

Reversible Manipulation of the Magnetic Coupling of Single Molecular Spins in Fe-Porphyrins to a Ferromagnetic Substrate

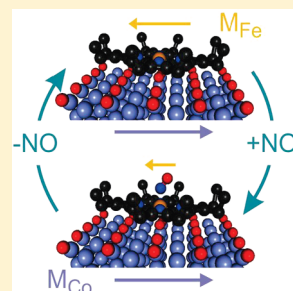
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S Supporting Information

ABSTRACT: We demonstrate by means of X-ray magnetic circular dichroism that the magnetization of paramagnetic Fe-octaethylporphyrin (FeOEP) molecules coupled antiferromagnetically to an oxygen-covered Co ultrathin film grown on Cu(001) can be reduced by about 50% by the adsorption of nitrogen monoxide (NO). From the similarity of Fe X-ray absorption spectra before and after NO adsorption, we conclude that this effect is the result of a reduction of the magnetic superexchange coupling between the Fe ions and the substrate caused by physisorbed NO molecules, leading to the reduced molecular magnetization. After thermal desorption of the NO from the Fe ion, the original FeOEP magnetization is restored. The reversibility of the process is proven by successfully repeating the NO dosing—desorbing procedure.

SECTION: Surfaces, Interfaces, Catalysis



The magnetic properties of molecules have attracted tremendous interest in recent years.^{1–7} Magnetic metallorganic molecules are considered the main building blocks of future molecular spintronic devices, provided that they can be immobilized on solid substrates. Studying the chemical and magnetic interactions between such molecules and well-defined surfaces is therefore mandatory. One of the key issues is to gain control over the magnetic properties of adsorbed molecules by external stimuli. A chemical stimulus affecting the molecular magnetization could, for example, be the attachment and detachment of additional small molecules.

The spin of paramagnetic Fe-porphyrin molecules adsorbed on a ferromagnetic substrate can be stabilized up to room temperature and above by superexchange interactions with the substrate.^{8–10} This coupling can be considered equivalent to a huge magnetic field acting on the magnetic moment of the paramagnetic molecules, providing the necessary stability against thermal fluctuations. The sign of this magnetic coupling to the substrate can be furthermore tailored to be either ferromagnetic or antiferromagnetic by adsorbing the molecules directly on a metallic ferromagnet or by inserting oxygen atoms between the molecules and the metal, respectively.¹¹

The adsorption of small molecules onto adatoms or molecules that are already adsorbed on the substrate can be a means to influence their properties. Oxygen adsorption, for example, leads to a change in the easy magnetization direction of Fe adatoms laterally coordinated by organic molecules on a Cu surface.¹² The reversibility of such an influence is an obvious condition for the true control of the magnetic properties. Only recently, Wäckerlin et al. have shown the feasibility of reversible switching of magnetic properties of adsorbed porphyrin molecules by the adsorption and thermal desorption of NO. Exposing a complete molecular monolayer of Co(II)-tetraphenylporphyrin (CoTPP) on Ni/Cu(001) to 6000 L of NO (1 L = 1 Langmuir = 1×10^{-6} mbar·s)

at room temperature quenches the spin state of the CoTPP molecules from $S = 1/2$ to $S = 0$.¹³ After thermal desorption of the NO molecules at 615 K, the initial $S = 1/2$ state is restored. This change goes hand in hand with an oxidation of the Co ion, as evidenced by the corresponding energy shift of the Co 2p core-level photoemission signal.

If the magnetic properties of single molecules are to be controlled by NO adsorption and desorption, the interaction of NO with uncovered parts of the magnetic substrate is also an issue. The magnetism of a metallic ferromagnetic substrate may be influenced by NO adsorption as well. Also, previous studies of NO exposure to CoTPP on Ag(111) have shown that on this substrate, NO adsorbs preferentially between the organic molecules, and such causes a structural rearrangement of the coadsorbate system.¹⁴ In the optimal case, the adsorption of NO leaves the magnetic properties of the substrate unaffected while at the same time inducing a sizable reversible change of the molecular magnetism. Last but not least, it is very interesting to see whether magnetic molecules with a spin higher than 1/2 can be reversibly influenced by NO.

