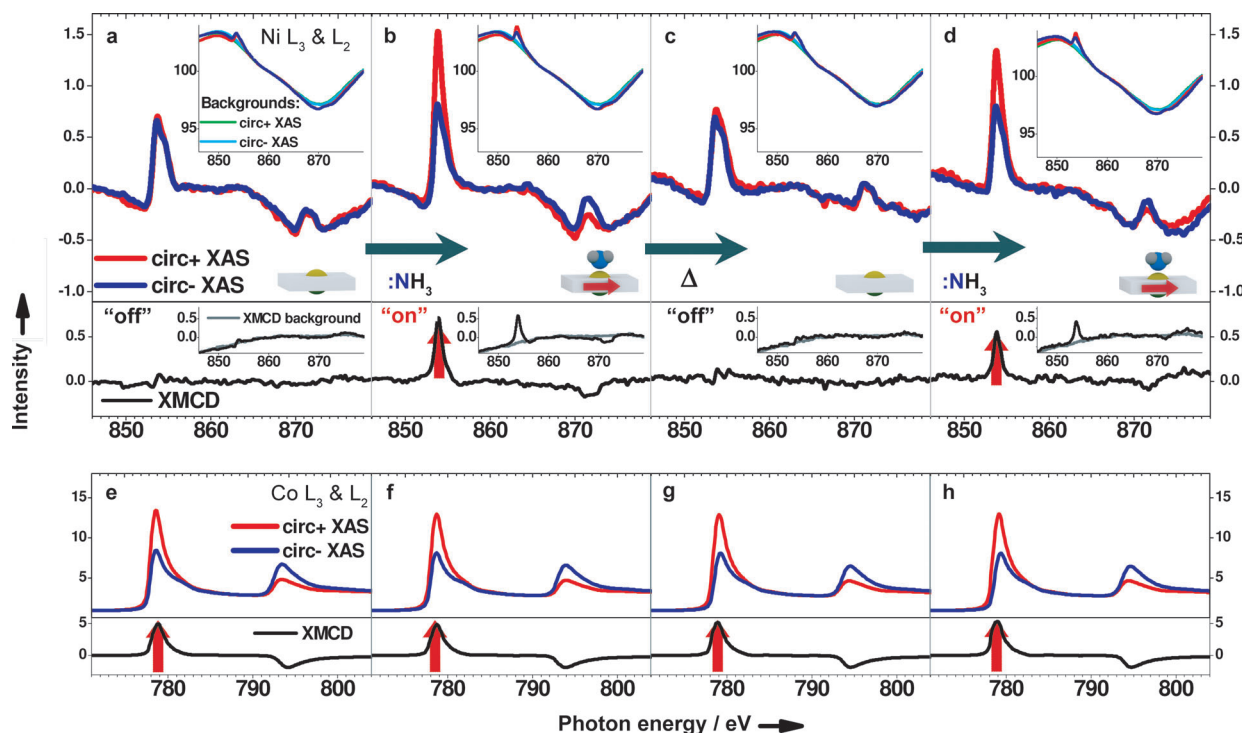


Figure 2. XAS/XMCD of Ni in the molecule and the Co substrate of the native NiTPP/Co (a,e), after exposure to NH_3 gas (b,f), after thermal desorption (Δ) of NH_3 (c,g) and after re-exposure to NH_3 gas (d,h). The spectra were recorded at about 70 K. At the Ni $L_{3,2}$ edge XAS/XMCD data, the respective backgrounds as shown in the insets (green/cyan for circ+/circ- XAS and gray for XMCD), have been subtracted. The original spectra (red/blue for circ+/circ- XAS and black for XMCD) are also shown in the insets. In absence of NH_3 (a,c), no XMCD signal is observed in Ni (spin-off state). The red arrows indicate the presence of magnetic dipole moments.

For native NiTPP/Co, the absence of an XMCD signal demonstrates that the adsorption of the molecules on the Co substrate alone does not induce a magnetic dipole moment in the Ni^{2+} central ion (Figure 2a). The exposure with NH_3 , however, results in a clear XMCD signal evidencing the presence of a magnetic moment on the Ni^{2+} center (Figure 2b). Annealing to 300 K restores the initial spin-off state and subsequent NH_3 exposure leads to the recovery of the spin-on state (Figure 2c and d). The spin-on state is characterized by a FM coupling to the substrate as indicated by the parallel red arrows in Figure 2. Such coupling for paramagnetic porphyrins and phthalocyanines in contact with ferromagnetic substrates has been observed earlier^[5a] and studied in detail.^[4,5] However, in the case presented here the FM coupled spin, confirmed by the observed change in the sign of the Co and Ni XMCD signals after remagnetizing the substrate in the opposite direction, is observed only in presence of the axial NH_3 ligand. The magnetic signature of the substrate remains unaffected (see Co-XMCD signals in Figure 2e–h) in the sequential processes of NH_3 coordination/decoordination, that is, the switching between the molecular spin-off and spin-on states occurs in the presence of the substrate magnetization and its exchange interaction with the central metal ion of the molecule.

