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

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

Christian Wäckerlin, Kartick Tarafder,[‡] Jan Girovsky, Jan Nowakowski, Tatjana Hählen, Aneliia Shchyrba, Dorota Siewert, Armin Kleibert, Frithjof Nolting, Peter M. Oppeneer, Thomas A. Jung* and Nirmalya Ballav*

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], i.e. 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 metal-organic 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 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 Fig. 1a.

To study this effect, Ni(II) tetraphenylporphyrin (NiTPP; cf. Fig. 1a) 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.

[*] C. Wäckerlin, J. Girovsky, J. Nowakowski, T. Hählen, Dr. D. Siewert, Prof. T. A. Jung
Laboratory for Micro and Nanotechnology, Paul Scherrer Institute, 5232 Villigen-PSI (Switzerland), E-mail: thomas.jung@psi.ch

Prof. N. Ballav
Department of Chemistry, Indian Institute of Science Education and Research, Pune 411008 (India), E-mail: nballav@iiserpune.ac.in

Dr. K. Tarafder,[‡] Prof. P. M. Oppeneer
Department of Physics and Astronomy, University of Uppsala, Box 516, S-751 20 Uppsala (Sweden)
[‡]Present address: Materials Science Division, Lawrence, Berkeley National Laboratory, CA 94720 (USA)

A. Shchyrba
Department of Physics, University of Basel, 4056 Basel (Switzerland)

Dr. A. Kleibert, Prof. F. Nolting
Swiss Light Source, Paul Scherrer Institute, 5232 Villigen-PSI (Switzerland)

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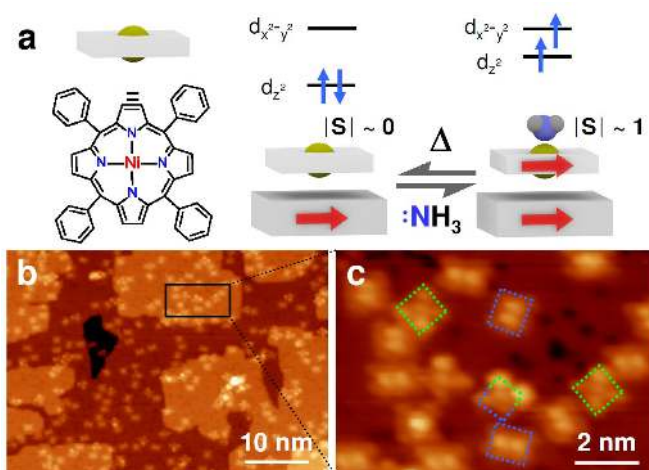


Figure 1. (a) Schematic representation of NiTPP and of the reversible spin *on-switch* ($S=0 \leftrightarrow S=1$). The molecular orbital diagram shows that the NH₃-ligand increases the energy of the 3d_{z²} orbital and thus allows a $S=1$ high-spin state (vide infra). (b) Constant current STM image of NiTPP on Co(001) (tunneling parameters: 20 pA, 650 mV, W-tip) without NH₃. 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).

In scanning tunneling microscopy (STM) experiments (Fig. 1b), 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] (Fig. 1c), while a minority of the molecules is observed as four-leaf clovers,^[5f] i.e. 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 the flat conformation has been observed in our previous studies.^[4] Note, that an intermediate conformation (half flat, half saddle-shape) is also observed (Fig. 1c, marked half green, half blue). STM data obtained after NH₃-exposure at 78 K depicts bright blurry protrusions which partly have a streak-like appearance^[5j,10] (see Supporting Information). This suggests considerable degrees of freedom of the NH₃-ligand or partial removal of NH₃ during the scanning process.^[5j,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 NH₃-ligand were investigated by element-specific X-ray absorption spectroscopy (XAS) and X-ray magnetic circular dichroism (XMCD)^[11a] measurements (Fig. 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→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.

Fig. 2 shows the Ni and Co L_{2,3} edge XAS/XMCD signals sequentially obtained at ~70 K with the substrate kept in its remanent magnetization on the native NiTPP/Co system (a), after exposure to NH₃ gas (b), after thermal desorption of NH₃ (c) and, finally, after re-exposure to NH₃ 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.

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 Ni²⁺ central ion (Fig. 2a). The exposure with NH₃, however, results in a clear XMCD signal evidencing the presence of a magnetic moment on the Ni²⁺ center (Fig. 2b). Annealing to ~300 K restores the initial *spin-off* state and subsequent NH₃ exposure leads to the recovery of the *spin-on* state (Fig. 2c and 2d). The *spin-on* state is characterized by a FM coupling to the substrate as indicated by the parallel red arrows in Fig. 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 presented here case 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 NH₃ ligand. The magnetic signature of the substrate remains unaffected (cf. Co-XMCD signals in Fig. 2e-h) in the sequential processes of NH₃ coordination/decoordination, i.e. 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.