We present an X-ray spectroscopic study of the adsorption of NO on top of a submonolayer of adsorbed Fe-octaethylporphyrin (FeOEP) molecules. As a substrate, we use a ferromagnetic Co film covered with an ordered $c(2 \times 2)$ layer of oxygen atoms, as in ref 11. We find that this oxygen layer protects the substrate magnetic properties from being influenced by NO adsorption. The magnetization of the adsorbed FeOEP molecules is strongly reduced after the dosage of a relatively small amount of only a few L of NO to the system. Although, after thermal desorption, some NO is dissociated and remains at the surface, the FeOEP

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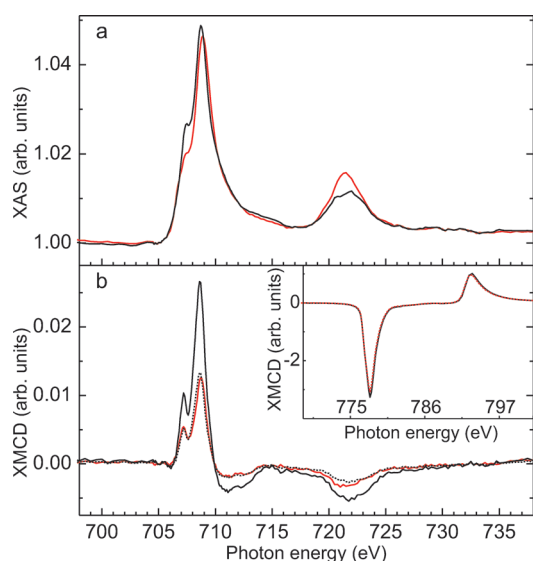


Figure 1. Fe $L_{2,3}$ XAS (a) and XMCD (b) spectra of 0.6 ML FeOEP on O/Co measured at 70° grazing incidence at 120 K before (black lines) and after (red lines) dosing 24 L of NO. The black dotted line in (b) is the spectrum before NO dosage, scaled by 0.5. Inset: XMCD spectra at the Co $L_{2,3}$ -edges before and after dosing NO.

molecules are found to stay intact. The process of influencing the magnetic properties of the metal ions is completely reversible and can be conducted over again.

X-ray absorption spectra of the Fe $L_{2,3}$ -edges show that this system represents a case where the reversible change of the molecular magnetism by the adsorption and desorption of NO occurs without change of the oxidation state. We conclude that in this case, it is mainly the strength of the magnetic coupling between the substrate and the molecules that is influenced by the NO adsorption, leading to a lower magnetization at finite temperatures. This mechanism is applicable to a much broader range of molecular systems because it does not rely on a change of the oxidation state, as in ref 13. A chemically induced switching of the coupling between “strong” and “weak” is potentially interesting for future spintronic devices.

Angle-resolved XAS spectra taken with linearly polarized X-rays at the N K-edge of the FeOEP molecules prior to NO exposure confirmed that the molecules are adsorbed flat on the O/Co surface (see Supporting Information), as published previously.¹¹ Figure 1a shows the X-ray absorption spectra at the Fe $L_{2,3}$ -edges of 0.6 molecular monolayers (ML) of FeOEP molecules, before and after dosage of 24 L of NO, measured at 120 K and grazing incidence and averaged over the signals for positive and negative helicity of the incoming circularly polarized light. It is evident that the energy position of the peaks is almost unaffected by the NO adsorption. The most prominent changes are the reduction of the shoulder in the low-energy flank of the L_3 peak at $E = 707$ eV and the increase in intensity of the L_2 peak at about 722 eV. The inset in panel (b) shows the XMCD spectra of the Co substrate before and after NO dosage. The two curves are nearly identical, confirming that the NO does not significantly affect the magnetism of the Co substrate, which appears to be protected by the oxygen adatoms.¹⁵ This is in contrast to other uncovered ferromagnetic surfaces, where, for instance, a modification of the easy magnetic axis was observed for thin Co films on a stepped Cu surface upon NO adsorption.¹⁶