The origin of the induced magnetic moment is related to the increase of the coordination number of the Ni ion upon exposure to NH_3 . Four-coordinated Ni^{2+} complexes are usually in the low-spin ($S=0$) state.^[12] Ni^{2+} ions with a coordination number of five (square pyramidal) or six (octahedral) are usually paramagnetic high-spin ($S=1$) species.^[13] However, the nature of the ligand, that is, whether it acts as a σ donor or as a π acceptor, plays a crucial role for the thermodynamic stability of the coordination bond.^[13c] Notably, we can observe this low-spin to high-spin transition also by X-ray photoelectron spectroscopy (XPS) as an increase in the full-width-at-half-maximum of the $\text{Ni}2\text{p}_{3/2}$ spectral feature (see the Supporting Information).

To explain our experimental observations and to provide detailed insight into the on-surface molecular spin-switching, numerical simulations based on density functional theory were performed taking additional Hubbard interactions (DFT + U) into account (Figure 3). The calculations were performed on Ni-porphine, that is, without phenyl substitution, to manage the computational efforts.^[4b,5b–e,14] Note that in view of the coexistence of different conformations, local experiments, for example, spin-polarized STM, would be desirable to correlate conformation and magnetochemistry. For Ni-porphine on Co (NiP/Co), we find that the 3d orbital local magnetic density of states (LMDOS) of Ni is equally distributed over the two spin-channels, that is, spin $\uparrow$ and spin $\downarrow$; hence the magnetic dipole moment of NiP on Co is not present ($S=0$). The calculated electronic configuration, approximately $(d_{xy})^2 (d_{yz}, d_{xz})^4 (d_{z^2})^1 (d_{x^2-y^2})^0$, corresponds well to the free Ni^{II} porphyrin.

Through NH_3 coordination, the 3d LMDOS of Ni^{2+} changes into $(d_{xy})^2 (d_{yz}, d_{xz})^4 (d_{z^2})^1 (d_{x^2-y^2})^1$, revealing singly occupied and FM coupled d_{z^2} and $d_{x^2-y^2}$ orbitals. The magnetic moment is about $1.61 \mu_B$ on the Ni ion and $0.06 \mu_B$ on each of the nitrogen atoms of the porphyrin. Moreover, the Ni ion is

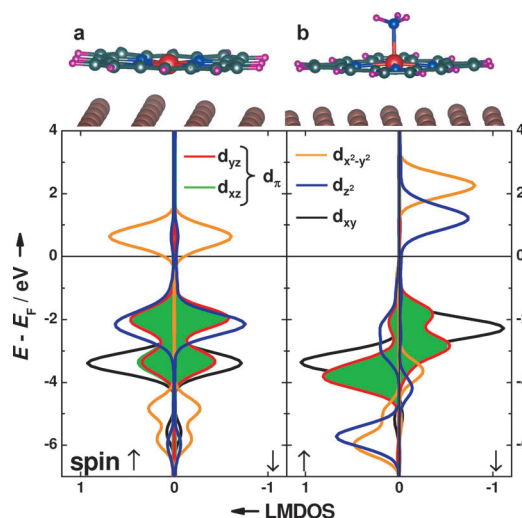


Figure 3. DFT + U calculations presenting the spin-projected 3d orbital local magnetic density of states (LMDOS) for the Ni-porphine/Co system with $S=0$ before (a) and with $S=1$ after (b) reaction with NH_3 . The given energies are with respect to the Fermi-level (E_F). The calculations show that the NH_3 ligation leads to an increased energy of the d_{z^2} orbital (because of interaction with the lone-pair of the NH_3 ligand), shifting it closer in energy to the $d_{x^2-y^2}$ orbital and allowing for a high-spin ($S=1$) state being FM coupled to the Co substrate.

pulled-up from the porphyrin plane towards the NH_3 ligand. Note that, depending on the electronic configuration NH_3 can also act as a spin-off switch.^[5i,7] The calculated Ni–Co distance for NH_3 -NiP/Co ($3.59 \text{ \AA}$) is significantly longer than the value obtained for the native NiP/Co ($3.09 \text{ \AA}$) system, consistent with the observation of a surface spin-trans effect.^[4] Notably, the coordination of the Co surface ligand^[4,15] to the Ni^{2+} ion is identified by a broadening of the calculated $3d_{z^2}$ LMDOS, however, this occurs without modification of the total molecular magnetic moment. Furthermore, the calculations show an increase of the Ni–N_{porphine} distance from 1.98 to $2.05 \text{ \AA}$. This increase has been attributed for a similar system to the reduced formal bond order because of the presence of an unpaired electron in the anti-bonding $d_{x^2-y^2}$ orbital of NH_3 -NiTPP.^[13b] Note, that the NH_3 -induced FM coupled spin density is distributed across the nitrogen atoms of the Ni-porphyrin and the NH_3 ligand ($0.06 \mu_B$). The spin density sums up to about $1.92 \mu_B$, corresponding to a molecular spin state of $S=1$, consistent with the two singly occupied levels seen in Figure 3b.

In conclusion, we have provided evidence for the capability of NH_3 to act as an on-switch for the spin of the NiTPP/Co system and confirmed the surface spin-trans effect.^[4] Notably, the observation of a magnetic moment in the molecule only after exposure to NH_3 rules out that the ligand quenches the magnetic moment of the substrate. The presented findings are of fundamental interest and provide a showcase for magnetochemistry in an on-surface setting. The consequence of ligation-induced transitions on spin multiplicity and magnetic moment are uniquely probed by XPS and XMCD, respectively. Moreover, they open-up new possibilities to control magnetic moments down to the single-molecule level by chemical stimuli. Possible applications

include the use of this system in a magnetochemical sensor and in molecular spintronics.

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