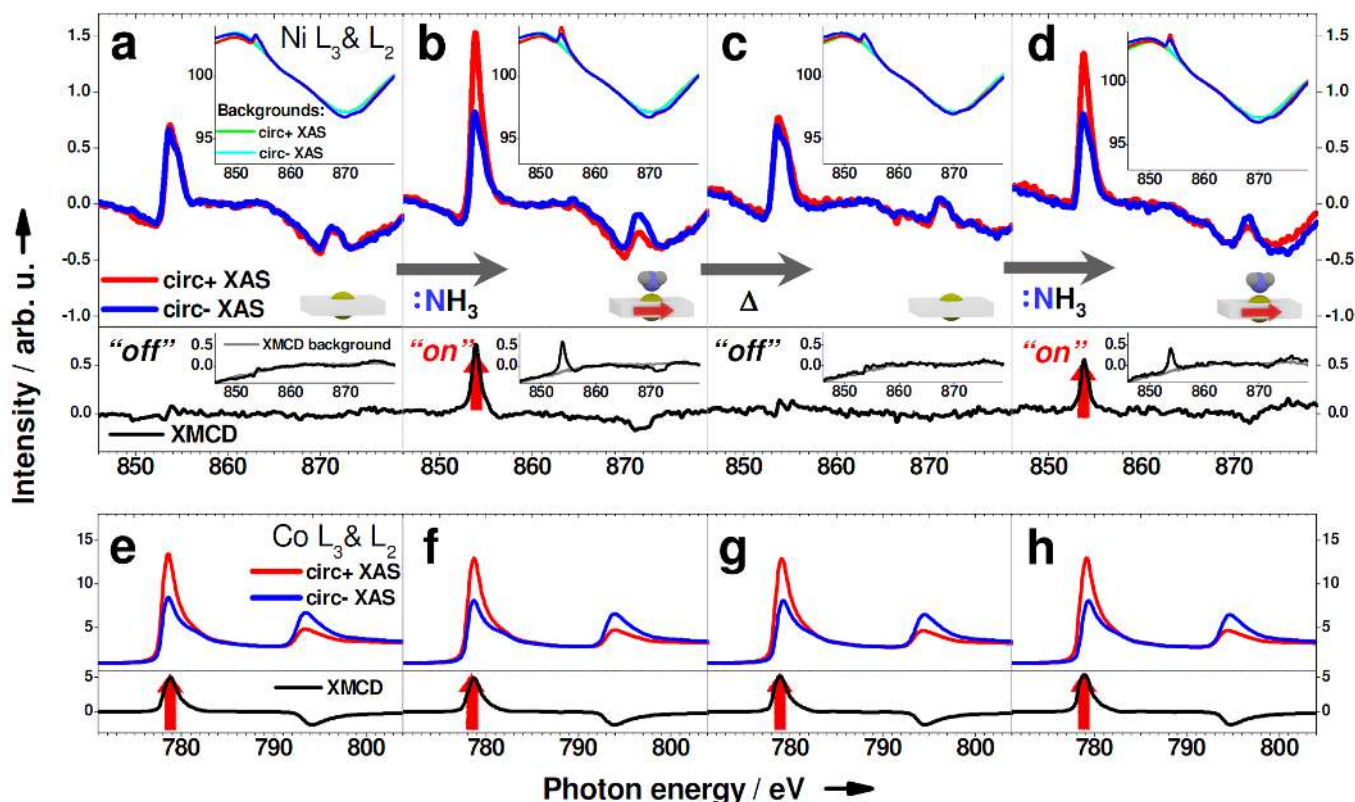


Figure 2. XAS/XMCD of Ni in the molecule and the Co substrate of the native NiTPP/Co (a,e), after exposure to NH₃ gas (b,f), after thermal desorption (Δ) of NH₃ (c,g) and after re-exposure to NH₃ gas (d,h). The spectra were recorded at ~ 70 K. At the Ni L_{3,2} edge XAS/XMCD data, the respective backgrounds 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 NH₃ (a,c), no XMCD signal is observed in Ni (*spin-off* state). The red arrows indicate the presence of magnetic dipole moments.

The origin of the induced magnetic moment is related to the increase of the Ni ion's coordination number upon exposure to NH₃. Four-coordinated Ni²⁺ complexes are usually in the low-spin (S=0) state.^[12] Ni²⁺ 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, i.e. 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 XPS as an increase in the full width at half maximum of the Ni2p_{3/2} spectral feature (see 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 (Fig. 3). The calculations were performed on Ni-porphine, i.e. without phenyl substitution, to manage the computational efforts^[4b,5b-e,14]. Note that in view of the coexistence of different conformations, local experiments, e.g., 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, i.e. 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_z²)² (d_{x²-y²)⁰, corresponds well to the free Ni(II) porphyrin.}