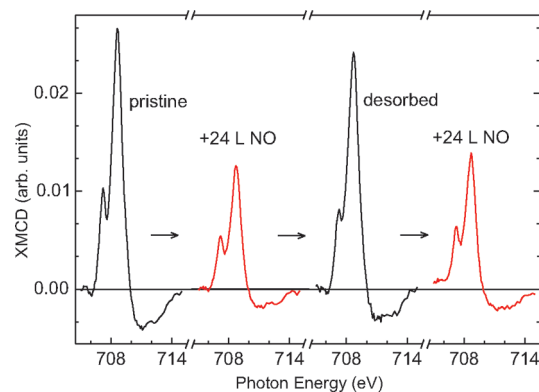


Figure 2. Fe L_3 XMCD signals measured at 120 K at each NO dosage step. From left to right, the spectra correspond to the sample in the pristine state, after dosing with 24 L of NO, after subsequent desorption of NO by warming up to 350 K, and after dosing with 24 L of NO once more.

In Figure 1b, we compare the XMCD spectra, that is, the difference between absorption spectra taken with opposite helicity, at the Fe $L_{2,3}$ -edges of the FeOEP molecules before (black continuous line) and after dosage of 24 L of NO (red line). The signs of both spectra are opposite to the ones of the Co substrate shown in the inset, proving the antiparallel alignment of the Fe spins and the magnetization of the oxygen-covered Co layer, as observed before.¹¹ Strikingly, the Fe XMCD signal after NO dosage is a factor of two smaller than that of the pristine sample, as can be seen by comparing to the black dotted line, which shows, for better comparison of the line shape, the XMCD spectrum of the pristine sample scaled by a factor of 0.5. Except for a slightly higher XMCD signal at the L_2 -edge relative to that at the L_3 XMCD and a small difference in the relative amplitudes of the two XMCD peaks at the Fe L_3 -edge, the line shape of the XMCD spectrum remains unaffected by the adsorption of NO.

To test for reversibility of this NO-induced change of the Fe XMCD signal, the system was brought to 350 K to desorb the NO molecules and cooled down again to measure the resulting XMCD signal. Figure 2 compares, from left to right, the XMCD signals at the Fe L_3 -edge of the pristine sample, of the sample after dosing with 24 L of NO, after annealing to 350 K, and after a second dosage of 24 L of NO, all measured at 120 K. It is evident that after the desorption of NO from the sample, the initial Fe XMCD intensity is almost completely recovered and that dosing NO again causes once more a reduction by nearly a factor of 2.

The N K-edge XAS signal can be used to gain information on the adsorption behavior of NO on FeOEP/O/Co. Figure 3a shows from the bottom to top the grazing incidence N K-edge XA spectra corresponding to the series of spectra displayed in Figure 2, that is, of the pristine sample, after dosing with 24 L of NO, after warming up, and after dosing again with 24 L of NO. For the sake of clarity, the spectra after subtraction of the one of the pristine case are shown in panel (b). Additional intensity after the first NO dosage is seen in the π^* resonance energy region, with a shoulder at $E = 398.7$ eV and a peak at $E = 399.9$ eV, as well as a broad σ^* shape resonance around 412.5 eV. The peak at 399.9 eV agrees with that found for gas-phase NO¹⁷ and suggests the presence of a weakly interacting NO species on top of the FeOEP molecules. The shoulder at 398.7 eV might be assigned to some NO chemisorbed on the oxygen-covered Co surface. After annealing the sample, the additional intensity at 399.9 eV disappears,

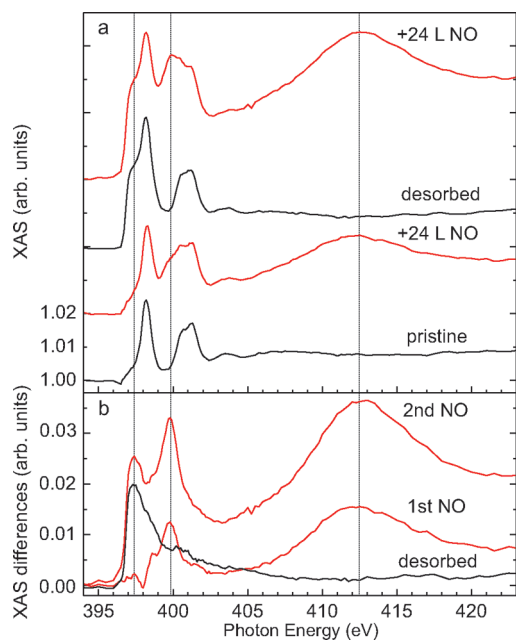


Figure 3. (a) From bottom to top, N K-edge XAS spectra of the sample in the pristine state, after dosing with 24 L of NO, after subsequent desorption of NO by warming up to 350 K, and after dosing with 24 L of NO once more. Spectra are shifted vertically for clarity. (b) Difference between the top three XAS spectra of panel (a) and the XAS spectrum of the pristine sample.

consistent with the desorption of the weakly bonded NO molecules, while a new peak at 397.4 eV emerges. We suggest that the latter may be ascribed to a chemisorbed atomic N species that could result from the dissociation of NO on Co. Fe $L_{2,3}$ absorption spectra taken at temperatures between 120 and 350 K show a gradual transition between the two spectra shown in Figure 1a, such that we conclude that no transition to chemisorption takes place before desorption (see Supporting Information). The second dosage of NO leaves this peak unaffected, while the signals at around 399.9 and 412.5 eV reappear. The detailed surface chemistry of nitric monoxide on transition-metal surfaces can be rather complex, depending on surface reactivity, temperature, or NO dosage, and can be found elsewhere.^{18,19}

In order to demonstrate how the change of the magnetization of the Fe atoms is linked to the adsorption of NO, we show in Figure 4 the dosage dependence of the N K- and Fe $L_{2,3}$ -edge signals at 412.5 and 721.4 eV, respectively, normalized to their values prior to NO exposure. Both intensities feature a sharp increase at low dosages, saturating already after about 4 L of NO, which approximately corresponds to 3 NO molecules per FeOEP molecule on the surface (see Figure S2 in the Supporting Information). The similarity of the dosage dependence of these nitrogen and iron signals allows one to conclude that the modification of the Fe electronic structure is indeed due to the adsorption of NO in the vicinity of the Fe ions.

Let us first examine the Fe oxidation state. By making use of the XAS charge sum rule²⁰ and using the Co $L_{2,3}$ XAS signal as a reference, we find that the Fe 3d occupancy number is five, irrespective of the presence of NO. On the basis of previous density functional theory calculations of the same system without NO¹¹ and the similarity of the Fe $L_{2,3}$ absorption spectra to those of Fe₂O₃,^{21–25} we conclude that Fe is in a 3+ state. Such an Fe

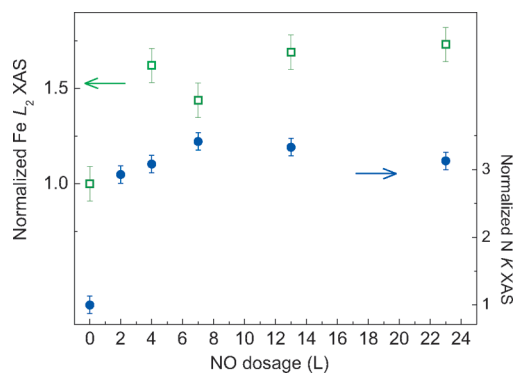


Figure 4. NO dosage dependence of the Fe $L_{2,3}$ and N K XAS signals at $E = 721.4$ (squares) and $E = 412.5$ eV (circles), respectively, relative to the corresponding intensities of the pristine sample.

valence state is consistent with the substitution of the Cl ligand of the powder evaporant by the oxygen-covered surface as the fifth ligand (see Supporting Information), while maintaining the Fe ion displaced from the porphyrato plane toward the center of the coordination polyhedron, so that the five-coordinated Fe ion is subject to a C_{4v} symmetry ligand field.²⁶ Because oxidation or reduction is usually accompanied by a change in absorption energy,^{24,25,27} the absence of any appreciable energy shift in the Fe $L_{2,3}$ absorption spectra upon NO adsorption indicates that, unlike in the coordination of NO to the metal center of CoTPP molecules adsorbed on Ag(001)²⁸ or on Ni/Cu(001),¹³ the oxidation state of the Fe ion is preserved. As a consequence, the spin state of the Fe ion is not necessarily modified by the NO molecules. This is supported by the striking similarity in the spectral shape of the Fe XMCD signals before and after NO dosage.