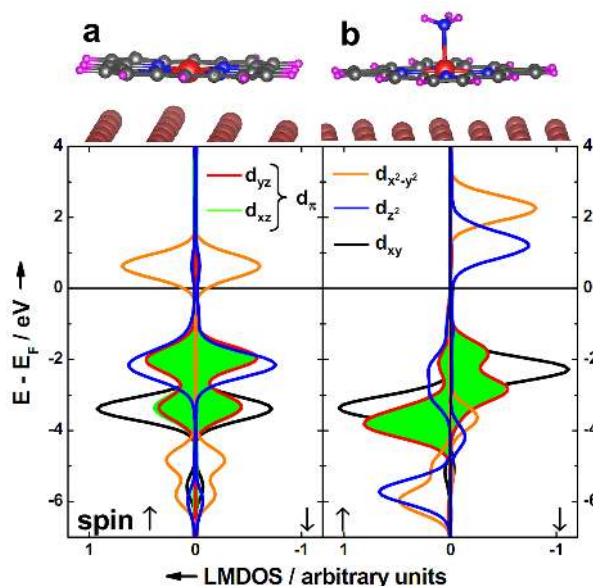


Figure 3. DFT+U calculations presenting the spin-projected 3d orbital local magnetic density of states (LMDOS) for the Ni-porphine/Co system with S=0 before (a) and with S=1 after (b) reaction with NH₃. The given energies are with respect to the Fermi-level (E_F). The calculations show that the NH₃ ligation leads to an increased energy of the d_z² orbital (due to overlap with the lone-pair of the NH₃-ligand), shifting it closer in energy to the d_{x²-y²) orbital and allowing for a high-spin (S=1) state being FM coupled to the Co substrate.}

Through NH₃ coordination, the 3d LMDOS of Ni²⁺ changes into (d_{xy})² (d_{yz}d_{xz})⁴ (d_z²)¹ (d_{x²-y²)¹, revealing singly occupied and FM coupled d_z² and d_{x²-y²) orbitals. The magnetic moment is $\sim 1.61 \mu_B$ on the Ni ion and $\sim 0.06 \mu_B$ on each of the nitrogens of the porphyrin. Moreover, the Ni ion is pulled-up from the porphyrin plane towards the NH₃ ligand. Note that, depending on the electronic configuration NH₃ can also act as a spin-off switch.^[5i,7] The calculated Ni–Co distance for NH₃–NiP/Co (3.59 Å) is significantly longer than the value obtained for the native NiP/Co (3.09 Å) system, consistent with the observation of a surface *spin-trans* effect^[4] Notably, the coordination of the Co surface-ligand^[4,15] to the Ni²⁺ ion is identified by a broadening of the calculated 3d_z² 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 Å to 2.05 Å. This increase has been attributed for a similar system to the reduced formal bond-order due to the presence of an un-paired electron in the anti-bonding d_{x²-y²) orbital of NH₃–NiTPP.^[13b] Note, that the NH₃-induced FM coupled spin-density is distributed across the Ni-porphyrin's nitrogens and the NH₃ ligand (0.06 μ_B). The spin density sums up to $\sim 1.92 \mu_B$, corresponding to a molecular spin state of S=1, consistent with the two singly-occupied levels seen in Fig. 3b.}}}

In conclusion, we have provided evidence for the capability of NH₃ 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 NH₃ exposure 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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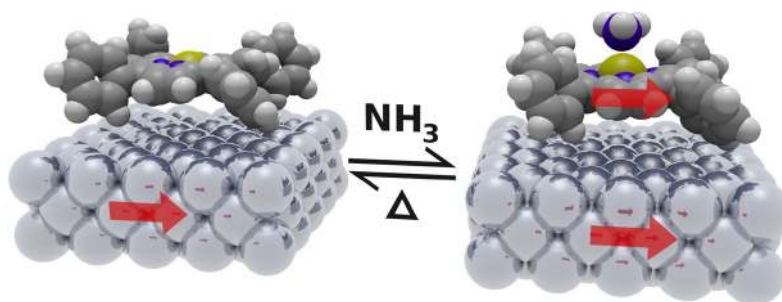
Layout 2:

On-Surface Magnetochemistry

Christian Wackerlin, Kartick Tarafder, ‡
Jan Girovsky, Jan Nowakowski, Tatjana
Hahlen, Aneliia Shchyrba, Dorota
Siewert, Armin Kleibert, Frithjof Nolting,
Peter M. Oppeneer, Thomas A. Jung*
and Nirmalya Ballav*

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Magnetic Moment in On-Surface Low-
Spin Porphyrin



Amazing ammonia! The molecular spin state of Ni(II) porphyrin, supported on a ferromagnetic Co surface, can be reversibly switched between *spin-off* ($S=0$) and *spin-on* ($S=1$) states upon coordination and decoordination of gaseous ligand NH_3 , respectively. This finding clearly indicates the possible use of the system as a magnetochemical sensor and could also find applications in molecular spintronics.