The spin XMCD sum rule is customarily employed to determine the value of the effective spin moment of transition-metal systems.²⁹ Unfortunately, its applicability to Fe³⁺ is questionable due to the mixing of intensities at the $L_{2,3}$ -edges caused by multiplet effects, the 3d spin–orbit coupling, and the presence of the magnetic dipole operator $\langle T_z \rangle$, which can be significant in low-symmetry systems³⁰ (see Supporting Information). Nevertheless, the spin XMCD sum rule yields a thermal expectation value of the effective spin operator $\langle S_{\text{eff}} \rangle = 0.27(2)$ per vacancy in the Fe 3d orbitals for the pristine sample and of 0.14(2) after dosing with 24 L of NO. Assuming a constant trivalent oxidation state for the Fe atoms, this leads to $\langle S_{\text{eff}} \rangle = 1.37(10)$ and 0.71(10) before and after NO adsorption, respectively. Because the Fe spins are subject to thermal fluctuations at finite temperatures, these averaged values represent lower limits for the effective spin (see Supporting Information). Therefore, we can exclude the possibility of a low spin state for the Fe ions before and after NO dosage. For the case of Fe³⁺ ions with no charge transfer from the ligands, the value of the magnetic dipole operator $\langle T_z \rangle$ in the effective spin moment would be very small for the $S = 5/2$ high-spin state, and a value of $S_{\text{eff}} = 0.5$ per vacancy would be expected for the effective spin. Previous temperature-dependent XMCD measurements on FeOEP/O/Co/Cu(001) yielded an extrapolated effective spin of 0.35 per vacancy,³¹ compatible with our values at 120 K as presented above, such that we conclude that the Fe ions are most likely in the intermediate $S = 3/2$ or in an admixed $S = 3/2, 5/2$ spin state.^{11,32}

The branching ratio, defined as the ratio between the Fe L_3 and the total Fe $L_{2,3}$ XAS intensities, has been used as an

alternative manner to gain information on the spin state.²¹ Dosing the FeOEP molecules with NO causes the Fe $L_{2,3}$ XAS branching ratio to decrease from 0.77(3) to 0.70(3). In the absence of a strong ligand field and of charge transfer, a higher branching ratio would suggest a higher spin state of the Fe ions. However, these conditions are, in particular, not met by the Fe ions of the system under study, so that there might not be a straightforward correlation between the branching ratio and the spin state. The orbital angular momentum m_L , as obtained from the corresponding XMCD sum rule,³³ is 0 within the error regardless of the presence of NO, although the comparison of the XMCD spectra of Figure 1b suggests a slightly lower orbital to spin moment ratio after NO adsorption.

If the Fe spin is not changing upon NO adsorption, the smaller Fe $L_{2,3}$ XMCD signal upon NO dosage can only be explained by a reduction of the magnetic superexchange coupling to the ferromagnetic Co substrate. In previous reports on the effect of NO dosage to adsorbed porphyrin or phthalocyanine molecules, this was found to be due to the shift of electron density in the d_z orbitals by the trans effect due to the strong σ -donor and π -acceptor characters of NO.^{28,34} For CoTPP, these effects are sufficient to alter the oxidation state and thus the spin.¹³ In our case, the oxygen atoms on the Co surface are likely to inhibit the oxidation of Fe upon NO uptake. The bond to the oxygen leaves the Fe ion already in a 3+ state and thus makes further oxidation more difficult. The spin-pairing energy of Fe³⁺ prevents a spin crossover transition, as evidenced by the striking similarity of the Fe XMCD signals before and after NO dosage. A decrease of the coupling energy to about a fourth of the initial value of around 37 meV¹¹ leads to the observed change in FeOEP magnetization at the experimental temperature of 120 K. The physisorption of NO onto the FeOEP molecules is thus obviously causing such a reduction of the strength of the magnetic superexchange coupling between Fe ions and the Co substrate across the oxygen atoms. The mechanism could be a slight influence on the bond distance or possibly also a conformational change of the porphyrin molecule.

To understand the small changes in the Fe $L_{2,3}$ XAS and XMCD spectra after adsorption of NO, it might be necessary to consider charge-transfer effects as a consequence of the covalency of the Fe atom in FeOEP. In this case, an integral oxidation state does not fully describe the Fe ion. Physisorption of NO might then cause slight shifts in the weight of the charge between Fe and ligands, even though the NO is not establishing a covalent bond with the Fe itself. The identical energy position of both the XAS and XMCD signals suggests that the net charge transfer between the Fe ion and the ligands before and after NO adsorption is nearly the same. It might, however, lead to the observed change in the XAS branching ratio and the slight change in the orbital moment ratio. It is not very likely, though, that such a small change in the charge transfer leads to a change in the spin state. The main effect has therefore to be assigned to the weakening of the magnetic superexchange coupling between the Fe moment and the magnetization of the Co substrate.

We have shown how the magnetization of Fe-porphyrin molecules coupled to a ferromagnetic substrate can be reversibly tuned in a bistable manner by adsorbing and thermally removing NO molecules. We conclude that the NO uptake reduces the strength of the magnetic superexchange interaction of the Fe ion in the porphyrin molecule. In contrast to results in similar systems, no oxidation of the Fe ion is found as a consequence of the NO uptake, suggesting that the Fe spin remains unperturbed.

The fact that the effect saturates at rather low NO dosages of less than 4 L is evidence of the efficiency of the switching process reported here, minimizing at the same time any possible chemical modification of the surface properties upon NO adsorption. The NO remains only weakly bound to the porphyrin molecules. The resulting reversibility of the magnetic switching process, proven here both for the attachment and the desorption of NO, allows manipulation of molecular spins in a truly bistable manner, potentially on a single-molecule basis, paving the road toward a repeatable control of the spin of individual molecules on surfaces.

EXPERIMENTAL SECTION

Co films were prepared by electron beam evaporation on a preoxidized Cu(001) single crystal at room temperature, following ref 35. Co growth on the Cu surface covered by 0.5 monolayers of atomic oxygen occurs in a surfactant-assisted mode,^{35,36} with the oxygen atoms at $c(2 \times 2)$ positions. Fe(III)-2,3,7,8,12,13,17,18-octaethylporphyrin-Cl molecules were subsequently evaporated by sublimating molecular powder from a crucible at around 485 K onto the O/Co surface held at room temperature. NO was dosed into the vacuum chamber at a pressure of 8×10^{-8} mbar while the sample temperature was 120 K. Experiments were performed using linearly p- and circularly polarized X-rays of the beamline UE56/2-PGM1 of BESSY II in Berlin, with degrees of polarization larger than 99 and of about 85%, respectively. Absorption spectra were acquired in total electron yield mode, recording the sample drain current as a function of photon energy while monitoring the incoming beam intensities by the total electron yield of a freshly evaporated gold grid. Spectra were taken at normal and grazing incidence, defined by angles of 0 and 70° between the k vector of the X-rays and the surface normal, respectively. The photon energy resolution was set to 150 and 300 meV for the N K and Fe, Co $L_{2,3}$ absorption edges, respectively. Typical photon flux densities at the sample of about $10^{13} \text{ s}^{-1} \text{ cm}^{-2}$ were used to prevent radiation damage, which can be excluded here from the comparison of spectra taken immediately after sample preparation and at later times.

ASSOCIATED CONTENT

S Supporting Information. Additional XAS and XPS spectra and discussion of the applicability of the XMCD sum rule. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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